Report of the Materials Research Council (1971)

December 1971

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REPORT

of

THE MATERIALS RESEARCH COUNCIL

December 1971

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Department of Materials & Metallurgical Engineering
The University of Michigan
Ann Arbor, Michigan 48104
(313) 764-3302

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INTRODUCTION

This report describes the activities and output of the Materials Research Council for the year ending December 13, 1971, the fourth year of operation of the Council.

The idea of a Materials Research Council originated in 1966 when several individuals in materials and materials sciences including Dr. Robb Thomson, Director of the Materials Sciences Office of ARPA, discussed the possibility of bringing together 20-30 outstanding people in the materials field for an extended period each year to examine this area of study and relate their concerns and interests to those of DoD in these fields. The group was to be briefed on the current state of emerging problems and was to be challenged to develop solutions, or a consensus for approaches to the possible solutions of such problems.

Subsequent development of this idea led to the formation of the ARPA Materials Research Council and the bringing together of a group for an extended period of study during the summer of 1966 for the first summer conference. The concept proved to be so fruitful that the Council was continued through 1969, 1970, 1971, and plans are currently being projected through 1972.

It has not been the principal purpose of the Council to concentrate on current high-priority and highly-focused materials problems. This type of problem is usually in very competent hands,

and is invariably part of a larger systems problem. The intrusion of the Council into such problems, while possibly of some benefit, would be divisive and cause back-tracking and be wasteful of the efforts of all groups involved. The Council has indeed occasionally worked on such problems and expects to do so in the future, but the real value of the Council lies in using it for its long-range and broad vision. A primary strength of the Council lies in its ability to recognize and work on future critical needs, rather than on current critical problems.

The initial concept that the members of the Council should be among the most able and highly qualified individuals in the country in their respective fields in order to bring their expertise to bear on the complex materials problems of DoD has proved to be a wise decision. The quality of the people in their respective fields has been such that the entire group, physicists, chemists, and engineers, have interacted in such a fashion that they are probably one of the most coherent, versatile and knowledgeable groups working in materials science and materials engineering in the country. It is noteworthy that the group has maintained a high degree of continuity throughout its four-year history.

Since the personnel of the Council is drawn largely from the academic community it was felt that exposure to longer range materials problems would have a beneficial influence on research undertakings of Council members and their students. This has indeed been the case. Follow-on work from problems encountered

in the Council has emerged at most of the institutions represented by the Council membership. Several graduate students are actively pursuing problems first formulated by the Council. They include such topics as surface chemistry, the physics of surfaces, fracture analysis, stress corrosion, plasticity, high-temperature thermodynamics, composite materials, refractory materials, electronic properties, optical properties, carbon thermodynamics, etc. The interdisciplinary nature of the group is reflected in the wide range of researches that have been generated as a result of the problems discussed in the Council.

PROJECT ORGANIZATION

The technical direction of the ARPA Materials Research Council is delegated to a nine-man Steering Committee, which is representative of the various disciplines embodied in the Council. Membership on the Steering Committee is normally for a period of three years with replacements occurring each year. The functions of the Steering Committee are:

a) Work with ARPA and interested parties who contact ARPA, to select problem areas for consideration by the Council.

b) Select Council members, specialists and consultants to work with the Council.

c) Evaluate and direct project activities.

d) Participate in project management.

The current Steering Committee is as follows:

Professor Elliott W. Montroll
Secretary of the Steering Committee
Department of Physics & Astronomy
University of Rochester
Rochester, New York 14534

Professor Morris Cohen
Department of Metallurgy & Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Professor John P. Hirth
Metallurgical Engineering Department
Ohio State University
Columbus, Ohio 43201

Professor John L. Margrave
Department of Chemistry
Rice University
Houston, Texas 77001

Professor Frank A. McClintock
Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Professor Howard Reiss
Department of Chemistry
University of California
Los Angeles, California 90024

Professor James Rice
Division of Engineering
Brown University
Providence, Rhode Island 02912

Professor Michael Tinkham
Department of Physics
Harvard University
Cambridge, Massachusetts 02138

Dr. George H. Vineyard
Brookhaven National Laboratory
Upton, Long Island, New York 11973

To carry out the work of the Council a contract has been arranged between ARPA and The University of Michigan. The

Project Director is Edward E. Hucke, Professor of Materials and Metallurgical Engineering.

The following functions are performed by the University:

a) Coordinating planning, through the Steering Committee.

b) Providing a central, responsive contact point and clearing house for all Council affairs.

c) Negotiating consulting agreements with the project participants, and handling all administrative and financial affairs.

d) Publishing the reports issued by the Council.

The current contract terminates April 30, 1972.

The members of the Council in addition to the members of the Steering Committee are as follows:

Professor Michael B. Bever
Department of Metallurgy & Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Professor Nico Bloembergen
Division of Engineering & Applied Physics
Harvard University
Cambridge, Massachusetts 02139

Professor Bernard Budiansky
Division of Engineering & Applied Science
Harvard University
Cambridge, Massachusetts 02138

Dean Daniel C. Drucker
Engineering College
University of Illinois
Urbana, Illinois 61801

Professor Pol E. Duwez
W. M. Keck Laboratory of Engineering Materials
California Institute of Technology
Pasadena, California 91109

Professor John D. Ferry
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Professor Willis H. Flygare
Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois 61801

Dr. John J. Gilman, Director
Materials Research Center
Allied Chemical Corporation
Morristown, New Jersey 07960

Professor Robert Gomer
James Franck Institute
University of Chicago
Chicago, Illinois 60637

Professor Alan Heeger
Department of Physics
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Professor Robert A. Huggins
Center for Materials Research
Stanford University
Stanford, California 94305

Professor Walter Kohn
Department of Physics
University of California
La Jolla, California 92037

Professor James A. Krumhansl
Department of Physics
Cornell University
Ithaca, New York 14850

Professor Erastus H. Lee
Department of Applied Mechanics
Stanford University
Stanford, California 94305

Professor Donald J. Lyman
Materials Science & Engineering
The University of Utah
Salt Lake City, Utah 84112

Professor Paul L. Richards
Department of Physics
University of California
Berkeley, California 94720

Professor Albert J. Sievers
Laboratory of Atomic & Solid State Physics
Cornell University
Ithaca, New York 14850

Dr. Robb M. Thomson
National Bureau of Standards
Institute of Applied Technology
Washington, D.C. 20234

PROBLEM SELECTION

In 1968 the Steering Committee, working with the ARPA Materials Science Office, arranged a series of briefings with various DoD agencies to examine those areas which were believed most appropriate for consideration by the Council. As a result of these meetings and subsequent discussions with the entire Council, four general topics were chosen for detailed examination: composite materials, shock propagation, constitutive relations at high temperatures and pressures and underground sensing. At the 1968 summer conference, consultants and specialists worked with the Council to define more closely the problem areas, and to inform the Council members of related programs and progress. Individual members then worked either independently or in small subgroups on various segments of the problem areas and, after discussion and analysis, issued reports.

While the above procedure was reasonably successful in directing the work of the Council, further improvements were

put into effect in the 1969 operation. The original concept of holding a summer conference where the entire Council could devote its concentrated efforts to a few selected issues proved to be fruitful, but it was evident that more detailed preparation prior to the summer conference was necessary in order to use the talents of the Council efficiently. Consequently, procedures were established for individuals or subgroups of the Council to undertake activities such as visits to DoD installations and DoD contractors or continuing investigations at home institutions in preparation for the following conference. The technical report of the activities of the 1969 conference stimulated several meetings of Council members with representatives of DoD laboratories. The results of this interaction were conveyed to the Steering Committee's May meeting enabling modification and addition of subject areas for the 1970 conference. Out of this meeting arose the following major areas of investigation:

1) Shock - continuation of efforts were to examine studies of the Grüneisen constant; electrical effects; dispersion by periodic structures; and dislocation structures.

2) Fracture - continuation of efforts to define crack propagation criteria, particularly in multiphased materials; define strain conditions at moving cracks; formulation of dislocation models of fracturing materials undergoing plastic deformation; and examination of surface energy considerations.

3) Composites - continuation of metal matrix composite investigation; examination of gradient composites; study of

carbon composites; and analysis of wave propagation in composites.

4) Optics - continuation of analysis of laser glass materials problems; and optical properties of special composites.

5) New Materials - continued examination of materials and property measurements at extreme conditions of temperature; novel chemical combinations; and disordered carbon structures.

6) Stress Corrosion - continuation of survey of the field; examination of specific mechanisms.

7) Materials for Meeting Societal Needs - examination of superconductors for a magnetically suspended transportation system.

8) Bio-Materials - examination of materials compatibility in human bodies; materials problems in artificial organs; blood clotting; biological polymers.

The Steering Committee in its 1970 fall meeting in Washington recommended that the Council conduct more small meetings during the year for the purpose of preparing a given subject area for the summer conference. In this way it would be possible to have the necessary outside consultants contacted early enough to allow them to plan to attend portions of the conference and to identify, secure, and screen the relevant literature. It was proposed that aside from problem areas continuing or arising from previous Council activities, that a closer link be established between the Council and the ARPA Materials Science Director. In this way the talents of the Council could be brought to bear

for the purposes of evaluation of future research directions in a particular problem area so as to serve as a long-range advisory group for the ARPA Materials Science Director. This objective was carried forward in the selection of problems for the 1971 summer conference. Plans for small preparation meetings were laid and the following subject areas suggested and planned.

Environmental Degradation of Materials

Materials Factors in Design with Brittle Materials

Gradient Materials

Infra-red Transmitting Materials

Amorphous Semiconductors

Stable Disordered Carbon Systems

Amorphous Metals

Applications of Superconductivity

Properties of Non-Biological Polymers

Fracture Mechanics

Materials at High Temperature

Stress Waves in Composite Solids

Surface Thermodynamics Problems

Irreversible Thermodynamic Problems

Solid Electrolytes

SUMMER CONFERENCE - 1971

The conference was held during the entire month of July, 1971, at the Quissett Campus of the National Academy of Sciences, Woods Hole, Massachusetts. A list of the invited

guests and consultants to the Council is appended. Pre-conference organizing meetings were held for planning in the case of the Environmental Degradation of Materials, Amorphous Semiconductors and Stable Disordered Carbon Systems.

In line with a previous decision of the Steering Committee, several of the subject areas were organized into short meetings of one to three days duration, during which presentations by outside experts took place. These meetings prompted considerable discussions and in most cases lead to the writing of technical memoranda or, in some cases, published papers. In the case of the first six of the previously listed subject areas, considerable use was made of outside consultants with a structured program of presentations. For these meetings a short summary of the meeting is given in the appendix of this report as a technical memorandum. In the case of the meeting on Environmental Degradation of Materials, the final written output will be bound as a separate volume of the yearly report of the project.

