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13. ABSTRACT *(Maximum 200 words)*

This Technical Report gives a summary of the research performed in the support of the Wright Laboratory Materials Directorate under a Student Support contract. The report contains a summary of the activities undertaken in administering the contract as well as the research and results for each of 284 Tasks completed under the contract.

Tasks included technical support and research in such areas as: Nonmetallic materials(structural materials, mechanics and surface interactions, polymers, nonstructural materials), metals and ceramics (processing and high temperature materials, metals behavior, structural metals, nondestructive evaluation), electromagnetic materials (hardened materials, electronic and optical materials), system support materials integrity, materials engineering, computer activities and manufacturing (material processing control paradigms, feature-based material/product design, self-improving systems).

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WL-TR-97-4037

A SUMMARY OF VARIOUS MATERIALS RESEARCH EXPERIMENTS

Wanda G. Vogler

Southwestern Ohio Council for Higher Education
3171 Research Blvd, Suite 141
Dayton, Ohio 45420-4014

FEBRUARY 1997

FINAL REPORT FOR 05/27/92 - 05/26/97

MATERIALS DIRECTORATE
WRIGHT LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AFB OH 45433-7734

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SUMMARY OF CONTRACT ACTIVITIES

Since May 1992, the Southwestern Ohio Council for Higher Education (SOCHE) has administered a contract to provide (1) opportunities for students to experience and participate in activities involved with materials development for the Air Force, and (2) student support for the conduction of experiments at an appropriate level for the various materials research programs within the Air Force Wright Laboratory/Materials Directorate. The contract allowed for 313,038 person hours on-site for research activities in nonmetallic materials, metals and ceramics, electromagnetic materials, and system support and manufacturing. The award made it possible for SOCHE to continue activities delivered to the Materials Directorate since 1986.

The Student Support Program Office in Miami Valley Research Park has all the necessary equipment and support to fulfill the Contract requirements. The Director has been with the Program since the beginning Contract in 1986. The Administrative Assistant has been with the Program since 1990. This half-time Director and full-time Administrative Assistant delivered 12,438 hours of the approved 12,539 person hours for five administrative/management Tasks. People and processes already in place allowed us to dovetail activities and transition to this Contract activity.

Systems to monitor and control the budget and individual tasks were already in place. However, we wanted a more comprehensive approach to managing the ever changing and growing information about the students, budgets, and Tasks. A Management and Information Systems class at Wright State University took on our needs as a class project. They designed a data base management system that allows us to perform contract requirements with less duplication of effort, greater accuracy and ease. This allowed us to have the information necessary to prepare required reports readily: monthly Funds and Man-Power Expenditure Report, monthly Management Reports, technical reports for each Task, quarterly Contract Funds Status reports and vouchers for billings.

During the 55 months of technical activity, SOCHE received and filled 284 Tasks Orders. The Student Support Program hired 177 students for technical research at ML and FIBG. SOCHE students delivered approximately 92% of the 245,493 approved person hours. Of the funds allocated for the Contract, expenditures were less than 90% of the budget.

Approach to Establishing and Maintaining Positive Relationships

Maintaining rapport with the Materials Directorate personnel continued as a priority. This was done in a variety of ways. Before the recruitment process began, the Director consulted the Government Task Leaders to determine the academic and technical background needed to do the Task. We sought their opinion in critiquing the technical qualifications of student applicants. The Task Leaders received information throughout the Task about anything that could affect the student worker or Task performance. Anytime there was a problem, the staff tried to resolve the issue to all parties' satisfaction. Task Leaders were kept informed by correspondence, telephone calls and site visits. We asked Task Leaders to rate strengths and weaknesses of the program procedures and staff. Sixty-two respondents rated us "Above Average" or "Outstanding" in most areas (See Attachment 1).

Recruiting and Selecting Students

Since this was our third Student Support Contract, the contacts on campuses were already in place. Liaison persons, previously designated by the college/university presidents, gave Student Support a point of contact on each campus to recruit students. It also gave students an accessible place to pick up brochures, applications and Task descriptions.

Task descriptions ran the gamut in science and engineering - chemistry, computer science, physics and engineering (material science, mechanical, electrical, electro-optics, chemical, etc.). Campus liaison persons, deans, department chairs and individual faculty members received information describing Tasks to recruit interested and qualified students. On those campuses that produced newsletters, they publicized Tasks in the newsletters. Campus departments with electronic mail publicized Tasks for us also. Students already working in Tasks received publicity about openings.

Recruitment activities were ongoing throughout the year. The Director made visits to campuses to generate interest, answer questions and generally keep the Program visible. Anytime there was an opportunity to meet with staff or faculty on a campus, it was done. We also attended special events for cooperative education, internships or career fairs. The Director belongs to state and national education associations and is active at the state level to increase interaction with campus personnel and recruitment options.

Students from 14 institutions submitted credentials for consideration. Credentials consist of an application, course listings/transcripts, and resume plus letters of reference if the student wishes. To maintain a prospective file of qualified applicants, Student Support encouraged and accepted credentials continuously. Besides campus referrals, Task Leaders would sometimes refer a student they knew. Materials Directorate personnel often teach and do research on campuses. They have occasion to get to know students through these or through other student oriented programs on Base.

Student Support screened credentials to determine academic standing (GPA), citizenship status, previous work experience and academic preparation. Student Support forwarded credentials of students qualified for the Task. The Task Leaders reviewed credentials and decided which students should be invited to see the work setting. Student Support staff contacted those students to set up appointments with ML personnel. We asked Task Leaders to assess the technical qualifications of the students. After conferring with the Task Leader, the Director ranked the students according to their qualifications. The Director negotiated with the most qualified candidate first. If this student did not accept the position, the Director contacted the next student.

After the Director selected the student, a written cost estimate (Task proposal) was prepared and submitted for approval. The person hours and schedule of work were determined after conferring with the Task Leader and the student. The 177 students hired by Student Support attended Cedarville College, Ohio University, Sinclair Community College, The Ohio State University, the University of Cincinnati, the University of Dayton and Wright State University.

Supporting, Directing and Supervising Students

New students hired received an orientation to the Program. Contracts, time sheets, general correspondence and telephone calls all serve to support and direct the students' activity. To help new students and Task Leaders in setting goals and to make expectations clear, Student Support developed a "Handbook of Information" that each received at the beginning of a Task. Students also received a copy of their Task description as prepared by the Task Leader.

As they completed Tasks, students submitted technical reports about their research activity. Part II of this report contains all the technical reports. Technical reports cover such areas as: Nonmetallic materials (structural materials, mechanics and surface interactions, polymers, nonstructural materials), metals and ceramics (processing and high temperature materials, metals behavior, structural metals, nondestructive evaluation), electromagnetic materials (hardened materials, electronic and optical materials), systems support (materials integrity, materials engineering, computer activities), and manufacturing (material processing control paradigms, feature-based material/product design, self-improving systems). Student Support used the technical reports in evaluating the students' performance. We asked that Task Leaders evaluate the students' strengths and weaknesses in Task performance through written and oral assessments, at least once during a Task assignment. We asked that they do this with the student and to allow the student to have input (See Attachment 2 for summary).

The Director contacted Task Leaders throughout the Task to see if things were going well. We encouraged Task Leaders to let us know immediately if problems arose that needed attention.

Predominantly, students worked the 1040 hour Tasks in a schedule that was part-time during the academic year and full-time during the summer. Whenever the Task Leader stated a preference, we selected students who could work full-time, alternating quarters. While most of the Tasks were 1040 hours for 12 months, we were flexible in providing Tasks for summer or other short periods.

Other Evaluations

Task assignments have enriched students' academic preparation in a variety of ways: two masters' theses; senior research projects; co-authorship of articles submitted to professional journals; presentations at professional conferences; cooperative education credit; internships for career related work experience and financial support that made higher education possible for many. As students completed their Tasks, Student Support asked them to complete a questionnaire about all aspects of their assignment. According to survey results, students said that the number one reason they participated in this Program was for the opportunity for hands-on experience related to academic study. The second most important reason was for part-time employment for pay (Attachment 3). Survey results also show that students were positive in most cases about their experience.

Summary

The Student Support Program was a success based on all the responses we received. Responses were more positive than not in all aspects of our surveys. A high quality program that meets the requirements of the Contract, while providing customers, whether a student or a person, with service and consideration was our goal.

Credit should be given to those who made it possible and rewarding for us to administer this Contract. Task Leaders were always willing to give information or cooperate with the Student Support staff whenever asked. Students gained mentors, as Task Leaders took an interest in them and spent time guiding them. The positive relationship and level of communication between the Project Engineers, Contract Negotiators and Director was a key factor in keeping the Program running smoothly.

Students and Wright Laboratory personnel alike benefited from this Contract. Government Task Leaders had the benefit of ongoing efforts by students to support the work of the division. Students brought new ideas and enthusiasm with them and potential colleagues were identified. State of the art laboratory settings allowed students to see real applications for their classroom experiences. Task assignments provided research opportunities for students not readily available from other sources.

ATTACHMENT 1
123 Surveys Sent
65 Responded

PROGRAM STAFF EVALUATION RESULTS

We are interested in your comments and suggestions concerning the effectiveness of our services to the WL/ML. Would you please take a few minutes to complete the following:

Rating Scale: A - Outstanding
B - Above Average
C - Average
D - Below Average
E - Not Applicable or No Experience

	A	B	C	D	E
1. Student selection procedures.	23	36	3	0	3
2. Match of applicants to Task Assignments.	23	36	3	0	3
3. Communication of information.	28	28	9	0	0
4. Timeliness of information.	37	25	3	0	0
5. Willingness and ability to resolve problems.	36	23	1	0	5
6. Responsiveness to your inquiries.	43	19	0	0	3

7. What has been the major benefit of our Program to you/your organization?

Increased Productivity	= 13
Outstanding students for unique technical requirements	= 8
Excellent research support	= 17
Get extra help in a reasonable time	= 3
Provides much needed technical support	= 12
Chance to encourage students	= 1
Allows time to devote to non-research duties	= 1
Energy of young engineer helps revitalize older civil servants	= 2
Student's research has provided critical new materials and scientific data to our lab	= 1

8. How many students have we placed with you?

9. Comments/Suggestions:

Excellent return on investment = 11
Good way for students to get hands-on experience = 1
Experience with SOCHE has been very positive = 2
Keep up the good work = 8
Flexibility of student schedules = 1
Good Program - everyone benefits = 11
Important to match applicants to specific assignments = 1
Program is a success largely due to Wanda Vogler's leadership and effort = 1
Selection process is awkward = 1
Students are making significant contribution = 1
Your selection of students has been outstanding = 1
Have students log in and out for work with Task Leader = 1
SOCHE is not well known outside of ML, spread the word = 1

ATTACHMENT 2
269 Sent
156 Received

Southwestern Ohio Council for Higher Education
Miami Valley Research Park
3171 Research Blvd., Suite 141
Dayton, Ohio 45420-4014
(513) 259-1375 • FAX (513) 259-1380

STUDENT SUPPORT PROGRAM
STUDENT EVALUATION

Student: ______

Task Order Dates: ______

Government Task Leader ______

Organizational Symbol: ______ Extension: ______

Task No: ______ Objective ______

Performance Evaluation: 1. ____ Outstanding 2. ____ Above Average 3. ____ Average 4. ____ Below Average 5. ____ Not Applicable

	1.	2.	3.	4.	5.
1. Leadership characteristics	36	54	25	1	40
2. Sensitivity to problems and ability to resolve	65	78	11	0	2
3. Effective in preparing and organizing work	69	69	16	1	1
4. Takes initiative, self-starter	92	46	15	2	1
5. Demonstrates willingness to accept responsibility	99	49	6	2	0
6. Demonstrates analytical ability	57	87	6	1	5
7. Demonstrates original and creative thinking	67	58	23	1	7
8. Demonstrates accuracy and thoroughness	82	63	11	0	0
9. Exhibits diligence and perseverance	103	41	10	1	1
10. Demonstrates ability to learn	100	53	2	0	1
11. Has healthy attitude toward organization	98	45	10	0	3
12. Is cooperative in working relationships with others	112	39	2	0	3
13. Quality of work performed	89	59	6	2	0
14. Effectiveness in oral communication	57	72	19	1	7
15. Effectiveness in written communication	27	69	17	1	42

Overall Performance:

Outstanding	Above Average	Average	Below Average
85	63	3	1

No Response: 4

Attendance: 142 Regular 3 Irregular No Response: 11
Punctuality: 138 Regular 9 Irregular No Response: 9

Comments on potential growth and development for student in major field of study: ______

Have you discussed this evaluation with the student? ____ Yes ____ No

Student's Comments: ______

Signatures:

Student ______ Government Task Leader ______ Date ______

White copy-S Support Office copy. Canary copy-Government Task Leader; Pink copy-Student copy

ATTACHMENT 3
261 Sent
105 Responded

STUDENT TASK ASSIGNMENT SURVEY

The following questionnaire is designed to assure complete anonymity. As a student worker, your evaluation of the Program is important to us in planning and improving the Program, so please be candid.

I. How did you learn about the Student Support Program? Check one.

16	Advertisement (flyer, brochure, campus paper)
21	Faculty member
28	Student worker
7	WPAFB employee
32	Other (please specify) Internship Co-op or Career Services
1	No response

II. Please rank your first and second most important reasons for participating in this Program.

First	Second	
20	47	Part-time employment for pay
12	27	Opportunity to conduct research work (Senior project, graduate thesis, etc.)
1	7	Co-op position for credit
72	15	Opportunity for hands-on experience related to academic study
	9	No 2nd choice

III. Do you feel you received adequate information and assistance from the Student Support staff in carrying out your Task Assignment?

Yes	No	If no, please elaborate.
103	2	Task description was entirely different from actual work.

IV. Did your guiding engineer or scientist establish clear expectations about your Task Assignment?

If no, please elaborate.

Yes	NO	
99	6	Seemed to be a lot of small tasks rather than a project that I could work on. Expectations seemed to change daily.

V. Did the Task Assignment meet your expectations?
If no, please elaborate.

Yes	No	
98	7	1 No response -Lack of support from Task Leader. Not enough to keep me occupied. -Many times I ended up performing menial tasks like washing dishes or retrieving library materials. -I thought my work was going to involve my major. -As a student worker, I expected somewhat tedious, repetitious work, that's exactly what it was.

VI. How much were you exposed to each of the following during your Task Assignment? (Circle one letter per line).

***A** = A LOT* ***B** = SOME* *C = A LITTLE* *D = NOT AT ALL* ***E** = NOT APPLICABLE*

A	B	C	D	E		
39	38	24	2	2	1.	Philosophy of research
38	37	26	1	3	2.	Use of scientific method to solve problems
51	37	14	1	2	3.	Use of experimental checks and controls
73	17	11	2	2	4.	Measurement techniques
34	22	22	15	12	5.	Design of equipment
32	32	27	6	8	6.	Process of design of an experiment
6	23	12	2	2	7.	Data analysis (with or without computer assistance)
25	19	21	21	19	8.	Computer programming
47	29	20	5	4	9.	Acquisition and use of scientific literature (books, audio visual, etc.)

A	B	C	D	E		
43	31	29	0	2	10.	Identification of new questions as a consequence of scientific exploration
55	31	15	1	3	11.	Teamwork in scientific research
76	20	6	2	1	12.	Use of advanced scientific equipment
43	34	19	7	2	13.	Other students with similar interests and goals
44	37	19	4	1	14.	Scientists working in different areas of research
24	32	40	8	1	15.	Information on scientific careers

VII. How much has your experience in this Task contributed to your development in each of the following?

(Circle one letter per line).

***A** = A LOT* ***B** = SOME* ***C** = A LITTLE* ***D** = NOT AT ALL* ***E** = NOT APPLICABLE*

A	B	C	D	E		
68	32	5	0	0	1.	Working with professionals
62	30	10	2	1	2.	Responsibility on a job
44	44	16	0	1	3.	Understanding of scientific principles
50	34	21	0	0	4.	Scientific vocabulary
33	33	26	10	3	5.	Ability to write a technical report
52	39	13	1	0	6.	Understanding of your interests and abilities
35	47	19	4	0	7.	Educational goal setting
43	44	15	2	1	8.	Insights into career opportunities in science
49	50	4	2	0	9.	Professional career development

VIII. To what extent did you benefit from the following?
(Circle one letter per line).

***A** = A LOT* ***B** = SOME* ***C** = A LITTLE* ***D** = NOT AT ALL* ***E** = NOT APPLICABLE*

A	B	C	D	E		
61	26	12	4	2	1.	Explanations of work by government task leader
15	27	23	15	25	2.	Tours of other laboratories or installations
56	27	19	3	0	3.	Informal talks with government task leader
56	31	13	3	2	4.	Discussions with other scientists or engineers
37	35	19	9	4	5.	Interactions with other student workers
13	24	26	25	17	6.	Guidance from campus personnel; i.e., faculty, co-op education, internship or placement offices.

IX. How do you feel about your Task Assignment experience?
(Circle one letter per line).

***A** = STRONGLY AGREE* ***B** = AGREE* *C = DISAGREE* ***D** = STRONGLY DISAGREE*

A	B	C	D		
67	36	1	1	1.	I enjoyed the experience
62	37	6	0	2.	I liked the scientific research
58	41	5	1	3.	I was satisfied with the way I spent my time
78	26	1	0	4.	I learned a lot
63	37	5	0	5.	I feel I contributed to the research results

X. What did you like most about the Program?

Valuable research/work experience - 38
The people I worked with - 21
Flexible schedule - 15
Exposure to lab hands on experience -14
Liked how it enhanced what I was studying in school - 8
Helped to focus career goals - 4
Guidance of working engineers - 5

Being responsible for a project - 5
Task leader was fantastic - 2
Part-time position lead to full-time position - 1

XI. Please include any comments or suggestions for improving the Program.

Fine Program - 4
More interaction with other students - 3
I consider myself very luck to have had this opportunity - 2
GTL didn't seem to understand the limits of the hours I was supposed to work. Always wanted me to work more - 1
Survey more frequently - 1
Tuition assistance for graduate students - 1
Have more accurate Task description - 1
Give students the opportunity to attend scientific meetings talks -1
Quality of research experience depends on the Task Leader to which the student is assigned. -1
Give students more choices for work -1
Talk with Task Leaders to determine amount of time needed on a task; then reduce that amount by a factor of two. -1
Offer tours of other government and private laboratories -1
Number of hours not emphasized so much -1
I had a great experience and learned a lot -1
Thank you -1
More research, less bookkeeping -1
More frequent review of expectations by GTL -1
I don't feel I should have to wash a weeks worth of dishes each month when I never use any of them -1

ELECTRONICS AND COMPUTER SUPPORT IN ELECTROMAGNETIC MATERIALS RESEARCH

Task Order No. 2
Student Support Program
Southwestern Ohio Council for Higher Education

Tyson B. Whitaker
Wright State University

5 July 1993

Government Task Leader
Mr. Ronald E. Perrin
WL/MLPO

ACKNOWLEDGMENTS

Thanks must go out to Mr. Ron Perrin for his leadership, patience and tolerance, and for his technical insights. It would be unthinkable not to mention Ms. Laura Rea in appreciation for her support. Special thanks are given to Mr. Tom Kensky, for his influence and motivation. The list could continue, but I will thank the rest of MLPO for making my experiences here this year colorful, realistic and growth promoting.

TASK ASSIGNMENT

The first area of activity is in hardware development, the second is in software. Hardware development specifies activities such as circuit fabrication, system packaging and electronics design. The highlights of the hardware development activities include a power modulator, low impedance pre-amp and a temperature controller. Computer support activities and system control programming fall into software activities. Included will be summaries of two projects, the polling system and the x-y stage controller.

The need for a variable power generator that can be driven by a DC voltage, from a variety of controllers lead to the design of the power modulator. This circuit converts a 0VDC to 10VDC input voltage into a 120VAC or 240VAC output which is time-modulated from 0% to 100%. The input is compared to a 10V ramp which represents 100 half cycles of the AC source (33.3 msec period), thus generating a digital pulse train which dictates the on and off parts of the 100 half-cycle string. This pulse train is used to control the AC signal, turning it on and off at the zero crossing points which minimizes switching transients. This circuit was converted to a PC board with the Douglass Professional software and farmed out for production.

It seems that the lab's materials development sometimes exceeds the industries' measurement capabilities or attention, because commercial instruments are not fast enough or geared toward certain applications. This is the real meat of what the engineering staff here is for. There were a few cases where custom development was required. One of these in particular, was a low impedance photo detector. This is essentially a pre-amp for an existing analyzer which interfaces a low impedance (superconductor) sample to a unit designed to analyze samples of higher impedances. The pre-amp consists of a constant current source, an amplifier and signal filtering. The current source drives the sample to a specific voltage determined by it's resistance. Variations in this resistance due to specific stimulus cause the voltage drop across the sample to change. This voltage change is then amplified and received by the unit for analysis.

A particular temperature controller/heater driver was designed by Mr. Ron Perrin to interface to a front end temperature sensor designed by Mr. Tom Kensky for the purposes of crystal analysis. The design was bread boarded and tested for stability. The printed circuit board layout and fabrication were done and the controller tuned to the application. The output has to remain still for any constant input. Therefore, the controller was tuned to be critically damped or slightly over damped to avoid oscillations. Packaging was also designed since it was developed for laboratory use.

A particular material characterization test involves polling, data gathering over long periods of time. This test applies a moderate voltage across a material at certain temperatures and measures leakage current. This can be accomplished with existing instrumentation, but since the tests can be drawn out for hours with many data points, automation is desired. Software was written for the Zenith Z100 computer that pulls all the elements together using RS-232 and IEEE-488 and the disk drive for data storage. Since there are many parameters involved, voltages, temperatures, polling times, etc. the parameters also can be saved and recalled to ease user interface. The output data file contains all the testing parameters, data and any additional information the user deems necessary.

Another software project is the X-Y positioning software for some sort of film deposition. Similar to the above, there are the necessary program parameters from the user and interfacing needs. The main object of control is a linear actuator that moves a mirror, thus allowing a laser to scan along a material in a preprogramed manner. The actuators have position feedback that allows very precise control and repeatability.

RESULTS

For the most part, the above projects are continuous efforts because as they are used, a better understanding of the devices and data they provide, serves to focus and tighten the performance specifications. A broad sink of time and effort is the seemingly never ending job of improving and fine tuning. Many other activities and responsibilities are not mentioned in the above summary, not necessarily due to lack of importance, but because of the variety. Some of these, for example, are instrument repair and calibration, auxiliary electronics assembly and design and computer-based documentation including CAD and report writing.

COMPOSITES

Task Order No. 3
Student Support Program
Southwestern Ohio Council for Higher Education

Douglas W. Barlage
Wright State University

15 August 1992

Government Task Leader
Dr. Ronald J. Kerans
WL/MLLM

ACKNOWLEDGMENTS

I would like to thank T. A. Parthasarathy (UES), S. Sambasivan (Systran Visiting Scientist) and Dr. Kerans for their guidance during my Task assignment.

TASK ASSIGNMENT

The objective of the Task was to identify the mechanisms that control the high temperature failure of ceramic composites. The primary mechanism explored was the behavior of the fiber matrix interface. Further work was done in training another student, Kim Andrews, about hot pressing and sample preparation requiring geometric regularity. Further work was completed on the epoxy matrix-plexiglass rod mock-up composite experiment.

It has become evident that interfacial roughness plays a large role in the behavior of the interface of ceramic matrix composites. There was a need to gain insight into how these effects influenced push-out behavior. To do this, it was suggested that a model composite be created that had large rods that acted as fibers. It was relatively unimportant what material this was constructed of. Plexiglass rods were chosen to be imbedded into an epoxy matrix. Several different epoxies were tested with the same plexiglass rods. It turned out that during setting, the epoxy bonded to the plexiglass rods. This voided the possibility of push-out testing. The plexiglass rods deformed before they could be pushed out of the epoxy matrix. Different coatings to the fibers were then examined to prevent this bonding. A Teflon type substance was found to coat the fibers evenly and sufficiently enough to prevent bonding in a consistent manor. The next large problem to be overcome was controlling the geometry of the fibers to be imbedded in the matrix. A good deal of machining skills had to be learned to create molds with tight enough tolerances to provide consistent results.

A sufficient model composite was created and tested for viability in push-out testing. The rods were then manipulated to provide different interfacial roughness. Four large groups of model composites were then created, as applied roughness. These were then tested for the push-out and push back sliding frictional load. This load was then normalized with respect to thickness and plotted vs. the assumed amplitude of the roughness. A linear relation was then found as predicted by the model created by Dr. Kerans and Dr. Parthasarathy. Two things were slightly disturbing about the resulting plot. The coefficient of static friction that was derived from the plot was an order of magnitude that was lower than expected. There was also considerable scatter in the data. It was determined that there should be some direct measure of this roughness. We assumed that the roughness was directly related to the grit of the polishing material used on the rods. Optical methods proved to be qualitative at best so a stylus probe that dragged across the surface, much like a needle on a record player, was used. From this, a direct measure of roughness could be obtained for each fiber pushed out.

Originally, it was assumed that the average peak to valley of this roughness should be used as the value for roughness. Examination of the plots obtained from the stylus probe indicated that this simple measure would be somewhat misleading. It was suggested that some type of RMS value should be used. It was also proposed that some type of Fourier analysis should be done of the roughness data to measure spatial period and amplitude. This was confirmed by others that this was a reasonable thing to do and a program was written to analyze roughness in this way. Most of the fibers were then measured and analyzed for roughness in this way. This new measure of roughness was then plotted vs. sliding load. This did reduce scatter in the data and produce a reasonable coefficient of static friction.

The coefficient of static friction was then directly measured using polished surfaces and the inclined plane method. This returned a value compatible with that derived from the plot of normalized load vs. roughness from Fourier analysis. Thus, initial confirmation of the experimental results was achieved.

Further tests were conducted using rods with random roughness and very regular interfacial roughness. In terms of Fourier space, a wide band roughness vs. a narrow band roughness was considered. The same push-outs test and roughness measurements and analysis were performed. No relation of band width and push-out load was available from the results. The initial experiment was confirmed within error by this second test also.

The last 6 weeks have involved exposure to many different types of equipment and techniques including computer data acquisition and analysis, laser interferometers, optical microscopy, SEM and microprobe. The most important thing learned during the Task was sound experimental science. Observing experiments develop completely and working with many excellent researchers is an invaluable asset universal to any technical training.

PROCESS CONTROL RESEARCH FOR MOLECULAR MANUFACTURING

Task Order No. 4a
Student Support Program
Southwestern Ohio Council for Higher Education

John G. Jones
University of Cincinnati

30 September 1993

Government Task Leader
Dr. James C. Malas
WL/MLIM

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TASK ASSIGNMENT

The primary goal of the work was to develop a computer program that would interface a Macintosh computer to two separate pulse laser deposition (PLD) processes which shared a common laser. Two programs were written in LabVIEW, a graphical object-oriented programming language, which was used to first setup the instruments and then collect data. With the addition of a second chamber, this program needed to be rewritten to accommodate two sets of instruments and preferably be consolidated into a single program.

The instruments that were to be interfaced consisted of a Lambda Physik Laser, an Oriel Mirror Controller, a mass spectrometer, two different XTC thickness gauges, two ion gauges and an oscilloscope that was used for spectroscopy. All instruments were interfaced to a Macintosh using a general purpose interface bus, GPIB, which ensured that the data could be obtained from the instruments in real time. The first step in getting a working system was to write program modules that would allow the user to set parameters for any instrument before a run would begin.

Modules already existed for the laser, the two ion gauges and the mass spectrometer. The routines that needed to be developed were for the mirror controller and the two different XTC thickness gauges. An XTC is a quartz crystal microbalance and requires three different parameters to give an accurate thickness as the deposition precedes. The module developed to initialize these instruments requires the user to enter three parameters: Tooling, Density and Z-ratio; or they can use the parameters that were previously used. Both XTC modules reset the thickness counter so that all thickness measurements begin at zero. In addition the new XTC, the XTC/2, requires that the program open the shutter, which prevents undesired thickness measurement. Once the three parameters have been entered and the shutter has been opened, if available, the instruments are ready to begin a deposition.

Since the target, Molybdenum Disulfide, which was being ablated by a high energy laser has a limited life, it was determined that using a mirror, that had two degrees of freedom, left right and up down, would allow a computer program to move the laser beam across the target in a way to prolong the life of the target as much as possible. A computer module was developed that sent a program to the mirror controller based on the requirements of the operator. The controller may be directed to only move left and right, or perhaps only up and down. If desired, the operator can calibrate the laser to the four outer-most edges of the target - left, top, right, and bottom, and use a complex raster pattern. The raster pattern adjusts the laser beam back and forth, much like the pattern with which someone would mow a square lawn. Once the pattern has reached the top or bottom, it merely continues in the other direction. While the mirror controller is constantly moving the laser beam, the target is simultaneously rotating to help increase the life of the target.

Once the modules that control each instrument were developed, they were integrated into one main program. The program permits the operator to select and initialize whichever instruments are required for a deposition. As the selections are made, the information is logged to a data file for convenience so that there is no misunderstanding about what instrument settings were used. The program also will log the readings of selected instruments to a file at a selected sampling interval in any one of four application file formats: Matlab, Microsoft Word, Microsoft Excel and Cricket Graph. A typical deposition takes about 3 hours, so the sample rate was limited to seconds - one set of data points recorded on a desired integer number of seconds. While a deposition is proceeding, the operator can turn the laser on or off, set the laser parameters of repetition rate, energy density and triggering mode of energy density or high voltage.

During a deposition a graph of the ion gauge, which indicates the vacuum of the chamber, and a graph of the thickness from the XTC are displayed. In addition, the operator can request any one of the 17 parameters that can be displayed from the laser. The parameters include the pressure of the gases, current settings of parameters, the wavelength that the laser is currently adjusted for and other parameters. The operator also has the ability to set a desired thickness. Once the desired thickness has been reached, the laser will automatically shut off.

Once a deposition has been completed, a module was developed that will automatically shut-down all the originally selected instruments. The ion gauges will be turned off to prevent the filaments from remaining on. The XTC/2 will be turned off so that the shutter will close, the laser will be turned off, the mass spectrometer will be turned off, and the mirror controller will be returned to the center of the target. If the mirror controller is not bumped before the next deposition and the same chamber is used, the mirror controller will not need recalibration since its position is known.

The use of this program resulted in an increase in efficiency of performing depositions, as well as the ability to analyze the data much more efficiently. The program does not perform actual closed-loop control of the process, but was the first step that allowed data to be collected in real time to see how the process evolves. The data collection program was also written with the expectation that a closed- loop control program could be embedded within it to allow the deposition of superior quality coatings. The control algorithm would affect the process by adjusting the laser parameters in real time. The user interface of the data collection program would remain the same.

STRUCTURAL FAILURE ANALYSIS

Task Order No. 5
Student Support Program
Southwestern Ohio Council For Higher Education

Joseph T. Hunter
Wright State University

15 July 1993

Government Task Leader
Mr. Ronald H. Williams
WL/MLSA

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TASK ASSIGNMENT

As a co-op student, my job was to aid in structural and electronic failure analysis investigations. I used standard metallographic techniques to prepare metal, composite and electronic specimens for microscopic analysis. I also used an image analysis system for composite research including determination of percent void content. I am currently working as a co-author to publish an article on void content analysis techniques.

There are several procedures required in analyzing a failed component. Photographing the part before any work has begun is important for documentation purposes. The next step is typically nondestructive evaluation (NDI), which encompasses many techniques to identify defects. A part is then sectioned for chemical analysis to identify any contaminates or processing defects. Another section is used for hardness and/or micro-hardness measurements for specification comparisons. Destructive analysis of the fracture surface or failed region is then performed. This was the bulk of my work as a co-op, and included standard metallographic procedures such as sectioning, mounting, grinding, polishing, etching and photographing defects under a microscope. Further analysis included the use of a high magnification, large depth of field microscope called a scanning electron microscope (SEM). These are the main procedures in conducting failure analysis investigations; others, such as mechanical testing and field testing are performed when necessary.

Over a 1 year period, I have worked on many projects, two of which I shall describe in some detail.

Void Content Analysis of Graphite/Epoxy Composites

One main project was to compare techniques for measuring the percent of voids in graphite/epoxy composite panels. I coauthored a paper on this project that is currently being reviewed for publication by the international journal, *Composites Engineering*.

Three techniques including matrix digestion, image analysis and grid technique were described, tested and discussed. Void contents of four graphite/epoxy panels were measured using each procedure. The advantages and disadvantages of each technique were then discussed.

Matrix digestion involved measuring the density of a sample, removing the resin from the sample via acid, weighing the remaining fibers and using various equations to calculate the void content. The grid technique was performed by placing a transparent grid over a photomicrograph of the composite's cross-section, counting the void/grid intersections and calculating the void percentage. Image analysis uses an image processor that creates a binary image of the voids from the original image and measures the area percentage of the voids.

After documenting the results, it was found that the void contents measured by image analysis were lower than the results obtained by matrix digestion and grid techniques. One large difference was noted in one panel, where image and grid methods measured void content under 2% while matrix digestion measured over 6%.

The most significant advantage of matrix digestion is that it takes into account the volume of the sample, therefore, a much greater amount of material is examined than with the other two methods. However, matrix digestion assumes accurate measurements of sample densities, complete removal of the matrix (and any filler material in the matrix), and no loss of fibers. It also assumes the bulk densities of the fibers and matrix are identical with the densities of the fibers and matrix in the cured composite. Inaccuracies in any of these parameters will alter the void content result. Samples that contain internal cracking cannot be correctly analyzed utilizing matrix digestion. The cracks will alter the density of the sample, thus affecting the void content calculations. Grid and image analysis, however, can be used in measuring the void content of internally cracked specimens. This is performed by excluding the cracks in the grid technique and eliminating the cracks during the processing of the binary image with the image analysis. The advantage of the grid and image analysis techniques is especially useful in failure analysis investigations where the presence of internal cracking is possible.

The void size and distribution can be examined by microscopically examining the specimens with image and grid techniques. This technique may be especially useful if the sample has a concentration of voids in one or more areas. If only one small area has a high concentration of voids and the remaining sample is void free, the overall void content of the sample will be relatively low. All three techniques would produce this lower content, however, matrix digestion could not identify the location of the void concentration. This result may not be significant unless the area of high void concentration is under more stress than the remaining area. If the concentration of voids was significant, the grid and image analysis techniques could be used to measure the void content in the concentrated areas.

The number of man-hours needed to perform the image analysis and grid techniques is much greater than matrix digestion due to the sample preparation (mounting and polishing) and analysis. However, the time to complete the image and grid techniques can be less than matrix digestion. Therefore, the urgency of the results is another factor in determining the method to be used.

Failure of HH-60J Helicopter Cable Antenna Wire

Another assisted investigation was to determine why high frequency (HF) antenna wire from HH-60J helicopters (Coast Guard) was failing. Teflon-coated wires were clamped to the outside of helicopters in such a way to allow for vibration and exposure to a corrosive environment. The Teflon coating was found to be abraded by rubbing of the clamp.

One of the fracture ends of the separated wire was removed and ultrasonically cleaned in acetone. The fracture surface indicated that the fracture mechanism was fatigue due to beach marks emanating from the crack initiation site. With the aid of the SEM the beach marks showing intermittent crack propagation were more visible, as was the stage III overload area. The fibrous nature of the latter region indicated a ductile overload. Further identification of fatigue failure was proved when identifying fatigue striations at high magnifications; a striation represents the crack propagation due to a single cycle of stress.

An energy dispersive spectrometer (EDS) map was produced from the fracture surface. The system mapped the location of four elements: iron, copper, aluminum and silver. There was a presence of aluminum between the steel wire and the copper coating as well as between the silver and copper coatings. Both copper and iron are cathodic to aluminum in the galvanic series, which means if a corroding medium is present (salt-water air) a galvanic cell will initiate the deterioration of the thin aluminum coating. This cell will provoke a galvanic cell between the copper and iron, where the more active iron will be corroded by the more noble copper. There is no known application in industry for an aluminum-coated steel wire, indicating its presence as a contaminate. The only possible explanation for the occurrence of aluminum is that aluminum-based materials were coated in the same copper baths as those in which the steel wires were plated. The aluminum is present on the outer surfaces of the copper coating because of its limited solubility in copper, and because aluminum is a surface-active element in relation to copper; i.e., the surface energy of aluminum is less than the surface energy of copper so aluminum diffusion occurs in an effort to reduce the surface energy of copper.

Galvanic corrosion of the aluminum further induced a galvanic cell between the copper and iron, which created a region of stress concentration after sufficient corrosion of the steel wire took place. This corrosion-induced stress concentration, together with the cyclic stresses created by vibration, allowed for the initiation and propagation of a fatigue crack.

Failure occurred by a combination of successive events that led to fatigue cracking. Three factors were considered important in the elimination of antenna wire failures. First, the manufacturer should address their copper plating process with emphasis on requirements for inspecting and maintaining contamination free baths. Second, a better insulating coating for the wire was suggested so that abrasion does not lead to corrosion. Lastly, a different clamping device for the cable on the helicopter, which minimizes vibration is recommended so cyclic stresses do not promote fatigue.

STRUCTURAL FAILURE ANALYSIS

Task Order No. 5a
Student Support Program
Southwestern Ohio Council For Higher Education

Joseph C. Leone
Wright State University

15 July 1993

Government Task Leader
Mr. Ronald H. Williams
WL/MLSA

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I would like to extend my appreciation to Mr. Ron Williams and Mr. William E. Berner for allowing me the opportunity to complement my education while working in the Structural Integrity Branch of Wright Laboratory.

Additionally, I would like to thank Dr. Kumar Jata, from the University of Dayton Research Institute, Mr. Tom Dusz, Mr. Michael Oliver and Mr. Brad Pinnell for their patience and assistance in guiding me through my Tasks.

In the short time I have worked at Wright Laboratory, I have learned a great deal about failure analysis. I am grateful for the opportunity to work in a field that I am pursuing as a student. I hope to continue working and learning from the engineers in the Structural Integrity Branch through my final years of schooling.

TASK ASSIGNMENT

The Task was to perform laboratory evaluation on metallic and composite materials using metallographic techniques; optical and electronic microscopy. To accomplish this it was necessary first to understand what metallography was (the study of microstructures) and the proper procedures involved in that science.

The sample preparation was the initial step, which was the key to obtaining an accurate interpretation. A properly prepared sample had to be flat, void of scratches and all other imperfections. The first stage was sectioning, using a high speed cut-off saw that was liquid cooled, to remove a representative area from the parent piece. Second was mounting, using a compression mounting press. The specimen was placed in the chamber and a thermosetting material placed over the sample. Heat and pressure were applied per manufactures specification. When the mount cooled it was removed to begin the next stage. Using a 60 and then a 120 grit wheel, the sample was finely ground to remove any deformation caused by sectioning. Next, rough polishing starting with 240, 320, 400, then finally 600 grit sanding disk was used to remove deformation caused by fine grinding. Final polishing was next, using a 6 micron diamond paste, then .3 and .05 aluminum oxide compound to remove any deformations caused by rough polishing. The final stage in sample preparation was to chemically etch the surface. Different etchants were used depending on the type of material and what was to be exposed in the microstructure. The etch solutions were acid based and was made each time etching was necessary.

For examination of the microstructure, an optical microscope was used to view the surface at magnifications up to 1000X. They were then analyzed to aid in decision making per individual project.

The first project was research of jet engine turbine blades made of a nickel-based superalloy. Three samples were used, the first was a control sample, second was heat exposed, and the third was sprayed with carbon then heat exposed. All three samples were mounted, polished and etched. Photographs of each were taken at various magnifications to compare microstructures. From the photos it was apparent each of the three microstructures was different. Further investigation was done by Dr. Jata.

The second project involved a sample of Weldalite 049, an aluminum alloy that is being considered for future space vehicles. The sample was sectioned in three pieces to show the longitudinal, transverse and rolling planes. Each sample was polished and micro-hardness testing was completed using a micro-hardness apparatus. The next steps were etching and photographing at various magnifications. The data was then given to Dr. Jata.

The third project was failure analysis on a compressor hub made of 6061-T6 aluminum alloy. Microstructures were compared to determine if there was any heat damage to the failed surface. Cracked blades were removed and sectioned below the fractured surface. Samples in all three planes were mounted, polished and etched. Photographs were taken of the microstructure. The same procedure was carried out on a control sample taken from the hub. From the viewed photos, it was concluded that the blades were heat damaged to the point of physical change to the microstructure.

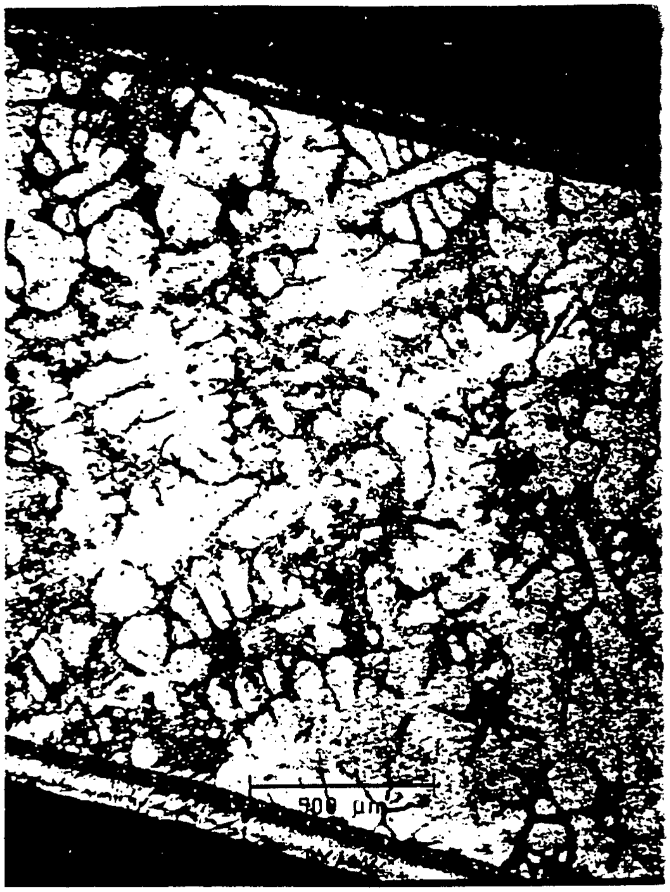
The fourth project was quality assessment of an F-15 UHF L-Band Antenna. The task was to determine whether or not cracks found on the surface coating extended through the aluminum base material. The first step was to send the part to Non-Destructive Evaluation for X-ray analysis, which showed that the antenna was made of sections of aluminum and glass epoxy composite. The coating cracks were observed to correspond to the interface of aluminum and composite. However, testing for aluminum cracking was inconclusive. Next, the part was sectioned, mounted and polished. Using an optical microscope, it was determined that the cracking was in the coating and did not affect the aluminum. During viewing of samples, it was discovered that cracking was present in the composite sections. Using the scanning electron microscope (SEM), a sample of the composite fracture surface was viewed. It was established that the failure occurred within the composite structure and not at the bond joint between aluminum and composite. The conclusion in this project was that cracking did not occur within the aluminum structure. However, further testing must be conducted to verify if composite cracking would affect the integrity of the system.

The four projects were only a partial listing of work completed. Many assignments were identical in procedures and testing methods to those that were discussed.

Microstructure of Turbine Blades

Nickel-Base Super Alloy

50X



125X

Microstructure of Weldalite 049

Longitudinal Plane #413

Microhardness:
Metallic area: 200.7 HV
Non-metallic: 176.1 HV

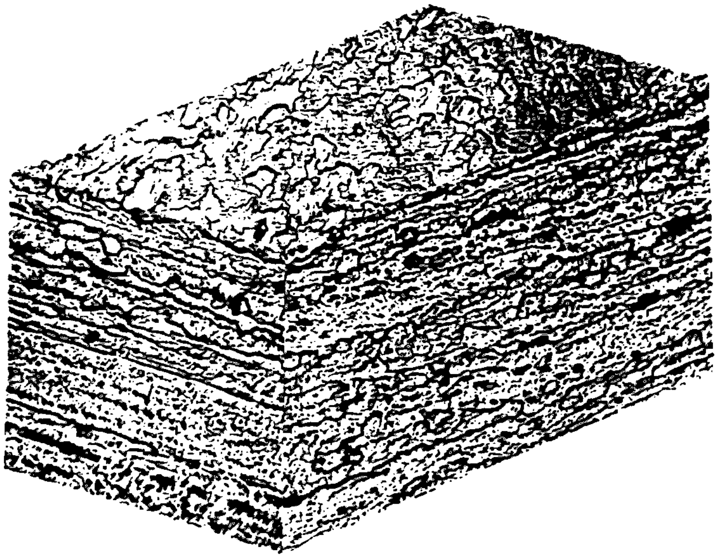
Rolling Plane #414

Microhardness:
Metallic area: 190.5 HV
Non-metallic: 174.5 HV

Transverse Plane #415

Microhardness:
Metallic area: 195.7 HV
Non-metallic: 174.5 HV

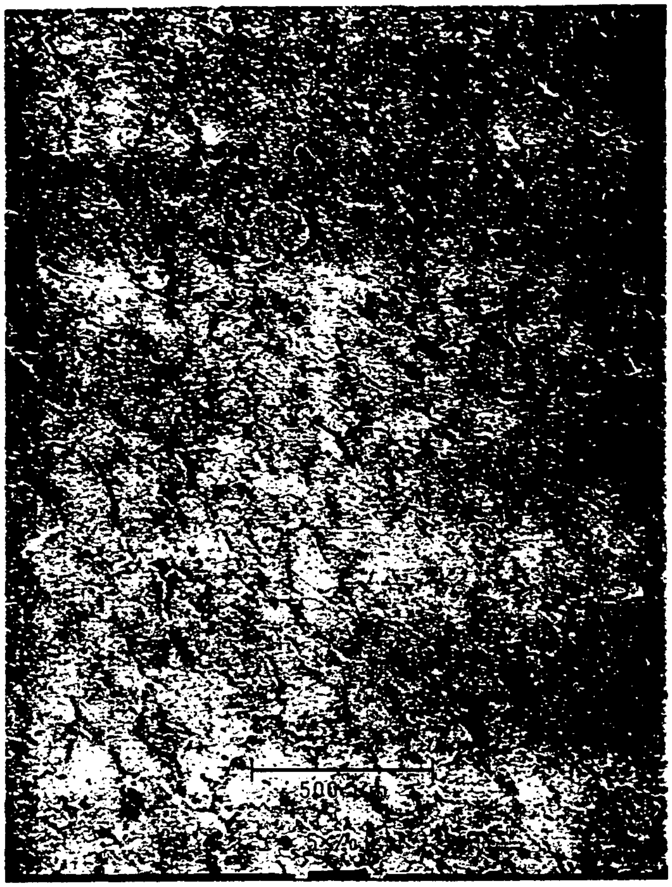
250X



Microstructure of Compressor Hub

6061-T6 Aluminum

50X



100X

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 7a
Student Support Program
Southwestern Ohio Council for Higher Education

Debbra L. Tron
Wright State University

12 July 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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I would like to thank Dr. Tom Cooper, my Task Leader, for all the training and assistance he gave me during my Task. I also would like to thank Lt. Brian Sennett for providing a large portion of my training as well as Scott Brittain, a fellow student employee in my lab who answered many of my questions.

TASK ASSIGNMENT

Solid Phase Peptide Synthesis (SPPS) was worked on to utilize the Fmoc protecting group. This group is the key component of the orthogonal approach to solid phase synthesis where this amino blocking group is removed under non-acidic conditions because of the base liability of the Fmoc group while the side-chain protecting groups are base stable.

Monitoring techniques to determine the completion of a reaction during synthesis are usually a function of free amine or activated amino acid concentration. The test primarily used is the ninhydrin test that is destructive to the portion of the product tested. Another type of method

experimented with for monitoring Fmoc SPPS reaction completions was through UV spectrophotometric monitoring during amino group de-protection. This type of monitoring would be preferred because it is faster and not destructive to the product. Also, these UV monitoring techniques are being used to study the kinetics of the de-protection and coupling stages of peptide synthesis.

After synthesis was completed for the chain, the peptide was cleaved from the solid phase upon which it was built. After this cleavage was completed, analysis techniques were employed. Size-exclusion chromatography was performed for the purpose of separating out small molecular impurities. Capillary electrophoresis, the next step for analysis, was also explored.

The preparation of an ester of glutamic acid was done for the next project. Sometimes after a peptide chain is completed it is desirable, after cleavage, to attach a dye along a peptide onto a side-chain. When cleaving, however, all side-chains are de-protected and, when dye attachment is performed, the dye is attached to all the side chains and not selectively to only one side-chain since the state of all side-chains are similar (basic) in composition. If, however, prior to synthesis of the peptide chain one amino acid side- chain could be altered so that different reaction conditions could be used to de-protect only that side-chain, a dye could be attached to only that side-chain. The purpose for the dye attachment is for certain monitoring techniques during analysis after the peptide chain is completed.

The method of monitoring Fmoc SPPS reaction completions is through UV spectrophotometry during the amino group de-protection. A fulvene-piperidine adduct is formed during the de-protection and this adduct has UV absorption at a specific wavelength. These UV monitoring techniques were also used to study the kinetics of the de-protection and coupling stages of peptide synthesis. The study involved taking aliquots at specific time intervals and performing UV monitoring on these samples. These results were plotted on a graph to find the maximum and the leveling of the curve beginning at the maximum indicated that the reaction had reached completion.

Peptide synthesis was performed using an automated peptide synthesizer, although in order to monitor the kinetics of the reaction a semi-manual approach was used (i.e., adding solvents and ingredients manually instead of having them automatically pumped in). The completed peptide was purified using size-exclusion chromatography. Using certain size beads in a chromatographic column, the larger size polymers will pass on through the column within a certain time frame that is determined by monitoring at a certain wavelength while the smaller impurities are retained on the column longer, collected and disposed. An analysis technique that was used after purification was capillary electrophoresis that determines the composition of the peptide chain (to help verify that the completed peptide is the same as the intended peptide). This is done by comparing the mass-to-charge ratio of the completed product to a known standard that is run prior to the sample. The task of attaching the ester side-chain to glutamic acid was performed using normal wet chemistry techniques (i.e., stirring, filtering, cooling, drying). Analysis at various stages of completion was performed by sending portions of the product out for elemental analysis and by using infrared spectroscopy, both to help determine purity and structure.

The monitoring of the kinetics during peptide synthesis gave the desired results in that it was determined that the rate of the reactions could be monitored via non-destructive testing methods. The drawback, initially, was that since the samples were manually drawn, time was lost in the process. It was determined that if a continuous-flow system was devised, the reaction could be monitored on-line at the actual time of occurrence and be much more accurate. The manual project was suspended until the equipment for a continuous-flow system could be obtained and made operational.

Analysis procedures were learned for analyzing completed peptides although some equipment problems were encountered that gave less than satisfactory results.

The attachment of the ester to the glutamic acid was successful and elemental analysis showed above 90% purity of products sent out for analysis. IR spectroscopic analysis also showed the expected functional groups to be present.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 7b
Student Support Program
Southwestern Ohio Council for Higher Education

Steven M. Cline
University of Dayton

12 July 1993

Government Task Leader
Dr. Robert Crane
WL/WLPJ

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A special thanks to senior chemist Dr. Tom Cooper and Lt. Brian Sennett for their time, effort, guidance and understanding in attempting to help me grow as a scientist and a person. I am privileged and honored to have the opportunity to work with people of their stature. Finally a special thanks to Cadette Tim Ritceshouse for his humor and friendliness, making the lab a much more enjoyable place to work.

TASK ASSIGNMENT

As of June first, olgonucleotide polymers have been synthesized by utilizing the Stepwise Chain-lengthening method for polypeptide synthesis. The process consists of linking amino acids together one by one to produce a desired amino acid sequence. By controlling the order that the amino acids are linked together, one can create peptides to mirror the structure of biologically active polymers. For example, if a synthetically fabricated amino acid sequence is created identical to a sequence occurring in nature, the two are the same. They will emulate each other in shape, chemistry and function. The only difference between the two peptides is the way they were created, the former being in a reaction vessel and the latter on the ribosome of a living organism. By being able to synthesize proteins of specific sequence, ideal materials can be created. For example, peptides can be created with the strength of collagen and the structure of muscle or with the elasticity of ligament and the density of bone. By understanding and being able to utilize *in situ* peptide synthesis, materials production capabilities are limitless.

In the Stepwise Chain-lengthening method for protein synthesis, the peptide chain is initiated by linking an amino acid (i.e., tyrosine) to a polystyrene bead, such as Rink resin:

Once the amino acid is sufficiently attached to the resin, a second amino acid can be coupled to the first, a third to the second and on down the line until a lengthy polymer has been amassed. Peptide synthesis relies on the formation of peptide bonds. A peptide bond between two amino acids occur between the amine group of the alpha carbon on one amino acid, and between the carboxyl group of the alpha carbon on another. The net product is the release of a water molecule (dehydration) and the formation a secure covalent peptide bond.

Following the coupling of two amino acids, it is always necessary to apply the Kaiser test to check for a successful coupling. The Kaiser test identifies the presence of uncoupled amines which is a sign of unsuccessful bond formation. Assuming the Kaiser tests have been negative throughout coupling and the desired polymer has been synthesized properly, the final step is to cleave the peptide from the resin. At this point, the resin support is no longer of value and is discarded. The peptide is cleaved from the resin by washing the protein complex in an acid strong enough to break the bond between the resin and the peptide, yet weak enough to avoid rehydrolyzing the peptide bonds formed between the amino acids (i.e., TriFlouroAcetic Acid).

During the 6 weeks of work at WPAFB Materials Directorate, a host of peptides has been synthesized. In particular, peptide polymers of the following sequences are being researched in attempt to identify their refractive indices:

$$\text{TYR-GLU}_{(2n-1)} \quad n = 1, 2, 3, 4, 5, 6.$$

When synthesis for these peptides is complete they will first be tested for purity using the High Pressure Liquid Chromatogram and the High Performance Capillary Electrophoresis system. If the peptides prevail as relatively pure samples, they will be examined using polarized light to determine their relative degree of alpha helical development.

Helical research is just a piece of the huge puzzle of knowledge which will ultimately be directed toward the manufacturing of laser sensitive materials. It is important to know the helical content of amino acid residues when manufacturing optically sensitive materials because light absorbent dyes are attachable to amino acid backbones (i.e., glutamic acid polymers). The attachment of a dye to this material provides the polymer chain with light absorbent properties. The shape of the structure to which the dye is coupled is important to know because the amino acid support's shape will ultimately determine the orientation of the dye. The spatial orientation of a dye is a major factor in its effectiveness in absorbing light. Knowledge of the helical structure of peptides is, without a doubt, a research topic of value.

LIQUID LUBRICANTS

Task Order No. 8
Student Support Program
Southwestern Ohio Council for Higher Education

Joseph R. Demers
Wright State University

15 September 1993

Government Task Leader
Ms. Lois J. Gschwender
WL/MLBT

ACKNOWLEDGMENTS

I would like to acknowledge and thank Ms. Lois Gschwender, Mr. Ed Snyder and Mr. George Fultz for helping and guiding me to the very successful completion of this Task.

TASK ASSIGNMENT

A common means for evaluating the performance of a liquid lubricant, short of field testing it, is the Oxidation Corrosion Test (OC test). This test has been used extensively to model the environmental conditions that a lubricant would encounter during use in a jet engine; from temperatures present to types of metal present. It has become a rigorously investigated (ASTM 4636) international standard.

OC testing involves four measurable quantities; weight loss of lubricant sample, viscosity change of lubricant sample, weight change of metal test sample and change of lubricant sample acid number. A test is generally run for a set time with the temperature and airflow being the adjustable variables. After the test time has elapsed, the four previously stated characteristics are examined for change. If no change has occurred, then the test temperature is raised and the test repeated. At some point, the fluid "breaks" as decided by a set amount of change in one of the four test qualities. Unfortunately, it is not currently possible to tell at what point during the test the fluid actually broke.

Another integral part of lubricant evolution is additive development. Additives are homogenized into base lubricants to improve, among other things, oxidation characteristics. The means by which additives change the breakdown characteristics, of the base fluids into which they are introduced, is still not completely understood. Because of this, the development of the chemical compounds used as additives borders on artistry and magic rather than chemistry. This is specifically true in the development of additives for the high temperature, non-flammable, perfluorpolyalkylether (PFPAE) liquid lubricants studied here.

To develop an anti-oxidant additive for a PFPAE lubricant, it is necessary to understand what process causes oxidation. Because of a PFPAE's large chemical difference from a hydrocarbon (fluorine atoms replacing all hydrogen atoms in the "hydro-carbon"), old models for degradation mechanisms were not applicable. Further, old additives used in hydrocarbon lubricants are not soluble in PFPAE's. It became necessary to develop a new model for metal catalyzed lubricant breakdown for the PFPAE's and to develop new additives from this model. A step in investigating the process by which PFPAE lubricant degradation occurs is to observe the process temporally.

Conductivity refers to the ability of a given material to carry an electric current. As the number of charge carriers (generally electrons) in the material increases, the conductivity increases. Double distilled water has very few free charge carriers and, therefore, has a conductivity of approximately zero. Because of water's polar nature, however, it will homogenize almost any ion. It was hoped that by monitoring the effluent gasses from an OC test, the time of fluid lubricant breakdown would be discovered. As the test fluid breaksdown, it releases ions. These ions become mixed with the air passing through the fluid and during an OC test, are generally released into an exhaust hood. With an OC test, however, these effluent gasses are passed through a conductivity test cell that contains distilled water and a conductivity probe. As the ion concentration of the effluent gasses increases, the number of the ions passed into the water also increases causing a subsequent increase in the water's conductivity. As was hoped, the conductive nature of the effluent gasses does indicate, temporally, the kinetics of fluid breakdown.

After an antioxidant additive disappears from the fluid lubricant package, fluid lubricant breakdown will increase nonlinearly. It has been shown with OC that for some additives this is true, while for others it is not. The qualifying term is "disappears." Figure 1 displays the temporal monitoring of the conductivity of a PFPAE with an additive that does get "used-up." Notice the sudden increase in conductivity after 400 minutes. This denotes the point where the anti-oxidative characteristic of the additive has ended. For the same PFPAE with a different additive, however, failure occurs without the characteristic induction curve (Figure 2).

Further work employing the OC apparatus is too extensive to report here, but has been very successful. The Task has been very fulfilling and has been exemplary in the illustration of how a project can succeed. My Task Leader and affiliate have decided to continue OC testing as a means for lubricant characterization. This is a success itself.

Figure 1
O.C.C. #100592 : Fluid Z, Additive 1
Test Performed at 315C

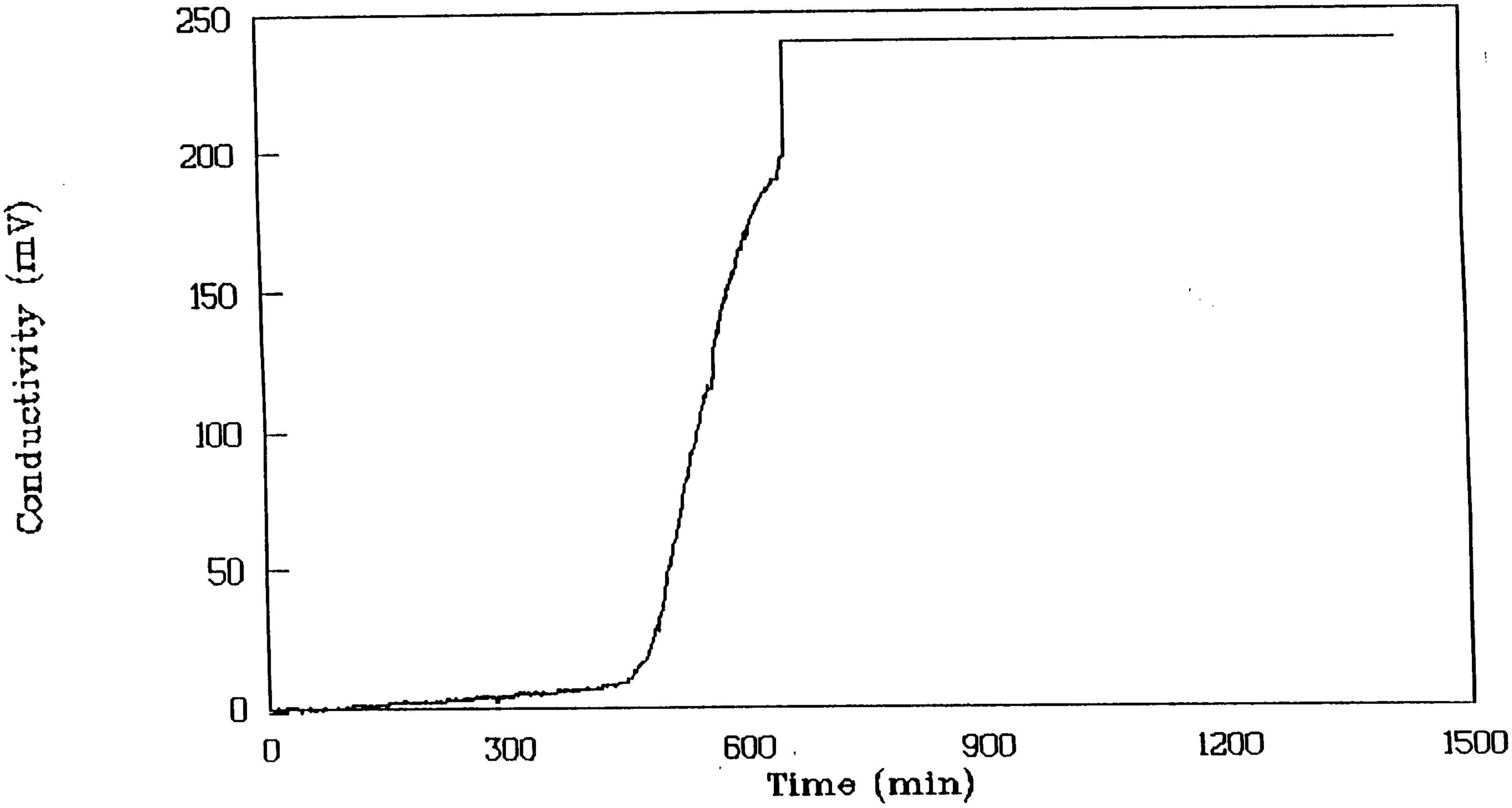
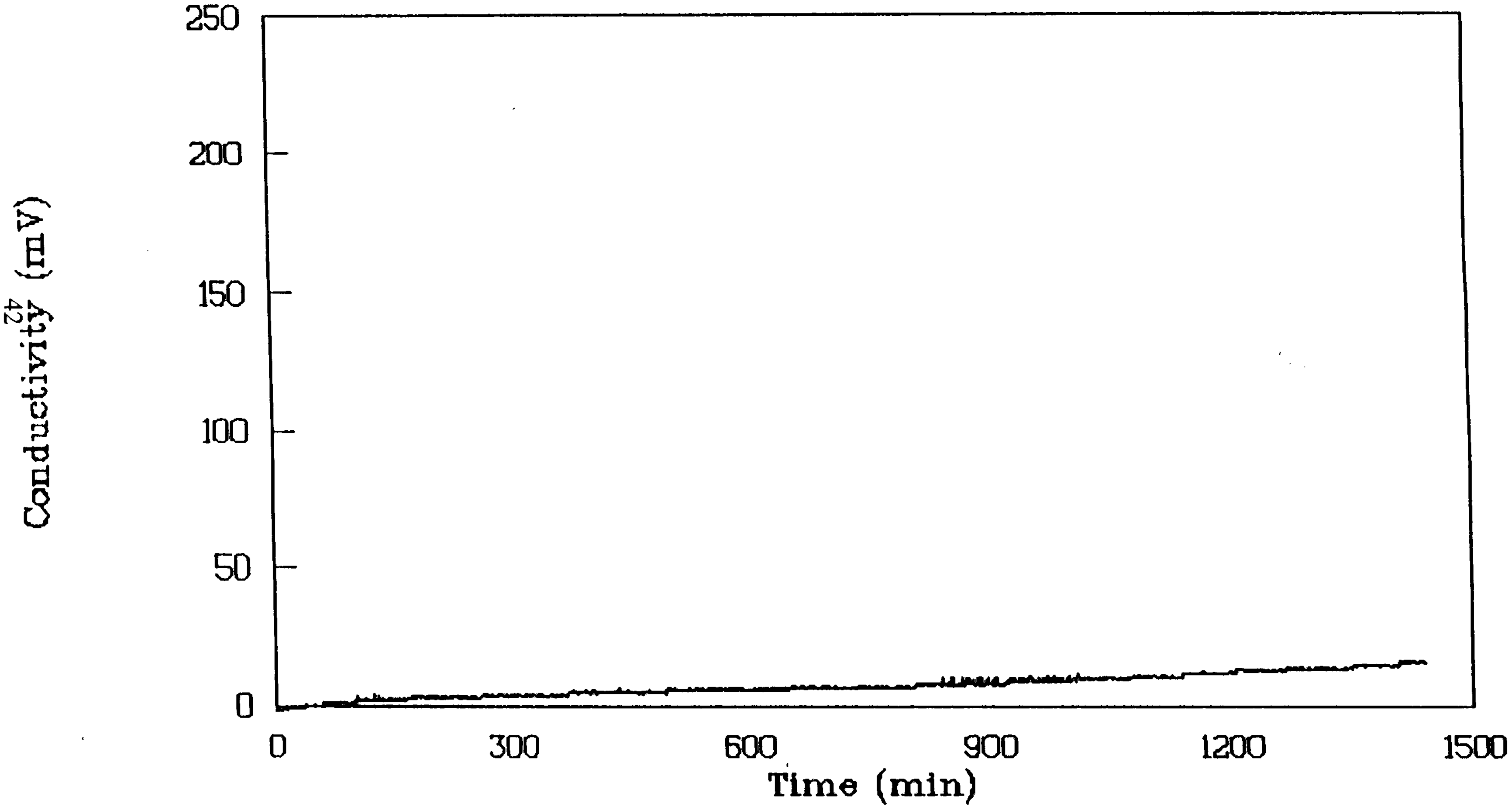


Figure 2

O.C.C. #032393 : Fluid Z, Additive 2
Test Performed at 315C



SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND EVALUATION

Task Order No. 9
Student Support Program
Southwestern Ohio Council for Higher Education

Steve C. Medeiros
Wright State University

15 March 1993

Government Task Leader
Mr. Robert B. Urzi
WL/MLSE

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I would like to thank all the personnel in the Systems Support Group for creating a work environment that is both enjoyable and educational. Special thanks to those individuals I worked directly with: Mr. Robert Urzi, Mary Cooper, MSgt. Bryan Cramer, Jim Mazza, and Mark Forte of MLSE; James McKiernan, and Bill Lawless of the University of Dayton Research Institute; and fellow SOCHE students Richard Huff, Cathy Gustafson and Rob Cassoni.

TASK ASSIGNMENT

The tasks performed were surface preparation, mechanical testing and data acquisition and reduction. Due to the lack of knowledge of research methodology, the level of input into the decision making process at the beginning of the quarter was minimal. However, as the quarter progressed, and with increased knowledge of research methodology, the level of input into the decision making process increased.

Over the course of the quarter work was primarily focused on two projects. The first was a continuation of a project headed by Mr. Bill Lawless. This project was to determine the effects of vacuum curing on the strength of various structural adhesives. Adhesives can be cured under positive pressure as well as vacuum. This study was to determine the drop off, if any, in the strength of the adhesives. The data obtained would help determine the optimum vacuum level to cure various structural adhesives. The second project was the continuation of a study to determine the most suitable surface preparation for the field level repair of a fighter aircraft. The reason for this study is one of today's advanced tactical fighters in the Air Force is experiencing a fatigue crack around the fuel vent hole located on the bottom of the wing. A patch has been developed which, when bonded in place will stop the crack growth. A suitable adhesive was also chosen to bond the patch to the aircraft wing skin. This study was to determine which surface preparation of the aircraft wing skin provides the most environmentally durable adhesive surface. The results were used in the first repair of the aircraft at another facility.

DESCRIPTION OF RESEARCH

The vacuum effects study involved nine adhesives, two surface preparations, and four processing methods. Lap shear panels were made of each adhesive subjected to the four processing methods for each of the two surface preparations. The processing methods involved were: processing under 29" Hg vacuum, 20" Hg vacuum, 14" Hg vacuum, and the positive pressure equivalent to 29" Hg vacuum, 14.5 psi. The two surface preparations were: clean with grease cutting detergent, abrade with a scotchbrite pad and rinse with distilled water and; Phosphoric acid anodization, and priming with a corrosion inhibiting primer.

A vacuum bag was prepared from nylon bagging material and tacky tape, and the lap shear specimens were cured in the vacuum bag under these various vacuum pressures. The positive pressure panels were cured in a Wabash press under a constant load.

The lap shear panels were sent to the U.D. campus to be cut and milled to 1 inch, and sent back to be further examined. The samples were sanded and polished so that an accurate bond line thickness could be measured. The porosity, due to vacuum curing, of the adhesive was also measured so that a relationship between porosity and vacuum level could be established. The bond line thickness and porosity measurements were preformed by Mr. Brad Pinell of MLSA, since the equipment used for the measurements were not available for use. Due to time constraints, the specimens were sent to the U.D. campus to be tested, and the results obtained were sent to Mr. Bill Lawless for analysis.

The second project was on the surface preparation study for the fighter aircraft repair. The study involved fabricating wedge panels from the same aluminum alloy that the aircraft wing skin is fabricated from. The wedge panels were fabricated by sandwiching the adhesive to be used for the repair between two aluminum panels that had been subjected to a particular surface preparation. The panels were then cured in the Wabash press under a positive pressure of 40 psi. Next, the panels were cut into five specimens and milled so that each specimen was 1 inch wide. Each specimen was measured for width and bond line thickness. A wedge was driven between the two panels of each specimen so that a crack was introduced. The initial crack length was marked for each specimen and all specimens were placed in a controlled humidity cabinet of 120 degrees F and 95-100% relative humidity. Measurements of crack growth were taken at intervals of 1 hour, 4 hours, 24 hours and 7 days.

The particular surface preparations under study at the beginning of the quarter were phosphoric acid anodizing, a pasa gel treatment, and a silane surface treatment. The first two were ruled out, however, since there are high strength steel rivets within the area to be patched, and the hydrogen in the acid and pasa gel can cause embrittlement of the steel rivets leading to failure of the rivets. Therefore, concentration was placed on the silane surface treatment, and methods to improve results obtained from this method.

The crack measurements for each specimen of a particular panel were then averaged to give an average crack growth for the panel. The acceptable crack growth after 1 week was .25" and significant improvements to the silane preparation method achieved acceptable results. The specimens were broken apart so that the failure mode could be analyzed. The crack growth rates and the failure modes were examined by the engineers to determine which direction the study should go.

RESULTS

Toward the end of the winter work term the aircraft repair was performed. The aircraft will fly a set amount of hours and then be examined by nondestructive inspection methods to learn if the crack is still advancing. The inspection methods used will also show if the adhesive is performing as intended. These results will not be known for sometime during the spring work term.

The vacuum effects study will continue as an ongoing project for another month or so. The study showed that as a result of curing under vacuum the shear strength of all adhesives declined. The higher the vacuum pressure the further the decline in the strength, and the higher the vacuum level the greater the porosity of the adhesive. This leads to the conclusion that the strength of a structural adhesive is related to the porosity created during the cure cycle.

The experience at the lab proved to be both educational as well as practical. The basic use of composite and adhesive materials was learned, which is of tremendous importance to a materials engineering student. More demanding tasks were preformed as the quarter progressed such as, phosphoric acid anodizing, corrosion inhibiting primer application and mechanical testing. The importance of establishing communication between the engineers, managers, and technicians also was learned as well as documentation of work plans and work performed. In general, the co-op experience allowed the workings of a materials laboratory to be more fully understood. Much practical experience and knowledge was gained that will be helpful in the future.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND EVALUATION

Task Order No. 10
Student Support Program
Southwestern Ohio Council for Higher Education

Robert P. Cassoni
Wright State University

31 December 1992

Government Task Leader
Mr. Robert B. Urzi
WL/MLSE

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TASK ASSIGNMENT

The Task was broken into three different projects. Project 067 was an ongoing study of the effects of different storage conditions on three adhesives. Project 076 was a study on the effects of vacuum and adhesive bonding strength. Project 083 was an unprecedented bonding procedure to be implemented into our military immediately.

Project 067 was initiated in June of 1992 to determine the effects of different storage temperatures and periods of storage on three aircraft bonding adhesives. Many tests were involved, as one type of test is not sufficient to determine bond strength. The project incorporated a lap shear test to determine the shear strength, a flatwise tension test to determine the tensile strength, a peel test to determine the peel strength, and a wedge test to determine the effects of humidity on adhesive crack growth. A particularly important aspect of this project was a process referred to as phosphoric anodizing. Phosphoric anodizing is used to remove the natural oxide layer from the bonding surface of aluminum and replace it with an oxide layer that is optimal for bonding. The preparation of the test specimens was mainly done by curing the specimens either in a vacuum environment or by positive pressure. This was accomplished by using a 75 ton press with built in heat platens. Monitoring of the cure cycle was necessary to ensure a good bond. Upon curing, the test samples were labeled and tested using a Tinius Olsen or Instron test machine. The data acquired was then logged into a computer using the Microsoft Excel spreadsheet and Cricket Graph. While the results of project 067 are incomplete at this time, the data to this date is enabling engineers to assess the optimal and practical temperature to store aircraft bonding adhesives.

Project 076 was an ongoing project to determine the effects of different vacuum pressures during the cure cycle of a lap shear panel on shear strength and percentage of porosity within the cured adhesive. This project involved over ten different adhesives and several different panel lay-ups. Preparation of the panels involved an abrasive soap and water scrub to degrease the aluminum surfaces. The lap shear lay-up was nearly identical to the process used on the 067 project, however, a different method of creating a vacuum bag was used. The 076 vacuum bag was constructed of high temperature nylon bagging film and two sided tape. Although this type of bag may seem basic and limited in capability, it has proven to have many applications throughout the aerospace adhesives industry. The panels were cured according to engineers specifications and monitored closely throughout their curing process. Upon curing, the panels were cut, labeled, checked for percentages of porosity and tested. The results conclusively showed what had been predicted by the senior engineers as far as the strengths were concerned, however, the porosity readings were not consistent enough to draw any definite conclusions on the effects of porosity versus strength. This could be due to the method used to measure porosity which only considers four values from across a panel. The data that had been derived from the testing of these samples was entered into a computer using Microsoft's Excel and Cricket Graph. Graphs made on the computer enhanced the project meetings which were held to receive input from the entire staff.

Project 083 was started in November 1992. It involved an unprecedented patch bonding procedure that must be implemented by January 1993. A military aircraft currently in service develops crack growth around a fuel vent hole located on the wing. The solution was to bond a boron composite patch around this vent hole to hinder the spread of the crack. One problem arose in the proposal of this project. The problem was to heat the patch area to a good curing temperature while trying to keep the heat blanket at a reasonable temperature. This problem was overcome by insulating the regions around the patch and using additional heat sources to supplement the curing process. A complete thermal survey of the patch area was mapped and helped to give valuable heat data. A hot bonder was used to create a vacuum around the area and to monitor the thermocouples that had been placed around the patch. Accurate record keeping was necessary as there were 23 curing cycles employed in the thermal survey, each having a different insulation lay-up. The data that had been supplied by the thermal survey of the patch area was of critical importance, as this process has very high priority and urgency. The data aided the engineers in choosing the most practical field lay-up possible.

The experience gained this quarter was far more than an engineering student could gain in the classroom. The phosphoric anodizing process is a very important concept in the adhesives industry which is rarely touched upon in the classroom. Of particular interest was the thermal survey on the aircraft wing. This tested the theory against the experiment. Much was gained in that respect. The knowledge gained in the different standard adhesive tests also will prove to be beneficial with further exposure to the adhesives industry.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 11
Student Support Program
Southwestern Ohio Council for Higher Education

Timothy M. Grinstead
Wright State University

11 August 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

Task involved the synthesis and characterization of various monomers and polymers. These polymers were synthesized to examine how the addition of Nonlinear Optical (NLO) groups affected the structure and properties of these polymers. Each additional polymer synthesized led to a better understanding of how an ideal Nonlinear Optical polymer can be produced.

New methods of synthesizing NLO-substituted polymers were explored during this Task. Three different methods were employed in hopes of finding the most efficient way to accomplish this.

The first method was the same method used in the last Task Assignment (69), where an alcohol was substituted onto a poly amino acid using p-toluene sulfonic acid (PTSA) as catalyst. This method did result in substituted polymers, but the products proved difficult to purify and low modification was also a problem.

The second method involved using PTSA again, but the reaction used a monomer of the amino acid rather than a polymer. This allowed for easier purification methods and complete modification. Once the monomer units were synthesized, it was then possible to use triphosgene to make an anhydride of the monomer. Once the anhydride has been made, it can be polymerized to form the final product. Before the triphosgene could be used, a safety and handling report had to be compiled. This task was accomplished and set the standards for future use of triphosgene at Wright Laboratory. The only problem with this method is the number of synthetic routes that are necessary and the toxicity of the reagents involved (namely triphosgne). The third reaction employed is a recent development in the field of polymers. It is a one pot reaction where a diphenylphosphoryl azide is used to attach an alcohol to the amino acid and then initiator can be added to polymerize the product. It is much safer than triphosgene but has not been thoroughly tested on the compounds that are being used for this Task.

Each reaction explained above has both advantages and disadvantages to them. The most successful of the three involves using triphosgene to synthesize the cyclic anhydride and then polymerize the anhydride. This allows for highly substituted polymers (100% theoretically) that can be purified easily. The downfall of this method is the toxicity of the reagents involved and how much the introduction of the bulky NLO dyes will affect the reactions involved. The most promising of the three methods is the new one involving diphenylphosphoryl azide. Although limited reactions have been attempted, it has been shown by other researchers to be an effective tool in the synthesis of poly amino acids.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 11a
Student Support Program
Southwestern Ohio Council for Higher Education

Christine S.Yoon
Wright State University

11 August 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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TASK ASSIGNMENT

Task Assignment 11 involved synthesis and classification of various photosensitive materials that contain optical chromophores for use in laser hardening devices. The main objective or goal was to synthesize various substituted tetraarylporphyrins and determine the ideal conditions of the reaction necessary to produce and successfully isolate p-nitrotetraphenylporphyrins and then reduce it to an amine. Products will then be characterized into various photosensitive materials that contain optical chromophores for use in laser hardening devices.

DESCRIPTION OF RESEARCH

New methods of synthesizing NLO-substituted porphyrins, star-shaped porphyrins, were explored during this Task Assignment. Many different reaction conditions were employed with hopes of finding the most efficient way, producing the highest yield of p-nitrotetraphenyl porphyrins. The tetraaylporphyrins have been widely used as models for the naturally occurring porphyrins. The synthesis of these numerous substituted tetraayl porphyrins has been reported, however, most of these findings were largely out of date and were hardly of any help. Thus, it became necessary to experiment with the reaction conditions, performing each reaction with slight deviations in the molar concentrations of reactants, the rate of addition, solvent of choice, the length of time of reflux and the presence of an anhydride.

The most successful reaction gave a product yield of 26% and demanded the following conditions: 0.01 molar ratio of both p-nitrobenzaldehyde and pyrrole in 250ml of glacial acetic acid, 3ml of acetic anhydride addition before the slow drop-wise addition of pyrrole over 30 minute period. The reaction was refluxed at 117 degrees for 30 minutes and then cooled to no lower than 32 degrees and immediately filtered. The crystals were washed with methanol and isolated with chloroform.

Visible spectrum (pyridine): 646, 590, 554, 518 and 428.

Reported visible Spectrum (pyridine): 647, 593, 554, 518 and 428.

RESULTS

The results of this research showed that glacial acetic acid was the solvent of choice. Acetic acid gave a higher yield of the porphyrin product than any other solvents such as propionic acid. The results of this research also showed that the reaction of interest involved a condensation of pyrrole with p-nitrobenzaldehyde and therefore and addition of acetic anhydride prior to pyrrole addition controlled the immediate water formation in this exothermic reaction, thus reducing the amount of tarry by-product from precipitating. Pyrrole-pyrrole polymer, also an unwanted product, was controlled by slowing down the rate of pyrrole addition. Because pyrrole's high reactivity, pyrrole rings can react with itself. Therefore it became necessary to keep pyrrole concentration low and only to add drop-wise over a 30 minute period. Also, results showed many isomers to exist in synthesis of substituted tetraphenylporphyrins. These compounds were very difficult to separate and isolate.

Many factors such as these complicated the task of separation and isolation. The poor percentage yield of this research has caused many chemists to shy away from this type of research. However, these star-shaped porphyrins could be a valuable photosensitive material and possess very important optical properties.

MECHANICAL PROPERTIES OF METAL MATRIX COMPOSITES

Task Order No. 12
Student Support Program
Southwestern Ohio Council for Higher Education

Evan J. Dolley, Jr.
University of Dayton

14 October 1993

Government Task Leader
Captain William Revelos
WL/MLLN

ACKNOWLEDGMENT

The author would like to thank Capt. William Revelos, WL/MLLN, Dr. Jim Larsen and Wayne Jones* for their guidance, support and the great leadership that they showed daily. A special thanks also to the personnel working for the University of Dayton Research Institute and Wright Labs. All personnel perform their work very professionally and maintain a high degree of motivation and dedication toward the research field in engineering. The author also would like to give appreciation to the personnel working in the metallurgical lab, as well as the personnel that assist with the scanning electron microscope.

*Department of Materials Engineering/University of Michigan

TASK ASSIGNMENT

The main requirement of this Task was to assist Capt.William Revelos with the necessary testing and analysis required to characterize a certain metal-matrix composite's response to thermal conditioning. The characterization of the composite was done in support of United States Air Force initiatives which involve the use of metal-matrix composites. One Air Force initiative that is affected by this material characterization is the National Aerospace plane institute for the Mechanics Life Prediction of High Temperature Composites (NIC), which uses the composites for hypersonic vehicle applications. The other Air Force initiative that plans to utilize the composites is the turbine engine industry. Since there is a significant coefficient of thermal expansion (CTE) mismatch between the fibers and the metal matrix, there is a need to characterize the response of the composite to thermal conditioning under different conditions. The different conditions should simulate conditions seen if the composite were to be used in a turbine engine or on a hypersonic vehicle. The characterization of the composite included testing to investigate the effects of environment, temperature range, maximum temperature, time at temperature and cycle count on composite residual strength and damage accumulation processes. The interpretation of the test results required analytical evaluation techniques such as the operation of optical and scanning electron microscopes. Other work was also done on a project that compared this composite to other conventional materials currently used in turbine engine and hypersonic vehicle applications.

The environment plays a very important role when the composite is used at elevated temperatures. This material was tested at temperatures which encouraged the formation of an oxide on the surface of the composite. The high temperatures would cause an oxide to form on the composite which would enhance the reduction of residual strength after the thermal conditioning test. Tests were run in lab air and in an inert environment. The purpose of running tests in an inert environment was to quantify the loss in residual strength as a result of oxygen in the lab air. Residual strengths were recorded after testing in an inert environment and then identical tests were run in lab air. The difference in the residual strengths between the inert and lab air tests showed proof of the effects of the environment since there was a reduction of residual strength in the specimens which were tested in lab air.

Time at temperature, maximum temperature and temperature range all play a role in the reduction of residual strength after thermal cycling. Time at temperature is the time the specimen spends at the maximum temperature of the test. Each specimen is cycled with a minimum and maximum temperature which is the temperature range. It was shown that the time in which the specimen spends at the maximum temperature has a great effect on the residual strength after thermal conditioning. The temperature range has the greatest effect when the maximum temperature is held and the minimum temperature is changed. The specimen will heat up to the maximum temperature and then cool down to the minimum temperature for a certain number of cycles which is called the cycle count.

The cycle count has a great effect on the residual strength of the composite after thermal conditioning. The longer the cycle count, the longer the specimen has to spend at the maximum temperature of the test. If this maximum temperature is high enough to cause oxidation, the effects of the environment are amplified. The cycles also fatigue the specimen similarly to an out of phase TMF test with no load applied.

As the testing was completed, the results needed to be analyzed using analytical analysis techniques. These techniques included polishing specimens, use of optical and scanning electron microscopes, Bromine etching of specimens, micro-hardness analysis of cross-sectioned specimens and data analysis of stress-strain and residual strength plots. All the analytical evaluation techniques were used to evaluate the results of the thermal conditioning tests to properly characterize the response of the composite to thermal conditioning.

All testing for the thermal conditioning characterization was completed in July 1993 and the results of the testing will be submitted for publication to Metallurgical Transactions in November 1993. The authors of the paper are William Revelos, Wayne Jones and Evan Dolley, Jr. Since August 1993, another small project was started to aid with the plots and figures which accompanied a paper that compared the composite system which is being evaluated to conventional alloys which are currently being used in hypersonic vehicles and turbine engines. This work was presented in Paris, France by Dr. Jim Larsen of WL/MLLN.

The purpose of the Task assigned was to provide aid with testing and analysis of data from thermal conditioning tests which characterize a metal-matrix composites response to thermal conditioning. Several tests were run under different conditions which simulate conditions seen in turbine engine and hypersonic vehicle usage. Evaluation of test data required analytical evaluation techniques such as optical and scanning electron microscopy.

The experience obtained from the work performed at WL/MLLN is very valuable. Wright Laboratory is considered a world class laboratory with leading edge technology. There are also many scientists and engineers from all over the world who offer a variety of knowledge and experience to pass on to others. Employment at Wright Labs has given the opportunity to be a co-author on a paper which will be published in a refereed journal. There have also been opportunities to present finds to colleagues which helps to hone communication skills. The

SOCHE program enables students to obtain valuable skills in a world class laboratory which the student will use for the rest of his/her career.

MECHANICAL PROPERTIES OF METAL MATRIX COMPOSITES

Task Order No. 13
Student Support Program
Southwestern Ohio Council for Higher Education

Michael P. Moran
University of Dayton

15 September 1993

Government Task Leader
Mr. Stephan Russ
WL/MLLN

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TASK ASSIGNMENT

The objectives of the Task were to assist Mr. Steve Russ in performing thermal mechanical fatigue testing of fiber reinforced metal matrix composites (MMC's) as well as data analysis, fractography and metallographic evaluations. Fatigue characteristics were obtained from these tests.

The investigation of the fatigue life of MMC's is of interest to the researchers involved in this Task, since these materials show great potential for aerospace applications in high temperature and high stress environments. The National Aerospace Plane (NASP) program is currently considering this class of materials to supplement ceramic materials in aerospace applications.

The Task was mainly devoted to the investigation of the Beta 21-S material system. Beta 21-S is a titanium-aluminide composite with interwoven silicon-carbon fibers. The fibers in the metal matrix are oriented in three different lay-ups. They are: [0], [0/90] and [0/±45/90].

A horizontal servo-hydraulic and a pneumatic test machine, in conjunction with load and displacement transducers, were utilized as the testing equipment. The data obtained by the test machine and the transducers were recorded and stored on the connected IBM computer system. The data was then copied from the computer to floppy disks and formatted on a Macintosh computer.

Experiments were conducted under thermal-mechanical fatigue conditions in laboratory air at a wide range of temperatures and loading conditions. The data collected is then analyzed to determine stiffness and damage accumulation as a function of the number of cycles. Plots are made with stress vs. strain, stress vs. cycles, strain vs. cycles, loading modulus and strain vs. cycles and temperature curves. The plots are used for engineering evaluation and presentation.

Tests are run in cycles until the specimens failed. Then the fractured surfaces are taken to the metallography lab. There the specimens are first cut and polished in order to reveal any cracking or oxidation as a result of thermal- mechanical cycling of the material. Three different orientations of the fibers are mounted in Epomet mounting material and then polished. This procedure of polishing MMC's is very difficult. Great care must be taken to ensure that an optimum polish is obtained. After polishing, the specimens are chemically etched and photographs are taken with a Riechert-Jung optical microscope. If needed, the scanning electron microscope (SEM) is used to show a greater depth of field. This is why the polishing procedure is so important. The optical microscope cannot focus if there is a height differential between the fibers and the metal matrix. This may be difficult since the fibers are much harder then the metal matrix and tend to polish away at a slower rate than the metal matrix. The SEM is also used to do the fractography work. Fractography shows the fracture surface of the material, possibly showing the mechanism of failure. The reduced data and metallographic results are then looked at together and an evaluation is made to show how the material behaves at high temperatures and stresses when cycled.

RESULTS

As was the objective of this Task, the fatigue characteristics of some advanced MMC's were investigated. Resulting from this study, certain aspects of the fatigue properties of the MMC's were discovered. The thermal-mechanical fatigue data is only a small part of a large data base generated for the material. Other areas include thermal fatigue, creep data, high cycle fatigue and low cycle fatigue. All of the data from the lab is sent to NIC, and at the end of the testing, a decision will be made as to the use of the material Beta 21-S.

METALLIC COMPOSITES II

Task Order No. 14
Student Support Program
Southwestern Ohio Council for Higher Education

Kevin L. Kendig
The Ohio State University

30 September 1993

Government Task Leader
Dr. Dan Miracle
WL/MLLM

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For their support and insight during my research this summer, I would like to thank the following: Dr. Dan Miracle, Dr. Winston Soboyejo, Dr. Sion Picard, Mr. Bob Lewis, Cameron Begg, Michael Scott and Mark Dodd.

TASK ASSIGNMENT

During this Task, samples were prepared and experiments performed to examine the residual stresses present in both as-processed and heat treated composites. The composite material used was Ti-15V-3Cr-3Sn-3Al(Ti-15-3) continuously reinforced with SCS-9 Textron fibers. Two of the residual stress components for the matrix were determined using an x- ray technique. The axial residual stress in the fibers was measured using the fiber extension, matrix under-cut removal (FEMUR) test. The goal of this Task was to correlate changes in composite microstructure to changes in the residual stress state of the composite.

DESCRIPTION OF RESEARCH

Required heat treatments were performed. The Ti-15-3 composite material was cut into several 1 cm by 1 cm pieces. These were individually vacuum encapsulated in quartz tubing. Heat treatments were performed at 540°C and 815°C each for 10 hrs, 50 hrs and 100 hrs. Two samples were prepared for each condition, one for the x-ray analysis and one for the FEMUR test.

The following is the experimental procedure used for the FEMUR test:

I. Sample preparation

A. Cut the sample ~ 1 cm by 1 cm

B. Mount sample in a triplex mount

1. Place the sample in a plastic clip and place this on the stage of the mounting equipment such that the fibers are normal to the stage.

2. Add a layer of non-conducting mounting powder.

3. Add a layer of conducting mounting powder; this must provide an electrical conducting path from the sample to the edge of the mount.

4. Add a second layer of non-conducting mounting powder.

5. Press the mount.

C. Mechanically polish the sample down to a 1 μm diamond surface using the Maximet.

D. Jet electropolish.

1. Paint the surface of the sample with an electrolyte resist leaving 1 mm of the center of the composite exposed.

2. Electropolish for 6-7 hours using a perchloric acid solution.

II. Measurement

A. Etch depth--measured before fiber extension

1. Take optical micrographs of etched area overlay with transparencies so they may be written on without damage to the photos.

2. Inspect depth of etch with an optical microscope; if nothing can be seen, place sample in an ultrasonic cleaner until the etch reflects light--this may take several hours.

3. Measure depths.

a. Use a calibrated optical microscope with adequate working distance such that it is possible to focus to the bottom of the etched region.

b. How.

(1) Focus on the fiber ends.

(2) Focus to the bottom of the etch.

(3) Record the difference in focusing positions.

c. Where.

(1) Along both sides of each row of fibers i.e., if there are n rows of fibers, then there should be n+1 rows of measurements.

(2) At the gap between each set of 2 fibers along the side of the row of fibers not in the row of the fibers.

(3) For most fibers, this will provide four depth measurements arranged in a square array about the fiber.

d. Record the measurement on the photo--on the transparency--where the reading was taken.

B. Fiber extension

1. Sample preparation

a. Fill the etched region with carbon paint and allow it to dry.

b. Remove the excess carbon using putting a solvent on a paper towel and then wiping the sample on this.

c. Depth around fibers must be minimized due to the limited travel of the profilometer-- see 2a.

d. All carbon must be removed from the fiber ends because the fiber extension is small and this carbon would therefore introduce a large error.

2. Measure extensions

a. Align a fiber row in the sample with the stylus trace of the profilometer, a mechanical device used to measure surface roughness.

b. Perform a trace.

c. Manipulate the recorded trace such that it is leveled and zeroed with respect to the fibers outside of the etched region.

d. Carefully label the trace printout as to which row the trace corresponds on the photo as well as the direction of the trace.

The above procedure was followed with the exception of an inspection of each sample after mechanical polishing. The microstructure and fiber-matrix interface of each was examined using a scanning electron microscope (SEM).

The following is the procedure used in the x-ray study:

I. Sample preparation

A. Cut the specimen to ~ 1 cm by 1 cm

B. Mechanical polish

    1. Mount on an aluminum block using a low temperature thermoplastic.
    2. Polish with the 6 μm diamond suspension on an 8" wheel using silk cloth.
    3. Remove ~90% of the oxide and/or roughness.
    4. Remount the sample and polish the other side similarly.

  C. Electropolish
    1. Mount in the alligator clip sample holder.
    2. Use a perchloric acid solution and 20 volts.
    3. Measure distance from surface of composite to first row of fibers.
    4. Run for an appropriate time to remove ≥10m--Ti alloys have a removal rate -1μm/min.
    5. Re-measure distance from surface of composite to first row of fibers to check amount of material removed.

II. Measurement

  A. X-ray set-up
    1. use 55mA/190kV
    2. slits
      a. 1_DS
      b. 1_SS
      c. .15 mm RS

  B. q translation
    1. The datum--the system calibration--q setting must be altered to achieve the necessary translations on the q axis **find datum** Rigaku x-ray software > qualitative programs > qualitative data collection program > datum.

2. Change the datum's q value to the sum of the current calibration + the desired translation angle (psi).

3. Translations should be at equal intervals of $\sin^2$(psi) e.g. $\sin^2$(psi)=.1 > psi=18.43.

4. One run should be done at each psi including psi=0.

C. Sample mounting

1. Affix the specimen to scotch tape on the x-ray sample holder in the center of window.

2. Specimen orientation should be either with the fibers horizontal or vertical.

3. One set of runs should be done for each specimen at each orientation allowing two stress constants to be determined.

To check the calibration of the x-ray unit, a beta titanium alloy powder was analyzed.

ANALYSIS

The micrographs taken using the SEM were used to examine the microstructure of the matrix and the interface between the matrix and the fibers. This was a cursory examination to develop a qualitative knowledge of the samples. The x-ray diffraction data was used to determine the longitudinal and cirumferential residual stress components in the matrix. This was done by monitoring the position of a high-angle peak with successive translations on the Θ axis. Six translations from 0° to 45° were used. The peak position was determined using a curve-fitting algorithm on Peakfit software. The 2Θ peak positions were changed to d-spacings using Bragg's Law then plotted versus $\sin^2(\phi)$ where ϕ is the translation angle on the Θ axis. The residual stress can be determined using equation 1. In this equation 'm' is

$$(1)\quad \sigma=\frac{mE}{d(\varphi=0)[1+\nu]}$$

the slope of the best fit line to the data, d(φ= 0) is the d-spacing at $\varphi = 0$, and E and ν are respectively the Young's Modulus and Poisson's ratio of the matrix. For the horizontal specimen geometry, $\sigma\varphi$ is the longitudinal residual tensile stress in the matrix. For the vertical specimen geometry, $\sigma\varphi$ is the circumferencial residual tensile stress in the matrix.

The FEMUR test was used to examine the axial residual stress in the fibers. The average of the depth measurements around each fiber was assigned to that fiber. A scatter plot of fiber extension versus etch depth--using the same units-- was then produced. A least squares linear regression was performed on the data. The slope of the line is equal to the average residual axial compressive strain in the fibers.

RESULTS

The SEM micrographs provided qualitative knowledge of the microstructure and matrix-fiber interface. The samples heat treated at 540°C showed an increasing amount of precipitated α_2 phase and no change in the matrix-fiber interface with increasing time at temperature. The samples heat treated at 815°C showed no precipitated of $\alpha2$ while the matrix-fiber interface coarsened with increasing heat treatment length.

The collection of data for the x-ray analysis was completed. Figure 1 shows the d vs. $\sin^2(\varphi)$ plot for the beta titanium powder sample. Due to the lack of macrostresses in a fine powder, any shift in peak position upon translating the θ axis must be due to mis-calibration of the x-ray unit. The zero slope shown in Figure 1 establishes that the x-ray unit was successfully calibrated. Data in two orientations for each sample was collected and is yet to be analyzed.

The FEMUR test was held up due to unavailable equipment. The FEMUR procedure was carried out (see Description of Research) on the as-processed sample and the fiber extension versus etch depth was plotted (Figure 2). The linear regression gave an average residual strain of .16%. Access to a profilometer will allow the remainder of the samples to be tested.

The goal of this Task was to correlate changes in composite microstructure to changes in the residual stress of the composite. Most of the data for this project has now been collected, but correlations have yet to be drawn.

Figure 1

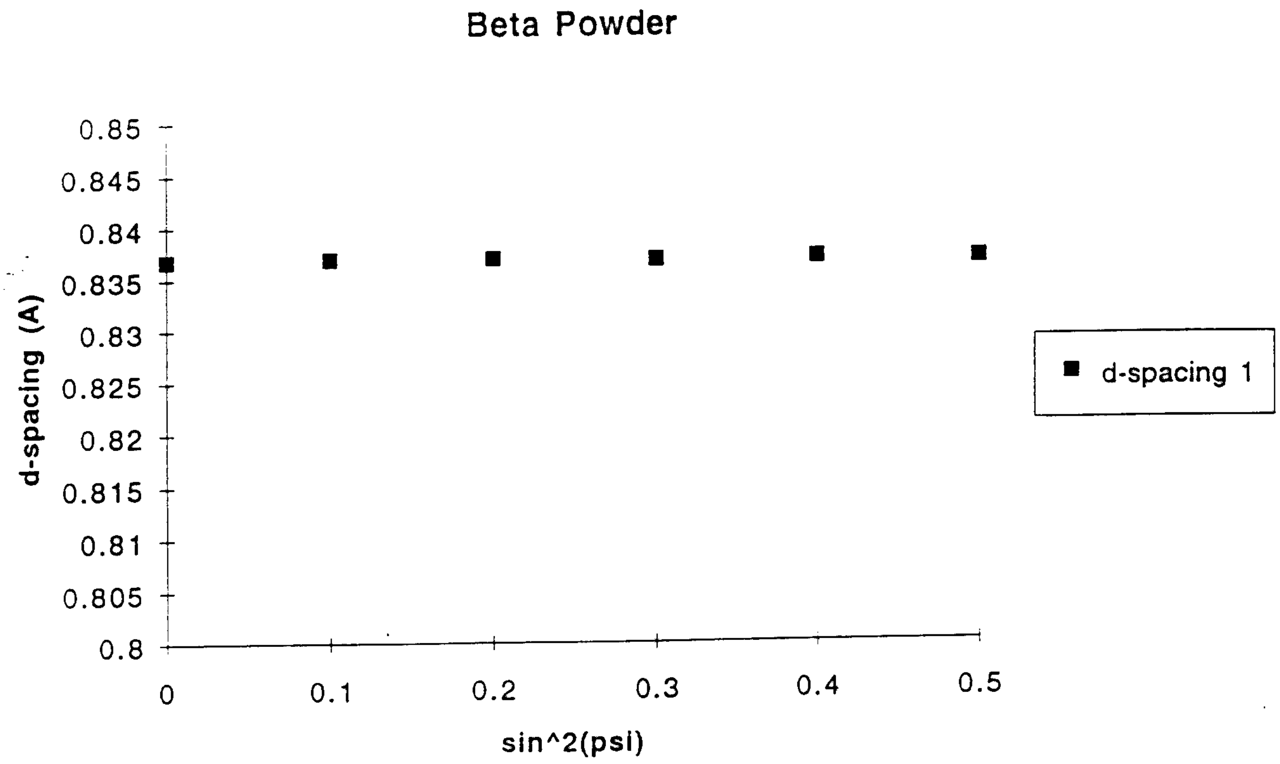
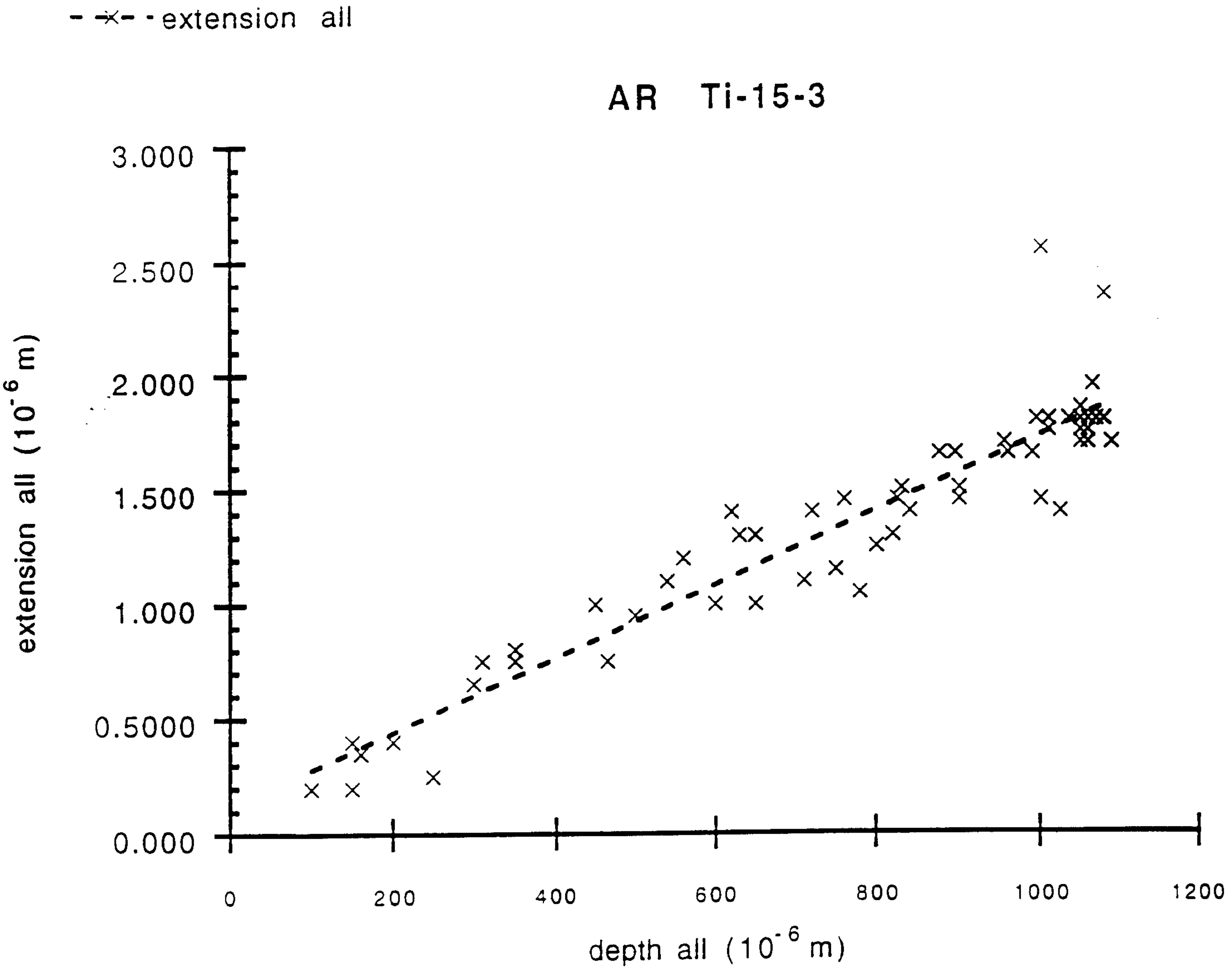

Beta Powder
0.85
0.845
0.84
0.835
0.83
0.825
0.82
0.815
0.81
0.805
0.8
d-spacing (A)
0
0.1
0.2
0.3
0.4
0.5
sin^2(psi)
■ d-spacing 1

Figure 2



- -×- - extension all
AR Ti-15-3
3.000
2.500
2.000
1.500
1.000
0.5000
0.000
extension all (10^{-6} m)
0
200
400
600
800
1000
1200
depth all (10^{-6} m)

ELECTRICAL AND MAGNETIC PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

Task Order No. 15
Student Support Program
Southwestern Ohio Council for Higher Education

Douglas A. Buchanan
Wright State University

17 November 1993

Government Task Leader
Mr. Timothy L. Peterson
WL/MLPO

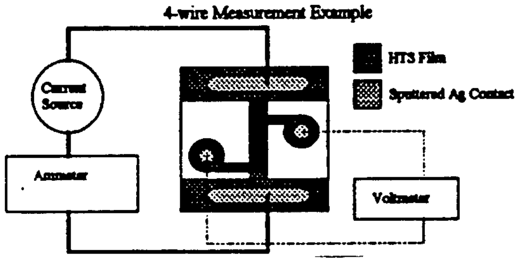
ACKNOWLEDGMENTS

Overall, this Task has been one to further help students gain experience to the laboratory setting and controlled experimentation. I would like to thank Southwestern Ohio Council for Higher Education (SOCHE) for their on going support and my Government Task Leader Tim Peterson.

TASK ASSIGNMENT

Task number 15, Electrical Properties of High Temperature Superconductors, involves the application of many scientific techniques to investigate the properties of high temperature superconductors. Throughout this Task assignment, it has been required to gain training on the basic experiment that is used to measure superconducting properties, the DC transport property measurements, where one determines the conducting ability of a superconductor by applying a direct current at various temperatures. Other areas of training have come from having to learn scanning electron microscopy, X-ray diffraction, clean room operations, and sample patterning. This was all accomplished to help the MLPO group in its ability to gather data for analysis of superconductors. The overall training has helped the MLPO group to have more time for its investigation of superconductors and saved them time from manual data gathering, which is the student's primary role.

Figure 1



The first thing that the student must learn is to operate the cryogenic dewar for transport measurements. The electrical properties of high temperature superconducting (HTS) materials in both bulk and thin-film form are measured to evaluate material quality and to better understand the nature of high temperature superconductivity. A 4-wire measurement technique capable of measuring very low values of resistance is used (see Figure 1). All experiments are completely automated with computer control to set the sample temperature, set the sample current, and collect all current and voltage readings. The properties which are measured include the normal state resistivity, p, the critical temperature, T_c, and the critical current density, J_c.

The resistivity is measured as a function of temperature from room temperature down to the temperature at which the transition to superconductive behavior occurs (the critical temperature). Critical temperatures of about 90 Kelvin with transition widths of about 1 Kelvin have been measured for high quality $YBa_2Cu_3O_{7-x}$ films grown in-house by pulsed laser deposition.

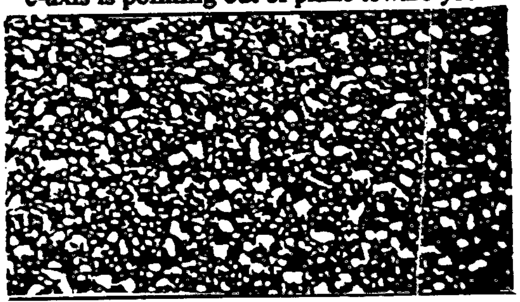
Voltage, as a function of current, is measured at different temperatures to determine the maximum current density (the critical current density) which can be carried by the material in the superconducting state before the material begins to show a resistance. High quality thin-films grown in-house have critical current densities of 5×10^6 Amp/cm^2 at 77 Kelvin (the temperature of liquid nitrogen).

The next area of training is learning to use scanning electron microscpy (SEM) work in conjunction with the HTS films (see Figure 2). The microscopic structure of $Yba_2Cu_3O_{7-x}$ tells the experimentalist what type of crystal structure exists for a sample. The latest technique is to try to look between the large granular structures on the surface of $YBa_2Cu_3O_{7-x}$ and see how one certain axis, the c-axis, is oriented. Until recently, the MLPO group was not getting a deep enough view between the grains using the SEM's provided to general use, or the ones used by the students. The ETEC scanning electron microscopes do not have the resolution capabilities needed, therefore, the student now has to operate a Hitachi Microscope with support of the SEM support group. There are other instruments that now provide a better view than the scanning electron microscope which can resolve down to 5 nanometers (5×10^{-9} m). The Atomic Force Microscopes (AFM) can easily resolve to much lower orders of magnitude, and has hence become the standard way of visually observing the structure of the HTS thin-film.

Figure 2

a and b axis run inside plane

c-axis is pointing out of plane toward you.



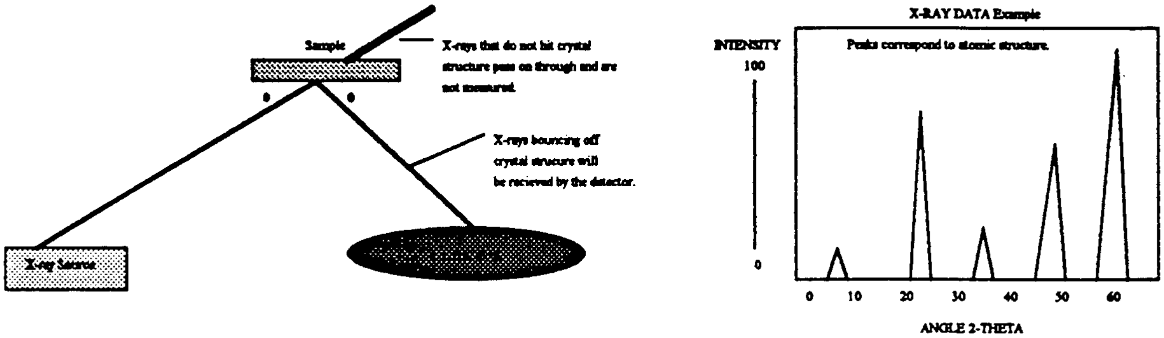
MLPO is interested in what lies between the grains.

X-ray diffraction is another measurement used to gather data on HTS thin-films. To operate X-ray equipment, training is mandatory as well as the acquisition of an X-ray badge that requires a small physical examination and blood test. Once qualified to operate an X-ray diffractometer the student can take measurements of the crystals structure by measuring the return of X-rays (see Figure 3).

figure 3

The left diagram corresponds to how the X-ray Diffractometer works.

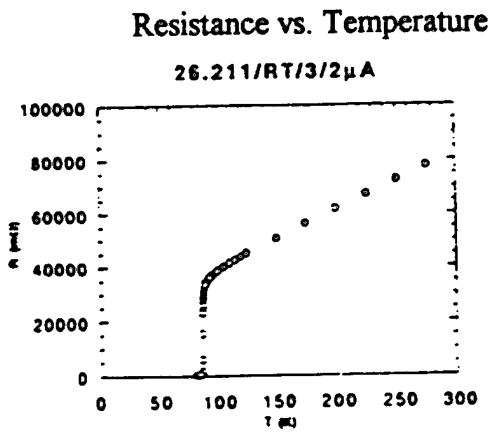
The right diagram is an example of the data obtained from the X-ray Diffractometer.

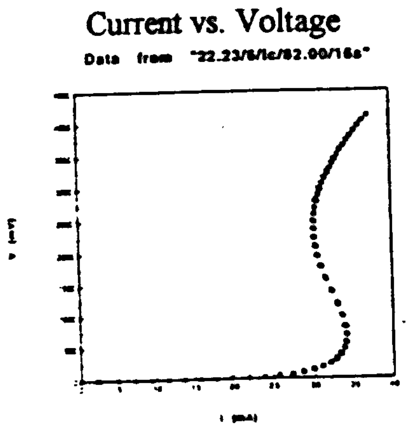


The X-ray data can be used to determine the exact composition of the material being used by how the peaks of one sample compare to the peaks of nearly the same material of known composition. Remember that $YBa_2Cu_3O_{7-x}$ has a 7-x at the oxygen location. When deposited by the laser the amount of oxygen present there helps correspond to the quality of the superconductor. X-ray diffraction can help one to determine the x value. The lower the x value, the higher the quality of the superconductor.

Another responsibility of the student is to clean substrates, which is usually a 1 x 1 x .2 centimeter crystal that the superconducting material will be grown on. To have good contact between the superconductor and the substrate, it is extremely important to have a well cleaned substrate. The process involves chemically cleaning the substrates using trichloroethylene, acetone and methanol. After a good chemical cleaning, the films are "baked" in an ozone oven for 1 hour and taken out to be placed in a clean substrate holder.

Using the above techniques, a large amount of data can be acquired and compared to samples of extremely similar composition. For the most part, this Task is concerned with analyzing the transport measurements and providing resistance versus temperature plots, and current versus voltage plots at set temperatures. Examples of both are provided below.





The other techniques in this Task are used to support and gather extra information that the transport measurements alone cannot provide. The data is used mainly used to try to understand the principles of superconductivity. Much of the data is used in publications and ongoing research with outside contractors to Wright Laboratory.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 16
Student Support Program
Southwestern Ohio Council for Higher Education

Sungmee Yoon Kim
Wright State University

28 October 1993

Government Task Leader
Dr. Robert Crane
ML/MLPJ

ACKNOWLEDGMENTS

I need to recognize Dr. Tom Cooper, Dr. L.V. Natarajan, Dr. Zbigniew Tokarski, Dr. Tim Bunning and Karen Hussong for their assistance with my research at the ML/MLPJ.

TASK ASSIGNMENT

The Task Assignment involves the synthesis and characterization of siloxane based macromolecule incorporated with spiropyran molecules and other mesogenic groups (a component of a molecule that induces a mesomorphic or liquid crystalline phase) for use as matrices for optically active materials.

DESCRIPTION OF RESEARCH

Synthesis: Various carbon length leader groups, allyloxybenzoic acid (3C leader group), penteneoxybenzoic acid (5C leader group) and vinylbenzoic acid (2C leader group) were synthesized by following a procedure modified by Tim Bunning from reference literature 167, except the vinylbenzoic acid (Aldrich). Dicyclohexylcarbodiimide (DCCI) coupling reaction was used with a catalyst, dimethylamino pyridine (DMAP), to attach various compounds such as hydroxybiphenyl, cholesterol, 1'- hydroxy ethyl -6-nitro BIPS ("T") and 1'- methyl-6-hydroxy BIPS ("I"). Different solvent systems were used to purify the products in trying to find the best systems (cost and toxicity). Further purification of the allyloxybenzoate-nitrobenzospiropyran (3C T BIPS) and penteneoxybenzoate-nitrobenzosp (5C T BIPS) was done by flash column chromatography but allyloxybenzoate-spiropyran (3C I BIPS) cannot be purified by flash column due to its tailing. Silanization reactions were conducted using 100% 5C T BIPS in a D5 ring system and 100% 3C T BIPS. The silanization reactions were done under positive argon pressure with platinum catalyst in toluene at 90°C. The reactions were monitored by comparing the ratio of Si-H peak (2160 cm-1) to C=O (1742 cm-^{1}) peak with the FTIR (Fourier Transfer Infra Red Spectroscopy). These reaction products were purified by reprecipitations in methanol from toluene until TLC (Thin Layer Chromatography) shows clear. These products were analyzed by either FTIR, Lambda 9 Spectrophotometer, NMR (Nuclear Magnetic Resonance), elemental analysis, mass spectroscopy, microscopy and/or DSC (Differential Scanning Calorimeter).

Results: The photochromic units (3C T BIPS, 5C T BIPS) have very low yield after purifying by flash column chromatography. The yield may improve when washed with hot ethanol before purifying by column. The silanization reaction requires high purity reactants and therefore rigorous and time consuming purification process is necessary. The thermal transitions of the various compositions of 3C T B IPS, cholesterol-4-allyloxy benzoate (CAB) and biphenyl-4-allyloxy benzoate (BAB) attached to siloxane ring was studied. As ABNS percentage increase, liquid crystallinity decreases. Holographic grating can be written on sheared thin-film of these materials and can be erased by heating. The potential of these materials as reversible optical data storage will be studied.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 17
Student Support Program
Southwestern Ohio Council for Higher Education

Linda Wood
Wright State University

16 December 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

I would like to thank the following individuals for their support and assistance in my Task assignment: Dr. Robert Crane, Wade Adams, Sue Kirchoff, Dr. Tom Cooper, Dr. Ruth Pachter, Steve Fairchild, Donald Brinkman, Jim Lupo, Soumya Patnaik and Dr. Zbig Tokarski.

TASK ASSIGNMENT

Work was completed on software used in molecular modelling for translating files from Z-Matrix to PDB file formats. Code was written in C for appropriate input and output format statements. Additional fields were created in existing structures for required data description. The code involving these structures was edited appropriately throughout the software. The input and output statements were incorporated into related software for molecular modelling. Searching methods were developed for key word searches of existing PDB files to increase efficiency of locating possible PDB files of interest. These methods include renaming of a group of files and transference of a group of files working from a remote computer station. Although the methods are very involved, they provide an effective tool for searching within a large group of PDB files.

Extensive investigation of remote access software has been conducted and tutorials have been given to individuals on the usage of this software.

With the purchase of additional hardware, more efficient methods have been developed for the transfer of data between computers with different operating systems. Tutorials have been given to individuals on the usage of these methods of transfer.

Methods of searching, ordering and printing inventory materials have been investigated on available network software. Tutorials have been given to individuals on the usage of these methods.

Available scanning software packages, including text and pictorial packages, have been investigated. Instruction has been given to individuals on the usage of these software packages and the scanners.

Data base files of chemical disposal have been restructured and reorganized to include additional satellite points. This system has been developed to allow for tracking of chemical disposal materials.

Some maintenance has been performed on computer systems. Optimization, backups and software installation and removal have been performed on the different Macintosh systems within the department.

When describing software requirements, the user may believe the specifications are completely clear. Many factors are involved in the development and maintenance of software that are not obvious or considered from the start. It has been found that a method that includes creating a prototype, a small scale version of the software to be developed, can save much confusion and time. Once a prototype has been developed, it can be demonstrated to the user and communication breakdowns are, therefore, avoided. After any additional requirements are investigated, a full-scale version of the software required may commence. The result is to save time and confusion on the development of the software development.

Many different computer systems were used in this Task. Many computers, UNIX, Macintosh, IBM and IBM compatible were utilized. In addition, CD-Roms, magnetic tape drives, portable external hard drives with removable disks, other external hard drives without removable disks and digital scanners were used in this Task.

Clear communication has been discovered to be an important element in software design. Clarity of software specifications by the user is necessary for efficient software design. Documentation of code by the designer is necessary for software development by multiple designers and is effective and efficient debugging by the designer.

Documentation of code also plays an important role in future maintenance of software. For future development of software, it is necessary to have clear communication of programming code to efficiently make any required changes in programming code. Without this documentation, much time may be wasted in reevaluating the code.

Possibly the most important factor, without proper software documentation the user may forget the application of the program and the software could become a bundle of useless code.

In conclusion, I have learned many aspects of software design in a research environment. I believe that clear and effective communication plays an integral role in this process. Although documentation of software is a considerable time-consuming effort, I have discovered that the outcome of this effort is to save time and increase efficiency.

CONSOLIDATION OF NDSANDS COMPUTER CODE

Task Order No. 18
Student Support Program
Southwestern Ohio Council for Higher Education

Anthony D. May
Wright State University

15 September 1993

Government Task Leader
Dr. Nicholas Pagano
WL/MLBM

ACKNOWLEDGMENTS

Thanks go out to Dr. G. P. Tandon for his time and guidance; to the technical initiator Dr. Nicholas J. Pagano, and to Mrs. Wanda Vogler and Mrs. Pamela Douglas of the Southwestern Ohio Council for Higher Education.

TASK ASSIGNMENT

The purpose of this Task is to create a consolidated, user friendly version of the NDSANDS application software for use on Apple Macintosh computers. NDSANDS is an acronym for N-Directional Stiffness AND Strength. A user of the NDSANDS software package is able to carry out a number of complex materials science computations. NDSANDS is an entirely menu driven system. NDSANDS users make selections by clicking on menu items with a mouse.

This software package allows its users to create and maintain a library of constituent materials (Fibers, Coatings, Matrices, and Particles). Each constituent material has its own specific properties which are supplied by the user. Users then combine these constituents to form composite materials. These composite materials are then stored in a separate library. NDSANDS then calculates the resulting properties of the new material created by combining the constituent materials according to the user's specifications. After computing these properties the program allows the user to specify various loading conditions. Resulting stresses, strains, displacement components and strength ratios are then able to be computed by the software package. These results are then able to be displayed in either tabular or graphical format.

The graphical format has been the focus of the recent work done on the program. Users are now able to simultaneously plot the results of the computations (i.e., stresses, strains, etc.) of up to five composites. The program plots these computed values against either the radius or the angle theta. Plots allow users to recognize the effects of their decisions quickly and clearly. This enhances the usability of the software package whose goal is to be as user friendly as possible. Another area in which modifications have been carried out involves the manner in which the data libraries are handled. Each constituent material type has its own data file stored on a disk. This information is then read into memory when the program requires the information. One problem was that the format statements for storing the data only allowed three significant figures to be stored. This bug caused values entered by the user to be truncated in many instances and unnecessarily limited the precision of the program.

Another problem involved the way in which the composite data was stored. In the case of the composite materials, only references to the data in the constituent's data files were stored. If a constituent material present in one of the composites was subsequently deleted by the user, the program would fail the next time it tried to analyze that composite, as the data it needed was no longer available. The solution opted for in this case was to store a copy of each constituent's data directly in the composite data file at the time of its creation.

Colors were also added to the software package. The color scheme was designed to provide a consistent appearance for the user to get used to. All titles are displayed in one color while prompts for user input are displayed in another. Another use of colors was to help distinguish between the different plots when more than one composite is plotted at a time. This is another attempt to make the program as user friendly as possible.

One of the next features to be added to NDSANDS is an on-line help mechanism. This will allow users to get clarification if they are unsure of the action they must take next, what a particular variable represents or other information relating to a particular phase of the program. Users will be able to get help at any stage of the program by clicking a help button with the mouse.

Another possible feature would be a contour plot with different colors representing different ranges of values. For example, blue and green (cold) might be at the low end of the values while red and yellow (hot) might be at the high end. Other improvements still to be made include stricter error checking of user entered values. Many values, at this point, are not checked to insure that they are within an allowable range.

Benefits gained from participation in this Task include the improvement of project management and analytical skills, and Macintosh programming experience. Because NDSANDS is a large program, approximately 650 kilobytes of executable code, it has been very important to remain organized in the programming effort. The experience in tracking down program bugs has also been useful in improving analytical abilities. This Task has also provided an opportunity for programming in the Macintosh environment, which is useful experience.

CONTROL FOR DEPOSTION PROCESS

Task Order No. 19
Student Support Program
Southwestern Ohio Council For Higher Education

Stephen Adams
Wright State University

15 September 1993

Government Task Leader
Dr. James Malas
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank the following people for their help in making my second contract here very pleasant and rewarding: Dr. Walter M. Griffith, Chief, Manufacturing Research Branch, Dr. Steven LeClair, Visiting Scientist, Dr. James Malas, Materials Research Engineer, Mr. Oliver Patterson, Visiting Scientist, Capt. Elizabeth Stark, Mr. Jeffrey Heyob, Mr. David Tucker, Mr. Doug Moore and Victor Hunt. I would like to thank the Student Support Program for allowing students the opportunity to work with the Wright Laboratory. I have found the people in this group to be very friendly and willing to help you if you are having problems with your project. They also seem to go out of their way to make you a part of both the professional and the social groups that are formed at work. The exposure to technology and equipment the Air Force has to offer is an experience that I am glad to be part of and is something that has changed my outlook on future job prospects.

TASK ASSIGNMENT

The objective of this Task was to provide support development of an advanced process control for the thin-film semiconductor growth process, Molecular Beam Epitaxy (MBE). Develop a compensator to eliminate shutter opening induced flux transient and associated automated system identification procedure. A secondary objective is to assist in the development of a fuzzy logic controller for Pulse Laser Deposition.

Molecular Beam Epitaxy (MBE) Process

MBE is a process where material is heated to its evaporation temperature and deposited on a substrate. In most cases more than one material is being deposited on the substrate at a time. As the material is deposited on the substrate, layers are formed. If the composition of the material being deposited on the substrate is inaccurate, then the desired characteristics will not be possible. Also, if the interfaces between the layers are not sharp, the desired characteristics are not achieved.

DESCRIPTION OF RESEARCH

The purpose and function of MBE is best said in the following sentences. "Future Air Force weapons systems, whether new platform or upgrades to existing ones, will require more capable and sophisticated electronics and electro-optic systems to maintain qualitative superiority over potential adversaries. These future electronic and electro-optic devices will rely more and more on materials grown in epitaxial thin-film forms. This GaAs based technology has and will continue to lead to enormous increases in analog device capability in the microwave applications areas. Much of the current technology is based on ion implantation into bulk GaAs wafers, but an ever increasing number of applications are turning to devices such as High Electron Mobility Transistors (HEMT) and Heterojunction Bipolar Transistors (BHT) that are made entirely from epitaxial III-V semiconductor films grown on substrates such as GaAs and InP." [1]

The main components of the MBE machine are the ultrahigh vacuum chamber, Knudsen Cells, ion gauge and substrate. The Knudsen Cell is comprised of a crucible, heater and shutter. The crucible holds the material to be deposited on the substrate. A Eurotherm 818 PID Controller regulates the power applied to the cell heater. A thermocouple located at the rear of the Knudsen Cell's crucible monitors the temperature of the material within the cell. This thermocouple signal is used by the PID controller to control the cell's temperature. The Knudsen cell's shutter is used to block the flow of material (flux) from the cell when the cell is at operating temperature. The ion gauge is used to monitor flux measurements for calibration purposes prior to a growth. During a growth, a substrate replaces the ion gauge. A side view of the MBE machine is shown in Figure 1.

When the Knudsen cell's shutter is opened, the material in the cell is released into the chamber. As the material radiates from the cell, the temperature at the front of the cell decreases to a new equilibrium as shown in Figure 2. When the PID controller detects the change in the thermal couple signal, additional power is applied to the Knudsen cell's heater. Currently it is not possible to measure the temperature at the front of the cell during a growth without interfering with the flux. When the cell temperature reaches equilibrium, the amount of material emitted from the cell is constant.

When making a growth, it is important to maintain the composition of the material being deposited on the substrate. Each type of material has a particular lattice constant. If the substrate is composed of GaAs, it will have a lattice constant of 5.65325 ü. If the material being deposited on the substrate does not have the same lattice constant as the substrate, it will try to conform to the lattice of the substrate. This is known as a strained layer.

As seen in Figure 2, the amount of flux leaving the cell just after the shutter opening is about 4% greater than the flux leaving the cell at steady state. This amount of change will cause the composition of the material to vary and change the lattice constant of the composition.

Figure 3 shows a schematic of a double-heterojunction laser structure, with a superlattice at each GaAs/AlGaAs interface. To obtain the lattice matching, the composition of the material deposited on the substrate must be controlled to within 1% of the calculated amount.

To be able to compensate for the shutter disturbance, three steps are involved. The first step is to identify the disturbance and the process. The second is to calculate the setpoint compensation signal. The third is to apply the compensation signal to the system during a growth. The first step is the process identification tests. This consisted of two separate tests. The first is to measure the flux readings after a shutter opening. The second is to measure the change in the flux measurements when a pulse is applied to the setpoint of the 818 PID Controller. The disturbance experiment will indicate the time constant of the shutter disturbance and its magnitude. The second experiment will describe the response of the system to a temperature setpoint change. Figure 4 displays the process identification test for the Indium cell.

The second step is to apply a first order least-squared fit to the disturbance data D(z) and the pulse response data H(z). The form of these equations are:

$$D(z)=\frac{N_1}{t_1-z} \qquad H(z)=\frac{N_2}{t_2-z}$$

From this a difference equation for the setpoint signal is calculated C(n). The form of this equation is:

$$C(n)=k_1S(n)-k_2S(n-1)+k_3C(n-1)$$

where:

$$k_1=\frac{N_2}{N_1}$$

$$k_2=k_1\times t_1$$

$$k_3=t_2$$

S(n) is the non delayed shutter value.

S(n-1) is the one increment delayed shutter value.

C(n-1) is the one increment delayed compensation value.

The third step is to apply the compensation equation to the actual MBE Knudsen Cell during a growth. This is done by having a program that will control both the setpoint values of the PID controller and the shutter of the cell. In the case of the Indium cell the compensation equation will start execution when the shutter is opened.

RESULTS

Figure 5 displays a compensation waveform of the Indium cell. When analyzing the wave form notice that for the first 50 seconds the flux signal is constant, but at 200 seconds the temperature applied to the setpoint is not able to compensate and the flux begins to decrease. At 400 seconds the flux begins to recover and after 1000 seconds the initial pressure is maintained.

Two important pieces of data can be extracted from Figure 5. The first is that after 1000 seconds the flux readings are the same as when the shutter was first opened. This indicated that the total amount of temperature change for the shutter disturbance was correct. The second piece of data is that at 200 seconds the flux readings begin to decrease. This shows that the rate at which the compensation signal is being applied to the PID controller setpoint is too slow.

CONCLUSIONS

Further analysis of the first order least-squared fits will indicate the accuracy of the equations for generating the compensation signal. A second order fit was tested and found that due to the noise that is present on the flux reading it is not feasible to fit.

A future enhancement of the calculation test will be to incorporate a noise reduction system. This noise reduction system will be able to fitted out the high frequency data from the flux readings. The new noise reduced data could lead to an increased accuracy in the least-squared fit of the data. The other possibility is that a second order fit can be used to fit to the data. This would enable a more accurate approximation of the disturbance.

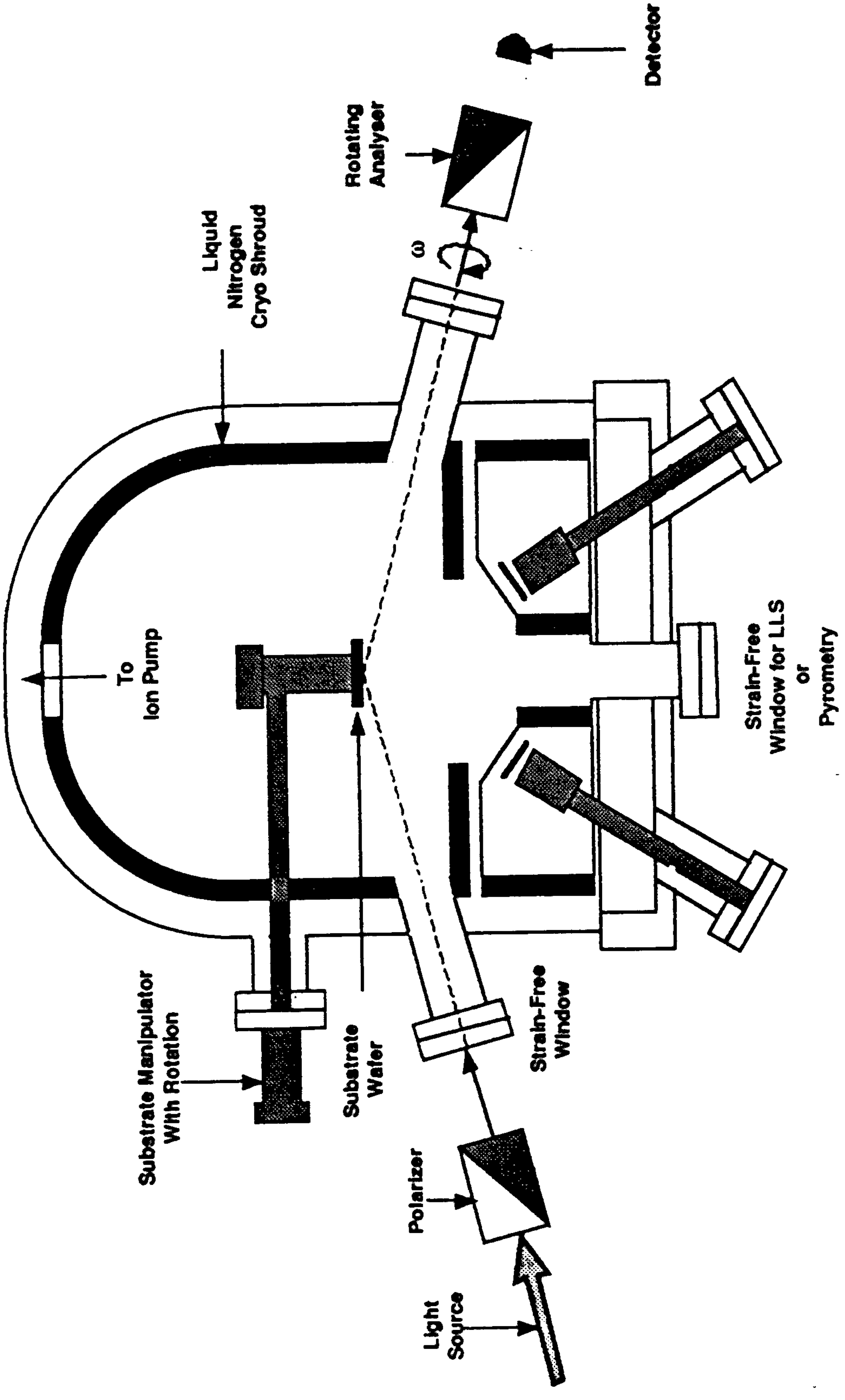


Figure 1. Side View of MBE Machine

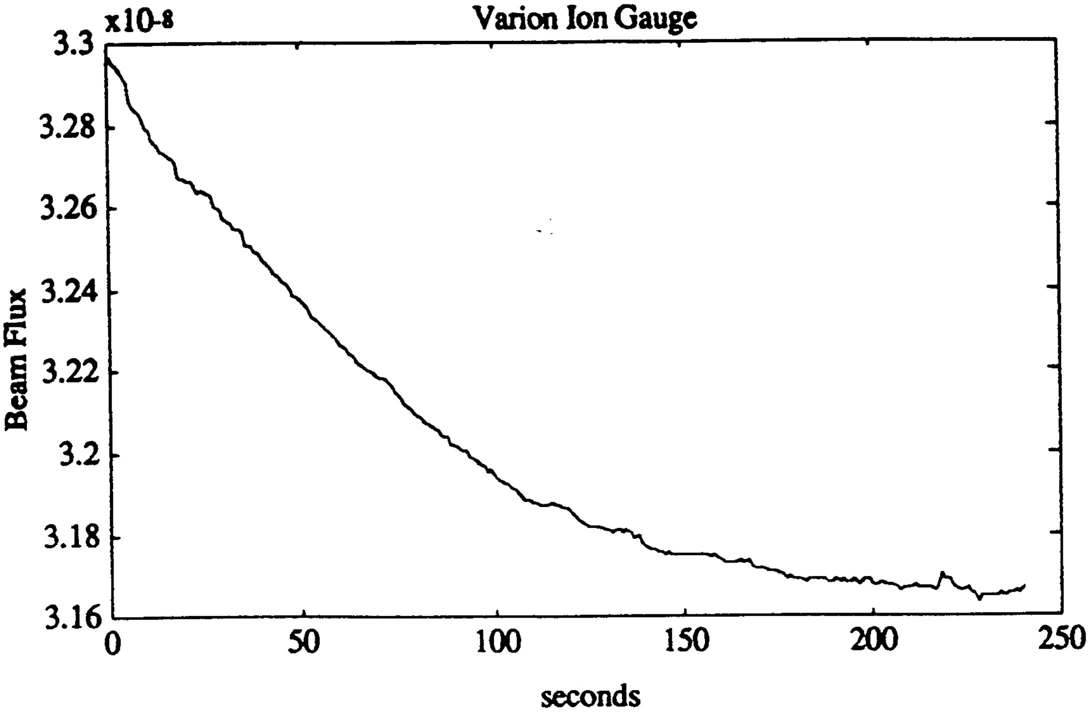


Figure 2 Shutter Disturbance

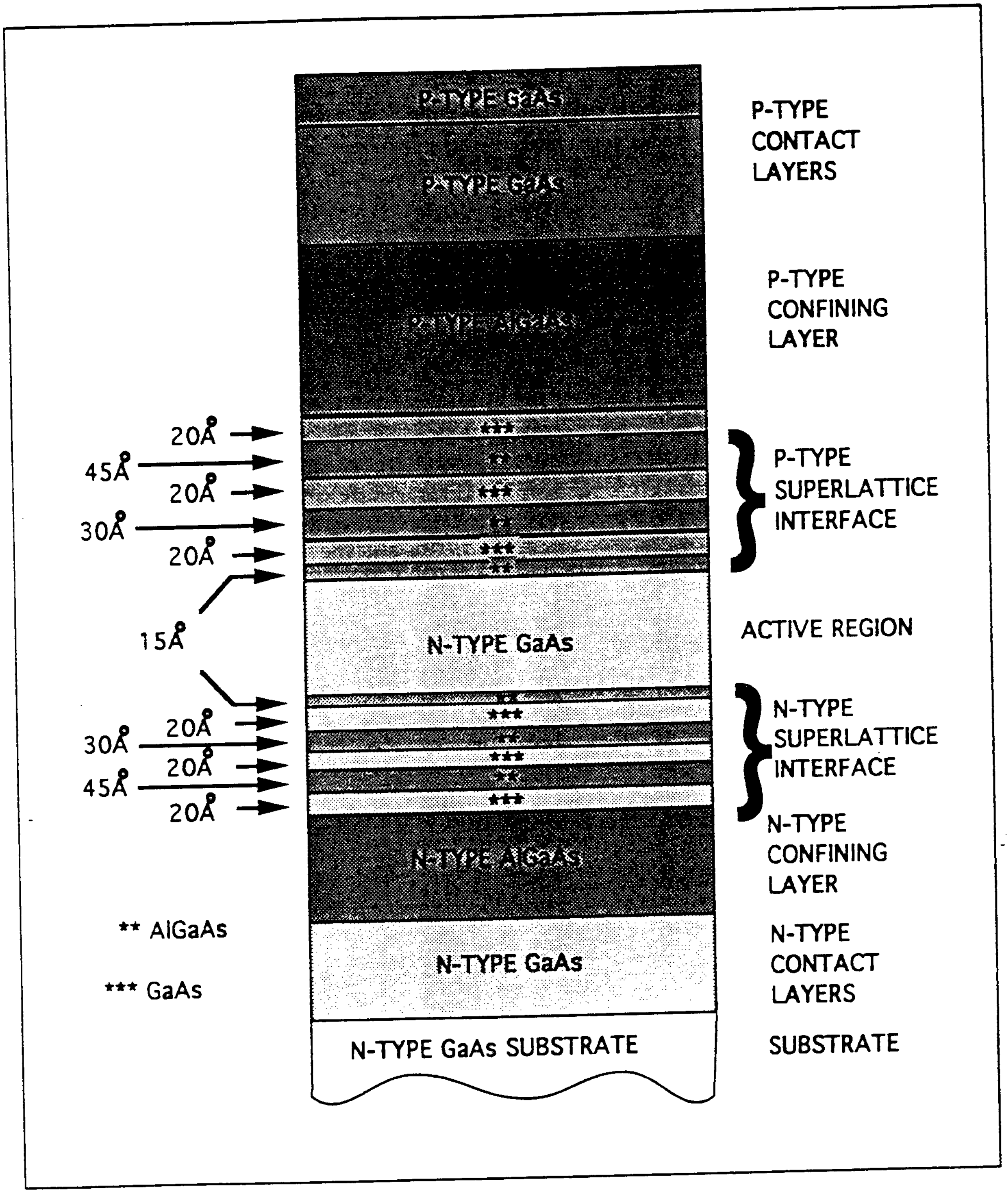


Figure 3

Schematic of a double-heterojunction laser structure, with a superlattice at each GaAs/AlGaAs interface, illustrates the complexity of devices possible with MBE

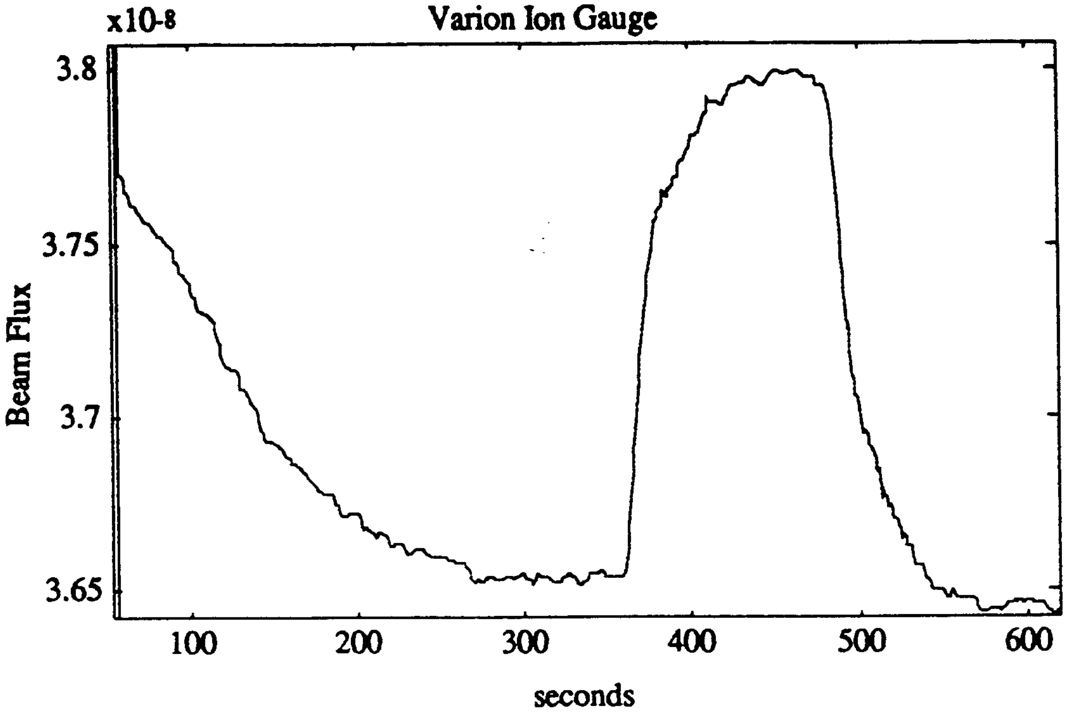


Figure 4. Process Identification Test

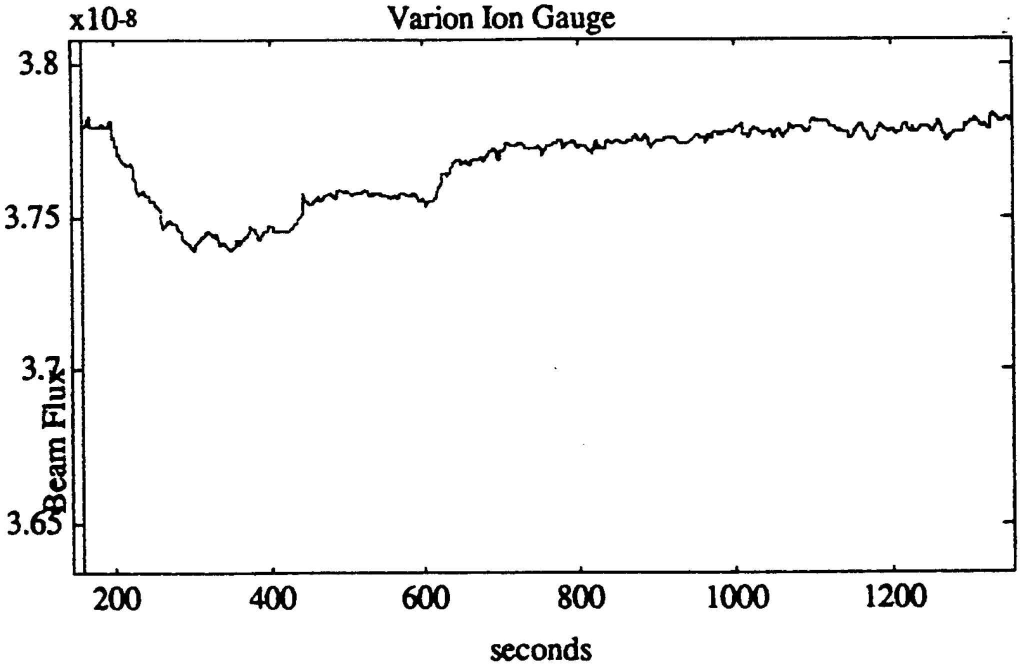


Figure 5. Compensated Ion Measurement

NON-PRISMATIC PART CREATION

Task Order No. 20
Student Support Program
Southwestern Ohio Council for Higher Education

Barry Caslin
Wright State University

30 June 1993

Government Task Leader
Dr. Jim Malas
WL/MLIL

ACKNOWLEDGMENTS

I would first like to thank Dr. Jim Malas and all the members of the Rapid Design System working group for the faithful assistance and abundant patience that every member of the RDS team extended. I would be remiss if I failed to mention the insightful and critical direction that was shown me by Dr. Radack, who was the researcher under whom I completed the majority of my Task and was the person I worked closely with on a regular basis.

TASK ASSIGNMENT

The primary Task was in the area of development of a generic feature in the Rapid Design System (RDS).

The Rapid Design System (RDS) is a project of the Materials Directorate, a unit of the Air Force Wright Laboratory. The goal of the project is to reduce design and production time and improve quality, particularly for small lot size jobs. The technical approach is to couple feature-based design with a memory that can retrieve past designs based on similarities to the current design, thus providing a "corporate history" function that enables the designer to profit from the experience of the past.

There are four major "environments" within the RDS.They are: The Feature-Based Design Environment (FBDE) that is used to create a specification of the part's geometry. This is done by adding, modifying or deleting features from the part model. The features handled by the FBDE are form features, which give the nominal geometry of the part, and Geometric Dimensioning and Tolerancing (GD&T) features, which specify the allowable deviation of a manufactured part from the ideal shape given by the form features. The FBDE has the ability to do some constraint checking and constraint satisfaction.

The Fabrication Planning Module takes the part specification (the collection of form and GD&T features) and produces a process plan for machining. The process plan includes tool selections, operation sequencing, tool paths, feeds and speeds.

The Inspection Planning and Evaluation Module (IPEM) takes the part specification and produces a process plan for inspection. Currently, only inspection by a 3-axis coordinate measurement machine is supported.

The Episodal Associative Memory provides for retrieval of past designs based on similarities with a given design. Search is based on geometric similarity; however, other types of search (e.g., based on functional similarity) will be supported in the future. The Rapid Design System (RDS) is a high-level design system that incorporates expert knowledge about producibility and inspectibility. A feature-based approach is used to describe part geometry, manufacturing information and inspection information. In traditional CAD systems, design information is represented in terms of geometric and topological primitives (points, lines, surfaces, vertices, edges, faces, etc.) and text. Feature-based design is an attempt to establish a higher level of representation, i.e., primitives (features) which have meaning and are interpretable by both the design system and the designer. It is also the intent of the designers of the RDS system to make this feature-based system very intuitive and simple for the designer to use, which today means using a Graphical User Interface (GUI). This Task was to update and modify the tool set available so it would meet the needs of the designers and future consumers.

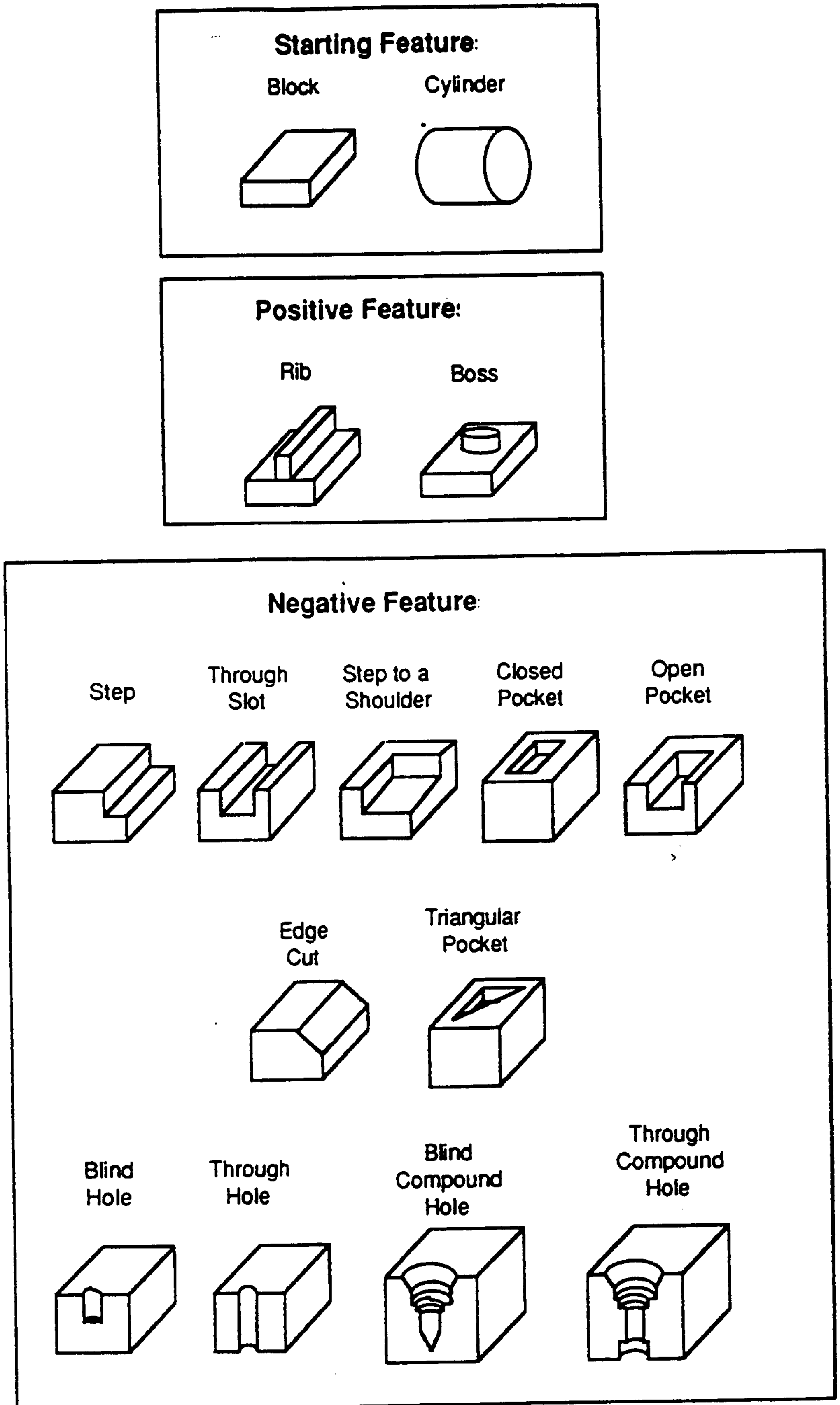


Figure 1: Features currently supported by the FBDE

Feature Attributes

The shape of an individual feature can be controlled using attributes of the feature. For features whose basic geometries are simple shapes such as rectangular block or cylinder, a small set of attributes can completely specify the shape.

Generic (non-prismatic) Feature Description

The generic (non-prismatic) feature can be an extrusion of an arbitrary two-dimensional profile, although in principle any three-dimensional solid could be used. The designer designs by adding and deleting features, and by modifying the attributes of already existing features. Feature can be categorized into three based on how they modify the geometry. Positive features, represent an addition of material; negative features, represent the removal of material, and modifier features, modify existing geometry, and can either cause addition or removal of material. Each feature has many attributes that must be given values to fully specify the feature. Attributes are used to specify the internal dimensions of a feature, the relationship of a feature to other features and other miscellaneous items. Each positive or negative feature has a basic geometry. For example, the basic geometry of a rectangular pocket is a block; the basic geometry of a hole is a cylinder. The basic geometry of a part is specified in a local coordinate system, and is generally centered around the origin. The attributes of the feature that are used to specify its relation to other features can then be used to determine the position of the features geometry in the world coordinate system.

DESCRIPTION OF RESEARCH

The RDS was a system that runs on a Sun work station and runs under UNIX. The RDS exists within an Emacs environment and is coded in Common LISP under a package called Wisdom which has many features that allow the programmer to interact with the part geometry, as well as allowing the user to manipulate the GUI in an efficient manner. Also, at times it was necessary to program in C.

RESULTS

In completing this project, I had to learn Emacs, Wisdom, Common LISP, UNIX system support and some X-windows programming. To accomplish the intended goals of this project, the rules for a generic feature were laid down and further developed. A generic starting block was added to the partmodel.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 21
Student Support Program
Southwestern Ohio Council for Higher Education

David P. Stitzel
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30 June 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

I would like to recognize the following persons who helped guide me through my Task Assignment; Dr. Robert Crane, Dr. Zbigniew Tokarski, Dr. Tom Cooper, Dr. L.V. Natarajan, Tim Grinstead, Sungmee Yoon Kim and Karen Myers.

TASK ASSIGNMENT

Task Assignment 21 involved the synthesis and classification of optical polymeric material which contained nonlinearly active molecules for use as laser hardening materials. The synthesized polymers led to a better understanding of what exactly nonlinear optically active polymers were and how the polymers could be produced.

Benzyl L-glutamate (BLG) was synthesized, via a transesterification reaction, by reacting L-glutamic acid (LGA) and benzyl alcohol (BA) with p-toluenesulfonic acid (PTSA) acting as the acid catalyst. The purified product of this reaction (BLG) was then used in the synthesis of the BLG anhydride using triphosgene and tetrahydrofuran. Polybenzyl L-glutamate (PBLG) was synthesized from the polymerization of the previously produced BLG anhydride with triethylamine (TEA) acting as the initiator and N, N- dimethylformamide (DMF) as the solvent.

Nitrobenzyl L-glutamate (NBLG) was synthesized, via a transesterification reaction, by reacting L-glutamic acid (LGA) and p-nitrobenzyl alcohol (NBA) with p-toluene sulfonic acid (PTSA) acting as the acid catalyst. The purified NBLG was then used in the synthesis of the NBLG anhydride using triphosgene and tetrahydrofuran. Polynitrobenzyl L-glutamate (PNBLG) was synthesized from the polymerization of the previously produced NBLG anhydride with sodium hydroxide (NaOH) acting as the initiator and DMF as the solvent.

Five carbon p-nitroaniline (5CPNA) was synthesized by reacting p-nitrofluorobenzene with 5-amino-1-pentanol. Poly 5 carbon L-glutamate (PC5LG) was synthesized, via a DCCI (N,N-dicyclohexylcarbodiimide) reaction, by reacting PBLG and pentanol with 4-dimethylaminopyridine (DMAP).

A copolymer was then synthesized, via atransesterification reaction, by reacting the previously produced 5CPNA and PC5LG with PTSA acting as the acid catalyst and a mixture of dichloroethane (DCE) and DMF as the solvent.

Another copolymer was synthesized, via a transesterification reaction, by reacting disperse red 1 (DR1) and PC5LG with PTSA acting as the acid catalyst and a mixture of DCE and DMF as the solvent.

The synthesis of disperse red 1 L-glutamate (DR1LG) was recently attempted, via a transesterification reaction, by reacting L-glutamic acid and DR1 with PTSA acting as the acid catalyst and a mixture of dioxane and DMF as the solvent.

The product of each reaction was purified and analyzed using various high technology instruments. Some instruments that were used include a mass spectrometer, a fourier transfer infra-red spectrometer (FTIR), and a nuclear magnetic resonance spectrometer (NMR).

The data that was collected from these various high technology instruments was analyzed by the interpretation of the spectra produced. Once the spectra had been interpreted, it was possible to examine the results of the numerous reactions. For example, after analyzing the data that was collected for the 5CPNA/PC5LG copolymer, it was determined that a .859% modification of the dye (5CPNA) onto the parent polymer (PC5LG) was obtained. Likewise, the data that was collected for the DR1/PC5LG copolymer indicated that a .868% modification of the dye (DR1) onto the parent polymer (PC5LG) was obtained.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 22
Student Support Program
Southwestern Ohio Council for Higher Education

Colin M. McHugh
University of Dayton

31 December 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

I would like to thank Dr. Timothy J. Bunning and 1st Lieutenant Kyle D. Gresham for their assistance and support in this research project. Their guidance and knowledge in the subject matter made the project fun and interesting. I am especially thankful for their assistance in my professional development.

Financially, there are several people and organizations that made this research possible. I would like to thank the Student Support Program (SOCHE) and Wright Laboratory/Laser Hardened Materials Branch for allowing me to perform the research at WPAFB.

TASK ASSIGNMENT

This Task involved the synthesis and characterization of liquid crystalline(LC) polymers for use in optical data storage materials and optical notch filters. A LC polymer system examined at WPAFB was cyclic siloxane rings with attached cholesterol and biphenyl-based esters. These ring compounds possess unique optical properties, in the cholesteric mesophase, that are favorable to applications.

Several derivatives of these mixed esters have been synthesized in MLPJ in which the length of the tail unit on the steroid was varied to allow structure/property relationships to be explored. The steroids chosen were stigmasterol, and rosterone and pregnenolone. These molecules possess different functionalities such as the presence of a ketone, double bonds and increased branching. LC mesophase textures of these mesogens were studied using POM and DSC. The type of mesogen packing will be determined using x-ray analysis.

Both vinyl and allyloxybenzoic acids were used as the spacer groups in making the LC mesogens. Vinylbenzoic acid was purchased from Aldrich and used as received. Allyloxybenzoic acid was prepared according to the method of Apfel. The attachment of the steroid molecules to vinyl- or allyloxybenzoate was performed using a mild, room temperature, peptide esterification reaction according to the method of Hassner. The reaction allows for the conversion of one equivalent of carboxylic acid to ester by using both a carbodiimide and aminopyridine catalyst.

The LC mesogens were attached to cyclictetramethylhydrosiloxane rings using standard hydrosilation chemistry with dicyclopentadienylplatinum (II) chloride as the catalyst. Reaction progress was followed by monitoring the ratio of C=O to Si-H in the infrared, as stated in Dr. Bunning's thesis. Thermal transitions of all liquid crystalline materials synthesized were determined using DSC and POM.

All vinyl LC mesogens thermally polymerized upon heating and only first heating scans were used. Under POM, the polymerization is observed as the initial birefringent texture of a cholesteric obtained upon melting that turns black in the microscope. Upon cooling, no birefringence is observed indicating an irreversible, chemical reaction has occurred. The LC texture observed before polymerization, a strong blue color with oily streaks, is characteristic of a cholesteric mesophase. The allyl LC mesogens do not polymerize and, therefore, the breadth of the LC mesophase is observed. Increasing the tail length from cholesterol's eight carbon aliphatic unit to stigmasterol's ten carbon unit resulted in a disruption in packing that decreased the breadth of the LC mesophase. This is seen in an increased crystalline temperature and a decreased cholesteric to isotropic temperature. The breadth of liquid crystallinity changes from 106 degrees to 15 degrees for cholesterol and stigmasterol, respectively.

The effect of attaching LC mesogens to polymeric systems is known to increase the range of liquid crystallinity. This is due in part to the restrictions the polymer imposes on the mesogenic side-chains. The attachment of vinyl LC mesogens to the polymer resulted in broad LC mesophase ranges and the formation of a layered smectic phase. Increasing the spacer group length to an allyl resulted in a diminished glass transition temperature and an increased mesophase range that has become multiphasic, cholesteric and a smectic phase.

X-ray experiments are underway to determine the packing behavior of these liquid crystals. Synthesis and attachment of LC mesogens that have different functionalities will be studied in an attempt to gain further understanding of structure on mesophase packing.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 23
Student Support Program
Southwestern Ohio Council for Higher Education

Karen Hussong
Wright State University

30 June 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

I would like to thank Dr. L. V. Natarajan and Dr. Tom Cooper who have directed and assisted me in developing and performing the goals of my Task. Dr. Zbig Tokarski has been very helpful, often guiding me in solving problems that arise. I would like to thank Tim Grinstead and Sungmee Kim for their help in the synthesis procedures.

TASK ASSIGNMENT

The objectives of this Task were to synthesize and characterize biopolymers that contained nonlinearly active molecules. These polymers are then used as matrices for laser hardening devices. This involved coupling reactions with polypeptides and nonlinear optical (NLO) compounds. Synthesis was followed by characterization procedures, which involved various measurements of the compound's properties to compare with starting materials. Using this information, conclusions about the possible NLO properties and applications of these materials can be formed.

Using coupling reactions, compounds containing non linear optical properties such as, Disperse Orange 13, 1- pyrenyl methanol and p-nitrobenyl alcohol are attached to a polypeptide backbone. The polypeptides used were poly(l- glutamic acid), poly(methyl l-glutamate), and poly(benzyl l- glutamate). The two synthesis procedures involved were carbodiimide coupling and transesterification. The reaction set-up was similar for both techniques using a round bottom flask, heating mantel, stir plate and a condensor. Purification of the substituted polypeptides was performed by consecutive precipitations until all starting materials were removed. Once synthesis and purification was complete, the substituted polypeptides were characterized. Various equipment used in the research was Fourier Transform Infrared spectroscopy (FTIR), Circular Dichroism spectroscopy (CD), UV-Vis spectroscopy, rotovap, a clean room spin coater and a Dektak scanner.

The substituted polypeptides were analyzed to determine many properties. The percent substitution of the dye was determined through various methods. These were UV-Vis spectroscopy, elemental analysis and NMR spectroscopy. CD spectroscopy was used to determine the structure of the polypeptide and to determine if the dye exhibited an induced dichroism, once attached to the polypeptide. Thermal gravimetrical analysis (TGA) was performed on each polypeptide to determine at what temperature the polymer will begin to decompose. Differential scanning calorimeter (DSC) results were analyzed for melting points and other types of phase changes.

Producing thin-films of the various substituted polypeptides involved mostly trial and error combinations of various solvents and concentrations. Eventually, some acceptable films of p-nitrobenzyl alcohol with each polypeptide were made in which aligning and NLO properties were tested.

The poly-L-glutamic acid substituted with pyrenyl methanol, disperse orange 13, and p-nitrobenzyl alcohol yielded gave the following percent modification respectively, 23%, 16% and 35%. The other substituted polypeptides were modified less than 10%. The poly-L-glutamic acid substituted with disperse orange 13 and nitrobenzyl alcohol were alpha helix with an induced dichroism.

The poly-L-glutamic acid substituted polymers yielded better films. This was due to the higher percent modification and greater processibility. It was also found that the NLO response increased with increasing film thickness. The poly-L-glutamic acid modified with p- nitrobenzyl alcohol produced the greatest NLO results. This polypeptide has good clarity and a second order response; however, the temporal stability of the polymer needs to be improved. A crosslinking agent is currently being incorporated into the polypeptide in an attempt to improve this weakness. The crosslinking also may "lock-in" the alignment after corona poling. From the systems synthesized, a foundation for the future will be established.

CERAMIC FIBER MATRIX COMPOSITES

Task Order No. 24
Student Support Program
Southwestern Ohio Council for Higher Education

John R. Welch
Wright State University

15 June 1993

Government Task Leader
Dr. Ronald J. Kerans
WL/MLLM

ACKNOWLEDGMENTS

I wish to thank Dr. Randall Hay and Dr. Ronald Kerans for the opportunity to learn and work in an experimental materials laboratory. I also wish to thank the rest of the ceramics group and the staff of the metallography laboratory for their assistance as I learn the different aspects of ceramic fiber matrix composite processing, metallography, and characterization.

TASK ASSIGNMENT

The recently concluded Task at the Wright Laboratory/Materials Laboratory has consisted of many processes. The majority of this Task was the lay up, processing, heat treatment and characterization of ceramic fiber matrix composite samples. Other work included characterization of experimental fiber samples produced by other laboratories. Zirconium and zirconium compound samples were also produced for creep testing.

The ceramic fiber matrix composites produced were almost exclusively samples of YAG (Yttrium-Aluminate) powder with sapphire fibers. The sapphire fibers were coated with a variety of materials that included molybdenum, palladium, silica, charcoal and combinations of the before-mentioned materials.

The fiber coating process was performed on an apparatus designed and patented by Dr. Randall Hay. The fiber coating apparatus consists of a fiber spool mount, a specially designed glass apparatus that holds the coating material, a small vacuum pump to recirculate the coating material, a furnace and a fiber winding spool mount driven by a small motor on top of the apparatus.

The fiber is pulled through the coating solution into the furnace for drying. At times, an argon introduced controlled atmosphere stage was placed between the coating and drying phases of the operation. The fiber is wound on a spool after the drying phase. This process is repeated several times to ensure the fiber is thoroughly coated.

After the coating process, the fibers are cut to length and laid parallel on tape. When this process is completed, the fiber layouts are sectioned into 1/4 inch squares for insertion into a cylindrical graphite die that has a 1 1/4 inch rectangular opening through its center. The fiber section squares are loaded in the graphite die between measured layers of YAG powder. The graphite die is lined on the top and bottom with two layers of graph foil at each end. The graphite die is then placed in the hot press. The chamber of the hot press is pumped to induce a vacuum and the pressure on the die is gradually increased to approximately 200 pounds per square inch. The temperature in the press is then slowly raised to around 1,700 degrees centigrade. When this temperature is attained, the pressure is raised to 300 pounds per square inch. An optical thermometer and gauges are used to monitor the temperature, pressure, vacuum and sample compression. The sample is allowed to cool and the pressure is released while still inside the hot press.

After the sample is removed from the hot press and graphite die, the characterization process is begun. Small sections of the sample are cut on low speed diamond saws. One of these pieces is then mounted in a Bakelite material called epomet, put in a mounting press and polished. Other pieces are heat treated in high temperature ovens to observe various composition changes that may occur. These pieces are then mounted in epomet and polished.

The polishing phase is a step process where the sample is ground flat on a diamond enmeshed disk and then polished on a rotating brass wheel covered with a piece of silk. A variety of diamond compound and diamond suspension polishes are used. The grains of the diamond compounds/suspensions range from forty-five micrometers to one-tenth micrometer. The polished epomet mounted sample specimen is then mounted on a glass slide. The sample is cut on a low speed diamond saw such that the piece attached to the slide is approximately 1 millimeter in thickness. The exposed portion of the sample is then ground and polished until the sample is approximately 5 micrometers in thickness. The remaining portion of the epomet mounted sample is also reground and repolished.

Small copper grids are glued on the thin section of sample and the grids are removed from the glass slide with the sample sections attached to them. Photographs are sometimes taken of the sample prior to this step. Photography is accomplished on a microscope that is designed to hold a camera. The copper grids are placed in an ion milling device where argon atoms are "shot" at the sample at a 15 degree angle to cut a hole through it.

The sample is then viewed and photographed on a transmitted electron microscope. The epomet mounted sample is sometimes viewed under a scanning electron microscope. The high resolution reveals reactions and inconsistencies in the interphase between the ceramic material and the fiber.

The desired result is to find a combination where the fiber remains separated from the ceramic matrix during the processes of hot pressing and heat treating. Most of the results have shown a reaction between the fiber and the ceramic material due to a breakdown of the fiber coating. The most recently produced sample, utilizing a thick fiber coating of molybdenum and palladium, has shown promise. The fiber coating was nearly continuous around the fibers after processing and heat treating at a temperature as high as 1,400 degrees centigrade for a 10 hour duration.

The ultimate usage of a successful ceramic fiber matrix composite would be as a light weight, strong, durable material in an aircraft. Other testing of a successful composite will test the stress and strain capabilities of the material under large applied loads. "Bend bars" are made for such purposes. These are merely long rectangular sections of the composite material that will be subjected to the applied loads in specialized testing equipment with monitors attached.

Other characterizations were made for pollusite without fibers. Heat treatment of pollusite has resulted in various chemical reactions at this time, but additional testing and characterization is continuing. Heat treated samples of natural pollusite were recently made and show some promise of being a durable ceramic material.

Characterizations of various types of experimental fibers have also been performed. The material composition of these fibers has included YAG, mullite and silicon carbide treated and cured with various reagents. These fibers have not yet been used in the ceramic fiber matrix composites during this Task.

Creep testing of zirconium and zirconium compound materials was also performed. The zirconium samples are ground into a rectangular box-like shape and the ends are ground parallel. The samples are then subjected to large pressures in testing equipment. The sample is then analyzed to identify dislocations and slip planes caused by deformation under the extreme loads. Very limited amounts of this testing were performed during this Task.

STRUCTURAL CERAMIC COMPOSITES

Task Order No. 25
Student Support Program
Southwestern Ohio Council for Higher Education

Kimberly Andrews
Wright State University

30 July 1993

Government Task Leader
Dr. Ronald Kerans
WL/MLLM

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

Research

Continuous ceramic fibers present an attractive package of properties. They combine high strength and elastic modulus with high-temperature capability and a general freedom from environmental attack. These characteristics make them attractive as reinforcements in high-temperature structural materials.

There are three types of ceramic fiber fabrication methods: chemical vapor deposition, polymer pyrolysis and sol-gel techniques.

The latter two routes involve novel techniques of obtaining ceramics from organo-metallic polymers. The great breakthrough in the ceramic fiber area has been the concept of pyrolysis. Under controlled conditions, polymers containing silicon, carbon or nitrogen are used to produce high-temperature ceramic fibers. The pyrolysis route of producing ceramic fibers have been used with polymers containing silicon, carbon, nitrogen and boron with the end products being silicon carbide, silicon nitride, boron carbide, and boron nitride in fiber form, foam or coatings.

An important type of ceramic fiber is the alumina fiber. Different types of this fiber are produced by several companies. Du-Pont produces a continuous filament polycrystalline alpha-alumina yarn. The Sumitomo Chemical Company produces a mixture of alumina and silica fiber. The process starts with polyaluminoxanes of a mixture or polyaluminoxanes and one or more kinds of silicon-containing compounds and a precursor fiber is obtained by dry spinning. This precursor fiber is then calcined to produce the final fiber. The 3M Company produces a ceramic fiber composed of 62% alumina, 14% boria and 24% silica. The fiber has the trade name Nextel 312. The manufacturing process involves a sol-gel technique, and the starting materials are solutions of metal alkoxides. Metal alkoxides are M(OR)n type compounds where M is the metal, n is the metal valence and R is an organic compound. Selection of an appropriate organic group is very important. It should provide sufficient stability and volatility to the alkoxide so that the M-OR bond is broken and MO-R is obtained to give the desired oxide ceramics. Hydrolysis of metal alkoxides results in sols that are spun and gelled. The gelled fiber is then densified at intermediate temperatures. The high surface free energy available in the pores of the gelled fiber allows for a relatively low-temperature densification. Currently, the process of carbon coating single crystal alumina fibers via phenolics is being investigated.

DESCRIPTION OF RESEARCH

Experimental Procedure

Single crystal alumina fibers were acetone washed, sonicated for 5 minutes, and air-dried. A 5 weight percent phenolic-isopropanol was prepared to dip coat the fibers one to three times with a 10 minute air dry between coatings. The following experiments were performed on the fibers:

1. Three fibers were double coated, heat-treated to 600C @ 1C/min. flowing nitrogen and soaked for 0.01 hr.

2. Three fibers were double coated, heat-treated to 525C @ 1C/min. flowing nitrogen and soaked for 0.50 hr.

3. Three fibers were double coated, heat-treated to 475C @ 1C/min. flowing nitrogen and soaked for 1.5 hr.

4. Three fibers were double coated, heat-treated to 480C @ 1C/min. flowing nitrogen and soaked for 1.0 hr. A rectangular alumina boat was used and poured coating mixture completely over fibers.

5. Three fibers were double coated, heat-treated to 480C @ 1C/min. flowing nitrogen and soaked for 1.0 hr. Used rectangular alumina boat and poured coating completely over 2 of 3 fibers.

6. Three fibers were double coated, heat-treated to 480C @ 1C/min. flowing nitrogen and soaked for 1.0 hr. Used rectangular alumina boat and poured coating mixture into basin of the boat, but did not immerse fibers.

7. Three fibers were double coated, heat-treated to 500C @ 1C/min. flowing nitrogen and soaked for 0.50 hr. Used rectangular alumina boat.

8. Three fibers were double coated, heat-treated to 230C @ 1C/min. in flowing oxygen and 3.0 hr. soak, followed by a heat treatment to 400C @ 1C/min in flowing nitrogen and soaked for 0.01 hr. Used rectangular alumina boat.

9. Three fibers were double coated, heat-treated to 220C @ 1C/min. in flowing oxygen and 3.0 hr. soak, followed by a heat treatment to 400C @ 1C/min in flowing nitrogen and soaked for 0.01 hr. Used rectangular alumina boat.

10. Three fibers were double coated, heat-treated to 220C @ 1C/min. in flowing oxygen and 0.5 hr. soak. Used rectangular alumina boat.

11. Three fibers were double coated, heat-treated to 300C in flowing nitrogen gas @ 1C/min, 1.0 hr. soak.

12. Three fibers (3/16"length) were double coated, heat-treated to 260C @ 0.5C/min and from 260-460C @ 1C/min. in flowing nitrogen gas in DTA (density thermo analyzer).

RESULTS

Experiments 1-3 yielded poor results. The coating was totally removed in the first experiment, while the coatings from experiments 2 and 3 were barely visible. The carbon coatings from experiments 4-11 were poor, i.e., the coating was not dark in color and not continuous along the length of the fiber. At first, it was thought that the cause of these undesirable results was that after the heating cycles, the tube furnaces used were not able to cool to room temperature but to 200C, which probably allowed the carbon coating to burn off the fiber surface. Thus, experiment 12 involved use of the DTA, which was set to heat at a lower rate and cooled to room temperature. However, the coating yielded was barely visible. It was later found that phenolics yield only approximately 40% carbon. Carbon products probably would form in bands since the phenolic loses 50% of its volume to degradation products. The fiber expands with heat to produce distinct bands of carbon products and clean fiber along the length of the fiber. Future work will involve heating the fibers in an inert atmosphere at a rate of 0.1C/min. If poor results are obtained, then a polyaeroacetylene solution, which yields 90% carbon, will be tested on the fibers.

STRUCTURAL CERAMIC COMPOSITES

Task Order No. 25b
Student Support Program
Southwestern Ohio Council for Higher Education

Ayman S. Amara
University of Dayton

30 July 1993

Government Task Leader
Dr. Ronald Kerans
WL/MLLM

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TASK ASSIGNMENT

Bending and indentation tests have been used to determine the mechanical property of the interfacial layer in ceramic matrix composites. Previous tests (push-in and pull-out tests) have shown a significant relationship between roughness of the interface and Possions effects.

The effects of the interfacial roughness which contributes to the sliding resistance have been neglected by most researchers. The objective of the Task is to test the theoretical models that provide an insight into the effects of the interfacial roughness during progressive debonding.

MODELS: 1. The specimen of the first model is a Cylindrical fibers "YAG" of a finite radius and 1 inches length embedded in a tetrahedral matrix (L=1.25', W=8/64', T=17/64") made of B Alumina. An artificial crack notch of about 1 millimeter was made in the matrix at the midpoint of the specimen. The specimen is supported at both ends where the notch was made while load is applied on the opposite face at the midpoint. This model is considered to be independent of deflection and stress distribution along the bonded interface.

2. The specimen of the second model is Tetrahedral Crystals of finite dimensions where l=5 mm, w=2 to 3 mm and t=1 to 2 mm embedded in a tetrahedral matrix (L = 25 mm, W = 3 mm, T = 6.7 mm). The crystal was made of "YAG doped in Calcium or undoped" or Neodymium while the matrix was made of B Alumina. An artificial crack notch of about 1 millimeter has been made at the midpoint of the specimen. The specimen is supported at both ends where the notch was made while load is applied on the opposite face at the midpoint. This model is independent of any deflection and stress distribution along the bonded interface.

PROCEDURE

Both models have been prepared adequately by using a Hot Press technique where 30 grams of B Alumina was used for the first model, while 13 grams of B Alumina was used for the second model. Square die of 1.25" was used for the first model, while round die of 1 inch was used for the second model. For both models, Molefoil and Grafoil, have been used to isolate hot press powder B Alumina from any leakage out of the center of the chosen die. Applied pressure was held constant at P = 50 psi on ram while the temperature was changed from 0° C to 1425° C by changing applied power from the set point of 28 KW to 38 KW.

Samples from both models have been annealed at 1400° C for about 72 hours at the rate of 10° C. The polishing technique from grade 36 to 3 micron was then applied. Thin and sharp blades were used to slice samples of either models into several slices of given dimensions. An artificial crack notch of about 750 micron was made perpendicular to the cut plane. Then several Metallographic pictures were taken for later comparison.

A bending test has been applied using digitalis 8562 INSTRON machine where load has ranged from 80 to 100 psi. Then Indentation test using Vicker hardness head has been applied along the interface of fiber or crystal and matrix to study the crack behavior and the toughness of the interface. (See Figure 1)

1. Bending test:

$$K_{lc}=3\frac{PL}{2bw^2}a^{0.5}f(\frac{a}{w})$$

$$f(\frac{a}{w})=1.99-2.47(\frac{a}{w})+12.97(\frac{a}{w})^2-23.17(\frac{a}{w})^3+2.48(\frac{a}{w})^4$$

where:

a = depth of the notch.

B = width of the slice

L = length of the slice

w = thickness of the slice.

Example:

a = 0.8mm, w=5.9mm, b=3.4mm, L=19mm, P=87lb

$$f(\frac{a}{w})=1.834$$

$$K_{lc}=\frac{3(87)(0.019)}{2(0.0034)(0.0059)^2}(0.008)^{0.5}(f(\frac{a}{w}))=12.288(10)^3$$

$$K_Q=4.784MPa\sqrt{m}$$

2. Indentation test:

$$HV = \frac{Test\ Load\ (kgf)}{Surface\ area\ of\ the\ Indentation\ (mm^2)}$$

$$HV = \frac{2F sin(\frac{x}{2})}{D^2} 1000$$

$$HV = 1854(\frac{F}{D^2})$$

where:

HV - Vicker hardness

G - Test Load (gf)

D - Arithmetic mean of the two diagonals D1 and D2 (micrometer)

X - Angle between the opposite faces at the vertex of the pyramid indenter, (136)

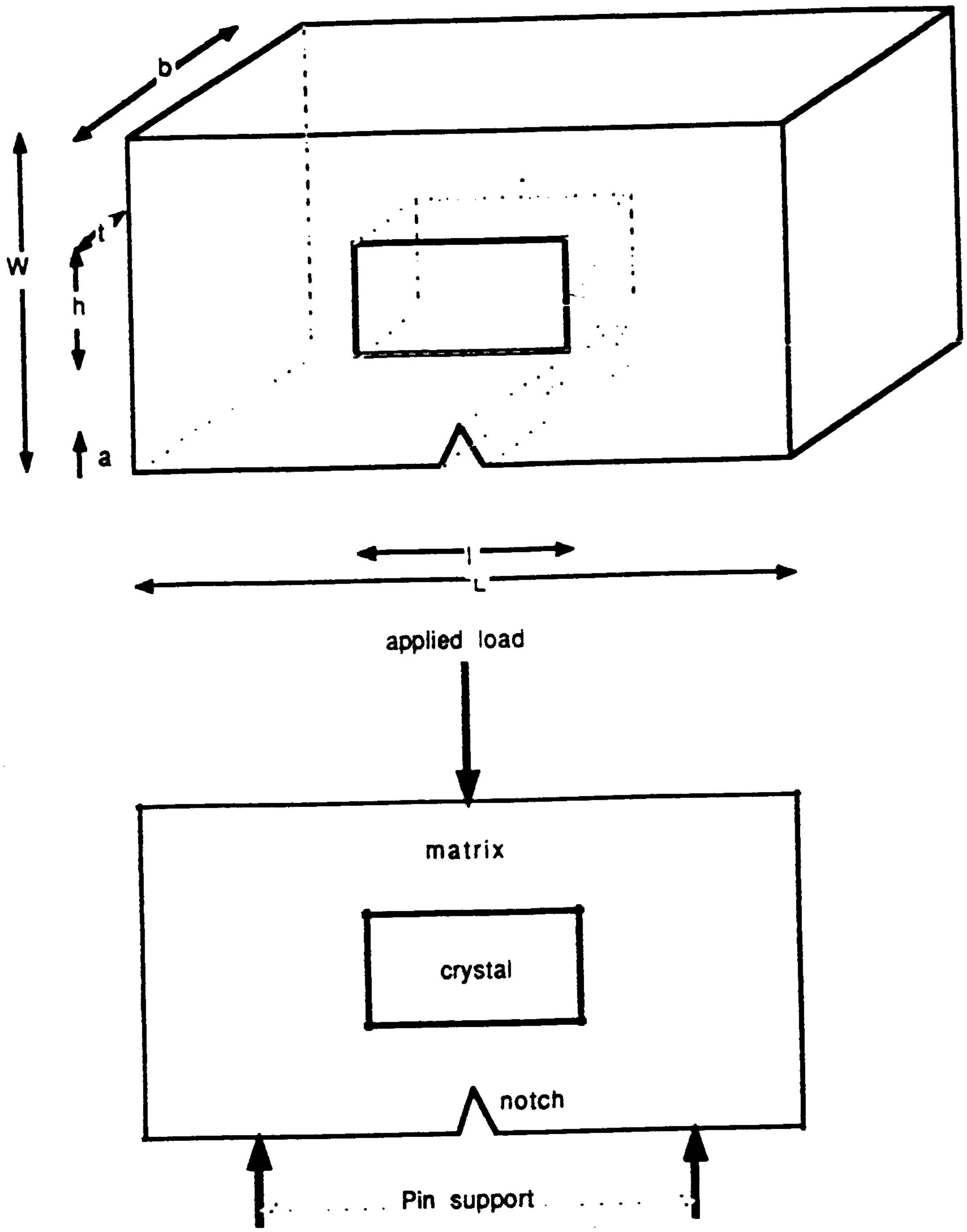

Figure 1

Illustrated Bending and Indentation Testing

RESULTS

1. Debonding has been noticed clearly along one side of the crystal interface. It might be due to thermal expansion during annealing process.

2. A crack has been noticed bridging over the crystal and fiber. It might be due to applied pressure during hot press or thermal stresses during annealing process.

3. Cracks also have been noticed in the matrix along grain boundary in doped specimen. This could be due to absorption of calcium from doped crystal into boundary layer of matrix.

4. Cracks tend to go in different directions at triple point following neither parent cracks.

5. Cracks in two neighboring slices have shown similarity in behavior. Cracks might be a 3D phenomenon.

CERAMIC POWDERS

Task Order No. 26
Student Support Program
Southwestern Ohio Council for Higher Education

Cynthia L. Emerick
Wright State University

5 June 1993

Government Task Leader
Dr. Ronald Kerans
WL/MLLM

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I would like to thank Dr. Paul Jero for his guidance during this year. He has helped me understand the significance of the research. It is truly amazing how the scientific ideas become projects in the research laboratories. I also would like to thank Dr. Ronald Kerans for recommending me for this Task so that I could become a part of this productive group. The experience working in the environment of Wright Patterson Air Force Base and interacting with the people have enhanced my future in the engineering field.

People that I would like to thank in the other departments are Mike Scott, Bob Lewis and Eric Fletcher. They have all helped me learn to operate all the metallography equipment. I also want to thank all other facility members of WPAFB, I have learned from everyone.

TASK ASSIGNMENT

The properties of the fiber/matrix interface in ceramic matrix composites (CMC's) are a current interest in the research of the Ceramic Division at WPAFB. These properties are important factors in determining the mechanical behavior of CMC's. Many techniques have been advanced to measure interfacial properties by a push-out or push-in fiber testing method. Fiber push-out and push-in tests have been used to examine the interfacial behavior in a variety of ceramic composites. Numerous push-out tests have been performed and the data analysis calculated so that the interfacial behavior of CMC's can be evaluated. This process of making and preparing the samples to be tested, testing the samples, and evaluating the properties and the behaviors of the composites are all part of my responsibility in the Ceramic research department. These behaviors will be very important for determining the methods of use of ceramic matrix composites.

To perform tests on CMC's, the specimens must first be fabricated from packing a ceramic powder then adding rows of fibers followed by more powder. The compact powder composite is then hot pressed in a vacuum at a high temperature until it has cured. This is the general process for making the specimens. Then the specimens are made suitable for testing by cutting, polishing and taking photos of them.

The samples for push-out and push-in testing are becoming more complex. Sample preparation and testing skills need to be very precise. Currently, the testing is moving to single microcomposites imbedded in layers of glass, which is again a form of ceramic powders. These microcomposites are bringing new complications in the interfacial measurements that need to be evaluated.

Knowledge of most of the equipment is necessary in all the labs. In the metallography lab, the use of all the polishing equipment, microscopes, photography and chemicals is a basis for preparing specimens for testing. Another piece of equipment that is introduced is the push-out tester. The fiber push-in/out apparatus includes a loading probe mounted on a load cell and an

X-Y stage on a slider that allows precise positioning of a sample. The use of a microscope and a video camera allows the sample to be viewed on a video monitor. The specimens' fibers range from 13 µm to 125 µm in size; therefore the accuracy of the positioning is important. This entire apparatus is mounted on a universal test machine that provides a constant displacement rate and load. These tests are performed with two types of loading probes, a tungsten carbide cylinder or a truncated diamond cone. After the tests have been performed, a series of data analysis was done on different computers, different programs and different ideas. Therefore, a background in computers is useful for research.

The tests for this report have all been performed and the analyses have been calculated. The analysis begins with subtracting the compliance of the testing system from the raw data so that the data holds only the behavior of the fiber debond. Results of this type of research depend on the fabrication of the samples, the preparation of the samples and the analysis of the data. So much more still needs to be learned on this subject to derive conclusions; but the continuation of guided experiments and interpretation can only yield answers in the discrepancies of research. The processes of research techniques are an important factor that is taught working as a student at WPAFB.

CERAMIC COMPOSITES

Task Order No. 27
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Southwestern Ohio Council For Higher Education

Cathleen M. Gustafson
Wright State University

15 June 1993

Government Task Leader
Dr. Ronald Kerans
WL/MLLM

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I would like to thank Dr. Ronald Kerans for recommending me for this Task. It is an enjoyable and enriching experience to work with such a helpful group. I would especially like to thank Dr. Rollie Dutton for all his help and guidance. He is helping to prepare me for when I will be an engineer and become familiar with all the aspects of an engineering project. Dr. Dutton has shown me that the work we do is significant for more than just us.

I would like to thank all the other people I worked with. Everyone is very helpful and supportive. Special thanks go to people in other departments, especially Mike Scott, Bob Lewis and Eric Fletcher in the metallography lab for all their help and patience.

TASK ASSIGNMENT

Ceramic matrix composites (CMC's) are of current interest in the research of the Ceramic Division at Wright Patterson Air Force Base. The processing procedure of CMC's is important in creating a good quality, reusable part. Many processes were used in the past to make fiber reinforced CMC's using whiskers. The area of producing CMC's reinforced with continuous fibers is still wide open.

One main way of making continuous fiber reinforced CMC's is by packing the ceramic powder around the fibers and hot pressing the compact. This process is time consuming and costly. An alternative to this approach is a process called tape casting, which is currently being used for metal matrix composites. The adaptation of this process for the production of CMC's has been the focus of this Task.

Tape casting is the process of creating a very thin-film (about 8 mils = .008 inches thick) of ceramic foil. The tape is cast on a long, level clean piece of glass. The film is made of a ceramic slurry. The slurry is poured in front of a doctor blade. The doctor blade is set to the required height and is pushed over the glass by a motor. The slurry is then allow to dry for about 2 hours. The CMC's are then made from this foil.

There are many steps involved in the creation of CMC's. With all projects, the selection of the materials used is very important. Other steps include determing the correct formula of the slurry to use, how to lay-up the fiber/matrix mats, the exact sintering process to use and the testing of the developed CMC's.

One goal of the group is to create a versatile procedure that will work for a variety of ceramics and fibers. Because a variety of things was examined and compared, it was important to take very accurate notes. These notes made it possible for formulas and procedures to be compared precisely.

It was decided to start working with a glass matrix before going on to other types of polycrystalline matrices. This would allow a working formula and procedure to be created and not be too costly. Silicon Carbide fibers are extensively used in industry, especially SCS-6. This and another comparable fiber called Sigma fibers were to be used in these CMC's.

In developing a formula to use, the ratio of binder to glass and glass to solvent is very important. Too much binder made the foil stick to the glass and tear upon removal. Too little binder made the ceramic foil brittle and hard to handle. Putting too much solvent in the formula made the slurry to thin and there was too much shrinkage upon drying. Not having enough solvent in the slurry greatly decreased the yield and made it hard to work with. Once the ratios were worked out, the decision had to be made on the type of glass to use.

An important factor to consider when chosing the type of glass was the coefficient of thermal expansion. The relationship between the fiber and matrix was solved prior to formula seven. With minor modifications in the amount of binder, this formula can be used for many different types of ceramics.

How to lay-up the fiber/matrix mats at first was thought to be the simplest and perhaps the least important part of the whole process. Through the ongoing research it was determined that the lamination step is important in creating a good final product. The lamination step was done by putting the fibers, either singularly or as a mat, on the tape and then partially imbedding them. The fibers were imbedded by heating the foil and fiber to approximately 200°F and using a minimum amount of pressure to force the fibers half their diameter into the tape. These foil/fiber layers were then laid on top of each other with a blank tape on top. This stack was heated and light pressure was applied to the layers so they would remain together. The shape needed could then be cut from the finished laminate.

The final processing of CMC's in the past was done by a process called hot pressing. This process requires high temperatures and high pressures. The equipment is very expensive. It was hoped that a process could be developed to get a fully dense sintered product without hop pressing. The sintering process is done in a regular tube furnace at lower pressures. This greatly reduces the cost. Much work has been done and is still being done on developing this process. The final process is almost completed.

A few good specimens have been produced. Samples are being mounted and polished to determine the fiber indexing and the amount of porosity in the specimen. Other specimens had many tests performed on them. The main tests are non-destructive and tensile tests. The results of these tests indicate that the processing method currently being examined shows great promise.

RESEARCH ON TERNARY AND HIGHER-ORDER SILICIDE INTERMETALLIC ALLOYS

Task Order No. 28
Student Support Program
Southwestern Ohio Council for Higher Education

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15 September 1993

Government Task Leader
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WL/MLLM

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I want to thank the entire Metallography Laboratory staff who answered my questions throughout the 2 years I have worked here. In addition, thank P.R. for his guidance and helpfulness.

TASK ASSIGNMENT

During this Task Assignment, several engineers were assisted with technical support for their projects. Heat treatments of metal alloys were conducted, preparation of specimens for metallographic examination was performed and utilization of an optical microscope and a scanning electron microscope (SEM) to observe the surface of a variety of specimens.

DESCRIPTION OF RESEARCH

The heat treatments were performed in a temperature range of 1200°C - 1500°C. For the alloys that contain Niobium, Titanium, Hafnium, Aluminum, Silicon and Chromium they were heat treated in the temperature range of 1300°C - 1500°C for a period of 24 - 100 hours. The specimens that were heat treated at very high temperatures for long periods of time were required to be wrapped in Ta foil and placed in a furnace with flowing argon. To prevent the oxidation and disintegration of the alloy specimens at these high temperatures, the sample was wrapped in Ta foil and the furnace chamber was evacuated with flowing argon. The specimens that were heat treated at approximately 1200°C were usually oxidation tests which required no Ta foil or Argon. The specimens were just placed in the hot air furnace for the allotted time. The heat treated specimens were then prepared for metallographic examination.

The samples were cut, if needed, by diamond saws and mounted in Konductomet in a mounting press. Fastening the specimens in a metal ring, they were attached onto the sweeping head of the Maximet automatic grinding/polishing machine. The head would spin, whether it was sweeping or in a fixed position, in the opposite direction of the rotating motion of the platen. The platen was covered by descending grit paper (240-600). The next step was to rough polish the samples with the 15µ and the 6µ perforated Teximet cloth platens. The samples were then released from the ring, secured in weighted holders and placed on the Vibromet for 24 hours or less depending on the type of material.

After this procedure, the polished surfacemicrostructure was examined by an optical microscope and by a scanning electron microscope (SEM, Leica 360, Jeol 840). In the Leica 360 a type of SEM, the images of the microstructure are digitized and loaded onto a computer disk. These images can later be manipulated using the computer software Adobe Photoshop. Other SEM machines and optical microscopes require Polaroid film. Graphs of load versus displacement from tension were converted, compression and bend bar tests to stress versus strain plots were done. This Task was completed by using computer software such as Kaleidagraph and Microsoft Excel.

The equipment used was an automatic specimen grinder/polisher (Maximet) and a Reichart - Jung Xenon Microscope to optically observe the surface of the metal. In addition, scanning electron microscopes were used to analyze the microstructure of the surface. The two types that were used were the Jeol 840 and the Leica 360. The images from the Leica 360 were digitized and loaded onto a computer disk so evaluation of theses images could be conducted at a personal computer. Diamond embedded blades were used to cut material. The conversion of data from the load versus displacement was completed by using the displacement formulas:

$$stress = \frac{load}{area} \text{ and } strain = \frac{displacement}{original\ length}$$

RESULTS

The procedure for running the Leica 360 was learned, as well as the software used, to manipulate the images obtained from the scanning electron microscope. In addition, TiAl was found to react badly, when exposed to a long period of time on the Mastermet Vibromet. Mastermet will react with TiAl causing cracks in the material.

COMPUTATIONS ON INTERMETALIC COMPOUNDS

Task Order No. 29
Student Support Program
Southwestern Ohio Council for Higher Education

Carlos Hernandez
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31 August 1993

Government Task Leader
Dr. Dennis M. Dimiduk
WL/MLLM

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TASK ASSIGNMENT

The 2D graphics package developed during the previous Task has grown twice fold during the current Task and has the potential to grow even further. The user's guide and reference manual have been revised and expanded to reflect these changes.

The package was developed to be general in nature to provide maximum flexibility in its utilization, without losing its user friendly interface. The necessary capabilities were built into the software by breaking it down into modules. These modules can be used separately or be used together as a whole. Every module was written so that the user could allow the package to take care of everything, or let the user take full control. In this way, an attempt was made to satisfy everyone's needs. This software provides screen output capabilities under systems supporting the X environment and as output for postscript devices. This package was developed under the GKS (the Graphical Kernell System [ANSI85b]) on a Sun Mycrosystem Sparc Station 2, the Open-Look interface and the UNIX operating system. It supports the grouping of logically related primitives (such as lines, polygons and character string) and their attributes into collections called segments. These segments may not be nested.

The software was initially implemented using the C programming language, however, a full Fortran interface has been added to it. In addition, an on-screen tutorial has been added that enables newcomers to get a friendly introduction. This on-screen tutorial is not a substitute for the user's guide. It was simply intended to make users feel more comfortable and get results quickly.

Two 3D graphic packages are currently being developed. The first one is being developed under the Precision Visual platform, commonly known as PVWAVE.

This package has a very user friendly interface. A user needs only to point and click to get results. Using this package, the scientist can manipulate data interactively and display the results as volumes, surfaces, contours or any three dimensional geometric figure. The package goes beyond this, compared to other graphics software commercially available, it allows the user to take four dimensional data (which is mostly used in scientific research) and represent it as a three dimension object. It begins with a simple point and click user interface: the scientist may rotate, translate the entire object or better yet pick the object apart. The package enables the scientist "to go inside the object," take slices, i.e., planes of any regions within, with any kind of orientation and display the results as surfaces, contours, etc.

The capability of this software is a powerful one, because it allows the materials' scientist to analyze the results of the atomistic and quantum mechanical simulations in a new way.

The drawback of this package is its unfriendly interface with software written in other programming languages (this is the gap expected to be filled by the second package). It is possible for other software to interact with it. However, its limitations and front face interface is cumbersome and painful enough to discourage almost everyone. This module is powerful as a stand-alone, capable of fulfilling almost everyone's needs.

The second package currently being worked on is built under PHIGS (Programmer's Hierarchical Interactive Graphic System [ANSI88]). This package, as its name implies, does support nested hierarchical groupings of 3D primitives, called structures. In it, all primitives, including invocations of substructures, are subject to geometric transformations (scaling, rotation and translation) to accomplish dynamic movement. It also supports a retained data base of structures that the programmer may edit selectively; it automatically updates the screen whenever the data base has been altered.

Several mathematical tools have been developed tosupport the displaying of information from large input data decks involving differential displacement of atoms, local strains etc. Among these a method of transformation of non-uniform data grids, into uniform ones, via interpolation was developed. This is an area currently being studied by experts in the field of mathematics for no perfect method exists, only approximations. In trying to get the best possible results, every library in the area, was visited and many books consulted. Different mathematicians in the area, whose field of expertise is numerical approximations were consulted. In doing, new information and approaches were learned. The result from these led to an algorithm, which although not a perfect one, was satisfactory.

The researcher also served as the System administrator, performing such tasks as restoring lost files from backup tapes, managing UNIX processes, planning and performing backups, setting-up printers and the spooling system, making the system secure, etc.

PHYSICS OF CONDUCTING POLYMERS AND OPTICAL FILMS

Task Order No. 30
Student Support Program
Southwestern Ohio Council for Higher Education

Henry Derstine
University of Dayton

31 December 1993

Government Task Leader
Dr. Robert Spry
WL/MLBP

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TASK ASSIGNMENT

The Task had four major areas of emphasis; 1) to measure the conductivity of various polymer samples, 2) determine whether the conductivity of a polymer is ionic or truly an electronic characteristic, 3) use the Brewster angle technique to measure the refractive index of optical polymer samples, 4) and measure the optical quality of samples.

The procedure for measuring the conductivity of the polymers is done by using a four point probe technique. This experiment is run off a Keithley S110 test system. Dr. Bai would present a sample that was to be tested. The sample would then be prepared for measurement in S110 test system. This preparation was done by cutting a strip from the sample, measuring the effective length, placing the sample in the test module mounting the module in the system and then beginning the computer sequence.

The cutting of a sample involved using a razor blade and a straight edge and cutting a strip from the larger film approximately 2 cm long by .2 cm wide. The precise dimensions for the calculation of the effective length were then measured under the microscope. The effective length is equivalent to the (Width*Thickness)/Length (between the contacts). The sample was then placed in a Teflon holder that was then connected to the S110 circuit. The program that controlled the current and did the calculations for the resistivity of the sample was then run. The program to calculate the proper resistivity and conductivity of the sample needed the effective length to be entered into the system. Other information was also entered for sample identification and record keeping.

The second major task undertaken was to determine if the conductivity of a sample is either ionic or electronic. The experiment used to determine this is known as a depletion experiment. The methodology of the experiment is to run a constant voltage across the sample and observe the effect of time on the current through the sample. If the sample is truly electronic, the current will remain constant as the voltage is held constant. If the sample is ionic, the current through the sample will display some kind of decay. The experiment was set up to a Keithley 617 unit and a computer for data acquisition. Most of the time spent in this area dealt with one specific type of sample. Numerous trials were run at different voltages for 20 hour periods. This was to show that the results were reproducible. The data from each of the runs were then plotted using a log/log current vs. time format. The results seem to show that the polymer was an ionic conductor and not an electronic one. The third area of work was that of using a Brewster angle measurement to determine the refractive index of a sample. This was done using an old ellispsometer set up, which included a polarizer, laser source and a detector. The samples were mounted on the center stage of the ellispsometer. Calibrations were then done to insure the alignment of the system was optimized. P-wave polarized light from the laser source would strike the sample on its surface at a specified angle, the reflected light would then be collected in a detector (power meter), this value along with the angle of the sample would be recorded. The angle would then be varied (.5 degrees) and the new values recorded. The data would then be plotted on a semi-log plot of reflected intensity vs. wavelength. The graph would display a minimum intensity value at an arbitrary angle. By taking the tangent of the angle you would then have the value of the refractive index.

The fourth and last area of focus was using the Hitachi UV 4001 (spectrophotometer) to do optical characterization of samples. The experiment was computer driven and only mounting the sample required time. The system parameters were set up before a base line was run. The parameters that were set included range and speed of scan, time/wavelength scan, absorbency/transmittance, etc. The base line is then run, the sample is placed in the center of the unit and the test scan is run. The data is plotted on screen and can be manipulated in several ways. This information can aid in determining the thickness and composition of the sample.

PHYSICS OF CONDUCTING POLYMERS AND OPTICAL FILMS

Task Order No. 30a
Student Support Program
Southwestern Ohio Council for Higher Education

Joseph R. Demers
Wright State University

31 December 1993

Government Task Leader
Dr. Robert Spry
WL/MLBP

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I would like to acknowledge and thank Dr. Spry and Dr. Bai for help and guidance during the application of this Task.

TASK ASSIGNMENT

As batteries are required to produce more current over longer periods in more extreme environments, new processes for battery construction become necessary. One of the present hopes is that conductive polymers offer a means to reduce battery weight and environmental sensitivity. By developing polymers which can conduct ions, it would be possible to remove the fluid which is commonly used for this purpose. In a lead-acid battery this fluid is usually sulfuric acid. The removal of this fluid would not only decrease the weight of the battery, but also would eliminate a highly corrosive substance from the battery.

The inverse of resistance is conductivity. By measuring the resistance per unit length of a polymer, it is possible to calculate the conductivity. Unfortunately, in polymers, unlike in metals, conduction characteristics can be dependent upon direction of measurement. In the past, a conductivity measurement involved four contact points across the surface of the polymer sample. The possibility that this configuration would only measure the surface conductivity forced the development of a technique to measure the conductivity through the sample. A new sample cell was fabricated out of non-conductive teflon. The cell sandwiches the polymer between two rows of contacts, each row containing four contact pins. By doing resistivity measurements across the sample as well as through the sample it is possible to make surface and bulk measurements without moving the sample. Initial tests with the new cell indicate that there is little difference between bulk conductivity and surface conductivity.

Another developing application for polymers (not necessarily conducting polymers) is optical computing. It is hoped that by developing polymers which are sensitive to electromagnetic radiation it will be possible to create optical switches, or optical transistors. This sensitivity to electromagnetic radiation is generally referred to as "non-linear behavior," and effects the index of refraction of the polymer. Polymers with indexes which are easily changed by local electrical fields offer great promise for optical computing.

Currently, a metricon unit is used to measure the index of refraction of a thin-film polymer. The metricon uses a rotating prism to couple a laser to the polymer through a range of incident angles. Generally the polymer is mounted on a 3 inch silicon wafer. By measuring the reflected intensity of the laser as a function of the angle, it is possible to very accurately calculate the index of refraction for the thin-film polymer. These calculations are performed automatically by the metricon unit. A method was sought to employ the high accuracy and utility of the metricon unit for measuring the non-linear behavior of polymers due to applied electric fields.

Under contract F33615-92-5904 for 1993, a technique for measuring non-linear optical behavior using the metricon unit has been developed and almost completed tested. The method employs sandwiching the polymer to be tested between two electrodes upon which a potential has been placed. This potential will establish an electric field through the polymer. This "sandwich" of polymer and electrodes fits in the metricon easily allowing index measurements with or without the electric field applied. Before successfully making index measurements, however, it was necessary to develop a process for sandwiching the polymer between the two electrodes.

First, the bottom electrode is sputtered onto the silicon wafer. Using 500 angstroms of a gold palladium alloy has produced a highly reflective and conductive bottom electrode. Following this, the polymer is then deposited (or glued) to the electrode. The difficulty lies in producing a top electrode which will still permit the laser to couple into the polymer film. Since the laser must pass through this highly reflective metal layer it must be thin, but conductive. Experimentation revealed that the gold palladium alloy was unsuitable as an upper electrode. A film of the gold palladium alloy which was thin enough to pass the laser through would not conduct even a slight current. Experiments with pure gold, however, were successful. It was found that a 35 angstrom gold film was conductive, and would pass the laser.

The next step is applying a 100 volt potential to the two electrodes while the "polymer sandwich" is mounted in the metricon unit. A comparison of the index of refraction of the sample before and after the application of the field should immediately indicate whether non-linear behavior is present. Even slight changes in the polymers index of refraction should be measurable with the metricon unit.

QUASI-PARTICLE POLYMERIC SYSTEMS BASED ON AIR FORCE POLY(BENZOBISTHIAZOLES) (PBX)

Task Order No. 32
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer Clager
University of Dayton

31 December 1993

Government Task Leader
Dr. Loon-Seng Tan
WL/MLBP

ACKNOWLEDGMENTS

At this time, I'd like to thank my Task Leader, Dr. Loon-Seng Tan, for giving me all the responsibilities that he did. I'd also like to thank my co-worker, Ms. Sharon Simko, for elaborating on my responsibilities further and teaching me how to use the lab instruments with which I was unfamiliar. She was very easy to talk to and made work enjoyable for me. Ms. Marlene Houtz is another who deserves thanks, for she helped me to fix instrument failures. Without her help I would have become very frustrated. Finally, I'd like to thank all the Polymer Branch personnel for being so friendly. The people here made coming to work enjoyable, not a chore.

TASK ASSIGNMENT

The Task assignment was to monitor organic synthesis experiments based on the established procedures for the preparations of monomers and polymers; to isolate monomers and polymers from the reaction media; to perform preliminary characterizations, using IR, NMR, UV/VIS, melting point, and viscosity determinations; to tabulate experimental data and to use computer graphics to illustrate the synthetic schemes.

For the most part, these tasks have been completed. The majority of the work dealt with the preliminary characterizations of the products of the reactions ran by the Task Leader and members of his group using IR, NMR and UV/VIS analysis. The purpose of doing IR (infared) characterizations is to determine if the reaction has run to completion or to determine whether the product obtained matches the expected product. The purpose of NMR (Nuclear Magnetic Resonance) characterizations is to determine, by the placement of the proton, if the correct product has been made. Ultraviolet/Visible (UV/VIS) is generally done to see how a certain product reacts in different solvents. For example, most products will turn a different color in each different solvent. Some solvents dissolve certain products better than others. It is also easy to compare the absorption of similar products run in the same solvents using UV/VIS.

Many melting points of products, both crude and pure, were taken. The melting point range indicates the purity of a product. If the melting point is within a few degrees, then it indicates that the product is pure. Larger ranges in melting point indicate that the product is not pure or that the product does not pack well in the capillary.

One viscosity was done. This information had to be obtained because the branch was trying to make polymers of high viscosity. This involved not only chemistry but mathematics as well. Calculations had to be done for intrinsic viscosity, inherent viscosity and the concentrations.

Another significant assignment was to run a column. The purpose of the column is to extract a product from the impurities that surround it. Once a column is run, the solvent has to be removed from the product using a rotovap.

Finally, a project was assigned to determine how to use the new software that was bought for the UV/VIS Perkin Elmer computer. This was a time consuming project, but it was helpful in learning all the different functions that could be performed. Until that point, only the scan function had been introduced. New functions learned included concentration and peak pick. With known concentrations of a particular solution entered into the computer, a plot could be displayed that enabled the absorptivity to be solved and saved to a disk.

DESCRIPTION OF RESEARCH

There were many jobs which required new procedures to be learned. This involved a variety of equipment and methods of analysis. The first process learned was Fourier Transform Infrared (FTIR). The instrument used to do this is the BIORAD unix system. Most of the samples run were in crystalline form, but some were liquids. To begin, 1 milligram of the sample is put into a small plastic vial with 15 milligrams or more of potassium bromide. Then a small ball is placed inside the vial with the chemicals, and with the cap on, the vial is put on a stirrer. When the product is thoroughly mixed with the potassium bromide, a few milligrams are sprinkled evenly around the potassium bromide die and placed in a press. Once the crystals form a nice film, it is put in an apparatus containing a laser beam. Meanwhile, a background scan is performed which is to be subtracted from the sample scan. This laser beam scans the sample and the aborption pattern is printed out graphically by following the commands given on the computer screen. A listing of the peaks is also printed out with the graph.

For UV/VIS, a dab of the product is dissolved in a solvent in a small vial. The parameters are then set on the Lambda 9, Perkin Elmer device. Next, two cuvettes (sample holders) are filled with the reference solvent and a background reading is taken so it can be subtracted from the actual reading. Then, approximately 4 drops of the solution in the vial are placed in one of these cuvettes. This solution is scanned and a graph is printed out. If the graph does not fit on the page, a more dilute solution has to be created and the solution rerun. After an adequate graph is plotted, the peaks are found and labelled. This procedure is repeated for each product and each different solvent. When a new solvent is chosen another background scan must be run.

For NMR analysis, a solvent must be found in which the product dissolves. It is very important that the product dissolve completely or else the proton peak(s) are hard to find, unlike the UV/VIS in which, it is not important that the product be completely dissolved because it takes such a small concentration of product to produce a plot. Nonetheless, once the solvent is found it is filtered into a capillary tube to ensure that the solution is clear. Adjustments are made on the Hitachi NMR machine, the reference solution is run and the background recorded. The desired solution is placed in the machine, the instructions on the computer screen are followed, and the results are printed. All three methods, NMR, UV/VIS and IR, have spectrum characteristics listed in a book. These spectrum characteristics are compared with the ones generated by the computer and a product is inferred.

Melting point determinations consist of filling a capillary tube with a quarter inch of the product and placing it in the melting point apparatus, called Mel-Temp II. It records temperature with a K-type thermocouple. Viscosity determinations are a little more complicated. These involve making exact concentrations of solutions of the product and running them in the viscosmeter placed in a temperature bath of 30 degrees Celsius. The time it takes the solution to travel from the top etch mark to the bottom etch mark is recorded. However, before any of this can be done, the solvent must be run through the viscometer and its time recorded. The procedure for running a column begins with making the column itself. First, silica gel for dry column chromatography is mixed with the solvent system of choice. Solvent system means that a mixture of solvents can be used. A pure solvent need not be used. One common solvent system used is 2:1 methylene chloride and hexane. Second, the silica that has become gel-like is poured into a glass column which looks much like a wide buret. Third, sand is placed on top of the silica gel solution. Fourth, the product that is desired to be cleaned is dissolved and placed dropwise on top of the sand. Fifth, the solvent system is poured into the column. This causes the product to separate from its impurities by polarity. A very weak solvent system should be used to begin, such as 2:1 hexane/methylene chloride to ensure separation. As the separation becomes more evident, increasing the more polar solvent, in this case methylene chloride is acceptable. The separation of the product produces a variety of colors. Each color is to be collected in an erlenmeyer flask. After each color is collected, a thin layer chromatography (TLC), is performed. This indicates exactly which color or colors the product is present. Those solutions containing the product are then rotovapped. This draws the solvent system off and leaves only product. This procedure is done only when recrystallization is not possible for it is very time consuming.

A great deal has been learned in this job. It is now easier to guess which solvents will dissolve certain substances, which comes from experience. Three different computer systems have been learned, NMR, IR and UV/VIS. It has become easier to identify spectrum characteristics, which helps in identifing trends between alcohols and esters. Running a column was also a new experience and quite rewarding to see the actual solid product appear from an apparent colored solution. Interpreting the FTIR, UV/VIS and NMR data is complicated process and takes years of experience to become proficient at it. Thus, only simple analysis was done such as matching a FTIR spectrum with one given in literature and identifying hydroxide groups. Everything done in this job gave a greater understanding of the interactions of polymers and solvents. Much emphasis was place on learning the safety factors involved in using the chemicals.

FATIGUE OF CERAMIC COMPOSITES

Task Order No. 33
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer Finch
Wright State University

31 December 1993

Government Task Leader
Capt. John Pernot
WL/MLLN

ACKNOWLEDGMENTS

First, special thanks should be given to the two engineering Task Leaders, Capt. John Pernot and Mr. Larry Zawada. They offered professional opinions, took time to explain matters thoroughly and gave advice on related homework problems. Next, the author would like to extend gratitude to every professional within the lab for lending me their time, patience and expertise. Lastly, I'd like to acknowledge the Student Support Program, thank you for this opportunity.

TASK ASSIGNMENT

The objective of this Task was to analyze the fatigue characteristics of certain Ceramic Matrix Composite (CMC) materials. The CMC system of interest during this examination is C/SiC (carbon reinforced silicon carbide). The fatigue properties of C/SiC were assessed by subjecting test specimens to the influence of both high-cycle and low-cycle loading at elevated temperatures.

A host of other related tasks were performed prior to investigating fatigue behavior of CMC's. Data on CMC's and related information was gathered from both outside sources and the Wright Laboratory Technical Library. The requests and proposals for the purchase of materials themselves and for various types of equipment needed for testing were written. Raw CMC material was C-Scanned, documented and prepared for machining so that it could be subjected to testing.

Several activities also were involved with this Task pending fatigue testing. Tested CMC specimens were sectioned and prepared for characterization by metallography techniques. Micrographs and negatives of final polished specimens were processed. Other documentation of fatigue test results included the creation of plots, tables, displays, briefings and procedures.

The investigation of the fatigue life of Ceramic Matrix Composites (CMC's) is of interest to the researchers involved in this Task, since these materials show great potential for high-temperature aerospace applications. One organization which realizes the capabilities of these materials is ARPA (Advanced Research Projects Agency). The Ceramic Insertion Program initiated by ARPA is geared toward inserting a component made of a CMC material into an existing Air Force engine. The component of interest is the divergent seal for the nozzle in the F110 which is currently manufactured out of a nickel alloy material. It is the goal of the CMC researchers and support personnel, which have been involved with this ARPA program over the past year, to provide data on the durability of different CMC's and to aid in the preliminary material selection for this component. Another program which the researchers of this Task have been involved in is TTCP (The Technical Cooperation Program). One of this program's efforts is to exchange information between NATO countries on the high-temperature capabilities of CMC's. The investigation of CMC's has shown them to be low density, high strength materials with high moduli and to have the ability to withstand increasing temperatures. Those properties an attractive alternative for aerospace applications. This concept of CMC integration into society has made them a vital research consideration to government agencies worldwide.

Fatigue and other behavioral characteristics of C/SiC, the ceramic matrix composite material of interest, were obtained from a series of tests at elevated temperatures. Tension and creep rupture tests at elevated temperatures provide strain rate information which is indicative of environmental effects on the material's mechanical behavior. Isothermal fatigue tests provide the information needed on the life limiting properties of the material. The test matrices performed on C/SiC were consistent with the outlined goals of the CMC researchers.

A horizontal servohydraulic test machine, in conjunction with load and displacement transducers, was utilized as the testing apparatus. Other equipment was essential for the characterization of C/SiC following testing. Microscopes (such as a scanning electron microscope, a traveling microscope, and a Xenon illuminated microscope), various cut-off saws, diamond wheels, pneumatic hotpresses and vibratory polishers also were used.

The data obtained by the test machine and the transducers was recorded and stored on the connected MS-DOS computer system. The data was copied from the computer to floppy disks and formatted on a Macintosh computer. The data associated with fatigue properties was arranged and plotted so the researching engineers of this Task could analyze the results.

The testing and characterization analysis performed on C/SiC revealed several important characteristics. Prior to any exposure to load or heat, the stress state of the matrix of a C/SiC composite is in tension while the carbon fiber is in compression. This is due to the thermal expansion characteristics of both the matrix and the fiber. The existence of microcracking in this state may be attributed to residual tensile stresses at the matrix-fiber interfaces. Its stress state also causes an effect which raises its UTS at room temperature. Subjecting this material to high-cycle fatigue at room temperature proved to be a strengthening mechanism due to the nature of crack propagation during fatigue. At approximately 1000°C, the matrix material is close to its processing temperature. Therefore, the stress state is somewhat relieved by the glassy flow of the matrix material. This causes a lower UTS and a reduction in the fatigue life of the material. In C/SiC specimens which did not contain a layer of coating material around the inner lying fibers, the temperature exposure caused them to weaken and fail.

The fatigue and other behavioral characteristics of C/SiC, a ceramic matrix composite material, were investigated. It was found that the characteristic mechanical behavior of C/SiC is not suitable for extended life applications at elevated temperatures. It is concluded that this material should not be utilized in such applications as the F110 nozzle divergent seal. However, further testing and documentation of the high-temperature capabilities of C/SiC could prove essential to the advancement of material development.

ANALYTICAL PROCESS MODELING

Task Order No. 34
Student Support Program
Southwestern Ohio Council for Higher Education

Jay C. Soper
Wright State University

13 December 1993

Government Task Leader
Mr. S. L. Semiatin
WL/MLLN

ACKNOWLEDGMENTS

Special thanks go to Mr. Lee Semiatin. He was an excellent mentor who guided me through the research process from beginning to end, explaining everything that was being done in great detail. He allowed the author to explore his fullest capabilities in research. This included tasks ranging from participation in the experimentation, to computation and computer modeling, to participating in the actual writing of the paper.

All the research carried out above proved to be exciting as well as beneficial. Mr. Lee Semiatin was very enthusiastic about his work which made me very enthusiastic. I learned that research is a very dynamic process; <u>not</u> the slow drawn out process which most people think.

Thanks also should be given to all the members of the Metals and Ceramics Division of the USAF Materials Directorate of Wright Laboratory. During the experimentation and specimen preparation, the assistance of Messrs. Jones, T. Brown, P. Fagin, J. Brown, T. Goff, M. Dodd and all the members of the Metallography Laboratory was appreciated.

TASK ASSIGNMENT

The objective of this Task was to develop a model of the hot tension test incorporating cavitation effects. This was to be carried out by modifying an existing finite difference computer program for the simulation of the hot tension test. This computer program would incorporate the effects of cavity and microcrack formation on flow stability. The results of the computer program would then be validated by comparing it to the measured values of hot tension testing of gamma titanium aluminide.

The first modification of the existing computer program was to make the program more user-friendly. This program was modified to predict the engineering stress and strain of a specimen under hot tension. The program also predicted various initial conditions and the true strain at each of the original elements in the specimen from the center (the reduced section) to the shoulder of the specimen. A finite difference approach was used. This approach divides a specimen into several small elements. These small elements can then be evaluated individually, with each successive element depending on the previous element. This type of process generally yields accurate results. This first modification was based on the effective stress not being a function of the effective strain. It was also based on no cavity or microcrack formations in the specimen.

Later modifications took into account the dependence of the effective strain on the effective stress. This was carried out by utilizing data that was found experimentally. At this point, graphs of engineering stress versus engineering strain were drawn using the predicted values. These graphs were then compared to the graphs based on experimental values. It was shown that the predicted values yielded a higher engineering stress than the experimental values. This was expected since cavity and microcrack formation was ignored.

Finally, cavity and microcrack formation was taken into account. First the program was modified to find the final radius versus the final distance from the center to the shoulder of the specimen. This was done without taking the cavities into account. Then, taking the cavities into account, the final radius versus the final distance and the volume fraction of voids versus the final distance were found experimentally. Finally, the volume fraction of voids versus the apparent true strain and the apparent true strain versus the final position were found.

The dilemma of how to accurately get the computer predicted values of engineering stress versus engineering strain to correlate with the experimentally found values is still under investigation. The information found in the previous paragraphs by the author, with future research, will be used to eventually correlate this data. After concluding that further thought would be required to complete the above Task in its entirety, Mr. Semiatin and the author decided to move onto another topic.

The topic next pursued was that of finding a simple model for conventional hot rolling of sheet materials. The material used in this investigation was Ti-6Al-4V. An existing computer program was modified so that it would find the temperature transient from the center to the surface of a bare sheet of Ti-6Al-4V as it passed through the rolling mill. This program played an integral role in the research. This modified computer model was applied to the analysis of rolling pressure behavior and microstructure development in Ti-6Al-4V processed above and below the beta transus temperature. Other duties performed included metallographic preparation of the samples of the Ti-6Al-4V used in the experimental rolling; and various calculations and graph preparations.

Other research pursuits included showing that for continuous heating cycles, the differential form [$dD^n=k(\exp(-Q_g/RT))dt$] of the classical isothermal grain growth equation [$D^n-D_0n=k(\exp(-Qg/RT))t$] can be used to find n, k, and Q_g for a specific experiment. In the above equations D and D_o denote the final and initial grain sizes; T and t are the annealing temperature and time; n, k, and Q_g represent the grain growth exponent, the rate constant, and the activation energy; and R is the gas constant. A simple experimental method can be employed that will result in the measuring of n, k, and Q_g, which are independent of time and temperature; and, in essence, can be considered material properties. This will lead to the ability to find the beta grain growth for supertransus peak temperatures of alpha-beta titanium alloys for an entire spectrum of heating rates ranging beyond that of the initial experiment.

Along with writing an initial rough draft of a paper to be published, a computer program was written that directly integrated $dD^n=k(\exp(-Q_g/RT))dt$ using an optimization technique on n, k, and Q_g. The computer program found the values of n, k, and Q_g which was the basic subject of the paper.

INFRARED SPECTROSCOPY

Task Order No. 35
Student Support Program
Southwestern Ohio Council for Higher Education

Mark Roselius
Wright State University

31 December 1993

Government Task Leader
Dr. Harvey Paige
WL/MLBT

ACKNOWLEDGMENTS

I wish to extend my sincere appreciation to Dr. Harvey Paige of the Wright Laboratory Material Directorate for his guidance and assistance during the performance of this Task.

I also would like to thank Dr. Jim Liang of UDRI for his assistance with infrared data analysis.

TASK ASSIGNMENT

The interactions of lubricant model compounds and decomposition products with active surfaces under a variety of environmental conditions were studied insitu using Fourier Transform infrared spectroscopy (FTIR). The model compounds studied were perfluorinated ethers and ketones. The decomposition products studied were acyl fluorides. Decomposition products of lubricants and model compounds will be studied using gas chromatography/FTIR and other suitable techniques.

DESCRIPTION OF RESEARCH

Infrared data was initially analyzed with a Perkin-Elmer model 1750 FTIR. Additional infrared analysis was conducted with a Hewlett Packard GC/FTIR and analysis confined to conformer study.

Surfaces used were alumina (Al2O3) and silica (SiO2) applied to either a potassium bromide crystal or a tungsten mesh. The active sites studied were the hydroxyl groups (O- H) on the surface of the alumina and the surface silanol groups of the silica. Both sites were produced by reduction with hydrogen gas.

Three cells were used or are under development for these surface studies. The first cell used was a custom built 10 centimeter gas cell developed at the University of Utah and consists of a 10 centimeter glass tube sealed at both ends with potassium bromide windows. The surface of interest was applied to a centrally located potassium bromide window with an airbrush. A heating and cooling element supporting the window was used to control the temperature of the surface during the experiment. The temperature range of this cell is 150 K to 700 K with very limited control below 275 K.

To conduct controlled low temperature and high temperature surface studies a metal gas cell was developed based on a design of Dr. John Yates, University of Pittsburg. This cell was constructed from a standard ultra high vacuum (UHV) stainless steel cubic junction machined for 2 3/4" knife edge flanges. The IR ports were potassium bromide windows mounted in knife edge flanges. The active surface material was airbrushed onto a tungsten mesh screen. Temperature control of the surface was accomplished by passing a variable electric current through the mesh for resistive heating of the surface. Low temperatures could be reached by the addition of liquid nitrogen to a dewar, attached to the mesh supports, to cool the surface by conduction.

A variation of the metal cell previously described is presently under construction. The chief differences in this cell consists of a greatly simplified mesh holder for ease of repair and maintenance and the substitution of high density polyethylene windows for the potassium bromide to permit studies to be conducted in the far infrared region.

Conformer analysis was conducted by a novel use of the GC/FTIR. The method is intended specifically to look at vapor state model compound degradation products but can be used with any compound that undergoes conformal change with temperature. The method consists of holding the injector port, column and IR detector at the same temperature (isothermal) and injecting a small quantity of the sample. This is repeated for several temperatures, typically 5 to 7. The resulting spectra is then compared.

The sample injected will be a mixture of conformers whose percentage of the population varies with the amount of thermal energy available. In other words, the conformer requiring the least amount of energy will predominate at lower temperatures and vice versa. Vibrational bands associated with a particular conformation will change in intensity with the change in population. Using the Van't Hoff equation, the natural log of the ratio of two band intensities from different conformers can be plotted against the inverse of the temperature (1/K) and ãH° obtained.

The study of the interaction of a sample species (model compound, degradation product, etc.) with a metal surface was conducted by admitting a controlled amount of the species of interest into one of the cells previously described. Infrared spectra were obtained of the sample/surface interaction at a series of temperatures and stored for later analysis. Changes in the spectra give an indication of what processes are occurring on the metal surface.

RESULTS

Conformer Analysis

Work completed to date consists of method development and a preliminary test using 1,2-diiodotetrafluoroethane. The ãH° for the trans and gauche conformers was found to 1.1 to 1.3 kcal/mol. This is in good agreement with the calculated value of 1.9 kcal/mol. These results will be published in the February 94 issue of Applied Spectroscopy.

Additional tests using 1, 2-dichloroethane, 1, 2-dichlorotetrafluoroethane and 1, 2 -dibromotetrafluoroethane are being conducted to confirm the method along with experiments to determine what, if any, influence the flowrate and nature of the carrier gas have on the results.

Surface Interaction Studies

At present, one study using alumina and a perfluoro acyl fluoride in the glass cell has established that the acyl fluoride hydrogen bonds to the surface hydroxyl group through the carbonyl oxygen. The results of this study have been accepted for publication in the Journal of Fluorine Chemistry. Results from additional studies using alumina doped with iron and rhodium are inconclusive.

Two studies using the Yates metal cell copy have been completed. Data from the first using silica is presently being analyzed. A second study using alumina and hexafluoroacetone has been completed. Preliminary analysis of the spectra suggests that hexafluoroacetone reacts with the surface hydroxyl groups. Initially, the carbonyl carbon is subjected to electrophilic attack by the hydroxyl oxygen. This leads to formation of a surface carboxylate group and the loss of a CHF_3. The carboxylate will then decompose losing CO_2 and CF_3-. The CF_3-ion will then react with another hydroxyl group to form a perfluorinated methoxy group on the surface.

The metal cell dedicated to far-IR is still under construction and will not be ready for use until January of 1994.

A replacement for the original Yates cell is under construction at present. Unfortunately, a power outage occurred shortly after completion of the hexafluoroacetone test resulting in the original cells destruction. The replacement is expected to be operational by the end of December.

In addition to the surface and conformer studies, a substantial amount of time was used to develop temperature control methodology for all the IR cells in use or under development. A separation method using an ultra high vacuum system (UHV) and liquid nitrogen was devised to purify some of the lubricant model compounds for use in the surface studies.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 36
Student Support Program
Southwestern Ohio Council for Higher Education

Aric Rothman
Wright State University

15 June 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

Thanks to Soumya Patnaik for her patience and insight during the development of the BEAN molecular modeling software. Thanks also to Jim Lupo for supplying Xviewit, an X Windows' graphic utility.

TASK ASSIGNMENT

The objective of this Task Assignment was to assist a senior chemist in the characterization of siloxane polymer materials incorporating spiropyran molecules for use as matrices for optically active materials. Results of this research could be employed in the creation of practical nonlinear optical materials.

Several programs have been developed to assist molecular modeling tasks:

BEAN: Is a program to assist in visualization of molecular networks in space. Input to BEAN consists of a Protein Data Bank (PDB) format file containing the coordinates of individual atoms for each molecule. BEAN outputs a file of coordinates for the endpoints of line segments defining the axes for the equivalent inertial spheroids that enclose each molecule. This file may be input into Xviewit, an X Windows' visualization program to generate a 3-dimensional display of molecule "skeletons," or axes that approximate the shape and size of the molecules. This type of molecular display clarifies the spatial relationship between complex networks of large molecules. BEAN also generates a table of angles each axis makes with an average axis of each molecules' primary axis, quantifying the interaxial angles displayed by Xviewit.

PDBFY: Soumya Patnaik was supplied with a series of time iterations for a network of liquid crystal simulations by Dr. George Plimpton. This data was to be input to BEAN. PDBFY translates the file format supplied by Dr. Plimpton to the PDB format BEAN accepts.

GETRINGS: GETRINGS extracts the central benzene rings in a PDB file of molecules.

GETMES: GETMES extracts the mesogen branches from a network of molecules in a PDB file.

In addition to development of software, I assisted co-workers with use of the UNIX operating system and UNIX-based applications. I also assisted in maintenance and updating of hard drive archives for researchers' personal Macintoshes.

BEAN assisted Soumya Patnaik in the interpretation of simulation data for liquid crystal systems. BEAN was used to generate illustrations for a publication by Soumya Patnaik.

ENGINEERING AND DESIGN DATA

Task Order No. 37
Student Support Program
Southwestern Ohio Council for Higher Education

Brian J. Knapke
University of Dayton

31 December 1993

Government Task Leader
Mr. Clayton Harmsworth
WL/MLSE

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This year I have worked with several engineers and technicians on a variety of projects. The government and UDRI employees have assisted me in all the projects and provided advice whenever needed. I would especially like to thank Mr. Neal Ontko, Mr. Dave Watson, Mr. Russ Cervay, Mr. John Ruschau, Mr. John Eblin, Mr. Dayle Pearson and Mr. Bill Fortener for their extraordinary effort to assist and instruct me while I was working on the projects.

TASK ASSIGNMENT

The first project was the continuation of the ARALL-3 specimens that was worked on most of the last year. This is a laminate material that consists of 6 plys of aluminum and 5 plys of kevlar. Iosipescu shear, Rolfes compression, tensile and compression tests were performed with a 4507 model Instron mechanical testing machine. The compression tests were performed using the SATEC compression fixture with a MTS extensometer measuring displacement. All tests were performed to determine the change in properties of the material in differing environmental conditions. Therefore, tests were run at 3 different temperatures: 180°, room temperature and -65° Fahrenheit. At each of these temperatures, half the specimens were exposed to high humidity conditions prior to the tests. The high humidity specimens were pre-soaked in a 90%, 180°F environment in a Cincinnati Sub-Zero oven. During the high temperature high humidity tensile testing, the epoxy used to bond the tabs to the specimen failed before the specimen would fail. To alleviate this problem, the tabs were removed by freezing them in a dry ice-alcohol mixture and the specimen was then tested without tabs. During this project, I became very proficient with the technique of strain-gaging specimens and converting the output of the strain gages through amplifiers and conditioners to obtain a useful load/strain plot.

I then worked with 7075 aluminum specimens to collect data for Military Handbook V. These tests were performed to determine the consistency of the heat treatment methods of differing manufacturers of 7075 aluminum. The tests performed for this project were tensile, shear, bearing and compression using the SATEC compression fixture. These tests were performed on the 1125 Instron mechanical testing machine and data was collected using Instron Series IX Data Acquisition Unit. The data from the tensile tests was used to calculate ultimate strength, yield strength and modulus of elasticity. The bearing test data was used to calculate the bearing load strength. The shear test data was used to calculate the shear strength of the material. After all the tests were performed, the data was analyzed. A Lotus 1-2-3 spreadsheet was used to organize the data for the project engineer. Throughout this project I had to familiarize myself with a new data acquisition program with which I had no prior experience. It was a great experience to learn how to program this unit so the data would be collected properly. A X-Y-Y plotter was used to verify that the unit was collecting the data correctly. Several times the use of this plotter caught discreet errors in the data acquisition program.

The final project consisted of testing samples from a wing section of a C-141. The weep holes in the wing had cracks growing in them and the group had to find a material to patch these cracks. In the process, it was determined that the wing had to be raised to a temperature of 250°F to cure the epoxy applied to the cracks. Specimens from the wing were heated to 275°F to determine if the properties of the material changed dramatically when exposed to these temperatures for varying times. The exposure times were as follows: 0, 10, 20, 30 and 50 hours. After the specimens were heat treated, tensile, hardness and conductivity tests were performed on them. The hardness tests were measured on a Rockwell B scale and were taken before the tensile tests to avoid strain hardening of the material during the tensile tests. The conductivity tests were measured on a scale of percent conductivity with 100% copper being the standard at 100%. The tensile tests were used to calculate ultimate strength, yield strength, % elongation, reduction of area and modulus. The conclusion of this series of tests was that the material properties of the aluminum did not change significantly for heat treatments of 275°F for 50 hours or less.

I then helped with precracking fatigue specimens on a MTS hydraulic machine. These specimens had to have a crack grown into them 0.75 inches long. To grow the crack, a cyclic load was applied with the maximum load being 7800 psi and the minimum load 10% less than that. This was my first experience with the MTS hydraulic machines and it proved to be a good learning experience.

When I couldn't test or was between projects, I continued to update all the groups' specimen drawings on AutoCAD files. Maintenance work on the electric motors was provided for the weight pans in the creep frames.

The experience I received for the past 2 years has been very beneficial, not only for introducing me to the metallurgical field and its research, but also for teaching me to analyze problems and find solutions. Often the test wouldn't go as planned and the problem wouldn't be evident immediately. The problem had to be fixed to complete the testing and get good data. This experience will benefit me throughout my career as a mechanical engineer no matter what field I choose.

SYNTHESIS OF NOVEL POLYARYLENES FOR NONLINEAR OPTICAL EVALUATION

Task Order No. 38
Student Support Program
Southwestern Ohio Council for Higher Education

Paul Roderer
University of Dayton

30 June 1993

Government Task Leader
Mr. Bruce Reinhardt
WL/MLBP

ACKNOWLEDGMENTS

I would like to thank Gibby, Marilyn, Jay and Rom for their patience and assistance during this Task. I look forward to continuing my status as an apprentice and co-worker with this group of highly talented individuals. As always, I am extremely grateful for the kindness and guidance presented by Mr. Bruce Reinhardt. The longer I work with him, the more respect I develop for him and appreciate what a remarkable chemist and individual he is.

TASK ASSIGNMENT

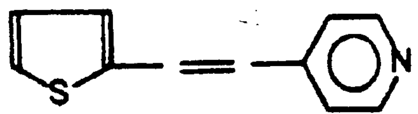
Several different Polyarylene compounds were synthesized for nonlinear optical (NLO) study. NLO research is on the cutting edge of physical and chemical research with ultimate goals of improving communication and computer technology by compounds that refract electromagnetic radiation in a non-linear fashion. This Task focuses on the development of organic NLO compounds with emphasis on synthesis of possible NLO compounds.

Extensively conjugated organic compounds have shown a high degree of promise in NLO activity. Since polyarylenes are highly conjugated compounds, they theoretically may exhibit a high degree of NLO activity. As a result of polyarylenes' theoretical NLO potential, this Task focused on synthesis of model polyarylene compound for NLO testing. This Task focused solely on the organic characterizations necessary to determine NLO activity. The structures of the major polyarylenes developed during this Task are outlined in Figure 1.

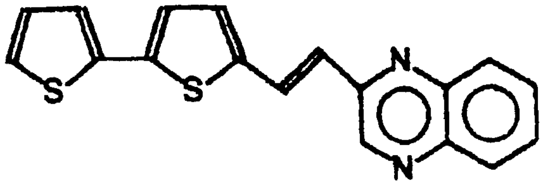
All compounds listed in Figure 1 were successfully synthesized . However, NLO data has not been compiled for these compounds. Since NLO testing is not performed as a duty of this Task, obtaining this data generally lags a couple of months behind successful synthesis of the compound.

Figure 1

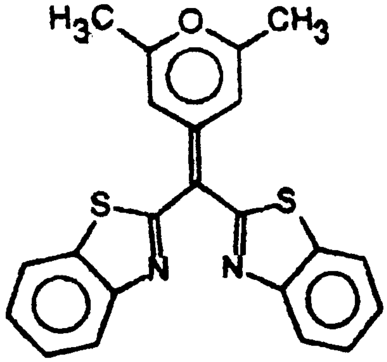
Some Polyarylenes developed during this task.



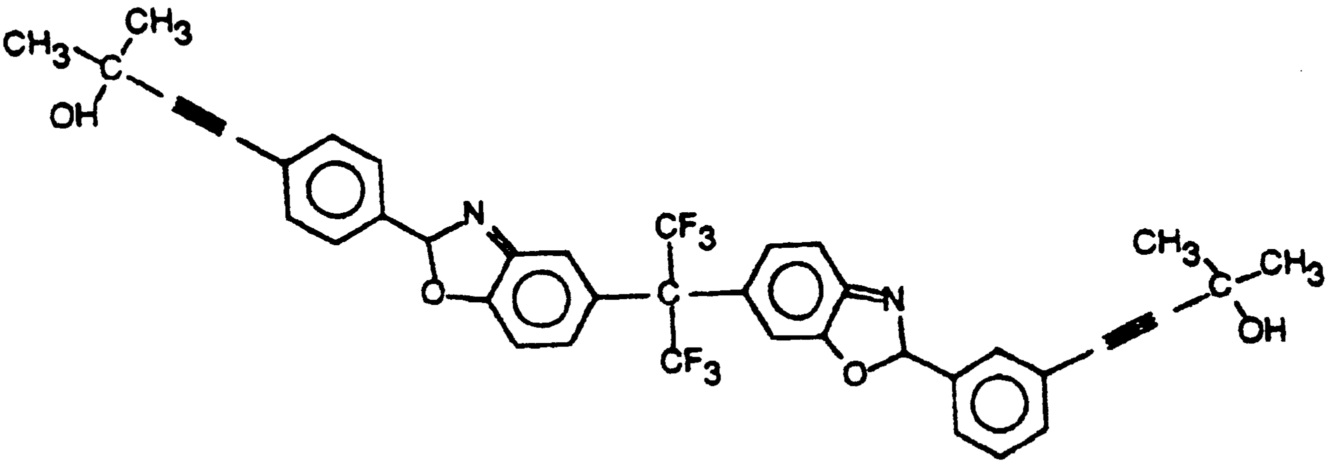
$C_{11}H_9NS$



$C_{18}H_{12}N_2S_2$



$C_{22}H_{16}N_2OS_2$



$C_{39}H_{28}N_2O_4F_6$

During this Task, library research projects were assigned that provided expectant synthesis methods for the model compound. After completing the library work, synthesis methods were selected to locate all necessary starting materials for the reaction. All necessary lab equipment was set up and the reaction run. The reaction was done with standard work up procedures such as vacuum filtration, extraction, neutralizations and vacuum removal of reaction solvents. The crude products were purified by recrystallization, column chromatography, charcoal treatment, distillation and mechanical filtration was then characterized. Finally, the purified characterized compounds were mailed to Buffalo, New York for NLO testing.

This Task concentrated on the synthesis of novel polyarylenes for NLO evaluation. The main polyarylene compounds developed during this Task are indicated in Figure 1. As in the last several tasks, many challenging research and experimental techniques were used to develop these compounds. While NLO data has not yet been compiled on these compounds, their successful production will hopefully provide further insight into NLO activity.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 39
Student Support Program
Southwestern Ohio Council for Higher Education

Scott M. Brittain
Wright State University

15 July 1993

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

Those helpful on this Task Assignment include 1st. Lieutenant Brian Sennett for research assistance and advice, and theoretical suggestions by Dr. Tom Cooper. In addition, I would like to thank my fellow students for helpful advice and assistance and the SOCHE administrators.

TASK ASSIGNMENT

The Task Assignment goals included the synthesis and characterization of peptides for laser hardened applications. This process is an integral step in the eventual goal of producing laser hardened materials that can and may be used to protect the eyes of pilots or protect the sensors of delicate and expensive satellites and other weapons systems. Protection of pilots is accomplished by coating goggles with laser light absorbing material so that their eyes are protected at all times. It is apparent that this research plays a role in the safety of our military. The synthetic peptides are only the first step in a long and tedious process of studying these nonlinear optical materials so that they can be used for practical purposes within the Air Force and Department of Defense. Also, the current research is founding important research that may develop in many years to come. This research is interesting and unique in that it involves the use of biomolecules (protein/peptides) derivitazed with synthetic chromophores for materials applications. All other protein/peptide research is exclusively biomedically related. Synthetic peptides form the backbone by which optical materials can be attached and subsequently applied to various substances. The peptide synthesis, accomplished by using the solid phase method, produced material to be further modified chemically and subsequent applications would include laser hardening and optical applications. These applications would utilize the chromophore (light absorbing) molecules (which were attached to the peptides) for previously mentioned applications.

DESCRIPTION OF RESEARCH

The Task research included the synthesis and characterization of peptides. This involves the solid phase synthesis technique, and many separation and analytical techniques. The synthesis involves attaching amino acids, which are protected at their N-termini, to an insoluble support. By repeated removal of the blocking group and then amino acid coupling, one can obtain a complete polypeptide. The peptide chains are then removed from the insoluble support by acidolysis. Of the analytical techniques, chromatography, amino acid analysis, protein/peptide sequencing, capillary electrophoresis and mass spectrometry were used. The chromatography included reverse phase, ion exchange and gel permeation chromatography.

The equipment used include an automated peptide synthesizer controlled by a PC, a low pressure chromatography device, a high pressure liquid chromatography device (HPLC), a protein sequencing machine and many smaller but important research tools. The synthesis of peptides includes the coupling of amino acid residues together in a unique sequence. The solid phase technique involves attachment of the first amino acid to an insoluble support and when synthesis is complete, chemical removal from the support can be accomplished. This process involves using base labile N- terminus protecting groups and acid labile links (via ester or amide bonds), to the polymeric support. In addition, the amino acid side chains are also "protected" with chemical groups that are acid labile so they can be removed when the peptide is removed from the polymeric support. Eventually, the desired peptide sequence can be purified and characterized. Once removed, the analysis begins.

Some analytical data is obtained by taking a small sample of the synthetic peptide, breaking the peptide bonds (holding amino acids together) and quantitating what kind and how much of the various amino acids is present in the peptide. This is known as amino acid analysis. The data obtained gives insight into the actual sequence of the peptide.

Capillary electrophoresis is a technique used to characterize peptides by their mass to charge ratios, and concerning a peptide standard of varying mass to charge ratios, the peptide elution time can be predicted. Also, mass spectrometry can be done on the samples and a molecular weight (or weights) of the synthetic peptide can be obtained. These data enable one to know the exact sequence of the peptide. Purity is important in peptide synthesis and that is why analysis is very important and difficult in this process.

RESULTS

Interpretation of the data shows that the process is delicate, and a mixture of peptides is usually obtained. Purification and analysis steps are important in this process. Without analytical confirmation, the subsequent experiments are not supported. Upon analyzing the synthetic peptides, a mixture of closely related peptides present was found. These "deletion" peptides are those that contain less than the full sequence that was desired. This is shown on a HPLC profile. In addition, capillary electrophoresis yields the same results with a mixture of peptides with varying mass to charge ratios. This led to the belief that HPLC purification and subsequent mass spectrometry would be a sufficient analytical sequence, and this is now being undertaken.

The amino acid analysis technique has been developed and is useful, but limited. The vacuum hydrolysis of the peptides may be the problem. It has been found that the resulting phenylthiocarbomyl (PTC) amino acids are reactive and the subsequent HPLC profiles afford qualitative data at best. This is probably due to the hydrolysis equipment or that one only detects picomole levels of these compounds. The synthesis studies indicate that the dynamics of the reactions may depend more on having a suitable solvent system than the actual type of reagents used. Side reactions are unique to the various reagents. Preformed symmetrical anhydrides, activated esters or in situ couplings seem to do the job. A negative, but extremely important, result is there is no means of quantifying the coupling, deprotecting and cleaving steps in solid phase peptide synthesis with the current methods used at the Materials Laboratories. The synthesis conditions are not optimal, and this involves somewhat of a guessing game. However, attempts have been made to convert the peptide synthesizer into a continuous flow apparatus where the chemical reactions can be monitored photometrically.

SYSTEMS SUPPORT-MATERIALS BEHAVIOR AND EVALUATION

Task Order No. 40
Student Support Program
Southwestern Ohio Council for Higher Education

Richard K. Huff
Wright State University

15 September 1993

Government Task Leader
Mr. Robert B. Urzi
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank all the personnel in the Systems Support Division for making my work experience enjoyable and educational. Special thanks to those I worked directly with or around: Mr. Robert Urzi, Mary Cooper, Mary McGiver, MSgt Bryan Cramer, Jim Mazza, Mark Forte and Mark Kistner of MLSE; James McKiernon, Bill Lawless and Ron Kuhbander of the University of Dayton Research Institute. I also would like to thank fellow SOCHE students Steve Medeiros, Rob Cassoni, Jim Stubbs and Cathy Gustufson.

TASK ASSIGNMENT

In the time spent with the Materials Lab System Support Group, as lab technician in the composites supportability lab, many tasks were performed. These included specimen fabrication, mechanical testing of these specimens and reporting the data from these tests. This data would then be given to the engineers for them to evaluate and decide if changes were needed in methods or a different direction in research was needed. Other times, the data was being generated to form a data base of information on certain products. The main areas of study at the time were the evaluation of composite materials, closed cell structural foams, film adhesives and the development of processes to bond boron patches to aircraft. The main project exposure was received from the study of closed cell structural foams. The main purpose of this project was to evaluate the mechanical properties of existing foams and create a data base of these properties. The main properties of interest were strength and modulus. The foams were tested dry and after humidity aging to compare the effects of humidity.

Another project was testing the effects of storage conditions of film adhesives. The adhesives were stored at room temperature, in a refrigerator and in a freezer. Several tests were performed on these adhesives as received and every 3 months thereafter. This project is ongoing and will be for some time.

Another project was the research of surface preparation techniques to bond patches to aircraft successfully. The patches would have to stop existing cracks from growing and restore structural integrity to the aircraft. They also must be able to withstand the elements and conditions they would be exposed to on the aircraft. Therefore, the preparation of the bonding surface is critical in the performance of the patch. A couple of different surface preparation techniques that could be done out in the field were researched and evaluated. Also, thermal surveys were conducted to determine a method to bond a patch to the prepared surface on the airplane out in the field.

Other projects included the study of the effects on different film adhesives of vacuum during bonding and a study of bonding kevlar to aluminum.

DESCRIPTION OF RESEARCH

The study of the close cell structural foam was mainly to develop mechanical property data. The main tests used were compression shear, compression and dog bone tensile. Specimens were fabricated and tested at room temperature, 180 degrees and either 220 or 250 degrees depending on the type of foam. Another set of specimens was fabricated and stored in a humidity chamber at 180 degrees and 65 % relative humidity until they were saturated by weight with moisture. These specimens were then tested in a humid environment at room temperature, 180 degrees and 212 degrees Fahrenheit. The results of the humidity tests were compared to the dry tests. The tests used a pen recorder that plotted a force vs. strain graph from which the modulus of the foam could be calculated. The strain acting on the foam during testing was measured using an extensometer.

The investigation into the storage effects of film adhesives was to determine the best way to store these adhesives and how long they can be stored before they become unusable. The tests used to evaluate these adhesives were flatwise tension, lap shear and floating roller peel. The fabrication of the flatwise tension specimens was by far the most time consuming. The fabrication involved bonding aluminum face plates to aluminum honeycomb core to form a sandwich structure. Before bonding, the aluminum face plates were abraded and then phosphoric acid anodized. After drying, they were primed with a spray on primer which aided the adhesive to bond to the surface and stopped the surface from reoxidizing. The aluminum honeycomb core was then placed between the two aluminum sheets with a piece of adhesive on each side of it. This panel would then be bonded together under positive pressure and varying temperature depending on the adhesive. The panel would then be cut into 2 by 2 specimens which would be bonded to 2 by 2 aluminum blocks using a paste adhesive. The blocks were then pulled on a testing machine until failure between the honeycomb core and the aluminum face plate occurred. The ultimate load was then recorded and strength calculations were then made. The lap shear specimens were easier to prepare as they consisted of two 9 by 4 sheets of aluminum, that were prepared the same as the flatwise tension sheets. They were bonded together with a half-inch overlap on the long side with a strip of adhesive in the middle. These were bonded under positive pressure and vacuum and then compared. They would then be cut into 1 inch wide strips, measured and tested for ultimate load until failure occurred. The peel specimens were bonded but sent out to be tested. All testing for this project was done at room temperature on either an Instron or Tinius-Olsen testing machine.

The research that was done on the surface preparation project was mainly conducted using wedge tests. The wedge tests were done by preparing two 6 inch by 6 inch by 1/8 inch pieces of aluminum with the particular surface preparation under investigation. The two pieces were then bonded together with a film adhesive in a Wabash press under positive pressure. The panel was then cut into 1 inch wide strips and a wedge drove down into one end. The wedges were then put into a humidity cabinet and left there for a week or two while the crack propagation was monitored periodically. The rate of crack growth and total crack growth determined the effectiveness of the surface preparation.

RESULTS

During the time spent with this group, a lot of testing was accomplished on the closed cell structural foam. This project is very large, however, and still has a long way to go to complete it.

The 6, 9, and 12 month tests were conducted on different adhesives for the storage conditions project. No real conclusions were drawn on the effects of storage conditions as this project is continuing for another year. There were some general trends noticeable such as a loss in strength over time, a loss in flow during cure over time. The colder storage seems to have a longer shelf life. These were the trends expected.

As for the surface preparation project, a method involving gritblasting and silane wiping, the surface yielded acceptable results in the lab. Patches were actually bonded on two different types of aircraft. The performance of these patches will not be known until they are on the planes for about a year and can be checked for their effectiveness.

MECHANICAL PROPERTIES OF METAL MATRIX COMPOSITES

Task Order No. 41
Student Support Program
Southwestern Ohio Council for Higher Education

Alisha Hutson
Wright State University

15 June 1993

Government Task Leader
Mr. Jay Jira
WL/MLLN

ACKNOWLEDGMENTS

I would like to thank Mr. Jay Jira for his patience and thorough explanations. I also would like to thank the other people working in building 655. Seeing you in action has helped me make career decisions. Finally, I would like to thank the people at Tech Photo. You have all been very informative.

TASK ASSIGNMENT

The Task required assistance in the data analysis aspects of the Materials Lab Metal Matrix Composites (MMC's) research being conducted in the Wright Patterson Materials Lab. Duties included both quantitative and qualitative analyses. A significant amount of time was spent running raw test data through data analysis programs on a MicroVAX computer system. Time was also spent analyzing the data from photos taken during fatigue crack growth tests. In addition to these, Mr. Jay Jira requested information from smaller scale studies and required help collecting the necessary materials by the contractor.

The analysis of the raw test data was a multi-step process that started with analysis of each photo taken during the test. (Photos were taken of each test specimen at regular intervals as a record of the crack growth rate.) Data providing crack lengths at regular intervals during a test would be recorded with a program on a Textronix 4052 computer. Then the data would be transferred to the MicroVAX. The next step was to merge the optical crack length file with the run time data file. (This file contained crack lengths measured by a different method.) The resulting file contained the most meaningful data from both files and allowed for easy comparison of the two crack length measurement methods. After merging the first two files, another program was run on the merged data file to generate a fourth file containing new calculated values. This file allowed for easy comparison of crack growth rates from several specimens. (In some cases the above programs had to be rerun several times on the same specimen because of changes in the analysis programs.)

After reducing and plotting the numerical test data, 8x10's were printed of the picture taken just before the specimen broke, or the last picture taken during the test if the specimen didn't break. This was also done to the photo just prior to failure if the specimen did fail; and the first picture in each test, for reference. Although someone outside the materials lab actually printed the photos, it was necessary to make sure the prints were good enough quality that the necessary features were visible, and the prints could be used for presentations and papers. The prints were then organized for quick reference.

Material collected from each specimen is on a data base. Each specimen tested under the NASP contract is contained here and is entered in the data base as soon as a test is complete and the measurements taken directly from the specimen. Along with this data base, test log sheets, test film, computer directories and digitizing sheets must be maintained and updated.

Periodically, symposiums are held that require specialized presentation materials to be generated. These materials include color transparencies, transparencies of test photos, special analysis photos and a generalization of all NIC data collected to that date. For various presentations specimens have been mounted and polished using metalography techniques to view various features of fatigue and failure not visible from outside the specimen.

During the past few months, I have continued to learn new skills and have gained invaluable experience. Mr. Jira assigns more difficult and challenging tasks as I learn more, which has helped make things interesting. I have enjoyed working with Mr. Jira and his colleagues in the Materials Lab and look forward to the upcoming year.

METALLIC COMPOSITES III

Task Order No. 42
Student Support Program
Southwestern Ohio Council for Higher Education

Christopher W. Palser
Wright State University

30 June 1993

Government Task Leader
Dr. Dan Miracle
WL/MLLM

ACKNOWLEDGMENTS

I would like to sincerely thank everyone whom I work with at the Materials Laboratory who make working there both fun and a great learning experience. I'd like to thank most, Dr. Dan Miracle, who continues to be patient with my frustrations and lack of all-encompassing knowledge and whose "table-side lectures" continue to help me see materials engineering in a completely different light.

TASK ASSIGNMENT

The overall objective of this Task was to determine interface properties and deformation characteristics in advanced metallic composites for high temperature applications.

The specific objective of this Task was to establish techniques to produce single fiber composites and multi-fiber composites in a range of geometries and for a number of matrix/reinforcement combinations. Additionally, the Task was to produce composites for determination of interface properties and deformation characteristics in advanced metallic composites and to conduct mechanical tests of the single and multi-fiber composites and to analyze the data resulting from the composite production and testing.

The purpose behind this Task is to produce lighter, stronger high-temperature materials for use in jet engines and aircraft airframes and structures. A structure or engine component made of a metal-matrix composite (MMC) will be significantly stronger at both normal temperatures and at the higher operating temperatures found in jet engines and also will have a lighter density. Given these improved mechanical properties, less material of a lighter weight will be used in production to form a much lighter component, resulting in substantial savings in aircraft weight and fuel. It is obvious that advancements in the production of MMC's that would enable them to be manufactured in a cost-efficient, reliable manner and therefore be widely used in aircraft production, would provide long-term savings in fuel usage for aircraft using MMC's in major components.

The student's role in this research was to prepare samples, perform analyses on the prepared samples and to understand and assist in the interpretation of the results of the analyses performed.

The bulk of the research performed on this Task was in the area of long-term heat-treated matrix alloys and MMC's. Long-term heat-treatment of MMC's very closely simulates the long-term exposure of MMC's to a high-temperature environment such as a jet engine. Research in this area is important, since long-term exposure to high-temperatures can drastically affect the mechanical properties of materials used.

Studies were performed on a completely new class of Titanium-Aluminide-Niobium alloys consisting of 55 atomic percent Titanium, 22 atomic percent Aluminum, and 23 atomic percent

Niobium (commonly referred to as Ti-22-23), with Silicon Carbide (SiC) or SCS-6 fibers. This composite is generally known as Ti-22-23 with SCS-6 fibers, or simply, Ti- 22-23 composite. Ti-22-23 matrix is composed purely of Ti- 22-23 alloy, while the composite is formed of unidirectional layers of SCS-6 fibers pressed at high-temperatures and pressure between thin foils of the matrix alloy.

Samples were sectioned from the as-received sheet into approximately 1 x 2 x 0.1 cm specimens for heat treatment and subsequent analysis. Heat treatments were performed at varying temperatures and times, varying from 500-800°C and 500-1000 hours. Following heat treatment, specimens were sectioned and mounted in a thermoset mount for metallography. After mounting, metallography was performed by rough grinding through final polish for scanning electron microscope (SEM) and microprobe analysis.

Scanning electron microscopy was performed to analyze the phases present in the as-received and heat-treated samples so that the phase transformations that occurred during long-term exposure to high temperatures could be determined. Microprobe analysis and x-ray diffraction was performed to analyze the specific chemical composition and crystal structure of each phase present in the matrix alloy.

The bulk of the material investigated during this report period was the Ti-22-23 composite. The results of the research are summarized in the following table:

T(°C)/t(hr)		$\propto^2$	Orthorhombic	β
As rec'd	Ti	61.2 ±0.4	54.9 ±0.7	53.9 ±1.2
	Al	24.7 ±0.2	24.2 ±0.3	12.2 ±0.4
	Nb	14.2 ±0.4	20.9 ±0.7	33.9 ±1.2
500°/500 h	Ti	60.1±0.3	53.9±1.0	53.2±0.4
	Al	24.5±0.4	24.1±0.4	12.7±1.1
	Nb	15.4±0.5	22.1±1.2	34.1±0.9
800°/500 h	Ti	61.9±0.7	54.3±0.7	50.3±0.5
	Al	24.0±0.3	23.8±0.7	11.1±1.3
	Nb	14.1±0.7	21.9±0.9	38.6±1.7
500°/1000 h	Ti	59.1±1.0	53.5±1.3	53.3±1.0
	Al	24.7±0.2	21.1±1.6	13.6±0.2
	Nb	16.2±1.0	25.4±0.7	33.2±0.8
800°/1000 h	Ti	61.8±0.6	54.4±0.9	49.6±0.7
	Al	24.3±0.1	24.4±0.2	10.9±0.4
	Nb	13.9±0.5	21.2±0.7	39.6±1.1

This table shows the changes in compositions that occur during long-term/high temperature exposures of Ti-22-23 composite.

