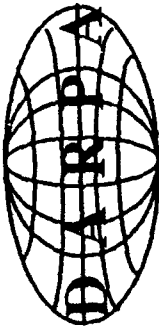


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DARPA - Advanced Composite Materials

Annual Presentation

November 19-20, 1992

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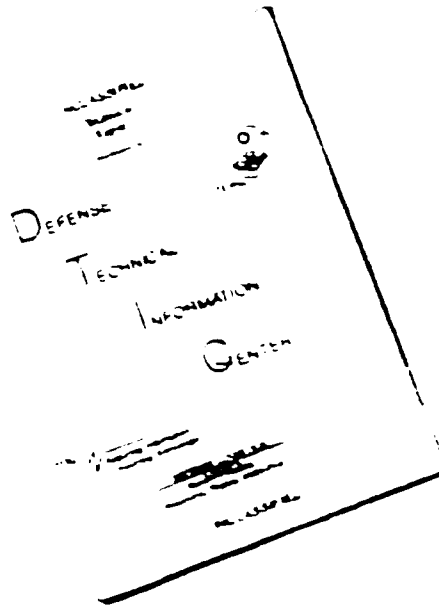
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DARPA - Composites Annual Review November 19-20, 1992

University of Florida, Gainesville, Florida

Thursday, November 19

1:30-1:45	Opening Remarks - Drs. Wilcox, Coblenz, Fishman
1:45-2:00	Overview - Reza Abbaschian
2:00-2:50	SiC Fibers - Chris Batich, Michael Sacks, Bill Toreki
2:50-3:20	Mullite Fibers - Joseph Simmons, Anthony Brennan
3:20-3:50	CVD Approaches to Composites - Tim Anderson
3:50-4:00	Break
4:00-6:00	Poster Presentation and Refreshments - Students

Friday, November 20

8:00-8:50	Intermetallic Composites - Michael Kaufman, Reza Abbaschian
8:50-9:40	Ceramic Composites - David Clark, Michael Sacks
9:40-10:10	Tapecast Laminated Composites - Jack Mecholsky
10:10-10:30	Break
10:30-11:15	Future Plan and General Discussions - R. Abbaschian
11:15-12:00	Summary and Comments
12:00-1:30	Lunch
1:30	Informal Subgroup Discussions and Tour of the Facilities

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List of Poster Presentations

Arredondo Room - 4:00 pm to 6:00 pm

Fiber Synthesis/Coating

- 1) "Atomic Layer Epitaxy"
R. Aparicio,* E. Allen, J. Wolan, and T.J. Anderson
- 2) "Chemical Vapor Infiltration"
R. Aparicio, E. Allen,* J. Wolan, and T.J. Anderson
- 3) "Chemical Vapor Deposition of TiC_x on Refractory Substrates"
R. Aparicio, E. Allen, J. Wolan,* and T.J. Anderson
- 4) "Chemical Vapor Infiltration and Atomic Layer Deposition of TiC on Ceramic Substrates"
R. Aparicio, E. Allen, J. Wolan, and T.J. Anderson*
- 5) "Sol-Gel Processing of Continuous Mullite Based Fibers"
S. Al-Assafi,* T. Cruse, T. Miller, A.B. Brennan, and J.H. Simmons
- 6) "Sol-Gel Processing of Continuous Mullite Based Fibers"
S. Al-Assafi, T. Cruse,* T. Miller, A.B. Brennan, and J.H. Simmons
- 7) "Polymer-Derived Silicon Carbide Fibers with Low Oxygen Content and Improved Thermomechanical Stability"
W. Toreki, C.D. Batich, M.D. Sacks, M. Saleem,* G.J. Choi, and A. Morrone

Microwave Processing

- 8) "Microwave Processing of High-Performance Ceramics and Composites"
D.E. Clark, Z. Fathi,* A.D. Cozzi, D.C. Folz, I. Ahmad, S. Al-Assafi, A.S. De',
and R.C. Dalton
- 9) "Microwave Processing of Sol-Gel-Derived Glass-Ceramics for High Temperature Composite Matrices"
A.D. Cozzi,* Z. Fathi, and D.E. Clark

Ceramic Matrix Composites

- 10) "Fabrication of Mullite and Mullite-Based Composites by Transient Viscous Sintering (TVS) and Pressure-Assisted Transient Viscous Sintering (PATVS)"
N. Bozkurt, G.W. Scheiffele,* Y.J. Lin, A. Ulicny, and M.D. Sacks
- 11) "Fabrication of Composites with Low Dielectric Constant Using Microcomposite Particles"
R. Raghunathan,* I.Y. Park, G.W. Scheiffele, and M.D. Sacks
- 12) "Processing, Microstructure and Properties of SiAlONs Prepared from Microcomposite Particles"
A. Bagwell, R. Raghunathan,* and M.D. Sacks
- 13) "Fabrication of SiC-Based Composites by Reactive Infiltration of Metals (RIM)"
K. Wang,* G.W. Scheiffele, P.J. Sanchez-Soto, and M.D. Sacks

* Indicates Presenter

Intermetallic Matrix Composites

- 14) "Processing of Compositionally Tailored Silica-Free MoSi_2/SiC Composites"
S. Jayashankar,* A. Costa e Silva, and M. Kaufman
- 15) "Phase Relations in Some Systems Relevant to MoSi_2 Processing"
A. Costa e Silva,* S. Jayashankar, and M. Kaufman
- 16) "Modelling and Design of Toughened Composites"
L. Xiao, M. Somerday,* and R. Abbaschian
- 17) "Microstructures and Properties of MoSi_2/Nb Coated and Uncoated Interfaces and Their Effects on Toughness"
L. Xiao* and R. Abbaschian
- 18) "Toughening and Strengthening of MoSi_2 with SiC Whiskers and Ductile Reinforcement"
L. Xiao* and R. Abbaschian
- 19) "Fabrication of Toughened Composites via Reactive Hot Compaction and In-situ Coating"
H. Doty,* L. Lu, A. Gokhale, and R. Abbaschian
- 20) "Development and Characterization of Interface Coatings in NiAl Matrix Composites"
P. Krishnan* and M. Kaufman
- 21) "Fiber-Reinforced TaTiAl_2 Alloy Composites"
I. Hwang* and R. Abbaschian

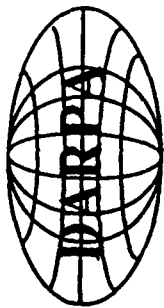
Mechanical Behavior

- 22) "Optimization of Creep and Fracture Properties by Microstructure Design"
B. De Aragao,* J.R. Castillo, and F. Ebrahimi
- 23) "Fracture Energy Anisotropy of Single Crystals"
L. Kalwani* and F. Ebrahimi
- 24) "Toughening by Metallic Lamina in Tape Casting Nickel/Alumina Composites"
Z. Chen* and J.J. Mecholsky Jr.
- 25) "Fracture of CVD Diamond Films on Silicon"
Y.L. Tsai* and J.J. Mecholsky Jr.

Other Contributed Posters on New Processing Technologies

- 26) "Surface Modification of BaTiO_3 Particles Via Oxalic Acid, Polyethyleneimine in Aqueous Systems"
R.E. Chodelka* and J.H. Adair
- 27) "Electrothermal Synthesis of BaTiO_3 Thin Films at 55°C "
S. Venigalla,* P. Bendale, T. Tsukada, J.R. Ambrose, and J.H. Adair
- 28) "Glycothermal Synthesis of $\alpha\text{-Al}_2\text{O}_3$ Particles at Ultra-Low Temperature"
S.B. Cho,* S. Venigalla, R.E. Chodelka, and J.H. Adair
- 29) "Monodispersed Nanosize Pt Particles Using Microemulsion Technique"
V. Nagabushnam* and J.H. Adair

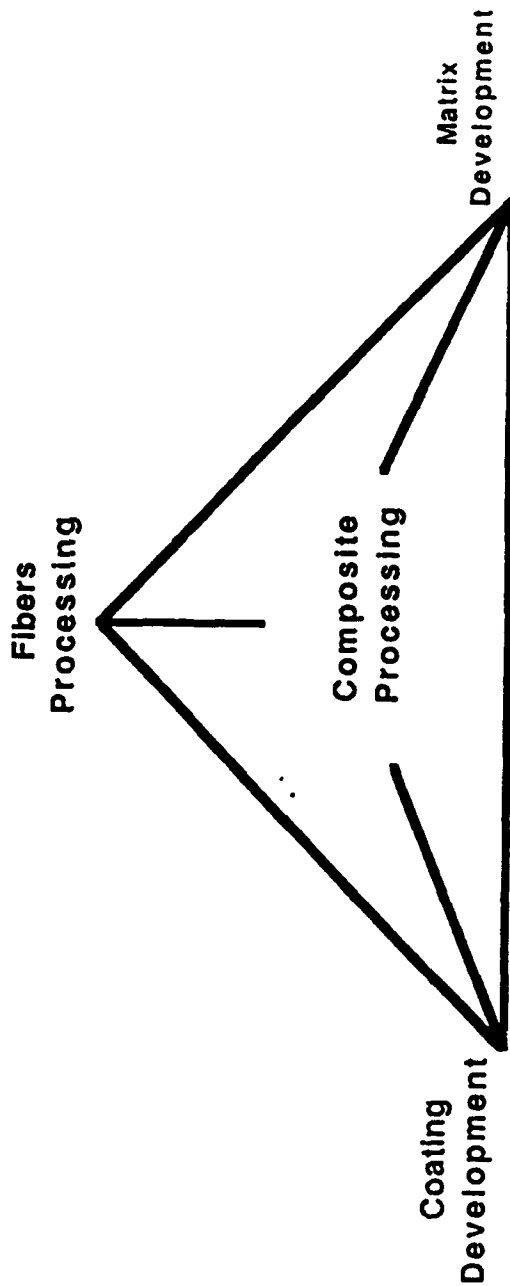
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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

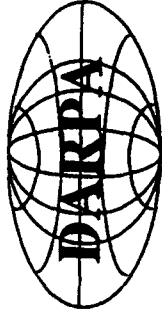
PROGRAM OVERVIEW

Reza Abbaschian



MSIE

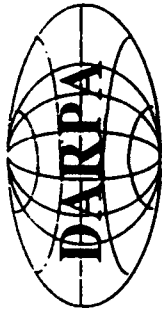
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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Program Objective

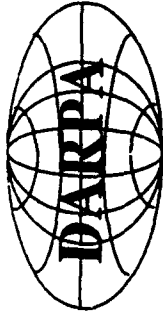
Provide a fundamental understanding of the processing science and technology necessary for cost-effective fabrication of ceramic-matrix and intermetallic-matrix composites with superior mechanical properties in high temperature and oxidizing environments. The composites are intended for use as structural materials for advanced aerospace applications at temperatures exceeding 1200°C.



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Critical Property Requirements

- High stiffness
- High strength
- High toughness
- Low density
- Thermal shock resistance
- Creep resistance
- Fatigue resistance
- Environmental stability
- Structural stability

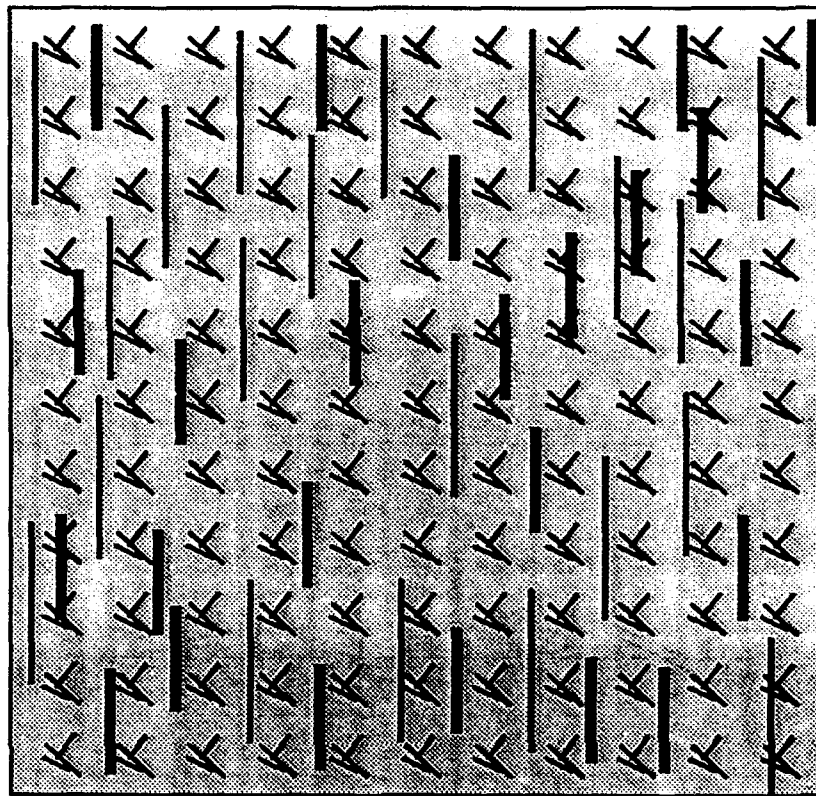


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

High Temperature Composite Needs

- Reinforcement materials with desired geometry, property and stability
- Matrix materials with appropriate properties and stability
- Interfacial control between reinforcement and matrix during processing and service
- CTE mismatch adjustments
- Cost effective processing and consolidation techniques

HYBRID COMPOSITES



COMPOSITE ELEMENTS



Environmentally Stable Matrix With Fine Dispersions For CTE Matching



Dispersions For Increased Strength and Creep Resistance

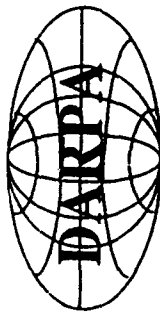


High Strength, High Aspect Ratio Reinforcing Phase For High Temperature Strength



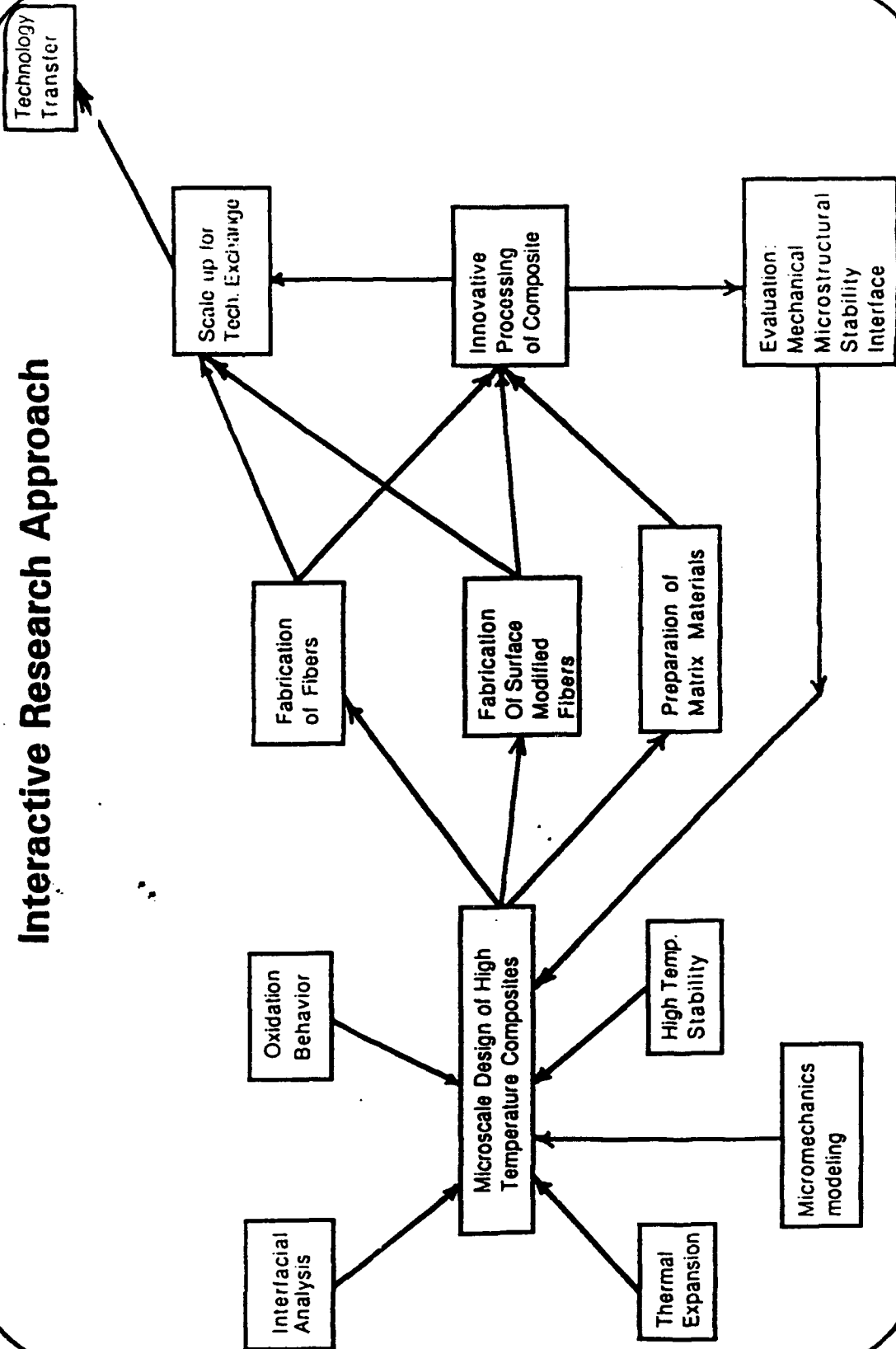
Ductile Phase Reinforcement For Low Temperature Toughness

Interfacial Tailoring For Optimum Mechanical and Chemical Stability



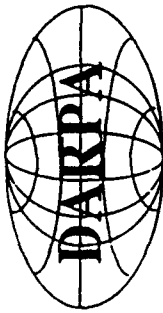
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Interactive Research Approach



MSE

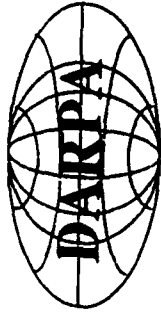
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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Major Thrusts of the Program

- A fundamental approach to microscale design of high temperature composites with tailored mechanical, chemical and physical properties.
- Development and scientific understanding of processes for the fabrication of refractory ceramic fibers with improved high temperature mechanical properties and stability.
- Development and scientific understanding of processes and properties necessary to control the chemical and mechanical integrity of the matrix/reinforcement.
- Development of innovative methods for the preparation of dense intermetallic-matrix and ceramic-matrix composites containing fiber and/or whisker reinforcement.
- Technology transfer.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Current Program Emphasis Areas

- FIBER FABRICATION
 - Mullite-based Fibers - A.B. Brennan and J.H. Simmons
 - SiC-based Fibers - C.D. Batich, M.D. Sacks, and W. Toreki
- COATINGS
 - Chemical Vapor Deposition of Refractory Carbides - T.J. Anderson
- COMPOSITE FABRICATION
 - Intermetallic Matrix Composites - R. Abbaschian and M.J. Kaufman
 - Ceramic Matrix Composites - M.D. Sacks
 - Microwave Processing of Composites - D.E. Clark
 - Laminated Ceramic/Metal Composites - J.J. Mecholsky, Jr.

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4. S-M. Sim, "Processing and Microstructural Characterization of Alumina-Dispersed Zirconia Fibers," Doctoral dissertation, University of Florida (1990).
5. W. Toreki and C.D. Batich, "Effects of Molecular Weight and Cross-Linking on Two Preceramic Polymers," presented at the American Chemical Society National Meeting in Miami Beach, FL, September 1989. Published in *Polymer Preprints*, 30 (2) pp. 237-238 (1989).
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11. W. Toreki, C. Batich, M.D. Sacks, M. Saleem, and G. Choi, "Polymer-Derived Silicon Carbide Fibers with Improved Thermomechanical Stability," pp. 761-769 in *Better Ceramics Through Chemistry V*, edited by M.J. Hampden-Smith, W.G. Klemperer, and C.J. Brinker, Mat. Res. Soc. Symp. Proc., Vol. 271, Materials Research Society, Pittsburgh, PA (1992).
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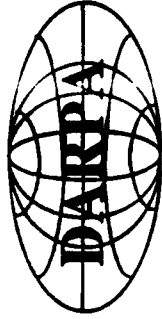
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Patent Disclosures and Applications

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2. "Polysilazane Preceramic Polymer via Free-radical Initiation," W. Toreki and C.D. Batich, August, 1990, patent disclosure.
3. "SiC Fibers Having Low Oxygen Content and Methods of Preparation", W. Toreki and C.D. Batich. Patent application approved for issue by U.S. Patent Office, July, 1992.
4. "Alumina- or Alumina/Zirconia-Silicon Carbide Whisker Ceramic Composites and Methods of Manufacture," M.D. Sacks and H.W. Lee, U.S. Patent No. 5,009,822, April 23, 1991.
5. "Silica-Coated Composite Powder," M.D. Sacks and C.S. Khadilkar, U.S. Patent Application Serial No. 07/714/438.
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**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

**POLYMER-DERIVED SILICON CARBIDE FIBERS WITH
LOW OXYGEN CONTENT AND IMPROVED THERMOMECHANICAL STABILITY**

Principal Investigators: C.D. Batch and M.D. Sacks

MSIE ————— UNIVERSITY OF FLORIDA

OUTLINE

- **BACKGROUND**
Nicalon™ Fibers
Other SiC fibers
- **OBJECTIVE**
- **RESULTS**
UF SiC Fibers
- **FUTURE DIRECTIONS**
R & D Needs

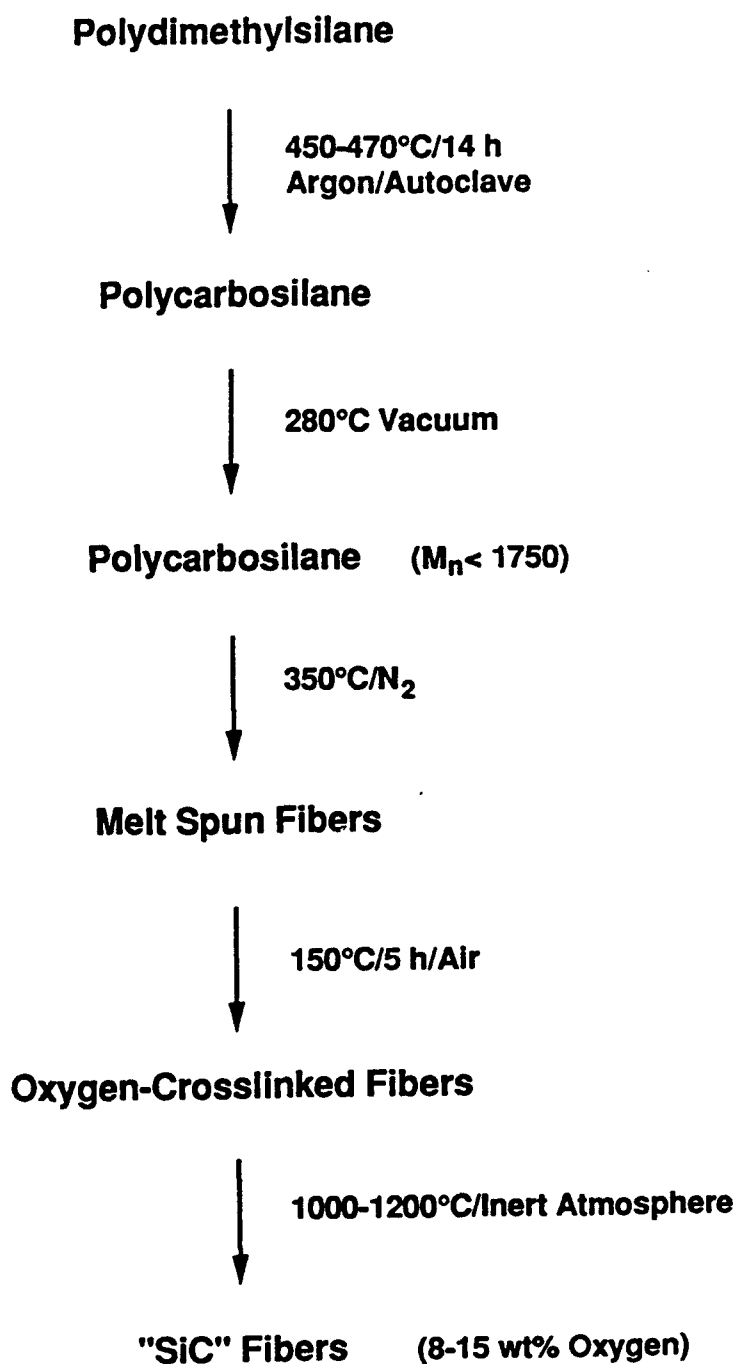
NICALON™ "SILICON CARBIDE" FIBERS

Processing: Melt Spinning of Polycarbosilane, Oxygen Cross-Linking, Pyrolysis

Structure: Continuous, Fine-Diameter Fibers; Weakly Crystalline, Fine-Grained SiC; Large Excess of Oxygen and Carbon

Properties: High Tensile Strength, High Rupture Strain, Low Modulus, Poor Thermal Stability

CONTINUOUS SILICON CARBIDE FIBERS (Yajima et al.)



DEGRADATION OF NICALON FIBERS

- **Reactions Involving SiO_2 and Excess C**
- **Large Weight Losses - Volatilization of CO, SiO**
- **Development of Porosity and Growth of Flaws**
- **Rapid Grain Growth**

FINE-DIAMETER SILICON CARBIDE FIBERS

Organosilicon Polymer-Derived

Hi-Nicalon (Nippon Carbon Co.)¹ - melt spun, radiation-cured, low oxygen content, excess carbon, good thermal stability, high tensile strength, improved elastic modulus

Lipowitz et al.² (Dow Corning Corp.) - melt spun, oxygen cross-linking and boron doping, near stoichiometric SiC, good thermal stability, high tensile strength and high elastic modulus, heterogeneous microstructure, continuous?

SiC Powder-Derived

Frechette et al.³ (Carborundum Co.) - powder/polymer melt extrusion, larger fiber diameter ($\geq 25 \mu\text{m}$), near stoichiometric SiC, good thermal stability, low tensile strength, high elastic modulus

Silverman et al.⁴ (Du Pont Co.) - slurry-processed (with organosilicon binder), larger fiber diameter ($\geq 25 \mu\text{m}$), near stoichiometric SiC, good thermal stability, low tensile strength, high elastic modulus

-
1. M. Takeda et al., Ceram. Eng. Sci. Proc., **13** [7-8] 209-217 (1992).
 2. J. Lipowitz et al., Ceram. Eng. Sci. Proc., **12** [9-10] 1819-1831 (1991).
 3. F. Frechette et al., Ceram. Eng. Sci. Proc., **12** [7-8] 992-1006 (1991).
 4. L.A. Silverman et al., J. Appl. Polymer Sci.: Appl. Polymer Symp., **47** 99-109 (1991).

Objective

- **Synthesis of continuous SiC fibers with small diameter, high tensile strength, and good thermomechanical stability**

Approach

- **Fabricate SiC fibers with low oxygen content**
- **Dry spinning of organosilicon polymers *without* oxidative or irradiative curing step**

CONTINUOUS SILICON CARBIDE FIBERS (Toreki et al.)

Polydimethylsilane



Heat Treatment

Polycarbosilane



**Solution/Filtration
Precipitation/Filtration
60°C/Vacuum**

Polycarbosilane (M_p = 5,000-10,000)



Solvent, Spinning Aids, etc.

Spinning Dope



**Dry Spinning
Ambient Atmosphere**

Green Fibers



Pyrolysis (~1000°C)

"SiC" Fibers (<2 wt% Oxygen)

KEY PROCESSING VARIABLES

Polycarbosilane Molecular Weight

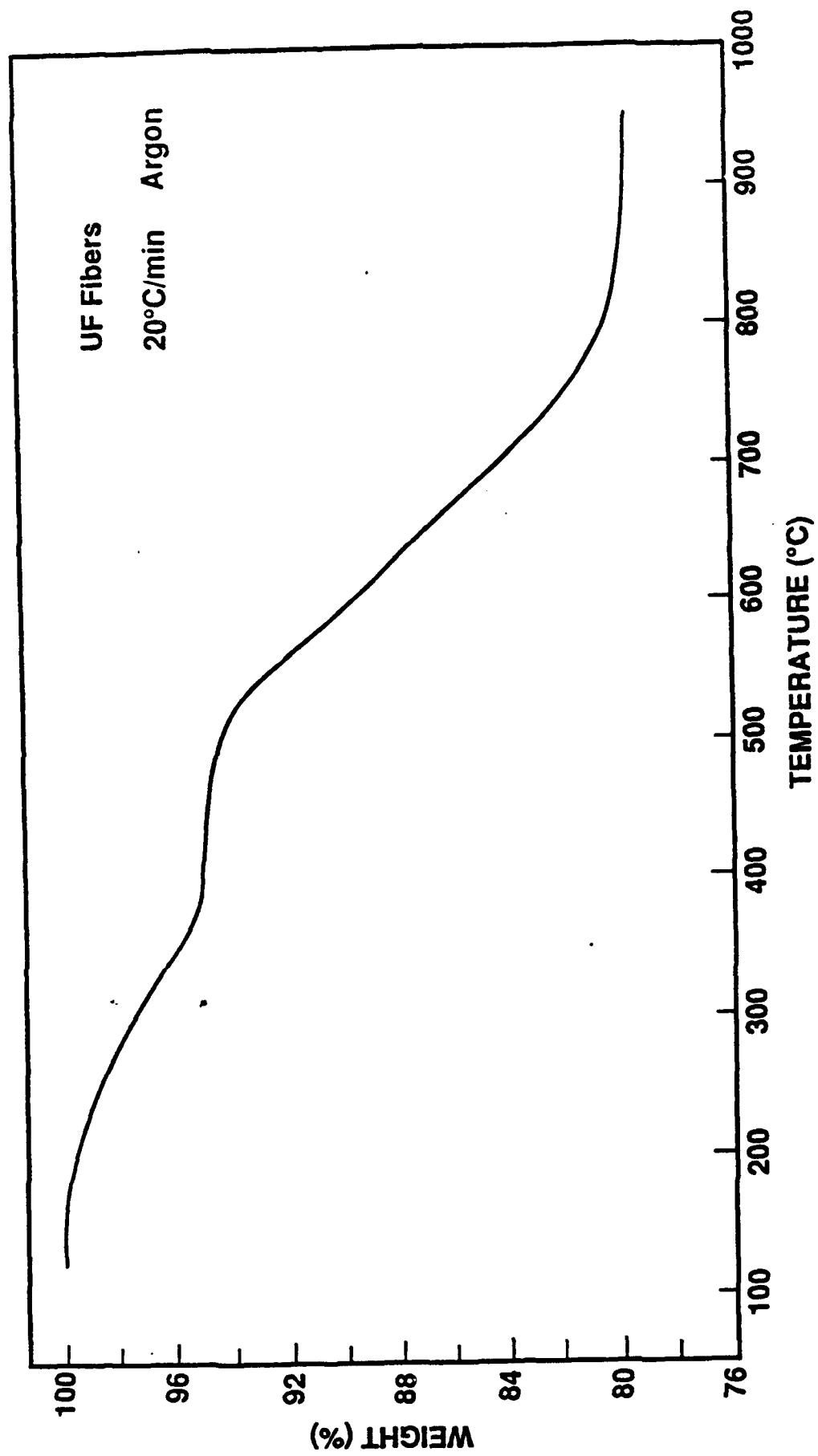
MW < 5,000	Highly soluble, but melts; Low ceramic yield
MW > 10,000	Does not melt, but insoluble; High ceramic yield
MW ~ 5,000-10,000	Does not melt, highly soluble; High ceramic yield

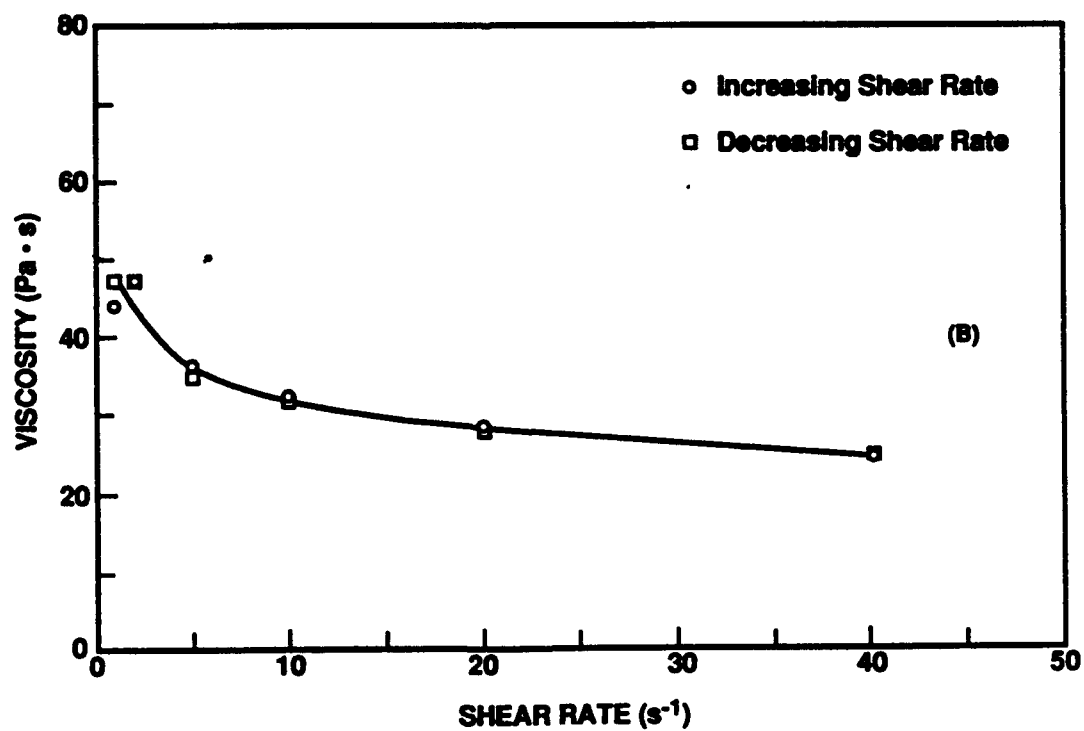
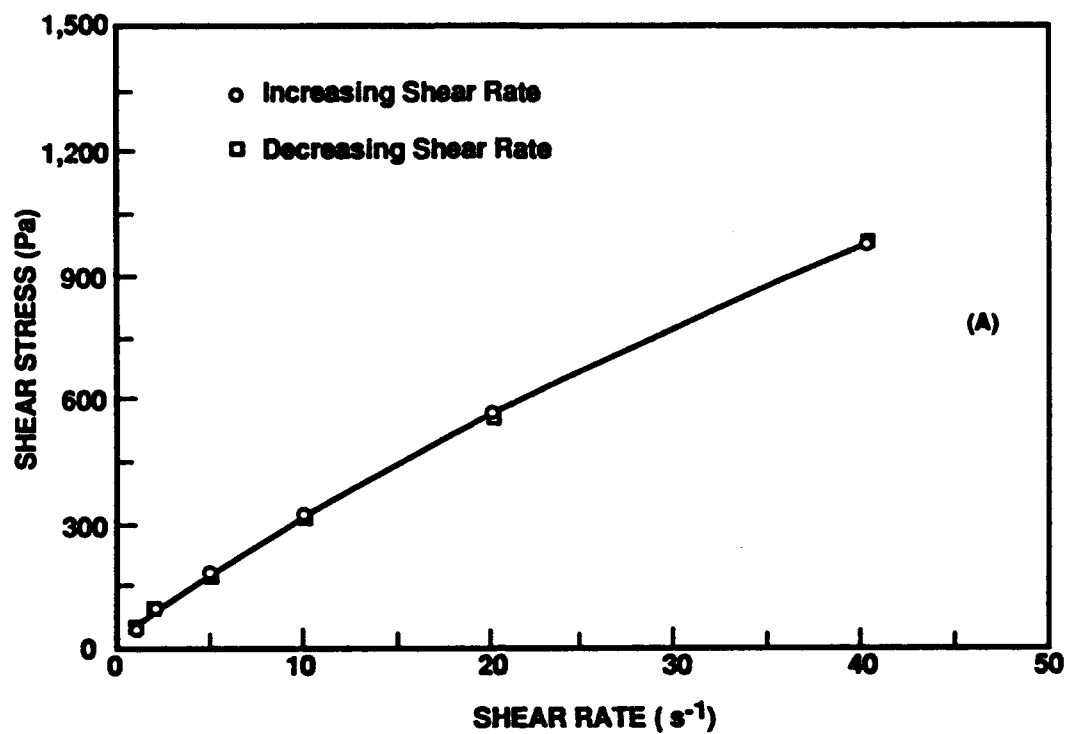
Polymer/Solvent Ratio in Spinning Dope

- Excess of solvent - fibers stick together
- Deficiency of solvent - difficult to extrude, rough fiber surfaces
- Optimum ratio - excellent spinnability, relatively smooth fiber surfaces

"Spinning Aids" (e.g., PIB, PVS, etc.)

- Modify solution rheological characteristics
- Modify "green" fiber properties

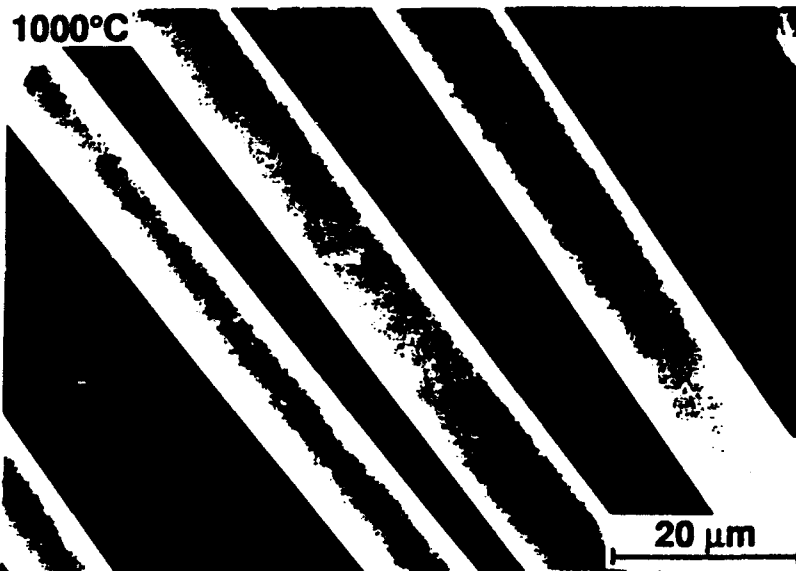


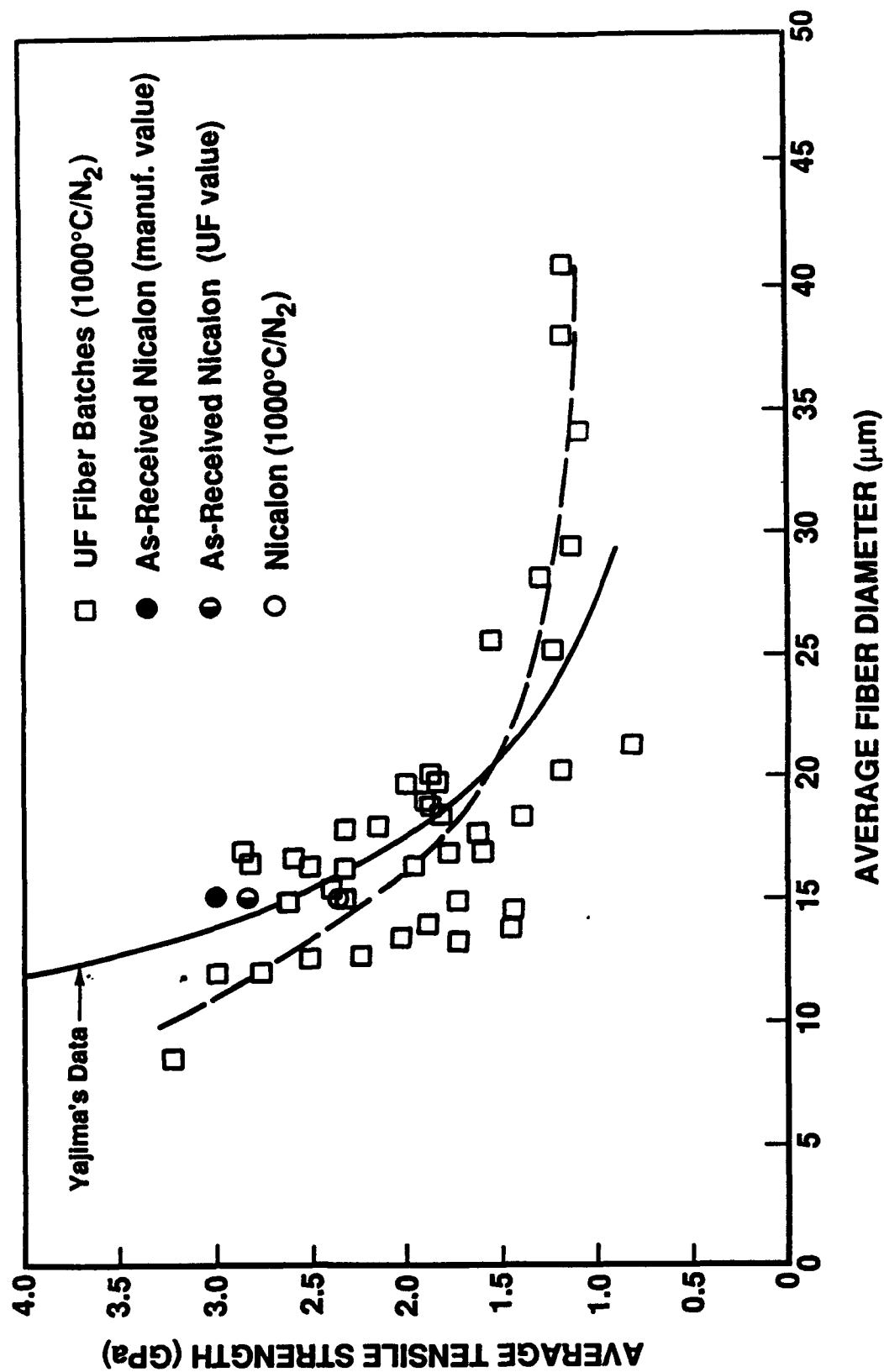


MECHANICAL PROPERTIES OF GREEN AND PARTIALLY-PYROLYZED FIBERS

	<u>Tensile Strength (MPa)</u>	<u>Rupture Strain (%)</u>
UF Fibers Green (as-spun)	20	1.0
UF Fibers (400°C)	44-52	3.5-7.6
Nicalon-type Fibers* (400°C)	~50	~4

-
- * Y. Hasegawa, M. Imura, and S. Yajima, J. Mater. Sci., 15 720-728 (1980)





ELEMENTAL ANALYSIS

<u>Sample</u>	<u>O (wt%)</u>	<u>Si (wt%)</u>	<u>C (wt%)</u>	<u>N (wt%)</u>	<u>H (wt%)</u>
UF Fiber	1.1-2.6 [†]	55 ^{†,‡}	42 [†]	1-2 ^{†,†}	<0.5 [†]
Nicalon	13.5-15 [†]	55 [†]	29 [†]	<0.5 [†]	<0.5 [†]
Nicalon*	10	58	31		

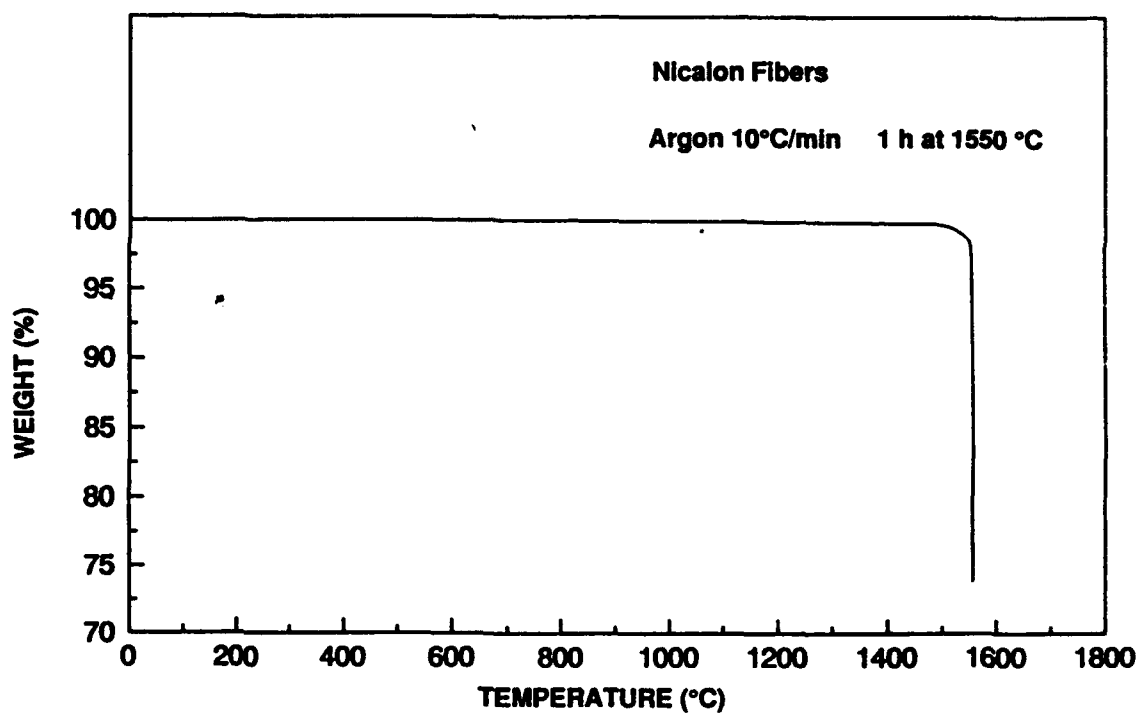
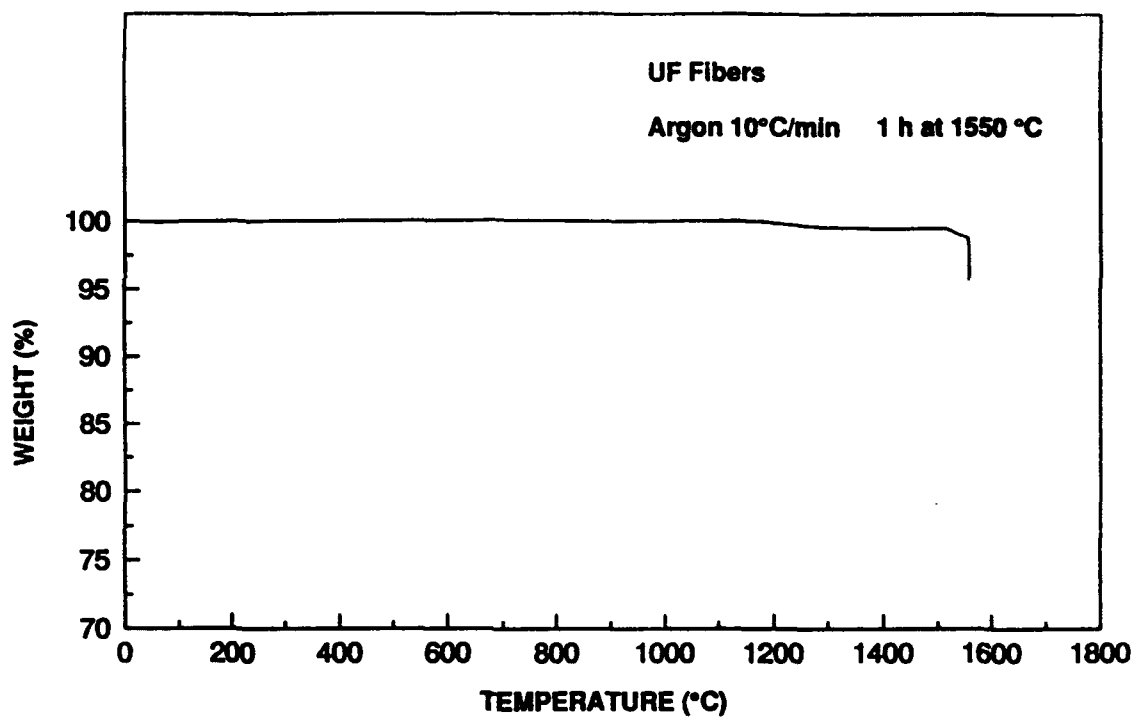
* Reported by manufacturer

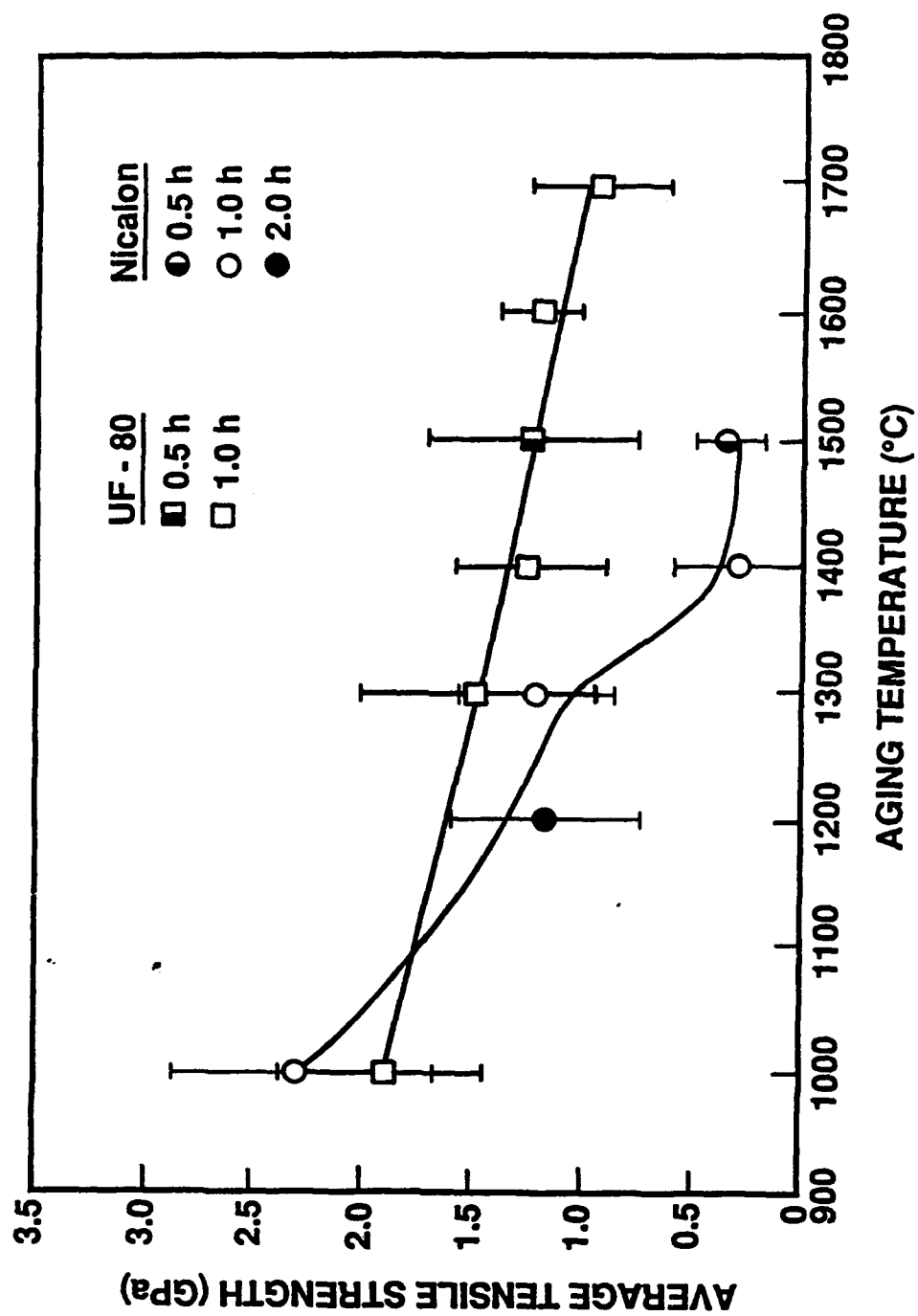
† Determined by neutron activation analysis

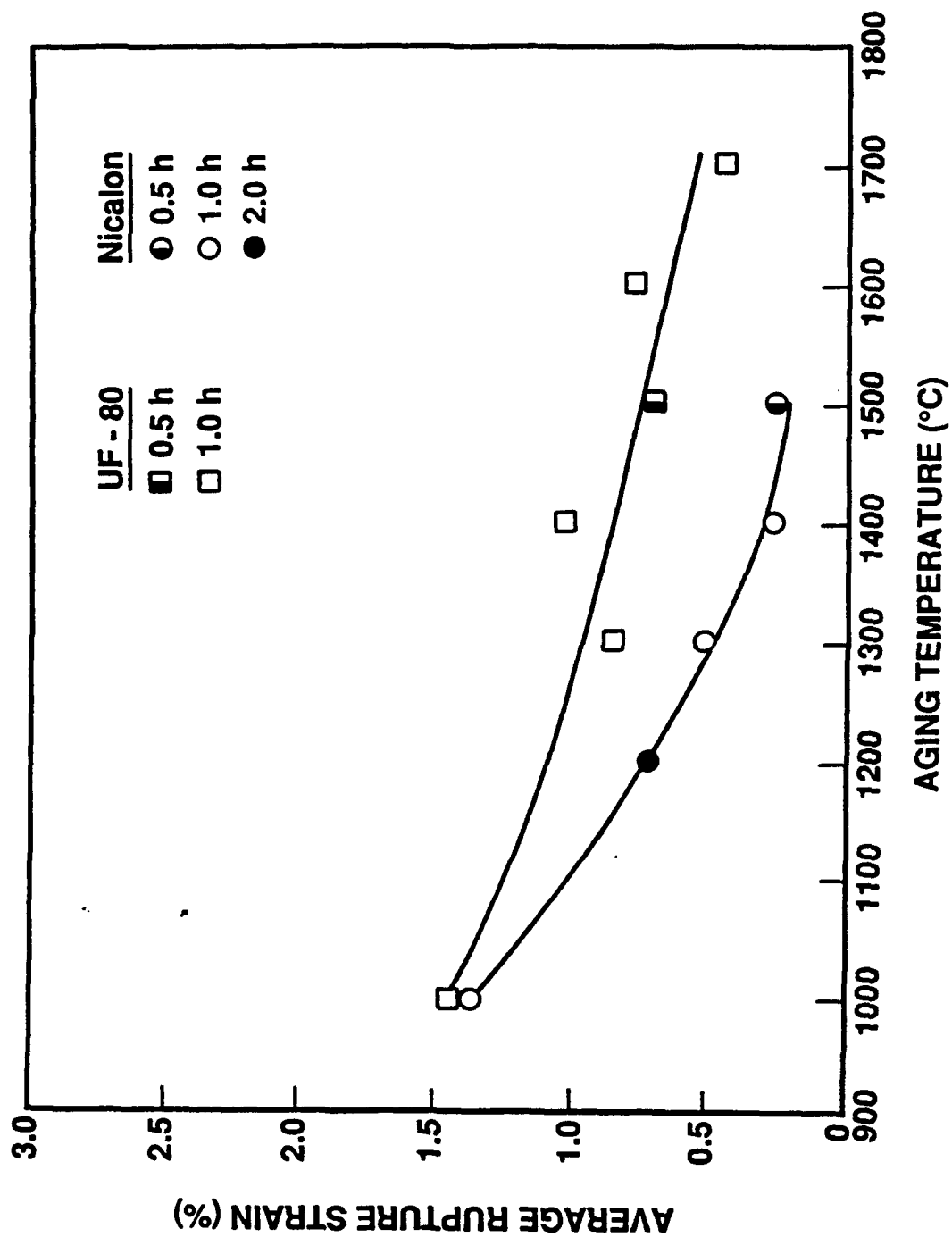
‡ Determined by atomic absorption

△ Determined by LECO combustion method

▽ Determined by difference







Processing Modifications

- **Improve Filtration of Spinning Solution**
(2-4 μm glass filter $\rightarrow$ 0.1-0.2 μm PTFE filter)
- **Reduce Oxygen Content in Fibers**
(Lower oxygen partial pressure during pyrolysis)

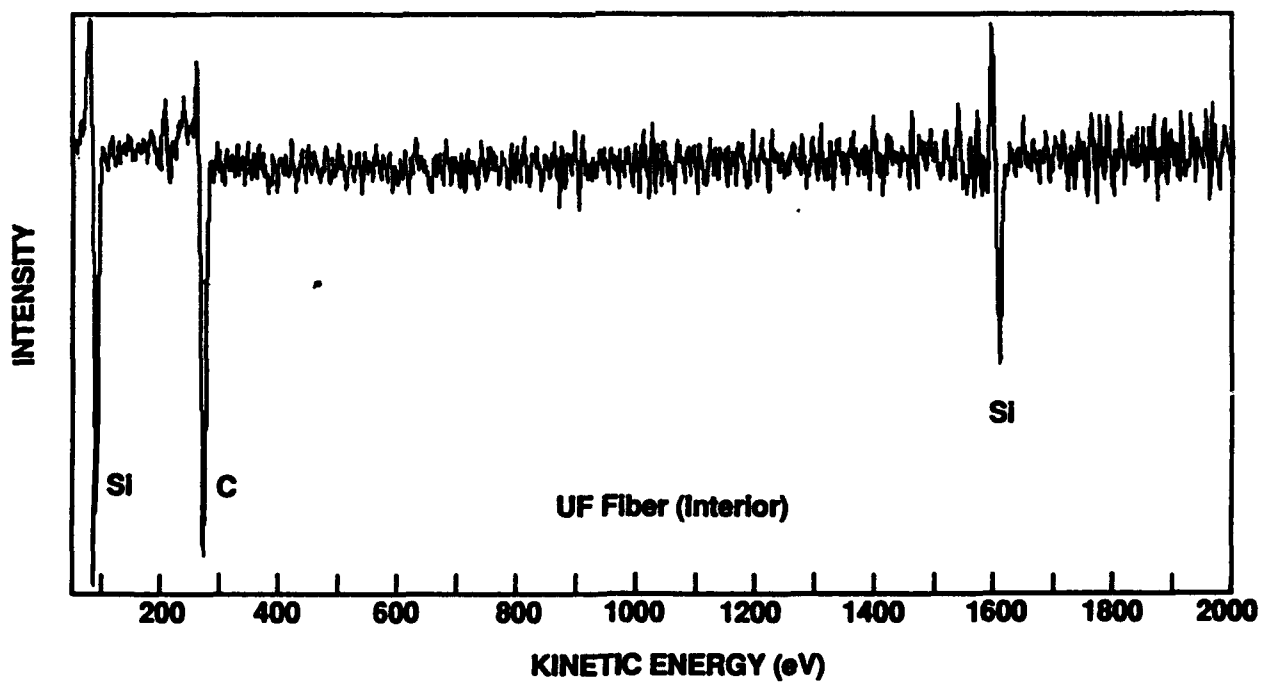
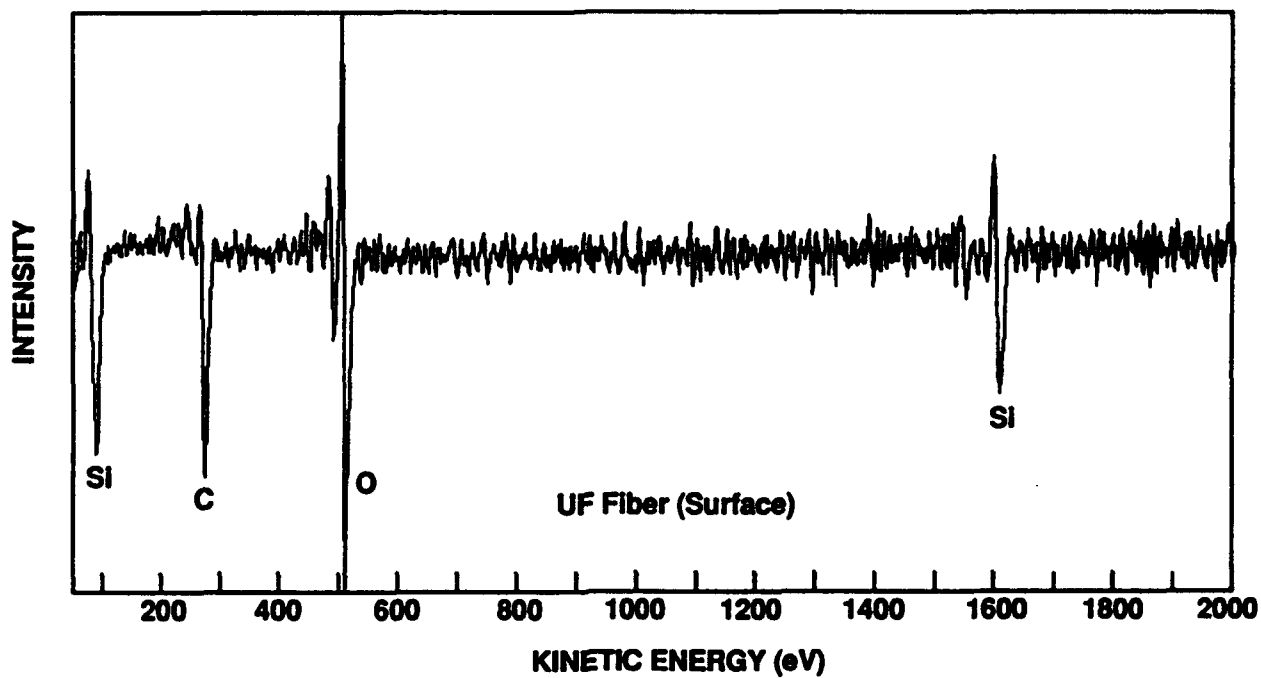
OXYGEN ANALYSIS*

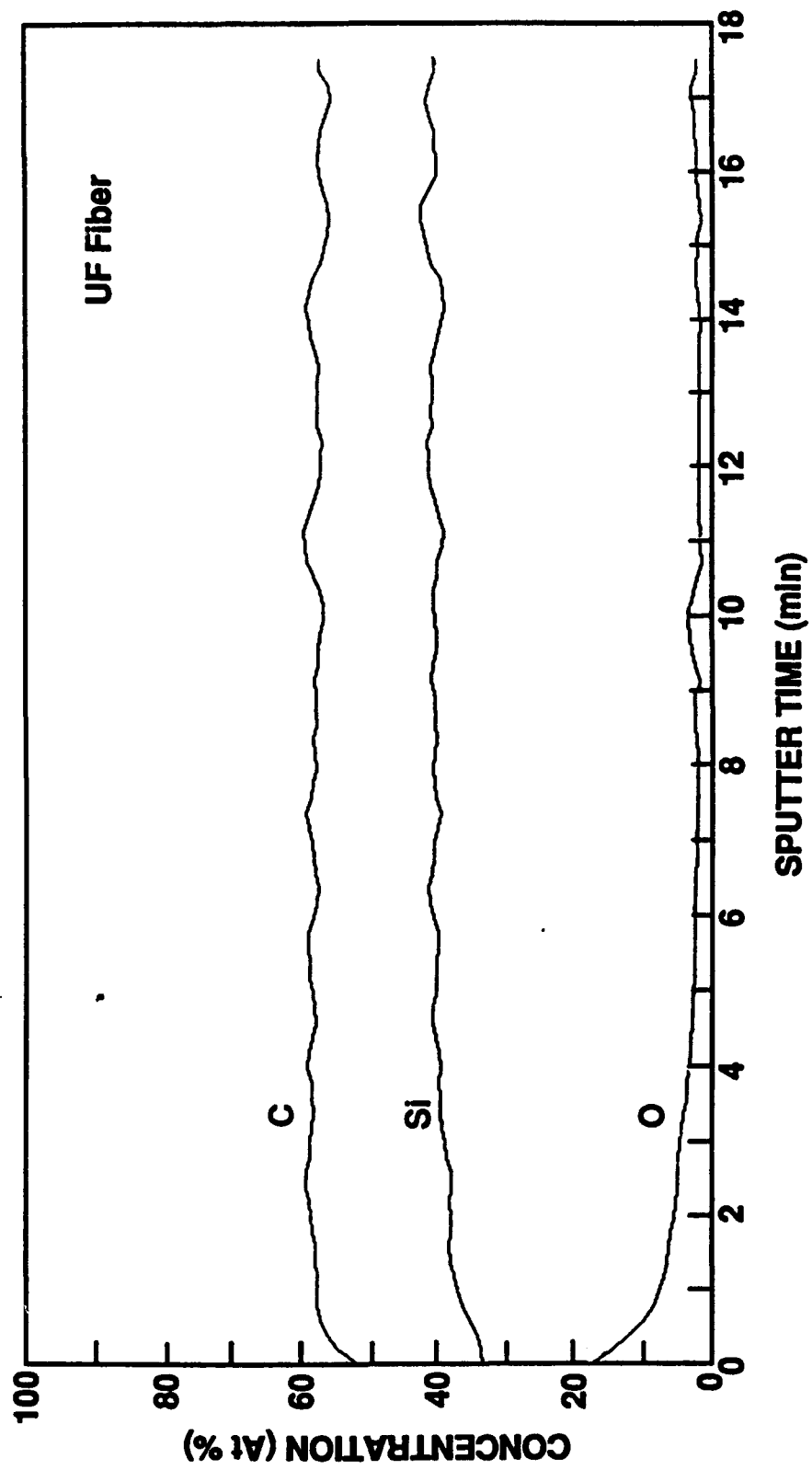
<u>Sample</u>	<u>Weight %</u>
Polydimethylsilane	0.3 - 0.4
Polycarbosilane	0.3 - 1.3
UF FIBER	1.1 - 2.6

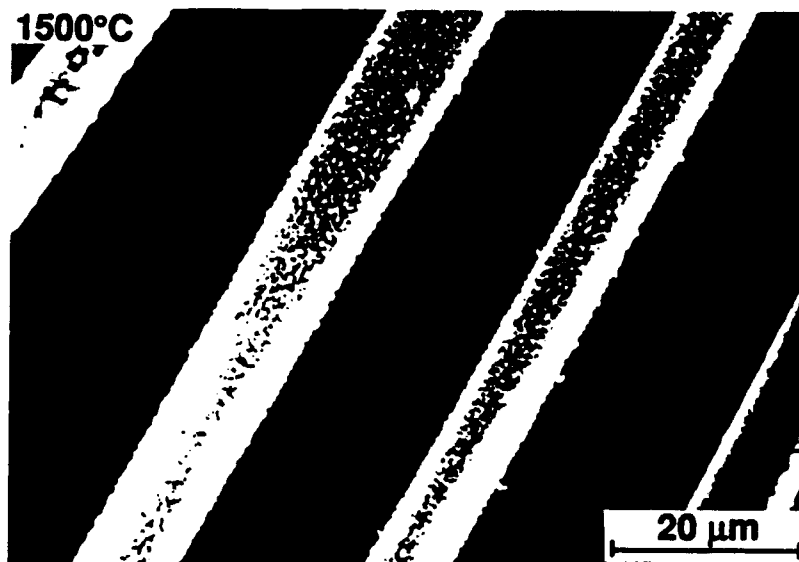
*** Determined by neutron activation analysis**

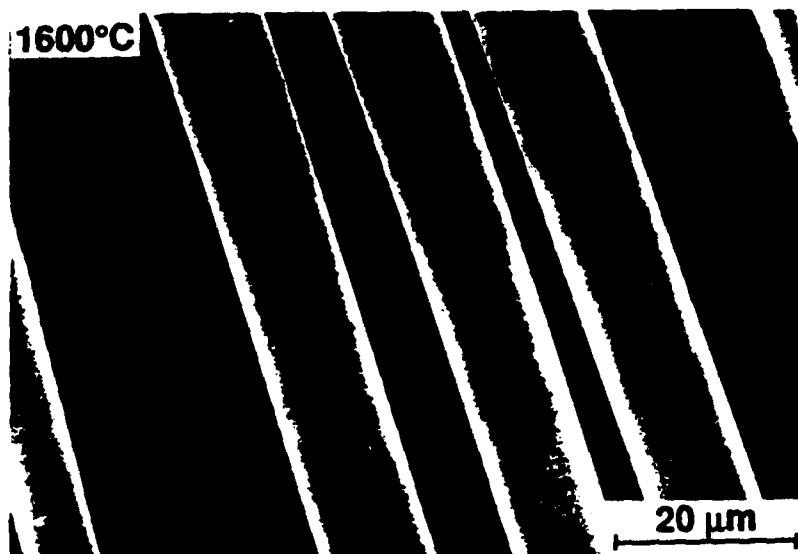
Oxygen Contamination During Fiber Fabrication

- **Spinning (ambient air atmosphere)**
- **Pyrolysis (ungettered furnace, nitrogen)**

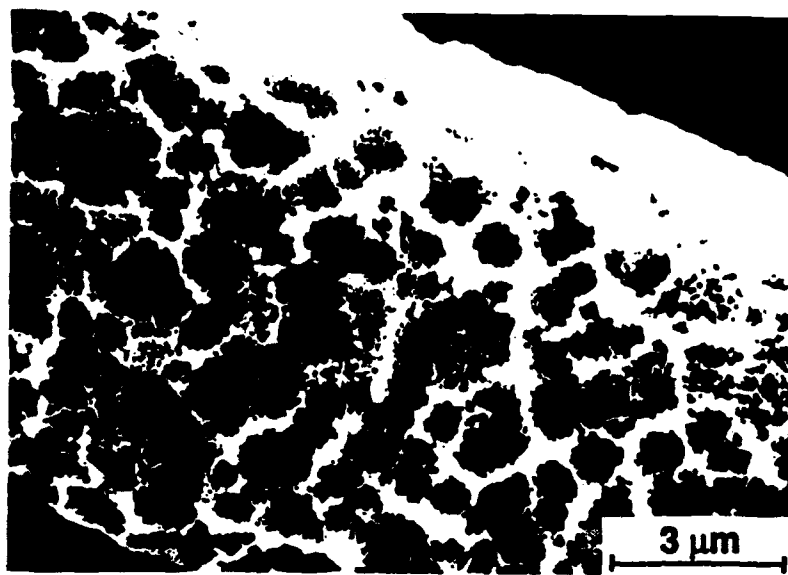


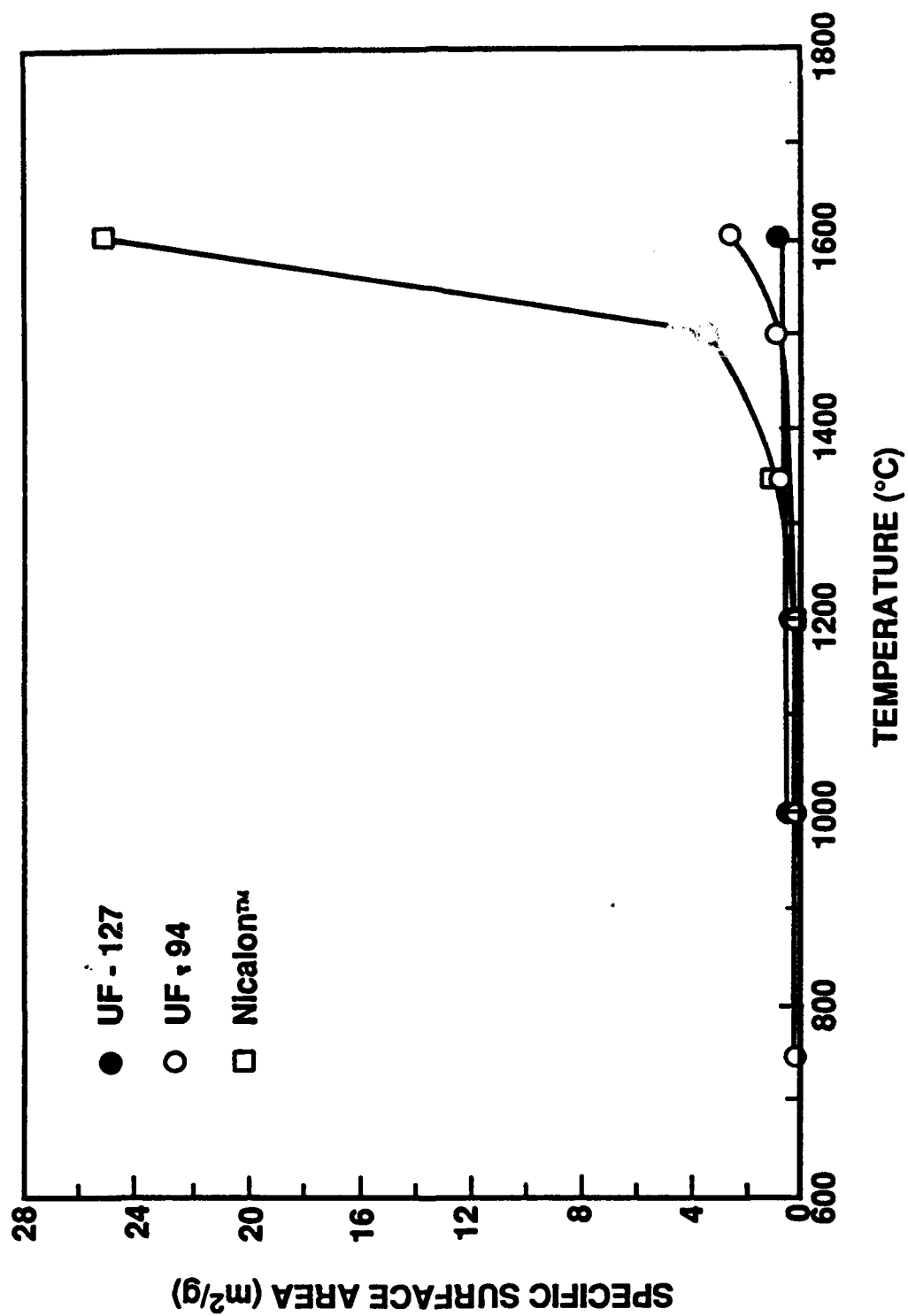


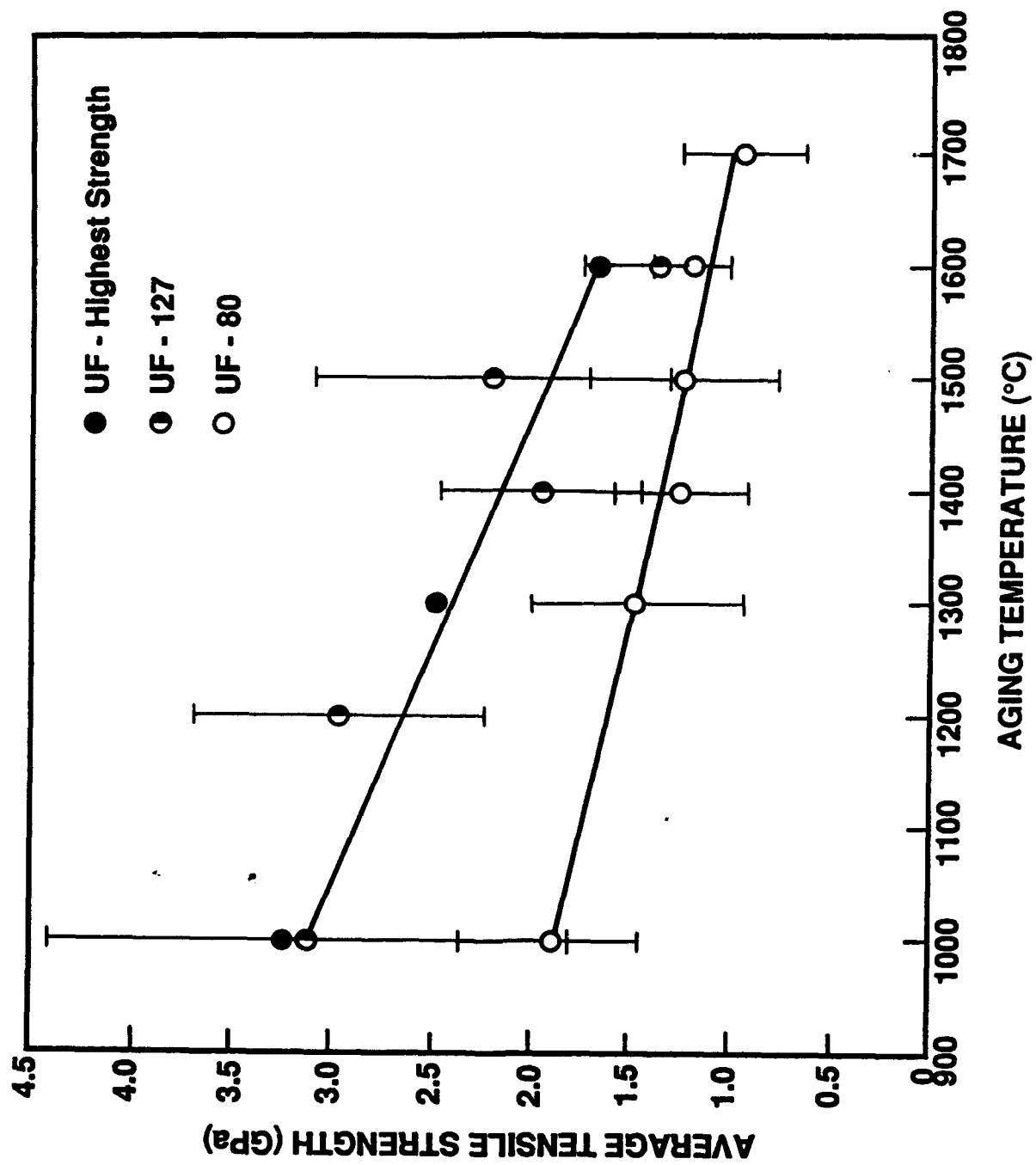


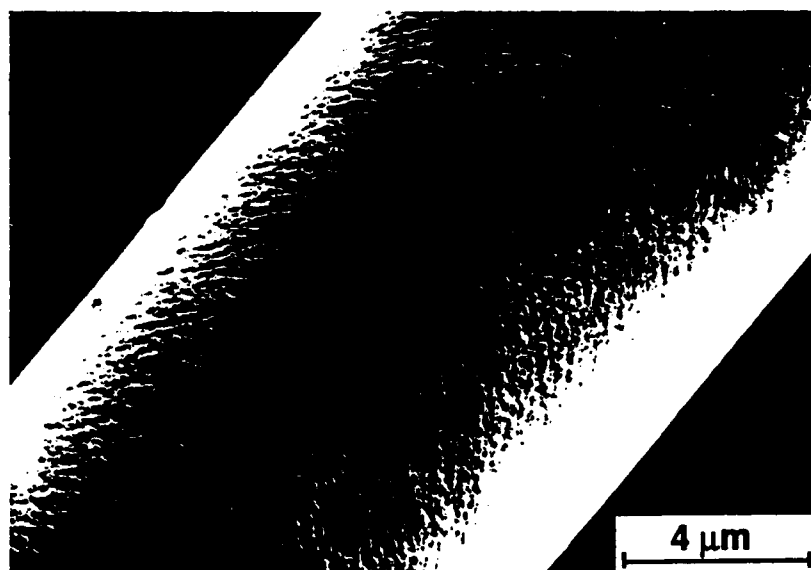
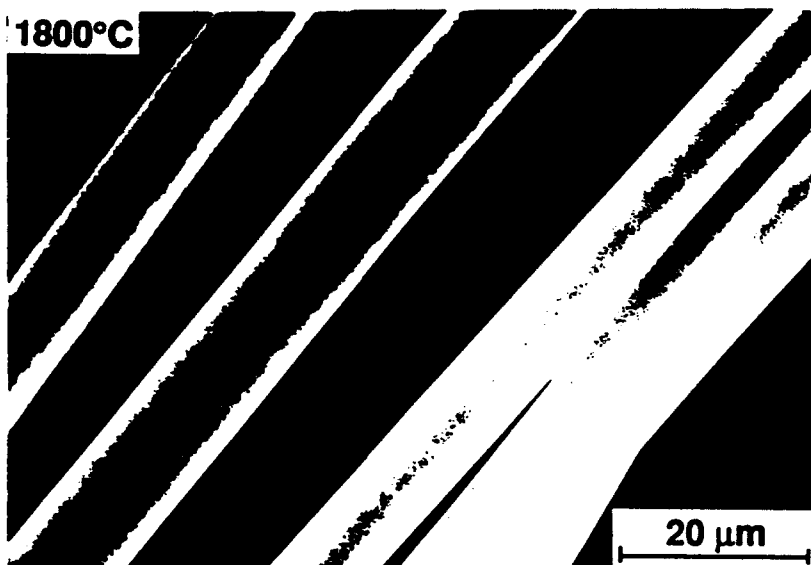