The activity in the remaining subject areas was carried out in the more traditional means by individuals or two to five man discussions. The Council members and consultants participating in each of the subject areas are listed below.

Environmental Degradation of Materials: J. P. Hirth, M. Cohen, F. A. McClintock, D. C. Drucker, E. E. Hucke, J. J. Gilman, R. Gomer, J. R. Rice, R. M. Thomson, S. H. Bush, B. Cohen, H. L. Gegel, H. H. Johnson, R. P. Kambour, R. Latanision, J. R. Low, Jr., R. A. Oriani, P. C. Paris, H. W. Paxton, R. Pelloux, E. N. Pugh, A. J. Sedriks, M. O. Speidel, R. W. Staehle, A. R. Troiano, H. H. Uhlig, H. G. F. Wilsdorf, J. Westbrook, and A. R. C. Westwood.

Materials Factors in Design with Brittle Materials: D. C. Drucker, M. Cohen, J. P. Hirth, E. H. Lee, J. R. Rice, F. Baratta, J. I. Bluhm, D. E. Harrison, R. N. Katz, A. F. McLean, A. Paluszny, R. J. Schaller, and M. J. Sinnott.

Gradient Materials: M. B. Bever, P. E. Duwez, E. E. Hucke, G. H. Bishop, W. J. Croft, D. Goldstein, G. Quinn. M. Shen, M. L. Wilkins, and R. Weiss.

Infra-red Transmitting Materials: N. Bloembergen, W. H. Flygare, A. S. Barker, B. Bendow, T. Deutsch, F. Horrigan, J. R. Jasperse, R. N. Katz, P. Miles, R. J. Sanford, M. Sparks, C. M. Stickley, H. V. Winsor, and A. Yariv.

Amorphous Semi-Conductors: J. A. Krumhansl, M. Cohen, P. E. Duwez, J. J. Gilman, R. Gomer, E. E. Hucke, R. A. Huggins, H. Reiss, P. L. Richards, M. Tinkham, G. H. Vineyard, A. Bienenstock, H. Ehrenreich, D. Emin, S. C. Moss, L. F. Salzberg, W. W. Scanlon, R. A. Smith, and D. Turnbull.

Stable Disordered Carbon Systems: E. E. Hucke, P. E. Duwez, J. J. Gilman, J. A. Krumhansl, J. C. Bokros, R. H. Bragg, J. M. Carpenter, S. Ergun, D. Fischbach, B. Granoff, D. F. R. Mildner, W. G. Ramke, M. C. Smith, G. L. Tingey, P. L. Walker, and G. S. Y. Yeh.

Amorphous Metals: P. E. Duwez and M. B. Bever

Applications of Superconductivity: M. Tinkham, P. L. Richards, G. T. Danby, and J. Powell

Properties of Non-Biological Polymers: H. Reiss, E. E. Hucke, E. H. Lee, F. Chompff, J. D. Hoffman, M. Shen, and G. S. Y. Yeh.

Fracture Mechanics: F. A. McClintock, J. P. Hirth, B. Budiansky, J. J. Gilman, E. H. Lee, J. R. Rice, R. M. Thomson, and E. Sternberg.

Materials at High Temperatures: J. L. Margrave, N. Bloembergen, E. E. Hucke, M. Flemings and D. V. Ragone

Stress Waves in Composite Solids: E. H. Lee, J. A. Krumhansl, G. H. Vineyard and J. B. Keller.

Surface Thermodynamic Problems: R. Gomer, R. M. Thomson, and J. A. Appelbaum.

Irreversible Thermodynamics: J. P. Hirth and G. M. Pound

Solid Electrolytes: R. A. Huggins and W. H. Flygare

As in the past, considerable use was made of a computational system utilizing by telephone the University of Michigan Computing Center. Professor J. O. Wilkes was again available to help formulate member's problems.

In addition, representatives of the various service laboratories were invited to the conference so as to provide a two-way communication between the Council and the respective laboratories. In this manner the results of the Council's efforts could be more directly communicated to the service laboratories. Also, the problem areas most deserving of consideration could be discussed with the Council so that they might be considered as topics at future conferences. The following service laboratory representatives attended portions of the conference:

Dr. Alvin E. Gorum, Director, Army Materials & Mechanics Research Center

Mr. T. F. Kearns, Naval Air Systems Command, Department of the Navy

Professor W. G. McMillan, University of California

Dr. Wayne W. Scanlon, U.S. Naval Ordnance Laboratory

Dr. M. J. Sinnott, Director, Materials Science Office, Advanced Research Projects Agency

Dr. C. M. Stickley, Deputy Director, Materials Science Office, Advanced Research Projects Agency

The interaction proved to be quite valuable to the Council.

As in prior years, the results of the Council's effort are divided into two broad categories; namely, 1) papers in a state ready for publication, and 2) reports and memoranda for

limited distribution representing work in progress. The former category is available for general distribution and in some cases are in the process of publication in the appropriate technical journals. In many instances, the reports arising from the 1971 meeting were the completed forms of work started at earlier conferences. The restricted distribution reports and memoranda represent initial ideas, problem suggestions, position papers, and status reports and are aimed primarily to stimulate discussion within the Council. However, they are available by request to the Project Director subject to the authors' release.

The breadth of activity of the Council during the 1971 conference can be seen from the following list of papers produced. The abstracts are given in the Appendix. Titles marked with an asterisk are reports and memoranda for limited distribution; those marked with (†) are being published.

†Gradients in Polymeric Materials
M. B. Bever and M. Shen

Effect of Strain on the Fermi Energy
R. Gomer and R. M. Thomson

Note on Density Determination of Amorphous Materials
R. Gomer

Modified Null-Flux Magnetic Suspension and Propulsion System for High-Speed Transportation
M. Tinkham and P. L. Richards

†Magnetic Suspension and Propulsion Systems for High-Speed Transportation
M. Tinkham and P. L. Richards

Conservation Laws and Energy Release Rates
B. Budiansky and J. Rice

Application of a Defect Model to Vitreous Solids
R. A. Huggins

Thermodynamic Properties of Liquid Metals
J. L. Margrave

Stress Corrosion Cracking in Plastic Solids Including the Role of Hydrogen
J. J. Gilman

Estimating Prediction and Tolerance Limits for Extreme Value Distribution
F. A. McClintock and J. O. Wilkes

A Unified Theory for the Free Energy of Inhomogeneous Systems
L. A. Swanger, G. M. Pound and J. P. Hirth

Theory of Ionic Transport in Crystallographic Tunnels
W. H. Flygare and R. A. Huggins

Effect of Stress on Electrochemical Dissolution
R. Gomer and R. M. Thomson

Amorphous Metallic Alloys
P. E. Duwez

Diffusion Through Anisotropic Polymer Systems
J. D. Ferry

Remarks on Montroll's Nonlinear Wave Equation
G. H. Vineyard

Random Close Packing of Spheres
G. H. Vineyard

Note on IR Windows
N. Bloembergen

Line Tension on Kinks on Fracture Cracks
J. J. Gilman, J. P. Hirth and R. M. Thomson

States of Ease of Polymeric Entanglement Networks Crosslinked in Strained States
J. D. Ferry

Diffusion Through Composite Polymer Systems
J. D. Ferry

Some Problems in Bulk Polymeric Systems
H. Reiss

A Note on the Ground State Energy of an Assembly of Interacting Electrons
A. Isihara and E. W. Montroll

A Rigid-Plastic Model of Spall Fracture by Hole Growth
F. A. McClintock

SD Effect
D. C. Drucker

Energy to Create New Surface During Crack Propagation
D. C. Drucker

On Gradient Materials: Phenomena and Fundamentals
M. B. Bever

Analysis of Stress Intensity Factors in a Plate with Any Given Distribution of Cracks: A Translation
M. Ishida

Edge Dislocation Arrays Around a Crack Under Tension
F. A. McClintock

High-Temperature Stability of Silicon Nitride
J. L. Margrave

The Use of Levitation in Inorganic Synthesis
J. L. Margrave, J. A. Treverton and P. W. Wilson

High Temperature Properties of Nb and Zr
J. L. Margrave and A. J. Valerga

Pyrolysis of Polymers and Simple Organic Molecules
J. L. Margrave

Emissivities of Liquid Metals
J. L. Margrave, D. W. Bonnell and A. J. Valerga

Heats of Formation of Various Types of Carbon and Graphite by Combustion Calorimetry
J. L. Margrave

The Li/CFX Electrochemical Cell and Related Problems
J. L. Margrave

Stress Waves Generated by Prescribed Pressure Histories on a Laminated Composite Half-Space
J. A. Krumhansl and E. H. Lee

Propagation of Transient Elastic Waves in Periodic Composites
J. A. Krumhansl and E. H. Lee

Determination of Stress Profiles for Waves in Periodic Composites
L. Bevilacqua, W. Kohn, J. A. Krumhansl and E. H. Lee

A Proposed Method for the Evaluation of the Thermodynamic Properties of the Glassy Carbon-Graphite Equilibrium
E. E. Hucke and S. K. Das

Flow Via Dislocations in Ideal Glasses
J. J. Gilman

Hardness - A Strength Microprobe
J. J. Gilman

Stress Corrosion Cracking Papers
Summary Report
M. Cohen, H. H. Johnson and A. J. Sedriks
Comments on Adsorption - Sensitive Cracking
A. R. C. Westwood and R. M. Latanision
Unit Processes in Stress Corrosion Cracking
R. W. Staehle
Defect Physics in Stress Corrosion Cracking
R. Thomson and J. P. Hirth
Fracture Mechanics for Stress Corrosion Cracking
F. A. McClintock and J. P. Hirth
Boundary Segregation Effects in Environmental Degradation
J. H. Westbrook
Fractography of Stress Corrosion Failures - Mechanistic Aspects
E. N. Pugh
Practical Problems of Stress Corrosion Cracking in High Strength Metallic Materials
M. O. Speidel
Stress Corrosion in Nuclear Systems
S. H. Bush
Some Thought on SCC Problems
B. F. Brown
Notes of Electrochemistry
R. A. Oriani
Stress Corrosion Cracking in Plastic Solids Including the Role of Hydrogen
J. J. Gilman

Meeting Summaries

Environmental Degradation of Materials
J. P. Hirth

Design with Brittle Materials
D. C. Drucker

Gradient Materials
M. B. Bever

IR Windows
N. Bloembergen

Amorphous Materials: Semiconductors
J. A. Krumhansl

Massive Disorder Carbon Systems
E. E. Hucke

POST CONFERENCE ACTIVITIES

Many of the Council found that they could take full advantage of the presence of the other Council members by utilizing most of the time during the conference in small group sessions. In this way problems could be formulated and subdivided with maximum effort on interchange of ideas. This resulted in a need to spend considerable time after the conference in writing the results. In addition to report preparation, in some cases it was thought desirable to arrange some additional small meetings between Council members and other individuals.

