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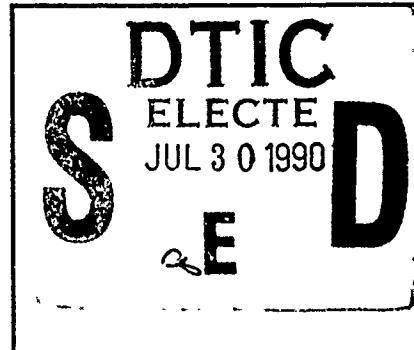
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AFOSR-TR- 90 0786

~~THE CHEMICAL PROCESSING OF STRUCTURAL CERAMICS
FOR USE IN SEVERE ENVIRONMENTS~~

AD-A224 410

A Workshop Sponsored
by
The U.S. Air Force Office of
Scientific Research

~~July 16 - 18, 1984~~

Workshop Summary
Prepared by

Norman L. Hecht
George A. Graves
and
Wendell E. Rhine

University of Dayton Research Institute
Dayton, Ohio

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THE CHEMICAL PROCESSING OF STRUCTURAL CERAMICS
FOR USE IN SEVERE ENVIRONMENTS

-A WORKSHOP-

INTRODUCTION

Recent advancements in several new and promising technologies have resulted in the availability of a diversity of improved structural ceramic materials through the development of novel chemical processing methods. As a result, the potential for utilizing ceramic materials in a number of advanced Air Force applications has been significantly expanded. The purpose of this Workshop was to understand the current "state-of-the-art" for chemical processing technologies of ceramic materials and to identify and suggest research needs and goals which would enable the successful Air Force utilization of improved structural ceramics in advanced systems.

It was the purpose of this Workshop to bring together leading scientists from academic institutions, industry, and the Government to direct their attention to defining the research needs for chemical processing technologies such as organo-metallic decomposition, organic to inorganic conversion processes, sol-gel, chemical vapor deposition, and related areas. All attendees were encouraged to participate in the series of discussions on the future requirements for structural ceramic and ceramic coating processes and aid in the identification of future research programs. An outline of the Workshop Agenda is presented in Table 1. A list of Workshop Attendees is presented in Appendix 1.

TABLE 1

THE CHEMICAL PROCESSING OF STRUCTURAL CERAMICS
FOR USE IN SEVERE ENVIRONMENTS
OUTLINE OF WORKSHOP AGENDA

MONDAY, JULY 16

Manager - Dr. D. Ulrich, AFOSR

Morning Session - 8:00 a.m.

1. Introduction of Co-Managers (8:00-8:15 a.m.)
General Announcements
2. Welcome - Dr. Don Ball, AFOSR (8:15-8:30 a.m.)
3. Description of Workshop Objectives and Format - Dr. H. C. Graham, AFWAL (8:30-8:45 a.m.)
4. Identification of Major Systems/System Objectives and System Needs - Dr. H. C. Graham (8:45-9:45 a.m.)
 - a) Rocket Motors
 - b) Heat Shields
 - c) Radomes
 - d) Turbine Engine Components
 - e) Discussion (9:25-9:45 a.m.)
5. Break (9:45-10:00 a.m.)
6. Carbon/Carbon Composites (10:00 a.m.-12:00 Noon) - Ms. Frances L. Abram, AFWAL
 - a) Advanced Polymer Starting Materials
 - b) Improved Processing
 - c) Improved Protective Coatings

Evening Session - 7:30-9:30 p.m.

1. Ceramic/Ceramic Composites - Dr. K. M. Prewo, UTRC
 - a) Materials/Processes for Matrix Development
 - b) Materials/Processes for Fiber Development
 - c) Composite Fabrication
 - d) Protective and Barrier Coatings

TUESDAY, JULY 17

Manager - Mr. J. Mazdiasni, WPAFB

Morning Session - 8:00 a.m.

1. Introduction and Overview for Chemical Processing - Mr. J. Mazdiasni (8:00-8:15 a.m.)
2. Colloid Chemistry - Dr. E. Matijevic, Clarkson College (8:15-10:15 a.m.)
3. Break (10:15-10:30 a.m.)
4. Sol-Gel Processing - Dr. L. L. Hench, Univ. of Florida (10:30 a.m.-12:30 p.m.)

TABLE 1 (Concluded)

OUTLINE OF WORKSHOP AGENDA

Evening Session - 7:30 p.m.

1. Thermal Treatments for Organic Polymer Precursors - Dr. R. West, Univ. of Wisconsin (7:30-9:30 p.m.)

WEDNESDAY, JULY 18

Manager - Dr. H. C. Graham, AFWAL

Morning Session - 8:00 a.m.

1. Chemical Vapor Deposition (and other gas phase reactions) - Dr. J. J. Gebhardt, GE (8:00-10:00 a.m.)
2. Coffee Break (10:00-10:15 a.m.)
3. Summary of Technical Discussions and Outline of R & D Needs (10:15 a.m.-12:15 p.m.)
 - a) Carbon/Carbon Composites
 - b) Ceramic/Ceramic Composites
 - c) Colloid Chemistry
 - d) Sol-Gel Processing
 - e) Polymer Processing
 - f) Chemical Vapor Deposition
4. Concluding Comments and Workshop Adjournment (12:15-12:30 p.m.)

(Note: The Topic Chairmen are expected to initiate their session, with a 30 minute presentation describing the current state-of-the-art and identifying some of the more promising opportunities. The Chairmen presentations would be followed by panel and floor discussions. The panel serves as discussion resources and facilitators.)

CHEMICAL PROCESSING WORKSHOP OVERVIEW

GREETING AND WORKSHOP INTRODUCTION

Dr. Donald L. Ball
Director of Chemical Science
Air Force Office of Scientific Research

Dr. Ball welcomed the workshop participants and presented a brief discussion defining the scope of the term "chemistry". He presented three different views: (a) Professor G. N. Lewis, who described physical chemistry as everything that is interesting, (b) Dudley Hirschbach, who distinguished chemistry from physics by saying that in chemistry there is always an irreducible residue of magic, and (c) Paul Flory, who defined chemistry as the science of molecules. Dr. Ball concluded his comments by extending his best wishes to the participants for a fruitful workshop that would take the fullest possible advantage of the magic in chemistry.

WORKSHOP OVERVIEW/SYSTEM DESCRIPTION AND IDENTIFICATION OF NEEDS

Dr. Henry C. Graham
AFWAL/MLLM
Wright-Patterson Air Force Base, Ohio

Dr. Graham discussed the workshop objectives and format, identified some of the major Air Force systems and the material needs associated with these systems. Figure 1 describes the workshop objective and Figure 2 outlines the workshop format. Dr. Graham initiated his presentation by pointing out that in the context of this workshop the term "chemical processing" is meant to represent a departure from traditional or conventional ceramic processing technologies. The goal of these advanced chemical processing techniques is to fabricate good, consistent ceramic products. Dr. Graham continued his presentation by presenting definitions for the terms "structural ceramic" and "severe environment" which are defined in Figure 3.

Dr. Graham also emphasized the current interest in ceramic-ceramic composites as a means for obtaining materials capable of

FIGURE 1
WORKSHOP OBJECTIVES

TO GENERATE WELL-FOUNDED IDEAS AND PLANS FOR
THE AIR FORCE PROGRAM TO DEVELOP HIGH
TEMPERATURE STRUCTURAL CERAMICS

FIGURE 2

FORMAT

- INTRODUCTION OF EACH TOPIC BY DISCUSSION LEADER PLUS 3 OR 4 HELPERS
- FLOOR IS OPEN - USE THE OPPORTUNITY
- NOT LOOKING FOR PROPRIETARY IDEAS - ONLY SCIENTIFIC DISCUSSION OF TOPICS
- GORDON CONFERENCE RULES
 - NO QUOTING OF DATA OR DISCUSSIONS WITHOUT SUBSEQUENT PERMISSION OF THE INDIVIDUAL
- WEDNESDAY LEADERS WILL FEEDBACK - OPPORTUNITY FOR FINAL COMMENTS/CORRECTIONS/ETC. BY PARTICIPANTS
- ADDITIONAL TOPIC WILL BE CONSIDERED - PRESENT SUGGESTIONS TO MAZDIYASNI/ULRICH ASAP OR WHEN THEY OCCUR TO YOU
- MEETINGS WILL START ON TIME
- BREAKS WILL BE A LITTLE FLEXIBLE
- WE WILL BREAK FOR LUNCH ON TIME
- WE WILL REOPEN ANY UNCOMPLETED DISCUSSIONS IF AT ALL POSSIBLE
- AFTERNOONS ARE FREE

FIGURE 3

DEFINITIONS

- CHEMICAL PROCESSING

DEPARTURE FROM TRADITIONAL COMPACTION OF POWDER (GREEN BODY) FOLLOWED BY HIGH TEMPERATURE DENSIFICATION/REACTION

- STRUCTURAL CERAMICS

COMPONENT CARRIES A LOAD - HOPEFULLY MORE THAN JUST SUPPORTING ITSELF (ELECTRONIC PROPERTIES ARE SECONDARY OR OF NO INTEREST)

- SEVERE ENVIRONMENT

X HIGH TEMPERATURE	2000 TO 4000°F
X LONG TIME	4000 TO 10 HOURS
X IMPACT/POINT LOADS	DIRT TO JOINTS
X VIBRATION	LOW TO HIGH CYCLES
X FUEL	JP10 TO B-SLURRY (OXIDIZING)
X CYCLIC	

withstanding the severe environments anticipated for advanced Air Force systems. The need for candid discussions in the workshop sessions was emphasized. Dr. Graham concluded this section of his presentation by emphasizing that the participants should not be inhibited by traditional ideas and concepts and that right brain (ideas) were encouraged for the workshop.

Dr. Graham initiated the second portion of his presentation by presenting a series of Graham's truisms (see Figure 4). In essence these truisms identified requirements and material concepts common to major Air Force systems. The first truism pointed out the lack of a single test available to qualify materials for components in major Air Force systems. Dr. Graham also pointed out that system designers are the people that the materials scientists and technologists are working for, and it is important to build up their confidence in the materials being developed; however, in many cases adequate tests are not available to achieve this goal. This is particularly true for the new ceramic composites systems being developed, for which basic testing techniques and methodologies have not been developed.

The importance of processing and how it is the key to the formation of any good material was identified by Dr. Graham. It was further mentioned that effective processing controls can limit the need for costly inspection systems. The key to effective processing control is contained in understanding the material and how to process it.

The final Graham truism identified the need to develop procedures which will provide near-net-shape or net shape capabilities for monolithic and composite ceramic systems.

As shown in Figure 5, there are four major Air Force systems of interest. These systems represent a considerably diverse array of material needs. Each system utilizes a diversity of components which require a wide variety of materials capable of operating in severe environments. In the general sense, it can be stated that all of these systems need good materials, and a good material can

FIGURE 4
TRUISMS (GRAHAM'S)

- NO SINGLE TEST IS AVAILABLE TO EVALUATE THE PERFORMANCE POTENTIAL OF MATERIALS USED IN SEVERE ENVIRONMENTS.
- QUALITY CANNOT BE "INSPECTED IN" (AND INSPECTION IS COSTLY).
- PROCESSING IS THE KEY TO "GOOD" MATERIAL.
- KEY TO PROCESSING IS AN UNDERSTANDING OF THE MATERIAL AND HOW TO PROCESS IT.
- WE MUST DEVELOP NET OR NEAR-NET SHAPE CAPABILITY.

FIGURE 5 SYSTEMS

- ROCKET MOTORS
- HEAT SHIELDS
- RADOMES
- TURBINE ENGINES

PROPERTY REQUIREMENTS FOR INDIVIDUAL
COMPONENTS ARE NUMEROUS AND VARIED

AND

THE KEY IS TO MAKE "GOOD" MATERIALS
THAT DESIGNERS HAVE FAITH IN

be defined as a consistent material that is stable and has a given set of properties that can be relied upon. Many of the material requirements offer the potential for the use of monolithic and composite ceramic materials.

When ceramic or ceramic composite materials are potential candidates, a major requirement is toughness. Toughness can be described as graceful or controlled failure. The second major requirement for ceramic materials is stability. Stability in both chemical and mechanical characteristics is required. For example, in rocket motors the material must be capable of maintaining its shape even though significant material loss can be tolerated. However, in the case of man-rated turbine engines, the material must be stable up to 4,000 hours at temperatures from 1800 to 2500°F. In missile systems, the material must be stable up to 10 hours at temperatures to 4000°F (see Figure 6).

The use of analytical process modeling techniques will be playing an ever increasing role in improving production technologies. The use of computer-aided engineering for computer processing applications looks quite promising. Dr. Graham discussed some of the current activities in his AFWAL Materials Laboratory exploring the potential for computer aided engineering in materials processing. Dr. Graham described the development of dies, designs, and preforms for extrusion processes (see Figure 7). The studies described by Dr. Graham showed how these techniques can be employed for developing unique processing routes and how the results demonstrated that intuition may not always be an accurate guide for the development of die designs and or processing routes.

The Processing and High Temperature Materials Branch of the AFWAL is initiating an internal program to also look at extrusion of selected glasses with whisker reinforcement. However, this project is only in its initial phase, and there is some difficulty in obtaining the necessary property data needed for effective process modeling. The utilization of these analytical procedures can reduce material processing programs that normally took two to three years to a few days. Computer processing techniques look very exciting and should find a large role in chemical processing.

FIGURE 6
SYSTEM NEEDS

TOUGHNESS

(GRACEFUL FAILURE)

STABILITY

(CHEMICAL AND MECHANICAL)

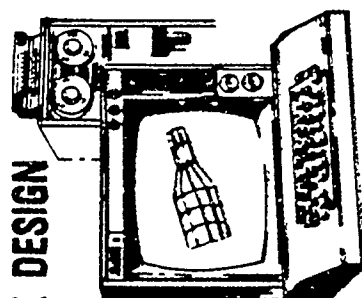
ROCKET MOTORS: HAS TO MAINTAIN SHAPE
BUT SIGNIFICANT MATERIAL
LOSS IS ACCEPTABLE

TURBINE ENGINES:

MAN-RATED	UP TO 4000 HOURS	1800-2500°F
MISSILES	5-10 HOURS	UP TO 4000°F

FIGURE 7
COMPUTER AIDED ENGINEERING

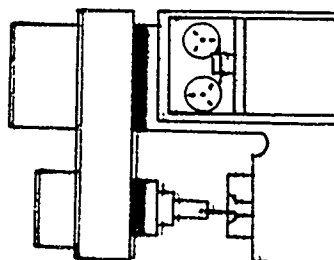
- PART DESIGN
- PROCESS ANALYSIS
- DIE DESIGN



PROCESS MODELING

DIE
GEOMETRY

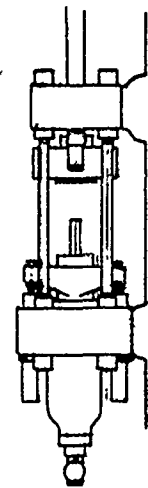
- NC DIE MANUFACTURING
AND INSPECTION



CNC MACHINE

DIES

- NET SHAPE
EXTRUSION



EXTRUSION PRESS

PROCESS CONTROL

An area of considerable importance to the Air Force is carbon-carbon composites. However a major problem is the lack of fundamental information about this family of materials. The current state of technology could almost be described as primitive. This situation has arisen partially because of the ease with which carbon-carbon composite products can be fabricated without really understanding the material or process fundamentals. However, as the structural application requirements become more demanding and the applications more sophisticated, the promise of these materials has been somewhat diminished. A major problem area is the inability in controlling the precursor material and the infiltration and reinfiltration processes. However, this situation is beginning to change.

Carbon-carbon composites are being considered to meet the need for materials to be used in both limited-life and man-rated turbine engines at temperatures to 3500-4000°F. These materials should have both toughness and stiffness. Because of the nature of the carbon-carbon composite materials, protection systems will be required to provide the necessary oxidation resistance. If it is not possible to devise effective coatings or other type of inhibitor mechanisms, the use of carbon-carbon systems may not be possible for these high temperature applications. However, to effectively design for these composite materials, more data is going to be required and this precipitates the need for effective test techniques of these anisotropic materials.

Dr. Graham also pointed out the need to better understand carbon fiber degradation mechanisms in order to design composites with improved strength and greater resistance to interlaminar shear. Poor interlaminar shear resistance of carbon-carbon composites is a critical problem and limits design application for many components. However, Dr. Graham stated that although there are still many problems with the utilization of carbon-carbon composites and there is considerable risk in their utilization, the payoff can be very great if successful systems can be developed.

In its simplest form, mats of carbon fiber are impregnated with carbon bearing precursors and then graphitized. In order to obtain desired densities and strength, the mats are subjected to multiple reimpregnation of the organic precursor and subsequent graphitization heat treatments. As densities are increased, the mechanical properties of the fiber are somewhat decreased, and it is quite usual to have the fiber strength reduced to one-half of its original value as a result of the processing procedure. These fabrication processes are also quite time consuming. A brief description of what carbon-carbon composites are and are not is presented in Figures 8 and 9.

The end product composite consists of carbon fibers that are loosely bonded in a carbon matrix that contains numerous cracks and holes. This type of structure presents a number of problems when nondestructive evaluation procedures are employed for composite analysis. Although the promise for carbon-carbon composites is quite high, it is important to recognize that there are conditions which would prohibit or rule out the use of carbon-carbon for turbine engine applications. These conditions are enumerated in Figure 10. As pointed out in Figure 10, it is important that compatible attachments to metallic structures in the engine are possible. However, only little effort is devoted to developing techniques for effective attachments, and this is an area that should receive greater attention.

Dr. Graham stated that if carbon-carbon composites prove to be unreliable, they would not be utilized in turbine engines. However, if they prove to be reliable, carbon-carbon composites would be used even if they could not be made as lightweight structures or very inexpensively. As better material becomes available, they will be used to replace the more expensive as less desirable systems. In response to questions from the floor, Dr. Graham pointed out that there were applications for carbon-carbon as heat shield materials in turbine engines if they could maintain strength of 10,000 ksi for thousands of

FIGURE 8

WHAT IS CARBON-CARBON?

- CURED AND GRAPHITIZED ORGANIC N-DIMENSIONAL CLOTH OR PREFORM
- TIME CONSUMING TO PROCESS (HAND LAYUPS, MULTIPLE IMPREGNATIONS/CURES/GRAPHITIZATIONS)
- C-FIBERS WITH LOOSELY BONDED C-MATRIX WHICH IS FULL OF CRACK AND HOLES
- TOUGH
- LIGHT
- ANISOTROPIC
- PROMISING

FIGURE 9

WHAT ISN'T CARBON-CARBON?

- OXIDATION RESISTANT (>800 F, CO_x)
- WELL CHARACTERIZED (UNDERSTOOD)
- HERE TODAY FOR "HIGH" STRENGTH APPLICATIONS

WHAT WILL KEEP C-C COMPOSITES OUT OF M/R TURBINE ENGINES

- X TOO SHORT A LIFE (SHORT UNDEFINED, BUT AT LEAST 600 H IS REQUIRED FOR MAN-RATED)
- X TOO LOW MECH. PROPS. (LESS THAN 10 KSI? HOW MUCH LESS?)
- X NON-COMPATIBLE ATTACHMENTS
- X UNRELIABLE (EITHER AS PRODUCED OR IN SERVICE)
- X LT. WGT. STRUCTURES UNAVAILABLE
- TOO COSTLY (DON'T KNOW COST WELL)
- X A "BETTER" MATERIAL (FOR 2D) NOZZLE MUST BE LIGHTWEIGHT, I.E., C-CR CERAMIC COMPOSITE)
- HIGH OBSERVATIONS (DESIGN AROUND?)
- X NON-REPAIRABLE
- X NON-INSPECTABLE
- X PREJUDICIAL

hours (4000); however, strengths of 20,000 ksi to 30,000 ksi are more desirable and would open up the potential for use in several structural applications. It should also be recognized that this materials gets stronger as temperatures increase and it is at its worst at room temperature. It is also important to recognize that carbon-carbon composites have poor shear strength resistance, frequently less than a 1,000 psi and sometimes only several hundred psi. As pointed out, multidimensional weaving of the fibers could overcome some of this, but it tends to reduce the overall strength properties of the composite. The current goal is to obtain composites with 30 ksi for use at 2500°F with the expectation that systems could be developed with 40 ksi at temperatures to 3500°F. Improvement in interlaminar shear strength can probably be achieved through a better understanding of the interface character of fiber and matrix.

Ceramists tend to think that a very dense matrix and good bonding are extremely important. However, for carbon-carbon composites, this may not be necessary, or for that matter desirable. It is quite apparent that nondense matrices can be quite acceptable. What is required is a tough, stable material that has a high degree of reliability. Both coated and uncoated applications are available for carbon-carbon composites, however, the carbon-carbon community is almost split into two camps on the subject. This need not be the case since a large amount of the development needed for coated systems is also required for the uncoated systems. The role and scope anticipated for coated carbon-carbon composites is described in Figure 11 and 12. Successfully developed coated carbon-carbon systems utilized in turbine engine systems would allow for higher inlet temperatures thereby increasing thermal efficiency, reduced cooling losses, and dramatically decreased engine size. This could be utilized in reduced fuel consumption, increased vehicle range, increased payload, or some combination of these. However, all of these benefits could not be enjoyed simultaneously.

FIGURE 11

Impact of Carbon/Carbon Material on Engine and System Performance

ADVANCED TURBOJET
INLET

TURBOJET
INLET

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ADVANCED
TURBOFAN

Fuel Consumption vs. Turbine Inlet Temperature (°F)

FIGURE 12

COATED CARBON-CARBON COMPOSITES

- FOR BOTH LIMITED-LIFE AND MAN-RATED ENGINE APPLICATIONS
- NEW BALL GAME (TOUGHNESS NOT STIFFNESS)
- AIR FORCE CONCENTRATING ON 2500°F, BUT WORKING WITH DARPA ON 3500°F APPLICATION
- COVERING FUNDAMENTAL UNDERSTANDING AS WELL AS PRODUCING PARTS WITH SOA MATERIAL FOR ENGINE TESTING
- TECHNOLOGIES INTERESTED IN
 - COATINGS
 - DESIGN (CRITICAL PROPERTIES AND METHODOLOGY)
 - PROPERTY DETERMINATION (INCLUDES MATRICES AND FIBERS SEPARATELY)
 - PROPERTY IMPROVEMENT (PRINCIPALLY STRENGTH) FABRICATION
- RISK IS HIGH
- PAYOFF IS VERY HIGH

Dr. Graham stated that there has been considerable effort in the development of carbon-carbon composite systems over the past 10 years. Initial flexure strengths were about 13 ksi and presently experimental systems now have flexure strengths as high as 70 ksi. It was also pointed out by Dr. Graham that there has not been sufficient basic studies of carbon-carbon systems and few studies have looked at the microstructure of these systems. The basic criteria used in most studies to determine whether the carbon-carbon system was effective or not has been percent weight change as a function of time and temperature. Little emphasis has been devoted toward developing composite toughness.

A tabulation of material systems of current interest is presented in Figure 13. Figure 14 describes the major protection approaches currently employed for carbon-carbon systems. Generally the carbon-carbon matrix is impregnated with silicon to form a silicon carbide phase. The surface of these systems are covered with one or more coating layers. For applications in the 3500°F range, consideration is being given to the use of thermal barrier coatings. In addition, there is some consideration being given to the use of cooling methods for these components.

In showing a micrograph of coated carbon-carbon composites, Dr. Graham pointed out that the major problem for the coatings developed to date is the development of surface cracks. This cracking is primarily due to the difference in the thermal expansions of the coating and the substrate (and it gets worse as the strength of the substrate increases!). Coatings tend to form cracks when brought down to room temperature, and sealing these cracks to prevent oxygen from entering the carbon matrix is a major problem (see Figure 15). Dr. Graham indicated that these coated carbon-carbon composites can perform quite differently depending upon the evaluation procedures used (see Figures 16 and 17). This variation in performance is a function of the evaluation procedure employed and is another problem encountered in dealing with coated carbon-carbon composite systems.

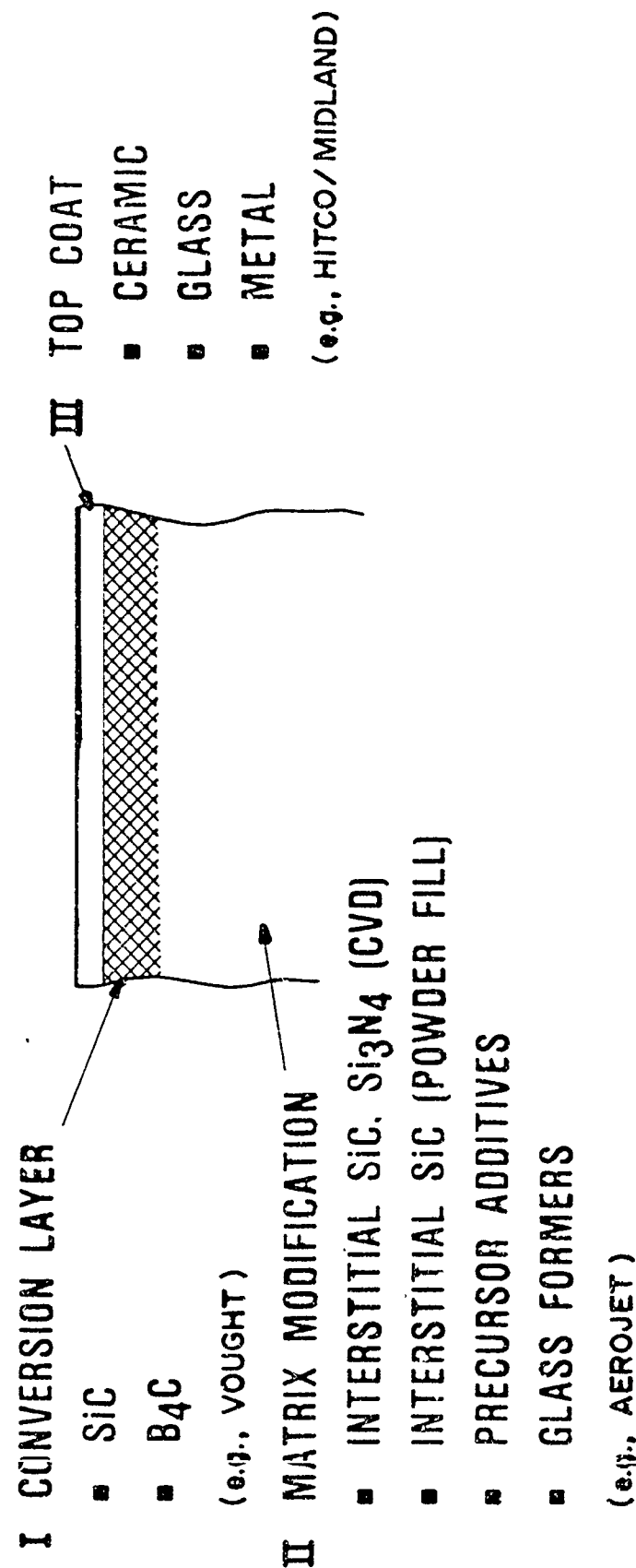
FIGURE 13

Carbon/Carbon Material Systems

PARAMETERS	SHUTTLE PARTS C/C	ADVANCED C/C	CO-PYROLYZED C/C
Materials Resin Reinforcement	R-120 WCA Graphite	T-300 Graphite Karbene 640	Pan Karbene 640
Process Pyrolyzation Time To Reach Required State	848 Hours	18 Hours	4 Hours
Post Pyrolysis Treatment	Oxidation CTG Applied	Oxidation CTG Applied	Oxidation CTG Optional
Development Status	Production	Prototype Fabrication	Experimental
Properties Flexure Strength Modulus Density	13,000 2.2×10^6 1.36	40,000 1.6×10^6 1.54	70,000 40×10^6 1.5
Applications	Space Shuttle L.E. and Nose Cone Multimission 100 Missions	2nd Generation Shuttle Multimission > 500 Missions A/C Engine/ Nozzle Parts	Missile Nose Cones Nozzles Turbine Engine Components

FIGURE 14

PROTECTION APPROACHES



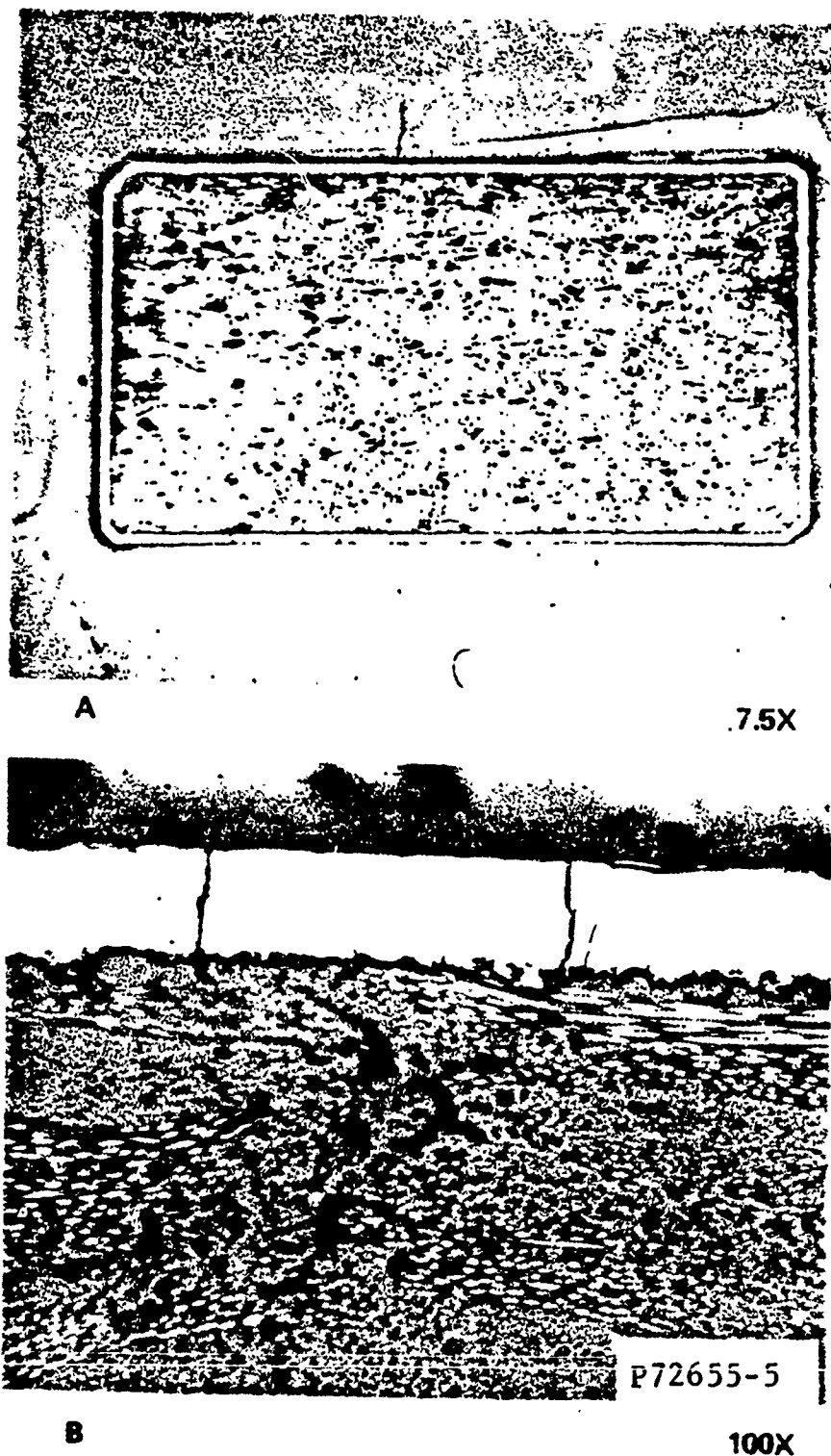


FIGURE 15

Hitco Ultra-Carbon Sample II-9-A Showing Uniform Top Coat: Coverage (A) but Extremely Shallow SiC Conversion (B).

FIGURE 16

STRENGTH DEGRADATION

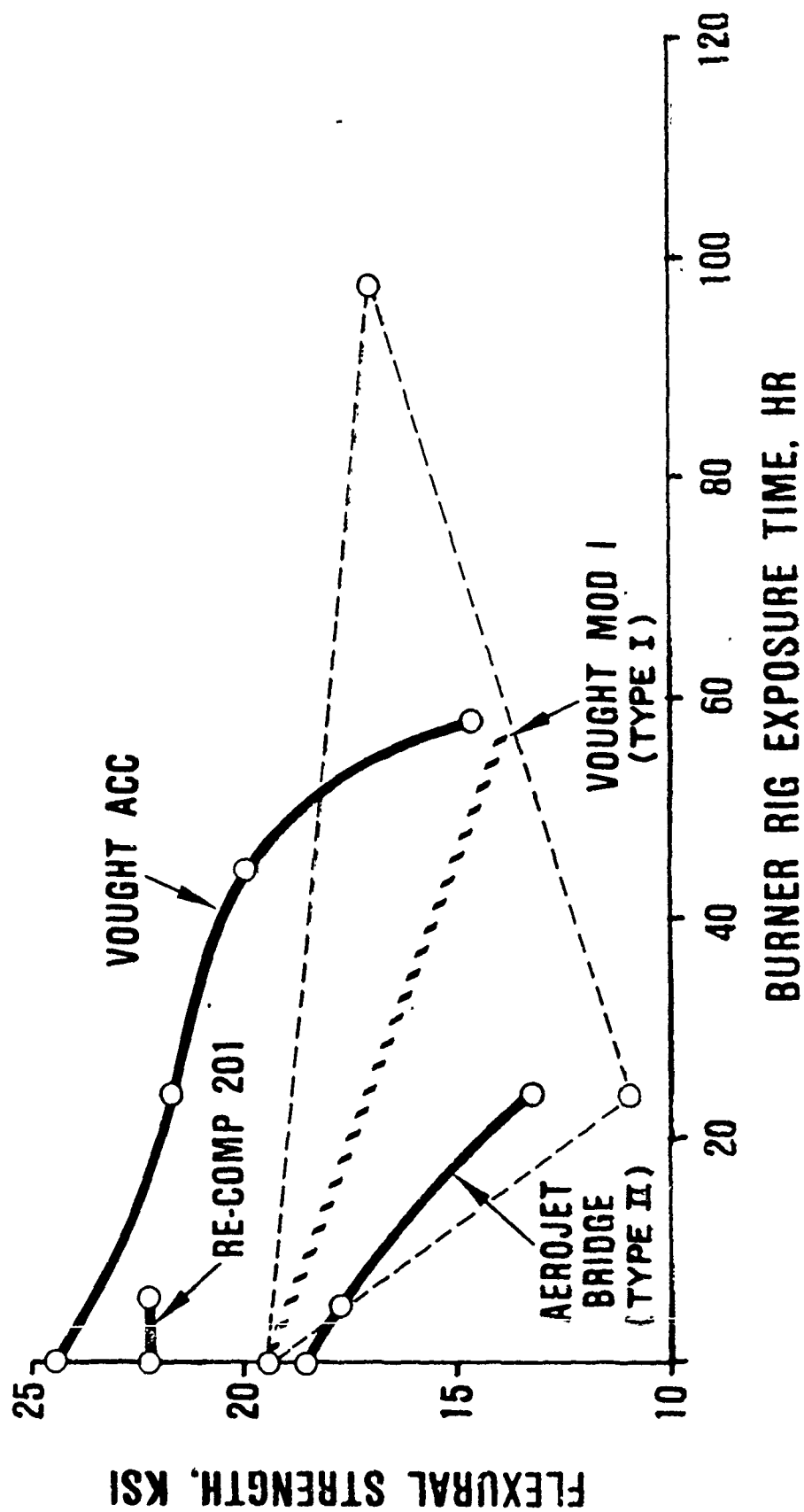
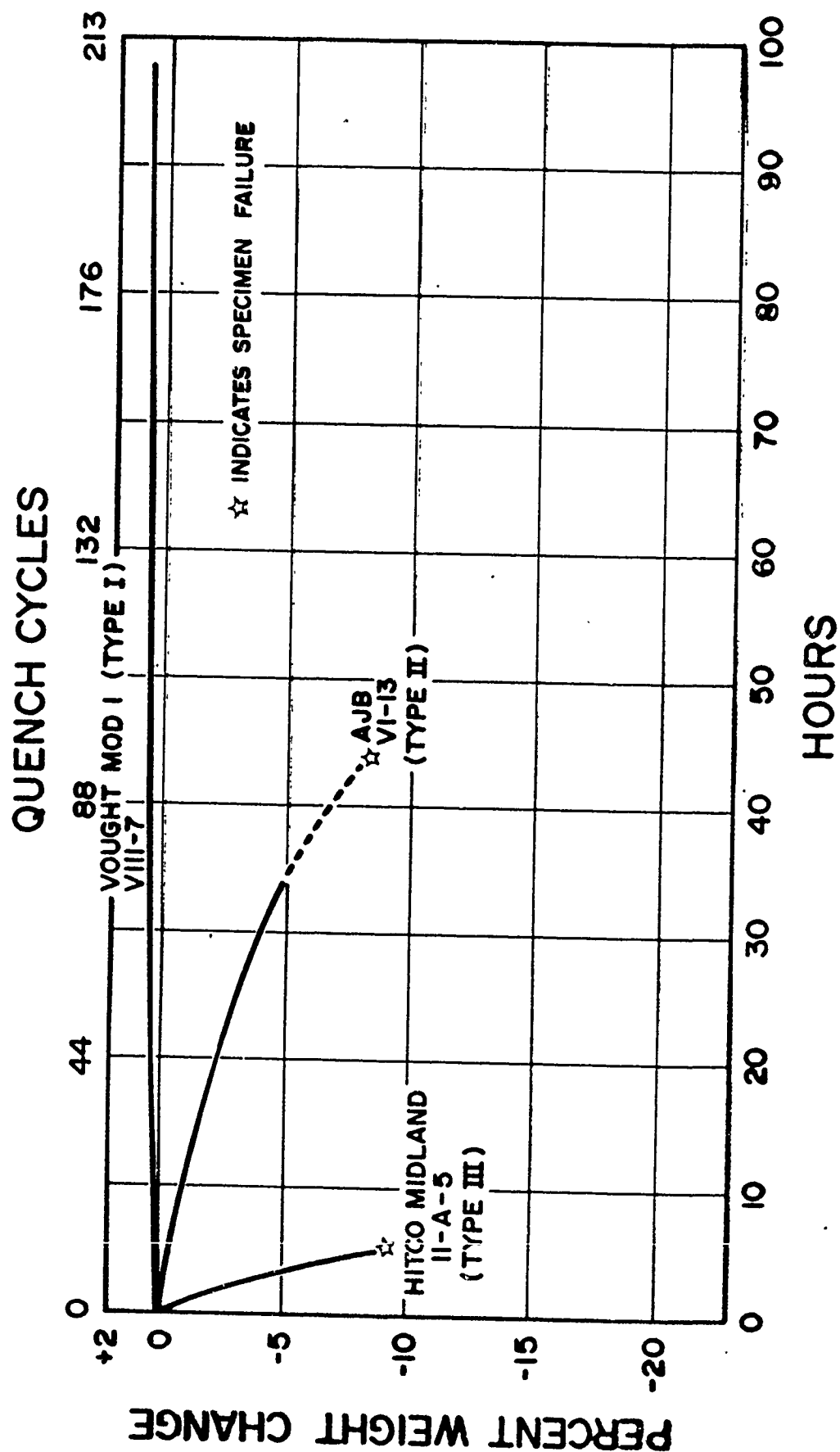


FIGURE 17

2500° F BURNER RIG DATA



In summary, Dr. Graham pointed out that it was important to be able to fabricate materials with good properties that would be stable throughout the life of the component. Although system needs were quite varied, the primary goal is the production of good materials. A good material was defined as one that is tough, stable, and can be fabricated into the desired shapes. A summary of the "State-Of-The-Art" for oxidation resistant carbon-carbon composites and the projected goals is presented in Figure 18.

Floor Discussion

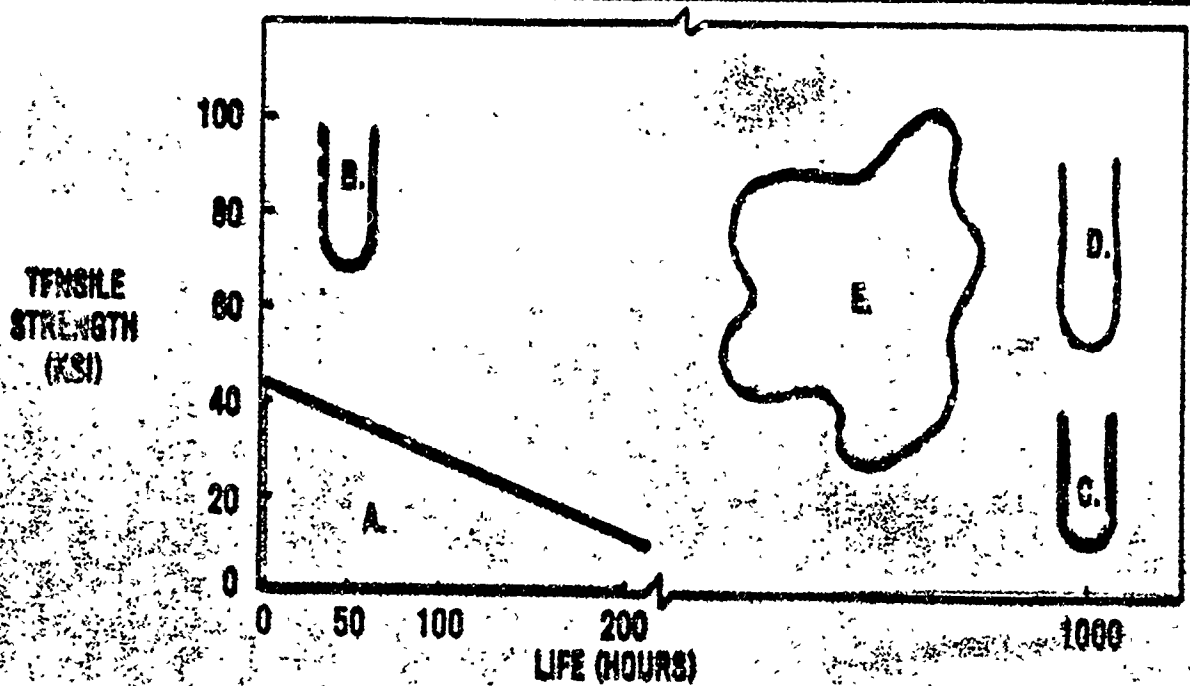
In comments from the floor it was pointed out that monolithic ceramics should not be dismissed. That the true strength and toughness which might be obtained for these materials has not yet been obtained. Further it was pointed out that near-net-shape fabricability might be much more easily achieved with monolithic ceramics than with composites. It was also suggested that chemical processing, by and of itself, would not provide a total solution to current material problem needs. Multiple approaches combining design and engineering technologies would also be needed.

The need for better understanding starting materials both in the precursor and final phase was pointed out, as was the need for new ways of viewing ceramics and ceramic composites. It was recommended that ceramists not take the conventional view of starting with macro sized things and putting them together to make objects. Chemical processing should be viewed as a new means of achieving end products rather than a vehicle for doctoring up current systems. The patch-up approach focuses on the immediate goals, (next five years) while the long-term (twenty year) goals require the development of processes based on new concepts and new ideas.

The need for better understanding the fundamentals of what forces are required for particles adhering and some of the

FIGURE 18

SOA OF OXIDATION RESISTENT C-C



APPLICATION				REQUIREMENT IMPROVEMENT
A.	BR	STATIC	FULL LIFE	STATE-OF-THE-ART
	M/R	NON-STRUCTURAL	1/5 LIFE	
B.	BR	ROTATING	FULL LIFE	2-3X STRENGTH OF SOA
C.	M/R	NON STRUCTURAL	FULL LIFE	WTR OXIDATION PROTECTION
D.	M/R	STRUCTURAL	FULL LIFE	2-3X STRENGTH W/WTR PROTECTION
E.	M/R	HOT AEROSTRUCTURAL	FULL LIFE	MATERIAL "D" WILL WORK

surface science phenomenas that have to be understood in order to make better materials and develop better processes was pointed out. Another suggestion from the floor was for the use of chemical skills to try to emulate the mechanisms found in nature (such as in the formation of jade) be used to produce ceramic-ceramic composites of superior properties. The need for greater attention to fundamentals associated with the fracture process and the physical, chemical interaction between matrices was also stressed.

It was pointed out that the problems associated with the development of superior composites are not simply chemical or mechanical problems but are a combination of these elements. By better understanding the mechanisms at the molecular level, it might be possible to develop improved materials. The utilization of sol-gel processing for ceramic composites was brought up and it was suggested that much more needs to be known to better control the large degree of shrinkage which occurs. The need for improved impregnation techniques and methods for reducing the number of impregnation cycles was also suggested.

The term composites applies to the use of fibers, whiskers, and particulates dispersed in a matrix, and all of these second phase or third phase systems need to be better evaluated. The use of transformation toughened particles was suggested as a particular area which might play an important role in developing stronger, more reliable ceramics. The interaction of pores and cracks is also an area which requires further elucidation.

It should be recognized that fiber-matrix interaction varies considerably according to both the composition of the materials involved as well as the environment in which they are employed. These factors will greatly affect the interface reactions that occur between fiber and matrix. Carbon-carbon composites can be described as a system of patches and that coatings applied on these composites are also patches, and each patch in the system should be considered as an important element. Efforts should be devoted toward better understanding how each patch works within the system.

Another important factor brought out in the discussion was that when any material system is initially selected, it is expected that it will be well suited to meet the goals of the particular applications. However, unanticipated problems can be encountered because sufficient study and consideration was not given to potential problems prior to selection. This was best summarized by saying that the best thing you hear about any materials system is the first thing.

The problem of reproducibility of results was also brought up. In much of the literature the starting material composition, presence of impurities, microstructure, etc., is not specified. More should be done by the referees to insist upon sufficient detail in the articles presented for publication.

CARBON-CARBON COMPOSITES

Ms. Frances L. Abram, AFWAL

Frances Abram presented a general description of carbon-carbon composites, and described some of the current and potential applications and general fabrication processes for these composites. She also discussed some of the current problems with these materials and some of the materials developments to meet the identified needs of current and advanced systems. Ms. Abram initiated her presentation by passing around some samples of typical carbon-carbon composites and pointed out that these composites can be multidimensional (directional). She then pointed out that the fabrication process used to prepare these composite materials is very time consuming and could take anywhere from 30 days to six months. Ms. Abram stated that the most rapid recorded process time was 14 days.

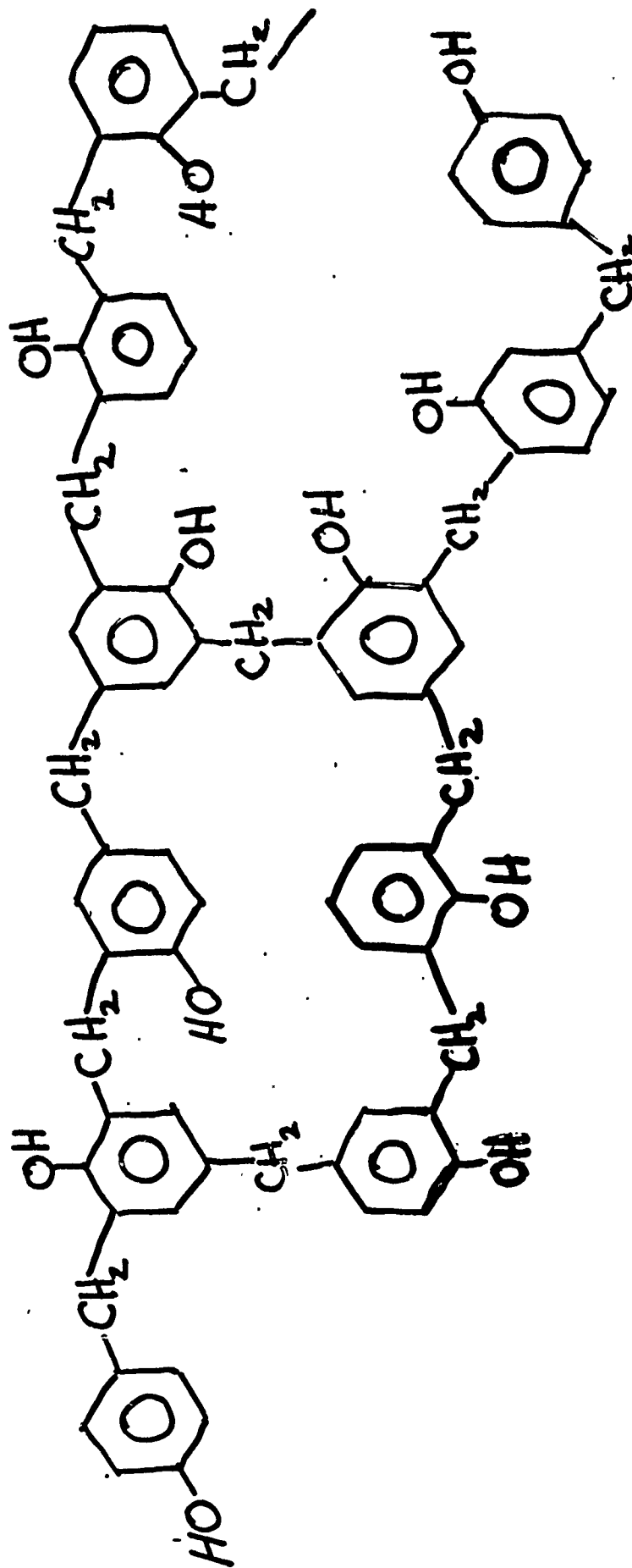
In carbon-carbon composites, unlike many of the ceramic-ceramic composites currently produced, there does not appear to be a real chemical bond between the carbon fiber and the carbon matrix. The matrix contains many pores and cracks and

there tends to be a considerable number of cracks running parallel with the fibers. Ms. Abram pointed out that these carbon-carbon composites were initially designed as ablative materials for application in aerospace systems. Current carbon-carbon systems are quite refractory, lightweight (densities as low as 1.4 gr/cm^3), highly anisotropic, but susceptible to oxidation. The anisotropic nature and susceptibility to oxidation of carbon-carbon composites present considerable limitation to their utilization. However, Ms. Abrams felt that these carbon-carbon composites offered significant promise for many applications, particularly those in non-oxygen atmospheres (space, etc.). Although coatings and protective systems are available for carbon-carbon composites to be used at high temperature oxidation environments, these systems need considerable improvement.

The more advanced carbon-carbon systems have demonstrated flexural strengths up to 40 ksi. Many of the current carbon-carbon composites have matrices prepared from thermal setting phenolic precursors. However, the stoichiometry of these precursors can be quite varied resulting in considerable variation in char content after carbonization. Typical phenolics provide a yield of 50% char (see Figure 1). However, some thermal setting matrices (Figure 2) have been developed which produce higher char yields. Current laboratory efforts have demonstrated that 20 to 30 percent increases in char yield could be obtained, but this resulted in a considerably higher cost precursor material.

For most carbon-carbon composite systems, a mat of graphite or carbon fibers is infiltrated with the matrix precursor and then cured. Most of the thermal sets are cured in an autoclave or hydroclave (see Figure 3).

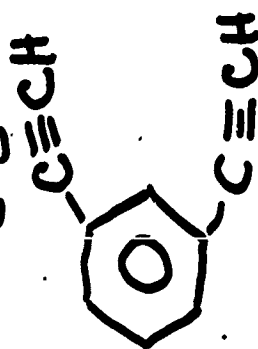
A number of different cure cycles are employed by carbon-carbon manufactures (see Figure 4). However, the end results



Cross linked Phenolic

FIGURE 1

m-Diethynyl benzene



M.P. < R.T.

Cure = 110-130°C

Char Yield = 94%

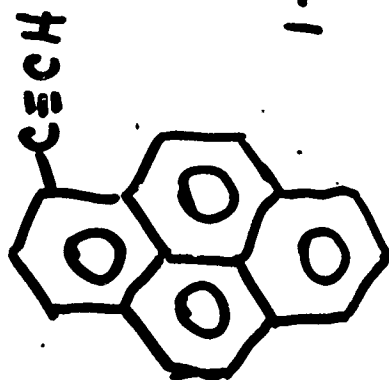
Diethynyl diphenyl methane



M.P. < R.T.

Cure = 130-140°C

Char Yield = 75%



1-Ethynyl pyrene

M.P. = 105°C

Cure = 130-140°C

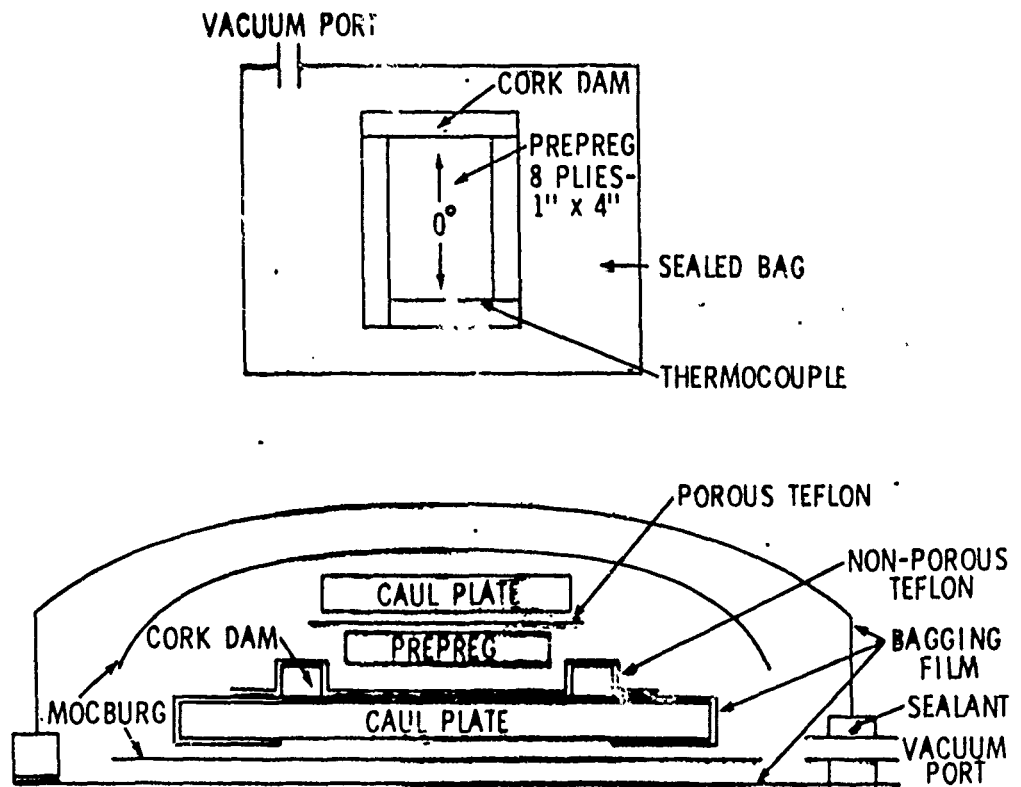
Char Yield = 57%

High Char Yield Thermosets

FIGURE 2

FIGURE 3

ATB COMPOSITE LAYUP A



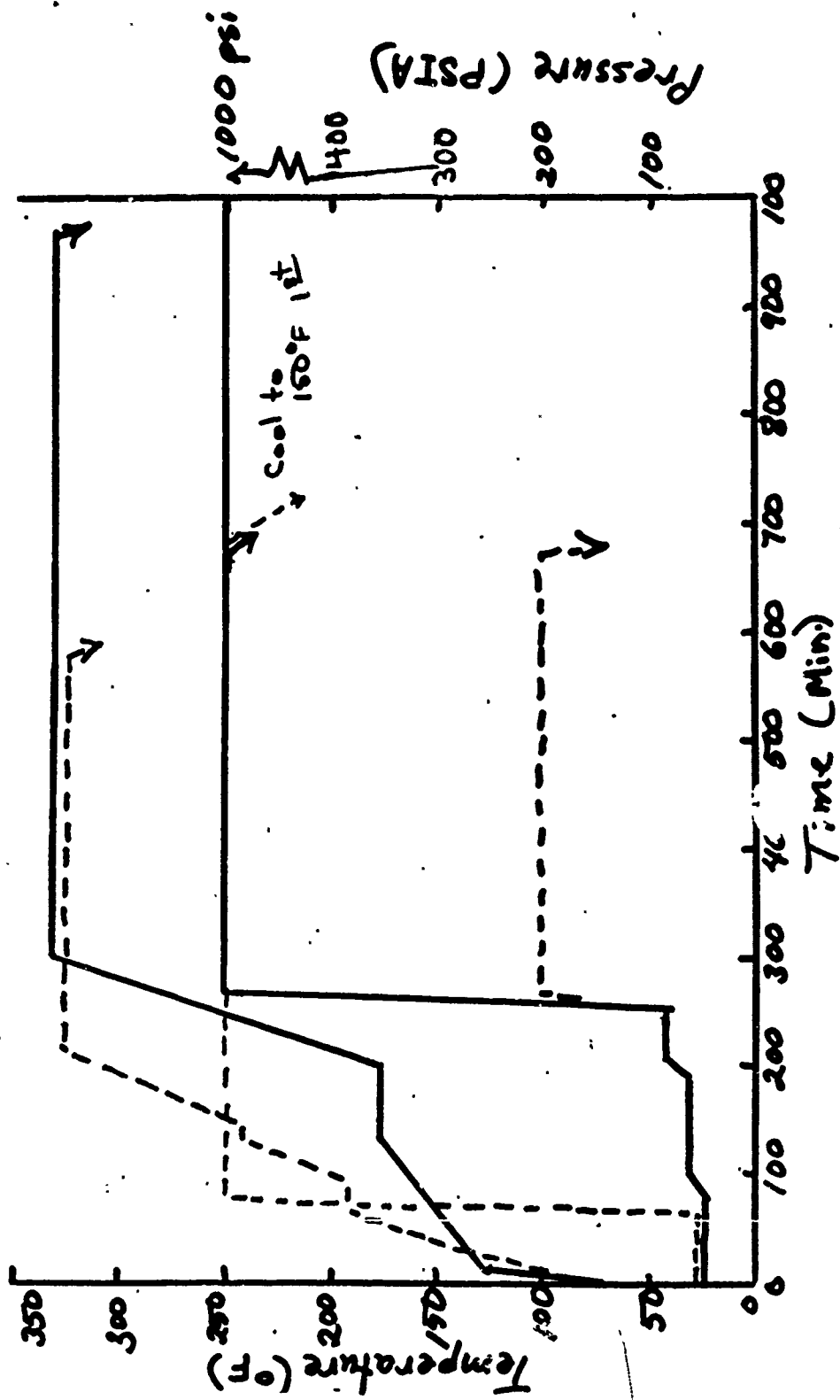


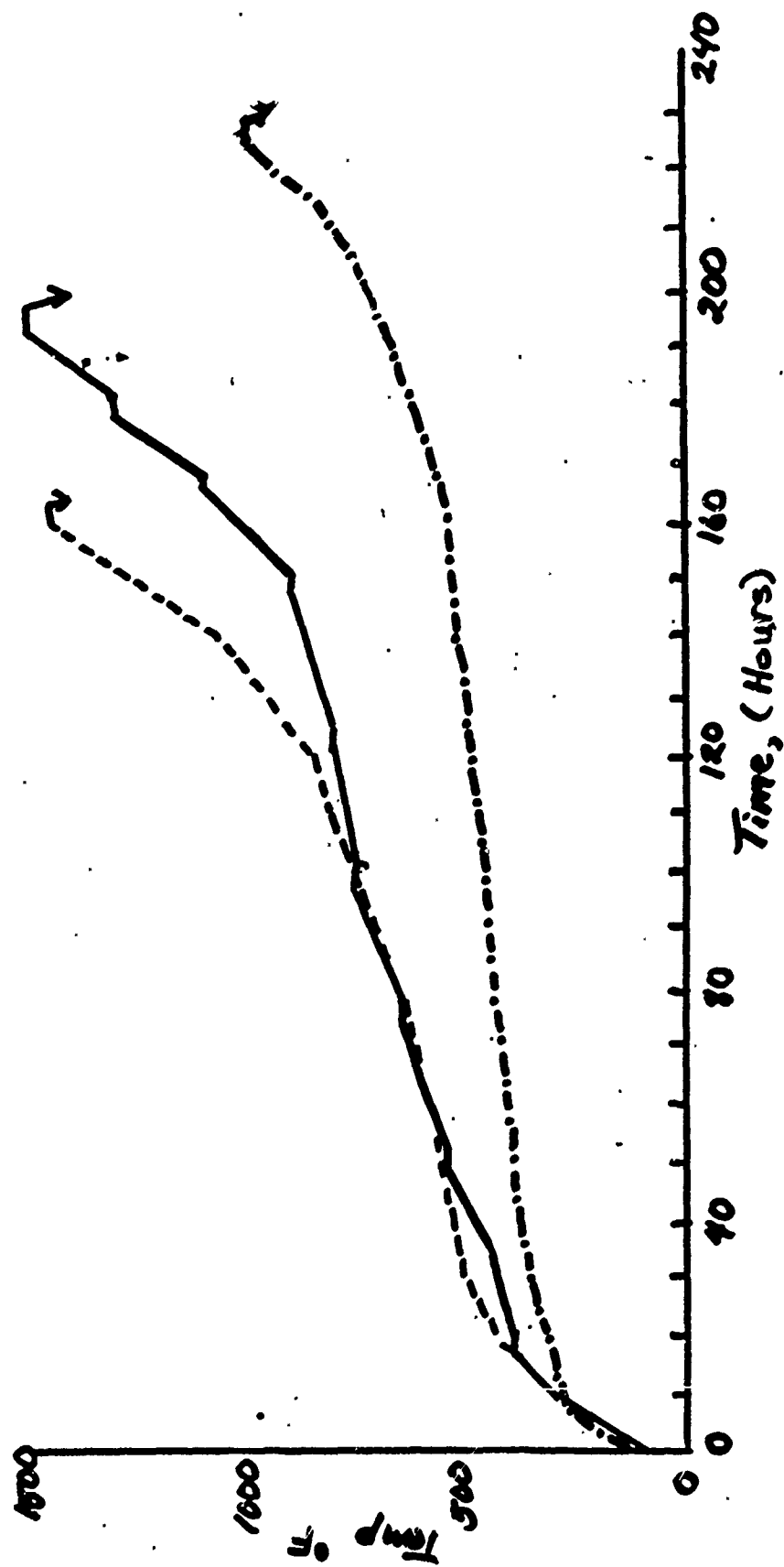
FIGURE 4

Typical Autoclave (200 PSIA) or Hydroclave (1000 PSIA)
Cure Cycles (Vacuum Bagged)

do not appear to be much different as a result of these different treatments. During the curing stage, primary volatiles are given off. From 50°C to 150°C the solvents are released and from 100°C to 200°C reaction product water is given off. Considerable shrinkage occurs during the curing cycle resulting in transverse cracks across the fiber bundles. These cracks run through the matrix along the side of the fibers.

Ms. Abram described a laboratory program currently under way to produce higher density, crack and pore-free cured laminates. The cure cycle is then followed by a carbonization cycle. This cycle is a drawn out thermal process which converts the organic material to a carbon (amorphous phases, graphitic phases, or intermediate phases). During carbonization process, all but the carbon atom/molecules are eliminated. The bonding and structural configuration of the matrix material will determine how readily the organic bonds are broken in order to leave a carbon residue. As with the cure treatment, there are a number of different carbonization cycles which have been developed (see Figure 5). Many of the higher temperature carbonization cycles are initiated by a precure cycle which heats the material to 500°C for a period of 240 hours. The time for the carbonization process will vary and is primarily a function of component size. However, specific mathematical relationships for this correlation have not been established.

Below 600°C, no carbonization takes place (see Figure 6). At about 600°C, some of the more lightly bounded groups (methyl phenol, water, etc.) are lost. At about 1000°C, there is usually a large weight loss with little shrinkage and at times even a slight expansion can occur. However, above

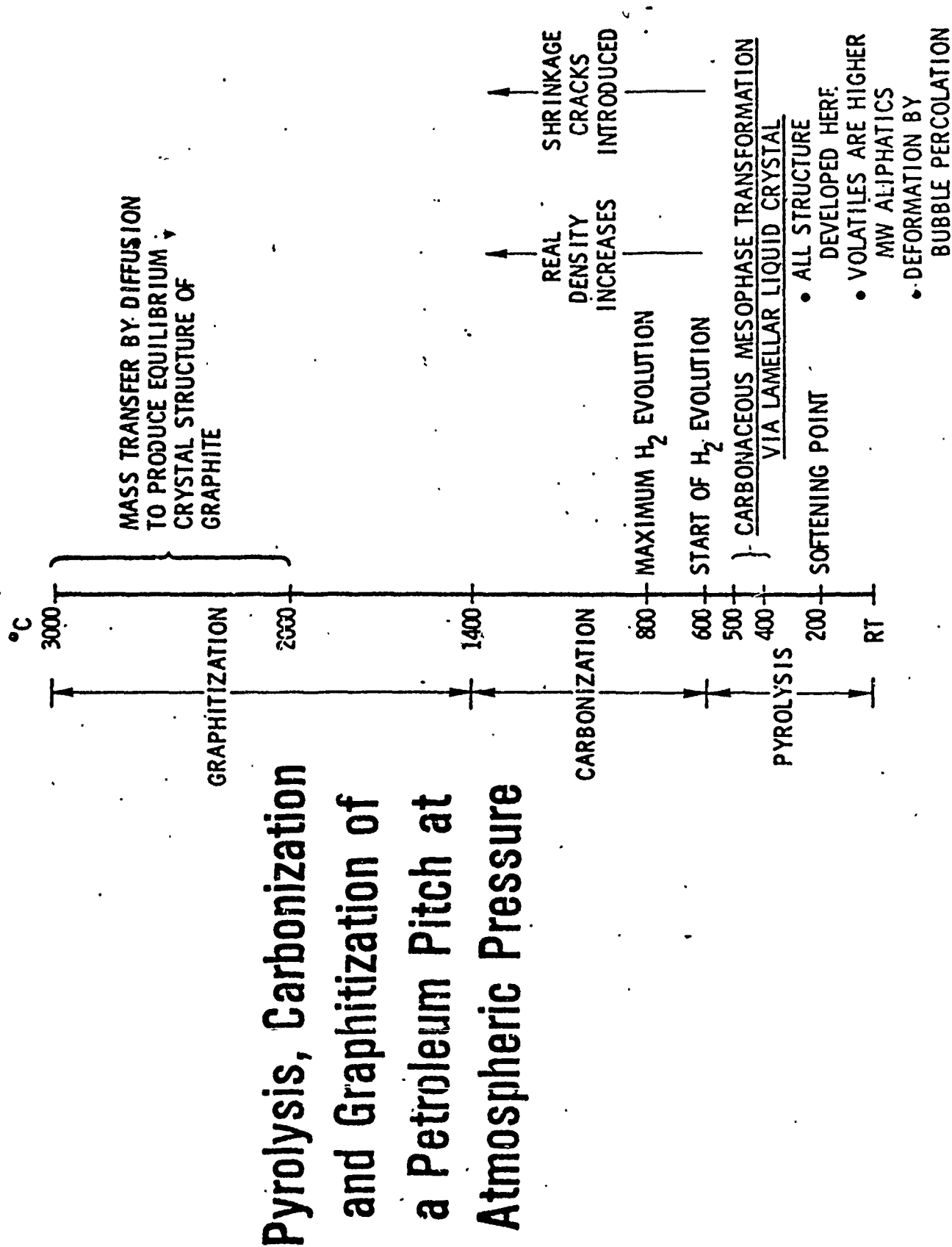


3 Carbonization Cycles

INERT ATMOSPHERE OVEN

FIGURE 5

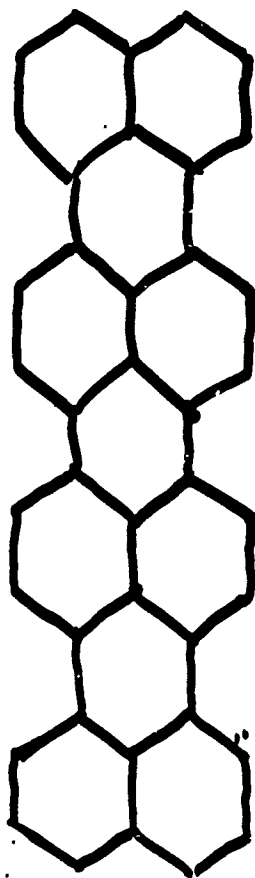
FIGURE 6



1000°C, there is little weight loss but tremendous shrinkage which is caused by structural network rearrangement. Below 600°C, all but hydrogen is given off and above 600°C, hydrogen is given off causing the structural rearrangement resulting in a saturated carbon structure.

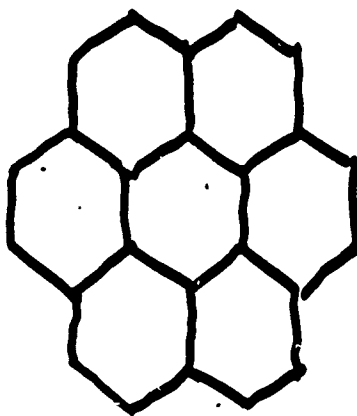
Carbonization process profiles are based more on equipment capabilities and tradition than on science. Temperatures are not well monitored, and DTA, TGA, etc. are not extensively used to develop time-temperature cycles. This lack of careful control during the carbonization process results in poor reproducibility from ingot to ingot which is a considerable problem for the industry. The slow carbonization cycles employed are based primarily on graphite manufacturing technology. The need to better study this process was identified, and the potential of NMR as a tool for these studies was also described. In addition, to better understand the carbonization cycle, the need to better control the preparation of the prepreps was also pointed out. Stoichiometry, degree of advancement, degree of polymerization, amount and type of volatiles, and moisture all need to be better defined.

After carbonization, the entire process cycle is repeated several times. The specimens are usually reimpregnated with pitch to increase component density. Pitches tend to have better char yields (up to 90%) and provides a very oriented graphic matrix (see Figure 7). However, it was noted that pitch compositions can vary from lot to lot. After pitch or phenolic reimpregnation, the specimen is again cured and recarbonized. After carbonization, the ingots are graphitized (see Figure 8). This successive reimpregnation and recarbonization results in considerable fiber damage, reducing virgin fiber properties. In addition, during the recarbonization process, there is further rearrangement of the structure and a more planar carbon network is developed.



M.W. = 500
M.P. = 295°C
Char Yield = 92%

Benzo(1,2,3-cd;4,5,6-c'd') diperylene



M.W. = 300
M.P. = 440°C
Char Yield = 0

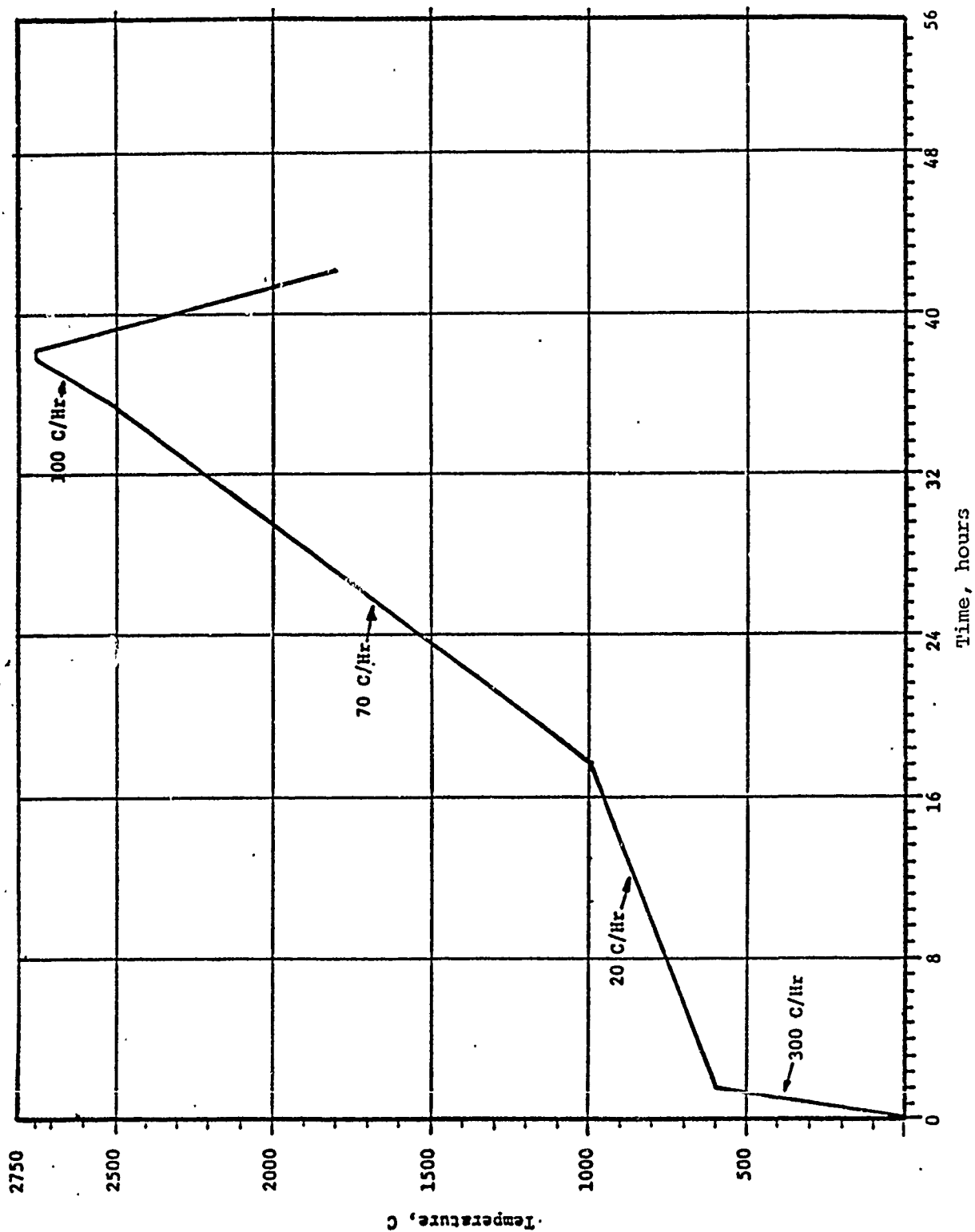
Coronene

Some Components of Pitch

FIGURE 7

FIGURE 8

TYPICAL COMPOSITE GRAPHITIZATION CYCLE



The reimpregnation, recarbonization, and regraphitization is carried out until the desired density is achieved. Figure 9 demonstrates the fabrication process employed for producing three dimensional carbon-carbon composites. It was again pointed out that char yields will vary with starting composition and processing procedures and these variations tend to be rather unpredictable.