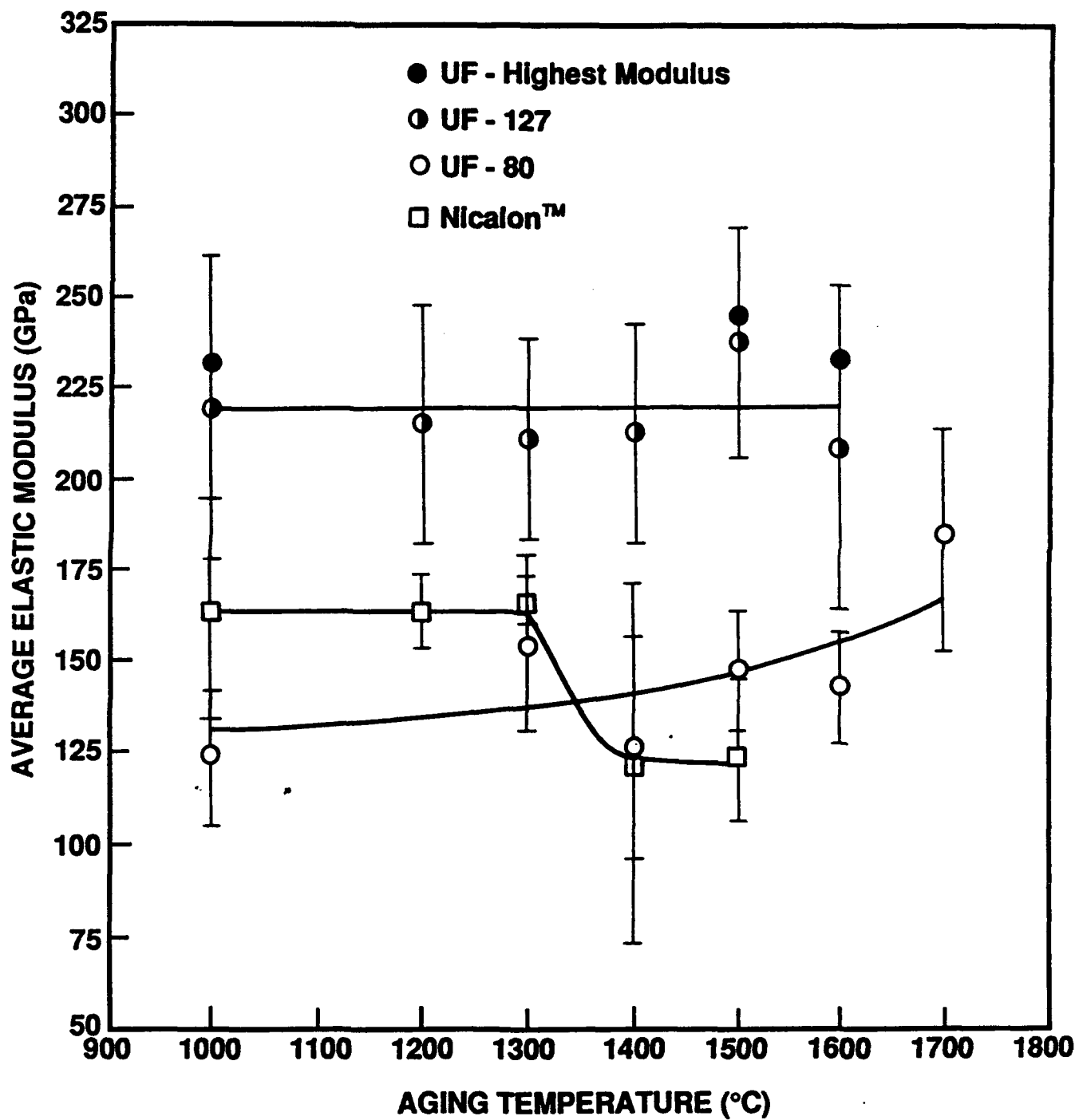
Nicalon™ 1600°C in Argon

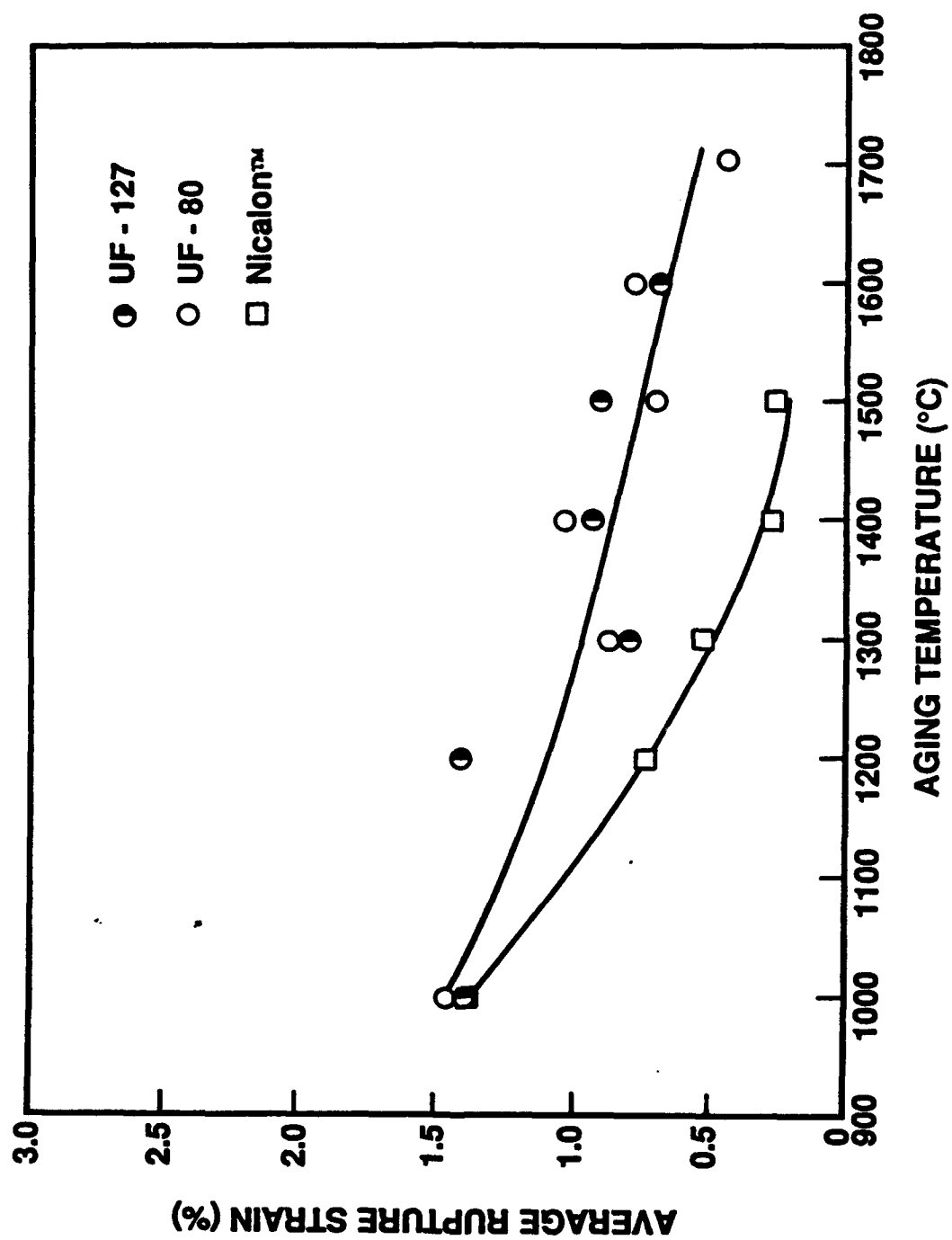












SUMMARY

UF fibers were prepared by dry spinning of concentrated solutions of high molecular weight ($\sim 5,000$ - $10,000$) polycarbosilane (PC) (with spinning aids) and subsequent pyrolysis of the polymer fibers

Processing

- **No oxidative or irradiative cross-linking step**
- **Polymers solutions have excellent spinnability**
- **High ceramic yield after pyrolysis**
- **Green and partially-pyrolyzed fibers have good mechanical properties**

Properties

- **Fibers with low oxygen content (~ 1 - 2%), range of diameters (~ 8 - $50\ \mu\text{m}$), round cross-sections, and relatively smooth surfaces**
- **Average tensile strengths as high as ~ 3.3 GPa for as-pyrolyzed fibers**
- **Average rupture strain $\sim 1.5\%$ for as-pyrolyzed fibers**
- **Average tensile strength as high as 2.3 GPa and average elastic modulus as high as 250 GPa after 1500°C (1 h) heat treatment in argon**
- **Average tensile strength as high as 1.9 GPa and average elastic modulus as high as 235 GPa after 1700°C (1 h) heat treatment in argon**

FUTURE DIRECTIONS

- **Optimization of Fiber Processing Conditions**
- **Additional Characterization of Fibers**
- **Compositional Modification/Microstructural Development**
- **Scale-Up**

Optimization of Fiber Processing Conditions

Polymer Characteristics

PC molecular weight distribution

Spinning aid characteristics (e.g., molecular weight)

PC/spinning aid ratio

Purity

Spinning Dope Characteristics

Solution rheological characteristics

Polymer/solvent ratio

Solvent type

Purity

Spinning Process

Spinneret geometry

Extrusion pressure

Drying conditions (temperature, atmosphere, gas flow)

Winding conditions

Pyrolysis conditions

Heating schedule

Atmosphere

Continuous vs. batch process

Tensioning

Process Controls/Sensors for Optimization of Fiber Fabrication

Metering pump

De-airing station

In-line filtration station

Viscosity sensor

Spinneret head temperature and pressure sensors

Multistage spinning/drying chamber (temperature/atmosphere controls)

Sensors to monitor temperature, gas composition, gas flow rate, and fiber diameter in spinning/drying chamber

Frictionless winders

Continuous pyrolysis facility

Fiber Characterization

Microstructure and Properties

High temperature testing (e.g., strength, creep) in oxidizing and non-oxidizing atmospheres

Detailed TEM analysis and compositional mapping

Fracture analysis

Suitability for Composite Fabrication

Fiber weavability

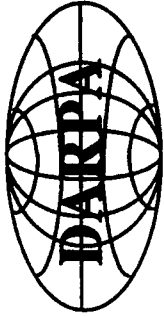
**Stability under compositing conditions (e.g., high temperature/
high pressure)**

Microstructural Development/Compositional Modification

- **Lower Oxygen Content**
- **Increased Si:C ratio**
- **Oriented Grain Structures**

Co-Workers/Contributors

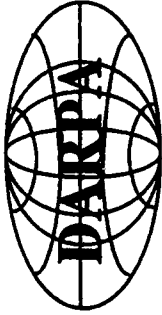
**Wm. Toreki
M. Saleem
G.J. Choi
E.J. Serrano
B.J. Madana
A.A. Morrone
E. Lambers**



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

Solution or Melt Spinning?

- **Earliest fibers were solution spun:**
natural - silk
synthetic - cellulose, i.e. rayon
- **Current high volume fibers are melt spun:**
glass fiber
nylon
PET, i.e., Dacron
(Nicalon)



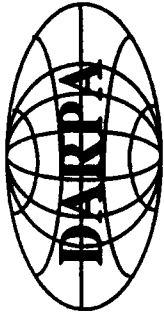
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Advantages of Melt Spinning

**Simple process (no solvent)
High speeds
Complex cross-section (trilobal, etc.)**

Disadvantages

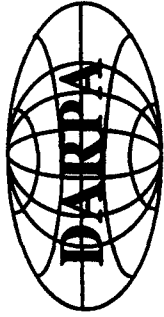
**Narrow range of operation
Hard to include additives**



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

High Performance Fibers Now Are Solution Spun

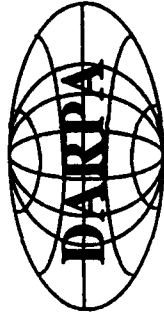
**Kevlar (DuPont)
Spectra (Allied-Signal)**



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

UF-SiC Fiber Technology Extendable Since

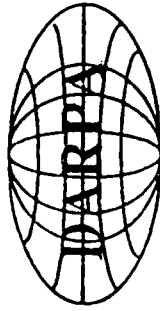
- **Very robust (wide range of conditions work)**
- **Additives easy to incorporate by viscosity changes (even if immiscible)**



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

Extendable (continued)

- **Same solutions can be used for coatings
(original goal)**
- **Synthesis modification has potential for
infiltration**
- **Same benefits for BN precursors and others**



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

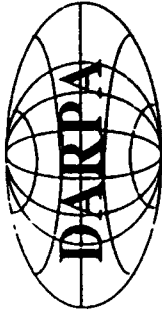
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

Joseph H. Simmons, Anthony B. Brennan, Michael D. Sacks

Salwan Al-Assafi, Tom Miller and Terry Cruse

**Department of Materials Science and Engineering
University of Florida
Gainesville, FL 32611**

**Help with the Electron Microscopy was provided by:
Augusto Morrone**



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

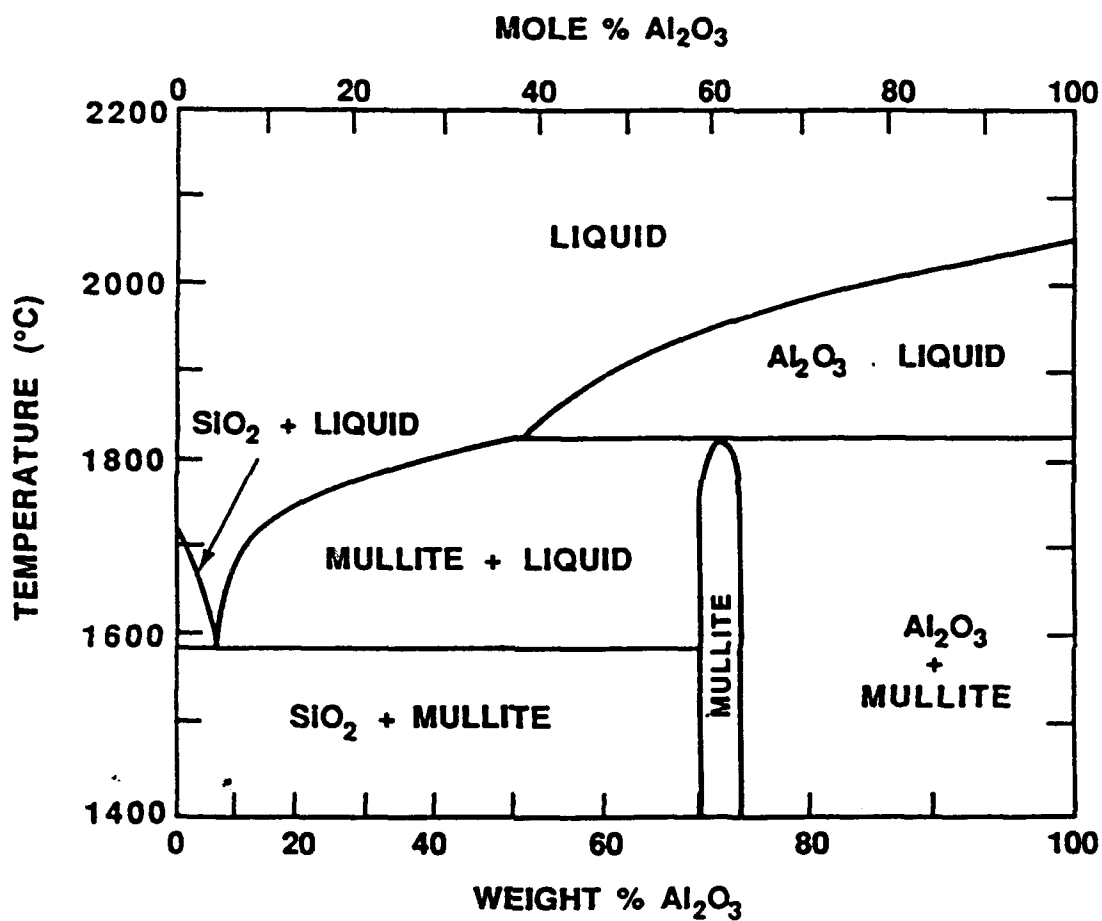
OBJECTIVE

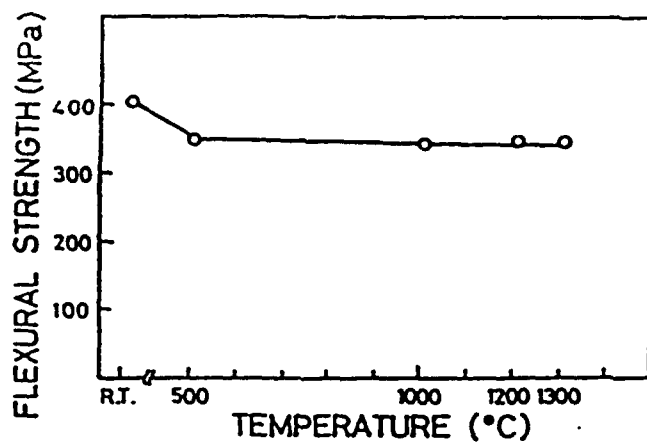
- To develop a solution-based process for the continuous and AI controlled spinning of high-strength mullite and composite mullite fibers with improved high temperature ($> 1200\text{C}$) properties.

APPROACH

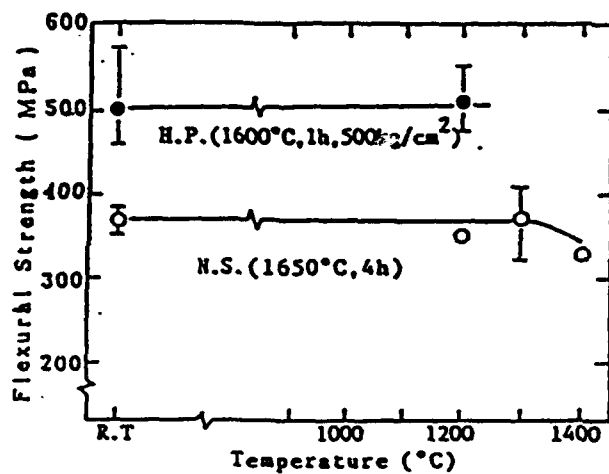
- Use a precursor sol approach to produce fine-grained mullite and mullite matrix composites with no intergranular glass phase.
- Develop a relationship between precursor sol chemistry and fiber spinning / ceramic processing characteristics in order to pre-determine and control sintered fiber properties, composition and phase structure.
- Relate processing conditions and microstructure to high temperature mechanical characteristics.
- Develop AI-based fiber spinning and processing operations.

SiO₂ - Al₂O₃ PHASE DIAGRAM

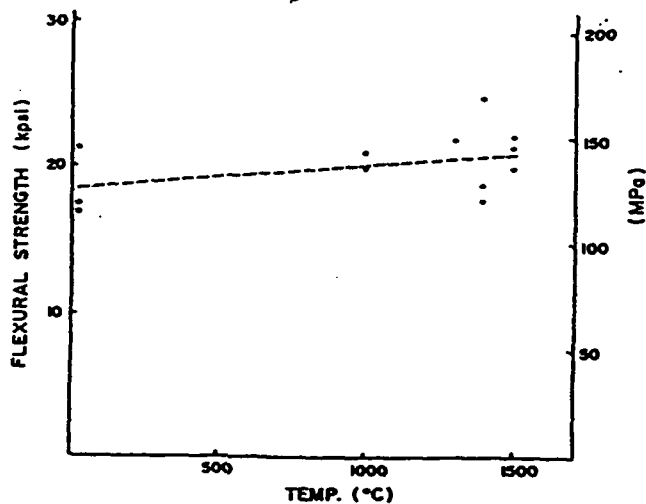




M.G.M.U. Ismail, Z. Nakai, and S. Sōmiya,
J. Am. Ceram. Soc., 70(1) C-7 - C-8 (1987)



S. Kanzaki and H. Tabata, pp 51-61 in "Mullite"
edited by S. Sōmiya, Uchida Rokakuho
Publishing Co., Tokyo, Japan, 1985



T. Mah and K.S. Mazdidasni, J. Am. Ceram
Soc., 66 (10) 699-703 (1983)

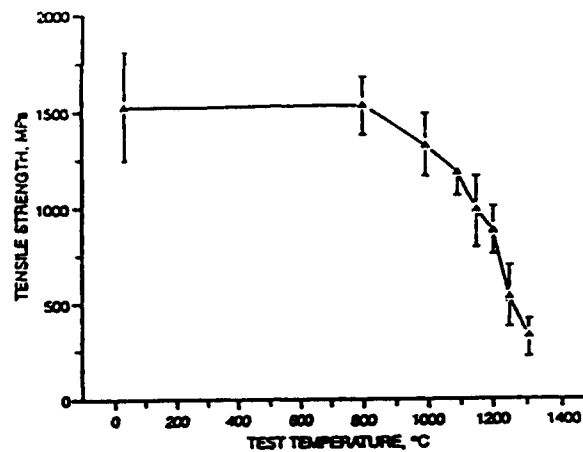


Fig. 7. Hot tensile strength of Nextel 480 filaments measured at various temperatures in air.

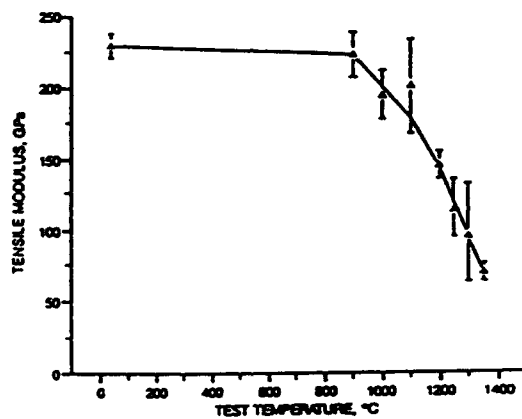


Fig. 8. Hot elastic modulus of single filaments of Nextel 480 measured at various temperatures in air.

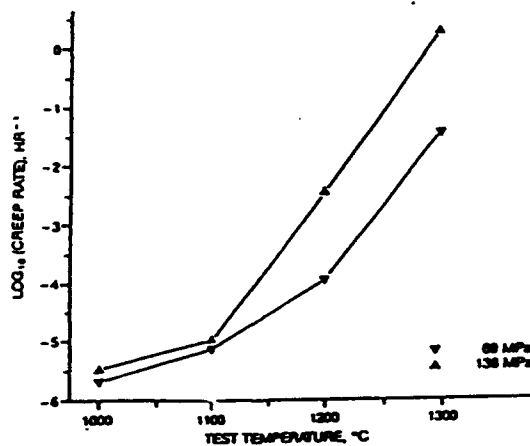


Fig. 9. Creep rate of Nextel 480 roving measured at various temperatures in air.

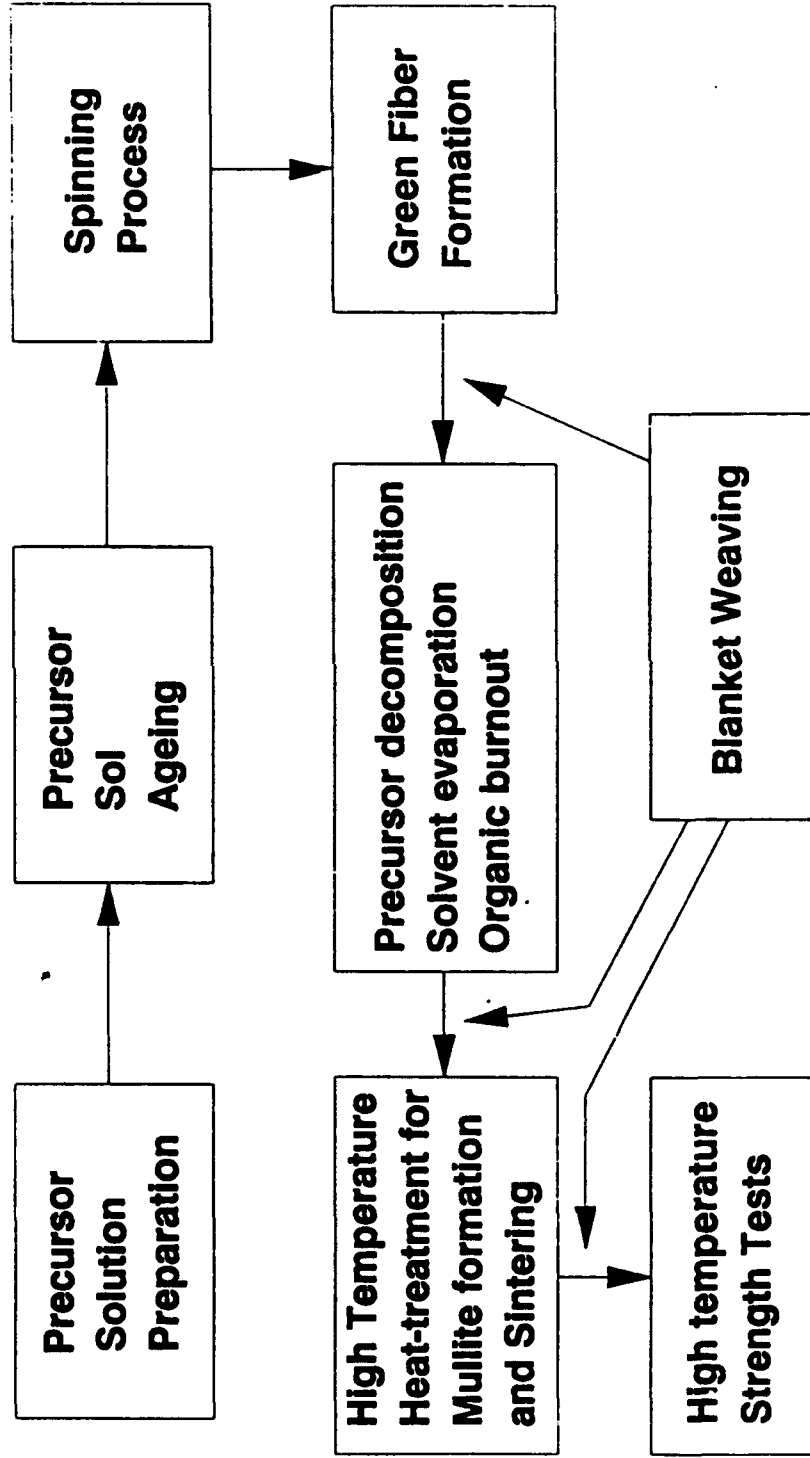
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

STATEMENT OF PROBLEM

- Degradation in mechanical behavior of composite fibers limits applications to temperatures below 1200°C.
- Non-oxide composition of most high temperature fibers limits their ability to withstand high temperature exposure to oxygen-containing atmospheres.
- Possible causes for mechanical degradation of composite fibers at high temperatures:
 - Residual glass phase at grain boundaries
 - Chemical reactions with ambient atmosphere or matrix material
 - Microstructure instabilities (e.g. grain growth) at high temperatures
 - Activation of slip (dislocation motion or generation) and/or diffusional creep
 - Incomplete densification (Modelling studies show that voids act as stress concentrators and nucleation sites for cracks)

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

TYPICAL PROCESS



SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

ADVANTAGES OF PROCESSING WITH SOL PRECURSORS

- Access to a wide range of precursor compositions and structures
 - Control over intermediate phases and final phase structure
 - Potential avoidance of intergranular glass phase
- Potential for independent control over sintering and crystal phase formation
 - Full density without sintering aids
 - Control of grain growth
- Low temperature fiber spinning and better AI controls
- High temperature sintering after handling can heal surface flaws from handling-spinning-weaving

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

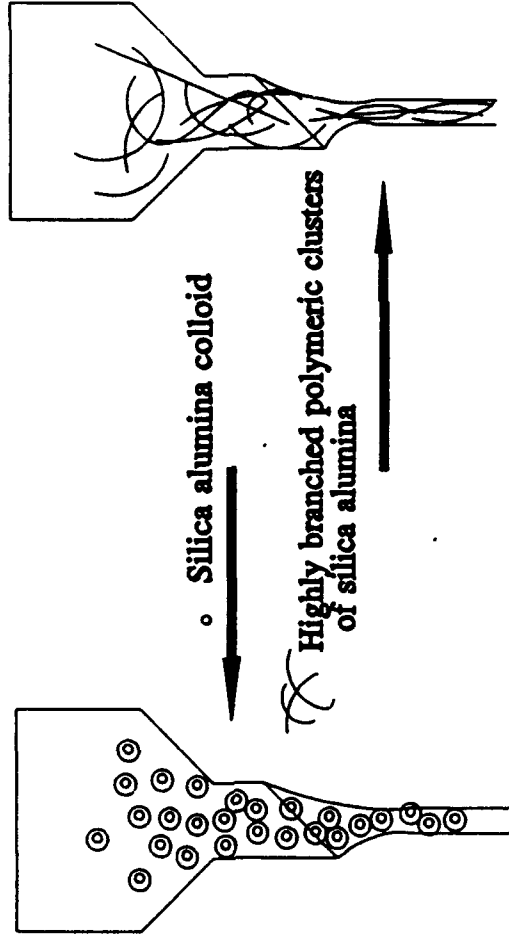
CRITICAL PROBLEMS IN CONTINUOUS FIBER SPINNING FROM SOL-GEL PRECURSORS

- Selection of solution precursors: colloidal vs polymer vs seeding
 - Component compatibility (prehydrolysis, sol stabilization, etc.)
 - Timing of hydrolysis/condensation reactions for each component
- Development of desirable rheological behavior in the precursor sol
 - Sol must be stable at low viscosity in the holding tank
 - Sol must quickly reach spinning viscosity at the spinneret
 - Spun fiber must solidify rapidly after extrusion past the spinneret
- Green fiber characteristics
 - Green fiber must be flexible and strong in order to withstand spooling on take-up drum
 - Fiber surface must resist handling and spooling damage in green condition
- Drying and sintering
 - Pronounced shrinkage during heating
 - Polymer burnout and carbonaceous residues
 - Phase transformations vs viscous phase sintering / no residual glass phase
 - Continued handling damage

Comparison of Fiber Processing Methods

Colloidal Method

Sol-gel Method



Method #1: Centrifugal Spinning

Method #2: Pulled by Hand

Continuous Spinning

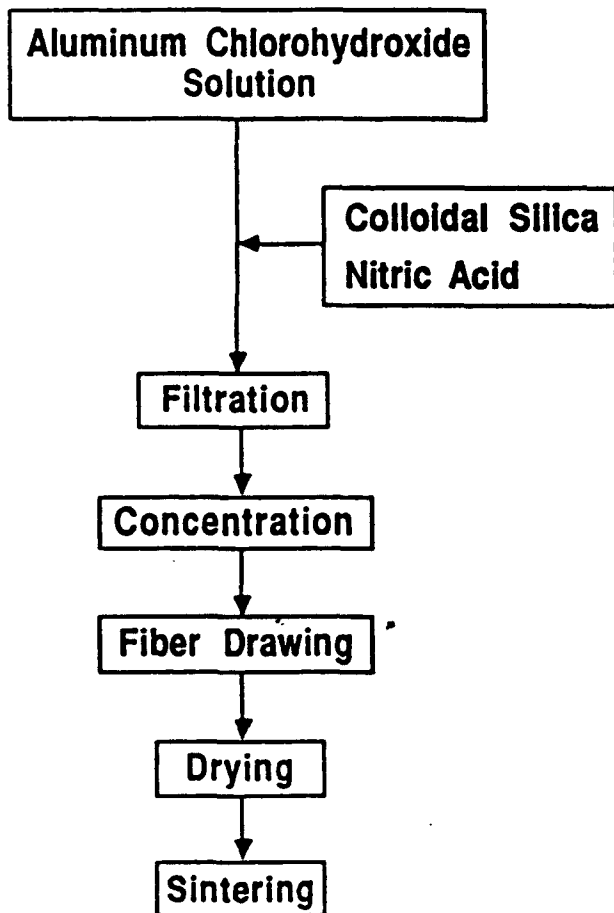
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

DETAILED APPROACH

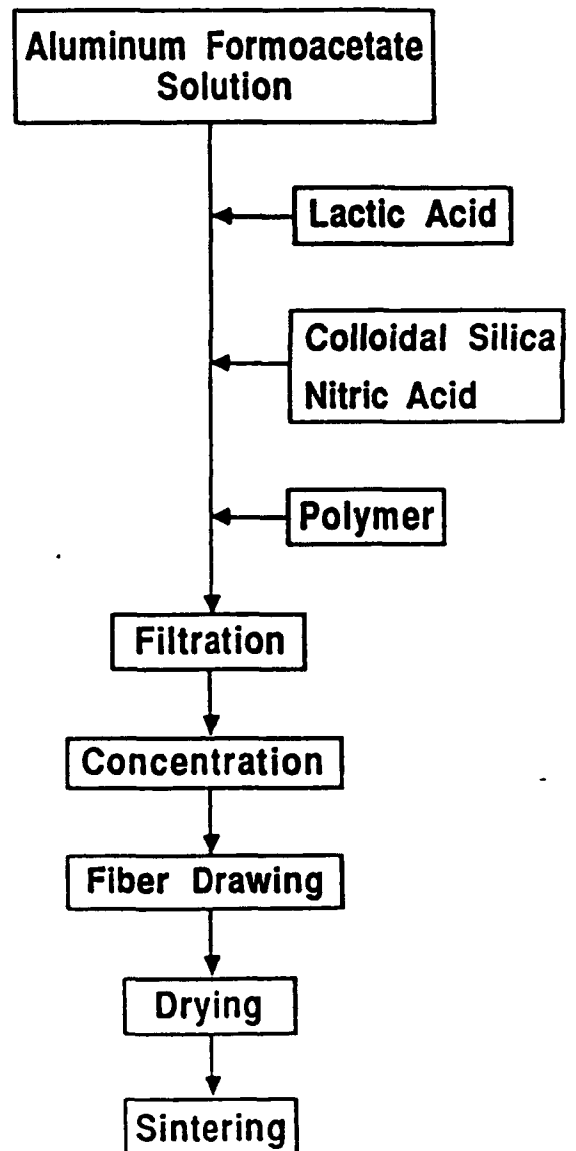
- Precursor sol chemistry variations:
 - alkoxide precursors (polymeric) vs colloidal precursors vs seeding
 - effect of solution stabilization aids
 - effect of fiber spinning aids
- Process variations:
 - treatment of fiber at spinning nozzle
 - precursor decomposition and organic burnout
 - mullite transition reaction and effect of intermediate phases
 - sintering kinetics and grain size control

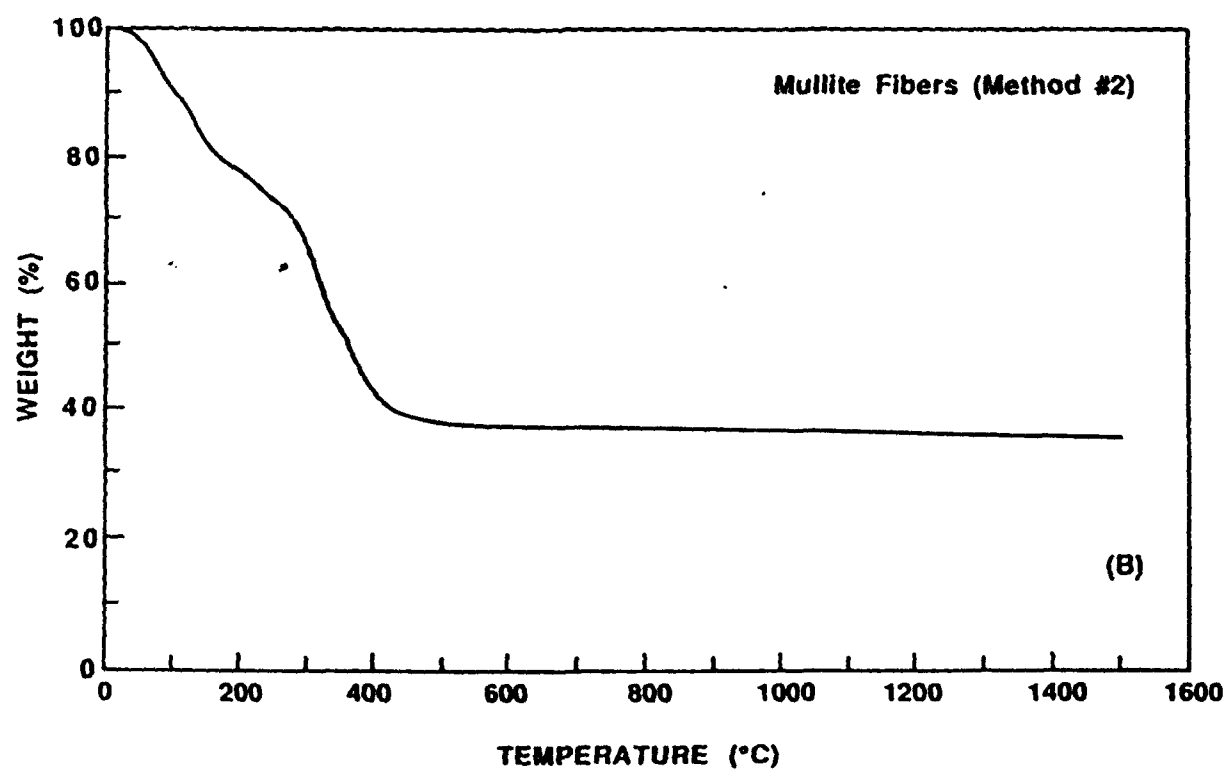
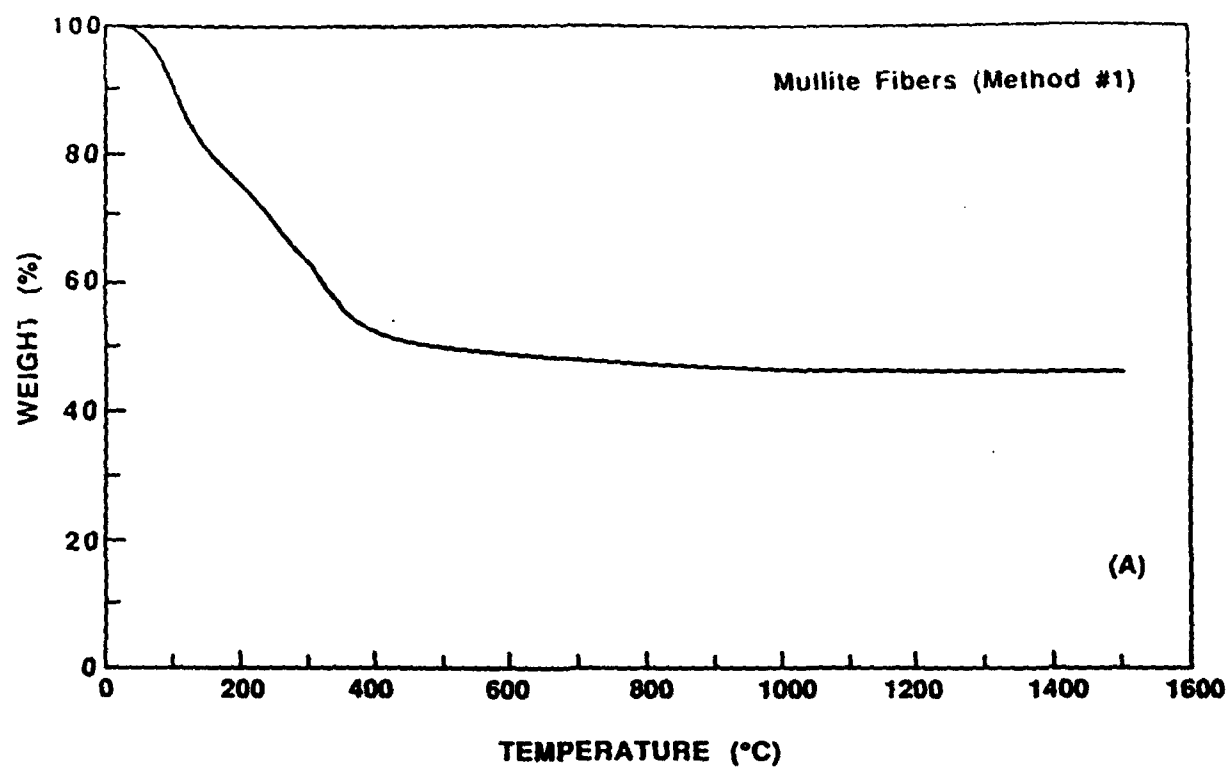
MULLITE FIBER FABRICATION

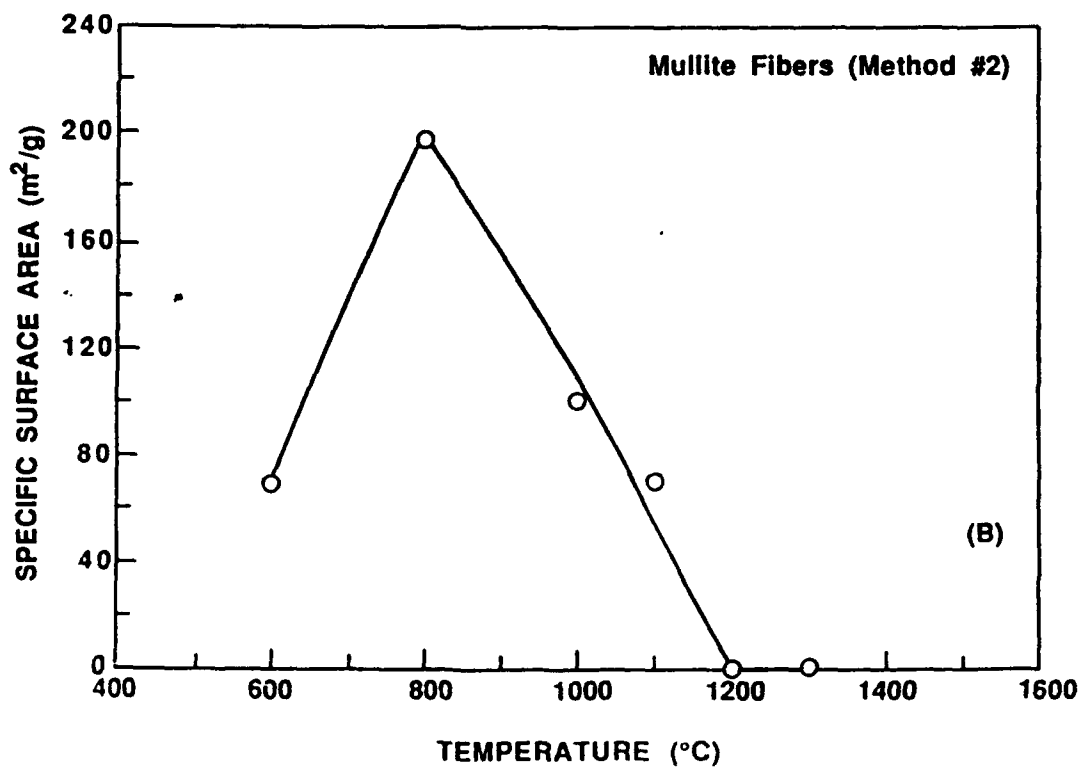
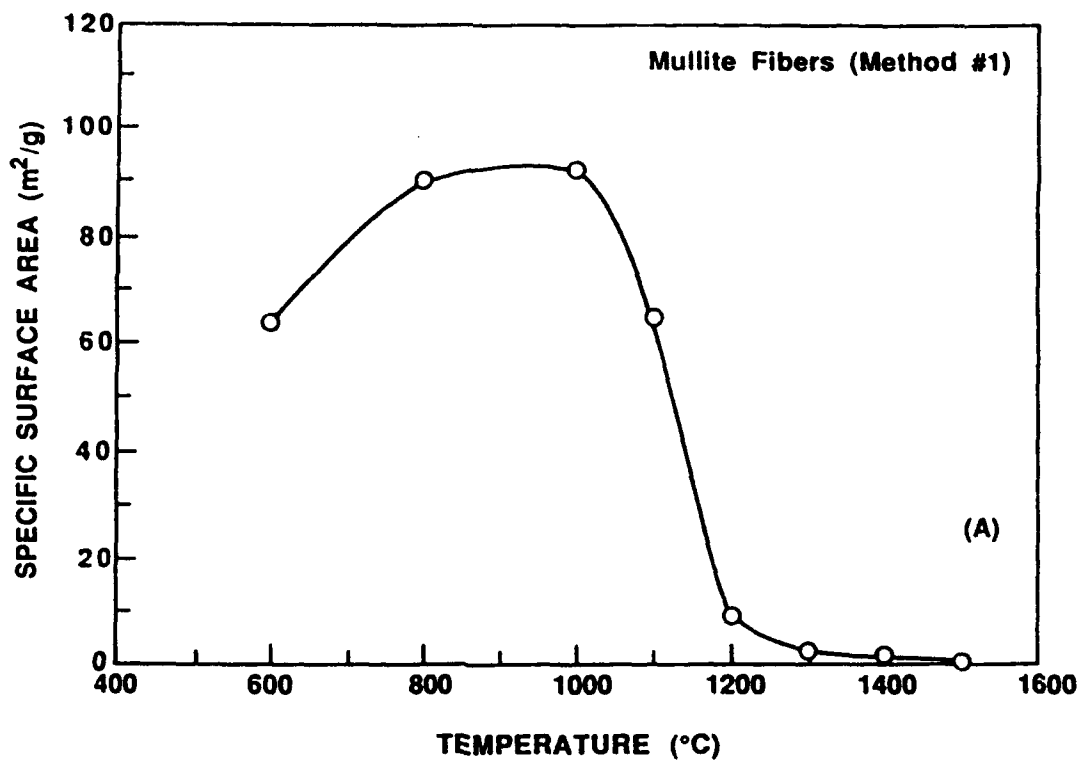
METHOD #1

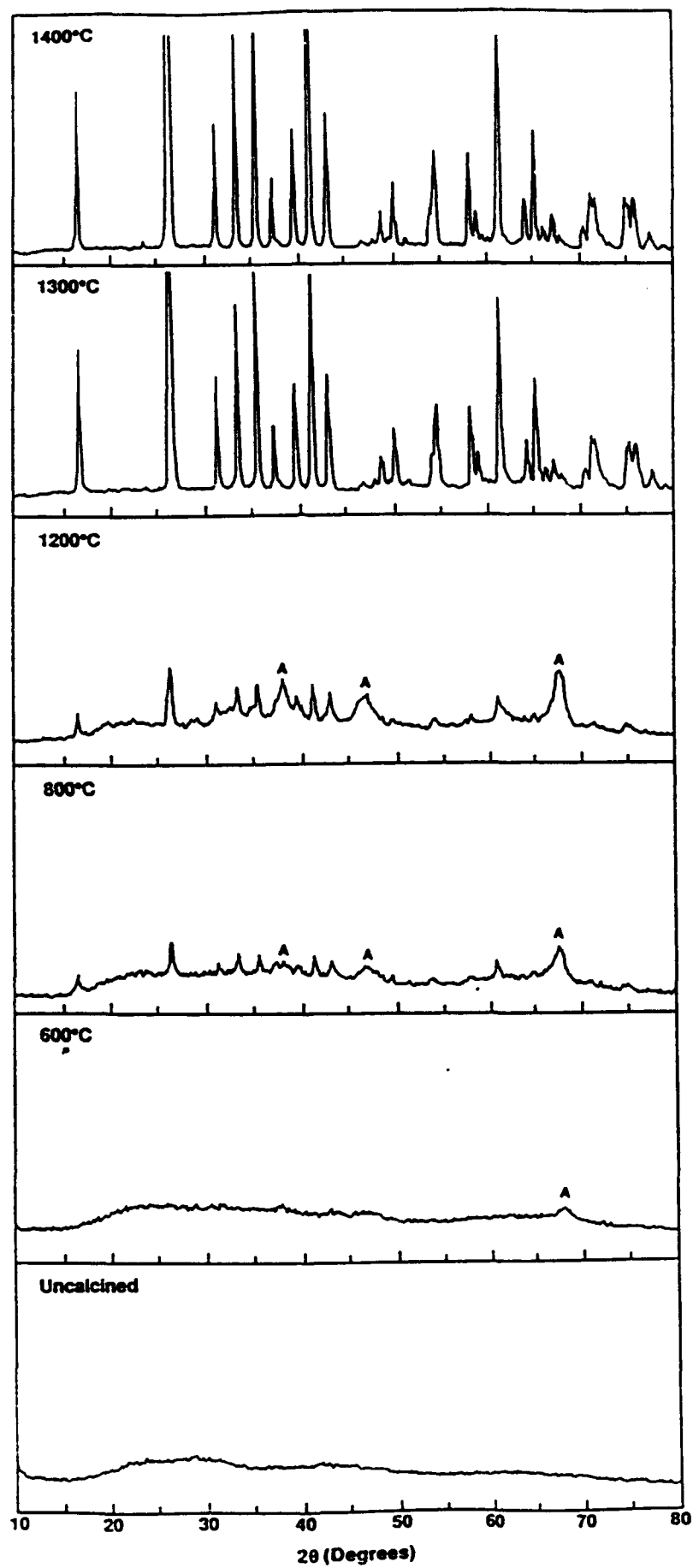


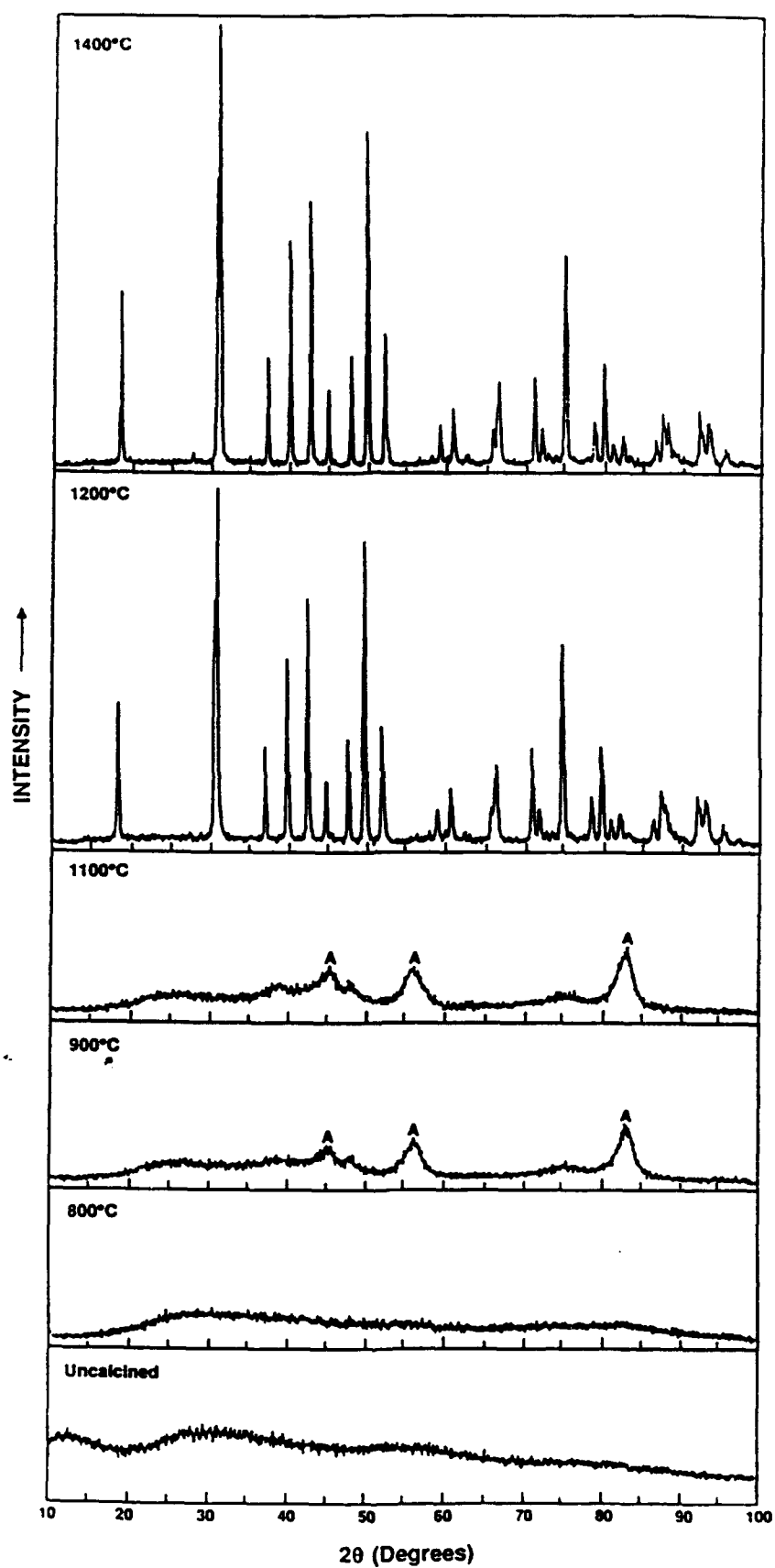
METHOD #2



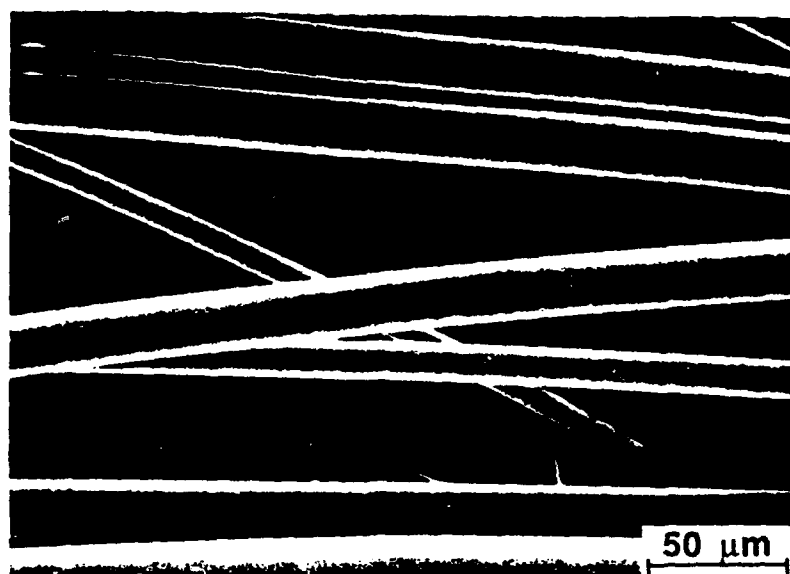
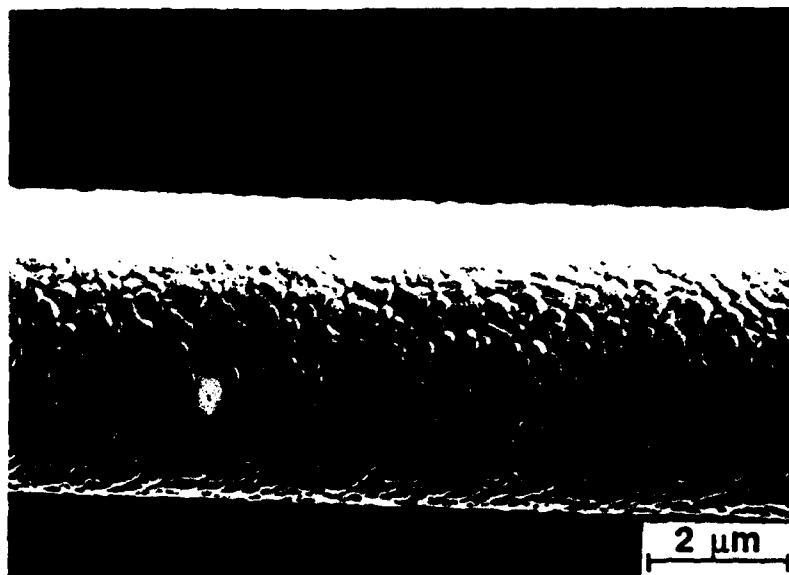




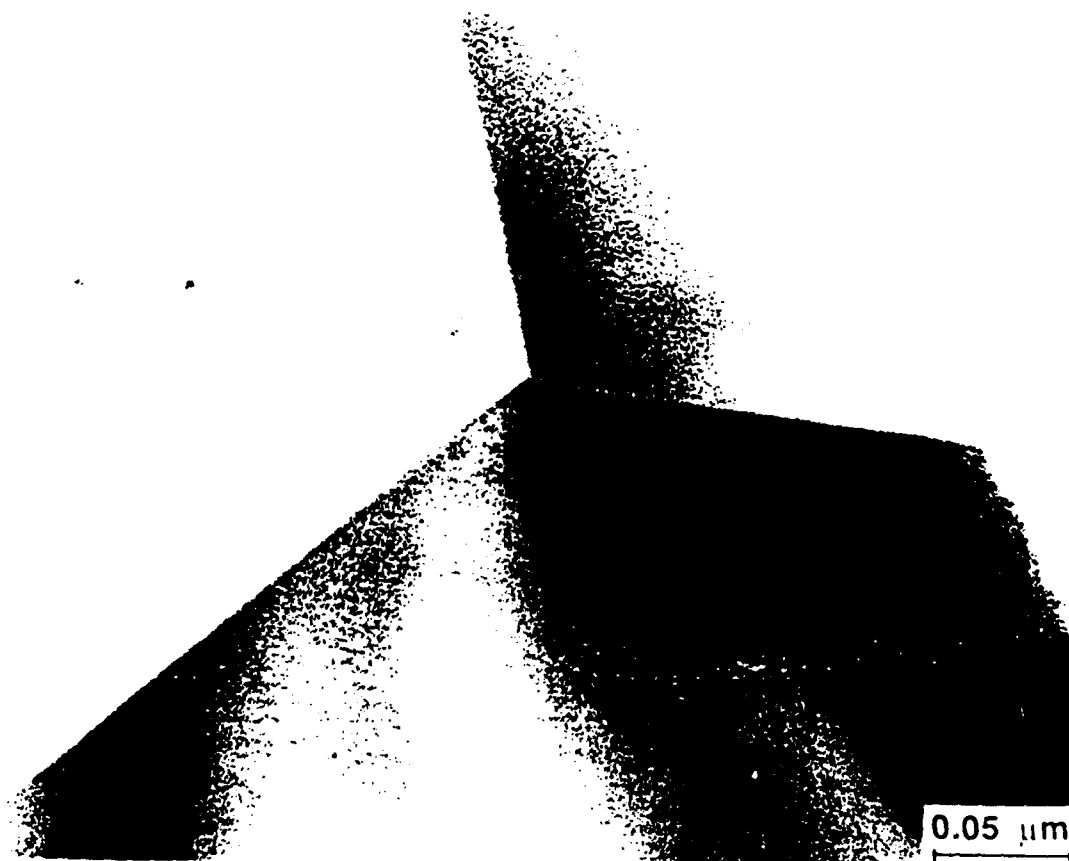




Mullite Fiber (Method #1)



Mullite Fiber (Method #1)

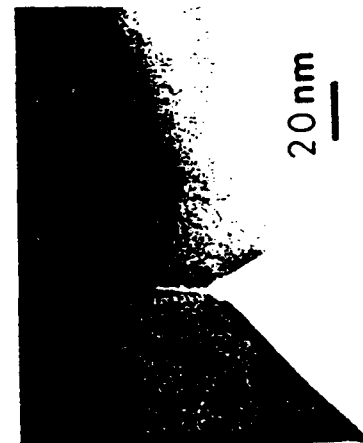


MULLITE BASED FIBERS (SOL-GEL PROCESS)

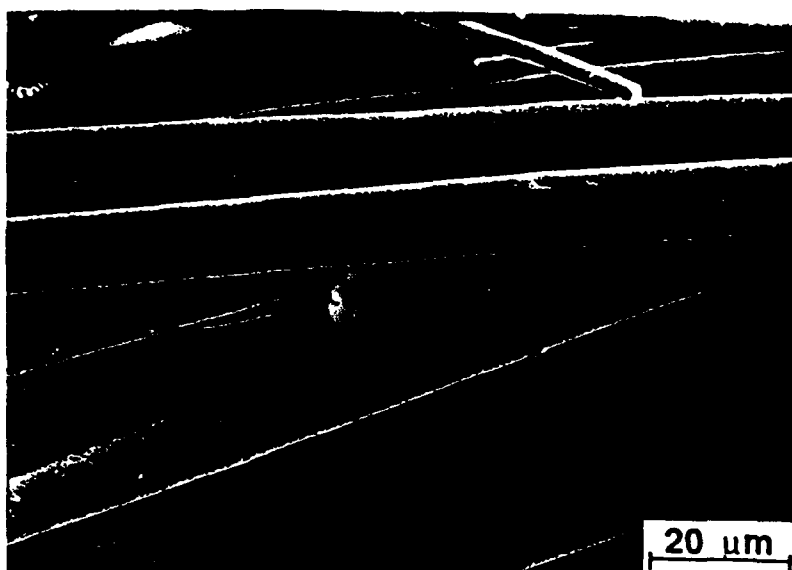
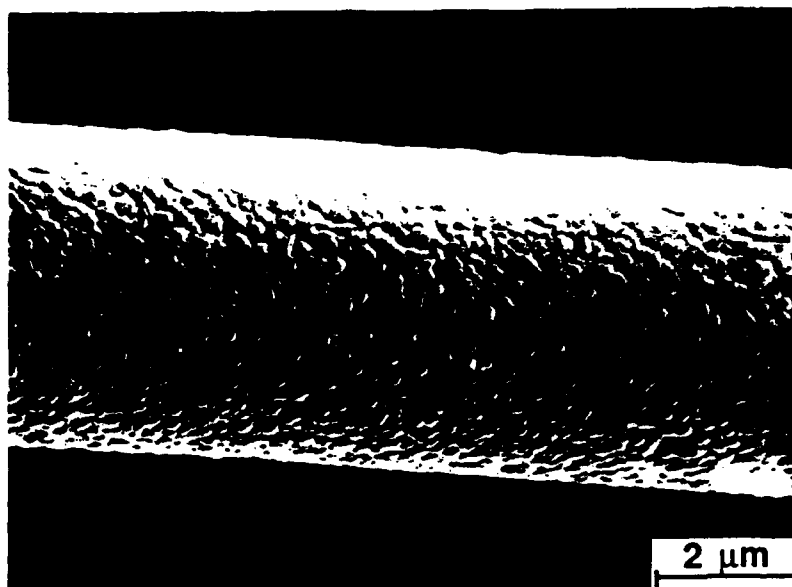
Al-CHLOROHYDROXIDE-SILICA SOL PRECURSOR, 1500°C



3M NEXTEL 480
AFTER 2hr. AT 1500°C

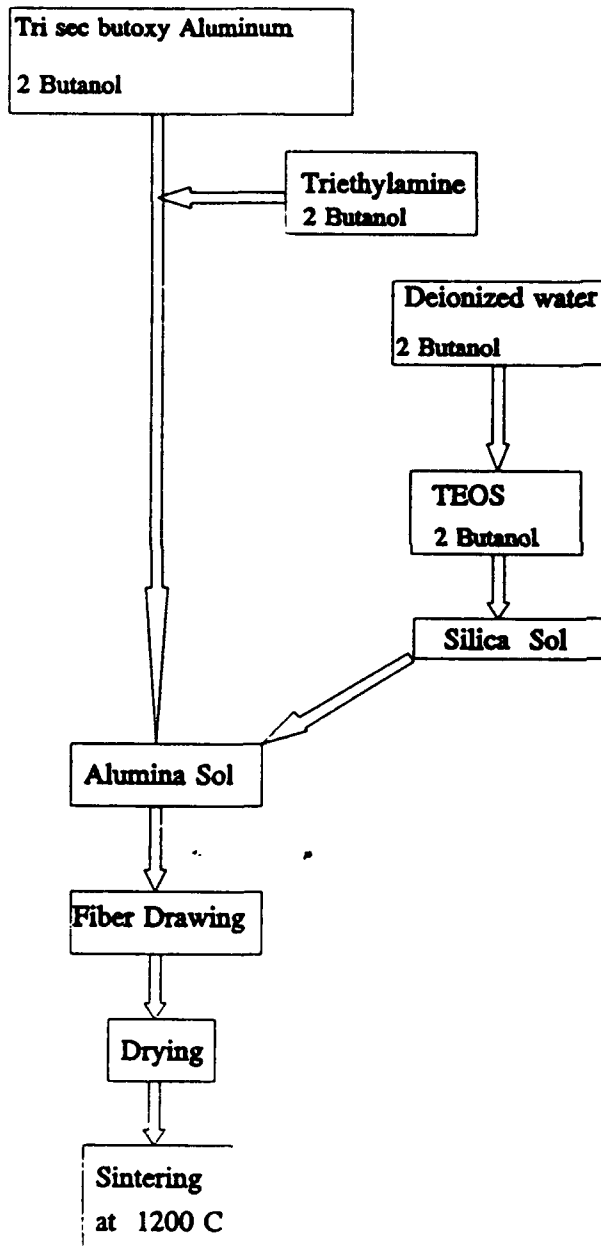


Mullite Fiber (Method #2)

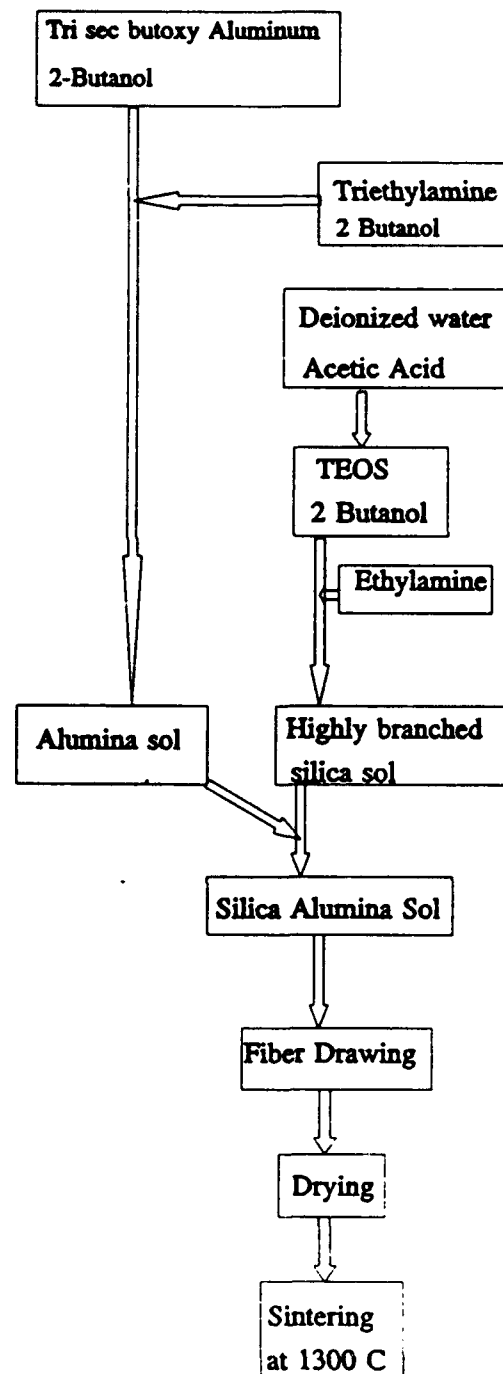


Silica Sol Methods

Method #3



Method #4

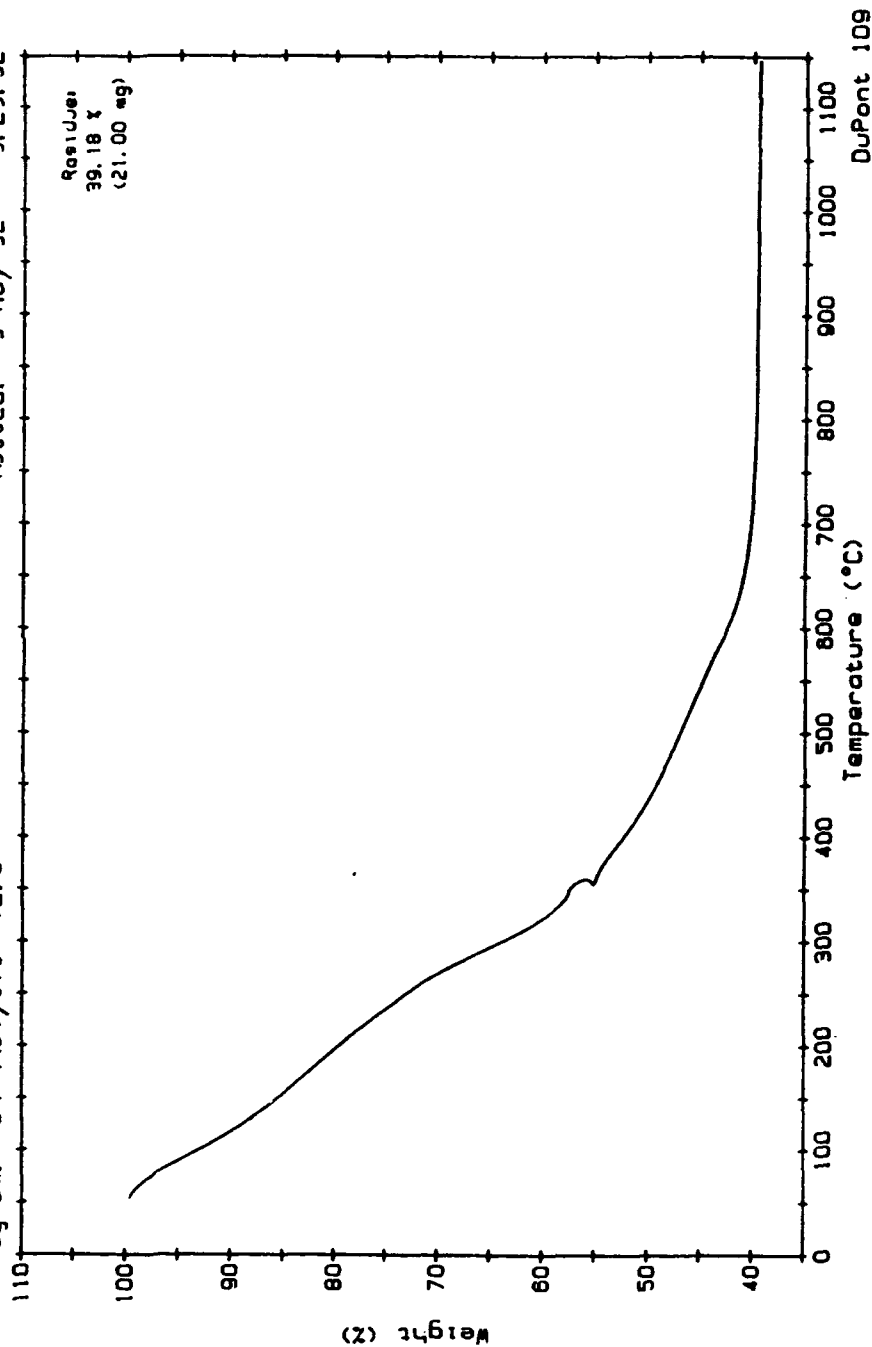


SILICA SOL METHODS

METHOD # 3

Sample: S1
Size: 53.60 mg
Rate: 10C/MIN
Program: TCA Analysis V2.0
Date: 6-May-92 Time: 23:14:41
File: SAATCA.01 ZACHARY
Operator: SAA
Placed: 9-May-92 3:25:32