A meeting of the Steering Committee held in Washington, D.C. in November, 1971, was held to formulate plans for the 1972 summer meeting and to discuss additions to the Council membership. ARPA Materials Science Director, M. J. Sinnott, reviewed subject areas of emerging importance to his office. After his presentation and a review of the member's proposed activities, it was decided that the Council would continue work in the areas now active and in addition attempt to organize some effort toward Failure Analysis. A pre-meeting in this area was suggested.

Past Council activities have lead to technical presentations and laboratory visits in the areas of Stress Wave Propagation in Composites, Applications of Superconductivity to Transportation Systems, Glassy Carbon, and Gradient Materials.

APPENDIX

GUEST CONSULTANT LIST

GUEST CONSULTANT LIST
Materials Research Council
July, 1971

Dr. Joel A. Appelbaum
Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey 07974
(201)582-2156

Dr. Francis Baratta
Army Materials and Mechanics
Research Center
Watertown, Massachusetts 02172
(617)926-1900

Dr. A. S. Barker, Jr.
Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey 07974
(201)582-3000

Dr. Bernard Bendow
Air Force Cambridge Research
Laboratories
L. C. Hanscom Field
Bedford, Massachusetts 01730

Professor A. Bienenstock
Materials Science Department
Stanford University
Stanford, California 94305
(415)321-2300 Ext. 2617 or 2534

Dr. G. H. Bishop
Metals Division
Army Materials and Mechanics
Research Center
Watertown, Massachusetts 02172
(617)926-1900

Dr. Joseph I. Bluhm
Army Materials and Mechanics
Research Center
Watertown, Massachusetts 02172
(617)926-1900

Dr. J. C. Bokros
Medical Products Division
Gulf Energy & Environmental
Systems Company
P.O. Box 608
San Diego, California 92112

Professor R. H. Bragg
Department of Materials
Science
University of California
Berkeley, California 94720
(415)642-3815

Dr. S. H. Bush
Battelle-Northwest
P.O. Box 999
Richland, Washington 99352
(509)946-2223

Professor John M. Carpenter
Nuclear Engineering Department
300 Automotive Laboratory
University of Michigan
Ann Arbor, Michigan 48104
(313)764-4260

Dr. Fred Chompff
Polymer Science Department
Scientific Research Staff
Ford Motor Company
P.O. Box 2053
Dearborn, Michigan 48121
(313)323-1423

Mr. B. Cohen
Aeronautical Systems Support
Branch
Materials Support Division
AF Materials Laboratory
Wright-Patterson AFB, Ohio 45433

Mr. W. J. Croft
Army Materials & Mechanics
Research Center
Watertown, Massachusetts 02172
(617)926-1900

Dr. Gordon T. Danby
Brookhaven National Laboratory
Upton, Long Island,
New York, 11973
(516)924-6262 Ext. 2471

Dr. Thomas Deutsch
Raytheon Research Division
28 Seyon Street
Waltham, Massachusetts 02154
(617)899-8400

Professor H. Ehrenreich
Pierce Hall
Harvard University
Cambridge, Massachusetts 02138
(617)495-3213

Dr. David Emin
Division 5134
Sandia Laboratories
Albuquerque, New Mexico 87115
(505)264-3431 or 5156

Dr. Sabri Ergun
U.S. Bureau of Mines
4800 Forbes Avenue
Pittsburgh, Pennsylvania 15213

Professor David Fischbach
Ceramic Engineering Division
Roberts Hall, FB-10
University of Washington
Seattle, Washington 98195
(206)543-8573

Professor Merton Flemings
Room 8-407
Department of Materials Science
Massachusetts Institute of
Technology
Cambridge, Massachusetts 02139
(617)864-6900 Ext. 3233

Dr. H. L. Gegel
Advanced Metallurgical Studies
Branch
Metals & Ceramics Division
AF Materials Laboratory
Wright-Patterson AFB, Ohio 45433

Dr. David Goldstein
Code 211
Naval Ordnance Laboratory
Silver Springs
White Oak, Maryland 20910

Dr. Alvin E. Gorum
Director, Army Materials
& Mechanics Research Center
Watertown, Massachusetts 02172
(617)926-1900 Ext. 275

Dr. Barry Granoff
Sandia Laboratories
Sandia Base
Albuquerque, New Mexico 87115
(505)264-5458

Dr. Donald E. Harrison
Manager, Materials Science
Research & Development Center
Westinghouse Electric Company
Pittsburgh, Pennsylvania 15235
(412)256-7000 Ext. 7336

Dr. J. D. Hoffman, Director
Institute of Materials Science
National Bureau of Standards
Gaithersburg, Maryland

Dr. Frank Horrigan
Raytheon Research Division
28 Seyon Street
Waltham, Massachusetts 02154
(617)899-8400

Dr. John R. Jasperse
Solid State Sciences Laboratory
Air Force Cambridge Research
Laboratories
L. C. Hanscom Field
Bedford, Massachusetts 01730
(617)232-5464

Professor H. H. Johnson, Head
Department of Materials Science
& Engineering
Cornell University
Ithaca, New York 14850
(607)256-4135

Dr. R. P. Kambour
Research & Development Center
General Electric Company
P.O. Box 8
Schenectady, New York 12301

Dr. R. Nathan Katz
Chief, Ceramics Research Division
Army Materials & Mechanics
Research Center
Watertown, Massachusetts 02172
(617)926-1900 Ext. 415

Mr. T. F. Kearns
AIR 320A-Research & Technology
Group
Naval Air Systems Command
Department of the Navy
Washington, D.C. 20360
(202)692-7416

Dr. R. Latanision
Research Institute for Advanced
Studies
1450 South Rolling Road
Baltimore, Maryland 21227
(301)247-0770

Dr. J. R. Low, Jr.
Department of Metallurgy &
Materials Science
Carnegie-Mellon University
Schenley Park
Pittsburgh, Pennsylvania 15213
(412)621-2600

Mr. Arthur F. McLean
Manager, Turbine Research
Ford Motor Company
20000 Rotunda Drive
Dearborn, Michigan 48121
(313)322-3859

Professor W. G. McMillan
Department of Chemistry
University of California
Los Angeles, California 90024

Mr. David F. R. Mildner
Department of Nuclear Engineering
University of Michigan
Ann Arbor, Michigan 48104
(313)764-6220

Dr. Perry Miles
Raytheon Research Division
28 Seyon Street
Waltham, Massachusetts 02154
(617)899-8400

Dr. S. C. Moss
Energy Conversion Devices, Inc.
1675 West Maple Road
Troy, Michigan 48084
(313)549-7300

Dr. R. A. Oriani
E. C. Bain Laboratory
United States Steel Corporation
Research Center
Monroeville, Pennsylvania 15146

Mr. Antoni Paluszny
Supervisor, Turbine Research
Ford Motor Company
20000 Rotunda Drive
Dearborn, Michigan 48121
(313)337-5515

Dr. P. C. Paris
Del Research Corporation
427 Main Street
Hellertown, Pennsylvania 18055
(215)838-7069

Dr. H. W. Paxton, Head
Materials Science Department
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213
(412)621-2600

Dr. R. Pelloux
Room 8-305
Massachusetts Institute of
Technology
Cambridge, Massachusetts 02139

Professor G. M. Pound
Department of Materials Science
Stanford University
Stanford, California 94305
(415)321-2300 Ext. 4257

Dr. James Powell
T-318
Brookhaven National Laboratory
Upton, Long Island,
New York 11973
(516)924-6262 Ext. 7789

Dr. E. N. Pugh
Department of Metallurgy &
Mining Engineering
University of Illinois
Urbana, Illinois 61801
(217)333-4692

Mr. G. Quinn
Army Materials & Mechanics
Research Center
Watertown, Massachusetts 02172

Dean David V. Ragone
Thayer School of Engineering
Dartmouth College
Hanover, New Hampshire 03755
(603)646-2238

Dr. W. G. Ramke, Chief
Ceramics & Graphite Branch
Metals & Ceramics Division
Air Force Materials Laboratory
Wright-Patterson AFB
Ohio 45433

Mr. Leo F. Salzberg
Chief, Materials Physics Division
AF Materials Laboratory
Wright-Patterson AFB
Ohio 45433
(513)255-2433

Dr. Richard J. Sanford
U.S. Naval Ordnance Laboratory
Code 431
White Oak, Silver Spring
Maryland 20910
(301)495-8539

Dr. Wayne W. Scanlon
Applied Physics Department
U.S. Naval Ordnance Laboratory
White Oak, Silver Spring
Maryland 20910
(301)495-7773

Dr. R. J. Schaller
Research & Development Center
Westinghouse Electric Company
Pittsburgh, Pennsylvania 15235
(412)256-7000

Dr. A. J. Sedriks
Research Institute for Advanced
Studies
1450 South Rolling Road
Baltimore, Maryland 21227
(412)621-2600

Professor Mitchel Shen
Department of Chemistry
University of California
Berkeley, California 94720
(415)642-2111

Dr. M. J. Sinnott, Director
Materials Science Office
Advanced Research Projects
Agency
1400 Wilson Boulevard
Arlington, Virginia 22209
(202)694-3010

Dr. Morton C. Smith
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Dr. Richard A. Smith
TREE Section Head
U.S. Naval Ordnance Laboratory
Code 431
White Oak, Silver Spring
Maryland 20910
(301)495-8334

Dr. Marshall Sparks
The Rand Corporation
1700 Main Street
Santa Monica, California 60406
(213)393-0411

Dr. Marcus O. Speidel
Boeing Scientific Laboratory
P.O. Box 3981
Seattle, Washington 98124
(206)655-6279

Professor R. W. Staehle
Department of Metallurgical Engineering
Ohio State University
116 West 19th Avenue
Columbus, Ohio 43210
(614)422-6255

Professor Eli Sternberg
Division of Engineering and Applied Science
California Institute of Technology
Pasadena, California 91109
(213)795-6841 Ext. 1178

Dr. C. Martin Stickley
Deputy Director
Materials Sciences Office
Advanced Research Projects Agency
1400 Wilson Boulevard
Arlington, Virginia 22209
(202)694-3010

Dr. Garth L. Tingey
Technical Leader
Ceramics & Graphite Section
Battelle-Northwest
P.O. Box 999
Richland, Washington 99352
(509)946-2419

Dr. A. R. Troiano
Department of Metallurgy and Materials
Case Western Reserve University
Cleveland, Ohio 44106
(216)368-4234