Another method for producing carbon-carbon composites relies on the CVD processing (see Figure 10). In this process, the carbon fibers are coated by a carbon vapor deposition process. This rigidizes the preform which then is impregnated with pitch or phenolic, cured and then carborized. Total densification is achieved by additional CVD treatments. This technique offers considerable promise for the preparation of thin walled components.

Although carbon-carbon components offer a number of promising opportunities, it was again stated that these materials are not oxidation resistant. Two primary methods are employed to improve the oxidation resistance of carbon-carbon composites. One is the application of a coating or series of coatings and the second is the infiltration into the composite of a material which inhibits oxidation. To date, the protective coatings have shown some promise, however, the most promise has been demonstrated by the combined use of both techniques. A major problem with coatings has been the mismatch in thermal coefficients of expansion between the coating and the substrate. This problem is exacerbated by the anisotropic nature of carbon. The cracks that occur in the coating result from the mismatch in thermal expansion. A number of compositions are being investigated for sealing these thermal cracks in the protective coatings.

The glassy sealants that are being developed are affected by several problems. At high temperature high volatilization of glass components are a problem while at low temperatures the problem is that the glassy sealant may not be sufficiently molten. This problem highlights one of the difficulties in selecting a sealant material which is capable of operating effectively through the entire temperature range. This problem is of particular concern in a cyclic application.

FIGURE 9

3D CARBON/CARBON CIRCULAR PIERCED FABRIC PROCESS

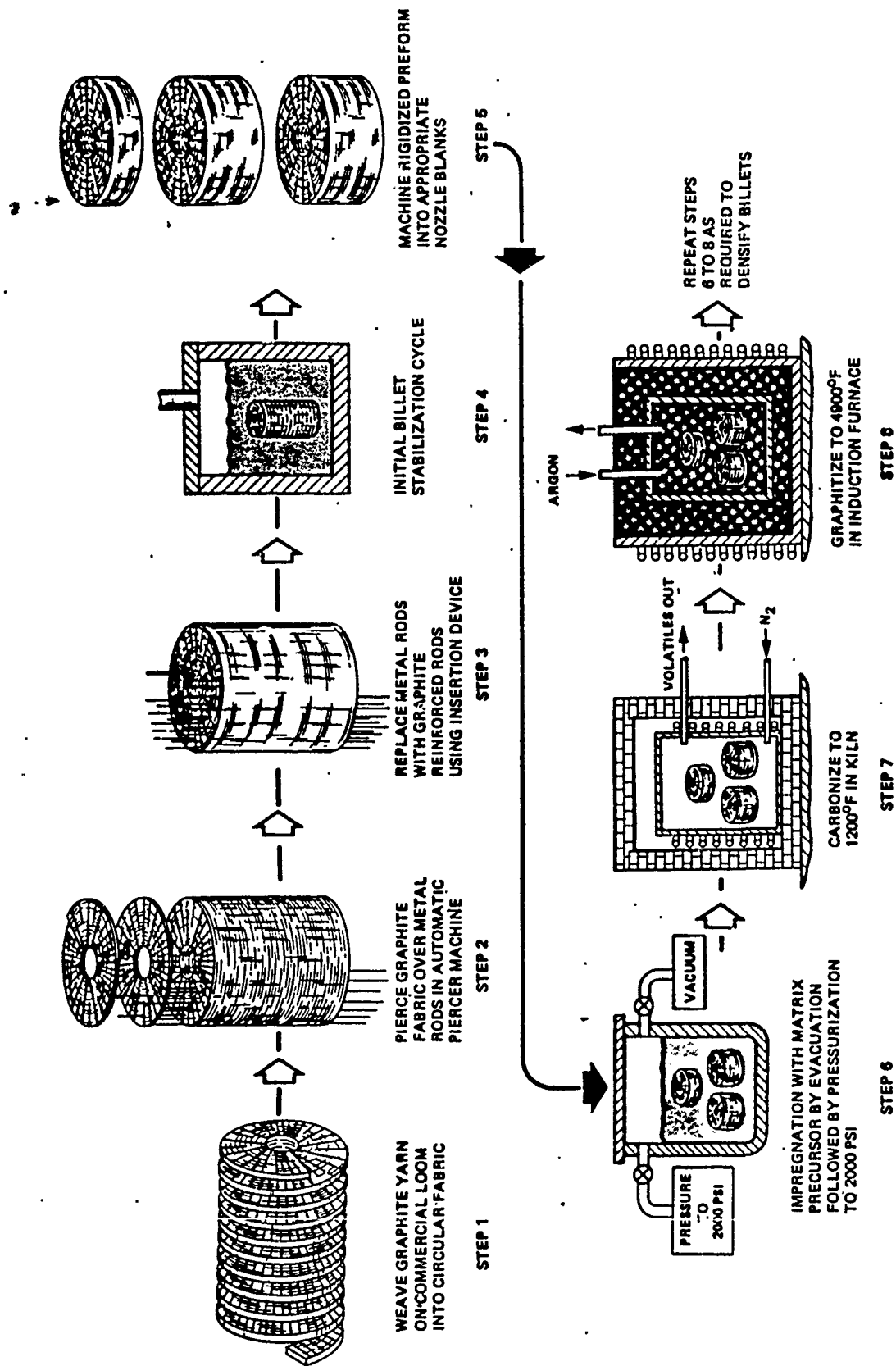
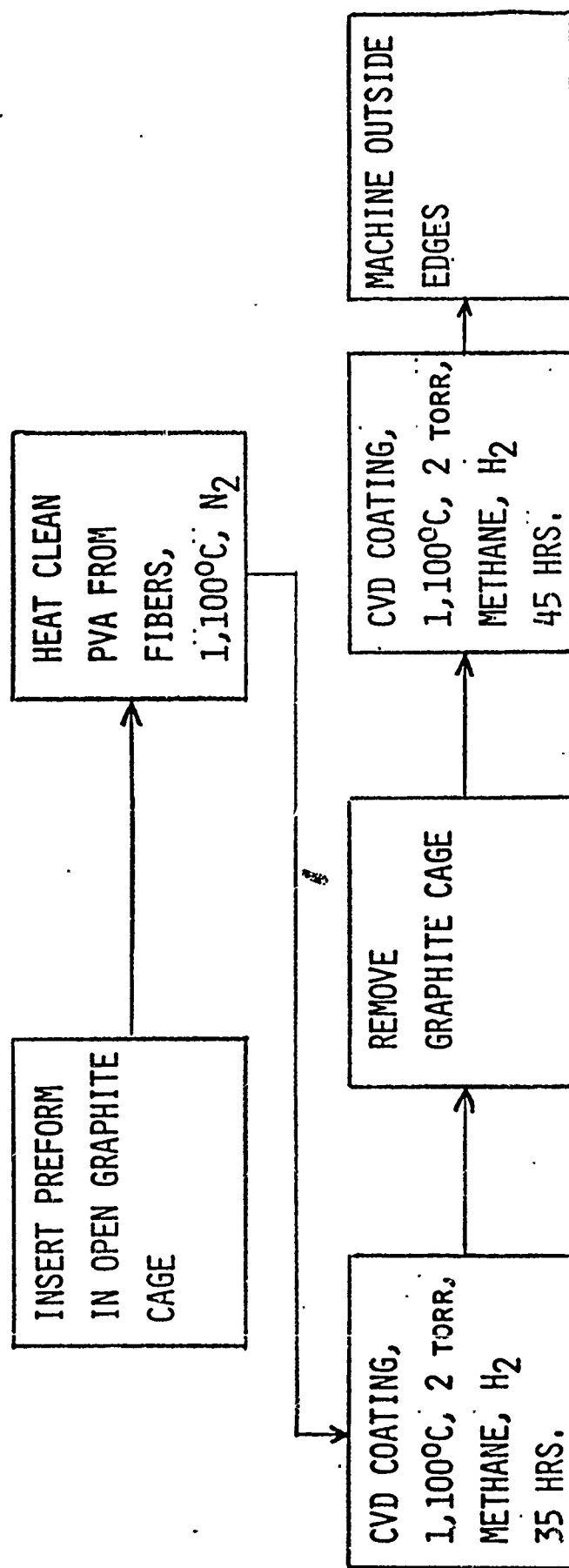


FIGURE 10

CVD PYROLYTIC GRAPHITIC COATING PROCESS



The use of hafnium and zirconium additives for increased oxidation resistance is also under study. The oxides formed from these additives have higher viscosities and help to retain the oxide scales which form on the surface. This is particularly important when the component is to be used in rotating applications.

The silicon pack coating process is commonly used for carbon-carbon composites. In this process, the silicon infiltrate reacts with the carbon matrix and forms a silicon carbide. However, because the pack coatings are hard to control the thicknesses can be quite variable. Generally, coatings are a few thousand thick and take up the first two layers of the carbon-carbon laminate. With the buildup of additional coating layers, the average coating thickness can be ten to twenty thousandths of an inch. For thin section components, the coating can be ten to forty percent of the component's thickness and this can be a problem since coatings are not structural members.

Borosilicate glasses are sometimes used to seal cracks and are effective at the intermediate temperatures where the cracks are still open. However, at high temperatures the cracks tend to close. The low viscosity glasses used to seal cracks during the intermediate temperature range exposures seem to be reasonably effective. However, at the higher temperatures and high gas velocity or centrifugal loading applications, the sealing glasses are hard to keep on the surface of the composites. Pure silica tends to resemble water at these high temperatures and it does not stay on the component. Addition of ZrO_2 to the silicate glass can be used to improve protective coating adherence. It was also pointed out that it might be desirable to use layered coatings for the formations of diffusion barriers to protect the carbon-carbon composite. Ms. Abram indicated that the technology of fiber production and the nature of the carbon fibers is well understood. However, the role of the fibers in the matrix is not as well understood. This is particularly true for the interface and the interfacial reaction between matrix components. The role of cracks and pores distributed throughout the matrices is also not well understood. The need to develop techniques to chemically tailor the matrix structure and the required coating was mentioned.

The graphitic nature of the matrix and the role of pores and cracks need to be better understood. The structure of the matrix can vary from a glassy carbon generally derived from phenolics to very graphite type structures which are derived from pitch. The graphite obtained from pitch tends to be highly planar and tough but has low shear strength. While the glassy carbons obtained from the phenolic are strong they have lower toughness. It was also pointed out that an important goal for improving carbon-carbon composites is the development of a matrix material that will be reproducible and have a high char yield.

Floor Discussion

In the floor discussion, the relation between processing pressure to be used and size limitations of the components which can be handled was brought up. Since process time can be significantly reduced by using higher pressure processing, a cost tradeoff between higher initial capital for larger pressure processing systems vs the time saving in processing time is possible.

Another matter brought up for consideration was the use of purification treatments of the graphite by chlorination to improve the matrix material. Also proposed for providing improved oxygen resistance of the fibers was the use of silicon nitride coatings. In addition, consideration of noncarbon matrices which are self-protecting was brought up. The use of silicon polymer matrices which would yield a high ceramic char at low temperatures (1200°C) after four to five hours exposure was proposed to provide an effective means of eliminating fiber degradation during processing. The use of protective coatings less than 1000Å (solution coating) was also suggested. Although the carbon matrix has a number of advantages there is a need for better control to insure reproducibility and provide a tough highly stable system.

It was stated that a major Air Force goal is the application of chemical processing technology to achieve the needed oxidation resistance or inhibition for carbon-carbon composites in high temperature environments. It was agreed that if technology

could be readily employed to obtain carbon-carbon composites which could be used in turbine engine environments, cost would not be a limiting factor. It was also indicated that there is also an important role for carbon fibers to reinforce intermediate temperature matrix that is still much higher than the organic polymer matrices currently being used.

The importance and influence of chemical bonding and the need to better understand it in order to develop improved composites was another matter brought up for consideration. The work that the French are doing in adding zirconium carbide to carbon-carbon composites in order to improve oxidation resistance was also raised. This would suggest that the use of organo-zirconium, hafnium, or niobium chemistry may offer promising opportunities for improving oxidation resistance through the formation of high temperature glassy phases. However, the question of reactivity with carbon fibers needs to be considered.

The importance of pursuing right brain thinking was again pointed out. So was the importance of not inhibiting the exploration of new ideas. 6.1 funding is designated for risk taking if the concepts are based upon good scientific principles. It was recommended that efforts be initiated to seek new polymer systems for advanced generation matrix materials. The final comment made highlighted the importance of phase relationship data for preparing oxidation resistant carbon-carbon composites.

CERAMIC-CERAMIC COMPOSITES
Dr. K. M. Prewo
United Technologies Research Center

Dr. Prewo initiated his presentation with a discussion about work that the British are doing to develop high-performance cements which are macro-defect free. These materials are made up from a series of thin sheets the same way nature made laminated seashells. Dr. Prewo continued his presentation on fiber reinforced ceramics concentrating primarily in three areas - fabrication techniques, mechanical properties, and environmental stability. Dr. Prewo pointed out that traditionally, people have made ceramics with higher fracture toughness by the addition of fibers to the ceramic matrix, for example, by the many types of different fibers that

have been added to plaster. In the 1700's, the British were noted for their fiber reinforced plaster ornaments. The fibers used in these applications were primarily wood pulp or horse hair. The use of cellulose fiber reinforced plasters was used introduced in the United States in the late 1700's and early 1800's.

The goals for today's fiber reinforced composites are higher reliability, greater fracture toughness, and high durability. Using the experience gained from fiber reinforced polymer composites, Figure 1 outlines the requirements necessary to obtain high performance ceramic matrix composites. Dr. Prewo pointed out that it is also very important to have people committed to using these advanced ceramic composites for established engineering and design systems. Dr. Prewo also showed some examples of graphite fiber reinforced glass and silicon carbide fiber reinforced glass.

The correlation between stress strain behavior of the reinforcing fiber and the matrix was discussed. Figure 2 compares the stress strain behavior of some of the advanced fiber materials and matrix compositions. The important consideration is the strain to failure properties of the fiber and matrix and the resultant strain to failure for the composite. One way to evaluate and model the correlations of the elastic modulus for the fiber versus the matrix is to prepare a series of glass matrix composites using graphite fibers of different elastic modulus values. This kind of study was conducted and the data for the different fibers used are presented in Figure 3. Using the P-100 fibers it was possible to obtain a composite with twice the strength in the axial direction parallel to the fibers of about 80,000 psi (see Figure 4). As shown in Figure 4 this graphite-reinforced borosilicate has a very low strain-to-failure which is dictated by the properties of the fiber. This combination allows you to make a very high modulus composite which is quite strong and can be quite serviceable in a number applications.

FIGURE 1

FIBER REINFORCED POLYMER COMPOSITES FORMAT PROVIDES EXEMPLARY APPROACH TO RELIABLE CERAMICS

- **Low failure strain composites (1%)**
- **Acceptable statistical reliability**
- **Adequate toughness (crack growth resistance)**
- **Established engineering design and utilization**

FIGURE 2

MATERIAL STRESS-STRAIN BEHAVIOR

$$\left[\frac{E \text{ (GPa)}}{\epsilon_f \text{ (\%)}} \right]$$

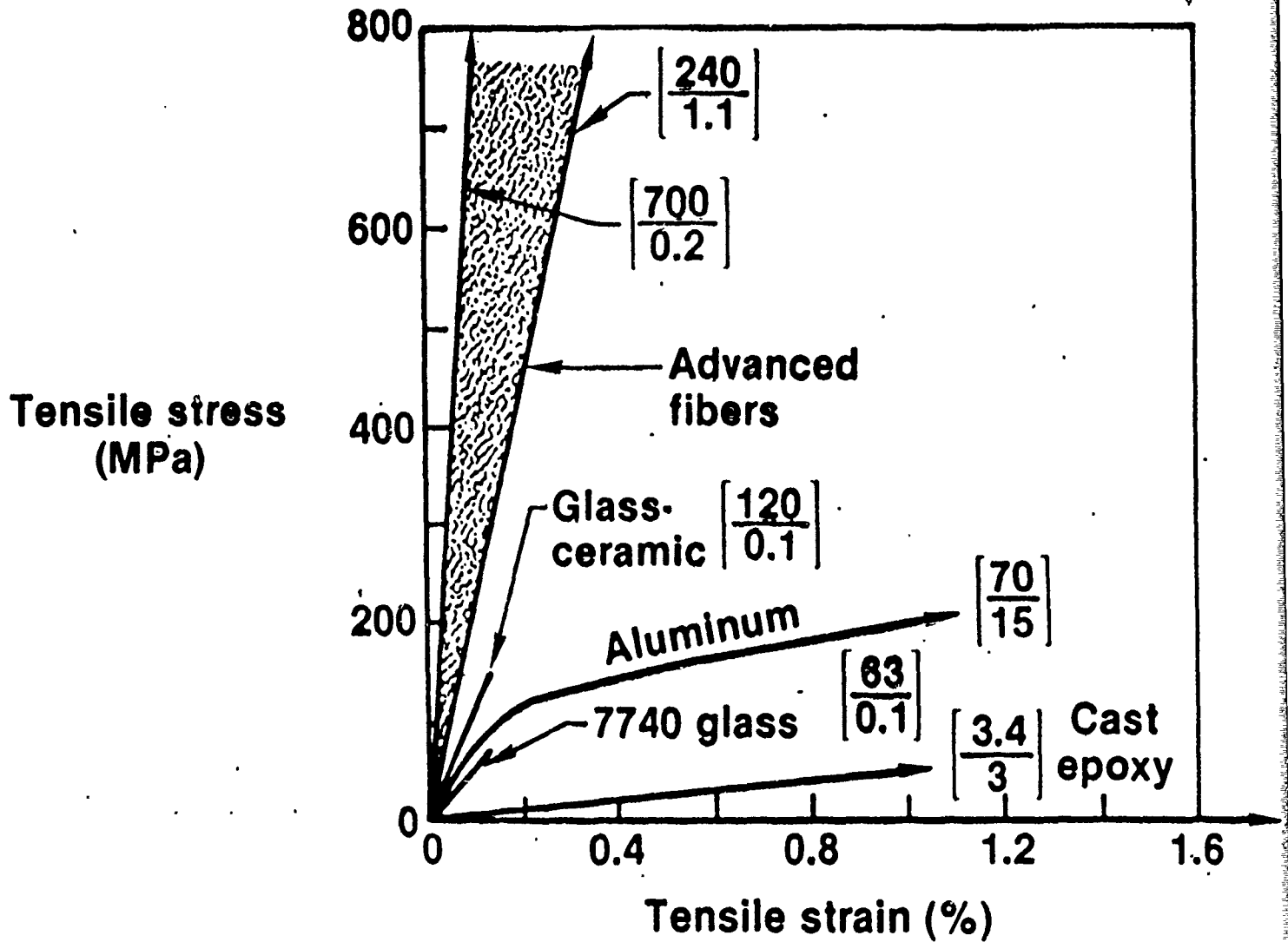


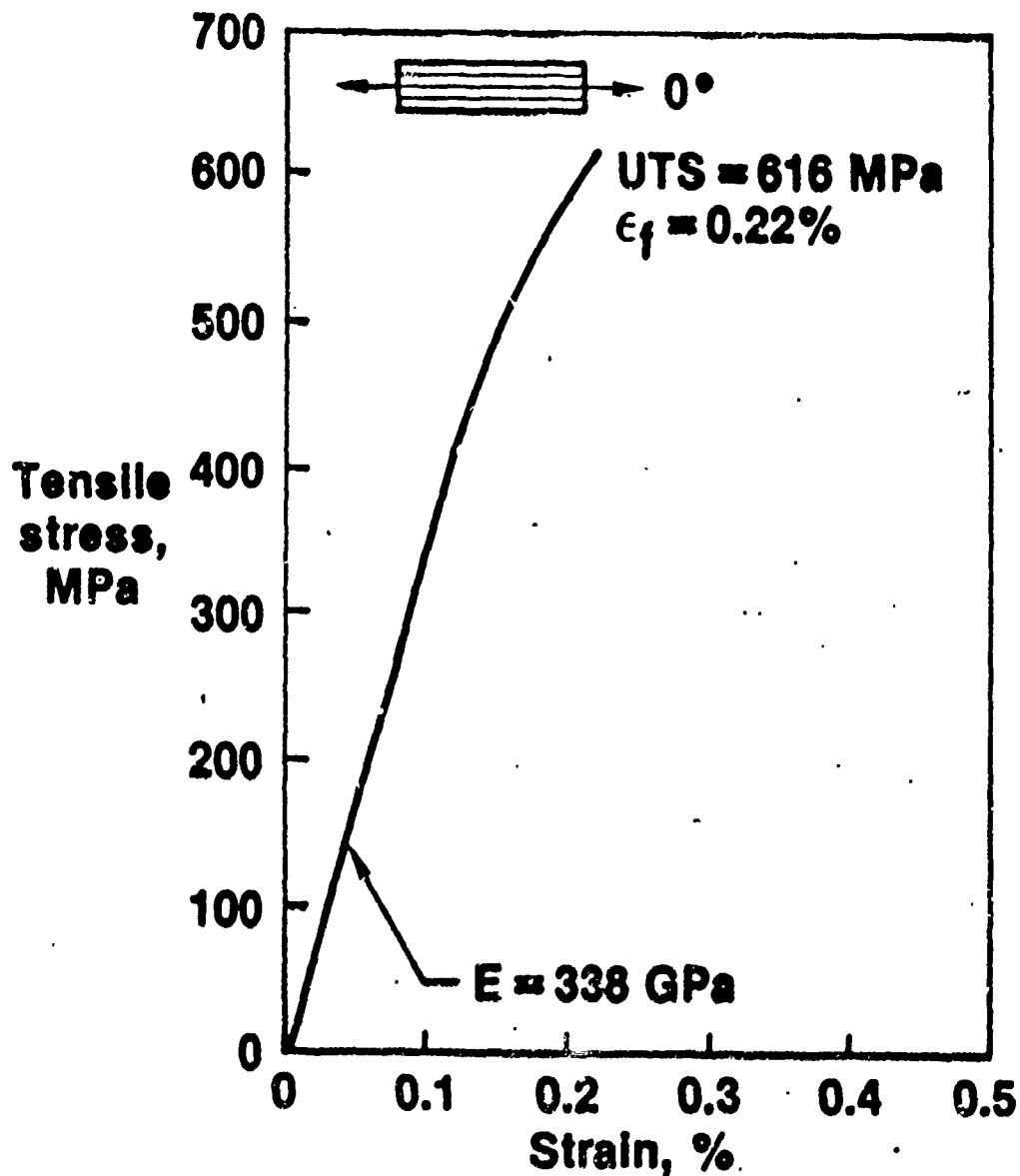
FIGURE 3

GRAPHITE FIBERS USED TO MAKE GLASS MATRIX COMPOSITES

<u>Fiber type</u>	<u>Density</u> gm/cm ³	<u>Elastic modulus</u> 10 ⁶ psi (GPa)	<u>Tensile strength</u> 10 ³ psi (MPa)
Thornel 300	1.76	34 (234)	425 (2930)
Cellon	1.76	34 (234)	400 (2760)
HTS	1.66	37 (256)	410 (2830)
Fortafil-5	1.77	48 (330)	400 (2760)
HMS	1.80	50 (350)	390 (2700)
GY-70	1.96	75 (516)	270 (1860)
P-100	2.10	95 (654)	300 (2070)
G-50	1.77	60 (413)	500 (3450)

FIGURE 4

TENSION TEST OF 54 v/o — 0° THORNEL P-100 GRAPHITE REINFORCED BOROSILICATE



In selecting the reinforcing fiber, consideration should also be given to the correlation between diameter and fiber strength. As shown in Figures 5 and 6, strength tends to increase with decreasing fiber diameter. However, the data is somewhat inconsistent.

A number of different techniques were employed in the fabrication of fiber reinforced composites. Figure 7 outlines the fabrication methods used for preparing glass matrix composites. A number of composites using silicon carbide (Nicalon®) fiber reinforcement in several different lithium aluminum silicate glass matrices were prepared. Tensile strength, modulus rupture, fracture mode, and the effects of fiber orientation were studied (see Figures 8-20).

As shown in Figure 9 there is considerable fiber pullout indicating that these composites can be made very tough. Fibers used in the composite were extracted and their strength measured. It was observed that there is a reduction in fiber strength during processing which may cause reduced composite strength. It was found that during processing the fibers developed a certain degree of curvature. It was also found that kinking of the fibers can occur during fabrication and this will also result in a reduction of composite strength. As shown in Figure 10, there is also a considerable dropoff in strength with a change in fiber orientation. It is believed that this dropoff of strength is due to low interfacial strength which occurs in these types of composites.

Several composites using a number of different lithium aluminum silicate matrix compositions were prepared with Nicalon® fiber reinforcement. These composites had tensile strengths of 100 ksi, modulus of rupture of 200 ksi, and almost 1% strain to failure. Figure 11 shows the tensile stress strain behavior for this composite as compared to an epoxy reinforced composite using the same Nicalon® fiber reinforcement. The epoxy composite doesn't fail until the fibers fail. For the lithium aluminum silicate II matrix composite with a 0.3% strain, the effects of microcracking are seen from the change in slope

FIGURE 5

DEPENDENCE OF INDIVIDUAL FIBER STRENGTH ON DIAMETER FOR AS RECEIVED FIBER

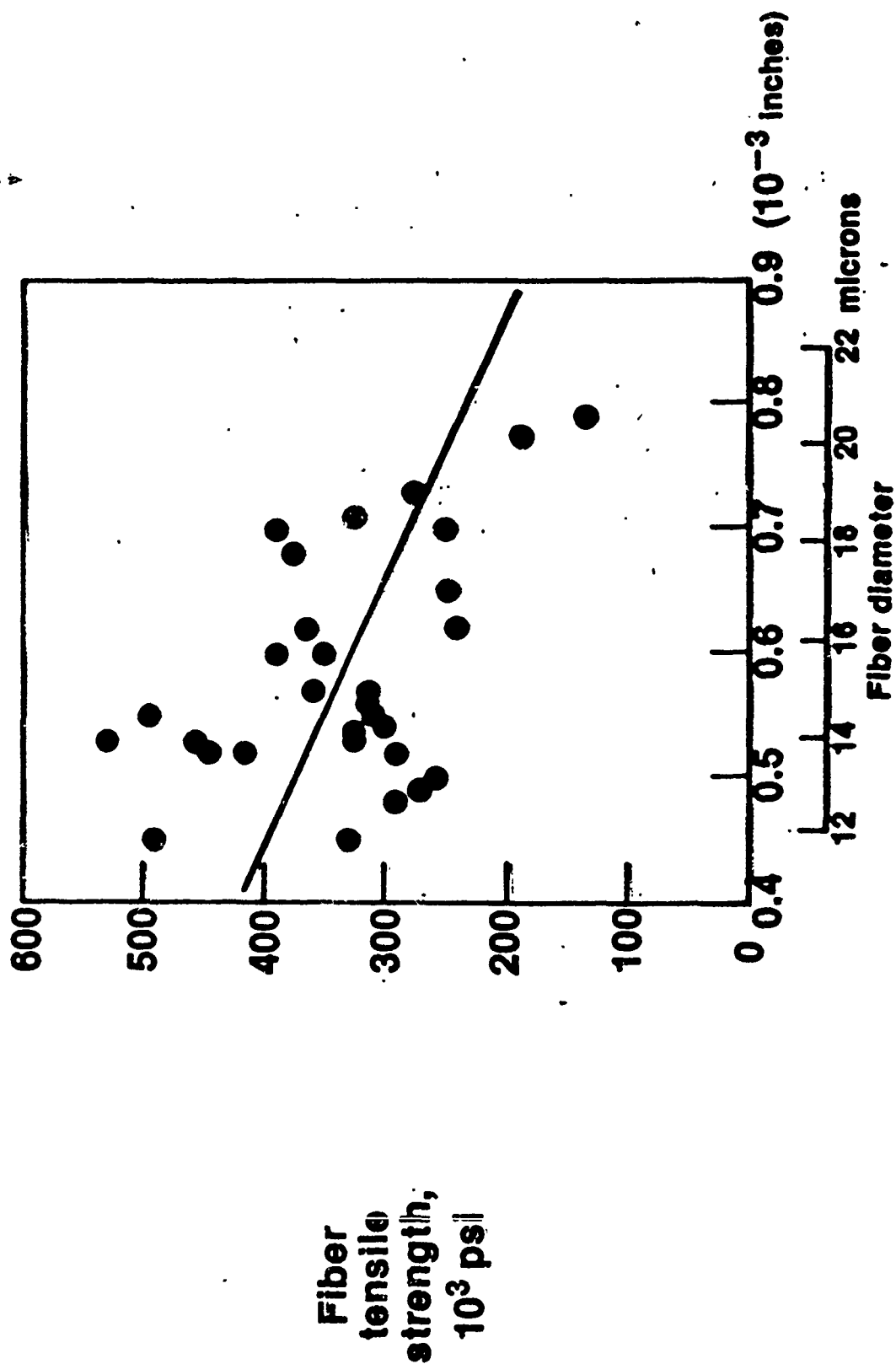


FIGURE 6

OVERALL DEPENDENCE OF AS RECEIVED FIBER STRENGTH ON AVERAGE SPOOL FIBER DIAMETER

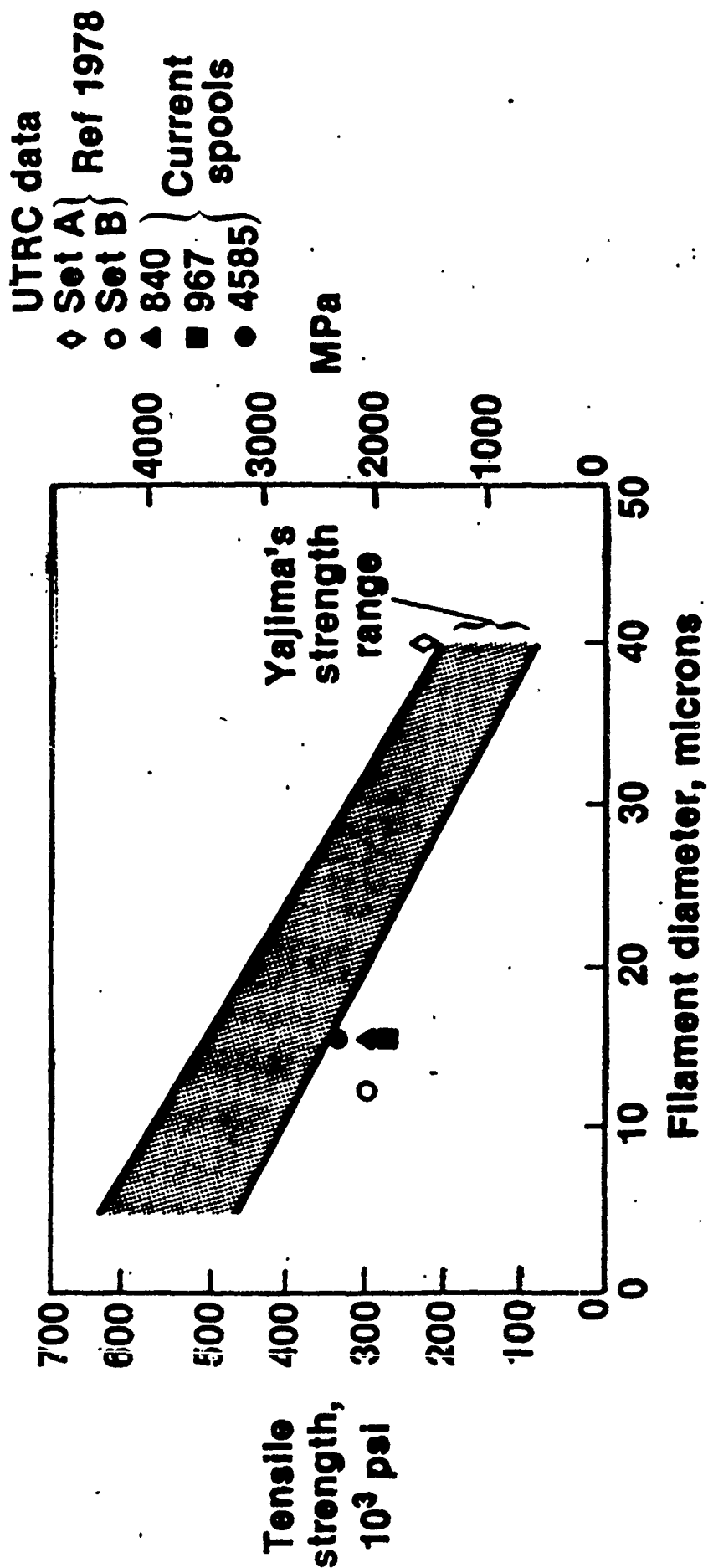


FIGURE 7

ADVANCED COMPGLAS™ FABRICATION **(Analogous to fiber reinforced resins)**

	Fiber arrays		
	Uni-tape	Woven	Chopped
Hot pressing	✓	✓	✓
Matrix transfer molding	✓	✓	✓
Chopped molding compound	—	—	✓
Injection molding	—	—	✓

FIGURE 8

TENSILE STRESS-STRAIN CURVE FOR CERAMED 0° SiC/LAS-I AT RT

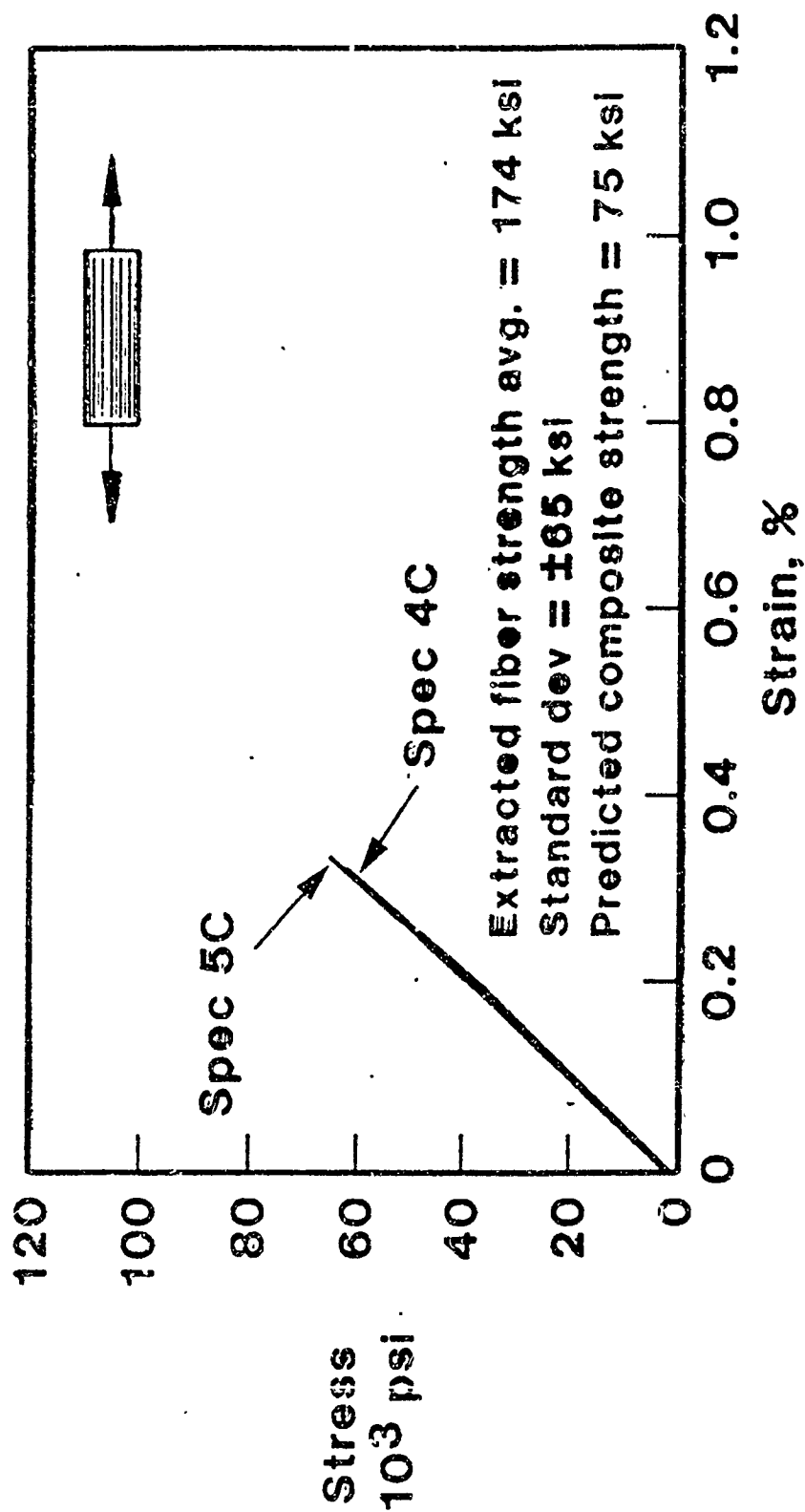


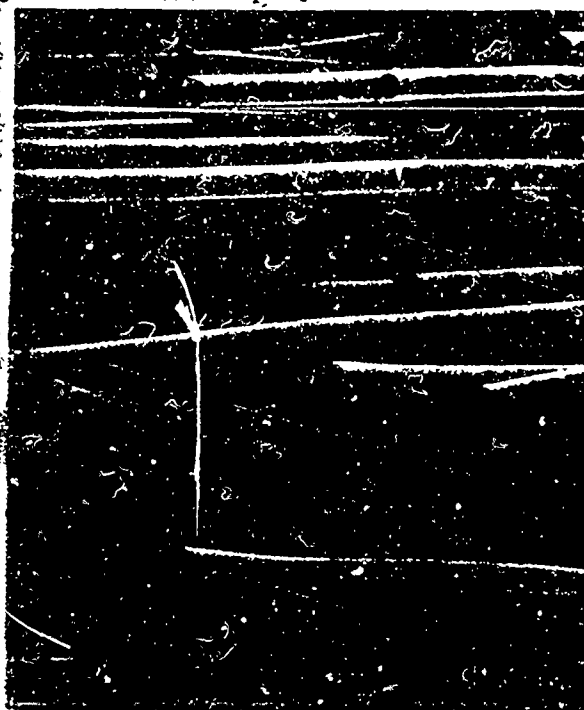
FIGURE 9

**0° SIC/LAS-1 COMPOSITE TENSILE
TESTED AT R.T.**



500 μm

a) Overall tensile fracture region



40 μm

b) Fibers on fracture surface

FIGURE 10

COMPOSITE TENSILE STRENGTH AS A FUNCTION OF ORIENTATION AND MAXIMUM STRESS FAILURE CRITERIA

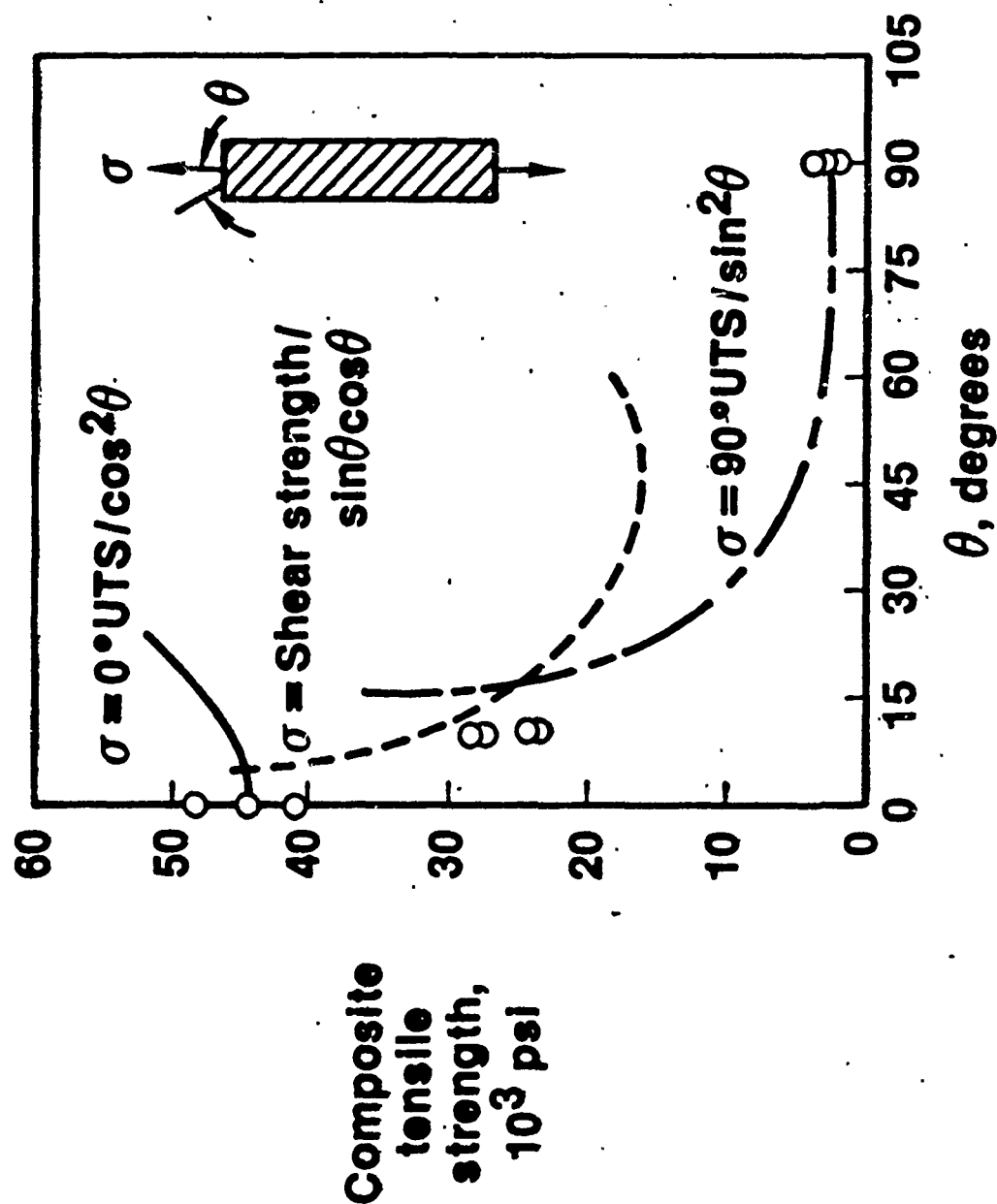
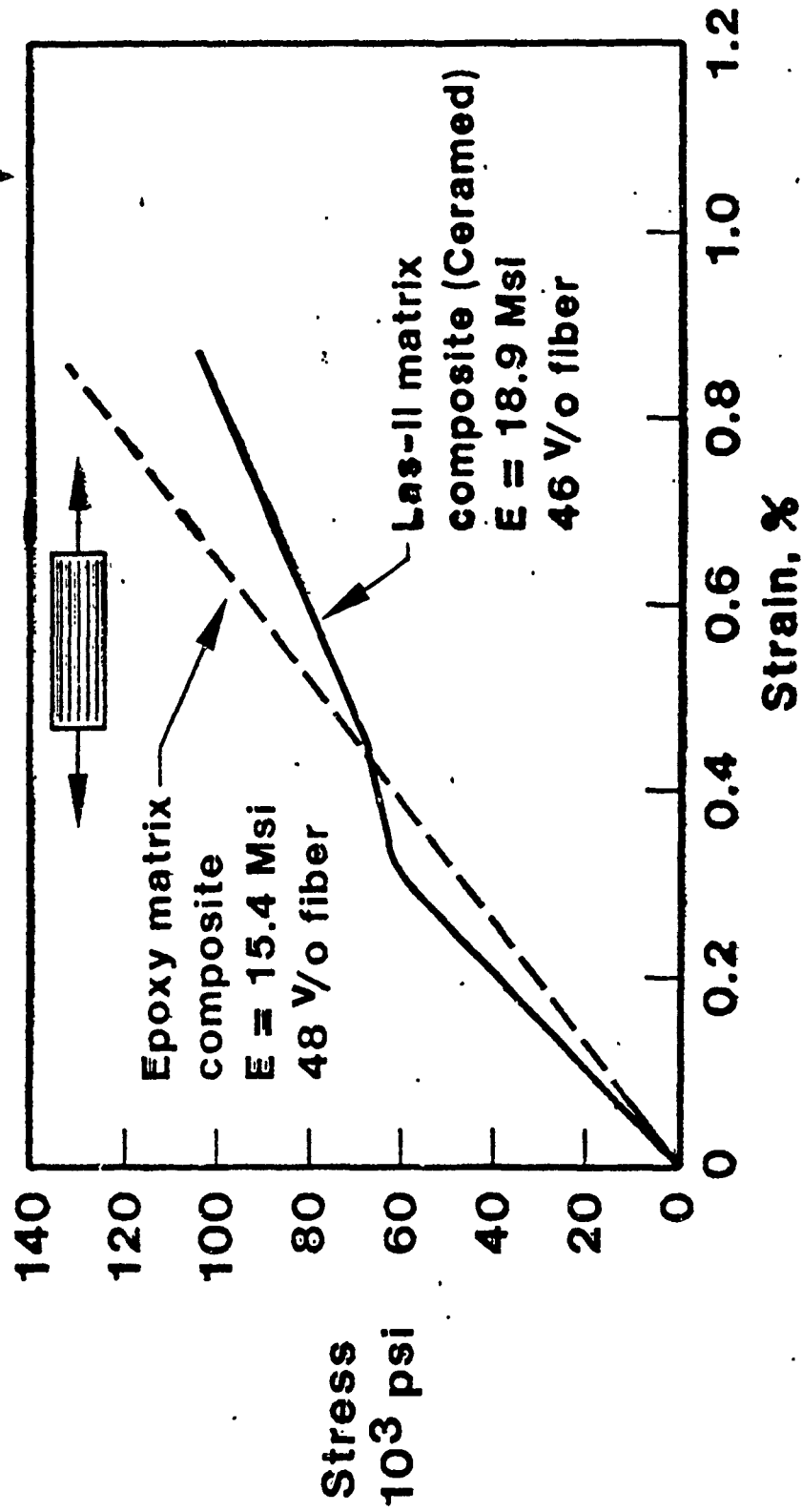


FIGURE 11

TENSILE STRESS-STRAIN COMPARISON FOR 0°-SiC REINFORCED COMPOSITES



of the stress-strain curve. Under cyclic loading, as shown in Figure 12, a change in elastic modulus does occur; however, the specimen does not appear to fail catastrophically. This change in elastic moduli is attributed to matrix microcracking.

Slight misalignments of the fibers during fabrication can result in regions of lower tensile strength due to shear failure in those regions where the fibers can be misaligned by 5 to 10 degrees. Composites reinforced with woven cross ply fibers were also prepared and tested on a 45 degree bias at room temperature and at 1000°C. The results obtained are shown in Figures 14 and 15. In both cases, failure was extremely fibrous demonstrating that these composites are very tough.

For some of the samples prepared, compression failure stress was not always greater than tension failure stress and in fact, for some samples it was less. This occurs when you have very low interfacial strength between fiber and matrix or high matrix porosity. The Nicalon® fiber reinforced glass composites prepared showed high tensile strength, good shear strength, good compression strength, fibrous failure, and a high degree of toughness. However, these materials cannot be employed at very high temperatures. Above 600°C we see a major drop in strength as shown in Figure 18. In examining the composite samples tested in the flexure mode at 900°C in air, we see that the compression side of the specimen had a very fibrous fracture, whereas the tensile side was not very fibrous at all (see Figure 19). It was also reported by Dr. Prewo that at the elevated temperatures in air, there appears to be a change in the nature of the fracture process. The flat fracture surface obtained could be due to severe degradation of the fiber in the presence of air or a change in the interface.

Dr. Prewo also initiated a discussion on the role of the interface and the importance of interfacial bond strength in a fiber reinforced composite structure. Dr. Prewo referenced a 1964 article by Cook and Gordon entitled, "A Mechanism for the Control of Crack Propagation in All Brittle Systems." Cook and Gordon pointed out that at the tip of a crack you have a complex

FIGURE 12

CYCLED TENSILE STRESS-STRAIN CURVES FOR CERAMED 0° SiC/LAS-II AT RT

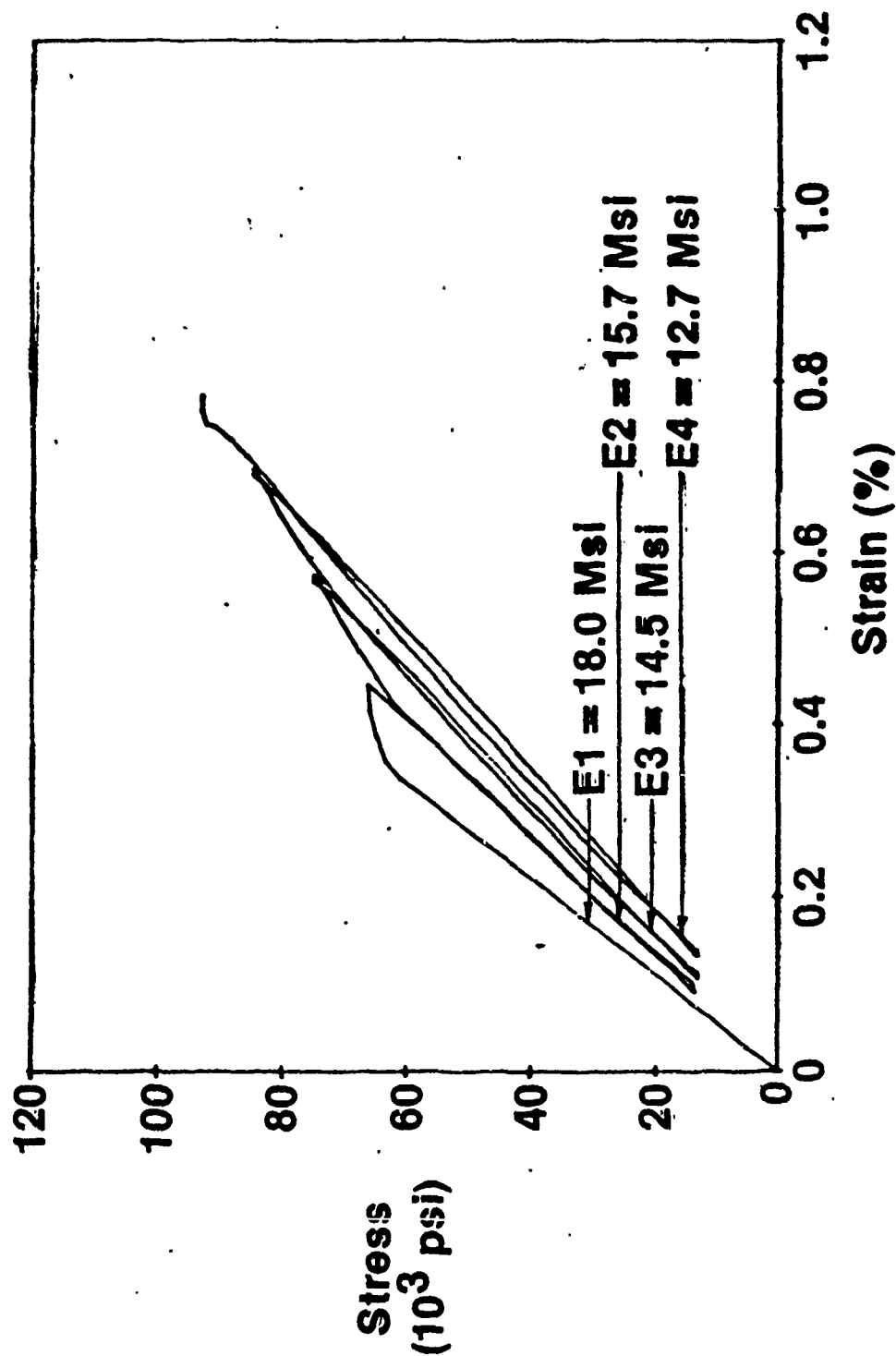


FIGURE 13

0°-SiC/LAS-II FRACTURED TENSILE SPECIMEN

As pressed condition



a) Optical photo of fracture profile



b) S.E.M. photo of fracture surface

FIGURE 14

22°C TENSILE STRESS-STRAIN RESPONSE FOR 0/90 SiC/LAS-I TESTED AT 45° IN AIR

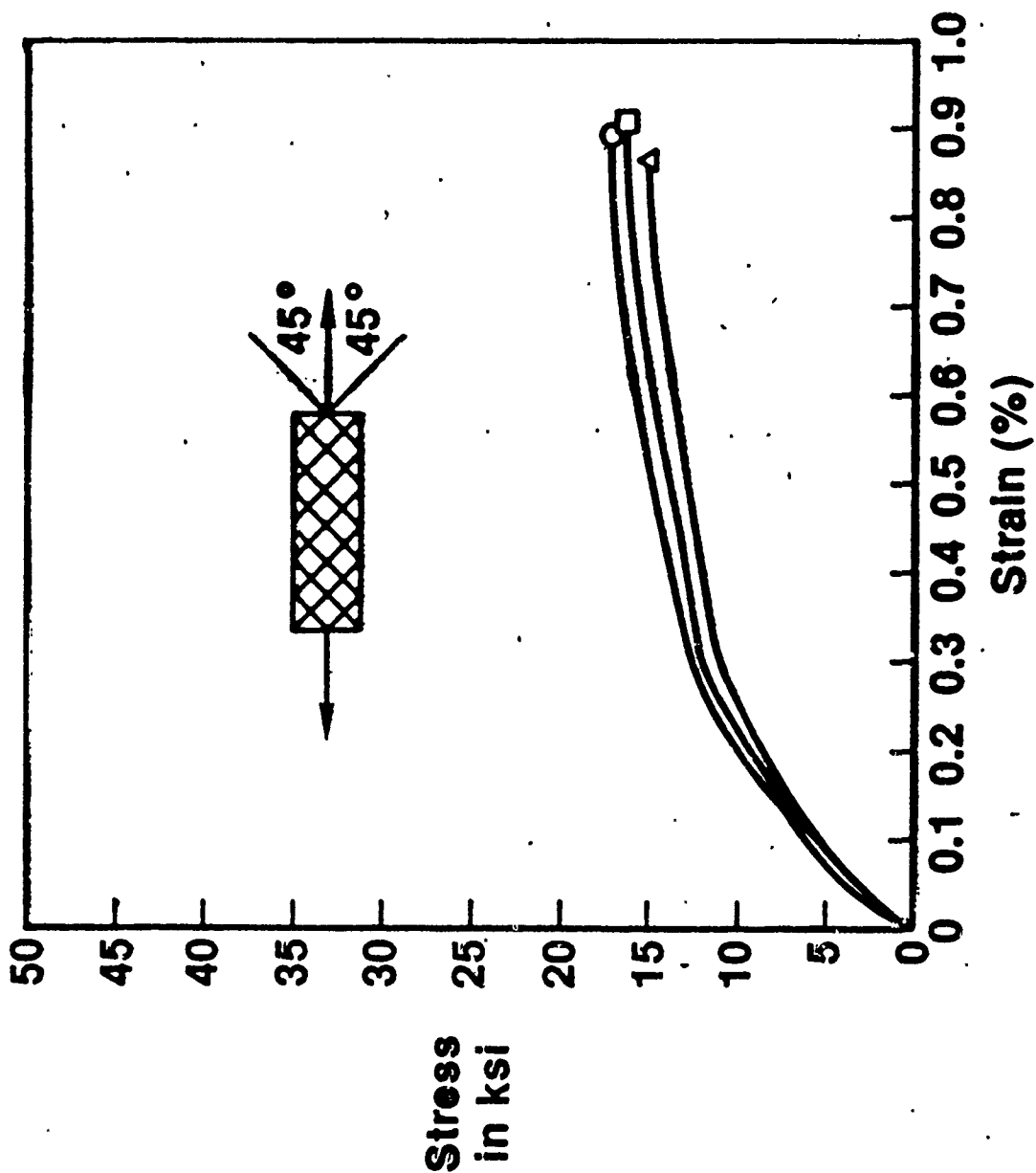


FIGURE 15

1000°C TENSILE STRESS-STRAIN RESPONSE FOR 0/90 SiC/LAS-I TESTED AT 45° IN AIR

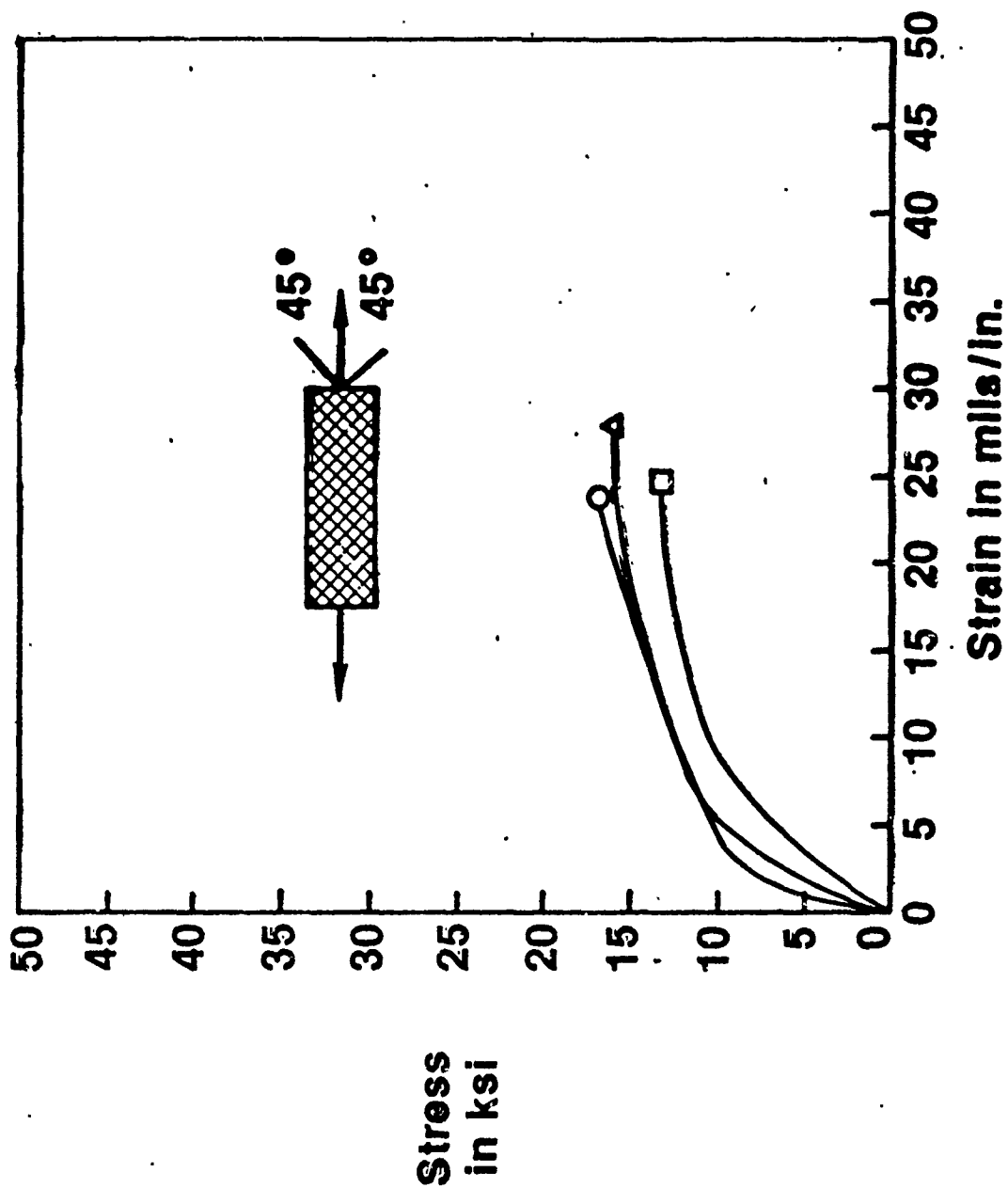


FIGURE 16

**FRACTURED 0/90 SIC/LAS-I
TENSILE SPECIMENS TESTED AT
45° TESTED IN AIR**

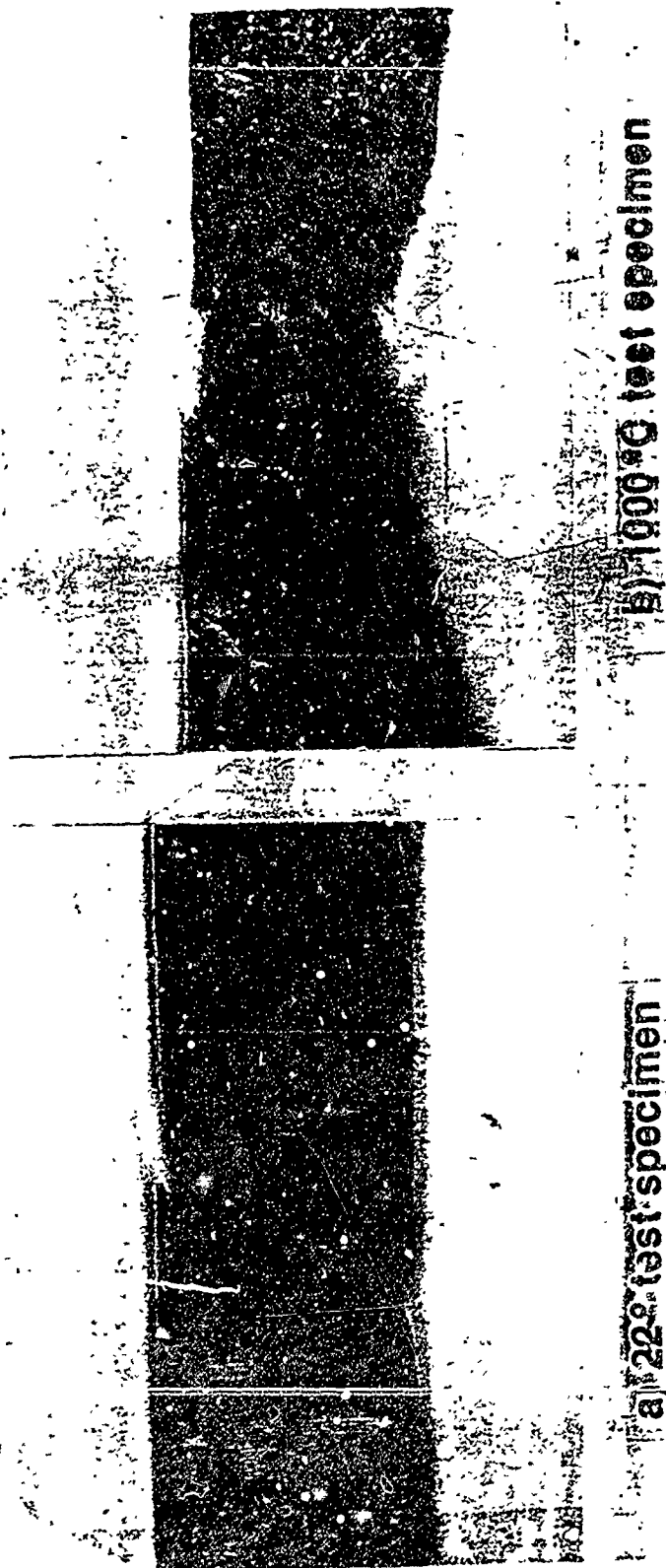


FIGURE 17

FRACTURED UNIDIRECTIONAL SiC/LAS-I COMPRESSION SPECIMENS TESTED IN AIR AT 0°

Shown normal to the ply layup



22°C



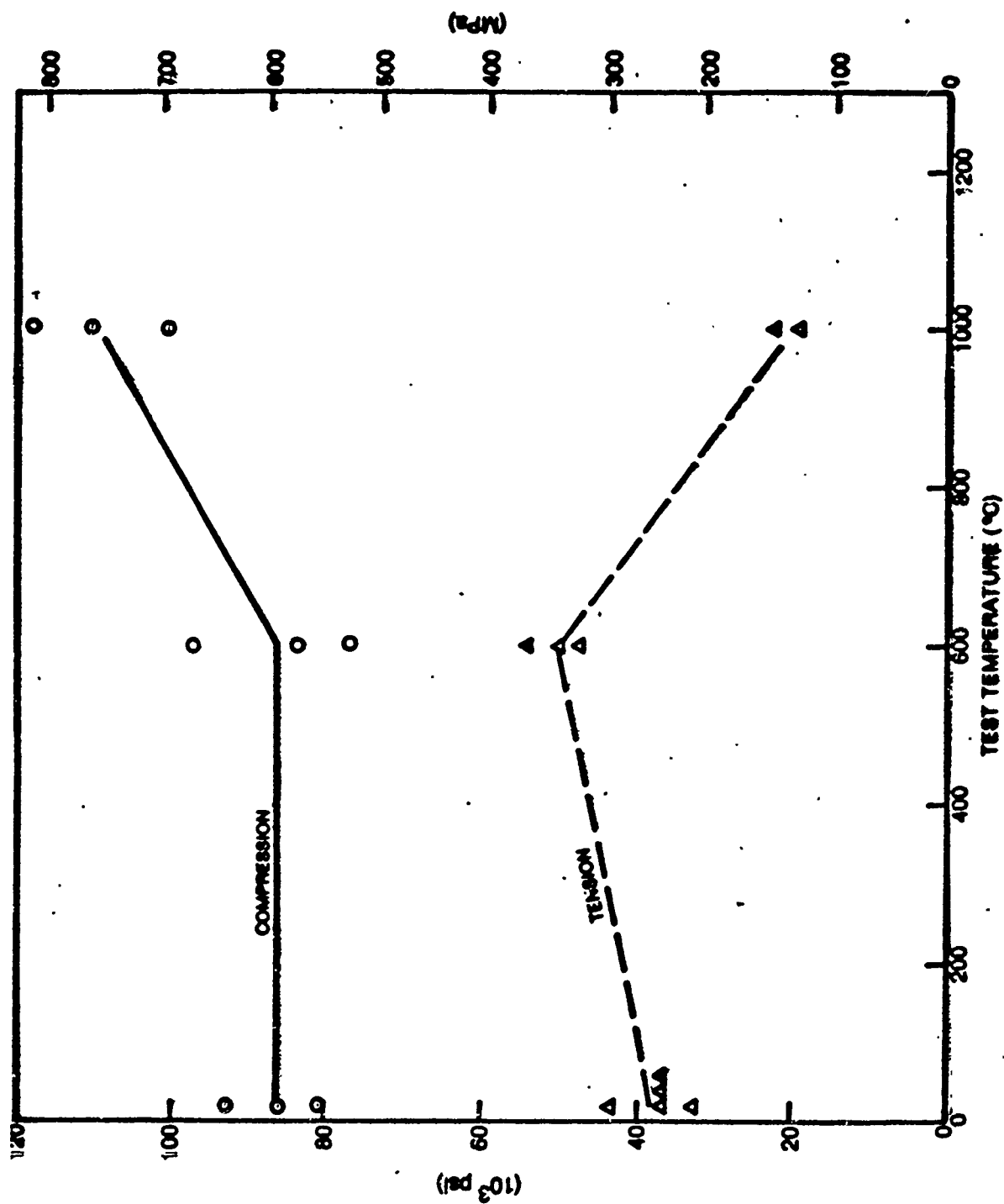
600°C



1000°C

(All specimens 2.5 in. long)

FIGURE 18



0° Tension and Compression Strength of Unidirectionally Reinforced IAS-1 Matrix Composites Tested in Air.

FIGURE 19

**0° SIC/LAS-II FLEXURE SPECIMEN
ON THE TENSION SIDE**



100μm



10μm

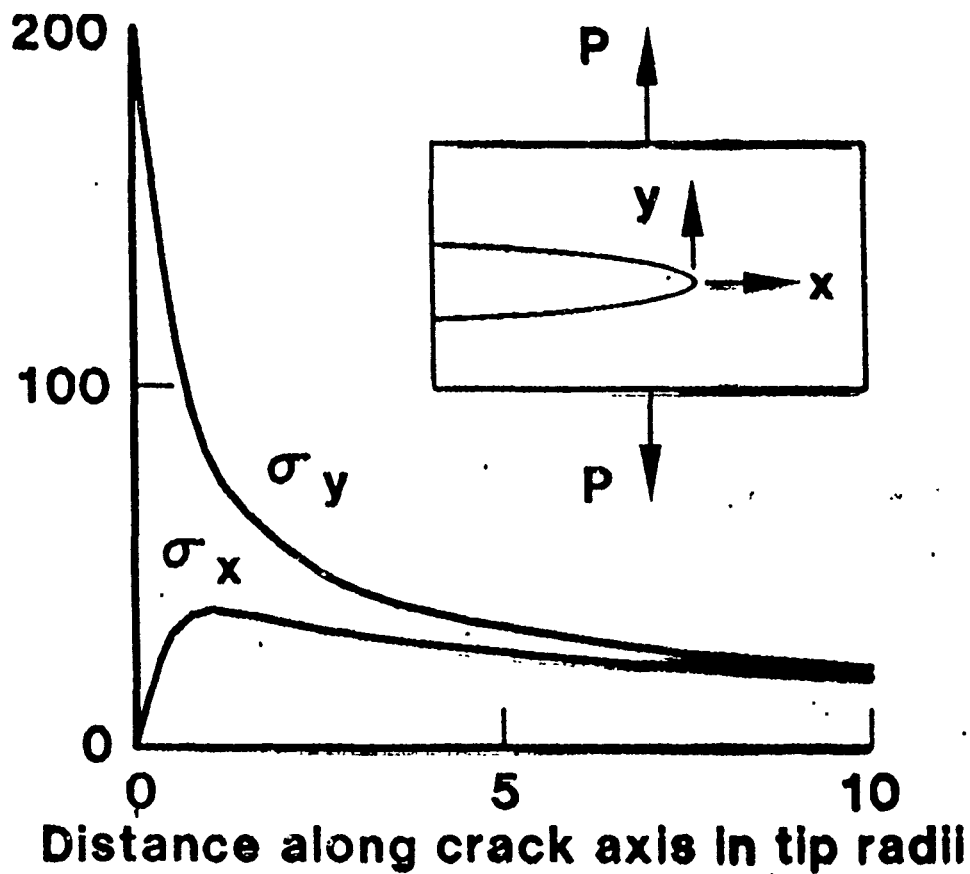
stress state as shown in Figure 20. As the crack approaches an interface (plane of weakness) a perpendicular gap can be generated. This open crack at the interface can serve to blunt a crack advancing perpendicular to it as seen in Figure 21. As shown in Figure 21, shear occurs off the primary axis of the propagating crack.

The relationship of fiber pullout and bond strength and the correlation of fiber pullout with composite toughness was discussed using the model developed in Figure 22. After matrix microcracking is initiated and as the stresses increase, fiber failure will be initiated in the path of the crack. The stress needed to pull the fiber out of the matrix increases with increasing length of fiber buried within the matrix. As expressed by the relationship shown in Figure 22

$$\sigma \pi r^2 = 2 \pi r l_c \quad \text{and} \quad \sigma_f = \frac{2 \tau l_c}{r} \quad .$$

If the fiber is very strong then interfacial strength can therefore be strong and you can still get good pullout length and a good degree of toughness. If the fiber is not very strong, a weaker interface is needed in order to blunt the crack. The relationship developed does not predict a constant fiber length since the fibers want to fail at a variety of different positions.

It was also pointed out that the properties of the interface would change with time and temperature since oxidation and other environmental conditions affect the fiber matrix interface. The exact nature of these rate controlling mechanisms are not well understood. However, the reactions which occur at elevated temperatures can also change the state of stress and can create new stresses. Dr. Prewo pointed out that the change in fracture mode observed at elevated temperatures in oxidizing atmospheres does not occur in inert atmospheres. When tested in inert atmospheres, the composites maintain their fibrous failure mode and show no loss of strength, in fact, a dramatic increase in strength was observed with increasing temperatures up to 1300°C. Strength well above 100 ksi were recorded at temperatures of 1300°C.



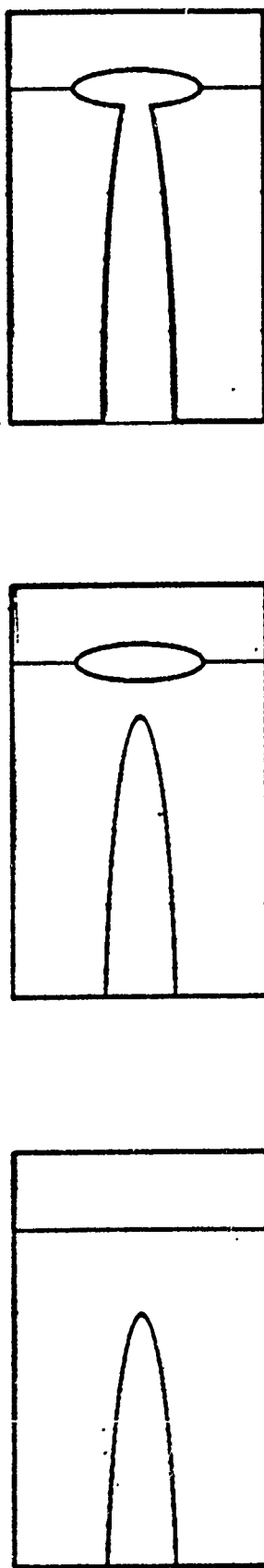
J. Cook and J.E. Gordon

"A Mechanism for the Control of Crack Propagation in All-Brittle Systems" 1964

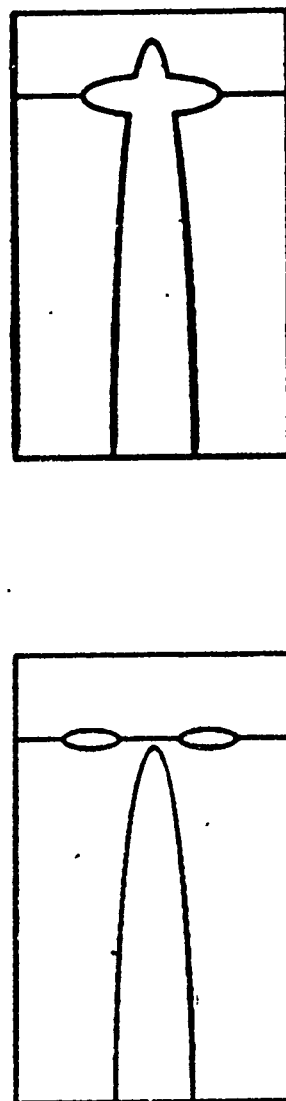
FIGURE 20

FIGURE 21

INTERACTION BETWEEN AN ADVANCING CRACK AND A PLANE OF WEAKNESS



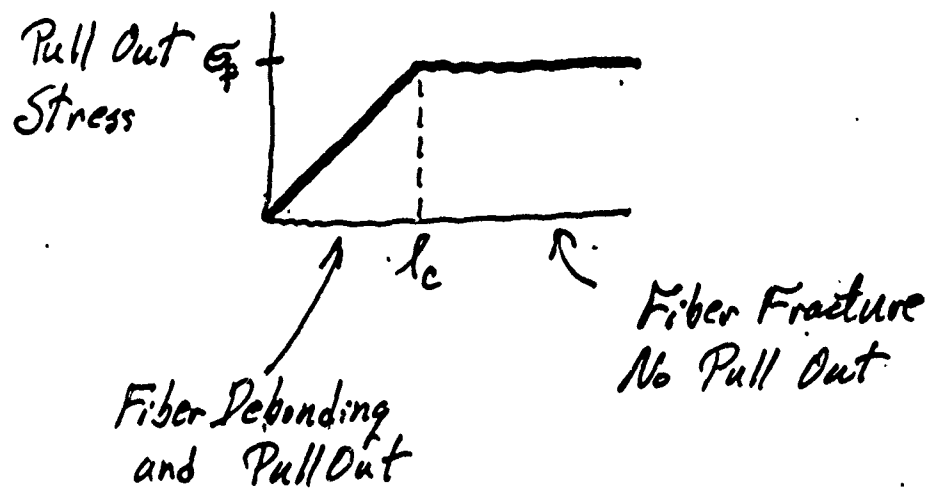
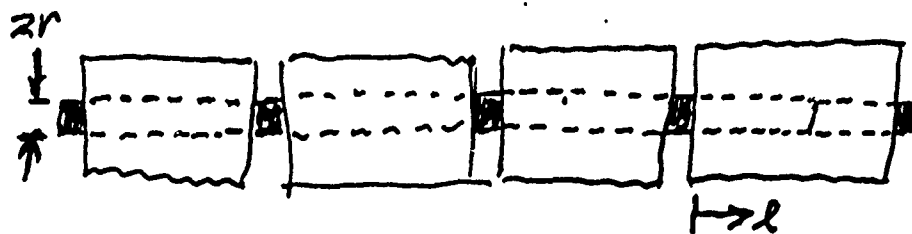
σ induced failure



τ_{xy} induced failure

FIGURE 22

Fiber Pull-Out



$$\sigma_f \pi r^2 = 2 \pi r l_c \tau$$

$$\boxed{\frac{l_c}{r} = \frac{\sigma_f}{2\tau}}$$

The fabrication of fiber reinforced composites using chopped fibers was also discussed by Dr. Prewo. These composites were prepared by chopping graphite and silicon carbide fibers which were then processed into randomly arrayed sheets. These sheets are stacked up and densified after the matrix is diffused into the system (see Figure 23). Both graphite and Nicalon[®] fibers were used in lithium aluminum silicate and borosilicate matrices.