METALLIC COMPOSITES I

Task Order No. 43
Student Support Program
Southwestern Ohio Council for Higher Education

Andrew Johnson
University of Cincinnati

22 March 1994

Government Task Leader
Dr. Dan Miracle
WL/MLLM

ACKNOWLEDGMENTS

I would like to thank the following people for their assistance on this project: Dr. Dan Miracle, Dr. Sion Pickard, Visiting Scientist and Joe Henry, UES Technician.

TASK ASSIGNMENT

Residual stress is an important component in the study of metal matrix composites. Residual stresses are stresses that are present in a material at room temperature without a load being applied. In the case of metal matrix composites (MMC), the residual stresses are created by a mismatch in coefficient of thermal expansion.

Titanium Aluminides are the metals used as the matrix in the composites studied. Silicon carbide, SCS-6 fiber, is the material used as the fiber reinforcements in the composite. Titanium aluminides have a larger coefficient of expansion than silicon carbide. This situation creates a problem during the cooling of a processed MMC.

The matrix contracts more than the fiber during the cooling process. This places the fiber in compression and the matrix in tension. The residual stresses present in MMC's are due to this situation. The magnitude of the residual stresses is not known. MMC's were only developed in the past two decades. Previous testing techniques could be applied to MMC's due to the unique geometry of MMC's.

The residual stresses present in MMC's have been divided into three components along or centering at the fiber; the axial stress, the radial stress and the hoop stress. This particular testing technique measures the axial strain present in the fiber. The stresses present in the metal deform the lattice structure of the material. These deformations change the d-spacing of the lattice structure. The change in d-spacing can be determined by comparing the unstressed matrix to the composite. This gives a reliable change in d-spacing which determines the residual stress present in a composite.

The composite material Ti-24AL-11Nb/SCS-6 was chosen as a test material for the process. The X-ray residual stress testing must first be examined before the technique can be used for research. The surface of the composite was first polished at 1 micron to remove surface oxidation. The polishing itself induces stresses into the composite which alters the actual residual stresses present in the sample. The sample must then be quickly electropolished to remove the surface damage from mechanical polishing. To properly electropolish the sample, a new jet electropolish set-up was created. This new jet electropolish has only been recently completed.

At this point, the project focused on the reliability of the X-ray scans. A mechanically polished sample was used for these experimental runs. The sample was run in orientations of 0, 15, 30, 45 and 60 degrees with respect to the X-ray source. This was done in both the vertical and horizontal positions for the composite corresponding to the axial and hoop stress respectively.

A matrix sample was also run at the previously mentioned orientations. The peak examined was at 144.6 degrees in the matrix.

Each data file was converted to an ASCII format and then converted to a graph on the Kaliedagraph software package. The peak was curve-filled to produce a second order polynomial equation. The derivative of this equation was taken and solved at y=0. The peak of the equation is present at the point y=0. The peak for each run was determined in this way. Numerous runs were done in the 0 and 45 degree orientations to establish the precision of these measurements.

Numerous problems with this technique must be corrected before reliable data can be obtained. The matrix peak shows a double peak. The stresses in the composite broaden the peaks to the point that only one peak is present. This artificially changes the peak of the sample. This can be corrected by choosing a peak with a higher intensity. This peak will be less subject to the problems of peak broadening. Another problem is the focusing radii of the diffractometer. The intensity values of the X-ray runs should be highest at the 0 degree orientation but, instead the 45 degree run has the highest intensity values. This stems from the incorrect focusing radii of the diffractometer.

The runs completed cannot be used for actual research, as of yet. Now that the jet electropolisher is complete, actual measurements of residual stress for research can be completed. This is subject to the correction of the above stated problems. Even with all the problems stated before, the basic principle of the technique is sound. As the angle of orientation increases, the peak of the sample shifts to a lower two-theta value. This shift was predicted prior to the beginning of the project.

METALLIC COMPOSITES I

Task Order No. 43a
Student Support Program
Southwestern Ohio Council for Higher Education

Lisa Rothenflue
Wright State University

22 March 1994

Government Task Leader
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WL/MLLM

ACKNOWLEDGMENTS

For their patience, insight and assistance, I would like to thank the following people: Dr. Dan Miracle, Dr. Mark Waterbury, Mr. Bob Lewis, Mr. Michael Scott, Mr. Kevin Kendig and Mr. Hou Jeing.

TASK ASSIGNMENT

The Task objective was to determine interface properties and deformation characteristics in advanced metallic composites for high temperature applications.

During this Task, samples were prepared and experiments performed to determine the residual fiber strains present in as-processed, heat treated and mechanically tested composites. The statistical method for performing a weighted linear regression analysis and for determining the standard errors for the resulting slope and intercept on the results from the FEMUR tests was researched. From this research, a spreadsheet was developed to perform these calculations.

Additionally, single and multi-fiber composites were produced in a range of geometries and matrix/interface combinations for the purpose of determining interface properties and aided in preparing samples for analysis.

The purpose of this Task was to improve the understanding of the interface properties and deformation characteristics of advanced metal matrix composites. Continuously-reinforced titanium-based metal matrix composites are being developed as potential materials for high temperature aerospace applications. Upon cooling from the processing temperature, residual stresses are introduced into these composites by the differences in the coefficients of thermal expansion (CTE) for the matrix and the fibers of the composite. These residual stresses can affect the mechanical behavior and failure characteristics of the composite. Therefore, determining a method by which the residual stresses can be measured is important. The reduction of these stresses through either heat treatment or mechanical processing is also of interest.

DESCRIPTION OF RESEARCH

The majority of the research performed for this Task involved the determination and analysis of axial residual fiber strains in composite materials.

The residual strains were determined using an electropolishing technique nicknamed FEMUR for Fiber Extension, Matrix Under-cut Removal. This procedure involved sectioning the specimen normal to the fiber axis, mounting in a triplex mount (two non-conducting layers with a conducting layer in the center in contact with the specimen), and polishing the sample to a 1μm finish using the Maximet. The specimen surface was then 'masked' with an acid resistant lacquer with the exception of a ~1mm wide region in the center of the composite. The sample was then jet electropolished using a perchloric acid solution for 11-12 hours. This procedure removed the composite matrix around the fibers by electropolishing to a depth of 0.5-1mm. The axial residual stresses in the fiber are due to constraint by the matrix (the CTE of the matrix is greater than that of the fiber). Therefore, upon removal of the matrix, the fibers relax. The magnitude of the fiber extension is related to the depth of matrix material removed. This depth (D) is approximated by using a calibrated optical microscope with a depth of field sufficient to measure the exposed fiber length by focusing on the fiber end and then on the matrix where the fiber entered the composite and recording the difference in positions. The magnitude of the fiber relaxation (ãH) was determined by surface profilometry. A surface profilometer scanned individual rows of fibers with a diamond-tipped stylus. The output for each row was a trace of the surface roughness. The fiber relaxation (ãH) was determined by measuring the difference in height of the exposed fiber to the height of the fibers in the unexposed regions.

The data was analyzed by entering the values for etched depth (D) and fiber extension (ãH) into the spreadsheet the student developed with the aid of the Task Leader. This spreadsheet calculates the weighted slope and intercept values from linear regression and the standard error for these values (with a confidence interval of 68%). This weighted method accounts for errors in both X - etched depth (D) and Y - the axial fiber extension (H). The procedure for this analysis is too long to describe in this report, but an outline of the procedure by page or section number and source is given on the attached printout of the results for a Ti-15-3 (15% fiber, tensile tested) composite. The residual fiber strain is the negative of the slope obtained from the spreadsheet. From this value, the residual stress can be calculated.

During this Task, analysis was performed on several continuous fiber reinforced composites: Ti-15V-3Cr-3Sn-3Al wt% (Ti-15-3) and B21S with SCS-6 SiC fibers.

When not performing other tasks, the student was involved with the production and sample preparation of composites of various geometries for interface characterization. Using a screw driven cutting tool in a piece of equipment designed for this purpose, grooves were cut in the matrix material of a specific size and location. Others were responsible for the subsequent steps in production. The finished composites were prepared for testing by grinding the specimens on 180 grit SiC paper to a uniform finish. After testing, basic metallography was performed on the specimens utilizing the Maximet to a 1µm finish and the Vibromet to 1/2/m finish prior to SEM examination.

RESULTS

The majority of the results from this Task will be published in an upcoming paper. In this paper, the results from FEMUR testing and analysis of Ti-15-3 continuous fiber reinforced composites will be presented. The results obtained by the spreadsheet developed during this Task are given in TABLE 1 under the heading - linear regression. The student analyzed all the FEMUR data for this section of the table, but was only responsible for performing the FEMUR test on the 0.30 (Tensile Tested at room temperature) sample. The Task Leader compared the results of the FEMUR analysis to other methods of residual stress determination and concluded that this method was reasonably accurate in assessing the residual strains within the stated error.

FEMUR testing and analysis was performed on a B21S/SCS-6 continuous fiber composite in both the as processed and tensile tested (500/C) conditions. The residual strains (%) obtained from analysis were -0 .137 ± 0.035 and -0.101 ± 0.016, respectively. The values were very similar due to the fact that residual stresses were reintroduced into the composite upon cooling from the testing temperature of 500°C. In the future, these materials will be examined to attempt to characterize the interface.

Knowledge of the statistics involved in linear regression analysis was greatly expanded. The resulting statistical research was the documentation of a method which was not clearly described in any of the texts that were examined. The resulting spreadsheet quickly performs these calculations upon the data entered.

Param Error WKS 15% TT

ENTER x(1) y(1) VALUES

ENTER x n y MEASUREMENT ERROR
Measurement Error (x) = 25
Measurement Error (y) = 0.2

RESULTS

SLOPE = 0.000871 ± 0.000265768
Eqn 12.45 Mandel
INTERCEPT = -0.454184 ± 0.156016614

Intermediate Results

N = 25
XAVG = 575.2
YAVG = 0.0467

LAMBDA = 15625	Eqn 12.38 Mandel
U = 8.60+06	Eqn 12.41 Mandel
W = 5.36E+01	Eqn 12.42 Mandel
P = 6.84E+03	Eqn 12.43 Mandel
S = 1.92955799	Eqn 12.52 Mandel
SIGMA = 0.28964431	Eqn 7.2 Mandel
VAR(x) = 4472.68856	Eqn 12.50 Mandel
VAR(y) = 0.28625207	Eqn 12.51 Mandel
w(x) = 0.00022358	Mandel p 290
w(y) = 3.49342455	Deming Sec 11
L = 0.28964431	Deming pp 154, 178
aa = 86.312761	Deming Sec 61
ab = 49647.1001	Deming Sec 61
bb = 29744758.4	Deming Sec 61
DET = 1.03E+08	
c11 = 0.29014273	Deming Ex 2, p 162
c22 = 8.4193E-07	Deming Ex 2, p 162

x(1)	y(1)
640	.654
660	.5
540	-.038
600	.37
680	.333
710	-.133
570	.233
730	.4
690	.533
580	.118
770	-.118
300	.0882
790	0
420	-.3225
620	0
530	-.12903
400	.2
440	-.2
560	-.5
580	-.3
450	-.26
550	-.26
550	-.174
480	-.087
540	.087

TABLE 1
Experimental Residual Fiber Stresses and Strains in Ti-15-3 Composites

	Linear Regression		'Mean Slope'	
V_f	Residual Strain (%)	Residual Stress (Mpa)	Residual Strain (%)	Residual Stress (MPa)
0.15 As processed	-0.206±0.020	-810±79	-0.257±0.053	-1010±208
0.15 Tensile Tested	-0.087±0.027	-342±106	0.004±0.050	16±197
0.30 As processed	-0.188±0.012	739±47	-0.159±0.023	-625±90
0.30 Tensile Tested	0.012±0.002	47±8	0.015±0.062	59±244

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SMART SKINS AND STRUCTURES

Task Order No. 44
Student Support Program
Southwestern Ohio Council for Higher Education

Thomas J. Witman
Wright State University

15 September 1993

Government Task Leader
Capt. Michael Holl
WL/MLBC

ACKNOWLEDGMENTS

I would like to give a special thanks to Capt. Michael Holl for his leadership and guidance through this Task. He has made this Task both enjoyable and knowledgeable. He is well respected and an excellent role model. I also would like to thank Mr. Jim Lute for helping with all the procedures done in the lab.

TASK ASSIGNMENT

Foreign objects are being embedded into advanced composite laminates for smart skin and smart structures purposes. The objective is to study the effects these inclusions have on the mechanical properties. If successful, continued testing will be done to determine other uses and advancements involving fiber optic embedment into composite laminates.

The composite laminates used consist of epoxy resin with graphite fibers. Epoxy resin with graphite fibers are used together to give the composite high performance characteristics. However, other resins are currently being tested. The fiber optics embedded in this particular composite are 240μm outer diameter fibers with a polyimide coating.

The composite material is received on a large roll 12 inches wide. Panels are made by cutting sheets, called plies and stacking each ply on top of one another. The orientation of each ply is determined by the engineer. The fiber optic is usually placed in the middle of the plies at 90° with respect to the horizontal 0° ply. The fiber optic is placed between two 0° plies. This is done so that the fiber optic may be surrounded by pure resin, called a resin eye. Since the fiber optic and the composite's fibers are not parallel, this is the weakest combination. Tests are run for the worst possible case so that any other case will be successful.

The panel is cured in an autoclave for 2 hours at 350°F. An ultrasonic c-scan is performed on the panel after it has been cured. This procedure detects impurities in the panel. Sound waves are sent back and the impurities in the panel can be seen. A diamond wet saw is used to cut the panel into separate specimens. The specimens are then tabbed on each end for gripping purposes in the test. The specimen length between each tab is referred to as the gage length, which is determined by the engineer.

From the pieces left over from the panel, a fiber volume content and photo-micrograph is obtained. Fiber volumes tell the engineer how much fiber is in the panel on a weight basis. Therefore, as the fiber volume increases, the strength also increases. Photo-micrographs are used with the scanning electron microscope (SEM) to examine the state of the composite. Microcracking, crack propagation and voids (air bubbles in the composite) can be seen and studied in this manner.

Standard tension tests were run until the specimen failed. The load at which failure occurred was recorded and the ultimate strength of each specimen was determined. The ultimate strength was found by dividing the ultimate load by the cross-sectional area of the specimen.

The results show that the embedded fiber optic specimen had little or no decrease in strength from the control specimen. Micro-cracking did not occur around the fiber optic, nor did micro-cracking initiation occur due to the fiber optic's placement. Fiber volumes were in the range of 55-60%.

Additional experiments that are recommended to study crack propagation and initiation are "cycling" experiments. This could be done as follows: 1) prepare specimens in the same manner as mentioned previously; 2) polish specimens on both sides before testing; 3) use SEM to document status of specimen before testing; 4) apply tension load in increments; and 5) after each increment, use SEM to follow crack propagation.

The second project involves the use of a different type of resin called AFR-700 resin. This uses the same graphite fiber, but the AFR-700 has different properties than the epoxy resin. The objective of this project is to determine the thermal residual strain that exists in the material after curing.

The AFR-700 panels were prepared in the same manner as the graphite epoxy. The AFR-700 consisted of only two plies: one at 0° and one at 90°. The AFR-700 panels were cured in an autoclave for 2 hours at 350°. During the cure cycle, the resin shrinks, inducing tension in the fibers. Due to the fibers being in tension, the panel, after curing, is curved into a half circle.

One-half inch specimens were obtained and post-cured at 750°F, held for 10 hours at 750°F and cooled. During this post-curing, the specimen flattens out, which relieves the stress existing in the specimen. About 5 hours into the post-cure, the specimen acquires some stress. Hence, the specimen curls slightly. This curl increases gradually for the remaining post-cure period. The specimen curled more after the post-cure was complete due to these stress relaxations. During the post-cure cycle, the specimen flattened out, which relieved the stress existing in the specimen. Therefore, the specimen is curled more after the post-curing is complete. During the post-cure cycle, the time, temperature and height of specimen to the apex was recorded. A fiber volume content and photo-micrograph was used to document the specimen's microstructure.

The thermal train can be found both experimentally and theoretically. This can be done using the following equation:

$$\epsilon th = E^{1} b(\alpha^{t} - \alpha^{1})(T^{1} - T^{2})/(E^{1} b + Ed) \qquad (1)$$

where:
E^1 = longitudinal modulus
E^t = transverse modulus
b = 0° ply thickness
2d = 90° thickness
T^1 = stress-free temperature
T^2 = room temperature
α^t = coefficient of thermal expansion (transverse)
α^1 = coefficient of thermal expansion (longitudinal)

theoretically,

$$(\alpha^t-\alpha^1)(T^1-T^2)=(b+d)/2p+(E^1b^3)[(E^1b)^{-1}+(E^{td})^{-1}]/6p(b+d)$$

where
p = radius of curvature of the specimen

The radius of curvature can be found using the equation:

$$p=(v^2+x^2))/2v$$

where
2x = chord length of specimen
v = height of specimen from apex

To find the thermal strain experimentally, Schapery's equations are used in the following manner:

$$\alpha^1=(E^m\alpha^mV^m+E^f\alpha^fV^f)/E^mV^m+E^fV^f)$$
$$\alpha^t=\alpha^mV^m(1+\nu^m)+\alpha^fV^f(1+\nu^f)-\alpha^1\nu^1$$

where superscripts m and f stand for matrix and fiber respectively and
V = volume fraction
E = modulus
α = coefficient of thermal expansion
u = poisson's ratio

After α^1 and α^t are found, this result can be plugged into equation 1 to find the experimental thermal strain. These procedures for finding the thermal strain are currently in progress.

ADVANCED COMPOSITES

Task Order No. 45
Student Support Program
Southwestern Ohio Council for Higher Education

Robert C. Weber
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13 December 1993

Government Task Leader
Ms. Kristen Kliner
WL/MLBC

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TASK ASSIGNMENT

The advanced composite Task consisted of a software engineering project dealing with data acquisition from the carbon-carbon composite pyrolysis process. The general design collected data acquired from the process, and manipulated the data for display purposes. The program also served as the main storage and retrieval system for the data. In the future, the program also will serve as a closed loop control source from which the carbon-carbon pyrolysis process can be controlled to aid in the efficiency of the process. The main goal then, of the computerization of the process, is the idea of speeding up the process while at the same time preventing deficiencies (i.e., cracks and delaminations) in the composite formation.

DESCRIPTION OF RESEARCH

The design of the program to collect data began with gaining a familiarization with the data acquisition equipment and the data processing unit. The data acquisition equipment included an 8900 Locan AT acoustic emissions analyzer, and an ACRO-400 data acquisition and control unit. The main processor used was an Intel '286 based personal computer (PC).

The Locan AT acoustic emissions analyzer was used to collect information relating to sounds generated by the cracking of the carbon-carbon composite as it was heated. At some point, it is hoped that this information will lead to signature signals that are easily identified by artificial intelligence (AI) software. This information will then be used in the carbon-carbon composite process to prevent such cracking from occurring.

The user interface to the program was studied and finally modeled after a typical PC application such as Excel, with menu and sub-menu type pull-down windows. The interface was constructed from scratch, and the whole framework of the program was composed modularly and incrementally.

RESULTS

The program to obtain the data from the carbon-carbon pyrolysis process was named DacqPro. As of December 3, 1993 the program is in Beta testing. The program is functional, but needs to be more fully tested. The program is also constructed so that it can evolve easily, and be the center of future applications as previously mentioned.

From the work so far on this software project, several things have been learned from the software production process. First, the importance of documentation, rigor and formality was learned. An earlier version of the software application existed, but its documentation was nonexistent, the code was sloppy, and the program was incorrect. Because of this, the program was useless. Second, a knowledge of the importance of separation of concerns, abstraction, and modularity principles were gained. Application of these principles allowed the complexity of this project to be tamed. Finally, the importance of designing for change was firmly established in the programmer's knowledge base. By keeping the program evolvable, it should be useable for many other projects including the current one. Hopefully, it will be used for the current project successfully.

The program needs to be more thoroughly tested and verification and validation of the program's correctness need to be performed. Furthermore, the use of the program in the analytical aspect of data acquired from the pyrolysis process needs to be further studied.

NONDESTRUCTIVE EVALUATION

Task Order No. 46
Student Support Program
Southwestern Ohio Council for Higher Education

Edward D. Fisher, II
Wright State University

31 December 1993

Government Task Leader
Mr. Curtis Fiedler
WL/MLLP

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I would like to thank Mr. Curtis Fiedler for his constant support and undying patience. He has been an easy person to work with and has overloaded me with valuable insight and information that I am sure will be useful in future work.

TASK ASSIGNMENT

Ultrafast Laser Generated Ultrasound Background

Conventional ultrasonic inspection methods, which use piezoelectric transducers and a fluid coupling medium, have proven to be very useful for characterizing and evaluating the integrity of conventional structures. The thickness of a structure can be characterized by measuring the time for an ultrasonic pulse, propagating at a known velocity, to travel through a part. If the part is made of subassemblies, bonded with a process such as diffusion welding, the integrity of the weld can be characterized by measuring the amplitude of the ultrasonic echo from the weld. The integrity of parts can be evaluated by an analysis of the ultrasonic echos from defects. Because of it's usefulness in inspecting parts ranging in thickness from 0.1mm to tens of centimeters thick, we would like to use conventional ultrasonic inspection techniques to characterize the thickness and bond quality of thin coatings, ranging in thickness from 500nm to 0.1mm. Unfortunately, we cannot merely scale up conventional ultrasonics to examine thin coatings.

The minimum thickness of a part that can be inspected by conventional ultrasonics is limited by the frequency and bandwidth of the piezoelectric transducer used. By increasing the center frequency of a conventional transducer to 50 MHz with a bandwidth of 50 MHz, the thinnest layer we can inspect is 120 microns. While we can increase the center frequency of the transducer to 100 MHz or higher, the useable bandwidth remains at 50 MHz, which does not give any better resolution than a 50 MHz transducer. In addition, by increasing the center frequency of a conventional transducer, the overall signal to noise ratio is decreased because the attenuation of ultrasound, which increases as the square of the frequency, becomes a problem.

Laser generated ultrasound (LGU) has the capability to inspect materials without using conventional transducers or water couplants. A short pulse of laser light is used to rapidly heat the surface of the material. Thermal-elastic expansion of the material causes an ultrasonic stress wave to be generated. LGU has been shown to be especially effective in inspecting complex geometries and regions with a high degree of curvature.

Ultrafast laser generated ultrasound (UFLGU), which uses an extremely short pulse of laser light (0.1-5ps), can generate correspondingly short pulses of high frequency ultrasound necessary to inspect these thin layers. UFLGU generates ultrasound right at the surface of the coating, and uses the first few atomic layers of the coating itself as the transducer. This ameliorates the problem of attenuation of high frequency ultrasound through coupling and buffer layers. By generating the ultrasound with a very short pulse of light a correspondingly short pulse of ultrasound is generated. These short pulses of ultrasound can then be used to measure the thickness and bonding of thin coatings.

REQUIREMENTS

A technique to rapidly inspect thin coatings, ranging in thickness from 500nm to 200um is required. This technique must be non-contact to eliminate the possibility of contaminating the coatings. This technique must be rapid enough to be able to map out coating thickness and bonding over a 5mm by 5mm region (512x512 points) in a reasonable time. This technique must be able to inspect materials which are not piezoreflective.

RESEARCH PLAN

Initially we will develop a piezoreflective UFLGU system. This system will be tested on fiber coatings, oxidation resistant coatings and coatings for electronics. For coatings which are not piezoreflective, we will deposit a thin (25nm) nickel overlayer which is piezorelflective, to make the coating inspectable. Unfortunately, this overlayer makes this a destructive inspection technique. We also will develop a set of specimens with coatings of varying bond quality to demonstrate the ability of this technique to evaluate bond quality.

This UFLGU system will then be extended so that coatings which are not piezoreflective can be nondestructively inspected using interferometric detection of the ultrasound. We believe that a pulsed interferometer will be able to rapidly detect the ultrasonic echos of a coating. The signal to noise ratio (SNR) of good interferometers is shot noise limited, so the ultimate SNR is only a function of the amount of light through the system. Since we using pulses of light, the instantaneous light power through the system will be 50 kW, which is significantly more than the 2 mW which has successfully detected LGU. We believe that this interferometer should be able to detect the ultrasonic echo from the back surface of the coating in less than 1 second, and it should be able to detect the amplitude of the echo to within 1.0% of the actual value.

This work is high risk new science development which will have significant payoffs for both coatings currently being developed and in use. This technique will give us the new capability of being able to inspect the quality of bond between a coating and grabber) so that we can grab successive frames of these beams and process them in the form of a graph of intensity vs. position, in essence creating a spectrograph. I have written a program which will accomplish this goal of creating a spectrograph and have been trying to think of better ways to accomplish the real-time effect.

2. In order for the experiment to run, you must have a program which will take data, process that data, and effectively communicate that data via a graph so that it can be scrutinized. Instead of jumping directly into writing a C program to accomplish this, we started with a Macintosh program called Labview 3.0, to get a skeleton view of what exactly was needed. Labview enables you to create virtual instruments which allow you to manipulate real instruments from a sometimes elaborate panel via the computer. It also eliminates any coding by using icons and "wires" to literally wire up an experiment solely by sight. The downside of this method, of course, is speed. After the experiment has been successfully executed using Labview, it will determined if speed is an issue, all the Labview code and will have to be translated into C code. Some of the instruments that need to be designed as virtual are: SR530 Lock-in Amplifier, which will be used to take the data, that is, to convert the laser light signal used to examine a specimen into an electrical signal; the Aerotech Unidex 11 Translation Stage, which will be used to move the specimen in one dimension so that the entire area of a specimen can be scanned; and an autocorrelator, which will be used to calculate the full width half maximum (FWHM) of the laser light pulse (used also for calibration).

DEVELOPMENT OF A CONCEPT MEMORY AS A METHODOLOGY FOR SOLVING THE GENERALIZATION PROBLEM

Task Order No. 47
Student Support Program
Southwestern Ohio Council for Higher Education

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30 March 1993

Government Task Leader
Dr. Steven LeClair
WL/MLIM

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TASK ASSIGNMENT

The Task involved working on the development of the Rapid Design System (RDS). The RDS system is an attempt to develop a NEXT GENERATION design system that enables the coupling of design intent directly to product geometry. The central purpose of RDS is the integration of product and process design across materials and processes. The RDS is a feature based system in which the designs are made from basic blocks that are the design features. The uniqueness of RDS comes from the fact that it uses the Episodal Associative Memory (EAM) to store past designs. The designer can retrieve past designs by providing partial descriptions. This means that a designer could use past experience to improve their designs.

The main goal of this Task was to develop a system that is capable of performing feature sequencing in RDS. The premise is that the problem of feature sequencing is a complex enough problem that if a strategy (system architecture) is developed to solve this problem then the same strategy could be applied to solve many real world problems. Most problems involve some type of sequencing or scheduling activity.

The architecture that was agreed upon is shown in Figure 1. There are three components to this architecture:

1. The Machinist (the human).
2. The Genetic Algorithm (Conceptual memory).
3. The Neural Net (Perception memory).

This architecture allows for self improvement by allowing all three components to interact with one another. In a typical session, the machinist would design a part, ask the system for the feature sequence by using the memory or the genetic algorithm. If the machinist doesn't approve of the sequence produced by the system, the machinist may query the system for an explanation. The system will provide them with the rules that led to the sequence. If the machinist still does not approve of the sequence the system provided, they may provide their own sequence. The system will then take this sequence and run it through a module to find out which rules were used to arrive at the sequence. The sequence is then stored in memory.

Another possibility being considered here is to allow the genetic algorithm to develop the sequencing (scheduling) rules. This may be achieved by providing the GA with an initial pool of rules, and allowing the GA to combine the rules in different ways to produce new rules. The GA would then store the rules that provided the best sequence.

DESCRIPTION OF RESEARCH

The research involves using neural networks, genetic algorithms and Evolutionary Simulated Annealing (Pao, Percy). A functional link net (Pao) will be used to implement the memory. The Evolutionary Simulated Annealing algorithm and the genetic algorithm are being compared.

The programming is being done in C and LISP programs that communicate with one another via the foreign function interface provided by the concept modeler. At this point, we are running on Sun Sparc-10, and Sparc-2 stations.

RESULTS

The research here involves working in two separate, but related areas:

1. Memory
2. GA (s) and ESA

The approach used here to solve this problem is unique. It allows for self improvement, by allowing the different components to interact with one another and with the user.

Comparing the performance of the GA and ESA should provide an insight into how these two algorithms work and behave.

We started implementing the memory as an associative memory, which has proven to be ineffective for the problem because of data representation problems. We are trying to implement a clustering algorithm that will organize and store the data in a useful format.

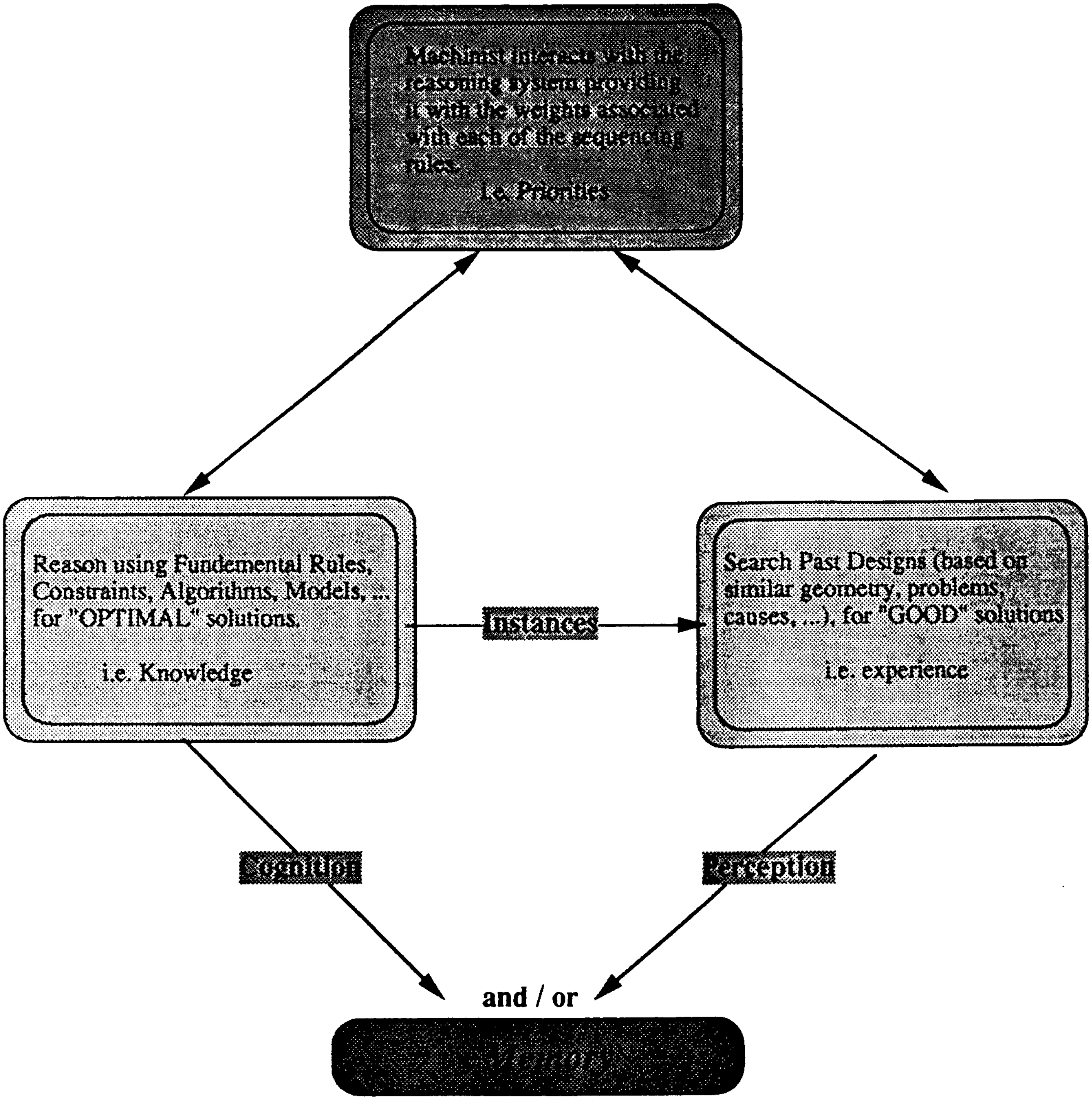

Figure 1, Overall System architecture

TRIBOLOGICAL EVALUATION FLUID AND LUBRICANT MATERIALS

Task Order No. 48
Student Support Program
Southwestern Ohio Council for Higher Education

Scott A. Long
Wright State University

15 July 1993

Government Task Leader
Mr. Shashi Sharma
WL/MLBT

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TASK ASSIGNMENT

While working under this Task, a variety of projects was completed. Continuing from the previous Task, the B-1 Pump Tests were completed, various software was learned and applied, and the design of an upgrade for a Traction Rig occurred.

Beginning in January, the B-1 pump test stand was up to grade and two tests, consisting of three 30 minute stages, were run. However, the practice tests had a few problems, which helped the main tests run smoothly. The three tests had minor problems, but as a whole, the tests ran well. The inlet temperature of the Hydraulic fluid, in the B-1 pump, began at 180 degrees F, and was raised by 30 degrees F each succeeding stage. The fluid ran at 50 gallons per minute at a pressure of 4150 psi. After examining the pumps at the end of each stage, the hydraulic fluid proved to be useful because the pumps looked like new. Therefore, the test was a success and the stand is awaiting new orders. As a result of the test, the software MacDraw was learned and a schematic was designed of the pump stand locating every feature. MacDraw made the process easy because every time there was a change with the stand, the file could be changed instead of redrawing it by hand. Next, two drawings of Oxidation-Corrosion Apparatuses were developed with MacDraw. MacDraw was very easy to learn and became very beneficial in these cases. By using the software Microsoft Excel, the data from the pump test was placed into a spreadsheet so all the data could easily be read throughout the test. Due to the test results and the software used, the B-1 Pump Test was given high marks.

In May, a third task involved reading old line graphs of the Physical Properties of Hydraulic Fluids from AIR 1362, May 1975, and creating charts of data points. The software Kaliedograph was learned and several graphs were designed from the charts produced. In all, about 60 graphs were designed and presented in a report on the physical properties of hydraulic fluids. Again, the software Kaliedograph was very user friendly and produced quality work without being time consuming.

In July, the software File Maker Pro was used and a data base was created to keep track of the computer systems in the branch. However, this software had its limitations, as do most programs, but its main drawback is the time it takes to learn its operation. Finally, during the last week of the Task, the Traction Disc Rig was being redesigned and certain components had to be sketched. This involved taking the old rig and designing new parts to work in conjunction with it. Most of the rig was designed outside the branch, but a few parts needed to be designed within.

After the design was completed, they had to be drawn to scale and checked for accuracy. At this time, the sketches are completed and the final touches are taking place.

I have learned a great deal throughout my Task, mostly to work with others. I gained the hands-on-experience needed in today's world, and learned how to use valuable software packages. I am very grateful to be placed in a fantastic atmosphere and am looking forward to continuing.

NONDESTRUCTIVE EVALUATION

Task Order No. 50
Student Support Program
Southwestern Ohio Council for Higher Education

Erik A. Jenkins
Wright State University

7 February 1994

Government Task Leader
Dr. Thomas J. Moran
WL/MLLP

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TASK ASSIGNMENT

Routine ultrasonic scans were performed to evaluate the suitability for study or the effects of experimental procedures on samples. These scans were performed as a service to members of other departments of the Materials Lab. A series of scans were performed as an interdepartmental study of the effects of residual stress on ceramic composites. In the pursuit of reproducible experiments, a form for recording scan parameters and the innovation of sketching samples insitu were introduced.

Software for controlling the apparatus of a small ultrasonic scanner and acquiring the data from an IBM PC compatible computer was developed. Modifications to the previous software were desired, but it was decided that modifying the previous software would have been more difficult than writing new control and acquisition software. Improvements in the software include: greater flexibility in choosing scan sizes including the ability to perform much larger scans, higher display resolution, and expanded color resolution. Ultrasonic scans are performed with transducers. Avoltage pulse is sent to the transducer generating a high frequency sound pulse which propagates to, and interacts with, a sample. Typically, the transmitting transducer is also used to convert signals echoing from the sample into voltage signals. These echo signals then are the data. More specifically, the average peak-to-peak amplitude of the echo signal was recorded. This technique is known as the pulse- echo or backscatter method.

The transducer is mounted on a frame which allows precise positioning in three dimensions. The position is controlled, via either servo motors or stepper motors, by a computer. The transducer is moved through a series of positions by the computer and the data for each position is recorded by the computer. The resulting array of data is then displayed graphically with colors and/or greyshades representing varying signal strengths forming an ultrasonic picture of the sample.

These pictures then are analyzed qualitatively by observing variations in amplitude and quantitatively by comparison with scans of samples of known quality and properties. The performance of this Task was very educational. The complexity of the experimental apparatus and procedure underlined the importance of consistency and carefulness in research. The practical nature of the work made it very interesting and relevant. The real world demands more creativity than the classroom. The opportunity to "stretch" was much appreciated. The software development experience was particularly rewarding.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND EVALUATION SECTION, WL/MLSE

Task Order No. 51
Student Support Program
Southwestern Ohio Council for Higher Education

Steve C. Medeiros
Wright State University

13 June 1994

Government Task Leader
Mr. Robert B. Urzi
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank all the personnel in the Systems Support Group for creating a work environment that is both enjoyable and educational. Special thanks to those individuals directly worked with: Mr. Robert Urzi, MSgt. Bryan Cramer, Jim Mazza, Mark Forte, and Mary Cooper of MLSE; Ron Kuhbander and James McKiernan of the University of Dayton Research Institute; and fellow SOCHE students Rob Cassoni and Jim Stubbs.

TASK ASSIGNMENT

During the final term of employment with the Materials Lab Systems Support Group, work was preformed as a lab technician. As such, the tasks performed were specimen preparation, mechanical testing and data acquisition and reduction. Work was primarily focused on three projects during this period. The first of these projects was the continuation of a study to determine the effect of various storage conditions on the mechanical properties of two film adhesives. The data obtained would be used to qualify the candidate film adhesives for field level repair use on existing aircraft. The second project participated in was the fabrication of graphite/epoxy composite panels for a study on composite repair concepts. These panels simulated a field level patch for a battle damaged aircraft. This study was to determine which method of affixing the patches to the aircraft was superior. The third project was a study to evaluate a water base adhesive primer. The adhesive primers currently being used contain chromates which is environmentally unfriendly. This study was to determine if the water base primers would have similar performance as the chromated primers.

DESCRIPTION OF RESEARCH

The storage effects study involved two film adhesives, three storage conditions and was carried out for 2 years. The adhesives were candidates because they were able to cure below the boiling point of water and were room temperature storable. The adhesives were stored at room temperature, at 38°F and at 0°F. Testing was performed at 3 month intervals for a total of 2 years. There were four tests run on each storage condition: tensile lap shear, floating roller peel, flatwise tensile and flow. All specimens were prepared using a phosphoric acid anodizing surface preparation to ensure that the failure modes were consistent and that the failure occurred within the adhesive. The lap shear panels were cured in a vacuum bag for pressure and were processed at full vacuum. The floating roller peel panels were cured under positive pressure in a heated press at 40 psi. The flatwise tensile sandwich panels were fabricated the same as the peel panels however, the pressure was only 15 psi. The lap shear and peel panels were sent to the U.D. campus to be tested and the results were sent back to be tabulated and analyzed. The flatwise tensile specimens were tested on the Instron 4505 and the flow test involved measuring the percent increase in the adhesive area after cure. These results were also tabulated and analyzed.

The second project work performed was the fabrication of graphite/epoxy panels for the composite repair concepts project. To simulate the battle damage repair of todays aircraft, graphite/epoxy panels were fabricated and either bonded or bolted to a composite parent laminate. The parent laminate, which was supplied by the customer, was autoclave cured and simulated the wing skin of today's advanced aircraft. The patch laminate was hand laid up using a three ply weaved graphite cloth which was then impregnated with a two part laminating resin. The particular orientations were cut from the cloth and stacked in sequence. The laminate was then cured under vacuum in a vacuum bag while heat was supplied from the platens of the press. Tensile lap shear specimens were fabricated using one adherent of repair laminate and one adherent as the parent laminate. The first specimens were adhesively bonded using a two part epoxy adhesive, while the remaining specimens were bolted using a special rivet for composite repairs. Some specimens were humidity aged prior to testing to determine the effect of moisture on the repair. The specimens were tested at room temperature and 90°C. The results were tabulated and analyzed by Mr. Ron Kuhbander.

The final project work was performed on the evaluation of a water base adhesive primer. The standard primer has chromates for corrosion resistance, but is being phased out by the E.P.A. This study was to determine if a water base primer will have mechanical properties similar to the standard primer. Wedge panels were fabricated since the wedge test is a good method of evaluating surface preparation. The manufacturers recommended surface preparation was a scuff sand/silane procedure followed by a water base primer. This method as well as grit blast/silane and phosphoric acid anodization surface preparations were examined. The wedge panels were placed in a humidity cabinet at 120°F and 95-100% relative humidity. Crack growth measurements were made initially after the crack was introduced, after 1 hour, 4 hours, 8 hours, 24 hours, 7 days and 28 days. The crack growth as a function of time determines the performance of the water base primer.

RESULTS

The 2 year storage effects study will finish in July. So far the study shows that the one film adhesive has better mechanical properties after room temperature storage and that the properties reach a maximum at 15 months aging time. The composites repair concepts study was finished and the results showed that the failure occurred within the patch laminate, and that the bolted patches took a much higher load than the bonded patches. As for the water base primer evaluation, the study is on hold until a new batch of primer is received. The results from the study so far indicate that the primer is not as good as the standard chromated primer. It was unclear if the data was inaccurate due to the primer being past its shelf life. Once the new primer is received, and the tests rerun, a better conclusion about the water base primer will be drawn.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND SYSTEMS SUPPORT SECTION, WL/MLSE

Task Order No. 52
Student Support Program
Southwestern Ohio Council for Higher Education

James W. Stubbs
Wright State University

31 December 1993

Government Task Leader
Mr. Robert B. Urzi
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank the following people at the Wright Laboratory for all their help and guidance during this Task: Mr. Robert Urzi, Mr. Jim McKiernan, Msgt. Brian Cramer, Mr. Mark Forte, Mr. Jim Mazza, Mr. Bill Purcell, Mr. Ron Kuhbander, Mr. Mark Kistner, Mr. Frank Fechek and Mr. Rob Cassoni.

TASK ASSIGNMENT

The objective of this Task was to conduct short investigations in-house to assist in the evaluation of various materials and processes for Air Force applications. The Task was divided into two full-time quarters of employment during the spring and fall of 1993. During both quarters of work, the student assisted in the fabrication, testing and evaluation of test specimen made from experimental and existing materials. The students were involved to some extent in many active projects during the work periods. The bulk of these projects required the students to fabricate and test various test specimen to examine the feasibility of adhesive systems for possible Air Force applications. The students were also exposed to composite repair procedures on actual aircraft for the Air Force. These procedures included adhesive bonding of precured boron fiber patches on the wing skins of an Air Force cargo airplane to restrict weep hole crack growth, and the design and construction of a fiberglass skin that was secondarily bonded to a wind tunnel model of the vertical stabilizer of a sub-orbital space vehicle.

Adhesive evaluation was conducted on two projects during this Task. The first of these was a series of tests to determine the shelf life of certain adhesives subjected to different storage conditions and times. Samples were prepared for overlap shear, flatwise tension and floating roller peel. The samples were then tested on an Instron 4505 testing machine. The results were compared with the original testing results to judge the loss of strength due to long-term storage.

The other project dealing with adhesive evaluation was a series of tests to find an adhesive with good high temperature qualities that could be cured at low temperatures. The adhesive was for repair of an Air Force airplane that required an adhesive that could be cured below 250°F to prevent structural damage to the aircraft, yet maintain 1800 psi at 350°F. Specimens were fabricated under 35 psi positive pressure and temperatures under 250°F for various cure time for overlap shear testing at 350°F.

Research was also done to determine if it is possible to find non-visual damage on composite fiber panels that have been exposed to a heat source. Test panels were obtained from the flight dynamics division and cut into 1 inch by 4 inch test coupons. These panels were then exposed to radiant heat from a bank of quartz lamps. The samples were exposed for different times and distances to obtain a range of damage on the sample's surface. The panels were then sent to be examined by the non-destructive evaluation section of Wright Laboratory to see if damage had occurred that was not visual. After it was determined that the project should continue, panels were taken to a thermal flash test facility for further testing. The panel size was increased to reduce heat losses near the edges and allow for a larger region of constant surface temperature.

In the adhesive storage project, the candidate adhesives were stored at room temperature, under refrigeration and at 0°C. It was found that the adhesives under study had the longest shelf life when stored at 0°C, with the greatest loss of strength when stored at room temperature.

Only one adhesive tested thus far in the repair concepts program has shown any promise. Four of five adhesives cured at or below 250°F only had overlap shear strengths of 1200 psi or less. The other adhesive tested showed a strength of approximately 2000 psi even when cured as low as 180°F. This adhesive is currently under more testing to examine the repeatability of these values.

In the heat damage project, several ways to find damage that is not visible are being tested. Research is also continuing to design a system of panel size and lamp setup to create a larger surface area of constant temperature on the panel's surface. This project is expected to continue for some time.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND EVALUATION SECTION, WL/MLSE

Task Order No. 53
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Cassoni
Wright State University

31 December 1993

Government Task Leader
Mr. Robert Urzi
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank Mr. Jim Mazza, Mr. Brian Cramer, Mr. Robert Urzi, Mr. Ron Kuhbander, Mr. Jim McKiernan, Mr. Jim Stubbs and especially Mr. Mark Kistner for the help they have given me over this past work Task. My efforts have been productive due to their experience and help.

TASK ASSIGNMENT

Over the past work term, three projects have been concentrated on. These include; Project 96, the evaluation of closed cell structural foam, Project 81, the study of slippage and foam characteristics within helmet liners and Project 109, the repair of weep hole cracking in wings of cargo planes.

Project 96, the evaluation of closed cell structural foam, has been an ongoing project which studies the strength and modulus (stiffness) for closed cell foam. It will eventually develop into a baseline for foam in the supportability of military aircraft. Due to the unorthodox results achieved in testing thermoplastics (foams) compared to metal alloys, much has been learned. Three test methods have been employed to determine the structural properties of the foams. These include Flatwise Compression, Dog Bone Tension and Compression Shear. All the tests are being performed at room temperature, 180°F and 212°F for both dry aged specimens and those aged at 85% relative humidity to saturation by weight. This project, which includes over 1600 test specimens is nearing completion. It should be completed in early 1994 during the next Task.

Project 81, the study of slippage and foam characteristics within helmet liners, has been actively ongoing since September 1993. Through meetings with Air Force personnel in Armstrong Laboratories/WPAFB, the problems involved in helmet instability and comfort were addressed and identified. The main factor involved in the slippage and instability was the coefficient of friction between the sanitary liner and the comfort liner. The comfort was based on the stiffness of the foam and surface area of contact between the pilot's head and the helmet liner. The test matrix thus includes a coefficient of friction test, a compression modulus (stiffness) test and a Creep test of foams aged at 180°F. Due to the softer and less structural nature of these foams, a different test machine with a lower load capacity had to be incorporated. Also, many innovative techniques and fixtures have been employed to simulate real life situations. Project 81 is still in the beginning stage and will be dealt with more in the next Task.

Project 109, the boron patch repair of weep hole cracking within the wings of cargo planes, has taken the greatest priority over this past Task due to the national impact of this problem. Many planes have been grounded and are not permitted to fly, thus a repair method was needed very quickly. The repair method consists of surface preparation on both the outer wing skin and on internal wing tank risers as well as two boron patches on the risers and one on the outer wing skin. Much is involved in the surface preparation and patching of these planes as it takes nearly 3 days to repair each crack.

Over this past work term, I have gained a wealth of knowledge and matured as an engineer and technician. I am the lead technician on Project 096 and have completed nearly all the testing myself.

On Project 81, my role has moved from mainly a technician into more engineering as I helped the lead engineer develop the necessary test matrix. On Project 109, I was involved in a repair developed by our group which was of national and immediate importance, one of the largest projects ongoing in the Air Force right now. I learned a lot on this project about surface preparation, priming a surface and boron patching. I have also been involved in the construction and repair of a wind tunnel model to test flutter on the National Aerospace X-30 plane. This has been very interesting and has taught me a great deal about composite skin construction and adhesion to kevlar honeycomb.

DEVELOPMENT OF GENERATIVE PROCESS PLANNING ALGORITHMS FOR FEATURE BASED DESIGN

Task Order No. 54
Student Support Program
Southwestern Ohio Council for Higher Education

David Domermuth
University of Dayton

30 July 1993

Government Task Leader
Dr. Steve LeClair
WL/MLIM

ACKNOWLEDGMENTS

The author's sincere appreciation is extended to Dr. Steve LeClair and the employees of the Material Process Design Branch.

TASK ASSIGNMENT

Documentation was performed of research to create a computer model for automatic feature based process planning.

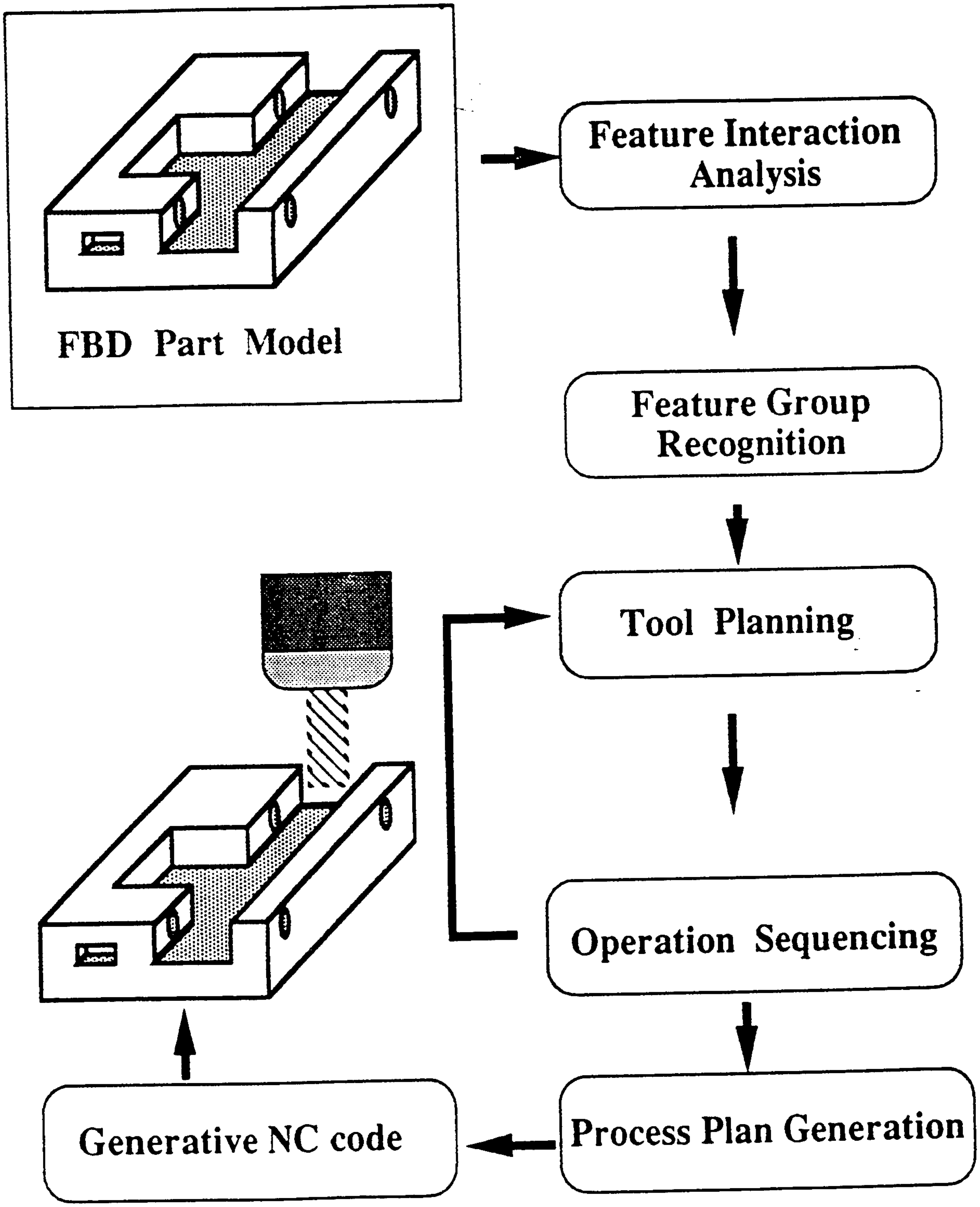
Work was performed to document, evaluate and correct a 3 year research effort in Generative Process Planning. A description of this work follows in the next paragraph. The work is described pictorially in the attached Figure. The documentation was performed on three different computer platforms as follows: text was produced with Word Perfect on DOS computers, figures were produced with MacDrawPro on Macintosh computers and the program was documented and produced with Framemaker on Unix work-stations. The final 250 page document represents the foundation of the authors' PhD Dissertation and will be submitted to the Air Force for reference.

DESCRIPTION OF RESEARCH

Commercial Computer Aided Process Planning (CAPP) systems for milled parts are dependent on the user to supply the operation sequence, the tools and the machining parameters. This dissertation presents an integral program of rule-based algorithms to automatically generate a process plan for milled parts directly from a solid feature based, object oriented, part model. The uniqueness of this effort is the development and application of techniques for feature group recognition, the determination of feature interactions and operation sequencing at the tooling level. The tooling and operation sequencing are optimized by an objective function of time and cost minimization. The optimization is based on setup order, minimization of tooling, minimization of tool changes, minimization of tool travel, standard machining practices and the use of similarity measures for group recognition, and the determination of feature interaction.

A data structure has been developed to generate the process plan and to drive a program to automatically generate numerical code to machine the part. This research represents the culmination of the manufacturing research performed by the University of Dayton for the Rapid Design System initiative of the Manufacturing Research Branch at Wright Patterson Air Force Base.

SOCHE has served as a very efficient Task management facility. The overhead rates were better than the competitive contract management firms and SOCHE does not require the long project lead time. As a result, SOCHE is providing an economical source of labor to the Air Force and helping to increase the educational level of the region by providing student employment.



PROCESS PLANNER

FIGURE 1. Process Planner

ELECTRONIC FAILURE ANALYSIS

Task Order No. 55
Student Support Program
Southwestern Ohio Council for Higher Education

George Baujan
University of Dayton

21 March 1994

Government Task Leader
Mr. George Slenski
WL/MLSA

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I would like to extend my thanks to the following for their help and assistance thoughout the course of my Task: George Slenski, Dale Hart, Bill Berner, John Ziegenhagen, Rick Reibel, Eddie White, Tom Duse, Ed Porter and others in the associated labs.

TASK ASSIGNMENT

A general description of this Task was failure analysis of electrical devices used in military equipment. The purpose of the assignment was to aid in the examination of electrical parts, components, circuits, and devices which may have been related to some failure. The objective was to determine quality of construction, mode of potential failure, and service capacity of electrical devices. The goal of the research is to assure that these devices conform to standards and will provide fail proof operations. The ultimate benefit of the research is the saving of human lives, increased reliability of products, better qualification standards, improved processing techniques, and innovation.

The general procedure used to evaluate a device was a multiple step process. The device is first visually inspected as received. Photographs are taken displaying this condition. Data is collected relevant to the accident and the conditions of use. Hypothesis and modes of testing are developed. Frequently, a new device will be compared to the failed device. Non-destructive evaluation and tests are performed first. The device is tested in a manner which simulates the intended use. Notes and results are recorded and compared to standards. If a problem is found, the device will be radiographed. The radiograph is followed by mechanical disassembly. During disassembly, each step is photographed, viewed under microscope, and re-evaluated. Each part of the device must be qualified. All components of the device are evaluated because the device is only as good as the sum of its parts. Suspected bad parts are then further evaluated until some conclusion is reached. Once a conclusion is reached, it must be tested for repeatability. A report is made of the evaluation indicating findings and future suggestions.

During the course of this Task, several projects were evaluated. Boost pump circuit breakers, from an aircraft, were examined because they were prematurely tripping and in some cases causing fires. The internal components of the circuit were tested for anomalies. Corroded contacts caused a condition of high resistance. This condition resulted in an excessive amount of power transfer through the contact interface. This voltage drop across contacts resulted in reduced thermal dissipation of energy by the circuit breaker.

Another project was to examine the circuit board and parts of an avionics computer. The device was inspected for corrosion, chipped parts, poor solder joints, and general condition. In this case, parts of the board were cut out, potted in epoxy and cross sectioned. Evidence of poor solder joints and cracked plated though holes was discovered using a high powered microscope.

Other projects involved the evaluation of wire samples used in aircraft devices. In one case, plated ire was oxidizing causing a condition known as Red Plague. The samples were placed in a humidity tank, removed several days later, and inspected under microscope. Exposed areas of copper were evident where plating had been oxidized. In a second case, wire which was plated and insulated with teflon was tested. The objective was to determine the breakdown temperature of the insulation and plating. Small samples were placed in an oven at different temperatures for a specific amount of time. The samples were then potted, sectioned, and inspected under microscope to find breakdown conditions. The findings were then compared to the conditions that occurred in an accident.

The work at the lab was a very beneficial experience. Perhaps the most beneficial aspect of the job was discovering the processes used to get to the root of a problem. The process used to work backwards from an accident to discover the cause of the failure is more complex than it might seem. Many aspects of the event must be taken into consideration. Each direction must be well thought our and documented before proceeding. No conclusion reached can be tagged the cause of the accident or failure, but it may prevent a failure in the future. Continual testing and searching for answers is what the research is all about. The ultimate goal is to make a safer, better and more reliable product for the future.

SYNTHESIS OF CONDENSED HETEROCYCLES FOR NONLINEAR OPTICAL EVALUATION

Task Order No. 57
Student Support Program
Southwestern Ohio Council for Higher Education

Vera M. Marsico
Wright State University

9 May 1994

Government Task Leader
Dr. Robert Evers
WL/MLBP

ACKNOWLEDGMENTS

I would like to thank Dr. Robert Evers, My Dotrong and Minhhoa Dotrong for their patience, understanding, cooperation and assistance throughout this Task. I have gained valuable experience and knowledge of chemistry that I will use in future endeavors. I am grateful to them, for their guidance has been essential to my growth and understanding of chemistry.

TASK ASSIGNMENT

This Task focuses on the synthesis of 4-(5-amino-6-hydroxybenzoxazol-2-yl)benzoic acid. Each of the seven steps in this monomer synthesis was developed such for the improvement of the quality and a higher percent yield of each compound obtained. This results in a more productive and cost effective synthesis.

The synthesis began with a nitration reaction of mphenylene diacetate. It was very important to maintain the reaction temperature at 10 C to have a maximum yield with minimal side products. From an analysis with thin layer chromatography, it was determined that a mixture of both dinitro and trinitro products were obtained. Purification began with boiling the yellow crystals in water to remove the trinitro product (soluble in the boiling water) followed by a recrystallization in ethyl acetate.

The purified dinitro product was then taken into a reduction reaction with tin chloride followed by the addition of acetic anhydride to form the amide compound. In this reaction, it was found that grinding the starting material into a fine powder was necessary for it to dissolve in the reaction mixture. Due to this, a product of appreciable yield was obtained. Thin layer chromatography was used to determine the purity of the product, which was washed with dilute hydrochloric acid and water to remove preliminary residues. After drying, the compound was recrystallized from acetic acid.

Next, the hydrochloric acid salt of the compound was obtained. Constant monitoring of the hydrochloric acid reflux was necessary with periodic shaking of the flask due to the high volume of HCl gas being released as the compound reacted. Upon cooling, a black compound precipitated and was collected.

This compound was dissolved in a minimum of hot water and neutralized with a saturated sodium acetate solution. Upon cooling, crystals were obtained and recrystallized from toluene. Purification of the product was checked using thin layer chromatography to show only one spot.

The fifth step of the synthesis reacted the compound with mono-methyl terephthalate in a nitrogen atmosphere to form the ester. Upon cooling, the product was precipitated using methanol. For purification, it was charcoaled and recrystallized from glacial acetic acid twice. Thin layer chromatography was used to check the quality.

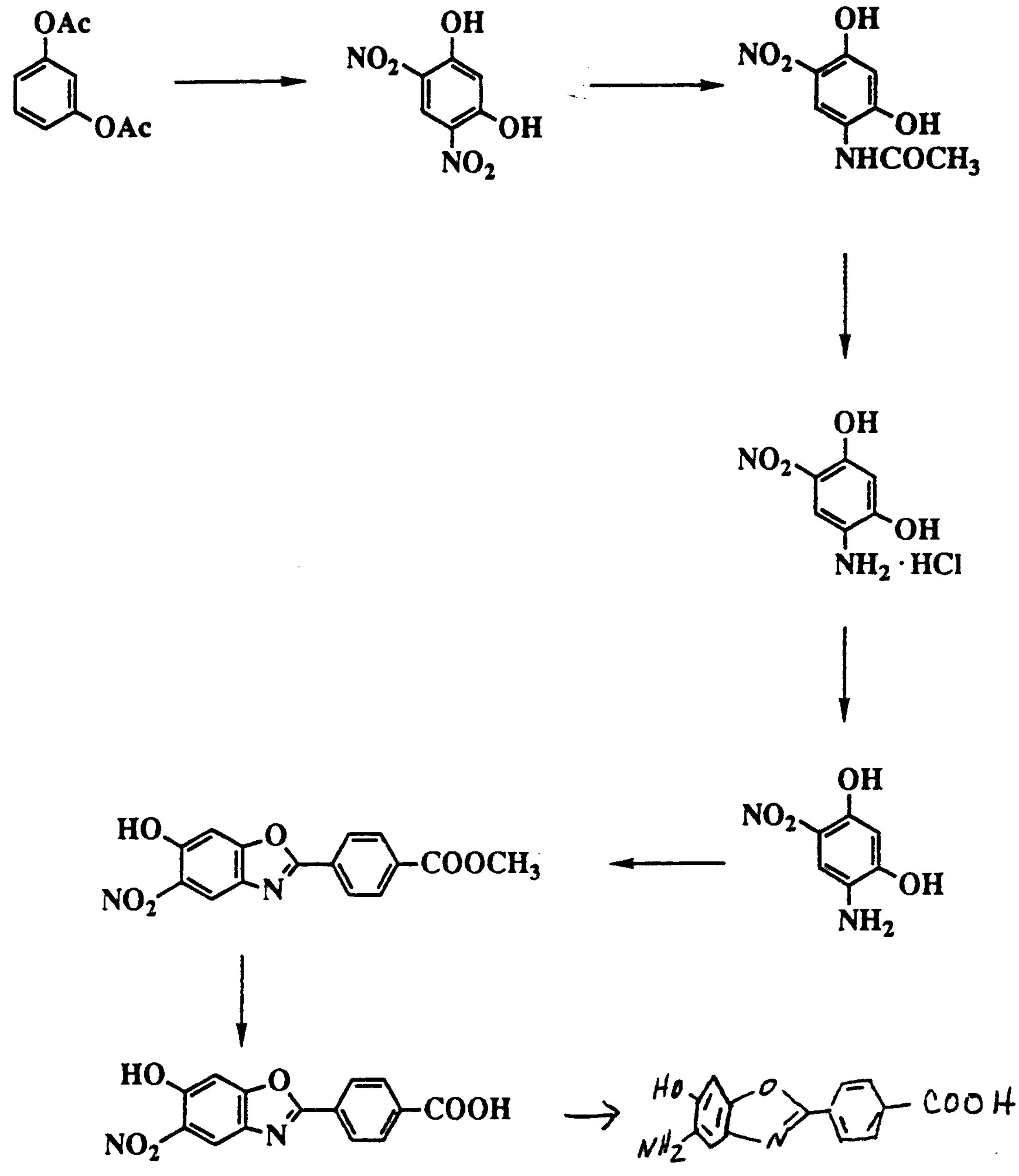
The carboxylic acid was formed from the ester in the next step using potassium hydroxide. Following the reaction, the mixture was poured into a 1:1 methanol/water solution, which allowed for the neutralization and collection of the product. To achieve a high level of purity for the final reaction, charcoal was used in two recrystallizations with dimethylformamide.

The final step in this synthesis involved a hydrogenation reaction with palladium and charcoal. The reaction suspension was placed in a parr bottle and shaken under 60 psi of hydrogen for approximately 24 hours. A degassed methanol/water mixture was used to precipitate the final product.

Analysis of products throughout the seven step synthesis included infrared spectroscopy, elemental analysis (carbon, hydrogen and nitrogen) and thin layer chromatography as mentioned before. From these, the compounds could be identified as the desired products along with their degree of purity to proceed with the synthesis.

This Task centered on the synthesis of a monomer compound, 4-(5-amino-6-hydroxybenzoxazol-2-yl)benzoic acid, which is outlined on the following page. Refinement of this synthesis resulted in a more efficient method of obtaining this compound, which has been used in a successful polymerization. Further research is being conducted on this polymer to provide further insight into it's properties.

Synthesis of 4-(5-amino-6-hydroxybenzoxazol-2-yl)benzoic acid



SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC COMPOUNDS FOR NONLINEAR OPTICAL PROPERTY EVALUATION

Task Order No. 59
Student Support Program
Southwestern Ohio Council for Higher Education

Paul Roderer, Jr.
University of Dayton

14 June 1994

Government Task Leader
Mr. Bruce Reinhardt
WL/MLBP

ACKNOWLEDGMENTS

Because I have now completed my education, I unfortunately will not get a further opportunity to work with Mr. Reinhardt's group in the Polymer Branch. I will undoubtedly miss the patience, guidance and camaraderie I have felt during the last 4 years as a member of this very special group of individuals. Furthermore, I am forever grateful for the knowledge these people have taught me and the invaluable experience I have received as a member of this group. Mr. Reinhardt's group is a unique blend of talented, insightful, hard-working chemists who accomplish whatever they set out to do. Thank you Gibby, Marilyn, Jay and Rom. I will miss all of you very much, and I wish you all success and happiness out of life. With your talents I'm sure you will achieve both. Most of all, thank you Mr. Reinhardt. I will miss your insight and guidance in not only matters pertaining to chemistry, but life in general. You are a much appreciated friend and I hope this does not change.

TASK ASSIGNMENT

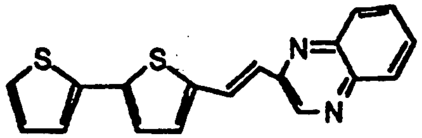
Several different hetrocyclic and aromatic compounds were synthesized for nonlinear optical (NLO) study. NLO research is on the cutting edge of physical and chemical research with ultimate goals of improving communication and computer technology by compounds that refract electromagnetic radiation in a non-linear fashion. This Task focuses on the development of organic NLO compounds with emphasis on synthesis of possible NLO compound.

Extensively conjugated organic compounds have shown a high degree of promise in NLO activity. Since hetrocyclics and aromatics are highly conjugated compounds, they theoretically may exhibit a high degree of NLO activity. As a result of hetrocyclics and aromatics' theoretical NLO potential, this Task focused on synthesis of model hetrocyclic and aromatic compounds for NLO testing. This Task focused solely on the organic synthesis of these compounds and involved none of the physical characterizations necessary to determine NLO activity. The structures of the major hetrocyclics and aromatics developed during this Task are outline in Figure 1.

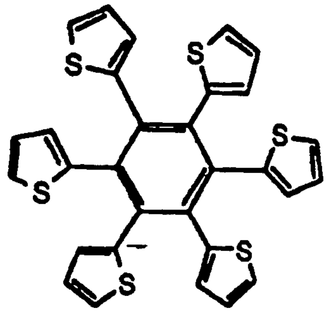
In addition to the synthesis of the above mentioned compounds, Task 59's duties also consisted of extensive training and learning how to operate a Perkin-Elmer 7700 Dynamic Mechanical Analyzer (DMA). Learning this instrument required an intensive review of the instrument's manuals and developing an understanding of the physical properties measured by the instrument and how they interacted. Much research was necessary to meet this goal. After developing competent understanding of the instrument and its parameters, the student measured several parameters on thin polymer film including storage modulus, loss modulus and Tg. The Task included plotting these polymer film properties and preparing them for presentation.

Figure One: Some Hetrocyclics and aromatics developed during this task

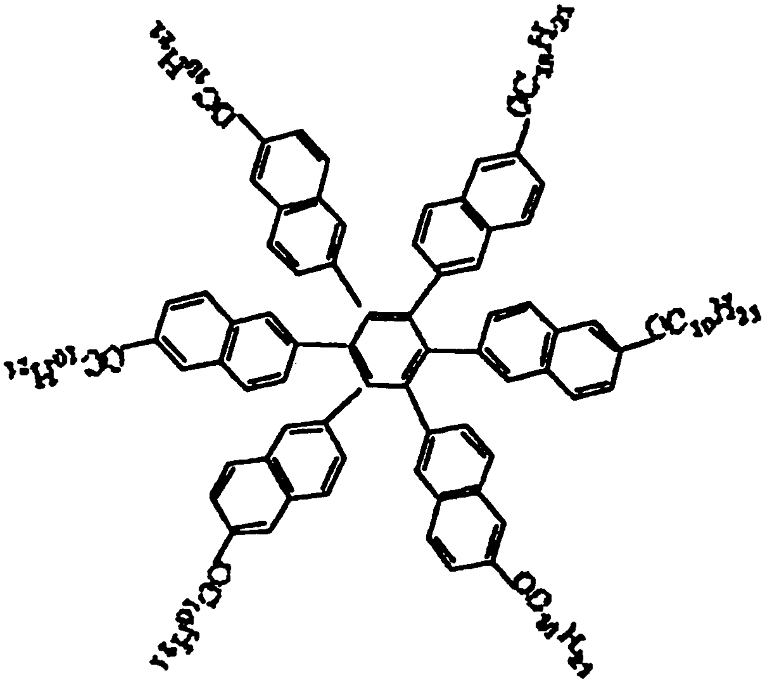
Compound A



Compound B



Compound C



Compound D

RESULTS AND DISCUSSION

All of the above mentioned compounds were successfully synthesized except compound D. The Task time ended before the completion of this project. However, my successor will probably complete this synthesis since the synthesis route and mechanism is identical to the synthesis route and mechanism of compound C.

Typical duties during this Task were as follows. Mr. Reinhardt assigned library research projects that provided expectant synthesis methods for the model compound. After completing the library work, Mr. Reinhardt determined which synthesis methods would be used to synthesize the compound. The lab inventory system was searched to locate all necessary starting materials for the reaction. The necessary lab equipment was set up and the reaction run. The reaction was worked up with standard procedures such as vacuum filtration, extraction, neutralizations and vacuum removal of reaction solvents. The crude products were purified by recrystallization, column chromatography, charcoal treatment, distillation and mechanical filtration. The purified products were characterized by melting point determination, thin-layer chromatography, nuclear magnetic resonance and infrared spectroscopy. Finally, the purified characterized compounds were mailed to Buffalo, New York for NLO testing.

CONCLUSION

This Task concentrated on the synthesis of novel and aromatic compounds for NLO evaluation. The main hetrocyclic and aromatic compounds developed during this Task are indicated in Figure 1. As in the last several tasks completed by this student, many challenging research and experimental techniques were used to develop these compounds. While NLO data has not yet been compiled on these compounds, their successful production will hopefully provide further insight into NLO activity.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC COMPOUNDS FOR NONLINEAR OPTICAL PROPERTY EVALUATION

Task Order No. 59a
Student Support Program
Southwestern Ohio Council for Higher Education

Gina Hess
Wright State University

14 June 1994

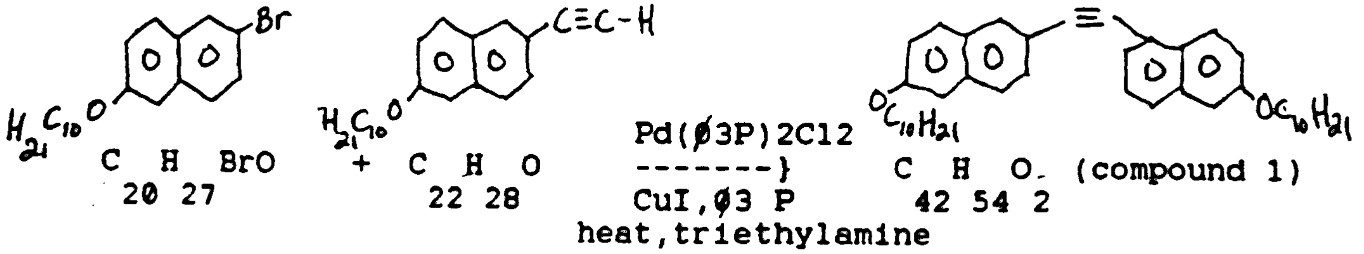
Government Task Leader
Mr. Bruce Reinhardt
WL/MLBP

ACKNOWLEDGMENTS

I would like to express my appreciation to Mr. Bruce Reinhardt, Gibby Dombrowskie and Paul Roderer who helped me in this Task Assignment and have shown much patience.

TASK ASSIGNMENT

The purpose of this Task was to synthesize aromatic compounds for nonlinear optical properties. One compound of interest is shown as the product in the following reaction:



The acetylene and bromo compounds in triethylamine were degassed with nitrogen. The catalysts were added, and the mix was heated for 24 hrs. at 90 degrees Celsius. After this, the mixture cooled to room temperature and was filtered to remove triethylamine salts. The triethylamine was removed with a rotovap. Recrystallization with hexane was performed, and both the mother liqueur and crystals were eluted through a chromatographic column. Yield was very low - only 1.46%. Portions of the product were sent for elemental analysis and mass spectrometry measurements. As of yet, the results have not returned to either confirm or deny whether the product obtained is truly compound 1.

It is hoped that this compound will be useful in synthesizing materials which demonstrate nonlinear optical properties.

NOTCH FATIGUE OF METAL MATRIX COMPOSITES

Task Order No. 60
Student Support Program
Southwestern Ohio Council for Higher Education

Alisha Hutson
Wright State University

15 June 1994

Government Task Leader
Mr. Jay Jira
WL/MLLN

ACKNOWLEDGMENTS

I always seem to find something new to learn here, and I thank everyone in ML for helping me learn. Mr. Jira has continued to be an excellent mentor and has supported my efforts at school in every way. I look forward to the coming year. I'm sure it will be as challenging and educational as the last one has been. I would like to thank everyone again.

TASK ASSIGNMENT

Duties required for this Task included continued support for the Mechanical Behavior Branch in the research of Titanium Aluminum Composites. Specific tasks ranged from data reduction and analysis of center hole tension fatigue specimens to qualitative analysis of the same using metalographic techniques and fractography. In addition, specimen tracking and bookkeeping were required for both the lab and the contracting company, as well as assisting in data collection and "dressing" for in-house reports, technical report publications and materials symposium presentations.

Data reduction proceeds as follows. Optical data must be obtained from photos taken during the test. This is obtained by measuring the length of the crack on each photo taken at various intervals during the test using a digitizing unit with a TEK computer to store the data. It is then correlated with crack growth data also taken during the test. This step requires running both files through a program that takes the pertinent information from both files and merges it into one file with a standard header and column labels. This file is then run through another program that generates a data set which represents the data without all the scatter. The two new files are then transferred to the Macintosh and used to generate plots that will tell the engineer most of what he needs to know about the test at a glance. Any discrepancies producing an error of greater than 10% are assumed to have occurred as a result of a test error. The source or sources of the discrepancy are searched out and the error is explained as much as possible. It is assumed that the optical data is more accurate than the data taken during the test because of the presence of material features that can easily bias readings during the test. This assumption is confirmed by a crack length measurement from a blow-up of the last photo taken before the end of the test, and by taking a crack length measurement from the unfailed specimen or by using the oxide layer occurring on the fracture surface of high temperature specimens that have failed to determine the point of failure. A method of measuring crack length just prior to failure for room temperature specimens is currently undergoing testing.

In addition to the above data reduction, it must be decided which photos will be enlarged, and in some cases enhanced. The student places the order for the enlargements, or for the bitmap files of various frames from the test. If bitmap files are required, the student also enhances the photo files and then places the order for the enlargements after enhancement.

Metalographic techniques are employed to view various cross-sections of a specific test. Once the specimen is mounted and polished, documentation of the surface features is done using high precision optical microscopes, or a scanning electron microscope (SEM). Several specimens required qualitative analysis after testing. Some were mounted and polished or etched to view features inside the specimen. These were observed using microscopes and the SEM. Others were placed in the SEM whole to view the fracture surface, and get a clearer view of the region changing from fatigue to fast fracture.

The current material investigation is nearing a close. Most of the necessary tests have been conducted; however, both quantitative and qualitative analysis is still under way. During this research, it has been found that some of the techniques used were unacceptable for the purpose they were used for. As a result, new techniques are being formulated and tested to replace those that were less than perfect.

HALF-TIME STUDENT AIDE

Task Order No. 61
Student Support Program
Southwestern Ohio Council for Higher Education

Ayman S. Amara
University of Dayton

1 August 1994

Government Task Leader
Dr. Randy Hay
WL/MLLM

ACKNOWLEDGMENTS

I would like to sincerely thank the persons at the ceramic composites group who gave me the chance to achieve my goal, namely Dr. Ronald Kerans, Dr. TAP and Dr. Shankar Sambasivan. Also I would like to thank Cindy Emerick (SOCHE), and especially Dr. TAP and Dr. S. Sambasivan for helping me to achieve this Task and for teaching me more useful lessons in materials than any classroom or textbook.

TASK ASSIGNMENT

Bending and indentation tests have been used to determine the mechanical property of the interfacial layer in ceramic matrix composites. Previous tests (push-in and pull-out tests) have shown a significant relationship between roughness of the interface and Possions effects.

The effects of the interfacial roughness, which contributes to the sliding resistance, have been neglected by most researchers. The objective of the Task is to test the theoretical models that provide an insight into the effects of the interfacial roughness during progressive debonding.

MODELS:

1. The specimen of the first model is a Cylindrical fibers "YAG" of a finite radius and 1 inches length embedded in a tetrahedral matrix (L=1.25', W=8/64', T=17/64") made of B Alumina. An artificial crack notch of about 1 millimeter was made in the matrix at the midpoint of the specimen. The specimen is supported at both ends where the notch was made while load is applied on the opposite face at the midpoint. This model is considered to be independent of deflection and stress distribution along the bonded interface.

2. The specimen of the second model is Tetrahedral Crystals of finite dimensions where l=5 mm, w=2 to 3 mm and t=1 to 2 mm embedded in a tetrahedral matrix (L = 25 mm, W = 3 mm, T = 6.7 mm). The crystal was made of "YAG doped in Calcium or undoped" or Neodymium while the matrix was made of B Alumina. An artificial crack notch of about 1 millimeter has been made at the midpoint of the specimen. The specimen is supported at both ends where the notch was made while load is applied on the opposite face at the midpoint. This model is independent of any deflection and stress distribution along the bonded interface.

PROCEDURE: Both models have been prepared adequately by using a Hot Press technique where 30 grams of B Alumina was used for the first model, while 13 grams of B Alumina was used for the second model. Square die of 1.25" was used for the first model, while round die of 1 inch was used for the second model. For both models, Molefoil and Grafoil, have been used to isolate hot press powder B Alumina from any leakage out of the center of the chosen die. Applied pressure was held constant at P = 50 psi on ram while the temperature was changed from 0° C to 1425° C by changing applied power from the set point of 28 KW to 38 KW.

Samples from both models have been annealed at 1400° C for about 72 hours at the rate of 10° C. The polishing technique from grade 36 to 3 micron was then applied. Thin and sharp blades were used to slice samples of either models into several slices of given dimensions. An artificial crack notch of about 750 micron was made perpendicular to the cut plane. Then several Metallographic pictures were taken for later comparison.

A bending test has been applied using digitalis 8562 INSTRON machine where load has ranged from 80 to 100 psi. Then Indentation test using Vicker hardness head has been applied along the interface of fiber or crystal and matrix to study the crack behavior and the toughness of the interface.

CALCULATIONS:

1. Bending Test:

$$K_{Ic}=\frac{3PL}{2bw^{2}}a^{0.5}f(\frac{a}{w})$$

$$f(\frac{a}{w})=1.00-2.47(\frac{a}{w})+12.97(\frac{a}{w})^{2}-23.17(\frac{a}{w})^{3}+2.48(\frac{a}{w})^{4}$$

Where: a = depth of the notch
b = width of the slice
L = length of the slice
W = thickness of the slice

Example a=0.8mm, b=3.4mm, L=19mm, w=5.9mm, P=87lb

$$f(\frac{a}{w})=1.834$$

$$K_{Ic}=\frac{3(87)(0.019)}{2(0.0034)(0.0059)^{2}}(0.008)^{0.5}(f(\frac{a}{w}))=12.288(10)^{3}$$

$$k_{Q}=4.784MPa\sqrt{m}$$

2. Indentation Test:

$$HV=\frac{Test\ load\ (kgf)}{Surface\ area\ of\ the\ Indentation\ (mm^{2})}$$

$$HV=\frac{2F\sin(\frac{x}{2})}{D^{2}}1000$$

$$HV=1854(\frac{F}{D^{2}})$$

RESULTS AND DISCUSSIONS

1. Debonding has been noticed clearly along one side of the crystal interface. It might be due to thermal expansion during annealing process.

2. A crack has been noticed bridging over the crystal and fiber. It might be due to applied pressure during hot press or thermal stresses during annealing process.

3. Cracks also have been noticed in the matrix along grain boundary in doped specimen. This could be due to absorption of calcium from doped crystal into boundary layer of matrix.

4. Cracks tend to go in different directions at triple point following neither parent cracks.

5. Cracks in two neighboring slices have shown similarity in behavior. Cracks might be a 3D phenomenon.

6. Struntum nitrate react with plain Alumina glommrising grain along the matrix. Consequently increase the porosity of the matrix in the fiber region. It is believed that Struntum nitrate dopped, dissolved or mixed with Alunima would not form B Alumina structure rather than weaken the matrix by having more voids.

HALF-TIME STUDENT AIDE

Task Order No. 61a
Student Support Program
Southwestern Ohio Council for Higher Education

Gregory Meyer
University of Dayton

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Government Task Leader
Dr. Randy Hay
WL/MLLM

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TASK ASSIGNMENT

Task Assignment 61 consisted primarily of two separate research objectives in an attempt to further the understanding of the behavior, characteristics and usefulness of ceramics within the scope of the U.S. Air Force. The two primary research objectives consisted of a study of the strength performance of YAG ceramics and Yttrium-doped ceramics and analysis of several Fiber Push-Out tests which were performed on fiber reinforced ceramic matrix composites. Both objectives are being researched because of the apparent high strength, high temperature and light weight properties available in processed ceramic composites as compared to the corresponding properties of the much more commonly used metals in use today.

All the researching time and effort is being spent in the hope of eventually producing a fiber reinforced ceramic matrix composite which will perform as well as, if not better than the metal composites which are currently in use in such applications as turbine engines for the U.S. Air Force. The knowledge gained from this research, if found to be successful in replacing metal in turbine engines, also may move on to generate interest in ceramic composites in a much wider scope of applications for both government and non-government purposes.

The process through which this research is performed differs widely between the two primary projects, one having it's emphasis on the technical procedures of research and the other emphasizing analysis of data and results. Beginning with the former, leads us to the study of the YAG ceramics and Yttrium-doped ceramics. This study involves preparation of the initial powders through basic chemistry techniques. These powders are then formed into their final condensed state through a process called hot pressing and are subsequently tested to evaluate their strength.

Such strength testing, called Creep Testing, evaluates a ceramic's reaction to high stresses under elevated temperatures, to mimic the conditions encountered within a turbine engine. This testing is performed with the use of an Instron loading cell which collects the temperature, load and displacement data whereby the ceramic is then analyzed to characterize it's stress to strain behavior.

The condensed ceramics are also evaluated for the growth size of their crystal grains, which indicates optimum strength and processing techniques, through the use of a scanning electron microscope (SEM). A SEM is necessary because of its ability to view objects at much higher magnifications than normal optical microscopes. Before any analysis on the ceramics can be performed, however, the specimen must be cut and ground to an appropriate size and shape and then polished to a mirror-like finish, all of which is done using diamond edged blades, grinding wheels and polishing solutions.

The second primary project consists of data analysis of fiber push-out testing using KaleidaGraph, a spread sheet graphing package, on an Apple Macintosh. The raw data obtained during the push-out test of a fiber reinforced ceramic matrix composite is manipulated through the use of a theoretical set of guidelines which were developed to determine behavioral and strength characteristics of the composite. This involves identifying and accounting for the compliance of the equipment used in the testing as well as the elastic behavior of the composite itself. Through such manipulation certain characteristics of the composite, such as coefficient of sliding friction, radial stress, interface toughness, etc., can be calculated.

Performing the actual push-out testing on these fiber reinforced ceramic matrix composites involve a fairly simple arrangement of equipment set up to produce a stress on the fiber which is imbedded within the matrix while at the same time recording the displacement of the fiber from it's original position. An Instron loading cell is used to produce the stress upon the fiber, while the displacement and acoustic emissions are recorded to an IBM data file and a graph of the stress behavior is plotted. The specimen being tested is, as before, prepared by cutting and grinding to the appropriate shape and size followed by polishing it to a mirror like finish.

To date, much new knowledge has been gained in the area of ceramics and ceramic composites. The purpose of this Task has been to concentrate on the processes and techniques used in the preparation and evaluation of the materials being studied. Hot pressing, use of a SEM and fiber push-out data analysis have now become familiar techniques in the research of ceramics and how they behave and are characterized. Interpretation of much of the data and results is still ongoing and requires more time to fully understand where these ceramics and ceramic composites stand when placed within their ultimate goal.

HALF-TIME STUDENT AIDE

Task Order No. 62
Student Support Program
Southwestern Ohio Council for Higher Education

John R. Welch
Wright State University

15 June 1994

Government Task Leader
Dr. Ronald J. Kerans
WL/MLLM

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I would like to extend my appreciation and thanks to Dr. Randall Hay and Dr. Ronald Kerans for the opportunity to work and learn in the ceramics division of the Materials Lab at Wright Patterson Air Force Base. I also wish to thank the other engineers who have provided opportunities for me to work and learn, including Dr. Michael Cinibulk, Larry Matson, and Dr. Craig Folsom. I also want to thank the staff of the Metallography Laboratory for their assistance in the accomplishment of my tasks.

TASK ASSIGNMENT

The majority of the Task was spent doing metallographic characterization of ceramic materials and ceramic fiber matrix composites. Preparation of ceramic fiber matrix composites for hot pressing, heat treating, preparation of ceramic materials, production of creep specimens, bend bars, and push-out samples for mechanical testing of strength and stability of ceramic materials was also performed. Additionally, characterization of experimentally produced fibers was performed for government contractors and other industries.

Most of the work was done under the supervision of Dr. Randall Hay. During the first 6 months of the Task, the emphasis was production of samples with a YAG (Yttria Alumina Garnate) with Saphikon (TM) fibers coated with various combinations of molybdenum, zirconium and carbon. The goal was to find a composite material suitable for usage in aircraft, possibly in the afterburners of the engines.

The production of these composites consisted of coating the fibers by so-gel solution in a specially designed coating machine equipped with a high temperature furnace. The fibers were sectioned after coating and laid parallel on paper held in place by tape. This was then sectioned into 1 1/4 inch square sections, placed between layers of YAG in a graphite die, and then hot-pressed.

The hot-pressed composites were then sawed into sections and heat treated at various temperatures for varying lengths of time. These sections were then mounted in Epomet (TM) for production of thin foils to be viewed in the TEM and, also, occasionally a scanning electron microscope (SEM). Micrographic photography would often be performed on the samples, if aspects of the material were noticeable under that magnification.

Production of thin foils for TEM is an often lengthy process that consists of several phases. The mounted samples are ground flat on diamond impregnated disks until a smooth surface is obtained. The mounted sample is then polished in stages on a mechanically rotating brass wheel covered with cloth (usually silk) with a combination of diamond paste and diamond suspension fluid in a slurry, ranging in coarseness from 45 microns to as small as 1/4 micron. The mounted sample is polished until all noticeable scratches are removed or the best possible finish is obtained, as samples will sometimes tend to disintegrate or have grains "pluck out" when polished with certain sized diamonds. If the sample is stable enough, the final polish will sometimes be done on a machine called a Vibromet, which is just a vibrating surface where diamond pieces are immersed in a lubricating fluid.

The polished surface is then epoxied on to a glass slide with a heat sensitive epoxy (crystal bond, usually). The sample is then cut as close and as parallel to the glass slide as possible. The part of the sample mounted on the slide is then ground and polished with diamond disks, pastes, and suspensions until the sample is around 5 microns (or less) thick. The final polished thickness depends on a number of factors, including the type of material, whether the material has a fiber-matrix interface in it, and the stability of the material under the pressures and stresses of polishing. Grain size of the material is also a factor in the final thickness of the sample, since materials tend to disintegrate when polished with materials that are nearly the same size as the grains. The thin foils need to be as thin as possible in most instances to minimize the amount of thinning required in the next phase. Micrographic photography is performed at this stage, if desired.

The next phase of preparation consists of appeasing small grids on the sample in places of interest. An oval is then epoxied over the grid and the grid is removed from the glass slide. The sample is then placed in an ion mill which fires argon atoms at the sample. The milling continues until the sample is so thin that it almost has a hole in it, perhaps in the tens of nanometer range. The sample is then ready to be observed in the TEM The remainder of the mounted sample can be polished and observed in the SEM.

The results for the ceramic fiber-matrix composites with fibers coated by molybdenum and palladium have not, in general, been very successful. The coating has a tendency to be sporadic and not completely protect the fiber from the matrix. Heat treating has shown a tendency to burn up or dissipate the coating. The coatings have also shown a tendency to "squash" into the matrix under the applied loads during hot pressing.

During the last 6 months of the Task, the emphasis has been on producing a viable ceramic from pollucite, which is a substance of Cesium oxide, Silicon oxide, and alumina ($CsAlSi_2O_6$). The interest in this polycrystalline ceramic is due to its very low coefficient of thermal expansion at temperatures above 200 degrees Celsius, and a favorable dielectric constant. Creep testing has shown the flow stress of pollucite to be comparable to that of polycrystalline mullite and YAG at temperatures of 1400-1500 degrees Celsius. Pollucite may have an even greater flow stress, but processing problems have prevented the production of a high density or pure sample. The samples produced by hot pressing have shown to undergo incongruent vaporization of cesia, causing the formation of mullite glass toward the outer edges of the sample due to cesia loss to the atmosphere. Another processing problem experienced has been the inability to produce a sample near the theoretical density of pollucite ($3.3 g/cm^3$). Samples produced to date have only attained 80-90% of the theoretical density. The last sample produced was by hot isostatic pressing instead of hot pressing. Purity for this sample was high (TEM analysis has not been performed yet), but much porosity was prevalent in the sample.

Characterization has been performed on many experimentally produced fibers, including some SiC fibers and some SiN fibers grown from a laser. The latest emphasis has been on coated "tows," which are tiny (15-25 microns in diameter) ceramic fibers that are bound together much like the strings in a rope. Characterization of these fibers takes a few extra steps in that they have to be mounted in epoxy and compressed together in a thin glass tube to be polished successfully. Some tows have been produced in cooperation with industry. No TEM analysis has been performed on the samples at this time, but will be soon.

The outlook for next year includes further investigation of the properties and processing of pollucite. Additional work in coated fiber tow characterization is forthcoming, as Dr. Hay intends to assemble a new fiber coater. Recently, some coating of Saphikon fibers with gallium oxide has been performed and they are the current TEM foil project.

HALF-TIME STUDENT AIDE

Task Order No. 63
Student Support Program
Southwestern Ohio Council for Higher Education

Cathleen M. Gustafson
Wright State University

15 June 1994

Government Task Leader
Dr. Randall Hay
WL/MLLM

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TASK ASSIGNMENT

Interest in brittle matrix composites has increased since the 1970's. This interest was largely due to the need to develop new advanced materials to deal with today's needs. By making fiber reinforced ceramics, most of the overall properties of the ceramic improve. Two of the most noticeable improvements are in the tensile strength and fracture toughness.

The scope of this project was to investigate the effect of fiber volume fraction, spacing regularity, thermal expansion mismatch, and fiber coatings upon the "matrix cracking stress" (MCS) of ceramic matrix composites. Matrix cracking stress is the minimum stress required to initiate a crack in the matrix. Theoretical models have been developed which predict that fiber spacing and residual stresses due to thermal expansion mismatch between the matrix and fiber, greatly affect the MCS. It has been predicted by the Full-Cell Cracking Model[1] that by increasing the fiber volume fraction, the MCS would increase. The model was based on a Brittle Matrix Composite (BMC) with a parallel, uniform, hexagonal array of fibers in a fully dense brittle matrix. Previously, these ceramic composites had not been made. BMC's, made by tape casting and lamination, were used to validate these model predictions.

A number of processes has been used in the past to make fiber reinforced CMC's using whiskers. One of the current ways of making continuous fiber reinforces CMC's is by packing the ceramic powder around the fibers and hot pressing the compact. This process is time-consuming and costly. An alternative to this approach is with a process called tape casting. Tape casting is a process that is currently being used for metal matrix composites.

The main steps to the Task were 1) determining the materials to use; 2) determining the correct formulas for the slurry to use; 3) casting tapes; 4) laminating composites; 5) sintering and hipping the samples; 6) having the samples tested; and 7) analyzing the data.

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[1] Pagano, N. J. And Kim, R. Y., "Progressive Microcracking in Unidirectional Brittle Matrix Composites." Winter Annual Meeting ASME, New Orleans, LA, 28 Nov. - 3 Dec. 1993.

DESCRIPTION OF RESEARCH

Tape casting is the process of creating a very thin film (about 0.008 inches thick) of ceramic. This is called a ceramic tape. The CMC's are then made out of this tape. Fiber mats are laid on the tape and pressed together to form laminates. The laminates can be made to size or cut to shape.

It was decided to start working with a glass matrix before going on to other types of polycrystalline matrices. This allowed a working formula and procedure to be created and not be too costly. Developing an actual working formula for the glass slurry took time because the ratios of the ingredient were hard to determine. Slight changes in the ingredients could throw off the whole recipe.

The actual tape caster consists of a smooth, even surface, a doctor blade and a moveable arm to slide the blade over the surface. It consisted of a reservoir to hold the slurry and an adjustable blade to control the thickness of the tape. The speed of the arm was also adjustable to help control surface roughness and thickness. The slurry was poured into the reservoir and the blade set in motion.

Once the tape was dry, it was removed from the substrate. It could be cut into strips for later use or used immediately in the making of "neat" samples or fiber laminates. A "neat" sample is a multi-layered specimen with no fibers. Fiber laminates were made by warm bonding fiber mats to the tape.

How to lay-up the fiber/matrix laminates at first was thought to be the simplest and perhaps the least important part of the whole process. Through the ongoing research it was determined that the lamination step is one of the most important steps in creating a good, uniform final product. The lamination step was done by putting the fibers on the tape and then partially imbedding them. These tape/fiber layers were laid on top of each other with a blank tape on top, heated up and light pressure was applied to the layers so they would remain together. The shape needed could then be cut out of this finished laminate.

It was hoped that a process could be developed to get a fully dense sintered product without hot pressing. The sintering process was used because it was done in a regular tube furnace at a much lower pressure. This greatly reduced the cost. At the end of the sintering cycle, there was still 2% to 3 % porosity left in the specimen so a final HIP (Hot Isostatic Pressing) run was done. The final product was fully dense.

Before testing, the samples were polished on the sides and edges. This was to ensure a smooth surface on which to detect the cracks and to remove most of the surface imperfections. The samples were then coated with a thin layer of an epoxy coating to reduce surface effects. Next, an acoustic emissions detections device was placed on one side and horizontal and vertical strain gages were placed in the gage length on the other side. A tensile load was slowly applied until an acoustic emission sensor detected the sound of the first crack. This load was determined to be the composite cracking stress.

After the sample had been completely tested, it was then cold mounted and an end was cut off. This piece was polished to check the indexing and the fiber volume fraction. The actual fiber volume fraction was checked by the rule of mixtures.

RESULTS

The cross-sections of the tested samples showed uniform spacing. The tensile results were compared with the Full-Cell Cracking model. The results of these tests indicate that the processing method currently being examined showed great promise. Because a variety of things was examined and compared, it was important to take very accurate notes. These notes made it possible for formulas and procedures to be compared precisely. The note became invaluable for reference to past work.

One of the most important things learned was patience. Nothing ever goes completely right, materials run short, equipment breaks down, people go on vacation, all causing slowdowns and setbacks. New ideas are thought of and procedures changed. This is life.

ELECTRONICS AND COMPUTER SUPPORT IN ELECTROMAGNETIC MATERIALS RESEARCH

Task Order No. 64
Student Support Program
Southwestern Ohio Council for Higher Education

Ty Whitaker
Wright State University

5 July 1994

Government Task Leader
Mr. Ron Perrin
WL/MLPO

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I would like to thank Mr. Ron Perrin for his leadership, patience and technical insights. I would like to thank the other people in MLPO that I worked with for the opportunities and help.

TASK ASSIGNMENT

In the last 6 months, time was spent on the following projects: the laser position-flash control system, the Hall system magnet controller and the crystal growth tank temperature controller. The other areas of Task responsibilities were in general maintenance of hardware, software and related activities.

The laser positioner-flash controller is used to position a laser onto a film carrier and flash it with a burst of energy. This causes particle scatter to achieve a thin-film deposition on another substrate. This system consists of a x-y controller, a laser supply and the central computer. Software was developed that communicates the desired position and laser flashing scheme to the auxiliary equipment. The system worked well, but needs a better IEEE interface for repeat performance.

The hall system measures electrical characteristics of materials at low temperatures in different magnetic fields. The controller is a stepper motor that adjusts the field. The motor is sequenced by a computer until the desired field is achieved. The software has other functions such as instrument communications, auxiliary I/O and user interface.

The crystal growth tanks are controlled environments for crystal growth. The controller will control up to 6 tanks through D/A and A/D converters which set and measure the temperatures. Circulators, controlled by the fore-mentioned instruments, maintain the temperature. The system runs continuously for months because of the time needed for control. It is always attentive to the users input however.

All the above systems required software development, hardware development and fabrication and testing. As the designer of these systems, it was necessary to fine tune and improve them constantly.

ELECTRONICS AND COMPUTER SUPPORT IN ELECTROMAGNETIC IN MATERIALS RESEARCH

Task Order No. 64a
Student Support Program
Southwestern Ohio Council for Higher Education

Rick Dorsten
University of Dayton

5 July 1994

Government Task Leader
Mr. Ronald E. Perrin
WL/MLPO

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TASK ASSIGNMENT

The projects taken on during the completion of this Task fall into three categories; programming, computer controlled devices and miscellaneous. The programming languages used included Basic and C. Programs were written in Basic for data acquisition and equipment control. These programs were integrated into another program as subroutines, and, when running, controlled every aspect of an experiment called the Hall System, therefore, replacing the need for an individual to be present during testing. The C program was a file transfer program used to shorten files containing mass quantities of data retrieved from testing.

The computer controlled devices consisted of switching circuits that could be controlled manually, or automatically by the Basic program previously mentioned. These devices helped the computer control the Hall System.

Finally, many miscellaneous tasks were completed that dealt with the repair and regular maintenance of equipment, support for the in-house physicists and routine duties such as monthly reviews of technical journals requiring philosophical discussions on the contents.

GENERAL DESCRIPTION OF DEVELOPMENT

Once a project was assigned by the Task Leader the appropriate solution was discussed and development would begin. This consisted of creating an initial working model in which testing could be done. The initial model was as simple as possible to allow for quick and easy changes according to need. Testing was completed using multi-meters, oscilloscopes, power supplies, computer analysis, and other various testing devices. The equipment was modern and the best money could buy. Once a working model was thought to be completely tested as close to actual operating conditions as possible the final model was constructed and implemented.

RESULTS

This Task was a valuable learning experience. In school not much emphasis is placed on the practicality of the theory being taught. This experience allowed for a connection between the theory and the many facets in which it can be applied. This Task gave knowledge that could never be taught in the classroom; for instance, the social aspect of the job environment, and something every employer wants; job experience. The program SOCHE offers is an invaluable one. The hours are flexible while attending classes, and the monetary reward helps pay for school. Any time one can get paid to gain knowledge instead of paying for it, one should consider themselves fortunate.

HALF-TIME STUDENT AIDE

Task Order No. 65
Student Support Program
Southwestern Ohio Council for Higher Education

Cynthia Emerick
Wright State University

6 June 1994

Government Task Leader
Dr. Ronald Kerans
WL/MLLM

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TASK ASSIGNMENT

An objective of this Task was to identify any significance in surface roughness of a fiber. This was explored by extracting the interfacial properties between the fiber and the matrix. Interfacial properties such as sliding friction and residual stresses in ceramic matrix composites (CMC's) are measured by fiber push-out and push-back tests. The Kerans and Parthasarthy push-out testing model has been accepted to represent the mechanical behavior of the interface between the fiber and matrix. This model is used to measure such properties as shear strength, frictional shear stress and residual axial strain. Previous studies have found the parameters of surface roughness was important in improving the toughness in CMC's. Therefore, interfacial behavior may be optimized by varying the surface roughness. When the matrix of a CMC fractures and if an easy debond occurs, then the optimum surface roughness may make the component stay intact, an increase in fracture toughness. The value of knowing the correlation between surface roughness and the overall toughness will bring more CMC applications.

Interfacial properties in ceramic matrix composites have been predominantly studied by fiber push-out and push-back tests at WPAFB A fiber push-out test is described as a fiber partially pushed out of the matrix block by a flat tungsten probe attached to an Instron. The push-back test is performed after a push-out test. The specimen is flipped over and the protruding fiber is pushed back to the original position of the fiber/matrix. During the tests, the amount of load applied to the fibers and the distance the fiber is pushed is recorded by a computer. These push-out and push-back tests exhibit a substantial magnitude of fiber displacement decreasing the amount of load as the fiber is pushed out and subsequently pushed back into the original position of the fiber. The load decrease is observed to be related to the interfacial roughness of the fiber/matrix. Surface roughness of a fiber causes the push-out and push- back testing behavior to change over all, which proves the significance of the roughness parameter. Presently, the variations of roughness observed have been with fibers of different composition and fabrication technique, also different roughnesses.

British Petroleum (BP) has established a technique to fabricate fibers by Chemical Vapor Deposition and is able to vary the surface roughness controlability by this method. This can give WPAFB the opportunity to prove the surface roughness theory. The comparison of interfacial properties of this project was between three different surface roughnesses; 700-800, 800-900 and +1500 angstroms, of Sigma (silicon carbide) fibers and 500-600 of SCS-6 fibers. The surface roughness of these fibers was additionally characterized by the Atomic Force Microscope (AFM) and the scanning electron microscope (SEM) to measure the roughness of each fiber before testing. The interfacial properties were extracted by push-out and push-back testing data, using the Kerans and Parthasarthy model for the data analysis procedures. The data was analyzed by software programs, Mathematica, Kaleidagraph and a fortran program. The results will bring research closer to accurately characterizing the toughness and the debonding strength of ceramic matrix composites. To make a correlation between fiber roughness in the push-out model, fiber roughness had to be measured and characterized on a fiber with a variation of roughness, but from the same fabrication technique. The purpose of this work was to observe how surface roughness effects the behavior of fiber push-out tests.

The topography of each fiber was first studied so that the roughness values given by BP were valid and an understanding of the morphology was obtained. The surface topography was observed by using the Atomic Force Microscope (AFM) and scanning electron microscope (SEM). The AFM measured the amplitude of roughness and an average roughness value that was compared to the roughnesses given by the manufacturer. Finally, SEM allowed the roughness of the fibers to be seen in adequate depth of field. The initial interface topography background will be important in the understanding of the parameters measured by the push-out tests.

The four different fibers with surface roughnesses, 500-600, 700-800, 800-900 and +1500 anstroms, was fabricated in the same conditions so that the Kerans and Parthasarathy Model could be used and correlations of the model can be recognized more easily. From this composite, push-out samples approximately 2 millimeters thick, was cut and polished to a 1mm finish on the two parallel sides. Push-out and push-back testing was performed on these different fibers and the data was collected on a computer attached to the push-out apparatus. This data was transferred to a Macintosh computer and analyzed using data analysis software. The data analysis was from the methods of the Kerans and Parthasarathy model. From this project the interfacial roughness was further understood so that the toughness can be optimized in ceramic matrix composite.

This research project proved many theories. By extracting the interfacial parameters of the fiber and matrix, a different behavior was observed between the different fibers. This was mainly seen in the sliding friction that was measured in the push-back tests. There were still discrepancies in some values that will mean work will continue this subject.

SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE POLYMERS

Task Order No. 66
Student Support Program
Southwestern Ohio Council for Higher Education

Scott M. Brittain
Wright State University

15 July 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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TASK ASSIGNMENT

The Task goals were to synthesis materials that are thought to be (1) liquid crystalline in nature and (2) show promise in being adequate substrates for chromophore attachment. These materials included synthetic peptides and other polymers. The synthetic peptides in this study are alpha-helical in secondary structure. The alpha-helical conformation would enable the attached chromophores to be oriented in a certain fashion. This orientation could allow desirable absorption of electromagnetic radiation. The liquid crystalline properties previously mentioned also would add structural alignment and specific orientation. These materials then could be used for laser absorption experiments and applications. Some commonly mentioned applications included satellite device protection from laser damage, and pilot vision protection by special goggles coated with these materials.

DESCRIPTION OF RESEARCH

The Task research is much more esoteric than goals previously mentioned. The synthesis and purification of peptides is both difficult and complicated. The synthesis involved building an amino acid chain from an insoluble support, called resin. The growing peptide chain is achieved by repeating chemical steps. First, the N-terminus of the amino acids must be blocked due to their reactivity. The subsequent attachment of the next amino acid is achieved by first deblocking or deprotecting the attached amino acid. Then the coupling is achieved by using activated species of the amino acids. This usually involved activating the C- terminus by using activated esters or carbodiimides. After the coupling takes place, the resin is washed and the steps are repeated until a peptide of the desirable chain and sequence is synthesized. The peptide must then be removed from the resin, usually by using a strong acid. Lastly, the peptide must be extracted from the acid mixture. Unfortunately, this is only the first step in obtaining a pure peptide. The subsequent purification steps include gel permeation, ion-exchange and over liquid chromatographic procedures, such as high performance liquid chromatography (HPLC) which is probably the most commonly used method of separation. The pure product is then checked for chemical make-up by using other methods such as amino acid analysis, nuclear magnetic resonance (NMR) and mass spectrometry. These are only a few of the methods employed in solid phase peptide synthesis, purification and characterization. Others include capillary electrophoresis, gel electrophoresis, protein/peptide sequencing and thin-layer chromatography (TLC). Some analytical data is obtained by taking a small sample of the synthetic peptide, breaking the bonds (holding amino acids together) and quantitating the various amino acids present. This amino acid analysis and the data obtained, gives insight into the actual sequence of the peptide. These data enable one to know the exact sequence of the peptide. Once a pure peptide is obtained, subsequent conformational tests must be conducted. The secondary structure of the peptide must be determined so that orientation of the chromophores can be accomplished. These tests are accomplished by doing circular dichroism spectroscopy or 2-D NMR (nuclear magnetic resonance). The data obtained from these tests gives us exact locations of the important amino acid side chains. Next, the attachment of the chromophores was attempted using carbodiimide medicated couplings of the dyes to the functional groups of the amino acids contained in the peptide. These dyes were attached as esters or amide bonds that would endure electromagnetic radiation exposure. Once attached, the new polymer is purified and processed for the specific application.

The use of spiropyran as a functional group chromophore was attempted using an alanine rich peptide consisting of 12 residues. The sequence was YAEAAAAEAAAA, with the tyrosine being the n-terminal amino acid and the last alanine as the c-terminal amino acid. The peptide was synthesized by using a Wang resin which would result in a free amino peptide. The couplings were achieved by using activated esters of the Fmoc-amino acids (fluorenylmethoxy carbonyl), primarily the pfp-esters (pentafluoraphenyl). Deprotection was conducted with 10% piperidine in DMF (dimethyformamide), and cleavage employed 100% TFA (trifluoroacetic acid). Extractions of the material were accomplished using diethyl ether. Crude peptide was centrifuged, dried, reextracted, dried and then removed. The attempted attachment of the spiropyran dyes and other chromophores included using DICI (diisopropyl carbodiimide) and other catalysts. Again, purification of the dye attached peptides required the use of many separatory techniques. The structural analysis of the materials was the next step in the research, but time did not allow for it. This would have been accomplished by employing 2-D NMR and CD spectroscopy. These data would show which materials are exhibiting alpha-helical like spectra and allow us to differentiate between varying sequence peptides and from the various chromophores used. Eventually, the material would be made into thin films and further laser hardening experiments would be performed.

RESULTS

The process of solid phase peptide synthesis (SPPS) is difficult and problematic and requires a lot of time. Many things were discovered about lab techniques involved in SPPS as well as the many purifying methods used. Firstly, yields of crude peptide were greatly increased when "capping" methods were discarded. The "capping" involves using acetic anhydride as reagent that when amino acid coupling in complete, the acetic anhydride can be applied and any un-reacted sites would be covalently blocked to reduce the occurrence of deletion and insertion peptides. This process caused large reductions in peptide yield, most likely due to inefficient coupling and loss of growing peptide chains by capping.

Another method responsible for lowering peptide yield was the inclusion of "scavengers" in the cleavage mixture. These reagents, such as ethane dithiol, reduce many of the side reactions that occur as the peptide is cleaved from the resin. The scavengers are necessary to a certain extent, but inclusion of them in the cleavage mixture caused ether extractions to become emulsive with the peptide being dissolved in the aqueous fraction. Removing the crude peptide from the emulsion was problematic with much of the product being lost in the process.

Many separatory problems were experienced including HPLC problems. The use of peptide standards was found to be esoteric and specific to certain systems in HPLC. Thusly, the peptide mixture being separated was usually accomplished using the common solvent systems. Many pH problems were found to be associated with both HPLC and solubilizing the peptides. Peptides with acidic side chains were separated better using basic solvent systems. Analysis and characterization problems were common also. Amino acid analysis of the peptides involved both hydrolysis and chromatographic problems. The vacuum hydrolysis problems were alleviated by hydrolyzing and transferring under vacuum (partial). The ptc-amino acids analyzed usually yielded qualitative rather than quantitative data.

A negative but extremely important result is there is no means of quantifying the coupling, deprotecting and cleavage steps involved in SPPS with the current methods used in the peptide lab at WPAFB, and this ultimately caused for many separatory and characterization problems. It is my opinion that employing continuous couplings detected spectrophotometrically would aid in determining coupling efficiency and peptide yield loss. If the couplings and deprotections are made to become more efficient, then the remaining procedures would be much more simple. The separation of the peptide mixtures would be possible for many complex peptide and chromophore-peptide mixtures. This has been a valuable scientific experience and an enjoyable time working with the scientists at the Materials Laboratories.

SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE POLYMERS

Task Order No. 66a
Student Support Program
Southwestern Ohio Council for Higher Education

Lynn R. Frock
Sinclair Community College

15 July 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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TASK ASSIGNMENT

The Task goals were first to survey materials for optical limiters and second to prepare samples that were to be tested in the laser labs. Working as part of a laser lab support team, the project focus was primarily the investigation and characterization of optical limiters. The materials that are being studied are materials of application for the laser lab scientist. Much interest of the assignment is in the application of device protection from laser damage and pilot vision protection by night vision goggles layered with materials that process precise optical properties.

DESCRIPTION OF RESEARCH

The investigation and characterization of materials is approached in the lab by research studies of the different properties of solvents, suspensions and optically active organics. C60 is a material of much interest. It contains sixty carbon molecules and is in a class of organic molecules known as the Buckminster Fullerenes. Fullerenes are synthesized by evaporating graphite rods in a modified Denton evaporator according to the literature procedures.[2] The optical properties and charge-transfer complexes of Fullerenes are a part of the research investigations. Lab procedures evoke an assortment of instrumentation that include, but are not limited to, UV-Vis spectroscopy, SEM, NMR and IR. All the samples tested are on a microlevel and, therefore, must be tested on equipment more sensitive than the human eye.

A comparison study of the different properties of C60 in toluene with several suspensions was an approach taken. The suspensions were made in ethanol for each of the following materials; India Ink (II), Carbon Black (CB), Silica Aerogel (SI-A R), and Cauliflower Carbon (CC). Concentrations were adjusted to give approximately 50% transmission in regular UV-Vis absorbance scans. Absorbance spectra was taken in 1cm cells. This spectra data was compared to Intergrating sphere absorbance scans. It was found that the Intergrating sphere collects all scattered light from the particles in the suspensions. Larger particles gave a larger angle of scatter from the cuvette cell. This indicated that the CC and the SI-AR particle sizes are larger than the

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[2] Haufler, R. E.; Conceicao, J.; Chibante, P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smally, R. E. J. Phys. Chem. 1990, 94, 8634.

II, which have been particle size analyzed to be 200nm in diameter. Light refracts at a shallower angle for smaller particles. II scattered light was nearly identical for both absorbance and Intergrated sphere measurements. Change in the CB scatter was 50% to 53%, which is not as noticeable as the change for CC and SI-AR. This also shows that the II components have a positive effect on the low angle scattering. While the CC and SI-AR transmitted light was 49% vs. 69% and 49.9% vs. 75.4% respectively for regular absorbance vs. integrated absorbance. These samples were submitted for optical laser testing and laser wavelength set at 532nm. CC and SI-AR did not perform as well as II. CB has not been laser tested.

Another approach to investigation of optical limiting properties was in the thermal effects in reverse saturable absorbers (RSA). RSA are materials where the excited state is larger than the ground state population. A thermal effect is also seen in many materials where heat dissipated to the surrounding solution after being absorbed by the active molecules. Different solvents have different heat capacities. The larger the heat capacity, the more noticeable the thermal effect will be. If a solvent has low heat capacity, it cannot absorb much thermal heat from the absorbing molecule. If the heat capacity is large, then the amount of thermal heat absorbed by the solvent is large and easily observable. By testing two solvents of widely varying heat capacities, it could be seen if the thermal effect is a major part of the function of absorption of light, or if RSA is the major component of this function. PbTPP (lead tetraphenyl porphyrin) was chosen as the absorbing molecule in solution. Testing was done in 31 solvents. Of the 31 solvents, it was soluble in only 6. Of the six, the one with the highest heat capacities and the lowest heat capacities were chosen for further testing. 1mg/1ml sample sized solutions of dibromomethane and carbon disulfide were prepared. Heat capacities are 8.65 and 25.00 respectively. Percent transmission was taken on UV-Vis at 694nm wavelength.

RESULTS

Dibromomethane and carbon disulfide registered 47.25% and 41.80% respectively on UV-Vis. The information gathered from the UV-Vis spectra indicates the optical properties of the materials tested. Laser testing requires knowledge of the information gathered by these tests to set precise parameters on the instruments in the laser labs. This information was submitted with the samples to be tested. The laser specialist will investigate further the components mentioned. If laser testing warrants further investigation, the other solvents will be tried for their thermal effect. Preparation and characterization of solvents for laser testing is still ongoing for nonlinear absorption laser test.

SYNTHESIS AND CHARACTERIZATION OF OPTICAL POLYMER

Task Order No. 67
Student Support Program
Southwestern Ohio Council for Higher Education

Karen Hussong
Wright State University

30 June 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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TASK ASSIGNMENT

The objectives of this Task were to synthesize and characterize biopolymers which contained nonlinearly active molecules. These polymers are then used as matrices for laser hardening devices. This involved coupling reactions with polypeptides and nonlinear optical (NLO) compounds. Synthesis was followed by characterization procedures, which involved various measurements of the compound's properties to compare with other similar systems. Using this information, conclusions about the possible NLO properties and applications of these materials can be formed.

DESCRIPTION OF RESEARCH

The biotechnology division has researched the ability to use functionalized polypeptides with nonlinear optical chromophores to produce laser harden materials with second harmonic generation (SHG) characteristics.

The functionalized polypeptide is coated on an ITO (indium tin oxide) coated glass slide by various methods. This film is then heated above its Tg, an electric field is applied, and then cooled below its Tg. This gives the film an overall net orientation, needed for SHG. However, one downfall of these systems is their low thermal stability. The film will again randomize once the electric field is off. This research investigates the addition of a crosslinking agent along with the chromophore on the polypeptide to increase stability of the film once the electric field is removed. The crosslinking may "lock-in" the alignment after corona poling.

The systems chosen to study was p-nitrobenzyl alcohol or Disperse Red 1 attached to poly(l-glutamic acid). The crosslinking agent also added to poly(l-glutamic acid) in some of the reactions was cinnamyl alcohol. The synthesis procedure performed was a carbodiimide coupling reaction. By varying the amount of cinnamyl alcohol and nitrobenzyl alcohol (or Disperse Red 1) to the number of monomer units in the polypeptide, the amount of substitution could be optimized and the ratio of nitrobenzyl alcohol (or Disperse Red 1) to cinamyl alcohol could be adjusted to some extent. Purification of the substituted polypeptides was performed by consecutive precipitations in methanol until all starting materials were removed. Once synthesis and purification was complete, the substituted polypeptides were characterized.

The substituted polypeptides were analyzed to determine their properties. The percent substitution of the dye was determined by UV-Vis spectroscopy and NMR spectroscopy. CD spectroscopy was used to determine the structure of the polypeptide and to determine if the dye exhibited an induced dichroism, once attached to the polypeptide. Differential scanning calorimeter (DSC) results were analyzed for the Tg and any other types of phase changes.

Producing thin films of the various substituted polypeptides involved mostly trial and error combinations of various solvents and concentrations. Eventually, some acceptable films of the polypeptides were made in which crosslinking, aligning and/or NLO properties were tested. The polypeptides with the cinnamate groups attached were then crosslinked. Due to decomposition of the chromophores when irradiating at the absorption maximum of the cinnamate groups, a sensitizer was added in the solution or doped into the film. This sensitzer was irradiated and transferred the energy to the cinnamate group. A medium pressure Hg lamp at 300 W produced a broad band spectra. A monochromator was then utilized to only pass 311 nm light. Films were typically irradiated for 1-2 hours. The crosslinking can be monitored by UV-Vis. In FTIR the carbonyl group and one of the amine groups mask the depletion of the C=C breakage.

RESULTS

The poly-L-glutamic acid was modified approximately 25% with p-nitrobenzyl alcohol and 4% with cinnamyl alcohol. Without the cinnamyl alcohol the polypeptide was approximately 30% substituted. Both of these polypeptides have good clarity and generate second order response. However, the increase in temporal stability of the polymer after crosslinking has not been determined. This will be investigated as soon as the experimental apparatus is calibrated and reassembled. The crosslinking in this system has been determined to be second order kinetics. The Tg should increase with crosslinking. However, due to the presence of the sensitizer acting as a plasticizer, the Tg decreased from 45-62°C in the uncrosslinked system with nitrobenzyl alcohol to 25-45°C for the crosslinked system.

The poly-L-glutamic acid was approximately 20% substituted with Disperse Red 1 and 15% cinnamyl alcohol. Without the crosslinking agent, the peptide was approximately 20% substituted with the dye. The Disperse Red 1 system did not need the addition of a sensitizer for crosslinking, however, the crosslinking takes much longer. DSC analysis has not been performed on these compounds. Good clarity films for the DR1 system are harder to obtain than for the other system. The best films were obtained by dropping the solution on the slide at approximately 50°C and placing under a weak vacuum. SHG measurements will be made along with the nitrobenzyl alcohol system. From the trends found in these systems, we hope we will be able to choose better systems for the desired properties in the future.

SYNTHESIS AND CHARACTERIZATION OF OPTICAL LIMITERS

Task Order No. 68
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Southwestern Ohio Council for Higher Education

David P. Stitzel
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Government Task Leader
Dr. Robert Crane
WL/MLPJ

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TASK ASSIGNMENT

Task Assignment 68 involved the synthesis and characterization of numerous macromolecules containing nonlinear optically active side chains that can be aligned in an electric field. The long-term orientational stability of the side chains is a property that will be measured by second harmonic generation. It is believed, that liquid crystalline cyclic siloxane macromolecules and rigid rod polypeptides will enhance this stability by hindering side chain motion.

DESCRIPTION OF RESEARCH

Liquid crystalline cyclic siloxane macromolecules were synthesized by substituting various ratios of two mesogens, namely C4AB and Cin4AB, onto a five membered cyclic siloxane.

4-allyloxybenzoic acid (4ABA) was synthesized as follows. 4-hydroxybenzoic acid was placed into a round bottom flask equipped with a reflux condenser, an addition funnel, a heating mantle and a magnetic stirrer. The 4-hydroxybenzoic acid was dissolved in methanol at 25°C which produced a brown solution. To this solution was added drop-wise potassium hydroxide in distilled water. The reaction was heated to reflux and allyl bromide was then added drop-wise over a 1 hour period. The reaction mixture was allowed to reflux for 8 hours, at which time approximately half the methanol volume was removed by single stage distillation. The remainder of the reaction mixture was cooled to 25°C and added to distilled water in a separative funnel. The aqueous solution was extracted three times with diethyl ether to remove organic impurities and the ether layer was discarded. The remaining aqueous phase was heated to 40°C and neutralized with 37% aqueous HCl, which caused the product to precipitate out. The crude acid was obtained by filtration and purified by recrystallizing three times from ethanol.

The C4AB mesogen was synthesized as follows, via a coupling reaction: 4-allyloxybenzoic acid (4ABA), cholesterol, 1,3-dicyclohexylcarbodiimide (DCCI), and 4-dimethylaminopyridine (DMAP) were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, a magnetic stirrer and dissolved in dichloromethane. The reaction was heated to reflux and allowed to run for 6 days, at which time the reaction was allowed to cool to 25°C. Once cool, the reaction mixture was filtered to remove the insoluble 1,3-dicyclohexylcarbodiimide urea (DCCI Urea). The filtrate was placed on rotovap and reduced to dryness to remove dichloromethane. The solid material that remained was purified by recrystallizing three times from ethanol.

The Cin4AB mesogen was synthesized as follows, via a coupling reaction. 4-allyloxybenzoic acid (4ABA), cinnamyl alcohol, 1,3-dicyclohexylcarbodiimide (DCCI), and 4-dimethylaminopyridine (DMAP) were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in dichloromethane. The reaction was heated to reflux and allowed to run for 6 days, at which time the reaction was allowed to cool to 25°C. Once cool, the reaction mixture was filtered to remove the insoluble 1,3-dicyclohexylcarbodiimide urea (DCCI Urea). The filtrate was placed on rotovap and reduced to dryness. The solid material that remained was purified by dissolving the crude product in a minimal amount of dichloromethane and eluting it through a column packed with silica gel to remove unreacted starting materials and any residual DCCI Urea. Once the product was obtained from the column, it was further purified by recrystallizing three times from methanol.

cSi[80,0,20]100 was synthesized as follows. The five membered cyclic siloxane, along with the two previously synthesized mesogens, C4AB and Cin4AB (4:1 ratio), were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, a magnetic stirrer and dissolved in toluene. Once the reaction was at reflux, the platinum catalyst was added. The reaction was monitored by FTIR to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in toluene three times.

cSi[60,0,40]101 was synthesized as follows. The five membered cyclic siloxane along with the two mesogens, C4AB and Cin4AB (3:2 ratio), were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in toluene. Once the reaction was at reflux, the platinum catalyst was added. The reaction was monitored by FTIR to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in toluene three times.

cSi[40,0,60]102 was synthesized as follows. The five membered cyclic siloxane along with the two mesogens, C4AB and Cin4AB (2:3 ratio), were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in toluene. Once the reaction was at reflux, the platinum catalyst was added. The reaction was monitored by FTIR to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in toluene three times.

Nitrobenzyl L-glutamate (NBLG) was synthesized as follows: L-glutamic acid (LGA), p-nitrobenzyl alcohol (NBA), and p-toluenesulfonic acid monohydrate (PTSA) were placed into a round bottom flask equipped with a distillation apparatus, a heating mantle, and a magnetic stirrer and dissolved in benzene. The reaction was at reflux while water was removed by azeotropic distillation. The reaction mixture was cooled to 25°C and diethyl ether was added with stirring for 15 minutes at which time the resulting mixture was filtered. The solid was stirred in chloroform for 10 minutes and the resulting mixture was then filtered to collect the PTSA salt of

NBLG. Triethylamine and chloroform were added to the salt and the resulting solution was stirred for 15 minutes. After stirring, diethyl ether was added and the resulting solution was filtered to collect the crude product. The crude product was purified by recrystallization with water using decolorizing charcoal.

The anhydride of nitrobenzyl L-glutamate was synthesized as follows, via a triphosgene reaction: NBLG and triphosgene were placed into a round bottom flask equipped with a condenser, a receiving flask which contained potassium hydroxide (to neutralize any phosgene produced), a heating mantle, and a magnetic stirrer and dissolved in dry tetrahydrofuran (THF). The crude product, which was dissolved in THF, was precipitated out of solution by the addition of hexane and then purified.

RESULTS

Once the previously mentioned macromolecules were synthesized and purified, the final product was verified by analytical methods such as E.A., FTIR and NMR analysis. Elemental Analysis was used to determine %C, %H, %O, %N (if applicable), and %Si (if applicable) of the purified product Once these analytical values were obtained, they were compared to the theoretical percentages to determine how well they correspond. A Fourier Transfer Infra-Red spectrophotometer was used to determine whether characteristic bands of the desired compound were present in the purified product. For example, if NBLG was indeed produced then the FTIR of the final product should have an ester peak at 1700cm^{-1}. Nuclear magnetic resonance spectroscopy was also used to verify the structure of the final product. Further analysis will be performed using DSC (Differential Scanning Calorimeter) and POM (Polarized Optical Microscopy) data.

SYNTHESIS AND CHARACTERIZATION OF BIOPOLYMERS

Task Order No. 69
Student Support Program
Southwestern Ohio Council for Higher Education

Steven M. Cline
Wright State University

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Government Task Leader
Dr. Robert Crane
WL/MLPJ

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TASK ASSIGNMENT

The Task Assignment consists of the synthesis and characterization of biopolymers for optical applications. Efforts were concentrated on biochemical materials which consist of attaching chromophoric dyes to an amino acid polymeric backbone. The Task involves synthesizing proteins of known sequence, their purification, observing their stature, attaching optically liable dyes to them, and observing resultant chromophoric packing and optical properties of the particular protein/chromophore arrangement. The interest in using biologically based materials lies in the recent popularization of genetic engineering and the ability to insert genes of specific sequences into bacteria. This process will provide a cost effective method of producing large volumes of desired protein. Biological materials have proven to be very valuable in that they are strong and durable, yet can be manipulated easily by a changing environment.

Currently, a suitable protein support is being sought for the chromophoric attachment. The process of finding such a support consists of, first, synthesizing a number of foreseeable useful proteins. The peptides of sequences TYR- GLU(2n-1) n = 1,2,3 . . . 6 were synthesized by utilizing the Stepwise Chain-lengthening method of polypeptide synthesis. This method consists of linking amino acid residues together one by one to create proteins of known sequence and length. Sequence specificity is ultimately the most important element of the Stepwise Chain-lengthening method of protein synthesis. Sequence specific proteins provide scientists with a definite primary structure that can be used to develop a working understanding of how the individual residues of the peptide effects each other. Sequence specificity is a necessity for computer modeling and thus, it is evident why this method of peptide synthesis is being used.

Once the protein has been synthesized, it is necessary to purify the protein of all impurities such as organic solvents, detergents, salts, etc. Protein purification also consists of removing unwanted protein sequences created during the Stepwise Chain-lengthening method. These sequences deviate from the desired sequences of TYR-GLU(2n-1) n = 1,2,3 . . . 6. The Stepwise method of protein synthesis is not 100% efficient, meaning it is not perfect. There are instances during the synthesis in which a sequence may be deleted from the chain of amino acids, producing a protein of undesirable sequence (as mentioned above) and must be removed from the sought proteins. Protein purification has proven to be most difficult. It entails ion exchange chromatography, gel permeation chromatography, high pressure liquid chromatography and gel electrophoresis. The application of the purification results provides the scientist with a step by step procedure of how to recover a specific protein free of impurities. Throughout the purification process, fractions of the sample are analyzed by mass spectrum analysis. This provides a quantitative measurement of the amount of different compounds in the sample and the mass of each compound. Results from mass spectrum analysis provide an excellent measurement of the purity of the sample.

DESCRIPTION OF RESEARCH

Methods of protein synthesis are initiated by deprotecting or removing the Fmoc group from the Fmoc-TYR- resin to expose the amine group (NH3) of the TYR residue.

(1) Fmoc-TYR-resin + piperdine -> H2N-TYR-resin + Fmoc- piperdine The free amine of the TYR was then reacted with the carboxyl group (COOH) of Fmoc-GLU-COOH in the presence of the catalyst HOBt to couple the GLU to the TYR. It is necessary to catalyze the coupling reaction of CLU and TYR with the catalyst HOBt.

(2) Fmoc-GLU-COOH + H2N-TYR-resin + HOBt-> Fmoc-GLU-TYR- resin The Fmoc group was then removed from the Fmoc-GLU-TYR-resin complex, as described above, and coupled to a second Fmoc-GLU to produce Fmoc-GLU-GLU-TYR-resin. The process was continued until the desired protein sequences were synthesized. The protein was then cleaved from the resin using 10% TriFlouroAcetic acid and was ready for purification.

(3) protein-resin + TFA -> protein + resin-TFA To avoid long chain deletion sequences, acetic anhydride was applied after each coupling step to cap any resin bound amino acids which had not reacted during the coupling reaction.

(4) Acetic anhydride + H2N-protein-resin -> Acetate- protein-resin + acetate. This leaves the protein-resin complex inert and unable to form large unwanted sequences. Such lengthy sequences may become confused with that of the desired sequence during purification and, therefore, are kept short to aid in the purification process. The efficiency of amino acid coupling is monitored by applying the Kaiser test to check for the presence of free amines. The synthesis reactions are performed on the peptide synthesizer by Advanced Chemtech.

Purification procedures began by precipitating the TYR-GLU(2n-1) n = 1,2,3 . . . 6 sequences in hexane, chilling, centrifuging, aspirating, and drying the precipitated pellet over KOH overnight. The proteins were then resuspended in a highly concentrated NaCl solution. The peptide salt solution was concentrated by dehydration. This leaves the peptide bound to the salt in precipitated form. This step is an attempt to evaporate impurities binding to the protein. Each sample was then re suspended in a sodium bicarbonate buffer and run through p-2 gel permeation gel at a flow rate of 0.12ml/min. in a 1.7 cm diameter column. This is a method of desalting. The process allows high molecular weight proteins to elute from the gel before the low molecular weight salts. Gel elution was monitored by spectrometric observation, revealing two large peaks. One identified as having free amines (protein) and the other as not having free amines (salt). Free amines are identified by using the Kaiser test.

The peptides peaks from the gel were collected by a Bio-Rad fraction collector and concentrated evaporation. The TYR-GLU 11 protein was run on a Waters HPLC system using C-4 and C-18 columns at a variety of Acetonitrile/H2O gradients. No gradient produced reproducible peptide peaks. However, the peptide was identified on the Waters Spectrum Index Plot to peak in absorbance at 205 and 280 nm. This provided a spectrotopic identification which will be valuable during future purification procedures.

The unpurified peptide sequence YAEA4EA4 was measured using circular dichroism to reveal a positive band at 190 and a negative band at 215, revealing the presence of an alpha helical protein in the presence of 10 mM sodium phosphate buffer. The peptide was run on the HPLC through C-4, C-18, and C-8 columns at a variety of Acetonitrile H2O gradients and again was not reproducible. A spectrum index plot was collected however, and will provide spectroscopic identification for future purification. The YAEA4EA4 peptide was analyzed by mass spectrum analysis providing detailed information on the variety and mass of contaminants present in the peptide samples. Future research is presently focused on the YAEA4EA4 peptide sequence and is presently being purified by ion exchange chromatography.

RESULTS

Circular Dichroism measurements reveal the YAEA4EA4 peptide as being alpha helical, protein mass and relative impurity have also been confirmed. It appears that further purification is necessary to achieve sample purity. The spectrum chromatography has been recorded and will be an asset in future work. The TYR-GLU(2n-1) n = 1,2,3 . . . 6 sequences are in the midst of purification. The Glu 11 and Glu 7 spectrum have been measure and saved. A great deal of what was learned is based on the discovery of lack of resolution on the HPLC and will provide a boundary which future lab workers will not have to encounter during protein purification. Future work consists of further protein purification and dye coupling for optical measurement.

METALLIC COMPOSITES IV

Task Order No. 70
Student Support Program
Southwestern Ohio Council for Higher Education

Christopher W. Palser
Wright State University

30 June 1994

Government Task Leader
Dr. Dan Miracle
WL/MLLM

ACKNOWLEDGMENTS

I would like to sincerely thank Dr. Dan Miracle for his guidance in how to properly conduct research, whether you like the results or not. I would also like to thank Dr. Harry Lipsitt (Wright State University) for his assistance and teaching this year. Both these men challenged me and encouraged me in this research, not letting me take the easy way out at any time, but always pushing me to keep on track and press on, no matter how slow it seemed to go at times. I also would like to thank Mr. Paul Smith for his suggestions for my senior project and providing of the material and his experience and guidance in this project.

TASK ASSIGNMENT

The objective of this Task was to further advance the knowledge of advanced metallic composites for high temperature applications. To this end, research was conducted toward the investigation of the embrittlement of a titanium-aluminide orthorhombic alloy being investigated as a candidate as the matrix for metal matrix composites. The specific objective of the project was to measure the ductility of and investigate the mechanism of embrittlement in Ti-22Al-23Nb neat panels after isothermal exposures. The end-goal for the materials being developed is to develop lighter, stronger materials which will withstand higher jet engine operating temperatures and, thus, increase jet engine efficiency.

Research has been previously performed which indicates that the ductility of the orthorhombic class of alloys decreases significantly after an exposure simulating jet engine operation. The intent of this project was to document more thoroughly this loss of ductility and to determine whether this phenomenon is caused by microstructural changes initiated by an environmental effect which occurs during the annealing process. All experiments were conducted on Ti-22- 23 "neat panels," that is, material processed exactly as a metal matrix composite would be, without the fibers' present.

DESCRIPTION OF RESEARCH

To meet the assigned goal of investigating the mechanism and extent of embrittlement in Ti-22Al-23Nb neat material, the following process was outlined: Dog-bone tensile specimens are to be heat-treated for 1, 10, 100 and 1000 hours in air and argon. After 1 and 10 hour exposures, a small amount of each specimen was removed for metallography and Vickers' hardness testing; the remainder of the tensile specimens will then be heat-treated for the completion of the 100 and 1000 hour exposures. The as-received and heat-treated specimens will then be tensile tested and fractography will be conducted on the fracture surfaces. Chemical analysis will be conducted to determine pick-up of environmental contaminants and metallography will be performed to determine the microstructural and phase stability of the neat material. The mechanical properties will be rationalized based on the chemistry, fractography and microstructural observations.

To date, the 1, 10, 100 and 1,000 heat treatments are completed. Additionally, the as-received and 100 hour treatment tensile testing is complete and the Vickers' hardness testing, metallography and fractography is still in progress.

RESULTS

Tensile testing has shown a decrease in the ductility and ultimate tensile strength of the air-exposed samples, as compared to the argon-exposed samples. Additionally, initial Vickers' hardness testing has shown a significant increase in hardness on the exterior of the air-exposed samples, but not the argon-exposed specimens. Also, chemical analysis has shown a significant increase in oxygen content of the air-exposed samples compared to the argon-exposed samples.

In conclusion, it appears that (at least in initial results) the Ti-22Al-23Nb neat panels are not stable in exposures in air to high temperatures. The cause of this instability in mechanical and microstructural properties has yet to be determined, but there is evidence that environmental factors are the root cause for the loss of ductility seen.

TRIBOLGICAL EVALUATION OF CANDIDATE FLUID AND LUBRICANT MATERIALS

Task Order No. 71
Student Support Program
Southwestern Ohio Council for Higher Education

Scott A. Long
Wright State University

31 December 1993

Government Task Leader
Mr. Shashi K. Sharma
WL/MLBT

ACKNOWLEDGMENTS

I would like to extend my gratitude toward Mr. Shashi Sharma, Mr. Ron Mortimer, Mr. Bruce Schreiber, Mr. Vince Vidoni and all my other co-workers throughout my Task. I was encouraged to ask questions and ask for help when needed. I always felt welcome. I appreciated the opportunity to gain their confidence. Quite often, I was given challenging tasks to perform on my own. These actions helped me expand as a professional and an individual.

TASK ASSIGNMENT

The Task began with the designs of various equipment to be integrated with a previously designed apparatus. The Traction Rig, used to test the contact resistance of two metal disks with certain fluids, had been redesigned and needed more additions to operate safely. In all, a safety shroud for a hinged and fixed spindle, a base for the torque sensor, and the front, rear and middle bases for the complete apparatus were designed. The final design of the entire base took the greatest amount of time because each leg had to be designed precisely so the pre-drilled screw holes align.

The next assignment dealt with learning the computer program File Maker Pro and assisting another employee in creating a data base. The data base is to be used to keep track of all the computers, printers, monitors, keyboards and any other computer equipment assigned to everyone in the branch. This assignment was to elevate all the paperwork and files on each system, and to allow someone to easily review a computer or a user. The program seemed very complicated at first, but with time, it became easier to understand, but it still had its drawbacks. Once an initial data base was created, a test was run. It was found that a great deal of work remained in the creation. Finally, the data base was prepared and the data could be entered by a second employee. Once all the data was entered, each file underwent extensive verification. After about 4 months, the data base was completed.

The final assignment involves converting parts of the present Traction Rig to an Optical EHD Apparatus. Once the Traction Rig upgrade is installed, some of the replaced mechanisms will be used to create this Optical EHD Apparatus. The design of this apparatus is in the very beginning stages and will be completed later.

DESCRIPTION OF RESEARCH

To design the extra components for the upgraded Traction Rig, the sketches of the system had to be examined thoroughly. These examinations showed that several key errors were made on the designs. However, everything was finally corrected, and the extra components could then be designed. All the designs were completed with pencil and paper to the appropriate scales. Once the designs were double and triple checked, they were taken to the machine shop on base to be produced.

The creation of the data base will organize all the computer information now and in the future. Each computer system is now linked with its user and whenever there are any changes, they can be performed easily and quickly. The FileMaker Pro program was used on a Mac IIfx system. It was found that a number of the inputed data was incorrect, proving that this Task will be very beneficial.

The design of the Optical EHD Apparatus is being drawn on paper by using existing designs of the Traction Rig. As written previously, this Task is in its beginning stage and will be completed by another employee.

RESULTS

Throughout the Task, there was a great deal of learning and discover. Within the first project, designing components for the Traction Rig, the errors found were completely surprising. It was felt that the designs were quickly checked and then sent to the branch. There were errors such as dimensions not adding up correctly. As a result, each design had to be thoroughly checked to insure proper fits.

The second task of creating the data base, displayed the fact of how difficult it can be creating a complicated structure. It was also discovered that the program had various limitations and was not suited to be used for all applications. For instance, the cut and paste function of the program did not allow for the cutting of a strand on one file to be pasted to another file. This drawback was very crucial to this project and to future projects also.

The final project, the design of the Optical EHD Apparatus, involved the use of creativity in some aspects. There were many different ways the apparatus could be designed. They all had to be considered to design the most appropriate system. Even though a design looks good on paper, it does not always mean that it will work when produced.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS FOR INTRINSIC CONDUCTING SYSTEMS

Task Order No. 72
Student Support Program
Southwestern Ohio Council for Higher Education

D. David Carpenter
Wright State University

14 July 1994

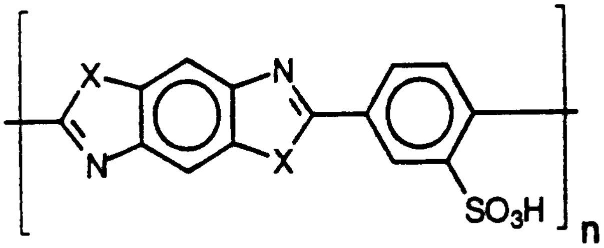
Government Task Leader
Dr. Fred E. Arnold
WL/MLBP

ACKNOWLEDGMENTS

I would like to thank everyone at the polymer research laboratory for their assistance and kindness. Special thanks go to Thuy Dang and Jerry Burkett for their guidance.

TASK ASSIGNMENT

Extensive studies have been focused on conjugated rigid-rod polymers for their opto-electronic technological applications. These rigid-rod polymers have been widely researched because of their high thermal stability, mechanical strength, chemical resistance, and p-electron delocalization. These unique features are the foundation for technological success in the research of conductive rigid-rod polymers. The heterocyclic aromatic polymers of PBX, as illustrated in Figure 1, is one of the more successful rigid-rod polymers. These PBX polymers appear to be cost-effective replacements for various other polymers used in engineering fibers for structural applications.



I. X = NH Poly-p-phenylene benzobisimidazole sPBI
II. X = S Poly-p-phenylene benzobisthiazole sPBT
III. X = O Poly-p-phenylene benzobisoxazole sPBO

Figure 1. Chemical structure of 2-sulfo PBX rigid-rod molecules.

Polymer Synthesis Polymer (I) was synthesized by the polycondensation of 1,2,4,5-tetraminobenzene tetrahydrochloride with 2,5- dicarboxy benzenesulfonic acid in polyphosphoric acid (PPA). Polymer (II) was synthesized by the polycondensation of 2,5-dicarboxy benzenesulfonic acid and 2,5-diamino-1, 4-benzene dithiol dihydrochloride in PPA. Polymer (III) was synthesized by the polycondensation of 2,5-dicarboxy benzenesulfonic acid and 1,3-dihydroxy-4, 6-diamino dihydrochloride in PPA. (See Figure 2 below)

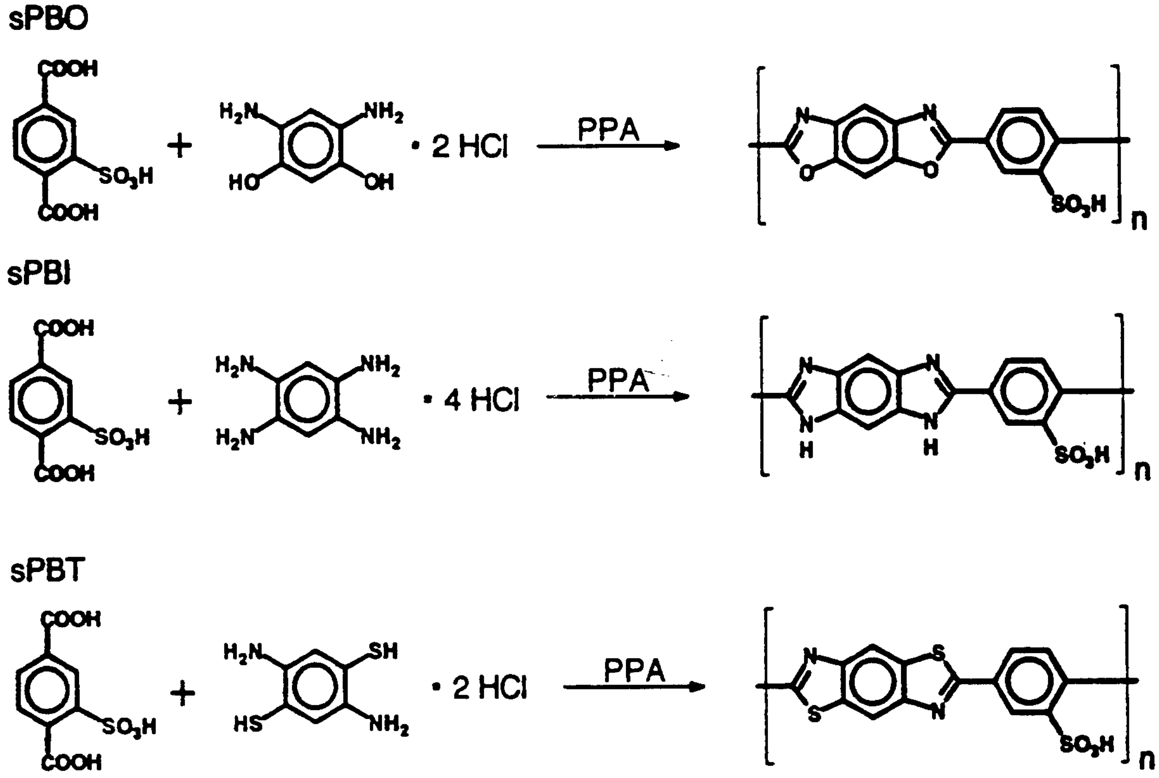


Figure 2: Polymer Synthesis

Monomer Preparation

The monomers used in the polymerizations have to be very pure and weighed accurately for the polymerization to occur properly. In general, the bigger and whiter the crystals of the finished monomer are, the less chance they have for impurities. The 2,5-dicarboxy benzenesulfonic acid, 1,2,4,5- tetraminobenzene tetrahydrochloride, 2,5-diamino-1,4-benzene dithiol dihydrochloride, and 1,3-dihydroxy-4,6-diamino dihydrochloride are recrystallized in the lab from a crude product produced by Daychem Chemical Co. The sulfonic acid is structurally verified by infrared spectrum analysis, mass spectrum analysis, and elemental analysis.

Synthesis Procedure

The procedure for preparing these polymers is the same. The two monomer compounds are added to a reaction flask equipped with nitrogen inlet/outlets and a mechanical stirrer. PPA is added and the mixture is stirred. The solution is heated to 60°C for 24 hours. Then, the solution is cooled to room temperature and diphosphorous pentoxide is added. The solution is then heated to 100°C for 24 hours, 145°C for 24 hours and 160°C for another 24 hours. Finally, the solution is heated at 180°C for approximately 2 hours. This heating procedure builds up the molecular weight in the polymer, which derives a polymer with a higher viscosity. The next step is extracting the polymer from the polymer dope. The dope consists of the polymer in the acid and must be beaten in a blender with water. The blender beats the dope until the polymer becomes fiber-like or powdery. In general, fibrous correlates to a higher viscosity of the polymer than powdery. The polymer is then soxhlet extracted with water. This is the process of removing any residual acid in the polymer by a continual washing of the polymer with water. The final step is drying the polymer. This is accomplished by heating the polymer in a sample jar under vacuum in a drying pistol.

Processing and Characterization

The polymer is dissolved in methane sulfonic acid (MSA) at various concentrations to determine its viscosity. The viscosity is measured using a viscometer in a viscosity bath at 30°C. The viscosity is the natural log of the ratio of the flow times of the polymer in solvent (MSA) compared to the solvent (MSA) itself through the viscometer divided by the concentration of the polymer in the solvent (MSA).

If a polymer appears to have some potential, samples are used to prepare thin films and fibers. The fibers are tested for the amount of tension they can withstand before breaking or becoming physically damaged. Conductivity measurements are performed on the films in transverse and longitudinal directions. The two methods of preparing the isotropic films are by using a sublimation apparatus for casting films or a gravimetric filter funnel for forming aggregated films. An example of DC electrical conductivity of sPBI for the two film types are 1.8×10^{-4} S/cm (cast film) and 8.3×10^{-2} S/cm (aggregated film).

RESULTS AND CONCLUSION

The aromatic heterocyclic rigid-rod polymers are synthesized at various concentrations and various viscosities are determined for each type of polymer. Maintaining the correct synthetic procedure and using pure monomer compounds are helpful in producing viable ionic conductive polymers. Research throughout the past has determined that the sulfonated PBI polymer has achieved the best conductivity. The sPBI's conductivity has surpassed the conductivity of its counterparts (sPBT and sPBO) by over 100 times. With this fact, the sPBI is the focus for future research at Wright Labs.

SYNTHESIS AND CHARACTERIZATION OF BIOPOLYMERS

Task Order No. 73
Student Support Program
Southwestern Ohio Council for Higher Education

Aric Rothman
Wright State University

20 June 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

Thanks to Soumya Patnaik for her patience and insight during the development of the BEAN molecular modeling software. Thanks also goes to Jim Lupo for supplying Xviewit, an X Windows graphic utility.

TASK ASSIGNMENT

The objective of this Task Assignment was to assist a senior chemist in the characterization of siloxane polymer materials incorporating spiropyran molecules for use as matrices for optically active materials. Results of this research could be employed in the creation of practical non-linear optical materials.

DESCRIPTION OF RESEARCH

Several programs have been developed to assist molecular modeling tasks.

BEAN

BEAN is a program to assist in visualization of molecular networks in space. Input to BEAN consists of a Protein Data Bank (PDB) format file containing the coordinates of individual atoms for each molecule. BEAN outputs a file of coordinates for the endpoints of line segments defining the axes for the equivalent inertial spheroids that enclose each molecule. This file may be input into Xviewit, an X Windows visualization program to generate a 3-dimensional display of molecule "skeletons," or axes that approximate the shape and size of the molecules. This type of molecular display clarifies the spatial relationship between complex networks of large molecules. BEAN also generates a table of angles, each axis makes with an average axis of each molecule's primary axis, quantifying the interaxial angles displayed by Xviewit.

PDBFY

Soumya Patnaik was supplied with a series of time iterations for a network of liquid crystal simulations by Dr. George Plimpton. This data was to be input to BEAN. PDBFY translates the file format supplied by Dr. Plimpton to the PDB format BEAN accepts.

GETRINGS

GETRINGS extracts the central benzene rings in a PDB file of molecules.

GETMES

GETMES extracts the mesogen branches from a network of molecules in a PDB file.

SHIFT

SHIFT fixes a spatial "folding" error introduced to a PDB file by SANDIA software. SHIFT detects gross distortions caused by SANDIA and corrects them.

In addition to development of software, I assisted co-workers with use of the UNIX operating system and UNIX-based applications. I also assisted in maintenance and updating of hard drive archives for researchers' personal Macintoshes. Numerous simulation iteration files were processed using the above software.

RESULTS

BEAN assisted Soumya Patnaik in the interpretation of simulation data for liquid crystal systems. BEAN and other programs listed above were used to process data for use in journal articles by Soumya Patnaik.

SYNTHESIS AND CHARACTERIZATION OF BIOPOLYMERS

Task Order No. 73a
Student Support Program
Southwestern Ohio Council for Higher Education

James J. Richardson
Wright State University

20 June 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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TASK ASSIGNMENT

The main goal of student support to WL/ML regarding Task Order #73 was to explore analytically the potential compositions and properties of new biopolymers under the direction of a senior computational chemist. The student was to explore compositions of optical materials to guide the in-house synthesis efforts.

The main tasks, which the student was required to complete, involved the introduction of new software application programs as well as updating current programs. The major portion of programs was written in the 'C' programming language. The FORTRAN language was minimally used and UNIX script files as well as other UNIX internals were periodically used in the interaction and development of new and existing software programs.

DESCRIPTION OF RESEARCH

Following is a brief list of major programs written and modified as well as a description of the operation and reason for modifications/creations: USERSB.SRC . . . This is a FORTRAN sub-routine written specifically to interface with the software package. CHARMM (a research instrument for theoretical studies of the properties and biological function of molecules). The program will read in a set of x, y, z coordinates and determine a linear, best-fit line through this data. It will then calculate the angle between two lines and submit the result into the package CHARMM for further data evaluation.

modify.c . . . This is a 'C' program written exclusively for the modification of a previous program. The previous program would update an already modified coordinate file with more specific criteria.

modify2.c, modify4.c . . . These 'C' programs will read a given data file of z coordinates and will produce a new file composed of specific x, y, z coordinates.

add.c . . . This 'C' program will calculate the average vector given a set of particular vectors. This average vector will be used in subsequent data manipulation.

vector.c . . . This 'C' program will compute the length of each required vector and will find the ratio between specified vectors and output to the corresponding files.

rings.c . . . This 'C' program will find the center of a ring of atom coordinates, and it will manipulate this data to more specific criteria. These are a few of the programs written during this Task.

The major pieces of hardware used by the student consisted of the following: Silicon Graphics Work stations SUN/Sparc stations (utilizing the SunOS operating system).

RESULTS

During this Task many different aspects relating to programming form, structure, and technique were incorporated into applications software. The value of reasonable and generous structure relating to the source code of the designed software was of major importance to the proper readability and execution of the program. A realistic approach to implementing solutions to solve problems in the area of computational chemistry is more easily understood. Though the student's academic interests centered around computer applications relating to electrical/biomedical engineering, applying algorithms to chemistry oriented research provided new insights into programming.

STRUCTURAL FAILURE ANALYSIS TECHNICIAN

Task Order No. 74
Student Support Program
Southwestern Ohio Council For Higher Education

Joseph C. Leone
Wright State University

15 July 1994

Government Task Leader
Mr. William E. Berner
WL/MLSA

ACKNOWLEDGMENTS

I would like to extend my appreciation to Dr. Ronald H. Williams and Dr. William E. Berner for allowing me the opportunity to complement my education while working in the Structural Integrity Branch of Wright Laboratory. Additionally, I would like to thank Tom Dusz, Michael Oliver, and Brad Pinnell from the University of Dayton Research Institute, for their assistance and direction in completing my Task.

TASK ASSIGNMENT

During the last 12 months, the Task objective was to assist engineers and technicians in performing structural failure analysis on metallic and composite weapon system components.

The first major project completed was the assessment of heat damage induced by the application of a thermoplastic powder coating (TPC) on aluminum substrate. A TPC was applied to a prototype munitions container designed and fabricated by the Air Force. It was suspected that the elevated temperatures (greater than 300° F) of application might degrade the properties of the aluminum substrate.

Overall and detailed photographs of the container were taken before sections were removed for inspection. Samples of aluminum from each section were then removed and chemically analyzed to determine their composition and compared to the corresponding specifications. Next, the coating thickness was measured on each side of the container. Measurement values varied between 0.001 to 0.011 inches, a variation in surface texture and gloss was also observed. Temper of the substrate material was verified through conductivity and hardness testing. Samples were selected from each material and representative coating thickness. The samples were measured for conductivity using the percent indicated annealed copper standard (I ACS). Hardness measurements were taken using the Vicker's hardness scale (HV). All the measured conductivities fell within the range specified by AMS 2658 for their respective alloys and tempers. All measured hardnesses met the minimum hardnesses specified by AMS 2658 for their respective alloys and tempers. No correlation between hardness and coating thickness was observed. No significant variation in hardness across the thickness of the substrate material was detected.

From the gathered data, it was determined that there was no thermal degradation of any of the substrate aluminum materials. The elevated temperature exposure during application of the TPC was not sufficient to thermally degrade the aluminum. Final recommendation made was that further studies of this coating material for potential application should focus on aspects other than thermal degradation of aluminum substrates. Factors such as adherence, thickness consistency, gloss, and resistance to chemical agents may be more relevant for evaluating the suitability of this coating for potential government application. After the testing was completed, the evaluation report was written and submitted for review.

The second project completed was the failure analysis of an idler shaft from the LSV-16 diesel engine. The engine powered a three megawatt generator used for electricity at an Air Force station in Alaska. The idler shaft was manufactured by welding an inner shaft to a circular base then machined to the proper specifications.

Cracking was observed in the filet region at the interface of the shaft and base extending through both sections. Fluorescent dye penetrant was applied to the fractured area and black light photographs were taken. Samples of the shaft and filler material were removed and chemically analyzed to determine their composition. The result was then compared to the corresponding specifications. It was determined that the shaft material was 8620 steel. Next, the two sections of the shaft were separated to expose the mating fracture surfaces. The relevant section of the fracture surface was photographed then viewed using a scanning electron microscope (SEM). From the macro photographs, crack arrest lines were discovered, an indication of fatigue. Concentrating on the crack arrest lines, fatigue striations were revealed using the SEM. Next, the multiple initiation sites of the fracture were documented and showed that the fracture started along the outer edge and propagated inward toward the center. Excess weldment material at the initiation sites indicate a lack of penetration during welding process. Micro-hardness measurements were taken through the weld zone and base metal area. Readings indicate a relative hard zone in the weld at the outer edge of the shaft. A significant difference in hardness values was observed between the weld zone and base metal areas. A photomicrograph of the hardened zone was viewed. The microstructure indicates the area has undergone plate martensitic transformation. Using Energy Dispersive Spectrometry (EDS), a carbonized layer region at the outer edge of the weld zone was observed. This layer indicates that the shaft was heat-treated prior to welding. This would cause a diffusion of carbon into the base metal during welding forming a martensitic region. The failure initiated in the defects in the weld zone which then propagated the high cycle fatigue then low cycle fatigue until the shaft could no longer support the load being applied. Final recommendation made was to find an alternative welding method other than fusion welding. This material (8620 steel) is not considered a "fusion weldable" material. If welding is the only method of joining possible, then the alternatives could either be solid state diffusion or friction welds. After the analysis was completed, the evaluation report was written and submitted for review.

Many smaller projects included metallographic sample preparation, characterization of microstructures, photographic documentation, and macro/micro hardness readings.

SYNTHESIS AND CHARACTERIZATION OF OPTICAL CHROMOPHORES

Task Order No. 75
Student Support Program
Southwestern Ohio Council for Higher Education

Christine S. Yoon
Wright State University

11 August 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

Task Assignment 75 was composed of different projects involving the synthesis, classification, and purification of various photosensitive materials derived from Tetraphenylporphyrins (TPP). This Task also required the analysis of the products using UV/VIS spectrometer, FTIR and proton NMR. The main objective was to synthesize various substituted tetraphenylporphyrin ring complex derivatives and determine the ideal conditions for purification. A tetraphenylporphyrin ring was used as the building block for the attachment of differing metals to produce novel photosensitive materials that contain optical chromophores for use in laser hardening devices.

DESCRIPTION OF RESEARCH

Project 1 involved the synthesis and purification of p-nitrotetraphenylporphyrin (${}_{NO2}$TPP) and tetra- nitrophenylporphyrin (T_{NO2}PP) ring complexes. The p- nitrotetraphenylporphyrin (${}_{NO2}$TPP) had to be purified and isolated through column chromatography which separated it from any unwanted isomeric compounds and by-products. The tetra-nitrophenylporphyrin (T_{NO2}PP) was focused for reduction reaction thus producing tetra-phenylporphyrinamine (T_{NH2}PP). The purified forms of tetraphenylporphyr in ring derivatives were analyzed through TLC, UV/VIS spectra, elemental analysis and FTIR.

Project 2 involved the separation of ortho-T_{NH2}PP from its isomeric components. The isomers were separated into different fractions through column chromatography and recrystallized for purification. The isolated compounds were also analyzed through TLC, elemental analysis, FTIR and NMR.

Project 3 involved the separation of $T_{CO2CH3PP}$ into different number of functional group (COOCHE) containing TPP's. Depending upon the number of the functional group it holds, the longer or shorter the retention time is in the column. Thus, the different number of functional groups was separated into different fractions through a dry column and recrystallized for purification. The separated compounds were analyzed through TLC, UV/VIS spectrometer and FTIR spectra.

RESULTS

Project 1: p-nitrotetraphenylporphyrin was synthesized by using the most optimal reaction condition of 0.01 M of pyrrol, added drop-wise, to 0.01 M of p-nitrobenzaldehyde dissolved in 250ml of acetic acid. This was then followed by the addition of 3ml of acetic anhydride. For isolation of p- nitrotetraphenylporphyrin from its crude p- nitrotetraphenylporphyrin ring complex, the crude compound was dissolved in benzene:hexane solution and eluted through a silica gel column with the same solvent solution (HPLC grade) until a color change was observed (dark purple to yellow-orange). The solvent was then changed to a 2:1 benzene:hexane solution. Once the $_{NO2}$TPP band was clearly visible on top of the sand layer, the column was washed with acetone. The UV/VIS spectra displayed absorption at 647, 590, 547, 518 and 440nm. Literature values for purified p- nitrotetraphenylporphyrin are 647, 593, 554, 518 and 428nm. The tetra-nitrophenylporphyrin ($T_{NO2}PP$) was synthesized and reduced to produce tetra-phenylporphyrinamine ($T_{NH2}PP$) with Sn_{Cl2} and HCl to obtain crude $T_{NH2}PP$. The crude $T_{NH2}PP$ was washed through a column and recrystallized in a CH_2Cl_2: CH_3OH solution.

Project 2: This project involved the separation of ortho-$T_{NH2}PP$ from its isomeric components. The $T_{NH2}PP$ was washed through a column and recrystallized in a CH_2Cl_2: CH_3OH solution. To isolate only the *aaaa* $T_{NH2}PP$, a column chromatography was designed with silica gel as the stationary phase and chloroform as the eluent for the separation. The $T_{NH2}PP$ sample was dissolved in chloroform and loaded on to the column. Once the first band traveled to the bottom of the column, the eluent was exchanged with a 1:1 chloroform: diethyl ether solution. When a color change was observed from dark violet to light brownish orange, the eluent was again changed with a 1:1 acetone:diethyl ether solution. The final band, being most polar, eluted with 100% acetone and the crude *aaaa* $T_{NH2}PP$ atropisomer was obtained. The crude *aaaa* $T_{NH2}PP$ was re-crystallized and washed through another column to obtain the purified form.

Project 3: This project involved the separation of crude $T_{CO2CH3}PP$ complex into the individual components, separating based upon its polarity strength (i.e., the number of functional groups it contains). A dry column was prepared with silica gel as the stationary phase and chloroform as the eluent. There were 6 components in all $T_{CH3}PP$, $C0_2CH_3TPP$, $(COCH_3)_2TPP$ in two forms at 5 and 15 positions and at 5 & 20 positions, $(COCH_3)_3TPP$ and $(COCH_3)_4TPP$. Five fractions were isolated, experimentally, and TLC, UV/VIS spectra, and FTIR spectrum all confirmed our findings as well as the identification of the isomeric compounds. J. Heteracyclic Chemistry 1975 reported similar findings and confirmed the results of our data.

HALF-TIME STUDENT AIDE

Task Order No. 76
Student Support Program
Southwestern Ohio Council for Higher Education

Kimberly Andrews
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8 August 1994

Government Task Leader
Dr. Ronald Kerans
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TASK ASSIGNMENT

Carbon coatings must meet several requirements such as stability, adherence with minimal fiber damage and uniform thickness. Coatings are used to coat ceramic fibers for three important reasons: (1) modifying fiber/matrix interface properties such that bonding is weak, allowing load transfer in ceramic-matrix composites, (2) reducing stresses resulting with coefficient of thermal expansion mismatch in ceramic-matrix composites and (3) protecting fibers from damage during preparation and use.

Carbon coatings are attractive coatings for ceramics for many reasons. These coatings have a low coefficient of thermal expansion, are usable at temperatures greater than 600°C in inert environments and can be used up to 426°C in oxidative environments. Carbon coatings produced by pyrolysis of a polymeric-based resin system should have a high char yield, minimum shrinkage during carbonization and heat treatments and be reproducible. During this Task, two polymeric-based resin systems were studied in carbon coating alumina fibers and preforms.

Fibers cut to 3 inches in length were placed in a glass beaker containing acetone and sonicated for 5 minutes. These fibers were air dried for 10 minutes at room temperature or oven dried at 110°C for 5 minutes. In some cases, the sizing was removed from the fibers and preforms by heat treating in air, oxygen, nitrogen or argon atmospheres.

The fibers were dip coated after cleaning for approximately 5-10 seconds in the polymeric-based resin system, air or oven dried for 10 minutes and desiccator dried for 10 minutes. These steps were repeated 1 to 3 times until all coatings were applied. The preforms were dip coated using various methods such as immersion, saturation or vacuum impregnation approximately 3 times with a polymeric-based resin system. After dip coating, the fibers and preforms were heat treated.

Alumina fibers coated with a phenolic-based resin system and pyrolysis did not develop a uniform carbon coating despite the application of various thermal treatments. Along the length of the fibers, there were areas of carbonaceous and non-carbonaceous coating. Gaps in the carbonaceous coating were believed to be caused by a coefficient of thermal expansion mismatch between the alumina fiber and carbon-based material. In addition, the phenolic resin system has a low char yield (40%) and shrink by 50% upon pyrolysis. Similar results were observed for the preforms.

A carbonaceous coating did not develop on fibers dip coated with a polyarylacetylene based resin system. The fibers were thermally treated to remove sizing. However, the fibers were neither wetted or coated by the polyarylacetylene system. This is believed to be caused by a surface energy problem. To alleviate this problem, surfactants or additives may be needed. Uniform coatings were obtained for preforms using different heating schedules and a flowing nitrogen atmosphere. The best conditions for processing preforms coated with the polyarylacetylene system occurred between 700-1000°C at a heating rate of 1-5C/min in a tube furnace. The polyarylacetylene system has an 80% char at 1000°C in a nitrogen atmosphere. This resin expands to the point of pyrolytic degradation. A shrinkage of approximately 4.9% begins as the resin-to-carbon transformation occurs between 485-500°C. However, the char yield is reduced due to significant decomposition prior to pyrolysis. The polyarylacetylene system produced better carbon coatings than the phenolic resin system since this system has a higher char yield and lower shrinkage than the phenolic system.

Using polymeric systems to coat ceramic fibers and preforms yields poor to adequate results. The only attractive property of carbon coating by pyrolysis is that the carbonaceous coating produced appear stable at high temperatures. The preforms may be damaged, however, when producing carbon coatings via pyrolysis of the phenolic resin system, due to bloating of the preform and brittleness.

The polyarylacetylene system did not wet the fibers. The surface energy of the alumina fibers was such that the polyarylacetylene resin would not wet the fibers. Thus, surfactants may have to be used in combination with this resin system to adjust the surface energy such that it will wet the alumina fibers. Carbon coating of preforms via pyrolysis of the polyarylacetylene system was excellent when using a nitrogen atmosphere, a 1/2 to 2 hour soak time, and 700-1000°C temperatures.

For future work, other processing environments may be used to produce carbon coatings via pyrolysis of polymeric-based resin systems. The surface energy of the resin system may be altered to obtain better results. Other polymeric-based systems may be investigated to carbon coat fibers.

HALF TIME STUDENT AIDE

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8 August 1994

Government Task Leader
Dr. Randy Hay
WL/MLLM

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TASK ASSIGNMENT

The majority of the Task Assignment completed during the last 8 months stemmed from the desire to gather an understanding, control and/or alteration of fiber-matrix and fiber-coating interface behavior.

The types of materials being used are Yttrium aluminates such as YAG ($Y_3Al_5O_{12}$), Yap ($YAlO_3$), YAM ($Y_4Al_2O_9$) and other Alumina-Yag Eutectic fiber in Alumina matrices with various coatings. Fiber reinforced ceramics such as YAG-alumia exude many beneficial and applicable characteristics such as extremely high operating temperatures, resistance to cracking, oxidation resistance, light weights and chemical stability. Applications of such fiber reinforced ceramic matrices are high temperature environments such as turbine blades and exhaust nozzles of military aircraft. The replacement of these new materials with previous metal alloys is greatly beneficial due to their ability to withstand much higher temperatures, oxidizing atmospheres and centrifugal elongation (creeping). All of these factors allow the engine to operate at higher RPM and higher temperatures.

Specifically, the primary evaluation methods for fiber-matrix and fiber-coating technology included the following: X-ray diffraction analysis for chemical composition, scanning electron as well as transmission electron microscopy and sample preparation, optical microscopy, hot pressing of fiber-matrix composites, sol gel generation for fiber coating, computer assisted crystallographic diffraction pattern analysis and fiber diameter analysis utilizing laser imagery.

X-Ray Diffraction Analysis

The main purpose of analyzing a piece of material with X-ray radiation is to gain an understanding of the chemical composition of the material by comparing the diffraction pattern with known substance's patterns. The Rigaku Rotaflex RU-200b series X-ray diffractometer is used for these comparative evaluations. For example, suppose two separate pieces of material with different chemical composition (such as YAG and pervoskite) are placed in a face-to-face fashion within a high temperature atmosphere and it is desired to know if and what type of reaction has taken place between the two materials. The diffractometer can give accurate information about the chemical composition of a material and can be used to determine if a reaction has indeed taken place by comparing both specimen's diffraction patterns to the known patterns of the original material (YAG or for pervoskite in this case).

Transmission Electron Microscopy

The transmission electron microscope is an essential tool in the design of fiber coating and fiber-matrix interface technology. Although the samples being evaluated are ceramic, mettalographic principles are applied in the production of TEM specimens. This includes properly arranging the fibers in a mounting press (such as the Simplimet 200), slicing the sample to small thicknesses using a diamond cutting saw and then using grinding and polishing surfaces to thin the sample to approximately 100 micrometers. Once these steps are completed, the sample is placed in an ion milling machine to perforate its surface. This is done so that an electron beam can penetrate the sample in a transmission electron microscope (such as the Joel 2000 FX or Hitachi). The desired information regarding the fiber-matrix or fiber-coating interface micro structure can then be obtained.

Scanning Electron Microscopy

Much of the work put into the production of TEM samples is merely a continuation of SEM preparation. The samples are mounted, cut and polished until a smooth, reflective surface is produced on the mounted sample. The advantage of SEM sample preparation is that the samples do not have to be thin since a scanning electron microscope requires the electron beams to be reflected from the surface of the material. The recently purchased Leica 360 FE is essential to this type of single surface imagery as well as energy dispersive spectroscopy (EDS).

Alumina SOL Preparation From Alkoxides.

One of the problems facing the full scale use of fiber-matrix composite material is that of interface design. An approach used to reduce the amount of stress cracking within the composite material is to use a weak interface that oxidizes at high temperatures. Originally, carbon has been used as the primary coating on fibers to provide this weak interface after oxidation. Another possibility is the use of alumina. The precursor of this coatable alumina is a clear sol obtained from aluminum alkoxides. The main steps involved in the production of the alumina are: hydrolysis of aluminum alkoxides, peptization of the hydroxide to a clear sol, gel formation and the pyrolysis to alumina. Once the gel sol is produced, it is then applied uniformly to the fiber and allowed to dry.

Crystallographic Diffraction Pattern Analysis of the hexagonal molecular crystal structure of sapphire fiber and it's orientation relative to its surrounding matrix is done using diffraction patterns from TEM and assisting computer programs. The main programs used are CRYSTAL and DIFFRACT which uses measured lengths and angles between atoms on the diffraction pattern negative (done manually) to display several possibilities of the orientation of the sapphire crystals using a four digit hexagonal coordinate system.

Fiber Diameter Analysis

The Velmex Lasermike 162 is used to determine the elongation ratios and reduced diameters of YAG and sapphire fiber that have undergone creep testing. This is done by applying a laser beam orthogonal to the fiber length and placing the fiber in the beam's path. The diameters are read every 25/1000 of an inch and then accumulated manually in attempts to see exactly how the fiber diameter changes along the portion that was creep tested.

The work spent assisting the production of ceramic matrix composite materials for aerospace applications has been immeasurable in terms of real life educational experience. The well rounded engineering environment at Wright Laboratory has allowed for a genuine understanding of micro-evaluation equipment, techniques and methodology. The previously mentioned evaluation methods for fiber-matrix and fiber-coating technology were by no means a complete list, but rather a general synopsis of the more crucial evaluation techniques and equipment. The work experience at Wright Laboratory has played a crucial role in the education of engineering methods and skills. The majority of the time spent at work has provided a practical and realistic perspective on specific aspects of materials science and engineering.

DISCOVERY SYSTEMS

Task Order No. 77
Student Support Program
Southwestern Ohio Council For Higher Education

Barry Caslin
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31 August 1994

Government Task Leader
Dr. James Malas
WL/MLIM

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I would first like to thank Dr. Jim Malas and Dr. Steve LeClair as well as all the members of the Rapid Design System working group for the faithful assistance and abundant patience that every member of the RDS team extended. I would be remiss if I failed to mention the insightful and critical direction that Dr. Al Jackson provided in the accomplishment of my Task. Dr. Jackson was the lead researcher under whom I completed the majority of my Task and was the person I worked closely with on a regular basis.

TASK ASSIGNMENT

Research will investigate the comparative similarities between semiconductor and natural protein crystal structures. The focus of the work will be to design a heuristic and adaptive engine that designs experiments, and based on the results, build the next experiment to optimize the design of a material in a given set of properties.

Introduction to KnowBE

Extracting new insights (associations and relations) from experimental data and/or databases is fundamental to the discovery process practiced by scientists and engineers for: verification of experimental results, mapping of casual (ingredients to property) relations, or synthesis of data to create a new view(s) of a phenomenon. Currently this process is strongly defined by the expertise of the user. Knowledge bases (KBs) are helpful, because they reduce the amount of tedium required in hunting for data and rules about phenomena, but they are also static, i.e., they are limited to the rules included in them. Evolutionary methods for searching KB's are being developed that can take the process a step further by assessing the data for regularities and singularities present. KnowBE is a first step in this direction.

DataBases/Knowledge Bases

Databases are by nature passive entities that wait for users to send queries regarding a subset of the stored data but do not provide a means for finding the patterns present. Knowledge bases do enable pattern matching and classification, but in a severely limited sense defined by a rule set inserted along with the databases.

KB's are, thus, semi-active in nature. When searches are required that lie outside the domain of the rules, the search fails.

Knowledge discovery from databases is a relatively new and exciting research direction. It is concerned with extraction of an extra dimension of non-trivial information from empirical data, information which is normally hidden in the form of interrelationships between data items. Knowledge discovery techniques are to a large extent based on earlier research results obtained in such areas as statistics, theory of databases, machine learning or rough sets theory. In particular, the theory of rough sets provides means of data analysis on various levels of abstraction analysis of data dependencies and primary factors contributing to such dependencies, and rule discovery.

KnowBE Features

The coupling of methods which are evolutionary in their storage and recall enables an active system that provides a means of generating associations and functional mappings. KnowBE contains features of a simple data base in which calculations can be accomplished on certain parameters, results of searches on data can be plotted to provide visual opportunities for the user to observe patterns and suggestions about the data patterns. In addition, concepts can be generated autonomously or via human intervention to build an evolving memory in the form of mappings between data. Thus, KnowBe knowledge base can grow in two ways - each new experience can be used to 1) refine existing associations or clusters of similar experiences, and 2) evolve existing and enables new functional mappings or causal relations. The structure of KnowBE is hierarchical. The opening screen shows a periodic table from which the user chooses elements of interest and then moves to the next screen where the type of search desired and any parameter bounds of interest are chosen. The results of the search are shown in the Compounds window. Here are displayed the parameters and reference numbers from which the data was obtained. The user can move to other windows related to chemical-physical parameters associated with a specific material, to the reference list, to a graphics window to plot associations and relations, or to a print window for hard copy of results. A special window for creating a new type of display is also provided for those who want to create their own sets of parameters. The graphics window allows the parameters to be plotted in bar chart form or in x-y scatter plot form. Other windows allow the user to turn searches over to the system and then display the results for approval, archiving, printing, or plotting.

E-O Example

The initial domain applied to KnowBE is in electro-optical materials. A data base of semiconductor compounds has been created containing a number of parameter values obtained from the literature and experimental sources. Access to the data is direct, and the interface is specifically designed to be simple in use and to display information clearly to the user. The Hypercard environment is attractive for this application because of the ease of use.

DESCRIPTION OF RESEARCH

The KnowBE was a system that runs on a Mac and Sun work station. The KnowBE is coded in Apple Script and C which has many features that allow the programmer to interact with the Apple environment, as well as allowing the user to manipulate the GUI in an efficient manner. Also at times it was necessary to program in C on the UNIX side.

RESULTS

In working on this project I had to Hyper Card, UNIX system support and some X-windows programming. I coded and developed methods of defining the orientation of crystals within a unit cell.

DISCOVERY SYSTEMS

Task Order No. 77a
Student Support Program
Southwestern Ohio Council for Higher Education

Marc Reiter
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31 August 1994

Government Task Leader
Dr. Steve LeClair
WL/MLIM

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TASK ASSIGNMENT

The objective of this Task is "To investigate and develop a system for the prediction of similarities within molecules." This is the goal of the project that is being worked on, KnowBE: Knowledge Based Elicitation. KnowBE is a program that takes data already known about an application and uses it to identify other items. The first application of KnowBE is crystal structures.

This application of KnowBE is broken down into several parts. Most of the KnowBE project is already completed and all current work is directed at the specific application of crystal structures. One part of the project is data entry. Data for specific compounds is in the process of being entered. This data includes the Compound Name, Structure type, Archtype and other information that describes the compound's composition and structure. Another set of data is the Spacegroup Data. This is also an important part of describing the compound's structure. This data is an essential part of the project's application because it makes up the data base upon which other items will be compared to.

Another part of this project is writing programs to use the data specific to this application. One program currently being written uses the data in the compound information data files and the spacegroup data files to build a unit cell for a compound. The data files describe what specific atoms are found in the compound and their specific coordinates. The program will read this information and manipulate the coordinates to make them all fall within the given unit cell.

Another program currently being written uses data that result from the first program to render a 3d image of the unit cell. This image of the unit cell can be rotated to be viewed from any angle. This program is important to get a grasp of what the compound actually looks like.

These programs are being written on Macintosh systems. These systems are very different because of their graphical interfaces that requires much specialized coding. Several small programs were written to get a feel for programming on a Macintosh system. Macintosh computers require extra coding to set up pull down menus, windows used on the screen, events such as mouse button down and other Macintosh specific coding. While this extra coding may be tough to implement and maintain, it is fairly easy to get used to and make programs look better and easier to use. Programming in C on a Macintosh is also different because the Macintosh seems to have many of it's own functions to use rather than the standard C library. While the standard C library can be used, the Macintosh functions seem to be preferred.

This experience has been a very rewarding one. Programs that are written that actually have a purpose give much more satisfaction than those written for programming classes. It is also a very beneficial experience working in a business atmosphere. It is an immense change from working in food service or a factory. This experience will be very good preparation for the future.

SMART SKINS AND STRUCTURES

Task Order No. 78
Student Support Program
Southwestern Ohio Council for Higher Education

Thomas J. Witman
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15 September 1994

Government Task Leader
Mr. John Russell
WL/MLBC

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TASK ASSIGNMENT

The objective of this project is to study the thermal and shrinkage residual strain and stress characteristics of a recently developed high temperature polyimide resin matrix system known as AFR-700. The post-cured resin shrink is known to be large. High stresses and strains develop within the composite as a result of the large resin shrink and coefficient of thermal expansion mismatch between the fiber and resin. The focus of this project was to determine how large these stresses and strains become.

The strains were determined for four different cases involving AFR-700 resin with S-2 glass fibers. The first two cases were on a microscopic level. Two fiber configurations were studied to represent the fiber arrangements in the composite. A single fiber with surrounding matrix was the first. Second, four fibers touching in a regular square pattern were examined. The next case involved a macroscopic study of a 0°/90° cross-ply laminate. The level of residual thermal strain was determined from the curvature of an unbalanced 0°/90° cross-ply laminate. A representative aircraft structure was constructed and analyzed for the final case.

The results show, on a microscopic level, that the failure strain is exceeded for both fiber configurations. The 0°/90° cross-ply laminate yielded large strains also. This is an extreme case, therefore large strains were expected. The aircraft structure shows the effect of the large resin shrink on a macroscopic scale. The residual strains were found to be quite small (when compared to the microscopic analysis results).

The development and implementation of high temperature resin systems in composites has created a need for similarly high temperature adhesives. An adhesive system based on the polyimide resin system AFR-700 is currently being studied. Several single-lap shear tests were conducted with various parameters changed. Tests were performed at room temperature and at elevated temperatures on dry specimens and on saturated specimens. Other strength tests were completed on thermally shocked and thermally aged specimens.

Three different modes of failure occurred in the shear strength tests. The first type of failure is first ply composite failure. This occurs when the adhesive bond is stronger than the composite. The first ply of the composite peels away and breaks (see Figure 1). The second mode of failure is called an adhesive failure. This occurs when the adhesive fails at the adhesive/composite interface. Adhesive failures occur when a good bond was not obtained between the adhesive and the surface of the composite which usually occurs due to surface preparation. The last mode of failure is a cohesive failure. This occurs when only the adhesive fails.

The tensile shear strengths obtained through all the tests were lower than expected. Shear strengths in the order of 1500 psi were anticipated. The mode of failure was the 1st. ply composite for a majority of the specimens. This indicates that good adhesion was had and was as strong as the composite itself. Water had no significant effect on the shear strength of the AFR-700 adhesive although water saturation and high temperatures combined produced a cohesive failure. Temperature (both aging and test temperature) had a large impact on the shear strength of the adhesive. The thermally aged specimens produced a standard deviation of about half the average shear strength. Due to the lack of materials, more tests could not be run to determine the effect of thermal aging.

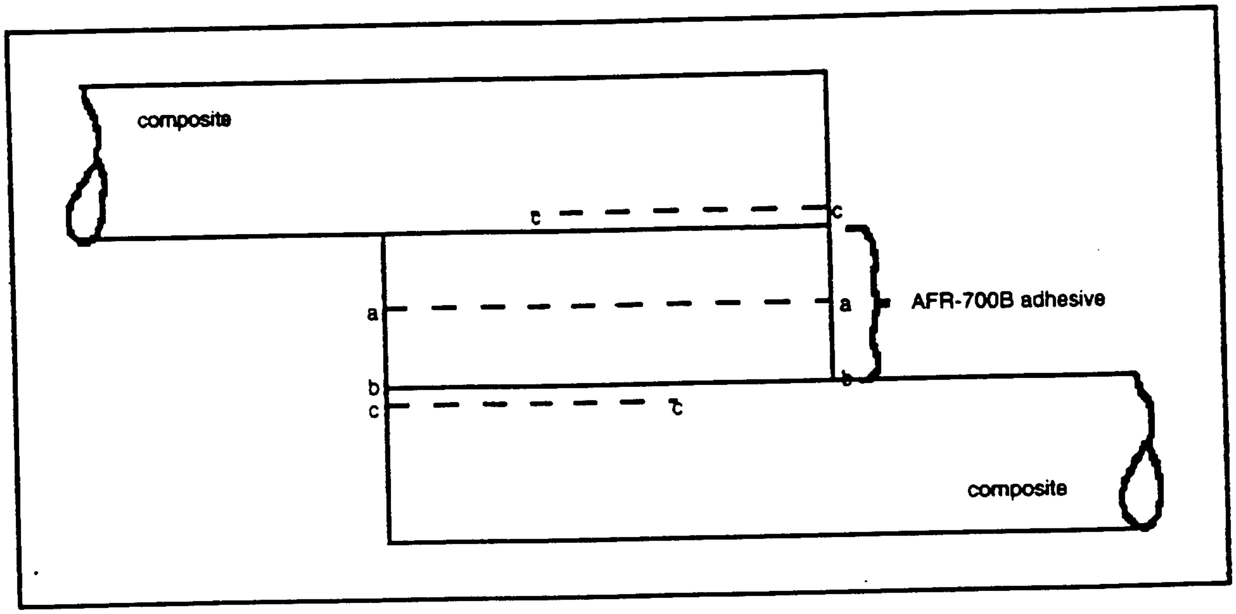

Fig 3. Diagram showing side view of a specimen and where the three modes of failure occur. Line a-a indicates where a cohesive failure would occur, line b-b indicates where an adhesive failure would occur, and lines c-c indicates where a first ply composite failure would occur.

MECHANICAL PROPERTIES OF METAL MATRIX COMPOSITES

Task Order No. 79
Student Support Program
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15 September 1994

Government Task Leader
Dr. Steve Russ
WL/MLLN

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TASK ASSIGNMENT

The objectives of the Task assignment were to assist Dr. Steve Russ in performing thermal mechanical fatigue testing of fiber reinforced metal matrix composites (MMCs) as well as data analysis, fractography and metallographic evaluations. Fatigue characteristics were obtained from these tests.

The investigation of the fatigue life of MMCs is of interest to the researchers involved in this Task, since these materials show great potential for aerospace applications in high temperature and high stress environments. The National Aero-Space Plane (NASP) program is currently considering this class of materials for airframe and skin applications.

The Task was mainly devoted to the investigation of the SCS-6/Timetal R 21S material system. SCS-6/Timetal R 21S is a titanium matrix composite with silicon carbon fibers. Testing has been conducted on three different laminates: [0], [0/90], and [0/±45/90].

Two test machines have been utilized. One was a servo hydraulic and one a pneumatic test machine. Both are horizontal frames equipped with load and displacement transducers and radiant energy lamps. The data obtained by the test machine and the transducers were recorded and stored on the connected computer system. The data was then copied from the DOS-based system to floppy disks and formatted on a Macintosh computer.

Experiments were conducted under thermal mechanical fatigue conditions in laboratory air at a wide range of temperatures and loading conditions. The data collected is then analyzed to determine stiffness and strain histories (damage accumulation) as a function of the number of cycles. Plots are made analyzing stress vs. strain at various cycles, strain vs. cycles, loading modulus vs. cycles, and temperature profiles. The plots are used for engineering evaluation and presentation.

Test specimens are cycled until failure, at which point the fractured specimens are taken to the metallography lab. There the specimens are first cut and polished to reveal any cracking or oxidation as a result of thermal mechanical cycling of the material. Three different orientations of the fibers are mounted in Epomet mounting material and polished. This procedure of polishing MMCs is very difficult. Great care must be taken to ensure that an optimum polish is obtained.

After polishing, the specimens are chemically etched and photographs are taken. Photographs are taken with a Riechert Jung optical microscope. If needed, the scanning electron microscope (SEM) is used to show a greater depth of field. This is why the polishing procedure is so important. The optical microscope cannot focus if there is a height differential between the fibers and the metal matrix. This may be difficult, since the fibers are much harder then the metal matrix and tend to polish at a slower rate than the metal matrix. The SEM is also used to do the fractography work. Fractography shows the fracture surface of the specimen, possibly revealing the mechanism of failure. The reduced data and metallographic results are then looked at together and an evaluation is made as to how the material behaves at high temperatures and stresses under cyclic conditions.

Over the last 8 months, a new material (Ti-6242), has been tested under tensile, iso-thermal mechanical fatigue and creep conditions. The test and data collection procedures for Ti-6242 specimens were the same as those described for SCS-6/Timetal R 21S. Testing on Ti-6242 specimens will continue for several months. After which, a test matrix will be created describing Ti-6242's strengths and weaknesses.

RESULTS

As was the objective of this Task, the fatigue characteristics of some advanced MMCs were investigated. Resulting from this study, certain aspects of the fatigue properties of the MMCs were discovered. The thermal mechanical fatigue data is only a small part of a large data base generated for the material. Other areas include tensile, thermal fatigue, creep, high cycle fatigue, low cycle fatigue, and fatigue crack growth. All the data from the lab is sent to NIC and at the end of the testing a decision will be made as to the use of the SCS-6/Timetal R 21S and Ti-6242 composite systems.

MECHANICAL PROPERTIES OF METAL MATRIX COMPOSITES

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Southwestern Ohio Council for Higher Education

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Government Task Leader
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TASK ASSIGNMENT

The primary objective of the Task was to develop a working understanding of the material behavior and properties of advanced fiber-reinforced titanium metal matrix composites (MMC's). Various conditions of thermal and mechanical fatigue and stress loadings are tested experimentally, and data from the tests is collected, reduced, and ultimately plotted for engineering evaluation and analysis. Test data and post-test specimen fractographic and metallographic evaluation are used to develop a comprehensive picture of the strength, stiffness, damage accumulation, and failure characteristics of the titanium MMC's.

The Air Force is particularly interested in characterizing the fatigue and loading behavior of titanium MMC's because this class of materials shows potential in a variety of engineering applications, particularly those requiring materials resistant to high temperatures and high loading conditions. As a result, titanium MMC's have been indicated as promising candidates for advanced aerospace structural applications such as the National Aerospace Plane (NASP).

RESEARCH METHOD

The titanium metal matrix composite systems investigated during the course of the Task consisted of titanium aluminide matrix (primarily Ti-22-23 or Ti-6242) with interwoven fibers of silicon carbide (typically SCS-6 fibers). Three standard fiber configurations or lay-ups were evaluated to determine their relative strengths and weaknesses under different loading scenarios. The lay-ups were [0], [0/90/0], [0/45/90/45/0] having fibers along one, two, and three axes respectively.

For testing, the sheets of as-delivered MMC were typically cut into smaller testing samples of roughly 5"x.5" in size. Samples were either tested as straight sided rectangular strips or cut further into "dog bone" samples with narrow test sections to concentrate the maximum axial stress in the center of the sample.

Tests were conducted on horizontal and vertical servo-hydraulic testing machines. Extensometers and transducers mounted on the test machine, as well as thermocouples (for elevated temperature tests) provided test data to IBM computers attached to the testing apparatus. In addition to recording and making initial plots of test data, the computers were also used to control many of the parameters of the test in accord with the machine's own instrumentation. Tests performed on the servo-hydraulic machines included static (tensile), creep, and fatigue tests, any of which could be conducted at room temperature or elevated temperatures up to 1000° C.

Test data is retrieved and plotted to allow engineering analysis. Plots are examined to determine the sample's stress/strain response and modulus. Graphs are also analyzed to obtain information about damage and plastic deformation that occurs in the material. Data may be evaluated based on a number of criteria (cycles, stress, strain, modulus, etc.), as needed by the engineer for evaluation or presentation of the test results. In addition to this method of analysis, the data obtained from the testing of the MMC's is also used in conjunction with a computer micromechanics model, FIDEP. Using test data to establish the empirical constants required by the modeling software's algorithms, it is hoped that the model may be refined to the point where it can be used to accurately predict MMC stress/strain responses for a variety of fiber volume fractions over a broad range of thermal and mechanical loading regimes.

After testing, the test samples typically undergo metallographic and/or fractographic analysis. In samples that were tested to failure, a fracture surface is cut from the broken sample and cleaned for examination and photographing under a scanning electron microscope (SEM). Careful inspection of the fracture surface can provide insight into the critical failure modes of the samples. Zones of cracking and ductile failure can be distinguished using the SEM, as well as regions of debonding at the fiber/matrix interface.

In addition to careful inspection of the fracture surfaces of tested samples, examination of the interior of the sample also provides insight into the mechanisms of failure and damage accumulation. Such examination is typically accomplished by sectioning a portion of the sample to obtain different views of the sample interior near the failure zone. Cut samples are mounted in Epomet/Konductomet resin using a Buehler mounting press. This mounting facilitates the polishing and lapping required to prepare the samples for close examination under optical microscopes or and SEM.

Once the samples are mounted, the lengthy process of polishing begins. Samples are first ground with rough silicon carbide paper to expose the uppermost layer of fibers at the sample's exposed surface. Mounted samples then undergo a sequence of progressively finer lapping steps (polishing with diamond powder/paste) using either small polishing wheels or the automated Maximet polisher. The sequence of lapping steps removes scratches and pits from the samples' surfaces, allowing careful examination of the fibers, matrix, and fiber/matrix interfaces. The final step in the lapping process involves Vibromet polishing to achieve a very finely polished surface. Once the samples have been completely polished, they are typically etched to make the microstructure of the matrix alloy visible. The samples are then examined and photographed with either advanced optical microscopes (Reichert-Jung) or with a SEM. Photographs are used in conjunction with the plotted data for analysis and presentation of test results.

RESULTS

In accordance with the objective of this Task, the behavior of titanium MMC's under various conditions of fatigue and loading was investigated. All results obtained from testing and all observations made during fractographic and metallographic evaluations become a part of the data base of information being gathered for the titanium metal matrix composites. Ultimately, this data base will allow engineers to determine the usefulness of the titanium MMC's and their applicability to the challenges of aerospace structural design and various other engineering problems.

GRAPHICS DISPLAY OF COMPUTER SIMULATIONS

Task Order No. 80
Student Support Program
Southwestern Ohio Council for Higher Education

Carlos Hernandez
Wright State University

31 August 1994

Government Task Leader
Ms. Monica A. Stucke
WL/MLLM

ACKNOWLEDGMENTS

I would like to thank the whole group for their support and camaraderie, which made the Task very enjoyable. The office is one of the friendliest and most pleasurable environments in which one would ever expect to work. Special thanks to Mr. Satish Rao for his support, expertise and collaboration in several projects. I also would like to thank the people at SOCHE (Southwestern Ohio Council for Higher Education) not only for their professionalism, but also for their service and assistance provided during the course of this Task. I only hope that my work and contribution to the community were as invaluable, as the experience and knowledge I gained.

TASK ASSIGNMENT

During the course of the Task, several graphical tools were completed in order to support the displaying of information from large input data decks involving differential displacement of atoms, local strains, forces, etc. Among these tools, some were built around the previously developed graphical packages, while others are stand alone utilities. The main objective of these utilities has been to improve the quality of the graphical results to give a more professional and ready to publish output.

The main focus of work during this Task, however, has been the development and optimization of several scientific programs; while some of them are simply innovations and improvements to old problems, others are new to the field of materials within our community.

To accomplish these problems, a "complete" scientific mathematical library that will fit and satisfy the necessities of the group had to be developed. It has been proven time and time again, that although much has been and is being done in this area, our community has always had special needs that are best served from within.

A new atomistic method was researched and developed to find local stress in materials, applying Kroèner's Quantum theory. The main difficulty this method presented was the cumbersome and misleading use of notation found in the different literature which had to be examined, rather than in the methodology approach and the understanding of the Kroèner's theory.

Elasticity theory has played a major role this year in most of the projects worked on. A new series of programs has been developed to find the self induced stress field at point due to a line segment, for both isotropic and anisotropic mediums and thus the capability to find the self stress induced in a loop. This program is a first step in an ongoing research, that will allow the material scientist to discover the generation and spreading of dislocation lines within a material, as well as computing force, torque, etc. This research is the first move by the group in the meso scale direction and hopefully will lead to new discoveries about the structural properties of metals.

A new series of programs was developed using Green's function for two and three dimensions, which allow the scientist to study displacements and forces between interacting atoms. The scientist can apply a relaxation to a region of the core and find the change in displacements caused by it, and subsequently how these changes affect the forces. These series of programs will eventually be interlaced with the new molecular dynamics' code, which still needs developing, to give the material scientist a very powerful set of tools with which to fully study the fundamental properties of materials.

The development of these programs, has raised one of the major problems that the CMS (computational material scientist) has to face, that of time. Most algorithms employed by the CMS group grow exponentially with the number of atoms. This fact has shown the impossibility of running some simulations, as well as, the enormous amount of wait between simulations, even with today's computational power.

This problem and the need for running larger cores, e.g., cores approaching 1,000 atoms, has led to the need for not only optimization of code, but for research and testing of new methods that will allow faster turn around times. New methods might allow the possibility of running some of today's unfeasible simulations.

Many frustrations were encountered during this crazy race against time. Not only were test results that begun with 15 minutes time dropped to that of merely 0.07 seconds, but accuracy of results was preserved and at times improved. To most people, the mere wait of minutes would have been acceptable. One has to realize that these are just sample tests and that actual simulations require billions of iterations, thus making time a critical factor.

In spite of these time reductions, the time problem has shown the group that it is time to parallelize the codes. The next step will be in employing distributed systems.

All the projects developed during this Task are fully portable across all systems. This may seem like an insignificant point, but after working and maintaining some old projects, it is gratifying to know that others will not have to deal with this annoying issue. Furthermore, this allows the material scientist to work on the machine of their choice.

The researcher also served as the system administrator, performing such tasks as adding new users, managing UNIX processes, planning and performing backups, restoring lost files from backup tapes, adding new terminals and disk drives, setting up a printer and the spooling system, and making the system secure. The researcher is proud of this last job, since our system was the only one in our LAN Network capable of withstanding the break-in attempts that the DOD (Department of Defense) conducted as tests in our networks.

METALLIC COMPOSITES II

Task Order No. 81
Student Support Program
Southwestern Ohio Council for Higher Education

Michael A. Foster
The Ohio State University

12 December 1994

Government Task Leader
Dr. Dan Miracle
WL/MLLM

ACKNOWLEDGMENTS

Thanks need to be given to everyone at Wright Laboratory who made the job a little easier and a lot more understandable. Special thanks need to be given to Chris Palser (SOCHE student), Dr. Dan Tilly (visiting scientist), Mr. Paul Smith (Research Engineer), and especially Dr. Dan Miracle, who was always there to answer questions and give meaningful advice.

TASK ASSIGNMENT

This Task's objective was to determine the interface properties and deformation characteristics in advanced metallic composites for high temperature applications.

The specific work to be done consisted of establishing new techniques to produce both single fiber and multi-fiber composites that had a range of geometries for a number of matrix/reinforcement combinations. The Task also called for the production of composites for the determination of interface properties and deformation characteristics in advanced metallic composites. Also involved was the testing of the mechanical properties of these single and multi-fiber composites and assisting in the analysis of the data.

The research proposed in this Task is very important. The United States Air Force's Integrated High Performance Turbine Engine Technology initiative (IHPTET) deals with the doubling of a jet aircraft's thrust to weight ratio by the year 2000. Metal matrix composites (MMC's) and other high technology materials are vital to the initiative's success. This is because MMC's are a good bit stronger, yet much lighter, than conventional materials. These MMC's are to be used in the engine of a jet aircraft, where it is necessary for a material to be able to withstand large stresses at elevated temperatures. One of the most important groups of metal matrix composites is continuously-reinforced titanium matrix composites (TMC's). These composites are necessary because they have the sort of high-temperature mechanical properties that are needed for an IHPTET jet aircraft engine application.

DESCRIPTION OF RESEARCH

Research has been conducted in three different areas. The first project dealt with the slice compression test, a test designed to evaluate the strength of the interface between the matrix material and the reinforcement fiber in a metal matrix composite. This research was done under the guidance of Dr. Dan Tilly. The material used for the tests was a TMC that had a matrix consisting of 90 atomic percent titanium, 6 atomic percent aluminum, and 4 atomic percent vanadium (Ti-6-4) along with SCS-6 or SCS-0 silicon carbide fibers. These fibers were manufactured by Textron Specialty Materials. Experimentally, the slice compression test is fairly straight forward. The TMC test specimen is placed in an Instron tension/compression machine between a hard silicon carbide anvil and a much softer brass plate. The specimen has a square geometry with a square array of nine fibers positioned in the center of it. The fibers are oriented parallel to the loading direction. At the beginning of the test, the specimen is compressed between the brass and silicon carbide plates using a constant displacement rate. At a certain stress level, the fibers start to debond from the matrix. Since the brass is much softer than the silicon carbide and the elastic modulus of the fiber is greater than the modulus of the brass, the fiber will start to protrude from the TMC specimen and indent into the brass. This compressive stress continues to a given load level, and then the load decreases linearly back to zero. For an analytical model to be used, several different parameters must be physically measured after the test is completed. The depth of the indentations in the brass was measured, which represented the maximum fiber protrusion length. The length of the final fiber protrusion was also measured, since at the end of the test the fiber relaxed back into the matrix but did not relax the entire way. Both these measurements were made using a surface profilometer, which uses a small stylus that moves over the sample and detects very small changes in height.

The other two projects dealt with a new titanium alloy that has been shown to have promising mechanical properties. This alloy consists of 55 atomic percent titanium, 22 atomic percent aluminum, and 23 atomic percent niobium (Ti-22-23). These projects were done under the guidance of Mr. Paul Smith. When Ti-22-23 is rolled to sheet thickness, it is rolled in only one direction, which causes the material to have anisotropic mechanical properties. Several heat treatment studies have been conducted on this alloy to determine which treatments have the best effect on the room temperature tensile and elevated temperature creep properties of this alloy when it is oriented in the rolling direction of the material. No work had been done to find which heat treatments had the best effect on the properties in the transverse orientation (perpendicular to the rolling direction). This is the subject of the first Ti-22-23 project.

Samples were obtained which were oriented in the transverse direction. The idea of the project was to see whether the heat treatments that had the best effect on longitudinal properties were also favorable to the transverse properties of the alloy. Two heat treatment schemes were picked which produced good ductility and creep resistance in the longitudinal orientation. These heat treatments were very similar, except one had a rapid cooling rate while the other had a cooling rate that was a factor of ten slower. Four specimens were heat treated at each condition, two of which were used for tensile tests and two for creep. Chemical analysis of the as-received alloy was also done.

The other Ti-22-23 related project had to do with the alloy's phase stability. This material is intended to be used in a jet aircraft's engine, where the operating temperature approaches approximately 650°C. A study had been conducted to ensure that the alloy's microstructure is stable at this temperature and above, but there has been no such study dealing with the phase stability of the alloy at temperatures lower than the operating temperature. Such a study is necessary though, due to the fact that in the aircraft's engine the alloy would experience these lower temperatures. Samples of the alloy were obtained and heat treatment conditions were set. The alloy was subjected to three different heat treat schemes which were 300°C, 450°C, and 600°C for 1000 hours in an inert argon environment.

RESULTS

An accurate analytical analysis of the slice compression test is still being worked on. Once a model is formulated, all the experimental measurements that were taken can be used in the model to get a good idea of the interfacial shear strength.

Most of the tests for the Ti-22-23 transverse property project are completed. The as-received material had a strain-to-failure on the average of 1.30%. The two heat treatments that had beneficial effects on the longitudinal tensile properties of the material also had a good effect on the transverse tensile behavior. The specimens that underwent the heat treatment with the faster cooling rate had an average strain-to-failure of 3.29%, while the slower cooling rate specimens had an average of 2.51%. Creep studies were also conducted for the as-received and heat treated materials. The as-received samples took an average of 7.27 hours to 0.4% creep strain and 198.6 hours to rupture. The specimens' heat treated with the faster cooling rate took an average of 59.8 hours to 0.4% creep strain and were removed from the machine after 300 hours because they had not fractured yet. The specimens at the other heat treatment are still undergoing creep testing.

The specimens for the 350°C - 600°C phase stability study are still undergoing their 1000 hour heat treatment.

CONSOLIDATION OF NDSANDS COMPUTER PROGRAM

Task Order No. 82
Student Support Program
Southwestern Ohio Council for Higher Education

Anthony D. May
Wright State University

19 September 1994

Government Task Leader
Dr. G. P. Tandon
WL/MLBM

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

The purpose of this Task was to create a user friendly software application, entitled NDSANDS, for use on Apple Macintosh computers. N Directional Stiffness AND Strength (NDSANDS) is an interactive program that evaluates composites' effective properties, does point(composite) stress analysis, and predicts the initial or first failure of multidirectional coated continuous fiber composites. The code, written in FORTRAN, can be used to study the effects of mechanical and hygrothermal loads on the microstress distribution within the constituents, namely the fiber, coating and matrix. It has been developed for the Apple Macintosh family of computers.

The program calculates the effective elastic properties, thermal conductivity, thermal expansion coefficients and moisture expansion coefficients of multi-directional coated continuous fiber composites. The microstress distribution within the constituents, namely the fiber, coating and the matrix, can be determined under a three-dimensional mechanical and/or hygrothermal loading. Some of the commonly used theories of failure, such as maximum stress theory, maximum principal normal stress theory and maximum shear stress theory can be employed to determine the initial or first failure of composite materials.

NDSANDS gives the user the option to do the stress analysis in cartesian or polar position coordinates. The evaluated stress distribution and the strength ratios can either be listed in a tabular format or plotted. Graphs of constant radius or constant angle can be obtained. The user has been given the complete flexibility of defining the number of grid points for listing, defining limits of minimum and maximum radius or angle for plots, prescribing external mechanical and/or hygrothermal loading and changing any or all of these at any stage of the analysis.

The computer code has also been set up to conduct parametric study. This means that the user can change either the material property or geometry of the composite one single variable at a time. Thus by assigning five different values for the variable selected, the influence of changing the parameter value on the effective properties, stress distribution etc., can be very easily studied.

A Help system has been provided as well. The purpose of this Help system is to provide on-line documentation clarifying the nomenclature used throughout the program. The Help system is designed so that a Help button will appear in sections of the program where the user may desire clarification. When the user clicks on the Help button they will be shown a screen of text with information relevant to the section of the program that the user is currently involved with. When the user clicks on the Continue button thus leaving the Help screen they will be returned to the section of the program where they originally clicked on the Help button.

Finally NDSANDS has the constituents material library and a composite material library that can be modified and updated.

RESEARCH ON HIGH TEMPERATURE INTERMETTALIC ALLOYS

Task Order No. 83
Student Support Program
Southwestern Ohio Council for Higher Education

John E. Florkey
The Ohio State University

12 December 1994

Government Task Leader
Ms. Monica A. Stucke
WL/MLLM

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I have had so much help this last work period from people who were more than willing to put their work on hold for a second to show me what I needed to know. Thanks to Ms. Monica Stuckey for being such an understanding and helpful Task Leader; to Sonya Boone for teaching me most of the metallurgical techniques I used; and to Bob, Mike, and Eric of the Met Lab, for teaching me how to speed things up by doing more than one sample at a time.

TASK ASSIGNMENT

Titanium aluminum alloys of varying compositions and processing backgrounds (forging, casting, etc.) were heat treated, tensile or creep tested and analyzed.

This was done to see the varying effects of chemical composition, processing and grain size and type on the physical characteristics of the alloy. Time was also spent determining how the temperature and duration of heat treatment affected the type and size of the grains in the microstructure.

By noting the changes in chemical composition, processing and heat treatment that exert changes in the physical characteristics of the alloy toward the desired physical characteristics, progress can be made.

DESCRIPTION OF RESEARCH

Samples were received after tensile or creep testing to be prepared for microscopy. The sample was sectioned perpendicular to the fracture surface. The fracture surface is the area of interest, so great care is taken to preserve that surface as it was immediately after testing. The sample was then sectioned parallel to the fracture surface to make it the proper size for mounting.

Next, the sample was mounted using a mounting press. The sample was placed on a stage, so that the flat, sectioned side was face down and lowered into the press. The sample was then encased in a mounting medium by application of heat and pressure. A variety of mounting media was available. Generally a conductive media was preferred because it could be placed directly into a scanning electron microscope (SEM) without further preparation.

After mounting, the sample was ready for grinding. Grinding could be done using several different means. For one or two samples, the roll grinder or the 12 inch grinding wheels could be used. The roll grinder was used most often because it removed material at a slower rate, therefore, it was easier for beginners to use. Generally, the sample was first ground on 240 grit silicon carbide paper. The sample was ground until all the scratches from cutting were removed and all the scratches from grinding ran in the same direction. When it seemed that all the scratches from grinding ran in the same direction, the sample was placed on a low magnification microscope. Under the microscope it could be seen clearly whether or not all the scratches were indeed running in the same direction and if all areas were receiving the same amount of grinding. It was especially important that the fracture surface was free of any abnormal scratches. The process was repeated with successively smaller grits, generally 320, 400 and 600 grits. When all this was accomplished, the samples were ready to be polished.

Polishing consisted of moving the sample back and forth over a note card that had some 15 micron diamond paste put on it. This continued until the scratches from grinding disappeared and all the scratches from polishing ran in the same direction. The above process was repeated with 6 micron diamond paste.

Next was the final polishing step. The samples were placed in a Vibromet overnight, which contained MasterMet, a .06 micron diamond polishing solution.

When processing four or more samples, the Maxi-Met could be used. The machine allowed the samples to be ground and polished by changing the medium used to remove the material. Using a platen made for grinding, the samples were ground using the same grit sequence as for hand grinding. The samples were checked periodically to make sure that there were no large scratches left from a previous grit. After the specimens were ground, the platen was changed to one designed for polishing. Using this platen, the samples were polished using 15 micron diamond polishing fluid. After the samples were polished with the 15 micron diamond fluid, they were removed from the Maxi-Met and placed in a Vibromet overnight, which contained one micron diamond polishing fluid. They were then removed from 1 micron Vibromet and placed in Vibromet containing .5 micron diamond polishing fluid for about 4 hours. Finally, they were placed in the Vibromet that contained MasterMet, for about 2 hours.

After the samples were polished, they could be examined several different ways. They could be viewed under polarized light on an optical microscope to see the grain outlines. They also could be etched, a process that involves eating away the top layer of material with an acid solution, and viewing under normal light to see the grains in more detail. Optical microscopy was only useful to about 1000x magnification. If higher magnification was desired, the samples must be viewed in a SEM. If the samples weren't mounted in a conductive medium, the sample must be carbon coated or silver painted to keep the specimen from becoming charged, which hampers the viewing of the sample. When the effects of heat treatment were to be studied, much the same process was followed. A small piece of material would be cut from a forged plate or cast billet and placed in the 1700°C muffle furnace. The furnace was equipped with a computer that controlled the temperature and the length of time the specimen was held at that temperature. The furnace was capable of having programs with many steps. After the heat treatment, the specimen was allowed to cool in air or it may have been oil or water quenched. After the sample was cooled, it was sectioned, mounted, ground, polished and viewed as described above.

I was not involved in the analysis of the data gathered, but I did learn about the microstrutures of metals, how failure occurs in metals, and the processes used in metallurgical research.

RESEARCH ON HIGH TEMPERATURE INTERMETALLIC ALLOYS

Task Order No. 83b
Student Support Program
Southwestern Ohio Council for Higher Education

Michael Jackson
Wright State University

12 December 1994

Government Task Leader
Ms. Monica Stucke
WL/MLLM

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Thanks go out to all the people at the metallography lab for their support as this Task was started. A special thanks to Dr. Young Kim for taking the time to make sure all information and direction on assignments was understood.

TASK ASSIGNMENT

The work that was done consisted of specimen preparation of intermetallic alloys for metallographic examination, including optical metallography and hardness testing. Selected specimens had various heat treatment trials performed and then had metallographic examinations again performed on the specimens. These analyses are being done to further the research in advanced intermetallic alloys. The aircraft industry is in need of a suitable alloy to be used as a high-temperature structural material for use in different parts of an airframe or engine component.

The methodology used for sample preparation was that of standard metallography practices either performed by hand or in automated machinery. The equipment employed in the preparation of samples was, but not limited to, silicon-carbide abrasive saws, diamond saws, mounting presses, automatic grinders and polishers, optical microscopes of various types, and a hardness testing machine. As of yet, the data analysis portion of the assignment has not been reached.

The extent of learning in the first few weeks on this project was quite large. The methodology of taking a raw specimen and converting it into something where the microstructure can be analyzed under an optical microscope was daunting at first, but became a valuable learning experience as time progressed. Although all the data has not been analyzed, the initial results do seem to indicate that there is potential for the particular intermetallic combination being studied at this time.

LIQUID LUBRICANT

Task Order No. 84
Student Support Program
Southwestern Ohio Council for Higher Education

Amy T. Neidhard
Wright State University

30 June 1994

Government Task Leader
Ms. Lois Gschwender
WL/MLBT

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TASK ASSIGNMENT

The Task involved research and experimentation regarding oxidation corrosion conductivity (OCC) testing, the development of a computerized data acquisition system for OCC testing, and the reestablishment of an oxidation absorption test apparatus.

The OCC experiment consists of measuring the degree of degradation (or oxidation) that a sample fluid lubricant undergoes when subjected to elevated bath temperatures (ranging from 350°F to 650°F/177°C to 343°C) and constant air flow (source of oxygen). The lubricants, themselves, contain temperature-driven catalysts. The purpose of the experiment is to simulate the static degradation of the fluid lubricant which is implemented to decrease the friction between moving jet engine parts, under the stress of air flight. The sample fluid lubricants are composed of perfluoropolyalkylethers (PFPAEs), which are commonly utilized as gas turbine engine oils for the United States Air Force. The specific parameter of interest is the ability of various lubricants to prevent engine wear at elevated temperatures, with and without additives which serve to extend or prolong the life of the PFPAE (through preventing chemical breakdown). It has been noted in previous research that when additives break down at high temperatures, the successive breakdown of the PFPAE is nearly immediate.

The purpose of the OCC experiment was to compare results obtained from tests run on fluid lubricants, with and without the addition of metals to the sample solution. The comparison between the results of OCC tests with and without metals is significant because it demonstrates the relative behavior of a sample fluid lubricant. In addition, the student served to improve upon the efficiency of the data acquisition system through the implementation of a personal computer, rather than the previously utilized data logger (which exhibited an insufficient input voltage threshold for the measurement of conductivity).

DESCRIPTION OF RESEARCH

I. OCC Experimentation

In an OCC test, the degree of degradation is approximated by the level of conductivity measured in a collection cell, located at the exit of glassware apparatus. Specifically, the gases released by the chemical breakdown of the sample fluid lubricant, within a glass test tube, are passed through a series of glass connectors, a condenser, and finally, into a receiving cell of distilled water (within which the conductivity probe is placed). The principle of measuring conductivity is based upon the fact that as a chemical compound breaks down (due to exposure to elevated temperatures), the number of ions (or free electrons) measured within the conductivity cell increases. The increased electrical charge of the solution results in a decrease in the resistance to the flow of electric current throughout the solution, or an increase in the reciprocal of resistance; conductivity. The probe of an Orion Model #126 conductivity meter measures the level of conductivity (in units of milliSiemen/centimeter), which is interpreted as a voltage potential (in units of milliVolts) by a data logger. The recorded voltage versus time data points represents the trend of a tested fluid lubricant to degrade under the influence of temperature. The slope of a favorable test fluid lubricant's degradation (conductivity versus time) curve is low, implying the slow degradation of the fluid lubricant.

Additional parameters, including the change in sample fluid lubricant's weight, viscosity, and clarity prior to and following an OCC experiment, are measured to provide an indication of the occurrence of oxidation.

The procedure described was developed by a previous student employee, Joseph Demers, who provided instruction regarding the procedures for an OCC test. The previously run OCC tests included five metal coupons to the test fluid lubricant sample, to simulate the oxidation of the fluid lubricant by the metals parts of an engine. Specifically, the acid sites on each metal coupon react with the base sites on the lubricant molecular chain, resulting in the oxidative breakdown of PFPAEs. The respective conductivity data points for simultaneously run, duplicate tests of 24-hour duration were input to two channels and stored within the memory of a Science/Electronics Model 1201 Squirrel 19-channel data logger. The data was then downloaded from the Squirrel to a 486 personal computer via a connection cable to SuperCalc5 software, through which a plot of the conductivity versus time data points was developed (See Figure 1), analyzed, and submitted to a supervisor.

The above procedure was followed to perform OCC tests, without the addition of metal coupons. The results of the test performed with fluid lubricants MLO71-6 and MLO78-80 at various temperatures (See Figure 2) were compared to the respective results obtained from experiments including the metal coupons in the test fluid lubricant solution. A calibration was required to make statistically accurate comparisons between experiments with and without metals since these tests were performed with 6mL and 20mL sample volumes, respectively. At low temperatures (approximately less than or equal to 550°F/288°C for MLO71-6), the data from 20mL tests without metals was accurately, mathematically scaled to approximate a 6mL test for comparison with data from previous 6mL tests with metals (the scale factor was supported by experimental data) (See Figure 3). Analysis of the results concluded that oxidation/degradation of the test fluid lubricant occurs significantly more rapid in the presence of the metal coupons (See Figure 4).

In addition, the results of the duplicate tests per experiment (two identical apparatus placed in two separate baths) imply that there is an inconsistency in the regulation of the discrete bath temperatures. The inconsistency is based upon the error calculated between the data points recorded from the two individual conductivity meters, and is exhibited in the difference in measured conductivity per test run with equivalent temperature and volumes of sample fluid (See Figure 5). This percentage of error was later determined to be negligible by analyzing the trend of the data, rather than discrete numerical values and errors.

II. Establishment of Computerized Data Acquisition System

The conductivity plateau exhibited in the figures presented above is attributed to the 250mV measurement threshold (or maximum input voltage) of the Squirrel data logger, determined to be a hindrance to the potential outcome of the OCC experiment. The nature of the experiment results in a positive correlation and linearity between conductivity and time, which is underestimated by the achievement of the data logger's maximum voltage input capacity prior to the completion of the 24-hour test period. The previously implemented Squirrel data logger was replaced with a computerized system, whose component parts were ordered prior to the start of the Task. An extensive amount of time and assistance was devoted to the establishment of a functional computerized data acquisition system. The procedure included the installation and initialization of Computer Boards, Inc. Model #CIO-DAS08-AO Metrabyte compatible analog-to-digital conversion card to the mother board of an upgraded 486-33 personal computer; the installation, initialization, and operation of Microsoft Windows-based Snap-Master data acquisition software and respective hardware drivers; and the incorporation of the component parts to develop a working system, despite minor incompatibility.

The final data acquisition system is based upon the input of analog conductivity data into the appropriate channels of a termination board (with respect to a specific wiring schematic for the provision of differentially amplified voltage signals); the conversion of the voltage signal from analog to digital form (through the installed conversion card); and the input of the digital data to the Snap Master data acquisition software and successively, to Microsoft Excel general analyses is software. The digitally converted data is manipulated through the general analysis software to produce conductivity versus time plots and relevant statistical information. The plot of conductivity versus time can be viewed real-time, as the experiment progresses, through a monitor (which provides a precise method in which to monitor the test), while the data is simultaneously saved to the hard or floppy drive of the computer for future manipulation.

The completed data acquisition system provides an efficient and versatile method of collecting data, providing a more appropriate voltage input range, simplified user operation and detailed plots. The developed computerized data acquisition system can be applied to additional test stations in the future.

III. Re-establishment of Oxidation Absorption Test

The Oxidation Absorption (Ox Ab) test is based upon the same physical principle as the Oxidation Corrosion Conductivity test discussed above, i.e., the degradation of fluid lubricant is measured under the circumstances of elevated environmental temperature and exposure to a constant air flow. The Ox Ab test, however, provides closed-loop feedback control of the system through monitoring the amount of oxygen which is absorbed by the lubricant, resulting in the oxidation/degradation of the fluid lubricant and the reduction in the pressure of the system (due to the reduction in the partial pressure of oxygen). The frequency of valve-opening to admit additional replacement air into the system represents the relative degradation of the fluid lubricant, and is the primary parameter measured.

The Ox Ab test system, in approximation to its operation in previous years was re-established, with the implementation of the Squirrel data logger previously implemented for OCC experimentation. This activity will be continued to during the next Task.

RESULTS

I. OCC Experimentation

As previously mentioned, the analysis of the results of OCC experiments consistently concluded that oxidation/degradation of the test fluid lubricant occurs significantly more rapid and with greater amplitude in the presence of the metal coupons. In addition, it was determined that tests conducted with 20 mL of sample fluid lubricant resulted in an increased sensitivity to changes in bath temperature, and hence, conductivity; however, the 6 mL test reduces the consumption of expensive sample fluids and, therefore, increases the efficiency of the OCC test.

These results offer insight into the thermodynamic properties of the lubricants implemented to protect the engine parts of the Air Force jet aircraft. The knowledge gained increases the ability of the Materials Laboratory to improve upon the efficiency of aircraft flight dynamics.

II. Establishment of Computerized Data Acquisition System

The development of a computerized data acquisition system has significantly improved the collection of real-time data, with respect to user-friendliness of system operation, efficiency, and quality of acquired data and respective graphical output. The computerized data acquisition system exemplifies the upgrade of technology with respect to laboratory data collection techniques and will undoubtedly be applied to additional Materials Laboratory experiments in the future.

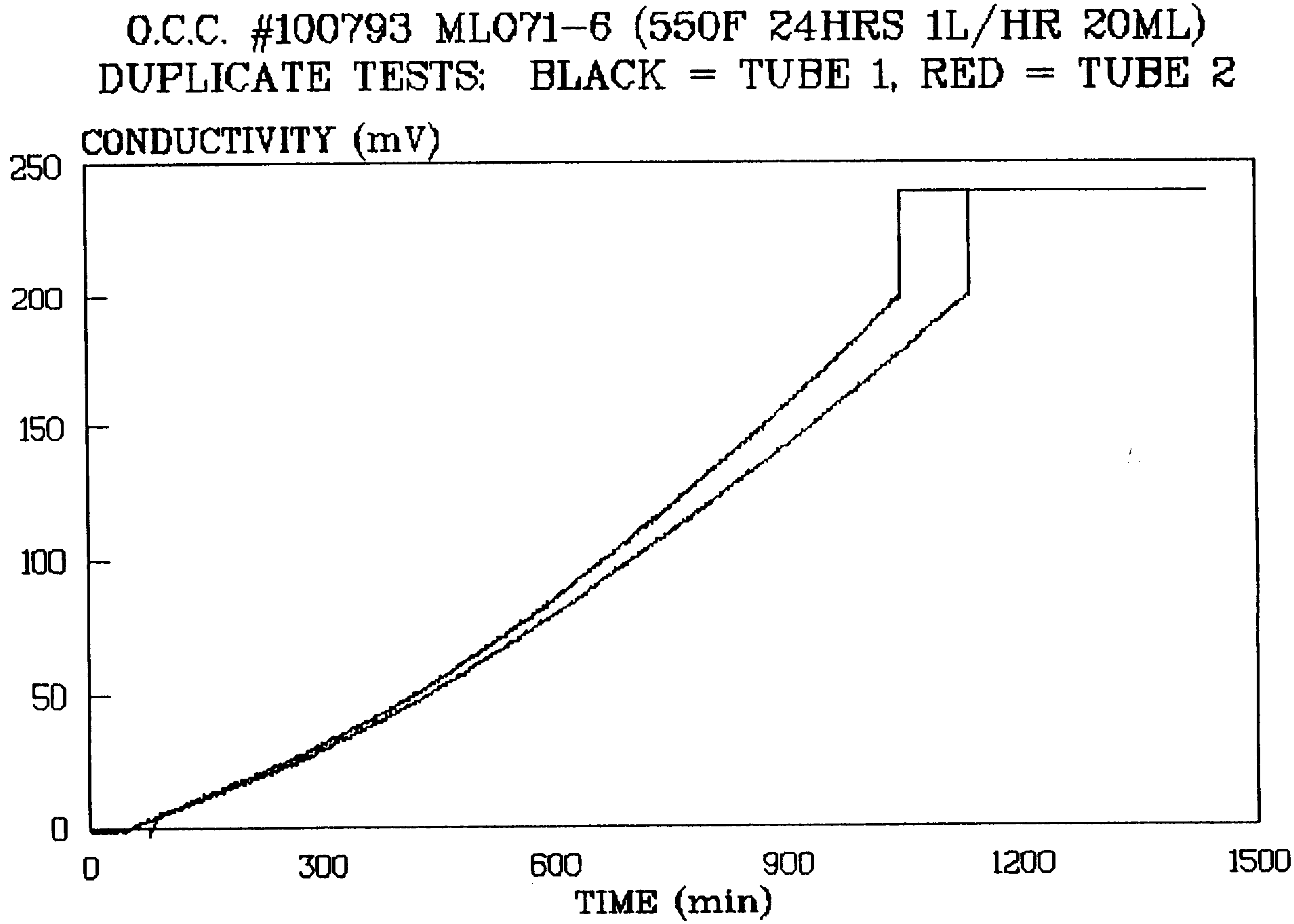

Figure 1: Example Plot of Conductivity versus Time from Collected Data

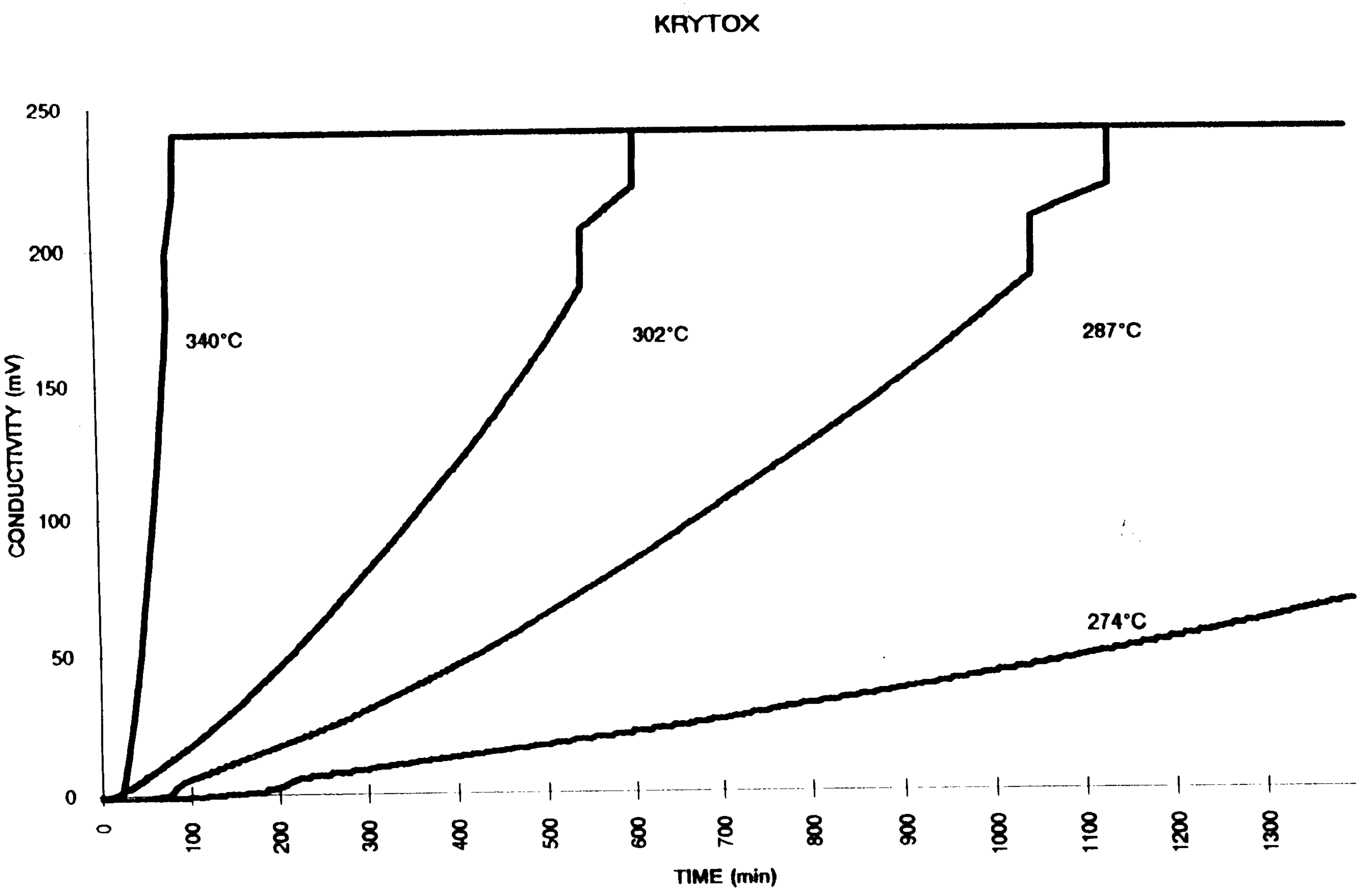

Figure 2: Conductivity versus Time Plots for MLO71-6 at Various Temperatures

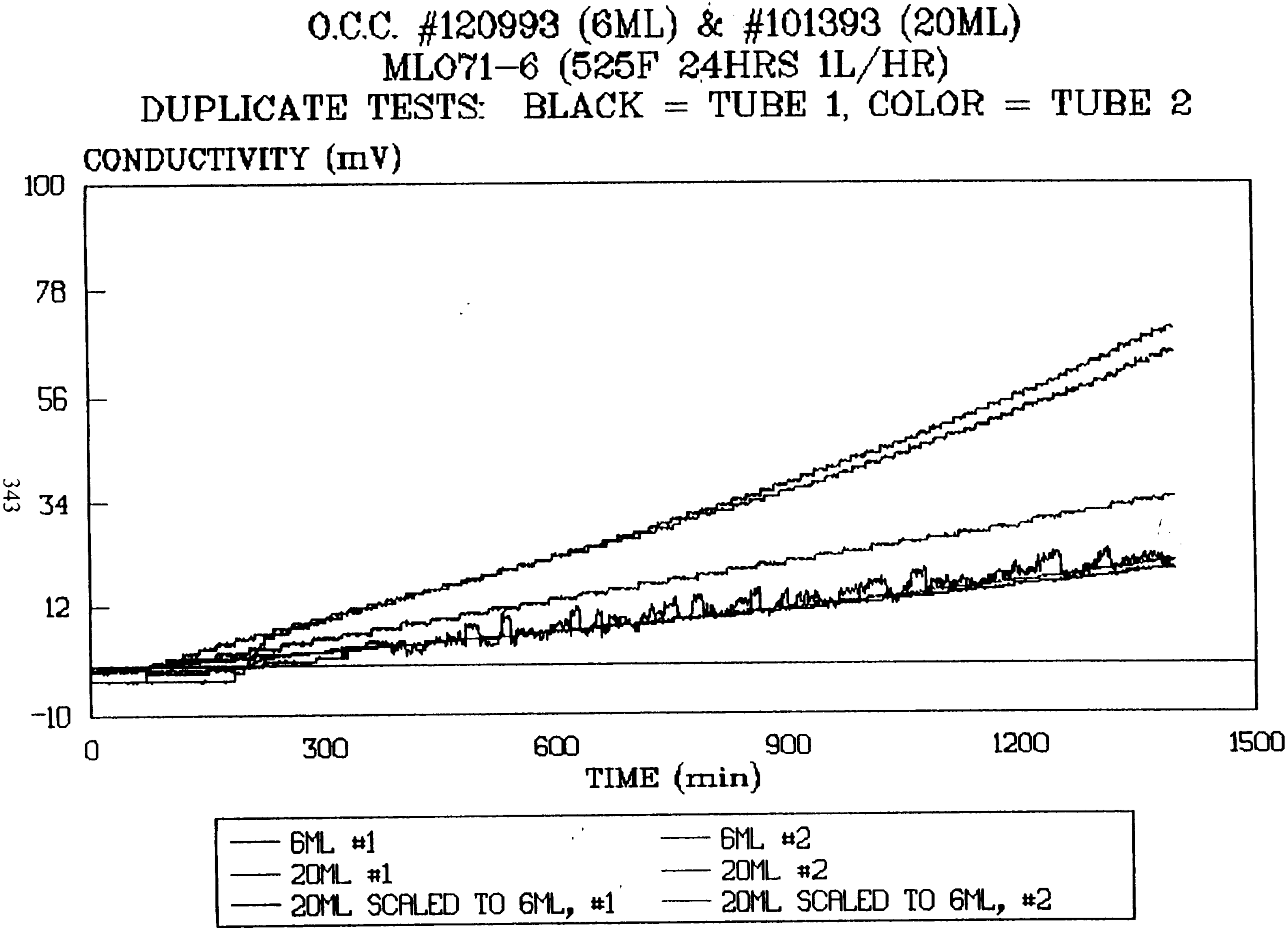

Figure 3: Conductivity versus Time Plots Exhibiting Difference Between 20mL and 6mL Tests

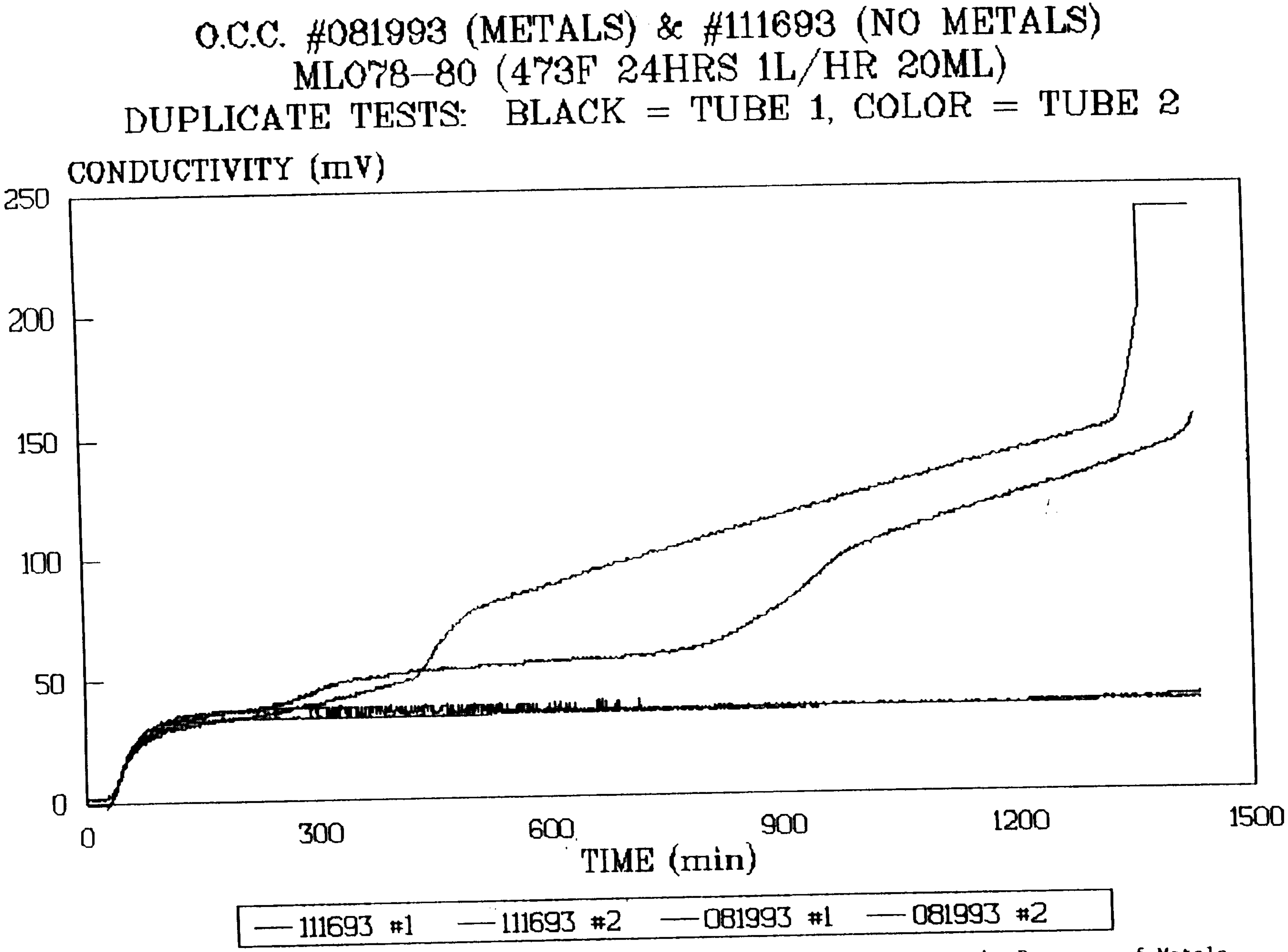

Figure 4: Conductivity versus Time Plots Exhibiting Difference Due to the Presence of Metals

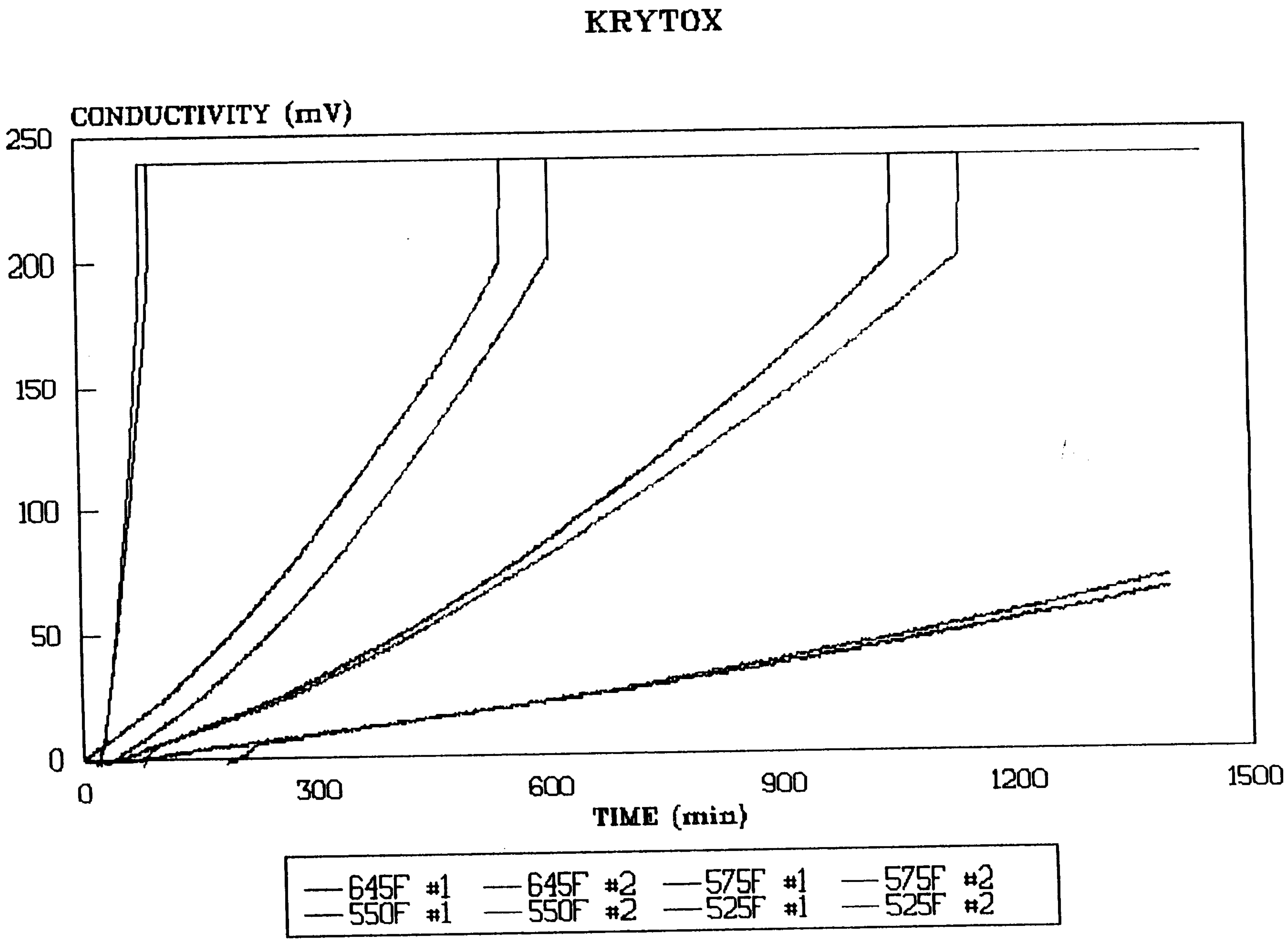

Figure 5: Conductivity versus Time Plots Exhibiting Difference Between Duplicate Tests

DAMAGE TOLERANCE OF ALLOWS AND METAL MATRIX COMPOSITES

Task Order No. 85
Student Support Program
Southwestern Ohio Council for Higher Education

Evan J. Dolley, Jr.
University of Dayton

14 October 1994

Government Task Leader
Dr. James Larsen
WL/MLLN

ACKNOWLEDGMENTS

The experience obtained while working at the Materials Directorate with Dr. James Larsen is invaluable. A special thanks is extended toward Dr. James Larsen and Dr. Jay Jira for the knowledge and experience which they have shared.

Others who were very professional and helpful, were the employees at the University of Dayton Research Institute, the personnel responsible for the scanning electron microscopes and the personnel who work in the metallurgical lab.

TASK ASSIGNMENT

Task 85 involved aiding Dr. James Larsen with projects which were pertinent to the area of crack initiation and growth in monolithic alloys and metal matrix composites. Theoretical and experimental work was performed to obtain knowledge of different materials system in support of United States Air Force initiatives. While assigned to this Task metallographic specimens were prepared and polished. Metallographic specimens were examined with the use of optical and scanning electron microscopies. Various theoretical models for fatigue crack growth in metal matrix composites were examined.

Following material testing, the tested specimen is examined using various techniques. During this Task the tested specimens were examined with an optical and scanning electron microscope (SEM). In preparation for examination, a piece of the tested material is cut from the tested specimen and mounted in Epomet compound. After mounting, the specimens are ground on an automated grinder and placed in a vibratory polisher for a final polish. If the microstructure of the specimen needs to be seen when using the optical microscope, the specimen must be chemically etched. The etching process causes a height differential between the different phases of the microstructure. The height differential between the phases produces a distinct outline of each phase so that they may be easily recognized. The specimen does not require a chemical etch for the microstructure to be seen when using the SEM. All optical microscopy is performed prior to the scanning electron microscopy since work performed on the SEM requires a carbon coating. Specimens cannot be seen with the optical microscope following the application of a carbon coating. The optical microscopy is performed to quantify the macro damage done to the specimen. Scanning electron microscopy is performed to quantify micro damage and microstructure characterization. The specimen is prepared for the SEM in two steps. The first step is to thoroughly clean the specimen in an ultrasonic cleaner using an alcohol solution. The second step is to coat the specimen with a thin layer of carbon and then bake the specimen at a low temperature in a vacuum furnace. The Epomet material which is used to mount the specimen is not conductive. Therefore, the carbon coating provides a path for the electrons to escape after they hit the specimen. Micrographs are taken with the optical microscope and the SEM. These micrographs are then used to document the damage tolerance of the tested specimen under the specific conditions in which it was tested. The micrographs are also used to characterize the microstructure of the material.

Theoretical work was done which compared two different approaches to determine the stress intensity factor for bridged cracks in an orthotropic material. A Microsoft Excel macro was written so that the derived equations could be used to determine $K_{bridging}$ for unidirectional fiber reinforced metal matrix composites. Hopefully, this analysis may be used in the future to assist in the prediction of fatigue crack growth of continuous fiber reinforced metal matrix composites.

Many different skills were obtained while working at the Materials Directorate. Probably, the most valuable skill learned was the ability to critically evaluate a problem and use the resources which are available to solve that problem. Other skills learned include the operation of Macintosh and IBM computers, the operation of MTS machinery which is used to perform material testing of optical and scanning electron microscopes, microhardness testers and metallographic specimen preparation and evaluation. All these skills were exercised while working under Task 85.

DAMAGE TOLERANCE OF ALLOYS AND METAL MATRIX COMPOSITES

Task Order No. 85a
Student Support Program
Southwestern Ohio Council for Higher Education

Julie L. Moran
Wright State University

14 October 1994

Government Task Leader
Dr. Jim Larsen
WL/MLLN

ACKNOWLEDGMENTS

Over the last year, I have had the pleasure of working with some exceptional individuals. Special thanks should be given to Dr. Jim Larsen for his guidance and great leadership. I also would like to thank all personnel working in MLLN and the University of Dayton Research Institute (UDRI). Everyone has helped in making this learning experience very valuable and it has been a pleasure working with a very professional engineering team.

TASK ASSIGNMENT

The objectives of the Task were to assist in performing data analysis, fractography and metallographic evaluations on thermally fatigued fiber reinforced metal matrix composites (MMC's). Mechanical properties of the materials were obtained from this thermal mechanical fatigue testing.

The investigation of the fatigue life of MMC's is of interest to the researchers involved in this Task, since these materials show great potential for aerospace applications in high-temperature and high-stress environments. The National Aerospace Plane (NASP) program is currently considering this class of materials for airframe and skin applications.

The Task was mainly devoted to the investigation of the SCS-6/Timetal R 21S material system. SCS-6/Timetal R 21S is a titanium matrix composite with silicon-carbon fibers. Testing has been conducted on three different laminates: [0], [0/90], and [0/±45/90].

Test specimens are cycled until failure, at which point the fractured specimens are taken to the metallography lab. There the specimens are first cut and polished to reveal any cracking or oxidations as a result of thermal-mechanical cycling of the material. Three different orientations of the fibers are mounted in Epomet mounting material and polished. This procedure of polishing MMC's is very difficult. Great care must be taken to ensure that an optimum polish is obtained. After polishing, the specimens are chemically etched and photographs are taken with Riechert-Jung optical microscope. If needed, the scanning electron microscope (SEM) is used to show a greater depth of field. When the SEM is intended on being used for photography the specimen must be mounted in Konductomet, which allows the electrons to flow into the specimen. This is why the polishing procedure is so important. The optical microscope cannot focus if there is a height differential between the fibers and the metal matrix. This may be difficult since the fibers are much harder than the metal matrix and tend to polish at a slower rate. The photographs taken are used for fractography analysis which shows the fracture surface of the specimen, possibly revealing the mechanism of failure.

The data collected during the mechanical fatigue testing is reduced for observation. The reduced data is analyzed by calculating mechanical properties using existing mechanical formulas and developing mechanical formulas. The bulk of the data and calculated properties require continuous updating, therefore, computer programs have been written to time efficiently standardize the data and calculate the mechanical properties.

The life expectancy of the material is a mechanical observation of special interest. During the Task work, research on the ability to evaluate this mechanical behavior has been done and the information gathered along with area individuals' additions have been applied to existing specimen data. Among the many mechanical properties required to evaluate life expectancy are stress intensity values at strategic areas of interest. The author has written a program that would evaluate stress intensity at one specific region of interest on the specimen and the author has also written other programs relating to this life expectancy topic.

The developing research and results have been modified for presentation. Plots are made to physically represent the mechanical relationships. Relating to the life expectancy research, Growth Rate vs. Cycles to failure would be a particular plot of interest.

RESULTS

As the objective of this task, the fatigue characteristics of some advanced MMC's were investigated. Resulting from this study, certain aspects of the fatigue properties of the MMC's were discovered. The thermal-mechanical fatigue data is only a small part of a large data base generated for the material. Other areas include tensile, creep, high cycle fatigue, and low cycle fatigue.

RAPID BETA ANNEALING OF CONVENTIONAL TITANIUM ALLOYS

Task Order No. 86
Student Support Program
Southwestern Ohio Council for Higher Education

Jay C. Soper
Wright State University

13 December 1994

Government Task Leader
Dr. S. L. Semiatin
WL/MLLN

ACKNOWLEDGMENTS

A special thanks goes to Dr. S.L. Semiatin. Dr. Semiatin was an excellent mentor. He guided the research process from the beginning to the end, explaining everything that was being done in great detail. He allowed me to explore my fullest capabilities in research. This included tasks ranging from participation in the experimentation, to computation and computer modeling, to participating in the actual writing of the paper.

Thanks should also be given to all the members of the Metals and Ceramics Division of the USAF Materials Directorate of Wright Laboratory. The assistance of Mr. T. Jones, Mr. T. Brown, Mr. P. Fagin, Mr. J. Brown, Mr. T. Goff, Mr. M. Dodd and all the members of the Metallography Laboratory was gratefully appreciated for their help and advise during the experimentation and specimen preparation.

TASK ASSIGNMENT

The objective of this Task was to investigate the beta grain growth of Ti-6Al-4V during moderately short time heat treatments. These heat treatments were *nominally* isothermal and were done above the beta transus temperature. The results of the investigation will hopefully show that the grain growth kinetics, above the beta transus, during these types of short time heat treatments can easily be modeled by the classical isothermal grain growth equation $[D^n\text{-}D_0n=k(\exp(-Q_g/RT))t]$ which is an equation normally used for conventional (long time) heat treatments.

The Task consisted of many parts. First, a finite difference computer model was modified to simulate various aspects of the experiment. Second, the heat transfer coefficient, an important parameter in the computer model, was found experimentally. This *independent* simple experiment was not the experiment simulated by the computer model. Next, the computer simulations were executed. Then, the experiments were carried out. Upon completion of the experiments, metallography of the experimental specimens was completed. This was completed by the members of the Metallography Laboratory. Finally, the results were determined from the analysis of the specimens.

The modified computer model used a finite difference approach to find the temperature change in samples of Ti-6Al- 4V with respect to time as the samples were dunked into a salt bath and as the samples were withdrawn from the bath and water quenched. The simulations were carried out assuming one dimensional heat conduction across the thickness (12 mil and 51 mil) of the two sets of thin sheet samples. Also entered into the simulation was the temperature of the salt bath, the room temperature, the material properties of the sample, the time that the samples spent in the salt bath, and the heat transfer coefficient between the salt bath and the titanium alloy samples. The output of the simulation was a graph of the temperature of the sample versus time, as the sample went from room temperature to the salt pot temperature; and then again from the salt temperature to the water quenching temperature.

This data showed that it took a significant amount of time for the thin samples to reach the salt temperature. Therefore, it is now known that the situation is not that of a perfect isothermal heat treatment; but, instead a *nominally* isothermal heat treatment. In other words, the heat treatment is basically isothermal except for a transient period at the beginning of the treatment that must be accounted for.

The heat transfer coefficient (between the salt bath and the titanium sample) used in the computer model was found by running a simple experiment, followed by a standard analysis. A thermocouple was inserted into the center of a 1 inch cube. This cube was then dunked into the salt bath and temperature versus time data was recorded. Finally, the energy entering the cube was set equal to the energy stored in the cube; and the heat transfer coefficient was determined.

The experimental part of this project consisted of dunking thin sheets of Ti-6Al-4V into a salt bath for various times. The thin sheets consisted of roughly forty 12 mil and forty 51 mil thick samples. These samples were then dunked into a salt bath of 1900°F and 2000°F. These are temperatures well above the beta transus which is roughly 1820°F. The samples stayed in the salt for various times ranging from 1 to 64 seconds, with a few extraneous trials at 240 and 960 seconds. This wide variety of dunking times allowed a wide spectrum of grain sizes to be created.

Upon completion of the metallography of some of the experimental samples, it can be shown through preliminary observations that there is a trend in the kinetics of the grain growth. The grains grew exponentially (as expected) as the heat treatments became longer. In conclusion, an experiment such as the one conducted in this research can be used to achieve a specific grain size as predicted by *some form* of the classical isothermal grain growth equation. The reason for the intentional ambiguity with respect to the grain growth equation above is because the short transient stage at the beginning of the already short heat treatment yields a non-isothermal condition at the beginning of the heat treatment which needs to be taken into account. At this point, the task is completed and Dr. S.L. Semiatin will finish the analysis and the write-up of the paper.

All of the research carried out above proved to be exciting as well as beneficial. Dr. S.L. Semiatin was very enthusiastic about research. This in turn made the author very enthusiastic. The author also learned that research is a very dynamic process; not the slow drawn out process which is what most people think.

RAPID BETA ANNEALING OF CONVENTIONAL TITANIUM ALLOYS

Task Order No. 86a
Student Support Program
Southwestern Ohio Council for Higher Education

Julia A. Bettlach
University of Dayton

12 December 1994

Government Task Leader
Dr. S. Lee Semiatin
WL/MLLN

ACKNOWLEDGMENTS

I would like to thank my Task Leader, Dr. Lee Semiatin, for all his guidance, support and encouragement throughout my Task. I also would like to thank the lab workers in the metallography lab for their patience and help in training me in the art of metallography.

TASK ASSIGNMENT

This Task has centered on the effects of rapid heat treating of Titanium alloys. The purpose of this study was to help prove that rapid heat treating can give better material properties in a more economical way than traditional heat treatments can. Investigation of this topic was performed by examining the change in microstructure of thin sheets of Timetal 21s, a Titanium Aluminum alloy, after they were heated above the Beta transus temperature. This data was then interpreted in analytical models used for conventional heat treatments.

Research for this Task can be broken down into three parts: study of recrystallization, study of grain growth and analysis of data. For measuring recrystallization, .0045" samples of B21s were heated in molten salt at 1500 and 1640° F. Before performing the heat treatments, the heat transfer rates from the salt to the metal had to be determined by modeling a computer program to obtain numerical solutions. To verify that the numerical solutions were reasonable, the heat transfer rates were calculated analytically. Once these rates were established, the isothermal heat treatments were run at 1500 and 1640° F at different times by dunking small samples into a salt pot filled with molten salt followed by a water quench. To determine the effects of the heat treatments on the microstructure, metallography was employed on all the samples and microscopic pictures were taken. From the pictures, the amount of Beta grains recrystallized was measured at each time for each temperature. The percent of recrystallization versus time was plotted for both temperatures.

The process of studying grain growth was similar to the study of recrystallization. For grain growth, .022" thick samples of B21s were heated in a furnace. Again, the heat transfer rates had to be established. This time, the rates were solely calculated analytically considering that heat transfer was due only to radiation. After plotting the heat transfer versus time, the heat treatments were performed on the samples at 1550 and 1650° F for various times. Next, metallography was performed and from the pictures taken of the microstructure grain sizes were measured. A graph of grain size versus time was then generated.

To analyze the data, focus was on the experimental results of the recrystallization study. Analysis was performed by fitting the data to the equation for recrystallization $X = 1 - \exp\{(-\ln2)(t/t_{.5})^n\}$ where X is the percent of grains recrystallized, t is the time, $t_{.5}$ is the time it takes to reach 50 % recrystallized, and n is the recrystallization exponent. To determine n, $\ln(\ln(1/(1-x)))$ versus $\ln(t/t_{.5})$ was plotted for both 1500 and 1640° F, and n was measured as the average slope of these two curves. The recrystallization activation energy was also found by using the data found for 1500 and 1640° F in the equation $(t_{.5})_1/(t_{.5})_2 = \exp(Q/RT_1)/\exp(Q/RT_2)$.

A graph of temperature versus $t_{.5}$ for temperatures ranging from 1500 and 1975° F was then plotted.

Analyzing the data found from the grain growth study was done by using the classical equation for isothermal grain growth $d^n - d_0 n = kt(\exp(-Q/RT))$where d_o is the original grain growth, d is the grain growth after time t, and Q, R, and k are the activation energy, the gas constant, and the rate constant respectively. Using this equation with the relationship that $k(t_1)\exp(-Q/RT_1) = k(t_2)\exp(-Q/RT_2)$where t_1 and t_2 are the times when the grain size of both temperatures is equal, k, Q, and n was solved. The analytical solution of grain growth versus time for 1550 and 1650° F was then plotted.

After fitting the data for recrystallization and grain growth to classical isothermal heat treating equations, the next step was to determine the effects that a 3 second heat up time would have on these two properties. To determine the recrystallization that would occur, approximate graphs of a 3 second heat up of B21s to the peak temperatures of 1650 and 1975° F were used. The graph was broken down into average time segments spent at each temperature between 1500° F and the peak temperature. These average times were then transferred to recrystallization versus time curves within the same temperature range. The percent of recrystallized grains at the end of the total time spent between the two temperature ranges found from the 3 second heat up graphs was determined. The grain growth that would occur during this time was also found by using a modification of the equation for grain growth during isothermal heat treatments $d^n - d_0 n = (kR\Theta(Q)\{T_f 2\exp(-Q/RT_f) - T_i 2\exp(-Q/RT_i)\}$where Θ is the heat transfer rate. Knowing d from previous experiments performed during a 3 second heatup, d_o was determined and the change in grain growth during the time spent between 1500° F and the peak temperature was calculated.

This study has shown that the microstructure, in particularly recrystallization and grain growth, of Beta grains can be altered during short time heat treatments and lead to enhanced mechanical properties of the metal. From the experiments performed and the analysis of the data, it was found that higher temperatures produced more effective results than temperatures closer to the Beta Transus temperature of 1470° F. My Task has supported the hypothesis that rapid heat treatments at high temperatures have much promise for being a successful, more economical alternative to conventional heat treatments.

MICROSTRUCTURE DEVELOPMENT IN ALUMINUM-LITHIUM ALLOYS

Task Order No. 87
Student Support Program
Southwestern Ohio Council for Higher Education

Robert M. Wilson
University of Dayton

31 December 1994

Government Task Leader
Mr. James T. Morgan
WL/MLLN

ACKNOWLEDGMENTS

A great deal of thanks and appreciation is extended to the Student Support program and Dr. Lee Semiatin for making this work contract possible. I appreciate the opportunity to work in such a professional environment and the valuable experience I gained throughout the Task. Special thanks are extended to Mr. Patrick Fagin of Universal Energy Systems for his help in preparing the material specimens and to Mr. Jim Morgan for his continued support and patience throughout the work term.