Professor David Turnbull
Pierce Hall
Department of Applied Physics
Harvard University
Cambridge, Massachusetts 02138
(617)495-2838

Dr. H. H. Uhlig
Department of Metallurgy & Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
(617)864-6900 Ext. 3313

Professor P. L. Walker, Jr.
Department of Materials Science
101 Minerals Industry Building
Pennsylvania State University
University Park, Pennsylvania 16802
(814)865-0497

Professor James O. Wilkes
Department of Chemical Engineering
University of Michigan
Ann Arbor, Michigan 48104
(313)764-2385

Dr. Mark L. Wilkins
L-24
Lawrence Radiation Laboratory
East Avenue
Livermore, California 94550
(415)447-1100 Ext. 8611

Dr. H. G. F. Wilsdorf, Chairman
Department of Materials Science
Thornton Hall
University of Virginia
Charlottesville, Virginia 22901
(703)924-3462

Mr. Harry V. Winsor
Air Force Weapons Laboratory/LRO
Kirtland Air Force Base
New Mexico 87117

Dr. Richard Weiss
Army Materials & Mechanics Research Center
Watertown, Massachusetts 02172

Dr. J. Westbrook
Bldg. K-1, Rm. 3A44
General Electric Research & Development Center
Schenectady, New York 12305

Dr. A. R. C. Westwood
Deputy Director, RIAS
1450 South Rolling Road
Baltimore, Maryland 21227
(301)247-0700

Professor A. Yariv
Department of Electrical
Engineering
California Institute of
Technology
Pasadena, California 91109
(213)795-6841 Ext. 1821

Professor G. S. Y. Yeh
Materials & Metallurgical
Engineering
University of Michigan
Ann Arbor, Michigan 48104
(313)764-9236

APPENDIX

MEETING SUMMARIES

SUMMARY OF MEETING
ON
ENVIRONMENTAL DEGRADATION OF MATERIALS

J. P. Hirth

Drs. Cohen, Sedriks and Johnson are preparing a summary paper of the proceedings to appear in the Council Report as well as a brief summary to appear in Materials Sciences and Engineering. Seven other extended abstracts or papers will also appear in the report.

Of the three subgroups, that on silicon nitride concluded that the engineering development work in achieving working silicon nitride turbine engines (except turbine wheels) was remarkable but that supporting applied and basic research was now needed to anticipate operational problems with the material. Critical problems centered on the microstructure of the reaction sintered material, containing 25% void; calculations of the elastic properties of the material, and diffusion and oxidation data.

The group on stainless decided that the two most promising theories of stress corrosion cracking, film-rupture and hydrogen embrittlement, were both still in the running. Future promise lay in the use of low-alloy steels with thicker sections to allow for corrosion; of higher-alloy stainless which would be expensive; or of stabilized grades if weldability could be enhanced.

The group on aluminum and titanium alloys felt that reasonable progress was being made in these areas. They were concerned with the likelihood of payoff as a consequence of research fund distribution and suggested 50% in empirical-type research, 25% in more fundamental research and 25% in education and prevention.

Some key problems that were pinpointed were:

(a) Corrosion-fatigue operates at lower stress intensities and seemingly by different mechanisms than stress corrosion cracking.

(b) What is the configuration of a crack tip at the atomic level -- atomically sharp, blunted by dissolution, blunted by shear steps, or effectively blunted by irregularities? What is the local stress intensity at this scale for a crack buried in inhomogeneous, locally plastic surroundings?

(c) Can the overaging-microstructural control technique that has been successful in improving aluminum alloys be extended to high strength steels?

SUMMARY OF MEETING
ON
DESIGN WITH BRITTLE MATERIALS

D. C. Drucker

The two day meeting concentrated almost exclusively on the design of gas turbines with silicon nitride components. Presentations were made by the representatives from the Ford Motor Company who are developing automotive and slightly larger turbines for a mass market and by the representatives from Westinghouse who are looking into the possibility of constructing a 30 megawatt turbine for peaking or emergency use as well as steady use. AMMRAC personnel joined in a spirited discussion with many members of the Council which followed and often interrupted the presentations.

Ford has been in the silicon nitride and other ceramics component development phase for several years and will soon produce commercial turbine units of 400 Hp or so with ceramics replacing metal for most components other than the rotor and its supports. For the small automotive turbine, a major problem is cost per horsepower. Reaction bonding (sintering) has enormous cost advantage over hot pressing (sintering) for the complex shapes needed and can be used for the silicon nitride stator which is subjected to low mechanical stress. However, the reaction bonded material at present is only about 75% dense and has a much lower modulus of rupture than the 100,000 psi

as hot pressed; so much lower that it cannot be employed for a rotor with a 2500 psi mechanical stress level.

Westinghouse has much less restraint on a cost per pound basis and can employ hot pressing without much penalty. The increase in thermal efficiency permitted by an increase in operating temperature make a ceramic turbine very attractive. Their problem as they see it, is a much "dirtier" fuel which can lead to corrosion and erosion.

The design procedure to be followed by both Ford and Westinghouse is to make an accurate three dimensional stress analysis by computer using finite element techniques for both mechanical loading and thermal shock. Maximum stresses are limited to some fraction of the modulus of rupture value. Except for the great care in analysis, fabrication, and probably inspection as well, the plan does not seem to differ from that for a high strength steel or other sensitive but somewhat ductile materials.

Serious doubt was raised that a brittle ceramic rotor can be operated repeatedly through drastic thermal cycles at a mechanical stress as high as 1/4 the modulus of rupture. The advantages to be gained however, clearly warrant the effort. Hope was expressed of a healing process at operating temperature. Silicon nitride shows creep at 1800°F which is well below the planned maximum operating temperature of 2500°F. In the Ford turbine, present estimates are that the rotor stress due to mechanical loading will be 2500 psi and due to thermal loading

3300 as compared with 7000 and 15,000 psi for the stator.

An enthusiastic discussion ranged over chemical, metallurgical, and mechanical topics including recommendations for K_{1C} tests and their use, size of critical flaws.

All agreed that this fascinating development, which until recently has advanced much farther in Britain than the USA, was well worth careful and continuing attention.

SUMMARY OF MEETING
ON
GRADIENT MATERIALS

M. B. Bever

The group interested in gradient materials met for a one day session. Apart from the speakers, the meetings were attended by several Council members, several consultants, and guests.

Bever introduced gradient materials in terms of compositional and structural gradients and the resulting gradients in properties. He pointed out that the program included presentations on gradients in metals, ceramics and polymers and would also deal with structural analysis. His introduction to gradient materials is now being expanded and written up as a memorandum. The first discussion period was concerned with general aspects of gradients and particularly with the differences between a gradient and an interface.

Goldstein reported on a development in induction hardening of steel which permits the three-zone concept of armor design to be realized by producing a gradient layer of appreciable thickness between the hard surface layer and the rough back-up layer. He called for a "dictionary of gradient terms", which he thought might be prepared during the conference. An extensive discussion of the requirements of various kinds of armor ensued.

Bishop presented an analysis of the connectivity in the transition zone between a structure of all α-phase to one of all $\tilde{\beta}$. He showed that the minority phase in such a zone can have a high degree of connectivity; this may be significant for crack propagation. Later in the day, Weiss questioned the relation of 2-D connectivity to 3-D connectivity and the significance of the former for crack propagation.

Wilkins' motion picture illustrated the penetration mechanics for various simulated conditions. A projectile penetrating a two-layer armor was shown to initiate fracture at the interface. This observation and subsequent discussion of the requirements of armor reinforced the conclusions drawn from Goldstein's presentation.

Weiss reported on experimental work with gradient materials in the system titanium-boron and on the properties and relations of various phases in this system. Titanium monoboride forms exothermally from titanium and titanium diboride; gradients can be produced by mixing of the reactant powders in varying proportions. Weiss concluded that the titanium-boron system is particularly well-suited for the production of gradient materials.

Shen surveyed possible gradients in polymeric systems using the following concepts as his outline: (a) crosslinking, (b) supramolecular structure, (c) chemical composition and (d) degree of crystallinity. He drew examples from various polymeric systems and considered the major methods of producing

gradients in supramolecular structure such as blending, co-polymerization and grafting; he also considered an analysis of gradients in hydrophilicity by Ferry (ARPA Materials Research Council Report for 1970, pp. 594-602). Shen related various aspects of gradients in polymeric systems to the analysis of gradients in composite materials by Bever and Duwez (Council Report for 1970, pp. 109-115). He also suggested possible applications of gradients in polymers. Since the meeting, Shen and Bever have written a memorandum on "Gradients in Polymeric Materials", copies of which are available.

Two major conclusions may be drawn from the presentations and discussions at these meetings: gradient materials are important and their characteristics and applications merit further research.

SUMMARY OF MEETING
ON
IR WINDOWS

N. Bloembergen

The meeting was organized by C. M. Stickley and N. Bloembergen with the dual purpose to familiarize members of the ARPA Materials Research Council with the materials problems posed by the transmission of high power infrared laser beams through windows, and to serve as a starting point for a NRC-NAS panel study on this problem.

The program of the meeting was as follows:

C. M. Stickley - Introduction, ARPA Interest in IR Windows

H. Winsor - Air Force Applications and Requirements for IR Windows

A. Yariv - Absorption Mechanisms in IR Window Materials

M. Sparks - Principles for Selection of IR Window Materials

A. S. Barker - Optical Phonon Processes and IR Radiation

J. Jasperse - Optical Beam Focusing, Distortion and Aberration in IR Windows

T. Deutsch - IR Absorption Data and Measurement Techniques

R. Katz - Crystal Growth Problems

N. Bloembergen - Nonlinear Optical Processes

From the presentations by Barker, Sparks and Yariv, it was evident that the lowest absorptivity region in the infrared between the highest TO phonon frequency and the electronic band edge energy is determined by high order optical phonon processes,

in the absence of absorption by impurities. For materials with intrinsic absorption coefficients $\beta \lesssim 10^{-3}$ cm^{-1}, which are of primary interest, these higher order processes cannot be calculated with any precision, since five or more optical phonons may be involved. It does not seem worthwhile to make an extensive theoretical or experimental search for materials with a lower intrinsic value of the absorption coefficient, say $\beta \sim 10^{-4}$ cm^{-1}, for several reasons:

1. Theoretical predictions are not reliable within one or two orders of magnitude,
2. Experimental methods are not reliable for values of $\beta < 10^{-3}$ cm^{-1},†
3. It is doubtful that impurity absorption levels could be pushed down much below this limit,
4. Values of $\beta \simeq 10^{-2} - 10^{-3}$ are acceptable in window operation.††

It was clear that oxygen impurities are especially harmful and that great care must be exercised in producing oxygen-free materials and oxygen free surfaces. In low gap semiconductors, such as Ge, the conduction electron concentration must also be controlled.