The flexure strength of chopped graphite fiber reinforced borosilicate glass is shown in Figure 24. The tensile strength of the sample is about 50 ksi and it had a failure strain of 1%. It is interesting to note that the elastic modulus of these composite systems was less than the elastic modulus of the starting modulus fiber. Although these composites have low elastic modulus, they have good strength and good strain to failure. The tensile fracture surface was very fibrous (see Figure 25). In Figure 26, the tensile stress strain curve obtained for the chopped graphite fibers in the borosilicate matrix is compared to chopped graphite fiber in an epoxy matrix composite. The flexure strength of the glass matrix composite exceeds that of the resin matrix composite. The tensile strength of the epoxy composite was 180 ksi and 150 ksi for the borosilicate glass composite. The flexure strength of the epoxy composite was 268 ksi and 400 ksi for the borosilicate glass composite.

Chopped silicon carbide fibers reinforced aluminum silicate glass composites were also prepared. These composites had a tensile strength of about 50 ksi with a failure strain a little over 1% (see Figures 27 and 28).

Experiments were conducted to determine the critical fiber length for chopped silicon carbide fibers. It was found that about 1/4- to 1/2-inches in length was desirable. Lengths shorter than 1/4 inch or longer than 1/2 inch created problems in the fabrication of the composites. Fiber length was to some extent determined by requirements to bridge the network of microcracks in the matrix. Aspects ratio did not seem to be too important a factor.

FIGURE 23

COMPOSITE STRUCTURE

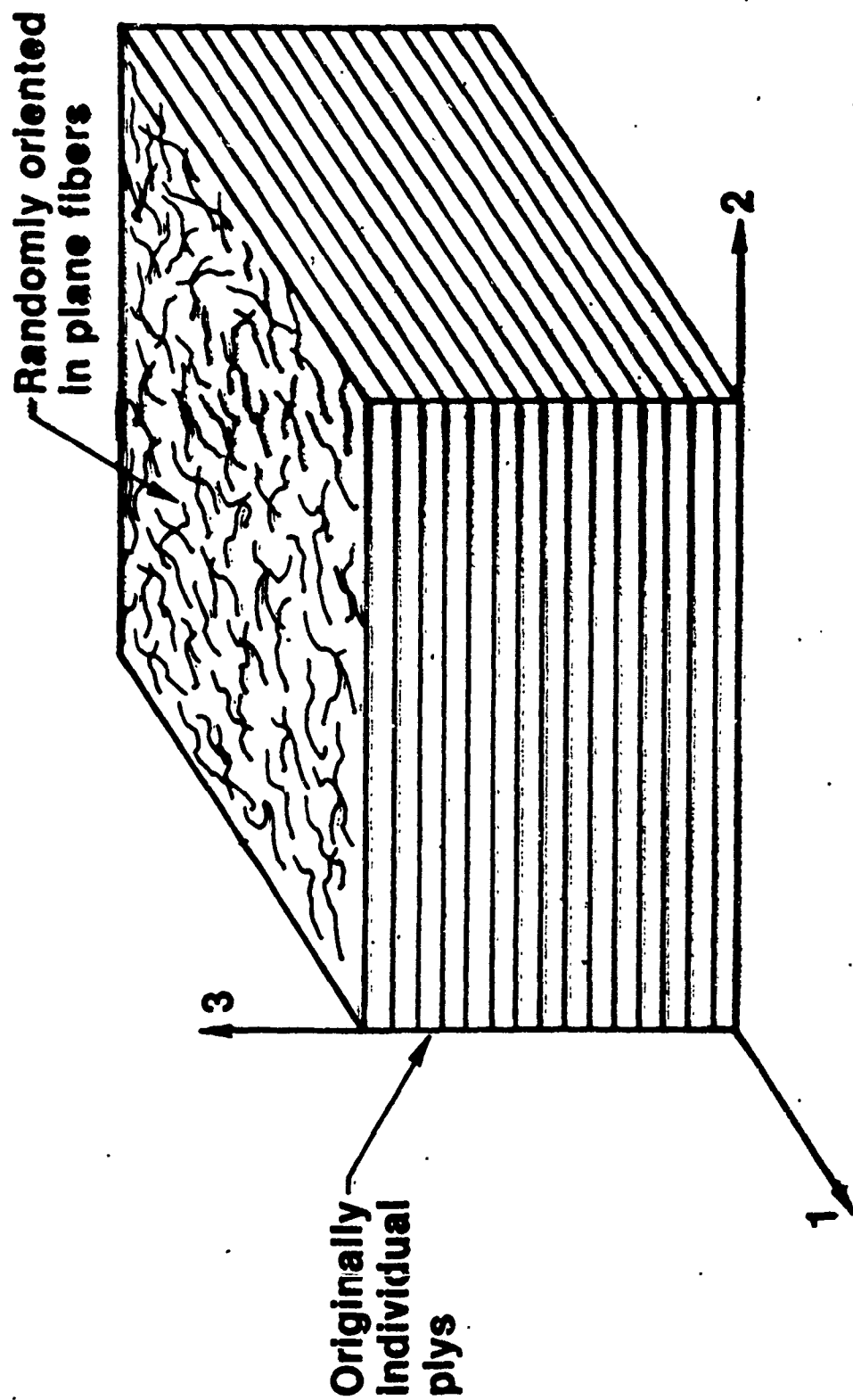


FIGURE 24

STRAIN GAUGED FOUR POINT BEND TEST

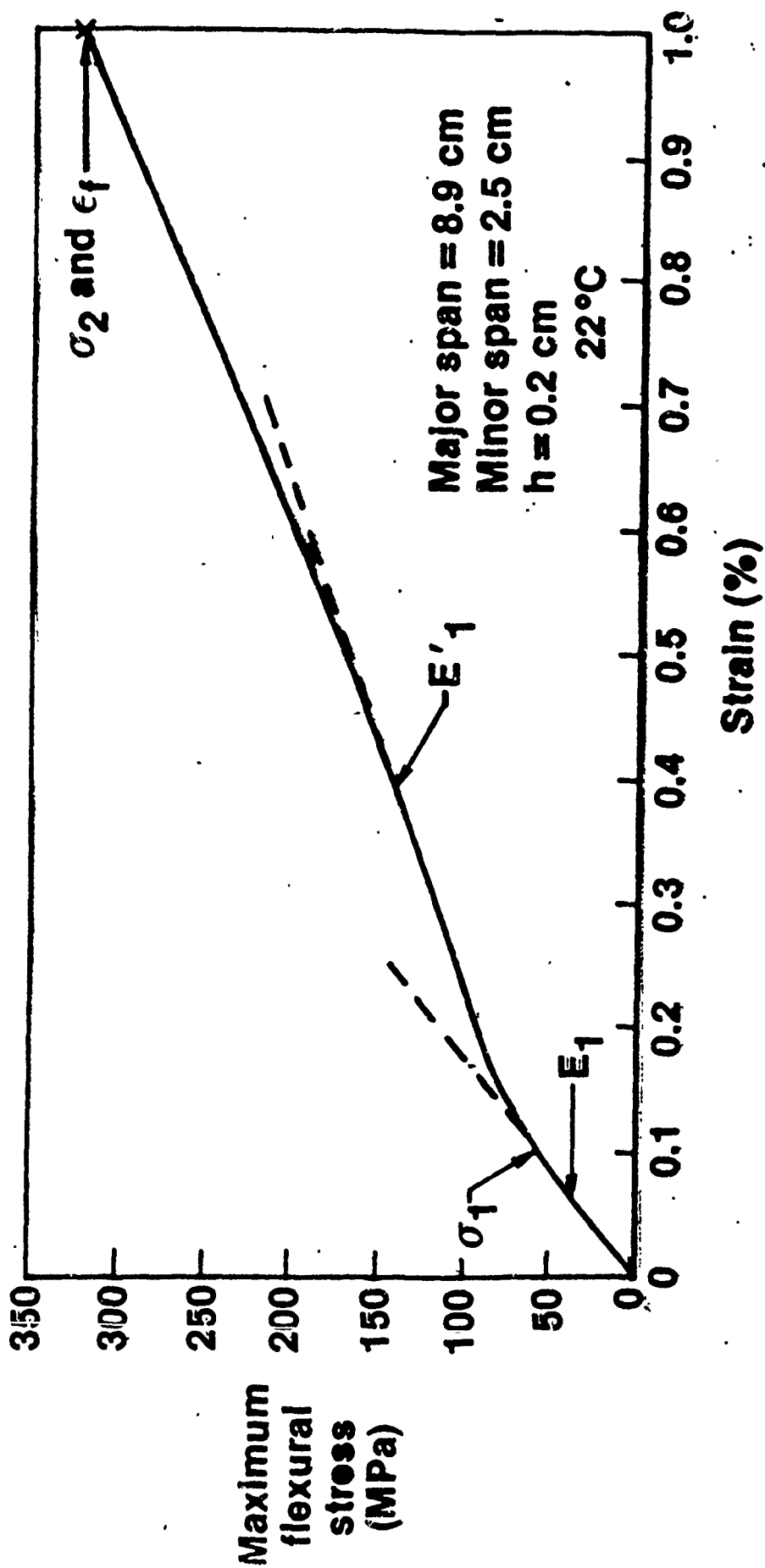


FIGURE 25

TENSILE FRACTURE SURFACE



20 μ m

TENSILE STRESS STRAIN COMPARISON FOR DISCONTINUOUS GRAPHITE REINFORCED COMPOSITES

FIGURE 26

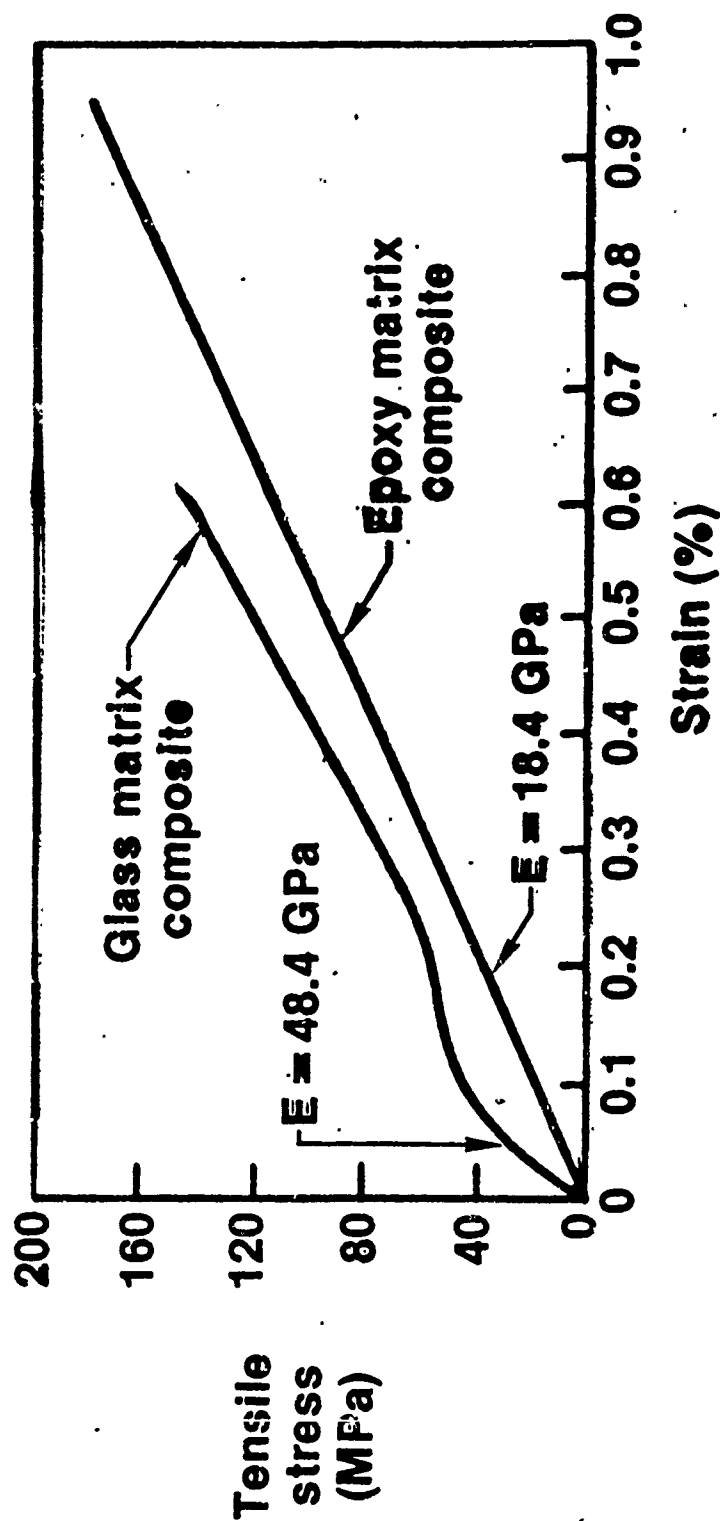


FIGURE 27

LONGITUDINAL SECTION MICROSTRUCTURES OF DISCONTINUOUS SIC REINFORCED LAS

Composite 2169 — 0.75 in. fibers



200 μm

Composl

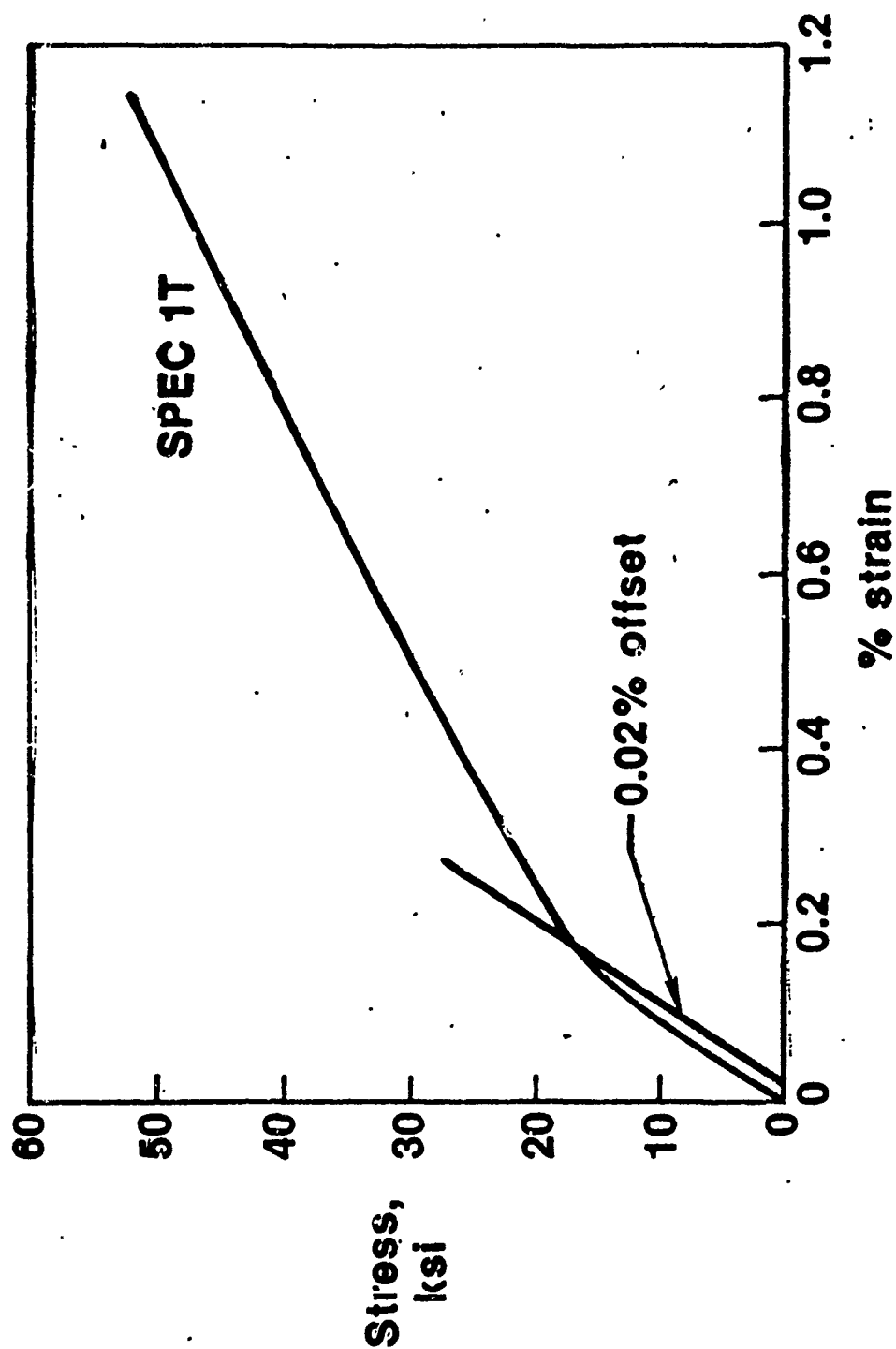
— 0.25 in. fibers



200 μm

FIGURE 28

RT 4 PT BEND STRESS STRAIN BEHAVIOR FOR 0.25 IN. DISCONTINUOUS SIC REINFORCED LAS-II COMPOSITE (AS PRESSED)



In his closing remarks, Dr. Prewo pointed out that in the efforts to achieve composites of optimum properties or what is perceived to be optimum properties, we shouldn't throw anything away. Systems developed along the way might have attractive potential for use in many noncritical applications. At the present time, there appears to be fiber reinforced glass ceramic composites which can be used to 1300°C and some systems which may be able to go to as high as 1500°C.

Dr. Allan Katz, AFML

The second presentation in this session was given by Dr. Allan Katz of the Air Force Materials Laboratory. Dr. Katz's presentation was concerned with the nondomestic technology developed by the French firm SEP for the preparation of composites by the CVD process. Although the SEP Group has been investigating a number of different composite systems they only provided samples of silicon carbide fiber reinforced silicon carbide matrix composite systems to the Air Force for evaluation. These unidirectional reinforced Nicalon[®] fiber composite systems are fabricated by a chemical vapor infiltration process, using low temperature, low pressure, and low gas flow rates. The deposition rates obtained in this CVI process are a factor of six lower than those reported for conventional CVD type processes.

The bars provided by SEP were 2 in long x 1/4 in x 1/8 in in cross section. These samples had a density gradient that extended from the edge of the bar toward the center with an average porosity of about 30%. Methyltrichlorosilane is used as the gaseous precursor for the infiltration process. The samples obtained seemed to consist of four separate deposition layers but it is not clear how these different layers around the Nicalon[®] fibers were formed. It was evident from the information available that the development for these composite materials is still evolving.

The mechanical strength of these composites was studied and there did not appear to be any evidence of fracturing between the four distinct layers observed in the composite microstructure.

In tensile initiated failures, cracks are formed, delaminate, and propagate through the sample in a semi-graceful fashion. The load deflection curves at room temperature did not display very much tailing. At elevated temperatures in air there was a substantial amount of tailing, however, on a macroscopic level the fracture mode did not appear to change. A degree of fiber pullout was observed on the microscopic level which may be related to changes at the interface due to the high temperature exposure. Room temperature tensile strength of these materials was approximately 40 ksi. Room temperature flexure strength for these materials was between 55 ksi and 60 ksi. In air at 1000°C, 1200°C, and 1500°C, the flexure strength measured was 52 ksi, 38 ksi, and 35 ksi, respectively. It would certainly appear that these samples retain a reasonable amount of flexure strength at elevated temperatures in air.

Dr. Katz also reported on a recent program initiated by Amercom of Chatsworth, CA under the small business program for the development of Nicalon[®] fiber reinforced silicon carbide composites prepared by similar CVD processes. In this study, a number of deposition parameters and a number of fiber reinforced architectures were investigated. Flexure strength for these composites at room temperature reached a high of 40 ksi. Processing times were less than 20 hours per sample which is considerably less than that reported by the SEP process. A continuation of the Amercom program is planned which would systematically examine key issues concerned with fiber pretreatment, effects on interface, how the interface relates to open viscosities, reinforcement architecture, and optimization of CVI processing parameters to achieve high quality reinforced composite materials.

Dr. R. Baney, Dow Corning

A third and final paper of this session was presented by Dr. Baney and was concerned with the environmental effects on ceramic matrix composite materials. Dr. Baney pointed out that only a very limited amount of work had been done in studying the environmental effects on ceramic matrix composites. Most of the

work reported in the literature is concerned with studying the high temperature performance of Nicalon[®] fibers in oxidizing or vacuum environments. Dr. Baney indicated that there has only been a little bit of work studying Nicalon[®] fiber exposed to high temperature nitrogen atmospheres even though there is some evidence that nitrogen is picked up by these fibers at elevated temperatures. Dr. Baney also made the point that very little work has been done in studying the nitrogen-carbon-silicon systems under the high temperature environments necessary for processing these advanced ceramic composite systems. Dr. Baney reported that Dow Corning had some studies in progress looking at reaction bonded silicon nitride and reaction bonded silicon carbide in high temperature environments.

In discussing the studies on the Nicalon[®] fibers, Dr. Baney referenced the work of the University of Dayton and Systems Research Laboratories where the effects of high temperature exposure in air, vacuum, and argon on mechanical strength were studied. A summary of the mechanical test results obtained from this study is presented in Table 1. As shown in Table 1 high temperature exposure degrades fiber strength and exposure in vacuum had the most deleterious effect on the Nicalon[®] fiber. It should also be noted that fibers exposed to 1200°C in air showed more serious degradation than those exposed to air at 1400°C. These studies also showed that there was significant grain growth of the β silicon carbide above 1200°C. These results would suggest that the limited degradation observed for fibers exposed to 1300°C and 1400°C in air should not cause composite degradation during processing. The strength degradation mechanisms observed in the composite do not appear to be significantly related to the fiber degradation observed during processing. It was suggested that a more significant problem is the formation of a silica film on the surface of the fiber during high temperature exposure in air.

Dr. Baney went on to describe some work at Dow Corning which used infrared spectroscopy to investigate Nicalon[®] fibers that had been heat treated for 12 hours at 1500°C in air. This

Table 1
SUMMARY OF TENSILE TEST RESULTS

Fiber Treatment	No. of Tests	Tensile Strength, MPa ($\times 10^3$ psi)	Young's Modulus, GPa ($\times 10^6$ psi)
As-Received	10	1765 (256)	106 (15.4)
Sizing Removed with Acetone	14	2110 (306)	118 (17.1)
1200°C in Argon	13	1234 (179)	108 (15.6)
1300°C in Argon	13	1262 (183)	110 (15.9)
1400°C in Argon	15	848 (123)	104 (15.1)
1200°C in Vacuum	5	345 (50)	94 (13.6)
1300°C in Vacuum	10	200 (29)	47.6 (6.9)*
1200°C in Air	15	660 (95.7)	110 (16.0)
1300°C in Air	12	1262 (183)	114 (16.6)
1400°C in Air	13	1379 (200)	102 (14.8)

NOTE: Tests on fibers heat treated in vacuum at 1400°C could not be made due to the extreme brittleness of the specimen.

*Due to low failure loads, significant error may have been introduced in the extension measurement. Load-deflection curves have a minimal linear portion.

work showed very distinct silicon-oxygen bonds in heat treated fibers resulting from the formation of complex silicon-oxygen-carbon systems. Dr. Baney also points out that there was a whole series of intermediate spectra which indicated the formation of a number of intermediate phases during treatment. The Nicalon® fibers heat treated for 12 hours in argon to 1400°C showed distinct grain growth in the center and in a layer around the outside of the fiber. Fibers made from the silicon-carbon-nitrogen system developed by Dow Corning showed some structure when subjected to the same heat treatment. However, these showed considerably less layering effects than was observed for the Nicalon® fibers.

Dr. Baney also reported on some work in their laboratory making ceramic matrix composites using the same type of process that is used for preparing carbon-carbon composites. Selected polymers were used to infiltrate an array of Nicalon® fibers. The composites were then pyrolyzed to obtain a silicon-carbon-nitrogen matrix around the silicon carbide fibers. Silicon resin matrices were also investigated in this study. Three-point bend strengths were measured for the samples prepared. Strengths from 20 to 70 ksi were recorded for these composites. The load deflection curves obtained were quite similar to those reported for the SEP materials and deflection curves did not have a tail. The fracture surface showed some fiber pullout and some delamination. Composite samples exposed to an air environment for 12 to 12-1/2 hours at 1200°C were quite brittle and failed without any apparent fiber pullout or delamination. It is believed that after exposure to oxygen at high temperatures, the composite becomes a complex silicon-oxy-carbide. It would appear that the silicon-carbon-oxygen phase formed is independent of the starting composition and under flexure more regions of the interface continue to become exposed to reaction with the oxygen resulting in the formation of a uniform phase within the interfacial reaction zone.

On exposure to a high temperature oxidizing atmosphere silicon carbide, silicon nitride, and complex silicon-carbon-nitride compositions form a passifying layer of silica on the

outside surface as well as through the interface. Of major concern is the extent to which an oxide phase forms through the internal structure of the composite and to what extent the surface layer forms a barrier which inhibits further oxygen transport through the surface. The impact of porosity, the effect of microcracks opening under loading, the role of the partial carbon monoxide pressures generated in the interior of the composite are all not well understood in determining the effective sealing that may be obtained by the formation of a silica coating around the surface of a composite. Another important question raised during this presentation was the degree to which information obtained from monolithic silicon carbide and silicon nitride composites can be utilized. It was also pointed out that much more information about both the fiber, matrix, and the interface of these different composite systems is needed.

Oxide formation at the interface between the fiber and the matrix seems to be responsible for composite embrittlement. The possibility for protecting the fibers by coating them prior to composite fabrication was suggested. However, efforts to develop an effective coating for silicon carbide fibers has not been encouraging to date. More information is also needed about this oxidation embrittlement phenomena in order to engineer high strength composite ceramics.

Another way to influence interface stability may be by changes in the composition for both the fiber and the matrix. Dr. Baney reported on some of the many different polymer systems Dow Corning was investigating in the silicon-carbon-nitrogen system in order to identify promising compositions. Polymers with a high carbon-to-silicon ratio oxidize all the way to silica while other compositions appear to be little changed in the presence of oxygen. These compositions may have formed an unstable oxide layer but apparently do not oxidize through the bulk of the specimen. It was suggested that perhaps there is a carbon path that allows continuous oxidation without the formation of a stable oxide layer.

A number of different composite compositions were prepared in order to study composite stability in an oxidizing environment. Samples prepared for the study were heated to 800°C and 1200°C in air for 12 hours. For some compositions there was a complete conversion to silica. However, it was noted that some of the samples which did not oxidize at 1200°C showed complete oxidation at 800°C. This would suggest that higher oxidation rates could occur for long time exposure at lower temperatures. TGA studies showed that a weight loss initially occurs as carbon is oxidized away and then a weight gain occurs at high temperatures as silica is formed. The results presented by Dr. Baney would clearly suggest that chemical composition can play a significant role on the thermal stability of composites made from the carbon-silicon-nitrogen system.

Dr. Baney continued his presentation with a discussion about the effect of excess carbon in the structure of silicon carbide fibers, particularly the Nicalon[®] fibers. It was pointed out that carbon is a grain growth inhibitor and fiber degradation by the evolution of carbon monoxide and/or silicon monoxide would result in coarsening with loss of carbon on subsequent thermal exposures. However, even when a silica surface layer is formed on the fiber preventing carbon monoxide evolution there still is considerable fiber degradation. Exposure of the fibers at 1400°C also results in considerable fiber porosity. The slides used by Dr. Baney in his presentation are presented in Figures 1-9.

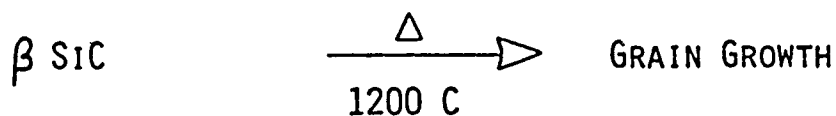
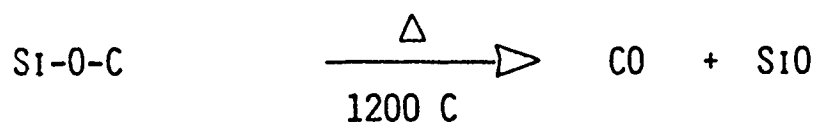
Floor Discussion

The floor discussions served as an extension to the subject areas presented by the three speakers. It was again pointed out that the relationship of the elastic modulus between fiber and matrix needs more study. The earlier concept that a high modulus fiber was required for use in a low modulus matrix may require reevaluation. For example, in a silicon carbide-silicon carbide composite the fiber has a modulus of 26×10^6 psi and it is possible to obtain silicon carbide matrices with modulus

FIGURE 1

THERMAL STABILITY EFFECTS

NICALON[®] FIBERS



- * T. MAH, ET AL, J. MATERIALS SCIENCE, 19 (1984) 1191-1201.
- * M. TAYLOR, ET AL, CORNING
- * R. ARONS, ET AL, CELANESE
- * R. CHI, DOW CORNING

RONB4

FIGURE 2

ENVIRONMENTAL STABILITY
CONSIDERATIONS
FOR
CERAMIC MATRIX COMPOSITES

- * THERMAL STABILITY EFFECTS?
- * OXIDATIVE STABILITY EFFECTS?
- * EFFECTS OF NITROGEN AT HIGH TEMPERATURES?
- * PROCESSING ENVIRONMENTS AND INTERFACIAL PHENOMINA?
- * EFFECTS OF COMBUSTION GASES AND ETC?

RONB4

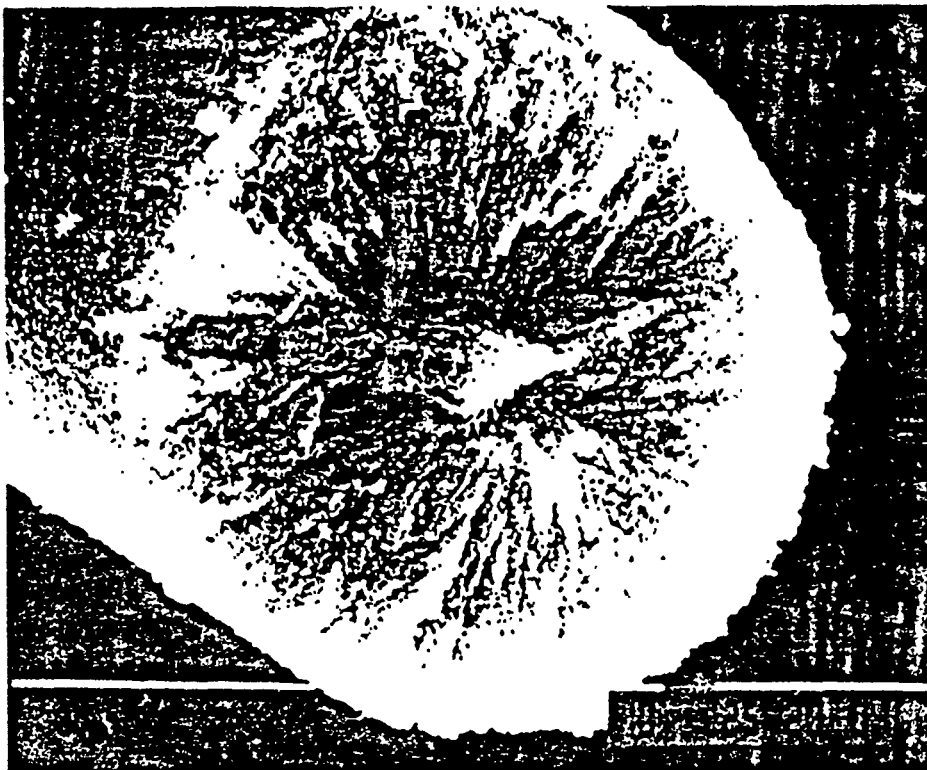


FIGURE 3

MPDZ based fiber refired 12 hours in Argon at 1400°C.

CELANESE



FIGURE 4

MPDZ based fiber refired 12 hours in Argon at 1400°C.

CELANESE

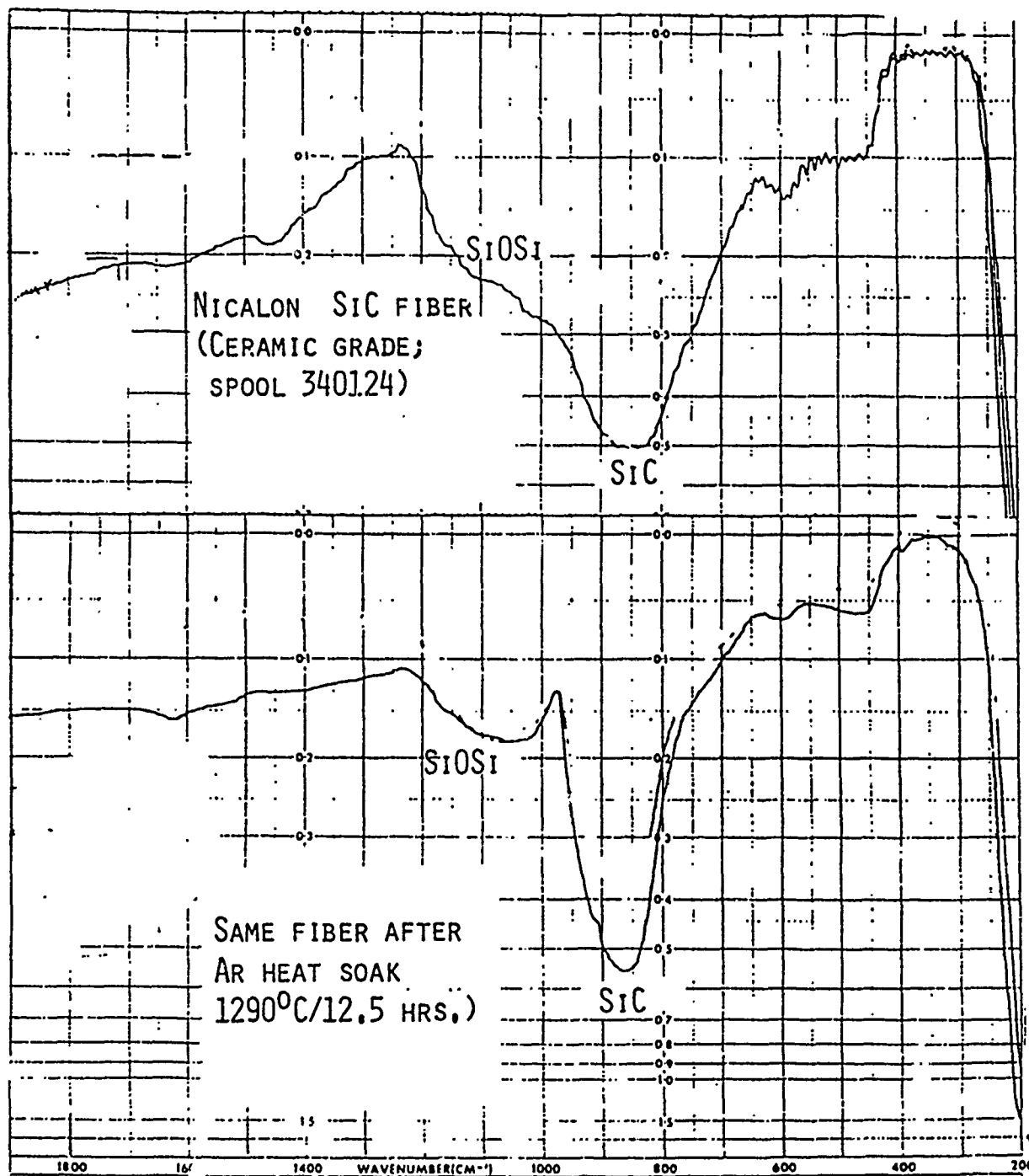
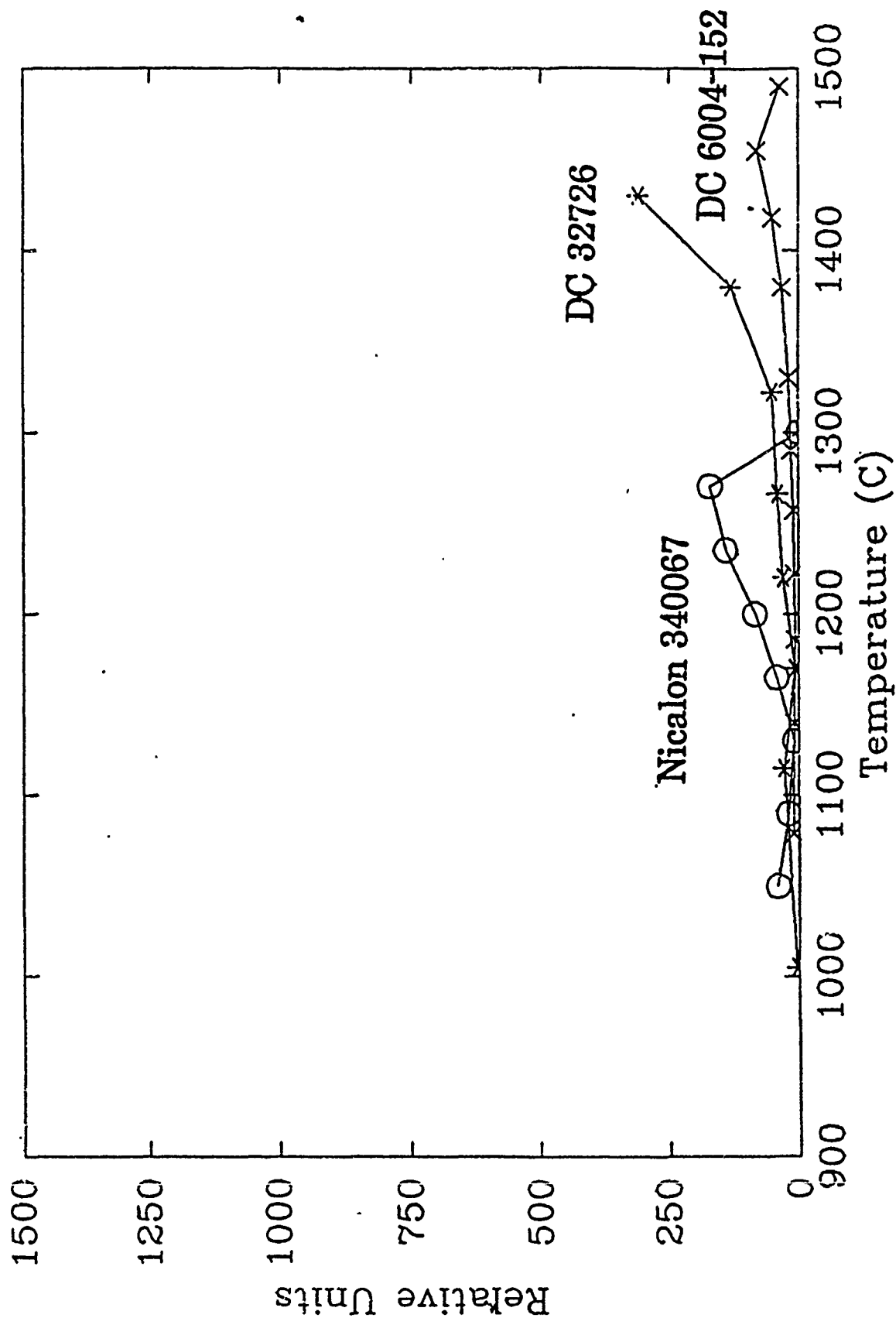


FIGURE 5
IR SPECTRA OF CERAMIC GRADE NICALON SiC FIBER
(A) BEFORE AND (B) AFTER AR HEAT SOAK,

FIGURE 6

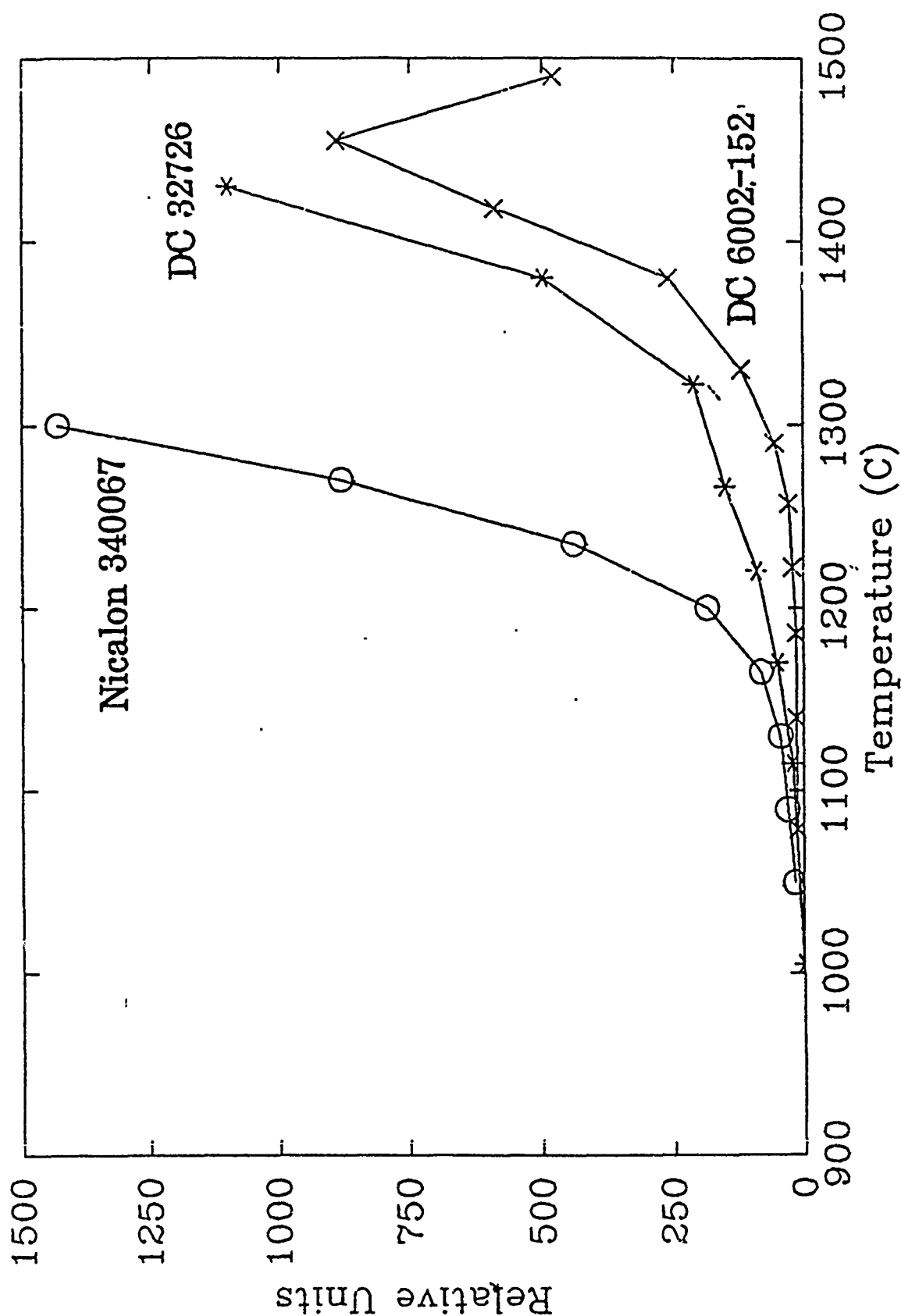
SiO Evolution by Dow Corning and Nicalon Fibers



TAYLOR - CORNING

FIGURE 7

CO Evolution by Dow Corning and Nicalon Fibers



TAYLOR - CORNING

FIGURE 8

10/14/83
3.6KV, 25.000MA
PT# = 2

XR= 2.5, YR= 2.5
CND= 345

OXIDIZED 2 2PT9.P304

AES PROFILE
10.00KV, .100UA
FILE: FC306

"Atomic Conc. vs. Sputter Time" of fired X9-6329 matrix after oxidation. Sputter rate: 100Å/min. to 10 mins., 250Å/min. at 10 mins. to the end.

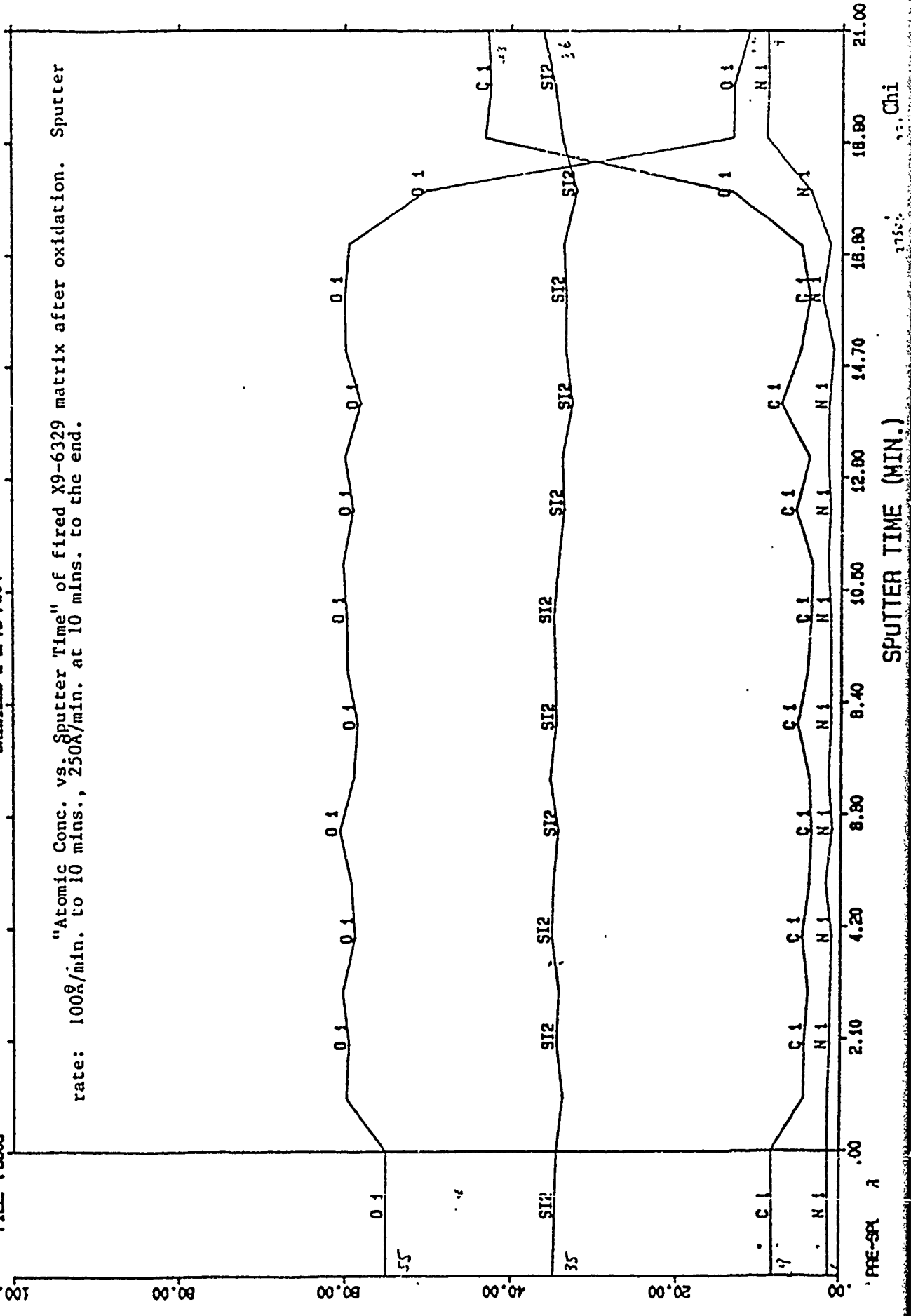


FIGURE 9

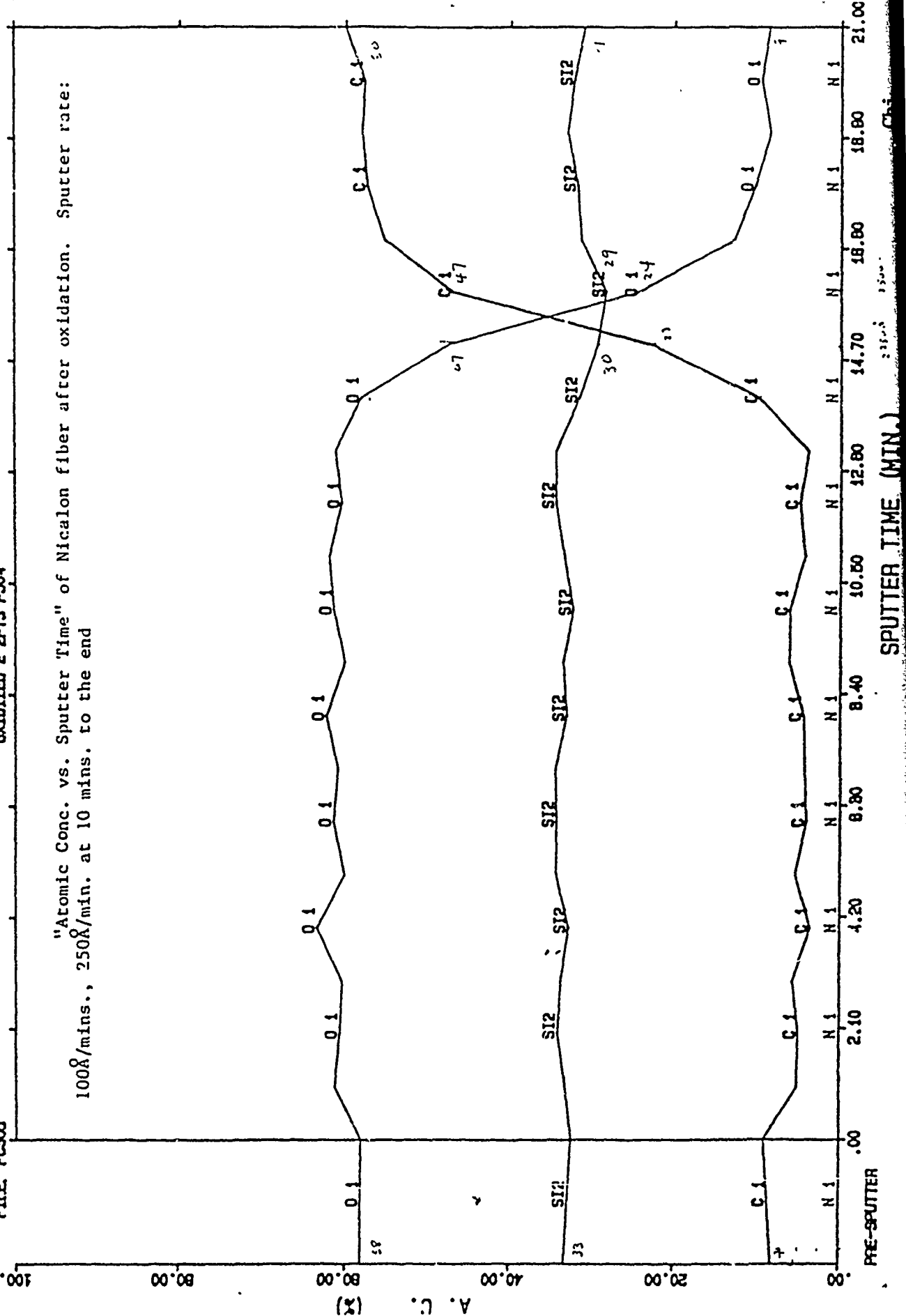
10/14/83
3.6KV, 25.000MA
PT# = 1

XR= 2.5, YR= 2.5
CND= 345

OXIDIZED 2 2PT9 P304

AES PROFILE
10.00KV, .100UA
FILE: FC306

"Atomic Conc. vs. Sputter Time" of Nicalon fiber after oxidation. Sputter rate:
100Å/mins., 250Å/min. at 10 mins. to the end



as high as 40×10^5 psi. However, this is based on the assumption that you have a fully dense composite and this may not necessarily be the case.

The need for the development of fibrous materials with a variety of different compositions as well as the need for more effective data characterizing these materials was stressed. Initially there is going to be a need for small samples of these newly developed fibers for analysis and incorporation in ceramic matrix composites. From these couples it will be possible to evaluate both the fiber and the composite interface. Another real need is the development of metal organic precursors that can be cured without oxygen. It was reported that the Japanese are investigating radiative techniques for curing fiber precursors by crosslinking.

The discussion then shifted to the potential of silicon-sulfur-nitrogen systems for obtaining crosslinked polymers that did not require oxygen and might be employed for the development of high temperature ceramic composites. It was suggested that the silicon-sulfur system had not been well studied if not totally neglected yet the potential appears very promising on initial considerations.

The effect of coefficient of thermal expansion mismatch between fiber and matrix also needs to be better understood. The rule of thumb is to select a matrix whose coefficient of expansion is similar or less than the coefficient of expansion of a fiber in order to maximize compressive forces in the composite. The degree of mismatch which can be tolerated and the impact of coefficient mismatch needs much greater study.

It was pointed out that the Air Force has interest in the development of material systems for applications in the temperature range of 150°C to 1550°C . Although major interest is for high temperature materials for application in turbine engines there is still need for a variety of material systems to be used in other applications like space structures, etc., where application environments are not as severe.

Initial emphasis has been for high density materials for use in gas turbine engines with minimum temperature stability to 1200°C. It was suggested that for applications with severe temperatures between 550°C and 1200°C major emphasis should be on the development of ceramic-ceramic composites. This approach would result in some pretty lightweight gas turbine engines. Since temperatures within the turbine engines have quite a range of variation there are effective regimes where all three categories of materials can be effectively employed.

Another area brought up for consideration is the development of composite systems using whisker reinforcement in ceramic matrix systems. It is estimated that effective composites can be made with whisker loadings of 30 to 35 volume percent. The chopped fibers or whiskers' length to diameter ratio required will depend upon the interfacial strength and the length of cracks that will have to be bridged. However, there is still a good deal more information needed to more effectively design whisker reinforced ceramic matrix composites.

Another point made during this floor discussion was that frequently these applications do not require excessively high strength materials. 30 ksi is a sufficiently strength for many of the high temperature applications of interest. The potential of coatings for silicon carbide fibers was the final point raised in the floor discussion.

INTRODUCTION AND OVERVIEW FOR CHEMICAL PROCESSING

K. S. Mazdiasni

AFWAL

Wright-Patterson Air Force Base, Ohio

Mr. Mazdiasni began his talk by giving a review of the last 25 years of materials development, as he perceived it, from his position and work within the Wright-Patterson Materials Laboratory. He began with the Air Force's interest in graphite and carbide materials for use in rocket motors within the space program in the early 60's and the work of Hasselman on dispersed particles (polyphase ceramics). He pointed out that the work presently being discussed as high tech ceramics actually began a quarter of a century ago and it has taken the ceramic community until now to accept these innovative concepts.

He went on to say that he hopes that it will not take that long for ceramists and chemists, both organic and inorganic, to work cooperatively to develop the next generation of high temperature structural ceramics and coatings.

Mr. Mazdiasni stressed understanding organic chemical reactions and the importance of characterizing the reactions involved in the process. He mentioned that work done in the Materials Laboratory with fine particle size ZrO_2 (Figures 1-5) originated when a graphite coating process did not reach the desired result and the ZrO_2 powder occurred as a by-product. He stressed that the organo-metallic type approach to ceramics allows the materials processor to tailor the material for a specific application.

He said in using this approach one must consider the organic radicals, the molecular structure, the vapor pressure, and other characteristics of precursor compounds in order to be successful.

Mr. Mazdiasni then showed the apparatus he was using to coat graphite with ZrO_2 (Figure 6) when he inadvertently deposited angstrom size ZrO_2 powder on the walls of the vessel.



M = Ge, Ti, Zr, Hf, Nb, or Ta

R = i - C₃H₇, R' = C₄ - C₅

FIGURE 1

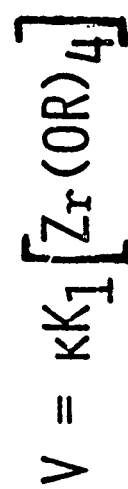
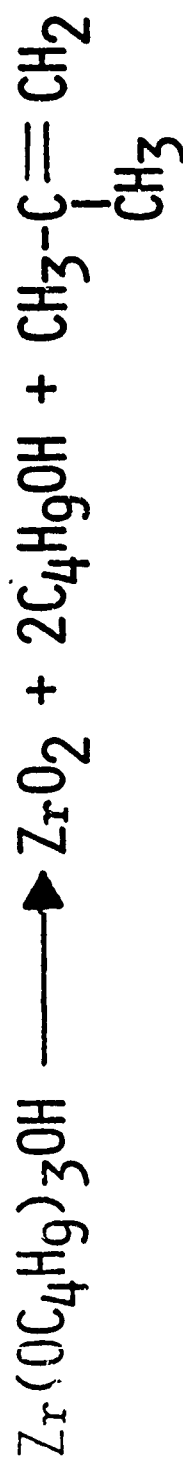


FIGURE 2

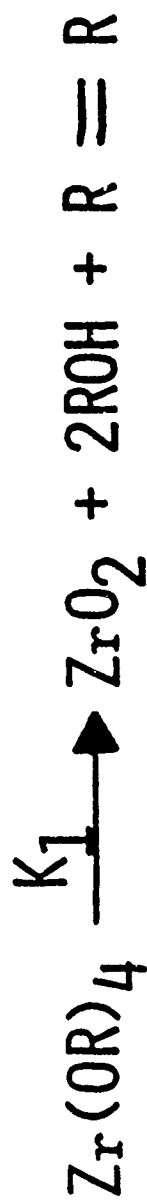


FIGURE 3



FIGURE 4

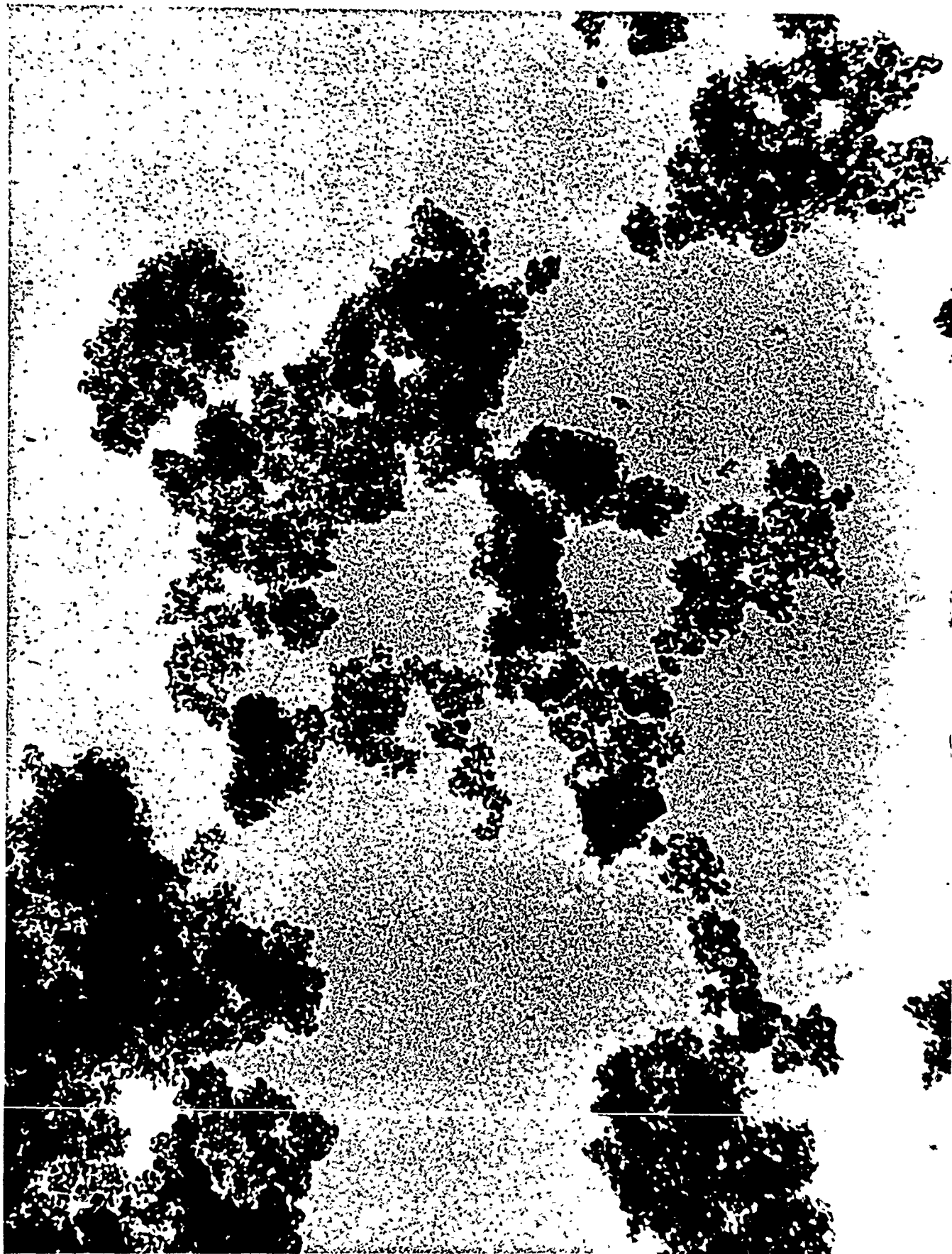
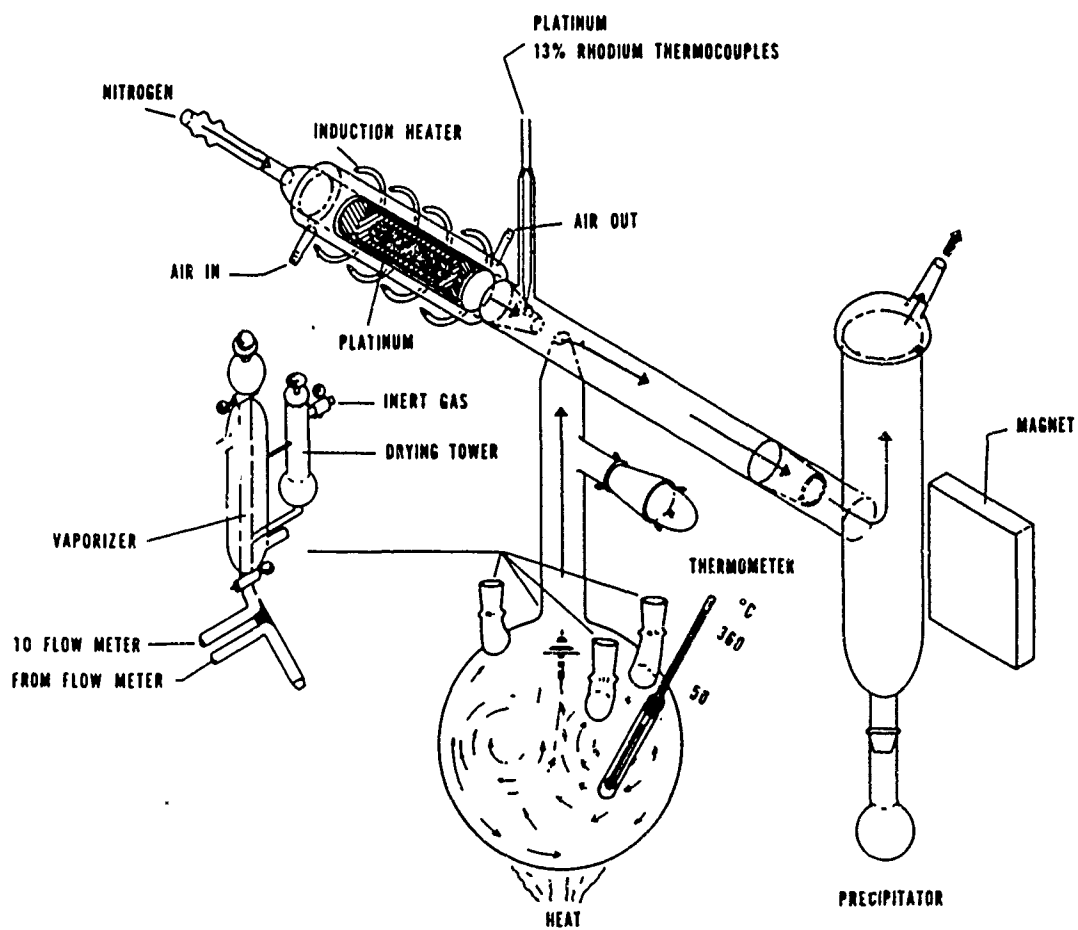


FIGURE 5



FLOW DIAGRAM FOR PREPARATION OF MIXED OXIDES

FIGURE 6

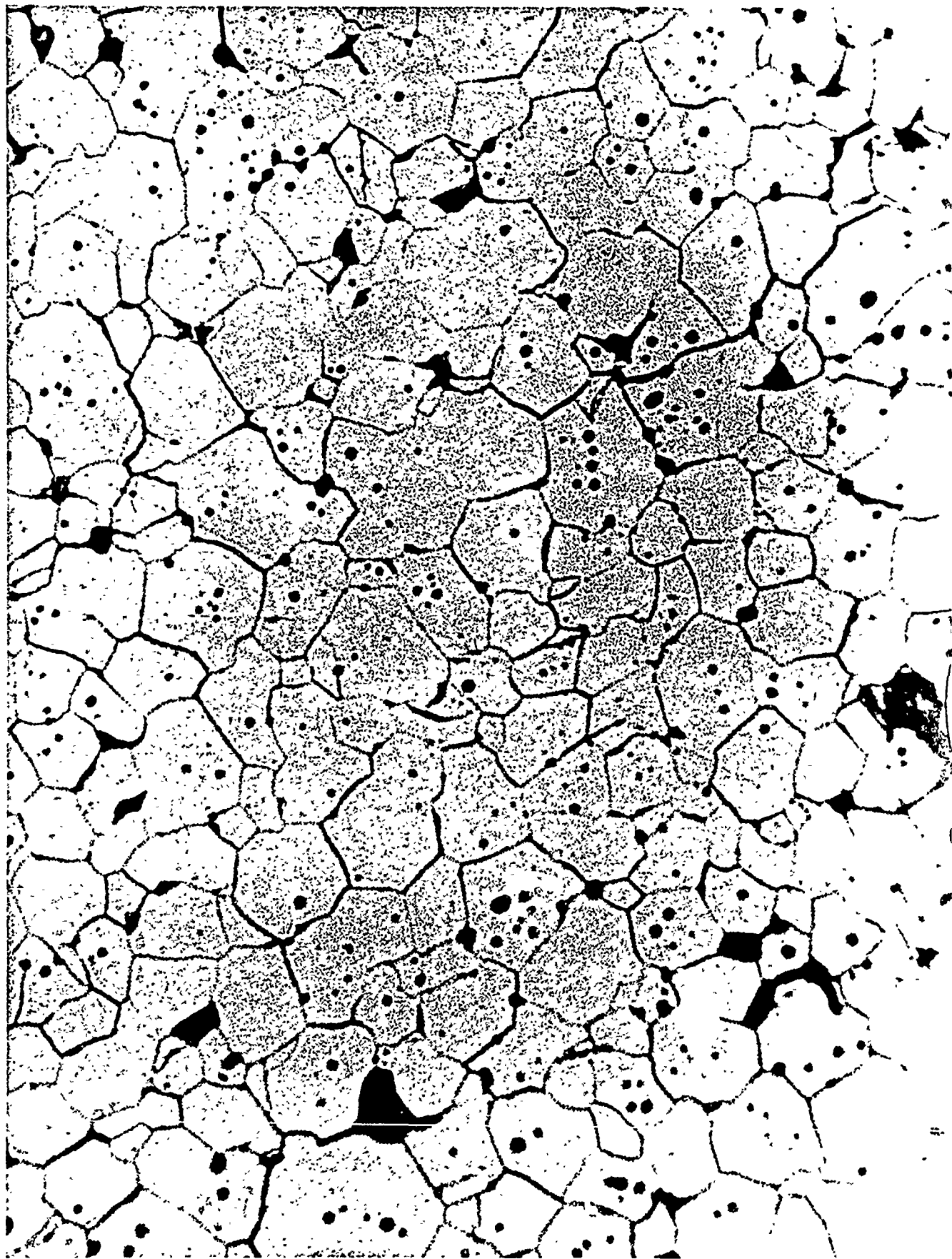


FIGURE 7

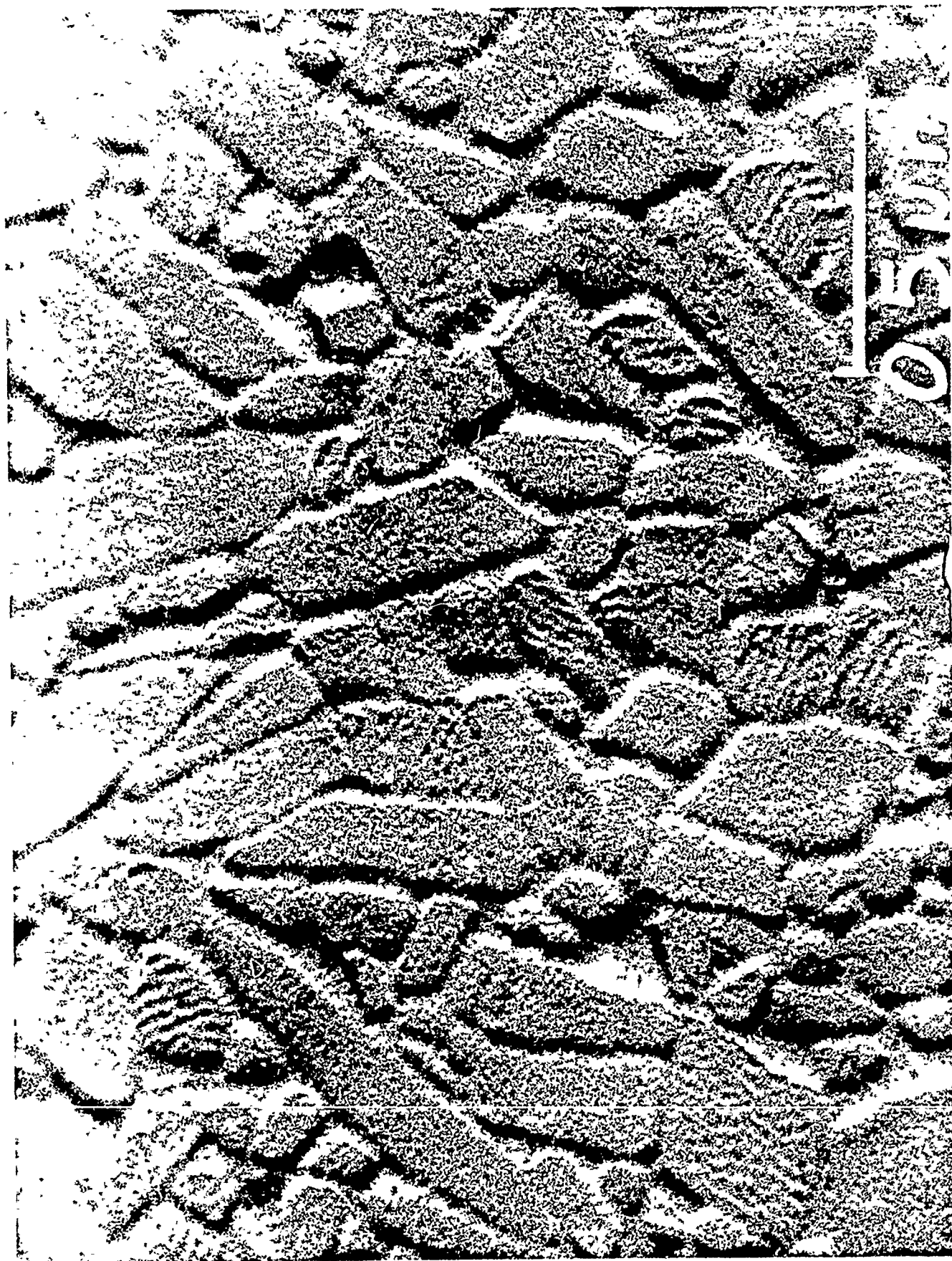


FIGURE 8



FIGURE 9

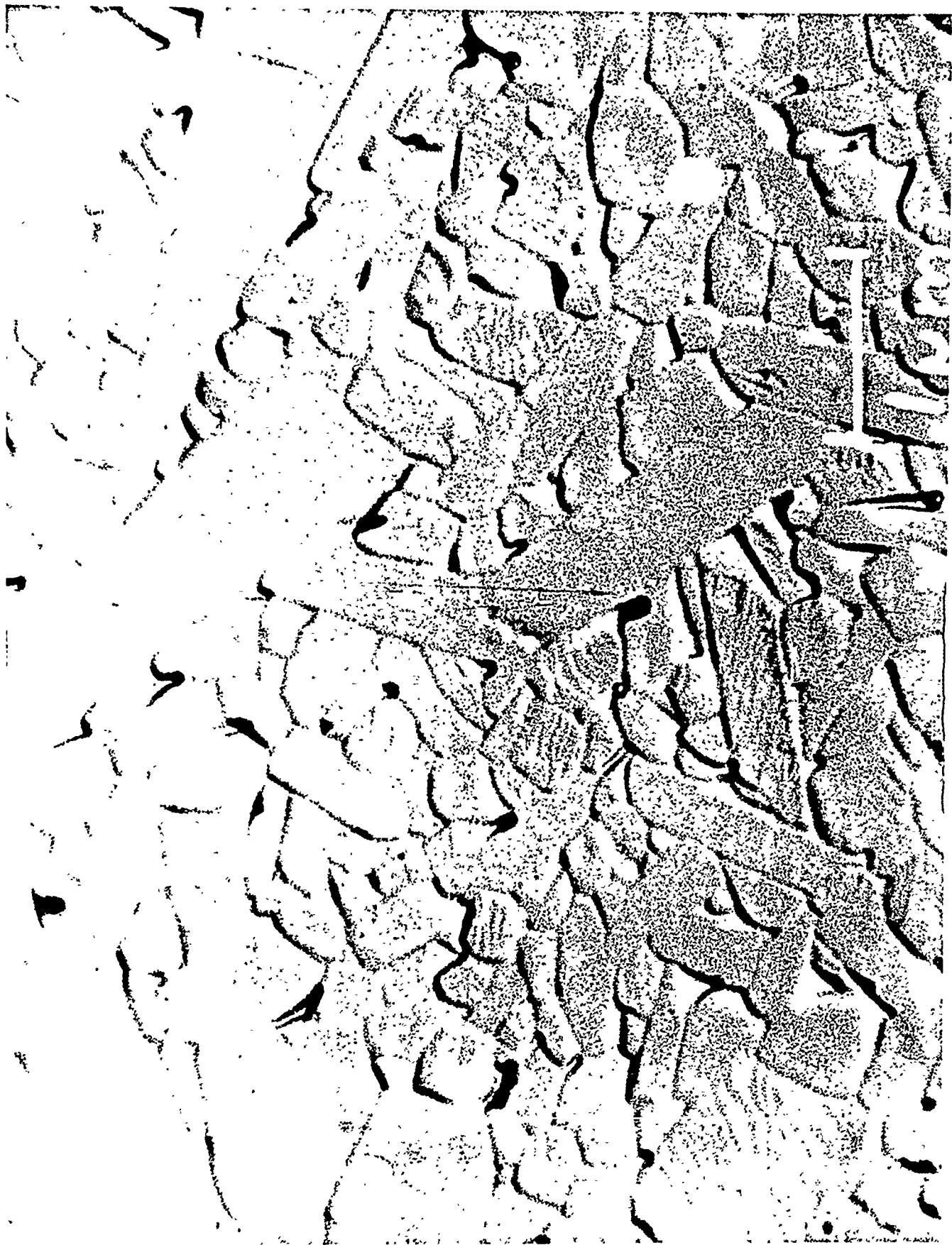


FIGURE 10



FIGURE 11

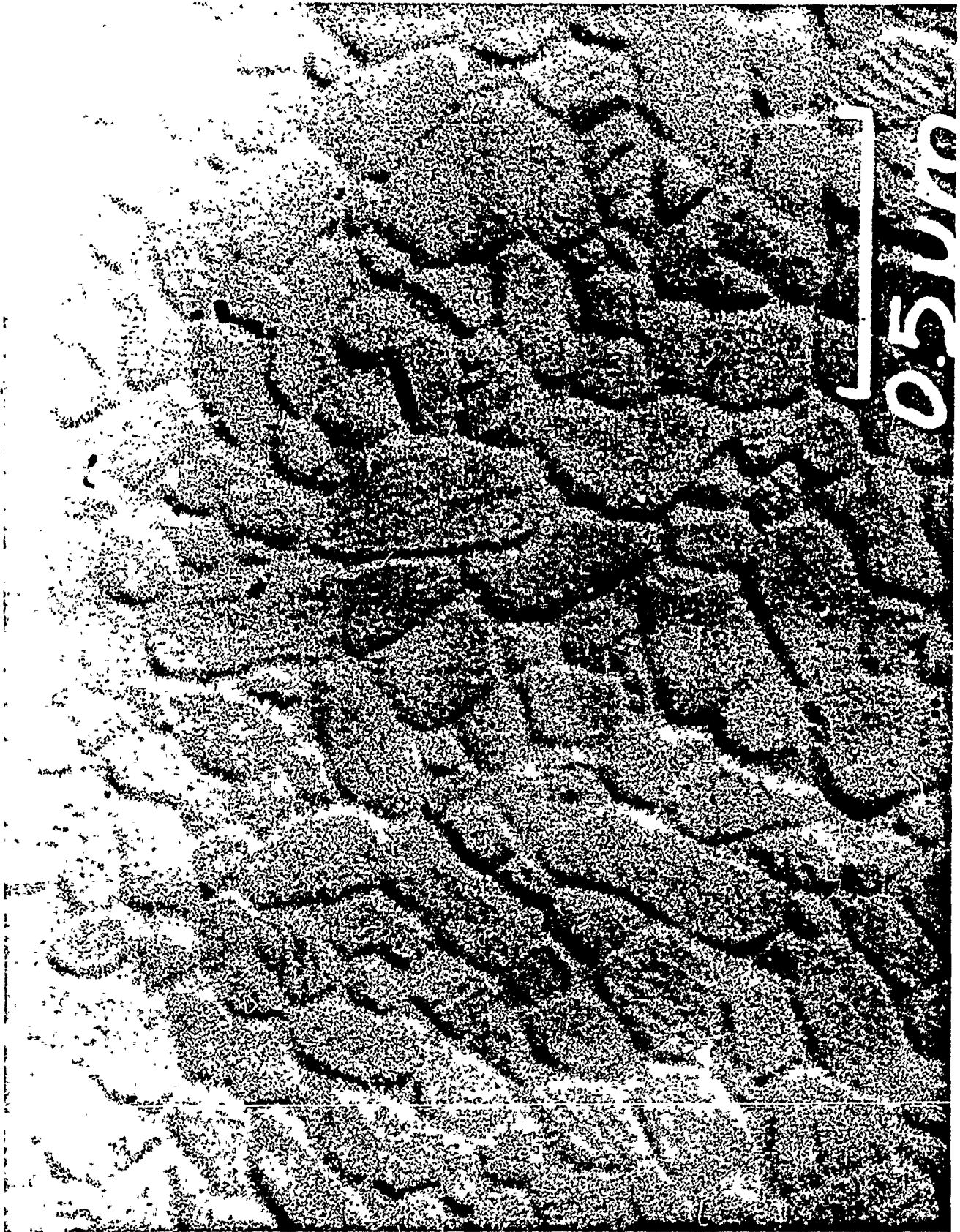


FIGURE 12

TABLE 1

POLYCRYSTALLINE BULK CERAMIC POWDERS REQUIREMENTS

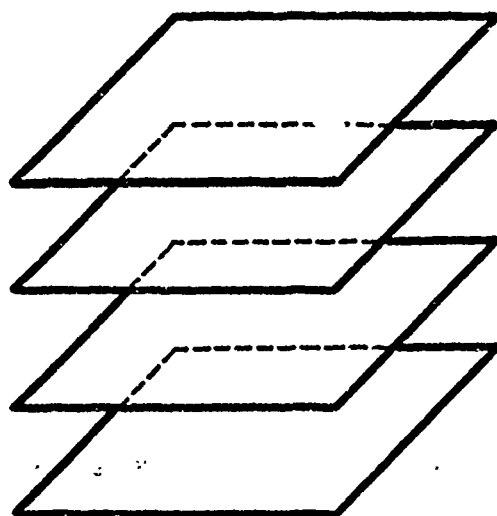
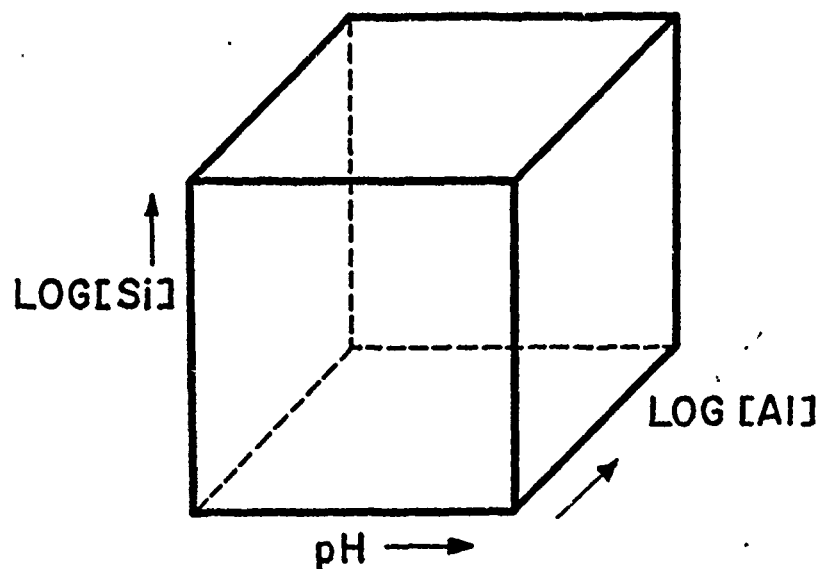
- HIGH PURITY / KNOWN IMPURITIES
- HIGH SURFACE AREA (REACTIVE POWDER)
- SMALL PARTICLE SIZE, $< 500 \text{ \AA}$
- UNIFORM PARTICLE SIZE DISTRIBUTION (LOG NORMAL)
- READILY AVAILABLE
- WITH
- NO BATCH TO BATCH VARIATIONS
- LOW COST (END ITEM PRODUCTS)
- REPRODUCEABLE AND RELIABLE PRODUCTS

He stressed the importance of being able to design a specific microstructure using organo-metallic processes and the ability to vary the process slightly in order to tailor the final product. He showed several microstructures of aluminum silicate (Figures 7-12) to illustrate his point. His criteria for bulk ceramic powders are summarized in Table 1.