TCA

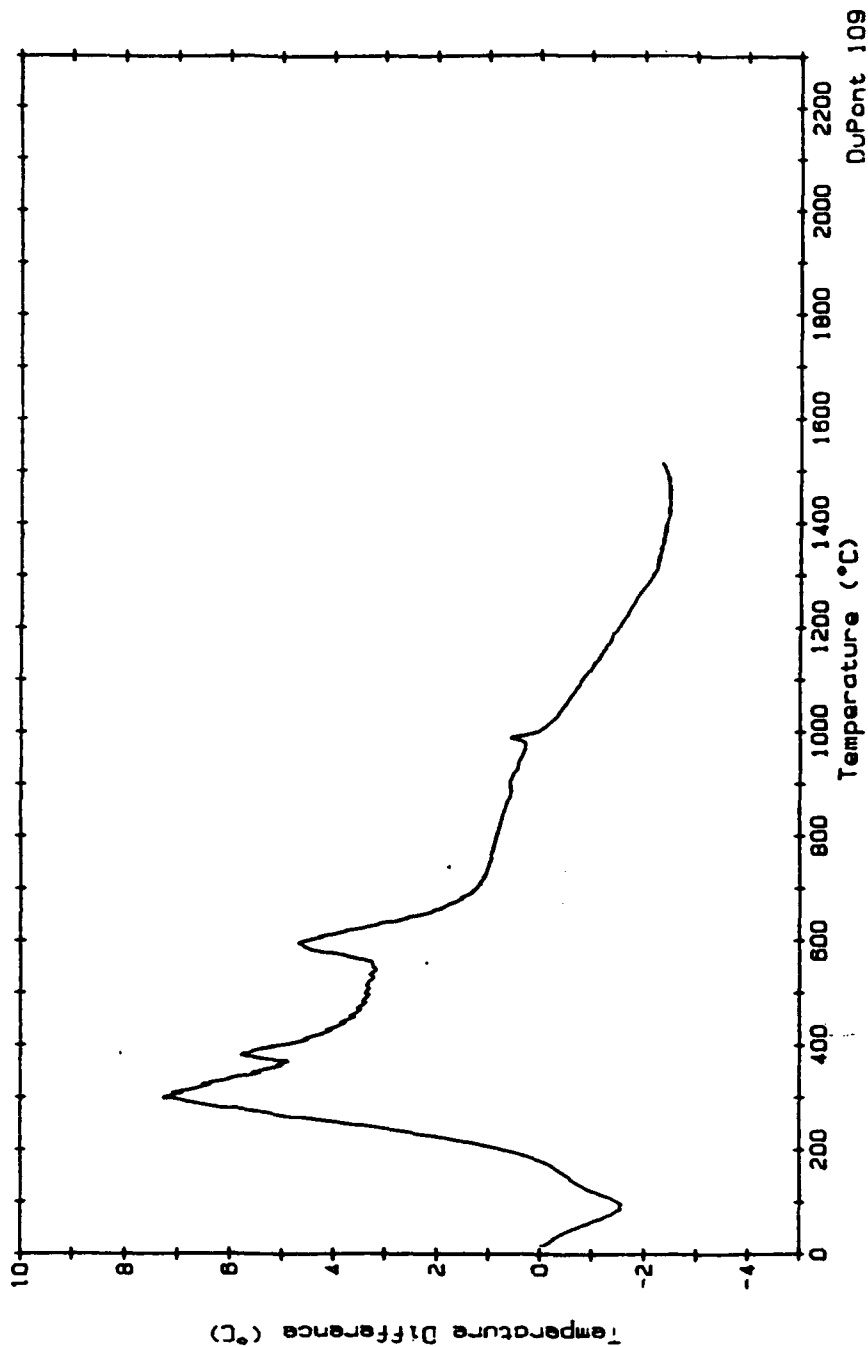


SILICA SOL METHODS METHOD # 3

Sample: S2
Size: .1037
Rate: 10

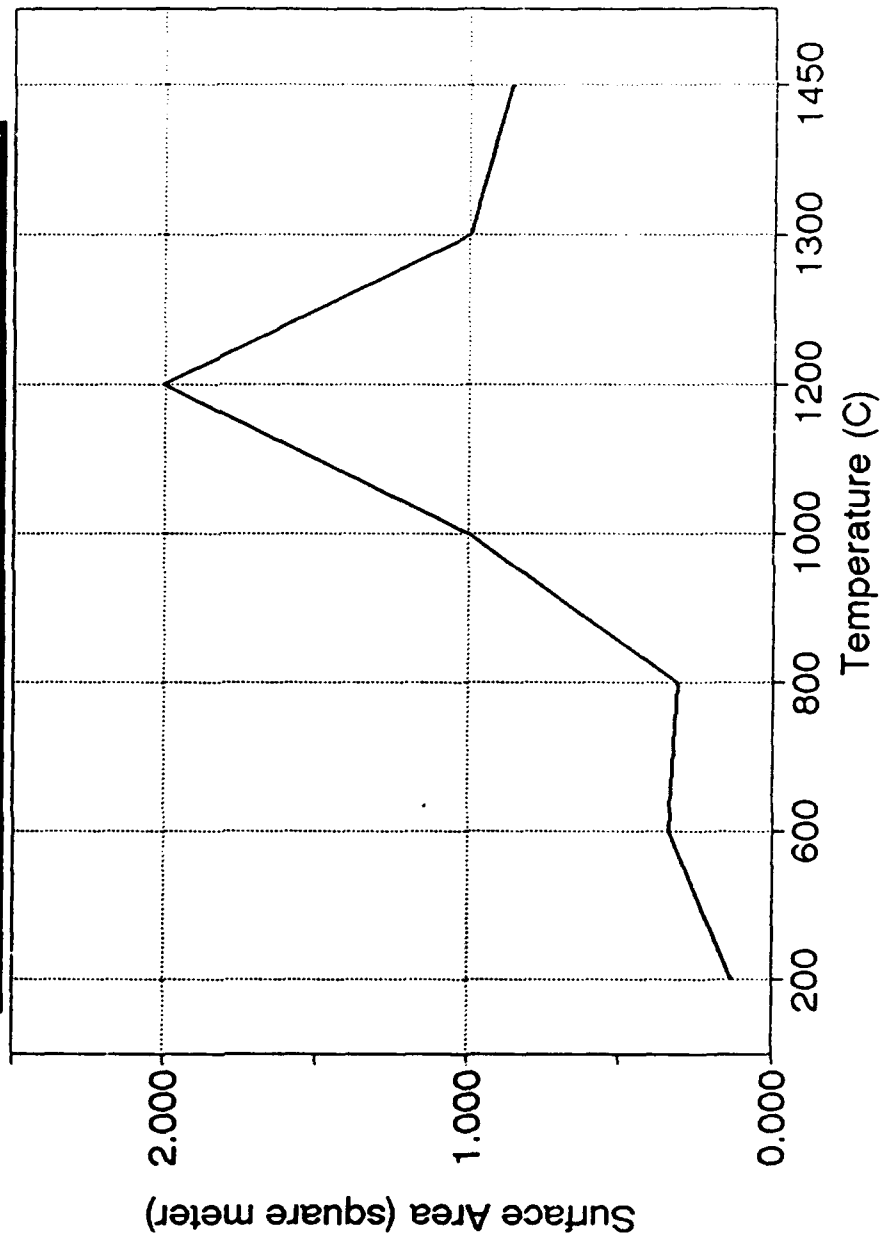
Date: 18-May-92 Time: 10:04:53
File: SAADTA.02 ZACKTA/1
Operator: SAA

DTA



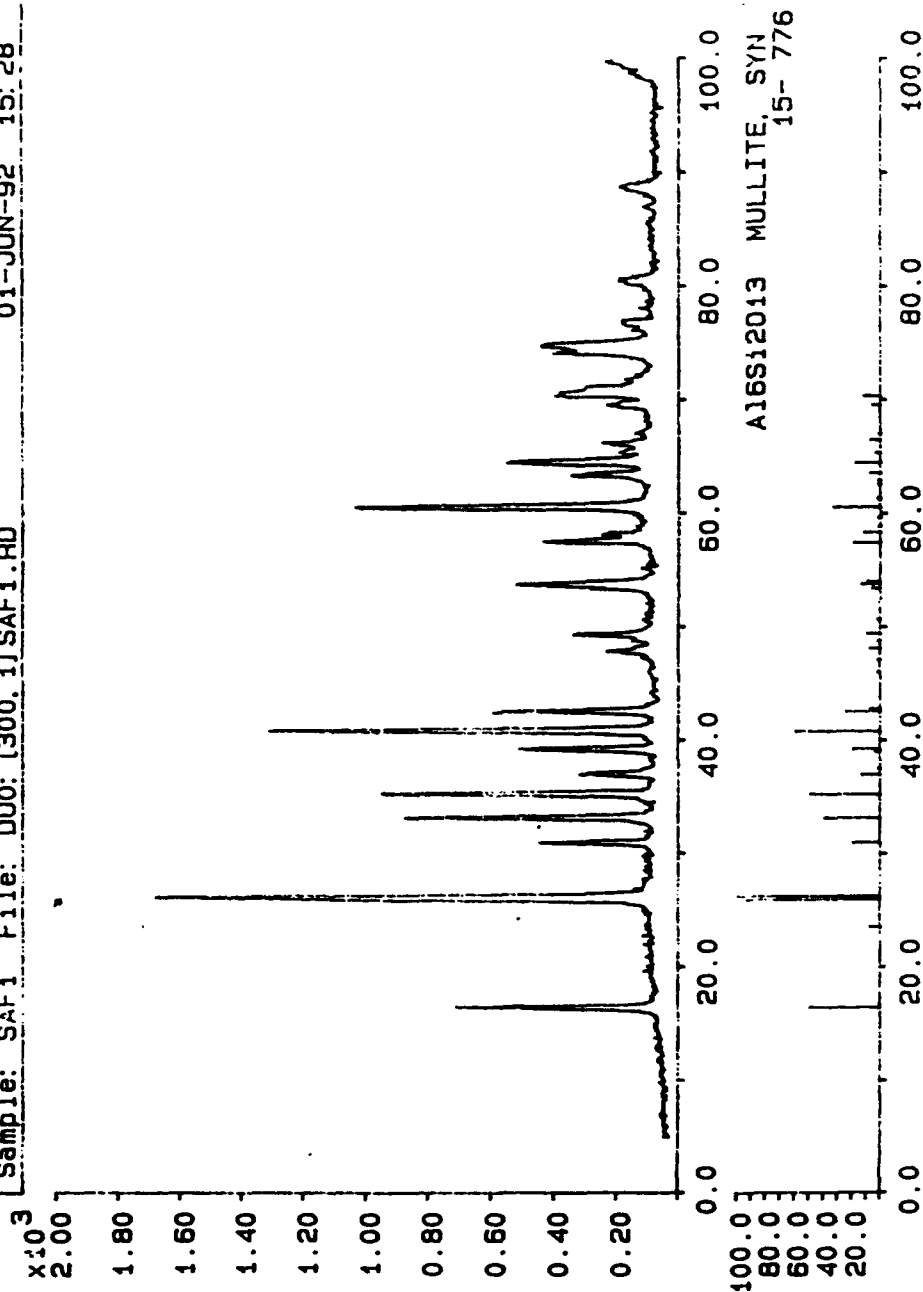
SILICA SOL METHODS METHOD # 3

Surface Area Change with Temperature
for Mullite Fibers



SILICA SOL METHODS METHOD # 3

Sample: SAF1 File: DUO: [300.1]SAF1.RD 01-JUN-92 15:28



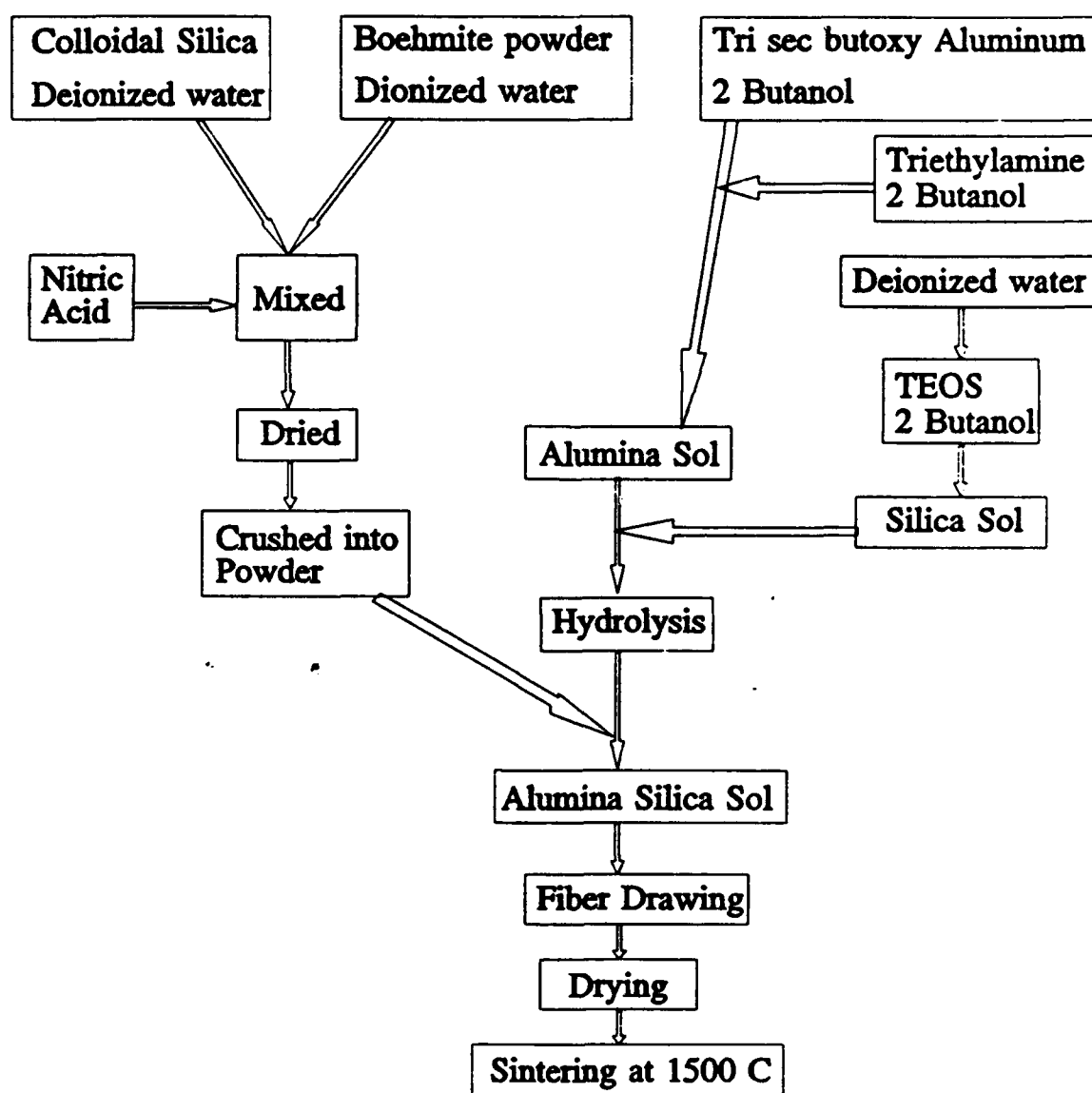
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

SOL-GEL APPROACHES FOR PRODUCING MULLITE

	Results:	Problems:
Colloidal Sols	Mullite phase formed (1200C) Full densification No intergranular glass phase Fine grain structure	Spinnability difficult to achieve
Polymer Sols	Mullite phase formed (1000C) Fine grain structure Spinnability excellent	Full density difficult to achieve
Seeded Sols	Promise: Full density No glass phase Spinnability Fine grain structure	Process control has many variables
Glass Leaching	Starts with woven blanket	Borate glass phase Process control

Seeded Sol Methods

Method #5



SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

A. GENERAL PROCESSING ISSUES

- Identified role of sol microstructure on mullite transition kinetics and sintering kinetics.
 - Colloidal silica retards mullite transition to 1250°C.
 - Colloidal silica enhances sintering kinetics below 1200°C.
 - Al-Si alkoxide precursors are mixed on the molecular scale and trigger the mullite transition at 980°C.
 - Early mullite transition has a detrimental effect on the sintering kinetics.
- Identified the role of sol microstructure on continuous fiber spinning.
 - Colloidal precursors have not produced adequate sols for continuous spinning.
 - Continuous spinning is achieved successfully when cross-linking of linear polymers occurs, as with alkoxide precursors.
- Identified formation of $6 \text{ Al}_2\text{O}_3 \cdot 1 \text{ SiO}_2$ spinel phase at 1000°C in the presence of alumina grains.
 - Spinel phase retards mullite transition to 1350°C.
 - Spinel phase liberates silica to allow for viscous phase sintering.

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

B. SPECIFIC RESULTS OF RESEARCH EFFORTS

- Colloidal Silica Methods (Methods #1, #2)
 - Formed fully dense mullite fibers
 - Formed structure with no intergranular glass phase
 - Formed sub-micron grain structure
 - Did not achieve continuous spinning
 - Centrifugal spun fibers were difficult to handle.
- Silica Sol Methods (Method #3)
 - Achieved continuous spinning of fibers
 - Spun fibers were processed up to 1450°C without handling problems
 - Formed mullite at 980°C
 - Resolved 2nd phase formation problem by improving polymer burn out below 600°C
 - Did not achieve full density at 1450°C
 - Formed 2-3 micron grain structure.

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

C. ONGOING STUDIES

- Colloidal Silica Methods
 - Addition of polydimethylsiloxane to form linear polymer structure as spinning aid
 - Formation of new Alumina sol precursors.
- Silica Sol Methods
 - Improved heating schedule to burn off carbonaceous residues and avoid formation of silicon carbide precipitates (this precipitate enhances glass phase formation upon decomposition of silicon carbide to silica)
 - Development of intermediate silica condensation process in basic solution (Method #4) to produce a more colloidal microstructure in the sol.
- Seeded Sol Methods (Method #5)
 - Studies of Boehmite seed volume fraction effect on intermediate spinel phase formation
 - Studies of the relationship of silica sol microstructure to sintering kinetics and full mullite conversion
 - Studies of tolerance of spinning process for partial colloid addition.

SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

PROGRESS STATUS

D. FUTURE WORK

- Full scale investigation of seeded sol methods
- Strength tests vs processing conditions
- High temperature mechanical tests
- Modification of spinning process to include on-line heat treatment processes
- Development of on-line tests for AI controlled processing.



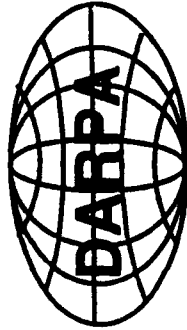
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

CHEMICAL VAPOR DEPOSITION APPROACHES TO IMPROVED COMPOSITE STRUCTURES

Tim Anderson
Chemical Engineering Department

MSE

University of Florida



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

OBJECTIVES

- Develop chemical vapor infiltration (CVI) processes for densifying composite structures
- Develop CVD processes for coating applications

control interfacial bonding, reactivity and diffusion
improve mechanical properties
increase wetting by metals
improve polishability

APPROACHES

- Construct general purpose cold-wall CVD system
- Understand deposition chemistries and mechanisms
- Investigate novel reactor designs for CVI
- Explore atomic layer deposition (ALD) mode

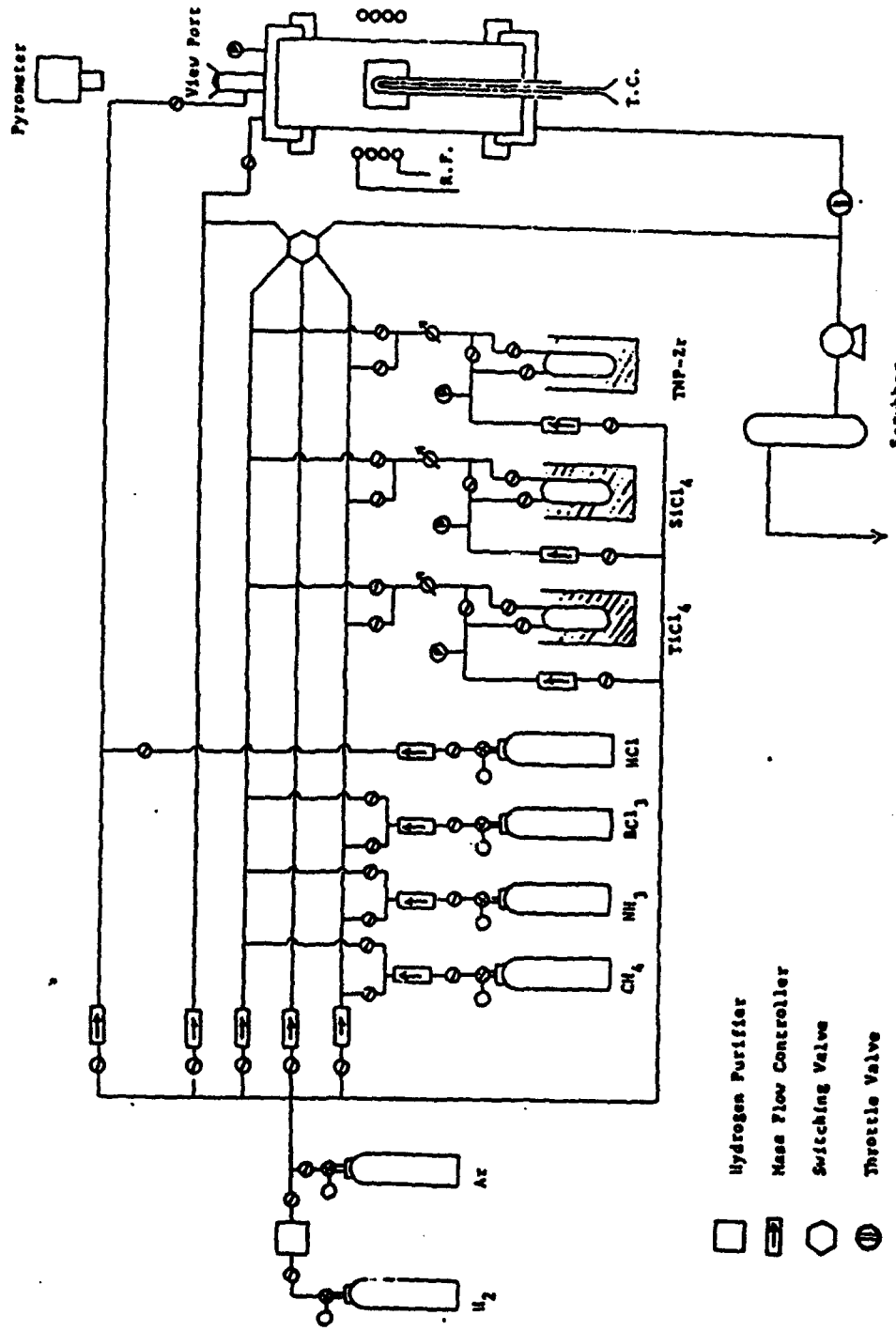
MSE

University of Florida



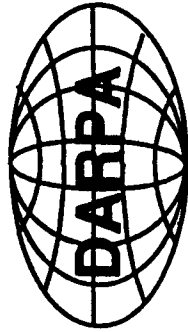
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

New CVD Schematic
Low Pressure, Fast-Switching Manifold, Multiple Species



MSE

University of Florida



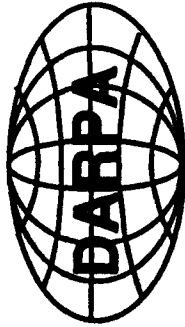
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

System Features

- Four Independent Gaseous Sources (Currently BCl_3 , SiH_2Cl_2 , CH_4 , and NH_3 or HCl)
- Three Independent Liquid Sources (Currently TiCl_4 , SiCl_4 , and PCl_3)
- Computer Operated Mass Flow Controllers
- Pressure Control
- Rapid Switching Run-Vent Radial Manifold
- Impinging-Jet Flow Reactor Design

System Capabilities

- Various Carbide, Nitride, Boride and Silicide Chemistries
- Compositional Grading
- Multilayer Structures
- In-situ Chemical Etching
- Extended-Time Atomic Layer Deposition



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

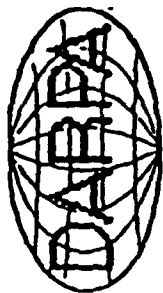
TiC

Properties

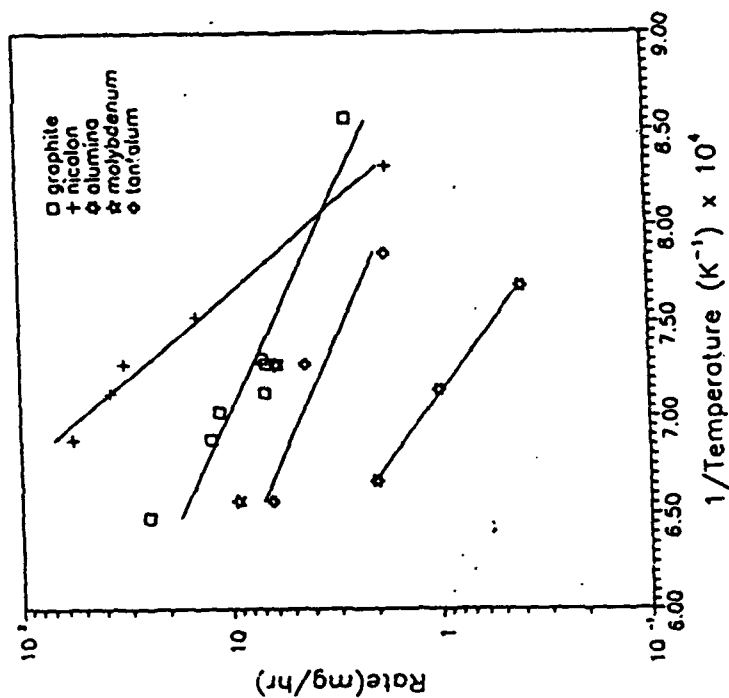
- High melting temperature (2940°C)
- High microhardness (2000-3000 GPa)
- High transverse rupture strength (240-400 GPa)
- Wear resistant
- Oxidation resistant

Applications

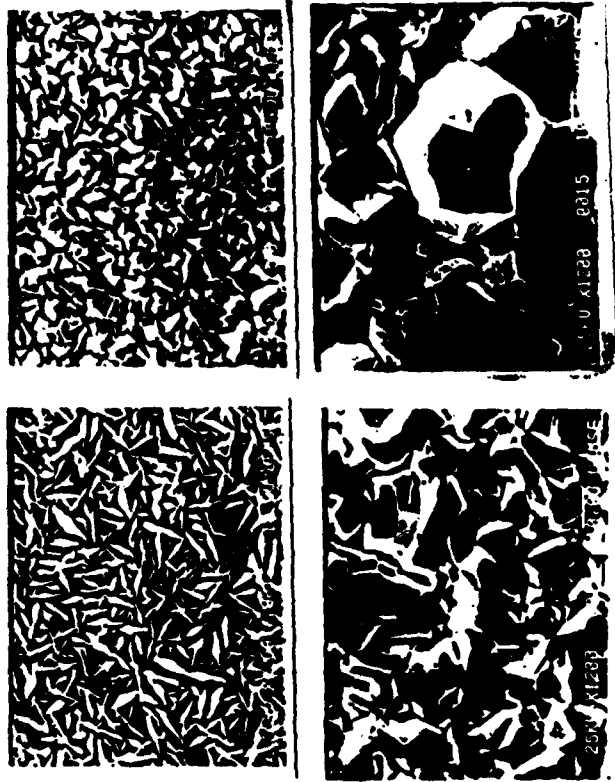
- Protective coatings on steels, ceramic inserts and bulk ceramic cutting tools
- Matrix phase in hybrid carbon/carbon composites
- High temperature applications



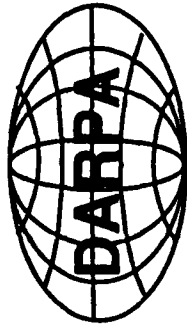
REACTION LIMITED DEPOSITION OF $TiCl_x$



Growth rate of $TiCl_x$ on various substrates as a function of reciprocal temperature.



Microstructure of $TiCl_x$ on Alumina, clockwise from upper left-hand side corner, $T=1300^\circ C$ and $CH_4/TiCl_4 = 0.5$, $T=1300^\circ C$ and $CH_4/TiCl_4 = 1.0$, $T=1300^\circ C$ and $CH_4/TiCl_4 = 3$, $T=1300^\circ C$ and $CH_4/TiCl_4 = 4.0$.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

COMPARISON OF ACTIVATION ENERGY AND ORIENTATION FOR DEPOSITION OF TiC_x

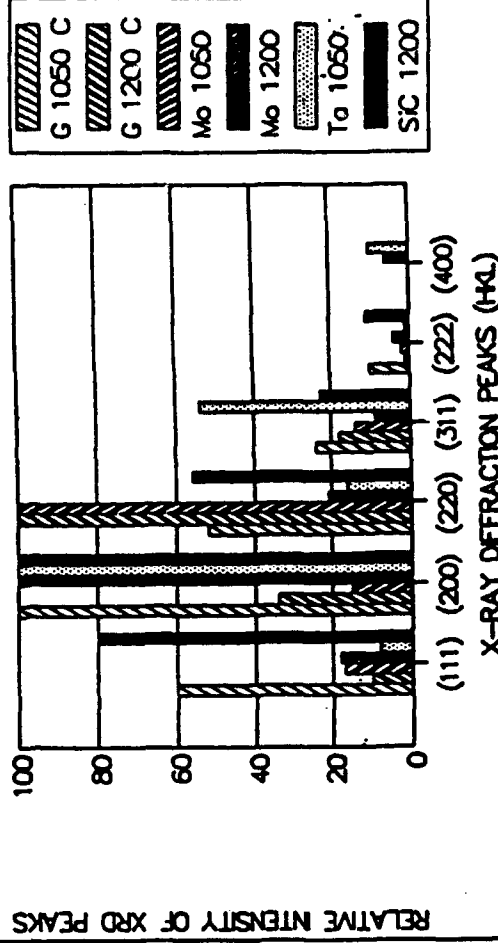
SUBSTRATE **EA(KJ/MOL)**

Al_2O_3 130
GRAPHITE 109
NICALON 210

PREFERRED ORIENTATIONS

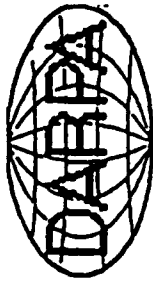
SUBSTRATE	T(°C)	(HKL)	T(°C)	(HKL)
GRAPHITE	1050	(200)	1200	(220)
NICALON	1050	(200)	1200	(200)
Al_2O_3	1050	(111)	1200	(111)
Mo	1050	(220)	1200	(200)
Ta	1050	(200)	-----	

PREFERRED ORIENTATIONS OF TiC GROWN ON DIFFERENT SUBSTRATES



MSE

University of Florida



MICROHARDNESS AND FRACTURE
TOUGHNESS OF CVD TiC_x

=====					
DEPOSITION TEMPERATURE		GRAPHITE		NICALON	
T (°C)	H (GPa)	K _c ^{1/2} (MPa·m ^{1/2})	H (GPa)	K _c ^{1/2} (MPa·m ^{1/2})	
1050	21	3.5	22	2.6	
1200	27	2.1	26	2.1	

INCREASING THE DEPOSITION TEMPERATURE INCREASES THE HARDNESS AND DECREASES THE FRACTURE TOUGHNESS OF THE TiC MATRIX. INCREASED CRACKING IS OBSERVED AT DEPOSITION TEMPERATURES OF > 1100°C.

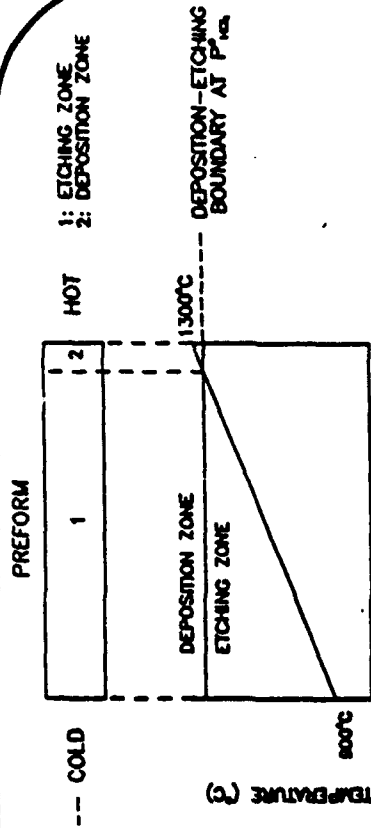


15 482 0405 0010 0



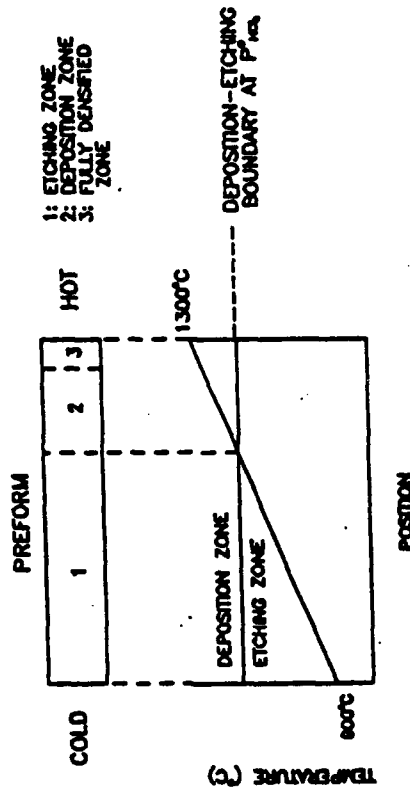
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

CVI WITH THERMAL GRADIENT AND HCL FLOW CONTROL



2-39

CVI BY THERMAL GRADIENT AND HCL ETCHING.
 P_{HCl} IS THE INITIAL INLET PARTIAL PRESSURE OF HCL.



2-40

CVI BY THERMAL GRADIENT AND HCL ETCHING.
 P_{HCl} IS LESS THAN P_{HCl} .

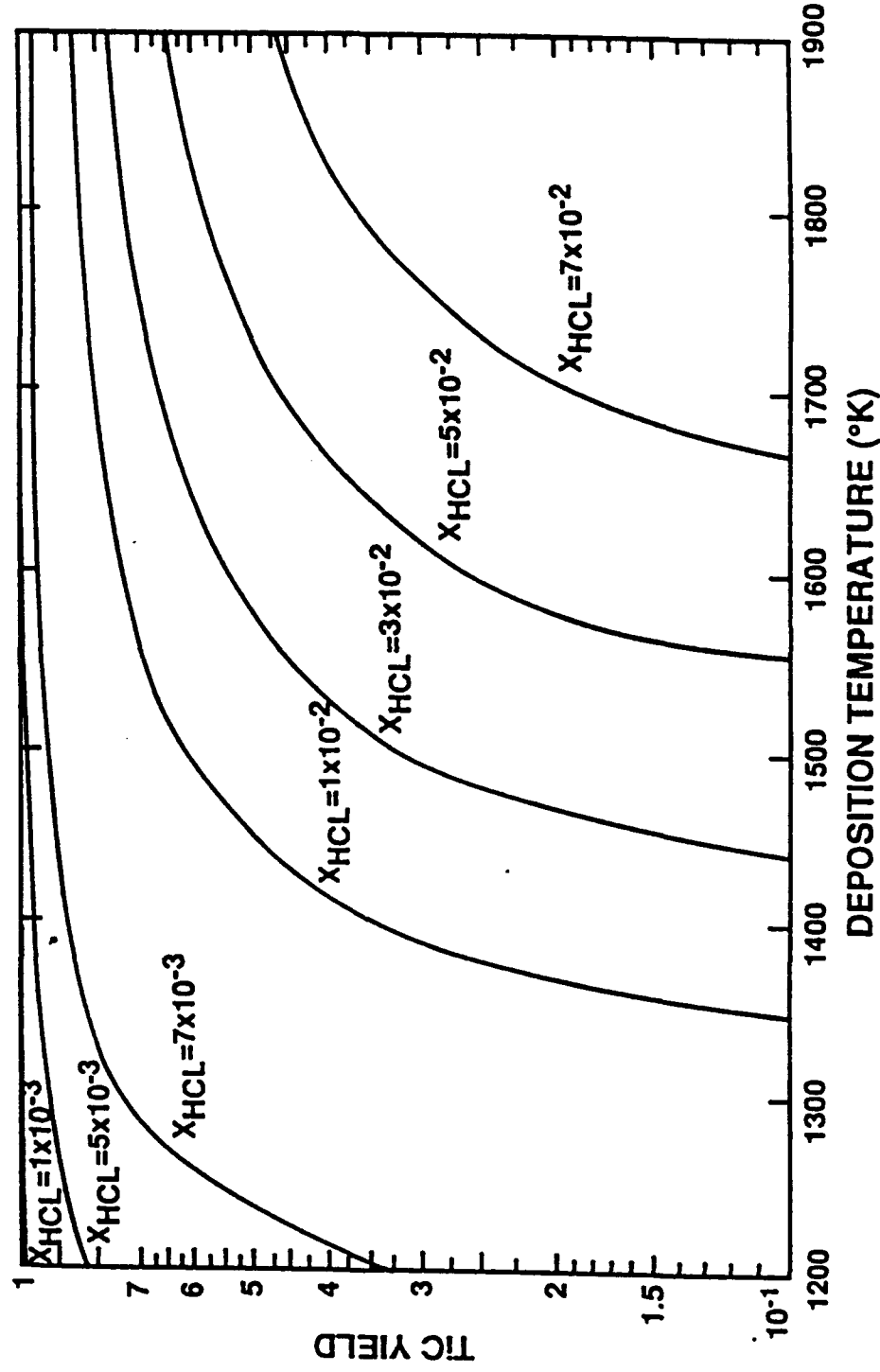
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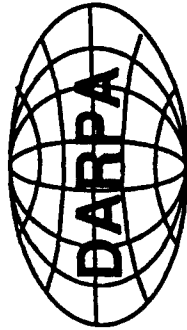
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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

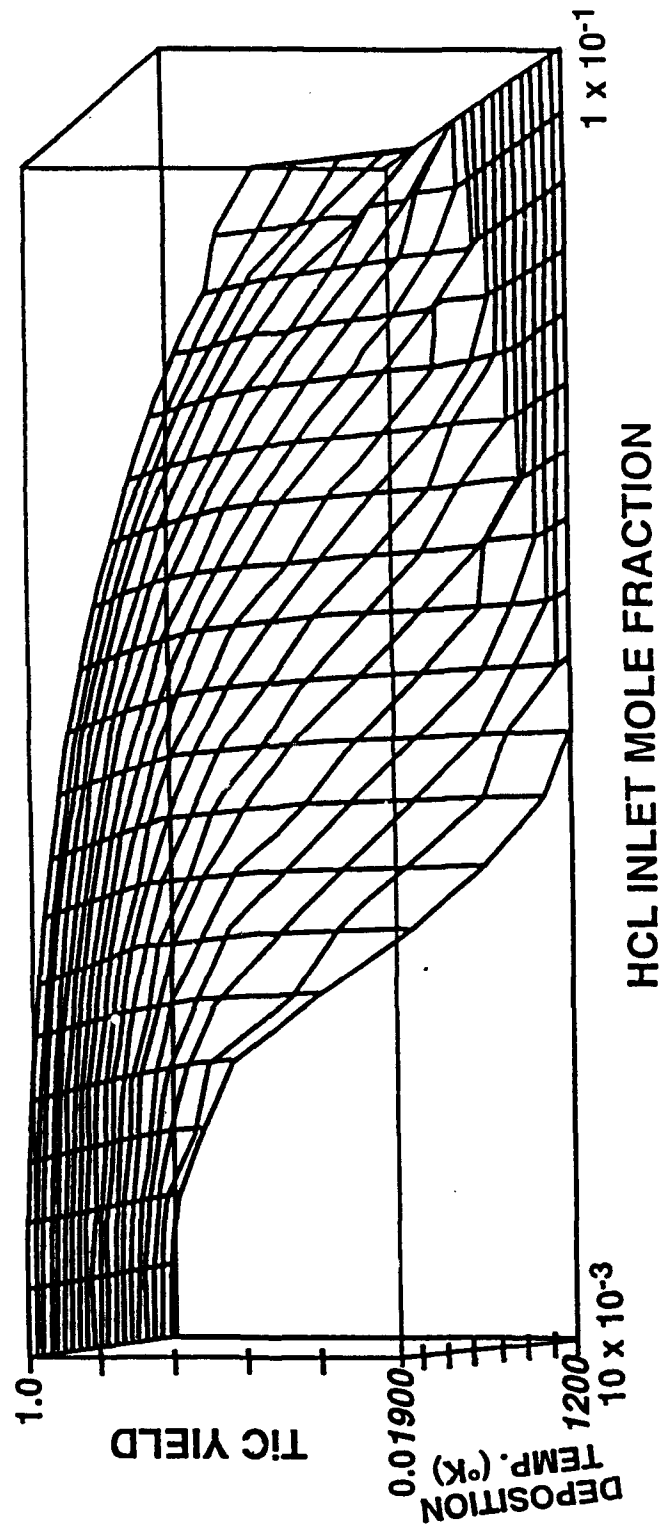
TiC YIELD vs DEPOSITION TEMPERATURE and HCl
CONCENTRATION





INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

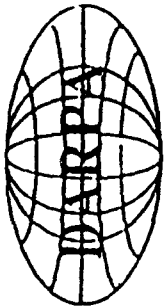
TiC YIELD vs. TEMPERATURE and HCl CONCENTRATION



CH_4 Inlet Mole Fraction = 0.01
 TiCl_4 Inlet Mole Fraction = 0.0001

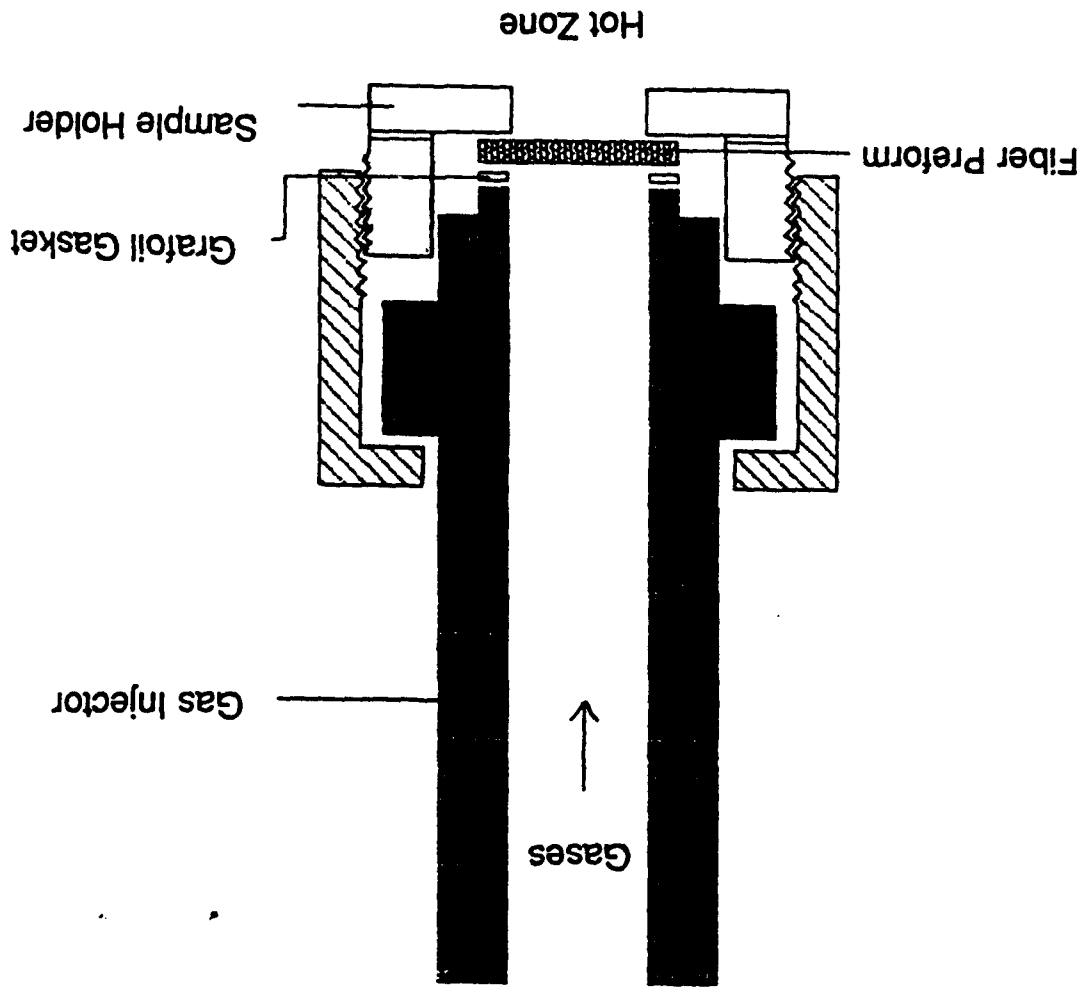
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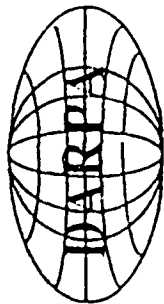
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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

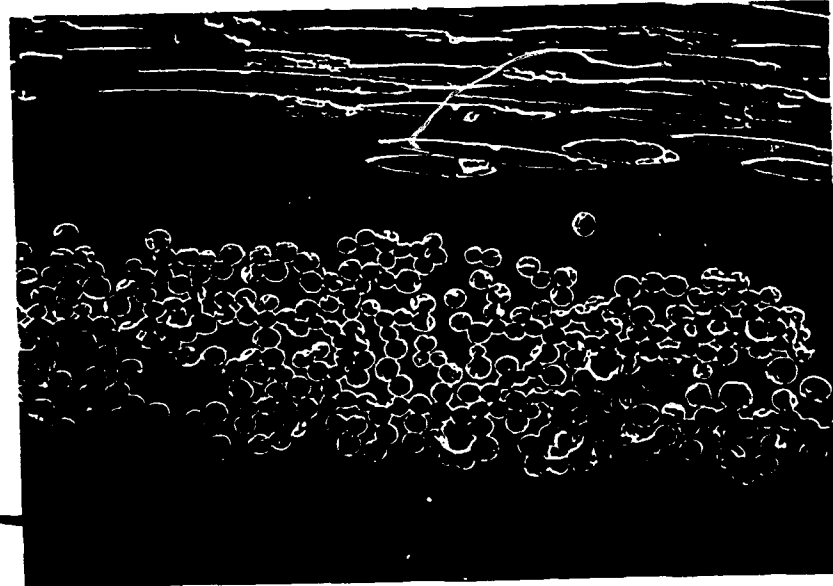
Sample Holder Set-up For
Forced-flow Temperature-Gradient CVI



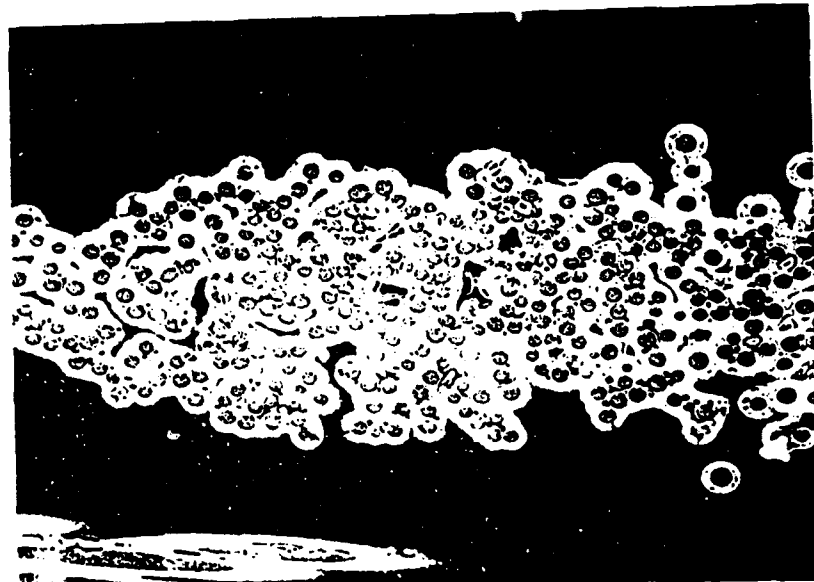


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

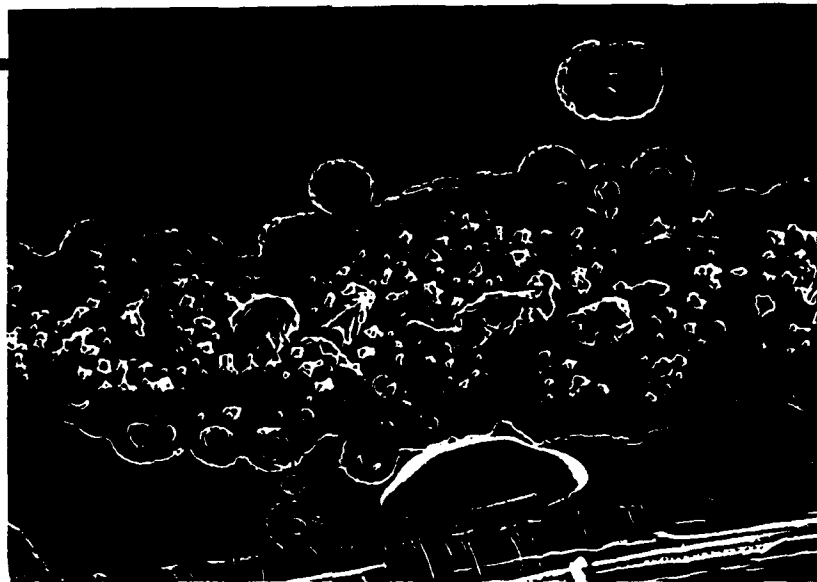
CONVENTIONAL CVI AT LOWER
C/Ti RATIO (2/1)



Top Layer (1000°C)



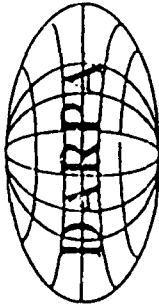
Middle Layer



Bottom Layer (1300° C)

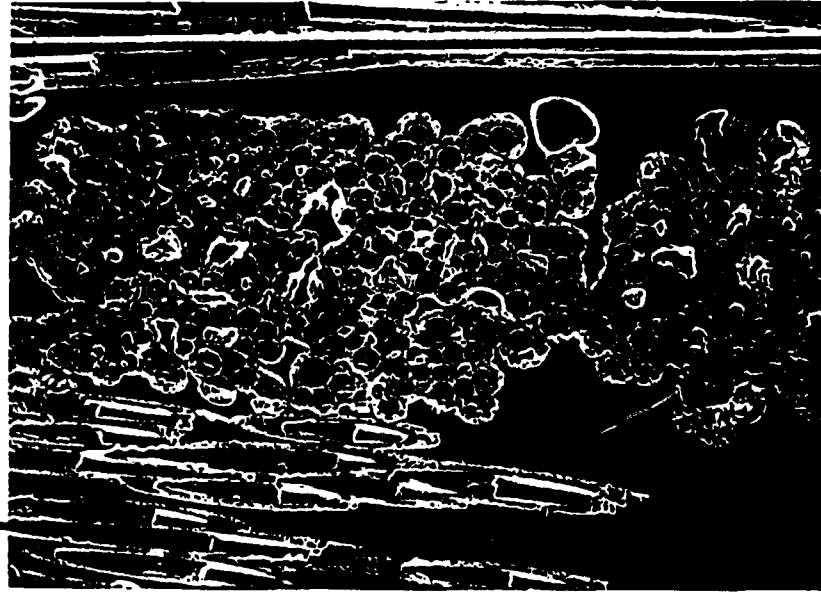
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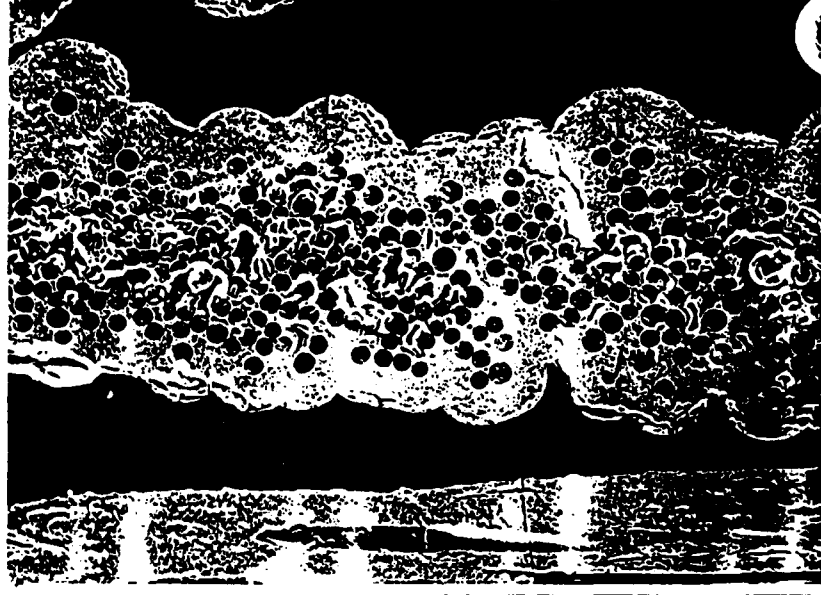


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

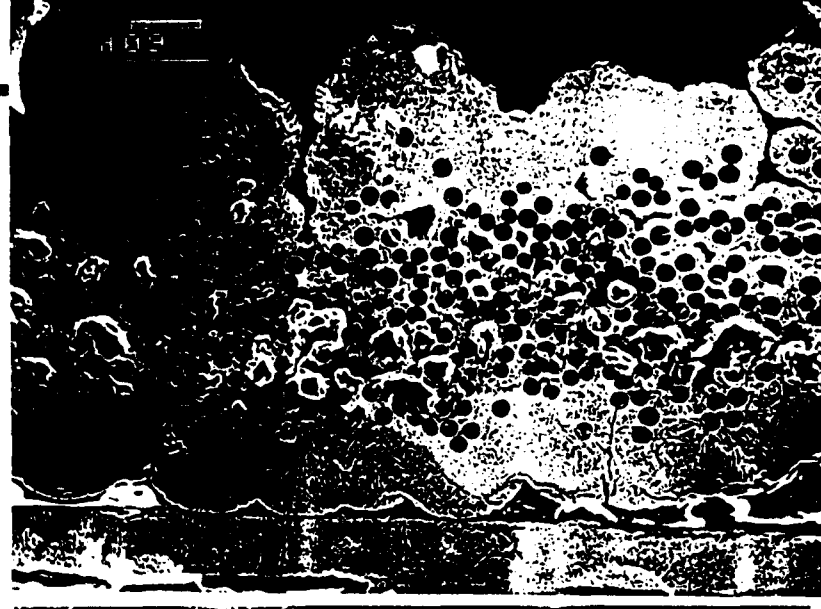
Conventional Forced-flow CVI of a Nicalon Preform with TiC_x .



Top Layer (1000°C)



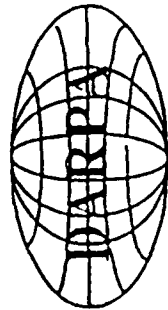
Middle Layer



Bottom Layer (1300° C)

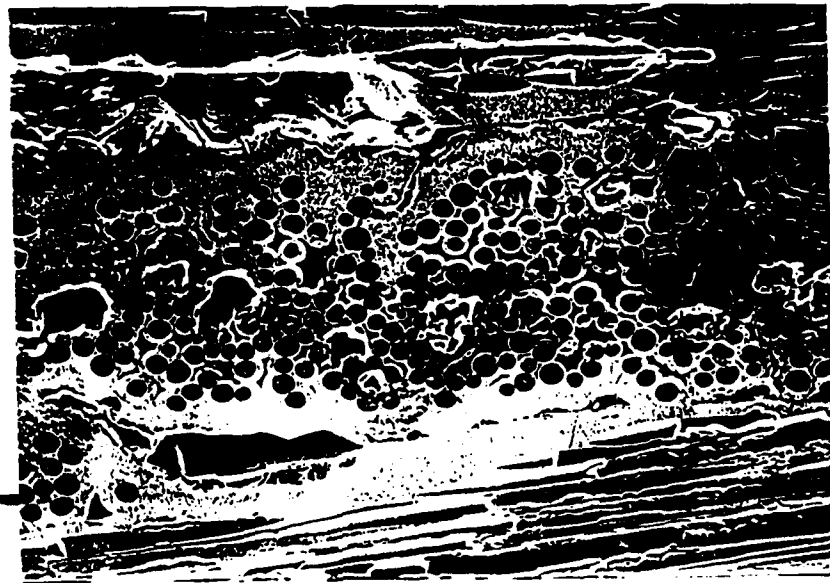
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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

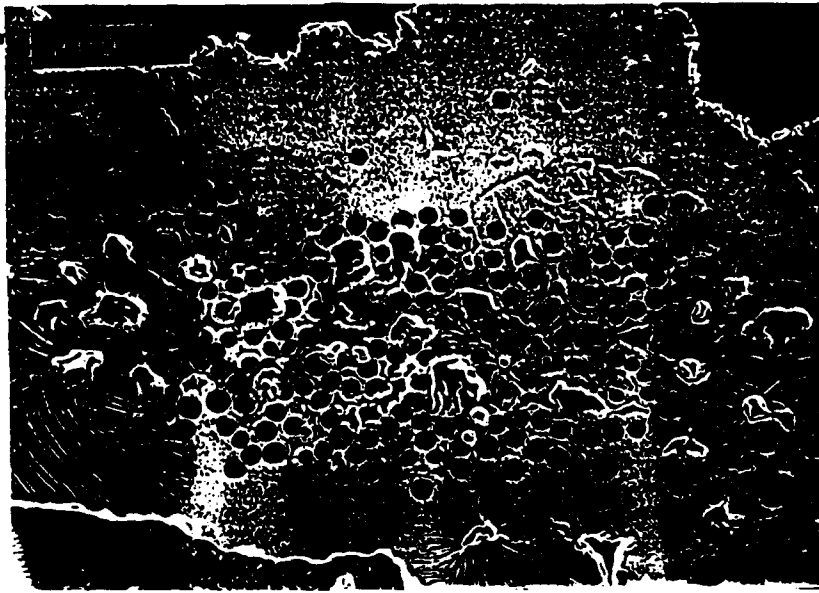
FORCED-FLOW CVI COUPLED WITH HCL ETCHING



Top Layer (1000°C)



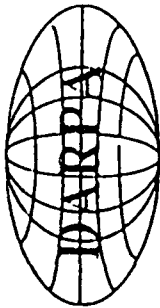
Middle Layer



Bottom Layer (1300°C)

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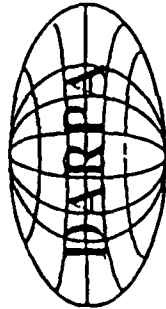
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

FIBER PULL-OUT AFTER POLISHING
INFILTRATED NICALON PREFORM



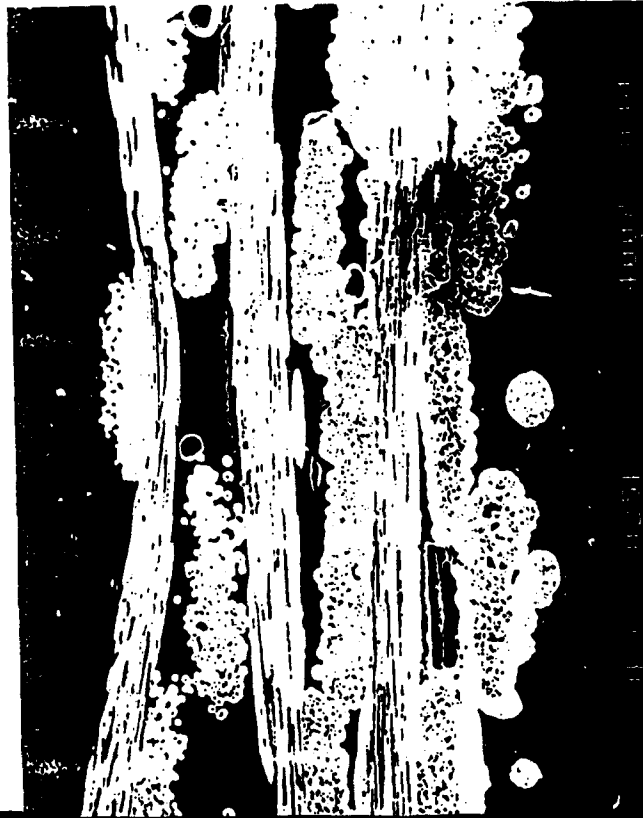
MSIE

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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

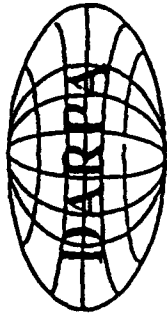
COMPARISON OF CVI PROCESSES



Conventional Forced-flow CVI
of a Nicalon Preform with TiC_x



Forced-flow CVI coupled with
 HCl injection



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

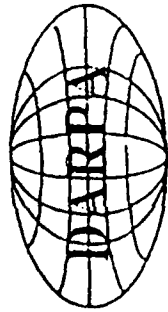
Silicon Carbide Deposition Parameters

Temperature 1523K
Pressure 200 torr
Inlet Gas Conditions
SiH₂Cl₂ 40 sccm
CH₄ 40 sccm
H₂ 420 sccm
Time 45 min.
Film Thickness 100+ μ m
Substrate Si (100)

Carburization Parameters

Done Immediately Prior to SiC Deposition

Temperature 1523K
Pressure 200 torr
Inlet Gas Conditions
CH₄ 10 sccm
H₂ 420 sccm
Time 10 min.
Film Thickness (est.) 1 μ m

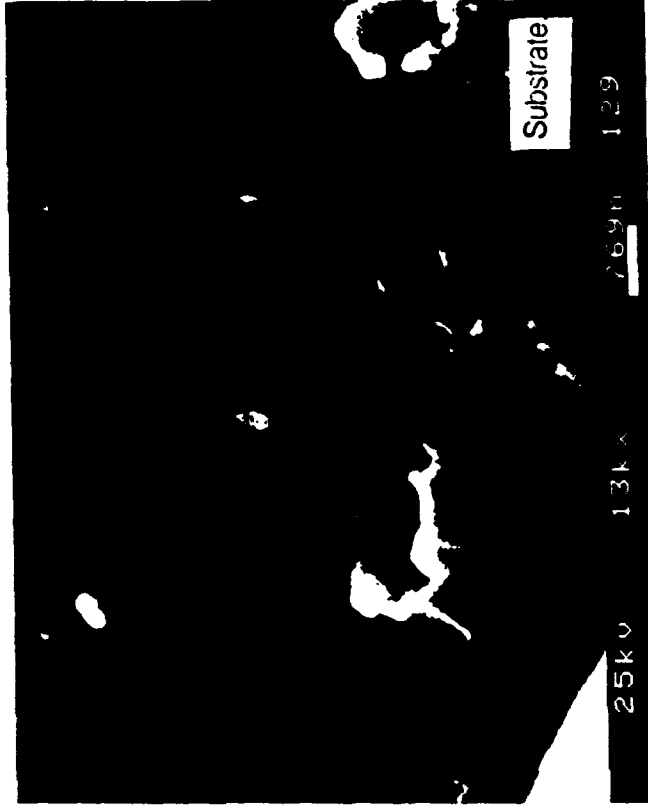


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Interface Without Carburization



Interface With Carburization

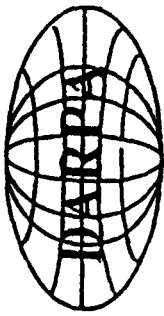


1 µm



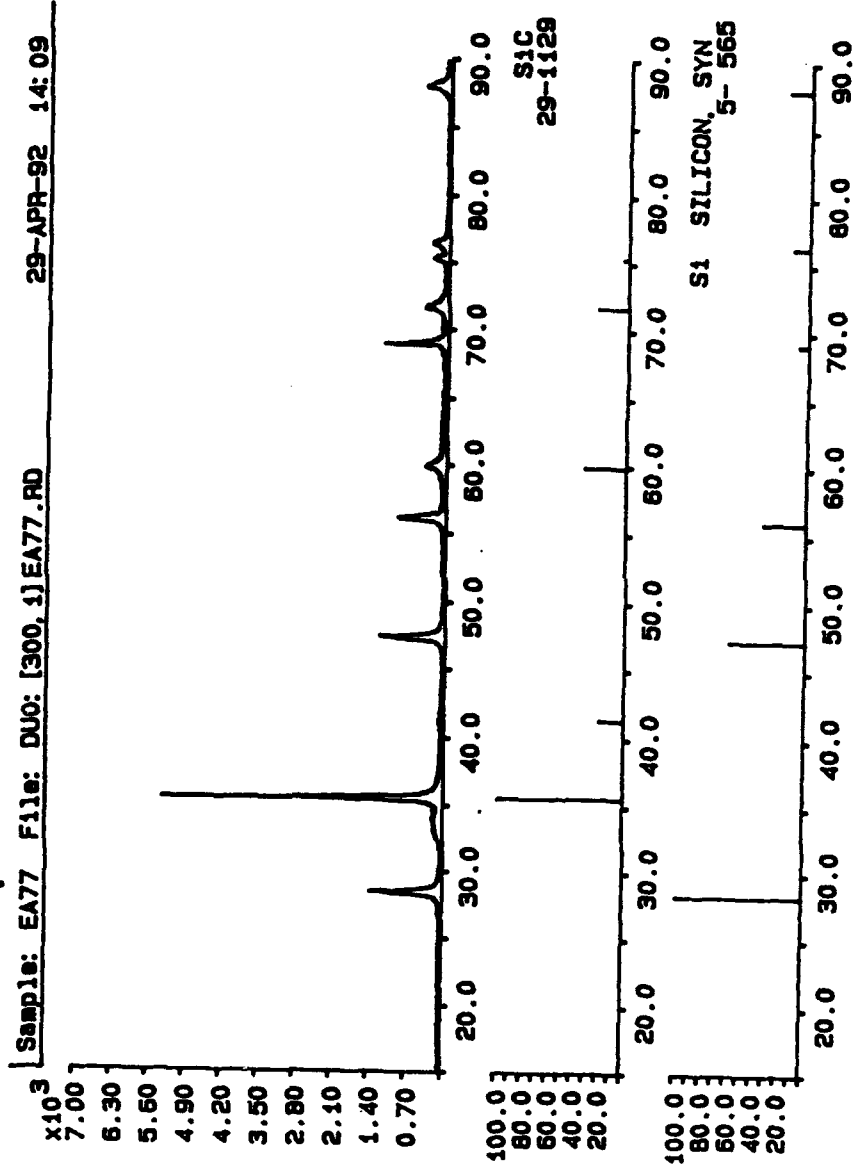
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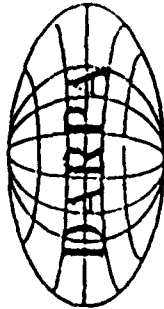
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

With Carburization



MSE

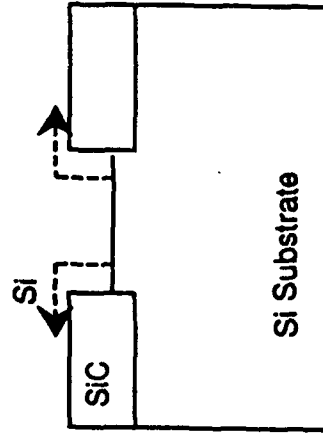
UNIVERSITY OF FLORIDA



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

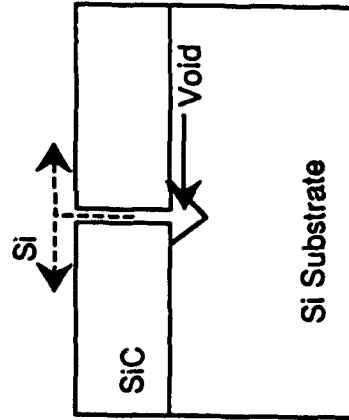
Void Formation During Carburization

$\text{CH}_4 + \text{H}_2$



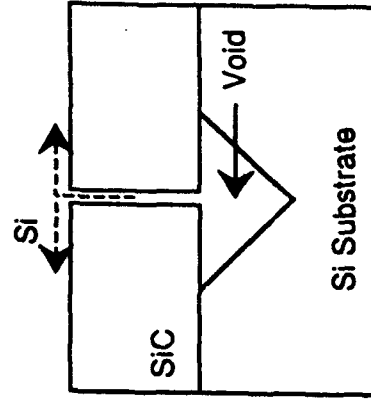
Nucleation and 3D Growth:
Uncovered areas provide
silicon at growth interface
via surface diffusion