Systematic collection of physical data on the same specimen must be made. It is especially important to increase

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† Note added in proof: Improved calorimetric low measurements in 5cm. long samples (at 1.06μ) have been shown to be possible by Pinnow and Rich of BTL with a precision of $\pm 1 \times 10^{-6}$ cm^{-1}. (CMS)
††Note added in proof: This may be questionable. (CMS)

the information on physical parameters in chalcogenide glasses and on hot-pressed sintered materials.

Low absorption coefficients should be measured on the same specimen by several different methods and as a function of wavelength and temperature by one method. Transmission measurements, calorimetric measurements and low power laser beam scattering experiments should be performed on the same window specimen.

On a short term basis single crystals grown by the gradient furnace technique, as discussed by Katz, appears to be the most promising avenue to produce large IR windows with low absorption. On a longer term basis, attention should be given to the production of low absorption, hot-pressed, sintered materials, and to the improvement of absorption and heat conductivity in chalcogenide glasses.

More attention should be paid to the thermal behavior of IR windows, subjected to very short pulses with a duration of less than 10^{-5} sec. Nonlinear optical effects would be expected to become important only at peak power levels exceeding 10^{7} watts/cm^{2}. These points are discussed in a separate research note by N. Bloembergen.

Another area which has not been treated at all are the constraints on window material selection imposed by mechanical strength requirements of the window. Clearly, these should be developed, at least to the first order, before even serious material improvement studies are initiated.

The results of the meeting may be summarized in the following conclusions:

1. There is a need for a systematic collection of data on systematically prepared and defined materials. Absorption should be measured vs. temperature and wavelength near 10.6μ. Different physical parameters should be measured on the same specimen, and, where possible, the same physical parameter should be determined by different experimental methods.

2. Since alkali halide crystals are strong contenders from the standpoint of low thermal optical distortion, high priority should be given to find ways to improve their surface and mechanical properties. Coatings to prevent water absorption should be studied. Ternary system crystals with infrared mechanical strength should be investigated.

3. The most promising semiconductor materials should be grown in larger sizes and anti-reflection coatings for them must be developed.

4. More theoretical analysis for the case of short laser pulse excitation ($<10^{-5}$ sec.) should be carried out and experimental work on the window properties, subjected to these shorter pulses, should be started immediately.

5. Long range fundamental work on the development of better chalcogenide glasses and other ternary systems, as well as on the improvement of polycrystalline, hot-pressed window materials should be continued.

6. First order analyses of constraints imposed by

mechanical strength requirements for windows should be developed immediately for guidance in all materials improvement and development efforts.

SUMMARY OF MEETING
ON
AMORPHOUS MATERIALS: SEMICONDUCTORS

J. A. Krumhansl

The subject of amorphous materials is not a new one, if one considers that glasses, amorphous oxides and elemental materials, glassy carbon, amorphous metal alloys and amorphous photoconductors have been with us for some time. However, much remains to be understood about their character and properties. It is apparent that there has been increasing interest in these materials, and that the ARPA Materials Science Program is involved.

Therefore, ARPA Materials Research Council decided some of its 1971 effort should be devoted to selected topics in amorphous material and they were chosen to be: Amorphous semiconductors, amorphous carbon, amorphous metal alloys.

This report covers activities on the first of these, amorphous semiconductors. Before describing work carried out in 1971 to date, let it be noted that the objectives were twofold:

1) To survey the basic materials science of amorphous materials.
2) To become cognizant of technological applications of particular interest to the Department of Defense.

In either case we were following the tradition of the Materials Research Council which looks for trends in the science

of materials, and for particular problems to which individual members can contribute advice or problem solutions. Lest there be any confusion, it was not our purpose to make a studied analysis of the general amorphous semiconductor technology, or current civilian applications.

The components of our activity were:

1) A literature survey of the basic science of amorphous materials, and attendance at the technical information meetings of the National Academy of Sciences Committee on Amorphous Semiconductors, H. Ehrenreich, Chairman. That committee's comprehensive report is expected to issue in 1971.

2) A one-day information meeting was held January 27, 1971 for ARPA Materials Research Council members (Duwez, Vineyard, Huggins, Krumhansl) and various interested DoD participants invited by the ARPA Materials Science Office. The program included general background, a summary by ARPA contractors of research sponsored in this area, and an introduction to planned programs on radiation resistant capabilities of amorphous semiconductor devices.

3) Planning of a small summer conference at the Council's summer study site, together with a background survey for that conference (J. A. Krumhansl, included as an appendix to the present summary). The conference was held at the National Academy site, Quissett Campus, July 7,8,9, 1971. The program was as follows: July 7, Structure and General Properties of Amorphous Materials; July 8, Electronic Properties, and Special Device Applications; July 9, General Discussion. Consultants

attending were: H. Ehrenreich, Harvard University; D. Turnbull, Harvard University; A. Bienenstock, Stanford University; S. C. Moss, Energy Conversion Devices; D. Emin, Sandia Laboratory; R. A. Smith, W. Scanlon, NOL; D. Salzburg, AFML. Council members attending included Duwez, Huggins, Gomer, Hucke, Reiss, Cohen, Tinkham, Richards, Gilman, and Krumhansl. It may be said that the discussions were successful and productive. The inter-disciplinary nature of diverse backgrounds represented was apparent in the discussion.

Principal Conclusion:

As a result of these activities the following observations on the state of the subject, as it pertains to the Materials Research Council's aims, seem to stand out:

1) The characterization of amorphous materials by experimental methods (X-rays, reaction diffraction, electron diffraction), and by comparison with analog and computer model building has progressed during the past few years to the point where the main features of network, polymeric, and elemental amorphous materials are generally known. Not known satisfactorily are: (a) how unique the configurations are, (b) how to decide how stable these are, (c) what is the nature of fluctuations from a "standard" configuration? It is apparent that the radial distribution experimental technique becomes difficult to carry out beyond a few neighbors, and that characterization on the 10-100 Å scale is difficult. Other methods are needed.

2) Changes of structure due to diffusion, phase separation, radiation damage are important aspects in the preparation and long-term behavior of amorphous materials.

3) It goes without saying that it is important now for good science that work be done on relatively few well characterized materials, by standardization or exchange of samples.

4) The theory of the properties of amorphous materials is in an evolving state. The overall energy level systematics are understood in a general way, but too often based on idealized models. Inferences from the energy level structure alone which make use of traditional band theoretic concepts to analyze transport phenomena (particularly) and other experimental properties are not justified. What is needed now are theories which are: (a) specific to real materials and situations, but b) general enough to describe either the short range or long range properties. With respect to the latter a foundation for describing the transition from hopping to drifting transport exists in the older literature of polaron theory; it needs to be extended and translated to current situations. A corollary of such work would be the design of experiments particularly suited to amorphous materials.

5) Of particular concern in the case of semiconductors is the whole question of fluctuations in composition, space charge density, or anything else which leads to spatial variation of the energy level systematics, because these can profoundly affect properties and their analysis.

6) The low temperature thermal properties of a wide variety of amorphous systems have been recently examined and found to be quite different from crystalline materials. Both in regard to this program, and in polymer physics, the time is ripe for further analytical work.

7) Amorphous semiconductor devices show distinct promise in applications which call for two terminal switching elements or non-volatile read mostly memory and must operate in a radiation environment. Compared to conventional semiconductor technology in the same applications the indications so far are that they are significantly more stable. In the immediate future it is important to push through test programs on actual devices; if they continue to show promise, much more must be determined about the nature of radiation damage and its relation to device operation.

All of this may be summarized by stating: Considered as a branch of materials science there is ample reason to support continued research on the basic science of amorphous materials because real progress with potential future application is being made, but much remains to be done; in addition, within the special interests of the Department of Defense some of the amorphous semiconductor devices are promising. Finally, a critical comment which the writer makes in passing is that the main body of effort in the "semiconductor" part of the subject is often quite embedded in its own history, without recognizing

that studies of non-electronic properties and amorphous materials other than semiconductors have encountered and solved problems with results which are applicable to electronic phenomena.

With this report this phase of the organized activity of the Materials Research Council has come to an end. Further activity will be up to individual members. The participation of all those mentioned above is gratefully acknowledged, as well as the opportunity to attend the ONR sponsored NAS-NMAB Panel technical meetings chaired by Dr. Ehrenreich.

APPENDIX

Amorphous Materials

Notes and Bibliography
J. A. Krumhansl

Familiar crystalline solid state physics is now highly developed; in some sense it may be regarded as in its baroque era now, but many of us will recall that just after World War II it was a conceptually rich but all too unquantified subject (no one has measured an effective mass, all transport theories assumed spherical energy bands, phonon spectra were inferred from thermal data). It seems fair to say that the science of amorphous materials is only at that point now.

The subject has made strides during the last several years, particularly regarding microscopic structure and properties. Indeed, it now appears that a threshold which is important to good science is being crossed in several areas - that is, standardization and characterization of materials are coming of age, forums now exist for critical discussion of the subject, and there are many actively communicating groups at the working level. But this is just a beginning.

Specific areas of progress are:

(1) Experiments and (computer) models have now been reasonably successful for determining primary structure of representative amorphous materials: vitreous oxides, amorphous silicon and germanium, some chalcogenides, metal-metalloid glasses, dis-

ordered alloys.

(2) A generally agreed upon classification of disordered materials runs like: I. Disorder on a Lattice: alloys, mixed valence semiconductors, etc. II. Amorphous Structures: random network (oxides, amorphous silicon, mixed chalcogenides), polymeric (vitreous selenium, polyethylene), random dense packing (organic glasses, metal-metalloid). Short range coordination is usually molecular-like.

(3) A number of properties have been measured. The gross properties are more or less understandable, and frequently resemble either a related crystalline solid, or molecule. For example, the optical absorption involving electronic transitions in amorphous silicon is largely a broadened version of that found in crystalline silicon; vibrational excitations studied in quartz, crystoballite, and vitreous silica are very similar in main features; infra red spectra in chalcogenide glasses show many features directly relatable to molecular bonds of various types.

(4) While the gross features are fairly well understood, low absorption tails and other fine features are not, and here must begin the next era in this part of this science. The optical properties of amorphous Si and Ge are yet to be explained in the tail regions and frequently the absorption is much lower than expected from the electron density of states inferred from electrical measurements, assuming a spatially uniform medium.