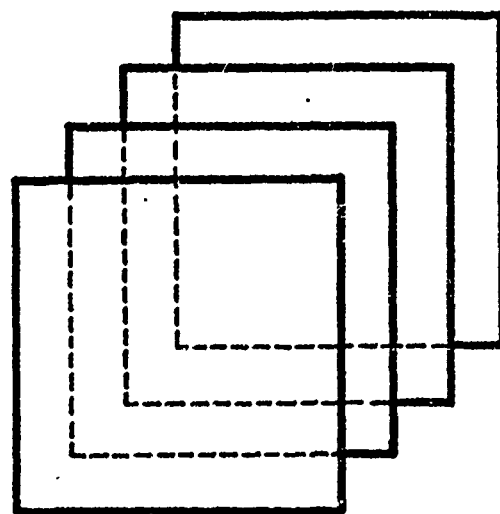
In conclusion, Mr. Mazdiyasni expressed his desire that organic chemist, ceramist, and materials users work together in the future to develop new techniques for preparing useful high temperature structural ceramics and coatings.

COLLOID CHEMISTRY
E. Matijevic
Clarkson College

Dr. Matijevic began by stating that colloid science is more than just making particles. Now that it has advanced beyond studying ideal single systems, using uniformly charged perfect spheres in KCl solutions, he believes we can begin to understand useful multiple systems. Due to advances in instrumentation we have developed advanced theories on multiple colloid systems of practical ceramic mixed dispersions. He presented a series of figures (Figures 1-6) on two component systems versus pH to illustrate the systematic approach one must use to investigate the effect of altering parameters: in this case the concentration of two components, and the pH of the solution. He stressed the point that no theories are adequate to predict the outcome because it is all "pure chemistry"; so you must carefully perform the experiments by partitioning a three-dimensional domain into two-dimensional domains (Figure 1) and methodically obtain data (Figures 2-6). He also mentioned the importance of the charge on a particle and that predicting the effect on a particle's behavior is virtually impossible due to the lack of sufficient thermodynamic data. Dr. Matijevic also discussed the importance of particle size and particle size distribution in altering the behavior of colloidal systems. He then showed another series of figures (Figures 7-14) to illustrate the



DOMAINS: ALUMINUM CONC.
VERSUS pH (SEE FIG. 5)



DOMAINS: SILICATE CONC.
VERSUS pH (SEE FIG. 3)

Figure 1

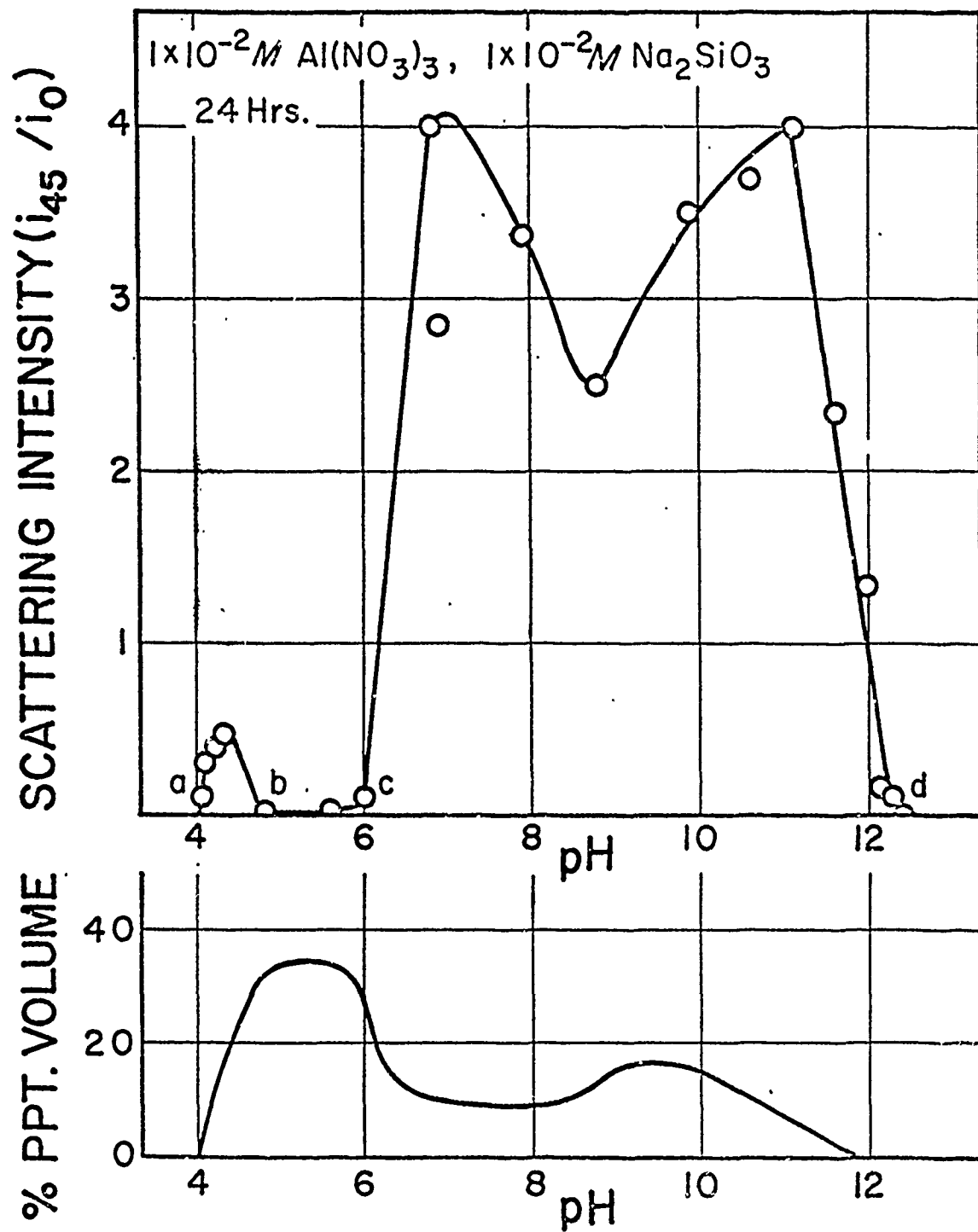


Figure 2

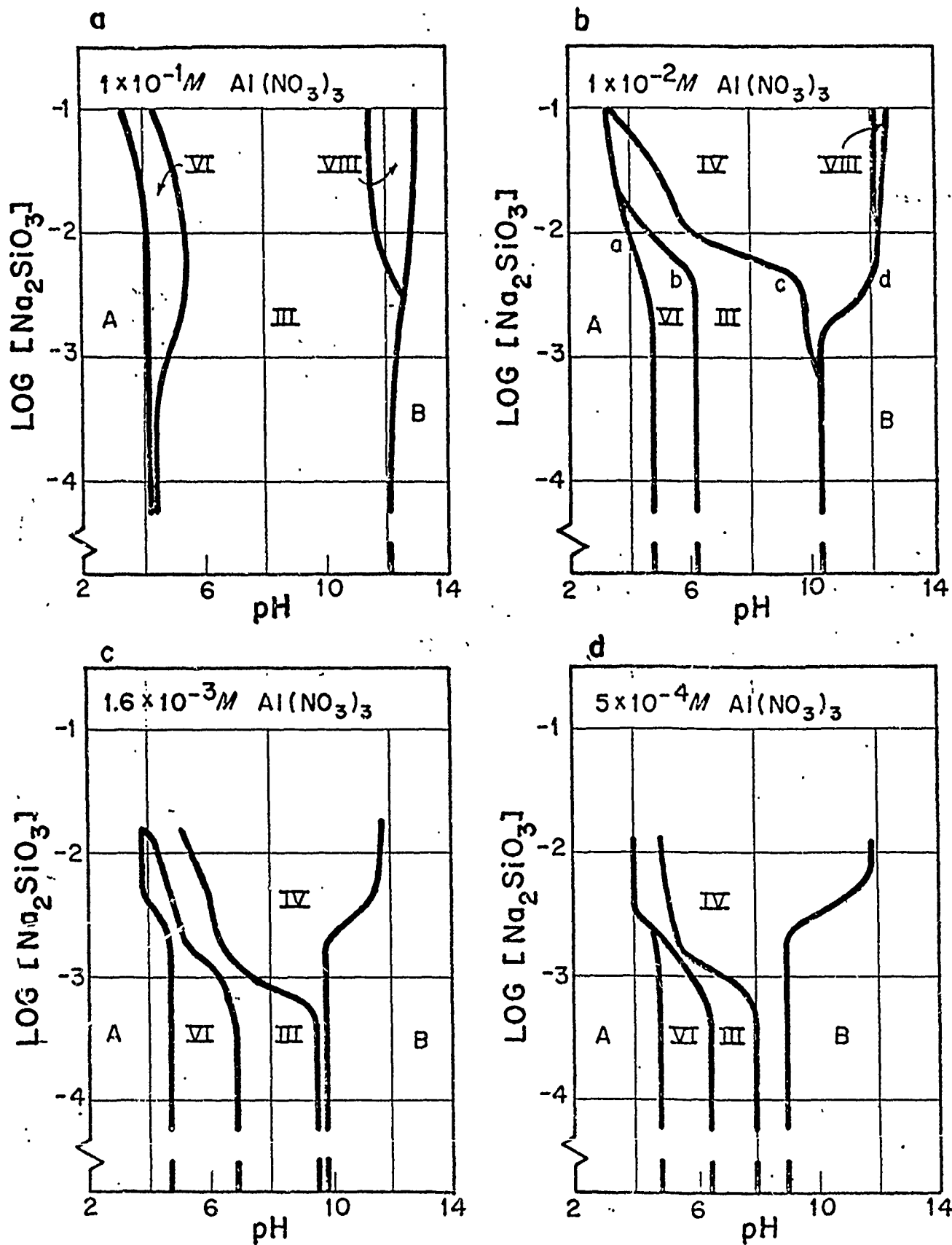


Figure 3

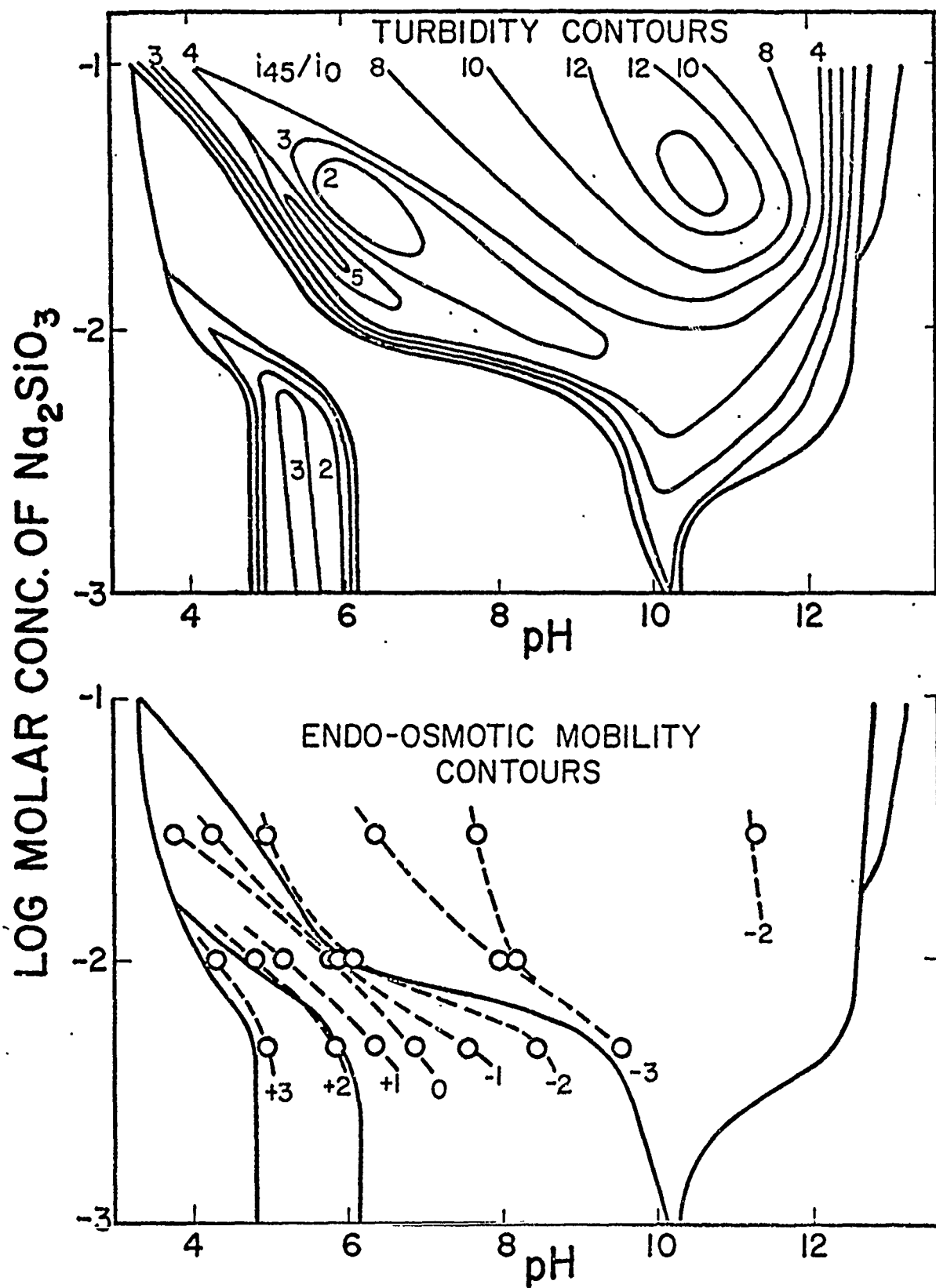


Figure 4

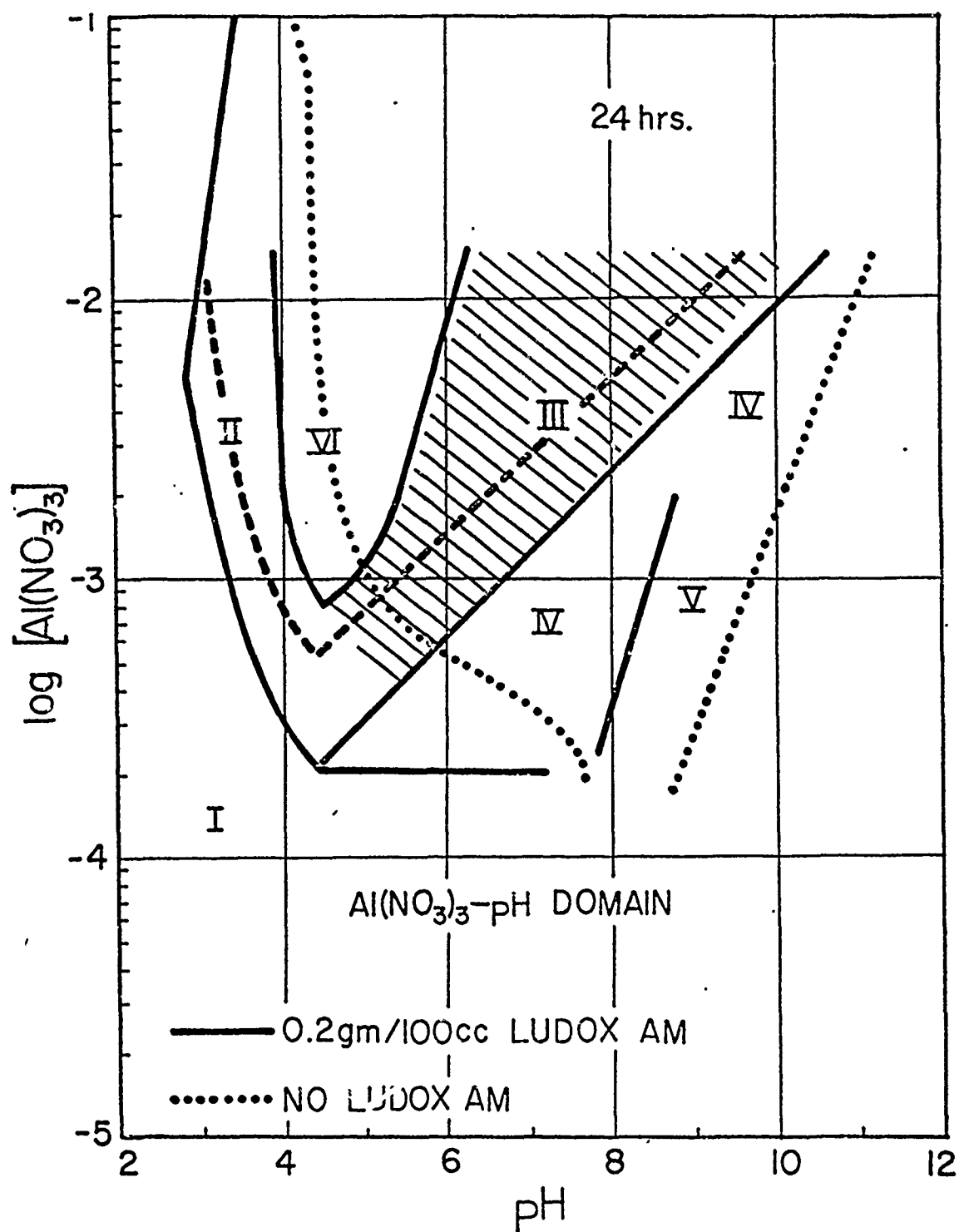
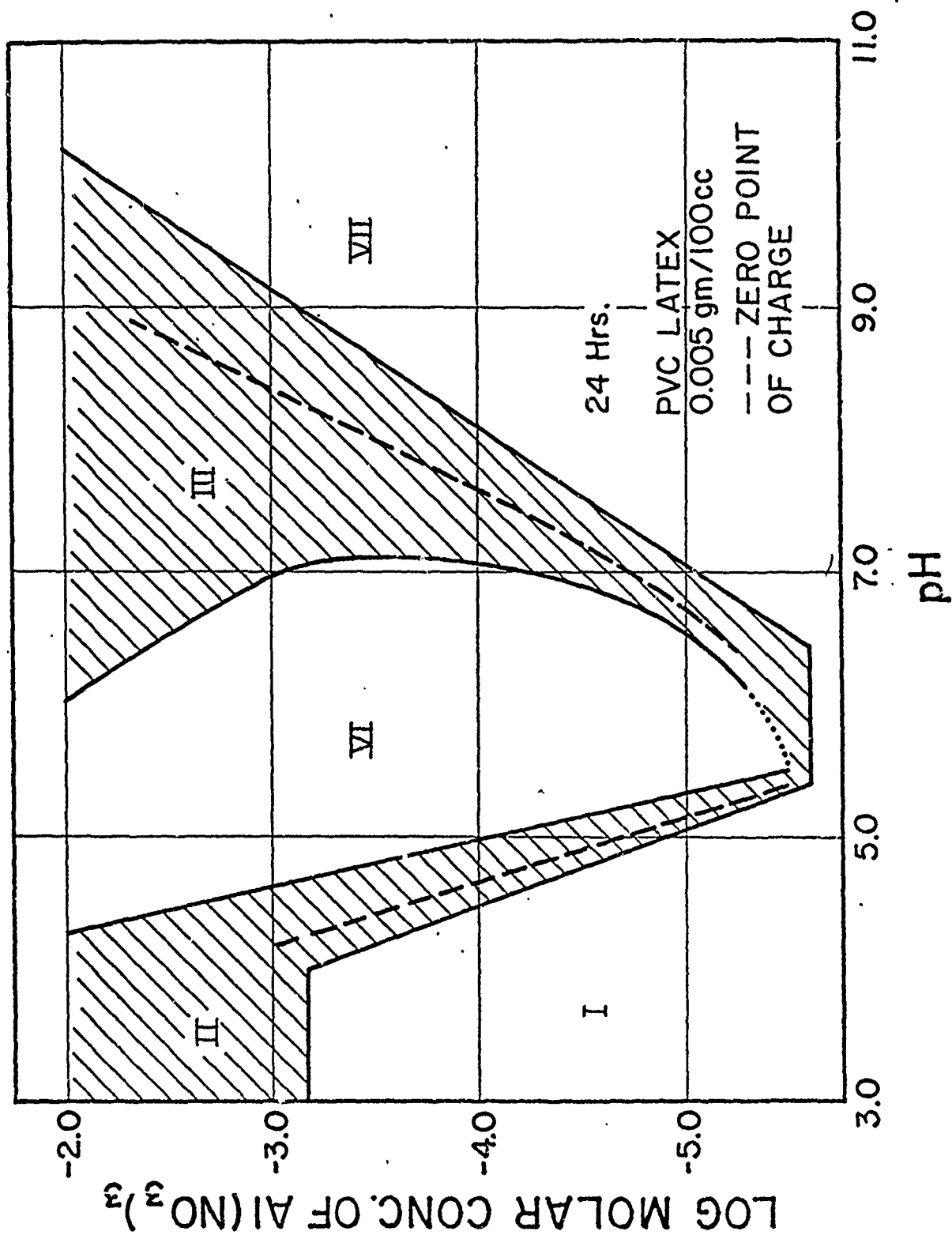


Figure 5



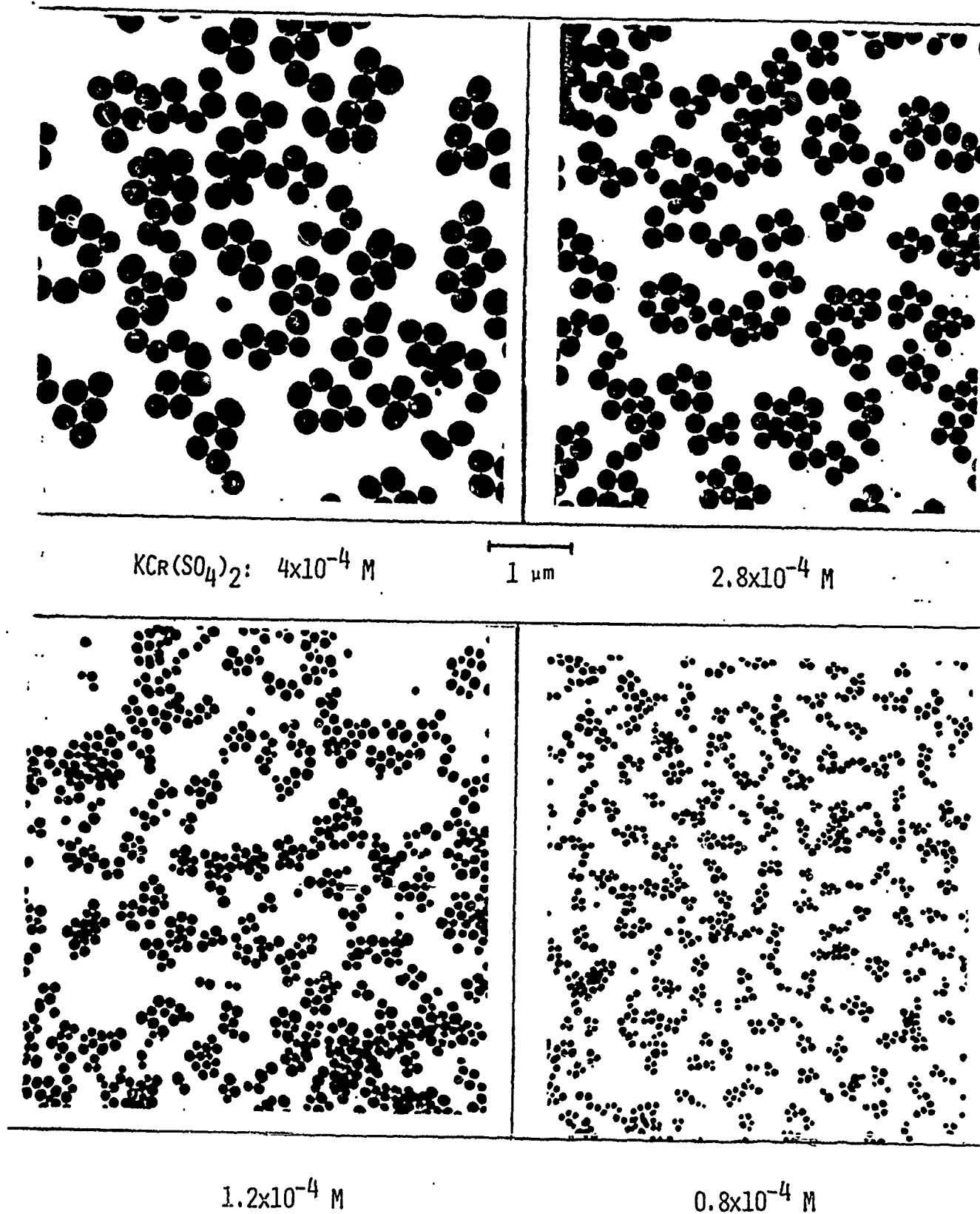
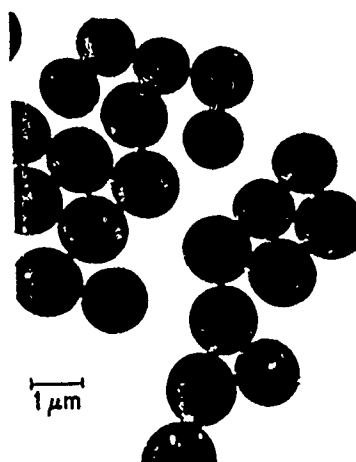
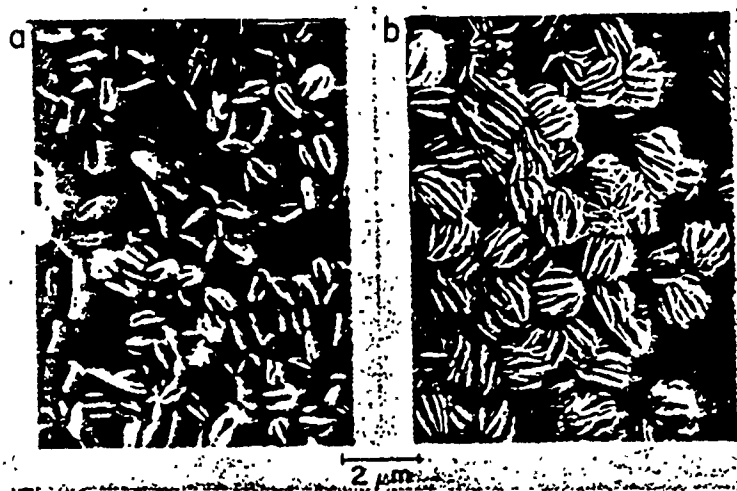


Figure 7

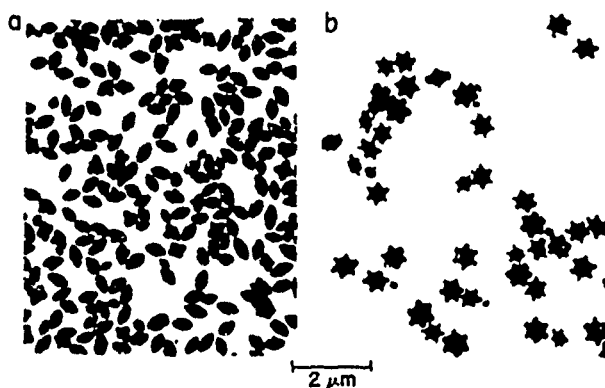


Electron micrograph of aluminum hydrous oxide particles obtained by aging for 48 hr at 97°C a 2×10^{-3} M solution of $\text{Al}_2(\text{SO}_4)_3$. Initial pH, 4.0; final pH, 2.5.

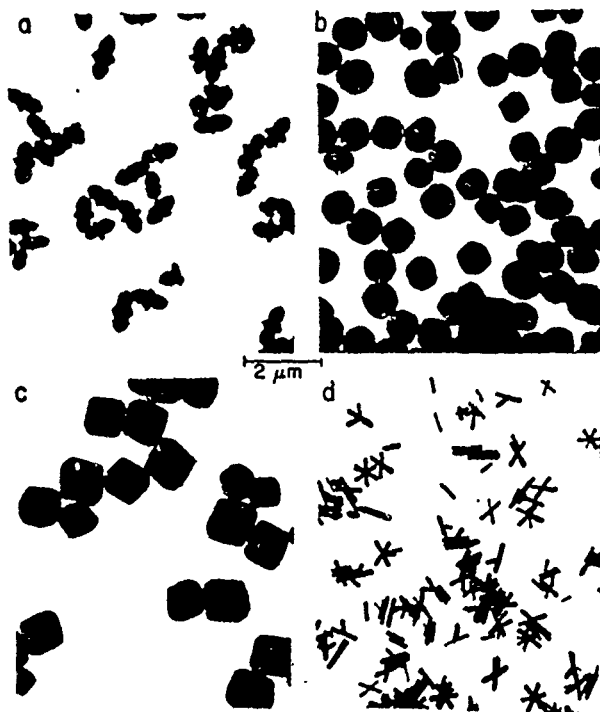


Scanning electron micrographs of aluminum hydrous oxide particles obtained by aging (a) for 24 hr at 150°C a 5×10^{-3} M solution of AlCl_3 (initial pH 3.7, final pH 2.1); (b) for 25 hr at 125°C a 5×10^{-3} M solution of $\text{Al}(\text{ClO}_4)_3$ (initial pH 3.8, final pH 2.1).

Figure 8



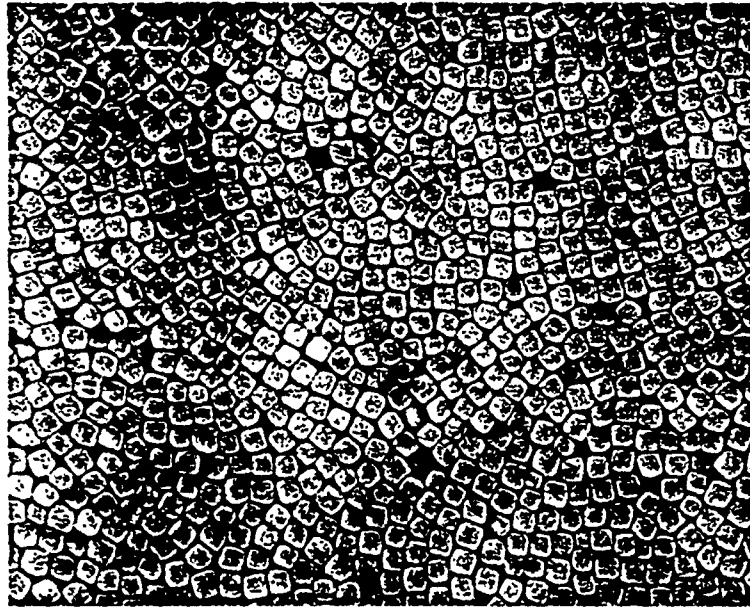
Electron micrographs of particles obtained by aging two different solutions of ferric salts at 100°C for 24 hr; in both cases the original pH was 1.3-1.4 and the final pH was 1.1-1.2. Concentrations: (a) System $\text{Fe}(\text{NO}_3)_3 + \text{HNO}_3$; $[\text{Fe}^{3+}]$, 0.018 M; $[\text{NO}_3^-]$, 0.104 M. (b) System $\text{Fe}(\text{ClO}_4)_3 + \text{HClO}_4$; $[\text{Fe}^{3+}]$, 0.018 M; $[\text{ClO}_4^-]$, 0.104 M.



Electron micrographs of particles obtained in solutions of $\text{FeCl}_3 + \text{HCl}$ under the following conditions:

$[\text{Fe}^{3+}]$ (M)	$[\text{Cl}^-]$ (M)	pH (initial)	pH (final)	Temp. of aging (°C)	Time of aging
(a) 0.013	0.104	1.3	1.1	100	24 hr
(b) 0.315	0.005	2.0	1.0	100	9 days
(c) 0.09	0.28	1.65	0.88	100	24 hr
(d) 0.09	0.28	1.65	0.70	150	6 hr

Figure 9



HEMATITE (α -Fe₂O₃)

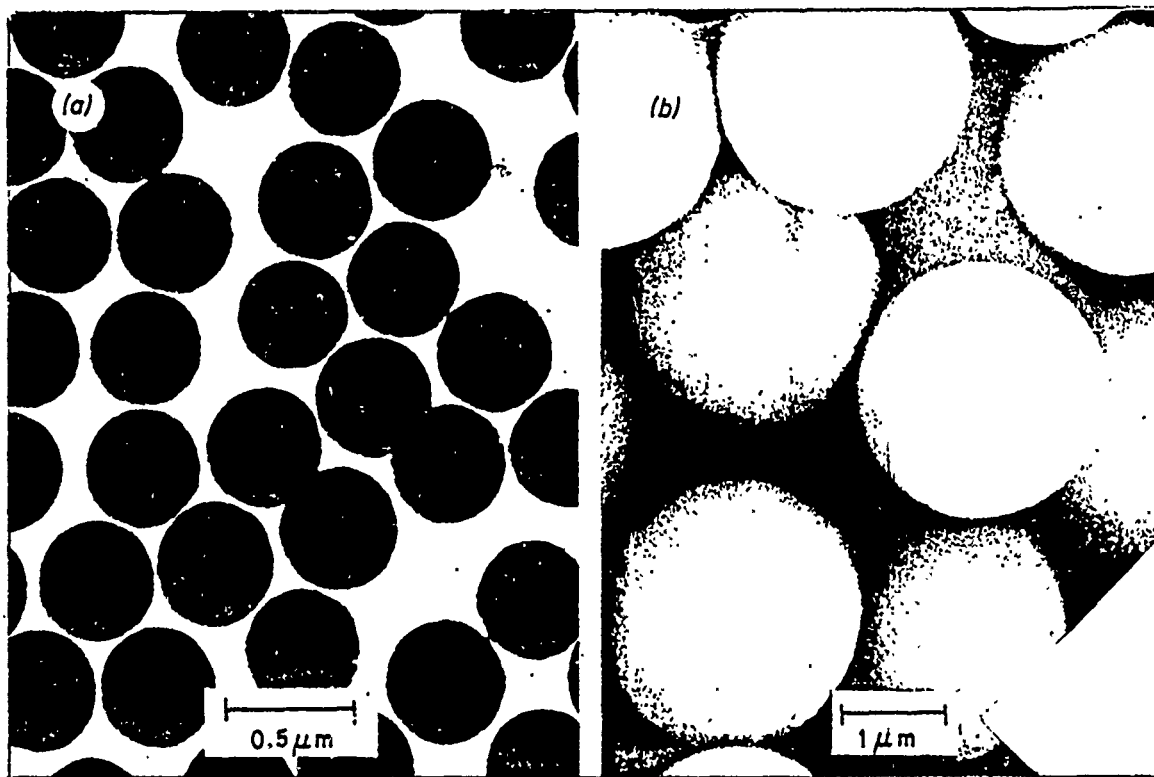
1 μ m

Figure 10



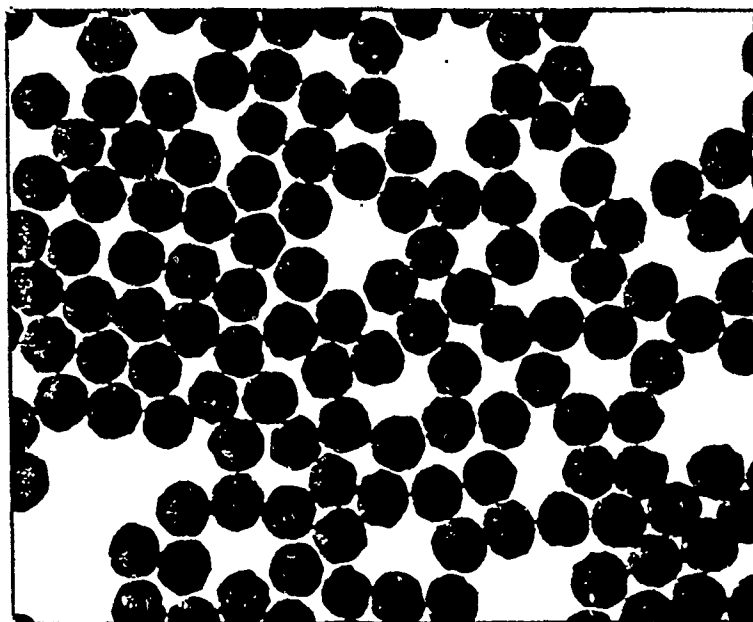
HEMATITE

Figure 11

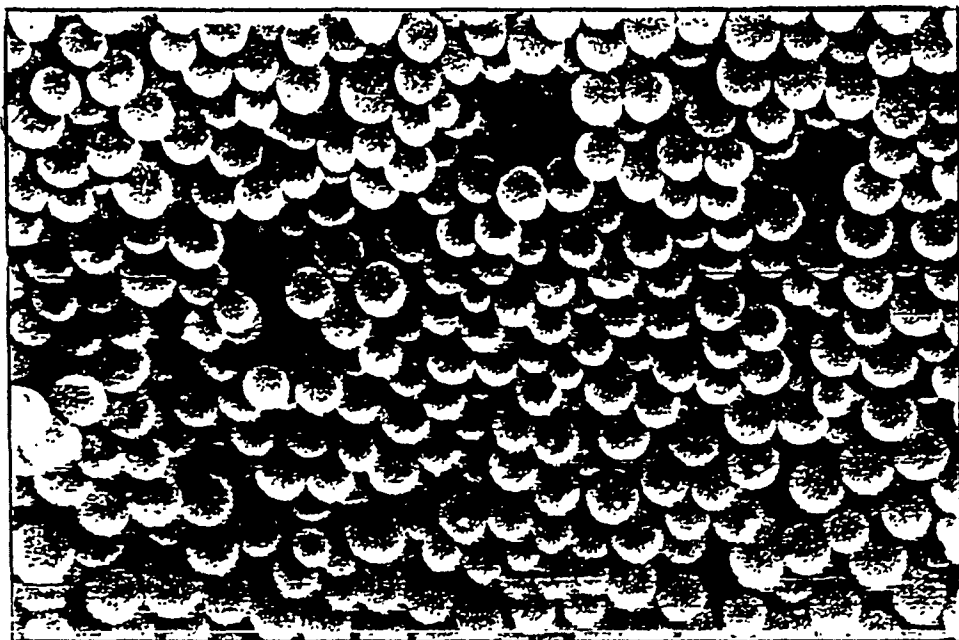


ZnS (Sphalerite)

Figure 12



Cd-Selenide



FePO₄

Figure 13



CaCO_3

Figure 14

variety of particle shapes it is possible to achieve by carefully controlling the chemistry. The importance of interfacial phenomena was also stressed as well as how the position of a molecule on a surface, and the number of bonds it forms, can influence properties. He placed emphasis on the importance of anions, even when they do not show up in the final product, because they can influence the final concentration and morphology.

Dr. Matijevic then mentioned the homogeneous precipitation of uniform metal oxides, especially iron oxides, to illustrate what can be done to obtain various particle sizes and shapes through careful control of the parameters.

Dr. Matijevic then described a method for obtaining the kinetics of various reactions using the light scattering apparatus shown in Figure 15. He also discussed the influence of particle shape and refractive index on the color of a material. Magnetic properties versus particle size was also briefly discussed (Figure 16).

Emphasis was then placed on interfacial chemistry and electrokinetics, especially the effect of organic-inorganic mixtures like EDTA and hematite (Figures 17-27) to alter surface charges. The importance of where molecules sit on a surface versus its ability to act as a dissolution agent was pointed out in Figures 22-27. Particle to particle interactions were then discussed using the silica-latex and FeOOH-latex systems as examples (Figures 28-32). Dr. Matijevic then explained the changes that occur in unlike particle potential profiles due to particle separation, particle size, and potentials (Figures 33-36).

Dr. Matijevic then switched his attention to adhesion phenomena (Figures 36-46) and the importance of understanding the basic phenomena which allows you to modify the system to achieve maximum adherence.

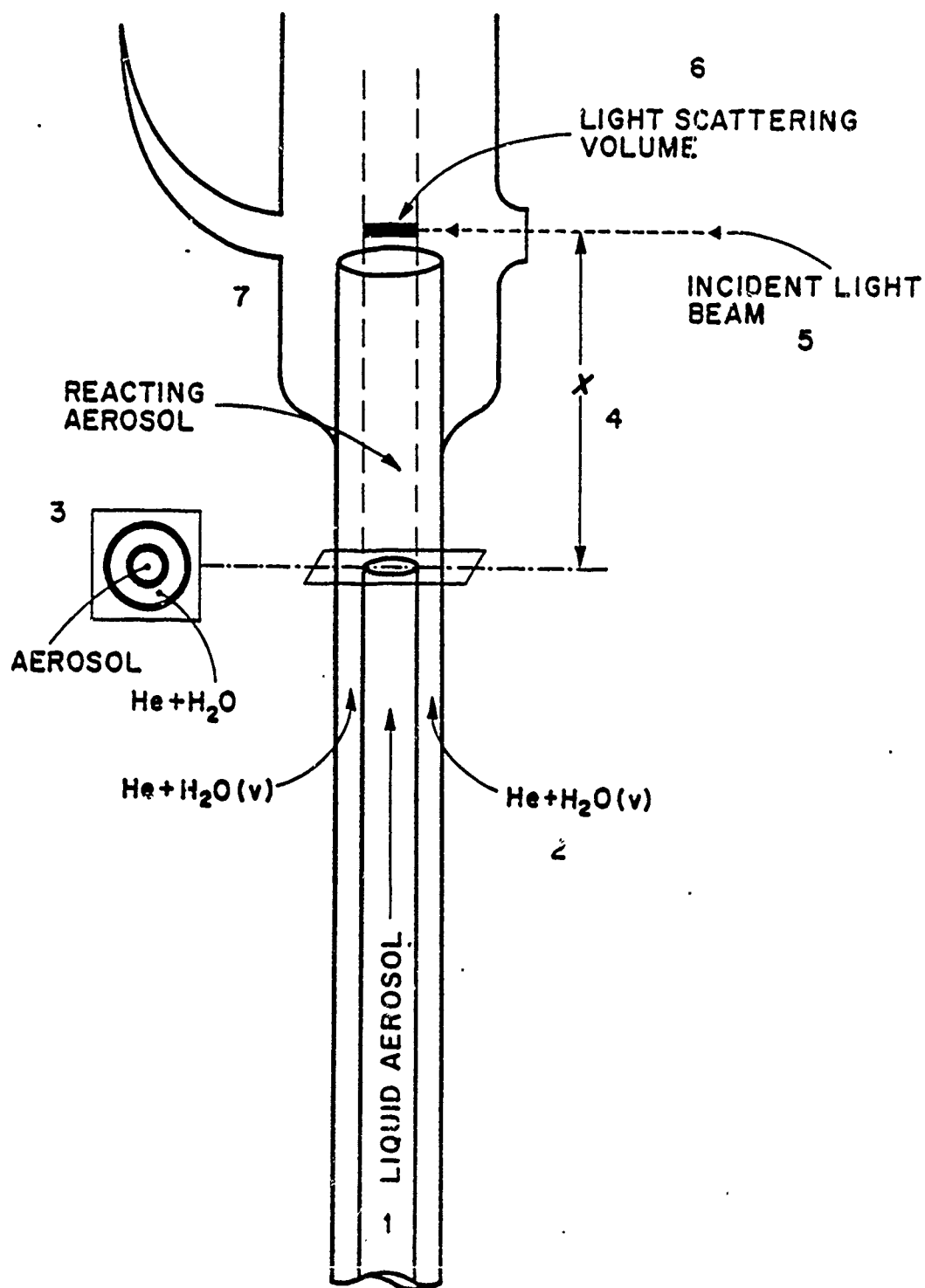
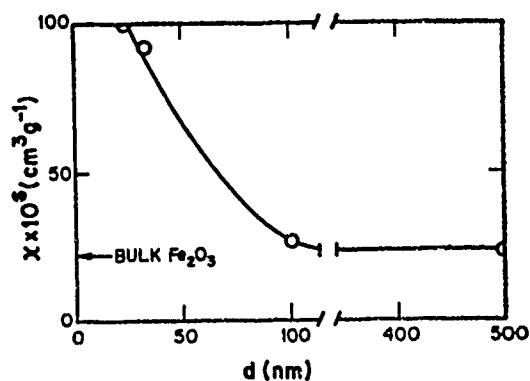
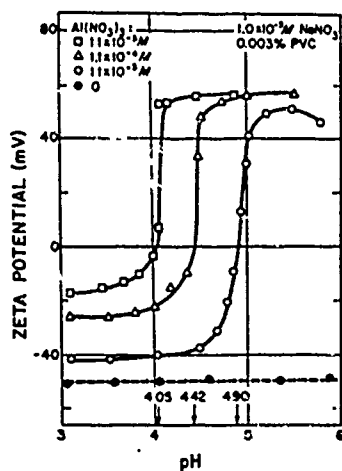


Figure 15



Magnetic susceptibility of spherical α - Fe_2O_3 particles as a function of their diameter.



Zeta-potential of a polyvinylchloride (PVC) latex (0.003% by weight) as a function of pH in the absence ($\bullet$), and in the presence of $\text{Al}(\text{NO}_3)_3$: $1.1 \times 10^{-5} \text{ M}$ ($\square$), $1.1 \times 10^{-4} \text{ M}$ ($\triangle$), and $1.1 \times 10^{-3} \text{ M}$ ($\circ$). Arrows indicate the isoelectric points. All systems contained $1.0 \times 10^{-3} \text{ M NaNO}_3$.