TASK ASSIGNMENT

The purpose of this Task was to determine the effect of thermomechanical processing variables on the development of microstructure on a low zirconium, aluminum-lithium (Al-Li) alloy. Processing variables of specific interest were the effects of rolling parameters such as reduction per pass, number of passes, rolling temperature, and rolling speed on dynamic and static recrystalization, whose combined effects were interpreted in terms of a pre-existing material process evaluating computer program. The computer program output a material processing map which predicted several temperature and strain-rate combinations for processing the alloy. These temperature and strain-rate combinations were then applied to the alloy microstructure during directly applied axial compression tests to evaluate the processing map's reliability. The information of all the tests was to be combined to construct a reliable material processing map to refer to in the future when processing the Al-Li alloy. Such a material processing map would eliminate expensive material testing and preparation uncertainties in the future, and allow manufacturers to go directly to production after selecting the desired material characteristics.

DESCRIPTION OF RESEARCH

The methodology behind the research was to physically roll several plates of the alloy starting at a known temperature and plate thickness, and work the plates down to a desired final plate thickness with the use of the Wright Lab's rolling mill. A total of eight plates was rolled at various selected speeds and temperatures by varying the number of passes and percent reduction per pass. These variations in speed, reduction per pass, etc. were recorded and entered into a pre-existing material process evaluating computer program, which through calculation of strain-rate, roll load per pass, and average and predicted pressures, printed out a material processing map which predicted suitable temperature and strain-rate combinations for working this particular alloy.

To check the computer program's output, the necessary mathematical calculations were done by hand. The reliability of processing map was then evaluated by physically working the alloy by direct axial compression tests using the selected temperature and strain-rate combinations. The compression tests were done by Mr. Patrick Fagin of Universal Energy Systems Inc., who aided in the material research. Compression tests of the alloy consisted of compressing small cylindrical billets of the alloy at the selected temperature and strain-rate combinations on a compression test machine. From here, the compressed billets were cut in half using a diamond blade cutter. Half of each specimen was mounted, ground, polished, etched, and finally photographed to record the state of the microstructure of each individual compression specimen. The microstructure was evaluated on the basis of grain size. A smaller average grain size was more desirable than a larger one due to internal stress concentration factors. After the initial evaluation, the second half of each compression specimen was solution heat treated and evaluated in the same manner. The heat treated specimens were then compared to the non-heat treated specimens to see if microstructure characteristics had been improved or not.

This general procedure was carried out on many temperature and strain-rate combinations throughout the Task period, due partly to the fact that the initial Al-Li material to test and do research on was of poor quality due to porosity and improper casting conditions. This material was later replaced with material that was cast under the correct conditions, with practically no porosity.

RESULTS

Due to the quality of the materials received to test with compression tests of the material were continuing at the time of the end of this Task order. However, a general material processing map existed that could, with limited accuracy, predict acceptable temperature and strain-rate combinations for processing the Al-Li alloy. The testing which continued at the end of this Task would ultimately narrow down an optimum combination of temperature and strain-rate at which to process the material.

LIFE PREDICTION OF COMPOSITE MATERIALS

Task Order No. 88
Student Support Program
Southwestern Ohio Council for Higher Education

Joseph Scheckel
Wright State University

31 December 1994

Government Task Leader
Lt. Jeff Schaff
WL/MLBM

ACKNOWLEDGMENTS

My thanks go to whomever started the Student Support Program. It is an excellent opportunity for hard working students to obtain experience in their field of study while continuing their studies on a full-time basis. Special thanks to my co-workers at Wright Labs Nonmetallic Materials Division who have taught me everything I know about composites, especially my Government Task Leader, Lt. Jeff Schaff. His patience and leadership have guided me to a potentially bright future.

TASK ASSIGNMENT

The main objective of this Task was to experimentally study the life prediction of composite materials as a follow-on to theoretical research conducted by Lt. Jeff Schaff and Dr. Barry Davidson, Syracuse University. A part of this research compared the effects of cyclic loading during fatigue where two sets of experiments undergo two stress level loading. In one set of experiments, the loading consisted of "large" cycling blocks at two stress levels intermittently. The other set of experiments consisted of "small" cycling blocks at the same two stress levels. Preliminary results indicate that both the fatigue life and the residual strengths of such composite specimens are greatly reduced due to the increased number of amplitude changes known as a "cycle mix" effect. Therefore, the Air Force believes this to be a critical issue in increasing the life of aging weaponry systems. For this research, the material chosen was AS4/3501-6, whose properties have been well documented.

To perform such research, there are several tasks that must be undertaken, including:

1) Understanding the make-up of prefabricated composite material and know that they consist of both unidirectional hair-like fibers and uncured resin.

2) Fabricating composite laminates by "sandwiching" several layers of this prefabricated material and curing them in an autoclave.

3) Performing fiber volumes on these panels to ensure that specimens from one panel to another are comparable, as well as performing nondestructive evaluation and making microscope plugs.

4) Preparing test specimens from each panel by tabbing, cutting and instrumenting them.

5) Manipulate existing computer program to perform the intermittent load changes described in the opening.

6) Investigate the mode of failure using both simple microscope and scanning electron microscope and report and present the results.

A significant task that required a lot of organizational skills was managing the whole test matrix. A lot of data had been taken and it was easy to lose sight of the main goal by getting involved in new ways of specimen investigation along the way. While making necessary changes to each portion of the test program, the effects of those changes on the rest of the test matrix had to be considered.

The test program was divided into seven phases that were also performed in this order: static tension, S-N fatigue, fatigue life distributions for two different stress levels, large block fatigue life, and small block fatigue life. The number of test specimens required for each test is as follows:

static tension	5
S-N fatigue	7
fatigue life distribution @ S1	5
fatigue life distribution @ S2	5
large block fatigue life	6
small block fatigue life	6
residual strength	5

The static tension testing was performed for specimens from each panel to determine the static strength distribution including panel-to-panel variability. Using strain gauges, the axial and transverse strains were calculated along with Poisson's ratio and Young's modulus.

Sinusoidal tension-tension fatigue testing was necessary to develop an S-N curve, plotting various percentages of the average static strength (S,ult = 91.24 ksi) versus the number of cycles to failure. From this curve, a low stress level, S1, corresponding to a fatigue life of 1,000,000 cycles and a high stress level, S2, corresponding to 20,000 cycles was chosen for fatigue life distribution testing. It turned out that S1 was approximately 0.57S,ult and that S2 was about 0.70S,ult.

The next step was to determine the fatigue life distribution for stress levels S1 and S2. Five specimens for each stress level were fatigue loaded, again at a stress ratio of 0.1, until failure; however, periodically, these specimens were removed from the test frame for extensometer placement and statically loaded to determine Poisson's ratio, Young's modulus, and axial and transverse strain. For the lower stress level, S1, this was accomplished at intervals of 250,000 cycles and for the higher stress level, S2, at intervals of 5,000 cycles, both of which are one-fourth of the expected fatigue life.

Next, two computer programs had to be written and generated to determine specific Weibull scale and shape parameters used in the mathematical model proposed by Lt. Schaff from the fatigue life distribution data. From this data, the intervals for the large and small block fatigue testing were determined. The number of cycles per block in the small block fatigue test was chosen so that each would experience one tenth the number of cycles per block at the same stress levels in the large block fatigue test. Still, the total number of cycles between both tests remained the same. Comparisons are then made between the fatigue life of specimens having undergone large block loading versus those having undergone small block loading. During these tests, the specimens are to be removed periodically to investigate the progressive damage that occurs during this fatigue testing. Thus, the effects of cycle mix can be readily observed while the specimens undergo fatigue loading and upon failure.

To this point, the fatigue life distributions have been performed and the large and small block fatigue testing is ready to begin for the first material. The hopes of finishing that portion of testing by year's end have been diminished due to problems encountered with the computer program that changes stress levels back and forth for the large and small block loading.

There is a high level of difficulty in understanding most every aspect of this test matrix, especially the Weibull distribution with all its different variables. However, the most labor intensive part of this Task took place in the test lab. The computer program that operates the test frame took a very long time to perfect because the original program, which was written in an unfamiliar language, had to first be decoded and then manipulated. The original program is highly sophisticated and interfaces with an asynchronous function generator that both sends and receives signals to and from the load cell. Because the computer is not synchronous with this function generator, manipulating the program was a project in itself that required many grueling hours of troubleshooting.

The most satisfying part of this Task was learning how to conduct research and incorporating one's own ideas into the research process while dealing on a professional level with some of the highest rated researchers in the country.

SYNTHESIS AND CHARACTERIZATION OF OPTICAL CHROMOPHORES

Task Order No. 89
Student Support Program
Southwestern Ohio Council for Higher Education

Sungmee Yoon Kim
Wright State University

28 October 1994

Government Task Leader
Dr. Robert Crane
ML/MLPJ

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I would like to thank Southwestern Ohio Council for Higher Education (SOCHE) for the opportunity to obtain valuable experience working with some great scientists and equipment. I also would like to recognize Dr. Tom Cooper, Dr. L.V. Natarajan, Dr. Zbigniew Tokarski, Dr. Timothy Bunning, Dr. Mike DeRosa, Karen Hussong, Linda Wood and Colin McHugh for their assistance with my research at the ML/MLPJ.

TASK ASSIGNMENT

The Task involved the synthesis and characterization of polymers that are siloxane based macromolecules, some incorporated with spiropyran molecules and other mesogenic groups (a component of a molecule that induces a mesomorphic or liquid crystalline phase) for use as matrices for optically active materials.

RESEARCH

Synthesis: Two different length spacer groups were synthesized: allyloxybenzoic acid (3C leader group) and pentenyloxybenzoic acid (5C leader group). The procedure used was modified by Dr. Timothy Bunning from reference literature 167. Dicyclohexylcarbodiimide (DCCI) coupling reaction was used with a catalyst, dimethylaminopyridine (DMAP), to attach various compounds such as hydroxybiphenyl, cholesterol, 1'- hydroxy ethyl -6-nitro BIPS ("T"), and phenylazophenol. Different solvent systems were used to purify the products in trying to find the best systems (cost and toxicity). Further purification of the allyloxybenzoate-nitrobenzospiropyran (3C T BIPS), pentenyloxybenzoate-nitrobenzosp (5C T BIPS) and allyloxybenzoate-phenylazophenol (3C PAP) was done by flash column chromatography. Silanization reactions were conducted using 100% 5C T BIPS and 100% 3C T BIPS in a D5 ring system. Also 100% 3CTBIPS were silanized onto linear dimethylhydrosiloxane. Using the 5 carbon spacer group, various percentages of biphenyl and cholesterol system were attached and silanization reactions were done with linear polysiloxane backbone. The silanization reactions were done under positive argon pressure with dicyclopentadienylplatinum (II) chloride catalyst prepared by method of Drew. The silanization reaction were performed in toluene at 90°C. The reactions were monitored by comparing the ratio of Si-H peak (2160 cm- ^{1}) to C=O (1742 cm-^{1}) peak with the FTIR (Fourier Transfer Infra Red Spectroscopy). These reaction products were purified by precipitations in methanol from toluene until TLC (Thin Layer Chromatography) shows one spot. These products were analyzed by either FTIR, Lambda 9 Spectrophotometer, NMR (Nuclear Magnetic Resonance), elemental analysis, microscopy and/or DSC (Differential Scanning Calorimeter).

RESULTS

The photochromic units (3C T BIPS, 5C T BIPS) have very low yield after purifying by flash column chromatography. The yield may improve when washed with hot ethanol before purifying by column. The silanization reaction requires high purity reactants and, therefore, rigorous and time consuming purification process is necessary. The thermal transitions of the various compositions of cholesteryl-4-pentenyloxy benzoate (C4PB) and biphenyl-4-pentenyloxy benzoate (B4PB) attached to linear siloxanes were studied. One 100 % biphenyl system with five carbon spacer group showed lowest mesophase range and compared with the corresponding three carbon spacer groups, the upper temperature limit (isotropic) increased. Fifty % and 100% cholesterol systems also had lower glass transition temperatures (Tg) as well.

For the cyclic siloxane systems (D5), 3 carbon spacer group was used to link various percentages of ABNS. As ABNS percentage increase, liquid crystallinity decreases by increasing the Tg and lowering the clearing temperature. Above 20% ABNS composition products are amorphous. Spiropyran molecule destabilizes the order necessary for the formation of a liquid crystalline phase. Increasing ABNS content causes the selective reflection band (characteristic of the cholesteric mesophase) shifted to lower wavelengths. The photochromic reaction leading to the blue merocyanine formation resulted in a narrowing of the reflection band width. Steric effects imposed by cholesterol, biphenyl and bulky spiropyran groups dominate the thermal decoloration kinetics of the merocyanine form. Aggregation of merocyanines was observed in nonpolar solvents, whereas in thin glassy films formed by shearing in the liquid crystalline state such an observation was not evident. Molecular stacking was observed in the 100% ABNS system by evidence of a shift in the thermal equilibrium toward merocyanine aggregate formation. Short spacer length of the leader group in spiropyran inhibited 100% attachment to the cyclic siloxane backbone. Possible explanation may be the steric effects. Longer spacer groups facilitated 100% attachment. Linear polysiloxane reaction times were much longer than the cyclic siloxanes since the reaction sites are much greater in the linear systems (D=35) than the cyclic (D=5). The 3C-PAP will be attached to the cyclic siloxane system with varying percentages of biphenyl and cholesterol based mesogens with same spacer groups. The thermal transition of these compounds will be analyzed and compared with other chormophores.

CONTROL FOR DEPOSITION PROCESSES

Task Order No. 90
Student Support Program
Southwestern Ohio Council for Higher Education

John G. Jones
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31 October 1994

Government Task Leader
Dr. James C. Malas
WL/MLIM

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TASK ASSIGNMENT

The automation of the actuators of a fiber Chemical Vapor Deposition, CVD, process has been accomplished to make the deposition process much more repeatable, easier and safer to accomplish, and much more flexible. The tasks which were performed included modifying existing equipment as well as installing new equipment to meet the requirements of having a fully automated fiber CVD process which allows computer control of reactor temperature, reactor pressure, mass flow of gases, and fiber velocity. Each of these requirements has been met with the current hardware and software implementations which are being utilized. Preliminary process models of the system utilizing a neural network have also been developed.

Automating the temperature control allows an operator to specify a desired operating temperature of the furnace before the deposition takes place. Since the operator uses a computer, the tedious task of programming three PID controllers, one PID controller for each zone of the furnace, with appropriate commands and numbers is removed. In addition, the use of a computer allows graphs of the temperature in each zone of the furnace to be displayed on the screen as opposed to just a current temperature reading from a segment display for each zone. The automation task of this subprocess consisted of replacing three LFE PID controllers, which were provided by the manufacturer in a cabinet with power electronic circuitry, with Eurotherm PID controllers. Since no documentation was provided, this involved understanding how the new three zone furnace system worked before it could properly be rewired and installed.

Another major task was to modify 14 pneumatic valves which controlled the flow of gases into the reactor system so that they could be controlled either manually as they always have been, or automatically through a computer. The valves were each controlled from 120VAC switches which are 35' from the computer. This task was accomplished after deciding upon a design which retained existing capability, provided computer control which was safe and expandable, and required a minimum number of additional components. Modifications to the existing equipment included wiring changes to each of 14 120VAC switches, the addition of a fuse for safety, and the addition of a selector switch to select between MANUAL/OFF/COMPUTER modes of operation. A metal enclosure which would sit next to the computer and contain 16 120VAC relays, 35' from the manual control panel, had to be designed and assembled. The box had to accept a 50-pin ribbon cable from the computer's I/O card and two 14 pin 1 20VAC connectors which were used to connect the 36 120VAC wires from the manual control panel. Using LabVIEW, software was developed which had graphical switches arranged in an identical manner as the manual control panel allowing an operator to easily understand its use.

The automation of pressure control of the reactor and the mass flow control of gases injected into the reactor was also accomplished. Both pressure and mass flow control was automated by adding an MKS 232, available from MKS Instruments Inc., which allows both the pressure and mass flows of up to three gases to be controlled from any RS-232 serial port. The pressure controller, MKS 250B, had to be internally modified by removing wiring and adding components to meet the OEM specifications of being computer controllable. These modifications were documented and appended to the equipment manuals. LabVIEW software was developed which allows the operator to graphically select the desired pressure and mass flow rates of each of three channels, as well as graph their current values.

The software which was developed for each of the subprocesses was integrated into a single program which allows an operator to easily manipulate the CVD process from a single computer terminal. The program automatically records the process parameters as the deposition proceeds while showing the operator how those parameters are changing in the form of graphical displays in real time. The automation of the process makes possible the linking of subprocess components which would otherwise not be possible, making the process much safer and more flexible. Actual sensors have not been obtained to allow the process to be operated in a closed loop manner, but the integrated data collection program was written with the expectation that a closed-loop control program could be embedded within it to allow the deposition of superior quality coatings.

A preliminary neural network model of the deposition growth rates for each of two precursors onto the fiber has been developed from data which has been provided by modeling efforts performed by Manthenein Technologies, Inc. The neural network was written in C++ for speed of execution, functions as a stand alone application, and generates data files which can be used for analysis by LabVIEW and Matlab. Manthenein Technologies, Inc. has developed a finite difference model of the specific CVD reactor which is in use and the associated precursors which are being deposited. The neural network has been trained on the available data and a preliminary process model has been developed. The current neural network model can be used in real time to provide deposition growth rate predictions from the temperature and pressure of the reactor. Although the model needs to be expanded to include mass flow rates and precursor concentrations to be useful for initial feedforward control of the deposition process, it has already been useful in understanding the deposition process.

ELECTRICAL AND MAGNETIC PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

Task Order No. 91
Southwestern Ohio Council for Higher Education
Student Support Program

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17 November 1994

Government Task Leader
Mr. Timothy L. Peterson
WL/MLPO

ACKNOWLEDGMENTS

Overall, this Task has been one to further help students gain experience to the laboratory setting and controlled experimentation. I would like to thank Southwestern Ohio Council for Higher Education (SOCHE) for their on going support, my Government Task Leader Mr. Timothy L. Peterson, and the many other fine people at Wright Lab that I have been given the opportunity to work with.

TASK ASSIGNMENT

Task 91, electrical properties of high temperature superconductors, involves the student helping to characterize the properties of high temperature superconductors by doing such things as measuring the DC electrical components of the thin superconducting thin films. This year there has also been a detailed study in the oxygenation of thin-film superconductors, which was also the student's senior project.

The experiment was originally set out to do several items centered around annealing a $YBa_2Cu_3O_{7-x}$ thin-film. These items were as follows:

1. To anneal a sample in Argon at different temperatures to drive out vacant oxygen atoms on the $YBa_2Cu_3O_{7-x}$ and rid the sample of its ability to be a superconductor.

2. Anneal a sample in oxygen to replace or fill vacant oxygen sites improving the films' superconductivity. (measured by changes in Tc)

3. Anneal a multicomponent film, or one that has different superconducting qualities over different regions of the film, and measure the results to the different components

4. Measure other properties of the films.

   a) X-ray Diffraction

   b) Atomic Force Microscopy

When one anneals in argon, the oxygen atoms diffuse out due to argon providing a zero oxygen partial pressure. After annealing, superconductivity was shown to be completely removed using AC susceptibility measurements. Next, the argon annealed sample was annealed in oxygen. Though traces of superconductivity returned, the sample showed chipping and flaking most notably at the edges. This was due to the slight crystal mismatch between the thin layer of $YBa_2Cu_3O_{7-x}$ and the substrate which it was grown on. The argon anneal creates stress between the two and when one starts to replace the oxygen in the $YBa_2Cu_3O_{7-x}$, the $YBa_2Cu_3O_{7-x}$ begins cracking. There is also the possibility that when one annealed in argon and removed the oxygen, the $YBa_2Cu_3O_{7-x}$ was converted to the tetragonal phase. When one anneals the tetragonal phase at higher temperatures (≈ 400° C), the $Yba_2Cu_3O_{7-x}$. Crystal twinning disappears and reappears when cooling below the transition temperature for twinning. This would cause a shearing of the $YBa_2Cu_3O_{7-x}$ structure mostly at the edges of the substrate where the most twinning occurs. It was at this point that the argon anneal was stopped as a method of removing oxygen from the film.

It has also been reported that annealing in vacuum will remove oxygen in $YBa_2Cu_3O_{7-x}$. The annealing furnace was set up so that a sample could be mounted in the furnace, a vacuum could be applied by hooking the inner quartz tube to a mechanical and diffusion pump, with other outlets to the quartz tube closed off. The sample could be heated to a given temperature in vacuum and annealed.

Bulk superconductors can be annealed in argon to remove oxygen thus producing a poor or non-superconductor. They can then be annealed in oxygen and restored to near original superconducting conditions. The thin films annealed in this experiment could be made oxygen deficient. The oxygen also could be replaced but unlike bulk samples, thin films are grown on top of a substrate that does not match the crystal structure of the $YBa_2Cu_3O_{7-x}$. The $YBa_2Cu_3O_{7-x}$ is thus strained when annealed in argon removing the oxygen, and then cracks when the oxygen is replaced. This also agrees with the experimental results in that the outer edges of the sample showed cracking first which is the least matched part of the film. It is believed that the cracking of the surface film is why the film could never be returned to pre-annealing conditions, not because oxygen could not be replaced.

The explanation of the vacuum annealed samples remain illusive. It was known prior to the experiment that oxygen could be removed by annealing in vacuum. It was also known that one could gradually degrade the film when annealing at lower temperatures in vacuum. This experiment showed no difficulty in arriving at these results, however, it has been reported that vacuum annealed samples could be annealed in oxygen and returned close to pre-annealing conditions. A. Mogro-Campero reported that samples deoxygenated by annealing in air could not be recovered but a reason was not included.[3] This experiment annealed samples in a minimum of 10^{-2} mTorr vacuum by using both a mechanical and a diffusion pump connected to a cold trap. There is a slight possibility that this is not a strong enough vacuum and that one would arrive at the same results as when annealing in air. There is also an anisotropic nature to the oxygenation of a film in that oxygen will diffuse into ab planes with a much greater probability than the c axis. This seems to be a weak explanation because the sample surface is not perfectly smooth and has many available oxygen sites in protruding ab oriented planes for oxygen to rediffuse into the sample. This is also inconclusive with the x-ray diffraction data in that oxygen was not returned to the annealed samples. The two vacuum annealed samples were both annealed in oxygen after their respective vacuum anneals that removed superconducting abilities. Another possibility is that the $YBa_2Cu_3O_{7-x}$ crystal grain boundaries that allow the sample to conduct have been damaged and even though oxygen may be returned to the film it does not have the needed grain boundaries for superconductivity. The last possibility is that there is something wrong with the experiment or the experimental process. One item of recent concern is the hour annealing period may be too long.

The results of the experiment to date can lead one to arrive at several conclusions. A sample will degrade, if annealed in argon but cannot be recovered due to the chipping and flaking of the film. Therefore, argon is not an annealing option to study the properties of films. Vacuum annealing will degrade and de-oxygenate a film but also appears unrecoverable when reannealing in oxygen, although the film does not appear damaged like the argon anneals. Samples only annealed in oxygen can be improved upon by increasing the samples' critical temperature (Tc) but from past measurements, oxygen annealed samples also show increases in resistivity after annealing.

INFRARED SPECTROSCOPY

Task Order No. 92
Student Support Program
Southwestern Ohio Council for Higher Education

Mark Roselius
Wright State University

30 June 1994

Government Task Leader
Dr. Harvey Paige
WL/MLBT

ACKNOWLEDGMENTS

I wish to extend my sincere appreciation to Dr. Harvey Paige of the Wright Laboratory Materials Directorate for his guidance and assistance during the performance of this Task. I also would like to thank Dr. Jim Liang of UDRI for his assistance with infrared data analysis.

TASK ASSIGNMENT

The interactions of lubricant model compounds and decomposition products with active surfaces under a variety of environmental conditions were studied in-situ using Fourier Transform infrared spectroscopy (FTIR). Temperature controlled infrared gas cells were constructed to perform conformational analysis of lubricant model compounds both in the vapor phase and on active surfaces. A new conformation analysis technique was developed using GC/FTIR. Compounds from the 1,2-dihalotetrafluoroethane family served as model compounds to evaluate the procedure.

RESEARCH METHODOLOGY

Infrared Instrumentation

Infrared data was analyzed with Perkin-Elmer model 1750 and a Nicolet 740 FTIR spectrometers. The GC/FTIR conformer study was conducted with a Hewlett Packard 5980 GC with a 5965A FTIR detector.

Surface

The surface used was alumina (Al2O3) applied to a potassium bromide crystal. The active sites studied were the hydroxyl groups (O-H) on the surface of the alumina. These sites were produced by reduction with hydrogen gas.

IR Cells

To conduct controlled low temperature and high temperature surface studies a metal gas cell was developed based on a design of Dr. John Yates, University of Pittsburgh. This cell was constructed from a standard ultra high vacuum (UHV) stainless steel cubic junction machined for 2 3/4" knife edge flanges. The IR ports were potassium bromide windows mounted in knife edge flanges. A potassium bromide (KBr) crystal was attached to a tungsten mesh mounted in nickel clamps. The KBr crystal acted either as a support for active surface materials or as a surface to which vapor samples were condensed. Active surface materials will be applied to this crystal. Temperature control of the crystal was accomplished by passing a variable electric current through the mesh for resistive heating, which in turn, heated the crystal by radiation and conduction. Low temperatures could be reached by the addition of liquid nitrogen to a dewar, attached to 0.098" diameter solid copper rods which chilled the nickel mesh supports by conduction.

A second metal cell, based on the previously described design, has been constructed. The chief difference in this cell is of a simplified mesh holder of solid copper mounted on hollow 0.250" diameter copper tubes mounted in a 2.750" Conflat^{R} flange. Liquid nitrogen is allowed to flow into copper mesh holder by way of the hollow tubes, greatly increasing thermal efficiency.

Conformer Analysis

Conformer analysis was conducted by a novel use of the GC/FTIR. The method consists of holding the injector port, column and IR detector at the same temperature (isothermal) and injecting a small quantity of the sample. This is repeated for several temperatures. The sample injected will be a mixture of conformers whose percentage of the population varies with the amount of thermal energy available. In other words, the conformer which requires the least amount of energy will predominate at lower temperatures and vice versa. Vibrational bands associated with a particular conformation will change in intensity with the change in population. Using the Van't Hoff equation, the natural log of the ratio of two band intensities from different conformers can be plotted against the inverse of the temperature (1/K) and ãH° obtained. For this study 1,2-dihalotetrafluoroethanes of the general formula CF_2XCF_2X were X = chlorine, bromine or iodine. Possible effects of injection volume and column flowrate were evaluated. Both were conducted with 1,2- diiodotetrafluoroethane.

In addition, conformer analysis will be conducted using the variable temperature gas cell. Sample gases will be condensed to the surface of the KBr crystal at low temperature. Spectra at various temperatures can be taken as the crystal is heated and will be studied with particular attention being paid to band shifts, differences in intensity, band appearance and disappearance.

RESULTS

Conformer Analysis by GC/FTIR

1. It has been clearly demonstrated that the GC/FTIR can be used to perform conformational analysis.

2. Flowrate variation substantially changes ãH° values.

Flowrate	ãH° (kJ/mol)
1 ml/min	5.3
2 ml/min	6.5
4 ml/min	7.8
Neat Vapor Phase Technique: 6.7 kJ/mol	
Theoretical: 7.5 kJ/mol	

Table 1. Flowrate data from tests using 1,2- diiodotetrafluoroethane.

3. Injection volume changes had no observable effect.Results from the initial qualification test using 1,2- diiodotetrafluoroethane were published in the February 94 issue of Journal of Applied Spectroscopy. Additional work involving flowrate effect, injection volume effect and determination of ãH° for the trans and gauche conformers of CF_2ClCF_2Cl and CF_2BrCF_2Br will be published as a master's thesis.

Surface Studies

At present, one study using alumina and a perfluoro acyl fluoride in the glass cell has established that the acyl fluoride hydrogen bonds to the surface hydroxyl group through the carbonyl oxygen. The results of this study have been published in the May 1994 issue of Journal of Fluorine Chemistry.

The two metal IR cells based on the Yate's design have been completed and are under evaluation at present.

In addition to the surface and conformer studies, a substantial amount of time has been used to develop temperature control methodology for all the IR cells in use or under development.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS

Task Order No. 93
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer Clager
University of Dayton

30 November 1994

Government Task Leader
Dr. Loon-Seng Tan
WL/MLBP

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At this time, I'd like to thank my Task Leader, Dr. Loon-Seng Tan, for giving me the responsibilities that he did. I'd also like to thank my co-worker, Mrs. Sharon Simko, for answering questions as they came up and for being a great conversationalist. She made work very enjoyable for me. Others who deserve thanks are Mrs. Marlene Houtz and Dr. K.R. Srinivasan. Mrs. Houtz helped me fix instrument failures. Without her help I would have become very frustrated. K.R. helped me analyze data and guided me through the process of making films. Moreover, he could always bring a smile to my face with one of his bad jokes. Finally, I'd like to thank all the Polymer Branch personnel for being so friendly. The people here made coming to work enjoyable, not a chore.

TASK ASSIGNMENT

The Task Assignment was to monitor organic synthesis experiments based on the established procedures for the preparations of monomers and polymers, to isolate monomers and polymers from the reaction media, to perform preliminary characterizations, using IR, NMR, UV/VIS, melting point, and viscosity determinations, to tabulate experimental data, and to use computer graphics to illustrate the synthetic schemes. All this is done for conductivity studies of the monomers and polymers.

For the most part, these tasks have been completed. The majority of the work, however, dealt with the preliminary characterizations of the products of the reactions run by the Task Leader and members of his group by performing IR, NMR, and UV/VIS analysis. The purpose of doing infared (IR) characterizations is to determine if the reaction has run to completion or to determine whether the product obtained matches the expected product. The purpose of Nuclear Magnetic Resonance (NMR) characterizations is to determine, by the placement of the proton, if the correct product was made. Ultraviolet/Visible (UV/VIS) is generally done to see how a certain product reacts in different solvents. For example, most products will turn a different color in each different solvent. Some solvents dissolve certain products better than others. It is also easy to compare the absorption of similar products run in the same solvents using UV/VIS.

Many melting points of products, both crude and pure, were taken. The melting point range indicates the purity of a product. If the melting point is within a few degrees, then it indicates that the product is pure. Larger ranges in melting point indicate that the product is not pure or that the product does not pack well in the capillary.

A couple of viscosities were done. This information had to be obtained because it is the goal of the branch to make viscous polymers, and anything over 1.0 is considered acceptable. This involves not only chemistry but mathematics as well. Calculations have to be done for intrinsic viscosity, inherent viscosity and the concentrations.

Another significant assignment was to run a column. The purpose of the column is to extract a product from the impurities that surround it. Once the column was run, then the solvent had to be removed from the product using a rotovap.

Lastly, polymeric films were made. This was the only new assignment given during this work period. Once a film was cast, it was sent to the physical chemistry section of the branch to test its conductivity characteristics.

DESCRIPTION OF RESEARCH

There were many jobs for which new procedures had to be learned. This involved a variety of equipment and methods of analysis. The first process learned was Fourier Transform Infrared (FTIR). The instrument used to do this is the BIORAD unix system. Most of the samples' run were in crystalline form, but some of them were liquids. To begin, 1 milligram of the sample is put into a small plastic vial with 15 milligrams or more of potassium bromide. Then a small ball is placed inside the vial with the chemicals, and with the cap on, the vial is put on a stirrer. When the product is thoroughly mixed with the potassium bromide, a few milligrams are sprinkled evenly around the potassium bromide die and placed in a press. Once the crystals form a nice film, it is put in an apparatus containing a laser beam. Meanwhile, a background scan is performed which is to be subtracted from the sample scan. This laser beam scans the sample and the absorption pattern is printed out graphically by following the commands given on the computer screen. A listing of the peaks is also printed out with the graph.

For UV/VIS, a dab of the product is dissolved in a solvent in a small vial. The parameters are then set on the Lambda 9, Perkin Elmer device. Next, two cuvettes (sample holders) are filled with the reference solvent and a background reading is taken so that it can be subtracted from the actual reading. Then, approximately four drops of the solution in the vial are placed in one of these cuvettes. This solution is scanned and a graph is printed out. If the graph does not fit on the page, a more dilute solution has to be created and the solution rerun. After an adequate graph is plotted, the peaks are found and labeled. This procedure is repeated for each product and each different solvent. When a new solvent is chosen another background scan must be run.

For NMR analysis, a solvent must be found in which the product dissolves. It is very important that the product dissolve completely or else the proton peak(s) is hard to find. In the UV/VIS it is not important that the product be completely dissolved because it takes such a small concentration of product to produce a plot. Nonetheless, once the solvent is found it is filtered into a capillary tube to ensure that the solution is clear. Adjustments are made on the Hitachi NMR machine and the reference solution is run and the background recorded. Then the desired solution is placed in the machine, the instructions on the computer screen are followed, and the results are printed. All three methods, NMR, UV/VIS, and IR, have spectrum characteristics listed in a book. These spectrum characteristics are compared with the ones generated by the computer and a product is inferred.

Melting point determinations consist of filling a capillary tube with a quarter inch of the product and placing it in the melting point apparatus, called Mel-Temp II. It records temperature with a K-type thermocouple. Viscosity determinations are a little more complicated. These involve making exact concentrations of solutions of the product and running them in the viscosmeter placed in a temperature bath of 30 degrees Celsius. The time it takes the solution to travel from the top etch mark to the bottom etch mark is recorded. However, before any of this can be done, the solvent must be run through the viscometer and its time recorded.

The procedure for running a column begins with making the column itself. First, silica gel for dry column chromatography is mixed with the solvent system of choice. (Solvent system means that a mixture of solvents can be used. A pure solvent need not be used. In fact, one common solvent system used is 2:1 methylene chloride and hexane.) Second, the silica that has become gel-like is poured into a glass column which looks much like a wide buret. Third, sand is placed on top of the silica gel solution. Fourth, the product that is desired to be cleaned is dissolved and placed dropwise on top of the sand. Fifth, the solvent system is poured into the column. This causes the product to separate from its impurities by polarity. A very weak solvent system should be used to begin, such as 2:1 hexane/methylene chloride to ensure separation. As the separation becomes more evident, increasing the more polar solvent, which in this case is methylene chloride, is acceptable. The separation of the product produces a variety of colors. Each color is to be collected in an erlenmeyer flask. After each color is collected, a thin layer chromatography is performed. This indicates in exactly which color or colors the product is present. Those solutions containing the product are then rotovapped. This draws the solvent system off and leaves only product. This procedure is done only when recrystallization is not possible, for it is very time consuming.

Making polymeric films involve calculating the proper amount of polymer needed to make the desired concentration, measuring it out, and then diluting it in 25 ml of solvent, which in this case happened to be methane sulfonic acid. Part of the solution is then poured into a petri dish, just enough to cover the bottom face. Next, it is put into a sublimator. The solution stays in the sublimator for a couple of days and is then washed and dried in a vacuum oven. The former solution is now a film.

CONCLUSIONS

A great deal has been learned in this job. It is now easier to guess which solvents will dissolve certain substances, and this knowledge can only come from experience. Also, three different computer systems have been learned, NMR, IR and UV/VIS. However, interpreting the FTIR, UV/VIS and NMR data is a complicated process and will take years of experience to become proficient at it. Thus, only simple analysis was done such as matching a FTIR spectrum with one given in literature and identifying hydroxide groups. Making polymeric films was a new Task which I thoroughly enjoyed. After making the film, I was then able to do the initial analysis on the IR before sending it to the physical chemistry department. This just proves that everything learned will be used again. Much of chemistry is inter-related. Furthermore, everything done in this job gave a greater understanding of the interactions of polymers and solvents. A lot of emphasis was placed on learning the safety factors involved in using each of the chemicals.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS

Task Order No. 93a
Student Support Program
Southwestern Ohio Council of Higher Education

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University of Dayton

30 November 1994

Government Task Leader
Dr. Loon-Seng Tan
WL/MLBP

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TASK ASSIGNMENT

The description of the given Task was to monitor organic synthesis experiments based on the established procedures for the preparations of monomers and polymers, to isolate monomers and polymers from the reaction media, to perform preliminary characterizations, to tabulate experimental data, and to use computer graphics to illustrate the synthetic scheme.

Due to my brief stay in the polymer branch, many of these objectives were not completed. The majority of the work was time spent performing preliminary characterizations using FTIR, NMR, UV/VIS, and melting point determinations of the productions of reactions completed by Dr. Tan and his group members. Different characterizations were performed to predict different things. The Fourier Transforms Inferred characterization (FTIR) was used to determine if a reaction was complete. By comparing an FTIR of the product with and FTIR of the material prior to the reaction, it is quite apparent whether or not the expected product has been obtained. Another characterization test frequently used was a test for melting point. This determined if a reaction product was actually a single product or if it was still an impure combination of several products. Other analysis used less frequently were the Nuclear Magnetic Resonance characterization (NMR) and the Ultraviolet/Visible (UV/VIS) characterization. The NMR tested if a product was the expected product, similar to the FTIR, but did so by the placement of additional protons to the sample. The UV/VIS tested a product's reaction in different solvents.

DESCRIPTION OF WORK

The FTIR was the one test that was used the most. Once a reaction was completed by a member of the group, and some product was obtained, tests were performed on it to determine it's characteristics. The first of these tests was usually the FTIR. A small amount, about 1 milligram, of the sample was placed in a small vial with about 15 milligrams of potassium bromide and then ground thoroughly to ensure even mixing. When the sample was completely mixed, a few milligrams were spread across one surface of a die and placed in a press. The sample was compressed under 12,000-15,000 psi until a transparent thin-film was produced (for about 10 seconds). The thin-film was then placed in the BIORAD (a device containing a laser beam). Beams of inferred light at different wavelengths were passed through the thin pellet and the transmittence was recorded in the form of a graph. The graph and a data table were then printed.

Each element absorbs a certain characteristic wavelength of light, for example, a peak appearing in the graph of a sample at around 2300 Hz indicates the presence of carbon dioxide. In this manner a sample tested before and after a reaction and the FTIR graph will show which elements have been added or removed from the sample.

The second test run frequently was the melting point test. This test was similar to what everyone does is General Chemistry Lab. A small amount of the sample was packed into a capillary tube, the tube was placed in a microscope like device that both gave a magnified view of the sample and heated it at the same time. The sample was heated quickly to determine approximately where the sample melted, then a second tube was run, heating it more slowly to determine to the nearest tenth of a degree where the sample started and stopped melting. If the sample became completely liquefied over a 2 degree interval or less, the sample was defined to be pure. More often the case was, however, that it began to melt, then remained partially solid, partially liquid for 20 or 30 degrees, then became completely liquefied. This indicated two separate melting points, therefore, two separate products and the sample was defined to be not pure. The device used to take a melting point was the Mel-Temp II which used a type K thermocouple to accurately record the temperature to within one tenth of a degree.

Again due to the brief stay at MLBP, many of the previously stated objectives were not completed. The NMR and UV/VIS characterizations tests were run only a few times each, so they were not the primary focus of the Task, and they will not receive any further attention here. The days were filled with the numerous other tasks involved in using and maintaining a synthesis laboratory. Everything, from the FTIR's potassium bromide die to the spatulas and glassware used had to be properly cleaned with soap and water, distilled water, and acetone, then dried and put away so it could be found again. Certain devices used in the laboratory acquired some nasty stains that had to be specially treated with chromic acid. Our laboratory alone housed over 800 bottle and jars of chemicals, all which had to be bar-coded, categorized and accounted for. When any characterization test was run, the results had to be recorded and kept on file for future reference, so an extensive system of filing was devised.

CONCLUSION

In conclusion, a great deal was learned from this Task. Several different computer systems were learned, careful chemical handling was learned, and an appreciation for the complexity of hazardous waste disposal was acquired. The need for careful record keeping was stressed in this job. Careful record keeping of procedures used to obtain a product also careful record keeping of orders, dates, materials, supplies, etc. Safety precautions were continually emphasized in this job. The handling, disposal, proper use and storage of all types of chemicals was a constant question. This type of knowledge can only come from direct hands on experience. As a result of this job, a better understanding of the interaction of chemicals and solvents and of the many uses they have in our society was learned.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS

Task Order No. 93b
Student Support Program
Southwestern Ohio Council For Higher Education

Bradley J. Keller
University of Dayton

30 November 1994

Government Task Leader
Dr. Loon-Seng Tan
WL/MLBP

ACKNOWLEDGMENTS

Special thanks are given to Dr. Loon-Seng Tan and Ms. Sharon Simko for their guidance and teaching throughout the course of this Task. They provided the knowledge and helpful hints to make this Task work on schedule.

TASK ASSIGNMENT

Task 93 involved many things. Analytical techniques were used to characterize organic compounds that were used in the synthesis of monomers and polymers. These techniques included Fourier Transform Infrared Spectroscopy (FTIR) and viscosities. Also, proper usage and storage of chemicals was practiced. A complete chemical inventory was processed as well as ordering of needed chemicals for the organic reactions.

One of the most useful techniques used was FTIR. It is used to give clues about the structure of the monomer or polymer being analyzed. In this procedure, a solid sample is pressed into a clear window with potassium bromide. This window is then scanned at varying wave numbers from 450 to 4000cm $^{-1}$. This produces a spectrum that has peaks at the wavelengths where certain functional groups absorb the light. By matching the peak wave numbers to the functional groups, one can get a good idea of the structure of the solid sample being tested.

This Task necessitated that a complete chemical inventory be made of chemicals in the lab. This was accomplished through the use of an old inventory and cross-referencing that with the HAZMAT computer inventory. This was needed for several reasons; (1) to be able to promptly locate a needed chemical in the lab, (2) to know what chemicals were diminished in supply and needed to be ordered. This new inventory includes the chemical names, their identification bar code number, their location in the lab, their quantity, and their manufacturer. The manufacturer name was completely new from the old inventory and greatly aids in identification of the needed chemical. It helps by letting one know what kind of label to look for and eliminates many other chemical bottles stored on the same shelf.

Another part of this Task included the ordering of chemicals and lab equipment to assist in the production of monomers and polymers. This was necessary whenever a chemical was out of stock or could not be borrowed from another person. Also, at the end of the year, money is allotted for government orders. This money is used primarily for the purchasing of new lab equipment such as beakers and reaction flasks.

Finally, the importance of proper handling and disposal of chemicals was learned. Care was taken when using all chemicals. Safety procedures were learned in case of an accidental spill. This is very important in preventing contaminants from entering the water supply and preventing injury to people working in the lab.

A great deal was learned while working on this Task. Most parts of the Task are ongoing processes which require constant attention and updating. The search of science into the synthesis of aromatic and aromatic heterocyclic polymers is one of great interest and has just begun.

ADVANCED COMPOSITES

Task Order No. 94a
Student Support Program
Southwestern Ohio Council for Higher Education

Jeremy D. Focht
University of Dayton

13 December 1994

Government Task Leader
Dr. Howard W. Brown, III
WL/MLBC

ACKNOWLEDGMENTS

I would like to thank everyone who has aided in making my stay at Wright Laboratory not only highly educational, but enjoyable as well. Specifically, I would like to thank Mr. Charles Hill and Dr. Howard Brown for their instruction, support and leadership. I also would like to thank the other members of the Carbon-Carbon Branch (MLBC) and the University of Dayton Research Institute (UDRI) team who have made this experience all the more worthwhile through the devotion of their time and knowledge.

TASK ASSIGNMENT

Carbon-carbon is one the most advanced materials around today. Possessing great strength, low density, resistance to extremely high temperatures, a high degree of stiffness, and a low coefficient of thermal expansion (CTE), carbon-carbon has become a vital part of the aerospace industry, making equipment stronger pound for pound than any metal can. Even with such excellent properties, this material is expensive due to its processing conditions. To create a strong carbon-carbon composite, a woven carbon fiber precursor must first be laid up into a panel, or similar shape. Using a phenolic resin (or other resin with a high char yield), the precursor is impregnated with resin. The composite is then heated to thermally crack the resin, depositing carbon on the fabric to bind the matrix together. The matrix is impregnated and heated again until the composite is fully densified (which can be a very lengthy process). Finally, the composite is heated to 2400° C to graphitize the carbon and give it its final strength. Much of the cost of the fabrication process occurs in the repeated densifications. Each impregnation and densification requires not only time, but a heating of an oven to ~800° C.

Low Cost Carbon-Carbon

The main objective of this project was to develop a technique of fabrication of carbon-carbon composites that would cut the lengthy and costly step of reimpregnation. This was hoped to be accomplished by using a mesophase pitch microbead powder to replace the phenolic resin as a binder. This powder gave an approximately 90% char yield upon first carbonization (a yield only obtained after many resin impregnations and heating cycles). While some actual carbon-carbon composites were synthesized, much of the project was spent characterizing the mesophase microbeads to see under what conditions they would fuse (or sinter) that, upon the addition of carbon fiber, the beads would form a strong composite.

Graphitic Foams

The aim of this project is to create an extremely lightweight and very strong material for use in a variety of aerospace applications. Foams are already used in many places in the aerospace field. However, graphitic foams show superior strength and better material properties than any existing today and seem to promise low processing costs also.

It has been shown that carbon fibers are extremely strong in the axial direction. Graphitic foams rely on the theory that the ligament structure in an open-cell foam will act as a three dimensional system of carbon fibers, each strong in their axial direction, thereby creating a network strong in any direction. Open-cell foams are at least 80% porous, making these materials extremely light weight.

The foams are synthesized by crushing a mesophase pitch into a fine powder. This powder is then heated to just above its softening point and pressurized to ~700 psi or more with a gas such as nitrogen. The nitrogen is slightly soluble in the mesophase pitch and dissolves there. As the pressure is released the gas in the pitch expands, creating the open cell foam structure. The pitch then cools slowly and hardens into the foam. The foam then needs to be heated to ~250° C in the presence of oxygen to insure oxidation. The foam then is carbonized to 700-900° C, and graphitized to 2400° C to give its final strength.

In this paper, only the processing conditions of the foams oxygen stabilization, carbonization and graphitizations are discussed. The synthesis of the foams remained a constant throughout the experimentation.

Computer-simulated Carbon-Carbon Composites

Part of the study of carbon-carbon composites is to create a mathematical model of the material so that it can be understood better. Development of better materials would become easier because different variables could be changed using the model and no actual material (expensive material) would have to be wasted. However, these mathematical models are so complex that they have no real hope of being solved by hand.

This project uses the model set down by Dr. N. J. Pagano in his article "Axisymmetric Stress Fields in Involute Bodies of Revolution" in Journal of Spacecraft and Rockets. A program written in FORTRAN exists for a limited set of conditions to predict the behavior of a composite material. The aim of this Task was to reprogram it more generally to make it useful by letting it apply to a larger set of conditions.

DESCRIPTION OF RESEARCH

Low Cost Carbon-Carbon

Two D2 hardened steel molds were obtained for testing purposes. Two pitch powders were available for use, one with an average particle size of 6 microns and the other with an average size of 20 microns. The mold was filled with powder and placed in an oven press for anywhere from 40 minutes to 4 hours. The press was set to temperatures anywhere from room (72° F) to 370° C (700° F) during the runs. Six runs were done with just microbead powder to determine the best conditions for sintering. Carbon fiber and microbead powder layers were alternated in the mold to create a carbon-carbon composite. Four runs were made using this method. Vapor-grown carbon fibers were mixed with the microbeads for two runs in attempt to see what interface between the two species would develop. Finally, layers of green mesophase fibers and microbeads were alternated in the mold to try a different approach to composite synthesis. Pieces of each sample were taken for analysis immediately after pressing.

After pressing, each sample was then carbonized for up to 2 hours at 700 to 900°C. Pieces were cut from each sample for analysis. Each sample was then graphitized to 2400°C in an induction furnace. Pieces were cut for analysis and tested for strength using a four-point bend test.

Analysis of samples was achieved using visible and polarized light microscopy. Samples were prepared by vacuum resin impregnation with a mixture of resin, hardener, and Epodye 828. A cross section of each sample was taken using the polishing wheels, sandpaper, and the Vibromet automatic polisher. These plugs were then mounted into the microscope and pictures were taken to characterize the microstructure. The percent porosity was also examined using image analysis software hooked up to the microscope using an IBM machine. Polarized light was used to characterize further the microstructure by showing the alignment of the molecules in the material.

Scanning electron microscope imaging was also used. Samples were mounted from each one and representative picture to show the degree of sintering of the beads and the interfaces (or lack thereof) between the two different material components of the composite.

Graphitic Foams

Foams were made under the relatively same conditions. The processing changes were all made in the degree of oxygen stabilization and carbonization. Graphitization could not be controlled well enough using the induction furnace to permit experiments in that arena. Oxygen stabilization was done in a tube furnace at 200-280°C for 6-48 hours. Carbonization was done in a tube furnace in a completely nitrogen atmosphere for 50 minutes to 6 hours at 700-900°C.

The foams were prepared for optical and scanning electron microscopy before stabilization, after stabilization, after carbonization, and after graphitization. This was done using the same methods as above for the carbon-carbon processing.

Computer Simulated Carbon-Carbon Composites

Experimentation consists of seeing if certain programming changes accomplish what needs to be done.

RESULTS

Low Cost Carbon-Carbon Processing

It was found that a pressure upwards of 8000 psi was required (through the examination of microscopy pictures) before any serious sintering (bonding between particles of mesophase powder) began. It was also found that increasing the temperature to 200°C and above increased the amount of sintering taking place.

In the two component samples, little interface between the components was detected. In the vapor grown carbon fiber mix, no gain in strength was detected, and the interfaces between the fibers and beads were poor at best. In the carbon fiber mix, there was almost no interface between the layers. Upon carbonization, delamination occurred in the carbon fiber runs. However, it was observed that a small amount of interfacing occurred upon elevation of temperatures to above 200°C and pressures above 8000 psi (however, not enough to make the composite cohere). The green carbon fibers worked better. There was much more bonding between the beads and the fibers. The problem here was that the fibers would not lay flat enough in the mold, so uneven pressing would result.

At this point, an experimental matrix is being set up based on the data gathered from these tests to find under what conditions low cost processing will work.

Graphitic Foams

Problems occurred with cracking and bloating of the foams upon carbonization. This was found to be due to incomplete oxygen stabilization. A method has still not been found to effectively stabilize the foam to prevent cracking and bloating consistently. Efforts are still being made in this area.

Computer Simulated Carbon-Carbon Composites

The adapted program is ready to run. No debugging has taken place. This process will occur next work term.

NONDESTRUCTIVE EVALUATION

Task Order No. 95
Student Support Program
Southwestern Ohio Council For Higher Education

Edward D. Fisher, II
Wright State University

31 December 1994

Government Task Leader
Mr. Curtis Fiedler
WL/MLLP

ACKNOWLEDGMENTS

I would like to thank Curt Fiedler for his unwavering support and confidence. I feel that I have gained valuable experience and skills under his leadership.

TASK ASSIGNMENT

Although conventional ultrasonic inspection methods have proven useful for characterizing and evaluating the integrity of structures, these methods are limited by the frequency and bandwidth of the piezoelectric transducer used. Therefore, the use of ultrafast laser generated ultrasound (UFLGU), which incorporates an extremely short pulse of laser light (0.1-5 ps) thereby generating short pulses of high frequency ultrasound, is necessary to inspect extremely thin layers in the nanometer range.

To test UFLGU, an experiment was constructed which would scan a small area of a metallic sample (Titanium). The thickness of this sample, at various points of its area, could then be measured by interpreting the ultrasonic echoes that would originate from the specimen. Therefore, a means for gathering and processing this data was needed.

DESCRIPTION OF RESEARCH

A Ti:sapphire laser was used to generate the extremely short pulse of laser light. This light was then directed via mirrors to the specimen which was to be analyzed. The ultrasonic pulses which resulted from the collision between the specimen and the light were then converted to electric signals via a photodetector. These signals were then amplified and filtered using a lock-in amplifier. The lock-in amplifier provided the connection between experiment and data acquisition.

Voltage magnitudes produced by the lock-in were collected via an IEEE interface between the computer and the lock-in. Labview, a software program which allows the implementation of virtual instruments, was used to gather and store the data collected from the experiment. The data could then be represented by a graph of voltage vs. time. This graphing process was implemented by Labview as well.

The specimen was moved in small increments via a translation stage which was controlled using Labview.

RESULTS

The final goal of this research project was not yet complete at the time of the completion of this Task. Promising data had been realized via the data acquisition program, which was the main component of the Task. The project is still in its infancy.

NONDESTRUCTIVE EVALUATION

Task Order No. 95a
Student Support Program
Southwestern Ohio Council for Higher Education

Michael D. Nelson
University of Dayton

31 December 1994

Government Task Leader
Dr. Curtis Fiedler
WL/MLLP

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I would personally like to thank Dr. Curtis Fiedler for allowing me to work with him on this Task. I also would like to thank all the other staff in the Materials Directorate department for their help on various computer tasks. Finally, I would like to thank Dr. Karim for his help during this Task and the staff at SOCHE Student Support Program for all the various help they have given me.

TASK ASSIGNMENT

Experimental Summary

The first phase of this experiment was to set up to duplicate the work done by Maris and was satisfactorily completed. The Fourier spectroscopy analysis of the various peaks of the spectra obtained using this method was only started and will hopefully yield more information later. The second phase was to produce results using the interferometric methods. Although this method has not yet been completed, the progress we have made in the past few months is encouraging. The initial peak seen in the piezoreflective method was detected, but further refinement and noise reduction was needed to allow for echo detection.

The aforementioned experiments were all set up and run within the 10 week duration of the Task. Assignments included experimental setups, which included securing and aligning lasers, optics, detectors and so forth as well as running the experiments and various amplifiers, extenders, oscilloscopes, function generators etc., that were necessary for successful experimental procedures. Also, computer programming in "C" and LabView to do various tasks and data analysis was required.

Ultra fast Laser Generated Ultrasound is a non-destructive testing technique that utilizes femtosecond pulsed lasers and ultrasonic stress waves to non-destructively measure the characteristics of thin films. Coatings as thin as 120 nm. are examined using UFLGU and characteristics such as thickness and weld integrity can be tested using this technique. This technique may have applications in MBE, optics, electronics and other areas where thin films are used. The research described below was completed using two different methods, the first being piezoreflective UFLGU and the second was interferometric UFLGU. The first method was used in an attempt to replicate previous work in the field and to gather data to be compared against the newer interferometric procedures. Both the methods and various tasks of each method will be described.

The general layout for UFLGU is shown below in Figure 1.

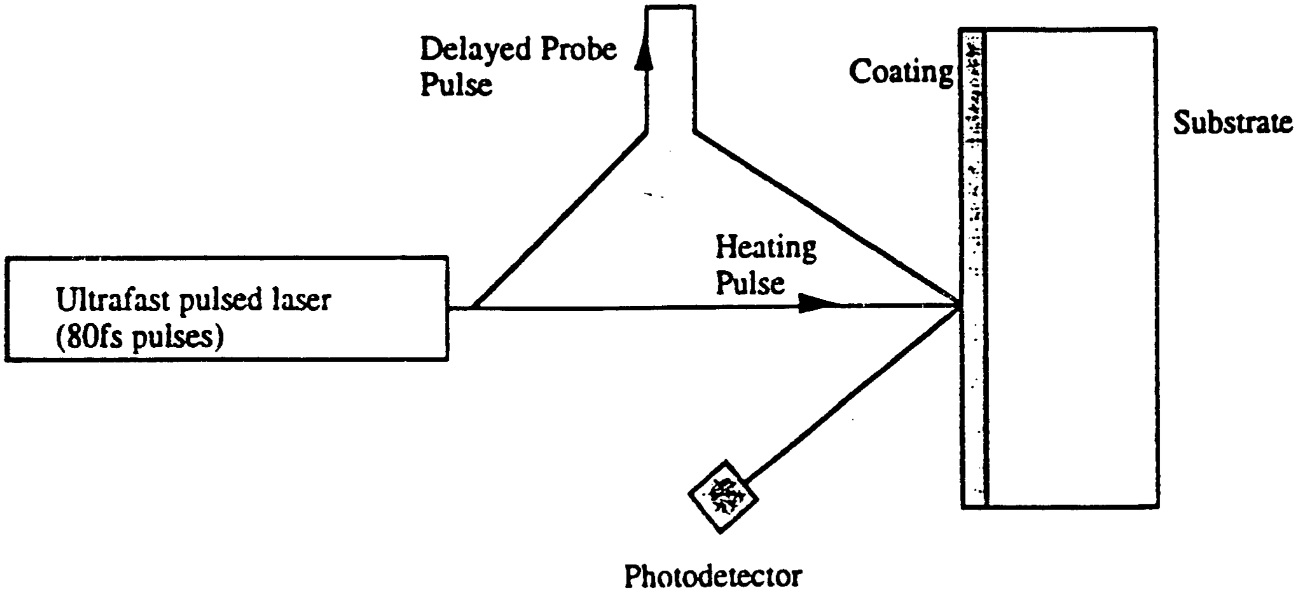

Figure 1

Experimental Set-up

To do UFLGU a Spectra-Physics Ti:SAP pulsed laser pumped by a cw Argon Ion laser was used. The Ti:SAP laser has a repetition rate of 82 MHz and is operated in the femtosecond pulse range. The Ti:SAP laser emits radiation between 720 nm. and 1080 nm., but the experiment is done at 720 nm., near the infrared region. The general setup consists of two beams, a heating beam and a probe beam, reflecting off a sample and into a detector. The heating beam is sent through a variable path length, then runs parallel to the probe beam and finally is focused onto the sample. When the heating beam strikes the sample, the rapid increase in heat causes an ultrasonic wave to be produced. This ultrasonic wave will propagate through the medium and reflect off the substrate. The probe beam is also focused onto the sample and it's subsequent reflection is captured by a detector. As the heating beam's path is varied, the phase difference between the two beams will be reduced. When the probe beam and the heating beam are coincident, the change in the reflectivity (or the displacement) of the surface of the sample will correspond to a peak in the reflected probe beam signal. As the ultrasonic wave travels through the sample and back toward the surface, the reflectivity of the sample will again be changed and a smaller secondary peak will appear and so on. If one knows the velocity of sound in the particular sample, then measuring the time it takes for the probe beam to reach a secondary point will allow one to measure the thickness of the particular sample being studied. Also, by looking at the amplitude of the reflected signal, information can be obtained on the integrity of the interface between the sample and the substrate.

To increase the signal to noise ratio, the polarized nature of the light emitted from the laser is utilized. Upon detection of the probe beam after it strikes the sample, we want as little of the heating beam to enter the detector as possible. To do this, the polarization of the probe beam is changed so that it is perpendicular to that of the heating beam. The light is originally S polarized and after the beam is split, a half wave plate or a set of orthogonal mirrors can be used to change the polarization of the probe beam to P polarized light. Once this is done, any diffusely reflected light from the heating beam can be eliminated by the use of a good polarizer. In the piezoreflective case, a polarizing cube is used to eliminate diffusely reflected light and an iris to eliminate the majority of the spectrally reflected heating beam.

Since the Ti:SAP laser is a tunable one, a make shift spectrometer had to be assembled. To do this, part of the beam was split and sent down the optics' bench. There it was split again, sent through an iris and onto a blaze grating. The first order diffraction was then sent into a video camera and displayed on the screen. The setup was then calibrated using an actual spectrometer on loan for this purpose. The beam placement on the video screen was then recorded for various wavelengths. With this setup, it is possible to dial the laser from 720 nm. to 790 nm. and still have a rough idea of the actual wavelength of the laser line being used. This was necessary because the UFLGU was shown to be most fruitful at 720 nm. even though the optimum laser power was delivered at 790 nm. Another feature of the makeshift spectrometer was that it allowed the user a quick look at the laser spot configuration. Do to the large bandwidth caused by the high pulse repetition rate, when the laser was mode locked (pulsing), the spot would be elongated in the various orders after diffraction. However, if the laser was not mode locked, this would correspond to a single frequency output and, therefore, the spot would be a tight circular round beam. This could be easily seen on the video screen. It also should be noted that it is essential to have a mode locked laser when running the actual experiment.

Finally, the beam that was split and run into the make shift spectrometer was also split and run into an autocorrelator. When properly aligned, this would show an autocorrelation signal which is used to measure pulse width. This setup was utilized for tuning purposes. The remainder of the beam was sent back along the table and onto a screen, where the proper alignment was marked for future reference. The entire setup (piezoreflective UFLGU) is shown below in Figure 2.

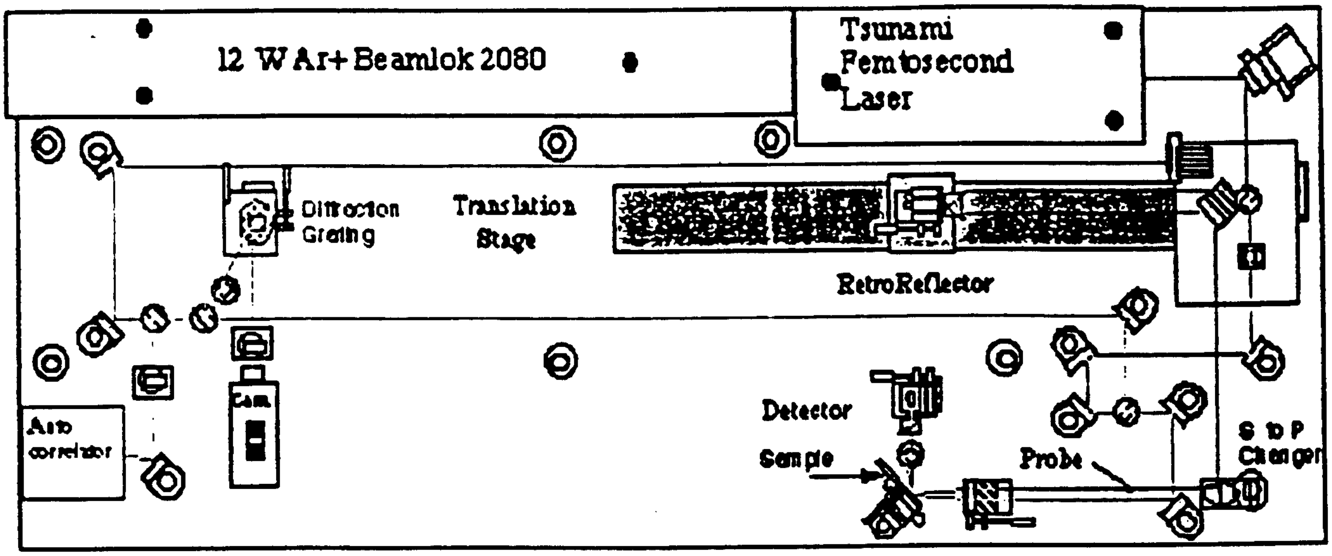

Figure 2

Piezoreflective UFLGU

Maris et al.[1] have shown in previous work that Ultra Fast Laser Generated Ultrasound can be a useful tool in measuring the thickness of samples for piezoreflective materials. Piezoreflective materials are those materials that show a change in reflectivity due to mechanical strain[2]. The initial work that was done was an attempt to reproduce the results obtained by Maris and his colleges. The experimental setup for the Piezoreflective UFLGU is shown in Figure 2.

As seen in Figure 2, when the retroreflector is moved along the translation stage, the path length of both the heating beam and the probe beam become coincident. When this occurs, the change in reflectivity due to the ultrasonic pulse created by the heating beam is detected by the probe beam which is directed into the detector. As the probe beam continues to move, the path length continues to change, which has the effect of delaying one beam relative to the other. This delay allows for the detection of subsequent echoes that occur as the ultrasonic pulse reflects off the substrate and back to the surface of the film. The plot of the average of several runs using a 120 nm. thick As_3Te_2 is shown below in Figure 3. As seen, the first peak occurs around 86 mm. (this being the relative position of the translation stage) and subsequent echos follow. Using the speed of sound in the particular medium, the thickness of the film as well as the integrity of the weld can be determined by looking at the positions and amplitudes of the echos. Other data analysis techniques such as Fourier Spectroscopy have also been applied when analyzing the various echoes.

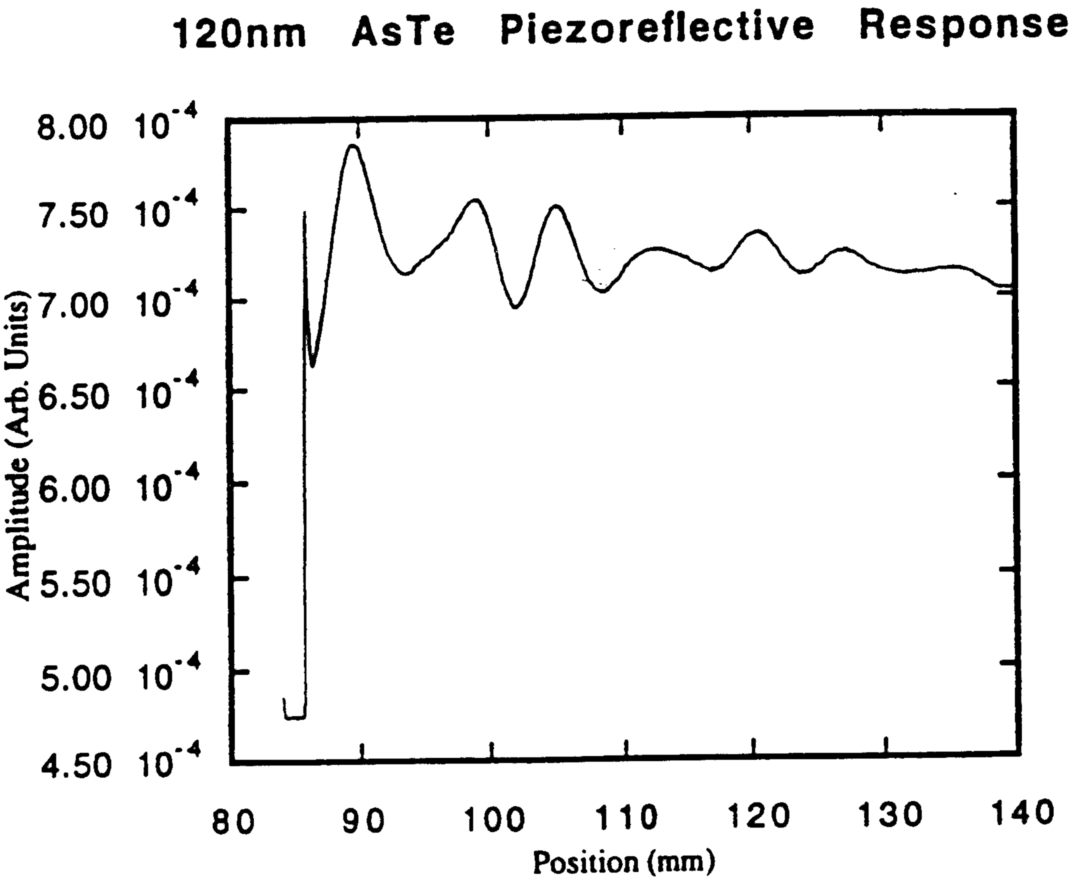

Figure 3

Interferometric UFLGU

Interferometric UFLGU takes advantage of the phenomena known as interference to obtain information about thin films. The main difference between interferometric and piezoreflective UFLGU is that interferometric methods measure displacements caused in the thin films due to the ultrasonic pulse whereas piezoreflective methods measure a change in reflectivity. Interferometric UFLGU then has the advantage that the material need not be piezoreflective in order for it to work.

To do interferometric UFLGU, we constructed an interferometer that splits the probe beam then recombines it to form an interference pattern. Then, when there is a change in the path length of one of the two beams due to the displacement caused by the ultrasonic pulse, the change in the interference pattern will be detected and the data can be obtained. The interferometer used consisted of a beam splitter cube aligned so that the two beams are reflected off the sample and then recombined. The configuration is shown in Figure 4.

The interferometric UFLGU method is currently being tried and will hopefully prove to have applications in nondestructive testing of thin films. As of the time of this report, the experimental setup was being perfected and preliminary experiments showed promising results.

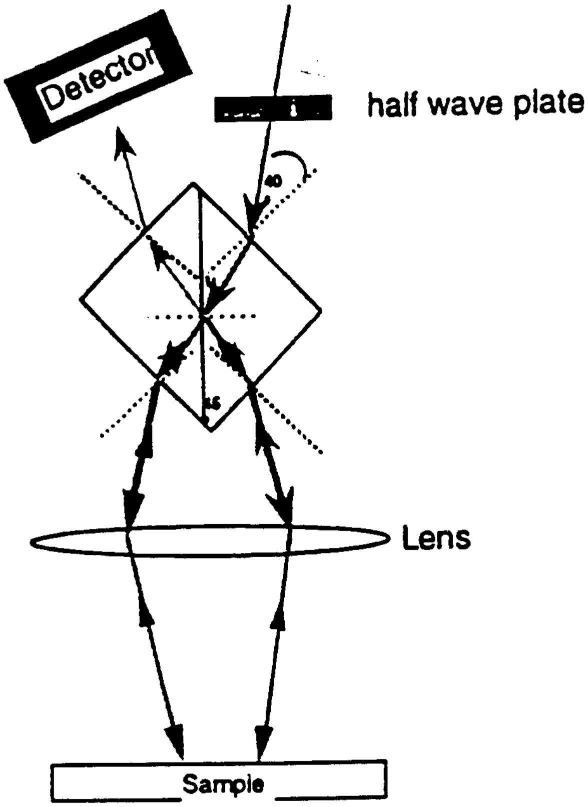

Figure 4

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[1] H.T. Grahn, H. J. Maris and J. Tauc, Picosecond Ultrasonics. *IEEE Journal of Quantum Electronics*, Vol. 24, NO. 12, December 1989.

[2] Frank L. Pedrotti, S. J. and Leno S. Pedrotti, *Introduction to Optics*, 2nd Ed. Prentice Hall, Englewood Cliffs, NJ.

NONDESTRUCTIVE EVALUATION

Task Order No. 95b
Student Support Program
Southwestern Ohio Council for Higher Education

David Lomely
University of Dayton

31 December 1994

Government Task Leader
Dr. Curtis Fiedler
WL\MLLP

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TASK ASSIGNMENT

Ultrafast Laser Generated Ultrasound

Introduction

Ultrafast laser generated ultrasound, UFLGU, is a method by which one may potentially measure and evaluate the properties of applied thin coatings. It is an attractive measurement technique because of its nondestructive nature. UFLGU relies heavily upon femtosecond pulsed lasers to induce an ultrasonic shock wave in the material being studied. By knowing certain facts about the material in question, it is possible to obtain information about the quality of the coating. For example, if one knows the speed at which sound propagates through the material, then by measuring the time it takes for the ultrasonic wave to travel from the surface to the back of the coating one may determine the thickness of the coating. In any case, there are two general types of UFLGU concerned, piezoreflective UFLGU and interferometric UFLGU. The actual details of these two methods of UFLGU are beyond the scope of this Task, so far. Thus, they are beyond the scope of this paper. A brief description of the techniques is given below to clarify the distinction between the two.

Piezoreflective UFLGU

For the purposes of this experiment, use was made of a Ti:Sapphire laser that was capable of producing femtosecond pulses. This laser was pumped by an Argon Ion laser. The beam from the Ti:Sap was split into a heating beam and a probe beam. The heating beam was sent to the target by following a variable path. The effect of this beam was to heat the surface of the sample rapidly enough to produce an ultrasonic shock wave in the material. This ultrasonic wave has the effect of producing a mechanical strain in the sample. In a piezoreflective material, this can easily be detected as a change in the reflectivity of the surface of the sample. Thus, the probe beam is focussed onto the sample. By analyzing the reflected light, one is able to determine the reflectivity. From this it is possible to obtain the required information about the coating. Unfortunately, to use this method the coating must be piezoreflective. There are a number of cases in which this criteria is not met. It would be desirable to have another method that does not depend upon the piezoreflectivity of the sample.

Interferometric UFLGU

Interferometric UFLGU has the advantage that the material in question need not be piezoreflective. Interferometric UFLGU utilizes a phenomena known as interference. The basic principles that underlie piezoreflective and interferometric UFLGU are the same. The main distinction relies upon how the information regarding the sample is obtained. Interference occurs as a result in the discrepancy between the phase of two coherent wavefronts. Since the wavelength of light is small, in this case, about 790nm, it is possible to measure small variations in the surface of the sample. Such a minute displacement will create an interference pattern. By analyzing this pattern, it is possible to determine how much the surface was displaced and thus, determine the properties of the coating. Where piezoreflective UFLGU measures the difference in reflectivity induced by the ultrasonic shock wave, interferometric UFLGU measures the actual displacement the ultrasonic wave causes in the material.

To accomplish this, a beam splitter cube was used to split the probe beam and then recombine it upon reflection from the sample to produce an interference pattern. (See Figure 1) When the ultrasonic wave creates a displacement in the material, then a corresponding change in the interference pattern occurs. This change in the interference pattern is used to obtain the data. A diagram of the beam splitter cube and its incoming and outgoing rays are included.

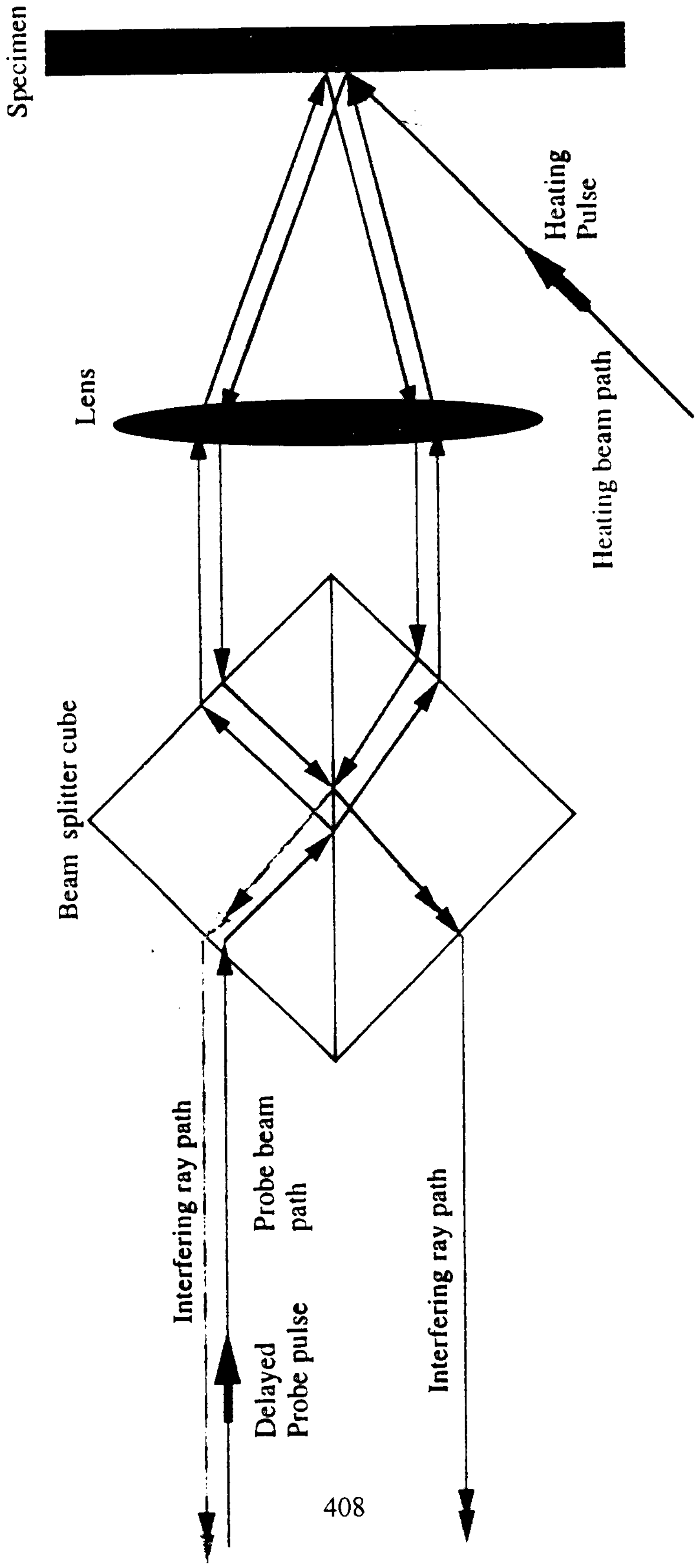
In preparation for future work, it was found necessary to create a C program that duplicated the effects of the beam splitter cube to a high degree of accuracy. From the data obtained from the program and the diagrams that it generated, it was possible to determine orientations for the cube and beam that resulted in interference. A sample of the program output is included in the last page of this report. (See Figure 2) Having no previous experience with programming, this was quite an assignment. This garnered a familiarity with the C language itself, which will be particularly useful as the Task is extended into the next year. It, also, fostered an understanding of the physical phenomena involved.

In addition with programming in C, a familiarity was gained with DEC vuit, LabView, Fortran, and the vax computing system.

The majority of this Task was spent learning enough of the basics so that it will be possible to play a more integral part in the future of this experiment.

In conclusion, while more research needs to be done concerning interferometric UFLGU, the results, thus far, tend to show promise. As the Task ends, a C program is currently under development that would allow serial communication between the Vax and the Macintosh computers. This will facilitate information gathering, processing and storage greatly.

Figure 1


Specimen
Heating
Pulse
Lens
Heating beam path
Beam splitter cube
Interfering ray path
Probe beam
path
Delayed
Probe pulse
Interfering ray path

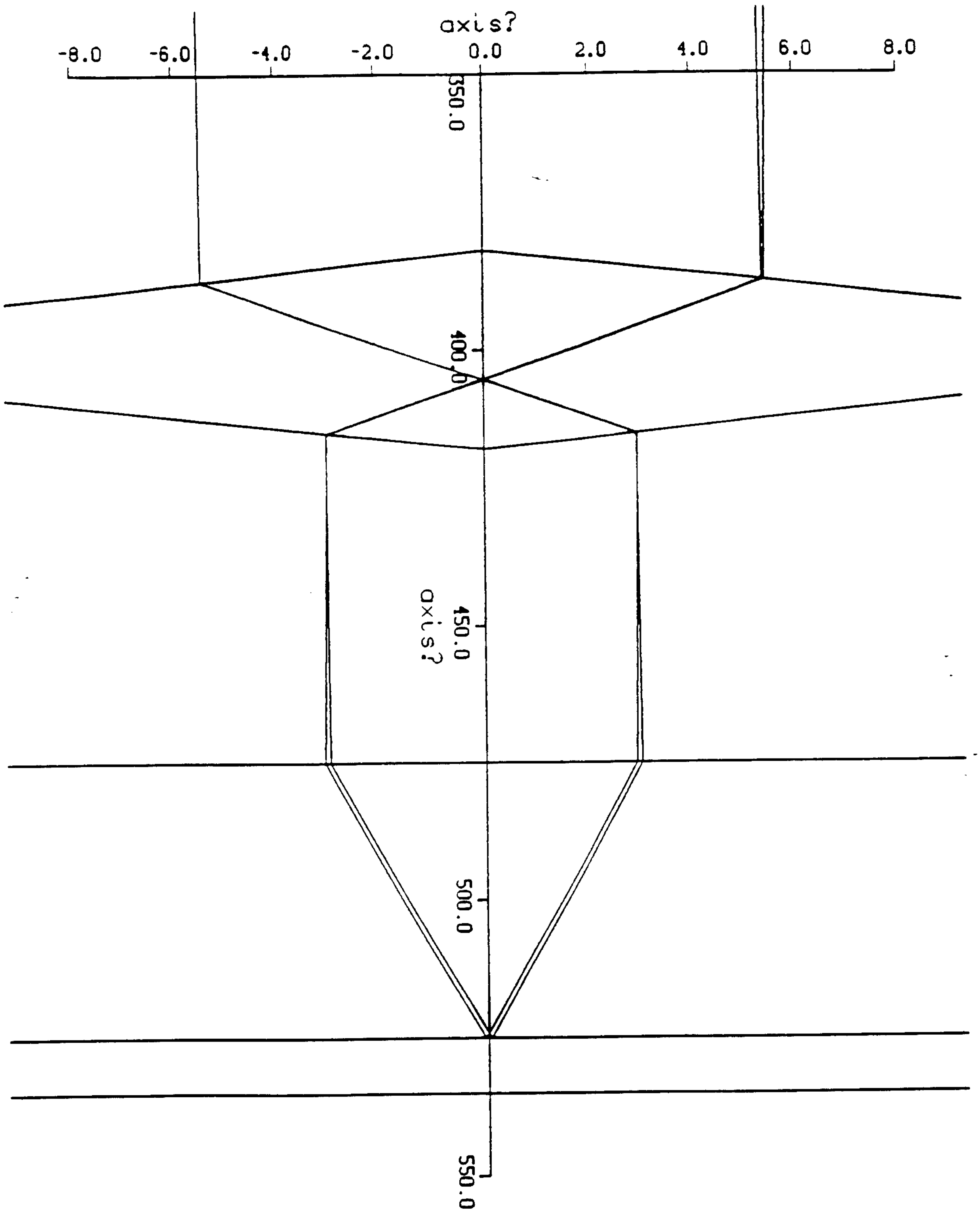


Figure 2

STRUCTURAL MATERIALS TESTING

Task Order No. 96
Student Support Program
Southwestern Ohio Council for Higher Education

Rodney B. McLaughlin
Wright State University

31 December 1994

Government Task Leader
Mr. Neal Ontko
WL/MLSE

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TASK ASSIGNMENT

Due to lack of specimens available, there were very few chances to perform the mechanical testing described in the Task title. Although more testing was anticipated later in the spring, the work never materialized. This was an extreme disappointment.

The first testing performed involved determining the ultimate load to failure of the weld attachment of an aircraft missile. This involved performing the test set-up for the test and recording the load at failure. The testing was needed because these missiles were literally falling of the aircraft while they were sitting on the runway. The results were presumably used to determine if the weld attachment was the reason for the failure.

My role in the next test was more involved. The dimensions of graphite/PEEK composite lap joint specimens were measured for shear testing. The joints were loaded to failure. PEEK (polyetheretherketone) is a relatively high temperature thermoplastic which provides good resistance to many common solvents. The joints consisted of various bonded and bolted fastening geometries. The testing was performed to help determine the optimum joining technique. The data was then transferred to spreadsheets. The results were summarized and submitted to the Task Leader.

The final testing concerned high temperature lap shear tests of F-111 aircraft repair adhesive. The objective of the testing was to determine the strength of the adhesive. The principal task included loading specimens into the machine grips and recording the load at failure. The conditions of the test were that the oven was preheated to 350°F. Two different soak techniques were used:

1) Measured the time for the air to reach 350°F after loading

2) Measured the time for the specimen to reach 350°F after loading

Two soak times were also used, 3 minutes and 10 minutes at 350°F. The data was then transferred to spreadsheets.

Most of the remaining time was spent at the computer either editing part drawings or transferring data to spreadsheets. At times, this became very monotonous.

There were, however, some tasks not associated with testing that stimulated my interest. Statistical analysis of T-62 and T-42 aluminum data was performed on the computer. This involved executing f-tests and t-tests for statistical variance of two populations. Another challenging job involved the design of a specimen grip. My job was to provide the specific dimensions of the specimen grip given the basic design from the engineer. This proved much more difficult and time consuming than was first anticipated. With help from the engineer, the grip was drawn on the computer. The drawing was then sent to the machine shop for fabrication.

DESCRIPTION OF RESEARCH

The testing was done using either Instron testing machines, Tinius-Olsen machines or MTS machines. Depending on how the part is mounted in the grips, the machines basically apply an axial load to the part or specimen. The data reduction was done using ASCII. The data was transferred to spreadsheets using EXCEL. All part drawings were done on AutoCad-Release 12.

Specimen dimensions were measured using calipers or micrometers. For extremely small distances a Nikon microscope and a digital measuring device were used. All the data was analyzed by the supervising engineers.

RESULTS

Through the jobs described previously, I became familiar with Excel and AutoCad. In attempting to design the specimen grip, it became apparent that the mechanical design process is extremely difficult without job experience.

Overall, this was not a great learning experience. There was just not enough testing done to become familiar with the machines.

SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE POLYMERS

Task Order No. 97
Student Support Program
Southwestern Ohio Council for Higher Education

Colin M. McHugh
University of Dayton

6 May 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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Financially, there are a number of people and organizations that made this research possible. I would like to thank the Student Support Program (SOCHE) and Wright Laboratory/Laser Hardened Materials Branch for allowing me to perform the research at WPAFB.

TASK ASSIGNMENT

Task 97 involved the synthesis and characterization of liquid crystalline (LC) polymers for use in optical defense applications, such as optical notch filters. This Task was subdivided into two main projects: 1) synthesis of mesogens leading to LC cyclic siloxane polymers, and 2) X-ray analysis of cyclic and dimeric LC siloxanes to investigate how the compounds pack on the molecular scale.

Experimental General Procedures

A Nikon Optiphot-Pol microscope, Mettler FP90 Central Processor, and a Mettler FP82HT hot-stage were used to perform polarized optical light microscopy. Thermal analyses were performed on a Perkin-Elmer DSC-2C and a Thermal Analyst DSC at 10°C/ min and only second heating and cooling curves were used to report data. FTIR spectra were recorded on a Perkin-Elmer 1725X, spectrometer. H^1 nuclear magnetic resonance spectra were determined at 360 MHz on a Bruker AM- 360 spectrometer using deuterochloroform as the solvent. Elemental analysis was performed by WL/MLSA, WPAFB. All compounds and reagents not referenced were obtained from the Aldrich Chemical Co. and were used as received unless otherwise stated.

Synthesis of Liquid Crystalline Alkene Mesogens

The attachment of steroid molecules, shown in Figure 1, to varying length benzoate units was performed using a mild peptide bond esterification reaction. The reaction allows for the conversion of one equivalent of carboxylic acid to ester by using both a carbodiimide and an aminopyridine catalyst. A general reaction diagram is shown in Figure 2. Thermal properties of the LC mesogens synthesized are shown in Table 1.

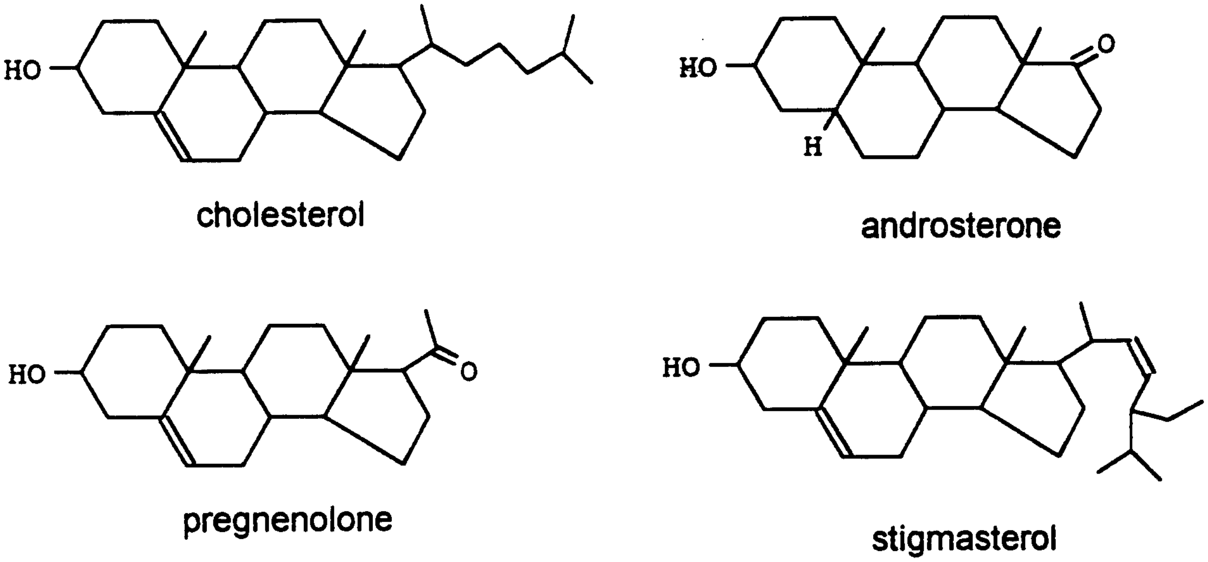

Figure 1: Steroid structures with various length and functional tail units

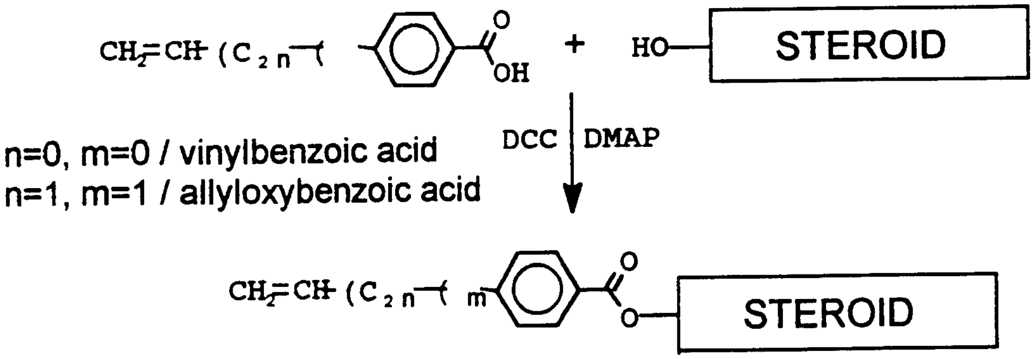

Figure 2: General reaction scheme for the synthesis of the mesogens

Table 1: Thermal transitions for the vinyl-terminated steroids. M and n refer to Figure 2

Cmpd #	m	n	Mesogen	Thermal Transition (°C)
1	0	0	stigmasterol	k 152 n* pol
2	0	0	cholesterol	k 168 n* pol
3	0	0	pregnenolone	k 170 ? pol
4	0	0	androsterone	k 141 n* pol
5	1	1	stigmasterol	k 150 n* 165 I
6	1	1	cholesterol	k 124 n* 234 I
7	1	1	pregnenolone	k 103 n* 157 I
8	1	1	androsterone	TBD

k-crystalline; n*-cholesteric; i-isotropic; pol-polymerized; TBD-to be determined; ?-undetermined due to the rapid loss of birefringence

Synthesis of Liquid Crystalline Cyclic Siloxanes

Cyclic tetramethylhydrosiloxane (Figure 3) was purchased from Huls America and purified by vacuum distillation before use. The liquid crystalline alkene mesogens, Table 1, were attached using standard hydrosilation chemistry with dicyclopentadienylplatinum (II) chloride as the catalyst. Stigmasterol was chosen as the first steroid after cholesterol because of its highly branched tail unit. The vinyl-terminated steroids were attached to the hydrogen atom on each silicon atom as shown in Figure 3. The hydrosilation reactions were performed in toluene at 80-100°C under a positive argon pressure. Reactions were run at a 10% molar excess of LC mesogen with enough catalyst to obtain a $1{:}10^3$ to $1{:}10^6$ mole ratio of catalyst mesogen. Reaction progress, using FT-IR, was followed by monitoring the disappearance of the Si-H stretch, at 2155-2170 cm-1. Addition of methanol after complete disappearance of the Si-H peak caused the LC siloxane polymer to precipitate. Further precipitation's were performed until thin layer chromatography showed only product remained. H^1 NMR confirmed no Si-H remained and the structure of the final product. Thermal transitions of the LC cyclic siloxanes are listed in Table 2 and are discussed in the next section.

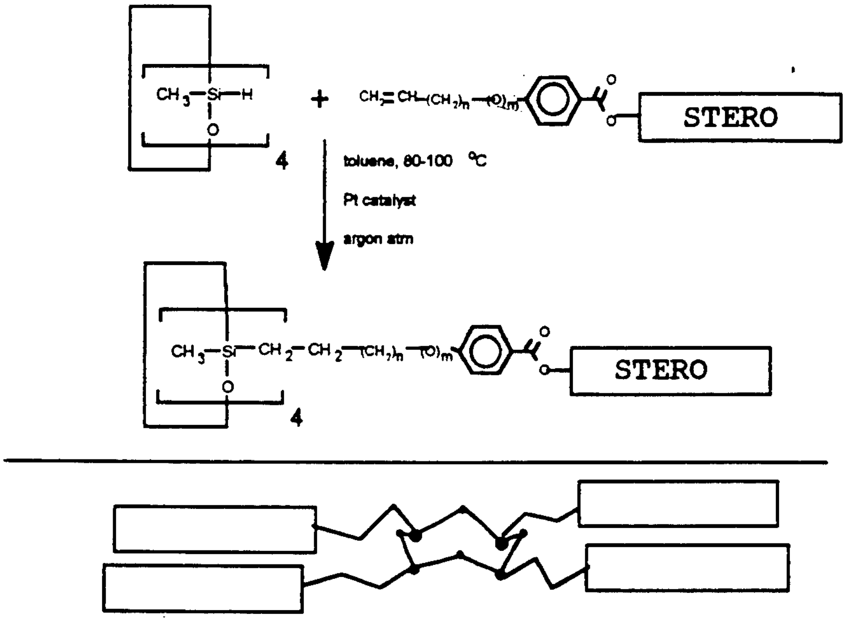

Figure 3: Hydrosilation reaction scheme for vinyl terminated steroid mesogens

Table 2: Liquid crystalline behavior of steroidal-based siloxane compounds

Compound	Thermal transition (°C)
D4-1	g 106 S_A 210 i
D4-2	g 100 S_A 232 I
D4-3	NLC
D4-4	NLC
D4-5	g 70 S_B 240 I
D4-6	g 76 S_A 270 n^* 277 i

g-glassy; n^*-cholesteric; S_A-smectic-A;S_B-smectic-B;
I-isotropic; NLC-not a liquid crystal

Project 1:

RESULTS

Steroids with varying length tail units, as well as different functionality's, were chosen to elucidate the effects of increased branching and polar substituents on the LC packing phase. The three steroid molecules, shown in Figure 1, possessing functional tail groups different than the eight carbon aliphatic unit in cholesterol were chosen for modification. All of these steroids possess the cyclopentanophenanthrene ring system with a hydroxy reactive site. In addition, androsterone, is completely saturated in the beta ring.

The steroids in Figure 1 were attached to a vinylbenzoate spacer group because higher glass transition temperatures are expected with shorter length leader groups. Stigmasterol and androsterone were also attached to an allyloxybenzoate leader group for comparison purposes to C4AB. Thermal transition data, for the LC mesogens and siloxane polymers, are shown in Table 1 and 2.

It should be noted that POM of three of the four vinyl mesogens showed a narrow cholesteric (n^*) phase upon polymerization. Compound #3, pregnenolone-4-vinylbenzoate, is undetermined if it has an LC phase due to the rapid loss of birefringence upon polymerization. The allyloxy mesogens did not polymerize and revealed the LC phase to be cholesteric (n^*). Modulated DSC of the vinyl mesogens show a broad crystal melt followed by a strong exothermic, irreversible polymerization.

The thermal transitions data for the siloxane polymers is very interesting. It is well known, that the attachment of a LC mesogen to a polymer backbone increases the mesophase temperature range. Tables 1 and 2 show that compound #6 increases its LC mesophase range from 110°C to 200°C. From this attachment, D4-6, is now multiphasic with the addition of a S_A phase. Compound #5 also follows this phase broadening (15°C to 170°C) but the phase changes from n^* to a higher ordered SB phase. Compound #4 and possibly #3 were n^* before polymerization, but attachment to the siloxane ring (D4-4 and D4-3) shows no LC phase just an amorphous glass. Apparently, the rigidity of the leader group and the cores of androsterone and pregnenolone do not favor LC mesophase packing. Compounds D4-1 and D4-2 both have long tails, have nearly the same temporal stability, and are liquid crystalline.

From these results, it would seem that the coupling of other steroids with different terminal polar groups, such as in acetoxypre gnenolone or estrone, to a vinylbenzoate leader group would result in mesogens and siloxanes that are not liquid crystalline. However, increasing the length of the leader group may decouple the mesogen interactions and allow a liquid crystalline state, as seen in compound #7, to be adopted.

RESULTS

[illegible]tion into cyclic and dimeric siloxane polymers is in the process of [illegible] to study the structure property relationship of these low molecular [illegible]mine what types of packing occur. X-ray diffraction experiments were [illegible] spacings of each molecule for aligned and unaligned samples. The data [illegible]eady for correlation.

DEVELOP A SOFTWARE DATA BASE FOR HAZARDOUS MATERIALS

Task Order No. 98
Student Support Program
Southwestern Ohio Council for Higher Education

Linda Wood
Wright State University

16 December 1994

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

A hazardous waste data base has been developed to document individual waste containers from satellite points. This system allows the user to view the waste containers generated in each satellite point chronologically. Individual container amounts, chemical composition, and amount of each chemical may easily be retrieved from the data base. Work has begun to expand the data base to relate individual containers within a satellite point and each satellite data base to the others.

A waste container record in the data base includes six input fields. The input is collected from hazardous waste container log sheets.

Procedures for completion of a hazardous waste container log sheet as well as waste container opening, closing, deposits and storage have been developed. Training for these procedures has been given in individual and group sessions.

Many different types of software have been investigated including software for spreadsheets, word processing, relational databases, scanning, drawing, graphing, converting file types, making forms, networking, system recovery, virus detection and instrument data collection. Tutorials have been given to individuals on the usage of the software.

Maintenance has been performed on computer systems. Optimization of hard disks, computer backups, software installation and removal, system upgrades, installation of hard disks, reformating of hard disks, recovery of systems from backups, and troubleshooting system failures and user errors have been performed on Macintosh systems within the division.

Evaluation and documentation of computer systems' software within the department were performed in preparation for computer inspections.

Investigation and documentation of branch computer systems' hardware were performed and compared with hardware available. Cost analysis of available hardware and the branch system analysis were scaled to create a plan for future computer system replacements and upgrades.

DESCRIPTION OF RESEARCH

Computers have become an essential tool in research and can make or break the ability to remain on the cutting edge. The capabilities and cost of computers are continually changing.

Flexibility and planning (and luck sometimes) in choosing a system, creating software, or purchasing software that doesn't become useless in less than a year are crucial factors in staying current with utilizing computer capabilities.

Within the planning aspect, user friendliness of systems and software plays a major role. If the computer environment follows a state of the art path but the user is incapable of keeping the pace because of a complex user, interface the computer system becomes useless.

The flexibility of a system and software either allow for growth or become obsolete. If they become obsolete within a short period of time, cost factors for total replacements can be devastating.

Many different computer systems were used in this Task. UNIX, VAX/VMS, Macintosh, IBM and IBM compatible were utilized.

In addition, CD-Roms, Magnetic tape drives, portable external hard drives, external eternet cards, and digital scanners were used.

RESULTS

Computer systems and software are constantly being improved. Equipment that is innovative and necessary today may be backward and useless in 8 months in both hardware and software. Careful planning with considerations for flexibility, as well as costs, are necessary to utilize computers effectively and efficiently.

In research, computers more than ever can make or break the speed of discovery. The user friendliness of computer systems and software, as well as the flexibility of the computer system and software design, can make the difference in being the leaders or followers in research.

PHYSICS OF CONDUCTING POLYMERS AND OPTICAL POLYMER FILMS

Task Order No. 99
Student Support Program
Southwestern Ohio Council for Higher Education

Joseph R. Demers
Wright State University

31 December 1994

Government Task Leader
Dr. Robert Spry
WL/MLBP

ACKNOWLEDGMENTS

I would like to sincerely thank my research advisors Dr. Bob Spry, Dr. S. J. Bai and Dr. Gust Bambikidis for their guidance and support during this project. Without their theoretical insight and practical laboratory experience this project would have failed. I, also, would like to thank the United States Air Force for funding this project and Southwestern Ohio Council for Higher Education for employing me on this contract. I am grateful for all the opportunities granted me while working here.

TASK ASSIGNMENT

Generally, in a material being illuminated with low light intensities, changes induced in the material are small and linear. The electrical field of light passing through the material causes a polarization of the material's electrons. This polarization, if non-linear, can change the dielectric properties of the material. This investigation focuses on Pockel's Effect; a change in the material's refractive index induced by an external electric field. The applied electric field shifts the equilibrium point of electrons which are coupled to the incident laser's alternating electric field. Because of charge de-localization and bond conjugation, organic materials, polymers mostly, are highly susceptible to non-linear optical effects. Further, polymers are easily processed, have highly adaptable physical properties and may easily be doped to improve non-linear optical behavior. This makes polymers primary candidates as a material for non-linear optical studies.

Research has been conducted to develop optical methods (photonics) for integrating digital communications. Most photonic applications involve fiber optics, or, more generally, guided wave phenomena. For thin-film applications waveguiding is generally achieved by coupling a laser through the upper surface of a film with a prism. At certain discrete angles of incidence, the equations governing the propagation of the light in the thin-film medium are satisfied and the laser light couples to the planer waveguide. Generally, the equations governing the propagation are satisfied for a number of different angles, each one denoting a different mode of propagation. The polarization of the incident laser changes the boundary conditions of the waveguide. Mode solutions are also dependent upon the thickness of the sample. Therefore, accurate measurement of the coupling angle for each mode makes it possible to calculate both the index of refraction and the thickness for the sample.

In the past, reflection techniques have been employed to study changes in the polymer's refractive index. A new method employing waveguiding was developed which allows repeatable, highly accurate, measurements of index changes in thin-film polymers induced by external electric fields. Unlike other methods, this technique also allows the simultaneous measurement of sample thickness or possible changes in the sample thickness due to the external electric field. A turn-key waveguiding apparatus produced by Metricon Corp. of New Jersey was employed for all measurements. The Metricon allowed optical studies to be performed with both transverse electric (TE) and transverse magnetic (TM) polarizations. The completeness of this unit allowed quick and accurate measurements of the polymer's refractive index. It is hoped that the methodology developed during this project can be used to pre-evaluate non-linear optical polymer candidates.

To measure Pockel's Effect, it is necessary to place the poled sample between two electrodes, apply a field and measure the refractive index in-situ. For waveguiding studies performed on thin-film polymers, this could be difficult to achieve since the upper electrode covers the same surface through which the laser is to be coupled. For coupling to occur, the upper electrode must be fairly transparent, be very thin or both. In the literature, upper electrode compositions and thicknesses vary, the only condition being that the conducting electrode be transparent to the wavelength of the incident laser at the chosen thickness. Although not expected, a further complication was that the upper electrode also must be conductive at the thickness which allowed optical transmission. The bottom electrode was simply sputtered onto the substrate before the thin-film polymer sample was epoxied into place.

The polymer used for developing the methodology was agar; an economic, biologically derived, highly refined animal protein. The oxygen on the carbonyl group and the trans-hydrogen on the nitrogen promote strong hydrogen bonds between separate protein molecules. Further, conformational changes of the protein allow every carbonyl group to participate in this hydrogen bond. This "cross-linking" produces a surprisingly rigid polymer. Because the agar came in a dehydrated form, it was necessary to mix approximately 0.15% of it, by weight, with double distilled water. The mixture would then be heated to 98°C and stirred until the agar dissolved. This fluid could then be poured into a casting dish and allowed to gel. Formation of the gel required approximately 5 minutes at room temperature, while complete drying into the polymer form required 14 hours. It was found, that approximately 10 ml. of the agar solution would evenly coat the bottom of the 3.5 inch casting dish and produce a film about 10 m thick. Large NLO responses have been displayed by doping the agar with water soluble 4-nitrophenol. For this reason, 4-nitrophenol was employed as the dopant for this series of tests.

Pockel's Effect was studied in a cast agar film doped with 10% 4-nitrophenol. The film was epoxied to a silicon wafer coated with a 150Å gold-palladium electrode. After adhering the doped agar film to the substrate, a 35Å gold electrode was sputtered on top. These electrodes were then connected to a high voltage source and a prism was used to couple a HeNe laser (632.8 nm) through the gold electrode into the film. Rotating the multi-layer sample with respect to the incident laser beam produced multiple waveguide propagation modes. From these mode positions, the Metricon unit, previously mentioned, calculated the refractive index and thickness of the doped agar film. The refractive index and thickness were then determined as a function of the applied DC potential.

The largest shift in the refractive index for the doped agar was observed with the TE polarization to be 0.0006. This shift occurred with an applied potential of 400 volts. The application of this 400 volt potential also induced the largest shift in the thickness of the doped agar film. This thickness increase was observed with the TE polarization to be 0.7μm. While shifts in both the index and thickness of the doped agar film for the TM polarization were observed, damage caused by the application of 400 volts prevented shifts as large as those recorded for the TE polarization.

While it was hoped that the change in the observed refractive index could be attributed solely to Pockel's effect, this was not the case. It was discovered that when a DC potential was placed across the doped agar thin-film it under went a conformational change. The agar film showed a significant increase in the thickness as a function of the applied potential. This significant increase in the sample thickness prevents a quantitative or even a qualitative evaluation of Pockel's effect. If an AC field of high enough frequency had been employed for this study then, presumably, the stress on the sample would have been effectively zero and only index changes due to Pockel's effect would have been measured. While the project was deemed very successful, future work should concentrate on preventing conformational changes to the polymer of study.

PHYSICS OF CONDUCTING POLYMERS AND OPTICAL POLYMER FILMS

Task Order No. 99a
Student Support Program
Southwestern Ohio Council for Higher Education

Max D. Alexander, Jr.
Wright State University

31 December 1994

Government Task Leader
Dr. Robert J. Spry
WL/MLBP

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TASK ASSIGNMENT

The work conducted at Wright Labs was focused around the following areas:

1) To review the condition of excess equipment from other groups and determine its suitability for use by the polymer physics group.

2) To measure the optical mode patterns and optical loss from a scratched and unscratched non-oriented thin-film of mylar containing filler particles.

3) To measure the optical mode pattern of a PBT film.

4) To measure the optical mode pattern and optical loss from an oriented unconstrained mylar/co-polymer, oriented constrained mylar/co-polymer, and an extruded mylar/co-polymer film.

The review of excess NON-NSN equipment was the first task undertaken at the beginning of the summer. Several dozen items were inspected, at various locations on Area B, 17 usable items were located. This equipment included several detectors, gratings and a lock-in amplifier. This equipment will be used as needed for studying photoluminescence of polymer films. This Task required approximately 2 weeks, at which time it was completed.

The second project, the measurement of optical mode patterns, and losses in scratched and unscratched mylar was performed on a Metrican Model 2010 prism coupler. The mylar samples were prepared by Mr. S. J. Bai by using a silicon wafer with a 2 micron SiO_2 substrate, upon this substrate an optical epoxy was coated and the mylar film adhered. The mylar sample was then placed in Metricon against the 1024 high refractive index prism where it was held in place by a pneumatically-operated coupling head. A laser beam of 632.8nm or 1152nm then strikes the base of the prism and is reflected out the other side at varying intensities depending upon the angle of incidence. The angles at which there is local minima in the intensity pattern are called the optical modes. It is at these incident beam angles that thin-film exhibits waveguide characteristics, which are clearly visible as a propagation streak in the mylar along the direction of the incident laser beam. Once the mode angles are determined, the Metrican is carefully aligned by hand to each of these positions. The beam is then attenuated, by means of neutral density filters, until the streak in the mylar is only faintly visible and the laser then turned off. At this time, the measurement of optical loss is acquired. The lights in the darkroom, where the Metricon is located, are turned off and a carefully cut piece of KODAK Technical Pan film is placed against the mylar. The laser beam is then turned on and allowed to expose the film for approximately 4 seconds, after which the film is removed and developed. The washed and dried photographic film is then scanned at a resolution of 50 microns per pixel on a Molecular Dynamics personal densitometer. The scan data is then analyzed by acquiring a "line scan" along the length of the streak, one to seven pixels wide, and generating a graph of optical density vs. distance from the prism. This technique extends from the equation $I(x)=I_o=\exp(-\alpha x)$ where $I(x)$ is the intensity of a beam propagating in a medium with absorbtivity α at a position x from a reference point where the intensity is I. The information was then saved to diskette and imported into Origin, where it was reconstructed and the log of the optical density plotted vs. distance traveled in cm. The slope of this graph is then calculated and was determined to be the α value, or lose of the signal while in the waveguide in cm^{-1}.

However, the data collected did not agree with the previous values obtained for the material. Several oversights were soon recognized. First, there was no ability to calibrate from optical density to incident intensity due to the use of an improper developer for the film. This problem was eliminated by using KODAK Technidol Liquid Developer. Calibration from optical density to incident intensity ($ergs/cm^2$) was achieved by scanning in a calibration sheet for the film/developer combination used, transferring the scanned data points to EASYPLOT and fitting three exponential functions to it. This provided a mathematical mapping function from optical density to incident intensity. With the incorporation of this technique and the remeasurement of the sample, better values were obtained. Also, another difficulty is acquiring the streak produced by the 1152nm laser. KODAK infrared film was used initially. It was discovered that the signal is too far into the infrared to be recorded by any photographic means available. A solution to this problem is being sought.

It was determined that the filler particles in the mylar resulted in too much scattering to provide consistent values and that a more suitable sample was required. DuPont Chemical Co. was contacted and asked to provide the materials listed in Task # 4.

While waiting on the new filler, free mylar to be fabricated and arrive, a small amount of time was spent analyzing the optical properties of PBT. The PBT was mounted by a similar technique to the mylar's. The PBT sample had poor optical quality with only four faint modes present. The material had such a high optical loss, no streak was visible in the film and, therefore, no measurement of α was possible.

The fourth project, consisting of the measurement of optical loss and mode patterns in constrained and unconstrained mylar/co-polymer and extruded mylar, is now underway. Initial results are much more consistent than in the previous study. This work will be continued over the next few months, with the results published around April 95.

The materials studied have potential for use in waveguiding, and optoelectronic applications such as optical computation and communication for both the Air Force and industry. Many improvements in optical loss measurement techniques have been the result of these studies, and many more are in the works.

FATIGUE OF CERAMIC COMPOSITES

Task Order No. 100
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer Finch
Wright State University

31 December 1994

Government Task Leader
Dr. Larry Zawada
WL/MLLN

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TASK ASSIGNMENT

The objective of this study is to develop an experimental procedure for testing material coupons under laboratory conditions to simulate the thermal conditions experienced by the divergent flaps and seals in the exhaust nozzle of a gas turbine engine during service testing. The material to be examined is an advanced ceramic matrix composite consisting of continuous silicon carbide fibers in a carbonaceous matrix. Tensile type dogbone specimens of this material will be subject to a designed test matrix based on measured thermal exposure data from previous engine tests. The residual properties of the simulated specimens will then be compared to those of specimens machined from the flaps and seals of an F414 gas turbine engine after service testing. It is hypothesized that thermal conditions of the exhaust components can be reproduced under laboratory conditions and therefore, the resulting data will show that there is less than a 15% difference in residual strength between the simulated and the engine tested specimens.

The significance of conducting the proposed investigation lies in the validation of laboratory simulation testing as an effective life predicting design tool for high temperature applications. Currently, the amount of live afterburner engine testing deemed necessary for the design of gas turbine engine exhaust nozzle components is both extremely time consuming and costly for engine producers. Although it is not plausible to eliminate engine service testing for final verification of an engine coponent's designed specifications, there are great economic implications in reducing the number of engine tests needed at the design stages of an engines component's development.

Implicitly, it follows from the validation of laboratory simulated testing that more often alternative materials such as ceramic matrix composites (CMC's) will be incorporated into high-temperature component design. Investigation into the properties of CMC's has already shown them to be potential replacements for high-temperature superalloys in certain aerospace applications. They have low densities, high strengths and moduli, and the ability to withstand temperatures in excess of 1800°F (1000°C). Due to these qualities, there is current interest to utilize CMC's such as silicon carbide fiber reinforced carbon (SiC/C) as exhaust components in several gas turbine jet engine families. Presently, SiC/C has replaced Rene'41 as the bill of materials for the flap and seal in General Electric's F414 gas turbine engine. Therefore, the ceramic matrix composite material SiC/C is a candidate material for the design of mission profile simulation testing.

RESEARCH

The designed engine simulation testing must show that SiC/C will meet the performance limits defined by the F414 exhaust components design. Although exact design criterion is not available for this study's purposes, the following approximate magnitudes are known to conform. The mission life of the exhaust components is defined by thermally induced low cycle fatigue constraints. The parts should endure 1500 thermal cycles resulting between engine cruise and acceleration to full military power. Operating temperatures in the exhaust nozzle during one cycle start around 800°F at the point of acceleration and reach as high as 2000°F at full afterburner. As a result of an extended service mission profile (N=1500) the parts accumulate approximately 10 hours at the formerly specified temperatures. The overall minimum material strength requirement for the flap and seal applications is around 100 MPa.

The proposed procedure for thermal condition engine testing will include testing and characterization of as-received service production material and F414 engine tested SiC/C specimens.

Material

The as-received SiC/C material coupons to be simulation tested under laboratory conditions have been machined from service production flaps and seals. The material was manufactured to conform to the design specifications for the flap and seal construction and then machined into dogbone specimens which conform to the newly proposed ASTM standard for CMC materials. The coupons have been given a 0.17mm. dual coating, as previously described, on all surfaces. The specimen dimensions after being coated are shown in Figure 6a. The material coupons will be simulation tested in this geometry. However, before residual strength testing, the specimens will be machined down to a straight-sided geometry. The machining of dogbone specimens will be done at WPAFB on a traversing table saw by a support technician employed by Universal Energy Systems (UES).

The engine tested SiC/C specimens will be machined upon receiving the F414 tested flaps and seals. The machining of the flat components also will be done at WPAFB by a UES technician. Textured tabs will be mechanically bonded to all the straight-sided specimens prior to gripping for residual strength testing.

Test Equipment

I. Preliminary Fatigue Testing

The preconditioning fatigue treatment and residual strength testing will be performed on an MTShorizontal servohydraulic test machine. The specimens will be held in place by rigid hydraulic clamping grips during cyclic loading and be MTS-647 wedge grips for postcycle monotonic loading. The fatigue test will be load controlled, whereas the tensile test will be controlled be the cross-head displacement. Strain measurements will be performed using an MTS clip-gage extensometer attached to the specimen gage section.

II. Thermal Cycling

The thermal cycling test simulation will be performed using a resistance heated tube furnace, with a computer-controlled in-line pneumatic actuator to position the specimen in and out of the furnace hot zone. Barber-Colman[* ***] temperature controllers in conjunction with a PC based data acquisition system fed from S-type thermocouples allows the thermal cycle to be defined by the specimen temperature. The software will be programed to move the specimen out of the furnace when the specimen temperature reads the maximum desired temperature of 2000°F for the set soak time, and into the furnace when the minimum test temperature of 800°F is reached. Fan cooling may be used to accelerate the cooling rate of the specimen. Inert atmosphere thermal cycling also will be performed using the same equipment. However, the specimen will be encapsulated in a quartz tube which has been purged with high purity argon gas (99.999%) and evacuated to a partial vacuum of $5x10^3$ torr[7].

The furnace temperature is currently controlled by a type K thermocouple which is placed in the center of the hot zone of the furnace. Type K thermocouple wire (nickel-chromium+nickel-aluminum) is stable to 2300°F (1250°C). An initial temperature profile performed revealed that the thermocouple readings showed a marked loss in temperature reading stability around 1950°F (1050°C). Modifications are being requested to convert the furnace assembly to monitor temperature by type S thermocouples (platinum+platinum and rhodium) which are stable to higher temperatures. This equipment modification will be headed by University of Dayton Research Institute support personnel.

The manufacturer's trade name for silicon carbide fiber is NICALON.
Engine testing will be performed by General Electric.
MTS is a trademark of MTS Systems Corporation, Minneapolis, MN.
Barber-Colman Company, Industrial Instrument Division, Rockford, IL.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND EVALUATION SECTION
WL/MLSE

Task Order No. 101
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Cassoni
Wright State University

31 December 1994

Government Task Leader
Mr. Robert Urzi
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank the following individuals for their technical support on this Task: Mr. Ron Kuhbander, Mr. Bryan Cramer, Mr. Doug Carter, Mr. Bob Urzi, and especially Mr. Mark Kistner. Their help was greatly appreciated.

TASK ASSIGNMENT

Several projects were involved in this Task. The first investigated the mechanical properties of pilot helmet comfort liners. The second investigated the mechanical properties of closed cell structural foams to be used in the support of military aircraft. Other projects involved the fabrication and testing of composite, adhesive, and metal specimens as well as the design and fabrication of various test fixtures.

The first project was proposed, as there is a stability problem within the helmet liner when night vision goggles are attached to the front of the helmet. The additional weight of the goggles creates an adverse moment, which tends to create a shearing condition through the comfort liner. This instability can cause misalignment of the pilot's eyes to the target which can hinder the pilot's ability to complete their mission. This project involved three phases of testing. The first was flatwise compression, which was used to measure the compressive modulus of the material that places a numerical value on the comfort of the liner. The second was static coefficient of friction testing, which was a measure of the friction between the comfort and sanitary liners of the helmet. The last phase was a creep test, which investigated the amount of deflection created when a force is applied normal to the surface over a period of time.

The use of structural foam materials is being considered as a replacement for the aluminum and Kevlar based honeycomb cores that are currently being used to stiffen structural panels. This project consisted of several different test methods that created a data base of mechanical properties. The first was flat wise compression, that measured the compressive strength and modulus of the material. The second was dog bone tension, that measured the tensile properties of the core material. The third was compressive plate shear, which considered the shear modulus and strength of the material. This project is nearly completed and has involved the fabrication and testing of approximately 3,000 specimens.

Several other projects were involved on this Task. Some of these projects have considered the effects that vacuum curing has on the strength of an adhesive or composite system, while others have investigated field methods of repair to combat damaged aircraft. The design and fabrication of test fixtures was necessary in both projects and presented additional work necessary beyond the test matrix involved in each project.

During this Task, I gained a lot of experience. I was the lead technician on two Tasks and was a co-author on an Air Force technical paper titled "The Evaluation of Pilot Helmet Comfort Systems." I also had the opportunity to operate many new pieces of mechanical test equipment, which are the forefront of technology. Also involved on this Task more than on prior tasks was the engineering role over the technician role. This allowed me to be involved on the design of test matrices as well as design test fixtures which were necessary to complete our projects. Involved in the design of test fixtures was the communication with the machine shop to build what the plans called for. Overall, I found this Task to be a very good opportunity to gain experience as well as contribute to the project goals of WL/MLSE.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND SUPPORT SECTION WL/MLSE

Task Order No. 102
Student Support Program
Southwestern Ohio Council for Higher Education

James W. Stubbs
Wright State University

31 December 1994

Government Task Leader
Mr. Robert B. Urzi
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank the following people at Wright Laboratory for all their help and guidance during this Task: Mr. Robert Urzi, Mr. Jim McKiernan, Mr. Ron Kuhbander, Msgt. Brian Cramer, Mr. Mark Forte, Mr. Jim Mazza, Mr. Doug Carter, Mr. Mark Kistner, Rob Cassoni and Mr. Dan McCray.

TASK ASSIGNMENT

The objective of this Task was to conduct short investigations in-house to assist in the evaluation of various materials and processes for Air Force applications. The Task was completed through continuous part-time work over the course of the year. During the Task, the student assisted in the fabrication, testing, and evaluation of test specimen made from experimental and existing materials. The students were involved to some extent in many active projects during the work periods. The bulk of these projects required the students to fabricate and test various test specimen to examine the feasibility of adhesive systems for possible Air Force applications. The student also had the opportunity to conduct research for a senior design project involving two aircraft battle damage repair adhesive systems that was conducted in conjunction with Wright State University. This project involved the development of a process by which a specific adhesive system could be bonded with a vacuum process while removing the negative effects of the vacuum process on the adhesive system.

DESCRIPTION OF RESEARCH

Adhesive evaluation was continued on two projects during this Task. The first of these was a series of tests to determine the shelf life of certain adhesives subjected to different storage conditions and times. Samples were prepared for overlap shear, flatwise tension, and floating roller peel. The samples were then tested on an Instron 4505 testing machine. The results were compared with the original testing results to judge the loss of strength due to long-term storage. The other project, dealing with adhesive evaluation, was a series of tests to find an adhesive with good high temperature qualities that could be cured at low temperatures. The adhesive was for repair of an Air Force airplane that required an adhesive that could be cured below 250° F to prevent structural damage to the aircraft, yet maintain 1800 psi at 350° F. Specimens were fabricated under 35 psi positive pressure and temperatures under 250° F for various cure times for overlap shear testing at 350° F. The research conducted in the evaluation of adhesive properties involved mechanical testing of tensile overlap shear panels and floating roller peel panels. These panels were bonded, machined, and tested using various bonding procedures. Also involved in this project was the evaluation of the pot life of two adhesive systems that were the basis for the Task. Research was also continued on the overheat damage project that was started during the last Task. A wide range of panels was tested in flexure and shear after exposure to varying levels of radiant energy. Conditioning and testing of these panels was also done during this Task.

RESULTS

In the adhesive storage project, the candidate adhesives were stored at room temperature, under refrigeration, and at 0° C. It was found that the adhesives under study had the longest shelf life when stored at 0° C, with the greatest loss of strength when stored at room temperature.

Only one adhesive tested thus far in the repair concepts program has shown any promise. Four of five adhesives cured at or below 250° F only had overlap shear strengths of 1200 psi or less. The other adhesive tested showed a strength of approximately 2000, psi even when cured as low 180° F. This adhesive is currently under more testing to examine the repeatability of these values.

In the overheat damage project, several ways to find damage that is not visible are being tested. A lamp-bank and fixture system was designed that allowed for large panels to be tested while maintaining constant temperatures over the majority of the panel. Approximately half the data for the completion of this project has been taken. Many of the thick panels are still being exposed to humidity prior to thermal exposure and, therefore hav,e not been tested.

Panels have been tested that were bonded with positive pressure, full vacuum, and partial vacuum cure processes.

Seven of the eight required pot life studies have also been completed. The research for this project is expected to be completed within the next 2 months.

METALLIC COMPOSITES

Task Order No. 103
Student Support Program
Southwestern Ohio Council for Higher Education

Lisa Rothenflue
Wright State University

22 March 1995

Government Task Leader
Dr. Dan Miracle
WL/MLLM

ACKNOWLEDGMENTS

For their patience, insight, and assistance, I would like to thank the following people: Dr. Dan Miracle, Dr. Mark Waterbury, Bob Lewis, Michael Scott, Kevin Kendig and Hou Jeing.

TASK ASSIGNMENT

The Task objective was to determine interface properties and deformation characteristics in advanced metallic composites for high temperature applications.

During this Task, samples were prepared and experiments performed to determine the residual fiber strains present in as-processed composites. The fiber extension, matrix undercut removal (FEMUR) technique was employed to ascertain the axial residual strains in the fibers. The $\sin^2\psi$ method was utilized to determine the residual stress in the matrix. A spreadsheet was developed to calculate the lattice parameters of orthorhombic materials from x-ray data. Commercial computer programs were used for peak location and identification.

Another focus of this Task was to determine a method to prepare composite materials for the fiber push-out test. The method employed for this will be presented in the next section.

The purpose of this Task is to improve the understanding of the interface properties and deformation characteristics of advanced metal matrix composites. Continuously-reinforced titanium-based metal matrix composites are being developed as potential materials for high temperature aerospace applications. Upon cooling from the processing temperature, residual stresses are introduced into these composites by the differences in the coefficients of thermal expansion (CTE) for the matrix and the fibers of the composite. These residual stresses can affect the mechanical behavior and failure of the composite. Examination of residual stresses provides important information about the interface. Therefore, determining a method by which the residual stresses can be measured is important. The reduction of these stresses, through either heat treatment or mechanical processing, is also of interest.

DESCRIPTION OF RESEARCH

The majority of the research performed for this Task involved the determination and analysis of axial residual fiber strains in composite materials.

The residual strains in the fibers were determined using an electropolishing technique nicknamed FEMUR for Fiber Extension, Matrix Under-cut Removal. This procedure involved sectioning the specimen normal to the fiber axis, mounting in a triplex mount (two non-conducting layers with a conducting layer in the center in contact with the specimen), and polishing the sample to a 1 μm finish using the Maximet. The specimen surface was then 'masked' with an acid resistant lacquer with the exception of a ~1 mm wide region in the center of the composite. The sample was then jet electropolished using a perchloric acid solution for 11-12 hours. This procedure removed the composite matrix around the fibers by electropolishing to a depth of 0.5-1mm. The axial residual stresses in the fiber are due to constraint by the matrix (the CTE of the matrix is greater than that of the fiber). Therefore, upon removal of the matrix, the fibers relax. The magnitude of the fiber extension is related to the depth of matrix material removed. This depth (D) is approximated by using a calibrated optical microscope with a depth of field sufficient to measure the exposed fiber length by focusing on the fiber end and then on the matrix where the fiber entered the composite and recording the difference in positions. The magnitude of the fiber relaxation (ΔH) was determined by surface profilometry. A surface profilometer scanned individual rows of fibers with a diamond-tipped stylus. The output for each row was a trace of the surface roughness. The fiber relaxation (ΔH) was determined by measuring the difference in height of the exposed fiber to the height of the fibers in the unexposed regions.

The data was analyzed by entering the values for etched depth (D) and fiber extension (ΔH) into the spreadsheet, developed in the previous Task, to calculate the weighed slope and intercept values from linear regression and the standard error for these values (with a confidence interval of 68%). This weighed method accounts for errors in both X-etched depth (D) and Y-the axial fiber extension (H). The procedure for this analysis is too long to describe in this report, but an outline of the procedure by page or section number and source is given on the attached printout of the results for the Dutton 18 ply composite (see Figure 1). The residual fiber strain is the negative of the slope obtained from the spreadsheet. From this value, the residual stress can be calculated.

During this Task, FEMUR analysis was performed on several continuous fiber reinforced composites: two unknown samples and Ti-22Al-23Nb.

The residual stress in the matrix was determined for Ti-22Al-23Nb. The specimen was cut to ~ 1 cm by 1 cm and ultrasonically cleaned in acetone. X-ray measurements were then taken using Cu Kα radiation at 40 mA and 150 kV. The slit configuration consisted of 1° DS, 1°SS, and 0.15mm RS. The $\sin^2\psi$ method consists of a number of inclined measurements rather than one. To perform the inclined measurements, the datum - the system calibration θ setting must be altered. Using the Rigaku x-ray software the datums θ value was altered by adding the translation angle (ψ) to the current calibration. The translation angles were at equal intervals of $\sin^2\psi$ (e.g.,$\sin^2\psi$=.1 --- ψ = 18.43). Six runs (ψ = 0° through 45°) were done for both composite fiber orientations (vertical and horizontal). The peak of interest is identified as the peak with the highest 2θ value with a useful intensity. The exact peak location was determined by the computer peak fitting program in Table Curve. The peaks were identified by the diffractometer calculations from the computer program Diffract. The values of 2θ for each orientation were plotted versus $\sin^2\psi$ to determine the stress constants.

The method for sample preparation for the fiber push-out test involves machining the specimens to a width of 1.6mm, mounting the sample in thermoplastic mounting material with a small amount of thermosetting powder around the surface for edge retention. The specimens are polished using the Maximet to a 1 μm finish (checking frequently to prevent excess removal of materials). The specimen is then removed from the mount and remounted on the other side and polished using the same procedure. A final polish to a 1/2 μm finish is preformed on the Vibromet. The specimen is removed from the mount and ultrasonically cleaned in acetone.

RESULTS

The majority of the results from this Task have yet to be determined. The results from FEMUR testing and analysis of the two unknown Dutton (18 and 28 ply) continuous fiber reinforced composites are complete. The residual strains (%) obtained from analysis were - .000009 ± 3.79946E-06 (28 ply) and -0.001884 ± 6.6103E-05 (18 ply).

The results obtained by the spreadsheet developed during this Task are given in Figure 2. From this spreadsheet, it was determined that the lattice parameters for the orthorhombic phase present in the Ti-22Al-23Nb are a = 6.076 Å, b = 9.637Å, and c = 4.654Å. This information was then used in the program to identify the peak.

FEMUR testing and analysis on the continuous fiber composite Ti-22Al-23Nb in the as processed condition were performed and analyzed but the stresses have not been calculated at this time.

The x-ray data on the Ti-22Al-23Nb continuous fiber composite has been completed. The values of 2θ for each orientation have yet to be plotted versus $\sin^2\psi$ to determine the stress constants.

The results of this Task will be completed in the near future.

Figure 1

P-Error cutton 18 ply

ENTER x(I) &y(I) VALUES
ENTER X & Y MEASUREMENT ERROR

Measurement Error (X) = 25

Measurement Error (Y) = 0.2

RESULTS

SLOPE = 0.001884 ± 6.61013E-05

INTERCEPT = 0.176586 ± 0.030446626

Intermediate Results

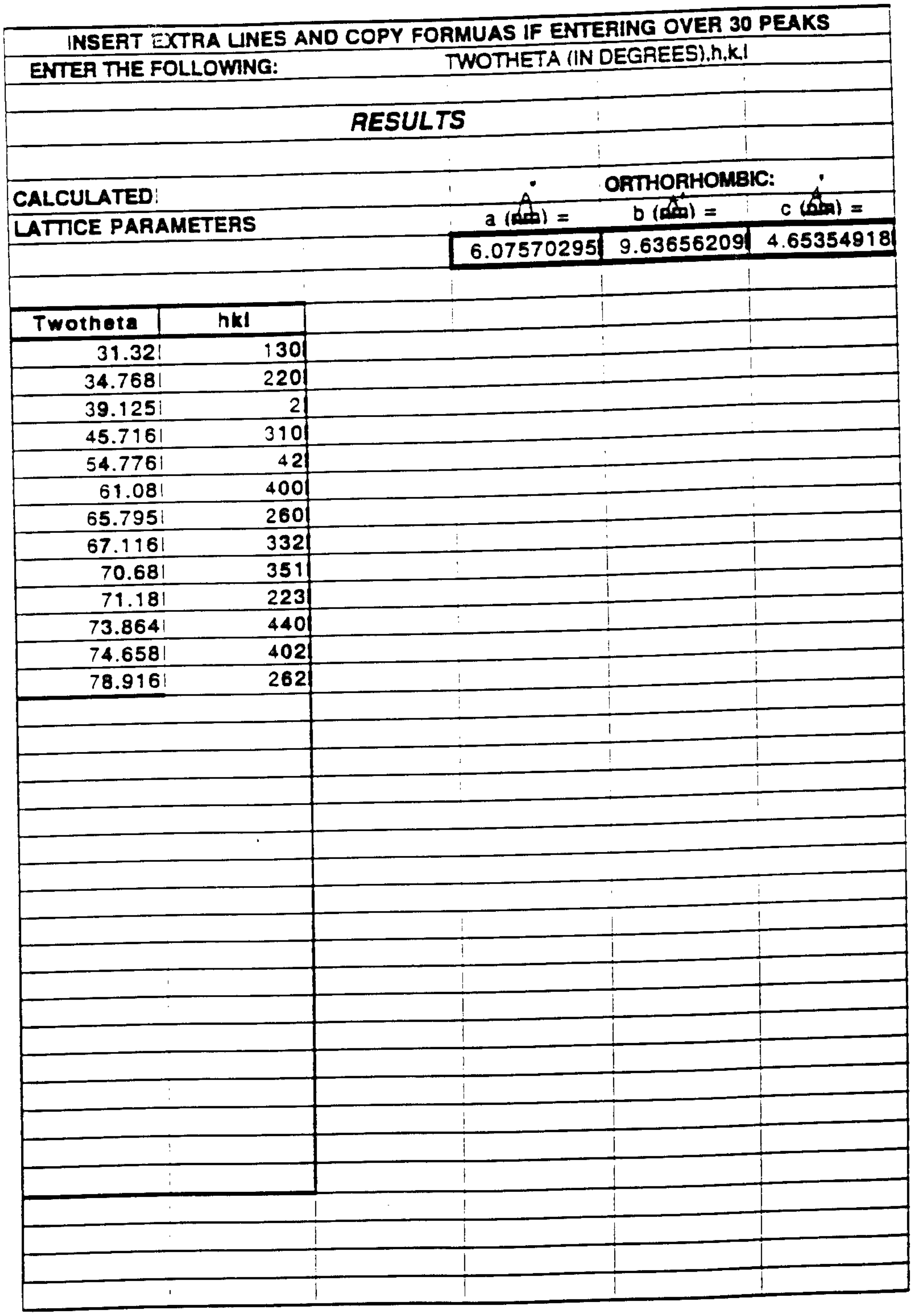
N = 103		
XAVG = 420.9214		
YAVG = 0.9697		
LAMBDA = 15625	Eqn 12.38 Mandel	
U = 3.71E+08	Eqn 12.41 Mandel	
W = 1.90E+03	Eqn 12.42 Mandel	
P = 6.81E+05	Eqn 12.43 Mandel	
S = 6.34447087	Eqn 12.52 Mandel	
SIGMA = 0.25063229	Eqn 7.2 Mandel; Deming p 168	
VAR(x) = 3710.29964	Eqn 12.50 Mandel	
VAR(y) = 0.23745918	Eqn 12.51 Mandel	
w(x) = 0.00026952	Mandel p 290	
w(y) = 4.21125018	Deming Sec 11	
L = 0.25063229	Deming pp 154,178	
aa = 410.96062	Deming Sec 61	
ab = 172982.103	Deming Sec 61	
bb = 87188395.2	Deming Sec 61	
DET = 5.91E+09		
c11 = 0.01475721	Deming Ex 2, p 162	
c22 = 6.9558E-08	Deming Ex 2, p 162	

Slope from Eqn 12.45 in Mandel
Intercept from Eqn 12.46 in Mandel
Variance in slope and intercept from Deming Sec 62

x(I)	y(I)
98.8	0.12
433	0.7
689.5	0.98
680.3	1.1
603.5	0.72
477.3	0.65
423.5	0.5
401.5	0.28
163	0.59
517.3	1.46
688.5	1.54
611	1.55
500.8	1.59
451.5	1.15
332.8	0.95
105.3	0.35
337	1.15
669.3	1.45
633.5	1.52
554.3	1.25
473.3	1
261.8	0.83
41	0.03
406.5	1.4
581.8	1.45
619.8	1.48
580.3	1.32
517	1.08
233	0.79
29	0.05
182.8	0.61
467.8	1.2
566.5	1.37
601.5	1.42
550.5	1.23
420.5	1.01
226.5	0.76
320	1.1
507.8	1.2
561	1.5
873	1.25
371.3	0.85
236.5	0.81
231.8	0.82
486.8	1.3
561.5	1.15
530.3	1.19
383	0.75
215.5	0.72

Figure 2

ORTHO-LAT-TI-22AL-23NB (OURS)



INSERT EXTRA LINES AND COPY FORMUAS IF ENTERING OVER 30 PEAKS

ENTER THE FOLLOWING: TWOTHETA (IN DEGREES),h,k,l

RESULTS

ORTHORHOMBIC:

CALCULATED LATTICE PARAMETERS	a (~~nm~~ Å) =	b (~~nm~~ Å) =	c (~~nm~~ Å) =
	6.07570295	9.63656209	4.65354918

Twotheta	**hkl**
31.32	130
34.768	220
39.125	2
45.716	310
54.776	42
61.08	400
65.795	260
67.116	332
70.68	351
71.18	223
73.864	440
74.658	402
78.916	262

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TRIBOLOGICAL EVALUATION OF CANDIDATE FLUID AND LUBRICANT MATERIALS

Task Order No. 105
Student Support Program
Southwestern Ohio Council for Higher Education

Mark Diller
University of Dayton

30 September 1994

Government Task Leader
Mr. Shashi Sharma
WL/MLBT

ACKNOWLEDGMENTS

I would especially like to thank Mr. Shashi Sharma for the opportunity to work at Wright Patterson Air Force Base. I also would like to thank Vince Vidoni and Bruce Schreiber for the tremendous aid they provided me in my Task.

TASK ASSIGNMENT

The majority of the Task was spent working toward the design of a traction rig which uses current interferometry techniques to measure EHL (elasto-hydrodynamic lubrication) film thicknesses of a lubricant between a rotating ball and disk under known temperature and loading conditions. This concept had been tried once before at WL/MLBT; however, due to a lack of precision and rigidness in the design there was too much wobble in the ball and disk rotations for accurate measurements to be made from the interference patterns. There is also a traction rig at WL/MLBT which is used almost strictly to measure traction coefficients of lubricants between two rotating balls under controlled loading and temperature conditions. Currently this traction rig is undergoing transformations to allow it to handle high temperature test conditions. In making these changes, the entire center section of the test rig has been removed to be replaced with the new apparatus. This center section consisted of a rigid base, two precision spindles, and a number of other possibly reusable parts. By combining these parts with the optical equipment from the original film thickness test rig, a new optical traction rig is to be developed. This recycling of parts should greatly reduce the cost of the new machine.

Procedure

Initial steps in this project included reading papers about the current use of interferometry in measuring lubrication film thicknesses and getting familiar with current traction rig test equipment. Several experiments were run with the previous interferometry traction rig to find flaws in the system and to gain even more familiarity with the optical equipment used to view the interference patterns. A FORTRAN program written to calculate theoretical film thicknesses under known loading conditions, temperatures, and rotation speeds was studied and revised according to the needs of the new test apparatus. Until more testing on the specific method being used by the new machine is done, no modification or creation of drawings and parts can begin. That is the extent of the progress made so far.

Inventory Data Base

The remainder of the Task was spent creating an inventory data base containing all items which government personnel is held accountable for at MLBT. Until now, the only inventory system available was kept by LMCA (the group with complete power over these accountable items). Government personnel only receive computer printouts of their own inventories from year to year and are denied direct access to this system, yet they are the ones held accountable if they are unable to come up with all of their inventory at the appropriate time (i.e., retirement, departure, etc.). Because LMCA provides this system for the entire Base, there is often great confusion in dealing with these inventories. There are often misprints in nomenclature and numbers, sometimes items mysteriously jump from one inventory list to another, many items are nearly impossible to find with the description provided by LMCA, and the turn-in process is so terribly slow that having an outside organization handle inventory has changed from a convenience to a common fear among government workers. By tracking items with their system, hopefully, much of this confusion will disappear.

Procedure

The new data base was created with File Maker Pro software on an Apple Macintosh computer. As soon as sufficient time was taken to learn the new software and hardware, a suitable format was created to which LMCA's inventory listings were copied. To improve upon LMCA's system, each inventoried item was found, and all nomenclature and numbers were updated to provide maximum convenience with the new system. Along with detailed descriptions, a picture of each item was taken with a digital camera and stored on the computer. With these additions, items should be much easier to locate in years to come assuming the new data base is kept current with the addition of new items to the list and the careful track of items turned in. Finally, a presentation of the new data base was given to the government personnel to assure proper use of the new system.

SYNTHESIS OF MULTIDIMENSIONAL HETEROCYCLIC STRUCTURES FOR NONLINEAR OPTICAL EVALUATION

Task Order No. 106
Student Support Program
Southwestern Ohio Council for Higher Education

Andrew E. Schade
University of Dayton

4 May 1995

Government Task Leader
Dr. Robert Evers
WL/MLBP

ACKNOWLEDGMENTS

I would like to thank Dr. Robert Evers, My Dotrong, Minhhoa Dotrong, and all those in the Polymer Branch at WPAFB who encouraged and helped me throughout my work experience.

TASK ASSIGNMENT

The Task to which I was assigned was an ongoing project in the Polymer Branch. I began my work while the scientists were already entrenched in the project. I was introduced to a variety of instruments and techniques that otherwise may not have been made available.

The exact nature of this Task involves work relating to the synthesis of 4-(5-amino-6-hydroxybenzoxazol-2-yl)benzoic acid in a seven-step process on a laboratory scale. Previously, this compound had been synthesized and extruded into a fiber form for mechanical testing. The chemistry of this synthesis was not successful at the industrial level though, so the project was sent back to the labs for more work.

The applications of this novel material being developed are numerous, both in the military and civilian sectors of society. The material shows mechanical properties rivaling those of composites, but will hopefully have lower production costs and many versatile uses.

The student was involved in several of the steps of the synthesis procedure, although participation was initially limited due to a lack of background knowledge in organic chemistry and organic lab techniques. As knowledge was acquired through instruction and practice, participation in the reactions extended more in-depth.

One of the first tasks was working up the polymer, in a fiberous polymeric material was ground and its acid content neutralized. Simple distillations were carried out for purification, usually of the solvents. Throughout the Task a portion of time was spent cleaning glassware and doing odd jobs such as recovering solvents, monitoring simple reactions, running ultraviolet and infrared tests on samples, and working in the processing lab. The broad array of involvement in many facets of the research and development process served the student well and was a positive contribution to the overall work experience.

Due to very low levels of yield on the laboratory scale, and the necessity for a minimum amount of raw material for processing, many of the reactions in the synthesis process must be carried out many times. This ensures that sufficient material is present for the process engineers. Since the reactions, for the most part, take considerable time to setup and run to completion, many times the same reaction would be repeated for up to a week or more. An example is when the product is being recrystallized from the solvent. As with this particular experiment, very often small amounts of product must be recovered from large amounts of solvent, and this can take time to accomplish.

SYNTHESIS OF MULTIDIMENSIONAL HETEROCYCLIC STRUCTURES FOR NONLINEAR OPTICAL EVALUATION

Task Order No. 106a
Student Support Program
Southwestern Ohio Council for Higher Education

Jodi L. Hemmelgarn
The University of Dayton

4 May 1995

Government Task Leader
Dr. Robert C. Evers
WL/MLBP

ACKNOWLEDGMENTS

First I would like to say thank you to everyone in the Polymers Branch who helped me get acquainted with the policies and instrumentation of MLBP. I would like to also thank Dr. Robert Evers and Dr. My Dotrong for such a wonderful opportunity and for making me feel welcome in the Polymers Branch. Most of all, though, I would like to thank Dr. Minnhoa Dotrong for having all the patience in the world answering my questions and making chemistry fun to learn.

TASK ASSIGNMENT

There were many different tasks performed during the four-month period of employment at Wright Lab. In addition to general housekeeping, waste control forms were completed, and ordering of chemical reagents was done. Several organic reactions were carried out from the initial preparations and calculations to purification of intermediate products, and finally finishing the process with different spectrophotometric procedures.

DESCRIPTION OF RESEARCH

Many different items of equipment were used to purify, dry, and analyze samples. Rinsing samples with various solvents (depending on the initial solvent used in the reaction) was done to further purify the samples. This purification was done following vacuum filtration. A vacuum oven was then used to dry the purified sample. Once the purification process had been finished, several different spectrometers were used. The most commonly used spectrometer was the Perkin Elmer Infrared Spectrometer. The Lambda 9 UV/Vis Spectrometer was also used, although not nearly as often. In addition to these two techniques, thin layer chromatography was also performed. Further along in the research process, viscometers were used in addition to basic stopwatches to determine the viscosity of the polymer of interest. The viscosity of a substance is an indication of how quickly or slowly a fluid will flow.

RESULTS

There was much learned during this employment, especially about spectrometers and other basic laboratory equipment. Over the 4 month period, a noticeable improvement of personal laboratory techniques was noticed. Most importantly though, the purity and integrity of samples were stressed and appropriate measures taken to obtain the most efficient yield with the best purity possible.

DEVELOPMENT OF A DESIGN ENVIRONMENT FOR A MATERIAL DISCOVERY SYSTEM

Task Order No. 107
Student Support Program
Southwestern Ohio Council for Higher Education

David Giovannini
Wright State University

20 September 1994

Government Task Leader
Dr. Steven LeClair
WL/MLIM

ACKNOWLEDGMENTS

Special thanks are given to: Dr. Steven LeClair for the opportunity to work in a science and research environment; Dr. Al Jackson for many ideas and a lot of patience; Jeff Heyob for innumerable technical insights and to Marc Reiter for working hard to learn foreign programming concepts.

TASK ASSIGNMENT

The Task is related to a product in development called KnowBe. The name KnowBe is an acronym for "Knowledge Base Elicitation." The main intention behind KnowBe's design is to aid researchers and developers in solving manufacturing problems. This is accomplished in two ways. First, KnowBe simply aids researchers in extracting and viewing compound and element information from existing data bases. The other aspect of KnowBe is to accumulate data, analyze it, and find patterns and best and worst case scenarios. The job associated with this Task is primarily to design software allowing the user to view data in perceptible ways.

The first accomplishment was the design of an intuitive periodic table. Using the presentation software HyperCard, a periodic table was developed to allow users to view element data by color, and to access elemental data by just a click of the mouse. In case the user had more information to add to the extensive element data base, an editor was merged into the viewer. When the periodic table was completed, a much more difficult program needed to be developed.

KnowBe's quest to give its users natural views of data called for an application that would render crystal unit cells (the building blocks of crystals) in three dimensions. The user could then rotate and magnify the unit cell image by the mouse. This application, when complete, will be linked to HyperCard. The linkage will allow the user to control the unit cell viewer from KnowBe. A program is being designed simultaneously which will convert information in KnowBe's data base to Cartesian coordinates to be used by the unit cell viewer. The unit cell viewer will eventually have the capability of stereo imaging. This capability will give the users a true three dimensional image. The development of the viewer was temporarily curtailed by a more immediate software need.

Two small applications were, at the time, immediately needed. The first application converted an ASCII file of float numbers to a binary file of integers. The binary file will be used for pattern recognition. The second application simply opened the binary file and displayed it in binary (series of 1's and 0's). The viewer's sole purpose is to aid the researcher in developing the pattern recognition program.

METHODS OF SOFTWARE DESIGN

Periodic Table Interface

The design problems surrounding the periodic table viewer and editor were the limitations of HyperCard. The application needed to have an attractive and intuitive interface. HyperCard did not lend itself well to the tasks the application needed. The application is such an integrated part of KnowBe that to pull it out of HyperCard would have been a horrendous task.

Unit Cell Viewer

The Unit Cell Viewer has to be fast, intuitive, and expandable. To easily design the intuitive and expandable aspects of the application, the language C++ and the PowerPlant application framework are being used in its development. The application needs to be expandable for two reasons. First, ideas like the stereo imaging need to be implemented without having to rewrite half the original program. Second, the three-dimension rendering engine should be exportable to other applications. The speed aspect is being accomplished through creative code optimization.

The data file format used has to be a compromise between the needs of the exportable three-dimension rendering engine and the needs of the application whose job it is to convert KnowBe's data to Cartesian coordinates. The format is believed to be set, but only time will tell.

ASCII to Binary Converter and Binary Viewer

These programs had to be created quickly. To do this, the application specific code was essentially jammed into executable example programs of the PowerPlant application framework. Three needs had to be met: a) the converter had to convert the floats into one byte integers, b) the converter had to keep track of the number of columns of data in the original ASCII file, and c) the viewer had to view the binary data in sets of 8 (equivalent to a byte) in the original column count.

CONCLUSIONS

Working in a professional science and research environment gives someone a chance to test, expand and tune their skills. It is an environment where a person gets a chance to explore new fields and new possibilities. One would be hard pressed to find these opportunities in the service industry.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS FOR INTRINSIC CONDUCTING SYSTEMS

Task Order No. 108
Student Support Program
Southwestern Ohio Council for Higher Education

David Carpenter
Wright State University

14 July 1995

Government Task Leader
Dr. Fred E. Arnold
WL/MLBP

ACKNOWLEDGMENTS

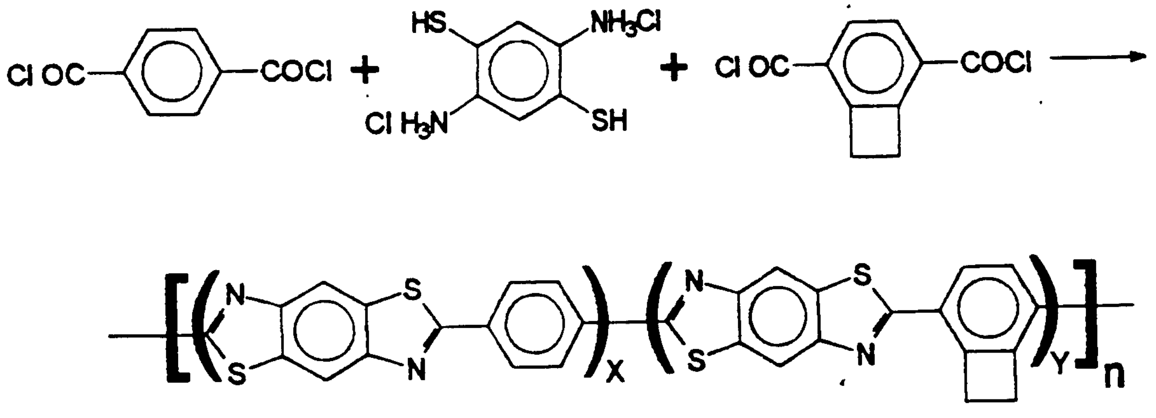
I would like to thank everyone at Wright Laboratory polymer research branch for their assistance and kindness. Special thanks go to Thuy Dang and Jerry Burkett for their guidance.

TASK ASSIGNMENT

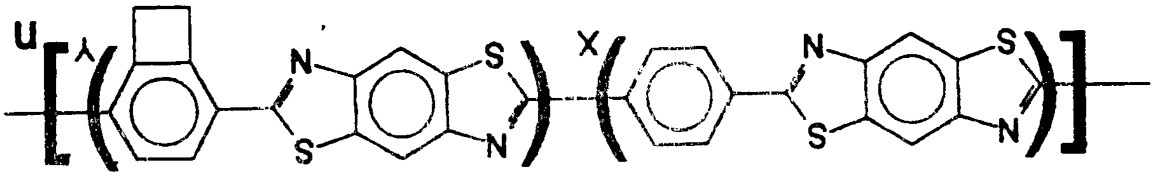
In this study, poly(p-phenylene benzobisthiazole) (PBT) polymers with benzocyclobutene (BCB) crosslinking moieties were prepared. Rigid-rod benzobisazole polymers demonstrate excellent modulus and tensile strength, but lack essential compressive properties for advanced structural composites. The poor axial compressive strength of these polymer fibers is believed to be due to insufficient lateral interactions between the supramolecular structures, causing them to buckle under an axial compressive load. To improve fiber axial compressive strength, many approaches have provided little success. However, the most promising approach to provide permanent lateral support to the supramolecular structures appears to be chemical crosslinking. Crosslinking between benzocyclobutenes is known to be an addition reaction that does not produce volatiles. The object is to investigate the significance of chemical crosslinks through addition reactions on the fiber axial compressive strength of rigid-rod polymers.

PROCEDURE

The preparation of the benzocyclobutene-polybenzobisthiazole (BCB-PBT) homopolymer and copolymers were carried out in polyphosphoric acid at 10 weight % concentration. High molecular weight rigid-rod polymers were synthesized from the polymerization of 2,5-diamino-1,4- benzenedithioldihydrochloride and 1,2-dihydrocyclobutabenzene-3,6-dicarbonyl dichloride.



These monomers were heated in 77% polyphosphoric acid (PPA) at 65°C for 24 hours to remove hydrochloric acid from the amine monomer. Also, to help removal of the HCl, nitrogen at a pressure of 60 mmHg was applied to the system. After dehydrochlorination was complete, the temperature was lowered to 50°C and phosphorous pentoxide was added under a nitrogen atmosphere to bring the PPA concentration up to 82-84%. The reaction mixtures were slowly heated to 140°C and remained at this temperature for 16 hours. This mixture was then cooled to room temperature. As with all polymerization reactions, aliquot samples were removed for determination of intrinsic viscosity. The rest of the sample is used for dry-jet wet spinning. The polymer reaction mixture showed lyotropic behavior as evidenced by persistent stir-opalescence and birefringence as observed under a microscope. Stir opalescence occurs when the polymer is heated at its highest temperature upon formation. It appears as a glowing and shiny metallic or even fluorescent mixture. However, temperatures above 140°C produced gels. Gels are an unwanted product of the polymer and occur from improper structuring.



Polymer mole % X Y	Polymer Conc. Wt %	Reaction Temperature (°C)	Intrinsic Viscosity (dl/g)
0 100	10	160	gels
0 100	10	140	35.0
50 50	10	160	gels
75 25	10	140	24.0

BCB-PBT homopolymer and copolymer (75/25) were spun into fibers by a dry-jet wet spinning process. Before mechanical evaluation, the fibers are soaked in distilled water to remove excess acid, air-dried, then heat treated at 330°C and 450°C for a length of time. (See table below)

Homopolymer	Length (in)	Tensile Strength (Ksi)	Compressive Strength (Ksi)
450°C/30 sec	1	430	15
450°C/30 sec	3	387	
450°C/30 sec	5	309	
330°C/20 min	1	317	70
330°C/20 min	3	300	
330°C/20 min	5	375	
Copolymer	Length (in)	Tensile Strength (Ksi)	Compressive Strength (Ksi)
330°C/10 min	1	339	18
330°C/10 min	3	335	
330°C/10 min	5	345	
330°C/20 min	1	448	16
330°C/20 min	3	427	
330°C/20 min	5	348	

CONCLUSION

The tensile properties of these fibers are comparable to those of regular PBT fiber itself. The BCB-PBT homopolymer fiber heat-treated at 450°C has a very low axial compressive strength, only 15 Ksi, while the heat treated at 330°C has an axial compressive strength about twice as high as regular rigid-rod PBT fibers. This improvement in axial compressive strength of the BCB-PBT homopolymer heat-treated at 330°C compared to regular PBT may be due to the formation of chemical crosslinking. However, the low axial compressive strength of BCB-PBT copolymer may have resulted from undesirable reactions that occurred during heat treatment.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS FOR INTRINSIC CONDUCTING SYSTEMS

Task Order No. 108a
Student Support Program
Southwestern Ohio Council for Higher Education

Leslie M. Tack
Wright State University

14 July 1995

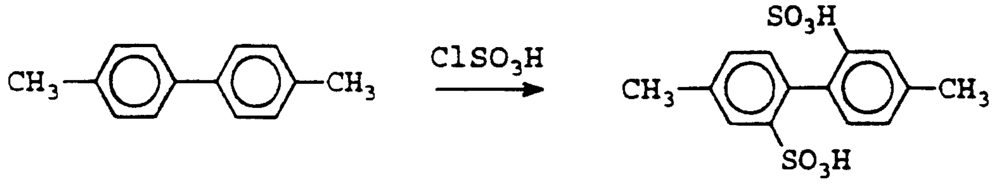
Government Task Leader
Dr. Fred E. Arnold
WL/MLBP

ACKNOWLEDGMENTS

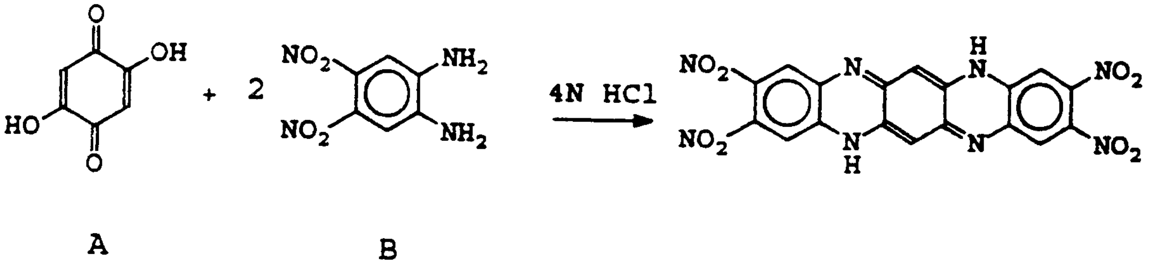
Special thanks goes to Dr. Fred E. Arnold and Mr. Thuy D. Dang.

TASK ASSIGNMENT

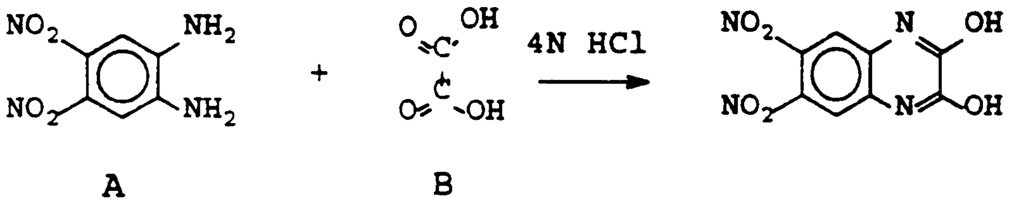
Throughout the past 6 months many reactions were performed in an attempt to produce not only polymers, but also monomers suitable for use in the synthesis of polymers. The experimental procedure for several of these reactions is as follows:



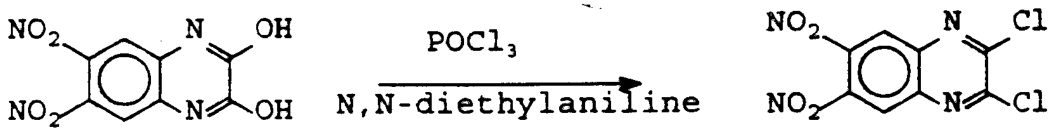
Into a round bottomed flask equipped with a stir bar was added 10.0g (0.05 mol) of 4,4' dimethylibiphenyl and 30ml of CLSO3H. After adding a condenser and a nitrogen inlet/outlet, the reaction mixture was refluxed at 140°C for 3 hours. After cooling to room temperature, the mixture was poured over ice and filtered to afford the product.



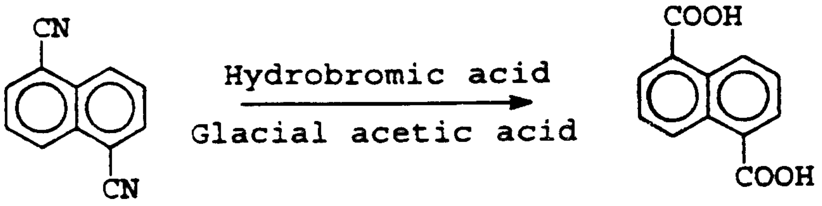
Into a round bottom flask with a stir bar was place 1.401g (0.01 mol) of compound A, 3.9628g (0.02 mol) of compound B and 100mL of 4N HC1. After cooling to room temperature, the mixture was filtered and the product was washed with water. To purify, the product was recrystallized using about 400mL of 2-propanol. Melting point: +400°C.



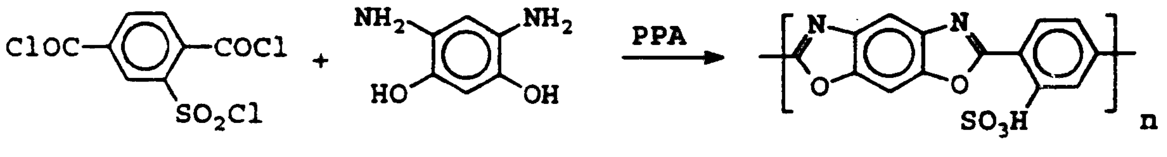
Into a round bottom flask with a stir bar was placed 10g (0.05 mol) of compound A, 4.544g (0.05mol) of compound B and 200mL of 4N HCl. The reaction mixture was refluxed overnight and then allowed to cool. After cooling, the reaction mixture was filtered and washed with water. 7.88g of product was produced giving a yield of 62.5%. The melting point was 384° - 386°C.



Into a round bottom flask with a stir bar was placed 7.75g (0.03 mol) of the starting material, 22.37 mL POCL$_3$, and 4.89mL of N,N-diethylaniline. The mixture was refluxed for 3 hours. After cooling to room temperature, the solution was poured into 100mL of ice water and filtered. The reaction produced 7.68g of product giving a crude yield of 86.4%. The melting point was 199-206°C. The product was purified using benzene.



Into a round bottom flask with a stir bar was placed 7.19g (0.04 mol) of 1,5-dicyanonaphthalene, 50mL of hydrobromic acid, and 100mL of glacial acetic acid. The mixture was refluxed for 2 days. After cooling, it was filtered and washed with ether. The product, was purified using hot toluene, and then dried overnight in the drying pistol. 6.73g of the diacid product were produced (77.8% yield).



A

B

Into a flask with a mechanical stirrer and a nitrogen inlet/outlet, was placed 4.4035g (0.02 mol) of compound A, 3.116g (0.02 mol) of compound B, and 22.45g of 77% polyphosphoric acid (PPA). The mixture was heated at 160°C for several days with constant stirring. The resulting polymer was precipitated in water, broken up with a blender, and collected by suction filtration. Then, it was washed with water by soxhlet extraction, and dried in a drying pistol overnight. An intrinsic viscosity of 1.19 dl/g was obtained in methane sulfonic acid at 30°C.

Various tests were performed on both monomer and polymer compounds to determine their chemical makeup and thus the success of the reaction. Melting points were used to characterize the compounds in terms of thermal stability. The actual chemical composition was determined in several ways: IR, NMR, and mass spectra and elemental analysis.

The IR spectrum is obtained when an infrared beam is passed through a thin sample of compound. The beam is absorbed at different wavelengths. This absorption causes the bonds in the compound to stretch or bend, forming peaks on the spectrum. These peaks correspond with known peaks for different organic functional groups.

The NRM spectrum involves the use of a magnetic field to detect where hydrogen atoms are located in the compound being sampled. The hydrogen atoms of different functional groups absorb energy from the magnetic field to form different peaks in the spectrum. These peaks can be compared to the known values for each functional group to determine not only the location of the hydrogen atoms, but also the number of hydrogens at each location.

The mass spectrum is used to determine the molecular weight of the sample being tested. The sample is bombarded with high-energy electrons. This removes a valence electron and a cation radical is produced. Due to the large amount of energy transferred to the cation, it fragments into smaller pieces. These fragments pass through a magnetic field and are deflected according to their mass to charge ratio. Since the charge is usually equal to one, the mass of the fragments is automatically known. This is then used to find the molecular weight of the entire compound.

The final method for determining the composition of a compound is elemental analysis. Elemental analysis determines the percent composition of each type of atom. These values can be compared to the calculated theoretical percentages.

SYNTHESIS OF AROMATIC AND AROMATIC-HETEROCYCLIC COMPOUNDS FOR NONLINEAR OPTICAL PROPERTY EVALUATION

Task Order No. 109
Student Support Program
Southwestern Ohio Council for Higher Education

Gina Hess
Wright State University

14 June 1995

Government Task Leader
Mr. Bruce Reinhardt
WL/MLBP

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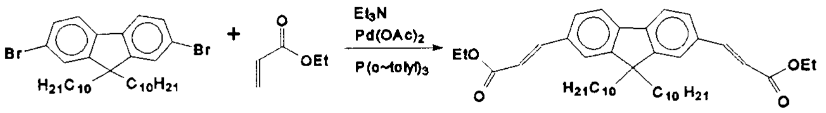
TASK ASSIGNMENT

The purpose of this Task was to synthesize new molecules for possible application in the area of electro-optic modulation, frequency doubling, all-optical switching and two photon pumped upconverted lasing. Second-order nonlinear effects are best seen in asymmetric molecules with long chains of conjugation. Molecules with long conjugated chains and easily polarizable bond structures are suited for third-order effects. The following is a summary of some reactions performed over the past year in an attempt to synthesize such nonlinear materials.

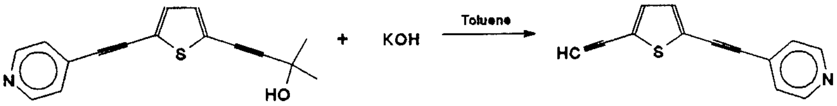
Experimental Procedures:

Experiment 1:



The dibromo compound was dissolved in Et_3N and degassed. The catalysts were included. Ethyl acrylate was also dissolved into Et_3N and then was added dropwise into the reaction mixture. While stirring, the reaction was heated to 80° C for 24 hours. The solution was cooled, filtered, and the residue washed with Et_3N. The Et_3N was distilled off. The first extraction was performed using methylene chloride and a 10% HCl solution. It was then extracted with several portions of water. The methylene chloride was rotoevaporated off and the crude product crystallized upon refrigeration. It was recrystallized from ethanol. Elemental analysis (found %, theoretical %): C- 80.32, 80.33; H- 9.65, 9.72.

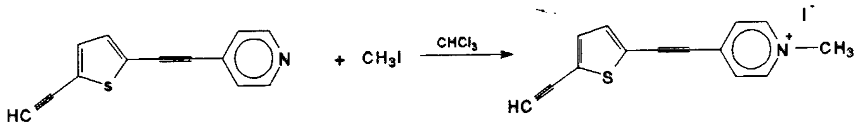
Experiment 2:



(A)

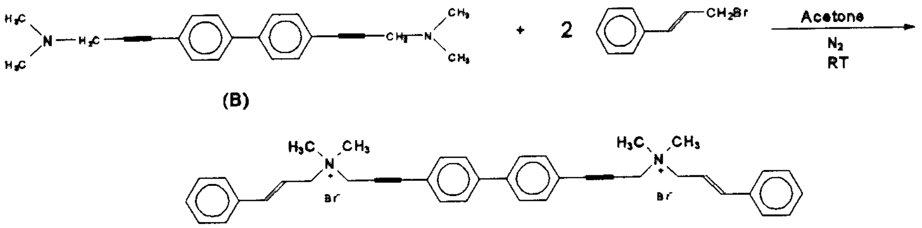
A distillation apparatus was set up to receive (A), KOH in methanol, and toluene. This solution was heated to about 90° C until the methanol and all the acetone formed in the reaction had collected in the receiving flask (about 1.5 to 2 hours). The toluene was removed under vacuum, and the reddish residue was purified by chromatography on silica gel using 2:8 THF/hexane. The product had a light yellow color. Yield: 72.7%.

Experiment 3:



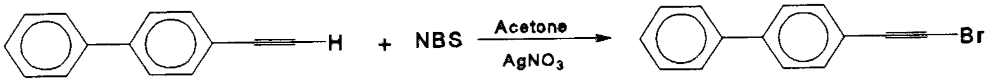
The ingredients were combined in a round bottom flask and stirred at room temperature until the product precipitated. The salts were filtered, placed into ether, and the ether was boiled. The product was filtered again and air dried. Yield: 96.0%.

Experiment: 4



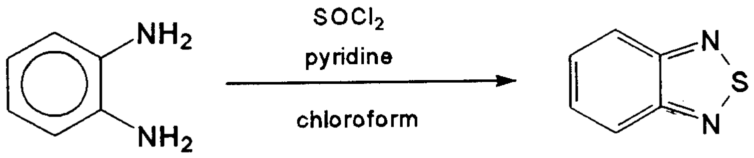
The starting material, (B), was dissolved in acetone and degassed. Cinnamyl bromide was added with stirring, and the mixture was heated to reflux for 2 hours. The resulting filtrate was chopped in a blender and filtered. It was then rinsed with acetone and dried in a desiccator. Yield: 92.7%.

Experiment 5:



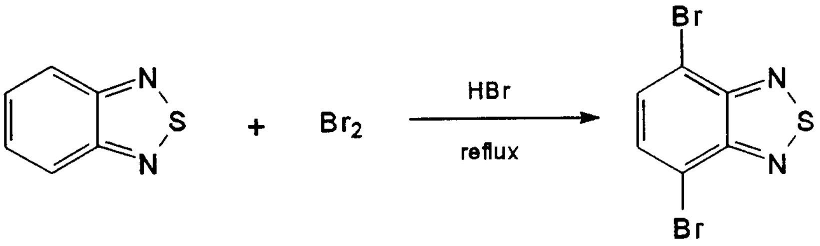
The biphenyl compound was dissolved in acetone, and NBS was added while stirring. Before adding silver nitrate, the solution was cooled. It was then allowed to warm to room temperature, and stirring continued overnight. The solution was poured into ice water, and the precipitate which formed was filtered and dried. The solid was stirred into methylene chloride, filtered, and rotoevaporated. The yellow product was then dried in a desiccator. Yield: 88.9%.

Experiment 6:



A solution of thionyl chloride in chloroform was added over 15 minutes to a suspension of o-phenylene diamine in chloroform and pyridine. For 15 minutes the solution refluxed, and the chloroform was distilled off. The brown solid was stirred in water and filtered. It was then refluxed in acetone, and filtered again. After rotoevaporating the acetone away, the residue was refrigerated; crystals formed and were purified by sublimation.

Experiment 7:



To a mixture of benzothiadiazole and HBr, Br_2 was added dropwise while stirring. When all the bromine had been added, the mix was refluxed for 2 hours. The solid which had formed was filtered and stirred with water. After filtering again, it was recrystallized from ethanol. The crystals were cream-colored needles. Yield: 36.1%.

CONCLUSION

The above reactions and their procedures are a sampling of the work accomplished in the past year. None of these products were nonlinear materials, but rather were used as intermediate steps in more complicated reaction schemes.

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LIQUID LUBRICANTS

Task Order No. 110
Student Support Program
Southwestern Ohio Council for Higher Education

Amy T. Neidhard
Wright State University

30 June 1995

Government Task Leader
Ms. Lois Gschwender
WL/MLBT

ACKNOWLEDGMENTS

Certain individuals contributed to the success of the student's Task , through professional guidance, example, and assistance in learning and performing the duties of the assigned Task. Those individuals include Keith Clendenon, George Fultz, Ms. Lois Gschwender, Ron Mortimer, Dr. Harvey Paige, Bruce Schreiber, Ollie Scott, Dr. Shashi Sharma and C. E. Snyder. Their appreciated efforts contributed to the success of the job and provided the student with retained scientific knowledge.

TASK ASSIGNMENT

The Task involved research and development of the Oxidation Absorption (Ox Ab) test system. The Ox Ab system is based upon the principle of measuring the degradation of a sample fluid lubricant under the external influence of elevated environmental temperature and exposure to gas flow, consisting of oxygen.

The Ox Ab apparatus was previously constructed by and purchased from the Phoenix Chemical Laboratory in Chicago, IL. Tests were run with the system in past years; the goal of the current Task was to reestablish a working system. The apparatus consists of an intricate arrangement of glass reaction cells, bulbs, and traps (See Figure 1) which is "monitored and controlled" by two autonomous instrumentation systems: a pneumatic measurement and control system and an electrical measurement and control system, the former consisting of three subsystems: an oxygen charging system, an oxygen metering system, and a sample exposure system (Krawetz, Page 1).

A sample fluid lubricant is placed within the primary reaction cell, which in turn is heated by a furnace-driven oil bath and exposed to a current of oxygen gas. As the sample fluid lubricant becomes heated, oxidation (or degradation) occurs, the partial pressure of oxygen within the system is reduced, and products of carbon dioxide and water are released into the system. The purpose of the condenser and various other ambient, cold, and absorption traps is to maintain the sample fluid lubricant within its reaction cell and reduce the amount of carbon dioxide and water within the system.

The reduction in the partial pressure of oxygen results in the alteration of the fluid level monitored by photoelectric receivers and scanners, which in turn close an electrical relay. This relay controls a valve which opens to admit more oxygen gas into the test system. An additional relay (also directed by the photoelectric system) controls a valve which opens to vent extraneous pressure to the atmosphere, during warm-up of the system and in the event that pressure within the system increases due to the formation of carbon dioxide and water products.

The purpose of the Ox Ab test system is to measure and record the frequency of the opening of the two valves, described above. By analyzing the results, the characteristics of a given sample fluid lubricant with regard to oxidation at discrete temperatures, and the speed of such a reaction, can be determined. More specifically, a high frequency of valve openings to admit oxygen would indicate rapid sample fluid lubricant degradation with respect to other tests. Likewise, a high frequency of valve openings to vent the system would imply warming of the system with respect to temperature and the high tendency of the sample fluid lubricant to yield products during degradation. The behavior of the valves is monitored in conjunction with thermocouple readings from the furnace bath and ambient air, to analyze the sample fluid lubricant's reaction with respect to temperature (temperature commonly serves as a catalyst to the oxidation of the lubricant).

DESCRIPTION OF RESEARCH

The research conducted consisted of learning the chemical and electronic principles of Ox Ab system and reestablishing a working system. The relays which control the above discussed valves, as well as the thermocouples, must be wired to a data logger to record the frequency of valve operation and temperature, respectively. The Ox Ab system previously employed a Rustrak Ranger data logger, but reliability problems constituted the implementation of a more sophisticated Squirrel data logger. A significant amount of time was devoted to increasing the compatibility of the Squirrel data logger with the Ox Ab system.

Specifically, a 15-pin female to 25-pin female connector cable was ordered to interface the relays with two event channels of the Squirrel data logger and a termination panel (with screw-down terminals for wires). A voltage divider circuit was additionally designed for insertion between the relay signal and the termination panel due to the discovery that the voltage measured across the relay was twice the maximum voltage input to the Squirrel data logger. The designed interface system will be operational upon the arrival of the ordered components.

RESULTS

The Ox. Ab. system was tested for functional mechanical and electrical operation and reestablished for data-collection during the Task. However, tests on specific sample fluid lubricants were not performed. An additional employee, involved in reestablishing the Ox Ab system, was assigned the task of performing Ox Ab tests upon the finalization of an upcoming government contract with a fluid lubricant vendor.

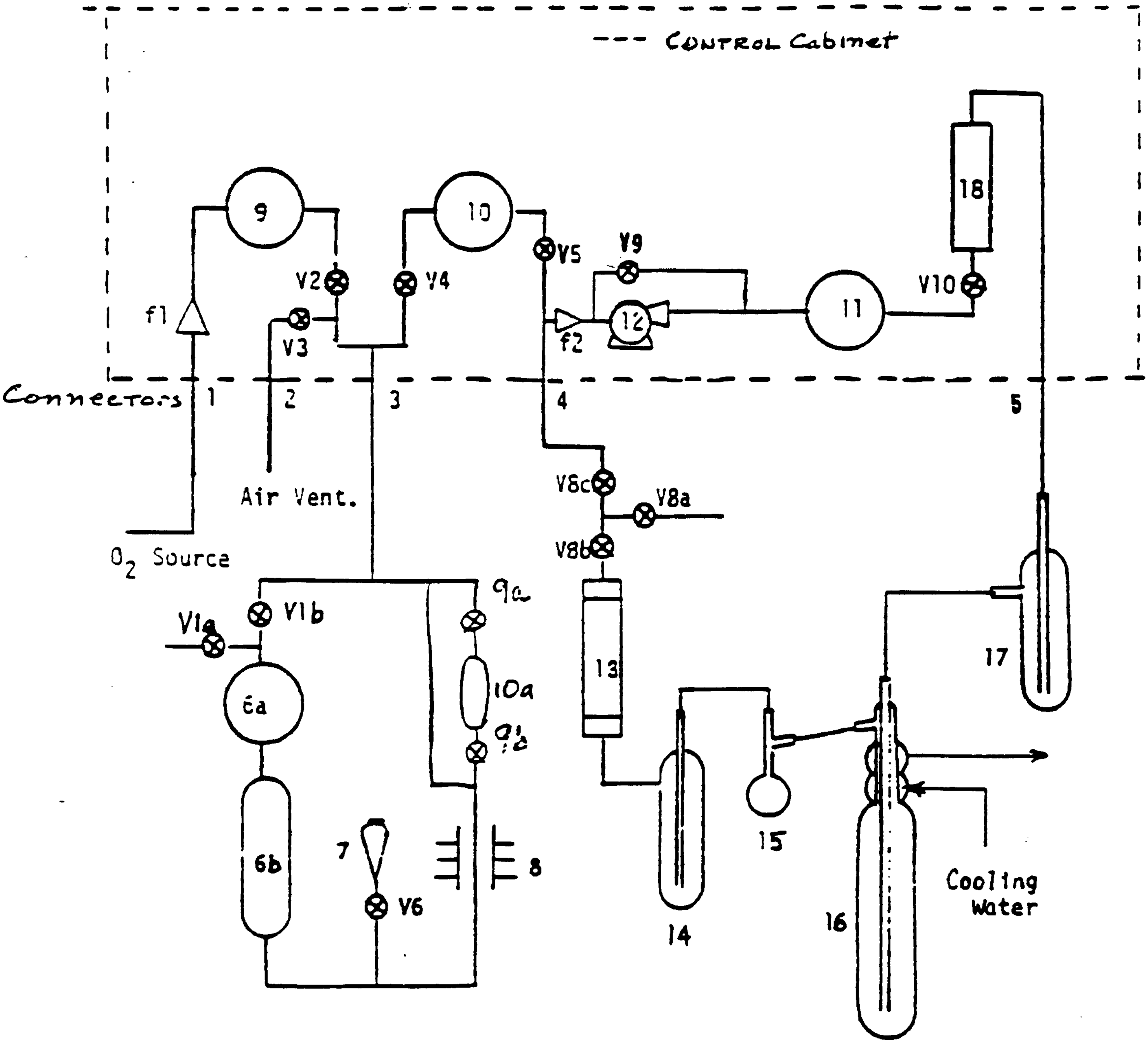


Figure 1: Apparatus for Oxidation Absorption System
(Krawetz, Pages 3-4)

KEY FOR FIGURE 1

1 - To oxygen source.
2 - To atmospheric ventilation.
3, 4, 5 - Connections between pneumatic systems inside and outside of control unit.
6a, 6b - Balancing bulbs: 6a, surge space and 6b, expansion.
7 - Leveling bulb.
8 - Photoelectric system.
9 - Surge bulb.
10 - Expansion bulb 10, resevoir.
10a - Auxiliary bulb (used for testing sensitive samples).
11 - Expansion bulb 11, resevoir.
12 - Circulation pump.
13 - Absorber.
14 - Cold trap.
15 - Ambient trap.
16 - Reaction cell.
17 - Ambient trap, reaction cell.
18 - Flowmeter.

V0 - Oxygen regulator.
V1a - System balancing valve.
V1b - Atmospheric balancing valve.
V2 - Oxygen solenoid valve (NC).
V3 - Air ventilation solenoid valve (NC).
V4, V5 - Oxygen evolution solenoid valves (NO).
V6 - Leveling valve.
V8 - Purge valve Assembly.
V9 - Bypass valve.
V9a, V9b - Auxiliary valves for 10a isolating bulb.
V10 - Flow control valve.
V11 - Pump isolation valve.

f1 - Filter #1
f2 - Filter #2

References:

Krawetz, Arthur A. Manual for Operation of Oxygen Absorption Apparatus. Chicago, IL: Phoenix Chemical Company, Inc., 1991.

LIQUID LUBRICANTS

Task Order No. 110a
Student Support Program
Southwestern Ohio Council for Higher Education

Matthew Argenbright
University of Dayton

30 June 1995

Government Task Leader
Ms. Lois Gschwender
WL/MLBT

ACKNOWLEDGMENTS

The success of the Task can be contributed to the following individuals who, through professional assistance and guidance, led to a successful Task. Those individuals are Keith Clendenon, George Fultz, Ms. Lois Gschwender, Dave Hahn, Ron Mortimer, Dr. Harvey Paige, Bruce Schreiber, Ollie Scott, and C. Ed Snyder.

TASK ASSIGNMENT

The Task involved research in the studies of stability and degradation of perfluoropolyalkylethers(PFPAE) and other related fluids, both with and without performance improving additives. The Task also included establishing evaluation protocol and data gathering procedures for an oxygen absorption apparatus and then to evaluate the performance of the apparatus using a stable hydrocarbon and finally studying the degradation of an ester using the oxygen absorption apparatus.

OXIDATION CORROSION CONDUCTIVITY

The research of the PFPAE's and related fluids was conducted using an Oxidation Corrosion Conductivity (OCC) testing method. The OCC method utilizes five measurable parameters in determining fluid lubricant breakdown. The parameters are: weight change of metal specimens, weight loss of lubricant sample, viscosity change of lubricant sample, acid number of lubricant sample, and conductivity of secondary cell (test beaker). The test involves the polishing and weighing, to the nearest 0.00001g, of five ferrous or titanium based metal specimens. The metal specimens are placed on an air tube (Figure 1) which is then inserted into an OCC tube. This is weighed to the nearest 0.05g. Then 6mls of the fluid lubricant sample are placed inside the OCC tube which is then weighed again to obtain the weight of the fluid sample. The enclosed OCC tube is connected to a secondary cell. The secondary cell contains both double distilled water and a conductivity probe. The air flowrate and bath temperature are set prior to the test. The test begins when the air tubes are connected to the tanks and air is circulated through the fluid and bubbles out through the distilled water. The test is allowed to run for 24 hours. The data acquisition system is started at the beginning of the test.

In determining the results of an OCC test, the five measurable parameters are evaluated again for any deviation from the pre-test results. For example, if the metal specimens weight change is greater than ± 0.2 mg/cm^2 than this would denote a test failure. The fifth parameter, conductivity, is shown to give an indication when fluid lubricant breakdown starts to occur. The air flowing through the lubricant removes effluent gases generated during fluid breakdown. The gases are circulated into the distilled water. Upon mixing with the distilled water, ions are formed and the water becomes conductive. With the increase in the breakdown of the fluid and the generation of more ions, the distilled water becomes more conductive, which is measured by the probe.

$$3\ COF_2 + 3\ H_2O\ \ 6\ HF + 3\ CO_2$$
$$SiF_4 + 4\ H_2O\ \ \ 4\ HF + Si(OH)_4$$
$$2\ BF_3 + \ 6\ H_2O\ \ 3\ HF + H_3BO_3$$

The data acquisition system continually reads the conductivity vs. time. This data is gathered and converted into a Microsoft Excel graph. The data and the graph are then studied to determine the characteristics of the fluid and evaluate the performance of additives, if used. The graph could illustrate that the fluid might undergo an initial induction period as is Fomblim Z fluid MLO 78-80 (Figure 2) at 245°C or that the fluid oxidizes almost immediately as with Demnum S65 fluid MLO 94-62 (Figure 3) at 330°C. The performance improving additives added to base stocks like MLO 94-62 are designed to improve oxidative stability by either creating an induction period or improving upon the inherent one. MLO 94-153 (Figure 4) shows the base stock MLO 94-62 with a 1% perfluoroalkyl substituted diphenyl ether additive at 330°C. Clearly, the graph shows the additives antioxidant capabilities. Subsequently, the experiment temperature is increased to 345°C. More ions are formed and at an earlier time. This can be shown in Figure 5. It shows MLO 94-153 at 345°C up from the previous 330°C. The conductivity sharply increases and the metal specimen weight change denotes a test failure.

The task of performing research on the stability and degradation of perfluoropolyalkylethers and related fluids, with and without performance improving additives, has led to an understanding of the behavior of fluid lubricants during oxidation.

OXYGEN ABSORPTION APPARATUS

The Oxygen Absorption Apparatus (Figure 6) is a test method in which the oxidation characteristics of a sample fluid are derived. The test relies on the principle that when a fluid oxidizes, it consumes oxygen. The test measures the direct amount of oxygen consumed by the fluid during the testing period. The test is performed by placing a fluid sample in the reaction cell. Once the reaction cell is placed back onto the apparatus, a closed test loop is completed. The test loop is then pressurized about 1-2 torr above ambient with oxygen. This pressurized gas is circulated through the loop by a diaphragm pump. In similarity to the OCC test, the Oxygen Absorption test method also thermally stresses the fluid being tested. This stressing causes the fluid to oxidize thus consuming the oxygen inside the test loop. The test loop is connected to a manometer monitoring system which detects this consumption of oxygen by the decrease in pressure in the test loop. The manometer system is monitored by photoelectric sensing detectors. These detectors, when activated, can trigger either an event that introduces the same amount of oxygen consumed back into the system or it can relieve the test loop of overpressurized gas by venting. Overpressurization and venting should only occur during heating of the sample cell at the start of the test.

The Task involved the implementation of a data recording device and the establishing of a testing procedure. The data gathering device is a series 1200 Grant Squirrel Logger. Prior to being electronically gathered, data was taken off a Rustrak chart recorder. The new Squirrel logger was directly connected to the apparatus and information was stored and transferred to a computer integration program. With this program, the data could easily be transferred to either a QP4 or Excel graph program and interpolated. After the logger was fitted to the oxygen absorption apparatus, it was then necessary to establish a testing procedure. This was primarily done through day to day familiarization of the apparatus and consulting previous operating manuals. An initial procedure was established though it would be continually modified with subsequent modifications in the apparatus.

The long-term goal of the oxygen apparatus program was to re-establish a working system using a stable hydrocarbon as the initial testing fluid and to develop glassware and procedure for taking fluid samples during the test to conduct analyses on these samples. Once a repeatable system was developed, the program would then move to testing a known ester, pentaerythritol tetraheptanoate, and then test newly developed ester based lubricants. The goal of re-establishing a working system was completed and a repeatable system was obtained. A stable hydrocarbon, hexadecane, was used initially in all tests performed. Figure 8 shows the results from the oxygen absorption runs using hexadecane and the oxygen consumed under different temperatures. Once the system showed good results, it was evaluated by an independent consultant who recommended changes to the system eliminating as much system volume as possible. These changes were to increase its sensitivity due to the nature of the esters being tested and short test times, looking at just the initial oxidation period. Figure 7 shows the modified glassware configuration. The ambient and cold traps were eliminated to reduce system volume. As well as making modifications in the glassware, it would also be necessary to initiate another intermediate and post-test evaluation in determining the oxidization of the lubricants being tested. The new test would determine quantitatively analyze the hydroperoxide formed during the oxidation of the fluid. Peroxides are the primary oxidation products formed when both the hexadecane and the ester based fluids are oxidized. The peroxide test would help in determining the kinetic oxidation rate of the fluid by analyzing the rate of peroxide forming in the fluid. Significant time was spent on determining which procedure would be best for determining the peroxide products. Finally it was suggested that the iodine liberation titration be used. The procedure "Determination of Organic Peroxides by Iodine Liberation Procedures" by Mair and Graupner was used. The titration uses sodium thiosulfate in iodine liberation after the iodine has reacted with the peroxide formed. The titration follows these equations:

$$\mathrm{O{=}COOH + 2e + 2H^{+} \quad O{=}C0H + H2O}$$

$$\mathrm{2I^{-} \quad I^{2} + 2e^{-}}$$

$$\mathrm{I_{2} + 2e^{-} \quad 2I}$$

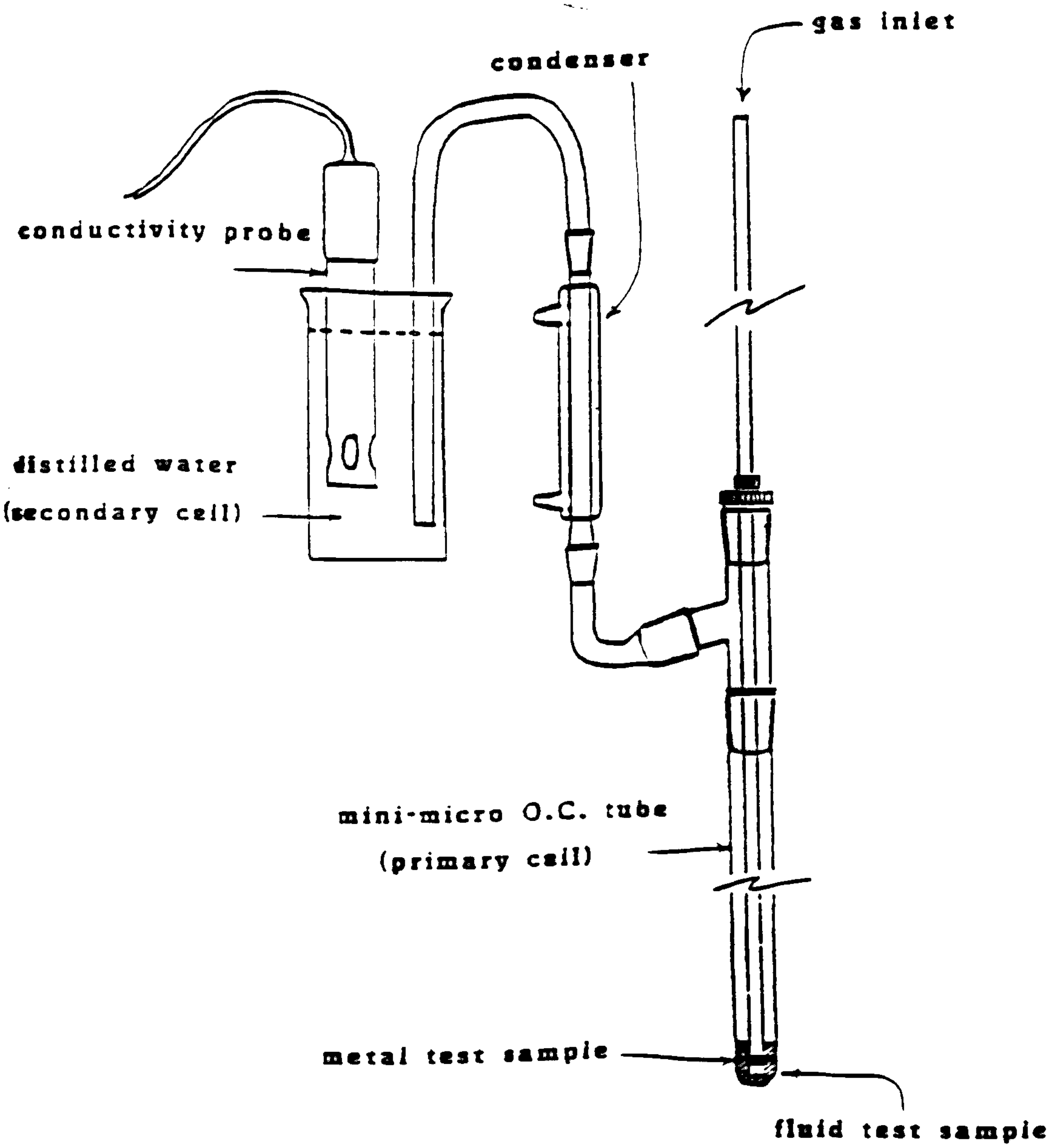
$$\mathrm{2S_{2}O_{3}^{3-} \quad S_{4}O_{6}^{2-} + 2e^{-}}$$

The titration proved sensitive enough in detecting the levels of peroxide that were being generated even at temperature around 150°C. The titration procedure was continually standardized and calibrated using benzoyl peroxide and t-butyl hydroperoxide as standards with known concentrations of peroxide. Figure 9 shows the relative peroxide concentrations for MLO 94-166 (hexadecane) at three different temperatures. The slope of the lines for both the oxygen absorption and the peroxide concentrations, should be approximately equivalent, since 1 mole of oxygen consumed should initially produce 1 mole of peroxide. In the later periods of a test, the peroxide can begin to react again changing the peroxide to other products which then would not obtain the 1 to one ratio peroxide to oxygen. This was evident in a test conducted at 190°C (Figure 10) were the peroxide concentration peaked and then leveled off.

The Oxygen Absorption apparatus has proven to be an effective device in determining the oxidation rates and degradation of fluid lubricants. A great deal of general, lab and technical knowledge has been and will be gained from this project. The testing of the pentaerythritol tetraheptanoate was just getting under way at the end of this contract. Only two tests were performed on this fluid and data is not yet available. The continuation of this contract should lead to extended learning in the oxidation of fluid lubricants by analysis of oxygen absorption and peroxide formation in the ester based fluids.

Apparatus

An OCC Test apparatus is set up in the same general format as a micro-OC Test. The only differences are (Figure 1): the air tight seal at the air tube, a condenser for cooling the sir, the secondary cell containing 150 ml of double distilled water and the conductivity probe. Any apparatus which incorporates these characteristics should be acceptable.



Oxidation Corrosion Conductivity Test Apparatus

Figure 1

FIGURE 2

OCC MLO 78-80 6ml 245°C

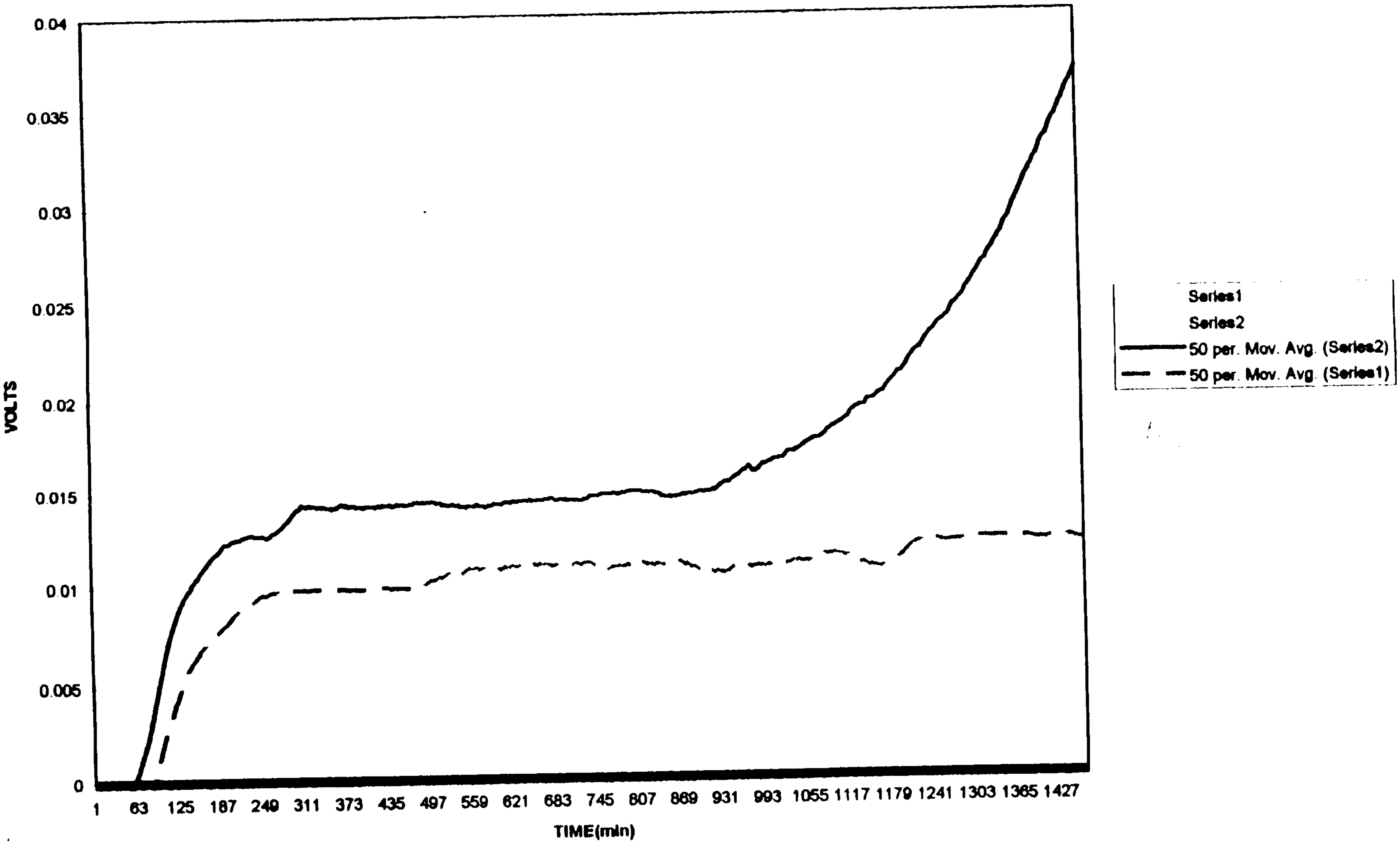


FIGURE 3

OCC MLO 94-62 6ml 330°C

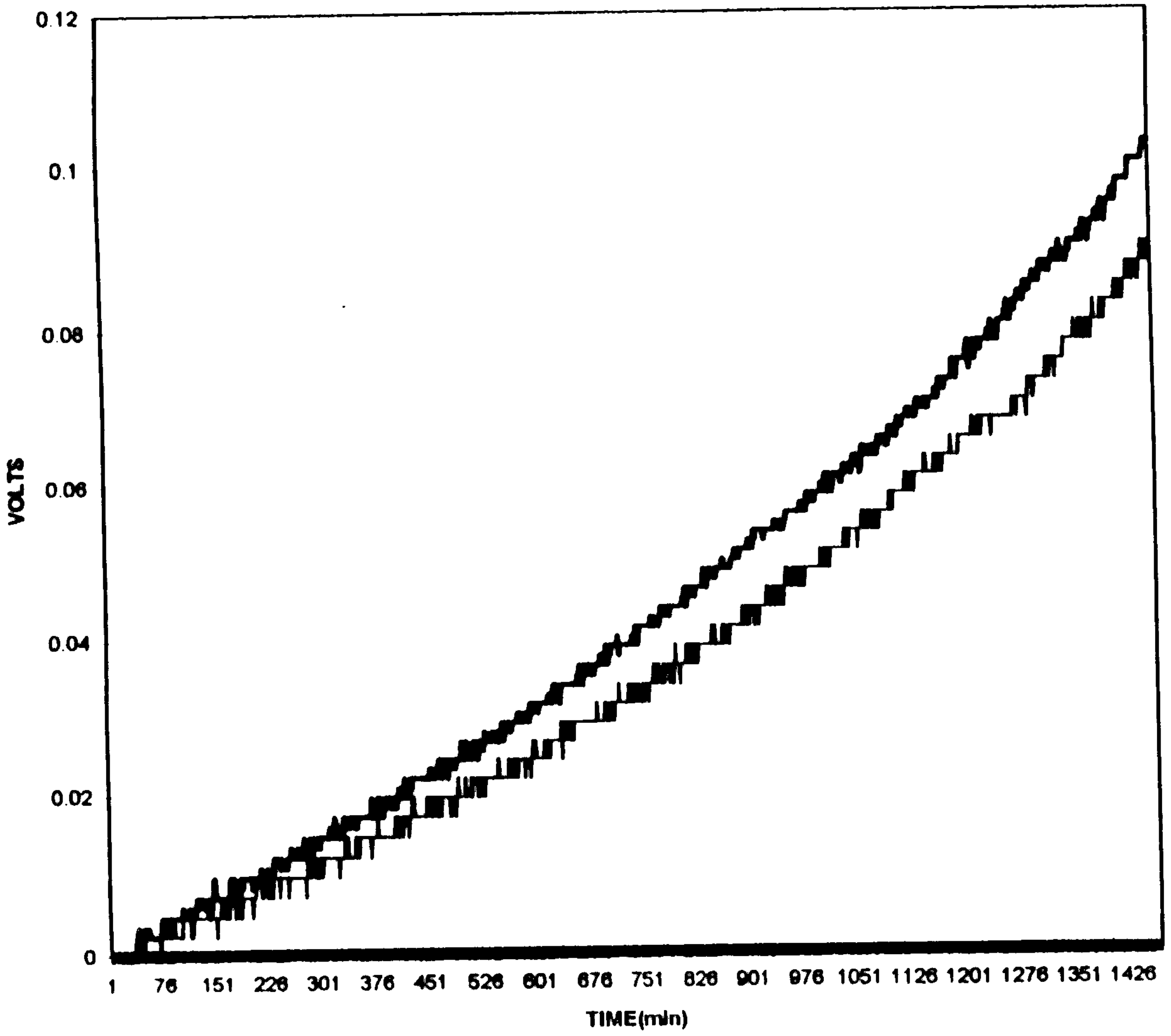


FIGURE 4

OCC MLO 94-153 6ml 330°C

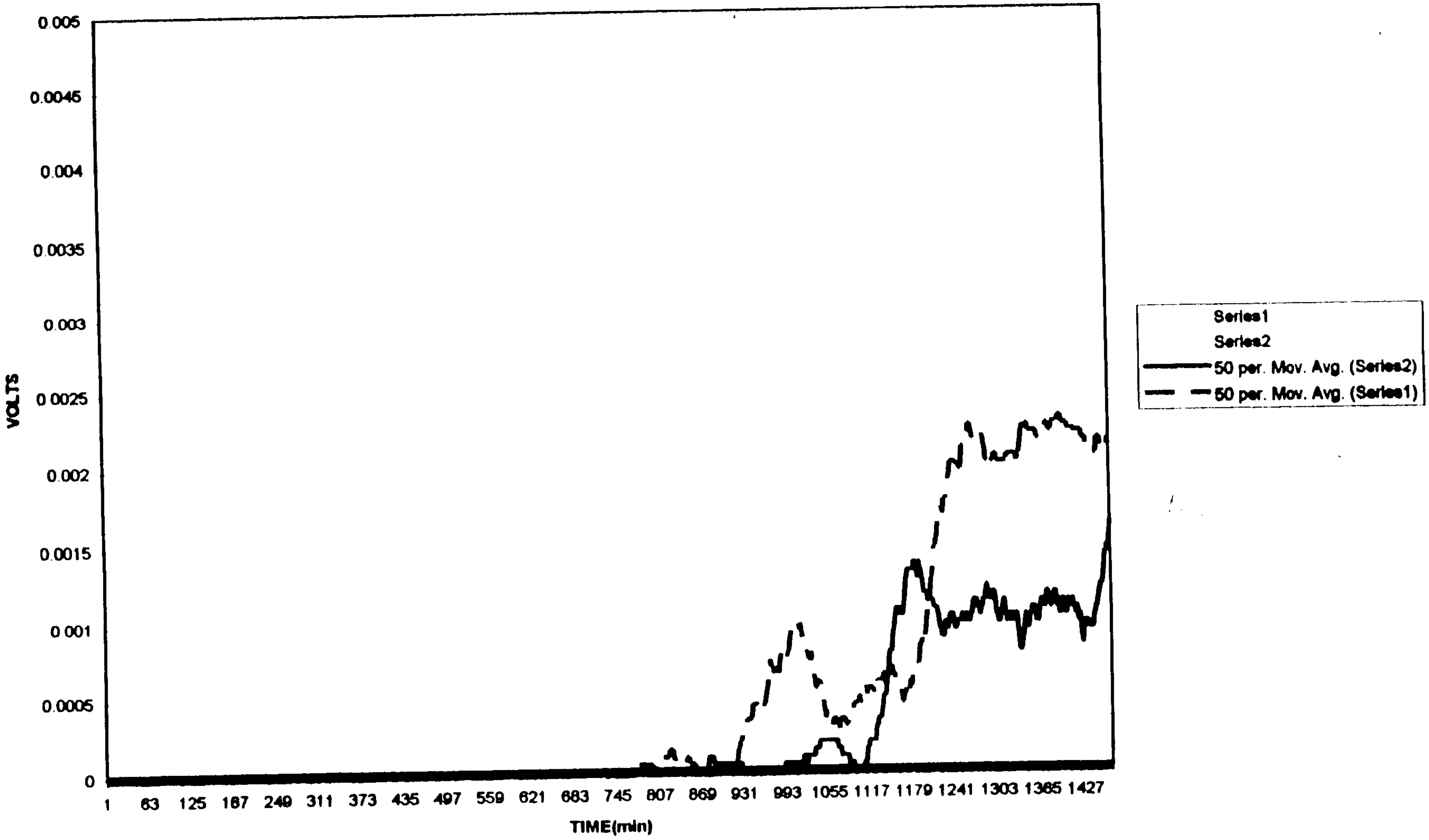


FIGURE 5

OCC MLO 94-153 6ml 345°C

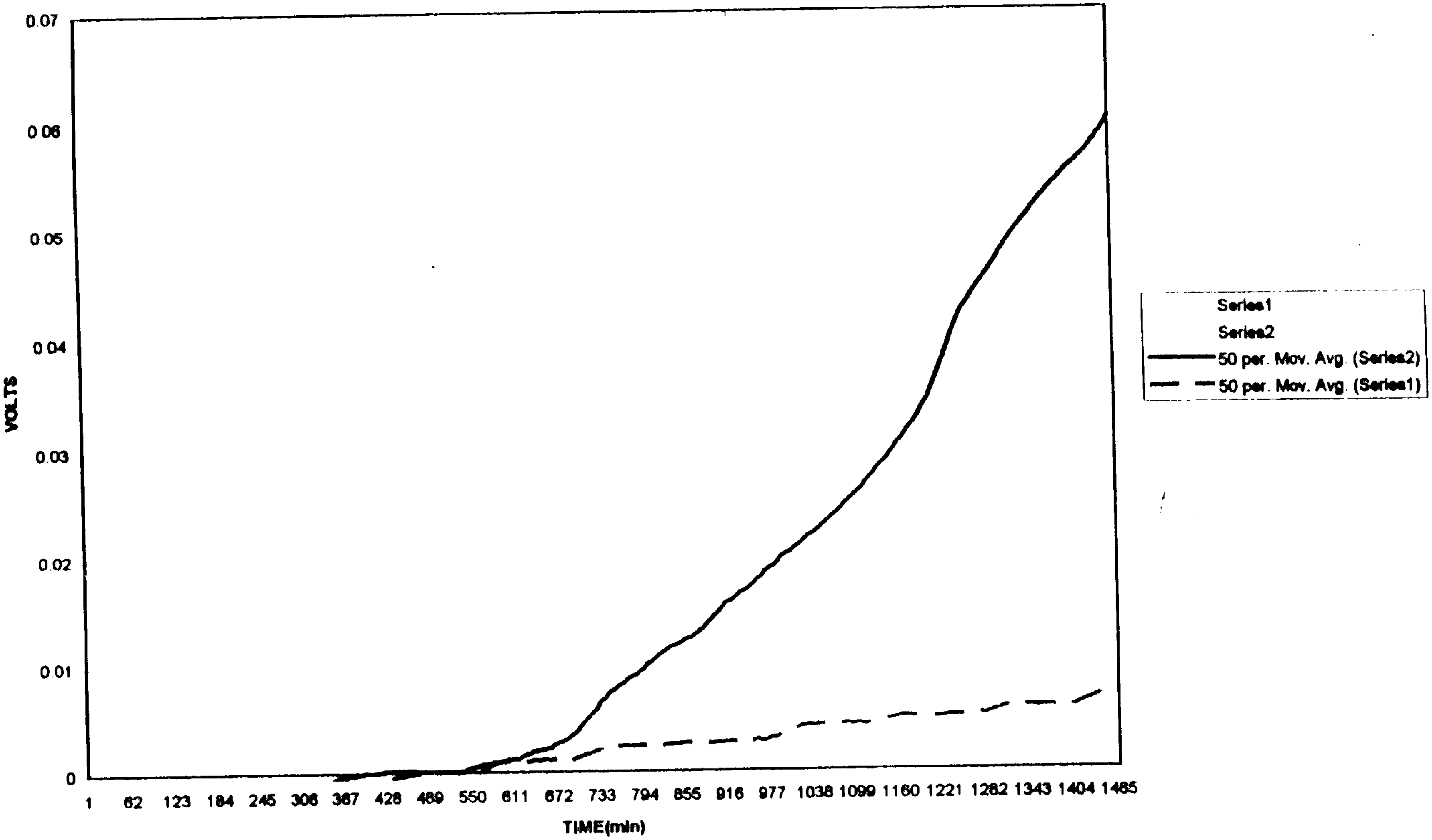
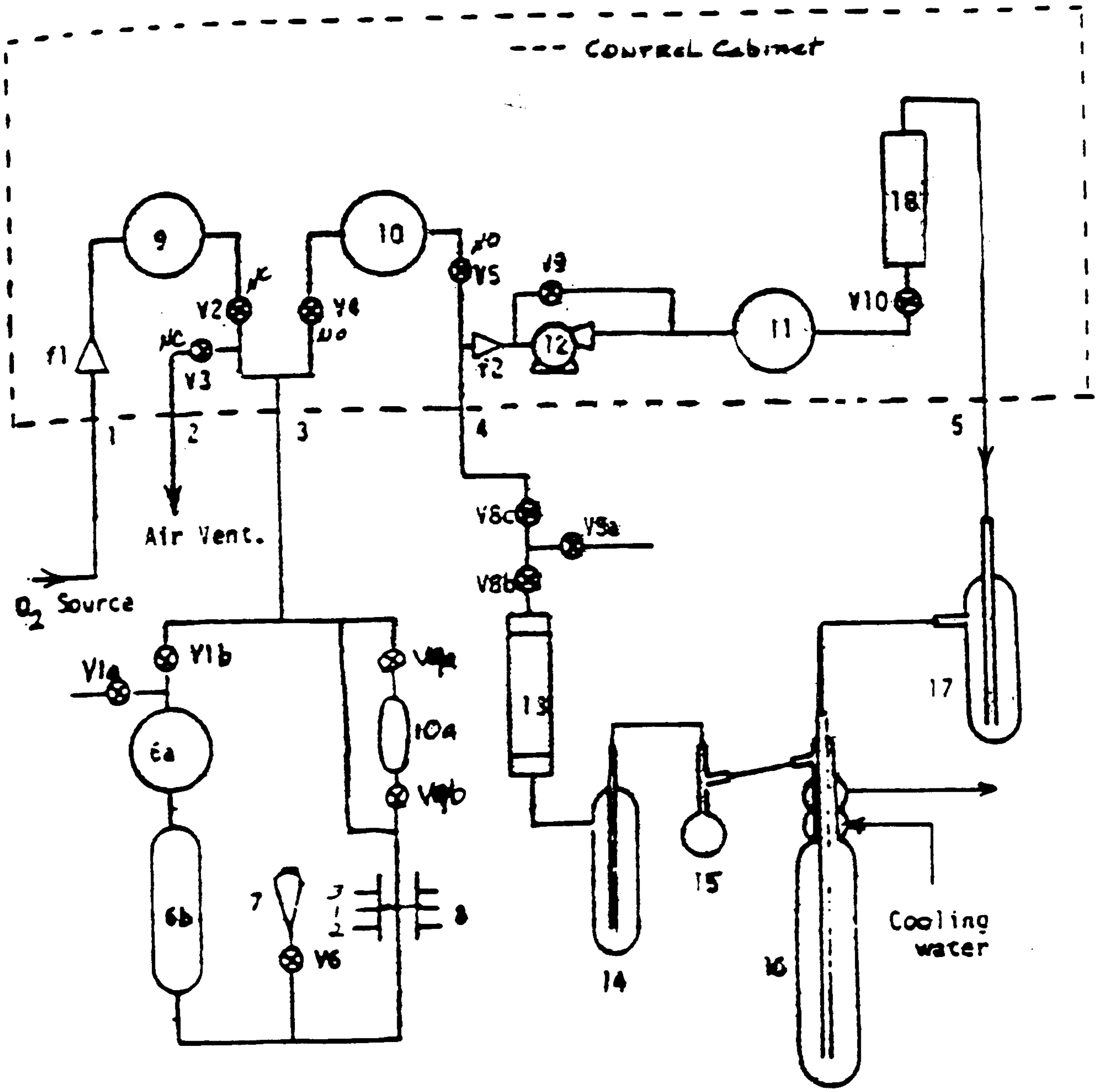
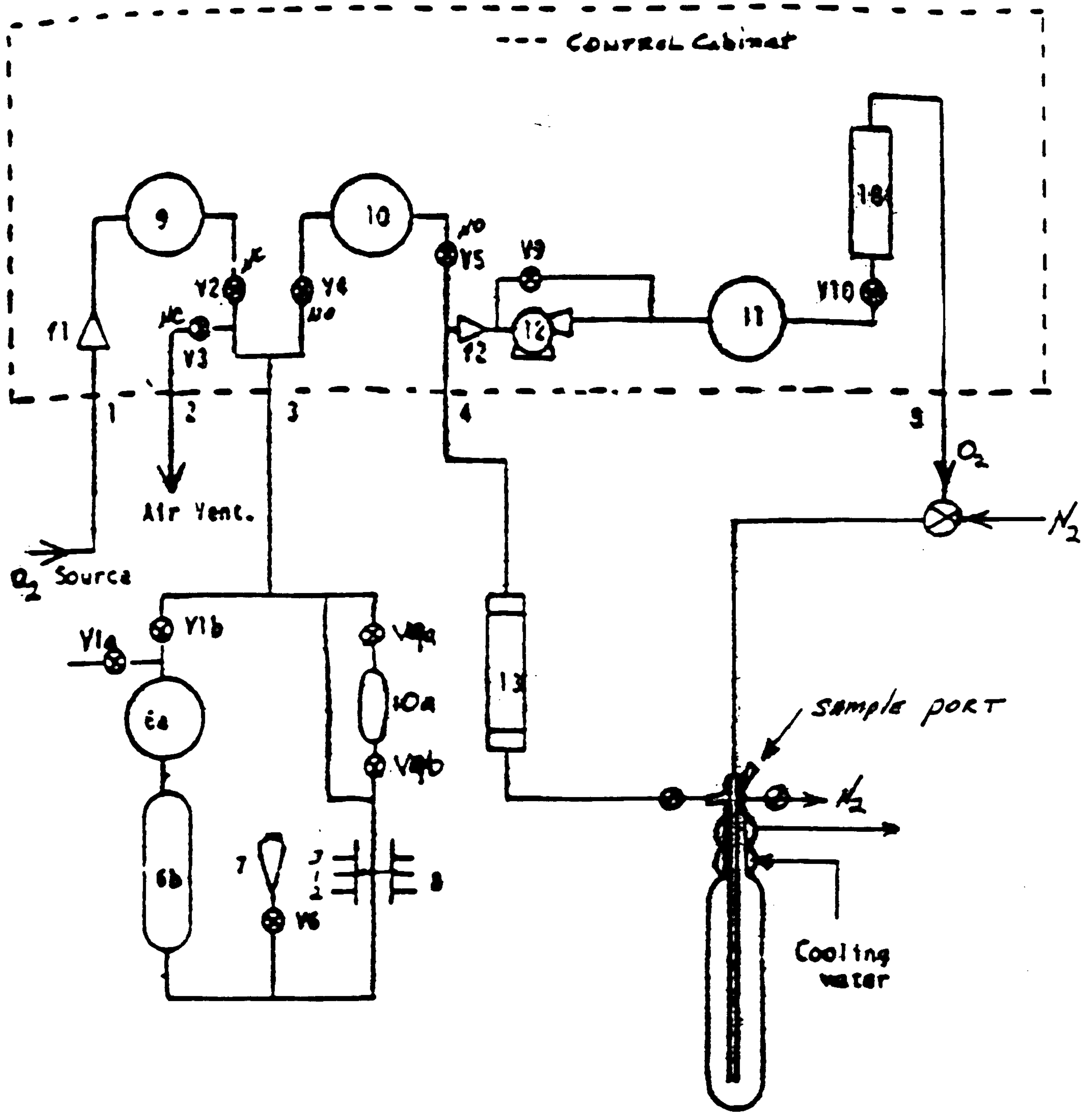


Figure 6



Flow Diagram - Oxygen Absorption Apparatus
Original

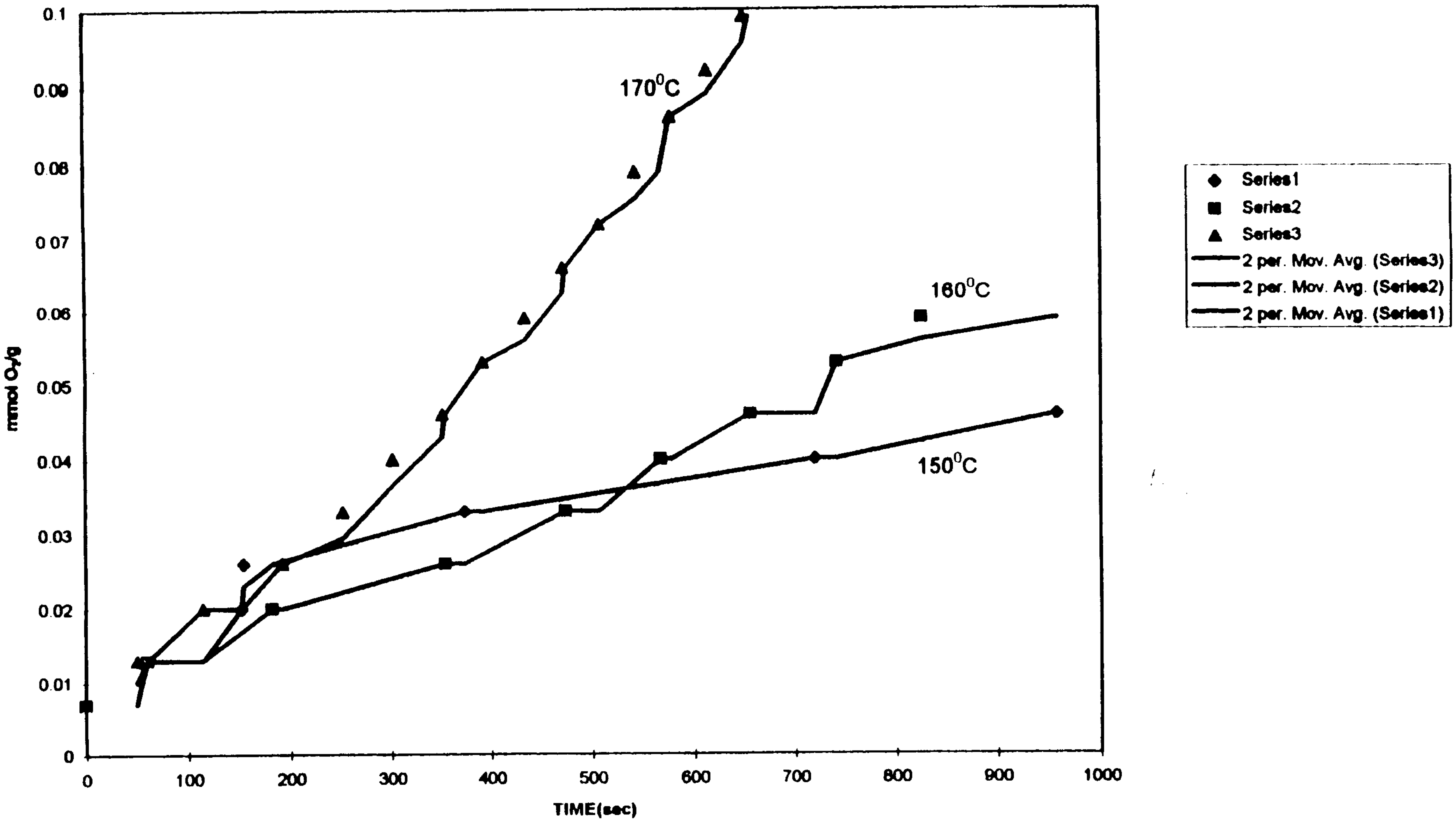
Figure 7



Flow Diagram - Oxygen Absorption Apparatus
After Modification

Figure #8

Oxygen Absorption Comparison at 170^{0}C, 160^{0}C & 150^{0}C of MLO 94-166



Peroxide Formation in MLO 94-166 at 150°C, 160°C & 170°C

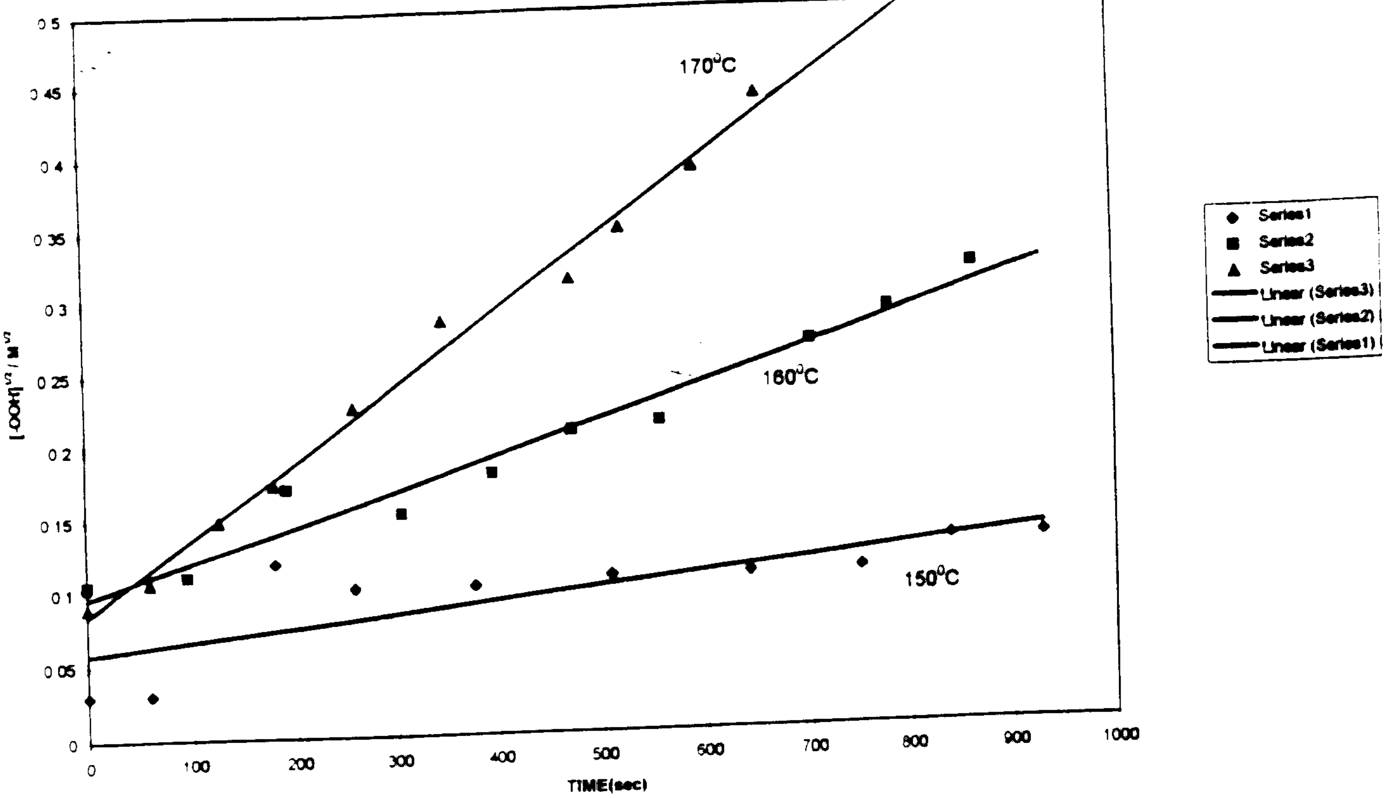
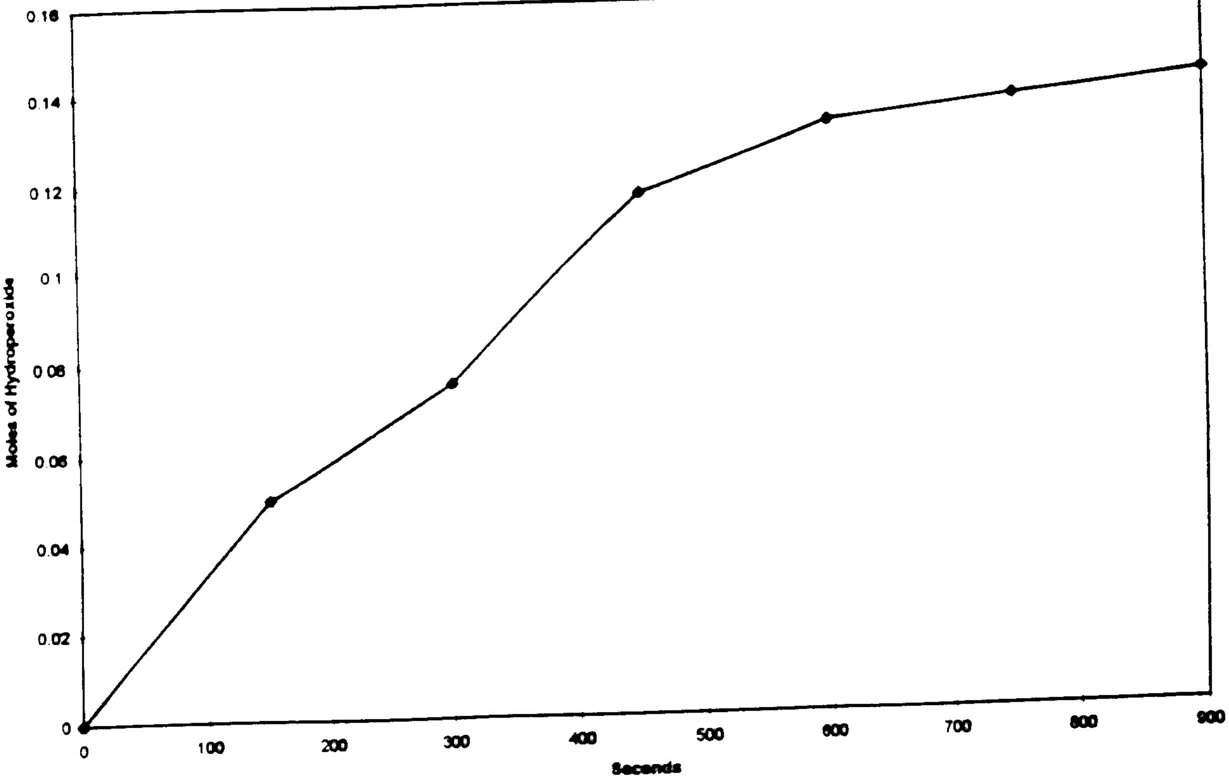


Figure #10
Peroxide Concentration MLO 94-166 190°C 19 June 95
7.0ml per event



BEARING FATIGUE OF METAL MATRIX COMPOSITES

Task Order No. 111
Student Support Program
Southwestern Ohio Council for Higher Education

Alisha Hutson
Wright State University

15 June 1995

Government Task Leader
Mr. Jay Jira
WL/MLLN

ACKNOWLEDGMENTS

This Task has proved to be the most interesting and educational yet. The opportunity to complete research from testing to documentation has helped me tie things together in a way I had not done before. I would like to thank Mr. Jay Jira and Mr. Jim Larsen for allowing me that opportunity. I would also like to thank Mr. Jay Jira and Mr. Rick Kleismit for assisting me throughout the study, and for their continued support in my academics as well as my practical experience.

TASK ASSIGNMENT

The duties involved in this Task included continued support for the Mechanical Behavior Branch, as well as responsibility for a small segment of the lab's research. Specific tasks performed under this contract were the same as for previous contracts. Included were reduction of data from mechanical behavior tests of metal matrix composites, some small scale data acquisition, specimen characterization for specific test specimens, and documentation of various test anomalies. The research project that was assigned involved quantifying the behavior of the region between the matrix and the fibers that make up the composite, as a function of temperature. The project was also used to complete requirements for the senior design series at Wright State University.

The purpose of the assigned study was to determine the interface sliding stress between the matrix and fibers in a fatigue cracked region at several test temperatures. This was accomplished by the following steps. First available literature was studied to determine approaches taken by other researchers, and to develop a background for the theories behind them. The test methods were determined and a schedule for the project was developed. Once a sufficient understanding of the theory had been acquired, the necessary theoretical values were calculated and tabulated. Finally, testing was conducted, and results were analyzed and documented.

Two different test methods were chosen to quantify the interface sliding stress: fiber pushout tests, and a variable temperature tension-tension fatigue test. The pushout tests involved taking a very thin slice of the composite and pushing on the end of the fibers, one at a time, until they slipped. The load required to make each fiber slip was recorded, and used to calculate the sliding stress between the fiber and the matrix. Since this method could not be used to measure sliding stress at elevated temperatures, a fatigue test was used to produce measurements from which the sliding stress could be calculated. This method required running a standard fatigue test until an 8 millimeter (tip to tip) bridged fatigue crack had developed. Then, several pairs of hardness indents were placed along the bridged section of the crack, and measurements were made of how far the crack would open at each of these points when the specimen was subjected to a specific load. These measurements were made for temperatures ranging from room temperature to 500°C. Finally, measurements were used to calculate the average sliding stress by correlating them with a model from the literature.

Successful completion of this study has reduced the number of tests required to fully and accurately model the material, by allowing researchers to interpolate fatigue crack growth rates between the room temperature and high temperature tests they have already conducted. In addition, it has given the student a better understanding of the focus of the laboratory's research, and the scientific methods involved in that research.

INFRARED SPECTROSCOPY

Task Order No. 112
Student Support Program
Southwestern Ohio Council for Higher Education

Sophia J. Briley
Wright State University

12 June 1995

Government Task Leader
Dr. Harvey L. Paige
WL/MLBT

ACKNOWLEDGMENTS

I would like to thank Dr. Harvey Paige for allowing the opportunity to work under his supervision in the WPAFB Materials Laboratory. Also, Dr. Jim Liang for teaching all the needed skills to work in the laboratory and allowing me to work with him in his research, Mark Roselius for helping me get started, and the entire MLBT branch for making my first year a nice learning experience.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Experiments were run to observe the surface interaction of perfluoropolyalklyether (PFPAE) compounds against an iron fluoride (FeF_3) surface. Scans were run with an FTIR Spectrometer after different amounts of the PFPAE were deposited on the FeF_3 surface and while the surface was at different temperatures to observe any noticeable amounts of concentration enhancement or decline in a reaction peak due to either the type of PFPAE deposited or the temperature.

These experiments were run to study chemisorption of CF_3COF onto an iron fluoride surface.

The results of the experiments were used to assist Dr. Jim Liang in his research of surface interactions of oils and lubricants and model compounds. Through these experiments, he was able to observe the interaction of these model compounds against an iron fluoride surface and conclude at the formation of a perfluorocarboxylate species being formed at this surface.

DESCRIPTION OF THE RESEARCH

The methodology of running a chemisorption experiment starts with cutting a tungsten mesh to fir small brackets held on two copper rods connected to the top of the cell which is held in place for the IR beam to pass through. The mesh is placed with about 1.0 g of solid powdered FeF_3 under a laboratory press at 20,000 psi for 3-12 hours. After being pressed, the FeF_3 should be snugly pressed between the small holes of the tungsten mesh. The mesh is carefully placed in the brackets and tightly secured. A thermocouple tip, connected to two thermocouple rods located in the tip flange of the cell, is spot welded to a clean corner of the mesh. This top portion is placed in the cell with a copper gasket between the flange and the cell. It is tightly bolted together to ensure that there will be no leaks from this part of the cell. The cell is then checked for leaks by hooking it up to a vacuum which should read 0.004 torr or thereabouts. Current is also checked by hooking up a power supply to the two Cu rods and viewing the temperature change as the current is raised. If everything checks out okay, the temperature of the mesh is set at $500^{\circ}C$ overnight and 0.004 torr to ensure a pure sample of FeF_3 and to vacuum out any impurities along the walls of the cell. The next morning, the cell is placed in the IR and scanned to see that the FeF_3 peak is visible. When it is assured that everything is working properly, the power supply is turned off and the cell is allowed to cool to room temperature. It is then further cooled with liquid nitrogen to the lowest temperature possible (about -130°C). A container of CF_3COF is hooked up to the vacuum line to be deposited onto the surface of the mesh at a rate of 0.001 torr/min. One hundred to 200 scans are taken every 5 minutes with the FTIR Spectrometer and the spectra resulting are observed to see if the CF_3COF is chemisorbing onto the FeF_3 surface at the lowest temperature. It is kept at this low temperature until an equilibrium is reached which is noticeable by the peaks being the same size with consecutive scans. At this point, the cell is pumped on to make sure that the peaks were actually due to the chemisorption of the CF_3COF and not merely gas phase. The cell is then heated to room temperature and the substrate is deposited again to view the chemisorption activity at room temperature. Finally, the cell is heated by the power supply and the desorption experiment is run to see at what temperature the surface interacted species will disappear. Once that point is reached, the experiment is finished and the cell is again heated up to 500°C to possibly be used for later experiments.

EQUIPMENT USED

Nicolet 740 FTIR spectrometer
2 3/4" Cubical Stainless Steel Cell
KBr Flanges for two opposite sides of the cell
Blank flanges for the bottom and back of the cell
Flange with two copper rods, two thermocouple rods, and a deposition tube all welded to the flange so they can be located both inside and outside the cell.
Carver Laboratory Press
FeF_3 solid powder
Unitek Dual Power 125 spot Welder
Cole-Parmer Digi-Sense^R Thermocouple Thermometer
Styrofoam worm bucket with two holes, which the copper rods go through, to hold the liquid nitrogen.
Electronics Measurements, Inc., TCR Power Supply
CF_3COF gas in a UHV gas container
Microspatula
Various wrenches

RESULTS

Throughout the year, the use of many instruments was learned including the Nicolet FTIR Spectrometer, Hewlett Packard GC/FTIR, and Perkin Elmer Grazing Angle Microscope/FTIR. All these are very useful in studying surface species, as well as the composition of a substance. Along with these instruments, many concepts that are useful in analytical research were learned including figuring out the concentration of an acid solution and making solutions up yourself and the interpretation of the various peaks shown on the spectrometers.

It was concluded by this experiment that the chemisorption of CF_3COF onto FeF_3 resulted in a perfluorocarboxylate surface species which desorbed at 300°C. These results were collaborated into a paper written by Dr. Jim Liang entitled "Chemisorption Study of CF_3COF on FeF_3 by FTIR," to be published at later date.

METALLIC COMPOSITES

Task Order No. 113
Student Support Program
Southwestern Ohio Council for Higher Education

Christopher W. Palser
Wright State University

30 June 1995

Government Task Leader
Dr. Dan Miracle
WL/MLLM

ACKNOWLEDGMENTS

I would like to sincerely thank Dr. Dan Miracle for 2 1/2 years of patience and guidance. Working under Dr. Dan Miracle has been a great learning experience for me. I have learned numerous lessons and much experience in the research atmosphere. I would also like to thank Dr. Harry Lipsitt (Wright State University) for his assistance and teaching this year. Both these men challenged and encouraged me in this research, not letting me take the easy way out at any time, but always pushing me to keep on track and press on, no matter how slow it seemed to go at times. I also would like to thank Mr. Paul Smith for his suggestions for my senior project and providing of the material and his experience and guidance in this project.

TASK ASSIGNMENT

The overall objective of this Task was to further advance the knowledge of advanced metallic composites for high temperature applications. To this means, research was conducted to investigate the effects of environmental exposure upon the embrittlement of a titanium-aluminide orthorhombic alloy which is currently being investigated as a matrix candidate for metal matrix composites. The specific objective of this project was to measure the ductility of and investigate the mechanism of embrittlement in Ti-22Al-23Nb neat panels after isothermal exposures. The end-goal for the materials being developed is to develop lighter, stronger materials which will withstand higher jet engine operating temperatures and, thus, increase jet engine efficiency.

Research previously performed indicates that the ductility of the orthorhombic class of alloys decreases significantly after an exposure simulating jet engine operation. The intent of this project was to more thoroughly document this loss of ductility and to determine whether this phenomenon is caused by microstructural changes, or whether it is initiated by an environmental effect which occurs during the exposure. All experiments were conducted on Ti-22-23 "neat panels," that is, material processed exactly as a metal matrix composite would be, without the fibers present.

DESCRIPTION OF RESEARCH

To meet the assigned goal of investigating the mechanism and extent of embrittlement in Ti-22Al-23Nb neat material, the following outline was followed: Dog-bone tensile specimens were heat-treated for 1, 10, 100, and 1000 hours in air and argon. After 1 and 10 hour exposures, a small amount of each specimen was removed for metallography and Vickers' hardness testing; the remainder of the tensile specimens was then heat-treated for the completion of the 100 and 1000 hour exposures. The as-received and heat-treated specimens were then to be tensile tested. Chemical analysis was conducted to determine pick-up of environmental contaminants and metallography was performed to determine the microstructural and phase stability of the neat material. The mechanical properties were rationalized based on the chemistry and microstructural observations.

To date, all groundwork has been laid for the research project to be completed. That is, all testing and evaluations have been performed, with only the final, formal write-up to be completed.

RESULTS

Tensile testing has shown a decrease in the ductility and ultimate tensile strength of the air-exposed samples as compared to the argon-exposed samples. Additionally, Vickers' hardness testing has shown a significant increase in hardness on the exterior of the air-exposed samples, but not the argon-exposed specimens. Also, chemical analysis has shown a large increase in oxygen content (but no significant increase in carbon or nitrogen) of the air-exposed samples compared to the argon-exposed samples.

Scanning electron microscopy (in both scanning and back-scatter electron mode) has been conducted. Electron micrographs reveal that there is an oxygen-affected phase transformation going on at the surface of the air-exposed samples, but not in the argon-exposed samples. It has also been seen that there is substantial oxygen diffusion into the air-exposed samples, but not into the argon-exposed samples. This diffusion zone corresponds to the increase in hardness seen from the Vickers' hardness measurements.

In conclusion, it appears that the Ti-22Al-23Nb neat panels are not stable in exposures in air to high temperatures. The results of this lack of environmental stability are a drastic decrease in ductility of air-exposed specimens. The cause of this instability appears to be oxygen embrittlement of the surface layers, which has been seen through hardness testing, back-scatter electron images, and chemical analysis.

METALLIC COMPOSITES

Task Order No. 113a
Student Support Program
Southwestern Ohio Council for Higher Education

Christopher M. Penick
Wright State University

30 June 1995

Government Task Leader
Dr. Benji Maruyama
WL/MLLM

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

The objective of the current Task is to determine interface properties, residual stresses, and deformation characteristics in advanced metallic composites for high temperature applications. However, as with all endeavors, the main objective is split into increasingly smaller objectives (goals) that need to be met daily to reach the ultimate objective (as stated above).

The workload of the Task consists of establishing known techniques for producing single and multiple fiber composites for their various geometries and matrix/reinforcement combinations. Also, it may become necessary to develop new techniques for composites production when known techniques are too inadequate to handle new geometries and matrix/reinforcement combinations. Then, with these composites, the Task work description calls for the determination of interface properties, residual stresses, and deformation characteristics in the advanced metallic composite. Often, it will be necessary to perform testing (mechanical, chemical, etc.) on the single fibers, the single fiber composites, and the multiple fiber composites. Therefore, data analysis will become a necessary operation to perform to complete the Task objectives.

Composites, in general, have been in use in the public for years. However, the difficulties and high cost in the production of metal matrix composites have kept them from public use. However, it has become increasingly apparent that there is a growing demand for high strength, light weight, high temperature materials. Some of this demand may be met with the development of metal matrix composites. A metal matrix composite, formulated to withstand the high temperatures and stresses found in a high performance military turbine engine, may be incorporated into the blades of the various stages of the turbine, the walls and lining of the turbine, and the actuator rods of the exhaust nozzles. This combination of applications will allow the turbine engine to perform far superior to current turbine standards. This is a large scale example of an application. On a day-to-day level, metal matrix composites can be used in electronics packaging to produce electronic devices that run much more efficiently than current material technology allows. A metal matrix composite would provide electronic packaging with the stiffness and toughness, thermal conductivity, and weight ratio that it would need to compete with the demand for faster and better electronics.

The applications for metal matrix composites are extensive. They can provide many advances in design and engineering that have, thus far, been held back by the lack of what a metal matrix composite can provide. With the research from this Task, perhaps these barriers will be realized and conquered.

DESCRIPTION OF RESEARCH

The research for this Task involves a constant reiteration of basic research methods. The first step consists of developing a feel for what the problem at hand is. The second step, in general, is to determine the desired solution with the third step being a plan of attack to attain the desired results. The fourth step is to put the plan into operation. The fifth, and final step is to analyze the progress obtained during the fourth step. This analysis determines what the next step will be. Thus, the process continues.

During this Task, several projects are often in progress at any given time. These projects all tie into the main objective of the Task by dealing with every aspect of the objective separately.

In terms of the determination of interface properties, the Task allows for many different experiments. During the term of this Task, it was determined that the interface properties of standard silicon carbide fibers were to be examined and optimized. The interface in concern was between silicon carbide fibers and a titanium matrix known as Ti-6Al-4V (titanium with six parts aluminum and four parts vanadium).

To study the interface properties between a titanium matrix and a silicon carbide fiber, it is necessary to introduce the fiber to a consolidated matrix. This process utilizes a hot isostatic press machine, in which a fiber-foil-fiber combination is placed into a pressing die and submitted to very high pressures and temperatures. At such high temperatures and pressures, the titanium foils "flow" so that the product is a consolidated plate of titanium with silicon carbide fibers inside. The second step is to section the plate such that the sections containing fibers may be mounted in a thermoset plastic mold. With the sample properly mounted, it is possible to polish the titanium matrix composite using various polishing cloths and diamond polishing solutions. It has been determined that the optimal polish is obtained by starting the sample on a Metlap Platen #8 with a 45-micron diamond solution. Using the same platen, the sample is polished with successively smaller micron diamond solutions with the successive steps being 15 micron 9 micron, and 6 micron. The next step is to polish the sample on glass with a three-micron paste. This step flattens the surface of the sample so that the final polishing steps will be effective. The next step is to take the sample onto a Texmet 1000 cloth with a 1 micron diamond solution. The final step is to use a Chemomet cloth with a colloidal silica solution on the sample. This is the step that is necessary to obtain a mirror-like final polish. At this point, it is possible to perform microscopy on the sample. Microscopy is the form of analysis performed on a sample to determine its interface reactions. Microscopy often takes one of two forms. The first form is optical microscopy which utilizes an ordinary microscope to observe the reaction between the fiber and the metal matrix in ordinary light. The second form is scanning electron microscopy which utilizes scanning electron microscope (SEM) to image the sample at magnifications as large as 500 thousand times. Often, this magnification is unwieldy, and smaller magnifications are used, but the images obtained from this type of microscopy are far superior to the images obtained from optical microscopy. The benefit to using scanning electron microscopy is that the images obtained from this process are digitized in the computer and are able to be analyzed using various computer programs.

In the analysis of an interface, it is desirable to determine how much of the fiber reacts with the metal. When a fiber reacts with the metal matrix, the fiber becomes essentially useless since the applied load will not transfer to the fiber. Thus, it is desirable to stabilize the interface by applying various coatings to the fibers in hopes that its reactibility with titanium is very low. However, titanium is very reactive with very many elements and chemical compounds. Sometimes it is necessary to subject the sample to a heat treatment in vacuum to try to initiate a reaction between the fiber and the matrix. Determining the coating for a fiber is very difficult, but the processing and analysis of each sample are the same. It is hoped that a fiber coating can be found so that the interface between a fiber and its metal matrix will be stable and allow the fibers to carry the loads applied and increase the strength of the composite.

The residual stresses of composites is a topic that is rarely utilized during this Task. However, it is a useful topic in preparing titanium foil plates for a hot press session in the hot isostatic press. The plates have residual stresses from their cold rolling initial processing. To relieve these stresses, a separate hot press runs on plain plates is necessary. Thus, the plates are then capable of being pressed with fibers such that, since the residual stresses are relieved, the fibers do not incur any extra stresses during the hot press process.

Another attempt to utilize the objectives of the Task, the idea of processing titanium matrices with diamond fibers has become a hot topic in the study of interface properties and deformation characteristics. The topic is still in its infancy, however, it has been seen that even in heat a treated sample of a diamond reinforced composite, the diamond fibers do not react with the titanium.

A diamond fiber is formed by depositing on a tungsten wire substrate a diamond layer through the process of chemical vapor deposition. Thus far, the fibers have not been of a reputable quality. This has led to difficulty in determining their mechanical characteristics. However, the procedure for testing the mechanical characteristics of individual diamond fibers is becoming more mature with each consecutive testing procedure. Presently, the fibers are glued to a customized plastic holder which can then be attached to the simple tweezer-like grips. The entire fiber tester rig depends upon an Instron« load cell to determine the load applied to the fiber. The voltage readout from the load cell is then read by a DOS based computer which has the programming necessary to determine the mechanical properties of the individual fibers. Again, since the fibers were of poor quality, the values obtained for the yield strength, ultimate tensile strength, and Young's Modulus for the fibers are not as high as is desired. However, since this project is still so young, it is hoped that the obstacles it is presenting will be overcome.

RESULTS

During this Task, many modes of learning have been employed. The main mode was that of reading many scientific journals on the topics of chemical vapor deposition and diamond properties. This has been an endless source for picking up on the technology employed in the research field. By doing most of the sample preparation and microscopy, it also has become an important source of enrichment.

STRUCTURAL FAILURE ANALYSIS TECHNICIAN

Task Order No. 114
Student Support Program
Southwestern Ohio Council for Higher Education

Joseph C. Leone
Wright State University

15 July 1995

Government Task Leader
Mr. William E. Berner
WL/MLSA

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I would like to extend my appreciation to Mr. Ronald H. Williams and Mr. William E. Berner for allowing me the opportunity to complement my education while working in the Structural Integrity Branch of Wright Laboratory.

Additionally, I would like to thank Larry P. Perkins and, from the University of Dayton Research Institute, Tom Dusz, Michael Oliver, and Brad Pinnell, for their assistance and direction in completing my Task.

TASK ASSIGNMENT

During the 9 months, the Task 's objective was to assist engineers and technicians in performing structural failure analysis on metallic and composite weapon system components.

The first major project completed was a material evaluation on steel roller segments used in the manufacturing of manganese brickets. The Edison Material Technology Center (EMTEC) submitted two roller segments for analysis. The purpose was to determine the cause of enhanced wear resistance observed infrequently during production. Twelve roller segments make up each of two opposing circular roller which compact manganese powder. The rollers are condemned once surface wear prevents them from pinching the brickets apart during production. One submitted segment demonstrated a useful life approximately three times longer than the other.

Samples from each segment were chemically analyzed and compared to their nominal specification. Because the chemical composition is controlled by a proprietary specification, determination of material conformation was inconclusive. However, the analysis did show that both segments possess nearly identical compositions. Next, the cross section of the two rollers were polished and etched to enable comparison of their microstructures. Both rollers possess carbides in a martensitic matrix. The volume fraction of carbide to matrix for both rollers was approximately the same.

From the analysis it was determined that carbide size and dispersion was the determining factor on how the roller segment would perform during use. The segment that demonstrated the longer life had a microstructure composed of carbides that did not exceed 20 microns in length, evenly dispersed throughout the matrix. The other had carbides as large as 50 microns.

Carbides may serve to enhance a material's wear resistance because they possess higher strength and lower ductility than the parent matrix. The elements chromium, molybdenum, and vanadium (present in the roller's composition) all form carbides when they are compounded with carbon. These refractory metal carbides form at very high temperatures during casting and are relatively unaffected by the comparatively lower temperatures of heat treating. The mechanical work of forging may serve to break up the carbides once they have formed.

The second project completed was a weld repair qualification on a second stage fan blade. A repair procedure was developed for repairing and extending the service life of the fan blade. The repair involves the removal of an area near the midspan where fatigue cracks initiate during service. A forged insert is electron beam (EB) welded in its place. The insert is designed to offer improved fatigue resistance. The qualification followed the specification for electron beam welding (AMS 2680B).

Nondestructive testing was performed using visual, fluorescent penetrant and X-ray. No evidence of defects was found. Next, five transverse sections were removed from each side along the weld at varying blade thickness. Examination of the cross section showed no defects in either the initial EB weld or the cosmetic pass. The blade was then sectioned through the midspan to allow visual inspection inside the weld, referred to as the pocket. The inspection revealed two areas of minor underfill and small cold lap. Samples of the weld repair were chemically analyzed to determine the composition. The insert and blade material were determined to be Titanium 6Al-4V. Photomicrographs of the microstructure in the weld zone, weld interface and base metal were taken. The microstructure consists of acicular alpha with alpha at prior austenite grain boundaries, typical for annealed Ti 6-4.

On the basis of the gathered information obtained in this evaluation, the weld schedule used to produce this weld is satisfactory and should be approved for production hardware.

The third project completed was a material evaluation to determine the chemical composition and hardness of the submitted case and fragment samples from an antipersonnel mine.

Microhardness measurements were taken along the cross section of the case material. Each fragment was hardness tested using a bench Rockwell hardness tester. One fragment was cross sectioned and a microhardness traverse was made through the thickness. The measurements taken were consistent with a low carbon steel.

The chemical composition of the fragment sample contained a high amount of sulfur and phosphorus, as compared to the case sample. The addition of sulfur in the fragment sample crates sulfide stingers that enhance fragmentation characteristics. The prevalent chemistry, however, may not have been intentional due to the presence of both phosphorus and sulfur in high quantities. It is possible the weight percent sulfur is an indication of poor control in the steel making process rather, than a design specification.

From the gathered data, it was concluded that both the case and fragments were manufactured from a low carbon steel.

Many additional smaller projects included metallographic sample preparation, characterization of microstructure, photographic documentation, and hardness measurements.

STRUCTURAL FAILURE ANALYSIS TECHNICIAN

Task Order No. 114a
Student Support Program
Southwestern Ohio Council for Higher Education

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Sinclair Community College

15 July 1995

Government Task Leader
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TASK ASSIGNMENT

Due to the brevity of this initial Task, goals were kept to a minimum. Laboratory equipment familiarization and hygiene, metal and composite mold making, as well as metal and composite polishing were stressed. In addition to what was stressed, an individual is given an educational conductive environment to proceed and acquire more knowledge.

In a failure analysis laboratory, as in any technical work place, there are many forms that serve as records for various procedures. There are log books for molds manufactured, supply purchase requisitions, chemical analysis requests, requests for film development, and appropriate waste disposal requisition forms. These forms and logs serve both as written communication between departments and agencies or as tracking devices for materials submitted to different offices or agencies.

Within the failure analysis lab, there is a variety of analysis equipment. There are microscopes of various magnifications, sanding devices, polishing devices, a band saw, rotary saws, and a mold press. All of the aforementioned devices must be properly maintained. A technician must fully understand cleaning procedures and replacement procedures of minor parts.

Initially, a large amount of a sample is given to a laboratory technician. The aide must reduce this sample to a smaller sample in order for it to be analyzed easier by the engineer. A mold makes it easier for the sample to be handled while it is being evaluated. The proper use of saws is important to obtain a small enough portion of the sample without increasing the damage to it. Depending on the material of the sample, it is cleaned using appropriate chemicals. There are many materials to use in making a mold. The decision to select the proper materials is dependent on the material of the sample and the evaluation it will undergo.

Once the mold is made and documentation of the mold is accomplished, it has to be polished. The technician uses various sanding methods, fixed or rotating, to polish the sample to get a closer look at its intergranular structure. Once sanding is complete, the sample is polished using wheel-mounted polishing cloths to further reduce scratches. Finally the sample, if metal, is etched. The etching reveals the intergranular structure just below the polished surface. By evaluating the intergranular structure under a microscope, an engineer makes a determination about why a substance failed.

The basic microscope an undergraduate technician may have come into contact with in his/her curriculum takes on a much more complicated state in the laboratory. Not only is there a power source and a few lenses, there are monitors, photographic equipment, personal adjustments as far as the eyepiece, and even large control panels such as those seen on high magnification electron microscopes. A beginning technician learns the basics of operation such as proper ways to focus, multiplication factors of magnification, and how to produce photographic images he/she sees.

Lastly, but definitely as important as other information, is disposal of waste. Everything is disposed of according to its chemical content. Very little goes into a waste paper receptacle. Even some photographic byproducts have special receptacles. The majority of waste is documented about what it is, where it was, how it was used, how much of it was used, and where it went when it left the laboratory.

A beginning laboratory technician should observe as much as he can. In this conducive environment, questions are encouraged and welcomed. No one turns away someone who wants to learn. One very valuable lesson learned is a strong reinforcement of communication. Communication, especially written, is of the utmost importance and should never be neglected. It is a very good experience to be able to increase knowledge of things mentioned in undergraduate textbooks by using the equipment and standing face to face with a qualified professional.

NONDESTRUCTIVE EVALUATION (NDE) EXPERIMENTAL SUPPORT

Task Order No. 115
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Willson
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14 March 1995

Government Task Leader
Dr. Thomas J. Moran
WL/MLLP

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I would like to give my thanks and appreciation to Mr. Mark Blodgett, Dr. Renee Kent and Mr. Mark Ruddell, who gave much of their time to help me in understanding aspects of non-destructive evaluation.

TASK ASSIGNMENT

This Task consisted of two separate areas of NDE. The first was conducted from 3/94 to 8/94. Mr. Mark Blodgett was the chief coordinator throughout this operation, which dealt with ultrasonic imaging of flawed specimens. These specimens included the liquid cooled outer skin components of the national aerospace plane, consisting of a channelled piece fit atop a flat piece, so that the channels became conduits through which liquid hydrogen or another coolant would flow. The defects examined consisted of the debonds in the channelled/flat metal interface. Since the specimens in question were relatively thin (the bonds being less than 2 mm. from the surface), ultrasonic imaging was used to examine the debonds nondestructively.

The ultrasonic imaging setup included a 100 Mhz piezoelectric transducer, which both produced an ultrasonic wave and detected the resulting echoes, a gated spectrum analyzer, and a computer to record and plot the intensities of the echo in question as a function of position on the specimen. Once a particular echo was chosen (by determining the transit time for an ultrasonic pulse to be sent from the transducer, bounce back from a certain depth, and return to the transducer), and the intensities of the echo plotted, the areas of debonding could be easily seen by noticing areas in the plate that did not fit with the symmetry, such as blotches or speckles.

The equipment used was relatively portable and easily transported to an active site. This is the main incentive for a program of nondestructive evaluation: to actively determine the quality of a part without interfering with it, and possibly while the part is still in service. Ordinary destructive evaluation of parts is the current defect- detecting mechanism, mainly due to its economic advantage over a nondestructive system. There is no doubt that a nondestructive evaluative system, though not currently practical for general use, would bring in many advantages.

The second part of this Task occurred from 8/94 to 3/95. This Task was coordinated by Dr. Renee Kent and Mr. Mark Ruddell. The main objective was to determine properties of fibers introduced to various stresses in a non-contact scheme. The stresses introduced into the fibers, which among other types included Sigma and SCS-6 fibers, were delivered by shear and longitudinal piezoelectric transducers that were affixed to one end of the fiber. The other end was kept out of contact with any physical device. Instead, a Michelson interferometer, powered by a He-Ne laser was focused on the other end of the fiber. Through this setup, minute changes in the displacement of the fiber were detected by the interferometer and recorded by an oscilloscope. In this way various echoes were picked up from the onset of a shear or longitudinal wave sent from the transducer. Analyzing these echoes gives information about the shear modulus of the fiber, and in cases of fiber-reinforced composites, evidence of debonding. In the future, it is hoped that a pulsed laser of considerably more power will produce the ultrasonic wave now being produced by the transducer. This will allow for a completely non-contact analysis of fibers, and fiber-reinforced composites. The pulsed laser will allow yet another way to non-destructively determine the quality of crucial parts, and to determine properties in matter not normally seen through contact testing.

MECHANICAL PROPERTIES TESTING OF CERAMIC COMPOSITES

Task Order No. 117
Student Support Program
Southwestern Ohio Council for Higher Education

John R. Welch
Wright State University

15 June 1995

Government Task Leader
Dr. Randy Hay
WL/MLLM

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I would like to extend my appreciation and thanks to Dr. Randall Hay and Dr. Ronald Kerans for the opportunity to work and learn at the ceramics division of the Materials Lab at Wright-Patterson Air Force Base. I also wish to thank the other engineers that have provided opportunities for me to work and learn, including Dr. Michael Cinibulk, Dr. Peter Brown, and Larry Matson. I would like to express special thanks to Dr. Scott Walck for his assistance and expertise while I was learning to use the tripod polisher. I would also wish to thank the staff of the Metallography Laboratory for their assistance in the completion of my Tasks.

TASK ASSIGNMENT

The majority of this Task consisted of preparation of thin foil specimens for transmission electron microscopy analysis. The decision of the Ceramics Division of Wright Laboratory to shift the research emphasis from Alumina based Saphikon@ fiber to fiber tows presented special problems in the performance of these duties. Ceramic fiber tows are similar to a rope, containing many fibers, but the fibers are generally between 8 and 15 microns in diameter, whereas the Saphikon fiber is usually between 135 to 150 microns in diameter. After several months of non-productive attempts to produce thin foils of coated tows in the traditional preparation techniques, a new technique designed by I.B.M. for semi-conductor thin foil preparation was attempted.

This method incorporates the use of a device called a tripod polisher. This device is designed with 3 micrometers attached to a precision made steel base. A sample is mounted with epoxy onto a small piece of microscope slide which is mounted onto a specially made stub that clamps in a bracket attached to the tripod polisher. The sample is then polished in stages ranging from-30 to 0.1 microns on diamond embedded myelar disks. The polished sample is then removed from the piece of microscope slide, flipped over, and remounted on the slide with the polished side down. The sample is then thinned in stages on the diamond embedded myelar disks until the sample is as thin as possible.