(5) Theory of both structure and properties seems to fall into two parts: Phenomenological and formal modeling. Phenomenological

theories are necessary in the early stages of a subject, and later on in the initial design of experiments, but they are limited. It is the writer's impression that the phenomenological theory is not yet very convincing in detail, being mainly troubled by the extension of (frequently oversophisticated) constructs previously developed in band theory or many body theory to situations in which they are quite inappropriate. Alternatively the formal models suffer in being too highly idealized, at least regards amorphous materials. They are useful, as was the Kronig-Penney model in energy band theory, but detailed results may often contain artifacts or be idealized to the point of omitting essential physics. Computer experiments based on models are quite instructive. Both these and formal solutions give useful insight into many major features of observed properties, but as to finer details and critically reasoned general results much remains to be done.

(6) Certain features particularly relevant to amorphous semiconductors have now been recognized as extremely important. Both computer models and formal theories have led to the concept that in sufficiently disordered materials, in so-called "tail-states" regions, there is a behavior not previously found in crystalline systems. That is, even though the energy of the state lies in a continuous spectrum the state may be spatially localized (Mott, Anderson). The point about semiconductors, as compared with metals, is that the electrons which dominate the behavior lie in just these states. This has led (Cohen, et al.)

to a differentiation between state densities, and mobile state densities. There seems little doubt at this point that these ideas are conceptually correct. However, critical experiments and comparison with equally relevant theory is much needed.

(7) The description of transport in amorphous semiconductors frequently uses the language of band theory. In part, this is because a convenient substitute to use in disordered systems has not developed very far. Basically, what is needed is a melding of hopping and drift theory, and the origins of such may well lie in the literature of transport in narrow band systems and by polarons. For this reason, reference to some of that literature is included in the bibliography attached.

(8) Technological Applications: This subject is moving rapidly enough that an overly brief summary would not do it justice. Indeed, by the time this report issues two extensive up-to-date reports covering applications of amorphous semiconductors should be forthcoming: National Academy of Sciences - National Materials Advisory Board Report on Amorphous Semiconductors; and Proceedings of the International Conference on Amorphous Semiconductors, Ann Arbor, August 8-13, 1971.

These views have been presented in general terms, but the supporting details may be found by browsing over the bibliography which follows; it is intended to provide the interested reader with an introduction to various aspects of the subject of amorphous materials, and is not intended to be all-inclusive.

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SUMMARY OF MEETING
ON
MASSIVE DISORDER CARBON SYSTEMS

E. E. Hucke

As a part of the discussion of amorphous materials, a subgroup met in Woods Hole to consider disordered carbon (glassy carbon and isotropic low temperature vapor deposited carbon). In addition to a consideration of technical questions, the meeting had a secondary objective of coordination of the recently established ARPA research programs in this field.

The meeting was especially structured to bring together a interdisciplinary group including polymer specialists, metallurgists, physicists, chemists, crystallographers, as well as carbon specialists. In addition, the group was chosen to represent those in governmental and military laboratories as well as those in the academic field.

During the first session, Professor Walker presented his views of the outstanding research developments in the carbon field from the just completed International Carbon Conference. While his talk and the ensuing discussion covered a variety of topics, several new thoughts were stressed. In particular, for a variety of reasons, related in many cases to environmental problems of air and water treatments, it appears that a new emphasis on the use of carbon for adsorption and catalysis will emerge in the next five years. In particular, new results show-

ing very large oxygen pick-up from atomic oxygen sources were discussed. In a related development, recent German work has shown the possibility of using a very cheap, porous disordered carbon for economically concentrating the oxygen content in air up to about 50%. Such a development could have obvious implication in large scale oxygenation processes such as sewage treatment and steelmaking. Professor Walker also presented recent work on the systematic variation of crystallinity of solid carbons made from antracene-biphenol solutions. The former was shown to yield well defined crystalline graphite, while the latter gives a glassy carbon. A smooth transition can be made by using mixtures of the two. The important, and as yet largely unknown effects of carbonization under pressure were also cited as areas showing promise for yielding different new variants of carbon.

Professor Walker projected the following areas for the growth of new applications in the next ten years.

1) "Alloyed" carbon structures - materials with either of two phases continuous or discontinuous, or with metal or metalloid elements dissolved.

2) Chemically active carbons - new, more versatile molecular sieve materials of the low temperature glassy carbon type for absorption and catalysts.

Professor Fischbach gave a short discussion of the current state of evidence for the various "new" crystalline forms of carbon. The discussion centered upon "Chaoite" (white

graphite); "Lonsdalite" (hexagonal variant of diamond) and a newly reported ion deposited carbon with "diamond-like" properties. While much of the evidence is controversial, it seems clear that there still remains much to be learned about even the crystalline states of carbon.

One day of the conference was given to the discussion of evolution of structure in disordered systems. To that end, Dr. Chompff developed an interesting theoretical model of the cross-linking of thermosetting polymers. His mechanism, one of developing density fluctuations over regions of about 70 angstroms forms a believable explanation for many of the structural characteristics of glass carbon produced by pyrolysis of these resins.

Further discussion by the group centered on the inter-relation of crosslinking and the actual destructive pyrolysis of the resin during carbonization. The importance of chemical as well as procedural variations was stressed. Professor Fischback presented his views and lead a discussion of the evolution of structure in the high temperature range (after carbonization). Several ideas concerning the remarkable difficulty in graphitization of glassy carbons were presented. Among these was the possibility that graphitization was limited by nucleation problems involving the lack of any embryos of large enough size for growth to proceed.

Dr. Eugun gave a very detailed review of the structure of disordered carbon as determined by X-rays. He presented a radial

destruction function indicating a structure of random faults, with about 50 Å mean distance between faults and imperfect layered structure. According to Ergun, a quinoid layered structure gives a slightly better fit than does a graphite layered structure.

The need for more discriminating atom-atom coordination studies was made apparent. Professor Carpenter gave a preliminary neutron diffraction pattern on a glassy carbon prepared at the University of Michigan. Further work on this sample and two others should yield radial distribution function precise enough to answer many of the questions remaining concerning local bonding in glassy carbons.

Measurements to be carried out at Michigan aimed at a clearer determination of the thermodynamics of the various disordered forms were reviewed. This work, together with calorimetry should yield directly vibrational and configuration measures of bond energy and entropy.

A group discussion was held concerning the need for standardization of certain experimental techniques, especially X-ray, used in this field. A subgroup will attempt to address this problem. Efforts to coordinate sample exchange among the various research groups were also discussed.

The final session on potential applications discussed the unusual properties already known and the directions in which further improvements are probable. It was concluded that potential applications will lie in several areas where unusual

combinations of strength, chemical stability, and density are the key factors. Applications data must await a better understanding of the possible ranges of properties that can be produced with more sophisticated control of structure, particularly through variation in polymer precursor.

APPENDIX

ABSTRACTS

GRADIENTS IN POLYMERIC MATERIALS

M. B. Bever and M. Shen

In this memorandum we consider the structure and properties of polymeric materials possessing spatial gradients. Potential applications of such materials are also discussed.

Gradients in the structure of polymeric systems may be generated by varying the chemical nature of the monomers, the molecular constitution of the polymers and the supramolecular structure or morphology of the polymers. Gradients in each of these categories are possible for single-phase as well as heterophase systems. Such gradients are associated with gradients in properties.

The properties considered are chemical, mechanical, biomedical and transport properties. Structural gradients in the polymeric system may lead to a desired gradient in a single property, or to a combination of more than one property which may assume optimum values in different regions of the material. In the latter case, one of the properties is frequently related to mechanical integrity.

Possible applications of gradient polymeric systems include plastic gasoline tanks, biomedical implants, and damping materials for a wide frequency range.

EFFECT OF STRAIN ON THE FERMI ENERGY OF SIMPLE METALS

R. Gomer and R. M. Thomson

The effect of the strain on the chemical potential and work function of a metal is reinvestigated. The result is of some importance for electron emission from metal tips under high fields and at crack tips. The results show that the chemical potential change is more complex than that predicted in an earlier work by Schrieffer and Tiller, but usually of the same sign.

NOTE ON DENSITY DETERMINATION ON AMORPHOUS MATERIALS

R. Gomer

A possible method of measuring the density of amorphous films is described.

MODIFIED NULL-FLUX MAGNETIC SUSPENSION AND PROPULSION SYSTEM FOR HIGH-SPEED TRANSPORTATION

M. Tinkham and P. L. Richards

A detailed Fourier analysis is given for a new hybrid system for magnetic suspension and propulsion of high-speed trains (~300 mph). The hybrid system combines the advantages of null-flux (low drag and feasible synchronous propulsion) with those of the image-force scheme (a cheap smooth track, typically 1/4" aluminum sheet); its disadvantage is that it requires a double set of opposing train magnets (as does one of the null-flux systems already proposed by Powell and Danby). The analysis shows that a drag/lift ratio as low as 1/80 should be obtained with reasonable parameter values, far superior to any simple image-force system, and much less than air drag over the useful speed range. Another advantage of this system to the image-force scheme is that its strong magnets facilitate synchronous propulsion. It is shown that the active track required for this propulsion could be energized in sections of several miles without undue power loss. The stability of this drive is studied, and shown to offer no serious problems for small fluctuations, but there may be a serious problem in maintaining synchronism during planned or accidental accelerations and decelerations.

MAGNETIC SUSPENSION AND PROPULSTION SYSTEMS FOR HIGH-SPEED TRANSPORTATION

P. L. Richards and M. Tinkham

High speed transportation vehicles (trains) carrying superconducting magnets can be levitated by repulsion from diamagnetic currents induced in a conducting track. Various approximate methods are presented for calculating the lift and drag forces for such magnetic suspensions. Fourier analysis of periodic train magnet fields is used to analyze "image force" and "hybrid null flux" systems which involve homogeneous conducting sheet tracks. A lumped circuit analysis is used to discuss the "null flux" principle and related systems with structured tracks. The stability and efficiency of linear induction and linear synchronous motor propulsion systems are studied using related methods.

CONSERVATION LAWS AND ENERGY RELEASE RATES

B. Budiansky and J. R. Rice

New path-independent integrals recently discovered by Knowles and Sternberg are related to energy release rates associated with cavity or crack rotation and expansion. Complex-variable forms are presented for the conservation laws in the cases of linear, isotropic, plane elasticity. A special point concerning plastic stress distributions around cracks is discussed briefly.

APPLICATION OF A DEFECT MODEL TO VITREOUS SOLIDS

R. A. Huggins

The translation of the concepts of defect chemistry developed for crystalline solids to the description of the structure of one class of "amorphous" materials, the vitreous oxides, is discussed. Of specific interest are the types and concentrations of unusual local structural configurations and the influence of oxygen activity and solute concentrations.