$\text{CH}_4 + \text{H}_2$



Substrate Coverage:
Silicon provided only
through grain boundaries

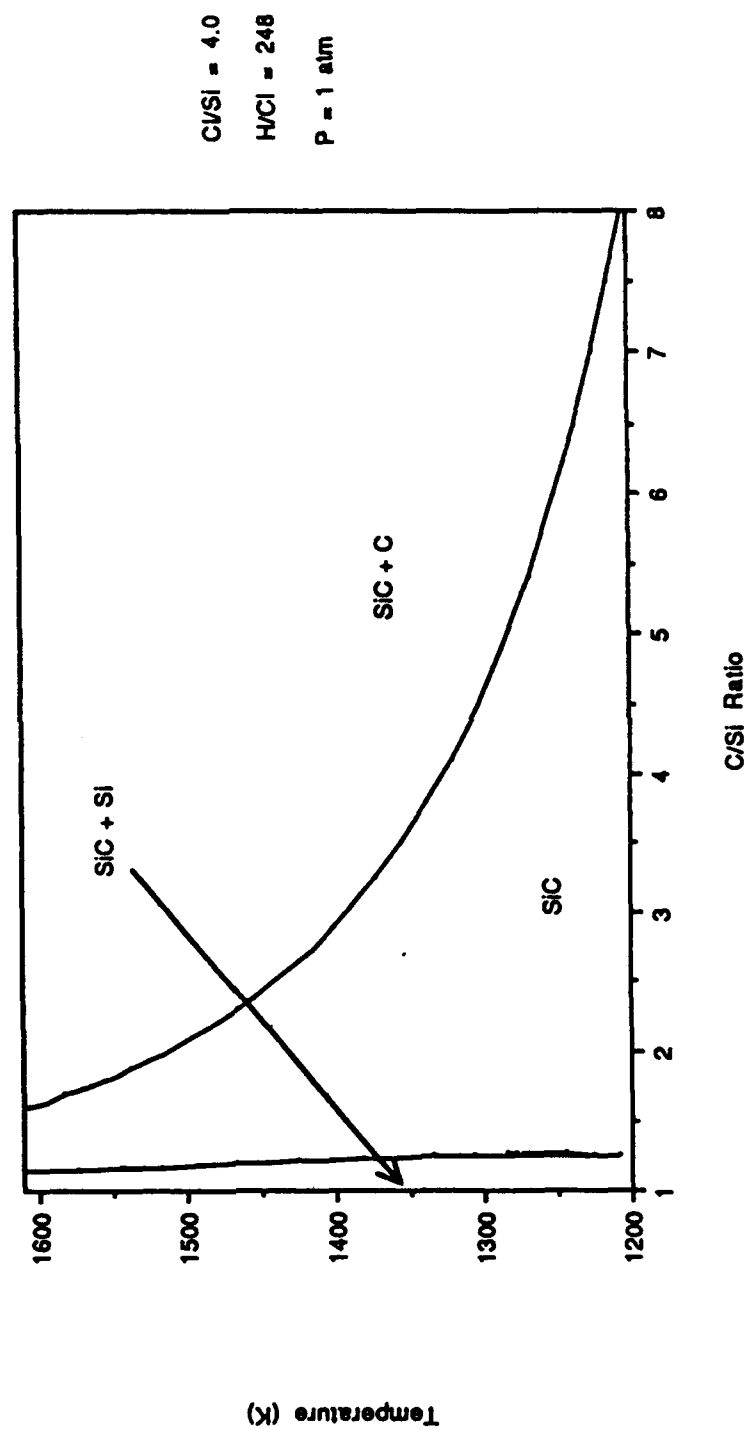
$\text{CH}_4 + \text{H}_2$



2D Growth:
Continued silicon
diffusion through grain
boundary results in pitting

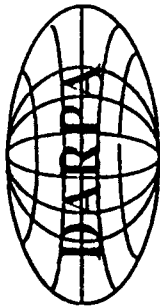


Equilibrium Deposition Diagram



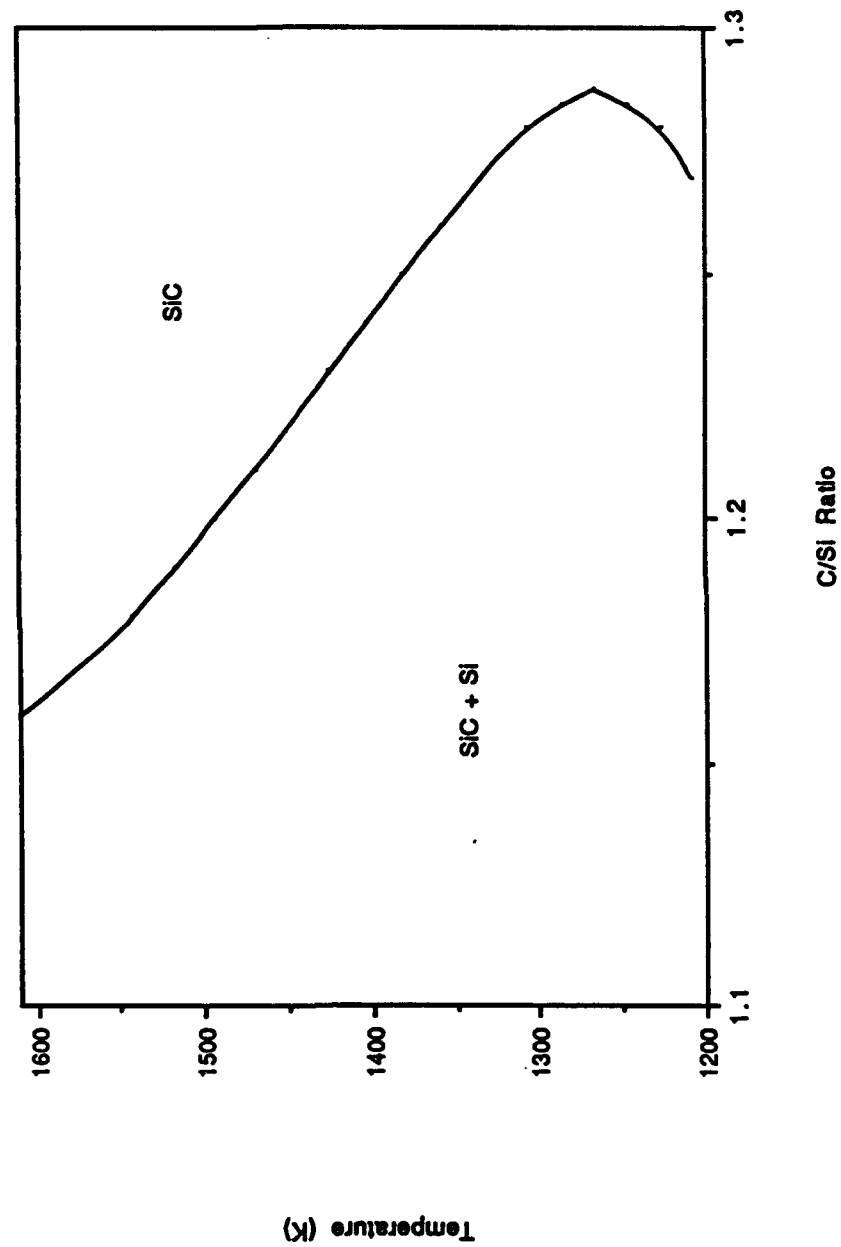
MSE

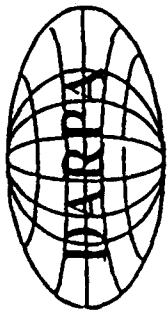
UNIVERSITY OF FLORIDA



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

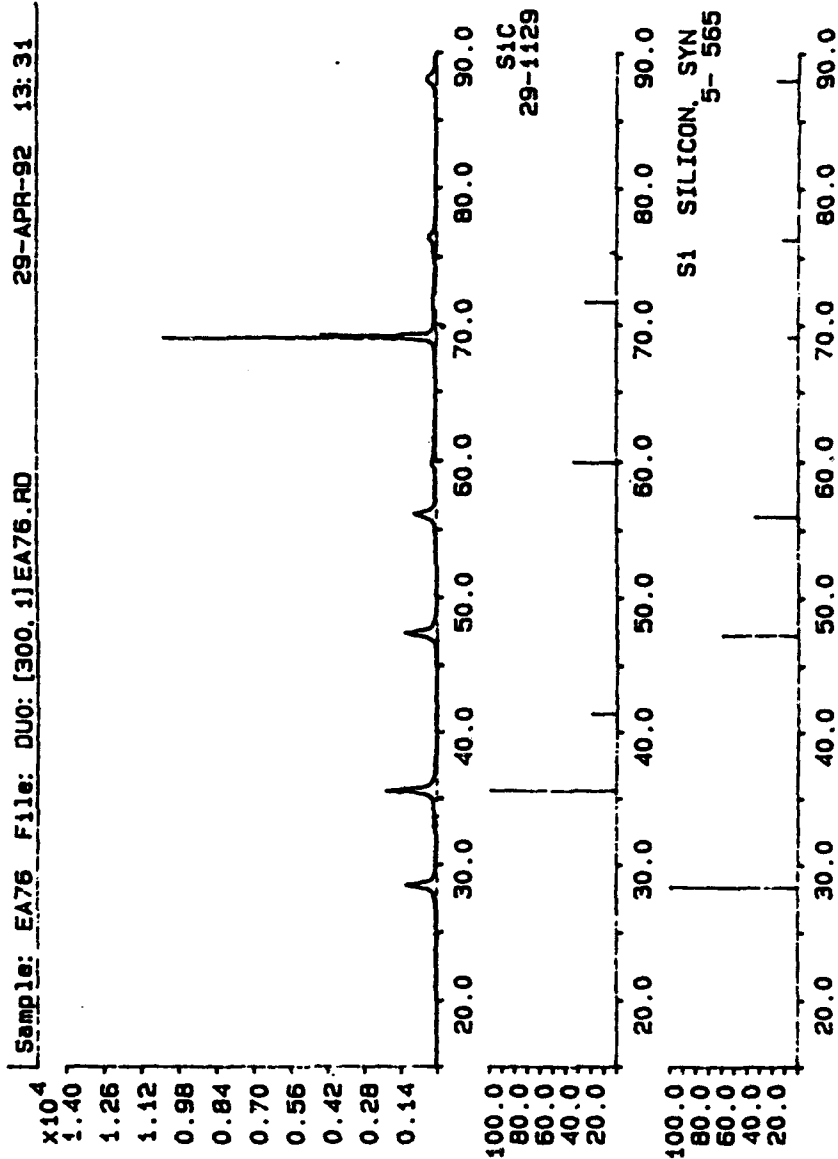
Equilibrium Deposition Diagram





INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

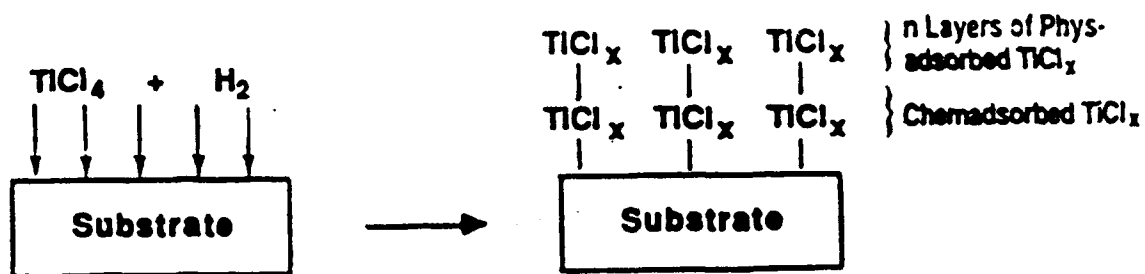
Without Carburization



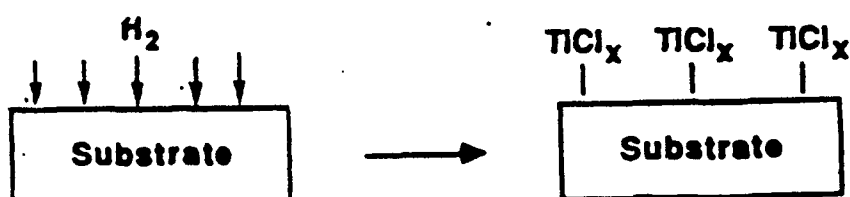
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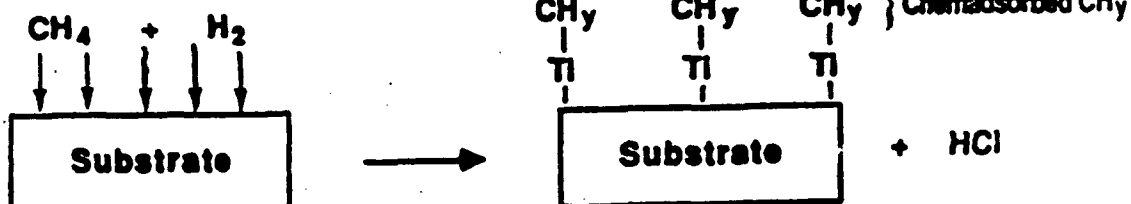
ATOMIC LAYER DEPOSITION (ALD)



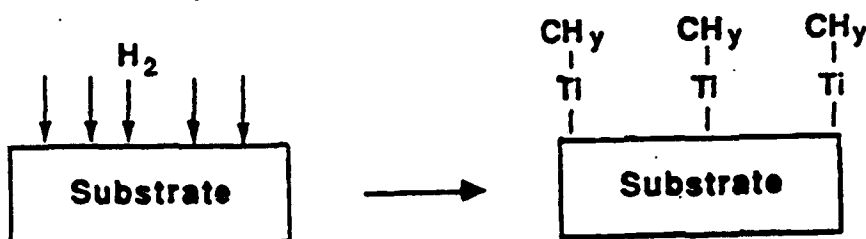
Step 1:
Ti Adsorption



Step 2:
Desorption of
Physadsorbed
 TiCl_x



Step 3:
C Adsorption



Step 4:
Desorption of
Physadsorbed
 CH_y

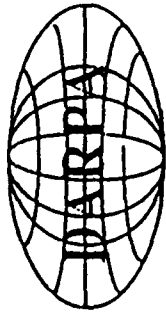
Repeat Steps 1-4



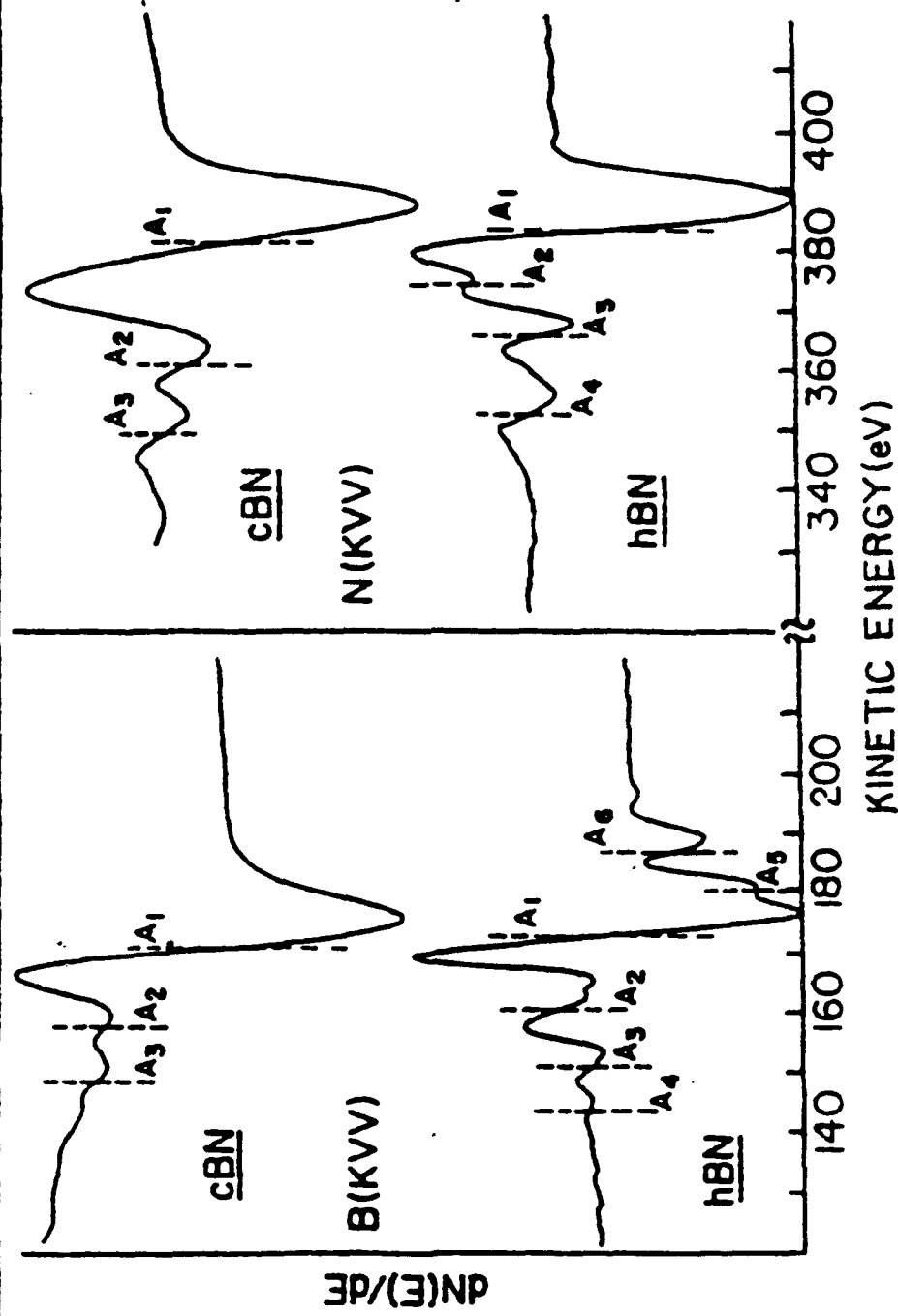
**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

**Cubic Boron Nitride
Properties**

Hardness:	4.7×10^9
Thermal Conductivity:	10 W/cm
Thermal Expansion:	1.5×10^{-6}
B-N Bond Strength:	152 kcal/mol
Lattice Constant	3.61 Å
	3.57 Å (diamond)

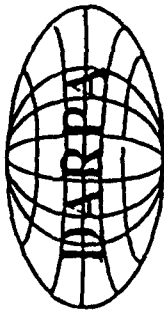


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



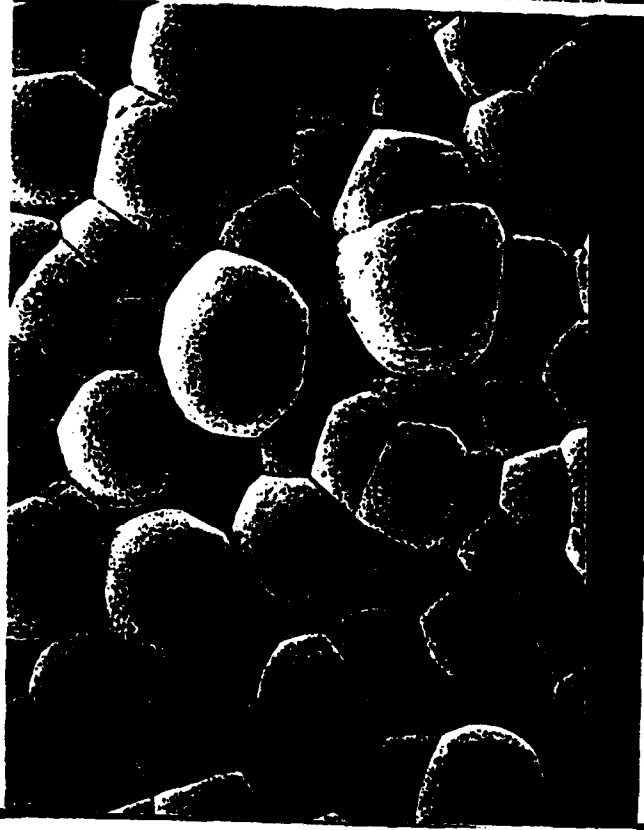
B-KVV and N-KVV Auger spectra of hexagonal and cubic BN.

R. Trehan, Y. Lifshitz, and J.W. Rabalais,
J. Vac. Sci. Technol. A, Vol. 8, No. 6, Nov/Dec 1990



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

CVD BN on Si(100) via BCl_3/NH_3 System



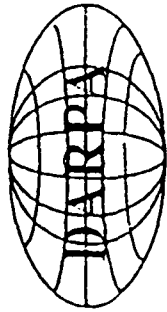
Surface (200 torr, 1000°C)



Cross-section

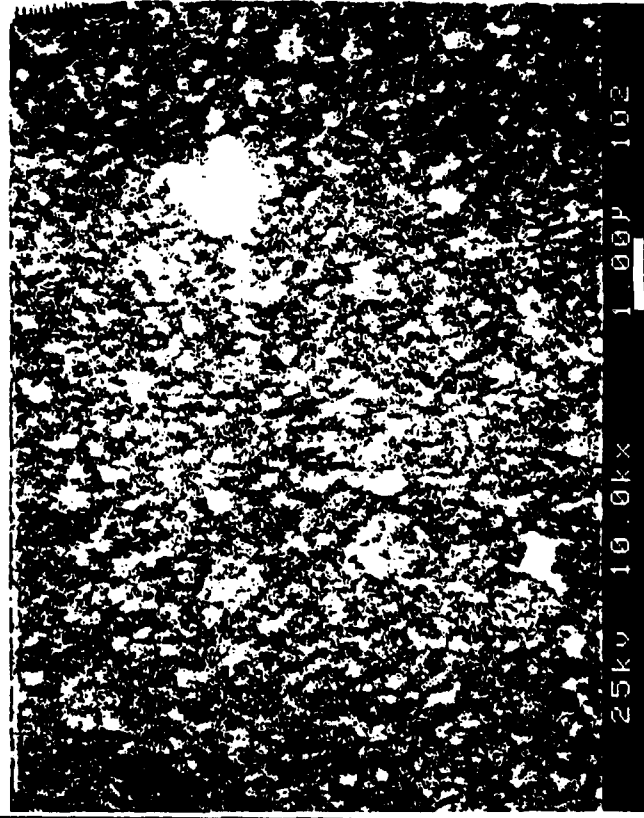
MSIE

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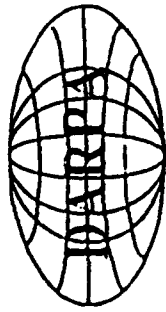


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

CVD BN on Diamond via BCl_3/NH_3 System

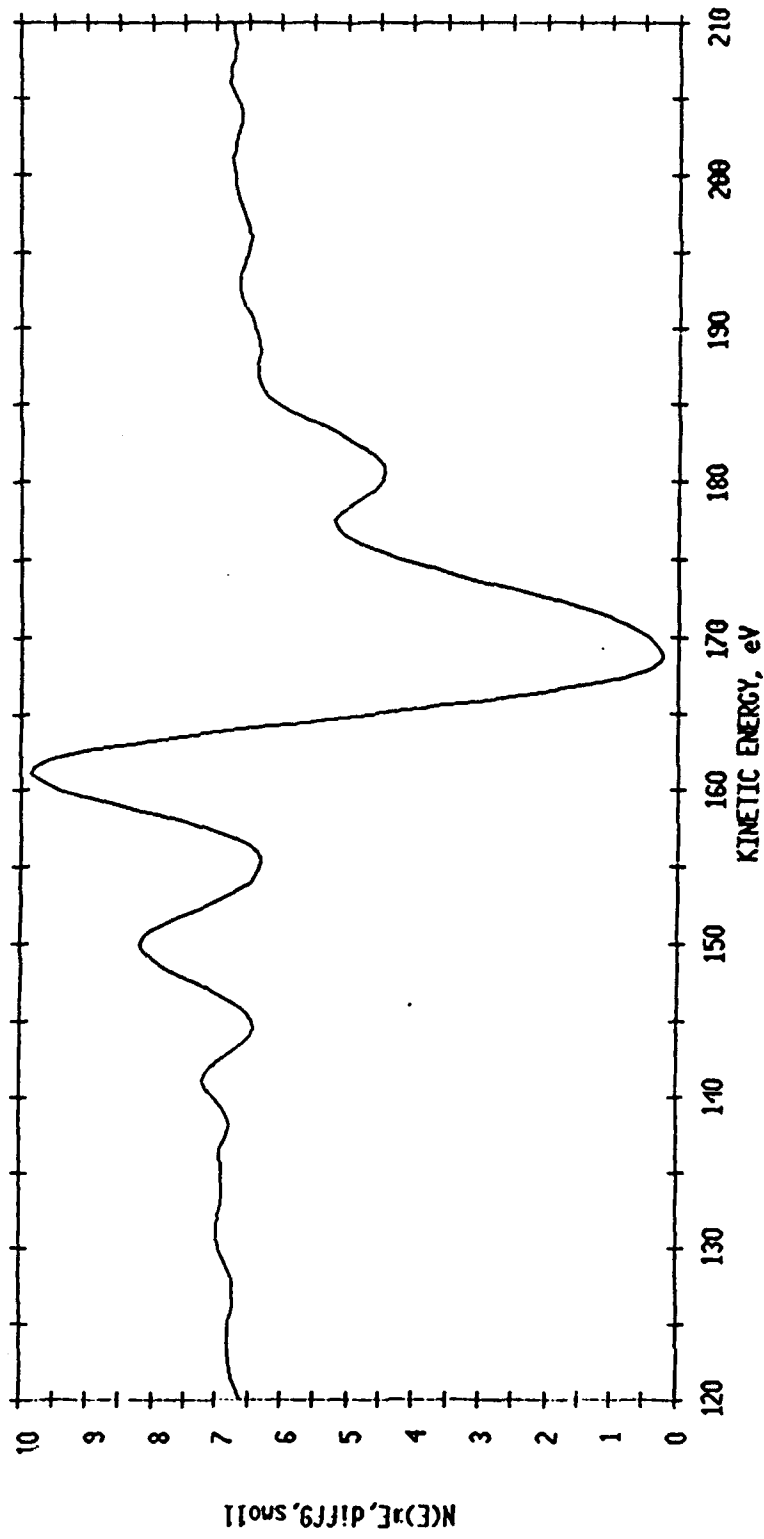


Surface (200 torr, 1000°C)



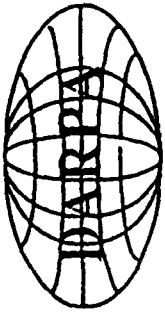
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

B-KVV CVD BN on Diamond(110)



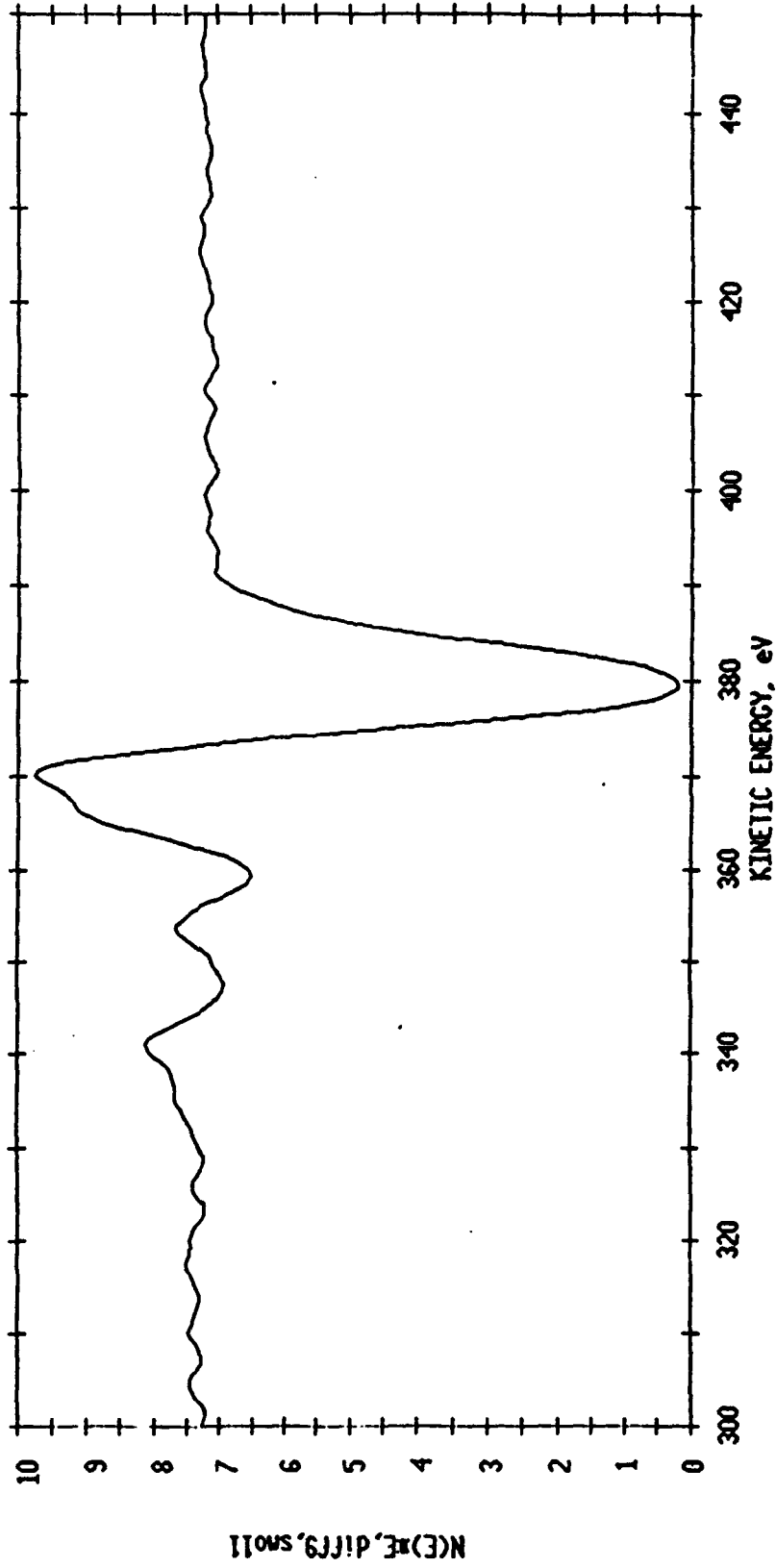
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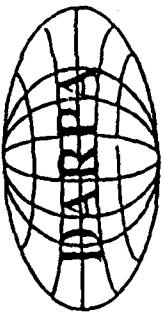
MSIE



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

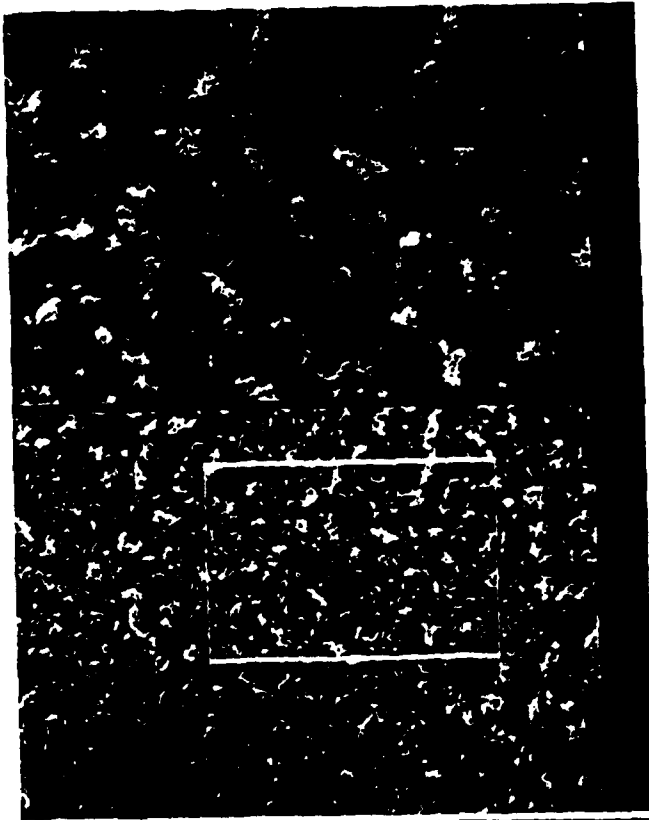
N-KVV CVD BN on Diamond(110)



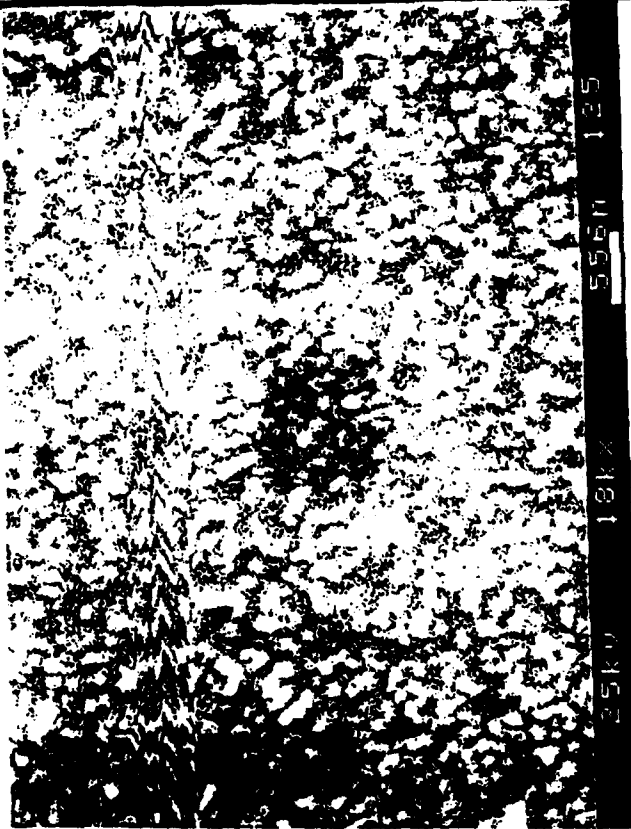


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

ALE BN on Si(100)



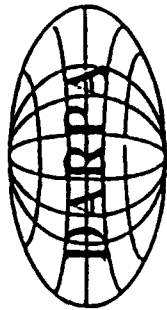
ALE BN on Diamond(110)



Surface (200 torr, 1200°C)

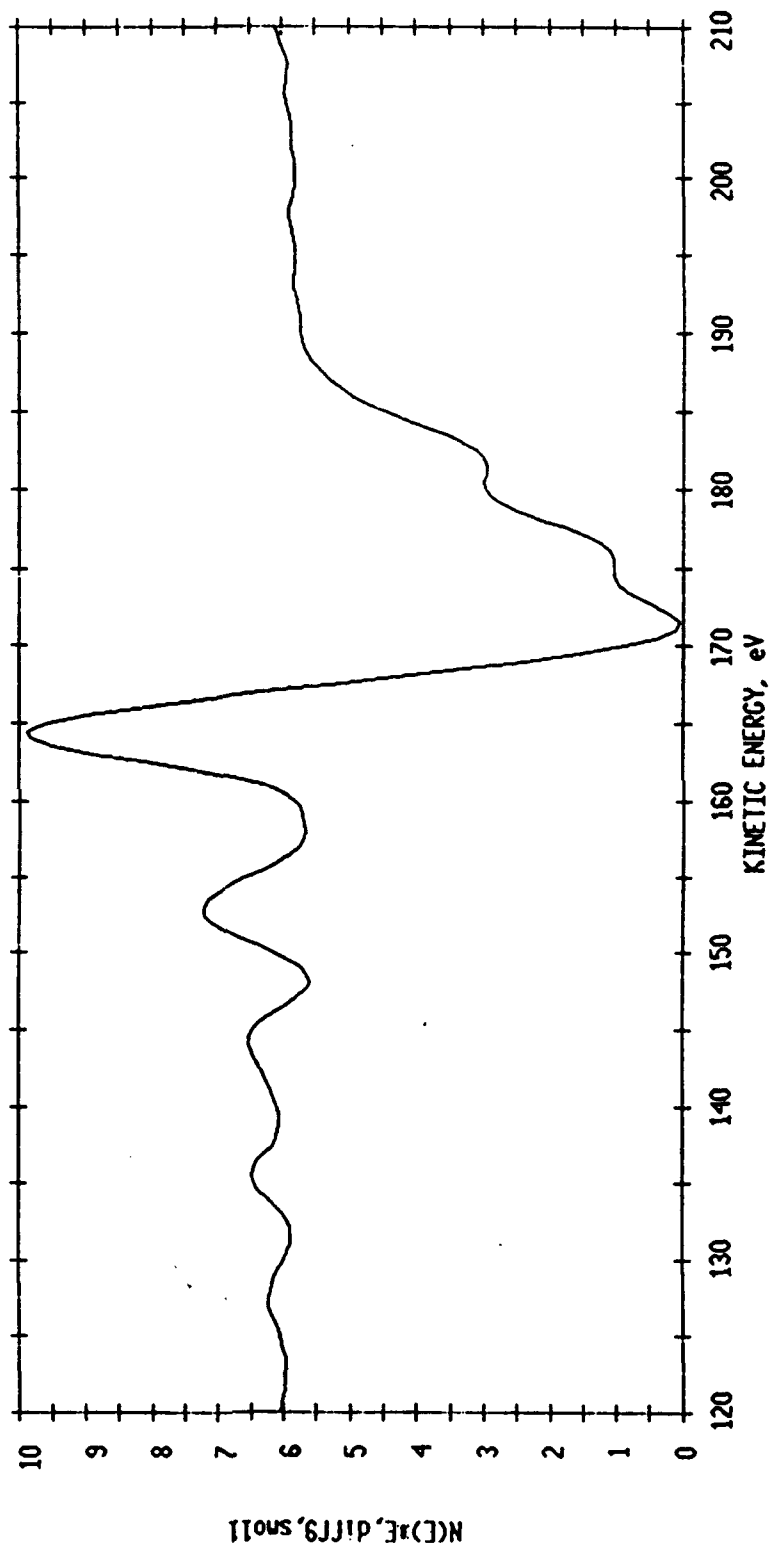
MSIE

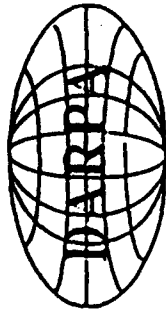
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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

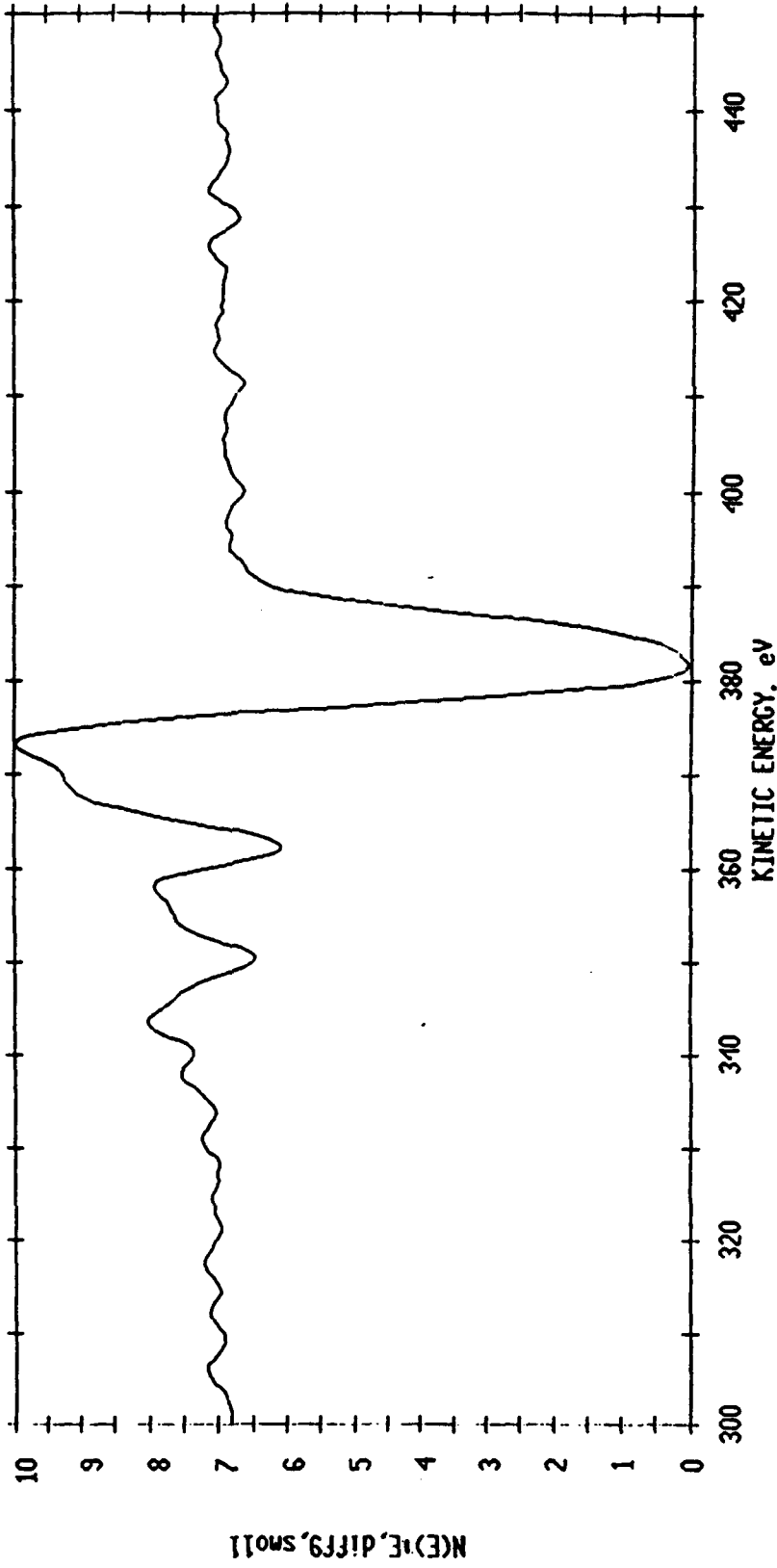
B-KVV ALE BN on Diamond(110)

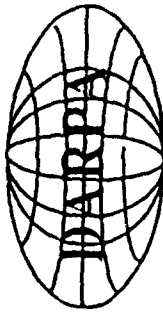




INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

N-KVV ALE BN on Diamond(110)





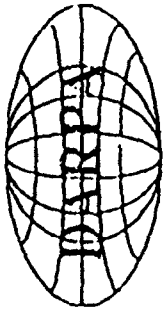
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

TIN FILM GROWN BY ALE ON Nb



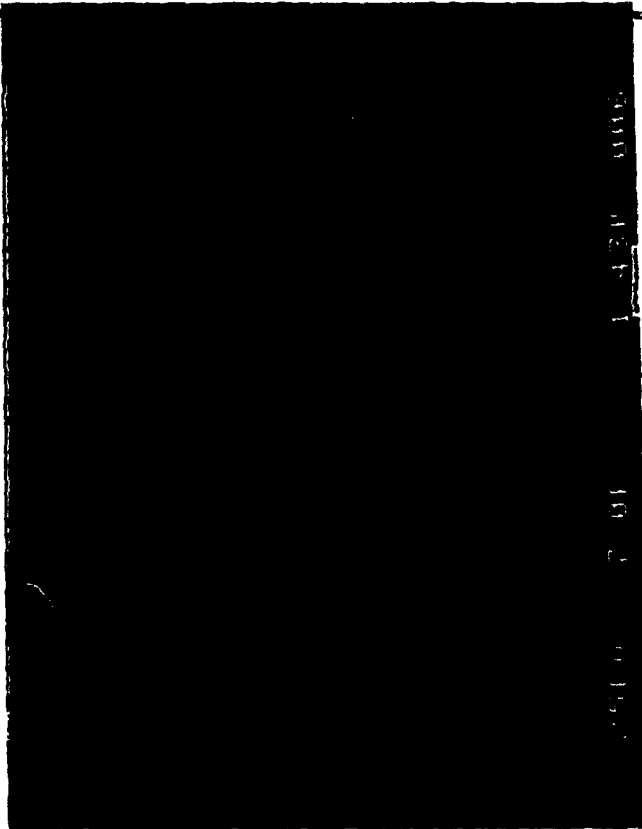
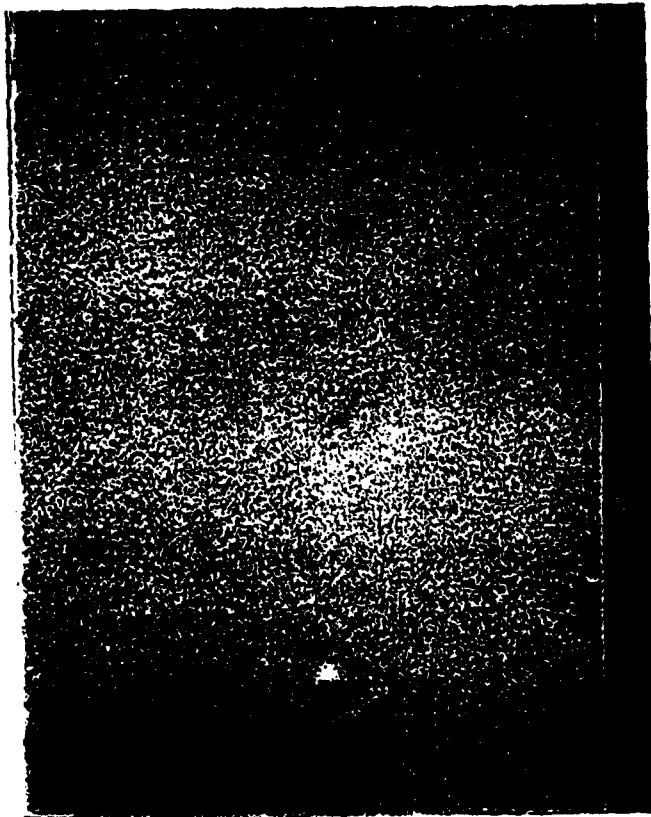
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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Nb SUBSTRATE PRIOR TO ALE

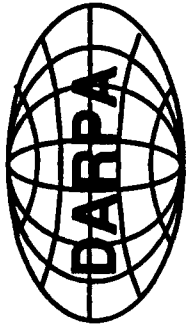


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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

FUTURE PLANS

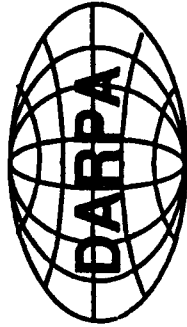
- Study Novel Chemical Vapor Infiltration Schemes
- Promise:
 - Uniform and economical densification of composites with improved mechanical, chemical and thermal properties
- Applications:
 - CVI of fibrous and powder preforms to fabricate ceramic matrix composites
- Studies:
 - Optimize HCl injection process for CVI of Nicalon with refractory carbides
 - Process modelling



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

FUTURE PLANS

- Develop ALD Process
 - Promise: Perfect uniformity, stoichiometry control, interface abruptness
 - Applications: - Uniform coatings for surface modification without mass transfer limitations
 - Growth of heterostructures with defined composition and thickness
 - Studies:
 - Understand influence of deposition parameters for various chemistries: TiC, TiN, BN
 - Investigate microstructure, stoichiometry mechanical properties, mixed crystals
 - Investigate new materials: SiC, TiB₂, ZrC, HfC, HfB

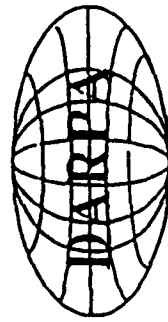


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

FUTURE PLANS

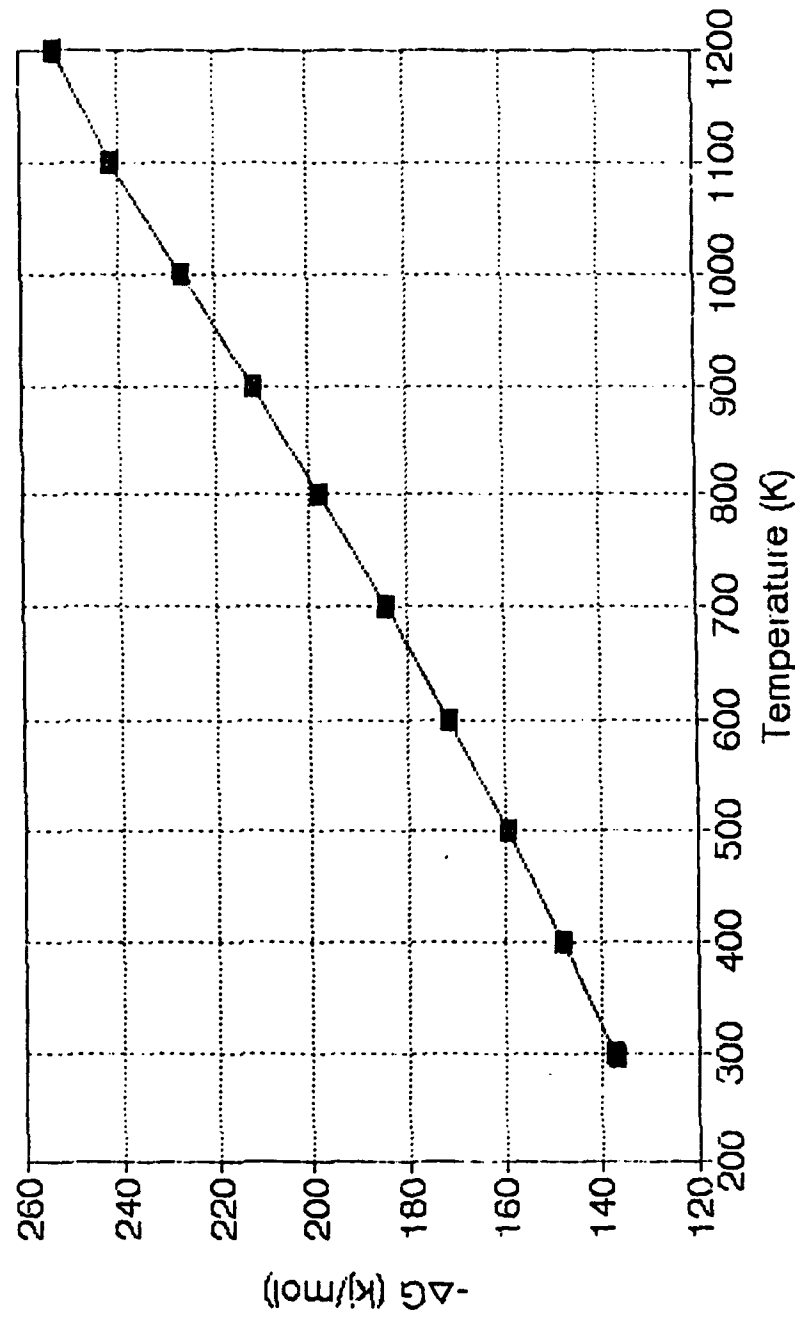
- Investigate CVD of Cubic BN
- Promise: Hard, high temperature and stable coating/particle material
- Studies: N reduction of BP to stabilize the cubic structure

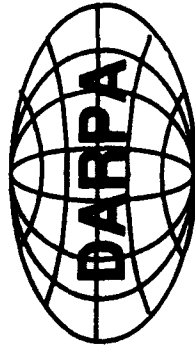
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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

ΔG vs Temperature for the Reaction





INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

INTERMETALLIC MATRIX COMPOSITES

R. Abbaschian and M.J. Kaufman

NOVEL
PROCESSING

MATRIX
DEVELOPMENT

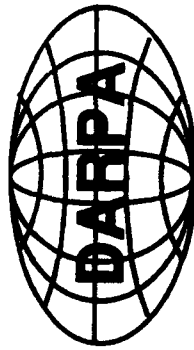
MECHANICAL
PROPERTIES

MICROSTRUCTURAL
CHARACTERIZATION

ENVIRONMENTAL
CONCERNS

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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Personnel

MoSi₂

- £ L. Xiao - Ductile phase toughening, SiC matrix modification - *TMS Best Graduate Student Paper Award - 1992.*
- S. Jayashankar - Silica-free, SiC reinforcements via mechanical alloying
- S. Riddle - Ductile phase toughening with mechanically alloyed powders
- A. Costa e Silva (ONR) - Interface development & characterization
- * Y.S. Kim - Mechanical alloyed vs. commercial purity material, dispersoid effects - *Professor in Korea*
- * J.D. Cotton - Powder processing studies - *Los Alamos National Laboratory*

NiAl

- H. Doty - Hybrid (niobium + SiC) composites, RHC studies
- P. Krishnan (ONR) - Interface development & characterization

NbAl₃

- * L. Lu - RHC and in-situ alumina coatings in Nb-reinforced composites *Technetics, Inc.*
- * A. Gokhale - RHC development & in-situ coating studies - *Post Doc on NASA program*
- * R. Erickson - Matrix development in combination with in-situ coating - *Alcoa Technical Center*

TaTiAl₂

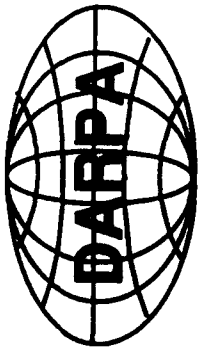
- I. Hwang - Hybrid (Nb + Al₂O₃) composites, in-situ alumina coatings
- * M. Weaver - Matrix development & phase equilibria studies - *PhD studies on NASA program*

£ - Recognition

* - Formerly associated with program

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INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

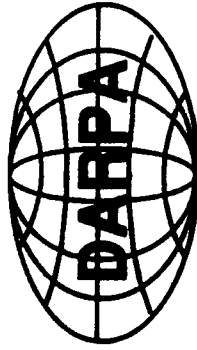
Need for Intermetallics & Intermetallic Matrix Composites

- ***Structural Materials for Next-Generation Aircraft Engines***

Higher temperature capabilities
Lower densities (higher thrust-to-weight ratios)
Environmental stability
Processability

➔ ***Ceramics and Intermetallics***

- ***EXAMPLE: Use of NiAl as high pressure turbine blades would reduce the turbine rotor weight (blades and disk) by up to 40% due to lower centrifugal stresses. Also lower tendency for hot spots due to higher thermal conductivity. (Source -- R. Darolia, et al. @ GE)***



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

*Characteristics of NiAl**

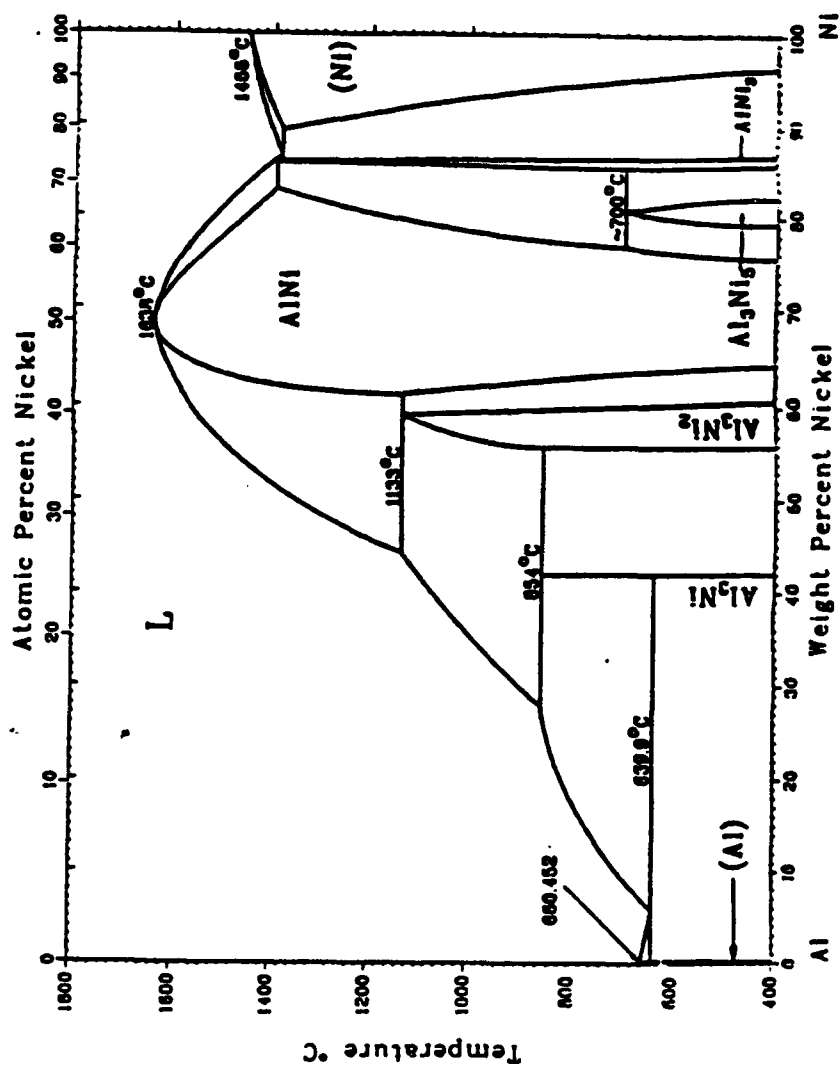
Advantages

- Density $\sim 2/3$ that of state-of-the-art nickel base superalloys
- Thermal conductivity 4 - 8X that of nickel base superalloys
- Excellent oxidation resistance
- Simple ordered bcc-like (CsCl) structure
- Lower ductile-to-brittle transition temperature (DBTT) than many other intermetallic compounds
- Higher melting temperature ($\sim 300^\circ\text{C}$) than current superalloys
- Wider solubility range than many other compounds (MoSi_2 , NbAl_3)

Disadvantages

- Low ductility and fracture toughness below DBTT
- Low strength at temperatures above the DBTT

*Source: Darolia, et al. at GE Aircraft Engine Division





INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

*Approaches for Enhancing
the Mechanical Properties of Brittle Intermetallics*

Low Temperature Properties

- Increase # of active deformation mechanisms by alloying/processing.
- Introduce second phases by alloying or compositing.

High Temperature Properties

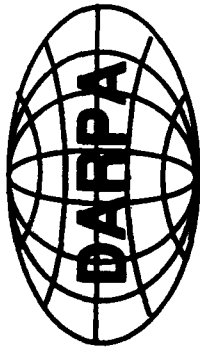
- Increase strength by appropriate alloying and processing.
- Introduce second phases by alloying or compositing.

Problem

- Difficult to enhance both low and high temperature properties of a particular compound by alloying/processing.

Possible Solutions

- Use alloying/processing to effect one property and artificially composite to effect the other.
- Use hybrid composite approaches.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Objectives and Strategy

Overall Objectives

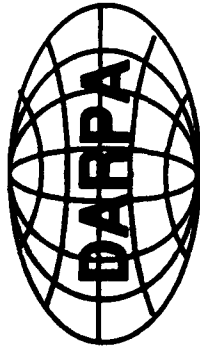
Synthesize intermetallic matrix composites with high fracture toughnesses at ambient temperatures and high strength and creep resistance at elevated temperatures.

Strategy

Use ductile refractory filaments to improve room temperature fracture toughness and ceramic fibers or matrix modification to improve the high temperature properties.

Where possible, select reinforcements which are compatible both chemically and mechanically (similar CTE's). If not available, use appropriate interface coatings as diffusion barriers or compliant layers.

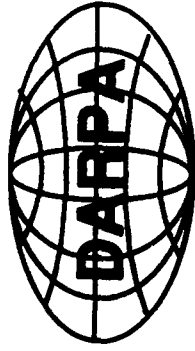
Explore novel processing routes to improve microstructural and compositional control, increase process efficiency, minimize contamination, and control reinforcement alignment.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Areas of Focus

- **Novel Processing:**
 - Reactive Hot Compaction
 - In-situ* Displacement Reactions
 - In-situ* Coatings
 - Other Coating Schemes (sol-gel, PVD, CVD)
 - Multiple Reinforcements
- **Matrix Development:**
 - Alloying Effects
 - Phase Equilibria and Transformations
 - Microstructural Evolution
 - Thermal Stability
 - Second Phase Toughening
 - Deformation Characteristics
- **Characterization:**
 - Mechanical Properties (vs. Temperature)
 - Structure/Property Relationships
 - Environmental Effects



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Reactive Hot Compaction

Impetus

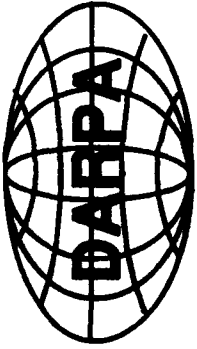
- Simple application of temperature + pressure
- Uses transient liquid phase -- easier densification
- High density compacts are easily achieved
- Lower processing temperatures required - less fiber degradation)
- Can control reaction rates to some extent
- Can combine with in-situ compositing schemes
- Cost effective

Important Parameters

- Temperature, pressure and time
- Heating rate
- Initial stoichiometry and powder size(s) and distribution (mixing)
- % elemental vs. prealloyed powders (for reaction control)

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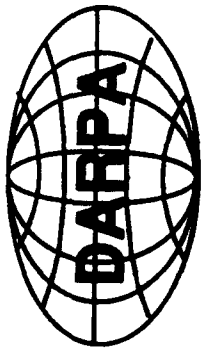
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**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

RHC of Aluminides

- Intermetallic formed from elemental powders
- Highly exothermic reaction
- Slow controlled heating → Al melts first
- Reaction rate depends on rate at which ΔH_{form} can be dissipated
- Application of pressure fills pores
- Time at T & P to densify and homogenize



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

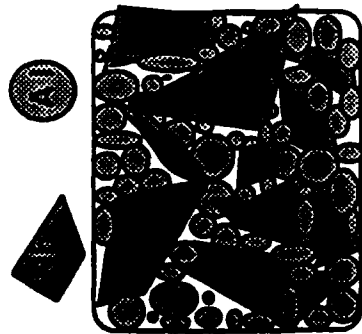
(1) Mix Nb and Al Powders in desired stoichiometry

(2) Produce green compact

(3) Hot press in BN lined graphite die

(4) During hot pressing, apply pressure
during reaction propagation (~ after 15 min at 1350°C)

RHC Processing Sequence



Green Compact



T > 660°C



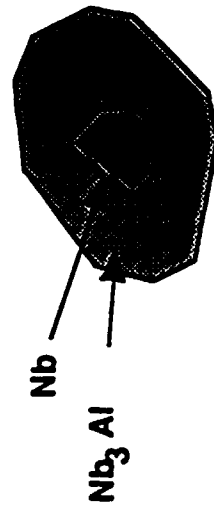
T > 1000°C



Densification of
NbAl₃ After
Pressurization

*Effect of Powder Particle Size
on the Composition of Second
(or multi) phase particles*

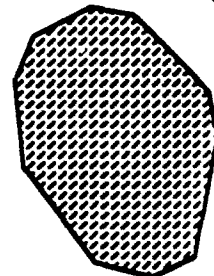
Nb < 44 μm
Al 20 μm
(average)



Nb

Nb₃Al

Nb < 37 μm
Al 6 μm
(average)

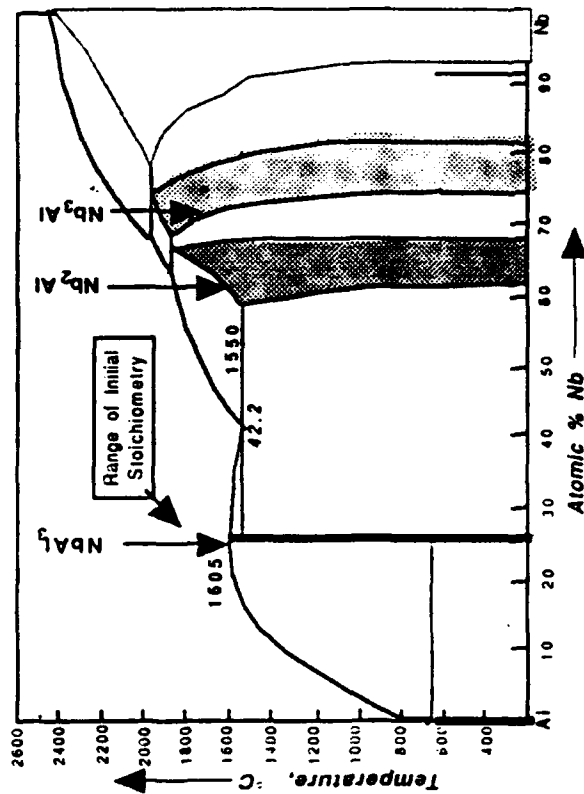


Nb₂Al

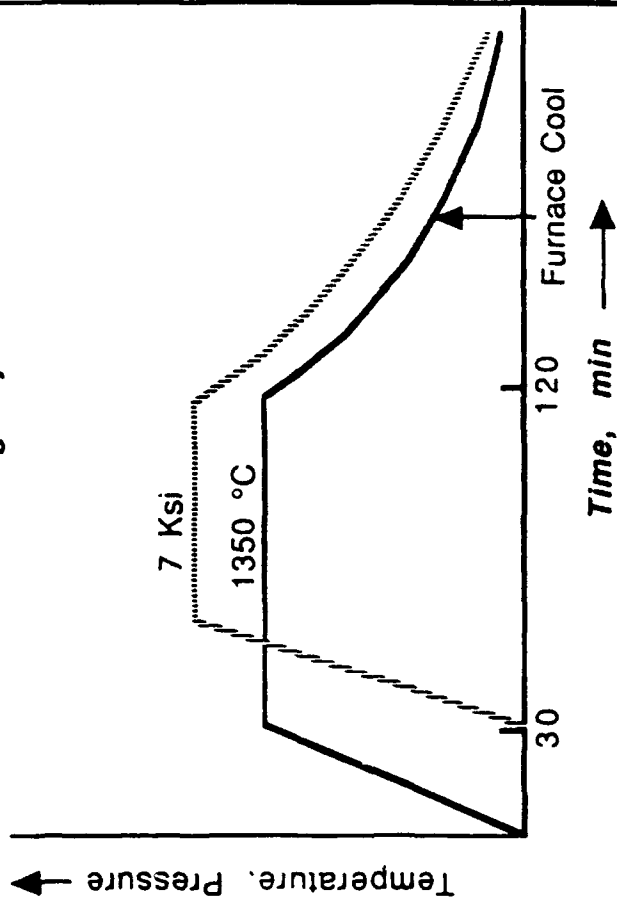
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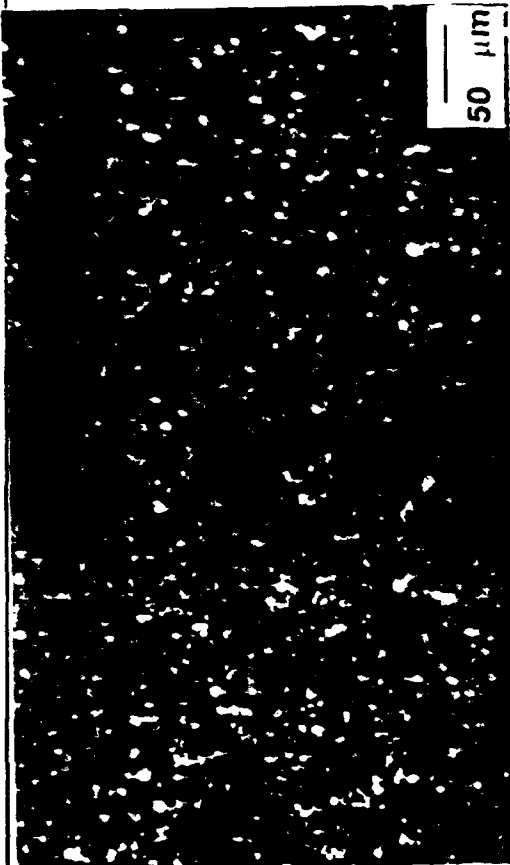
The Nb-Al System



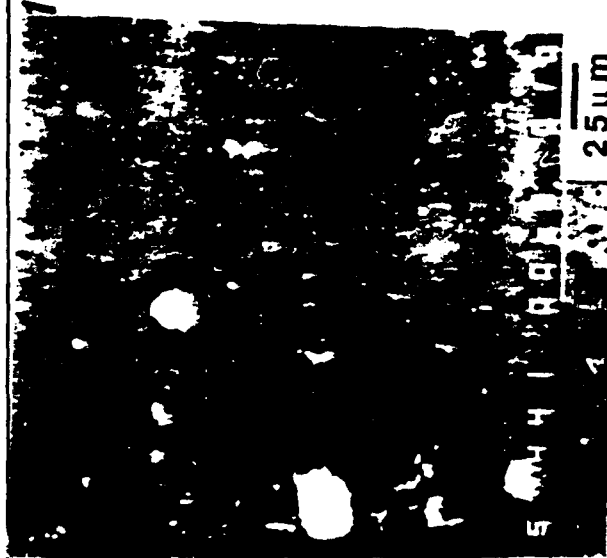
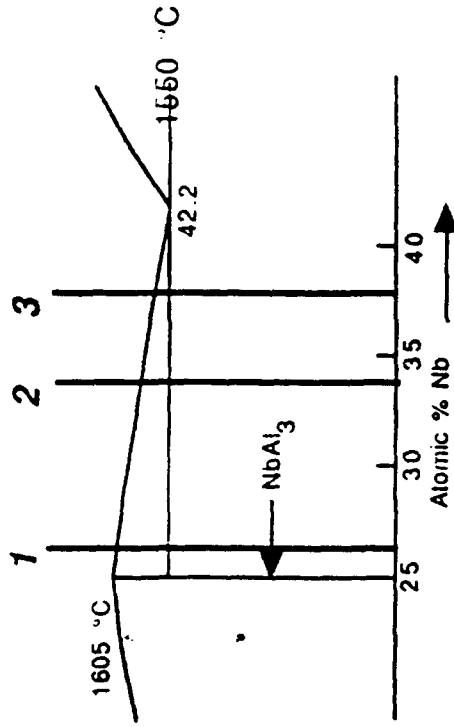
Processing Cycle



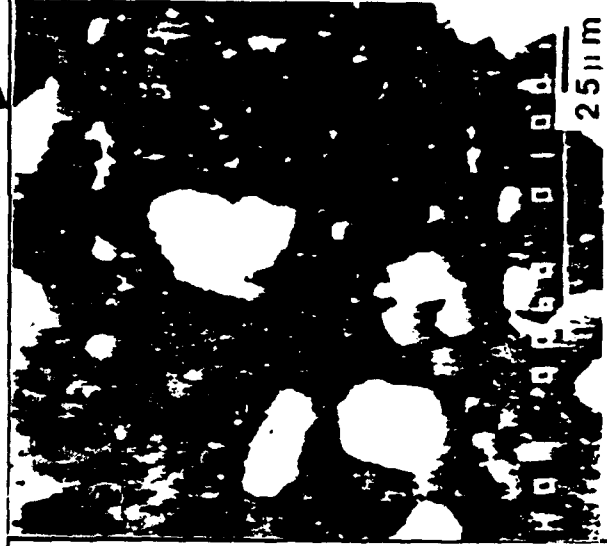
RHC Processed NbAl₃
Volume Fraction
of Porosity < 2%



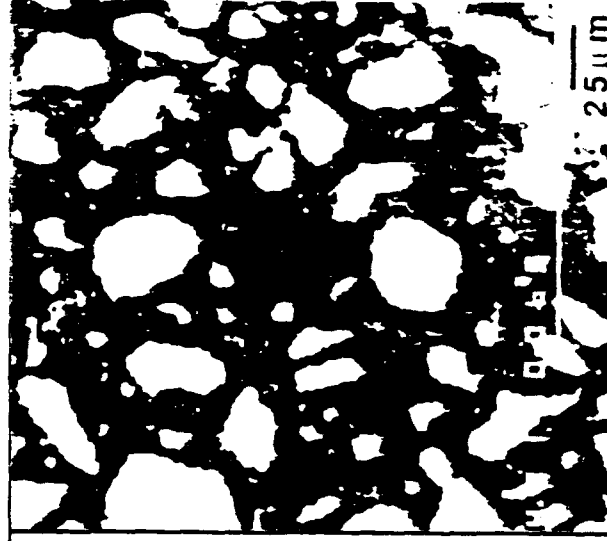
Green Compact Compositions



Volume Fraction 6.9%
Mean Spacing 383.8 μm



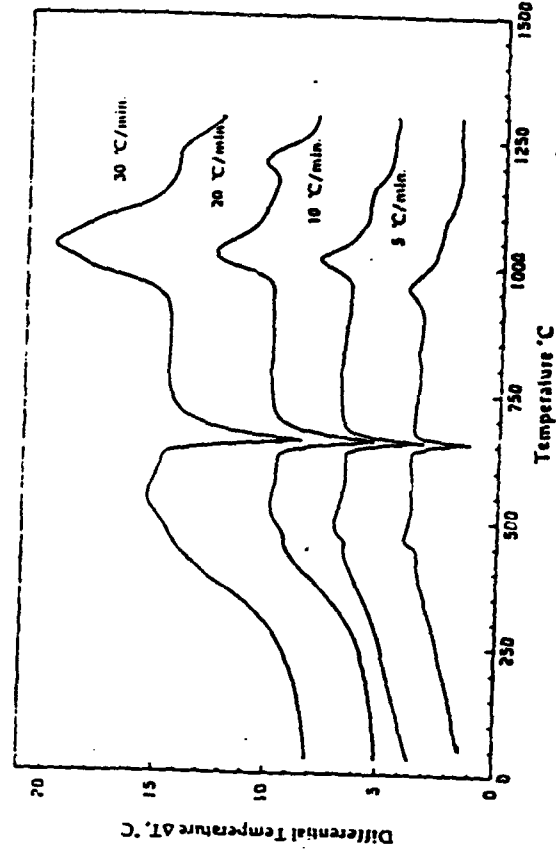
Volume Fraction 14.6%
Mean Spacing 142.4 μm

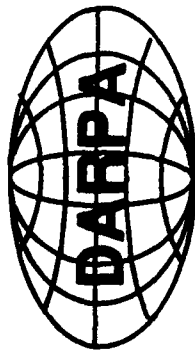


Volume Fraction 27.68%
Mean Spacing 75.1 μm

Effect of Heating Rate

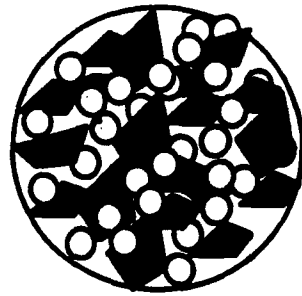
DTA profile of Nb and Al powder samples (NbAl₃ composition)
performed at four heating rates





INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

T < 600 C



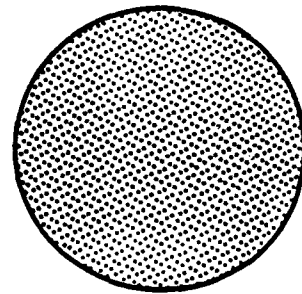
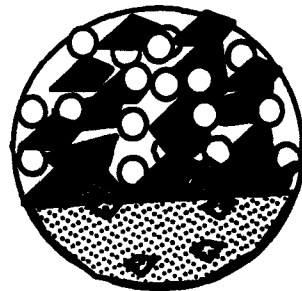
○ Al



■ Ni

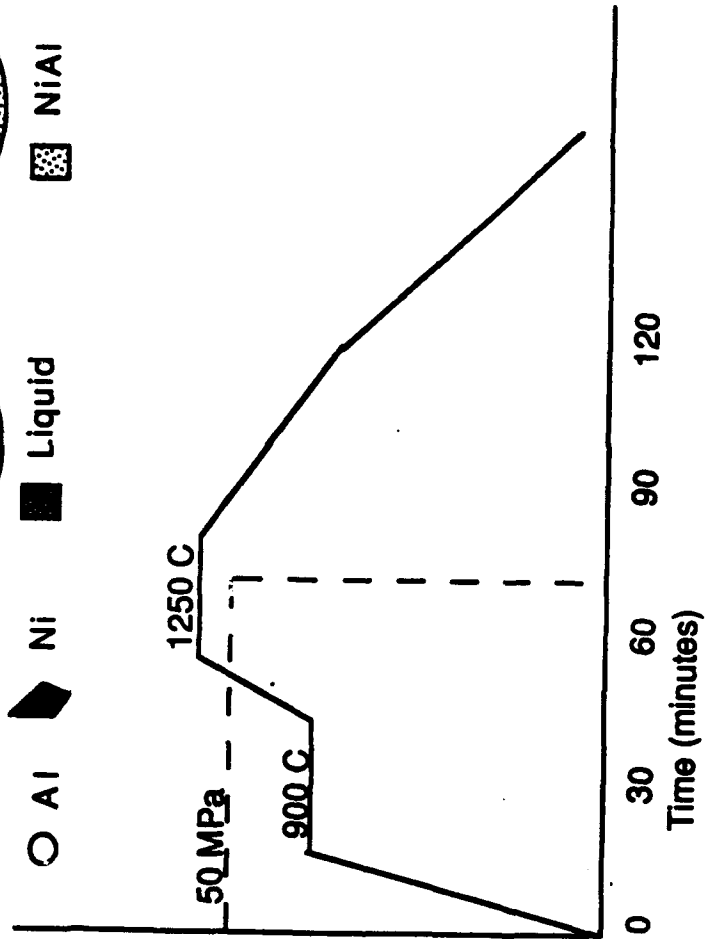
■ Liquid

T = 600 C



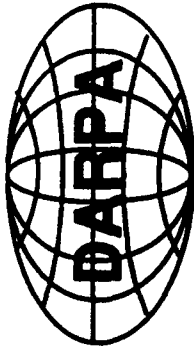
■ NiAl

Temperature/Ram Pressure



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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Differential Thermal Analysis

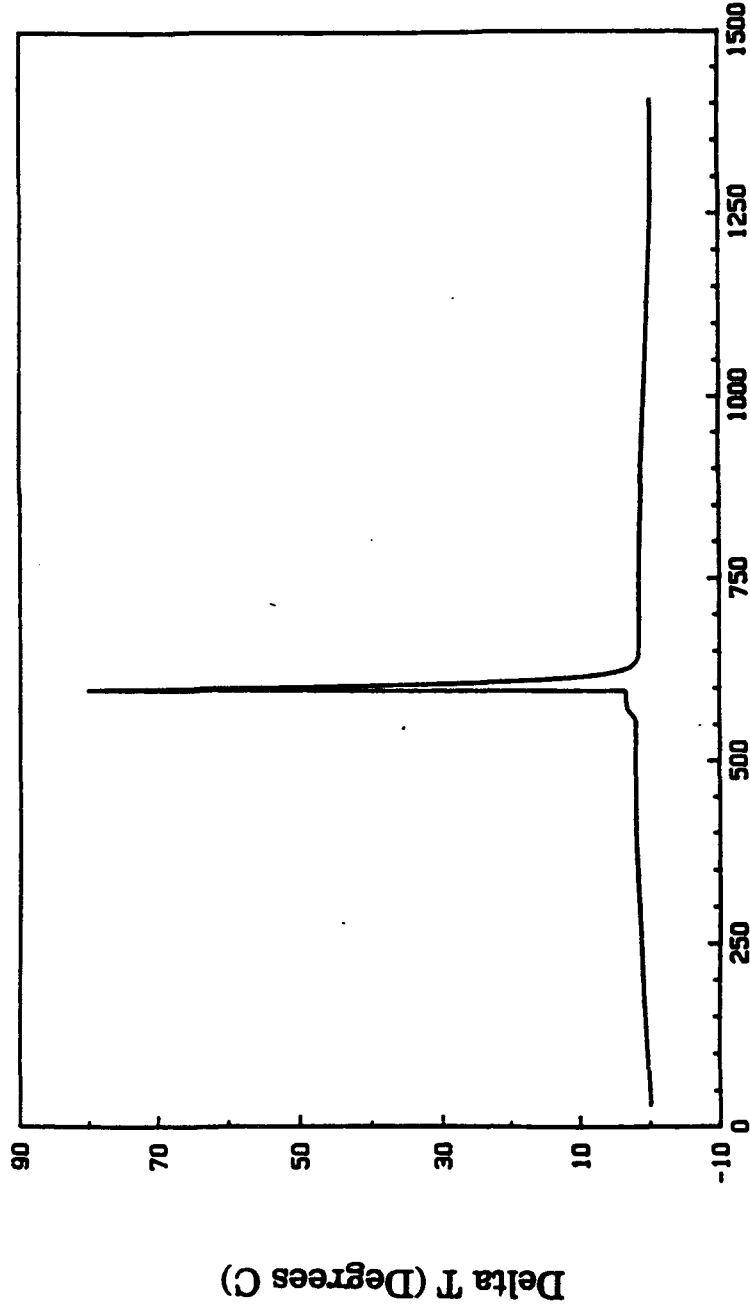
Sample : NiAl

Reference : Al₂O₃ CR75

Heating Rate : 10 Degrees C per minute

Atmosphere : Argon

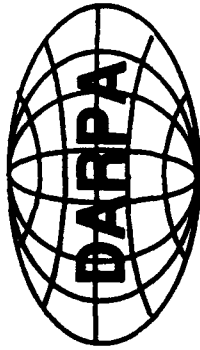
Peak Delta T = 87 at 590 Degrees C



Temperature (Degrees C)

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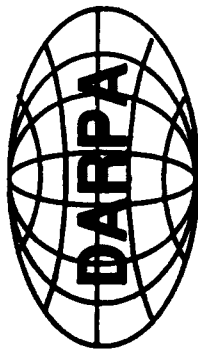


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Matrix-Reinforcement Considerations

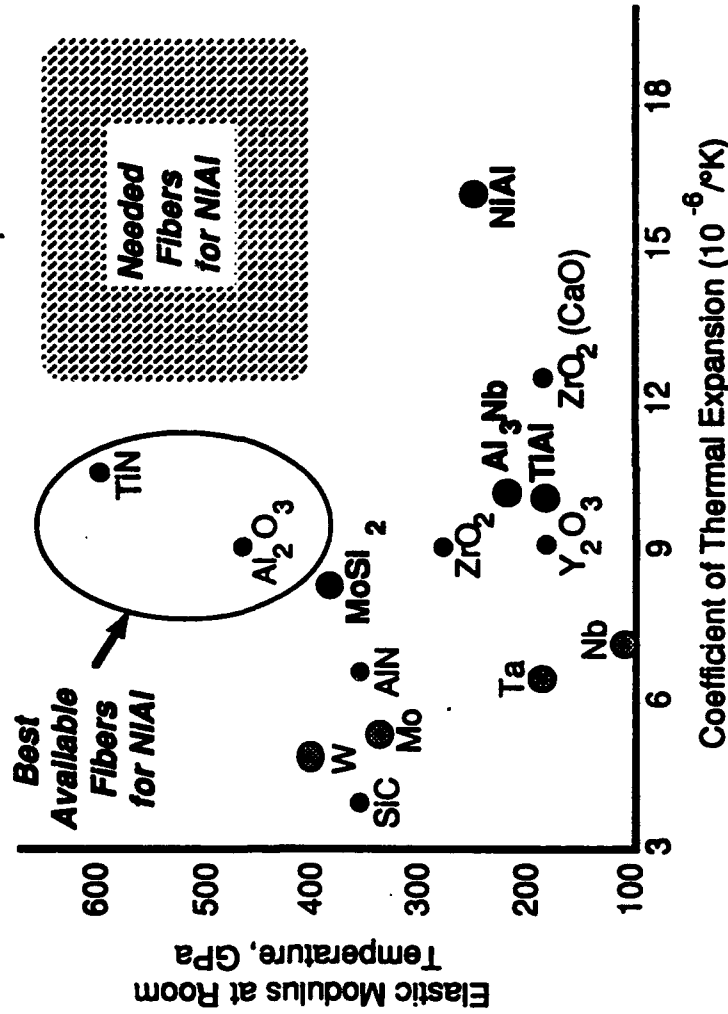
- Mechanical Properties of Matrix and Potential Reinforcements
- Microstructural Stability (Anticipated Reactions)
- Mechanical Stability (CTE & Modulus Mismatch)
- Interface Properties (Weak vs. Strong; Nature of Bonding)
- Effect of Reinforcement on Environmental Stability (e.g., Refractory Metal Toughening)

Note: For most matrix/reinforcement combinations, there are problems with one or more of the above issues and interface modifications are required!! Unfortunately, it is difficult to solve all problems with a single interface.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Fiber Selection



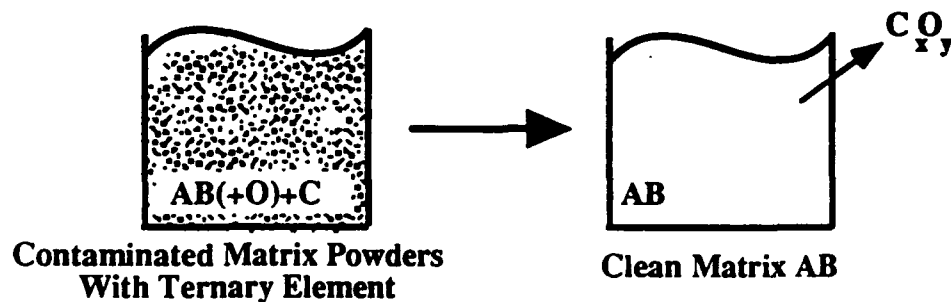
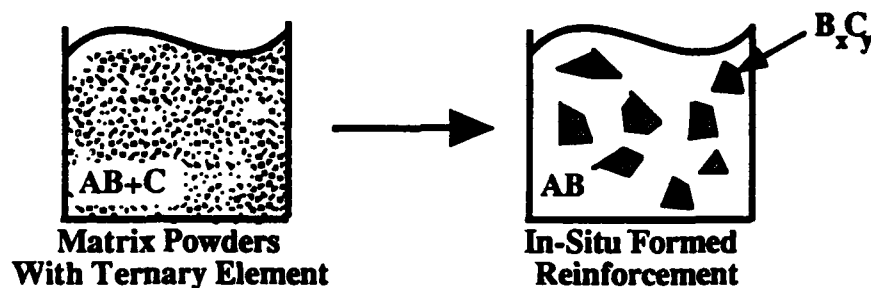
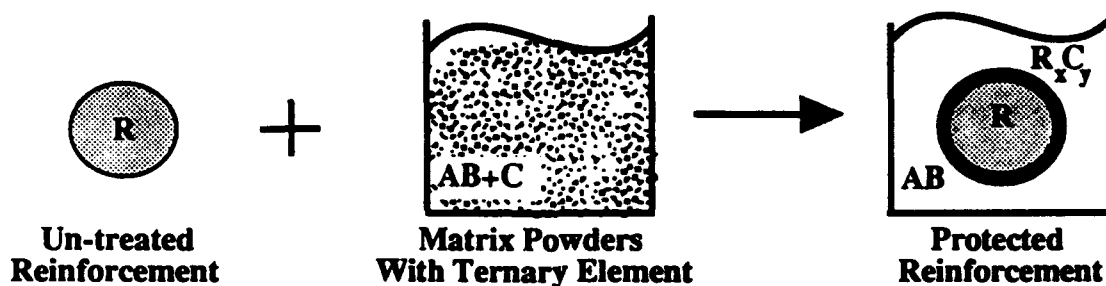
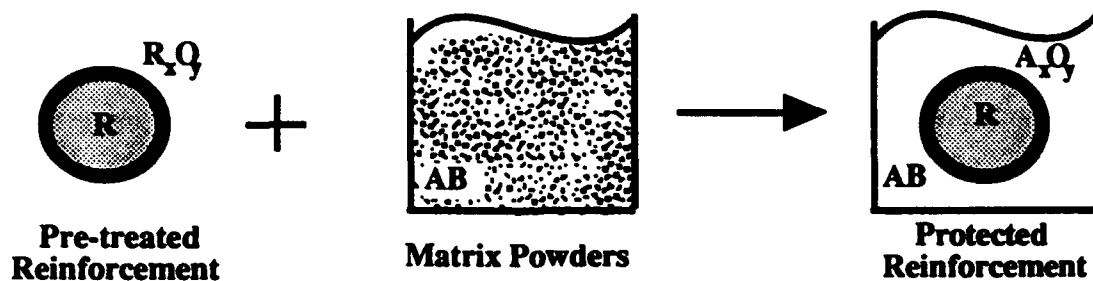


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

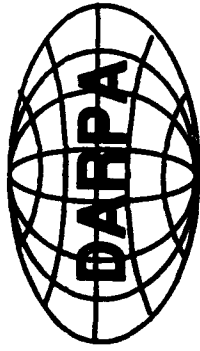
Impetus for In-Situ Reactions

- Traditional coating schemes (sol-gel, CVD, PVD, etc.) tend to be expensive and unreliable.
- Need for simple, reliable processing schemes that are cost effective.
- In-situ reactions offer numerous advantages over traditional schemes.
 1. *Form dispersoid or reinforcements in-situ with uniform distributions.*
 2. *Form uniform interface coatings readily in some systems.*
 3. *Product phases are usually more compatible from a thermodynamics standpoint.*

Typical Reaction Scenarios



Combinations of the Above



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Application to Intermetallic Matrix Composites

- ***Microstructural Stability***

Thermodynamic & Kinetic Considerations
(Diffusion Couples, Equilibrium Calculations)

- ***Mechanical Stability***

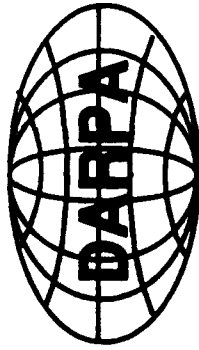
CTE Mismatch Considerations
(Compliant Layers, Matrix CTE Modification)

- ***Optimum Interface Properties***

Weak Interface for Toughening
Strong Interface for Strengthening
Reliable Measurement Techniques (Push-out, Pull-out, etc.)