This technique can produce outstanding results when all goes extremely well. Homogeneously composed materials can sometimes be thinned to near TEM transparency. Unfortunately, the materials produced in this laboratory are generally non-homogeneous. Ceramic fiber matrix composites have been the next easiest to produce specimens. Several of these specimens were thinned during this Task to thicknesses of approximately 2 microns or less, requiring minimal ion-milling time and allowing a large area (for TEM) of a given specimen to be readily analyzed in the TEM Most of the specimens produced have been simply coated tows or coated weaves (woven tows) without a matrix. These presented very special difficulties, requiring a substantial amount of trial and error procedures before consistently successful specimens could be produced.

The solution to the coated fiber tow sample preparation was accomplished by taking several short lengths (around 4 inches) of the tow, stuffing these tows in a tapered glass pipette, and injecting epoxy around the fibers with a hypodermic needle. The sample would then be placed in an apparatus in which the sample would undergo vacuum infiltration to try to eliminate as many air bubbles as possible. When this was completed, the sample would be heated in a low temperature oven at approximately 70° centigrade to harden the epoxy. The initial attempts at thinning specimens in cross section proved to be failures, so most samples were produced longitudinally. Recently, a new approach was attempted and has so far proved to be fairly successful. This approach requires taking small sections of the pipette after it has gone through all of the other procedures and additionally mounting them in epomet in a sample press. This requires making a sample clip become circular, sifting fine ground epomet powder, placing a fine layer of powder on the ram piston, placing the circular sample clip on the layer of fine powder, partially filling the circular clip with more fine powder, delicately placing the pipette sections perpendicular to the sample press ram piston, covering any still exposed areas of pipette with more fine powder, and then filling the remainder of the space with a coarser grade of epomet. The specimen then has to be carefully cut on a diamond saw to remove the excess epomet mounting from around the center circular sample clip. This piece is then carefully ground around the sides of the sample clip until the clip can be removed from the specimen. The remaining piece is then mounted on the slide as usual. Some very nice results have been obtained using this method. The coated fibers need to be extremely thin when the sample is completed, for the area of interest is the interface between the coating and the fibers. The coating on these fibers typically is 1 micron or less and experience has indicated that the sample thickness should be substantially less than 5 microns to produce a truly qualitative and quantitative TEM analysis of this interface. This sample preparation technique has produced several samples with substantial areas showing some level of thickness fringes, an excellent indication that the sample is fairly near TEM transparency, requiring a short duration of ion-milling time.

The weave characterization problem had an added dimension of difficulty to solve. The woven tows lie roughly planar and perpendicular to each other in a weave. The initial attempts involved trying to make inplane thin foils of the weaves. The weaves were mounted in a pool of epoxy, vacuum infiltrated, mounted on a piece of glass slide and the mounting stub. The results of this method generally were failures. The individual fibers displayed a tremendous tendency to pull out of epoxy mounting media whenever the specimen thickness neared the fiber diameter. By the time the sample reached less than 5 microns thickness, there would be almost no fibers left and the remaining fibers would be very poorly polished, showing very little resemblance to their original columnar shape.

The solution to this problem required eliminating the many exposed voids present in the epoxy and orienting the specimen such that not all of the fibers would be longitudinal in respect to the plane of polish. Many methods were tried, many destroyed samples were produced, and many hairs were pulled from scalps before a successful method was discovered. The successful method entailed mounting the fibers in the pool of epoxy as before. These pieces were then thinned as closely to the weave as possible on both sides. Small squares were then sectioned from these flat, thin pieces. The squares were then immersed in liquid epoxy, removed, stacked in a rectangle on a small piece of flat Teflon mounted on the bottom jaw surface of a 1 inch C-clamp, oriented so the edges of the little squares roughly lined up, clamped together to squeeze the epoxy into the remaining voids, and placed into the low-temperature oven to cure and harden. The hardened piece was then sectioned to provide a small piece to be mounted on the tripod polisheris stub. The results proved to be outstanding. The amount of time required to prepare one of these weave specimens was reduced to approximately 1/3 of the inplane method time, fiber pull out was substantially reduced, plus the majority of the remaining fibers were in cross section instead of longitudinal, a very desirable result for analysis.

The most significant other duty performed during this Task was training on the Transmission Electron Microscope. Some progress has been accomplished, but much more experience and perfection of technique are required for type of analysis done on this Task. A course on the TEM was taken at Wright State University during the spring quarter which provided much theoretical and analytical background necessary for successful specimen analysis. More training is expected during the next year and with the tutelage and assistance of Dr. Randall Hay during the summer, sufficient refinement should result in this Task producing significant analytical evaluations of specimens during the next year.

The upcoming Task promises to contain much more of the same TEM sample preparation and hopefully the tripod polisher method will continue in its refinements to produce even better results than have been produced to date. Part of the next year's Task should also include some operation of the fiber coating apparatus designed, built, and patented by Dr. Randall Hay.

FIBER COATING SYNTHESIS

Task Order No. 118
Student Support Program
Southwestern Ohio Council for Higher Education

Cathleen M. Gustafson
Wright State University

15 June 1995

Government Task Leader
Dr. Randy Hay
WL/MLLM

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I would like to thank SOCHE for hiring me and Dr. Ronald Kerans for having me work at WL/MLLM. It has been an enjoyable and enriching experience to work with such a cooperative group. I would especially like to thank Dr. Rollie Dutton for all his help and guidance. He has helped to prepare me for when I will be an engineer by having me become familiar with all the aspect of engineering. He has also shown me that the work we do is significant. I also would like to thank Dr. Nick Pagano who has taught me much about the theoretical aspects of engineering. Also, I would like to thank all the rest of the people I worked with. Everyone was very helpful and supportive.

TASK ASSIGNMENT

This Task deals with ceramic matrix composites and consists of tape casting, laminating, sintering, testing and data analysis. Ceramic matrix composites are being considered as an alternative material for high temperature applications and better ways of processing them need to be developed.

The main criteria for these samples are continuous fibers in a uniform array and in a fully dense matrix. The reason for making the samples is to test a model that was developed to predict the matrix cracking stress of these types of composites. Until this time, ceramic matrix composites with continuous fibers could not be made with a uniform fiber array. A uniform fiber array is predicted to greatly increase the stress at which the composite cracks compared to a composite with a nonuniform array.

DESCRIPTION OF RESEARCH

Tape casting, laminating and sintering are part of a process being developed to make ceramic matrix composites with continuous reinforced fibers. Tape casting is done by spreading a ceramic slurry over a flat plate of glass with a doctor blade. After the tape is dry it is then removed and cut into sections about 8 inches by 6 inches. These sections are used in lamination. Laminating is done by warm press bonding either the sections of tape together (monoliths) or tape and fibers together (composites). During lamination, the fibers are uniformly spaced on aluminum to form mats. The fibers are presses about one half their diameter into the tape and the aluminum backing is removed. The different layers of fiber/tape sections are then stacked with an extra layer of tape on top. These stacks are in turn pressed together to form a "green" composite laminate. These green laminates can be made to size or larger and cut to size and shape.

Next, the green laminate is placed in a tube furnace for burnout and sintering. All of the extra ingredients (i.e., binder and plasticizer) in the tape are removed during burnout. This is done at 460°C in flowing oxygen for 1 hour. After this step, the temperature is raised to just above the softening point of the glass (about 700°C) for 1 hour in vacuum. The vacuum removes any gases that may have been caught in the pores of the sample. The tube furnace is then filled with argon to collapse the pores and to reduce the residual porosity to less then 3%. The sample is then cooled and removed. The last processing step is to HIP (Hot Isostatic Pressure) the sample to remove the last of the porosity. This is done at 650°C and 35 MPa for 30 minutes.

After the sample is made, it is then tested. There are three main tests which are done. The first test is a Non- Destructive Evaluation (NDE) which is an internal evaluation done using sonic waves. This test helps to determine consolidation and if cracks are present. The next test is a transverse tensile test which is used to determine crack growth. The last and main test is a tensile test in the fiber direction. This test is used to determine crack initiation, crack growth, composite cracking stress, and the ultimate tensile strength of the composite.

RESULTS

Data analysis is a very important part of this project. Proper record keeping is vital to correct and timely analysis of the results. It is very important to be able to repeat a process that yielded a good sample or to learn what went wrong. The samples made during this Task have lead to a greater understanding of both processing ceramic matrix composites and of the model developed to predict the composite cracking stress.

FIBER COATING SYNTHESIS

Task Order No. 118a
Student Support Program
Southwestern Ohio Council for Higher Education

Rodney B. McLaughlin
Wright State University

15 June 1995

Government Task Leader
Dr. Randy Hay
WL/MLLM

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

As with the previous Task , work was slow during the first month or so from the start. During this period, time was spent reading literature and becoming familiar with the facilities. The technical papers of relevance concerned work that would be done later. Specifically these papers were about the theory behind push-in and push-out testing.

The bulk of my work during the first 4 months consisted of cutting small specimens from a larger piece of material for future analysis. This work was very tedious and time consuming.

Lithium aluminum silicate composite samples were cut and cleaned for future analysis by the engineers. Bend specimens were cut for failure analysis of silicon carbide combuster plates. Samples from three different manufacturers were prepared. A failure analysis involves determining the causes of failure and providing solutions to prevent future failures. Fiber push-in samples were also prepared from nicalon silicon carbide composite materials.

Cleaning of ceramic composite specimens in an ultrasonic bath of acetone is essential for any kind of analysis. Metallographic techniques were also learned. Metallography involves (1) mounting small specimens in a cold epoxy and (2) polishing the samples by using progressively finer grit sizes in order to bring out the microstructure for analysis.

The most recent work consisted of performing fiber push-in testing and reducing the data. The push-in and push-out tests are useful in determining properties of the interface between the fibers and the composite matrix. Fiber push-in testing consists of pushing individual fibers of about 20 microns in diameter into the matrix until sufficient debonding occurs. Reducing the data involves generating plots of load versus displacement on the computer for analysis.

DESCRIPTION OF RESEARCH

Conventional methods were used in the research and testing. The cutting of samples was done using low-speed saws with 5" diamond impregnated saw blades. Polishing was performed on 8" polishing wheels using TBW diamond polishing disks. Fiber push-in testing was done on an Instron testing machine using a conical tungsten carbide probe. Data reduction was done on Apple Macintosh machines and the plots were generated using Kaliedagraph software.

RESULTS

The most recent work involving the fiber push-in testing was the most rewarding in terms of learning and overall job experience. After some instruction, the testing and data reduction was performed without any assistance. Along the way I have learned some theory behind the testing, as well as a basic interpretation of the data (load vs. displacement plots). In addition, I have learned the basic techniques of metallography.

METALLOGRAPHY OF CERAMIC COMPOSITES

Task Order No. 119
Student Support Program
Southwestern Ohio Council for Higher Education

Gregory R. Meyer
University of Dayton

1 August 1995

Government Task Leader
Dr. Randy Hay
WL/MLLM

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TASK ASSIGNMENT

Development of ceramic matrix composites requires that the behavior of the composites be tested and fully understood. Several methods are used to perform this testing so that the data acquired can be analyzed efficiently and comprehensively. In particular, fiber tensile testing was performed to determine the tensile strength of the various fibers of interest. This data is then used together with data from other types of testing, such as fiber push-out testing and creep testing, to develop a strong understanding of the overall behavior of the material in interest. The goal of this testing is to develop a suitable ceramic matrix composite which will have a strength comparable to steels and a thermal behavior which will surpass that of the current standards.

Once this material has been developed, it can then be used to replace many parts within a turbine engine which are currently made of steel. The composites, will hopefully, enhance the performance of the turbine and lessen it's weight.

Tensile testing was performed using an Instron testing machine which was equipped with a computer data acquisition program. Analysis of this data was performed using a computer program which evaluated several properties of the test subject. Analysis of the data acquired from fiber push-out testing was also performed via computer. This procedure, however, required direct human evaluation using the computer as an aid and not as the analytical tool. Also involved in this Task term, was simulation of fiber placement throughout the thickness of the matrix in an attempt to obtain a more accurate view of the behavior of the fibers during the push-out test procedure. All of the data analysis and the fiber simulation was performed using Macintosh computers and Kaleidagraph and Mathematica software packages. Data acquisition was performed using a PC equipped with LabMate software.

The second primary project consists of data analysis of fiber push-out testing using KaleidaGraph, a spread sheet graphing package, on an Apple Macintosh. The raw data obtained during the push-out test of a fiber reinforced ceramic matrix composite is manipulated through the use of a theoretical set of guidelines which were developed to determine behavioral and strength characteristics of the composite. This involves identifying and accounting for the composite itself. Through such manipulation certain characteristics of the composite, such as coefficient of sliding friction, radial stress, interface toughness, etc., can be calculated.

Performing the actual push-out testing on these fiber reinforced ceramic matrix composites involve a fairly simple arrangement of equipment set up to produce a stress on the fiber which is imbedded within the matrix while the same time recording the displacement of the fiber from its original position. An Instron loading cell is used to produce the stress upon the fiber while the displacement and acoustic emissions are recorded to an IBM data file and a graph of the stress behavior is plotted. The specimen being tested is, as before, prepared by cutting and grinding to the appropriate shape and size followed by polishing it to a mirror like finish.

By performing the tests described above, understanding of the behavior of ceramic matrix composites continues to grow. It has been learned that alignment of fibers within a matrix is less than optimum and that interpretation of data acquired from push-out testing may be misleading. The fiber's behavioral deviation from theory during the actual push-out test may be dependent upon it's alignment and, therefore this factor needs to be studied in greater detail.

From analysis of tensile test results some fibers have been dropped from interest due to their poor behavior. Still, others have shown remarkable and sometimes unexpected behavior and are, therefore, being studied in more detail to determine their eligibility for the final ceramic matrix composite.

Throughout the Task, many new pieces of equipment have been used along with new techniques and theories to provide for an excellent hands-on education.

METALLOGRAPHY OF CERAMIC COMPOSITES

Task Order No. 119a
Student Support Program
Southwestern Ohio Council for Higher Education

Cohen King
Sinclair Community College

1 August 1995

Government Task Leader
Dr. Randy Hay
WL/MLLM

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Thanks to Dr. T. A. Parthasarathy for allowing me to work with him and to help me learn some techniques involved in research and development. Also, thanks goes out to other people of (Universal Energy Systems) UES for demonstrating how to operate and work different machines used for doing these types of tasks. A couple of scientists that stand out are Charles Cooke and Dennis Petry.

Many things have been done during the time spent in the Wright Laboratory/ Materials Directorate. First, tensile tests were done on some nicalon fibers to find their maximum load capacity before breaking. During this testing, displacement readings were also taken and recorded. The purpose of the tests was to find the Modulus of the fibers and compare them to other tests done and to determine whether they would be beneficial to the operation of the engines where they would be placed. Also, other tests were done on some Nextel aluminum oxide fibers where some were coated with boron nitride (BN) and some were not.

Before any tensile tests were done on these fibers, a laser was used to determine the diameter of the individual fibers. Later, the same tensile testing as mentioned above was conducted. Lastly, a couple of ceramic samples were cut, ground, and polished to a desired size that later would be examined under a microscope.

In preparing the fibers, some metal frames were designed and made of a particular size in which the individual fiber's diameter could be determined. Then those same fibers were tested and their maximum loads determined as well.

The equipment used to do the above tests was a Spectra Physics Class 2 laser (low-powered helium-neon laser) to determine the fiber diameter and an ATS - Universal Test Machine with a 100-lb load cell in conjunction with a Modular Testing Panel that was hooked up to a computer to find the load capacity of the fiber. In finding the diameter of the fibers, the laser is shot directly at the fiber producing an interference pattern. By using a known distance marked off on a note card for the distance between the first points of interference and the distance between the laser and the note card, the diameter of the fibers can be determined. This was done by using geometry and the known wavelength of the laser.

During the testing procedure, the Modular Testing Panel transfers voltage readings taken at regular intervals and transfers them into loads to be recorded by the computer. At the same time, a displacement reading is taken at the same regular intervals and recorded by the computer.

Once the testing is done, the maximum load is found using Microsoft Excel and then corresponded to the diameters found so that the Modulus of the fibers can be determined. Kleidagraph 3.0 was also used in plotting the load vs. displacement of the individual fibers (when necessary).

A lot has been learned so far working in the laboratory, both from an individual aspect and the actual knowledge attained. In addition, some of the painstaking processes that scientists and engineers go through during the research and development stage of a process were witnessed. There is still a lot to be done and accomplished while working for SOCHE at the Wright Laboratory.

COMPUTATIONAL EXPLORATION OF BIOPOLYMERS

Task Order No. 121
Student Support Program
Southwestern Ohio Council for Higher Education

Paul Bulson
University of Dayton

31 May 1995

Government Task Leader
Dr. Ruth Pachtor
WL/MLPJ

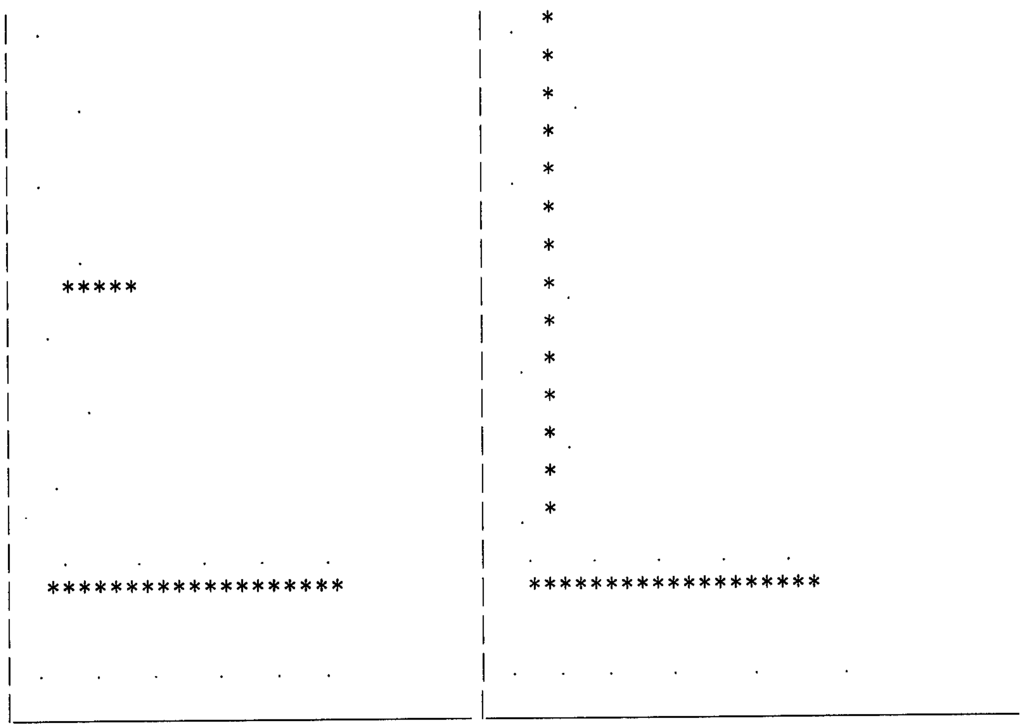
ACKNOWLEDGMENTS

I would like to take this time to thank everyone who assisted me in understanding the different concepts of chemistry and biology that I needed to perform my Task and to all those who trusted and had faith in me to perform work for them. This list includes Dr. Ruth Pachtor, Dr. Souyma Patnaik Dr. John Wangz, and Captain George Gates. Also, a special thanks to Dr. James Lupo for assisting me with the Unix operating system and the compilation of several important programs.

The Task objective was to provide computer support to various researchers in MLPJ. The Task called upon both professional and educational computer experience to write and/or modify code that would be beneficial. In addition, skills in mathematics were utilized to help Dr. Patnaik graph a molecule on a three-dimensional grid.

The first assignment was to continue some work of the previous student in this position. Basically, what was needed was a program to use one of the user entry points to the CHARMm software to modify how the energy was being calculated. The program written included a subroutine (user) to calculate a number to be added to the energy determined by CHARMm. The number calculated was based upon the principal axis of the two molecules. The two axis would determine an angle and from that angle code was written to calculate an energy value. The major problem faced was to determine the principal axis of each molecule. After several different graphing/interloping techniques were implemented to try to find the principal axis, the decision was made to use the jacobi method since it yielded the best results. The jacobi method was used to find the eigenvectors of the matrix determined by the equation #1 were alpha and beta each take on the values 1,2,3, thus forming a 3 X 3 matrix. The sum is taken over all atoms i. The positions are measured relative to the center of mass. The jacobi method results in three eigenvectors and the three corresponding eignevalues. The overall algorithm for the solution to the problem is as follows. First, determine the center of mass for each molecule. Then calculate all the inertia tensors. This results in 2 matrices and for each one apply the jacobi method to determine the eigenvector used to represent the principal axis of the molecule. The two principal axis are then used to determine the angle between the two molecules. That angle is used in an energy equation to determine an energy value with this subroutine will then pass back to the CHARMm program.

The first method attempted was least squares, but it would fail every time the angle was greater than 45 degrees. This was a theoretical problem and not an implementation problem. Originally the idea was that there was an error in the code that only affected those angles greater than 45 degrees. Thus, an attempt was made to search for a programming error. In reality, after consulting several numerical methods books and thinking back to numerical methods class, the realization was that the code was correct and that the idea of using least squares was wrong. The least squares method was taking vertical lines and graphing them to be horizontal. This determination was made by using several different graphing programs to graph the results. In addition, the results of the jacobi method were tested at the University of Dayton on their vax system using the MAPLE software that was used in Numerical Analysis class. This is probably the best example in my computer career where something learned in class (both theoretical/applied) was used in a real world application. The code wrote was the first code I ever wrote in Fortran. Time was also spent learning how the code would interface with the CHARMm software. Below is an example of what the least squares method was doing wrong compared to what it should have been doing.



Least Squares Method Jacobi Method

Each . represents an atom and the * represents the lines that each method would determine. Notice how the Least Squares Method takes the vertical line and makes it horizontal, while the Jacobi Method more accurately determines the true principal axis.

Since then, the majority of time has been spent on a molecular dynamics package called MD. This project started when I was handed a brief document describing what the MD code did, where you could find it, who wrote it, etc. Based on that information, the software was downloaded on to the biotech system. The software was then compiled successfully on that system. It was also successfully run on that system. Since then, the software has also been ported to the Curie system. The first problem encountered was molecular dynamics was a foreign subject to this person. Specifically, molecular dynamics that utilized the fast mulitpole algorithm (FMA), like MD did. To solve this problem, numerous papers were read that were written by John A. Board, who described his work with the FMA and from that a very general idea of what MD utilizing FMA was acquired. The second problem encountered was that the MD code had little or no documentation and several people were interested in exactly how it worked. Due to the lack of documentation, much time was spent running tests on the code and studying the output to determine exactly what was going on. Some of that information is contained in document.txt in my directory /md_mine on Curie. I have included that with this paper.

As the work progressed, there was a desire to run our own simulations with our own molecules, rather than the molecules provided in the MD package. The first problem that occurred in this process was that our .psf file did not match up with their .psf file. Testing proved that it was necessary for us to change our .psf so that it corresponds to what the MD code expects. The problem was traced back to the "atom" structure. In "atom" (struct.h) there are, among other variables, type, and typeind. Type is a name (char[4]) and typeind is an index (integer). Originally the thought was that our .psf supplied typeind and that MD contained a conversion list because the function typeindex existed. What typeindex did however was simply check to see whether a certain type of atom is in the structure. Upon going through our .psf and changing the 6th column to stings similar to what the MD expected, the .str file was created.

The second problem that occurred was the following error: "Error in struct: entering mderror:" "Illegal binary file format". The cause of this error was that print statements added to the code were being routed to the .str file that was being created. Those print statements in the .str file were what was causing the error. At this point, it also was observed that several lines to the parameter file param19.pro had to be added in order for certain angles to be defined.

The third problem that occurred was the following question from Dr. Patnaik , "Are the k's (a constant) in both CHARMm and MD the same?" According to all the information that was found, they are. Between the documentation provided by CHARMm and the MD code (there was no documentation to speak for MD), they appear to be the same.

The fourth problem that occurred was that the CHARMm parameter file that was to replace the MD parameter file first had to be converted to the form that was expected by the MD program. After this conversion,. another problem arose. That problem was that several atoms (NH1 for example) are not listed in the CHARMm parameter file, yet MD expects them. The solution was to look up the missing CHARMm parameters in the CHARMm parameter book and insert them in the file. For NH1, the values for NT were used. After these problems were solved, a run of the MD package using our own molecule, rather than one provided was finally completed.

After studying the system some more, the introduction to Alan McKenney occurred. The purpose of this was to speed up the study of the MD code, the FMA and the PFMA code. We have talked on several occasions and all that can be done has been done to assist him in understanding how the MD code works. He currently y has taken over the MD research.

Some time was also spent assisting Captain George Gates with the optimization of his genetic algorithm code. This process has involved the studying and modifying of the code. The first change was needed was to change part of the routine compatible were the original programmer had used unnecessary loops and if statements. After studying the code and discussing with Capt. Gates about what was actually going on, the changes that we agreed to were implemented.

This is the included document mentioned above.

```
main        --> reads in parameters
(dyn.c)     --> str_read reads in .str file
                (struct.c)
            --> coor_load reads in coordinates
                (coor.c)
            --> maxwell generates Maxwell distribution of velocities
                (temper.c)
            --> verl_init initializes file wide variables
                (dynamics.c)
                --> ener_init calls nb_setup, inittemp, dc_init
                    (energy.c)
                    --> nb_setup initializes file wide variables
                        (nbond.c)
                    --> inittemp initializes the variable temp
                        (bonde.c)
                    --> dc_init initializes the grid, pairlist
                        and nonbonddata list (dist.c)
                        --> pfma_init initialize necessary stuff
                            (pfma.c)
                            --> init_PFMA create grid structure
                                via subroutines (PFMAinit.c)
                                --> create_tree sets up grid structure
                                    (PFMAinit.c)
                                    --> insert_points sets up grid structure (PFMAinit.c)
                                    --> init_constants sets up grid structure (PFMAinit.c)
                --> verl_velo updates the coordinates
                    (dynamics.c)
                    --> potential interfaces with the energy calculation routines
                         (energy.c)
                         --> bondenergy calculates the bond energy
                             (bonde.c)
                         --> angleenergy calculates the angle energy
                             (bonde.c)
                         --> dihedenergy calculates the dihederal energy
                             (bonde.c)
                         --> impropenergy calculates the improp energy
```

```
                (bonde.c)
            --> dc_ener
                (dist.c)
                --> pfma_ener calls PFMA_adjust and PFMA
                    (pfma.c)
                    --> PFMA_adjust
                        (PFMA_adjust.c)
                    --> PFMA is the main driver routine to FMA
                        (PFAM.c)
                        --> PFMA_shell is interface to FMA
                            (PFMA.c)
                            --> step2 executes steps 1 and 2 of FMA
                                (step2.c)
                            --> step3 executes steps 3, 4 and 5 of FMA
                                (step3.c)
--> verl_ceiling limits excessive velocities
    (dynamics.c)
--> printenergyrecord() prints the energy record
    (energy.c)
--> simulation loop
    --> verl_step updates the coordinates and
        velocities of the atoms (dynamics.c)
        --> potential interfaces with the energy calculation routines (energy.c)
        --> bondenergy calculates the bond energy
            (bonde.c)
        --> angleenergy calculates the angle energy
            (bonde.c)
        --> dihedenergy calculates the dihederal energy
            (bonde.c)
        --> impropenergy calculates the improper energy
            (bonde.c)
        --> dc_ener
            (dist.c)
            --> pfma_ener to call PFMA_adjust and PFMA
                (pfma.c)
                --> PFMA_adjust
                    (PFMA_adjust.c)
                --> PFMA is the main driver routine to FMA
                    (PFMA.c)
                    --> PFMA_shell is interface to FMA
                        (PFMA.c)
                        -> step2 executes steps 1 and 2 of FMA
                           (step2.c)
```

```
                    --> step3 executes steps 3, 4 and 5 of FMA
                        (step3.c)
        --> nb_energy calculates nonbonded energy
            (nbond.c)
        --> dc_nbond
            (dist.c)
            --> dc_build sets up a grid structure
                (dist.c)
            --> nb_pl calculates energy affected by pair interactions
                (nbond.c)
--> verl_ceiling finds the atoms with excessive velocities
    (dynamics.c)
--> harm_check does some sort of error check that I'm not familiar with.
    (harme.c)
--> printenergyrecord prints the energy record to stdout
    (energy.c)
--> temperature
    (temper.h)
--> verl_scale scales the velocities
    (dynamics.c)
```

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 122
Student Support Program
Southwestern Ohio Council for Higher Education

Karen Hussong
Wright State University

30 June 1995

Government Task Leader
Dr. Thomas Cooper
WL/MLPJ

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I would like to thank Dr. L. V. Natarajan and Dr. Tom Cooper who have directed and assisted me in developing and performing the goals of my Task. They have been a great source of knowledge and encouragement, whenever I get discouraged. Also, Dr. Zbig Tokarski has often helped guide me in solving problems that arise. I also would like to express my appreciation to Dave Stitzel for his synthesis work and knowledge of the monomer units used in this research.

TASK ASSIGNMENT

The objectives of this Task were to synthesize and characterize biopolymers which contained nonlinearly active molecules. These polymers are then used as matrices for laser hardening devices. This involved coupling reactions with polypeptides and nonlinear optical (NLO) compounds. Also, synthesis of modified monomer units was performed and polymerized to obtain fully substituted polypeptides. Synthesis was followed by characterization procedures, which involved various measurements of the compound's properties to compare with other similar systems. Using this information, conclusions about the possible NLO properties and applications of these materials can be formed.

RESEARCH DESCRIPTION

The biotechnology division has researched the ability to use functionalized polypeptides with nonlinear optical chromophores to produce laser harden materials with second harmonic generation (SHG) characteristics.

The functionalized polypeptide is coated on an ITO (indium tin oxide) coated glass slide by various methods. This film is then heated above its Tg, an electric field is applied, and then cooled below its Tg. This gives the film an overall net orientation, needed for SHG. However, one downfall of these systems is their low thermal stability. The film will again randomize once the electric field is off. This research investigates the addition of a crosslinking agent along with the chromophore on the polypeptide to increase stability of the film once the electric field is removed. The crosslinking may "lock-in" the alignment after corona poling.

To obtain highly functionalized polypeptides, polymerization of the modified monomer units was investigated. The goal is to produce a copolypeptide with either the NLO chromophore or the crosslinking agent substituted on all the glutamate units. Substitution with p- nitrobenzyl alcohol and cinnamyl alcohol, or disperse red 1 and cinnamyl alcohol was pursued.

Once the modified monomer units were synthesized by a co-worker, the monomer was converted to the anhydride to perform polymerization. The synthesis of the modified polypeptide required anhydrous reaction conditions which involved drying all solvent and heat treatment of all glassware. The first synthesis step was reacting the monomer with triphosgene to form the anhydride. Upon reduction of the reaction solution, an oil was obtained which contained the anhydride. This was decolorized with activated carbon and filtered, then precipitated with hexane. The resulting oil was polymerized in dioxane with triethylamine (TEA) as the initiator.

Continued investigation of previously synthesized modified poly glutamate peptides was also performed. These peptides were modified by coupling the NLO chromophore and a crosslinking agent to the a-helical poly(L-glutamic acid). Crosslinking of these samples was performed and analyzed.

The substituted polypeptides were analyzed to determinethe change in their thermal properties before and after crosslinking. This was probed by differential scanning calorimetry (DSC) and monitoring the Tg and any other types of phase changes.

The polypeptides with the crosslinking agents attached were then crosslinked. Due to decomposition of some of the chromophores when irradiating at the absorption maximum of the cinnamate groups, a photoinitiator was added in the nitrobenzyl substituted polypeptide or doped into the film. This photoinitiator was irradiated and transferred the energy to the cinnamate group. A medium pressure Hg lamp at 300 W produced a broad band spectra. A monochromator was then utilized to only pass 311 nm light. All other films were irradiated at 255 nm without a photoinitiator. Films were typically irradiated for 1-2 hours. The crosslinking can be monitored by UV-Vis. In FTIR, the carbonyl group and one of the amine groups mask the depletion of the C=C breakage.

RESULTS

Polymerization of the p-nitrobenzyl alcohol modified monomer has been successfully performed. This is supported by the FTIR spectrum. A peak is present at 1660 cm^{-1}, which is indicative of the α-helix formation. To form an α-helix, approximately 15 monomer units must be connected. The substituted polypeptide is soluble in DMF and is tan in color. Synthesis and isolation of the cinnamyl alcohol modified monomer is currently being performed by myself and Dave Stitzel. Once this monomer can be polymerized, a copolymer can then be made where there is control over the percent substitution of the substituents. Then will be able to check for increases in thermal stability and SHG stability with time.

The previously synthesized polypeptides were analyzed for increased thermal stability with crosslinking. The disperse red 1 system with cinnamyl alcohol also attached to poly(L-glutamic acid) had a Tg of 15-19°C before crosslinking and 22-27°C after crosslinking. This supported the theory that crosslinking would increase the thermal properties. However, the Tg was well below that of the substituted peptide with only the disperse red 1 substitution (no crosslinking agent). Its Tg was 80-85°C. The decrease of Tg with the addition of the cinnamate side chain groups could be due to their low melting point of 33-35°C. The change, also, may be a result of differences in side chain interactions with and without the addition of the cinnamate groups.

The other system with p-nitrobenzyl alcohol and cinnamyl alcohol attached to poly(L-glutamic acid) exhibited a Tg at 53-55°C. As previously stated, to crosslink this system the addition of a photoinitiator was added to prevent decomposition of the chromophore. With the photoinitiator present and after crosslinking the Tg of the system fell to 35-39°C. It seems the photoinitiator is acting as a plasticizer when embedded in the functionalized polypeptide.

More research into these systems is needed to understand fully the variations found in this Task. However, it can be seen that crosslinking does increase the Tg for systems with no added photoinitiator. The investigation of changes in second harmonic generation need to be performed once the equipment is assembled. The combined results, once performed, may offer knowledge for choosing other systems that will result in the desired properties.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 122a
Student Support Program
Southwestern Ohio Council for Higher Education

Robert L. Haaga
Wright State University

30 June 1995

Government Task Leader
Dr. Robert Crane
WL/MLPJ

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I would like to give special thanks to the people who made this job a positive learning experience in my academic career: Dr. Lalgudi Natarajan, for his personal guidance and knowledge in chemistry and his effective ability to teach; V.P. Tondiglia for his extreme patience in teaching me the laboratory techniques involved with lasers and optics; and Dr. Cooper, Dr. Robert Crane and SOCHE, for their positive attitudes and helpfulness over the past year. Finally, I'd like to thank all MLPJ personal for their bits and pieces of information that made my Task a little easier. This is a great team to work with.

TASK ASSIGNMENT

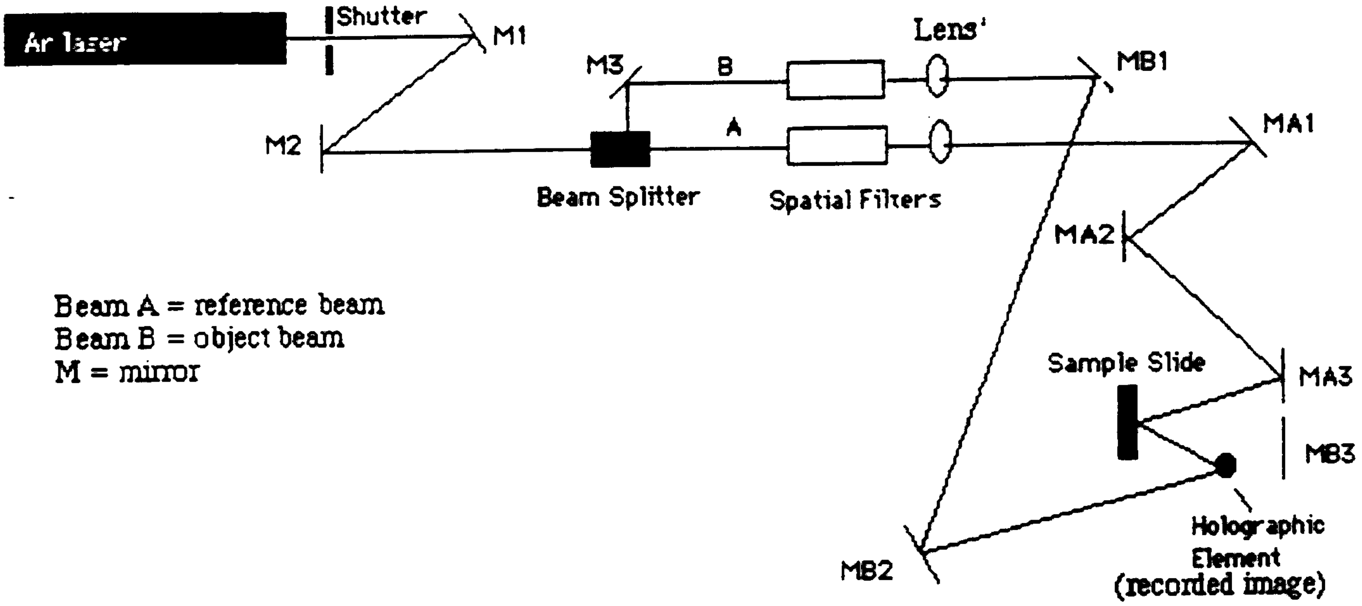
Task No. 122 dealt with the synthesis and characterization of polymers. The polymer systems that were studied in detail consisted of nematic liquid crystals dispersed in a prepolymer syrup. When polymerization is induced, these polymer-dispersed liquid crystals (PDLC's) can be used for a variety of holographic applications. My Task was to create different prepolymer syrups and study the effects those varying concentrations of components of these syrups has on the resulting holograms and their optical properties.

DESCRIPTION OF WORK

The first part of the Task was to create prepolymer syrups containing the liquid crystal of interest. The syrups ingredients consisted of the monomer dipentaerythrol hydroxy penta acrylate, a crosslinking monomer N-vinylpyrrollidone, co-initiator N-phenylglycine (NPG), a photoiniator Rose Bengal or Methylene Blue, and a liquid crystal. The liquid crystal used in all experiments was E7. The components of the syrup were mixed accordingly with emphasis in studying the different effects of changing the weight percentages of each component in most cases the liquid crystal. Numerous syrups were made by varying the percent liquid crystal and adding a small percentage of surfactant octanoic acid. Once the syrups had been produced, the system had to undergo photoinitiation to be able to record the desired holographic application. Two types of holograms were desired. The first was to record Bragg gratings in the prepolymer syrup samples to study which component of the syrup greatly affected optical characteristics like diffraction efficiency. Another desired characteristic of these Bragg gratings were the ability of these samples to be tuned with an applied electric field to produce an optically clearer grating with lower diffraction efficiency. Most of the gratings were written with an argon laser split into two beams with a prism at 488 nm. The absorption by the photo-initiator (Rose Bengal) excites it to an excited triplet state that undergoes an electron-transfer with the co-initiator creating an NPG radical which, in turn, induces free radical chain polymerization. The gratings are written when the regions of constructive interference of the two laser beams undergo the described polymerization which in turn leave the dark fringes as unpolymerized sample (Sutherland et. al. 1983). The diffusion of these molecules to regions of ensuing polymerization cause the liquid crystal droplets to separate into distinct phases. Different dyes were also used (Methylene Blue) which allows the gratings to be written at different wavelengths.

The second desired hologram was to be able to record various images in these polymer systems and see which syrup produced the clearest tunable images. Transmission holograms were recorded in the following fashion. An argon laser was used at 488 nm and split into two beams which are known as the reference beam and the object beam. The beams were passed through spatial filters and then through a lens. The reference beam remains unchanged from the lens to the sample and the object beam is directly reflected off the image to the sample slide. Both beams travel the same distance from the beam splitter to the sample. The sample was the prepolymer syrup which was pressed between two ITO glass slides with various spacing between the two slides and then fixed with clips to hold the two slides together. OD filters were fitted on the slides to reduce the scattering of the light entering and exiting the slides. The ability to record images as holograms in these polymer systems prove to be challenging. The intensities of both the reference beam and the object beam must be carefully adjusted depending upon the initial intensity of the laser light. The objects that record the best images are those that are very shiny and reflect light very well. A diagram outlining this setup is shown.

Laser Setup for the Writing of Holograms



RESULTS

Much was learned about these liquid crystal systems. Numerous syrups of various concentrations of liquid crystal were made and tested. Experiments run with syrup RB77 had the following composition which was used to determine a good laser intensity to record Bragg gratings.

dipentaerythrol hydroxy penta acrylate	61.3%
N-vinylpyrrollidone	6.4%
N-phenylglycine	1.5%
E7	30.6%
Rose Bengal	0.15%

The intensity decided upon was approximately 25 mw/cm^2. It was found, using laser intensities less than this caused a pinkish tint to the samples that concluded that all of the Rose Bengal had not been excited to its triplet state. It was also found, intensities higher than this were hard to obtain using the proper optical density filters, which are required to reduce the scattering of the laser light entering the sample slides. When OD filters are removed to reach higher intensities, the grating usually consists of numerous cross gratings which reduce diffraction efficiency.

Other syrups tested were to study the effects of added amounts of surfactant octanoic acid. Four syrups were constructed with the following amount of octanoic acid Syrups with real high concentrations of surfactant, as in RB82S and RB83S, produced samples with low diffraction efficiency and poor tunability; so, samples with acid contents of 1-5% were thought to be the best.

RB80	0%
RB81S	4%
RB82S	7%
RB83S	9.3%

A slight variation to the addition of this acid was also tried. It was found when images were recorded as holograms it was better to add the acid directly to the sample slide and mix a syrup with low or no acid already premixed with the other components directly on the ITO slides, and stir with a pipette. By adding the acid directly to the prepolymer syrup on the sample slide, no accurate measurement of how much you've added has been discovered. The surfactant, however, seems to lower the voltage needed to tune the sample but at the cost of losing some diffraction efficiency.

The polymer systems worked with proved to be very challenging in narrowing down which factors greatly affected the desired optical properties. It was proven through the experiments performed, that five or six factors must be considered when working with these systems. Among a few are % liquid crystal, % octanoic acid, laser intensity, and the various percentages of crosslinker and co-initiator. Now, emphasis must be put on trying to put all these variables together to get the "ideal" syrup.

Works Cited

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SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 123
Student Support Program
Southwestern Ohio Council for Higher Education

Lynn R. Frock
Sinclair Community College

19 July 1995

Government Task Leader
Dr. Tom Cooper
WL/MLPJ

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TASK ASSIGNMENT GOALS

The Task goals are twofold. First, to survey materials for optical limiters and second to prepare samples for laser testing. The primary focus was the investigation and characterization of optical limiters. In the process of looking at materials for their durability and optical activeness, C60 was chosen as a material of much interest. The properties of interest are optical limiting, nonlinear absorption and photoluminescence of C60 in select solvents. Expanding the useful list of solvents for C60 in nonlinear optic applications has led to the investigation of the behavior of C60 in complexing solvents. The comparison of C60 complexes in toluene and methylcyclohexane with aromatic amines, DEA, BZN, NMP, and TPA was the primary focus of investigations.

RESEARCH

Two sets of samples where made, one for laser testing and a second set for determination of the equilibrium constants. Complex formations in C60 solutions have already been noted in diethyl aniline[1]. A wide survey of solvents was conducted and several additional solvents gave evidence of complexing behavior with the C60 when analyzed with UV-Vis and fluorescence spectroscopy. All of the solvents with complexing behavior contained nitrogen. They are benzonitrile, N-methylpyrrolidone, and triphenylamine. A careful study was done to characterize the formation of the complexes formed in C60 / toluene solutions when each complexing agent was added. Diethyl aniline was added to the study, as a reference complexing system. Formation of the complexes was followed by UV-Vis and fluorescence spectroscopy. Nash plots of the complexes were done to determine the equilibrium constant and the isosbestic point for each system.

Stock solutions of C60 in MCH and toluene were doped with higher and lower concentrations of each complexing ligand and examined. The stock solution of C/60\toluene (ss), ligand\toluene (ls), and C/60\ligand\toluene (lss), {toluene =(s)}, was made. The concentration of C/60 was 4.37E-4. Two titration's were made for each ligand. The first consisted of the addition of lss to ss to obtain increasing ligand concentration while maintaining substrate concentration. The second consisted of adding ss to lss to obtain dilution's of the ligand concentration. The method used here allowed for full ligand concentration range. For TPA, ligand was added to the reference cell because of internal absorption of this ligand at test wavelengths. The absorbance was monitored using UV spectroscopy. UV spectra were taken on a Perkin-Elmer Lambda 9, and fluorescence spectra were taken using a Perkin-Elmer LS51B. Full spectra were taken at intervals in the titration's. Absorbance scans were recorded and monitored at 600nm and 694nm.

RESULTS

C_{60} is known to be the acceptor in complexes formed with aromatic amines[5]. In the MCH systems, the K value for DEA in MCH matches the literature value of .18 with a .005% error[1]. In the $C_{60/toluene}$ system DEA has a K value of 0.71. This is approximately four times greater than in MCH.

Broadening of the spectra and the appearance of isosbesic points indicative of complex formation in a 1:1 stoichiometric ratio[2] was observed for DEA, BZN, TPA and toluene in C60 / MCH solutions. Similar results were seen in C60/ toluene solutions for DEA, BZN, NMP and TPA. Evaluation of the equilibrium constant (K) was calculated from Nash plots[3] whose linear fit shows 1:1 complex formation. [4]Table I shows the measured K values, and location of the isosbestic points for each system.

Table 1. Equilibrium Constants and Isosbestic Points for Complex Systems

Solvent System	Complex Agent	K(ml mol^{-1})@600nm	Isosbestic pt.@ nm
C_{60}/toluene	DEA	00.71	422
	NMP	01.18	420
	BZN	04.76	418
	TPA	11.00	--------
C_{60}/MCH	DEA	00.17	464
	NMP	-------	-------
	BZN	53.18	473
	TPA	00.2*	468
	Tolune	00.06	410

The absorbance of C_{60} at the specified wavelength was improved in the presence of the complex agent. DEA is clearly a better donor than toluene in solution. However, the slightly electropositive aromatic structure of the toluene may aid DEA in complexation. To be sure that toluene was not contributing significantly to the complex formation by acting as a complexing agent, toluene was tested alone in a C_{60}/MCH solution. The K value for toluene was measured to be 0.06 and an isosbestic point was observed. Thus, the effect of toluene as a complexing agent is minimal.

The K value for NMP could not be calculated in MCH, because of immiscibility, and had a small value in toluene. TPA data is inconclusive for MCH and is still being analyzed. The literature value for TPA in MCH is 0.2[6]. There may be some stearic hindrance with the TPA structure in the MCH system which interferes with complex formation. Interestingly, in toluene TPA has a K value indicating possible solvent enhancement, similar to that seen for DEA in the two solvent systems. BZN shows a very large K value of 53.18 in MCH and a much smaller value in the toluene system. This behavior is opposite to that of DEA and TPA in the two solvent systems. A possible explanation may be that in MCH there is no solvent assistance for complexation. In toluene the electronegative rings on the DEA and TPA are getting slight donor assistance from toluene, while BZN has an electropositive ring and it must compete with toluene, which is a weak donor. To be sure, electron donating functional groups can be put onto the BZN in the para position and tested in the toluene system.

Fluorescence spectra were taken of C_{60} in the pure solvents for toluene, BZN, NMP and DEA. A broadening of the fluorescence spectra is evident with the complexing agents indicating the formation of other species not present in the solvent.

Charge transfer complexes form in solutions of C_{60} and aromatic amine solvents. The equilibrium constant is enhanced by toluene for amine solvents with electronegative aromatic rings. The nonlinear absorption behavior has been studied and found to correlate with the concentration of the charge transfer complex and the equilibrium constant.

Large effects in the excited state cross sections at 694nm due to different aromatic solvents has been demonstrated. New techniques have been introduced. The first technique studies nonlinear absorbers by varying the solvent and leads to the establishment of a large data base of nonlinear properties. A new simple technique to extract an effective excited state crosssection at a single wave length has been introduced also.

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SYNTHESIS OF CHARACTERIZATION OF POLYMERS

Task Order No. 124
Student Support Program
Southwestern Ohio Council for Higher Education

Christine S. Yoon
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11 August 1995

Government Task Leader
Dr. Tom Cooper
WL/MLPJ

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

Task 124 focused on nearinfrared absorbing materials. The goal of this investigation was to explore, via literature searches, the available material for nearinfrared absorbing dyes in the range 700-1400 nm with minimal loss of transmission in the visible range. The nearinfrared (NIR) region of the spectrum covers the interval from about 0.7 μm (14285 $cm^{-1)}$ to 2.5 μm (4000 cm^{-1}) and contains a great deal of spectral data that is mostly concerned with overtones or combination vibrations. Only the overtones or combination bands of vibrations involving hydrogen (such as C-H, O-H, and N-H) were observed at appreciable intensities. Because of their comparatively small absorptivities, sample paths had to be longer than those required for fundamental bands. The origin of the NIR absorption bands was kept in mind when using this region for analytical purposes.

DESCRIPTION OF RESEARCH

The compatibility of the dyes displaying nearinfrared absorptions with polycarbonates was based on chemical structures. An intense literature search was done and all nearinfrared dyes were investigated and evaluated for our purposes. The dyes were classified and grouped according to their journal, chemical name, chemical formula, chemical structure, maximum wavelength, maximum band width, extinction coefficient, and the availability of the compound.

The literature search was performed in two sets, the first being a search from 1960 to 1985 and the latter being a search from 1985 to 1995. When absorption spectra was available, the spectrum was extrapolated to calculate the maximum wavelength, band width at half maximum, and the extinction coefficient. The following aspects were stressed and researched in detail:

* Chemical structure of the material

* Organometallic coordination complexes that are known to have absorption bands in the nearinfrared region.

- Synthetic organic dyes of the merocyanine class as well as quinones with metal complexes.
- The search focused on the state of the art dye technology in developing dyes that display nearinfrared absorptions.
- A complete literature search from 1960 to 1995.
- The dyes were grouped according to the band width, extinction coefficients, and wavelength maximum.
- The availability of these materials, whether the dye is commercially available or not and, if the latter, then what the best means to synthesize the compounds were all investigated.
- Dyes with multi pass bands, containing multiple high narrow transmission pass bands, were considered for further investigation.
- Notch filters-narrow band absorbers, in the visible spectrum with good OD and minimal loss in the rest of the band, were also to be investigated.

RESULTS

The primary focus of the research was to explore compounds whose spectral properties would provide attenuation of light in the 700 - 1600 nm region. In particular, attenuation of generally non-agile lasers of several different wavelengths were considered. What was discovered was that the rhodium complexes have strong absorption properties. It has strong absorptions in the 835 nm to 860 nm region.

The Leuco-dye, as published by Yoshida and Kubo, displays a maximum wavelength at 343 nm. When placed in the oxidant $FeCl_3*6H_2O$, the λ_{max} shifted to 495, 905, and 1002 nm. When placed in the oxidant $Cu(ClO_4)_2*6H_2O$, the λ_{max} shifted to 491, 897, and 985 nm.

Chrysochoos and Tokousbalides investigated the splitting of the nearinfrared absorption bands of samarium ions in phosphoryl chloride:Tin(IV) chloride, phosphoryl chloride:Zirconium chloride, and phosphoryl chloride:Titanium (IV) chloride. Several absorption bands of Sm^{3+} in $POCl_3$: $SnCl_4$ display a spectrum extending from 350 to 1600 nm. The absorption spectrum does not extend beyond 1600 nm since any absorption bands of Sm^{3+}, located in the nearinfrared, exhibit a characteristic band structure which is repeating itself from band to band. Three distinct components are present in each band envelope. Other compounds investigated were magnesium phthalocyanines which were found to display absorption maximum at 827 and 830 nm with maximum band widths of 85 and 115 nm, respectively.

Primarily, the search was focused on the bis(benzene-1, 2-dithiolato)Ni(II) complexes. This compound has been shown to display intense nearinfrared absorptions, with a maximum of intensity at 990 nm, 1055 nm, and at 1163 nm with corresponding band widths of 180, 250, and 245 nm, respectively. Consequently, the dithiolato-nickel complexes attracted strong attenuations because of their unique physiochemical properties. This made the application of the dithiolato-nickel complexes as low-dimensional conductors (O_2 quenchers) possible. The most significant characteristic of Ni complexes is that it displays a very intense NIR absorption (λ_{max}) at 1055 nm (with an extinction coefficient of $\varepsilon = 15400$). The NMe_2 substitution, onto the benzene-1, 2-dithiolato ligand, shifts the original NIR band to a much longer wavelength. The corresponding parent Ni(II) complex exhibits the NIR absorption band at $\lambda_{max} = 881$ nm.

Another discovery was that the nickel chelates, which as a liquid crystal, has an unusually strong absorption in the nearinfrared region (810-850 nm). The nickel chelates has a much lower absorption in its visible absorption region (580 nm), but more importantly, because of the phenyl substitution, it is a highly soluble compound. This makes it an excellent compound for absorption of laser radiation in the 810-850 nm region.

An example of a nickel chelates that displays a good nearinfrared attenuation would be bis (4-dimethylaminodithiobenzil)nickel and bis(4-diethylaminodithiobenzil)-nickel. Both display a broad, intense nearinfrared absorption centered at 1050 nm and 1075 nm, respectively. Other nickel chelates with attenuation potential include nickel thiobisphenon. Also, it has been reported that several of these compounds have been incorporated into a polymethacrylate (PMMA) polymer including the rhodium chelates.

The Chemistry department of York University synthesized and characterized the charge distribution of bis(4-*tert*-butylpyridine)-bis(3,5-di-*tert*-butylquinone)ruthenium. They showed the nearinfrared spectrum of $Ru(t\text{-}Bupy)_2(DBQ)_2$ showing absorptions in the 1100 nm region and disappearance of these absorptions upon coulometric oxidation of the complex. The optical absorption spectrum consists of bands at 280nm ($\varepsilon = 13000\ M^{-1}\ cm^{-1}$), 325 ($\varepsilon = 4060\ M^{-1}cm^{-1}$), 400 ($\varepsilon = 3780\ M^{-1}cm^{-1}$), and 580 ($\varepsilon = 1100\ M^{-1}cm^{-1}$) in the UV and visible regions. The most interesting feature is an intense, structured band centered at 1160 nm ($\varepsilon = 35300\ M^{-1}cm^{-1}$) in the nearinfrared region (Haga et al. 1986).

Upon analyzing all the information in terms of structural features and characteristics of the nearinfrared dyes, an extracted strategy for the design of NIR dyes was discovered. Considering only nickel complexes, a summarization was published by Mueller-Westerhoff et al. in 1991. It discusses the effect of the substituents and how the substituents offer the opportunity to shift the absorptions. The absorption shifts are possible because the substituents provide electron donating groups in one or several of the positions on the dithiolene nucleus.

The following factors are important to shift the absorption maximum of the dithiolenes to a lower energy as expressed by Mueller-Westerhoff:

1. Coplanarity of ligand pi-system and dithiolene
2. Presence of an extended pi-system
3. Presence of electron donating substituents
4. Fixing of the substituents into rigid coplanarity with the ligand
5. Attachment of sterically bulky substituents to increase solubility
6. Variation of the central metal to obtain different shifts and to tune the relaxation time.

Other nickel complexes include bis[3-(4'-dialkylaminophenylimino)-pyrido[2,3-a]phenothiazine]nickel(II). This complex dye has a maximum wavelength of 838 nm and a extinction coefficient of 782 /l $mol^{-1}cm^{-1}$.

This NIR project has not yet been completed and needs further investigation and additional work on seeking other infrared absorbing dyes.

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SYNTHESIS OF CHARACTERIZATION OF POLYMERS

Task Order No. 124a
Student Support Program
Southwestern Ohio Council for Higher Education

Laura A. Porter
Wright State University

11 August 1995

Government Task Leader
Dr. Tom Cooper
WL/MLPJ

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

The goal of Task 124 is to explore the available materials for Near IR absorption in the range 700-1400 nm with minimal loss of transmission in the visible range. The available materials are selected from literary searches of Near IR absorption related experiments. These dyes may have specific properties which would allow them to absorb the harmful effects of a variety of lasers. This technology could be used to protect the eyes of pilots and aircraft instruments from the damaging effects of lasers.

DESCRIPTION OF RESEARCH

The information collected for this Task was acquired by way of literary searches. Chemical abstracts were organized and by their journal, chemical name, chemical formula, chemical structure, maximum wavelength, maximum band width, extinction coefficient, and the availability of the compound. When absorption spectra were available, the spectrum was extrapolated to calculate the maximum wavelength, band width at half maximum, and the extinction coefficient. The following aspects were stressed and researched in detail:

* Chemical structure of the material

* Organometallic coordination complexes that are known to have absorption bands in the nearinfrared region.

* Synthetic organic dyes of the merocyanine class as well as quinones with metal complexes.

* The search focused on the state of the art dye technology in developing dyes that display nearinfrared absorption.

* A complete literature search from 1960 to 1995.

* The dyes were grouped according to the band width, extinction coefficients, and wavelength maximum.

- The availability of these materials, whether the dye is commercially available, or what the best means to synthesize the compounds were all investigated.
- Dyes with multi-pass bands, containing multiple high narrow transmission pass bands, were considered for further investigation.
- Notch filters-narrow band absorbers in the visible spectrum with good OD and minimal loss in the rest of the band were also to be investigated.

RESULTS

The chemical abstracts from the final literary search are still being complied. Only the data from the first search has been recorded. The abstracts of all other searches will be recorded when the remaining abstracts have been ordered.

SYNTHESIS AND CHARACTERIZATION OF POLYMERS

Task Order No. 125
Student Support Program
Southwestern Ohio Council for Higher Education

David P. Stitzel
Wright State University

6 July 1995

Government Task Leader
Dr. Thomas Cooper
WL/MLPJ

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TASK ASSIGNMENT

Task 125 involved the synthesis and characterization of numerous macromolecules containing nonlinear optically active side chains that can be aligned in an electric field. The longterm orientational stability of the side chains is a property that will be measured by second harmonic generation. It is believed that liquid crystalline cyclic siloxane macromolecules will enhance this stability by hindering side chain motion.

RESEARCH

A series of cyclopentylsiloxanes were synthesized containing different ratios of two mesogens, namely Cinnamyl-4-Allyoxybenzoate (Cin4AB) and Cholesterol-4-Allyoxybenzoate (C4AB) (Table 1).

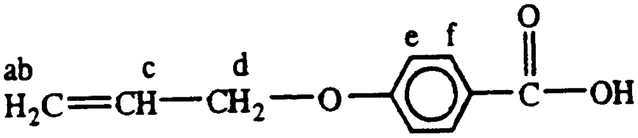
Table 1

	(Cin4AB)	(C4AB)
cSi 100	20%	80%
cSi 101	40%	60%
cSi 102	60%	40%
cSi 103	80%	20%
cSi 104	100%	0%

Once the substituted cyclopentylsiloxanes were synthesized, purified, and characterized they were placed into solution and crosslinked via 2 + 2 cyclo addition of the cinnamic moieties upon UV irradiation.

4-allyloxybenzoic acid (4ABA) was synthesized [1] as follows. 4-hydroxybenzoic acid (90.15g, 0.6527mole) was placed into a round bottom flask equipped with a reflux condenser, an addition funnel, a heating mantle, and a magnetic stirrer. The 4-hydroxybenzoic acid was dissolved in methanol (400ml) at 25°C which produced a brown solution. To this solution 15M potassium hydroxide (106.05g, 1.89mol) in distilled water was added dropwise over a 30 minute period. The reaction was heated to reflux and allyl bromide (65ml, 0.75mol) was then added dropwise over a 1 hour period. The reaction mixture was allowed to reflux for 26 hours, at which time approximately half of the methanol volume was removed by single stage distillation. The remainder of the reaction mixture was cooled to 25°C and added to distilled water (1L) in a seperatory funnel. The aqueous solution was extracted three times with diethyl ether (600ml total) to remove organic impurities and the ether layer was discarded. The remaining aqueous phase was heated to 40°C and neutralized with 37% aqueous hydrochloric acid (183ml, 2.23mol), which caused the product to precipitate out. The crude acid was obtained by filtration and purified by recrystallizing four times from ethanol to give pure 4-allyloxybenzoic acid (4ABA).

Yield: 48g (41%) white platelet crystals
IR: 3200-2500 (br, OH), 1700 (C=O), 1613 (C=C), 1261cm-^{1}(C-O)

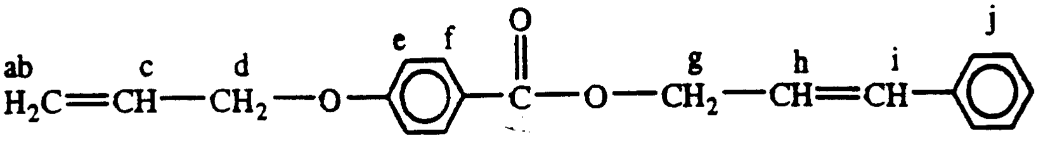


^{1}H NMR (CDCl3):
(a) δ = 5.33 (d, 0.98H),
(b) δ = 5.45 (d, 0.98H),
(c) δ = 6.07 (m, 0.96H),
(d) δ = 4.64 (d, 2.08H),
(e) δ = 7.00 (d, 2.01H),
(f) δ = 8.09ppm (d, 1.99H)
Elemental Analysis (3X1C):

Calc.	C 67.41	H 5.66	O 26.94
Found	C 67.12	H 5.50	O 26.60

The Cinnamy-4-Allyoxybenzoate (Cin4AB) mesogen was synthesized via a coupling reaction as follows. 4-allyloxybenzoic acid (4ABA) (10.04g, 0.05632mol), cinnamyl alcohol (7.566g, 0.05639mol), 1,3-dicyclohexylcarbodiimide (DCCI) (11.58g, 0.05610mol), and 4-dimethylaminopyridine (DMAP) (0.6891g, 0.005641mol) were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in dichloromethane (500ml). The reaction was heated to reflux and allowed to run for 8 days, at which time the reaction was allowed to cool to 25°C. Once cool, the reaction mixture was filtered to remove the insoluble 1,3-dicyclohexylcarbodiimide urea (DCCI urea). The filtrate was rotary evaporated to dryness. The solid material that remained was purified by dissolving the crude product in a minimal amount of dichloromethane and eluting it through a column packed with silica gel to remove unreacted starting materials and any residual DCCI urea. Once the product was obtained from the column, it was further purified by recrystallizing four times from methanol to give pure Cin4AB.

Yield: 5g (30%) white needle-like crystals
IR: 3046 (aromatic CH), 2929-2871 (aliphatic CH), 1719 (C=O), 1612 (C=C), 1263cm-^{1} (C-O)

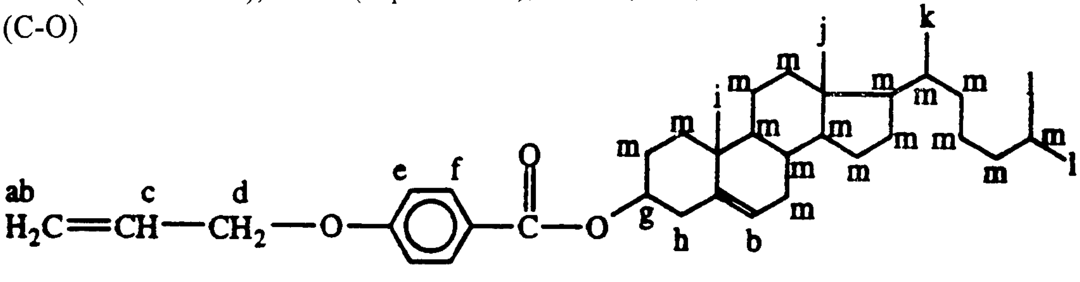


^{1}H NMR (CDCl3):
(a) δ = 5.30 (d, 0.96H),
(b) δ = 5.40 (d, 0.96H),
(c) δ = 6.05 (m, 1.02H),
(d) δ = 4.92 (d, 2.01H),
(e) δ = 6.95 (d, 2.07H),
(f) δ = 8.05 (d, 1.59H),
(g) δ = 4.63 (d, 2.35H),
(h) δ = 6.45 (m, 1.10H),
(i) δ = 6.65 (d, 1.09H),
(j) δ = 7.3-7.4ppm (m, 4.86H),
Elemental Analysis

Calc.	C 77.53	H 6.16	O 16.31
Found	C 77.45	H 6.36	O 16.19

The Cholesterol-4-Allyoxybenzoate (C4AB) mesogen was synthesized via a coupling reation as follows. 4-allyloxybenzoic acid (4ABA) (6.090g, 0.03418mol), cholesterol (12.27g, 0.03172mol), 1,3-dicyclohexylcarbodiimide (DCCI) (7.061g, 0.03422mol), and 4-dimethylaminopyridine (DMAP) (0.4220g, 0.003454mol) were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in dichloromethane (475ml). The reaction was heated to reflux and allowed to run for 14 days, at which time the reaction was allowed to cool to 25°C. Once cool, the reaction mixture was filtered to remove the insoluble 1,3-dicyclohexylcarbodiimide urea (DCCI urea). The filtrate was rotary evaporated to dryness. The solid material that remained was purified by recrystallizing three times from ethanol to give pure C4AB.

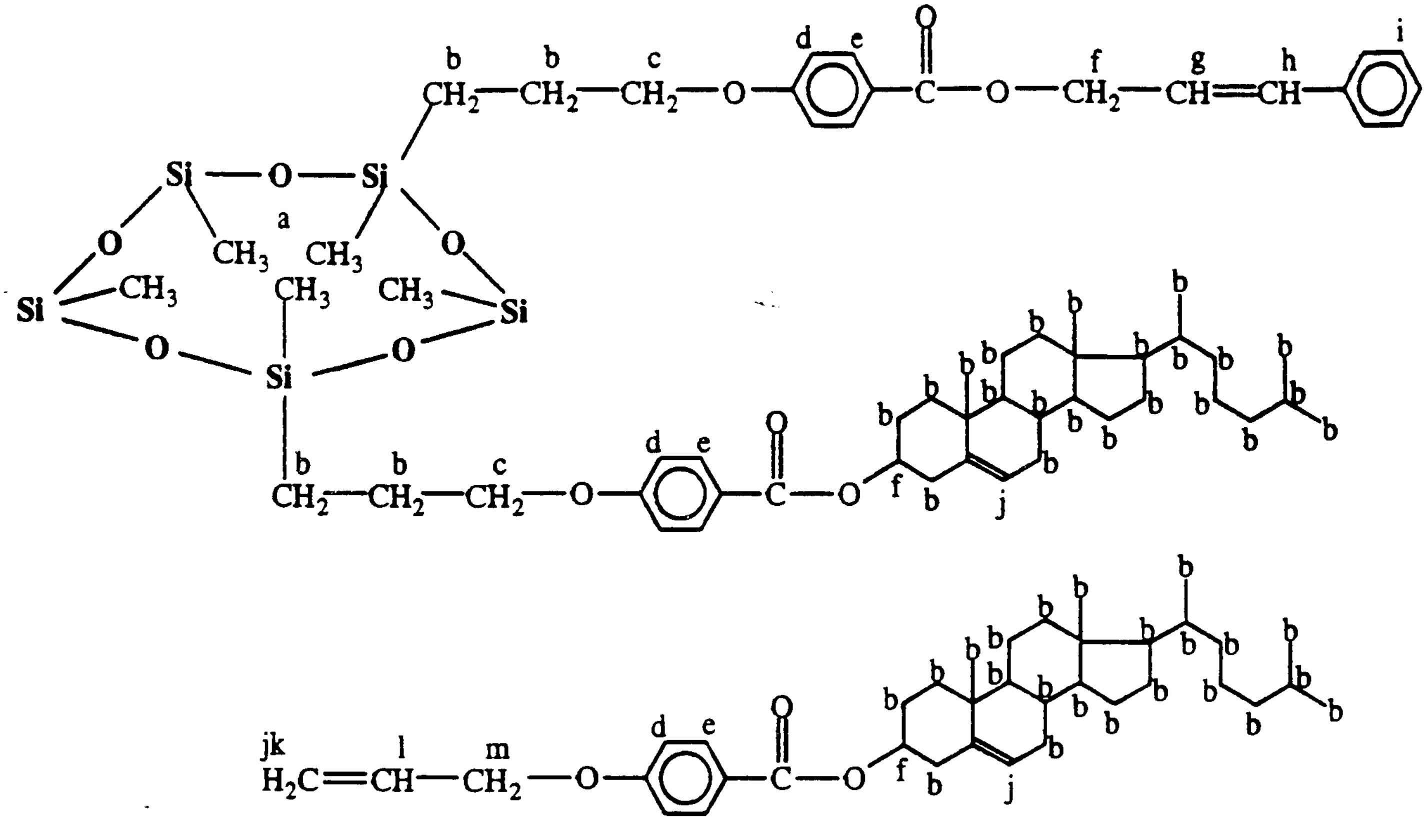
Yield: 5g (29%) white powder
IR: 3070 (aromatic CH), 2941 (aliphatic CH), 1717 (C=O), 1613 (C=C), 1257cm-^{1} (C-O)



^{1}H NMR (CDCl3):
(a) δ = 5.30 (d, 1.03H),
(b) δ = 5.40 (d, 2.07H),
(c) δ = 6.05 (m, 0.90H),
(d) δ = 4.60 (d, 2.24H),
(e) δ = 6.90 (d, 2.22H),
(f) δ = 7.90 (d, 2.24H),
(g) δ = 4.85 (m, 0.88H),
(h) δ = 2.45 (d, 1.22H),
(i) δ = 1.00
(j) δ = 0.80
(k) δ = 0.91
(l) δ = 0.88
(m) δ = 0.60-2.10ppm (collection of peaks, 41.24H)

cSi[20,0,80]100 was synthesized as follows. The 5 membered cyclic siloxane (108ul, 0.0003594mol) along with the two previously synthesized mesogens, Cin4AB (0.1192g, 0.0003954mol) and C4AB (0.8659g, 0.001581mol) (1:4 ratio), were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in toluene (6ml). Once the reaction was at reflux the dicyclopentadienyl platinum (II) chloride catalyst (80ul) was added. The reaction was monitored by FTIR to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in a minimal amount of toluene three times. Detection of unreacted cholesterol-4-allyloxybenzoate (C4AB) was determined by ^{1}H NMR.

IR: 3050 (aromatic CH), 2945 (aliphatic CH), 1715 (C=O),
1609 (C=C), 1270 (C-O), no peak at 2170cm-^{1} (therefore no Si-H present)



^{1}H NMR (CDCl3):

(a) δ = 0.15 (s, 15H),

(b) δ = 0.50-2.50 (collection of peaks, 256.4H),

(c) δ = 3.95 (t, 6.9H),

(d) δ = 6.75-7.00 (two d, 11.5H),

(e) δ = 7.75-8.05 (two d, 10.4H),

(f) δ = 4.70-4.95 (broad m, 5.5H),

(g) δ = 6.35 (q, not present),

(h) δ = 6.65 (d, not present),

(i) δ = 7.10-7.40 (m, 10.4H, includes residual protons present in chloroform-d @ 7.24),

(j and k) δ = 5.30-5.45 (two d, 8.5H),

(l) δ = 6.05 (m, 2.5H),

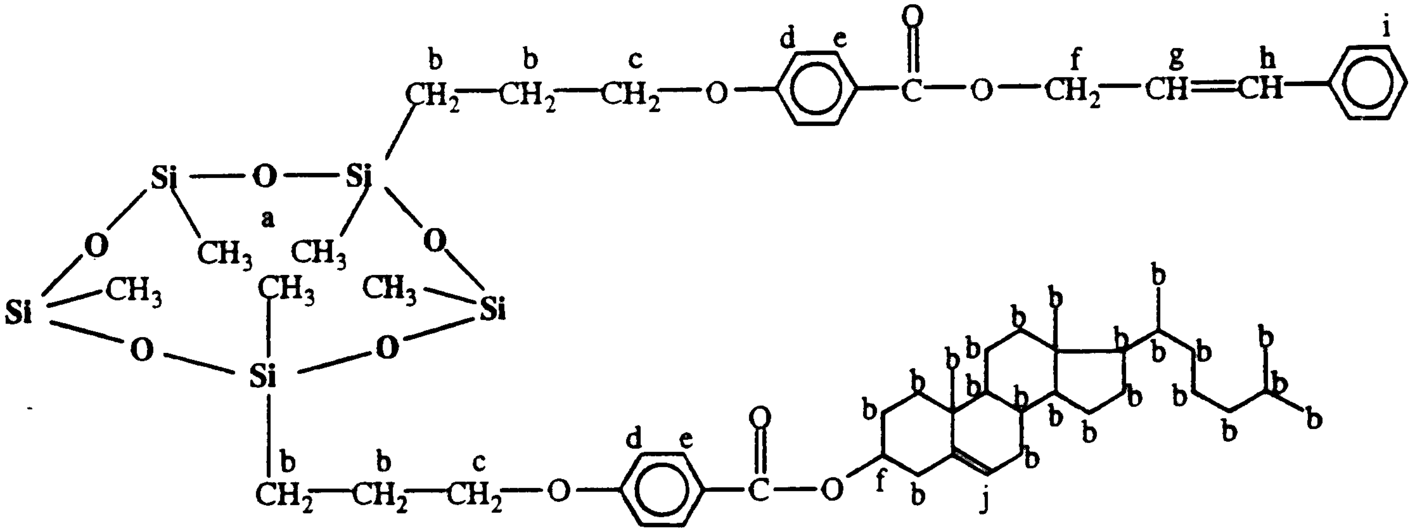
(m) δ = 4.60ppm (d, 3.7H)

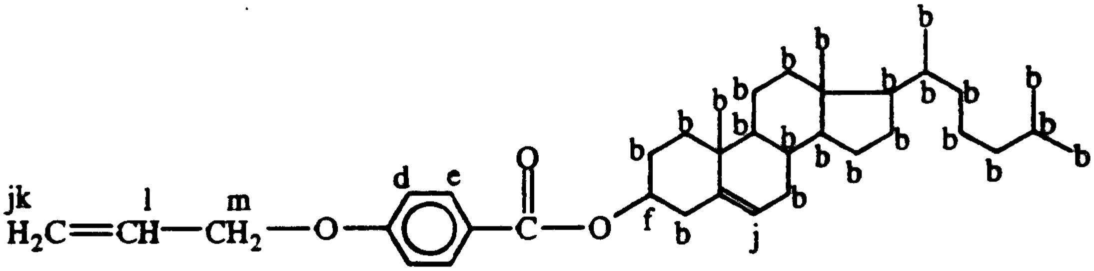
Elemental Analysis:

Calc.	C 74.25	H 9.20	O 11.50	Si 5.05
Found	C 72.87	H 9.47	O 10.88	Si 6.78

cSi[40,0,60]101 was synthesized as follows. The 5 membered cyclic siloxane (119ul, 0.0003953mol), along with the two previously synthesized mesogens, Cin4AB (0.2560g, 0.0008696mol) and C4AB (0.7140g, 0.001304mol) (2:3 ratio), were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in toluene (6ml). Once the reaction was at reflux the dicyclopentadienyl platinum (II) chloride catalyst (60ul) was added. The reaction was monitored by FTIR in order to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in a minimal amount of toluene three times. Detection of unreacted cholesterol-4-allyloxybenzoate (C4AB) was determined by ^{1}H NMR.

IR: 3059(aromatic CH), 2945 (aliphatic CH), 1720 (C=O),
1614 (C=C), 1281 (C-O), no peak at 2170cm^{-1} (therefore no Si-H present)





^{1}H NMR (CDCl3):

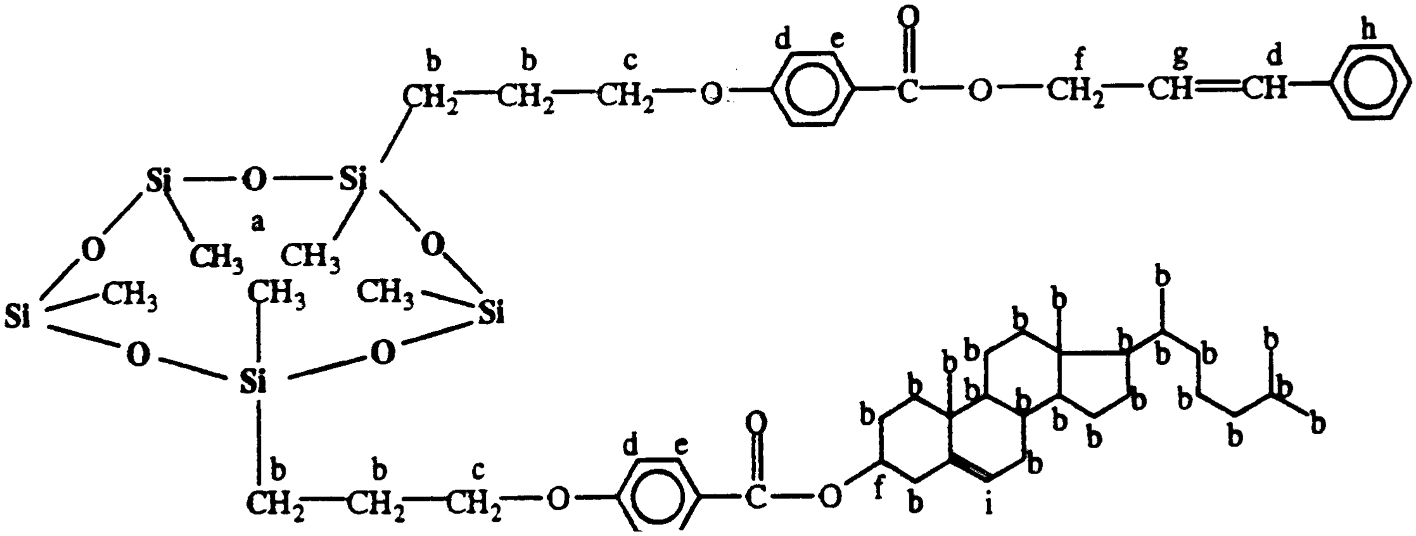
(a) δ = 0.15 (s, 15H),
(b) δ = 0.50-2.50 (collection of peaks, 164.2H),
(c) δ = 3.95 (t, 3.8H),
(d) δ = 6.75-7.00 (two d, 7.3H),
(e) δ = 7.75-8.05 (two d, 6.3H),
(f) δ = 4.70-5.00 (broad m, 4.0H),
(g) δ = 6.35 (q, present but very small, therefore not integrated),
(h) δ = 6.65 (d, present but very small, therefore not integrated),
(i) δ = 7.10-7.45 (m, 7.3H, includes residual protons present in chloroform-d @ 7.24),
(j and k) δ = 5.20-5.50 (two d, 6.2H),
(l) δ = 6.05 (m, 1.7H),
(m) δ = 4.60ppm (d, 2.7H)

Elemental Analysis:

Calc.	C 73.11	H 8.69	O 12.65	Si 5.55
Found	C 72.78	H 9.29	O 11.51	Si 6.42

cSi[60,0,40]102 was synthesized as follows. The 5 membered cyclic siloxane (135ul, 0.0004481mol) along with the two previously synthesized mesogens, Cin4AB (0.4264g, 0.0004829mol) and C4AB (0.5269g, 0.0004818mol) (3:2 ratio), were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in toluene (6ml). Once the reaction was at reflux, the dicyclopentadienyl platinum (II) chloride catalyst (70ul) was added. The reaction was monitored by FTIR to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in a minimal amount of toluene three times.

IR: 3060(aromatic CH), 2945 (aliphatic CH), 1720 (C=O), 1614 (C=C), 1271(C-O), no peak at 2170 cm-^{1} (therefore no Si-H present)



^{1}H NMR (CDCl3):

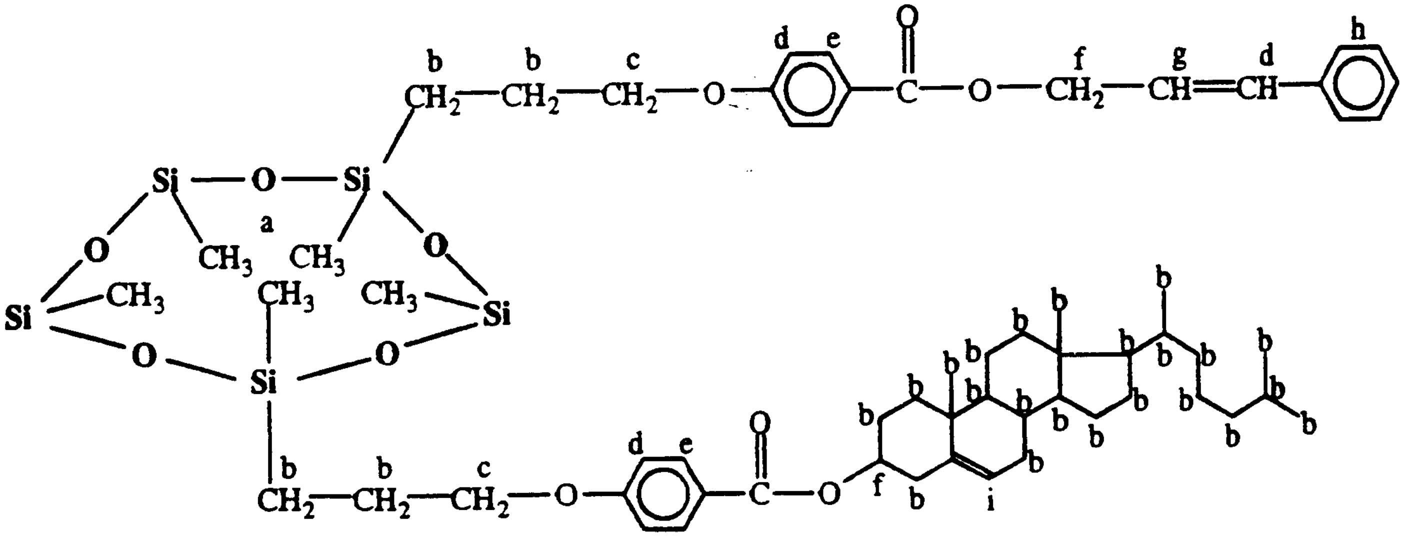
(a) δ = 0.15 (s, 15H),
(b) δ = 0.40-2.50 (collection of peaks, 99.6H),
(c) δ = 3.95 (t, 5.8H),
(d) δ = 6.60-7.00 (two d, 10.1H),
(e) δ = 7.75-8.05 (two d, 7.6H),
(f) δ = 4.70-5.00 (broad m, 6.6H),
(g) δ = 6.35 (q, 2.2H),
(h) δ = 7.10-7.50 (m, 13.9H, includes residual protons present in chloroform-d @ 7.24),
(i) δ = 5.20-5.50ppm (d, 6.2H),

Elemental Analysis:

Calc. C 71.73	H 8.05	O 14.05	Si 6.17	
Found	C 71.33	H 7.99	O 13.99	Si 6.69

Si[80,0,20]103 was synthesized as follows. The 5 membered cyclic siloxane (150ul, 0.0004979mol) along with the two previously synthesized mesogens, Cin4AB (0.6374g, 0.0005414mol) and C4AB (0.2972g, 0.0005435mol) (4:1 ratio), were placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in toluene (6ml). Once the reaction was at reflux, the dicyclopentadienyl platinum (II) chloride catalyst (40ul) was added. The reaction was monitored by FTIR to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in a minimal amount of toluene three times.

IR: 3061(aromatic CH), 2945 (aliphatic CH), 1715 (C=O),
1614 (C=C), 1266(C-O), no peak at 2170 cm-^{1}(therefore no Si-H present)



^{1}H NMR (CDCl3):

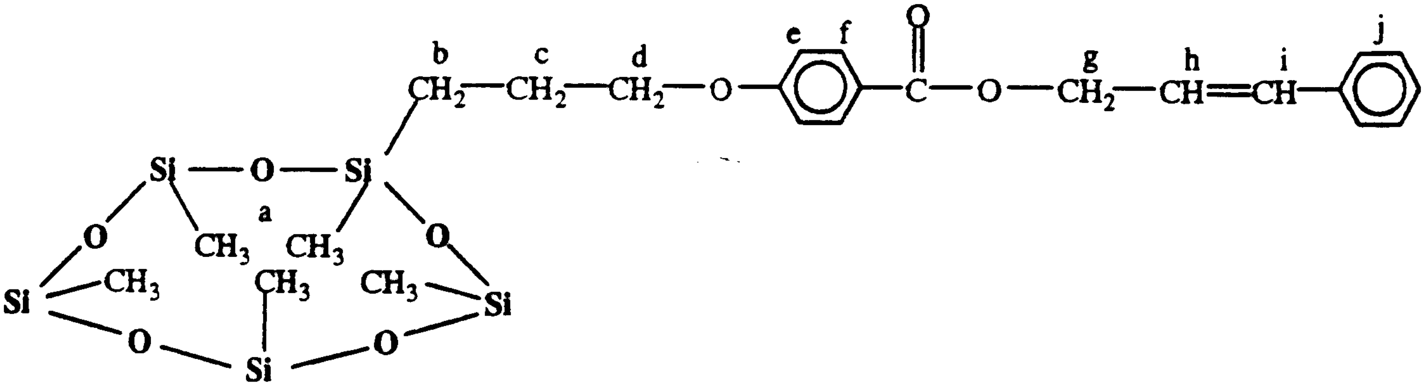
(a) δ = 0.15 (s, 15H),
(b) δ = 0.40-2.50 (collection of peaks, 76.4H),
(c) δ = 3.95 (t, 10.1H),
(d) δ = 6.60-7.00 (two d, 12.6H),
(e) δ = 7.75-8.05 (two d, 10.9H),
(f) δ = 4.70-5.00 (broad m, 7.3H),
(g) δ = 6.35 (q, 2.6H),
(h) δ = 7.10-7.50 (m, 13.9H, includes residual protons present in chloroform-d @ 7.24),
(i) δ = 5.20-5.50ppm (d, 6.2H),

Elemental Analysis:

Calc. C 69.99	H 7.27	O 15.80	Si 6.94	
Found	C 69.61	H 7.32	O 16.34	Si 6.73

Si[100,0,0]104 was synthesized as follows. The 5 membered cyclic siloxane (170ul, 0.0005643mol) along with one of the previously synthesized mesogens, Cin4AB (0.9158g, 0.0006222mol) (5:0 ratio), was placed into a round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in toluene (6ml). Once the reaction was at reflux, the dicyclopentadienyl platinum (II) chloride catalyst (80ul) was added. The reaction was monitored by FTIR to determine when the reaction was complete. Once the reaction had gone to completion, the crude product was purified by precipitating it with methanol and redissolving it in a minimal amount of toluene three times.

IR: 3061(aromatic CH), 2935 (aliphatic CH), 1715 (C=O),
1609 (C=C), 1271(C-O), no peak at 2170 cm-^{1}(therefore no Si-H present)



^{1}H NMR (CDCl3):

(a) δ = 0.10 (s, 15H),
(b) δ = 0.70 (t, 7.73H),
(c) δ = 1.80 (m, 7.85H),
(d) δ = 3.90 (t, 8.42H),
(e and i) δ = 6.65-7.00 (two d, 9.81H),
(f) δ = 7.75-8.05 (broad d, 6.52H),
(g) δ = 4.70-5.00 (broad m, 8.42H),
(h) δ = 6.15-6.50 (q, 2.13H),
(j) δ = 7.10-7.50ppm (m, 18.35H, includes residual protons in chloroform-d @ 7.24),

Elemental Analysis:

Calc.	C 69.99	H 7.27	O 15.80	Si 6.94
Found	C 69.61	H 7.32	O 16.34	Si 6.73

Once the previously mentioned substituted cyclopentylsiloxanes were synthesized, purified, and characterized they were placed into solution and crosslinked via a 2 + 2 cyclo addition of the cinnamic moieties upon UV irradiation. Figure 1 illustrates the 2 + 2 cyclo addition process upon UV irradiation to form the photo crosslinked polymer.

Figure 1

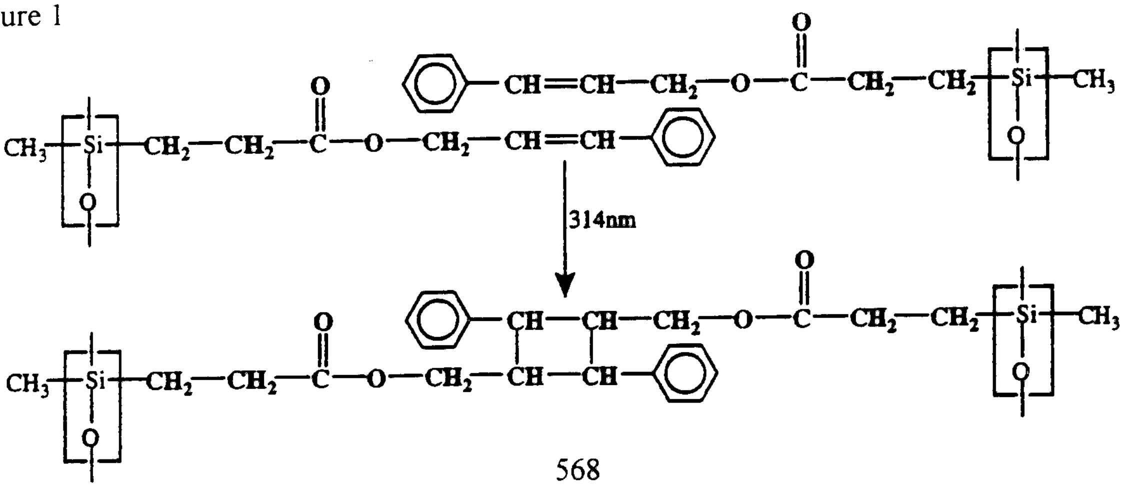
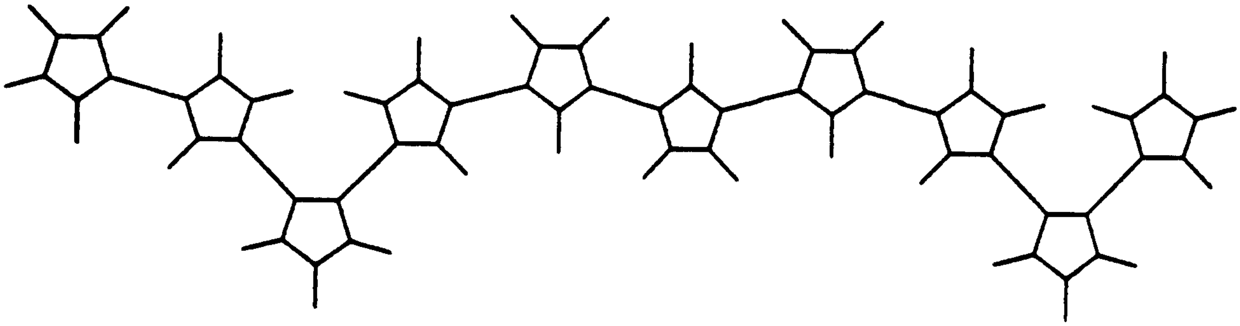


Figure 2 illustrates what the polymer product of cSi[40,0,60]101 would look like after photo crosslinking.

Figure 2



The nonlinear optically active side chains present in the cyclopentylsiloxane polymers can be aligned in an electric field. The long-term orientational stability of the side chains is a property that will be measured by second harmonic generation in the future. It is believed that the liquid crystalline cyclic siloxane polymers will enhance this stability by hindering side chain motion.

RESULTS

Once the previously mentioned macromolecules were synthesized and purified, the final product was verified by analytical methods such as FTIR, 1H NMR, and EA. FTIR (Fourier Transfer Infra-Red) spectrophotometry was used to determine whether or not characteristic bands of the desired compound were present in the purified product. 1H NMR (Proton Nuclear Magnetic Resonance) spectroscopy was used to verify the structure of the purified product. EA (Elemental Analysis) was used to determine %C, %H, %O, and %Si of the purified product.

Once these analytical values were obtained, they were compared to the theoretical percentages to determine how well they correspond. Kinetic experiments were performed on the photo crosslinking reactions and it was determined that each reaction followed secondary kinetics, as was expected.

References

1. M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Laab, B. H. Luhma, A. Price, W. L. Roberts, T. J. Shaw, and C. A. Smith, **Analytical Chemistry**, 1985, 57, 651-658; Synthesis and Properties of High Temperature Mesomorphic Polysiloxane Solvents: Biphenyl and Terpheny Based Nematic Systems.

ELECTRONICS AND COMPUTER SUPPORT IN ELECTROMAGNETIC MATERIALS RESEARCH

Task Order No. 126
Student Support Program
Southwestern Ohio Council for Higher Education

Rick Dorsten
University of Dayton

5 July 1995

Government Task Leader
Mr. Ronald E. Perrin
WL/MLPO

ACKNOWLEDGMENTS

First and foremost, the deepest appreciation is extended to the following people for whom without their time and guidance this Task would not have been possible. To Mr. Ronald E. Perrin, Task Leader, Mr. Thomas E. Kenskey and Mrs. Laura Rea, all Technical Supervisors from whom many valuable skills and much needed knowledge was learned. Their superior attributes in the engineering field, complemented by their patience and ability to teach, were as crucial to the learning experience as the projects and resources that were assigned. Also to Mrs. Wanda G. Vogler and the staff at SOCHE for making the experience possible.

TASK ASSIGNMENT

The Task title was "Electronics and Computer Support in Electromagnetic Materials Research," and the objective was to provide needed technical support for in-house engineers and physicists at Wright Labs. The task objectives were met through the design of PC and Macintosh software, the design and construction of custom electronic circuits, the construction of mechanical interfaces for laboratory systems, and the fulfillment of various other engineering requirements.

One project that was worked on was the design and construction of a temperature controller for a high temperature Hall system. The temperature controller had to accept a reference input in the range of 0V - 10V DC from a digital to analog converter and compare that to a DC voltage that was fed in from the heater. The heater was a silicon carbide heater capable of temperatures approaching 1800°C. The power for the heater was supplied by a large variac which adjusted its output via a DC motor. The system was complex and detailed.

Along with the design and construction of custom circuits, programs were written to control complex experiments. The programming languages used included Basic and C. Programs were written in Basic for data acquisition and for equipment control. These programs were integrated into other programs as subroutines, and when running, controlled every aspect of an experiment, therefore replacing the need for an individual to be present during testing.

Finally, many miscellaneous tasks were completed that dealt with the repair and regular maintenance of equipment, support for the in-house physicists and routine duties such as monthly reviews of technical journals.

GENERAL DESCRIPTION OF DEVELOPMENT

Once a project was assigned by the Task Leader, the appropriate solution was discussed and development would begin. This consisted of creating an initial working model in which testing could be done. The initial model was as simple as possible to allow for quick and easy changes according to need. Testing was completed using multi-meters, oscilloscopes, power supplies, computer analysis and other various testing devices. The equipment was modern and on the leading edge of technology. Once a working model was thought to be completely tested, as close to actual operating conditions as possible, the final model was constructed and implemented.

RESULTS

The time spent at Wright Labs was a valuable learning experience. In school, not much emphasis is placed on the practicality of the theory being taught. This experience allowed for a connection between the theory and the many facets in which it can be applied. From this Task, I gained knowledge that could never be taught in the classroom. For instance, the social aspect of the job environment and something every employer wants, work experience. The program SOCHE offers is an invaluable one, the hours are flexible while attending classes and the monetary reward helps pay for school. Any time you can get paid to gain knowledge instead of paying for it one must consider themselves fortunate.

ELECTRONICS AND COMPUTER SUPPORT IN ELECTROMAGNETIC MATERIALS RESEARCH

Task Order No. 126a
Southwestern Ohio Council for Higher Education
Student Support Program

Charles E. Culp, Jr.
Wright State University

5 July 1995

Government Task Leader
Mr. Ron Perrin
WL/MLPO

ACKNOWLEDGMENTS

I would like to recognize several people who have assisted in my accomplishment of the Task assigned at the Materials Division of Wright Laboratory. First, I would personally like to thank Mr. Ron Perrin and Mr. Tom Kensky for their instruction and proper technical guidance in beginning level electrical engineering. The knowledge provided by the two listed individuals has aided me in widespread information that will be beneficial in my future college studies. This information will also provide me with the essentials needed throughout my future career as an engineer. Last, I would like to thank Wanda Vogler and the staff of Southwestern Ohio Council for Higher Education for this unique opportunity to work in such an educational environment. All these people listed have given me the proper assets needed to accomplish my Task. Thanks to all of you for everything.

DESCRIPTION OF TASK ASSIGNMENT

The student's responsibility is to aid Mr. Perrin in the engineering process that surrounds the requirements that the research scientists are requesting. This may differ each time due to the multitude of scientists and the scientists' needs may vary from experiment to experiment. Assistance will be in the following forms: building and testing customized circuitry, modifying computer hardware, and writing computer programs. These are just the basics that the student may be involved in. The needs of Mr. Perrin may go outside the basic guide lines listed due to the level of involvement that he may require. This assistance directly gives the scientist better equipment to conduct more valuable experimentation, and to accomplish their task.

DESCRIPTION OF RESEARCH

The method of research is not that typical of a person working in a research laboratory. This is because the Task is not that of a particular experiment or research type. Instead, engineering assistance is provided to scientists in the form of specialist equipment or circuitry. This does not mean there is any research done. The student uses a form of self experimentation, due to the variation in the project types. This way, the student may use his own ideas on how to accomplish the task and sees if the method was effective or not. The results of this are learning proper technical skills and valuable habits essential to be an electrical engineer.

There is an abundance of equipment used to acquire the technical skills and habits. The most common of these is a bread board used to build electrical circuitry. This helps the student easily test and get an indication that the circuitry will operate according to its design specifications. Along with the bread board, there is some basic test equipment used such as an oscilloscope, function generator, power supply and volt meter. These items aid in getting the circuitry into working order. They will also provide the signals necessary for the circuitry to function. The last piece of equipment used is a computer, either a Macintosh or an IBM compatible. The computer provides a means of programming for certain circuitry or it could be used as an aid to illustrate the functional layout of a circuit. The equipment is essential because without it there would be no clear indication of the circuit functioning in a correct manner.

In performing every research method there is always some form of data collected. For this project, there are two forms of data collected. The first, to see if the circuit functioned correctly according to what it was designed to achieve. The second question to research is if the methods were efficient and did it cause the least amount of obstacles to overcome. This data will be retained by the student and will allow a similar project to be done in a more efficient manner for the future.

RESULTS

This Task has given me a great deal of knowledge in the field of electrical engineering. This information was acquired through hands-on experience and has enhanced my knowledge of working circuitry. An example of this is learning how a control circuit works and the variables involved in its operation. This one piece of information now allows me to look at schematic drawing of this type of circuit and clearly understand it in a working operation. This is important because, as an engineer, it is important not to just know the numbers involved but to also know the theoretics of how it operates. This has been shown numerous times in everything from transformers to operational amplifiers.

My knowledge was also increased in the use of equipment used to manipulate and test circuitry. The best example of this is the use of a computer to control circuitry and to produce various effects. For example, on one project, a computer aided card was programmed to put voltages out on various pins of a connector. This type of learning is very important due to the swing of sophistication in our world today. Because of ever changing technology, it is important for an engineer to be able to use all the resources available to them. This lesson will be applied repeatedly on different computer cards and test instrumentation.

CERAMIC FIBER CREEP STUDIES

Task Order No. 127
Student Support Program
Southwestern Ohio Council for Higher Education

Andrew Knall
Wright State University

8 August 1995

Government Task Leader
Dr. Randy Hay
WL/MLLM

ACKNOWLEDGMENTS

Thanks to: Larry Matson, Scott Apt, Chris Pierce, Rob McLaughlin, Cohen King, Peter Brown, Charlie Cook, Kristy Keller and SOCHE.

TASK ASSIGNMENT

The assigned Task was as following:

- To assist with the preparation of ceramic fibers for creep studies.
- To aid in the conduction of creep studies and reduction of data.
- To perform metallography on creep samples to determine microstructural responses to creep.
- To assist in the characterization of creep samples.

The main purpose for this work was to assist in the measure the creep resistance of ceramic fibers and to determine the dependence of creep resistance on microstructure. It was important to know the amount of elongation over a period of time for a specific temperature and load.

Ceramic fiber plays an integral role in any high temperature and high strain oxidizing environment. The use of ceramic fiber is predominantly found in aircraft engines, rocket engines, turbines for generating electricity and also some use in the automotive industry. The main purpose for using ceramic fiber is due to the fact that its melting point far exceeds that for any known alloys and that it has a high creep resistance (it tends not to elongate or stretch when large forces are applied in these high temperature environments.)

DESCRIPTION OF RESEARCH

The fibers used were Yttrium alumina garnet (YAG) / alumina directionally solidified at its eutectic composition. These fibers were manufactured by either Sapphicon or UES which were grown at various pull rates from .25 inches per minute to 2 inches per minute. The range of temperatures was 1400c, 1500c, 1600c and 1700c. The device used to test the fibers was a creep rig. The rig consisted of a clamp at the top to hold the fiber vertically, a sapphire tube furnace that was heated by induction and at the bottom was another clamp where the load was suspended. A magnetic coil wrapped around the sapphire tube provided the heat in the heat zone (approx. 3 inches) and argon gas was fed into the system to prevent oxidation of the fiber. The amount of time the fiber was allowed to remain in this state varied from less than 1 hour to over 100 hours. The temperatures were kept constant by electronic control and the temperature, elongation and time were all graphed on chart paper. Once the fiber broke or sufficient time had elapsed, the heat was discontinued, the charted data was collected and the fiber or fiber pieces were saved for microstructural analysis.

Microstructure was analyzed by using a Leica 3000 Scanning Electron Microscope (SEM) and was prepared for the transparent electron microscope (TEM). The fiber pieces were mounted in epoxy either vertically or horizontally, depending on what information was needed, and then polished using a polishing wheel and decreasing sizes of diamond paste. Once the surface of the sample had been polished sufficiently (usually to a 1 micron polish), it was then given a carbon coat using a carbon coating machine to prevent conduction in the SEM. If a TEM sample was needed, the sample was cut and polished on both sides using a tripod polisher. The tripod polisher allowed extremely small thicknesses to be obtained (20 micron) without breaking the sample. Once this thickness has been reached, the thinned fiber was then removed and glued to a small copper grid. This grid was then put in an ion milling machine which perforated the fiber with an argon beam. It was carbon coated and then ready for the TEM.

The data obtained from the SEM was a magnified view of the crept area of fiber which revealed microstructural information such as cracking, plane slippage and creep. Also, the grain size, orientation and changes in cross sectional area could be determined in the SEM. Numerous pictures were taken of interesting areas and features up to a magnification of 20,000 X.

From the TEM, more information could be determined that was unavailable in the SEM. A higher magnification could be obtained and crystallographic diffraction patterns could be recorded or photographed.

More information was obtained by measuring the amount of elongation and using the respective cross sectional area to determine actual stress strain and strain rate. From the analysis of the above information and data, it was determined that the microstructure of the fibers was responsible for the creep resistance as well as strength. The fibers with a smaller microstructure in cross section were stronger and were able to resist creep more easily. It was also found that the more elongated the microstructure is in the longitudinal direction, the higher the creep resistance. Therefore, a fiber which is uniaxially loaded can obtain high strength as well as high creep resistance, if it has a high aspect ratio and aligned phases.

SYNTHESIS AND CHARACTERIZATION OF BIOPOLYMERS

Task Order No. 128
Student Support Program
Southwestern Ohio Council for Higher Education

Steven M. Cline
Wright State University

12 July 1995

Government Task Leader
Dr. Thomas Cooper
WL/MLPJ

ACKNOWLEDGMENTS

A special thanks to senior chemist Dr. Thomas Cooper for the time, effort, and guidance he has provided in helping me mature as a scientist and person. He has allowed me to work independently on my Task which ultimately has instilled personal growth and an increase in self confidence. I would like to express sincere thanks and gratitude to SOCHE and Dr. Robert Crane for giving me the opportunity to work and learn at WL/MLPJ of Wright-Patterson Air Force Base. The experience and insight I have gained here have enhanced my life and attitude toward the world in which I live.

TASK ASSIGNMENT

The Task initiated consists of the synthesis and characterization of non linear optics and laser hardening materials. The goal of the Task is to utilize readily available biological and biochemical materials and to incorporate their functional properties into electro-optical systems. Currently, the Task is directed toward the understanding and manipulation of simple systems. The long-term goal of the Task is to incorporate simple materials into functional devices involved in properties such as: selective wavelength absorbance, spectral rearrangement, photo-electric communication, and visual protection.

DESCRIPTION OF RESEARCH

Due to the molecular arrangement and perfectly repetitive symmetry of atoms in crystalline compounds, crystals possess amazing photo-manipulative properties. Proteins and amino acids, individually and in complex with metals and organic dyes have proven to be excellent secondary harmonic generating materials (SHG).

These SHG materials consist of molecules which under normal optical conditions possess a stable separation of charge (i.e., the most simple amino acid, glycine $^{+}H3N\text{-}CH_2\text{-}COO^{-}$), called a zwitterion. When zwitterions are oriented properly in crystals, they often have the ability to generate a harmonic frequency different from the frequency initiated by an exciting light. A harmonic frequency is generated by photons of light (i.e., 1080 nm) passing into a crystal and eliciting a momentary period of absorption. The net result of the absorption is the excitation of the electrons within the crystal. The electrons are normally located in their ground state but when excited by a photon of light, leap into a high energy orbital. The electrons soon return to their ground state and upon returning release the absorbed energy in the form of light and heat. In most cases, the transmitted or exiting light is released from the crystal in the same frequency as the incident or entering light. However, in the case of crystals made up of zwitterions, the frequency of the transmitted light is shortened significantly. In fact, it is cut in half (i.e., from 1080 nm to 540 nm); therefore, gaining its classification as an (SHG). Such materials provide a mechanism of transferring retinal damaging frequencies of infrared light into harmless frequencies found in the visible spectra. Thus, the extreme interest in categorizing and understanding second harmonic generating materials.

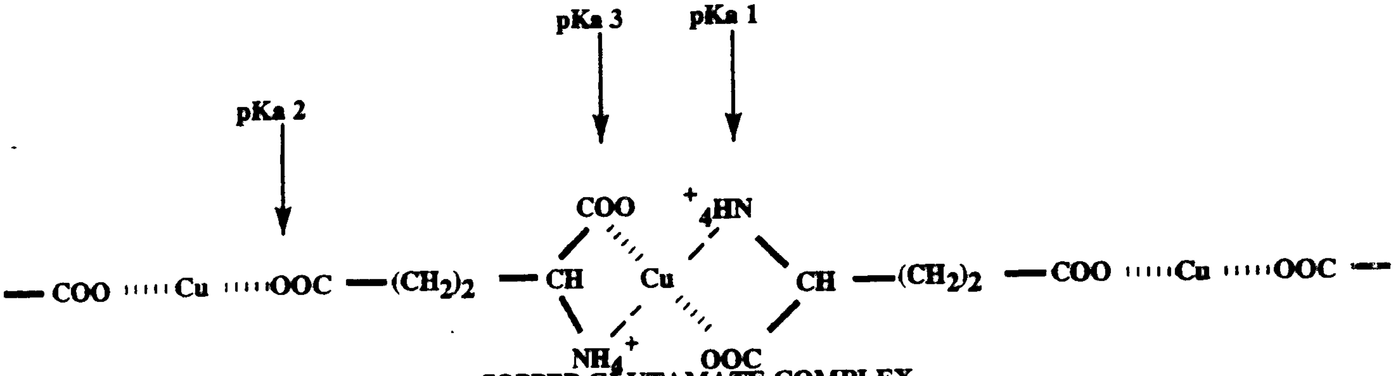
The research involved in this Task consists of synthesizing a group of suspected SHG materials, determining their ability to harmonically generate secondary frequencies, and crystallizing the more promising SHG materials into macromolecular sizes. Once large crystals have been grown, their resultant molecular structure can be determined using X-ray crystallographic techniques.

RESULTS

The following group of compounds were synthesized and tested for SHG properties:

* 1) Copper Acetate - Glutamic Acid complex
* 2) Copper Chloride - Glutamic Acid complex
* 3) Calcium Chloride - Glutamic Acid complex
4) Iron (ii) Chloride - Glutamic Acid complex
5) Iron (ii) Sulfate - Glutamic Acid complex
* 6) Mercury Acetate - Glutamic Acid complex
7) Manganese (ii) Nitrate - Glutamic Acid complex
8) Strontium Nitrate - Glutamic Acid complex

* signifies a material w/sufficient SHG properties upon (1080 nm) laser light exposure



COPPER GLUTAMATE COMPLEX

POLYMER

The Copper Glutamate Complex (above) was synthesized under basic conditions and titrated with HCl to determine its relative pKa values. The blue compound was solublized in acidic conditions and successfully crystallized by vapor diffusion in the presence of Sodium Acetate to dimensions exceeding a cubic millimeter. Crystalline copper glutamate is in the process of SHG loci determination and X-ray structure determination. A series of photographs were taken confirming crystalline morphology relative to crystallization conditions using a NIKON UFX IIA camera.

Mercury Glutamate Complex was synthesized under basic conditions. The compound has been successfully crystallized and stoichiometrically confirmed by elemental analysis. Photos of this white crystal were taken to confirm crystal morphology.

Zinc Glutamate complex was synthesized under basic conditions. It has been confirmed stoichiometrically by elemental analysis.

A small peptide Ac-AEAEAKAKAEAEAKAK-NH3, has been confirmed as pure, by migration during Capillary Electrophoresis. The peptide awaits electrostatic attachment with ionic dyes and spectrophotometric measurements. Thin-film processing is also being done.

ENVIRONMENTALLY COMPATIBLE MAINTENANCE CHEMICALS

Task Order No. 129
Student Support Program
Southwestern Ohio Council for Higher Education

Matthew J. Laufersweiler
Wright State University

30 April 1995

Government Task Leader
Ms. Lynne Pfledderer
WL/MLSA

ACKNOWLEDGMENTS

I would like to extend a note of appreciation to Ms. Lynne Pfledderer and Gary Stevenson for this opportunity. Additionally, appreciation goes to Bill Lawless, Joe Hunter, Ken Chitwood, Albert Foster, Andy Louge, John Buhrmaster, Roger Visoc, Tom Dusz, Michael Oliver, and Brad Pinnell for their support and guidance throughout the Task.

TASK ASSIGNMENT

The Task's main objective over the last 12 months was to determine the effectiveness, and the ability to support substitute aerospace materials/processes which are environmentally acceptable in relation to corrosion control.

To successfully complete the Task, many testing procedures had to be mastered. The first procedure was the abrasion resistance test. This test involves placing a coated specimen (4 in. X 4in.) of known weight on a revolving surface. Weighted abrasive wheels are then placed on the specimen and the specimen is rotated for a set number of cycles. Once this is completed, the specimen is re-weighed and the weight change is reported. In order for a coating to pass it must not lose more than 100 mg in a 10,000 cycle test with 1000g loads on the abrasive wheels.

The second test method learned was salt spray resistance. This method involves conforming to parameters set in ASTM B 117. During this test specimens are painted, scribed, placed in a salt spray cabinet, and exposed to a 5% NaCl solution for 2000 hours. Specimens are periodically taken out, inspected, and photographs are taken for documentation. Once the 2000 hours is done, the specimens are rated according to a scale in ASTMB117.

A third test method learned during the Task is a relatively new process, prohesion. This is a similar test to the salt spray resistance test, however it is believed to more accurately represent atmospheric corrosion mechanisms. A scribed specimen is placed in the prohesion cabinet and is fogged with an ammonium sulfate/NaCl solution for 1 hour, then exposed to a drying period of 1 hour where the cabinet temperature is at 35 degrees Celsius and then repeats the cycle. This is carried out for 2000 hours and is periodically inspected in the same way as the salt spray resistance test.

In addition to these two test methods, the Task involved becoming proficient with numerous other testing procedures. These involved fluid resistance, filiform corrosion testing, gloss measurements, thickness measurements, freezing point determination for runway deicers, and wet tape adhesion testing. Work was also done in becoming familiar with a new testing capability that is being brought into the laboratory. This is electrochemical impedance spectroscopy (EIS). This capability enables the users to quantitatively monitor the corrosion process. It involves applying a current, over a range of frequencies, to a sample and plotting the log of the impedance verses the frequency. This gives information on the corrosion process and is valuable in assessing the quality of a coating.

Recently, the Task has involved preparing and carrying out an evaluation of a chemical conversion coating. The conversion coating in question is a trivalent chromium based solution. This trivalent chromium is more environmentally acceptable than the hexavalent chromium conversion coatings currently used in the field. Samples were prepared using the standard method for preparing samples for conversion coating: alkaline clean, rinse, de-oxidize, rinse, conversion coat, dry. Samples that were conversion coated with the trivalent chromium conversion coating were immersed in the solution for 10 minutes, immersed in a hydrogen peroxide solution for 20 seconds, and then dried before painting. Samples conversion coated with the hexavalent conversion coating were immersed in the solution for 3 minutes and then dried before painting. The test samples are currently undergoing salt spray resistance and prohesion testing in both the bare and painted states. Painted specimens will also be tested for wet tape adhesion. Bare panels will be subjected to high temperatures to evaluate the performance of the conversion coating at elevated temperatures. In addition to these tests, the Task also involves researching a method of measuring the thickness of the conversion coatings. The method under consideration involves making a cross section of a sample and looking at it using a scanning electron microscope (SEM). Then using Energy Dispersive Spectrometry (EDS) the region containing the coating is scanned. This gives a map of the areas of high chromium concentration. The thickness of this region can be measured and that is the thickness of the conversion coating. Once the evaluation is complete, a report will be written and submitted for review.

Before the conversion coating evaluation, many smaller evaluations were conducted according to ASTM methods. The bulk of these involved reviewing results of previously performed tests and submitting the data to be used in evaluation reports.

SYSTEMS SUPPORT-MATERIALS BEHAVIOR AND EVALUATION SECTION WL/MLSE

Task Order No. 130
Student Support Program
Southwestern Ohio Council for Higher Education

Daniel B. McCray
Wright State University

15 June 1995

Government Task Leader
Mr. James Folck
WL/MLSE

ACKNOWLEDGMENTS

I would like to express my gratitude to a few of the people involved in making my Task a success. Mr. Robert Urzi was the former Task Leader until he retired in December of 1994. Mr. James Folck replaced Mr. Urzi in February of 1995. Both of the Task Leaders were very helpful in giving instruction and answering questions. Mr. Ron Kuhbander of the University of Dayton Research Institute assisted in giving daily assignments and providing training. MSgt. Brian Cramer and Doug Carter were helpful in giving guidance on certain projects.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The main objective of this Task was to conduct short, in-house investigations and evaluate various materials and processes for Air Force applications. Most of these investigations were associated with projects headed by government engineers. Most of the work associated with this Task was experimental, however, some interpretation of results was conducted.

One project conducted during this Task was a study of a new corrosion inhibiting primer. The primer that is presently being used for Air Force applications contains chromates and other hazardous materials. This primer is not only dangerous for people exposed to it, but also devastating to the environment. A new primer that is safe for humans and environmentally safe is being investigated to determine if it has similar properties to the presently used primer.

Another project conducted during this Task involved the repair of battle damaged aircraft canopies. Presently, aircraft canopies damaged during battle are repaired with aluminum plates. It is not always possible to replace the canopies due to availability and time constraints. The aluminum plates are not good repairs because they can seriously decrease the pilot's visibility. The present research is geared toward a new repair concept that will include a transparent patch so that the pilot's visibility is not affected. This repair concept utilizes an acrylic plug that is adhesively bonded to the canopy. In order to pass all requirements the plugs must be tested at high pressures and temperatures.

The last major project that was conducted during this Task was a research project aimed at determining the effect of applying mechanical fasteners to adhesively bonded patches. These fasteners are used to apply pressure to the bond area and is essential for proper adhesive bonding. However, these fasteners can create uneven adhesive thicknesses along the bond line. The effect of the fasteners was determined by fabricating bolted-bonded panels and measuring the bond line adhesive thicknesses at various points on the panel.

RESEARCH DESCRIPTION

The corrosion inhibiting primer research project used a mechanical property test to test the effectiveness of the primer. The name of the test is a wedge panel test. Two 6" x 6" aluminum plates are surface prepped and adhesively bonded together. The surface prep consists of a solvent wipe, phosphorus acid anodizing, and primer application. The two aluminum plates were bonded with film adhesive. The bonded panel was cured and machined into 1" wide specimens. Each specimen had an aluminum wedge hammered into the top of the specimen. The initial crack in the adhesive was measured. The wedges were then stored in a humidity cabinet at 120°F and 95-100% relative humidity. The crack growth was measured after 4 hours, 8 hours, 24 hours, 1 week, and 28 days. The data from the panels with the new primer was compared to the data from old primer. Surface preps were also varied to obtain an optimum strength. The best mechanical properties were found on the panels with the smallest crack growth.

The research conducted on repair concepts for aircraft canopies was very interesting. Actual repairs were conducted on actual aircraft canopies. An acrylic, ultraviolet light curing resin was used to plug the damage. An ultraviolet light was used to cure the resin. When exposed to ultraviolet light, the resin hardened in place in less than 15 minutes. Transparent tape was placed over one side of a 1.5" diameter hole. Resin was poured into the hole from the other side, and the panel was exposed to ultraviolet light. Once the patches were completed, they were tested for mechanical strength. The plugs were tested with the use of a vacuum pump and convection oven at 12 psi and 250°F.

In the bond line thickness project, aluminum and epoxy-graphite composite panels were used to determine the effect of mechanical fasteners on adhesive thickness. Aluminum and composites are commonly used materials in the aerospace industry for aircraft applications. The composite and aluminum panels were only 2" x 4" in size. Holes were drilled in the panels with a drill press and then the panels were surface prepped. The aluminum panels were solvent wiped and scuff sanded with scotchbrite pads. The composite panels were solvent wiped and abraded with 120 grit silicon carbide abrasive paper. Epoxy adhesive was applied to the bond areas of the panels and the fasteners were inserted into the drilled holes. The panels were placed together and the fasteners were tightened. Once the resin cured, the fasteners were removed and the panels were sectioned with a saw. The adhesive thickness was measured along the panel in various points with the use of an optical microscope.

RESULTS

The new, environmentally safe, corrosion inhibiting primer did not exhibit the same mechanical properties as the existing primer. The crack growths in the wedge panels primed with the new primer were much longer than the crack growths observed in the panels primed with old primer. Thus, the new primer did not perform as well as the old primer under identical conditions. The new primer had other faults as well. The primer was difficult to mix and apply. The primer was composed of two parts. Before applying, the two parts were mixed. The two parts did not mix well and did not remain in solution with each other without constant mixing. Application was only possible by brush application. The primer was unable to be removed from the brush after application so the brush was disposed of after every application. The old primer could be applied with a spray gun and was easily cleaned. To this point, the new primer's only benefit is its safety related benefits.

The canopy repair concept developed was tested on 1.5" diameter holes in actual canopies. The patches remained intact under 250°F and 12 psi. However, when larger holes of up to 4" in diameter were tested, the patches failed. Additional research for this project is still underway.

After analyzing the adhesive thicknesses at various points along the aluminum and composite panels, it was determined that the adhesive was thinnest around the fasteners and thickest at the points farthest from the fasteners. This matches the expected results. Additional work is being conducted on this project to quantitize the results so that bond line thickness can be predicted for actual aircraft patches.

DISCOVERY SYSTEMS FOR E-O MATERIALS

Task Order No. 131a
Student Support Program
Southwestern Ohio Council for Higher Education

Marc Reiter
University of Dayton

31 August 1995

Government Task Leader
Dr. Steve LeClair
WL/MLIM

ACKNOWLEDGMENTS

Several people deserve thanks for allowing this experience to take place. Thanks goes to Dr. Al Jackson who helped guide the project and helped give direction to what was done. Thanks to David Giovannini for help with getting over stumbling blocks in programming. Thanks to Steve Adams and Jeff Heyob for their support and experience in programming. Thanks to Dr. Steve LeClair for running an excellent office environment. Thanks to Rob Ray for some very stimulating conversation. And a special thanks goes to SOCHE for their help in providing the opportunity for this wonderful experience.

TASK ASSIGNMENT

The main project that is being work on is called KnowBe (Knowledge Based Education). KnowBe is a development tool that will help engineers chose a compound to work with based on what they require it to do. KnowBe is composed of many smaller programs. The program being worked on, Unit Cell Builder was originally part of KnowBe. Recently the idea of marketing Unit Cell Builder and it's companion, Unit Cell Viewer by themselves has been explored.

Unit Cell Builder uses data from raw crystalline compound data files to build the compound's unit cell and save it in a useful format to be used by other programs. A unit cell is the smallest sample of repeating atoms that make up the structure of a compound. This program started with only building basic unit cells, but over the past 8 months many features have been added that allow different types of unit cells to be built and several options on how to build them.

Unit Cell Builder's companion program, Unit Cell Viewer, is also currently being written. Unit Cell Viewer reads in the data files created by the Unit Cell Builder program and displays a 3-D rendering of the unit cell to the screen. The unit cell displayed on the screen can be rotated on all three axis so that it is easy to comprehend exactly what the unit cell looks like.

In the past unit cells were built by hand. The coordinates of each atom had to be carefully computed. This process could easily take 5 to 10 minutes on even the simplest unit cells. Unit cells that are much more complex could take hours to build by hand. Unit Cell Builder can build even the most complex unit cells in seconds. Another advantage of Unit Cell Builder is it does not make mistakes. If a unit cell that contains hundreds of atoms is built by hand, there is a very good chance many mistakes could be made.

Unit Cell Viewer is also a big improvement over plotting the unit cell by hand. In the past, unit cells were plotted by hand in 2-D on paper. Using this method, it would be very difficult to grasp an understanding of exactly what the unit cell looks like. When plotted out on paper, only one level of the unit cell can be viewed at one time, or all levels could be plotted in a 2-D representation. This makes it extremely hard to understand what the unit cell looks like and what patterns and properties it may possess. The unit cell could be plotted in 3-D on paper, but plotting in 3-D is a difficult process and mistakes could be made. Using Unit Cell Viewer, the cell is plotted in 3-D with no mistakes, and can be rotated so a good understanding can be made of what the unit cell looks like and patterns or properties the cell may possess become obvious.

In the near future, Unit Cell Builder and Unit Cell Viewer will be combined to form one complete program. This program will be easy to use and will contain everything necessary to build a unit cell and display it.

These programs are being written on a Macintosh platform. A Macintosh IIcx and a Quadra 840 are being used to write the programs. The programs are being written in the C and C++ languages using the Metrowork's Code Warrior compiler. Once the next version of the Code Warrior compiler is released, Unit Cell Builder and Unit Cell Viewer will be able to be ported to work with IBM compatibles using a Pentium Processor.

This experience has been a very valuable one. It has been a chance to work in a professional office environment. This experience can be invaluable in the search for a permanent job after graduation. Much was learned about programming in a research environment. This type of programming is very different from programming for a class or for personal use. This will also be very valuable for a permanent job. All together this has been an invaluable experience for the future and again, many thanks are deserved to all those who made it possible.

DISCOVERY SYSTEMS FOR E-O MATERIALS

Task Order No. 131b
Student Support Program
Southwestern Ohio Council for Higher Education

Keith M. Andrews
Wright State University

31 August 1995

Government Task Leader
Dr. Steven R. LeClair
WL/MLIM

ACKNOWLEDGMENTS

The guidance of Jeff Heyob, Steve Adams and Dr. Steven LeClair has been greatly appreciated throughout this Task. Over the past few years Jeff Heyob has developed a robust data logging and data management system known as InfoScribe. His vast knowledge of both the InfoScribe project and C++ programming on the Macintosh has been instrumental to the furtherance of this Task. Steve Adams, who is also working under Jeff Heyob on the InfoScribe project, has devoted a great deal of time to procuring the software and hardware required for the completion of this Task. His guidance and knowledge of the InfoScribe project, C++ programming and many other applications on the Macintosh have proven invaluable to this Task. As project manager for a majority of the projects at MLIM, Dr. Steven LeClair, has encouraged other projects to utilize the software developed by this Task. This interaction has helped to expedite the beta-testing phase of InfoScribe and the Inter-Application Communication(IAC) software developed by this Task.

TASK DESCRIPTION

This Task was originally described as the "Discovery Systems for E-O Materials." However, due to previous experience with National Instruments LabVIEW, a graphical tool for the development of virtual instruments and controls, the focus of the Task shifted to a broader project dealing with Inter-Application Communication(IAC). The primary objective became the utilization of the IAC Link between LabVIEW and InfoScribe that Keith developed during the previous contract.

With the near completion of Jeff Heyob's InfoScribe software, it was decided that several projects at MLIM should utilize InfoScribe as a common platform for storing experiment results. The InfoScribe project was founded on the notion that eventually the entire Materials Lab will utilize its data logging capabilities to store experiment results in a universal format that could later be retrieved and utilized by other projects. This ability to share experiment results throughout the facility would greatly reduce the time previously wasted in duplicating the work of another project that might have stored its results in an incompatible format.

Several projects at both MLIM and throughout the Materials Lab utilize LabVIEW for experiment control and data acquisition. Therefore, it was understood that a method of communicating between LabVIEW and InfoScribe would need to be developed to accomplish the previously mentioned goal. Thus, an Inter-Application Communication(IAC) Link was developed between LabVIEW and InfoScribe and was named LabVIEW Bridge.

Once the bidirectional communication capabilities of LabVIEW Bridge was thoroughly tested, it was decided that the IAC link should be incorporated into two material processes. The two discovery systems chosen include a Copper Vapor Deposition(CVD) process and Pulsed Laser Deposition(PLD) process. It was hoped that, if LabVIEW Bridge could be applied to both experiments, this would demonstrate its ability to fulfill the previously mentioned goal of making InfoScribe a universal data logging and management depository.

DESIGN METHODOLOGIES

To accomplish the Task objective as quickly and efficiently as possible, the existing data acquisition and experiment control aspects of each process was first studied. It was determined that LabVIEW Bridge could be used to log the data and instrument settings for both experiments. The PLD process would also benefit from InfoScribe's ability to remotely control and monitor the status of the laser. The CVD process, however, involved logging arrays of spectrum data that would vary in length throughout the experiment. Previously, to store data within InfoScribe the process was required to preregister the known data specifications to allow for precise memory allocation. However, because the specifications of this spectrum data could change throughout the experiment, it was clear that this would not be possible.

Once the existing control systems of the PLD were analyzed, it was determined that reworking the existing code would not be possible. A future goal for this project included incrementally converting it from the LabVIEW environment to C code to improve efficiency. Unfortunately, the existing code was not designed with a high level of modularity and would not allow for incremental conversion. Therefore, it was concluded that the entire control system be rewritten to accommodate future incremental development. The new PLD program would divide tasks into smaller Virtual Instruments (VIs) that could be initiated and controlled using the Apple Event protocol. These VIs could then eventually be replaced with routines written in C and initiated through Apple Events.

The CVD process was studied in more detail to determine if either the spectrum array could be forced to maintain a specified length or limited to a known set of varying length arrays. Unfortunately, this proved to be false, the situation was discussed with the initial designer of InfoScribe. It was concluded that the only way to store a varying sized array within InfoScribe would require registration of a new array every time its length was changed. The LabVIEW program would also have to remember if a specific sized array has already been registered to prevent duplicate data allocation errors within InfoScribe. Also, it was concluded that data logged using this method would be difficult to decipher and analyze from within InfoScribe.

When the results of this discussion were relayed to the CVD process manager, he claimed that monitoring the data within InfoScribe was not required. The current system converts the spectrum data into binary files that are later analyzed by a mathematics program called MATLAB. Therefore, despite the fact that other users of InfoScribe might not be able to benefit from the CVD spectrum data being stored, the LabVIEW program to log variable length arrays could now be implemented.

TASK RESULTS

The new PLD control shell was completely coded by the completion of this Task. However, the specific Virtual Instruments (VIs) for each device in the experiment have not been developed. Therefore, the testing of the control shell was limited to simulated experiments. The task of coding the new instrument VIs will now be completed by the PLD process manager with the help of the InfoScribe development team.

The CVD LabVIEW VI for storing variable length arrays was completed and tested by the end of this Task. It successfully registers new data specifications as a new spectrum array is presented for data logging and remembers if arrays have been previously registered. The CVD process manager was also able to store comments with his data to describe how the spectrum should be analyzed outside InfoScribe. This was done to help future users of the InfoScribe data depository utilize the experiment results. This project also allowed for the testing of InfoScribe's export data capabilities. Several spectrum arrays were successfully converted to MATLAB binary files and manipulated using MATLAB functions.

Overall, both tasks were completed successfully. Due to the unique requirements of each process, the work completed during this Task should help to prove the robustness and flexibility of LabVIEW Bridge and the InfoScribe data logging and data management system.

GRAPHICS DISPLAY OF COMPUTER SIMULATIONS

Task Order No. 132
Student Support Program
Southwestern Ohio Council for Higher Education

Carlos Hernandez
Wright State University

31 August 1995

Government Task Leader
Ms. Monica A. Stucke
WL/MLLM

ACKNOWLEDGMENTS

I would like to thank the whole group for their support and camaraderie, which made the Task very enjoyable. The office was one of the friendliest and most pleasurable environments in which one would ever expect to work. Special thanks go to Mr. Satish Rao and Mr. Jeff Simmons for their support, expertise and collaboration in several projects. I would also like to thank the people at SOCHE (Southwestern Ohio Council for Higher Education) not only for their professionalism, but also for their service and assistance provided during this Task.

I am proud to be currently involved in the writing of a paper, in collaboration with Mr. Satish Rao and Mr. Jeff Simmons to be published in the Materials Science Phil. Mag, about Green's function boundary conditions methodology, including extensive graphical, theoretical, computational and timing analysis.

TASK ASSIGNMENT

During the Task, several graphical tools were completed to support the displaying of information from large input data decks involving differential displacement of atoms, local strains, forces, etc. Among these tools, some were built around the previously developed graphical packages, while others are stand alone utilities. The main objective of these utilities has been to improve the quality of the graphical results to give a professional and ready to publish output.

The main focus of work during this Task, however, has been the development and optimization of several scientific programs; while some of them are simply innovations and improvements to old problems, others are new to the field of materials within our community.

Several flexible boundary schemes have been proposed in the material science community to relieve inconsistencies which arise at the boundary region in atomistic simulations of defects, like dislocations and crack tips. These flexible techniques can be classified into two categories: (1) finite element methods and (2) Green's function methods. With the finite element techniques, the difficult part is the proper treatment of the transition between the lattice and the continuum which has recently been described in terms of non-local elasticity theory. Green's function techniques suffer from the disadvantage that the Green's function of the defected lattice, even in the long range part, is dependent of the core structure and of the size of the defect that is being simulated. Therefore, in atomistic simulations of crack propagation, the appropriate Green's functions for the defect problem, needs to be updated continuously as the simulation proceeds. However, the Green's function of a perfect lattice is relatively unperturbed around line defects like dislocations. Therefore, for simulations of dislocations in a single crystal, Green's function techniques can be applied with relative ease, since only the perfect lattice Green's functions are required for a proper treatment at the boundary region.

The requirements specification phase of a project was completed to implement Green's functions techniques, to describe the inconsistencies arising at the boundary region in atomistic simulations of infinite dislocations, for both two and three-dimensional dislocation problems for the Materials Lab at WPAFB. The system was analyzed, designed and developed to run on all type of RISC workstations, including the Power Macintosh, and on CRAY Supercomputers (X-MP, Y-MP and C-90). This required, in addition to the development of the system, a complete design and development of a time library and an extensive scientific mathematical library. As a result of the large core structure used by the CMS (Computational Materials Science) group, the system was optimized for all the running architectures and was improved by a 700% factor. Optimization techniques employed varied, from loop unrolling techniques, instruction scheduling etc. on the software side, to cache, registers, processors etc. utilization on the hardware front.

Once the system was operational, the researcher, analyzed and "costed" the development of the system to run in parallel, distributed and in multiprocessor workstations, to accommodate for future larger simulations. The researcher then, proceeded to design and develop the system to run on the Intel Paragon™ using the NX library for message passing. The system was then optimized after a thorough study of the hardware available, e.g., message routers etc. The system, as well as, the libraries were developed completely using C and the UNIX™ Operating System.

As a project leader, the researcher, also completed the requirements specification phase of a molecular dynamics (MD) system, which uses embedded atom method (EAM) potentials for the CMS. This system was implemented using new MD algorithms that are more precise and faster than existing ones. The system was developed first for RISC workstations and CRAY Supercomputers and then ported to the Intel Paragon™. This system was developed using C, FORTRAN and the UNIX™ Operating System.

This system was refined and optimized through the course of the Task several times, to be, not only more accurate, but also friendlier and more efficient. As a result of this, the CMS group is now in a position to analyze larger core structures in a fairly reasonable amount of time, leaving more time for the material scientist to devote to the study and analysis of the simulation results. Additionally, this performance improvement, allows the CMS group to run their simulations "in house" without having to request computer time from other outside facilities.

The development of these systems, has raised one of the major problems that the CMS has to face, that of time. Most algorithms employed by the CMS group grow exponentially with the number of atoms. This fact has shown the impossibility of running some simulations, as well as, the enormous amount of wait between simulations, even with today's computational power.

This problem and the need for running larger cores, e.g., cores approaching 1,000,000 atoms, have led to the need for not only optimization of code, but also the need for research and testing of new methods that will allow faster turn around times, as well as, the possibility of running some of today's unfeasible simulations.

This Task also involved various other projects, such as, the development of a program to calculate "Schmid Factors" and displaying these using isometric projections, Monte Carlo simulations, "Zenner and Pinning" studies, finding and displaying local strains, finding the self induce stress field at point due to a line segment, for both isotropic and anisotropic mediums, displaying embedded surfaces and contour plots, for the analysis of electronic structures etc. The activities also included being the system administrator, performing such Tasks, as adding new users, managing UNIX™ processes, planning and performing backups, restoring lost files from backup tapes, adding new terminals and disk drives, setting up a printer and the spooling system, and especially making the system secure.

MICROSTRUCTURE DEVELOPMENT IN SUPERALLOYS

Task Order No. 133
Student Support Program
Southwestern Ohio Council for Higher Education

Jamsheed Reshad
Wright State University

12 June 1995

Government Task Leader
Mr. Lee Semiatin
WL/MLLN

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TASK ASSIGNMENT

The primary objective of the Task was to establish the effect of processing variables on microstructure development in nickel-base superalloys. Specifically, the effect of forging strain, strain rate, and temperature and subsequent supersolvus heat treatment conditions on abnormal grain growth have been determined. The resulting data of microstructures in as compressed and compressed and heat treated samples can later be interpreted using computer simulations of the deformation process and conventional metallurgical descriptions of abnormal grain growth kinetics.

A secondary objective of the Task was to determine solvus temperatures of various phases present in a titanium based alloy. The solvus temperature determinations were studied using isothermal heat treatments. The results obtained will ultimately determine the mechanical properties of this material.

RESEARCH METHOD

The steps for research and analysis for both objectives were very similar. These three main steps were heat treatment, specimen preparation, and specimen analysis.

Before an actual heat treatment, a certain methodology must be followed. The material to be heat treated is received in bulk form and sectioned to a desirable shape using an abrasive cutting machine. The sectioned material, or slices, are then cleaned in acetone and encapsulated in quartz tubing under vacuum. The cleaning and encapsulation of these specimens before heat treatment are done to prevent contamination which can occur under high temperatures in atmosphere. The actual heat treatment takes place in a muffle furnace with a temperature range of up to 1200° Celsius. For both primary and secondary objectives of this Task, the heat treating methodology consisted of an isothermal forming heat treatment for all specimens and subsequent heat treatments for individual specimens. The forming heat treatments were used to precipitate the phase or phases under evaluation and cooled in the atmosphere. The individual heat treatments were used to determine the solvus temperatures and were water quenched so that the resulting microstructure will represent the material at the specific heat treating temperature.

Specimen preparation begins with sectioning the heat treated material by using a gravity fed diamond saw. The material is then mounted in Konductomet in a mounting press to ease the handling of the specimen during the polishing phases. The polishing process is composed of an initial polishing phase, an intermediate phase, and a final polishing phase. The initial polishing phase is composed of subjecting the specimen to silicon-carbide grit paper from 240 grit to 600 grit. This is done to make the surface as level as possible while decreasing the size of surface scratches. The intermediate or lapping phase includes polishing the specimen using a suspended diamond solution on a wheel. The lapping stages use 9 micron diamond suspension in stepwise increments through 1 micron suspension. The final polish consists of placing the specimens in a vibromet containing neutralized .06 micron colloidal silica. This final stage produces a pristine scratch free polish.

Analysis of these specimens is usually done in the scanning electron microscope (SEM). Due to the nature of the SEM, all specimens must be thoroughly cleaned and baked out under vacuum to insure safe operation of this expensive equipment. While on the SEM, the presence of phases under analysis can be detected by electron dispersal spectroscopy (EDS). Also, digital images of the surface are collected at various magnifications. These digital images can then be analyzed using computer software such as NIH image which can determine the volume fraction of phases in question.

RESULTS

As outlined with the objectives of this Task, the behavior of the nickel-base superalloy while under various processing variables and its effect on microstructure have been determined. The digital images and data collected from them have been compiled for further examination. The solvus temperature for the various phases in the titanium alloy has been determined and will be used for further investigation.

CONVERSION OF CONTROL SOFTWARE FOR DEPOSITION PROCESSES

Task Order No. 134
Student Support Program
Southwestern Ohio Council for Higher Education

Keith M. Andrews
Wright State University

26 June 1995

Government Task Leader
Capt. Elizabeth Stark
WL/MLIM

ACKNOWLEDGMENTS

The guidance of Jeff Heyob, Steve Adams and Dr. LeClair has been greatly appreciated throughout this Task. Over the past few years Jeff Heyob has developed a robust data logging and data management system known as InfoScribe™ His vast knowledge of both the InfoScribe™ project and C++ programming on the Macintosh has been instrumental to the furtherance of this Task. Steve Adams, who is also working under Jeff Heyob on the InfoScribe™ project has devoted a great deal of time to procuring the software and hardware required for the completion of this Task. His guidance and knowledge of the Info Scribe™ project, C++ programming and many other applications on the Macintosh have proven invaluable to this Task. As project manager for a majority of the projects at MLIM, Dr. Steven LeClair, has encouraged other projects to utilize the software developed by this Task. This interaction has helped to expedite the beta-testing phase of InfoScribe™ and the Inter-Application Communication(IAC) software developed by this Task.

TASK DESCRIPTION

This Task was originally described as the "Conversion of Control Software for Deposition Processes." However, due to previous experience with National Instrument's LabVIEW™ a graphical tool for the development of virtual instruments and controls, the focus of the Task shifted to a broader project dealing with Inter-Application Communication(IAC). The primary objective became the development of an IAC Link between LabVIEW™ and the InfoScribe™ data logging and data management software.

With the near completion of™ software, it was decided that several projects at MLIM should utilize InfoScribeTM as a common platform for storing experiment results. The InfoScribe TM project was founded on the notion that eventually the entire Materials Lab will utilize its data logging capabilities to store experiment results in a universal format that could later be retrieved and utilize by other projects. This ability to share experiment results throughout the facility would greatly reduce the time previously wasted in duplicating the work of another project that might have stored its results in an incompatible format.

Several projects at both MLIM and throughout the Materials Lab utilize LabVIEW™ experiment control and data acquisition. Therefore, it was understood that a method of communicating between LabVIEW™ and InfoScribe™ would need to be developed to accomplish the previously mentioned goal. Thus, with the help of Jeff Heyob and Steve Adams, the main objective of this Task has been broadened to encompass several experiments by developing and Inter-Application Communication(IAC) Link between LabVIEW™ and InfoScribe™.

DESIGN METHODOLOGIES

To accomplish the Task objective as quickly and efficiently as possible, it was determined that the IAC Link should initially attempt to utilizing existing Virtual Instruments(VIs) provided by National Instruments with their LabVIEW™ software. The InfoScribe™ project was originally designed to communicated with other C++ programs utilizing a Macintosh Apple Events(AE) communication protocol. Several VIs were included with LabVIEW™ that appeared to provide limited AE communications.

If the Task objectives could not be accomplished with the existing VIs, it was initially decided that the second alternative would be to write a Code Interface Node. National Instruments realized, as they improved upon earlier versions of LabVIEW™ that to perform certain specialized tasks it was far simpler to write a small C program than to implement it using the graphical interface of LabVIEW™ Therefore, they provided the means to incorporate the functionality of a small C program into their VIs through a Code Interface Node(CIN). This CIN was designed to load a resource file written by an external C Compiler. This compiler would be used to design and debug the original C program and incorporate specific functions and variable type definitions required for the program to work with LabVIEW™ as a CIN. Symantec's Think C++ compiler was utilized because National Instruments provided these functions and variable type definitions in a library format compatible with this development software.

The computer systems upon which this IAC Link was developed include several different Macintosh platforms. Initially, it was developed on a Macintosh IIcx as a means to test the software's capabilities on one of the slower systems at the Materials Lab. Next, it was tested on a Macintosh IIfx as an example of how the IAC link would perform on a faster and more commonly used computer. Finally, the software has been tested and redesigned on a Macintosh Quadra 700 for the past few months to test its functionality of a much faster platform.

It was determined that the results of this Task will be analyzed upon completion of the software. As stated earlier, it is has been deemed necessary to incorporate the InfoScribe™ data logging and data management software into several different experiments. The evaluation of the performance of this IAC Link between LabVIEW™ and InfoScribe™ will most likely be based upon its speed, efficiency, and how well it meets the needs of other project leaders.

TASK RESULTS

In the initial months of this Task, it was discovered that utilizing the original Virtual Instruments(VIs) provided by National Instruments for LabVIEW™ would not be possible. The goal of developing bi-directional communication between LabVIEW™ and InfoScribe™ would not be accomplished using the existing VIs. However, a uni-directional link was established to send data acquired by LabVIEW™ to InfoScribe™ for storage. Unfortunately, to properly manage files, parameter names, and time constraints in InfoScribe™ it was discovered that bi-directional communication was crucial.

In the second phase of this Task, it was also discovered that constructing a Code Interface Node(CIN) to serve as the IAC Link would not be possible. Due to National Instruments desire for LabVIEW™ compatibility on both the IBM and Macintosh platforms, they have developed their own memory management routines. These routines are incompatible with those provided by Apple in their Apple Toolbox ™ and are therefore incompatible with the C++ software written by Jeff Heyob for Apple Event communication with InfoScribe ™.

Eventually, after exhausting all methods of communicating with InfoScribe™ via Apple Events(AE), it was decided that a third alternative was available. On the Macintosh platform the AE communication protocol was built upon an earlier communication technique called PPC. With the extensive work over these past few months devoted to LabVIEW™ communications it was discovered that bi-directional communication via the PPC protocol was possible using the original VIs provided by National Instruments. Therefore, because Jeff Heyob and Steve Adams have both been developing C++ programs to communicate with InfoScribe™ it was decided that a separate bridge program could be developed. This C++ program, referred to as LabVIEW™ Bridge, has been designed to communicate with InfoScribe™ using the AE protocol and to likewise communicate with LabVIEW™ using the PPC protocol. The LabVIEW™ Bridge utilizes the code previously written to help InfoScribe™ efficiently manage files, parameter names, and time constraints. This final phase of the Task was started within the past month and is expected to continue into the second contract.

CONTROL OF PLD FOR DEPOSITING SUPERCONDUCTING FILMS

Task Order No. 135
Student Support Program
Southwestern Ohio Council for Higher Education

Steve Murray
University of Cincinnati

12 June 1995

Government Task Leader
Capt. Elizabeth Stark
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank a number of people who helped to make this project possible. First, a special thanks to both Dr. Steven LeClair and Capt. Elizabeth Stark for funding both the initial Task and subsequent equipment purchases. Also, thanks to Dr. Rand Biggers and Mr. David Dempsey whose numerous suggestions on the new system's capabilities helped to push me in the right direction when it came time to design the software/instrumentation interface. Finally, a huge thanks to Dr. Samuel Laube, who had enough faith in my abilities to keep me in the lab. Without his direction and encouragement, this project would have never gotten off the ground.

TASK ASSIGNMENT

The main objective of this Task was to develop a Pulsed Laser Deposition (PLD) system for producing thin films of High-Temperature Superconductors (HTSCs). This goal was accomplished through the use of a Macintosh IIfx computer and a number of instruments coupled in with the computer. The reason for developing a sophisticated system for PLD of HTSCs deals with the fact that superconductors exhibit the unique characteristic of having no resistance to the flow of electricity. The fact that these materials have essentially zero resistance means that no power will be dissipated in them due to current flow. This simple fact has profound implications in the engineering world. The target material for this system is Yttrium-Barium-Copper-Oxide, usually referred to as YBCO. This material has a relatively high transition temperature of around 90 deg K, which implies that refrigeration costs to keep the material in the superconducting state can be kept low.

This essentially means that using superconductors in various applications may be cheaper than using other 'normal' conductors such as copper. Besides this, there are applications in which normal conductors could never approach the performance of superconductors no matter what the cost. One example of this is extremely high-Q filter circuits (theoretically infinite) due to 'lossless' inductors. To meet the expected increased demand for thin-film High Temperature Super Conductors (HTSCs), many researchers have turned to fairly inexpensive and reliable PLD-based systems since this technique has had success in other thin-film applications. Currently, however, PLD of HTSCs is essentially limited to the laboratory environment because the physics of the underlying process is not well understood. While many researchers have been able to produce HTSC films, the quality of these films varies from deposition to deposition. To eliminate some of the uncertainty of process conditions, a highly automated PLD system was developed at the Materials Directorate, WPAFB. In addition to simply replacing manual control elements with a sophisticated computer interface, the system is also capable of real-time data collection. This data will be used to model the effect of various system parameters on film quality.

DESCRIPTION OF RESEARCH

Again, the goal of the Task was to build a new PLD system from the ground up. This included assembling the chamber and various instruments and writing automation/data collection software. Scientists at the base had been experimenting with PLD of HTSCs for some time, and hence were able to relate problems with other PLD systems they had worked with. The major problem with other PLD systems was that data collection was typically done by hand. In light of this, the major goal was to automatically collect data in a real-time fashion.

The following two sections will describe the work done during this Task period.

Chamber Assembly and Instrument Selection: The chamber assembly consisted of mounting both the chamber and the pump station on a movable base. Also, the various ports of the new chamber were fitted with either instrumentation interfaces or view windows to allow for process observation. The following list provides a small description of each instrument used in the new system.

1. LPX-305i Lambda Physik Excimer Laser - the source of energy for the deposition.
2. IRCON MODLINE Two Color Pyrometer - measures the substrate temperature, much faster than a standard thermocouple.
3. OMEGA Thermocouple Gauge - also measures the substrate temperature, more accurate than the pyrometer.
4. GRANVILLE-PHILLIPS CONVECTRON VACUUM GAUGES (2) - measures both chamber pressure and pump pressure, capable of high pressure measurements.
5. BARATRON PRESSURE GAUGE - measures chamber pressure, capable of making precision low pressure measurements.
6. HEWLETT PACKARD 54502A DIGITIZING OSCILLOSCOPE - measures the voltage response of plume intensity.
7. LFE PID Controller - regulates the temperature of the substrate.
8. National Instruments relay cards - allow standard AC relay switching, used to regulate the chamber pressure.
9. Newport Programmable Motion Controller PMC200-P - allows a mirror to scan the laser across the surface of the target.
10. INFICON DEPOSITION CONTROLLER - measures film thickness.

Software Development: Software was written to direct both the deposition procedure overall and the various functions of each instrument as listed above. The deposition software was written with the goal of giving the operator complete control of every device from the keyboard/mouse. Prior to the actual deposition, any instrument can be selected/deselected as required, and those devices which require some type of setup information can be configured either interactively or quickly through the use of disk-based device setup files. During the deposition, all actuator settings can be changed any time. Instead of manually collecting the data with pen and paper, the operator simply supplies a file name for data storage. Finally, all sensor measurements are displayed graphically in real time.

CONCLUSIONS

Apparently, the new system has a definite advantage over other manually operated systems. At the lowest level, the new computer controlled system automates many of the tasks the operator(s) needed to perform manually. More important, however, it gives the scientist the ability to collect large amounts of data effortlessly. This data will be used by scientists to develop a model for PLD of HTSCs. This model can then be used to develop a comprehensive control structure. Since the system was designed with this goal in mind, it is already capable of supporting a complex control structure implementation.

Without an efficient means to collect experimental data, it would be nearly impossible to understand the dynamics of PLD of HTSCs. When a comprehensive control structure is added, it is probable that film consistency will increase dramatically. Only then will the benefits of thin film superconductors be realized.

TRIBOLOGICAL EVALUATION OF SOLID LUBRICANT COATINGS

Task Order No. 136
Student Support Program
Southwestern Ohio Council for Higher Education

John E. Florkey
The Ohio State University

12 June 1995

Government Task Leader
Dr. Jeff Zabinski
WL/MLBT

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

An experiment was created to try to increase the corrosion resistance of Titanium Nitride, to be used on turbine engine bearings in perfluoropolyalkylether, by code position with Chromium Nitride. The TiN film is generally porous, which leads to poor protection against chemical attack. CrN is also a hard coating. It is not as hard as TiN. But, it can be made to be free of pores, which makes it a better protector against chemical attack than TiN. It is hoped that the code position of Cr, Ti and Nwill yield a hard coating with good protection against corrosion.

Another experiment was done to ascertain the usefulness of Graphite Fluoride (Cf_x) as an additive to Tungsten Disulfide (WS_2) to make it less sensitive to moisture.

DESCRIPTION OF RESEARCH

The TiN coatings were deposited using Plasma Arc Deposition on 440C and M50 substrates at Hohman Plating and Mfg. Inc. The partial pressure of nitrogen and substrate bias were the controlled variables. The coatings were characterized for chemistry and crystal structure by X-ray Photoelectron Spectroscopy and x-ray Diffraction, respectively. The coatings were tested for friction and wear properties with a pin-on-disk type tester.

The WS_2-CF_x films were deposited onto 440C substrates using an excimer laser that provided a beam of ultraviolet radiation at 248 nm. The beam was directed at a cold pressed WS_2-CF_x target. Film uniformity was maximized by: (1) rotating the target and substrate during deposition and (2) rastering the laser beam across the target face under computer control. The substrates were cleaned in an ultrasonic cleaner in acetone and methanol before deposition to maximize adhesion. The substrates were also polished prior to deposition to minimize roughness and increase deposition rates. The coatings were characterized for chemistry and crystal structure by X-ray Photoelectron Spectroscopy and x-ray Diffraction respectively. The coatings were tested for friction and wear properties with a pin-on-disk type tester. Humidity was controlled by bubbling air through a flask of water.

RESULTS

Resistance to corrosion and crystal orientation of the TiN coatings was affected by changing the substrate bias and nitrogen partial pressure. The coatings were found to have excellent corrosion resistance, surpassing the target temperature at which they would be used. At higher temperatures, pinholes were observed in the films. This problem was overcome by coating the substrate with electroless nickel. The XRD data shows that the films have a crystalline structure. The relative intensities of the XRD peaks suggest that the films have a preferred orientation that changes with bias and nitrogen partial pressure. Data from the XPS suggests that the C and F found in the film is bonded differently than in graphite fluoride. This difference in bonding and dispersion in the WS_2 may account for the improved friction coefficient and insensitivity to moisture. The films had hardness values in the range of 30 - 40 Gpa. The coefficient of friction for the films varied between $\mu = 0.6 - 0.7$. So far the TiN has been the only film deposited. The target to be used for the deposition of CrN is being acquired.

The 10:1 WS_2-CF_x films grown at room temperature exhibited ultra low friction at low humidity, below the detectable limit for the tribometer (μ=.01). The film reacted similarly to pure WS_2 films with increasing humidity but remained lower until about 50-60% humidity. The 10:1 WS_2-CF_x films grown at 300° C showed higher initial friction but were insensitive to humidity after an initial jump on moving from dry conditions. As humidity increased, from 15 - 75% the humidity decreased slightly from 0.14 to 0.1.

For the 1:1 WS2-CFx films grown at room temperature, friction increased with humidity but never reached μ0.1. The 300° C 1:1 WS2-CFx films had higher friction than the other films throughout the tests.

These coatings could be used in a couple of different ways. If the application called for a lubricant to be used in an environment where there was little or no humidity such as space, the 10:1, room temperature films would be suitable. If the application called for a lubricant to be used in terrestrial environments where sensitivity to moisture is harmful, the 300° C, 10:1 and room temperature, 1:1 films would be useful.

SELF-DIRECTED CONTROL OF CHEMICAL VAPOR DEPOSITION

Task Order No. 137
Student Support Program
Southwestern Ohio Council for Higher Education

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Wright State University

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Government Task Leader
Capt. Elizabeth F. Stark
WL/MLIM

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Also, many thanks to Dr. Samuel Laube and Dr. Al Jackson for involving me in the X-ray project. Their generosity in sharing their knowledge and experience in scientific and engineering matters is very much appreciated.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The objective of the Task was to implement control strategy for Chemical Vapor Deposition (CVD). The Task undertaken, however, did not involve CVD, rather, the design, construction and testing of a 30 kilovolt power supply used to provide high voltage to an X-ray machine being developed by Dr. Jackson's group. This technical report, therefore, describes the development of this high voltage power supply, covering early designs that failed to provide a high enough voltage output or that operated at such high temperatures that the electronics failed after only a few moments of operation. Since these designs were not complete failures, the details of their designs are included here for two reasons. The first reason is so that these projects will not be unnecessarily redesigned in the future. The second reason is that since these designs 'almost' worked, there may be some merit in further developing them.

Motivation for developing this high voltage power supply 'in-house' comes from a desire to produce a complete, yet inexpensive X-ray system that can be used in conjunction with a computerized data acquisition system to measure consistency in the thickness of carbon fibers. Fiber consistency can be determined by measuring the variation in X-ray intensity as the fiber is passed between an X-ray source and a radiation detector. The absorption of X-rays by the fiber is proportional to the mass of the fiber and so X-ray transmission can be used as a measure of fiber thickness.

At present, the most successful high voltage power supply available to the project is a 24 kilovolt, 3 kVA transformer. This transformer provides sufficient A.C. voltage and current to power the X-ray tube, however, it is excessively bulky and heavy, weighing in at 225 pounds. For this reason work is continuing on the design of a lighter, more compact power source. Preliminary testing on the latest design, a switched-capacitor voltage multiplying arrangement, shows very promising results. The design is complete and the circuitry is expected to be operational in the first week of November 1995.

DESCRIPTION OF RESEARCH

The original design was based on a 12-volt automobile ignition coil. In this circuit, the current in the primary is slowly ramped up to some peak value and then abruptly cutoff. Since the voltage across the secondary coil is proportional to the time rate-of-change of current in the primary, a high voltage appears at the secondary coil. Unfortunately, the ignition coils used were not able to withstand the extreme voltages, and would begin arcing internally between 15 and 20 kilovolts. Therefore, another approach was necessary.

Color television sets typically operate at 30 to 40 kilovolts and so their circuitry provides a promising model for the X-ray's power supply. The second approach was to drive the flyback transformer from an old color television set with a field-effect transistor (FET) current switching circuit as shown in Figure 1. The principle of operation is as follows. The amplified output of a variable duty-cycle Schmidt trigger oscillator is used to switch a n-channel power MOSFET. This FET sends pulses of current through the primary winding of the flyback transformer, inducing a high voltage across the secondary winding.

Ten milliamps of electron current in the X-ray tube at 30 kilovolts was achieved, however sustained operation caused the flyback transformer and the FET switching circuit to overheat. This obstacle could probably be overcome by using a larger flyback transformer, by better tuning the resistor-capacitor circuit in parallel with the primary coil on the flyback, and by using small fans to cool both the transformer and the FET. Since a larger flyback could not be found, development on this design was halted so that other designs could be explored.

A radar pulse transformer was experimented with next. According to the literature that accompanied the transformer, a pulse of current through the primary would induce > 20 kilovolts on the secondary. Perhaps due to improper impedance matching, this was never realized and the project was quickly scrapped.

The latest experiment is with a switched-capacitor voltage multiplier circuit. Unlike the previous designs that generate a high A.C. voltage via inductive mechanisms, the switched-capacitor voltage multiplier uses a diode-capacitor arrangement to generate high D.C. voltage.

The input-output relationship of the voltage multiplier circuit is ideally

$$V_{out} = 2\,n\,V_{in}$$

where 'n' is the number of stages in the circuit. The diodes and capacitors used in the circuit are rated at 1 kilovolt, and the largest voltage across any element in the circuit is twice the input voltage; therefore, the maximum safe input voltage is 500 volts. Ideally, at this input voltage, 30 stages should generate 30 kilovolts at the output. Experiment shows that the actual output voltage is only about 75% of what theory predicts; therefore, the number of stages in the circuit will need to be roughly forty to fifty to reach the required 30 kilovolts.

The circuit was designed as three subcircuits: the oscillator, the FET switching circuit and the voltage multiplier. Figure 2 illustrates the oscillator circuit. A 556 timer integrated circuit is configured to generate a variable duty cycle, 10 to 0.1 Hz pulse that gates a second 15-khz square wave.

The gated 15 kHz output signal is optically coupled via optoisolators to the gates of the four FETs in the second subcircuit, a 500 volts switching circuit, illustrated in Figure 3. The input signals to the 6N135 optoisolators are configured in such that only two of the FETs are on at any one instant. For example, referring to Figure 3, the upper-left and the lower-right FETs are turned on while the upper-right and the lower-left FETs are turned off. This places the upper output terminal at +V and the lower output terminal at -V. During the next cycle of the 15 kHz input signal the FETs switch state, thus reversing the polarity of the output terminals. The maximum voltage difference between the output terminals is limited to 500 volts.

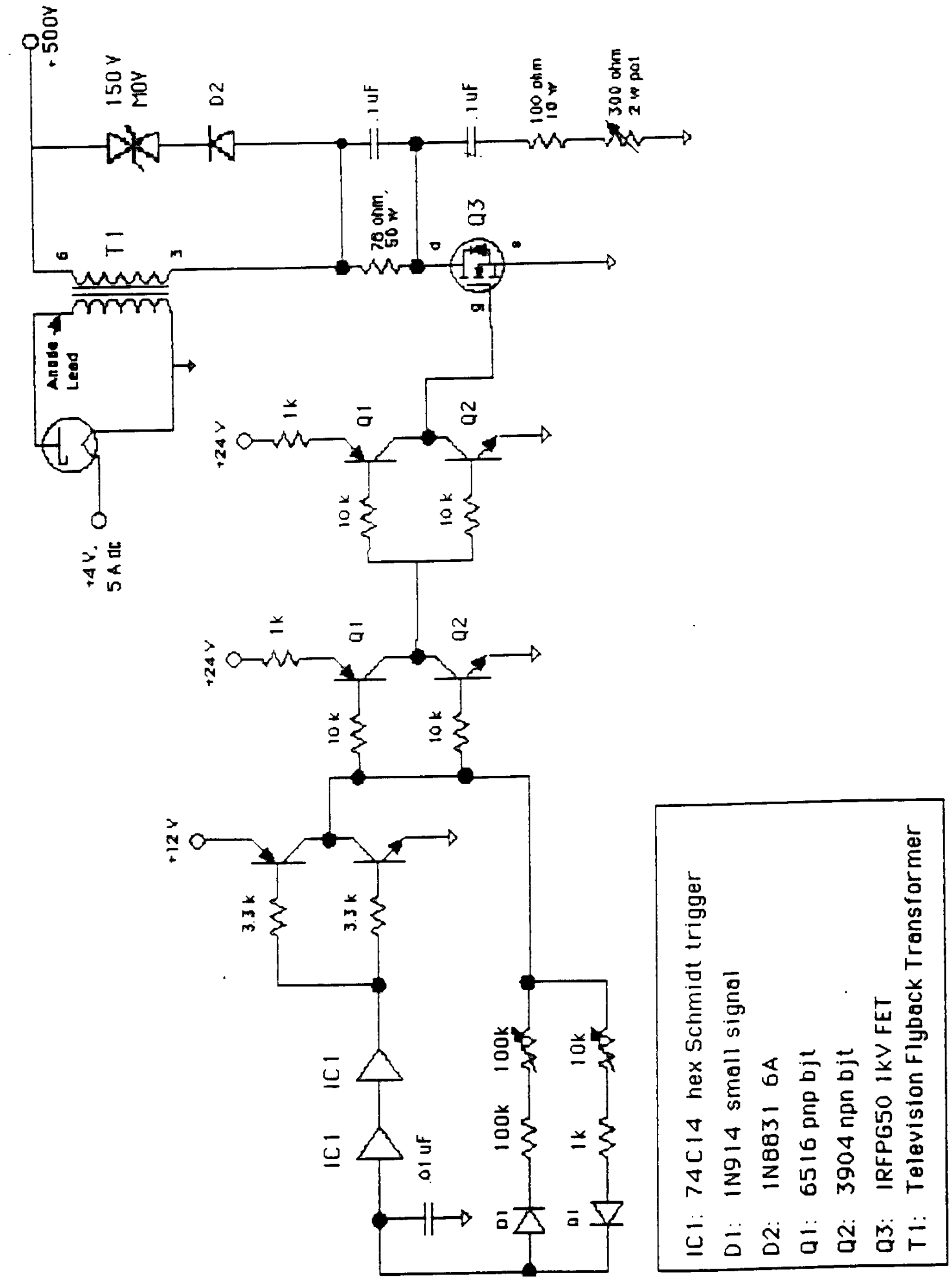
The last subcircuit is the switched-capacitor voltage multiplier shown in Figure 4. The output from the second subcircuit drives this one. Each time the input voltage switches polarity, the diodes pump electrons into successively higher capacitor stages (each stage consisting of two adjacent diodes in parallel with two capacitors). This pumping action incrementally charges each capacitor in the chain to a voltage twice that of the input voltage. The high voltage output is tapped off of the lower set of capacitors as indicated in Figure 4.

RESULTS

Variation upon variation has been tried with the flyback transformer and ignition coil circuits. These designs would be successful if higher voltage transformers and transistors could be acquired, however this is not the case.

The switched-capacitor arrangement is the most promising design yet for the following reasons:

1. All of the parts that are required are easily accessible.
2. The output voltage is scalable. Simply add more stages to increase the voltage.
3. The oscillator circuit is electrically isolated from any high voltage. This allows a control computer to be safely interfaced with the power supply.



IC1:	74C14 hex Schmidt trigger
D1:	1N914 small signal
D2:	1N8831 6A
Q1:	6516 pnp bjt
Q2:	3904 npn bjt
Q3:	IRFPG50 1kV FET
T1:	Television Flyback Transformer

Figure 1

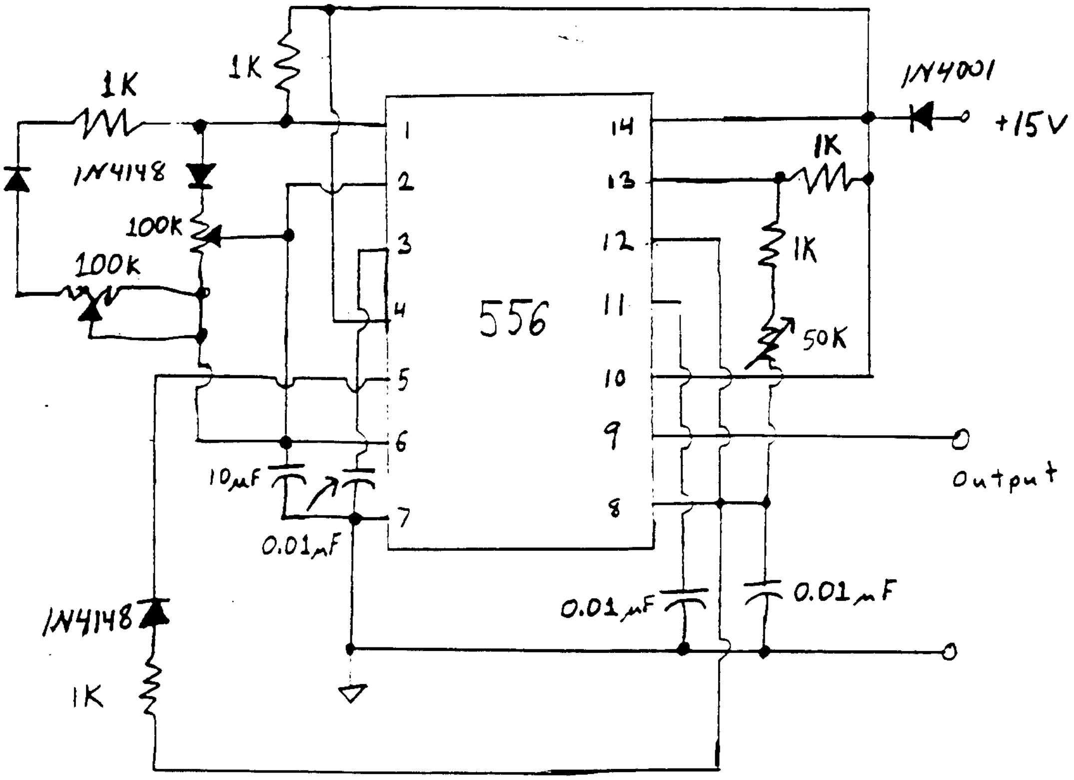


Figure 2 Oscillator Circuit

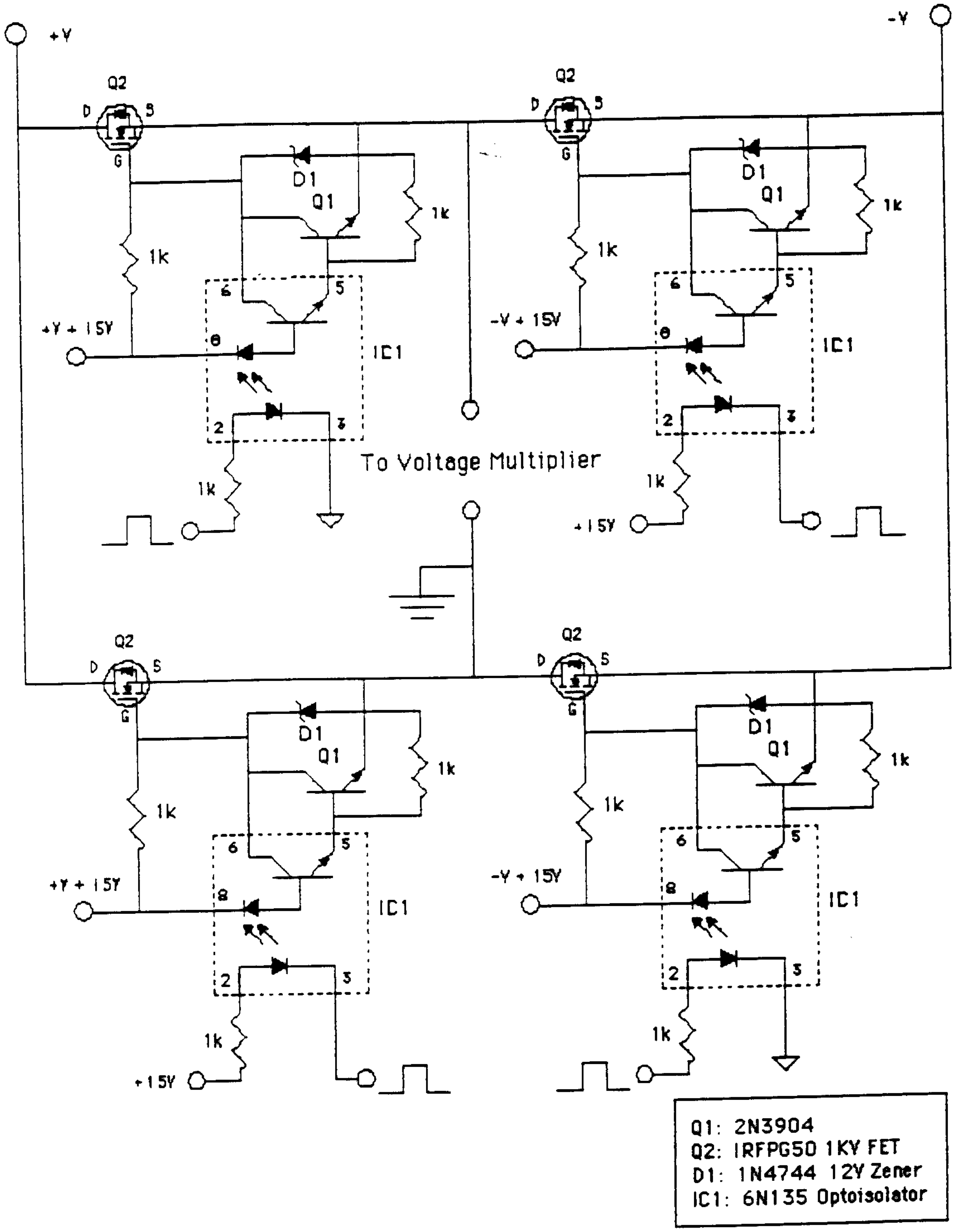


Figure 3 FET Switching Circuit

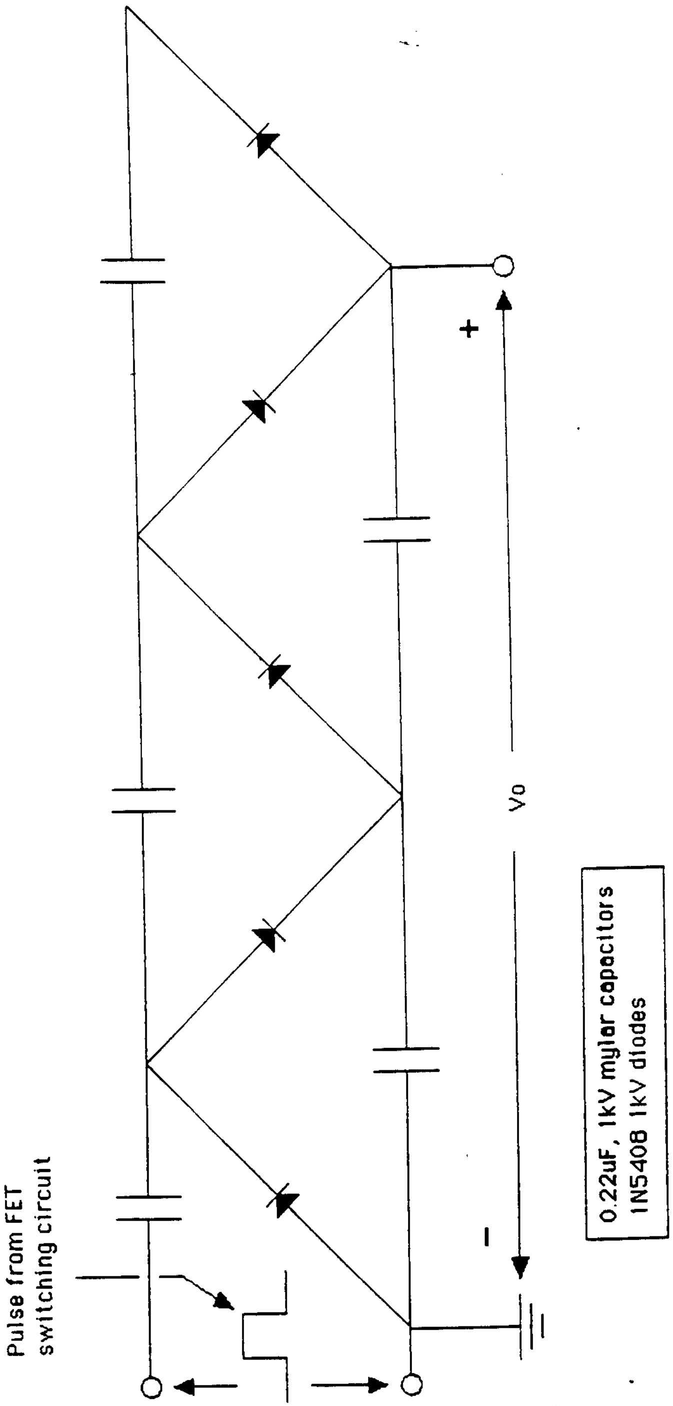


Figure 4 Voltage Multiplyer Circuit

AXIOMATIC DESIGN OF MATERIAL PROCESSES

Task Order No. 138
Student Support Program
Southwestern Ohio Council for Higher Education

Robert M. Ray, III
Ohio University

26 June 1995

Government Task Leader
Dr. James C. Malas, III
WL/MLIM

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TASK ASSIGNMENT

The objective of this Task was to study the feasibility of using the Axiomatic Design Approach to aid in the improvement of the shear die design process. The Axiomatic Design Approach is a systematic, methodological view of the design process, which can be utilized to design any system or product, from the initial design of new parts to increasing the quality of existing parts and/or manufacturing processes. This Task attempted to increase extruded aluminum product quality by systematic design of the tooling which produced the parts. With the use of design matrices and the general knowledge of the axioms, theories and corollaries involved in Axiomatic Design, a specific order of design emerged to lead a designer in the proper direction.

DESCRIPTION OF RESEARCH

Extrusion is utilized to produce continuous, long, straight, semi-finished metal products which have a constant cross sectional area. Parts are produced by inserting a preheated cylindrical billet, made up of the material which is to be deformed, into a preheated, cylindrical, non-lubricated container and then pushed by the force of a mechanical or hydraulic ram against an opening or orifice cut into the face of the die in the specified shape of the product. The die is a thin disk of tool steel with an opening cut into it which matches the required shape of the product. There are certain die parameters which can be altered to affect the quality of the extrudate or product.

The Task began as a design of the entire process of extrusion from the choice of process parameters such as the extrusion temperature and speed, to the design of the auxiliary process needed to acquire the correct shape, such as the run out manipulation and subsequent machining and heat treatment. This Task was deemed too extensive for the allotted time, and not what was really needed out of this project. The conclusion was, that the geometrical configuration of the part was most affected by the configuration of the die parameters.

The changeable die parameters include the following: (a) die diameter, which is usually constrained by the size of the container; (b) the orifice dimensions, which are decided after taking into account thermal shrinkage of the part, thermal expansion of the heated die and die deflection; (c) the orifice placement in the die to help give uniform metal flow, since metal flows faster at the center of the billet as opposed to the edges where container friction is present; (d) land length, which is the surface into the die at right angles from the die face. These serve as brakes on the metal as it exits the die, since metal seems to flow faster in larger cross sectional areas; (e) the surface quality of the die land lengths, which directly affects the quality of the product surface.

These parameters were chosen to control the quality of the product, namely: (a) the surface roughness (b) the product dimensions and (c) the flow of the product out of the die.

Axiomatic design can be summarized into two fundamental axioms namely: (a) maintain the independence of the functional requirements and (b) minimize the information content. These axions state that proceeds through four design domains. The first is the customer domain and gets mapped into the functional realm. Second is a minimum list of functional requirements (FRs) which the system must meet in order be improved or designed. These FRs are to be physically realized by a vector set of design parameters (Dps), the third domain, in the physical domain. The DPs are in turn mapped to the fourth domain process variables (PVs) these can be specified to produce the desired part.

RESULTS, CONCLUSION AND FUTURE WORK

When the vector of design parameters of the part is mapped to the vector of process variables in the process domain, a design matrix emerges which show the designer an order of design which must be followed to keep it an uncoupled design. What the results say is that the die orifice dimensions must be determined first, then the land length will need to be designed in light of the already specified dimensions, and then the surface roughness of the die can be specified. These parameters are decided while holding the other die parameters constant, such as, the orifice placement and the die diameter.

The conclusion is, that tooling for shear die extrusion can be designed relatively accurately using the Axiomatic Design Approach. This approach eliminates the "trial-and-error" method to die design where the die is designed and corrected multiple times until it performs properly. More work should be done to use the axiomatic approach to design the entire process and then the aluminum extrusion process may be more understandable and controllable. This is the direction that the current work is leading toward. The next short-term project is to quantify the relationships, if possible, between the physical domain and the process domain, to determine how sensitive the part features are to the specified die parameters. Once this is accomplished, different solutions to the same problem will be analyzed using axiom #2 to determine which design system is the "best" one to use.

MECHANICAL PROPERTIES OF METAL MATRIX COMPOSITES

Task Order No. 139
Student Support Program
Southwestern Ohio Council for Higher Education

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15 September 1995

Government Task Leader
Mr. Stephan M. Russ
WL/MLLN

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TASK ASSIGNMENT

The objective of the Task was to participate in the ongoing characterization and evaluation of titanium-based metal matrix composites (MMC's). The Air Force is interested in assessing the potential of this class of materials for use in advanced aerospace applications, particularly high performance jet engines and airframe structural components. To safely and efficiently employ titanium MMC's in such roles, it is necessary to obtain a full understanding of how the materials behave under various conditions of thermal and mechanical loading.

Tensile and creep testing are used to evaluate the usefulness of the material in load-critical structural applications. Fatigue testing is also conducted to help predict the materials' response to cyclic loadings such as those experienced by engine components. Metallographic and/or fractographic analysis of tested MMC specimens provides insight into the damage mechanisms and failure modes of the material when subjected to various thermal and mechanical loads. Metallographic examination of untested MMC samples is also useful as it provides a general idea of the overall quality and microstructural characteristics of composites fabricated by various methods.

RESEARCH METHOD

Through the course of the Task, MMC research focused on composites consisting of a titanium-aluminide matrix such as Ti-6Al- 4V, Ti-15-3, or Ti-22-23 surrounding SCS-6 silicon carbide reinforcing fibers. Testing focused largely on composites with unidirectional longitudinal [0] fiber orientation, but tests were also conducted on specimens with transverse [90] and tri-axial [0/+45/90/-45/0] fiber orientations. In addition, some fiberless or "neat" specimens were tested for refining the present understanding of the behavior of the matrix material. The research effort was essentially broken down into three interrelated segments: testing and data analysis, computational modeling, and microscopic examination.

MMC test samples were cut from composite plates received from the manufacturer. Test specimens were either straight-sided or dogbone configurations and typically ranged in length from 4 to 6 inches and were between 1/3" and 3/4" wide in their gage (center) sections. Some samples were heat treated prior to testing to alter their mechanical properties by producing microstructural changes.

Specimens were primarily tested on horizontal servo-hydraulic MTC testing machines. The machines were linked to PCs which provided computer control and recorded data from the tests. Due to the flexibility of the computer control and data retrieval scheme, the same machines could be programmed for tensile (static) testing, elevated temperature creep tests, and both thermal and mechanical fatigue tests. Thermocouples attached to the surfaces of the test specimens provided feedback control for heating lamps which made it possible to conduct tests anywhere from room temperature to temperatures in excess of 800°C. Extensometers mounted on the edge of the test specimen were used during testing to collect strain data in real time.

After testing, data was transferred from the data retrieval computers to be plotted and analyzed. From static tests, data on the yield stress, ultimate tensile strength, and elastic modulus of the material could be obtained. Creep tests provided information about the composite's behavior under high temperature loading conditions. Examination of fatigue data indicated the crack nucleation and propagation characteristics of the material.

One objective of gathering material property data was to use the experimental data to establish and refine mathematical models which attempt to predict the behavior of the material. Data gathered for the titanium MMC's was used to establish a set of material constants for the Bodner-Partom model of MMC behavior. This set of equations served as the basis for the FIDEP finite difference and LISOL finite element modeling programs which were used to attempt to predict MMC behavior. Comparison of computer model results with empirical data allowed for adjustments to be made in the computer models' constitutive equations. The ultimate goal of this process was to refine the computer models to a point where their predictions would very closely match the results of any given experiment.

Beyond the quantitative material property data obtained from MMC testing, qualitative information about the tests was gathered through metallographic and fractographic analysis. The fracture surfaces of MMC's tested to failure were cut and cleaned for examination in the scanning electron microscope (SEM). The SEM was used to scan the broken specimen surface and gather information about how the sample failed. Inspection of a fracture surface with the SEM indicated whether the failure had been primarily ductile or brittle in nature and could illustrate the overall mechanism by which the specimen had failed. Examination of the surface at higher magnifications made possible the identification of likely sites of failure initiation as well.

In addition to fractographic analysis of tested specimens, test samples were sectioned by low-speed diamond rotary saw for metallographic analysis. Sectioned pieces of test specimens were then mounted in thermoplastic resin such as Epomet or Konductomet. After mounting, samples were polished in a series of progressively finer lapping (diamond polishing) steps. Rough polishing was carried out using either a Maximet auto-polishing machine or smaller grinding wheels in conjunction with diamond suspensions of varying particle size. Finer polishing was carried out using diamond paste on index cards or vibratory polishing machines (Vibromets). After taking samples through all the steps in the lapping process, finishes of up to 0.05 micron were possible (a 1 to 0.5 micron polish produces a mirror-like surface).

After polishing, samples were sometimes etched using an acid-based Kroll's Reagent etchant. Etching would selectively erode certain metallic phases on the sample's surface, leaving fibers intact and effectively bringing out microstructural details such as grain boundaries, precipitates, and lamellar microconstituents. Polishing and etching were also carried out on untested material so these samples could be used to obtain a basic characterization of the material and to evaluate microstructural changes arising from different heat treatments.

After polishing and etching, both tested and untested samples were examined by optical or scanning electron microscope. Optical microscopy was used to obtain information at relatively low magnifications (not more than 1000X) on such things as fiber distribution, gross microstructural variations, and foreign inclusions in the material. Using specialized metallographic microscopes with integrated Polaroid cameras, specimen features could be documented with photomicrographs.

When specimen examination required greater magnification and resolution than that provided by optical methods, scanning electron microscopy was employed. Using the Leica360fe SEM, it was possible to obtain digital images at magnifications well in excess of 25000X. Scanning electron microscopy was used to obtain high-magnification images for microstructure characterization, examination of fiber/matrix interface regions, and evaluation of damage features such as cracks and fatigue striations. Images from the SEM were digitally recorded and stored for use in documenting microstructural features and formations. Images from both optical and SEM examination were used in conjunction with numerical test data for analysis and presentation of test results.

RESULTS

Further steps were taken in the characterization and description of the structure and mechanical properties of titanium-aluminide metal matrix composites. Data obtained from tensile, creep, and fatigue testing was used to enhance the present understanding of the performance of these materials under various conditions of thermal and mechanical loading. This data also contributed to the refinement of various mathematical models used to predict the behavior of these MMC's. Microscopic analysis provided insight into the failure mechanisms and microstructural characteristics of this class of materials. Eventually, this mass of information will enable engineers to make informed decisions on how best to apply metal matrix composites to solve various engineering problems. Potential applications currently being considered for titanium MMC's include aerospace structures and propulsion system components.

DAMAGE TOLERANCE OF AEROSPACE ALLOYS AND METAL MATRIX COMPOSITES

Task Order No. 140
Student Support Program
Southwestern Ohio Council for Higher Education

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Wright State University

14 October 1995

Government Task Leader
Dr. Jim Larsen
WL/MLLN

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TASK ASSIGNMENT

At the Materials Directorate at Wright-Patterson Air Force Base (WPAFB), advanced materials are researched to produce extensive mechanical behavioral data bases that can be referenced for potential engineering applications. Specifically, the Task involved data processing to analyze fatigue data of titanium matrix composites in various environmental conditions. Digitizing was also performed on other researcher's titanium matrix composite fatigue data. Lastly, metallography and photo microscopy was completed on titanium matrix composites before and after fatigue testing. The most extensive investigation into the mechanical behavior of titanium matrix composites during this Task was completed to both enhance previous research done at WPAFB, and to achieve a senior project requirement for Wright State University. The research was successful enough to submit for publication in Scripta Metallurgica. The submitted paper was titled "An Evaluation of Interfacial Degradation in [0]4 SCS-6/Timetal®21S." A more extensive description of the need, procedure, and results of the investigation is detailed below.

Titanium-matrix composites have been extensively studied due to their potential capabilities in elevated temperature and high strength-demanding environments. Of particular interest, is the fiber/matrix interface degradation occurring in composites with carbon-coated silicon carbide fiber reinforcements. Interface damage decreases the ability of the fibers to bridge a matrix crack and, in effect, allows more of the applied stress to focus at the crack tip. Initially, the crack tip stress is reduced by transferring some of the load to the fibers in the crack wake. The occurrence of bridging requires an interface allowing the fiber to slip through the matrix as it cracks. If the fiber is unable to slip, the load will cause fiber failure. After the initial bond between the fiber and matrix is broken, frictional stress works against the applied load to hold the crack at an equilibrium opening.. This frictional stress is defined as Tau. If Tau is too large, then slip will not occur and the fiber will fail; however, if Tau is too small, the crack will continue to grow as it would in a monolithic alloy.

The magnitude of Tau is dependent upon many factors, such as: temperature, fiber and matrix stress states, and interface condition. Previous studies have shown the fiber/matrix interface degrading over many fatigue cycles, and thus reducing Tau. Tau varies in magnitude along the crack length due to corresponding fatigue cyclic exposure. Specifically, the fibers near the crack initiation region have seen the most fatigue cycles, while the fibers near the crack tip have seen only the last few fatigue cycles. However, life predicting computer models for titanium matrix composites (TMC's) often use a constant Tau value in their evaluations, thus reducing the effectiveness of the model. This inaccuracy produces a need to establish a relation between Tau and fiber position along a fully bridged fatigue crack to be applied to these preexisting predictive models. Production of accurate life predictive data bases are significant to design engineers choosing appropriate materials for their applications.

The project was conducted in correspondence with research performed at WPAFB in the production of a life predictive model for the TMC, $[0]^4$ SCS-6/Timetal®21S. The objectives of this project were to determine the regions of interfacial damage within a [0]4 SCS-6/Timetal®21S fatigued specimen and, then, to establish a relation between Tau and fiber position along the fully bridged fatigue crack within the defined interfacial damage regions. This will then be accommodated into this material's preexisting life predictive model. The approach taken was to simulate a realistic environment for these high performance composites by performing the push-out procedure on a [0]4 SCS-6/Timetal®21S composite fatigue tested at approximately 650°C and Smax = 300 MPa until a desired crack length of 2a = 10 mm was produced. The push-out testing models the interfacial degradation by pushing a fiber through the matrix with a probe controlled by a load-cell. Push-out testing produces load-displacement data used to evaluate Tau all along the push-out distance. Performing this procedure on fibers along a fatigue crack will produce Tau magnitudes for a sequential range of cycle exposures. The regions of interfacial damage are determined by performing an acoustic microscopy scan (SAM scan) on the fatigued material.

The results of this approach discovered fibers with an effective Tau magnitude of zero lying completely within the interfacial damage regions identified by the SAM scan. The fibers experiencing partial interfacial damage, (the interfacial damage boundary intersects the fiber), had intermediate Tau magnitudes between the maximum Tau value and zero Tau value. The Tau versus fiber position relation observed with this approach can effectively identify the zero Tau and transitional Tau region; however, the Tau magnitudes are not accurate in the transitional region due to the room temperature push-out procedure not effectively modeling the 650°C tensile fatigue testing process. More accurate Tau magnitudes may be obtained if a fiber pull-out procedure, in agreement with the Poisson Effect of the fatigue testing process, was performed at elevated temperature.

PROCESSING OF POLYIMIDES

Task Order No. 141
Student Support Program
Southwestern Ohio Council for Higher Education

Thomas J. Witman
Wright State University

15 September 1995

Government Task Leader
Mr. John Russell
WL/MLBC

ACKNOWLEDGMENTS

I would like to thank Mr. John Russell and SOCHE for this opportunity.

TASK ASSIGNMENT

A major existing problem for engineers today is the need for repairing the infrastructure which is deteriorating at a rapid pace. According to the Federal Highway Administration, more than 40% of the highway bridges in the United States are in need of replacement or rehabilitation. These bridges were also initially designed for low volume traffic which is not the case today. Therefore, a procedure for repairing the infrastructure (concrete) must be obtained.

Currently, a method used to repair concrete beams consists of bonding or bolting large steel plates to the concrete beam that is in need of repair. This method does provide adequate strength increases although other factors have forced engineers to develop a new procedure. Due to environmental conditions, steel plates corrode over time. Corrosion significantly affects the bond between the steel plate and the concrete which may result in the plate peeling off the concrete beam.

To avoid this corrosion problem, the steel plates have been replaced with CFRP (Carbon Fiber Reinforced Plastics) plates. CFRP plates will not corrode and have higher strength characteristics than that of steel. Using CFRP plates also allows engineers to repair a beam that will last for years.

The problem is then to develop a suitable procedure for repairing concrete beams with CFRP plates. This includes application and design of the plates. The ease of application is essentially the same as the steel plates. Epoxy glue is sandwiched between the CFRP plate and the concrete and left to cure.

For the past 8 months, Wright-Patterson Air Force Base has been developing such a suitable procedure. Since WPAFB is the leader in composite technology, industry has asked WPAFB to aid in this development. To develop such a procedure requires many hours of experiments and analytical verifications.

I was assigned to do the analytical procedures. This requires predicting the strength increases, determining stresses in the beam, and predicting failure modes. Of the few beams tested, the analytical results were within 30% of the experimental results. This prediction is satisfactory, although more accurate predictions are required.

Currently, I am working on a finite element analysis of the beam. This simply consists of drawing the problem on the computer (modeling), applying the loads (corresponding to traffic on the bridges), and the finite element software solves the problem and can predict more accurately the results in need. There are many different ways to model this situation to obtain accurate results. Each case will be thoroughly examined. I have modeled and solved the case for the concrete beam alone and found that accurate results are achievable. Another student is taking over this part of the project and will add the CFRP plate to the model to check for accuracy. This step is crucial in the development of a procedure for this repair method.

HIGH TEMPERATURE SUPERCONDUCTING PULSED LASER DEPOSITION

Task Order No. 142
Student Support Program
Southwestern Ohio Council for Higher Education

C. Brandon Lovett
Wright State University

11 September 1995

Government Task Leader
Dr. Rand Biggers
WL/MLPO

ACKNOWLEDGMENTS

I would first like to thank Dr. Pat Hemenger for funding this contract and his genuine interest in my work. A special thanks goes out to Mr. David Dempsey and Mr. Steve Murray for their assistance in the lab, leading me in the right direction. Numerous other persons contributed to the success of this Task including Mr. Tim Peterson, Dr. Eric Moser, Dr. Iman Maartense, and Mr. Doug Buchanan. Finally, I would like to thank Dr. Biggers for his guidance throughout this Task. He has communicated his expectations clearly while allowing me the freedom to design this data base. Dr. Biggers has shown great faith in my abilities and continues to provide me with thought provoking insights.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The purpose of this Task was to create a data base consisting of information obtained on thin film high-temperature superconductors (HTSCs). The data base consists of several parameters observed throughout the life of the HTSCs. Most of the HTSCs are the ceramic yttrium-barium-copper-oxide (YBCO) deposited on lanthanum aluminate substrates by the process of pulsed laser deposition. This data base is the most rational way to track and view this information. The data base was created using 4th Dimension 3.1 software. The data base is a rather extensive compilation of the data gathered on the YBCO films, starting with the makeup of the substrate, through the growth process, and technical measurements of the film.

The reason for this database is the ability to track what growth parameters produce certain film characteristics. This allows researchers to see the effects of certain growth parameter combinations on the micro structure and properties of the HTSCs. The data base currently tracks fifty different growth parameters subdivided into four major categories. These fifty parameters alone times 425 films show the need for this data base.

This data base not only tracks growth parameters but, also measurements made on the properties in the film. The information stored in the data base serves several purposes. The main purpose is a table for the application of growth parameters. However, another important aspect of the data base is acting as an easily accessible information resource needed for publications.

DESCRIPTION OF RESEARCH

As stated earlier, the objective of this Task was to create a data base for storing and referencing data collected on HTSCs. This data base was constructed and modified using 4th Dimension 3.1 software. The data base currently occupies approximately 1.6 megabytes of information. The data base contains information concerning 425 different films grown at this WL/MLPO facility. Each entry contains 177 different fields of information. The data base is divided into sections with each section having smaller categories. The major divisions consist of growth parameters, Atomic Force Microscopy (AFM) and scanning electron microscopy, AC susceptibility measurements, and critical current transport measurements. Information obtained from Dr. Biggers (growth parameters), Dr. Moser (AFM/SEM), Dr. Maartense (AC susceptibility), and Mr. Peterson (transport), is entered into the data base. The data is made available to all who wish to view it by means of file sharing.

The equipment needed to complete this Task is fairly basic:

1. Apple Macintosh II computer controls the main computing requirements.
2. 4th Dimension 3.1- the software program in which the data base is written.
3. Delta Graph Pro 3- the application program used to graph and view the data in the data base.

Most of the information in the data base was retrieved from technical lab journals. More recent films were grown by automation, thanks to Mr. Murray, and the information was obtained through computer interface over the network.

The data is analyzed and used by importing the information into Delta Graph Pro 3. Delta Graph allows different parameters of the data to be viewed together in graphical form. Once the graphs and tables are viewed, trends can be observed from the presented information.

RESULTS

This Task has provided an easily accessible data base for use throughout the high temperature superconducting team. The data base has given insights to what growth parameters can be modified to produce a high critical temperature. This is the first step in the development of HTSCs for industry. Superconductors will revolutionize electronics once they are understood. Superconductors have the ability, once reaching a super conducting state, to allow the flow of electricity with no capacitance or loss of energy. High temperature superconductors become superconducting around 90°K that is easily attainable at liquid nitrogen temperatures. Conventional superconductors work at very low temperatures not easily attained.

The data base work is continually being modified and enlarged. Currently, the format is growing to include HTSCs grown at other facilities for WL/MLPO using similar and other growth techniques. Attaining a working knowledge of the growth mechanisms will provide a means of further understanding HTSCs. Once fully understood, HTSCs could be tailor made for specific purposes that may bring another technical revolution.

NONLINEAR OPTICAL MATERIALS (NLO)

Task Order No. 143
Student Support Program
Southwestern Ohio Council for Higher Education

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University of Dayton

25 September 1995

Government Task Leader
Dr. David Zelmon
WL/MLPO

ACKNOWLEDGMENTS

This work was accomplished largely due to the generosity of the personnel of the Nonlinear Optics Division of the Materials Directorate at Wright-Patterson Air Force Base. In particular I would like to acknowledge the sponsorship of Dr. Pat Heminger, the experimental expertise of Dr. Steve Caracci and Dr. Uma Rhamabar, and the laboratory facilities of Dr. Dave Zelmon. This work was also performed in coordination with efforts at the University of Dayton Center for Electro-Optics. In particular, Dr. Vincent Dominic is largely responsible for the development of theoretical analysis and experimental procedures at all levels of this work.

TASK DESCRIPTION

The primary assignment was to assist in characterizing the optical properties of various poled polymer optical samples to aid in the development of improved polymers. Of particular interest were the electro-optic properties of the polymers. To perform the experimental characterization of the sample various optical setups were utilized including a Mach-Zehnder type interferometer and a transmission-type, rotating Fabry-Perot etalon. Related theory was developed and acquisition and analysis software was programmed into a control setup to extract the desired material parameters.

The initial task was to develop a visible wavelength Mach Zehnder interferometric setup that would independently measure the orthogonal principal electro-optic coefficients of a poled polymer sample. (Presently only one of the principal electro-optic coefficients is measured. The second coefficient is inferred from the measurement of the first based upon an approximate relationship.) This effort revealed an unexpected and significant instability in the measurement which is now attributed to an electro-chromic (or identically electro-absorption) effect in the poled-polymer. This is significant since the present measurement techniques cannot distinguish between electro-optic and electro-chromic effects.

The new direction of the Task was then to understand and to characterize the electro-chromic effect. An experimental understanding of this effect has been developed resulting in a novel experimental technique based upon a transmission-type, rotating Fabry-Perot etalon used to measure the related electro-optic and electro-chromic coefficients. Acquisition and analysis software has been developed and an initial wavelength dependence study has been performed.

DESCRIPTION OF RESEARCH

The poled polymer samples studied consist of a microscope-slide substrate coated with a transparent ITO electrode, a thin polymer/chromophor, and finally an evaporated gold contact. The ITO and gold contact layers serve as the electrodes across the poled regions of the polymer whereas the glass/air interface and gold contact act as the mirrors of the Fabry-Perot etalon. The experimental setup consists of a tunable HeNe laser beam passed through the poled region of the sample and focused onto a photodiode. A ± 16V sinusoidal voltage is applied across the poled-polymer which induces electro-optic and electro-chromic effects. These effects cause small variations to the transmissivity of the etalon, resulting in a weak modulation signal that can be detected with a vector lockin amplifier. The sample is then rotated from -3(to +3(with a controlled actuator.

Results of this technique are shown in Figure 1 which demonstrate the angular variation of the average photodiode signal as well as the magnitude of the modulated lockin signal. The average signal shows the typical Airy function behavior of a low finesse Fabry-Perot etalon, however, the modulated signal has asymmetric peaks. These asymmetric peaks result from constructive and destructive interference between the electro-optic and electro-chromic effects, and can be fit to a theoretical model to extract the appropriate coefficients.

This technique was applied to study the dispersion of the electro-optic and electro-chromic effects in a Dow Chemical sample labeled TP86. The sample is a golden yellow and has an absorption edge at approximately λ=520 nm. Figure 2 shows that at the shortest HeNe wavelength the Fabry-Perot signal is completely dominated by electro-absorption. Figure 3 shows the wavelength dependence of both effects.

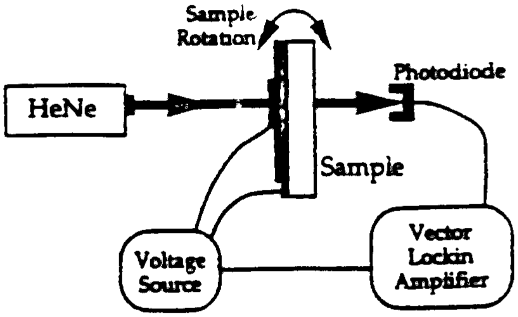

Figure 1) Schematic drawing of the experimental setup. A photodiode monitors the laser transmission through our poled-polymer Fabry-Perot structure. The rotation axis is centered on the incidence spot within the poled region. The sample consists of the following layers: gold electrode, polymer layer, ITO contact, and the glass substrate.

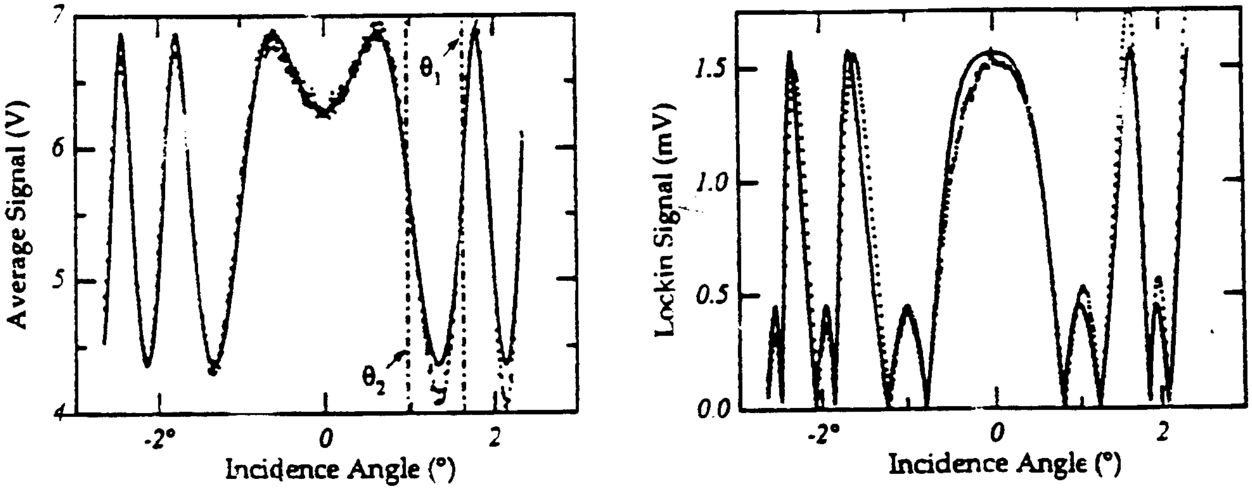

Figure 2) a) Average photodiode signal and theoretical fit (dots=data, line=fit) at $\lambda = 632.8$ nm as the Fabry-Perot is rotated. b) Lockin signal dependence on the incidence angle with the raw data (dots) and the theoretical fit (solid line).

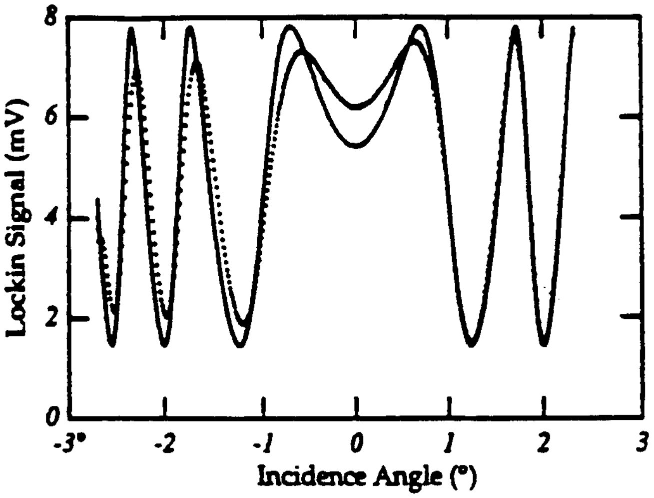

Figure 3) Lockin signal dependence on the incidence angle at $\lambda = 543.5$ nm. The dots are raw data and the solid curve is the theoretical fit. The signal magnitude does not reach zero because the electro-absorptive effect dominates.

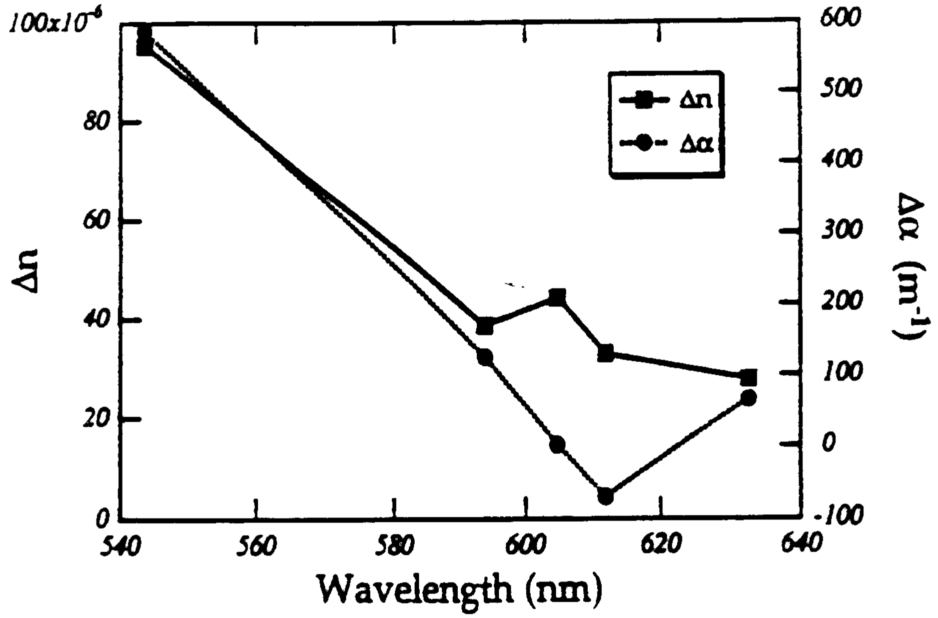

Figure 4) Dispersion of the electro-optic and electro-absorptive effects for the five HeNe wavelengths. Notice that the electro-absorption changes sign near 615 nm. The sample (labeled TP86) was supplied by the Dow Chemical Company.

RESULTS

Through this Task, it was learned that the electro-chromic effect has a significant effect on electro-optic measurements, particularly near the absorption of the poled polymer chromophor. Furthermore, a novel technique was developed utilizing a rotating Fabry-Perot etalon to measure the electro-optic and electro-chromic coefficients simultaneously.

The results of this experiment may be used to distinguish preferred regimes to set the operating wavelength (or conversely to set the chromophor absorption) in order to minimize the electro-chromic effect while maximizing the electro-optic effect.

DEVELOPMENT OF A DESIGN ENVIRONMENT FOR A MATERIAL DISCOVERY SYSTEM

Task Order No. 144
Student Support Program
Southwestern Ohio Council for Higher Education

David Giovannini
Wright State University

3 April 1995

Government Task Leader
Dr. Steve LeClair
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank Dr. Steve LeClair for opening such a door of opportunity and experience. Dr. Alan Jackson has been a wonderful inspirational director with much patience. Lastly I would like to thank Mr. Jeff Heyob for endless technical support from programming to computer systems on the fritz.

TASK ASSIGNMENT

The objective of this Task was to develop an application to create and display crystal structures. Users of the application should have full control over the crystal creation process and the viewing display. Another objective was to create source code that can be easily modified for other applications. One example of reusable code is modification of the crystal structure application to display manufacturing simulation. To satisfy the objectives, certain steps had to be taken.

The first hurdle was learning how to implement the functions of a 3D graphics library. A small application was created solely for testing purposes. This application allowed for experimentation and was the basis for drawing routines. When the time came to start the development of the crystal structure application, one very important question had to be answered. What development environment should be used?

The language chosen was C++ with a strong emphasis on object-oriented programming. C++ was an obvious choice in languages due to the available resources and the flexibility of the language. The choice to use object oriented programming as a development method had more of a downside. The positive aspect of using object oriented programming are the steep learning curve and program speed. Due to the robustness of object-oriented programming, the final products are often slower than their counterparts written in ordinary C or C++. The object-oriented method of programming was chosen primarily for its tendency to yield reusable code.

Reusability of code is achieved through abstraction, which is the ability to encapsulate segments of the application into groups of behaviors associated with a single conceivable object. An example is associating the calculations to be performed on data with the data itself. Such encapsulations can be ported from application to application with little modification. As mentioned before, reusability of source code was desired. Reusable code also cuts development time by using a framework.

Choosing the appropriate framework was the next step. A framework is a complete library of encapsulations that will allow the programmer to immediately create a complete standalone application. He would only have to modify certain behaviors to coerce the application to his needs. There were three commercial frameworks available for the development of the crystal structure application. “Power Plant” by Metrowerks was the obvious choice because of its small memory need, speed, and the intuitiveness of its associated compiler.

The initial development was slow due to learning the nuances of "Power Plant" and the 3D graphics library being used. As the developers experimented with the framework, the application began to take form. The application was originally designed to only view crystal structures. Another application is being developed concurrently with the crystal structure application. The alternative application creates the tb dimensional data from textbook data to display the crystal structures.

The next step is to merge the two applications into a seamless whole where the user can create a crystal structure and view it in one step. When this is done, the application will be ready for general use. Unfortunately, a major problem in three dimensional rendering has been ignored. The problem is called partial-hidden-line-removal. This occurs when one face of an object partially obscures another. How does a programmer figure out what face to draw first? When Apple Computer releases "QuickDraw 3D," the application will use that library to solve the problem. Only then will the application be ready for commercial release. The development of the crystal structure application gave new insights into object-oriented design. It is a good example of code reusability and the incremental process of creating a stable application.

CONSOLIDATION OF MINC(MICROMECHANICAL IN-PLANE CRACKING) COMPUTER CODE

Task Order No. 145
Student Support Program
Southwestern Ohio Council for Higher Education

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30 October 1995

Government Task Leader
Dr. Nick J. Pagano
WL/MLBM

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DESCRIPTION OF TASK ASSIGNMENT

The Task assignment was the consolidation of MINC (Micro mechanical In-Plane Cracking) Computer Code. More specifically to the past year's Task, the development of a pre-processor for the 2-dimensional inplane damage model. The pre-processor automates the task of determining the input data from the geometry and load description of the problem of interest. The pre-processor allows an easy interface for the MINC code. The pre-processor gives the user the ability of specifying the physical geometry of the problem, and then converting this to input data for the MINC code. The user is then free of the internal workings of the MINC code itself. This pre-processor adds greatly to the versatility of the MINC code.

DESCRIPTION OF RESEARCH

The geometry of the problems is that of a cylinder, with cracking in all three coordinate systems, radial, angular, and z coordinate plane. This pre-processor deals with only cracking in the r and theta directions. This is equivalent to taking a radial, two dimensional slices from the complete model for the composite fiber. In other words, r and theta coordinates are variable and z is constant. Due to the amount of work necessary to change the physical description of the problem to input data for the MINC code, the pre-processor code is broken into several relevant subroutines. These six subroutines are INPUT, SECTIONS, LAYERS, TRCON, ANGCON, and OUTPUT. All these are described below.

INPUT

The INPUT subroutine is the only direct link for the user to enter the description of the problem. There are two subroutines that make up the INPUT routine. The INPUT1 routine prompts the user to enter data from the keyboard. INPUT2 subroutine takes input from a file specified by the user. Both subroutines ask the user for the same information. These subroutines are used to enter the physical constants of the problem, the position of radial and angular cracks, and the boundary conditions on the cracks. This data is used by all other subroutines.

SECTIONS and LAYERS

The SECTIONS subroutine breaks the geometry of the problem up into radial sections, with these sections being radial divisions originating from the center of the model. These radial sections are based on the position of radial and angular cracks. The radial positions of the center of radial cracks and the tips of angular cracks define the sections. The LAYERS subroutine imposes layer structure upon the problem. Layers are arranged as concentric circles within the radius of the problem. Layer positions are determined by the centers of angular cracks, the endpoints of radial cracks, and the position of material regions. Both subroutines then perform a sorting routine on these new sections and layers, with their locations being held in an array. The arrays and size of arrays are then used by the other subroutines.

TRCON and ANGCON

Both TRCON and ANGCON use the boundary conditions imposed on the problem to find the end conditions for the section and layers. TRCON deals with all boundary conditions in the radial sense, those being SIG-r, tau-r theta, and tau-z theta values. These values are the imposed boundary conditions on radial cracking. TRCON looks at each section defined by a radial crack, and at every layer interface assigns an end condition value based on whether traction, displacement, or continuity is present. Also at this time, numerical values are assigned based on whether traction or displacement is taking place between sections. The ANGCON subroutine does the same, only this time looking at the boundary conditions on angular cracks and on the surface of the composite fiber. ANGCON deals with all boundary conditions in the angular sense, which is SIG-theta, tau-r theta, and tau-theta Z. ANGCON looks at every layer, and at each section interface, assigns a value based on whether continuity, traction, or displacement exists at the interface. It is both TRCON and ANGCON that comprise the bulk of computations for the pre-processor. These two subroutines are where the actual real world problem is defined in terms of input data for the MINC code.

OUTPUT

The OUTPUT subroutine takes all arrays and variables generated by the pre-processor and prepares them for the MINC code. This routine sends these values to an output file. This output file is used as input for the MINC code.

The pre-processor is coded in FORTRAN 77 programming language. This was used because all work done previously for the MINC code and the MINC code itself was done in FORTRAN 77. Also, the decision was guided by the number of personnel who work on this code and are familiar with FORTRAN 77.

Data used by the pre-processor will be taken from models simulating cracking in composite fibers. These models for this pre-processor will only deal with the r and theta coordinates, with the z direction being held fixed.

RESULTS

The development is still an ongoing process. The subroutines INPUT, SECTIONS, and LAYERS are all complete and have been tested. All have performed well within defined parameters and do provide the correct output for a given geometry. Subroutine TRCON is in the final stages of development now, with minor changes being made to algorithm structure in the main body of the program. The entire pre-processor should be completed by the beginning of the year. After this is done, work will begin on the post-processor for the MINC code.

PROCESS DEVELOPMENT FOR CERAMIC MATRIX COMPOSITES

Task Order No. 146
Student Support Program
Southwestern Ohio Council for Higher Education

Chris Pierce
Wright State University

30 October 1995

Government Task Leader
Dr. Edmund Moore
WL/MLLN

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

The majority of the work during the Task period was dedicated to analyzing the degradation of mechanical and physical properties inherent to ceramic matrix composites at elevated temperatures. At elevated temperatures, the physical and mechanical properties of a ceramic matrix composite can degrade by chemical interactions. These interactions can occur between the environment and either the fibers, the matrix, or the interface compounds. Mechanical property degradation can be detected by mechanically testing the specimen, and physical property degradation is detectable under moderate to high magnification.

During the early stages of the Task, a decision was made to test individual Nicalon^{TM} fibers coated with Blackglas^{TM} B-stage resin, in lieu of testing Nicalon^{TM} tows. The decision was based upon the fact that single fibers give a better representation of the mechanical properties. With that decision made, the Nicalon^{TM} fibers were coated and heat treated at different temperatures. Upon the completion of heat treating, the coated and uncoated fibers were tested on an Instron testing machine. Data from this test revealed the load bearing capability of the fibers. This data was manipulated and then statistically analyzed on a computer. Physical properties were then examined under a scanning electron microscope (SEM).

DESCRIPTION OF RESEARCH

Individual Nicalon^{TM} fibers have to be first separated from the two. Fiber separation begins with the removal of sizing, which is a bonding substance that holds the two together. Sizing is removed by heating the two for 20 minutes at 600^{0}C. After the sizing is removed, tweezers are used to separate the fibers.

Mounting the fibers on a coating frame, follows the separation of the fibers from the two. The frame is a flat piece of aluminum with a rectangular hole in the center. Outer dimensions of the frame are 4" X 3 ½," while the hole dimensions are 2 ½" X 2". Adhering the fibers to the frame was a problem at first, but through trial and error, double-sided tape was found to be the best solution. With the fibers mounted to the frame, the coating process begins. All coating operations are conducted under a vacuum hood, due to the release of siloxane vapors from the Blackglas^{TM} resin. The resin is applied to the fibers with a fine paint brush. Patience is a must during the application process because the fibers are very delicate. After the coating of the fibers is complete; the mounted fibers are placed in a vacuum curing oven for 1 hour at 150^{0}C. The fibers are removed from the oven at the end of the curing period and cut from the mounting frame with a sharp razor blade. Some of the fibers were put aside for mechanical testing, while the others were heat treated at 900°C for 30 minutes. Originally the heat treatment was for 1 hour at 1000°C, but this would cause extreme degradation, to a point where the fibers would break at the slightest touch.

Mechanical testing was performed on uncoated, coated and cured at 150°C, and heat treated at 900°C fibers. An Instron testing machine was implemented for this purpose. The Instron consists of opposing specimen grips, one that is mobile and one that is not mobile. A fiber is placed between the two grips and the machine is activated. The mobile grip will move away from the opposing stationary grip, until the fiber specimen breaks. During this operation, a computer is recording the extension and the amount of uniaxial load being applied to the fiber. Data stops being recorded at the point of fracture. The recorded data is later manipulated for statistical analysis.

When the mechanical testing is complete for a specific set of fibers, the broken fiber ends are saved for SEM analysis. Scanning electron microscopy revealed the physical effects of the curing and heat treating processes. Regions specifically looked at, were the coating-fiber interface and the overall quality of the fiber coating.

RESULTS

Statistical data and SEM analysis were both in agreement that the coating had weakened the fibers. The mechanical properties of the fibers declined after curing and declined even farther with heat-treating. The degradation of mechanical properties is probably the result of a chemical reaction between the fiber and the coating resin. Physical properties also deteriorated at elevated temperatures. The SEM analysis revealed a good interface between the coating and the fiber, however, the coating quality was very poor. Droplets had formed along the length of the fiber, indicating some sort of wetting problem. These droplets would become embrittled at elevated temperatures, due to chemical reactions, and serve as crack initiation sites. Embrittled droplets would actually come off the fibers after the application of the 900°C heat treatment, leaving regions of coated and uncoated fiber.

Personally, this Task has been a good learning experience for me. I have become efficient at operating the SEM and Instron machine, as well as, having learned a great deal about ceramic matrix composites, a topic that is only briefly touched upon at the university. Additionally, I gained experience in statistical analysis of collected data, and manipulation of that statistical information.

MORPHOLOGY OF NOVEL MATERIAL SYSTEMS DEVELOPED IN-HOUSE AT MLPJ

Task Order No. 147
Student Support Program
Southwestern Ohio Council for Higher Education

Colin M. McHugh
Wright State University

30 October 1995

Government Task Leader
Dr. Tom Cooper
WL/MLPJ

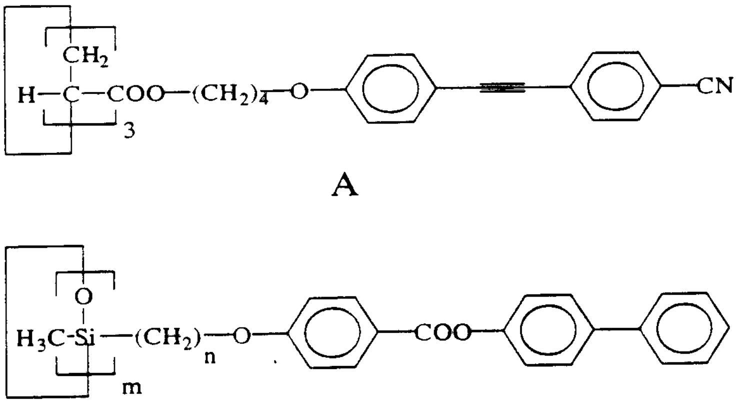
ACKNOWLEDGMENTS

I would like to thank Dr. Timothy J. Bunning for his guidance throughout the course of this work. His knowledge and enthusiasm toward the project are much appreciated. I would also like to thank the Student Support Program (SOCHE) and Wright Laboratory/Laser Hardened Materials Branch for financial assistance and for allowing me to perform the research at WPAFB.

TASK ASSIGNMENT

Objective: To provide feedback on the structure/morphology of material systems being developed in-house in support of the laser hardened material's program through the use of spectroscopy, image analysis, and X-ray densitometry techniques.

Procedure: X-ray diffraction was used to probe the morphology of the four compounds shown in Figure 1. Compound A is based on a cyclohexane ring system while compounds B-D is based on some cyclic siloxane ring systems. The synthesis and thermal transitions of these materials have been previously reported[1]. The goal of the present study was to examine the effects of small structural changes(m=4 or 5, n=3 or 5) with changes in the mesophase packing and resulting alignment.



A

B, C, D

Figure 1. Structural formulas of compounds investigated: B) m=4, n=3, C) m=5, n=3, and D) m=5, n=5

Nickel filtered CuKα radiation, operating at 0.908 or 0.914Å, from the Cornell High Energy Synchrotron Source(CHESS) was used as the radiation source. A typical experiment consisted of two 0.5 mm gold-plated stainless steel electrodes separated by a distance of 100μm (see Figure 2) held in a Mettler FP 82HT hotstage. Samples were melted between the electrodes and held in place by capillary forces. Voltage and frequency of the applied field were controlled using a function generator coupled to a high voltage operational amplifier. Diffracted radiation was recorded on either flat-film(Kodak DEF) or a CCD detector at sample-to-film distances of 92-94 mm. Exposure times varied from 1-20 seconds depending on the flux of incident X-rays. Data is reported as intensity as a function of s (defined as 2sin(theta)/lambda) due to the radiation wavelength differences. Samples were probed at approximately 1V/micron in the frequency ranges of 10-10,000 Hz through the mesophase range. All data analysis was accomplished using a subroutine developed for Matlab which allows for various data manipulations to be performed. Orientation parameters and column correlation lengths were calculated in a manner similar to compound C as reported in a previous publication[2].

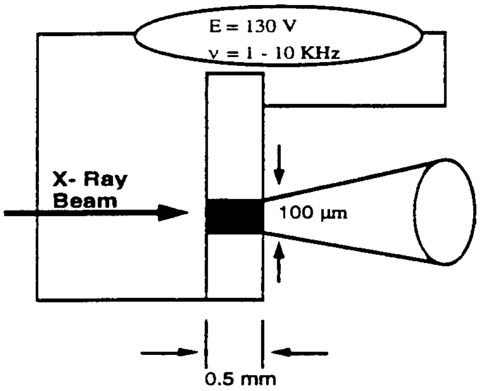


Figure 2. Schematic of electrodes showing the voltage and frequencies used.

Results and Discussion: Compound A was analyzed, relative to the applied electric field, through the liquid crystal mesophase, as a function of a) frequency and b) change in the orientation parameter S_d calculated as (3cos^2(phi)-1)/2. Figure 3. shows typical diffraction images at 10Hz with the e-field director pointing in the vertical. Compound A aligned nicely at all frequencies from 10-10000Hz, with the long axis parallel to the e-field direction. As the temperature is decreased large crescents develop along the equator (characteristic of the nematic LC mesophase) as well as faint periodicites along the meridian indicating strong orientational order and poor translational order respectively. Radial scans through the crescents(shown above for 60°C) plotted as intensity versus phi for five temperatures (Figure 4) show that the orientation parameter S_d increases with a decrease in temperature and ranges from 0.22-0.66. This is consistent with conventional thinking in that a decrease in viscosity of the system leads to more molecular order. Comparable images and orientation parameters were observed at 10000Hz, illustrating that their is little or no frequency dependence on alignment or orientation.

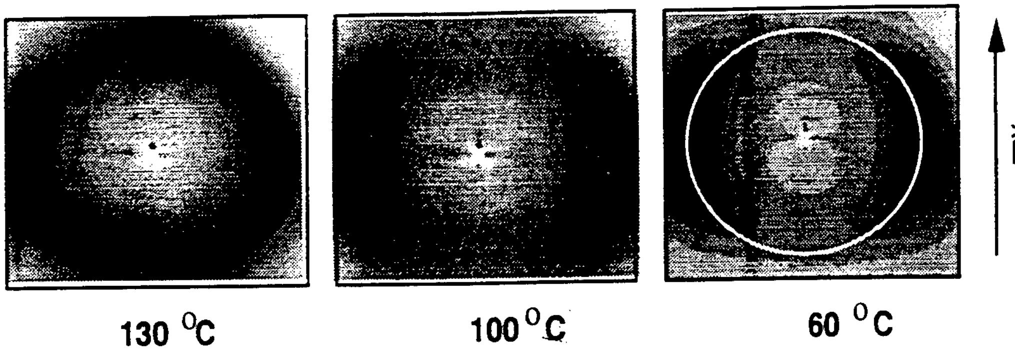


Figure 3. Compound A diffraction patterns cooled from the isotropic(130°C) to the nematic mesophase(60°C).

Radial scans through the crescents(shown above for 60°C) plotted as intensity versus phi for five temperatures (Figure 4) show that the orientation parameter S_d increases with a decrease in temperature and ranges from 0.22-0.66. This is consistent with conventional thinking in that a decrease in viscosity of the system leads to more molecular order. Comparable images and orientation parameters were observed at 10000Hz, illustrating that their is little or no frequency dependence on alignment or orientation.

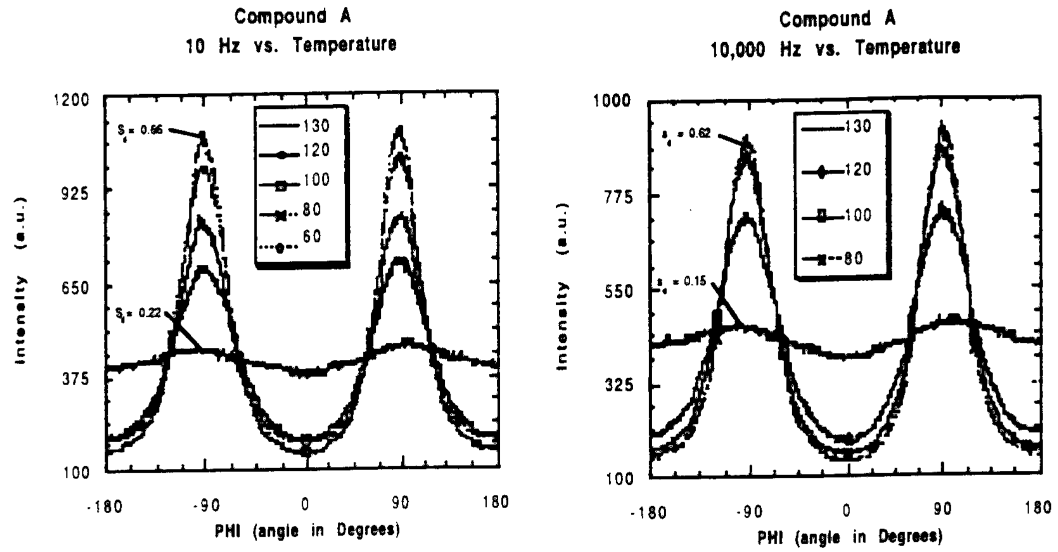
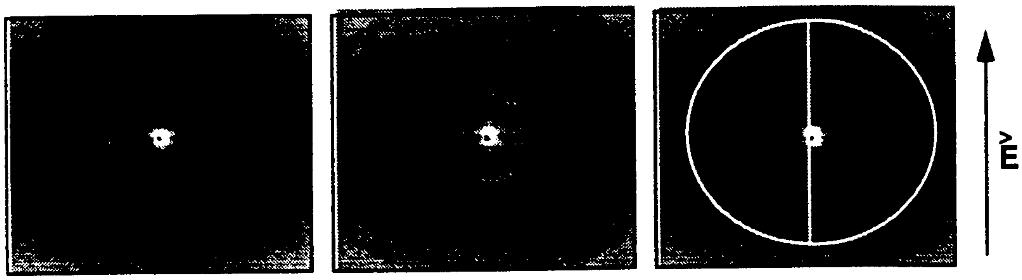


Figure 4. Radial scan determination of S_d showing no dependence on frequency.

Similar data treatment on compound B indicates unusually strong orientational and translational order. Figure 5 shows the diffraction patterns at 10000Hz vs. temperature and Figure 6. shows a meridional line scan vs. intensity through the beam stop(image center). The straight, equidistant diffuse streaks, with a defined periodicity, along the meridian, can readily be described as a Fourier-Transform of a linearly modulated object along the director. In a nematic system this might correspond to molecules aligning in rows along the director over a short range. By looking at the breadth of these reflections, you can determine the correlation length L. The full width at half maximum (FWHM) were measured as a function of S, and plotted as S^2 vs. ΔS^2 for each reflection. By assuming a gaussian intensity profile, the intercept of a best fit line through these points equals $1/L^2$, where L is the correlation length of a column containing n molecules that are d long(in angstrom units).



180 **175** **170**

Figure 5. Compound B diffraction patterns cooled from the isotropic(185 °C) into the nematic mesophase(180-170 °C) at 10000Hz.

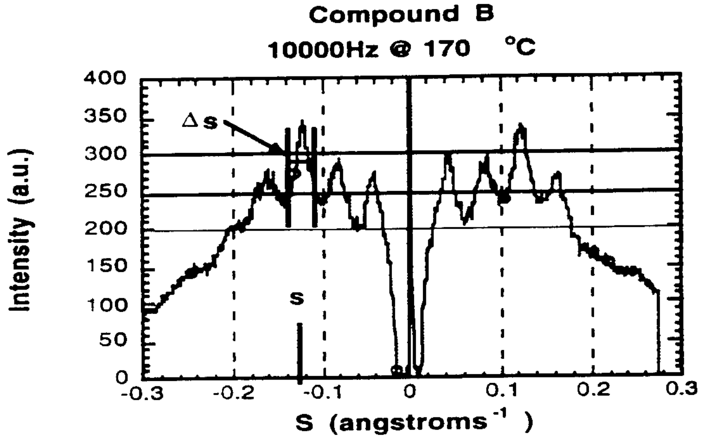


Figure 6. Meridional line scan showing periodicity and determination of ΔS and S.

Correlation lengths at 10Hz and 10000Hz were calculated and found to increase as the temperature was decreased. Figure 7. shows a plot that was used to determine that the short range molecular order corresponds to 3-4 molecules (60-80 Å) aligned in rows.

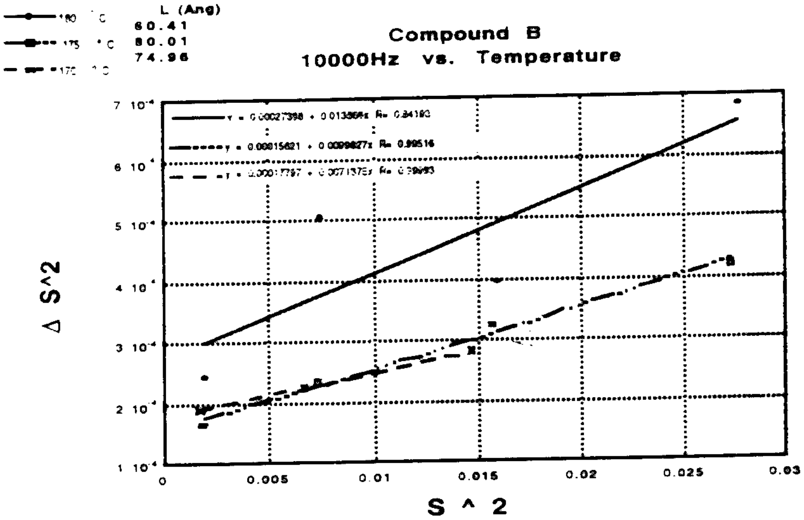


Figure 7. Column correlation determination for compound B at 10000Hz

Compound C was analyzed in the same matter as compound B. The only difference between these two structures is the slightly bigger ring size. As a first approximation, it is believed that the mesogens attached to the rings alone control the orientability of the system. One would then expect that a bigger ring would have little effect on the packing or diffraction patterns in the system. However, this is not what is found. It appears that the addition of one Si-O unit to the ring system is sufficient to cause very complex packing schemes, as shown in Figure 8. The direction of orientation rotates through an angle of 90° at temperatures of 120, 130, and 140°C for 10000Hz and at 120°C for 1000Hz as indicated by the negative values of S_d as shown in Figure 8. This rotation about the director, to the equatorial position, corresponds to a switch in the sign of the dielectric anisotropy. The frequency dependence at a given temperature, shown in Figure 8b, is weak throughout the mesophase except where a switch in orientation occurs.

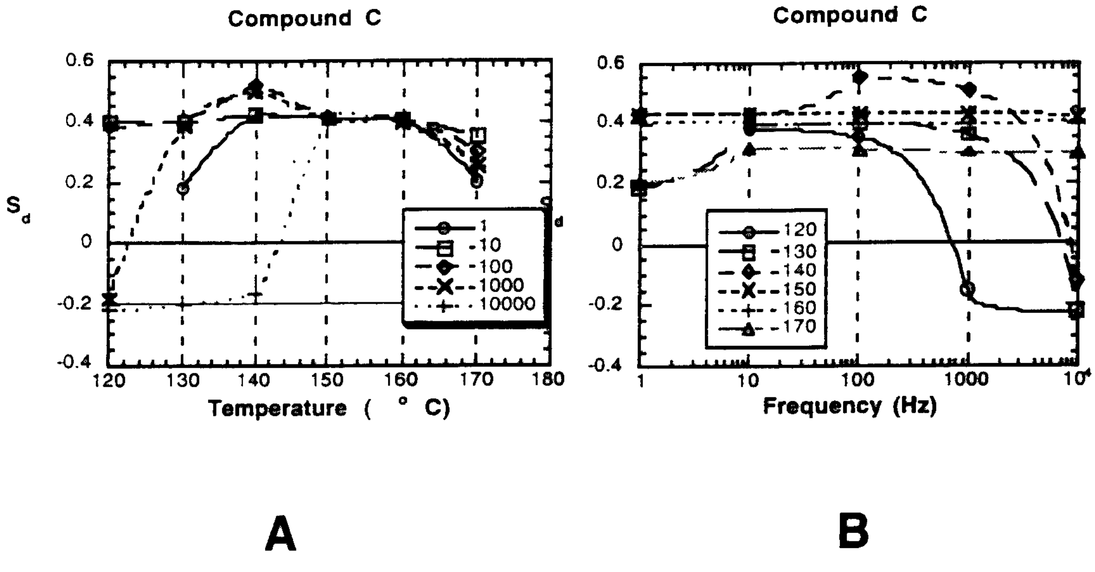
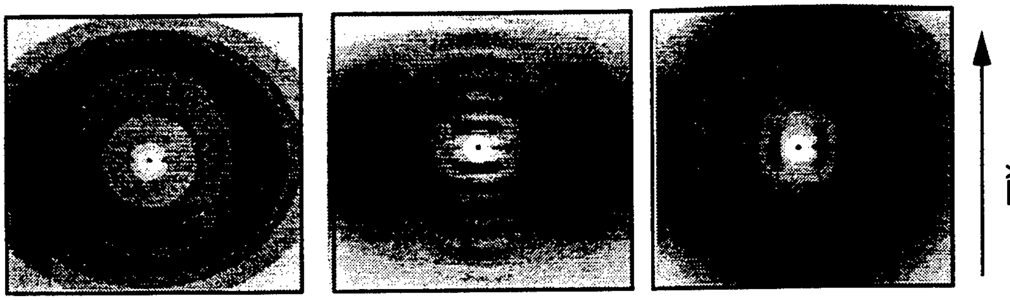


Figure 8. Director orientation parameter as a function of a) temperature and b) frequency.

For the electric fields used to study compound C, orientation parameters ranged from 0.3 to 0.55 with the highest values being observed in the middle of the mesophase range (140-150° C). For a given frequency, the orientation parameter first increased and then decreased as the temperature was increased as shown in Figure 8a. The loss of order at higher temperatures is consistent with Maier-Saupe theory, in that the thermal fluctuations within the system overwhelm the ordering fields as the isotropic temperature is approached. The Si-O bond has a good deal of ionic character due to the differences in electronegativity between oxygen and silicon. The resulting (+) inductive effect of silicon decreases the basicity of the oxygen, due to the strong effect of the (p⇒d)π bond, which withdraws electrons from oxygen. The addition of one more Si-O bond changes the polarity slightly and the packing greatly.

Compound D was analyzed in the same manner as above. The only difference between compound C and D is the increase in the length of the alkyl spacer from three to five carbons in the mesogen. Diffraction images at 10000Hz vs. temperature are shown in Figure 9.



185 °C **155 °C** **150 °C**

Figure 9. X-ray diffraction images as a function of temperature showing reorientation about the director from 155°C - 150°C for Compound D at 10000Hz.

The packing behavior of compound D was much more complicated than compound B and C. At low frequency (10Hz), weak periodic reflections were present orthogonal to the electric-field axis at all temperatures with a measured orientation parameter of 0.4 at 155°C as shown in Figure 10. At high frequency (10000Hz), strong periodic reflections were present parallel to the electric field axis with an S_d almost twice in value.

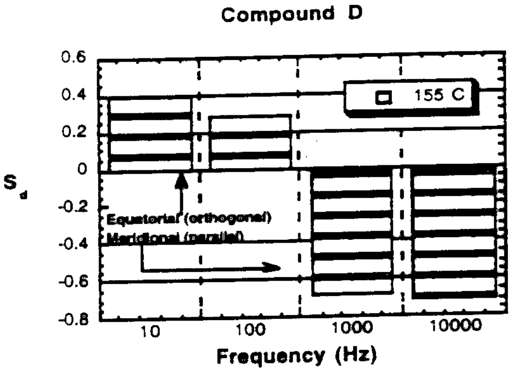


Figure 10. Frequency dependence of the orientation parameter at 155°C.

Upon further investigation at 10000Hz it was found that parallel orientation (S_d) increased on cooling from the isotropic to a value of 0.71, decreased to 0.61 upon switching to an orthogonal orientation, and then increased to a final value of 0.67 in the smectic mesophase. Figure 11 follows the change in orientation versus temperature at 10000Hz. In addition, the much larger orientation parameter at 10000Hz (155°C) than at 10Hz (155°C) indicates a strong frequency dependence of the effectiveness of the applied field. The similarities of the behavior to compound C at the higher frequency is reassuring. The opposite orientation at the low frequencies given by the similarity of the structures is not clear.

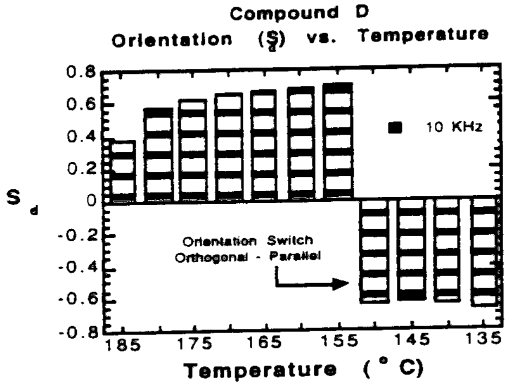


Figure 11. Orientation parameter versus change in temperature at 10000Hz.

To summarize, very simple changes in structure have pronounced effects on the electric-field alignment of these compounds. The subtle differences in the electronic and/or physical structure of these compounds induced by small chemical changes in their composition is not understood fully at this time.

References

1) Bunning, T. J., 1992, Ph. D. Dissertation, University of Connecticut

2) Bunning, et. al, 1994, Liquid Crystals 17, 2, 179-190.

ELECTRICAL AND MAGNETIC PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

Task Order No. 148
Student Support Program
Southwestern Ohio Council for Higher Education

Douglas A. Buchanan
Wright State University

17 November 1995

Government Task Leader
Mr. Timothy L. Peterson
WL/MLPO

ACKNOWLEDGMENTS

Overall, this Task has been one to further help students gain experience to the laboratory setting and controlled experimentation. I would like to thank the Southwestern Ohio Council for Higher Education (SOCHE) for their on going support, my Government Task Leader, Mr. Timothy L. Peterson, and the many other fine people at Wright Labs that I have been given the opportunity to work with.

TASK ASSIGNMENT

Task Order 148, Electrical Properties of High Temperature Superconductors, involves the student helping to characterize the properties of high temperature superconductors by doing such things as measuring the DC electrical components of superconducting thin films, measuring other physical properties of the film (thickness or patterned line width), and occasionally helping adjust the experimental technique by altering the way data is collected or altering the experiment itself. There was also a very long, detailed study of current direction dependence on a circular patterned superconducting thin film.

The measurements of DC electrical properties of a superconducting thin film are rather simple, but the preparation of the film to be measured can be rather tedious and taxing. First, the films are grown by pulsed laser deposition, where a pulsed laser is used to blast a Yttrium Copper Barium Oxide (YBCO) target. The blasted particles then fall onto a crystal substrate that is heated to 700 degrees Celsius. The substrate is heated so that the particles fall into a specific orientation on the substrate. The substrate is then cooled to room temperature and is ready to be patterned and have contacts applied for measuring DC current and voltage. The sample is patterned using photolithography, a technique where a photosensitive chemical is placed across the entire film and then using high intensity light, shined on the areas that you want superconductor to remain, acid can be applied to eat off the remaining area. The film is then patterned. The patterned film will have gold wires attached, but to make good low resistance contact between the film and wire, silver is sputtered onto the film in small circular areas. Gold wire is finally attached using special silver paint for good contact and low resistance (typically $10^{-3}\Omega$). Figure 1 is given to show what a patterned film looks like. In the Figure, the black areas are the superconducting region, the silver areas are points that wires can be attached to run current across the film and to measure voltage. Using the DC current and controlling the temperature one can measure the dependence of current and temperature, also called the critical current measurement.

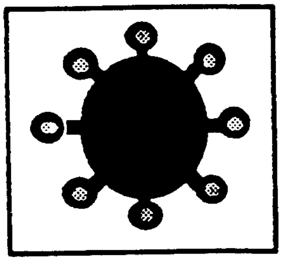


Figure 1: Superconductor Pattern
This particular pattern was used to study directional dependence of applied current.

Superconductors have no electrical resistance for certain currents applied, but as current is increased, the superconductor will lose its superconducting ability. The current at which a superconductor switches to a normal metal is called the critical current. This current passes through the entire volume of the film, and dividing the critical current by the cross sectional area of the superconducting film gives critical current density, a typical reported measurement of a superconductor that tells its quality. One commonly uses microscopes to determine patterned line thicknesses (usually about 1 μm wide) and uses an instrument called a Dektak to measure the films' thickness (usually 300 nm).

This year the experiment was modified so that a magnetic field could be applied to the superconductor. This involved having the magnet delivered and set up in the lab into the proper position. Water pipes were also laid to cool the magnet and the magnet's power supply. Lastly, a gaussmeter was set up to measure the strength of the magnetic field. The magnet is now being applied to the superconductors and the effects are being measured.

One large component of the work done on this Task this year was the detailed study of how an applied current across a superconducting film at different angles affected the superconducting properties. Using the pattern of the superconductor in Figure 1, current was applied across one of the pairs of contacts that were 180 degrees from each other. Voltage was then measured by the pair of contacts that ran perpendicular to the contacts sustaining current. This type of measurement is called a transverse voltage measurement. Each set of contacts was studied for voltage dependence as a function of temperature while a constant current was applied and also voltage dependence as a function of current while the temperature was held constant. The results were that the films have superconducting properties that are based on the fact that the film is anisotropic, or that the film is not the same across the substrate. This data also help refute a superconducting model that said the effect we saw was based on electrical properties of the film.

In the next year, with the continuation of this Task, it is hoped that the magnetic effects of the superconductor can be further studied. There is also the possibility that the magnet will be set up to be controlled by computer rather than manually adjusted as it is now.

ELASTOHYDRODYNAMIC LUBRICATION

Task Order No. 149
Student Support Program
Southwestern Ohio Council for Higher Education

Mark Diller
University of Dayton

31 December 1995

Government Task Leader
Mr. Shashi Sharma
WL/MLBT

ACKNOWLEDGMENTS

I would especially like to thank Mr. Shashi Sharma for the opportunity to work at Wright-Patterson Air Force Base in the Non-Structural Materials Branch of the Materials Directorate. I would also like to thank Vince Vidoni and Bruce Schreiber for the tremendous aid they have provided me with in my Task.

DESCRIPTION OF TASK ASSIGNMENT

In elastohydrodynamic lubrication (EHL), a thin film of lubricant under great pressure separates two bearing surfaces and allows them to slide or roll together exposing the surfaces to less friction and wear. There is much theoretical information on the subject of EHL, but experimental information is always needed for specific fluids to back theory up. This has created a need for tribological testing of the new lubricants at the Materials Directorate of Wright Laboratory providing a role for the mechanical engineer.

Although the Materials Directorate is capable of measuring many characteristics of EHL for specific fluids, they have no means at their disposal to measure the film thickness formed by a fluid between two bearing surfaces. Since a current traction rig was being replaced, it was decided that by recycling many parts from this machine, a new apparatus could be created to measure film thickness using current interferometry techniques.

Using the principles of interferometry to measure EHL film thickness has already been accomplished by several other research groups. The setup consists of a rotating ball loaded against the side of a rotating glass or sapphire disk coated with a very thin semi-reflective layer of material. The lubricant is fed onto the ball creating a thin film layer between the two surfaces as they rotate. Intense light is then directed through the glass disk, with some reflected back off the thin metal coating and the rest continuing through the lubricant and reflecting back off the surface of the ball. The light that passes through the fluid medium is slowed according to the properties of the fluid and must also travel a longer distance than the light reflected off the thin metal coating on the disk. Due to these differences in path, when the two beams of light meet again they are out of phase and cause interference. Because of the spherical surface of the ball, the many different path distances send back beams at several different phases resulting in several different interference patterns. When viewed under a microscope, these interfering beams appear as alternating light and dark rings around the contact region due to the constructive and destructive interference of the light waves. These rings can be calibrated to give film thickness using the known geometry of the ball as a base. The amount of error associated with these measurements is about the magnitude of the wavelength of light used.

PROCEDURE

In designing this apparatus, first a general plan was worked out to make the best use of the parts already available. The basic design uses a 1 inch stainless steel ball connected through a high speed flexible coupling to a variable speed (up to 3000 rpm) pancake motor. The flexible coupling gets rid of most vibration caused by eccentricity of the ball pressed onto a shaft. The ball is sealed inside a small reservoir and rests on three ball bearings connected to a small pad. The four-inch diameter sapphire disk sits on top of the ball and is fastened to a spindle that comes up through the bottom of the reservoir. To keep fluid from leaking out of the hole where the spindle comes through, the sides of the hole are raised and a special fanning device is attached beneath the disk to blow away any fluid spray while the ball and disk are rotating. The disk is driven by another variable speed pancake motor with a torque cell mounted between the spindle and the motor to check traction coefficients. Pressure between the ball and disk is applied with a pneumatic cylinder that is attached to the ball pad and is mounted just below the reservoir.

Since the metal coating on the disk wears fairly quickly leaving an uncoated ring around the disk after a test is run, it is important to maximize the amount of usable surface area on the disk. To be able to run tests at different radii on the disk's surface, the disk and ball have to be able to move relative to one another. In this design, the disk and its driving system are mounted permanently while a base plate that contains the ball and reservoir along with part of the ball driving system is free to move in one direction. This makes over a half inch of the disk's 2 inch radius usable.

In this design, parts that were salvage from other equipment include the fluid reservoir, steel balls, steel disks, a precision spindle, and both pancake motors, all of which are precision items and would normally be high cost. Parts that must be machined include the disk adapter with the fan flinger, the ball pad, the base plate and rails, the spindle mounting plate, and the motor mount along with small modifications to some reused parts. Finally, parts that can be purchased commercially include ball bearings, flexible couplings, a pneumatic cylinder, torque cell accessories, and a machine table.

Most of the final drawings for the design are finished, however, due to time constraints, the project is far from complete. Once money is made available for the purchase of commercially available parts, then machining can also begin. As with any design project, nothing is perfect the first time and even after all of the parts are ready, it will still take much time to work out all of the bugs in the system.

SPECIFIC PARTS DESCRIPTIONS

Pneumatic Cylinder

The pneumatic cylinder chosen can supply a load of up to 150 pounds between the ball and disk. By leaving only an eighth inch wall thickness between the cylinder and the spindle hole on the reservoir, it can achieve a maximum use of 0.6875 inches on the sapphire disk's radius. The base of the air cylinder requires some machined modification to leave room for the disk spindle.

Ball Pad

The ball pad uses three ball bearings to support the rotating ball. The dimensions of the pad are critical both because of the lack of space within the fluid reservoir to allow for error and the importance of having a well-balanced support for the ball.

Reservoir Modifications

First, the reservoir needs to be lengthened for disk travel relative to the ball. The two holes through the width of the reservoir must be plugged permanently. To accompany the air cylinder, a half inch hole must be bored through the bottom along with a machined relief to allow for the top raised portion of the cylinder. To make room for the ball pad, the bed of the reservoir requires some machining. The bottom of the reservoir nearest the disk spindle will have to be machined to a 0.120 inch bottom wall thickness while even deeper machining is necessary further away from the disk spindle to accompany the lower mounted bearing of the ball pad.

Disk Adapter

The disk adapter consists of a fan flinger, washer and nut. The fan flinger slides on the spindle first and is designed to keep fluid spray from leaking through the spindle hole. The sapphire disk rests on top of the fan flinger and is tightened on with the washer and nut.

Base Plate

The base plate supports the reservoir and most of the ball drive system and can move freely between two rails to make several tracks on the sapphire disk. There is a mounting hole for the air cylinder and an elongated hole for the spindle. There are also mounting holes for the driven shaft and holes for locator pins that will be used to position the reservoir on the plate.

Mounting Plate for Disk Drive

This plate will contain the entire sapphire disk drive system below the machine table. There is room for the attachment of the spindle cradle, a torque sensor, and a pancake motor mount. A method to attach this plate to the table and align the disk spindle still needs to be determined.

Mounting Table

The table chosen is 36” x 48” x 32” high. It leaves plenty of room for working area along with the test set up. Specific layout of the test set up on the table still needs to be determined.

ELASTOHYDRODYNAMIC LUBRICATION

Task Order No. 149a
Student Support Program
Southwestern Ohio Council for Higher Education

Jeremy Schmidt
University of Dayton

31 December 1995

Government Task Leader
Mr. Shashi Sharma
WL/MLBT

ACKNOWLEDGMENTS

Many people here at Wright-Patterson Air Force Base made my Task enjoyable and informative. I would like to express my thanks to Shashi Sharma, my Task Leader, for his patience with my questions and his helpful nature. I would also like thank Bruce Schreiber for his willingness to share his technical knowledge and awareness with me. I worked primarily with Bruce on my Task, and thanks to him I am ahead in my knowledge of computers, electronics, and engineering applications. He introduced me to many new ideas and technologies, and my education has grown because of it. I would also like to thank Professor Larry Helmnick of Cedarville, whom I assisted in the Cameron Plint Humidity Test. These three individuals expanded my knowledge greatly. It has been a pleasure working along with them.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

In this Task, the primary objective is to study the behavior of research lubricants under Elastohydrodynamic lubrication, commonly referred to as EHL. More specifically, a testing device called the traction rig is used to measure the behavior of lubricants when the lubricant is pumped between two round, rotating steel specimens, which are rotated on shafts at different speeds. The lubricant is tested between parameters 80 to 750 F, and the steel specimens are rotated at a certain revolution per minute (rpm), between 1000 RPM to 25,000 RPM. The rig is setup to rotate each specimen at a certain rpm, have the specimens forced together at a certain load, and have the lubricant pumped between the rotating specimens. The data comes from monitoring torque, temperature of the lubricant, RPM's of the shafts spinning the specimens, and various other temperatures such as the shaft and heater temperatures. All of the apparatus is used to acquire data concerning the lubricant's properties at different temperatures and torques. Ultimately, coefficient of traction friction is calculated. This data will be used in analyzing how lubricants react under certain conditions, and what lubricants act favorably. The lubricants tested will eventually be used in high altitude hydraulic systems. Under high atmospheric conditions, all types of weather, and changing temperatures, the hydraulic system must not fail. The traction rig apparatus has been created to test the lubricant under the most extreme conditions. The lubricant's practical purposes will be two to three times lower than the EHL testing. This test will ensure the lubricant's dependability under excessive conditions. Unfortunately, no data has been taken up to this point. We are on the verge of starting testing in early 1996.

For this test, there are a variety of equipment and testing methods used. First of all, there is the traction rig itself. It measures roughly 9 feet long, 4 feet wide, and 3.5 feet high. It has a concrete base, along with an I-beam construction, which most of the rig is mounted to. The rig had to be leveled to eliminate noise and vibration. There are two motors, one on each side of the traction rig. The motor is hooked up to a transmission system, which turns the shafts where the specimens are located. The transmission shafts had to be lined up with a torque cell and the shaft which the steel specimen is mounted to. The amount of error had to be within .002 inches, or else the shafts would vibrate and fail. The shafts turn the specimens between 1000 and 25,000 rpm inward towards each other. There is a load cell that pushes the moving specimens together, so rolling friction is created between them. The lubricant is pumped through a jet which shoots the lubricant between the two specimens. The lubricant is heated by two heaters in the fluid reservoir, ranging from room temperature to 750 F. The data from this setup comes from the torque created between the shafts moving at different RPMs, relative to each other.

Other equipment used in this test is the data acquisition program developed by Bruce Schrieber. This program, written in Basic, displays the load cell force, the temperature of the shaft bearings, the test fluid, and the motors, and motor speed. It also acquires data from torque cell every 1 to 2 seconds. Along with this acquisition program, there is a console where meters display the same variables as the acquisition system, along with controlling power supply of system, emergency stoppage, and power to heat the fluid reservoir to get the desired temperature of the lubricant. Both the computer program and the control console are able to change parameters, adjust rpm and temperature, and shutdown the system. Most of the data going to the computer is first seen on the console. Having both systems allows the display of data, the ability to save it, as well as having safety precautions. If the computer system or the console is malfunctioning, the other can still control and shut down the system, if need be.

The data will be analyzed by taking into account the rpm difference at the start of the test, the temperature of the lubricant, and the torque as a result of the two conditions. The traction coefficient, calculated from the measured torque, will entail what type of conditions the lubricant is capable of performing at. Unfortunately, no data has been taken to show a lubricant's coefficient of traction and its properties at certain conditions.

RESULTS

Even though no test was run before this contract ended, the knowledge and experience is beneficial to my future. I entered many areas which I was familiar with, but expanded on all of them. My knowledge of computers, electronics, manufacturing, dimensional metrology, and design was broadened by this experience. These areas are essential to understanding the complicated world of engineering, and yet I was able to comprehend it all with the help of my Task Leader and my advisors. I received many chances to put all of these areas into practice on my Task, which improved my skills and confidence in engineering. The learning I have done here has given me a solid base on which to grow.

RAPID RECRYSTALLIZATION ANNEALING OF TITANIUM ALLOYS

Task Order No. 151
Student Support Program
Southwestern Ohio Council for Higher Education

Julia A. Bettlach
University of Dayton

13 December 1995

Government Task Leader
Dr. Lee Semiatin
WL/MLLN

ACKNOWLEDGMENTS

I would like to thank Dr. Lee Semiatin for all of his guidance, support, and encouragement throughout my Task. I would also like to thank the lab workers in the metallography lab for their patience and help in training me in the art of metallography.

TASK ASSIGNMENT

Task 151 focused on the effects that rapid annealing has on recrystallization of cold-worked conventional Titanium-Aluminum alloys. The goal of this Task was to prove that rapid heat treating can give better material properties in a more economical way than traditional heat treatments can. To reach this goal, the change in microstructure of thin sheets of B21s (a type of Ti-Al alloy) was examined after being rapidly heated above the Beta transus temperature. By examining the microstructure, the changes of recrystallization and grain growth with respect to both time and temperature can be determined. Once these properties are known, estimates of the effectiveness of rapid annealing for the short times of 0.3 and 3 seconds can be calculated.

To begin the Task, the first step taken was to perform heat treatments on the 0.0045" thick samples of the alloys. The samples were to be heated at 843°, 899°, and 982° C for 0.5, 1, 2, 3, and 4 seconds. In the past, these types of heat-treatments were done in the Materials Lab by dunking the samples in molten salt in a salt pot. The time the samples were heated was monitored by using a stop watch and completing the heat treatments by water quenching. However, because the heating times were so short, this type of heat treatment could not ensure accurate heating times. Consequently, the heat treatments had to be contracted out to another facility with more accurate means of doing heat treatments. Tests were done by Paul Bonniwell at the Ohio State University under the guidance of Professor Baeslack. The machine used to do the heat treatments is called a Gleeble machine. The Gleeble machine could heat precisely and cool the samples at a rate of 10,000°C/s for the specific times requested. Due to the thinness of the samples, some mechanical problems were encountered causing the results of the tests to be delayed.

Once the heat treated, samples were received from The Ohio State University, the second step was to perform metallography on the samples. Only part of each sample was actually heat treated, so much care had to be taken in cutting and mounting them. When taking the samples through the polishing stage of the metallography, some problems with pitting arose which caused the process to be very slow and to take much patience. Once the metallography was finally completed, microscopic pictures were taken of the samples.

From the photographs taken, the grain structure of the samples was analyzed. To decide the percent of grains recrystallized in each sample, a grid was laid over the photograph. The number of points that fell on top of grains was counted and then divided by the total number of points on the grid to give a percentage of recrystallization.

$$\% \text{ Recrystallized} = (\text{Points on Grains} / \text{Total Points}) \times 100$$

Using this method of determining the percentage of recrystallization present in each sample, the objective was to see how the recrystallization changed with time and exactly when the grains became fully recrystallized. However, of the 15 samples photographed, 12 were already recrystallized by 0.5 seconds. The samples heated at the lowest temperature of 843°C showed some unrecrystallized grains, but the samples seemed to have been out of order. The samples heated at the shorter times of 0.5, 1, and 2 seconds were fully recrystallized while those heated for 3 and 4 seconds were not. For this reason, and that the grains were fully recrystallized at the higher temperatures, new heat treatments had to be performed. New samples were sent to The Ohio State University to be heated at the same temperatures for 0.1 and 0.3 seconds as well as repeated at 0.5, 1, and 2 seconds for the temperature of 843°C. At the time this report was written, the heat treatments had not yet been completed.

For the samples heated at 899° and 982°C's, the grain size of each sample was also measured. From 0.5 to 4 seconds, the grains seen in the samples from both temperatures showed steady grain growth. The grain size of the samples heated at the higher temperature of 982°C's was consistently higher than those heated at 899°C's for the same amount of time.