Figure 16

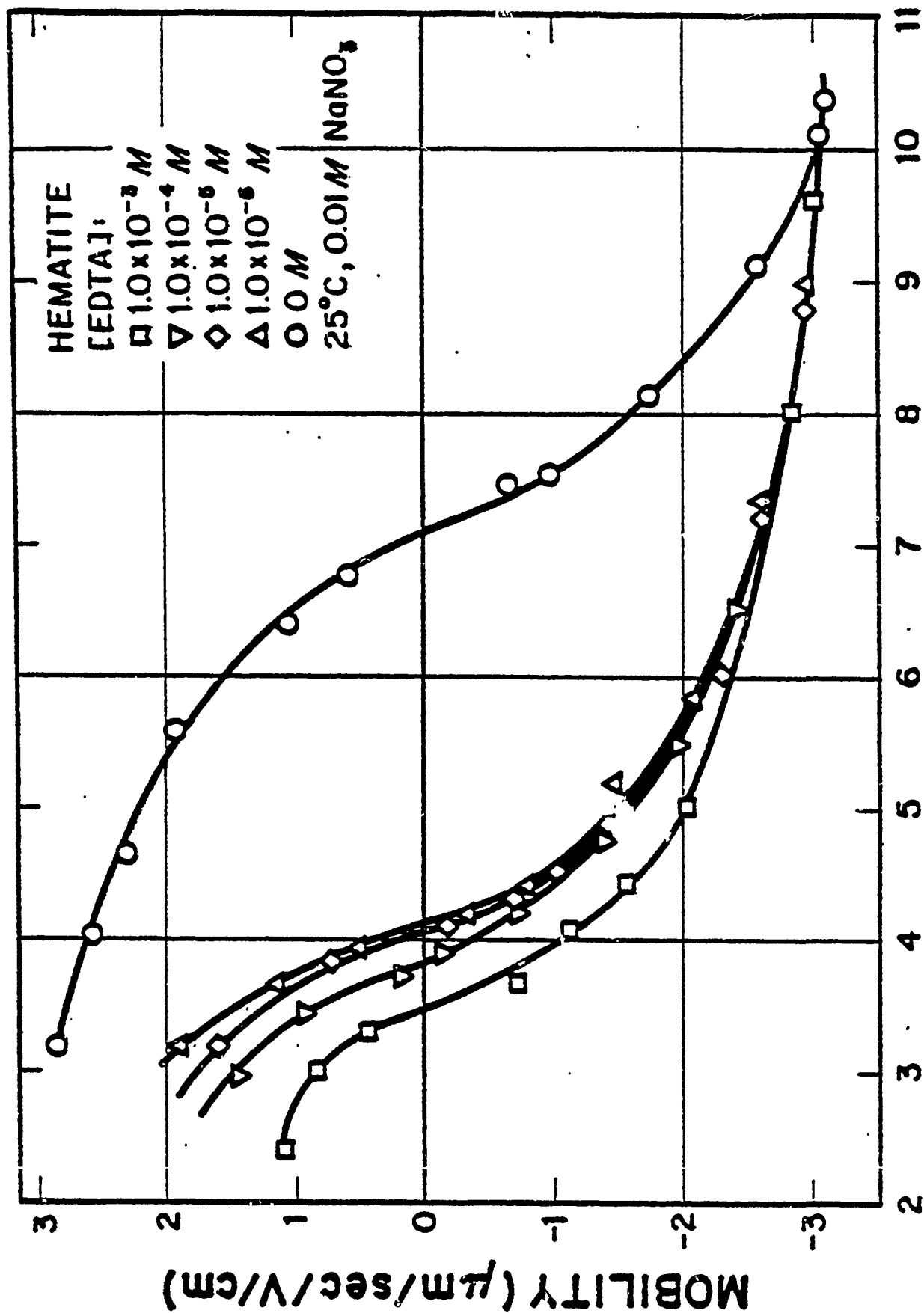


Figure 17

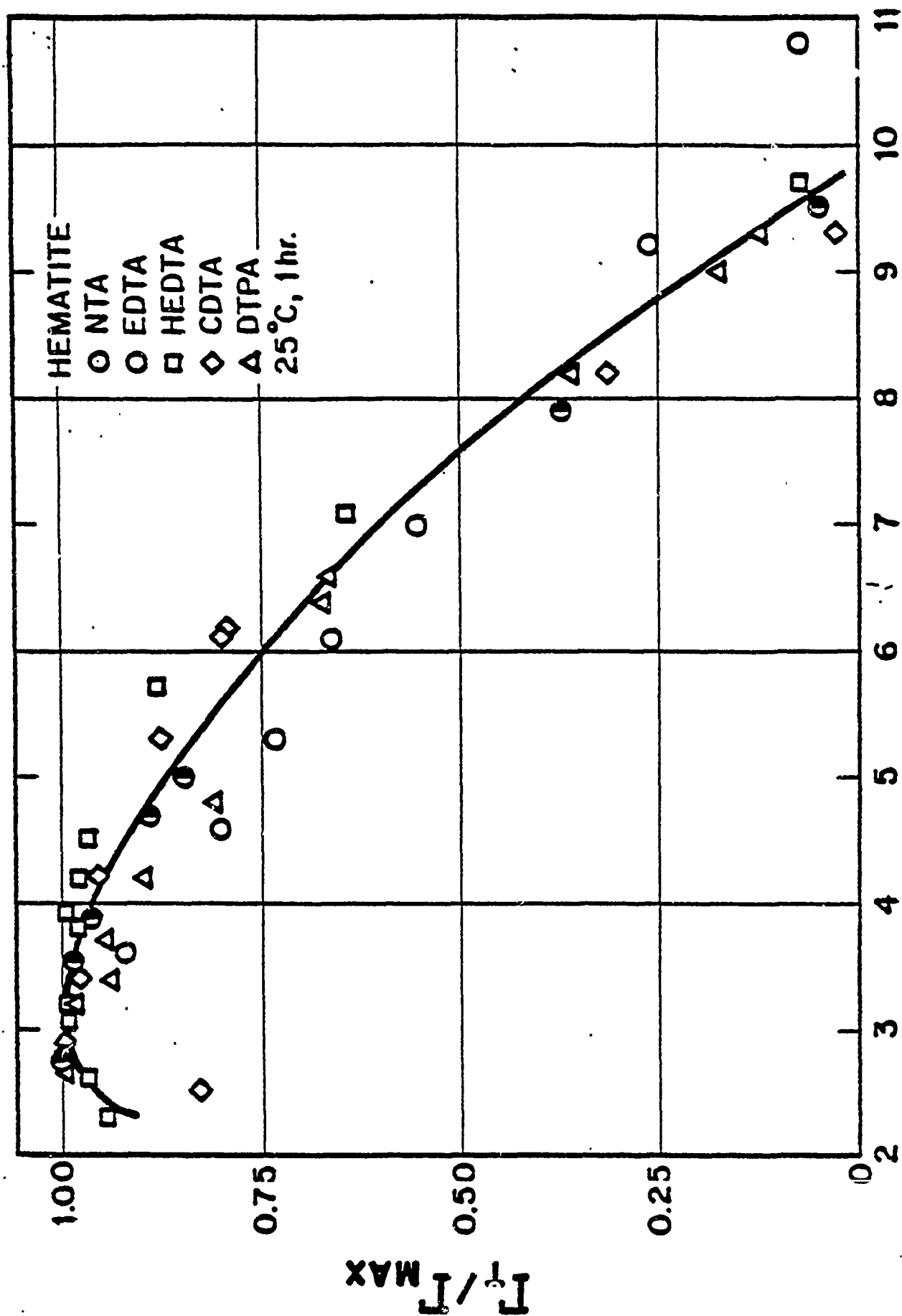


Figure 18

pH

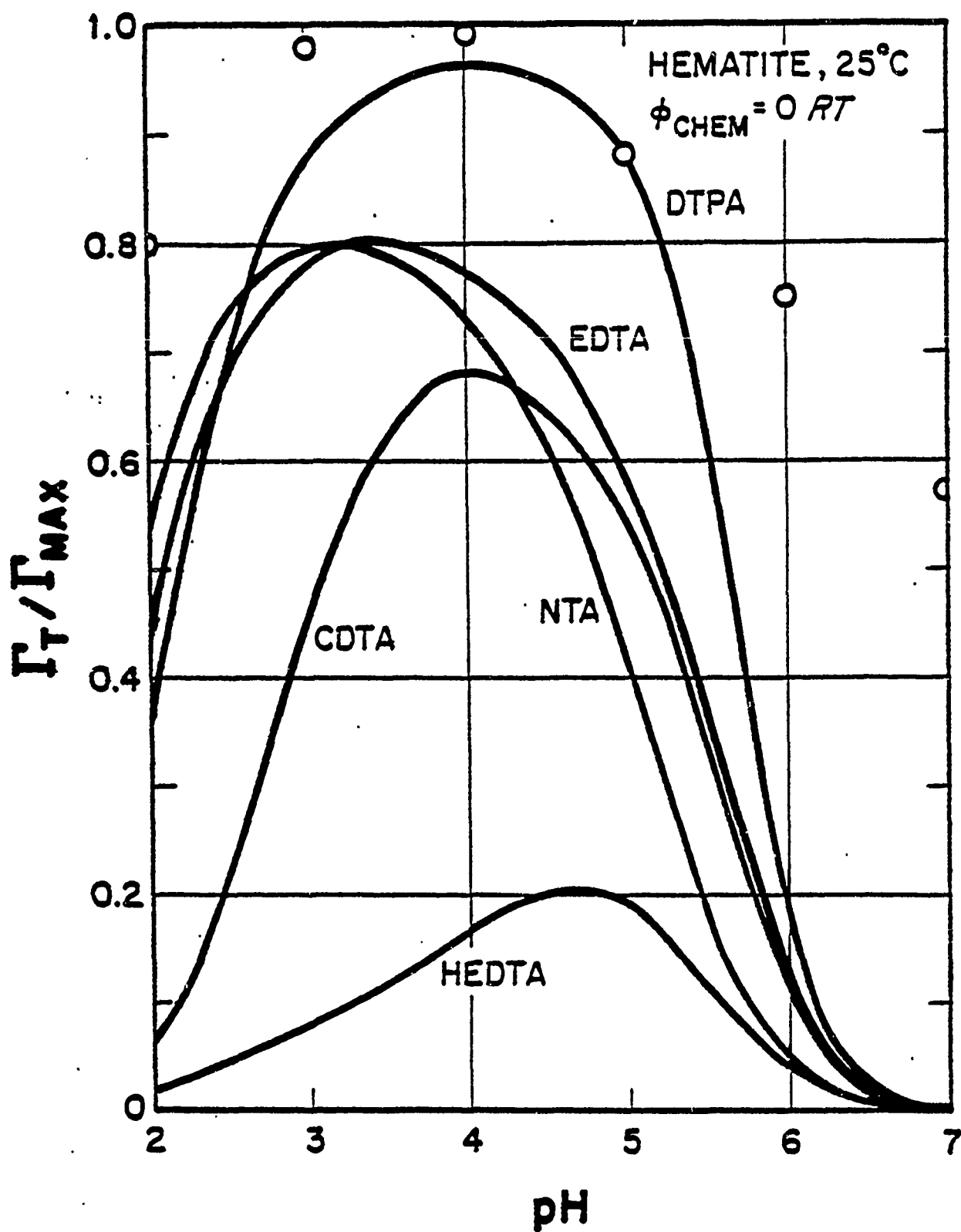


Figure 19

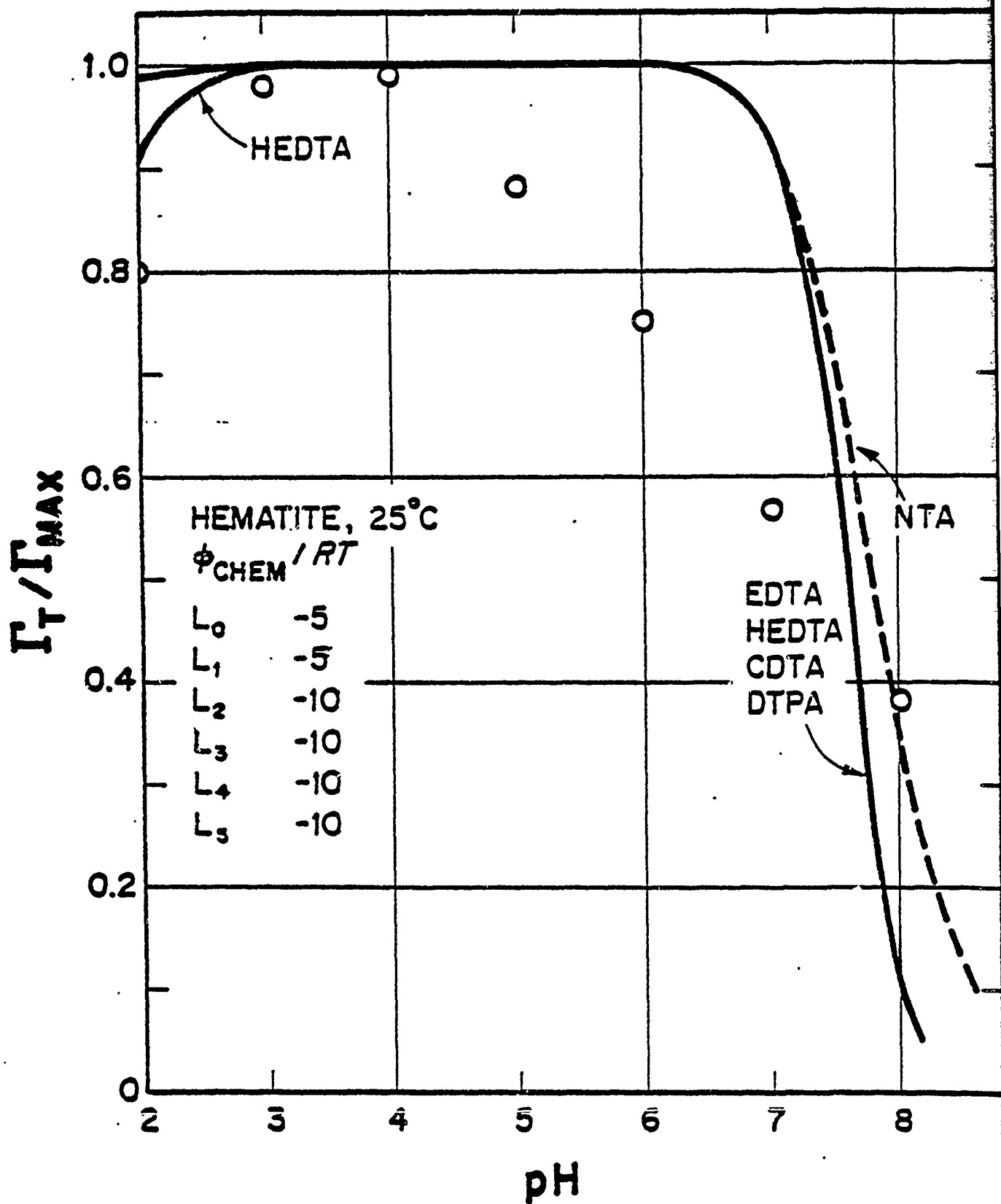


Figure 20

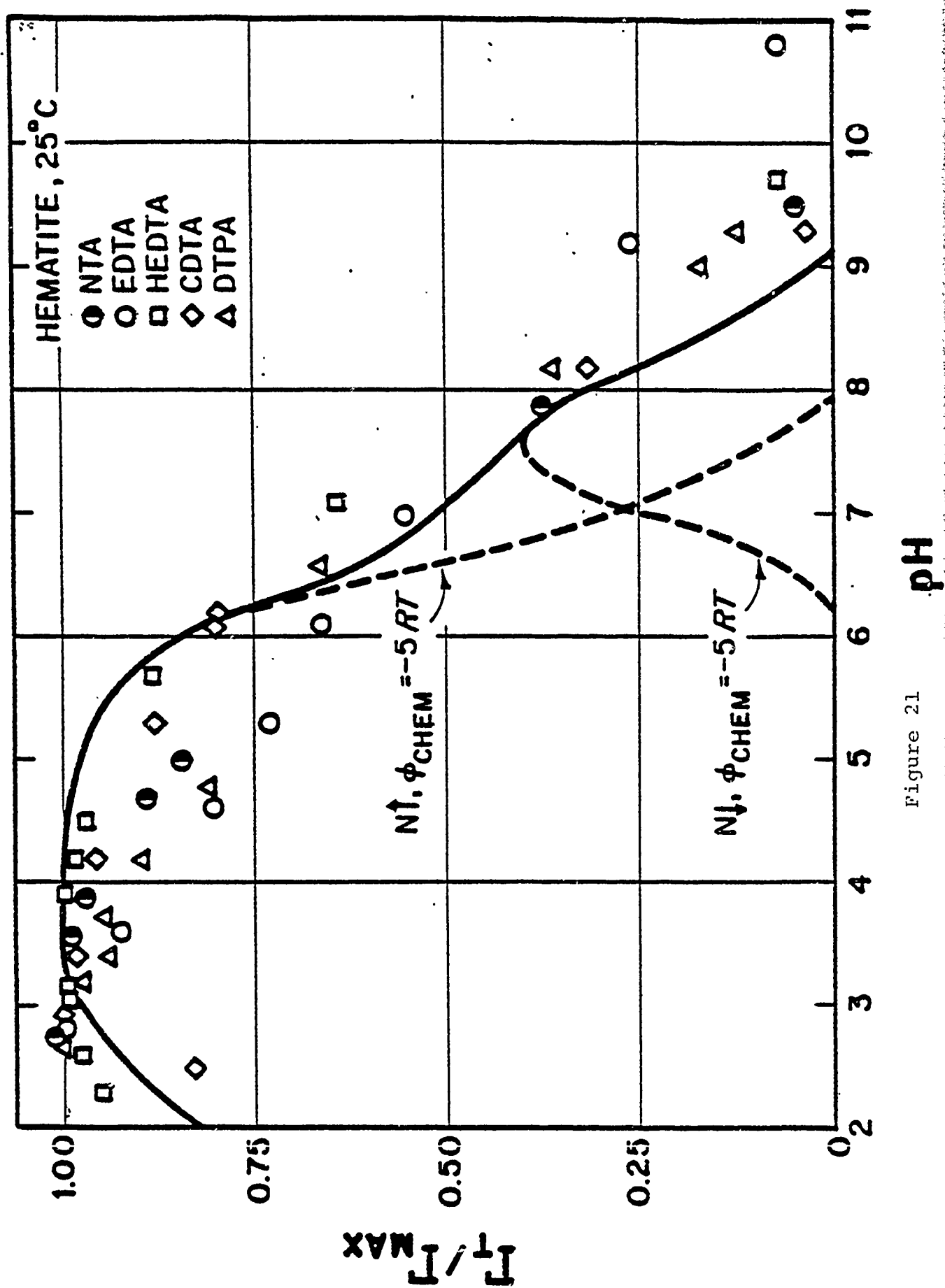


Figure 21

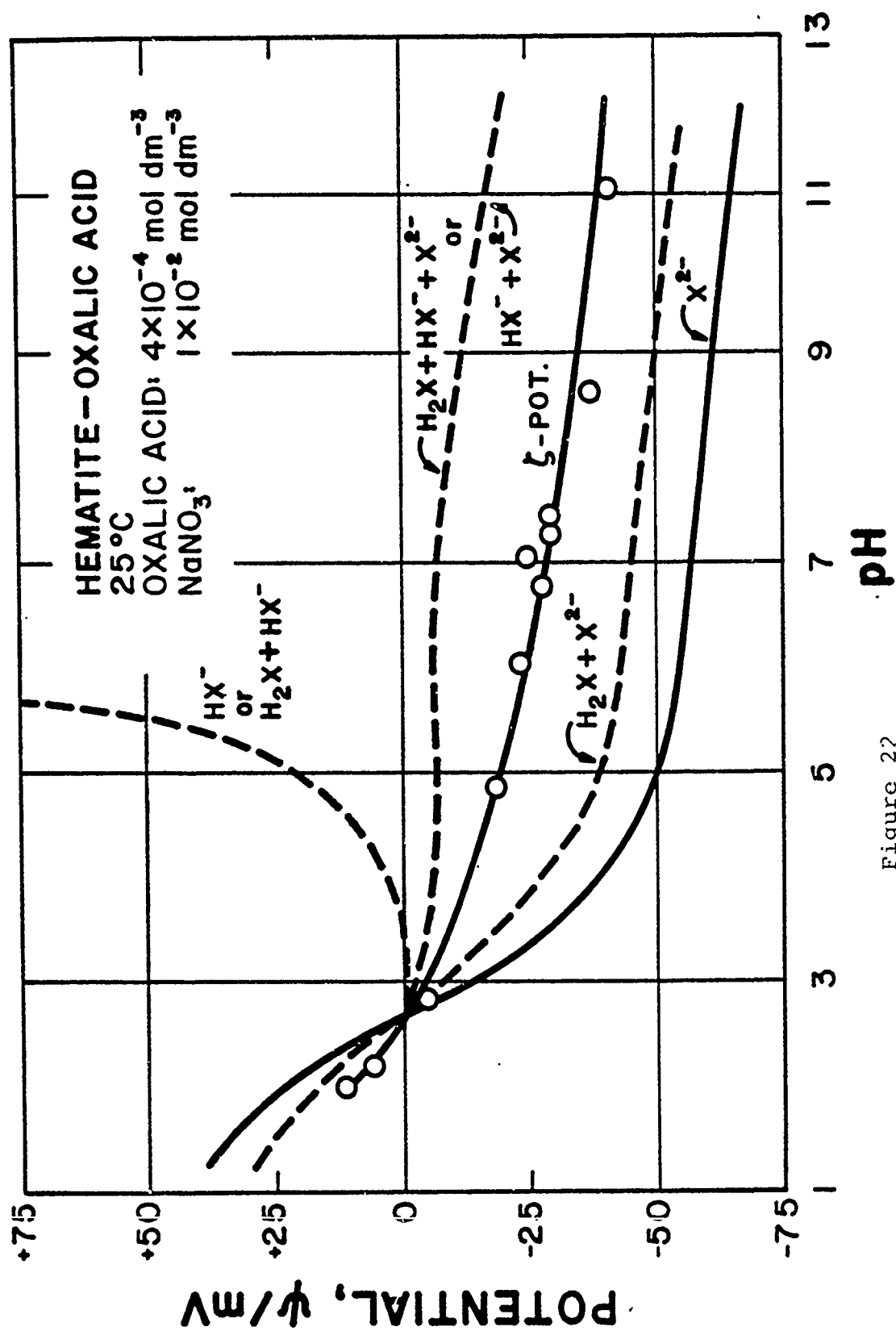


Figure 22

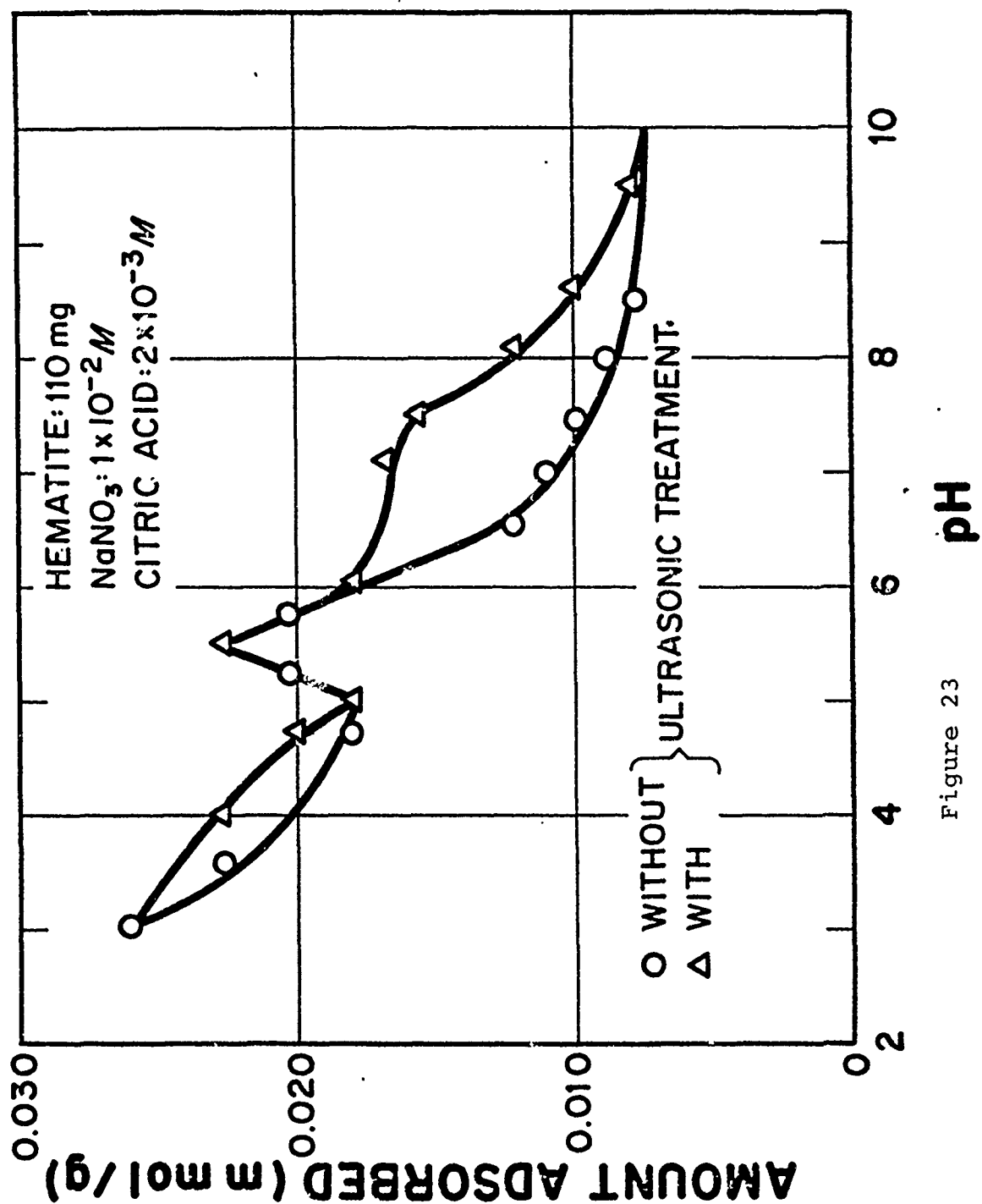


Figure 23

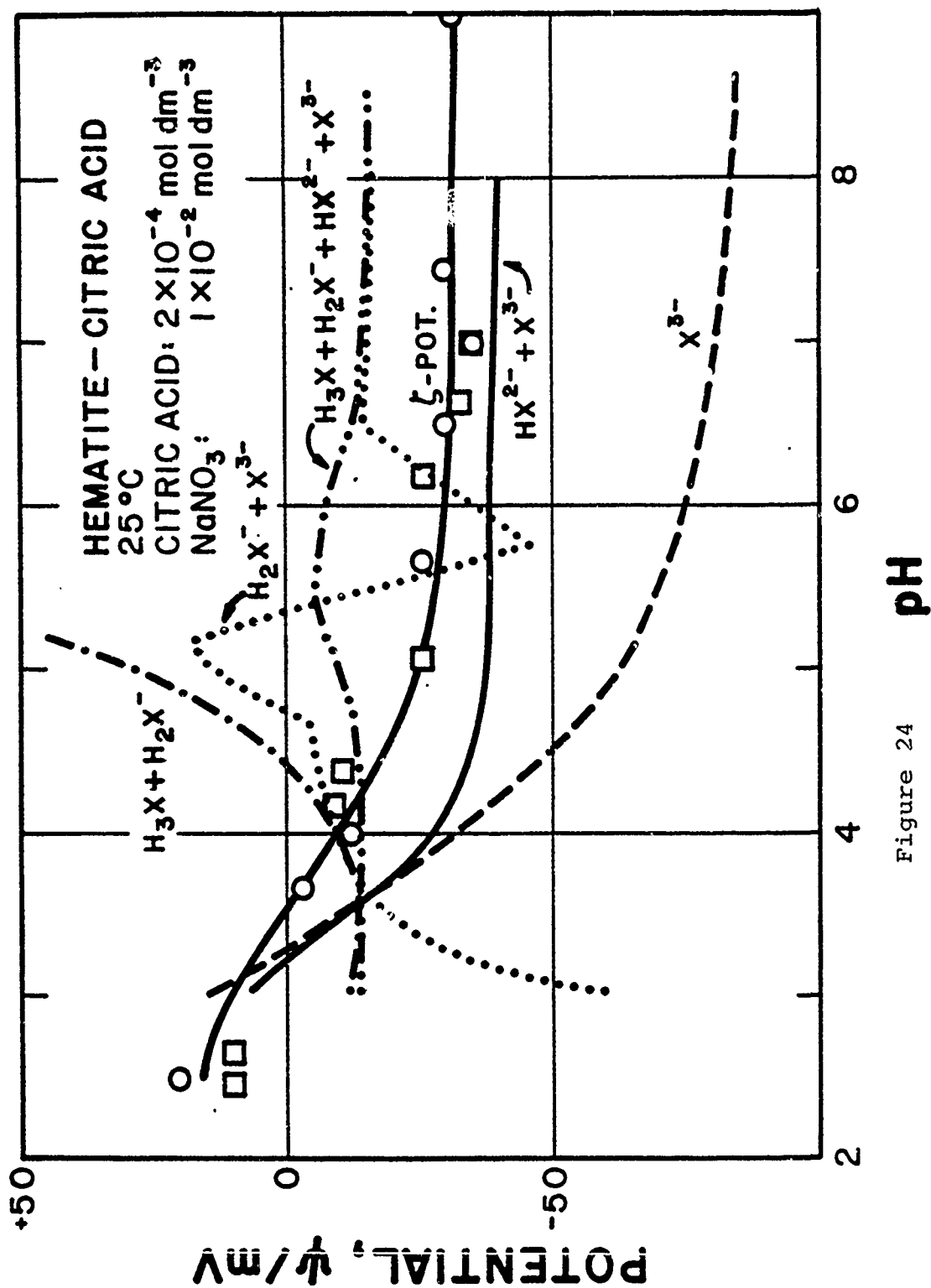


Figure 24

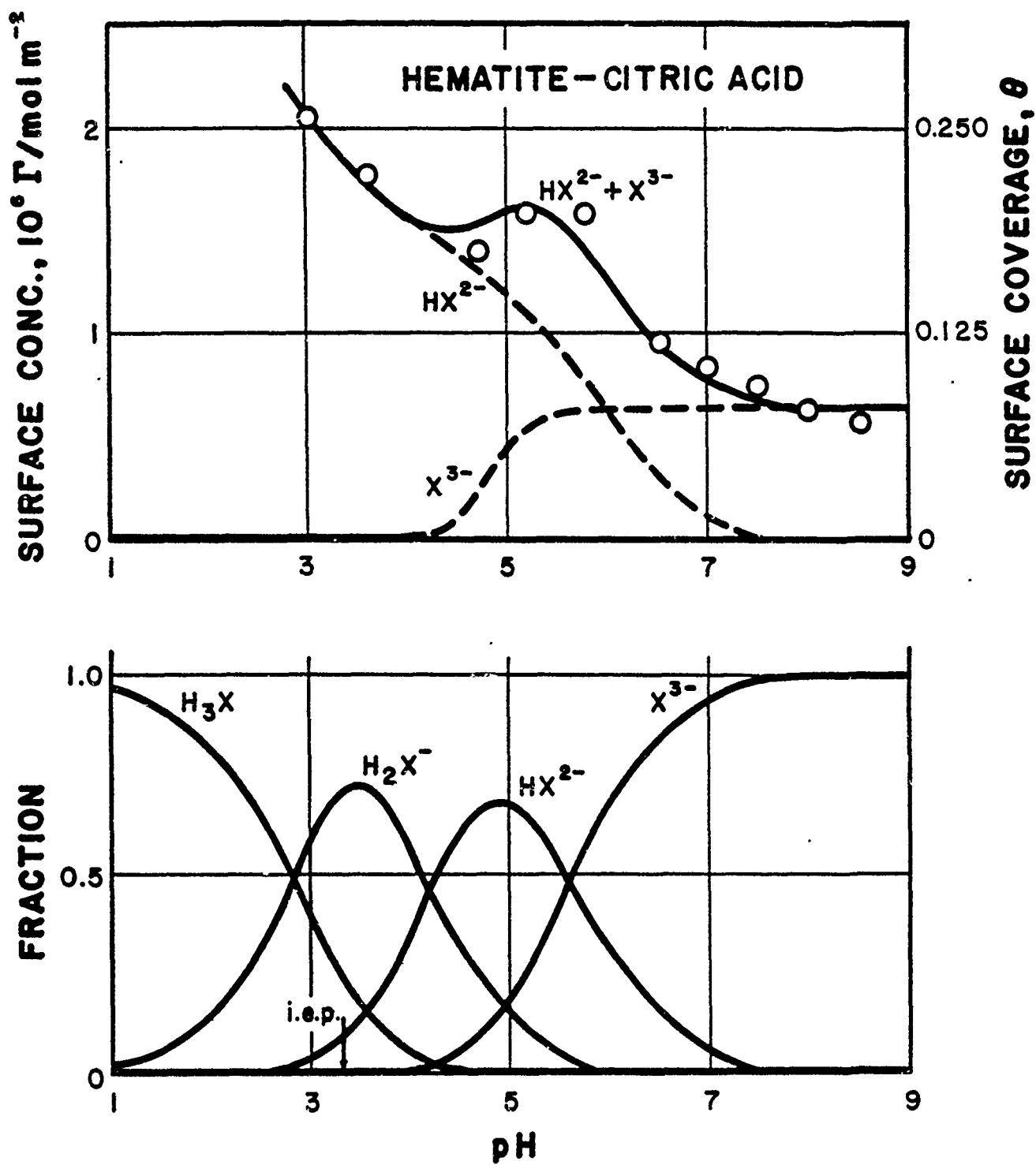


Figure 25

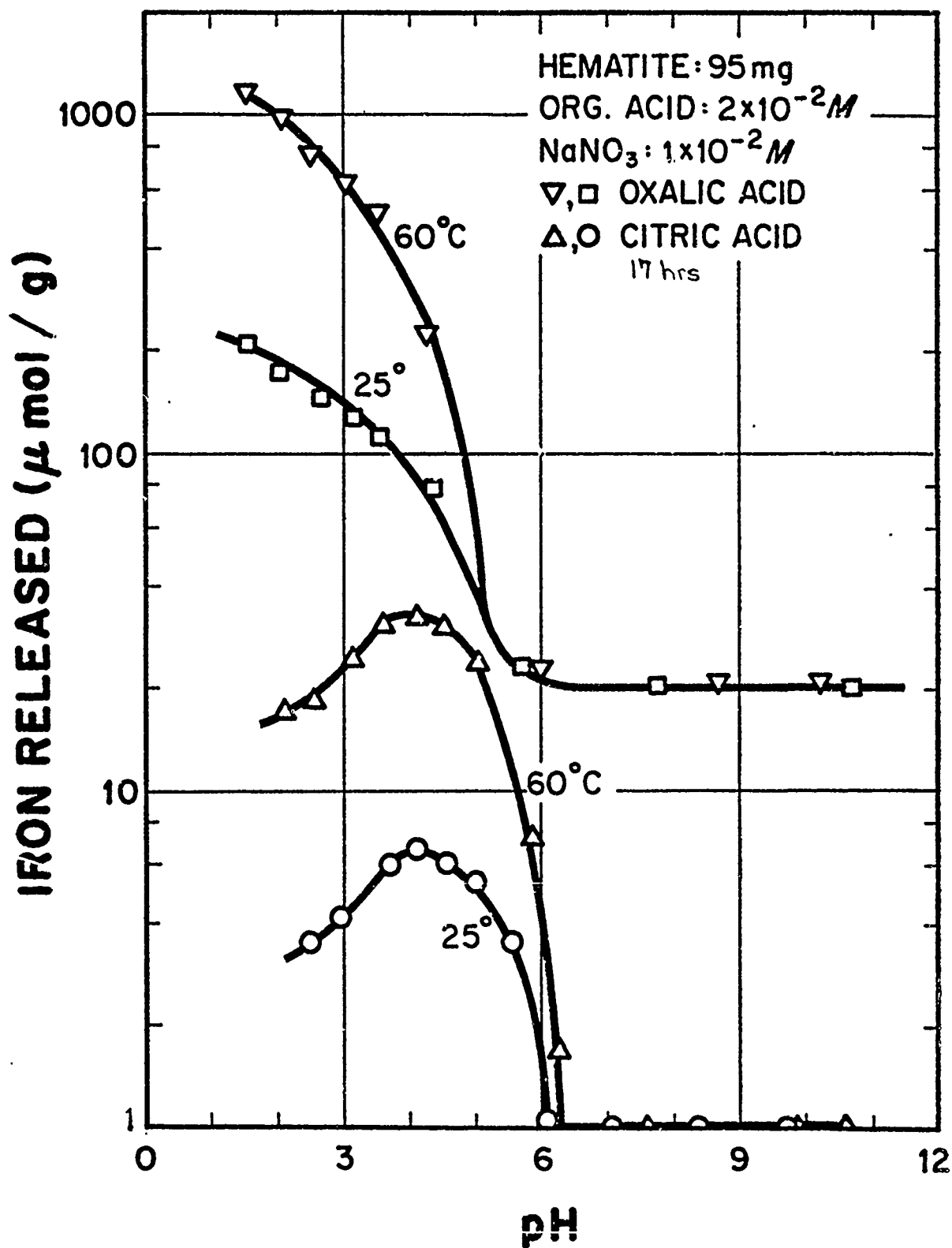


Figure 26

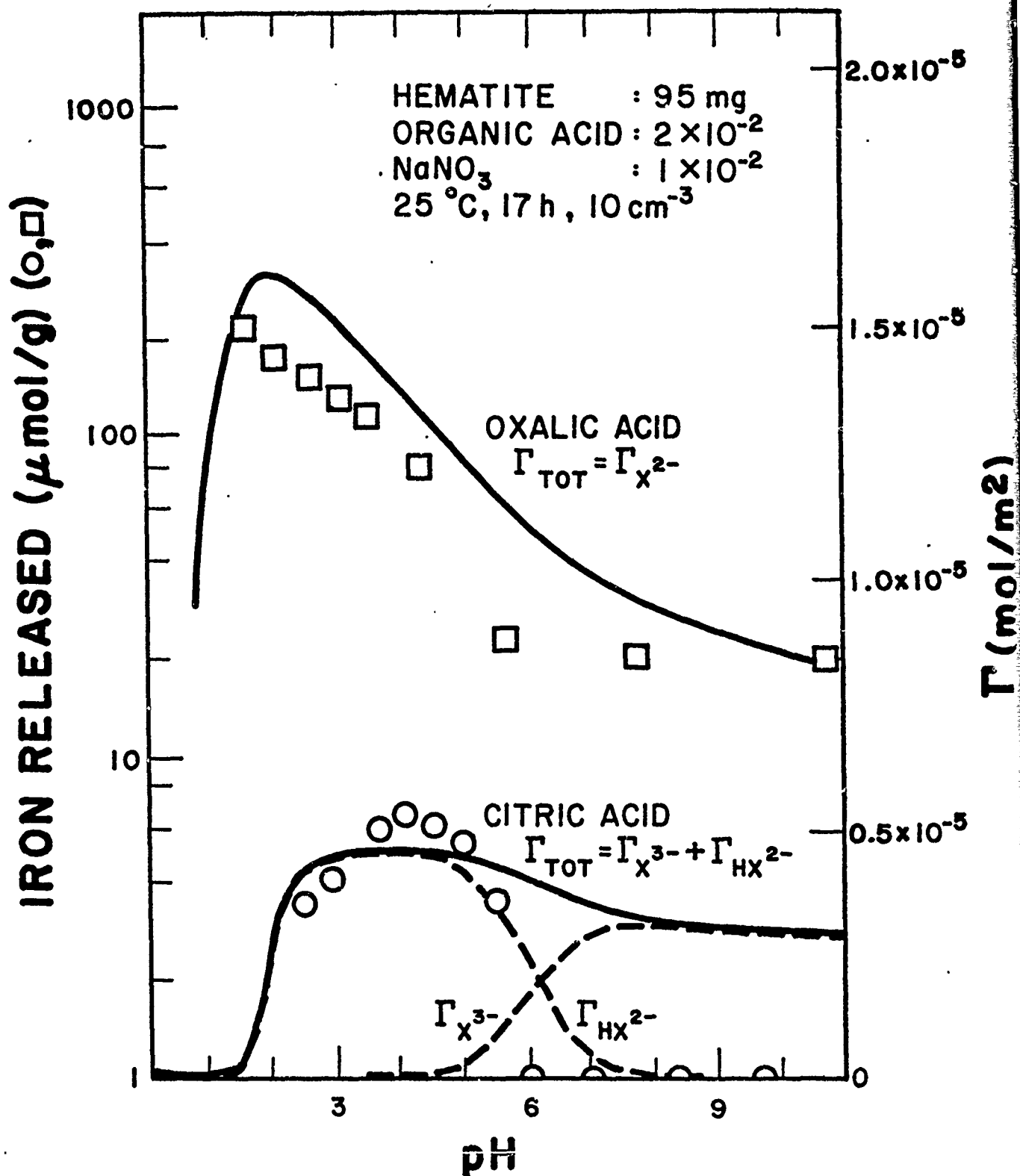


Figure 27

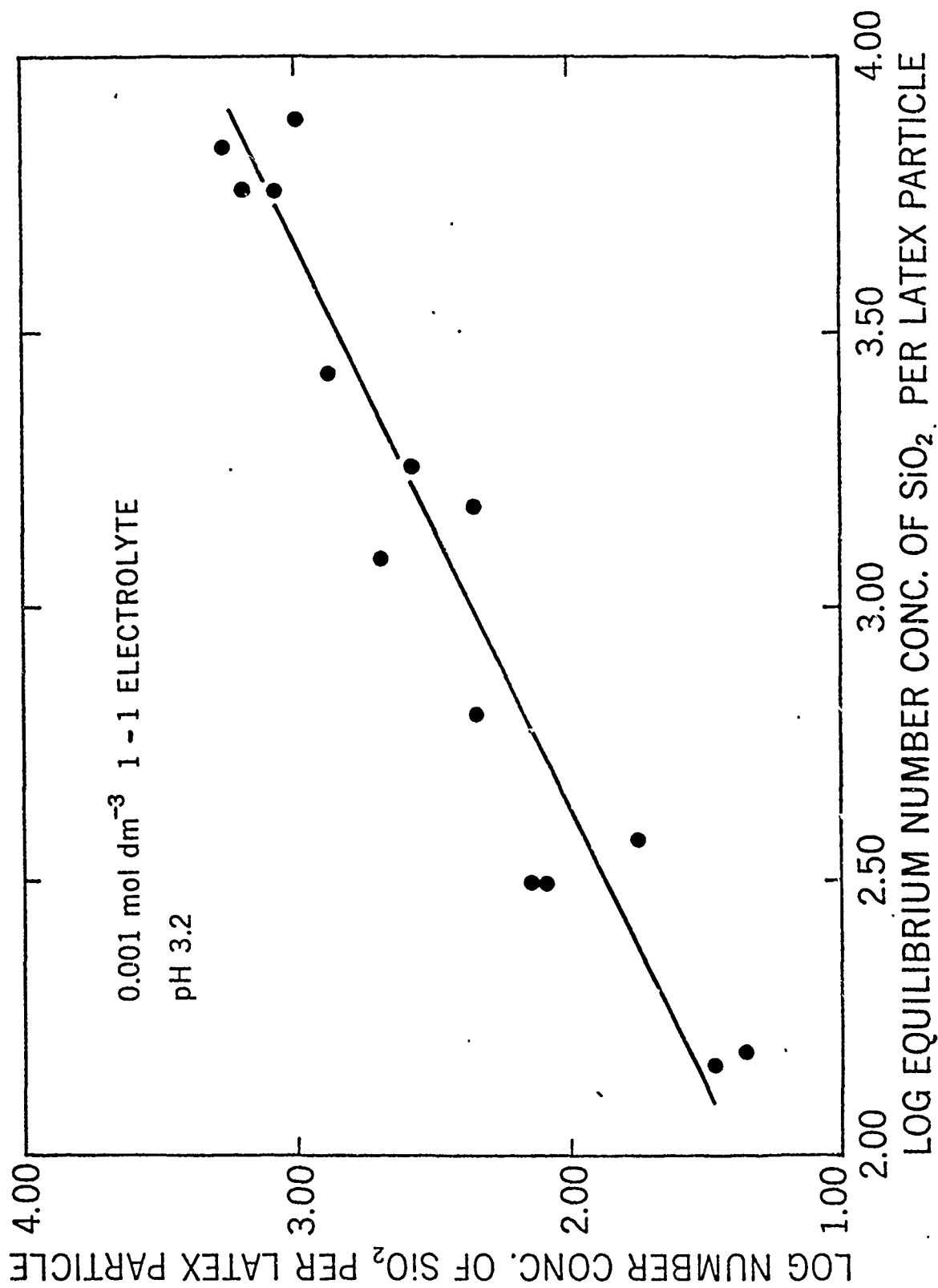
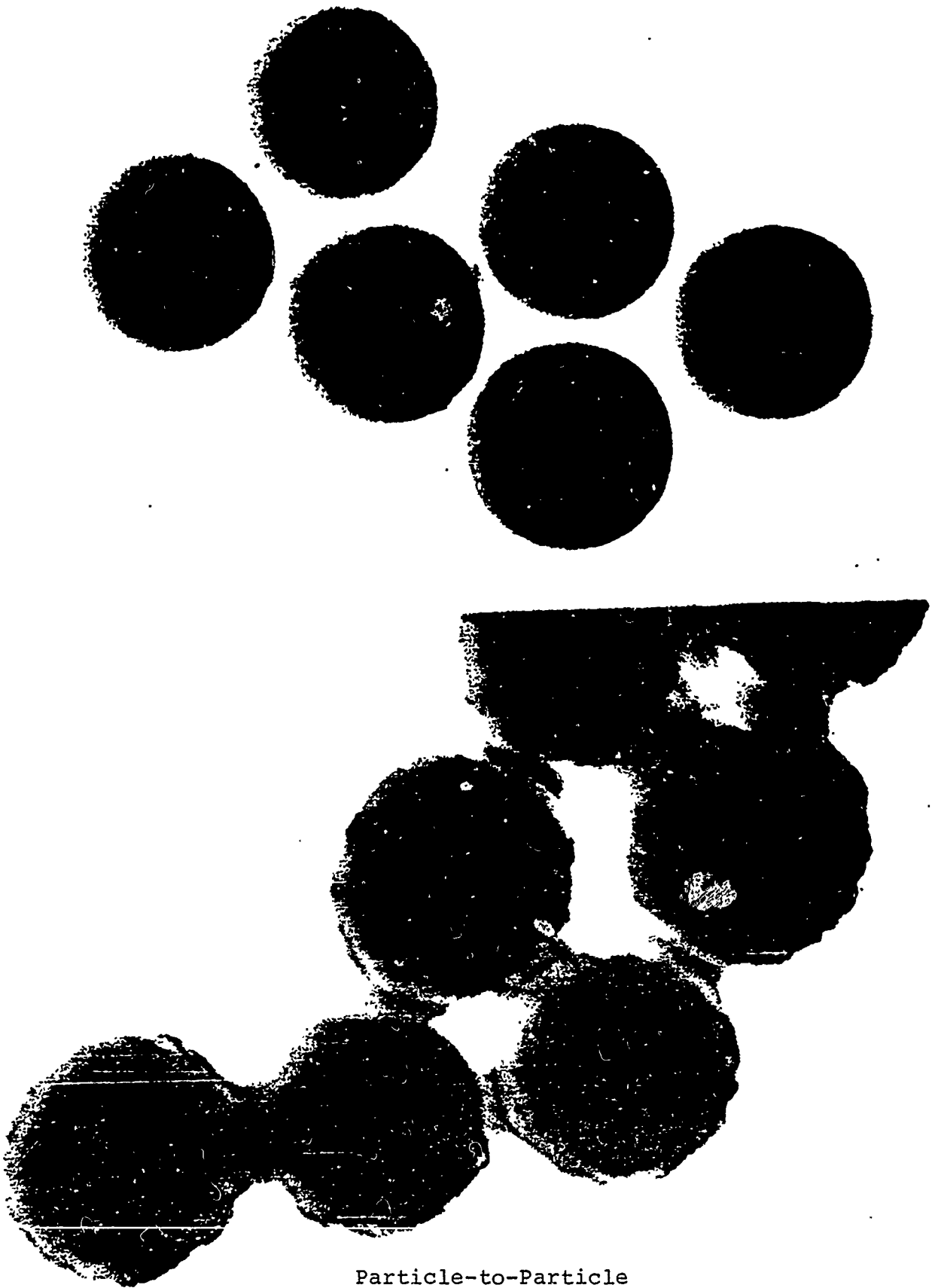


Figure 28



Particle-to-Particle
Interaction

Figure 29

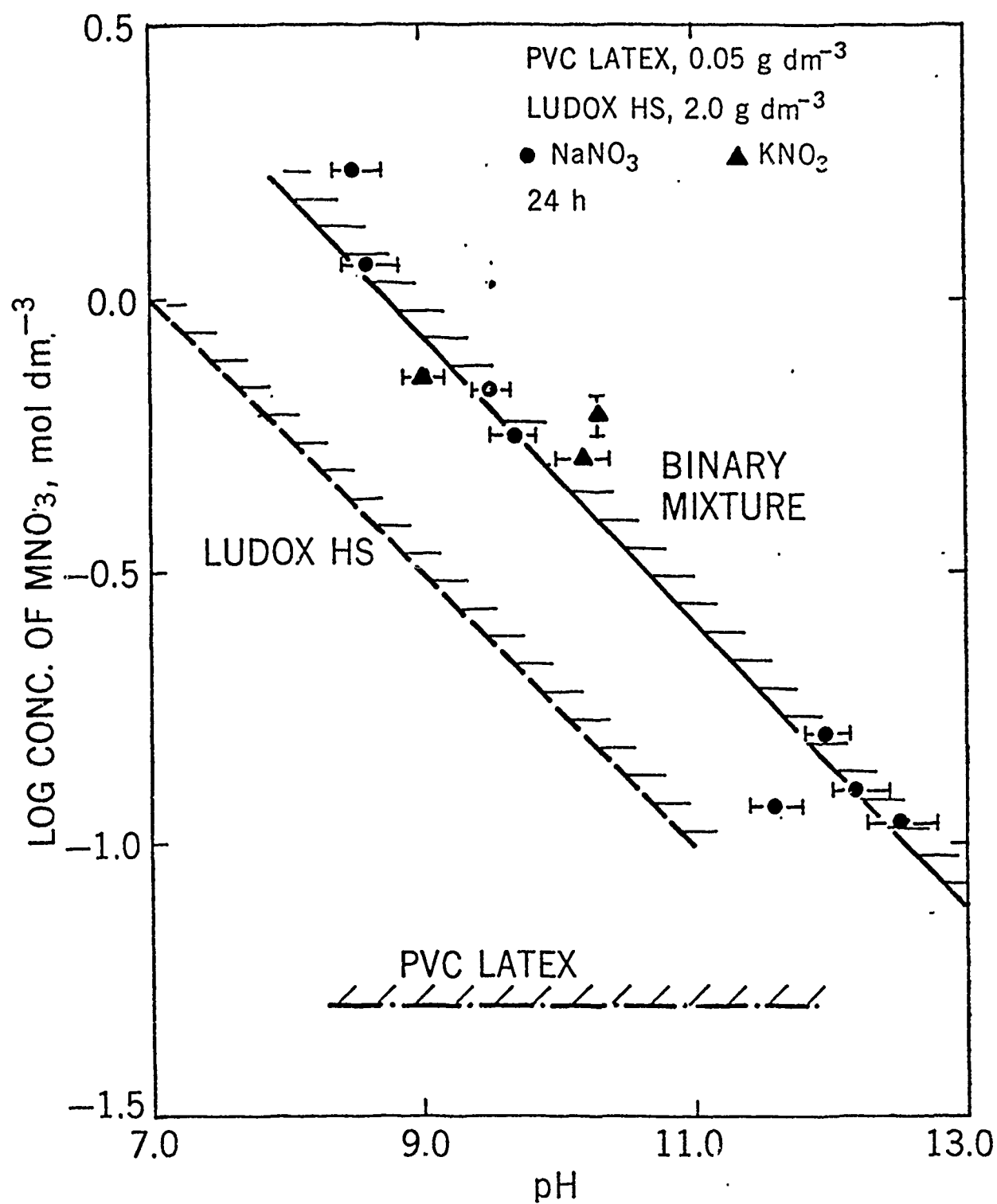


Figure 30

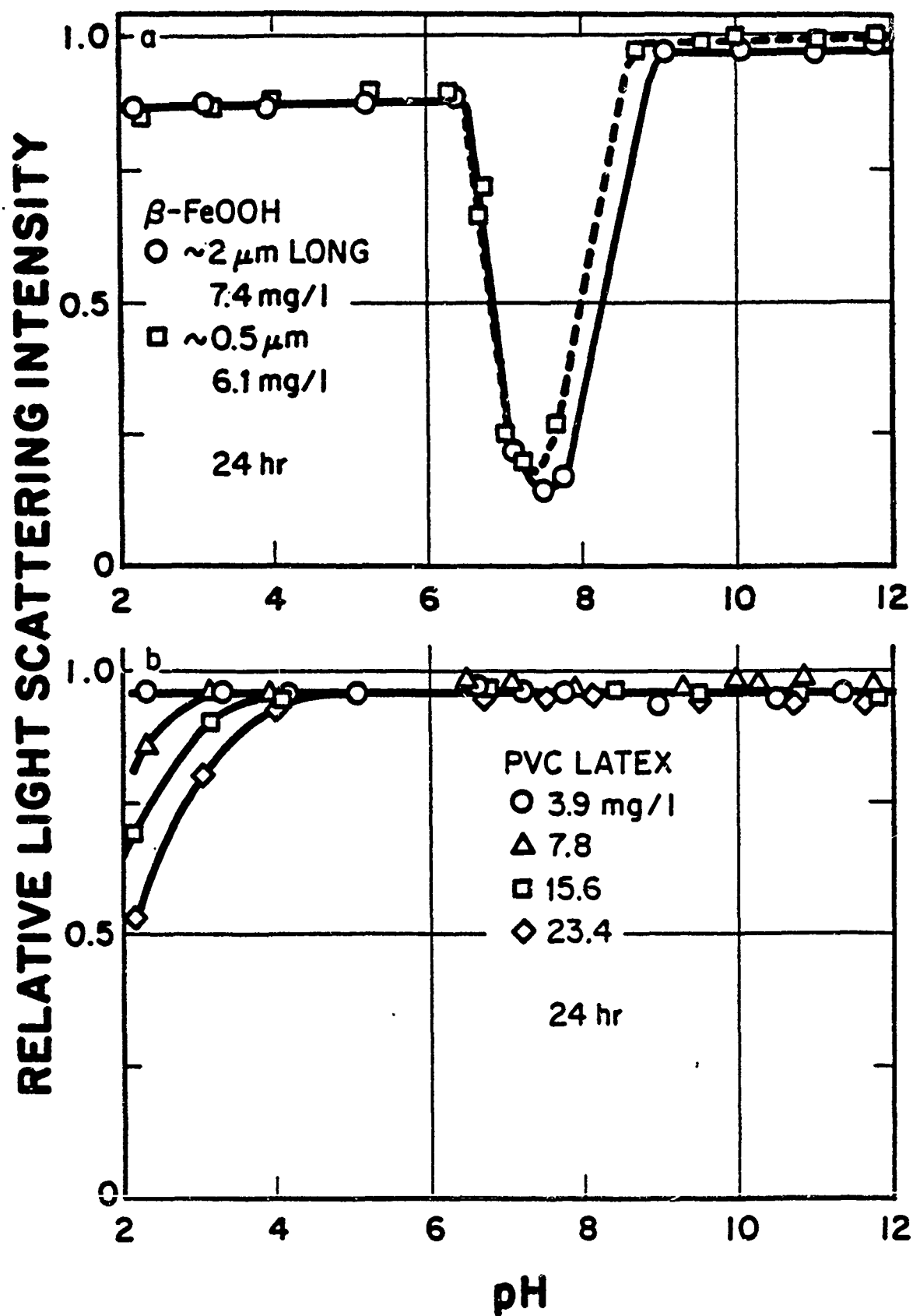


Figure 31

REL. LIGHT SCATT. INTENSITY (L.S.) or
FRACTION COAGULATED (F.C.)

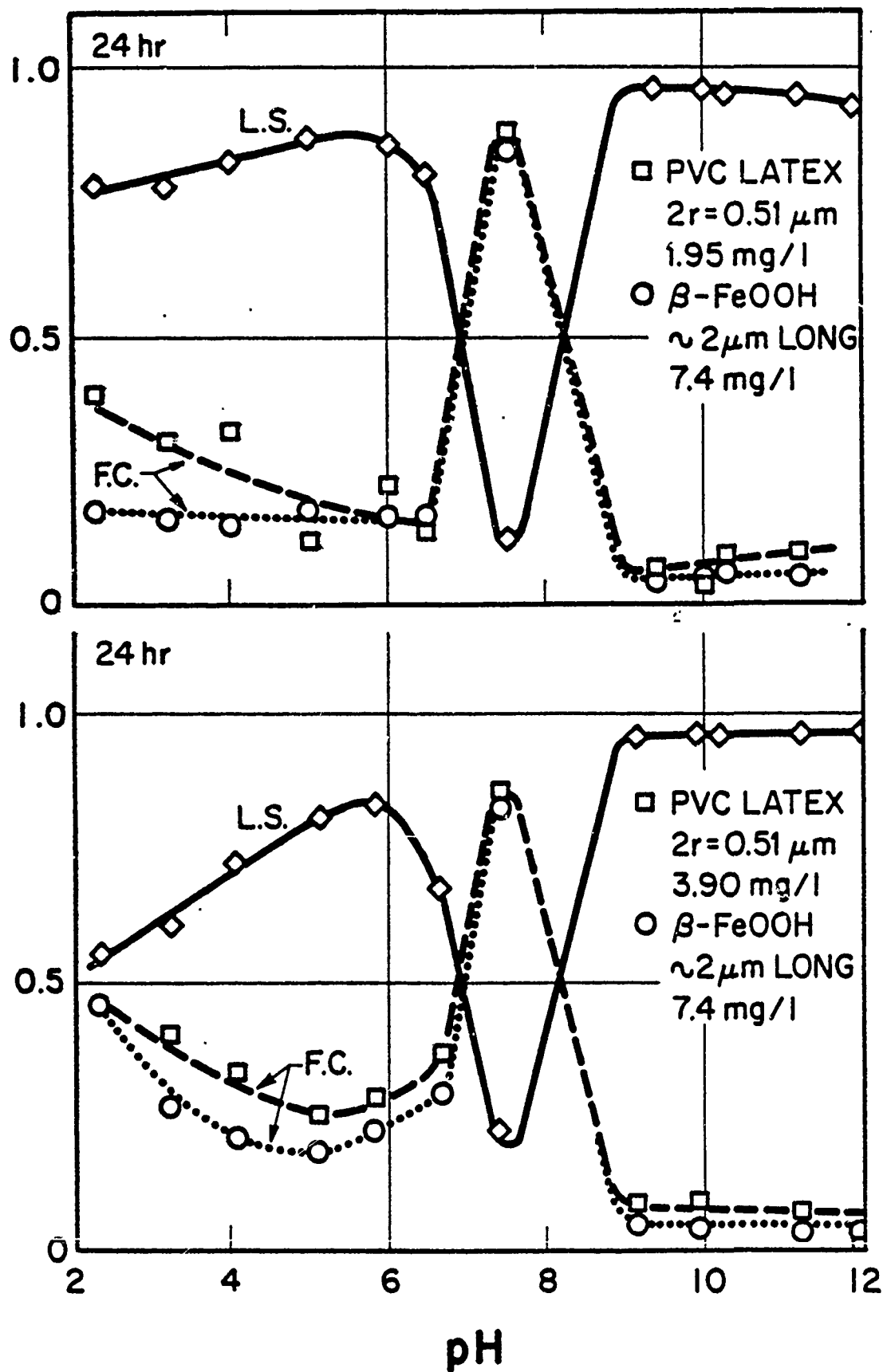


Figure 32

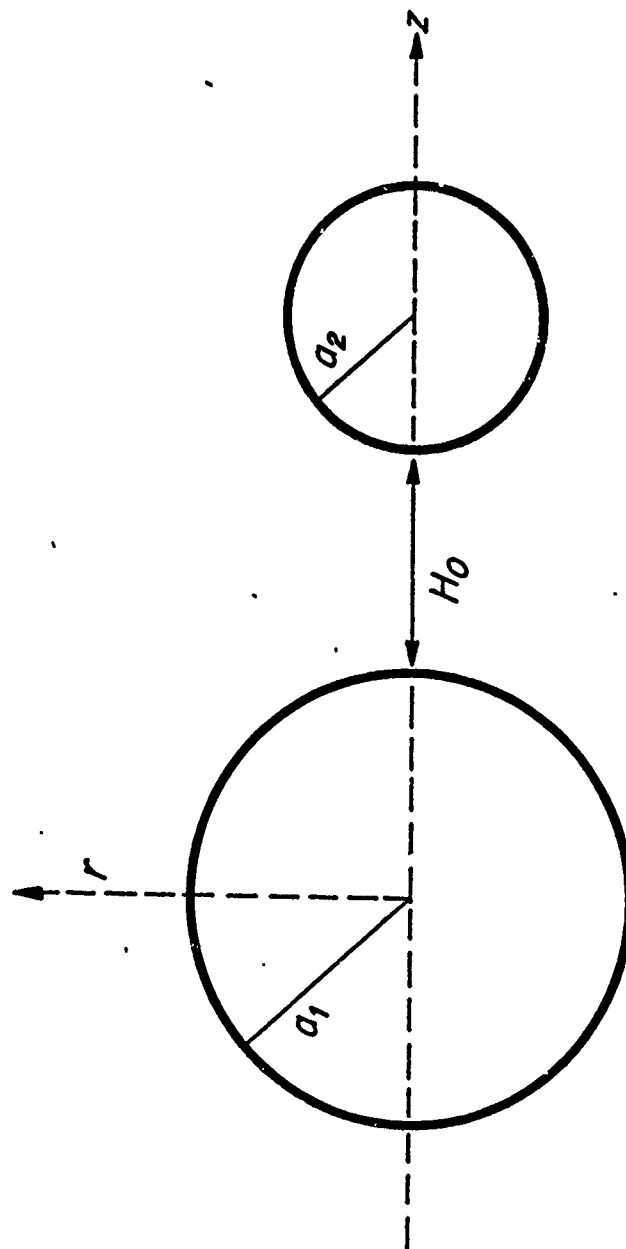
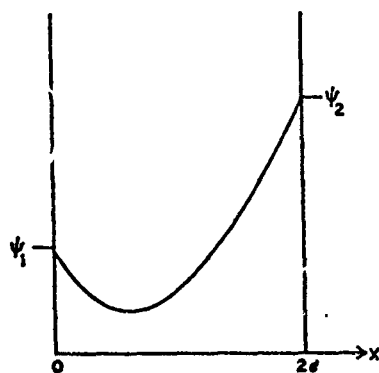


Figure 33



Schematic representation of the electric potential between unequally charged surfaces.