THERMODYNAMIC PROPERTIES OF LIQUID METALS

J. L. Margrave

As a continuation of the project started earlier, an extended effort has been made to collect the best available data on the themodynamic properties of liquid metals, including heats and entropies of fusion, heat capacities and surface tensions. Attention has been concentrated on the heats and entropies of fusion and the heat capacities in a search for parameters which would allow correlation and make possible reasonably reliable predictions for the many high melting elements yet unstudied - Cr*, Hf, Ir, Mn*, Os, Re, Rh, Ru, Ta*, W and Zr - as well as the hundreds of important refractory compounds and alloys. A mutually consistent table of such liquid metal properties has been assembled and various correlations are presented graphically.

Special attention has been given to correlations of the entropies of fusion with structure parameters and the literature has been surveyed for information regarding theoret-

*Currently under study.

ical approaches for explaining the rise of the specific heats of both elemental solids and liquids far beyond the 3R predicted by either the Debye or the Born-von Karman theories. The predominant literature explanation is "anharmonic effects" but new experimental data* show strong correlations with electronic configurations and suggest that new calculations which take into account the actual densities of states at high temperatures might yield more realistic electronic contributions to the specific heat than those usually predicted by the equation

$$C_{e\ell} = \left(\frac{\pi i^2 Nk}{2T_F}\right)T = \gamma T$$

when applied in the evaluation of γ from low-temperature heat capacity data.

*Various publications making use of levitation calorimetry in High Temperature Science and in Journal of Chemical Thermodynamics.

STRESS CORROSION CRACKING IN PLASTIC SOLIDS INCLUDING THE ROLE OF HYDROGEN

J. J. Gilman

Small changes in surface environments can change the energy needed to create a surface shear step. Increases in this energy tend to shift a delicate balance between glide and cleavage initiation at a crack tip. By inhibiting plastic deformation this causes an increased tendency for cleavage. Thus a material that is ductile in a vacuum can become quite brittle in the presence of certain surface active environments; particularly atomic hydrogen.

The quantitative criterion for deciding whether flow or cleavage will prevail is the ratio of the appropriate glide plane's surface energy to the cleavage plane's surface energy.

A survey of the strengths of the interactions between hydrogen and metals has been made. Throughout the periodic table strong diatomic interactions occur. At surfaces the interactions remain strong although they are somewhat weaker. In solid hydrides they tend to be much weaker or nonexistent. Thus the strength of the interaction depends on the metal-metal distance. It is shown that for a typical transition metal the interaction with hydrogen is strong enough to readily cause embrittlement.

ESTIMATING PREDICTION AND TOLERANCE LIMITS FOR EXTREME VALUE DISTRIBUTION

F. A. McClintock and J. O. Wilkes

Abstract not available.

A UNIFIED THEORY FOR THE FREE ENERGY OF INHOMOGENEOUS SYSTEMS

L. A. Swanger, G. M. Pound and J. P. Hirth

Recent theories for the free energy of inhomogeneous systems are considered and shown to be consistent when certain apparent discrepancies in coordinate systems are removed. The question of reduction of symmetry of a crystal to that of the group $C_{\infty v}$ in the presence of a field gradient is discussed. Conditions for the existence of odd-order gradient terms in a free energy expression are presented.

THEORY OF IONIC TRANSPORT IN CRYSTALLOGRAPHIC TUNNELS

W. H. Flygare and R. A. Huggins

A theoretical model has been developed for the treatment of the motion of ions through crystallographic tunnels, as are found in materials that are interesting solid electrolytes. This model, which includes consideration of both point charge and higher order attractive terms as well as overlap repulsion effects, allows the calculation of the minimum energy positions of mobile ions and the activation energy barrier that they must surmount to move through the lattice. Calculations have been made for ions of different sizes in the AgI lattice which show the experimentally observed dependence of mobility on ionic size, and initial steps have been taken toward extensions to more complicated structures.

EFFECT OF STRESS ON ELECTROCHEMICAL DISSOLUTION

R. Gomer and R. Thomson

Some simple thermodynamic considerations are applied to the dissolution of material from a surface under stress such as obtained at a crack tip. We estimate that the EMF generated at the crack tip in iron is of the order of four millivolts.

AMORPHOUS METALLIC ALLOYS

P. E. Duwez

During the last ten years, a relatively large number of amorphous alloys with metallic properties have been obtained by very rapid cooling from the liquid state. This paper presents a brief review of the chemical compositions of these alloys and the factors which appear to be important in obtaining the amorphous state after quenching from the melt. The unusual electrical and magnetic properties of these alloys are discussed. There is some strong indication that these properties are unaffected by rather high doses of radiation. References are given to 52 papers published on the subject before June 1971.

DIFFUSION THROUGH COMPOSITE POLYMER SYSTEMS

John D. Ferry

The factors influencing the diffusion coefficient for a small molecule through a composite structure of permeable (polymeric) and impermeable domains are discussed. Calculations of the geometrical structure factor based on various models with a continuous permeable phase are reviewed; they are similar enough so that deviations of experimental data therefrom may be interpreted in terms of other features such as modification of the local molecular mobility in the continuous phase, failure of contact between phases, and gross alterations of morphology.

REMARKS ON MONTROLL'S NONLINEAR WAVE EQUATION

G. H. Vineyard

A solvable non-linear integro-differential equation which is a conceivable model for shock wave phenomena is examined. Conditions for the existence of an energy integral of the equation are determined and found to impose severe restrictions on the coefficients.

"RANDOM CLOSE PACKING" OF SPHERES

G. H. Vineyard

Elementary considerations of the density of a "random close packed" arrangement of hard spheres are given.

NOTE ON IR WINDOWS

N. Bloembergen

Considerable attention has been devoted to the thermal loading with resultant deformation and beam distortion, when an infrared laser beam traverses a window material. In comparing window materials, it has typically been assumed that the laser beam would be on for a period of many milliseconds or longer. It is pointed out in this note that a different situation prevails when the duration of the laser pulse is shorter than the time required by a sound wave to traverse the window. In the limit of very short pulses the beam deformation due to residual absorption in the window is largely determined by $(\partial n/\partial T)_{strain}$. Since the peak powers in the short pulses will be orders of magnitude higher than in pulses lasting milliseconds or seconds, attention should be paid to other possible modes of window failure in this regime.

LINE TENSION AND KINKS ON FRACTURE CRACKS

J. J. Gilman, J. P. Hirth & R. M. Thomson

The concept of line tension for a crack is explored and applied to the atomic kink on a crack. The line tension turns out to be so dependent upon shape that a simple use of it as in dislocation theory is not possible. For atomic kinks, the argument leads to the prediction of an abrupt kink shape. The activation energy of the kink is not unique, but has values over a range from zero to a maximum value. This range of activation energies results from the lattice trapping plateau for the crack.

STATES OF EASE OF POLYMERIC ENTANGLEMENT NETWORKS CROSS-LINKED IN STRAINED STATES

John D. Ferry

An experiment is proposed to provide information about the nature of "entanglement coupling", a somewhat vague concept which is widely applied to interpret mechanical and other physical properties of polymers of high molecular weight. A sample of such a polymer, visualized as a network of entanglement loci, is deformed in simple extension and subjected to chemical cross-linking; upon release it contracts and approaches a first state of ease in which the forces exerted by the effective networks of entanglement loci and of cross-links are

balanced. If some of the entanglements remain untrapped by the cross-links and can rearrange, the sample then more slowly extends again and approaches a second state of ease. The dimensions in these states have been evaluated numerically for various cases, based on existing theories for the related problem for chemical cross-links in two successive stages. Experimental measurements of equilibrium dimensions, as well as the kinetics of dimensional change, and also changes in dimensions on subsequent swelling in solvent, can clarify the nature of entanglement coupling and trapping.

DIFFUSION THROUGH ANISOTROPIC POLYMER SYSTEMS

John D. Ferry

An experiment is proposed to provide information about the effects of large deformations on the local molecular mobility in rubbery polymers, and the mechanism of translatory motion of foreign molecules, either small (molecular weight about 200) or polymeric (10^4-10^5). Diffusion of a radioactively tagged penetrant from a point source in a stretched strip is monitored by autoradiography, giving the ratio of diffusion coefficients in the two principal directions. The absolute coefficient in the stretch direction is obtained by diffusion from a line source, and compared with that for the isotropic polymer. Free volume fluctuation theory can be used to provide a coefficient which measures the relative ease of penetration in different directions, probably influenced also by the shape and flexibility of the penetrant molecule. Polymeric penetrants may reveal additional effects associated with entanglement coupling, related also to the density of cross-links in the polymer matrix.

SOME PROBLEMS IN BULK POLYMERIC SYSTEMS

H. Reiss

A condensed summary of some of the statistical techniques used in the study of polymer chain configurations is presented.

In connection with the theory of polymers containing rings, a new variation principle is developed which can be used in connection with associated configurational problems. This variation principle leads to a "self-consistent field" solution of the configurational problem. The theory of rubber elasticity is discussed, and the possibility of applying the variation principle to this phenomenon considered.

Glassy polymers and the glass transition are discussed, and some ideas connecting the glass transition and what appears to be a related phenomenon involving a fluid-solid transition observed in a system of hard spheres are considered. The hard sphere transition is really a glass-avoiding transition for which we have coined the term "hyalo-phobic transition".

Block copolymers and their participation in the formation of heterophase polymer bulk polymers are also discussed. It is suggested that the fairly well developed field of the statistical thermodynamics of curved surfaces might be of use in connection with the heterophase transition.

Inhomogeneous bulk polymers resulting from the formation of inhomogeneous networks are discussed. Some corrections are applied to the "gel ball" theory of Labana, Newman, and Chompff. Polymer crystals are also treated.

Finally, frictional and dynamical effects in bulk polymers and polymer solutions are considered. The Rousse model is outlined and possible future directions are indicated.

A NOTE ON THE GROUND STATE ENERGY OF AN ASSEMBLY OF INTERACTING ELECTRONS

Akira Isihara and Elliott W. Montroll

The ground state energy of an assembly of charged particles of density ρ imbedded in a continuum of charge of the other sign in an electrically neutral system is considered. Asymptotic formulae for the ground state energy of such systems are known in the high and low density regimes. An interpolation formula covering the entire density range is derived using the method of two point Padé approximants. A phase transition from an electron lattice to an electron gas seems to occur at $r_s \simeq 14$, r_s being the radius of a sphere which, on the average, contains a single charge, in units of the Bohr radius of the electron in a hydrogen atom.

A RIGID-PLASTIC MODEL OF SPALL FRACTURE BY HOLE GROWTH

F. A. McClintock

A numerical procedure is formulated for calculating spall fracture by hole growth, as approximated by the spherical growth of holes in rigid-plastic material. An order-or-magnitude

estimate indicates that inertia effects are more important than rate effects and that this model is likely to be appropriate for 6061-T6 aluminum alloy at stresses up to twice the static strength.