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ULTRA-HIGH TEMPERATURE APPLICATIONS

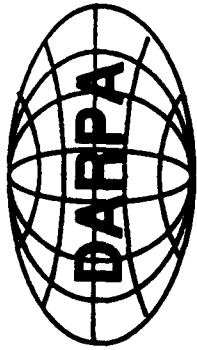
NbAl₃ Composites

Ductile phase toughening

- RHC studies
- *In-situ* interface coatings
- Mechanical properties

Matrix development

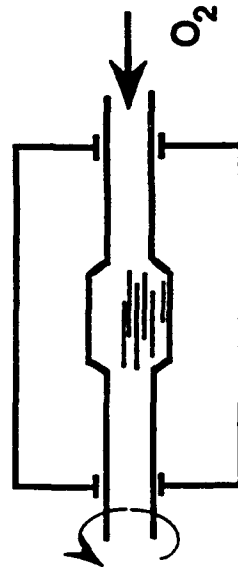
- Alloying to effect the $\text{DO}_{22} \rightarrow \text{L1}_2$ transformation
- Alloying to enhance slip and/or twinning
- Second phase effects
- Combination of enhanced matrices with *in-situ* coating scheme



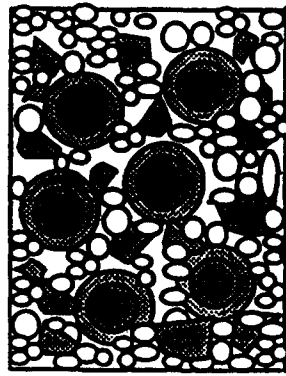
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Processing Sequence for Fabrication of In-Situ Alumina Coated
Nb/NbAl₃ Composites : Coupling of Pre-Oxidation and RHC

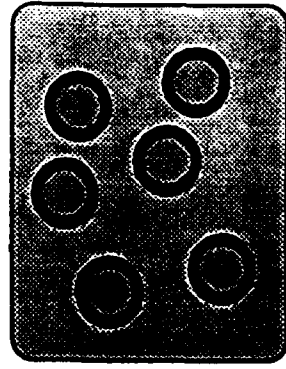
Pre-surface-oxidation
of Nb filaments



Green compaction of
mixture of Nb, Al
powder and the
oxidized Nb filaments



Final product of
in-situ coated
Nb/NbAl₃ composite



○ Al ▽ Nb

■ NbAl₃

○ Oxidized Nb

○ Alumina coated Nb

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Nb Filaments Without Diffusion Barrier

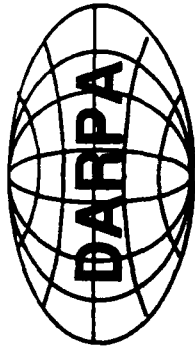


Absence of Diffusion Barrier Results in
Embrittlement of Nb Filaments by Al and an
Extensive Interaction Zone

Nb Filaments With Diffusion Barrier



Preoxidized Nb Filaments Produce an
"In-Situ" Alumina Diffusion Barrier During
RHC. Note the Absence of Nb Embrittlement
and Interfacial Reaction Zone



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

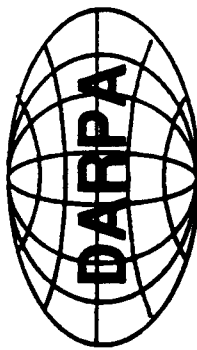
THERMAL STABILITY AT 1200°C. ANNEALED FOR 100 HOURS

Uncoated Nb Filament



"In-Situ" Coated Nb Filament





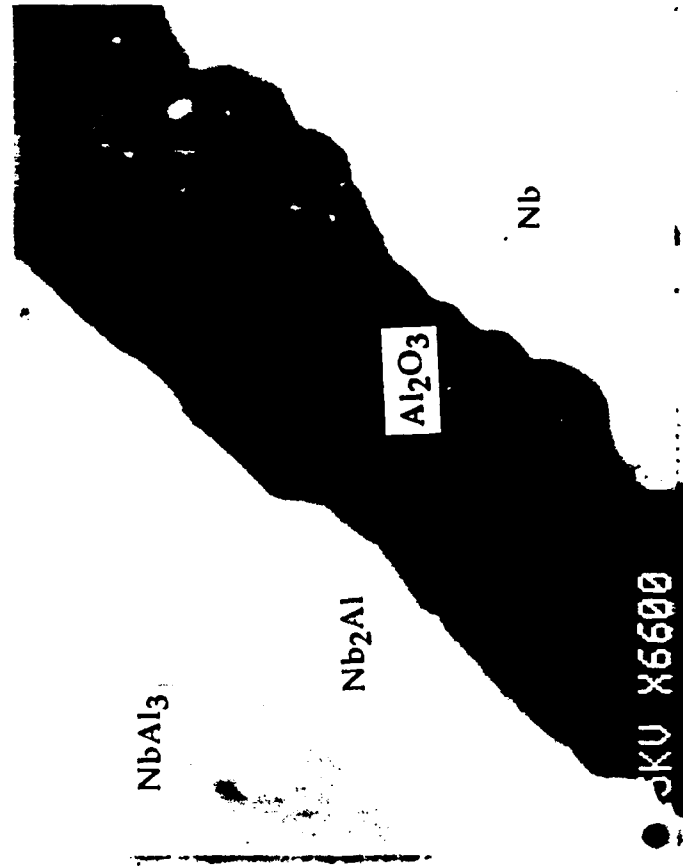
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



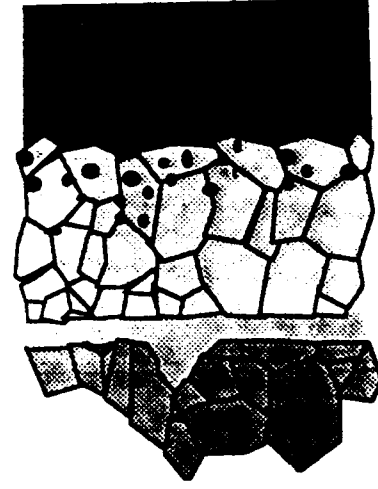
- (A) General view of the debonded interface
- (B) Surface geometry of Nb filament corresponding to the area labeled "a" in (A)
- (C) Surface geometry of in-situ formed alumina layer corresponding to the area labeled "b" in (A), showing typical intergranular fracture surface

Microstructure of In-Situ Formed Alumina Interfacial Layer

SEM Micrograph.



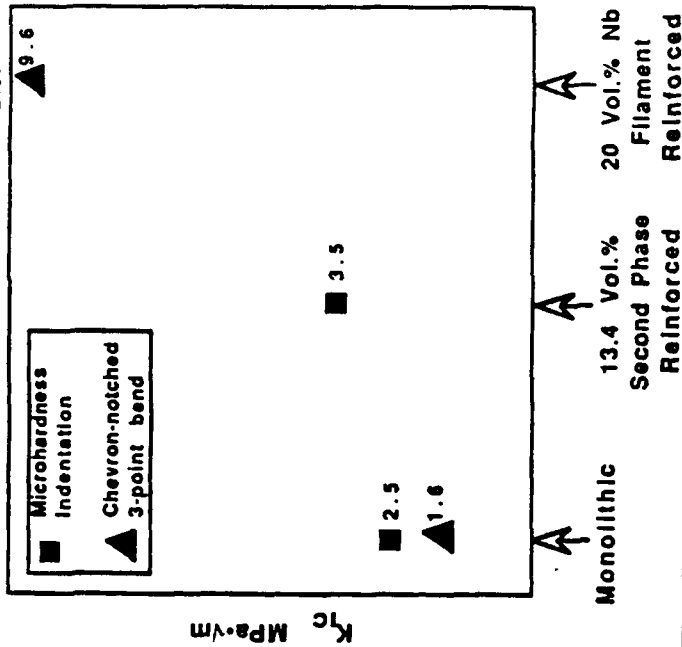
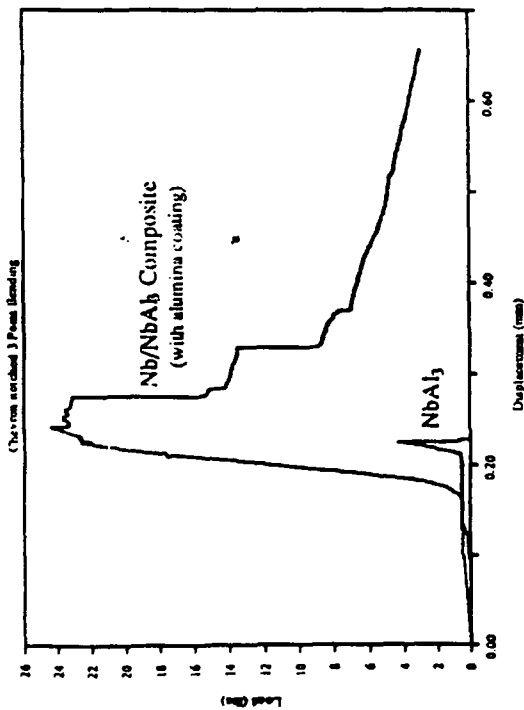
TEM Micrograph



Key	NbAl ₃	Nb ₂ Al	α-Al ₂ O ₃	Nb

Toughening Effect of Nb Filament Reinforcements With Alumina Diffusion Barrier Produced "In-Situ"

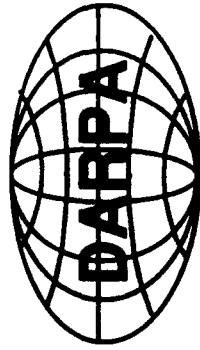
FRACTURE TOUGHNESS TEST



Toughening
Due to
Interfacial
Debonding



Toughening
Due to
Filament
Pull-Out

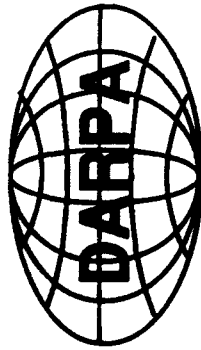


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

NbAl₃ -- Matrix Development

Highlights

- Additions of Fe, Ni, Ti, V, Cu, Cr and Pd were investigated for possible "ductilizing" effects. In many cases, the segregation during solidification is severe.
- Only marginal improvements in toughness are possible by alloying to form second phases.
- Lamellar eutectics were observed in the Al-Nb-V and Al-Nb-Cr systems.
- Corrections were proposed for the ternary Al-Nb-V isotherm.
- Formation of alumina on niobium filaments using prealloyed NbAl₃ powders was successful.
- Alloying to promote the $DO_{22} \rightarrow L1_2$ transformation is not possible for this compound.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

NiAl-Matrix Composites

RHC studies

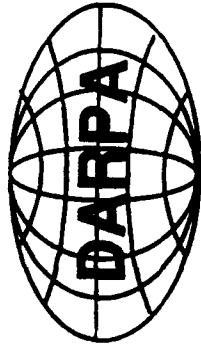
- Effect of processing schedule
- DTA to investigate enthalpy changes during processing

Interface development

- Alumina formation on niobium reinforcements
- Carbide formation on Mo and W reinforcements
- Interface formation on selected fibers

Property measurements

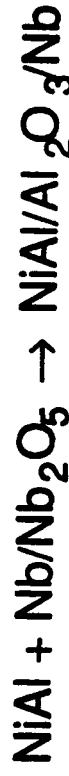
- Influence of refractory metal diameter on mechanical properties
- Interface strength compared with uncoated reinforcements
- Composite properties vs. reinforcement schemes



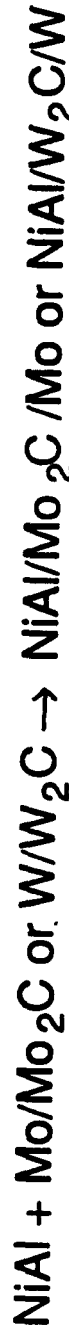
INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Reaction Schemes for NiAl Matrix Composites

Extension of Nb/NbAl₃ Work



Related Approaches for Molybdenum & Tungsten Reinforcements



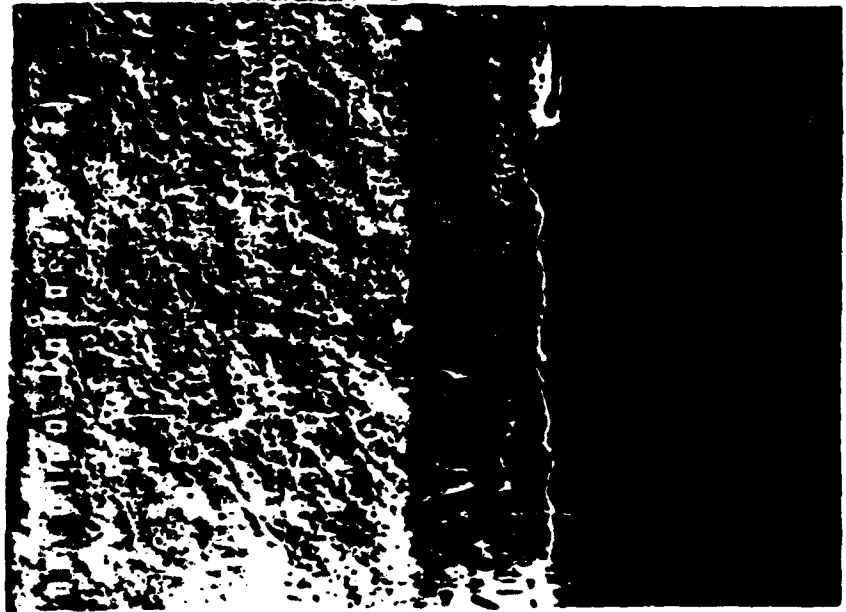
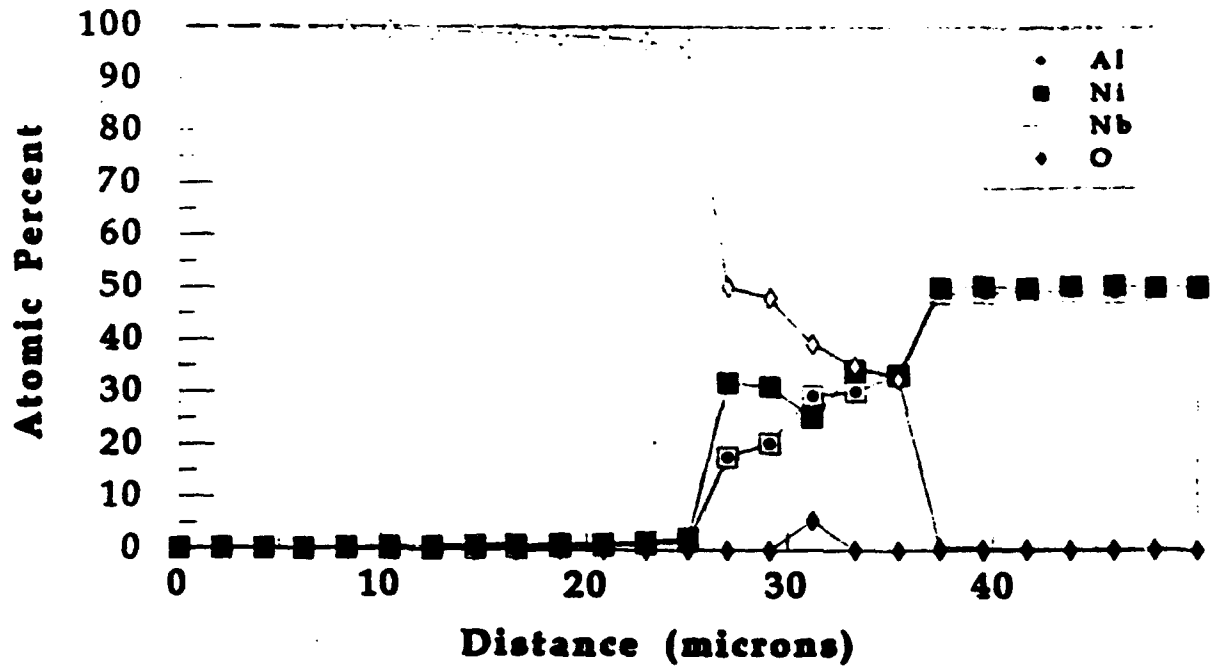
Related Approaches for Sapphire Reinforcements



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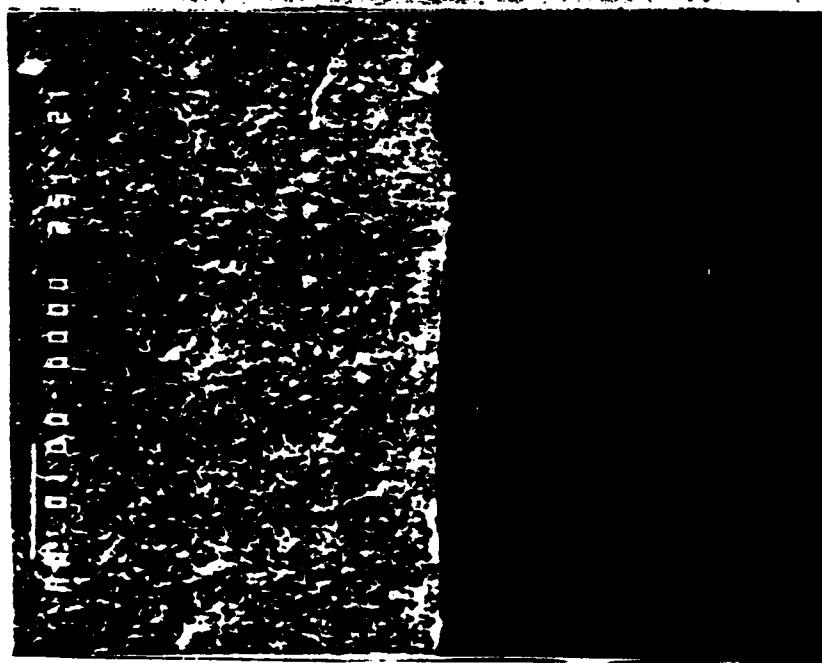
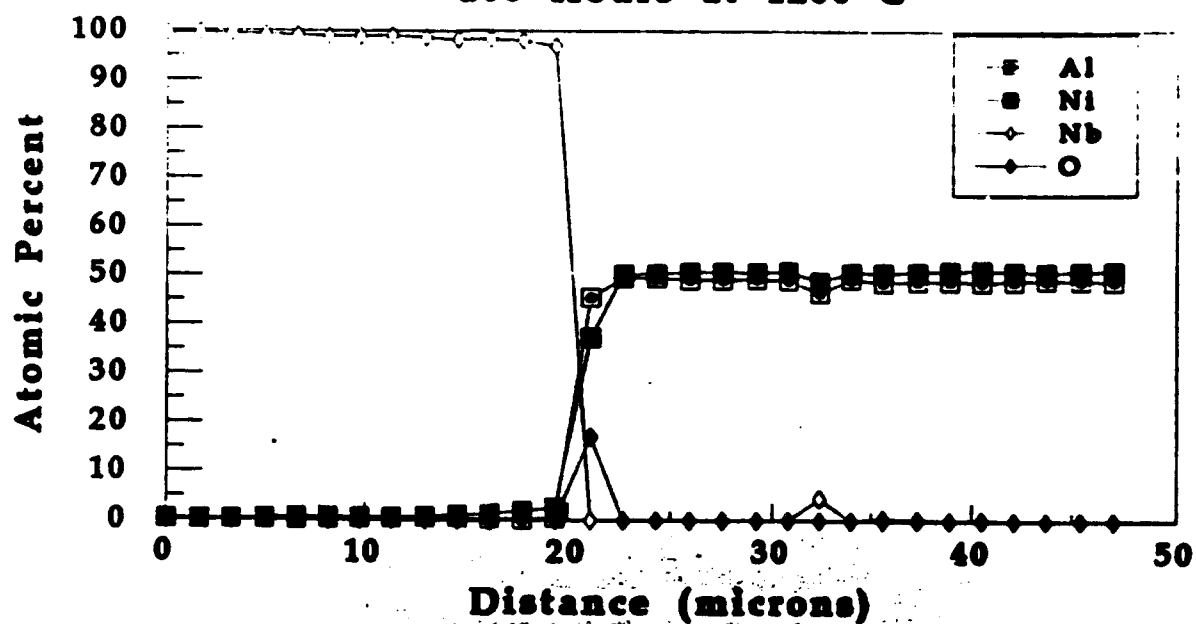
University of Florida

Nb-NiAl Diffusion Couple 4 Hours at 1200 C



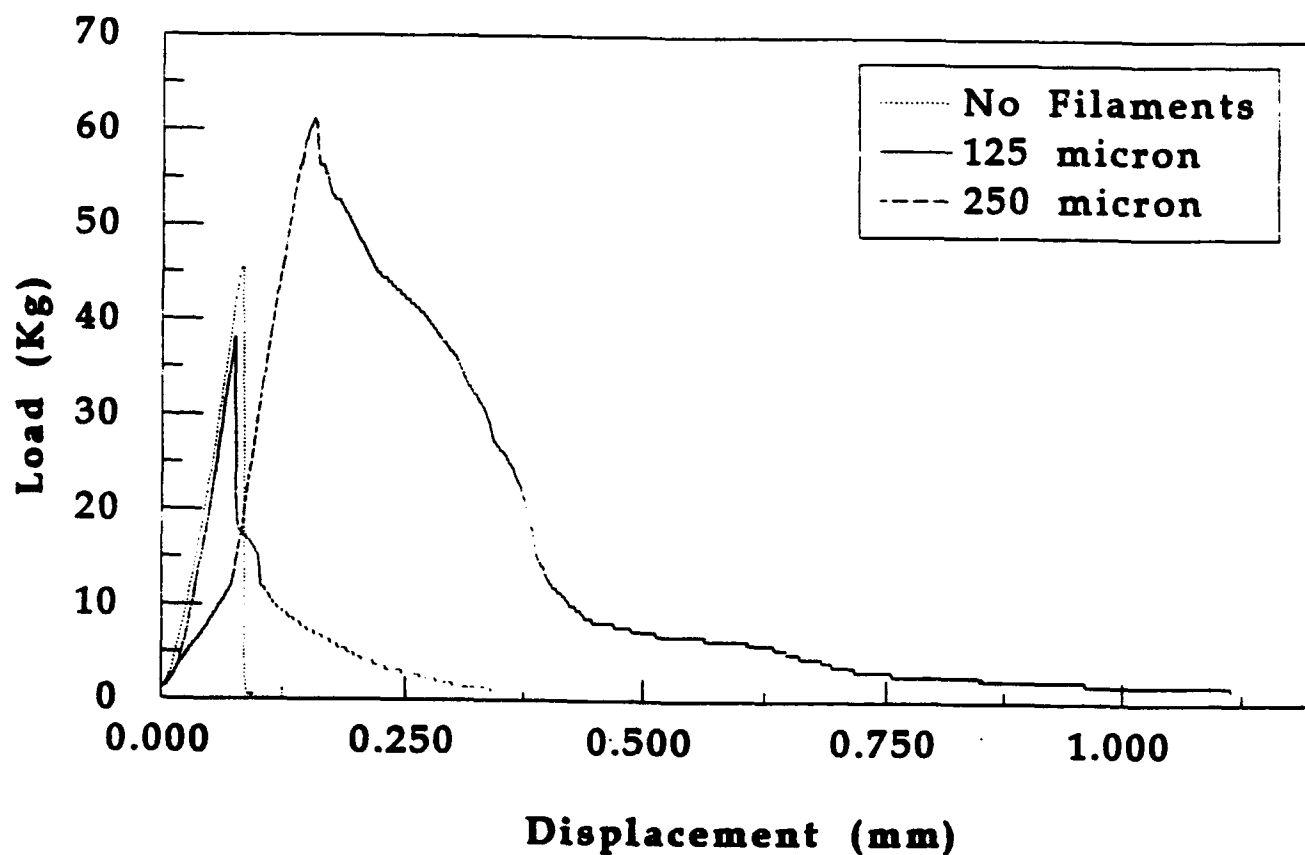
Electron microprobe linescan showing extensive reaction zone between the NiAl matrix and untreated niobium reinforcement.

In-situ coated Nb-NiAl Diffusion Couple 100 Hours at 1200 C



Electron microprobe linescan showing reactively formed alumina interface between NiAl matrix and pretreated niobium reinforcement.

4 Point Bend Test - Chevron Notch NiAl Matrix - Nb Filaments

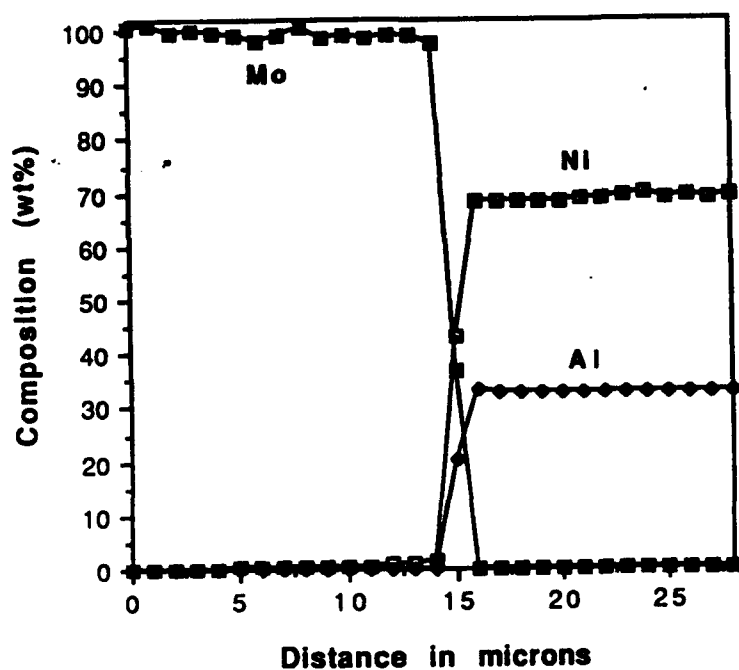
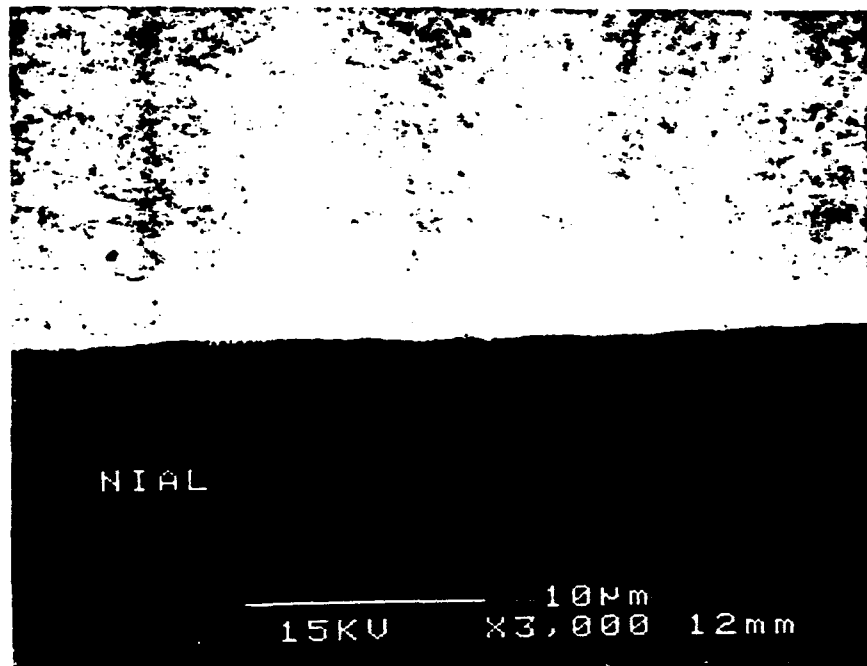


SAMPLE	K_{IC} (MPa $\sqrt{m}$)	FRACTURE ENERGY (J/m ²)
00-000	11.03 $\pm$ 1.09	1253.6 $\pm$ 289.6
00-125	7.15 $\pm$ 1.21	1481.5 $\pm$ 183.0
00-250	12.75 $\pm$ 1.62	6794.8 $\pm$ 2157.9



INTERMETALLIC MATRIX COMPOSITES

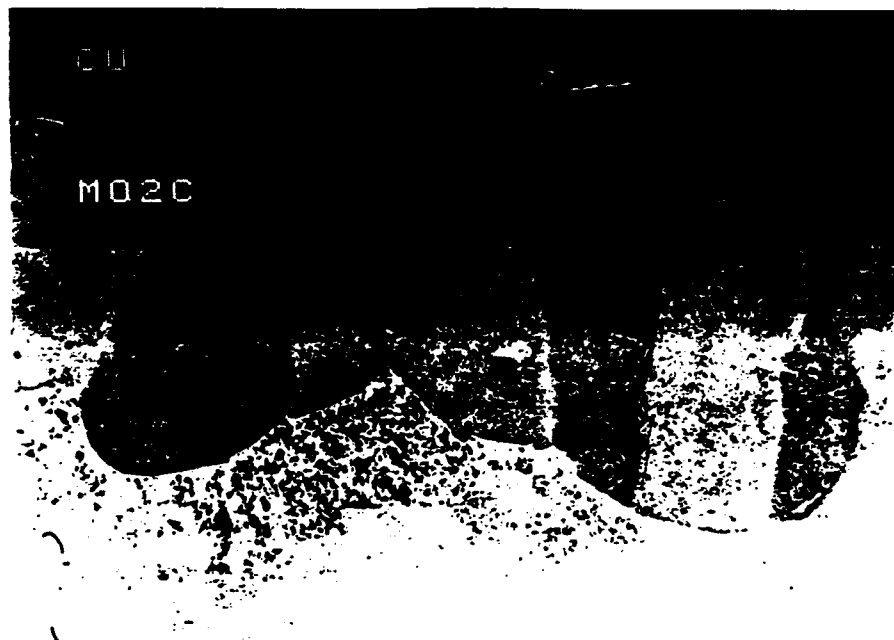
NiAl / Mo diffusion couple



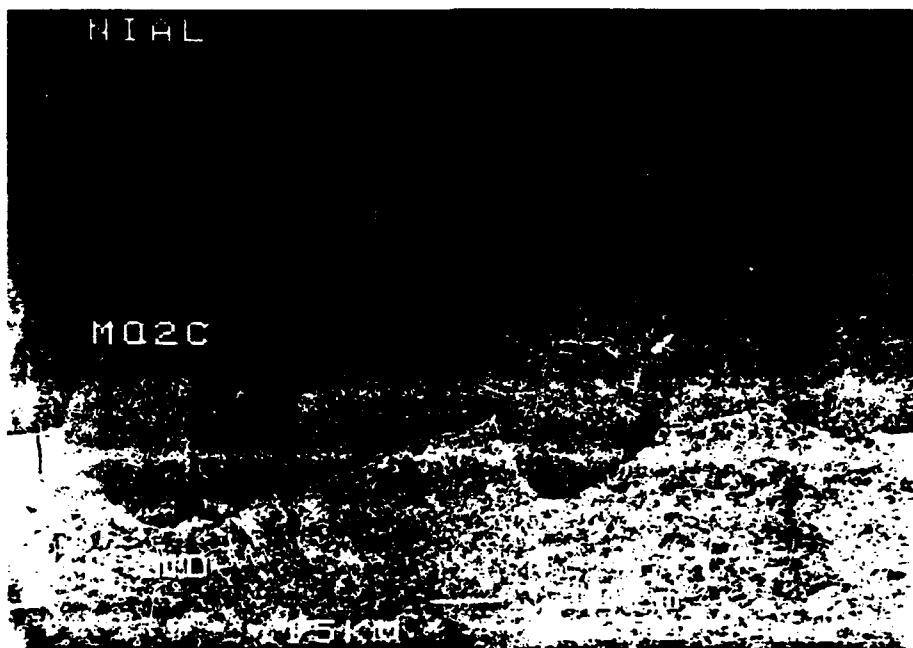


INTERMETALLIC MATRIX COMPOSITES

Precarburized molybdenum



NiAl / Mo₂C / Mo diffusion couple

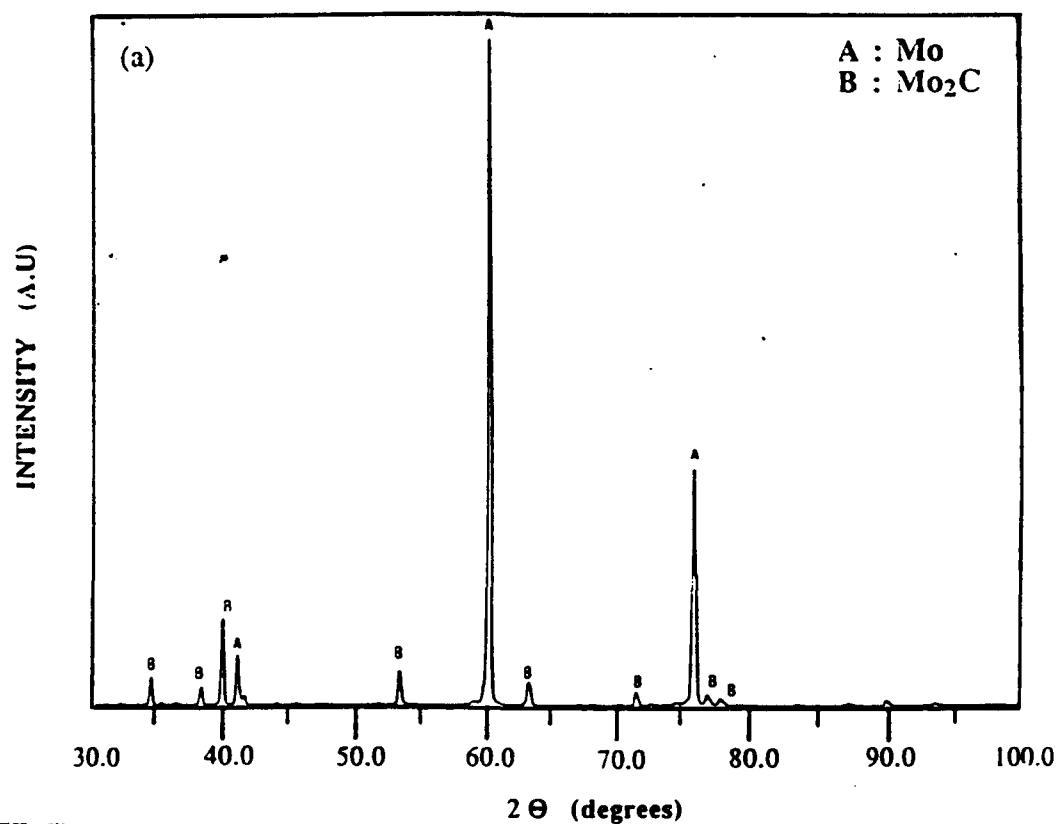
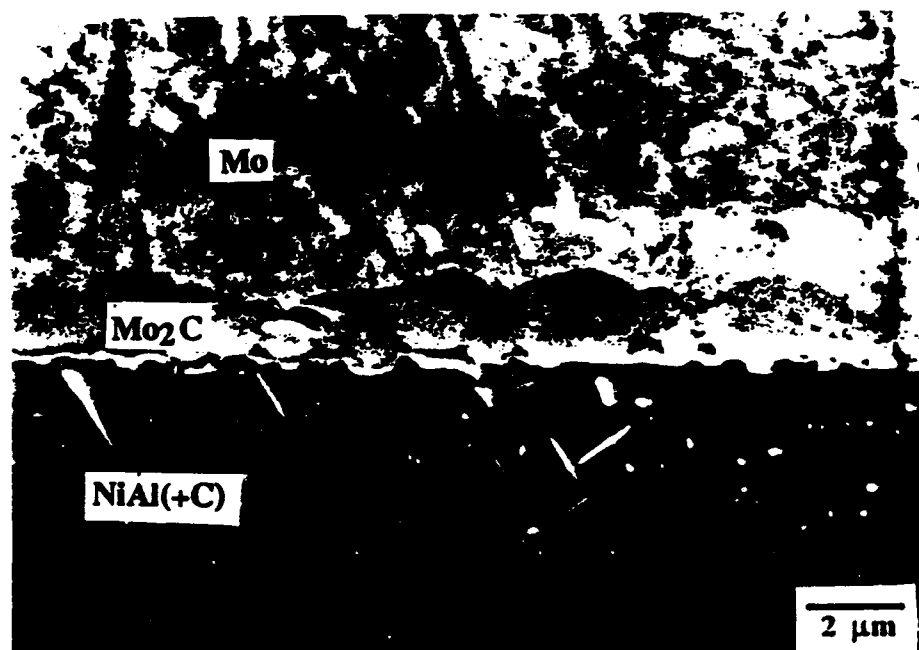


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INTERMETALLIC MATRIX COMPOSITES

NiAl(+C) / Mo diffusion couple

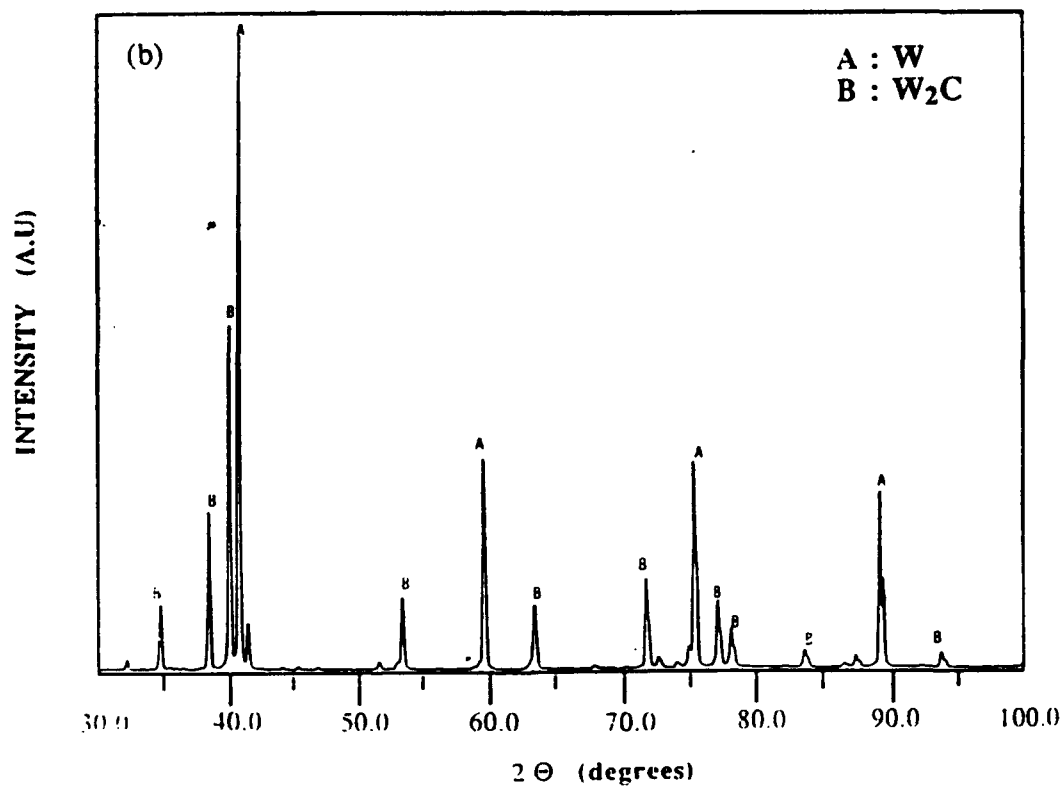
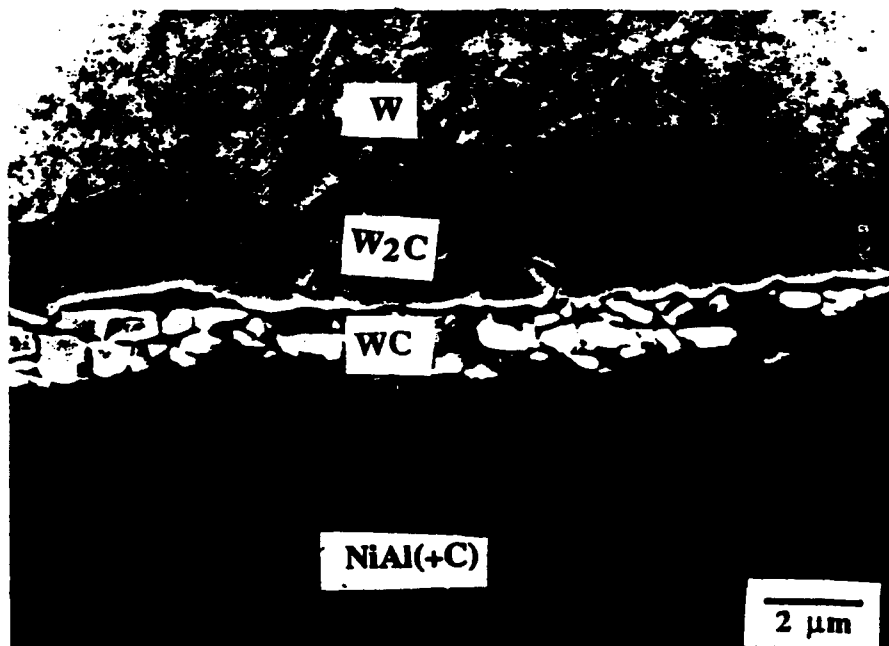


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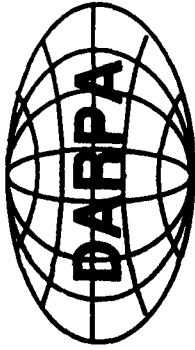


INTERMETALLIC MATRIX COMPOSITES

NiAl(+C) / W diffusion couple



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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

MoSi₂ Studies

Ductile phase toughening studies

Chemically stable

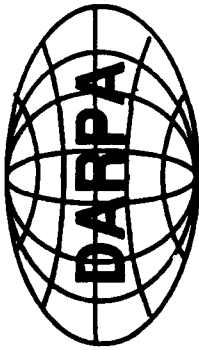
- Niobium/MoSi₂ laminates
- Coating studies
- Modeling

Matrix development

- Tape casting of MoSi₂ containing SiC whiskers
- Mechanical alloying -- carbon additions for reducing silica and forming SiC dispersion
- Microstructural evolution of carbon-modified materials

Thermochemistry studies

- Estimation of Mo-Si-C phase equilibria using existing thermochemical data
- Verification by microstructural analysis



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Physical Properties of MoSi_2

Density : 6.14 g/cc

Elastic Modulus : 380 GPa

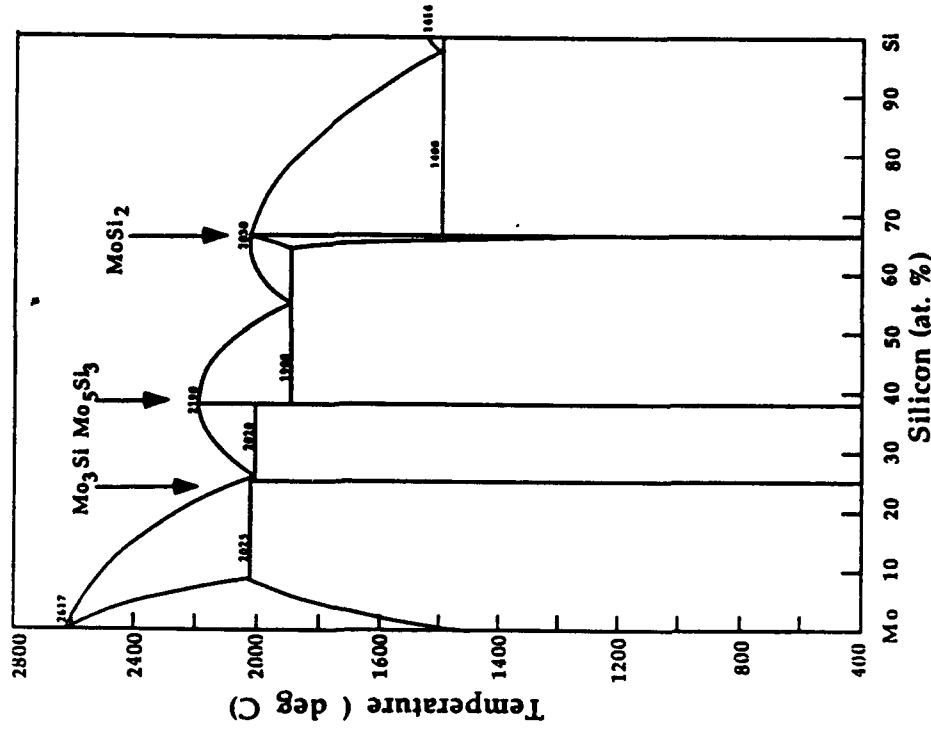
Poissons Ratio : 0.17

Hardness : ~ 1300 kg/mm²

Thermal Conductivity : 0.49 W/cm^{°C}

Excellent Oxidation Resistance

Fracture Toughness : 3 ~5 MPa-m^{1/2}



(From Brewer and Lamoreaux, 1980)

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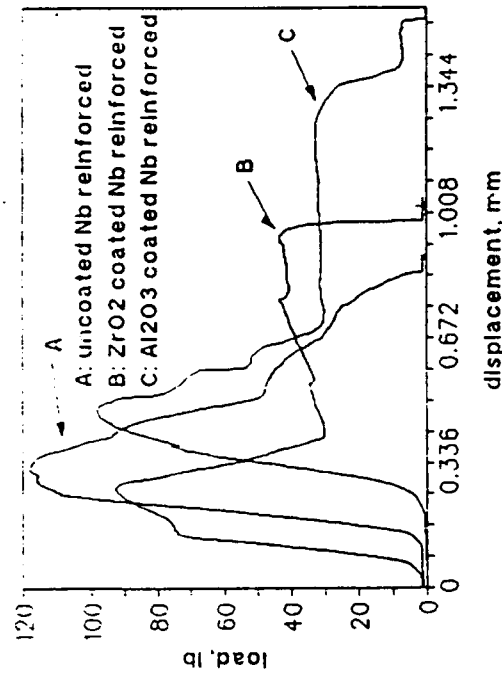


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

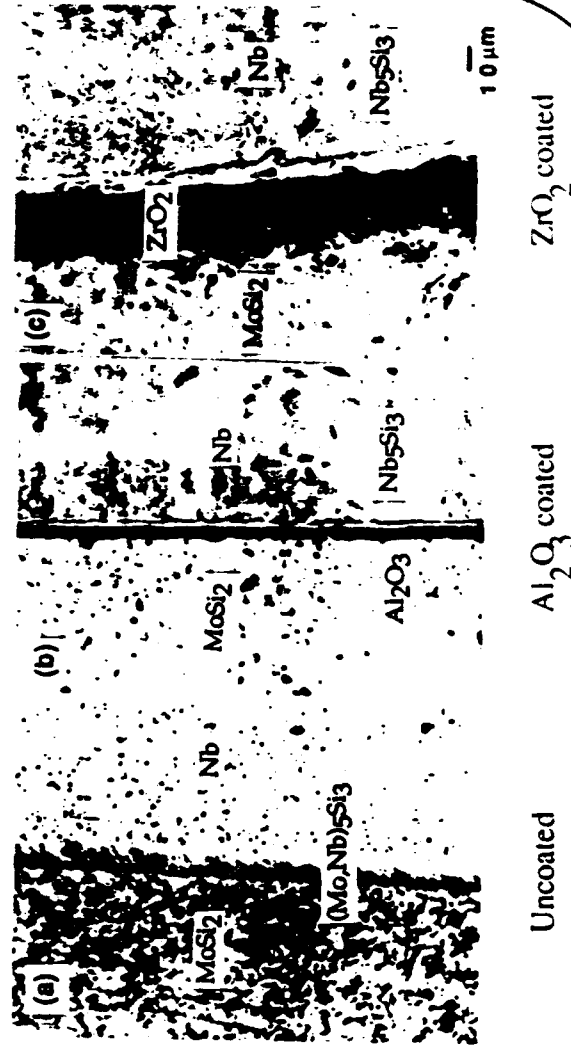
Toughness and Interfacial Fracture Energy of MoSi₂ Composites with 20 vol.% of Nb Laminae

Materials	MoSi ₂	uncoated Nb reinforced	Al ₂ O ₃ coated Nb reinforced	ZrO ₂ coated Nb reinforced
Interfacial				
fracture energy (J/m ²)	-	> 33.7 ± 1.4	16.1 ± 1.3	12.8 ± 1.0
Damage tolerance (MPa.m ^{1/2})	3.3 ± 0.3	15.2 ± 1.3	14.0 ± 1.5	12.8 ± 1.5
Work of fracture (J/m ²)	690 ± 30	21,600 ± 3,000	28,700 ± 1,900	28,700 ± 4,600

Typical load-displacement curves of
the chevron notched specimens with
different interfacial conditions



Interfacial microstructures





INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Effects of Size of Ductile Phases on Toughness of MoSi₂ Composites with 20 vol. % of Nb Laminae

Thickness of Nb laminae (mm)	0.127	0.25	0.5	1.0
Damage tolerance (MPa.m ^{1/2})	12.2 ± 0.5	15.2 ± 1.3	15.4 ± 0.6	17.6 ± 0.1
Work of fracture (J/m ²)	5,490 ± 200	21,600 ± 3,000	30,900 ± 1,700	35,900 ± 3,500

Fracture Surfaces of the Composite Laminates



Thickness of Nb lamina = 0.127 mm



Thickness of Nb lamina = 0.25 mm

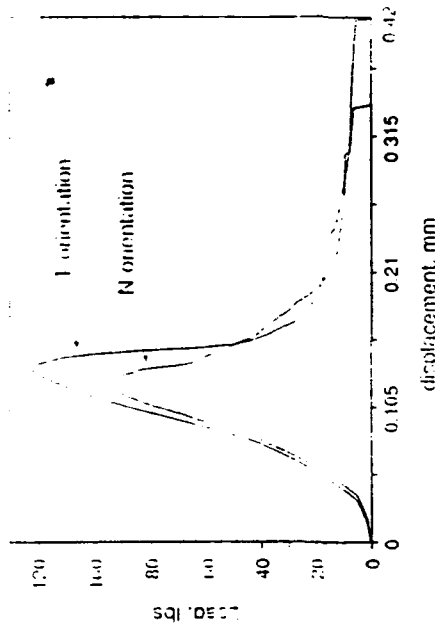


Thickness of Nb lamina = 0.5 mm



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Representative Load-Displacement Curves of Chevron Notched Specimens with Different Orientations



Orientation Dependence of the Toughness of the Composites

Orientation of crack propagation	N	T
Damage tolerance (MPa.m ^{1/2})	12.2 ± 0.5	14.9 ± 1.4
Work of fracture (J/m ²)	5,490 ± 200	6,960 ± 350

Fracture Surfaces of the Composite Laminates



Crack
propagates
normal to the
lamina plane
(N-orientation)

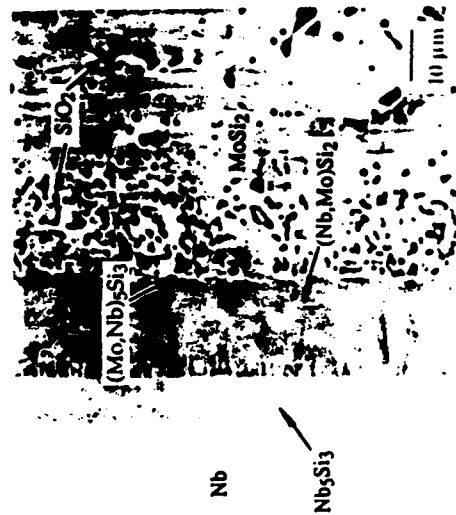


Crack propagates
transverse to the
lamina plane
(T-orientation)



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

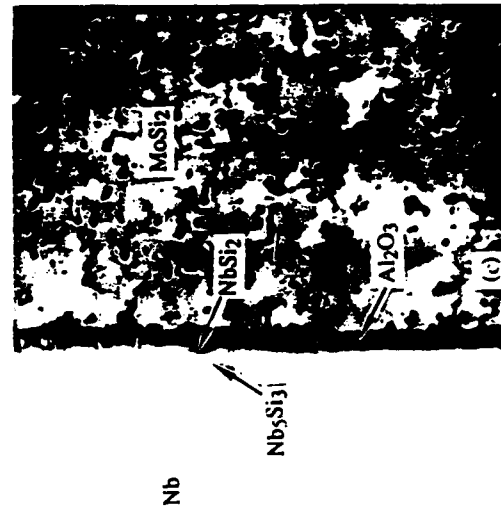
Interfacial Microstructures in MoSi_2 /Nb Composites



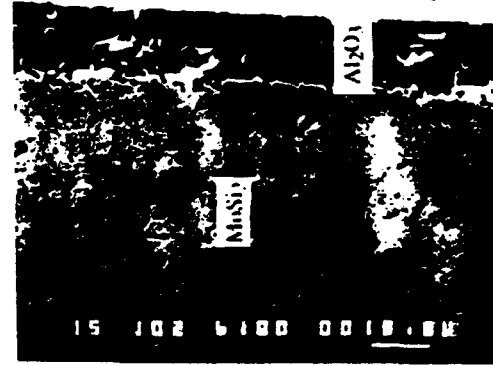
Uncoated



Al_2O_3 coated
via sol gel
technique



Al_2O_3 coated
via PVD

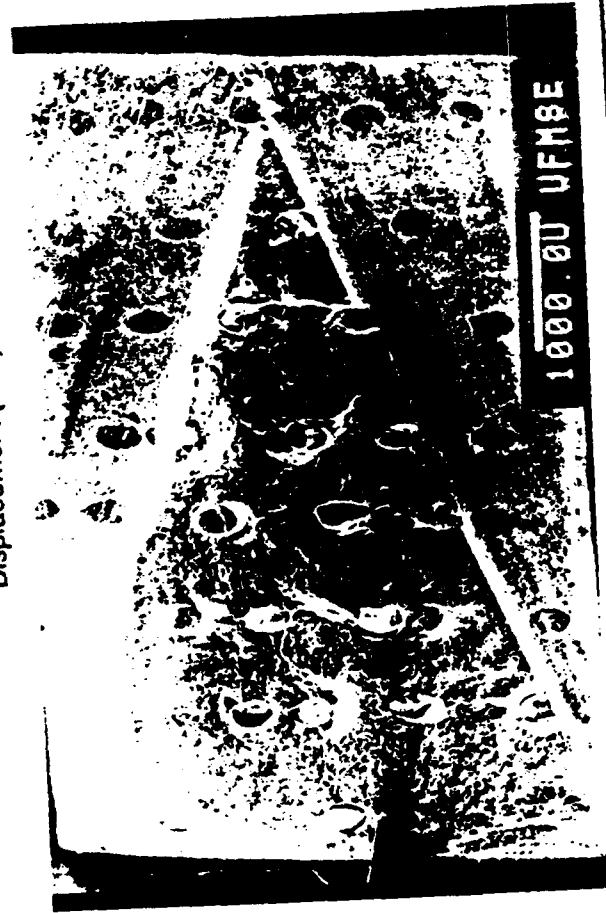
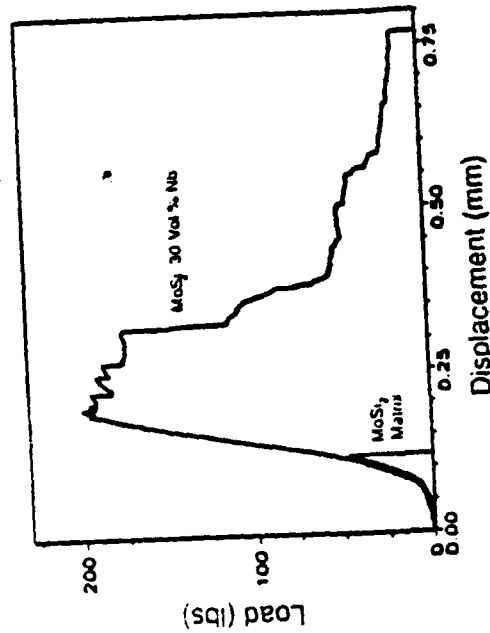


Al_2O_3 coated
via aluminum
anodizing

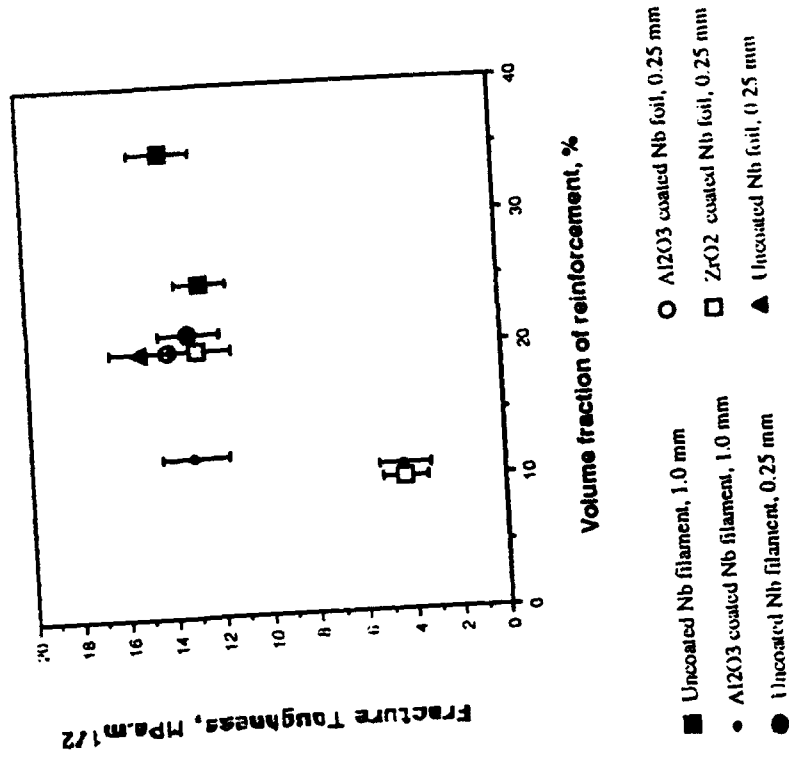


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load-displacement curves of the Chevron
notched samples



Fracture Toughness of MoSi₂/Nb Composites



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Strengthening of MoSi_2 with SiC Whiskers

Incorporation of SiC whiskers was done via tape casting. The incorporation of SiC whiskers is to improve high temperature strength and creep resistance, and at the same time to modify the thermal expansion coefficient of the matrix to enhance ductile phase toughening.



General Image of Green-tape of MoSi_2 with 30 vol. % SiC_w



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

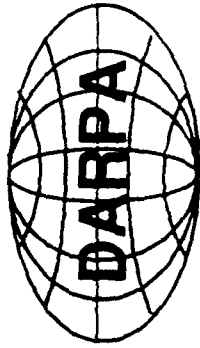
Microstructures of the Hot Pressed MoSi_2 Tape With 30 vol.% SiC Whiskers



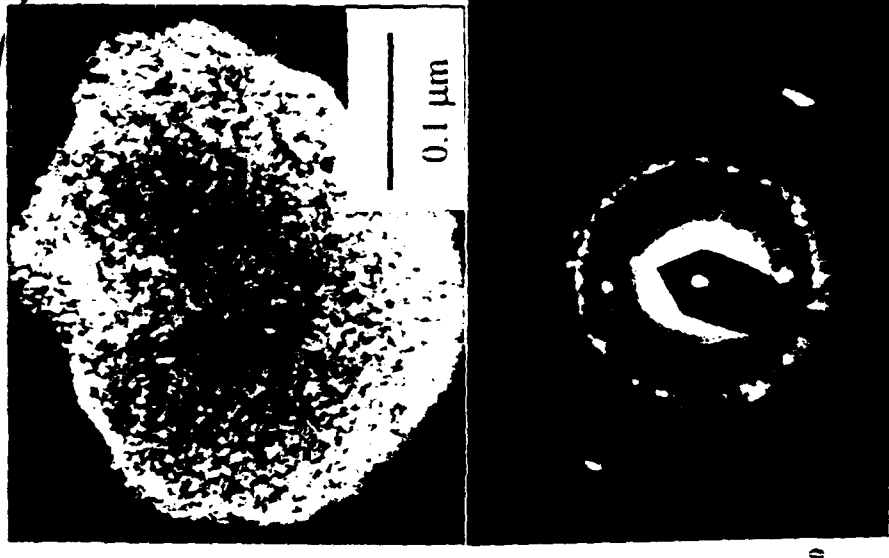
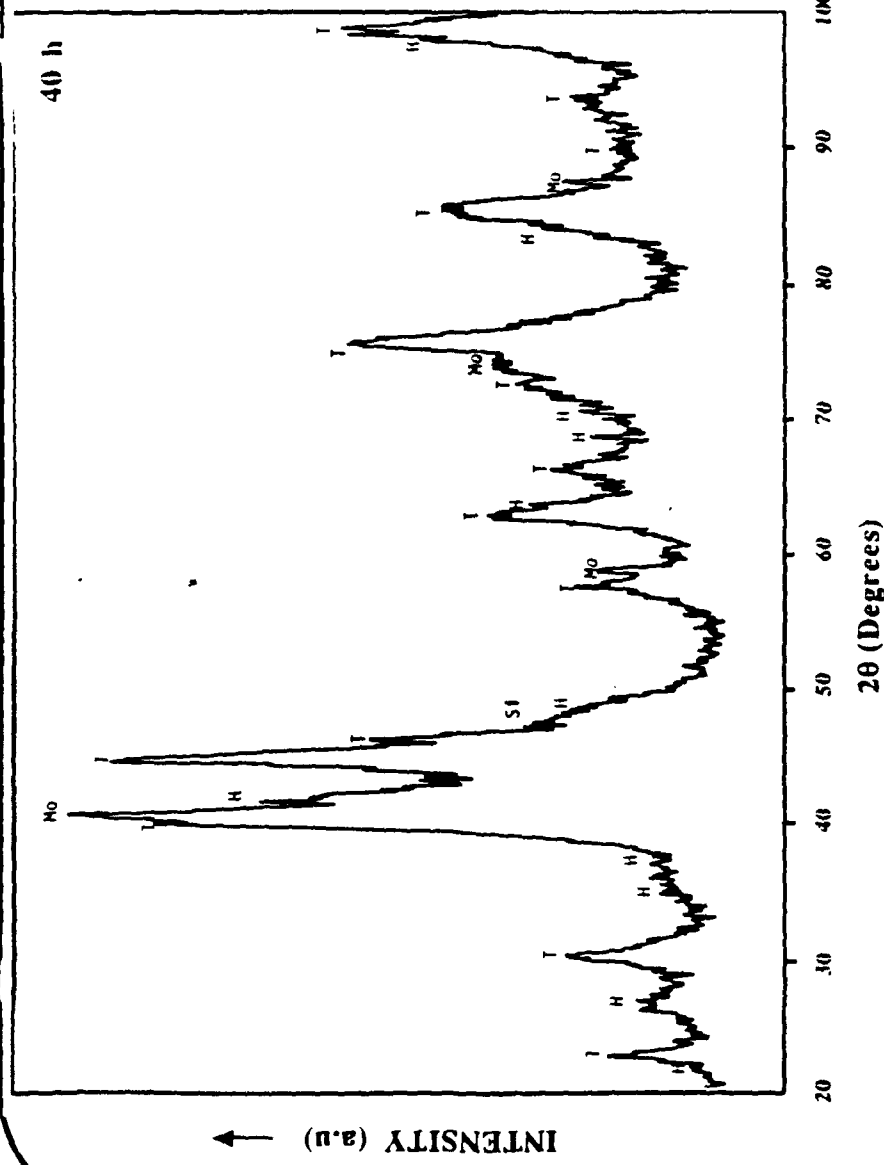
Typical microstructures (SEM) of MoSi_2 -30 vol.% SiC composites produced via hot pressing of the tape cast laminae. The cross sections shown are perpendicular to the tape casting direction. (a) Higher magnification view, and (b) overall view of the microstructure.

Why Mechanical Alloying?

- Defects (SiO₂ and/or porosity) in MoSi₂ made from commercial powder — MoSi₂ can be synthesized at room temperature by mechanical alloying. Carbon can be added to both reduce SiO₂ and form SiC.
- High temperature strength of MoSi₂ decreases rapidly at temperatures approaching 1200°C — can use MA to introduce dispersoids into MoSi₂.
- Refractory metal toughening is desirable but a problem due to the mismatch in CTE's — can lower CTE of matrix by introducing a uniform dispersion of a lower CTE phase (e.g., SiC) via mechanical alloying.
- High temperatures required to consolidate MoSi₂ — can consolidate MA'd powders at relatively low temperatures (e.g., 1200°C)



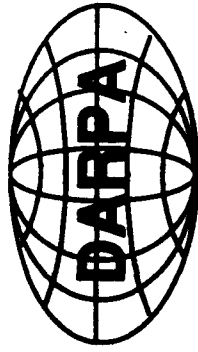
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



X-ray diffractogram of a typical powder sample attritted for 40 hours showing the presence of α -MoSi₂ (labelled T), β -MoSi₂ (labelled H) and molybdenum (labelled Mo). Inset shows a dark field TEM of a powder particle showing a fine distribution of crystallites (4-7 nm) of Mo and α -MoSi₂.