Figure 34

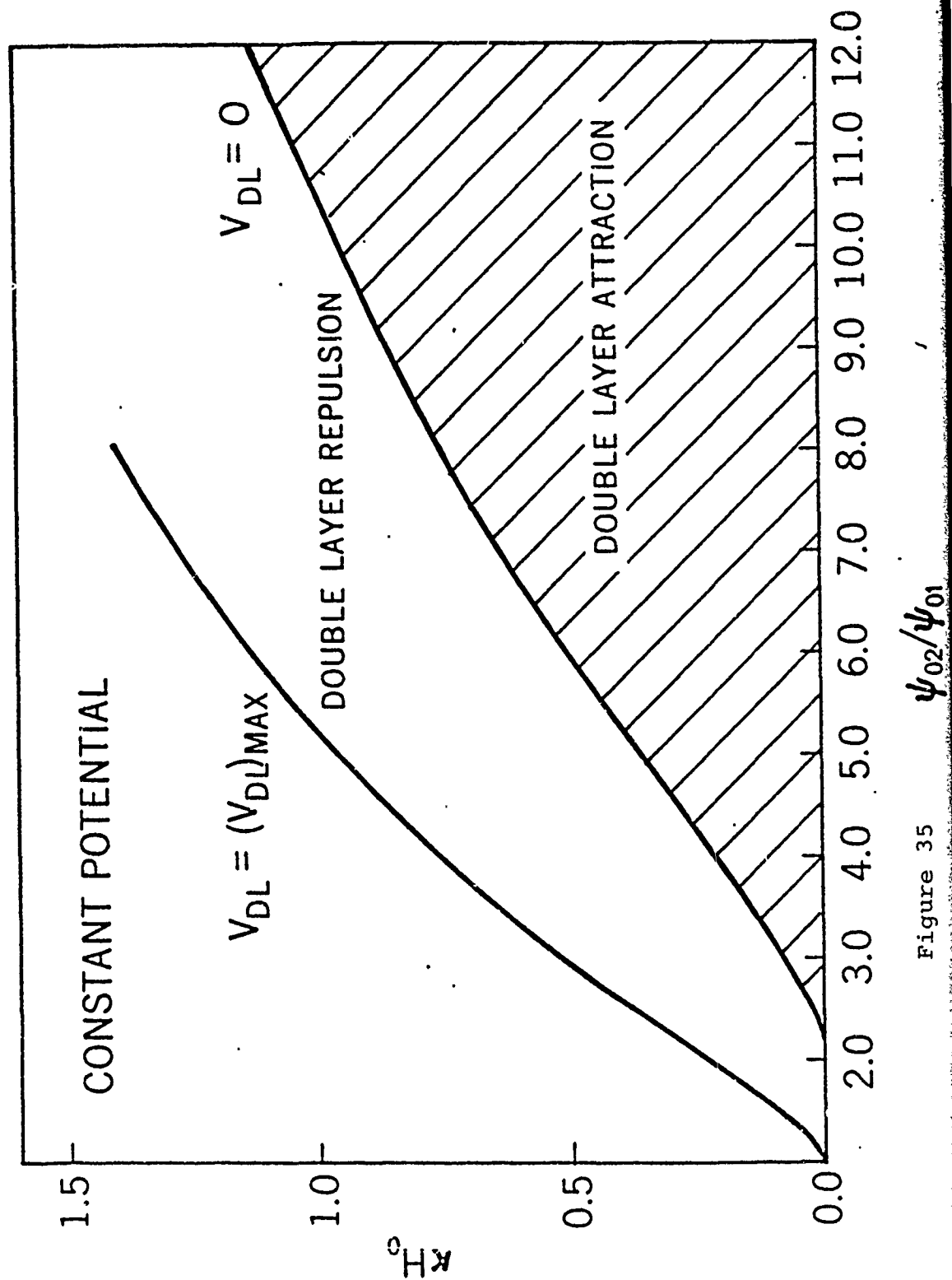


Figure 35

ψ_{02}/ψ_{01}

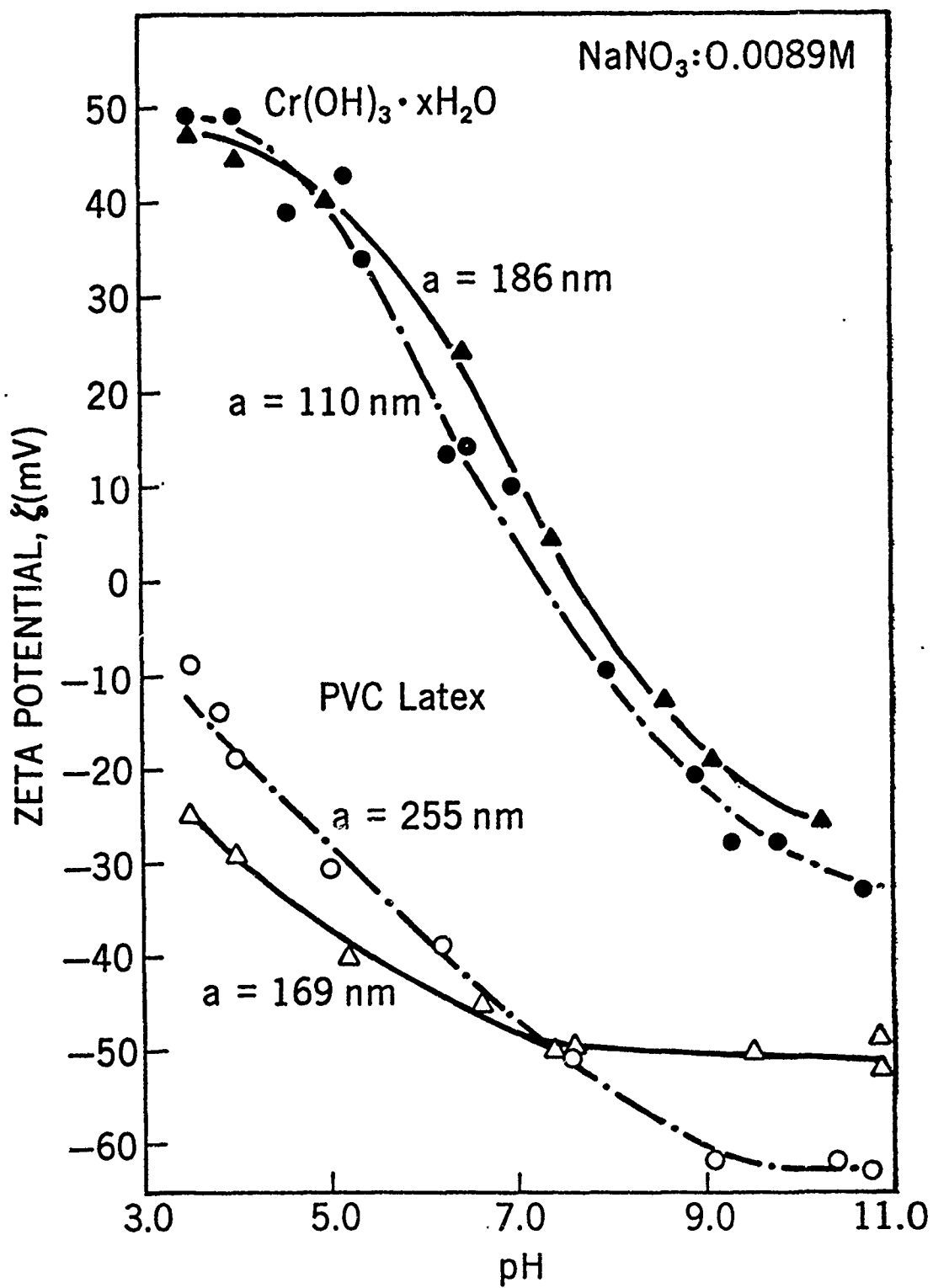


Figure 36

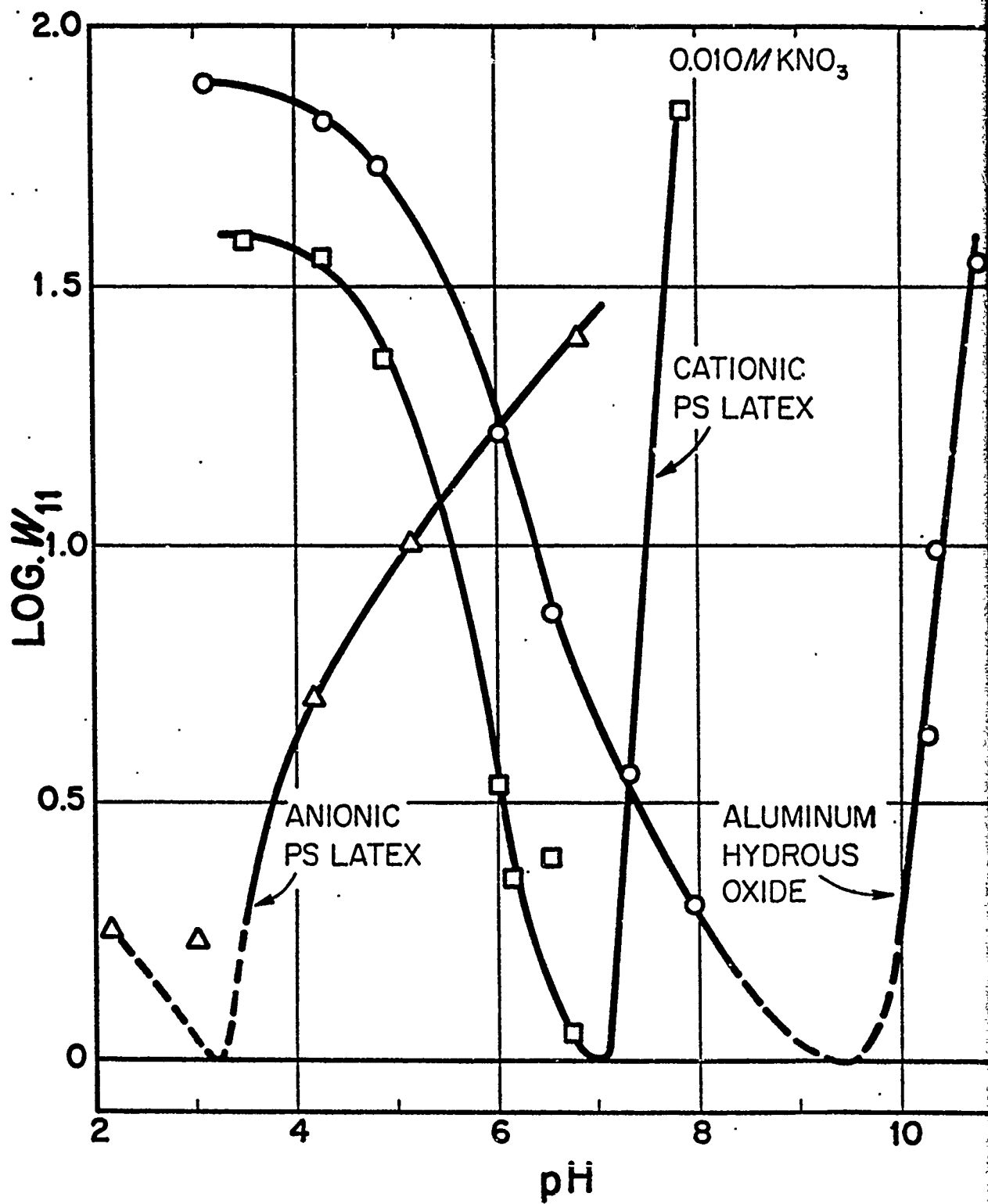


Figure 37

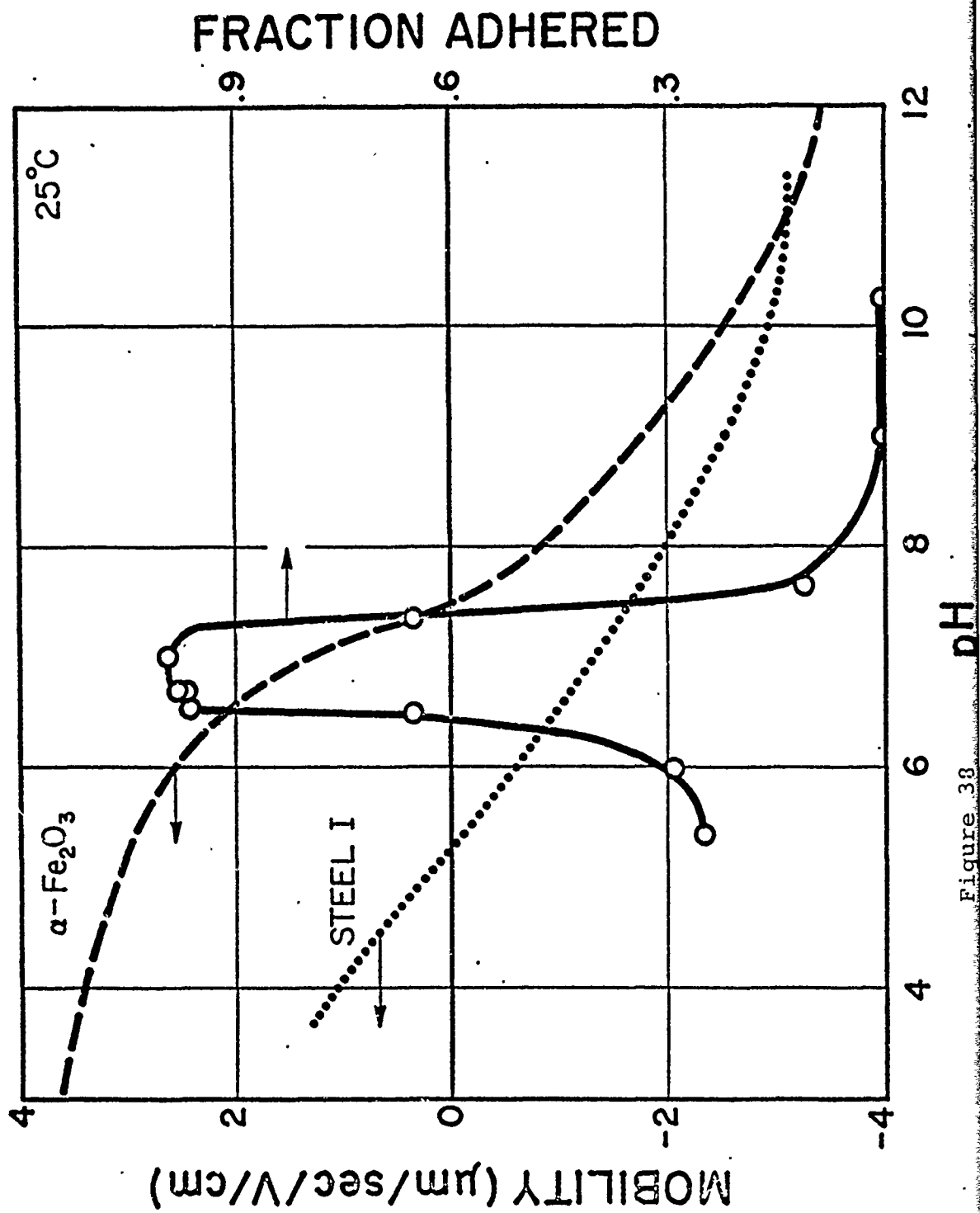


Figure 38

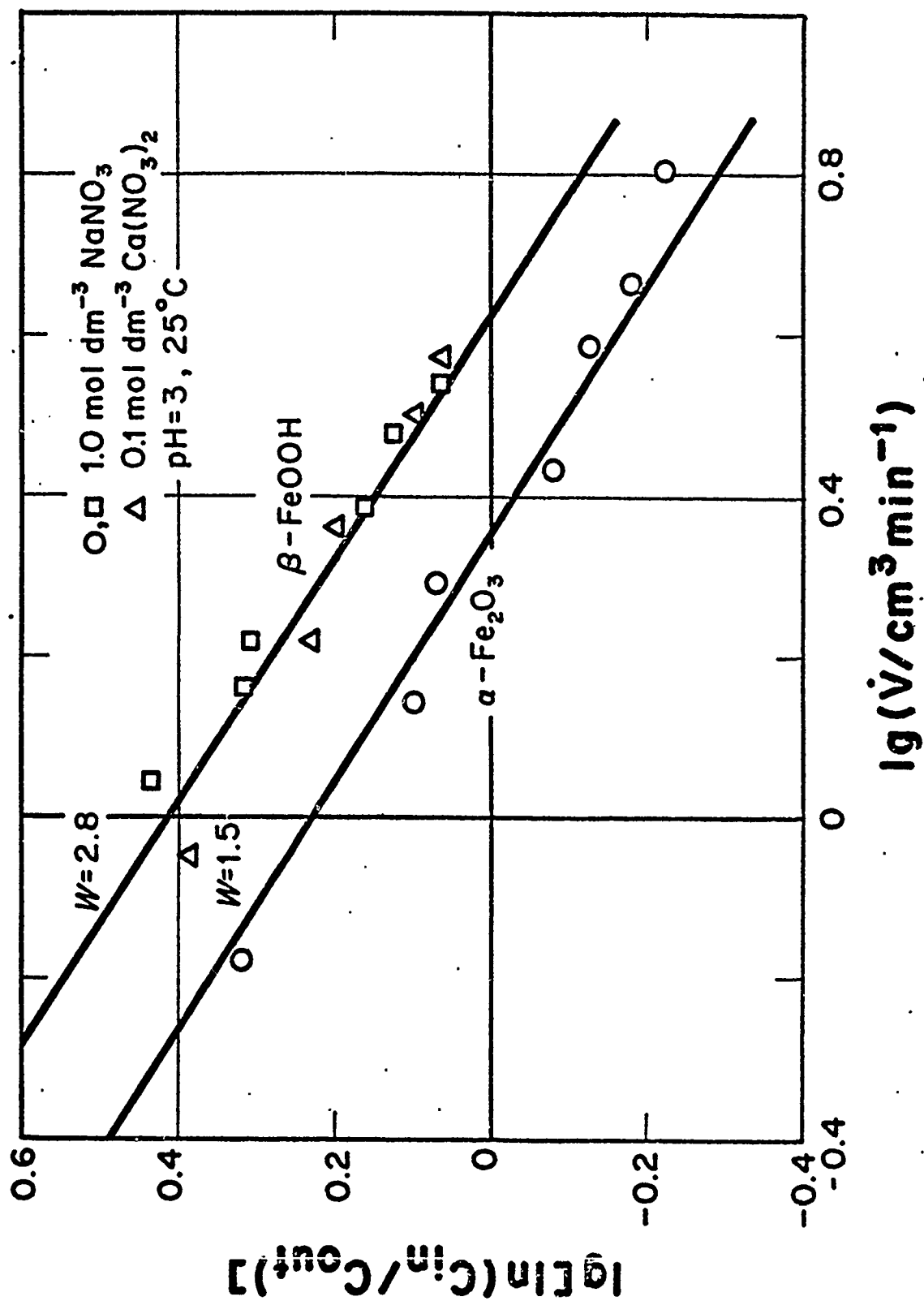


Figure 39

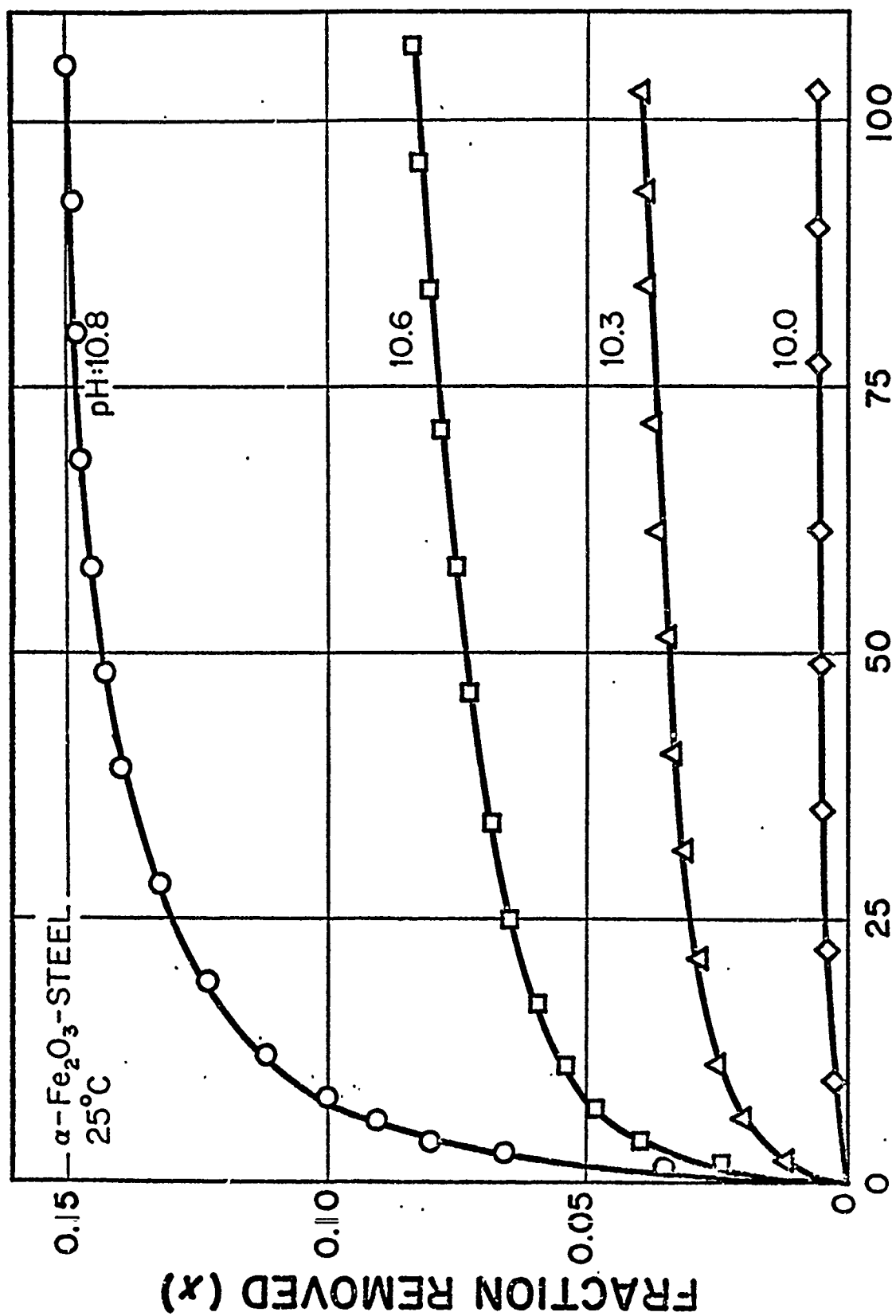


Figure 40

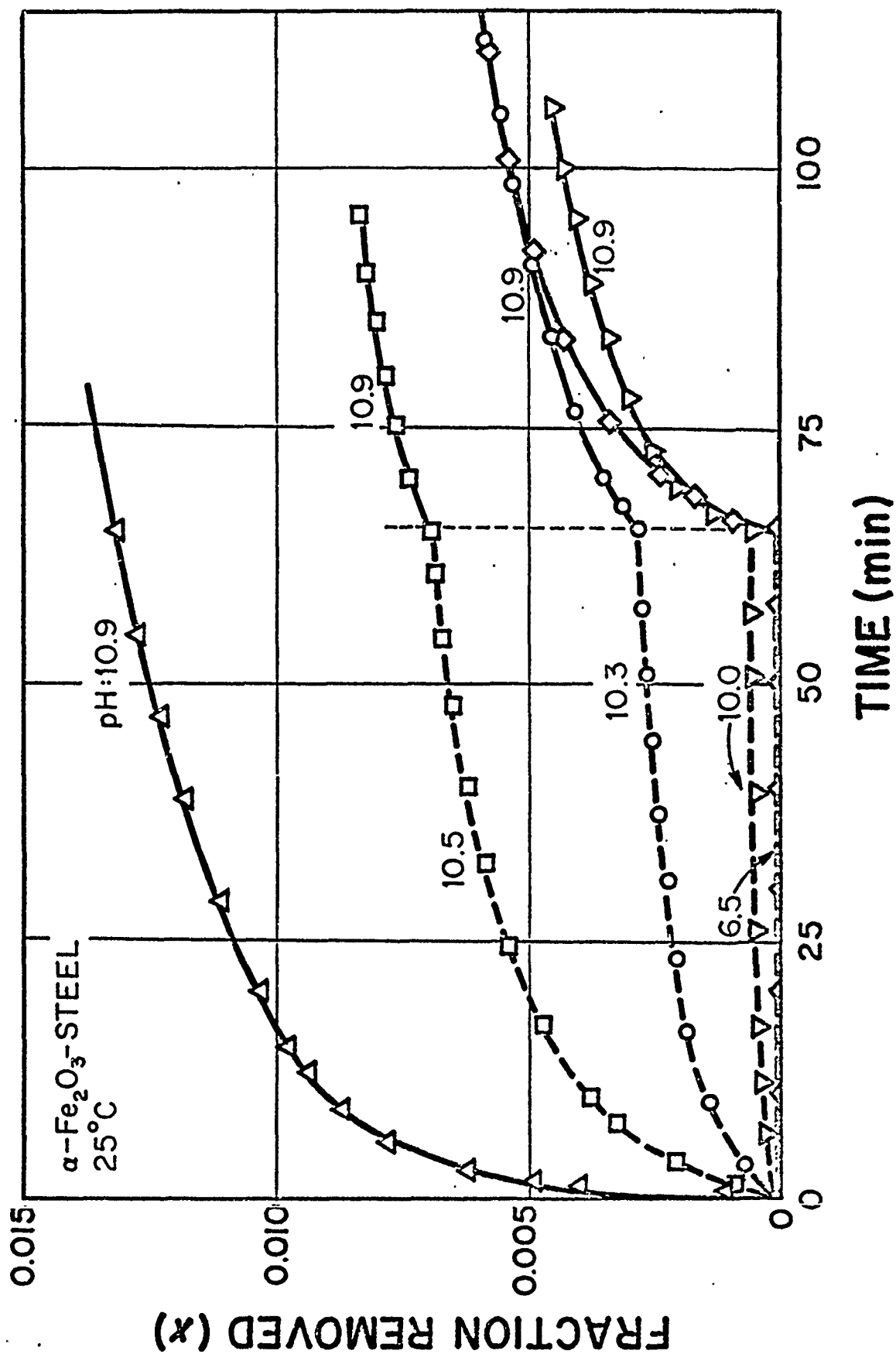


Figure 41

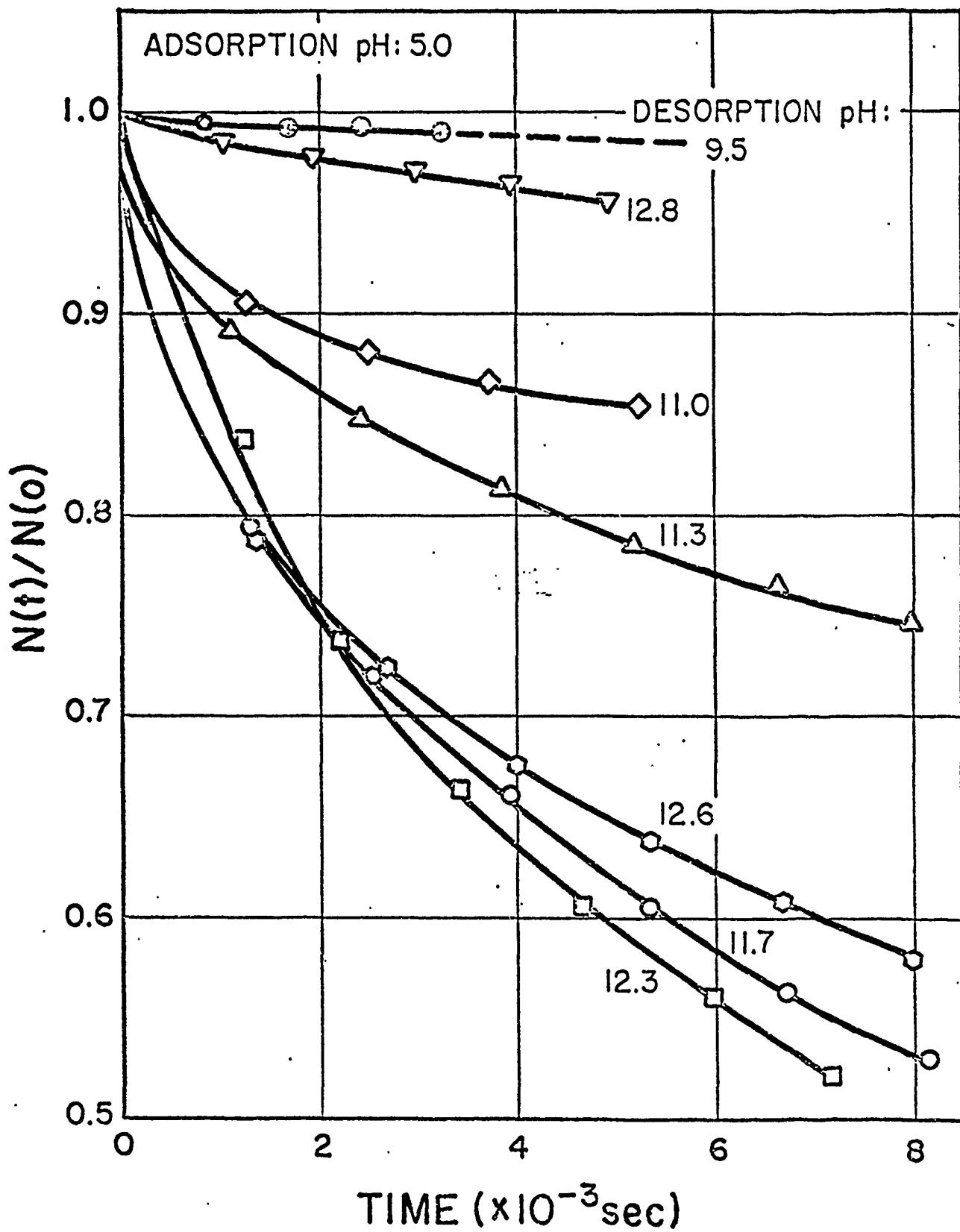


Figure 42

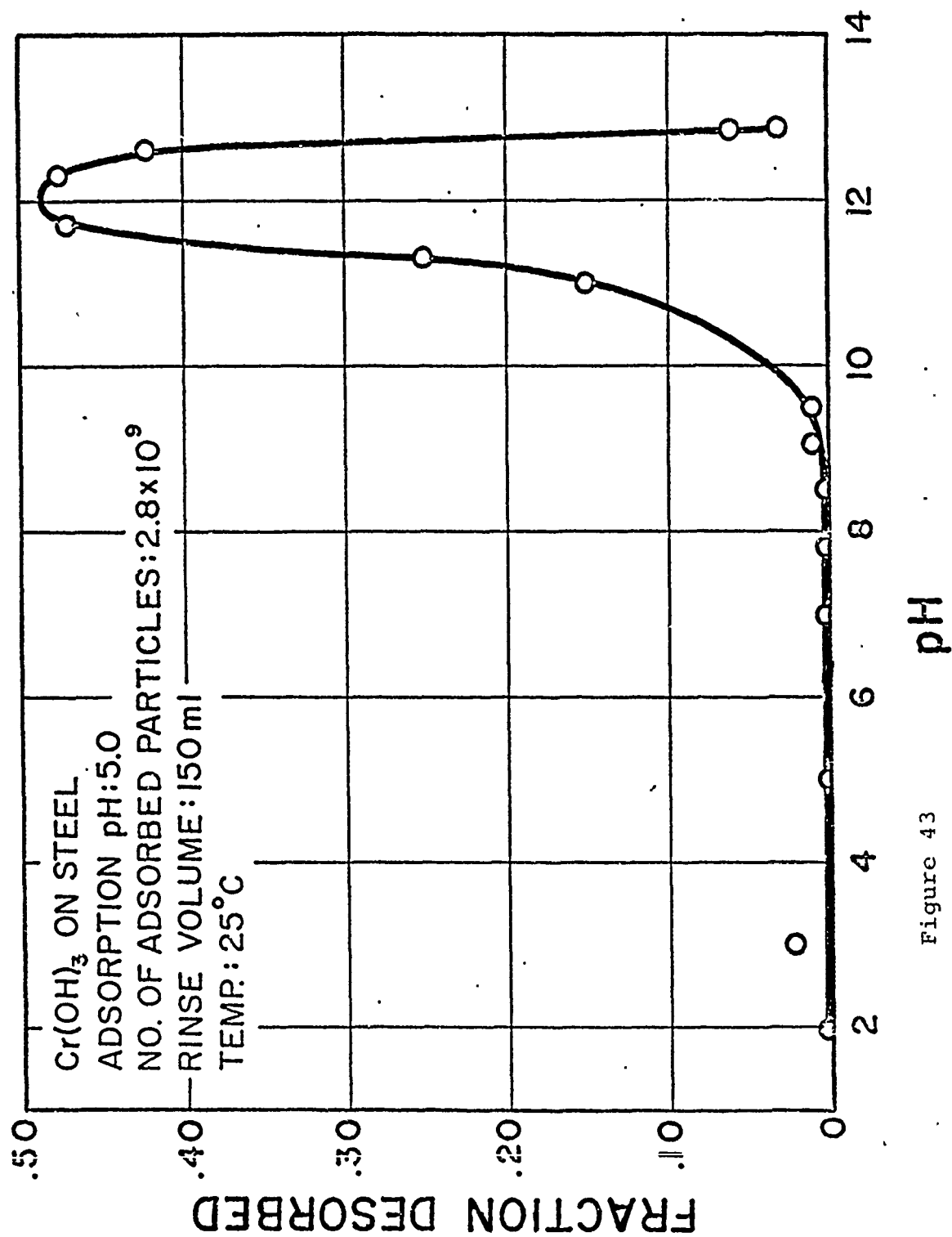


Figure 43

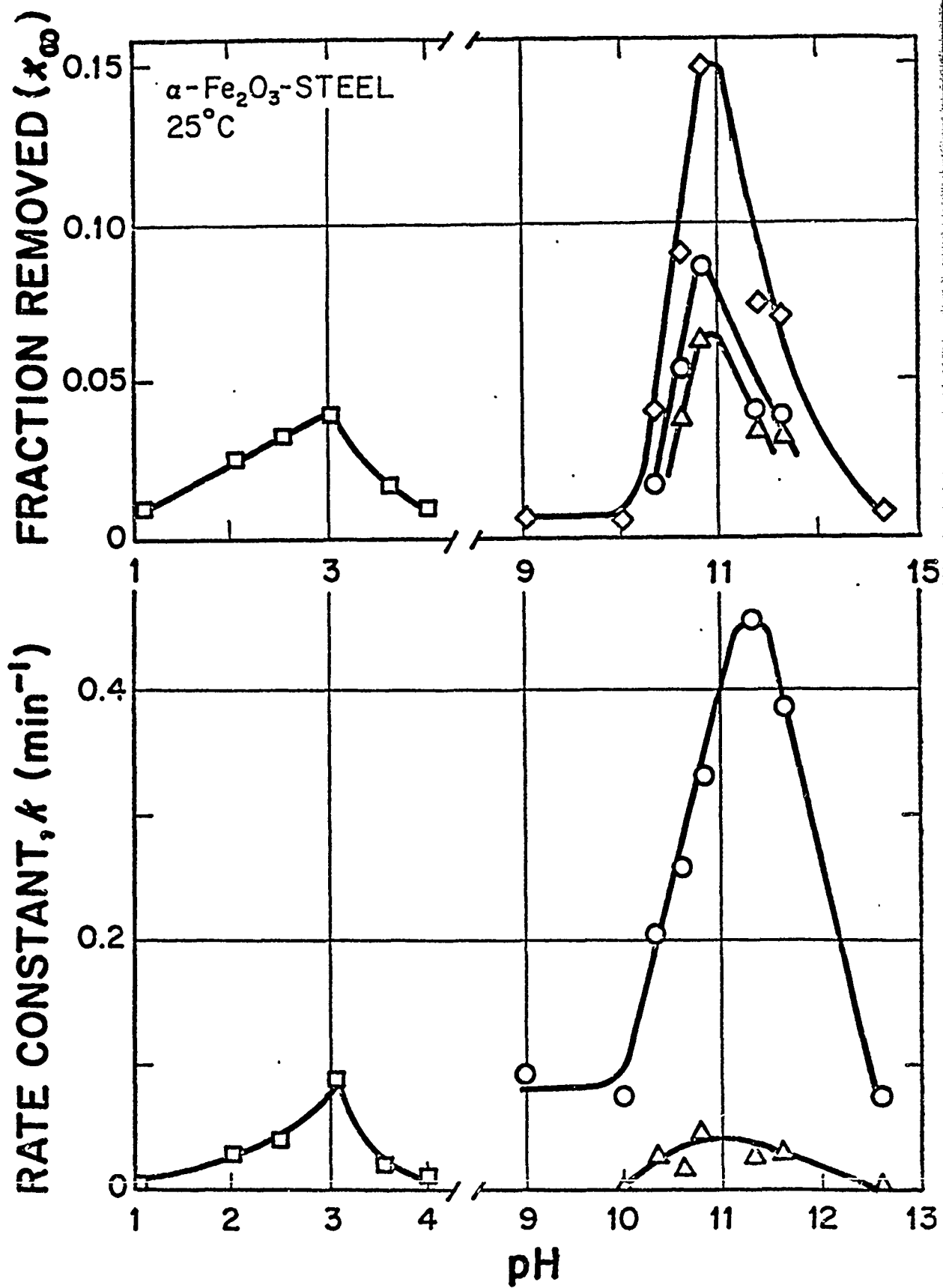


Figure 44

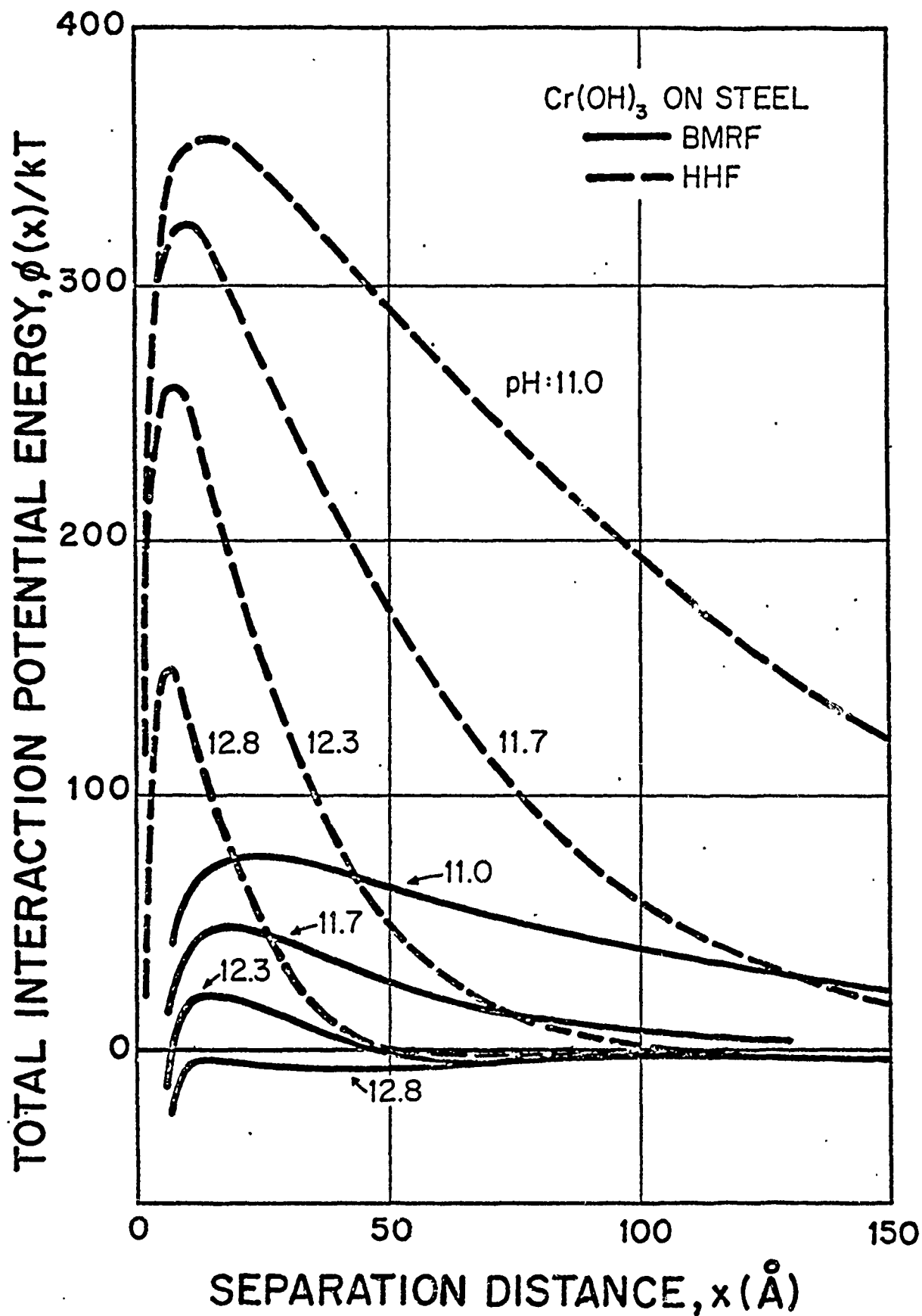


Figure 45

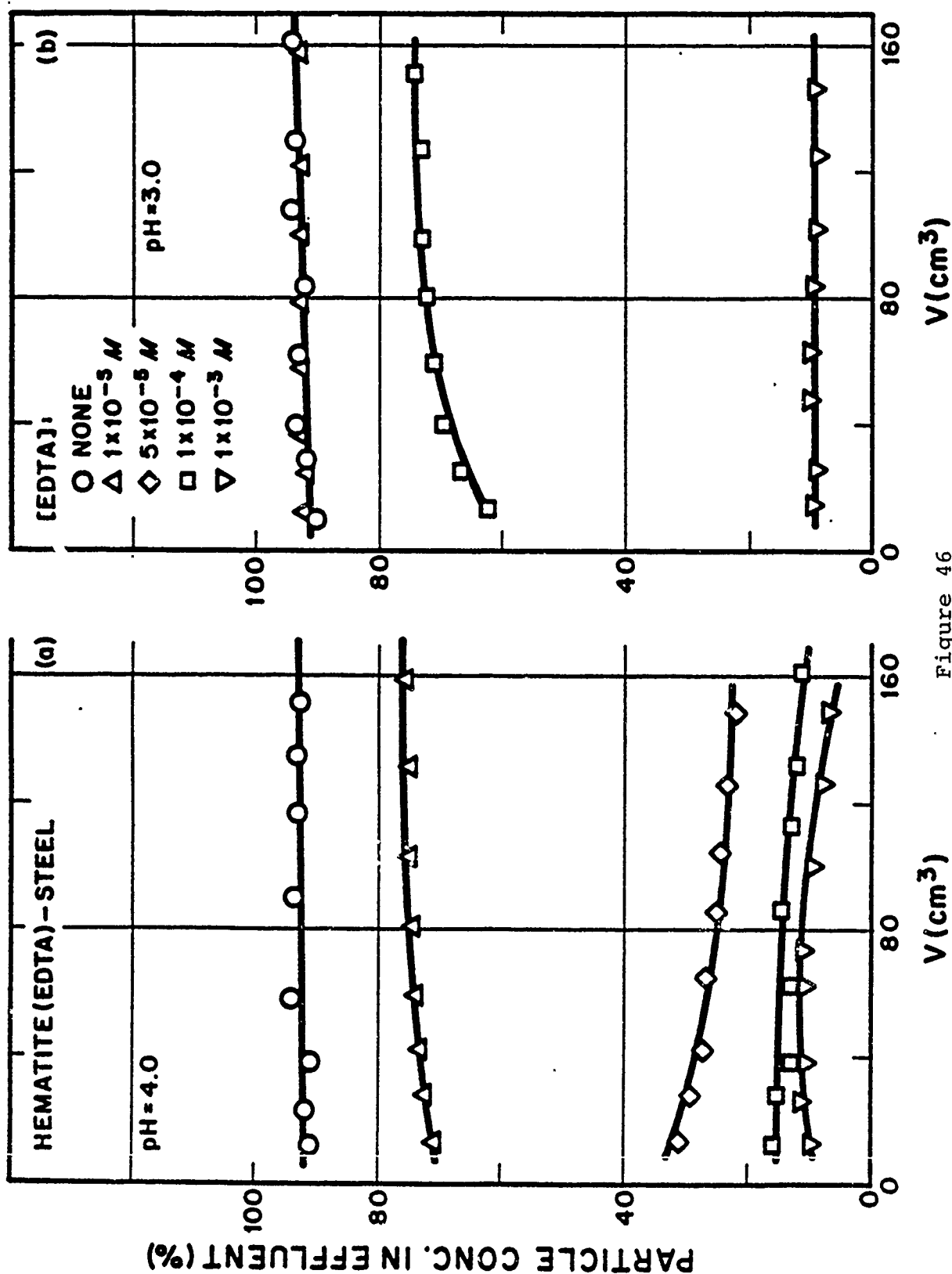


Figure 46

Floor Discussion

Comment - In talking about producing colloid systems, in the case where you mentioned that the anion is critically important, in terms of the shape of the particle produced, it seems that another aspect that would be critically important, and more inherent would be the basic crystal structure of whatever material you are trying to produce. It is going to be the interplay of the anion across the growing interface of the particle. That brings in another aspect and that would be the number in the hematite case, where you had the hexagonal shape, the number of iron sites, and the absorption of the iron on one or more of the iron sites to inhibit the growth along a given crystallographic direction.

Question from the Floor - Have you tried to model that?

Reply - Well absolutely a proper point to be raised. Let me go back a little. The anion effect depends on their concentration. For example, we now know that phosphates have a phenomenal effect. If you take very, very small concentrations of phosphates you influence the morphology. You add a little more and influence the composition, the structure. If you add even more, you change the chemical composition. The whole thing has to be related to the nature of the species of the solution attraction at the interface. What we are talking about here is phosphate complexes. So the difficulty is, we have to identify all of the species in solution to see which sit on the surface. That is our prerequisite, and once we have that the next absolutely essential step is to see how it absorbs - what amount, which position, what ion is absorbed, and how does it influence crystal growth.

Comment - One of the other areas where we are looking at, where there is a lot of data, is in the phase transformation theory of metals, in terms of crystal growth out of the melt.

Reply - OK, you are again pointing out a very important problem, which I could not cover in the lecture and that is, in solution as well as in the melt, phase transformation. Many more systems are produced by phase transformation than people tend to believe. Because we form first one phase, it may be exceedingly small in the nuclei state, which then in turn changes to something else. For example, we know the precursor to many hematite particles.

Comment - I wondered about that. Isn't that really a metastable phase to Fe_2O_3 ?

Reply - You know metastable is something that when you don't understand something, give it a name, metastable. I don't know what metastable is. It is obviously not stable because it changes. You use metastable and you think you understand it. I hate the term symbiotic effect, you know, antagonistic effect, metastable effect. People who use them who don't understand the bloody business, you see. Obviously it is not stable, it changes. Now that we have systems that are attractable, you can make a bloody sphere over and over again. Now you can go into solution kinds of studies to see what species are involved, how they change with time, and so on. We have done it in a few cases. It is a very fascinating science, but it is very hard work.

Comment - I know intermediate phases form in a hydrothermal process, you take advantage of those phases. In fact they sometimes act as a reservoir for your cations, your cationic species.

Reply - As a matter of fact, I have shown this to be the case. When you change hematite to magnetite you can do it by phase transformation. And if you add, say, a complexing agent (adherent), you can get perfectly spherical hematite particles into an octohedral magnetite particle.

Comment - the solution is what one has to emphasize. You seem to say that everything ceramic depends on the colloidal state of the solution.

Reply - When did I say so? I didn't say so. First of all, let me clarify. I think we are getting mixed up on something. When I talked about alkoxide, I didn't talk about solution, I talked about an aerosol where you have a droplet of an alkoxide reactor. So it has nothing to do with solution work, right? That is Number 1.

Comment - Fine.

Reply - So what are we talking about? It is not solution work.

Comment - I want to add something.

Reply - All right, now before I forget what you said. When the particle forms by polymerization, inorganic particles, the case of aluminum hydroxide spherical, chromium hydroxide, there is no difference between organic and inorganic chemistry. Period. You have a degree of interaction, you follow your chain and so on. When your particle forms a crystal growth, and I can show you beautiful crystal particles, then you don't have polymerization you have very well defined monomeric or dimeric species interacting. And that is a dramatic difference. Then when we do not disagree, we have a different situation from polymer, organic polymers, so we have to be careful to distinguish very different formation mechanisms. Chromium tends to polymerize, aluminum tends to polymerize in the presence of sulfide ions, which is a polymerizing agent which gives you spherical amorphous particles.

Comment - Providing that you carry the reactions to the limit of it. We in polymer solutions control the extent of reaction.

Reply - So do I in inorganic.

Comment - Yes, but the thing is you could make polymers, polymers with linear polymerization or the spherical polymerization, or actual branching that with terminating and crystallizing method. I don't think metal organic compounds, you never go to the hydroxides or oxides, they are always aqueous groups left on the terminating point.

Reply - Well first of all I don't use alkoxides or organo metallics to make these particles, you use plain aluminum, alumina solution and you form it, so again I never said so. If you take pure aluminum solute, chromium solution, add sulfide iron, that is your polymerizing agent, there I can go into details. You

form your inorganic polymer, you roll it up into spherical particles and you have an amorphous particle. That is one case. It has nothing to do with organic versus inorganic. I think that it is a very important point that in our thinking we get away from this classical separation of inorganic and organic chemistry and think as chemists, whether you form individual molecules or long chain molecules, and so on. Under certain conditions you can do it with inorganic chemistry, certain conditions you can do it with organic chemistry. When you have the same mechanism, you will get essentially the same product. When you have different mechanisms, you will get different products. That is the way I look at it.

Comment - I would like to ask a question along a different line. The field reached a point where it is possible to generalize the principles or rules of thumb with respect to control of size and aspect ratio in single systems. Does every composition have to be dealt with individually?

Reply - Let me give you an honest thought. The whole field was pure art. They have started to introduce science into it. In some cases now it's 50/50. So with someone experienced in science it is predictable. Now, for example, we are able to extend to sulfides and make sulfides, selenides, and so on. But you still have to perform experiments because we don't know enough chemistry. Nobody knows enough chemistry! Then you have to play some of this to conditions and adjust it, but we can narrow down for example the matrix of conditions that we want to explore and focus on one that might succeed. That's where we stand. The same thing with yields, in some cases it still will produce experimental quantities, in some cases now we can make large quantities of matrix. So that's where we stand.

Question - Are there any articles or books that are published that are trying to identify such principles besides an

aspect ratio control even if it is debatable that the principles are correct?

Reply - Not in the sense of making perfectly uniform particles. That has been mostly an empirical field.

Question - Is it possible to make very high aspect particles, maybe to use as reinforcements?

Reply - Oh yes, we make particles of any aspect ratio, so that's no problem.

Comment - What are the forces or interactions which shape the particle if it's amorphous?

Reply - Oh, if it's amorphous it's very simple. Amorphous particles I can understand, our problem is how to understand spherical particles. Amorphous particles are essentially spherical if you make it in uniform shape. They are properly done by controlled kinetics, which makes them come out spherical.

SOL-GEL PROCESSING

Dr. L. L. Hench
University of Florida

Dr. Hench began by discussing the potential advantages of using sol-gel processing in preparing high performance ceramic structures. He stated that they show promise in providing for the simple forming of complex shapes using low temperature infiltration and densification techniques resulting in the ability to control volume porosity and interfacial chemistry. He felt that control of these parameters would result in good oxidation resistance coatings for non-oxide systems. He suggested a gel matrix with alumina, carbon, or silicon carbide fibers as possible composite systems to be made by the process. He showed specimens prepared at the University of Florida that demonstrated their ability to prepare some of these materials at the present time. He then discussed the use of controlled drying agents that provide one method of controlling the final grain size and pore structure of a sol-gel processed ceramic, especially in composite systems that may require multiple step infiltration where interfacial cracks may form due to matrix shrinkage away from the second phase.

The possibility of preparing ceramic fiber, mat, or weave composites using a gel matrix by standard organic preform technology was discussed. The advantages would be a concurrent preform conversion and matrix densification. The present concern with this approach is the weakening of the fibers resulting from an interfacial reaction between the fiber and matrix.

Dr. Hench indicated that a porous gel matrix could be used in conjunction with CVD or CVI to impregnate the matrix with SiC, Si₃N₄ or C followed by a final densification step. This has the potential for providing a very small diameter second phase, high aspect ratio, uniform distribution, and good control of the interface and volume porosity. Dr. Hench voiced concern about the fact that this is not a standard SOA process, the second phase may not act as high strength fibers and that densification of the matrix may not occur.

The potential advantage of preparing gel-derived SiC, Si₃N₄, or Si-C-N monoliths were also mentioned; e.g., ease of forming at lower densification temperatures and control of pore size distribution. However, Dr. Hench expressed concerns about the possibility of a lower fracture toughness material resulting and the unknown oxidation resistance of the materials prepared by this method.

Dr. Hench suggested that sol-gel processing techniques might also be used to provide protective coatings for fibers, weaves, mats, etc., prior to their use in ceramic composite systems.

Dr. Hench summed up by explaining that there are five major stages in the sol-gel process (Figures 1-3): sol preparation, gelation, aging, drying, and densification. He also pointed out the importance of the aging process (no loss of liquid from the pores) where a large change in solid-solid particle contact area can occur with virtually no change in pore size. This can substantially affect the final strength of the material.

Dr. Hench believes that the use of DCCA stops the growth of network polymers very early in the process, ultimately resulting in uniform particles, more uniform evaporation, lower drying

FIGURE 1

CONTROL OF SOL-GEL PROCESSING WITH
ORGANIC ACID DCAA'S

STEP 1: Sol FORMATION

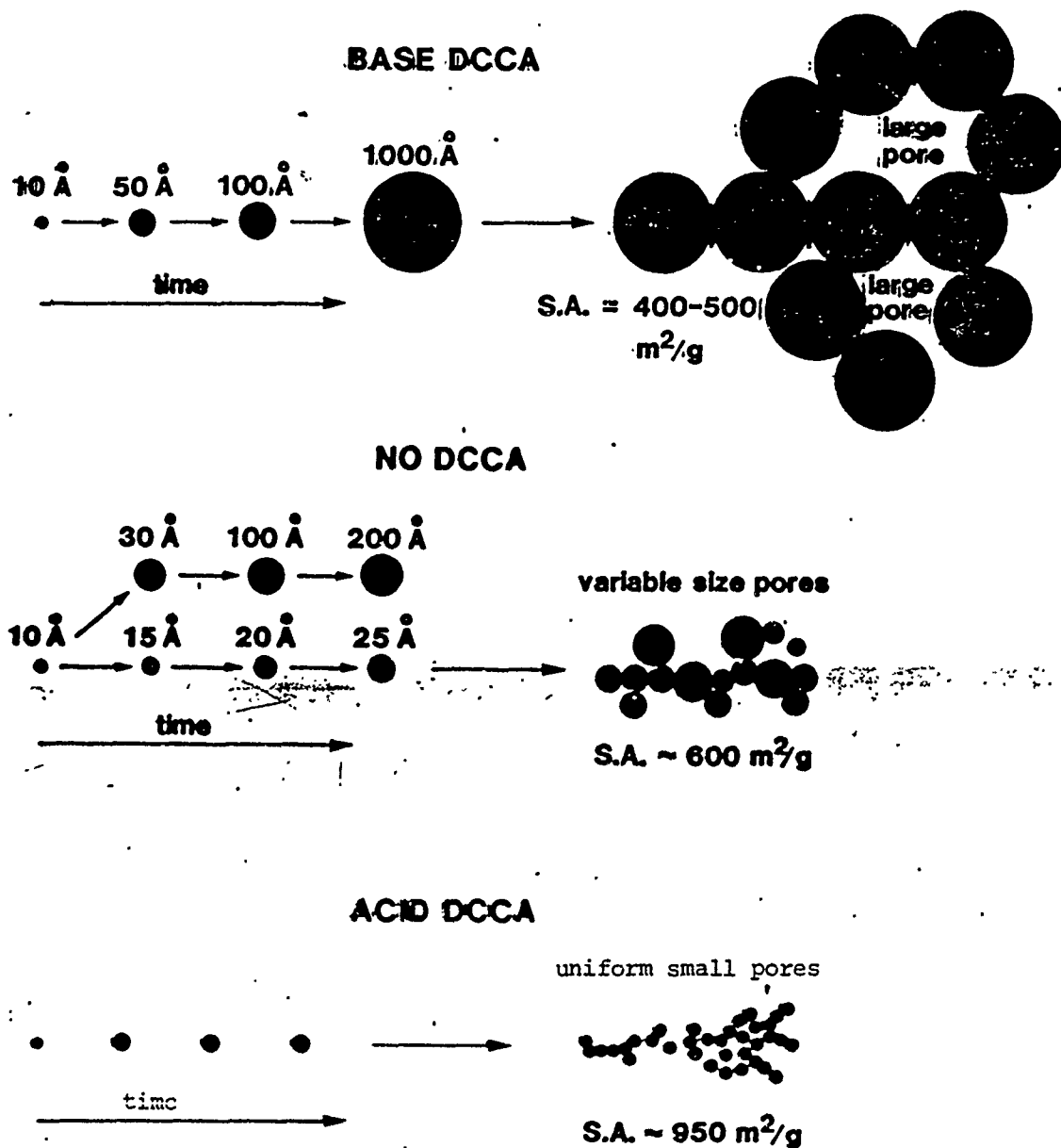
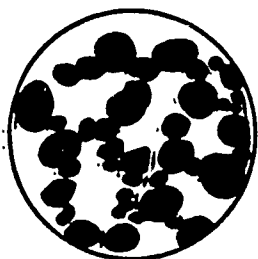


FIGURE 2

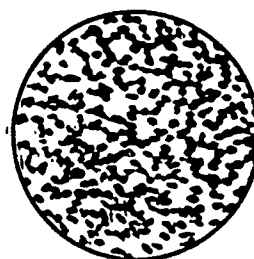
STEP 2: GELATION

(A) Without DCCA



large pore distribution

(B) With DCCA



Si(OR)_4
+
 Si(OH)_4
+
 H_2O
in pores

small pore size distribution

STEP 3: AGING

(A) Without DCCA



(B) With DCCA

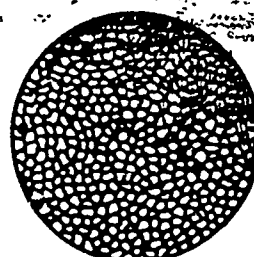


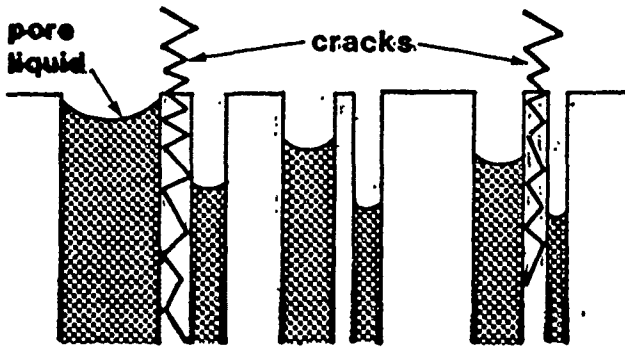
FIGURE 3

STEP 4: DRYING (Minimize Drying Stress Due to

$$p_i = \frac{2\gamma \cos \theta}{d_{ii}} \text{ by}$$

Minimizing Δd_{ii} ; $\Delta p_i = 0$ when $\Delta d_{ii} = 0$

(A) Without DCCA



large differential evaporation
large stresses, large σ
distribution
→ CRACKING

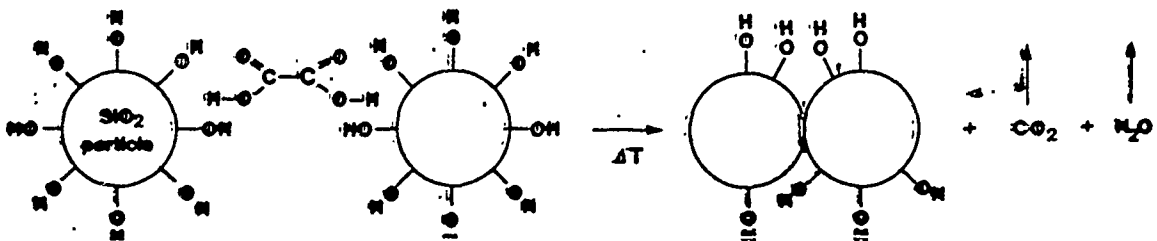
(B) With DCCA



little differential evaporation
uniform σ
uniform stress distribution
→ NO CRACKS

STEP 5: DENSIFICATION

DCCA Eliminated as Vapor before Pore Closure



stresses, and uniform neck formation between particles. The control of these parameters ultimately results in eliminating crack formation (Figure 4).

Dr. Hench concluded by stating that he believes that innovative ideas are a result of researchers having the freedom to try new approaches without fear of reprimand if your ideas don't work and that breakthroughs cannot be targeted within specified time periods.

In his concluding remarks he listed questions he felt would have to be answered before sol-gel processing can be considered practical in the fabrication of structural ceramics for use in high performance applications;

1. Can we apply the same principles to multiphase systems that are currently being used to prepare single phase systems?
2. What are the effects of higher pressures on gel formation and densification?
3. Can we precipitate second phases at the ultrastructural level?
4. Can full impregnation of high surface areas be achieved, and can precursors be developed that will not produce excessive volatiles which would result in high shrinkage and unwanted porosity?
5. Can proper densification be achieved in multiphase systems?

Floor Discussion

Comment - I don't recall your listing many principles, even for single phase systems. Are there any?

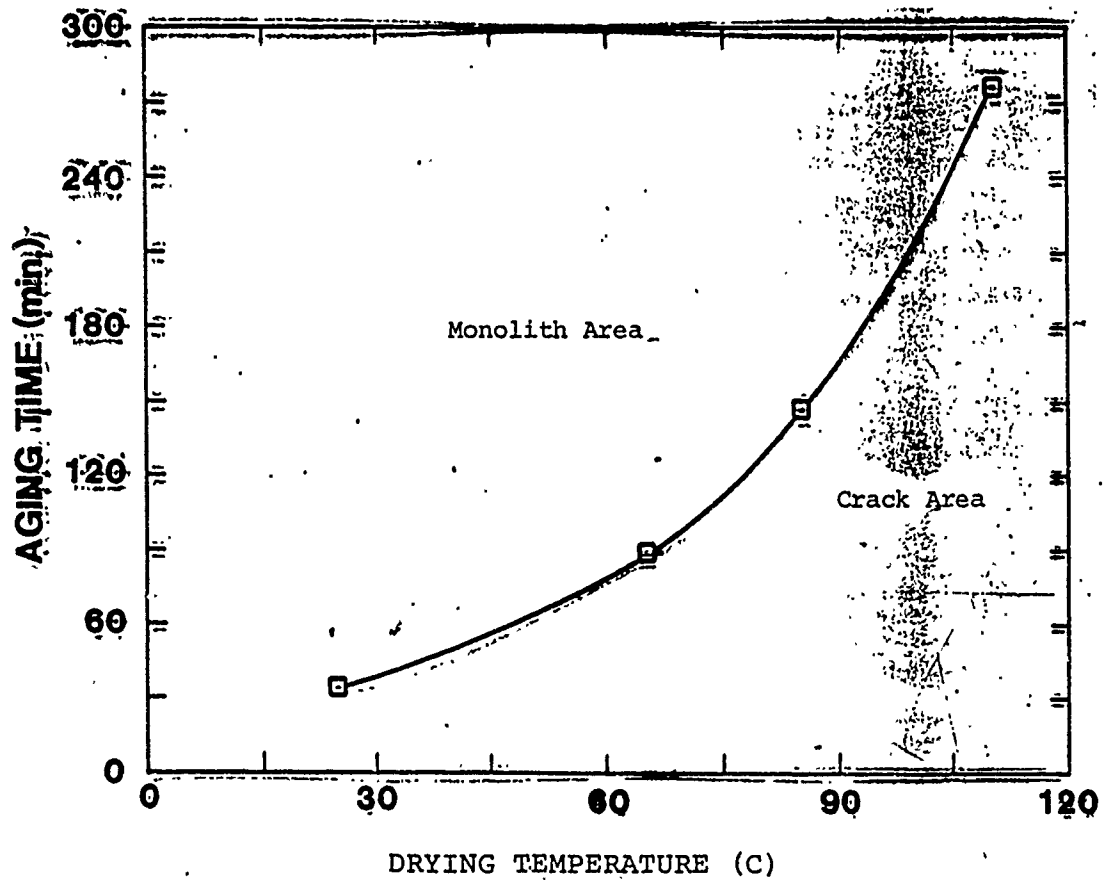
Reply - Not really, however, we can generalize about the behavior of certain additives and feel fairly confident about the results. This simplifies moving from one composition to another. We haven't seen how we can do even that in multiphase systems.

Comment - Isn't that just for the one material, silica, that you have some principles worked out?

Reply - Yes, we use the silica system as the vehicle to determine the number of functional units and the size of the

FIGURE 4

MONOLITH & CRACK AREAS BETWEEN THE AGING TIME vs. TEMP.
CURVE SAMPLES WERE AGED 65C X MINS. THEN OPENED & PLACED
IN DRYING OVEN



molecules that can be made. We have it bound on a couple of sides, but we don't have it boxed in.

Comment - We did a similar thing with binders that was reported at the Cocoa Beach meeting. Instead of drying agents we used methylbimethoxysilane which hydrolizes to methylsilanetriol. This allowed us to make very large pieces without having drying agents that had to be removed.

Question - It's not one of your questions, but thinking about these drying additives, the glycerol is not going to be volatile as far as removing, right. So that you have a problem with getting that out of the alumina system. The other question is, the two that are seen are oxalic acid and glycerol, and it seems to me then that the picture you seem to be drawing is of a difunctional catalyst which is pulling two things together, causing aggregation, catalyzing the aggregation if you will, of the dehydration. In general, is that true that you think things that activate catalysts are difunctional?

Answer - That's right. They're at minimum difunctional, but they can also be multifunctional. A study of this is something that would really be worth a long-range research effort. This isn't going to come easily because so much less is known, both about the precursor molecules and the solvents.

Comment - There is a study that graduate students are doing at Penn State and if I understood what you said, would suggest that what you said is correct. We've been doing nitridization of surfaces and that involves first-stage reaction to produce an active chlorine group. Then an ammonium reaction that leads to a silicon nitride film on the surface with the attendant of optical index of the silicon nitride on the surface. It's been a very exciting program, and I think it could work.

Comment - It came to my attention that in the original classical paper of liquid ammonia, and the similarity of its chemistry with water, it was done by a chap, whose name I forget, at Stanford. He considered reactions of this kind, silicon disulfide and many more. That's what often happens in chemistry. The guy that

starts it often does conceptually most of the chemistry that's going to be involved, and then it gets forgotten.

Answer - That would be very useful to have that available and reviewed.

Comment - It is also possible to make composites this way. You could fill those pores with another phase of organic. The monomers can penetrate and you can polymerize it with UV or something. You'd have a continuous two-phase by making an open foam structure and fill pores with second phase.

Answer - David Clark and a student named Chuck Davies reported at Cocoa Beach in January their preliminary observations of using one of the alumina gels and then doing RF polymerization to form silicon carbide within the pore structure of the alumina gel. There is some spectral evidence that they actually did have the silicon carbide structure formed inside the pores. I think that this is an area that could be one of the most exciting ways to get super-tough materials.

Question - How is the shrinkage of the gel accommodated when you use this technique?

Answer - We don't know. The black samples that were passed around -- in that case there was almost no shrinkage. As you densify that, which eventually has to be done to have anything of any real interest for most applications, we don't know. We've taken a composite like the black ones around up to 1650°C in an inert atmosphere with no shrinkages, no densification at all.

Comment - It's never going to be 100% theoretically dense because you're always going to take a volatile out of the species you put in the pores that you're trying to fill.

Answer - So you can get 100% density. You'll get the volatiles out before you get more shrinkage closure and then the pore closure would just be driven as in any sintering process. If you keep the pore size down, you should be able to get 100% dense matrix.

Question - But you're saying densification after forming the second phase.

Answer - Yes, then you have to go to a higher temperature or some method using high-temperature and pressure. The problem is the ultra submicron pores in the matrix are the fibrous kind. The question was, are the pores that are in the matrix, when they go away, there has to be shrinkage that takes place if you can get residual volatiles out of the pores before they close and keep the size down assuming you can generalize the silica system to the composite system. The size is so small that the driving force for the pore removal is very high and you should get pore collapse closure, and elimination 300°-400° lower than you can get with the pore distributions that presently are found in powder compacts. The comment about the monoliths without the whiskers, I can't see that the matrix should behave any differently than the monolith. You should get the lower temperature densification of the matrix around the whiskers. But we've not been able to see whether that can happen because we haven't solved the problem of getting the matrix fully impregnated, so there's always some big cracks present when you do any measurements. Those control the properties. You'd have to get the macro-defects out of the first stage of making the composite in order to test whether the full potential can ever be achieved. Does that make sense?

Question - I'm having trouble with that. Is not the density of the matrix after the volatiles are out, is the matrix fully densified? Is not the density of that matrix less than the theoretical density of the material?

Answer - The density before it's densified is definitely less.

Question - But what I'm saying is that, after the volatiles are out, at that stage the density is less than the theoretical density. Well, in that case, if the external shape retains its dimensions, there's got to be shrinkage.

Answer - There's no controversy on that point. The question is how much shrinkage and how much will be accommodated and we don't have the answer there because all the data is skewed by the presence of the nonimpregnated portion which has the macrocracks. If you can achieve the ideal, which is full impregnation of a

whisker array with the gel -- if it's fully impregnated like that one corner of that SEM showed that portion was, then the pores that are present will have only the same very narrow distribution with a mean around 50-100 angstroms. When densification occurs they should all go down at the same time and there should be no large pores present so there's nothing to trigger the formation of the cracks.

Comment - If the fibers form a rigid framework, then they're going to oppose densification and you go into an Oswald wiping mode where you get more pore growth.

Question - In the weaves, for example, that you get to anything greater than say 90% densification, the matrix which would then require impregnation to get the rest of the strength. But in a whisker composite, what we've seen is that the whiskers move with the gel as the gel is densified. The whiskers aren't connected together so they are free to respond to this elastic motion of the matrix as it's densified. I think that is the most likely system to go to full density without macrocrack development, whether you can do it with a weave or mat type where the fibers are already connected, I think it's pretty questionable, too.

Question - Do you think there is any possibility, in the alumina kinds of matrices, of retaining a microporous structure at temperature. I think it would be very interesting if they make this kind of material to have a kind of foam structure at the end which would effectively give you kind of a low modulus to accommodate this kind of volumetric change. One could have a porous structure with a pore size small compared with the reinforcing phase, I would think that would be an extremely interesting kind of material.

Answer - Until this meeting, I didn't know that there was any possible interest in that sort of thing, so I looked at the black sample as a failure. We heated the silicon matrix/silicon carbide whisker composite up to 1650°C, held it for a weekend, and came down with the temperature and it hadn't densified. How far that can go without losing the porosity and what its properties are, we're encouraged to do some measurements on that material.

Comment - There's one more general solution to the drying problem and that is to reduce the total amount of shrinkage by putting in densified grog. I think that is very important work that was done at Dow Laboratories, making optically transparent silica or fiber optics. What they've done really is they've gone back to the old ceramic traditional processing where you cut down the drying shrinkage by putting in a fraction that doesn't shrink.

Reply - Along those same lines, one of the things we've seen is when we've tried to add colloidal monomers of silica powders to the silica gels, certain combinations of process conditions can lead to non-crack, but others will just degrade the whole compact. Also, the process conditions that work to contain an uncracked second phase filled system, at least in our hands, are not the same combinations of things that lead to the uncracked, single phase unfilled system. It looks like there's a lot of areas for investigation to put together the two concepts that we've been talking about. We have not been able to just routinely add a second phase to the same process and have it end up working. It has to be manipulated independently.

Comment - Along those same lines, I know you're familiar with it, the other approach of a similar type is in George Sherer's work, where you start with a system of colloids and gels that you can certainly make monoliths with. That, in a crazy way, could be viewed as almost a combination of the two views. That is, that colloids end up going through a gel and then goes through all these other sorts of operations.

Comment - Let me say a few things about that, because I think there's going to be a lot happening there in the near future. Of course, we are presenting diphasic gels as though they have just suddenly been discovered. While there are a lot of new things to do there, the concept is really rather old. Silica gels have been impregnated with things for many years and catalysts so produced. But things have gone on already that are in the literature that are quite interesting. For example, if

you take something like dispurol, which you can gel very nicely to make grinding grain. In our work on the radioactive wastes, we absorbed the radioactive elements on the dispurol (as many as 30 elements in the periodic table) and can gel that stuff up and go through this process with that. What becomes immediately evident is that all the additives to the gel really change the way the unheated gel develops. In particular, when you get these super-amorphous materials, then at higher temperatures you get all kinds of coupled crystallization phases. The act of one phase crystallizing from this rather ill-defined amorphous sort of material tends to throw out another crystalline phase, and so on. What we are doing now is copolymerizing our alkoxides by two new techniques, without alcohol or water. This exaggerates these effects, because then you have a very, very dense polymer. For example, we're doing alumina zirconia this way. You can fire it all the way to 1700°C and the coupled grain growth is so inhibited that a trigonal zirconia is obtained with no stabilizing additives at all. I think a lot of the zirconia is getting engulfed within the alpha alumina as it develops. Another thing we have seen from these polymerized materials is alpha alumina forming on the gamma-phase material at 850°C which is quite low. It is not the lowest that has been seen before, but I just throw this out because I think there is a lot of phenomena here. It is going to be very interesting from the ceramics point of view, because first of all there's the colloidal interests and what happens there. Also, there are the new ceramic situations.

A general discussion of silicon carbide (SiC) matrix and fiber materials prepared by sol-gel techniques ensued. Problems with the one SiC fiber commercially available (Nicalon®) were also referred to. The discussion then focused on the possibility of copyrolysis as a method of preparing ceramic/ceramic composites.

Comment - I think you can fabricate many structures by that technique. There are a lot of places that try to do it in combinations of very stable carbon fibers and polymer precursors and things that create structure in a material. But I think just a word of caution again regarding the relationship of the tensile strength of the fiber and the interfacial strength. Generally,

it is difficult to make strong fibers in any case, and to try to do it in some process where you have the matrix and the fiber being generated at the same time, I don't think you're going to make very strong fibers. So we degraded the tensile strength of the fibers. In addition, generally in these processes we do generate much higher interfacial strengths between the reinforcing stage and matrix so we upped that because that's generally why you find that although you've broken a lot of structures you have very effective component strength.

Comment - I was wondering if there is any objection to wetting fibers with an iron oxide. You can produce it very easily. There's no problem in any isometric shape. They're very interesting rod-like particles, so you can almost tailor the reinforcing agent. It would react with this matrix very nicely because iron oxide surface is a reactive surface and it would form bonds and you can have here a lot of different materials that you could control and relate to the final properties. They are easily made and you can control anisotropic properties without much difficulty. You could make long, elongated, shorter, stubbier particles and so on. That would be a good experimental case. Also, zinc oxide can be made nicely like that. But I think this is the cheapest, most easily made material with good quality.

Comment - I'd hoped that this discussion would have spent more time on coatings. Because I think in general we find that there are more techniques to generate a very high-strength and a very high elastic fiber. But with very little latitude in the chemistry of those things that are generated, I think we're going to have to solve all the chemical problems that come up through the use of coatings on fibers or whatever you're working with.

Comment - In these last few minutes here are some thoughts on achieving super-tough, super-performance composites. It seems to me that we have three general approaches that can be considered.

1. One is to make the strong fibers, lay those up in some way, put a matrix into them, and see if you can get better performance by the control of the microstructure of the matrix, the interface between the matrix and the fiber, and the coatings.

2. To have a pre-fiber in a matrix and then achieve the densification of both, with the limitations that have been mentioned where you tend to have difficulty in getting the strength of the fiber under those conditions, and the control of the interface due to the tendency for a reaction between the two.

3. A third general alternative is to start with a single phase system by using, for example, the sol-gel processing and then through manipulation of temperature, atmosphere, or some other means, induce a second phase to appear in the matrix with high enough aspect ratio that it can act as a reinforcing phase. with a substantial enough composition difference to provide a large difference in modulus that it also acts as an effective reinforcing phase.

Comment - You left one option out of there. How about putting something in there about transformation of the ceramic approach?

Answer - Right, that would be a fourth category.

Comment - Just one note on that. The ultrastructure that you're talking about where you are able to make very finely dispersed second phases that allow you to control the small cracks. However, when you get the large strain fields associated with cracks, the very fine structures will actually have no effect in toughening the material and that is an argument of scale. In the engineering sense what we're trying to do is generate a reliable material. We're talking about large strain fields and microstructures will not stop them.

Comment - We're talking about the importance of the K_{IC} value. They still fail in the same way that a ceramic fails and that is that you'll end up with two pieces at the end of the test. You may have a fracture toughness number and you may be able to use that in some instances, but that's not the general structure of the material.

Comment - Transformation toughness is also very useful because it generates a large strain field. The larger strain field the larger the area that goes through the transformation toughness process. It depends on the surface properties and on the fiber matrix coupling. You can't separate the thing. You can't just answer it that way. It's a more complicated question.

Question - Are you all saying as a group that all you can do is go in the lab and use whatever comes to mind and cookbook up something and still have to wait upon the design ... you wait until down the road a year and a half later some engine tester gives you some feedback and says yes or no it isn't going to do it.

Answer - Well, it would be nice if we had a test and a criteria for toughness. Banking against the chair is very cute and all but it doesn't really help much because that's not a quantitative test in my lab.

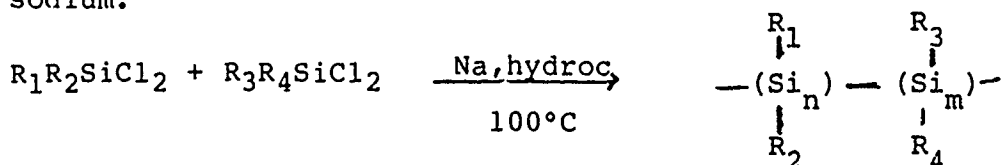
Comment - It's a very good point, but the point about composites is that you don't have a single toughness, and you can't use the standard criteria for a toughness for a material. And the other thing is that the toughness numbers that you get only give people a warm feeling. They don't use them in design. It is just a warm feeling. If you tell a guy who is familiar with a metal that he's got a certain fracture toughness number, he can only use that in reference in regard to other metals he's working on. If you tell him the same fracture toughness number for a composite that failed in a different mode, there's no relationship between them.

THERMAL TREATMENTS FOR ORGANIC POLYMER PRECURSORS

Dr. Robert West, University of Wisconsin

Professor West began his presentation with some definitions concerning polymer chemistry (Figure 1) and the types of organo silicon polymers that have been investigated (Figure 2). The interest in ceramic precursors began when Yajima and his coworkers (Figure 3) showed that permethylpolysilane can be used as a precursor for silicon carbide. In Yajima's process, the polysilane is first heated at 400°C to produce a polycarbosilane. The polycarbosilane was fractionated from solvents, spun into fibers, oxidized on the surface with air to give rigidity, and finally pyrolyzed at 800-1350°C to produce SiC. Professor West also discussed several other polymers which contain boron and titanium. However, all of these polymers contain substantial amounts of oxygen (Figure 4). The products obtained upon pyrolysis contain oxygen as well as carbon and are complicated materials.

Robert West and others have found that introducing other groups besides the methyl group greatly decreases the crystallinity of polysilanes. Over 70 new homo- and copolymers have been synthesized by co-condensation of diorganodihalosilanes with sodium.



These polymers are usually soluble in organic solvents such as ether, THF, toluene, and benzene (but not hexane), and can be melted, molded, cast into films or drawn into fibers. Most of Professor West's work has been done with polysilastyrene which is prepared from dimethyldichlorosilane and methyl phenyl dichloro silane.

FIGURE 1

SOME POLYMER TERMINOLOGY

R,(S) : Repeat Units

ADDITION POLYMER : $nR \rightarrow \{R\}_n$
(polyethylene)

CONDENSATION POLYMER : $n \text{ XRX} \rightarrow \{R\}_n + 2nX$
(nylon)

HIGH POLYMER : $n > \sim 50$

OLIGOMER : $n = 2 \text{ to } \sim 10$

RANDOM COPOLYMER : -RRSRSSSRSS-

BLOCK COPOLYMER : $\{R\}_n \{S\}_m \{R\}_n$

"LIVING" POLYMER : $-R-\{R\}_n-R-$ (active ends)

END-CAPPED POLYMER : $E \{R\}_n -E$ (inactive ends)

LINEAR POLYMER : 

CROSSLINKED POLYMER : 

FIGURE 2

Types of Organosilicon Polymers ("Polly who?")

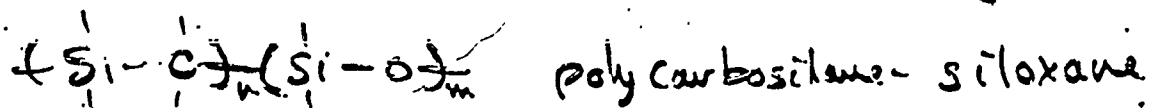
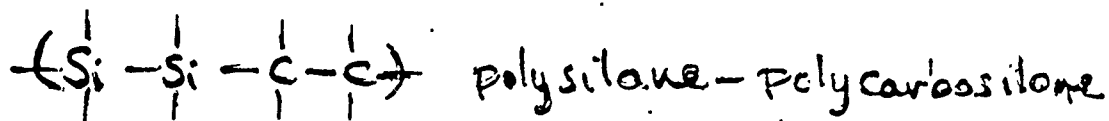
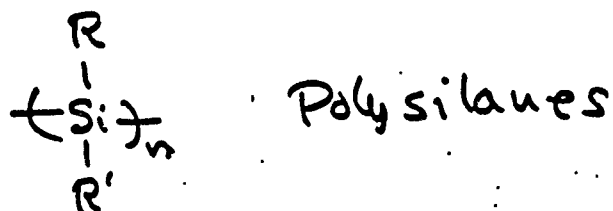
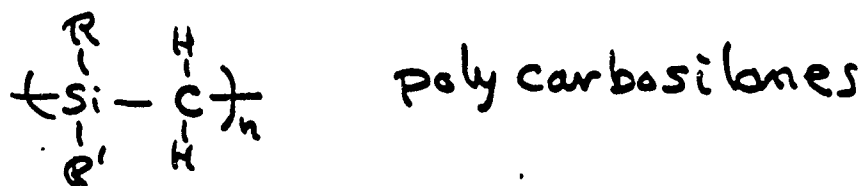
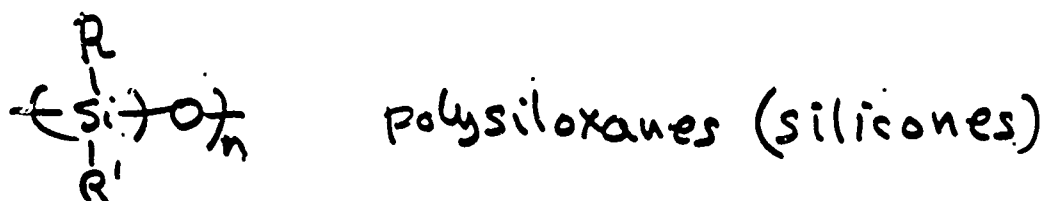
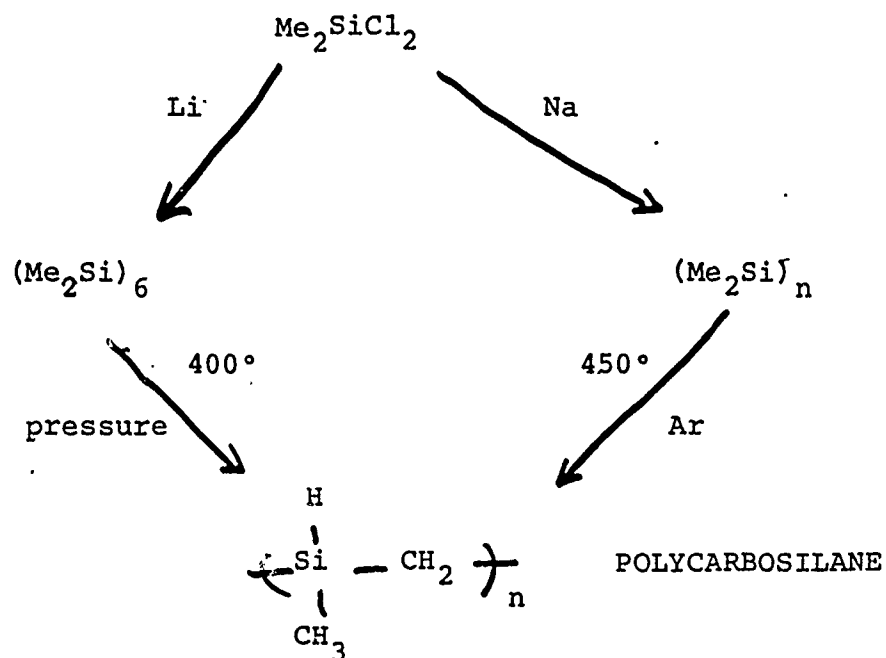


FIGURE 3

YAJIMA-NAYASHI PROCESS



- a. Δ VACUUM TO REMOVE VOLATILES
- b. FRACTIONATE BY PRECIPITATION
- c. SPIN INTO FIBERS
- d. Δ , 200 IN AIR TO OXIDIZE SURFACE (SiO_2 ,
- e. FIRE TO 800°C

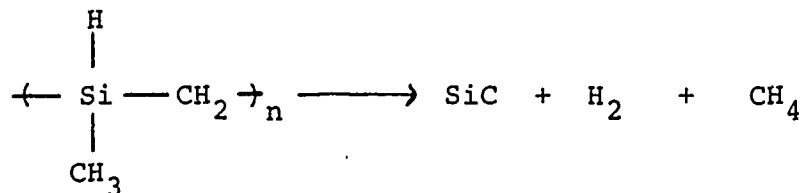
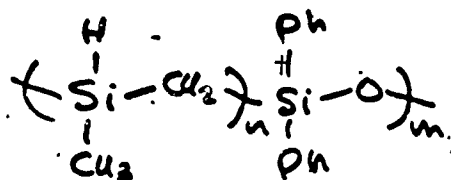
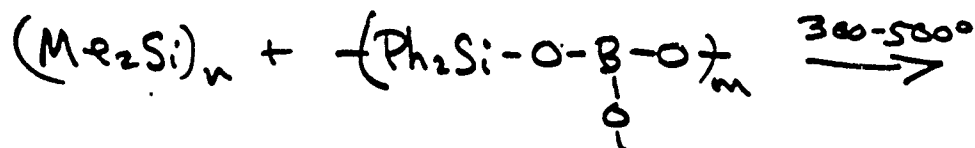


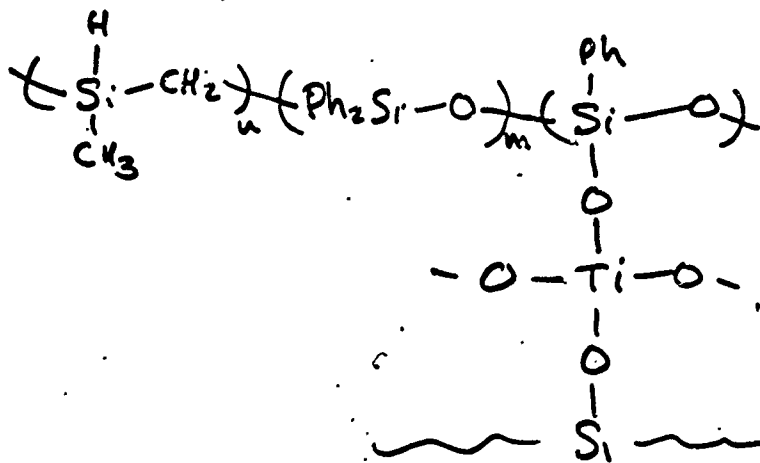
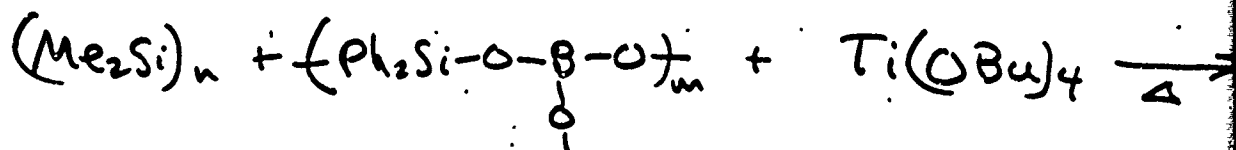
FIGURE 4

Nippon Carbon : Improved Polycarbosilane
"PYTHON"



$$\frac{n}{m} = 5 \text{ to } 200$$

Use Industries : Polycarbosilane Precursor
to SiC-TiC



After firing:

Si 45, Ti 30, C 25, O 23 %

Molecular weights of these polymers have been measured by size exclusion or gel permeation chromatography using polystyrene as the standard. These polysilanes have three molecular weight ranges which include a very high molecular weight fraction, a moderate molecular weight fraction and then oligomers. Molecular weights of the high molecular weight fraction are over 1 million based on polystyrene calibration.

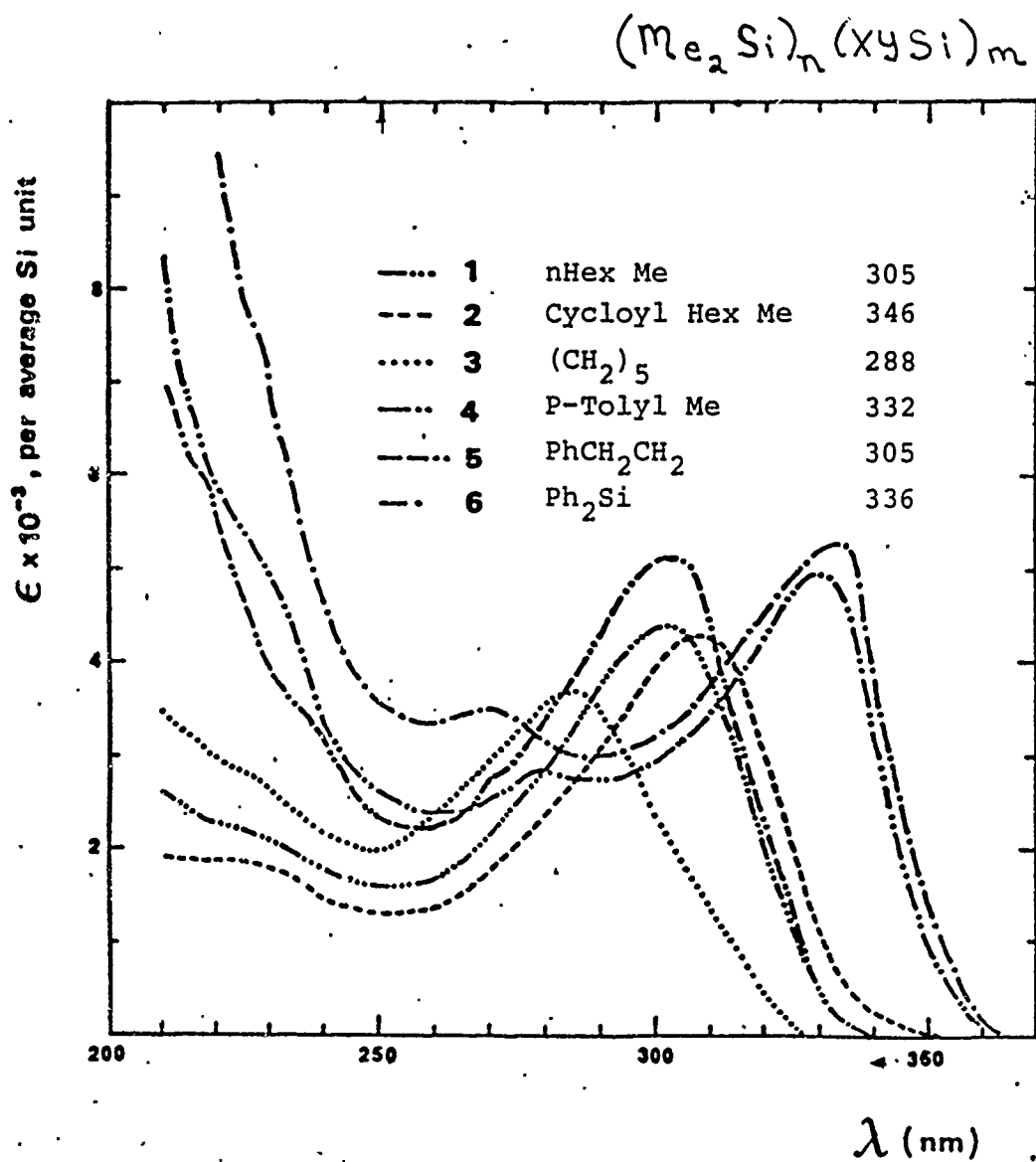
The formation of soluble, meltable polysilanes offers the possibility of preparing silicon carbide directly from the polysilane, rather than going through the polycarbosilane. For this process to be successful, the polysilane must be crosslinked, otherwise weight retention upon pyrolysis is low. Polysilastylene and other polysilanes which have aromatic groups attached to the silicon can be photo crosslinked by irradiation with low-energy ultraviolet light in an inert atmosphere. The resulting crosslinked polymer converts to SiC. Figure 5 shows the UV absorption spectra for these types of polysilanes. Irradiation at 300-330 nm induces crosslinking.

The crosslinked polymer becomes stiffened, insoluble in organic solvents, infusible, and films adhere to the substrate. Thermal gravimetric analysis shows that weight loss begins at a little over 200°C and the ceramic yield is 30%. If all Si were converted to SiC the yield would be at best, 50%.

This polymer has been converted to fibers at the 3M Company. The drawn fibers were photopolymerized so that the outer layer has been crosslinked and converts to SiC upon pyrolysis. The inside volatilizes during pyrolysis leaving a hollow tube. (Figure 6.)

These types of polymers are also good materials for photo resists, and photo resists can be made in either the positive or negative mode (Figure 7). In the positive mode, the polymers that are used as photo resists undergo photo scission upon expo-

FIGURE 5



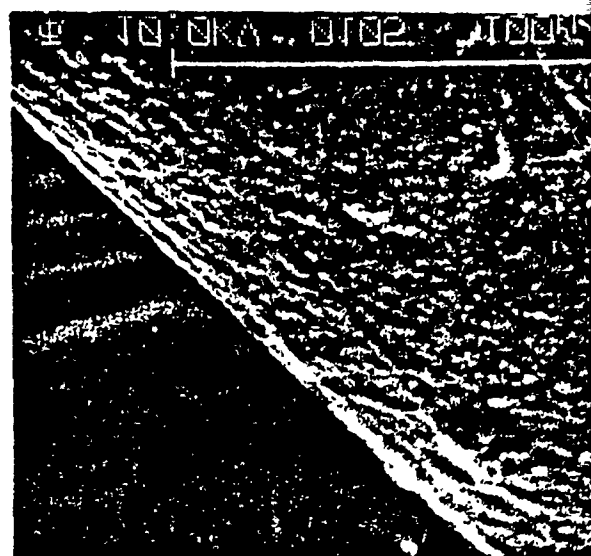
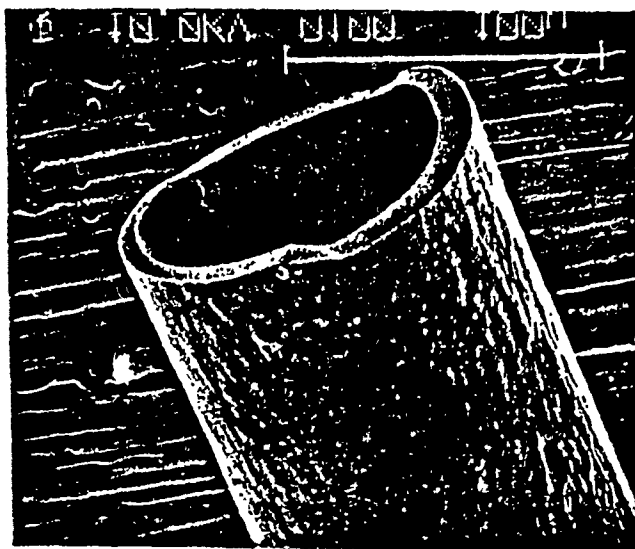
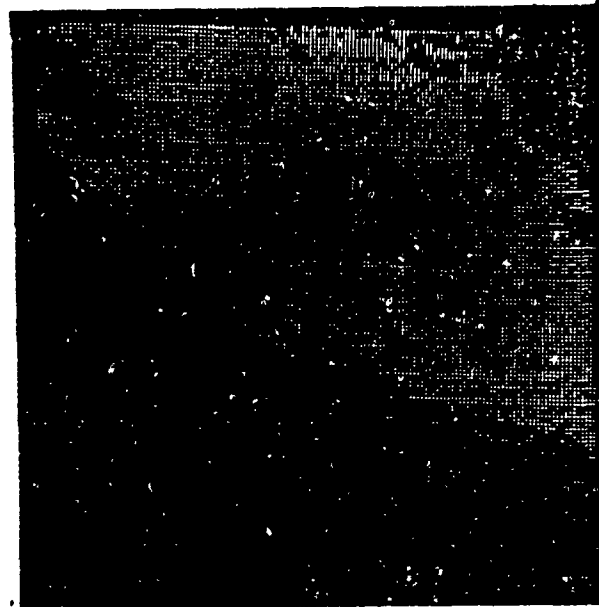
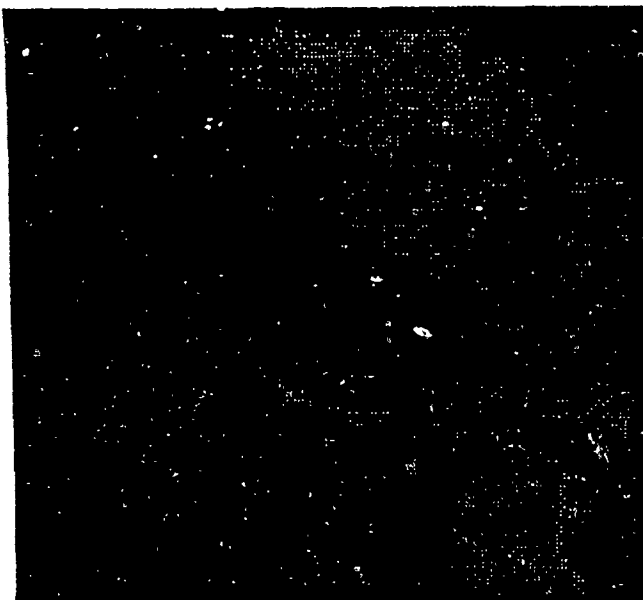
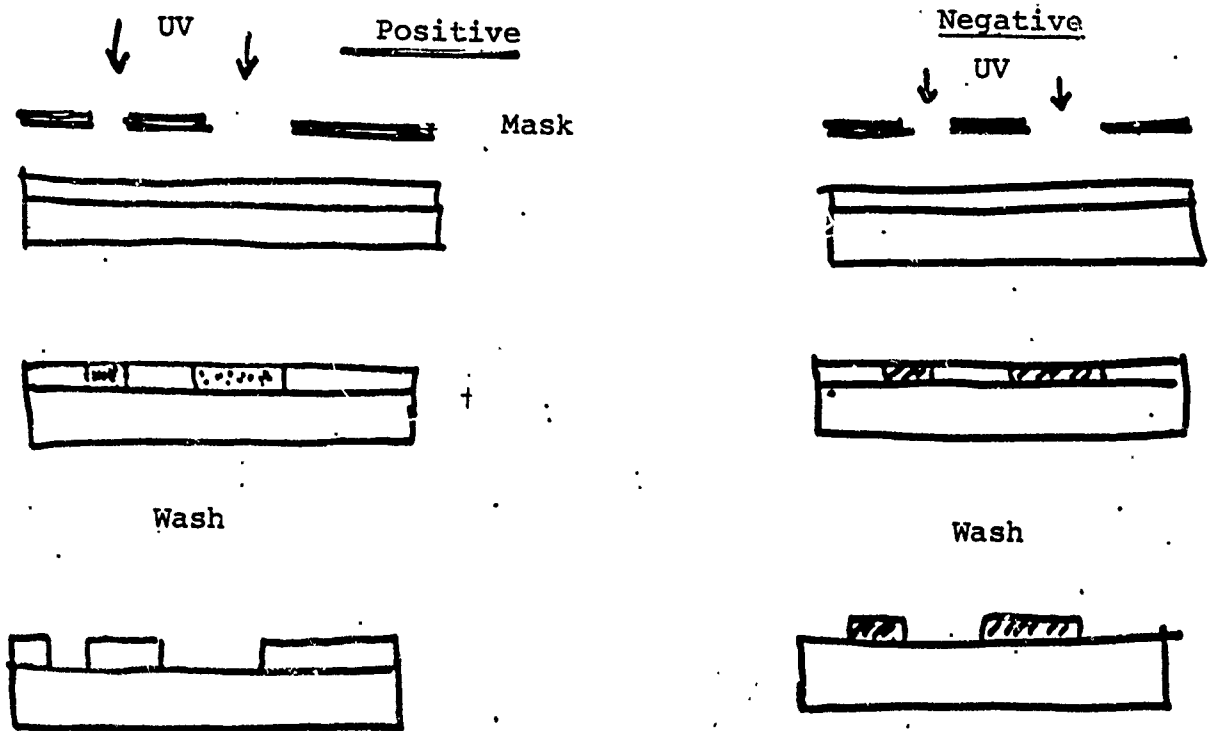


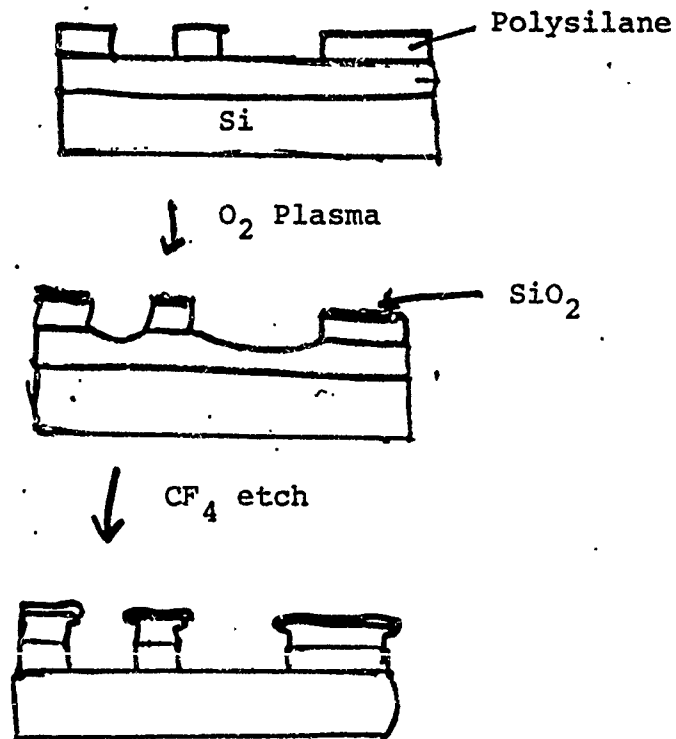
FIGURE 6.

FIGURE 7

POLYSILANE PHOTORESISTS



POSITIVE BILAYER



sure to UV light (they contain no aromatic or unsaturated groups). The polysilane is degraded where the light gets through the mask and the degraded polymer is washed off using the appropriate solvent.

In the negative mode, a polysilane is used that contains aromatic groups and crosslinks when exposed to UV light. In this case, a solvent is used that dissolves the polysilane and the crosslinked polysilane remains in place. Some examples of etched silicon chips using polysilane photo resists are shown in Figure 8.

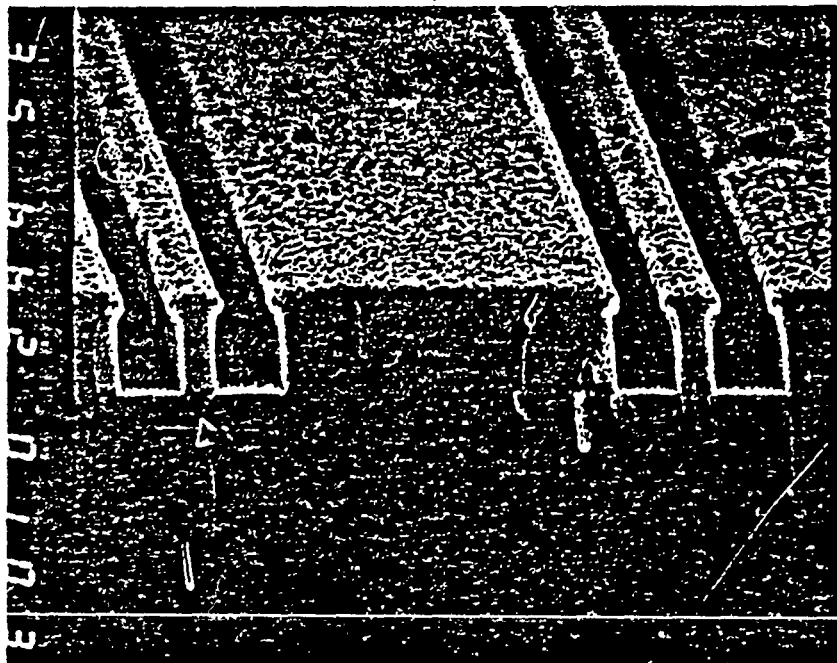
Crosslinking is vital for good yields of SiC. Therefore, Robert West has looked for other crosslinking mechanisms. Allyl groups survive the condensation reactions and can be crosslinked with UV radiation. The polymers containing allyl groups rapidly gel by irradiation at 300 nm.