Although the study of the recrystallization of Titanium-Aluminum alloys could not be completed, it was seen from the samples heated at 899° and 982°C that short-time annealing is effective in causing recrystallization and grain growth at high temperatures. The next step in the study will be to find the exact rate of recrystallization and grain growth of B21s at these given temperatures. Once both properties are known, estimates can be made of how much recrystallization and grain growth that will occur during heat-up times of 0.3 and 3 seconds. These estimates can be used to predict the microstructure that will result due to specific heating parameters. Once completed, this research will have much potential to help lead to new methods of annealing Titanium-Aluminum alloys.

PROCESSING-MICROSTRUCTURE RELATIONSHIPS FOR ALUMINUM-LITHIUM ALLOYS

Task Order No. 152
Student Support Program
Southwestern Ohio Council for Higher Education

Robert M. Wilson
University of Dayton

31 December 1995

Government Task Leader
Mr. James T. Morgan
WL/MLLN

ACKNOWLEDGMENTS

Much thanks and appreciation is extended to the Student Support program, Dr. Lee Semiatin, and Mr. James T. Morgan for making this work contract possible. I appreciate the opportunity to work in such a professional environment and the valuable experience I gained throughout the Task. Special thanks is extended to Mr. Patrick Fagin of Universal Energy Systems for his help in preparing the material specimens and to Mr. Jim Morgan for his continued support and patience throughout the work term.

DESCRIPTION OF TASK ASSIGNMENT

The purpose of this Task was to find the effect of thermomechanical processing variables on the development of microstructure on a low zirconium, aluminum-lithium (Al-Li) alloy. Processing variables of specific interest were the effects of rolling parameters such as reduction per pass, number of passes, rolling temperature, and rolling speed on dynamic and static recrystalization. These combined effects were interpreted for a preexisting material process evaluating computer program. The computer program output a material processing map that predicted several temperature and strain-rate combinations for processing the alloy. These temperature and strain-rate combinations were taken from directly applied axial compression tests used to simulate a rolling process. The information of all the tests was to be combined to construct a reliable material processing map to refer to in the future when processing the Al-Li alloy. Such a material processing map would eliminate expensive material testing and preparation uncertainties in the future, and allow manufacturers to go directly to production after selecting the desired material characteristics.

DESCRIPTION OF RESEARCH

The methodology behind the research was physically to roll several plates of the alloy starting at a known temperature and plate thickness, and work the plates down to a desired final plate thickness with the use of the Wright Lab's rolling mill. A total of eight plates was rolled at various selected speeds and temperatures by varying the number of passes and percent reduction per pass. These variations in speed, reduction per pass, etc. were selected from the processing map that the preexisting material process evaluating computer program output. To check the computer program's output, the necessary mathematical calculations were done by hand. The reliability of the processing map was then evaluated by physically working the alloy by rolling-mill tests using the selected temperature and strain-rate combinations obtained from the axial compression testing. The compression tests were done by Mr. Patrick Fagin of Universal Energy Systems Inc., who aided in the material research. Compression tests of the alloy consisted of compressing small cylindrical billets of the alloy at selected temperature and strain-rate combinations on a compression test machine. From here, the compressed billets were cut in half using a diamond blade cutter. Half of each specimen was mounted, ground, polished, etched, and finally photographed to record the state of the microstructure of each individual compression specimen. The microstructure was evaluated based on grain size. A smaller average grain size was more desirable than a larger one due to internal stress concentration factors. After the initial evaluation, the second half of each compression specimen was solution heat treated and evaluated in the same manner. The heat treated specimens were then compared with the non heat treated specimens to see if microstructure characteristics had been improved or not. This general procedure was carried out on many temperature and strain-rate combinations throughout the Task period, due partly to the fact that the initial Al-Li material to test and do research on was of poor quality due to porosity caused by improper casting conditions. This material was later replaced with material that was cast under better conditions, with little to no porosity.

RESULTS

Due to the quality of the materials received for testing, compression tests of the material were continuing at the end of this Task. However, a general material processing map existed that could, with limited accuracy, predict acceptable temperature and strain-rate combinations for processing the Al-Li alloy. The testing, which continued at the end of this Task, would ultimately narrow down an optimum combination of temperature and strain-rate at which to process the material.

PROCESSING-MICROSTRUCTURAL RELATIONSHIPS FOR ALUMINUM-LITHIUM ALLOYS

Task Order No. 152a
Student Support Program
Southwestern Ohio Council for Higher Education

Roger Gural
University of Dayton

31 December 1995

Government Task Leader
Dr. Lee Semiatin
WL/MLLN

ACKNOWLEDGMENTS

I would like to thank Mr. James Morgan for his advice and direction: Dr. Lee Semiatin for all of his guidance, and explanations, Dr. Venkat Seetharaman for his patience and understanding, and Mr. Bob Lewis for his expertise in the metallography lab.

The experiences gained from this cooperative education reinforced the notion that not all learning takes place in the classroom. Past school experience provided sufficient preparation for this engineering position, but learning on the job was a prerequisite for success. Every day usually presented a new and different challenge to be mastered.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

This Task was created to learn the effect of process variables on microstructure development in aluminum-lithium alloys under the guidance of Mr. James Morgan, WL/MLLN, within the Metals and Ceramics Division (WL/MLL) of the Materials Directorate.

Working with members of the MLLN and MLLM, the effects of rolling, forging, and extrusion on aluminum-lithium alloys were observed. Several aluminum-lithium strips were heated in a furnace and then mechanically deformed. Strip chart data taken during this hot rolling procedure was reduced and plotted using a Macintosh equipped with Microsoft Excel and Kaleidagraph. Computer simulations of deformation during rolling were written and compiled using MacFortran. The large aluminum strips were cut using a high speed band saw. The strips were further reduced using the metallography lab's low speed diamond saws. After reaching a suitable size, the newly sawed specimens were mounted and ground. After repeated sandings, the specimens were polished with diamond paste and placed on Vibromets for a final polishing. After the specimens achieved a suitable finish, their micro structures were photographed using a Reichert-MeF3 photo microscope.

When the aluminum samples were photographed, work on titanium alloys was begun. titanium-aluminide samples were cut with the diamond saws and mounted in a conducting compound. After grinding and sanding, they were polished using diamond paste and placed on the Vibromet machines. Despite the high magnification of the microscope used, surface features could not be seen on the samples. An acid etchant was used to make grain boundaries and other microstructural elements visible. These specimens were also photographed. Several thin metal coupons were ground to remove oxide layers, but were not polished.

During the heat treating of samples, a time trace of temperature and thermal expansion was made using a Dilatometer. Before computer analysis, the strip charts were digitized using a Power Macintosh, Adobe Photoshop software, and a flatbed scanner. The resulting data was plotted using Kaleidagraph. The beta-titanium samples were ground and polished using the Maximet Autopolisher and then placed in the Vibromets for a final polishing.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS

Task Order No. 153
Student Support Program
Southwestern Ohio Council for Higher Education

Bradley J. Keller
University of Dayton

30 November 1995

Government Task Leader
Dr. Loon-Seng Tan
WL/MLBP

ACKNOWLEDGMENTS

Thanks are given to everyone at the Polymer Branch who helped and assisted in this Task. This Task often required the help of others, and someone was always there, ready and willing to share their knowledge.

TASK ASSIGNMENT

Over the past year, Task 153 has included many duties and completion of many projects. These duties, along with acquired analytical skills, provided the necessary keys for making this Task a success. Among these duties was Fourier Transform Infrared Spectroscopy (FTIR), Ultra-Violet/Visible/Nearinfrared Spectroscopy (UV/VIS/NIR), viscosities, and melting point determinations. Other duties included maintaining a chemical inventory, ordering and receiving chemicals for reactions, ordering supplies and equipment to be used in experimentation, maintaining a clean lab area, following government guidelines for disposal of hazardous wastes, and computer work.

A technique most used in this Task was FTIR. It is used to give clues about the structure of the monomer or polymer being analyzed. In this procedure, a solid sample is pressed into a clear window with potassium bromide. This window is then scanned at varying wave numbers from 450 to 4000 cm^{-1}. This produces a spectrum that has peaks at the wavelengths where certain functional groups absorb the light. By matching the peak wave numbers to the functional groups, one can get a good idea of the structure of the solid being tested. Near the end of the Task, a new spectrometer was installed. This new spectrometer greatly simplified the Task of obtaining an FTIR. It was much quicker to use this than the old equipment once the new procedures were learned. This new spectrometer also allows one to transfer spectra to other programs such as Origin and Power Point. The spectra can then be used in presentations.

Another part of this Task included performing UV/VIS/NIRs. One study included the analyzing of a series of seven compounds. The first time the series was analyzed, a trend of sorts was noticed. This apparent trend brought about the need to more carefully analyze the series to see if the 'trend' was really a trend. After several more tests of the series, the 'trend' was a trend. Careful measurements and testing were necessary to accomplish this study.

The determination of viscosities was another part of Task 153. Viscosities are done to decide the intrinsic viscosity of the compound. This is done by recording times it takes for varying concentrations of the solution to flow though a capillary-size tube. These times can then be used along with the concentration values to calculate inherent and reduced viscosities at each concentration. These values can then be plotted on the same graph to find the intrinsic viscosity.

During this Task, the program Origin was learned. Over a 2-week period, the program was learned through use of the manuals and the tutorial guides and just plain experimentation with the program. It is a graphing program that was very useful in determining intrinsic viscosities.

Once calculations were entered into a template, time values could be entered into the program, and the intrinsic viscosity was quickly and neatly determined. The graph could then be manipulated to create a neat and professional presentation of the data.

Other computer applications learned were the HAZMAT, ChemDraw, Word for Windows, Excel, and Teamlinks E-mail. These programs were very useful in many aspects of the Task. HAZMAT is a chemical inventory program for the Material Labs. It keeps track of all chemicals in all of the labs. It can be used to order depleted chemicals or to find someone who has the chemical to lend for an experiment. ChemDraw is used to draw chemical structures. These structures can be copied and pasted into other applications for presentations. Excel was used to maintain a chemical inventory for the lab in which Task 153 was done. It includes name, location, manufacturer, quantity, and a government bar-code for HAZMAT tracking purposes. Teamlinks E-mail was used to talk with others involved in this Task. It was also used to order chemicals, and to request pickup of hazardous waste containers from the lab. It proved useful when someone was not around and time was not available to wait around to call them back.

An important part of Task 153, was ordering and receiving chemicals and equipment for the lab. Chemical ordering is easy to do and requires little paperwork. On the other hand, equipment ordering is done through the government and requires extensive paperwork. The problem with government ordering was that the procedure was changed several times throughout the Task, and what was needed was often not clarified. All this aside, no major problems resulted with equipment orders besides a few messed up orders and an extreme amount of time spent on the paper work. A suggestion was made to simplify the government ordering procedure and to drop some paperwork. With the information highway buzzing past as endless paperwork is being processed, one would become envious to jump on the highway and leave the paper behind. A suggestion is only a suggestion until action is taken. When Task 153 was completed, nothing had yet changed in the ordering procedure.

The Task was very educational and a good bit of knowledge was acquired. Task 153 ends where the next begins, because most facets of the Task are ongoing processes that require constant attention and updating. Polymer research is very important for developing new technologies that aid in the construction of new and better equipment for the Air Force. This research is an integral part of maintaining state-of-the-art technologies.

BRITTLE MATRIX COMPOSITE STUDIES

Task Order No. 154
Student Support Program
Southwestern Ohio Council for Higher Education

John Schuck
Sinclair Community College

4 December 1995

Government Task Leader
Dr. Rollie Dutton
WL\MLLN

ACKNOWLEDGEMENTS

Many thanks to Rollie Dutton. All his help and guidance made this Task a truly educational and enjoyable experience. Special thanks goes to Wanda Vogler for giving me the opportunity to work on this Task.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The focus of this Task was largely dedicated to the processing of ceramic matrix composites reinforced with unidirectional SiC fibers for the investigation of initial matrix micro cracking under tensile loads. The composites are a borosilicates glass matrix. The composition of the glass was varied to allow for the thermal expansion coefficient mismatch between the fiber and the matrix. This resulted in varying radial thermal stresses from tensile too compressive after processing. The fibers used in the composite were a TiB_2 coated Sigma fiber and an uncoated SCS fiber uniformly spaced on aluminum mats at 120 or 68 fibers per inch. The volume fraction of the composites was therefore varied by selection of fiber spacing. The glass strongly bonded to both fibers allowing investigation into the role of a weak layer at the $C\backslash TiB_2$ interface. The various composites were tensile tested to figure out initial matrix cracking, which varies with the fiber volume fraction, and then loaded to failure. A SEM was then used to evaluate the physical properties of the composites. The collected data was compared with earlier predictions based on a semi-empirical and axisymmetric damage models for model verification.

DESCRIPTION OF RESEARCH

The matrix for the composites was prepared via tape casting. The recipe for the glass slurry is given in Table 1. The binder, PEG, and solvent are mixed and paddle stirred for 15 minutes then set aside. The fish oil and remaining solvent are paddle stirred until the fish oil is well distributed. The glass powder is added and the mixture is paddle stirred for 15 minutes. The binder mixture is added to the glass mixture and paddle stirred for 15 minutes. The glass slurry is cast on the Tape Casting Machine and allowed to dry for at least 3 hours. Tape thickness averages 7 mils with 50% relative density.

Each layer of the composite was prepared individually. The green tape and fiber mat of the desired fiber spacing were cut to size then laminated into the green tape at 180°F using 100k Pa on a Carver Press installed with heated platens. Six layers were processed by the same procedure and stacked together to make the final composite laminate.

The composite laminates were loaded into a tube furnace for binder burnout and sintering. The heating schedule is given in Table 2. After sintering, the composites were hot isostatically pressed at 650°C's for 30 minutes with an applied pressure of 35M Pa to remove approximately 2% residual porosity. The final composites were 10cm long by 2cm wide and 0.2cm thick.

Before tensile testing the composites were coated with a thin coat of 828 epoxy to reduce any surface flaws. The composites were tabbed and the edges were polished to 1μm. Polishing was required to improve microscopic imaging used for crack detection. Strain gauges and an acoustic emissions detector were mounted and then the composites were tensile loaded. The load was incremented so that initial matrix cracking could be detected by photomicrographical and acoustic emissions techniques before the composites reached ultimate failure. The micrographs produced by the MTS machine were used to determine the initial matrix cracking stress. The failed composites were analyzed on a Leica 360 SEM to determine micro crack growth and the roles that the fiber, coatings, and matrix played on the crack growth.

RESULTS

The composite cracking stresses obtained from mechanical testing for the Sigma fiber showed the 7040 and F glasses to agree with model predictions. The E glass cracking stresses fell below the predicted level suggesting a previous debond at the fiber/matrix interface. Composite cracking stress versus fiber volume fraction was plotted against the model predictions and is shown in Figure 1. Test results for the SCS fiber are inconclusive and more testing needs to be done to compare it with model predictions.

This has been a very educational experience for me. I have learned how to operate various scientific instruments and how to interpret the data obtained from them. The methods of research I have learned will be an invaluable asset to me as I pursue my degree in chemical engineering.

Table 1

48 gm glass powder (ave. particle size ~8μm)

35 ml Ethanol (add 20 ml\15 ml)

35 ml Toluene (add 20 ml\15 ml)

1.9 gm Manhaden Fish Oil

4.3 gm B-90

4.1 gm PEG

Table 2

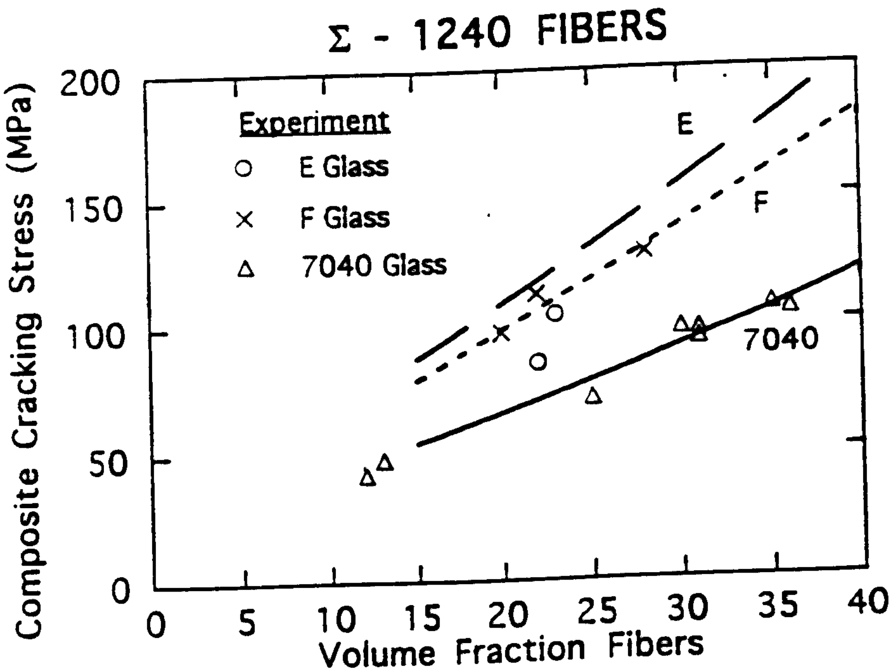
200°C ⇒ 450°C @ 2°C/min in oxygen, 1 hr hold, binder burnout

450°C ⇒ 710°C @ 4°C/min in argon in vacuum, 1 hr hold, sintering

backfill with argon, 20 minute hold

710°C ⇒ 200°C @ 5°C/min in argon, cool down

Fig 1



NONDESTRUCTIVE EVALUATION (NDE) EXPERIMENTAL SUPPORT

Task Order No. 155
Student Support Program
Southwestern Ohio Council for Higher Education

David Lomely
University of Dayton

31 December 1995

Government Task Leader
Mr. Curtis Fiedler
WL\MLLP

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INTRODUCTION

An ultra fast laser generated ultrasound, UFLGU, is a method by which one may potentially measure and evaluate the properties of applied thin coatings. It is an attractive measurement technique because of its nondestructive nature. UFLGU relies heavily upon femtosecond pulsed lasers to induce an ultrasonic shock wave in the material being studied. By knowing certain facts about the material in question, obtaining information about the quality of the coating is possible. For example, if one knows the speed at which sound propagates through the material, by measuring the time it takes for the ultrasonic wave to travel from the surface to the back of the coating, one may determine the thickness of the coating. In any case, there are two general types of UFLGU concerned, piezoreflective UFLGU and interferometric UFLGU. The actual details of these two methods of UFLGU are beyond the scope of this Task, so far. Thus, they are beyond the scope of this paper. Nevertheless, a brief description of the techniques is given below to clarify the distinction between the two.

Piezoreflective UFLGU

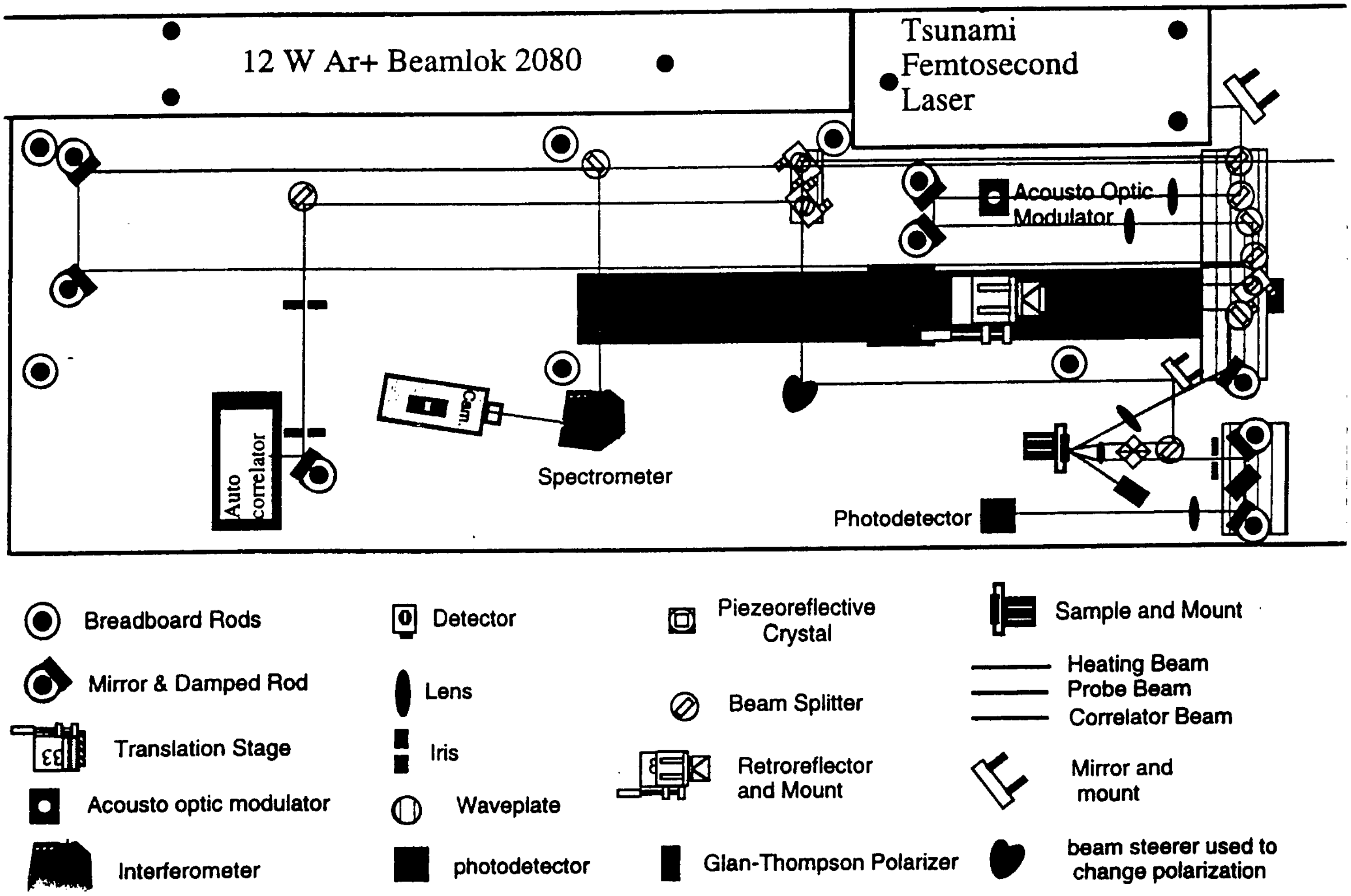
For the purposes of this experiment, use was made of a Ti: Sapphire laser that can produce femtosecond pulses. This laser was pumped by an Argon Ion laser. The beam from the Ti: Sap was split into a heating beam and a probe beam. The heating beam was sent to the target by following a variable path. The effect of this beam was to heat the surface of the sample rapidly enough to produce an ultrasonic shock wave in the material. This ultrasonic wave has the effect of producing a mechanical strain in the sample. In a piezoreflective material, this can easily be detected as a change in the reflectivity of the surface of the sample. Thus, the probe beam is focused onto the sample. By analyzing the reflected light one can determine the reflectivity. From this obtaining the required information about the coating is possible. Unfortunately, to use this method the coating must be piezoreflective. There are many cases in which these criteria are not met. Having another method that does not depend upon the piezoreflectivity of the sample would be desirable.

Interferometric UFLGU

Interferometric UFLGU has the advantage that the material in question need not be piezoreflective. Interferometric UFLGU uses phenomena known as interference. The basic principles that underlie piezoreflective and interferometric UFLGU is the same. The main distinction relies upon how the information regarding the sample is obtained. Interference occurs as a result in the discrepancy between the phase of two coherent wavefronts. Since the wavelength of light is small, about 790nm, measuring small variations in the surface of the sample is possible. Such minute displacement will create an interference pattern. By analyzing this pattern, learning how much the surface was displaced is possible and thus, determines the properties of the coating. Where piezoreflective UFLGU measures the difference in reflectivity induced by the ultrasonic shock wave, interferometric UFLGU measures the actual displacement the ultrasonic wave causes in the material.

To accomplish this, a beam splitter cube was used to split the probe beam and then recombine it upon reflection from the sample to produce an interference pattern. When the ultrasonic wave creates a displacement in the material, then a corresponding change in the interference pattern occurs. This change in the interference pattern is used to obtain the data.

A diagram of the optics bench setup is shown below:



TASK ASSIGNMENT

Tasks included the everyday startup and shutdown of the 1.5 watt Ti: Sapphire laser and the 12 watt Argon Ion lasers. Furthermore, optic bench layouts were continually being updated to reflect the changes in the experimental setup.

In addition, there was ample programming to be done. At the beginning of the Task, work was being done to translate an older outdated Fortran program that facilitated communications between the VAX and the Macintosh into C. C subroutines were used to call upon the already existing Fortran routines.

Work was done with the IGOR wavemetrics software package. With this software, writing a small program that would analyze the collected UFLGU data from a directory was possible. A programming sample is included at the end of this paper. However, work still needed to be done on the program. Adding enhancements that allowed the program to do an FFT of the data and sort through the proper files in a given directory, were necessary. These enhancements were eventually added by Mr. Fiedler.

In addition, a microscope system was set up using simple ray tracing techniques. It was designed so that the experimentalist can view the surface of the sample being studied, in good detail.

While there is still much work to do on the UFLGU project, much has already been accomplished. It seems that now the biggest step lies in the collection and processing of the data required to prove that the system is, indeed, feasible.

Laser Operating Procedures
for the
1.5 Watt Ti:Sapphire Laser
pumped with a
12 Watt Argon Ion Laser

Startup Proceedure.

1. The operator must remove all watches, rings and other jewelry.
2. Lock all three doors (hall, core, and room 192)
3. Turn on the safety light (the Argon Ion laser will not start without this light on)
4. Turn on the cooling water for both lasers
5. Verify that everyone in the lab is wearing Ti:Sapphire goggles
6. Turn on the electronic controls for both lasers. The Argon laser will start automatically after 10 seconds.

Shutdown Proceedure

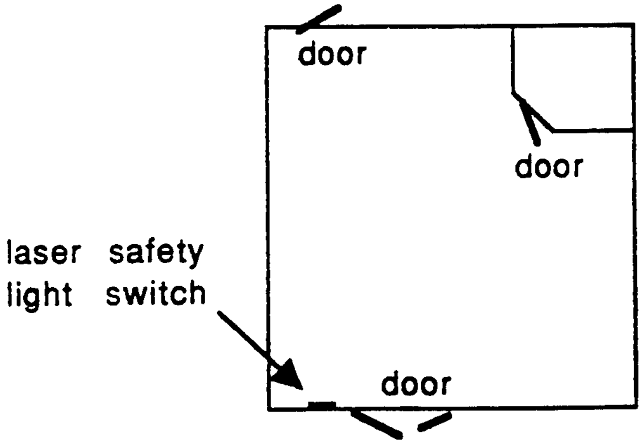
1. Turn off the Argon Laser
2. Turn off the electronic controls for both lasers
3. Let the cooling water for the Argon laser run for at least 5 minutes after the power has been shut off, and then turn the cooling water off for both lasers.
4. Turn the laser safety light off.

Emergency Shutdown Proceedure

1. Turn the laser safety light by the door off. This will shut the Argon laser down, and since the Argon laser pumps the Ti:Sapphire laser it will also shut down that laser.

Overexposure to Laser Radiation

1. Contact the Base Laser Safety Officer at 7-2010



```
#include <Strings as Lists>

function Analyze(pathname)
    String pathname                    |  name of symbolic path or "" to get get dialogue

                                       |  Variation from Igor Pro Users Manual pg 211


    String filename
    String graphname
    Variable index=0

    Make/N=101/D/O  Xvalue,Yvalue

    if  (strlen(pathname)==  0)        |if no path specified, create one
        NewPath/O temporaryPath        |this will put up a dialogue
        pathname ="temporaryPath"
    endif

    do
        filename = IndexedFile ($pathName, index, "TEXT")
        if  (strlen(fileName)==  0)   | no more files?
            break                      |break out of loop
        endif
        Load(filename, pathname)
        index+=1
    while(1)


    YWavesAverage("wave","Yvalue")
    SetScale/P x, 170, 0.2, "mm", Yvalue
    Display Yvalue

    KillWaves/A/Z                              |kill all waves not in use
    if  (Exists("temporaryPath"))    |kill temp path if it exists
        killpath  temporaryPath
    endif
End

function Load(fileName, pathName)
    String fileName                        |name of file to load or "" to get dialog
    String pathName                        |name of path or "" to get dialogue



    | load the waves and set the globals
    LoadWave/J/D/O/A=wave/P=$pathName  fileName
End

function  YWavesAverage(basename, destname)
```

```
                                      |From Igor Pro Users Manual pg. 613

    string basename                   |name for source wave
    string destname                   |name for destination wave

    string  wn                        |contains the name of particular wave
    string  wl                        |contains a list of wave names
    Variable index = 1

    | get list of waves whose name starts with the basename
    wl = WaveList (basename+"*", ";", "")

    |make destination wave based on first source wave
    wn = GetStrFromList (wl,0, ";")
    Duplicate/O $wn, $destname

    Wave dest = $destname             |create wave reference for destination
    dest = 0

    do
        wn = GetStrFromList(wl, index, ";")   |get next wave
        if (strlen(wn)  ==  0)                |no more names in list?
            break
        endif
        Wave source = $wn                     |create wave reference for source
        dest += source                        | add source to dest
        index += 2
    while(1)                                  |do unconditional loop
    dest=  dest/((index-1)/2)                  |divide by number of y waves
End
```

NONDESTRUCTIVE EVALUATION (NDE) EXPERIMENTAL SUPPORT

Task Order No. 155a
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer A. Foley
Wright State University

31 December 1995

Government Task Leader
Dr. Curtis J. Fiedler
WL/MLLP

ACKNOWLEDGMENTS

I would like to thank Curt Fiedler for all of his help. He has done an excellent job teaching me how to set up and run the experiment. Working with him on this experiment has really helped me to apply what I have learned in school. I have also obtained a lot of important knowledge on computers and programming. I know that as significant as computers have become in today's society, this knowledge will benefit me throughout life, as well as my career.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The general purpose of this Task was to develop experimental procedures using computer programming and hands-on technical work. In addition to running the experiment, the acquired data was to be processed and recorded. This allows for easier and more efficient interpretation of the results.

Data collected and recorded from the experiments performed during this Task, were done so to aid the research of Curt Fiedler in the Nondestructive Evaluation (NDE) branch of the Wright Laboratory Materials Directorate.

DESCRIPTION OF RESEARCH

The experiment underway deals with the development of a technique to inspect thin coatings, ranging anywhere between 10 nm and 500 nm. While methods for inspecting thin coatings already exist, this research sets out to find methods of inspection which are non-contact (to eliminate any contamination of the coating) and non-destructive. Experiment are also being conducted to expand on the types of materials used and to decrease the time it takes to inspect materials. For example, a technique is being explored to inspect materials which are not piezo-reflective.

The system used involves Ultrafast Laser Generated Ultrasound (UFLGU). Two beams, a heating beam and a probe beam are focused onto a sample. The intense heat on the sample causes an ultrasonic wave to be produced. As the ultrasonic wave passes through the sample, it affects the path length of the probe beam. The differences are detected when the probe beam reflects off of the sample and into a detector. For non-piezo-reflective materials, interferometric detection is used. The ultrasonic wave causes a displacement as it reflects off the surface. This displacement is detected with an interferometer. As the ultrasonic wave moves, changes in path length lead to changes in the interference pattern. This difference is then recorded by the computer. Piezo-reflective scans are different in that they detect a change in reflectivity. The resulting data consists of peaks and echos which are produced by the ultrasonic wave. The positions and amplitudes of these echoes are very important in determining the thickness of the thin-films.

The initial research and methods used were developed by Curt Fiedler. What has followed has been a modification of these methods to improve the outcome of the data. This has involved changes in the experiment itself and how data is taken. It has also dealt with the processing and manipulation of the data once it is received.

The first modification task undertaken was to design a new shelving system that would allow the instruments used to be taken off of the optics table while still being accessible. These instruments needed to be taken off of the optics table in order for the table to be able to float. Floatation of the optics table is one method of noise elimination for the experiment by reducing vibrations which offset the experiment.

Using a CAD software called MiniCad, along with input from Mr. Fiedler, a shelf was designed that would go over the optics table. Large instruments are placed on top of the shelf where they are easily seen. Instruments that must be easily accessible in order for the experiment to run are placed on a hanging shelf attached to the bottom of the top shelf. A shelf that covers that optics serves not only to hold valuable instruments, but adds extra protection for the optics from dust falling out of the heating vents above the table.

A software package called Labview is used to run the experiment. Through General Purpose Instrumentation Bus (GPIB), the computer controls the instruments used in the experiment. The computer also collects data via the GPIB bus. Many modifications have be made as to how the experiments are run. For example, the multiple scans program can be set to run scans at as many different angles as desired. It then takes a scan at each angle. Once it is done with its set of angles, it continues its scans from the first angle. This program was changed so that the scan taken at the first angle of every set is piezo-reflective while the others are interferometric. Using a Burleigh translation stage, a thumb card is moved in and out of the beam accordingly to either create fringes (for the interferometric scans), or not create fringes (for the piezo-reflective scan). A switch was also inserted into this program to allow the experiment to be halted after it is done with its present scan. This is done so that when the experiment has been running for a long period of time, the laser may be reset. The alignment of the laser is important because it ensures the best results.

Another significant change to the multiple scans program is that the scans can be run to collect x and y data versus the magnitude and phase data that was collected before. Before running the experiment, one must choose which type of data is to be collected and then simply press one button on the computer screen and either the x/y or magnitude/phase button on the Lockin Amplifier. X and y data is important for comparing results from the magnitude and phase data. Comparing and contrasting of the two sets of data will lead to a better understanding of the experiment and the data that is being received.

Currently Labview is being used to write a program which will measure the amount of noise from the laser itself. One has already been written to measure the noise in the system. By comparing the two and finding where the most noise is occurring, it will be easier to solve the problem.

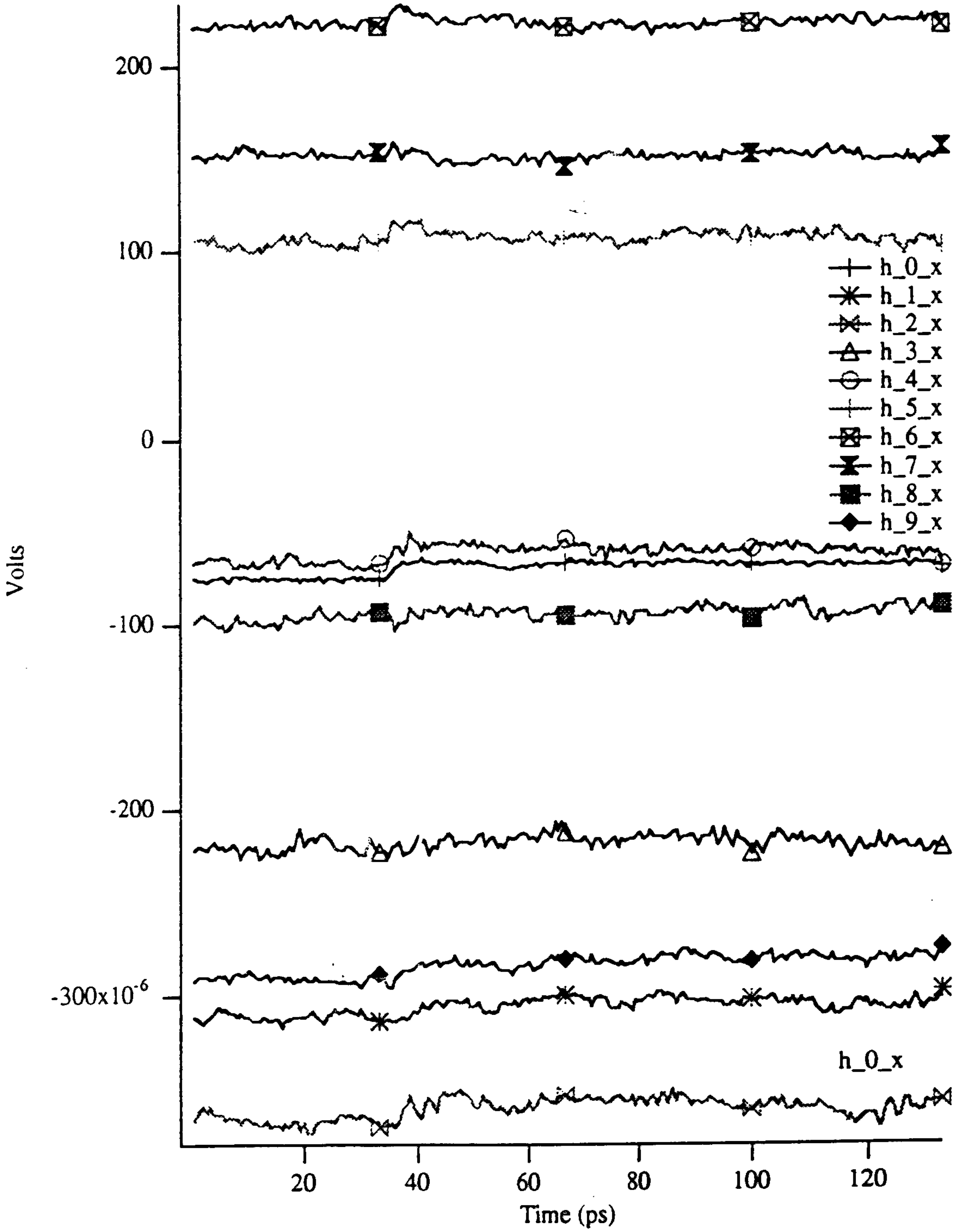
Igor is the software being used to process the data that is received. A macro has been written to average the data taken at each angle and then plot each of these averages on one graph. Another macro then subtracts each of these waves from a reference wave. The reference wave is the piezo-reflective wave. It is subtracted out because in an interferometric scan, reflection is also occurring. Subtraction allows the interferometric data to be plotted and viewed by itself. The original versions of these macros only worked with magnitude and phase data. They have been modified to now accept and process x and y data. A macro has also been written to convert the x and y data to magnitude and phase. This was accomplished using the following equations:

magnitude, R = SQR (x^2 + y^2)

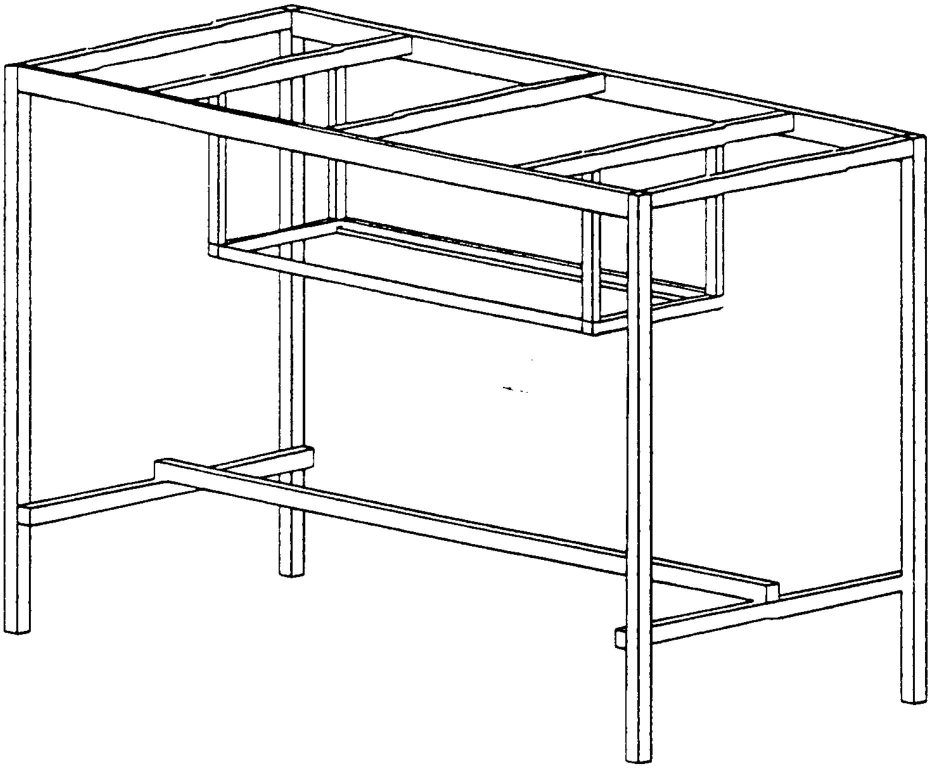
phase, q = arctan (y / x)

For the phase, Igor has a command which looks at the data and automatically decides which quadrant the angle q exists. This is important in keeping the data as accurate as possible. With the x and y data converted to magnitude and phase, the two sets of data may easily be compared.

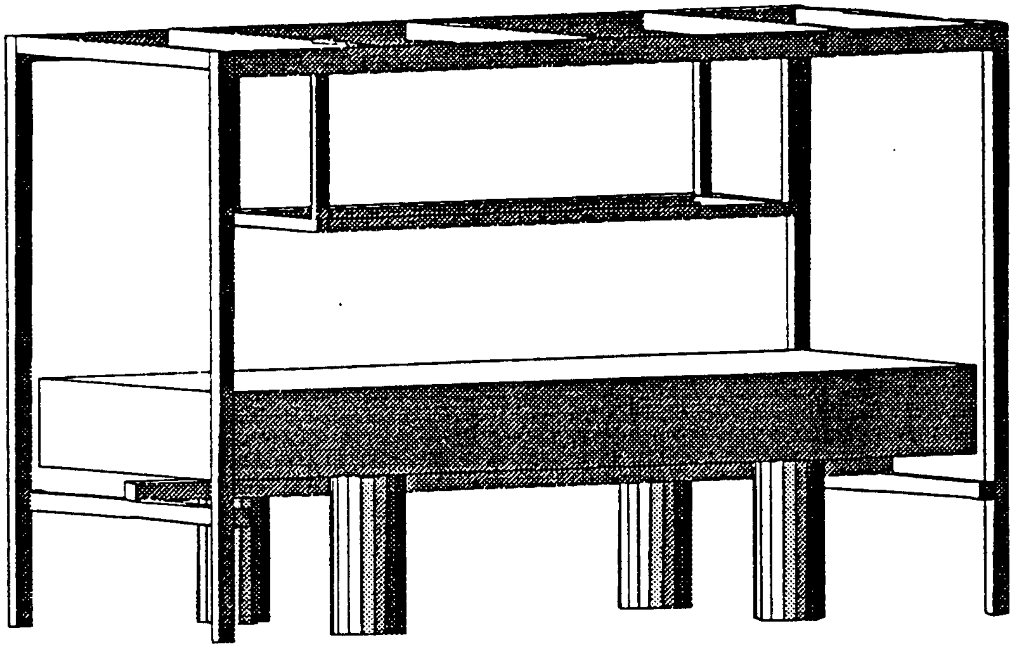
An important characteristic of the material is how it affects the ultrasonic wave as a function of frequency. Because this information is not given directly from the scans, a macro was written in Igor to calculate it. The macro first allows the user to choose the echoes that he wishes to analyze. The computer then calculates the FFT (Fast Fourier Transform) to find the frequency components of the signal. It plots the data in energy vs. frequency. With the known frequency, the ultrasonic attenuation of the material can be found. This can lead to further information on the characteristics, thickness, and other properties of the specimen.



Example of multiple scan: This data was taken December 5, 1995. It is the x data from a sample of 200 nm Al over 300 nm AuPd.



This is an illustration of the shelf that was designed to go over the optics table that holds the experiment.



This is an illustration of how the shelf fits over the optics table.

PHYSICS OF CONDUCTING AND NONLINEAR OPTICAL POLYMERS

Task Order No. 156
Student Support Program
Southwestern Ohio Council for Higher Education

Max Dudley Alexander, Jr.
Wright State University

31 December 1995

Dr. Robert Spry
WL/MLBP

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I would like to thank those who assisted my research during the my time in the polymer branch this year. Dr S.J. Bia, who I have worked with closely on the copolyester attenuation project, Dr. Barney Taylor and Mr. John Fergeson for assistance in the luminescence and spectroscopy area, Mr. Gerd Beutel for his expertise in the areas of computer languages and conductivity, Mr. Gary Price for his assistance in the acquisition of scanning electron microscope images of various samples, and Dr. Robert Spry for his direction and expertise in all aspects of my research.

GENERAL TASK DESCRIPTION AND ASSIGNMENT

Task: To measure the nonlinear optical properties of polymeric materials, to write and modify computer programs for nonlinear property modeling.

Project 1

The in plane absorption constant, α, was measured and correlated to molecular orientation in a copolyester planar waveguide. The copolyester film, ***Figure 1*** manufactured by DuPont Lab Circleville, Ohio[1] was uniaxially stretched to 3.5 times its initial length at a temperature slightly above the materials glass transition temperature, T_g.

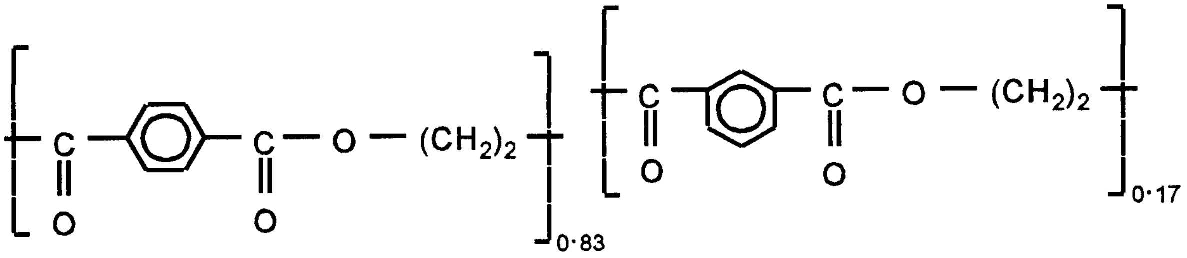

Figure 1. Random copolyester film, poly(ethylene terephthalate-co-isophthalate)

A sample of the film was adhered to a silicon wafer with a 2 micron SiO_2 layer. A Metricon 2010 prism coupler[2] was used to measure the reflected intensity of a 632.8nm He:Ne laser beam at various angles ***Figure 2***. At discrete angles the beam enters a mode in which total

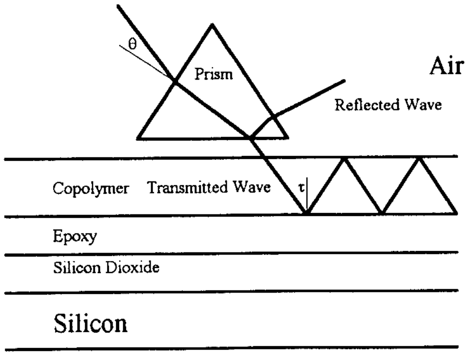

Figure 2. Set up of Metricon Prism Coupler

internal reflection inside the film occurs and the reflected intensity becomes a minimum ***Figure 3***. By knowing what angle at which these modes occur, the index of refraction and film thickness can be easily calculated. The index of the film was measured with both TE and TM laser beam polarizations parallel and perpendicular to the stretch induced molecular orientation of the film. These measurements showed the film to be highly anisotropic yielding in plane indices of 1.5464 and 1.6545, parallel and perpendicular to the stretch direction respectively. The out of plane index was also calculated, from the TM measurements, as 1.5428 with margin of error of 0.0001.

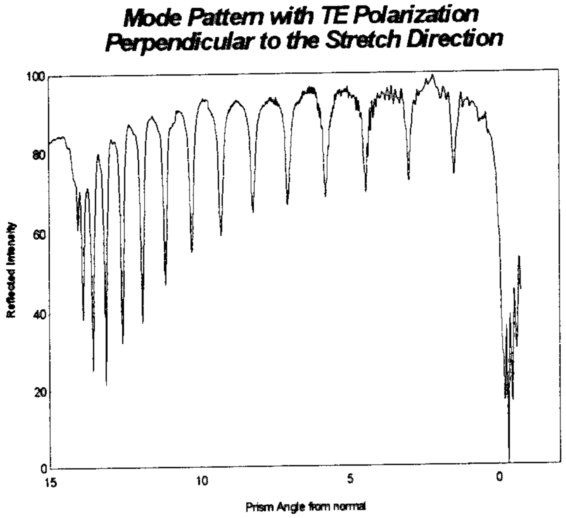

Figure 3. Mode Pattern produced by altering indident angle upon prism

The in plane optical loss was measured by direct contact imaging, of the propagation streak produced at each even numbered optical mode, onto Kodak Technical Pan Film[3]. The film was then developed and the intensity of the beam along the streak acquired by scanning the negative with a Molecular Dynamics Personal Densitometer[4] ***Figure 4***. A line scan along the propagation streak was taken at a width of 350 microns, the known full width half maxmima of the He:Ne laser to acquire the data points used in the absorption loss measurement calculation.

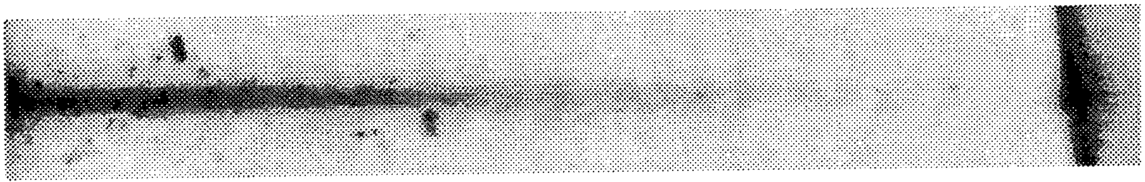

Figure 4. Propagation streak as recorded by densitometer

The data points from the line scan were then converted from optical density units measured by the densitometer to intensity units (required by Beer's Law) using a conversion curve published by Kodak Corporation[5]. Since the in plane optical absorption is given by Beer's Law as $I(x) = I_0 e^{(-\alpha x)}$, where I(x) is the intensity at some distance x along the propagation streak away from the reference point, and I_0 is the intensity at the reference point, the log of the intensity data when plotted against the propagation distance x will yield a straight line whose slope is α ***Figure 5***.

Because each mode takes a different path through the film, the in-plane attenuation coefficient was normalized for path length. This was achieved by multiplying the measured α by $\sin\tau_i$ as shown in ***Figure 2***

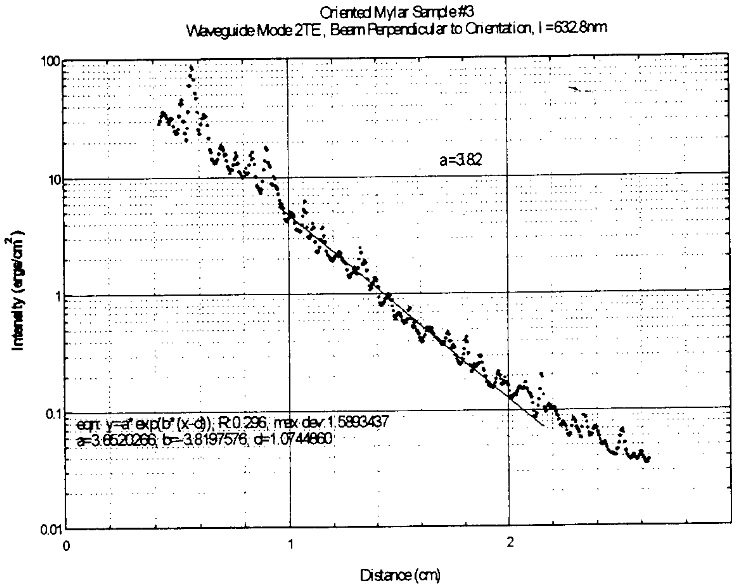

Figure 5. Example of Beer's Law plot to determine the in plane optical loss

After optical path normalization, a clear trend in the data was present with a summary shown in ***TABLES 1*** and ***2***. The TE polarization shows an increase in the attenuation coefficient with mode number while the TM remains constant and has a lower value than either of the TE mode 0 values. This is an unexpected result which is described elsewhere^6.

Mode Number	normalized attenuation coefficient
TE_0	1.90
TE_2	2.46
TE_4	3.34
TE_6	4.46
TM_0	2.05
TM_2	2.08
TM_4	2.02
TM_6	1.94

TABLE 1. Propagation parallel to the stretch direction of the copolymer waveguide

Mode Number	normalized attenuation coefficient
TE_0	3.16
TE_2	3.81
TE_4	4.83
TE_6	5.62
TE_8	6.80
TE_{10}	7.77
TM_0	2.01
TM_2	1.97
TM_4	2.03
TM_6	1.98

TABLE 2. Propagation perpendicular to the stretch direction of the copolymer waveguide

The significance of this work is in area of optical communication. Optical communication relies on the ability of a light signal to waveguide along in optical fiber with the minimal absorption and scattering. The mode or path dependence coupled with the beam polarization (TE or TM) was the focus of this study. It has been shown that the smallest losses can be achieved by using the TM polarization rather than the TE; and, the optical loss associated with the TM polarization is not dependent upon the waveguide mode chosen.

Project 2:

The debugging and re-coding of a series VAX Fortran code programs[7] was performed for the simulation of polarized light reflection and transmission through multiples anisotropic films. The goal of this project was to debug the FORTRAN code written for the VAX and translate it for use on a personal computer.

The reflection study software allows the user to input several parameters such as: number of layers in the system, the light wavelength, the in and out of plane indices, the in plane optical loss, the incident light polarization (p or s) and, the incident angles with respect to the normal to the surface. The program then generates an ASCII data table of reflection intensity vs. incident angle. This ASCII data table can then be incorporated into any variety of plotting packages available for visual interpretation. The program was given experimental data for the above parameters and then instructed to produce the experimental curve of reflection intensity. ***Figure 6*** shows a comparison between experimental reflection data and the Fortran simulation. The Figure indicates good agreement between the data sets; however, due to the method of measurement, the indices used in the FORTRAN simulation were scaled by 3.6 % to obtain their actual values. This scaling was a result of compression of the sample during experimental measurement.

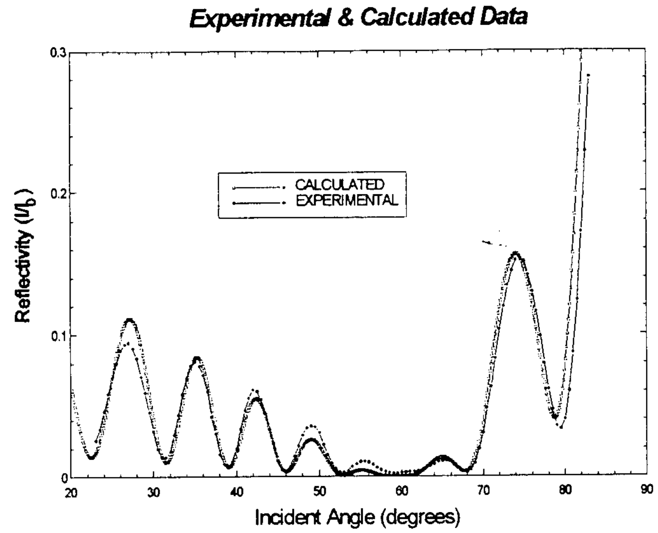

Figure 6. Comprison of Experimental to Calculated Data for p-polarized light, n_o=1.72678, n_e=1.57268, thickness= 6.8 microns, kappa=0.0025, wavelength=632.8nm

The transmission study software allows the user to input the number of layers, the in and out of plane indices for each layer, the thickness of each layer, the wavelength of the light source, and the angle of incidence from the normal to the surface. The software then outputs an ASCII data file of transmittance vs. wavelength which can be analyzed using a variety of software packages. An example of the program output is shown in ***Figure** 7*. The conversion of the software from the VAX to PC is now complete and it allows easy optical modeling of complex multi-layer non-isotropic films, saving hours of time in the lab setting up and taking ellipsometric.

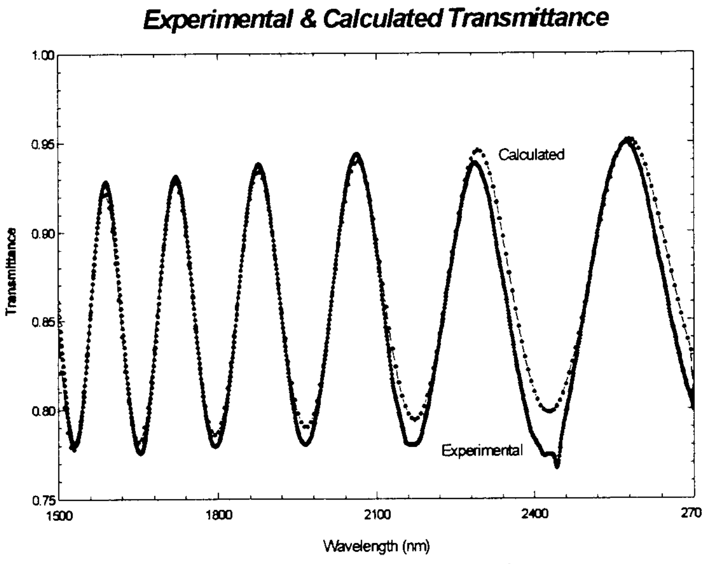

Figure 7. Comparison of Experimental and Calculated Transmittance

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2. Metricon Co. Pennington
3. Eastman Kodak Co., Rochester, N.Y.
4. Molecular Dynamics, Sunnyvale, Ca
5. Scientific Imaging Products 1995, Eastman Kodak Co., Rochester, N.Y
6. Bai, Spry, Alexander, WPAFB WL/MLBP; Barkley, Dupont (publication pending)
7. Optical Properties of thin Solid Films, Tom Vaughn, Wright State Univ. 1992

GROWTH AND CHARACTERIZATION OF NONLINEAR OPTICAL MATERIALS

Task Order No. 157
Student Support Program
Southwestern Ohio Council for Higher Education

David Small
Wright State University

11 December 1995

Government Task Leader
Dr. David Zelmon
WL/MLPO

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

This Task involves characterizing new non-linear optical materials, which come from universities, government labs, contractors and from in-house sources.

Measuring indices of refraction of crystals. The values of the indices of refraction are very important to people who wish to build devices out of new materials. Many of these new materials are being tested for the first time, and the properties are not known. The index of refraction of a material tells how fast light will travel through the medium compared to its velocity in a vacuum. When light enters a crystal, its phase velocity decreases and the direction of propagation changes. The magnitude of these phenomenon is dependent on the wavelength of the light and on the crystal and molecular structure of the material.

One of the major goals of the lab is to find materials which will efficiently convert the frequency of light. Conversion of light is important for applications in all of the sciences and engineering. Only certain frequencies of light are attainable by using lasers, but others are needed to study chemical reactions, build optical communications systems, laser targeting systems and a variety of other applications. To be able to predict whether or not it will be possible to obtain phase match ability, which is a measure of the efficiency of frequency conversion, the indices of refraction of the crystal to five decimal place precision must be found. The refractive index that light experiences when propagating through a crystal will differ depending on the direction it is traveling. There are three axis in the crystal called the dielectric axis, and there will be correspondingly be three different indices of refraction in a crystal if the crystal is bi-axial. If two of the indices are the same it is called uniaxial. Most of the crystals are bi-axial and we have to measure three indices of refraction. Two prisms made out of the material cut with different orientations are needed. The indices are measured using a spectrometer by the minimum deviation method for each crystal with each of two polarizations five to seven times each over a wide range of wavelengths. Indices of refraction are measured, calculations are made, the date fit to a curve, and the data reported. Because of the importance of the precision of the results, it is important to know the limitations of the system. The system is calibrated by measuring the indices of a prism of known composition and known indices. If my values are within 2 in the fifth decimal place, the system is good. If not, the system needs readjusting.

For a material called RTA, the indices of refraction from 403nm to 3500nm in steps of 50nm are measured using a special camera after the wavelength exceeded 1200nm. This data was used to predict the phase matching possibilities of the material and a paper on the work was presented at the Optical Society of America Annual Conference this past summer. Similar work was done on a material called ATCC which is also to be published. Good index data, especially at long wavelengths, is of great interest to the technical community.

Transmission spectra of materials were measured using standard spectrophotometers. The transmission spectra tells the relative amount of light that will pass through the material at different wavelengths. It is a property of molecules that they absorb light of certain wavelengths. Near these wavelengths, a very small amount of the light incident on the crystal will actually pass through. For device construction, it must be known where these absorptions will occur. The materials the lab is interested in developing are for use in a specific range of wavelengths, the nearinfrared. If there are absorptions in this range, the material is of no use to the Air Force. Looking at these graphs will tell whether or not the material may be useful.

The Kurtz powder experiment. When laser light, which is coherent and of very narrow spectral width, is passed through samples that have been crushed and sorted by particle size, a plot of intensity versus particle size can be obtained. The shape of this plot tells whether or not a material will be phase matchable, and if it is, over what range it will be so. To run the experiment, samples must be prepared. Crystals of the material were crushed into a powder and use industrial sieves and a shaker to sort the material by particle size. The sizes of the particles range from 5μ to 355μ where 1μ is one-millionth of a meter. The powders are packed into standard spectrophotometer cells and the experiment run.

The phase matching angles of a crystal can be calculated knowing the three indices of refraction. There will be three possibilities: second harmonic generation, sum and difference frequency generation. First, a curve-fitting program in FORTRAN was written to fit the index data to the Selmier equation which gives the index as a function of wavelength. A MATLAB program is being used to take the fitted Selmier coefficients and find the angles of phase matching for second harmonic generation and display the output intensity over the surface of a sphere. The program will be expanded to include sum and difference frequency calculations and optical parametric oscillation. An experiment which uses these types of predictions to build setups where these phenomenon could be used to tune the frequency of laser output.

Molecular orbital calculations are made to predict the non-linear optical properties of new materials. These new materials are variations of a small peptide, which is being altered molecularly to give new desired properties. Any promising results will be synthesized and tested in the lab.

Other aspects of the Task have included growing crystals for testing by mixing the solutions. Frequent literature searches are done at the technical library. Typically, as topics or titles are identified, research is conducted at the technical library.

The experience of working in the non-linear optical materials lab has been educational. I have not only learned about optical materials and non-linear optics, but I have also seen how basic research is done. I have gained a real appreciation for the importance of basic research and the pace at which it must proceed.

DEVELOP AND MAINTAIN A SOFTWARE DATA BASE FOR HAZARDOUS MATERIALS

Task Order No. 158
Student Support Program
Southwestern Ohio Council for Higher Education

Linda Wood
Wright State University

18 December 1995

Government Task Leader
Dr. Robert Crane
WL/MLPJ

ACKNOWLEDGMENTS

I would like to thank the following individuals for their support and assistance in my Task: Dr. Robert Crane, Dr. Wade Adams, Mr. Dennis Hagar, Dr. Tom Cooper, Dr. Ruth Pachtor, Mr. Marc Martin and Dr. Jim Lupo.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

A hazardous waste data base has been developed to document individual waste containers from satellite points. This system allows the user to view the waste containers generated in each satellite point chronologically. Individual container amounts, chemical composition, and amount of each chemical may easily be retrieved from the data base. Work has begun to create a data base with relational capabilities.

A relational data base design, an SQL data base design, appropriate for implementation using INFORMIX, a UNIX/VAX type data base software, or a comparable PC data base software has been created. The description of the problem the data base addresses, Entity Relation design, Relational Schema, and discussion of the design have been delivered. A data base implemented from this design will allow more complex data retrieval. It provides a mechanism for queries to be made associating many different types of related data. This type of data base will allow association of containers within a satellite point as well as association of contains of all satellite points. It would also allow manager to satellite point information retrieval such as start and end dates.

Procedures for completion of a hazardous waste container log sheet as well as waste container opening, closing, deposits, and storage have been developed. Training for these procedures has been given in individual and group sessions. A manual has been developed as a guide for these hazardous waste procedures. This manual is intended to be useful for research scientists and student employees involved with hazardous waste disposal.

Many different types of software have been investigated including software for spreadsheets, word processing, relational data bases, scanning, drawing, graphing, molecular modeling, converting file types, making forms, networking, system recovery, virus detection, and instrument data collection. Tutorials have been given to individuals on the usage of the software.

Maintenance has been performed on computer systems. Optimization of hard disks, computer backups, software installation and removal, system upgrades, installation of hard disks, reformatting of hard disks, recovery of systems from backups, and trouble shooting system failures and user errors have been performed on Macintosh systems within the division.

Evaluation and documentation of computer systems' software within the department were performed in preparation for computer inspections.

Investigation and documentation of branch computer systems' hardware were performed and compared with hardware available. Cost analysis of available hardware and the branch system analysis were scaled to create a plan for future annual computer system replacements and upgrades. Suggested purchases of number and type of computers was submitted.

Inventories of computer systems hardware and software were created. Hardware was grouped by location, user, computer type, amount of RAM, hard disk size, and monitor size. Software was grouped by manufacturer, name, serial number and user. The hardware inventor is intended to aide in computer tracking for replacements and upgrades. The software inventory is intended to aide in tracking and documentation for further computer inspections and software purchases.

DESCRIPTION OF RESEARCH

Computers have become an essential tool in research and can make or break the ability to remain on the cutting edge. The capabilities and cost of computers are continually changing. Flexibility and planning (and luck sometimes) in choosing a system, creating software, or purchasing software that doesn't become useless in less than a year are crucial factors in staying current with utilizing computer capabilities.

The consideration of user friendliness of systems and software should play a major role in computer purchases. If the computer environment follows a state of the art path but the user is incapable of keeping the pace because of a complex user interface, the computer system is no longer a tool to enhance production.

The flexibility of a system and software either allows for growth or becomes obsolete. If they become obsolete within a short period, cost factors for total replacements can be devastating.

Many different computer systems were used in this Task. UNIX, VAX/VMS, Macintosh, IBM, and IBM compatible were utilized.

In addition, CD-Roms, Magnetic tape drives, portable external hard drives, external ethernet cards, and digital scanners were used in this Task.

RESULTS

Computer systems and software are constantly being improved. What is innovative and necessary today may be backward and useless in 8 months in both hardware and software. Careful planning with considerations for flexibility as well as cost is necessary to utilize computers effectively and efficiently.

In research, computers can make or break the speed of discovery. The user friendliness of computer systems and software as well as the flexibility of the computer system and software design can make the difference in being the leaders in research or the followers.

ADVANCED COMPOSITE MATERIALS DURABILITY ANALYSIS

Task Order No. 159
Student Support Program
Southwestern Ohio Council for Higher Education

Joseph Scheckel
Wright State University

31 December 1995

Government Task Leader
Lt Jeff Schaff
WL/MLBM

ACKNOWLEDGMENTS

I thank my coworkers at Wright Laboratory Nonmetallic Material Division and at the University of Dayton Research Institute as their cooperation and recommendations were instrumental to accomplishing this Task. Special thanks goes out to Lt Jeff Schaff, my Government Task Leader. Because of his mentoring, I was allowed to make many of my own decisions and to take on more responsibility for my work.

One objective for this Task was to help researchers better understand the mechanical response of composite materials in Air Force structural applications, in particular, composite bolted joints. In this work, methods for drilling holes in composites were investigated to reduce the number of drill induced cracks, thus optimizing hole perfection. This allowed scientists to analyze failure mechanisms in these high-strength, low-weight materials by determining the origin of micro cracks.

Research also continued for determining why the sequence of cyclic loading affects composite fatigue life. This is essential for estimating aircraft life and durability and, thus, is a critical issue for Air Force weaponry longevity objectives.

The final objective for this Task was to help develop a crutch for the handicapped made from composites. The standard wrist-wrapping crutch is made from aluminum and there have been little if any advances with that model in forty years. The proposed composite crutch will be lighter in weight, will provide better mechanical response, and will be more aesthetically pleasing.

DRILLED HOLE INVESTIGATION

In this study, 12 drilling methods were investigated. Initially, four composite test panels were drilled with three holes each at speeds of 600, 900, and 1200 rpm's, respectively. The holes in the first and second panels were made with a 1/4" diameter helical circuit board drill bit while those in the third and fourth panels were made with a 1/4" diameter diamond-core drill bit.

The first panel was supported on the bottom side with a sheet of glass-epoxy material while the second panel was supported on both the top and bottom. The first method was designed to reduce cracks on the bottom side caused by "push through" from the drill bit. In the second method, the top reinforcement plate was incorporated to try to reduce tearing of the outer composite ply due to radial drill bit forces.

A diamond core bit was chosen for the third and fourth methods. This drill bit, designed for water submersion drilling, consists of a hollow cylinder with a fine diamond outer coating which grinds rather than cuts the material. Internal water flow in the bit flushes out any small blockages and washes away the particles as the drill bit grinds away at the composite. This drill bit was expected to reduce tearing of the material thus providing a better quality hole. Originally, there was an attempt to use a top reinforcement plate for one of these methods. But this was unsuccessful because the reinforcement material would completely block the internal water flow in the drill bit before reaching the composite panel. The drill bit then had to be removed for unclogging and repositioned in the drill chuck with the hope of realigning it with the hole. The third method consisted of a glass epoxy bottom reinforced panel with a plywood support. Because of flexing of the plywood, a fourth method was investigated incorporating an aluminum support.

After all specimens were drilled, zinc-iodide penetrant was applied to the hole edges. Once the penetrant was fully absorbed, the samples were x-rayed. These x-rays are simply photograph negatives and, therefore, were sent to the base Technical Photograph Department to obtain blow-up photos of each hole. This was necessary because the micro cracks were too small to observe with the naked eye. From these photos, the method producing the best quality hole was the second method at a velocity of 900 rpm's. More holes were then drilled with that method to obtain a better distribution to ensure that this was the optimum drilling method.

To insure that the lines on the photographs were indeed micro cracks, the specimens were cut in half at the holes and the hole edges were polished for viewing under a scanning electron microscope. This was not only a success, but it also provided a means of determining which plies contained the cracks.

The significance of this work is that it provides scientists with a high quality hole necessary for composite bolted joints research and an explanation for the extent of damage due to drilling and loading.

LOAD SEQUENCE EFFECT ON COMPOSITES

A comparison between the effects of cyclic loading during fatigue took place where two sets of experiments undergo two stress level loading. In one set of experiments, the loading consisted of large cycling blocks where the specimens intermittently experienced two stress levels. In the other set of experiments, the specimens experienced small cycling. The only difference between the large and small block loading was that the frequency of stress level changes was higher. The comparisons made included fatigue life and micro crack density.

This research involved the development and execution of a test plan that included the manipulation of computer software to perform the large and small block loading sequences on the test frame. The test specimens were methodically removed from the testing frame for the gathering of stress-strain plots, microphotographs and x-rays so that states of damage could be documented and compared. During this process, the limitations of the specimen design were recognized.

Other than the accelerated rate of change for the small block loading, the stress-strain plots showed no significant differences between the mechanical properties of large and small block loading. Both the axial and transverse elastic strains increase during fatigue life. Passion's

Ratio and Young's Modulus for both load types are primarily dependent on the transverse and axial strains, respectively. Average test data also indicates that small block loading adversely affects specimen fatigue life more than large block loading.

X-rays of small block and large block specimens show that their damage mechanisms are similar while de-laminations are the primary contributor to failure. Microphotographs of cross sectional areas of test specimens showed that de-laminations formed and expanded more slowly in large block specimens than in small block specimens.

Tapered glass-epoxy tabs were glued to the ends of the specimens so that they would not be damaged by the grips of the test frame. Due to tab design, the number of tab failures was high and redesigning was necessary to reduce premature specimen failure. Therefore, additional research was necessary to determine the effects of tab design on specimen performance. A series of experiments are being conducted on specimens with different tab designs. These tests consist of statically loading specimens with different tab configurations. Several strain gages were applied to the cross sectional edge of the specimen at the tab and at the far field to obtain a strain distribution. The results will then be plotted for several tab designs to select the one that provides the least stress concentration at the tabs. Future loading with the new configuration will then complete the testing portion of the program and final conclusions can be made.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND EVALUATION SECTION
ML/MLSE

Task Order No. 160
Student Support Program
Southwestern Ohio Council for Higher Education

James W. Stubbs
Wright State University

31 December 1995

Government Task Leader
Mr. Jim Folck
WL/MLSE

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GENERAL DESCRIPTION OF TASK

The objective of this Task was to conduct short investigations in-house to assist in the evaluation of various materials and processes for Air Force applications. The Task was completed through continuous part-time work over the coarse of the year. Work was done to assist in the fabrication, testing, and evaluation of test specimen made from experimental and existing materials. The students were involved to some extent in many active projects during the work periods. The bulk of these projects required fabrication and testing of various test specimen to examine the feasibility of adhesive systems for possible Air Force applications.

DESCRIPTION OF RESEARCH

Adhesive evaluation was continued on two projects during this Task. The first of these was a series of tests to determine the shelf life of certain adhesives subjected to different storage conditions and times. Samples were prepared for overlap shear, flatwise tension, and floating roller peel. The samples were then tested on an Instron 4505 testing machine. The results were compared with the original testing results to judge the loss of strength due to long-term storage. The other project dealing with adhesive evaluation was a series of tests to find an adhesive with good high temperature qualities that could be cured at low temperatures. The adhesive was for repair of an Air Force airplane that required an adhesive that could be cured below 250°F to prevent structural damage to the aircraft, yet maintain 1800 psi at 350°F. Specimens were fabricated under 35 psi positive pressure and temperatures under 250°F for various cure times for overlap shear testing at 350°F. Research was also continued on the overheat damage project started during the last Task. A wide range of panels was tested in flexure and shear after exposure to varying levels of radiant energy. This student was involved both in the conditioning and testing of these panels during this Task.

RESULTS

In the adhesive storage project, the candidate adhesives were stored at room temperature, under refrigeration, and at 0°C. It was found that the adhesives under study had the longest shelf life when stored at 0°C, with the greatest loss of strength when stored at room temperature.

Only one of the adhesives tested thus far in the repair concepts program has shown any promise. Four of five adhesives cured at or below 250°F had overlap shear strengths of 1200 psi or less. The other adhesive tested showed a strength of approximately 2000 psi even when cured as low 180°F. This adhesive is currently under more testing to examine the repeatability of these values.

In the overheat damage project, several ways to find damage that is not visible are being tested. A lamp-bank and fixture system was designed that allowed for large panels to be tested while maintaining constant temperatures over the majority of the panel. Approximately half of the data for the completion of this project has been taken. Many of the thick panels are still being exposed to humidity prior to thermal exposure and therefore have not been tested.

SYSTEMS SUPPORT MATERIALS BEHAVIOR AND EVALUATION SECTION
ML/MLSE

Task Order No. 160a
Student Support Program
Southwestern Ohio Council for Higher Education

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Government Task Leader
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WO/MLSE

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The people at Wright-Patterson have helped me perform my duties very well. The support that was given to me by all members of the Systems Support Team was instrumental in helping me complete the projects I worked on. Also, the engineers and technicians helped expand my interest in composite materials, which was the main purpose for my desire to obtain this job. I would personally thank the following people with whom I have worked for the last 8 months: Ron Khubander, Jim McKiernan, Doug Carter, Brian Cramer, Jim Mazza, Jim Folck, Mark Kistner, Greg Elam, Bill Hoogsteden, Dan McCray, Rob Cassoni, and Sean Friedman.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The projects on which I worked; bolted bondline thickness experiments, foam core physical property test, characterization of Magnolia Two-part Epoxy adhesive, and the characterization of low voc adhesive primer; were conducted for the advancement of composite aircraft repair. Each project represents a special area of composite repairs.

The bolted bondline experiments were used to understand the variation in the adhesive bondline when rivets are used to apply the bonding pressure. The thickness of the bondline was measured with respect of the distance between bolts. This rational helps engineers give proper design criteria for maximizing the strength of the adhesive bondline.

The foam core with which I worked was used in the fabrication of military shelters. The experiments performed were water absorption and flammability. Both tests relate to conditions which the shelter may be exposed. The foam that I worked with passed the test very well.

Magnolia Two-Part Epoxy is similar to an adhesive used frequently by the AIR Force. These types of adhesives are formulated for bonding materials with differing coefficients of expansion. The addition of aluminum powder in the adhesive increases its viscosity. This increased viscosity makes it perfect for composite repair. The tests ran helped clarify the processing parameters for this adhesive plus identify its similarity with presently used adhesives.

Low VOC (Volatile Organic Compounds) primers are of interest now because of the need to reduce pollution. The primer which was studied is a water based primer with epoxy particles in suspension. Tests performed were used to characterize the properties of the primer at several different conditions. Comparisons were made between this primer and presently used primers.

Presently primers used in the field are MEK (methyl-ethyl-keyton) based and posses some pollution problems.

DESCRIPTION OF RESEARCH

Most of the test performed was used to measure various types of strengths. Lap shear and floating roller peel tests were the key experimental strength measurements performed. These tests gave the engineers an idea of the adhesive strength as well as the bonding strength. Depending on what was being studied, one or both of these tests were prominent in the research plan. Other tests performed were environmentally and physical property related. Instron and Tinius-Olsen test machines were used for mechanical property testing. Humidity and salt fog cabinet were used for the environmental test. Data was analyzed on computer, as well as by hand.

RESULTS

I was able to gain common, as well as advanced, knowledge of composite design and processing. The test methods used are common throughout the industry, while some are very unique. Performing these tests were very interesting. In the short time I worked here, I gained more knowledge about polymer composites than could possibly be learned in the class room. This position helped me become familiar with several different types of equipment such as autoclaves, hydraulic presses, test machines, humidity cabinets, lathes, and spraying devices. Also, I gained some engineering experience in the interpretation of data by hand and with computer assistance.

SYSTEMS SUPPORT - MATERIALS BEHAVIOR AND EVALUATION SECTION
WL/MLSE

Task Order No. 161
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Cassoni
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31 December 1995

Government Task Leader
Jim Folck
WL/MLSE

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GENERAL TASK DESCRIPTION AND ASSIGNMENT

Task 161 consisted of many projects which involved composite and sandwich core research, development, and supportance. These projects will be considered individually and are as follows:

1. Project 003: High Temperature Composite Repair.
2. Project 081: Comfort Liners for Pilot Helmets.
3. Project 096: Closed Cell Structural Foam for Supporttability Applications.
4. Project 139: Core Materials for Shelter Structures.
5. Project 140: Bondline Temperature Monitor and Control.
6. Project 141: Heat Lamps for Primer Curing.

Project 003 involved the mechanical evaluation of composite lap shear specimens at room temperature, 700(F dry, and 700(F wet to determine the strengths of two different high temperature adhesives. The work was performed on an Instron 4507 tensile machine using a standard ASTM lap shear test method. The work was accomplished in conjunction with the Navy.

Project 081 involved the mechanical evaluation of pilot helmet comfort liner materials. Armstrong Laboratory expressed concern of the stability of these helmets when night vision goggles are attached as well as during high gravity maneuvers and asked Wright Laboratory (WL/MLSE) to develop a test matrix and test three of the currently leading helmet liners. The test matrix involved ASTM standard compression, creep, and coefficient of friction testing. Fixtures were constructed for both the creep and coefficient of friction testing as it was necessary to properly conduct the testing. All testing was conducted on a Sintech tensile machine (courtesy WL/MLB). Upon completion of the testing, an Air Force Technical Report was written.

Project 096 is an on going assignment which involves the mechanical evaluation of structural core materials to be used in the supporttability of aircraft. The test matrix involves the testing of approximately 15 different types and densities of core materials using ASTM standard flatwise compression, flatwise tension, dogbone tension, and compression plate shear at both dry and humidity aged conditions. All testing was performed at room temperature, 180(F, and 212(F. Modulus and strength were measured for each of the materials and testing configurations to determine the feasibility of its usage in supporttability applications. The equipment used on this project included various Cincinnati Sub-Zero and Blue M humidity cabinets, Instron 1125, 4505, and 4507 tensile machines, MTS screw-based tensile machines, various extensometers (MTS and Instron), and Wabash presses. The test matrix should be complete by the early part of 1996 with the results being written into an Air Force Technical Report.

Project 139 involved the mechanical evaluation of core materials to be used in the construction of shelter structures for disaster relief and other applications. Specifically, the project was to qualify an Israeli core material under U.S. Mil-Spec standards. The testing consisted of ASTM standard compression, tension, and plate shear which was performed on the Instron 4507 tensile machine. This work was conducted in cooperation with the Army.

Project 140 involved the research and development of various methods to place thermocouples and heating elements within the adhesive layer of a composite repair and determine the level of benefit or degradation caused by it. Several thicknesses of thermocouples and insulation have been investigated with promising results. To determine the effects of these objects within the bondline, several ASTM standard test methods were used including lap shear, peel, and fatigue lap shear. This work is currently being held due to higher priority projects.

Project 141 involves the research and development of various methods of curing primer coatings on aircraft. A large temperature gradient across the bonding surface is created under the current method which degrades the quality of the bond that can be achieved. The method being investigated has greatly reduced this temperature gradient and is being tested and optimized for possible wide spread field usage. This work is currently being held due to higher priority projects.

I felt that this Task has been a great learning experience. I have been actively involved on many projects in which I had the opportunity to be an author on the 081 technical report, as well as be one of only two developers on the heat lamp bank that was developed on project 141. I have also had the opportunity to use my knowledge on the testing machines to train other technicians. I look forward to my next Task to complete many of these projects.

TO EVALUATE THE FATIGUE CHARACTERISTICS OF SEVERAL ADVANCED CERAMIC MATRIX COMPOSITE MATERIALS

Task Order No. 162
Student Support Program
Southwestern Ohio Council for Higher Education

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Government Task Leader
Larry Zawada
WL/MLLN

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TASK ASSIGNMENT

The objective of this Task was to provide assistance in the study of the fatigue characteristics of several advanced Ceramic Matrix Composites (CMC) materials. Specifically, support was provided in the study of the durability of coated silicon carbide fiber-reinforced carbon (SiC/C). The durability of SiC/C was assessed by subjecting test coupons to a number of mechanical and thermal tests as well as optical and electron microscopy inspection.

TEST PROCEDURES

Under this Task, pre-conditioning fatigue tests were performed on a number of SiC/C material coupons in an MTS horizontal servo hydraulic test machine. The specimens were fatigue tested at a maximum stress of 125 Mpa for 1000 cycles at room temperature.

After pre-conditioning, isothermal heat treatments were conducted in both a digitally controlled box furnace and a tube furnace on several specimens. The designated specimens were heat treated for wither 10 hours or 30 hours at 1093°C (2000°F). By strictly conduction heat treatments without thermal cycling, the effect of time at temperature on the material can be evaluated and compared to thermal fatigued specimens.

Thermal fatigue tests were performed using a resistance heated tube furnace, with a computer-controlled in-line pneumatic actuator to position the specimen in and out of the furnace hot zone. Barber-Colman temperature controllers in conjunction with a PC based data acquisition system ged from S-type thermocouples allowed the thermal cycle to be defined by the specimen temperature. The software was programmed to move the specimen out of the furnace when the specimen temperature reached the maximum desired temperature of 1093°C (2000°F) , and into the furnace when the minimum test temperature of 427°C (800°F) is reached. The data acquired maximum and minimum temperature versus cycle count, as well as the thermal profile during heating and cooling. A designated number of specimens were tested at the condition described above for wither 1500 or 4500 cycles.

Upon completion of all thermal testing, the specimen were prepared for post-cycling strength testing. Each specimen was prepared by hand-grinding rough spots in the coating smooth using a 75um diamond wheel and applying tabs to each end. The tabbing technique and tab material was selected after several trial residual strength tests on SiC/C material. Residual strength tension tests were then performed on each of the thermally tested specimens.

RESULTS

Tensile curve were generated for each of the tested specimens using MATE software on a DOS based computer and Kaleidagraph on a Macintosh computer. The reduced data were then compared on the bases of maximum stress and strain, and shape. The specimens heat treated for 10 hours had strengths of 193 Mpa, 194 Mpa, 189 Mpa, and 22 Mpa, respectively. The strengths measured for 30 hours showed an average decrease in strength of 20 Mpa. The average residual strength for the 1500 cycle and the 4500 cycle thermal fatigue tests of 193 Mpa and 194 Mpa, are practically identical to the average strength measured for the shorter heat treatment. All tensile curves for the thermally tested coupons showed linear behavior and showed improved strength over as-received material coupons which were tension tested.

Other information obtained from the residual strength tests performed on SiC/C, include the modulus results, the strain at failure measured and the fracture location observed could also be considered for damage assessment. The method used for measuring the moduli during the residual strength tests used up to 12% of the maximum load-in stress as for linear regression and slope calculation. The modulus results showed that the average for the as-received tensile tests 77 Gpa. Upon pre-conditioning fatigue testing before thermal testing, the modulus fell and then stabilized at an average value of 53 Gpa in the case of each specimen. Then, during tensile loading the moduli measured in almost every case was increased slightly from the modulus measured on the 1000th cycle of the fatigue uet was decreased slightly from the as-received measured stiffness to average values of 60 Gpa, 59 Gpa, 57 Gpa, 60 Gpa, and 56 Gpa for each of the respective test conditions.

As well as stiffness of the material, the strain at failure may be indicative of the damage incurred by thermal testing. In general, the percent strain measured was smaller in the case of the weaker specimens and the strain was larger for the stronger specimens as was expected. The average percent strain for the as-received tension tests is 0.36% whereas the average percent strain for the other tested condition are 0.33%, 0.36%, 0.38%, 0.39%, and 0.38% respectively.

The last observations made from the residual strength tests to be included in the damage assessment of SiC/C is the failure location observed for each specimen. Almost every specimen failed inside the wedge grips on either the load cell side or the actuator side of the test machine. The fracture occurring inside the wedge grips implies the alignment of the machine may not have been accurate and may have induced bending stresses on the specimen as well. One of the specimens which did not have failure in the grip was heat treated for 10 hours, had a strength of 193 Mpa, and failed in the middle of the gage section. Since the strengths measured for all the specimens had the same strength, it was observed that failure location on the test specimen did not have an effect on the strength of the material.

In order to verify that none of the thermal simulation tests conducted induced significant damage to the microstructure compared to the as-received microstructure, optical and scanning electron microscopy were performed. So far, representative samples from two of the four different thermal test conditions as well as-received material samples have been prepared and inspected optically. Additionally, fracture surfaces from all the different test conditions after residual strength testing were inspected, including the fracture surfaces of an as-received and a pre-conditioned specimen.

CONCLUSIONS

The objective of this study was to characterized the thermal fatigue behavior of the advanced CMC known as SiC/C. Assessment of the material's performance was attempted through comparison of the residual properties measured for each test condition. Verification of the results was documented through microscopic inspection.

The conclusions made as a result of this study are as follows:

(1) There is no degradation in strength when coated SiC/C is subjected to mechanical cyclic loading to a maximum stress of 125 Mpa for 1000 cycles followed by isothermal heat treatment at 1093°C (2000°F) for either 10 or 30 hours.

(2) There is no degradation in strength when coated SiC/C is subjected to mechanical cyclic loading to a maximum stress of 125 Mpa for 1000 cycles followed by thermal cycling between temperatures of 427°C (800°F) and 1093°C (2000°F) for either 1500 or 4500 cycles.

(3) There was no significant variation in strength beyond the inherent scatter in the material between any of the tested coupons.

(4) SEM and optical microscopy studies revealed no distinct differences in the fracture surfaces or the micro structure of the thermally tested specimens which supports the observation of no loss in strength from any of the test conditions.

RESEARCH ON HIGH TEMPERATURE INTERMETALLIC ALLOYS

Task Order No. 163
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Southwestern Ohio Council for Higher Education

Michael A. Jackson
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Government Task Leader
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WL/MLLM

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GENERAL TASK DESCRIPTION

The description of work for the current Task is for the sample preparation and heat treatment of intermetellic alloys for metallographic examination. The Task was subdivided into smaller sections that generally needed between one week to several months to complete and was directed by either Dr. Kim or Dr. P.R. Subramanian. These smaller assignments were the basic building blocks to the completion of the overall goal of the Task.

The applications for the alloys studied during the Task are within the aerospace and automotive industries. In the aerospace industry, the quest for lighter weight components and ever increasing operating temperatures of jet turbine engines is a focus of today's research by DOD contractors and civilian companies alike. The realized material for the application would have to exhibit high tolerance to oxidation and creep, and have a low density, all of which contribute to a higher performance of the engine. The new material may find its way into applications involving the next generation fighter aircraft or the National Aerospace Plane effort.

An ongoing effort to transfer these new technologies to other industries has seen the beginnings of use in the automotive market. The engine of today's automobile needs to be lighter and more efficient than ever before, while still maintaining or increasing the performance and decreasing the environmental impact of the emissions. The alloys under study, while still in the experimental stage of development, are starting to find uses as engine components with superior wear resistance than today's common place materials. Although these alloys are promising, they still pose quite a problem in the manufacturing domain. One of the goals of the current Task is to refine the feasibility of the manufacturing process of such parts. While the process looks hopeful, actual implementation may be far away in time.

DESCRIPTION OF RESEARCH

The workload consisted of the heat treatment, metallographic examination, and microscopic examination of the experimental alloys. The heat treatments included using both the atmospheric and the argon atmospheric furnaces, where as the heat treatment could last as long as 500 hours. The heat treatments were used for several reasons, including, but not limited to the following, refining the microstructure, oxidation studies, studying the growth rate of lamellae and grains, and recovery of the microstructure from mechanical processes. After the completion of the heat treatment, the metallogrpahic preparation of the specimen was performed to facilitate one of many examination techniques.

These techniques included both the macroscopic and microscopic examination of the microstructure and to a limited extent, the mechanical properties of the alloy. An optical microscope was used for low magnification studies (50x to 500x) of the microstructure, while a Leica model 360FE Scanning Electron Microscope (SEM) was used for high magnification studies (500x - 50,000x). For the qualitative determination of the composition of the studied alloys, Back Scatter Electron imaging (BSE) and x-ray analysis was used leading to a total of approximately 100 hours of SEM time. The above microscopic instruments were used to help determine the mechanism by which deformation occurs in the alloy during heat treatments or mechanical testing. While the bulk of the mechanical testing was completed by outside contractors, limited tests were conducted during the Task, including the micro and macro hardness of the studied alloys.

RESULTS

Numerous relationships between the composition, heat treatment, stress, strain, fatigue cycles to failure, hardness, and aging were all studied during the Task. All are included in the characterization process of the materials. The data was given to the lead engineers to make the appropriate theoretical studies, from which, new tests and alloys are developed for further testing. The testing and development of these alloys will one day yield a superior material for use in wide ranging applications including, but definitely not limited to the aeronautical and automotive industries.

ADVANCED COMPOSITES

Task Order No. 164
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Government Task Leader
Dr. Howard W. Brown, III
WL/MLBC

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TASK ASSIGNMENT

In today's world, there is a great demand for higher performance and lower cost in nearly every area of manufacturing. One of the most promising ways for lowering costs and achieving higher performance levels is through the development and use of new materials. Carbon-carbon is one of the leading areas in material research today. Due to its great strength, low density, resistance to extremely high temperatures, high degree of stiffness, and low coefficient of thermal expansion (CTE), carbon-carbon has become a vital part of the aerospace industry already and is making great strides in becoming an important part of the automotive and construction industries. At this point, carbon-carbon composites are expensive, and so the most efficient manufacture of a composite possible is very important. To find the most efficient design of a carbon-carbon composite, experimental structural tests have been run in many cases. However, this report will focus on another aspect of the analysis: mathematical modeling.

Computer-simulated Carbon-Carbon Composites

This project uses the model set down by Dr. N. J. Pagano in his article "Axisymmetric Stress Fields in Involute Bodies of Revolution" published in Journal of Spacecraft and Rockets, so much of the actual mathematical modeling has already been set down in this paper. However, the calculations required to simulate an actual composite are so complex that a computer is necessary to solve them (realistically).

At the beginning of this Task, a program had been written in FORTRAN by Dr. Brown, that translated the mathematical model set down in Dr. Pagano's paper for a specific set of conditions. Since this program uses the method of finite element analysis, it can be applied to other applications. While the program worked very well, it was very limited in its usage and needed to be extensively modified for each new situation. It is believed that if the program is made easier to use and adapts more easily to different applications, then it could have possibilities for sale to the public. The aim of this Task was to reprogram it more generally to make it useful by letting it apply to a larger set of conditions.

This will also make it easier to model different types of carbon-carbon systems and will help in the understanding of what makes a composite stronger. Development of better materials would become easier because different variables could be changed using the model and no actual material (expensive material) would be wasted. A computer program makes the solving of many different models possible in a much shorter time frame.

SPECIFICS OF GOALS

Computer Simulated Carbon-Carbon Composites

The computer program gave little flexibility to the user. Each set of formulas had to have either 16 or 18 equations. Also, for accuracy, two equations were added to each of the major equation sets in the program (those found in the CORE and COATNG subroutines). Next, the program could only handle models with only two continuity conditions, which yielded only four different possibilities. Each possibility was dealt with on an individual basis. However, to make the program easier to use, it was felt necessary to be able to handle as many continuity conditions as necessary. This requirement also necessitated that a general case for handling each continuity condition be found (since for every N continuity conditions, there are 2^N possibilities). Finally, the method of eliminating derivative terms in the main array needed to be altered, since the locations of the derivative terms were known in the previous program and were dealt with on a case-by-case basis. Again, this had to be changed for the new program, since it was not known where the derivative terms would be located. A general method for their elimination needed to be devised.

WORK DONE ON EXISTING PROGRAM

Computer Simulated Carbon-Carbon Composites

First, the subroutine SCTN was altered to accommodate any number of equations, and the appropriate variable declarations were made throughout the program. Next, the two functions

were added to the CORE and COATNG subroutines as well as all the supporting equations used to develop and reference these functions.

The next Task was to rewrite the SCTN subroutine so that it would affect the appropriate continuity conditions regardless of how many were defined at the beginning of the program. This required nearly an entire rewrite of that subroutine. After some work, Dr. Brown submitted a subroutine to handle an indefinite amount of continuity conditions. After setting up a test design outside the framework of the program using small, much more manageable arrays, problems were found with this algorithm and were fixed accordingly. The code was then transferred to a developing subroutine called NWSCTN. The derivative elimination code was then programmed quickly and the subroutine was completed.

The new program was run and the output was compared to the original. After successive tests, it was found that the addition of two functions to CORE and COATNG subroutines affected the output so much that an altered program needed to be made to compare outputs properly. This was achieved by replacing CORE, COATNG, and SCTN2 in the old program only, but leaving the SCTN subroutine unmodified.

Through the comparison of these outputs, some minor problems with the CORE and COATNG functions were found and corrected. After extensive printing of arrays, it was found that the main arrays in both programs agreed before they were exposed to the alterations of continuity made in SCTN and NWSCTN. However, there was a serious discrepancy afterwards.

After much analysis, this problem was attributed to an error in the modification of the old program to the program used for comparison purposes and not in its extensive modification. The number of functions was increased by two in both CORE and COATNG, a couple other minor problems were fixed, and the data in the arrays agreed afterwards much more.

The discrepancy that remained was attributed to the derivative elimination. Upon further discussion with Dr. Brown, it was found that the algorithm for this process needed serious modification. Also, a test was done, eliminating this from the new program and the output did agree for no continuity conditions. Therefore, this is where the problem existed.

The derivative elimination code was rewritten. Some output comparisons were made. Further testing still needs to be done to make certain of the validity of the elimination code.

RESULTS

Computer Simulated Carbon-Carbon Composites

This modeling program, by all indications, has been adapted according to the goals outlined above. Equations have been added to CORE and COATNG according to Dr. Brown's specifications, and no problems have been found with these over the course of the last month. The program also has shown no problems with the changes made to accommodate different sized systems of equations.

The handling of the continuity conditions also shows no problems when only two continuity conditions are present. This is the only number of continuity conditions tested in the context of the program because the only matrix to compare with comes from the old program which can only handle two continuity conditions. However, in outside testing, the algorithm handling the continuity could handle up to five continuity conditions, but this has not yet been tested in the context of the large program.

Finally, the derivative elimination seeks to create a matrix in which there is only one non-zero term in any row or column. The derivative elimination routine in all tests up to this point has done this. However, the solutions of the problem do not agree with the solutions gained from the unmodified program. Upon analysis of the less modified program's output, it was found that the derivative elimination code in that program was not doing its job. There is at least one instance of two non-zero terms being in the same row. This does have an explanation. The less modified program has two functions added to CORE and COATNG to let the outputs be close enough to compare at all. This creates a problem in the subroutine SCTN. Since SCTN changes only specific spots in the matrix to eliminate the derivative terms and does not check to see if these are the correct terms (because the positions were figured out for each condition specifically), the derivative terms are not eliminated. Without the derivative terms eliminated, the output of the less modified program is not correct. This makes a comparison of the outputs invalid.

The next order of business is to adjust for the two functions added in the CORE and COATNG subroutines so that the derivative terms are eliminated properly in the less modified program. Later an accurate comparison can be made between the programs.

There is also further testing to be done on the program after the derivative elimination routine is verified. The program should be tested for additional continuity conditions and given many more sets of data to insure that there are no errors.

INFRARED LASER LABORATORY DATA ACQUISITION AND CONTROL (DAC) DEVELOPMENT

Task Number No. 165
Student Support program
Southwestern Ohio Council for Higher Education

Brian Deep
University Of Dayton

15 January 1996

Government Task Leader
Dr. Patrick Hood
WL/MLPJ

ACKNOWLEDGMENTS

The Task involves working primarily with Dr. Patrick Hood, Shekhar Guha, Chuck Lovett and Mike Thomas. Thanks are given to Dr. Hood for helping learn the basic overview of the program and for guidance and assistance in getting the Task started, to Shekhar for helping to learn the optical experimentation process, to Chuck for helping out with everything, and to Mike for helping to grasp a basic knowledge of optics.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

This Task mainly involves the learning and implementation of a software package called Labview. The purpose of implementing this software package is to experimentally automate optical experiments for laser hardening. This software is used in conjunction with General Purpose Interface Bus (GPIB) and relay card hardware to automate experimentation.

The purpose of the experimentation was to discover the optical characteristics of materials at 10.6 micron wavelength for optical detector purposes. Different materials are tested and the optical characteristics of the materials are charted to discover whether or not the material is suitable for optical detector or protector purposes.

The automation process involves designing Labview programs to emulate the experimental process and remove the user from tedious data gathering tasks. Labview is a graphical programming language that allows for a graphical user interface to the experimentation process. This software is used to communicate with data gathering devices via GPIB to gather and manipulate experimental data. The data is then graphed in real time so that the user can see experimental results as they occur.

The equipment involved in the automation is a ZEOS 486-66 with 16 MB of RAM running Windows 95, a Laser Precision RM6600 with energy probes for measuring laser beam energy at different positions in the optical setup, a PMC400 Newport motion controller for moving the sample within the beam path, and a Lakeshore 330 temperature controller for thermal control of the sample. Also, a proprietary relay-controlled device is used to control the placement of attenuators in the path of the laser beam to control the amount of energy reaching the test sample.

The major problem involved getting the devices to communicate with the computer and getting the software to recognize the devices. Once this was accomplished, the Task turned towards programming in Labview.

The developed Labview program runs and gathers data from each of the devices, graphs the necessary data and writes all data to file. In order to produce professional looking graphs, the data is taken to Microsoft Excel and a macro was developed to process the data quickly and produce a titled and dated graph of the desired data.

This Task also involves learning the basics of the optical experimentation setup. During the Task, a person learns the basics of optical lenses, the focusing and de-focusing of the laser beam, steering the beam and setting up energy detectors and pinholes for the laser to shoot at and through. The main concept in the learning process was learning laser safety. When working with a CO_2 10.6 micron laser, an invisible beam, the user must know the path of the beam and be constantly aware of whether the beam is on or not. The laser can cause extreme retinal damage so eye protection is always worn.

Another project that this Task involved transmission electron microscope (TEM) sample preparation. Glass samples are cut to microns thick and polished for use with the microscope. The preparation of the samples is a tedious and time consuming task that involves a lot of patience and care. These samples are then placed in a TEM for observation at high magnifications and examined at various temperature levels.

Another fun part of the Task involved the use of Night Vision Goggles (NVGs). The Task involves dealing with the use of NVGs for medical research. The lights are turned off in a room and an infra-red light is placed behind someone's hand. The night vision goggles are turned on and show the veins in the hand of the subject. The purpose of this Task is to find out how helpful these tests are for practical medical purposes and to discover just what can be seen through this technique.

The main portion of this Task involved a quick learning curve of the Labview software package. Once this knowledge was attained, the Task simply involved the development of programs to reproduce the desired experiment.

This Task shows that optics is an ever growing field and that there are many undiscovered ideas in the field of optics. The Task will involve many more experiments on untested or rarely tested materials and hopefully will give the world a better understanding of certain optical material properties.

ATION OF NONLINEAR INFRARED MATERIALS

Task Order No. 166
Student Support Program
western Ohio Council for Higher Education

Michael S. Thomas
University of Dayton

17 January 1996

Government Task Leader
Dr. Patrick Hood
WL/MLPJ

ACKNOWLEDGMENTS

First, I would like to thank Dr. Patrick Hood for his patience, guidance, wisdom, and understanding throughout this Task. The contributions and tutelage of the government personnel at WL/MLPJ are greatly appreciated.

I would also like to thank Mrs. Wanda Vogler of the Southwestern Ohio Council for Higher Education for giving me the opportunity to fulfill this Task at Wright-Patterson AFB.

The laboratory work on Task Order No. 166 has been performed in the CO_2 laser laboratory for Wright Laboratory at Wright-Patterson AFB under the direct supervision of Dr. Patrick J. Hood. The work on this Task has been performed in conjunction with a separate Task granted to Brian Deep (who is also subcontracted through SOCHE). The combined work lead to the automation of materials testing in the CO_2 laser laboratory. Laboratory automation was desired due to the amount of time required to manually characterize samples and also due to the large number of samples to be tested. The result of this effort decreased the amount of time required to characterize a single thin-film material from several hours to approximately 25 minutes.

During the extent of this Task, much work has been performed characterizing infrared nonlinear optical materials. Most of the materials and devices tested are optical switches and limiters, which means that these optical materials will decrease the throughput energy under large values of fluence. In order to characterize these materials, it is necessary to move the sample about a focused spot (in which the total fluence may be determined) of a laser beam while measuring the transmitted energy. The laser beam can then be manipulated to vary the amount of fluence incident on the sample.

A 4 x 8 foot optical table was used to mount the necessary optics to carry out this experiment. A tunable TEA (Transverse Electrode Atmospheric) CO_2 laser was used as the laser source. According to the manufacturer's specifications, this laser is capable of producing a maximum of 50 mW of power at the 10.6 μm laser line. (However, because we did not operate the laser at maximum power and due to losses on the optics table, the power in the laser beam incident on sample was approximately 7 mW.) Although this TEA CO_2 laser is capable of several far infrared laser lines, the primary wavelength used for materials testing was 10.6 μm.

The experimental optical setup is attached and can be seen in Appendix A. Gold coated infrared reflecting mirrors were used to guide the laser beam around the optical table. The laser beam was first directed through two water cooled Brewster Angle Polarizer's. These water cooled Brewster Angle Polarizer's consist of a plate of Zinc Selenide (ZnSe) which is positioned at the Brewster angle (hence the name) such that the exiting beam has a polarization that is dependent on the orientation of the ZnSe plate . These polarizer's were positioned such that the laser beam would be polarized in the vertical direction (perpendicular to the tabletop). Two polarizer's were used to better polarize the laser beam.

Next, two ZnSe aspheric lenses (f = 2.5 in.) were used to create an intermediate focus of the laser beam. This focal plane was for the position of an optical chopper when long pulse high energy testing was done. Then, a 50/50 beam-spliter was placed in the beam to redirect the beam into a Laser Power pyroelectric detector. The energy incident on this detector was used as a reference.

Attenuation of the laser beam was necessary to collect a full set of data at varying energies. Calcium Fluoride plates were used to attenuate the CO_2 laser beam. An attenuator box was constructed by George Orbits of Science Application International Company (SAIC). This attenuator box raised blocks (which contained different thickness' of Calcium Fluoride positioned in a binary form) into the laser beam. Each block was characterized with a Perkin Elmer 983 spectrophotometer. From this information, the energy to the transmitted laser beam could be calculated.

The laser beam was then expanded by an infrared laser beam expander. The beam was expanded such that it would be collimated and have a diameter greater than 1 inch. An iris with a clear aperture of 1 inch was then used to resize the laser beam. The laser beam was then guided through a series of aspheric ZnSe lenses. The lens directly after the iris had a focal length of 5 inches. The thin-film sample of the material to be tested was placed at this lenses focal point. Most of the samples were placed in a Dewar in order to lower their temperatures to cryogenic temperatures. A Lakeshore temperature controller was used to vary the temperature of the material being tested. This capability allowed many characteristic limiting curves to be taken at several different temperatures.

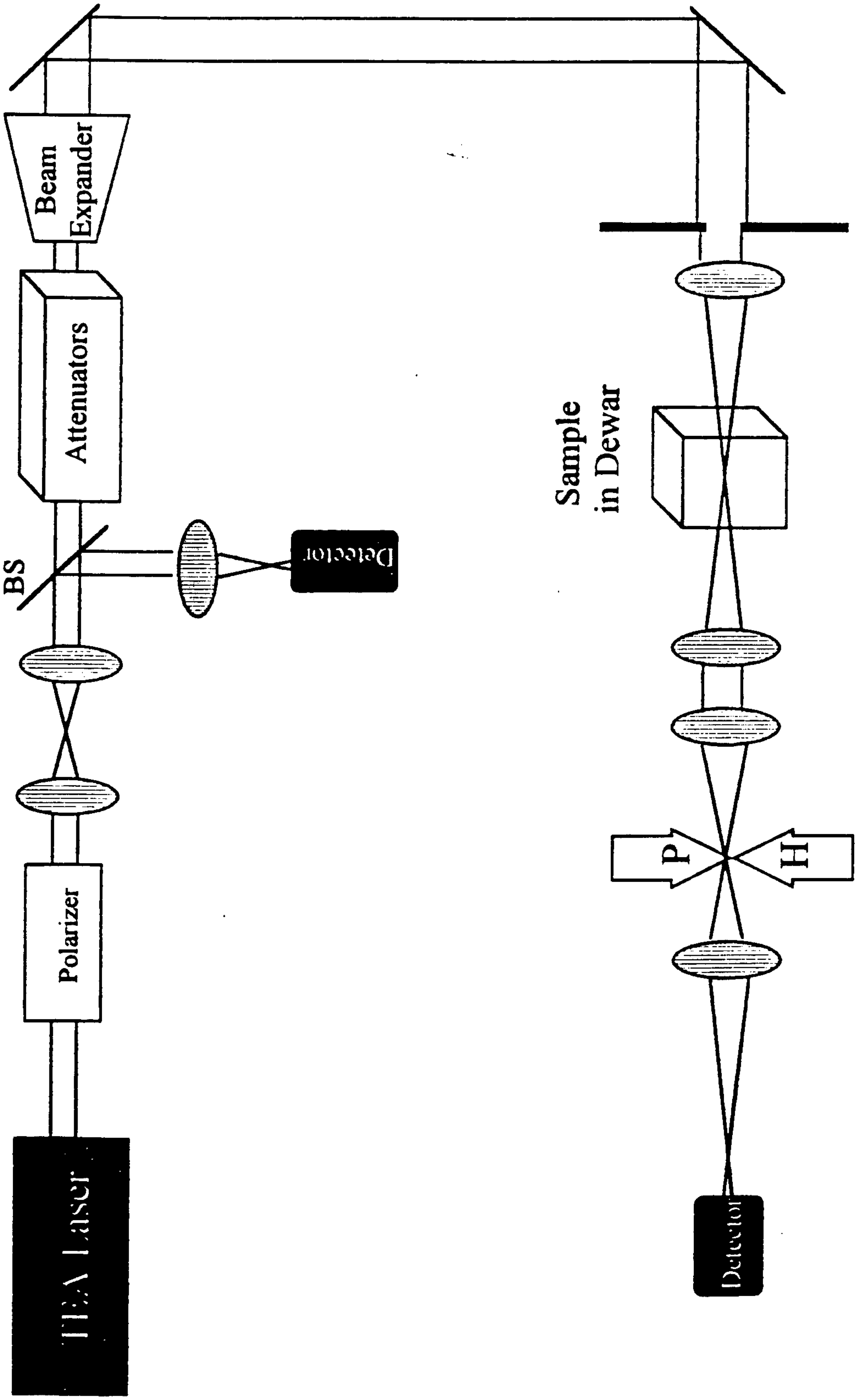
The laser beam was then recollimated and passed through another lens of 5 inch focal length. A pinhole was placed at this lenses focal point. Limiting curves could then be taken with and without the pinhole in place. From this data, the mechanism responsible for limiting could be determined.

After the pinhole, a lens was used to focus the beam onto a second Laser Power pyroelectric detector. The detected energy of this detector is that which was transmitted through the sample and also the pinhole. Calculations were then performed to analyze the data set.

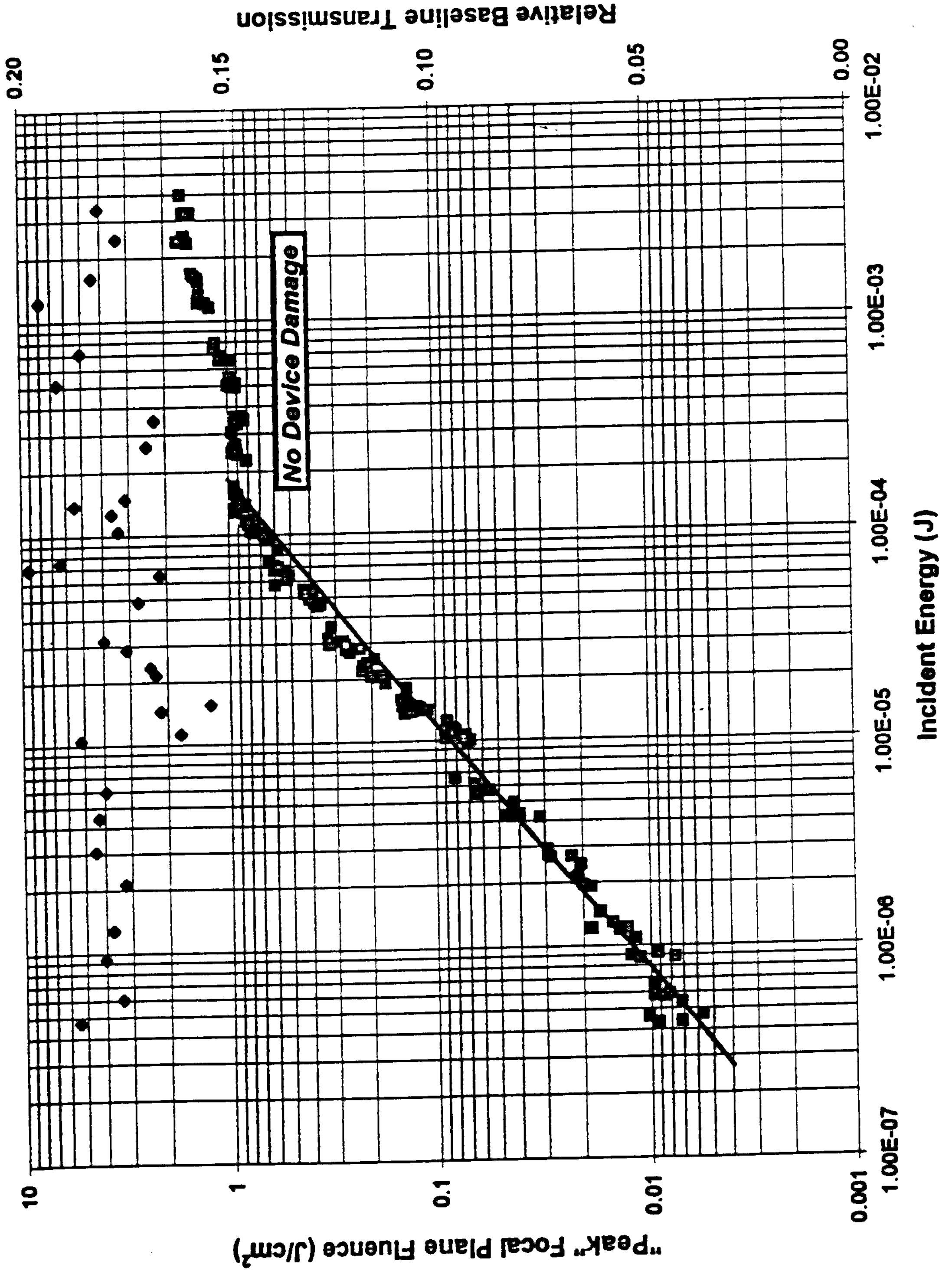
This entire process of collecting this data was computer automated. Brian Deep wrote a program in Labview (data acquisition software by National Instruments) which controlled the attenuator box, the temperature controller, and the sample position. It also collected data from the two laser power pyroelectric detectors. This program also enabled the limiting curves of the material being tested to be observed in real time. An example of the data acquired by this system can be seen in Appendix B.

The time required to take one limiting curve before the automation of this system was approximately 4 - 8 hours (providing no complications). Now, after the automation process, it takes approximately 25 minutes to take a full set of data. Hence, many samples may be characterized in a single day.

Appendix A Experimental Optical Set-up



Appendix B Sample Data



MATERIALS VISUALIZATION TECHNIQUES FOR CRYSTAL ENGINEERING

Task Order No. 167
Student Support Program
Southern Ohio Council for Higher Education

David Giovannini
Wright State University

3 April 1996

Government Task Leader
Dr. Steven LeClair
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank Dr. Steven LeClair and Dr. Alan Jackson for the opportunity to gain experience in software design and implementation. I would like to thank Jeff Heyob for the endless tales and technical advice. My final thanks goes to Mark Benedict for picking up where I left off with ambition and zeal. The time I spent in the WL/MLIM lab was been a positive and constructive experience. The skills and knowledge that I acquired during my employment cannot be denied. The individuals I worked with were skilled and wonderful teachers.

GENERAL TASK DESCRIPTION AND ASSIGNMENT

The Task objective is to "develop simulation of pulsed laser deposition plasma condensation, SiC crystal structures, and simulation of physical properties tetrahedron." The personal goal of the project was to further experience and knowledge of good software design and object oriented programming methods. In doing so, a large suite of C++ classes that both extend the Metrowerks application framework, PowerPlant, and give a foundation for future development projects, was created.

The Unit Cell Viewer application was to be developed first on the Macintosh 68K LC platform. The Macintosh was chosen because both the primary costumer of the application required that particular platform and the location of the development effort specialized in Macintosh software and hardware development. Metrowerks' compiler, linker, and application framework are being used for the actual development because of their quality and effectiveness in helping the programmer create modular and versatile code.

Metrowerks PowerPlant was chosen as the core application framework because it is light weight and yet powerful. It has continually and successfully supported all of Apple's operating system technologies. The 3D graphics library is built on both PowerPlant and the ideas outlined in the easy to understand book Engines of Creation , by Jon Blossom. In Engines of Creation the reader is taught how to create a 3D graphics library with lighting and partial and whole hidden line removal. When the time comes for the application to move to a PowerPC, Unix, and/or Windows platform it is strongly suggest using QuickDraw 3D for all 3D graphics handling. It out performs and is more robust than the graphics library already implemented in the application.

Application Framework, the Project Design

The application has three functions. The first is to record and edit basic unit cell information in a user readable format. This information includes items such as the Pearson symbol and the Wyckoff sites. The second function is to use that unit cell data and create a file containing 3D graphical data used to create a viewable image of the particular unit cell. The third function is to display various unit cells in one virtual world allowing the user to manipulate the unit cells independently or create more complicated structures.

There are two distinct interfaces in the application. The first and simplest is the unit cell input window. In a series of edit fields the user inputs all the unit cell molecular information. From this window the user can tell the application to make and display the resulting 3D image. The second user interface is the manipulation and viewing of the 3D image. There are five windows of controls containing translation, rotation (world and unit cell with idle time rotation), lighting (ambient and directional), perspective and magnification, color, and a trackable axis. In the main window, which contains the 3D world, each unit cell is selectable. The selected unit cell is the one affected by the rotation and translation controls.

TRIBOLOGICAL EVALUATION OF SOLID LUBRICANT MATERIALS

Task Order No. 168
Student Support Program
Southwestern Ohio Council For Higher Education

John E. Florkey
The Ohio State University

11 June 1996

Government Task Leader
Dr. Jeff Zabinski
WL/MLBT

ACKNOWLEDGMENTS

Everyone I have worked with has been very helpful, but I would like to thank these people for the time and patience they gave me: Dr. Jeff Zabinski, Dr. Mike Donley, John Bultman, Art Safreit, Wayne Polley, Donald Thomas, Jim Heirholzer, Dr. Scott Walck, Lt. Kate Havey and Bob Chaney.

DESCRIPTION OF TASK ASSIGNMENT

An experiment was continued to try to increase the corrosion resistance of titanium nitride to perfluoropolyalkylether (PFPAE) by codeposition with chromium nitride. The focus of this Task was to characterize the titanium nitride coating. The combination of titanium nitride and (PFPAE) is to be used as a high temperature liquid lubricant for jet engines. It has been proposed in the literature that PFPAE's breakdown, forming iron oxides and iron fluorides. In a wear situation, this debris is removed from the wear track exposing clean iron which is easily oxidized or fluoridated by the previously formed debris. Further degradation of the metal and the PFPAE lead to a synergistic corroding effect. It is hoped that coating the metal parts that come in contact with the PFPAE with titanium nitride will retard the corrosive action of the PFPAE. TiN is harder than chromium nitride, but is generally more porous, which leads to weaker resistance to chemical attack. It is hoped that the codeposition of chrome, titanium, and nitrogen will yield a hard coating with good protection against corrosion.

A project was also undertaken that involved the modification of an existing piece of equipment and installation of new piece of equipment.

DESCRIPTION OF RESEARCH

The TiN coatings were deposited using plasma arc deposition on 440C and M50 substrates at Hohman Plating and Mfg. Inc. The substrates were ultrasonically cleaned in trichlorotrifluoroethane, ultrasonically cleaned in a mild caustic solution, rinsed in deionized water, and blown dry. The partial pressure of nitrogen gas admitted and substrate bias were the controlled variables. The coatings were characterized for chemistry and crystal structure by X-ray photoelectron spectroscopy and X-ray diffraction respectively.

RESULTS

The X-ray data was taken in a series of six 2-theta scans per sample. Theta was fixed for each scan but varied from .05° to 10° over the series. The change in theta corresponds to how deep in the coating the x-rays penetrate. The higher the theta, the deeper into the coating the x-rays penetrate. The data clearly showed that the coating was stoichiometric titanium nitride as determined from the peak positions. The peak intensities showed a preferred orientation. The coatings deposited at -75V bias had a (111) orientation throughout the depth of the coating. The coatings deposited at -125V had a (111) orientation through the lower half of the coating, but

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The XPS data showed the coatings were oxidized on the surface, but the oxide was easily removed by sputtering. It also showed slightly more nitrogen than what is expected of stoichiometric TiN. This is somewhat unusual. There could be excess nitrogen trapped within the TiN lattice, but the coatings are still believed to be very close to stoichiometric as shown in the XRD data.

Hardness data was taken by Nano Inc. Different loads and conditions were used to avoid the substrate hardness affecting the coating hardness measurements. The hardness for the samples in general was 32.42 GPa, and falls within what would be expected of TiN

The corrosion test consisted of the test specimens submerged in the heated PFPAE for 24 hours with 1 liter of air bubbled through it per hour. The samples were classified into two classes: low energy and high energy. The low energy samples were those that were deposited at low bias or high pressure. The high energy samples were those that were deposited at high bias or low pressure.

Both types of coatings survived up to 330°C without the coating coming off or becoming discolored. At 345°C, the low energy coatings showed some minor corrosion, while the high energy coatings were unharmed. At 360°C, both the low and high energy coatings failed.

The low energy coatings are thought to be more porous and less dense than the high energy coatings. Those properties are thought to lead to the low energy coatings being more susceptible to corrosion than the high energy coatings. The TiN coating must be improved for use above 345°C. To improve the coating it could be made more dense by varying the deposition parameters. Or a layer of some material that is resistant to chemical attack could be deposited on the substrate first and the TiN deposited second.

So far, the TiN has been the only film that has been deposited by Hohman Plating. The target to be used for the deposition of chromium nitride has yet to be acquired.

An electron beam (e-beam) heater was purchased and installed to expand the research capabilities of the existing XPS system. The concept is to quickly heat a sample to up to 600°-700°C with a beam of electrons that strike the bottom of the sample. The sample would then be transferred into the main analysis chamber where data could then be taken. Phenomena such as phase changes and other chemical reactions could be observed using this equipment.

A problem was encountered after installation. The system was arcing when the high voltage was turned up to 2,000 volts. Ceramic sleeves had been placed around the sample stage supports before installation as a precautionary measure to avoid arcing. Those sleeves greatly reduced the clearance between heater and sample stage. The reduced clearance combined with metal that had been rubbed onto the ceramics or deposited there during heating made it easier for an arc to jump from the heater to the stage. This arcing caused several resistors and fuses to be burned out. The sleeves were removed from the stage supports. This relieved some of the arcing problem, effectively raising the voltage that could be achieved before arcing.

Somehow arcs were still being generated and blowing out fuses. It is thought that by heating the sample slowly the chamber was also heated up and outgassed. The pumping of these extra gasses required longer ramp up time. The higher pressure, due to the outgassing, also made it easier for an arc to jump. This problem was solved by following this procedure: warming up the filament for 5 minutes, turning up the high voltage, and adjusting the emission current to achieve the desired temperature. This procedure did not allow the chamber to warm up with the sample. Therefore, the pressure stayed lower making the voltage required to arc higher than what the heater required.

DEPOSITION OF THIN-FILM COATINGS

Task Order No. 169
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer M. Corneille
University of Dayton

16 April 1996

Government Task Leader
Dr. Jeffery S. Zabinski
WL/MLBT

ACKNOWLEDGMENTS

I would like to thank Dr. Jeff Zabinski who gave direction, John Bultman who always answered questions, Dr. Peter John who also answered questions, Art Safreit who solved "shop" problems, and Lt. Kate Havey who answered all my military questions and helped me get to where I am today.

GENERAL DESCRIPTION

The Task of the tribology group is to develop hard film lubrication coatings and to test their composition, hardness, friction, and wear life. The specimens are tested under various conditions, such as in air or under vacuum or in normal, dry or wet atmospheres. It is important to obtain lubricants that have a long life and low resistance to friction. This is so that the lubricated specimen will maintain its lubrication properties for a long period of time. Based on the results obtained, the lubricant could potentially be used on ball bearings for turbine blades or in other space related applications.

DESCRIPTION OF RESEARCH

Many of the properties of a specimen that need to be determined are mechanical in nature, such as the friction coefficient, the hardness, and the wear life. In this Task, these characteristics were found for TiC, CS_2, and various other films.

A wear tester was used in which the samples were exposed to varying humidity. This tested the life of the film under different atmospheric conditions. The pin on disc method was used in this particular tester.

The NanoIndentor determined the hardness of the film. Typically, hardness testers, such as the Rockwell or Brinell, are inaccurate and destructive, meaning the sample can never be used again. Using the NanoIndentor insured the integrity of the specimen and produced results that were much more accurate. The indentation device slowly approaches the specimen at the specified speed and loading. The programming of the indentor is dependent on the type of film, whether it is thick or thin, hard or soft. During testing, the NanoIndentor software collects the data and stores it until it can be properly analyzed. The indentor leaves a microscopic valley that does not really affect the surface - the specimen is able to be used for other tests.

The X-ray photoelectron spectroscopy (XPS) system determines the composition of a film. Theoretically, TiC contains the ratio of one titanium atom to one carbon atom. However, when a film is deposited, this ratio may not exist. The ratio could be 1.5 to 1 or .7 to 1. This difference in ratio could be due to how the film was deposited - the temperature of the chamber could vary or the target could be defective. By determining what the true ratio is, one could try to reproduce it if the results were favorable. A ratio of .7 to 1 may give excellent frictional properties, while a ratio of .9 to 1 might fall apart. While no sample that was worked with had this extreme, it is important to recognize the composition of the specimen. The XPS fires electrons at the specimen. Once it has hit the sample, it bounces back at some energy level. Depending on what element the electron hit, the energy level is changed. If these energy levels are read, then one can know how often a certain element was "hit" and a composition can be developed from there.

Vacuum systems are an important element in the study of tribology. Many materials will act drastically different in air than they do under vacuum. While under vacuum, it is understood that a material will behave in a "truer" sense and more accurate predictions can be made. In addition, many applications for the films are for space where vacuum conditions are prevalent. A number of vacuum chambers were assembled or brought on line. Among those were a high-speed tribometer and a heater system. A vacuum was generally drawn with two, sometimes three pumps - a rough pump, a turbo pump, and an ion pump. Each pump produces an advancing level of vacuum. Most work was done in the 1.0 E-7 to 1.0 E-9 torr.

METALLIC COMPOSITES (95-II)

Task Order No. 170
Student Support Program
Southwestern Ohio Council for Higher Education

Michael A. Foster
The Ohio State University

15 September 1995

Government Task Leader
Dr. Dan Miracle
WL/MLLM

ACKNOWLEDGMENTS

I would like to express my thanks to everyone at Wright Laboratory who made the job enjoyable and fulfilling. Special thanks needs to be given to Dr. Dan Miracle, who was always there to answer questions and give meaningful advice. I would also like to acknowledge Mr. Paul Smith and Dr. Mary Lee Gambone for their help in the understanding of material that was technically difficult.

GENERAL DESCRIPTION OF THE TASK ASSIGNMENT

This Task's objective was to determine phase relationships and thermal stability of Ti-Al-Nb alloys.

The specific work to be done consisted of conducting heat treatments, metallography, and microstructural analysis of Ti-Al-Nb alloys. Other characterization procedures, such as X-ray and chemical analysis, were expected to be performed as necessary. Any data collected was to be interpreted and presented, if needed.

The United States Air Force's Integrated High Performance Turbine Engine Technology initiative (IHPTET) deals with the doubling of a jet aircraft's thrust to weight ratio by the year 2000. Metal matrix composites (MMC's) and other high technology materials are vital to the initiative's success. These MMC's are to be used in the engine of a jet aircraft, where it is necessary for a material to be able to withstand large stresses at elevated temperatures. One of the most important groups of metal matrix composites is continuously-reinforced titanium matrix composite (TMC's). Research is underway on several titanium alloys that are being considered as possible matrix materials for the TMC's. One of the most promising titanium alloys is based on the orthorhombic phase Ti_2AlNb. The orthorhombic alloy system is not very well characterized, and an equilibrium phase diagram has not yet been prepared. This diagram is very important because it shows the temperatures at which the various phases of the orthorhombic system are stable. The development of this orthorhombic phase diagram was the subject of most of the work performed.

DESCRIPTION OF RESEARCH

Work has been done on two different projects. The first project dealt with the titanium alloy system based on the orthorhombic phase Ti_2AlNb, as described above. The other project dealt with the strength populations of fibers which were consolidated inside titanium matrix composites and then extracted from the composites by etching the matrices away.

The first project, constructing a phase diagram of the orthorhombic titanium alloy system, was a collaboration between Wright Laboratory and Rockwell Science Center. Forty alloys, which consisted of the elements Ti, Al, and Nb, were prepared for the study. All alloys had a constant aluminum level of 22at%, while the niobium level was varied from 5at% to 40at%. All the alloys were heat treated at temperatures ranging from 650°C to 1000°C for a time of 1000 hours, to ensure that the microstructures were close to equilibrium. Wright Laboratory received 25 of the alloys while Rockwell Science Center got the rest. Each alloy was made into two cubes, each approximately 1 cm^3 in volume. One of the cubes of each alloy was not used (saved for possible examination at a later date) while the other was cut in half using a diamond saw. Both halves of the cubes were then mounted in conductive mounting compound and labeled.

All the mounts were then polished to a surface finish of 1 μm. Both halves of the cubes had to be mounted because one half was to be used for X-ray analysis while the other half was to be studied using scanning electron microscopy and microprobe analysis. After the specimens were polished to a 1μm finish, the specimens to be used for X-ray analysis were broken out of their mounts so that they would fit into the X-ray diffractometer. Each of these 25 specimens was then individually scanned in the X-ray diffractometer, and the test data from each scan was analyzed to get a list of X-ray peaks for each alloy. The peaks from each scan were then indexed so that it could be determined which phases were present in each alloy. SEM was also performed on the 25 alloys to see what the equilibrium structure of each alloy was. After looking at the SEM micrographs, it could be determined which specimens could have microprobe analysis performed on them. All specimens could not be microprobed since this analysis technique requires that the phases in the specimen have a visible area of approximately 5μm^2. Several of the 25 specimens contained phases that were very much smaller than this required area, so they could not have microprobe performed on them. Microprobe analysis is a characterization technique which allows the chemical composition of each phase to be determined. The microprobe work is still in progress.

For the second project, seven different titanium matrix composites were sectioned so that pieces of the composites (approximately .25 in x 3.5 in) were obtained. These composite sections were then put into a bromine and methanol solution which was saturated with tartaric acid. This solution dissolved the titanium matrix away from the fibers, but it was gentle enough that it did not damage the fibers or the reaction zones that were on the exterior of the fibers. Once all the matrix was dissolved away, the diameters of 40 fibers from each composite were measured using a measuring microscope. After the diameter measurements were completed, tensile tests were performed on 50 fibers from three of the composites. The purpose for extracting the fibers from the composite is to see if the fibers lose any of their strength due to the composite consolidation process. The tensile tests on the fibers from the other composites are still being performed.

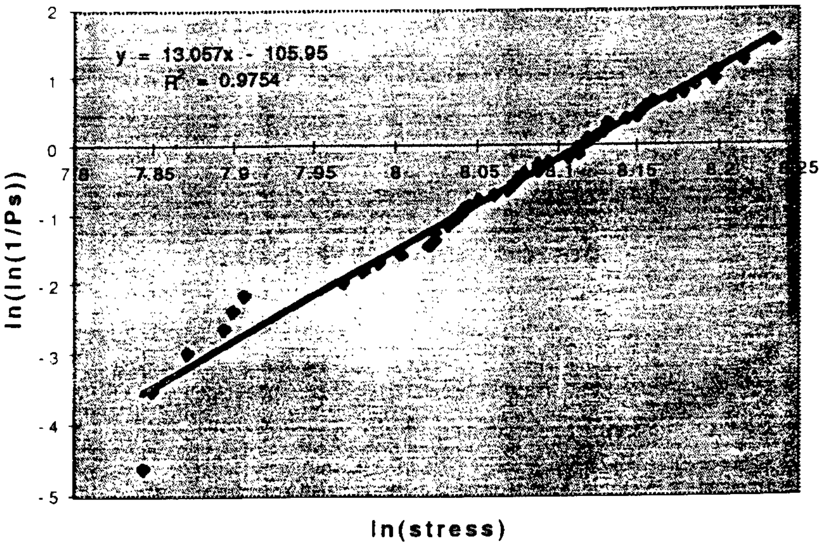
RESULTS

The X-ray diffraction scans performed on the 25 alloys were completed and the peaks have been indexed. These scans were supposed to tell which phases were present in each alloy. A problem that was run into, though, was that two of the phases being looked for had peaks that are extremely close together. It was therefore very difficult to discern between the peaks and decide which phase produced them. The X-ray scans are thus only going to be of marginal use for this orthorhombic system phase diagram project. No results are available as of yet from the microprobe analysis since it is still underway.

Three of the fiber populations which were extracted from titanium matrix composites have been tensile tested. The following chart is a plot of the data obtained from the fibers extracted from one of the composites. It shows the relationship between Ps (probability of survival of the fibers) and the stresses at which the fibers failed.

If only one type of defect is the cause for the fiber failures, the data in the plot should be linear. The data for this population of fibers appears to be linear in fashion, with an R^2 fit of .975. Several deviations from linearity can be seen toward the lower left portion of the chart. The fracture surfaces of those, as well as the rest of the fibers, will be looked at in the SEM to determine if the fracture mode of the deviated fibers was different from that of the other fibers. The other two populations of fibers also produced plots that were linear in fashion, showing that only one type of defect was causing fracture. The fracture surfaces of those fibers will also be examined in the SEM to see exactly what kind of defect was causing fracture.

Middle-Middle Series



METALLIC COMPOSITES (95-I)

Task Order No. 171
Student Support Program
Southwestern Ohio Council for Higher Education

Gregory F. Schieleit
The Ohio State University

18 June 1996

Government Task Leader
Dr. Daniel B. Miracle
WL/MLLM

ACKNOWLEDGMENTS

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

Through the Air Force's Integrated High Performance Turbine Engine Technology (IHPTET) initiative, the performance of turbine engines needs to be improved from a thrust to weight ratio of 10:1 to 20:1 by the year 2000. Titanium matrix composites (TMC's) have the mechanical properties including: low density, high strength and stiffness at elevated temperatures, that make TMC's prime candidates as a material in turbine engines. Current TMC's posses the needed properties along the axis of the fibers, however, they lack the needed off-axis properties. To improve the off-axis properties, work is currently being conducted to understand the interface's role in TMC's.

DESCRIPTION OF RESEARCH

Research, under the direction of Dr. Doug Gundel, is in progress to find the interface properties of the composite. Matrix-only panels and both single and multi fiber composites were subjected to transverse loads to measure the interface strength. By using strain gages, many different fibers and interfaces produced at Wright Patterson Air Force Base (WPAFB) and at the 3M company were evaluated by measuring the local strain experienced by the composite near the fiber-matrix interface.

The composite material was made by hot pressing SCS-6, SCS-0, and Trimarc I, fibers between two panels of a Ti-6Al-4V matrix. SCS-6 and Trimarc fibers both have carbon coatings while the SCS-0 fiber has no coating. The coatings are very important to the strength of the composite because they must protect the fiber from reaction with the matrix that can weaken the fiber. While protecting the fiber, the coatings must also form a strong bond with the matrix to provide the necessary tensile strength. Four-ply and single-ply multi fiber composites were made as well. The four-ply consisted of four rows of fibers and the single-ply composite contained one row of fibers in the Ti-6Al-4V matrix.

After manufacturing the composites via hot pressing, the panels were cut into a cruciform shape using wire electrical discharge machining. The fiber is in the horizontal arm of the cruciform. This shape and fiber placement provide an accurate means of measuring the load experienced by the interface. A strain gage was then placed above the fiber in the cruciform specimen. The cruciform specimen was then subjected to a tensile load transverse to the fiber orientation. From the tensile tests, stress-strain plots were made to find the interface failure stress. Along with the transverse tensile test, each specimen was sectioned under the strain gage perpendicular to the fiber axis. This section was mounted and prepared metallographically for evaluation in the scanning electron microscope (SEM) to reveal failure mechanisms and problems in the manufacture of the coating, fiber, and matrix.

RESULTS

In initial tests, the SEM revealed consolidation problems, voids near the fiber coating, in the composite material. The consolidation problems caused low stress values to be obtained. Applying a matrix coating to the fibers, before they were hot pressed between the titanium alloy sheets, eliminated the consolidation problems.

Even after solving these problems, the debond stress, or the initial change in slope of the stress-strain curve, in the composite panels occurred at a much lower stress value than the neat matrix panels. For the carbon coated fibers, the fully consolidated composite had debond stresses of approximately 340 MPa for the SCS-6 fiber, and an average stress of 231 MPa for the Trimarc fiber. The uncoated SCS-0 composite had a debond stress of 650 MPa. The neat matrix panels had yield strengths of 700MPa.

Significant decrease in transverse strength from the neat matrix panels to the composite material was due to interface debonding. SEM micrographs showed that in tested composites damage occurred in the fiber-matrix interface, while in untested composites no damage was present in the interface. While both the SCS-6 and Trimarc composite failed between the carbon coating and the matrix, the Trimarc composite also failed within the carbon coating. The SCS-0 composite failed in the reaction zone between the matrix and silicon-carbide. The SCS-0 composite had higher transverse strength values than the SCS-6 and Trimarc composites because the reaction product between the matrix and silicon-carbide is much stronger than the reaction product between carbon and the matrix.

The multi fiber composites produced results similar to the single-fiber composites. The four-ply composite had a debond stress of approximately 310 MPa while the single-ply composite initiated failure near 340 MPa. The similarities in the stress values, obtained from the single-fiber and multi fiber composite, show that an increase in volume fractions of fibers in a composite moderately effects the transverse strength of the material.

While this research is continuing, results thus far have proven that this approach is a viable means of understanding the interface properties of composite materials. Interface strength data compiled with metallographic evaluation has been an important technique for understanding the behavior of interfaces in transverse tension. Important information, such as the weak nature of carbon reaction product bond, has been revealed. Future work includes the testing and examination of interfaces altered through the use of fiber coatings in single and multi fiber composite.

ADVANCED NONDESTRUCTIVE EVALUATION

Task Order No. 172
Student Support Program
Southwestern Ohio Council for Higher Education

Gregg H. Jessen
Wright State University

2 April 1996

Government Task Leader
Dr. Renee M. Kent
WL/MLLP

ACKNOWLEDGMENTS

The author wishes to acknowledge and thank Dr. Renee M. Kent for making this Task possible, Mark J. Ruddell for teaching and explaining nondestructive evaluation techniques, and all of the people in MLLP who tolerated my presence and assisted in the completion of the Task.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Advanced Nondestructive Evaluation is any method by which advanced composites can be observed and tested without using intrusive or destructive methods that may change the characteristics of the sample of interest. The techniques of particular interest to this Task are ultrasonic and laser based. These evaluation procedures have value to many industries. The Air Force has several aircraft that need to be inspected for wear, damage, and corrosion. With ultrasonic and laser-based techniques, the aircraft can often be examined without dismantling them and stripping paint from them. Being able to examine existing components without taking them apart are very convenient and cost effective or causing damage to them. Other industries use Nondestructive Evaluation procedures to monitor the formation of fiber reinforced composites using the fibers as sensors. These methods help to observe the formation of the matrix about the fibers and provide useful information about what is happening during the cooling of the matrix. The information obtained here can be used to improve the processes to get a better product. The ultrasonic and laser-based evaluation methods are developed by examining fiber reinforced metal or glass matrix composites. Here, it is specifically silicon carbide fiber in a titanium or glass matrix.

DESCRIPTION OF RESEARCH

Since sound propagates as a wave, it must satisfy the boundary conditions of the partial differential equations that predict its motion. This means, that as the wave moves from medium to medium, the equations predict that there will be a wave deflected. This deflected wave is seen as an ultrasonic echo and is observed whenever there are cracks or changes in the elastic properties of the medium through which the ultrasound travels. The equations used to solve for the motion of the ultrasonic wave also predict that the propagation of the wave is dependent on the compression or tension of the medium. This is important when a fiber is embedded in a matrix and residual stresses formed by mismatching the coefficients of thermal expansion between the fiber and the matrix causes shear stresses between the two. This causes compression or tension in both materials. Since sound wave characteristics change due to stresses, ultrasonic pulses can be observed for changes to examine these stresses in different locations of the samples.

In this Task, three different combinations of ultrasonic and laser-based methods were used to detect flaws in samples. The first technique involves two ultrasonic transducers, the second technique uses only one transducer, and the third technique uses a laser interferometer and an ultrasonic transducer.

The first method uses one ultrasonic transducer that emits ultrasonic pulses about milliseconds. This transducer is then coupled to the sample of interest by a medium through which sound can pass easily. Sometimes this is water, but in several applications a more viscous medium is required for good coupling and epoxy is used. The other end of the sample is then coupled to another ultrasonic transducer that can detect the ultrasonic pulses that travel through the sample. The detected ultrasound can be observed on an oscilloscope (see Figure 1). From this information, the velocity of sound is calculated, the Fourier Transform of the signal is taken, and the amplitudes of the resulting pulses are observed. Each sample has a signature signal and many signals show patterns for similar types of properties and for similar types of damages. Stress in different parts of the sample can change the signals drastically and fractures or debonds in the material can change the signal completely. This method was used to monitor the formation of the SCS-6/glass composite and several individual fibers. When glass formed around the fiber, echoes were seen at the point where the glass adhered to the fiber and stress changes in the composite showed as velocity changes in the ultrasonic pulse. Fiber breaks showed as echoes that reflect before the sound should reach the end of the sample.

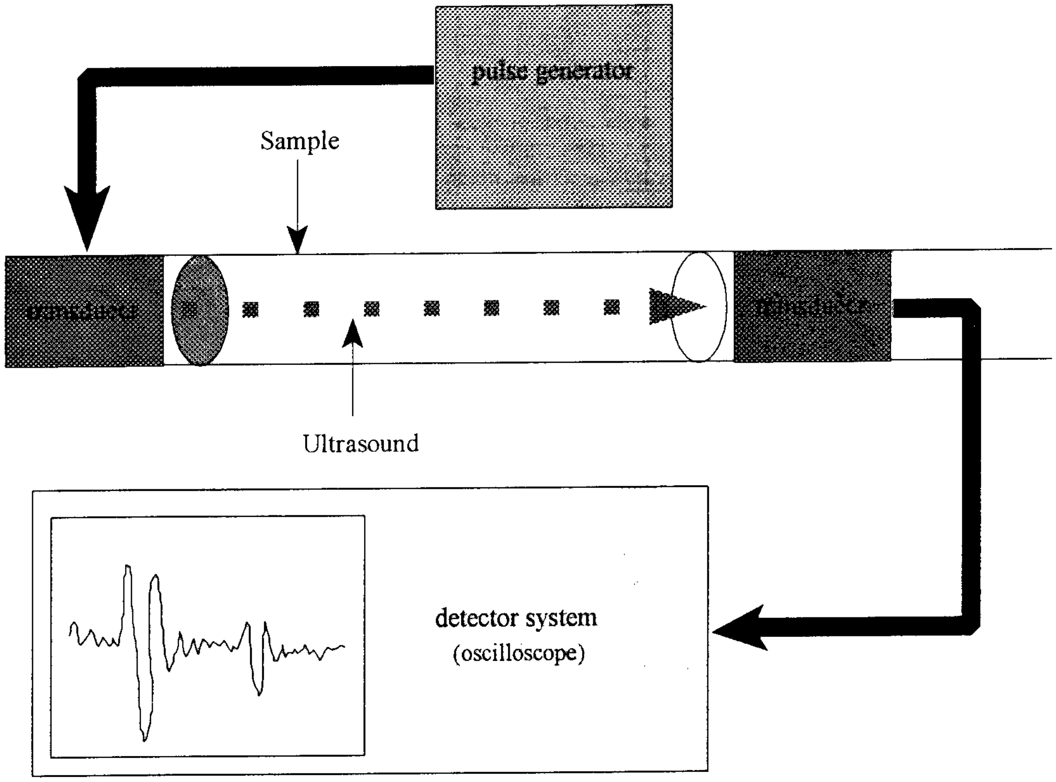

Figure 1. A schematic diagram of the transducer to transducer technique.

The second method uses only one ultrasonic transducer that both emits and detects ultrasonic pulses. The sample is placed in a tank of water and the transducer is typically focused such that the ultrasonic pulse that it emits reflects off fibers in the sample at the focal plane of the transducer. This pulse comes back to the transducer and the waveform is stored (See Figure 2).

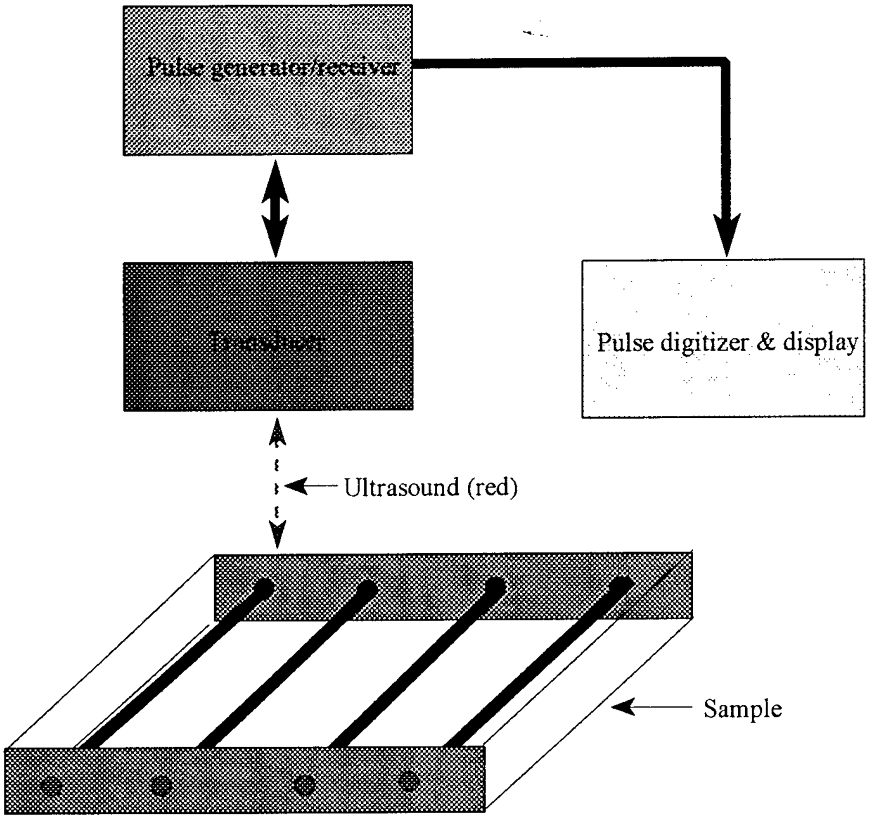

Figure 2. A schematic diagram of the single transducer method.

The transducer is traversed over the entire area of the sample and the peak to peak values of each waveform are stored and plotted against position on a computer screen. The resulting image is a false-color mapping of the internal structure of the sample in which the internal fibers and sometimes damage can be seen. Seeing broken fibers and fibers that are not bonded properly to the matrix is very easy. This method was used to observe SCS-6/glass and SCS-6/titanium composites. Fiber breaks were obvious and poor bonds between the fiber and matrix were seen as areas that were not cleanly defined. Apparently there were air bubbles between the fiber and matrix in cases of poor bonding.

The third method uses an ultrasonic transducer and a laser or a laser interferometer. Here, an ultrasonic transducer is coupled to a sample so that it can send ultrasonic pulses through the sample. The other end of the sample is polished and an interferometer is focused on the area of interest on the sample. When the ultrasonic pulses travel through the sample and reflect off the polished end of the sample, the end of the sample oscillates. This oscillation is picked up by the interferometer because the motion is large enough to cause fringe movement at the polished end of the sample. The change in fringes can be used to find the position of the edge of the sample and plotted the same as an ultrasonic pulse picked up by an ultrasonic transducer (See Figure 3). This is an interesting technique because the fibers in the sample act as ultrasonic waveguides so specific fibers can be observed by merely focusing the interferometer on these fibers. This method was used to examine SCS-6/titanium composites and the resulting signals were the same as the transducer to transducer method. The only difference is that individual fibers can be selected for investigation.

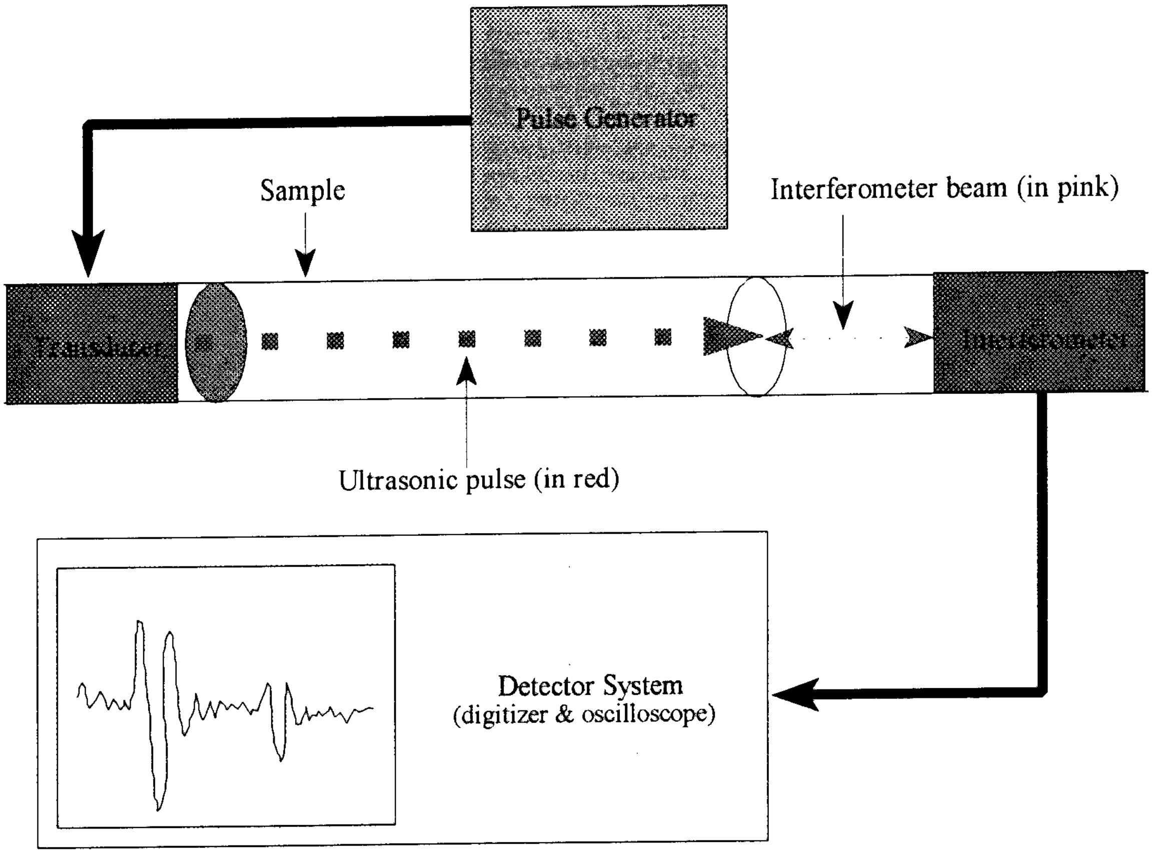

Figure 3. A schematic diagram of the interferometric technique.

RESULTS

Clearly these techniques are worth exploring. Examining specimens without altering their characteristics is always preferable. The eventual goal of Nondestructive Evaluation is to find ways to evaluate specimens without any characteristic changes at all. This not only reduces the chances of damaging or altering the sample, but these techniques allow people to save time and money by skipping steps such as dismantling the object of interest. Sometimes, the object of interest may not be accessible, and this is one main reason that Nondestructive Evaluation is necessary.

ENVIRONMENTALLY COMPATIBLE MAINTENANCE CHEMICALS

Task Order No. 173
Student Support Program
Southwestern Ohio Council for Higher Education

Matthew J. Laufersweiler
Wright State University

30 April 1996

Government Task Leader
Ms. Lynne M. Pfledderer
WL/MLSA

ACKNOWLEDGMENTS

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

The Task objective over the last 12 months was to determine effectivity, applicability, and supportability of substitute aerospace materials and processes that are environmentally acceptable, as it relates to the MLSS work with corrosion control.

During the Task, three major projects were completed plus several smaller projects. The major projects were analysis of an AGM-142 canard coating failure, coating evaluation of a 10-year outdoor exposure test sample, and evaluation of a proposed replacement aluminum alloy chemical conversion coating.

DESCRIPTION OF RESEARCH

The first project, analysis of an AGM-142 canard coating failure, involved the determination of the cause of paint blistering on the canard and to assess corrosion near the locking lug on the canard. The project consisted of a quality control check on the coating itself, removing liquid from the blisters, and checking the liquid for the presence of sodium. It was discovered that sodium was present in the blister. The conclusion was drawn that the primer contained sodium chromate contaminants within the primer, which are known to cause blistering in primers due to the high water soluble nature of the salt. It was then determined that the corrosion around the area of the locking lug was due to dissimilar metals that were not properly isolated from each another. It was recommended that all of the contaminated primer be stripped and repainted with uncontaminated primer to ensure no further blistering of the coatings. The second recommendation was that the locking lug pin material be changed to cadmium plated steel or titanium that is wet installed with either corrosion inhibiting sealant or primer.

The second project, coating evaluation of a 10-year outdoor exposure test sample, involved doing coating tests on a weathered sample to find out how effectively it held up in an outdoor test environment. The first step in this project was to take a color measurement of the material as received, compare that with color number 36118 (the original color of the specimen), and conduct a pencil hardness test. Once this was done, the sample was immersed in water at room temperature for 24 hours and a second pencil hardness was conducted once it was removed from the water. There was no change in the hardness of the coating. The sample was then immersed in Skydrol at room temperature for 2 weeks, pencil hardness was conducted once the specimen was removed, again there was no hardness change. A final color measurement was taken and compared with color number 36118. There were no recommendations made with this project because the data was taken for evaluation by the submitter of the sample.

The third project, evaluation of a proposed replacement aluminum alloy chemical conversion coating, involved a study of the corrosion protection and paint adhesion properties of a trivalent chromium conversion coating. Trivalent chromium conversion coating was considered as a possible replacement for the currently used and more toxic hexavalent chromium conversion coating. This evaluation involved salt spray and prohesion testing of the conversion coating on bare and clad aluminum 7075-T6 and 2024-T3, with and without a primer/topcoat system. Wet tape adhesion testing was also done to find the paint adhesion properties of the conversion coating. The unpainted trivalent specimens did slightly worse than the unpainted hexavalent specimens, but not significantly. The painted specimens of both the trivalent and hexavalent conversion coatings performed identically. Also, both sets of specimens passed the adhesion test. It was recommended that the trivalent chromium chemical conversion coating proceed further to field testing based on its performance in the painted condition.

During the Task, many smaller projects were completed. Some of these included DC plarisation scans on aluminum alloys in different aqueous solutions to determine the rate of corrosion of the materials in the solutions, and evaluations of corrosion products on submitted samples using capillary electrophoresis ion analysis methods to determine the presence of different cations and anions at the site of corrosion. This information could then be used to suggest the possible cause of the corrosion.

SYNTHESIS OF CONJUGATED AROMATIC SYSTEMS FOR OPTO-ELECTRONIC APPLICATIONS

Task Order No. 174
Student Support Program
Southwestern Ohio Council for Higher Education

Trista K. Schrickel
Wright State University

4 May 1996

Government Task Leader
Dr. Robert C. Evers
WL/MLBP

ACKNOWLEDGMENTS

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

The Task included the synthesis of organic compounds that can be used for nonlinear optics. Nonlinear optics is predicted to be important in the technology of photonics. Photonics is the analog of electronics in which photons instead of electrons are used to find, store, transmit, and process information. Examples of nonlinear phenomena useful in this area are the capability of altering the frequency or color of light and to amplify one source of light with another, switch it, or alter its transmission characteristics through a medium, depending on its intensity. The potential for providing these functions in suitable materials encourages research in the field of nonlinear optics.

Many nonlinear optical processes are currently under study, and one of the most visually dramatic is frequency doubling. This process can convert nearinfrared laser light from diode lasers into deep blue light. This can increase the capacity of stored information on optical disks immensely. Optical processing of information and optical computing are appealing applications of photonics.

All materials exhibit nonlinear optical phenomena to some degree. The important and useful nonlinear optical materials, however, are generally solids that require great stability with respect to ambient conditions and high intensity light sources. The first type of useful material, molecular material, consists of chemically bonded molecular units that interact through weak Van der Waals' force. Examples of these materials include organic crystals and polymers. The optical nonlinear relationship of these structures is derived from their molecular structures. Therefore, the primary step in optimizing optical nonlinear relationship in this class of materials is at the molecular structural level. Organic and other molecular materials are increasingly being recognized as the materials of the future. Their molecular nature combined with the versatility of synthetic chemistry can be used to change and optimize molecular structure to maximize nonlinear responses and other properties. Many organic materials, especially high-performance polymers, have high mechanical strength and, excellent environmental and thermal stabilities.

DESCRIPTION OF RESEARCH

The synthesis of a new polymer begins with an idea. Before that idea is exemplified in the laboratory, it undergoes many revisions. Then the process of gathering all of the needed reactants begins. Sometimes, it is as easy as ordering them from Aldrich; but, usually many long hours are spent synthesizing the reactants in the laboratory. Often the most trying part of the polymer synthesis process is ensuring that the functional groups are properly placed so that the reaction may take place. To ensure that the function groups are in place, tests are run on the products.

One comment test is running an IR. This is accomplished using an IR spectrometer (Beckman or Bio-Rad). Another test is thin layer chromatography (TLC). These procedures are carried out many times daily in the laboratory.

After all of the reactants are synthesized, they are used to make the model compound and the polymer. The model compound is simply a monomer of the polymer. Polymers have such huge molecular weights that it makes them difficult to study. The model compound has all of the properties of the polymer, except that it has a low molecular weight making it easy to study. The model compound is sent for elemental analysis to confirm its structure.

RESULTS

It takes many months and sometimes even years to advance from the idea of a certain polymer to the actual synthesis of that polymer. Organic chemistry is nothing like it looks in the textbooks. Those reactions work only sometimes and only under certain conditions. A polymer chemist must know so much more than those thousands of reactions of basic organic chemistry. He must realize that even if something looks perfect on paper, most likely it will not work in the laboratory.

The field of nonlinear optical research offers multi disciplinary challenges from the basic understanding of physics of nonlinear optical interactions, to molecular engineering and chemical synthesis of novel organic structures with enhanced optical nonlinear relationship.

SYNTHESIS OF CONJUGATED AROMATIC SYSTEMS FOR OPTO-ELECTRONIC APPLICATIONS

Task Order No. 174a
Student Support Program
Southwestern Ohio Council for Higher Education

Christine Zucker
University of Dayton

4 May 1996

Government Task Leader
Dr. Robert Evers
WL/MLBP

ACKNOWLEDGMENTS

There were many individuals with whom I have worked closely, and to whom I am most appreciative for allowing me the opportunity to gain hands-on experience in scientific lab research. These individuals include Dr. My Dotrong, Dr. Rob McKellar, and Dr. Bob Evers. In addition, I would also like to thank Sharon Simko for her time and patience in demonstrating the operation of the Bruker FT-IR.

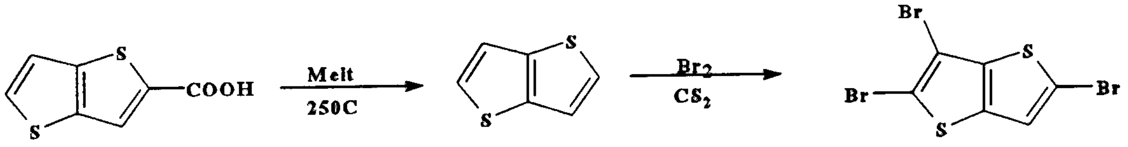
GENERAL DESCRIPTION OF TASK ASSIGNMENT

There were several projects in progress at the Polymer Branch at WPAFB. Several significant monomers were undergoing synthesis for future synthesis of the polymer. These polymeric materials are of much interest because their structure possesses unique properties of conducting electric current. Their development may provide useful future applications in such areas as computer technology and aircraft production. This task within the overall project included a two-step synthesis of an intermediate compound for synthesis of the monomer, besides purification of several products from reaction mixtures using extraction and column chromatography, and characterization of the synthesized compounds using melting point and infrared spectroscopy.

DESCRIPTION OF RESEARCH

Synthesis of 2,3,5-tribromothieno [3,2-b] thiophene

The two-step synthesis is two of many steps required in obtaining the monomer, 3-Dodecylthieno [3,2-b] thiophene that will be used to produce the polymer. The two-step synthesis of 2,3,5-tribromothieno [3,2-b] thiophene from thieno [3,2-b] thiophene-2-carboxylic acid is shown below:



From the above reaction scheme, thieno [3,2-b] thiophene was decarboxylated with melting at 250°C using a heat gun with reaction being done under N_2 conditions. The product thieno [3,2,-b] thiophene was collected at the end of the distillation tube for next steps. Thieno [3,2-b] thiophene, the starting material of the above synthesis was previously synthesized through a 3-step synthesis done by Daychem. The decarboxylation of thieno [3,2-b] thiophene-2-carboxylic acid was repeated twice to obtain enough thieno [3,2-b] thiophene for the bromination step. From each reaction 5.08 g and 31.15 g of the product was obtained from 24.22 g and 50.69 g of starting material giving relative yields of 27.5% and 81.2%. The low yield of the first reaction was a result of the first trial run. However, from the second reaction a higher yield was obtained showing a successful procedure for decarboxylation.

In the second step of the synthesis, thieno [3,2-b] thiophene was brominated by the drop wise addition of Br_2 in carbon disulfide with stirring in an ice bath for 20 minutes. A KOH trap was used to collect evolved HBr. The mixture was allowed to come to room temperature and left to react with stirring for 48 hours.

Purification of 2,3,5-tribromothieno [3,2-b] thiophene

After the bromination reaction, the product was extracted with saturated sodium bicarbonate to remove excess acetic acid. After several extractions with saturated sodium bicarbonate, the organic layer was washed with several portions of distilled water to ensure complete removal of acetic acid and other water soluble impurities. The organic layer containing the product was collected for characterization. The product 2,3,5-tribromothieno [3,2,-b] thiophene was obtained in a good yield of 80%.

Purification of 3-nitro-1,2,4,5-tetramethylbenzene

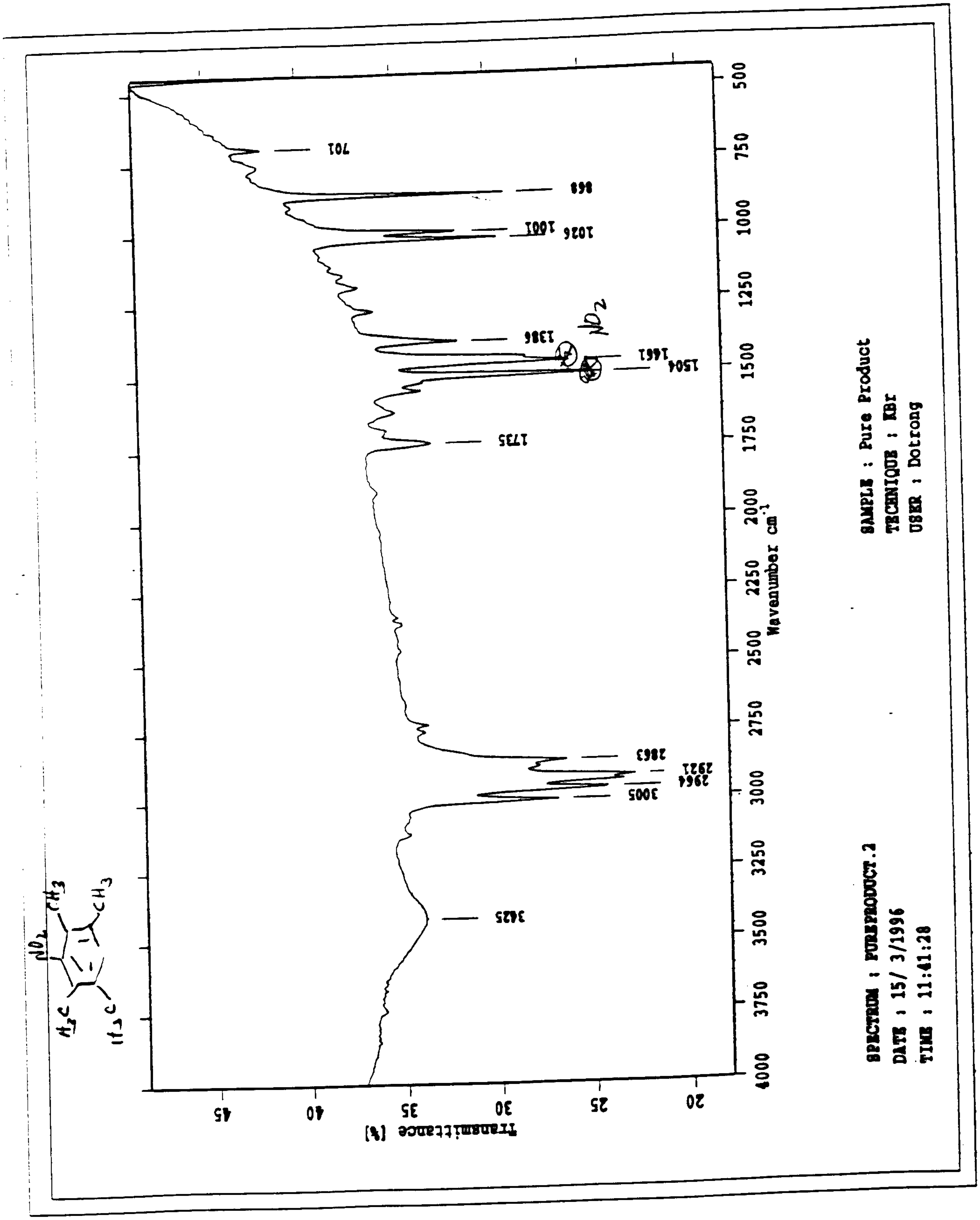
After nitration of 1,2,4,5-tetramethyl was completed, the reaction mixture was slowly poured into a sufficient amount of ice water (1 L of H_2O/ 500 mL of mixture) with continual stirring. The product, 3-nitro-1,2,4,5-tetramethylbenzene, precipitated as yellow crystals upon addition to H_2O. After the crystals were allowed to stir, the mixture was vacuum filtered. Results of thin layer chromatography showed a product with some impurities corresponding to the starting material, but in a minimal amount with respect to the product.

Characterization of 3-nitro-1,2,4,5-tetramethylbenzene

A sample of 3-nitro-1,2,4,5-tetramethylbenzene was prepared for infrared spectroscopy using Kbr. The IR spectrum (see attachment) displayed the characteristic aromatic stretching at 3005 cm^{-1}. Three peaks corresponding to an aromatic methyl group appeared at 2964 cm^{-1}, 2921 cm^{-1}, 2863 cm^{-1}. In addition, the nitro peaks at 1504 cm^{-1} and 1461 cm^{-1}, therefore, confirming the product was formed.

RESULTS

The synthesis of the intermediate compound 1,3,5-tribromothieno [3,2-b] thiophene was obtained in a high enough yield to move the to next step in the synthesis. Further synthesis is underway for 3-nitro-1,2,4,5, -tetramethylbenzene that involves work on a separate project. There are still several more steps from 1,3,5-tribromothieno [3,2,-b] thiophene to complete before obtaining the monomer required in synthesizing the polymer.



SPECTRUM : PUREPRODUCT.2
DATE : 15/ 3/1996
TIME : 11:41:28

SAMPLE : Pure Product
TECHNIQUE : KBr
USER : Dotrong

FATIGUE CRACK GROWTH IN METAL MATRIX COMPOSITE

Task Order No. 177
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Allen Lair
Wright State University

11 June 1996

Government Task Leader
Mr. Jay R. Jira
WL/MLLN

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TASK ASSIGNMENT

The objective of this Task was to help Mr. Jay R. Jira in the analysis of Titanium Matrix Composite Material and Titanium Matrix Monolithic (fiberless) Material. Within these two materials, two primary Titanium Matrixes were encountered, Ti-6Al-4V and Ti-22Al-23Nb, better known as PRDA (named for organization), and the latter as Orthorhombic (named for material). Fatigue Crack Growth Tests (FCG) were run with different conditions; some of which being high temperature; room temperature; stress ratio 0.1; stress ratio 0.7, etc. After the tests are completed, the data is then run through a series of data reduction techniques and the resulting data is then analyzed.

RESEARCH METHOD

In the analysis of Titanium Matrix Composite and Monolithic Materials, there are many "jobs"to be done. To explain these better, I will briefly run through a typical fatigue crack growth test.

In the first step, a group of engineers discusses the types of specimen they want cut out of a given Parent Plate (typically 6" x 6"). A machine drawing is created which reflects what was decided upon. The machine drawing is then sent, with the parent plate to the machining shop where it is cut into a number of specimens. After the specimens have been cut from plate, the specimen is assigned a five-digit "specimen ID" number. The specimen ID consists of the last two digits of the year, followed by a three-digit number reflecting a series of specimens (001, 002, etc.). When the specimens all have ID's, all the appropriate data are recorded for the specimen in an electronic log that is resident on our building's server.

After the specimens are recorded and have been labeled with the specimen ID, the test conditions the specimen will be run under are determined. The first step in the testing process is to cut the initial notch in the specimen. When the notch has been cut, the specimen is then loaded in one of several testing machines where it undergoes a series of maximum to minimum load cycles. After many cycles (can get into the millions) the specimen starts to form a crack that propagates from the initial notch tip. The test is then run until either a specified cycle count is met, a desired load is achieved, a desired crack length is present, or the specimen simply breaks (catastrophic failure).

At the completion of the test, the raw data (data created during the test containing test conditions and test data, such as crack length, cycle count, etc.) is run through several data reduction programs. One of these computer programs is "CRKCORR," (created by Reji John) a program which corrects any "jumps" or errors in the data. "CRKCORR" fitted the raw data to many optical measurements, which were recorded at varying times during the test. "MATE" is a program which calculates the closure load (event where the crack mouth actually closes during a cycle) if closure was present in the test. "SMOOTH" is a program designed to smooth the reduced data for scatter. Once the data reduction has been completed, the data created by the data reduction is plotted using "KaleidaGraph." Three main plots are usually created; A vs N Plot (Figure 1), Crack Length (a) vs Cycle Count (N); da/dN vs ΔK (Figure 2), Growth Rate vs Stress Intensity Factor; and Kcl vs Kmax (Figure 3), Closure Stress Intensity Factor vs Maximum Stress Intensity Factor. After these plots are created, they are analyzed, and important information is extracted.

When the specimens are machined from the parent plate, small pieces of scrap are left over. These scraps can be used to analyze the microstructure or specifically, analyze the layering of the specimen. The parent plate contains a number of small plates placed on top of each other and pressed into a "layered" specimen. In this Task, small 0.5" x 0.5" samples were cut out of the machining scrap. They were then mounted and polished in both the transverse (against the grain or fibers) and longitudinal (with the grain or fibers) directions. Then photographs of the samples were taken which showed the "layering" in the plate. These pictures were then scanned into a computer image and put into a viewgraph. These viewgraphs were then used in many presentations.

RESULTS

As was the objective of this Task, the fatigue of Metal Matrix (Titanium) Composite Material and Monolithic Material was explored. Resulting from this study and the analysis of the microstructure, the theory that a Ti-6Al-4V Plates contained an abundance of Molybdenum has surfaced. Investigation of this theory is pending until the resigning of this Task, after which work will be done on the scanning electron microscope (SEM) to learn where the extra amount of Molybdenum resides.

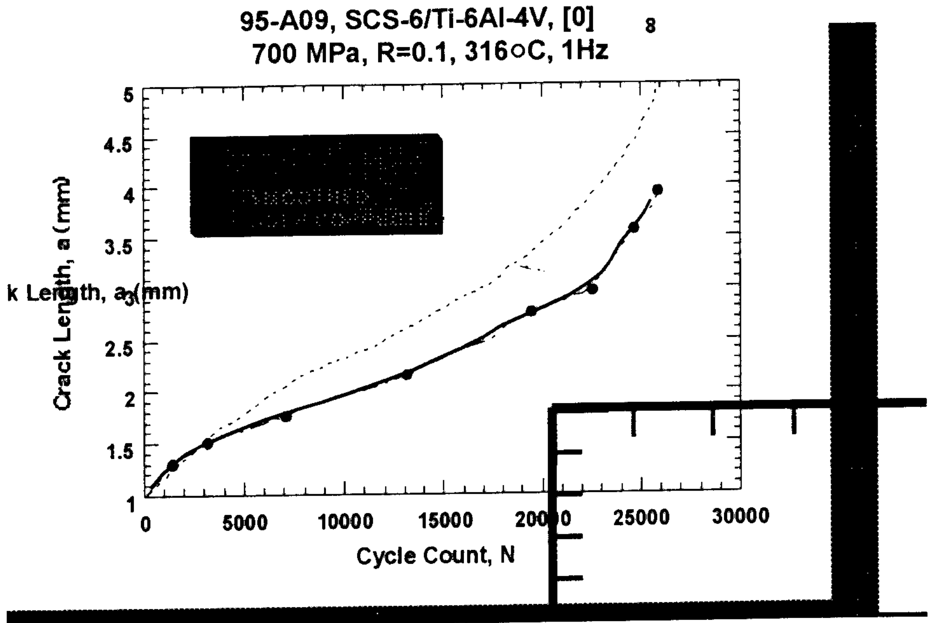

Figure 1- Typical A vs. N Plot (Crack Length vs. Cycle Count)

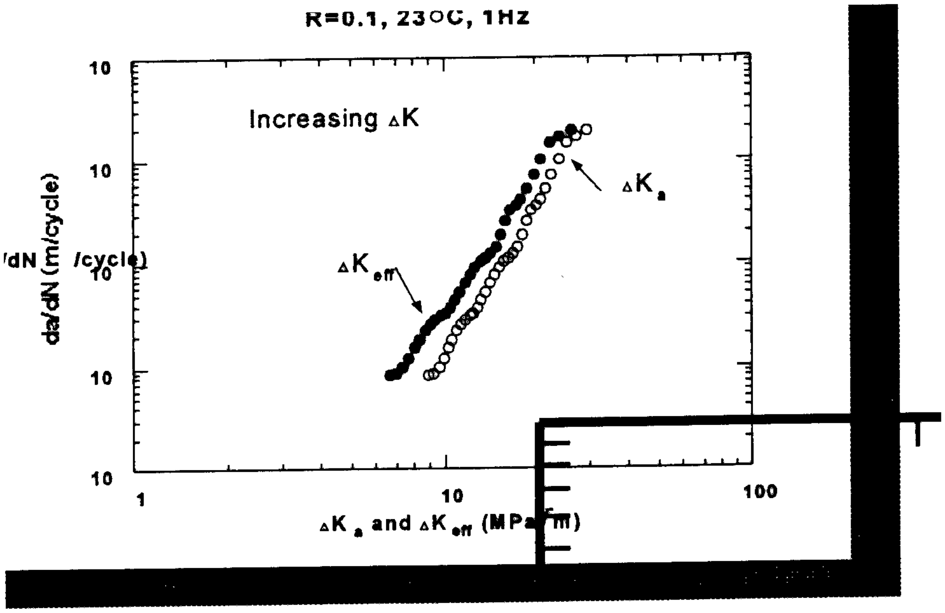

Figure 2- Typical da/dN vs. ΔK Plot (Growth Rate vs. Stress Intensity Factor). In this Figure Closure was present, (referenced by "ΔKeff")

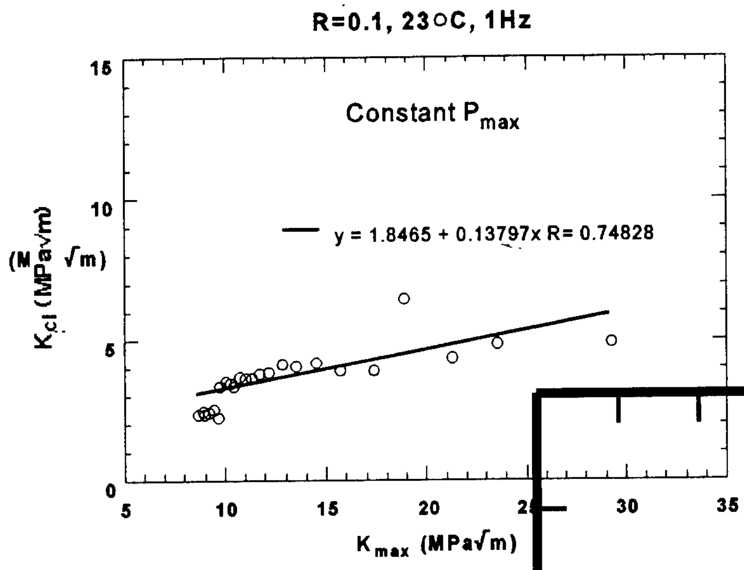

Figure 3- Typical Kcl vs. Kmax Plot (Closure Stress Intensity Factor vs. Maximum Stress Intensity Factor

METALLIC COMPOSITES (95-III)

Task Order No. 178
Student Support Program
Southwestern Ohio Council for Higher Education

Christopher M. Penick
Wright State University

2 July 1996

Government Task Leader
Dr. Benji Maruyama
WL/MLLM

ACKNOWLEDGMENTS

It is a necessity to thank everyone at the Wright Laboratory facilities for their unending help, guidance, and friendship. Special thanks goes to Dr. Benji Maruyama for his leadership, technical direction, guidance and encouragement. Also, thanks goes to Dr. Doug Gundel (a visiting scientist) for his endless help. Finally, Sunil Warrier (a visiting scientist) deserves special 'thanks' for his brevity and humor. Again, thanks to everyone, including the staff of SOCHE, for all the much needed help.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

As stated by the Task initiator, the objective of the current Task is to determine interface properties, residual stresses, and deformation characteristics in advanced metallic composites for high temperature applications. However, as with all endeavors, the main objective is split into increasingly smaller objectives that need to be met on a day to day basis so that the ultimate objective can be reached.

The work load of the Task consists of establishing known techniques for producing single and multiple fiber composites for their various geometries and matrix/reinforcement combinations. Also, it became necessary to develop new techniques for composites production when known techniques are no longer adequate to handle new geometries and matrix/reinforcement combinations. Then, with these composites, the Task work description calls for the determination of interface properties, residual stresses, and deformation characteristics in the advanced metallic composite. Often, it was necessary to do testing, mechanical, chemical, etc., on the single fibers, the single fiber composites, and the multiple fiber composites. Therefore, data analysis became a necessary operation in completing the Task objectives.

Composites have been in use in the public for years. However, the difficulties and high cost in the production of metal matrix composites have kept them from public use. Apparently, there is a growing demand for high strength, light weight, high temperature materials. Some of this demand may be met with the development of metal matrix composites. A metal matrix composite might be formulated to withstand the high temperatures and stresses found inside a high performance military turbine engine. Therefore, the goal may be to incorporate such a material into the blades of the various stages, walls and lining of the turbine, and the actuator rods of the exhaust nozzles. This combination of applications will allow the turbine engine to perform superiorly to current turbine standards. This is a large scale example of an application. On a day to day level, metal matrix composites may be used in electronics packaging to produce electronic devices that run more efficiently and cooler than current material technology allows. The problem with many modern computers and control systems, in an airplane landing gear control system for example, is that they run very hot as they do millions of computations per second and are subjected to unusual loadings. A metal matrix composite would give electronic packaging the stiffness and toughness, thermal conductivity, and weight ratios needed to compete with the demand for faster and better electronics.

The applications for metal matrix composites are extensive. They can provide many advances in design and engineering that have, thus far, been held back by the lack of what a metal matrix composite can provide. With the research from this Task, perhaps these barriers may become less burdensome.

MATERIALS TEST AND EVALUATION

Task Order No. 179
Student Support Program
Southwestern Ohio Council for Higher Education

Daniel B. McCray
Wright State University

15 June 1996

Government Task Leader
Mr. James Folck
WL/MLSE

ACKNOWLEDGMENTS

I would like to express my gratitude to some individuals involved in making my Task a success. Mr. Folck, the Task Leader, was very adapting when forming a work schedule. This allowed me to work and attend school with little conflict in schedules. Mr. Ron Kuhbander and Jim McKiernan of the University of Dayton Research Institute were responsible for providing guidance and giving daily assignments. MSG. Bryan Cramer, Doug Carter, Mark Forte, and James Mazza assisted in providing guidance and training in specialized areas including aircraft repair, aluminum surface treating, adhesive bonding, and composite fabrication techniques. I thoroughly enjoyed working with this group and will value the experience and knowledge that I have gained while working at WL/MLSE.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The main objective of this Task was to conduct short, in-house investigations and evaluate various materials and processes for Air Force applications. The investigations were associated with projects headed by government engineers. Work associated with these projects include: experimental setups, conduction of experiment, data reduction and organization, and project write up.

One project conducted during this Task centered on characterizing a new adhesive for use on aircraft repairs. This adhesive can be used as a laminating resin for composite structures. The manufacturer of this second generation epoxy resin system claims that this adhesive offers a better shelf life and working life over its predecessor without sacrificing mechanical properties. The objective of this project was to verify if this claim were true.

Another project conducted during this Task revolved around determining the effect of varying the mix ratio of an epoxy laminating resin system. The manufacturer of this resin system provides the optimum mix ratio. However, when used in the field, it is a common practice of technicians to alter the mix ratio to allow a patch to cure faster or slower depending on the specific need. The objective of this project was to learn the effect of mix ratios on the mechanical properties.

The final major project conducted was an effort as a part of the Four Powers Aircraft Battle Damage Repair Group. This group is composed of engineers from the United States, France, Great Britain, and Germany. Each of the four countries is responsible for certain activities that will analyze patched composite structures. The U.S. was responsible for fabricating composite test specimens with 6inch diameter holes in the middle. These panes were fabricated at the Flight Dynamics Directorate at Wright- Patterson Air Force Base. These panels were then delivered to WL/MLSE to be patched in several different ways. These repaired panels could then be delivered to France for testing.

RESEARCH DESCRIPTION

To characterize a resin, many tests must be done. To characterize the second generation adhesive as a laminating resin, laminates composed of epoxy and graphite cloth was fabricated under four different conditions. These four conditions are characteristic cure conditions for composite patches or panels fabricated in the field are: full vacuum, partial vacuum (20 in Hg), Navy debulk, and 35 psi positive pressure. Laminates were made for each condition so that mechanical properties could be found for in-plane shear, pin bearing, and IITRI compression. All of the panels were fabricated and specimens were cut out. The in-plane shear specimens were humidity aged to 1% weight gain, and then tested. The pin bearing and compression specimens are in the process of being humidity aged to 1% weight gain.

For the mix ratio project, laminates were made to learn the in-plane shear, pin bearing, and IITRI compression strengths of laminates made from an adhesive whose mix ratio was varied. Five mix ratios were used, including: control, a +15% hardener, -15% hardener, +50% hardener, and -50% hardener. Laminates were fabricated so that specimens for the four tests listed above could be conducted. The specimens were then humidity aged to saturation.

The Four Powers project was very interesting. Composite panels were received with the 6inch holes in them. Three different patch ideas were looked at. The first was a pre-cured patch. A graphite fabric/epoxy patch was fabricated under 20 inches Hg vacuum. It was then bolted to the test specimen with mechanical fasteners. The second patch was known as a "wedding cake" co-cured patch. The hole was filled with Bondo. A patch was then laid up directly over the filled hole. The patch was composed of circles. The bottom circle was 15.25 inches in diameter. The next circle was .75 inches smaller in diameter. This was continued until the top circle was 7inches in diameter. The patch was 12 plies thick. The patch was laid up directly over the hole and cured the specimen under 20 in Hg vacuum. The third patch was similar to the "wedding cake" patch. However, it was upside down so that the smallest ply was on bottom and the largest ply was on top. The patch was fabricated identically to the "wedding cake" patch.

RESULTS

To this point, it seems that the new generation adhesive does have superior shelf and pot life without a decrease in mechanical properties. However, further tests are still in progress. The pin bearing and IITRI specimens still need to be tested. It also appears, the way the panels are fabricated, has a large effect on the properties. The specimens fabricated under full and partial vacuum had more porosity and less strength than the panels fabricated under positive pressure and Navy debulk.

The effect of mix ratio is still waiting to be seen. The specimens are in humidity at this time and due to be tested in the future. It is expected that a difference in strength and glass transition temperature will be seen. The densities of the panels were seen to change greatly depending on the percent of hardener added.

The patched panels are completed and ready to be shipped to France for testing. It is not expected that a large difference in strength will be associated with the different patching concepts.

SYSTEMS SUPPORT-MATERIALS BEHAVIOR AND EVALUATION

Task Order No. 180
Student Support Program
Southwestern Ohio Council for Higher Education

Sean Friedmann
Wright State University

11 June 1996

Government Task Leader
Mr. Jim Folck
WL/MLSE

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I would like to express my gratitude to a few people who were involved in making this Task a success: Mr. Ron Kuhbander of the University of Dayton Research Institute, who was responsible for providing training and project assignments. Without his leadership and patience none of my assignments would have been accomplished; MSGT Brian Cramer and Doug Carter for providing technical knowledge to the importance of each project.

DESCRIPTION OF TASK ASSIGNMENT

The main objective of this Task was to conduct in-house evaluations of various material and the associated processes dealing with the support of Air Force aircraft repair. Most of the projects conducted were lead by government engineers.

One project done during this Task was a mix ratio study of Hysol 9396 two-part epoxy resin. This resin is approved for field level repair on aircraft. At the field level, the resin is obtained through a dispenser. One main problem is the tolerances on the dispensers, which vary the amount of hardener. Sometimes the hardener was varied either to speed up or slow the pot life and cure time. Another is the possibility that the resin is not being mixed well before use. Therefore, the reason for the study was to evaluate the mechanical properties when the hardener was varied.

Another project worked on was the Characterization study of BR6747 environmentally safe primer. This primer was being tested to possibly replace a hazardous primer, which contains chromates. This was an existing project from a previous Task.

RESEARCH DESCRIPTION

The project was split into two major components. The first part consisted of running a gel-time and exothermic temperature test. This was done in the hood using a total of 130gms of resin at a steady-state temperature of 72° F. The percentage of the hardeners was varied from 0%, +15%, -15%, +50%, -50%. Each part was placed in a water bath for several hours before mixed. Once each part was at the control temperature, they were mixed into a container. At the center of the mixture was a thermocouple to measure the exothermic temperature. The temperature was recorded every 5 minutes until the resin gelled. This was done per ASTM standard D2471-88.

The second part consisted of using the same mix ratios to impregnate 9 x 9 W133 carbon fiber composite. This was done by spreading the mixture through the carbon fiber and then cutting the fiber to size. Once to size, the fiber was placed in a vacuum bag and cured at 200° F for 65 minutes. When the temperature was below 150° F, the panel was removed and the edges squared. The panel was then labeled and cut into specimens. The specimens, in plane shear and pin bearing, were sent to be tested. The physical specimens were sent to be scanned and environmentally conditioned.

The primer study consisted of finishing the mechanical testing of prefabricated specimens and to verify the environmental condition test. These tests were used to check to reaction of the primer to different environmental conditions. The test started with three 3 x 5 inch aluminum panels. The surface prep was solvent wipe, scotch-brite, and P2 etch with carbo-sil. The panel was then primer and cured. The three panels were then tested under three conditions, which were water resistance, heat resistance, and corrosion resistance. The water resistance test consisted of immersing the panel in distilled water for 7 days and then exposed 120° F to 95-100% relative humidity. After exposure the panel must not show any cracking or blistering, and have a pencil hardness of 4H. The heat resistance test consisted of exposing the panel to 250° F for 70 hours. They would have the same after exposure results as the water resistance test. The corrosion resistance test consisted of scribing an X across the panel and exposing the panel for 40 days in a 5% salt fog. The panel would then follow the same after exposure conditions as the water resistance test.

RESULTS

The results of the gel-time and exotherm were acceptable. There was little difference among the 0%, -15%, +15% to require any recommendations. The remaining two were enough to recommend that the dispensers' tolerances be closer than +50% or -50%.

The results of the in plane shear specimens and pin bearing specimens are still in progress and should be done next quarter. The results of the physical properties are also still in progress and are being tested now.

The mechanical testing was finished and the results were given to the project leader who completed the report and data. The environmental testing was successful in all three areas. The primer was then combined with previous data collected by other project members and then given to the project leader.

THE SYNTHESIS OF BENZOTHIADIAZOLE MODEL COMPOUNDS AND POLYMERS FOR EVALUATION AS NONLINEAR OPTICAL MATERIALS

Task Order No. 181
Student Support Program
Southwestern Ohio Council for Higher Education

Gina Hess
Wright State University

14 June 1996

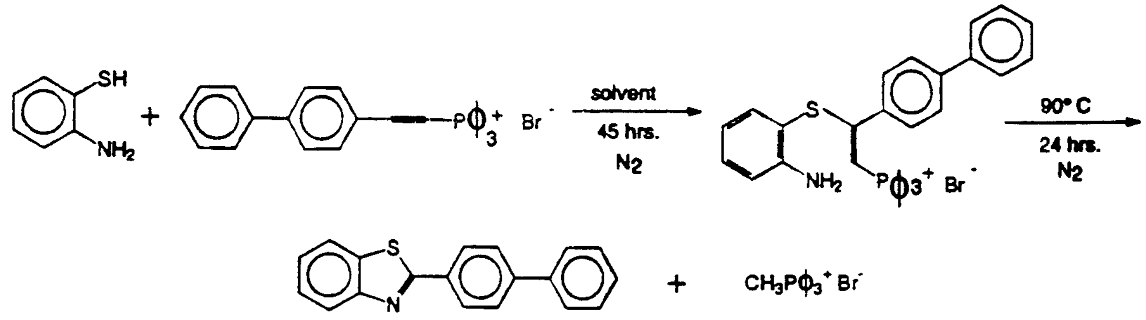
Government Task Leader
Bruce Reinhardt
WL/MLBP

ACKNOWLEDGMENTS

I gratefully acknowledge the help that Bruce Reinhardt has given me. I have learned a great deal from him.

TASK ASSIGNMENT

The objective of this Task was to synthesize and evaluate new benzothiadiazole model compounds and polymers as potential third order nonlinear optical materials. One reaction in particular has been examined to make a model compound and to try to maximize yields:



It was thought that a high yield could be obtained if the right solvent was found for the first step. Accordingly, nine experiments were done in which the solvent varied.

EXPERIMENTAL PROCEDURE

The salt was dissolved in solvent and degassed. Aminothiophenol was added, and the solution stirred for 45 hours under nitrogen at room temperature. After 45 hours, the product was heated under nitrogen at 90° C for 24 hours. Work up varied according to the experiment. Table 1 lists the details of the individual experiments.

Table 1

Experiment	Solvent	Solvent Volume (ml)	Yield (g)	Of D (%)
A	Ch_3CN	20	0.62	77
B	Nitromethane	20	0.63	78
C	NMP	20	0.50	62
D	Methanol	20	----	----
E	CH_3CN	20	0.60	74
F	NMP&DBU	20	----	----
G	NMP&DBU	20	----	----
H	CH_3CN& DBU	20	----	----
I	NMP	20	----	----
J	DMSP	10	----	----

For experiments A-E the starting material came from the same batch; 0.3 ml of A and 1.81 g of B were used. In experiments F-J, the starting material came from a different batch than that used for experiments A-E. For experiments F-J, 0.37 ml of A and 1.81 g of B was used. The discrepancy between the amounts of aminothiophenol used in the first five experiments and the last six were due to a miscalculation. The correct amounts for molar equivalency are those given for experiments F-J.

Experiment A: After 45 hours of stirring, the acetonitrile was removed. The yellow residue was heated for 24 hours, and the product was rinsed with water to remove salts. The water was decanted and the product was recrystallized from ethanol.

Experiment B: After the first step, most of the nitromethane was removed by rotoevapporation, and the product was heated for 24 hours. It was recrystallized from ethanol.

Experiment C: Because NMP has a high boiling point, it was not possible to remove before going on to the second step of the reaction. So, the solvent was left in the flask and heated to 90° C for 36.5 hours. It was poured into ice water, filtered, and stirred with methanol, and filtered. The product was recrystallized from ethanol.

Experiment D: Methanol degrades the starting material.

Experiment E: This reaction was performed to determine if the aminothiophenol was pure. Instead of using 0.30 ml of A, 0.45 ml was used to see if the yield would increase over that of experiment A. The procedure was the same as that of experiment A.

Experiment F: In this reaction, DBU (0.52 ml, one equivalent) was included to see if the addition of a base could catalyze the reaction to better yields. As in experiment C, no attempt was made to remove the NMP, and it was heated at 90°C for 24 hours. After heating, the solution was poured into ice water, but only an oily suspension formed. The pH of the water was adjusted to one with HCl, but this did not cause any precipitation.

Experiment G: The procedure for this experiment was the same as for experiment F; the workup differed. After pouring the mixture into ice water and getting an oily suspension, it was extracted with methylene chloride. The TLC (alumina, 2:1 methylene chloride, hexane) however, showed that very little product was present.

Experiment H: DBU (0.52 ml) was added to the solvent, and after the first step, the acetonitrile was removed. Because DBU boils at a high temperature, it remained in the flask while heating at 90°C for 24 hours. The oil which resulted did not solidify when placed into water. It was stirred in methanol and dissolved completely. The desired product does not dissolve in methanol, and it was concluded that no product was formed.

Experiment I: The procedure for this experiment mimicked that of experiment C, although this one was heated for 24 hours. When placed into ice water, an oily suspension formed. It was extracted with methylene chloride, but the TLC showed no product.

Experiment J: After the first step, the DMSO was extracted with ether (20 ml, 2x). The oil layer was placed back into the flask and heated. The dark green residue was poured into ice water and solidified. Attempts to recrystallize from ethanol were unsuccessful. The insoluble solids were hot filtered, and a TLC of the filtrate showed at least five spots, with the product spot being faint.

CONCLUSION

It appears that dielectric constant of the solvent is important for achieving good yields in this reaction. The best solvents also had the highest dielectric constants, 37.50 for acetonitrile and 35.87 for nitromethane.

It was postulated that adding base to the reaction would increase yield. Experiments F, G, and J that used DBU yielded nothing, but so did I and J that contained no DBU. These experiments did use the same batch of starting material though. Except for the starting material, experiment I mirrored that of experiment C and should have given a yield of at least 62%. It is believed that the starting material was the problem, and that the experiments with the base are inconclusive.

THE SYNTHESIS OF BENZOTHIADIAZOLE IN MODEL COMPOUNDS AND POLYMERS FOR EVALUATION AS NONLINEAR OPTICAL MATERIALS

Task Order No. 181a
Student Support Program
Southwestern Ohio Council for Higher Education

David P. Stitzel
Wright State University

14 June 1996

Government Task Leader
Mr. Bruce A. Reinhardt
WL/MLBP

ACKNOWLEDGMENTS

I would like to take this opportunity to thank Mr. Bruce A. Reinhardt and Dr. William A. Feld for their guidance, advice, and consultation. I would also like to express my sincere thanks and gratitude to SOCHE and the Polymer Branch at Wright-Patterson Air Force Base for giving me the opportunity to gain knowledge and work experience in organic synthesis. I am confident that the knowledge and laboratory experience that I have acquired will continue to be invaluable to me in the future.

TASK ASSIGNMENT

Task 181 involved the synthesis, characterization, and preliminary evaluation of tetraphenylnaphthalene in model compounds as potential third order nonlinear optical materials.

RESEARCH

The electron rich polycyclic aromatic compound 1,4,5,8-tetraphenyl-2-naphthaldehyde was synthesized via a five-step reaction scheme1[1].

The first step involved a Diels-Alder reaction between t-1,2-dibenzoylethylene and t,t-1,4-diphenyl-1,3-butadiene in re fluxing 2-propanol yielding 1,2-dibenzoyl-3,6-diphenylcyclohex-4-ene.

Experimental: t-1,2-dibenzoylethylene (28.20g, 0.1194mole) and t,t-1,4-diphenyl-1,3-butadiene (24.62g, 0.1194mole) was placed into a 1000ml single neck round bottom flask equipped with a magnetic stirrer, reflux condenser, nitrogen adapter, and a heating mantle followed by the addition of nitrogen purged 2-propanol (350ml). The reaction mixture was originally opaque yellow and upon heating became opaque orange. Once at reflux, the reaction solution was transparent orange. The reaction was allowed to reflux for 8 hours under nitrogen atmospheric conditions. The crude product 1,2-dibenzoyl-3,6-diphenylcyclohex-4-ene crystallized upon cooling (yield 49.99g, 95%) and was used in the next step without purification to reduce the possibility of retrosynthesis.

The second step involved dehydrogenation of 1,2-dibenzoyl-3,6-diphenylcyclohex-4-ene with bromine in re fluxing chloroform yielding 1,2-dibenzoyl-3,6-diphenylbenzene.

Experimental: Unpurified 1,2-dibenzoyl-3,6-diphenylcyclohex-4-ene (49.99g, 0.1130mole) was placed into a 2000ml three necked round a bottom flask equipped with a magnetic stirrer, reflux condenser, nitrogen adapter, addition funnel, and a heating mantle followed by the addition of nitrogen purged chloroform (351ml). The starting material went into solution immediately. Upon re fluxing under nitrogen atmospheric conditions, a solution of bromine (11.6ml, 0.225mole) in nitrogen purged chloroform (243ml) was added drops wise for 90 minutes. The reaction was allowed to continue re fluxing for and additional 3.5 hours (monitored by thin layer chromatography). The reaction solution was cooled and rotatory evaporated to dryness and the residue triturated with alcohol then recrystallized from ethanol to give stable 1,2-dibenzoyl-3,6-diphenylbenzene (yield 22.64g, 46%; MP 215-218°C, lit. MP 212°C).

The third step involved reduction of 1,2-dibenzoyl-3,6-diphenylbenzene with zinc and potassium hydroxide in re fluxing ethanol yielding 2,3,6,7-tetraphenylisobenzofuran.

Experimental: Sodium hydroxide (17.94g, 0.4485mole) was dissolved in water (60ml) followed by the addition of ethanol (1136ml). The solution was purged with nitrogen. 1,2-dibenzoyl-3,6-diphenylbenzene (6.64g, 0.0151mole) was placed into an aluminum foil wrapped 3000ml three necked round bottom flask equipped with a mechanical stirrer, reflux condenser, nitrogen adapter, and heating mantle. Upon reaching reflux, the starting material was in solution that was yellow in color. Zinc (17.94g, 0.2744mole) was slowly added and the reaction was allowed to reflux for 2.5 hours (monitored by thin layer chromatography) under nitrogen atmospheric conditions. The green reaction mixture was filtered hot to remove the zinc. Acetic acid (1200ml) was added to the yellow filtrate with stirring. Water (1800ml) was then added with stirring which resulted in the product precipitating out. This mixture was placed in a refrigerator overnight. The crude product was collected and washed many times with water to remove any residual acetic acid. The crude product 2,3,6,7-tetraphenylisobenzofuran (yield 5.41g, 85%) was dried and used in the next step without purification to reduce the possibility of retrosynthesis.

The fourth step involved a Diels-Alder reaction between 2,3,6,7-tetraphenylisobenzofuran and acrolein in refluxing benzene yielding a briged-oxygen aldehyde adduct.

Experimental: Unpurified 2,3,6,7-tetraphenylisobenzofuran (3.03g, 0.00717mole) was placed into an aluminum foil wrapped 100ml three necked round bottom flask equipped with a magnetic stirrer, reflux condenser, nitrogen adapter, and a heating mantle followed by the addition of freshly distilled acrolein (2.8ml, 0.043mole) containing trace hydroquinone, and nitrogen purged benzene (25ml). Upon refluxing, the starting material went into solution immediately. The reaction, was allowed to reflux for 1 hour (monitored by thin layer chromatography) under nitrogen atmospheric conditions. The light yellow reaction solution was allowed to cool to room temperature then submerged into an acetone dry-ice bath for approximately 30 minutes. Upon reaching room temperature, crystals remained. Nitrogen purged 2-propanol (30ml) was added with stirring for approximately 30 minutes. The crude bridged-oxygen aldehyde adduct was collected and dried (yield 2.53g, 74%; mp183-185~c, lit. MP 179-180°C) and used in the next step without purification to reduce the possibility of retrosynthesis.

The fifth step involved dehydration of the bridged-oxygen aldehyde adduct with anhydrous hydrochloric acid in acetic acid at room temperature yielding 1,4,5,8-tetrapheny-2-naphthaldehyde.

Experimental: Unpurified bridged-oxygen aldehyde adduct (2.53g, 0.00529mole) was placed into a 100ml three necked round bottom flask equipped with a magnetic stirrer, reflux condenser, and a nitrogen adapter followed by the addition of nitrogen purged methylene chloride (15ml), which dissolved the starting material, and acetic acid (15ml). The reaction solution was submerged into an ice-water bath for approximately 10 minutes. Anhydrous hydrochloric acid was bubbled into the reaction solution for 15 minutes when the ice-water bath was removed. The reaction was stirred at room temperature for an additional 2 hours and 45 minutes (monitored by thin layer chromatography) with anhydrous hydrochloric acid bubbling into the red solution at a steady state. Reaction solvents were allowed to evaporate off. The nearly dry reaction mixture had residual acetic acid present. As a result, the product was dissolved in nitrogen purged methylene chloride (20ml) followed by the addition of a nitrogen purged 10% sodium bicarbonate solution (30ml) to neutralize the acetic acid. The organic layer was obtained from a seperatory funnel and dried with magnesium sulfate. 1,4,5,8-tetraphenyl-2-naphthaldehyde is presently being purified by column chromatography and will be recrystallized from xylene.

Future Work

Once purified, the electron-rich polycyclic aromatic compound 1,4,5,8-tetraphenyl-2-naphthaldehyde will be attached to two electron-poor molecules, namely 4-picoline and bis-2-benzothiazoylmethane via a dehydration reaction to produce two model compounds. These compounds will be analyzed for potential third order nonlinear optical properties.

Reference

E. D. Bergmann, Sh. Blumberg, P. Bracha and Sh. Epstein, Tetrahedron, 1964, Vol. 20, pp. 195-209.

COMPUTATIONAL MATERIALS SCIENCE

Task Order No. 182
Student Support Program
Southwestern Ohio Council for Higher Education

Fateh Ullah Khan
Wright State University

25 June 1996

Government Task Leader
Dr. Ruth Pachter
WL/MLPJ

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TASK ASSIGNMENT

Objective: Design novel material for laser hardening applications using a variety of computational techniques. These range from ab initio quantum mechanical approaches to molecular mechanics and dynamics, and new methods and algorithms.

DESCRIPTION OF WORK

To develop and improve computer programs to be used for the design of novel laser hardened materials.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The work assigned this summer involved computer programming in C language for UNIX operating system. The assigned program was successfully completed in the given amount of time and has been installed on MLPJ Network as a working tool within bigger software.

Backups of hard drives of Macintosh computers were made through the Network and through the Bernoulli machine.

Different software packages were installed on the hard drives of Macintosh computers.

RESULTS

It was a good real world learning experience. Witnessing the interaction of various types of people in the office was an experience.

Computer skills like UNIX operating system and programming were enhanced. Networking skills were enhanced.

COMPUTATIONAL MATERIALS SCIENCE

Task Order No. 182a
Student Support Program
Southwestern Ohio Council for Higher Education

Steven Wiles
Wright State University

25 June 1996

Government Task Leader
Dr. Ruth Pachter
WL/MLPJ

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TASK ASSIGNMENT

The Task consists of the design of novel materials for laser hardening applications using a variety of computational techniques. These range from ad initio quantum mechanical approaches to molecular mechanics and dynamics, and new methods and algorithms. Currently, the Task is directed toward the understanding and manipulation of simple systems with the use of existing methods and algorithms.

DESCRIPTION OF RESEARCH

Three existing algorithms, of great interest are Charmm, ECEPP, and ASA. Charmm and ECEPP are both written in Fortran and ASA is written in C. The Fortran language is a place by value language, where the C language is place by reference language. This difference in language is overcome by using the Unix operating system on a middle size main frame computer like the Silicone Graphic Machine. The UNIX system has a C compiler with a Fortran option, making it possible to recompile both the C and Fortran program at once.

Charmm was developed by the Department of Chemistry at Harvard University. Charmm's main purpose is the evaluation and manipulation of the potential energy of a marcomeleclular system.

Adaptive Simulated Annealing (ASA), was developed by Lester Ingber Research. ASA is a very fast simulated reannealing meant to deal with the necessity of performing adaptive global optimization on multi-variate nonlinear stochastic systems.

ECEPP computes the atomic coordinates and relative conformational energy of a polypeptide chain in standard geometry, for any given sequence of residues and set of dihedral angles.

RESULTS

The ECEPP and ASA programs have been connected in series to take advantage of the global optimization ability of the ASA. This allows the global optimization of the conformational energy of a polypeptide chain in a simple system, but is limited. Work continues on the connecting of the Charmm and the ASA programs. Once Charmm and ASA are connected this will give a wide range of samples.

COMPOSITE THERMAL STRESS ANALYSIS

Task Order No. 183
Student Support Program
Southwestern Ohio Council for Higher Education

Christine M. Baker
University of Michigan/
University of Dayton

25 August 1995

Government Task Leader
Mr. Bryan C. Foos
WL/MLLP

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The author is deeply in debt to Mr. Bryan Foos for helping guide and direct in many ways. Mr. Foos dedicated an enormous amount of time in assisting with questions and any problems that arose.

TASK ASSIGNMENT

There were two major parts of the Task completed this summer. One of these was working with composite tensile coupons, both strain gage mounting and solvent cementing. The second part of the Task was running ultrasonic scans of graphite/epoxy plates with known delamination.

The summer passed in several different phases. The first few weeks was spent reading about solvent bonding, including chemical safety, and learning how to use the ultrasonic scanner. Also, the author became familiar with the mathematical theories behind the thermoelastic stress-based discrete layer plate theory which is under development. The next phase involved the actual experimentation behind the theories which had been so thoroughly studied. Scans were run on the ultrasonic scanner and strain gages were mounted on the coupons. The coupons were then solvent bonded in a variety of ways, which are explained in detail later in the document. The final phase was the documentation of all that been accomplished throughout the Task, including writing a manual for the ultrasonic scanner and designing a World Wide Web homepage. Also, the work accomplished toward solvent bonding was documented so that it could be continued.

COMPOSITE TENSILE COUPONS

A. Strain Gage Mounting

One on the steps in preparing the samples for testing is to mount strain gages. Strain gages are microscopic sensors that can be used to detect a strain within a specimen. Because of the size of the sensors, mounting them onto the composite coupons is difficult. Kits of chemicals with specific directions have been designed specifically for this purpose.

The series of steps to mount them involves cleaning the specimen, preparing the sensor, aligning the sensor on the sample, and then the actual cementing. Following those steps, most of which involve the use of chemicals from the kit, soldering a series of wires to the tiny sensor is necessary so that the strain can be read from it. This is one of the hardest parts, because of the size of the sensors. However, after practicing, mastering it is possible.

B. Solvent Cementing

Many steps taken were taken to find the most efficient way to cement two coupons together. The chemical used was methylene chloride. Because this is a hazardous material, special precautions were taken before using the chemical. Methylene chloride dissolves the composite materials upon contact, while it also evaporates very quickly.

The instructions for bonding include soaking a piece of felt or a sponge in methylene chloride, then touching the coupon to be bonded to the wet surface. Immediately after contact, the coupon is pressed upon another coupon to form the bond. In other words, the felt or sponge acts almost like an applicator of the chemical.

In the first trial, neither felt nor sponge was available, so a piece of foam was substituted. This turned out to be a mistake, because there was a bad reaction between it and the chemical. Not only did the fibers in the foam expand, but they also froze due to an endothermic reaction.

In the next trial, sponge was used. However, the sponge was too thick to absorb enough methylene chloride before it evaporated. After halving the thickness, the sponge seemed to work. However, the sponge, like the foam, froze from an endothermic reaction, and because of the porous nature of the sponge, it did not uniformly coat the surface of the specimen.

The next step was to try a piece of felt. Because the felt was so thin, it easily absorbed enough of the chemical to soak the coupon. However, many fibers of the felt stuck to the samples and were visible within the bond. Also, at times the coupons were almost bonded to the felt because the reaction is so rapid.

The final trial was to forgo the use of a medium to apply the methylene chloride. A small amount of the chemical was pored into the bottom of a pan, then the sample was literally dipped into the chemical. At first, it seemed as if this worked better than any other method. However, upon further examination, part of the sample had apparently dissolved within the chemical; when the chemical evaporated, the residue of the sample was left in the pan.

ULTRASONIC SCANNING

A. Graphite Epoxy Plates

During the experimentation for Mr. Foos' masters degree, *Damage Progression in Composite Pltes Due to Low Velocity Impact,* he had constructed graphite/epoxy plates of 12, 24, and 48 layers of both 0/90 and +-45 fiber orientation. These plates were all 7 inches by 7 inches. They were struck with various weights of varying velocities to find out the damage occurring within the plates. The damage, on most of the plates, is not apparent when one simply looks at the plate. Therefore, a scan of the interior delamination must be completed. Mr. Foos' did a simple c-scan showing the extent of the delamination. However, the scans he completed had no indication of the damage layer by layer.

The scans completed on the Large Tank Ultrasonic Scanner demonstrated the damage through the layer and as a result could be analyzed for the shape and extent of damage on each layer.

B. Equipment/Software Manual

Many days were spent learning how to use the Large Tank Ultrasonic Scanner from both Dick Martin and Bryan Frock. A few weeks after learning to use the equipment, another student, Craig Fortner, needed to learn how to use the scanner also. The author not only taught him to use it, but together they wrote a manual on the use of the ultrasonic scanner. Strangely, there had never been a manual written on the usage of the scanner. While Craig wrote about the hardware, the author wrote on the software of the scanner. There is an extensive computer program in which one enters the parameters and control settings before running a scan. Also, during the scan, the user can change the color formatting of the computer display so that it is apparent if the scan is accomplishing the needed task.

RESULTS AND CONCLUSIONS

The results of this summer's work are varied. On one hand, Mr. Foos now has a more finalized theory and directions with which he can follow to produce more samples easily. Also, he has many c-scans with which to base his theories on for damage progression throughout the layers of a graphite/epoxy specimen.

To display the results of the summer and other work that Mr. Foos has completed, the author and Craig Fortner designed a World Wide Web Homepage for Mr. Foos. The most notable feature of the page is the background, which is one of the more interesting c-scans. Also, all of Mr. Foos' personal references and information about the Materials Laboratory and Wright Laboratory are included.

This summer has been very productive and worthwhile. While learning engineering and reasoning skills in dealing with people, other skills necessary for working within an office and laboratory environment were acquired.

MICROSTRUCTURE DEVELOPMENT IN TITANIUM ALLOYS

Task Order No. 184
Student Support Program
Southwestern Ohio Council for Higher Education

Jamsheed Reshad
Wright State University

12 June 1996

Government Task Leader
Mr. Thomas F. Broderick
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TASK ASSIGNMENT

The primary objective of the Task was to establish the effect of processing variables on microstructure development in nickel-base superalloys. Specifically, the effect of forging strain, strain rate, and temperature and subsequent supersolvus heat treatment conditions on abnormal grain growth have been determined. The resulting data from microstructures in as compressed and compressed and heat treated samples, can later be interpreted using computer simulations of the deformation process and conventional metallurgical descriptions of abnormal grain growth kinetics.

A secondary objective of the Task was to learn solvus temperatures of various phases present in a titanium-based alloy. The solvus temperature determinations were studied using isothermal heat treatments. Results obtained will ultimately determine what types of aging treatments can be used for certain applications.

The tertiary objective of the Task was to learn the mode of failure for another titanium-based sheet alloy (in its as-received condition), which was initially having problems during certain stretch forming operations. The second step in this project was to alter the material's microstructure, through precipitation of a secondary phase, to improve its flow behavior over the as-received material. The results obtained will aid in understanding this material's flow behavior.

RESEARCH METHOD

The steps for research and analysis for all objectives were very similar (except that the third objective included a mechanical testing phase). These main steps were heat treatment, specimen preparation, mechanical testing (for the tertiary objective), and specimen analysis.

Before an actual heat treatment, a certain methodology must be followed. The material to be heat treated is received in bulk form and sectioned to a desirable shape using an abrasive cutting machine. The sectioned material, or slices, are then cleaned in acetone and encapsulated in quartz tubing under a vacuum. The cleaning and encapsulation of these specimens before heat treatment are done to prevent contamination that can occur under high temperatures in atmosphere. The actual heat treatment takes place in a muffle furnace with a temperature range of up to 1200 Celsius. For both primary and secondary objectives of this Task, the heat treating methodology consisted of an isothermal forming heat treatment for all specimens and subsequent heat treatments for individual specimens. The forming heat treatments were used to precipitate the phase or phases under evaluation and cooled in the atmosphere. The individual heat treatments were used to learn the solvus temperatures and was water quenched so that the resulting microstructure will represent the material at the specific heat treating temperature. The heat treatments for the tertiary objective were designed to precipitate a secondary phase with a desired size, shape, and distribution.

Specimen preparation begins with sectioning the heat treated material by using a gravity fed diamond saw. The material is then mounted in Konductomet using a mounting press to ease the handling of the specimen during the polishing phases. The polishing process is composed of an initial polishing phase, an intermediate phase, and a final polishing phase. The initial polishing phase is composed of subjecting the specimen to silicon-carbide grit paper from 240 grit to 600 grit. This is done to make the surface as level as possible while decreasing the size of surface scratches. The intermediate or lapping phase includes polishing the specimen using a suspended diamond solution on a wheel. The lapping stages use 9 micron diamond suspensions in stepwise increments through 1 micron suspension. The final polish consists of placing the specimens in a vibromet containing neutralized .06 micron colloidal silica. This final stage produces a pristine scratch free polish.

Mechanical testing for the tertiary step involved using previously prepared specimens for tension testing. These tests were done on a screw driven tensile test apparatus, at various strain rates, to obtain stress-strain data used in interpreting the material's flow behavior. Analysis of mounted and tensile tested specimens are usually done in the scanning electron microscope (SEM). Due to the nature of the SEM, all specimens must be thoroughly cleaned and baked out under a vacuum to insure safe operation of this expensive equipment. While on the SEM, the presence of phases under analysis can be detected by electron dispersal spectroscopy (E.D.S). Also, digital images of the surface are collected at various magnifications. These digital images can then be analyzed using computer software such as NIH Image that can determine the volume fraction of phases in question.

RESULTS

As outlined with the objectives of this Task, the behavior of the nickel-base superalloy while under various processing variables and its effect on microstructure have been determined. The digital images and data collected from them have been compiled for further examination. The solvus's temperatures for the various phases in the titanium alloy, for the secondary objective, have been determined and will be used for further investigations. The results from the tertiary objective have led to a much greater understanding of this material's flow behavior. Although the attempts to improve its flow behavior through precipitation of a secondary phase have failed, work is still underway to find a solution.

CERAMIC FIBER CREEP STUDIES

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John R. Welch
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Government Task Leader
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TASK ASSIGNMENT

The primary work of this Task was the production of thin foil specimens of coated ceramic fiber tows. Conventional thin foil preparation techniques to achieve this Task proved to yield specimens that were consistently inadequate for detailed analysis in a transmission electron microscope. This required the development of a new approach to allow adequate resolution and inspection of such specimens in the transmission electron microscope. The following is a detailed, step by step approach developed during the past 2 years to achieve such results.

To prepare the samples, they must first be mounted. The recommended minimum amount of fiber is 2+ meters. The fiber tows should be sectioned with a sharp pair of scissors in equal lengths of approximately 10-20 millimeters. A section of irradiated polyolefin shrink tubing of approximately the same length is needed. If 3/16 inch shrink tubing is used, approximately 50-60 of the fiber segments should be cut. Smaller tubing requires fewer fiber segments, and 30-40 will be enough for 1/8 inch tubing. Larger tubing diameters are not recommended due to the immense number of short fiber sections required and the difficulty of handling that volume of short fibers. The fibers should be compressed and bundled as evenly as possible. The fibers are then inserted into the shrink tubing section and the excess hanging out the ends should be trimmed very close to the ends of the shrink tubing with small, sharp scissors. The bundle is then carefully removed from the tubing and immersed in a prepared epoxy solution. A Petri dish works well for this process. The epoxy should be a fast curing heat sensitive type. A catalyst deficient "G-1" epoxy has proven to yield excellent results. The fiber bundle will need to be manipulated in the liquid epoxy to coat the fibers as thoroughly as possible. Rubber gloves are highly recommended at any stage of the process in which hands may contact the epoxy. The epoxy saturated fiber bundle is then carefully reinserted into the shrink tubing. This can be a difficult task, but if an end is compressed to a point without causing any significant elongation of the bundle, the difficulty will be minimal. Ends of fiber hanging out of the shrink tubing should be trimmed with scissors near the ends of the tubing. The shrink tubing is then placed on a preheated hot plate (100+°C) and rolled back and forth to promote even heating or exposed to a heat gun. A thin, flat piece of Teflon can be laid on the hot plate surface to ease cleanups. If very much fiber extends from the end of the shrink tubing, the epoxy may harden before the shrink tubing shrinks, causing the sample to be loosely packed with fibers and saturated with air pockets and voids. The sample is then placed in a low temperature oven and cured for at least an hour at 60-100°C to ensure that all the epoxy has hardened. The shrink tubing is then cautiously removed with an exacto knife or a razor blade. The removal of the tubing can be difficult but is an absolute necessity since the sample will not polish with the shrink tubing around it.

The "rod" section is then cut into shorter pieces on a diamond saw. A metal spring mounting clip (Buehler sampl-klip specimen support springs) can be used as the length guide. The metal spring mounting clip is rolled into a cylinder and the sample will be mounted in epomet in a sample mounting press. Some finely ground epomet will be needed and it is recommended that a small amount of this finely ground epomet be further sifted to produce a small amount of very fine powder. A thin layer of the fine powder should be place upon top of the raised clean ram piston of the mounting press and manicured with a razor blade to eliminate any large pieces that may have made it through the sifting process. The rolled up spring mounting clip (preferably 10 mm or less in diameter) is then placed gently with an open end toward the piston surface in the manicured epomet. The spring clip is then loosely filled with more of the sifted epomet and the short cylindrical rods of fibers are inserted into the epomet filled spring clip, as vertically as possible, fiber ends toward the piston surface. A small amount of sifted epomet is then carefully heaped on top of the cylinder to insure adequate coverage. The piston should then be lowered and the cavity around the spring clip should be filled with the finely ground epomet (not sifted). It is recommended that when raising the piston in the mounting press to expose the piston surface, the piston not be raised completely to the top. When the ram is later lowered, the jarring will be minimal, and the amount of sifted epomet will remain mostly in place as will the spring clip. The rest of the void in the mounting press can be filled with regular epomet.

After removing the mounted specimen from the mounting press, the cylindrical metal clip needs to be cut out of the mount using a diamond saw. Another metal mounting clip of the same type may be used as a guide about how far from the end the initial cross-sectional cut should be made. The end of the spring clip should be visible in the mount from the end that was in contact with the face of the lower piston's flat surface. This can be used as a guide to slice the excess mounting material away from around the spring clip. With practice, this will become easy to judge and minimal grinding will be needed. With a reasonable amount of grinding skill, the spring clip may be used repeatedly by cutting and grinding the excess mounting material away. The spring clip is "unwound," leaving a small cylinder of mounted fibers. If the cuts are made close enough to the spring clip, the sample may not need to be ground to remove the cylindrical specimen.

The next step is to prepare a small glass slide. A piece of a regular microscope slide will do, somewhat rectangular and just larger than the cylindrical specimen. This process can be done on a diamond saw if care is taken so as not to splinter the glass. A Struers' Accutom 2 with a table saw-like set up works very well, as it does for one of the next steps. The edges of the slide should be ground to straight, but not necessarily parallel edges to avoid damaging the polishing surface during the thinning phase of polishing. The flat surfaces of the glass should be roughed to facilitate adhesion of the wax epoxy that will be utilized to attach the slide and the specimen for polishing. A 600 grit silicon carbide finish is suggested (800 grit has proven to be too smooth a surface and 400 grit makes a very rough surface in the glass).

The specimen is then heated on a hot plate, along with a silicon glass (preferred) mounting stub that attaches to the L-shaped mount holding bracket on the tripod polisher. When the silicon glass stub has become just warm enough to melt the wax epoxy (a crystal bond is recommended for easy removal), a flat surface perpendicular to the cylindrical sides of the glass stub should be coated with a light, but thorough coat of the wax epoxy. The piece of glass is then placed upon the glass stub epoxy-coated surface. Care is needed to avoid letting the epoxy get too hot. The epoxy should be fluid like, but too much heat will cause the epoxy to boil, which may cause air bubbles to form under the sample. This is critical for the final polishing phase, since this may cause the specimen to disintegrate before it is sufficiently thin to ion mill. The exposed surface of the glass slide is then coated with a thin layer of the same wax epoxy and the cylindrical specimen will be placed flat side toward the epoxy coated surface of the slide. The side of the specimen that was in contact with the lower piston face of the mounting press is usually used, but if the surface is reasonably flat and the curved sides of the cylindrical specimen are roughly perpendicular to the flat surface of the glass, this is not a crucial requirement for the initial polish phase. After the epoxy has cooled and solidified, the specimen is usually cut in cross-sections several millimeters (discretionary, but the tripod polisher has a height limit) from the surface of the glass slide. Turning the cylindrical glass stub on the edge that has been flattened (by the manufacturer) and cutting the specimen with the table saw-like setup on the Struers Accutom 2 works very well for this step.

The glass stub is then placed in the slot in the L-shaped bracket with the specimen surface exposed. The clamping screw of the bracket is then tightened securely (over tightening the screw may strip the threads and/or crack the glass). The "feet" on the ends of the 3 micrometers should then be leveled. This can be easily accomplished by lowering the feet slightly below the surface of the L-shaped bracket, firmly placing a large glass slide on the bottom surface of the L-shaped bracket, and then raising the feet until they just contact the large glass slide. The feet are then raised equally until they are at a level that is just below or even with the lowest part of the exposed surface of the sample. The micrometer foot that is closest to the sample is then retracted and the other 2 feet are locked in place by the locking rings on the micrometers.

The specimen is then polished in steps, ranging from 30 microns to 0.1 microns, on diamond lapping films (the 3M type gives the best results) mounted on an 8-inch optically flat round piece of glass epoxied on an 8-inch brass polishing wheel. The diamond films are mounted on the glass by first thoroughly rinsing the disk with distilled water, letting the glass surface build up a layer of distilled water, carefully laying the diamond film over the layer of water on the glass with none or very few air bubbles visible through the film, squeegeeing the water out from under the disk (a shower squeegee works well for this), and thin spinning the wheel at high r.p.m. until the water is no longer visible on top or underneath the film. The wheel should then be slowed to low r.p.m.'s, the rear feet of the tripod polisher should then be brought carefully in contact with the film's surface, and then the specimen should be slowly lowered onto the film's surface. The specimen should then be moved alternately toward the center and then toward the film's edge slowly to reduce wearing the disk at one particular radius. The 30-micron polish on the first polish side of the specimen will serve mainly to attain a flat surface on the specimen. The 15 and

6 micron finishes will appear very rough, with the 6-micron finish starting to expose the roundness of the fiber shape when the polishing is nearly complete for that step. The 3-micron finish should produce fibers that are noticeably round, with many chips or pieces missing from the fibers. There will also probably be several small voids in the specimen where there are some air pockets present in the epoxy or where some pull out has occurred. These should be minimal, but virtually unavoidable. The 1 micron finish should significantly improve the appearance of the specimen's fibers, leaving mostly fibers that are obviously round, but contain some slight chipping on the fiber edges. The 0.5 micron finish should leave most fibers appearing perfect, but there may be many fine scratches visible at high magnification (1,000 X) under reduced lighting conditions. An inverted microscope is the best way to examine the specimen. The mount should not be removed from the L-shaped bracket until the final polish has been attained or the plane of polish may be lost, requiring the repetition of a previous step or steps. The 0.1 micron finish may be omitted if the 0.5 micron finish appears satisfactory, but the 0.1 micron will remove many small scratches from the fiber surface. Extraneous debris that may have collected upon the surface also had a tendency to put a few deep scratches in the surface that were not present earlier. Recommended polishing wheel speeds are as follows: 30 micron ~ 125 r.p.m.; 15 micron ~ 75-90 r.p.m.; 6 micron ~ 60-70 r.p.m.; 3 micron ~ 40-50 r.p.m.; 1 micron ~ 35-40 r.p.m.; 0.5 and 0.1 micron ~ 25-30 r.p.m. Cellulose-type sponges are recommended for the 3 - 0.1 micron steps and should be held behind the specimen to clear debris from the film's surface. A different sponge should be used for each micron size (and nothing else) and everything should be kept very clean as debris will cause a lot of problems, possibly even destroying the specimen when it nears adequate thinness. The feet and specimen surface have a tendency to "stick" to the surface of the film for the 0.5 - 3 micron sizes. The 0.5 micron (1 micron films have similar difficulties, but the 0.1 films do not tend to stick) films tend to stick the worst and should be replaced much more often than most of the other films. The films need to be replaced when several pits have appeared in them or when a lot of diamond begins sticking to the sample. The film surfaces are very fragile and can be damaged very easily, so care must be used at all times when handling them. Hands that may contact any of the surfaces should be clean. The surface of the specimen should always be rinsed with distilled water before being placed upon the film's surface. A duster can is useful for removing the water from the specimen's surface to allow inspection.

The glass stub is then removed from the L-shaped bracket when a satisfactory finish has been obtained. The stub is then placed on a hot plate and heated until the sample can be removed from the glass slide. More crystal bond epoxy is applied to the slide surface and when the epoxy forms a smooth puddle, the polished side of the specimen is placed in the epoxy puddle. The specimen should be oriented in a way that will have a small area of epomet at the center of the curved area of the stub. A small amount of pressure should be applied to the top of the specimen in order to assure the specimen is in close contact with the glass surface. After the epoxy has set, the specimen should be rough ground reasonably close to the glass surface. It is best to make the grind a slight wedge with the thin side in the direction that will be oriented toward the center of the polisher. A 68 micron diamond embedded steel disk works very well for this process. The corners of the microscope slide should have excess epoxy removed from the thinned side to expose small portions of the glass slide. The stub is then remounted in the L-shaped bracket of the tripod polisher, preferably with an inside edge of the glass slide roughly parallel to a tangent line to the rear 2 feet.

The tripod polisher's feet are again leveled, then raised evenly until the large glass slide will just barely clear the cleaned off corners of the glass slide upon which the specimen is mounted. The front foot of the polisher is again lowered completely out of the way of the polishing plane and the rear 2 feet will be lowered a total of six turns (3 mm), producing a "reverse" wedge (similar to the rough polish wedge) for the initial plane of polish. The rear feet of the polisher are placed in contact with the surface of the 30 micron film, the specimen lowered to the film's surface, and then the rear feet are then raised just barely above the film's surface to minimize the amount of wedging of the rear feet. When the sample becomes very thin at the rear (this is a judgment gained through experience), the rear feet are allowed to make contact with the film surface. This plane of polish should be continued until the disk makes contact with the edged of the glass slide. A straight line where the crystal bond epoxy is eroding away should be noticeable when the film makes contact with the glass slide. If the specimen is close enough to the edge of the slide and the specimen is oriented such that the thinnest portion of the specimen is composed mostly of epomet, the epomet should appear somewhat transparent. If a noticeable difference is noted in the transparency of the epomet, minor leveling adjustments to the rear feet are in order (if the initial leveling procedure was followed closely). The minor adjustments should probably not exceed 10 marks on the micrometer (100 microns) on either side.

The rear feet are then raised seven complete turns (3.5 mm) and the 30-micron polish will change the wedge to a "forward" wedge. A line should be visible at the intersection of the two planes of polish. The 30-micron polish should continue until this line of intersection reaches approximately 75-85% of the way back toward the rear of the sample or until the front edge of the sample becomes slightly transparent. Again, if a noticeable difference is noted in the transparency from side to side, minor leveling adjustments are in order. The rear feet should then be lowered toward the L-shaped bracket by approximately 25-30 marks on the micrometer. The polishing should then be continued on a 15-micron film until the epomet has all become slightly transparent (a dark gray color), possibly making minor leveling adjustments, if necessary. If too many leveling adjustments are made, the plane of polish will contact the glass slide and the specimen will be much thicker in one direction. A rough guide to where the current plane of polish lies may be made by placing the large glass slide in contact with the feet and the specimen. Fringes may be noted at the plane of polish's contact with the glass slide when the polish reaches the 3-6 micron stage. The polish is then continued the 6-micron film, lowering the feet approximately 10-15 marks on the micrometer, until the epomet turns a much lighter shade of gray. The polish will then be continued on 3-micron and efforts should be made to obtain a very even shade of gray throughout the sample at this point, if in fact this has not already occurred. The 3-micron polish should continue until the epomet is noticeably transparent (still slightly gray) or the front edge of the specimen begins eroding. The polish should then continue on 1-micron until a decent polish is obtained and there is minor erosion noticeable at the front edge of the specimen. The specimen is then polished on 0.5 micron film until several thickness fringes in fibers near the thinnest edge of the specimen are noted or severe erosion of the thin edge occurs.

At this stage, it is necessary to use a film that is in good condition and to make frequent specimen condition checks. Being partially destroyed is usual for areas of the specimen, but sufficient care should reduce this problem. When the thickness fringes become noticeable, the polish should continue on 0.1 micron film for as long as possible. With practice, specimens consistently less than 2 microns with areas ~ 1 micron or less can be produced.

The glass slide is then removed from the stub in the same manner in which it was mounted. The specimen can then be removed by directly epoxying T.E.M. grids on the sample surface, placing the glass slides on a hot plate, separating the grids with a razor blade (if necessary), and then removing the grids with tweezers when the crystal bond epoxy liquefies. Minimal ion milling times should be needed to obtain excellent specimens for T.E.M. analysis.

Additionally, research was undertaken to analyze the temperature and time dependence of grain growth in NEXTEL 720™ fiber tows. The fibers were heat treated for times ranging from 1 to 100 hours and temperatures ranging from 1200°C to 1700°C. Thin foil specimens were prepared for the specimens heat treated to 1500° and they were ion milled and analyzed in a T.E.M. Further analysis of the higher temperature specimens will be carried out by SEM analysis and mathematical relationships will be developed for the data that is and will be tabulated.

COATED FIBER CHARACTERIZATION

Task Order No. 186
Student Support Program
Southwestern Ohio Council for Higher Education

Rodney B. McLaughlin
Wright State University

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Government Task Leader
Dr. Randall Hay
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Overall, this was a good learning experience. For the most part, my coworkers were helpful. Most of the work was challenging and interesting.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

During the summer since my last report, much of the work consisted of finishing the fiber push-in testing started in the spring. The push-in and push-out tests are useful in determining properties of the interface between the fibers and the composite matrix. Fiber push-in testing consists of pushing individual fibers of about 20 microns in diameter into the matrix, using a conical indenter, until sufficient debonding occurs. The total displacement of the fiber is only about 3 to 4 microns. The material tested was silicon carbide/silicon nitrocarbide (SiC/SiNC). Reducing the data involved generating plots of load versus displacement on the computer for analysis. Specifically the aim was to remove the system compliance from the data using a corrected displacement equation. The term "compliance" is not usually recognized. Instead, the term "stiffness" (inverse of compliance) or modulus elasticity is the ability to resist deformation within the linear range of the curve. Load versus corrected effective displacement plots were then generated. The nonlinear portion of these curves was curve fit to determine various material parameters.

Work was done to examine how much fiber contact, interweaving, bending, and variation in orientation in an unidirectional SiC/1723 glass matrix composite by serial sectioning. This is thought to affect the results of fiber push-in and push-out tests. Specimens had been previously polished and photographed over a distance of 262 microns. First, 30 fiber diameters and their respective x and y coordinates were measured for each section using image analysis software. New coordinates were calculated for the fibers using two of the fibers as reference. These coordinates were then entered to a Mathematica® program to produce two dimensional and three dimensional plots of fibers.

Another task involved cutting a 4' length of sapphire fiber into 1 3/4" length to make a composite. The fibers were carbon coated in an oven using P-10 gas (10% argon) for 1 hour at 1280°C. Glass powder was added to form the matrix. The fibers and powder were loaded into a die and hot pressed at 850°C and 500 psi for 20 minutes to form the composite.

In my last report, bend specimens were cut for failure analysis of silicon carbide combuster plates. A failure analysis involves determining the causes of failure and providing solutions to prevent future failures. Samples from three different manufacturers were prepared. These specimens were recut and the width and thickness dimensions measured. Then the four-point bend testing was done. Next, the fractured specimens were gold/palladium coated for viewing under the SEM. The specimens were examined under low magnification, about 100 X. Evidence of fiber pull-out, particulate, and porosity were expected.

The remainder of time was spent working on templates for fiber push-in or push-out testing based on papers by various authors. These templates allow one to calculate various material parameters from data that the user inputs from the computer keyboard.

DESCRIPTION OF RESEARCH

Conventional methods were used in the research and testing. The cutting of samples was done using low-speed saws with 5 inch diamond impregnated saw blades. Polishing was done on 8" polishing wheels using TBW diamond polishing disks. Fiber push-in testing was done on an Instron® testing machine using a conical tungsten carbide probe. Four-point bend testing was done on a Sintech® testing machine. Data reduction was done on Apple Macintosh® machines, and the load versus displacement plots was generated using KaleidaGraph™ software. Fiber diameters were measured using NIH Image software. The two dimensional and three dimensional plots from serial sectioning was generated using Mathematica® software. The templates were created using Mathcad® for Windows™ software.

RESULTS

The work involving the fiber push-in testing was the most rewarding in learning and overall job experience. Along the way I have learned some theory behind the testing and basic interpretation of the data (load vs. displacement plots). The failure analysis of the silicon carbide combuster proved particularly rewarding, since I could follow the analysis from sample preparation to SEM viewing of the fracture surface. In addition, I have learned the basic techniques of metallography.

INFRARED SPECTROSCOPY

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WL/MLBT

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I would like to thank Dr. Harvey Paige for the opportunity to work with him in the WPAFB Materials laboratory. I would also like to thank Dr. Jim Liang for trusting my work to help with his research and teaching the needed skills to work in the laboratory with his research. I would like to thank the entire MLBT branch for making the Task an enjoyable learning experience.

GENERAL DESCRIPTION OF TASK

Experiments were run to study the wear scars of stainless steel M-50 specimens after they had been run on a tribometer. During the tribology experiment, an acid species was formed and its concentration had an inverse relationship to its relative humidity. These specimens were scanned with an FTIR spectrometer that contained a grazing angle objective lens attachment that allowed for the surface of the M-50 specimen to be examined.

These specimens were studied with the grazing angle microscope attachment to view the concentration of acid formed on the wear scar area during the tribology experiment.

The results of this experiment were used to help Dr. Jim Liang of UDRI and Dr. Larry Helmick of Cedarville College in studying the effect of humidity on a Perfluoropolyalkylether (PFPAE), namely Fomblin-Z, during a tribology experiment. Through these experiments, they could observe the relationship of humidity with acid concentration and try to measure the layer of thin-film created by the acid species.

DESCRIPTION OF RESEARCH

The initial tribology experiments were run by Dr. Larry Helmick on a Cameron-Plint High Frequency Friction machine. During these experiments, a round M-50 disc with two flat sides-one polished - is laid into a hole in the center of the machine made to fit the M-50 specimen. A small cylindrical roller (about 7 mm long) is placed on top of the M-50 disc and repeatedly rolled across the specimen for 2-5 hours in the presence of about 1ml of Fomblin-Z. This entire system is enclosed and the humidity in the system is regulated by a humidity controller. After the experiment is finished, the roller, M-50 disc, and Fomblin-Z fluid are removed and placed in vials for further analysis.

The M-50 discs have a wear scar in the middle of the specimen with a length of about 8mm and a width of about 3mm. Each disc is cleaned in an ultrasonic bath for 20 minutes with Freon 113. They are then placed on the diaphragm of the microscope containing the grazing angle attachment. The diaphragm of the microscope is equipped with a ruler along the top and the left side allowing for exact measurement of the wear scar. The microscope is initially in the view mode with a regular 10X objective lens. The wear scar is visible on a TV monitor connected to the microscope. The wear scar is viewed from left to right at each 0.5mm and recorded about what color the area appears which range from a dark blue to a yellow color. A background point was determined by moving the focus of the microscope to a point off the wear scar, but still on the disc. At this point, the regular objective lens is switched to the grazing angle and the light of the microscope is switched to full power. The disc is then put into the "grazing mode" by moving the focal adjustment until a very bright light appears on the screen. At this point, the lights of the microscope and the monitor are turned off and the microscope is switched from the view mode to the IR mode. A nitrogen purge is constantly flowing through the grazing angle attachment to make sure that the spectra are not affected by the atmospheric humidity. A background is taken with 100 scans. After the background is finished, a noise test is taken of the background point and saved. The recorded points are then each taken with between 50 and 300 scans depending on whether any interesting peaks were visible. If they were, 300 scans would be taken and the spectra would be printed out for further analysis. After each point is taken and saved, the experiment is completed and the disc is removed and placed back into the vial to be returned to Dr. Helmick for storage.

EQUIPMENT USED

Perkin Elmer 1750 Infrared Fourier Transform Spectrometer
Perkin Elmer 7700 Professional computer
Spectra-Tech Infrared Microscope
Spectra-Tech Grazing Angle Objective Lens
Branson 2210 Ultrasonic Bath
Freon 113
Pyrex 250 Ml Beaker
Perkin Elmer PR310 Printer
Cameron-Plint High Frequency Friction Machine Model TE77

RESULTS

During this Task, the grazing angle attachment on the FTIR was used to study surface residues. The exact procedure used to carry out the experiment was learned plus how to use the Perkin Elmer FTIR Spectrometer in a safe and productive way.

It was concluded from the experiment that the M-50 specimens at a low relative humidity, namely 1-5%, showed a higher concentration of the acid species than those of a high relative humidity. This was noticeable by the acid peaks on the spectra becoming smaller and smaller as the humidity was increased. It was also noticeable that the center of the wear scar had a higher concentration of the acid species than the sides of the wear scar. The results of these experiments were collaborated into a paper by Dr. Jim Liang and Dr. Larry Helmick entitled "Tribochemistry of a PFPAE Fluid on M-50 Surfaces by FTIR Spectroscopy" is to be published in <u>STLE</u> later.

INFRARED SPECTROSCOPY

Task Order No. 187A
Student Support Program
Southwestern Ohio Council for Higher Education

Heather Watrob
University of Dayton

12 June 1996

Government Task Leader
Dr. Harvey Paige
WL/MLBT

ACKNOWLEDGMENTS

I would like to take this opportunity to thank the many people that have contributed to my work experience at Wright-Patterson Air Force Base. I would like to Dr. Harvey Paige for his thoughtfulness and guidance. I would also like to thank Dr. Jim Liang for his inspiration, patience, and integrity that he displayed throughout my Task. I would also like to acknowledge Dr. Rajiv Berry, Vince Vidoni, and Bruce Schreiber for all their help and for making me feel an essential part of the work effort.

TASK ASSIGNMENT

The purpose of this Task was to study the interactions of lubricants and lubricant additives with metal surfaces and the decomposition products resulting from such interactions. The lubricants of interest were perfluoropolyalkyl ethers (PFPAEs). Their molecular formula is denoted as $R_f(CF_2CF_2CF_2O)_xR_f'$, $R_f(CF_2O)_x(CF_2CF_2O)_y(CF_2CF_2CF_2O)_zR_f'$, $R_f(CF_2CF(CF_3)O)_xR_f'$. They are of primary interest for aeronautical and computer applications. This Task was accomplished by employing Fourier Transform Infrared Spectroscopy (FTIR), grazing angle microscopy coupled with FTIR, and optical microscopy. This work has been published in such media as *Tribology Letters* and has been presented at many conferences.

Three separate research experiences were done during this Task. This was possible because my assigned advisor was on sabbatical for the first portion of the Task. This granted an opportunity to gain experience through three separate endeavors.

The first project was in conjunction with Shashi Sharma and Bruce Schrieber. The purpose of this project was to detect the effects of humidity and temperature upon a metal surface in the presence of a lubricant. To do this, a Cameron-Plint Tribometer was employed. The test cell was composed of a disk and a cylinder. A lubricant was present at the interface between the disk and the cylinder. The test itself involved the movement of the cylinder across the face of the disk in a repetitive motion done by a mechanical arm. This test was done at a range of different humidities and temperatures, each with a 2-hour duration.

Visual observation of the wear scar was made by optical microscopy. The size of the wear scar was measured and the volume, area, length, and average width were calculated. A trend had previously been reported correlating the wear scar area with percent humidity. The data obtained did not confirm the previous findings. Upon further investigation it was determined that the new data could not be compared with the data previously obtained due to a difference in the experimental conditions. A larger disk width was used in these trials. It was further discovered that this larger width influenced the fluid that was present at the cylinder-disk interface. This larger width put the fluid at a starvation level. The reaction that occurred at this lubricant deficient surface was different from the reaction that occurred in the previous tests. Although we were unable to confirm the previous results, the threshold of the amount of fluid necessary was identified.

The second project involved the research of Dr. Rajiv Berry. His research involves molecular modeling and calculating molecular geometries and the vibrational frequencies for the transition states, reactants and products of the reaction of fluoromethanes with H or OH. This was accomplished using Excel, Insight II, and Framemaker software. Insight II was the most interesting of the programs due to the molecular modeling capabilities. From this program, the bond lengths, bond angles, and dihedral angles for the transition states in question were determined.

The third part of the Task was done with Dr. Jim Liang. It has been a combination of laboratory experience, instrument manipulation and an introduction to the world that a Ph.D. chemist must work in. The laboratory experience involved the use of the FTIR to study surface chemisorption of metal oxides such as Al_2O_3 and SiO_2. These materials were examined by pressing the material onto a strip of tungsten mesh and then inserting this mesh into a reaction cell. Spectra were then taken of the reaction cell under different experimental conditions and recorded. Analysis of the spectra determined what species were present on the mesh and provided insight into what chemical reaction had taken place on the surface. Another technique used in the lab was grazing angle/ FTIR microscopy. By this method an infrared spectrum of the wear scar on the previously prepared disks was obtained. The chemical structure of the surface film present at this surface could be elucidated. This also provided insight into the tribochemistry occurring at the interface between the metal surface and the lubricant fluid.

The experience with Dr. Liang also provided an overall view of the profession of a chemist. Working with him, some non laboratory tasks required of every chemist were done. This included the preparation of scientific manuscripts and presentations, and assistance in the acquisition of new instrumentation while making minor repairs on the existing instrumentation. Reviewing the extensive literary resources that are integral to the advancement of research was another important part of the research conducted. Some work performed contributed to a poster presentation to be given at the Central Regional ACS meeting in Dayton on June 11, 1996.

KINETIC LUBRICANT DEGRADATION STUDIES

Task Order No. 188
Student Support Program
Southwestern Ohio Council for Higher Education

Matthew Argenbright
University of Dayton

31 December 1995

Government Task Leader
Ms. Lois Gschwender
WL/MLBT

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

The Task involved the continuing research in determining the kinetic degradation mechanism of the model ester pentaerythritol tetraheptanoate and evaluating the performance of the ester in a high temperature and high oxygen environment using the oxygen absorption apparatus.

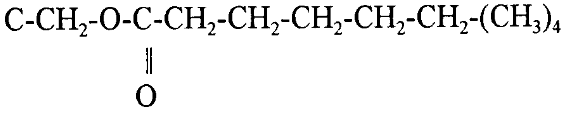
OXYGEN ABSORPTION APPARATUS

The Oxygen Absorption Apparatus (Figure 1) is a test method in which the oxidation characteristics of a sample fluid are derived. The test relies on the principle that when a fluid oxidizes, it consumes oxygen. The test measures the direct amount of oxygen consumed by the fluid during the testing period. The test is done by placing a fluid sample in the reaction cell. Once the reaction cell is placed back onto the apparatus, a closed test loop is completed. The test loop is then pressurized about 1-2 torr above ambient with oxygen. This pressurized gas is circulated through the loop by a diaphragm pump. The oxygen absorption test method thermally stresses the fluid being tested. This stressing causes the fluid to oxidize thus consuming the oxygen inside the test loop. The test loop is connected to a manometer monitoring system that detects this consumption of oxygen by the decrease in pressure in the test loop. The manometer system is monitored by photoelectric sensing detectors. These detectors when activated can trigger either an event that introduces the same amount of oxygen consumed back into the system or it can relieve the test loop of over pressurized gas by venting. Over pressurization and venting should only occur during heating of the sample cell at the start of the test.

The testing of the pentaerythritol tetraheptanoate however would require us to make changes to the apparatus. In the initial testing of the more highly oxidative pentaerythritol tetraheptanoate, it was noticed that the apparatus was cycling as fast as it could. This led to the suspicion that perhaps the apparatus was causing some oxygen limitations, meaning that the fluid could oxidize with more oxygen than what was present in the closed test loop. The apparatus was not cycling fast enough to replenish the consumed oxygen. This led to the need to ensure that the fluid was in an environment that had ample oxygen. The first idea was to attach more of the oxygen reservoirs (Figure 1, 10a) to the apparatus. This was expensive and still could not ensure an excess volume of oxygen in the test loop. Upon consulting with the original designer of the apparatus, it was decided to open the test loop directly with the oxygen cylinders. This was accomplished by ensuring that valves #2, #4 and #5 would stay open at all times. This would then allow the test loop to have unregulated access to all the oxygen it would need. The advantage of having ample oxygen available was only diminished by the fact that to facilitate this change, it would require the bypassing of the manometer system. A "cap" was place on the line #3 that branched to the manometer system. Again, the manometer system adjusts for change in the pressure in the test loop. A concern was that if the reaction were to increase pressure in the loop rapidly, how would we know when it occurred and how would the excess pressure be vented. This was remedied by opening valve #3 and placing a bubbler at the air vent line, #2. The bubbler contains a high molecular weight hydrocarbon. This would allow the test loop to be maintained at the 2.75 KPa , which is the regulated pressure coming out of the oxygen cylinder. The bubbler would also allow gas, if the pressure increased significantly, to "bubble-out" through the liquid in the bubbler. During actual testing, the bubbler proved sensitive enough to detect small changes in pressure caused from purging and the circulation pump. No over pressurization occurred during the experiments. Figure 2 shows the reconfigured system used for subsequent testing of the pentaerythritol tetraheptanoate.

PENTAERYTHRITOL TETRAHEPTANOATE

Pentaerythritol tetraheptanoate(PETH) was chosen as a test fluid because of the similar characteristics that it has with the fluid that Exxon is designing. Since it has been studied before, we have some comparative analysis to evaluate the performance of the apparatus. PETH



$$C\text{-}CH_2\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}(CH_3)_4$$

is representative of a class of neopentyl-type ester materials used in high temperature applications.

Due to the absence of hydrogens on the central carbon that is in a position to heptanoyloxy groups, PETH is not susceptible to the usual cyclic elimination processes that yield olefin and acid products. Thus, without oxygen, PETH possesses thermal stability comparable to that of hydrocarbons. The evaluation of the PETH was carried out on a temperature range of 190-220°C. Since the manometer system was removed from the test loop, it was not capable of looking at oxygen absorption for the test runs. The post test analysis of the fluid would rely on the iodometric titration for hydro peroxide determination and gas chromatography for the identification and rate formation of by products. This data would then be used, in comparison to the Hamilton, Korcek, Mahoney and Zinbo study, to ensure that the apparatus was sufficient in testing the autoxidation of the PETH.

The testing of PETH was dramatically simplified with the reconfiguration of and removal of the manometer system. The test is done by starting with a sealed test loop. The loop is purged with pure oxygen, ideally removing all air and having a 100% oxygen environment. The sample fluid is placed in the reaction and a stream of nitrogen is used to inert the cell during which the fluid is raised to the test temperature. Once thermal equilibrium is reached, the nitrogen stream is changed over to an oxygen stream, this begins the oxidation of the fluid. The pressures in the regulator on the cylinder, the fluid temperature and oxygen flow rate are the only test parameters to maintain. At predetermined intervals, 1 ml aliquot are extracted through the sample port for analysis while noting the exact time interval. These aliquots are used in the hydro peroxide determination and the gas chromatography analysis.

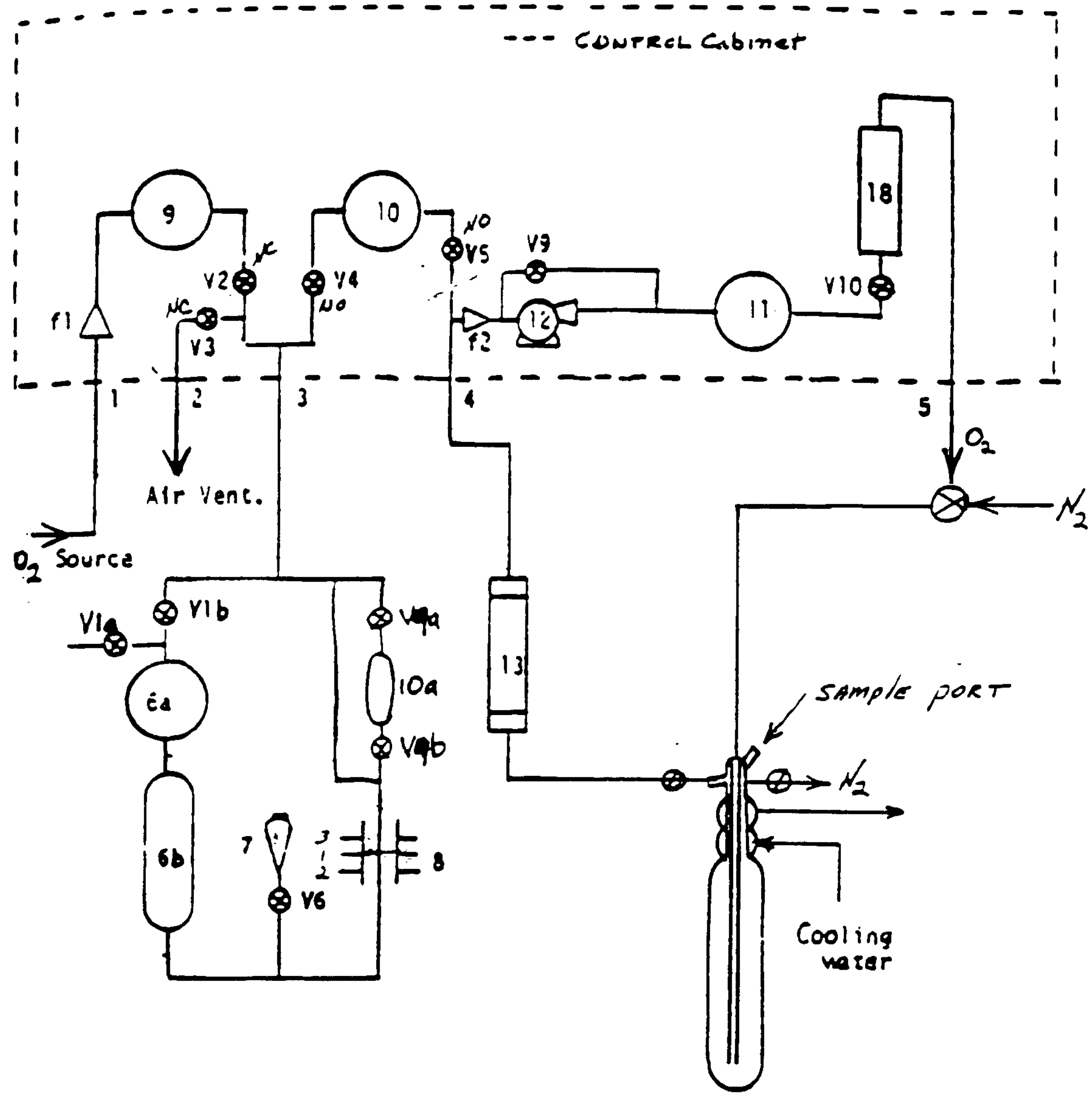
The post test analysis of the aliquot would determine if the apparatus could determine the kinetic oxidation of the PETH on a micro scale. The analysis would consist of the iodometric titration for peroxide formation and gas chromatography for by-product formation. The titration of the PETH samples yielded a linear formation of the hydro peroxide for the test temperatures 190° C. and 200° C. This shows that the PETH will continue to react with the oxygen until a saturation point is reached. However, starting at the 210° C. and especially at the 220° C. test, the hydro peroxide formation reaches a peak and then levels off or even decreases, as in the 220° C. This occurs because the hydro peroxide at a higher temperature is being reacted further into many by-products. This deviation can be clearly seen in Figure 3.

In analyzing the PETH by gas chromatography, Figure 4 shows an unstressed chromatograph of the PETH. Figure 5 shows the degradation of the PETH at 190, approximately 3 1/2% weight loss. The graph shows that the PETH is beginning to shows some by-product formation, but is still insignificant. At the maximum test temperature of 220° C, Figure 6 show that the fluid has lost approximately 50% of it weight. Not until the fluid is stressed for 1 hour at 220° C is there significant weight loss, approx. 75%, of the PETH into oxidation products (Figure 7).

The hydro peroxide and GC analysis of the stressed samples shows that the apparatus could determine the kinetic oxidation of the PETH. Though there are some reservations concerning whether or not the apparatus can determine the initial induction period of the fluid, the response so far has been positive. Not till after the next meeting with Exxon will a definitive answer be reached.

Much has been learned about the oxygen absorption apparatus, laboratory procedures and operations, and predominately the oxidation of fluids at high temperatures. With continued research, further understanding and knowledge will be gained.

Figure 1



Flow Diagram - Oxygen Absorption Apparatus After Modification

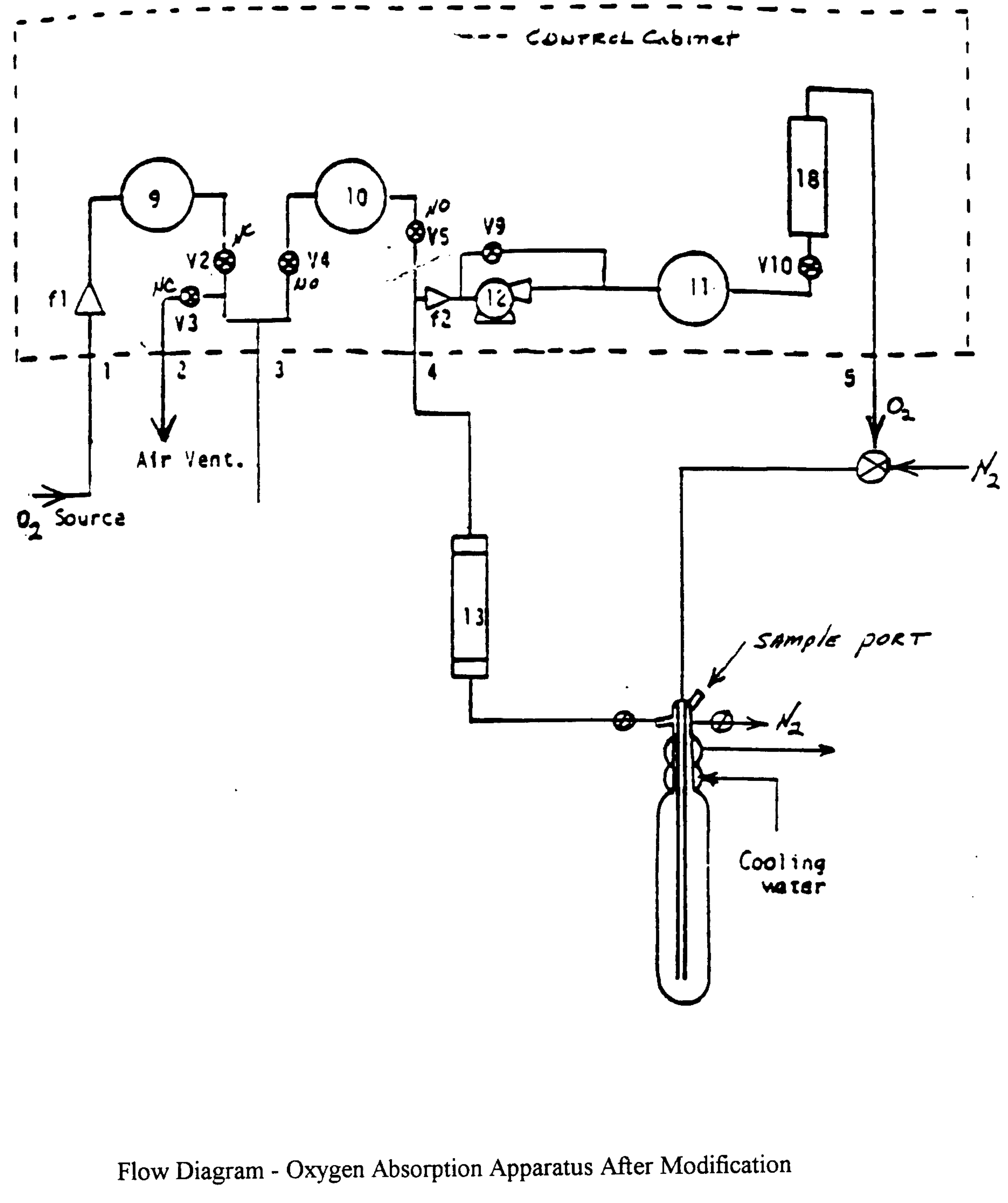
KEY FOR FIGURE 1

1 - To oxygen source.
2 - To atmospheric ventilation.
3, 4, 5 - Connections between pneumatic systems inside and outside of control unit.
6a, 6b - Balancing bulbs: 6a, surge space and 6b, expansion.
7 - Leveling bulb.
8 - Photoelectric system.
9 - Surge bulb.
10 - Expansion bulb 10, resevoir.
10a - Auxiliary bulb (used for testing sensitive samples).
11 - Expansion bulb 11, resevoir.
12 - Circulation pump.
13 - Absorber.
14 - Cold trap.
15 - Ambient trap.
16 - Reaction cell.
17 - Ambient trap, reaction cell.
18 - Flowmeter.