SD EFFECT

D. C. Drucker

The distinction between true and apparent strength-differential (SD) effects must be sharpened and definitive experiments performed to evaluate recent data and place plasticity theory in proper contect.

ENERGY TO CREATE NEW SURFACE DURING CRACK PROPAGATION

D. C. Drucker

An understanding of the effect of microstructural and atomic features and properties along with the influence of corrosive and other environments depends critically on the energy needed to create new surface, an energy which is neither the thermodynamic equilibrium surface energy nor the energy needed to deform bulk material.

ON GRADIENT MATERIALS: PHENOMENA AND FUNDAMENTALS

M. B. Bever

Materials with compositional and structural gradients are of considerable interest and importance, expecially as they are being used in an increasing number of applications. This memorandum will consider systematically the types of gradients which can occur in the major classes of materials. The basic characteristics of gradients and the effects of gradients on some properties will be discussed qualitatively. Brief attention will be given to the preparation of materials with various gradients.

Gradients occuring in single-phase and multiphase metals and alloys will be discussed in detail; examples will be drawn especially from the physical metallurgy of steel. Typical gradients in ceramics, polymeric materials and composites including cermets will also be reviewed. The mathematical analysis of gradients and the effects of gradients on properties will be dealt with in later memoranda.

ANALYSIS OF STRESS INTENSITY FACTORS IN A PLATE WITH ANY GIVEN DISTRIBUTION OF CRACKS

M. Ishida

A translation by Mr. Coe Ishimoto, M.I.T., for ARPA Materials Research Council.

EDGE DISLOCATION ARRAYS AROUND A CRACK UNDER TENSION

F. A. McClintock

Abstract not available.

HIGH TEMPERATURE STABILITY OF SILICON NITRIDE

J. L. Margrave

Within the last decade the level of interest in silicon nitride as a practical refractory has risen meteorically and it is somewhat surprising that the high-temperature thermodynamic properties have been so poorly characterized. In this paper, new calorimetric data on a variety of Si_3N_4 samples will be presented and a reliable value for the standard heat of formation derived. This information, coupled with available and/or estimated thermodynamic functions for the material at elevated temperatures, can be used for comparison with decomposition pressure measurements. Mass spectrometric studies allow one to demonstrate that only elemental species (Si(g) and N_2(g)) are important in ordinary decomposition but other complex species are known -- Si_2N and SiN -- which may play a role in forming techniques and in establishing ultimate use limitations.

THE USE OF LEVITATION IN INORGANIC SYNTHESIS

J. L. Margrave, J. A. Treverton and P. W. Wilson

The technique of electromagnetic levitation has been adapted for the synthesis of refractory compounds in inert or protective atmospheres. Thus, carbides, borides, silicides, nitrides, etc., can be prepared without worrying about contamination caused by crucibles or electrodes or other foreign objects in the reaction zone. Reactive gases can yield volatile species. A broad summary of the potential applications of this method will be prepared.

HIGH-TEMPERATURE PROPERTIES OF Nb AND Zr

J. L. Margrave and A. J. Valerga

Various high-temperature data available on these two important elements will be summarized and critically evaluated. New data from levitation calorimetric studies will be included and a complete set of thermodynamic properties will be presented for both the solid and liquid phases. The emissivities of both solid and liquid phases will be discussed.

PYROLYSIS OF POLYMERS AND SIMPLE ORGANIC MOLECULES

J. L. Margrave

The techniques of mass spectrometry and of matrix-isolation infrared spectroscopy may be combined to yield meaningful descriptions of the species which are formed in the primary mechanistic steps of pyrolysis. Decomposition of the hydrides of boron, carbon and silicon establish the presence of species like MH, MH_2 and M_2H as well as the expected MH_3, MH_4, M_2H_6, etc. Mass spectrometric characterization then facilitates the interpretation of infrared spectra of such pyrolysis intermediates when they are frozen out on surfaces at liquid helium temperatures.

Recent experimental work at Rice has identified species like $Si(CH_3)_2$, CCl_2, CCl_3, CCl_2Br, etc. Such studies are needed to allow reliable interpretation of pyrolysis data on hydrocarbon and other more complex polymers.

EMISSIVITIES OF LIQUID METALS

J. L. Margrave, D. W. Bonnell and A. J. Valerga

Emissivities for transition metals have been evaluated in the region of the melting points. Data for both solids and liquids will be presented.

HEATS OF FORMATION OF VARIOUS TYPES OF CARBON AND GRAPHITE BY COMBUSTION CALORIMETRY

J. L. Margrave

The literature for 1960-70 will be surveyed to assemble data on the combustion of various forms of carbon or graphite, usually in oxygen, to yield CO_2. This technique allows one to define energetic differences in materials prepared by different processes and thus, to get a feeling for strain and extent of graphitization. At the moment, there is sure evidence that the heat of formation of CO_2 (gas), a standard reference point in thermodynamic tables, is slightly in error because of ambiguity in the definition of just which kind of graphite is really the "reference" or "standard state".

THE Li/CFX ELECTROCHEMICAL CELL AND RELATED PROBLEMS

J. L. Margrave

Current efforts at the United States Signal Corp. Laboratories, Fort Monmouth, toward the development of a Li/CFX primary cell are being renewed with special attention to material problems -- preparation and characterization of CFX, container problems, electrical designs, and the general chemistry of the various stoichimetric forms of CFX.

STRESS WAVES GENERATED BY PRESCRIBED PRESSURE HISTORIES ON A LAMINATED COMPOSITE HALF-SPACE

J. A. Krumhansl and E. H. Lee

Floquet waves form a complete set of functions with which to represent transient motion by a Fourier type integral. Krumhansl (ARPA Mat. Res. Council Rep., p. 175, 1970) utilizes this approach to analyze the effect of impulsive pressure on the surface of a laminated composite half-space, with periodic laminations lying parallel to the plane surface. For a prescribed pressure variation over a short duration, such as arises from a plate slap experiment, the solution during pressure application can be obtained by wave refraction and reflection theory. The Floquet solutions for the whole space, which give odd functions for stress, provide a complete set of functions for the half space with zero traction on the surface. Using these, a Fourier-Floquet integral can represent the initial wave solution after contact has ceased, and provide a convenient

mathematical representation of the subsequent motion. This is carried out, and the corresponding head of the wave asymptotic solution formulated to provide the initial main influence in the far field.

PROPAGATION OF TRANSIENT ELASTIC WAVES IN PERIODIC COMPOSITES

J. A. Krumhansl and E. H. Lee

The propagation of transient elastic waves, particularly impulses, through a periodic medium is discussed in the linear regime. Basically, the method is the generalization of Fourier methods to Fourier-Floquet transient analysis. The "far field" solutions have certain common features, and can be related to "head of the pulse" solutions found by the equivalent of ray tracing.

DETERMINATION OF STRESS PROFILES FOR WAVES IN PERIODIC COMPOSITES

L. Bevilacqua, W. Kohn, J. A. Krumhansl and E. H. Lee

Floquet or Bloch wave theory provides a convenient basic set of functions for representation of the propagation of transient elastic stress waves in periodic composites (Krumhansl, ARPA Mat. Res. Council Report, p. 175, 1970). Variational principles for computing dispersion relations and hence phase velocities generate a band structure of pass and no-pass frequency bands (Kohn, Krumhansl and Lee, ARPA Mat. Res. Council Report, Vol. I, Paper No. 2, 1969 and ASME Preprint 71-APMW-21, to appear in Jour. Appl. Mech.) Dispersion curves (frequency versus wave number) were accurately evaluated for laminar composites by using smooth Fourier series test functions for displacement in a Rayleigh-Ritz approximation procedure, but the corresponding stress profiles were unsatisfactory since the required continuity of stress at the inclusion-matrix interface was ruled out by the use of the smooth test functions for displacement and corresponding continuous strain profiles.

In this paper exact stress profiles are calculated for waves propagated normally to the laminae, and satisfactory approximations to these are generated with the extended variational principle which permits independent test functions to be used in the matrix and inclusions. An augmented plane wave approach in the Rayleigh-Ritz procedure was adopted in which exact solutions of the wave equation were used as component

test functions in the filament. It was found that with this procedure, accuracy was essentially independent of the ratio of elastic moduli of the inclusion and matrix. The variational approach is applicable to two and three-dimensional composite configurations, which are not amenable to exact evaluation.

A PROPOSED METHOD FOR THE EVALUATION OF THE THERMODYNAMIC PROPERTIES OF THE GLASSY CARBON-GRAPHITE EQUILIBRIUM

E. E. Hucke and S. K. Das

The available thermodynamic data for the graphite-carbon oxide equilibrium are critically reviewed, together with the meager data presently existing for heat capacity and heat of combustion of glassy carbon.

Five different, experimentally feasible, solid oxide cells and one molten salt cell are proposed to measure directly and more accurately the equilibrium thermo-chemical properties of the following reactions in the range of 600-1000°C.

$$CO(g) + \tfrac{1}{2}O_2(g) = CO_2(g)$$

$$C_{graphite} + CO_2(g) = 2CO(g)$$

$$C_{glassy\ carbon} + CO_2(g) = 2CO(g)$$

$$C_{glassy\ carbon} = C_{graphite}$$

The above data can be combined with low temperature heat capacity data for glassy carbon and graphite to yield configuration entropy and enthalpy values of glassy carbon relative to graphite. The configuration entropy value is a direct measure of the degree of disorder and can be used to compare with structural models of glassy carbon deduced from other physical measurements such as X-ray and neutron diffraction.

FLOW VIA DISLOCATIONS IN IDEAL GLASSES

J. J. Gilman

Nature of dislocation lines in glasses
Experimental evidence for the existence of dislocation lines
Kinematics of flow via dislocation motion
Dynamics of dislocation motion
Implications of dislocation mechanics

HARDNESS - A STRENGTH MICROPROBE

J. J. Gilman

REPORT OF THE CONFERENCE ON ENVIRONMENTAL DEGRADATION OF MATERIALS

J. P. Hirth, et al.

The Conference was organized so that fundamental aspects of stress corrosion cracking was discussed on the first day from a number of different viewpoints. Next, three groups met to consider the possible application of these ideas to the diverse problems of cracking of stainless steel, particularly in nuclear reactors; of the corrosion of high strength alloys, particularly aluminum and titanium; and of degradation of silicon nitride. The results of these deliberations were presented and discussed with the entire group on the final day, on which a general discussion of the field also ensued.

The initial paper in the following report is both a summary of the results of the conference and an overview of the field generated by the authors subsequent to the meeting. The remainder represents the Proceedings of the Conference.