Another approach being investigated is to make hydrosilane polymers where the hydrogen is bonded to silicon atoms. This is not easy since Si-H bonds are reactive. The polymer is end capped with a monochlorosilane so that the polymer can be isolated under strictly neutral conditions which is necessary for the Si-H bonds to survive. Now the polymers can be crosslinked using conventional technology and using vinyl compounds such as $(C_2H_3)_3Si(CH_2)_4Si(C_2H_3)_3$, trivinylphenylsilane or divinylbenzene, and a little platinum tetrachloride. Hydrosilylation addition of the Si-H bond to the vinyl groups takes place and rapid crosslinking occurs. An easy way to do the crosslinking is to mix the polysilane with some polyvinyl compound, such as tetravinylsilane, and use either peroxide or UV light to generate free radicals to crosslink the polymer. Crosslinking can also be initiated thermally.

Questions and discussion followed Professor West's presentation. Most of the questions were about their use as SiC precursors but this work has not been done.

FIGURE 8

POLYSILANE BILAYER SYSTEM
SCAN SPEED 8000-POSITIVE TONE
(0.83 μ)



Conclusions:

- Crosslinking is necessary to get good yields of SiC.
- Polysilastyrene is available from Shin Miso Nako Co., Japan. Information is available from Robert West.
- UV radiation can cure sections about 10 μ m in thickness.

Questions which were asked but their answers were unknown.

- Why are U.S. companies not interested in making polysilanes developed by the University of Wisconsin?
- What is the mechanism of the photo crosslinking?
- How long does it take to crosslink by UV radiation?
- How does the degree of crosslinking effect SiC stoichiometry?
- What volatile compounds are formed during pyrolysis?
- What rearrangements occur during conversion to SiC?
- Should someone make quantities of polysilanes so that samples can be supplied to researchers interested in studying these compounds as SiC precursors?
- Should Government fund a pilot plant type of operation?

SiC PRECURSORS
Dr. Curt Schilling
Union Carbide

Following Professor West's presentation, Dr. Schilling (Union Carbide) presented his work on SiC precursors. This work was funded by Dr. Kenneth Wynne at the Office of Naval Research and is currently being continued with Union Carbide support. Samples of the polymers synthesized

in this effort will be supplied to people who ask for them, free of charge.

The first seven figures cover "prior art" and were not discussed in detail. When the program started at Union Carbide John Wesson was doing the work, and he began by synthesizing polydimethylsilanes to see if he got the objectionable sand that Burkhardt got. He did. However, by substituting other R Groups for some of the methyl groups, tractable, soluble, fusible polymers were obtained that could be worked with.

About this time, Yajima's work was published, so the polysilanes were pyrolyzed to see if SiC could be obtained from any of them. Since these polysilanes were linear polymers no SiC was obtained. However, if vinylmethyldichlorosilane is dechlorinated with K and then blocked with trimethylchlorosilane, a polymer was obtained that gives a 40% yield of SiC upon pyrolysis (Figure 8). This polymer was infusible and insoluble and not very useful.

Further work showed that when vinylmethyldichlorosilane is dechlorinated with K, the vinyl group becomes disilylated forming two new silicon carbon bonds as illustrated in Figures 9 and 10. After many experiments, they found that when a ratio of 0.85 Me_3SiCl , 0.3 Me_2SiCl_2 and 1.0 $\text{C}_2\text{H}_3\text{SiMeCl}_2$ was dechlorinated with K in THF a soluble, solid polycarbosilane was obtained (Figure 11). This particular product has been spun into fibers and converted to SiC. Figure 12 shows an idealized structure for this polymer which is a random polymer and not a block polymer. Dr. Schilling has determined that the silicon-carbon bonds are formed preferentially as the vinyl groups react and then the Si-Si bonds form (Figure 13).

FIGURE 1

ORGANOSILANE POLYMERS

OFFICE OF NAVAL RESEARCH

DR. KENNETH WYNNE

UNION CARBIDE CORPORATION

FIGURE 2

COMMERCIAL SiC PROCESS



CHEMICAL VAPOR DEPOSITION



ORGANOSILICON ROUTES

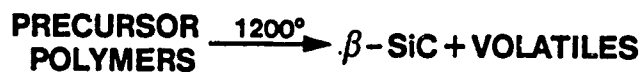


FIGURE 3

EARLY POLYMER ROUTES

- Commercial Siloxane Resins
- Crosslinked Polysilanes
- Rice Hulls
- Polycarbosilazanes from $\text{MeSi}(\text{NHMe})_3$

FIGURE 4

YAJIMA PRIOR ART

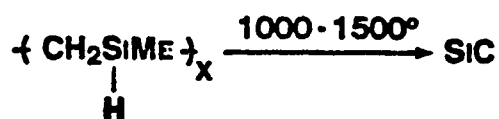
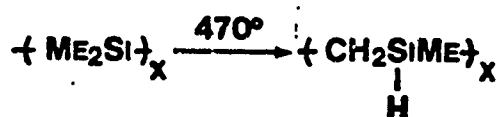
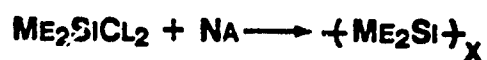
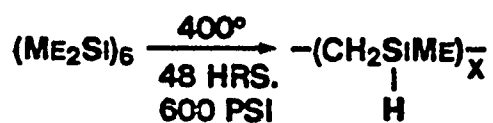
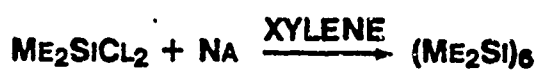
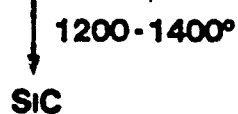
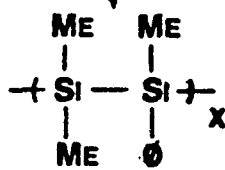


FIGURE 5

**ROBERT WEST PRIOR ART
"POLYSILASTYRENE"**



TOLUENE $\downarrow$ NA DISPERSION - 48 HR



FUNDED BY AFOSR

FIGURE 6

DOW CORNING PRIOR ART

DIRECT REACTION HEAVIES



X = N OR P

CHLOROSILANE

+ RESIDUE

MONOMERS

(US 2,842,580 TO GENERAL ELECTRIC)



**RESIDUE IS THERMOPLASTIC AND
SPINNABLE (GB APPL 2,021,545)**

FIGURE 7

**DOW CORNING
POLYSILANE DERIVATIVES**

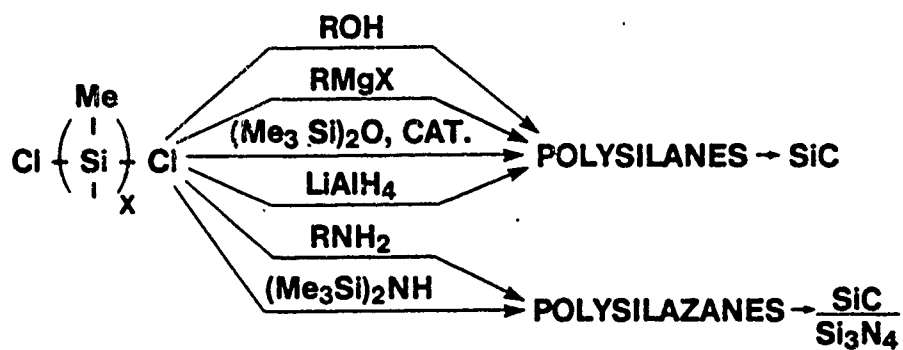


FIGURE 8

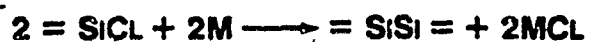
J. WESSON PRIOR ART

POLYDIALKYLSILANES



R = ME, ET, PR

ACTIVE METAL DECHLORINATION



M = NA, K, LI

VINYL SILANES



K | OCTANE



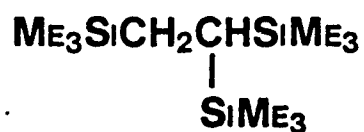
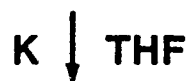
POLYMER

1200°C

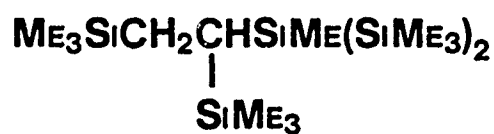
SIC

FIGURE 9

REACTIONS OF VINYL GROUPS



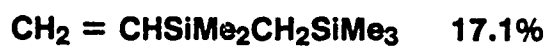
77.4% DISTILLED YIELD



24% DISTILLED YIELD

FIGURE 10

**REACTIONS OF
CHLOROMETHYL GROUPS**



+



FIGURE 11

OPTIMIZED PREPARATION

0.85 Me₃SiCl + 0.3 Me₂ SiCl₂

+ 1.0 CH₂ = CHSiMeCl₂

K ↓ THF

97.3% SOLUBLE SOLID

F = 2.53

POLYCARBOSILANE STRUCTURES



= SiSi = BONDS FORM MORE SLOWLY

FIGURE 13

REACTION MECHANISM

- 1. ELECTRON TRANSFER FROM K TO
VINYLSILANE GROUPS**
- 2. NUCLEOPHILIC ATTACK BY CARBANIONIC
INTERMEDIATES ON $\equiv$ SICI GROUPS**

The structural features that are considered as critical are listed in Figure 14. After examining many precursors, Dr. Schilling found that the polycarbosilane had to be branched, and the branching had to be at silicon atoms in the polymer backbone.

The importance of branching was proven by a couple of experiments. Linear polycarbosilanes were synthesized by methods published in the literature. Both of the polymers illustrated in Figure 15 gave no ceramic yield. However, if methyltrichlorosilane is added to create branching sites, products are obtained which convert to SiC (Figure 16).

Figure 17 lists the advantages of using K in THF. An important point that was made is that the reactions are terminated by adding a mixture of water and THF. The reactions are not terminated by adding water directly to the reaction. Also the reaction is cooled before the water/THF is added. The disadvantages are shown on Figure 18 which shows the by-products produced. Figure 19 lists the advantages of the vinylsilane route.

Figure 20 illustrates methods used to prepare hydrosilyl modified polycarbosilanes. These polymers are versions of earlier polycarbosilanes but use MeHSiCl_2 as a comonomer. Potassium dechlorination converts MeSiHCl_2 to both trifunctional $\text{MeSi}\equiv$ and difunctional $-\text{MeSiH}-$ units, both of which provide improved SiC yields (Figure 21).

Polysilahydrocarbons are copolymers derived from olefins such as styrene or isoprene and dichlorosilanes. The linear polysilahydrocarbons do not give good yields of SiC (Figure 22). The branched polysilahydrocarbons prepared with MeSiCl_3 do give SiC (Figure 23) and one of the better candidates is a copolymer derived from MeSiHCl_2 and isoprene as shown in Figure 24. The chemistry for the MeSiHCl_2 /isoprene polymer is shown in Figure 25, and the bad news is that the yield of copolymer is low from the synthesis. The copolymer which gave high ceramic yield is a

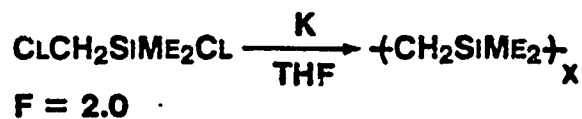
FIGURE 14

**CRITICAL STRUCTURAL
FEATURES**

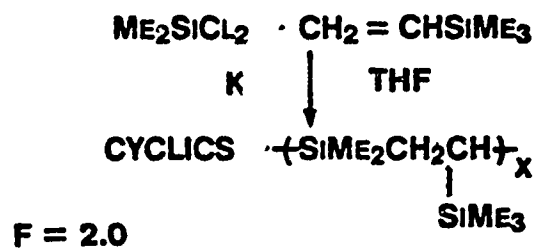
- 1. POLYMERS MUST BE BRANCHED**
- 2. BRANCHING MUST BE AT BACKBONE
SILICON ATOMS**
- 3. FORMATION OF BACKBONE SI-C
BONDS MUST BE FAVORED**

FIGURE 15

LINEAR POLYCARBOSILANES



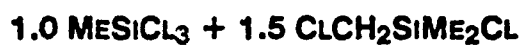
J. T. GOODWIN, U.S. PATENT 2,483,972



O. M. NEFEDOV ET AL,
PROC. ACAD. SCI., USSR 154, 76 (1964)

FIGURE 16

METHYLTRICHLOROSILANE POLYMERS



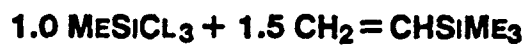
5% xs K THF

SOLUBLE SOLID PRODUCT 39%

1200°C

"SiC"

F = 2.4



5% xs K THF

SOLUBLE SOLID PRODUCT 20%

1200°C

"SiC"

F = 2.4

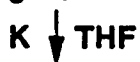
FIGURE 17

ADVANTAGES OF K/THF SYSTEM

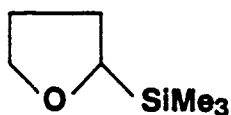
1. REACTIONS ARE EXOTHERMIC AND COMPLETE.
2. SOLID, SOLUBLE POLYCARBOSILANES ARE FORMED.
3. REACTION TEMPERATURE IS LOWER.
4. THF IS MISCIBLE WITH H_2O FOR HOMOGENEOUS TERMINATION.
5. THF IS A BETTER SOLVENT FOR POLYCARBOSILANES.

FIGURE 18

SILYLATED THF DERIVATIVES

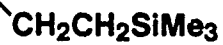
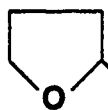


+



+

OTHER PRODUCTS



ISOLATED FROM
 $\text{CH}_2 = \text{CH SiMe}_3$ REACTIONS.

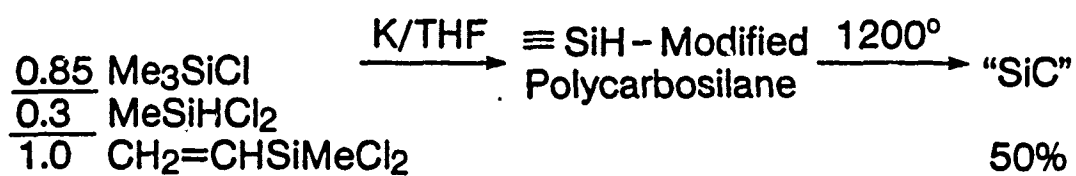
FIGURE 19

**ADVANTAGES OF
VINYLSILANE ROUTE**

1. LESS ACTIVE METAL USED
2. LESS BY-PRODUCT KCl FORMED
3. NO VISCOSITY PROBLEM
4. WELL DEFINED CHEMISTRY
5. GOOD MONOMER SUPPLY SITUATION

FIGURE 20

POLYCARBOSILANES FROM MeSiHCl₂



~ 20% Retention of $\equiv \text{SiH}$ Groups

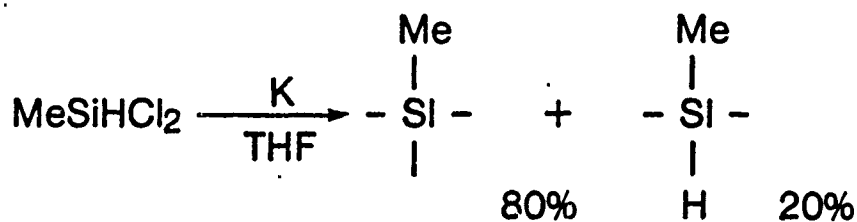


FIGURE 21

**Me₂SiCl₂/MeSiHCl₂
CERAMIC YIELD COMPARISON**

VINYL SILANE	COMONOMER	SIC YIELD
CH ₂ = CHSiMe ₃	Me ₂ SiCl ₂	0.3%
	MeSiHCl ₂	28.5%
CH ₂ = CHSiMe ₂ Cl	Me ₂ SiCl ₂	3.0%
	MeSiHCl ₂	31.0%
CH ₂ = CHSiMe ₂ CH ₂ Cl	Me ₂ SiCl ₂ (2/1)	0.3%
	MeSiHCl ₂ (1.5/1)	27.8%

FIGURE 22

LINEAR POLYSILAHYDROCARBONS

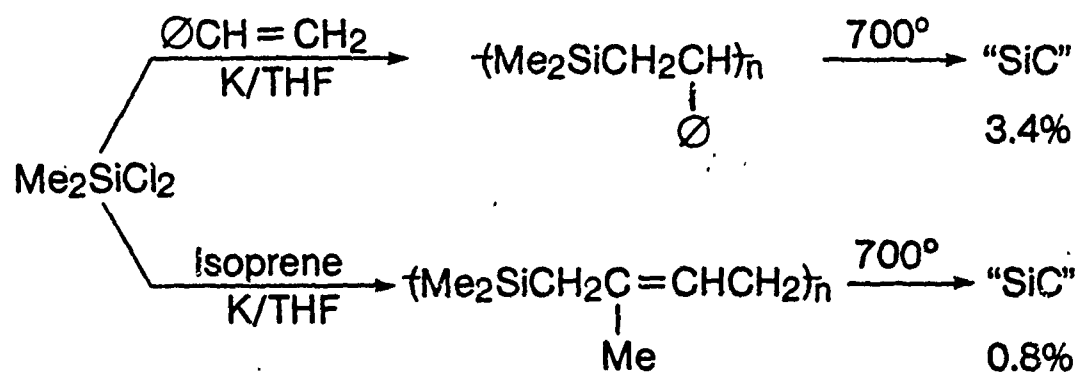


FIGURE 23

BRANCHED POLYSILAHYDROCARBONS

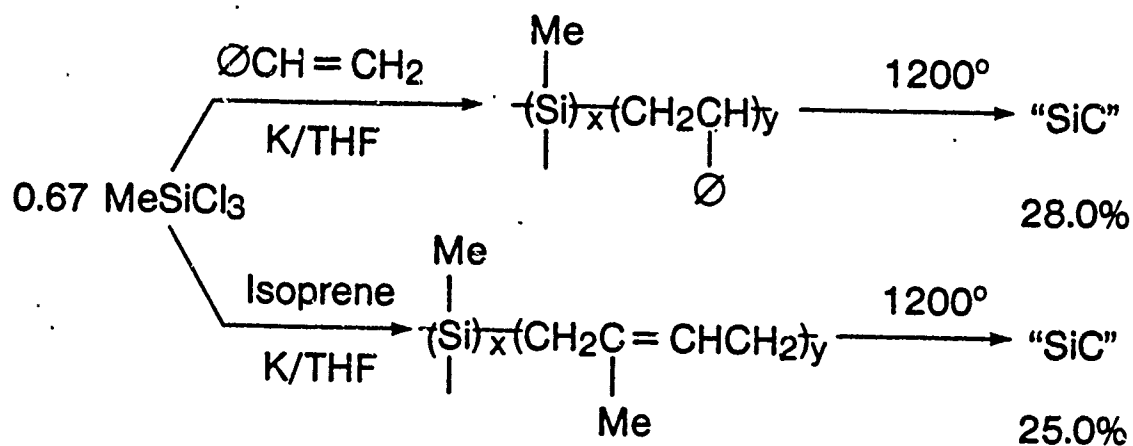


FIGURE 24

POLYSILAHYDROCARBONS FROM MeSiHCl₂

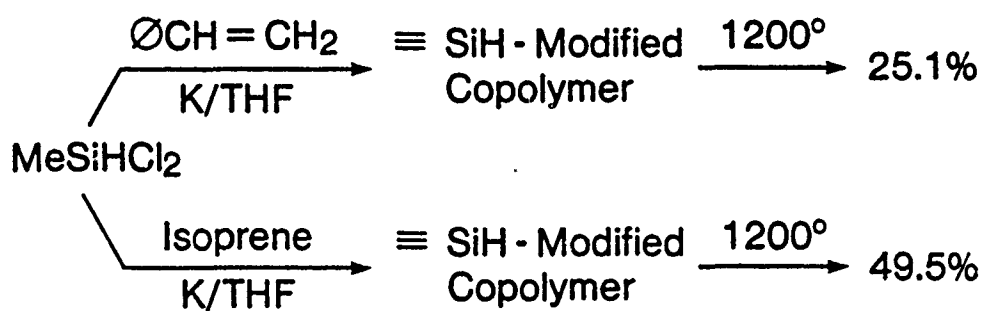
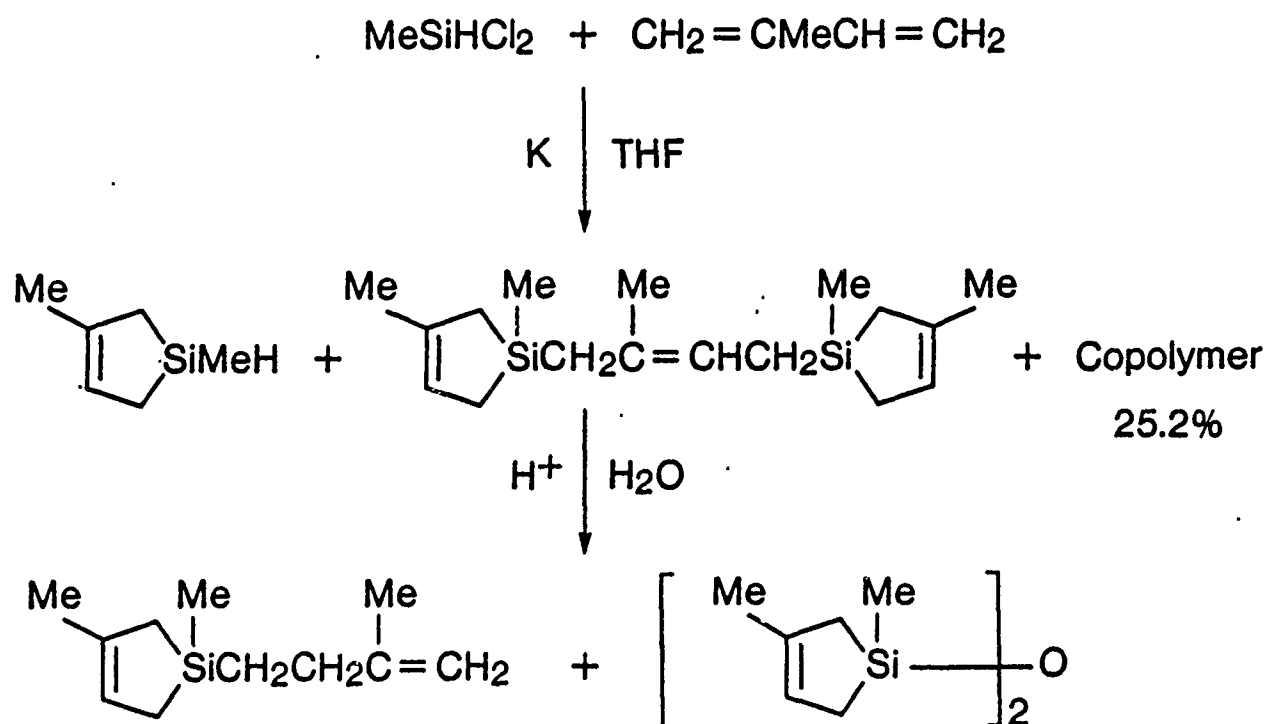


FIGURE 25

MeSiHCl₂/ISOPRENE REACTION



very low viscosity fluid, less than 50 cs, and would be ideal as an impregnant.

The sodium route to polyvinyllic silanes has also been studied, but the polymerization chemistry is different (Figure 26). The Na dechlorinated polymers are formally linear copolysilanes since Na does not cause disilylation of the vinyl group (Figures 27 and 28) and leaves the vinyl group unreacted (Figure 29). Using this chemistry, polysilanes can be synthesized that contain vinyl groups which thermally crosslink (Figures 30 and 31). The product shown on Figure 31 is a very low viscosity liquid and when heated at above 200°C, crosslinking occurs and a solid product is obtained that can be drawn into fibers.

The advantages (Figure 32) of the sodium route are largely commercial. Sodium is 1/20th the cost of potassium on the molar equivalency basis. The solvent used is a 7:1 mixture of toluene:THF which is less expensive than the pure THF solvent used in the K route. Sodium is less hazardous than potassium and the products give better ceramic yields. The reaction procedure is summarized in Figure 33.

Figure 34 shows the pyrolysis procedure used at Union Carbide. The sample is heated in two steps. First it is heated to 500°C and then pyrolyzed at 1000-1200°C to obtain SiC. It takes about 60 hours of heating to generate the X-ray pattern for SiC (Figure 35).

If you take a piece of the pyrolyzed product and run the TGA in air, virtually nothing will happen (Figure 36). However, if you crush it and run the TGA in air again, a different TGA curve is obtained (Figure 37). The weight loss is the result of CO being given off and the weight gain is the formation of SiO₂.

The conclusions derived from this work are listed in Figure 38 and are summarized below.

FIGURE 26

**SODIUM ROUTE
TO VINYLIC POLYSILANES**

- Na can replace K
- Polymerization chemistry is different
- Na - Derived polymers are effective SiC precursors.

FIGURE 27

K/Na REACTIVITY DIFFERENCE

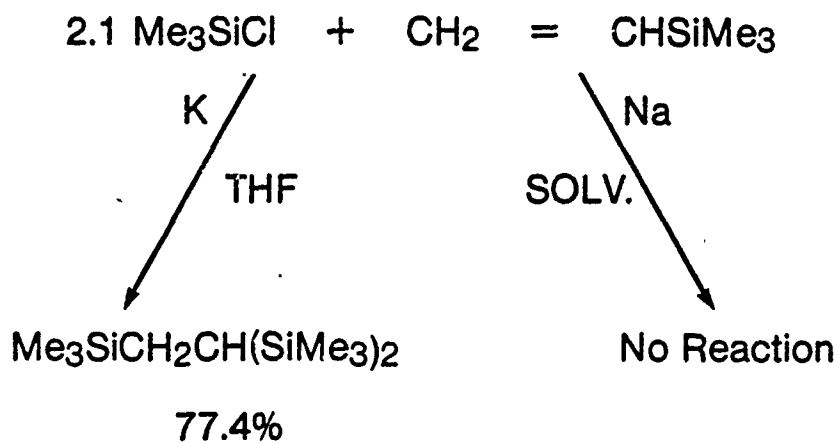


FIGURE 28

POLYMER UNITS FROM $\text{CH}_2 = \text{CHSiMeCl}_2$

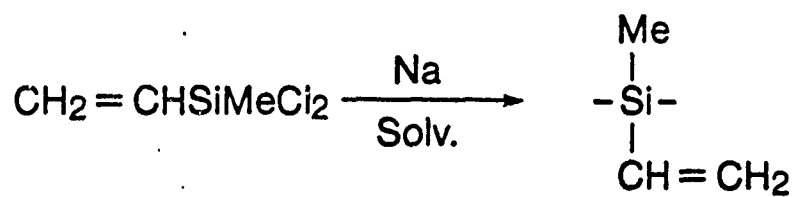
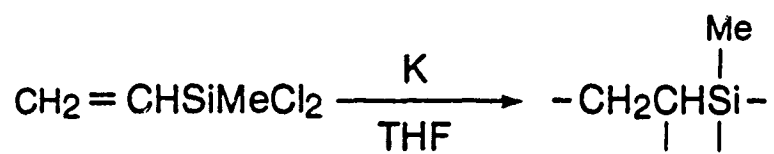


FIGURE 29

VINYLIC POLYSILANES

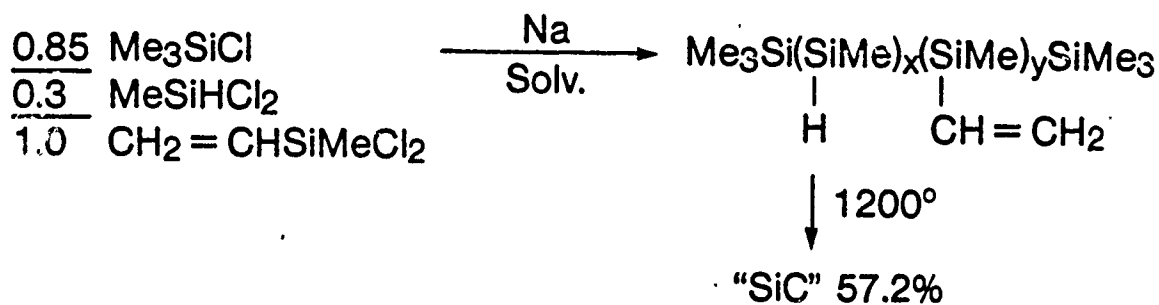
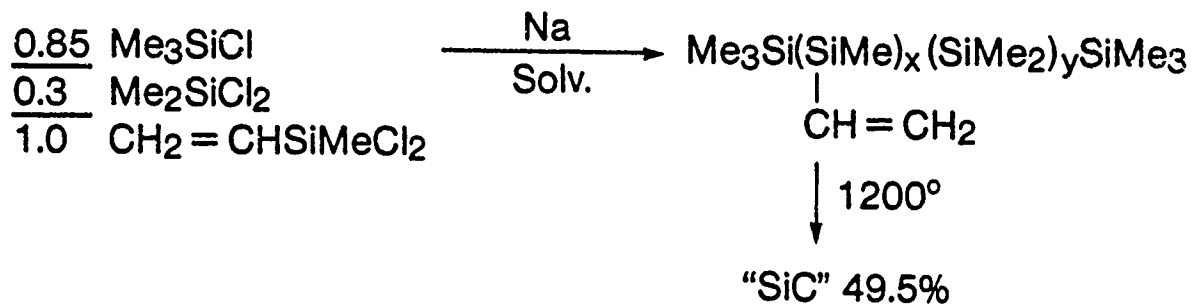


FIGURE 30

KEY CHEMICAL FEATURES

- Reactivity of Na versus K
- Use of Solvent Blends
- Chlorosilane Reactivities – $\text{CH}_2 = \text{CHSiMeCl}_2$
- Thermal Crosslinking

FIGURE 31

THERMAL CROSSLINKING CHEMISTRY

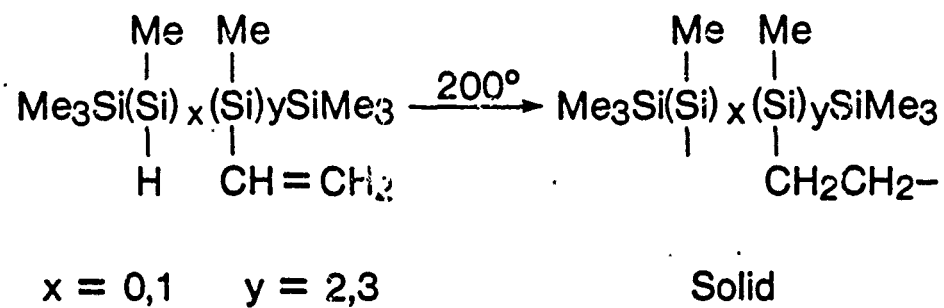


FIGURE 32

**ADVANTAGES
OF SODIUM ROUTE**

- Cost – Metal/Solvents
- Safety
- Precursor Performance

FIGURE 33

GENERAL REACTION PROCEDURE

1. Combine Active Metal/Solvent
under Inert Atmosphere
2. Heat to Reflux, Melting Metal
3. Add Monomer Mixture at a Rate
Which Maintains Reflux
4. Heat at Reflux after Addition
5. Cool, Terminate, and Neutralize
6. Remove Salt By - products
7. Isolate Polymeric products

FIGURE 34

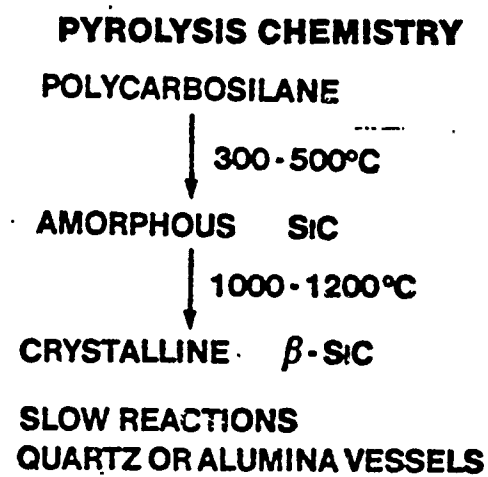


FIGURE 35

**GRAPHITE
MONOCHROMATOR**

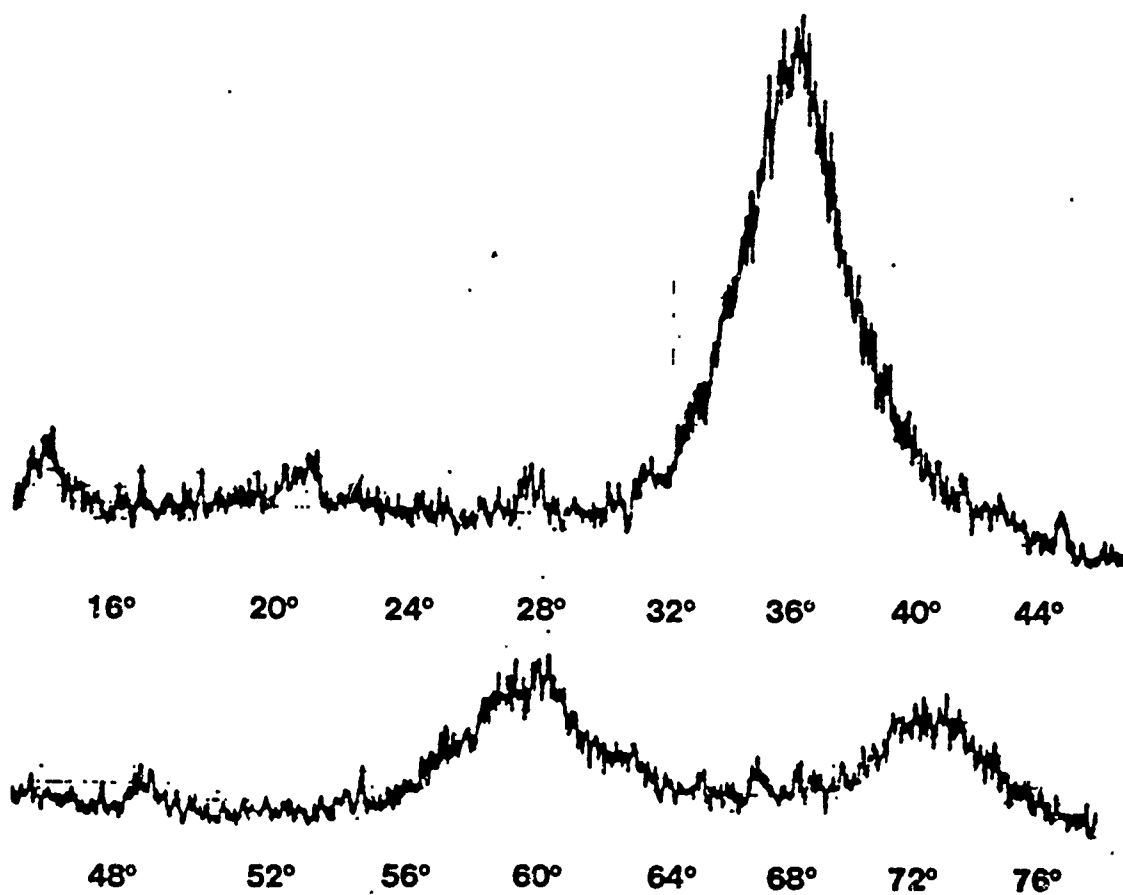


FIGURE 36

**TGA OF UNCRUSHED SiC SAMPLE
IN AIR**

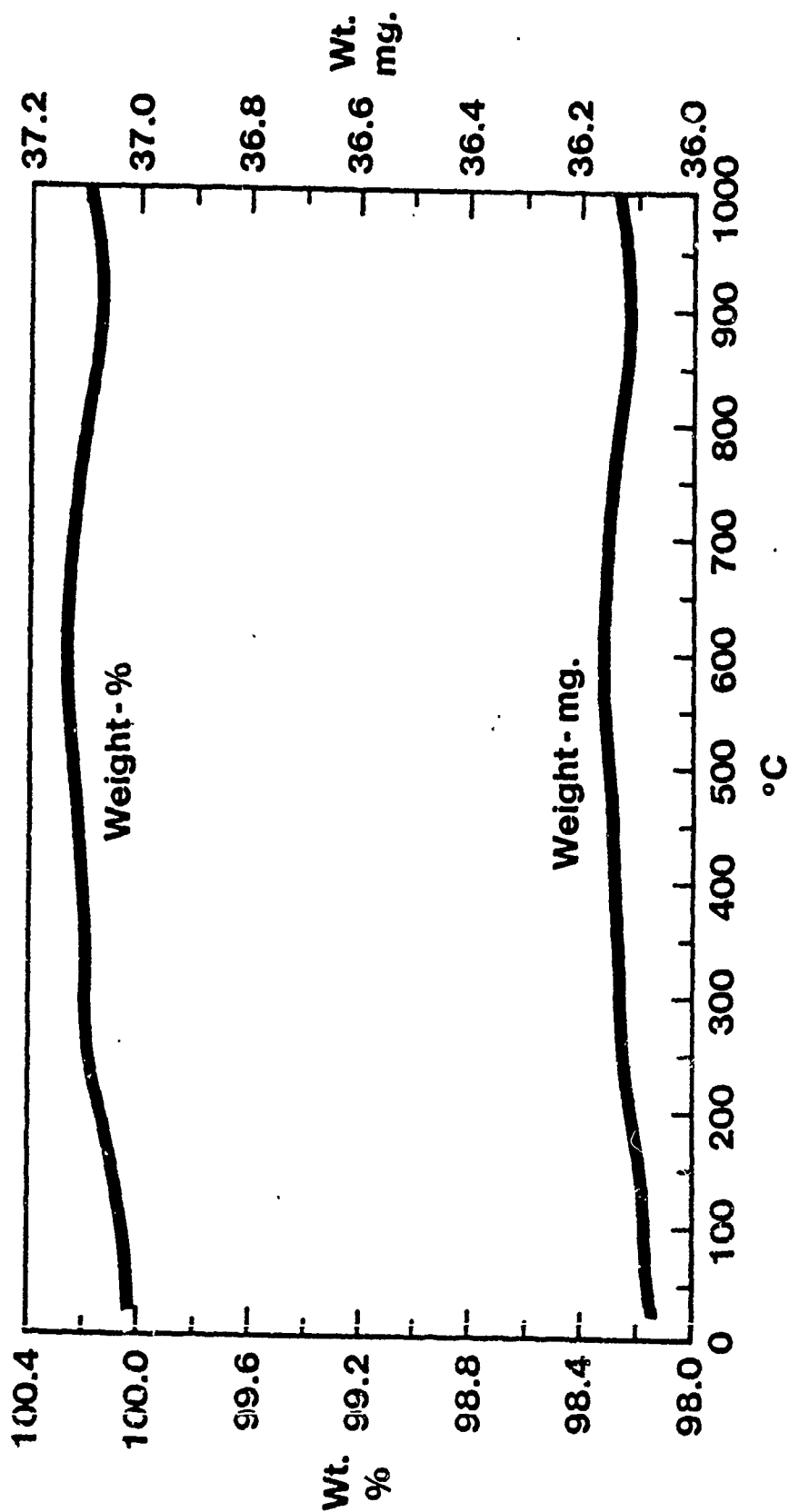


FIGURE 37

**TGA OF CRUSHED SIC SAMPLE
IN AIR**

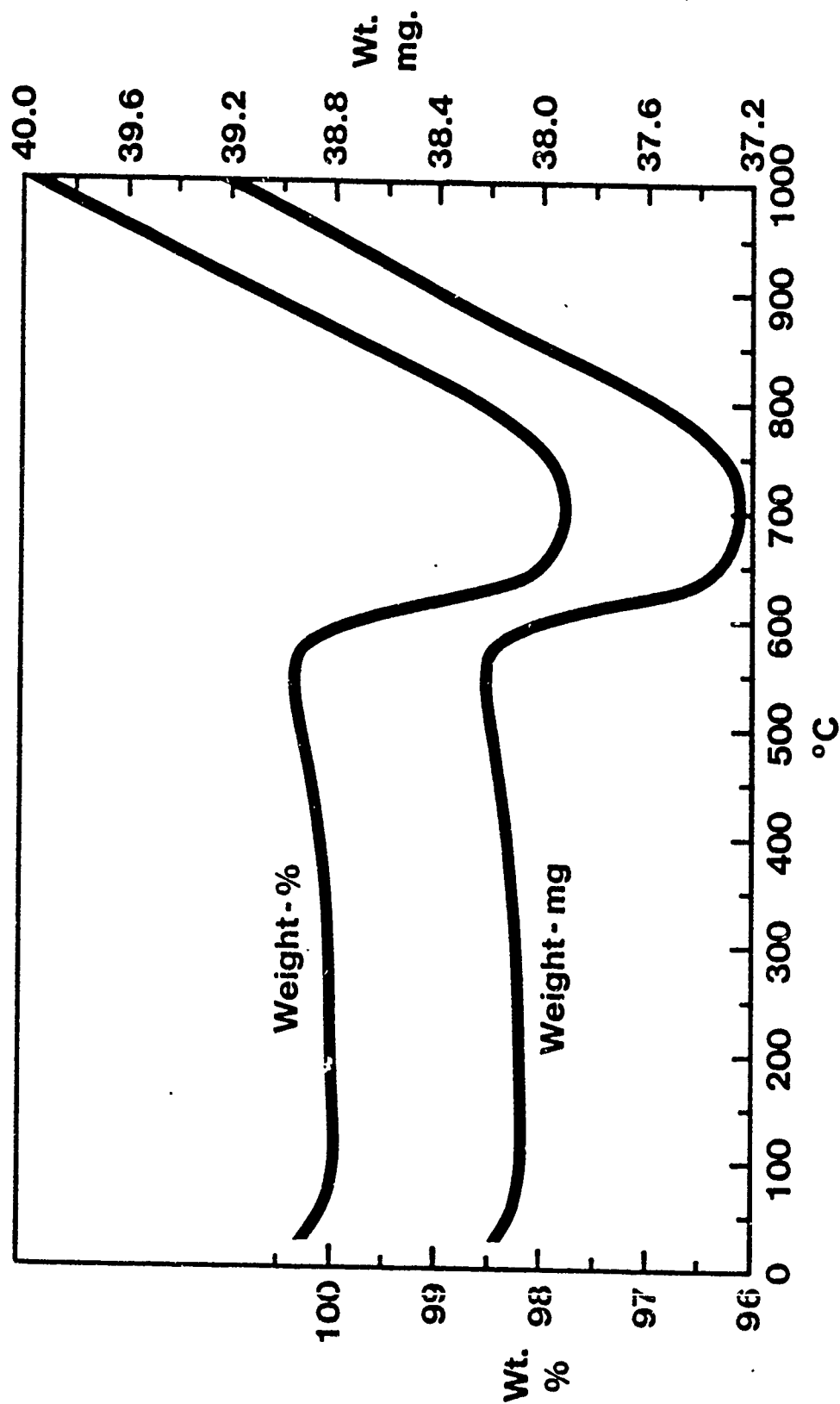


FIGURE 38

CONCLUSIONS

Three Classes of SiC Precursors

- K-Derived Polycarbosilanes
- Branched Polysilahydrocarbons
- Na-Derived Vinylic Polysilanes

Role of Backbone Branching

Role of Reactive Functional Groups

Conclusions:

- Many polymers have been synthesized but very little is known about the ceramic products.
- Analytical methods are not developed to completely characterize these materials. Solid state NMR has given the most success.
- Information is needed about the ceramic products. Should this be a separate research group?
- Mechanistic studies are needed so that hundreds of compounds are not needed to find those that work.
- Experimentalists' point of view is that many compounds must be synthesized to see what structural features are required.

Dr. Gary Legrow
Dow Corning

After Dr. Schilling's presentation, Professor West introduced Dr. Gary Legrow who presented Dow Corning's work on SiC and Si_3N_4 precursors. Dow Corning's approach is summarized in Figure 1 and involves both synthesis and processing of the polymer into fibers or matrix material with the final goal being a ceramic/ceramic composite. So far, every polymer Dow Corning has identified as being useful as a ceramic precursor is an oligomer with a molecular weight of 1000-2000 as determined by vapor phase osmometry. Gel permeation chromatography requires a new calibration standard (other than polystyrene) to be useful.

The polymers that are synthesized are screened as outlined in Figure 2, and so far out of 60 some polymers only three have passed. As far as the polymer itself is concerned, it must be tractable. If it's to be a precursor for a fiber, it has to be a solid, have a sharp deformation point so the material can be reproducibly spun on commercial equipment. The materials need to be curable (non oxygen) and give a char yield of at least 40%. It is important that the char be characterized so that its identity is known. If it's 50% free carbon it's useless. If it's SiC or Si_3N_4 or a combination of the two it passes the screening tests. The other two screening factors concern economics and safety.

The standard pyrolysis procedure is shown in Figure 3. One problem is evident here. It is entirely possible that another procedure would yield better ceramic products. If the procedure were different, other or additional polymers may have passed. Using this procedure three polymers have passed and look promising.

The next questions are, what is the ceramic's thermal stability in an inert atmosphere, what is its oxidative stability, what is its modulus, what is its strength, and finally, how compatible is it with a ceramic matrix or in a composite (Figure 4)?

FIGURE 1

ORGANOMETALLIC MONOMERS TO CERAMIC
MATRIX COMPOSITES
POLYMER PYROLYSIS

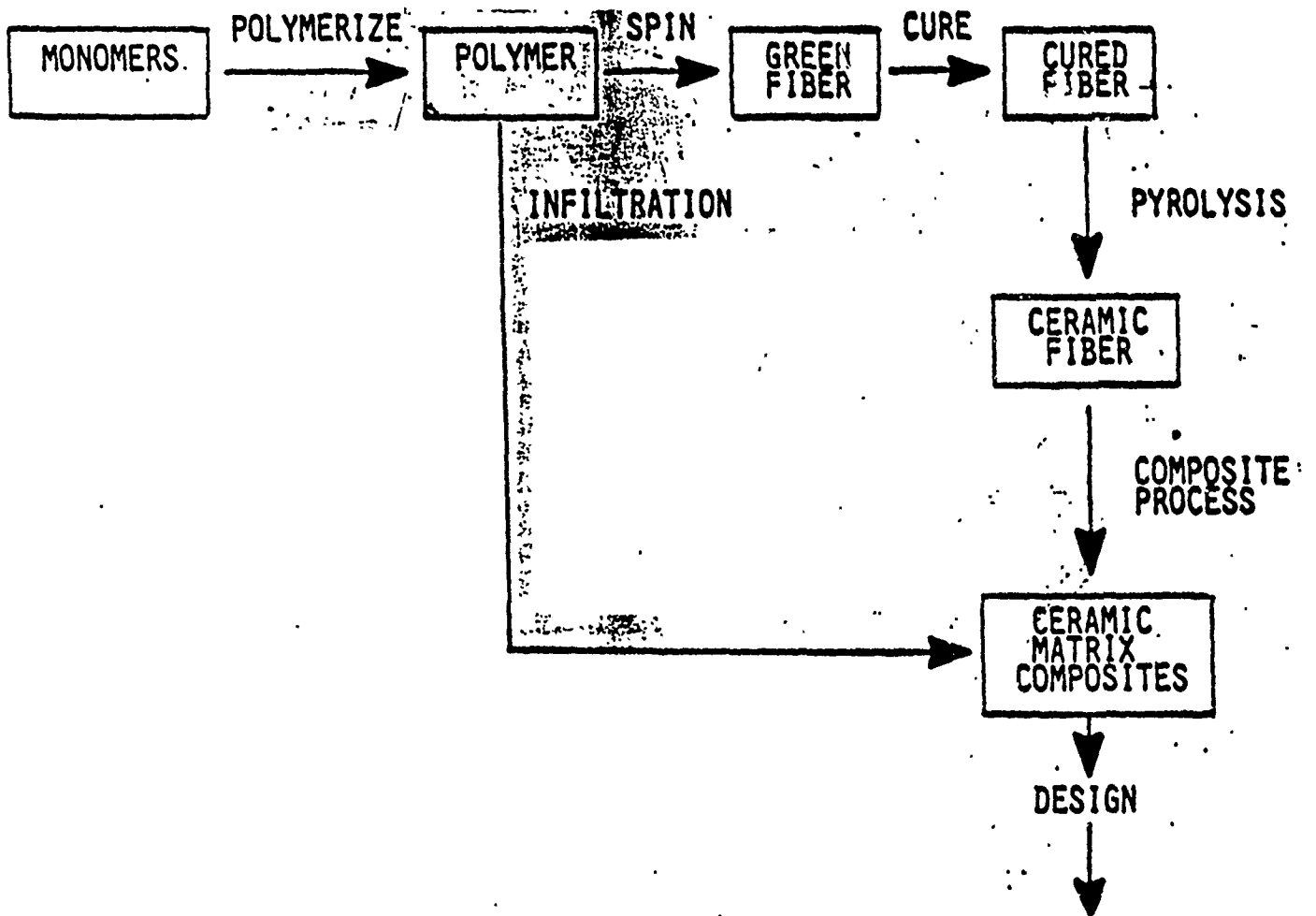


FIGURE 2
POLYMER SCREEN

- TRACTABLE
- CURABLE (NON-OXYGEN)
- CHAR YIELD $>40\%$ AT 1000°C
- $3(\text{RAW MATERIALS COST})^N$ \$300/LB
N = NUMBER OF PROCESS STEPS
- POTENTIAL PROCESS HAZARDS
EXPLOSIVE? TOXIC?

FIGURE 3

- PYROLYZE TO 1150 C
- RAMP RATE 5°/MIN
- 30 MIN HOLD TIME AT MAXIMUM T
- ARGON ATMOSPHERE

• USUALLY IN A LINDBERG TUBE FURNACE

FIGURE 4

CERAMIC ALLOY SCREEN FOR
HIGH TEMPERATURE STRUCTURAL CERAMICS

- DOES THE CERAMIC HAVE HIGH TEMPERATURE THERMAL STABILITY IN INERT ATMOSPHERES?
- DOES THE CERAMIC HAVE HIGH TEMPERATURE OXIDATIVE STABILITY?
- DOES THE CERAMIC HAVE A HIGH MODULUS?
- CAN THE CERAMIC HAVE A HIGH STRENGTH?
- IS THE CERAMIC COMPATIBLE IN CERAMIC MATRIX COMPOSITES?

FIGURE 4

The first question is addressed by the process shown in Figure 5 and the oxidative stability is determined by the process outlined in Figure 6. If the material passes these tests, then the whole process is started over to see if the material can be spun properly, cured, and so on.

Dow Corning has tried to make their polymers in a very organized way, and their approach has been to design polymers or oligomeric materials that are nonvolatile under the conditions used for curing. Ideally, Dow Corning's approach is to synthesize material that contains silicon and carbon in almost the exact stoichiometric ratio that is required to make SiC. One way to do that is to use the hydride functionality and make polymers that have the desired carbon to silicon ratio. So ideally, materials are made that will first have a high char yield and second the char will be SiC. The Si, C and N percentages for the three systems that Dow Corning is studying are shown on Figure 7 and the percentages for the systems that others have investigated are shown in Figure 8.

The starting material that is used to make two of the oligomeric systems is a product which is derived from a direct synthesis which is summarized in Figure 8. The methylchlorosilanes (MCDS) that are actually used, contains all of the underlined compounds shown on Figure 9. So there are five materials that are actually present in the MCDS that is used for the synthesis of the precursors.

In one of the processes, MCDS, phenylvinylchlorosilane and hexamethyldisilazane are mixed together and heated (Figure 10). A number of reactions take place which are summarized in Figures 11, 12 and 13. The very first thing that happens is that the tetrachlorodimethyldisilane reacts with the hexamethyldisilazane. The trichloro compound undergoes a similar reaction but the dichloro compound does not react. The phenylvinylchlorosilane reacts with the hexamethyldisilazane to form the

FIGURE 5

HIGH TEMPERATURE THERMAL STABILITY

CERAMIC POWDER EXPOSED TO 1500°C FOR 12 HOURS IN ARGON

- ELEMENTAL COMPOSITION CHANGE
- MORPHOLOGICAL CHANGES
- DENSITY CHANGES
- WEIGHT CHANGE

FIGURE 6

HIGH TEMPERATURE OXIDATIVE STABILITY

CERAMIC POWDER EXPOSED TO 1200°C FOR 12 HOURS IN AIR

- CHANGE IN PERCENT OXYGEN DETERMINED
- WEIGHT CHANGE DETERMINED

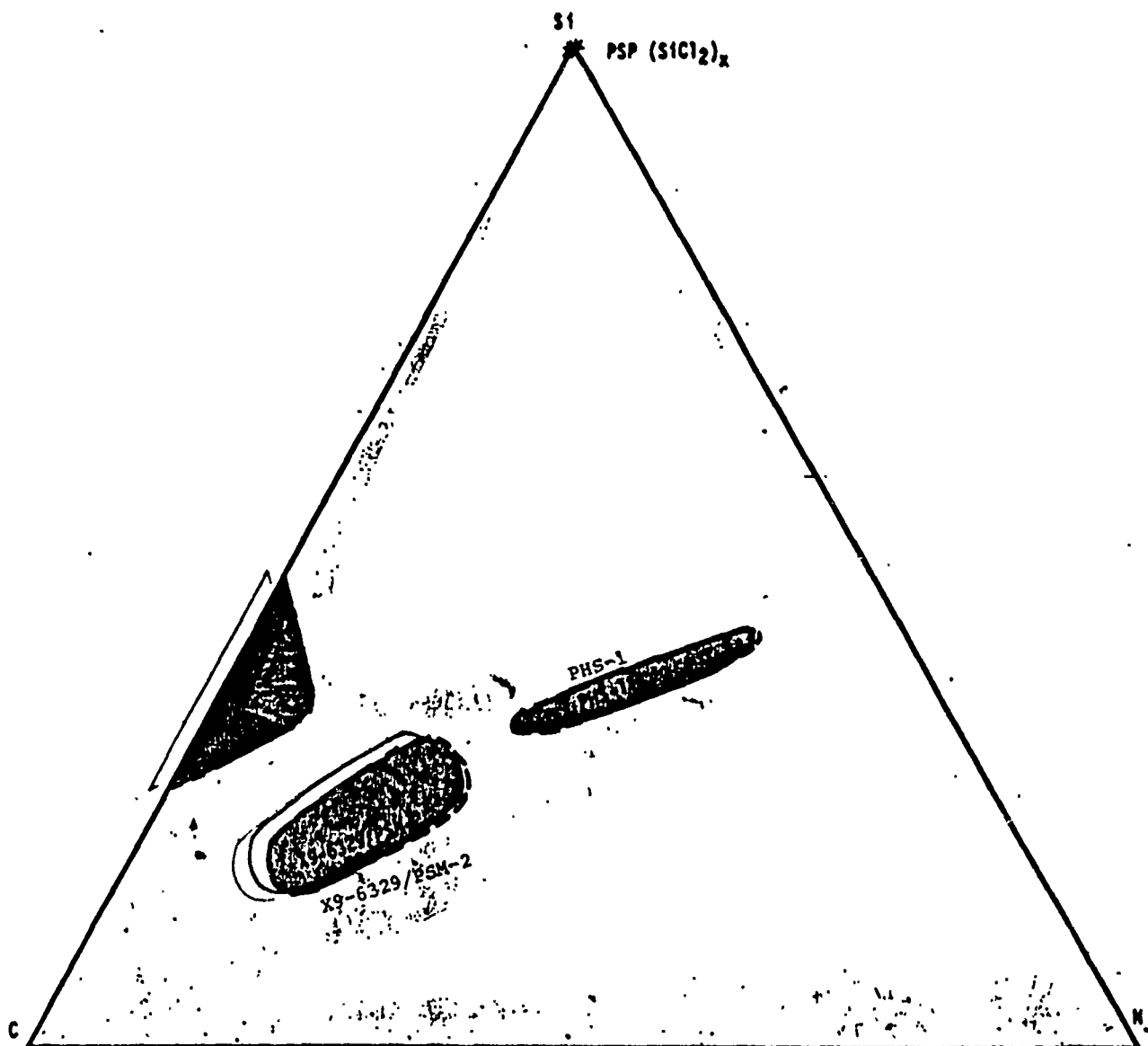


FIGURE 7.
DOW CORNING SYSTEMS

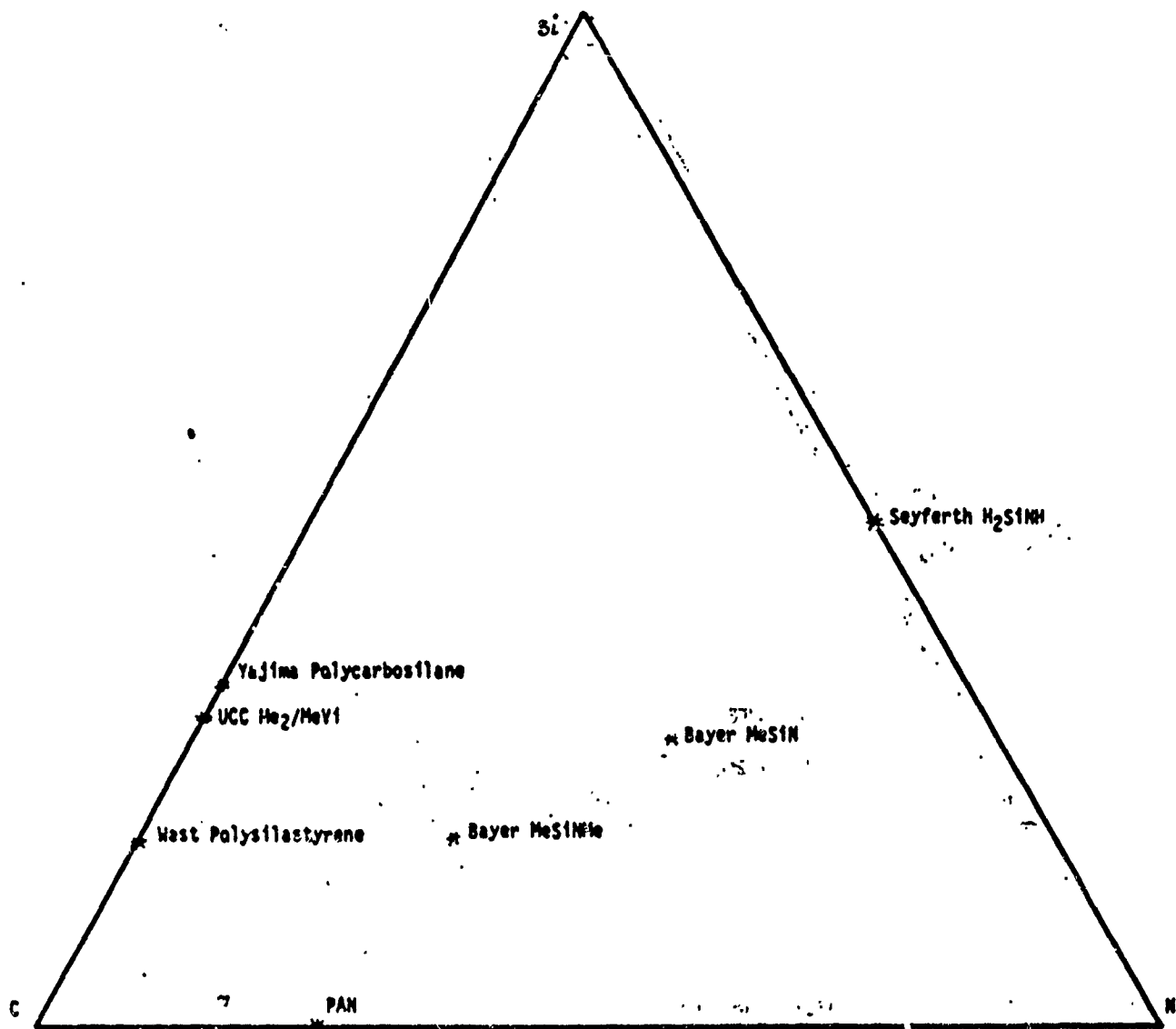
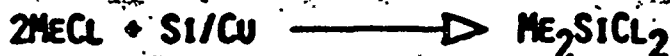
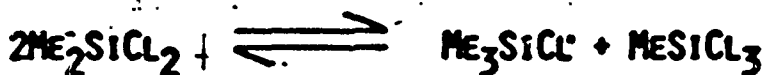
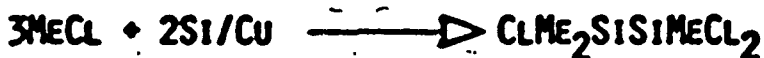
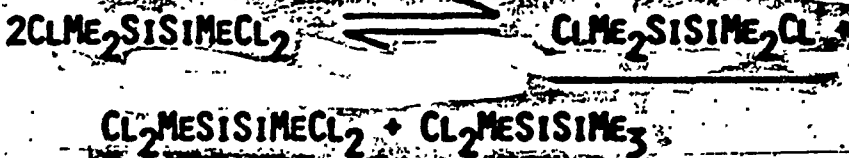
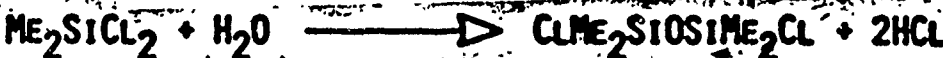


FIGURE 8.

FIGURE 9

SYNTHESIS OF MCDSDIRECT SYNTHESIS:LIGAND REDISTRIBUTION:INCOMPLETE SILICON REDUCTION:LIGAND REDISTRIBUTION:HYDROLYSIS:

• UNDERLINED CHEMICALS ARE COMPONENTS OF MCDS.

FIGURE 10

SYNTHESIS OF MPDZ-PHVI-CL

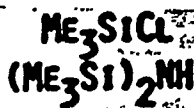
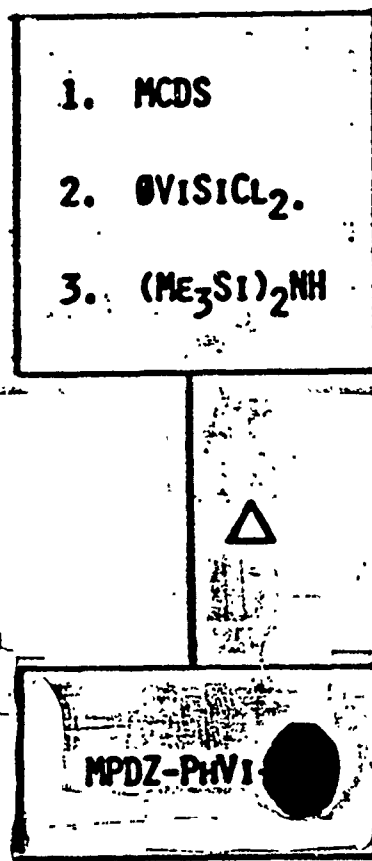


FIGURE 11

CHEMISTRY OF SYNTHESIS OF MPDZ-TYPE OLIGOMERS

1ST STEP

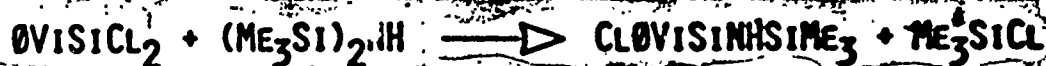
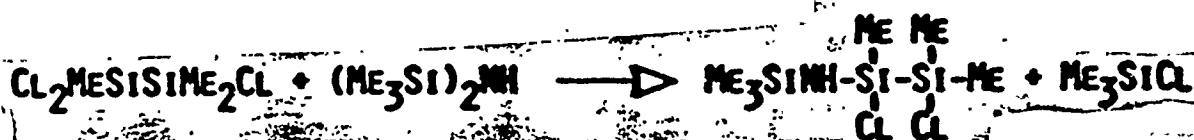
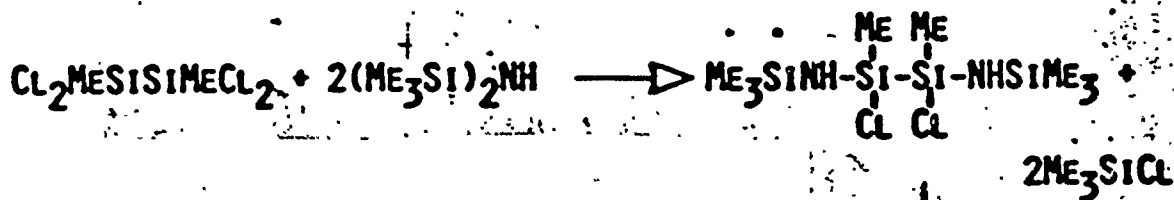


FIGURE 12

CHEMISTRY OF SYNTHESIS OF MPDZ-TYPE OLIGOMERS
2ND STEP

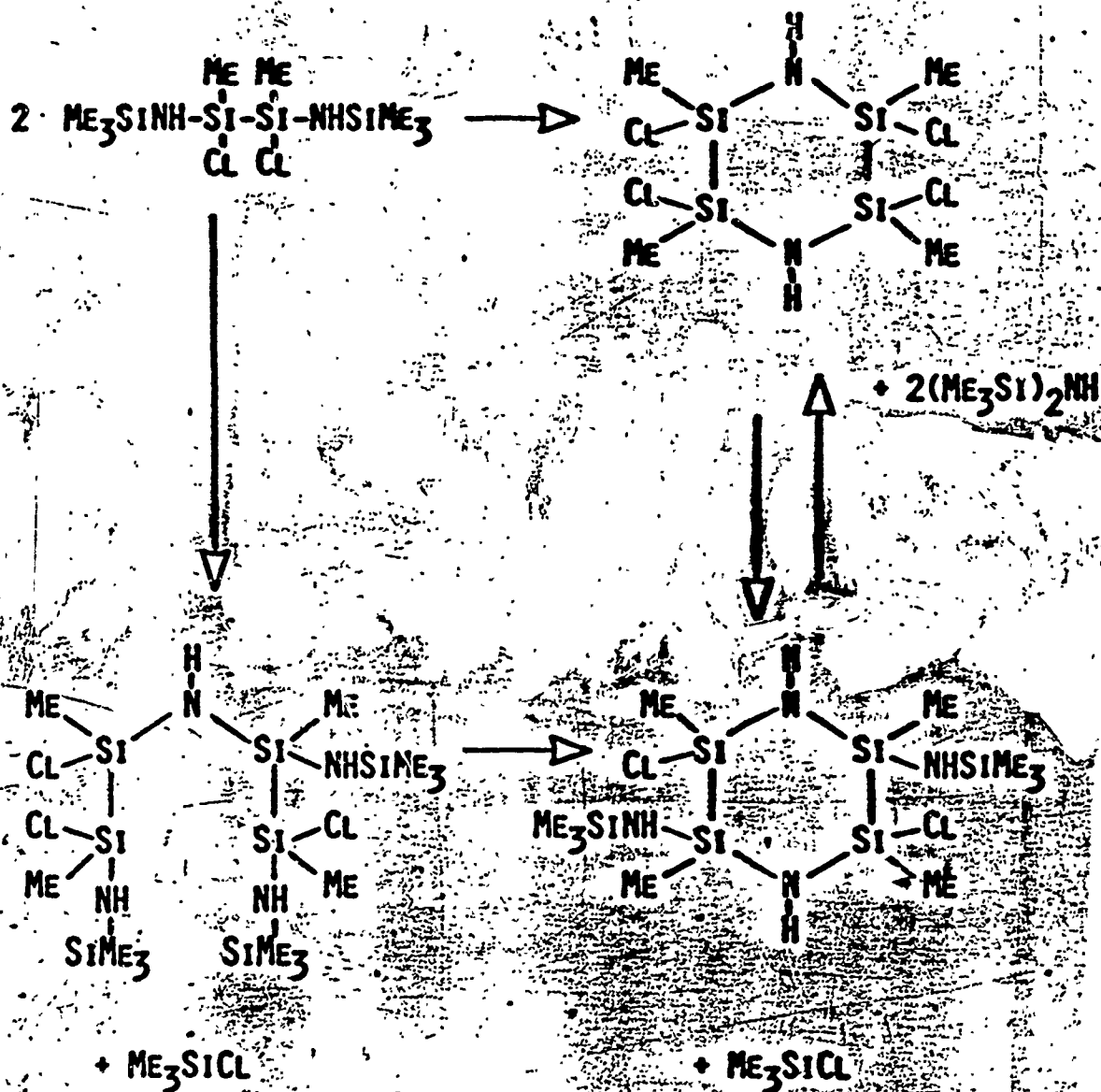
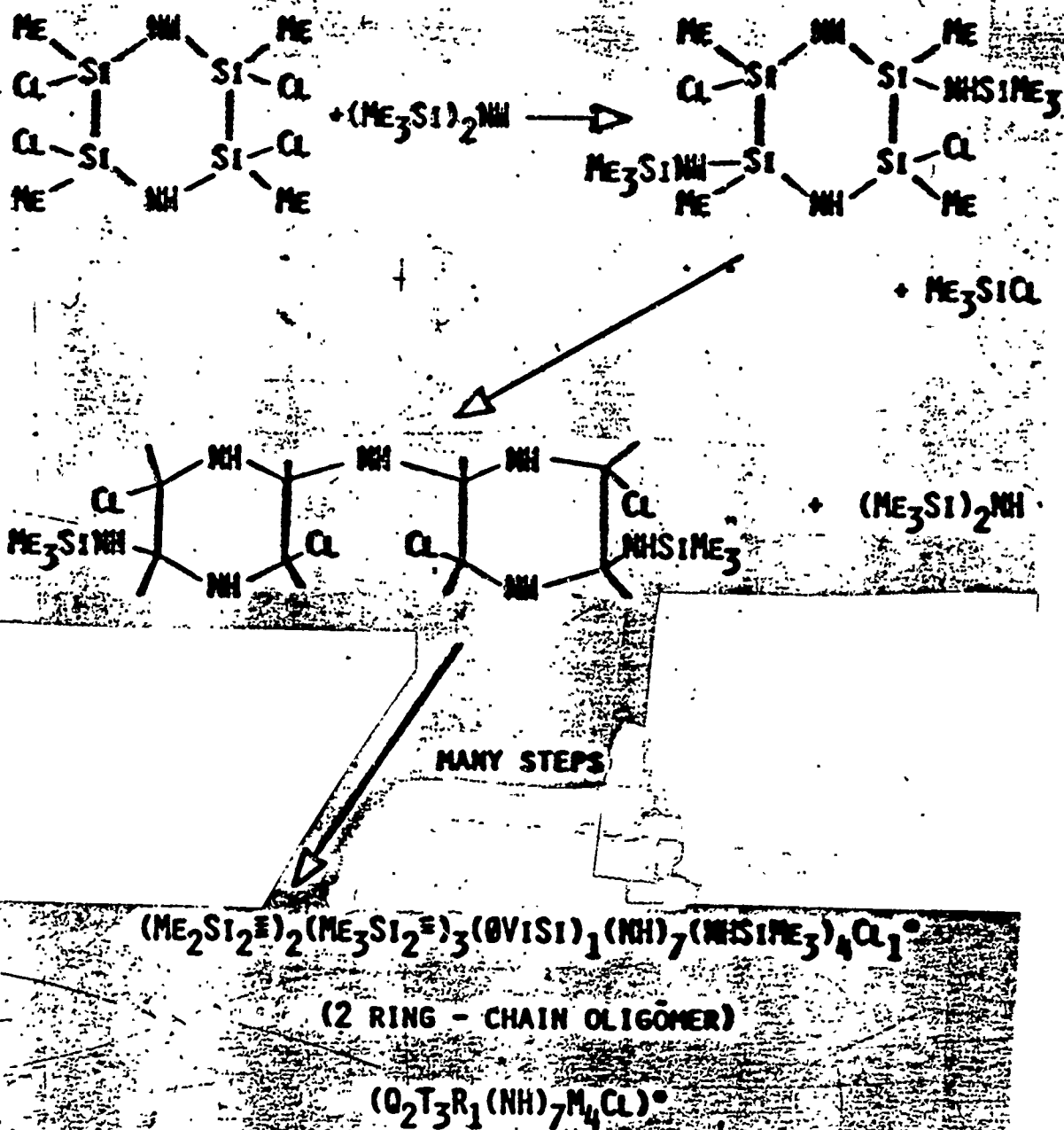


FIGURE 13

CHEMISTRY OF SYNTHESIS OF MPDZ-TYPE OLIGOMERS3RD STEP

• REFERENCE:

1984 1ST QUARTER REPORT - POLYMER CHARACTERIZATION SECTION

FIGURE 13.

phenylvinylchloro (trimethylsilylamino) silane. These reactions occur very quickly and are not reversible.

The products formed condense further as the system is heated (Figure 12). The compounds with one chlorine and one nitrogen bonded to each silicon are the most stable. The trimethylchlorosilane is removed to drive the reaction further (Figure 13). Possible structures for the final material are shown in Figure 14. In the average material there are two disilane molecules that originated as the tetrachlorodisilane and three disilane molecules that came from the trichlorodisilane. The dark areas on Figure 14 are residual trimethylsilylamino groups. Molecular models of these polymers show that this polymer is spherical with the trimethylsilylamino groups around the outside and the vinyl groups and chlorine are buried inside. In order to get at the vinyl group, this polymer needs to be swelled so that it is in a more linear configuration. This particular polymer is cured using oxygen and contains 10% free carbon after pyrolysis.

Alternatives to the Me_3SiNH group are shown in Figure 15. By using reactive groups on the pendant amino group, the oligomer can be cured by crosslinking reactions, and oxygen free ceramic fibers are possible. Figure 16 summarizes the approach for obtaining a high Si_3N_4 content ceramic fiber.

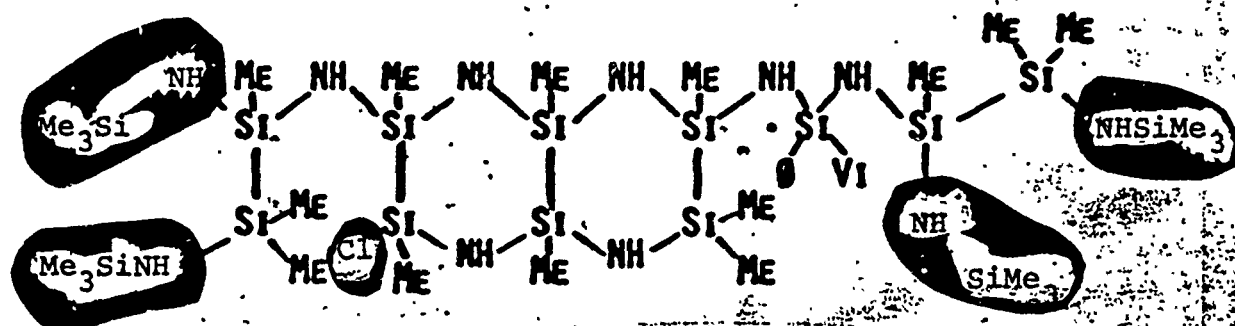
Floor Discussion

Materials that contain mixtures of SiC and Si_3N_4 have modulus properties expected for the mixed system and the modulus increases as the oxygen content decreases.