V0 - Oxygen regulator.
V1a - System balancing valve.
V1b - Atmospheric balancing valve.
V2 - Oxygen solenoid valve (NC).
V3 - Air ventilation solenoid valve (NC).
V4, V5 - Oxygen evolution solenoid valves (NO).
V6 - Leveling valve.
V8 - Purge valve Assembly.
V9 - Bypass valve.
V9a, V9b - Auxiliary valves for 10a isolating bulb.
V10 - Flow control valve.
V11 - Pump isolation valve.

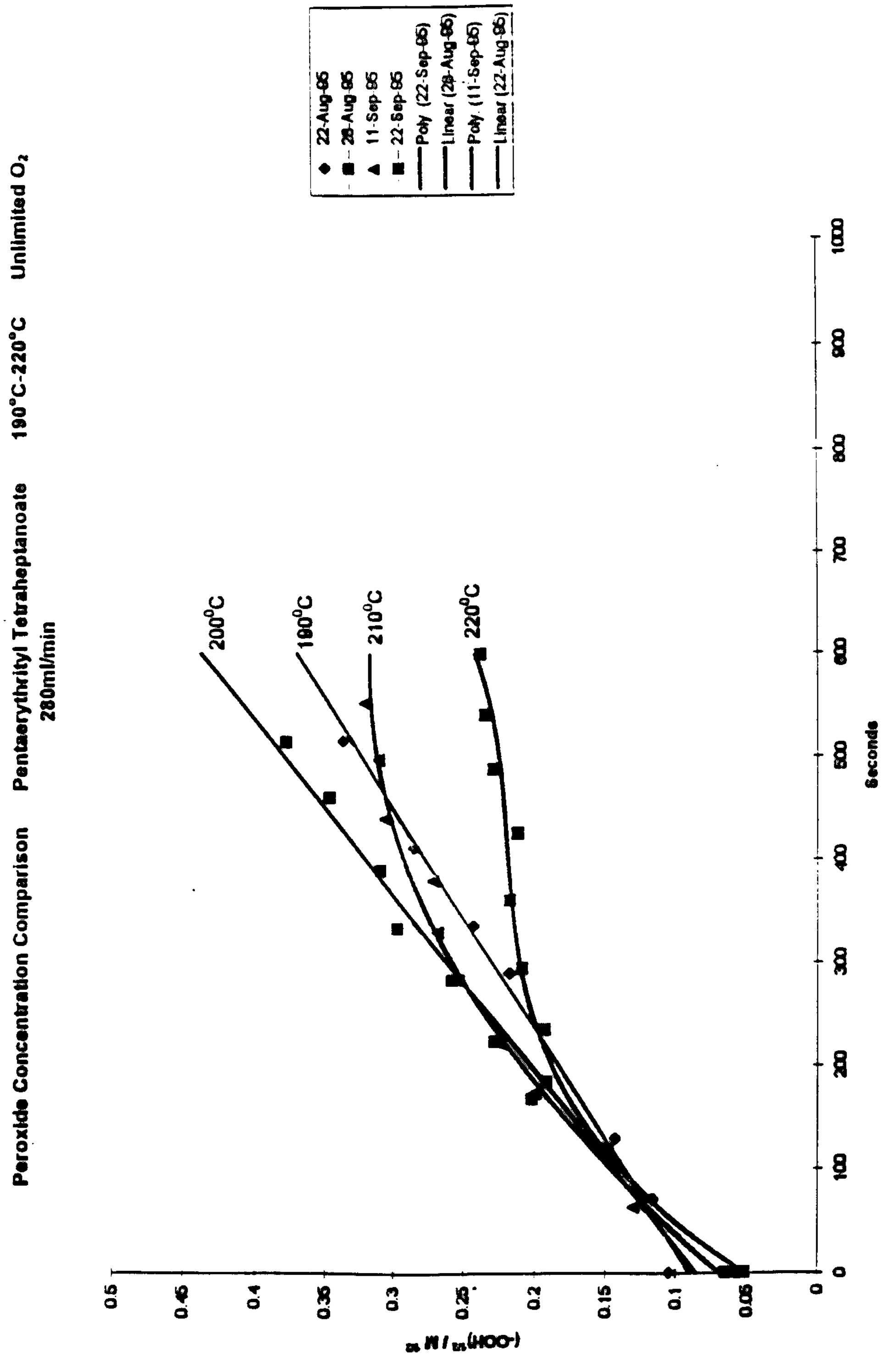
f1 - Filter #1
f2 - Filter #2

Figure 2



Flow Diagram - Oxygen Absorption Apparatus After Modification

Figure 3


Peroxide Concentration Comparison Pentaerythrityl Tetraheptanoate 190°C-220°C Unlimited O_2

280ml/min

Figure 4

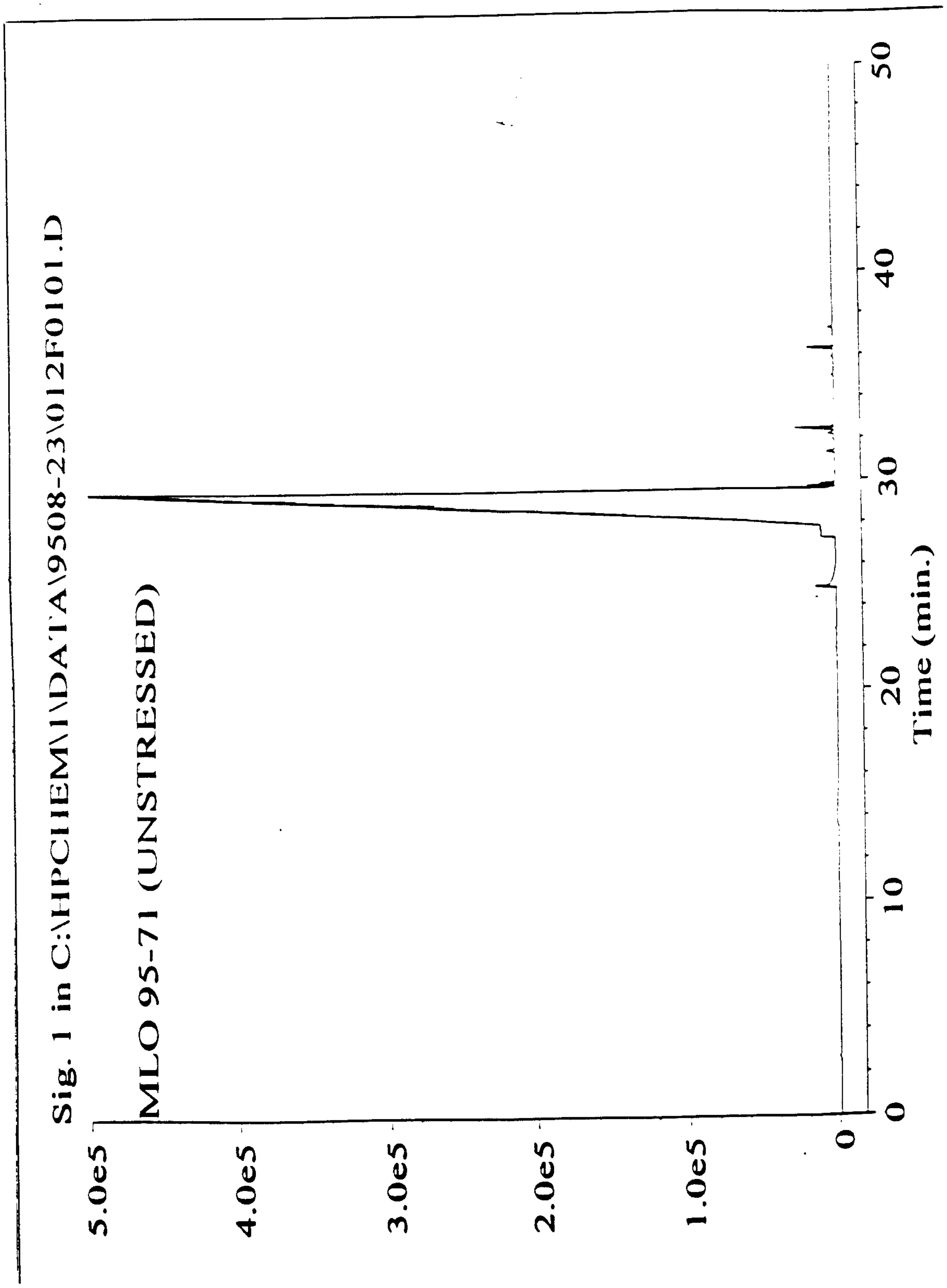

Sig. 1 in C:\HPCHEM\1\DATA\9508-23\012F0101.D
MLO 95-71 (UNSTRESSED)
5.0e5
4.0e5
3.0e5
2.0e5
1.0e5
0
0
10
20
30
40
50
Time (min.)

Figure 5

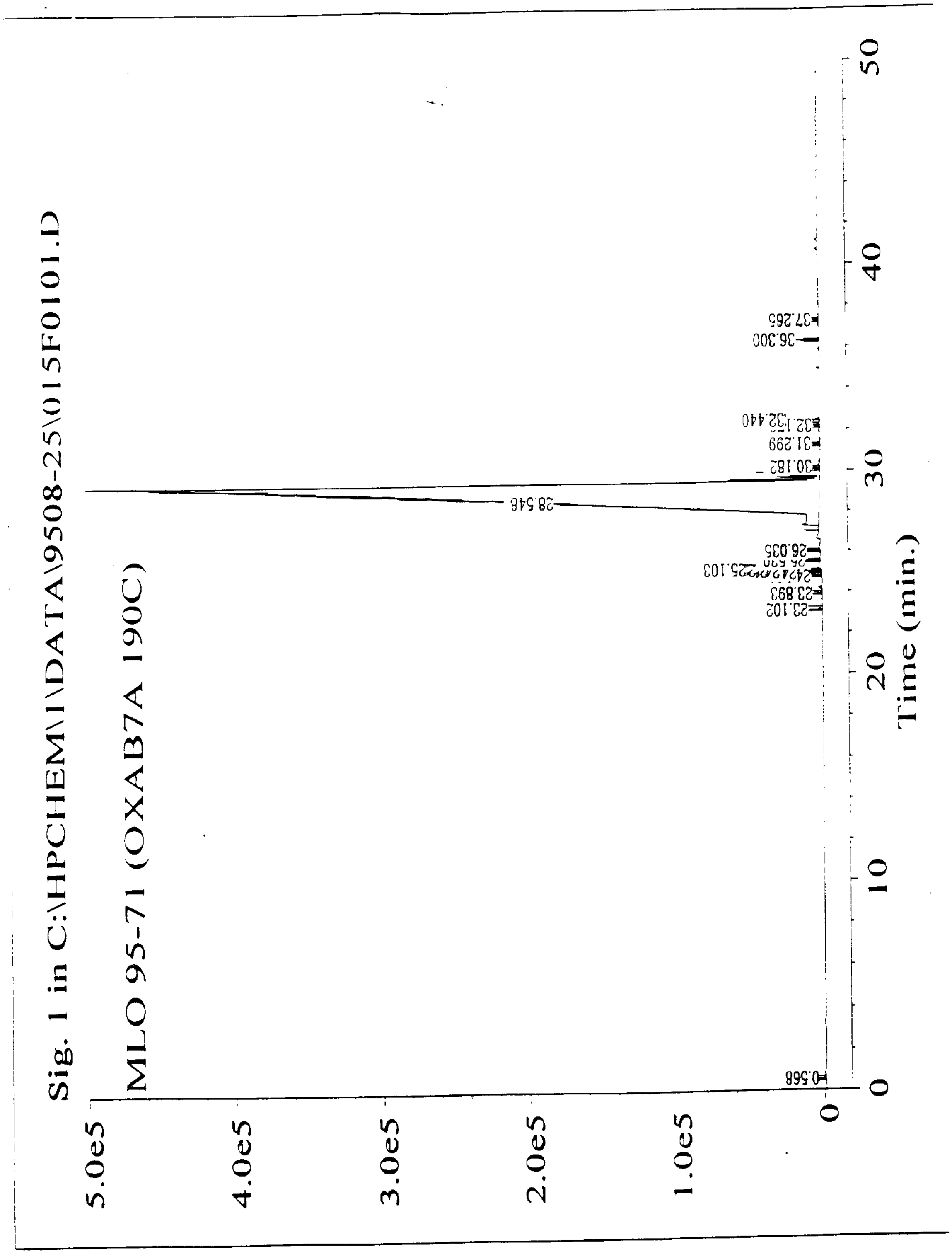

Sig. 1 in C:\HPCHEM\1\DATA\9508-25\015F0101.D
MLO 95-71 (OXAB7A 190C)
5.0e5
4.0e5
3.0e5
2.0e5
1.0e5
0
0
10
20
30
40
50
Time (min.)
0.568
23.102
23.893
25.103
26.035
28.548
30.182
31.299
32.440
36.300
37.265

Figure 6

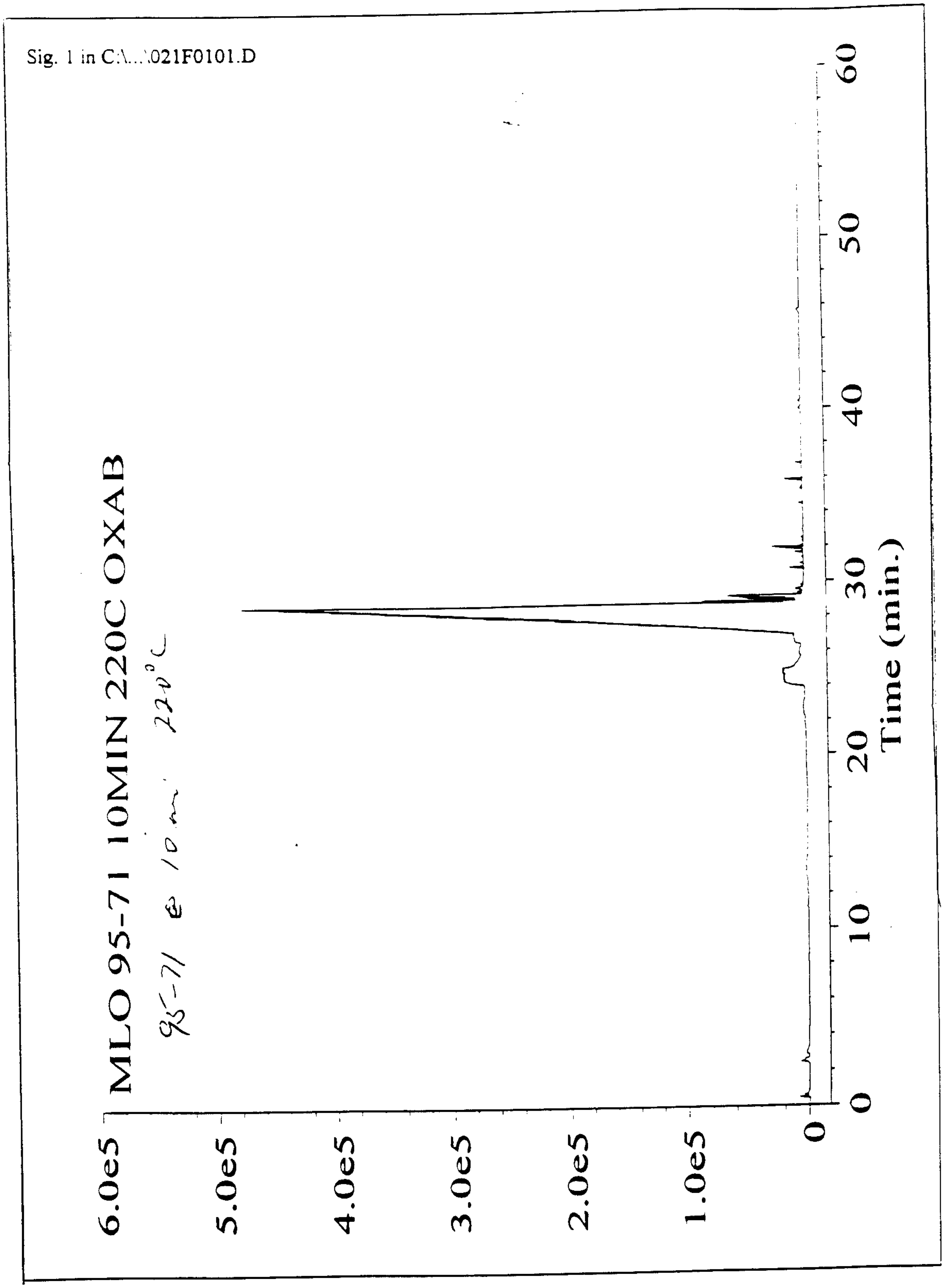
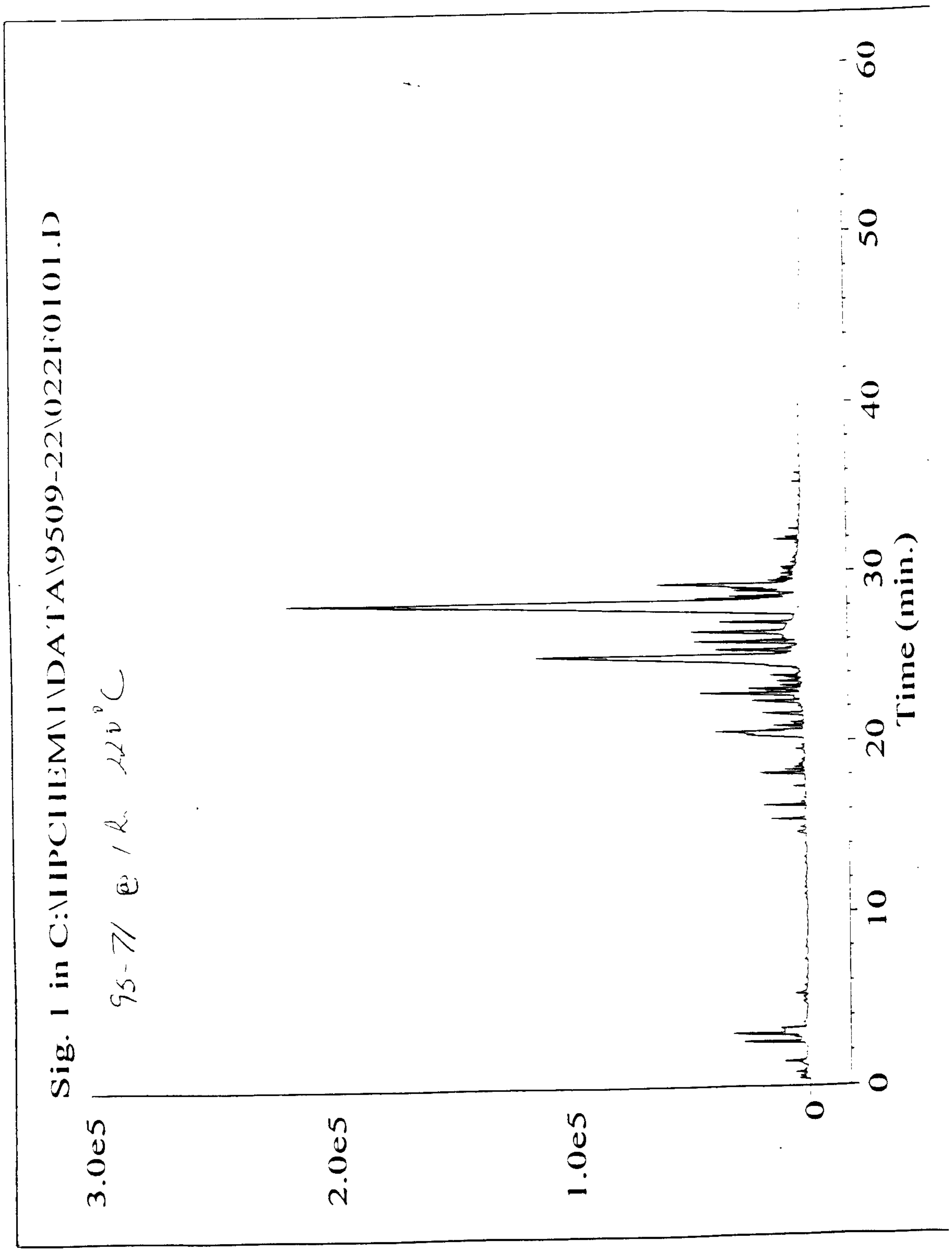

Sig. 1 in C:\...\021F0101.D
MLO 95-71 10MIN 220C OXAB
95-71 @ 10 min 220°C
6.0e5
5.0e5
4.0e5
3.0e5
2.0e5
1.0e5
0
0
10
20
30
40
50
60
Time (min.)

Figure 7



Sig. 1 in C:\HPCHEM\1\DATA\9509-22\022F0101.D
95-71 @ 1/2 220°C
3.0e5
2.0e5
1.0e5
0
0
10
20
30
40
50
60
Time (min.)

ELECTROMAGNETIC MATERIALS RESEARCH-ELECTRONIC AND COMPUTER TECHNOLOGIES

Task Order No. 189
Southwestern Ohio Council for Higher Education
Student Support Program

Charles E. Culp, Jr.
Wright State University

5 July 1996

Government Task Leader
Mr. Ron Perrin
WL/MLPO

ACKNOWLEDGMENTS

I would like to recognize several people who have helped me in accomplishing the Task assigned at the Materials Division of Wright Laboratory. First, I would personally like to thank Mr. Ron Perrin and Mr. Tom Kensky for their instructions and proper technical guidance in beginning level Electrical Engineering. The knowledge provided by these two individuals has enabled me to learn valuable information through accomplishments of tasks, teaching, and observance that will be beneficial in my future college studies. This information will also give me the essentials needed throughout my future career as an engineer.

I would also like to thank Mrs. Wanda Vogler and the staff of the Southwestern Ohio Council for Higher Education for this unique opportunity to work in such an educational environment. All the people listed have given me the proper assets needed to accomplish my Task. Thank you for your support and assistance.

DESCRIPTION OF TASK

My responsibility is to aid Mr. Perrin in providing engineering support to scientists working in the MLPO branch of the Materials Directorate of Wright Laboratory. The assistance provided differs from situation-to-situation due to the needs of the researcher at that particular moment of time. The usual role played is building and testing customized circuitry, modifying computer hardware, and writing computer programs. These are just a few of the main tasks completed for Mr. Perrin. His requirements may include going outside the basic tasks listed due to the involvement needed on a particular project. The Task's involvement allows for direct assistance to scientists with the technological advantages they may be required to aid them in accomplishing the goals of their research. It also allows for valuable knowledge to be gained about engineering that is not always taught in the classroom.

DESCRIPTION OF RESEARCH

The particular research that the Task is involved in is not ordinary research that can be listed on paper. There is not always a scientific experiment to use to obtain the information required. Instead, the Task provides direct technological support by finding the best possible means to obtain the data that the scientists require to complete their project.

This does not mean that there is no research done. The Task involved research in self experimentation methods, sometimes learning from trial and error. The result of this experiment is to learn the proper technical skills that are essential to become a good electrical engineer.

The most commonly assigned task is building and testing customized circuitry. This is the one area that research was completed. This is because putting a schematic of a circuit into functional reality given the physical limitations is much more difficult. These limitations come in the form of connecting components, dissipating heat that a circuit item emits, size limitations of the circuit container, and having it function as designed.

The area that was the source of the problem was approached in a different way. First, circuits must be built one section at a time, not all at once. The reason behind this method is that guarantees that each section of the circuit is working properly. This allows for all of the mistakes to be caught before it damages or destroys another circuit component. This has helped in the manufacturing process to solve potential problems as they occur, such as connection problems. The laying out of the circuit section by section also allows this process to overcome heat related problems by placing these circuit items in areas of the board where they can be properly arranged to dissipate heat.

The second method that has allowed for production methods to be improved as research is the use of test equipment to ensure that items are placed correctly and to ensure that they are operating in the way that the circuit has intended for them. This is accomplished by such aids as digital oscilloscope, digital multimeter, and functional generator. This equipment, when used in the proper manner allows the user successfully to test the specialized circuitry and avoid critical mistakes that may occur during scientific research. This method, is very important because the length of many experiments, using the technological aids provided, can last many days, months, etc. Therefore, if there is a faulty component, the experiment could be delayed.

This is just a sample of the research done. Though, this illustrates exactly what the task tries to accomplish when Mr. Perrin assigns a project. The goal is to find the best and most productive technique in which to accomplish it and then complete it in the way that generates the least amount of difficulty and the best results for the task. This enables the experimental data to be used in approaching tasks and apply this knowledge to other tasks and continue to grow in knowledge.

RESULTS

The Task completed has provided a great deal of knowledge in the field of Electrical Engineering. This information was found through dealing with the challenges that the Task provides and experimentally finding the most efficient way in which to overcome and successfully complete the projects assigned. This is important for future engineers, because the ability to solve ambiguous problems is what engineering is all about. Mr. Perrin has provided this ability by assigning various levels of tasks to complete and allowing them to be obtained by using a problem. This has provided hands-on experience that is not possible to attain from a classroom.

The valuable knowledge obtained from using self experimentation and creativity this past year has provided the incentive to continue an educational path of becoming an Electrical Engineer. This gives the desire for the next Task assigned and another year of working under the guidance of Mr. Perrin.

POLYMER AND DISPERSED LIQUID CRYSTAL

Task Order No. 190
Southwestern Ohio Council for Higher Education
Student Support Program

Robert L. Haaga
Wright State University

2 July 1996

Government Task Leader
Dr. Dennis S. Hager
WL/MLPJ

ACKNOWLEDGMENTS

A special thanks to Dr. Lalgudi Natarajan, Dr. Timothy Bunning, and Dr. Tom Cooper for their patience, guidance, and knowledge of chemistry that made this Task a positive learning experience. Also, thanks to all the MLPJ personal including my technical director Dennis S. Hager who made this Task possible, and to Dr. William Feld for his support and Mike Schulte who laid the groundwork for my research. Finally, thanks goes to all SOCHE employees who made life a little easier.

TASK ASSIGNMENT

Task order number 190 dealt with the synthesis and development of various nonlinear active molecules required for the material formation of polymer dispersed liquid crystal systems (PDLC). New liquid crystalline monomers to replace current monomers and/or cross linkers that make up the polymer matrix of these PDLC's was investigated.

DESCRIPTION OF WORK

Synthesis of new liquid crystalline monomers includes not only basic organic chemistry applications but an extensive research into groundwork already obtained in the current PDLC systems. Knowledge of these systems is vital before new monomers that are to be incorporated into these systems are produced. The first part of my Task was to learn the processing techniques of polymer dispersed liquid crystal systems and how holograms work and are prepared. This included initial research in the laser labs and actual production of holograms. Production of holograms in PDLC's is a one-step, photochemically induced, electrically switchable process which exploits the principles of constructive interference in the writing region of a suitable laser. A typical PDLC system is a homogenous mixture of monomer, liquid crystal, cross linker, co-initiator, and photo initiator that forms a viscous syrup. When a droplet of syrup is placed between two microscope slides and exposed to two crossing laser lines, the liquid crystal micro droplets migrate into clearly defined regions in the host polymer matrix. These clearly defined regions produce a Bragg grating. To optimize these systems, a maximum loading of liquid crystal is desirable to lower switching voltages and increase overall performance. In current systems, syrups only consist of 30% loading of liquid crystals due to incompatibility of the liquid crystal (E7), the principal monomer (dipentaerythrol hydroxy penta acrylate), and cross linker (N-vinylpyrrollidone). New monomers that can be used as cross linkers and/or principal monomers that is more compatible with E7 to allow higher doping of liquid crystal into these systems, were investigated. This incorporated the basic principles of organic chemistry and literature research.

Current liquid crystal E7 is a 4 component mixture of cyano-biphenyls with various functionality's on each. An overview of these systems is shown.

New monomers more thermodynamically compatible with E7 are needed to increase doping 5-10%. These new monomers should be long about the principal axis, posses a high pi electron conjugation along this axis, and liquid crystalline. Monomers synthesized were designed to have a biphenyl backbone to mimic E7 since this is the reoccurring backbone in all the above molecules. Also, esters were desired since the principal monomer is a multiester in hopes of increasing solubility of new monomers into current syrups. The first synthesis routes taken were DCCI coupling reaction. This is a one-step esterification process that is easily ran at room temperature. The reaction scheme is as follows (1).

This is a simple conversion of an alcohol and carboxylic acid into the corresponding ester. The experiment for this reaction was the following: A 100 mL, 3 neck round bottom flask was fitted with a stirbar, condenser and put under a positive nitrogen pressure. 4-Undecyloxybenzoic acid (2.9231g, 0.01mol) was added along with methylene chloride (20 mL). 4-Penten-1-ol (0.96g, 0.011 mol) was added in one portion along with another 10 mL methylene chloride. DCCI (2.264g, 0.011 mol) and the catalyst was added with another 10 mL of methylene chloride and the reaction was heated to 30¡C for 5days. The resulting solution was filtered and half the solvent was removed and filtered again. A yellowish white precipitate was recovered.

This reaction has not been confirmed but strong evidence is now present that it did proceed. The actual product hasn't been isolated in a pure enough form for analysis but the urea by-product present in these reactions has been recovered which indicates a reaction taking place. Further purification of this product is currently being investigated. Purification turns these relatively simple reactions into a struggle and usually leads to poor obtainable yields. DCCI is also a severe skin irritant and extreme caution must be taken when it is being used. Other reactions to replace DCCI coupling reactions were investigated.

Other reactions investigated were halide reactions. Again a one-step esterification but the by-product urea in DCCI coupling reactions is not present. An overview of the reaction (2).

The reaction was done under the following conditions: A 3 neck flask was equipped with septa, stirbar, condenser, and addition funnel. 4,4'-dihydroxybiphenyl (1.87g, 10.1mmol) and 4-dimethylaminopyridine (6.65g, 54 mmol) were added to the flask and the system was purged with nitrogen for 20 min. THF (100 mL) was added to the flask and the solution was heated until all the starting materials had dissolved. 10-undecenoyl chloride (11.14g, 55 mmol) was added to the addition funnel along with 20 mL THF. The acid chloride solution was dropped in over 40 min. A precipitate formed on immediate addition of acid chloride. The solution was heated to reflux for 4h then filtered hot. The solvent was removed to yield a light brown solid recrystallized from ether to afford white crystals. This reaction was very good and was improved drastically over the DCCI coupling reactions. The monomer synthesized was also found to have interesting characteristics. Also, under investigation was the ability to polymerize various monomers previously synthesized. One in particular was the following monomer (3).

This monomer was successfully synthesized via the DCCI coupling route byÊMike Schulte. This monomer was easily polymerized thermally with the radical initiator AIBN at 70°C for 1hour.

RESULTS

These two reactions taught us a lot about the synthesis of liquid crystalline monomers. As stated before the first monomer (1) was unobtainable in a pure form. This was, however, not a complete loss. Further purification via chromatography can be employed if so needed. The first reaction taught us however that DCCI coupling reactions should be avoided if the corresponding acid halide reaction can be done. DCCI coupling reactions have previously given good yields of pure materials, but none investigated in my research.

The polymerization of (3) was successful, but at a cost. The reaction went so well that it was found highly cross linked. This made solubility difficult and NMR was unobtainable. The polymerization was found to have gone by monitoring the disappearance of the double bond stretching via FT-IR. Nothing further has been done regarding this molecule.

Acid halide reactions were very successful. Yields were increased three times over their DCCI counterparts and purification was achieved via simple recrystalization. The monomer synthesized also proved to have interesting characteristics. Monomer (2) was found to exhibit a very highly ordered liquid crystalline behavior. Optical polarizing microscopy showed a texture associated with the smectic B phase. Differential scanning calorimetry also showed two very strong thermal transitions one assuming to be the melt and the second the clearing of the smectic B phase. Interestingly enough the second transition, the clearing, had a larger enthalpy than the first melt. This is very uncommon and suggests a higher order smectic phase. X-ray diffraction experiments on the unaligned samples at various temperatures shows six clearly defined peaks again indicative of smectic B phase. This monomer (1) was found to have a more complex micro structure than originally expected for such a simple molecule. This monomer has proven challenging to polymerize. No successful procedure has been found to induce the radicals needed for polymerization to take place. Thermal and photo-induced polymerization methods have failed. New acid halide reactions of new liquid crystalline monomers are now currently being investigated.

LIQUID LIMITER MATERIALS

Task Order No. 191
Student Support Program
Southwestern Council for Higher Education

Lynn R. Frock
University of Dayton

19 July 1996

Government Task Leader
Dr. Gregg Anderson
WL/MLPJ

ACKNOWLEDGMENTS

I would thank Dr. Tom Cooper, Mrs. Donna Brandelik and L. Natarajan for their support and guidance. I would also like to thank Mrs. Weiji Sue for her assistance and willingness to teach me useful techniques in my endeavors in the laboratory. I would also like to give special thanks to Mr. Dan McLean for giving me the opportunity to work independently and having the faith to allow me to do so. This past year has brought about wonderful and exciting developments toward the advancement of my education and career training. The team of scientists that I am so fortunate to work with, has given me the opportunity to excel beyond my own expectations. Thanks to this group, I have had the honor of completing my fourth co-authorization, published in *SPIE Journal.* The work I contributed toward this publication gave me the edge I needed to be selected for The Society of Applied Spectroscopy's Student of the Year Award. I would like to thank SOCHE for the effort maintained in keeping this program alive and giving students like myself the opportunity to learn and progress in such an excellent environment.

TASK ASSIGNMENT GOALS

The Task goals are to develop the next generation of reverse saturable absorber (RSA) optical limiter materials and devices by developing the understanding and control of materials, mechanisms and processes. This includes, but is not limited, to the preparation and characterization of various guest/host materials for use in electro-optical applications. The primary focus of these scientific investigations is to show nonlinear absorption enhancement in energy transfer designed material, and to investigate high fluence effects in the materials to confirm characterization techniques.

RESEARCH

Background information was needed to begin the RSA project. An intense literature search for the critical parameters of selected materials was done before laboratory investigation. The information was found through use of computer data banks such as Uncover. A library of research papers was developed and is still being reviewed for materials of usefulness concerning this project. An understanding of ideas and use of all available information is the backbone of the development of acceptable RSA molecules.

RSA organic dyes form the basis of advanced optical limiters. The drive of this project is toward understanding the principles required to achieve an engineering design capability for the RSA property. The current approach is to engineer a chromophore with specific ground state absorption properties and link it to a chromophore designed for its excited state properties in a way as to control energy and charge transfer. The focus of the work is to make a photosensitive optical switch. Photosensitive optical switch work is a refinement of an existing research effort. This effort includes computational chemistry, synthetic chemistry, chemical and optical characterization and processing techniques research.

The investigation and characterization of polypeptides covalently bound to photochromic molecules have been studied for use as model systems for coupling photo chemistry with conformational changes in the polypeptide backbone.[1] The study involves azo-modified and spiropyran modified polypeptides. Recently we have reported on the substituent effects in spiropyran photochromism, namely the acceleration of α-helix to coil transformation in a light adapted poly (L-spiropyran glutamates). Studies, thus far have shown that it is possible to accelerate the rate of backbone conformational changes by orders of magnitude through substitution in the spiropyran ring that may have some practical implications for making dynamic filters for lasers.[2]

RESULTS

We studied the spiropyran-attached PGA's in DMF (N,N-Dimethylformamide). There were two types of dyes used in this study, one electron withdrawing and the other electron donating 6-Nitro-8-methoxy-1'-(2 hydroxyethyl) Bips and 6-Bromo-8 methoxy-1'-(2 hydroxyethyl) Bips respectively. The third dye used in this study was selected as a model compound for comparative study and that is 6,8-Dibromo-1'-hydroxyethyl Bips. All three dyes were attached to PGA utilizing DCCI coupling reaction. The DCCI coupling reaction is an esterification reaction. Prior to coupling, FTIR scans were taken and again after reaction was done.

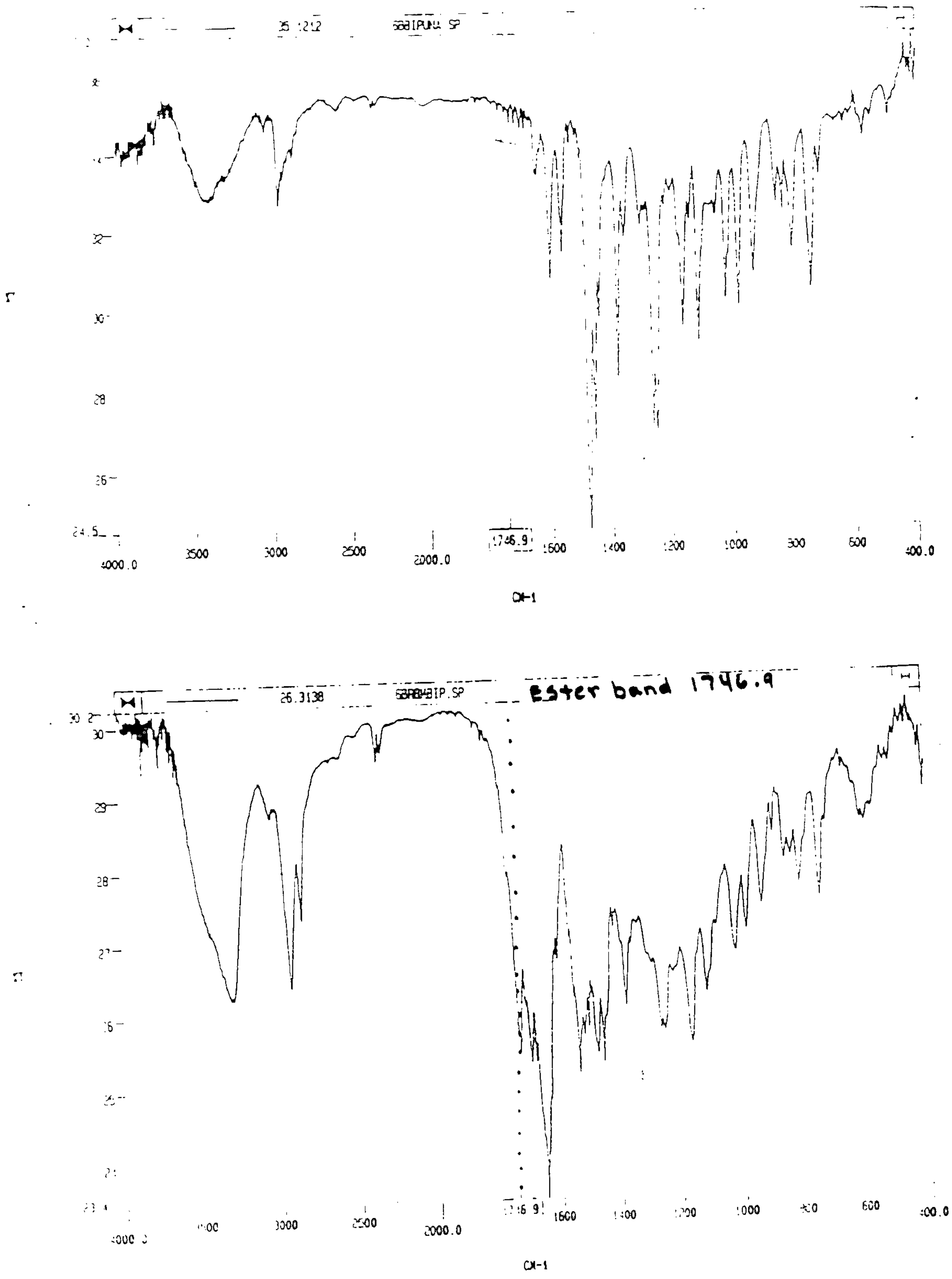
Figure 1 shows evidence of successful attachment because of the ester band that is not present in the scan of the unattached dye and suggests attachment. The dye shown here is 6-bromo-8-methoxy-1'-(2hydroxyethyl)Bips. Thin layer chromatography was also used to detect successful attachment and agreed with FTIR. Several purifications will be performed until the by-product of this reaction, and DCU is no longer present in TLC or FTIR.

The model compound reaction product is yet to be recovered. Due to the difficulty of separation of the alcohol-ester mixture, a column will be prepared using hexane and ethyl acetate mixture. The ratio of solvent mixture was determined by using the concentric ring method for selecting solvent ratio for column separation. This was followed up with a series of TLC experiments to give exact ratios of solvents. R_f. factors were calculated for both the ester and alcohol, the difference between each value was calculated and the percent ratio with greatest difference in the $_{Rf}$ factor was the one chosen for use in the column. Table 1 shows results of R_f. factor study.

The dyes used in this study were synthesized at an out source laboratory and have not been investigated for reverse photochromism properties. Uv-vis spectra were taken to determine reverse photochromism of the following dyes, 6-nitro-8-methoxy-1'-(2-hydroxyethyl)Bips, 6-bromo-8-methoxy-1'-(2-hydroxyethyl)Bips, 6-phenyl Azo-8-methoxy-1'-hydroxyethyl Bips, 6-methoxy-8-nitro-1'-hydroxyethyl Bips and 6,8-dibromo-1'-hydroxyethyl Bips. These dyes were run using both DCM and HFIP as solvent in two separate trials. Both trials were done, using a 366nm wavelength hand-held light source. Samples of known concentrations were prepared in the dark and exposed to equal amounts of a long wave length light source. Scans were taken of samples immediately following exposure. Data for 6-nitro-8-methoxy-1'-(2-hydroxyethyl)Bips gives no evidence of reverse photochromism, and thus eliminates this dye for any further testing. Figure 2 shows graphs of this dye with and without exposure of 366 nm wave length light source. A red shift in the peak absorbance, not seen here, would have suggested reverse photochromism. Data for the other four dyes is still being analyzed. Reverse photochromism for 6,8-dibromo-1'-hydroxyethyl Bips has already been determined previously and will be used as the model compound for this ongoing study. DCCI coupling reaction has been determined to be the most useful synthesis procedure for this study.[3] Upon conformation of characterization, the selected dyes mentioned above will also be used in DCCI coupling and evaluated for optical properties that may be useful in RSA materials. Following synthesis and purification of selected dyes a kinetic study of reverse conformation changes will be performed and calculated using the Hammett equation, which relates rates and equilibria for many reactions involving varying substituents in the pyran ring. It is known that varying the substituents in the pyran ring influence the rate of decolorization reactions and consequently the kinetics of helical conformational changes in the polypeptide backbone.[2] The ongoing study is an attempt to increase and control the rate of zwitterion ring closure in the side chain photochromophore. By doing so, the life time of the α-helical conformation of the poly(l-glutamate) is shortened by orders of magnitude.

The photochromism study is ongoing and results of experiments are expected within the next quarter of this fiscal year.

Figure 1



Ester band 1746.9

Figure 2

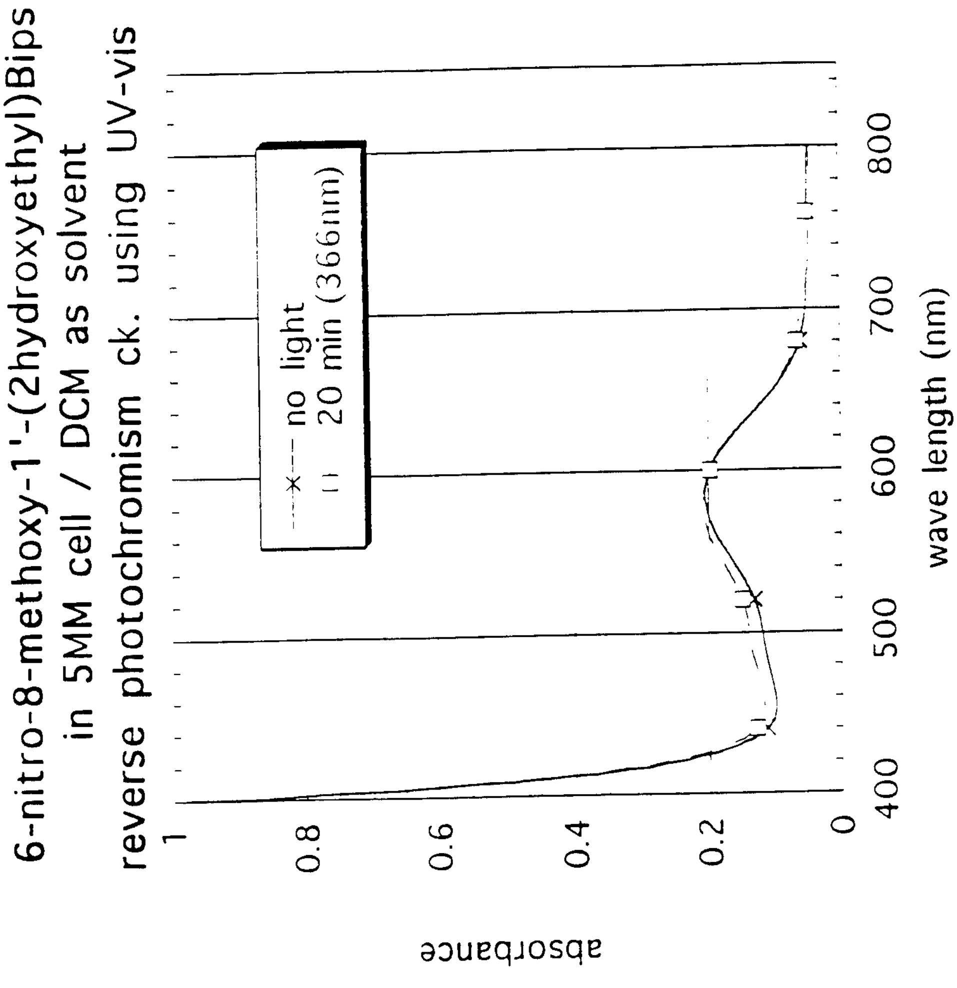

6-nitro-8-methoxy-1'-(2hydroxyethyl)Bips
in 5MM cell / DCM as solvent
reverse photochromism ck. using UV-vis
no light
20 min (366nm)
absorbance
1
0.8
0.6
0.4
0.2
0
400
500
600
700
800
wave length (nm)

Table 1

Ratio of solvent mixture	Rf value for ester	Rf value for alcohol	differe
100% ethyl acetate	0.7169	0.862	0.15
8:2	0.759	0.860	0.10
7:3	0.608	0.850	0.24
6:4	0.588	0.840	0.25
1:1	0.412	0.700	0.30
4:6	0.280	0.660	0.38
100% hexane	0.066	0.800	0.06

ratios given as ethyl acetate/ hexane respectively

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BIOPOLYMERIC MATERIALS

Task Order No. 192
Student Support Program
Southwestern Ohio Council for Higher Education

Steven M. Cline
Wright State University

12 July 1996

Government Task Leader
Dr. Dennis Hager
WL/MLPJ

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A special thanks to my advisory chemist, Dr. Thomas Cooper, for the time, effort, and guidance he has provided in helping me mature as a scientist and person. He has allowed me to work independently on my Task that ultimately has instilled personal growth and an increase in self confidence. Thank you, Dr. Dave Zelman, for the education and mentorship provided in enhancing my knowledge of electro-optics. Thank you for teaching me confidence and a willingness to persevere in times of adversity. Much of my research success has come from modeling myself after you. I would like to express sincere thanks and gratitude to SOCHE for giving me the opportunity to work and learn at WL/MLPJ of Wright-Patterson Air Force Base. The experience and insight I have gained have broadened my scientific interests and skills extensively.

TASK ASSIGNMENT

The Task consists of the synthesis and characterization of nonlinear optics and laser hardening materials. The goal of the Task was to use readily available biological and semi organic materials and to incorporate their functional properties into electro-optical systems. Currently, the Task is directed toward the understanding and the manipulation of simple systems. The long-term goal of the Task is to incorporate simple materials into functional devices involved in properties such as: high resolution spectroscopy, remote sensing, data storage and communication, and laser radar protection.

DESCRIPTION OF RESEARCH

Due to the molecular arrangement and perfectly repetitive symmetry of atoms in crystalline compounds, crystals possess amazing photo-manipulative properties. Proteins and amino acids, individually and in complex with metals and organic dyes have proven to be excellent secondary harmonic generating materials (SHG). The desirable material properties for second harmonic generating materials include high beam transmission in the spectral region of interest, high nonlinearity, physical and chemical robustness, easy growth and processing, and reasonable cost. The research goal was to find novel materials for high efficiency Second Harmonic Generation with these selective characteristics.

Second Harmonic Generation (SHG) is the electro-optical phenomenon of transforming the wavelength of light entering a transparent material to a wavelength of one half of that which it entered. Therefore, a wave of Infra Red light entering an SHG material at 1064 NM, emerges at 532 NM. The efficiency of this process is important in selecting materials to be used for SHG devices. To decide the appropriate material, many parameters must be examined. These parameters include determining: a nonlinearity coefficient (d), crystal semetry, an angular sensitivity coefficient (B), and spectral absorption regions. Unfortunately, only the crystal symmetry can be determined in materials of crystalline sizes less than 2mm3. Thus, there is a great necessity for crystals that can be grown to sizes larger than 2mm3.

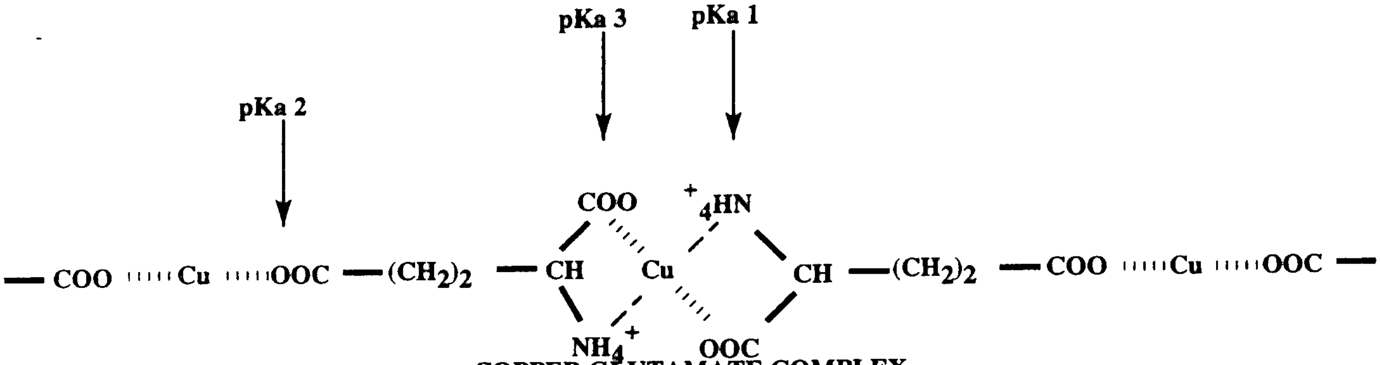
To produce crystals of high SHG efficiency, the molecular composition of the starting material to be crystallized must be carefully selected. According to Velsko, the probability of finding materials with SHG ability is greatly increased by examining materials with the combination of organic and inorganic characteristic (Materials for Nonlinear Optics, 1991). Thus, the compounds considered in the research for high SHG efficiency consist largely of semi organic materials. A number of chiral, hyperpolarizable, semi organic salts have been synthesized and crystallized into macromolecular sizes to decide second harmonic generation (SHG) in semi organic materials.

RESULTS

The following group of compounds was synthesized and tested for SHG properties:

*1) Copper (II) Acetate - Glutamic Acid complex
*2) Zinc Chloride - Glutamic Acid complex
*3) Cadmium - Glutamic Acid complex
*4) Magnesium - Glutamic Acid complex
5) Copper Citrate complex
6) Cobalt - Glutamic Acid complex
7) Copper (I) - Glutamic Acid complex

* signifies a material w/sufficient SHG properties upon (1080 NM) laser light exposure



COPPER GLUTAMATE COMPLEX

POLYMER

The Copper Glutamate Complex (above) was synthesized under basic conditions and titrated to examine supersaturating pH ranges. The blue compound was solubilized in acidic conditions and successfully crystallized by vapor diffusion in the presence of Sodium Acetate to dimensions exceeding a cubic millimeter. Crystalline copper glutamate was separated by particle size (20, 50, 75, 100, 150, 200, and 350 micrometer size groups) and tested for relative centrosymmetry and phase match ability by placing the samples in front of a Yttrium-Aluminum-Garnet (YAG) laser and measuring for nonlinear optical intensity. This process is called the Kurtz-Perry Powder Test and proved that the Copper Glutamate crystal is attractive material for Second Harmonic Generation.

Zinc Glutamate Complex was synthesized under basic conditions. The compound has been successfully crystallized and stoichiometrically confirmed by elemental analysis. Photos of this white transparent crystal were taken using a NIKON UFX IIA camera to confirm crystal morphology and birefringence. Phase match ability and high nonlinearity were confirmed by the Kurtz-Perry Powder Test.

Cadmium Glutamate was synthesized under basic conditions. The compound has been successfully crystallized and presently awaits having its crystal structure solved by X-ray Crystallographic Methods. Cadmium Glutamate is a white transparent crystal and shows high probability for being an attractive material for constructing SHG devices. Future work consists of optimizing conditions for growing larger crystals and, ultimately, measuring the nonlinear coefficient (d), angular sensitivity (B), and the spectral absorbance regions (as mentioned above). These values will provide a quantitative measurement of SHG efficiency and material relevance to the laser hardening program.

PHOTOCHROMIC POLYPEPTIDES

Task Order No. 193
Student Support Program
Southwestern Ohio Council for Higher Education

David P. Stitzel
Wright State University

14 June 1996

Government Task Leader
Mr. Dennis Hager
WL/MLPJ

ACKNOWLEDGMENTS

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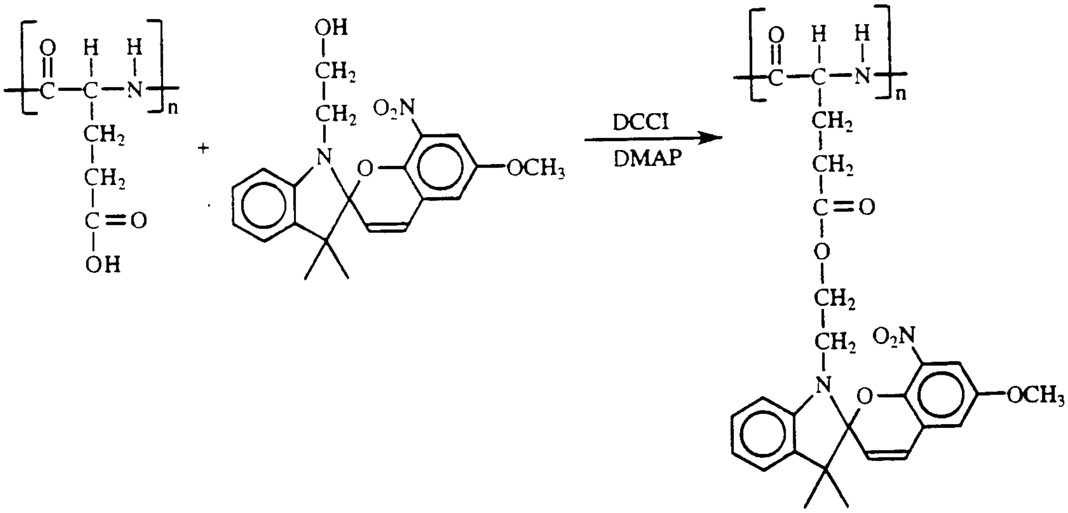
TASK ASSIGNMENT

Task Assignment 193 involved the synthesis and characterization of macromolecules containing nonlinear optically active side chains that can be aligned in an electric field. The long-term orientational stability of the side chains is a property that will be measured by second harmonic generation. It is believed that rigid rod polypeptides will enhance this stability by hindering side chain motion.

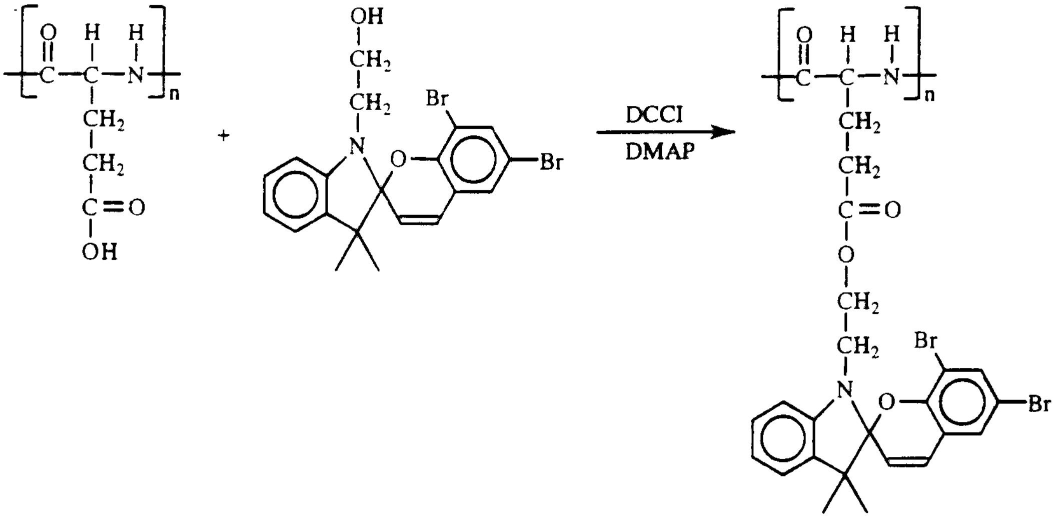
RESEARCH

A series of rigid rod polypeptides was synthesized, each containing a different nonlinear optically active dye. Each rigid rod polypeptide was synthesized by performing side chain transesterifications on a poly glutamic acid with one of the following nonlinear optically active dyes; 6-methoxy-8-nitro-1'-hydroxyethyl BIPS, 6,8-dibromo-1'-hydroxyethyl BIPS, and 6-phenylazo-8-nitro-1'-hydroxyethyl BIPS.



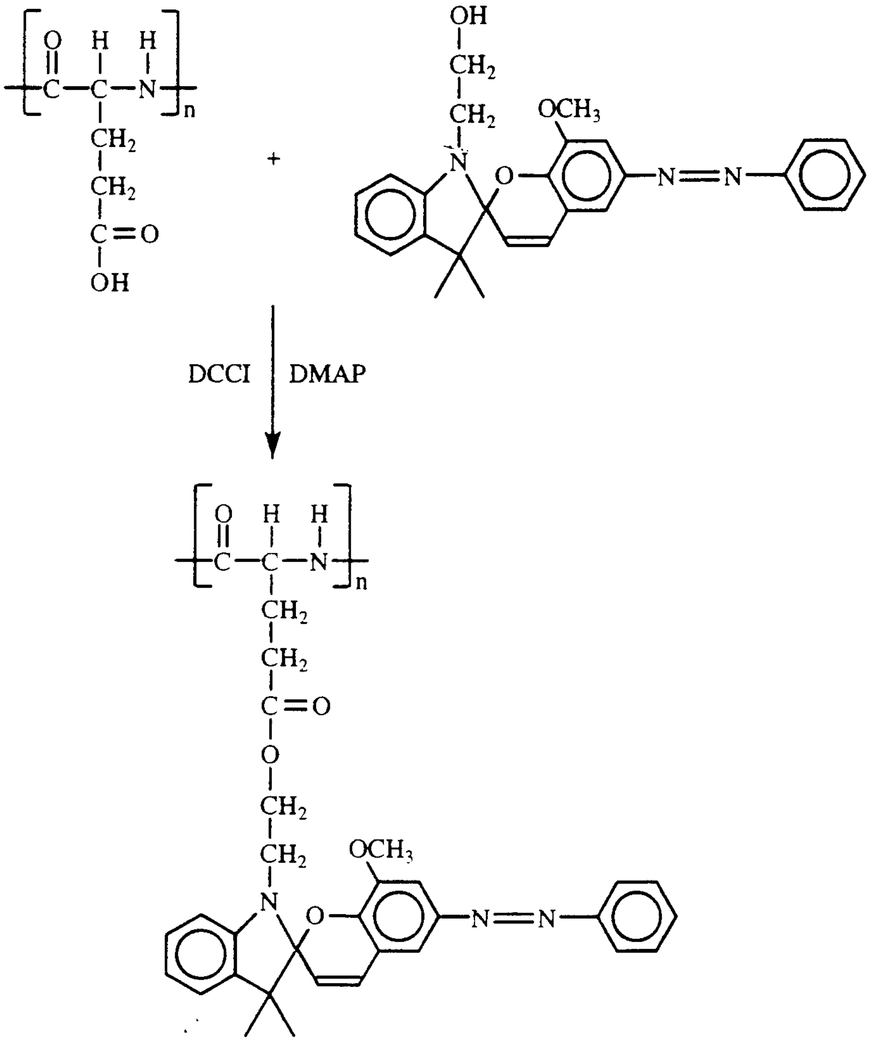
6-methoxy-8-nitro-1'-hydroxyethyl BIPS poly glutamate was synthesized as follows. Poly glutamic acid (0.1560g, 0.001208mol), 6-methoxy-8-nitro-1'-hydroxyethyl BIPS (0.9162g, 0.002396mol), 1,3-dicyclohexylcarbodiimide (0.2720g, 0.001318mol), and

4-dimethylaminopyridine (0.0751g, 0.0006147mol) were placed into an aluminum foil wrapped round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in dimethylformamide. The reaction was allowed to run for 6 days, at room temperature, under nitrogen atmospheric conditions. The crude product was purified by precipitating it with cold ethanol and redissolving it in a minimal amount of methylene chloride twice.



6,8-dibromo-1'-hydroxyethyl BIPS poly glutamate was synthesized as follows. Poly glutamic acid (0.1487g, 0.001152mol), 6,8-dibromo-1'-hydroxyethyl BIPS (1.0085g, 0.002168mol), 1,3-dicyclohexycarbodiimide (0.2613g, 0.001266mol), and 4-dimethylaminopyridine (0.0715g, 0.0005853mol) were placed into an aluminum foil wrapped round bottom flask equipped with a reflux condenser, a heating mantle, and a magnetic stirrer and dissolved in dimethylformamide. The reaction was allowed to run at 40°C for 4 days under nitrogen atmospheric conditions. The crude product was purified by precipitating it with cold ethanol and redissolving it in a minimal amount of methylene chloride two times.

Due to time restraints, 6-phenylazo-8-methoxy-1'-hydroxyethyl BIPS poly glutamate has not yet been synthesized.



RESULTS

Once the previously mentioned macromolecules were synthesized and purified, the final product was verified by analytical methods such as FTIR and NMR. FTIR (Fourier Transfer Infra-Red) spectrophotometry was used to find out whether characteristic bands of the desired compound was present in the purified product. One such band was the ester band that occurs at approximately 1750cm-^{1}. ^{1}H NMR (Proton Nuclear Magnetic Resonance) spectroscopy was used to verify the structure of the purified product.

PHOTOCHROMIC POLYPEPTIDES

Task Order No. 193a
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Earl Magness
Wright State University

6 July 1996

Government Task Leader
Dr. Angela Campbell
WL/MLPJ

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TASK ASSIGNMENT

Task number 193 was mainly concerned with electrostatic self assembled thin-films. Much of this research was a continuation of Dr. Angela Campbell and Dr. Thomas Cooper's work. Their most recent publication, T.M. Cooper, A.L. Campbell, and R.L. Crane, Langmuir, **11**, 1995, 2713-2718. should be consulted for a more thorough background on this subject. Optical, physical, and chemical properties of these films were investigated. The purpose of this investigation was to find out how various factors influence the assembly of the thin films and the limitations of these films. The ultimate purpose of the electrostatic self assembled films is the advancement of laser-hardening materials.

DESCRIPTION OF RESEARCH AND THE RESULTS

Several different aspects of the thin-film assembly research were conducted: literature searches on thin-film fabrication, UV/Vis/NIR, Fluorescence, and FT-IR Spectroscopy, solvent effects on the optical properties of certain compounds, substrate preparation (cleaning and deposition of coupling agents), and the synthesis of balodications and balodianions.

Several literature searches were conducted on the fabrication of thin films, recent and past techniques and research regarding thin films, the chemical synthesis of balodication and balodianions. These searches were conducted at the Wright Laboratory Technical Library and Wright State University's Dunbar Library.

UV/Vis/NIR Spectroscopy was obtained from a Perkin Elmer Lambda 9 Spectrophotometer. Various dyes and indicators were examined to learn the maximum absorbance wavelength of the dyes. Each compound was examined in several different concentrations. A calibration curve was then prepared for each compound, to decide the molar extinction coefficient. Beer's Law states absorbance is equal to the product of the pathlength, concentration, and molar extinction coefficient ($A = e*b*c$). The molar extinction coefficient can then be determined from a simple plot of absorbance versus the concentration yields a linear plot with the slope equal to the molar extinction coefficient.

Fluorescence spectroscopy was done on a Perkin Elmer 700 Series Fluorimeter. This information is useful in many applications. Several dyes used in thin-film fabrication exhibit fluorescence at room temperature. A comparison of solution fluorescence and thin-film fluorescence is useful information for further understanding the thin-filmoptical properties.

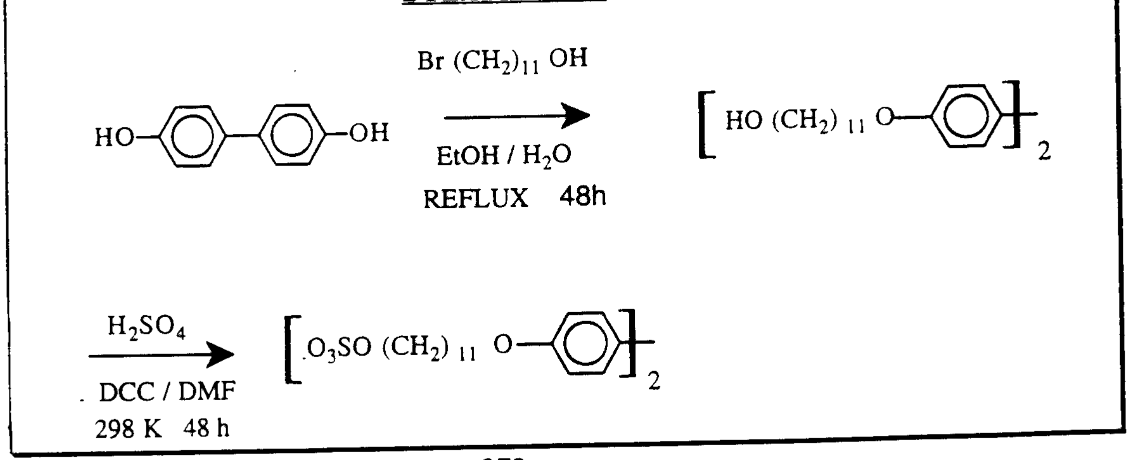
FT-IR Spectroscopy was obtained from a Perkin Elmer Model 1725 Infrared Spectrophotometer. This information is useful in determining the functionality of various compounds. By monitoring the functionality of a compound one could use this information to monitor the progress of a chemical reaction, i.e., the disappearance or appearance of a functional group. This information is also useful in characterizing products of reactions.

Several studies were performed to study the effect of a solvent. Something peculiar occurs with some group compounds, called the Metallo-phthalocyanine tetrasulfonates, in higher concentrations several of their optical properties deviate from what is expected. Aggregation, 'stacking' of the molecules in solution, is the main cause of this phenomena that often causes the quenching of fluorescence and other optical properties. This process can be avoided by changing the solvent of the solution, but doing this often causes other problems. For example, Aluminum Phthalocynanine Tetrasulfonate Tetrasodium salt (AlPCTS) is readily soluble in water, but in higher concentrations aggregation becomes a problem. AlPCTS is soluble in ethanol but aggregation is not a problem. Several different water ethanol solvents (different percentages) were then investigated to examine the optical and solubility properties. In the same category, acid base indicators deviate from Beer's Law. This deviation is often a function of pH, therefore, several solvents with varying pH's were prepared to examine the effect on the UV/Vis spectra.

A brief period was devoted to substrate preparation. This process of cleaning and deposition of coupling agents is very elaborate and difficult to describe. A very rigorous cleaning is performed, this goes well beyond the common soap/water/acetone routine, and involves the use of two very hazardous chemicals, concentrated sulfuric acid and 30% hydrogen peroxide. The deposition of coupling agents is arduous procedure. This process aides the adhesion of the thin-film components to the substrate.

Two relatively simple synthetic routes to balodication and balodianions were begun. Both contain the necessary 'rigid rod' center of the molecule for examining the build up of components on the substrate. The following diagram outlines the synthetic steps to balodianion:

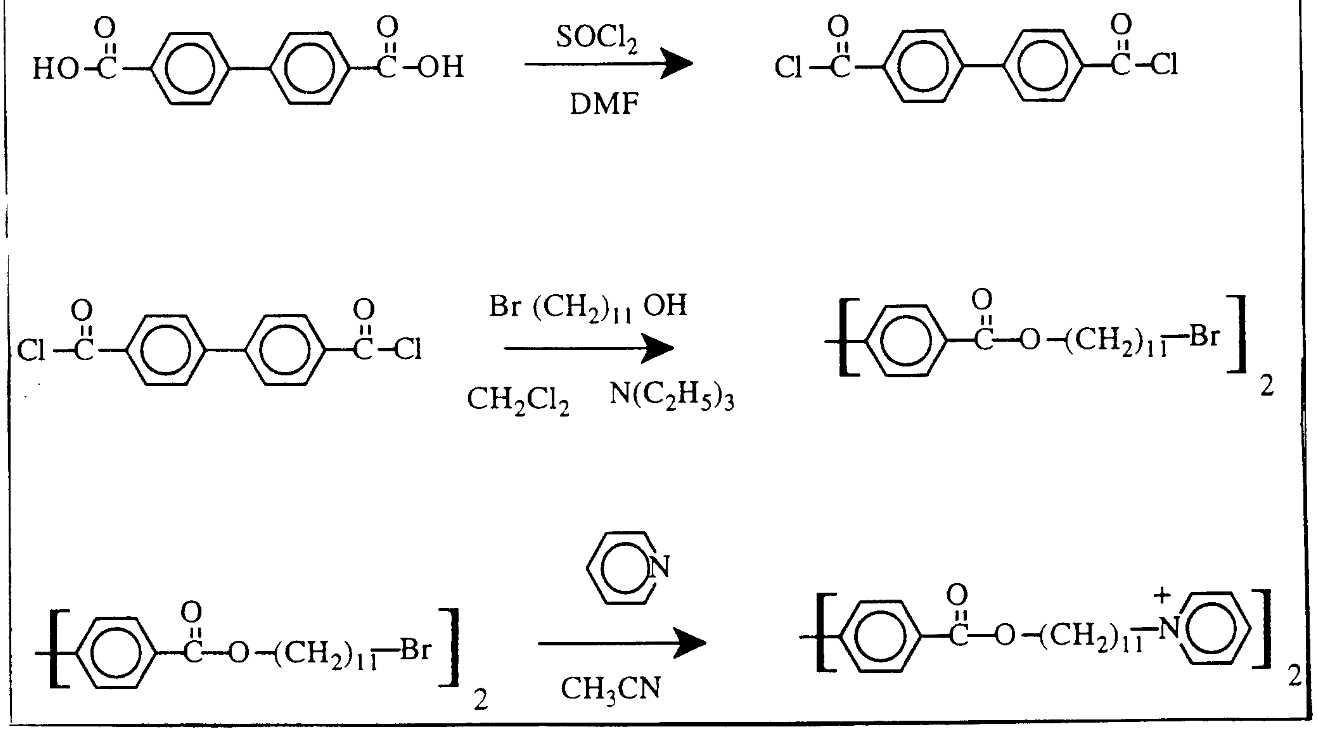
BOLADIANION



The first step in this sequence was done with yields approaching those in the literature cited. It is a simple reaction using the acidic phenolic proton to initiate the reaction. The reaction was monitored by Thin-Layer Chromatography and FT-IR. The product was recrystallized and characterized by FT-IR. The second step was not done by the time this report was written.

The following diagram outlines the synthetic steps toward the balodication:

BOLADICATION



The first step of this reaction sequence was done with yields approaching those of the literature cited. The second step did not turn out quite as well. The reaction was performed according to the literature, but the product was to be isolated by flash chromatography. This proved to be the limiting step. These reactions were also monitored by TLC and FT-IR. The third step in this sequence was not done at the time this report was written.

CONCLUSIONS

The research process in an industrial setting was eye opening experience. The time needed to obtain significant results, or any result is staggering. Exposure to the industrial setting was the most rewarding experience, and most beneficial.

DEVELOPMENT OF A VISUALIZATION ENVIRONMENT FOR A MATERIAL DISCOVERY SYSTEM

Task Order No. 194a
Student Support Program
Southwestern Ohio Council for Higher Education

Brian LaVelle
Wright State University

12 June 1996

Government Task Leader
Dr. Steve LeClair
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank Dr. Steve LeClair for this opportunity.

TASK ASSIGNMENT

Materials processing is an important field in today's world. We see applications in this area every day with such products like plastics to the radar absorbing skin on the stealth bomber. There is a need for this kind of study to develop new and better materials to make other products better.

There is usually a large amount of data that needs to be collected and processed. Normally, taking this data and processing it by hand can be a very time consuming method. We need an automated process that can do all of this tedious work and present it in a way that is easy to understand and learn. That is the motivation for the Unit Cell project.

The Unit Cell project deals with automating the method of information gathering and processing. The automation is being done currently on the Macintosh computer and written in Metrowerks C++, programming language. The code for the project was originally written in C. A conversion was made to C++ to take advantage of its many features. With C being a subset of C++ clearly it will offer more advantages. One of the most important features of C++ is that it has better facilities for mutual exclusion to different modules of code. An object can only gain access if it has inherited rights to certain modules in the code. It is better this way because it allows one to control more easily the flow of your application and (what object) has what access to your code.

Two general sections apply. First, there are the data entry and processing unit, and secondly, a graphical engine displays the processed data. Approximately 50% of the data entry and processing portion have been converted to C++. The data entry section has been complete, leaving only the processing section left to finish. The processing section can read in the input Unit Cell data and generate all of the atoms that it needs. It still needs to check for boundary conditions and do the appropriate scaling. The graphical portion of the project has been finished but is going through optimizations and minor debugging. An extensive graphical engine has been developed to aid in the visualization process. The engine has the abilities to do polygon clipping, painters' algorithm, lighting, multiple transformations and scaling. The function of the graphical engine is to display unit cell data after if has been processed.

To build the graphical user interface for the project a program called "Construct" was used. This small package enables a much faster approach at designing a graphical user interface. It focuses on designing the interface by dragging and drop icons and then generates resource files to be included in the code. The user interface now consists of its own drag and drop features, scrolls bars, and interface boxes. All of the features that can be done with the user interface can also be accomplished with the menu bar as well.

In conclusion, much was accomplished with this project. The graphical user's interface has been designed and is properly working. Most of the code has been converted to C++. The area that still needs work is the unit cell data processing portion. The code for this exists and does work but is very inefficient. Many optimizations can be done to speed up this section of the code. This project still has much potential. It is almost ready to start to add more functionality to do more operations on unit cell structures once the data processing portion is completed.

CERAMER TECHNOLOGY

Task Order No. 195
Student Support Program
Southwestern Ohio for Higher Education

Leslie M. Tack
Wright State University

16 July 1996

Government Task Leader
Dr. Fred E. Arnold
WL/MLBP

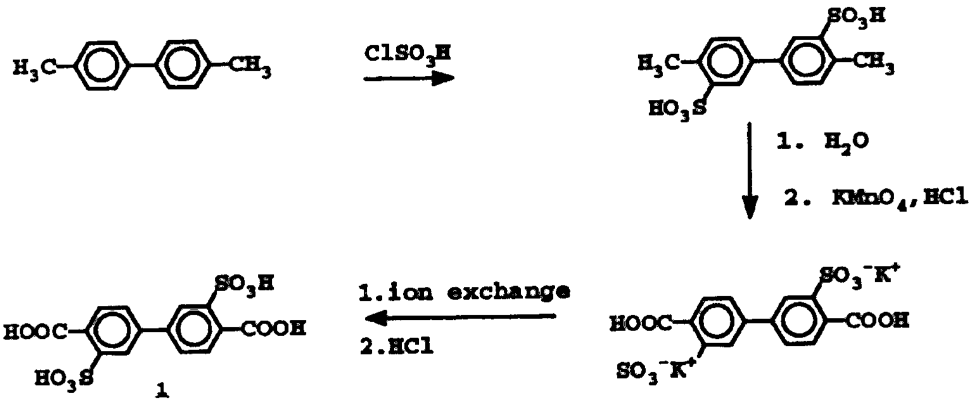
ACKNOWLEDGMENTS

I would like to thank Dr. Fred E. Arnold and Mr. Thuy Dang who have taught me so much. Thanks also to everyone at the Polymer Branch for their friendliness. They have made the past year an enjoyable one.

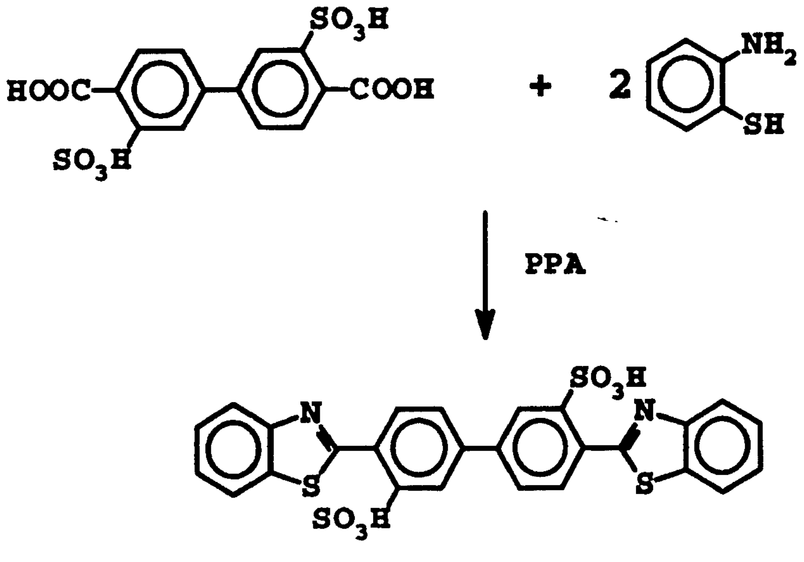
GENERAL DESCRIPTION OF TASK ASSIGNMENT

Ceramer materials have many potential applications for the United States Air Force. They possess many desirable qualities without the drawbacks of other polymer materials. These other aromatic heterocyclic polymer systems exhibit excellent high temperature properties, but only limited solubility (high boiling aprotic or acidic solvents). Organic ammonium salts of these ceramer materials have been found to exhibit high solubility in methanol. Silane coupling agents containing trialkylamine and trialkoxysilyl functional groups increase the solubility to produce homogenous gels.

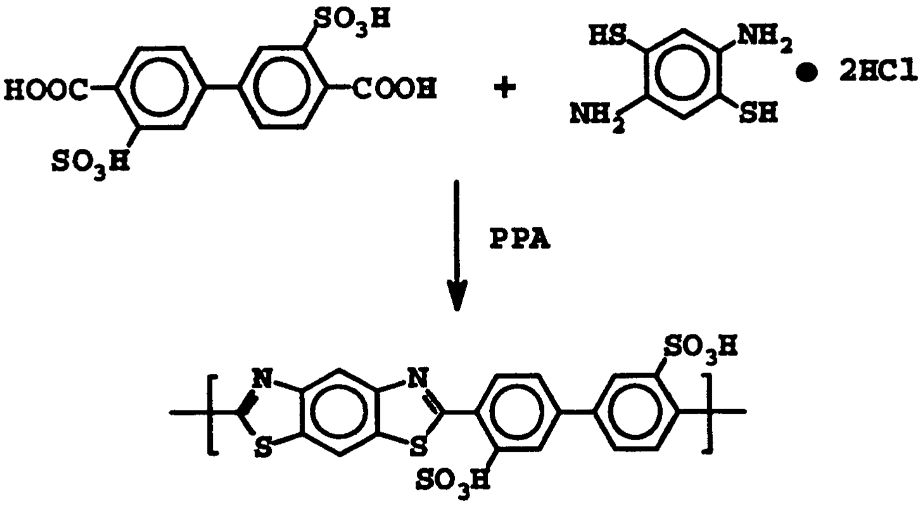
The following reaction scheme shows the synthesis of 3,3'-disulfodiphenic acid that will be later used to form a sulfonic acid pendant polymer.



Once the 3,3'-disulfodiphenic acid monomer was produced, a model compound was formed. The following scheme shows the synthesis of the model compound.

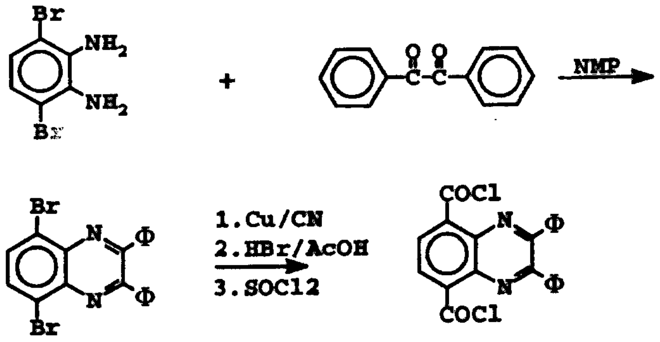


After the successful synthesis of the model compound, an attempt at polymerization was made.

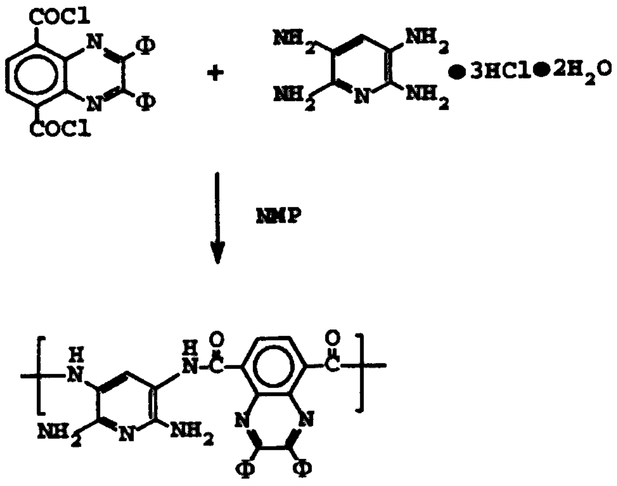


The synthesis of the 3,3'-disulfodiphenic acid monomer took quite a bit of time to accomplish. After many attempts to remove the potassium from the oxidation reaction by using a 10% hydrochloric acid solution, this method was determined to be unsuccessful. The elemental analysis results continually showed a high level of potassium. Finally, after using an ion exchange column, the potassium was removed and the synthesis was complete.

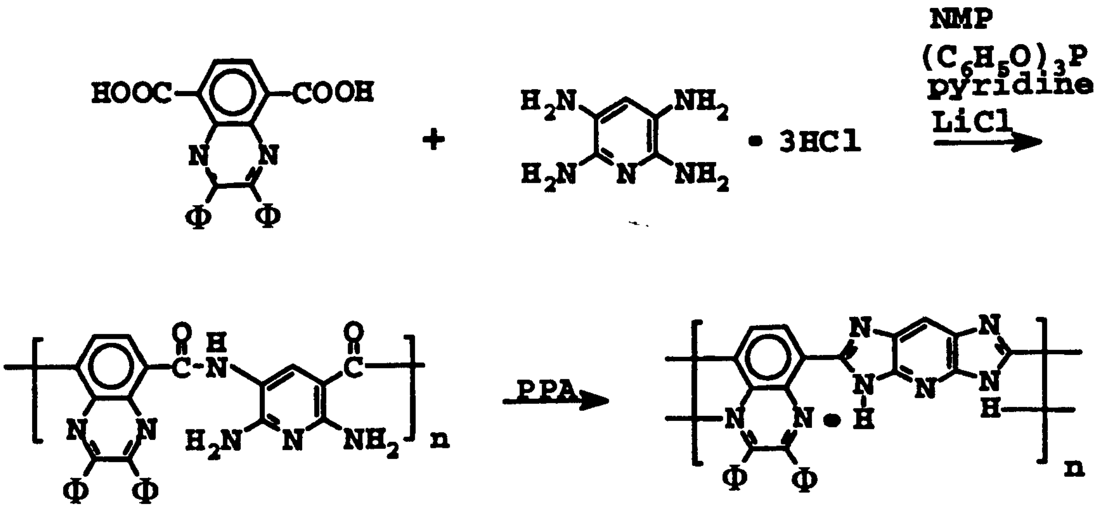
Another polymer made was a quinoxaline pseudoladder polymer. One of its monomers, a diacid chloride (1.0993g, 0.0027 mol.), was made according to the following synthetic reaction.



It was then reacted with 2,3,5,6-tetraamino pyridine (0.7195g, 0.0027 mol.) in 5.3 mL NMP. The reaction was stirred in an ice bath for 3hours and then at room temperature overnight. The resulting polymer had an intrinsic viscosity of 0.14 dl/g^3 at 30°C in sulfuric acid.



Similarly, another polymer was synthesized using a diacid monomer instead of a diacid chloride. The diacid monomer (0.9259g, 0.0025 mol.) was reacted with 2,3,5,6-tetraamino pyridine (0.6664g, 0.0025 mol.) to produce 1.275g of the polymer. An intrinsic viscosity of 0.26 dl/g^3 at 30°C in sulfuric acid was measured. The polymer was then placed in a resin flask with enough PPA to cover and heated overnight. An intrinsic viscosity of 0.45 dl/g3 was obtained at 30°C in methane sulfonic acid. The reaction scheme is as follows.



All compounds were identified using mass spectrometry, infrared spectrometry, and elemental analysis.

CERAMER TECHNOLOGY

Task Order No. 195a
Student Support Program
Southwestern Ohio Council for Higher Education

Pamela Bonds
Wright State University

16 July 1996

Government Task Leader
Dr. Fred Arnold
WL/MLBP

ACKNOWLEDGMENTS

I would like to thank Dr. Fred Arnold and Thuy Dang for their guidance and help during this Task.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The Task investigated the synthesis and characteristics of new aromatic-heterocyclic ceramers that would be compatible with current state-of-the-art sol-gel processing. The Task included the synthesis of alcohol/water-based polymer systems with functional groups which coreact with commercial coupling agents.

Most structural modifications on high performance benzazole and benzobisazole polymer systems have been carried out to promote this class of polymer materials amenable to the state-of-the-art sol-gel processing. The objective is to investigate the appropriate polymer, ceramic and processing technologies for fabricating ceramic polymer alloys, then address the modification of both polymer and ceramic technologies to enable a processing target temperature of 300-400°C.

It is anticipated that the improvement in ceramer technology would impact many structural and nonstructural Air Force applications. A variety of high performance thermally stable polymeric structures are known, but they are intractable and virtually impossible to process. The sol-gel ceramer technology is one solution to this problem. In the same manner, the optical quality of silicate glass can be continued with many high performance electrically conductive and non-linear-optically active polymers to produce low-cost opto-electronic and photonic components for telecommunications.

DESCRIPTION OF RESEARCH

The experiments that were done during this Task focused on the synthesis of monomers and polymers and the production of cast and aggregated films. Initial reactions included the synthesis of 4,4'-dimethylbiphenyl and 4,4'-dinitrobiphenyl monomers. Intermediate reactions were used to add functional groups, oxidize and acidify these monomeric materials before polymerization was carried out to form 2-sulfopolybenzobisimidazole (S-PBI).

The films produced were constructed from thermosettable secondary amines and thermoplastic molecular composites. Several films were cast of varying mole ratios in an attempt to generate homogeneous films that could be further studied after being heat cured. Aggregate films were made from blended polymeric material.

The analysis of materials was conducted by infrared spectroscopy, melting point, thin layer chromatography, nuclear magnetic resonance, mass spectrometry, and elemental analysis. Specific equipment used included the Bruker FTIR and Hatachi NMR.

RESULTS

High temperature, high performance polymer systems would offer many new desirable properties and eliminate many drawbacks of the polymer and ceramic technologies. Aromatic heterocyclic polymers are such polymer systems with excellent high temperature properties, but they only exhibit solubility in high boiling aprotic or acidic solvents.

High molecular weight S-PBI polymers are being synthesized along with a variety of 2-sulfo pendant benzazole and benzobisazole polymer systems to be evaluated for sol-gel processing. Organic ammonium salts of these polymers were found to exhibit excellent solubility in methanol. It was found that commercially available silane coupling agents containing trialkylamine and trialkoxysilyl functionality provided the required solubility in methanol leading to clear homogeneous gels.

COMPOSITES FOR INFRASTRUCTURE

Task Order No. 196
Student Support Program
Southwestern Ohio Council for Higher Education

Maggie Dougherty
University of Dayton

19 November 1996

Government Task Leader
Mr. John Mistretta
WL/MLBC

ACKNOWLEDGMENTS

I would like to thank all of the MLBC and UDRI staff who have helped me develop an understanding of composite materials, and acquainting me with the Materials Labs. Thanks to Ron Esterline, Chuck Fowler, and Ken Lindsay for guidance and materials testing. Thank you Allan Crasto and Brian Rice for insight into development of project agendas, and data interpretation. I greatly appreciate Ron Cornwell and James Lute for daily, if not hourly, advice on any question I may have. Thanks to Mrs. Wanda Vogler for providing me with this opportunity. Finally, a special thanks to my mentor, Mr. John Mistretta, for providing me with direction and encouragement, and opportunities to grow and excel.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The objective of this Task is to provide a civil engineering student the opportunity to develop an understanding of advanced composite materials. This Task is designed to further the transfer of technology to the civilian and commercial sector, specifically to the civil engineering realm. The development of this Task represents one civil engineering focus area. Other efforts to develop knowledge, interest, and future applications in the civil engineering community include short courses, seminars, and workshops, and development of design codes to regulate composite design in civil engineering applications.

This Task involves the development of an infrastructure rehabilitation system utilizing advanced composite materials. Many highways and interstates in the United States were constructed in the 1950's and are in need of repair as they approach the end of their design life. Advanced composites can be employed in this area as a more cost-effective means to repair the infrastructure, compared to traditional restoration methods. Greater cost efficiency is achieved through composite application because of lower maintenance and life cycle costs.

Specific responsibilities associated with this Task include the development of a thorough understanding of composite materials including composite constituents, composites processing procedures, and future composite applications. Additional responsibilities include testing and evaluation of structural adhesives for field applications, and development of in-house testing.

DESCRIPTION OF RESEARCH

Task work began with the characterization of graphite composite material AS4C/1919, commercially available through Hercules. AS4C/1919 is used to reinforce the tensile side of concrete beams in this project. The purpose of this reinforcement is to extend the life of the beam and delay or prevent catastrophic failure. This reinforcement will be used in concrete bridges. AS4C/1919 had been partially characterized in 1993. Characterization provided the development of more current and thorough results, as well as acting as an orientation to composites, and testing procedures required to decide optimal applications for a specific composite material.

An optimal composite lay-up had been previously determined. A field demonstration had also been initiated before the start of this Task. Further work associated with this project focused on the development of an optimal adhesive that would bond to both the concrete and the composite. Dexter-Hysol's EA9460 had been used almost exclusively in previous applications, including the field demonstration. EA9460 is highly recommended for concrete bonds, but does not bond to graphite composites exceptionally well. An adhesive's data base was developed as part of this Task to decide which companies produced adhesives that would provide an optimal bond for this project. The adhesive was required to maintain the bond through a wide range of temperatures, due to varied temperatures experienced in the field.

With satisfactory development of plate bonding to concrete beams, the project focus expanded to include the development of tendon reinforcement as opposed to composite plate bonding. Scaled beam tests with graphite composite tendon reinforcements were executed on both concrete beams and wooden beams. Wooden beams were tested to decide the feasibility of reinforcing wooden beams for use in construction.

RESULTS

Once the adhesive data base had been compiled and analyzed, Dexter Hysol EA9430 adhesive was selected as an alternative adhesive due to the strong bond formation with graphite. Double lap shear tests were performed using EA9430 and produced favorable results. EA9340 was used with EA9460 on a scaled beam test. EA9430 was applied to the composite while EA9460 was applied to the concrete. Unfortunately, the combined bond of EA9430 and EA9460 failed under a much lower loading than the EA9460 alone.

The first true test of composite plate reinforcement of concrete beams took place this summer. In the summer of 1995, the two exterior girders on a box span bridge were reinforced with composite plates using Dexter Hysol EA9460. The 28-foot span bridge is new and is located in Butler County. This project was made possible through the efforts of the Butler County Engineer's Office and civil engineering design firm LJB, Inc. This summer one of the reinforced exterior girders was removed and replaced with a typical box span girder. With 1 year of environmental exposure, the composite reinforced girder was brought to the Material Labs and tested. The beam showed a 20% increase in strength over a traditional girder beam. This was a 10% reduction in added strength produced with application of composite plates with no environmental exposure. The loss in additional strength is attributed to delaminations that occurred between the adhesive and composite plate as noted through nondestructive testing of the beam before testing.

Tendon reinforcement tests produced outstanding results, withstanding larger loading than plate reinforcement and preventing catastrophic failure that results with plate reinforcement. Plans to develop tendon reinforcement and determine the ultimate configuration for the tendons have been developed for the upcoming year.

A new composite material will be used in future composite plate reinforcement projects. This material is also made by Hercules and is similar to the AS4C/1919. The new material is AS4C/1995. These materials will be characterized as part of the next Task. In addition, the next Task will be expanded to include the responsibility of coordinating in house testing. Also, developing design skill so that the student plays a more active role in the design of composite reinforcement in infrastructure rehabilitation.

ENVIRONMENTAL DEGRADATION OF CMC'S

Task Order No. 197
Student Support Program
Southwestern Ohio Council for Higher Education

Isabel Rojano
Wright State University

27 August 1996

Government Task Leader
Dr. Craig Folsom
WL/MLLM

ACKNOWLEDGMENTS

Thanks must be given to the various government and contract workers of the Wright-Patterson Air Force Base Materials Directorate. Special thanks goes to Dr. Craig Folsom and Dr. Paul Jero for continuing to conduct the experiments of this Task.

TASK DESCRIPTION

The objective of the Task was to study the effects of water and high temperature on several ceramic matrix composites. Several corporations manufacture these composites however, to ensure favorable durability upon application of these materials, conducting extensive testing on the products of various corporations is necessary. More specifically, it is desirable for these ceramic matrix composites to resist fatigue, cracking, etcetera when they are used in the making of turbine engines for jet aircraft. The results of this testing would then be made available for materials research.

RESEARCH

There are several stages in the completion of this Task: background research, material acquisition, equipment acquisition, specimen preparation, material characterization, mechanical testing, data analysis, and research compilation. At this time, approximately half these stages have been completed.

A. Background research

This included conducting a literature search on the best types of shear testing that could be conducted and determining the type and number of experiments that would be conducted. This was completed by Dr. Craig Folsom before my arrival.

B. Material Acquisition .

The source of the materials was a series of government tests on CMC's called the Williams Program. The materials from this program are General Atomics C/Si_3N_4, Dupont Lanxide HPZ/SiC, Dupont Lanxide NiC/Al_2O_3, Dow Corning NiC/SiNC, Dupont Lanxide NiC/Al_20_3, Amercom NiC/SiC, and Kaiser Aerotech NiC/SiC. In addition, a plate of GEN4 was acquired from General Electric.

C. Equipment acquisition

The equipment needed for this testing includes a compression anti-buckling jig, DNC anti-buckling jig, humidity chamber, pump and tubing, sprinkler head, furnace tubes, rain-rapid heat rig, and self-aligning 4-pt bend rig. Some of this equipment has been obtained and/or located over time. A self-aligning 4-pt bend rig was found in a paper written by Professor R.G. Hoagland

(Battelle Columbus Laboratory). Professor R.G. Hoagland was contacted and the drawings of the rig were forwarded to MLLM.

D. Specimen preparation

Preparation of the CMC's involves cataloging, measuring, and weighing and prefatigue, humidity exposure, rain-rapid heat exposure, and specimen notching. To catalog the materials, each CMC was identified according to the layout and description of the same CMC's from the Williams Program. Each CMC was then placed in a separate bag and labeled. Then, the length and width of the specimens were recorded with a micrometer and the weight of each specimen was recorded with a gram balance.

E. Material Characterization

This involves sectioning, mounting, and polishing of the specimens and image analysis, optical microscopy, and SEM microscopy. To complete some characterization without waiting until the preparation of the specimens could be accomplished, optical microscopy and image analysis was conducted on samples that had been previously prepared by Dr. Paul Jero. Optical microscopy was done on a Reichert-Jung microscope. The resulting photographs were enlarged to 8'x10'. Image analysis was attempted on various computer programs available at WPAFB. Unfortunately, the results were relatively poor. Therefore, it was decided that the image analysis would be done from direct optical input. To aid in achieving satisfactory results by this method, the 8'x10' photographs were overlaid with transparencies. Then, the areas of fiber, matrix, coating, particulate, and porosity were filled in on the transparencies. The image analysis itself was then performed using the transparencies alone.

F. Mechanical testing

This involves DNC, 4-pt, and CND testing. None of these tests have been initiated at this point.

G. Analysis

Analysis of the CM's involves calculating their bulk densities and analyzing test data to determine their shear strength, flexural strength, and interfacial toughness. The bulk densities were calculated upon recording the length, width, and mass of the specimens. The shear strength, flexural strength, and interfacial toughness may not be determined until the mechanical testing has been completed.

H. Compilation

Upon completion of the Task, publication would be sought. To achieve this, all data, figures, graphs, etcetera would be presented. Throughout all other stages of the Task, the data has been transformed into tables for this purpose.

RESULTS

Because the experiments on CMC's for this Task are far from being completed, coming to any conclusions regarding their durability in rain-rapid heat conditions is not possible.

SUBSTRATE PREPARATION FOR ORGANIC THIN-FILM DEPOSITION

Task Order No. 198
Student Support Program
Southwestern Ohio Council for Higher Education

Swetang D. Patel
University of Dayton

4 September 1996

Government Task Leader
Dr. Angela Campbell
WL/MLPJ

ACKNOWLEDGMENTS

A special thanks to Dr. Lalgudi Natrajan, Dr. Tom Cooper and Dr. Angela L. Campbell for their patience, guidance and knowledge of chemistry that made this Task a positive learning experience. I would also like to thank Mr. Vince Tondiglia who helped and educated me in laser laboratory experiments. Thanks to MLPJ all personnel including Dr. Dennis Hager who made this Task possible. Finally, I would like to thank all SOCHE employees who made life a little easier.

TASK ASSIGNMENT

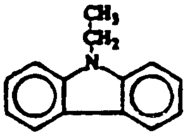
This Task dealt with thin-film processing of photo refractive materials and tests the photorefractivness by two-beam coupling experiment. Photo refractive (PR) polymers are a relatively new class of materials for photonic applications and are based on the phenomenon of photo refractivity that, by definition, is the modulation of index of refraction in an electro-optics material by internal electric fields caused by optical redistribution of charge carriers. There is tremendous potential for these materials in various electro-optics application such as optical signal processing, holographic and storage applications, to name just a few.

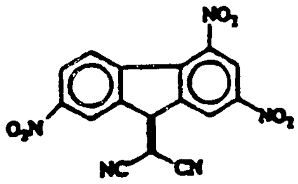
DESCRIPTION OF RESEARCH

The focus of this Task was to investigate and develop thin-film processing techniques of photo refractive (PR) materials and test the PR effectiveness by the interference of two-beam laser coupling experiment. In this laser experiment, a diffraction grating produced by the interference of two laser beams modulates the refractive index so that energy is transferred from the pump to the probe beam originally of equal intensity 1, 2. Usually, the irradiation of any PR materials by coherent light modifies the special distribution of photo generated charge carriers and produces an electric field dependent of the refractive index. It is crucial that the processing techniques control film thickness (beam interaction volume) and uniformity insuring the production of quality diffraction grating that would facilitate energy transfer from one beam to the other.

Molecular structure of each component in PR formulation is shown in Figure 1, where Poly(N-vinylcarbazole)(PVK), p-(N,N-dimethylamino)-w-nitrostyrene (DEANST), 9-ethylcarbazole (9EK), and 9-dicynomethylene-2,4,7-trinitrofluorene (DCMTNF), Table 1, lists the principal components, their thermal properties, and the function of each component in the mixture.

Figure 1


9-EK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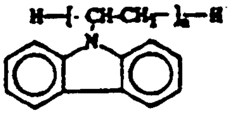
PVK

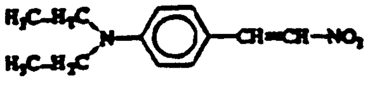
DEANST

Table 1

Compound	Function	Thermal Transition
Poly(N-vinylcarbazole) (PVK)	Photoconductive Polymer	Tg =212°C
p-(N,N-dimethylamino)-*w*-nitrostyren (DEANST)	Electro-optics Chromophore	m.p. =98°C
9-ethylcarbazole (9EK)	Plasticizer	m.p. =72°C
9-dicynomethylene-2,4,7-trinitrofluorene (DCMTNF)	Photosensitizer	m.p. =270°C

Preparation of ITO Etch Pattern:

Indium Titanium Oxide, ITO etches away with 20% HF solution. The rectangular ITO etch was created by placing transparent tape on the coated side and then putting the slide in the oven at 50°C for an hour. The slide was immersed in HF solution for a few minutes and the tape was cut with a razor blade, then, the unwanted portion was pealed away.

Material Formulation:

Two sets of different formulations were made in two separate vials, one containing the polymer and the other contained the remaining ingredients. Excess chlorobenzene was added to both vials to dissolve and dilute the mixture. This allowed the material to pass through a 0.45 mm nylon micro filter without clogging the filter paper. The two solutions were filtered into a third vial that was rinsed with methanol. A large portion of the excess chlorobenzene was removed by blowing a stream of dry nitrogen gas over the vial for several days. The increased concentration of the mixture constituted the working stock viscosity. One small drop was put onto each ITO plates and sandwiched them together trying to avoid formation of an air bubble.

Second, formulation of C_{60} and FDEANST were used instead of DCMTNF and DEANST respectively. PVK, 9EK, FDEANST, and C_{60} were mixed and dissolved in 4:1 toluene:cyclohexanone, for every 1 ml of solvents to 80 mg of solids. These ingredients were mixed by sonication for 20 minutes, placed on a hot plate at 110°C for 1 hour, then put in a vacuum oven at 70°C for 72 hours to drive off excess solvent. The spacer was placed on one ITO plate and dye was dropped on one side of the ITO plate. Then both plates were placed on a hot plate at 90°C for 3 minutes., and sandwiched together trying to avoid the formation of an air bubble. The sample was brought to room temperature by placing it on an aluminum plate.

The melting point and glass transition temperature was determined by TA Instruments modulated DSC instrument, Model 2920. A heat/cool method with several cycles was used with 10°C/min. heating and cooling rates.

In addition, 1 month was spent on designing and ordering laser optics for a two-beam coupling experiment.

RESULTS

Sample	PVK (wt%)	9EK (wt%)	DCMTNF (wt%)	C_{60} (wt%)	DEANST (wt%)	FDEANST (wt%)
PR#1	53.66	26.92	1.57	-----	17.85	----------
PR#2	53.67	26.85	1.57	-----	17.89	----------
PR#3	38.43	19.20	29.59	-----	12.77	----------
PR#4	50.00	16.00	33.00	-----	1.00	----------
PR#5	50.30	16.44	----------	0.49	----------	32.76

The above formulations were made but samples were not analyzed due to a laser break down. Results are under investigation.

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2. Meerholz, K., Volodin, B. L., Sandalphon, Kippelen, B. and Peyghambarian, Nature, 1994, **371**, 497-500, "A photorefractive polymer with high optical gain and diffraction efficiency near 100%."

STRUCTURAL FAILURE ANALYSIS TECHNICIAN

Task Order No. 199
Student Support Program
Southwestern Ohio Council for Higher Education

Erman L. Cole II
Sinclair Community College

24 July 1996

Government Task Leader
Mr. Ron Williams
WL/MLSA

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TASK ASSIGNMENT

Due to the brevity of the initial Task, goals from that Task were carried over into a new Task. Laboratory equipment familiarization and hygiene, metal and composite mold making, sample photography, and metal and composite polishing were stressed. In addition to what was stressed, an individual is given an educational conductive environment to proceed and acquire more knowledge of the procedure of analyzing failures.

In any technical work place, including a failure analysis laboratory, there are many forms to document and record various procedures. There are log books for molds manufactured, supply purchase requisitions, chemical analysis requests, requests for film development, and appropriate waste disposal requisition forms. These forms and logs serve both as written communication between departments and agencies or as tracking devices for materials submitted to or received from various offices or agencies located within or close to Wright Laboratory.

Various analytical equipment is used within the laboratory to provide many methods to approach any problem. There are microscopes of various magnifications, sanding devices, polishing devices, a band saw, rotary saws, and a mold press. All of the above devices must be properly maintained. A technician must fully understand cleaning procedures and replacement procedures of minor parts.

Upon receipt of a large sample, a laboratory technician begins a procedure. The aide must reduce this sample to a smaller sample in order for it to be analyzed easier by the engineer. A mold makes it easier for the sample to be handled while it is being evaluated. The proper use of saws is important to obtain a small enough portion of the sample without increasing the damage to it. Depending on the material of the sample, it is cleaned using appropriate chemicals. There are many materials to use in making a mold. The decision of which ones to select is dependent on the material of the sample and the evaluation it will undergo.

Following the completion of the mold assembly and documentation of this assembly, it has to be polished. The technician uses various sanding methods, fixed or rotating, to polish the sample to get a closer look at its intergranular structure. Once sanding is complete, the sample is polished using wheel-mounted polishing cloth to further reduce scratches. After polishing, if requested by the assigning engineer, the technician may accomplish hardness testing on the sample. Due to the small indents produced by this procedure, the sample must be polished again. Finally the sample, if metal, is etched. The etching reveals the intergranular structure just below the polished surface. By evaluating the intergranular structure under a microscope, an engineer makes determination why a substance failed. Failure may be caused by corrosion, stress, improper metal processing, or embrittlement, just to name a few.

The basic microscope an undergraduate technician may have come into contact within his or her curriculum takes on a much more complicated state in the laboratory. Not only is there a power source and a few lenses, there are monitors, photographic equipment, personal adjustments as far as the eyepiece, and even large control panels such as those seen on high magnification electron microscopes. A beginning technician learns the basics of operation such as proper ways to focus, multiplication factors of magnification, and how to produce photographic images he or she sees. To achieve the proper combination of these to produce correct reproductions can require many attempts by a novice and can even be trying for the more experienced lab technician.

Lastly, but definitely as important as other information, is disposal of waste. Everything is disposed of according to its chemical content. Very little goes into a waste paper receptacle. Even some photographic byproducts have special receptacles. The majority of waste is documented about what it is, where it was, how it was used, how much of it was used, and where it went when it left the laboratory.

Laboratory technicians should observe as much as he or she can. In this conductive environment, questions are encouraged and welcomed. Unfortunately, there are times that questions must go unanswered. The sensitivity of some information may exclude a lab technician from participating in some analysis. The previous year has been one in which these types of projects have been in abundance. Even in these situations, a laboratory technician may be called upon to do some tasks, such as polish a metal sample or even be given an assignment by an engineer from another group. No one turns away someone who wants to learn.

One very valuable lesson learned is a strong reinforcement of communication. In a failure analysis laboratory, as well as any organization, communications, oral and written, are very important and should never be neglected. An open line of communication between a lab technician and his immediate supervisor is of special importance. A breakdown of communication between these two individuals can lead to a detrimental crisis. During this Task it was possible to observe and learn how to deal with this kind of communication problem and communication problems between other colleagues.

A Task of this type teaches the technician, not only how to complete assignments in a laboratory environment successfully, but also how to function properly as a team member in a corporate team. It is a very good experience to be able to increase knowledge of things mentioned in undergraduate text books by using the equipment and standing side by side with a qualified professional.

GRAPHICS DISPLAY OF COMPUTER SIMULATIONS

Task Order No. 200
Student Support Program
Southwestern Ohio Council for Higher Education

Carlos Hernandez
Wright State University

31 August 1996

Government Task Leader
Ms. Monica A. Stucke
WL/MLLM

ACKNOWLEDGMENTS

I would like to thank the whole group for their support and camaraderie, which made the Task very enjoyable. The office was one of the friendliest and most pleasurable environments in which one would ever expect to work. Special thanks goes to Mr. Satish Rao and Mr. Jeff Simmons for their support, expertise and collaboration in several projects. I would also like to thank the people at the Southwestern Ohio Council for Higher Education (SOCHE) not only for their professionalism, but also for their service and assistance provided during this Task.

TASK ASSIGNMENT

During the Task, several graphical tools were completed to support the displaying of information from large input data decks involving differential displacement of atoms, local strains, forces, etc. Among these tools, some were built around the previously developed graphical packages, while others are stand alone utilities. The main objective of these utilities has been to improve the quality of the graphical results to give a professional and ready to publish output.

The main focus of work during this Task, however, has been the development and optimization of several scientific programs; while some of them are simply innovations and improvements to old problems, others are new to the field of materials within our community.

Several flexible boundary schemes have been proposed in the material science community to relieve inconsistencies that arise at the boundary region in atomistic simulations of defects, like dislocations and crack tips. These flexible techniques can be classified into two categories: 1) finite element methods and 2) Green's function methods. With the finite element techniques, the difficult part is the proper treatment of the transition between the lattice and the continuum that has recently been described in terms of non-local elasticity theory. Green's function techniques suffer from the disadvantage that the Green's function of the defected lattice, even in the long range part, is dependent of the core structure and of the size of the defect that is being simulated. Therefore, in atomistic simulations of crack propagation, the appropriate Green's functions for the defect problem, needs to be updated continuously as the simulation proceeds. However, the Green's function of a perfect lattice is relatively unperturbed around line defects like dislocations. Therefore, for simulations of dislocations in a single crystal, Green's function techniques can be applied with relative ease, since only the perfect lattice Green's functions are required for a proper treatment at the boundary region.

The requirements' specification phase of a project to implement Green's functions techniques were completed to describe the inconsistencies arising at the boundary region in atomistic simulations of infinite dislocations, for both 2 and three-dimensional dislocation problems for the Materials Lab at WPAFB. The system was analyzed, designed and developed to run on all types of RISC workstations, including the Power Macintosh, and, on CRAY Supercomputers (X-MP, Y-MP and C-90). This was required in addition to the development of the system, a complete design and development of a time library and an extensive scientific mathematical library. Because of the large core structure used by the CMS (Computational Materials Science) group, the system was optimized for all the running architectures and was improved by a 700% factor. Optimization techniques employed varied, from loop unrolling techniques, instruction scheduling etc. on the software side, to cache, register, processors etc. utilization on the hardware front.

Once the system was operational, the development of the system was analyzed and "costed" to run in parallel, distributed and in multiprocessor workstations, to accommodate for future larger simulations. The researcher then, proceeded to design and develop the system to run on the Intel Paragon™ using the NX library for message passing. The system was then optimized after a thorough study of the hardware available, e.g., message routers etc. The system, as well as the libraries, were developed completely using C and the UNIX™ Operating System.

As a project leader, the researcher, also completed the requirements specification phase of a molecular dynamics (MD) system, that uses embedded atom method (EAM) potentials for the CMS. This system was implemented using new MD algorithms that are more precise and faster than existing ones. The system was developed first for RISC workstations and CRAY Supercomputers and then ported to the Intel Paragon. This system was developed using C, FORTRAN and the UNIX Operating System.

This system was refined and optimized during the Task several times, to be, not only more accurate, but also friendlier and more efficient. Because of this, the CMS group is now able to analyze larger core structures in a reasonable amount of time. This leaves more time for the material scientist to devote to the study and analysis of the simulation results. Additionally, this performance improvement, allows the CMS group to run their simulations "in house" without having to request computer time from other outside facilities.

The development of these systems, has raised one of the major problems that the CMS has to face, that of time. Most algorithms employed by the CMS group grow exponentially with the number of atoms. This fact has shown the impossibility of running some simulations, as well as, the enormous wait between simulations, even with today's computational power.

This problem and the need for running larger cores, e.g., Cores approaching 1 million atoms, has led to the need for not only optimization of code, but also the need for research and testing of new methods that will allow faster turn around times, as well as, the possibility of running some of today's unfeasible simulations.

The researcher, was also involved in various other projects, such as, the development of a program to calculate "Schmid Factors" and displaying these using isometric projections, Monte Carlo simulations, "Zenner and Pinning" studies, finding and displaying local strains, finding the self induce stress field at point due to a line segment, for both isotropic and anisotropic mediums, displaying embedded surfaces and contour plots, for the analysis of electronic structures etc.

Currently a paper is being written in collaboration with Mr. Satish Rao and Mr. Jeff Simmons to be published in the Materials Science Phil.Mag, about Green's function boundary conditions methodology, including extensive graphical, theoretical, computational and timing analysis.

Other activities done during the Task included serving as the system administrator, doing such tasks, as adding new users, managing UNIX processes, planning and performing backups, restoring lost files from backup tapes, adding new terminals and disk drives, setting up a printer and the spooling system, and especially making the system secure.

SYNTHESIS OF LIGHT-SENSITIVE MATERIALS FOR LASER HARDENING APPLICATIONS

Task Order No. 201
Student Support Program
Southwestern Ohio Council for Higher Education

Laura A. Sowards
Wright State University

11 August 1996

Government Task Leader
Dr. Tom Cooper
WL/MLPJ

ACKNOWLEDGMENTS

I would like to take this opportunity to thank Dr. Lalgudi Natarajan for his assistance during the last year. He has advised and directed me toward accomplishing the goals of my Task. In addition, he has helped me to become acquainted with many different operations at Wright Laboratory. I would also like to express my sincere gratitude to Dr. Tom Cooper and SOCHE for giving me the opportunity to work and learn at WL/MLPJ. I have found the experience and knowledge gained here to be quite valuable.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The goal of Task Assignment 201 is to obtain light-sensitive materials to be used in laser hardening applications. These materials may consist of infrared-absorbing dyes, photochromic compounds and photochromic polypeptides. The research concentrated on dithienyl polyenes and related compounds obtained from Dr. Charles Spangler of Northern Illinois University. These compounds were analyzed by UV/VIS spectroscopy, steady state fluorescence, fluorescence quantum yield and fluorescence lifetime. Analysis of the resulting data determines whether the compounds can be used in laser hardening applications. These applications include optical filters used to block radiation in the near infrared region.

DESCRIPTION OF RESEARCH

The compounds received from Dr. Spangler were to be analyzed by four spectroscopic techniques: UV/VIS spectroscopy, steady-state fluorescence, fluorescence quantum yield, and fluorescence lifetime.

A Perkin-Elmer Lambda 9 Ultra-Violet/Visible/Infrared Spectrophotometer was used to obtain the spectra for the dithienyl polyenes. An abscissa range of approximately 300nm -700nm was used. The solvent for all compounds was dichloromethane.

Steady-state fluorescence measurements were taken with a Perkin-Elmer Luminescence Spectrometer (LS 50B). The excitation wavelength was determined from the maximum wavelength of the UV/VIS spectrum of the corresponding compound. The emission and excitation slits were adjusted to yield the best spectrum. Dichloromethane was used for the solvent.

The fluorescence quantum yield is calculated by taking the ratio of the emission of a sample to the emission of a standard. The quantum yield represents the ratio of the number of photons emitted to the number of photons absorbed. Perylene has a fluorescence quantum yield of .98 and was used as the standard. The standard and the sample were both adjusted to have equal absorptivities of approximately 0.10 at a specific wavelength on the UV/VIS spectrophotometer. Both samples were then analyzed on the steady-state fluorometer using the same specific wavelength as the excitation wavelength. The area under the resulting spectrum was determined by integration. The area of the sample was then divided by the area of the standard to yield the fluorescence quantum yield.

The fluorescence lifetimes were measured on a Photon Technology International (GS-302). Samples were prepared with dichloromethane. Spectra were measured on a picosecond scale.

RESULTS

The primary goal of this Task is to assess the feasibility of using these compounds in laser hardening applications. Many dithienyl polyene compounds have been found to have strong absorption bands of relatively narrow widths (20nm-50nm) which is a criterion for laser hardening applications.

Analysis of the compounds from Dr. Spangler is still in progress. Most of the UV/VIS spectra have been taken. The fluorescence spectra are difficult to obtain because steady-state fluorescence does not occur uniformly or at all in certain compounds. Some compounds have been analyzed, and most show atypical spectra. This may be because biphenyl compounds typically have irregular fluorescence spectra. Another probable cause is that increased length of conjugation chains decreases the efficiency of fluorescence scans. The quantum yields of several compounds have been calculated. The results are comparable to literature values. The fluorescence lifetime measurements taken are limited in number due to a short supply of high purity nitrogen. The lifetime measurements taken indicate isomerization during emission for certain structural isomers.

This research Task is progressing well. New information, such as the isomerization of the structural isomers, is being uncovered as the compounds are continuously being analyzed.

CERAMIC FIBER CREEP STUDIES

Task Order No. 202
Student Support Program
Southwestern Ohio Council for Higher Education

Aaron Minch
Wright State University

1 October 1996

Government Task Leader
Dr. Randy Hay
WL/MLLM

ACKNOWLEDGMENTS

I would like to thank two people, first, Larry Matson, my Task Leader, who spent time explaining the Task. Secondly, thanks goes to John Welch, who spent a lot of time showing me how to do the polishing correctly and how to interpret when to move to a different size micron disk. He also showed me how to know when the sample was nearing completion using the light in the room and the microscope. His Task paper must be credited because it was used as a reference when using the tripod polisher. The job could not have been done without him.

TASK ASSIGNMENT

This Task involved getting specimens ready for the scanning electron microscope (SEM) and the transmission electron microscope (TEM) to investigate the micro structure of ceramic fibers.

The problem was using only a 1/8 inch of fiber in which to prepare a sample. This small amount was used because not much fiber can be "scrapped" for sample preparation since different parts of the fiber may have different micro structures especially if, for example, a heat treatment or creep test is being performed. Before the sample preparation was done on the heat treated or crept samples, "junk" fiber was used until I became comfortable with a method of preparation.

The method used is putting the fiber of interest on a piece of Teflon, and then putting two junk fibers on either side of the fiber of interest to protect it from debris and erosion when the sample becomes very thin, as would happen for TEM preparation. Epoxy, type "G-1," is put on the fibers to keep them steady so they do not get pulled out when polishing. This assembly is put into a curing oven to allow the epoxy to cure.

A problem with this method is epoxy was put on top of the fibers, they moved from the original position next to each other, probably due to the viscous forces within the epoxy. This problem was solved by using double sided tape, which sticks to the Teflon. Next, the fibers are placed on the tape beside each other, so when the epoxy was dropped upon the fibers, they would not move because they were stuck to the tape. The sample is put in the curing oven for at least 1 hour. The specimen is taken out of the oven after curing and taken off the tape before it fully cures. This is done because the tape would have curled up and caused problems when the specimen had been polished down to the fibers. This would cause diamond or bits of fiber to put big scratches in the desired fiber when it became thin. The specimen is turned over and once the tape is removed, a thin coat of epoxy is applied to give good coverage to the other side of the fibers. The specimen is placed in the oven and this time it is fully cured.

When preparing for the SEM, the desired view is a transverse cross-section, which means the width of the fiber is being viewed. The cured specimen is ground on sandpaper to find the orientation of the fiber ends. The sample is placed in a clip on the ram of the mounting press so that the fiber ends are pointing straight up. Sifted epomet, which is a mounting material, is used around the base of the sample for better adhesion to the sample. Regular epomet is used to fill the remainder of the cylinder.

Once the specimen is mounted, it is taken out and polished on an 8-inch brass wheel with a piece of silk on it. Diamonds suspended in oil in 45, 15, 9, 3, and 1 micron sizes are put on different pieces of silk. The specimen is cleaned with acetone, 2-Propanol and put in a vacuum oven to keep it clean until carbon coating. The carbon coating is done for conduction of electrons to the sample because of the necessity of a bean of electrons to hit the sample for viewing the fiber's micro structure on a SEM.

The TEM procedure is quite different since the desired view is longitudinal or lengthwise. Once the specimen has cured, it is ground with silicon carbide paper so the specimen can be put in a clip ring. This clip ring makes the specimen approximately the size needed for mounting on the tripod polisher. The specimen and the ring are put on the ram of the mounting press and epomet of various ground is put on the specimen as follows: first sifted, to get good coverage around the specimen due to the lack of chunks, then fine ground, then the standard epomet. Once the mounting is complete, the specimen is cut until the ring is reached and the small ring-sized sample is taken out. This is mounted on the tripod polisher, which is a piece of metal with a place for putting the specimen and three micrometers for legs. The tripod polisher can be adjusted to get a desired plane of polish by using a large glass slide to get the rear 2 feet and the specimen in the same plane.

The sample rests on the stub. The stub is set on a hot plate and epoxy is placed on it and heated until the epoxy becomes fluid-like, then a glass slide is put on the epoxy. More epoxy is put on the glass slide and when it becomes fluid-like, the sample is put on the glass slide. The large glass slide is used to make the rear feet level with the lowest part of the sample, which acts as the third leg once the third micrometer is moved out of the way.

Once the sample is polished on 30, 15, 6, 3, 1, ½, and 1/10 micron diamond embedded disks, the sample is heated on a hot plate to make the crystal bond fluid. The sample is removed and turned over. The objective when polishing the first side is to be at the middle of the fiber when finished so the maximum area of the fiber can be seen.

The specimen is turned over and ground with a reverse bevel with a 68-micron embedded diamond disk until the back of the glass slide is about 1 millimeter thick. The feet of the polisher are leveled to the glass slide on which the specimen lies with the large glass slide used previously. The feet are lowered an additional six turns so that the reverse bevel is continued on the specimen. The specimen's reverse bevel is finished on the 30-micron diamond disk when the back of the glass slide on which the sample is mounted is seen. This is done by setting the rear 2 feet of the specimen on the disk and, setting the specimen on the disk. The rear feet of the tripod polisher are raised until they are not touching the disk. Once the reverse bevel is finished, the glass slide is used to level the feet to the part of the sample where the glass slide is exposed.

The feet of the tripod are raised seven turns and the front of the sample will be polished until 75-80° of the sample is polished. At this point, the 30-micron disk is removed and a 15-micron disk put on. The rear 2 feet of the tripod polisher are lowered 25 notches. The 15-micron disk is used until the top of the fiber is exposed and then it is removed to switch to the 6-micron disk. The 6-micron disk is used until the side being polished is getting close to the side that is already polished and the epoxy becomes nearly transparent. Look at the sample on the microscope and focus on the specimen so that the scratches can be seen. The light is turned down so that the outline of the fibers on the other side of the specimen can be seen. The sample must be checked often because it is becoming very thin at this point. The 6-micron disk is removed. The 3-micron disk is put on and used until the epoxy becomes transparent and the opposite side matches the side that is being polished fairly well. The 3-micron disk is removed and the 1-micron disk is used. Once a small amount of the surrounding epoxy is eroded away, the sample can be polished on the ½ micron disk. The sample is polished on the ½ micron disk until more of the epoxy is eaten away. If the sample is fairly diamond free when examined under the microscope, the sample is finished, otherwise the sample is polished with the 1/10 micron disk until the greater part of the diamond is removed. The 1/10 micron also seems to give the fibers a brilliance that the ½ micron polish lacks.

When the sample is finished, the stub is removed from the tripod polisher and put on the hot plate. The sample needs close attention while on the hot plate, because the specimen is so thin it will warp or crinkle. The glass slide should be pushed with tongs while heating the specimen on the hot plate to check and see if the slide is ready for removal. The sooner the slide can be removed the better. The specimen is placed in a small plastic bag and labeled with the given fiber name and description.

Further work is needed to get the specimen in the TEM for observation of the fiber micro structure. A certain microstructure is desired to give the fibers good strength so certain treatments and tests are done on the fibers to get these qualities.

A valuable lesson in the Task was learning that polishing does not get rid of all scratches, but exchanges larger scratches for smaller scratches. Therefore, if polishing is necessary, one grade of polishing would probably not be enough. Start with a larger grain size and then work downward to smaller grain sizes.

METALLOGRAPHY OF CERAMIC FIBERS

Task Order No. 203
Student Support Program
Southwestern Ohio Council for Higher Education

Cohen King
Wright State University

1 August 1996

Government Task Leader
Dr. Randall Hay
WL/MLLM

ACKNOWLEDGMENTS

Special thanks goes to Dr. T. A. Parthasarathy for allowing me to work with him in the Student Support Program. Also, thanks goes to Travis Brown of Universal Energy Systems (UES) for making the frames that will be explained later. In addition, thanks to Dennis Petry, also of UES, for helping set up the tensile test machine

I have learned a great deal working in the Ceramics Group at Wright Laboratory Materials Directorate. The knowledge and experience I have gained working with materials engineers and scientists, is very valuable. Throughout the Task, questions emerged about the relative findings of tests, but in the end, everything became clear. It has been an honor to work with such a staff of engineers while employed by SOCHE.

TASK ASSIGNMENT

Throughout the Task, there were various strength tests done on Nicalon^R and Boron Nitride (BN) coated Nicalon^R fibers. In determining the strength of the fibers, a four-step method had to be done for this to be accomplished. The four steps involved getting the fibers to the condition they would be tested. This included mounting the fibers to frames, measuring the fibers using a laser, and testing the fibers using a tensile test machine. The purpose of the tests was to find the strengths and the modulus of the fibers and compare them to other tests. The fibers were tested under several conditions including annealing in air and soaking in salt water, to understand better what will happen once the fibers are put into a composite and used for jet engine applications.

The four steps of conditioning, mounting, measuring, and testing will be explained below. The first step of conditioning the fibers involved heating and soaking the fibers and combinations of the two. The initial condition was taking the fibers as received and testing them. Some of the conditions were soaking the fibers in 0.05% salt water and 0.5% salt water solutions followed by annealing them at 1000° C for 2 hours. Other fibers were soaked as well, but only annealed at 800°C for 2 hours. Others still were not soaked, but annealed.

The second step involved mounting the fibers to a frame. This step initially needed some help from Travis Brown. He made the frames needed for mounting from aluminum. The frames were 3.5" x 4" dimensions with a 0.75" interior border. With the frames this size, there was usually enough room to place about 21 fibers. In addition, using two frames made it possible to test up to 42 fibers.

The third step involved measuring the diameter of the individual fibers to be tested. This was done by placing the frames vertically into a specially designed styrofoam base attached to a moveable stand and then shooting a laser directly at the individual fibers creating an interference pattern. Then, by using a standard distance from the fibers to a note card and measuring the distance between the fringes created, it was then possible to calculate the diameter of the fibers using geometry and the known wavelength of the laser. This was done at three different parts of the fiber and the average was recorded.

The fourth step involved testing the fibers for their maximum load capacity before breaking. This was done by using a tensile test machine connected to a computer. The fibers were taken from the frames and placed into grips with a foil wrapping over the grips. One grip stays in place while the other is connected to a load cell and sends signals to the computer at a set interval. This continues until the fiber breaks or shows signs of stretching where the testing is terminated.

One piece of equipment used to do the above tests was a 4mW class IIIa Helium-Neon laser made by the Uniphase Corporation. Other pieces of equipment used was a Universal Test Machine by ATS (Applied Test System, Inc.) with a 100 lb. load cell with a 408 Modular Testing Panel and an analog to a digital converter hooked up to a computer.

During the testing procedures, the Modular Testing Panel transfers voltage readings at regular intervals and transfers them into loads to be recorded by the computer. Simultaneously, a displacement reading is taken at the same intervals and recorded by the computer. Once the testing is done, the maximum load is found using Microsoft Excel and corresponded to the diameters found so the modulus and strength of the fibers can be determined.

HIGH TEMPERATURE SUPERCONDUCTING PULSED LASER DEPOSITION

Task Order No. 204
Student Support Program
Southwestern Ohio Council for Higher Education

C. Brandon Lovett
Wright State University

11 September 1996

Government Task Leader
Dr. Rand Biggers
WL/MLPO

ACKNOWLEDGMENTS

I would first like to thank Dr. Pat Hemenger for funding this Task and his genuine interest in my work. I would also like to thank Mr. David Dempsey, Mr. Steve Murray and Mr. David Lubbers for their assistance in the lab. Mr. Tim Peterson, Dr. Iman Maartense, and Dr. Eric Moser provided me with insights to each part of the HTS Team. Finally, I would like to thank Dr. Biggers for his guidance throughout this Task. He has communicated his expectations clearly while allowing me the freedom to design this database. Dr. Biggers has provided me with both opportunities to develop my technical abilities and professional skills.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The purpose of this Task was to maintain, modify, and update the data base consisting of information obtained on thin-film High-Temperature Superconductors (HTSCs). The data base was created under the previous Task. The data base consists of several parameters observed throughout the life of the HTSCs. Most of the HTSCs is the ceramic Yttrium-Barium-Copper-Oxide (YBCO) deposited on Lanthanum Aluminate substrates by the process of Pulsed Laser Deposition (PLD). This data base is the most rational way to track and view the information obtained from the films. The data base was created using *4th Dimension 3.1* software. The data base is a rather extensive compilation of the data gathered on the YBCO films, starting with the make-up of the substrate, through the growth process, and technical measurements of the film.

The reason for this data base is the ability to track what growth parameters produce certain film characteristics, desirable or undesirable. This allows researchers to see the effects of growth parameter combinations on the micro structure and properties of the HTSCs. The database currently contains 120 different parameters subdivided into four major categories. Those 120 parameters alone, times 658 films show the need for this database.

The information stored in the data base serves several purposes. The main purpose is a table for the application of growth parameters. However, another important aspect of the data base is acting as an easily accessible information resource needed for publications. The most recent publication was a poster at the August, 1996 ASC meeting in Pittsburgh.

DESCRIPTION OF RESEARCH

As stated earlier, the objective of this Task was to maintain, modify, and update the data basefor storing and referencing data collected on HTSCs. This data base was originally constructed and modified using *4th Dimension 3.1* software. The software has since been updated to *4th Dimension 3.2*. The data base currently occupies approximately 1.8 megabytes of hard disk space. The data base contains information concerning 658 different films grown at the WL/MLPO facility. Currently, modifications are being made to store information on films produced at other facilities. Each entry contains 120 different fields of information. The data base is divided into sections with each section having smaller categories. The major divisions consist of growth parameters, atomic force microscopy and scanning electron microscopy, AC susceptibility measurements, and critical current transport measurements. Information obtained from Dr. Biggers (growth parameters), Dr. Moser (AFM/SEM), Dr. Maartense (AC susceptibility), and Mr. Peterson (transport), is entered into the database. The data is made available to all who wish to view it by means of file sharing over the Ethernet.

The equipment needed to complete this Task is basic:

1 Apple Macintosh IIci computer controls the main computing requirements.

2 *4th Dimension 3.2*- the software program in which the data base is written.

3 *Delta Graph Pro 4.0*- the application program used to graph and view the data in the database.

Most of the information in the data base was retrieved from technical lab journals. More recent films were grown by automation, thanks to Mr. Murray and Mr. Lubbers. The information for the data base was obtained through a computer interface over the network.

The data is analyzed and used by importing the information into *Delta Graph Pro 4.0*. Delta Graph allows different parameters of the data to be viewed together in graphical form. Once the graphs and tables are viewed, trends can be observed from the presented information. This software is used to graphically show the trends observed with respect to a controlled variable. These graphical plots are used in publications.

RESULTS

This Task has provided an easily accessible data base for use throughout the High Temperature Superconducting Team. The data base has given insights to what growth parameters can be modified to produce a high critical temperature superconductor. This is the first step in the development of HTSCs for industry. Superconductors will revolutionize electronics once they are understood. Superconductors have the ability, once reaching a super conducting state, to allow the flow of electrical current with no resistance or loss of energy. High Temperature Superconductors become superconducting around 90°K, which is easily attainable at liquid nitrogen temperatures. Conventional superconductors work at very low liquid Helium temperatures not easily attained.

The data base work is continually being modified and enlarged. Currently the format is growing to include HTSCs grown at other facilities for WL/MLPO using similar and other growth techniques. Attaining a working knowledge of the growth mechanisms will provide a means of further understanding HTSCs. Once fully understood, HTSCs could be tailor made for specific purposes that may bring another technical revolution.

MORPHOLOGY OF NOVEL MATERIAL SYSTEMS DEVELOPED IN-HOUSE AT MLPJ

Task Order No. 205
Student Support Program
Southwestern Ohio Council for Higher Education

Colin M. McHugh
Wright State University

30 October 1996

Government Task Leader
Dr. Tom Cooper
WL/MLPJ

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Financially, there are many people and organizations that made this research possible. The author would like to thank the Student Support Program (SOCHE), Wright Laboratory/Laser Hardened Materials Branch, and Wright State University Department of Chemistry for allowing me to do the research at Wright-Patterson AFB.

INTRODUCTION

Thermotropic liquid crystals have been extensively examined in recent years as potential materials for optical device applications, including infrared spatial light modulators, light polarizers, optical information storage and communication modules, and frequency conversion films. Except the applications where electric or magnetic field-induced molecular orientation is critical, it is preferable that the desired liquid crystal mesophase is frozen into a glassy state to promote long-term orientational stability. To achieve this goal, glass-forming, low molar-mass liquid crystals (GFLMLCs) have emerged as a prominent new material class. GFLMLCs, with glass transition temperatures, T_gs, above room temperature, have been studied [1, 2] mainly due to their low melt viscosity, which facilitates easier processing into uniform thin films.

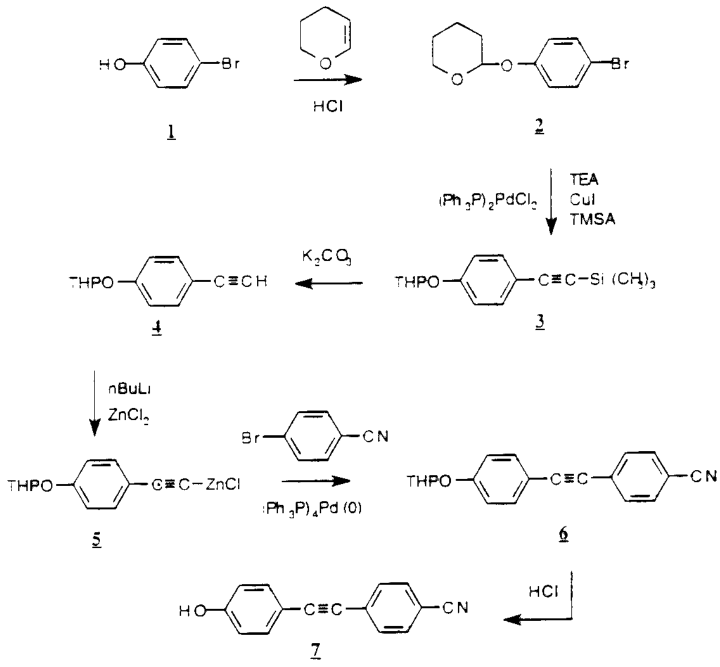
A recent series of articles reports the design and synthesis of GFLMLCs based on cyanotolane as a mesogenic group attached to cyclohexane [1, 3-5]. The cyclohexane ring acts as an excluded volume moiety capable of depressing crystallization while retaining LC mesomorphism. The tolane, which possesses an extended π-conjugation and perfect linear rod-like structure, exhibits extraordinary high birefringence and relatively low viscosity. The benefits of a large optical birefringence value are to lessen the thickness requirement in optical devices. Moreover, unsymmetrical tolane LCs that contain an electron donating group at one end of the molecule and an electron withdrawing group at the other, has been found to possess pronounced second order nonlinear optical properties [6].

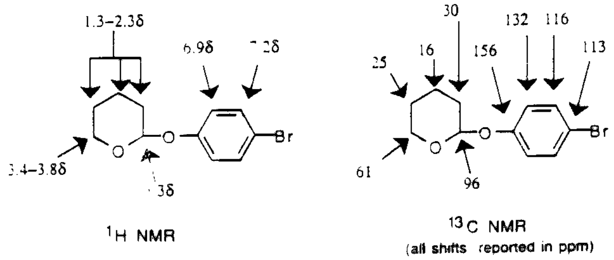
The objectives of the current work were: 1) to use cyclic 1,3,5,7-tetramethylhydrotetrasiloxane as an excluded volume moiety, 2) to attach pendant mesogenic tolane liquid crystals to cyclic 1,3,5,7-tetramethylhydrotetrasiloxane while avoiding unwanted by-products, and 3) to compare our yields, optical properties, and phase behavior with previous literature results.

RESULTS AND DISCUSSION

The results and discussion section are divided into three major parts. The first part discusses the synthesis and characterization of the cyanotolane liquid crystal. The second part examines the allyl tosylate methodology employed for attaching the cyanotolane to cyclic 1,3,5,7-tetramethylhydrotetrasiloxane. The last part discusses the pyranyl ether methodology that is currently being investigated.

Tolane Synthesis: The reaction of p-bromophenol (1) with 3,4-dihydro-2H-pyran was carried out in an acidic medium to protect the hydroxyl group as the pyranyl ether 2. The IR spectrum for compound 2 exhibited typical aromatic C-H stretching absorptions at 3098 cm^{-1}, an aliphatic C-H stretching absorptions at 2972 cm^{-1}, and an ether absorption at 1635 cm^{-1}. The ^{1}H NMR spectrum for compound 2 exhibited aromatic proton absorptions as a doublet of doublets at 6.9-7.5δ and aliphatic CH_2 proton absorptions as a multiplet at 1.3-2.3δ. The ^{13}C NMR spectrum for compound 2 exhibited absorptions for nine unique carbons. The ^{1}H and ^{13}C NMR assignments are shown in Figure 1.





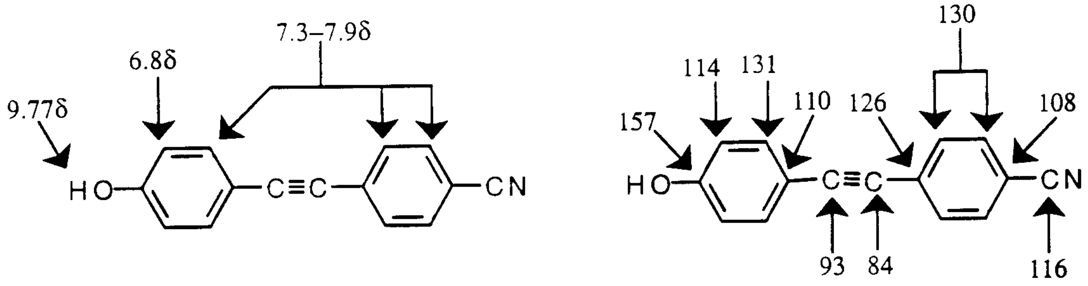
^{1}H NMR

^{13}C NMR
(all shifts reported in ppm)

Figure 1. ^{1}H and ^{13}C NMR Assignments for Compound 2.

Compound 2 then underwent a traditional, three-step synthesis of 1,2-(diaryl)acetylenes by a Pd(0)/Cu(I) catalyzed coupling of aryl halides with a monoprotected acetylene. Specifically, 2 was allowed to react with trimethylsilylacetylene (TMSA) in the presence of triethylamine (TEA), copper (I) iodide, and the catalyst bis(triphenylphosphine) palladium (II) dichloride to form the coupled product 3. After an extensive work-up, the trimethylsilyl group was removed using potassium carbonate to yield compound 4. n-Butyl lithium was added to abstract the alkyne proton and zinc chloride was added to form the alkynylzinc reagent 5. A solution of p-bromobenzonitrile and tetrakis (triphenylphosphine)palladium (0) were then added [7] to form compound 6 that was not isolated but subjected to deprotection forming 4-cyano-4'-hydroxytolane (7).

The IR spectrum for compound 7 exhibited a typical phenolic hydroxyl stretching absorptions at 3327 cm^{-1}, an aromatic C-H stretching absorption at 3070 cm^{-1}, and an acetylene and cyano absorption at 2210-2225 cm^{-1}. The ^{1}H NMR spectrum for compound 7 exhibited aromatic proton absorptions at 6.8-7.9δ and a hydroxyl proton absorptions as a singlet at 9.77δ. The ^{13}C NMR spectrum for compound 7 exhibited absorptions for 11 unique carbons. The ^{1}H and ^{13}C NMR assignments are shown in Figure 2.



^{1}H NMR

^{13}C NMR
(all shifts reported in ppm)

Figure 2. ^{1}H and ^{13}C NMR Assignments for Compound 7.

Allyl Tosylate Methodology:

Because of the well-documented problems associated with hydrosilation reactions of molecules containing both alkene and alkyne functions, a new methodology was envisioned for the attachment of the cyanotolane 7 to cyclic 1,3,5,7-tetramethylhydrotetrasiloxane. A two-step process involving 1) hydrosilation chemistry on an alkenyl tosylate followed by 2) a phase transfer catalyzed nucleophilic displacement of the tosylate group by the sodium or potassium salt of the cyanotolane 7. Specifically, allyl alcohol (8) was protected as the tosyl ester 9 by treatment with p-toluenesulfonyl chloride (TSCl) and sodium hydroxide. Allyl tosylate (9) was used immediately as it appeared to decompose even on standing in the cold.

The IR spectra for compound 9 exhibited typical aromatic C-H stretching absorptions at 3090 cm^{-1}, an aliphatic C-H stretching absorption at 2952 cm^{-1}, and an S-O absorption at 1599

cm^{-1}. The ^1H NMR spectrum for compound 9 exhibited aromatic proton absorptions as a multiplet at 7.3-7.9δ, an aliphatic $H_2C=\underline{C}H$ proton absorption as a multiplet at 5.8δ, an aliphatic $H_2\underline{C}=CH$ proton absorption as a doublet of doublets at 5.3δ, an aliphatic $\underline{C}H_2$-O as a doublet at 4.5δ and a $\underline{C}H_3$ proton absorption as a singlet at 2.4δ. The ^{13}C NMR spectrum for compound 9 exhibited absorptions for eight unique carbons. The ^1H and ^{13}C NMR assignments are shown in Figure 3.

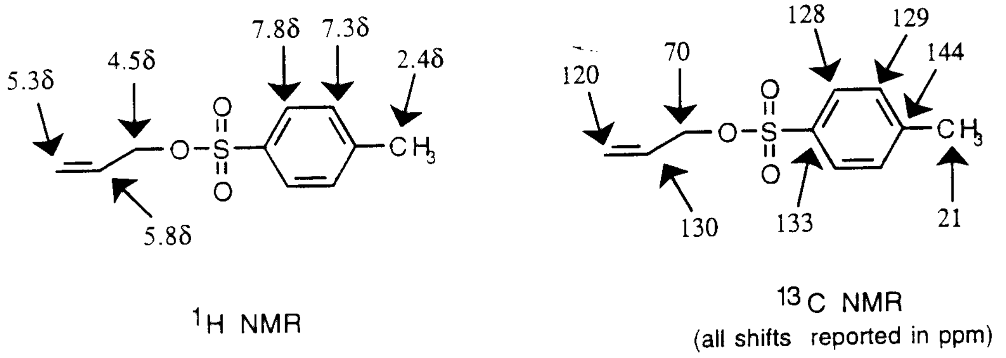
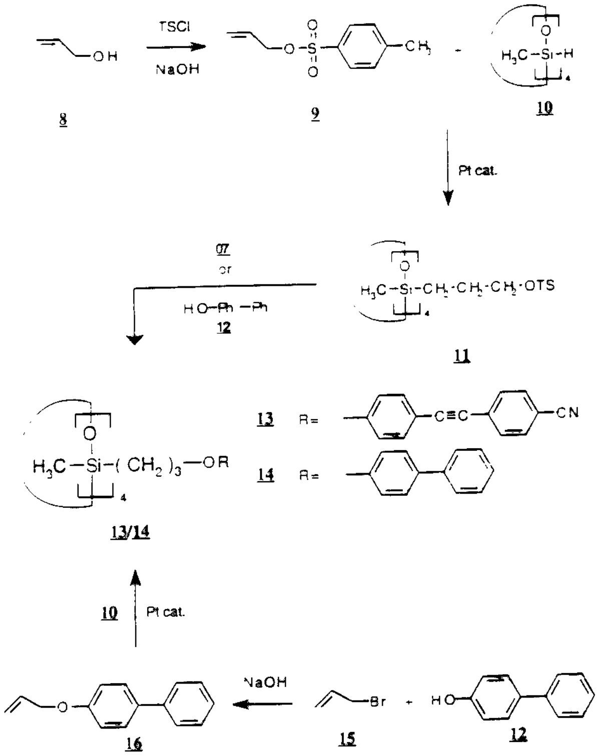


Figure 3. ^1H and ^{13}C NMR Assignments for Compound 9.

Compound 9 was then subjected to hydrosilation chemistry with 10 in the presence of dicyclopentadienylplatinum (II) chloride to yield 11. When FT-IR spectroscopy showed the disappearance of the Si-H bond at 2150 cm^{-1} the reaction solution was precipitated into methanol/water and collected. Unfortunately, once compound 11 precipitated out of solution it could not be redissolved. To get spectroscopic data (^1H and ^{13}C NMR) to confirm the structure and purity of 11, the reaction was conducted in deuterated chloroform.



An aliquot was removed upon reaction completion and NMR analysis was performed. The ^{1}H NMR spectrum showed the presence of unreacted allyl tosylate (9) which was due to an initial 10% molar excess of starting alkene to reactive Si-H. The ^{13}C NMR spectrum was inconclusive as 21 absorption peaks were found (nine were expected.) Another reaction, also run in deuterated chloroform, was performed using an exact 1:1 molar ratio of starting alkene to reactive Si-H. The ^{1}H NMR spectrum for compound 11 showed the complete disappearance of the terminal vinyl bond of allyl tosylate along with the presence of five other absorptions. The aromatic proton absorptions appeared as a set of doublets at 7.3-7.9δ, an aromatic CH_3 absorption from the tosyl function appeared as a singlet at 2.4δ, and two other broad absorption peaks appeared at 0.0-0.8δ. Integration of the five peaks resulted in the assignment of four hydrogens for the aromatic ring, three hydrogens for the methyl of the tosyl function, and a ratio of two hydrogens to one hydrogen for the last two peaks. In looking at the structure of compound 11, one would expect to see seven unique proton peaks. Only five peaks were encountered here, suggesting that the aliphatic methylenes between the siloxane ring and the tosyl function have the same chemical shift equivalence from tetramethylsilane (TMS), the internal standard.

The ^{13}C NMR spectrum for compound 11 exhibited absorptions for 14 unique carbon peaks. In looking at the structure of compound 11, one would expect to see only nine unique carbon peaks. This difference (14 vs. 9) can be attributed to the presence of starting alkene 9, as evidenced by the small peak at 70.6ppm corresponding to the unattached aliphatic CH_2-O. The lack of three distinctive, up-field, absorption peaks for the attached aliphatic methylenes suggests that compound 11 was not formed. The second step in the two-step process, phase transfer catalyzed nucleophilic displacement of the tosylate group by the sodium or potassium salt of 7 or 12, in the presence of tetrabutylammonium bromide (TBABr), will remain untested until a clearer understanding of the hydrosilylation reaction can be obtained.

Concurrently, an independent synthesis of compound 14 utilizing traditional hydrosilation chemistry and the commercially available starting material 4-phenylphenol (12) was explored.

Allyl bromide (15) underwent S displacement by the salt of 4-phenylphenol (12) to yield 1-(3-propenyloxy)biphenyl (16) which was subjected to a hydrosilation reaction, under the usual conditions, with 10 to form compound 14.

The IR spectrum for compound 14 exhibited typical aromatic C-H stretching absorptions at 3033 cm^{-1}, an aliphatic C-H stretching absorptions at 2936 cm^{-1}, and a Si-O absorption at 1077 cm^{-1}. The ^{1}H NMR spectrum for compound 14 exhibited aromatic proton absorptions as a group of multiplets at 6.8-7.5δ, an aliphatic CH_2-O proton absorption as a multiplet at 4.0δ, an aliphatic CH_2-CH_2-CH_2-O proton absorption at 1.9δ, an aliphatic CH_2-CH_2-CH_2-O proton absorption at 0.75δ, and a Si-CH_3 absorption at 0.17δ. The ^{13}C NMR spectrum for compound 14 exhibited absorptions for 12 unique carbons. The ^{1}H and ^{13}C NMR assignments are shown in Figure 4. Differential scanning calorimetry, polarized optical microscopy, and X-ray diffraction confirmed that 14 lacked liquid crystallinity.

Once the target molecule **14** had been synthesized and fully characterized via an independent pathway, the pyranyl ether methodology was undertaken.

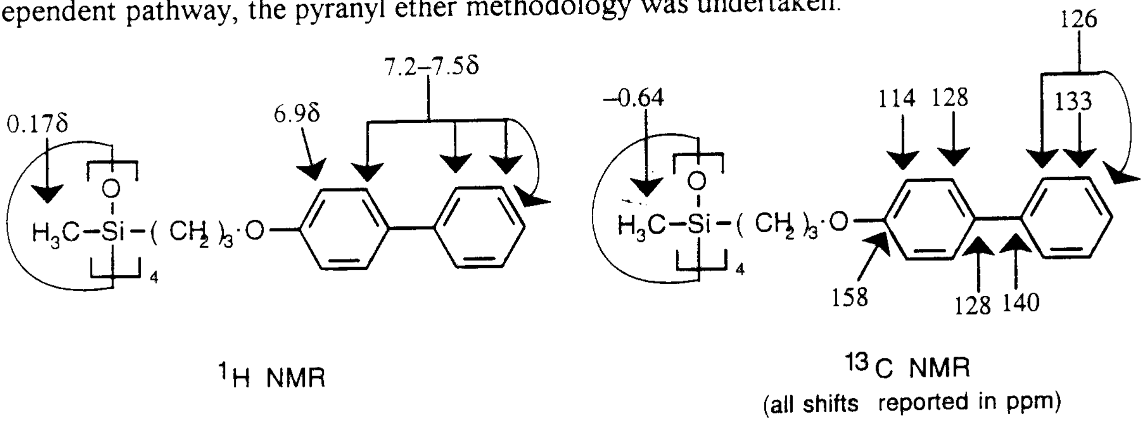
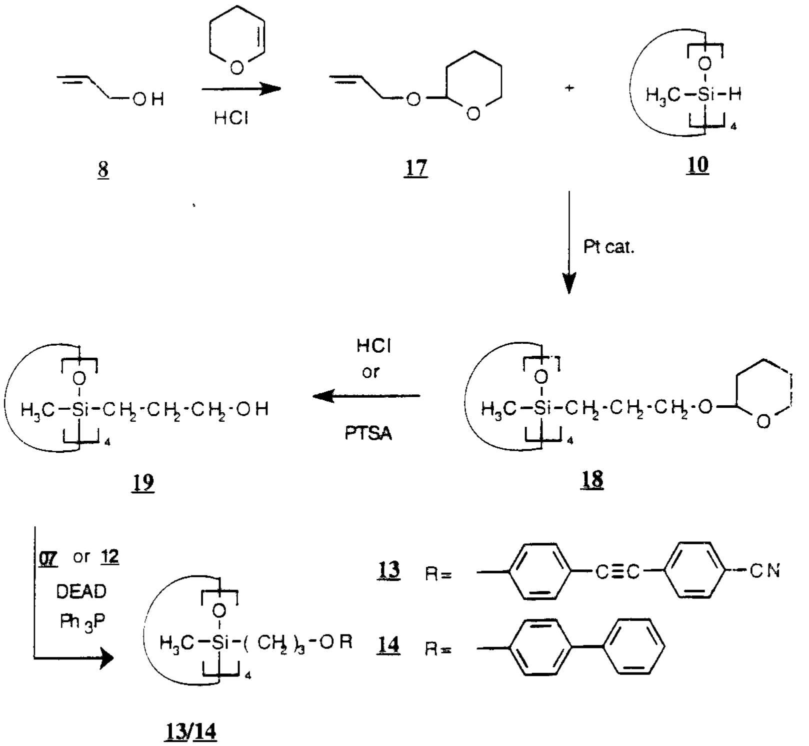


Figure 4. ^{1}H and ^{13}C NMR Assignments for Compound **14**.

Pyranyl Ether Methodology:

The pyranyl ether methodology is a three-step process involving 1) hydrosilation chemistry on an alkenyl pyranyl ether followed by 2) deprotection of the pyranyl group to yield a reactive hydroxyl group and 3) a Mitsonubu reaction coupling of a phenol to a deprotected hydroxyl function. Specifically, the reaction of allyl alcohol (**8**) with 3,4-dihydro-2H-pyran was carried out in an acidic medium to protect the hydroxyl group as the pyranyl ether **17**. The IR spectrum for compound **17** exhibited typical aliphatic C-H stretching absorptions at 2942 cm^{-1}, an alkene C-C stretching absorptions at 1648 cm^{-1}, and an ether absorption at 1030 cm^{-1}.



The ^{1}H NMR spectrum for compound 17 exhibited an aliphatic $H_2C{=}\underline{C}H$ proton absorption as a multiplet at 5.9δ, an aliphatic $H_2\underline{C}{=}CH$ proton absorption as a doublet of doublets at 5.1-5.3δ, an aliphatic O-$\underline{C}$H-O proton absorption as a singlet at 4.6δ, an aliphatic $\underline{C}H_2$-O proton absorption as a doublet at 3.5-4.2δ, and an aliphatic $\underline{C}H_2$ proton absorption at 1.0-1.9δ. The ^{13}C NMR spectrum for compound 17 exhibited absorptions for eight unique carbons. The ^{1}H and ^{13}C NMR assignments are shown in Figure 5.

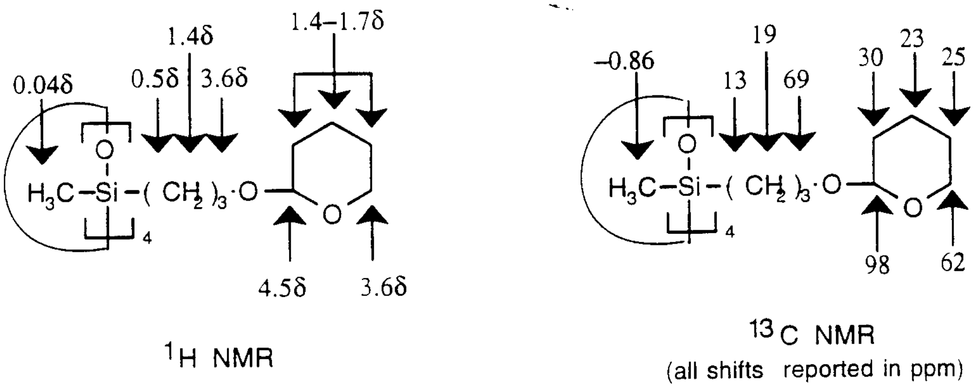


Figure 5. ^{1}H and ^{13}C NMR Assignments for Compound 17.

Compound 17 was then subjected to hydrosilation chemistry with 10 in the presence of dicyclopentadienylplatinum (II) chloride to yield 18. When FT-IR spectroscopy showed the disappearance of the Si-H bond at 2150 cm^{-1} the reaction solution was cooled and an aliquot removed for ^{1}H and ^{13}C NMR analysis.

The ^{1}H NMR spectrum for compound 18 exhibited an aliphatic O-$\underline{C}$H-O proton absorption as a singlet at 4.5δ, an aliphatic $\underline{C}H_2$-O proton absorption as a group of multiplets at 3.3-3.6δ, an aliphatic $\underline{C}H_2$ proton absorption as a broad multiplet at 1.4-1.7δ, an aliphatic Si-$\underline{C}H_2$ proton absorption as a singlet at 0.5δ, and an aliphatic Si-$\underline{C}H_3$ proton absorption as a singlet at 0.04δ. The ^{13}C NMR spectrum for compound 18 exhibited absorptions for nine unique carbons. The ^{1}H and ^{13}C NMR assignments are shown in Figure 6.

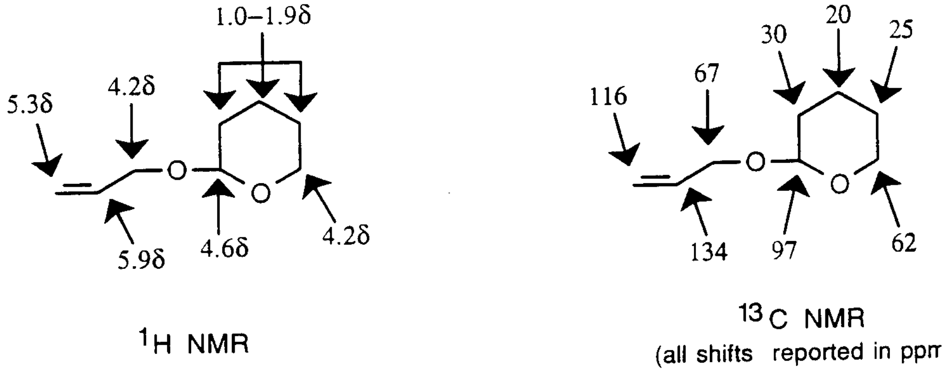
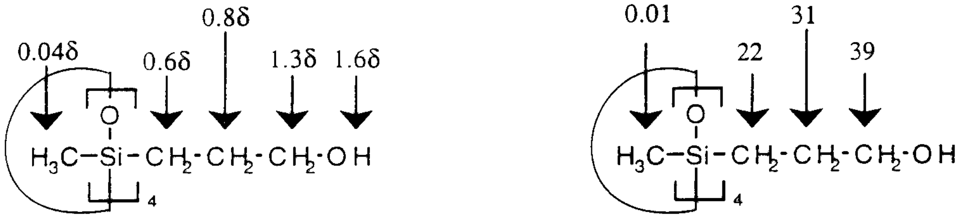


Figure 6. ^{1}H and ^{13}C NMR Assignments for Compound 18.

Compound **18** was then hydrolyzed in the presence of an ethanolic solution of either hydrochloric acid or pyridinum-p-toluenesulfonate to yield the deprotected hydroxy compound **19**. Work-up consisted of dissolving compound **19** in petroleum ether, washing the petroleum ether layer with water (100 mL), half-saturated brine (100 mL), and drying the petroleum ether layer over sodium sulfate. Petroleum ether was removed using a rotary evaporator and the residue was slowly stirred at 60°C and 0.3 kPa for 30 min. to yield compound **19**. The IR spectrum for compound **19** exhibited a typical hydroxyl stretching absorptions at 3486 cm^{-1}, an aliphatic C-H stretching absorptions at 2939 cm^{-1}, and a Si-O stretching absorption at 1078 cm^{-1}. The ^{1}H NMR spectrum for compound **19** exhibited an aliphatic CH_2-$\underline{C}H_2$-OH proton absorption as a singlet at 1.3δ, an aliphatic $\underline{C}H_2$-CH_2-OH, a hydroxy proton absorption as a broad singlet at 1.6δ, a Si-$\underline{C}H_2$ proton absorption as a singlet at 0.6δ, and a Si-$\underline{C}H_3$ proton absorption at 0.04δ. The ^{13}C NMR spectrum for compound **19** exhibited absorptions for four unique carbons. The ^{1}H and ^{13}C NMR assignments are shown in Figure 7. The mass spectral fragmentation pattern is consistent with the structure of compound **19**.

The last step in the three-step process, a Mitsonubu reaction utilizing diethyl azodicarboxylate (DEAD) and triphenylphosphine to couple a phenol to a deprotected hydroxy will remain untested until a sufficient amount of $3,3',3'',3'''$-(1,3,5,7-tetramethylcyclotetrasiloxan-1,3,5,7-tetrayl)tetrapropanol (**19**) can be obtained.



^{1}H NMR

^{13}C NMR
(all shifts reported in ppm

Figure 7. ^{1}H and ^{13}C NMR Assignments for Compound 19.

CONCLUSIONS

The tolane, 4-cyano-4'-hydroxytolane (7), was prepared utilizing a traditional, three-step synthesis of 1,2-(diaryl)acetylenes by a Pd(0)/Cu(I) catalyzed coupling of aryl halides with a monoprotected acetylene. Because of the well-documented problems associated with hydrosilation reactions of molecules containing both alkene and alkyne functions, two new methodologies were investigated for the attachment of the cyanotolane 7 to cyclic 1,3,5,7-tetramethylhydrotetrasiloxane. The first methodology involved 1) hydrosilation chemistry on an alkenyl tosylate followed by 2) a phase transfer catalyzed nucleophilic displacement of the tosylate group by the sodium or potassium salt of the cyanotolane 7. The second step will remain untested until a clearer understanding of the hydrosilylation reaction in step one can be obtained.

The second methodology involved 1) hydrosilation chemistry on an alkenyl pyranyl ether followed by 2) deprotection of the pyranyl group to yield a reactive hydroxyl group and 3) a Mitsonubu reaction coupling of a phenol to a deprotected hydroxyl function. The last step, the Mitsonubu reaction, will also remain untested until a sufficient amount of 3,3',3'',3'''-(1,3,5,7-tetramethylcyclotetrasiloxan-1,3,5,7-tetrayl)tetrapropanol (**19**) can be obtained.

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MORPHOLOGY OF NOVEL MATERIAL SYSTEMS DEVELOPED IN-HOUSE AT MLPJ

Task Order No. 205a
Student Support Program
Southwestern Ohio Council for Higher Education

Sanjiv Lakhia
University of Dayton

30 October 1996

Government Task Leader
Dr. Thomas Cooper
WL/MLPJ

ACKNOWLEDGMENTS

Thanks to Captain Mike DeRosa for demonstrating the proper technique needed to be successful in a laboratory environment and for making this Task an excellent introduction to materials science.

TASK ASSIGNMENT

The objective of the Task was to provide support in the preparation and development of laser hardened materials. The main project involved preparation of a gradient limiter polymer. Our goal was to develop a limiter that would have a higher level threshold capacity than the industry standard material polymethyl methacrylate. An epoxy material was chosen as the material to be used. Previous research by Captain Mike DeRosa showed that this epoxy material would be able to withstand higher levels of energy than the normal material.

After discovering which material to use, the next step was processing the material into a practical, presentable shape that could then be further characterized and shown to those interested. The first step in this process was developing a mold into which the material could be placed and cured. A rubber material was chosen as the mold. Next, the correct mixture of the epoxy materials had to be found to eliminate the tackiness of the material. Trial and error were used until the correct ratio of epoxy to epoxy hardener was found. The third problem to overcome was that the material was developing a hazy film upon curing. Acetone was found to be the culprit and proper steps were taken to reduce the haziness.

Once the samples were produced, light spectra was taken using a UV/VIS spectrophotometer. This data was placed into a spreadsheet to figure out the absorption and transmittance at 532 NM, the wavelength of characterization.

This Task has shown the tedious nature of research and specifically, material processing. Many minute problems arose each week that slowed the development of a transparent, high threshold material that in the future could help pilots fight blinding effects of lasers.

CONSOLIDATION OF MINC(MICROMECHANICAL IN-PLANE CRACKING) COMPUTER CODE

Task Order No. 206
Student Support Program
Southwestern Ohio Council for Higher Education

Greg Nichols
Wright State University

30 October 1996

Government Task Leader
Dr. N. J. Pagano
WL/MLBM

ACKNOWLEDGMENTS

I would like to thank Dr. Tandon, Dr. Pagano, and Greg Schoeppner for their support and guidance during the project development. Also, thanks goes to Joe Scheckel, Max Alexander, and Dave Small for their help with programming tips and hints.

DESCRIPTION OF TASK ASSIGNMENT

The Task was the consolidation of Micromechanical In-Plane Cracking (MINC) Computer Code. More specifically, the development of a preprocessor for the two dimensional in-plane damage model. The preprocessor automates the task of determining the input data from the geometry and load description of the problem of interest. The preprocessor allows an easy interface for the MINC code. The preprocessor gives the user the ability of specifying the physical geometry of the problem, and then converting this to input data for the MINC code. The user is then free of the internal workings of the MINC code itself. This preprocessor adds greatly to the versatility of the MINC code.

DESCRIPTION OF RESEARCH

The geometry of the problems is that of a cylinder, with cracking in all three coordinate systems, radial, angular, and z coordinate plane. This preprocessor deals with only cracking in the r and theta directions. This is equivalent to taking a radial, two-dimensional slice from the complete model for the composite fiber. In other words, r and theta coordinates are variable and z is constant. Due to the amount of work necessary to change the physical description of the problem to input data for the MINC code, the preprocessor code is broken into several relevant subroutines. These seven subroutines are INPUT, SECTIONS, LAYERS, TRCON, ANGCON, RIGID, and OUTPUT. These are described below.

INPUT

The INPUT subroutine is the only direct link for the user to enter the description of the problem. Two subroutines make up the INPUT routine. The INPUT1 routine prompts the user to enter data from the keyboard. An input2 subroutine takes input from a file specified by the user. Both subroutines ask the user for the same information. These subroutines are used to enter the physical constants of the problem, the position of radial and angular cracks, and the boundary conditions on the cracks. This data is used by all other subroutines.

SECTIONS and LAYERS

The SECTIONS subroutine breaks up the geometry of the problem into radial sections, with these sections being radial divisions originating from the center of the model. These radial sections are based on the position of radial and angular cracks. The radial positions of the center of radial cracks and the tips of angular cracks define the sections. The LAYERS subroutine imposes layer structure upon the problem. Layers are arranged as concentric circles within the radius of the problem. Layer positions are determined by the centers of angular cracks, the endpoints of radial cracks, and the position of material regions. Both subroutines then perform a sorting routine on these new sections and layers, with their locations being held in an array. The arrays and size of arrays are then used by the other subroutines.

TRCON and ANGCON

Both TRCON and ANGCON use the boundary conditions imposed on the problem to find the end conditions for the section and layers. TRCON deals with all boundary conditions in the radial sense, those being sig-r, tau-r theta, and tau-z theta values. These values are the imposed boundary conditions on radial cracking. TRCON looks at each section defined by a radial crack, and at every layer interface assigns an end condition value based on whether traction, displacement, or continuity is present. Also at this time, numerical values are assigned based on whether traction or displacement is taking place between sections. The ANGCON subroutine does the same, only this time looking at the boundary conditions on angular cracks and on the surface of the composite fiber. ANGCON deals with all boundary conditions in the angular sense that is sig-theta, tau-r theta, and tau-theta Z. ANGCON looks at every layer, and at each section interface, assigns a value based on whether continuity, traction, or displacement exists at the interface. It is both TRCON and ANGCON that comprise the bulk of computations for the preprocessor. These two subroutines are where the actual real world problem is defined in terms of input data for the MINC code.

RIGID

This subroutine will place rigid body constraints on the problem at a particular location on the body. This constraint will keep the body stable at that point, free from motion caused by the introduction of forces into the system (Traction on the surface and on cracking in the problem.).

OUTPUT

The OUTPUT subroutine takes all arrays and variables generated by the preprocessor and prepares them for the MINC code. This routine sends these values to an output file. This output file is used as input for the MINC code.

The preprocessor is coded in FORTRAN 77 programming language. This was used because all work done previously for the MINC code and the MINC code itself was done in FORTRAN 77. Also, the decision was guided by the number of personnel who work on this code who is familiar with FORTRAN 77.

Data used by the preprocessor will be taken from models simulating cracking in composite fibers. These models for this preprocessor will only deal with the r and theta coordinates, with the z direction being held fixed.

RESULTS

The development of the preprocessor is now complete. The subroutines are all complete and have been tested. All have performed well within defined parameters and do provide the correct output for all cases.

MECHANICAL PROPERTIES METAL MATRIX COMPOSITES

Task Order No. 207
Student Support Program
Southwestern Ohio Council for Higher Education

Michael S. Bartsch
University of Dayton

17 September 1996

Government Task Leader
Dr. Theodore Nicholas
WL/MLLN

ACKNOWLEDGMENTS

As I conclude my term as a member of the Materials Directorate team, I would like to take this opportunity to thank all those who have made my time here as fulfilling and educational as it has been. In particular, I would like to thank Dr. Ted Nicholas, Steve Russ, and Captain Brian Sanders for their excellent leadership and guidance. I would also like to thank Joe Kroupa and the other members of the University of Dayton Research Institute. Perhaps more than anything else, the people of the Materials Directorate have made my experience here so thoroughly enjoyable. All have been extremely generous in sharing their time and experience, and it is this sense of community and camaraderie that I will remember most.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The objective of this Task was to contribute to the ongoing efforts underway to characterize different titanium metal matrix composite (MMC) material systems. This class of materials has been selected by the Air Force for its potential applications in aerospace structural components and high performance jet engines. MMC's are ideal for such applications due to their strength and fatigue resistance at operating temperatures combined with their relatively low density. To apply MMC's safely and effectively, establishing the manner, in which they behave when subjected to various conditions of thermal and mechanical loading is essential. Once experimental data on the characteristics of a material have been accumulated, they are used to generate computer models of the material systems that then predicts the approximate behavior of the material for various testing or operating conditions.

DESCRIPTION OF RESEARCH

During the Task, MMC research focused on composites consisting of a titanium-aluminide matrix such as Ti-6Al-4V, Ti-15-3, or Ti-22-23 surrounding SCS-6 silicon carbide reinforcing fibers. Testing focused largely on composites with unidirectional longitudinal [0] fiber orientation, but tests were also conducted on specimens with transverse [90] and triaxial [0/+45/90/-45/0] fiber orientations. In addition, some fiberless or "neat" specimens were tested for refining the present understanding of the behavior of the matrix material. The results of numerous tensile, creep, fatigue, and stress relaxation tests conducted on the composite and neat specimens were used to create a data base of information on the behavior of each material system tested.

Specimens were primarily tested on horizontal servo-hydraulic MTC testing machines. The machines were linked to PCS that provided computer control and recorded data from the tests. Due to the flexibility of the computer control and data retrieval scheme, the same machines could be programmed for tensile (static) testing, elevated temperature creep tests, and both thermal and mechanical fatigue tests. Thermocouples attached to the surfaces of the test specimens provided feedback control for heating lamps that made it possible to conduct tests anywhere from room temperature to temperatures in excess of 800°C. Extensometers mounted on the edge of the test specimen were used during testing to collect strain data in real time.

One primary objective of gathering material property data was to use the empirical data to develop mathematical models capable of predicting the behavior of the various material systems. Ideally, the goal of computer modeling is to allow the engineer to accurately predict the behavior of the material system for virtually any thermo-mechanical loading scenario without the necessity of conducting costly experiments for each set of conditions. Similarly, accurate computer modeling for materials to be used in aerospace applications could enable the engineer to forecast a part's performance under adverse operating conditions. In this way, it may be possible to predict a failure without putting the part into operation in a testing situation where a failure could cause catastrophic damage and/or loss of life. Admittedly, these are idealized scenarios. In practice, the modeling of a complex material system such as a titanium MMC is no simple proposition.

The first step in the development of an accurate computer model is the establishment of a comprehensive material data base reflecting the material's characteristics for a wide array of temperatures and mechanical loading scenarios. A comprehensive model must reflect the performance of the material under all conceivable operating conditions. Not only the material's tensile behavior, but also its response to conditions of creep and cyclic fatigue must be described within the model. To accomplish this, experimental data for such varied situations must be obtained. Any model is only as good or complete as the empirical data on which it is based.

Computer modeling of composite systems can be conducted on both the macroscopic and microscopic level, and how much detail required determines, largely, the modeling method best suited to the task. For titanium MMC systems, micro-mechanical modeling has been the method of choice for capturing the complex behavior and characteristics of these materials. FIDEP, a proprietary finite difference micro-mechanics program, uses the Bodner-Partom model for MMC behavior. The model has a high degree of flexibility, allowing the simulation of virtually any loading scenario for any composite material for which a set of descriptive material constants has been obtained. These constants reflect the properties and response characteristics of the material at various temperatures, and serve as the inputs to the Bodner-Partom equations within FIDEP.

Material constants for a given material are obtained by a time-consuming iterative process based on the accumulated experimental data for the material. One primary objective to the Task was the formulation of a new set of material constants for Ti-6Al-4V. Experimental data from tests conducted on neat Ti-6-4 specimens was used to determine the accuracy of new constants. The Bodner-Partom equations were evaluated for a variety of loading conditions, mimicking those of the available experiments. The constants were adjusted by trial and error until the model's output duplicated the experimental data within a reasonable degree of error.

With a preliminary set of constants matching individual cases established, all the constants and their trends were evaluated together to arrive at a unified set of constitutive material properties. This phase of the process required some degree of compromise in the final values chosen for each parameter. While one set of constants for a given case might fit that particular experimental data best, its validity and utility were questionable if it failed to conform to the prevailing trends among the constants for the various temperatures. The constants were adjusted relative to each other to produce a set of parameters demonstrating logical trends and smooth transitions with varying temperature. These alterations were made in a way that produces the best overall modeling of material response, though at the expense of some accuracy in specific individual loading cases.

With a consistent and logically varying set of constants established for the Ti-6-4, the model and new constants were tested by attempting to reproduce the results of SCS-6/Ti-6-4 composite tests. Some additional refinement to the constants was made at this stage, primarily to reduce numerical difficulties encountered when the new constants were input to the FIDEP routines.

RESULTS

Progress was made in the characterization and modeling of titanium Metal Matrix Composites. Particularly valuable to this process was the development of an integrated and comprehensive set of material constants for the Ti-6Al-4V alloy that serves as the supporting matrix for one of the more promising titanium MMC systems undergoing evaluation. Though not perfect, the model captures the behavior of Ti-6-4 with sufficient accuracy to be highly useful to the ongoing testing effort. The computer model can be used to help judge which test scenarios are most worth conducting and which will be less cost effective in terms of the amount of new information they provide. Additionally, the model may be used to provide a rough analytical prediction of the response of Ti-6-4 composite components subjected to harsh operating conditions and environments. Such simulations can better help engineers to understand the design potentials and limitations of Ti-6-4 MMC, simplifying the design process and ultimately resulting in a better, more reliable product.

MECHANICAL PROPERTIES OF METAL MATRIX COMPOSITES

Task Order No. 207a
Student Support Program
Southwestern Ohio Council for Higher Education

Frank C. Boller
University of Dayton

17 September 1996

Government Task Leader
Dr. Theodore Nicholas
WL/MLLN

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I would like to express my gratitude to Joe Kroupa for his patience, guidance, and help as I completed this Task. To Dr. Theodore Nicholas, the Government Task Leader, and Joe Kroupa, I thank you for taking the time to explain the principals being used in this Task as I completed my work. Next, I want to thank all the members of the University of Dayton Research Institute team and the professionals at Wright Labs for giving me their time, patience, and expertise. Lastly, I want to thank the Student Support Program at the Southwestern Ohio Council for Higher Education for giving me the opportunity to gain this experience that has been immeasurable to me.

TASK ASSIGNMENT

The objective of this Task was to evaluate fatigue and thermomechanical fatigue characteristics of several advanced titanium matrix composites. The work completed under this Task was the development and evaluation of a FORTRAN computer code that accurately depicted a titanium matrix composites response to a given loading. The computer code developed under this Task was based on an existing computer code. This existing computer code was adapted into the new code by adding new material models of the titanium matrix composite. These new material models, which are essentially just a series of equations, were based on previous research done by University of Dayton Research Institute researchers. Another change to the existing code made was that a time cutting scheme was implemented to speed up the operating time of the program. Once the new material models and the time cutting scheme were inserted into the existing code the new code was checked for its accuracy relative to the previous version of the program.

METHOD OF RESEARCH

The process by which the new FORTRAN code was developed was an iterative process. The first step in the development of the new code was the addition of the new material models. After the addition of the new models, the new program was tested against the old program for both accuracy and efficiency time wise. Although the new program at this stage was found accurate enough compared with the old code, the time required to complete the calculations was far too large to make the program practical for use. The next step taken then was to decide the portion of the program in which the most time was being spent and then formulate a way to increase the efficiency of that portion. The solution devised was a time cutting scheme in which a section of code was not executed every time. This section of code was executed based on a ratio of the change in the answers from the program. At this point, the process of verifying that the program was still producing viable solutions was begun again. The testing consisted of comparing the solutions and time efficiencies of the various material types that the code was designed to emulate with the solutions and run times from the old code. This process was repeated several times to find a reasonable compromise between speed and accuracy. The solutions were considered the same when a 1% deviation or less was reached between the old program and the new program. Work was begun at the end of this Task to compare the results of the new code with a totally different FORTRAN code designed to serve the same purpose; however, this comparison was never completed as time did not permit for the completion of this comparison.

RESULTS

The newly developed code allows for a prediction of a material's response under a cyclic loading, which in turn allow engineers to be able to decide what processes through which to take a material to obtain a certain result without having to physically test a specimen. The other advantage to using this newly developed code is in running a simulation of a specimen being placed under a loading of many hours takes only a matter of minutes rather than the many hours it would take to do the actual test. Although this process will never be able to fully replace the need for physical testing of new materials, it may lead to a faster innovation of better materials.

ANALYTICAL MODELING FOR ENGINE DAMPING STUDIES

Task Order No. 208
Student Support Program
Southwestern Ohio Council for Higher Education

Jason J. Blair
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1 October 1996

Government Task Leader
Dr. Joseph Hollkamp
WL/FIBG

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I would like to take this time to thank Dr. Joe Hollkamp and Mr. Bob Gordon personally. They provided a wonderfully challenging and diverse environment that fostered an intense desire for learning. Their combined guidance and helpfulness have made the last year a true joy for me. I feel as though I have learned a considerable amount about what I am destined to do in my future. After spending this year with two people who define engineering in the truest sense of the word, I am sure, beyond all doubt, that I have chosen my profession wisely. I appreciate all of your help and support over the last year and I will never forget either of you and what you have shown me.

TASK ASSIGNMENT

Introduction

A series of projects to gain experience and understanding in the design and performance of viscoelastic material (VEM) damping concepts for increasing the high cycle fatigue (HCL) life of jet engine fan blades was conducted. These projects included; finite element model analysis, experimental model construction, modal testing, damping treatment testing, viscoelastic material characterization and DC servo motor testing and design. The result of this work was a greatly increased ability to model and accurately predict the response of damped structures. In particular, a process of modeling damping in jet engine fan blades was determined.

Objective

The main objective in this project was to evaluate the effect of damping concepts applied to hollow jet engine blades. The goal was to be able to accurately predict damping increases and to achieve an increase in critical damping in the frequency range of 2000-3500 Hz for first stage fan blades.

Approach

The approach used was to conduct a number of analyses and experiments on full scale and one half scale dynamic models of the fan blade. The exact method used in the approach was to construct experimental models, perform modal testing, add damping treatments, retest the model, and tune/retune the model as necessary. The method used was perfected by first considering only the half scale blade. Damping modeling, predicting, and testing methods were determined from these first tests. The damping treatment used was, at first, a well-characterized VEM. This meant that the material properties were well known and accepted. Once a solid working knowledge of the model was gained, the damping material was changed to the proposed VEM of the full scale model. While doing these tasks, several side issues arose. These were viscoelastic material processing and characterization.

The construction of experimental models consisted of building cantilevered aluminum plates of both half and full scale size. Besides construction, the models had to be equipped with sensors and means to excite the structures had to be determined. For sensing the displacements, piezoelectrics were used with video holography techniques. Magnetic drivers, electromechanical shakers and impact hammers were used as excitors. Several configurations of cantilevered plates were built and tested including: sandwich plates, free layer treatments, and plates with internal pockets. In each case care was taken to accurately reproduce the testing conditions from test to test.

Modal testing of the models was accomplished using an HP data acquisition system equipped with a Microsoft Windows front-end. The HP system, in conjunction with a WaveTek signal generator, and a Piezo Systems amplifier was used to gather data from the models. The testing procedure consisted of exciting the plate with either a magnetic driver, piezoelectric, electromechanical shaker, or an impulse hammer. The response of the plate was then sensed using a piezoelectric. The natural frequencies were found by plotting the plate's transfer function and picking the peaks off the plot. The damping was determined by using the half power bandwidth method. The half scale plates were tested after clamping them into a machinist's vise fixed to a vibration isolation table. The full scale models were tested in a similar way by clamping them into a specially designed fixture mounted to a vibration isolation table. Several excitation and sensing methods were attempted to arrive at the final method. It was found that the magnetic driver and piezoelectric sensor arrangement worked the best.

The damping treatments used in the testing consisted of two different types of material. ISD 113 and EAR Isodamp C1002 VEM were both used. The ISD 113 was used in the half scale model testing to establish whether damped plates could be accurately modeled by using the finite element method. ISD 113 is a well-characterized material. This means that its properties are well known and have had extensive testing done to validate them. The finite element was used to try to predict the natural frequencies of the plate and increases in damping. Finite elements were also used to try to back out the properties of the VEM, treating them as unknowns. This became important when the full scale testing began with the second VEM, EAR Isodamp C1002.

To attach the EAR Isodamp C1002 to the model plates, several methods were considered. The final solution was to either heat the material to a temperature of 350° F or to use a structural adhesive that heat cures. In either case, the VEM had to be heated to a temperature that was extremely close to its melting point. To determine the change in material properties of the VEM brought on by the heating, more modal testing had to be done and the VEM properties determined from the modal test and finite elements.

An extensive material's characterization was done on EAR Isodamp C1002. This testing included tests for melting point, adhesion properties, change in elastic moduli and shear moduli. The procedure for these tests involved baking the VEM in a large oven at a constant temperature for an established time. After baking, the VEM was bonded to a test specimen and modal testing was done. After testing, analytical methods and finite element analyses showed that the heating/cure cycle did not adversely affect the VEM but, the manufacturer's data was in fact, grossly in error. The reported properties were largely better than those that were found experimentally. The work of D. K. Rao, D. Ross, E. Ungar, and E. M. Kerwin, Jr., and, ASTM standard E 756-93 was consulted and several MATLAB programs were written to aid in the determination of material properties.

In addition to the model testing, a DC servo motor system was required for testing purposes. This was used to try to decide properties of a model while in rotation. All tests up to this point, while dynamic, were not truly representative of a real world situation. The blades tested, were not rotating. A method for testing a rotating blade was suggested and two DC servo motors and amplifiers were purchased. A calibration procedure was devised and a manual written. The goal of this project was to try to control one motor with the speed signal from the other. This procedure was also included in the calibration manual.

RESULTS

A method for accurately predicting added damping in a dynamically scaled jet engine fan bladed was determined. Finite element modeling of damped sandwich structures was investigated. Material characterization of VEM was done, thus casting doubt on the manufacturer's data. The tentative feasibility of adding damping through the addition of a VEM to fan blades was shown.

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DAMAGE TOLERANCE METHODS FOR AEROSPACE ALLOYS AND METAL MATRIX COMPOSITES

Task Order No. 209
Student Support Program
Southwestern Ohio Council for Higher Education

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Wright State University

15 October 1996

Government Task Leader
Dr. James Larsen
WL/MLLN

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

Advanced materials are researched to produce extensive mechanical behavioral data bases that can be referenced for potential engineering applications. The research done during the previous Task needed final compilation into a form suitable for publication. Specifically, the Task involved data processing to analyze fatigue data of titanium matrix composites in various environmental conditions. Digitizing was also done on other titanium matrix composite fatigue data. Lastly, metallography and photo microscopy was completed on titanium matrix composites before and after fatigue testing. The most extensive investigation into the mechanical behavior of titanium matrix composites during this Task was completed to enhance previous research. The research was successful enough that the Task Leader and the student will submit the investigation for publication in Scripta Metallurgica. The submitted paper will be titled "An Evaluation of Interfacial Degradation in $[0]^4$ SCS-6/Timetal®21S." A more extensive description of the need, procedure, and results of the investigation are detailed below.

DESCRIPTION OF RESEARCH

Titanium-matrix composites have been extensively studied due to their potential capabilities in elevated temperature and high strength demanding environments. Of particular interest is the fiber matrix interface degradation occurring in composites with carbon coated silicon carbide fiber reinforcements. Interface damage decreases the ability of the fibers to bridge a matrix crack and, in effect, allows more of the applied stress to focus at the crack tip. Initially, the crack tip stress is reduced by transferring some of the load to the fibers in the crack wake. The occurrence of bridging requires an interface allowing the fiber to slip through the matrix as it cracks. If the fiber is unable to slip, the load will cause fiber failure. After the initial bond between the fiber is unable to slip, the load will cause fiber failure. After the initial bond between the fiber and matrix is broken, frictional stress works against the applied load to hold the crack at an equilibrium opening. This frictional stress is defined as Tau. If Tau is too large, then slip will not occur and the fiber will fail. However, if Tau is too small, the crack will continue to grow as it would in a monolithic alloy.

The magnitude of Tau is dependent upon many factors, to include temperature, fiber and matrix stress states, and interface condition. Previous studies have shown the fiber matrix interface degrading over many fatigue cycles, and thus reducing Tau. Tau varies in magnitude along the crack length due to corresponding fatigue cyclic exposure. Specifically, the fibers near the crack initiation region have seen the most fatigue cycles, while the fibers near the crack tip have seen only the last few fatigue cycles. However, life predicting computer models for titanium matrix composites (TMC's) often use a constant Tau value in their evaluations, thus reducing the effectiveness of the model. This inaccuracy produces a need to establish a relation between Tau and fiber position along a fully bridged fatigue crack to be applied to these preexisting predictive models. Production of accurate life predictive data bases are significant to design engineers choosing appropriate materials for their applications.

The project was conducted in correspondence with research done at WPAFB in the production of a life predictive model for the TMC, $[0]^4$ SCS-6/Timetal®21S. The objectives of this project were to decide the regions of interfacial damage within $[0]^4$ SCS-6/Timetal®21S fatigued specimen and, then to establish a relation between Tau and fiber position along the fully bridged fatigue crack within the defined interfacial damage regions. This will then be adapted into this material's preexisting life predictive model. The approach taken was to simulate a realistic environment for these high performance composites by doing the push-out procedure on a TMC, $[0]^4$ SCS-6/Timetal®21S composite fatigue tested at approximately 650°C and Smax=300 Mpa until a desired crack of length 2a = 10 mm was produced. The push-out testing models the interfacial degradation by pushing a fiber through the matrix with a probe controlled by a load cell. Push-out testing produces load displacement data used to evaluate Tau all along the push-out distance. Performing this procedure on fibers along a fatigue crack will produce Tau magnitudes for a sequential range of cycle exposures. The regions of interfacial damage are determined by doing an acoustic microscopy scan of the fatigued material.

RESULTS

The results of this approach discovered fibers with an effective Tau magnitude of zero lying completely within the interfacial damage regions identified by the SAM scan. The fibers experiencing partial interfacial damage, (the interfacial damage boundary intersects the fiber), had intermediate Tau magnitudes between the maximum Tau value and zero Tau value. The Tau versus fiber position relation observed with this approach can effectively identify the zero Tau and transitional Tau region. However, the Tau magnitudes are inaccurate in the transitional region due to the room temperature push-out procedure not effectively modeling the 650°C tensile fatigue testing processes. More accurate Tau magnitudes may be obtained if a fiber pull out procedure, to agree with the Poisson Effect of the fatigue testing process, was done at elevated temperature.

DAMAGE TOLERANCE METHODS FOR AEROSPACE ALLOYS AND METAL MATRIX COMPOSITES

Task Order No. 209a
Student Support Program
Southwestern Ohio Council for Higher Education

Deborah Williams
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WL/MLLN

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TASK ASSIGNMENT

The need for materials that will provide better elevated temperature performance in advanced turbine engine components has led to the study of fiber reinforced titanium aluminides. One promising titanium aluminide is Ti-22Al-23Nb (atomic percent). Heat treatments have been shown to improve the properties of this titanium aluminide matrix. However, it is important that the elevated temperatures used in the heat treatments do not degrade the strength of the continuous fiber reinforcement.

The study was undertaken to determine the effect of heat treatment on the strength of silicon carbide (SiC) fibers. Four fibers were chosen for the study: Trimarc1, SCS-6, Ultra SCS, and Large Diameter (LD) Ultra SCS. The SCS-6, Ultra SCS, and LD Ultra SCS fibers have a carbon core surrounded by a silicon carbide mantle and a silicon doped carbon coating. The Trimarc1 differs from the other fibers in that it has a tungsten core. Two heat treatment schemes were applied to the fibers themselves and to the fibers consolidated in the titanium alloy matrix. (For testing, the fibers were extracted from the matrix after the heat treatments.) Characterization included room temperature tensile testing of the fibers, evaluation of the fiber/matrix reaction zone growth, fiber fracture and matrix microstructure.

Procedure

The fibers were tensile tested and examined in five conditions: (1) As received; (2) Heat treated at 1085°C; (3) Heat treated at 1160°C; (4) Consolidated, heat treated at 1085°C and then chemically extracted. (5) Consolidated, heat treated at 1160°C and then extracted. After each tensile test, the tensile strength was recorded and all fracture surfaces, except those that shattered or broke in the grips, were carefully mounted for further examination on the scanning electron microscope (SEM).

Using the SEM, each fiber fracture surface was photographed, examined, and a determination was made as to the possible source of the failure. Most fractures could be identified as being initiated at the surface, mid radius or core. A common practice in determining fracture initiation site is to follow the "river marks." For example, a surface-initiated flaw is characterized by lines "flowing" toward a defect at the edge of the fiber (see Figure 1 at the "10 o'clock" position).

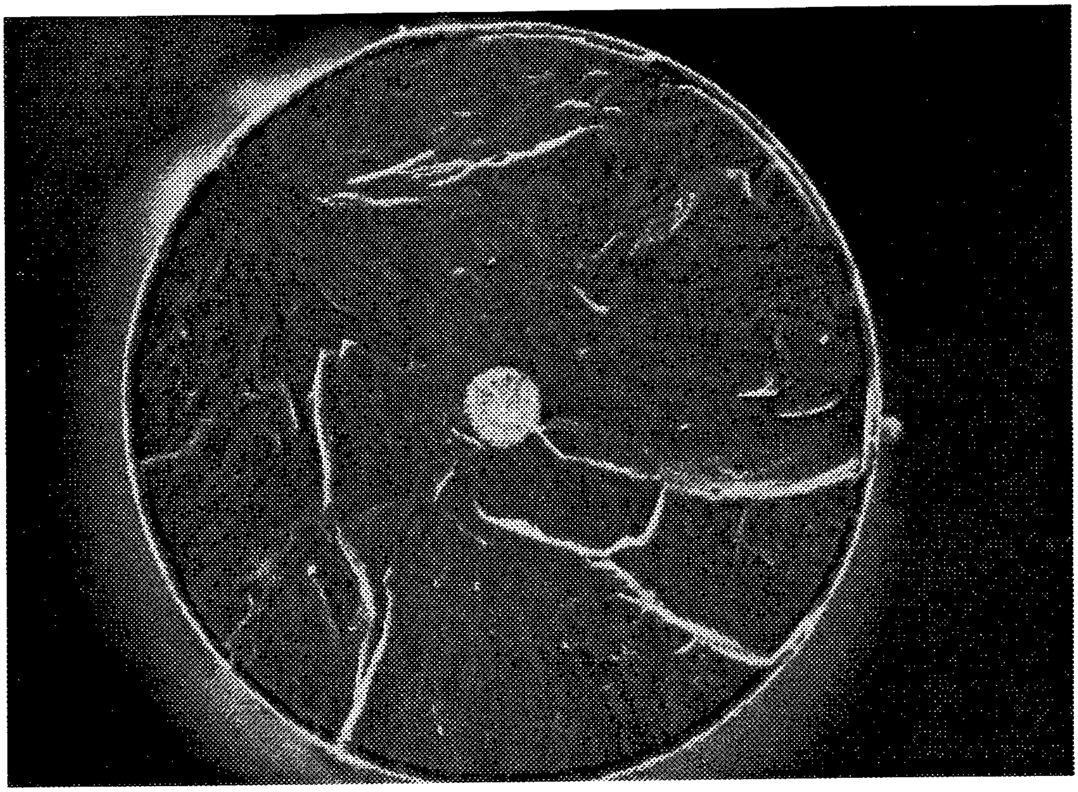

Figure 1

A mid radius flaw is characterized by lines converging toward an internal defect (see Figure 2 at the "6 o'clock" position).

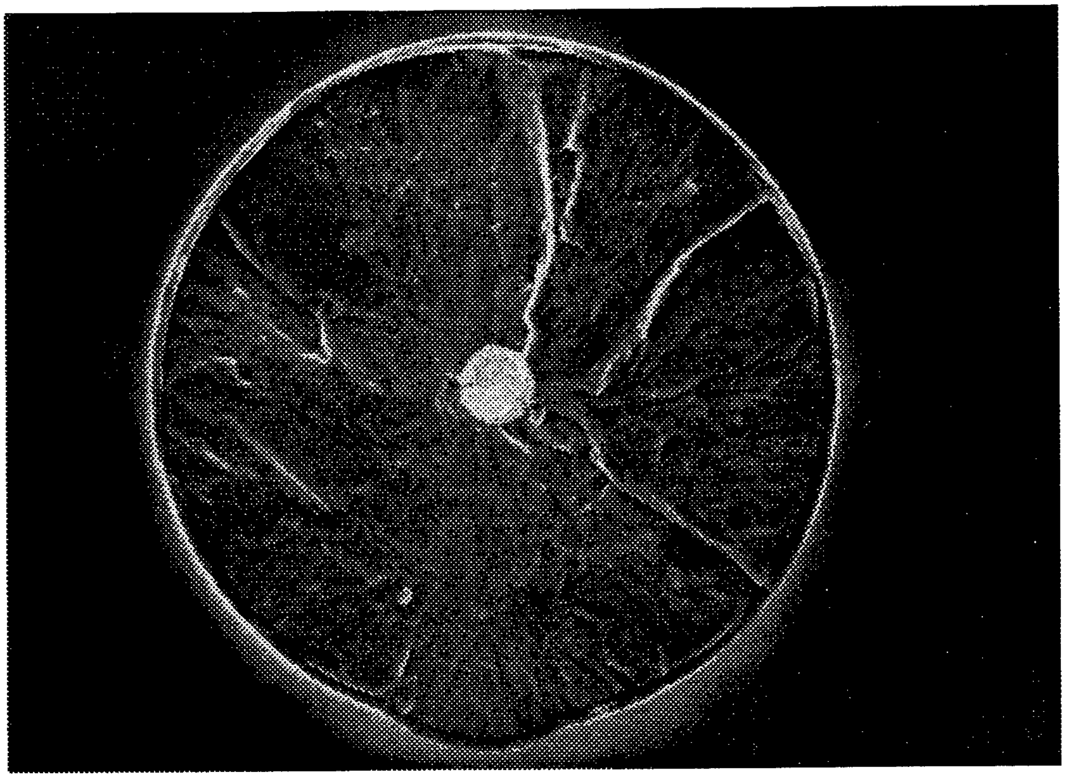

Figure 2

Both surface and mid radius failures usually corresponded to lower tensile strengths with surface failures having the lowest. Core initiated failures, which most often occurred at higher tensile strengths, were characterized by radial lines emanating from the core. Often the fracture initiation site was not evident because the primary fracture surface shattered off upon failure, thus leaving a secondary fracture (see Figure 3). These secondary fractures occurred at higher tensile strengths similar to core failures. Besides the characterization of the fiber fracture type, photos and measurements were also taken of the Trimarc1 reaction zone between the tungsten core and SiC mantle in the as received and heat treated conditions.

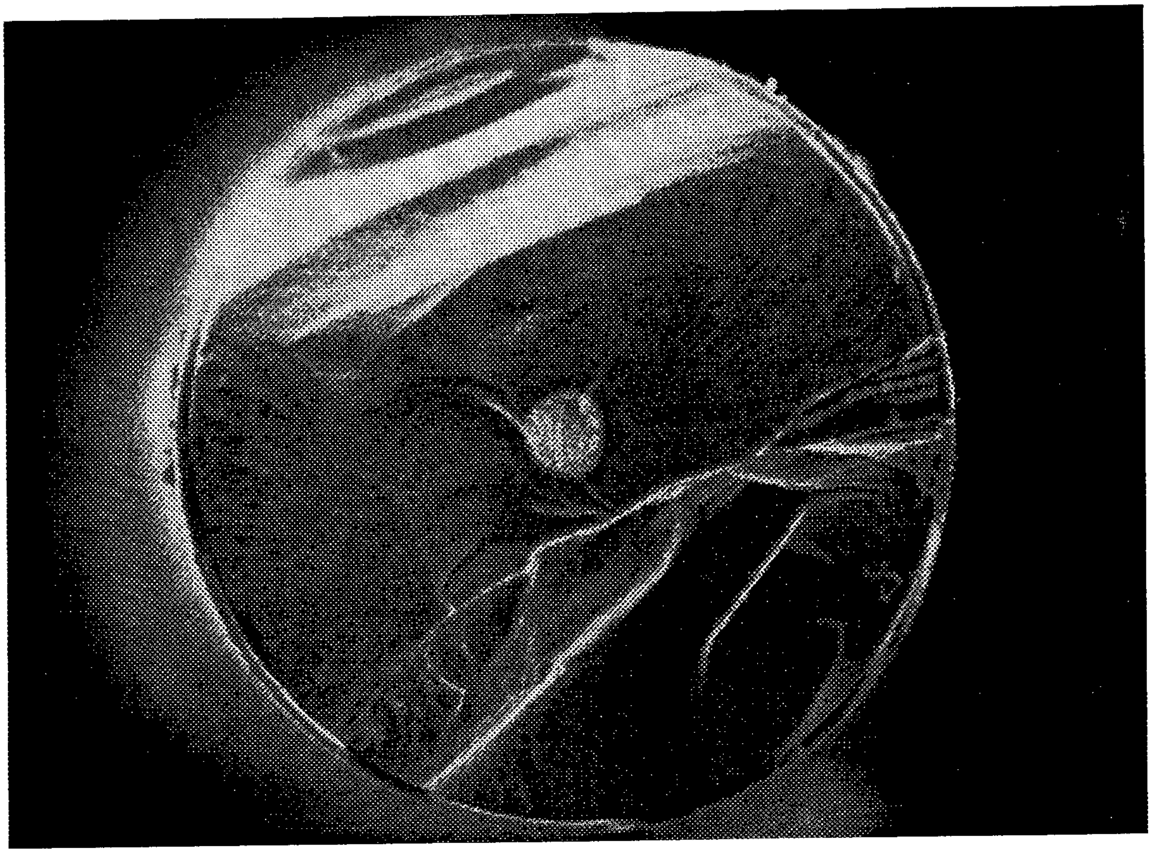

Figure 3

In addition to examining the individual fibers, the composite was also examined in the as received and heat treated conditions. For a comparison of the three conditions, photos were taken of the matrix microstructure and measurements were taken of the fiber/matrix reaction zone and the carbon coating thickness.

Results and Analysis

For analysis, tensile strengths were plotted against the probability of survival and compared with the information gathered on the SEM. At the .5 probability of survival, the strength of the SCS-6 and the Ultra SCS fibers were unaffected by the heat treatments; however, the Trimarc1 and Large Diameter Ultra SCS showed significant decreases in strength (see Table 1). This strength reduction in the Trimarc1 fibers was attributed to the Tungsten core/SiC mantle reaction and by internal defects exacerbated by the differing coefficients of thermal expansion between the fiber and matrix.

Condition	Trimarc1 (MPa)	SCS-6 (MPa)	Ultra SCS (MPa)	LD Ultra SCS (MPa)
As Rec'd	3100	4400	5600	6300
1085°C	3700	4000	5400	5600
1085°C + Extracted	2200	4500	5200	1000
1160	2200	4200	5000	5200
1160°C + Extracted	1600	4300	5400	1800

Table 1

These internal defects were evidenced in the higher number of mid radius failures in the extracted fibers. This was particularly evident in those heat treated at 1085°C in which the bare fibers had no mid radius failures. Forty five percent of the extracted fibers were mid radius failures. The strength degradation in the LD Ultra SCS appears to be due to insufficient thickness in carbon coating. Measurements of the carbon coating of the LD Ultra SCS compared to the Ultra SCS show that the thickness of the LD Ultra SCS carbon coating is much thinner.

DEVELOPMENT OF AN EMPIRICAL CONTROL SYSTEM DATA MATRIX FOR A MATERIAL DISCOVERY SYSTEM

Task Order No. 210
Student Support Program
Southwestern Ohio Council for Higher Education

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Government Task Leader
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WL/MLIM

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TASK ASSIGNMENT

Work was performed optimizing the controls for a pulsed laser deposition (PLD) process for the manufacture of the superconductor YBCO. Since basic environmental controls (temperature, pressure, position, and laser energy) were already in place the concentration was on in situ controls. The two in situ controls explored were Laser Induced Fluorescence and Raman Spectroscopy. Laser Induced Fluorescence is based on the emission of photons by the atoms during flight. Raman Spectroscopy involves the excitation and subsequent emission of coherent light on a material to monitor its stoichiometric properties. This report summarizes the control structure used.

While the environmental control minimizes process variability, in-situ process control is needed for complex processes to reduce process disorder. In-situ control establishes real time monitoring and actuation of process dynamics thus providing information not available at the process boundary. Therefore unknown and unmodeled variables that typically would upset a process can be compensated for during a process run. The result is a more robust process that can adjust itself for perturbations and anomalies. This is sometimes called self-directed control. An additional advantage is that process domain knowledge is enhanced by the collection of previously unavailable data.

To accomplish this, a proposed PLD control hierarchy was established (Figure 1). As shown the environmental controls are at the lowest control level. The references for these controls are provided by the in situ controller at the next level. These references are determined based on environmental measurements, in situ measurements, and in situ models. The in situ references are generated at the top hierarchical level from a knowledge base of all films produced at this plant. The in situ reference generator could be started with a neural network or an artificial intelligence routine.

The proposed in situ control hierarchy block is shown in detail in Figure 2. Fluorescent spectroscopy is used to monitor the elements in the plume and thus is input to the plume in situ controller. Raman spectroscopy is used to monitor the stoichiometry and morphology of the film as it is grown and thus is input to the deposition controller.

Since the plume dynamics are essentially independent of the deposition subprocess, the plume in situ controller operates at the lowest level in the in situ control hierarchy. It establishes most of the environmental references in an attempt to track the plume references. The plume references are generated by the deposition in situ controller that resides one level up in the in situ hierarchy.

The deposition controller is found at the top of the in situ hierarchy because it contains the highest degree of process knowledge as it is closest to the process output. From this level, the deposition controller can adjust the process by changing the plume references. This relationship creates a nested control structure suitable for this process. When the deposition controller wants to change the ratio of elements delivered, it adjusts the plume reference and lets the plume controller determine how to achieve this adjustment. In a sense, it treats the plume as an environmental variable to the deposition subprocess.

An important result of this structure is that it effectively partitions the process between the plume subprocess and the deposition subprocess. Partitioning provides effective decoupling for the subprocess variables. This allows for better modeling with higher intelligence and increased linearity.

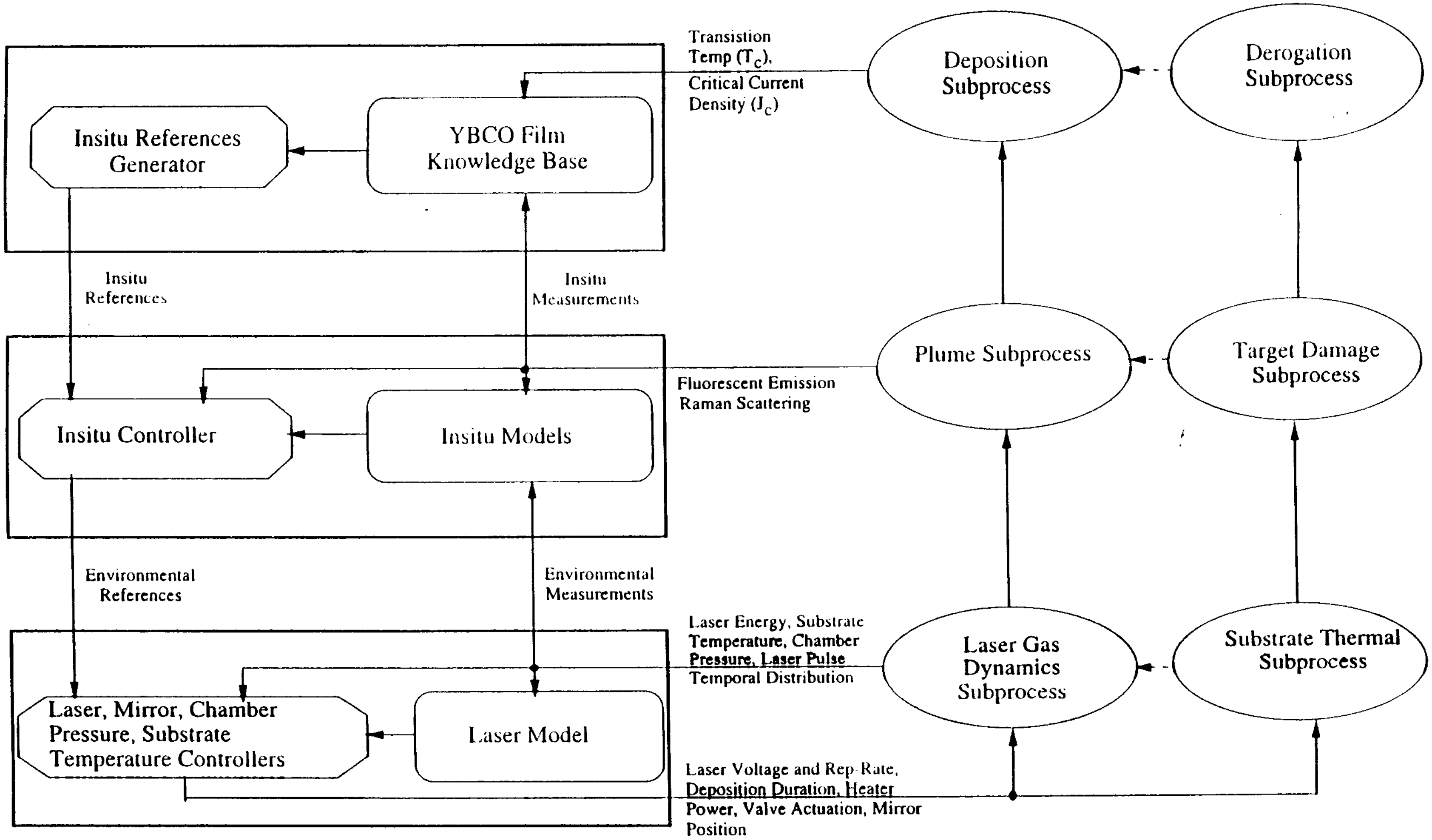

FIGURE 1 CONTROL HIERARCHY

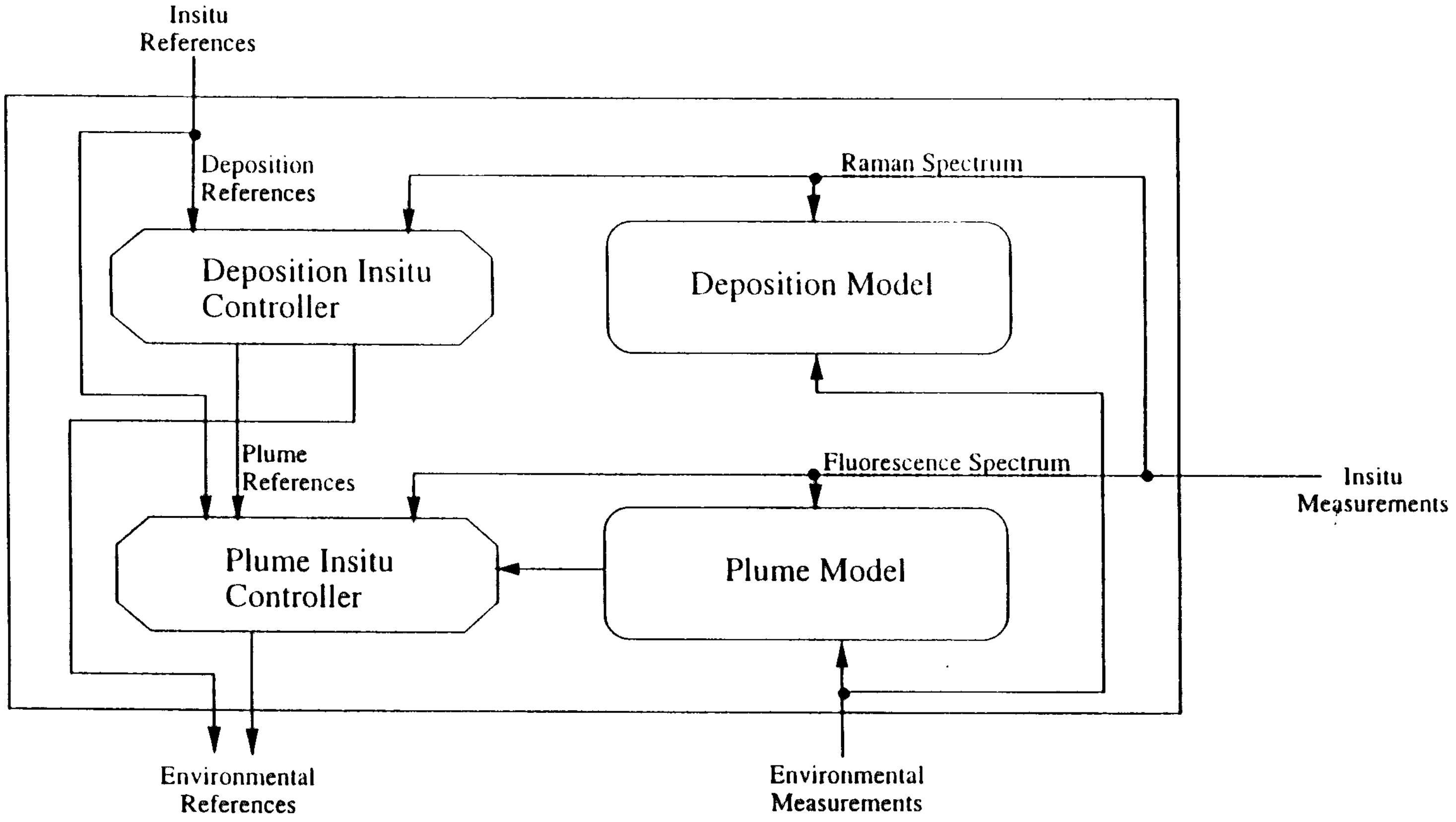

FIGURE 2 PROPOSED INSITU CONTROL HIERARCHY

PROCESS DEVELOPMENT FOR CERAMIC MATRIX COMPOSITES

Task Order No. 211
Student Support Program
Southwestern Ohio Council for Higher Education

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30 October 1996

Government Task Leader
Dr. Edmund Moore
WL/MLLM

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DESCRIPTION OF RESEARCH AND RESULTS

Coating Mixtures

The Cotronics Corporation, Inc. (CCI) ceramic adhesive material is being evaluated as a possible protective coating for ceramic aircraft tile. Initially, it was thought that the CCI ceramic adhesive would be too thick for application; therefore, the CCI adhesive would have to be thinned out before application to the ceramic aircraft tile. CCI recommended thinning their ceramic adhesive with their ceramic hardener, none the less they did not recommend mixing ratios. These ratios were determined by trial and error.

The CCI ceramic adhesive will be referred to as adhesive and the CCI ceramic hardener as hardener, moreover, the Xcc adhesive: Xcc hardener ratio will be referred to as a Xcc A: Xcc H ratio. The first mixing ratio that was evaluated consisted of 10.0cc A: 1.0cc H. This coating, and all following coatings, was applied with a paint brush to the smooth surface of a clean building brick. A sponge was also initially used as an applicator, but was too difficult to use for consistent results. The 10.0cc A: 1.0cc H coating was very thin, which made it difficult to apply a thick and even coating. Less CCI ceramic hardener was needed than was originally thought. To obtain a thicker coating the amount of CCI ceramic hardener added to 10.0cc of CCI ceramic adhesive was reduced by a 0.20 of a cc, which resulted in a ratio of 10.0cc A: 0.8cc H. This slight reduction in hardener made a very noticeable difference. The coating generated from this ratio was thicker, easier to apply with a brush and created a smooth coating that provided total surface coverage. CCI ceramic hardener content was reduced again by 0.2 of a cc, resulting in a ratio of 10.0cc A: 0.6cc H. This coating mixture did not appear to be much more different from the 10.0cc A: 0.8cc H ratio, however after applying the 10.0cc A: 0.6cc H coating, the surface was observed to be slightly rougher. The final coating applied was the CCI ceramic adhesive with no CCI ceramic hardener added. Surprisingly, the adhesive was not as difficult to apply as was first thought. However, the coating's surface was very rough. This rough surface would probably lead to spalling and subsequent coating erosion when placed under operating conditions, i.e., near the debris filled gaseous exhaust of a jet engine.

The coatings were then allowed to cure for 48 hours at room temperature. After the curing process, the coatings were examined. All coatings were well adhered to the clay building brick, offered complete surface coverage, and showed no signs of cracking or debonding. To prevent the waste of expensive ceramic aircraft tiles, (i.e., cost about $5,000 per tile) the coated clay brick was thermal cycled five times before any tiles were coated. One thermal cycle is composed of a 2minute dwell at 1,000°F followed by a 2minute dwell at room temperature

(72°F). Upon completion of the five thermal cycles, examination of the coatings revealed them to be in excellent condition. Therefore, coating of the ceramic aircraft tile could be conducted using the two best coatings determined by trial and error.

Tile Coating and Testing

The tiles were prepared for coating by first cutting 2.54cm X 2.54cm samples from the mother tile and clearing the tiles of cutting debris using compressed air. A total of six tiles were cut from the mother tile. The 10.0cc A: 0.8cc H coating was used to coat the tiles because it was easy to apply and rendered a smooth surface. CCI ceramic adhesive was also used to decide how the rough surface would be affected in the proposed operating environment. In both cases, the CCI coatings were applied to both the uncoated and existing coated regions of the ceramic aircraft tile. The CCI coated ceramic aircraft tiles were then cured at room temperature for approximately 12 hours, followed by a 2-hour cure at 212°F and a 24-hour static heat treatment at 1,000°F. Examination of the tiles after curing and heat treating, revealed the coatings to be in excellent condition. The four coated tiles and two uncoated tiles were then thermal cycled 100 times. The thermal cycle conditions used to test the tiles are the same as the thermal cycle conditions used to test the coatings on the brick, as discussed earlier. No evidence of coating cracks, debonding or spalling could be found after the thermal cycle testing was complete. Additionally, the uncoated tiles displayed no noticeable change in either the base material or the existing tile coating.

Upon the completion of the thermal cycle testing, six new samples were prepared for humidity testing. Before the CCI coatings were applied to the four test specimens, the samples were cleaned with compressed air and weighed. The coatings used for humidity testing were the same as those used for thermal cycle testing, i.e., 10cc A: 0.8cc H and as received CCI ceramic adhesive. These coatings were applied to both the uncoated and existing coated regions of the ceramic aircraft tile. After the ceramic aircraft tile had been coated with the CCI coating, they were cured for 48 hours at 212°F. Simulating 95°F/95% relative humidity conditions was done by placing the samples in a 95°F furnace with two 500ml beakers of water. Coated and uncoated ceramic aircraft tiles were placed in the furnace for 24 hours. The ceramic aircraft tiles were then removed and the four coated tiles were weighed. From the weight data collected before coating, after coating, and after humidity testing; the coating weight of the applied CCI coating could be calculated. Results of these calculations are as follows:

As received coating

1.) Weight gain per unit area: 90.33 g/ft^2 (Applied to existing coating)

2.) Weight gain per unit area: 56.97 g/ft^2 (Applied to base material)

10.0cc : 0.8cc coating

1.) Weight gain per unit area: 74.38 g/ft^2 (Applied to existing coating)

2.) Weight gain per unit area: 90.87 g/ft^2 (Applied to base material)

In the case of the CCI as received ceramic adhesive coating, there was a larger weight gain per unit area when the coating was applied to the existing coating than the 10.0cc A: 0.8cc H. These differences in weight gain can probably be attributed to an uneven application of coating with the paint brush and with the different weight loss associated with curing of the CCI ceramic adhesive and ceramic hardener. As in the previous tests the coatings appeared to be in excellent condition and the uncoated samples appeared to have suffered no changes.

The samples were then thermal cycled 25 times in the same manner as was discussed earlier. Results from the weight gain calculations after 25 thermal cycles are as follows:

As received coating

1.) Weight gain per unit area: 85.17 g/ft^2 (Applied to existing coating)

2.) Weight gain per unit area: 53.80 g/ft^2 (Applied to base material)

10.0cc : 0.8cc coating

1.) Weight gain per unit area: 70.54 g/ft^2 (Applied to existing coating)

2.) Weight gain per unit area: 86.97 g/ft^2 (Applied to base material)

The differences in weight gain data is probably attributable to the same reasons that caused weight gain differences in the data after the humidity testing. When comparing the data obtained after humidity testing and thermal cycle testing there is a slight reduction in weight gain per unit area in every case after the thermal cycle testing. This suggests the coating or the tile is picking up a slight amount of moisture. Again, the coatings suffered no cracking, debonding or spalling, and the uncoated samples also looked unaffected.

Personally, this Task has been a good learning experience for me. I have become efficient at operating the scanning electron microscope (SEM), X-ray spectrometer, the thermal cycling (fatigue) apparatus, and various high temperature furnaces. I have learned a great deal about ceramic matrix composites, a topic that is only briefly touched upon at Wright Sate University.

DEVELOPMENT OF SENSORS FOR DEFECT DETECTION IN COMPOSITE AIRFRAMES

Task Order No. 212
Student Support Program
Southwestern Ohio Council for Higher Education

David Liptak
Wright State University

31 October 1996

Government Task Leader
Lt. Ron Jon Annaballi
WL/MLIM

ACKNOWLEDGMENTS

Thanks go out to several people associated with this Task. Many thanks to Captain John Busbee for recruiting me into the in situ Raman sensor project. I am grateful for the instruction that you have provided, and for the introductions that you have facilitated between myself and others in the field.

Thanks to Dr. Steven LeClair, for making the position available to me and for providing guidance both on the details of this project and on my engineering career. Finally, thank you for accepting and respecting my ideas as professional and significant.

Thanks also to Dr. Sam Laube, who provided the motivation and direction necessary to keep the Task on track and on time.

TASK ASSIGNMENT

This Task involved the design, development and fabrication of a portable radiography system to be used for nondestructive defect detection in composite airframes. This system operates in the following manner. X-rays are produced, passed through a composite material and detected on the other side. Since the transmission of the x-rays is proportional to the density of the material through which they pass, a density profile of the material can be generated and then analyzed to detect stress fractures or manufacturing defects.

This system consists of three parts: the x-ray tube, power supply and the x-ray detector.

The x-ray tube uses an evacuated glass cylinder to isolate a filament electrically, sitting at ground potential, from a molybdenum plate, sitting at 30 kV. Heating causes electrons to be ejected from the filament. The electric field accelerates these electrons to a very high velocity. The rapid deceleration of the electrons as they impact the plate generates a continuous spectrum of x-rays with energies ranging from 30 kV down to 0 kV. A second form of emissions occurs when an electron transfers energy to the molybdenum atoms with enough force to eject an inner shell electron. As a higher energy electron falls to the lower energy state, an x-ray, with energy equal to the difference in energy levels, is produced.

The tubes for this project were designed and built in-house. Variations in tube length, the number of turns in the filament and the plate shape were explored to produce maximum x-ray intensity from the tube.

A high voltage (HV) power supply is necessary to generate the 30 kV plate voltage. Although HV supplies are commercially available, they are quite expensive. It was decided that an inexpensive supply would be designed and constructed in-house. Several paradigms were explored; the most successful was the result of coupling a high-frequency series resonant inverter with a three-stage voltage multiplier. The inverter was designed to operate at 100 kHz with an efficiency of 90%. The sinusoidal output of the inverter is the input to the voltage multiplier, which rectifies and amplifies the signal to 30 kV DC.

Finally, for the x-ray detector, a charge-coupled device (CCD) was selected due to its sensitivity and ability to provide two-dimensional information.

The next step in this project is to interface the detector with InfoScribe Technologies data logging software so that 2-D imaged can be acquired, stored and analyzed.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS

Task Order No. 213
Student Support Program
Southwestern Ohio Council for Higher Education

Michael Laufersweiler
Wright State University

19 November 1996

Government Task Leader
Dr. Loon-Seng Tan
WL/MLBP

ACKNOWLEDGMENTS

I would like to thank Dr. Seng Tan, Sharon Simko, Jerald Burkett, and Thuy Dang for their guidance and advice over the last year. It has been invaluable.

TASK ASSIGNMENT

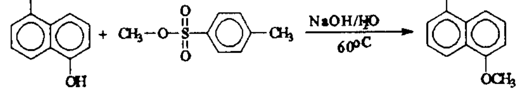
Synthesis of Aromatic and Aromatic Heterocyclic Polymers

As part of this Task, many techniques used in a modern organic polymer laboratory were learned, including laboratory safety techniques, preliminary characterization of organic compounds, the monitoring of organic reactions and scale up of organic monomer synthesis.

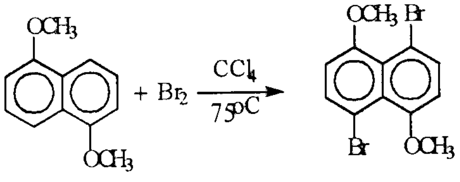
The safety techniques learned involved many aspects of hazardous waste accumulation and disposal. These involved maintenance of hazardous waste disposal logs, use of the hazardous material network, and the regular disposal of accumulated chemical waste. Purchasing and tracking chemicals used in the laboratory and keeping an up to date inventory of chemicals was also involved with following the lab safety standards.

Preliminary characterization of organic compounds using standard organic analytical techniques was also done. Regular use of Nuclear Magnetic Resonance spectroscopy, Fourier Transform-Infrared spectroscopy, and Ultraviolet-Visible light-Near infrared spectroscopy on monomer and polymer samples were performed. Viscosity determinations on several polyaniline samples were performed involving much use of the Origin spreadsheet software to report results. Other analytical techniques learned and performed were the uses of melting point apparatus, and methods of Thin-Layer and Column chromatography. These techniques allowed the performance of day-to-day laboratory duties in support of ongoing projects.

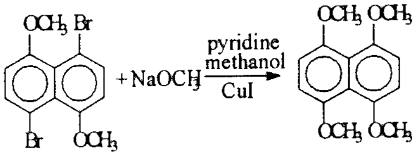
A large part of polymer synthesis is the synthesis of monomers that act as the starting material for the polymerization. Several syntheses were done to prepare monomers for use in the synthesis of nonlinear optical (NLO) polymers. The preparation of the monomer precursor, 1,4,5,8-tetramethoxynaphthalene, began with the preparation of 1,5-dimethoxynaphthalene from 1,5-dihydroxynaphthalene. The synthesis of 1,5-dimethoxynaphthalene was carried out by dissolving 1 molar equivalent of 1,5-dihydroxynaphthalene in an aqueous solution of sodium hydroxide (4 molar equivalents). Methyl *p*-toluenesulfonate was added drop-wise under nitrogen at 10°C. The solution was then heated to approximately 60°C for 3hours and allowed to cool. The product was filtered off and recrystallized in heptane. This reaction was repeated several times to increase yield and to obtain enough material to complete the next step in the synthesis, yield was approximately 80%.



The second step in the synthesis was to brominate the 1,5-dihydroxynaphthalene at the 4 and eight positions. A solution of bromine in carbon tetrachloride was added to a solution of 1,5-dimethoxynaphthalene in carbon tetrachloride at 74°C-76°C. Bromine was added over a period of 1hour. The solution was brought to reflux and allowed to stir for 30 minutes, after which the reaction mixture was allowed to cool. Upon cooling, a vacuum aspirator was used to remove excess HBr and Br_2. Solution was cooled with ice to 10°C where the precipitated product was filtered off with 70-75% yield. The product was recrystallized in toluene. This product will be used as a precursor for the next step in the synthesis.



The third step in the synthesis was to convert 4,8-dibromo-1,5-dimethoxynaphthalene to 1,4,5,8-tetramethoxynaphthalene. 4,8-dibromo-1,5-dimethoxynaphthalene was added to a solution of pyridine and methanol, followed by 25% sodium methoxide in methanol and copper iodide (CuI). The solution was refluxed for 16 hours, cooled, and precipitated into 5 liters of water. The solid salts and product were filtered off and repeatedly washed with water. The product was then dried in an oven and extracted with methylene chloride (3 x 200 mL). The methylene chloride solution was stripped off. The crude product was recrystallized in heptane. The synthesis gave 89% yield. This product was the starting material for the fourth step of the synthesis that has not yet been done.



These syntheses were done as scale ups of the reactions used to produce the starting material of an NLO polymer synthesis that has not yet been done. The product from each step of the synthesis was characterized using TLC, proton and C^{13} NMR, IR spectroscopy, elemental analysis, and mass spectrometry. The use of these synthetic steps has allowed the rest of the project to move forward. After the synthesis is completed, the product will be used to aid continuing research in NLO polymers.

DEVELOPMENT OF A MATERIALS KNOWLEDGE BASE FOR A MATERIAL DISCOVERY SYSTEM

Task Order No. 214
Student Support Program
Southwestern Ohio Council for Higher Education

Scott Blair
Wright State University

22 October 1996

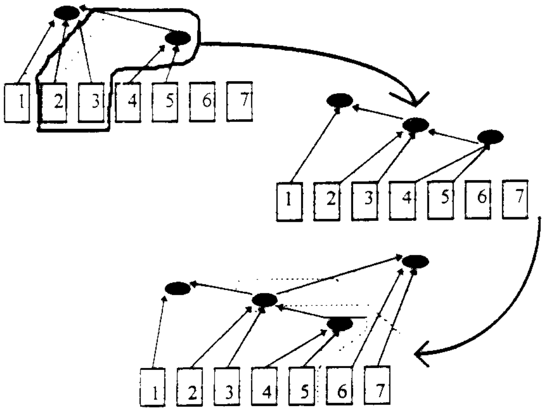
Government Task Leader
Lt. Ron Jon Annaballi
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank Dr. Al Jackson and Lt. Annaballi for their guidance on this Task.

TASK ASSIGNMENT

The Task required the use of a computer program call CONFOR (CONcept FORmation). This program takes large sets of data (i.e., physical and mechanical properties of compounds) and finds similarities in the different compounds and produces a pyramidal net. For example, it is possible to select all objects that include some combination of attribute values by tracing outgoing paths from the network vertex that corresponds to a certain combination. When the program finds a similar attribute, it produces a *node* or a *vertex* in the net.



New object generates new node

Pyramidal networks in combination with their construction have provided a convenient tool for massive data representation and prediction of unknown properties.

To predict if a new material will have the desired property, its attribute description was classified based on knowledge of a class of materials with the same properties. Thus, new materials with predefined properties were classified by calculating the node to which it belongs.

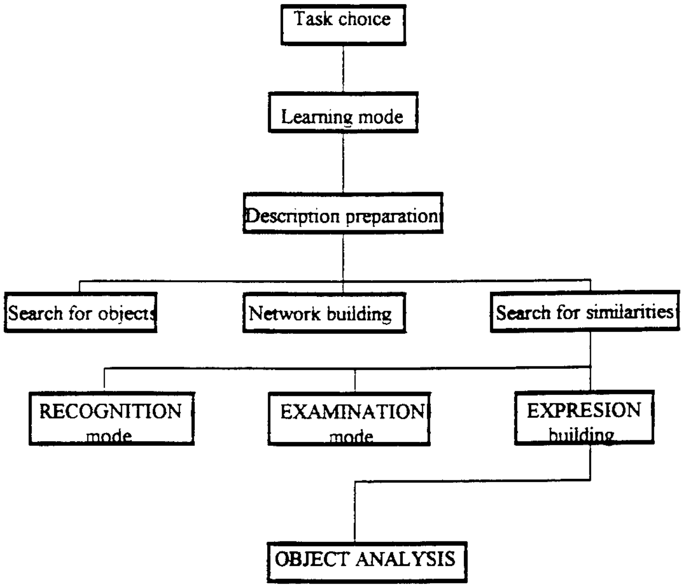
To produce the pyramidal nets a few steps that had to be carefully followed there were three modes:

- learning
- recognition
- examination.

In the learning mode, the data were objects of the training set that belongs to other classes. Objects of the training set were represented by attributive descriptions or attribute values. The set of attributes used for describing new objects was chosen and values were given to these sets. These sets were divided into bins. Therefore, every object contains a value for every attribute. Then class names were provided for each object. Initially, the data were object descriptions that are referred to some class, in the recognition mode. Finally, the object descriptions are in terms of attribute values chosen in the learning mode.

The network was then produced and the information was than compared with a test set. The test set was a set of compounds that had known values for certain physical and mechanical properties. The value for the same properties of the set of compounds that was ran through the CONFOR program were also known (because this experiment is in its infancy stage, but in the future the set will have unknown values and CONFOR will be used to predict these values). The output of the program was then compared with that of the test set. The prediction accuracy of the values decreased as the number of bins increased. This problem is being looked at presently.

To run the CONFOR program the following sequence was used:



Network Building

Objects with identical descriptions were found. If these objects belong to a different class, the object is not added to the network.

Search for Similarities

The program finds attribute values common for those whose names were entered by the user.

Search for Objects

The program finds attribute values combinations that occur in object descriptions more frequently.

Expression Building

A collection of check nodes that correspond to each concept formed was then described by a logical expression. These expressions included attribute values that were the most typical for the object class.

Recognition

The system analyzes new object descriptions comparing them with the pyramidal network.

Examination

The program analyzes the object description of examination sets and recognizes them.

Object Analysis

The program then finds objects that include those values of the test set that were entered by the user, and compares the results of the programs finding to the test set.

CONCLUSION

CONcept FORmation, CONFOR, is a useful tool in predicting what class an unknown value belongs to. This is a difficult program to learn how to use. It takes a lot of training. The use of CONFOR for predicting material selection may be in the near future!

DEVELOPMENT OF A MATERIALS KNOWLEDGE BASE FOR A MATERIAL DISCOVERY SYSTEM

Task Order No. 214a
Student Support Program
Southwestern Ohio Council for Higher Education

David Hanna
Wright State University

22 October 1996

Government Task Leader
Lt. Ron Jon Annaballi
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank Lt. Annaballi for his guidance during this Task.

TASK ASSIGNMENT

Classification of Data using Neural Recognition

There are various ways to classify data into their relative groups. To do this, one needs to know what the possible choices are. The classic way of approaching the classification process would be to use empirical data to support these predictions. Another way, this report will focus on, is by using neural recognition. The goal is to predict accurately where various substances should be grouped.

The use of neural recognition is realized by using artificial intelligence. For the artificial intelligence language to work, it needs a set of rules by which it can operate. This is called an algorithm. The algorithm being used is the creation of a group of people headed by Dr. Victor Gladun. Therefore, it is called the Gladun algorithm. The algorithm operates as follows: The program takes in a set of test data from which the algorithm sets up a group of neural pathways and nodes though which data can be sifted. By this operation the program theoretically can classify the data sifted. The program records all of the common nodes by which the data is related and these could result in new classification groups. From these new classification groups there could arise new materials with new properties that may help in the production of improved materials.

Two programs that used Gladun's algorithm were used but have not met with great success. The first one, created by Victor Gladun, is a program called CONFOR. The problems faced when using CONFOR are as follows: First, it is not a time-efficient menu-driven program. It requires a user to sit by the terminal and guide the program through the process through the uses of menus. This wastes too much time regarding the time spent between menu manipulation. The major problem regarding this program was most of the data filtered did not get classified in any group or if it was, usually, the wrong one. A second problem will be expressed later after an overview of another Gladun algorithm run program. The second program met with more success regarding classification. Instead of getting no classification, the information generated states that the data filtered was most probably not in a certain group. From this a lengthy iterative process, to narrow down how grouping an object would be classified by elimination, would occur. This is not the result looked for. The goal is to find objects that corresponded to nodes of new classification and using elimination does not help.

Some developments and insights occurred in this Task that may have an impact on this research. The first was that the second program was written using only two attributes with qualifying weights. The experiments used ran between five and eight qualifying weights. This most probably was the reason for the unsuccessful test runs. A new version that will incorporate more attributes is in the making. Second, during this research Dr. Steven LeClair and Dr. Allen Jackson brought forth the idea that the Gladun algorithm did not account for types of grouping. There are two types of groupings, structural and functional. Until this time data used had both types of groupings and therefore might have caused faulty results. The development or new path this research may take is in using cryptography. This is a method of breaking the code of a pattern and thus giving insight on why things are the way they are. All options as of yet are not depleted. Hopefully, a key will be discovered that will lead toward a more defined goal.

ELECTRICAL AND MAGNETIC PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

Task Order No. 215
Student Support Program
Southwestern Ohio Council for Higher Education

Douglas A. Buchanan
Wright State University

19 November 1996

Government Task Leader
Mr. Timothy L. Peterson
WL/MLPO

ACKNOWLEDGMENTS

Overall, this Task has been one to help students gain experience in a laboratory setting and controlled experimentation. With this final report, I would like to thank everyone with whom I have worked. I would like to thank those I have worked with directly including, Mr. Tim Peterson, Iman Maartense, Eric Moser, and Dr. Rand Biggers. I would also like to thank those not directly involved in superconductivity research, namely Ron Perrin, Dave Zelmon, and the many others that this Task has given me the opportunity to meet.

TASK ASSIGNMENT

This Task involved characterizing the properties of high temperature superconductors by doing such things as measuring the DC electrical components of superconducting thin-films, and measuring other physical properties of the film such as thickness or patterned line width. The Task also requires occasionally adjusting the experimental technique by altering the way data is collected or altering the experiment itself.

The measurements of DC electrical properties of a superconducting thin-film are simple, but the preparation of the film to be measured can be tedious and taxing. First, the films are grown by pulsed laser deposition, where a pulsed laser is used to blast a Yttrium Copper Barium Oxide (YBCO) target. The blasted particles then fall onto a crystal substrate heated to 700 degrees Celsius. The substrate is heated so that the particles fall into a specific orientation on the substrate. The substrate is then cooled to room temperature and is ready to be patterned and have contacts applied for measuring DC current and voltage. The sample is patterned using photolithography, a technique where a photosensitive chemical is placed across the entire film. High intensity light is then shined on the areas where the superconductor is to remain. Acid can be applied to eat off the remaining area. The film is then patterned. The patterned film will have gold wires attached, but to make good low resistance contact between the film and wire, silver is sputtered onto the film in small circular areas. Gold wire is finally attached using special silver paint for good contact and low resistance, (typically $10^{-3}\,\Omega$). Using the DC current and controlling the temperature, one can measure the dependence of current and temperature, also called the critical current measurement.

Superconductors have no electrical resistance for certain currents applied, but as current is increased, the superconductor will lose its superconducting ability. The current at which a superconductor switches to a normal metal is called the critical current. This current passes through the entire volume of the film. Dividing the critical current by the cross-sectional area of the superconducting film gives critical current density, a typical reported measurement of a superconductor that tells its quality. Microscopes are commonly used to determine patterned line thicknesses (usually about 1μm wide) and use an instrument called a Dektak to measure the film's thickness (usually 300 NM).

Magnetic field dependance is also investigated using a recently installed Dynaphysic 1.8 Tesla magnet. Magnetic field measurements have altered the experimental technique of acquiring data. Currently, different magnetic fields are applied to the superconductor while the temperature is maintained at a set value. Previously, the critical current was determined for a range of temperatures within the superconducting state.

Results of the magnetic field data are still being analyzed. The eventual goal is to use the magnetic field data with other transport data to further the understanding of superconductors.

ELECTRICAL AND MAGNETIC PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

Task Order No. 215a
Student Support Program
Southwestern Ohio Council for Higher Education

Kueiming Max lee
University of Dayton

19 November 1996

Government Task Leader
Mr. Timothy L. Peterson
WL/MLPO

ACKNOWLEDGMENTS

I would like to thank Southwestern Ohio Council for Higher Education (SOCHE) for their ongoing support and my Government Task Leader, Mr. Tim Peterson, for his technical support. I also would like to thank Douglas Buchanan, Dr. Eric Moser and Dr. Imann Maartenise from the superconductor team for their help when I started this Task.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Primarily this Task is to measure and take electrical and magnetic properties data of high temperature superconductor thin-film. It involves the application of many scientific techniques to investigate the properties of high temperature superconductors. The Task includes preparing samples for electrical and magnetic measurements, mounting samples in Dewar, cooling samples using liquid nitrogen and liquid helium, doing resistivity and critical current density transport measurements as a function of temperature, generating graphs and tables from computer-generated data. The collected and organized data are used to aid in analysis at the Wright Lab MLPO group. In addition, substrates are prepared and cleaned for deposition of thin superconducting films.

DESCRIPTION OF RESEARCH

The main task was to operate the cryogenic system including Dewar cooling (from room temperature to 77 K), sample temperature control (at a setting temperature) and controller system including sample current control, sample voltage readouts with electronic and the software package LabView. The electrical properties such as normal state resistivity ρ, critical temperature Tc, and the critical current density Jc of high temperature superconducting (HTSC) thin-film (for instance, $YB_2Cu_3O_{7-x}$ on substrates LAO or STO) are measured to evaluate material quality. This information will feedback to the laser ablation deposition group for improving HTSC thin-film growth quality and better understanding of the nature of high temperature superconductivity.

The sample mounting as illustrated in Figure 1 is based on 4-point probe technique similar to the standard semiconductor device measurement. This technique is used to eliminate the contact resistance along the measurement circuit. The resistivity of thin-films is measured as a function of temperature from room temperature down to the temperature at which the superconductivity occurs (the cool down process). The voltage across the thin-film, as a function of increasing current passing through the thin-film at a constant temperature, is measured to learn the critical current density that can be carried by the film from a superconducting state to a normal (non superconducting) state.

For the magnetic properties measurement as shown in Figure 1, the thin-film sample is placed parallel to or perpendicular to an external magnetic field ranged from 0 to 12k Gauss under the same environment as described in the electrical properties measurements. The relation between Tc, ρ and Jc and sample directions are then measured and recorded.

The other area was cleaning the substrates before the HTSC thin-film is grown on it. This involves chemical and ultrasonic cleaning processes. The samples are soaked in TCL, acetone and methanol solutions within an ultrasonic vibrating container in that sequence for a time. The cleaning substrates are very critical to the quality of grown HTSC thin-films. Any contamination can ruin the HTSC properties. After chemical cleaning, the substrates are baked in a UV ozone oven for an hour and stored in clean holders.

RESULTS

The typical resistivity as a function of temperature is shown in Figure 2. The range of resistivity for in-house thin-film is 200 to 300 μΩ-cm at transition temperature. The critical density measurement is illustrated in Figure 3. It has a typical value of 5 x 10^6 Amp/cm^2 at the temperature of 77 Kelvin.

B ⊥ line 2, B ⊥ film
filenames MCM6/Ic/77/xx, xx=Magnetic filed strength in KG

Device mounting diagram:

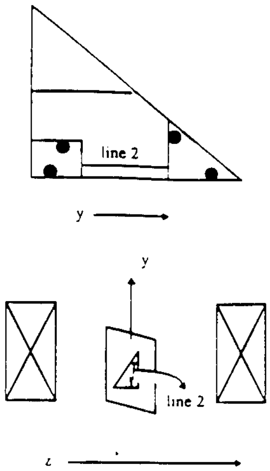


Figure 1

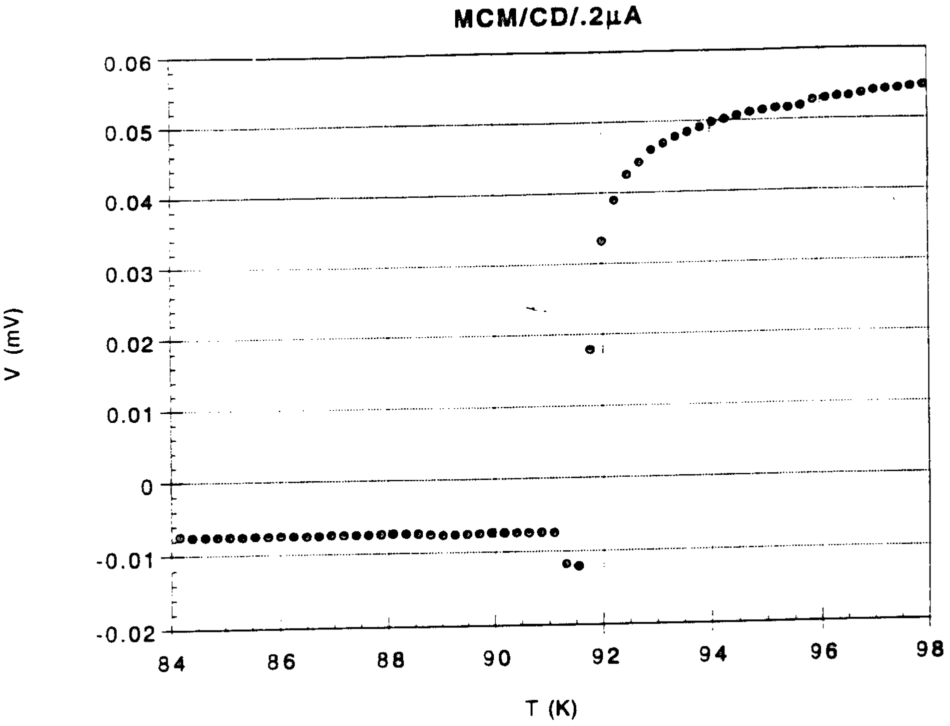


Figure 2

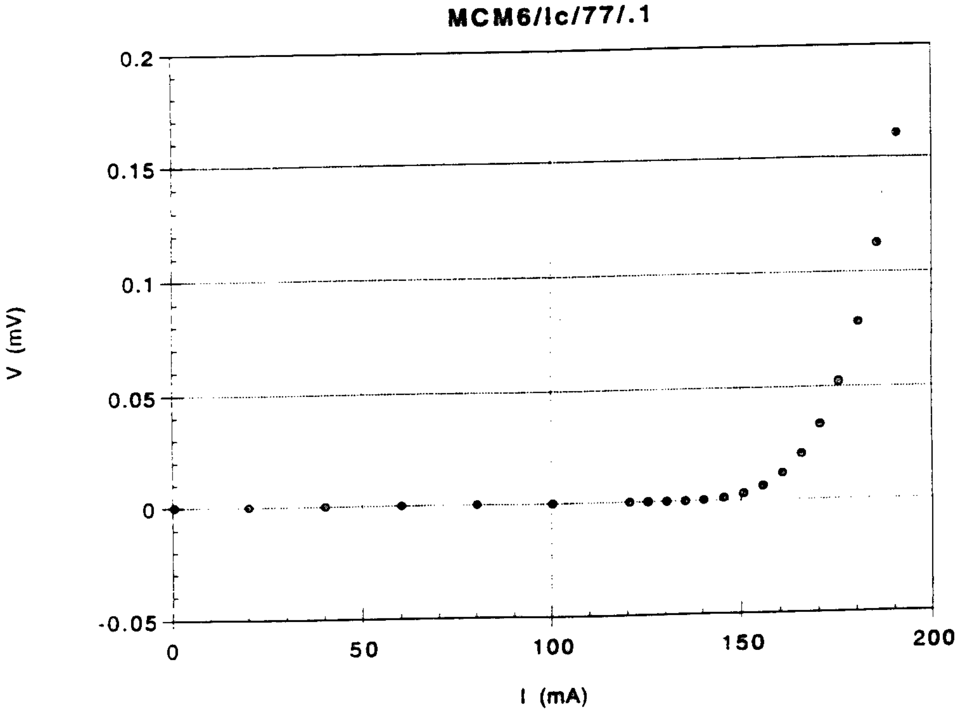


Figure 3

BRITTLE MATRIX COMPOSITE STUDIES

Task Order No. 216
Student Support Program
Southwestern Ohio Council for Higher Education

John Schuck
Sinclair Community College

4 December 1996

Government Task Leader
Dr. Rollie Dutton
WL\MLLN

ACKNOWLEDGMENTS

A big thanks goes to Dr. Rollie Dutton for his guidance and advice throughout the Task. He has made this Task truly educational and very enjoyable. Thanks to Peter Brown for the computer support. A special thanks to Mrs. Wanda Vogler and Dr. Nick Pagano for giving me the opportunity to work on this Task.

Working on this Task has been a very educational experience. I learned how to operate various scientific instruments and to interpret the data obtained from them. The methods of research learned will be an invaluable asset, as I pursue my degree in chemical engineering.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The focus of this Task was primarily the same as last years. Borosilicate glass composites reinforced with SiC fibers were prepared via the traditional tape casting method. Three glasses with differing coefficients of thermal expansion were used to vary the residual radial thermal stresses after processing from tensile to compressive. The unidirectional reinforced six layer composites were loaded to failure under tension to detect the initial matrix cracking stress and the effect of fiber coating on crack growth. The resulting data was used for comparison with a semi-empirical and axisymmetric model for model verification and the effect of coating/interface properties on micro cracking.

An increased emphasis was placed on the preparation and testing of 'transverse' composites. These composites consisted of the same glass matrix as the traditional composite, but employed only a single row of the TiB_2 coated Sigma fiber oriented 90 degrees to the length of the composite. The 'transverse' composites were prepared with the fiber ends covered and exposed from the matrix. This was done to show the significance of free edge effects on the effective response of the composite under combined thermal and transverse loading. The results were used to validate predictions based on an analytical model.

DESCRIPTION OF RESEARCH

The matrix for the composites was prepared via tape casting. The recipe for the glass slurry is given in Table 1. The binder, PEG, and solvent are mixed and paddle stirred for 15 minutes then set aside. The fish oil and remaining solvent are paddle stirred until the fish oil is well distributed then the glass powder is added and the mixture is paddle stirred for 15 minutes. The binder mixture is added to the glass mixture and paddle stirred for an additional 15 minutes. The glass slurry is cast on the tape casting machine and allowed to dry for at least 3 hours. Tape thickness averages 7 mil. with 50% relative density.

Table 1

48 gm glass powder (ave. particle size ~8μm)

35 ml Ethanol (add 20 ml\15 ml)

35 ml Toluene (add 20 ml\15 ml)

1.9 gm Manhaden Fish Oil

4.3 gm B-90

4.1 gm PEG

Each layer of the unidirectional composite was prepared individually. The green tape and fiber mat of the desired fiber spacing (120 fiber/inch or 68 fibers/inch) were cut to size. They were then laminated into the green tape at 82°C using 150kPa of pressure on a Carver Press installed with heated platens. Six layers were prepared by the same procedure and stacked together to make the final composite laminates. The 'transverse' composites were prepared using four layers of tape and a single row of fibers covered by four additional layers of tape.

The composite laminates were individually loaded into a CM Inc. tube furnace for binder burnout and vacuum sintering. The heating schedule is given in Table 2.

Table 2

200°C ⇒ 450°C @ 2°C/min in oxygen, 1 hr hold, binder burnout

450°C ⇒ 710°C @ 4°C/min in argon in vacuum, 1 hr hold, sintering

backfill with argon, 20 minutes hold

710°C ⇒ 200°C @ 5°C/min in argon, cool down

After vacuum sintering, the composites were hot isostatically pressed at 650°C for 30 minutes with an applied pressure of 35MPa to remove ~ 2% residual porosity. The final composites were 10cm long by 2cm wide and 0.2cm thick.

Before tensile testing, the composites were coated with a thin layer of 828 epoxy to reduce any surface flaws. The composites were tabbed and the edges were polished to 1µm. Polishing was preformed to improve microscopic imaging used for crack detection. Strain gauges and an acoustic emissions detector were mounted and then the composites were loaded in tension. The load was incremented so that initial matrix cracking could be detected by photomicrographical and acoustic emissions techniques before the composites reached ultimate failure. Micrographs produced by the MTS testing machine were used to determine and verify the initial matrix cracking stresses. The failed composites were analyzed on a Leica 360 SEM to learn micro crack growth and the roles that the fiber, coatings, and matrix played on the crack growth. Some data reduction, in the form of graphical analysis, was done using a Kalidagraph program.

RESULTS

The composite cracking stresses obtained from mechanical testing for the Sigma fiber showed the 7040 and F glasses agreed with model predictions. The E glass cracking stresses fell below the predicted level suggesting a previous debond at the fiber/matrix interface. The composite cracking stress versus fiber volume fraction was plotted against the model predictions and is shown in Figure 1. Test results for the SCS fiber were inconclusive as more testing needs to be done to compare it with model predictions.

The results of the study on the 'transverse' composites showed significant changes in the ultimate failure strength and failure strain observed between the two different types of composite designs. Failure stress for 7040 glass matrix composites with the ends covered were approximately four times that of the 7040 composites with the fiber ends exposed. The E glass matrix composites with fiber ends covered resulted in reduced strength and strain to failure. Overall, the theoretical predictions for damage development and propagation were in good agreement with experimental measurements and observations.

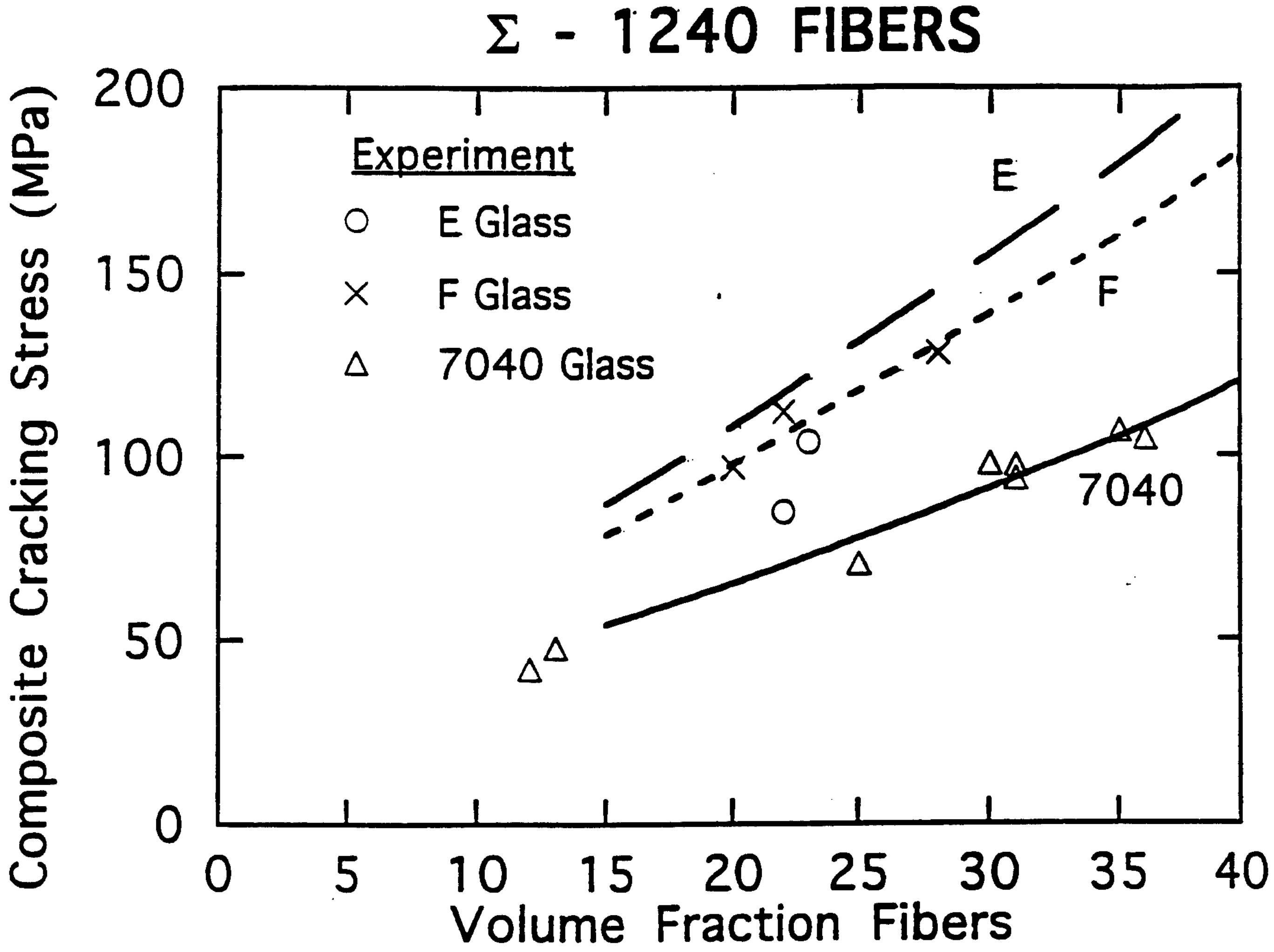


Figure 1

Figure 1

BRITTLE MATRIX COMPOSITES STUDIES

Task Order No. 216a
Student Support Program
Southwestern Ohio Council for Higher Education

Tracy Criswell
Wright State University

4 December 1996

Government Task Leader
Dr. Rollie Dutton
WL/MLLN

ACKNOWLEDGMENTS

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

Throughout this Task, the main objective was to fabricate borosilicate glass matrix composites with monofilament silicon carbide (SiC) fibers by tape casting. The green matrix glass tapes, which have 50% relative density, are then laminated with the SiC fiber mats that already have uniform fiber spacing. The samples are then sintered at 710° C, which then has a 98% relative density. The purpose of these samples is to see how the fiber/matrix interface reacts with the initiation of matrix cracking. A problem was encountered while fabricating the samples. Most of the work on the Task was spent trying to find where the problem was occurring. It was finally decided that the problem occurred because of too much binder on the fiber mats. It created its own layer and would not allow the glass to wet with the fibers.

DESCRIPTION OF RESEARCH

The recipe for the tape casting slurry is given in Table 1. The slurry is prepared in four steps. First, a paddle stirrer is used to disperse the Menhaden fish oil into 40% of the solvent. Next, the borosilicate glass powder (average particle size ≈ 9μm) is added to the slurry and mixed for 20 minutes. Following this, in a separate beaker, the binder and plasticizer are mixed into the remaining solvent until the binder is well dissolved (≈ 20 min.). Using the paddle stirrer is an advantage to ball milling because not as much material is wasted. Also, it takes a lot less time. The two slurries are then combined and mixed for another 20 minutes after which the tape is cast. The doctor blade is typically set at .32 mm above the glass bed of the tape caster. After casting the tape, it takes approximately 3 hours to dry. The tape has a final thickness of approximately .18mm and a relative density of approximately 50%.

The tape is then removed from the glass and cut into 3 by 3/4 inch rectangles. The fiber mats are cut 2 1/2 by 3/4 inch with the fibers perpendicular to the length of the tape. The tape and fibers are laminated in a Carver press with platens heated at 93°C. The laminate is separated from each heated platen by a sheet of Teflon and a thin silicon rubber sheet. When being laminated, five layers of tape with one layer of fibers are first laminated together and then another five layers of tape are laminated on the opposite side of the fibers.