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ULTRA-HIGH TEMPERATURE APPLICATIONS

Reaction Schemes for MoSi_2 Studies

Multi-step Reactions

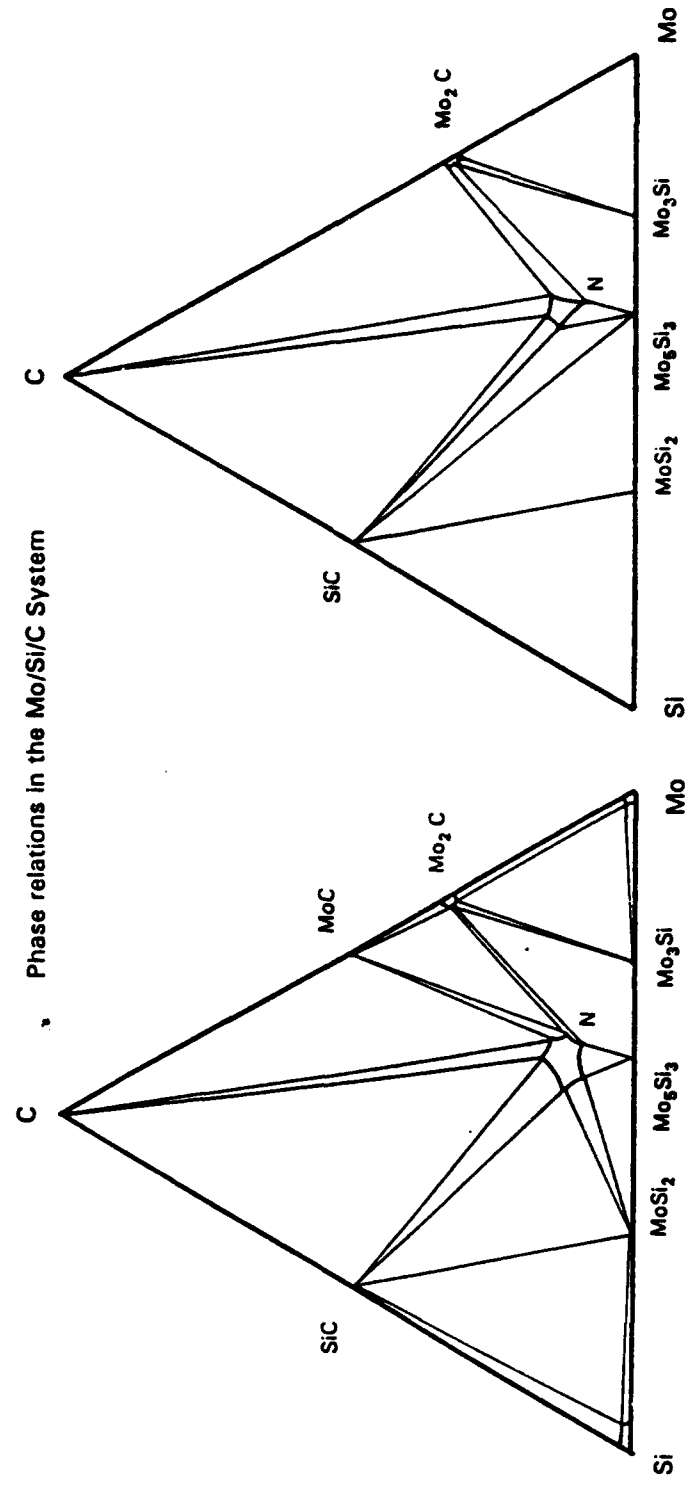


Overall Reaction





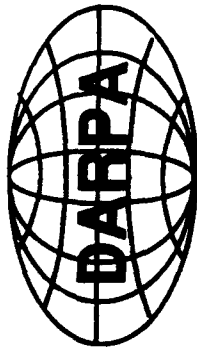
INTERMETALLIC MATRIX COMPOSITES



1600°C Isotherm by H. Nowotny et al.
Mh. Chem. 85(1954) 255

1200°C Isotherm by F. J. J. van Loo et al.
High Temp. - High Pres. 14(1982) 25

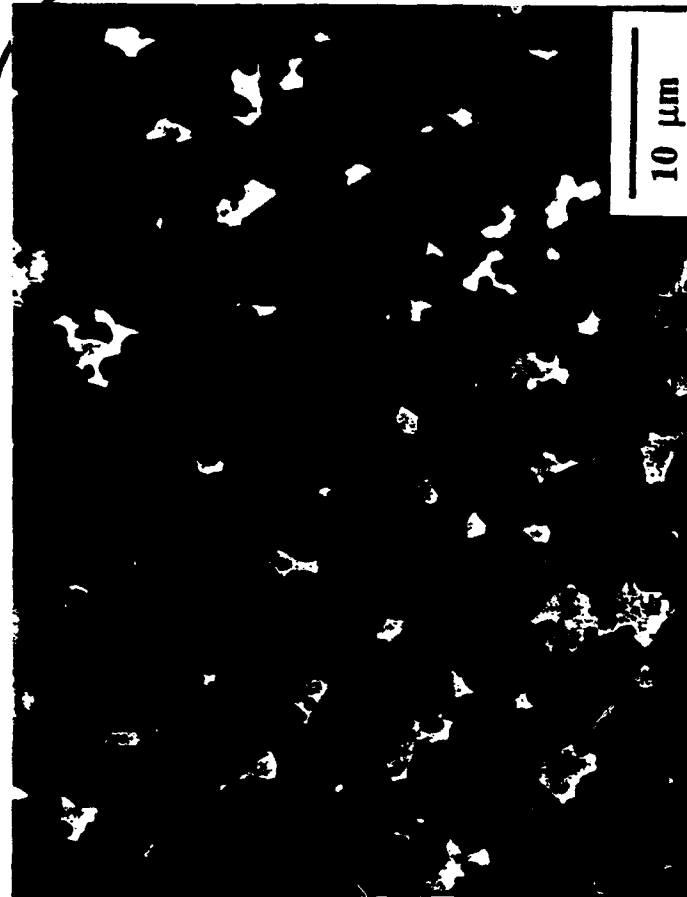
N = Mo₅Si₃C



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

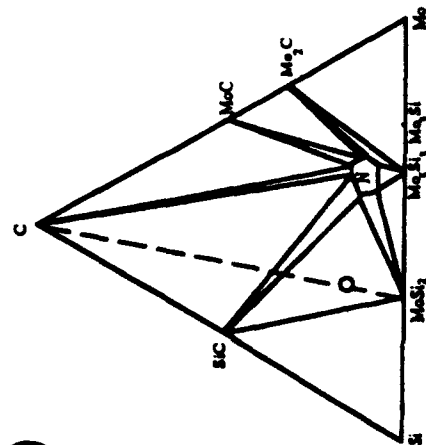


(a)



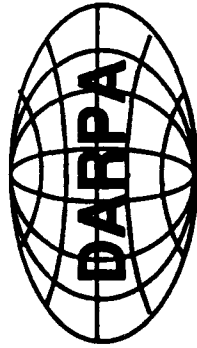
(b)

Microstructures of carbon-modified MoSi₂ processed using two different approaches, but having the same overall composition as indicated in the isotherm (a) Commercial MoSi₂ + 4 wt.% C, HP @1600°C (b) Mechanically alloyed powder, Si-28 Mo- 14C (at. %), HP @1600°C. Note the greater degree of homogeneity in the mechanically alloyed microstructure. The white phase is Nowotny phase, grey is MoSi₂, and black is SiC.

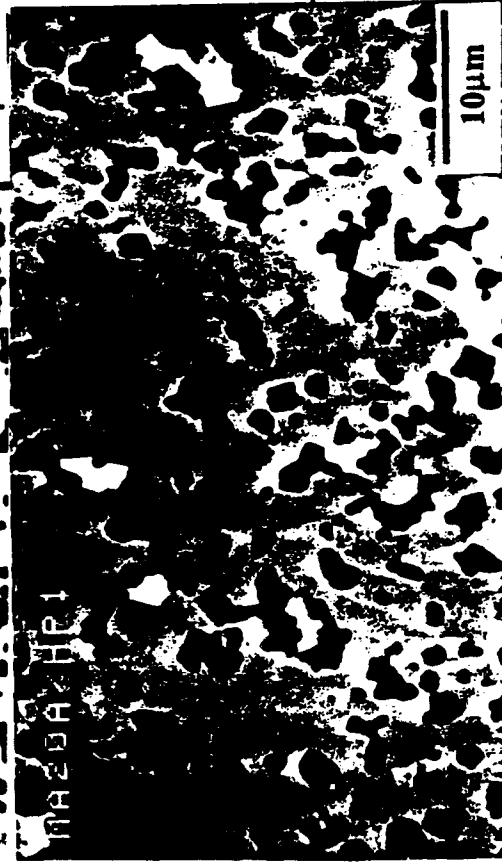


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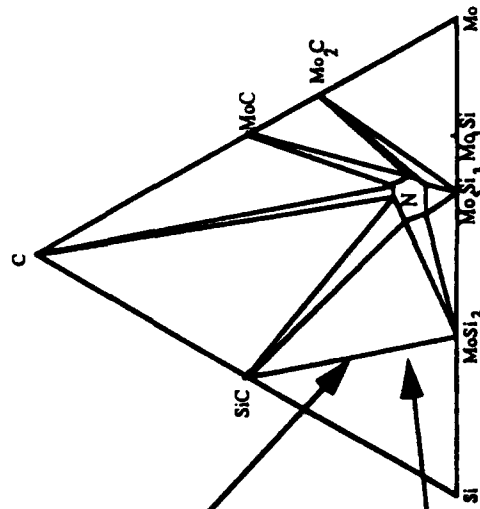
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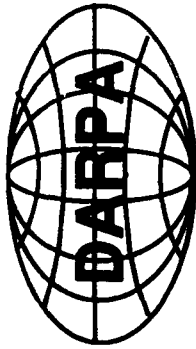


Backscattered electron images of the MoSi₂/SiC composites processed via the CTDS (Compositionally Tailored Displacive Synthesis) scheme along with the nominal composition of the precursor powders
(a) 40 v/o SiC content (b) 20 v/o SiC content

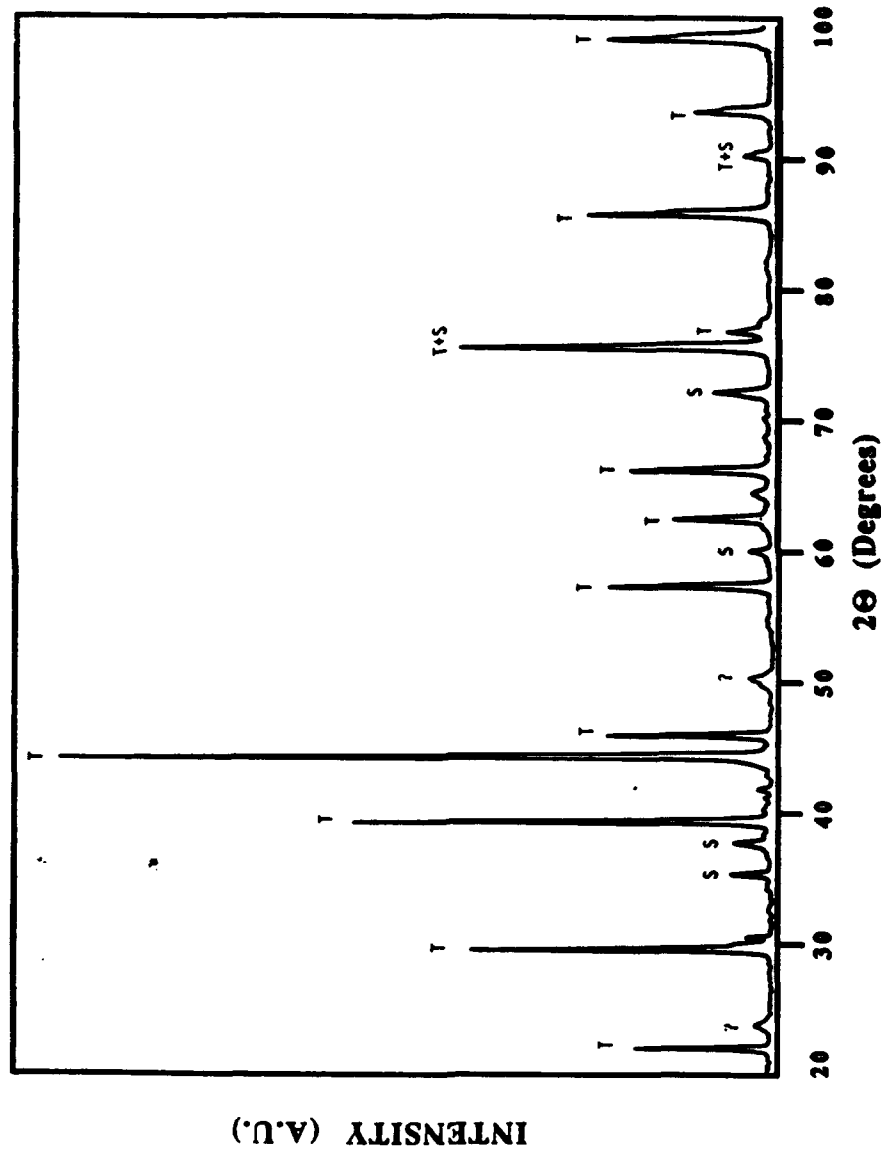


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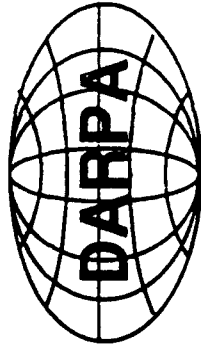
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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



X-ray diffractogram of an in-situ formed MoSi₂-20 v/o SiC composite showing the peaks corresponding to tetragonal MoSi₂ (labelled as T) and silicon carbide (labelled as S). Both the α - and β forms are present.



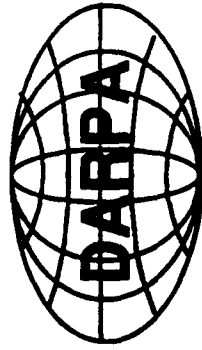
**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**



**Bright Field TEM of β -SiC particle formed in-situ in a typical ternary
(C-modified) MA MoSi₂ sample.**

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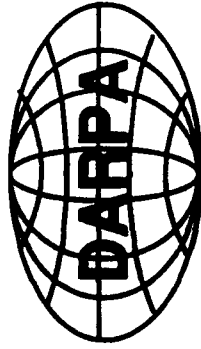
University of Florida



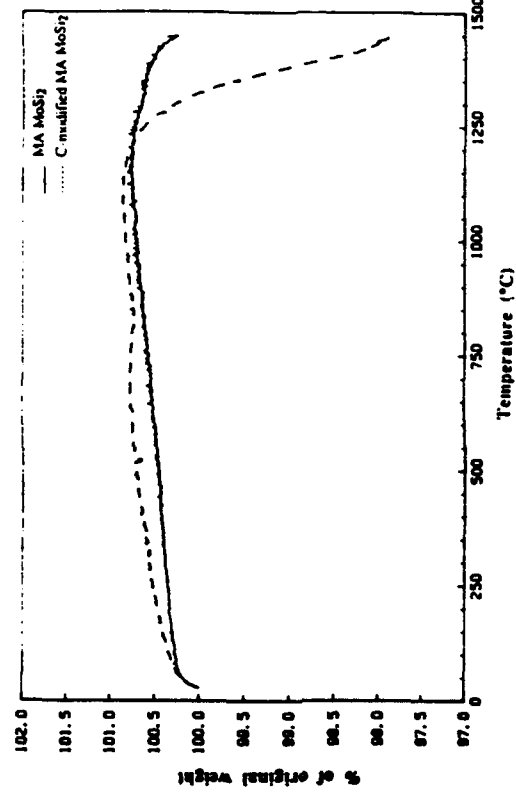
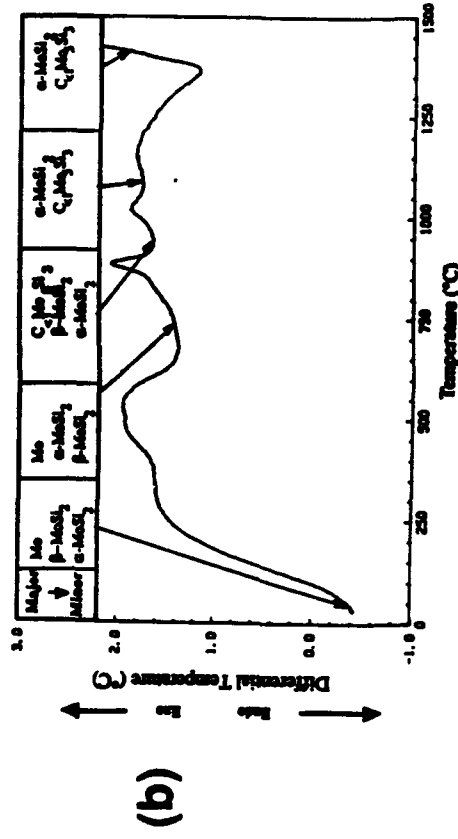
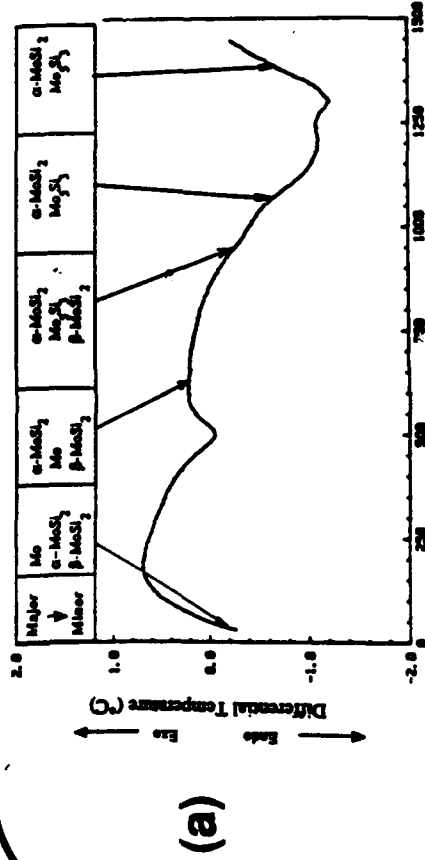
**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**



Bright Field Transmission Electron Micrograph of a typical ternary (C-modified) MA MoSi₂ showing the clean silica-free grain boundaries



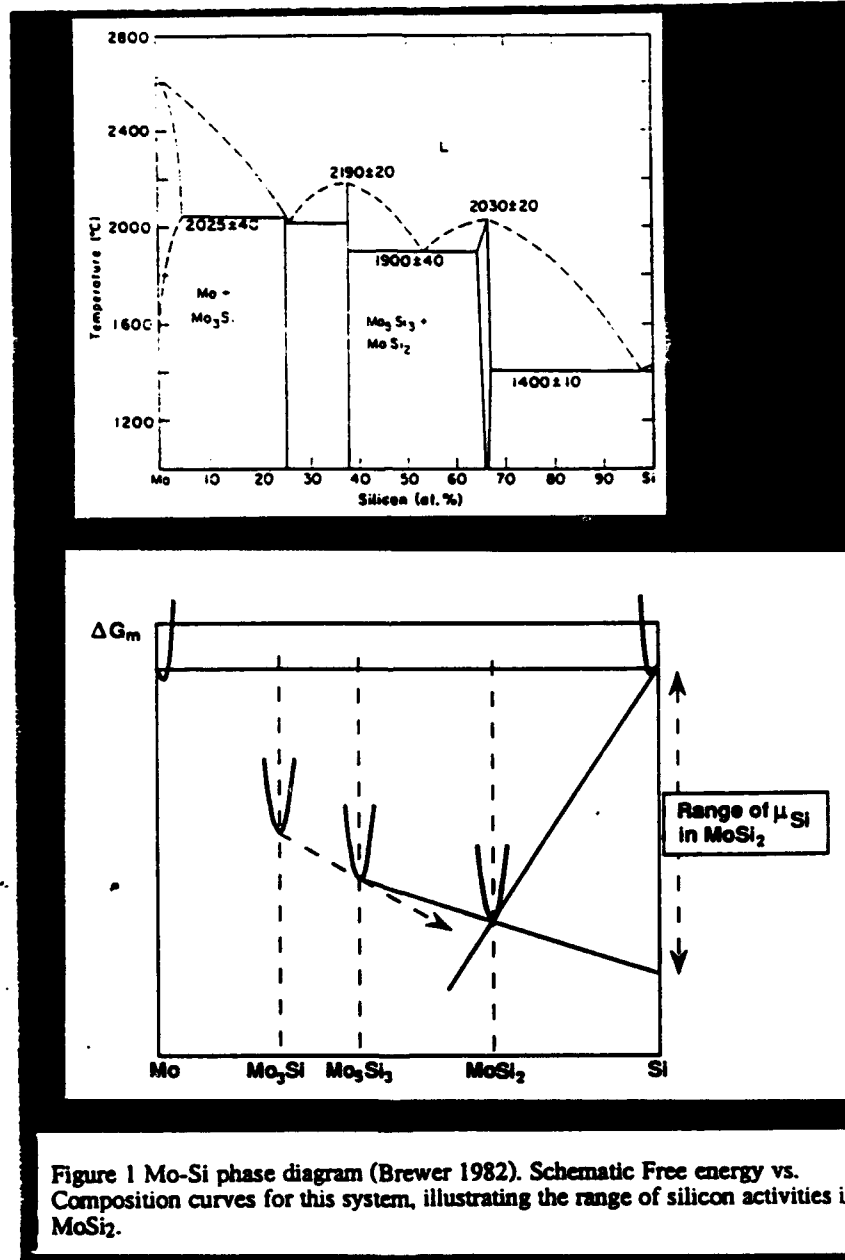
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



- (a) DTA of binary MA MoSi₂ powder indicating the phase formation sequence
- (b) DTA of a typical ternary MA MoSi₂. Heating rate 10°C/min under argon
- (c) TGA of binary and ternary MA MoSi₂ powders, 10°C/min under argon



INTERMETALLIC MATRIX COMPOSITES





INTERMETALLIC MATRIX COMPOSITES

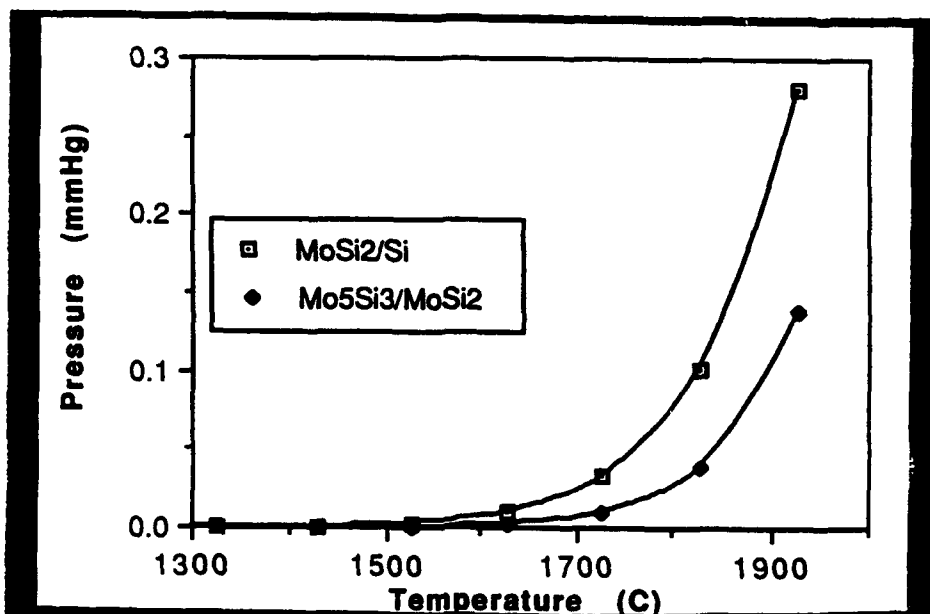


Figure 2 Equilibrium silicon vapor pressure over MoSi₂.

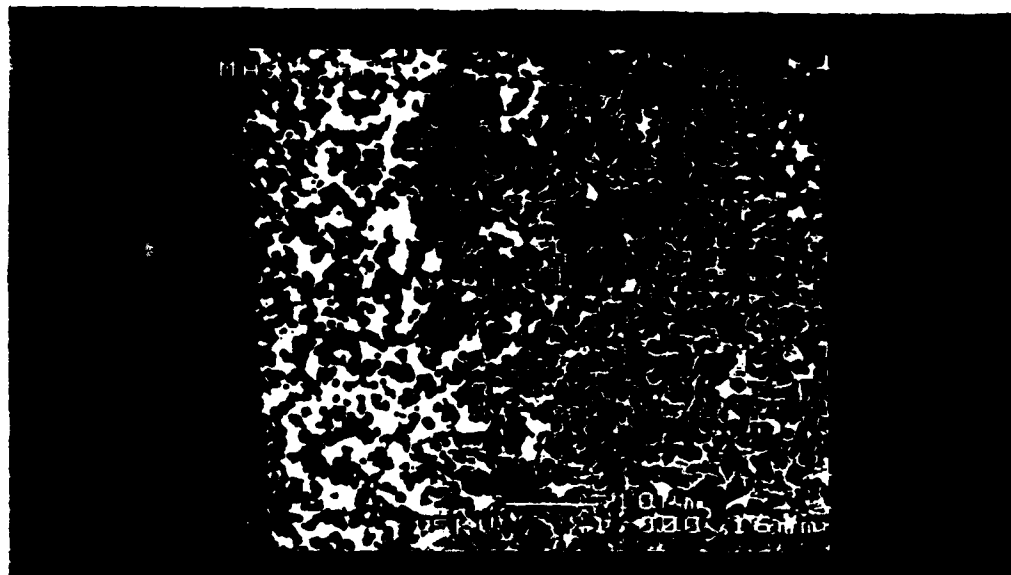
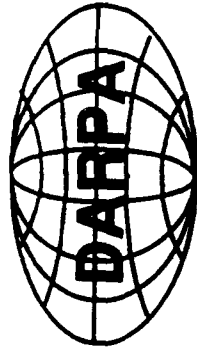


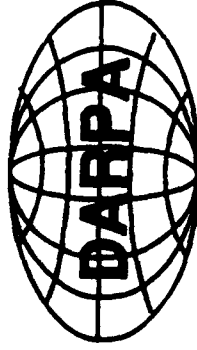
Figure 6 Mechanical alloyed Mo-Si-C vacuum hot pressed at > 1600C. The left side of the picture is close to the sample surface. The phases present indicate this area is poorer in silicon.
(Dark phase: SiC, Gray phase: MoSi₂, Light phase: Mo₅Si₃C)



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Highlights of MoSi₂ Studies

- Under optimized conditions, refractory metal toughening (Nb) leads to damage tolerances approaching $17 \text{ MPa.m}^{1/2}$.
- Reliable coating schemes (sol-gel and PVD) have been developed.
- SiC whisker reinforced MoSi₂ composites have been produced via tape casting and are being evaluated from the standpoint of high temperature properties.
- Carbon additions to MoSi₂ have been used to eliminate silica and to form SiC during consolidation. Both mechanically alloyed and commercial powders have been investigated. For the mechanically alloyed powders, it is possible to produce MoSi₂/SiC alloys with much less of the higher Mo phases (e.g., Mo₅Si₃ & Mo₅Si₃C).
- Important processing parameters have been identified and controlled during these studies.
- The phase equilibria in the Mo-Si-C system have been evaluated and the 1600°C isotherm proposed by Nowotny appears to be correct at lower temperatures as well.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

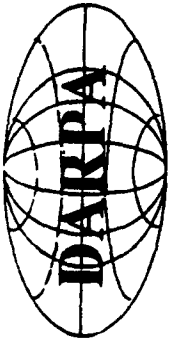
Ta-Ti-Al Composites

Hybrid Composites

- Compatibility studies
- Protection of ductile phases (niobium) using in-situ coating
- Processing schemes for fiber alignment
- Property studies

Matrix Development

- Phase equilibria studies
- Phase transformations and matrix optimization
- Microstructure/property relationships



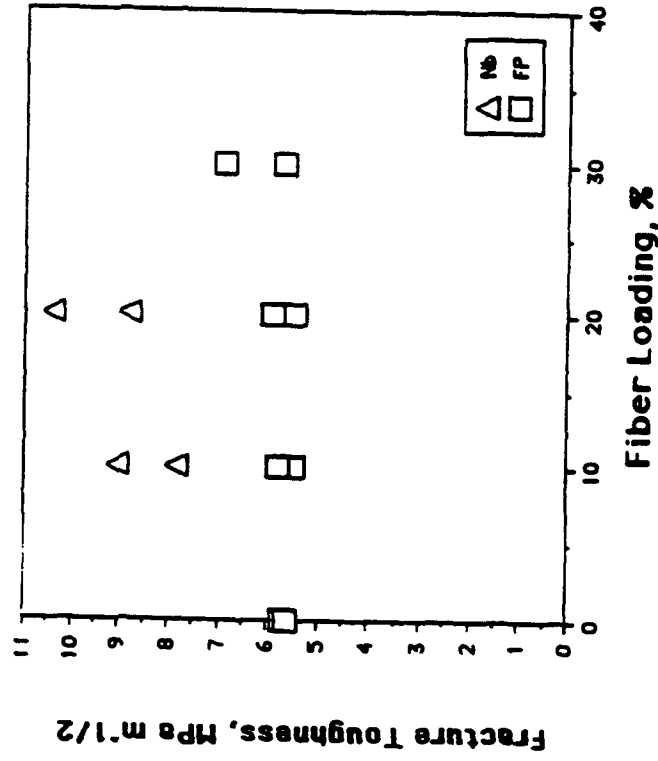
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

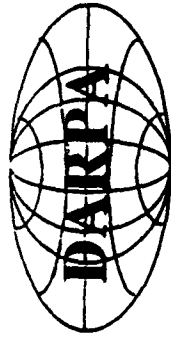
Ta-Ti-Al Hybrid Composites

Highlights

- Alumina was stable with TaTiAl₂ alloy
- Short fibers were aligned via cold extrusion
- Composites with in-situ alumina coated Nb fibers exhibit high toughness at room temperature
- FP alumina fiber reinforced composites exhibit higher elastic modulus and flexural strength at 1000 and 1200 C

**R.T. Fracture Toughness Values of
TaTiAl₂ Composites**





INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Matrix/Reinforcement **Thermochemical Compatibility**

<u>Reinforcement</u>	<u>Interaction</u>	<u>Comments</u>
Al ₂ O ₃	No Reaction	A
Y ₂ O ₃	No Reaction	A
ZrO ₂	Moderate	B
ZrN	Extensive	C
ZrC	Extensive	C
SiC	Extensive	C
TiB ₂	Extensive	C
Nb	Extensive	D
Nb (alumina coated)	No Reaction	A

Note:

- A - Limited Diffusion Layer
- B - Complex Oxides
- C - Reaction Phases
- D - Intermetallics

Processing conditions: hot pressed for 30 min under vacuum
and annealed for 50 h in Ar atmosphere



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

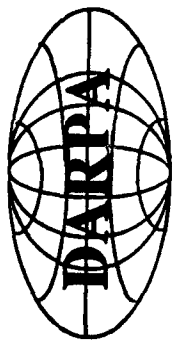
Ductile Phase Toughening

UNCOATED NB FILAMENT



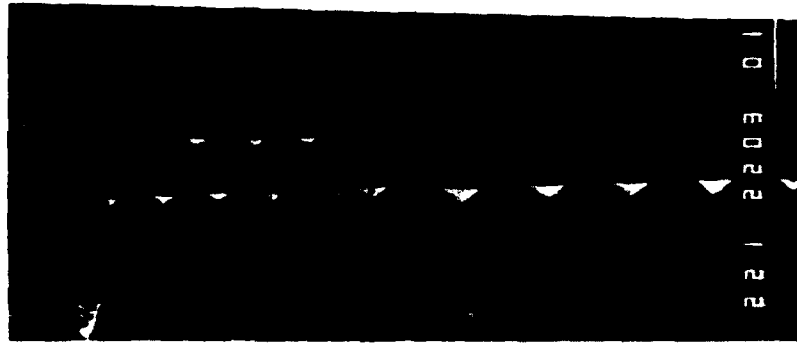
COATED NB FILAMENT

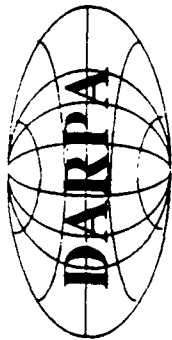




INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

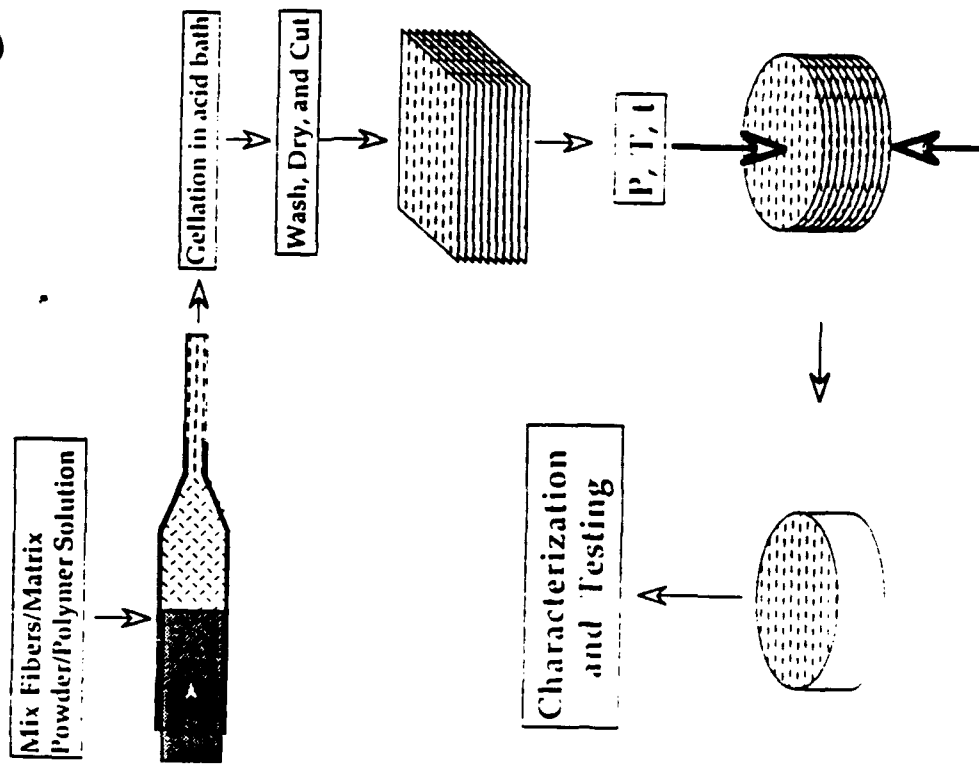
Coated Nb Filament
Microhardness Profiles

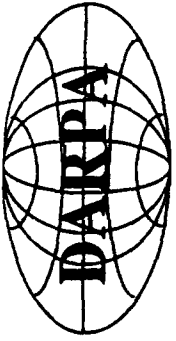




INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

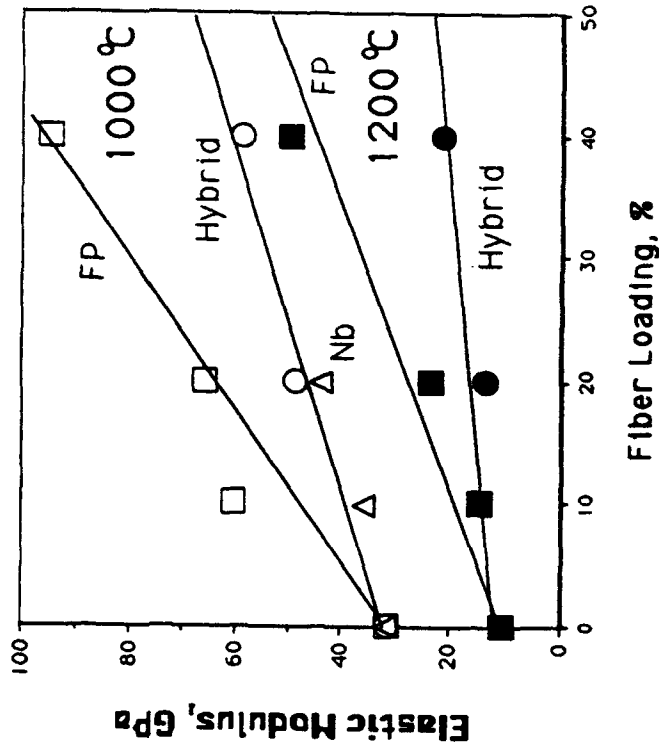
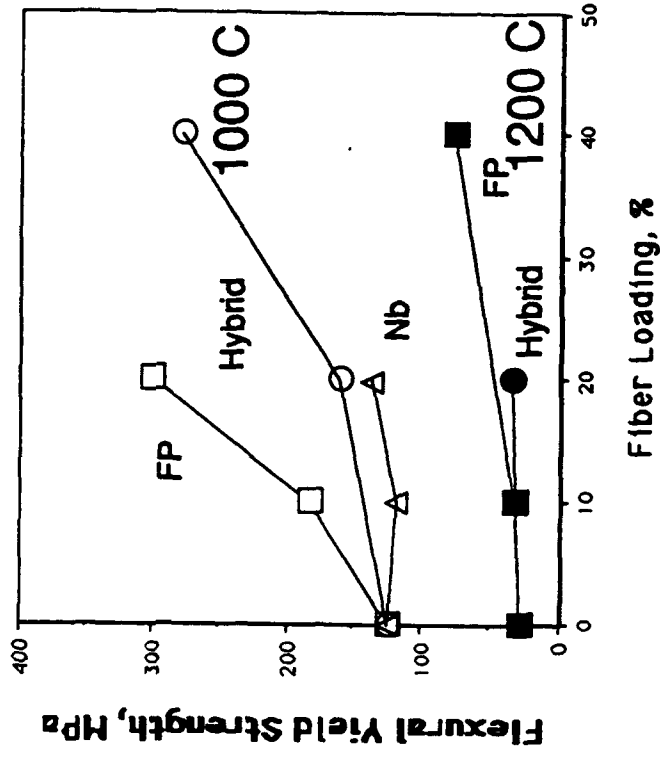
Short Fiber Alignment Process

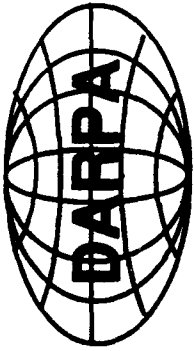




INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Flexural Yield Strengths and Elastic Moduli of Composites at High Temperatures



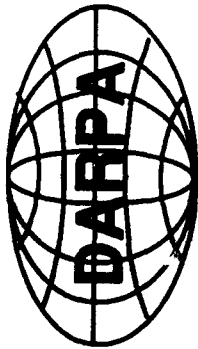


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Matrix Development in the Ta-Ti-Al System

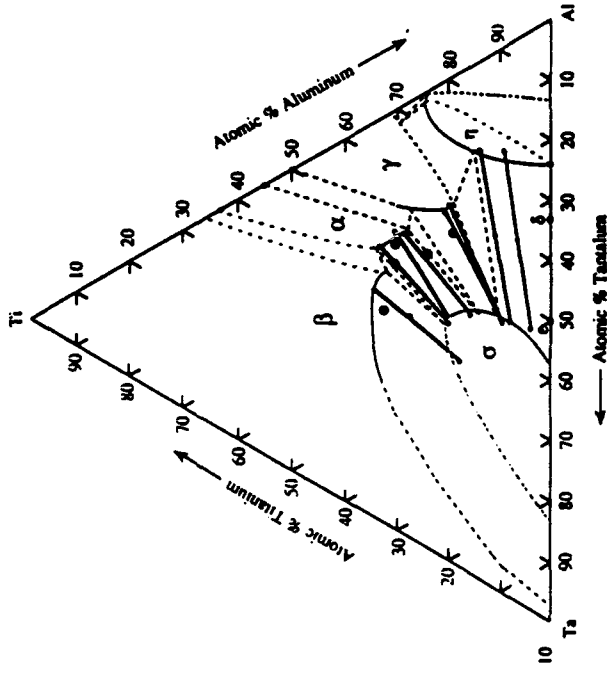
Highlights

- Heavy segregation occurs upon solidification
- Large α & β phase fields at 1450°C
- Complex decomposition sequences -- corresponding large variation in microstructures and properties
- γ forms massively from α upon water quenching
- Phase boundary positions vary considerably with temperature -- undesirable from an applications standpoint

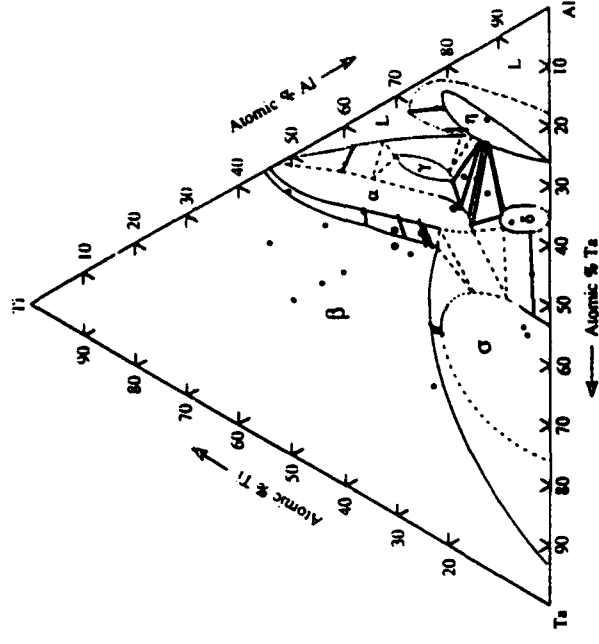


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

Experimentally-Determined Ternary Ta-Ti-Al Isotherms



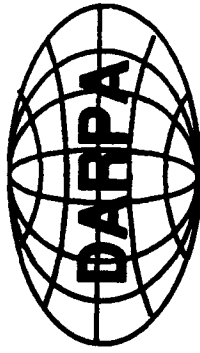
1350°C



1450°C

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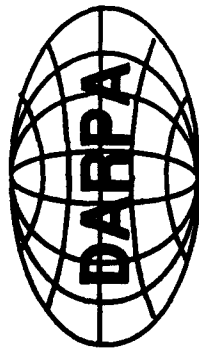
SUMMARY

- RHC can be used to form full density intermetallics
- Natural composites can be formed by control of stoichiometry
- Artificial composites can be produced readily combining RHC with in-situ reactions.
- In-situ displacement reactions can be used to:
 1. Remove undesirable phases -- silica in MoSi_2
 2. Form dispersoid phases -- SiC in MoSi_2
 3. Form interface coatings

Alumina in $\text{Al}_3\text{Nb/Nb}$ and NiAl/Nb composites

Refractory metal carbides in NiAl/W and NiAl/Mo composites

- Dual schemes (matrix enhancement vs. hybrid reinforcements) are required to achieve desirable low and high temperature properties.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Future Directions

RHC Processing

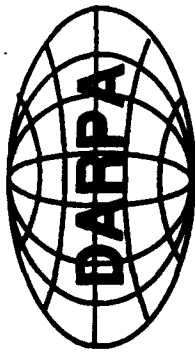
- Continue studies of alumina formation and matrix development in NiAl/Nb composites.
- Investigate the possibility of combining RHC, in-situ coating and fiber alignment.

MoSi₂ Matrix Composites

- Characterize the mechanical properties and environmental stability of enhanced silica-free matrices (vs. SiC content) -- origin of DBTT.
- Combine enhanced matrices with refractory metal toughening -- lower CTE mismatch and better creep strength?
- Complete phase equilibria studies in Mo-Si-C system.
- Develop of in-situ coating schemes to replace sol-gel approach (e.g., Si₃N₄).
- Investigate other in-situ formation sequences.
- Extend processing scheme to other silicide and silicide IMC systems.

NiAl Matrix Composites

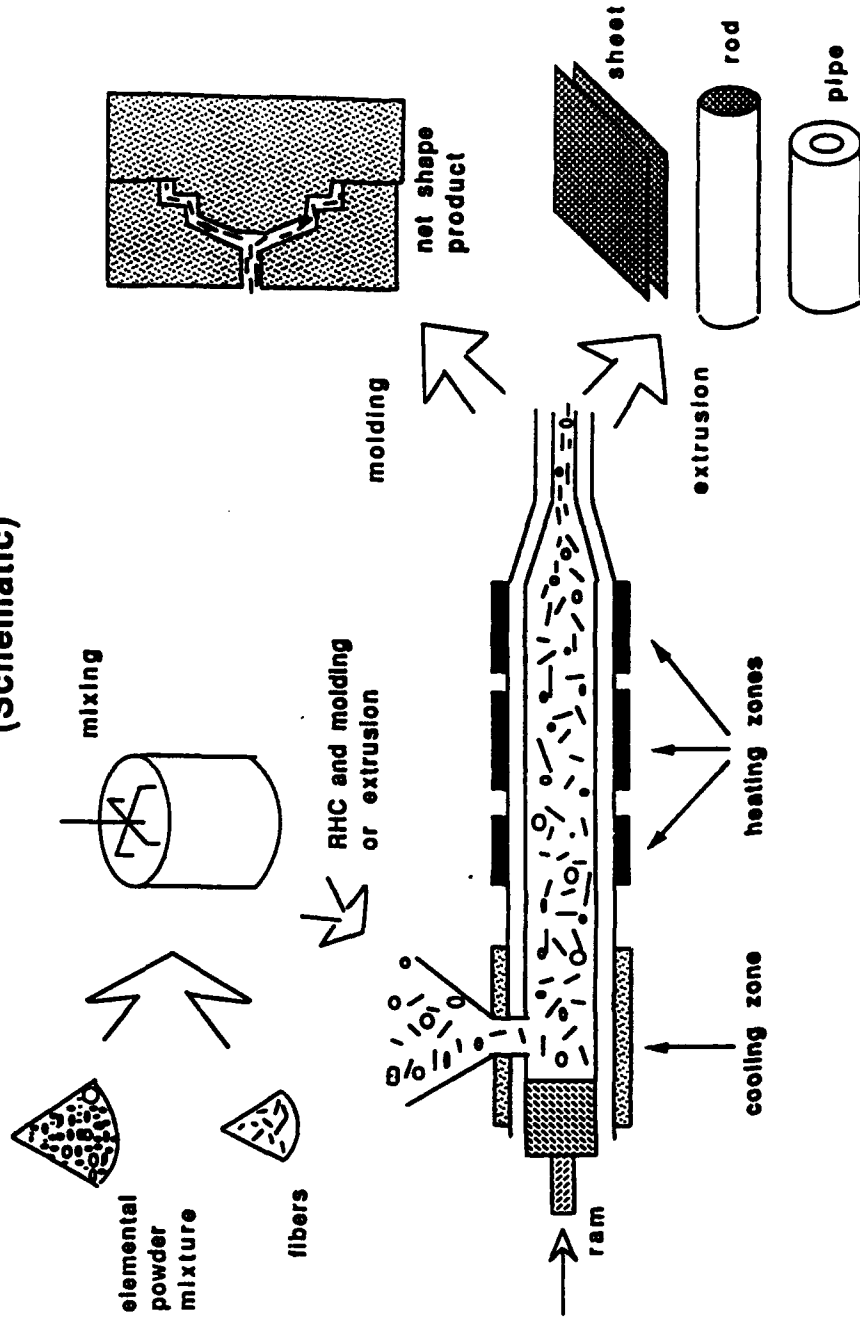
- Characterize and optimize the properties of NiAl reinforced with in-situ coated Nb and SiC particulate at both room and elevated temperatures.
- Continue investigation of alternative schemes for interface modification in Mo, W and alumina-reinforced NiAl.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

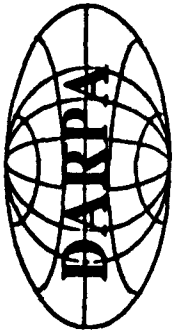
A Combination of RHC, In-Situ Coating and Fiber Alignment

(Schematic)



MSE

University of Florida

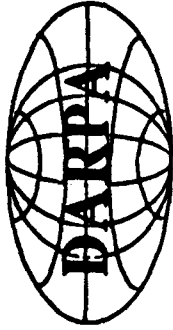


**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

CERAMIC COMPOSITES

Applications of Sol-Gel, Glass-Ceramics and Microwave Processing

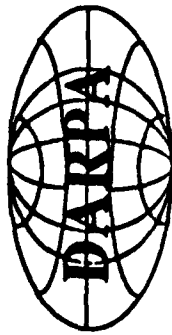
**D.E. Clark
D.C. Folz
A.D. Cozzi
Z. Fathi**



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

PROGRAM OBJECTIVE

*Develop alternative methods for processing
advanced ceramics and composites
with specific emphasis on microwave processing.*

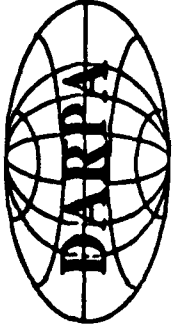


**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

OUTLINE

Microwave Processing

Low Expansion Matrix Development



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

MICROWAVE PROCESSES INVESTIGATED

Sintering

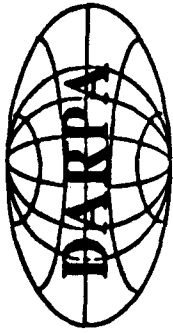
Annealing (superconductors)

Self-Propagating High-Temperature Synthesis

Joining

Surface Modification

Crystallization



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

MATERIALS SYSTEMS INVESTIGATED

High-Purity Alumina - Sintering and Joining
 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Superconductors - Sintering and Annealing

TiC

$\text{Al}_2\text{O}_3/\text{TiC}$

Others

Microwave SHS

$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ - Surface Modification

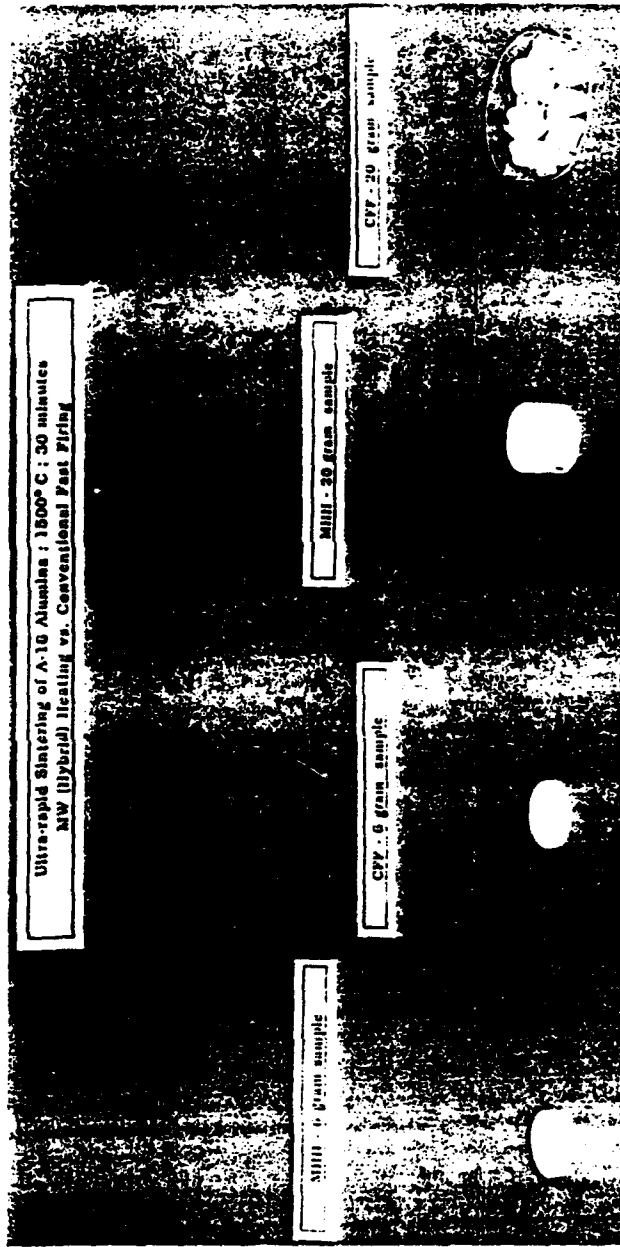
$\text{Li}_2\text{O} \cdot 2\text{SiO}_2$

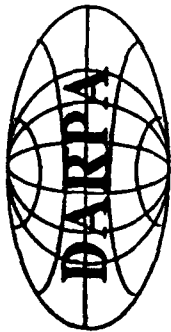
$\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

Crystallization

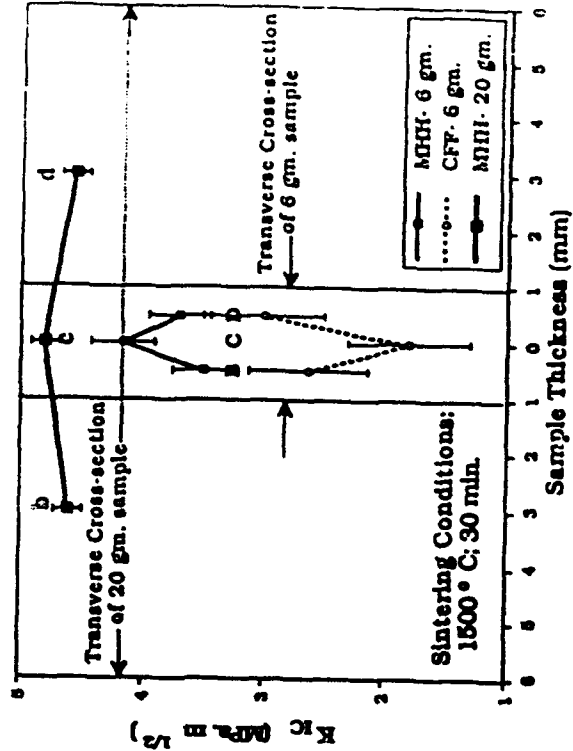
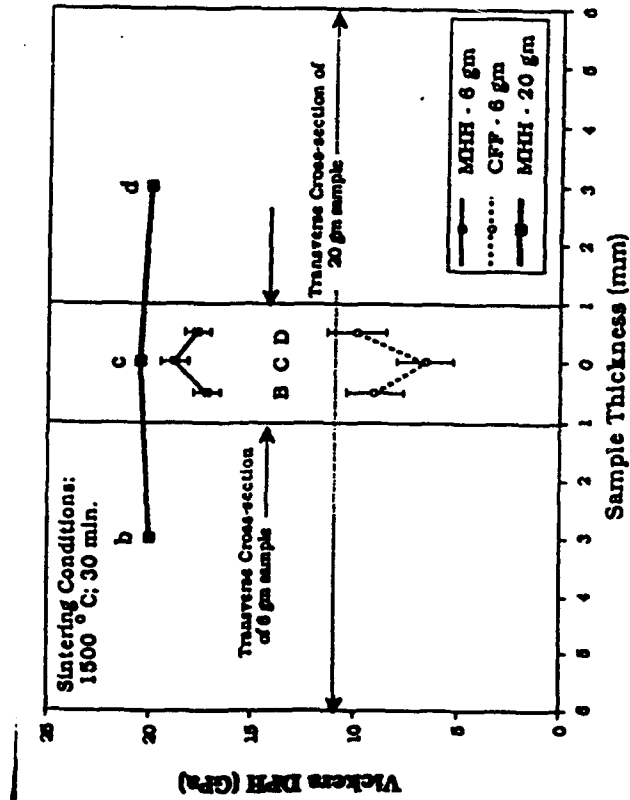


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



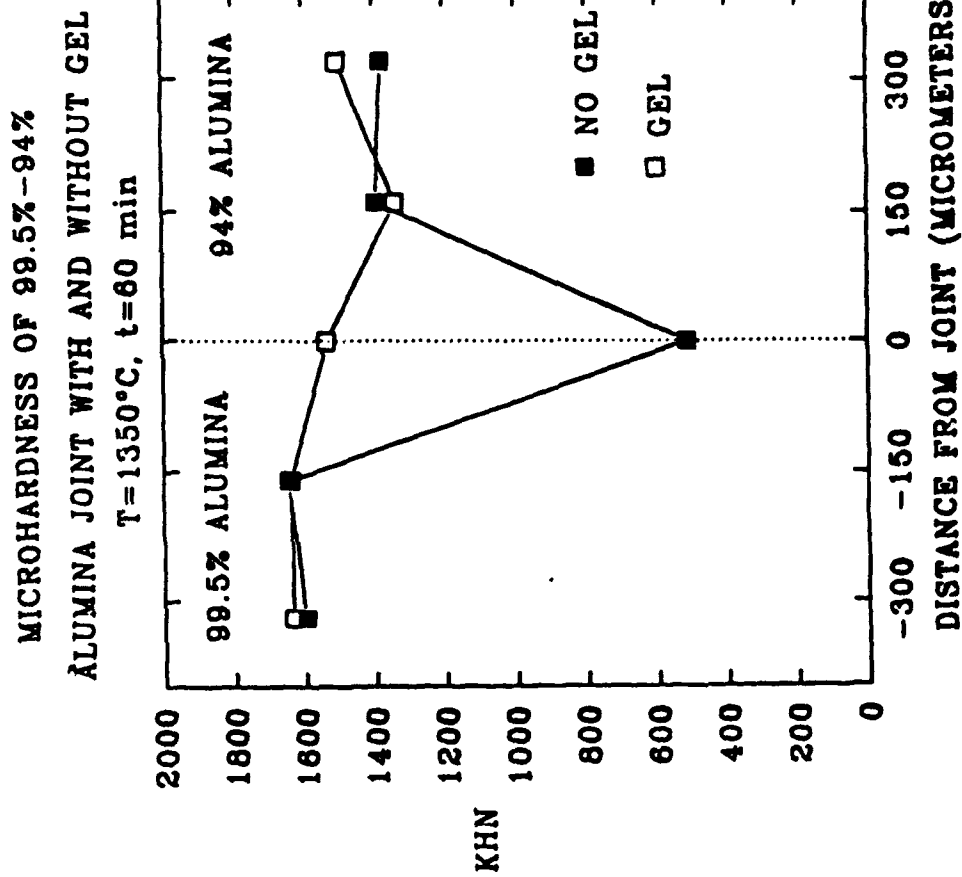


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS





INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS





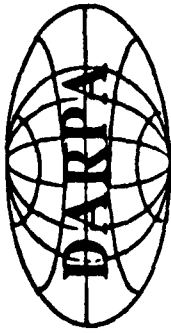
**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**



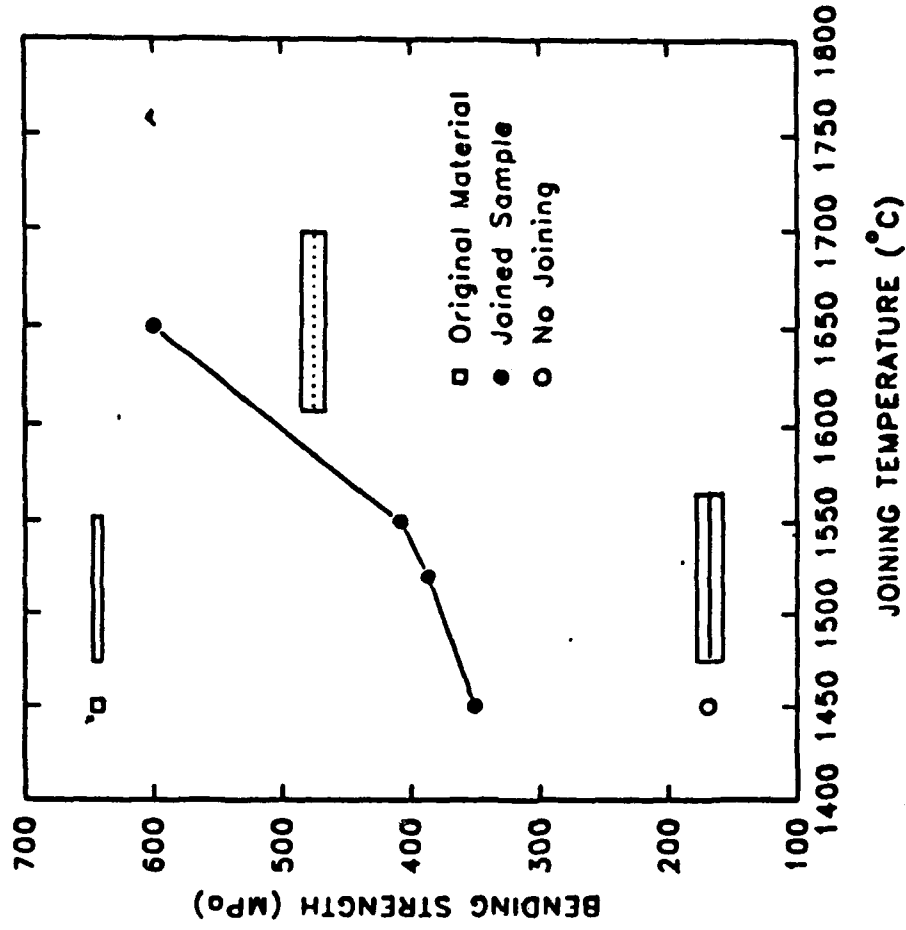
*** 99.5%-GEL-94% ALUMINA
 $T=1350^{\circ}\text{C}$, $t=60$ min**

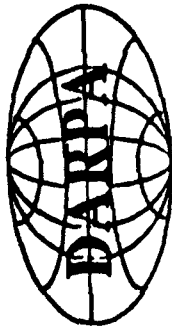


*** 99.5%-GEL-94% ALUMINA
 $T=1350^{\circ}\text{C}$, $t=60$ min**



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS





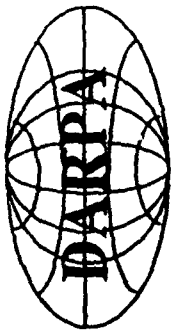
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

MICROWAVE CONTROLLED COMBUSTION SYNTHESIS (MICROCOM)

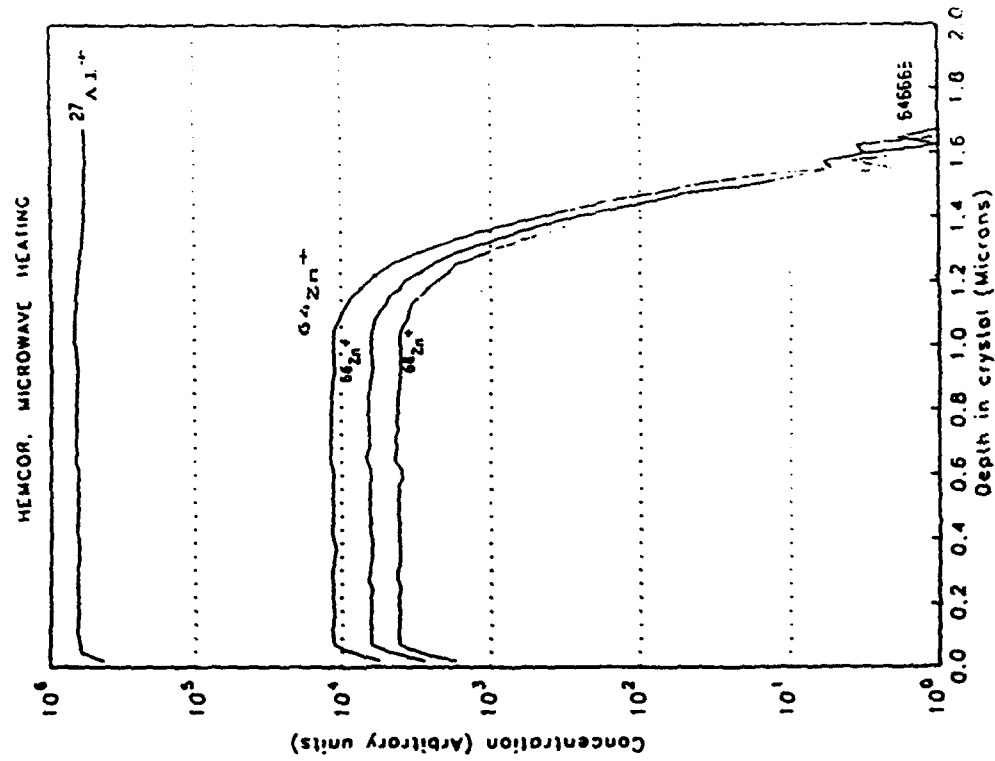
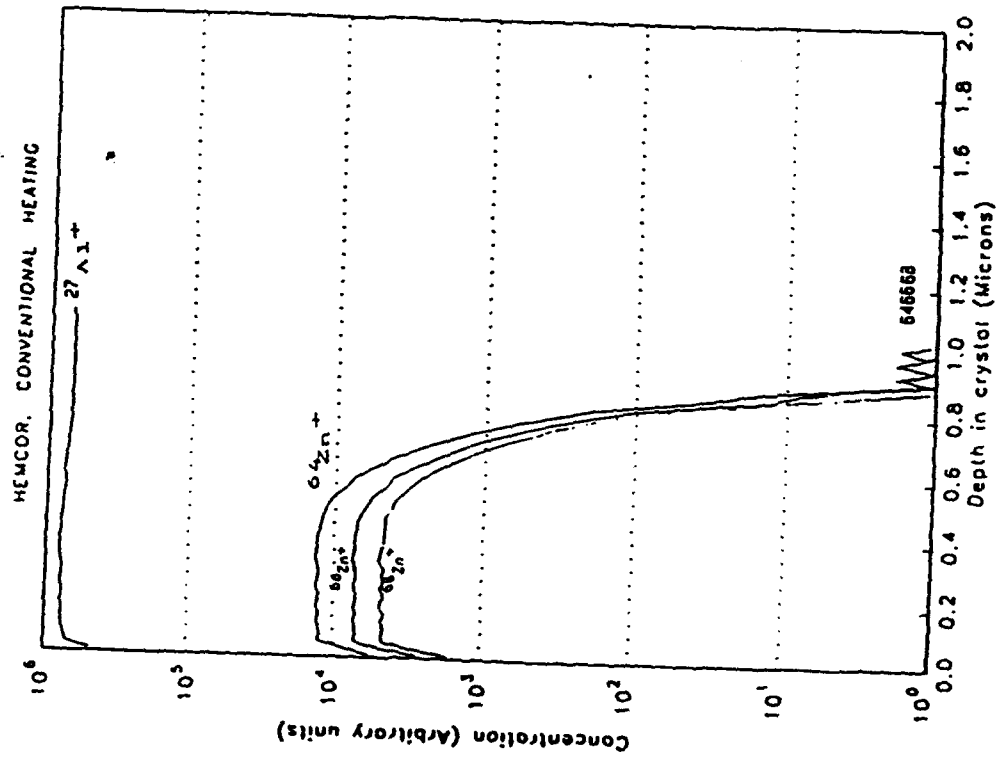
PROCESSING TIME:

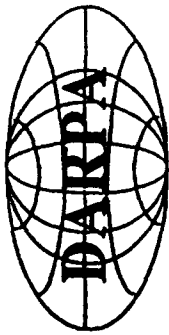


Microwave ignition and controlled combustion synthesis (MICROCOM). The reacted volume increases with increasing exposure to microwave energy. When the microwave energy is turned off, the combustion reaction halts.

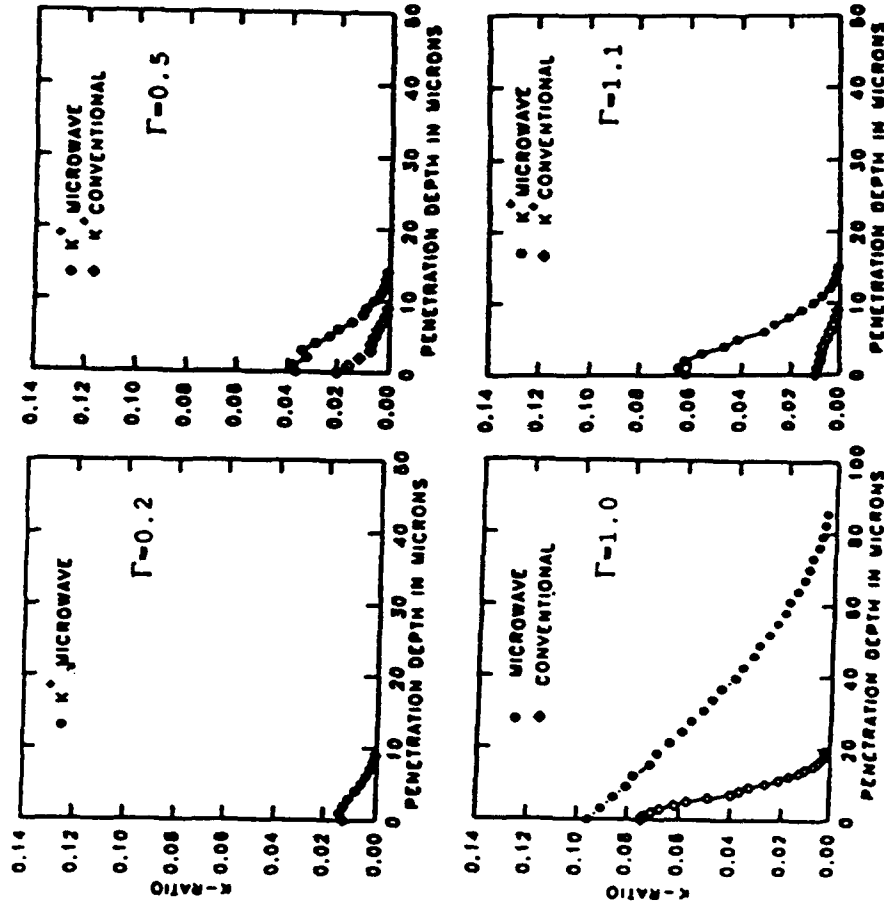


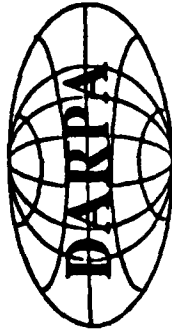
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS





INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS





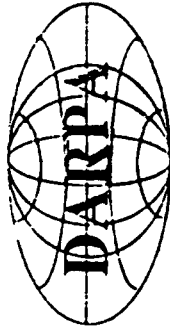
**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

**LOW EXPANSION MATRIX DEVELOPMENT
PROJECT GOALS**

*To evaluate $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ as
a potential matrix material.*

*To investigate sol-gel as an alternative processing route
to traditional glass-ceramic processing.*

*To investigate the use of microwave energy
for processing composites.*

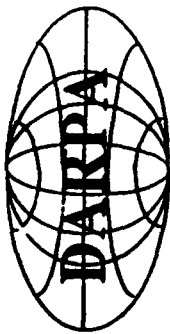


INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

WHY CELSIAN?