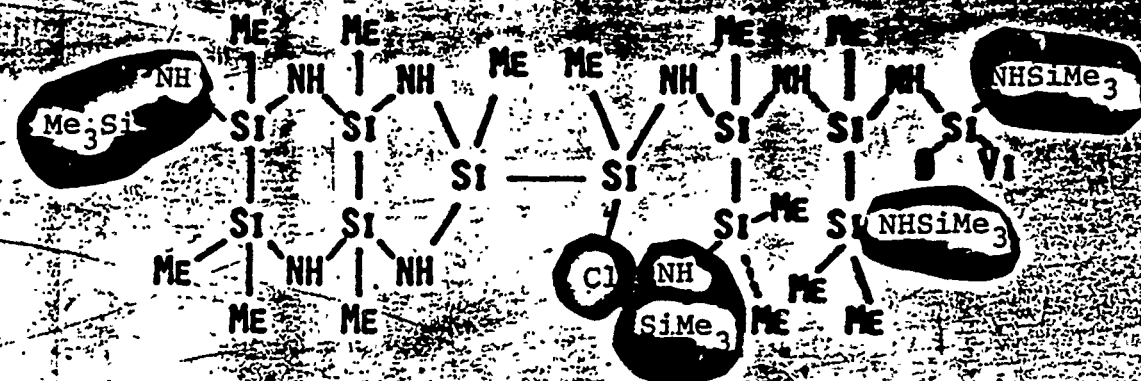
There was discussion that SiC and Si_3N_4 may not be the best systems to investigate. Perhaps HfC , TiC , AlN , BN , etc., would be better. AlN has interesting properties and is oxidation

FIGURE 14

EXAMPLES OF POSSIBLE STRUCTURES FOR
MPDZ-PHVI-CL



2 FUSED 6 MEMBERED RINGS



1-6, 1-5 FUSED RINGS

FIGURE 15

ALTERNATIVES TO $(\text{ME}_3\text{Si})_2\text{NH}$

CONTROL

$(\text{ME}_3\text{Si})_2\text{NH}$

1

$(\text{VIME}_2\text{Si})_2\text{NH}$

2

$(\text{HME}_2\text{Si})_2\text{NH}$ •

PURPOSE: ENHANCED CHEMICAL REACTIVITY, E.G.: CURE

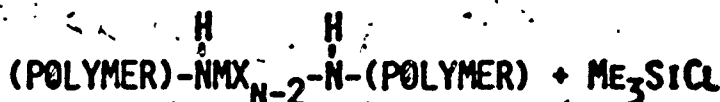
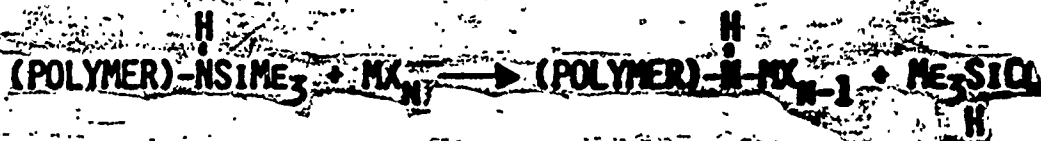
DRAWBACKS: • STABILITY OF MATERIALS NOT KNOWN

FIGURE 16

Si_3N_4 PRECURSORS + HP : HYDRODOPOLYSILAZANE
 TARGET - HIGH Si_3N_4 -CONTENT CERAMIC FIBER
 APPROACH - USE SI-, N- AND C- CONTAINING POLYMER WITH
 READILY ELIMINATED ORGANIC GROUPS

SYNTHESIS - $\text{HSiCl}_3 + \text{xs}((\text{CH}_3)_3\text{Si})_2\text{NH} \longrightarrow (\text{CH}_3)_3\text{SiCl} +$
 $\text{xSHMDZ} + \text{POLYMER}$

CURE/CONVERSION



- RENDERS POLYMER INFUSIBLE
-AND-
- REDUCES CARBON CONTENT

resistant once protected by an aluminum oxide scale. It may be a good idea to rethink and decide what kind of a fiber is really desired. The ceramics should list the materials that are desired so that the chemists can design and develop synthetic routes for these materials.

The organometallic synthetic community can probably make anything that is set as a goal when given some time and money to think about it. However, they may lack the capability to characterize the ceramics that are produced.

The need for facilities for scaling up promising materials that are available only in small amounts, and for preparing totally new materials was identified.

Every time you do something, like altering the pyrolysis step, or the cure step, you alter the ultimate ceramic. So you need to consider all steps and not just the polymer and what it gives as a ceramic.

The question was also raised about the feeling of academia toward working with the Government and national laboratories versus industry? Which is preferred and how is the path made smoother? The response -- "Whichever has less red tape."

Dr. Peter E. D. Morgan
Rockwell International

Peter E. D. Morgan discussed two approaches to molecular engineering. He discussed an approach for synthesizing a polyheterocyclic, high temperature polymer that may have high char yields for carbon-carbon composites. The synthesis begins by treating acenaphthene with glacial acetic acid and fuming nitric acid. The final material can be hot molded at 4000 psi up to about 400°C in which case it gives off H₂O. Polymer people can't do this but ceramics have the hot presses to do this type of thing.

The other synthesis presented was the use of silicon sulfur chemistry. Silicon sulfide has a chain structure that would be a polyspiro compound to polymer chemists. The extraordinary thing about SiS₂ is that when treated with NH₃ at 900°C, it converts to silicon nitride with no change in shape. Silicon sulfide fibers were converted to Si₃N₄ fibers with no change in shape. Heating these materials to 1250°C gives α-Si₃N₄.

CHEMICAL VAPOR DEPOSITION

Dr. J. Gebhardt
General Electric

Chemical vapor deposition (CVD) came into prominence during the 60's and it is a process for depositing solids, especially refractory solids by reactions in the gas phase. The applications, advantages, and disadvantages are summarized in Figure 1.

FIGURE 1

CHEMICAL VAPOR DEPOSITION

Formation or condensation of a solid deposit from the vapor phase from species generated by chemical reaction of appropriate precursors

Some Major Applications

Thin Films	- Passivating Layers	(Si_3N_4 , SiO_2)
	Doping	(P, B, As)
	Decorative	(Ni, Ir, TiN)
	Protective	(TiN)
Coatings	- Cutting Tools	(Al_2O_3 , TiB_2)
	Wear Surfaces	(SiC)
	Conversion Layers	(SiC)
	Internal Layers	(C, SiC)
Free Standing	- I.R. Windows	(ZnS, ZnSe)
	Crucibles, Tubing	(W, BN, C, Ta)
	Plates	(BN, C)
Raw Materials	- Powders	(C, TiO_2 , SiO_2)
	Plates	(PG, BN, W)

Advantages

High Purity
Dense, Impermeable
Lower Temperature Than Bulk Formation

Disadvantages in Starting Up

Development, Scale-up Costs, Proprietary
Batch Process, Empirical Origins
Equipment Design

The requirements for carrying out a CVD process are listed in Figure 2 along with some of the techniques that are used. An open substrate involves depositing a coating on something like carbon, while infiltration involves depositing material throughout the porous body (coating internal surfaces). Fluidized bed techniques are used for coating fuel particles. The fluidized bed technique does allow one to alter the microstructure of the deposit. Plasma assisted deposition involves passing the components into a chamber where a plasma exists, allowing the desired material to be deposited at a much lower temperature than normal. Conversion techniques involve using a mixture of powders that generate the gas phase species that eventually form the coating by reacting with the substrate.

A number of variables are associated with the CVD process (Figure 3). Some variables can be directly controlled and some cannot be directly controlled. CVD processes can be like a black box - gas goes in one side and the deposit comes out the other. A lot of things happen that are gradually being understood.

Optimization (Figure 4) usually involves optimizing the deposit itself, and that depends on the application. Electromagnetic windows are the most difficult to optimize because in addition to mechanical properties, purity is also critical. For example, in attempting to make AlN radar windows, we want a low dielectric loss; we want it to be constant with temperature, and we want thick deposits that are structurally sound. If you want a thick deposit, you must deposit it fast, and if you deposit it fast, you trap impurities that "screw up" the electromagnetic properties.

FIGURE 2

REQUIREMENTS

THERMODYNAMIC FEASIBILITY

VAPOR PHASE PRECURSORS

HEAT SOURCE (HOT WALL, COLD WALL)

SUBSTRATE

TIGHT SYSTEM

TEMPERATURE, PRESSURE, GAS CONTROLS

PUMPING CAPACITY

BY-PRODUCT DISPOSAL

TECHNIQUES

OPEN SUBSTRATE

INFILTRATION

FLUIDIZED BED

PLASMA-ASSISTED

CONVERSION

FIGURE 3

DEPOSITION VARIABLES

DIRECTLY CONTROLLED

PRECURSOR(S)
COMPOSITION, ADDITIVES
INITIAL FEED STOICHIOMETRY
TEMPERATURE
PRESSURE
FEED RATE (VELOCITY)
HEAT SOURCE, TYPE
SUBSTRATE

INDIRECTLY CONTROLLED

GAS DYNAMICS
REACTION KINETICS
GAS PHASE CHEMISTRY

DEPOSIT VARIABLES

STOICHIOMETRY
GRAIN SIZE
MICROSTRUCTURE, MORPHOLOGY
STRESSES
COMPOSITION
HABIT
UNIFORMITY
ANISOTROPY
CRYSTALLINITY

FIGURE 4
DEPOSIT OPTIMIZATION FACTORS

DEPENDS ON APPLICATION

COATINGS

ADHERENT
IMPERVIOUS
RESIDUAL STRESS
THERMAL COMPATIBILITY
HARDNESS
STRENGTH
TOUGHNESS

WINDOWS

PURITY
STOICHIOMETRY
INTRINSIC EM PROPERTIES
STRUCTURE
MECHANICAL PROPERTIES

COMPOSITE

DENSITY
DENSITY GRADIENTS
ADHERENCE
THERMAL COMPATIBILITY
MATRIX PROPERTIES, STRUCTURE

Figure 5 lists some of the CVD techniques which were mentioned before. Chemical vapor infiltration (CVI) is a technique that is summarized in Figure 6 and is used to seal up porosity. This process usually is run at lower temperatures for longer times than CVD processes. The precursors must penetrate the sample before any appreciable reaction occurs. Otherwise, the reaction would occur on the surface of the piece and not reach the internal surfaces.

Figure 7 lists some examples of conversion coatings. In carbon-carbon conversion coatings, Si vapor is generated using a mixture of powders. The Si vapor reacts with the carbon-carbon to form silicon carbide. In this case, the substrate takes part in the reaction, as denoted by the use of the term conversion.

Figure 8 lists the factors involved in the process modeling. There are a number of variables which have to be worked out empirically. You may try to carry out experiments in a small reactor, but then you find out that you have terrible problems when you try to scale up to a large reactor because the gas dynamics play a large part on how fast one deposits and how uniform the deposit is.

We can model the chemistry or the fluid dynamics or both. There are a number of factors to consider for determining what the most efficient set of conditions would be for depositing a material like SiC. All of the species involved are identified, or at least you write down as many reactions as you can that would occur. You might have twenty or thirty reactions and components that you think could be present in the reaction and environment. If you can find the free-energies or heats of formation, you can establish phase diagrams and presumably understand the thermodynamics of the situation.

Figure 9 shows some thermodynamic yields for the $\text{CH}_3\text{SiCl}_3\text{-H}_2$ system. In the diagrams the percent conversion of feed gases is on the ordinant. On the abscissa is the ratio of hydrogen

FIGURE 5
CVD VARIATIONS

OPEN SUBSTRATE

COATINGS, SHAPES
THIN FILM FORMATION, DOPING

INFILTRATION

COMPOSITE MATRIX FORMATION
COATING INTERNAL SURFACES
SEALING POROSITY

PACK CONVERSION

HARD COATINGS
PROTECTIVE COATINGS

FLUIDIZED BED

PARTICLE COATING
STRUCTURAL MODIFICATION

PLASMA ASSISTED

POWDER FORMATION
COATINGS
OPTICAL FIBER PREFORMS

THERMAL DECOMPOSITION/REACTION

POWDER FORMATION

FIGURE 6

CHEMICAL VAPOR INFILTRATION

DEPOSITION ON INTERNAL SURFACES OF POROUS OR FIBROUS SUBSTRATE

REACTION RATE SLOWER THAN DIFFUSION RATE

GRADIENT FORMATION

ACCESS TO PORES

REMOVAL OF SURFACE SCALE

EXAMPLES

CARBON
SILICON CARBIDE
BORON NITRIDE
TANTALUM
TITANIUM DIBORIDE
BORON CARBIDE
TITANIUM CARBIDE

LIMITATIONS

SPECIMEN THICKNESS
AVAILABLE POROSITY, GEOMETRY
DENSITY GRADIENTS

TECHNIQUES

ISOTHERMAL
TEMPERATURE, PRESSURE GRADIENT
RF HEATING

FIGURE 7
CONVERSION COATING

FORMATION OF COATINGS THROUGH REACTION OF
SUBSTRATE COMPONENT WITH VAPOR PHASE SPECIES

EXAMPLES

ALUMINIDES
BORIDES
NITRIDES
CARBIDES
CHROMIDES

VARIABLES

COMPOSITION OF VAPOR OR PACK
TIME
TEMPERATURE
CATALYSTS (ACTIVATORS)
SUBSTRATE SHAPE, SIZE
CARRIER
SUBSTRATE STRUCTURE
GLOW DISCHARGE, PLASMA ASSIST
PACK DENSITY, PART LOCATION

PACK COATING (CEMENTATION) - REACTIVE VAPORS
GENERATED BY REACTIONS AMONG PACK COMPONENTS.
ADVANTAGEOUS FOR LARGE, COMPLEX SUBSTRATES

FIGURE 8
PROCESS MODELING

A. CHEMISTRY

IDENTIFY MAJOR SPECIES GENERATED/DEPOSITED
DETERMINE FREE ENERGIES OF FORMATION
ASSUME THERMODYNAMIC EQUILIBRIUM
MINIMIZE FREE ENERGY OF SYSTEM
SOLVE FOR EQUILIBRIUM OVER T, P, COMP., CONC.
DERIVE CONCENTRATIONS OF MAJOR SPECIES
ESTABLISH EFFICIENCY AND PHASE DIAGRAMS

B. FLUID DYNAMIC

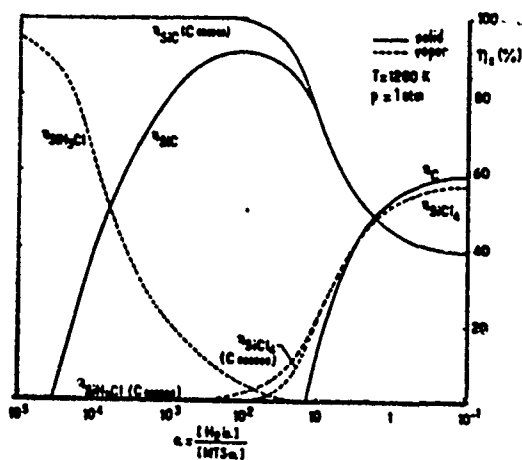
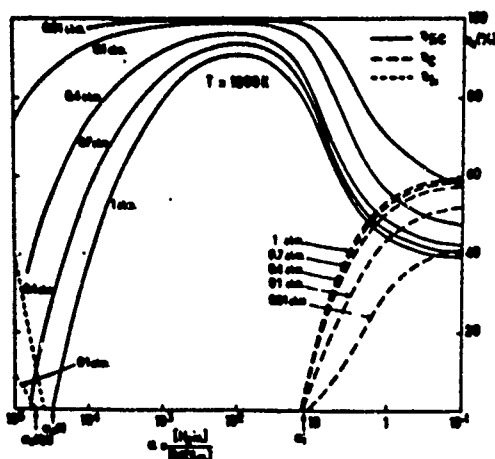
GAS DENSITY, VISCOSITY, VELOCITY
LAMINAR VS. TURBULENT; STAGNATION

UNCERTAINTIES

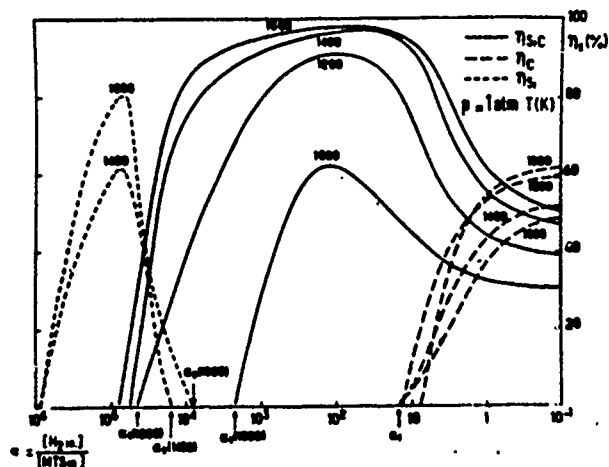
DEPARTURE FROM EQUILIBRIUM
IDENTITY OF POLYMERIZATION SPECIES
RATES, ENERGY OF FORMATION OF INTERMEDIATES
DIFFUSION RATES
GAS DYNAMIC EFFECTS

APPLIED TO MANY CVD PROCESSES (e.g. PROC. 7th CVD CONF. 1979)

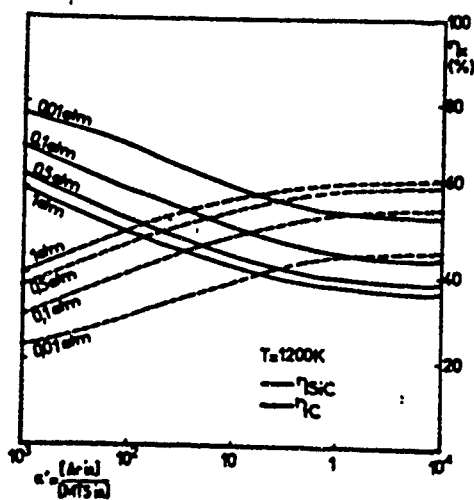
MANY COATING PROCESSES HAVE BEEN DEVELOPED EMPIRICALLY



$\text{CH}_3\text{SiCl}_3\text{-H}_2$: influence of a carbon excess on thermodynamic yields



System $\text{CH}_3\text{SiCl}_3\text{-H}_2$: variations of the thermodynamic yields as a function of T , p and initial composition



$\text{CH}_3\text{SiCl}_3\text{-Ar}$: variations of thermodynamic yields vs. p and initial composition

FIGURE 9

Thermodynamic Yields of CH_3SiCl_3

Ref. R. Naslain et al., EuroCVD-IV, 293-305 (1983), pub. Philips, Eindhoven

to methyltrichlorosilane being fed. A series of diagrams like these will allow you to determine experimental conditions to obtain the best yields of SiC.

Figure 10 illustrates gas dynamics analysis by looking at the geometry of the deposition. In Figure 10A, the gases are being fed up toward a substrate which is heated (cold wall reactor). In Figure 10B, the gas stream is coming down toward the substrate. By determining the hydrodynamic factors, one can analyze the flow lines and avoid stagnation points where very little deposition occurs.

Figure 11 shows the two types of reactors used in the CVD processes. Figure 11B is a hot wall reactor. In this case the heat is generated by radiation from the sides of the furnace so that the whole zone between the gas nozzle and the substrate is heated. Reaction parameters such as gas velocities, residence times, etc., can be calculated. In the cold wall reactor, only the substrate is heated and different reactions are involved. So the kinetics and conversions are going to be different.

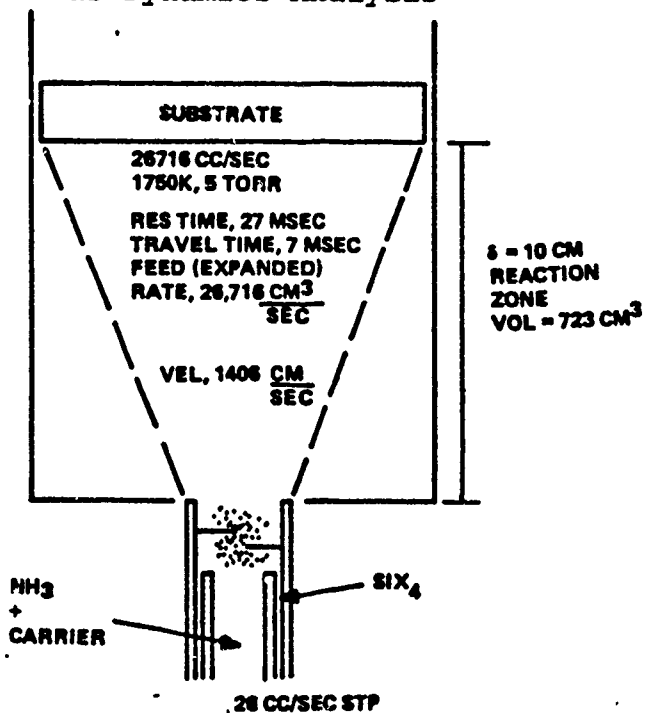
The boundary reaction zone (Figure 12) and the reaction rate can be controlled by knowing the reaction kinetics and rates at which the gas diffuses through the boundary to the surface. Sometimes you can overcome diffusion by having mass flow control.

The reaction sequence for a surface reaction is frequently described as consisting of six steps. The diffusion through the boundary layer, absorption on the surface, dissociation, surface diffusion/reaction to form the most favored structure, desorption of the by-product, and diffusion of the by-product out of the reaction zone. Intermediate reactions also occur where polymeric species form which may contribute to the deposit and affect its morphology.

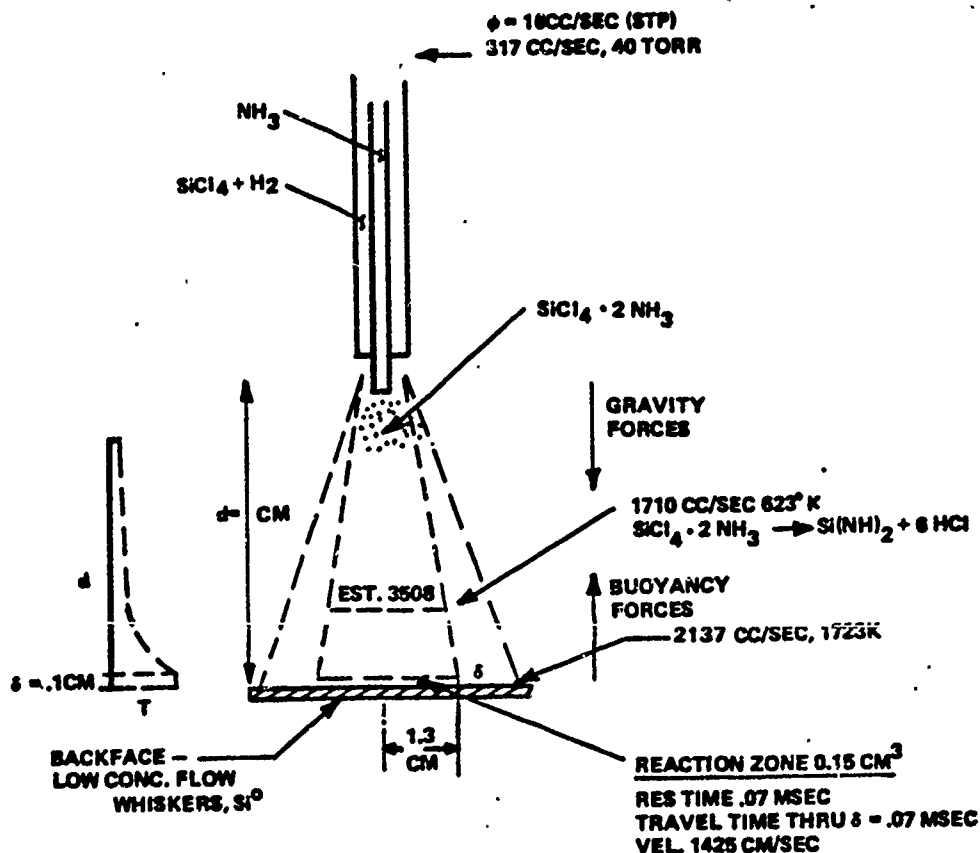
Figure 13 shows a tube reactor with a heated filament going through the tube. Figure 13B shows the temperature profile, and Figure 13C shows the concentration profile. This is an example of

FIGURE 10

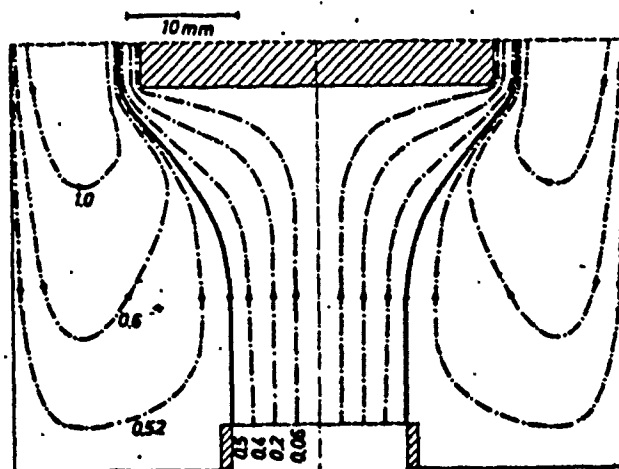
Gas Dynamics Analysis



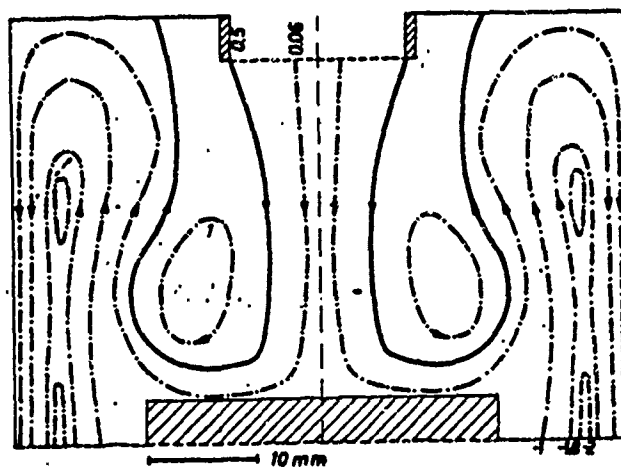
Typical Flow Conditions in HW-4 Using Deposition Surface Perpendicular to Flow.



Flow Conditions in Cold Wall Reactor.



Calculated flow lines: $Re = 50$, $T_d = 900$ K, $Gr/Re^2 = 22$ ($Fr = 0.09$).



Calculated flow lines: $Re = 50$, $T_d = 900$ K, $Gr/Re^2 = 22$ ($Fr = 0.09$).

FIGURE 11

Gas Reactor Flow Profiles.

Ref. G. Wahl, Thin Solid Films 40 13-26 (1977)

FIGURE 12

KINETICS

BOUNDARY LAYER REACTION ZONE RATE CAN BE CONTROLLED
BY:

REACTION KINETICS

DIFFUSION

MASS FLOW

REVERSE REACTIONS

REACTION SEQUENCE - SURFACE REACTION

DIFFUSION THROUGH BOUNDARY LAYER

ADSORPTION

DISSOCIATION

SURFACE DIFFUSION/REACTION

DESORPTION OF BY-PRODUCT

DIFFUSION OF BY-PRODUCT

INTERMEDIATE REACTIONS

GAS PHASE POLYMERIZATION/DISSOCIATION

DROPLET DEPOSITION, DECOMPOSITION

NUCLEI FORMATION

COMPLEX VS. SIMPLE CHEMISTRIES

HYDROCARBONS

CARBOSILANES

NITRIDES

METALS

SCALE-UP CORRELATIONS

TRAPPED SPECIES

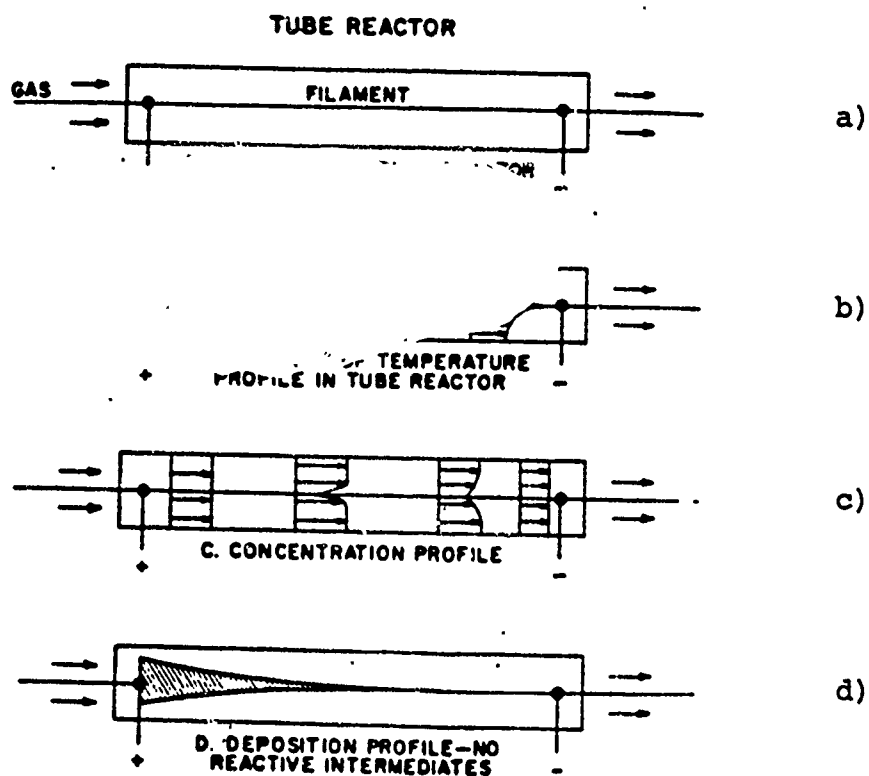


FIGURE 13

A cold wall deposition apparatus. (a) The deposition gas flows through a tube with a resistance heated, substrate filament placed along the cylinder axis. (b) The temperature profiles are shown for the pyrolysis gas as it flows down the deposition tube. (c) The concentration profiles are indicated for the pyrolysis gas. (d) The deposition profile along the filament is illustrated for the case when deposition occurs immediately without formation of an active intermediate.

a cold wall reactor so the walls of the tube are cold and the concentrations of reactive species are lowest at the filament.

Figure 14 shows the profiles for a hot wall reactor where the walls have the highest temperatures and the concentration of reactive species are the lowest at the walls. The deposit profile can be smoothed out to obtain a more even deposit by accepting a lower conversion of reactive species to the solid. The problem to contend with is that the conversion may be only 5 to 10%, and the by-products cannot be dumped into the environment as they were years ago.

The average molecular weight (Figure 15) of species in the gas environment tend to increase and then decrease as a function of temperature. In the case of methane, the maximum molecular weight occurs at about 700-800°C. In the case of methyltrichlorosilane, the temperature for maximum molecular weight might be somewhat lower. The fact is that these are dynamic systems, and if you deposit at 2000 or 1500°C, you cannot categorically say that you don't have some of these higher molecular weight species there. They will tend to form at varying rates depending on gas velocity and various other factors which are very complex.

One of the earlier studies involved pumping tetramethylsilane into a hot tube at a pretty good rate so that the residence times were about one minute. Some of the species identified are shown in Figure 16. Some of these molecules have fairly high molecular weights (~400). As the molecular weight increases, the chances are they will begin to lose hydrogen and methyl groups and eventually molecules will react with other molecules and reach the point where they will condense and deposit, some of them as droplets. A fair amount of work has been done on liquid drop nucleation. Rather than depositing atoms, more complex molecules are being deposited which tend to give the microstructure observed.

Figure 17 shows some of the relationships for making pyrolytic graphite from methane. Two common forms of pyrolytic

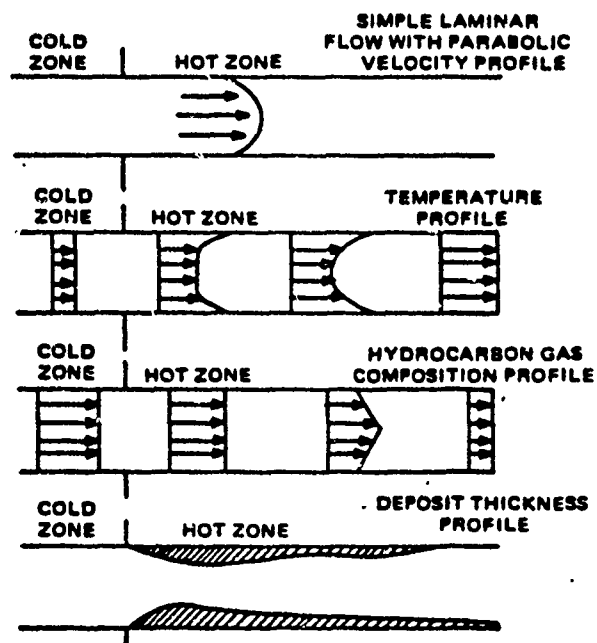


FIGURE 14
Hot Wall Reactor Profiles.

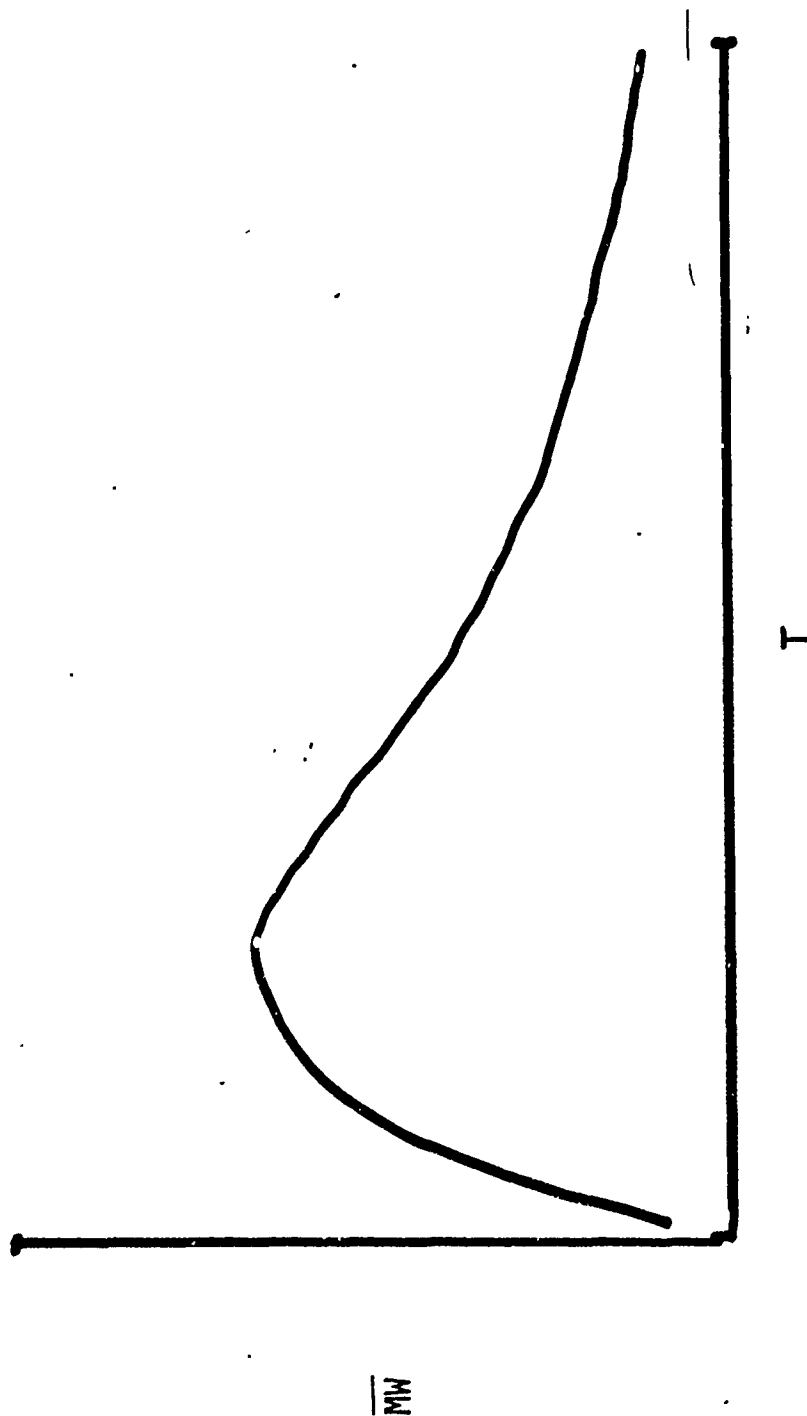


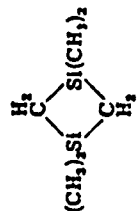
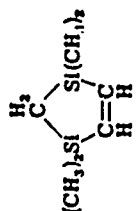
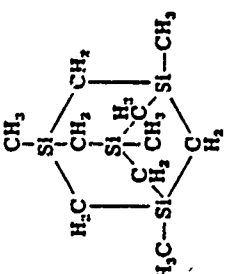
FIGURE 15.
Average Molecular Weight vs. Temperature in a Gas Environment.

DECOMPOSITION SPECIES

G. FRITZ, J. GROBE, AND D. KUMMER

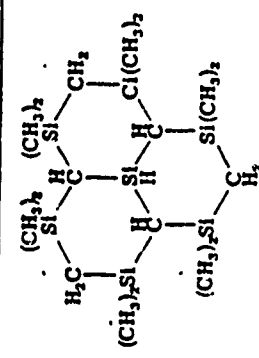
TABLE III

COMPOUNDS FROM THE PYROLYSIS OF $\text{Si}(\text{CH}_3)_4$

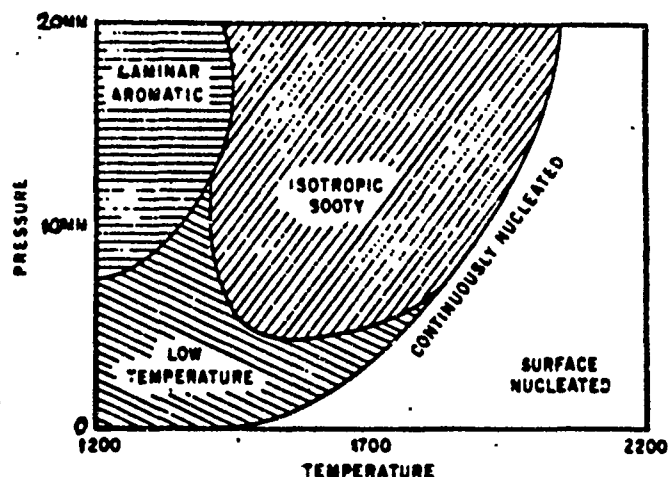
Compound	Vol % of product
1. $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{Si}(\text{CH}_3)_3$	2.4
2. 	3.2
3. $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{Si}(\text{CH}_3)_3$	6.9
4. 	0.7
5. $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$	5.6
6.  and $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{Si}(\text{CH}_3)_3$	7.5 (together)
7. 	-
8. $\text{Si}_4\text{C}_{13}\text{H}_{34}$ (pale yellow oil)	-
9. $\text{Si}_4\text{C}_{13}\text{H}_{34}$ (yellow viscous oil)	-

CARBOSILANES

TABLE III (Continued)

Compound	
10. $\text{Si}_4\text{C}_{18}\text{H}_{48}$	
11. $\text{Si}_6\text{C}_{30}\text{H}_{90}$	(yellow solid)
12. $\text{Si}_6\text{C}_{31}\text{H}_{98}$	(yellow-brown solid)
13. $\text{Si}_6\text{C}_{37}\text{H}_{114}$	(red-brown solid)

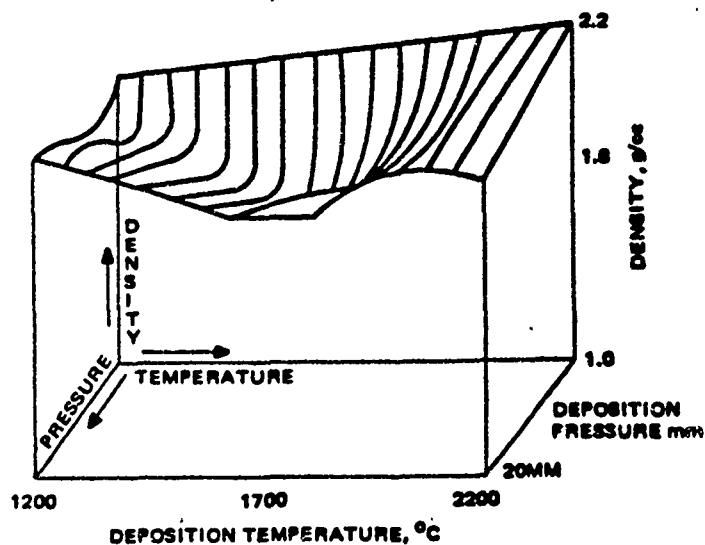
Ref. G. Fritz, J. Grobe and D. Kummer,
Advances in Inorganic Chemistry and
Radiochemistry, 7 349-418 (1965).



Fields of microstructure for pyrolytic graphite deposited from methane. Samples were obtained from 1/2-inch bore tubes, 3 inches from the inlet (Reference 1).

Ref. R. J. Diefendorf, Reactivity of Solids, pp 461-475, ed. J.W.Mitchell, Wiley, 1969.

Generalized relationship between density of pyrolytic graphite deposits and deposition pressure and temperature at a constant flow rate. Similar relationships have been obtained for different flow rates, and results have been correlated with microstructures and properties.



Ref. J. Bokros, Chemistry and Physics of Carbon, 5 1-110 (1969)
ed. P.L.Walker, Jr., M. Dekker

FIGURE 17
PYROLYTIC GRAPHITE

graphite are surface nucleated graphite and continuously nucleated graphite. In surface nucleated graphite, deposits nucleate at the surface and continues under very stable gas phase conditions and develops a fine comb structure. In continuously nucleated graphite you get larger amounts of nucleation from particles, and a new deposit starts rather than continuing to grow from the original deposit. Figure 17B shows the correlation between pressure, temperature, and density of pyrolytic graphite deposits.

Figure 18 illustrates the morphology - process relationships for SiC deposits. The $H_2/MeSiCl_3$ ratio is on one side, the pressure and temperature are on the other axes. The microstructures obtained at the various ranges of parameters are shown on the left side.

At higher temperatures pyrolytic graphite (PG) and silicon carbide can be co-deposited. Pyrolytic graphite and SiC are co-deposited to reduce the anisotropy of PG. In the case of thermal expansion (Figure 19), the thermal expansion in the "c" (cross the planes) and "ab" (along the planes) directions becomes almost equal as the percent SiC in PG is increased to 30-40%. The high degree of anisotropy was leading to mechanical scaling off of deposited layers, and better materials could be obtained by co-depositing PG and SiC.

The same phenomena were observed for the thermal conductivity of PG (Figure 20). In the "ab" direction, the thermal conductivity of PG is fairly high, and in the "c" direction it is low. By co-depositing SiC the thermal conductivity becomes more isotropic. These results occur by changing the microstructure and altering the preferred orientation of the deposit.

Other work which was discussed involved Si_3N_4 and AlN. The Si_3N_4 was deposited from SiF_4 and ammonia mixtures at about $1500^\circ C$, but fine grained deposits have not been obtained. One problem has been trace amounts of oxygen (Figure 21). A reproducible white crystalline Si_3N_4 could be deposited at about 1% oxygen.

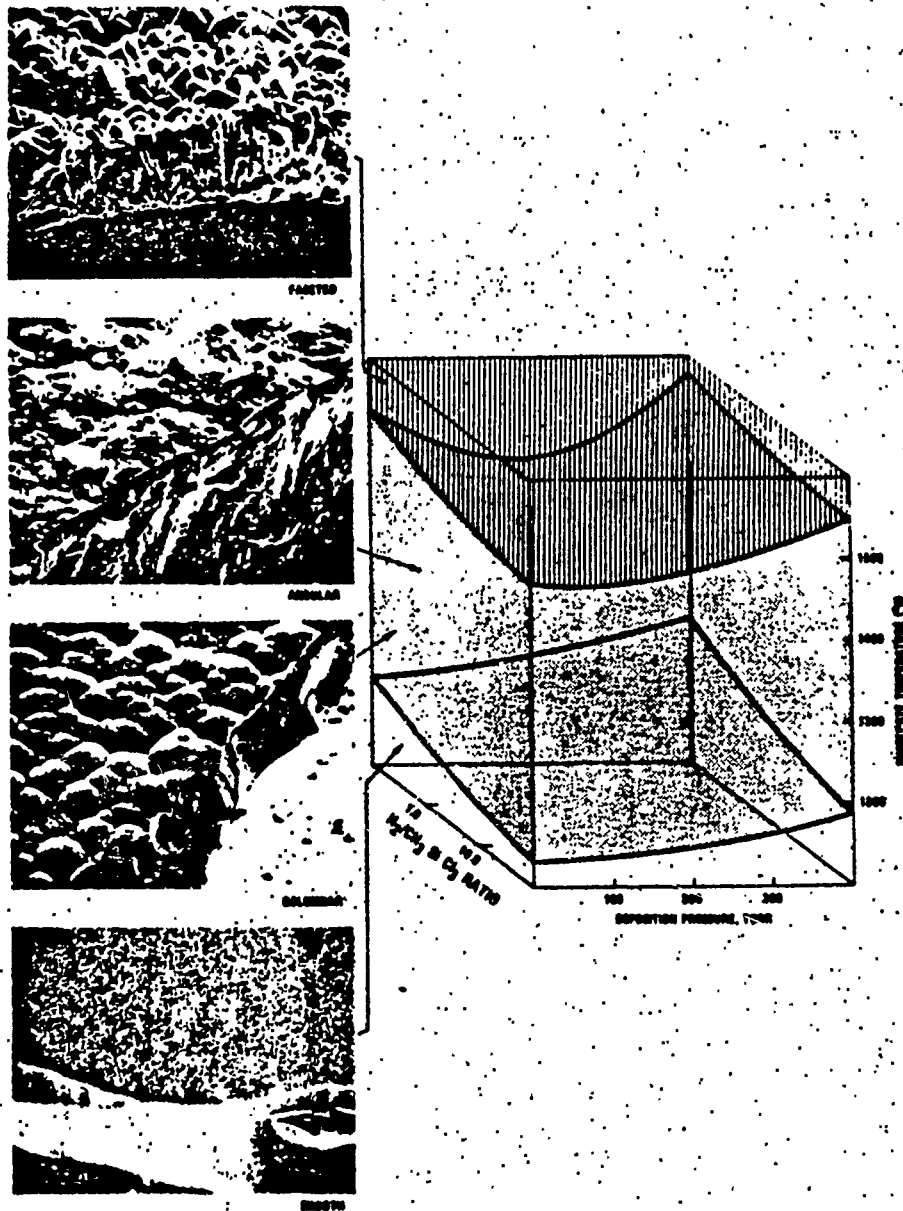
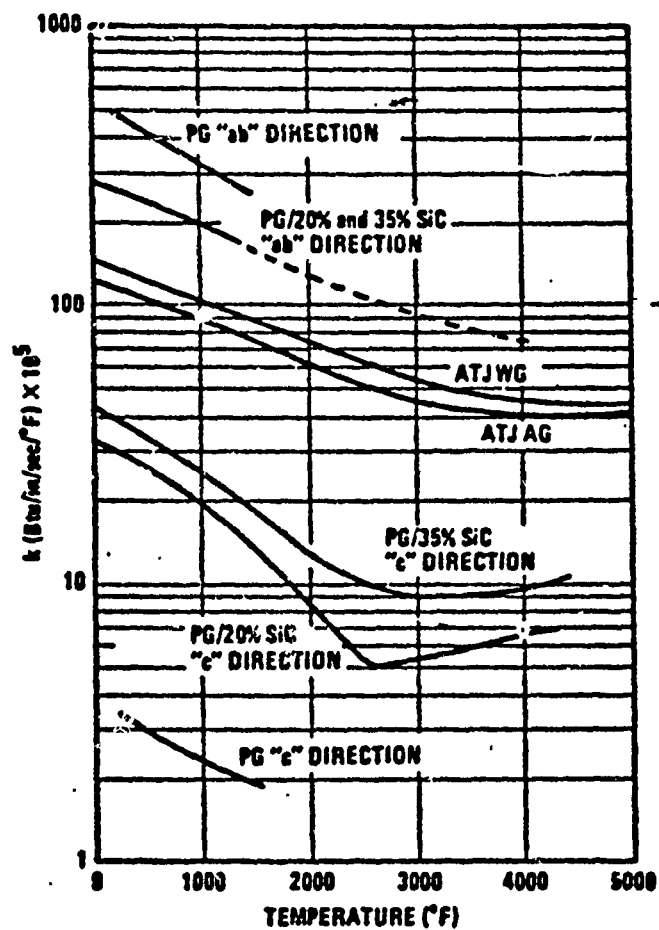


FIGURE 18

The morphology-process relationships in CVD SiC.

Ref. J. Chin, P.K.Gantzel and R.G.Hudson, Thin Solid Films 40 7-72 (1977)



References

PG	ab	Appendix B	Figure 15
PG	c	Appendix B	Figure 16
PG/20% SiC	ab	Appendix B	Figure 17
PG/20% SiC	c	Appendix B	Figure 18
PG/35% SiC	ab	Appendix B	Figure 19
PG/35% SiC	c	Appendix B	Figure 20

ATJ WG&AG Private communication 1972
from SRI

FIGURE 19

Thermal Conductivity of PG and PG/SiC Codeposit.

Ref. R. H. Singleton, AD 769-285 (1973) Atlantic Res. Corp. Contract
FO 4611-72-C-0047

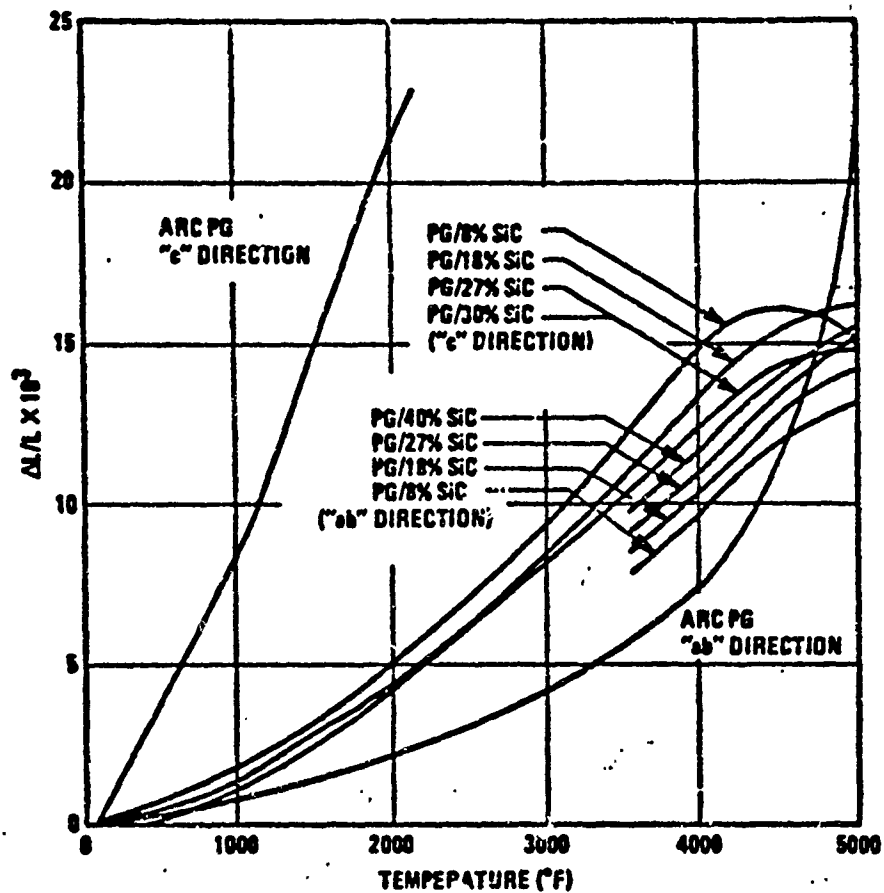


FIGURE 20

Thermal Expansion of PG and PG/SIC Codeposit.

Ref. R. H. Singleton, AD 769 285 (1973) Atlantic Research Corp. Contract
FO 4611-72-G-0047

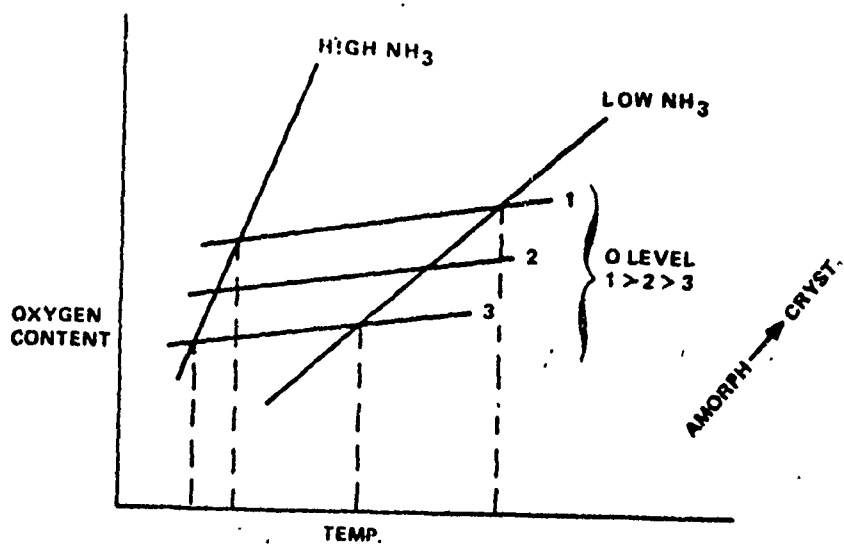


FIGURE 21

Schematic Representation of Effect of Oxygen Impurities on Formation of Amorphous and Crystalline Deposits at Various Temperatures.

Aluminum nitride has been investigated using the $\text{AlF}_3 \cdot \text{NH}_3$ complex. By reacting AlF_3 and ammonia one can get a 3:1 or a 1:1 ammonia to AlF_3 complex which is not too sensitive to moisture. It has a good vapor pressure and can be vaporized.

Figure 22 lists some of the aspects of coating carbon/carbon composites. Carbon has a low thermal expansion coefficient but has local thermal expansion variations. When a coating is deposited on carbon/carbon at high temperature, it usually cracks since the carbon shrinks less than the coating. The reactivity of the carbon varies, and a resin char reacts differently toward conversion coatings than a pitch base char. Other factors include carbon reactivity, diffusivity, and the coating stresses and low strain capability of most of the coatings. Also, the carbon/carbon properties vary with application. The carbon substrate varies and depends on who manufactured it. Coating every type of carbon may not be possible, and communication between the composite designer and CVD personnel is critical.

Floor Discussion

Areas where improvement is needed:

- More knowledge is needed about coating properties--
How do they match the substrate?
- More information is needed about coating stresses--
Can coating stresses be varied or controlled by
varying gas composition?
- How do various molecular species affect microstructure?
- Usually a conservative approach is taken since there
is never enough money to explore the extremes or new
approaches.
- How do you reproduce results to control deposits?
- Scale up is a problem.
- How do you coat fibers without sticking some of the
filaments together? Can you deposit uniform coating?

FIGURE 22

FACTORS RELATING TO COATINGS FOR C/C

LOW, ANISOTROPIC THERMAL EXPANSION

LOCALIZED EXPANSION VARIATIONS

VARIABLE CARBON REACTIVITY

MATRIX-RESIN, PITCH

FIBER-SURFACE, ENDS

PARTICLE SIZE

DEGREE OF GRAPHITIZATION, ANISOTROPY

CARBON REACTIVITY, DIFFUSIVITY

COATING STRESSES, LOW STRAIN CAPABILITY

C/C PROPERTIES VARY WITH APPLICATION

COATING WILL VARY WITH C/C PROPERTIES

COATING AND DESIGN INTERACTION CRITICAL

EFFECT OF GEOMETRY AND FIBER VARIATION IN
COMPOSITE SURFACE REGION - GRADED COMPOSITE

- More knowledge is needed about wetting and adhesion-- not much is known about wetting and adhesion of CVD coatings.
- Polymeric precursors should be investigated as coatings for fibers, but polymers should be designed for the application and should bond to the surface. Different polymers will probably be needed for each type of surface that needs a protective coating.

Some General References

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 13. P. Christin, R. Naslain and C. Bernard, "A Thermodynamic and Experimental Approach to SiC-CVD Infiltration of Porous C-C Composites," Proc. 7th Int. Conf. on CVD (1979) pp. 499-514.
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 15. N.E. Miller and P.F. Stablein, Jr., "CVD Scaling Study," Proc. 3rd Int. Conf. CVD,(1972) pp. 153-163, ed. F.A. Glaski, pub. Amer. Nucl. Soc., Hinsdale, IL.
-

SUMMARY OF TECHNICAL DISCUSSION AND OUTLINE OF R & D NEEDS

In the final session of this workshop, each of the discussion leaders summed up the technical highlights of their sessions and then a general floor discussion was held to review recommendations for research goals to meet identified Air Force requirements for high temperature materials. The summaries prepared by each of the floor leaders are presented in Tables 1 through 7. A summary of the audience recommendations developed in the final floor sessions of the workshop is presented in Table 8. The summaries presented in Table 1 through Table 8 describe the essence of the discussions carried on during the past three days of this workshop.

TABLE 1

AF NEEDS - DR. HENRY GRAHAM

Toughness
Stability } Still First Order Needs
Shrinkage
Chemical Purity
Processing Aid
Drying w/o Cracking
Alternate Materials/Processes
Coatings (Oxidation Resistance, Mechanical Strength, Chemical Stability)
Testing Techniques/Methodology
Fundamental Understanding

- Size of Second Phase
- Matrix, Fiber, Interface Properties

Computer Aided Design, Control, Feedback, Processing Window
Some Pores Are OK - Cracks Are Not
Technology Evaluation and Implementation

TABLE 2

OPPORTUNITIES IN CARBON-CARBON COMPOSITES - Ms. Frances Abrams

Innovative Processing

- Ceramists are accustomed to high temperature processes
Example: Superheating, carbonization

Innovative Materials

- In-depth inhibition (fluorinated carbon)
- Controlled char materials for matrices
- Chemistry of carbon fiber controlled for:
 - a) matrix compatibility
 - b) oxidation resistance
- Produce a material tailored and linked to processing and design

PROBLEMS

Application of Ceramics for Oxidation Protection Coatings

- Composite coatings
- Organosilicates
- Sol-Gel
- Coated fibers

Importance of integrating material process and design properties.

TABLE 3

CERAMIC-CERAMIC COMPOSITE ISSUES - DR. KARL PREWO

3 Component System - R & D for All Three

- Fiber
- Matrix
- Interface(s) - Interphases
- Relative Sizes

Toughness is Key, but Various Strengths Necessary

- Tension - Compression - Shear
- Fatigue, Stress - Rupture

Strengths of Components Must be Considered Relative to Each Other

Environmental Stability is a Composite Issue

- Not Single Component
- Under Stress

SUGGESTIONS

Study Mechanisms of Environmental Stability

- Fiber
- Matrix
- Interface

Provide Ceramics for Study to Determine Guidelines for What We Want

Push Existent Ceramic Composite Systems as Close to Use as Possible to Determine Important Factors for Success

- Elastic Modulus (E), Ultimate Tensile Strength (UTS), Fracture Toughness (K_{IC})
- Coefficient of Thermal Expansion (CTE), Thermal Conductivity
- Joining
- Nondestructive Evaluation (NDE)

Make Management Aware That Ceramic Composites Will Evolve Over More Than 3 Years

- "Superalloys were not developed overnight"

Don't Limit Scope of Applications

- Tribiology
- 800°F

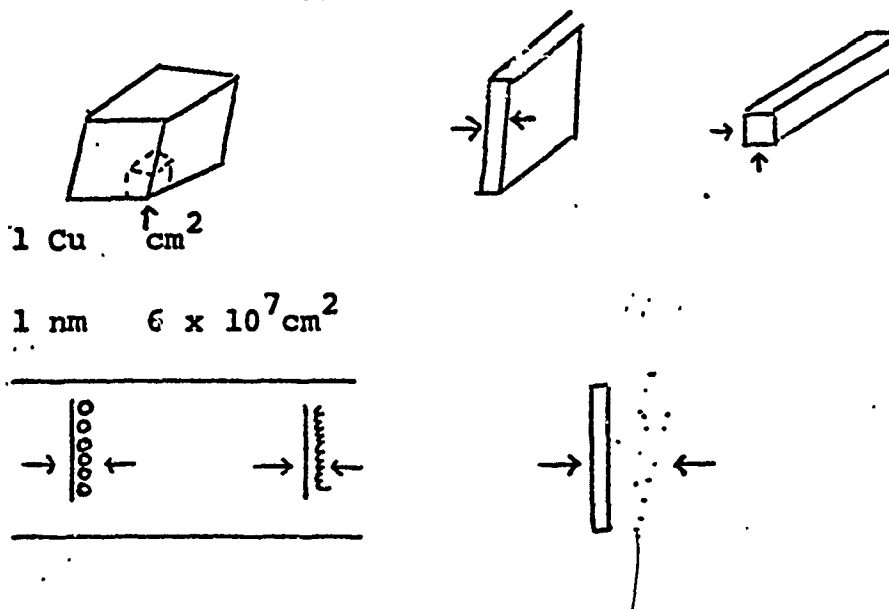
TABLE 4

SCOPE OF COLLOID SCIENCE - DR. EGON MATIJEVIC

$$V_T = E_i + \epsilon_s$$

$$V_T = e_i V + \gamma A/V$$

$$(V_T)_V = e_i + \gamma \left(\frac{A}{V} \right)$$



1. Materials for Study
2. Applications (center for materials preparation - synthesis - materials characterization)
3. Shopping list of needed materials behavior

TABLE 5

ROLE OF SOL-GEL PROCESSING IN HIGH PERFORMANCE
STRUCTURAL CERAMICS - DR. LARRY HENCH

- Al_2O_3 , $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, SiO_2 , or ZrO_2 Gel Matrix with Al_2O_3 , C, or SiC
Fibers or Whiskers

Potential Advantages:

Simple forming, complex shapes, room temperature infiltration,
low temperature densification, controlled volume porosity,
control of interface chemistry, oxidation resistance

Concerns:

Shrinkage control, redistribution of porosity, interfacial
voids

- Gel Matrix with Al_2O_3 , C, or SiC Weaves or Mats

Potential Advantages:

Same as above

Concerns:

Same as above, plus multiple step infiltration, interfacial
cracks due to matrix shrinkage away from 2nd phase

- Gel Matrix with Precipitated 2nd Phase

Potential Advantages:

Simple single phase processing, very small scale structures,
dense matrix

Concerns:

2nd phase may not act like fiber, difficult control of
interface chemistry

TABLE 5 (Continued)

- Gel Matrix with Fiber, Weave, or Mat, Preform Conversion Concurrent with Densification

Potential Advantages:

Use SOA technology, accommodate matrix shrinkage

Concerns:

Not demonstrated, fibers may be weak, interface may react

- Anisotropic Porous Gel Matrix with CVD or CVI Impregnation with SiC, Si₃N₄, or C Followed by Densification

Potential Advantages:

Very small diameter second phase, very high aspect ratio, very uniform distribution, control of interface and control of volume porosity

Concerns:

Several steps not SOA, 2nd phase may not act like high strength fiber, matrix may not densify, anisotropic gel matrix with pyrolyzed organometallic precursors

- Gel Derived SiC, Si₃N₄, or Si-C-N Ceramic Monoliths

Potential Advantages:

Ease of forming, lower densification temp. control of pore size distribution

Concerns:

Toughness? catastrophic failure, undemonstrated, gel densification processes, unknown oxidation resistance

TABLE 5 (Concluded)

- Gel Derived SiC, Si₃N₄, or Si-C-N with Coated Whiskers, Fibers, Mats, etc.

Potential Advantages:

Ease of forming, control of interface and volume (size of porosity), superior toughness

Concerns:

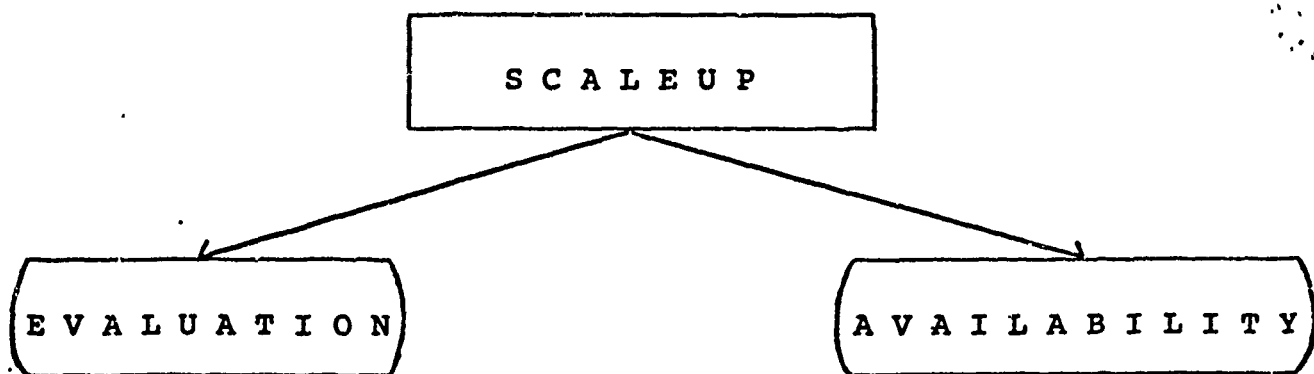
Undemonstrated, oxidation resistance

- Gel Coatings

- fibers
- weaves, mats, etc.
- composites

TABLE 6

ORGANIC POLYMER PRECURSORS - DR. ROBERT WEST



1. New approaches to "conventional" materials.
2. New chemistry to make "unknown" materials.

TABLE 7

CHEMICAL VAPOR DEPOSITION MULTI-SOURCE,
MULTI-DISCIPLINE APPROACH - DR. JOSEPH GEBHARDT

1. Design Coating First
Required Properties vs. Applied Conditions
Reactivity (Exhaust)
Thermomechanical Properties
Compatibility
Constituents (Multilayer)
Properties of Consistent Layers vs. Thickness
2. Design Process Steps
Consider All Options
Pack
Cud-Sputtered
Solutions
 - inorganic, chelates
 - colloidal, gas phaseMix and Match, Model
3. Design Substrate, Process
For Compatibility: Difference in Thermal Expansion,
Adherence, Residual Stresses
Estimate Response to Applied Conditions
Surface Modifications - Infiltration
4. Properties of Candidates
Existing Data
Determine Data - New Coatings
Fit Into Design Requirements
Attempt Selection
Compatibility
5. Fit Into Process Steps
6. Evaluate Feasibility for Various Applications

TABLE 8

SUMMARY OF AUDIENCE RECOMMENDATIONS

PROPOSED INVESTIGATIONS

1. Combination of thermodynamic & kinetic considerations
2. Computer aided process development
3. High strain material development
4. Continued development of promising monolithic ceramics
5. Better definition and understanding of "graceful failure"
6. Role of fillers
7. Crack sealing techniques
8. Me in organometallics (Hf, Nb, Ta, Zr)
9. Selective degradation of C fibers.
10.
 - a) Scale re-micro distances
 - b) Mechanical interactions of interface zone
 - c) Bonding vs. fracture toughness - optimum condition for each system
11. Information flow (and exchange)
12. Relevance of early polymer work
13. Techniques for evaluation of individual coated fiber
14. Process modeling

OTHER ACTIONS PROPOSED

1. Industry open to new and improved materials information exchange paths needed
2. Working group for interdisciplinary approach
3. Avoid problems by use of better application of fundamental technology

APPENDIX 1

List of Workshop Attendees

Abrams, Frances L.
AFWAL/MLBC
Wright-Patterson AFB, OH 45433

Adair, Dr. James
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201

Ball, Dr. Donald L.
Director of Chemical Sciences
Bldg. 410
Bolling AFB
Washington, D.C. 20332

Baney, Ronald H.
Dow Corning Corp.
3901 South Saginaw Road
Mail #540
Midland, MI 48640

Boudjouk, Prof. Philip
Dept. of Chemistry
North Dakota State Univ.
Fargo, ND 58105

Burte, Harris M.
AFWAL/MS
Wright-Patterson AFB, OH 45433

Chyung, Dr. Kenneth
Glass-Ceramic Research
Corning Glass Works
Sullivan Park
Corning, NY 14831

Coblentz, Bill
National Bureau of Standards
Bldg. 223, Room A221
Gaithersburg, MD 20899

Cranmer, David
The Aerospace Corporation
P.O. Box 92957, M2/242
Los Angeles, CA 90009

Dole, Steve
GE Corporate R & D
P.O. Box 8
Schenectady, NY 12301

Drzal, Dr. Lawrence T.
AFWAL/MLBM
Wright-Patterson AFB, OH 45433

Eitman, David A.
Science Applications, Inc.
18872 Berdeen Ave.
Irvine, CA 92714

Foley, Paul
Celanese Research Co.
86 Morris Avenue
Summit, NJ 07901

Forcht, Bremman
Kaiser Aero Tech.
P.O. Box 1678
San Leandro, CA 94577-0801

Gebhardt, Dr. Joseph J.
General Electric Space
Systems Division
P.O. Box 8555, Room U8614
Philadelphia, PA 19101

Gerstle, Dr. Frank P., Jr.
Sandia National Labs
Division 1845
Albuquerque, NM 87185

Goldfarb, Ivan
Polymer Branch
MLBP
Wright-Patterson AFB, OH 45433

Gonczy, Dr. Stephen
Signal UOP Research Center
50 UOP Plaza
Desplaines, IL 60016

Graham, Dr. Henry C.
AFWAL/MLLM
Wright-Patterson AFB, OH 45433

Graves, George A., Jr.
Univ. of Dayton Research Inst.
300 College Park, KL - 165
Dayton, OH 45469

Rager, Capt. Joseph W.
AFOSR/NE
Bldg. 410
Bolling AFB
Washington, D.C. 20332

Hasselman, Prof. D. P. H.
Virginia Polytechnic Inst.
Dept. of Matl's. Engineering
Blacksburg, VA 24061

Hecht, Norman L.
Univ. of Dayton Research Inst.
300 College Park, KL - 165
Dayton, OH 45469

Hench, Prof. Larry L.
Dept. of Materials
Science and Engineering
University of Florida
Gainesville, FL 32611

Hermes, Edward
AFWAL/MLLM
Wright-Patterson AFB, OH 45433

Hillig, Dr. William
General Electric Co.
Aircraft Engine Business Group
Cincinnati, OH 45215

Hurwitz, Fran
NASA Lewis - Mail Stop 106-1
21000 Brookpark Road
Cleveland, OH 44135

Jonas, Prof. Jiri
Univ. of Illinois
School of Chemical Sciences
1209 W. California
166 Roger Adams Lab, Box 53-5
Urbana, IL 61801

Katz, Dr. A. P.
AFWAL/MLLM
Wright-Patterson AFB, OH 45433

Kerans, Dr. Ron J.
AFWAL/MLLM
Wright-Patterson AFB, OH 45433

LeGrow, Gary E.
Dow Corning Corp.
3901 South Saginaw Road
Mail #540
Midland, MI 48640

Lillybeck, Eric
San Fernando Laboratory
10258 Norrif Avenue
Pacoima, CA 91331

Lynch, C. T.
ONR - Code 431
800 N. Quincy St.
Arlington, VA 22217

Mah, Dr. Tai-Il
Universal Energy Systems
4401 Dayton-Xenia Road
Dayton, OH 45432

Matijevic, Dr. Egon
Chairman, Dept. of Chemistry
Clarkson University
Potsdam, NY 13676

Matuszko, Dr. Anthony J.
Air Force Office of
Scientific Research
Bolling AFB, Bldg. 410
Washington, D.C. 20332

Mazdiyasni, K. S.
MLLM
Area B, Bldg. 450
Wright-Patterson AFB, OH 45433

McCormick, Scott
General Electric Co.
1 Neumann Way
Cincinnati, OH 45215

Morgan, Dr. Peter E. D.
Rockwell International
1049 Camino Dos Rios
Box 1085
Thousand Oaks, CA 91360

Prewo, Dr. Karl M.
Composites and Nonmetallics Group
United Technologies Research Ctr.
East Hartford, CT 06108

Prochazka, Dr. Svante
General Electric Corp. R & D
P.O. Box 8
Schenectady, NY 12301

Quinn, Dr. R. K.
Sandia National Labs.
Division 1846
Albuquerque, NM 87185

Rhine, Wendell
Univ. of Dayton Research Inst.
300 College Park, KL 562
Dayton, OH 45469

Rhodes, Dr. William H.
Ceramics and Metallurgy Tech. Ctr.
GTE Laboratories
40 Sylvan Road
Waltham, MA 02254

Rich, Michael J.
Univ. of Dayton Research Inst.
300 College Park
Dayton, OH 45469

Ruh, Dr. Robert
AFWAL/MLLM
Wright-Patterson AFB, OH 45433

Rybicki, Mr. George
NASA Lewis - MS 105-1
21000 Brookpark Rd.
Cleveland, OH 44135

Schilling, Curtis L., Jr.
Union Carbide Corp.
Techn. Center, Silicones 220
Tarry Town, NY 10591

Sheehan, James
GA Technologies, Inc.
P.O. Box 85608
San Diego, CA 92138

Stinton, D. P.
Oak Ridge Nat'l. Lab.
P.O. Box X
Oak Ridge, TN 37831

Tamborski, Dr. Christ
AFWAL/MLBT
Wright-Patterson AFB, OH 45433

Uhlmann, Prof. Donald R.
MIT
13-4005 MIT
Cambridge, Mass. 02139

Ulrich, Dr. Donald
Air Force Office of
Scientific Research
AFOSR/NC
Bolling AFB
Washington, D.C. 20332

Weber, Dr. William
Univ. of Southern California
Los Angeles, CA 90007

West, Prof. Robert
Dept. of Chemistry
University of Wisconsin
Madison, WI 53706

Yoldas, Bulent E.
Westinghouse Electric Co.
R & D Center
1310 Beulah Rd.
Pittsburgh, PA 15235