A single sample is placed between two pieces of graph foil placed on a graphite block. A graphite bar is placed on top with a weight of 20 gm to prevent the sample from curling up during sintering. The sample is inserted into a tube furnace for binder burn out and sintering. The burn out cycle happens when the sample is heated at 2°C/min to 450°C and held for 1 hour with flowing oxygen. The sintering cycle happens when the furnace is evacuated and the temperature increases to 710°C at 4°C/min, held for 1 hour, and an additional 20 minutes with flowing argon.

RESULTS AND DISCUSSION

The problem encountered was the SiC fibers were not wetting to the glass and would actually move in the glass. It became a little frustrating because this had not happened before. Looking at the sample, after being sintered, under the microscope, showed a lamination problem. When it seemed everything had been done that could be done, the sample was examined under the microscope before sintering. Binder on the fibers had been keeping the fibers from imbedding into the glass.

Table 1

Basic Recipe-Borocilicate Glass Composites

Glass Powder	48 gm
Tolulene (solvent)	35 ml
Ethanol (solvent)	35 ml
Menhaden Fish Oil (dispersant)	1.9 gm
Polyvinyl Butyral (binder)	4.3 gm
Polyglycol (plasticizer)	4.0 gm

RAPID, CONTINUOUS HEAT TREATMENT OF TIMETAL 21S

Task Order No. 217
Student Support Program
Southwestern Ohio Council for Higher Education

Roger J. Gural
University of Dayton

27 December 1996

Government Task Leader
Dr. Lee Semiatin
WL/MLLN

ACKNOWLEDGMENTS

I would like to thank Dr. Lee Semiatin for all of his guidance and explanations, and Mr. Bob Lewis for his expertise in the metallography lab.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Working with members of the MLLN and MLLM, the volume fractions of recrystallized microstructure in cold-rolled and rapidly annealed samples of Timetal 21S were determined. The small foil specimens were mounted in a press using fine ground epomet mounting material. After repeated sanding, the specimens were polished with diamond paste and placed on vibromets for a final polishing. After the specimens achieved a suitable finish, they were etched with various acids and their micro structures were photographed using a Reichert-MeF3 photo microscope.

The photographs were then analyzed for their respective micro structures. This included using point counting to learn the recrystallized percent of the samples. The method of point counting uses a small grid-like array to learn the actual number of recrystallized grains that exist within a predetermined area. By dividing the number of grains covered by the grid by the known number of points on the grid, it was possible to calculate the recrystallized percent of the sample. The data was plotted against each specimen's respective peak heating temperature. This was used to create a recrystallized sample curve for comparison to previous tests.

RESULTS

The experiences gained from this cooperative education reinforced the notion that not all learning takes place in the classroom. Past school experience provided sufficient preparation for this engineering position, but learning on the job was a prerequisite for success. Every day usually presented a new and different challenge to be mastered.

RAPID, CONTINUOUS HEAT TREATMENT OF TIMETAL 21S

Task Order No. 217a
Student Support Program
Southwestern Ohio Council for Higher Education

Matthew P. Simon
The University of Dayton

27 December 1996

Government Task Leader
Dr. S. L. Semiatin
WL/MLLN

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I would like to take this opportunity to extend my thanks to those individuals without whom completion of this Task would not have been possible, or perhaps even enjoyable. I would like to thank Bob Lewis and Eric Fletcher of UES for their guidance and assistance in the Metallography Laboratory, where many days were spent. I would also like to thank Tim Campbell, Mark Dodd, Travis Brown, and Tom Jones of UES for their assistance in heat treating and High-bay phases of the Task. Given the amount of computer work done in this Task, not thanking Pat Sponsel and the DOISM computer support staff for their assistance would be inappropriate. Finally, I would like to extend my heartfelt gratitude to Dr. Lee Semiatin for the opportunity to experience material sciences, not out of a text or lecture, but firsthand.

TASK ASSIGNMENT

To create a model from which the microstructure of annealed Timetal 21S could be predicted, it was first necessary to create, experimentally, a representation of the recrystallization behavior, about temperature of the rapid annealing, and the time at that annealing temperature. Therefore, small samples of the foil were rapidly annealed in a molten salt bath, for various durations, at various temperatures, and rapidly quenched in water to capture the microstructure for the corresponding time and temperature. These samples were polished, etched, and photographed so that point counting could be done quantitatively to assess the recrystalization that took place. However, the recrystallized microstructure is not always visually distinct from the uncrystallized microstructure. It was, therefore, theorized that heat treatment for a long duration at a low, subtransus temperature would highlight the recrystallized microstructure without further annealing the foil, a process called decoration aging. It was found, however, by comparing the decoration aged samples with nondecoration aged samples, that some annealing was taking place during decoration aging treatment and this method had to be dismissed, and careful point counting done on the original photographs.

The data collected from the point counting of the photographs was a measure of the percent recrystallized. This data was plotted as functions of time and temperature to quantify the effects of these variables on the recrystallization of the Timetal 21S foil.

For confirmation of results from the salt pot trials, tests were run by two independent organizations. The results of the first of these, when examined by point counting, indicated an apparent discrepancy between the indicated sample temperature (from testing equipment monitors) and the actual temperature experienced by the sample. This is currently being looked into. The results from the tests run by the second organization were identical to those gathered on-site. Further tests have been run and are currently in preparation for examination.

Results from all cases were made useful in plots of the sought data, as functions of the variable condition, to take steps closer to a model for prediction of the microstructure. When an appropriate model is created for the alloy's behavior, controlling processing appropriate to cast components, ranging from aircraft skin to engine parts, will be possible.

RESEARCH METHOD

Having enough data points on plots made from collected data was necessary so the dependence of recrystallization on those parameters would be clear. In this instance, a salt pot, which keeps a manufactured salt in a molten state for use in rapid heat treatments, was employed to anneal the samples rapidly. These samples were held in the molten salt for brief durations, then quickly drenched in water to capture it in its annealing state.

Once annealed in this manner, samples were cut, mounted, and polished, using various grit paper sizes and polishing cloths. The samples were etched in the Metallography Lab hood room, employing etchants that contained, chiefly, nitric and hydrofluoric acids that react differently with the phases of the alloy to highlight its microstructure.

For the decoration aging process, these samples would have been first wrapped in Tantalum foil and encapsulated in quartz tubing. These could then be placed in the heat treatment oven for a programable time and temperature.

Once etched, the samples were examined and photographed on a Reichert-Jung optical microscope. For clarifying the image or features of the image, the polarized light and direct interference contrast attachments could be employed. Photographs were then ready for point-counting.

Point counting involves laying a small 10 by 10-block grid on a transparent sheet over the photograph. When the intersection of two lines falls on a crystal, the point is counted, otherwise it is not counted. This gives a value for the percent of the foil recrystallized. This was carried out at several locations on each photograph, and then a mean value was tabulated, to insure a representation of the entire sample. Then the data from the photographs were plotted using varying types of plots. For example, plots of percent recrystallized versus temperature were made with the computer programs Excel and Kaliedograph.

To attempt an equational fit to the behavior of the metal while annealing, simulations have been and are being run and plotted with the data collected. These plots are examined and redone with a variation of a single parameter, which are narrowed until a fit the data is accomplished.

In the tabulation of slopes or confirmation of simulations results, hand-held calculators were employed. Ironically, these were instrumental in revealing minute error in simulations that could cause gross errors in the results of the simulation.

RESULTS

Unfortunately, at this stage, little in the way of results has been obtained. As mentioned, off-site results, employed as a comparison to the data obtained from the salt pot trials, have either not yet been run, or have just been received and not yet undergone examination. Once this data is collected and applied, a correlation of results is expected with the salt pot data (a lack of correlation led to an insistence on retesting and finer instrumentation of the off-site work). This is an indication that a model for predicting the rapidly annealed microstructure is near, based on the temperature, time of annealing, and heating rate.

ADVANCED COMPOSITE MATERIALS ANALYSIS

Task Order No. 218
Student Support Program
Southwestern Ohio Council for Higher Education

Joseph M. Scheckel
Wright State University

27 December 1996

Government Task Leader
Lt. Jeffery Schaff
WL/MLBM

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I would like to thank my coworkers at Wright Laboratory Nonmetallic Material Division and at the University of Dayton Research Institute for their cooperation and recommendations that were instrumental to accomplishing this Task. Special thanks goes to Lt. Jeffery Schaff, my Government Task Leader. His mentoring has aided in my preparation for the world of engineering.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The primary objective for this Task was to understand the mechanical response of composite materials in Air Force structural applications and assist in technology transition to industry. Experimental analysis of composite laminates and structures was planned to document the failure mechanisms of these high-strength, low-weight materials after experiencing a predetermined loading sequence. This loading sequence introduced a frequency dependent phenomenon known as "cycle mix." Another objective was to learn the ply orientation and stress analysis of a composite crutch designed for the permanently disabled. The final objective was to aid Wright Laboratory researchers in the transfer of composite materials' technology to local transportation officials for infrastructure applications.

In the cycle mix research, test specimens were to experience fatigue loading at one mean stress level for many cycles and then change to a different mean stress level for a different set of cycles. This loading sequence is then repeated until a specified number of these loading blocks are completed. One large block and one small block were used as test sets. Both sets were to experience the load sequence just described with the same number of total cycles, but the cycle intervals for the small block set were 1/100th of those of the first set. Therefore, the number of stress transitions for the small block set of specimens was 100 times that of the large block set. Fatigue life comparisons between the two sets were to verify a cycle mix prediction model for composites. Unfortunately, premature failure of test specimens occurred due to tab design. These tabs were glued to the ends of the specimen to avoid damage caused by the hydraulic grips.

A study was conducted on tab design to investigate two types of adhesives, materials and shapes. The adhesives investigated were Epon 828 with V-40 hardener and Epon 828 with D-230 hardener. The materials were aluminum and glass epoxy, and were either tapered or untapered. Strain gages were applied to the edges of the specimens at the tabs to find the strain distribution during static loading as this was the location of premature failure. The results showed that the two specimens with the least amount of strain were bonded with either aluminum tapered tabs and D-230 hardener or glass epoxy untapered tabs and V-40 hardener. These specimens were then fatigued with small block cycle mix loading and intermittently removed at regular intervals for microscopic investigation. Although the aluminum tabs needed frequent rebonding, this specimen type had a longer fatigue life than the glass epoxy specimen. Until a better specimen configuration is found, the cycle mix research should resume using aluminum tapered tabs and D-230 hardener.

RESULTS

Designing a composite crutch for the permanently disabled proved to be more difficult than was originally expected since the model supplied to the lab was arc shaped. The stress distribution was of little significance since the majority of bending was due to cantilever loading. A MATLAB computer program was developed to detect the ply orientation for a cylindrical composite tube based on cantilever bending stiffness. This orientation was then sent to a New England composite tubing manufacturer for prototype production. Wright Laboratory is waiting for the prototype to be sent back for stress analysis.

Unfortunately, there was little time to do research on composite infrastructure technology transfer. That program, however, appears to be excelling without additional assistance at this time.

ADVANCED COMPOSITE MATERIALS ANALYSIS

Task Order No. 218A
Student Support Program
Southwestern Ohio Council for Higher Education

John Schuck
University of Dayton

27 December 1996

Government Task Leader
Dr. David Curliss
WL/MLBC

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

This Task has involved many different duties. Initially, the Task focused on the aging of AS4/3501-6 prepreg and FM-300 resin. The study was conducted on samples that were both stored in a desiccator and open to the atmosphere for 1 month. The objective of the study was to learn how the prepreg and resin cured over time when stored in different conditions. The Task then shifted focus to the development of several different polyamide formulations. The base monomer units used were biphenyl dianhydride and 6-florodianhydride which were crosslinked with *p*-phenylenediamine and terminated using norbornene anhydride. Several different ratios of the monomer units were formulated to study the thermal characteristics of varying chain size and molecular weight polyimides. Recently, the Task has focused on the specific volume change of 3501-6 epoxy resins cured using varying cure cycles. The specific volume change is measured as a function of both temperature and pressure. Measuring the specific volume change of the resin will allow for the development of cure cycles to minimize volume changes during cure.

DESCRIPTION OF RESEARCH

The aging of AS4/3501-6 and FM-300 was analyzed using a BOMEM FTIR. This unit sends an infrared signal through a fiber optic cable to a movable probe and back through another fiber optic cable to the liquid nitrogen cooled detector. The FTIR is interfaced to a PC equipped with Lab Calc software to produce a spectrum for each scan. The software also corrects the baseline and determines peak heights of the spectrums. Using this equipment, scans and spectrums of the prepreg and resin was prepared each day for 1 month. The spectrums were analyzed to learn the peak heights of the carbonyl, primaryamine, and ester functional groups. The peak height of each functional group versus time was plotted to find if there was a correlation between the peak heights of these groups and the curing of the prepreg.

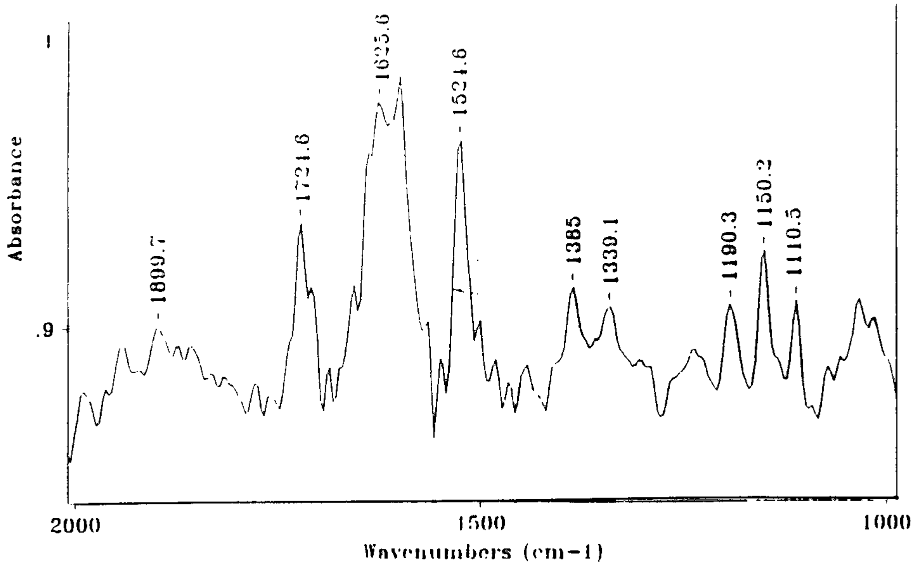

Figure 1. Typical spectrum of AS4/3501-6 prepreg

The BPDA/6FDA polyamides were formulated using 100, 75, 50, 25, and 0% BPDA/6FDA ratios with chain lengths of two, four and eight units. The desired ratio and chain length polyamide was prepared by refluxing the appropriate amounts of BPDA, 6FDA, and *p*-PDA in methanol until the solution was clear. The solution was then stirred and NA was added. The methanol was evaporated and the polyamide formed by placing the solution in an oven under vacuum and heating to 85°C. The polyamides were then sent for thermal analysis by another technician.

The specific volume change of 3501-6 resin was determined using a GNOMIX pressurized volumetric dilatometer. This apparatus is used to find the pressure-volume-temperature relationship of polymers. A 0.5-1.0 g sample is placed in a mercury filled cell and a hydrostatic pressure of silicon oil is applied to the sample by flexible metal bellows. The sample volume is changed by pressure or increasing temperature causing the bellows to deflect. An LVDT measures the bellows displacement that corresponds to a change in the sample volume. A sample of resin for each cure cycle was tested to analyze the volume change with temperature. A plot of specific volume change versus temperature was prepared to decide the optimum cure cycle.

RESULTS

The results, of the aging study of AS4/3501-6 prepreg and FM-300 resin, were inconclusive. The plots of the functional group peak heights versus time showed no definitive correlation between the peak height and how the prepreg and resin cured with time when stored in different conditions. The thermal analysis of the polyamide formulations has yet to be completed and the optimum cure cycle for 3501-6 epoxy resin is still under investigation.

EVALUATION OF COATINGS FOR CERAMIC MATRIX COMPOSITES

Task Order No. 219
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer Finch
Wright State University

27 December 1996

Government Task Leader
Mr. Larry Zawada
WL/MLLN

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TASK ASSIGNMENT

The requirements of Task 219 were to assist the technical initiator, Mr. Larry Zawada of the Materials Directorate at Wright-Patterson Air Force Base, in evaluating the high temperature performance of an advanced coated composite under thermal fatigue conditions. Experiments were performed using a thermal cycling test system in the laboratory. Several thermal profiles were used to characterize the role of temperature, delta T, cycle count, and time at temperature on the integrity of the coating and ultimately on the room temperature residual strength of the material. Tensile testing and microscopic characterization showed no degradation of the coating nor the material properties following thermal testing.

Continued support in the research of advanced materials is driven by the need for greater efficiencies in military aerospace turbine engines. Engine and exhaust components constructed from materials that operate at higher temperatures, which have increased strength-to-weight ratios, and greater stiffness over currently available materials, will provide the most significant improvements in the performance of advanced military aerospace turbine engines. One class of materials that has shown potential for replacing current high-temperature nickel-based superalloys in certain aerospace applications, particularly those with demanding thermal and acoustic environments, is ceramic matrix composite (CMC) materials. CMC's do suffer from oxidation at elevated temperatures, and often require an exterior coating for extended life. However, unlike their coated superalloy predecessors, coated CMC's tend to have a minimized coefficient of thermal expansion mismatch and therefore are not as likely to suffer degradation. Due to these unique material properties, there has been a recent increase in activities aimed at using coated CMC's such as silicon carbide fiber-reinforced carbon in such applications as exhaust nozzle flaps in afterburning turbofan engines. The goal of these activities is to maintain increased efficiency while providing greater durability over metal parts.

RESEARCH

1) Material

This Task was devoted to testing coated silicon carbide fiber-reinforced carbon (SiC/C). The reinforcement used in the composite is Nicalon® silicon carbide fiber. Fiber architecture for the material consists of 8-harness satin weave fabrics laid-up in a 0°/90° fashion. The matrix is mostly resin based inhibited pyrolitic carbon, which is then densified by the infiltration (CVI) of addition carbon. The entire composite structure is coated with a thermal barrier coating. The coating layer, silicon carbide (Chromalloy RT42), is plasma sprayed to the substrate.

2) Test Procedures

Before the SiC/C material specimens were tested, each had to be accounted for and prepared. The specimens were accounted for by being logged into the WL/MLLN's data via the network computer. Each specimen was then prepared for testing by (1) ultrasonic scanning to detect any defects, (2) measuring the length, width, and thickness, and (3) grinding the tab surfaces. The coated SiC/C material coupons were then thermally cycled, tested for residual properties, and examined microscopically.

The thermal fatigue tests were performed using a resistance heated tube furnace, with a computer-controlled in line pneumatic actuator to position the specimen in and out of the furnace hot zone. Barber-Coleman temperature controllers with a PC-based data acquisition system fed from S-type thermocouples allow the thermal cycle to be defined by the specimen temperature. The software was programmed to move the specimen out of the furnace when the specimen temperature reached the maximum desired temperature, and into the furnace when the minimum test temperature is reached. The data acquired during testing included maximum and minimum temperature versus cycle count, and the thermal profile during heating and cooling. The tests were performed using different cycle counts and different maximum and minimum temperatures.

After the specimens were thermally cycled, they were tensile tested at room temperature. A horizontal servo hydraulic test machine, with load and displacement transducers, was used as the testing apparatus. The data obtained from by the transducers were recorded and stored by a computer, which is directly connected to the testing apparatus. The stress-strain behavior, measured, recorded, and plotted by computer for each tensile specimen, illustrates such residual properties as strength, modulus and strain at failure. The magnitude of the properties measured on thermally cycled specimens compared with the properties measured for as-received specimens, gives insight to the rate of degradation and the overall durability of the material.

After residual strength testing and data reduction, metallographic evaluation was done on the thermally tested specimens. Representative specimen sections were cut, mounted, polished and examined microscopically for indications of damage to the coating and the material structure. Both optical and electron microscopes were used to examine and document the microstructure. Image analysis software was then applied to the images taken from the tested material to measure fiber and phase volume fractions, coating thickness, and crack length to document any damage from the thermal cycling.

RESULTS

The residual strengths measured for all test conditions fell well above the design stress for the exhaust nozzle application being considered for this material. Additionally, the results of the residual strength tests performed on each type of laboratory tested specimen showed no loss in strength due to thermal fatigue testing for either duration tested. SEM and optical microscopy studies revealed no distinct differences in the fracture surfaces or the microstructures of the thermally tested specimens, which supports the observation of no loss in strength from any of the test conditions. Nearly identical fiber volume fraction measurements for all tested specimens verified that there were no differences in the original material. Coating thickness measurements showed no degradation for the thermal fatigue specimens.

CONCLUSIONS

High temperature durability of an advanced coated composite, SiC/C under thermal fatigue conditions was evaluated. It was determined that coated SiC/C suffers no loss in strength under the conditions tested. In addition, the results generated in the laboratory suggest that the coated material investigated should perform above the design specifications for exhaust nozzle components in an after burning turbofan engine.

RESEARCH IN NONLINEAR OPTICAL MATERIALS

Task Order No. 220
Student Support Program
Southwestern Ohio Council for Higher Education

David Small
Wright State University

11 December 1996

Government Task Leader
Dr. David Zelmon
WL/MLPO

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Special thanks go to Dr. David Zelmon for his infinite patience in teaching the basics of optical materials and optical processes in crystals and his generosity in sharing credit. Thanks also to Dr. Pat Heminger, Bob Dennison and Dr. Ken Hopkins for allowing a student to be part of their branch, which is known and respected both inside and outside Wright Lab. To all the scientists, engineers and secretaries who make everyone feel welcome, a big thank you.

The experience of working in the Materials Lab for the past year has been especially beneficial. Three publications have been turned in for publication or presentation. A total of six papers, with more to come, has been an unexpected reward for working in the lab, as is a possible trip to the CLEO meeting in Baltimore, MA. Because of working at Wright Labs, my future is much brighter than could ever have been imagined, and for that, a big thanks goes to the SOCHE Student Support Program.

TASK ASSIGNMENT

The Task recently finished was carried out in the Non Linear Optics (NLO) lab that is part of MLPO in Wright Laboratory, Wright-Patterson Air Force Base. The nature of the work is interdisciplinary, with the NLO group consisting of physicists, electrical engineers and chemists. The goal of the research is to develop, synthesize and characterize materials for frequency conversion applications.

The most important Task in the lab is measuring indices of refraction of crystals. The values of the indices of refraction are very important to people who wish to build devices out of new materials. To build a workable device, the indices of refraction must be known to within .0001 for all wavelengths in the .4μ to 12.5μ spectral range. Hot bodies radiate with spectral distributions dependent on their temperature. Hot exhaust from an aircraft would, for example, radiate with a spectrum characteristic for its temperature. This gives the enemy a chance to track their airplanes. The materials being examined are mainly wanted for a frequency conversion application known as optical parametric oscillation (OPO). An optical parametric oscillator exhibits a nonlinear property. Monochromatic light of one frequency enters the OPO, but the output beam contains a component of a different frequency, the frequency being dependent on the direction of propagation the wave through the crystal. The Air Force wishes to develop crystals to convert the frequency of light for use in devices designed to mask the heat signature of their airplanes. The device must convert the single frequency laser radiation of a high power laser, most likely a CO_2 laser, to a continuous spectrum of radiation so that the enemy cannot see their airplanes in the air. The atmosphere has an absorption band between 8μ and 10μ, so the ability to tune the CO_2 laser between 3μ and 8μ and between 10μ and 12μ is most important. The crystal will only be useful over a small portion of the spectrum. In many of the possible directions of propagation through the crystal, the output intensity will be so low that using the crystal for frequency conversion is not possible. A locus of angles describes the direction of propagation where the output intensity is high. These angles are called the phase matching angles. Knowing the phase matching curve is very important for building a device. These angles can be measured, but they can also be calculated. To calculate these angles, the three indices of refraction of the crystal must be known over the frequency range. The indices are measured using a spectrometer by the minimum deviation method, which requires two separate measurements. The first is the apex angle of the prism. The second is the minimum deviation angle, which is frequency dependent, so it must be measured at .05μ increments over the .4μ to 5.5μ spectral range for each crystal with each of two polarizations five to seven times each. The indices are then calculated, and fit to a curve using a FORTRAN program written by our lab and reported in optical science journals. During the past 12 months, three such publications have been prepared in the WL/MLPO Non Linear Optics Lab, two of which are to be presented at the Conference on Lasers and Electro Optics (CLEO) in Baltimore in May.

Crystal growth is another active area of research in the lab. Crystals of new materials, engineered by chemists to have large optical nonlinearities are synthesized and small crystals grown using the solution growth method. Because these materials are new, often the solvent used and the pH. must be adjusted to produce the largest crystals. After the crystals are harvested, they are sorted by particle size and tested for their phase matcheability in a Kurtz powder test. This is a new capability of the lab, as the necessary YAG laser only arrived this year. The materials being investigated currently are mostly semi-organic compounds synthesized using amino acids such as glutamine and carnosine and metal atoms such as Zn and Cu.

Other projects under way include extending the capabilities of the index measurement experiments to measure the indices out to 12μ, designing an experiment to measure the change of the index of refraction as a function of temperature over a range of frequencies, and designing an experiment to measure the phase matching angles in a crystal ball directly.

MATERIALS AND PROCESSES FOR SYSTEM SUPPORT

Task Order No. 221
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Cassoni
Wright State University

27 December 1996

Government Task Leader
Mr. Jim Folck
WL/MLSE

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Thanks to the staff and engineers of the WL/MLSE group for making my adjustment to the Task comfortable. Special thanks are given to MSGT Bryan Cramer, Mr. Doug Carter, Mr. Ronald Kuhbander, Mr. Jim McKiernan, Mr. Jim Folck, and Mr. Mark Forte. My efforts have been productive due to their experience and help.

TASK ASSIGNMENT

Over the past work term, three projects have been concentrated on. These include project 096, the evaluation of a closed cell structural foam; project 140, bondline monitoring and control, and F-16 fatigue crack repair. Each of these will be considered individually.

Project 096, the evaluation of a closed cell structural foam has been an ongoing project that is investigating the mechanical properties of closed cell foam. Particularly, the strength and modulus are being calculated. It is intended eventually to develop into a baseline for foam in the support of military aircraft. Due to the differences inherent in thermoplastic materials relative to metal alloys, much has been learned. Three test methods have been employed to detect the structural properties of the foams. These include flatwise compression, dog bone tension, and compression plate shear. All of the tests are being done at room temperature, 180° F, and 212° F for both dry aged specimens and those aged at 85% relative humidity to saturation by weight. Due to involvement on other projects, 096 has been delayed in completion. The final specimens are currently being tested and a final data package will be constructed.

Project 140, bondline monitoring and control, involves the placement of thermocouples and heater elements in the bondline of composite patches during composite repair procedures. This has the advantage of getting accurate temperature readings of the repair area during cure as well as providing an integral heating system that could lower thermal gradients through the adhesive layer. This project began with attempts at coating bare thermocouple wires with an adhesive layer to prevent shorting of the wires when in contact with the aircraft skin. This proved difficult, as the small diameter of the thermocouple wires (1-3 mils) created large capillary forces that caused the adhesive to coalesce into beads. This method was eventually abandoned in place of precoated thermocouple wires that were slightly heavier. The second phase of this project involved the investigation of the mechanical degradation of an adhesively bonded structure when thermocouple wires were introduced into the bondline. Floating roller peel, static lap shear, and fatigue lap shear were used as the test methods. The static lap shear and floating roller peel was done at both room temperature and -65° F, while the fatigue lap shear was done at only room temperature. Control specimens were used throughout the testing to eliminate extraneous variables. This project is currently closed due to higher priorities on other projects.

The F-16 fatigue patch project involved all facets of repair of a fatigue cracked fuel vent hole. The process involves surface preparation, priming, and adhesive bonding. Surface preparation of the aircraft repair area includes grit blasting of the surface followed by a Silane surface treatment. A grit blast containment system was constructed to contain the grit and has proven to work well. The curing of the Silane and primer layers was accomplished via a heat lamp system developed in our lab. It has lowered thermal gradients across the aircraft skin significantly when compared with the former system. To test the current heat lamp system, a series of thermal surveys was done on a wing section. The settings of each bulb were marked for future reference when doing the repair in an actual field scenario. This project is currently on hold since the requested aircraft have been repaired.

Over this past work term, I have gained a wealth of knowledge and have matured as an engineer and a technician. My involvement in each of these projects has given me the opportunity to input as an engineer and a technician. The grit blast cabinet designed and built in this group might be submitted as a co-patent between MSGT Bryan Cramer and myself. The heat lamp system has proved to have significant application potential. Overall, it has been a wonderful learning experience.

MATERIALS AND PROCESSES FOR SYSTEM SUPPORT

Task Order No. 221A
Student Support Program
Southwestern Ohio Council for Higher Education

Christopher Michael Penick
Wright State University

27 December 1996

Government Task Leader
Mr. Jim Folck
WL/MLSE

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I would like to take this opportunity to acknowledge several people who have made my stay on the base a very enjoyable experience. Mr. Jim Folck should be recognized and thanked for his faith in my abilities. I wish to extend gratitude to Mr. Ron Kuhbander and Mr. Jim "Mac" McKiernan, both of UDRI, for their support, wisdom, and guidance. I would also like to thank my SOCHE compatriots, Belinda McKinney and Brian Wilhelm. Also, I would like to thank the office staff of SOCHE, particularly Mrs. Wanda Vogler and Mrs. Pamela Douglas.

DESCRIPTION OF TASK ASSIGNMENT

The Task for WL/MLSE was to find the effectiveness of adhesive repairs to aircraft components. These repairs come in a variety of shapes and sizes from ballistically impacted wing sections to hairline fatigue cracks in areas of stress concentration. Although this is the end goal, most of the work takes the form of in-house specimen preparation for mechanical testing. Doing mechanical testing is necessary so that affecting a repair upon an actual aircraft structure may be possible. Therefore, the bulk of the Task is in actual specimen fabrication, heat and moisture conditioning, adhesive curing and mechanical testing.

The major fields of interest at this juncture are on studying the effects of moisture and heat upon bonded panels and composite panels as well as the ratio between adhesive and hardeners used in the specimen fabrication. Several questions are worth asking. How much moisture will some of these specimens retain, and how long does it take to gain that much moisture? What is the best possible way to relieve the excess moisture from the specimen, and how long will it take to lose enough moisture to be an effective specimen again? How will this specimen handle under mechanical testing? How much is too much hardener? Is it better to add more hardener for a quicker cure time or will that hurt the mechanical properties of the specimen? These questions are just a few of the superficial ones that need to be answered.

To understand why this work is important, adding an example at this point may be necessary. The B-2 Stealth Bomber currently has a problem with a panel that is found near the blast nozzle for its two powerful engines. The panel is a graphite composite panel and takes on moisture quickly in a humid environment. If the B-2 Stealth Bomber is flown with these panels full of moisture, then the panels will blister, be ruined, and need to be replaced. Therefore, the object is to dry these panels before flight. However, this is difficult because the panels are attached to the plane. This makes the job of drying out the panels before flight very difficult. Using a drying oven on the part is not practical since it is attached to the plane, therefore, the only other method of drying the panel that is being considered is the process of desiccant bagging. This process requires that the panel be as completely covered by desiccant bags in as airtight of a seal as possible. The desiccant in the bags will absorb all moisture that is on and given off the panel and contained in the airtight seal. The major problem with this that it takes an inordinate amount of time to dry properly. As it is, the B-2 Stealth Bomber must sit with these desiccant bags on it for 48 to 72 hours prior to any flight. This is not convenient and practical.

Another example can be given in the flight hanger. An aircraft has been found to have a fatigue crack in its wing. It is grounded and the technicians set to work on patching it quickly so it can fly another sortie or two. They want to have it patched and ready to go as quick as possible, but the adhesive for the patch requires that a heat blanket be placed on the patch and allowed to cure for 24 hours. To speed up the process, they add more hardener to the adhesive in hopes that it will cure quicker and fly sooner. In fact, it does cure quicker and is ready to fly in 12 hours. However, is the patch 100% ready for flight loading conditions? Will it rip off in flight? Will the crack be allowed to propagate due to an ineffectual patch? Will the pilot and plane be in jeopardy on the next sortie?

These two examples may provide the explanation for why creating test specimens in controlled environments and test them in particular ways is necessary. The results from those tests may save lives, money and repair time if their results are properly analyzed and initiated into the aircraft battle damage repair process.

DESCRIPTION OF RESEARCH

The research that is conducted in-house is aimed at trying to answer the questions posed by the two previous examples. The first step in answering those questions is to prepare the sample specimen. For these two specific cases, the specimens were fabricated from a panel of material that comprises the makeup of the exhaust port panel on the B-2 Stealth Bomber. The second specimen was a graphite panel laid up in epoxy to create a composite panel.

The methodology employed by the researchers consists of specimen conditioning. Understanding what happens to the specimen is necessary for them as it undergoes heat and moisture conditioning. Therefore, they can make best guess estimates against which the actual data collected will be compared.

The next step is to test the various specimen according to the directions given by the senior researchers. These include moisture studies where the specimens are kept in humidity cabinets for long periods of time and periodically weighed to find out how much moisture they have absorbed. It also includes drying studies to find how long it takes the given specimen to lose that moisture in a drying oven or with desiccant bags in different atmospheric conditions (i.e., dry air, moist air, warm air). It may also include, as the hardener to adhesive ratio study has, the use of mechanical testing equipment to run various types of tests. These tests may include inplane shear tests that are very much like a standard tensile test except that the directions of the composite layers are at 45° to the axis of pull. As well, doing a wedge test may be necessary. This test consists of driving a wedge between two bonded panels to initiate a crack to grow between the two panels and then subjected to a moist atmosphere. They are checked frequently and the length of the crack is measured to detect how much effect humidity has on the adhesive between the two panels when a crack is present. The final test that is frequently done is a floating roller peel test to test the resistance of the adhesive to failure.

The equipment used varies from the average toolbox to the high-tech mechanical test equipment. There are heated presses for the fabrication of the specimen. These allow a specimen to set at high heat and pressure during the cure time of the adhesive so that the panels will bond properly. There are grit blasters for the preparation of the sample surface and primer spray booths, which are used for the same reason. There are several Instron mechanical testing machines to choose from when doing mechanical testing. Some are controlled by conditioners, amplifiers and similar old-technology controllers whereas some are controlled by sophisticated computer systems and personal computers. The importance in the accuracy of the results is the main factor in determining the sophistication of the machine to use for a particular test. As far as the mechanical tests done for the determination of the importance of hardener to adhesive ratio are concerned, using the old-technology machines to produce a pen plot of the results is possible. From the rudimentary pen plot, detecting several characteristics for the specimen tested during the reduction of the data is possible.

Once the tests are complete and the data has been reduced, learning the actual real-world results is possible. For instance, it has been shown, so far, that drying the panels on the B-2 Stealth Bomber with a drying oven versus desiccant bagging the section is best. While this is impractical in the real world, it may lead to research on developing a technique that is more practical. As well, it has been accurately determined how long it takes to dry a specimen using the desiccant bagging system in various atmospheres and conditions. This will be a help the flight technicians who are in charge of taking care of the B-2 Stealth Bomber program. Also, it has been shown that, in regard to the ratio of hardener to adhesive used, using less hardener will produce a better bond, but take longer to cure. If a shorter cure was wanted, and more hardener was used, the bond would be weaker than it should be under better conditions.

RESULTS

The experience here has been very exciting and helpful. The experience has been helpful in learning the test techniques and mechanical test machines. It has also been pleasing to see real world applications for most of the testing and results.

MATERIALS AND PROCESSES FOR SYSTEM SUPPORT

Task Order No. 221B
Student Support Program
Southwestern Ohio Council for Higher Education

Brian P. Milligan
Wright State University

27 December 1996

Government Task Leader
Mr. James L. Folck
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank Mr. Jim Folck for providing the opportunity for me to work as a student research assistant in my field of study. I would also like to thank Ron Kuhbander and Jim McKiernan for my training and their assistance with laboratory work.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

For this Task, short in-house investigations were done to evaluate various materials and processes for Air Force applications including repair and maintainability. These investigations included fabricating, testing, and evaluating experimental material test specimens. Evaluations of current practices in advanced composite materials repair and maintainability was also conducted.

Some Air Force projects included studies of various patching methods, evaluation of a self contained phosphoric anodizing system, and a composite moisture study. The patching methods were studied to learn which surface preparation would yield results suitable for aircraft repair. Since these repairs will be conducted on battle damaged aircraft, the feasibility of doing the various methods of surface preparation on location was considered. For this project, a PACS unit (Phosphoric Anodizing Containment System) was used during surface preparation. The results from the PACS unit were then compared with other methods of phosphoric anodizing to decide the effectiveness of the self-contained unit. A composite moisture study was also conducted to learn how a saturated composite would behave when exposed to elevated temperatures.

The in-house investigations include fabrication and testing of wedge panels and the testing of adhesives using various scrim cloths for fracture toughness. Wedge panels are tested to study the effects of moisture on the performance of the adhesive. The results are then used to decide which adhesive would be most suitable for aircraft repair. The fracture toughness test is used to study the effects of various scrim cloths (used to maintain a uniform bondline thickness) on the performance of the adhesive. The results are then used to establish which scrim cloth has the best performance characteristics, which then will be applied to other projects.

DESCRIPTION OF RESEARCH

One of the most important steps before bonding any type of panels together is the surface preparation of the aluminum. Two methods of surface preparation are used. The first method was the grit blast/silane process and the second was the phosphoric anodizing process.

The first step in the grit blast/silane process is solvent degreasing. This step removes gross contaminants such as oils from the surface to be treated. Degreasing was accomplished by wiping the surface with clean wipes dampened with solvent. Methyl ethyl ketone (MEK) was primarily used. The next step is Scotchbrite abrading. This step removes the old oxide layer from the aluminum surface. The aluminum was hand abraded using 3M Company Scothbrite pads wet with MEK. The surface was abraded until shiny in appearance. The surface is then solvent cleaned using aerospace wipes to remove any residual contaminants from the abrading. The panels are ready for the grit blast step. This step produces a macro-rough surface with greatly increased surface area. Fifty-micron aluminum oxide grit was used in a glove box with a portable blaster. The aluminum panel received a light grit blast until the surface had a uniform frosted appearance. Next, the residual aluminum oxide grit was removed from the surface by spraying it with dry, oil free nitrogen at 80 psi. The aluminum panel is ready for the silane hydrolysis. This step converts the silane coupling agent's siloxane groups into silanol groups that can couple with the oxide on the aluminum surface to be treated. For this process, 1% by weight Dow Corning Z-6040 silane in deionized water was continuously stirred in a glass beaker for 1 hour using a stir bar and a magnetic mixer. The aluminum was flooded with silane, using a camel's hair brush to keep the surface wet for 10 minutes. The excess silane is then removed from the surface and the panels are dried at 200°F for 1 hour in a circulating air oven. Once cooled to room temperature, the panels are then primed with BR 127 adhesive primer per manufacturer's recommended practices. The aluminum panels are ready for bonding.

The phosphoric anodizing surface preparation (PAA) follows some steps from the grit blast process. First the panels are solvent degreased, Scotchbrite abraded, and solvent cleaned as they were in the previous process. Next, the panels are processed using a PAA tank that contains a phosphoric acid anodizing solution that will treat the aluminum surface. Once treated, the panels are rinsed and dried in an air circulating oven at 140°F for 10 minutes. The panels are ready to be primed as they were in the previous process.

These panels were then bonded using roll film adhesive in a hydraulic press with a positive pressure of 35 psi. Next, they were milled into 1 x 6 inch specimens. A wedge was driven into one end and the initial crack length was scribed on the side of the specimen. The specimens were then placed in a humidity cabinet and crack growth was measured at set times. When the test was concluded, the data was compiled and submitted to the engineer in charge for analysis.

A composite moisture study was conducted to study the performance of two composites at elevated temperatures. First, the composite specimens were saturated with water in a humidity cabinet. The specimens were then exposed to various elevated temperatures for 5 minutes. Once this was completed, the specimens were c-scanned to reveal the internal structure of the composite. This test allowed the engineers to find the temperature at which each composite will delaminate while in a moist environment. This test was conducted to decide the feasibility of replacing a composite that is already in use with a better performing composite.

Another test conducted was the adhesive fracture toughness test. For this test, two aluminum beams were bonded together using adhesive and various scrim cloths. One end of the beam was then placed under a tensile stress while the crack growth was monitored. An Instron tensile testing machine and X-Y plotter were used for this test. The plotter was set up to plot the load applied to the specimen versus the extension of the tension testing machine. Various intervals of crack growth were marked on the plot. When all of the plots were finished, they were compared to find out which scrim cloth yields the best performance characteristics.

RESULTS

Many things were learned during this Task. While handling many different materials, some of which were hazardous, laboratory safety was discovered. Through various tests, interpreting data/plots and incorporating the results into practical applications was learned. While working closely with engineers, the methodology of conducting a test was also learned. Since there is a lot of hands-on laboratory work, a great deal was learned about working with sophisticated equipment and heavy machinery. This Task provided a great deal of learning about the overall process of conducting tests.

RESEARCH ON HIGH TEMPERATURE INTERMETALLIC ALLOYS

Task Order No. 222
Student Support Program
Southwestern Ohio Council for Higher Education

Michael A. Jackson
Wright State University

12 December 1996

Government Task Leader
Ms. Monica Stucke
WL/MLLM

ACKNOWLEDGMENTS

A thanks is needed for all of those at Wright Labs who contributed to the learning experience over the past year. Some people included are Mr. Bob Lewis, and Eric Fletcher whose knowledge of metallography and specimen preparation was a tremendous help for the current Task. Thanks to Mr. Scott Apt, Ms Luann Piazza, and John Woodhouse for their expert knowledge in electron microscopy, and Dr. Young Won Kim and Dr. P.R. Subramanian for their excellent leadership and teaching abilities. A special thanks goes to Ms. Monica Stucke for making this Task possible.

GENERAL TASK DESCRIPTION

The description of work for the current Task is for the sample preparation and heat treatment of intermetallic alloys for metallographic examination. The Task was subdivided into smaller sections that generally needed from 1 week to several months to complete and was directed by either Dr. Kim or Dr. P. R. Subramanian. These smaller assignments were the basic building blocks in the completion of the overall goal of the Task.

The applications for the alloys studied are within the aerospace and automotive industries. In the aerospace industry, the quest for lighter weight components and ever increasing operating temperatures of jet turbine engines is a focus of today's research by DOD contractors and civilian companies alike. The realized material for the application would have to exhibit high tolerance to oxidation and creep, and have a low density, all of which contribute to a higher performance of the engine. The new material may find its way into applications involving the next generation fighter aircraft.

DESCRIPTION OF RESEARCH

The workload consisted of the heat treatment, metallographic examination, and microscopic examination of experimental alloys. Heat treatments included using both the open air and argon furnaces. The heat treatments lasted as long as 500 hours. The heat treatments were used for several reasons, including, but not limited to the following; refining the microstructure, oxidation studies, growth rates of lamellae and grains, and recovery of the microstructure. After the completion of the heat treatment, the metallogrpahic preparation of the specimen was done to facilitate one of many examination techniques.

These techniques included both the macroscopic and microscopic examination of the microstructure and to a limited extent, the mechanical properties of the alloy. An optical microscope was used for low magnification studies (50x to 500x) of the microstructure. A Leica model 360FE Scanning Electron Microscope (SEM) was used for high magnification studies (500x - 50,000x). For the qualitative determination of the composition of the studied alloys, Back scatter electron imaging (BSE) and electron dispersion spectra (EDS) analysis was used that lead to a total of approximately 200 hours of SEM time. The above microscopic instruments were used to help determine the mechanism by which deformation occurs in the alloy during mechanical testing. When a suitable microstructure was found, larger sections would be treated similarly so testing specimens could be made from the material for strength evaluation at various temperatures. This testing was completed using a compression regime and a vacuum furnace for high temperature tests. Data analysis included writing small programs to reduce the amount of collected data, and then calculating the various strength characteristics of the test, i.e., yield strength, elasticity modulas, elongation, and reduction of area.

While researching heat treatment methods for the new materials, a computer system was procured for the testing of a new software package being developed by Wright Laboratory MLIM. The software would collect data from the furnace controllers and store this data to disk for later retrieval and use. This involved many hours in the heat treatment facility wiring the new system and trouble shooting the software with the engineers developing it. This system provided valuable furnace data on cooling rates achievable by the furnace.

A small project involving the failure analysis of high cycle fatigue specimens was completed within the Task. This used the SEM to identify the crack initiation and propagation paths of the material that lead to failure. This was correlated with the number of cycles to failure to gain a larger understanding of the fatigue properties of these new intermetallics.

RESULTS

Numerous relationships between the composition, heat treatment, stress, strain, fatigue cycles to failure, hardness, and aging were all studied during the Task. All are included in the characterization process of the materials. The data was given to the lead engineers to make the appropriate theoretical studies from which new tests and alloys are developed. The testing and development of these alloys will one day yield a superior material for use in wide ranging applications including, but definitely not limited to the aeronautical and automotive industries.

OPTICAL PROPERTIES OF POLYMERIC MATERIALS

Task Order No. 223
Student Support Program
Southwestern Ohio Council for Higher Education

Max D. Alexander, Jr.
Wright State University

27 December 1996

Government Task Leader
Dr. Robert J. Spry
WL/MLPB

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TASK ASSIGNMENT OBJECTIVE

The major objective of this Task will be to develop electroluminescent polymeric devices. A secondary objective will be to develop theory and experiments to analyze other polymer electro-optical devices.

Completion of the In-Plane Optical Attenuation Study

The in plane optical absorption constant, α was measured and correlated to molecular orientation in a copolyester planar waveguide. The copolyester film, **Figure 1**, manufactured by DuPonte Lab Circleville, Ohio was uniaxially stretched to 3.5 times its initial length at a temperature slightly above the material's glass transition temperature (T_g). A sample of the film was stuck to a 2-micron SiO_2 surface layer on a silicon wafer. A Metricon 2010 prism coupler was used to measure the reflected intensity of a 632.8 nm He:Ne laser beam at various incident angles **Figure 2**. At discrete angles, the beam enters a "mode" in which total internal reflection occurs inside the film, and thus the reflected intensity becomes a minimum.

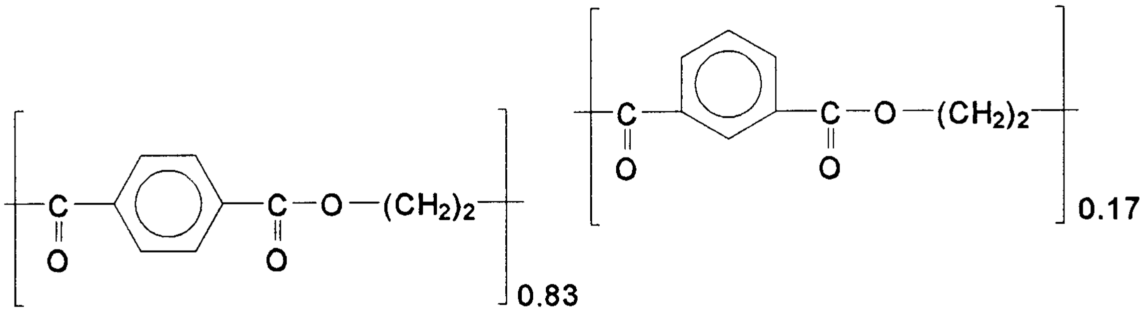


Figure 1. Random copolyester film, poly(ethylene terephthalate-co-isophthalate)

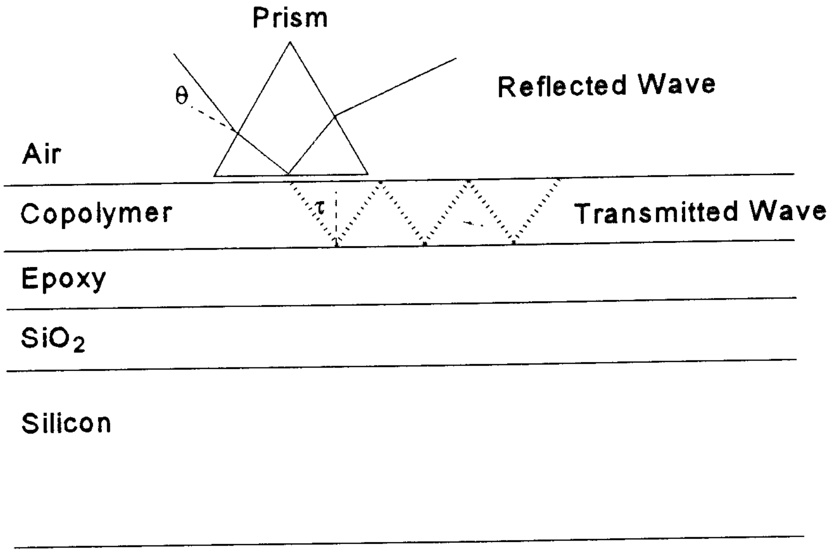


Figure 2. Layout of Metricon Prism Coupler

Knowing the angles at which the minima occur the film thickness and indices of refraction can be calculated. Rotating the film 90° and varying the polarization of the laser beam the index ellipsoid can be measured **TABLE 1**.

Propagation Direction	Parallel to the Stretch Direction	Perpendicular to the Stretch Direction
Refractive Index n	1.5464	1.6545
	1.5427	1.5429
Calculated Film Thickness (microns)	7.2292	7.1802
	7.3183	7.3357

Table 1. Indices along the axis of the index ellipsoid for the polyester copolyester waveguide.

The attenuation coefficient can be measured by positioning the prism at an angle at which total internal reflection occurs. A sheet of Technipan® film is placed on the copolymer surface and the image of the waveguide mode streak recorded. This film is then developed and scanned into a computer where the intensity of the streak along the propagation path is measured. The rate at which the intensity of the propagation streak decreases is related to the inplane attenuation coefficient, and can be correlated with the molecular orientation by comparison of films taken with TE and TM polarizations parallel and transverse to the stretch direction. **TABLE 2** details the results of this study.

Mode Number and Direction with respect to Stretch	Attenuation Coefficient
Parallel TE_0	1.90
Parallel TE_2	2.46
Parallel TE_4	3.34
Parallel TE_6	4.46
Parallel TM_0	2.05
Parallel TM_2	2.08
Parallel TM_4	2.02
Parallel TM_6	1.94
Transverse TE_0	3.16
Transverse TE_2	3.81
Transverse TE_4	4.83
Transverse TE_6	5.62
Transverse TE_8	6.80
Transverse TE_{10}	7.77
Transverse TM_0	2.01
Transverse TM_2	1.97
Transverse TM_4	2.03
Transverse TM_6	1.98

Table 2. Results of Attenuation Coefficient Study

This study has determined that the inplane attenuation coefficient increases with increasing mode number for TE polarization, while the attenuation coefficient is insensitive to mode number for TM polarization. This result suggests that TM polarized light may be more suitable than TE polarized light in polymeric waveguiding applications.

PMMA Waveguide Study

The waveguide characteristics of a PMMA film adhered to a SiO_2 substrate were investigated to detect the thickness and index of the film. The measurement configuration was the same as shown previously in **Figure 2**, with the following data obtained. The film was oriented in two directions 90° from each other that allows for the calculation of the index ellipsoid. **Figures 3** and **4** show the mode patterns at an arbitrarily chosen 0° while **Figures 5** and **6** show the mode patterns 90° from the initial measurement. The TE measurement determines the in plane index and the TM measures the out of plane index.

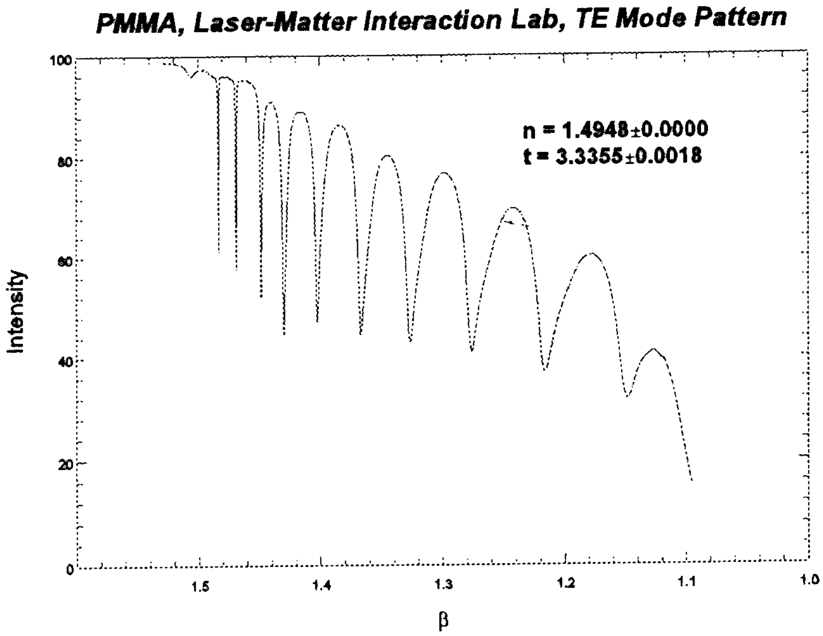


Figure 3. TE Mode Pattern of PMMA at 0°

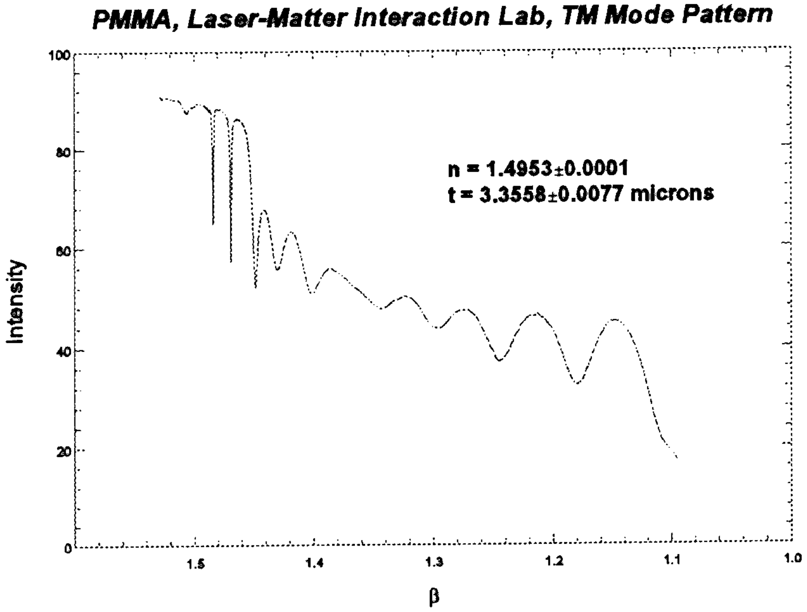


Figure 4. TM Mode Pattern of PMMA at 0°

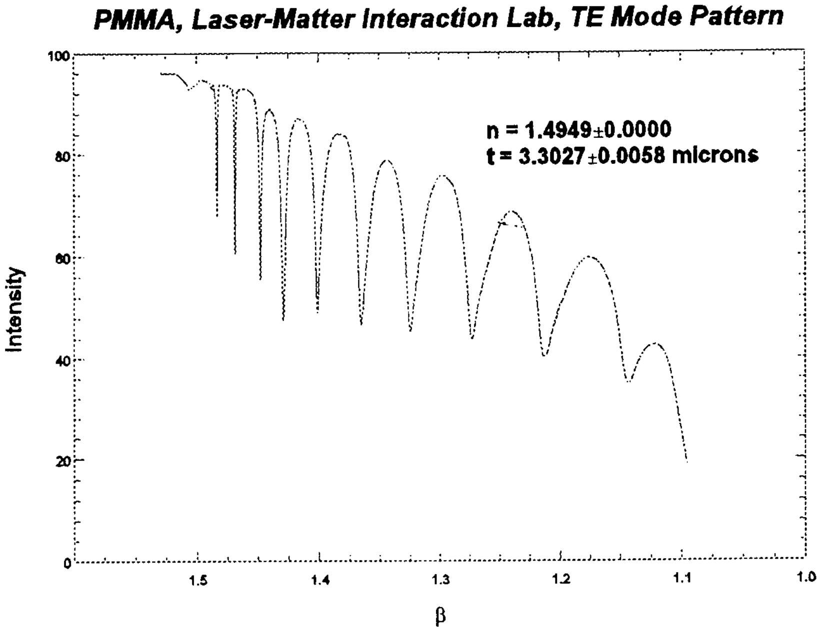


Figure 5. TE Mode Pattern of PMMA at 90°

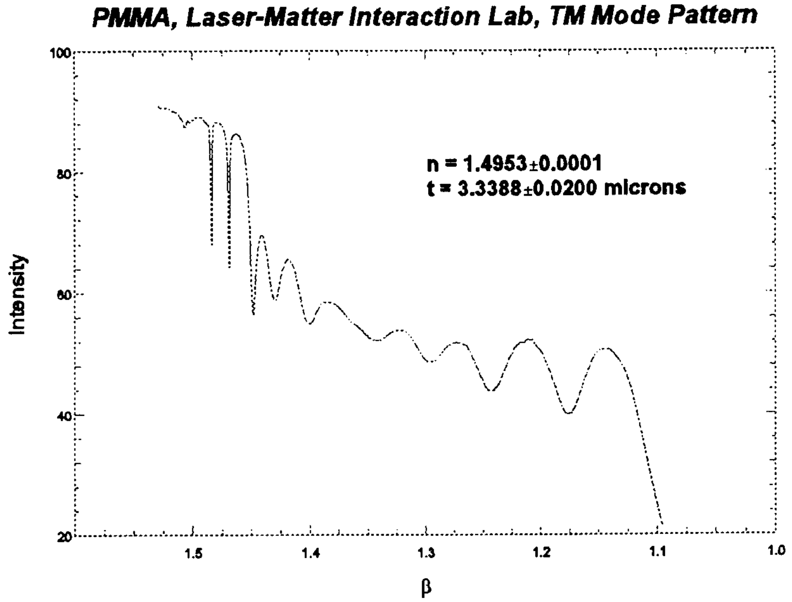


Figure 6. TM Mode Pattern of PMMA at 90°

The in plane and out of plane indices were determined to be identical with a value of 1.495 while the average film thickness was measured to be 3.33 microns. These measurements were done in support of work done at Laser Matter Interaction Labs.

Oxydecly-6F-PBO Luminescent and Properties Study

The optical properties of Oxydecly-6F-PBO, **Figure** 7 were studied to determine the suitability of the film for the manufacture of electroluminescent devices.

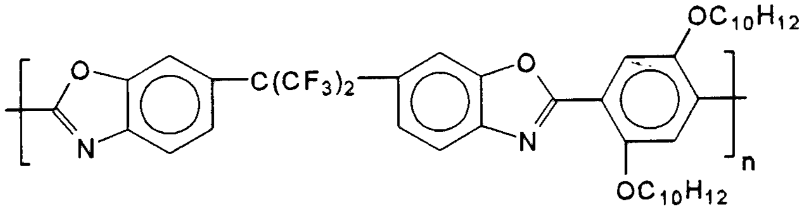


Figure 7. Structure of Oxydecly-6F-PBO Polymer

Optical loss measurements were done on the film as previously described, however only the 0th mode was measured.

Figure 8 shows the Beer's Law type attenuation in the TE configuration while **Figure 9** shows the attenuation in the TM polarization. The sample was determined to be amorphous with a higher optical loss (10.2 dB/cm vs. 9.37dB/cm) in the TE orientation.

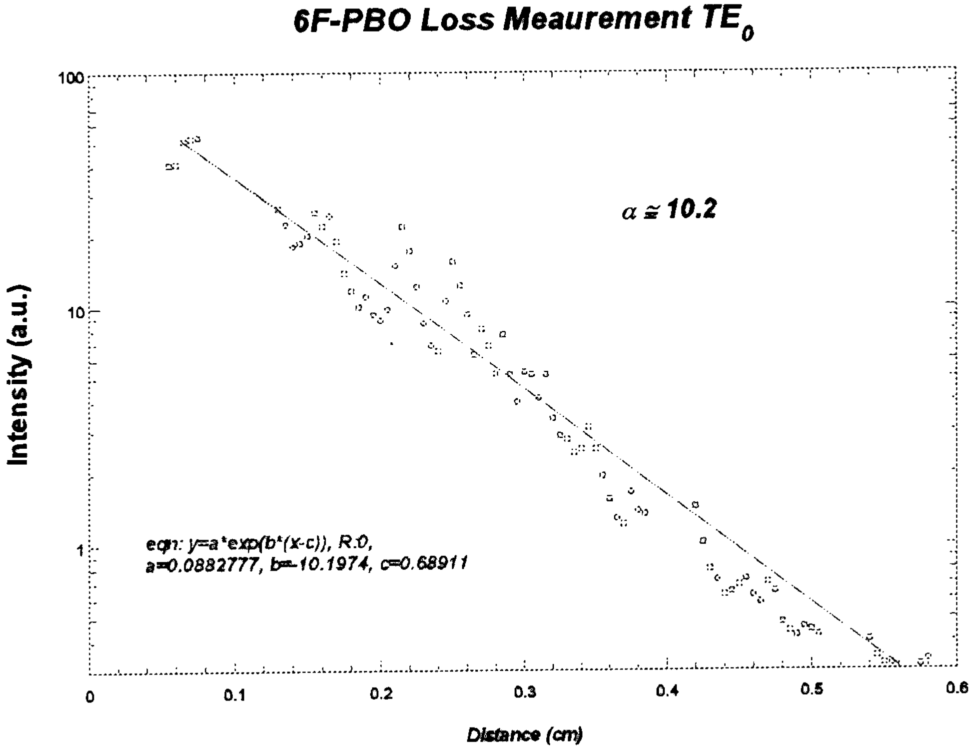


Figure 8. Optical loss of Oxydecly-6F-PBO at 632.8 nm using TE Polarized Light

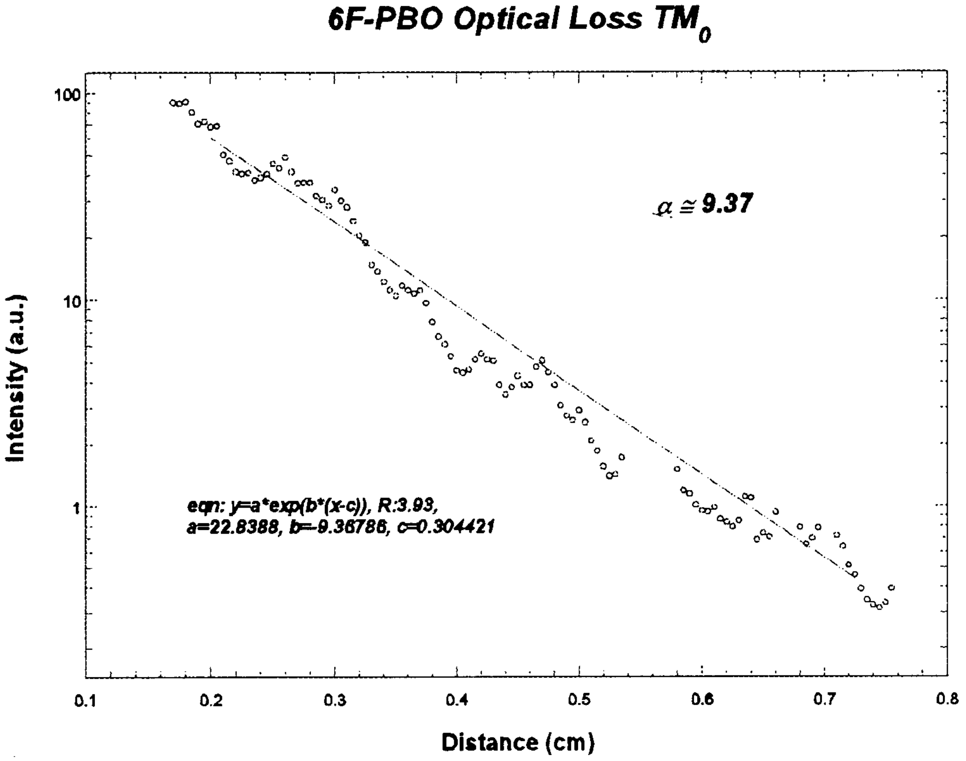


Figure 9. Optical loss of Oxydecly-6F-PBO at 632.8 nm using TM Polarized Light

- The thermal stability of the film was measured by thermal gravimetric analysis (TGA) as shown in **Figure 10**. The molecule shows minimal oxidation in air between room temperature and 360°C, when the $OC_{10}H_{12}$ groups begin to detach from the polymer backbone. The backbone remains intact until 500°C is reached when the polymer undergoes rapid and total decomposition. This analysis was done in air at atmospheric conditions. However, most electroluminescence experiments are done at reduced pressures, to prevent premature device burnout. Research done by others suggests that this material may not be thermally stable beyond 200° C at reduced pressures.

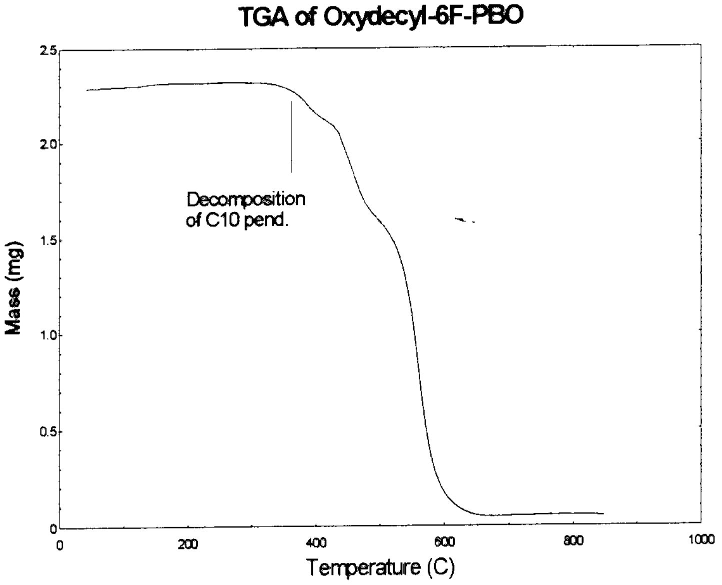


Figure 10. TGA Scan of 2.3 milligram sample of oxydecyl-6F-PBO from room temperature to 850° C

The attenuation coefficient of the polymer was measured using a Hitachi UV-4001 Scanning Spectrometer. The results of the scan are shown in **Figure 11** as the red colored trace on the right-hand side of the plot. The spectrum shows three distinct absorption bands centered at 3.2eV, 3.9eV, and 6.0eV. The sample was then placed in an optical multi-channel analyzer (OMA) to measure the photoluminescent output when pumped at each of the above absorption bands. The sample was found to respond identically when pumped at 3.2eV or 3.9eV resulting in a two-peak photoluminescent signal, shown as the green trace on the left side of the plot in **Figure 11**. No signal was collected when the sample was pumped at 6.0eV due to filtering difficulties. The overlap of the attenuation coefficient with the photoluminescence signal shows the energy of the polymer's bandgap. These traces overlap at 2.9eV as shown in **Figure 11**. With this information available the construction of electroluminescent devices from this material is now proceeding with great success.

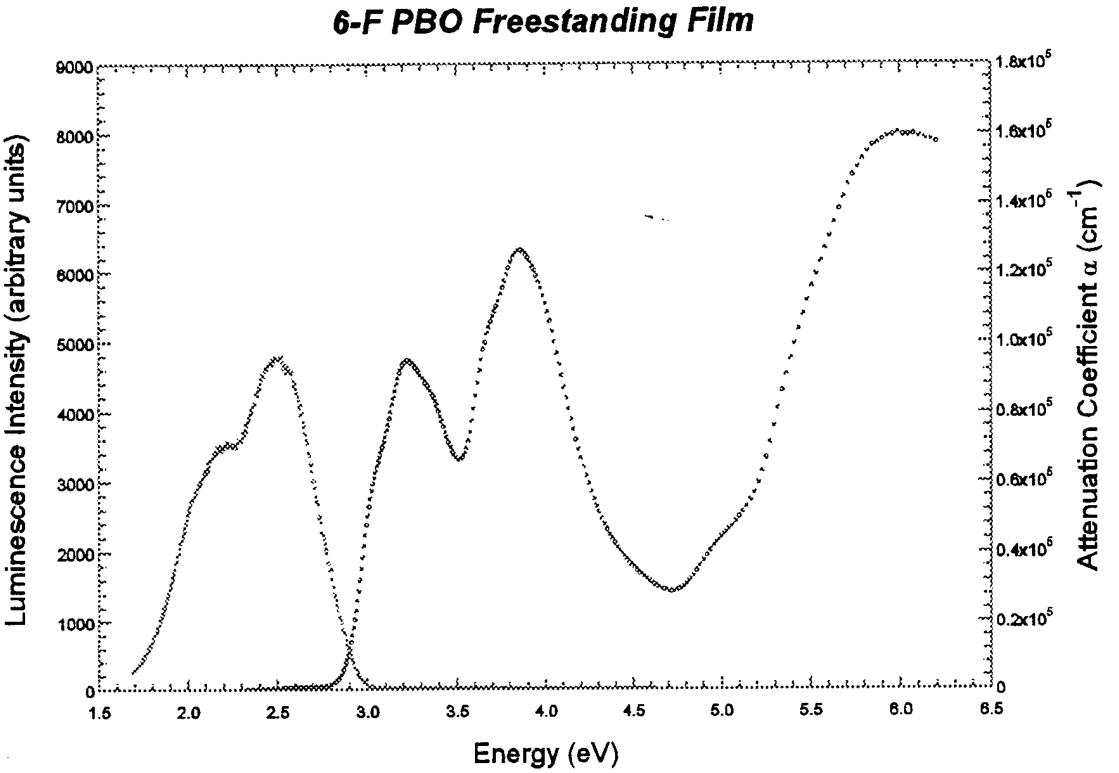


Figure 11. Overlay of the attenuation coefficient and photoluminescence of oxydecyl-6F-PBO in the solid state.

Study of the effect of Iodine doping and final washing on the conductivity of the DPA-PBI polymer system

The effect of iodine doping and washing of DPA-PBI (**Figure 12**) was studied to gain a better understanding of readily activated polymer films. The polymer was synthesized in MSA and then divided into two batches. One was water washed and the other washed in NH_4OH. The process of washing the films neutralizes or rids the film of any remaining acids dissolved in the polymer.

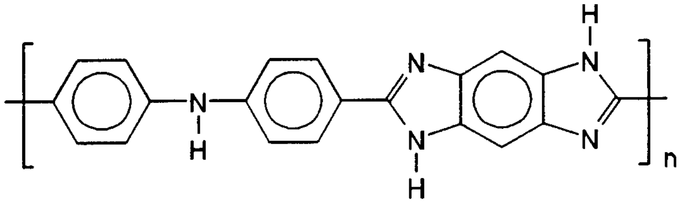


Figure 12. Structure of DPA-PBI Homopolymer

A sample of each batch was then measured using the standard 4-probe technique shown in **Figure 13**. In the 4-probe method four gold pins are spaced evenly apart and pressed onto the film. Current is injected at one end and recovered at the other, while the voltage is measured across the center two pins. This configuration results in a highly accurate measurement of conductivity down to 10^{-10} S/cm.

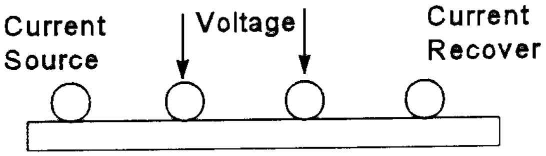


Figure 13. Four-Probe Measurement Configuration

The samples were then removed from the measurement apparatus and placed in an iodine environment for 48 hours. During this time, the iodine diffuses through the polymer, activating the backbone and freeing charge for easier movement, lowering the resistance of the film. The results of these measurements are shown in **TABLE 3**.

Sample Number	Description	Maximum Measured Conductivity (S/cm)
60520A02	Water washed undoped	less than 10^{-10}
60520A02	Water washed I_2 doped	2.11×10^{-6}
60520B02	NH_4OH washed undoped	3.01×10^{-9}
60520B02	NH_4OH washed I_2 doped	5.54×10^{-5}

TABLE 3. Conductivity of DPA-PBI Homopolymer

The results suggest two trends, first, iodine doping of this system increase conductivity by four orders of magnitude. Second water may not be a sufficient washing agent for neutralizing acid dissolved in the polymer since a stronger base wash can increase the conductivity by another order of magnitude.

Effect of Lithium Doping and Orientation on the TD-3 System

The TD-3 system (Figure 14) was studied extensively for use in Air Force battery applications and to resolve discrepancies between transverse and longitudinal conductivity. Several samples were prepared and measured by two techniques.

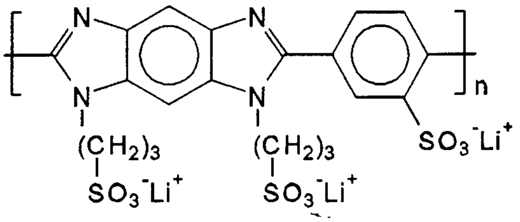


Figure 14. Structure of Lithium Activated TD-3 Homopolymer

The first method is identical to the 4-probe setup described above, but with an additional set of gold pins. This measurement scheme is called an 8-probe measurement (**Figure 15**). It allows for the differentiation of surface conductivity from that of the bulk. Pin 1 serves to inject the current while pins 2-3, 2-7, and 6-7 measures the voltage drop across the polymer. Pins 4 and 8 serve to collect the current. These pin combinations are then cycled until every permutation is collected. If the conductivity measurements are all identical then the bulk and surface have the same conductivity. Otherwise, the surface has a conductivity different from that of the bulk, often indicative of an oxide layer or non-uniform dopant distribution.

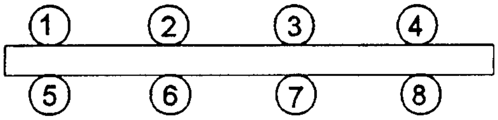


Figure 15. Eight-Probe Measurement Configuration

The second method is the transverse or 2-probe measurement (**Figure 16**), in which rubber electrodes of known conductivity sandwich the polymer sample. In this technique, the electric field is perpendicular to the film surface. By comparing the conductivity value obtained by the 2-probe to that of the 8-probe, sample morphology information can be obtained.

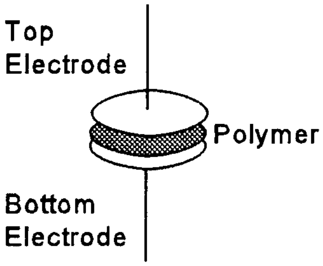


Figure 16. Two-Probe Measurement Configuration

TABLE 4 contains the information about the TD-3 system at various Lithium concentrations.

Sample Number	% Lithium	Measurement	Conductivity
60717A	2.76%	2-probe	1.22×10^{-8} S/cm
60717A	2.76%	8-probe	8.57×10^{-5} S/cm
60717B	2.76%	8-probe	10.96×10^{-5} S/cm
60822A	3.18%	8-probe	19.8×10^{-5} S/cm
60813A	3.33%	8-probe	35.4×10^{-5} S/cm

TABLE 4. Summary of Typical TD-3 Conductivity Measurements

It is clear that the conductivity of the TD-3 system increases with higher lithium loading. Also, the 8-probe measurements are all in agreement with each other indicating the surface and bulk conductivities are identical. However, the transverse measurement is three orders of magnitude less than the longitudinal measurements, implying a high degree of orientation in the system. These results were recently validated by wide angle x-ray scattering and scanning electron microscopy.

Conductivity Measurement of S-PBI/S-PANI 50/50 blend

A 50/50 blend of sulfonated PBI/ Sufonated PANI (**Figure 17**) was produced and the conductivity of the film measured using the 4-probe method, described earlier. The film's conductivity was 1.41×10^{-10} S/cm. After obtaining this low value, no other blends were produced.

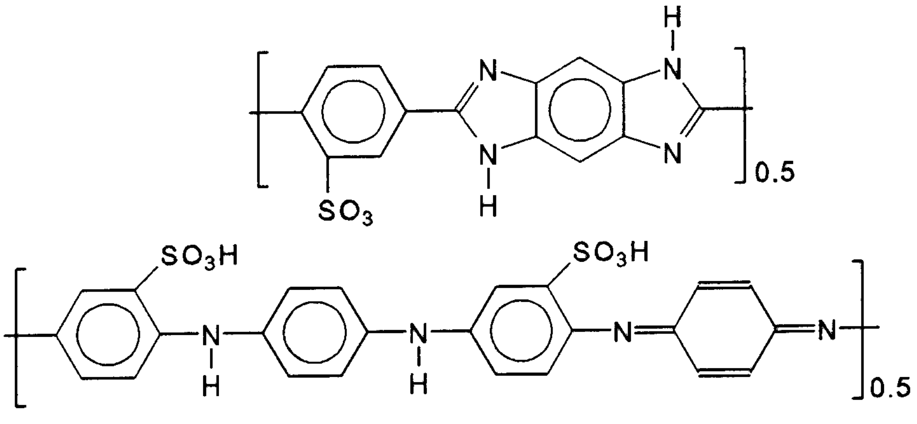


Figure 17. Structure of Sulfonated PBI / Sulfonated PANI Blend

Study of the Conductivity of DASA:PANI Copolymers

A series of DASA:PANI copolymers (**Figure 18**) were synthesized and pressed pellets formed. A PANI (**Figure 19**) homopolymer pellet was also made as a baseline for the conductivity values. Due to the nature of pressed pellets, the conductivity of the pellet is approximately three orders of magnitude less than that of a comparable film.

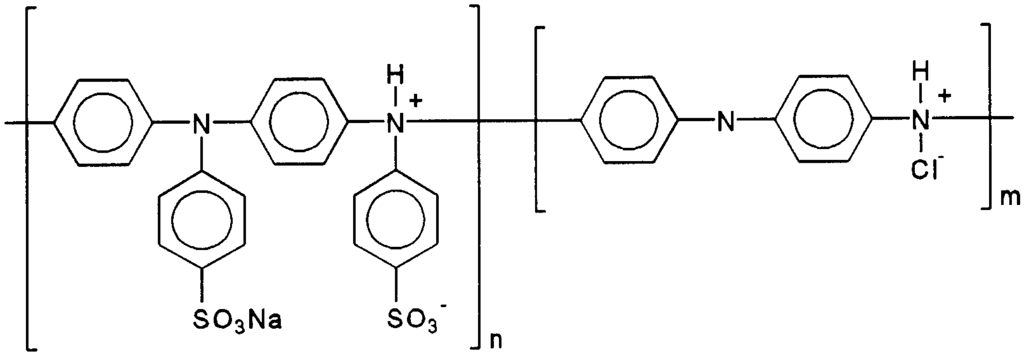


Figure 18. Structure of DASA:PANI Copolymers

Films were not made of the blends due to difficulty in casting, and time considerations. **TABLE 5** shows the results of the conductivity measurements.

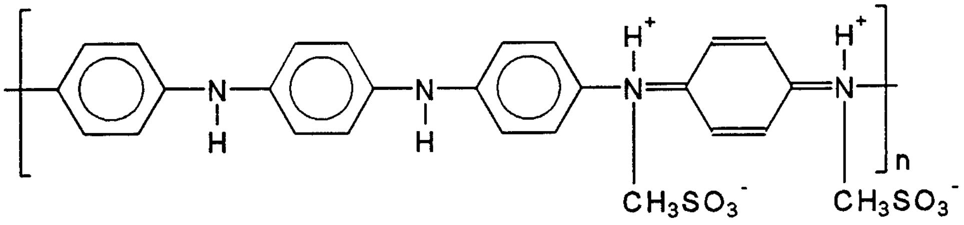


Figure 19. Structure of PANI·MSA

Sample Number	% DASA	% PANI	Conductivity S/cm
61028A02	0	100	0.139
61015A02	20	80	1.02
61029A02	30	70	0.258
61030A02	50	50	3.2×10^{-5} *

TABLE 5. Summary of DASA:PANI Conductivity Measurements

The values are all reasonable except the 50/50 copolymer. The 50/50 sample is being remade due to a possible problem in its synthesis. In addition, higher DASA concentrations are being made to complete the series.

Study of the Conductivity of DBSA-PPY Copolymers

The DBSA-PPY homopolymer (**Figure 20**) has been synthesized and its conductivity measured using the 4-probe technique. The material is as a pressed pellet, and no copolymers have been produced. The pellet's conductivity is 2.30 S/cm, much higher than the previous system.

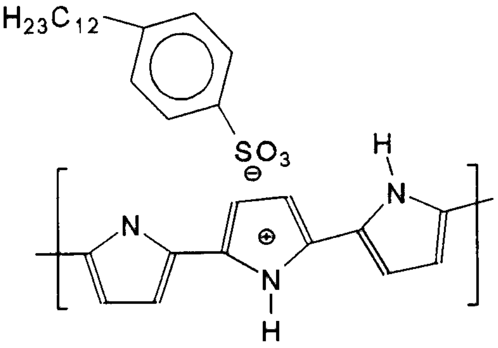


Figure 20. Structure of the DBSA·PPY Polymer

KINETIC LUBRICANT DEGRADATION STUDIES

Task Order No. 224
Student Support Program
Southwestern Ohio Council for Higher Education

Matthew Argenbright
University of Dayton

27 December 1996

Government Task Leader
Ms. Lois Gschwender
WL/MLBT

ACKNOWLEDGMENTS

The success of the Task can be contributed to the following individuals, who through professional assistance and guidance, led to a successful Task. Those individuals are Keith Clendenon, George Fultz, Ms. Lois Gschwender, Ron Mortimer, Dr. Harvey Paige, Bruce Schreiber, Ollie Scott and C. Ed Snyder.

TASK ASSIGNMENT

The Task involved the continuing research in the determining of the kinetic degradation mechanisms of a model synthetic polyol ester and pentaerythritol tetraheptanoate (PETH) in a high temperature, high concentration oxygen environment using the oxygen absorption apparatus.

Oxygen Absorption Apparatus

The evaluation of the PETH using the modified design had proven that the apparatus was capable of determining the kinetic oxidation of the PETH. Still some reservations existed on whether or not the apparatus was useful in evaluating the initial induction period of the fluid. To determine this capability, a matrix of gas chromatography experiments was used in making this determination. The experiments called for thermally stressing the PETH for very short run times. During these runs, samples were extracted. These samples were then analyzed by gas chromatography. The chromatograms were correlated with the mass spectrophotometer data in determining exactly what products that formed and degraded during the test runs. Hopefully, this method would produce the same product formation rates as the Exxon and Ford data had shown. If the rates were the same, this would insure that the apparatus could determine the kinetic oxidation rates of the liquid lubricants.

The PETH was evaluated using the modified oxygen absorption apparatus (Figure 1). The test is done by starting with a sealed test loop. The loop is purged with pure oxygen, ideally removing all air and having a 100% oxygen environment. The sample fluid is placed in the reaction and a stream of nitrogen is used to inert the cell during which the fluid is raised to the test temperature. Once thermal equilibrium is reached, the nitrogen stream is changed over to an oxygen stream, this begins the oxidation of the fluid. The pressure in the regulator on the cylinder, the fluid temperature and oxygen flowrate are the only test parameters to maintain. At predetermined intervals, 1-ml aliquot is extracted through the sample port for analysis by hydroperoxide titration and gas chromatography.

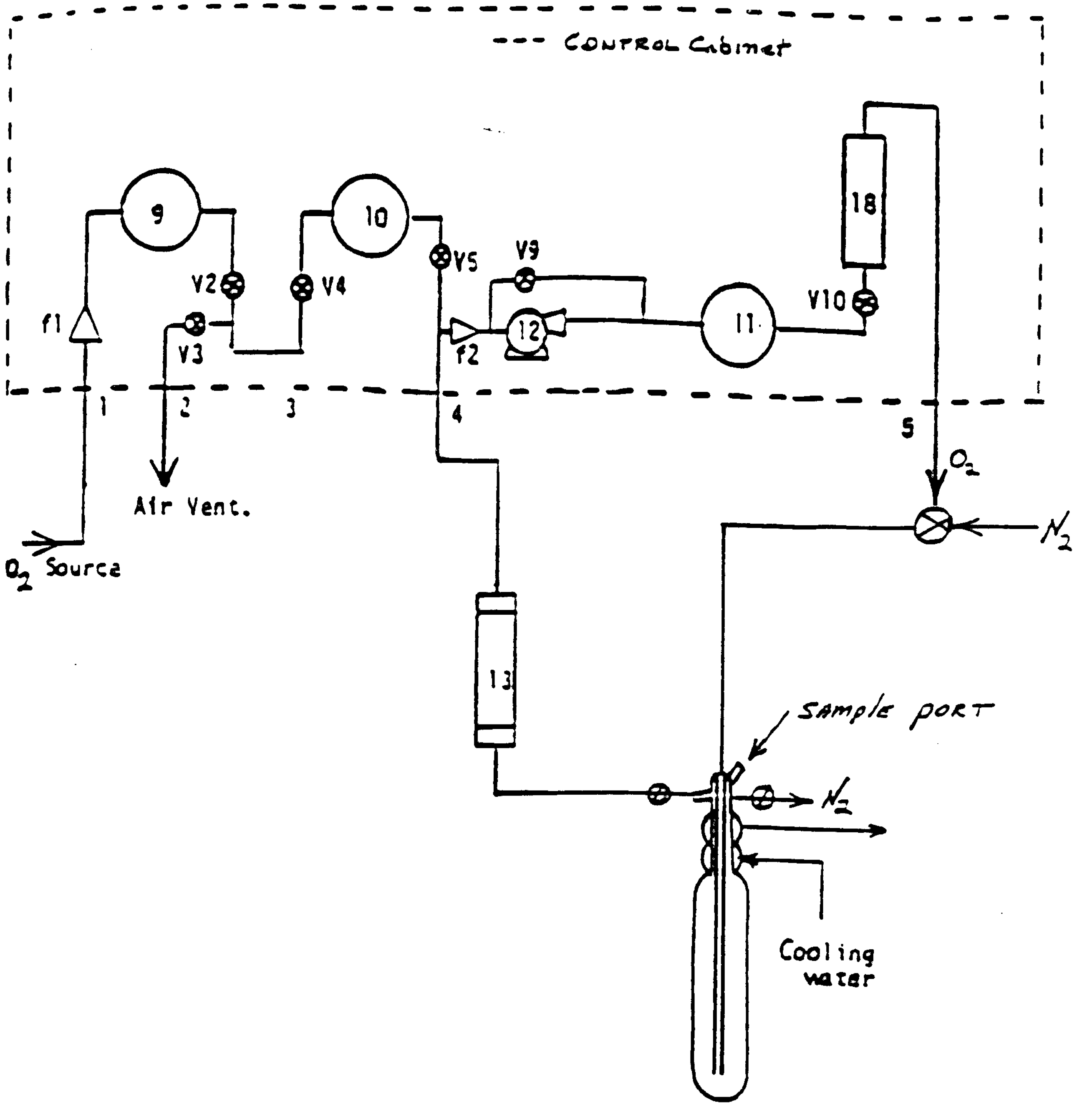
For the gas chromatography study, test temperatures of 205°C, 210°C, and 215°C were selected based on their formation of hydroperoxide. At 215°C, aliquots were extracted every 40 seconds up to and including 200 seconds. This meant that within the 200 seconds period hydroperoxide was not breaking down into further by-products, thus simplifying and reducing the number of peaks and peak identification. For ease of calculations, sample times were duplicated for all three test temperatures. However, at the lower two test temperatures, the experiment run was extended to 320 seconds because of the lower formation of by-products.

For the 210°C and 205°C experiments, aliquots were extracted every 40 seconds up to and including 320 seconds, the time when linear formation of hydroperoxide ends. Once the samples were extracted, they were placed in a vial that can be used on the GC autosampler. For consistency in analysis, all samples for a specific temperature were analyzed by GC the same day of the experiment. Also, the GC-MS analysis was done the same day of the experiment. This set up would eliminate any variations in the GC results that could have been caused by the fluid undergoing degradation, while in the vial, if the samples were tested on different days.

The individual peaks were identified by GC-MS. This analysis was done on the final sample of the experiment run. The GC was modified to duplicate the runs by the GC-MS. That meant the retention times of the two instruments were very close, which insured of proper peak identification when using the GC chromatograms for kinetic study calculations. From the mass spectrophotometer, twenty-eight peaks were numbered and identified. From that data, the peak retention time and shape was used to correlate and positively identify the peaks formed from the GC analysis. Each identified peak was placed in a column of data that compared sample time with peak area. This table (Table 1) could easily show peak growth or reduction based on area change. These criteria were selected by Exxon for their calculations. An example of the chromatograms used for this study are shown in Figure 2 and Figure 3. The prior showed a 40 second stressed sample having little degradation. The latter were a chromatogram after 30 minutes of being thermally stressed and showing significant peak formation and reduction.

The project spent much time on determining the hydroperoxide formation characteristics of the fluid. Determining the optimum sample time for the kinetic calculations was necessary. Also, significant time was spent on learning GC software and hardware and sampling techniques. The data derived will be forwarded to Exxon for evaluation and continuation of the project will be based on their results. If the project is continued, action items from the September meeting between Exxon and WPAFB will be carried out. Those include investigating the effect of storage condition variables on oxidized samples, quantitative data on product formation of PE sekanoate, peroxide formation on PE sekanoate, and computational chemistry studies.

Figure 1



FLOW DIAGRAM - OXYGEN ABSORPTION APPARATUS
MANOMETER SYSTEM REMOVED

Table 1

PETH 205°C OXAB 34

PEAK #
AREA(pA*s)

Sample Time(sec)	1	2	4	6	9	15	16	17	18	19	20	21
0		0.01				5.3	1.05		48.3	0.04		
40		4.14		0.71	0.67	34.9	0.66	0.91	4.87	0.53		12.8
80	15.9	8.34		0.13	0.31	26.2	0.67	1.18	4.02	9.4	0.76	8
120	21.2	11.1	0.17	2.15	0.51	15.5	0.86	1.01	11.9	14.3	1.56	10.8
160	28.7	14.6	0.52	3.19	0.59	14.1	1.24	1.04	2.45	13.8	2.04	10.7
200	30.4	16.4	0.82	3.82	0.65	18.8	1.71	1.28	6.96	18.1	3.39	11.3
240	35.5	18.7	1.19	5.06	0.62	11	1.87	1.91	8.75	22.1	5.1	11.2
280	41	21.5	1.07	5.62	0.81	24.1	2.69	2.85	9.09	24.6	7.69	13.2
320	45.9	24.5	1.46	8.03	0.89	28.8	3.19	4.43	3.61	28.3	9.74	16.5
RETENTION TIME(min)	1.455	1.8	2.542	3.961	6.367	8.949	9.991	10.521	20.386	20.576	21.255	22.741

Table 1 cont.

PETH	205°C		OXAB 34				
						PEAK # AREA(pA*s)	
Sample Time(sec)	22	23	24	25	26	27	28
0			2521.7	5.4	43.5	103.9	118932
40		3.01	2490.7	1.32	4.59	14.63	111589
80	9.71	17.7	2354.2	2.01	1.8	2.97	112334
120	17.3	23.2	2559.4	75.3	87.3	211.2	113901
160	23.3	34.9	2765.7	101.1	101.2	250.6	111645
200	28.3	23.9	2978.9	135.9	141.7	315.3	111025
240	33.3	52	2889.4	324.4	470.7	731.9	112341
280	37	60.2	3557.3	190.4	236.7	450.2	108773
320	42.5	78.3	3912.1	295.4	390.4	555.9	108575
RETENTION TIME(min)	**24.529**	**26.575**	**28.974**	**29.936**	**31.03**	**32.576**	**39.391**

Figure 2

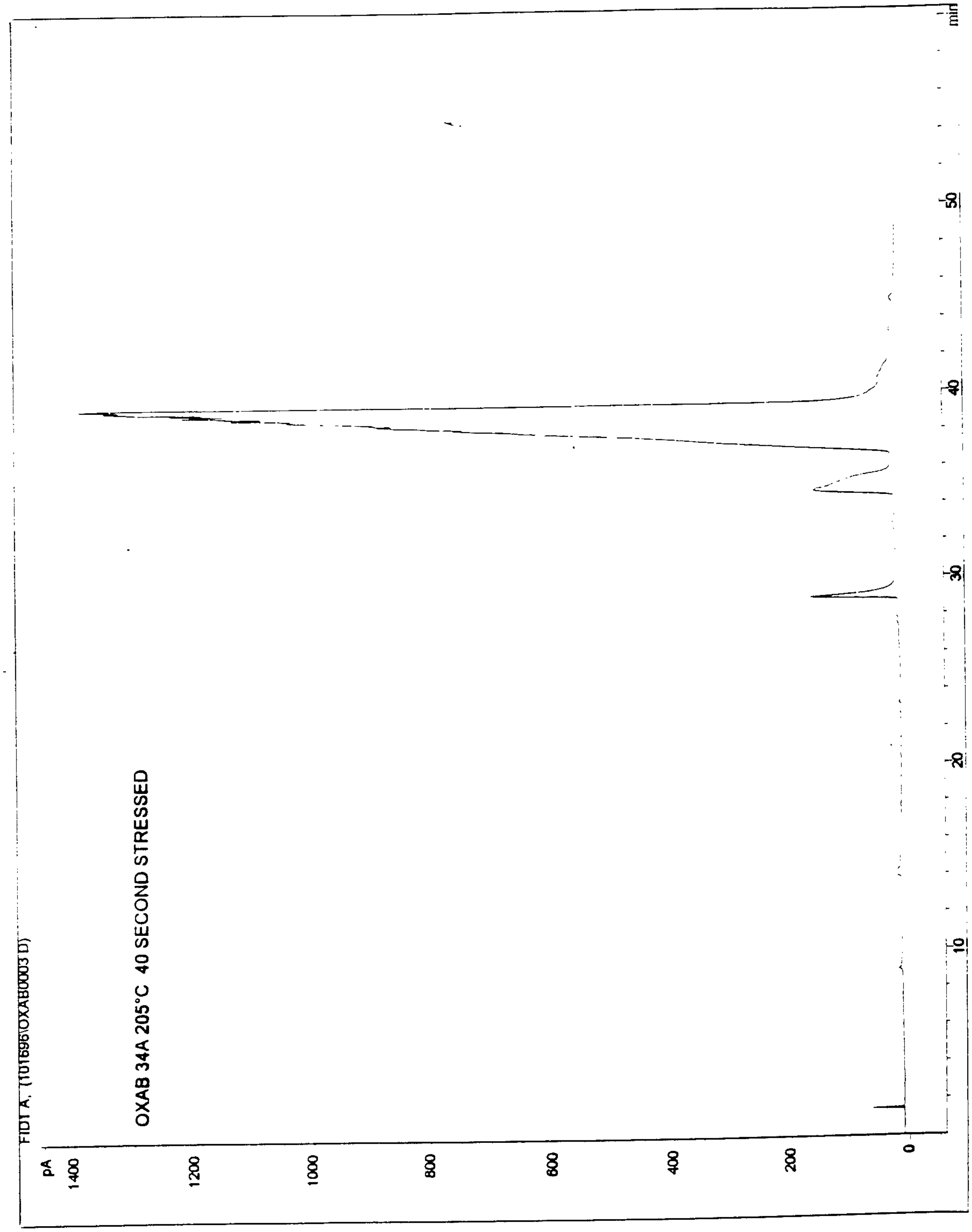
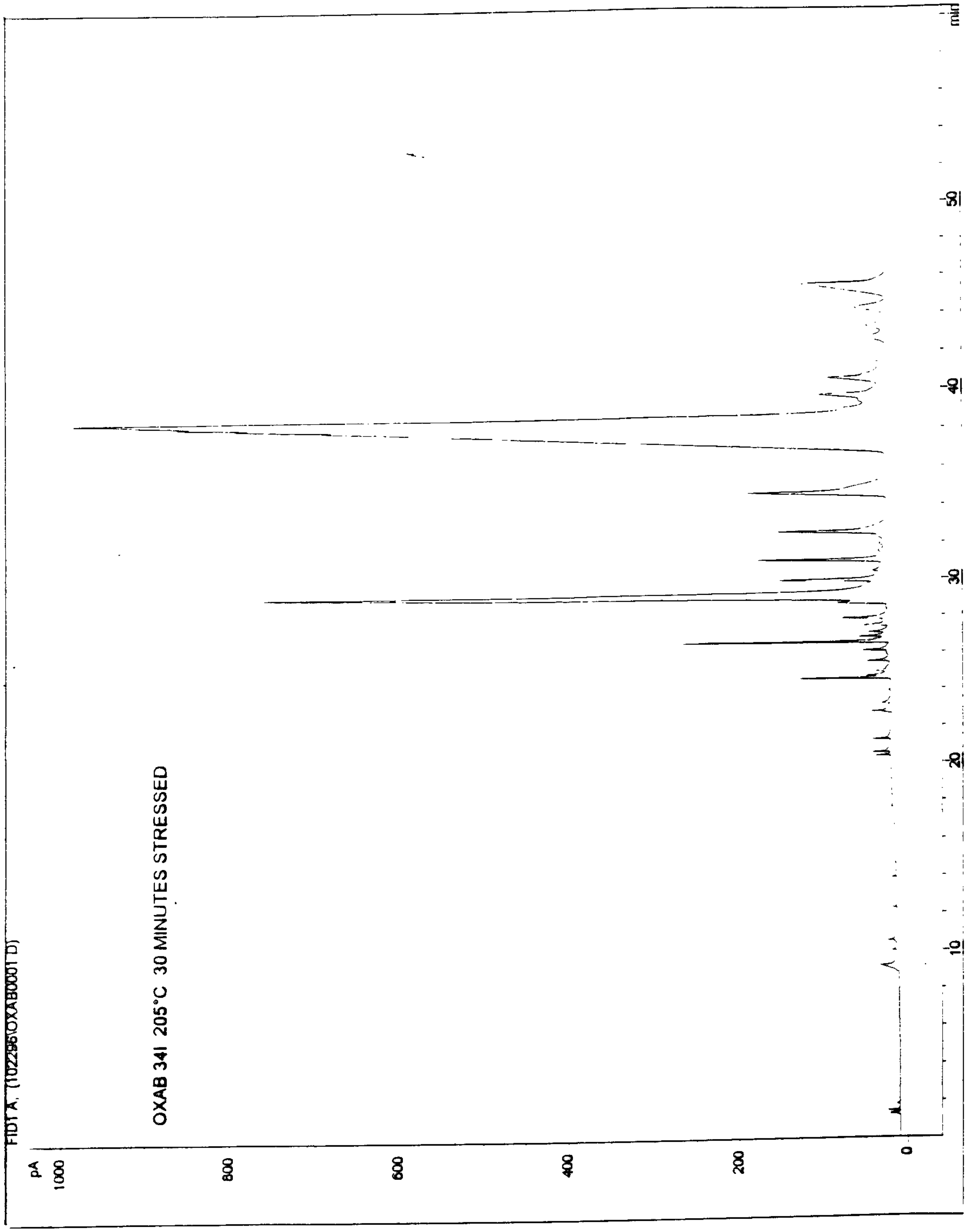

FID1 A, (101696\OXAB0003.D)
OXAB 34A 205°C 40 SECOND STRESSED
pA
1400
1200
1000
800
600
400
200
0
10
20
30
40
50
min

Figure 3


FID1 A, (102296\OXAB0001.D)
OXAB 341 205°C 30 MINUTES STRESSED
pA
1000
800
600
400
200
0
10
20
30
40
50
min

TRIBOLOGICAL EVALUATION OF CANDIDATE FLUIDS AND LUBRICANT MATERIALS

Task Order No. 225
Student Support Program
Southwestern Ohio Council for Higher Education

Jeremy Schmidt
University of Dayton

27 December 1996

Government Task Leader
Mr. Shashi Sharma
WL/MLBT

ACKNOWLEDGMENTS

I would like to express my gratitude and thanks to my Government Task Leader, Mr. Shashi Sharma. In the last year, I have learned a great deal from him about tribology and general engineering practice. He has been a help in answering my questions and checking my assumptions. He also has taught me about responsibility and thoroughness. I am grateful to have learned so many important things about education, engineering, and life in general.

I also would like to thank Vince Vidoni and Bruce Schrieber for their help in developing this Task. They have been available to answer any questions concerning this project. They also have been resourceful in giving new ideas and moving the Task along through the difficult times.

Finally, my sincere thanks go to Rick Kolb, whom I have been working side by side with this entire year. To take on a project of such size by two undergraduates was difficult. By working together using our different disciplines, we caused the successful manufacturing of this project. I hope in the future we will see the fruit of our efforts.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Most of the time spent on this Task was to develop a new tribology testing machine completely. The elastohydrodynamic lubrication rig, commonly known as the EHL rig, was designed to test different lubrications under boundary lubrication. Boundary lubrication occurs when two surfaces slide against each other with only a microscopic film between contacting points. The film is the only lubricant that the contact of the material has. This can lead to greater wear, quicker failure, and the lubricant changing its chemistry. Boundary lubrication often happens at the start of a machine, or other surfaces that have very little lubricant on them. The importance of this test is to develop new lubricants to help decrease wear on a material, and prevent the lubricant from losing its lubricating properties. The application of this development would be longer lasting engines, bearings, and decrease of wear and chemical changes on a surface.

DESCRIPTION OF RESEARCH

This project was a collaborative effort to develop a new EHL rig that required design, modification, and research into making the machine operate at a low vibration level and give consistent results. Essentially, the rig was designed to rotate a steel ball on a shaft against a transparent sapphire disk. The bottom side of the disk contained a film of the lubricant to be tested. At the point of contact (the steel ball with the disk), diffraction patterns occur due to the chemical changes from the heat and friction of the point. The diffraction patterns are observed by a high resolution microscope, and recorded onto a video tape and/or computer for analysis.

The main objective of this Task was to redesign the existing parts and design the fixtures to make the EHL rig work. The original machine had been manufactured, but never assembled for testing. The new project was to redesign the old rig into a testing apparatus that had very low vibration and record the necessary data to show differences in lubricating properties of fluids. The existing shaft, housing, and test chamber were redesigned to accept the new design of the new structure of the rig. Also, the drive shaft housing was modified to prevent any excess movement or vibrations of the sapphire disk. Some original designs were incorporated into the new design. One was the test plate, which attached the motor, torque cell, and test chamber to rotate the steel ball with very minimal vibration. Also, the main table, which was the support structure of the apparatus, was a new design. The table will hold the drive motor and the housing for the disk shaft. It also will be used for mounting the microscope in the correct spot to record the diffraction patterns. The development and manufacture of these objects are the present focus of the Task.

The EHL rig is in its final process of being manufactured and is almost ready for its final assembly. The microscope and computer system are still in their respective development stages. Hopefully, the next few months will lead to the recording and analysis of data concerning different lubricants under boundary conditions.

RESULTS

The development of this project uncovered a great deal about the cause and effect side of tribology. Every possible problem was analyzed before a clear design of the part was realized. The main goal of the design was to reduce the vibrations of the EHL rig so the recording of the diffraction pattern would give conclusive evidence. The size of this project was on a grand scale, since the incorporation of a computer system and a recording system are necessary for recording data. Unfortunately, the end of this Task came before the project could be fully realized. The testing of lubricants with this system will be realized during the next Task.

ULTRAFAST LASER GENERATED ULTRASOUND SUPPORT

Task Order No. 226
Student Support Program
Southwestern Ohio Council for Higher Education

Jennifer A. Foley
Wright State University

1 July 1996

Government Task Leader
Dr. Robert L. Crane
WL/MLLP

ACKNOWLEDGMENTS

I would like to thank Dr. Curt Fiedler for working with me during this Task. He initially showed me how to run the experiment and explained what it does. Whenever I encountered an obstacle while working with the experiment, it was always Curt I turned to for help. Working with this experiment gave me experience with hands-on research, and computer programming skills. It gave me insight into the world of research and opened new possibilities for career choices.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The objective of this Task was to acquire and document data from the Ultra-Fast Laser Generated Ultrasound (UFLGU) experiment. It also included any modifications to the current setup that might lead to improved results from the experiment or more accurate data collection. Examples of changes made to the current setup might be writing new programs to deal with how the data is collected and processed or changing the layout of the experiment.

DESCRIPTION OF RESEARCH

The Ultra-Fast Laser Generated Ultrasound (UFLGU) experiment deals with the development of a technique to inspect thin-films, ranging from 10 nm to 500 nm. While methods for inspecting thin coatings already exist, this specific experiment explores methods that are non-contact (to eliminate any contamination of the coating) and nondestructive. For this Task, scans were run to reproduce already existing data supporting the theory that interferometric and piezoreflective detection are valid methods for determining the thickness of thin-films. It was hoped that methods would be found- to improve upon the current data collection abilities of the experiment.

While analyzing the results of the multiple scans (scans taken many times and averaged together to subtract out the noise from the resulting signal), it was discovered that the signal from the first and the last angle were different. (See Figure 1) In theory, they should be the same because the angles are taken from what is called a fringe scan. The fringe scan shows the changes in the magnitude of the voltage as the specimen is tilted at different angles. For the multiple scans, a piezoreflective scan is run for the first angle. Then, interferometric scans are run at each of nine angles along one period of the resulting sine wave (from the fringe scan). Because the first and last angles are at the same position along the sine wave, they should have approximately the same magnitude and phase. (See Figure 2)

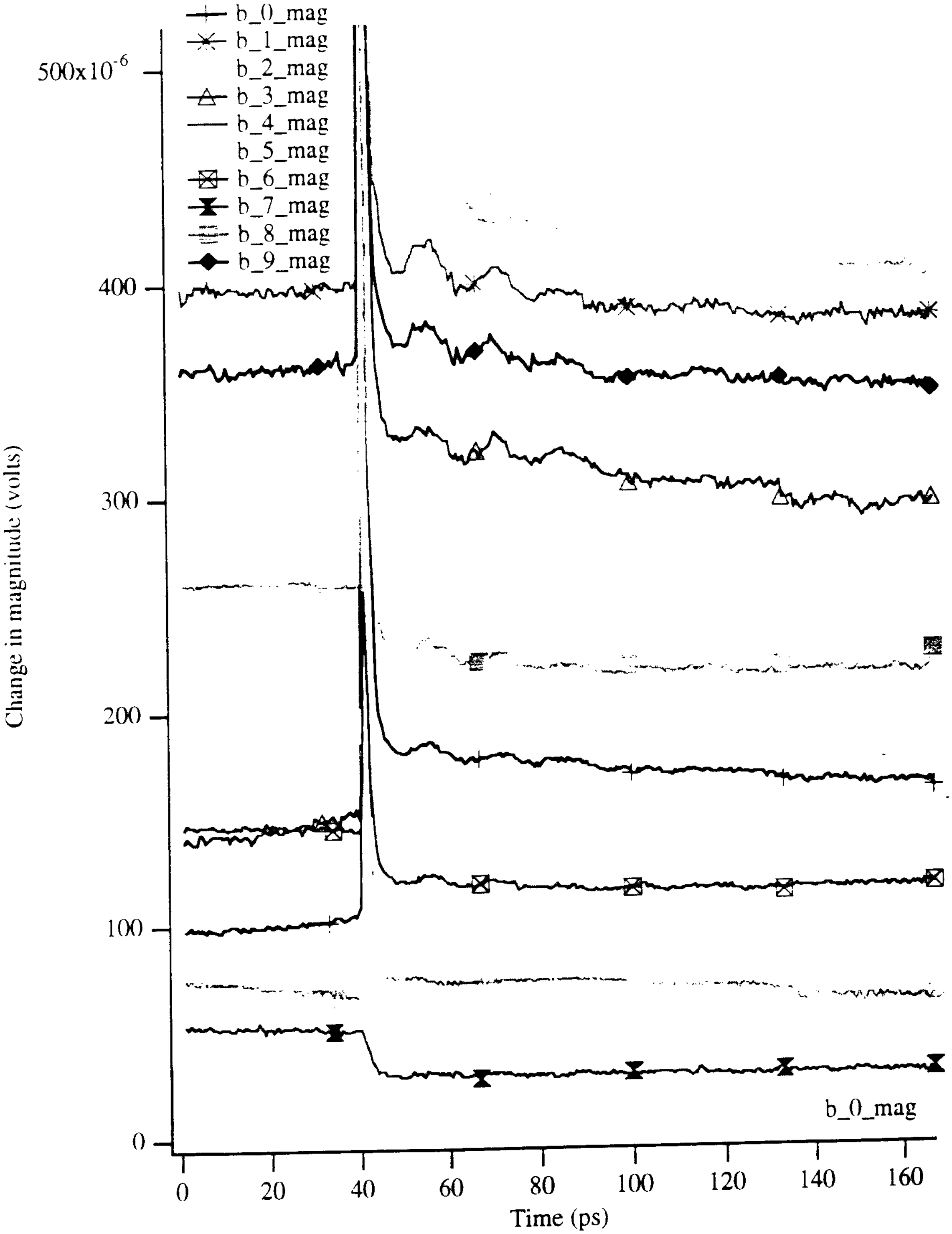


Figure 1. Multiple Scans-Magnitude (taken April 17, 1996)
*The first and last angle are represented by b_1 and b_9.

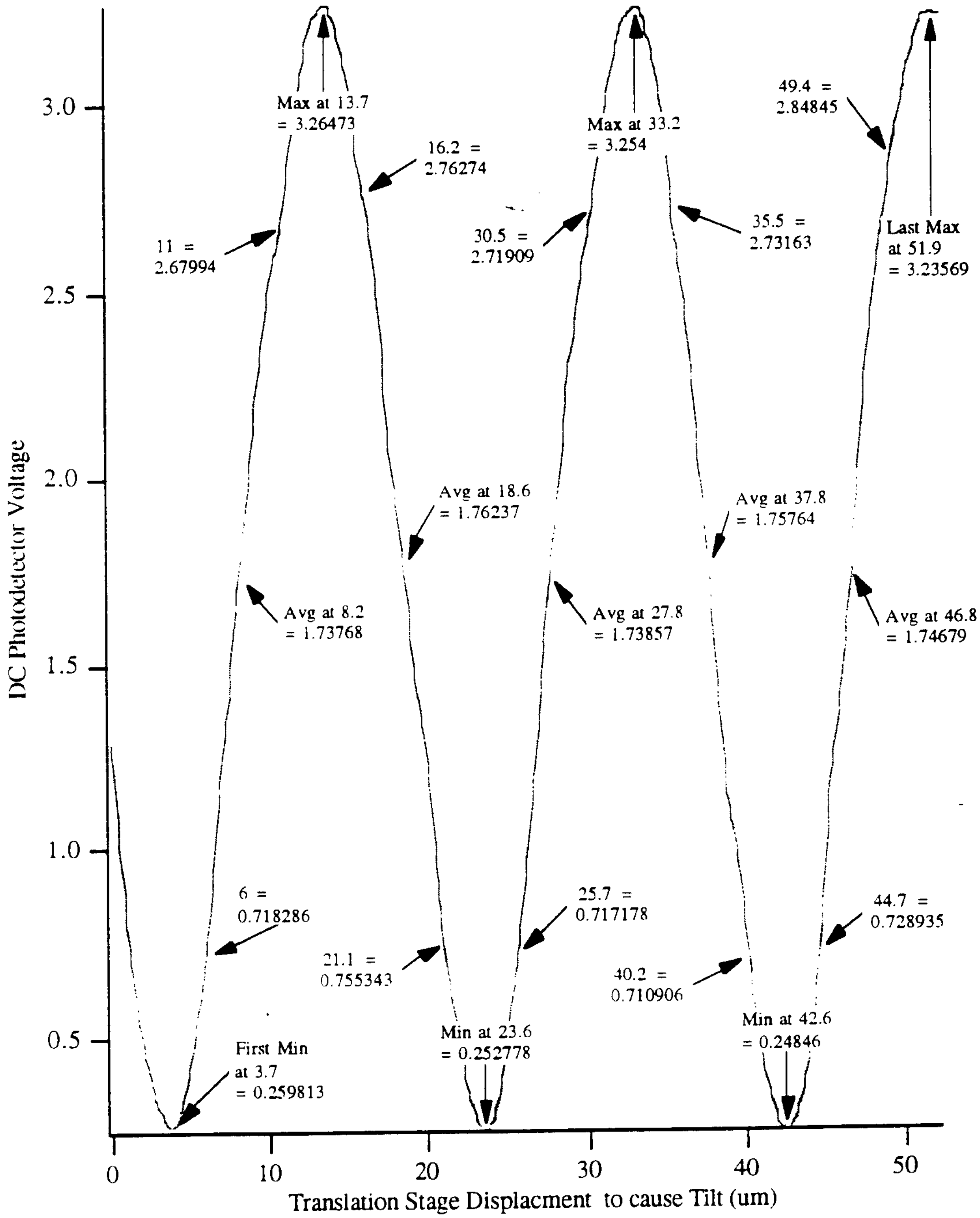


Figure 2. Fringes Scan taken on April 29, 1996

*The nine angles chosen for a multiple scan would consist of one time period (i.e. Avg at 8.2 to 27.8).

The results of the scans showed that the heating beam was walking across the specimen, causing it to fall out of alignment with the reference beam. While the walking of the beam itself is a slow process, it becomes highly evident with the multiple scans because they are run for long periods (around 16 hours). To fix this, the angle of the heating beam with respect to the reference beam was changed. In its original position, the heating beam was more likely to walk across the specimen because it was coming in at a wide angle. The experiment was changed so that the angle of the heating beam was more perpendicular to the specimen, creating a higher accuracy in the signal. (See Figure 3)

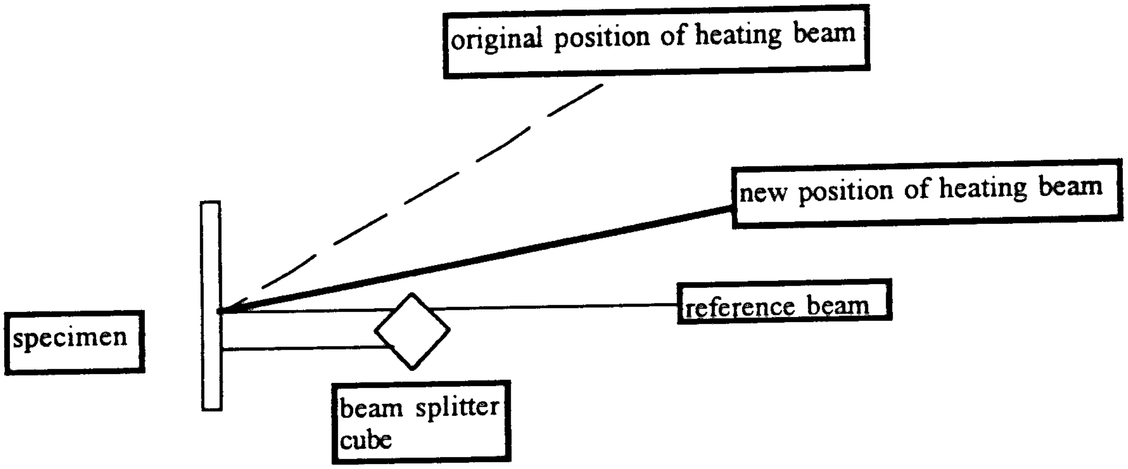


Figure 3. Heating Beam Positions

Another possible reason for the significant changes in the signal between the first and last angle could be the result of the apparatus that was tilting the specimen. A Burleigh 7000 Inchworm Controller was positioned on a plate behind and to the side of the specimen holder. Movement forward and backward leads to the tilting of the specimen. With a longer tilt arm on the specimen, while applying the same amount of force, the distance traveled (or the angle produced) will be less than with the shorter tilt arm. It is believed that smaller and more precise incrementation in the turning angle will produce more accurate results and fewer regions for error.

The results received from the two previous changes to the experiment proved positive. The signals at the first and last angle are more in sync with each other. (See Figure 4)

Another change made to the experiment dealt with the instruments being used to run the experiment. A new Lock-in Amplifier was received. Because the experiment is run through a computer using a software package called Labview, all of the programs were updated so that the experiment can be used with the new Par200 Lock-in Amplifier. The programs compatible with this instrument are kept under startup-experiment-2.vi. The previous lock-in, the SR530, can still be used in the experiment. The programs that it works with are listed under startup-experiment. vi.

Data has shown that inspection of thin-films by piezoreflective and interferometric detection is possible. Now, techniques must be found to produce signals with less noise and clearer peaks and echoes. By rearranging the setup of the experiment and using newer, more precise instruments to run the experiment, it is hoped that even better results than before will be found.

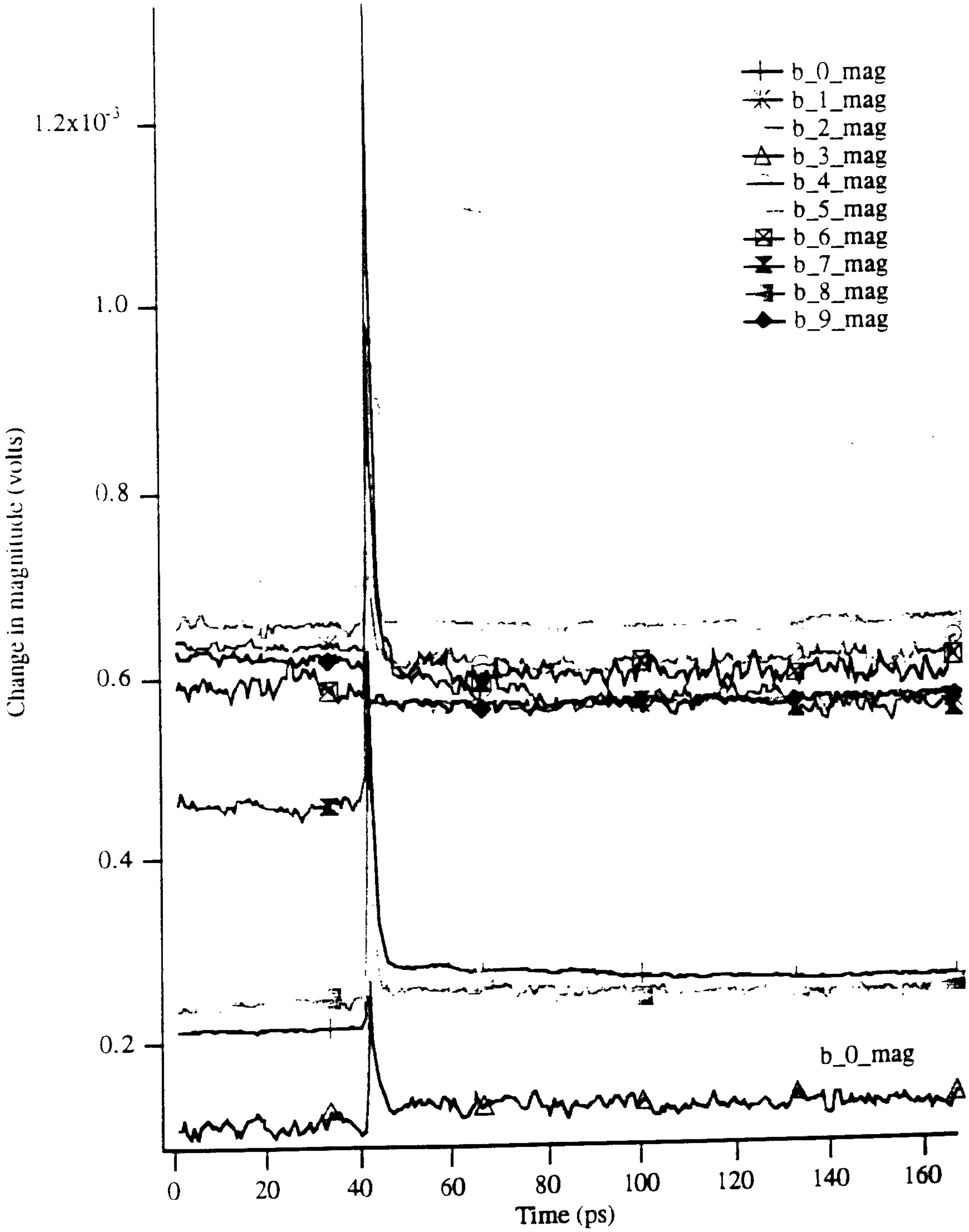


Figure 4. Multiple Scans-Magnitude (taken April 29, 1996)

METAL COMPOSITES (96-I)

Task Order No. 227
Student Support Program
Southwestern Ohio Council for Higher Education

Emily Warwick
University of Cincinnati

27 December 1996

Government Task Leader
Ms. Mary Lee Gambone
WL/MLLM

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

Literature on titanium alloys and titanium metal matrix composites was reviewed to obtain a general knowledge about the materials tested. Silican Carbide, SiC, fibers were received for metalographic preparation for the SEM. General metallography techniques were learned such as sample preparation and SiC fiber extraction so that future samples could be prepared for testing and evaluation. SEM training was completed in which basic skills for operating the SEM were obtained along with literature about some more advanced techniques.

Samples of tested SiC fibers were received and prepared for evaluation on the SEM. Other SiC fibers were first extracted and then tested, using a fiber tester, and then later prepared for evaluation in the SEM. The results of these tests were used to show strength and failure modes of different types of SiC fibers.

Different coatings were also put onto the SiC fibers within the metal matrix. This was done to determine bond strength between the coating and the titanium matrix and the coating and the SiC fiber. After being tested, these samples were prepared for and evaluated by the SEM to show which coating would give the desired properties under certain conditions.

Another experiment was done to learn the temperature uniformity of the furnace in which the titanium alloy was being heat treated. A sample bar of a heat treated titanium alloy was cut, mounted, and prepared for evaluation under the light microscope to see if there was any change within the microstructure along the length of the bar. Such a change would suggest a fluctuation in temperature within the furnace in which the bar was heat treated.

For the second half of the Task, two specific projects were assigned. The first was concerning the heat treatment of titanium alloys containing different levels of carbon. The alloy Ti-24Al-12Nb was chosen and carbon levels of .25, .5, .75, and one atomic percent were introduced. Samples were then analyzed to learn the exact chemical composition. DTA was done with a temperature range of room temperature to 1200°C, a heating rate of 30°C/min and a cooling rate of 30°C/min. During DTA, the temperature at which phase changes occur within a material, can be determined by monitoring energy fluctuations within the chamber. Other samples of the same materials were also heat treated at temperatures of 1125°C, 1100°C, 1075°C, 1050°C, 1025°C for 2 hours and then water quenched and at 815°C for 8 hours and water quenched. After being heat treated, microhardness measurements were taken using a 50 gm load and a 15-second dwell time. They were then metallographically prepared for SEM analysis.

The second project was done to find the effects of alloying elements on the oxidation rate of Ti-22Al-23Nb alloy. Samples containing no alloying elements, 1% at W, 1% at Cr, 1% at Hf, 1% at Mo, .1% wt. Si, and .2% wt. Si, were analyzed to learn their chemical composition and then cut and prepared for TGA, thermogravimetric analysis.

Another project completed during this time was the testing of several fibers coming from a sample bar of the titanium matrix composite. A crack had been deliberately introduced into the sample bar that was then fatigue tested. This resulted in several oxidized fibers whose strengths and levels of oxidation were unknown. Therefore, tensile testing and SEM evaluation were done. After these Tasks were done, weibull analysis on the data, obtained from the tensile testing, was performed to find the probability of survival of the test specimens under certain conditions.

DESCRIPTION OF RESULTS

From the work completed during the first portion of the Task, many methods were used to learn the microstructure and properties of the composite and its constituents. These are methods that are effective in evaluating all materials, not just Titanium Matrix SiC fiber composites, and would be helpful in future research.

From the tensile tester, information such as, the ultimate tensile strength, the modulus, and the type of failure, (shatter, gage, or grip) of an individual fiber, could be employed to compare different types of fibers. These results were used to support existing ideas about certain fiber types.

SEM evaluation was also used to learn properties of the composites. For the SiC fibers, the SEM was used to learn the cause of failure. This was accomplished by mounting the broken ends of the individual fibers. If the fiber tip was shattered, then the fiber most likely did not have an internal or external flaw and was not damaged during processing. However, if the fiber showed signs of fatigue, such as stress marks flowing from a point of origin, then the fiber presumably had an internal failure and could have been damaged during processing. The SEM was also used during the first portion of the Task to evaluate the SiC fiber coatings. After being tested and prepared, the bond strength between the coating and the fiber, and the coating and the titanium matrix could be determined. If the bond between the fiber and the matrix was heavily cracked or had completely disappeared, the bond was considered a "weak" bond. If the coating between the fiber and the matrix was and had few small cracks, it was classified as a "strong"bond.

During the second portion of the Task, other methods of materials evaluation, such as chemical analysis, heat treatment, TGA, DTA, and microhardness testing, were used. These, along with the methods previously discussed, were used further to investigate the properties of the materials being considered.

Chemical analysis was the first form of evaluation done on each sample. This was to ensure the quality and homogeneity of the received sample. DTA was then done on the samples containing varying levels of carbon. This determines the temperatures at which materials undergo phase changes. It was known that the material in question would have a phase change. However, it was not known what effect carbon would have on the temperature at which this occurred. By heating the sample at a constant rate, it can be determined at what temperature heat is absorbed or released by the material. It is at the temperatures, at which the heat is absorbed or released, when the material undergoes a phase change.

Heat treatments were done with small samples of the Ti-24Al-12Nb material. First, the samples are encased by glass in a nitrogen atmosphere. This is meant to prevent oxidation of the sample during heating. The samples are then placed in furnaces at temperatures and times by which a transformation of the sample will take place. This transformation should come as an increase or decrease in hardness or even a change in the microstructure of the sample. Microhardness testing is used to find the change in hardness and SEM evaluation was used to find microstructural changes.

The samples selected for heat treatment varied not only in heat treatment temperatures and times but also in the carbon content of the material. It was suspected that the carbon content would, increase the hardness of the material, and possibly change the microstructure. SEM evaluation of the samples was done on the samples to learn if the theory was correct.

TGA is an experiment done to find weight gains and losses of a material when subjected to certain temperatures and environments. Several alloying elements were introduced into samples of Ti-22A1-23Nb and heated to 800°C for approximately 8 hours in an oxygen rich environment. This was done to decide the effectiveness of the alloying elements in reducing the oxidation rate of Ti-22A1-23Nb. After the samples were tested, they were sectioned and prepared for SEM evaluation to find the oxidation.

The fiber testing, accomplished during the second part of the Task, done on a sample that had undergone fatigue testing was used to find the effects of oxidation on fiber strength. After the fibers were tensile tested, they were mounted and evaluated by the SEM. After the mode of failure was recorded, the fibers were ranked according to their ultimate tensile strength. The data was then manipulated, using weibull statistics to learn the probability of survival of fibers that had undergone different stages of oxidation.

RESULTS

During the first portion of the Task, the work was used to support ongoing projects. The determination of tensile strength of the SiC fibers and the mode of failure of those fibers was used to support a project being done by Mary Lee Gambone. Extensive research must be done to be able to find which is the best possible fiber that can be used in the metal matrix composites and to figure out the effects of processing on the fibers. The work done to find the effects of different coatings on the bond strength between the fiber and the matrix was in support of a project being done by Doug Gundel. It has not even been determined whether a strong or weak bond is needed for the composite being considered; however, a great deal has been learned about the reactions between coatings and both the matrix and the fiber.

During the second part of the Task, two projects were assigned to support existing theories on the effects of additional elements on titanium composites. For the project concerning the addition of carbon to Ti-24AL-12Nb, it was determined that carbon would add to the strength of the alloy and decrease the temperature at which the Ti-24A1-12Nb would undergo its phase change. This was true for each temperature at which the material was heat treated. It was also determined that as the heat treating temperature increased, so did the hardness of the alloy. This supported existing theory about the effect of carbon on titanium alloy systems.

For the project concerning the addition of several different alloys to Ti-22Al-23Nb, it was found that when Si, Mo, and Cr were added to the system, the oxidation rate was decreased, therefore having a beneficial effect. When the elements W and Hf were added, larger amounts of oxidation occurred, therefore having an adverse effect.

The work done on the tensile testing of the fatigue tested bar was not entirely completed, it was found that the oxidized specimens had a lower tensile strength and probability of survival.

TIME-DEPENDENT BEHAVIOR AND ENVIRONMENTAL EFFECTS ON MECHANICAL PROPERTIES OF HIGH TEMPERATURE AEROSPACE ALLOYS

Task Order No. 228
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 1996

Government Task Leader
Mr. Steve Balsone
WL/MLLN

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TASK ASSIGNMENT

The main objective of Task 228 was to help in the Study of High Temperature Aerospace alloys. The materials studied were gamma (γ) titanium in Ti-6Al-4V and PRDA 30. The major part of the Task was the microstructural analysis of various types of gamma titanium. This included the cutting, mounting, polishing, taking optical photographs of the microstructure, and volume fraction measurements of the titanium phases. This was done to help determine the size of the microstructure, which is important in gamma titanium because the properties of the material improve as the lamellar grain structure is decreased. In the PRDA 30 material, the main objective was to find the beta (β) transus temperature for the material by doing microstructural analysis of the material after heat treatment at nine different temperatures, using 10°C intervals.

Unfortunately, the Government Task Leader left government service during the third month of the Task. I was then transferred to work on a Task with Mr. Larry Zawada on the study of advanced ceramic matrix composites (CMC's) and to organize and computerize the procurement of all the supplies used by the branch. During this portion of the Task, duties included preparing presentations, logging in data, data organization, and material microstructure characterization. The three main projects in this Task were evaluating SCS-6/Si_3N_4, organizing and transferring 9 years of test data on CMC's to 100MB Zip disks, and preparing log information on all the purchases made in the branch over the past 2 years.

In evaluating SCS-6/Si_3N_4, microstructural analysis was done on the material in the as received condition for later comparison to the microstructure after the various tests had been run. The tests that were run included fatigue, creep, heat treatments, thickness and tensile testing. These different types of tests were run under various conditions. The results of these tests were plotted and given to the engineer for analysis. Tested material was cut and polished for microstructural analysis. Fracture analysis was done on the different types of tests run on the material using the scanning electron microscope (SEM). One special task involved heat treatment for 185 hours at 1309°C. This test clearly identified an oxidation problem in this CMC. The result showed that the material was not ready for a production application. All of this data was prepared for presentation at a detailed design review. This resulted in a decision not to use the material for the turbine engine seal. This was due to some unfortunate high temperature results for the material. This part of the Task was successful in helping to evaluate this material for this application.

The next project was compiling all of the reports on the purchases placed by the Branch in the last 2 years. This included a comparison of the length of time it took to get deliveries of needed supplies through both the credit card and LMCA. A difference in delivery time of 8.6 days for the credit card verses 161.2 days for the LMCA system was found. A tracking process was developed to speed up the LMCA system by performing timely phone calls to make sure the supplies do not get lost. This project ended with a work unit directorate (WUD) presentation to inform people that if they want to get their supplies on time they should try to order through the credit card or plan on a 4 to 5 month delay in getting what they need. The completion of this Task involved the transfer of spreadsheets to the on-site UDRI contractor, and closeout of four purchase requests that had remained open for several months.

The final project consisted of organizing all of the test data which Larry Zawada has generated over 9 years and organizing it onto zip disks to update the storage medium used for storing all of the plots and data which have been generated over the years. This new storage medium allows all the material for each different material type to be stored on one zip disk decreasing the chances that the data could be lost or damaged. This effort is culminating in the writing of a technical report to be published in the future that will contain all of this data. The main emphasis was to establish a directory hierarchy and a standard set of file names for each type of test data. The entire Task involved over 2GB of data and more than 10,000 files.

MECHANICS AND MECHANISMS OF DAMAGE ACCUMULATION IN AEROSPACE ALLOYS AND METAL MATRIX COMPOSITES

Task Order No. 229
Student Support Program
Southwestern Ohio Council for Higher Education

Brian Rigling
University of Dayton

27 December 1996

Government Task Leader
Dr. James Larsen
WL/MLLN

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I would like to acknowledge Dr. Jay Jira for his guidance over the past several months. His help was especially critical over the summer of 1996 by keeping me busy during Dr. Larsen's sabbatical. I would also like to thank Dr. Reji John of UDRI for the research opportunities he provided. Finally and most important, I would like to thank Dr. Jim Larsen for allowing me this time with the WL/MLLN family through the SOCHE program.

TASK ASSIGNMENT

The Materials Directorate at WPAFB is conducting basic research, exploratory development, advanced development, and materials process design. The Directorate works to reduce costs, improve reliability, and enhance performance of Air Force aircraft and equipment.

This Task was assigned to the Metals and Ceramics Division of the Materials Directorate and more specifically the Materials Behavior Branch, designated WL/MLLN. Engineers and scientists within the Branch deal mainly with the effects of high temperature, high pressure and extreme stress loads on Metal Matrix Composites (MMC). The purpose of the Task was to act as a research assistant to both government and on-site UDRI contracted researchers.

The first assignment in the department was the conversion of many macros from Excel 4.0 to VisualBasic (VBA) for Excel 5.0. The macros are used for analysis of bridged crack data. In summary, technicians run an experiment on a specimen of an MMC with a crack initiated on it. A computer interface monitors the specimen and measures the growth of the crack. The collected data is then processed by a program called SMOOTH that calculates crack growth rates and stress intensity factors. This SMOOTH data, and a plethora of other factors are combined into a large Excel spreadsheet. The macros translated and revised are used in analysis of all this data. Roughly 35-40 pages of macro language translated to an approximate equivalent number of pages in VBA. The crux of the difficulty of this Task was a lack of experience with either Excel macro language or VisualBasic. Therefore, the first few weeks of the assignment were used in self-instruction in Excel Macro language and Visual Basic for Applications. After doing a basic conversion, the code was then revised and optimized to allow more efficient performance and to correct shortcomings in the original code. Besides the above revisions, additional routines were added to the original analysis code.

Once the above bridging macros had been revised, all the previous data bases created by the old 4.0 macros had to be brought up to date. This was a task within itself because the old form had been in use for many years. During which a growing trend of inconsistencies, changes, and revisions had been affected on the format of the Excel spreadsheets used for analysis; by this time, there was no standard format. As such, all the old data bases had to be manually reformatted one at a time, case by case.

The next major assignment was dealing with general displacement solutions for the edge crack geometry. The purpose of this assignment was to fit general solutions to crack opening displacements and stress intensity factors, as well as the reverse, going from a crack opening displacement to a geometry. The crack opening displacements and stress intensity factors were determined as functions of two geometric variables, "a/W" which is the ratio of crack length to specimen width and "H/W" which is the ratio of the specimen length between clamps and the specimen width. Finite element analysis was used to produce raw data for crack opening displacements and stress intensity factors for a number of geometries. Equations to fit the data were then developed. The difficulty in doing this is fitting simultaneously to two variables makes it difficult to get a smooth fit. If the fit is not smooth, one cannot rely on the fit equations to give accurate answers for geometries between the data points that were fitted. In addition, one must also work to use the fewest number of constants in fitting as possible. These constants must have a reasonable number of significant digits. All these factors must be taken into account in order for the results to be effectively communicated and used by others. The fits have been completed, and the margin of error was under the goal of 1.5%. Currently, experiments are being run to test the validity of the solutions. So far, the data is matching nicely.

Afterwards another curve fitting problem was assigned. However, this surface crack geometry was defined in three dimensions, requiring a fit to three variables. After many attempts, experimenting, and discussion, it was decided that the solutions could not be fit with a reasonable number of equations and constants. Instead, an iterative solution to the problem was coded. The program inputs many initial values and then conducts a binomial search for the solution. This method is not as precise as a solution in equations, but is nonetheless effective.

The final task to be completed was to make an addition to the previously SMOOTH program. This programming had to be done in FORTRAN, in which there had been no prior experience. During the Task, instructing oneself in FORTRAN was obviously necessary, just as the VBA and the Excel 4.0 macro languages had been learned. The subroutine written simply inputs a delimiter character used to delimit a given string of text into separate substrings.

The remaining projects involves working with an engineer contracted by UDRI at the base. He is developing a new solution for the semi-elliptical surface crack geometry. The method in use is that of determining a weight function for a known reference solution. This weight function can then be used to determine other stress intensity factors.

INFRARED MATERIALS CHARACTERIZATION

Task Order No. 230
Student Support Program
Southwestern Ohio Council for Higher Education

Michael Thomas
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Government Task Leader
Dr. Patrick J. Hood
WL/MLPJ

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TASK ASSIGNMENT

An instrument has been designed and constructed in which the complex index of refraction of thin films can be measured through spectroscopic reflectometry and/or ellipsometry. This instrument is designed to measure the index of refraction in the 3 to 15-micron region. The instrument was designed to be flexible and may either be configured as a reflectometer or an ellipsometer. The measurement technique selected depends on the optical properties of the thin-film and substrate materials. When configured as a reflectometer, reflection measurements are made for s and p polarized light at single or multiple wavelengths and at various angles of incidence. The transformation to an ellipsometer consists of adding a variable compensator, a polarizer, and an analyzer to the reflectometer configuration. When configured for spectroscopic ellipsometry, a variable compensator is integrated into the system. The compensator is set to a quarter wave for the wavelength of interest that converts linearly polarized light to circularly polarized light before reflecting off a thin-film sample. Four-zone null ellipsometry is then done to extrapolate the complex index of refraction of the sample. Calibration measurements were done and are presented.

The objective of this project is accurately to measure the complex index of refraction, n and k, of materials in thin-film or bulk form as a function of temperature and wavelength. The spectroscopic instrument described in this paper is designed to be flexible and accurately traceable to reference standards.

The current design capability allows for a sample to be tested over a range of temperatures from 77 to 500 K. The ability to take measurements over a broad range of temperatures is very important, especially when characterizing thermochromic materials such as vanadium oxides and rare earth nickel oxides.

The designed instrument can be configured as a spectroscopic reflectometer or ellipsometer. Configured as a reflectometer, the system measures transmission and reflection simultaneously as a function of temperature and incident polarization. Figure 1 shows the instrument configured as a reflectometer.

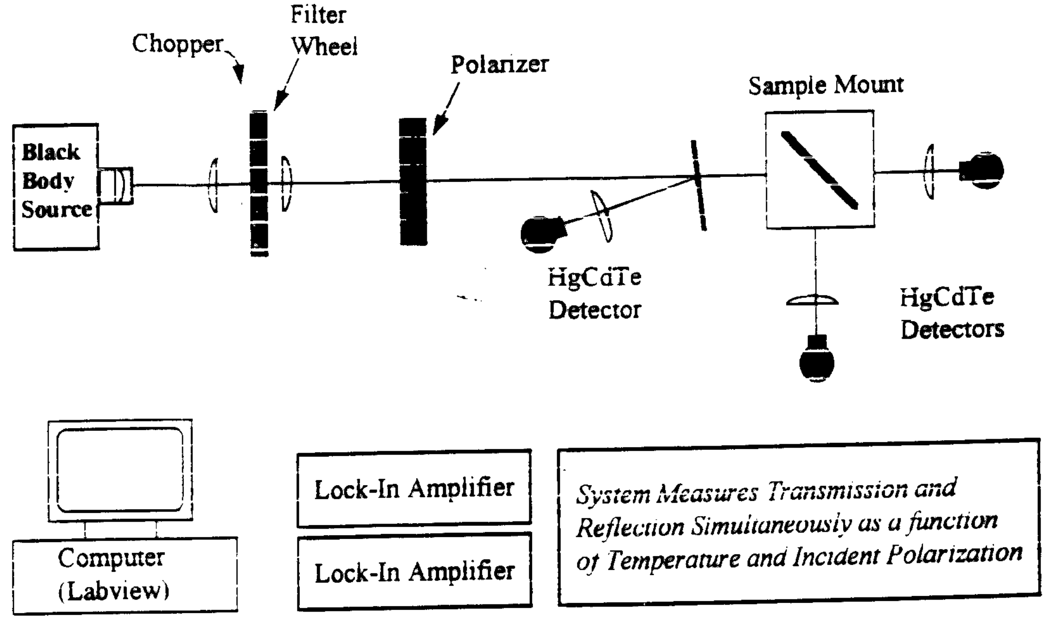

Figure 1. Instrument Configured as a Spectroscopic Reflectometer.

The conversion of this instrument from a reflectometer to an ellipsometer consists of adding a variable quarter-wave plate (Soleil-Babinet compensator) and an analyzer. Figure 2 shows the instrument configured as a spectroscopic ellipsometer.

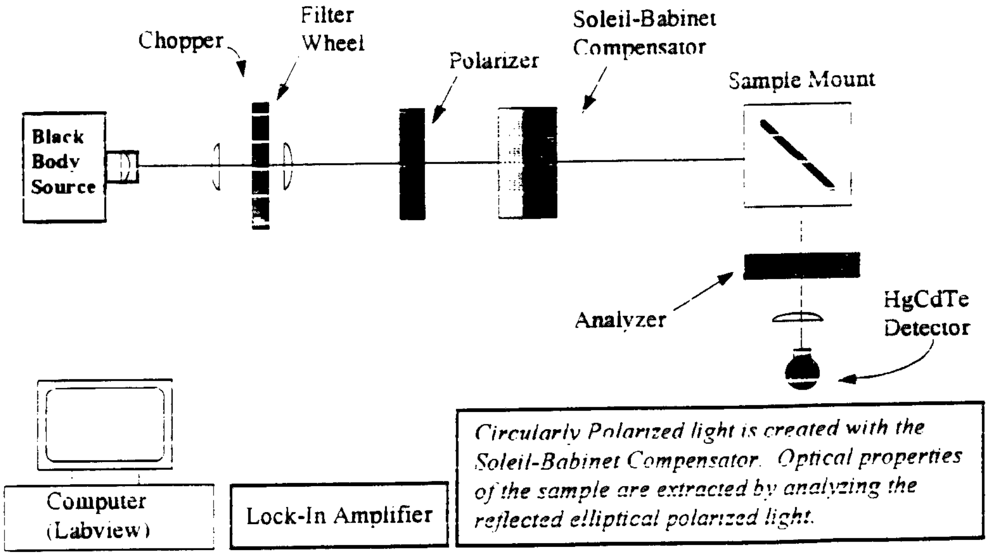

Figure 2. Instrument Configured as a Spectroscopic Ellipsometer.

First, all optical components are aligned and set to take measurements at the desired wavelength. A gold mirror with 99.7 % reflectance at infrared wavelengths is used to align the detector and collect the maximum amount of energy for the given setup. The normalized recorded value is used as a standardized reference. A reference detector is also used to monitor the source. The source used is an Oriel infrared lamp that is very steady (less than 2% variation per hour). For reflectometry, the sample is placed in the system and reflectance data is acquired for s and/or p polarized light at a single angle and/or multiple angles of incidence. For ellipsometry, the arrangement described above is setup and reflection data is recorded while rotating the analyzer (Rotating-Analyzing-Ellipsometry).

In conclusion, an instrument has been designed and assembled in which the optical constants of bulk or thin-film materials can be determined as a function of wavelength and temperature. The layout above has been proven to produce a set of reasonable data.

INFRARED LABORATORY EXPERIMENTAL AUTOMATION

Task Order No. 231
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Southwestern Ohio Council for Higher Education

Brian Deep
University of Dayton

27 December 1996

Government Task Leader
Dr. Patrick Hood
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TASK ASSIGNMENT

This Task at WPAFB Materials Labs mainly involves the implementation of a software package from *National Instruments* called Labview 4.0.1 to automate different experimental methods for characterizing infrared (IR) nonlinear materials and devices. The purpose of implementing this software package is to automate optical experiments for laser hardening experimentally. This software is used with GPIB and relay card hardware to automate experimentation.

The purpose of the experimentation is to discover the optical characteristics of materials at near and far IR wavelengths. Different materials are tested and the optical characteristics of the materials are charted to discover whether the material is suitable for optical detector or protector purposes.

The automation process involves designing Labview programs to emulate the experimental process and remove the user from tedious data gathering tasks. Labview is a graphical programming language that allows for a graphical user interface to the experimentation process. This software is used to communicate with data gathering devices via GPIB(General Purpose Interface Bus) to gather and manipulate experimental data. The data is then graphed in real time so that the user can see experimental results as they occur.

The equipment involved in the automation is a ZEOS 486-66 with 16 MB of RAM running Windows 95, a Laser Precision RM6600 with energy probes for measuring laser beam energy at different positions in the optical setup, a PMC400 Newport motion controller for moving the sample within the beam path, and a Lakeshore 330 temperature controller for thermal control of the sample. Also, a proprietary relay-controlled device is used to control the placement of attenuators in the path of the laser beam to control how much energy reaches the test sample.

The major problem involved with this Task is getting the devices to communicate with the computer and getting the software to recognize the devices. Once this was accomplished, the Task turned toward programming in Labview.

The developed Labview program runs and gathers data from each device, graphs the necessary data and writes all data to file. To produce professional looking graphs, the data is taken to Microsoft Excel and a macro was developed to process the data quickly and produce a titled and dated graph of the desired data.

This program and testing process were designed for far IR testing. The program was then adapted for use with a near IR system. The Laser Precision RJ7620 energy box was automated for these wavelengths. A Labview driver was written for all of the low-level calls to the energy box since none previous existed.

This Task also involves learning the basics of the optical experimentation setup. During the Task, the basics of optical lenses, focal lengths, focusing and defocusing of the laser beam are learned, *f* numbers of different optical setups, and steering the beam and setting up energy detectors and pinholes for the laser to shoot at and through. The main thing to learn is laser safety. When working with a CO_2 laser in the IR, the laser produces invisible light pulses. The user must be aware of the path of the beam and whether the beam is on or not. The laser can cause extreme retinal damage so eye protection is always worn.

This Task also involves the upkeep and maintenance involved with a local area network. This portion involved setting up the systems on the network and setting up file and printer sharing between computers. This also involves system upgrade and maintenance.

One final project of this Task is to automate the experimental systems to allow for remote monitoring. This system gathers data and sends it via TCP/IP to a remote terminal for user data analysis. The system also monitors sample temperatures so that the user does not waste time waiting for the sample to reach a given temperature. The experimenter can return to other tasks and remotely set and monitor the temperature of the test sample.

The main portions of this Task involve adapting the existing Labview programs to meet user needs and computer and network maintenance. As different experimenting methods become apparent, the desire is to have an automation program that fits those needs. Networks sometimes fail and this Task involves troubleshooting some of those problems.

This Task shows that optics is an ever growing field and that there are many undiscovered ideas in the field of optics. The Task will involve many more experiments on untested or rarely tested materials and hopefully will give the world a better understanding of certain optical material properties. The Task will also lead into other automation needs as new experimental methods are deemed necessary.

SUPERCRITICAL FLUID CHROMATOGRAPHY OF LUBRICANTS AND ADDITIVES

Task Order No. 232
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 1996

Government Task Leader
Dr. Harvey L. Paige
WL/MLBT

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ABSTRACT

The purpose of this Task was to examine a variety of high-performance fluids, lubricants, and additives: a Dionex Series 600 Supercritical Fluid Chromatograph (SFC) with a flame ionization detector (FID). Another goal under this Task was to examine the usefulness of an ultraviolet/visible light detector (UV/VIS) with SFC; this topic remains yet unexamined due to instrumental difficulties. Finally, a separation of perfluorinated ethers at ultra-high vacuum (UHV) conditions was carried out under the supervision of Jim Liang.

GENERAL DESCRIPTION OF TASK

The primary purpose of this Task was to employ supercritical fluid instrumentation and detection devices to evaluate the performance of perfluoropolyethers (PFPAEs) and performance-enhancing additives during stress testing. Supercritical fluid chromatography is a useful tool in the analysis of component mixtures that are not readily separated by GC or high performance liquid chromatography (HPLC). SFC is also compatible with a wide range of detection devices, which enhances its utility. Flame ionization detection (FID) was the primary detection method, but ultraviolet/visible light detection (UV/VIS) was also of interest because some additives were UV active (and thus detectable by UV/VIS). Thus, UV/VIS detection has potential as an alternative method to FID. Due to technical difficulties with the UV/VIS detector, the performance of this detection method was not tested during this Task. In addition, a supercritical fluid extractor (SFE) was obtained for use in preparation and delivery of a modified mobile phase. The modifiers under consideration for use were water and methanol. These modifiers could potentially enhance separation of the PFPAE sample components, and would be compatible with UV/VIS detection. The results of these studies may be applied to selection of the best high-performance hydraulic fluids, lubricants, etc. for use in Air Force aircraft and space vehicles.

DESCRIPTION OF RESEARCH

The methodology used in the completed chromatograms was as follows. A Dionex Series 600 SFC with a personal computer interface (ACI-450) and a Dionex FID 600 were used in these analyses. Unmodified carbon dioxide was used as the mobile phase. The chromatograph was equipped with a Chromegabond PFP packed column (10cm X 1.0mm); a 100-mm frit restrictor with 1/4 of the frit removed controlled the CO_2 flow into the FID. The program method used throughout this study was as follows: the method was isothermal, with T=140°C., the FID was set at 400°C., the initial CO_2 pressure was 120 atm and was increased to 200 atm with a ramp rate of 4 atm/min. This pressure was held for 10 minutes, underwent a pressure ramp rate of 2 atm/min to a final pressure of 350 atm. After a hold time of 45 minutes, the method was ended. After each sample, the SFC column was cleaned by using a cleaning method that cycled through an isothermal, high ramp-rate program to remove any residue of samples on the column. The base PFPAE fluids and those containing additives were formulated to wear-test specifications, tested, and submitted for SFC analysis. The stressed samples were then compared to nonstressed ("blank") samples to evaluate the performance of the sample fluids. Significant changes sought between the stressed and nonstressed samples were low molecular-weight changes in component amounts at early times in the chromatographic runs. Any major changes, if any, in the chromatograms were commented on as well.

RESULTS AND DISCUSSION

Two sets of samples were analyzed. It should be noted that the SFC was inoperative for about 2 months due to hardware problems, during which time the research in the "Addendum to Task 232" was carried out. After the SFC was operational again, these analyses were carried out. The first set of samples contained the PFPAE fluid, Demnum, with the additives in the following formulations (Table I). The results are given in the following paragraphs. Table I contains a summary of information about the various samples (where PH_3PFPAEP is PH_3(perfluoropolyalkyletherphenyl)phosphine).

Table I: Summary of Sample Information

Sample ID	**Formulation**
MLO 95-103	Demnum S65
MLO 95-105	2% proprietary add. in MLO 95-103
MLO 95-126	2% PH_3(PFPAEP) in MLO 95-103
MLO 96-62	Stressed MLO 95-103
MLO 96-63	Stressed MLO 95-103
MLO 96-73	Stressed MLO 95-103
MLO 96-74	Stressed MLO 95-126
MLO 96-75	Stressed MLO 95-103
MLO 96-76	Stressed MLO 95-103
MLO 96-81	Stressed MLO 96-105

In a comparison of sample MLO 95-103 with the stressed samples, some slight differences were noted between MLO 95-103 and the samples MLO 96-62, MLO 96-63, and MLO 96-76. The common difference among these samples was that in the time span of 20-30 minutes into the chromatograph, there were less intense peaks in the stressed samples than in the MLO 95-103.

No significant differences were noted between MLO 96-73 and MLO 95-103, or between MLO 96-75 and MLO 95-103.

The samples 95-105 and 96-81 both contained a proprietary additive. The chromatograms of these two samples, when compared to each other, showed that the stressed fluid was not significantly affected by the stress applied to the system, relative to the unstressed sample.

The samples MLO 95-126 and MLO 96-74 both contained a perfluoropolyetherphenylphosphine additive. There were very few differences between the chromatograms of the stressed and unstressed fluid. This indicates that this formulation of PFPAE and additive was relatively unaffected by the stress added to the system.

If any of these three sample lots could be evaluated to a best/worst situation based upon SFC data alone (which is not the case; there are other data to consider), the sample with the proprietary additive could be assumed to have the best performance, since its chromatogram was the most unchanged between the unstressed and stressed samples.

The second lot of samples was formulated in Demnum S65. The formulations, additives, and the conclusions drawn from the chromatograms, are discussed below.

The S65 fluid samples were formulated with additives as follows: MLO 96-250 and MLO 96-59 contained 1% DBZT; MLO 96-251 and 96-58 contained 1.5% TPE; and MLO 96-258 and MLO 96-65 contained 1% DPE. Also, there were some separation performance problems, most likely caused by an improper split ratio.

The samples MLO 96-250 and MLO 96-59 showed some proportionality differences in the fourth and fifth peak after the solvent peak. These could be in part due to a noise line caused by a FID adjustment (there was concern the flame was going to go out).

The samples MLO 96-251 and MLO 96-58 had some differences that were readily observable. In the unstressed sample, the last well-resolved peaks were observed at T=60 minutes. In the stressed sample (MLO 96-251), the regular, well-defined peaks ended at T=45 minutes. Otherwise, the chromatograms were similar between T=16 minutes and T=44 minutes.

The samples MLO 96-258 and MLO 96-65 exhibited no major differences in their respective chromatograms. However, the first three peaks in both chromatograms were not integrated by the SFC software, even after repeated adjustment of the integration program.

Again, based exclusively upon this data (which should not be the only data on which the overall conclusions about the fluids' performance are based), either the 1% DBZT formulation or the 1% DPE formulation has undergone the least changes when subjected to stress.

Overall, the most valuable learning experience throughout this Task was the troubleshooting expertise gained while the SFC was "down" due to oven malfunctions. The author has learned (from that situation) several valuable lessons about instrumental failure and means by which to address this. Also, the author's experience in the field of Chromatography was enhanced a great deal. Finally, the experience gained about "Real World" experience will no doubt serve the author at later terms in her career.

SUPERCRITICAL FLUID CHROMATOGRAPHY OF LUBRICANTS AND ADDITIVES

Task Order No. 232a
Student Support Program
Southwestern Ohio Council for Higher Education

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Government Task Leader
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WL/MLBT

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TASK ASSIGNMENT

During the research with Dr. Paige, fluid lubricants were analyzed to determine when the components of the fluid fell out of solution under high temperatures and pressures. This was done to determine if a lubricant fluid could be created such that the solution could be stable at a temperature at or above 345 degrees Celsius. The results of the data received have been used to refine lubricant fluids that show promise and to eliminate those that do not.

The research completed with Dr. Liang involved attempts to find environmentally friendly coatings for aluminum and titanium for aircraft and spacecraft. The metal strips were coated with varying solutions, including vinyl mixtures, some included the use of cerium in the form of cerium(III) nitrate.

The lubricant fluid samples of Dr. Paige were analyzed by use of a supercritical fluid chromatograph or SFC. The SFC used a Flame Ionization Detector or FID to detect when the components of the solution fell out of solution. Later an ultraviolet detector, or UVD was connected to the SFC. The results were analyzed by George Fultz and Dr. Paige.

Dr. Liang's samples were analyzed by using a grazing angle microscope lens to detect where the coatings and materials showed signs of wear. The coatings were analyzed using an FTIR, infrared spectrometer. Data were analyzed by examining the IR graphs of the samples given by the FTIR.

Due to the short amount of time spent with Dr. Paige on the SFC research, not much was learned from late November until the closing date of December 27. There are no confirmed conclusions as of the date of this report on Task 232.

Dr. Liang's research showed that cerium did affect the sample coatings, although more testing needs to be done to arrive at any conclusions about what, exactly is happening.

SPACE COATING MATERIALS DEVELOPMENT: MECHANICAL TESTING

Task Order No. 233
Student Support Program
Southwestern Ohio Council for Higher Education

John Florkey
The Ohio State University

13 September 1996

Government Task Leader
Lt. Kathleen Havey
WL\MLBT

ACKNOWLEDGMENTS

Thanks to everyone who has offered their knowledge and experience. Special thanks goes to the following: Dr. Jeff Zabinski, Dr. Peter John, Dr. Dave Rigney, Lt. Kate Havey, Art Safriet, John Agoston of GE Lighting, Nela Park Cleveland, OH, Dr. Sahai, John Bultman, Kurt Eyenk, Robert McAlister of McAllister Technical Services, Coeur d'Alene, Idaho.

DESCRIPTION OF TASK ASSIGNMENT

Perfluoropolyalkylethers (PFPAE) are a class of liquid lubricant under investigation for use in the high temperature areas of gas turbine engines. Similar types of fluids have been used in space applications but were limited to operation mainly at room temperature. PFPAE's are observed to degrade at high temperatures (above 400°C), under tribological conditions, in the presence of ionizing radiation, and in the presence of certain catalytic materials. The degradation of PFPAE under tribological conditions over a range of temperatures is the main focus of the research this project is supporting.

To understand the degradation of PFPAE under tribological conditions at various temperatures, the Tribology Group of Wright Laboratory has designed an ultra-high vacuum tribometer for use with an existing X-ray photoelectron spectroscopy (XPS) system. An XPS is an instrument used to find the chemistry of the surface of a material. The objective of this Task was to design, build, install, and calibrate a heater to be used with the existing tribometer.

DESCRIPTION OF DESIGN PARAMETERS

1) The heater can heat a sample (a 1.25" diameter, 0.125" thick disc) from room temperature to 350°C.

2) The heater can maintain the desired temperature within 20°C over the 1" working diameter of the sample.

3) The heater can reach the desired temperature in no more than 15 minutes.

4) The heater can maintain the desired temperature for several hours.

5) The heater must reside within a standard 6-way cross.

6) The cost of the heater must be kept to a minimum because of the length of time it takes to get large dollar orders through government procedures.

7) The heater must be vacuum compatible.

8) The electrical components of the heater will not interfere with the signal from the transducer or strain gauge used for measuring the friction force.

9) The heater will be designed such that the temperature can be measured during experiments.

DESCRIPTION OF DESIGN PROCESS

Several choices for heater designs were available. A wound filament could be used to heat the sample radiatively from above or below. A resistive heat source embedded in an electrically insulating material could be used as a sample stage on which the sample would sit. Magnetic samples could be heated by induction.

The inductive method of heating was ruled out because of the requirement that the samples be magnetic. The heater should be compatible with many different samples. Inductive heating also requires high frequency biasing that could cause noise in the transducer signal. The frequency generator would also have to be purchased.

The resistively heated table was not used because previous attempts at making one had not produced a reliable heater. Servicing when there were problems was difficult. It seemed that the design would be more massive than the alternatives.

The radiative method using the wound filament was chosen because the materials necessary to build the heater could all be found in-house. The heater could be retrofitted to the existing tribometer without much modification and there were no restrictions on sample type.

The existing tribometer designs were modified such that a cylinder, approximately 0.600" in diameter and 0.500" high, was created for the filament to reside. The shaft that rotated the sample was modified so lead wires for the filament could reside inside the shaft.

A brush system was designed that allowed power to be applied to the filament during rotation. It consisted of a copper disc attached to the rotation shaft, but electrically isolated by a ceramic spacer. A thick copper wire bent into a U shape was attached to the electrical feedthrough at the curved part of the U, while the prong parts of the U were put into contact with the copper disc. A spring was placed between the prongs of the copper wire to keep the prongs in contact with the copper disc while rotating. 0.020" tantalum wire was used to connect the copper disc to the filament.

Heat flow models were prepared to predict how much power required to reach the desired temperature. The worst case scenarios were chosen and the filament was designed with these in mind. Calculations showed that at worst approximately 30 watts would be needed to heat the sample to 350°C. So the filament was designed for 100 watts. It was soon realized that a filament of the required dimensions could not be produced in-house. So, on the advice of Dr.

Rigney, John Agoston, of GE Lighting, was contacted. He donated approximately 1 hundred 100 watt filaments. These filaments were suitably sized and of the correct wattage.

Experiments were first undertaken without rotating the heater. It was found that the filaments weakened and sagged at high temperatures, causing the filament to ground to the cylinder that surrounded it. This was combated by positioning the filament such that when it sagged, it did not meet the cylinder walls. The filament ends were slid over the ends of the tantalum lead wires instead of being spot welded. This offered easy changing of burnt filaments and structural support to decrease sag.

An optical pyrometer was to be used to measure the temperature of the sample during experiments. The pyrometer was calibrated by correlating the output of the pyrometer to the output of two thermocouples spot welded to the sample. One thermocouple was placed in the center of the sample and the other near the edge of the sample. The positioning of the thermocouples was used to ensure that the surface of the sample differed in temperature by no more than 20°C over the 1" working diameter.

Many experiments were undertaken to get a feel for the behavior of the filaments. As the heater was used frequently, it was noticed that filaments were burning out too quickly. Inspection of the side of the sample that faced the filament showed a build up of tungsten. This indicated that the filament was getting too hot and was evaporating. To combat this problem, the lead wires were modified to allow two filaments to be used at the same time. The added filament allowed more heat to radiate to the sample while allowing each filament to operate at a lower temperature.

RESULTS

The tribometer heater was not tested as thoroughly as was originally planned. The heater does achieve most of the original goals including: heats to a minimum of 350°C, maintains less than a 20°C gradient across the 1" working diameter of the sample, is completely vacuum compatible, meets cost qualifications, allows for temperature measurement during the experiment, and does not interfere with the signal from the transducer. Slightly modified from the original goals: heats to desired temperature in less than 30 minutes and has difficulty maintaining temperature while rotating.

The addition of the second filament should reduce the amount of time necessary to achieve the desired temperatures, but there was not enough time to verify this hypothesis. The electrical contact design is being evaluated and modified to improve performance while rotating.

SPACE COATING MATERIALS DEVELOPMENT: DEPOSITION AND PROCESSING

Task Order No. 234
Student Support Program
Southwestern Ohio Council for Higher Education

Barbara R. Lowery
Ohio University

6 September 1996

Government Task Leader
Lt. Kathleen Havey
WL/MLBT

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TASK ASSIGNMENT

The objective of Task 234 was to develop and deposit thin films (advanced surface coatings) for use in space applications. Development of the deposition equipment and analyzation of the surfaces to characterize them was also included.

DESCRIPTION OF WORK

Most of my time during this Task was spent characterizing nitrogen plasmas, which are electrically neutral yet highly ionized concentrations of gas. These plasmas, along with a target like Boron, are what is used to deposit the thin films on the substrates. To characterize the plasmas I worked with the Electron Cyclotron Resonance (ECR) chamber which Dr. Chen had developed. This was a high vacuum chamber that contained both a magnetron gun and an ECR apparatus that could create plasmas using a DC power supply and microwaves.

At the beginning of the assignment, the basic procedures involved were in using the chamber, such as bringing the chamber's pressure back up to air pressure so that it could be opened for cleaning and other maintenance, and then pumping the chamber's pressure back down to a low pressure to work with vacuum conditions. A substrate was removed on which a thin film had been deposited. Then a Langmuir probe was placed inside the chamber. This probe was the basis for all of the characterizations. It consisted of both a small flat disc and a Tungsten wire, and it could be moved to different distances from the magnetron gun.

A high voltage source was also used in characterizing the plasma. With this power source both negative and positive charges could be sent to the chamber and through the Langmuir probe, this process was called biasing. Once the probe was charged within the plasma, the oppositely charged particles from the plasma were attracted to the probe. This in turn caused a current to go through the probe that I could measure and record using a multimeter. Throughout the different characterization tests, several factors would be altered. Some of these included pressure, power of the magnetron gun, power of the ECR, and distance of the probe from the gun. After obtaining these data, the results were recorded and graphed using bias vs. current. During most of the characterization, nitrogen gas was used, which created a pink plasma, but at the end of the Task, argon was used, which created a blue plasma.

As another portion of the Task, I learned to use the Dektak IIA. This piece of equipment evaluated the thickness of the film by lightly running across the surface of the sample with a small diamond-tipped pin. When I first learned to use the Dektak, I used standard samples, then after more practice I moved on to analyzing actual test samples.

There were several other responsibilities during this Task. Some of these included doing research in the technical library to help Dr. Chen in making decisions about future equipment purchases, organizing and labeling samples, taking inventories of equipment, and filling out purchase request order forms. I also became more familiarized with using spreadsheets.

FUTURE GOALS

In the time allotted for my first Task, I was unable to accomplish all of my objectives. In the future I would finish the characterization of the argon plasmas to compare them with the nitrogen plasmas. I would also begin actual depositing of films onto substrates to create samples to analyze more closely. When analyzing these samples, I would not only be testing for their thickness, but also I would learn to test their hardness, durability, and responsiveness to lubricants. During this Task I concentrated on the ECR chamber, but in the future I would possibly work with another chamber more recently developed by Dr. Chen, the Magnetron Deposition chamber.

NONDESTRUCTIVE CHARACTERIZATION OF CORROSION

Task Order No. 235
Student Support Program
Southwestern Ohio Council for Higher Education

Scott Monnin
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27 December 1996

Government Task Leader
Dr. Robert Crane
WL/MLLP

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I would like to thank Dr. Crane for giving me the opportunity to join in his research, Mark Ruddell for answering the many questions I came upon, and the entire NonDestructive Evaluation (NDE) task force for helping me in the completion of my Task.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The purpose of the Air Force's NDE branch is to provide alternate means of testing and observing samples without altering the samples' characteristics. The major areas of interest in this Task were chemiluminescence based leak detection and the observation and analysis of compounds present in corrosion pits.

Chemiluminescence is the production of light because of a chemical reaction. This usually occurs as the result of a compound being excited to a higher state and then emitting a photon while dropping back to the ground state. A common example of this is the Cyalume® Lightsticks used both in the military and civilian sectors. One part of this Task dealt with the use of chemiluminescence in identifying leaks in fuel tanks. The method currently being employed is using fluorescence to find the cracks in the fuel tanks. The shortcoming of this procedure is the problem of being able to observe the fluorescence. NDE believes that the increased visibility of the chemiluminescence would solve this problem.

The second part of this Task involved the prevention of corrosion on airplanes. A careful analysis of airplane corrosion pits was needed to detect the chemicals present, and in what percentages they were found. These findings could help researchers to decide the best routes toward future experimentation in corrosion prevention.

DESCRIPTION OF RESEARCH

The goal of this research project was to develop a mechanism to detect leaks in fuel tanks. The main area of interest was fuel carrying (wet) wings on airplanes. The method that was explored involved two stable liquid components that when brought together would give off luminescence. One liquid would be used to coat the inside the wing, while the other would be sprayed on the outside the wing. By reducing the pressure inside the wing, pulling the outside liquid through any cracks was possible, causing the reaction to proceed. Observation of the inside of the wing would allow for the detection of leaks (areas of luminescence). Both liquids had to be at or near neutral pH and nonreactive toward metals, such as aluminum in the case of wet wings.

The second objective of this Task was to attempt to identify the chemical compounds present in corrosion pits found on airplanes. The method used to accomplish this was colorimetry. Pieces of corroded plane were rinsed with deionized water and this water was then collected for further testing. The tests involved measuring the micrograms/liter of each chemical thought to be present, using a Hach model spectrometer. Changing the μg/liter results into

Molarity (moles/liter) showed a definite trend from one sample to another. It also showed that the greatest effects of corrosion were due not to salt present in the air, but to acid rain. Knowing what is causing the most significant corrosive effects, will enable researchers to develop better systems for combating corrosion.

RESULTS

It has been shown through research accomplished in this Task that using chemiluminescence to detect cracks has practical applications. Further research still needs to be done to detect what magnitude of cracks this method can identify. If this application is found to identify cracks on the order of magnitude necessary for Air Force regulations, both the time and money spent on finding and repairing these cracks will decrease.

The Air Force spends millions of dollars a year dealing with the problem of shielding their airplanes from the corrosive affects of the environment to which they are subjected. Before an acceptable preventive method can be implicated, an understanding of the source of corrosion is needed. This involves the identification of the products of corrosion. Determining in what percentages these compounds are present will determine the best maintenance procedures. Research accomplished through this Task has led to a better understanding of this problem.

DEVELOPMENT OF NOVEL NONDESTRUCTIVE EVALUATION TESTS

Task Order No. 236
Student Support Program
Southwestern Ohio Council for Higher Education

Greg Tyler
University of Dayton

27 December 1996

Government Task Leader
Dr. Robert Crane
WL/MLLP

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Mark Blodgett supplied a great deal of technical and moral support during the last 6 months. He was also extremely patient during the initial stages of this project.

William Mullins provided technical assistance and access to many resources.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The last 6 months consisted of two concurrent projects. The first involved the design and construction of an acoustic microscope envisioned by Mark Blodgett. Unlike most acoustic data collection equipment, this new scanner could collect information about a specific point of interest from any number of vantage points. This will allow for more detailed and complete analysis of materials. Acoustic microscopes are designed to characterize the internal microstructures of polymers and metals. The key limitation of most devices is the line-of-sight nature of the scans. Most devices can only detect microstructural defects on a two-dimensional basis. The microscope under construction will provide extensive information from multiple locations in three-dimensional space, giving the operator more thorough information.

The second Task project, overseen by William Mullins, involves the characterization of metallic surface corrosion. This project has involved doing acoustic and radiographic scans on multiple samples of 2024 and 7075 alloys. Each sample has been exposed to carefully prepared corrosive baths for varying durations. By performing fractal analyses of the samples, it is hoped those models for corrosion can be constructed for the purpose of predicting the expected durations of metallic constructions such as aircraft. This purpose becomes increasingly important in an age where military aircraft are being used well beyond their original intended lifetimes.

DESCRIPTION OF RESEARCH

The acoustic microscope under construction, tentatively called ARNAM T MAW, incorporates numerous pieces of laboratory equipment. Data collection is provided by a high-frequency immersion transducer. The sample is mounted level within a small tank of water, into which the transducer is immersed. Signal collection and averaging is provided by a LeCroy 9310a digitizing oscilloscope, linked via GPIB interface to a standard PC. Data processing is handled within the PC, which also serves as the data storage device. Motive power is provided by five stepping motors, three for translation and two for rotation. The motors are linked through two daisy-chained Velmex controllers to a standard GPIB-equipped PC. Software control is provided through a GUI program written in G, the proprietary graphic programming language of National Instruments' LabVIEW.

Corrosion characterization has involved repeated acoustic and radiographic scans of approximately 2 dozen samples of aluminum alloy. Acoustic data collection was provided through a high-precision scanning acoustic microscope (HIPSAM), which is maintained by UDRI engineer Richard Martin. Radiographic data collection was provided by John Brausch. Once sufficient scans were done, the data was processed using a PV Wave routine. Fit curves will be created in an attempt to find consistent trends in exfoliation and pitting corrosion.

RESULTS

Both projects remain in progress at this time. The ARNAM T MAW acoustic microscope is nearly complete. The hardware has been successfully integrated, and the control program can direct transducer translation and rotation, managing data files, and accepting varied user inputs. What remains is to collect actual transducer data. Currently a function generator is being used to provide input to the oscilloscope. This has confirmed the viability of the control program in collecting, processing, and storing data. Once the control program is completed, which should be within a month, actual data collection can begin. The user will become familiarized with the user interface, and technical support will be provided, for future enhancements or modifications.

The corrosion characterization project will remain in progress for perhaps 1 additional year. Data collection of seven tensile specimens from Purdue University has been completed. The data will soon be processed and analyzed. Once the Purdue samples have been analyzed, preparation of new samples will begin. This will entail cutting a predetermined number of wafers of 2024 alloys, exposing each to the same corrosive bath but for different durations, and cleaning the samples for data collection. The data collection will again be provided by HIPSAM and perhaps the ARNAM T MAW acoustic microscope.

ADVANCED NONDESTRUCTIVE EVALUATION (NDE)

Task Order No. 237
Student Support Program
Southwestern Ohio Council for Higher Education

Gregg Jessen
Wright State University

27 December 1996

Government Task Leader
Dr. Renee M. Kent
WL/MLLP

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

Advanced NonDestructive Evaluation is any method by which advanced composites can be observed and tested without using intrusive or destructive methods that may change the characteristics of the sample of interest. Techniques of particular interest to this Task are ultrasonic and laser based. These evaluation procedures have value to many industries. The Air Force has several aircraft that need to be inspected for wear, damage, and corrosion. With ultrasonic and laser-based techniques, the aircraft can often be examined without dismantling them and stripping paint from them. Being able to examine existing components, without taking them apart, is very convenient and cost effective or causing damage to them. Other industries use NonDestructive Evaluation procedures to monitor the formation of fiber reinforced composites using the fibers as sensors. These methods help to observe the formation of the matrix about the fibers and provide useful information about what is happening during the cooling of the matrix. The information obtained here can be used to improve the processes to get a better product. The ultrasonic-based evaluation methods are developed by examining fiber reinforced metal or glass matrix composites. Here it is specifically silicon carbide fibers in a titanium or glass matrix. The laser-based evaluation methods are developed by examining various interference patterns generated by surfaces of different degrees of roughness.

DESCRIPTION OF RESEARCH

Two primary methods of NonDestructive Evaluation are investigated. The first method is the more common ultrasonic technique that can be used for finding internal flaws and monitoring processes while materials are being formed. The second technique is a laser scattering technique that is useful for determining surface corrosion and surface roughness.

The first method is based on very simple ultrasonic principles. Since sound propagates as a wave, it must satisfy the boundary conditions of the partial differential equations that predict its motion. This means that as the wave moves from medium to medium, the equations predict that there will be a wave that is deflected. This deflected wave is seen as an ultrasonic echo and is observed whenever there are cracks or changes in the elastic properties of the medium through which the ultrasound travels. The equations used to solve for the motion of the ultrasonic wave also predict that the propagation of the wave is dependent on the compression or tension of the medium. This is important when a fiber is embedded in a matrix and residual stresses formed by mismatching the coefficients of thermal expansion, between the fiber and the matrix, causes shear stresses between the two that in turn causes compression or tension in both materials. Since sound wave characteristics change due to stresses ultrasonic pulses can be observed for changes to examine these stresses in different locations of the samples.

The first technique uses one ultrasonic transducer that emits ultrasonic pulses on the order of milliseconds. This transducer is then coupled to the sample of interest by a medium through which sound can pass easily. Sometimes this is water, but in several applications a more viscous medium is required for good coupling and epoxy is used. The other end of the sample is then coupled to another ultrasonic transducer that can detect the ultrasonic pulses that travel through the sample. The detected ultrasound can be observed on an oscilloscope (see Figure 1). From this information, the velocity of sound is calculated, the Fourier Transform of the signal is taken, and the amplitude of the resulting pulses is observed. Each sample has a signature signal and many signals show patterns for similar types of properties and for similar types of damages. Stress in different parts of the sample can change the signals drastically and fractures or debonds in the material can change the signal completely. This method was used to monitor the formation of the SCS-6/glass composite and several individual fibers. When glass formed around the fiber, echoes were seen at the point where the glass stuck to the fiber and stress changes in the composite showed as velocity changes in the ultrasonic pulse. Fiber breaks showed as echoes that reflect before the sound should reach the end of the sample.

It is desired to automate this first ultrasonic technique so that it can be used by industry to monitor the formation of materials produced and use the data collected in real time to control the formation process. Software is currently being developed to control the measurement taking process, and an algorithm that controls the formation process will be the final product. At this point, the measurement software is ready to be implemented with some tuning, but the intelligent control algorithm is still only in the discussion stage.

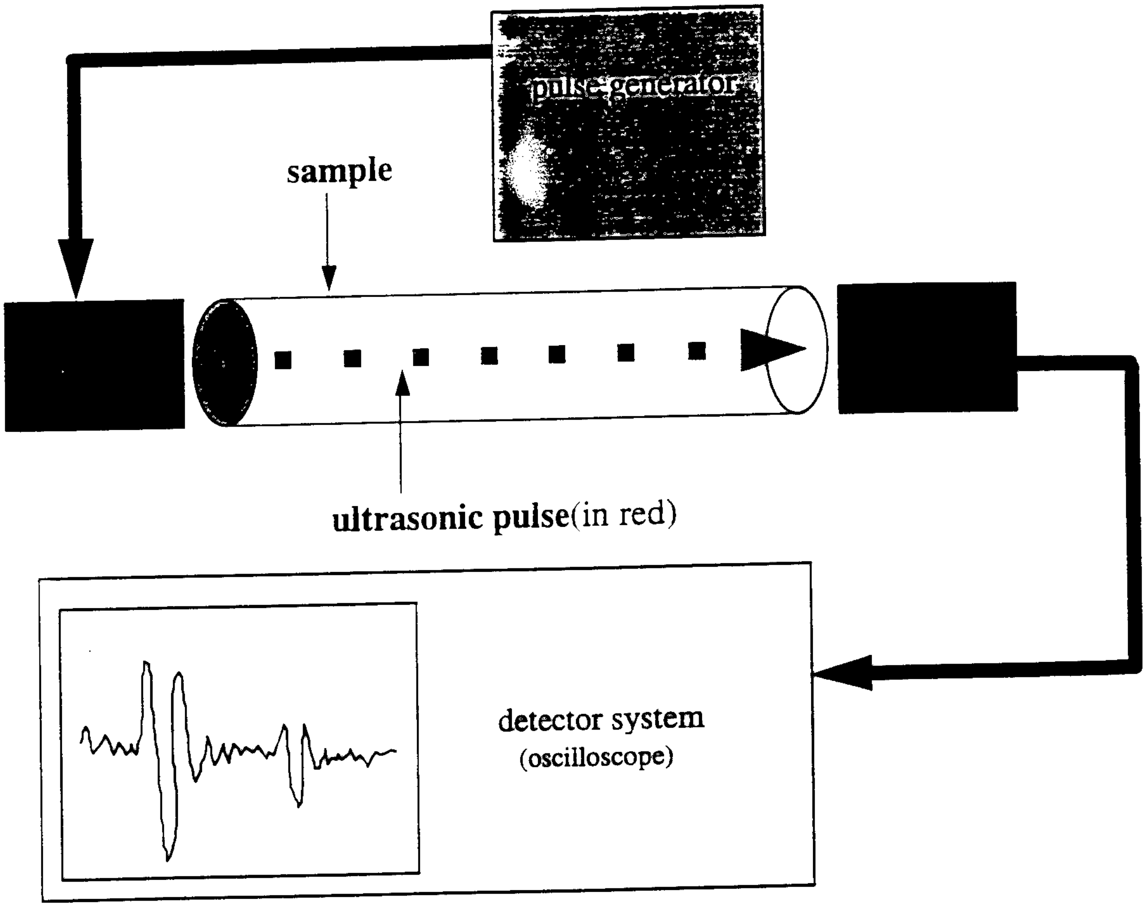

Figure 1. A schematic diagram of the transducer to transducer technique.

The second nondestructive technique is based on the ability of a rough surface to scatter laser light and relate this to its fractal dimension. The fractal dimension then gives a relative measure of the sizes and quantity of the flaws at the surface. This test shows areas of surface corrosion, frictional wear, or micro-cracking at the surface. It has already been shown that the intensity of the scattered light varies with the distance away from the scattering point and is related to the fractal dimensions of the object's surface. The relationship states that the intensity of the light is inversely proportional to the distance from this scattering point but the power to which the intensity is inversely proportional is directly dependent on the fractal dimension of the sample. The reason the intensity attenuates at a power related to the fractal dimension is because the fractal dimension is a direct measure of the curvature of the surface and the size of the flaws found there. These flaws are what determines the interference patterns generated and are directly responsible for the size and shape of the interference patterns from the laser light. As the flaw sizes change, the intensity as a function of distance away from the sample changes with respect to the fractal dimension.

The technique used collects intensity measurements as a function of distance and plot the log (intensity) versus the log (distance). Then the slope of this graph is related to the fractal dimension of the surface under inspection and the various surfaces can be distinguished simply by looking at the fractal dimensions. This is a good technique for finding areas of roughness or corrosion, but at this time it is not a good way to make detailed surface maps of an object. It represents degrees of deformity for any given region but does not draw an exact picture. Doing this is possible. However, this has not been investigated and would take large amounts of time to implement and analyze the data.

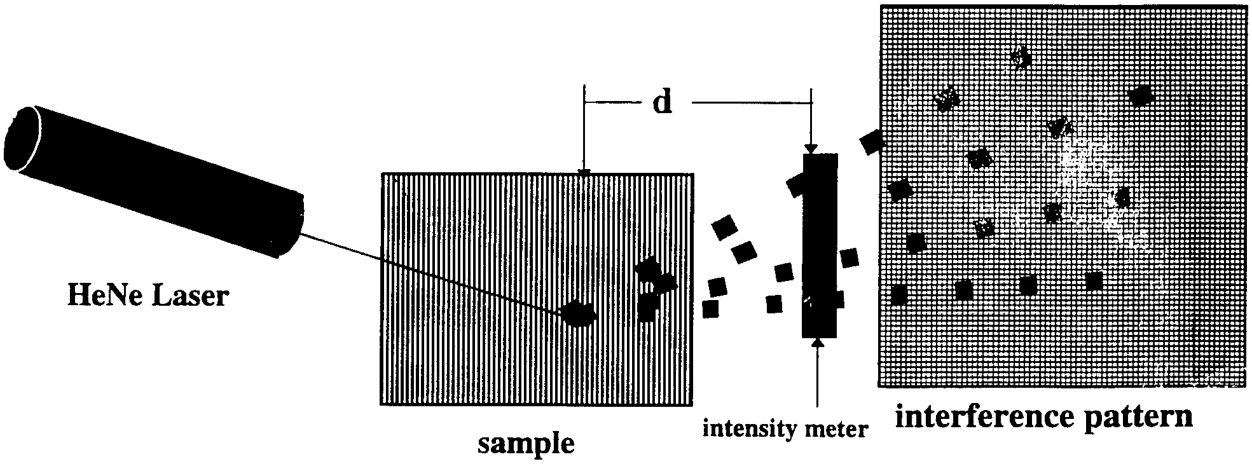

Figure 2. A Schematic Diagram of the Laser Scattering Technique.

RESULTS

Clearly these techniques are worth exploring. Examining specimens without altering their characteristics is always preferable. The eventual goal of NonDestructive Evaluation is to find ways to evaluate specimens without any characteristic changes at all. This not only reduces the chances of damaging or altering the sample, but these techniques allow people to save time and money by skipping steps such as dismantling the object of interest. Sometimes, the object of interest may not be accessible, and this is one main reason that NonDestructive Evaluation is necessary.

SPACE LIQUID LUBRICANT STUDIES

Task Order No. 238
Student Support Program
Southwestern Ohio Council for Higher Education

Kevin Gross
Wright State University

27 December 1996

Government Task Leader
Ms. Lois Gschwender
WL/MLBT

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First I would like to thank Ms. Lois Gschwender for having me work with her. Although my time spent on this Task was brief, I learned some important things--namely careful laboratory techniques. I would also like to thank Keith Clendenon who took me under his wing, so to speak. He showed me the "right" way to do things in the lab. I would like to acknowledge another important person whom I worked with: Bill Gaskins. Mr. Gaskins offered much insight in how things should be done in a laboratory setting. Finally, I would like to thank SOCHE for making this Task possible!

TASK ASSIGNMENT

This Task was mainly devoted to determining the lubricating capabilities of certain lubricant/additive mixtures to be used in space. This included performing wear testing on a Cameron Plint tribology machine and a standard 4-ball test rig. The ultimate goal from this wear testing was to find a lubricant/additive mixture that could be used in space applications keeping in mind the low volatility requirements for any lube used in such an environment.

DESCRIPTION OF RESEARCH

Several different aspects of lubricant testing were employed: reciprocating tribology tests, standard 4-ball tests, FT-IR spectroscopy and grazing angle FT-IR spectroscopy.

Reciprocating tribology tests were done on a Cameron Plint Reciprocating Tribometer. The tests were performed using 52100 steel discs and pins. Using the specific lube/additive concentration, the pin would reciprocate on top of the disc under a 250-newton load. After a set amount of time, the load was removed and the reciprocation stopped. A wear scar was the result of this test. The scar was measured using a Nikkon microscope. The lube's performance was proportional to the scar size. Standard 4-ball testing was done on a Falex 4-Ball Test Rig. Tests were performed using 1/2 inch 52100 steel ball bearings. Three balls were locked in place while the fourth was placed on top of the three and rotated at 1200 rpm under a 40-kg load. All four balls were immersed in the lube being tested.

FT-IR spectroscopy on the individual lubes and additives was done on a Nicolet 740 FT-IR Spectrometer. This testing was done to compare a lube both before and after it had been through tribology testing. This could help explain any type of chemistry with the 52100 steel or decomposition taking place by the lubricant.

Grazing angle FT-IR was done on a Perkin Elmer 1750 FT-IR. This type of spectroscopy made apparent what type of surface chemistry was taking place between the lubricant and 52100 steel by actually getting a spectrum of the steel surface itself.

RESULTS

What was ultimately learned is that there is a give and take relationship between lubricant and its application. Trying to find a lube that protects well and is suited for space application is difficult. Generally the better it protects, the less it is suited for space. This is due to the near-vacuum conditions in space. The better protecting lubes and additives were too volatile to be used in space. The less volatile lubes and additives better suited for space gave poorer results in the tribology tests.

SPACE LIQUID LUBRICANT STUDIES

Task Order No. 238a
Student Support Program
Southwestern Ohio Council for Higher Education

Maurice L. Massey
Wright State University

27 December 1996

Government Task Leader
Ms. Lois Gschwender
WL/MLBT

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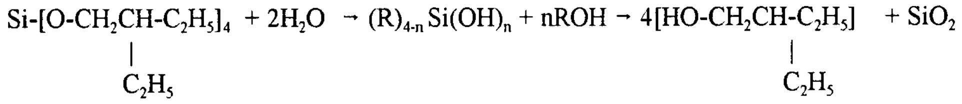
TASK ASSIGNMENT

The objective of this study was to follow the degradation of MLO 95-44, Coolanol 25R tetra(2-ethylbutyl) orthosilicate by analyzing for alcohol (2-ethylbutanol) through gas chromatography.

Coolanol 25R is a coolant known to react with water to form 2-ethylbutanol. The coolant is used mainly with radar systems in aircraft. An aircraft radar system fire brought out interest in this study. The flash point of 2-ethylbutanol is 163°C(325°C). It has been proposed that thermal degradation can also produce the alcohol. The purpose of this study was to learn under what conditions does the reaction take place, how time affects the reaction, and the possibility of the reaction causing a fire while in service.

REACTION SEQUENCE:



$$\mathrm{Si\text{-}[O\text{-}CH_2\underset{\overset{|}{C_2H_5}}{CH}\text{-}C_2H_5]_4 + 2H_2O \rightarrow (R)_{4-n}Si(OH)_n + nROH \rightarrow 4[HO\text{-}CH_2\underset{\overset{|}{C_2H_5}}{CH}\text{-}C_2H_5] + SiO_2}$$

COOLANOL **2-ETHYLBUTANOL**

By stoichiometric analysis, this reaction should take place with a mixture of Coolanol with 4.2% water added. Water was used in the amount of 5% to help ensure a reaction. The mechanism of the thermal degradation process has not been studied in sufficient detail to propose a specific mechanism to produce an alcohol. The results of this study will be used to help determine if this coolant is hazardous to use in service.

RESEARCH DESCRIPTION

Thermal Stability Test:

A 9" X 1/4" OD, stainless steel bomb was filled with 2 ml of Coolanol. The bomb was purged with nitrogen for 5-10 minutes, sealed weighed and placed into a preheated oven at selected temperatures for varying amounts of time. The bomb was allowed to cool to room temperature and weighed. The fluid was collected and analyzed for alcohol content by gas chromatography. The tests were conducted in duplicate at heating times of 6, 24, 48, and 72 hours and at temperatures from 50°C to 200°C in increments of 25°C.

Hydrolytic and Thermal Stability Test:

The procedure was the same as above except that after the bomb was purged, distilled water was added to the bomb to create a 2-ml sample of Coolanol and 5% distilled water by volume.

TEST MATRIX

One set of eight bombs that contained only Coolanol was prepared along with another set of eight with 5% distilled water added. The 16 bombs were placed in the oven at the beginning of the test cycle. After 6, 24, 48, and 72 hours, two bombs with water and two bombs without water were removed, cooled to room temperature, weighed, and analyzed for alcohol content. If the difference in the pretest and post test bomb weights was greater than 0.1 grams, the run was to be repeated because the loss in weight could have been due to inadequate sealing of the bomb resulting in a volatilization of the water. After collection of the specimens, the bombs were cleaned with hexane and acetone to dissolve any left over fluid in the bombs and brushed to help remove the inorganic SiO_2 or partially hydrolyzed products.

DISCUSSION OF RESULTS

The results of the thermal stability and the thermal and hydrolytic stability tests are summarized in the following appendices. The method for determining the alcohol content was gas chromatography area percent with a flame ionization detector. The original sample of Coolanol, MLO 96-44, was exhausted after the runs at 150°C. MLO 96-192 was used in subsequent runs. Both samples were tested for alcohol content before any tests were conducted and were found to contain less than .01% alcohol.

Generally, as the temperature increased, the thermal stability test samples showed some signs of alcohol content but the amounts were not very significant. The thermal stability samples started to change from clear to slightly yellow after the runs at 150°C. At the 175°C test temperature, the samples turned yellow consistently. In the graphical representation of the data, a linear relationship between % alcohol and time was observed.

In the hydrolytic stability study, the results were approximately the same as the thermal study until the 100°C tests were conducted. Test 96-44A produced a gel after only 6 hours at 50°C. This was considered an anomalous data point and disregarded. The alcohol content from the 100°C tests was noticeably higher and the samples were becoming opaque and cloudy. At the 125°C test points, gelatinous particles were starting to form. At the 175°C temperature, the samples were very cloudy and about 50-75% gelled. The test was halted after the 6-hour sample at 200°C because of the high amount of alcohol formed and the inability to collect the highly gelled sample. The gel is believed to be hydrated SiO_2 or partially hydrolyzed product. At point 96-192-AS, the sample was manually injected due to the small amount of sample collected. Please refer to the attachments for more detailed information about each individual run.

CONCLUSIONS AND RECOMMENDATIONS

1. Only negligible amounts of 2-ethylbutanol was formed from thermally stressing tetra(2-ethyl butyl) orthosilicate at temperatures up to 200°C for up to 72 hours.

2. Significant amounts of 2-ethylbutanol was formed when 5% by volume water was added to the stability tests with no indication that all of the water had reacted by the completion of the tests, at temperatures up to 175°C for up to 72 hours. At 200°C, too much degradation had occurred within 6 hours to obtain a representative sample for analysis.

3. While the duration of the thermal and hydrolytic stability tests were rather short (less than or equal to 72 hours), it appears that if Coolanol 25R systems are kept dry, there is negligible formation of 2-ethylbutanol. However, when water is present, the alcohol readily forms at temperatures as low as 100°C, well below the usual operational temperatures of most systems using that solvent.

4. The process of water in cooling systems using Coolanol 25R not only results in the formation of the corresponding alcohol to the alkyl group on the orthosilicate, but also a gelatinous precipitate form believed to be a partially hydrolyzed product.

5. This fluid can still be used for radar applications if necessary, but due to the possibility of such a flammable liquid being formed, high temperature and high water content must be avoided. MIL-C-87252, a polyalphaolefin-based coolant, is hydrolytically stable and can be used as a good alternative to Coolanol 25R.

COOLANOL 25R HYDROLYTIC AND THERMAL STABILITY

GAS CHROMOTOGRAPHY ANALYSIS FOR ALCOHOL(2-ETHYLBUTANOL) CONTENT

STRESSED COOLANOL 25R

SAMPLE	HOURS	TEMP°C	%ALCOHOL	COMMENTS
96-44-1	6	50ºC	0.00	
96-44-2	6	50ºC	0.00	
96-44-3	24	50ºC	0.00	
96-44-4	24	50ºC	0.00	
96-44-5	48	50ºC	0.00	
96-44-6	48	50ºC	0.00	
96-44-7	72	50ºC	0.00	
96-44-8	72	50ºC	0.47	
96-44-9	6	75ºC	0.00	
96-44-10	6	75ºC	0.00	
96-44-11	24	75ºC	0.48	
96-44-12	24	75ºC	0.00	
96-44-13	48	75ºC	0.48	
96-44-14	48	75ºC	0.46	
96-44-15	72	75ºC	0.49	
96-44-16	72	75ºC	0.51	
96-44-17	6	100ºC	0.47	
96-44-18	6	100ºC	0.46	
96-44-19	24	100ºC	0.52	
96-44-20	24	100ºC	0.52	
96-44-21	48	100ºC	0.53	
96-44-22	48	100ºC	0.53	
96-44-23	72	100ºC	0.00	
96-44-24	72	100ºC	0.54	

STRESSED COOLANOL 25R + 5% WATER

SAMPLE	HOURS	TEMP°C	%ALCOHOL	COMMENTS
96-44-A	6	50ºC	0.00	gel, acetone peak only
96-44-B	6	50ºC	0.00	
96-44-C	24	50ºC	0.00	
96-44-D	24	50ºC	0.00	
96-44-E	48	50ºC	0.00	
96-44-F	48	50ºC	0.00	
96-44-G	72	50ºC	0.00	
96-44-H	72	50ºC	0.00	
96-44-I	6	75ºC	0.00	slightly cloudy
96-44-J	6	75ºC	0.00	cloudy
96-44-K	24	75ºC	0.54	slightly cloudy
96-44-L	24	75ºC	0.49	slightly cloudy
96-44-M	48	75ºC	0.60	slightly cloudy
96-44-N	48	75ºC	0.54	slightly cloudy
96-44-O	72	75ºC	0.64	slightly cloudy
96-44-P	72	75ºC	0.65	slightly cloudy
96-44-Q	6	100ºC	0.65	slightly cloudy
96-44-R	6	100ºC	0.00	slightly cloudy
96-44-S	24	100ºC	0.84	slightly cloudy
96-44-T	24	100ºC	0.73	slightly cloudy
96-44-U	48	100ºC	1.83	slightly cloudy
96-44-V	48	100ºC	1.48	slightly cloudy
96-44-W	72	100ºC	1.86	slightly cloudy
96-44-X	72	100ºC	2.19	slightly cloudy

STRESSED COOLANOL 25R

SAMPLE	HOURS	TEMP°C	%ALCOHOL	COMMENTS
96-44-25	6	125ºC	0.48	
96-44-26	6	125ºC	0.47	
96-44-27	24	125ºC	0.54	
96-44-28	24	125ºC	0.51	
96-44-29	48	125ºC	0.56	
96-44-30	48	125ºC	0.57	
96-44-31	72	125ºC	0.58	
96-44-32	72	125ºC	0.61	
96-44-33	6	150ºC	0.48	
96-44-34	6	150ºC	0.48	
96-44-35	24	150ºC	0.57	
96-44-36	24	150ºC	0.57	
96-44-37	48	150ºC	0.60	slightly yellow
96-44-38	48	150ºC	0.66	slightly yellow
96-44-39	72	150ºC	0.63	slightly yellow
96-44-40	72	150ºC	0.73	slightly yellow

STRESSED COOLANOL 25R + 5% WATER

SAMPLE	HOURS	TEMP°C	%ALCOHOL	COMMENTS
96-44-Y	6	125ºC	1.84	slightly cloudy
96-44-Z	6	125ºC	0.83	slightly cloudy
96-44-AA	24	125ºC	3.43	slightly cloudy
96-44-AB	24	125ºC	2.53	slightly cloudy
96-44-AC	48	125ºC	5.39	slightly cloudy
96-44-AD	48	125ºC	5.35	slightly cloudy
96-44-AE	72	125ºC	10.56	slightly cloudy
96-44-AF	72	125ºC	10.37	slightly cloudy
96-44-AG	6	150ºC	5.27	slightly cloudy
96-44-AH	6	150ºC	2.01	slightly cloudy
96-44-AI	24	150ºC	19.38	higher coagulation
96-44-AJ	24	150ºC	9.96	slightly yellow
96-44-AK	48	150ºC	mistake point	no water added
96-44-AL	48	150ºC	22:06	very cloudy
96-44-AM	72	150ºC	19.56	very cloudy
96-44-AN	72	150ºC	10.06	very cloudy

NOTE: A NEW FLUID, MLO 96 -192, IS BEING USED DUE TO THE EXHAUSTION OF THE SUPPLY OF MLO 96-44.
NOTE: SAMPLE 96-192-AS WASN'T INCLUDED ON GRAPHICAL OUTPUTS

96-192-41	6	175ºC	0.15	yellow
96-192-42	6	175ºC	0.13	yellow
96-192-43	24	175ºC	0.18	yellow
96-192-44	24	175ºC	0.23	yellow
96-192-45	48	175ºC	0.18	yellow
96-192-46	48	175ºC	0.23	yellow
96-192-47	72	175ºC	0.21	yellow
96-192-48	72	175ºC	0.29	yellow

96-192-AO	6	175ºC	17.72	cloudy
96-192-AP	6	175ºC	16.10	cloudy
96-192-AQ	24	175ºC	37.81	cloudy
96-192-AR	24	175ºC	10.68	cloudy
96-192-AS	48	175ºC	manual inject:	low sample amount
96-192-AT	48	175ºC	54.87	cloudy
96-192-AU	72	175ºC	57.47	cloudy
96-192-AV	72	175ºC	43.29	cloudy

STRESSED COOLANOL 25R

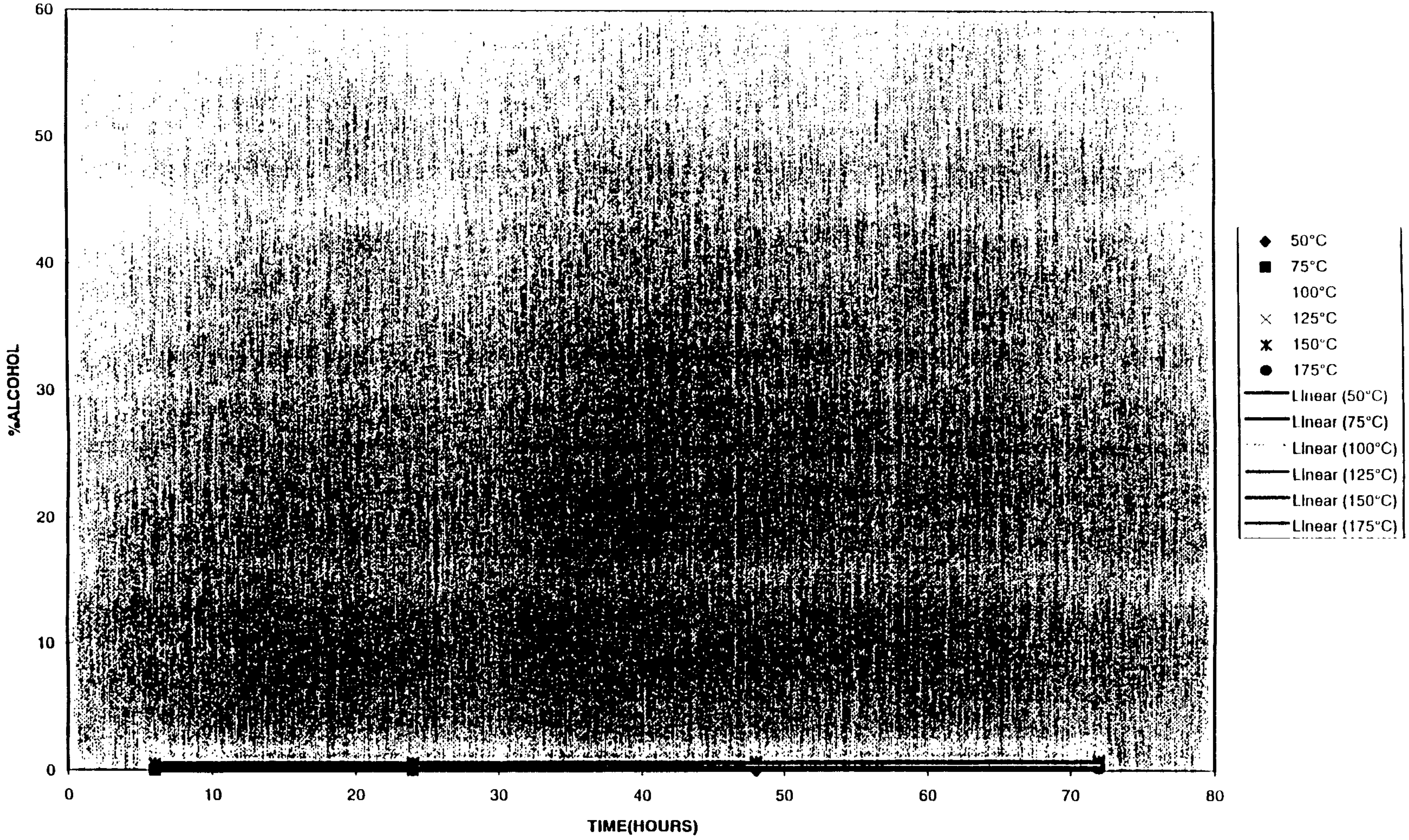
SAMPLE	HOURS	TEMP°C	%ALCOHOL	COMMENTS
96-192-49	6	200°C	0.29	
96-192-50	6	200°C	0.23	
96-192-51	24	200°C	0.30	
96-192-52	24	200°C	0.31	
96-192-53	48	200°C	0.25	
96-192-54	48	200°C	0.29	
96-192-55	72	200°C	0.00	
96-192-56	72	200°C	0.00	

STRESSED COOLANOL 25R + 5% WATER

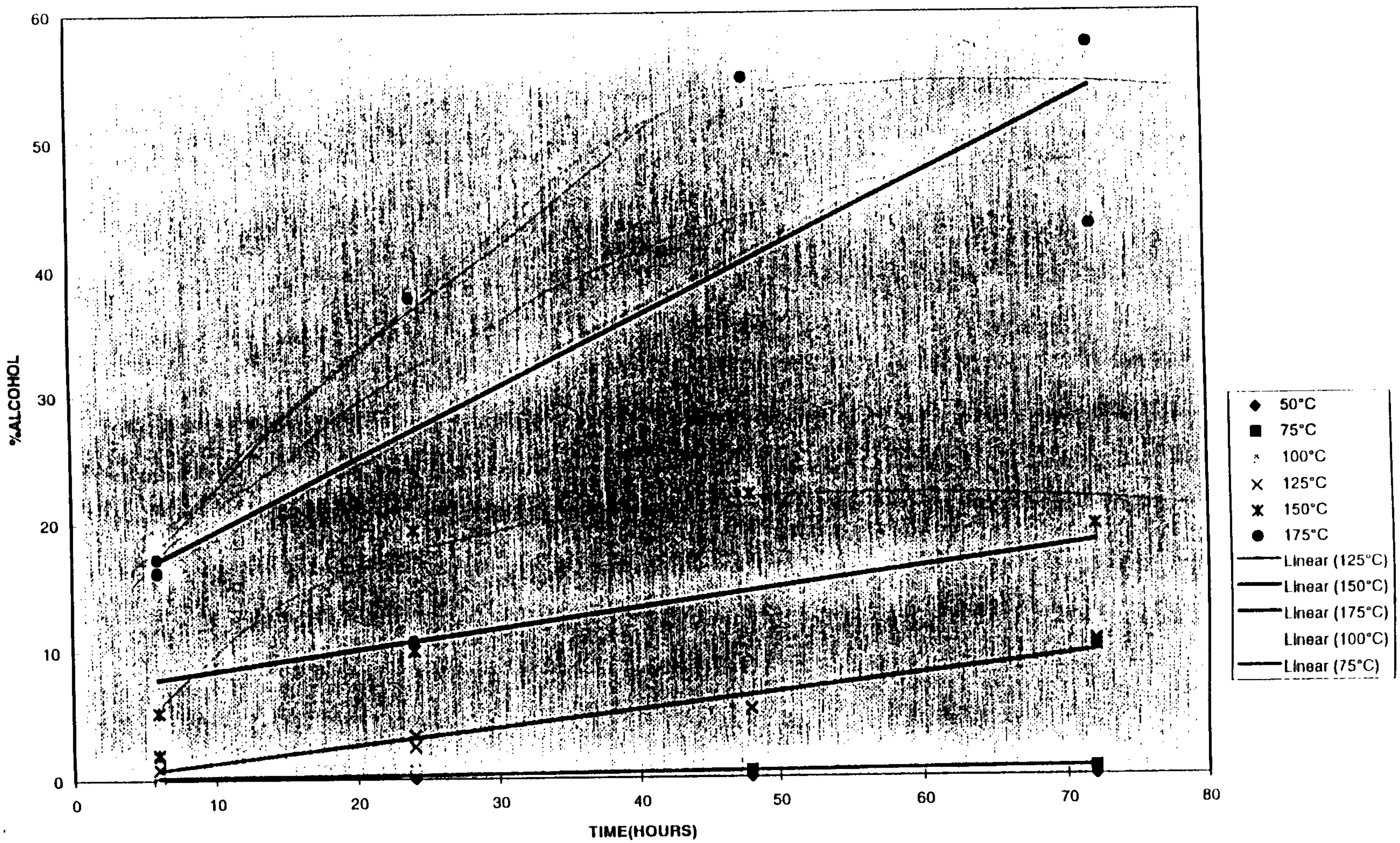
SAMPLE	HOURS	TEMP°C	%ALCOHOL	COMMENTS
96-192-AW	6	200°C	1.84	very cloudy
96-192-AX	6	200°C	0.83	very cloudy

A new column was placed in the GC for a different project. The results of this study were affected on sample points 96-192-AW, 96-192-AX, 96-192-55 ,& 96-192-56.

COOLANOL25R THERMAL STABILITY SUMMARY



COOLANOL25R & 5%WATER THERMAL STABILITY SUMMARY



SYNTHESIS OF CONDUCTING AROMATIC-HETEROCYCLIC POLYMERS

Task Order No. 239
Student Support Program
Southwestern Ohio Council for Higher Education

Christine Zucker
Wright State University

27 December 1996

Government Task Leader
Dr. Robert Evers
WL/MLBP

ACKNOWLEDGMENTS

I would like to take the opportunity to thank Dr. My Dotrong, Dr. Rob McKellar, and Dr. Bob Evers for making my experience at the polymer branch very valuable. Their time and patience have given me a greater interest and understanding of scientific research.

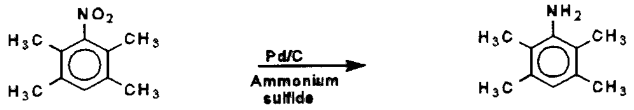
TASK ASSIGNMENT

Concurrently, there are several projects in progress at the Polymer branch at WPAFB. Continued synthesis on 3-nitro-1,2,4,5-tetramethylbenzene has been the main focus of my Task for the past 4 weeks, besides training the incoming student to take over the Task. Procedures such as extraction, infrared spectroscopy and column chromatography have been used routinely for completing the assigned Task over the four-week period.

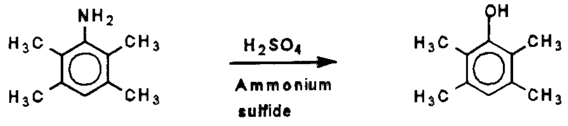
DESCRIPTION OF RESEARCH

The starting material 3-nitro-1,2,4,5-tetramethylbenzene was used in a 3-step synthesis to obtain the product. The reaction scheme for each step is shown below.

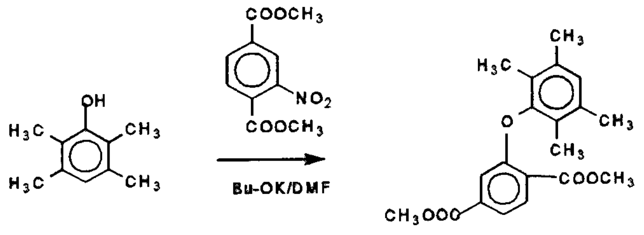
Step 1



Step 2



Step 3



In Step 1, 3-nitro-1,2,4,5-tetramethylbenzene was reduced using ammonium formate in the presence of Pd\C catalysts. Once reaction was complete, the corresponding amino product was extracted with ethyl acetate and analyzed with infrared spectroscopy. The distinctive amino peaks were present, thus suggesting the presence of the desired amino product.

In Step 2, the product from the previous step was converted to the corresponding phenol using ammonium sulfide and concentrated sulfuric acid. The product was extracted with chloroform and washed with several portions of distilled water. From infrared spectra, the amino peaks disappeared, and a distinctive O-H band was observed around 3500cm^{-1} indicating the presence of the tetramethylphenol product.

In Step 3, tetramethylphenol was reacting with dimethylnitroterephtalate in the presence of potassium t-butylate and DMF. The product was added to ice water, extracted with ethyl acetate, and washed with several portions of water. The infrared spectra showed the distinctive peaks for the esters and ether group, therefore, showing that the final product was obtained. The crude product was purified using column chromatography.

CONCLUSION

The final product was obtained successfully, and will be used as starting material in future reactions, in addition, to analysis for structural studies.

SYNTHESIS OF CONDUCTING AROMATIC-HETEROCYCLIC POLYMERS

Task Order No. 239A
Student Support Program
Southwestern Ohio Council for Higher Education

Colleen M. Dwyer
University of Dayton

27 December 1996

Government Task Leader
Dr. Robert C. Evers
WL/MLBP

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I would first like to thank everyone in the Polymer Branch who helped me become acclimated with the policies of MLBP. Furthermore, I would like to say thank you to Dr. Robert Evers and Dr. My Dotrong for this opportunity to enhance my scientific knowledge and for making me feel so welcome in the Polymer Branch.

TASK ASSIGNMENT

There were several assignments during the 7 month Task. Besides chemical ordering, cleaning glassware, and managing the waste control forms, I helped in the synthesis and analysis of several organic reactions via purification techniques and spectrophotometric procedures.

DESCRIPTION OF RESEARCH

A new project for the research team in the Polymer Branch was assigned. The nature of the project involved an interest in organic polymers that possessed very low band gaps. Since these materials display high intrinsic conductivity, the team decided to couple squaric acid with aromatic heterocycles to make conducting polymers. A work-up of the synthesis procedures was done.

One task involved running a model reaction consisting of 2,4-dimethyl pyrrole and squaric acid, in the presence of ethanol, to yield a 1,3 adduct of pyrrole. By running infrared spectroscopy and nuclear magnetic resonance tests, it was found that both the 1,2 and 1,3 adducts were present. Further purification was necessary to isolate the 1,3 adduct of pyrrole. Next, polymerization of squaric acid with 1-methylpyrrole was attempted. This reaction was run using three different solvents - ethylene glycol, ethanol, and acetic acid. The reaction that took place in the presence of ethylene glycol and acetic acid resulted in a blue metallic polymer. Along with further purification and synthesis techniques, thin layer and column chromatography was done plus ultraviolet and infrared spectroscopy tests.

RESULTS

A vast amount of knowledge and experience was gained during the 7 months at Wright Laboratory. As a result, laboratory techniques were improved and an appreciation for polymer chemistry developed.

TRIBOLOGICAL EVALUATION OF CANDIDATE FLUIDS AND LUBRICANT MATERIALS

Task Order No. 240
Student Support Program
Southwestern Ohio Council for Higher Education

Garrick W. Kolb
Wright State University

27 December 1996

Government Task Leader
Mr. Shashi Sharma
WL/MLBT

ACKNOWLEDGMENTS

I would like to thank Mr. Shashi Sharma for all the advising on the development of the elastohydrodynamic lubrication apparatus. His efforts aided in the modification of existing parts and fabrication of new parts to coincide and meet the specifications of the existing parts. I would also like to thank Vince Vidoni for his continual support with supplies and procedures of the Wright-Patterson Air Force Base machine shop. Lastly, I appreciated the insight of machining techniques from Arthur Safriet.

BACKGROUND

In the Tribology division of the Materials lab, several properties of fluids are determined. Two main apparatuses are used, the Cameron Plint and the Traction Rig. The Cameron Plint measures the contact resistance of a fluid and the corresponding wear scar produced from of oscillations of a head applied to a test specimen under a calculated load. From Traction Rig data the traction coefficient (resistance to fluid sheer) can be determined. Though several properties can be observed by current means, other properties are wanted. The film thickness between two rotating objects under a certain load is a desired property that currently cannot be measured.

TASK ASSIGNMENT

At the start of the task, the goal was quite clear: design an apparatus that could measure this fluid film thickness as needed. Earlier, there had been an apparatus designed to accomplish this. This apparatus focused on using a 1 inch ground steel ball, rotated by a motor, contacting a sapphire disk rotating on a precision spindle driven by a separate motor. This contact point was encapsulated by a test chamber containing the fluid that was of interest. The fluid film thickness would then be determined by optical interferometry, comparing the different diffraction patterns of light from the bottom of the sapphire disk and the top of the 1 inch ground steel ball.

The theory behind the design of the apparatus provided results, but due to undampable vibrations, the design could not produce the micro scale measurements wanted. Last year, work was started on a design to produce a more stable apparatus that could withstand these large vibrations. The idea was to incorporate as much of the original apparatus into the new design as possible. Several design changes were made. The fruits of these design change efforts produced a shorter high speed rotating shaft, a loading mechanism, and a revised test chamber to hold the new loading mechanism.

After much consideration only the test chamber was used from the original machine. It was determined that the task had to be divided into design steps. These steps would include the design of the spindle housing for the existing high speed spindle, a driving mechanism for the 1 inch steel ground ball, and a vibration less table.

The design of the high speed spindle housing was quite simple because the traction rig had been updated with a new arrangement that left a spindle housing. The housing was modified to fit the new shaft. A mounting bracket, with adjustable consideration, was designed to attach the housing to the table.

The driving mechanism for the ball was a combination of existing parts. A Motor Technologies 27 Volt D.C. motor in series with a Lebow torque sensor was used to drive the ball and record accurate motor speed and torque. A new mounting plate was designed to incorporate these changes with the test chamber and the 1 inch ground steel ball.

Finally the table had to be designed. With the previous vibration problems considered, the table was designed to have as much mass as reasonably possible. This idea lead to a 31 x 28 x 1 inch steel top mounted on a 3 inch square tubing frame. This setup yielded a table that weighed more than 400 pounds.

All the designed parts were drafted on AutoCAD, and taken to the machine shop on Base. The machinist has nearly completed all the parts designed. When the table is finished, the apparatus will be assembled.

CONCLUSION

The design of the EHL apparatus was clearly a mechanical engineering type of task. This project showed how a project of any nature, such as electrical engineering, is put together and completed. The completion of this apparatus will help WL/MLBT complete its mission of research and development of coatings and lubricants for aircrafts.

AEROSPACE CORROSION CONTROL AND ENVIRONMENTAL RESPONSIBILITY

Task Order No. 241
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 1996

Government Task Leader
Ms. Lynne Pfledderer
WL/MLSA

ACKNOWLEDGMENTS

I would like to extend my appreciation to Ms. Lynn Pfledderer and James Dante for providing an opportunity to supplement my education at the University of Dayton with practical work experience in the corrosion laboratory.

In addition, I would like to thank Joe Hunter and the technicians working in the corrosion lab for their assistance and support in furthering my lab experience and completing my Task, and their obvious interest in keeping me busy.

TASK ASSIGNMENT

During the last 6 months, the Task's objective was to help in the determination of performance, applicability, and supportability of substitute materials and processes for environmental compatibility and aerospace functionality.

This Task began with a great deal of reading. Becoming familiar with the materials and coating processes currently used on US aircraft was necessary. Once a basic understanding of the materials and coating processes used on the aircraft was achieved, the task turned more toward specific corrosion testing. Unfortunately, the corrosion lab was undergoing quite a renovation. A great deal of the equipment used in corrosion testing was not available for immediate use (including the prohession chambers and the now finished coating production line). The available corrosion work was necessarily on a smaller scale, most of which was done on the potentiostat and with capillary ion analysis (CIA).

The first major project completed was one in which some electrochemical properties (open circuit potential, pitting potential, etc.) of two aluminum alloys, 2097-T8 and 2124-T851, were compared. The 2124 alloy had been used on flight and safety critical bulkheads. It had also been shown to undergo severe fatigue cracking. The 2097 alloy was a possible replacement for 2124 on FS479 bulkheads on the F-16s. Two alloys were electrochemically tested several times in both a rain water solution and in 0.6 M NaCl solution, aerated and deaerated. Each trial included an open circuit and a potentiodynamic analysis. The results in both solutions suggested that 2097 exhibited higher pitting potentials, establishing that, electrochemically, 2097 would be a good replacement for 2124.

The next major project undertaken was analyzing the efficiency of a new corrosion preventive compound (CPC), Amlguard. Several magnesium alloy plates were cut and coated with the Amlguard, leaving two plates uncoated for reference. The plates were exposed either to rain water or to salt water in prohession chambers. The plates were then delivered to the base, where they were each rinsed thoroughly with DI water. The DI water rinses were then tested for cations and anions using CIA. The rinses of the plates exposed to the NaCl solution naturally tested positive for high amounts of Na^+ and Cl^-, while the rinses of the plates exposed to the rain water tested high for SO_4^{2-} ions. Besides these ions, several plate rinses had traces of other metal cations, including Al^{3+} and Mg^{2+} - two major components of the plate material.

These results showed that the magnesium alloy was degrading during exposure. The extent of the degradation, however, was inconclusive. When the results from the coated plates were compared with those from the uncoated plates, no discernible pattern was observed. The way the plates were handled immediately after exposure in the prohession chamber accounts for the results being inconclusive. To elaborate, the plates were rinsed before their arrival on the Base; the uncoated plates were not only rinsed, but also *scrubbed* when removed from the prohession chamber. However, all was not lost. This project is only in its beginning stages. This was also the first time that CIA had been incorporated in CPC analysis. Though the results were somewhat inconclusive, they did show that CIA is a plausible analysis technique for projects of this nature.

Other lesser projects involved lab maintenance. With the construction wrapping up in the neighboring laboratories, a little reorganization was necessary. In the spirit of reorganization and maintenance, the DI water filters were tested using an electrophoresis method on CIA. The filters were over a year old and their effectiveness was questionable. DI water samples were analyzed for the presence of cations and anions on a part per billion scale. It was determined that a sizable amount of several ions were present in the samples. The most abundant ion was Ca^{2+}. Filters were most likely close to saturated with Ca^{2+} ions from the hard water inlet. Due to the sensitive nature of CIA, any significant contamination in DI water used to dilute samples and standards for examination could result in a notable increase in the results' uncertainties. Consequently, new filters were ordered.

Many smaller projects included research assistance, bulk solution preparation, and metallographic sample preparation.

DEGRADATION STUDIES OF AIRCRAFT COATINGS

Task Order No. 242
Student Support Program
Southwestern Ohio Council for Higher Education

Nathan Grebasch
Wright State University

27 December 1996

Government Task Leader
Dr. Mike Donley
WL/MLBT

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I would like to thank the following members of the MLBT in-house coatings group: Dr. Mike Donley, for allowing me to become a member of this terrific research project; Dr. Jim Liang, for teaching me about FTIR surface analysis; Dr. M. Khobaib, for his help in electrochemical analysis; and Robert Parkhill, (from OSU) for his assistance as the sol-gel program developed.

TASK ASSIGNMENT

As the Air Force attempts to conserve its resources, longer life spans for planes are to be expected. A major problem with a longer plane life is the corrosion of the aluminum alloy (2024). Presently the degradation of the coating system is subjectively tested by either atmospheric or salt spray testing. Both methods fail to yield quantitative data on the mechanism of the failure.

To address this problem, an in-house coating and corrosion group (headed by Dr. Mike Donley) was formed. The purpose of the group was to research state-of-the-art methods to quantify the results seen in the atmospheric and salt spray testing. In addition, this research has used electrochemical testing as that evaluation method. By conducting these tests, current coating systems and far-term systems were evaluated.

Surface analysis was employed to study the coatings before and after electrochemical testing. Grazing angle FTIR (GA/FTIR) and specular reflectance was employed as the main surface analytical method. This allowed for nondestructive analysis.

During the summer of June 1996-September 1996 an AFOSR project was initiated between Oklahoma State University and Wright Labs. The purpose of this program was to: investigate the possibility of using sol-gel technology to replace the current aircraft coating system. In support of the in-house coatings program, Task #242 involved applying the surface analysis techniques to these sol-gel coatings. A sol-gel coating is formed by using a metal alkoxide. Here a silane compound such as Tetraethoxysilane was employed. A hydrolysis reaction is carried out followed by a corresponding condensation polymerization. This synthesis route is important because it is the key to understanding the way in which the coating does its barrier role.

The major advantage of using this type of technology is that it offers an environmentally benign coating system, and reduces or eliminates the volatile organic compounds (VOC). Present coating systems rely on chromates to reduce the corrosion of the aluminum alloy (2024). Under Federal Mandate these compounds must be removed from the paint systems. In addition the toxicity of chromates is a hazard during the application process.

Sol-gel technology offers the best solution for these problems. Sol-gel is a process by which a colloid is dispersed in a solvent and then allowed to polymerize on the surface. Currently spin coating is the preferred application technique, but eventually this process will be transformed to a spray on process. Research focused on the use of silicates as sol-gel treatments and the resulting surface analysis of those compounds. Silicates are environmentally friendly and offer easy application.

ORMOSILs are organically modified silicates. ORMOSIL compounds offer the possibility of dense layers in which passivating dopants (i.e., Ce, Mo and Zr salts) can be added to protect the aluminum substrate, should the coating become damaged. Sol-gel silicate coatings are also thought to posses the ability to bond covalently with the metal/metal oxide layer. Currently, the coatings used by the Air Force rely on a weaker hydrogen bond between the coating and the surface pretreatment for corrosion protection. Spectroscopic research has yet to prove conclusively that covalent bonding has occurred. Further research will concentrate on conclusively proving this fact. Further research will also focus on the role that the dopant plays in the matrix.

THE SYNTHESIS OF TETRAPHENYLNAPHTHALENE DERIVATIVES FOR NONLINEAR OPTICAL PROPERTY EVALUATIONS

Task Order No. 243
Student Support Program
Southwestern Ohio Council for Higher Education

David P. Stitzel
Wright State University

27 December 1996

Government Task Leader
Mr. Bruce A. Reinhardt
WL/MLBP

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I would like to take this opportunity to thank my mentors sincerely, Dr. William A. Feld, Department of Chemistry, Wright State University, Dayton, Ohio and Bruce A. Reinhardt, Polymer Branch, Materials Directorate, U.S. Air Force Wright Laboratory, Wright-Patterson Air Force Base, Ohio for their patience, support, guidance, advice and consultation. I would also like to express my sincere thanks and gratitude to the Southwestern Ohio Council for Higher Education and the Polymer Branch at Wright-Patterson Air Force Base for giving me the opportunity to gain knowledge and work experience in organic synthesis. I am confident that the knowledge and laboratory experience that I have acquired will continue to prove to be invaluable to me in the future.

TASK ASSIGNMENT

This Task involved the synthesis, characterization, and preliminary evaluation of 1,4,5,8-tetraphenylnaphthalene and a derivative as potential third-order nonlinear optical materials.

RESEARCH

The electron rich polycyclic aromatic compound 1,4,5,8-tetraphenylnaphthalene was synthesized via a six-step reaction scheme.

The first step involved a Diels-Alder reaction between *trans,trans*-1,4-diphenylbutadiene and *trans*-1,2-dibenzoylethylene in refluxing isopropyl alcohol to yield 1,2-dibenzoyl-3,6-diphenylcyclohex-4-ene. A mixture of trans,trans-1,4-diphenyl-1,3-butadiene (24.62 g, 0.1194 mole), trans-1,2-dibenzoylethylene (28.20 g, 0.1194 mole) and nitrogen purged 2-propanol (350 mL) were placed in a 1000 mL single-necked, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, nitrogen adapter, and heating mantle. The reaction mixture was initially opaque yellow and upon heating became opaque orange. At reflux, the solution was transparent orange. The reaction was refluxed for 8 h under nitrogen. The crude product crystallized on cooling to yield a light yellow solid used in the next step without purification (49.99 g, 95%): mp 178-182°C (lit.[1] mp 179-180°C); IR (KBr) cm^{-1} 3026 (Ar-C-H and Alkene-C-H), 1672 (Ph-C=O), 1597 and 1447 (Ar-C=C), 1211 (C-C-C stretching and bending in the C-(C=O)-C group), 757 and 699 (Ar-C-H).

The second step involved dehydrogenation of 1,2-dibenzoyl-3,6-diphenylcyclohex-4-ene with bromine in refluxing chloroform to yield 1,2-dibenzoyl-3,6-diphenylbenzene. Unpurified 1,2-dibenzoyl-3,6-diphenylcyclohex-4-ene (49.99 g, 0.1130 mole) and nitrogen purged chloroform (351 mL) was placed into a 2000 mL three-necked, round bottomed flask equipped with a magnetic stirrer, reflux condenser, nitrogen adapter, addition funnel, and heating mantle. The starting material went into solution immediately. At reflux, a solution of bromine (11.6 mL, 0.225 mole) in nitrogen purged chloroform (243 mL) was added dropwise over 90 minutes. The reaction was refluxed for an additional 3.5 h under nitrogen (monitored via thin layer chromatography (TLC); stationary phase silica gel; eluent methlene chloride: hexane 1:1). The reaction solution was cooled and evaporated to dryness and the residue triturated with alcohol to provide a solid which was recrystallized from ethanol to give 1,2-dibenzoyl-3,6-diphenylbenzene (22.64 g, 46%); mp 215-218°C (lit.[1] mp 212°C); IR (KBr) cm^{-1} 3056 (Ar-C-H), 1667 (Ph-C=O), 1595 and 1449 (Ar-C=C), 1236 (C-C-C stretching and bending in the C-(C=O)-C group), 760, 724 and 704 (Ar-C-H); ^{1}H NMR ($CDCl_3$) d 7.06-7.71 (m, 22H, Ar); ^{13}C NMR ($CDCl_3$) ppm 127.5, 127.7, 128.1, 129.1, 129.5, 130.9, 132.6, 137.6, 139.2, 139.3, 139.6, 198.6.

The third step involved reduction of 1,2-dibenzoyl-3,6-diphenylbenzene with zinc and potassium hydroxide in refluxing ethyl alcohol to yield 2,3,6,7-tetraphenylisobenzofuran. Purified 1,2-dibenzoyl-3,6-diphenylbenzene (6.64 g, 0.0151 mole) and a nitrogen purged sodium hydroxide solution (17.94 g, 0.4485 mole; sodium hydroxide dissolved in 60 mL water and 1136 mL ethanol) were placed into an aluminum foil wrapped 3000 mL three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, nitrogen adapter, and heating mantle. At reflux, the reaction solution was transparent yellow. Zinc (17.94 g, 0.2744 mole) was slowly added and the reaction was refluxed for 2.5 h under nitrogen (monitored via TLC; stationary phase silica gel; eluent methylene chloride: hexane 1:1). The green reaction mixture was filtered hot to remove the zinc leaving a transparent yellow filtrate. Acetic acid (1200 mL) was added to the yellow filtrate with stirring followed by the addition of water (1800 mL) which resulted in precipitation of the product. After cooling overnight, the crude product was collected and washed many times with water to remove any residual acetic acid. The crude product, 2,3,6,7-tetraphenylisobenzofuran was dried to yield a yellow solid then used in the next step without purification (5.41 g, 85%); slow melt mp 144-240°C (lit.[1] mp 258-259°C); IR (KBr) cm^{-1} 3031 (Ar-C-H), 1667 (Ph-C=O), 755 and 696 (Ar-C-H).

The fourth step involved a Diels-Alder reaction between 2,3,6,7-tetraphenylisobenzofuran and acrolein in refluxing benzene to yield 1,3,6,8-tetrapheny-11-oxatricyclo[6.2.1.$0^{2,7}$]undeca-2,4,6-trien -9-yl-1-methanone. Unpurified 2,3,6,7-tetraphenylisobenzofuran (3.03 g, 0.00717 mole), freshly distilled acrolein (2.8 mL, 0.043 mole) containing a trace of hydro quinone, and nitrogen purged benzene (25 mL) were placed into an aluminum foil wrapped 100 mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, nitrogen adapter, and heating mantle. At reflux, the reaction solution was transparent yellow. The reaction was refluxed for 1- hundred nitrogen (monitored via TLC; stationary phase silica gel; eluent methylene chloride: hexane 1:1). The light-yellow solution was cooled to room temperature then further cooled in an acetone/ dry-ice bath for approximately 30 minutes, which gave white crystals upon reaching room temperature. Nitrogen purged 2-propanol (30 mL) was added then stirring was continued for approximately 30 minutes The crude product 1,3,6,8-tetrapheny-11-oxatricyclo[6.2.1.$0^{2,7}$]undeca-2,4,6-trien-9-yl -1-methanone was collected, dried, and used in the next step without purification or characterization (2.53 g, 74%).

The fifth step involved dehydration of 1,3,6,8-tetrapheny-11-oxatricyclo[6.2.1.$0^{2,7}$] undeca-2,4,6-trien-9-yl-1-methanone with anhydrous hydrogen chloride in acetic acid at room temperature to produce 1,4,5,8-tetra phenyl-2-naphthaldehyde. Unpurified 1,3,6,8-tetrapheny-

11-oxatricyclo [6.2.1.0^{2,7}]undeca-2,4,6-trien-9-yl-1-methanone (2.71 g, 0.00566 mole), nitrogen-purged methylene chloride (15 mL), and acetic acid (15 mL) were placed into a 100 mL, three-necked, round-bottomed, flask equipped with a magnetic stirrer, reflux condenser, and nitrogen adapter. The reaction apparatus was purged with nitrogen. The light yellow reaction solution was placed in an ice-water bath (10-15°C) for approximately 10 minutes. Anhydrous hydrogen chloride was bubbled into the reaction solution for 15 minutes when the ice-water bath was removed. The red reaction mixture was stirred at room temperature for an additional 2.75h (monitored via TLC; stationary phase silica gel; eluent methylene chloride: hexane 1:1) while anhydrous hydrogen chloride addition was continued at a steady rate. The solvents were allowed to evaporate overnight. The nearly dry reaction mixture, which contained residual acetic acid, was dissolved in nitrogen-purged methylene chloride (20 mL) followed by the addition of nitrogen purged 10% sodium bicarbonate solution (30 mL) to neutralize the acetic acid. The organic layer was separated and dried with magnesium sulfate. The anhydrous solution containing the product was evaporated then triturated with a minimal amount of xylene to give yellow 1,4,5,8-tetra phenyl-2-naphthaldehyde (0.49g, 19%): mp 253-258°C (lit.[1] mp 245°C); IR (KBr) cm^{-1} 3053 (Ar-C-H), 1667 (CHO), 1492 and 1444 (Ar-C=C), 754 and 696 (Ar-C-H); ^{1}H NMR ($CDCl_3$) d 6.87-7.23 (m, 20H, Ph), 7.36 (d, 1H, Ar), 7.51 (d, 1H, Ar), 8.00 (s, 1H, Ar), 9.67 (s, 1H, CHO); ^{13}C NMR ppm 126.0, 126.1, 126.2, 126.3, 127.1, 127.3, 127.5, 130.0, 130.1, 130.7, 131.7, 132.0, 132.4, 133.2, 134.1, 136.7, 140.2, 140.7, 142.6, 143.5, 145.4, 193.5.

The sixth step involved decarbonylation of 1,4,5,8-tetra phenyl-2-naphthaldehyde with palladium on charcoal to generate the polycyclic aromatic compound 1,4,5,8-tetra phenyl-2-naphthalene. A mixture of 1,4,5,8-tetra phenyl-2-naphthaldehyde (0.89 g, 0.0019 mole), and 10% palladium on activated carbon (0.10 g), were placed into a 100-ml single-necked, round-bottomed flask equipped with a reflux condenser (without running water), heating mantle filled with sand, and a thermometer submersed in the sand. The reaction was heated for 5 h at 240-290°C during which time the product sublimed as light brown crystals on the upper inside the reaction flask. The product was extracted in boiling benzene (50 mL) then gravity filtered to remove the palladium on activated carbon. The light brown crystals (0.13g) were recrystallized three times from toluene to give white crystals (0.33 g, 40%): mp 276-279°C (lit.[1] mp 266°C); IR (KBr) cm^{-1} 3054 (Ar-C-H), 1443 (Ar-C=C), 836, 752, and 695 (Ar-C-H).

A derivative of 1,4,5,8-tetraphenylnaphthalene was synthesized by reacting the electron-rich polycyclic aromatic compound 1,4,5,8-tetra phenyl-2-naphthaldeyhyde with an electron-deficient nitrogen heterocyclic, namely bis(2-benzothiazoyl)methane, to yield, via a condensation reaction, the model compound 1,1-bis(benzothiazol-2-yl)-2-(1,4,5,8-tetra phenyl-2-naphthalenyl) ethene.

A mixture of 1,4,5,8-tetra phenyl-2-naphthaldehyde (1.77 g, 0.00384 mole), bis(2-benzothiazoyl) methane (1.08 g, 0.00384 mole), and nitrogen purged pyridine (25 mL) were placed into a 100 mL single-neck, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, nitrogen adapter, and heating mantle. The reaction was refluxed for 96 h under nitrogen (monitored via TLC; stationary phase silica gel; eluent methylene chloride: hexane 1:1).

The reaction was stopped at 96 h though the TLC showed that starting material was still present. The reaction mixture was poured, with stirring, into ice-water (200 mL) containing hydrochloric acid (35 mL). The acidic solution mixture was stirred until all of the ice had melted then the solution was filtered and dried (3.94 g). The solid was stirred in boiling ethanol (900 mL) then filtered hot to give a light brown solid (1.77 g). The solid was recrystallized from cyclohexane:benzene (100 mL:25 mL) then reduced to a total volume of 50 mL and cooled for 2 weeks to give brown crystals of 1,1-bis(benzothiazol-2-yl)-2-(1,4,5,8-tetra phenyl)-2-naphthalenyl)ethene (1.11 g, 40%): mp 146-148°C; IR (KBr) cm^{-1} 3056 (Ar-C-H), 1598 and 1432 (Ar-C=C), 1491 (C=N), 756, 696 (C-H or C-S); EIMS m/z 724 (M^+), 444 (M - isobenzothiazole-C-isobenzothiazole$^+$), 367 (444 - $C_6H_5^+$), 782 (isobenzothiazole-CH_2-isobenzothiazole$^+$), 108 ($C_6H_4S^+$), 69 ($C_3H_5^+$), and 45 (HCS^+). Anal Calcd for $C_{50}H_{32}N_2S_2$: C, 82.84; H, 4.45; N, 3.86; S, 8.85. Found: C, 82.91; H, 4.48; N, 3.74; S, 8.87.

Reference

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THE SYNTHESIS OF TETRAPHENYLNAPHTHALENE DERIVATIVES FOR NONLINEAR OPTICAL PROPERTY EVALUATIONS

Task Order No. 243a
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Haaga
Wright State University

27 December 1996

Government Task Leader
Mr. Bruce Reinhardt
WL/MLBP

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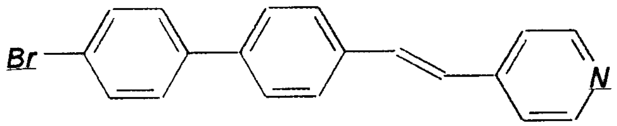
TASK ASSIGNMENT

Task order number 243 dealt with the development of tetraphenylnaphthalene derivatives for nonlinear optical property evaluations. The objection was the development of these novel model compounds for evaluation as 2-photon resonant nonlinear optical materials using standard organic synthetic procedures and analytical techniques.

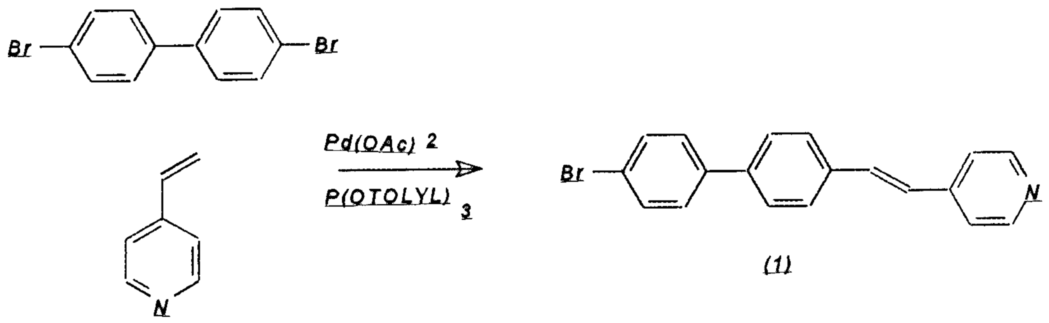
DESCRIPTION OF WORK

Synthesis and characterization of organic molecules for evaluation as 2-photon resonant nonlinear optical materials were investigated. The main portion of this Task has been the synthesis and optimization of a biphenyl structural unit substituted with a bromine and a pyridine bridged with a double bond (1)



(1)

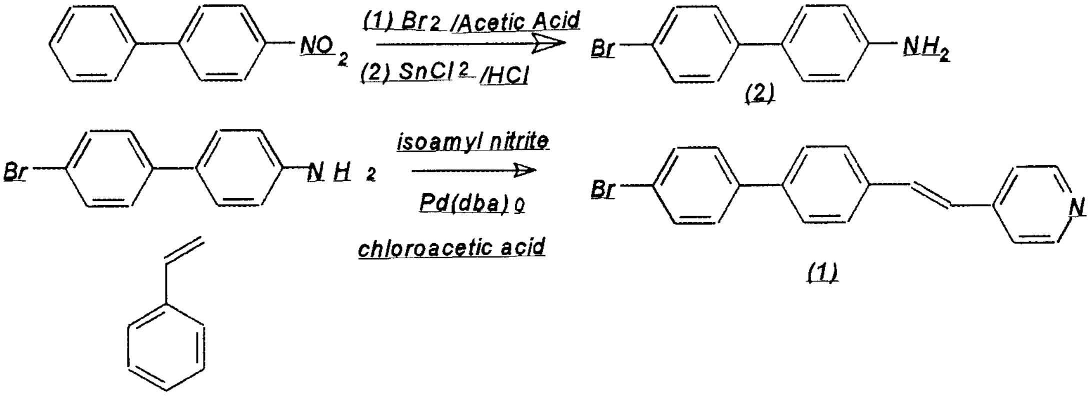
Two main routes to this biphenyl unit have been tried. The first is a direct attachment of vinyl pyridine to diphenyldibromo in a single step. This reaction is commonly referred to as the Heck reaction[1]. The following synthetic route was tried:



(1)

The above reaction is attractive due to its one pot reaction scheme but was found to be unrefined due to its yields between 30 and 40 %. Two attempts were made to improve these yields by changing the catalyst and solvent. The first was to replace the palladium catalyst [$Pd(OAc)_2$] with an arsenic catalyst, triphenylarsine. This showed no improvement in yield due to a miscalculation and hasn't been repeated. The second attempt was to use pyridine instead of triethylamine as the solvent and to use no tri-o-tolyl phosphine [P(OTOLYL)] which is added to stabilize the palladium catalyst. The reaction proceeded but product was not able to be isolated via chromatography.

A second synthetic route to the desired biphenyl unit (1) is now being investigated. This is the attachment of the vinyl pyridine to 4-bromo-4-aminobiphenyl through the amine[2]. The following route is now being investigated:



The above scheme is a three-step synthetic route which is attractive due to reported literature yields of greater than 90 % for the bromination and reduction of nitrobiphenyl to compound (2) and a 60 % conversion of (2) to the desired compound (1)[2]. The first two steps have proceeded as expected and results on the final step are still pending.

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(2) Matsuda, T.; Giam, C.S. *J. Org. Chem.* **1981**, 46, 4885-4888.

METALLIC COMPOSITES (96-II)

Task Order No. 245
Student Support Program
Southwestern Ohio Council for Higher Education

Gregory Schieleit
Ohio State University

27 December 1996

Government Task Leader
Ms. Mary Lee Gambone
WL/MLLM

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DESCRIPTION OF TASK ASSIGNMENT

The Task involved determining interface properties of titanium matrix composites. Titanium matrix composites (TMC's) have the mechanical properties including: low density, and high strength and stiffness at elevated temperatures, that make TMC's prime candidates as a material in turbine engines. Unfortunately, the environment in a turbine engine will cause the interface of the composite to undergo oxidation, degrading the composite's mechanical properties. Measuring the oxidation at the interface in a TMC would be helpful in developing future oxidation resistant composites. Overcoming this problem will help reach the goal of the Air Force's Integrated High Performance Turbine Engine Technology (IHPTET) initiative, which is to increase the thrust to weight ratios of turbine engines from 10 to 1 to 20 to 1 by the year 2000.

DESCRIPTION OF RESEARCH

Presently carbon coated fibers are a popular choice among interface systems. The focus of this research is to measure fiber protrusion from the matrix caused by oxidation of the fiber's carbon coating. Oxidation of the carbon layer on carbon coated fibers may cause a debonding between the matrix and fiber. At elevated temperatures interface, debonding will eliminate residual stresses in the composite, allowing the fiber freely to expand in the composite due to differences in coefficients of thermal expansion (CTE) between the fiber and matrix. If the fiber did not experience any residual stresses caused by the matrix then fiber protrusion, after exposing the material to a high temperature and cooling the material to room temperature, could be simply measured by the following equation.

$$af \times (25-T) \times L - am \times (25-T) \times L = h[T] \qquad (1)$$

Where af and am are the CTE's for the fiber and matrix, L is the initial length of the composite, if the fiber and matrix initially have the same length, T represents the temperature in Celsius and h[T] is the height difference between the fiber and matrix. A positive h[T] shows the fiber is above the matrix while a negative h[T] shows the fiber is below the matrix. However, h[T] can be measured only after eliminating the residual stresses. Oxidation of the carbon layer can eliminate these stresses. Assuming a linear relationship between length of carbon oxidation along the fiber and h[T] makes it possible for the height difference to be measured. This height difference is calculated in the following manner.

$$h[cl]=(h[T]/L) \times cl \qquad (2)$$

Cl is the length of carbon oxidation and h[cl] is the height difference or fiber protrusion as a function of the carbon oxidation length.

The following work was done to measure fiber protrusion. A .03 in. thick 4-ply unidirectional composite panel of AC-1 fibers and a Ti-22Al-23Nb matrix manufactured by Atlantic IMT, Wilmington MA, was sectioned into a ½ x ½ inch piece and a ½ x 1/4 inch piece via wire EDM and a diamond saw. The pieces were polished perpendicularly to the fiber direction. Fiber height with respect to the matrix was then measured using a confocal microscope. The ½ x ½ inch sample was then subjected to a heat treatment of 25 hours at 800°C while the ½ x 1/4 inch piece was subjected to a heat treatment of 600°C for 24 hours. After the heat treatment the fiber height was measured again using a confocal microscope. Then the pieces were mounted and polished along the length of the fibers to the second row of fibers in the composite. SEM work was done to measure the length of carbon oxidation along the fiber.

RESULTS

After the heat treatment of 800°C for 25 hours, the average height difference was 5.64 microns below the matrix. Before the heat treatment the average height of the fiber was .55μm above the matrix so the average fiber protrusion was -6.19μm. The average length of carbon oxidation was 4.21 mm. The heat treatment of 600°C for 24 hours provided an average fiber protrusion of .91μm and the average length of carbon oxidation was 280μm.

The heat treatment of 800°C for 25 hours proved to be too severe. While succeeding in oxidizing the carbon layer, the fiber and matrix oxidized as well. SEM images show that the space left by the oxidized carbon was filled by the growth of SiO_2 and TiO_2. This growth of SiO_2 and TiO_2 may have caused the formation of residual stresses after the carbon oxidized and prevented the fiber from freely expanding. The 600°C 24 hour heat treatment limited oxidation to mostly the carbon layer and the matrix. There was very little SiO_2 or TiO_2 growth that allowed the fiber to expand and show positive protrusion values.

The growth of oxide on the polished surface contributed to measured protrusion values being lower than their actual values. Subtracting oxide growth from the measured protrusion values gave an actual average fiber protrusion of 1.57μm. The actual fiber protrusion value of 1.57μm was .78μm or +99% larger than the predicted results. Predicted results were calculated using equations (1) and (2). The CTE values used to calculate the predicted results were 4.86E-06/ °C for the fiber and 9.8E-06/°C for the matrix. The length of oxidation, cl, used to calculate the predicted results, was the length measured in the SEM for each fiber. A possible reason for this large discrepancy could be the technique used to measure the protrusion. One problem with using the confocal is orienting the surface of the sample perpendicular to the direction of the laser scanning the sample. The poor orientation makes recording measurements difficult since the image that is being measured is at an angle relative to the measuring device of the confocal microscope. However, there are many different ways to record measurements using a confocal microscope and a better understanding of the microscope may produce a better method for recording measurements.

As stated earlier, the focus of this research was to measure fiber protrusion caused by oxidation of the composite. In the 600°C 24 hour heat treatment sample the carbon layer was oxidized and fiber protrusion was observed. The measured values taken using a confocal microscope varied significantly from the predicted values. To determine the extent of oxidation in a composite using this method, more accurate data needs to be recorded. Measuring fiber protrusion with a profilometer as well as a confocal microscope may produce more accurate data. When an accurate method for measuring fiber protrusion is developed, future work will include heat treating composites with oxidation resistant coatings and comparing their fiber protrusion values with the values obtained from the carbon coated fiber interface.

INFRARED SPECTROSCOPY

Task Order No. 246
Student Support Program
Southwestern Ohio Council for Higher Education

Heather Watrob
University of Dayton

27 December 1996

Government Task Leader
Dr. Harvey Paige
WL/MLBT

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I would like to take this opportunity to thank the many people that have contributed to my work experience at Wright-Patterson Air Force Base. I would like to thank Dr. Harvey Paige for his thoughtfulness and guidance. I would also like to thank Dr. Jim Liang for his inspiration, patience, and integrity that he displayed throughout this Task.

TASK ASSIGNMENT

The purpose of this Task was to study the interactions of lubricants and lubricant additives with metal surfaces and the decomposition products resulting from such interactions. The lubricants of interest were perfluoropolyalkyl ethers (PFPAEs). Their molecular formula is denoted as $R_f(CF_2CF_2CF_2O)_xR_f'$, $R_f(CF_2O)_x(CF_2CF_2O)_y(CF_2CF_2CF_2O)_zR_f'$, $R_f(CF_2CF(CF_3)O)_xR_f'$. These lubricants are of primary interest for aeronautical and computer applications. This task was accomplished by employing Fourier Transform Infrared Spectroscopy (FTIR), and grazing-angle microscopy coupled with FTIR. This work has been reviewed in such media as *Tribology Letters* and has been presented at numerous conferences.

This Task was carried out under the guidance of Dr. Jim Liang. A combination of laboratory experience, instrument manipulation and acquisition were an introduction to the world that a research chemist must work in. The laboratory experience involved the operation of a Nicolet FTIR to study surface chemisorption of metal oxides such as Al_2O_3 and SiO_2. These materials were examined by pressing the material onto a strip of tungsten mesh and then inserting this mesh into a reaction cell. IR analysis was then done on the reaction cell under different experimental conditions and recorded. These experimental conditions included variations in both pressure and temperature. Analysis of the spectra determined what species were present on the mesh and provided insight into what chemical reaction had occurred at the interface. The purpose of this technique is to simulate the reactions that occur between a metal surface and the lubricant fluid during triboreactions.

Another technique used in this study was grazing-angle/ FTIR microscopy. By this method an infrared spectrum of the wear scar present on the sample disks prepared by the tribology group was obtained. The chemical structure of the surface film present at this surface could be elucidated from the resulting GAM/FTIR spectrum. This method of analysis also provided insight into the tribochemistry occurring at the interface between the metal surface and the lubricant fluid. A major part of the research effort involved the acquisition of new software to drive this instrument. The Grams Analysis Model 1700 software package was acquired from Perkin Elmer after a power surge required the upgrade. An important feature to note is that the old software is not directly compatible with the new software. This makes retrieval and conversion of the old data a timely and arduous multi step process. Due to its inherent complexity, a short lab guidebook was developed and set up for future use.

The experience with Dr. Liang also provided an excellent overall view of what is required of a research chemist. Working with him, some nonlaboratory tasks required of every chemist were done. This included the preparation of scientific manuscripts and presentations, and assistance in the acquisition of new instrumentation while making minor repairs on the existing instrumentation. Reviewing the extensive literary resources that are integral to the advancement of research was another important part of the research conducted. Some work has contributed to a poster presentation to be given at the Central Regional ACS meeting in Dayton on June 11, 1996.

INFRARED SPECTROSCOPY

Task Order No. 246a
Student Support Program
Southwestern Council for Higher Education

Lynn R. Frock
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27 December 1996

Government Task Leader
Dr. Harvey Paige
WL/MLBT

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TASK ASSIGNMENT GOALS

The Task goals are to study the interactions of lubricants and lubricant additives with metal surfaces and the decomposition products resulting from such interactions.

RESEARCH

The chemisorption process is one basic tool used in the lubricants chemistry research.

The interactions of metal oxide and silane compounds with metal surfaces under a variety of environmental conditions are being studied using Fourier Transform Inferred Spectroscopy (FTIR). The system chosen for the chemisorption research is the interactions of alumina and silane compounds.

Presently, a new technique for preparation of metal oxide samples has been used for investigation of interactions between oxide samples and additives under high stress conditions studied by FTIR. This involves the preparation of an alumina oxide sample pressed onto a cm sized tungsten mesh. The sample is placed inside a cubed chamber designed to allow vacuum, atmosphere and temperature to be controlled and adjusted for various experiments. The sample is connected by weld to a copper electrical feed through inside the cubed chamber and electrical current is allowed to flow through the sample to control temperature as needed. A metal vacuum line is also connected to the chamber to allow the evacuation of the chamber and addition of chemical substances to the system within the chamber. The sample chamber has two ports, one on each side, capped with vacuum flanges mounted with KBr windows. These windows allow FTIR spectra to be taken during changes occurring in the system. The interactions and mechanisms of chemical reactions are studied by observing the differences in the peaks while temperature, pressure, and chemical changes are in process. The chamber is sealed by copper gaskets to ensure the system remains closed.

The focus of these studies has been on the interactions of alumina oxide with dimethylethoxySilane (DMES) as the additive. To insure no H_2O or O_2 is present, a method of freeze pump thaw is done on the additive before allowing it to be released into the sample chamber. Samples consist of 0.04g of Al_2O_3 mixed in with 20 ul of H_2O, placed onto a cm sized tungsten mesh subjected to 24,000 lbs. of pressure between two steel plates. A sample is placed into a sample chamber and then the surface of a sample is calcimined to prime the surface by gradually heating the surface to about 500°C. DMES is added at ambient temperature. Temperature is monitored by a digital thermometer. The chamber is then evacuated by means of a turbo molecular pump to a background pressure of 10^{-7} Torr, to remove any unreacted material. Current is applied again to the sample to heat it to see how much stress and/or heat is required to break any newly formed bonds. During this complete process, scans are being taken to monitor the chemsorption and any chemical interaction happening on the surface of the sample. Bonds are broken and formed simultaneously, which allows for the study of the mechanism involved in the chemical reaction process.

RESULTS

It has been determined that silane interacts with alumina at ambient temperature. Chemisorption bonds have been observed. The surface of the alumina sample is:] Al-O-H, this reacts with DMES at the hydrogen position to form ethanol gas as a by product of the reaction, the new bond formed on the surface is]Al-O-SiH(CH3)2. Addition of the DMES at ambient temperature rises to a peak at ~1075 cm^{-1}. This wave number is characteristic of Al-O-Si. The desorption of the-OH band at ~3730cm^{-1} as the new band appears suggests the replacement of the-OH with the Si molecule. EtOH leaves the system upon evacuation of the system, because it leaves as an unattached gas molecule formed as a by product resulting from the chemical reaction that took place on the surface of the tungsten mesh.

These mechanisms and other similar reactions will be investigated, reported and used as tools in studying the chemisorption process. Research is ongoing and data is still being analyzed for any new interesting changes.

COMPOSITE MATERIALS SUPPORTABILITY

Task Order No. 247
Student Support Program
Southwestern Ohio Council for Higher Education

Belinda McKinney
University of Dayton

27 December 1996

Government Task Leader
Mr. Jim Folck
WL/MLSE

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I would like to thank all those who helped me feel comfortable and a part of this work environment, especially Ron Kuhbander and Jim Mac Kiernan.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Currently, many projects are being worked on including the Mix Ratio Study, PMR-15, and Aircraft Battle Damage materials characterization, surface preparation using a PACS unit, and fracture toughness evaluation. For the Mix Ratio Study, the resin adhesive EA9394 was studied. Resin adhesives contain two parts, the epoxy (usually labeled part A) and hardener, part B, which upon mixing react and develop into a durable adhesive. Different ratios of the epoxy and the hardener are tested to decide which ratios weaken the strength of the resin. The PMR-15 project requires studying the composite PMR-15 to decide new drying methods of this composite for the B-2 plane. This four-ply composite part of the plane often blisters when the engines fire up because it picks up atmospheric moisture extremely quickly while sitting in the hanger. This moisture causes the part to blister upon contact with the 500° F temperatures the engines of the plane develop while running. The Aircraft Battle Damage Report materials' characterization is a study of the resin EA9396/C2 strengths and damage characteristics to use as adhesive in making composite patches for planes. The PACS (Phosphoric Acid Containment System) project is another procedure to acid anodize specimens. It is being studied and compared with other surface preparation procedures. The fracture toughness evaluation is being done to decide the strength of EA9396 at different bond line conditions.

The results of this work will contribute to using these projects in many applications. The results of the Mix Ratio Study helped to decide at what ratios the resin could be mixed and still function properly.

The PMR-15 results will develop a new method for workers to dry the part on the B-2 plane where the problem exists. These methods will be more time efficient and cost effective. The Aircraft Battle Damage characteristics' results will determine what kind of damage an adhesive can stand before failing when used in a patch. This will help in choosing the best adhesive to use when repairing an airplane. The results from the PACS project will compare this type of surface preparation to other surface preparation techniques for finding the best surface preparation that can be used in the field. The fracture toughness results will show how strong and what the limits of EA9396 adhesive are.

DESCRIPTION OF RESEARCH

The research was done by making specimens for each project and then testing the specimens under different conditions. For the Mix Ratio Study and the Aircraft Battle Damage characterization, wedge panels, floating roller peel panels, and inplane shear panels were tested using different ratios of hardener to epoxy and under dry conditions and saturated conditions.

The specimens were then tested using an Instron machine. The data were analyzed using graphs. Several wedge and peel panels were made using the PACS unit for surface preparation. These specimens were tested and compared to test results using other methods of surface preparation. The fracture toughness specimens were tested using an Instron machine. The results were analyzed by measuring points on the graphs made during each test. For the PMR-15 project, several different methods of drying the panels were tested.

These methods include using an oven at different temperatures, desiccant bags, a vacuum oven, and making a model of the part being studied and using large de-humidifiers at several different temperatures to determine how quickly the specimens would dry. The different methods of drying the specimens were compared and the data analyzed using graphs.

RESULTS

Several things were learned during this task. The importance of laboratory safety and lab behavioral skills were discovered for a safe working environment. Several different types of surface preparation techniques used for repairing aircraft with composite patches including acid anodizing, acid etching, grit-blasting, and the use of the coupling agent silane and the PACS unit were learned. Interpreting data and learning how to incorporate results into practical applications was discovered through helping and watching the engineers in the group. Also, because of the hands on work, laying up composite materials and curing them was learned along with the procedure for testing specimens using an Instron machine and interpreting the graphs of these tests.

COMPOSITE MATERIALS ENGINEERING AND ANALYSIS

Task Order No. 248
Student Support Program
Southwestern Ohio Council for Higher Education

Brian K. Wilhelm
Wright State University

27 December 1996

Government Task Leader
Mr. Jim Folck
WL/MLSE

ACKNOWLEDGMENTS

I would like to thank Ron Kuhbander and Jim McKiernan for their help in lab procedures, equipment familiarization, and testing methods for this task.

DESCRIPTION OF TASK ASSIGNMENT

Metal surface preparation is the initial process before testing any specimens. Four kinds of surface preparations are available depending on the test, and type of specimen chosen. All steps must be followed precisely to ensure a clean, contaminant free surfaces.

Phosphoric acid anodizing solution is used to decontaminate the metal surface. The metal specimen is initially cleaned with MEK (methyl ethyl ketone), and abraded with Scotchbrite pads and water. After drying, the specimens are placed in the acid solution for 20 minutes. A final rinse and drying, complete this process.

Grit-blast silane surface preparation starts with solvent degreasing with MEK, and is abraded with Scotchbrite pads and MEK. The specimens are then grit blasted with 50 micron aluminum oxides to produce a macro-rough surface. Hydrolyzed silane is applied so the metal surface stays saturated for 10 minutes. The specimens are dried with nitrogen to complete the surface preparation.