Celsian has several properties that make it attractive as a potential matrix material

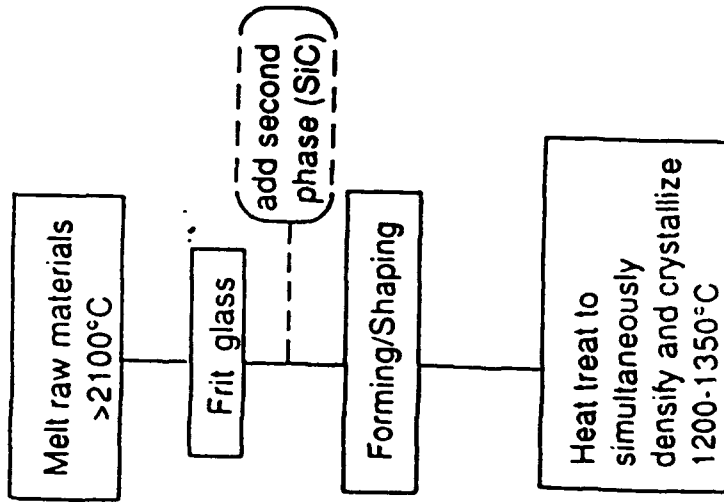
- CTE $2.3 \times 10^{-6}/^{\circ}\text{C}$
- Celsian phase stable to 1590 °C
- Formability
- Oxidation resistant
- Compatible with SiC fibers



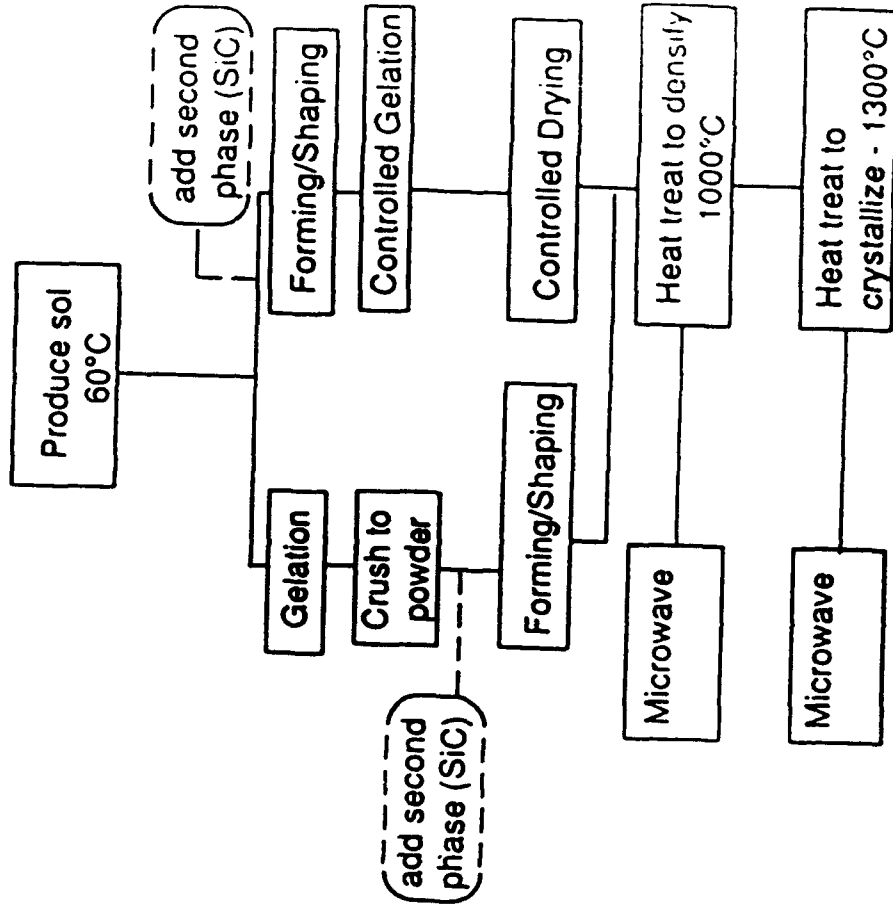
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

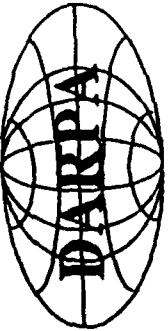
THE GLASS CERAMIC PROCESSING OF CELSIAN

TRADITIONAL



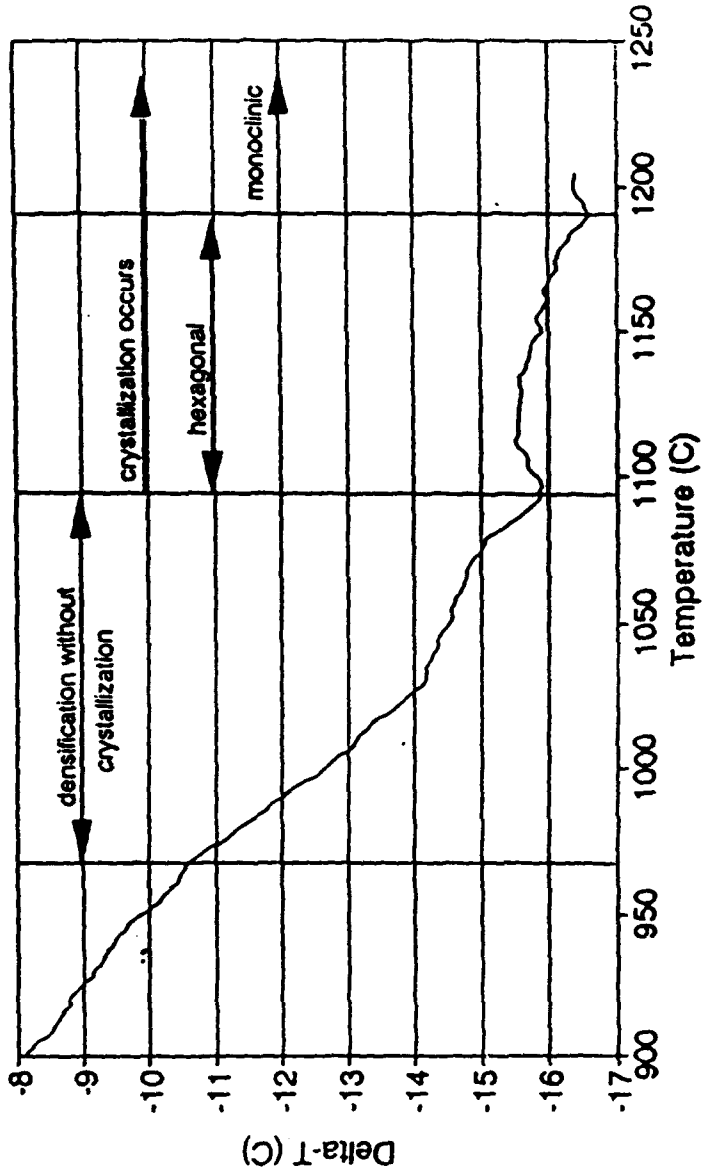
SOL-GEL PROCESS

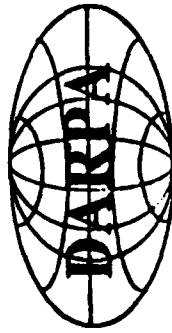




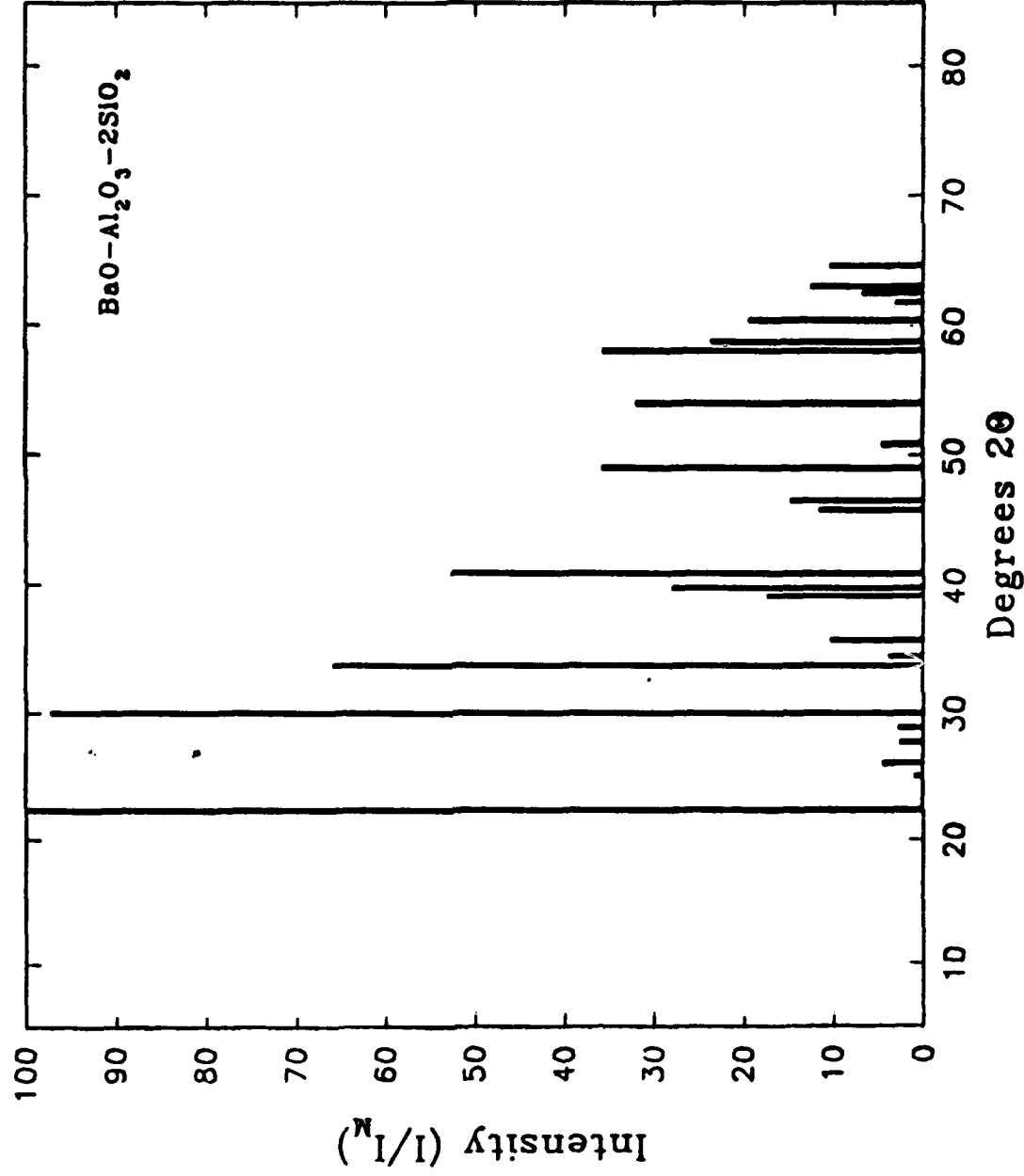
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Barium Aluminosilicate + 10 wt% CuO
dried at 850 C



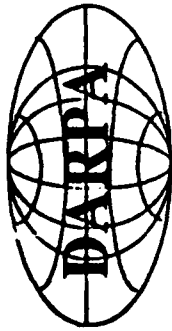


INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

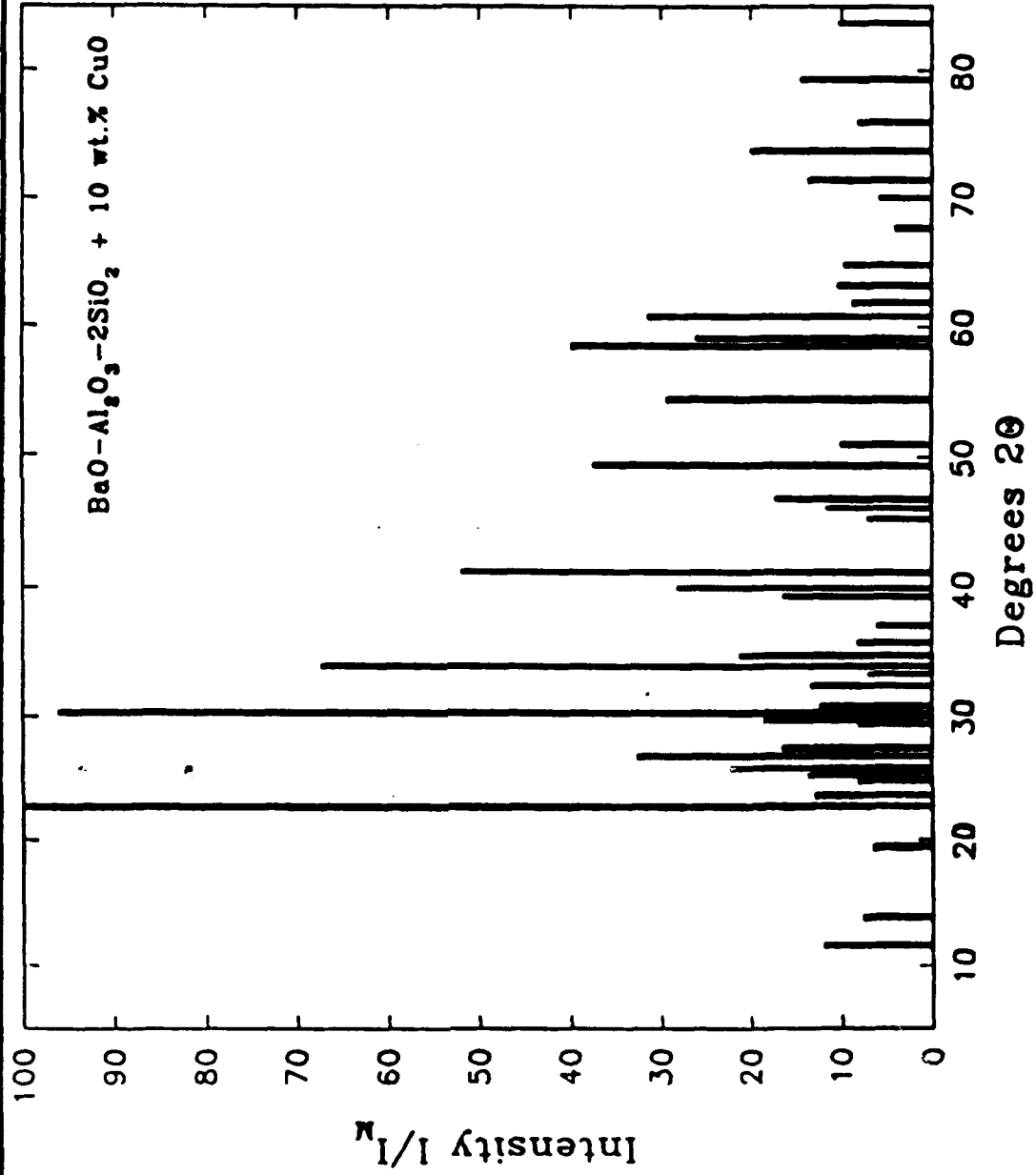


All peaks correspond to the hexagonal phase

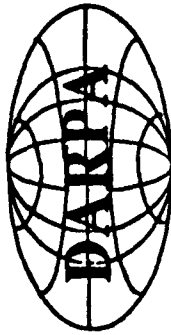
MSIE — UNIVERSITY OF FLORIDA



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS



most peaks correspond to the monoclinic phase



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

ACCOMPLISHMENTS

Sintering and annealing can be accomplished at lower temperatures and in less time.

Extremely rapid/uniform heating rates are possible without thermal shocking.

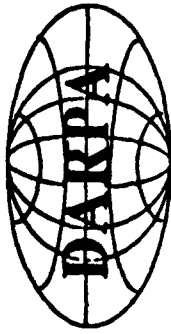
Better microstructural homogeneity and properties, and this improves even more with scale-up.

SHS reactions involving powders can be performed efficiently in the microwave. In some systems, SHS of shaped powders can be controlled with the potential for fabricating Functionally Gradient Materials (FGMs).

With the combined use of sol-gel processing, ceramics can be joined efficiently using microwave energy.

Surfaces can be modified to greater depths in shorter times in the microwave oven. Also of importance, the chemical profiles can be tailored (in systems studied) to improve the mechanical properties.

Crystallization can be performed at lower temperatures in the microwave oven.



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

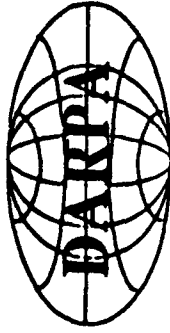
ACCOMPLISHMENTS cont.

**Produced amorphous $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ glass
using two different sol-gel routes.**

**Determined the processing temperatures
for densification and crystallization.**

**Evaluated CuO as a microwave-absorbing additive
to facilitate the crystallization of celsian.**

**Crystallized samples using microwave hybrid heating
and stand-alone microwave energy.**



INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

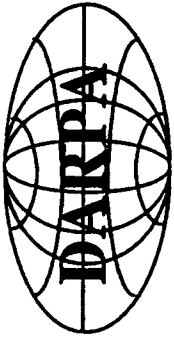
FUTURE WORK

Fabricate composites using both hybrid and stand-alone microwave heating.

Evaluate microwave-transparent matrix materials reinforced with

- microwave-absorbing SiC fibers
- microwave-transparent mullite fibers
- transparent and absorbing fibers with microwave-tailored coatings (i.e., CVD and sol-gel).

Pursue work proposed to other agencies to investigate fundamentals of microwave/materials interactions.



**INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS**

PROCESSING OF CERAMIC-MATRIX COMPOSITES

Principal Investigator: M.D. Sacks

MISE

UNIVERSITY OF FLORIDA

PROCESSING OF CERAMIC-MATRIX COMPOSITES

- **FIBER DEVELOPMENT**
- **MATRIX DEVELOPMENT**
- **COMPOSITE FABRICATION**

Approaches

- **Viscous Processing**
- **Infiltration Processing**

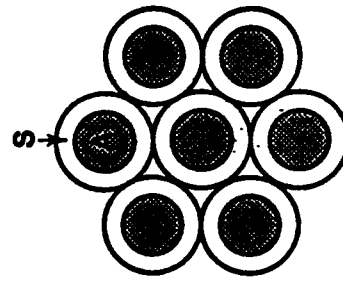
Potential Advantages

- **Near Net Shape Fabrication**
- **High Relative Density (Low Porosity)**
- **Low Processing Temperatures**

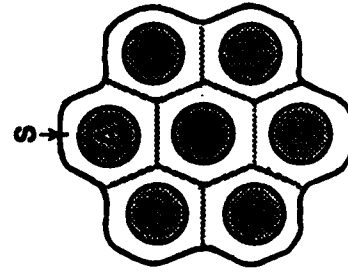
TRANSIENT VISCOUS SINTERING AND PRESSURE-ASSISTED TRANSIENT VISCOUS SINTERING

Consolidation of "microcomposite" powders by viscous deformation (with or without applied pressure) and subsequent transformation (partially or completely) to a crystalline ceramic.

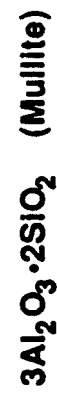
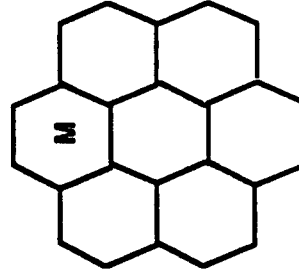
Transient Viscous Sintering of Mullite

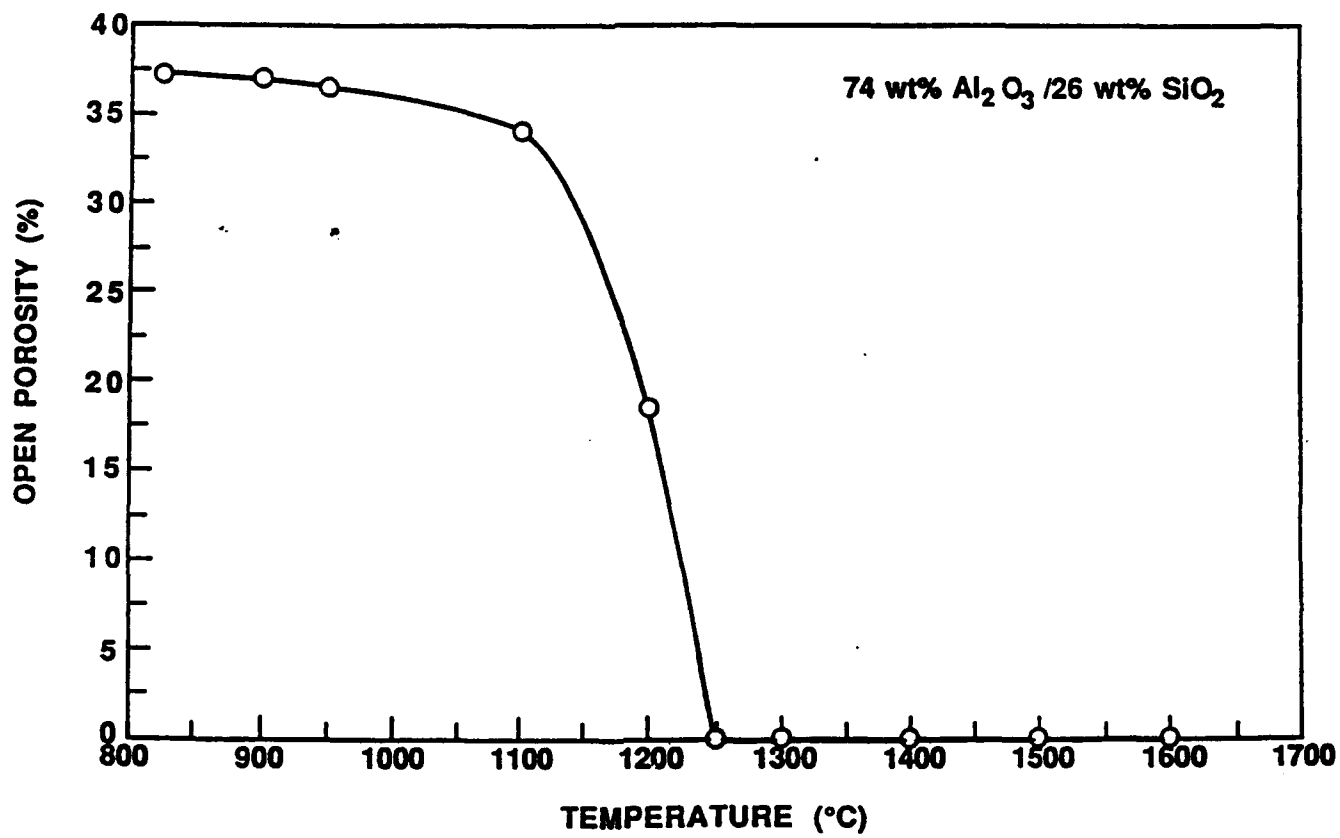
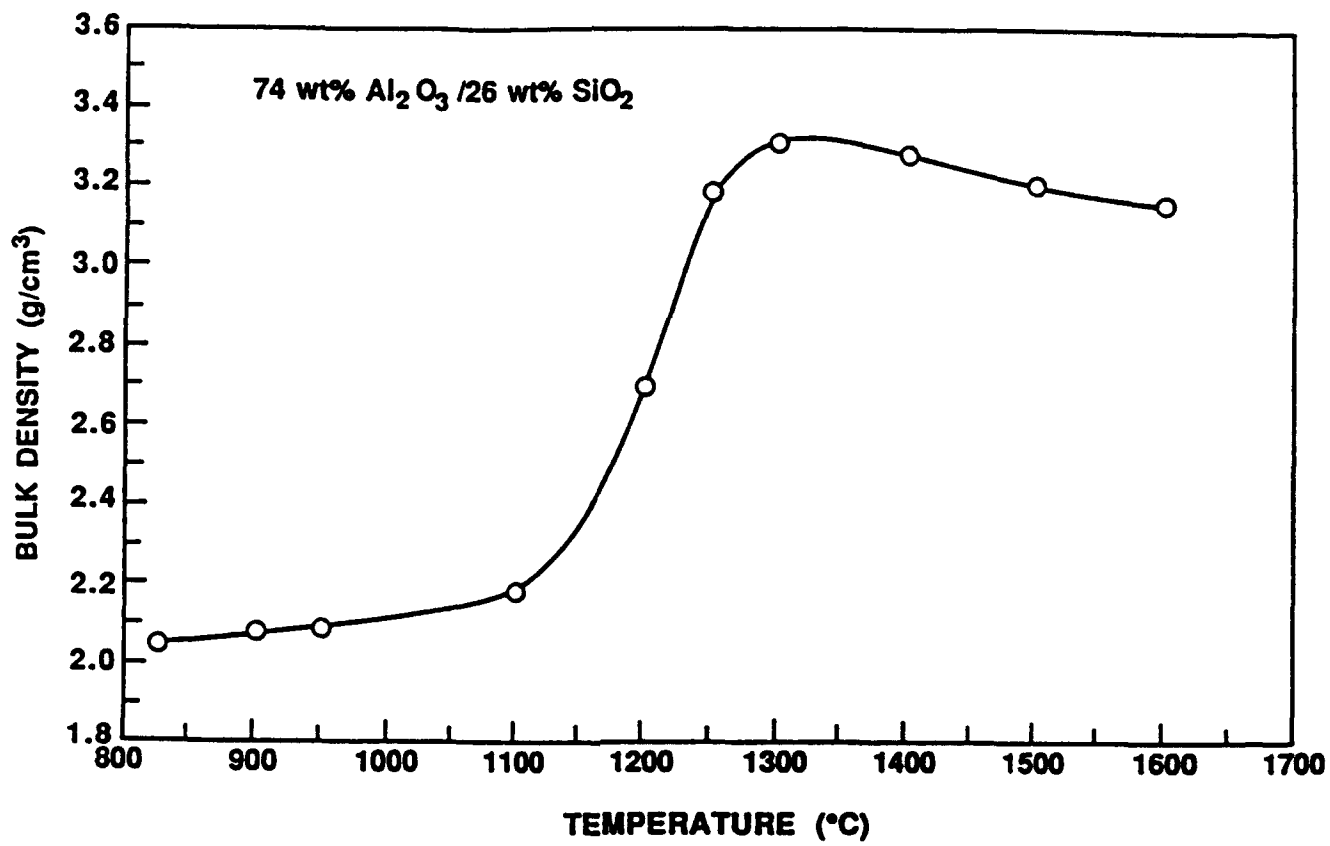


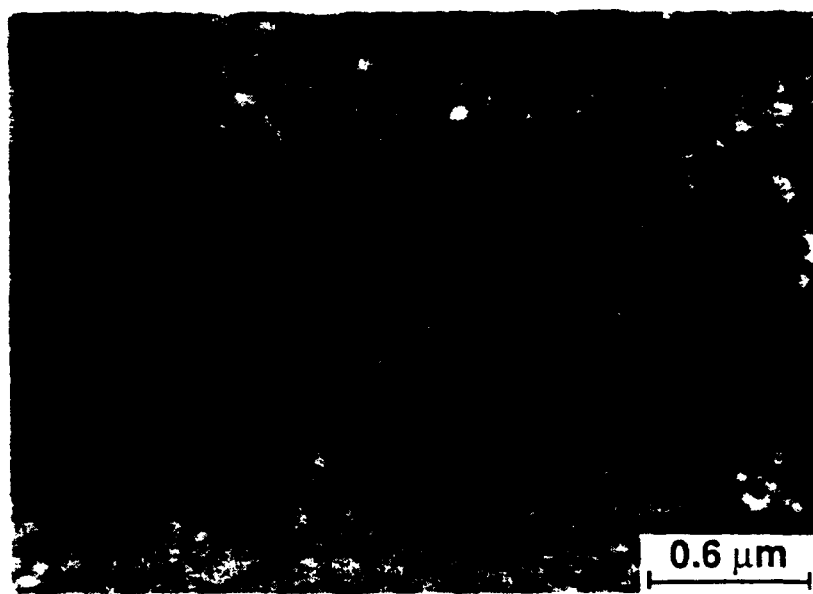
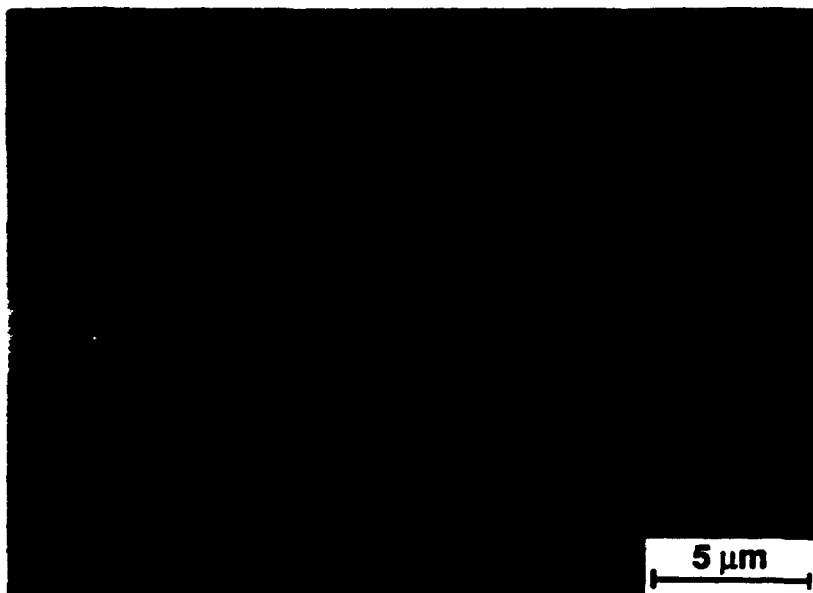
Densification

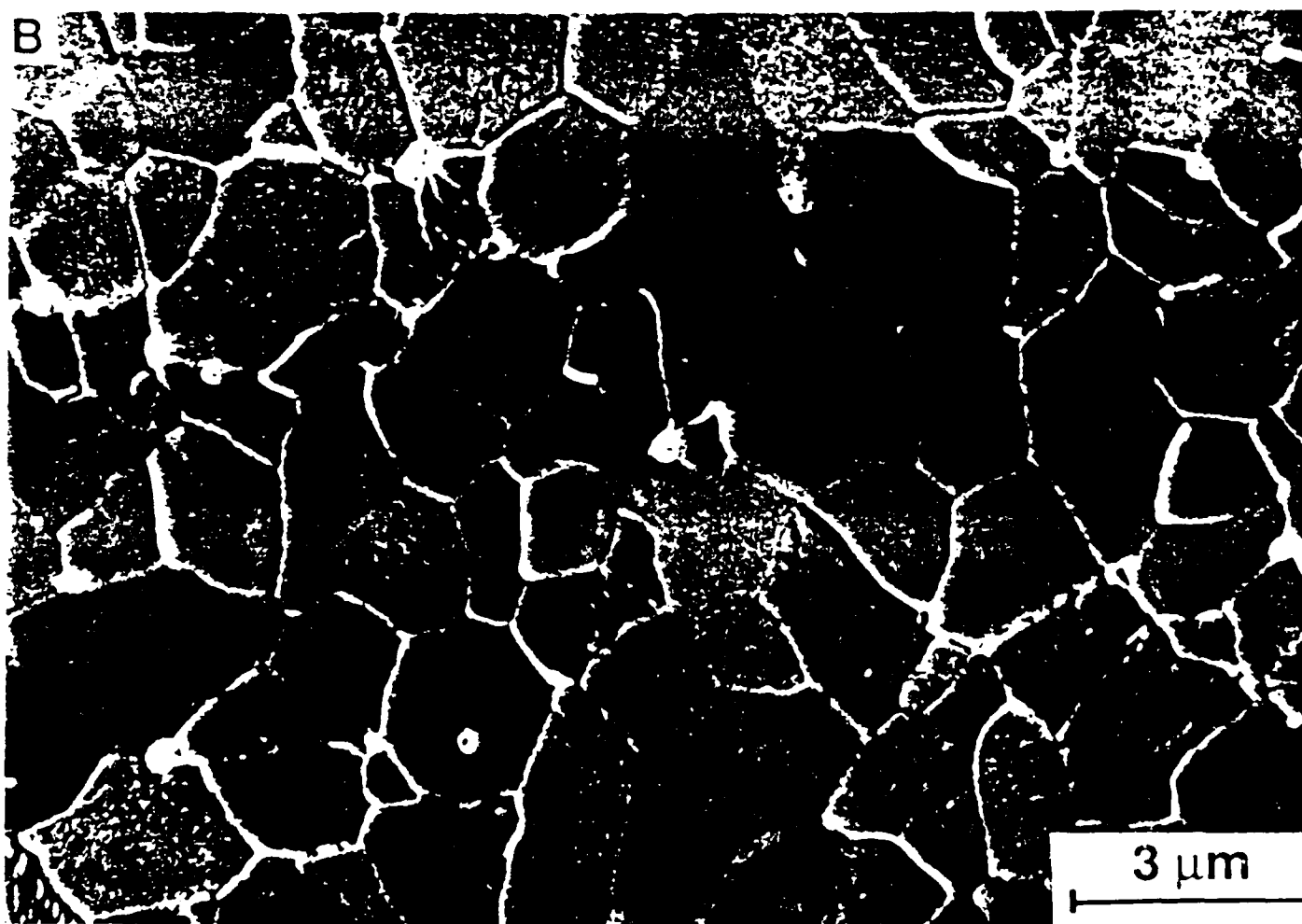
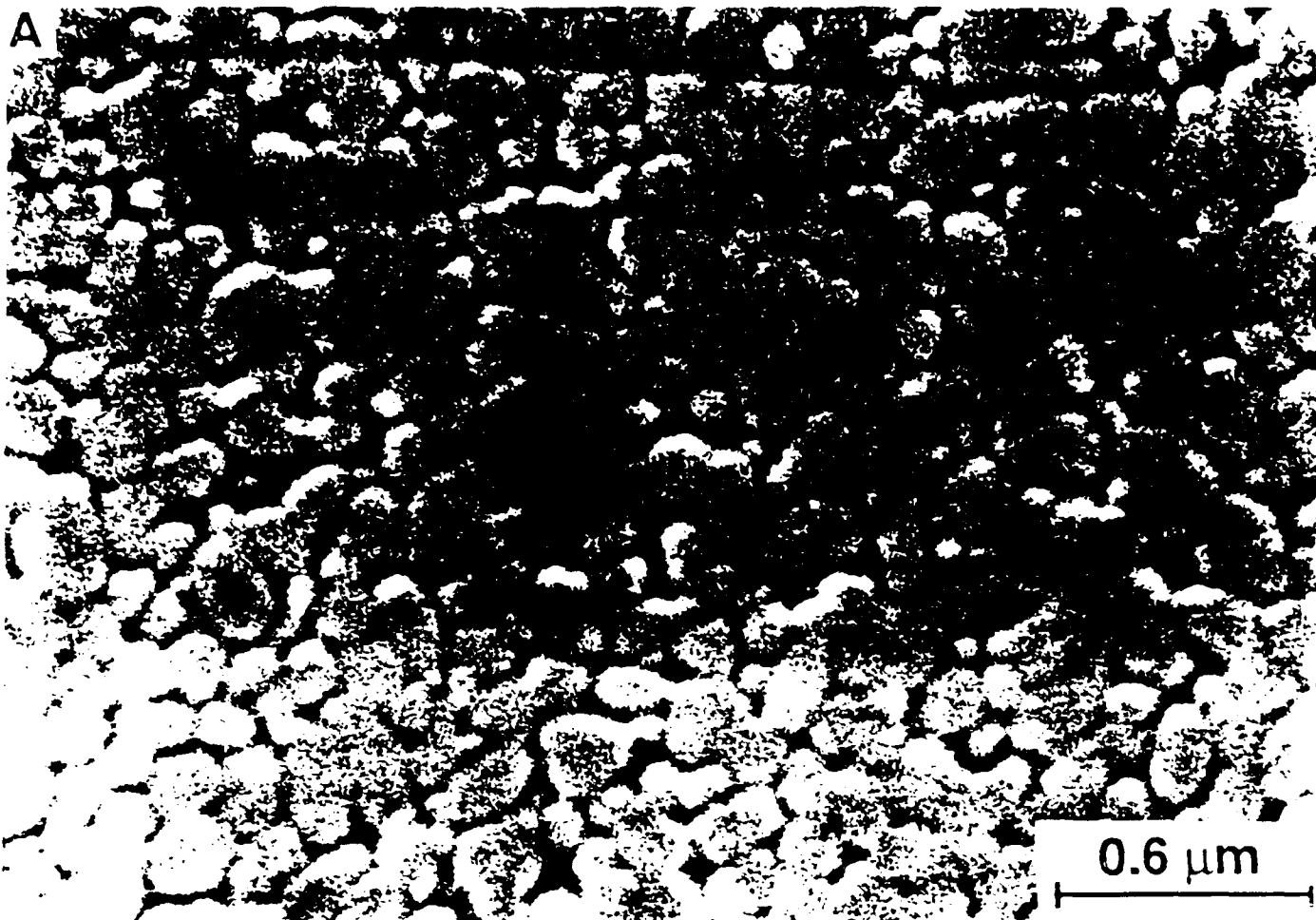


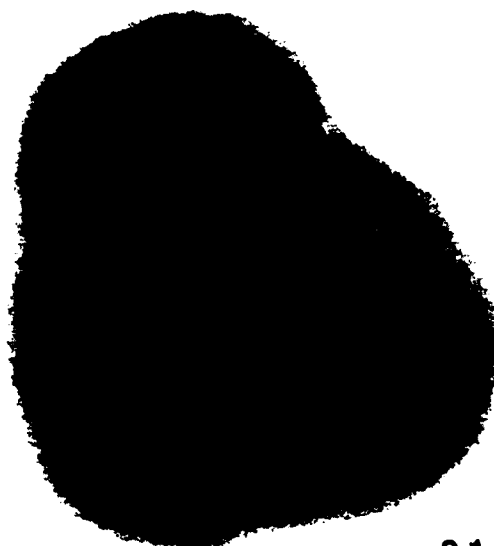
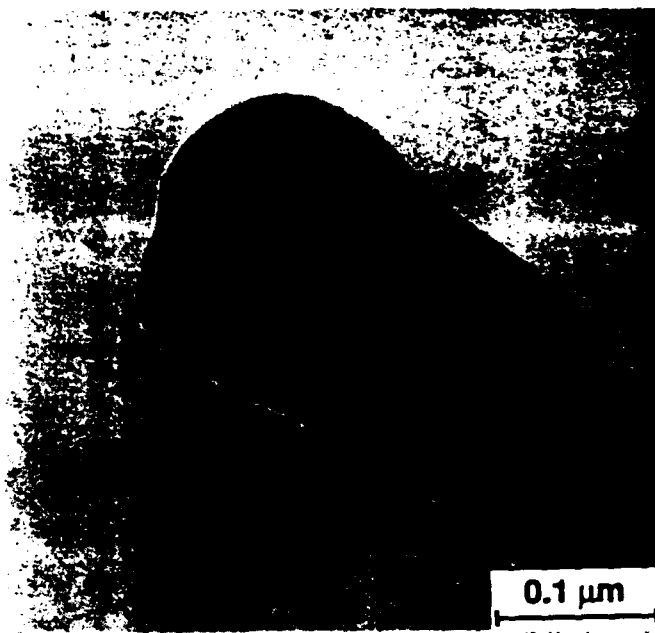
Chemical
Reaction



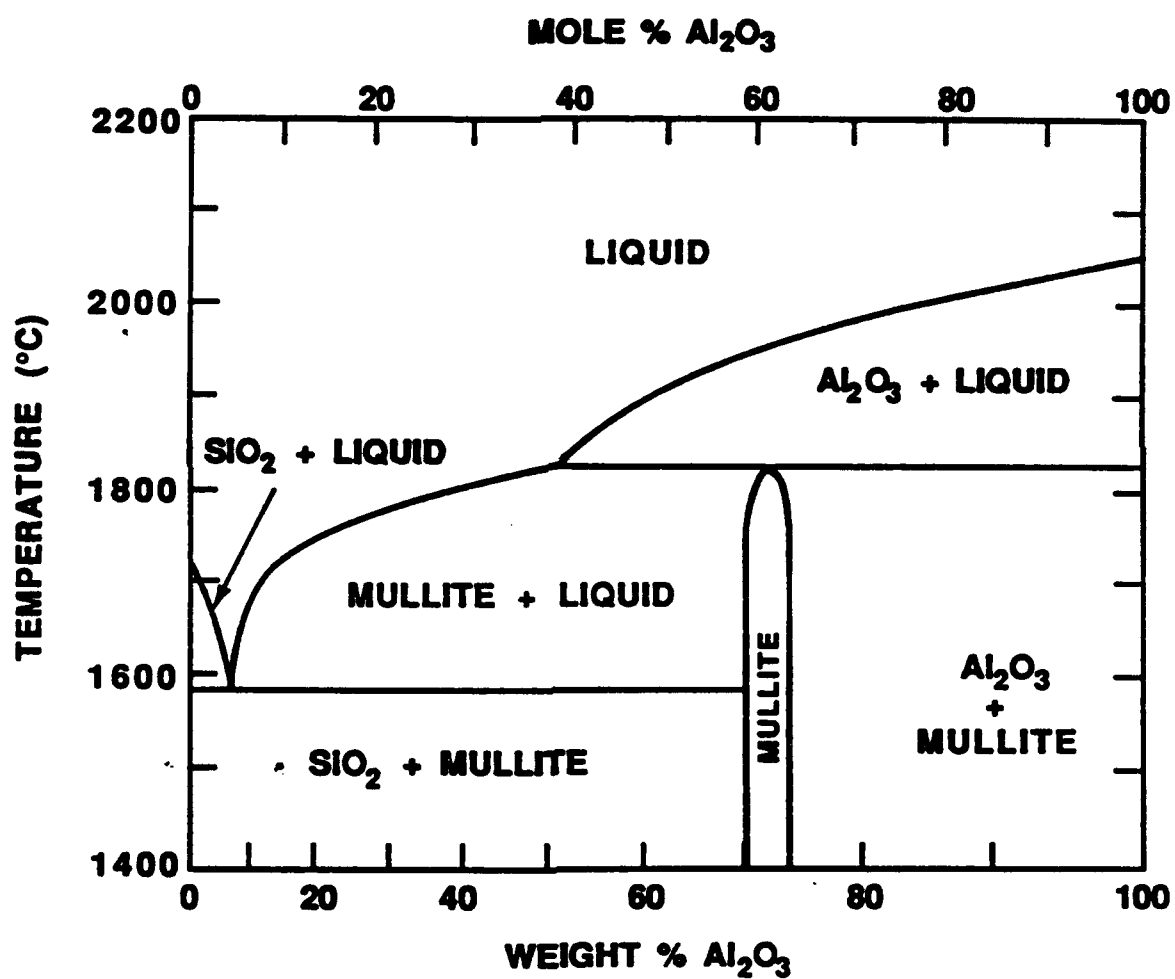




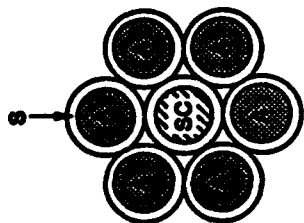




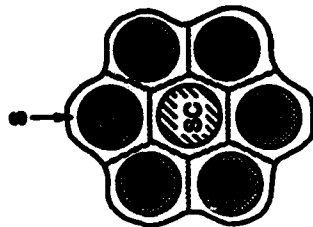
SiO_2 - Al_2O_3 PHASE DIAGRAM



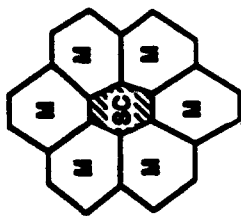
FABRICATION OF MULLITE/SILICON CARBIDE COMPOSITES



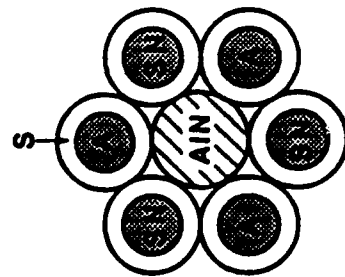
↑
Densification



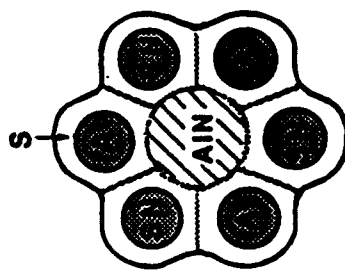
↑
Chemical Reaction



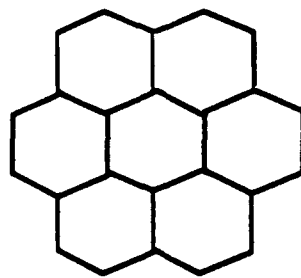
TRANSIENT VISCOUS SINTERING

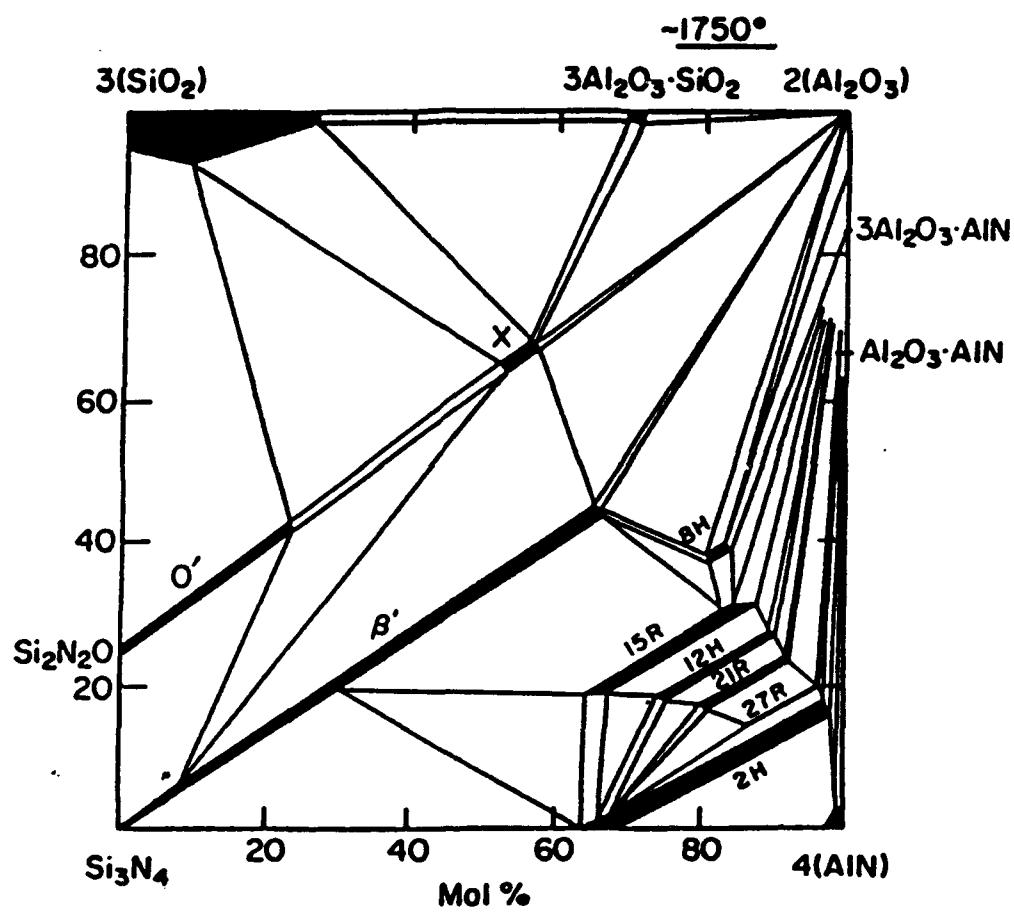


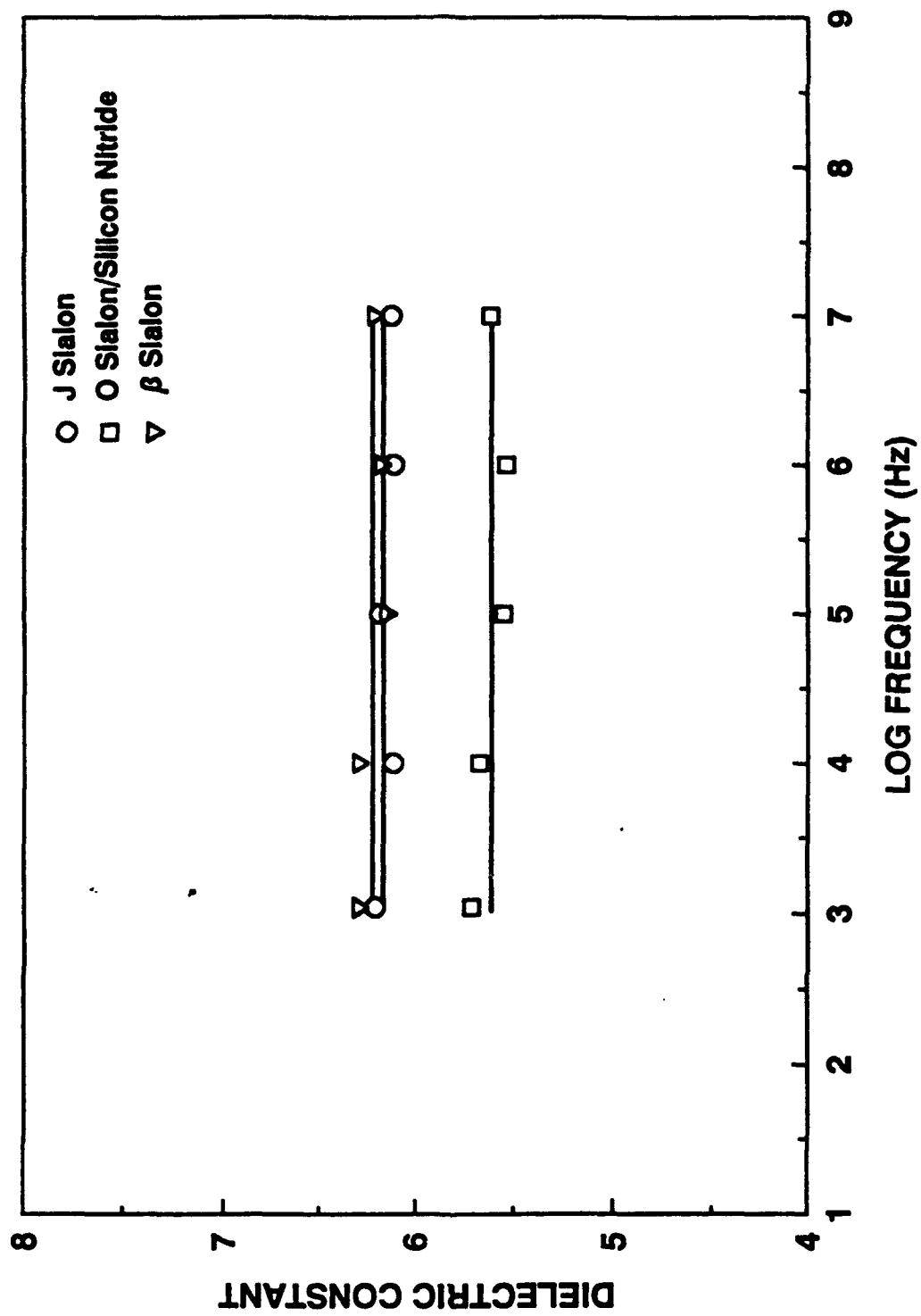
Densification



Chemical Reaction







**CERAMICS AND COMPOSITES PREPARED BY VISCOUS AND
TRANSIENT VISCOUS SINTERING OF SILICA-COATED PARTICLES**

MULLITE

SILICA/ALUMINA

MULLITE/ALUMINA

MULLITE/SILICA

MULLITE/ZIRCONIA

MULLITE/SILICON CARBIDE PARTICLES

MULLITE/SILICON CARBIDE WHISKERS

SILICA/SILICON NITRIDE

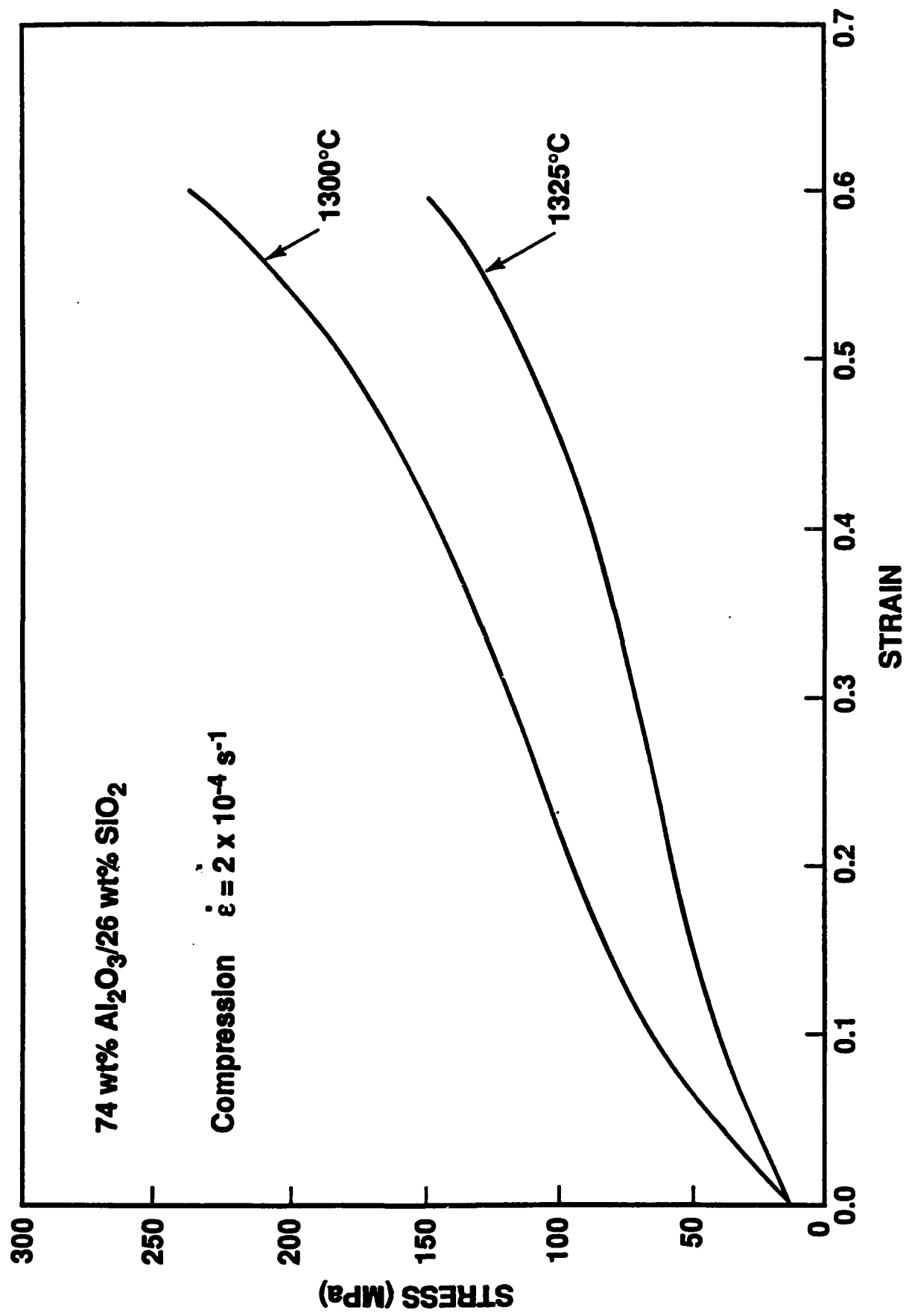
SIALON (β , O, J PHASES)

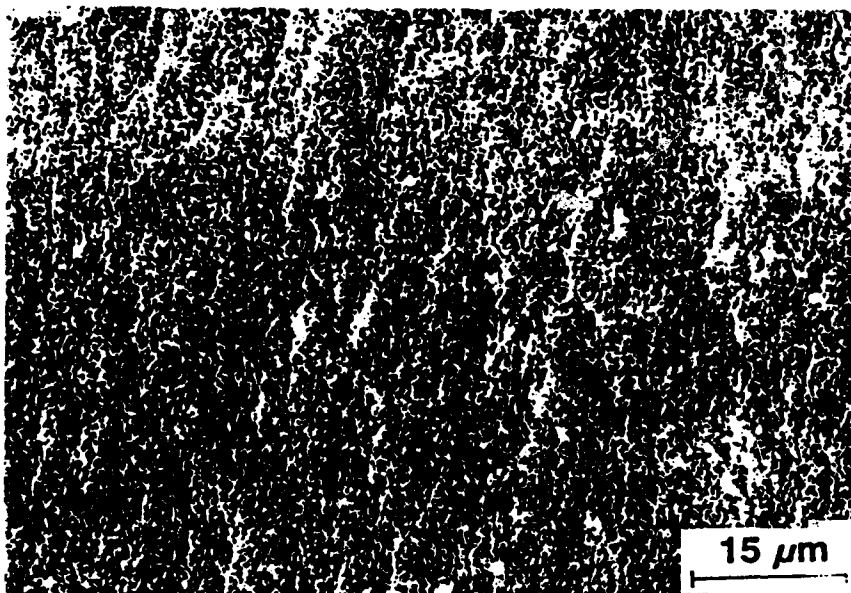
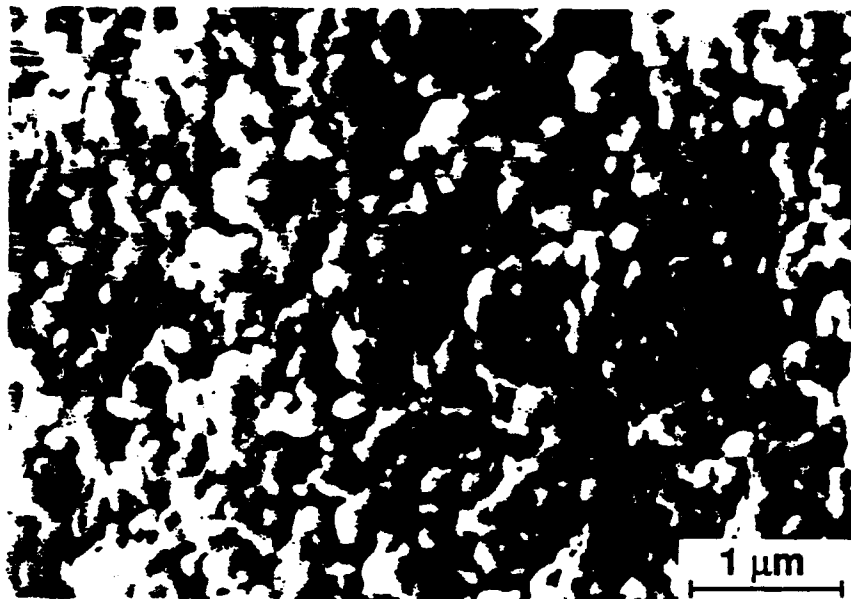
SIALON/ALUMINA

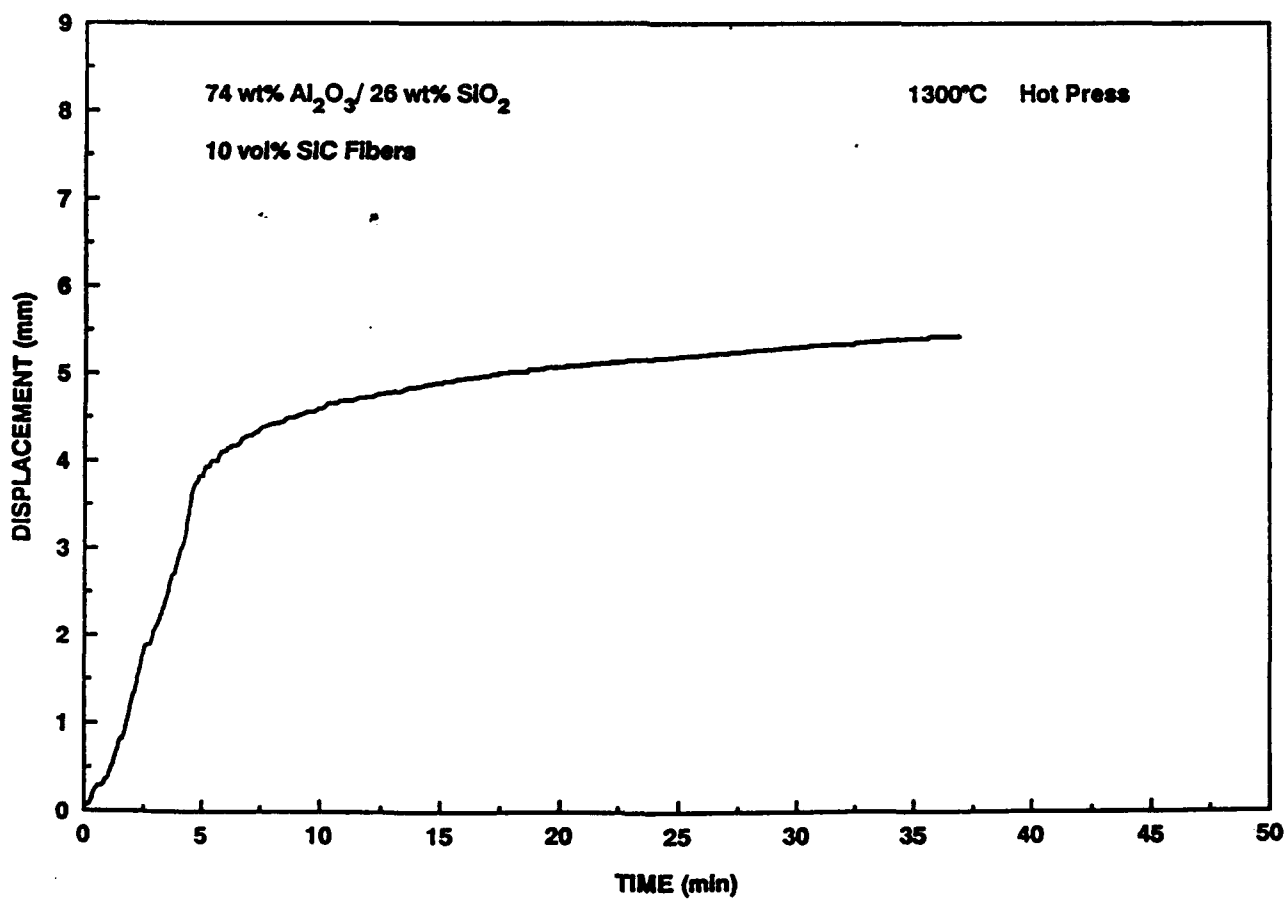
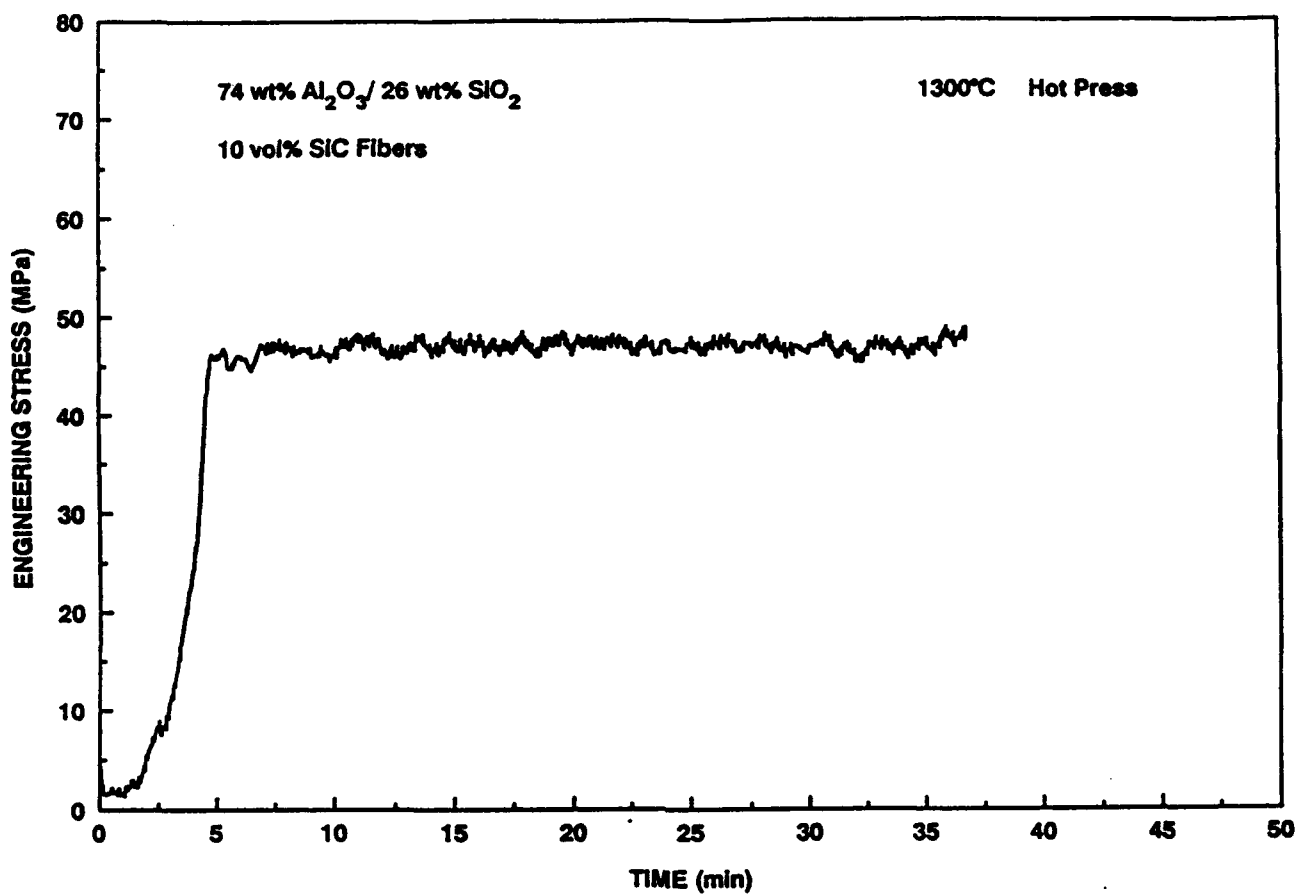
SIALON/SILICON NITRIDE

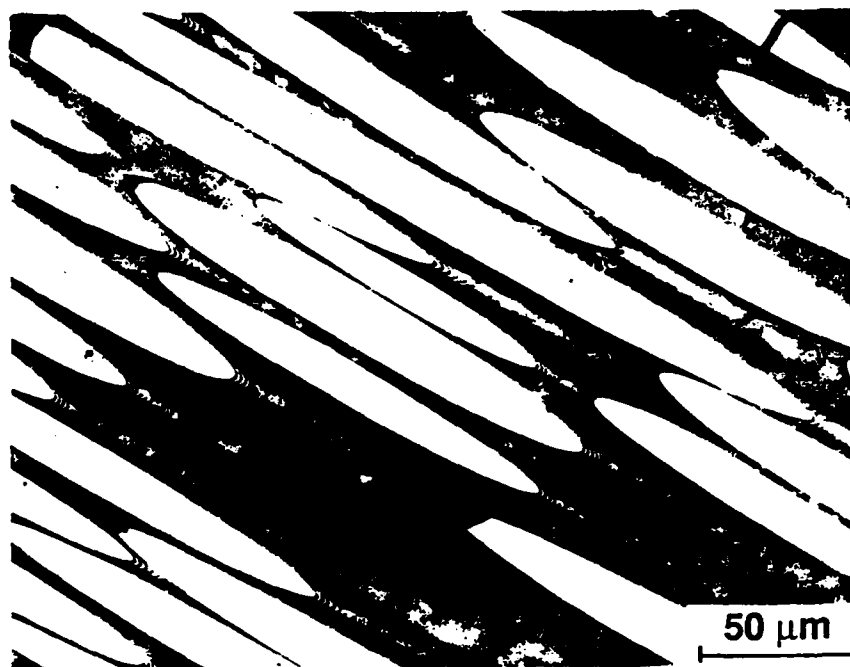
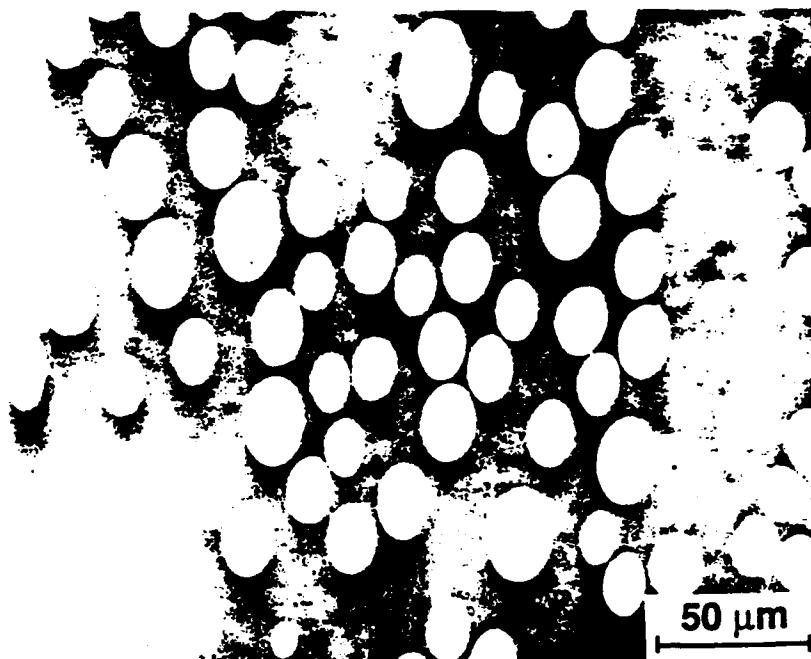
Recent Developments in Viscous Processing

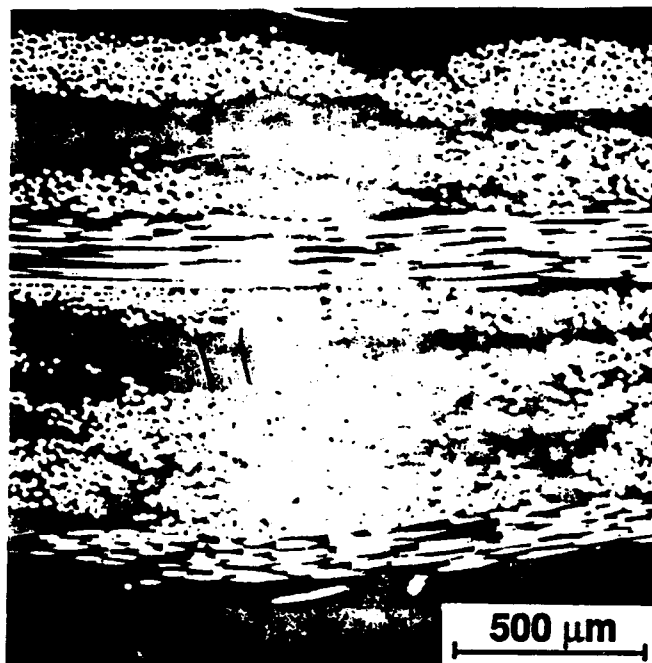
- **Pressure-Assisted Transient Viscous Sintering (PATVS)**
(fiber-reinforced composites)
- **Seeded Phase Transformations**
(lower processing temperatures, finer-grain microstructures)
- **Microcomposite Particles with Multicomponent Coatings**
(expanded range of compositions, lower processing temperatures)

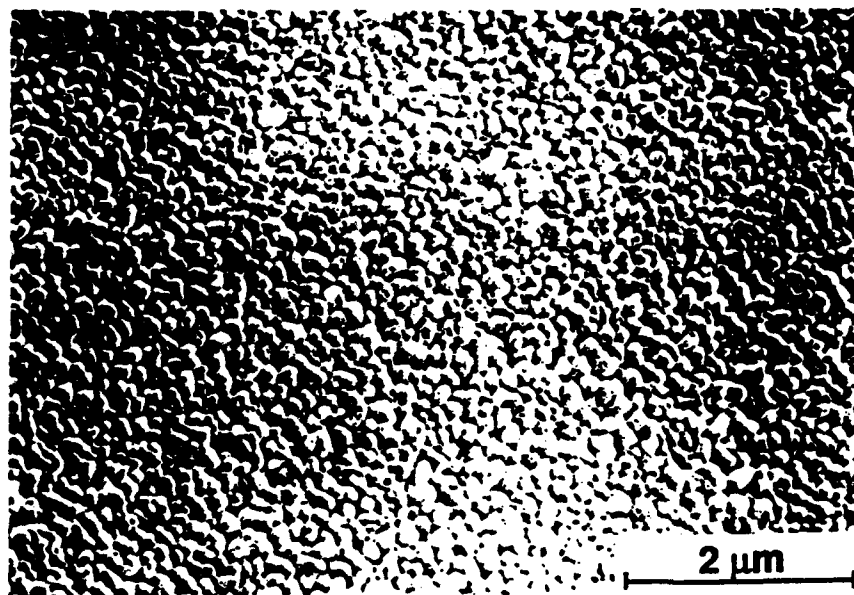
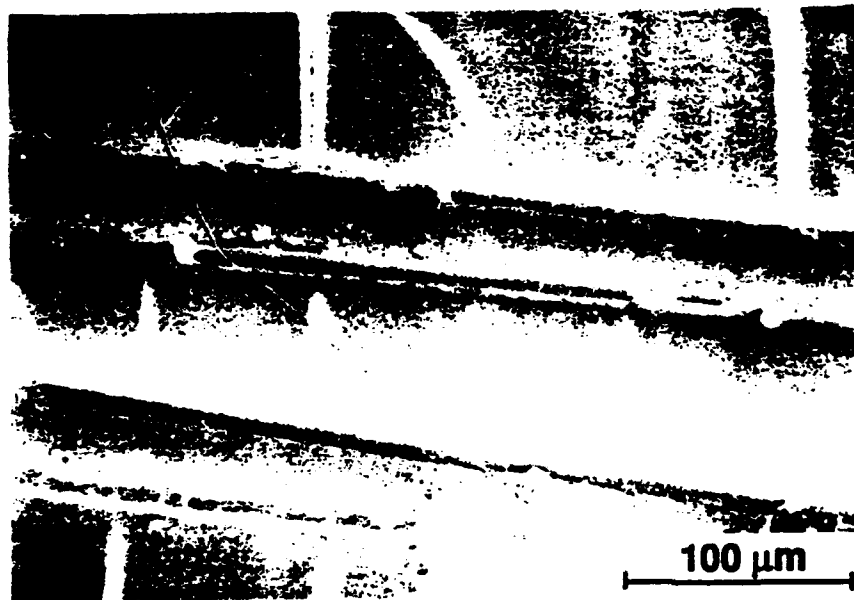






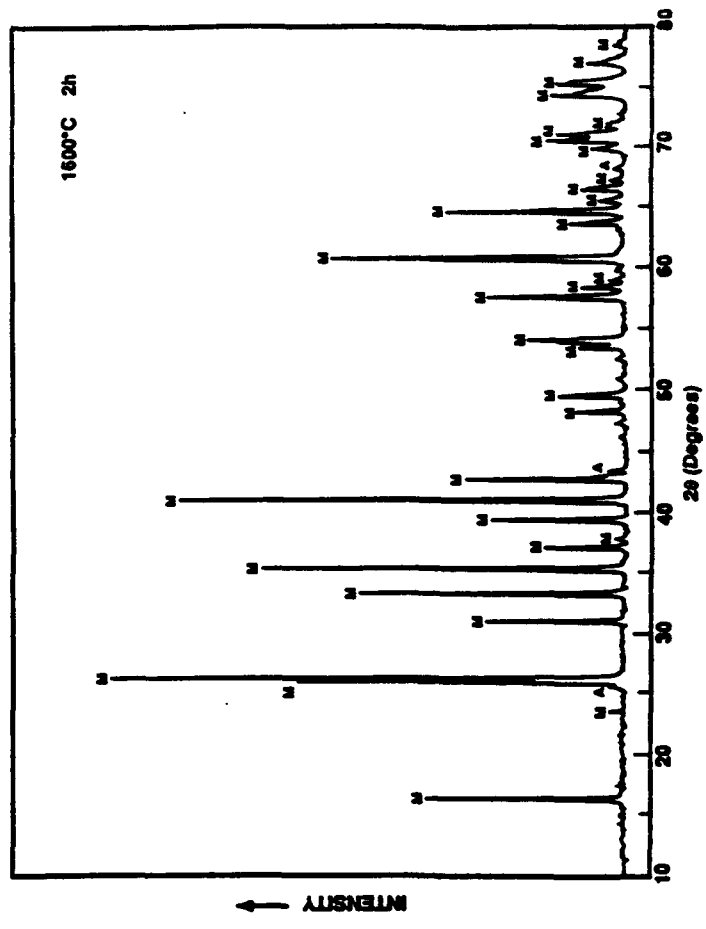
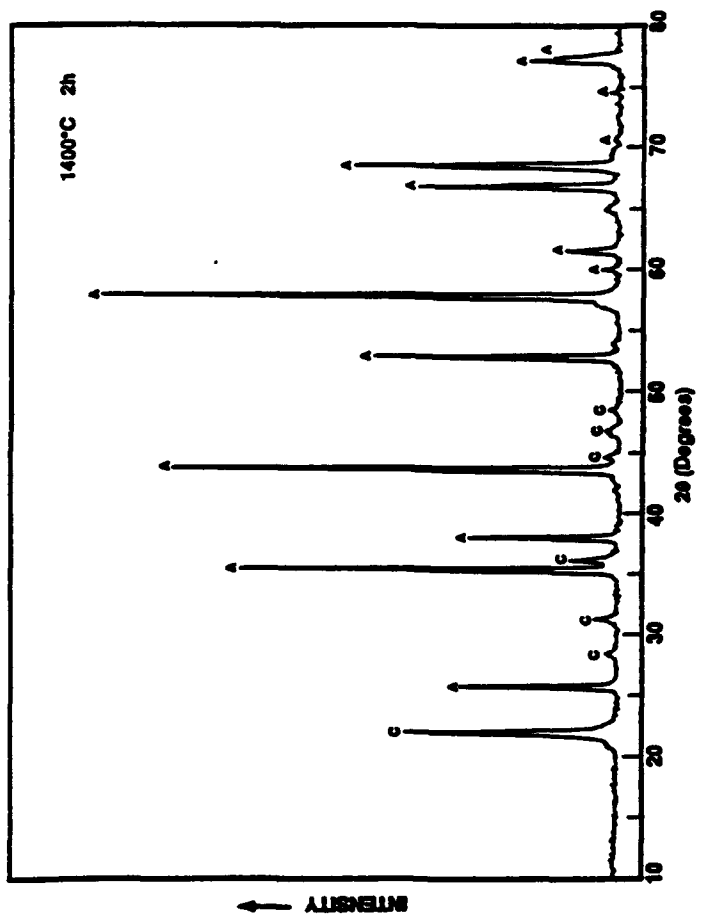
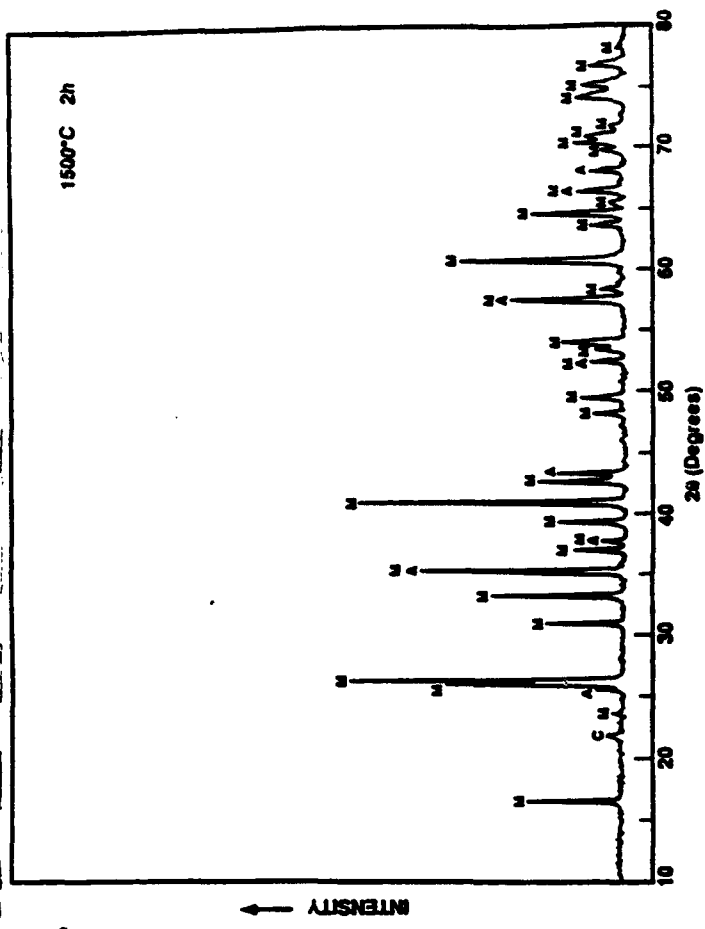
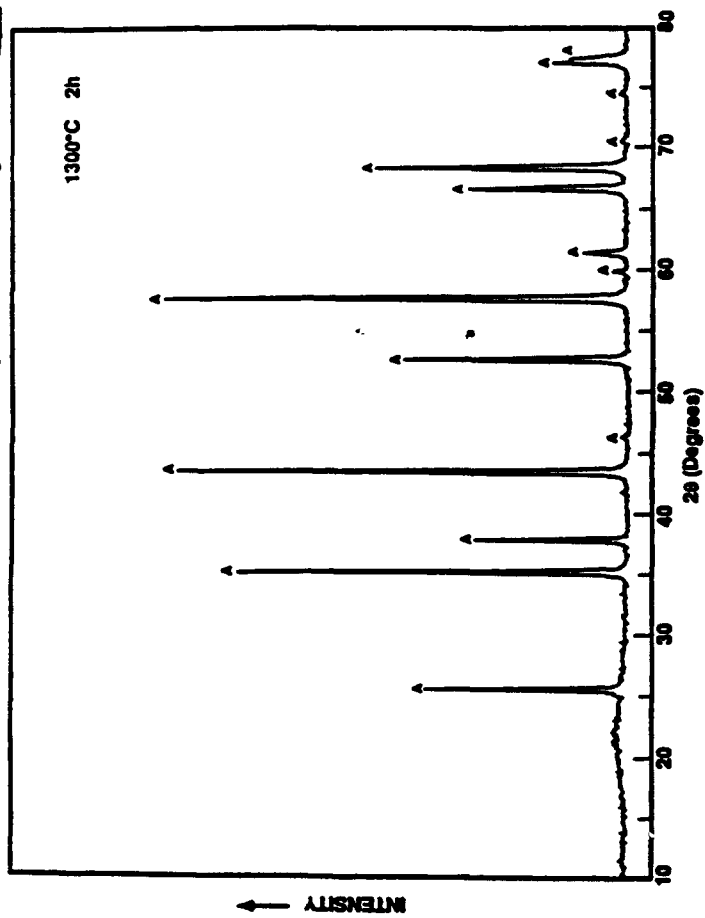