P2 etch, and Pasa-jel prepares the surface by removing oxide layers. They are solvent wiped with MEK, and Scotchbrite abraded and applied to the surface with acid brushes for 25 minutes, and rinsed with distilled water. The specimens are then completed by drying at 160°F for 15 minutes.

After the surface preparations are completed, some specimens require an application of BR127 primer. Specimens were primed in a paint booth to a desired thickness of .003 to .007 inches. After priming, specimens are cured in an oven at 250°F for 1 hour. When cooling is complete, specimens can be bonded with the appropriate adhesive.

Material testing is another task required for this work assignment. Fracture toughness evaluation for a double cantilever beam was tested by using an Instron tensile test machine. An optical microscope used to measure crack-length was connected to a precision dial caliper for exact measurements. The test machine output was recorded in real-time on an analog display of the load versus crack opening displacement, on an x-y recorder.

DESCRIPTION OF RESEARCH

Research was accomplished by using technical manuals, and engineering handbooks. Engineers aided in any further research required.

The following pieces of equipment were used during this Task. A portoclave was used to cure panels under positive pressure, and/or vacuum pressure at various temperatures. A vacuum oven dried-out the specimens for test purposes. Venturi air flow meters allowed the house air supply to be converted into a vacuum line. Various hydraulic presses allowed positive pressure tests to be obtained for all types of panels. A Phosphoric Acid Containment System (PACS) unit allowed surface preparation to be done at a remote location on aircraft. This system keeps all acid internal, with safety vacuum bags for precautionary measures. Grit-blast silane cabinets permit any specimen to be grit-blasted using nitrogen pressure at 80 psi. Measurements were taken by using electronic balances, or triple beams.

The Instron test machine was the most elaborate piece of equipment used. Instron's can be set up to accommodate any test scenario, including freezing, overheating, and full vacuum tests. The different equipment associated with the Instron involves an x-y recorder for stress-strain curves. The amplifier records output voltage, which is transferred to the plotter, to become the signal. A multimeter reads the output voltage of the amplifier to check the signal. An extensometer measures the amount of displacement that the test machine travels, which is converted into a signal to become the actual crack growth.

Instron test data was analyzed only to the extent to see if the plotter data corresponded with actual data. Further analysis was done by the engineer in charge.

RESULTS

Many tests were accomplished during a PMR-15 moisture study on graphite composites. The composite panels were fully saturated at 95-100% relative humidity. The tests involved methods of drying out the panels, while recording the time it took to reach 0.50% saturation. The results were very interesting by showing how the rate of drying varied so greatly due to the test conditions. A few specimen drying scenarios include using heat blankets, desiccant bags, a vacuum oven, and a dry air heater.

The fracture toughness evaluation revealed the effects of different bondline controls with EA 9396 as the constant adhesive used. The bondline control methods include using polyester, graphite, and fiberglass random mat, and a fiberglass and graphite knit. Test results concluded which bondline control could withstand the maximum load.

A mix-ratio study involved using a two-part adhesive, EA 9394. A base and a hardener were added with different ratios for 6 cases. The results showed different hardness, strengths, pot life's, and T_g's for each ratio, which determined the best ratio of adhesive.

Many different methods of surface preparation and bonding are available. This task presented many of these different methods, and allowed for actual results to be collected and analyzed. The Instron test machine proved to be the most exciting task accomplished. Future knowledge of this type of machine is inevitable, which makes this work experience even more important. This was a successful task, which allowed for many different kinds of materials testing to be observed, and practiced.

COATED FIBER CHARACTERIZATION

Task Order No. 249
Student Support Program
Southwestern Ohio Council for Higher Education

John R. Welch
Wright State University

27 December 1996

Government Task Leader
Dr. Randall S. Hay
WL/MLLN

ACKNOWLEDGMENTS

I would like to thank the following for assistance in developing the tripod polishing method: Dr. Michael Cinibulk, U.E.S., Dr. Scott Walck, Scott Apt U.E.S., and Frank Scheltens, U.E.S. I would also like to thank Emmanuel Boakye, U.E.S. and Dennis Petry for providing me plenty of coated fibers to test the method. I especially thank Dr. Randall Hay and Dr. Ronald Kerans for the opportunity to learn and work in Wright Laboratory.

TASK ASSIGNMENT

This task has consisted of the preparation and analysis of thin foil specimens of ceramic fiber tows. A process was developed to successfully thin these specimens to transmission electron transparency at Wright Laboratory over the last 2 years. A brief description of this process is detailed in the following paragraphs.

Fiber tow lengths of several feet are sectioned with scissors into pieces of approximately 0.5 inches. These pieces are then bundled together, immersed into a thermal setting epoxy, and inserted into a piece of shrink tubing of the same approximate length. This bundle is then exposed to heat via a hot plate or heat gun to cause the shrink tubing to contract, increasing the density of fibers, and simultaneously curing the epoxy. The bundled tows in shrink tubing are then placed in a low temperature oven to ensure full curing of the epoxy.

The fiber tow specimen is removed from the oven after approximately 1 hour and the shrink tubing is then removed with the aid of an exacto knife. The resulting tubular like pieces are then sectioned into lengths of about 1 quarter of an inch on a diamond blade saw. The pieces are placed in a cylindrical spring mounting clip filled with a Bakelite substance called epomet and further surrounded with more of the same material after placement. This arrangement is compacted and heated in the mounting press until cured. The spring clip is removed by sectioning the surrounding medium on a diamond blade saw until the spring clip is exposed. This piece is heated on a hot plate, mounted onto a piece of roughened glass microscope slide, mounted upon a glass stub with a temperature sensitive wax called crystal bond. After the wax has cured, the cylindrical section of mounted fiber tows immersed in epoxy is sectioned through the middle.

The glass stub is placed in a tripod polisher for polishing. The resulting exposed transverse cross section of thousands of filaments of fiber tows and mounting media is polished on a brass wheel with an optically flat glass mounted upon it where diamond lapping films of grades ranging from 30 microns to 0.1 microns have been placed, held in place by wet suction.

A fine polish is obtained, that results in fiber filaments with few defects. The stub is removed from the polisher, heated on a hot plate to allow removal of the cylindrical section from the glass slide, replaced on the glass slide with the polished side toward the slide, and allowed to cool to cure the wax.

The rough surface is ground at a wedge on a diamond embedded metal mesh disk until the remaining amount of specimen is thin. The stub is again placed in the tripod polisher. The sample is then ground on the diamond lapping films in the general direction of the wedge with the rear feet of the tripod polisher having been raised 3 millimeters from parallel with the surface of the glass slide. When the rear edge of the specimen begins to erode away, the wedge is reversed by lowering the rear feet of the tripod polisher approximately 3.5 millimeters. The sample is further thinned and more finely polished on progressively finer grades of diamond lapping films, periodically adjusting the rear feet of the tripod polisher to bring the specimen surface into near parallel with the previously polished side. This process continues until the thickness of the thin foil is approximately 2 microns or until the specimen begins to disintegrate catastrophically.

Copper mesh TEM. grids are attached to the thin foil section on areas containing fiber tow filaments with a quick curing epoxy. Oval copper washers are placed on top of the mesh grids for support. These grid sections are removed from the slide by heating the slide on a hot plate and removing as much of the wax as possible by pushing the grids over the surface of a hot glass microscope slide. The sample is further cleaned by squirting acetone on the surfaces.

The sample is then further thinned by placing the grids in an ion mill, where a beam of ionized argon gas is directed at the surface of the thin foil at angles of approximately 15 degrees above parallel. This process continues until the thin foil contains several filaments of fiber that are transmission-electron transparent, approximately 70 to 100 nanometers in thickness. The sample surface is coated with carbon to enable surface currents, while the sample is in the transmission electron microscope.

Most of the samples prepared during this Task have consisted of monazite coated, porous coated, and grain growth samples of Nextel 720™ fiber tows. The study of grain growth in the two phase fiber system is nearing completion, having been significantly expanded due to collecting data that may indicate a second cycle of growth at high temperatures and lengthy heat treatment periods. A presentation of the findings of this study is planned to be shown at the American Ceramics Society convention in the spring of next year. Additionally, a communiqué coauthored with Dr. Michael Cinibulk and Dr. Randall Hay was recently published in the *Journal of the American Ceramics Society*, detailing the thin foil preparation technique described in this report. Several inquiries have been made concerning the technique since publication, including a visit to Wright Laboratory by a doctoral candidate at the University of Illinois.

Plans include a possible detailed instruction of the thin foil preparation at a microscopy science meeting and a formal paper on the grain growth investigation. A possible return to characterization and processing of ceramic fiber matrix composites is being considered. Additionally, the thin foil preparation is continually being modified as improvements are found.

FATIGUE CRACK GROWTH BEHAVIOR OF ADVANCED MMC'S

Task Order No. 250
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Allen Lair
Wright State University

27 December 1996

Government Task Leader
Mr. Jay R. Jira
WL/MLLN

ACKNOWLEDGMENTS

I would like to give a special thanks to Mr. Jay R. Jira for providing professional guidance, patience and instruction throughout my Task. I would also like to thank Reji John for his additional advising during my Task. Finally, I would like to thank all of WL/MLLN for providing a professional work place.

TASK ASSIGNMENT

The primary objective of this Task was to help Mr. Jay R. Jira in studying the effects of Fatigue Crack Growth on Titanium Matrix Alloys. Within this study, the specific assignments included data organization, data reduction and analysis, and material microstructure characterization.

For each Titanium Matrix Alloy, many Fatigue Crack Growth tests are conducted, each with varying test conditions. Some examples of the varying test elements are the temperature the test is run at, the maximum load applied to the metal, and the stress ratio relating the maximum to minimum load cycles. With all the different test condition combinations, there is an enormous amount of tests conducted for a particular material. This stresses the importance of good organization and record keeping throughout the testing procedure. Thus, a large portion of this Task is made up of organizing and record keeping.

When a new material is received (generally a 6" X 6" panel), several test specimens are cut out of it. These specimens are then given a 5-digit specimen identification number. For the remainder of the time, the specimen will be called this specimen ID. The Specimen then needs to be logged into a specimen log sheet that contains the specimen's dimensions (for example the width and thickness), the specimen's testing conditions (for example the Maximum Load and Stress Ratio), and a few of the test results. This log sheet is kept electronically and posted for all of MLLN to access and use.

Another part of this Task is data reduction and analysis. For every test that is run, a "raw" file is created by the test machine containing the test results. In addition, optical measurements of the crack length are recorded periodically throughout the test. However, before the data can really be useful, it must be run through several data reduction programs. At times, the raw data may produce crack lengths that are off by a given factor. This is generally caused by inaccuracy in setting the computer. To correct the raw data of this, the data is run through a crack correction program. This program compares the raw data with the optical data recorded during the test to assure that the two match. In case of any difference, the raw data is adjusted to run through the optical measurements. Another problem that may be present in the raw data is caused by the sensitivity of the testing machines. Having a very rough crack length verses cycle is common count curve when using the raw data (or corrected data). To fix this problem, the data is run through another program called SMOOTH. This program literally "smooths" out the data to produce a smooth crack length verses cycle count curve. This type of data is easier to use when analyzing the results.

After the data is run through the data reduction, the reduced data is then plotted. Two plots are generally created to show the results, "Crack Length verses Cycle Count" and "Growth Rate verses the Change in Stress Intensity Factor." The first plot, referred to as the "A verses N Plot," shows the crack length through the progress of the test. During an FCG test, a load is applied to the specimen and then removed. Each time this is done it is called a Cycle. The second plot, referred to as the "da/dN verses delta K Plot," shows the crack growth rate (derivative of the Crack Length verses the Cycle Count Curve) in terms of the stress intensity factor (K). This will show the engineer things such as fiber bridging which is where fibers in a Titanium Matrix Composite (TMC's) remain unbroken through a crack in the matrix, thus holding the specimen together. This is the prime objective of composite material.

Once the plots are created, they are looked at to see if all the data look accurate. In case of any possible "problems" in the data, the data reduction process is run through backwards checking for mistakes in the reduction. If no problems are found, the test itself is considered. Most of the time, the problem lies in the reduction of the data. This is corrected by simply rereducing the data.

The final assignment in this Task is the material microstructure characterization. When a material is tested, the material is not considered "perfect." To do this, would make the data useless to the real world. Imperfections are predicted in the specimens. To find the imperfections and thus determine the effects they have on testing results, material characterization is done. Material characterization can come in many forms. Concerning this Task, a sample is cut from each material. The sample is then mounted and polished. After the sample has been final polished (0.06 microns), the sample is photographed. Both optical and Scanning Electron microscopes are used. The photographs are then given to the engineer to look for imperfections. If any imperfections are found, further investigation is conducted.

As outlined in the primary objectives involved with this Task, Fatigue Crack Growth tests for Titanium Matrix Composites data are reduced, plotted, and analyzed. In addition, material imperfections are considered by conducting material characterization. By looking at these results, materials can be compared and perhaps even be modified to produce a more efficient metal. However, whether any concrete solutions or discoveries are made, information is gained for each test conducted. As long as this is the case, the work for this Task is a success.

COMPUTATIONAL MATERIALS SCIENCE

Task Order No. 251
Student Support Program
Southwestern Ohio Council for Higher Education

Steven Wiles
Wright State University

27 December 1996

Government Task Leader
Dr. Ruth Pachter
WL/MLPJ

ACKNOWLEDGMENTS

A special thanks to Dr. Ruth Pachter for the time, effort, and guidance she has provided in helping me mature in this ever changing field of computers. I would like to thank Dr. Donald Wiff for offering his knowledge and guidance in an unselfish and patient way. I would like to express thanks and gratitude to SOCHE for giving me the opportunity to work and learn at WL/MLPJ at Wright-Patterson Air Force Base. The experience and knowledge gained is something I will remember my whole life.

TASK ASSIGNMENT

The Task initiated consists of the design of novel materials for laser hardening applications using a variety of computational techniques. These range from ad initio quantum mechanical approaches to molecular mechanics and dynamics, and new methods and algorithms. Currently, the Task is directed toward the understanding and manipulation of simple systems with the use of existing methods and algorithms.

DESCRIPTION OF RESEARCH

Three existing algorithms, of great interest are Charmm, ECEPP, and ASA. Charmm and ECEPP are both written in FORTRAN and ASA is written in C. The FORTRAN language is a pass by reference language, where the C language is place by value language. This difference in language is overcome by using the UNIX operating system on a middle size main frame computer like the Silicone Graphic Machine. The UNIX system has a C compiler with a FORTRAN option, making it possible to recompile both the C program and the FORTRAN program at once.

Charmm was developed by the Department of Chemistry, Harvard. Charmm's main purpose is the evaluation and manipulation of the potential energy of a marcomeleclular system.

Adaptive Simulated Annealing (ASA), was developed by Lester Ingber Research. ASA was developed as a very fast simulated reannealing to deal with the necessity of doing adaptive global optimization on multivariate nonlinear stochastic systems.

ECEPP computes the atomic coordinates and relative conformational energy of a polypeptide chain in standard geometry, for any given sequence of residues and set of dihedral angles.

RESULTS

The ECEPP and ASA programs have been connected in series to take advantage of the global optimization ability of the ASA. This allows the global optimization of the conformational energy of a polypeptide chain in a simple system, but is limited. Work continues on the connecting of the Charmm and the ASA programs. A program written in the C language is being used to call parts of the Charmm program as functions, with limited success. Once Charmm and ASA are connected, this will give a wide range of samples.

SUBSTRATE PREPARATION FOR ORGANIC THIN-FILM DEPOSITION

Task Order No. 252
Student Support Program
Southwestern Ohio Council for Higher Education

Kevin Gross
Wright State University

27 December 1996

Government Task Leader
Dr. Angela Campbell
WL/MLPJ

ACKNOWLEDGMENTS

First and foremost, a large thanks is due to Dr. Angela Campbell for giving me the opportunity to work with her in a very exciting field. I would also like to thank Dr. Thomas Cooper, who was – and still is – a fine scientist who instilled the enthusiasm in me necessary to be a successful scientist. I would also like to thank Nat Natarajan for help in understanding some common laboratory techniques. Finally, a special thanks is due to all the SOCHE students I worked closely with, namely, Laura Sowards, Steve Cline and Bob Haaga.

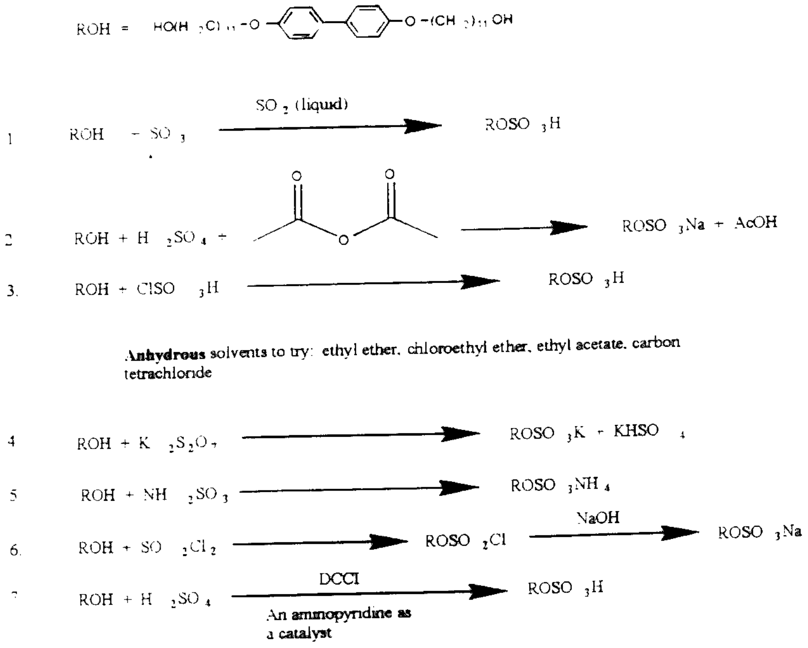
TASK ASSIGNMENT

Preparation of substrates for subsequent use in organic thin-film deposition by the electrostatic self-assembly technique and spin coating technique. Synthesis of monolayers to be used in the above mentioned thin films. Thin films are synthesized with the intent of having optical limiting properties.

WORK COMPLETED

Ultraviolet/visible spectroscopy via a Perkin Elmer Lambda 9 spectrophotometer was done on specific dyes to be incorporated into the above mentioned thin films. The dyes included are: Methylthymol blue, Pyrocatechol violet, Eriochrome Black T, Xylenol orange, 4-(2-pyridylazo)resorcinol, Ponceau S, Acid Fuchsin, Tropaeolin O and Murexide.

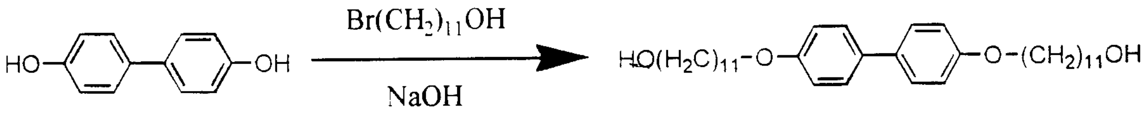
Next, routes to a sulfate ester, a substrate to be used in the thin films, were found via research in sulfur organic chemistry. The findings were as follows:



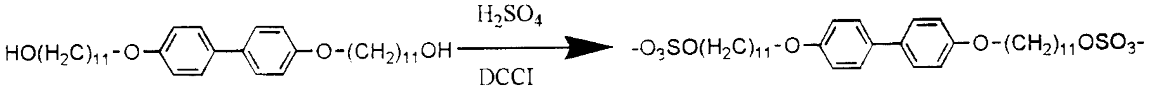
Anhydrous solvents to try: ethyl ether, chloroethyl ether, ethyl acetate, carbon tetrachloride

An aminopyridine as a catalyst

Synthesis of 4,4'-Bis(w-hydroxyundecanoxy)biphenyl was accomplished via the following procedure:



The reaction was done under reflux in ethanol for 48 hours. The material obtained from this was in good yield (88.2% crude) and was used in its crude form for the next step of the synthesis. The resulting 4,4'-Bis(w-hydroxyundecanoxy)biphenyl was used in an attempt to convert it into its sulfate ester analogue via the following reaction (#7 in the above table):



The DCCI (dicyclohexylcarbodiimide) was used in ~25% excess. The reaction was run in methylene chloride at room temperature for 48 hours. An ionic species was obtained by washing reaction material with 10% aqueous NaOH solution and evaporating off this aqueous phase. The yield was ~1%. Analysis to verify the product could not be carried out due to insufficient material.

A carbon dioxide supercritical fluid cleaning system was installed. This will allow for hassle free cleaning of silicon and glass – surfaces in which the thin films will be attached.

SUBSTRATE PREPARATION FOR ORGANIC THIN-FILM DEPOSITION

Task Order No. 252a
Student Support Program
Southwestern Ohio Council for Higher Education

Scott A. Bradley
Cedarville College

27 December 1996

Government Task Leader
Dr. Angela Campbell
WP/MLPJ

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When thanks are in order, two people immediately come to mind. The first is obviously to Dr. Campbell. What she is doing to help my career cannot be overstated, and for this I am truly grateful. It is exciting to be involved in research of this caliber. Secondly, special recognition is due to Dr. Hao Jiang. He has sacrificed much time teaching me how to run the instrumentation and the computer systems, which are intricate parts of my Task.

GENERAL DESCRIPTION

The intent is to synthesize organic thin films. Though many different methods for film preparation exist, Electrostatic Self-Assembly is the current method employed by the lab. This technique requires two oppositely charged materials and a charged substrate. Many strong, ionic bonds are responsible for the film's stability. The substrate is the solid supporting material that serves as the foundation for the film. Silicon wafers or glass slides work well for this function. Three stages are required to prepare the substrates: cutting, cleaning, and silanizing.

First, the silicon wafers and the glass slides must be cut into 15x10 mm pieces. This is done by the old technique of scribing a scratch into the surface and breaking along the scratch. Theoretically the substrates could be used in any size, but pieces at these dimensions are needed in order for them to fit into the Teflon holder. Secondly, since the film is known to take on the characteristics of the substrate's surface, it is imperative that the substrate is clean. To insure this cleanliness, the substrates are taken through a rigorous, three-step procedure. Starting with a special soap, each substrate is individually "scrubbed"(not rough or it will scratch). Next, an acid bath known as piranha is used, which is a boiling mixture of concentrated sulfuric acid and 30% hydrogen peroxide in a 7:3 ratio. Finally, an alkaline bath that uses water, concentrated ammonium hydroxide, and 30% hydrogen peroxide in a 5:1:1 ratio is used. Each step is followed by thoroughly rinsing with pure water and drying with a nitrogen stream. To protect against contaminants and outside particles, the final two steps are carried out in a cleanroom. In the third and final stage, the substrate must be charged to begin the film formation. An organosilane molecule, which is called a silanizing agent, is reacted with the surface of the substrate. A covalent bond is formed via the silanol functionality upon curing in an oven. The organic substituent contains another functionality that can be charged upon protonation with an acid, i.e., an animo group.

DESCRIPTION OF RESEARCH

Currently under investigation are different silanizing agents. It is important that the silanizing agent lays even and smooth, since the film will display the attributes of the silanizing layer and these are the attributes the film should have. Therefore, the goal is to decide which organosilane is giving a better coverage over the substrate. Presently under examination are `[3-(trimethylsilyl)propyl]ethylene diamine, 3-Aminopropyltrimethoxysilane, and 3-Aminopropyltriethoxysilane. The experiment is done by preparing silicon and glass substrates using each of the three silanizing agents. These substrates will be analyzed with atomic force microscopy to determine their smoothness, and ellipsometry to learn the film thickness and the refractive indices. A brief explanation of ellipsometry follows. Ellipsometers measure the change in polarization of light upon reflection from or transmission through the film. Film thickness and the refractive indices can be obtained using a set of equations called Fresnel's Equations and a good model. The data is graphed against the model, and the variables of the equation are altered until they coincide.

RESULTS AND FUTURE RESEARCH

The exploration of the silanization layer of the substrates with the ellipsometer and the atomic force microscope has not been completed. Therefore, no conclusive data on the film silanization has been obtained.

Upcoming work will be carried out to investigate ways to modify or change the cleaning process. The carbon dioxide snow jet stream cleaning technique will be studied further. This process uses a stream of solid and fluid carbon dioxide to remove microscopic particulates and hydrocarbons (greases, oils, etc.) from any surface. It is a nondestructive and non-abrasive method that wastes no chemicals. If this method cleans as effectively as the current method, switching would save many hours and chemicals (and frustrations).

The synthesis of a boladication and a boladianion will continue to be studied. These compounds have been produced by previous SOCHE Students; however, old routes will be improved and new routes may be employed. These molecules are desirable because they are amphiphilic and would be used in the making of films.

POLYMER DISPERSED LIQUID CRYSTALS

Task Order No. 253
Student Support Program
Southwestern Ohio Council for Higher Education

Robert Haaga
Wright State University

27 December 1996

Government Task Leader
Dr. Thomas Cooper
WL/MLPJ

ACKNOWLEDGMENTS

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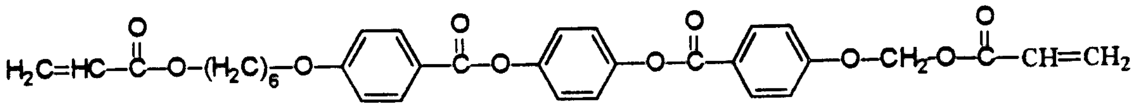
TASK ASSIGNMENT

This Task dealt with the development of various nonlinear active molecules required for the material formation of polymer dispersed liquid crystal systems (PDLC). New liquid crystalline monomers to replace current monomers and/or cross-linkers that make up the pre-polymer matrix of these PDLC systems were investigated.

DESCRIPTION OF WORK

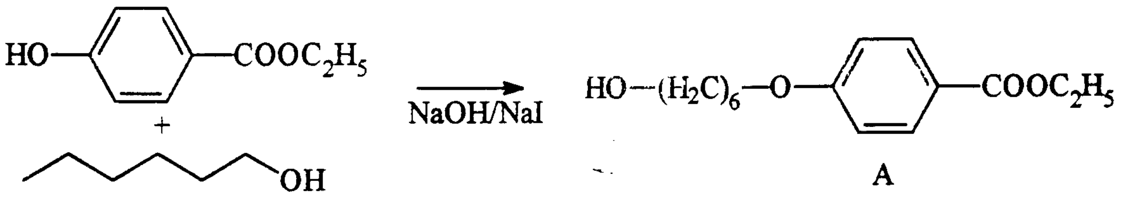
Synthesis and characterization of organic molecules reported in literature were investigated. Previous work has shown that novel liquid crystalline monomers have been successfully synthesized but have failed in current PDLC recipes. A literature search of other liquid crystalline monomers that would be compatible with our systems was done. An interesting compound was found that exhibited unique properties. The compound has been used quite extensively by Broer et. al., at Philips Research Lab in the Netherlands. The compound of their choice was a complex molecule with multiple functionality on both sides of a tri phenyl backbone joined via ester linkage.



It was decided that it would be beneficial to synthesize this molecule and try to incorporate it into our current PDLC system. The synthesis of this compound can be done in a five-step scheme with an overall yield of close to 20%. It was decided that it would also be good to find alternative routes to increase yields along the way.

The overall scheme of the synthesis route can be broken into five distinctive steps.

STEP ONE

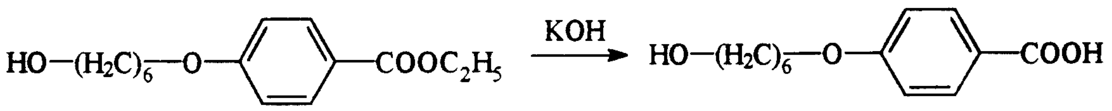


A

The following procedure was followed:

Ethyl-4-Hydroxy benzoate was added to sodium hydroxide in 2-Butanaone. After the addition of Sodium Iodide and 6-clorohexanol the solution was heated at 60° for 10 hours. The solvent was removed by vacuum and the residue washed with sodium hydroxide and extracted with ether. The ether was removed to give compound A. Characterization of this molecule was not done until after the second step had been run.

STEP TWO

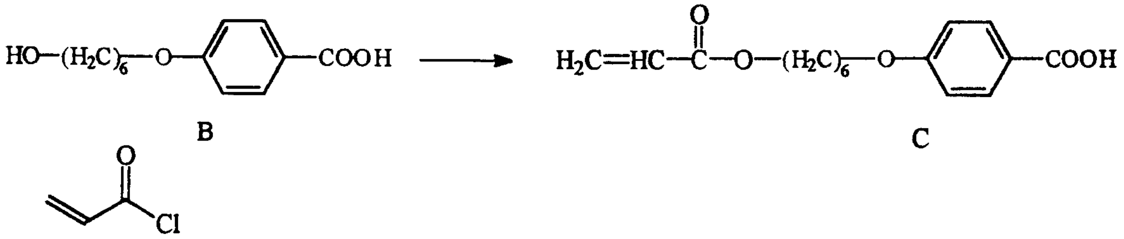


A

B

Compound A was then added to a potassium solution to convert the ester to the corresponding carboxylic acid. Compound B was obtained by washing the solution with ether and neutralizing the water phase with hydrochloric acid. The precipitate was recrystallized with ethanol to yield compound B. Compound B was easily characterized via thin layer chromatography and infrared spectrum.

STEP THREE

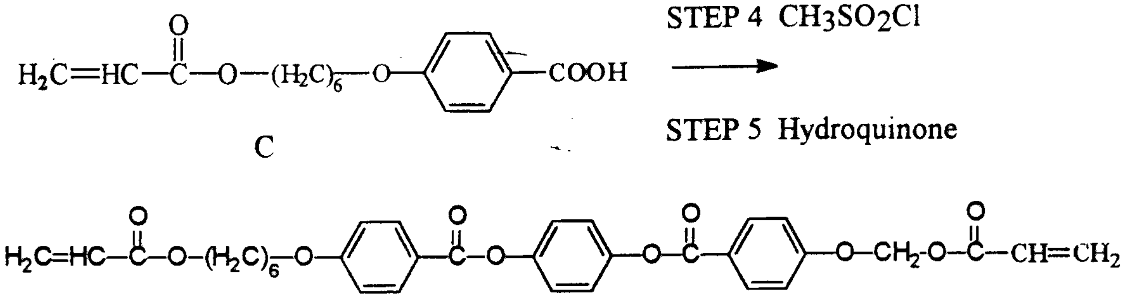


B

C

Compound C was obtained through the above acid chloride reaction. Compound B was added along with dimethylamaline in dioxane and heated at 60°. Acryloyl chloride was slowly added and the solution was stirred for 2 hours. Compound C was isolated by washing with water and recrystallized with 2-propanol.

STEPS FOUR AND FIVE



C

DESIRED PRODUCT

RESULTS

The above five-step synthesis scheme was not completed. Time constraints forced the synthesis to halt after compound C had been made and characterized. The last two remaining steps (4, 5) have not been run. Good success can be reported on the first three reactions and a new procedure was found for the synthesis of compound A which should increase overall yields and make the above reaction scheme more efficient. Future work will include steps 4 and 5 and then incorporate this new monomer into our PDLC systems.

ELECTROMAGNETIC MATERIALS RESEARCH-ELECTRONIC AND COMPUTER TECHNOLOGIES

Task Order No. 254
Student Support Program
Southwestern Ohio Council for Higher Education

Charles E. Culp, Jr.
Wright State University

27 December 1996

Government Task Leader
Mr. Ron Perrin
WL/MLPO

ACKNOWLEDGMENTS

I would like to recognize several people who have helped me in my accomplishment of the Task assigned at the Materials Division of Wright Laboratory. First, I would personally like to thank Mr. Ron Perrin and Mr. Tom Kensky for their instructions and proper technical guidance in beginning level Electrical Engineering. The knowledge provided to me by these two individuals has enabled me to learn valuable information through accomplishments of tasks, teaching, and observance that will be beneficial in my future college studies. This information will also provide me with the essentials needed throughout my future career as an engineer.

I would also like to thank Mrs. Wanda Vogler and the staff of the Southwestern Ohio Council for Higher Education for this unique opportunity to work in such an educational environment. All these people have given me the proper assets needed to accomplish my Task. Thank all of you for your support and assistance.

The valuable knowledge obtained from using self-experimentation and creativity this past year has provided an incentive to continue the educational path of becoming an Electrical Engineer. In the next year, the Task will increase considerably the fundamental abilities necessary for engineering and continue to provide challenges for a future engineer.

DESCRIPTION OF TASK

The responsibility of the Task is to aid Mr. Perrin in providing engineering support to scientists working in the MLPO branch of the Materials Directorate of Wright Laboratory. The assistance provided differs from situation to situation due to the needs of the researcher at the particular time. The role played was in support of building and testing customized circuitry, modifying computer hardware, and writing computer programs. These are just a few of the main assignments completed. The requirements may include going outside the basic tasks listed due to the involvement needed on a particular project. This part of the Task allows for direct involvement in scientific research by providing technological advantages needed to achieve the goals of the scientific experiments that a researcher may have to accomplish. These different parts of the task are combined to form the major objective and that is to provide fundamental knowledge about electrical engineering that is not always provided in a college classroom setting.

DESCRIPTION OF RESEARCH

The type of research accomplished by this Task is not normal variety found in the Materials Directorate. There is not always a scientific experiment to use to obtain the information required. Instead, it is in providing technological support by finding the most efficient means to obtain the data that the scientists require to complete the project.

This does not mean that no research is completed. The research involved in is self experimentation methods, sometimes learning from trial and error. The result of this is the learning of the proper technical skills that are essential to become a good Electrical Engineer.

The most commonly assigned task is building and testing customized circuitry. This is the one area that experimentation was used to find a better methodology. It was more difficult than anticipated to put a schematic of a circuit into functional reality given the physical limitations through which one might go. These limitations come in connecting components, dissipating heat that a circuit item emits, size limitations of the circuit container, and having it function as designed.

The research into finding a better method to accomplish this assignment was approached in two different ways. First, the circuit must be assembled 1 section at a time, not all at once. For example; building the main power supply before trying to assemble the main functional part of the circuit. The reason behind this method is that it allows for the verification that each section of the circuit is working properly, allowing for no mistakes to be made that may damage or destroy another circuit component. This has aided in the prevention of many potential problems that could have occurred, such as connection problems. The laying out of the circuit section by section also allows for the overcoming of heat-related problems by placing these circuit items in areas of the board where the circuit subassemblies can be properly arranged to dissipate heat.

The second method found which has aided in the research is the use of test equipment to ensure that items are placed correctly and to ensure the components are operating in the way the circuit was intended. This is accomplished by such aids as digital oscilloscope, digital multimeter, and functional generator. This equipment, when used in the proper manner, allows the user to test the specialized circuitry successfully and avoid critical mistakes that may occur during scientific research. This method is very important because the length of many experiments that scientists administer, using the technological aids provided, can last many days, months, etc. Therefore, if there is a faulty component, the experiment could be delayed.

This is just a sample of the research done. This illustrates what is needed to accomplish a project. The goal is to find the best and most productive technique to accomplish the job and complete it in the way that generates the least amount of difficulty and contributes the best results for the task. This enables the data gathered by this research to be used in future tasks and complete the work needed in a more expedient way.

RESULTS

The Task completed has given a great deal of knowledge in the field of Electrical Engineering. This information was acquired through dealing with the challenges that the Task provided and experimentally finding the most efficient way in which to overcome and successfully complete the projects assigned. This is important for being a future engineer because the ability to solve ambiguous problems is what engineering is all about. Mr. Perrin has allowed this ability to be gained by assigning various levels of tasks to be completed and allowing the skills to be developed and obtaining the problem solving skills necessary to complete the assignments. This provides the hands-on experience that is not possible to attain from a college laboratory or classroom setting.

LIQUID LIMITER MATERIALS

Task Order No. 255
Student Support Program
Southwestern Ohio Council for Higher Education

Lynn R. Frock
University of Dayton

27 December 1996

Government Task Leader
Dr. Gregg Anderson
WL/MLPJ

ACKNOWLEDGMENTS

I would like to thank Dr. Tom Cooper and L. Natarajan for their support and guidance. I would also like to thank SOCHE for allowing me the opportunity to learn and progress in my career field of chemistry.

TASK ASSIGNMENT GOALS

The Task goals are to develop the next generation of reverse saturable absorber (RSA) optical limiter materials and devices by developing the understanding and control of materials, mechanisms and processes. This includes, but is not limited to, the preparation and characterization of various guest/host materials for use in electro-optical applications. The primary focus of these scientific investigations is to demonstrate nonlinear absorption enhancement in energy transfer designed material, and to investigate high fluence effects in the materials to confirm characterization techniques.

RESEARCH

Background information was needed to begin the RSA project. An intense literature search for the critical parameters of selected materials was performed prior to laboratory investigation. The information was acquired through use of computer data banks such as Uncover. A library of research papers was developed and is still being reviewed for materials of usefulness concerning this project. An understanding of concepts and use of all available information is the backbone of the development of acceptable RSA molecules.

RSA organic dyes form the basis of advanced optical limiters. The drive of this project is toward understanding the principles required to achieve an engineering design capability for the RSA property. The current approach is to engineer a chromophore with specific ground state absorption properties and link it to a chromophore designed for its excited state properties in a way to control energy and charge transfer. The focus of the work is to make a photosensitive optical switch. Photosensitive optical switch work is a refinement of an existing research effort. This effort includes computational chemistry, synthetic chemistry, chemical and optical characterization and processing techniques' research.

The investigation and characterization of polypeptides covalently bound to photochromic molecules have been studied for use as model systems for coupling photo chemistry with conformational changes in the polypeptide backbone.[1] The study involves azo-modified and spiropyran modified polypeptides. Recently, we have reported on the substituent effects in spiropyran photochromism, namely the acceleration of α-helix to coil transformation in light adapted poly(L-spiropyran glutamates). Studies, thus far have shown that it is possible to accelerate the rate of backbone conformational changes by orders of magnitude through substitution in the spiropyran ring that may have some practical implications for making dynamic filters for lasers.[2]

RESULTS

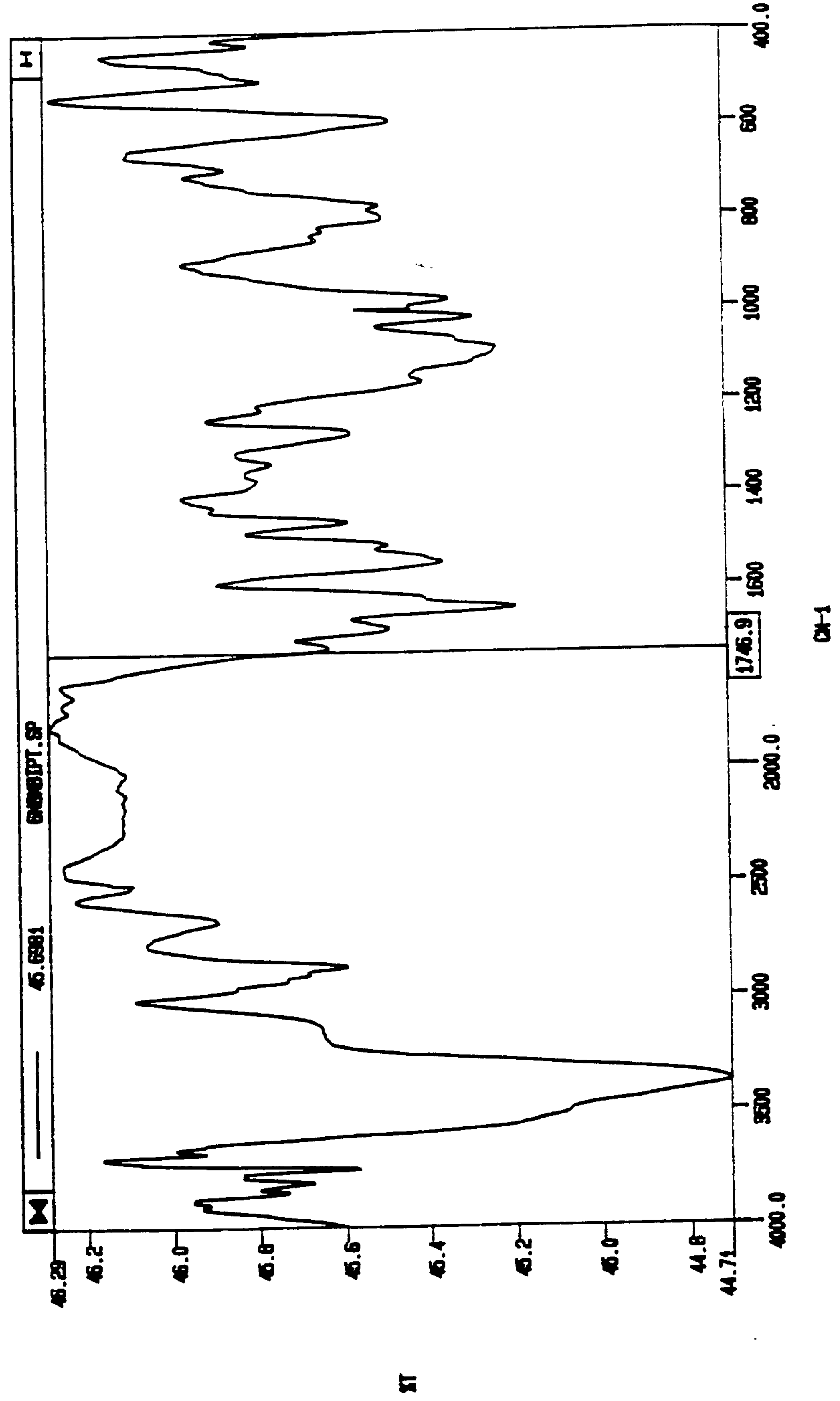
We studied the spiropyran-attached PGA's in DMF (N,N-Dimethylformamide). There were two types of dyes used in this study, 1 electron withdrawing and the other electron donating 6-Nitro-8-methoxy-1'-(2 hydroxy ethyl) Bips and 6-Bromo-8- methoxy-1'-(2 hydroxy ethyl) Bips respectively. The third dye used in this study was selected as a model compound for comparative study and that is 6,8-Dibromo-1'-hydroxyethyl Bips. The first two dyes were attached to PGA, utilizing DCCI coupling reaction. The model compound was attached to isobutyric acid via the same method. The DCCI coupling reaction is an esterification reaction. Prior to coupling FTIR scans were taken and again after the reaction was done.

Figure 1 shows evidence of successful attachment because of the ester band that is not present in the scan of the unattached dye and is indicative of attachment. The dye shown here is 6-nitro-8-methoxy-1'-(hydroxyethyl) Bips/PGA. Thin layer chromatography was also used to determine successful attachment and was in agreement with FTIR. Several purifications were done to remove the by-product of this reaction, DCU, and the product was monitored by TLC and FTIR to show reduced amounts of the by-product.

The model compound reaction product was difficult to recover. Due to the difficulty of separation of the alcohol-ester mixture, a column was prepared using hexane and ethyl acetate mixture. The ratio of solvent mixture was determined by using the concentric ring method for selecting solvent ratio for column separation. This was followed up with a series of TLC experiments to give an exact ratio of solvents. Rf. factors were calculated for both the ester and alcohol, the difference between each value was calculated and the percent ratio with the greatest difference in the Rf. factor was the one chosen for use in the column. The column, however did not give good separation, thus a silicon gel plate was used instead of using DMF as the developing solvent. This gave the best separation.

The dyes used in this study were synthesized at an out-source laboratory and have not been investigated for reverse photochromism properties. UV-vis spectra was taken to determine reverse photochromism of the following dyes, 6-nitro-8-methoxy-1'-(2-hydroxyethyl) Bips, 6-bromo-8-methoxy-1'-(2-hydroxyethyl) Bips, 6-phenyl Azo-8-methoxy-1'-hydroxy ethyl Bips, 6-methoxy-8-nitro-1'-hydroxyethyl Bips and 6,8-Dibromo-1'-hydroxyethyl Bips. These dyes were run using both DCM and HFIP as solvent in two separate trials. Both trials were done, using a 366-nm wavelength hand-held light source. Samples of known concentrations were prepared in the dark and exposed to equal amounts of a long wave length light source. Scans were taken of samples immediately following exposure. Data for 6-nitro-8-methoxy-1'-(2-hydroxyethyl) Bips initially gave no evidence of reverse photochromism, however when reduced concentrations of the same solution was tested, the data gave evidence of reverse photochromism. Figure 2 shows graphs of this dye with and without exposure of 366 nm wave length light source. An increase in the peak absorbance is indicative of reverse photochromism. Data for the other four dyes was analyzed and determined not to show evidence of reverse photochromism. Figure 3 is a graph of the reverse photochromism exhibited by the model compound and Figure 4 is an example of a dye that does not have this characteristic. Reverse photochromism for 6,8-Dibromo-1'-hydroxyethyl Bips has already been determined previously and will be used as the model compound for this ongoing study. DCCI coupling reaction has been determined to be the most useful synthesis procedure for this study.[3] Evaluation and conformation of the characteristics of the selected dyes mentioned above shows no need for DCCI coupling or evaluation for optical properties. Only the one showing reverse photochromism may be useful in RSA materials. Following synthesis and purification of selected dyes a kinetic study of reverse conformation changes was performed using Time Drive scans. The Time Drive scan monitors decay of the photochromic reaction. The dye alone and the attached dye both show the same decay rates. The next step in these experiments will be to run a circular dichroism test to decide if the decay rate is in conjunction with the rate at which the molecule goes from the alpha-Helix to the coil form. This will be calculated using the Hammett equation, which relates rates and equilibria for many reactions involving varying substituents in the pyran ring. It is known that varying the substituents in the pyran ring influence the rate of decolorization reactions and consequently the kinetics of helical conformational changes in the polypeptide backbone.[2] The ongoing study is an attempt to increase and control the rate of zwitterion ring closure in the side chain photochromophore and by doing so, shorten the life time of the α-helical conformation of the poly(l-glutamate) by orders of magnitude.

The photochromism study is ongoing and results of experiments are expected within the next quarter of this fiscal year.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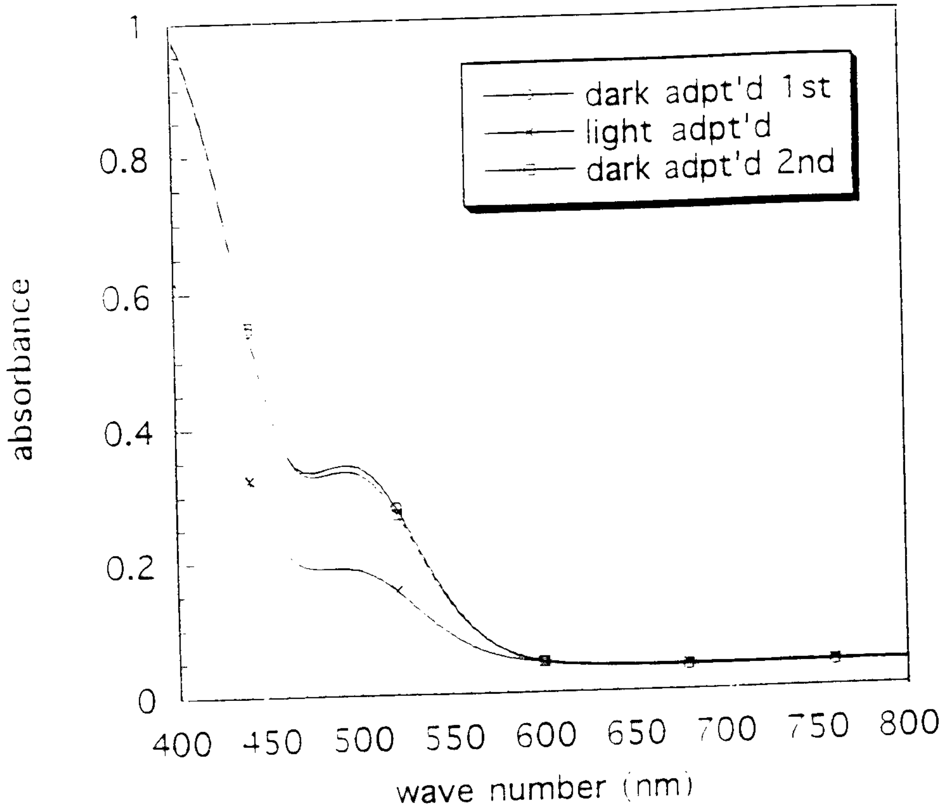
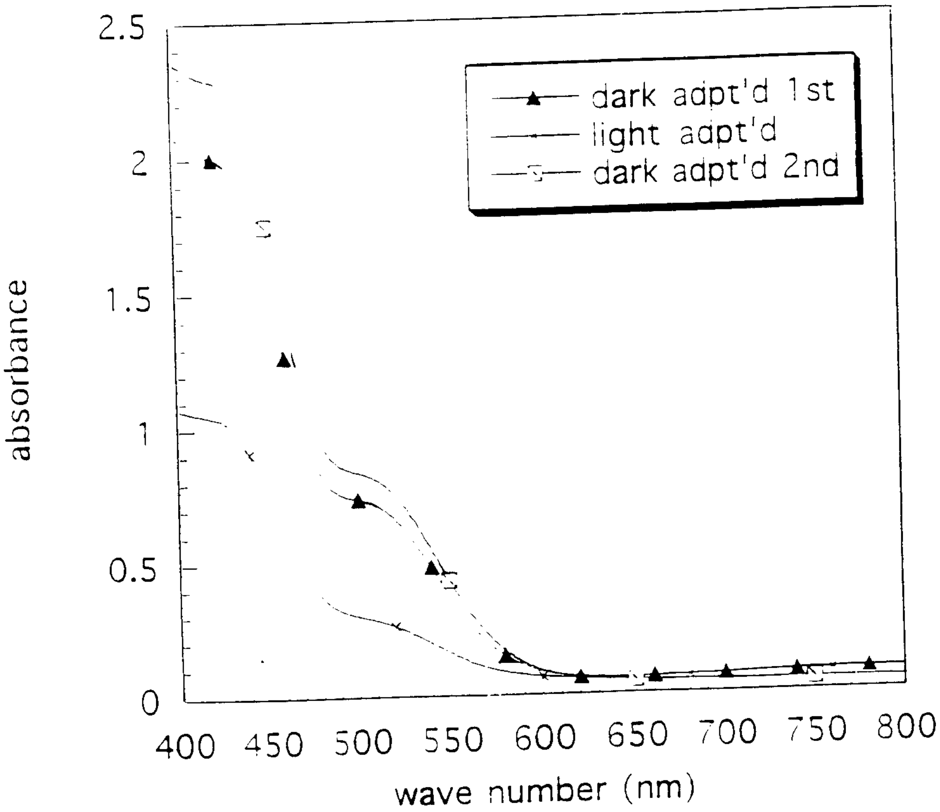
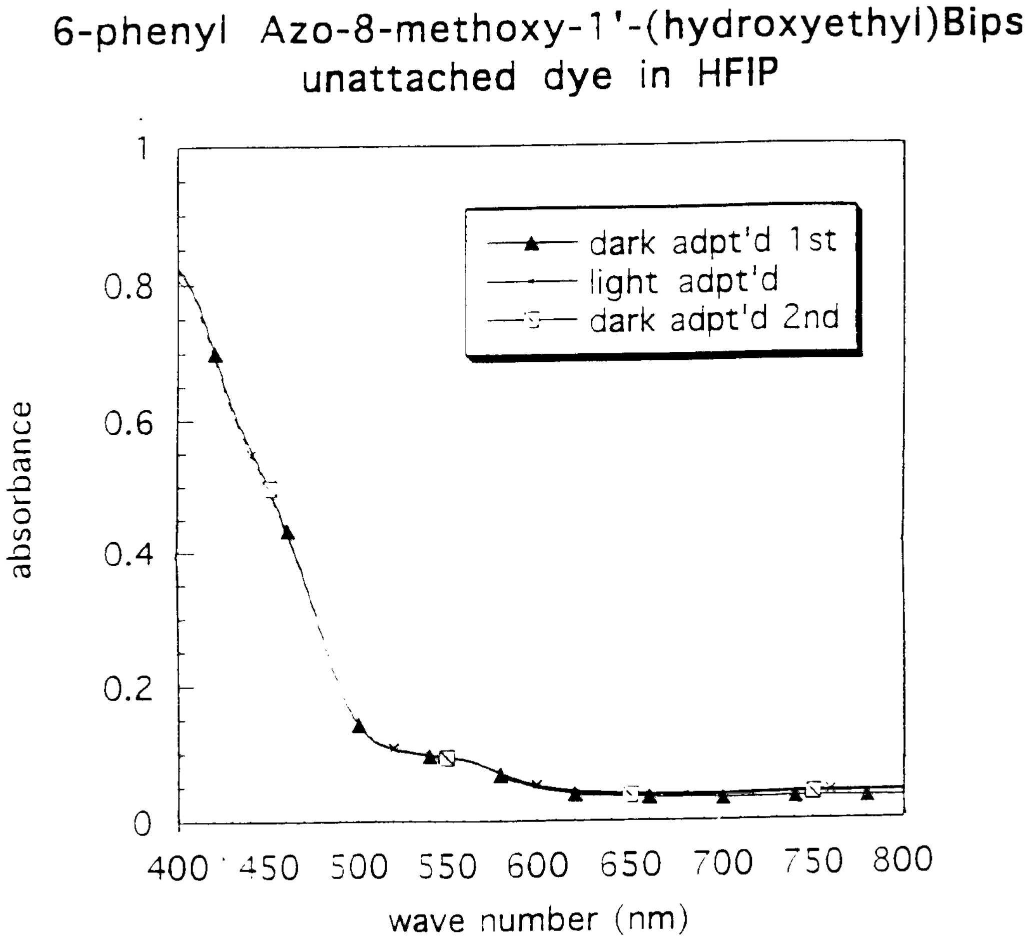


6-nitro-8-methoxy-1'-(2-hydroxyethyl)Bips
unattached dye in HFIP



6,8dibromo-1'-(hydroxyethyl) Bips
unattached dye in HFIP



6-phenyl Azo-8-methoxy-1'-(hydroxyethyl)Bips
unattached dye in HFIP

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LIQUID LIMITER MATERIALS

Task Order No. 255a
Student Support Program
Southwestern Ohio Council for Higher Education

Swetang D. Patel
University of Dayton

27 December 1996

Government Task Leader
Mr. Gregg T. Anderson
WL/MLPJ

ACKNOWLEDGMENTS

A special thanks to Dr. L. V. Natrajan, Dr. Tom Cooper and Mr. Gregg T. Anderson for their patience, guidance and knowledge of chemistry that made this Task a positive learning experience. I would also like to thank Mr. Vince Tondiglia who helped and educated me in laser laboratory experiments. Thanks to all MLPJ personnel including my technical director Mr. Dennis Hager who made this Task possible. Finally, I would like to thank all SOCHE employees who made life a little easier.

TASK ASSIGNMENT

The Task goals were to develop the thin-film processing of photo refractive materials and test the photo refractiveness by two-beam coupling experiment. Photo refractive (PR) polymers are an emerging, relatively new class of materials for photonic applications and are based on the phenomenon of photo refractivity that, by definition, is the modulation of index of refraction in an electro-optics material by internal electric fields caused by optical redistribution of charge carriers. There is tremendous potential for these materials in various electro-optics application such as optical signal processing, holographic and storage applications, to name just a few.

DESCRIPTION OF RESEARCH

The focus of this Task was to investigate and develop thin-film processing techniques of photo refractive (PR) materials and test the PR effectiveness by the interference of two-beam laser coupling experiment. In this laser experiment, a diffraction grating produced by the interference of two laser beams modulates the refractive index so that energy is transferred from the pump to the probe beam originally of equal intensity. The irradiation of any PR materials by coherent light modifies the special distribution of photo generated charge carriers and produces an electric field dependent of the refractive index. It is crucial that the processing techniques control film thickness (beam interaction volume) and uniformity insuring the production of quality diffraction grating that would help energy transfer from one beam to the other.

Molecular structure of each component in PR formulation is shown in Figure 1, where Poly(N-vinylcarbazole)(PVK), p-(N,N-dimethylamino)-w-nitrostyrene (DEANST), 9-ethylcarbazole (9EK), and 9-dicynomethylene-2,4,7-trinitrofluorene (DCMTNF), table 1, lists the principal components, their thermal properties, and the function of each component in the mixture.

Figure 1

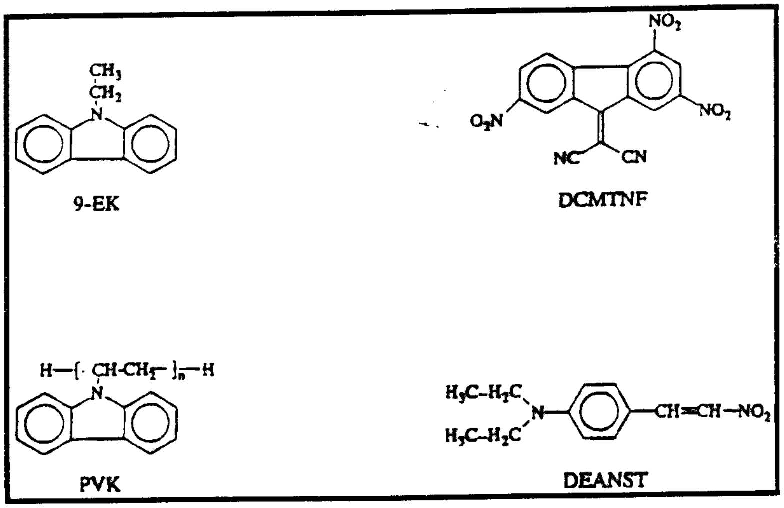

Table 1

Compound	Function	Thermal Transition
9-dicynomethylene-2,4,7-trinitrofluorene (DCMTNF)	Photosensitizer	m.p. =270°C
p-(N,N-dimethylamino)-ω-nitrostyrene (DEANST)	Electro-optics Chromophore	m.p. =98°C
9-ethylcarbazole (9EK)	Plastisizer	m.p. =72°C
Poly(N-vinylcarbazole) (PVK)	Photoconductive Polymer	Tg =212°C

Preparation of ITO Etch Pattern:

Indium Titanium Oxide, ITO etch away with 20% HF solution. The rectangular ITO etch was created by placing transparent tape on the coated side and then putting the slide in the oven at

50°C for an hour. Then the slide was immersed in HF solution for a few minutes, the tape was cut with a razor blade, then, the unwanted portion was pealed off.

Material Formulation:

Two sets of different formulations were made in two separate vials: one containing the polymer and the other contained the remaining ingredients. Excess chlorobenzene was added to both vials to dissolve and dilute the mixture. This allowed the material to pass through a 0.45 mm nylon micro filter without clogging the filter paper. The two solutions were filtered into a third vial that was rinsed with methanol. A large portion of the excess chlorobenzene was removed by blowing a stream of dry nitrogen gas over the vial for several days. The increased concentration of the mixture constituted the working stock viscosity. One small drop was put onto each ITO plate to sandwich them together, trying to avoid formation of an air bubble.

Second, formulation of C_{60} and FDEANST were used instead of DCMTNF and DEANST respectively. PVK, 9EK, FDEANST, and C_{60} were mixed and dissolved in 4:1 toluene: cyclohexanone, for everyone ml of solvents to 80 mg of solids. These ingredients were mixed by sonication for 20 minutes, placed on a hot plate at 110°C for 1 hour, then put in a vacuum oven at 70°C for 72 hours to drive off excess solvent. The spacer was placed on one ITO plate and dye was dropped on one side of the ITO plate. Both plates were placed on a hot plate at 90°C for 3 minutes, and then sandwiched together, trying to avoid the formation of an air bubble. The sample was brought to room temperature by placing it on an aluminum plate.

Melting point and glass transition temperature was determined by TA Instruments modulated DSC instruments, Model 2920. A heat/cool method with several cycles was used with 10°C/min. heating and cooling rates.

Two beam coupling experiment was performed using Dr. W. E. Moerner's sample. Because of a break down in the power supply, no results were achieved.

In addition, 2 months were spent on Polymer Disperse Liquid Crystal (PDLC) project.

RESULTS

Sample	PVK wt.%	9EK wt.%	C60 wt.%	FDEANST wt.%
PR#5	50.30	16.44	0.49	32.76
PR#6	50.00	16.50	0.50	33.00

Above formulations were made but samples were not analyzed due to power supply break down. Results are under investigation.

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BIOPOLYMERIC MATERIALS

Task Order No. 256
Student Support Program
Southwestern Ohio Council for Higher Education

Steven M. Cline
Wright State University

27 December 1996

Government Task Leader
Mr. Greg Anderson
WL/MLPJ

ACKNOWLEDGMENTS

A special thanks to my advisory chemist, Dr. Thomas Cooper, for the time, effort, and guidance he has provided in helping me mature as a scientist and person. He has allowed me to work independently on my Task that ultimately has instilled personal growth and an increase in self confidence. Thank you, Dr. Dave Zelman, for the education and mentorship provided in enhancing my knowledge of electro-optics. Thank you for teaching me confidence and a willingness to persevere in times of adversary. I would like to express sincere thanks and gratitude to SOCHE for giving me the opportunity to work and learn at WL/MLPJ at Wright - Patterson Air Force Base. The experience and insight I have gained have broadened my scientific interests and general skills.

TASK ASSIGNMENT

The Task initiated consists of the synthesis and characterization of nonlinear optics and laser hardening materials. The goal of the assignment is to use readily available biological and semi-organic materials and to incorporate their functional properties into electro-optical systems. Currently, the Task is directed toward the understanding and the manipulation of simple systems. The long-term goal of the Task is to incorporate simple materials into functional devices involved in properties such as: high resolution spectroscopy, remote sensing, data storage and communication, and laser radar protection.

DESCRIPTION OF RESEARCH

Due to the molecular arrangement and perfectly repetitive symmetry of atoms in crystalline compounds, crystals possess amazing photo-manipulative properties. Proteins and amino acids, individually and in complex with metals and organic dyes have been excellent second harmonic generating materials that include high beam transmission in the spectral region of interest, high nonlinearity, physical and chemical robustness, easy growth and processing, and reasonable cost. It is my research goal to find novel materials for high efficiency second Harmonic Generation with these selective characteristics.

Second Harmonic Generation (SHG) is the electro optical phenomenon of transforming the wavelength of light entering a transparent material to a wavelength of 1/2 of that which it entered. Therefore, a wave of Infra Red light entering an SHG material at 1064 nm, emerges at 532 nm. The efficiency of this process is very important in selection materials to be used for SHG devices. To decide the appropriate material for manufacturing, many parameters must be examined. These parameters include determining: a nonlinear coefficient (d), crystal semetry, an angular sensitivity coefficient (B), and spectral absorption regions. Unfortunately, only the crystal symmetry can be determined in materials of crystalline sizes less than 2 mm3. Thus, there is a great necessity for crystals that can be grown to sizes larger than 2 mm^3.

To produce crystals of high SHG efficiency, the molecular composition of the starting material to be crystallized must be carefully selected. According to Velsko, the probability of finding materials with SHG ability is greatly increased by examining materials with the combination of Organic and Inorganic characteristics (Material for Nonlinear Optics, 1991). Thus, the compounds considered in this research for high SHG efficiency consist largely of Semi-Organic materials. Many chiral, hyperpolarizable, Semi-Organic salts have been synthesized and crystallized into macromolecular sizes to decide Second Harmonic Generation in Semi-Organic materials.

Methods:

1.) Cadmium Glutamate crystals were synthesized by, first, heating 50 g's of Glutamic Acid (MW=147.1 g/mol) (0.34 mole) in 1 liter of Mili-Q water to 100 degrees C and gently stirred until solublized. The solution was pH adjusted to 7.0 by adding 6 M NaOH. A 1 liter solution of Cadmium Acetate [90.62 g's (0.34 mole)] was gently dripped into the Glutamic Acid solution over a period of 1 hour. The solution was removed from the heat and pH adjusted to 10.0 by adding 6M NaOH. As the pH was increased, a white precipitate began to form. The Cadmium Glutamate container was, then, covered with cheese cloth and left to evaporate at room temperature. Twenty-four hours later, the Cadmium Glutamate precipitate was removed from the solvent by suction filtration. The white crystals were rinsed with Mili-Q water, ethanol, and, then, ether. The rinsed precipitate was dried for 48 hours at 50° C in a drying oven.

The Cadmium Glutamate powder was, then, recrystallized by making a 15-mg/ml solution of Cadmium Glutamate in Mili-Q water. The solution was prepared by stirring the Cadmium Glutamate powder into the Mili-Q water and gently lowering the pH of the solution to 2.0 (6M HCl). Once the Cadmium Glutamate was completely solublized, the solution was pH adjusted to 5.88 and placed into 20 ml glass test tubes and allowed to evaporate in a dissector filled with drying stones. Two weeks later, the test tubes were removed from the dessicator containing transparent Cadmium Glutamate crystals.

2.) Copper Pthalocyanate was complexed with Bovine Globulin protein by, first, solublizing globin (purchased from Sigma) into Mili-Q water (3.1 uM). The pH of the globulin solution was 4.5. A 14.2 uM solution of Copper Pthalocyanate was pH adjusted to 2.5 before being dripped into the globin. The solution was gently stirred and stored at 4° C for 48 hrs. Upon removing the solution from the refrigerator, the solution was poured onto a 90x1.5 cm column filled with (G75) size exclusion gel, buffered with 25 mM sodium phosphate. Three peaks emerged from the column (0.5ml/min), the first was collected and saved as the Copper Pthalocyanate-Globulin complex product. The second and third peaks were non-complexed reactants.

RESULTS

1.) Cadmium Glutamate crystals were solved for structure at Miami University using CAD-4 instrumental software and SDP Structure Determination Package software to record: hkl values, intensity values, and angle measurements from the X-ray beam used to visualize the structure of the Cadmium Glutamate crystals. The X-ray crystallographic structure was solved from 1063 reflections at a 1.4% error. Cadmium Glutamate has a space group of p212121. These results are being reviewed for publication by the Acta Cryst Journal (1997).

2.) By solublizing Copper Pthalocyanate (CuPth) with the Globin protein, the solubility of Copper Pthalocyanate was increased dramatically. Without being complexed in a highly water soluble protein matrix, the porphyrin (CuPth) readily precipitated from solution even at very low concentrations.

SURFACE ANALYSIS AND THIN-FILM GROWTH

Task Order No. 257
Student Support Group
Southwestern Ohio Council for Higher Education

Dennis Walker, Jr.
Wright State University

27 December 1996

Government Task Leader
Dr. William Lampert
WL/MLBM

ACKNOWLEDGMENTS

I want to thank Dr. William Lampert for allowing me the opportunity to work with the Surfaces Group and for giving me guidance in my work at the lab. I want to thank Steve Fenstermaker for teaching me the essentials of vacuum work and surface analysis. I also want to thank Dr. John Grant for taking the time to explain some of the finer details of crystal structure and surface analysis techniques. I would like to thank Jimmy Hierholzer and Larry Grazulis for answering many questions I had in electronics and electricity and Don Thomas for answering some questions on computers. Finally, I want to thank Dr. Walt Haas, Robyn Anderson, Dr. Dave Tomich, Dr. Kurt Eyink, Jim Solomon, Scott Walck, Leanne Petry, and Rick Bach for helping me at various times of need throughout the quarter.

TASK ASSIGNMENT DESCRIPTION

There was much work completed this quarter in the Thin Films group at Wright-Patterson Air Force Base. Two major research efforts and various other tasks helped further the efficiency of the group. One major project begun this quarter is a thin-film deposition/examination project led by Dr. William Lampert. The other major project is the investigation into the effectiveness of different GaAs wafer cleaning methods led by Dr. Walt Haas.

The project led by Dr. Lampert has involved much work in both preparation and implementation. Thin films were deposited onto GaAs with 1/4 of the sample covered in a mask to form a set of contacts. Electrical characteristics of the films were studied using the contacts while the physical composition of the films was investigated using Auger depth profiling. The films will be heat treated and the effects of the annealing will be determined by the change in the electrical properties of the contacts and the change in physical composition as determined by depth profiling. These results will assist in engineering efficient contacts to GaAs wafers.

Much surface analysis was done in looking at various cleaning techniques and their effects on GaAs wafers. Among these was ion scattering spectroscopy (ISS), x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). This research will help determine the best technique to prepare samples for use in Molecular Beam Epitaxial growth chambers.

RESEARCH DESCRIPTION

In beginning the contact project, the deposition chamber had to be brought back into operation. This involved cleaning the system and getting the source materials in working order. Water lines had to be reconstructed and the chiller needed to be flushed and refilled after many years of use.

After preparing the chamber, 7 GaAs wafers were cut and prepared. For each sample, the system had to be cycled, the sample mounted, deposited on, and retrieved out of the system. This took an average of 2 days for each sample. Some problems were encountered and dealt with during the deposition. The manipulator/sample holder/heater assembly was taken out of the system and reworked to repair problems with the heater and thermocouple. The hearth was also removed often to repair a malfunctioning deflector assembly, an overheating contact, and the nickel source crucible destroyed during a deposition.

When this was complete, the samples were analyzed on the I-V analysis machine. The last time the machine was used the software and hardware were redesigned to allow only small voltages, totally unacceptable to the tests on the deposited samples. To correct this problem, the equipment was worked on often and the operating techniques were analyzed to obtain the best results possible with the equipment. After about a month, the technique was refined to the point that the results were satisfactory and reproducible. The probe tips on the machine were replaced and cleaned and the computer running the system was virtually replaced when a motherboard/CPU upgrade was started.

Also, in working on Dr. Lampert's project, another previously little-used piece of equipment was revived: the x-ray diffraction equipment. After getting the setup details worked out and doing an overall recalibration of the machine, the equipment is again in working order.

In working with Dr. Haas' project, an analysis system that had previously been mostly unused has come into the forefront of research efforts. Etched samples were placed in the system to be analyzed and often the equipment was cycled to atmosphere to be worked on. Reparation began with the ion gun that had never functioned properly owing partly to the manufacturer that refused to supply working schematics of the system. Details in the electronics and major faults in the gun itself were discovered and repaired. One of the most noticeable improvements to the ion gun was the addition of a missing setscrew to hold the filament in place.

After getting the ion gun to function properly, work shifted to the x-ray source. The safety cover was replaced on the source with a newer design to protect against any possible contact by users or bystanders with lethal high voltages. The chiller that supplied the source with cool water was worked on after a fault in the flowmeter was discovered and the x-ray source interlock would not close. Both anodes were cleaned to improve the amount of signal that could be produced. An aluminum window was removed from the source to allow low energy zirconium x-rays through and was replaced with a tungsten mesh to stop the electric field being produced which adversely affected the data. Both filaments were also replaced and aligned and the overall effect was a dramatic improvement in the amount of signal received.

Data collected from the study was imported into MS Excel. Manipulation of the data began, consisting of writing normalization equations and plotting the data in an informative way. All peaks of any significance were labeled and the results were submitted to Dr. John Grant for further analysis. In looking at manipulating the data, various software packages were reviewed in the attempt to find one especially suited to the needs of the lab. Igor and Microcalc Origin were two packages of special interest due to their possible ability to peak-fit Gaussian, Lorenz, and Voigt curves.

Another possibility in data analysis was to use a package specifically designed for use with XPS data analysis of which the lab had a copy. The difficulty in this plan was the problem with data importation. First, the data collected included a header different from that needed by the software package. Second, the data itself was in a different format with columns for the time and data. The software package needed only a header specifying the initial time, final time, and the amount of data taken followed by only the data. Using Microsoft C++, a short routine was written to allow easy transfer of the data into the software package by automatically replacing the times and the total data collected in the header with correct values and reformatting the data in a way that the software package could use. The result was easy analysis of XPS data with a package that could not only peak fit, but could also identify obvious peaks making XPS analysis much simpler. Unfortunately, the software cannot analyze ISS data resulting in the continued reviewing of the various software packages.

RESULTS

Overall, much work in the lab was completed this quarter. Many systems were improved upon and streamlined in an attempt to get data as quickly and efficiently as possible. Among the things studied this quarter were general ultrahigh vacuum techniques including cycling vacuum systems, adjusting equipment on the chambers, and leak-checking. This led up to the use of the deposition chamber and analysis equipment. The methods for analyzing data included x-ray photoelectron spectroscopy, Auger electron spectroscopy, and ion scattering spectroscopy.

The investigation into the various films deposited this quarter led to the finding that the equipment in the lab could be made to perform at satisfactory levels when compared with other equipment. The overall projects were not completed this quarter, but major stages were finished leading into the continuation of these projects in the upcoming year.

NONDESTRUCTIVE CHARACTERIZATION OF CORROSION

Task Order No. 258
Student Support Program
Southwestern Ohio Council for Higher Education

Edward J. Schumaker
Wright State University

27 December 1996

Government Task Leader
Dr. Robert Crane
WL/MLLP

ACKNOWLEDGMENTS

Thanks to Mark Blodgett who was consulted concerning the development of the acoustic scanner with five computer controlled axes of motion.

In the analysis of the corrosion samples and preparing corrosion test specifications, thanks goes to William Mullins who provided consultation.

Finally, thanks to Greg Tyler for his aide and help in working on both projects.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

One project is to design a computer program, which controls five motors, retrieves and analyzes data from an oscilloscope from each point, and saves the original waveform and the analysis results. Each data point has more than one waveform associated with it because it is scanned from different perspectives. The accompanying Figure illustrates that the sample is scanned at normal incidence then repeatedly scanned after rotating the transducer by the polar and azimuth angles. The polar angle is directly inputted and the azimuth angle is calculated based on user input. The purpose of this acoustic scanner system is to characterize the microstructure of the material.

The other project is to quantify the amount of corrosion on Al 2024 samples from an accelerated corrosion test (modified ASTM G34) and analyze corroded samples from Purdue University. The test samples will be corroded for varying lengths of time. The fractal dimensions of the samples increase with longer exposures to the corrosion bath. The goal is to decide if the lateral and depth fractal dimensions have a strong correlation. This may then be incorporated into a field test in which the approximate corrosion-caused material loss is known by measuring only the lateral fractal dimension. The Purdue samples are from the ASTM G44 test and were then cycled to failure. The purpose is to calculate the fractal dimensions of the top and bottom lateral surfaces using acoustic and optical data.

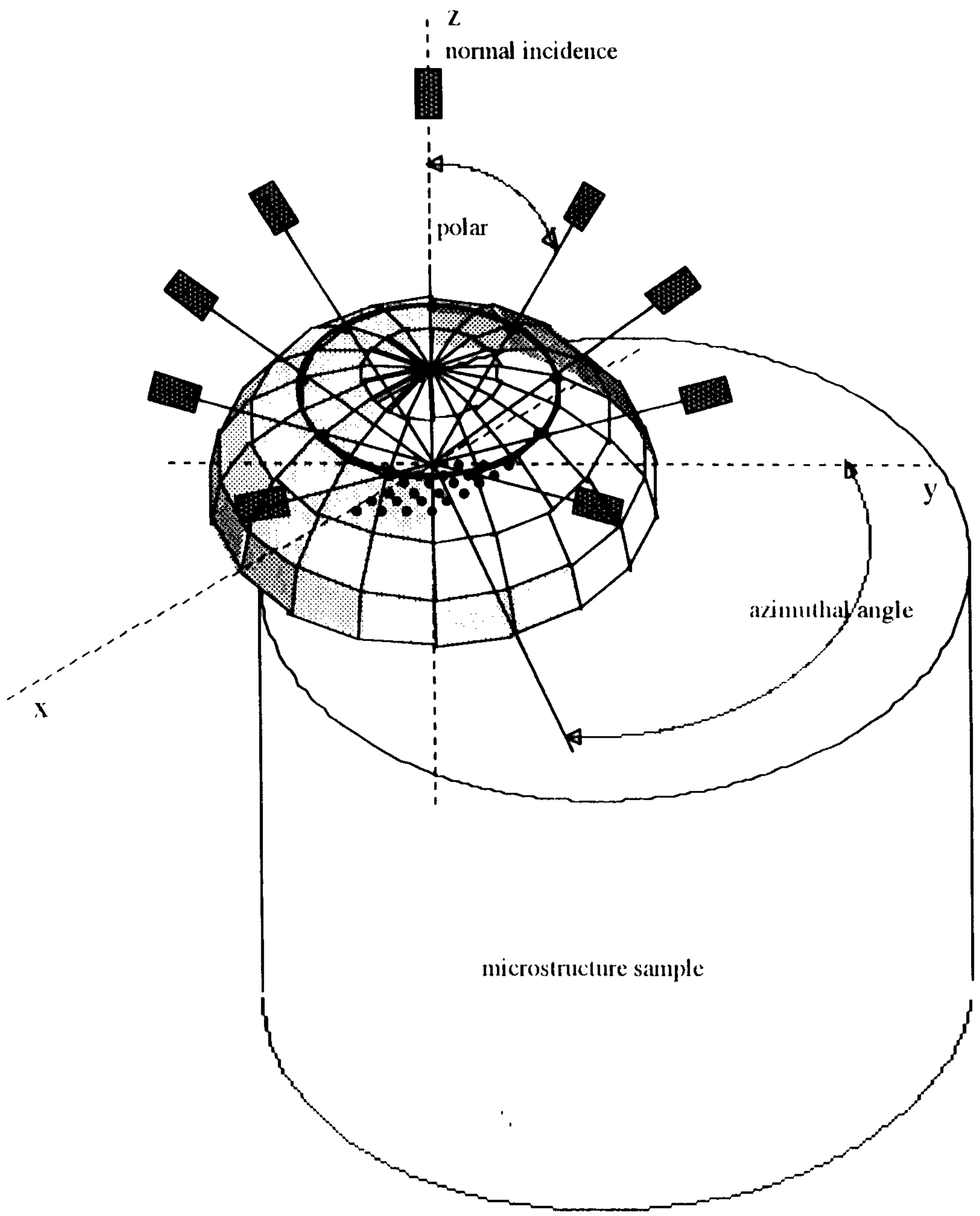
The NDE branch (Nondestructive Evaluation) is primarily concerned with evaluating materials used in the aircraft industry and others. The understanding of the microstructure of materials may lead to methods of finding microscopic flaws that would then cause the material to fail while in operation. The goal is to detect these flaws before accidents occur. The characterization of corrosion project is useful in determining the extent of corrosive damage on airplanes. This may then be used to determine the useful remaining lifetime expectancy of the airplane.

DESCRIPTION OF RESEARCH

The computer program will be used in the ultrasonic acoustic characterization of the microstructure of materials. It aids in controlling the motors for the five axes of rotation and saving the data in a consistent file structure. In the early stages, the program was written in QBASIC using a Velmex 86MM Stepping Motor Controller/Driver (two motors). The need for more motor controls required ordering two NF90 Stepping Motor Controllers (three motors / controller). The program was translated into LabView for several reasons, such as, easier control of the motors and better debugging techniques.

The Purdue samples were scanned using the HIPSAM (high precision sampling acoustic microscope) operating system and using an HP Scanner. The acoustic data was collected by using a front surface time of flight gate that measures the water path between the transducer tip and the surface of the sample. The specifications for the accelerated corrosion test (modification of the ASTM G34 test) were established.

Polar Backscatter Data Collection



RESULTS

The computer program allows the user to enter the size of the sample, the distance between points, the scanning radius, distance from bend joint to the sample chosen to return the transducer to its original position, the file path to store the data, the polar angle, and the number of arcs. The number of arcs is used to determine the azimuth angle. The program then uses the inputs to calculate how to move each motor and to number the files. The file format is ####_###.*. The first two sets of numbers correspond to the row and column of the data point. The next two corresponds to the arc number while the last one is the point on the arc. The * equals dat, rec, bck, or fft depending on the analysis of the signal. For example, 0103_122.dat is the original waveform corresponding to the second point on the twelfth arc from row one, column three. The number of steps for each move statement has to be rechecked because of the latest revisions.

The twenty-four data files from the Purdue samples have been collected and can be analyzed using a program in PVWAVE. The program performs a two-dimensional FFT on plots the real portion of the result. The fractal dimension can then be calculated from the slope of this plot. The program has to be modified to calculate the slope or the graph can be printed and the calculation done graphically. The current test specifications are included in the following pages.

MODIFICATION OF THE G34 TEST

NOTE: results reflect field tests more accurately

TEST SOLUTION: NOTE: reagent grade necessary

235 g/L NaCl
60.6 g/L KNO_3
5.40 g/L $AlCl_3 \cdot 6\, H_2O$

SAMPLE INFORMATION

≈ 30 Al 2024
Size 2" x 3"
Preparation
    wipe with solvent to eliminate grease
    clean with NaOH solution somewhat concentrated
    nitric acid
    rinse with di water then dry
    let stand for a couple weeks (builds oxide layer)
    tape edges carefully

TEST SPECIFICATIONS:

DURATION: $\approx$1 TO 8 DAYS??? 9 hr. sample
pH ADJUSTED TO 3.2 USING 0.01*M* HCl OR 0.01*M* NaOH
CLOSED CONTAINER OR LOOSE-FITTING COVER
SAMPLES MUST BE ABOVE THE BOTTOM OF THE CONTAINER
MILDLY STIRRED TO REMOVE CORROSIVE PRODUCTS
LOCATION: "SALT SPRAY LAB" BUILDING 652, Room 20
VOLUME:SURFACE AREA --------60 sq. into 184 sq. in

MORE DETAILS NEEDED:

disposal of used solutions--------their lab
    ordering sufficient quantity of reagents through UDRI

MATERIALS NECESSARY:

- SUFFICIENT QUANTITY OF REAGENTS (acid spill kit available from Bldg. 652)
- SUITABLE CONTAINER--
    - Glass container available (Bldg. 652)
- HEATING DEVICE
    - Magnetic hot plate available (Bldg. 652)
- METHOD OF STIRRING
    - magnetic stirrers on low speed to prevent agitation of the solution
- SUITABLE DEVICE/SETUP TO ENSURE SAMPLES ABOVE BOTTOM OF CONTAINER
    - Modified two household heat/air-conditioning registers
- SAFETY EQUIPMENT
    - PROTECTIVE EYE WARE - available(655)
    - GLOVES

ITEMS TO OBTAIN

Cover for container (plexiglass sheet)
Thermometer
Reagents
Gloves
Tongs remove samples and drop in distilled water
Beaker or other container for distilled water
Magnetic stir bars

NOTE: Let KEN CHIPWOOD know ahead of time before beginning b/c he has to service the corrosion tanks first. (every 10 days)

POLYMER BLENDS

Task Order No. 259
Student Support Program
Southwestern Ohio Council for Higher Education

Pamela Bonds
Wright State University

27 December 1996

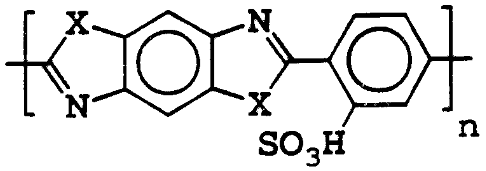
Government Task Leader
Dr. Fred Arnold
WL/MLBP

ACKNOWLEDGMENTS

I would like to thank Dr. Fred Arnold and Thuy Dang for their guidance and help during this Task.

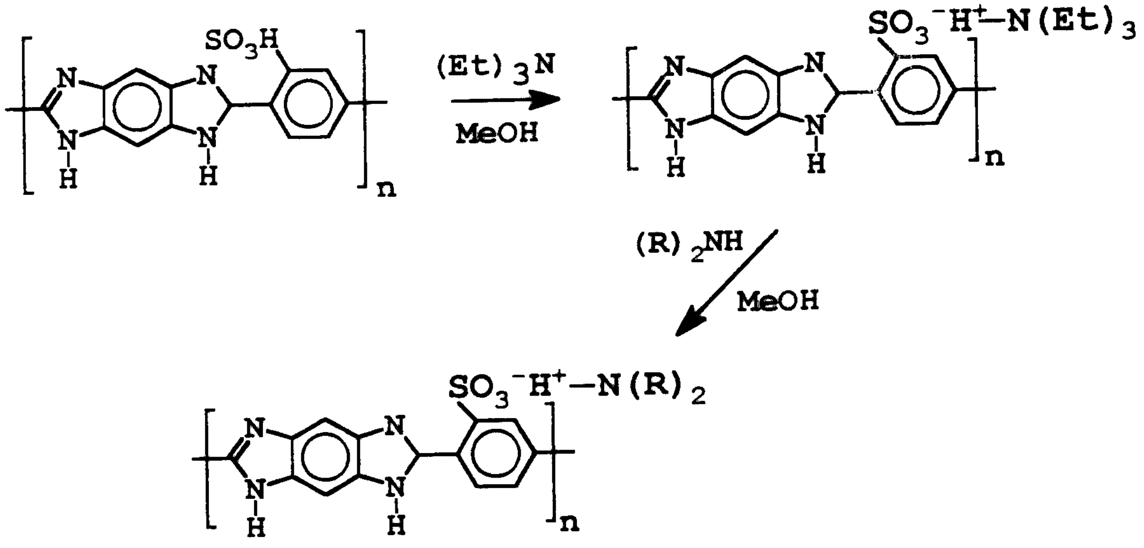
GENERAL DESCRIPTION OF TASK ASSIGNMENT

The Task investigated the synthesis and characteristics of new polymer blends. The Task began with the synthesis of thermoplastics. In this Task, two rigid rod polymer systems of the PBX series with sulfonic functional groups were used. The polymers had the following structure:

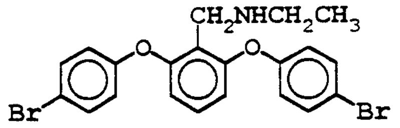
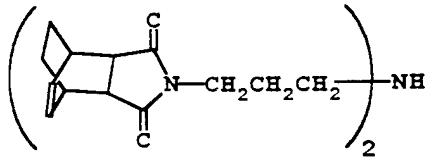
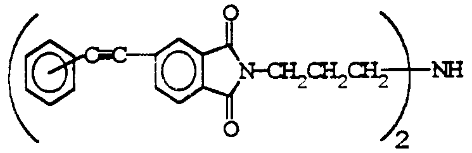
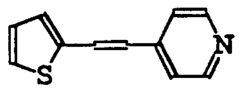
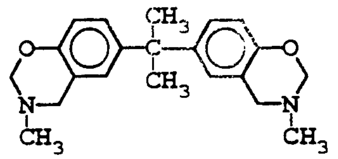


x = NH OR S

The rigid rod thermoplastics were then combined with thermoset table amines through the ionic interchange process according to the reaction scheme below:



Films were cast from methanol and observed for monodispersed systems. The results are tabulated in the table below:

Amide Thermoset	Mole Ratio	Wt Ratio TS/TP	Color	Homogeneous
	1:1	60/40	yellow-orange	no
	1:3	82/18	orange	yes
	1:1	58/42	orange	yes
	1:3	80/20	orange	yes
	1:1	65/35	orange-red	no
	1:3	85/15	orange-red	no
	1:1	37/63	yellow-orange	no
	1:1	52/48	orange	no

The objective was the development of new polymer blends with characteristics of the thermosets and the reinforcement of the thermoplastic that could be cast into homogeneous films that could be further studied after being heat cured. Additionally, other personnel of the polymer branch investigated the thermal and mechanical properties of the molecular composites and the potential application of the new materials for Air Force applications.

DESCRIPTION OF RESEARCH

The polybenzazoles were synthesized to contain sulfonic acid groups for the formation of organic ammonium salts. The thermosets used had to fit two criteria. First, they had to be soluble in methanol or an aprotic solvent. Second, they had to have some type of amine functionality for ionic interchange. The molecular composites were made via an ionic interchange and solvent casting process. A good molecular composite was indicated by a homogeneous optically clear film with thermal stability. Several films were cast of varying mole ratios in an attempt to generate homogeneous films that could be further studied after being heat cured.

The analysis of materials was conducted by infrared, ultraviolet and visible spectroscopy, melting point, nuclear magnetic resonance, mass spectrometry, and elemental analysis. Specific equipment used included the Bruker FTIR, PE Lambda 9 UV/VIS and Hitachi NMR.

RESULTS

Organic ammonium salts of the sulfo pendant benzazole polymer systems were found to exhibit excellent solubility in methanol. The thermosets containing amine functionality provided the required solubility in methanol leading to some clear homogeneous films.

PROCESSING OF ADVANCED AEROSPACE MATERIALS

Task Order No. 260
Student Support Program
Southwestern Ohio Council for Higher Education

Eric B. Shell
University of Dayton

27 December 1996

Government Task Leader
Dr. Lee Semiatin
WL/MLLM

ACKNOWLEDGMENTS

I would first like to thank both Dr. Tom Broderick and Dr. Lee Semiatin for their assistance and patience. The time I spent discussing the theories behind metallurgy was invaluable.

TASK ASSIGNMENT

The contract with Wright-Patterson Air Force Base has been a great learning experience. Approaching the job with a chemical engineering background, the job offered a chance to learn new ideas to work effectively in the mechanical engineering and metallurgical environment.

After arrival at the Base, first on the agenda was to learn in a broad sense about the skills necessary to acquire, and the concepts with which to become familiar. Four books written about the study of metal processing and the effects of processes on the mechanical properties of the material were read along with several pertinent published essays. After several days of reading, relevant issues such as dislocations, stress-strain diagrams, phase diagrams, and how certain key phases that are present in the metallic grain matrix affect the strength of the overall material, became more clear.

After forming a knowledge base in metallurgy, the history of the project was discussed. This included learning how all pertinent information and data were organized and the procedures used to run various experiments. An overview of why the project was initiated, where the project was in its overall completion, and what the particular role of the contract was in finishing the project was given.

To complete the project, a variety of skills had to first be obtained. The first skill learned was surface polishing. This had to be learned to view samples in the scanning electron microscope (SEM). Polishing involves using increasingly finer sanding papers and diamond pastes to remove successive layers of scratches on the surface of the metal. This continues until there are practically no visible scratches. This task is difficult to learn for two reasons. When polishing is done by hand, the surface of the specimen can easily become curved, by putting too much pressure on just one part of the sample. If this occurs, the surface will not become fully polished and scratches will remain visible. The second difficulty in polishing a specimen is even after no scratches are visible to the naked eye (or even under a light microscope), there still may be scratches present when viewing the specimen in the SEM. This means that the polishing must be accomplished by an intuitive sense of the quality of the surface. The only way to learn this is by trial and error. When this polishing is completed correctly, the specimen has a mirror finish with no scratches even at magnifications upwards of 20,000 times.

After learning how to polish the samples, training in how to view them in the SEM was started. This involved taking a three-hour training session and later working with Luann Piazza, who runs the SEM's, to learn more about the daily operation of the microscope. Being able to learn how to use a SEM as a student is a rare experience. Most companies that own SEM's, only one or two people are trained to operate the SEM. However, with the high volume of research done at WPAFB, individuals are trained how to operate one of the most advanced microscopes available. The use of the SEM enables a direct look at the microstructure, the metal from five to 500,000 times magnification. The particular needs of this project entailed looking at the grain size and grain patterns, the volume fraction of certain phases, and the chemical makeup of the different phases.

Digital photographs were taken on the SEM that served several purposes. First, the photographs served for recording what was found while using the microscope. If regions in the grain structure suggested abnormal conditions, photographs were used to remember this. Second, the photos served as a documentation of the history of the specimen. By looking at the grain structure, details of the previous heat treatments and mechanical working can be inferred. For example, when stress-strain data for the compression of test cylinders was different from the expected results, the SEM photographs were examined. From the volume fractions of the phases that were present, it was determined that the temperature of the compression test was done at well below the reported temperature. This resulted in greater stress at a given strain and strain rate. Armed with this new information, the validity of each new test may either be verified or questioned after SEM analysis. The third way in which the pictures were used was to decide the limiting values of certain material characteristics. The effect of strain was studied in the tensile tests to decide the maximum allowable cavity or void fraction. As a material begins to have a greater cavity fraction during a tensile test, the effect of strain on the sample becomes increasingly apparent. To determine the effect, a plot of cavity fraction versus strain is obtained by computer analysis of the photographs. At a certain cavity fraction, the metal begins to stretch easily and quickly break. This fraction is the critical cavity fraction. Metals with fractions above this value will not have the tensile strength to withstand the loads that are being tested.

The overall experience of working at Wright-Patterson was a great opportunity to work in one of the largest research facilities in the world. The resources of such a large complex offer great power for research capabilities and production.

CERAMIC FIBER CREEP STUDIES

Task Order No. 261
Student Support Program
Southwestern Ohio Council for Higher Education

Christopher Kelley
Wright State University

27 December 1996

Government Task Leader
Dr. Randall S. Hay
WL/WLLM

ACKNOWLEDGMENTS

My thanks goes to Dr. Jero for giving me the opportunity to work with him at Wright Laboratory. Thanks also to Kristy Keller and Charlie Cooke for their guidance in the chemical labs, and to Rollie Dutton for helping answer some of my questions.

GENERAL DESCRIPTION OF TASK ASSIGNMENTS

1) Preparation of fibers for a radial thermal expansion test, and the reduction of the preliminary test data.

2) Preparation of ceramic matrix composite (CMC) samples for push-out and push-in testing.

3) Other tasks include; the retrieval of documents related to current research pursuits, helping other researchers with polishing of CMC samples, and studying literature pertinent to the current Task.

DESCRIPTION OF RESEARCH

The preparation process of the fibers for the radial thermal expansion test consisted of:

- Cutting 1/2 inch strips of tape with fibers
- Removal of 1/2 inch fibers from tape
- Cleaning sizing from fiber surface
- Arranging fibers in a layered and stacked orientation in graphite test fixture

The arranging was accomplished by placing each fiber in the test fixture individually until the current layer was full, rotating the test fixture 90°, and completing the next row. This process was repeated until the test fixture was full with approximately 127 layers of 30 fibers, or 3810 fibers.

The fixture was then placed in a Dilatometer. An inert gas displaced the room atmosphere in the Dilatometer's heating chamber, while the fixture was heated to 1500°C and cooled to room temperature in steps of 2°C/min over a period of 24 hours. During this period, the displacement of the top of the test fixture was recorded by a strip chart recorder. The information on the strip chart was reduced in Mathcad and a preliminary plot was created of the thermal expansion of the fibers versus temperature.

Polishing of CMC was done in preparation for push-out and push-in tests. This process consisted of:

> -Rough cutting the samples using a diamond cut-off saw, to an approximate thickness of 0.4 millimeters.
>
> -Grinding the samples using diamond disks to an approximate thickness of 0.33 millimeters.
>
> -polishing the samples through various stages, using diamond suspensions on silk, to a final thickness of approximately 0.3 millimeters.

RESULTS

As of the writing of this report, I have only worked part-time for about 6 weeks and have not done any significant testing. When more data have been collected, a better assessment of the results can be made.

CREPT YAE CHARACTERIZATION

Task Order No. 262
Student Support Program
Southwestern Ohio Council for Higher Education

Aaron Minch
Wright State University

27 December 1996

Government Task Leader
Dr. Randy Hay
WL/MLLN

ACKNOWLEDGMENTS

Several people deserve to be thanked. Thanks to Larry Matson, my Government Task Leader, who spent time explaining the Task. Also thanks to John Welch, who spent a lot of time showing me how to do the polishing correctly and how to interpret when to change polishing grades. He also showed me how to detect when the sample was nearing completion using the light in the room and the microscope. His task paper must be credited because it was used as a reference when tripod polishing. The job could not have been done without him. Finally, Scott Apt, gave me a lot of help in the laboratory.

TASK ASSIGNMENT

Most ceramics are brittle and do not sustain a very large impact or tensile load. This task involved getting specimens ready for the Scanning Electron Microscope (SEM) and the Transmission Electron Microscope (TEM), to investigate the micro structure of ceramic fibers and to see how to get the micro structure with the best properties regarding strength and ductility.

The work done will determine whether these properties can be obtained with ceramic fibers. If these properties are obtained, then these ceramics may replace metals in many applications because they would have the good ductility and strength of metals, but with the high temperature resistance of ceramics.

The problem is using only 1/8 inch of fiber in which to prepare a sample. This small amount is used because not much fiber can be "scrapped" for sample preparation since different parts of the fiber may have different micro structures especially if a heat treatment or creep test has been done.

The method of preparation begins by putting a very little bit of "G-1" epoxy on a piece of Teflon. The fiber of interest is placed in the epoxy to keep the fibers from moving or getting "pulled out" when polishing. Then two "junk" fibers are put on either side of the fiber of interest to protect it from debris and erosion when the sample becomes very thin, which would happen for TEM samples. This assembly is put into a curing oven or on a hot plate to allow the epoxy to harden or cure. When the sample is finished hardening, more epoxy is put on the sample to protect the fibers when mounting the sample in Epomet, a hard mounting material.

When preparing for the SEM, the desired view is a transverse cross-section, which means the width of the fiber is being viewed. The cured specimen is ground on sandpaper to find the orientation of the fiber ends. The sample is placed in a clip on the ram of the mounting press so that the fiber ends are pointing straight up.

Once the specimen is mounted, it is taken out and polished on an 8-inch brass wheel with a piece of silk on it. Diamonds suspended in oil in 45, 15, 9, 3, and 1 micron sizes are put on different pieces of silk. The sample is finished when the cross-section of the fiber has scratches that are not observable with a light microscope and the edges of the fibers are not chipped. The specimen is cleaned with acetone, 2-Propanol and put in a vacuum oven to keep it clean until carbon coating. The carbon coating is done for conduction of electrons to the sample because it is necessity for a beam of electrons to hit the sample to view the fiber's micro structure on a SEM.

The TEM procedure is quite different since the desired view is longitudinal or lengthwise. Once the specimen has cured, it is ground with silicon carbide paper so the specimen can be put in a clip ring, which makes the specimen the size of the glass slide on the tripod polisher. The specimen and the ring are put on the ram of the mounting press and Epomet of various ground is put on the specimen as follows: first sifted, to get good coverage around the specimen due to the lack of chunks, then fine ground, then the standard Epomet. Once the mounting is complete, the specimen is cut until the ring is reached and the small ring-sized sample is taken out. This is mounted on the tripod polisher, which is a piece of metal with three micrometers for legs and a place parallel to the legs for putting the sample. The tripod polisher can be adjusted to get a desired plane of polish by using a large glass slide to get the two rear feet and the specimen in the same plane.

The sample rests on a glass slide on the stub. The stub is set on a hot plate and epoxy is placed on it and heated until the epoxy becomes fluid-like, then a glass slide is put on the epoxy. More epoxy is put on the glass slide and when it becomes fluid-like, the sample is put on the glass slide. The large glass slide is used to make the rear feet level with the lowest part of the sample, which acts as the third leg once the third micrometer is raised.

Once the sample is polished on 30, 15, 6, 3, 1, 1/2, and 1/10 micron diamond embedded disks and nearly no scratches or bits of diamond are observed, the sample is heated on a hot plate to make the crystal bond fluid. The sample is removed and turned over. The objective when polishing the first side is to be at the middle of the fiber when finished so the maximum area of the fiber can be seen.

The specimen is turned over and a similar, but not the same procedure is done. The 30 and 15-micron disks are used to get to the fiber. Then the 6-micron disk is used until the side being polished is getting close to the side that is already polished and the epoxy becomes nearly transparent. This can be checked by looking at the sample on the microscope and focusing on the specimen so that the scratches can be seen. The light is turned down so that the outline of the fibers on the other side of the specimen can be seen. The sample must be checked often because it is becoming very thin at this point. The 6-micron disk is removed. The 3-micron disk is put on and used until the epoxy becomes transparent and the opposite side nearly matches the side that is being polished. The 3-micron disk is taken off and the 1-micron disk is used. Once a small amount of the surrounding epoxy is eroded away, the sample can be polished on the 1/2-micron disk. The sample is polished on the 1/2-micron disk until more of the epoxy is eaten away. If the sample is fairly diamond-free when examined under the microscope, then the sample is finished, otherwise the sample is polished with the 1/10-micron disk until the greater part of the diamond is removed. The 1/10-micron seems to give the fibers a brilliance that the 1/2-micron polish lacks.

The stub may now be removed from the tripod polisher and put on the hot plate. The sample needs close attention and should be removed when possible, or it will warp or crinkle. A small plastic bag labeled with the given fiber name and description may be needed for storage. A grid is put on the sample so it can be removed from the glass slide and put into the ion mill, which uses ionized molecules to make the sample even thinner. Finally, the sample is carbon coated and placed in the TEM.

Another method in process for TEM preparation, under the direction of Robert Wheeler of UES, is to put the desired fiber on the end of a cotton swab to observe the fiber's surface with a microscope. Once imperfections are found, the orientation is marked on the swab so that the fiber can be put in the same position again and set in place with epoxy. The fiber is placed between two sapphire slides, which are similar in hardness to the fibers. Epoxy is put on the fiber and sandwiched between the slides. The part of the fiber with the imperfections is broken off when the epoxy cures. This assembly is placed under a Dimpler, which grinds the sample with a small metal wheel until a certain distance is reached. The same is done to the second side. The sample is then placed in the ion mill. The sample is carbon coated when it is thorough ion milling and placed in the TEM for observation. This is the procedure as I can best describe it. I have only begun to learn it for less than 2 days and I have not gone through the whole procedure on a sample yet.

A valuable lesson was learning that polishing does not remove all scratches, but exchanges larger scratches for smaller scratches. Therefore, if polishing is necessary, one grade of polishing is not enough. Start with a larger grain size and then work downward to smaller grain sizes. Another lesson is that once a method becomes comfortable, another method of preparation comes up.

ENVIRONMENTAL DEGADATION OF CMC'S

Task Order No. 263
Student Support Program
Southwestern Ohio Council for Higher Education

Cohen King
Wright State University

27 December 1996

Government Task Leader
Dr. Randy Hay
WL/MLLN

ACKNOWLEDGMENTS

Special thanks goes to Dr. T. A. Parthasarathy for allowing me to work with him in the Student Support Program at Wright Laboratory Materials Directorate at Wright-Patterson Air Force Base. Also, thanks goes to Charles Cooke of UES (Universal Energy Systems) for providing assistance and showing the operation of the hot press vacuum induction furnace.

TASK ASSIGNMENT

The following detailed description of the hot pressing procedure took place over the last task period. A hot press vacuum induction furnace was used to sinter a YAG (yttrium aluminum garnet) pellet within an alumina (Al_2O_3) powder surrounding. The purpose of the assignment was to do the hot pressing of the materials and to study the grain structure and sizes of the particular materials. The hot pressing was done under a variety of conditions. The conditions involved heating in different gases, at different temperatures, and under different pressures.

Initially, the YAG pellet had to be prepared by using a 3/8 in. (inner diameter) cold pressed die. One plunger is inserted into the bottom of the die and then the die is placed onto a manual press. Next, a small amount of the YAG eutectic powder was placed into the die and some acetone was squirted into the die as well. Then, the other plunger was placed into the die on top of the powder and the plungers pressed by the manual press until the pellet was made. To remove the pellet from the die, another half cylinder die was placed at the bottom of the original die. The second half cylinder die must have a larger inner diameter, otherwise, the pellet cannot be pressed out. Then the top plunger was pressed forcing the bottom plunger and the YAG pellet out of the bottom of the die.

Before the hot pressing could be done, the graphite die had to be loaded. In doing this, a 1 inch (inner diameter) round die was set up by placing a rolled piece of graphfoil inside the die and inserting a plunger on one end of the die. Next, about three one-inch diameter pieces of graphfoil were placed on the plunger. Once this was done, about seven or 8 grams of the alumina powder were poured into the die on top of the pieces of graphfoil. Then the YAG pellet was placed in the center of the alumina powder and another seven or 8 grams of alumina powder was poured into the die and the whole thing packed down. Next, three more 1-inch diameter pieces of graphfoil were placed on top of the alumina and the top plunger inserted. Once the die was loaded, it was then wrapped in insulation and placed in the hot press chamber. Then the ram was placed in the chamber and positioned above the top plunger and lowered until snug against the top plunger. Additional insulation was placed on top of the die and a site tube inserted into a previously drilled hole in the top of the die. The site tube was used to detect the temperature of the die during the hot press procedure. Following this, the door to the hot press chamber was closed and the chamber allowed to pump down for about an hour. Once the chamber was pumped down to almost a vacuum, the testing procedure was begun.

The testing procedure began when the generator control panel was activated and the power turned up. As the power was increased, the temperature of the die increased until the desired temperature was achieved. Once the die arrived at a specified temperature, pressure was applied to the ram at a specified amount using a manual press, located at the top of the chamber. The pressure remained constant until the temperature of the die reached its maximum specified temperature and was kept there for a specified amount of time. At the end of the specified amount of time the generator, was shut down and allowed to cool, but the pressure was allowed to remain applied. After the die cooled it was taken out of the chamber and the specimen removed by pressing the top plunger down until the bottom plunger and the specimen fell out.

Next, metallography was done on the specimen by grinding and polishing it with diamond wheels and diamond suspension. Once this was done with the polishing of the specimen it was then observed under a microscope to study the microstructures of the materials. The above process of hot pressing and metallography took about a week to do and was repeated throughout the last 4 months.

The equipment used to do the hot pressing procedure was a hot press chamber made by Vacuum Industries hooked up to a generator made by Inductotherm. Buehler diamond suspension was used on a Buehler grinding wheel to polish the specimen.

There was essentially no data to be taken, except periodical measurements of the temperature and pressure of the specimen inside the die.

The learning experience of the hot pressing showed how important the processing of ceramics and CMC's (ceramic matrix composites) is to the government and outside industries. Besides the knowledge gained, was the experience of working with and around engineers and scientists. There is a lot of respect given to the staff of engineers and scientists at Wright Laboratory Materials Directorate and it is an honor to be around them and to work side by side doing various research and development.

PLASMA ENERGETICS IN PULSED LASER DEPOSITION

Task Order No. 264
Student Support Program
Southwestern Ohio Council for Higher Education

Karla L. Strong
University of Dayton

27 December 1996

Government Task Leader
Dr. Jeffrey S. Zabinski
WL/MLBT

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I would like to thank Dr. Jeffrey Zabinski for all his guidance and giving me the opportunity to work in his laboratory. Mr. John Bultman and Art Safriet have been instrumental helping me design, specify, order and build the equipment required. Finally, thanks to Dr. Terry Murray for his advice and constant support.

TASK ASSIGNMENT

Plasma Energetics in Pulsed Laser Deposition

The task was to design, assemble and use a time-of-flight mass spectrometer to detect the angular distribution of species within the plume generated during pulsed laser deposition (PLD) of solid lubricants and/or hard coatings. In addition, the coatings grown are to be characterized with various techniques. The purpose of the research is to detect the distribution in the laser plume of the particles' energy, mass, and charge. It has been discovered that some tribological films grown by PLD exhibit a layered structure attributed to differences in the species arriving at the substrate as a function of laser plume angle. Film layering is important because the chemical composition of the layers varies, and the layers have been observed to control the crystallite size developed at elevated temperatures. For tribological coatings, using this phenomenon to control crystallinity may be desirable, or, more likely, to understand it so more uniform coatings can be deposited.

In the subject research, adaptive lubricants and other materials of tribological interest will be deposited by PLD, and the laser plume will be studied with angle-resolved time-of-flight mass spectrometry (AR-TOFMS). Properties of thin films grown at different angles will be correlated to the plume characteristics. This total research project is expected to take 2 to 3 years, thus only part of the task has been completed. In the following section, the accomplishments from 5 August to 27 December 1996 will be reviewed. No research results are yet available.

Accomplishments

In the past 5 months, several major accomplishments have been achieved in designing and assembling the AR-TOFMS equipment, and designing the subsequent experiments. Most important, the angle-resolved TOF chamber, which was previously ordered, was evaluated, and additional equipment required to perform TOFMS was specified and ordered. This equipment included vacuum parts (rotary feed through, vacuum gages and controllers, connecting hoses and clamps, air inlet, etc.), an oscilloscope for data collection, and a computer. Those parts received have been assembled.

In addition, a cart was designed and modified to make entire TOF system portable, as is required by the current laboratory configuration. A support system for the TOF tube, which will extend more than 1 meter above the chamber, has also been designed and is currently being machined. Mobility was also the reasoning behind modification of the turbo molecular pump to be air-cooled rather than water-cooled. Also, a mobile emergency shut-down system was designed and ordered. The TOFMS microchannel plate detector always requires vacuum, and so the pumps must always be running. To protect the equipment if power is lost, the pneumatic gate valve will seal the chamber, providing protection for several hours, if necessary.

The TOFMS equipment was also received, and the controlling equipment was mounted in an equipment rack, and partially wired. It was determined that using the equipment in the manual mode, rather than in the automated mode, will be beneficial to speed the experiments along. It is anticipated that the computer will be used initially for data acquisition and analysis, and will later be used to control the entire TOF experiment. A photodiode (looking at laser reflected light as it fires) will be used as a manual trigger for the TOF equipment.

A rotatable sample holder was designed for installation into TOF chamber. Design of this sample holder is critical as it will allow angle resolution of the mass spectrometry data. Its design is currently being completed, and it will be machined in the next month.

Future Research

Experiments were designed to complete the task. AR-TOFMS will be done on carbon, adaptive lubricants, and possibly also other materials such as TiC, Al_2O_3, MoS_2, PbO, Pd, and SiO_2. These materials were selected for utility as high-temperature solid lubricants, hardness coatings, or diffusion barriers, and for the distribution of atomic weights of the ablated species. Each selected material will be studied at various angles with mass spectroscopy, and thin films will be grown by PLD at these angles. Thin films will be characterized with x-ray diffraction, x-ray photoelectron spectroscopy, tribometry, and other appropriate methods. Care will be taken to collect duplicate data to ensure validity. A preliminary test matrix is included at Attachment 1.

Probably one of the most significant accomplishments regarding experimental planning was the identification of some major drawbacks with the experimental procedure dictated by the equipment currently available. In some AR-TOFMS experimental setups, particles from a fixed-position target are detected with multiple detectors located at different positions. In another set up, a single detector is scanned over several angles. A less satisfactory arrangement uses a fixed-position detector whose sampling angle (with respect to the target surface normal) is varied by simultaneously varying both the target tilt and the laser angle of incidence. Measurements of this type are inherently difficult, since laser-plume interactions may cause the plume energy, distribution, and composition to vary with laser angle of incidence on the target. Unfortunately, the latter tilting target experimental set up will be used in this research.

The problem arises from three sources. First, as the spot size increases (as it will as the target is tilted) at a given energy, the laser fluence decreases. This problem can be overcome by adjusting the laser energy to keep the fluence constant for a changing spot size. The second concern is that film thickness profiles become more narrow as the spot dimensions increase even when fluence is held constantly. To alleviate this effect, appropriate masks or optics will be used to keep the beam shape as constant as possible. Finally, laser-plume interactions may vary with laser angle of incidence on the target, causing the plume energy, distribution, and composition to change. This effect cannot be controlled with the current equipment. A new TOFMS chamber design is under consideration for future research to mitigate these effects. Experiments have been planned to characterize the beam energy and shape with changing target angle. These experiments will commence in early 1997.

Attachment 1. Preliminary Test Matrix

Film Composition	Angle	No. of Films	Sample Size	TOF	XPS	GAXRD	Raman	Micro-scopy	EELS	Tribo-testing
ZnO2/WS2	0	3	small	✓	1		1	1		
	10	3	small	✓	1		1	1		
	20	3	small	✓	1		1	1		
	40	3	small	✓	1		1	1		
	0	3	large	✓	1		1	1		2
	other	3	large	✓	1		1	1		2
DLC	0	3	small	✓	1		1	1	1	
	10	3	small	✓	1		1	1	1	
	20	3	small	✓	1		1	1	1	
	40	3	small	✓	1		1	1	1	
Also possibly: TiC	0	2	small	✓	1	1	1	1		
	10	2	small	✓	1	1	1	1		
	20	2	small	✓	1	1	1	1		
	40	2	small	✓	1	1	1	1		
Al2O3	0	2	small	✓	1		1	1		
	10	2	small	✓	1		1	1		
	20	2	small	✓	1		1	1		
	40	2	small	✓	1		1	1		
PbO	0	2	small	✓	1	1	1	1		
	10	2	small	✓	1	1	1	1		
	20	2	small	✓	1	1	1	1		
	40	2	small	✓	1	1	1	1		
ZnO	0	2	small	✓	1	1	1	1		
	10	2	small	✓	1	1	1	1		
	20	2	small	✓	1	1	1	1		
	40	2	small	✓	1	1	1	1		
Others?										

COMPOSITE THERMAL STRESS ANALYSIS

Task Order No. 265
Student Support Program
Southwestern Ohio Council for Higher Education

John C. Stewart
Wright State University

27 December 1996

Government Task Leader
Dr. Robert Crane
WL/MLLP

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The author of this document wishes to thank Mark L. Ruddell for his patient guidance and instruction in Non-Destructive Evaluation, and all of the people in the ML Branch.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Non-Destructive Evaluation is any method by which samples are tested without using destructive methods that may alter the physical composition of the sample. Many structures composed of wood, rot from exposure and suffer from termite infestation. Unfortunately, the classical method of determining the state of such structures often includes the use of an ice pick! In Non-Destructive Evaluation, the use of ultrasonics has shown great promise. The use of ultrasonics allows for the accurate evaluation of samples without damaging or disassembling of a given sample. In wood, the ability to learn the deterioration of certain portions of a structure and various other practical applications saves enormous time and effort/money in localizing a problem. These methods concerning use in wood were developed by examining the velocity of sound in wood and analyzing the results to detect the condition of the sample/structure. Furthermore, these analysis techniques have shown great promise for future testing environments. The only drawback to date is the equipment used in this form of testing is quite costly, which is part of the motivation of this project, to accomplish the same task at a lower cost.

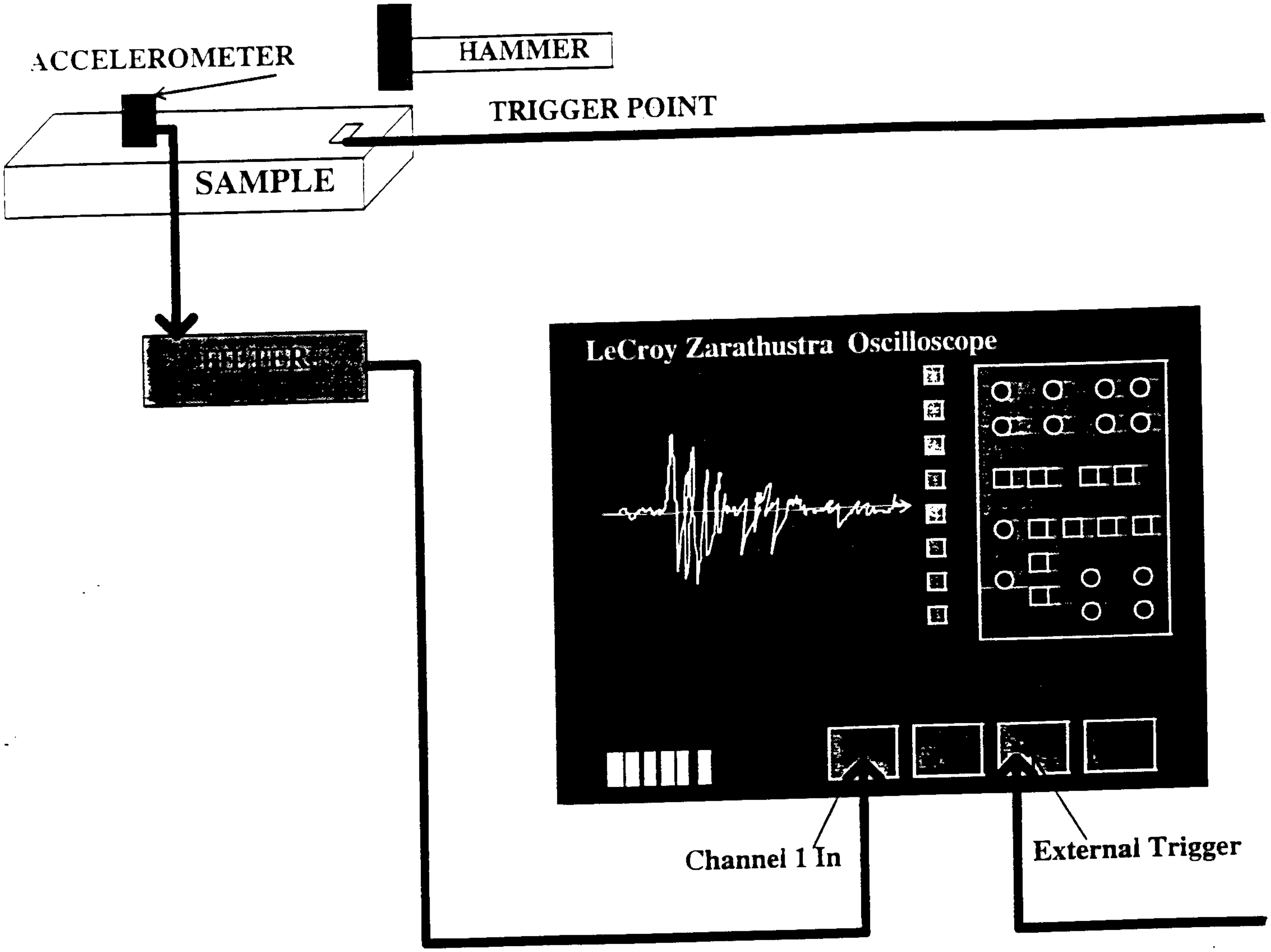
DESCRIPTION OF RESEARCH

Sound propagates in waveform. A good sample will allow ultrasonic waves to pass through it, unobstructed by unwanted sources of corrosion. In a rotten or otherwise damaged sample, sound waves propagate much more slowly. Take a sample of wood with extensive water damage for example. As water seeps into the fibers, it displaces the mass of the sample. The result is a change in the density of the sample (decrease) which causes the sound waves to propagate more slowly. The same is also true for wooden structures infested with termites. The experimentation process is done by performing the following steps. The testing setup includes (see Figure 1): an undamaged or rotten sample of a specific type of wood, a digital oscilloscope, a triggering mechanism (a ball-peen hammer in this case), a power source, a Band-Pass filter, and an accelerometer. A sound wave is generated by striking the sample on the trigger point. This sends a sound wave through the sample. The impact also triggers the oscilloscope. The accelerometer is attached to the sample a measured distance away from the trigger point, by an adhesive. As the wave propagates through the sample, it elicits a response from the accelerometer. This response is evident in the sample waveform from the LeCroy Digital Oscilloscope (see Figure 2). The first pass of the ultrasonic wave represents the initial contact of the wave with the accelerometer that is our chief point of interest. Since the impact at the trigger point initiated the oscilloscope reading at reference time zero, there is relatively little response from the system (other than some standard noise) until the first pass. This ‘zero response region’ represents the time it takes for the ultrasonic wave to propagate from the trigger point through the sample to the accelerometer. Knowing the time is measured by use of the oscilloscope, and the measured distance on the sample, the velocity of sound can be calculated through that sample. Since the setup is not the first of its kind, we can refer to known values of the velocity of sound through certain types of wood. Initial results illustrated that the setup had a large margin of error. Further analysis of the system showed sources of noise. As a result, the system performance improved so the level of noise decreased drastically. This was accomplished by designing a simple yet effective third order Band-Pass filter. Further testing showed that light and the magnetic fields around the power source influenced the behavior of the filtering process. The filter was encased in a metal housing to shield it from these sources of noise. The results produced from the subsequent tests showed marked improvement. The calculated velocity of sound through the pine sample had almost no correlation to the established value in the original setup. After shielding the filter, the accuracy of the measurements increased to a value more resembling the known.

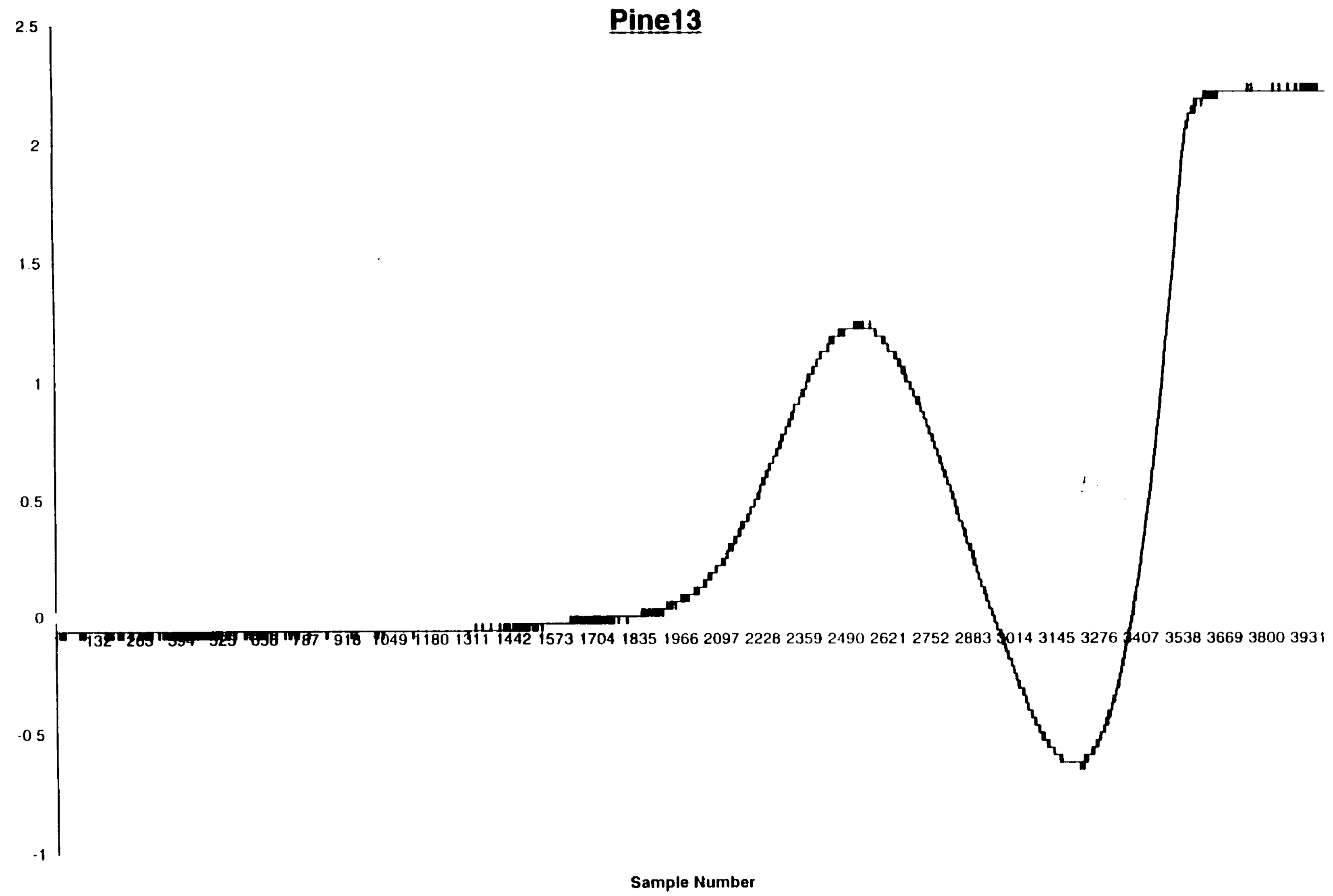
RESULTS

The shielding of the filter with the recalibration of lab equipment and the use of a relatively optimal lab setting has produced some excellent results. For example, the steady state of the system as seen on the oscilloscope shows that the filter has eliminated the vast majority of the undesired noise. Further, the exact setting of the trigger level decreased the noise in the system to a point such that now readable waveforms are produced during experimentation. This series of tests has a long way to go if it is ever to become useful in industry. However, these tests have illustrated that this form of testing can be done at a greatly reduced cost.

Figure One


ACCELEROMETER
HAMMER
TRIGGER POINT
SAMPLE
LeCroy Zarathustra Oscilloscope
Channel 1 In
External Trigger

PINE13 Chart 1



SYNTHESIS OF LIGHT-SENSITIVE MATERIALS FOR LASER HARDENING APPLICATIONS

Task Order No. 266
Student Support Program
Southwestern Ohio Council for Higher Education

Laura A. Sowards
Wright State University

27 December 1996

Government Task Leader
Dr. Tom Cooper
WL/MLPJ

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I would like to take this opportunity to thank Dr. Lalgudi Natarajan for his assistance during the last year and a half. He has advised and directed me toward accomplishing the goals of my Task. In addition, he has helped me to become aquatinted with many different operations at Wright Laboratory. I would also like to express my sincere gratitude to Dr. Tom Cooper and SOCHE for giving me the opportunity to work and learn at WL/MLPJ. I have found the experience and knowledge gained here to be quite valuable.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The goal of this Task is to obtain light-sensitive materials to be used in laser hardening applications. These materials may consist of infrared-absorbing dyes, photochromic compounds and photochromic polypeptides. The research concentrated on dithienyl polyenes and related compounds obtained from Dr. Charles Spangler of Northern Illinois University. These compounds were analyzed by UV/VIS spectroscopy, steady state fluorescence, fluorescence quantum yield and fluorescence lifetime. Analysis of the resulting data determines whether the compounds can be used in laser hardening applications. These applications include optical filters used to block radiation in the nearinfrared region.

DESCRIPTION OF RESEARCH

The compounds received from Dr. Spangler were to be analyzed by four main spectroscopic techniques: UV/VIS spectroscopy, steady-state fluorescence, fluorescence quantum yield, and fluorescence lifetime. Other techniques were also employed to evaluate the characteristics of these compounds.

A Perkin-Elmer Lambda 9 Ultra-Violet/Visible/Infrared Spectrophotometer was used to obtain the spectra for the dithienyl polyenes. An abscissa range of approximately 300nm -700nm was used. Octane and dichloromethane were the two solvents used during the measurements of the compounds.

Steady-state fluorescence measurements were taken with a Perkin-Elmer Luminescence Spectrometer (LS 50B). The excitation wavelength used was determined from the maximum wavelength of the UV/VIS spectrum for the corresponding compound. The emission and excitation slits were adjusted to yield the best spectrum. Dichloromethane and octane were used for the solvents.

The fluorescence quantum yield is calculated by taking the ratio of the emission, of a sample to the emission of a standard. The quantum yield represents the ratio of the number of photons emitted to the number of photons absorbed. Perylene has a fluorescence quantum yield of .98 and was used as the standard. The standard and the sample were both adjusted to have equal absorptivities of approximately 0.10 at a specific wavelength on the UV/VIS spectrophotometer. Both samples were then analyzed with the steady-state fluorometer using the same specific wavelength as the excitation wavelength. The area under the resulting spectrum was determined by integration. The area of the sample was then divided by the area of the standard to yield the fluorescence quantum yield.

The fluorescence lifetimes were measured on a Photon Technology International (GS-302). Samples were prepared with octane. Spectra were measured on a picosecond scale.

Compounds with an ethylene chain of length six will be analyzed by a much more sensitive pump-probe absorption technique that operates on a femptosecond time scale. Not all compounds in this category can be tested due to poor absorption at 532nm which is a requirement for detection.

Z scans will be done on the non substituted dithienyl polyenes. Currently, work is in progress on four of these compounds. The results will, hopefully, show that the compounds exhibit nonlinear optics with two photon absorption being evident in the spectra.

A solvent study will be done on two of the non substituted dithienyl polyenes. This will compare the spectra of compounds taken in acetone, ethanol, dichloromethane, and octane.

RESULTS

The primary goal of this Task is to assess the feasibility of using these compounds in laser hardening applications. Many dithienyl polyene compounds have been found to have strong absorption bands of relatively narrow widths (20nm-50nm) which is a criterion for laser hardening applications.

Analysis of the compounds from Dr. Spangler is still in progress. Most of the UV/VIS spectra have been taken. The steady-state fluorescence spectra does not occur uniformly or at all in certain compounds. Most of the compounds analyzed show atypical spectra. This may be because biphenyl compounds typically have irregular fluorescence spectra. Another probable cause is that increased length of conjugation chains decreases the efficiency of fluorescence scans. The quantum yields of several compounds have been calculated. The results are comparable to literature values. The fluorescence lifetime measurements taken are limited in number due to a short supply of high purity nitrogen. The lifetime measurements taken indicate possible isomerization during emission for certain structural isomers. This must be confirmed by further fluorescence lifetime tests.

The pump probe absorption spectra study and the Z scan studies are still in progress.

Some solvent effect experiments have been completed. They show a large variance in spectral peak intensities based on solubility. Spectroscopic shifts also occur due to changes in solvent. For example, the spectrum of a compound dissolved in octane exhibits better solubility and a blue shift when compared with a spectrum of the same compound dissolved in dichloromethane.

This research task is progressing well. New information such as the possible isomerization of the structural isomers is being uncovered as the compounds are continuously being analyzed. During the past year and a half, I have learned a great deal about light excitation and fluorescence emission.

GRAPHICS DISPLAY OF COMPUTER SIMULATIONS

Task Order No. 267
Student Support Program
Southwestern Ohio Council for Higher Education

Carlos Hernandez
Wright State University

27 December 1996

Government Task Leader
Ms. Monica Stucke
WL/MLLM

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The researcher, is proud to have contributed to the writing of a paper, in collaboration with Mr. Satish Rao and Mr. Jeff Simmons. The paper was published in the Materials Science Phil.Mag, regarding Green's function boundary conditions methodology, including extensive graphical, theoretical, computational and timing analysis. I hope that my work and contribution to the community were as invaluable, as the experience and knowledge gained.

TASK ASSIGNMENT

The main focus of work during this Task, has been the development and optimization of several scientific programs; while some of them are simply innovations and improvements to old problems, others are new to the field of materials within our community. New work was also begun on a very exciting and promising project code-name Xlat.

Several flexible boundary schemes have been proposed in the material science community to relieve inconsistencies that arise at the boundary region in atomistic simulations of defects, like dislocations and crack tips. These flexible techniques can be classified into two categories: (1) finite element methods and (2) Green's function methods. With the finite element techniques, the difficult part is the proper treatment of the transition between the lattice and the continuum that has recently been described about non-local elasticity theory. Green's function techniques suffer from the disadvantage that the Green's function of the defect lattice, even in the long range part, is dependent of the core structure and of the size of the defect that is being simulated. Therefore, in atomistic simulations of crack propagation, the appropriate Green's functions for the defect problem, needs to be updated continuously, as the simulation continues. However, the Green's function of a perfect lattice is relatively unperturbed around line defects like dislocations. Therefore, for simulations of dislocations in a single crystal, Green's function techniques can be applied with relative ease, since only the perfect lattice Green's functions are required for a proper treatment at the boundary region.

The requirements' specification phase of a project to implement Green's functions techniques were completed, to describe the inconsistencies arising at the boundary region in atomistic simulations of infinite dislocations, for both two and three-dimensional dislocation problems for the Materials Lab at WPAFB. The system was analyzed, designed and developed to run on all types of RISC workstations, including the Power Macintosh, and, on CRAY Supercomputers (X-MP, Y-MP and C-90). This required, besides the development of the system, a complete design and development of a time library and an extensive scientific mathematical library. Because of the large core structure used by the CMS (Computational Materials Science) group, the system was optimized for all the running architectures and was improved by a 700% factor. Optimization techniques employed varied, from loop unrolling techniques, instruction scheduling etc. on the software side, to cache, registers, processors etc. utilization on the hardware front.

Once the system was operational, the development of the system was analyzed and "costed" to run in parallel, distributed and in a multi processor workstation, to accommodate for future larger simulations. The system was designed and developed to run on the Intel Paragon™ using the NX library for message passing. The system was then optimized after a thorough study of the hardware available, e.g., message routers etc. The system, as well as, the libraries were developed completely using C and the UNIX™ Operating System.

The requirements' specification phase of a molecular dynamics (MD) system was completed, that uses embedded atom method (EAM) potentials for the CMS. This system was implemented using new MD algorithms that are more precise and faster than existing ones. The system was developed first for RISC workstation and CRAY Supercomputers and then ported to the Intel Paragon. This system was developed using C, FORTRAN and the UNIX Operating System.

This system was refined and optimized through the course of the task several times, in order to be, not only more accurate, but also friendlier and more efficient. As a result of this, the CMS group is now in a position to analyze larger core structures in a fairly reasonable amount of time, leaving more time for the material scientist to devote to the study and analysis of the simulation results. Additionally, this performance improvement, allows the CMS group to run their simulations "in house" without having to request computer time from other outside facilities.

The development of these systems, has raised one of the major problems that the CMS has to face, that of time. Most algorithms employed by the CMS group grow exponentially with the number of atoms. This fact has shown the impossibility of running some simulations, as well as, the enormous amount of wait between simulations, even with today's computational power.

This problem and the need for running larger cores, e.g., Cores approaching 1 million atoms, has led to the need for not only optimization of code, but also the need for research and testing of new methods that will allow faster turn around times, as well as, the possibility of running some of today's unfeasible simulations.

Xlat is a graphical interface that can solve several of the current needs that the CMS group currently has.

The proposed capabilities currently under work of such a project include the following: The software can construct virtual crystals, put a dislocation at arbitrary positions within said crystal, apply relaxation techniques according to Green's function elastic relaxation methods, as well as, applying Embedded Atom Methods (EAM) relaxation techniques. This project will be intelligent enough to apply such relaxation techniques, as many times as, the simulation requires it without human intervention. In addition, this project will also record and show flexible boundary conditions of the atoms based on the atomistic relaxation techniques already mentioned, it will also be used for other purposes, such as, straining a crystal and calculating frictional stress.

The software, will be of a graphical nature, displaying multiple crystals and performing operations on each of the crystals independently of one another. The scientist will have complete graphical control to perform operations on the crystals, such as, duplicate, cut elements from one crystal and possibly attach such elements to other crystals, performing any recalculations needed on said crystal, all of this is expected to be done in real time. The software will also allow the scientist to select specific atoms within the crystal, to use their forces to relax the remaining atoms in the crystal.

The researcher also served as the system administrator, performing such tasks, as adding new users, managing UNIX processes, planning and performing backups, restoring lost files from backup tapes, adding new terminals and disk drives, setting up a printer and the spooling system, and especially making the system secure.

STRUCTURAL FAILURE ANALYSIS

Task Order No. 268
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 1996

Government Task Leader
Mr. Ronald H. Williams
WL/MLSA

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TASK ASSIGNMENT

One of the most difficult problems arising during exploitation of aircraft is structural failure. Structural failure may be defined as failure of a structural component of any mechanical system due to unforseen stress magnitudes and modes such as fatigue, stress corrosion, creep and, etc. Structural failure may also take place because of material imbrittlement which is most often due to improper chemical treatment during manufacturing process. The set of procedures utilized to deal with these problems is called Structural Failure Analysis. The primary objective of Structural Failure Analysis is to determine the cause of any given structural failure instance, to determine the conditions under which such a failure was possible and to provide recommendations that would preclude such failures from happening in the future.

The main goal was to perform such an analysis on mechanical and metallurgical joining of aluminum, advanced nickel-based, titanium-based and refractory metals as well as unknown metallic materials, residues, contaminants and coatings. The structural components on which the analysis was performed included gears, shafts, nozzles and other engine parts, gasoline lines, impellers, tanks and other fuel system components, landing gear components, pylons, cables and various other aircraft parts.

The first thing done to a failed part or a component when it is brought to the lab is a visual observation. The primary purpose of the visual observation is to observe the surface of the failure, catalogue any visible abnormalities such as discolorations, cracks, burn or wear marks, and, etc. The information collected during the visual observation is recorded and multiple photos of the part are taken from various angles. Importance of the visual analysis cannot be overstated. Very often it gives very important clues about the causes of the failure. The visual analysis of the failed component is normally not intrusted to the students and is carried out to an experienced engineer with a rich background in these matters.

After the visual analysis phase is complete, a sample containing a portion of a failed surface is prepared. The determination of the sample selection is normally made by an experienced engineer as well. The most important requirement in preparation of the samples is that during the preparation process, the failed surface and microstructure of the sample material should not be tempered with. The microstructure of any sample could be ruined by overheating resulting from cutting to close to the failed surface. Excessively prolonged contact between the sample and a polishing surface will also lead to overheating. Additionally, cutting too close to the surface of interest may work harden the surface and lead to erroneous conclusion in further analysis. Therefore, the cutting techniques are normally dictated by such factors as physical dimensions of the failed component, chemical make-up of the component and available time. The equipment available for performance of the cutting procedures included a variety of saws such as band saw (used for cutting large parts), automatic saws with diamond wheels (used for cutting components of small size), as well as portable hand-held saw with plexiglass cutting wheels (used for cutting components made of titanium alloys). During the cutting process, additional attention was paid to the observance of all safety procedures and regulations.

After the sample is made, a sample mount is usually prepared for ease of handling the sample. The choice of sample mount material depends on such factors as sample size, hardness and topic of interest (such as depth of micro cracks and, etc). The material most often used for sample mount preparation is granular epoxy powder. Mounts are prepared by subjecting the powder to the pressure of approximately 80 PSI in conjunction with the heat of approximately 300°F.

After a mount is attached to the sample, the sample is polished to required specifications. The underlaying idea of the polishing process is to start with the coarsest polishing surface and to gradually move to finer surfaces until the specifications are met. During the polishing process it is important to remember to make sure that coolant is being poured on the sample while the sample is in contact with the polishing surface. When simultaneous cooling is not available, it is important to remember to allocate a sufficient amount of time for the sample to cool off. The equipment available for sample polishing included polishing wheels 80 grit to 600 grit. In addition, diamond pastes were available for samples to be polished to a degree where the depth of the cracks did not exceed 0.5 micron.

Sometimes, in a course of analysis, it is important to see the microstructure of the sample. In order to do this, it is necessary to remove a layer of microscopic sawdust that accumulated on the sample surface as a result of polishing. This is achieved by a procedure called etching. Etching is the treatment of the surface with various chemical compounds. Choice of the compound and duration of contact between the compound and surface depends on the sample material and surface area of interest. Since some of the etching compounds tend to be very chemically aggressive, it is also imperative to follow basic caution rules while executing etching procedure.

One of the most important procedures carried out in a course of failure analysis is surface hardness test. Hardness is a physical property of a material reflecting its tensile strength (tensile strength is the amount of tensile stress a material will withstand before failing). The basic idea behind hardness test is to apply steady pressure against a surface for a set interval of time using some kind of indentor powered by mechanical or hydraulic force. The size of indentation and its shape will give an idea about surface hardness of the material. The test exists in two basic forms: macro hardness and micro hardness tests. One differs from another by the size of the indentor used and the amount of load applied. Normally the surface hardness test is conducted across the whole cross-section of the failed part. Presence or absence of variations of results will give an idea about possible uniformity of strength as well as possible uneven chemical and thermal treatment of the component during the manufacturing process. The data obtained from the hardness tests was analyzed by engineers who presented their conclusions to the appropriate authorities.

Due to the fact that the author of this report got involved in the task almost right before it was completed, his experience in the matters of structural failure analysis could not be expanded beyond familiarization with basic techniques of sample preparation and surface hardness analysis described above. Absolutely all analytical work and procedures involving knowledge beyond execution of above-mentioned tasks were carried out by other personnel.

PROCESSING AND CHARACTERIZATION OF ELECTRO-OPTIC (EO) POLYMER FILMS

Task Order No. 269
Student Support Program
Southwestern Ohio Council for Higher Education

Michael Banach
University of Cincinnati

27 December 1996

Government Task Leader
Capt. Richard Vaia
WL/MLBP

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TASK ASSIGNMENT

Introduction

The future of optical communications may lie in the widely researched area of nonlinear optical (NLO) polymers. Polymers are an attractive alternative to inorganic materials, in which high dielectric constants offer fairly slow response times. Polymers are advantageous with respect to other NLO materials because they are less expensive and easier to process. NLO systems that meet strict specifications of magnitude, thermal, and temporal stability of the electro-optic (EO) response can be integrated into many communication devices. To obtain electro-optic behavior in a polymeric system, a noncentrosymmetric alignment of chromophores that posses high nonlinear polarizabilities is required. One approach is to dope a host polymer with the NLO-phore[1-3]. Although fairly strong NLO signals were obtained with these systems, in general the thermal and temporal stability did not meet device specifications. Polymers functioned with NLO-phores on the side or even the main chain have also been studied[4,5]. These studies usually reproduced the results seen in guest-host systems while improving both the thermal and temporal stability.

Electro-optic activity in guest host, side chain, and main chain systems depend on the eventual poling of the NLO-phores. The poling process begins, as the polymer is heated to its Tg to increase NLO-phore and matrix mobility. An electric field is then applied to induce alignment of the dipole moments in the NLO-phores. The polymer is then quenched, hopefully "locking in" the thermodynamically unstable alignment.

Research now is being focused on new NLO-phores with greater EO activity. The Air Force has synthesized novel NLO-phores with very high polarizabilities. The processing, in-situ characterization of poling and absolute EO behavior of these NLO-phores were studied by observing their orientational dynamics within many different polymer systems.

Methodology

The orthogonal components (n_x, n_y, n_z) of the refractive index of a poled polymer film can be illustrated as an ellipsoid, as seen in Figure 1.1 and described by Equation 1.1[6].

$$x^2/n_x^2 + y^2/n_y^2 + z^2/n_z^2 = 1 \qquad \text{EQ 1.1}$$

The z-axis is parallel to the aligned NLO-phores and contributes to the semi major axis of the ellipsoid. The refractive index along this direction is known as extraordinary (n_e). Perpendicular to the polar axis are the semiminor x and y axes. The refractive index along these directions is referred to as ordinary (n_o). A light beam which propagates through the uniaxial medium will be decomposed, due to birefringence, along two orthogonal linearly polarized components[6]. These components are known as the s and p components and are illustrated in Figure 1.1. The s-component is independent of incident angle (θ) and, for the geometry specified in Figure 1.1, is governed by n_o. While the p-component depends on the incident angle and is governed by $n_e(\theta)$.

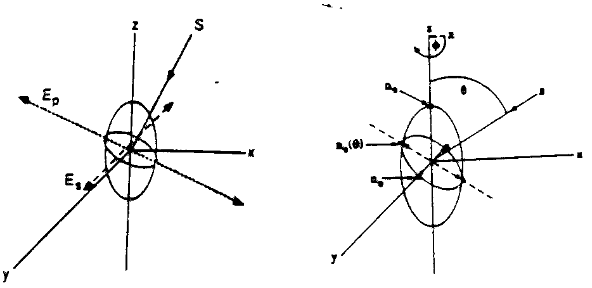


Figure 1.1 Illustrations of the refractive index ellipsoid. The S beam is the propagating incident beam and s and p refer to the components due to birefringence[6].

The electro-optic effect may be visualized as the change or rotation of the refractive index ellipsoid in the film by the application of an electric field. When the refractive index changes in proportion to the applied field, a linear or Pockels effect is observed. In this case the change in the refractive index ellipsoid can be computed as a function of the electric field by Equation 1.2 [6]:

$$\Delta(1/n^2)_i = \Sigma r_{ij} E_j \qquad \text{EQ 1.2}$$

where, E is the applied electric field, and r_{ij} are the Pockels coefficients. The Pockels tensor can be simplified through the symmetry of the film. The final relationships between the change in the refractive index in ordinary and extraordinary directions due to an electric field applied along the z-axis are Equations 1.3 and 1.4[6].

$$\Delta(1/n_o^2) = r_{13} E_3 \qquad \text{EQ 1.3}$$

$$\Delta(1/n_e^2) = r_{33} E_3 \qquad \text{EQ 1.4}$$

Most optical characterizations of EO polymers determine the r_{33} value of the material.

Testing Procedure

A slight variation to the Teng and Man[7] reflection method was used to determine r_{33}. A schematic of the experimental set-up is shown in Figure 1.2. Sample geometry is shown in Figure 1.3. The polymer sample is spun coated onto a patterned indium tin oxide (ITO) coated glass slide. The ITO provides an electrode for modulation and poling and is clear to avoid absorption of the incident laser beam. Gold is then evaporated on top of the polymer sample to be used as a reflector and the counter electrode.

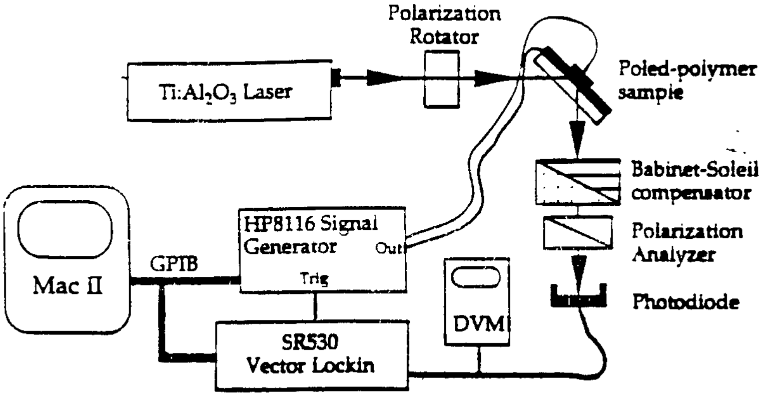


Figure 1.2 EO characterization set-up.

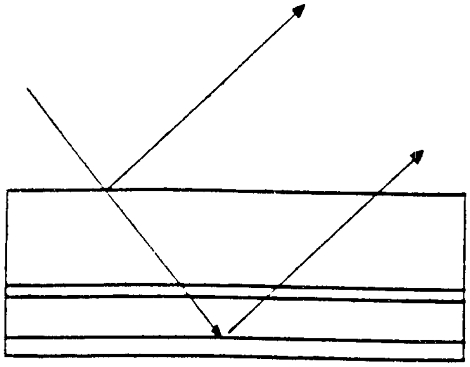


Figure 1.3 Sample geometry.

The sample is then placed in the sample holder seen in Figure 1.2, gold side against the holder. In this set-up a laser beam is sent through a polarizer set to 45°. The polarized beam then propagates through the glass and polymer where it is modulated by the polymer film and is eventually reflected by the gold. The reflected beam passes through the Soleil-Babinet compensator, which is set to let half the maximum intensity pass. This allows the most linear part of the sinusoidal wave to pass through. The beam then encounters an analyzer set perpendicular to the polarization direction. This allows only the modulated light to pass. A photodiode detects the final signal which is sent to a computer lock-in to give $\Delta I/I_o$. The final EO coefficient r_{33} can be calculated from

$$r_{33} = 3\lambda\surd(n\hat{}2 - \sin\hat{}2\,(\theta))/(4\pi n\hat{}2 * \sin\hat{}2(\theta)) * 1/V_{mod} * \surd 2\Delta I/I_o * 10\hat{}12 \qquad \text{EQ 1.5}$$

where λ is the wavelength of the laser, n is the refractive index in the polymer, θ is the incident angle (set at 45°), V_{mod} is the AC modulation voltage, ΔI is the intensity of the AC signal at the input frequency read at the lockin, and I_o is the intensity of the beam read at the photodiode.

In-situ observation of $\Delta I/Io$ while poling these polymer films allows for a closer look at the orientational dynamics of the NLO-phores. In this apparatus, poling of the NLO-phores is done by using large DC electric fields. An AC electric field is used to modulate the refractive index ellipsoid of the medium. Therefore, a generator is connected to the electrodes that can apply both an AC and DC field. The sample, which is mounted on a heating strip, is originally subjected to a 10-volt AC modulating field of 1 kHz. The computer lock-in determines intensity variation at the photodiode with the same frequency as the applied AC field, from this, an EO coefficient is calculated. The signal is continually monitored while a DC poling field of 75-100 V/µm is applied and the polymer is heated to Tg. Finally, the polymer is cooled and the DC field is withdrawn, and an absolute EO characterization is made.

Processing Conditions

In the testing procedure, a great deal of voltage is applied across the polymer. It is very important that the polymer layer be fairly thick and lack any holes or impurities which would allow the current to flow between the electrodes, shorting the sample. Therefore, all films should be spuncast to be between 1-2 microns thick, lacking any impurities or holes.

The polymer systems that were characterized included AF-80 NLO-phore in PMMA, 6FPBO, and connected as a side chain in a sulfonated polymer. Each system required different processing conditions to achieve quality films. Film preparation begins with the polymer system in solution being filtered onto an ITO slide in a spincaster. The polymer is then spread by using a slow speed for a small period of time, and then spun at a higher speed for a longer period of time. The spread time and speed were held constant for all the spuncasted films at 400 rpm for 5 seconds. The spin time and speed were adjusted according to the viscosity of the solution. The viscosity of the solution is controlled by the amount of solvent used. As the viscosity increases, the spin speed must increase to get the proper thickness. As a general rule the spin speed is not to be less than 750 rpm, because at slower speed uneven films may result. Table 1.1 shows a chart of the processing conditions which make quality films. The NLO-phore is counted as solvent in the guest-host systems.

Solution instructions	**Spinning instructions**	**Results**
12% PMMA in cyclopentanone/AF-80	1000 rpm for 60 sec	yellowish film 1-2 microns thick
7% 6FPBO in monochlorobenzene/AF-80	750 rpm for 40 sec under a heat lamp	yellowish film 1-2 microns thick
10% AF-85 polymer in cyclopentanone Mix overnight	800 rpm for 60 sec	yellowish film 1-2 microns thick

Table 1.1 Summary of spincasting EO polymer films.

Optical Characterization

After all the films are processed and gold is evaporated on top, optical characterization can be done. The first sample characterized was a PMMA sample doped with the commercial chromophore, Disperse Red 1 (DR1). This is a fairly well studied system, so some sort of characteristic poling behavior can be determined. Figure 1.4 shows the results of the DR1/PMMA sample tested with an infrared laser (787 nm). The original r_{33} is very low around

.01 pm/V, which indicates that the sample is unpolled. A huge jump to 1.6 pm/V is seen when the DC field is applied. This jump will be referred to as the DC offset. As temperature increases, the signal also increases indicating the alignment of the chromophores. It plateaus at 5.3 pm/V at a temperature of 85° C, which is the Tg for the material. A slight dip in the signal is seen as temperature drops which could be explained by the changing refractive index of the polymer. The larger dip is a result of the elimination of the DC poling field. The absolute r_{33} value at room temperature is 3 pm/V which agrees with other literature values. This sample was then depoled by increasing the temperature to Tg with applying a DC field. The behavior seen in DR1/PMMA will be used as a comparison for other systems.

The first test for the AF-80 NLO-phore was as a guest in a 6FPBO matrix. 6FPBO was selected because its rod-like structure should offer a favorable environment for poling of the large AF-80 molecules. Figure 1.5 shows the optical characterization results of AF-80/6FPBO system, done with the IR laser. The original signal is very small followed by a small DC offset. The EO coefficient does increase very rapidly with temperature to reach very large values. This large signal is then lost as the temperature is dropped, and a very small absolute EO is maintained. This behavior was very odd when compared with the DR1/PMMA sample. To help understand what happened, AF-80 was introduced to PMMA. This system showed a much more characteristic curve, as seen in Figure 1.6, but the absolute signal was only 1 pm/V. Since the nonlinear polariziablities of the AF-80 NLO-phore are so high, the lack of a significant signal was attributed to lack of poling. The dipole moment of this molecule is relatively low and the spaghetti like molecules of PMMA offers an appreciable barrier to movement. Therefore the fact that complete poling did not take place is not surprising. This does not help explain the 6FPBO behavior. A potential explanation to this behavior would be aggregation of the AF-80 molecules in a head to tail fashion. This would create a net dipole moment of zero and prevent any poling from taking place. The aggregation could be very temperature dependent which would allow for poling at higher temperatures. The forces of aggregation could then overcome the modest poling field applied as the temperature decreases. This would account for the large drop in the signal. Work on this theory is being carried out.

AF-85 is the same AF-80 NLO-phore attached as a side chain to a sulfonated polymer. DSC results show a Tg of about 215° C after the polymer was originally annealed at 225° C. Therefore, the AF-85 polymer was annealed and then optically characterized. Figure 1.7 shows a modest DC offset, but poling does not even begin until 190° C. After reaching a poling temperature of 215°C, an absolute r_{33} value of .4 pm/V is achieved. In this system, the small dipole moment still presents a problem along with the relatively little free volume available for such a large molecule to move. Therefore, the polymer was doped with propane sultone which, after reacting with the end group of the NLO-phore, will increase the dipole moment of AF-80 and improve the packing in the system. Figure 1.8 shows the promising optical characterization results. A very large DC offset is seen and the signal continues to climb as the temperature is increased. The propane sultone also produced extra charge carriers in the material which greatly increased the conductivity. Therefore, the poling temperature was only 95°C, and the absolute signal is 1pm/V. The sample was depoled at 170°C, which means that optimal poling conditions were not achieved.

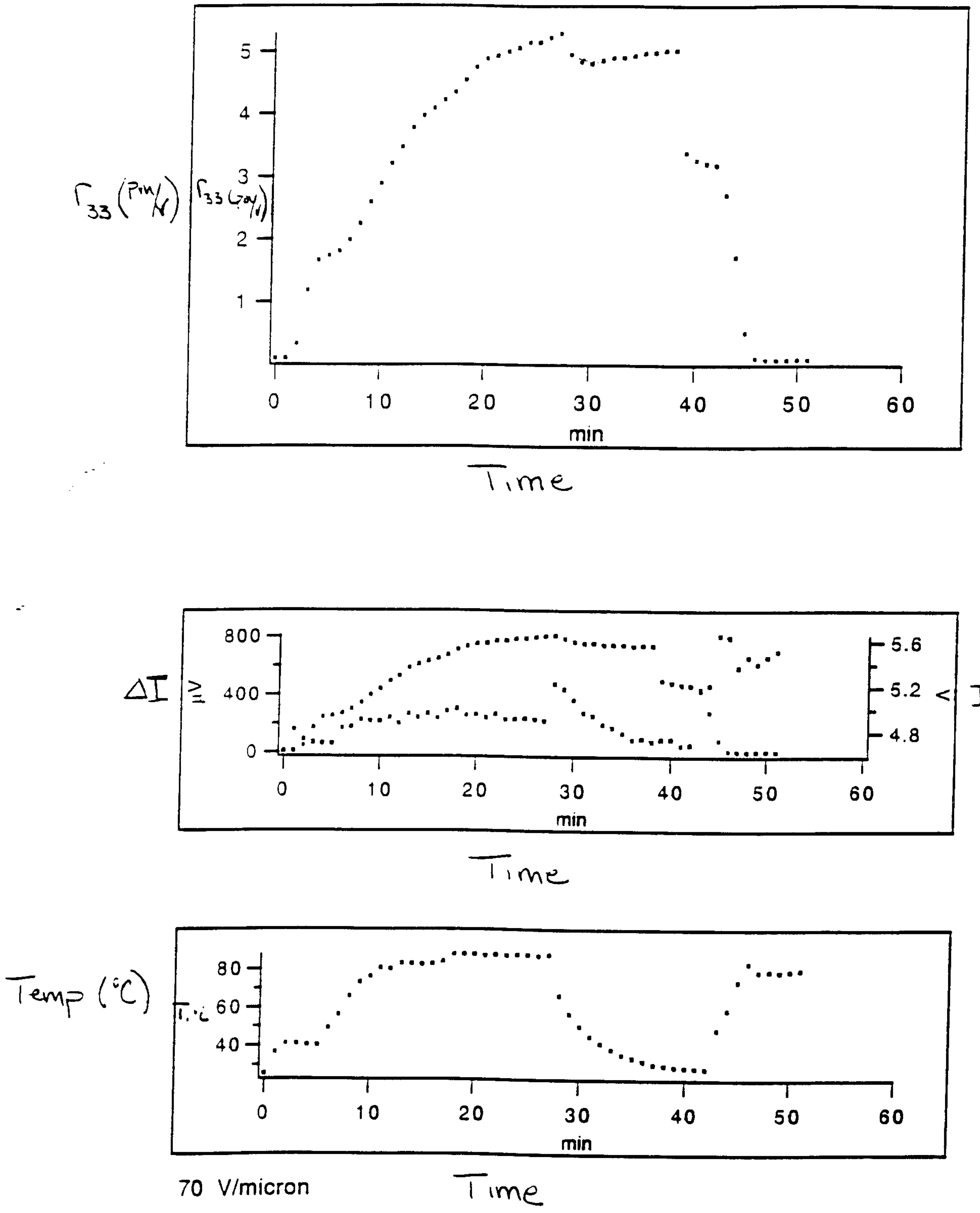
AF-85 doped with propane sultone indicated that poling of this chromophore is possible. The propane sultone increased the dipole moment and improved packing conditions in the polymer, but it also shifted the absorption spectrum of the system. The formerly yellowish film turned dark red when propane sultone was added. This film looked very similar to the DR1/PMMA films that have been poled in the past. To test how much of the effect this shifted absorption had on the EO calculation, a new laser at a visible wavelength (676 nm) was used to characterize the pure AF-80 chromophores. The expectations were that the IR laser that was originally used for the testing was too far away from AF-80's absorption peak to optimize the EO results. Figures 1.9 and 1.10 show the effect the new laser had on AF-80 in 6FPBO and PMMA respectively. The curves are slightly inflated, but overall the new laser had little effect on these samples. Figure 1.11 shows an AF-85 sample characterized with the new laser. A noticeable difference is seen with the new laser in this system. The absolute signal is doubled and the DC offset increased by 1 pm/V. Since the current stopped this test short, optimal poling conditions may not have been reached. This is definitely promising results in the pursuit of poling the pure AF-80 chromophore.

CONCLUSION

This project was started to gain a working knowledge of the processing conditions necessary to create films containing novel NLO-phores and then to characterize their optical properties, specifically the Pockels coefficient (r_{33}). Quality films were obtained by optimizing both the solution viscosity and spinning conditions. Optical characterization results lead to some understanding of the orientational dynamics of the AF-80 NLO-phore. The small dipole moment of AF-80 will definitely present a large obstacle in poling of the NLO-phores. This coupled with the large size of the molecule probably are the main contributors to the small signals achieved compared with what could be expected from nonlinear polarizibilities tests. Changing the wavelength of the testing laser did have a positive effect on the characterization results. More questions also came from the testing results. Most intriguing is the behavior of the NLO-phore in 6FPBO, which is being looked at much closer now. Progress was made in the understanding of the poling behavior of the AF-80 in many different systems.

Figure 1.4

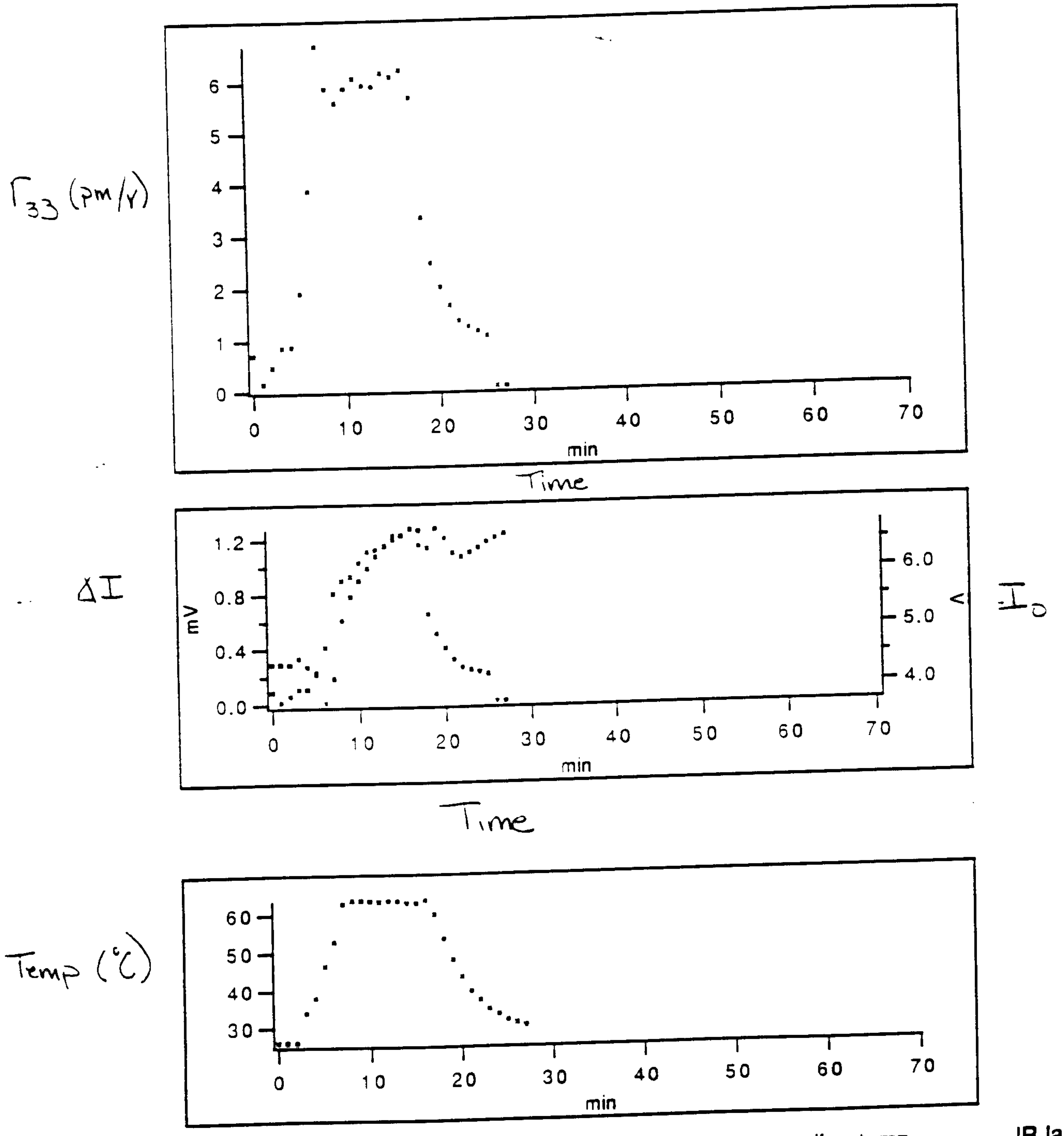
DR1/PMMA



70 V/micron

20% AF-80 in 6FPBO

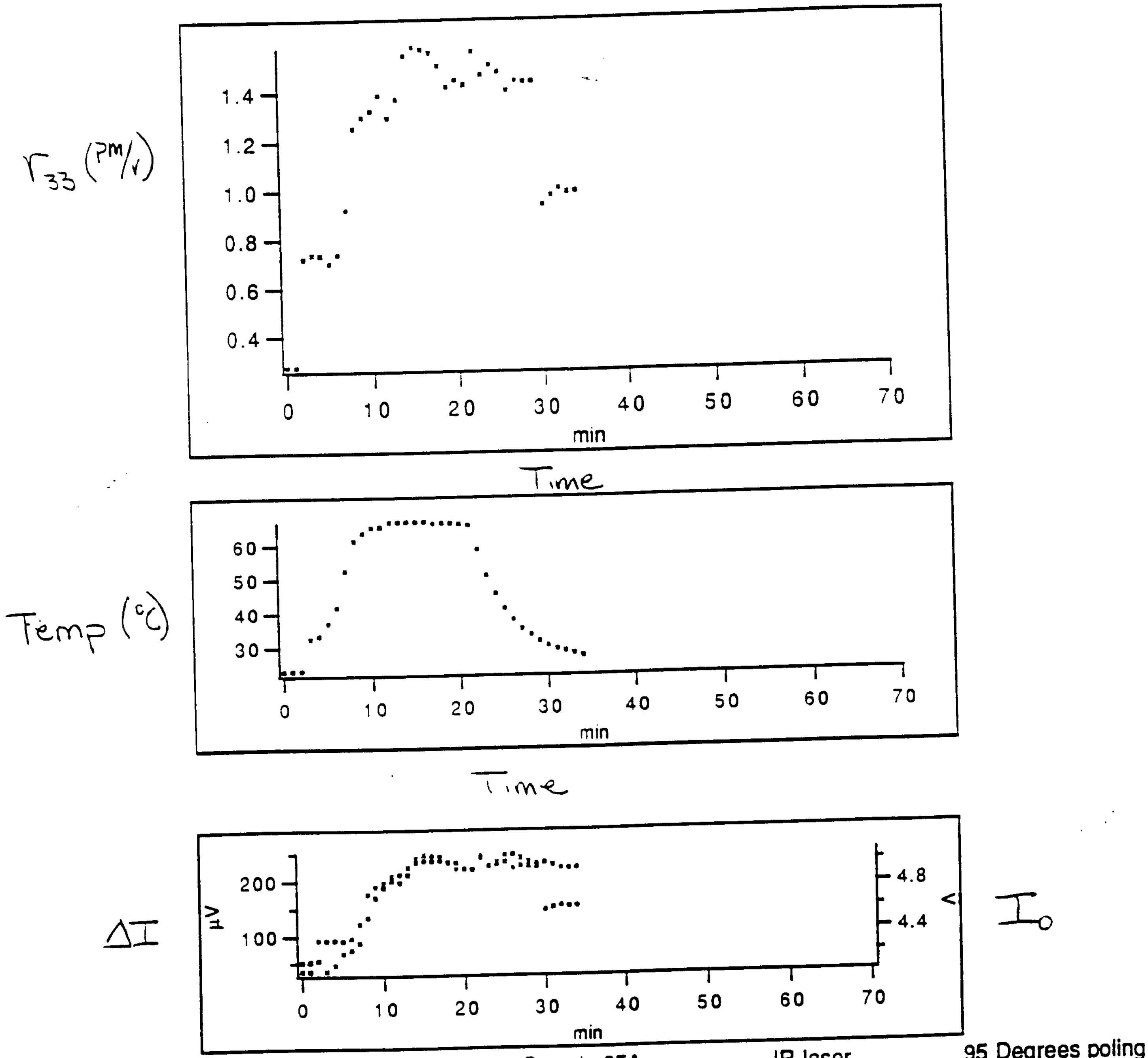
Figure 1.5



100 V/micron Sample 35D 95 degrees poling temp IR laser

Figure 1.6

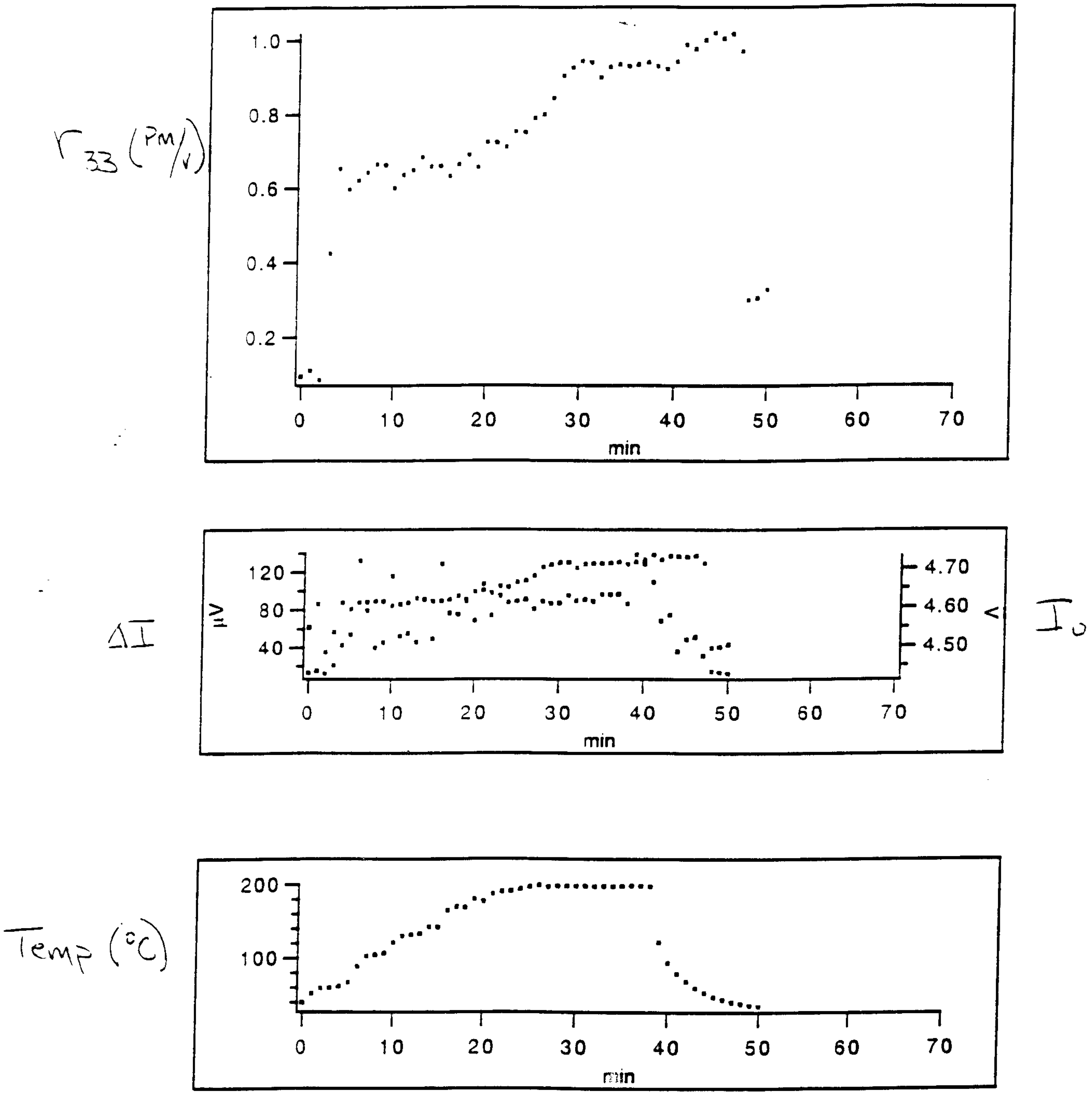
20% AF-80 in PMMA



95 V/micron Sample 35A IR laser 95 Degrees poling

Figure 1.7

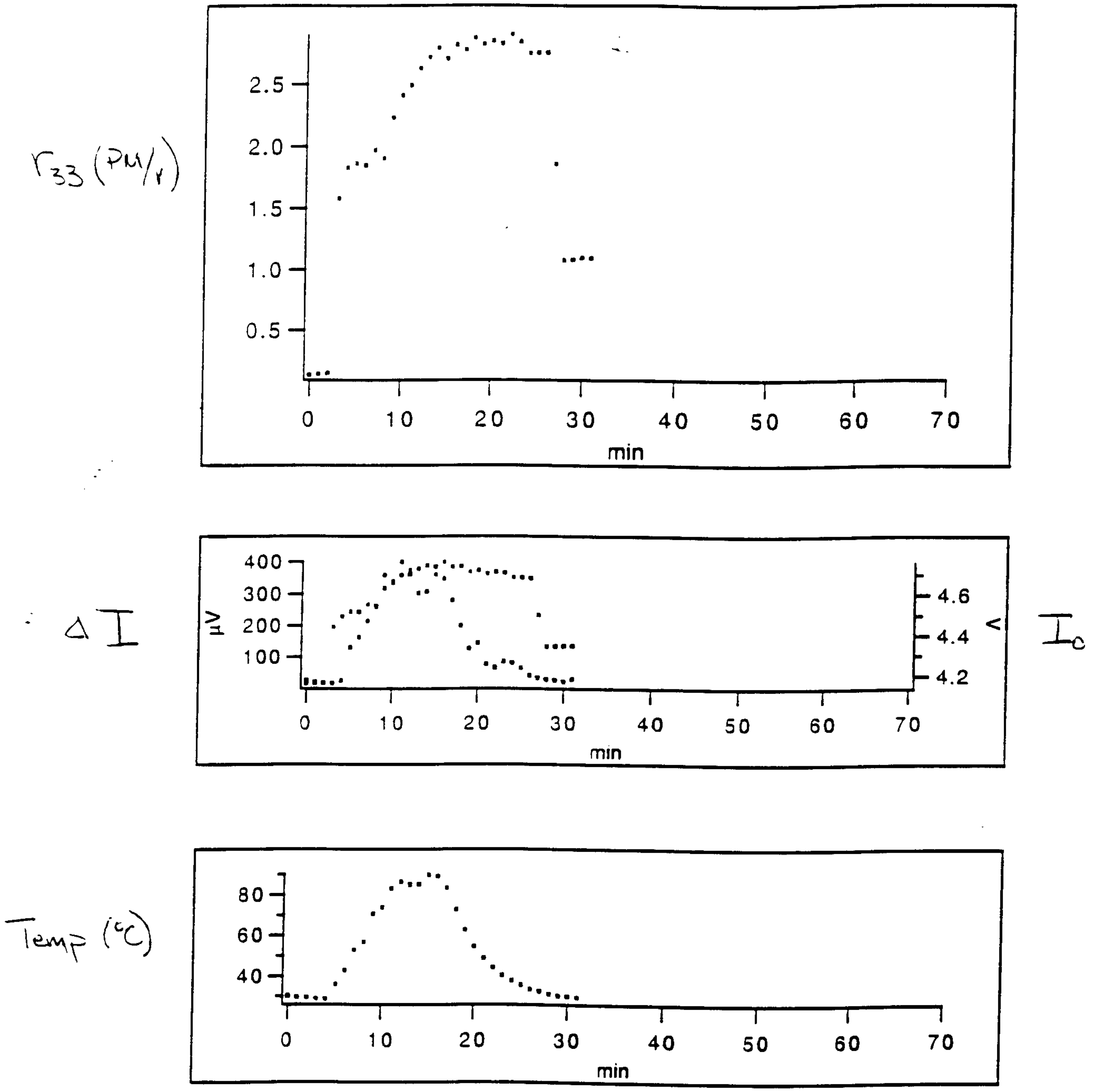
AF-85 with IR



Sample 27A 88V/micron After annealing

Figure 1.8

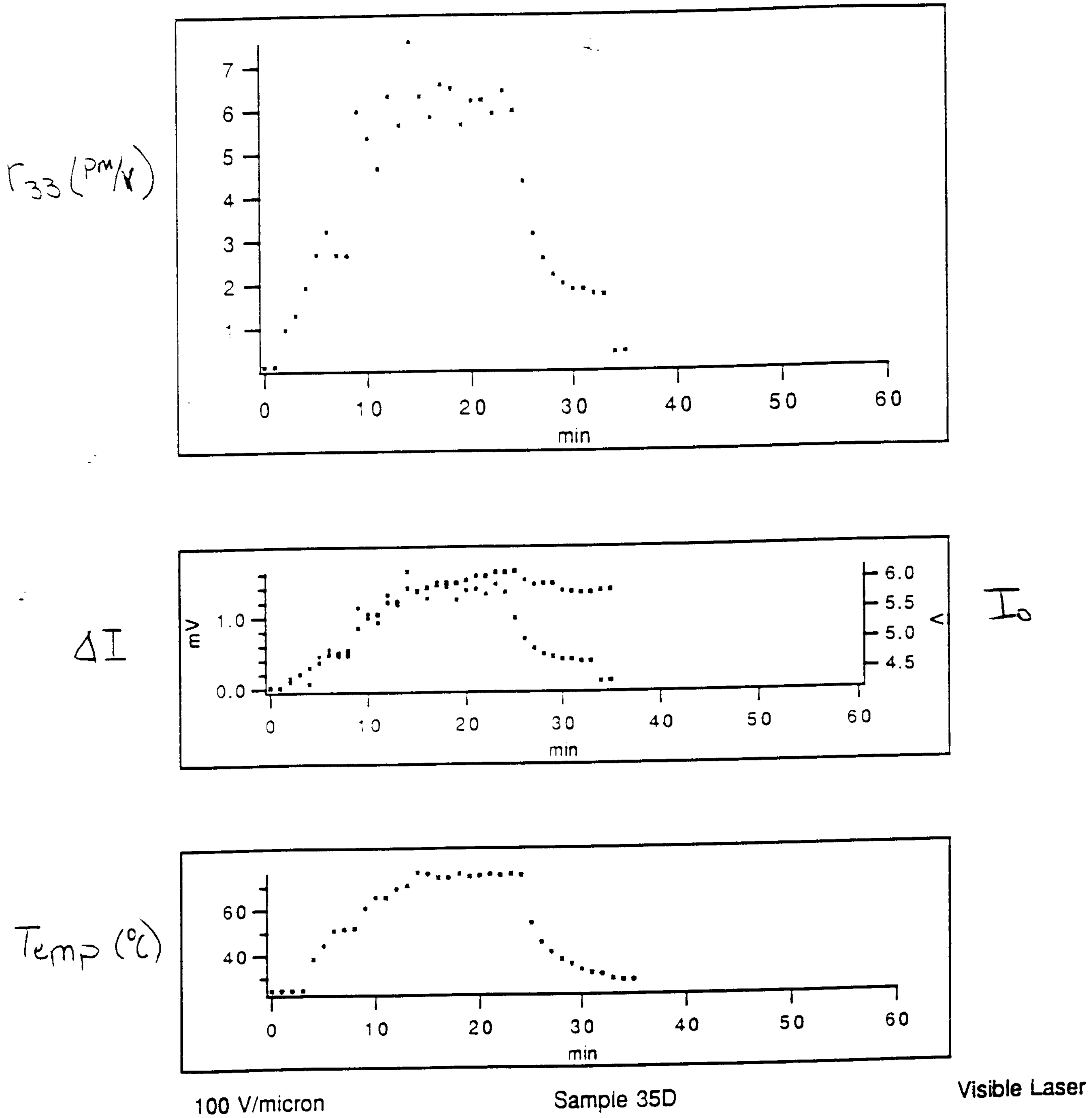
AF-85*



Sample 34B 100 V/micron IR

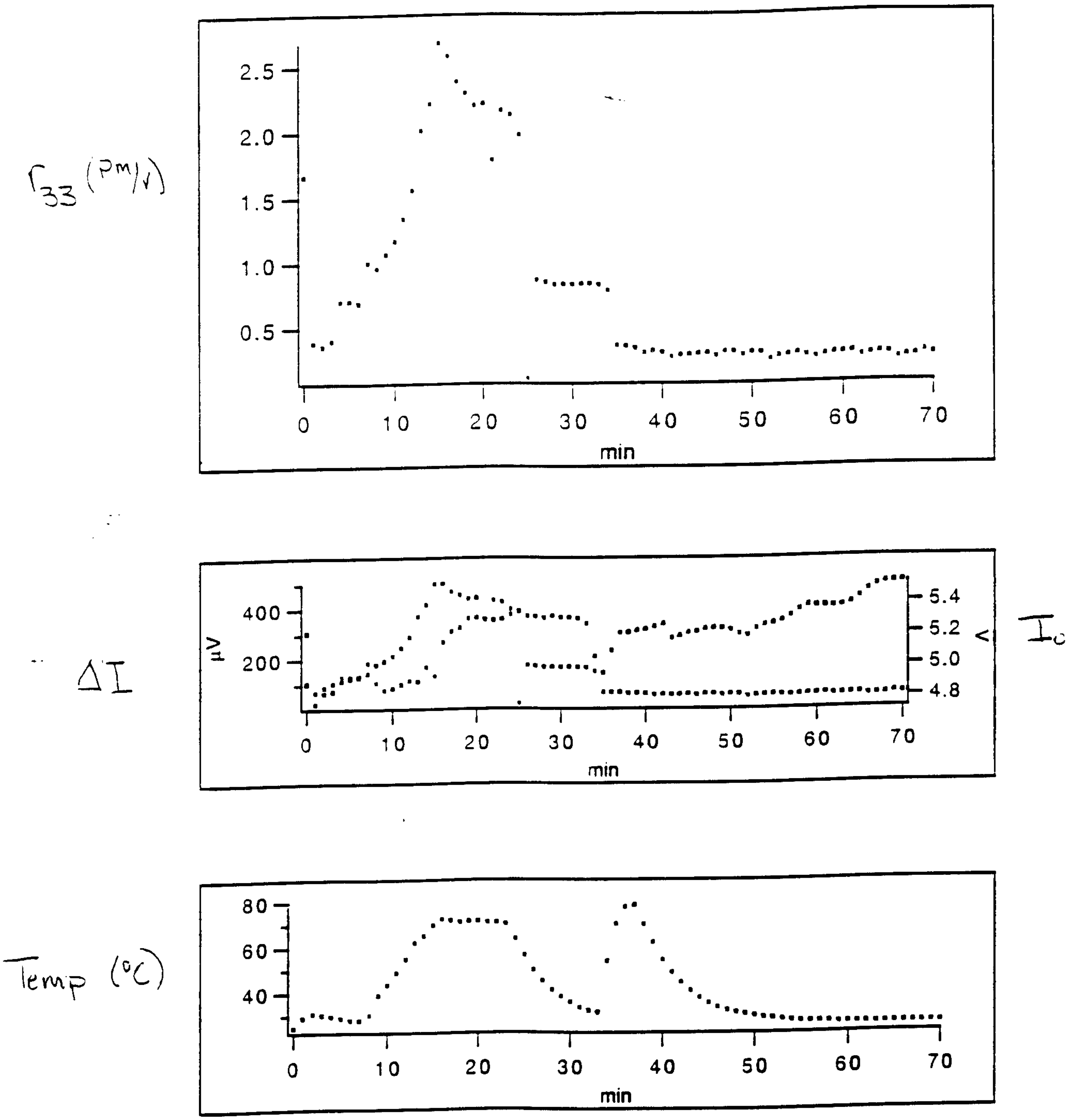
Figure 1.9

AF-80 in 6FPBO



20% AF-80 in PMMA

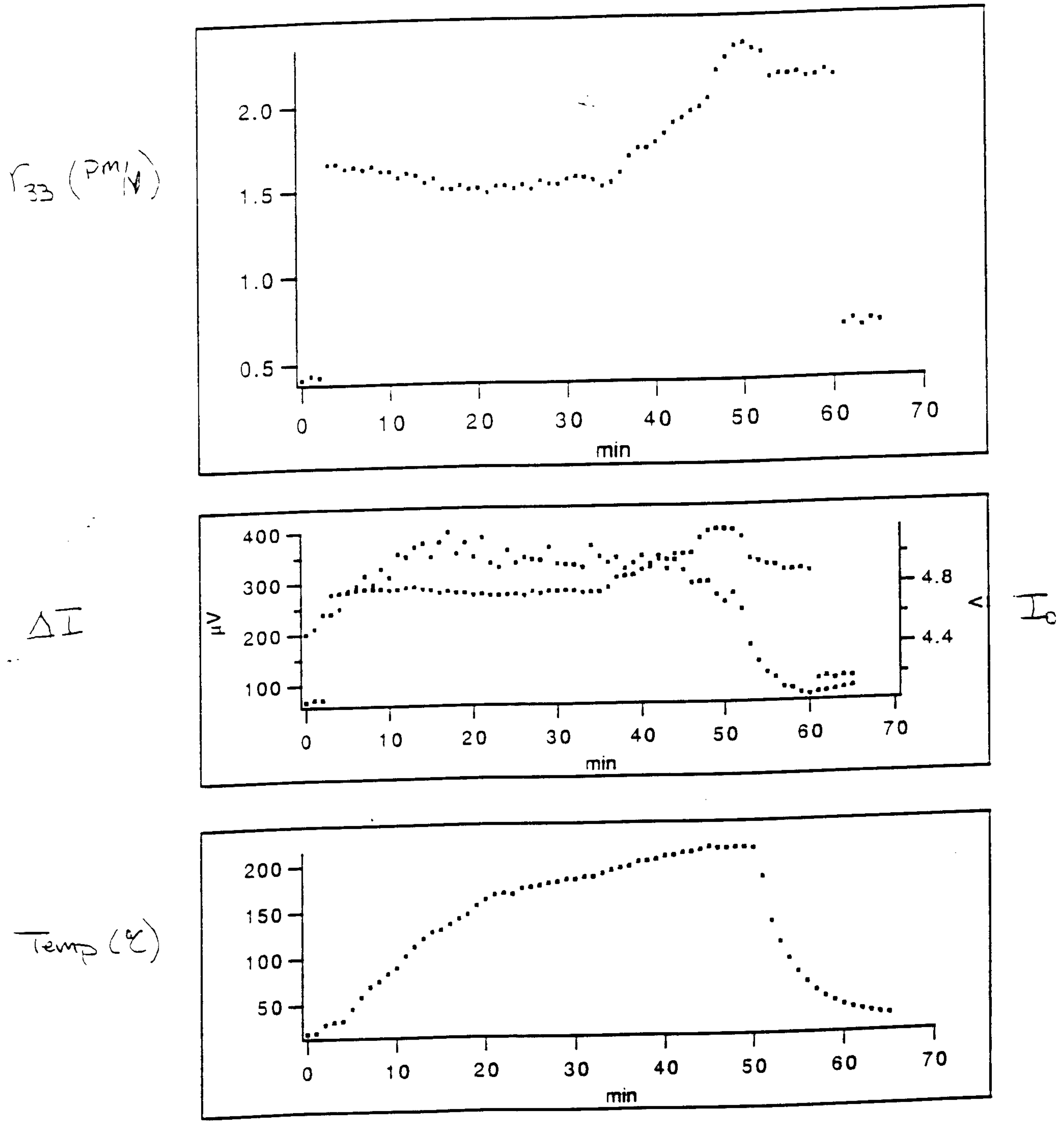
Figure 1.10



Sample 35A 90V/micron Visible

AF-85 with visible laser

Figure 1.11



Sample 27A

100 V/micron

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HIGH TEMPERATURE SUPERCONDUCTING PULSED LASER DEPOSITION

Task Order No. 270
Student Support Program
Southwestern Ohio Council for Higher Education

C. Brandon Lovett
Wright State University

27 December 1996

Government Task Leader
Dr. Rand Biggers
WL/MLPO

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GENERAL DESCRIPTION OF TASK ASSIGNMENT

The purpose of this Task was to maintain, modify, and update the data base consisting of information obtained on thin-film High-Temperature Superconductors (HTSCs). The data base was created under the previous Task , and continued under this Task. The data base consists of several parameters observed throughout the life of the HTSCs. Most of the HTSCs are the ceramic Yttrium-Barium-Copper-Oxide (YBCO) deposited on Lanthanum Aluminate substrates by the process of Pulsed Laser Deposition (PLD). This data base is the most rational way to track and view the information obtained from the films. The data base was created using *4th Dimension 3.1* software. The data base is a rather extensive compilation of the data gathered on the YBCO films, starting with the make up of the substrate, through the growth process, and technical measurements of the film.

The reason for this data base is the ability to track what growth parameters produce certain film characteristics, desirable or undesirable. This allows researchers to see the effects of growth parameter combinations on the micro structure and properties of the HTSCs. The data base currently contains 180 different parameters subdivided into four major categories. These 180 parameters alone times 750 films show the need for this data base.

The information stored in the data base serves several purposes. The main purpose is a table for the application of growth parameters. However another important aspect of the data base is acting as an easily accessible information resource needed for publications. The most recent publication was a poster at the August 1996 ASC meeting in Pittsburgh.

DESCRIPTION OF RESEARCH

As stated earlier the objective of this task was to maintain, modify, and update the data base for storing and referencing data collected on HTSCs. This data base was originally constructed and modified using *4th Dimension 3.1* software. The software has since been updated to *4th Dimension 3.2.* The data base currently occupies approximately 2.0 megabytes of hard disk space. The data base contains information concerning 750 different films grown at the WL/MLPO facility. Currently modifications are being made to store information on films produced at other facilities. Each entry contains 180 different fields of information. The data base is divided into sections with each section having smaller categories. The major divisions consist of growth parameters, Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), AC susceptibility measurements, and critical current transport measurements. Information obtained from Dr. Biggers and Dr. C Varanasi (growth parameters), Dr. Moser (AFM/SEM), Dr. Maartense (AC susceptibility), and Mr. Peterson (transport), is entered into the data base. The data is made available to all who wish to view it by means of file sharing over the Ethernet.

The equipment needed to complete this task is fairly basic:

1. Apple Macintosh IIci computer-controls the main computing requirements.
2. *4th Dimension 3.2*- the software program in which the data base is written.
3. *Delta Graph Pro 4.0*- the application program used to graph and view the data in the data base.

Most of the information in the data base was retrieved from technical lab journals. More recent films were grown by automation, thanks to Mr. Murray and Mr. Lubbers. The information for the data base was obtained through a computer interface over the network.

The data is analyzed and used by importing the information into *Delta Graph Pro 4.0*. Delta Graph allows different parameters of the data to be viewed together in graphical form. Once the graphs and tables are viewed, trends can be observed from the presented information. This software is used to graphically show the trends observed with respect to a controlled variable. These graphical plots are used in publications.

RESULTS

This task has provided an easily accessible data base for use throughout the High Temperature Superconducting Team. The data base has given insights to what growth parameters can be modified to produce a high critical temperature superconductor. This is the first step in the development of HTSCs for industry. Superconductors will revolutionize electronics once they are understood. Superconductors have the ability, once reaching a super conducting state, to allow the flow of electrical current with no resistance or loss of energy. High Temperature Superconductors become superconducting around 90°K which is easily attainable at liquid nitrogen temperatures. Conventional superconductors work at very low liquid Helium temperatures not easily attained. The cost of working at liquid Helium temperatures is much greater than that of liquid Nitrogen, thus making HTSC's a more cost effective alternative.

The data base work is continually being modified and enlarged. Currently, the format is growing to include HTSCs grown at other facilities for WL/MLPO using similar and other growth techniques. Another area of expansion is new superconducting ceramics and new substrate materials being researched by Dr. Varanasi. These new ceramics are showing a promising trend of Tc's in the low to mid 90°K range. Attaining a working knowledge of the growth mechanisms will provide a means of further understanding HTSCs. Once fully understood, HTSCs could be tailor made for specific purposes which may bring another technical revolution.

FATIGUE OF METALS AND METAL MATRIX COMPOSITES

Task Order No. 271
Student Support Program
Southwestern Ohio Council for Higher Education

Frank C. Boller
University of Dayton

27 December 1996

Government Task Leader
Dr. Theodore Nicholas
WL/MLLN

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I would like to express my gratitude to Joe Kroupa for his patience, guidance, and help as I completed this Task. To both Dr. Theodore Nicholas, the Government Task Leader, and Joe Kroupa I thank you for taking the time to explain the principals being used in this Task as I completed my work. Next, I want to thank all the members of the University of Dayton Research Institute team and the professionals at Wright Labs for giving me their time, patience, and expertise. Lastly I want to thank the Student Support Program at the Southwestern Ohio Council for Higher Education for giving me the opportunity to gain this experience that has been immeasurable to me.

TASK ASSIGNMENT

The objective of this Task was to evaluate fatigue and thermomechanical fatigue characteristics of several advanced titanium matrix composites as well as neat titanium matrix or pure titanium sample. The work completed under this Task was the development and evaluation of a FORTRAN computer code that accurately depicted a titanium matrix composites' response to a given loading. The computer code developed under this Task was based on a previous version of an existing computer code. The existing computer code was adapted into the new code by adding new material models of the titanium matrix composite. These new material models, which are essentially just a series of equations, were based on previous research done by University of Dayton Research Institute personnel. Another change to the existing code made was the addition of a time cutting scheme to speed up the operating time of the program. Once the new material models and the time cutting scheme were inserted into the existing code, the new code was checked for its accuracy relative to the previous version of the program.

METHOD OF RESEARCH

The process by which the new FORTRAN code was develop was basically an iterative process. The first step in the development of the new code was the addition of the new material models. After the addition of the new models, the new program was tested against the old program for both its accuracy and efficiency time wise. Although the new program at this stage was found to have an acceptable deviation from the old code, the time required to complete the calculations was far too large to make the program practical for use. The next step taken was to determine the portion of the program in which the most time was being spent and then formulate a way to increase the efficiency of that portion. The solution devised was a time cutting scheme in which a section of code was not executed every time, but the previous values of the section of code cut out was used again. The omitted section of code was executed when a certain amount of change in the answers from the program occurred. At this point, the process of comparing the solutions generated by the new program to that of the old program was used to verify that the program was indeed still producing viable solutions. This testing consisted of comparing not only the solutions of the various material types that the code was designed to emulate with the solutions and run times from the old code, but also with the time efficiencies of each program.

This process was repeated several times to find a reasonable compromise between speed and accuracy. The solutions were considered to be the same when a 1% deviation or less was reached between the old program and the new program. Work was begun at the end of this task to compare the results of the new code with a totally different FORTRAN code designed to serve the same purpose; however, this comparison was never completed as time did not permit for the completion of this comparison. The work completed on this other program included the introduction of the new material models into the FORTRAN code; however, testing of the code was incomplete at the end of this task, since viable solutions were not being produced by the program.

RESULTS

The newly developed code allows for a prediction of a materials' response under a cyclic loading, which in turn allow engineers to be able to determine what processes through which to take a material to obtain a certain result without actually having to physically test a specimen. The other advantage to using this newly developed code is that in running a simulation of a specimen being placed under a loading of many hours takes only a matter of minutes rather than the many hours or even days that it would take to perform the actual test. Although this process will never be able to fully replace the need for physical testing of new materials, it may lead to a faster innovation of better materials.

ORTHORHOMBIC TITANIUM MATRIX COMPOSITES

Task Order No. 272
Student Support Program
Southwestern Ohio Council for Higher Education

Michael J. Shepard
Wright State University

27 December 1996

Government Task Leader
Mr. Paul Smith
WL/MLLN

ACKNOWLEDGMENTS

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TASK ASSIGNMENT

Introduction:

Non-uniform distribution of fibers, particularly fiber clustering, in metal matrix composites can result in substantial degradation of mechanical and fatigue properties. It is believed that these distribution defects contribute to failure in most mechanical testing specimens. At this time processing complications make it impossible to ensure that fiber spacing is uniform, thus understanding the effects that these defects can have on the behaviors of metal matrix composites is crucial.

Background:

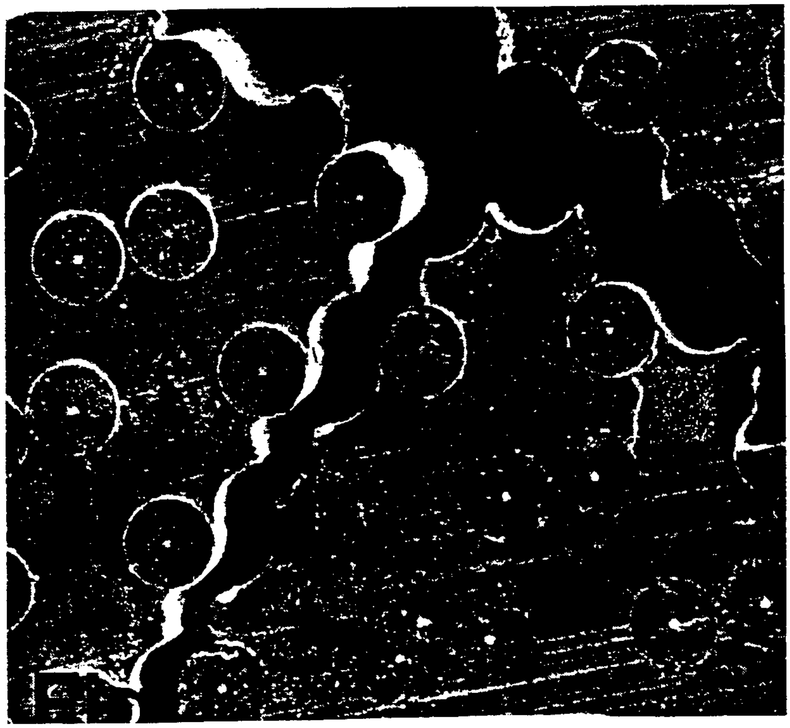
The non-laminate production methods used to produce the subject material have been shown to produce non-uniform fiber distribution in a very high percentage of production. This lack of uniformity means that significant variation can occur in the properties of different regions of one composite panel. Since materials of this class are required for use in next generation of high performance military aircraft, it was determined that it was necessary to develop tools to predict what properties one could expect in a composite panel with a given fiber macrostructure.

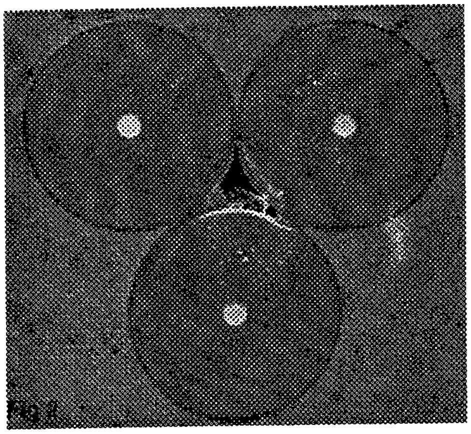
The first phase of this project consisted of an extensive series of fatigue, compressive and tensile strength testing on specimens from multiple panels from different production runs. Tensile and compressive strength tests were conducted both longitudinally and transverse to the fiber direction. This phase is nearing completion, with only the fatigue testing remaining incomplete.

The second phase of the project, now underway, is to collect data regarding the fiber macrostructure of the tested specimens, and to examine how this data correlates to the mechanical and fatigue properties of the tested specimens. Specimens are prepared using standard metallographic procedures for metal matrix composites and the structures are analyzed using both scanning electron and optical microscopy. Computerized image analysis is then used to facilitate the collection of a statistically significant amount of data. The data of chief interest in this analysis is the percentage of fibers that are part of doubled, tripled, or other fiber structures, and the angle between the major axis of any multiple fiber structure and the x-axis of the digitized image. This last statistic gives a good indication of the orientation of the fiber to fiber interface in multi-fiber structures. This interface may be acting as a small crack, and thus its orientation is relevant to the strength of the specimen. It is believed that mechanical and fatigue properties will be a strong function of these statistics, particularly under loading transverse to the fibers.

It is believed that there are two ways to predict the mechanical properties. First, the composites "weakest link" with respect to the loading conditions will fail first. Following this local failure, the remaining composite cross-section will be subjected to an increased load almost instantaneously, often causing global failure. Knowing that this "weakest link" will probably be some sort of multi-fiber structure, property prediction then becomes an issue of classifying which fiber structures will be the weakest under what loading conditions. This, however is only of limited use, because one cannot typically examine the fiber macrostructure of whole production runs. The second prediction tool, will be a statistical approach. Rather than searching a cross-section for the "weakest link," it is likely that it will be possible to accurately predict a range in which the strengths (and other properties) will be likely to fall, simply by calculating the percentage of fibers that are part of particular types of structures. Using computerized image analysis this is a quick and easy task. In order to develop this method, a substantial number of specimens must be thoroughly examined so it is understood what fiber macrostructures have a high probability of producing what properties.

The distribution defects fall into three categories. The most common structure produced by this non-uniform fiber distribution is the "doubled fiber," which occurs when one fiber lays directly against another. Preliminary results from scanning electron microscope analysis of fracture surfaces suggests that the fiber to fiber interface in doubled fibers may be acting like a stress crack in loading transverse to the fiber, thereby significantly reducing the potential mechanical strength of the composite. Failure has been noted to occur almost exclusively along fiber to fiber interfaces in doubled fiber structures in cases of loading transverse to the fiber. (Figure 1)





Also found, but much less commonly, is the "tripled fiber," which occurs when three fibers come to rest against each other. The tripled fiber seems to be an extremely weak structure, often having little or no matrix material in the area surrounded by the three fibers. (Figure 2) It is unclear whether on not tripled fibers contribute significantly to property degradation since the structure is so rare. It seems reasonable to assume, based on the significant voids usually present in the tripled fiber structure, that any specimen with a high proportion of tripled fibers would display inferior strength under loading both longitudinal and transverse to the fiber direction.

Also of significance are string type structures, which may contain numerous touching fibers. These structures are rare, although less so than the tripled fiber, but they can be quite large, sometimes containing five or more fibers. As a result it is conceivable that when these structures are present there may be a larger strength debit than would occur in a fiber macrostructure mostly composed of doubled fibers. This is probably more true in loading cases transverse to the fiber structures than in those longitudinal.

Summary:

Until processing difficulties can be overcome to produce uniform fiber macrostructures in metal matrix composites it will be critical that the behaviors of non-uniform structures are understood, and that accurate prediction tools are developed. The research now underway in this area holds the promise of soon providing these tools.

DEVELOPMENT OF RAMAN SPECTROSCOPIC SENSOR FOR INSITU MONITORING OF PULSED LASER DEPOSITION (PLD) PROCESS

Task Order No. 273
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 1996

Government Task Leader
Dr. Steve Leclair
WL/MLIM

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TASK ASSIGNMENT

The objective of this Task was to design a high-temperature Raman spectroscopic sensor which can be integrated into the control structure of a new Pulsed Laser Deposition (PLD) chamber being developed.

This Task supports a project directed at improving film quality and yield in the large-area YBCO superconducting thin-film manufacturing process. Traditional control techniques implement a feedback control law based strictly on environmental parameters such as chamber pressure, laser repetition rate, laser energy and substrate holder temperature. These methods have improved the deposition process. However, there are still inconsistencies between films even when grown under seemingly identical conditions. It is expected that the inclusion of film stochiometric and morphological data into the control scheme will improve the consistency with which quality films can be grown. To this end, work has begun on a new insitu sensor which can simultaneously monitor the stochiometry and morphology of the films. Additionally, this sensor can directly monitor the substrate temperature. At present, temperature measurements are of the substrate holder, not the substrate.

The insitu sensor consists of a modified Raman spectrometer that uses a high-temperature, low-noise Raman probe which can operate in the harsh environment present inside the deposition chamber. Modifications to the spectrometer include an improved Raleigh-line notch filter that allows acquisition of both Stokes and anti-Stokes Raman.

Several weeks were spent evaluating and characterizing the transmission characteristics of Rugate notch filters. These filters can be manufactured to have a very narrow stop band, which is exactly what is desired for anti-Stokes Raman. It was determined that the Rugate type filters performed better than the interference filters currently used in the spectrometer. As a result of these experiments, the manufacturers of the Raman spectrometer will be integrating Rugate filter technology into future spectrometer designs.

The focus of this Task has been to perform a set of exsitu experiments on YBCO thin films to define the relationship between the Raman spectrum and both the superconducting temperature, Tc, and the current carrying capability, Jc, of the films. This work builds on the preliminary research performed by David P. Lubbers earlier this year suggesting a relationship between the 336/500 cm^{-1} peak ratios and Tc. We have spent a great deal of time attempting to verify Mr. Lubbers' results. Although our conclusions differ somewhat on what the exact relationship between the 336/500 cm^{-1} peak ratios and Tc is, we are confident that this peak ratio is a significant indicator of Tc, and so we are continuing research in this area.

The second focus of the Task was designing a Raman probe that can operate inside the deposition chamber, while not interfering with the deposition process. The requirements for such a probe present difficulties from both materials and implementation perspectives. The materials' issues have been addressed in the technical report for SOCHE Task #212, presented in October 1996, therefore, only the implementation issues will be discussed in this paper.

Some of the most important issues are listed below:

1. Physical size. The probe must be as small as possible since the amount of room inside the chamber is limited. Also, the probe must be as lightweight as possible to allow for quick and accurate positioning. A lightweight probe also allows us to use a smaller positioning system.

2. Positioning stage. We have begun to consider what type of positioning system will be used to focus the probe at some point on the substrate. The stage must be able to move the probe in the x,y-plane to some predetermined location on the substrate. It must then have the ability to focus the probe in the z-plane for optimal signal strength. Finally, the stage must be able to reposition the probe to some protected location during deposition.

3. Separate laser excitation. Separating the collection optics from the excitation optics has advantages in terms of simplifying noise reduction. However, focusing both sets of optics at the same point will require an additional focusing and positioning system for the excitation laser. We are currently assessing the feasibility of such an approach.

Work will continue on integrating Raman spectroscopy into the PLD process. Discussions on a new probe design using micro-optics are currently underway. We expect to have a prototype operating by mid 1997.

PROCESSING AND MORPHOLOGY OF NOVEL MATERIAL SYSTEMS DEVELOPED IN-HOUSE AT MLPJ

Task Order No. 274
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 1996

Government Task Leader
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TASK DESCRIPTION

The objective of the Task was to continue to provide support in the preparation and development of laser hardened materials. The main project involved preparation of a gradient limiter polymer. The goal was to develop a limiter that would have a higher level threshold capacity than the industry standard material polymethylmethacrylate. An epoxy material was chosen as the material to be used. Previous research showed this epoxy material would be able to withstand higher levels of energy than the normal material.

RESEARCH

After discovering which material to use, the next step was processing the material into a practical, presentable shape which could then be further characterized and shown to those interested. The first step in this process was developing a mold into which the material could be placed and cured. A rubber material was chosen as the mold. Next, the correct mixture of the epoxy materials had to be found to eliminate the tackiness of the material. Trial and error were used until the correct ratio of epoxy to epoxy hardener was found. The third problem to overcome was that the material was developing a hazy film upon curing. Acetone was found to be the culprit and proper steps were taken to reduce the haziness. Once the samples were produced, light spectra was taken using a UV/VIS spectrophotometer. This data was placed into a spreadsheet to figure out the absorption and transmittance at 532nm, the wavelength of characterization.

The next step in the process was to add the dye to the epoxy material. Numerous concentrations of the dye solution were prepared and their absorbance and transmittance at 532 nm were taken using a UV/VIS spectrophotometer. From this data a calibration curve was developed using Kaleidagraph on the Macintosh computer. This was done by plotting absorbance versus concentration. Meanwhile, laser testing had found that in samples previously made, the dye was precipitating. Therefore, the next step was to determine the highest level of maximum solubility of the dye in the EPOTEK host. This project involved changing the mold to be used. A system that involved an o-ring and two microscope slides were used to develop smaller samples and save use of the expensive dye. The previous samples were then analyzed under a microscope to determine crystal size. The concentration of the smallest crystal was used as a starting point for investigation of maximum solubility. This concentration was held constant while the ration of EPOTEK B/A was manipulated. The maximum concentration that may be added to the gel host without precipitation is still yet to be determined.

Similar to the previous assignment, the milligram balance and vacuum oven were the primary equipment used. In addition, a caliper was used to determine the pathlength of each sample made. Data was analyzed on Kaleidagraph using linear regression curve fits to help generate the calibration curve. A long wavelength UV lamp was used to help curve the slide mold.

RESULTS

Recent work has suggested that the current dye being used will not be able to withstand strong enough levels of energy to be applicable. However, it has served as a good model for other dyes. Determination of maximum solubility of this dye will be an important task to complete. Research has also shown that the dye being added may need to be ultra sonicated to prevent crystals from forming. This will be a technique used, if varying the concentrations of the EPOTEK materials fails to increase solubility.

An important aspect of the Task was the use of the Wright-Patterson Technological Library. Research was done using both the library catalog and the Goldengate browser. Reports and journals were accessed that included information on techniques for determining solubility of dyes in polymer compounds.

PROCESSING OF CERAMIC/METALLIC COMPOSITE AND MONOLITHIC MATERIALS

Task Order No. 275
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 1996

Government Task Leader
Dr. Edmund Moore
WL/MLLM

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INTRODUCTION

The Cotronics Corporation, Inc. (CCI) ceramic adhesive material is being evaluated as a possible protective coating for ceramic aircraft tile. The criteria for the CCI ceramic adhesive coating is it must be able to stay attached to the aircraft tile during severe thermal conditions. These severe conditions are characterized by repeated steep thermal gradients, i.e., an increase in temperature from 70°F to 1000°F or a decrease from 1000°F to 70°F in approximately 60 seconds.

PROCEDURE

A total of six thermal fatigue specimens were sectioned from a ceramic aircraft tile. The dimensions of the sectioned test specimens were 12.7cm X 1.27cm X 1.27cm. Specimens were cleaned after sectioning with compressed air and then weighed. The ceramic aircraft tiles are composed of a porous white alumina base material that is coated with a dense black alumina silicate protective coating, in addition the alumina base material will be referred to as base material and the alumina silicate coating as dense protective coating. Two of the test specimens were not coated with the CCI coating, instead the base material of one specimen was tested and the dense protective coating of the other specimen was tested. This was done so that an observation could be made of how the aircraft tile material, by itself, reacts to a thermally demanding environment. Test specimens that were coated, received a coating of CCI ceramic adhesive or a mixture of CCI ceramic adhesive and CCI ceramic hardener. The ratio of ceramic adhesive to ceramic hardener for this mixture is 10cc:0.8cc. The CCI ceramic adhesive will be referred to as adhesive and the ÇCI ceramic hardener as hardener, moreover, the 10cc adhesive: 0.8cc hardener ratio will be referred to as a 10cc A: 0.8cc H ratio. An adhesive coating was applied to the base material of one test specimen and to the dense protective coating of another test specimen. The adhesive coating was then air cured at room temperature for 24 hours. The specimens were then weighed again. Adhesive coating weight was then determined by subtracting the uncoated specimen weight from the coated specimen weight. This procedure was repeated with two other test samples and the 10cc A: 0.8cc H coating. The coating weight data for both CCI coatings is displayed in Table 1 in the results section. Both the adhesive and 10cc A: 0.8cc H coatings were applied to the test specimens with a paint brush. The existing dense protective coating was roughed up with 240 grit sand paper before the CCI coatings were applied. This was done because the CCI coatings would not adhere to the smooth surface of the dense protective coating.

To simulate the severe thermal conditions that the CCI coatings will operate in, a special furnace and testing apparatus was developed. The furnace consists of a 59.38cm long X 6.35cm outer diameter alumina tube that sits within a 71.12cm long alumina shell which is covered with a metal heat shield. The diameter of the alumina shell is slightly larger than the outer diameter of the alumina tube and has a wall thickness of 16.51cm. Within the ceramic shell there are six electrical resistors configured in a radial orientation about the alumina tube. These resistors are the source of heat for the furnace. The furnace has a maximum temperature capability of 2912°F and the temperature is monitored and controlled by a Barber-Coleman temperature controller that is linked to an IBM compatible computer. The Barber-Coleman temperature controller is calibrated for R-type thermocouples, which is the type used, and the computer program is calibrated for S-type thermocouples. Therefore, there is a 3-4 degree difference in temperature monitored by the computer versus the temperature monitored by the controller. Positioned in front of the furnace is the specimen holding device. This device is comprised of a metal boom attached to a computer driven pneumatic cylinder. The metal boom is a piece of light weight corner steel that has equally spaced holes down its length. In the center of the metal boom there is a hollow, thermocouple containing, alumina rod which protrudes over the end of the boom. Test specimens are attached to this protruding portion of alumina rod with high temperature wire and ceramic adhesive. The alumina rod is also attached with high temperature wire to the metal boom. The specimen thermocouple, which is the thermocouple that resides within the hollow alumina rod, is attached to the specimen's surface with ceramic adhesive and a short piece of thermocouple wire. The ceramic adhesive is cured at 160°F for 1 hour followed by a cure at 572°F for 1 hour. A computer controlled cooling fan is located next to the test specimen to increase specimen cooling rates.

This system works on temperature set points and dwell times that are programmed into the computer. The temperature set points are specimen temperatures, not furnace temperatures. The computer monitors the specimen temperature through the thermocouple that is attached to the specimen's surface. For this particular experiment the computer was given minimum and maximum temperature set points of 73.4°F and 1094°F. Once either of the specimen temperature set points was reached, the computer would hold the specimens at the given set point for 120 seconds. During this 120-second dwell period, specimens would often reach a temperature that was three or four degrees higher then the programmed specimen temperature. At the end of the 120-second dwell time, the computer would activate the pneumatic cylinder and either extend the specimen into or retract the specimen out of the furnace. Once the specimen had been held at the maximum temperature for 120 seconds, the specimen would be retracted from the furnace and the computer would activate the cooling fan which would increase the specimen's cooling rate. All of the six specimens tested were cooled to the minimum set point temperature in less than 60 seconds. After the specimen had spent 120 seconds at the minimum set point temperature, the computer would activate the pneumatic cylinder and extend the specimen into the furnace. All of the six specimens tested were heated to the maximum set point temperature in less than 60 seconds. The computer counts the completion of the dwell time at minimum temperature and maximum temperature as one cycle. The six specimens' tested were cycled 150 times.

RESULTS

The CCI coating weights are given in Table 1. The goal is to have a coating that creates a weight gain that is no greater than 100 g/ft^2. Specimen numbers 4-6 meet this goal and specimen number one is very close to meeting the weight gain goal. The method used to apply the CCI coatings, a small paint brush, is the most probable cause for the variation in coating weight gain and the failure of the adhesive coating on specimen number three to meet the weight gain goal. The CCI coatings are all quite viscous and the paint brush used to apply the CCI coatings is unable to make coatings that have a uniform thickness. Therefore, there will be a variation in coating weight.

Previous to the thermal fatigue testing, the CCI coatings were scratched with a sharp object to roughly gauge the hardness and adherence of the CCI coatings. In Figure 1, the appearance of the adhesive coating put on specimen number three can be seen. Note the roughness of the coating and the paint brush contours. The 10cc A: 0.8cc H coatings are not as rough as the adhesive coatings, but the paint brush contours are still evident, as seen on specimen number six's 10cc A: 0.8cc H coating in Figure 2. There was no noticeable difference in the hardness, adherence or appearance of the CCI coatings when comparing those applied to the aircraft tile base material to those applied to the dense aircraft tile coating. Upon completion of thermal fatigue testing, the CCI coatings were scratched again with a sharp object. There was no difference in the hardness, adherence or surface appearance of any CCI coating, as seen in figures three and four. Additionally, there were no noticeable differences in the aircraft tile base material or the aircraft tile dense coating. The only notice difference was a slight discoloration of all the CCI coatings. Both the adhesive and 10cc A: 0.8cc H coatings met the criteria of surviving a severe thermal environment.

Table 1

Sample #	Sample Description	Uncoated Weight	Coated Weight	Weight Gain
3	Adhesive/dense coating	5.6671g	7.4085g	100.31g/ft^2
4	Adhesive/base material	4.8063g	6.4484g	94.59g/ft^2
5	10ccA:0.8ccH/dense coating	5.7929g	7.1884g	80.39g/ft^2
6	10ccA:0.8ccH/base material	4.8721g	6.5027g	93.93g/ft^2

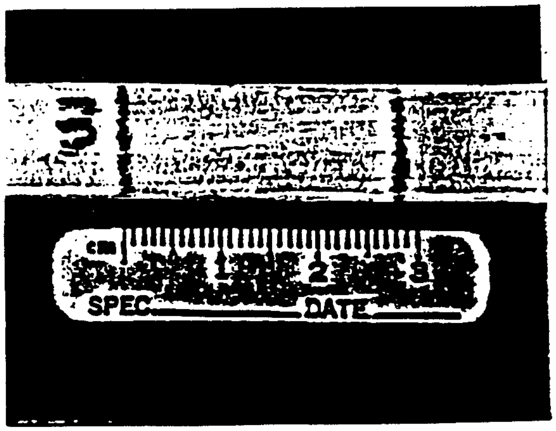

Figure 1. Adhesive coating applied to dense aircraft tile coating before thermal fatigue testing.

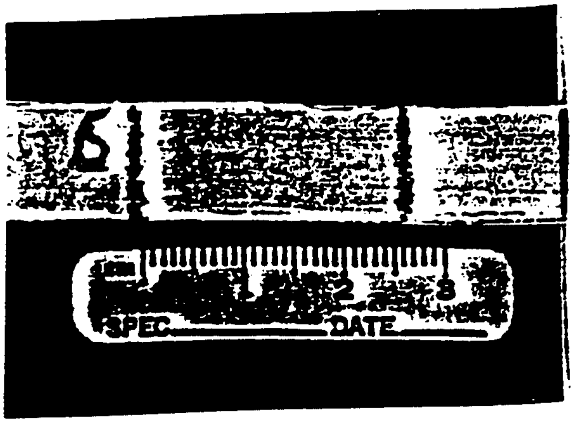

Figure 2. 10cc A:0.8cc H coating applied to base material before thermal fatigue testing.

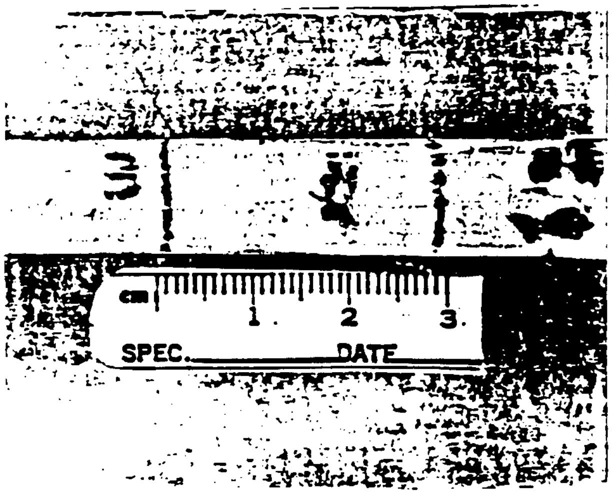

Figure 3. Adhesive coating applied to dense aircraft tile coating after thermal fatigue testing.

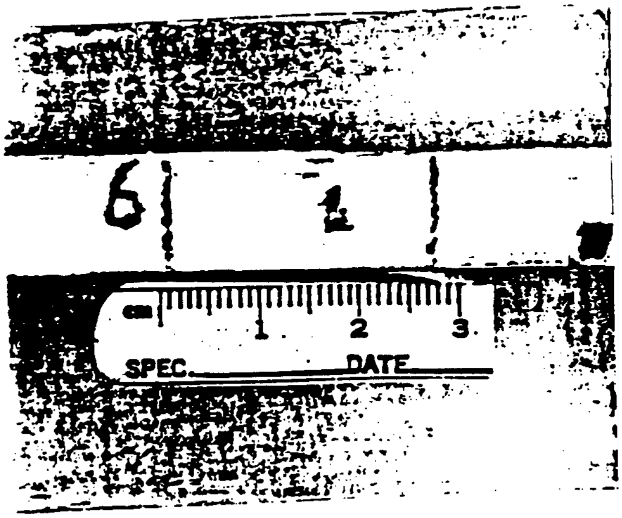

Figure 4. 10cc A:0.8cc H coating applied to base material after thermal fatigue testing.

LIFE PREDICTION METHODS FOR AEROSPACE ALLOYS AND METAL MATRIX COMPOSITES

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Southwestern Ohio Council for Higher Education

Deborah Williams
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Government Task Leader
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TASK ASSIGNMENT

Introduction

The need for materials that will provide better elevated temperature performance in advanced turbine engine components has led to the study of fiber reinforced titanium aluminides. One promising titanium aluminide is Ti-22Al-23Nb (atomic percent). Heat treatments have been shown to improve the properties of this titanium aluminide matrix. However, it is important that the elevated temperatures used in the heat treatments do not degrade the strength of the continuous fiber reinforcement.

The study was undertaken to determine the effect of heat treatment on the strength of silicon carbide (SiC) fibers. Four fibers were chosen for the study: Trimarc1, SCS-6, Ultra SCS, and Large Diameter (LD) Ultra SCS. The SCS-6, Ultra SCS, and LD Ultra SCS fibers have a carbon core surrounded by a silicon carbide mantle and a silicon doped carbon coating. The Trimarc1 differs from the other fibers in that it has a tungsten core. Two heat treatment schemes were applied to the fibers themselves as well as to the fibers consolidated in the titanium alloy matrix. (For testing, the fibers were extracted from the matrix after the heat treatments.) Characterization included room temperature tensile testing of the fibers, evaluation of the fiber/matrix reaction zone growth, fiber fracture and matrix microstructure.

Much of the following work was accomplished in the previous task. However, to present the information in a composite's workshop in Orlando, Florida and later in July 1997 at the Eleventh International Conference on Composite Materials in Australia, this task focused on pulling all the data together and filling in any missing parts.

Procedure

The fibers were tensile tested and examined in five conditions: 1) As-received; 2) Heat treated at 1085°C; 3) Heat treated at 1160°C; 4) Consolidated, heat treated at 1085°C and then chemically extracted, and 5) Consolidated, heat treated at 1160°C and then extracted. After each tensile test, the tensile strength was recorded and all fracture surfaces, except those that shattered or broke in the grips, were carefully mounted for further examination on the scanning electron microscope (SEM).

Using the SEM, each fiber fracture surface was examined, and a determination was made as to the possible source of the failure. Most fractures could be identified for being initiated at the surface, mid radius or core. A common practice in determining a fracture initiation site is to follow the "river marks." For example, a surface initiated flaw is characterized by lines "flowing" toward a defect at the edge of the fiber. A mid radius flaw is characterized by lines converging toward an internal defect. Both surface and mid radius failures usually corresponded to lower tensile strengths with surface failures having the lowest strength. Core initiated failures, which most often occurred at higher tensile strengths, were characterized by radial lines emanating from the core. Often the fracture initiation site was not evident because the primary fracture surface shattered off upon failure, thus leaving a secondary fracture. These secondary fractures occurred at higher tensile strengths similar to core failures. Photographs were taken of a representative fracture type for each fiber condition. In addition to the characterization of the fiber fracture type, photographs and measurements were also taken of the Trimarc1 reaction zone between the tungsten core and SiC mantle in the as-received and heat treated conditions.

In addition to examining the individual fibers, the composite was also examined in the as-received and heat treated conditions. For a comparison of the three conditions, photographs and measurements were taken of the fiber/matrix reaction zone and the carbon coating thickness.

RESULTS AND ANALYSIS

For analysis, tensile strengths were plotted against the probability of survival and compared to the information gathered on the SEM. At the .5 probability of survival, the strength of the SCS-6 and the Ultra SCS fibers were unaffected by the heat treatments; however, the Trimarc1 and Large Diameter Ultra SCS showed significant decreases in strength (see Table 1). This strength reduction in the Trimarc1 fibers was attributed to the Tungsten core/SiC mantle reaction and by internal defects exacerbated by the differing coefficients of thermal expansion between the fiber and matrix. These internal defects were evidenced in the higher number of mid radius failures in the extracted fibers. This was particularly evident in those heat treated at 1085°C in which the bare fibers had no mid radius failures. Forty-five percent of the extracted fibers were mid radius failures. The strength degradation in the LD

Condition	Trimarc1 (MPa)	SCS-6 (MPa)	Ultra SCS (MPa)	LD Ultra SCS (MPa)
As Rec'd	3100	4400	5600	6300
1085C	3700	4000	5400	5600
1085C + Extracted	2200	4500	5200	1000
1160	2200	4200	5000	5200
1160C + Extracted	1600	4300	5400	1800

Table 1

Ultra SCS appears to be due to insufficient thickness in carbon coating. Measurements of the carbon coating of the LD Ultra SCS compared to the Ultra SCS show that the thickness of the LD Ultra SCS carbon coating is much thinner.

MATERIALS DISCOVERY SYSTEM

Task Order No. 277
Student Support Program
Southwestern Ohio Council for Higher Education

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27 December 96

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I would like to thank the following persons for suggestions on how to handle difficulties faced throughout this Task, Dr. Allen Jackson and Dr. Steven LeClair. Their help on various subjects gave me insight into how to go about solving similar type problems and will be an asset in my future.

TASK ASSIGNMENT

Several methods were used in the attempt to classify known elements/compounds. The intention being to produce a reliable tool in classifying new substances in various ways toward a goal of improving existing technologies. The algorithm upon which these methods depend is a product of Victor Gladdun. The premise of these programs is to train a neural net using known data and then running the recognition data set through this information net. Once through the net the programs would give an analysis of how accurate these predictions were.

The focus of recent work is not in testing the existing programs, but is to make sure the data inputted is of correct format and to find a way to input multiple runs without taking up all the users' time. Running the existing programs has recently had some success to the point that the results produced can be checked against empirical data. The problem of the existing programs is that they require the user to be at the computer monitoring the programs and telling the programs what to do next at various points. This is seen as being not efficient use of users time which could be spent on other problems while the programs are running.

To become time efficient in the task set forth, a set of programs has been written to manage the programs. These programs ask the user to enter where the data is coming from for both the training and recognition set and where the results will go. Another piece of information asked for is how many runs of this data are required. Using this further information, the managing program can run the programs to create the neural nets and outputs the results in files that can be read at the convenience of the user. This set of managing programs is a great asset due to the fact some of these runs takes up to 2 hours each.

Output generation of the programs are greatly dependent of the quality of the input. At first, the only way to make sure the data is of correct format, the user had to scan through the entire data set to catch anything wrong. To make this particular task more efficient, several macros were written in Microsoft Excel addressing this problem. The following were the guidelines that the macros followed. The first column names had to be less than eleven characters long. The data had to be within the bin ranges listed at the top of the data set. All data excluding the first column was to be numerals only.

Using these various programs as tools in the process of data classification has greatly enhanced the productivity of the task set. Now all one has to do is get a data set, run it through the macros, and specify how many runs are to be tabulated on them. Upon receiving this information, the manager program takes over leaving the user to focus on other facets of the goal of new productive material for the growth of technology.

QUALITATIVE MATERIALS DESIGN

Task Order No. 278
Student Support Program
Southwestern Ohio Council for Higher Education

Kurt D. Keener
Wright State University

27 December 1996

Government Task Leader
Dr. Steven R. LeClair
WL/MLIM

ACKNOWLEDGMENTS

I would like to thank the following people for helping me during my Task. I would like to thank Jeff Heyob. Jeff helped me while I was learning new programming techniques that would be used throughout my Task. I would like to thank Steve Adams who helped me on several occasions with programming problems. I would like to thank Sam Laube for giving me challenging assignments which gave me an opportunity to use the knowledge accumulated during school. Sam also gave me several ideas and is helping me to fashion research and development tools I undoubtedly will use in my future. I would also like to thank Steve LeClair and the staff at SOCHE for making the position of student research assistant available. Finally I would like to thank all the employees in the lab who have assisted me during this Task.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

This particular Task involved several areas of knowledge. Being fluent in a computer language such as C was important; be able to look at a problem from several viewpoints, to reach a solution, and be willing to learn new ideas, while building upon one's on personal ideology, quickly and efficiently.

Most of the research involved in this Task was directed toward the field of Pulse Laser Deposition. A software controlled laser beam control system was developed, which would quickly allow the user to specify a rectangle target of desired dimensions.

The current process involves the laser being directed onto the PLD target in a predictable way. The beam progresses across the target in straight lines. This seemed to cause problems with overheating the surface of the target. This overheating may lead to reactions on the surface of the target which cause impurities to form. The goal was to increase the purity of the deposited film, by reducing the effects of excess heating. One way to reduce the effects of heating was to create a mirror control system that would scatter the laser pulses randomly across the surface of the target.

DESCRIPTION OF RESEARCH

The initial steps in the research process consisted of laying out a general plan and getting a good understanding about what was expected from the computer program. The computer program was to operate in a "stand alone" fashion so that it could be utilized on any Macintosh computer, independent of processor speed or system specifications. Once the expectations were laid out for the software, the code was ready to be written.

A National Instruments DIO 24 data acquisition board was installed in a Macintosh computer. This board was connected to a DSC2000 interface, which was directly connected to the XY3037 mirror system. The DSC2000 accepted three signals from the computer. It accepts the position data through a 16 bit bus, an X position strobe signal, and a Y position strobe signal.

The computer program had to generate 16 bit random numbers which would be sent to the DSC2000 and interpreted into mirror positions. The program sends random position data at a rate of at least 100 cycles per second. This process continues until another user interrupted the program via an Apple Event and sent the program data specifying a new range on the target. This range could be specified by four numbers. The four numbers are sent as a vector in the form, (X offset, Y offset, a scale, b scale), in which all numbers would be in the range zero to 65535. The X and Y offset values determine the starting point in the target field, a scale would determine the x axis width of the rectangle, and b scale determines the y axis width of the rectangle.

For the mirrors to function properly, the computer program had to send the data in the correct manner. The first step in the program was to create a random number within the specified range. This value was sent to the DSC2000 as the random X axis position. The next signal sent was the X strobe signal which informed the DSC2000 to interpret the number as an X position. This process was repeated for a Y axis value and both processes continued in a loop until an interruption was sent by another user.

The approach of writing the software consisted of building small components of the program and then connecting them all instead of attempting to write the complete program at once. The first module simply generated the X and Y random numbers and graphically displayed them on the screen. After inspection and approval, the program was updated to send the random data to an output port connected to LEDs. This let the user test the speed at which the data was being output, by setting up an oscilloscope.

During the construction of the software, it became obvious that the program would have to be separated into two components. The mirrors were going to be operated by a single computer that would be accessed through a network connection. Therefore, the computer program needed to be broken into "receiving" and "sending" programs. The "receiving" program was going to be constantly running on the computer connected to the mirrors. This constantly running program would center the mirrors and wait in that state until the "sending" program sent new positioning data.

RESULTS

Upon completion of the software, the mirrors were setup for testing. All connections were established and a laser pointer pen was used to view the patterns created by the movement of the mirrors. Within a few minutes the speed at which the data was obviously being sent to the mirror interface, was greatly exceeding the rate at which the mirrors could handle. After seemingly perfect operation the mirrors would simply stop. This was due to the overload of the data. The system was tested until a safe and steady operating speed was discovered. The program needed to wait 18 milliseconds between each data strobe signal. This delay was added to the program and the system ran as desired.

This mirror control upgrade is presently being used in the actual PLD process. Several films have been created but there is insufficient data to conclude any results about the upgraded control system. Several studies are currently underway.

Though the software is working as planned, there is still room for improvement. The "sending" program's user interface needs improvement. The user currently needs to specify things that could be coded into the program to make it easier for the user. Instead of having to enter the four data numbers, the user has to specify to which computer to send the data and then specify to which program to send the data. The ideal operation would be simply to enter the four data numbers and have the program do the rest. This addition is currently being explored.

SYNTHESIS OF AROMATIC AND AROMATIC HETEROCYCLIC POLYMERS

Task Order No. 279
Student Support Program
Southwestern Ohio Council for Higher Education

Michael Laufersweiler
Wright State University

27 December 1996

Government Task Leader
Dr. Loon-Seng Tan
WL/MLBP

ACKNOWLEDGMENTS

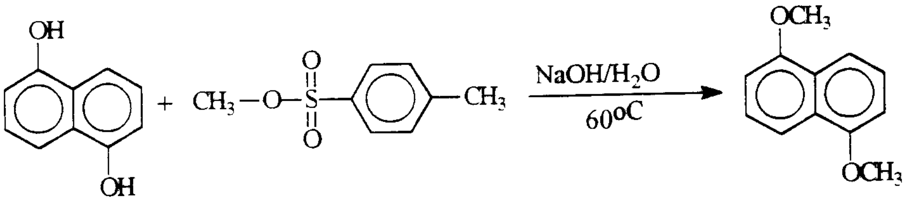
I would like to thank Dr. Loon-Seng Tan and Jerald Burkett for their guidance and advice and for the time and instruction that they have given me.

TASK ASSIGNMENT

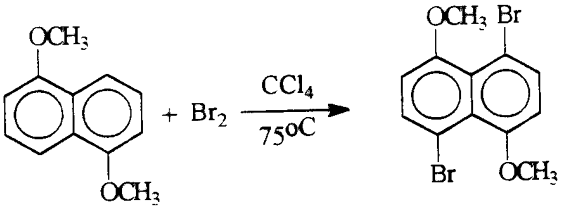
The fourth step of a multi-step synthesis was done. The fourth step was the final step in the synthesis of a material to be used as starting material in nonlinear optical (NLO) polymer applications. The product, 2,6-dibromo-1,4,5,8-tetramethoxynaphthalene, is the final product to be delivered to the NLO synthesis group. The reaction was scaled up to produce a good starting base for further syntheses. Two, 6-dibromo-1,4,5,8-tetramethoxynaphthalene may also have other polymer applications that will be explored, such as replacing the bromines with cyano or nitro groups and exploring polymerization possibilities.

The three previous steps in this multi-step synthesis were:

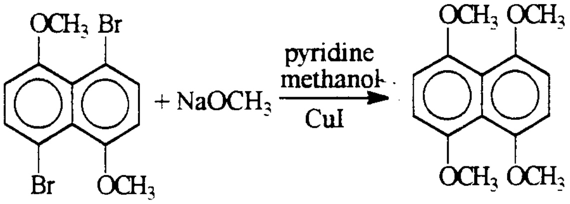
The synthesis of 1,5-dimethoxynaphthalene from 1,5-dihydroxynaphthalene:



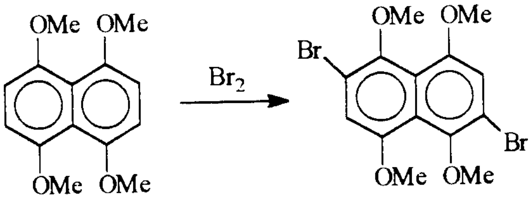
The synthesis of 4,8-dibromo-1,5-dimethoxynaphthalene from 1,5-dimethoxynaphthalene:



and the synthesis of 1,4,5,8-tetramethoxynaphthalene from 4,8-dibromo-1,5-dimethoxynaphthalene:



In the last step, into a 1000 mL three-neck flask was added 12g (48.36 mmol) into 450 mL of carbon tetrachloride (CCl_4). A condenser was attached and the solution was brought to reflux. A mixture of two molar equivalents of Bromine (Br_2) and 75 mL CCl_4 was added dropwise to the reaction solution. As bromine is added, a dark solid precipitates. After all bromine was added, 100 mL of CCl_4 was added to the solution and it was allowed to stir at reflux until all solid goes into solution and solution colors changes from brown to a light yellow. The solution was allowed to cool overnight and a vacuum aspirator was used to remove HBr. The Product precipitated as solution cooled. The product was recrystallized in Heptane.



The reaction was run with 85% yield. The product was characterized using melting point, elemental analysis, IR spectroscopy, Mass spectrometry, and C^{13} NMR. This product will be used as starting material in NLO polymer synthesis, and in future syntheses for polymer target molecules.

ELECTRICAL AND MAGNETIC PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

Task Order No. 280
Student Support Program
Southwestern Ohio Council for Higher Education

Kueiming Max Lee
University of Dayton

27 December 1996

Government Task Leader
Mr. Timothy L. Peterson
WL/MLPO

ACKNOWLEDGMENTS

I would like to thank the Southwestern Ohio Council for Higher Education (SOCHE) for their ongoing support and my Government Task Leader, Mr. Tim Peterson, for his technical support.

I also would like to thank Douglas Buchanan, Dr. Eric Moser and Dr. Imann Maartenise from the superconductor team for their help when I started this Task.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Primarily this Task is to measure and take electrical and magnetic properties data of high temperature superconductor thin-film. It is involved with the application of many scientific techniques to investigate the properties of high temperature superconductors. The task includes preparing samples for electrical and magnetic measurements, mounting samples in Dewar, cooling samples using liquid nitrogen and liquid helium, doing resistivity and critical current density transport measurements as a function of temperature, and generating graphs and tables from computer-generated data. The collected and organized data are used to aid in analysis for the MLPO group. Besides this, the secondary task is to prepare/clean substrates for deposition of thin superconducting films.

DESCRIPTION OF RESEARCH

The main task is to operate the cryogenic system including Dewar cooling (from room temperature to 77 K), sample temperature control (at a setting temperature) and controller system including sample current control, sample voltage readouts with electronic and software package LabView. The electrical properties such as normal state resistivity ρ, critical temperature Tc, and the critical current density Jc of high temperature superconducting (HTSC) thin-film (for instance, $YB_2Cu_3O_{7-x}$ on substrates LAO or STO) are measured to evaluate material quality. This information will feed back to a laser ablation deposition group for improving HTSC thin-film growth quality and better understand the nature of high temperature superconductivity.

The sample mounting, as illustrated in Figure 1, is based on the 4-point probe technique similar to the standard semiconductor device measurement. This technique is to eliminate the contact resistance along the measurement circuit. The resistivity of thin-film is measured as a function of temperature from room temperature down to the temperature at which the superconductivity occurs (the cool down process). The voltage across the thin-film as a function of increasing current passing through the thin-film at a constant temperature is measured to determine the critical current density that can be carried by the film from superconducting state to normal (non-superconducting) state.

For the magnetic properties measurement as shown in Fig. 1, the thin-film sample is placed in parallel to or perpendicular to an external magnetic field ranged from zero to 12k Gauss under the same environment as described in the electrical properties measurements. The relation between Tc, ρ and Jc and the sample direction are then measured and recorded.

The other area to work with is to clean the substrates before HTSC thin-film is grown on it. This is involved with chemical and ultrasonic cleaning processes; the samples are soaked in TCL, acetone and methanol solutions within an ultrasonic vibrating container in that sequence for a certain amount of time. The cleaning substrates are very critical to the quality of grown HTSC thin films. Any contamination can ruin the HTSC properties. After chemical cleaning, the substrates are baked in a UV ozone oven for an hour and stored in clean holders.

RESULTS

The typical resistivity as a function of temperature is shown in Fig. 2. The range of resistivity for in-house thin-film is 200 to 300 μΩ-cm at transition temperature. The critical density measurement is illustrated in Fig. 3. It has a typical value of 5×10^6 Amp/cm^2 at the temperature of 77 Kelvin.

B ⊥ line 2. B ⊥ film
filenames MCM6/Ic/77/xx.   xx=Magnetic filed strength in KG

Device mounting diagram:

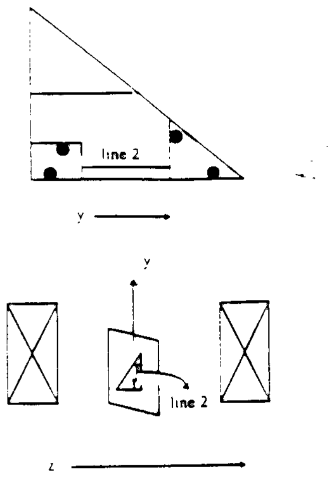


Figure 1.

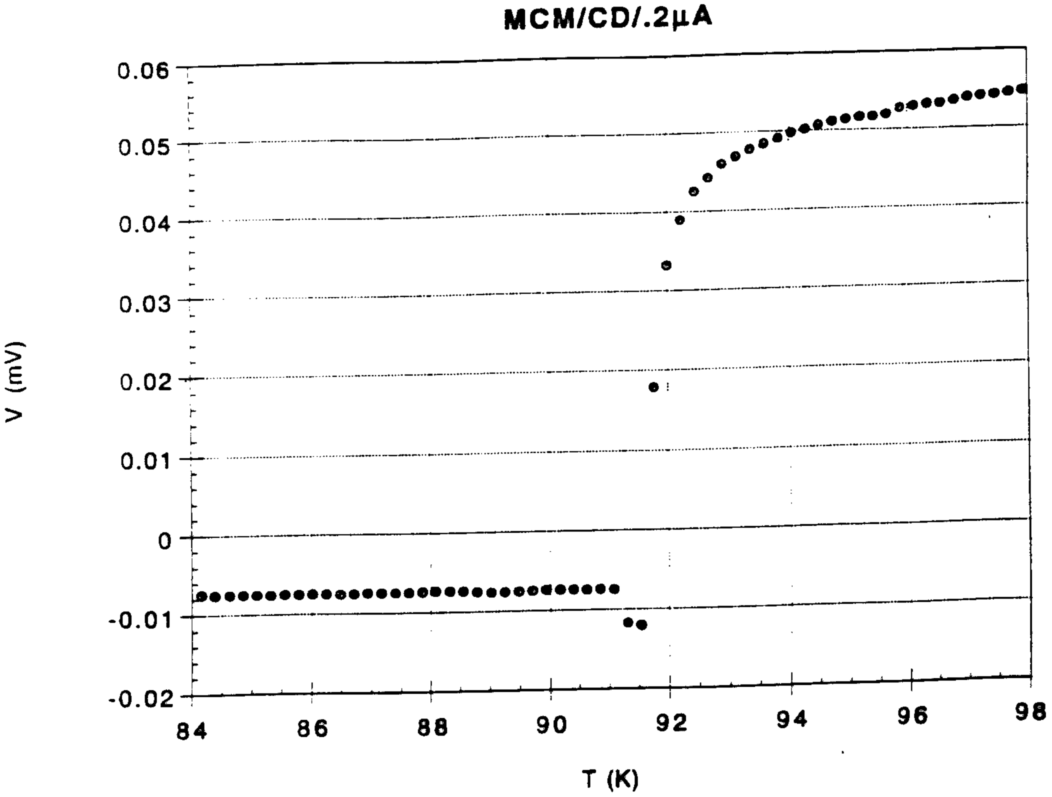


Figure 2.

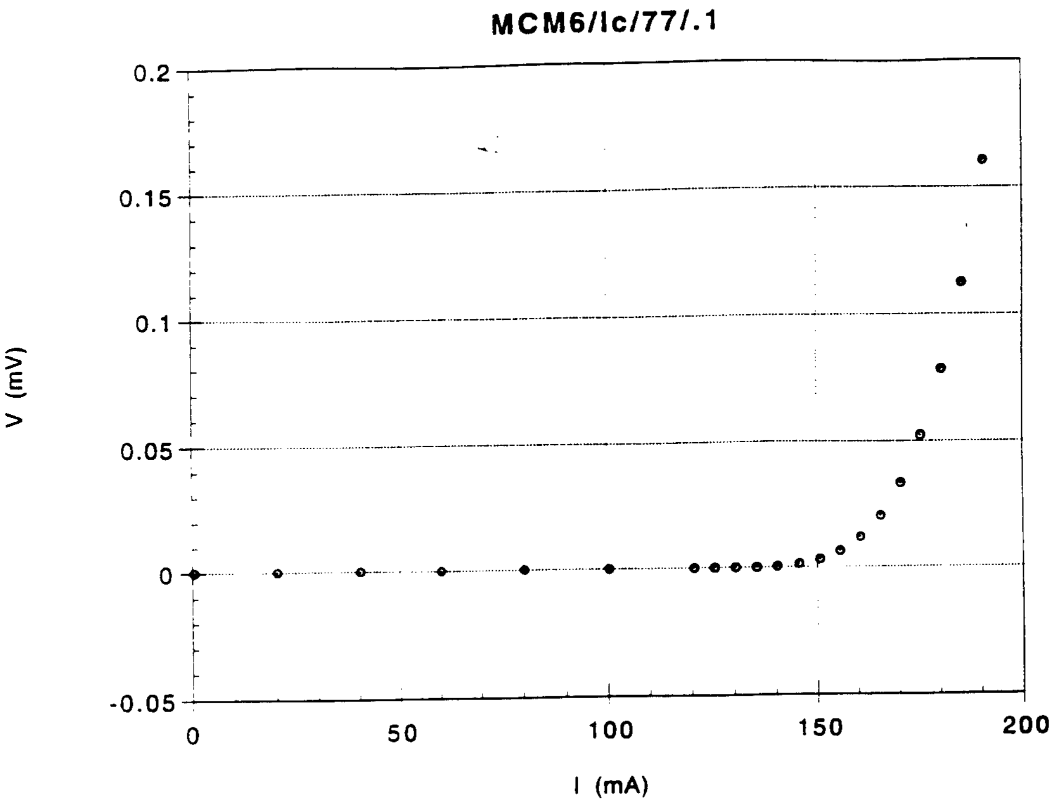


Figure 3.

BRITTLE MATRIX COMPOSITE STUDIES

Task Order No. 281
Student Support Program
Southwestern Ohio Council for Higher Education

Tracy Criswell
Wright State University

27 December 1996

Government Task Leader
Dr. Rollie Dutton
WL/MLLN

ACKNOWLEDGMENTS

Special thanks goes to Dr. Rollie Dutton for all of his help and guidance throughout the past 8 months. Thanks to Wanda Vogler and the SOCHE program for making this experience possible.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

Throughout this Task, the main objective was to fabricate a cruciform epoxy mold with monofilament Silicon Carbide (SiC) fibers. The epoxy needed to be at room temperature cure, to decrease the amount of stress on the fiber. Another objective was to fabricate borosilicate glass matrix composites with monofilament Silicon Carbide fibers by tape casting. The green matrix glass tapes, which have 50% relative density, are laminated with the SiC fiber mats that already have uniform fiber spacing. The samples are sintered at 710°C that has a 98% relative density. The purpose of these samples is to see how the fiber/matrix interface reacts with the initiation of matrix cracking.

DESCRIPTION OF RESEARCH

To make the epoxy D828 and a hardener is mixed by a ratio of 12.4/2.5. The solution is put in an oven for 1 hour at 100°C; the purpose of this is to get all the air bubbles out of the solution. The solution is then poured into the mold, which is made of silicon, and takes approximately 3 days to harden at room temperature.

The recipe for the tape casting slurry is given in Table 1. The slurry is prepared in four steps. First, a paddle stirrer is used to disperse the Menhaden fish oil into 40% of the solvent. Next, the borosilicate glass powder (average particle size ≈ 9(m) is added to the slurry and mixed for 20 minutes. Following this, in a separate beaker the binder and plasticizer are mixed into the remaining solvent until the binder is well dissolved (≈ 20 min.). Using the paddle stirrer is an advantage to ball milling because not as much material is wasted and it takes a lot less time. The two slurries are then combined and mixed for another 20 minutes, after which the tape is cast. The doctor blade is typically set at .32 mm above the glass bed of the tape caster. The tape takes approximately 3 hours to dry. It then has a final thickness of approximately .18mm and a relative density of approximately 50%.

The tape is removed from the glass and cut into 3 inches by 3/4 inch rectangles. The fiber mats are cut 2.5 inches by 3/4 inch so the fibers are perpendicular to the length of the tape. The tape and fibers are laminated in a Carver press with heated platens, which are heated at 93°C. The laminate is separated from each heated platen by a sheet of Teflon and a thin silicon rubber sheet. When laminating, five layers of tape and one layer of fibers are first laminated together, and then another five layers of tape are laminated on the opposite side of the fibers.

A single sample is placed between two pieces of graphfoil that is placed on a graphite block. A graphite bar is placed on top with a weight of 20 gm to prevent the sample from curling up during sintering. The sample is inserted into a tube furnace for binder burnout and sintering. The burnout cycle happens when the sample is heated at 2°C/min to 450°C and held for 1 hour with flowing oxygen. The sintering cycle happens when the furnace is evacuated and the temperature increases to 710°C at 4°C/min, held for 1 hour, and another 20 minutes with just flowing argon.

RESULTS AND DISCUSSION

The epoxy sample is progressing, and is still in its beginning stage. There have not been any samples that were good enough to test, but it looks like there will be in the future. There has been a lot of progress, and much has been learned. Within the next few weeks, a sample will possibly be ready to test.

Not much has been done with the borosilicate glass composites because of an insufficient amount of fibers. Within the next few weeks, the material needed will be received.

Table 1

Basic Recipe-Borocilicate Glass Composites

Glass Powder	48 gm
Tolulene (solvent)	35 ml
Ethanol (solvent)	35 ml
Menhaden Fish Oil (dispersant)	1.9 gm
Polyvinyl Butyral (binder)	4.3 gm
Polyglycol (plasticizer)	4.0 gm

COMPOSITES FOR INFRASTRUCTURE

Task Order No. 282
Student Support Program
Southwestern Ohio Council for Higher Education

Maggie Dougherty
University of Dayton

27 December 1996

Government Task Leader
Mr. John Mistretta
WL/MLBC

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I would like to thank all of the MLBC and UDRI staff for continual guidance and support. Special thanks to Allan Crasto for insight into development of project agendas, and data interpretation. I greatly appreciate Ron Cornwell and James Lute for daily, if not hourly, advice on any question I may have. Finally, a special thanks to my Government Task Leader, Mr. John Mistretta, for providing me with direction, encouragement, and opportunities to grow and excel.

GENERAL DESCRIPTION OF TASK ASSIGNMENT

The objective of this Task is to provide continued exposure for a civil engineering student to the arena of advanced composites and composite applications in civil engineering. Specifically, this Task involves the development of an infrastructure rehabilitation system utilizing advanced composite materials. Previous work included the development of composite plate and rod reinforcement of concrete beams. Concrete beams are reinforced to develop a means to provide a more cost effective way to repair an infrastructure. Traditional infrastructure rehabilitation includes steel plate reinforcement and beam removal and replacement. These rehabilitation forms are costly and time-consuming and result in delays or partial roadway closure to complete. The advanced composite reinforcement developed at the Materials Labs Directorate provides an efficient means of infrastructure repair.

Specific responsibilities associated with this Task include the development of overhead reinforcement installation and testing. Advanced composite reinforcement will be placed in an elevated concrete beam to mimic field conditions. Field application methodology will be developed for use in field application in the spring of 1997.

DESCRIPTION OF RESEARCH

Task work began with the development of reinforcement methodology. Advanced composite reinforcement consists of graphite composite rods, 5/16 inches in diameter. These rods are placed into grooves, precut in the concrete, 1/2 inch deep and 5/8 inch wide. The precut grooves are placed in the compression side of the beam. This is the top of the beam and is not reinforced with steel rebar. The beam is inverted with the steel-reinforced side on the top and the grooves on the bottom of the beam. This configuration forces the rods to act as the primary reinforcement instead of acting in combination with the steel rods to provide reinforcement. Rods are secured with Dexter-Hysol EA 9460. EA 9460 is a two-part epoxy material that has a working life of approximately 1 hour.

Methodology developed for the overhead application centers around the use of caulking guns to place the epoxy into the precut grooves. Several qualitative were then conducted to determine feasibility of overhead application and to detect the feasibility of overhead application in cold conditions. Materials, including empty caulking tubes and disposable jump suits to wear during the application, were also obtained. Additionally, the project was coordinated with in-house personnel and base personnel.

RESULTS

Qualitative tested showed an overhead application would be feasible. A beam mock up was created to mimic the concrete groove in the beam. A composite rod was placed in the groove and held in place with epoxy, without additional reinforcement. This was extremely important, as no additional means would be required to hold the rods in place while bonding with the adhesive. Testing could have continued even if additional reinforcement would be required during bonding. However, this would make the bonding process more difficult and time consuming.

Additional tests were executed to learn if bonding could be done in cold temperatures. Results of a parallel plates test of the adhesive suggest a twelve-hour cure time for the adhesive in cold temperatures, which is acceptable for field application. Internal concrete temperatures were developed and compared to concrete surface and air temperatures. The test indicated a five-hour lag time between the internal beam temperature and the air temperature. This means that it takes 5 hours for the beam too warm to air temperature. Lag temperature development time is a consideration in the length of time required for the adhesive to bond. In extreme temperatures, bonding should begin in the afternoon so that beam temperature has warmed to air temperature and an accurate prediction of the adhesive cure time may be developed.

EA 9460 adhesive was mixed at various temperatures to mimic field conditions. Mixing tests indicated that mixing below 50° Fahrenheit was impossible. As a result, adhesive mixing would have to be done in a heated truck if this application were to occur in the field during cold temperatures. Workability of the mixed adhesive was also tested. This test also indicated low workability levels at temperatures lower than 50° Fahrenheit. Since adhesive would be mixed in a warm environment and immediately applied, this factor is not a consideration on field development.

Qualitative tests show a field application in cold temperatures is feasible, if adhesive mixing occurs in a warm environment. However, field application in Butler County scheduled for this December has been rescheduled for this spring. The field application has been postponed to allow for additional time for in-house testing.

Overhead beam bonding took place in-house as scheduled. Bonding was completed by a two-person crew, Mr. Ron Cornwell and I. Bonding went smoothly and efficiently. As anticipated, rods stayed in place without additional reinforcement, and adhesive did not drip excessively. The beam remained in place for 1 week and was then tested in a four-point flexural test. The beam failed in compression at 29,000 psi. This failure is close to the failure of a previous beam test of the same configuration that failed at 297,500 psi. Based on this test, overhead bonding of composite rods is a feasible option. Failure was not catastrophic, which demonstrates one benefit of this type of reinforcement. In contrast, plate reinforcement failure has proven to be catastrophic. Plans to develop tendon reinforcement further and determine the ultimate configuration for the tendons have been slated for the upcoming year.

RESEARCH ON HIGH TEMPERATURE INTERMETALLIC ALLOYS

Task Order No. 283
Student Support Program
Southwestern Ohio Council for Higher Education

Michael A. Jackson
Wright State University

27 December 1996

Government Task Leader
Ms. Monica Stucke
WL/MLLM

ACKNOWLEDGMENTS

The following people deserve a special thanks for the instruction, guidance, and the deeper understanding that they brought to the Task, Dr. Young-Won Kim, Dr. Dennis Dimiduk, Tim Schock, and Mark Dodd. If not for these individuals, this Task would not have been completed successfully.

GENERAL TASK DESCRIPTION AND BACKGROUND INFORMATION

The work during the Task period consisted of the mechanical testing of two different alloys studied during the previous Task. These were alloys of the gamma titanium aluminide and a beta niobium alloy. During the previous Task, heat treatment studies were completed to find the optimum microstructures for these materials. With this information, a second set of heat treatments was completed to produce a wide array of microstructures for use during the mechanical testing portion of this task. In the beta niobium alloy, the grain size was merely refined to remove microstructural artifacts from the extrusion process.

<u>Gamma Titanium Aluminide</u>- The second set of heat treatments produced five lamellar structures, which differed in the size of the individual grains, and one duplex microstructure. Basic metallurgical theory says that small grain sizes will produce the strongest material at lower temperatures, <500°C, whereas larger grain sizes will produce the stronger material at higher temperatures, >500°C. Using this theory, the effect of the grain size and temperature on the strength of the K3 alloy was to be studied. Small round cylindrical specimens were machined using an EDM (Electronic Discharge Machining) machine with dimensions of 0.6 inches in length and 0.3 inches in diameter. After the specimens were machined, the ends were paralleled by either the student or "First Tool Corp." When the machining was complete, the testing began. It is at this point where the current task picks up. The testing was done in a compression mode using an Instron model 8562 testing frame. The test matrix of specimens consisted of six grain sizes, and five temperatures for each grain size, for a total of 30 specimens to test. The tests were carried out at room temperature, 600°C, 760°C, 870°C, and 1000°C in a vacuum furnace attached to the test frame. Testing usually took between 30 minutes for the room temperature tests and as long as 4 hours for the elevated temperature tests.

<u>Beta Niobium Alloy</u> - Less work was done on this alloy as the gamma took most of the time, but what was accomplished was to polish a precut compact tension specimen, and use a method called fatigue precracking to initiate a small crack in the specimen. This precrack is then measured for length and noted for each specimen. A general tension test is then completed on the specimen with the existing crack. From this combination of tests, the true fracture toughness of the material can be found along with its tolerance for microcracks during the service life of the material.

RESULTS

Gamma Titanium Aluminide - The initial results from the test show, that at elevated temperatures, the alloy was retaining around 50% of its room temperature yield strength. This is an improvement over conventional alloys that retain only 20% to 30% of their room temperature strength. The basic pattern of large grains showing higher strengths at elevated temperatures was also shown to be true. Creep tests, to be performed later, will help to refine the mechanical properties

Beta Niobium Alloy - Time only permitted the completion of the precracking of the specimens during this task, so results were not available at this time.

RESEARCH IN NONLINEAR OPTICAL MATERIALS

Task Order No. 284
Southwestern Ohio Council for Higher Education
Student Support Program

David Small
Wright State University

27 December 1996

Government Task Leader
Dr. David E. Zelmon
WL/MLPO

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TASK ASSIGNMENT

The Task recently finished was carried out in the Nonlinear Optics lab that is part of MLPO in Wright Laboratory, Wright Patterson Air Force Base. The nature of the work is interdisciplinary, with the N.L.O. group consisting of physicists, electrical engineers and chemists. The goal of the research is to develop, synthesize and characterize materials for frequency conversion applications.

The only Task undertaken was measuring indices of refraction of crystals. The values of the indices of refraction are very important to people who wish to build devices out of new materials. To build a workable device, the indices of refraction must be known to within .0001 for all wavelengths in the .4μ to 12.5μ spectral range. The materials being examined are mainly wanted for frequency conversion applications such as optical parametric oscillation and second harmonic generation. In many of the possible directions of propagation through the crystal, the output intensity will be so low that using the crystal for frequency conversion is not possible. There are a locus of angles describing the direction of propagation where the output intensity is high. These angles are called the phase matching angles. Knowing the phase matching curve is very important for building a device. These angles can be measured, but they can also be calculated. To calculate these angles, the three indices of refraction of the crystal must be known over the frequency range. The indices are measured using a spectrometer by the minimum deviation method, which requires two separate measurements. The first is the apex angle of the prism. The second is the minimum deviation angle, which is frequency dependent, so it must be measured at .05μ increments over the .4μ to 5.5μ spectral range for each crystal with each of two polarizations five to seven times each. The indices are then calculated and fit to a curve using a FORTRAN program written by our lab and reported in an optical science journal.