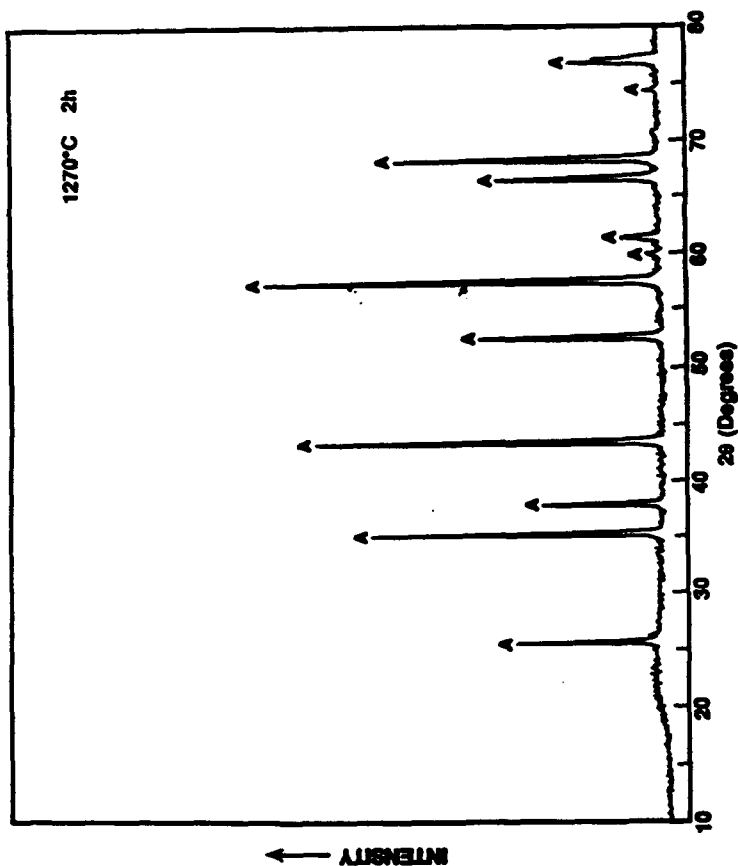
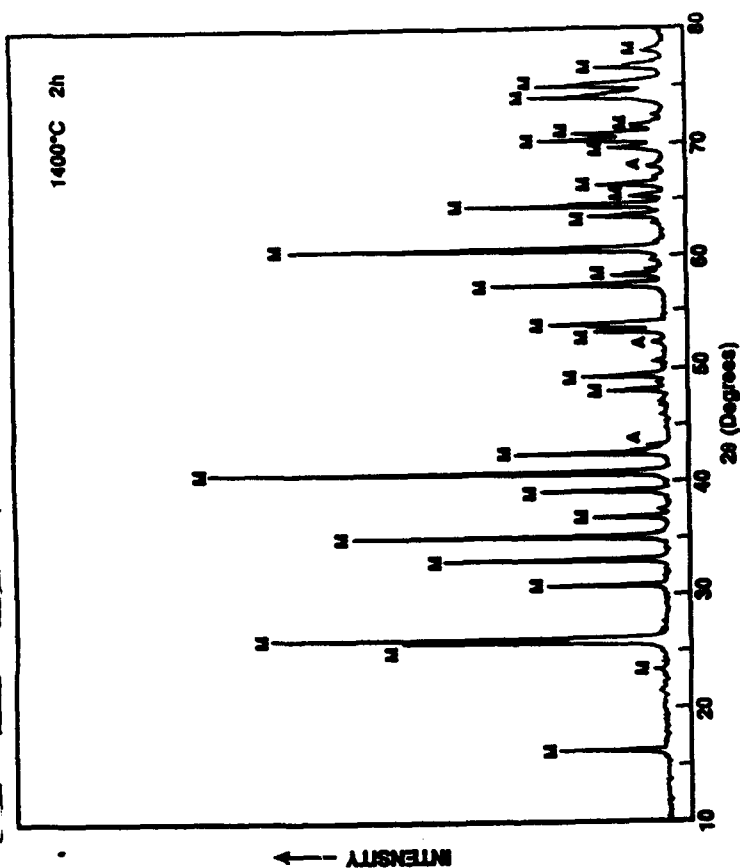
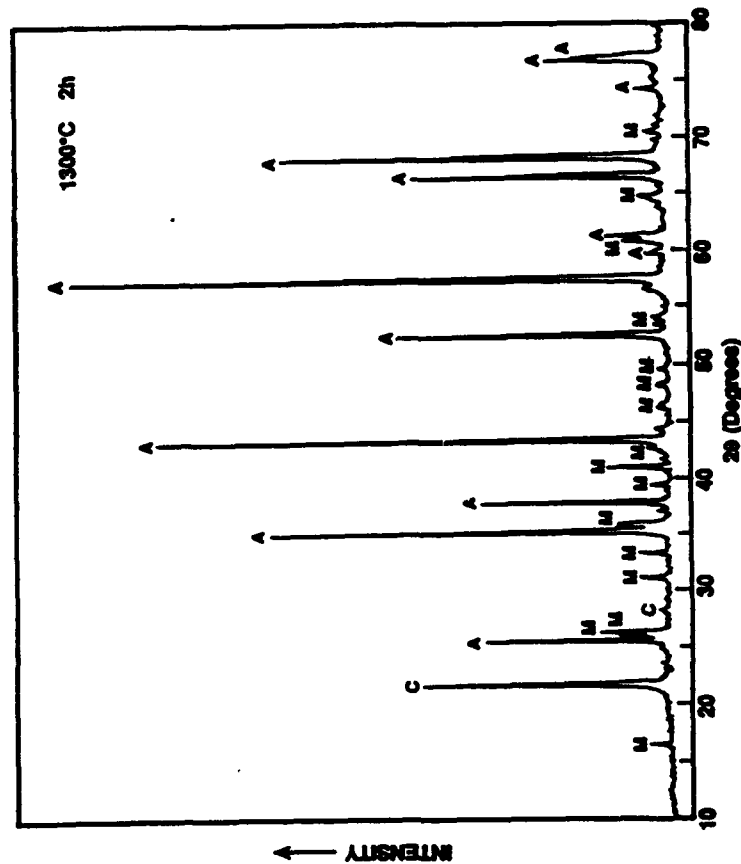
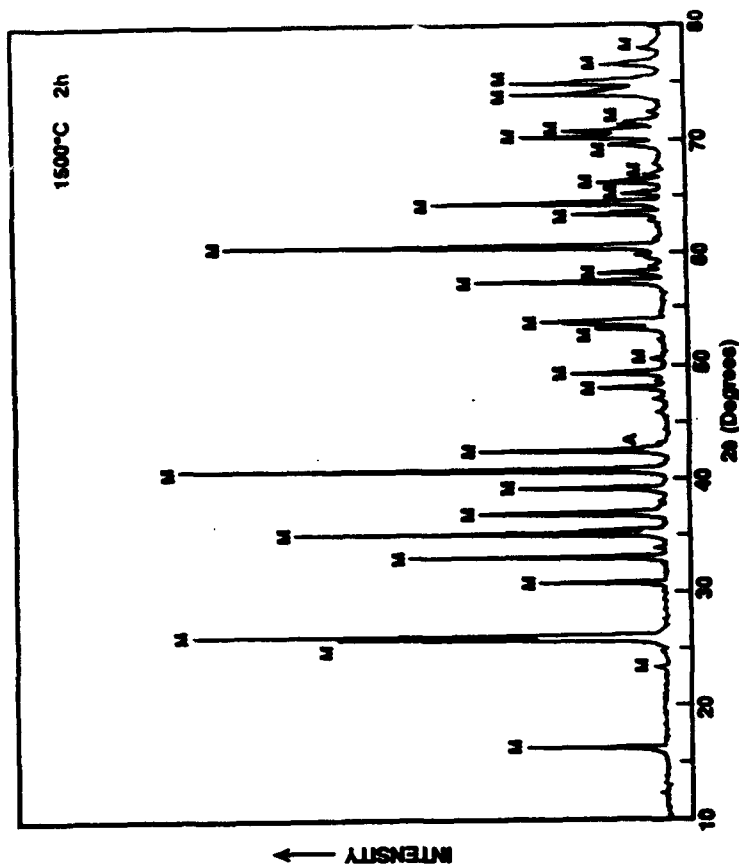




Recent Developments in Viscous Processing

- **Pressure-Assisted Transient Viscous Sintering (PATVS)**
(fiber-reinforced composites)
- **Seeded Phase Transformations**
(lower processing temperatures, finer-grain microstructures)
- **Microcomposite Particles with Multicomponent Coatings**
(expanded range of compositions, lower processing temperatures)

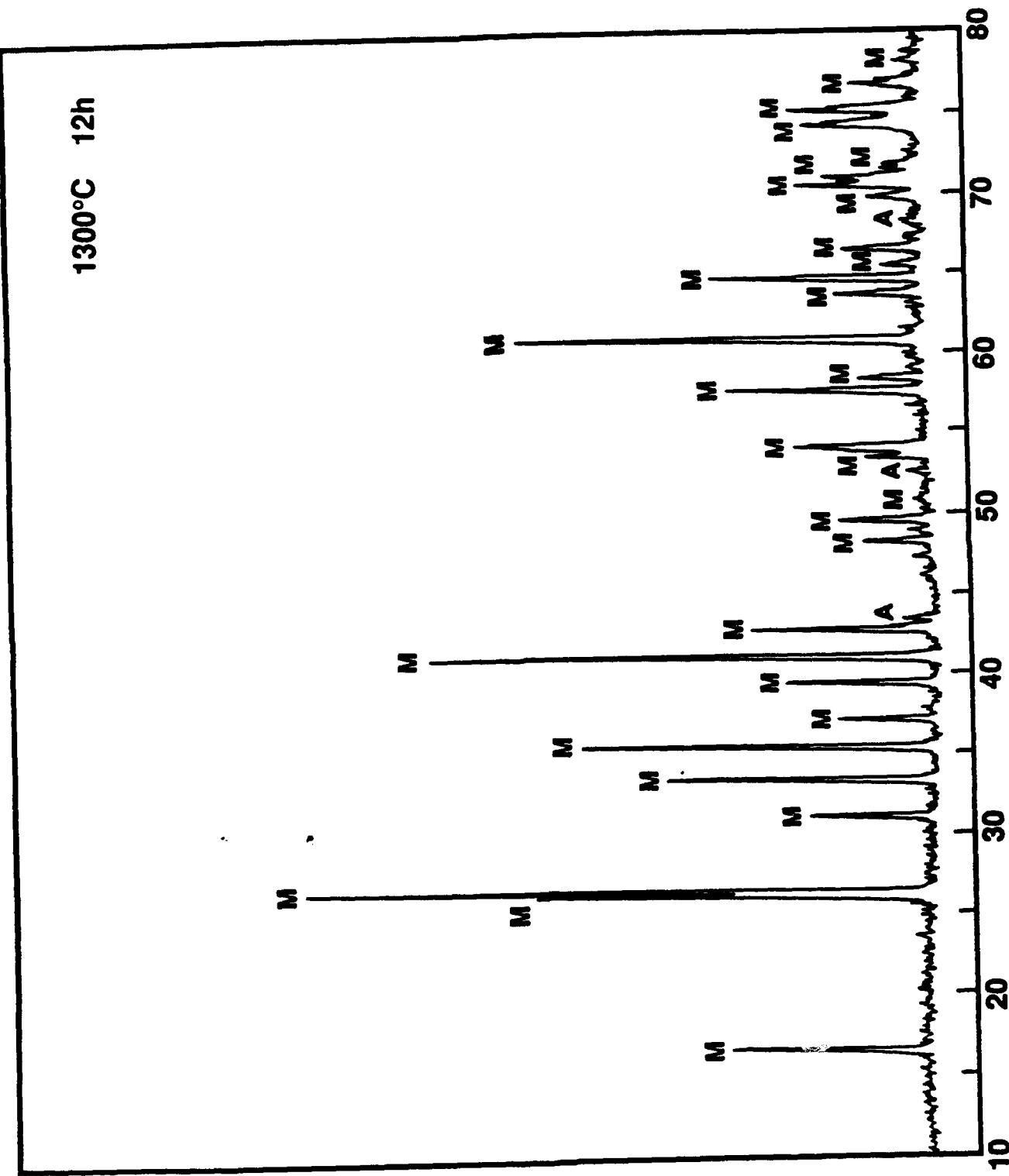




1300°C 12h

↑ INTENSITY

2θ (Degrees)

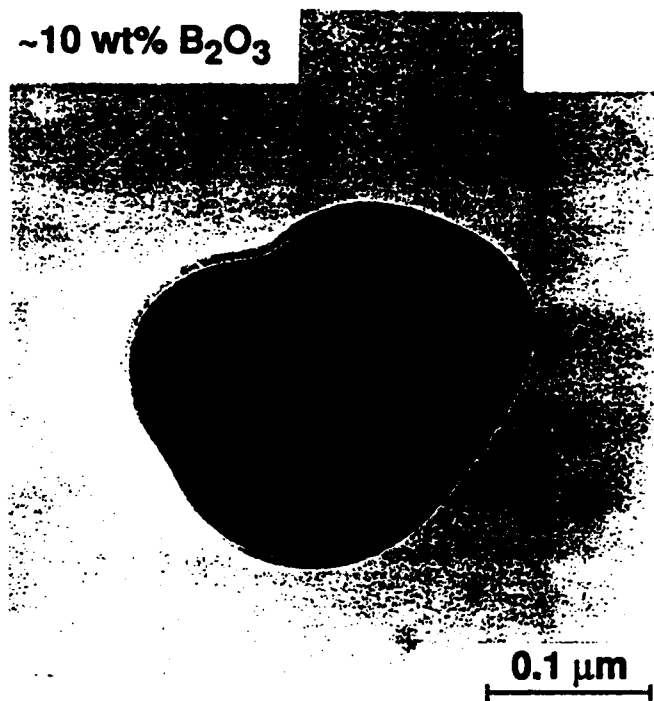




Recent Developments in Viscous Processing

- **Pressure-Assisted Transient Viscous Sintering (PATVS)**
(fiber-reinforced composites)
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(lower processing temperatures, finer-grain microstructures)
- **Microcomposite Particles with Multicomponent Coatings**
(expanded range of compositions, lower processing temperatures)

~10 wt% B₂O₃

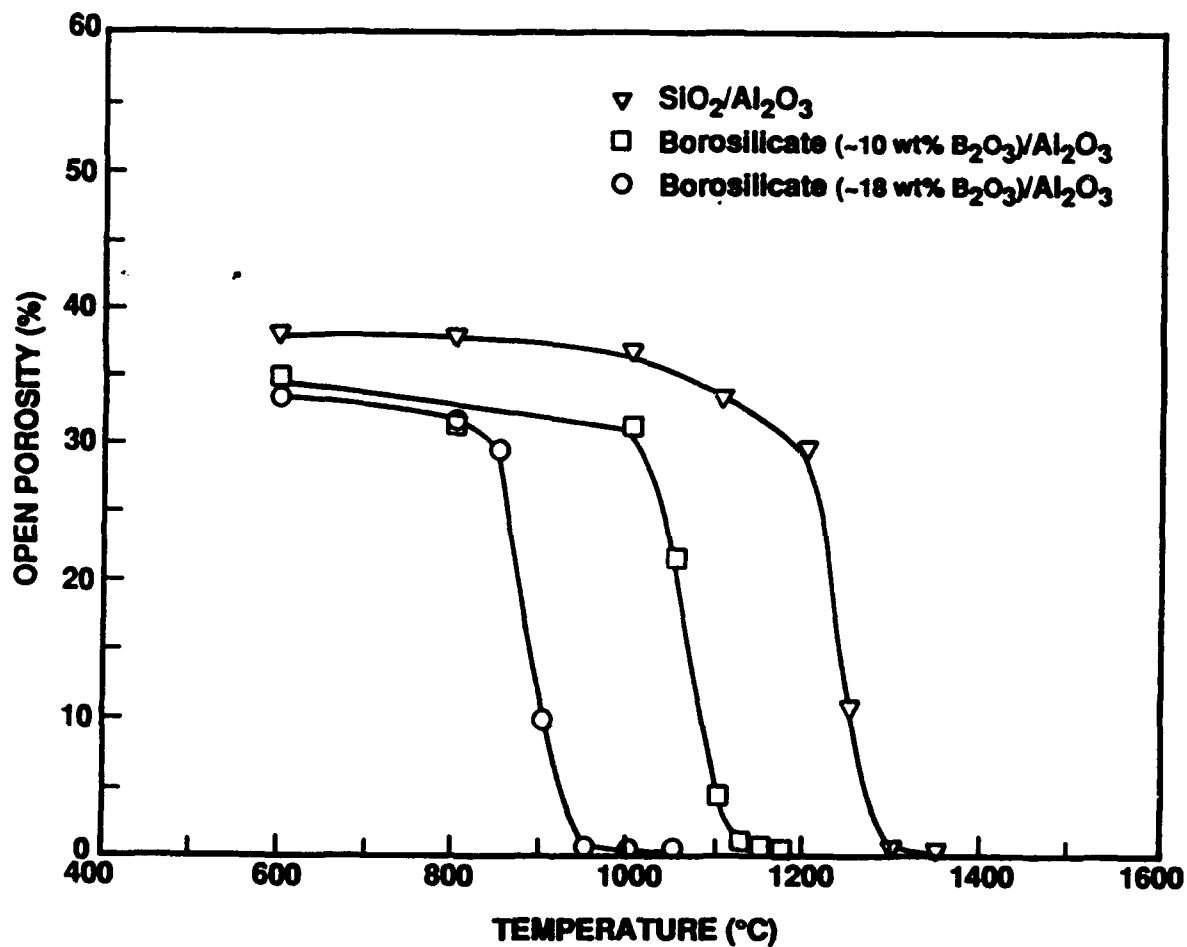
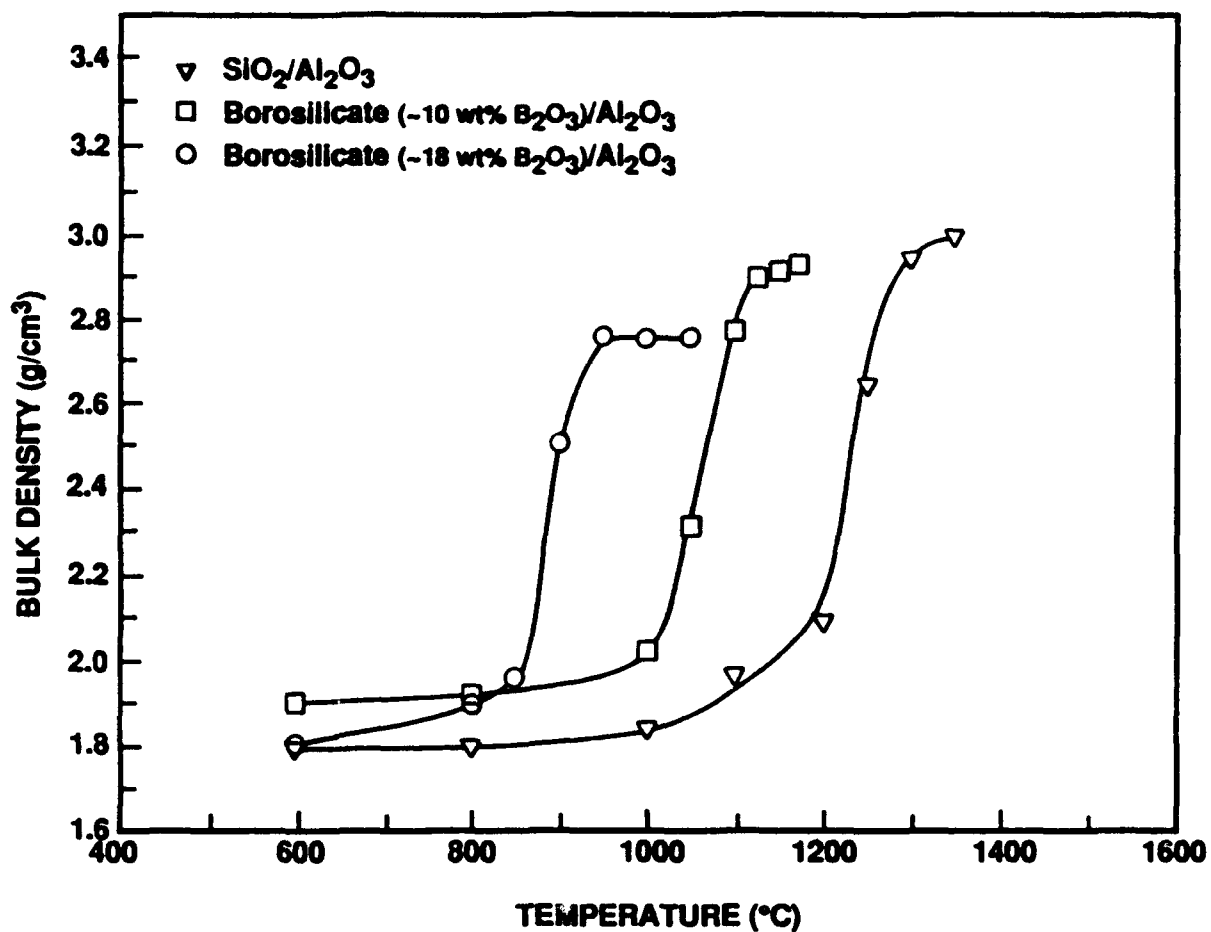


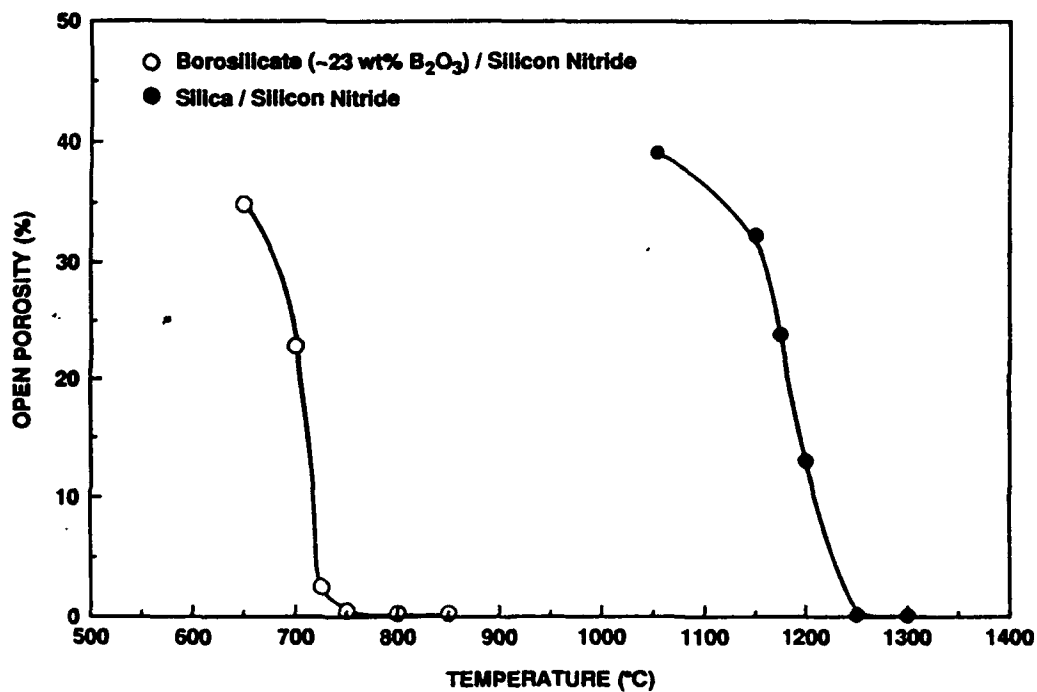
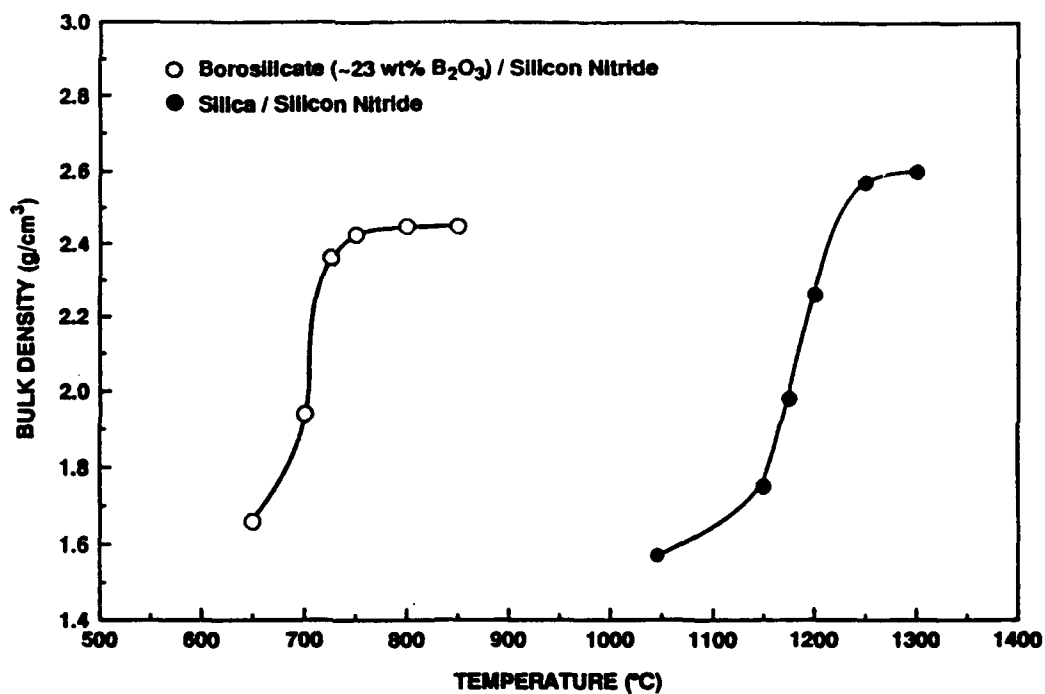
0.1 μm

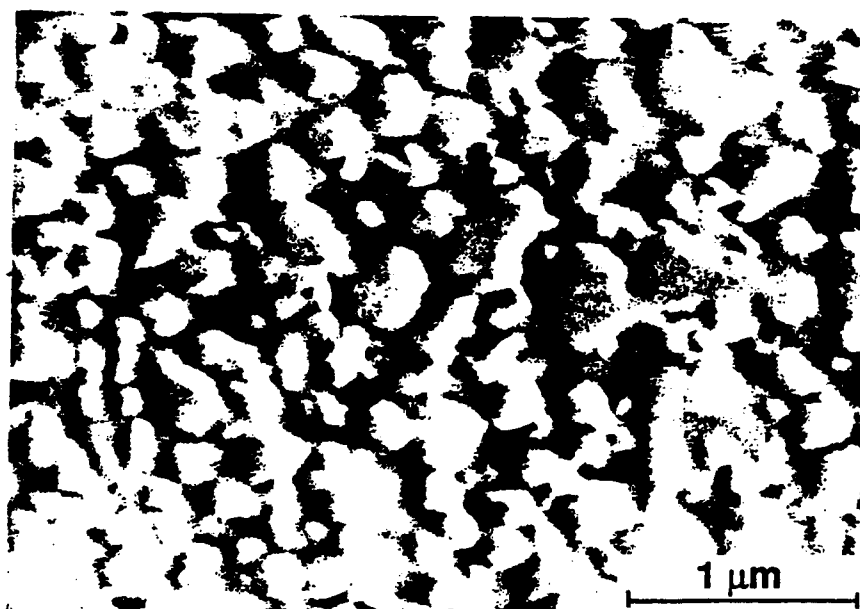
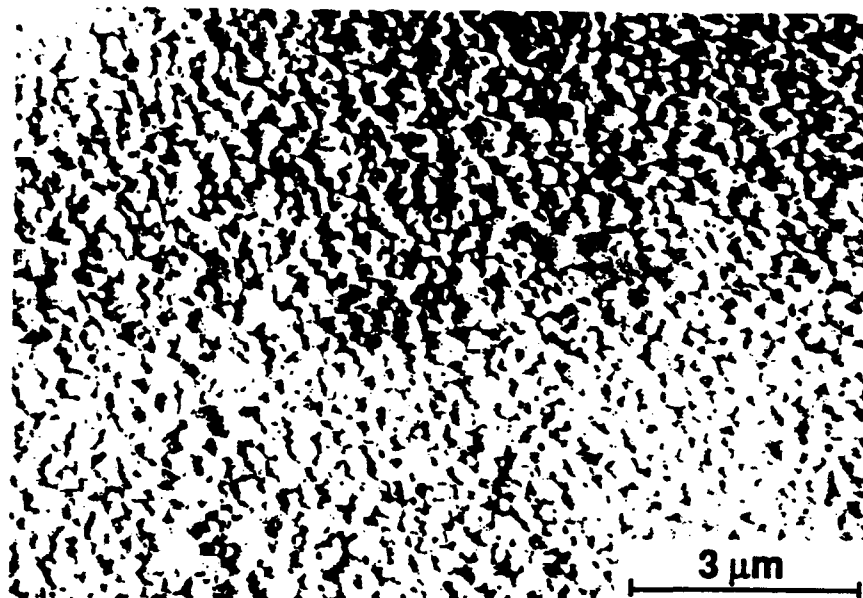
~17 wt% B₂O₃



0.1 μm







Reactive Infiltration of Metals (RIM)

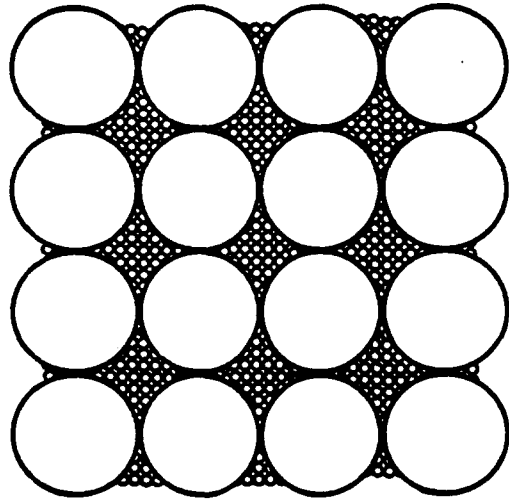
Objectives

- **Densification with little or no shrinkage**
- **SiC-based composites with little or no residual metal**

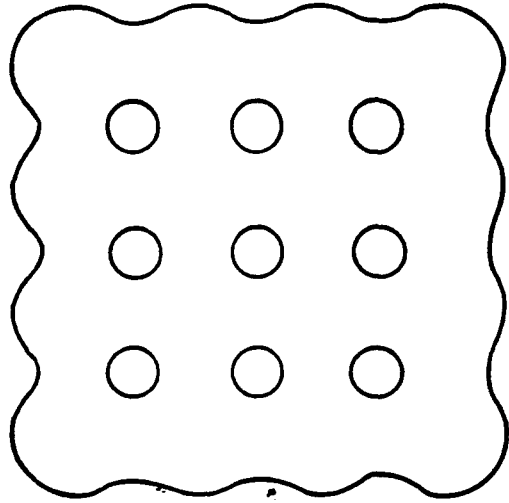
Approach

- **Low temperature infiltration of carbon precursor and high temperature infiltration of silicon alloy.**

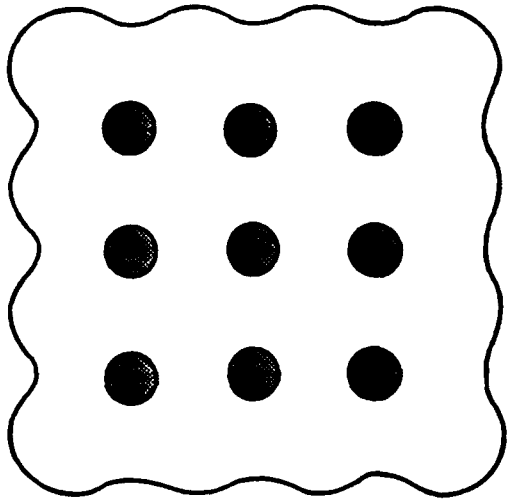
GREEN BODY



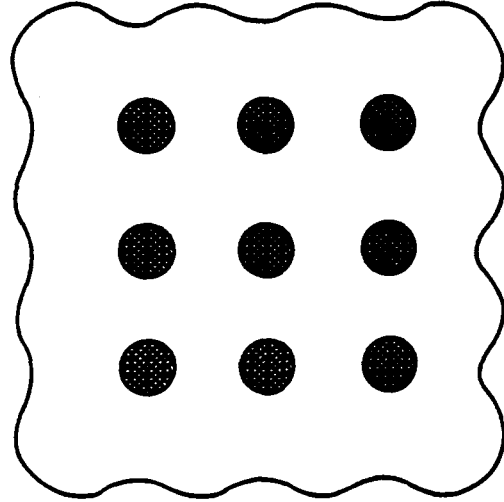
SINTERED BODY



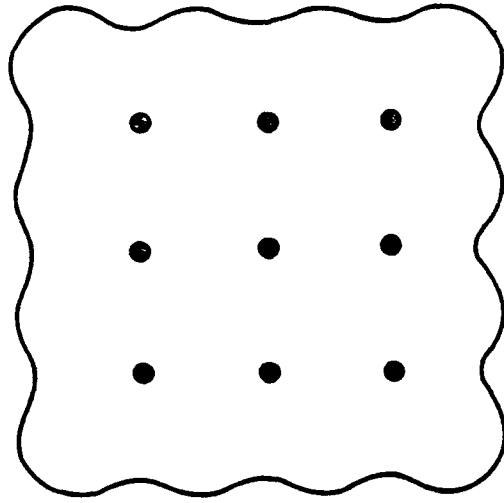
SILICONIZED BODY

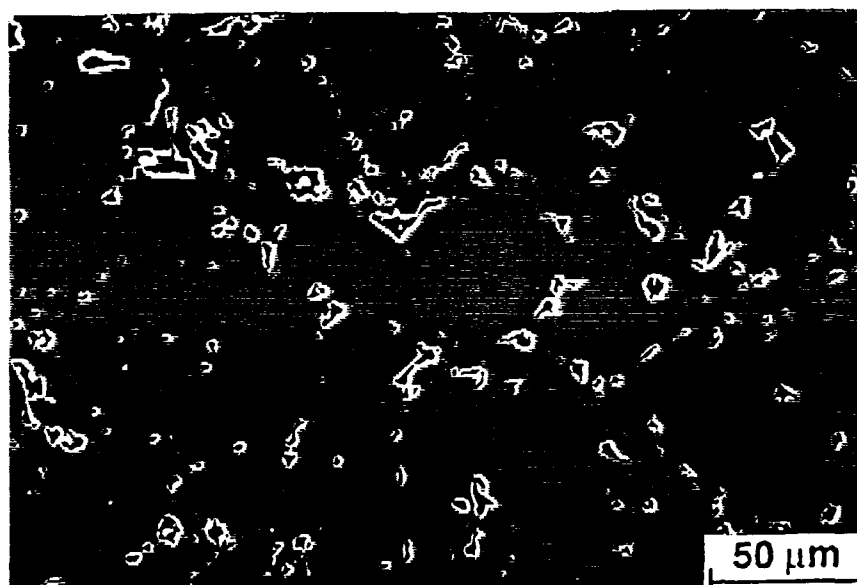
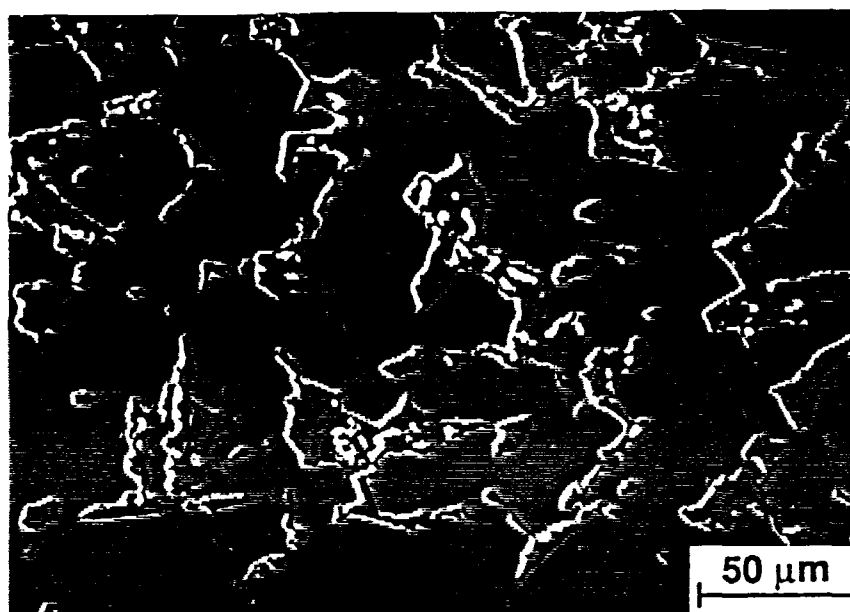
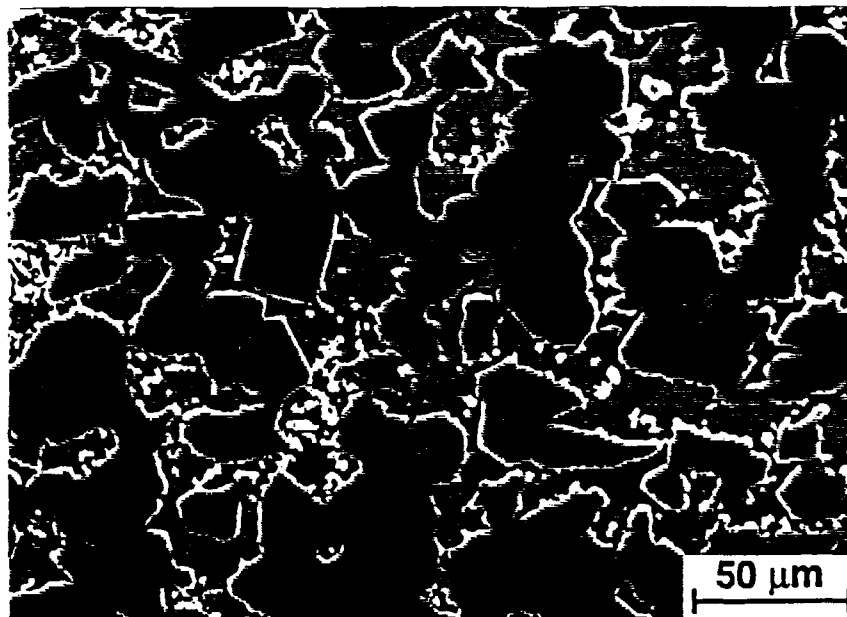


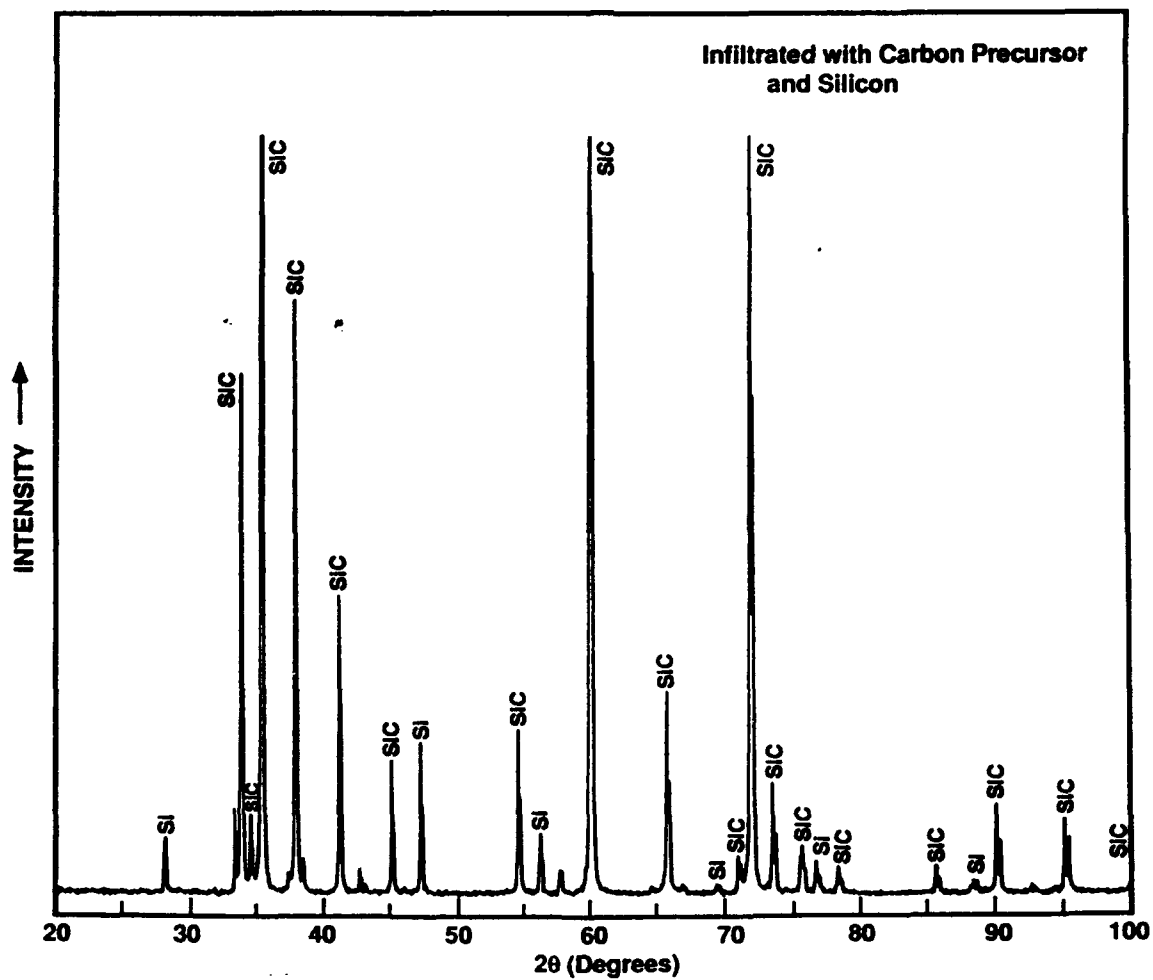
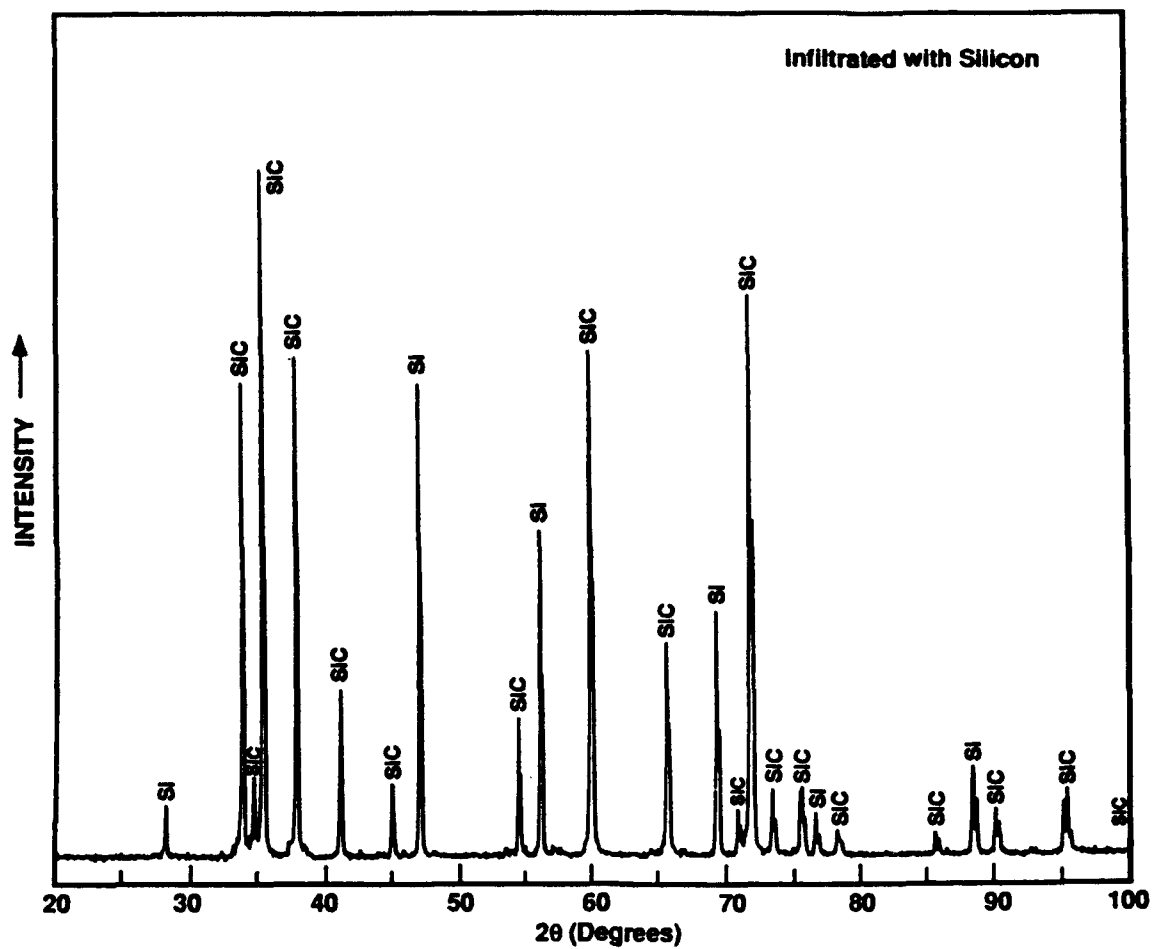
INFILTRATION WITH CARBON

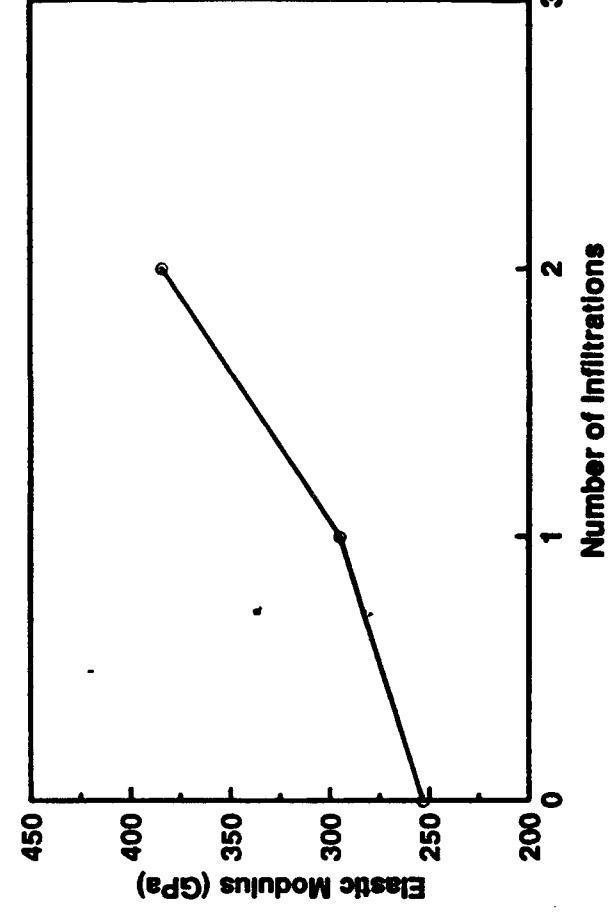
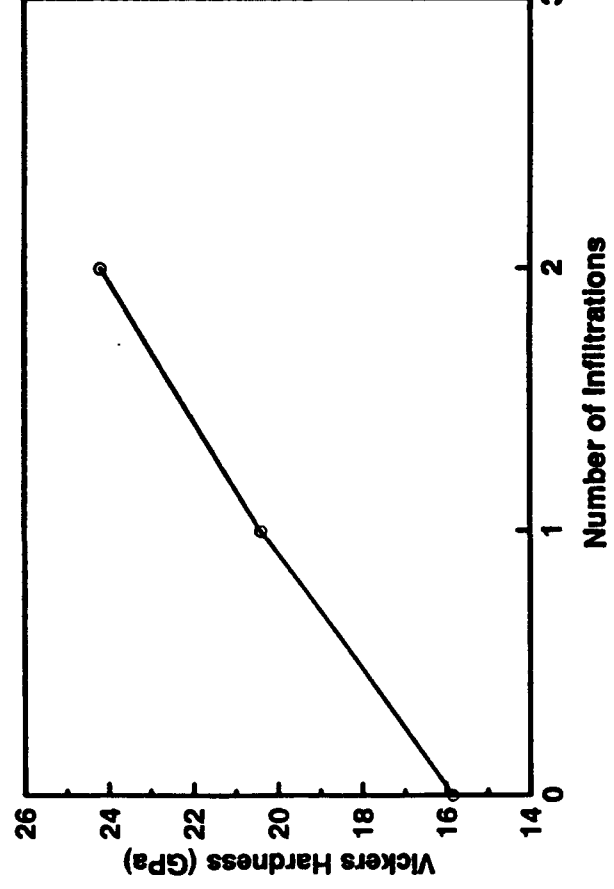
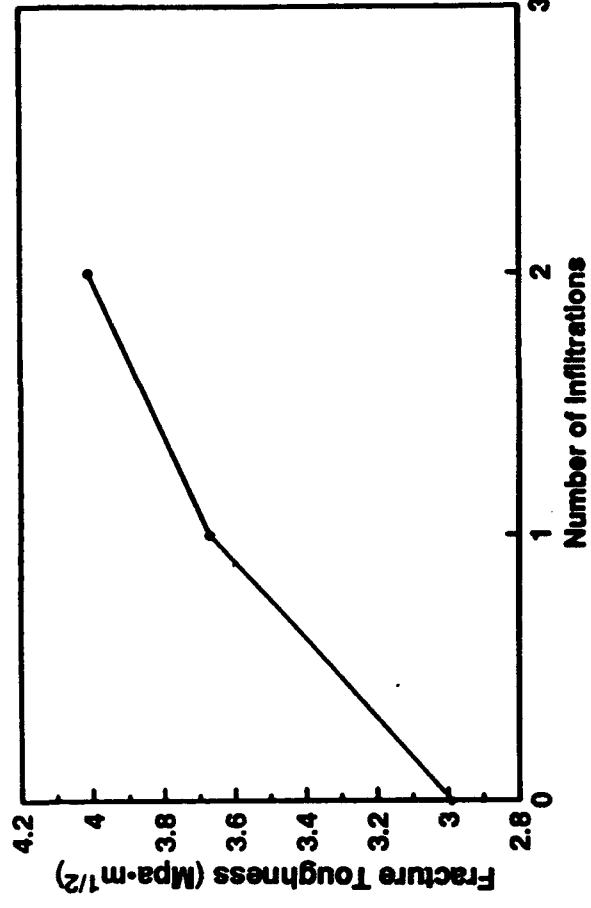
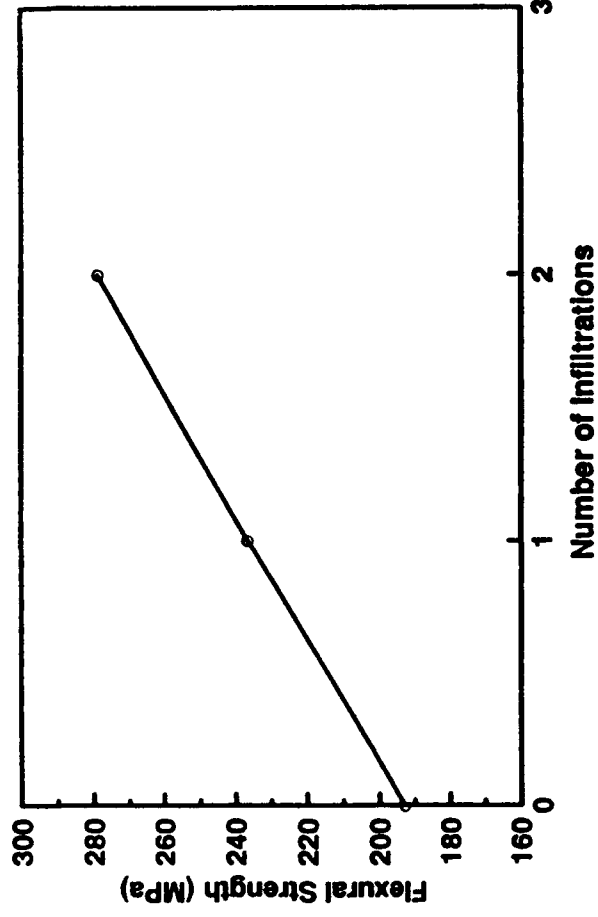


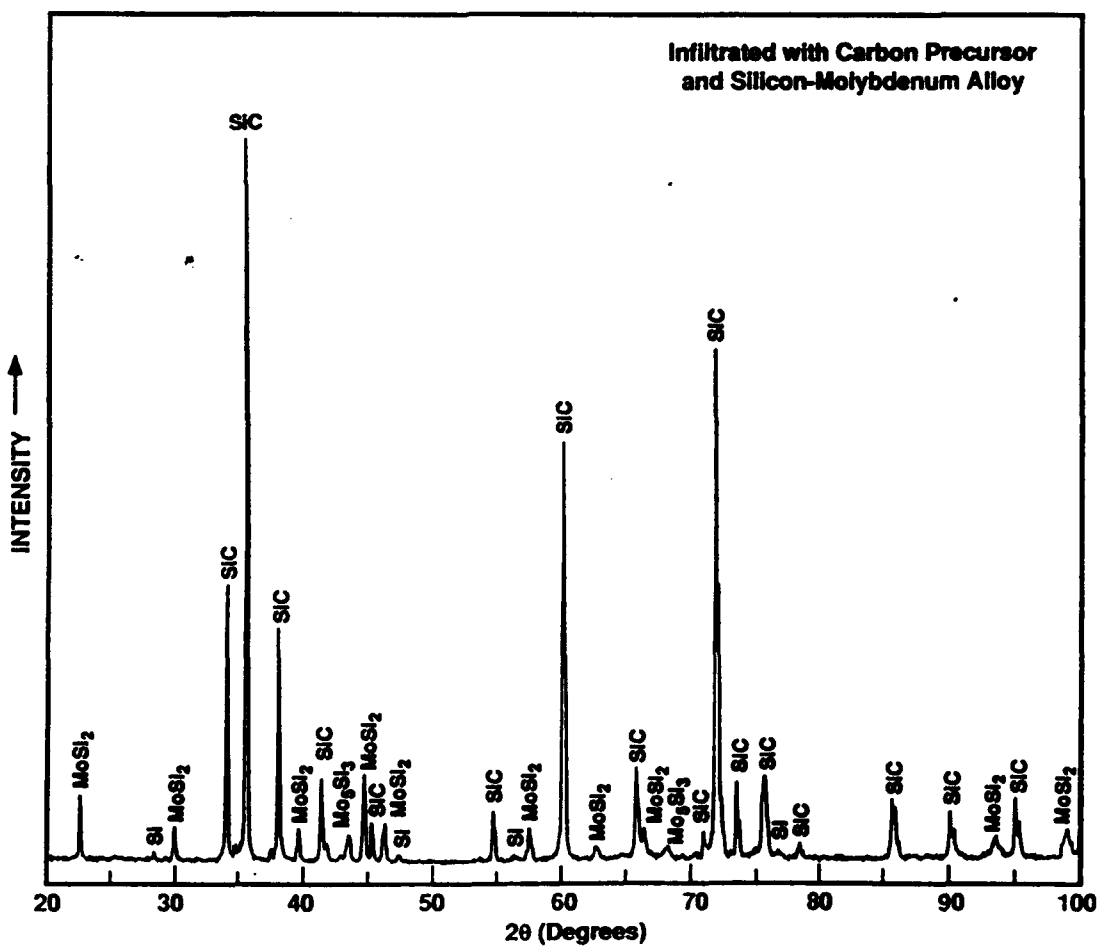
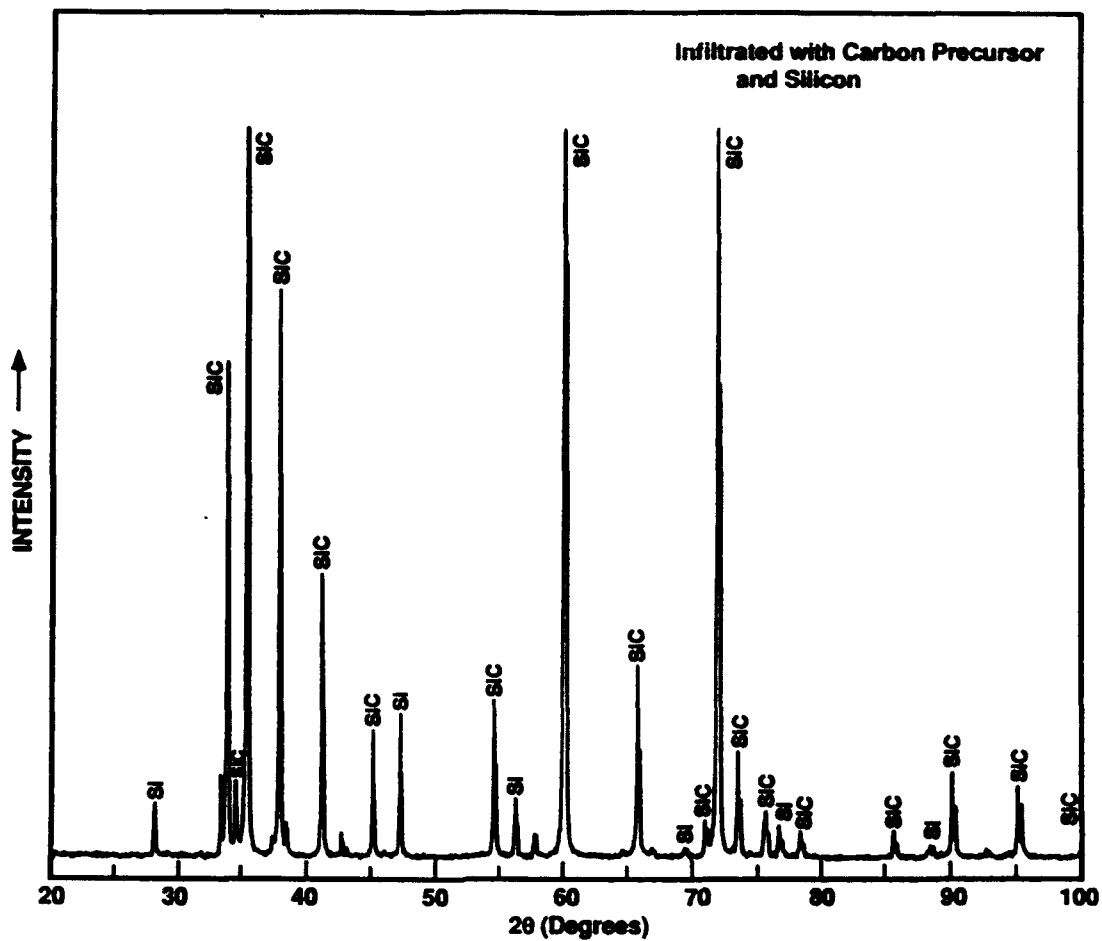
SILICONIZED BODY

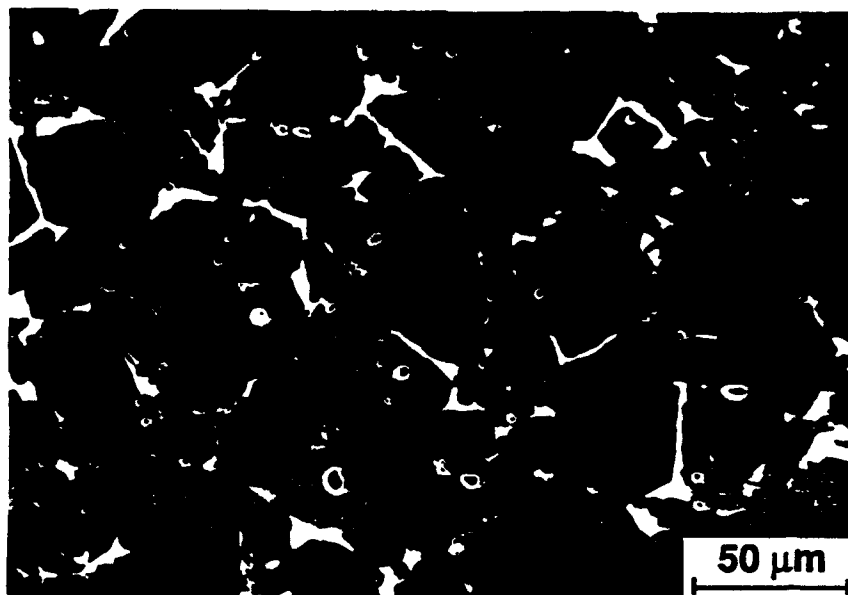




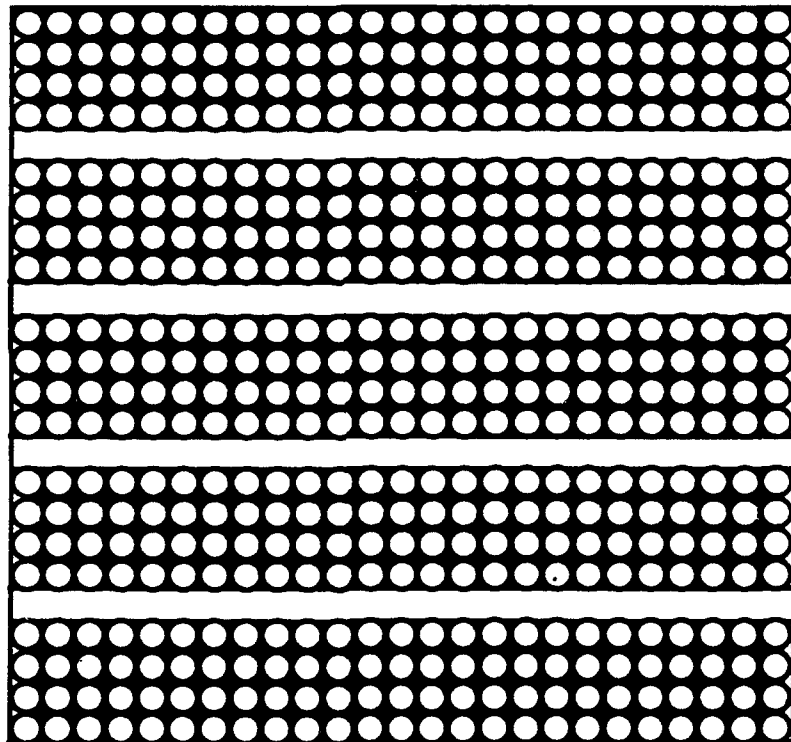


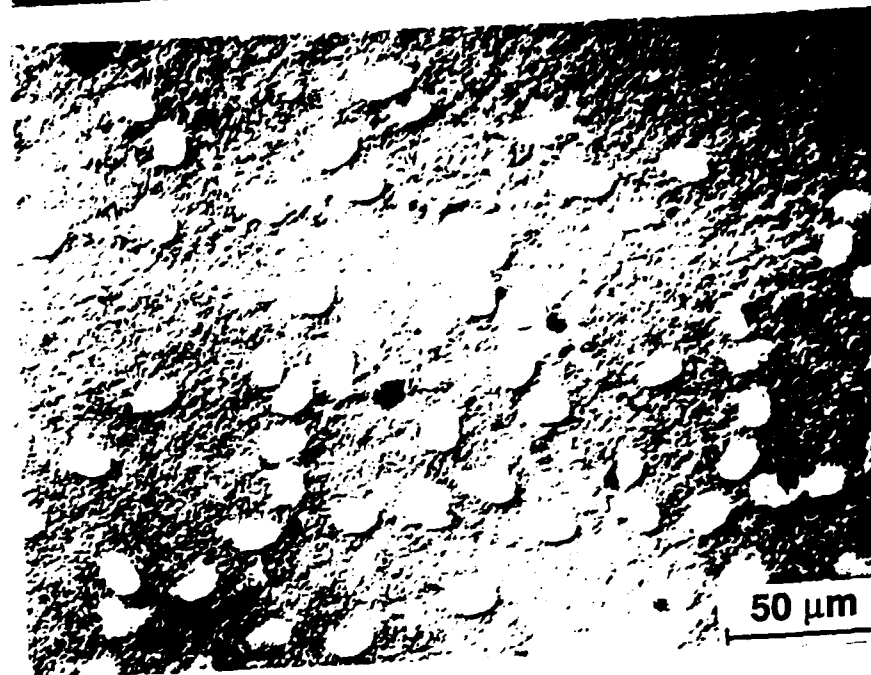
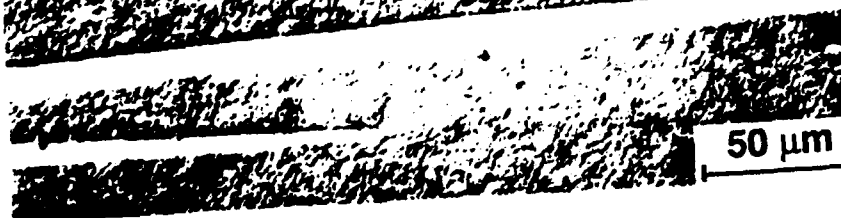
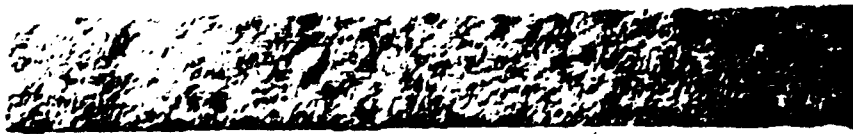
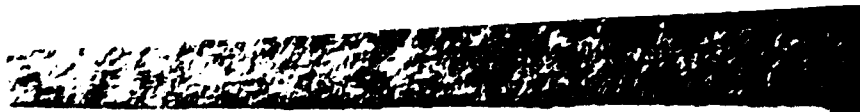






Fiber-Reinforced Green Body





SUMMARY

Viscous Processing of Microcomposite Particles

- **Fabrication of a Wide Range of Ceramics, Glass/Ceramic Composites, and Ceramic/Ceramic Composites**
- **Low Temperature Densification by Viscous Flow**
- **Unique Microstructures (e.g., High Volume Fraction of Well-Dispersed Inclusions)**
- **Hot Forming of Shapes**

Reactive Infiltration of Metals

- **SiC-Based Composites with Low Residual Si Content**
- **High Density (Low Porosity) Achieved without Shrinkage**

Co-Workers

G.W. Scheiffele

N. Bozkurt

I.Y. Park

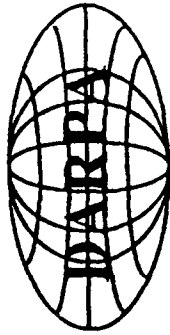
R.Raghunathan

K. Wang

Y.J. Lin

A.E. Bagwell

A.J. Ulicny



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

TAPECAST LAMINATED COMPOSITES

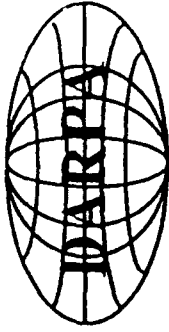
ZHENG CHEN & J. J. MECHOLSKY, JR.

DEPARTMENT OF MATERIALS SCIENCE &
ENGINEERING

UNIVERSITY OF FLORIDA

— MISIE —

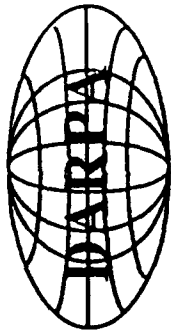
— UNIVERSITY OF FLORIDA —



INNOVATIVE PROCESSING OF COMPOSITES FOR
ULTRA-HIGH TEMPERATURE APPLICATIONS

OBJECTIVES:

- DEVELOP A DESIGN METHODOLOGY FOR TAILORED COMPOSITE STRUCTURES TO INHIBIT CRACK INITIATION AND PROPAGATION
- MEASURE PROPERTIES OF CERAMIC MATRIX - METALLIC LAMINATED COMPOSITES



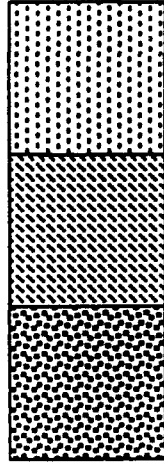
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

PROGRESS

- PRODUCED LAMINATES WHOSE STRENGTHS ARE CRACK SIZE INDEPENDENT.
- DEVELOPED A DESIGN METHODOLOGY TO CONTROL LAMINAE INTERFACES.
- IMPROVED LAMINATE TOUGHNESS TO $> 10 \text{ MPam}^{1/2}$ USING FUNCTIONALLY GRADED DESIGN.
- IMPROVED THERMAL SHOCK RESISTANCE OF ALUMINA UP TO $\Delta T = 1200^\circ\text{C}$.
- ACHIEVED LAMINATE STRENGTHS $> 700 \text{ MPa}$.

Toughening Can Occur Using Different Mechanisms

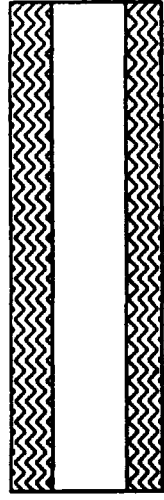
SECOND PHASE



COMPOSITES

(e.g. Heitzenrater)

RESIDUAL COMPRESSION



HYBRID LAMINATES

(Amateau and Messing)

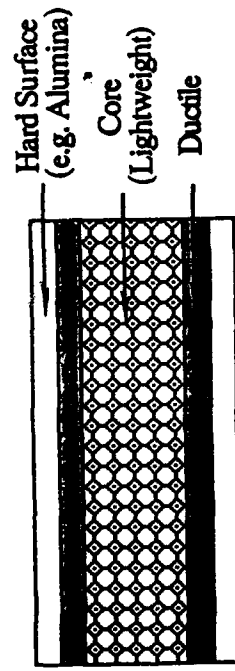
DUCTILE LAYER BRIDGING



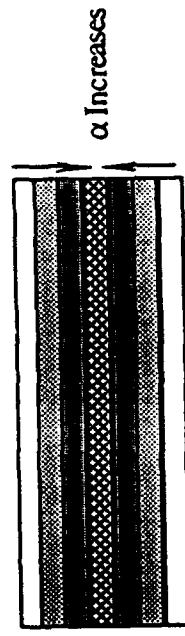
METAL-CERAMIC LAMINATES

(Evans and Cao et al.)

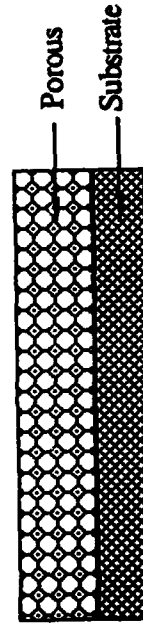
LAMINATE DESIGN OFFERS MANY POTENTIAL MULTILAYER STRUCTURES



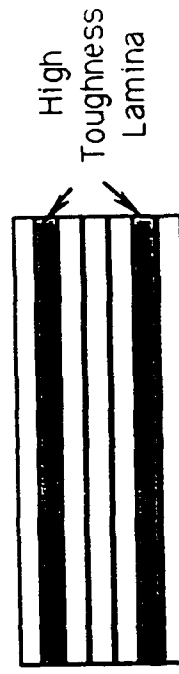
High Specific Strength



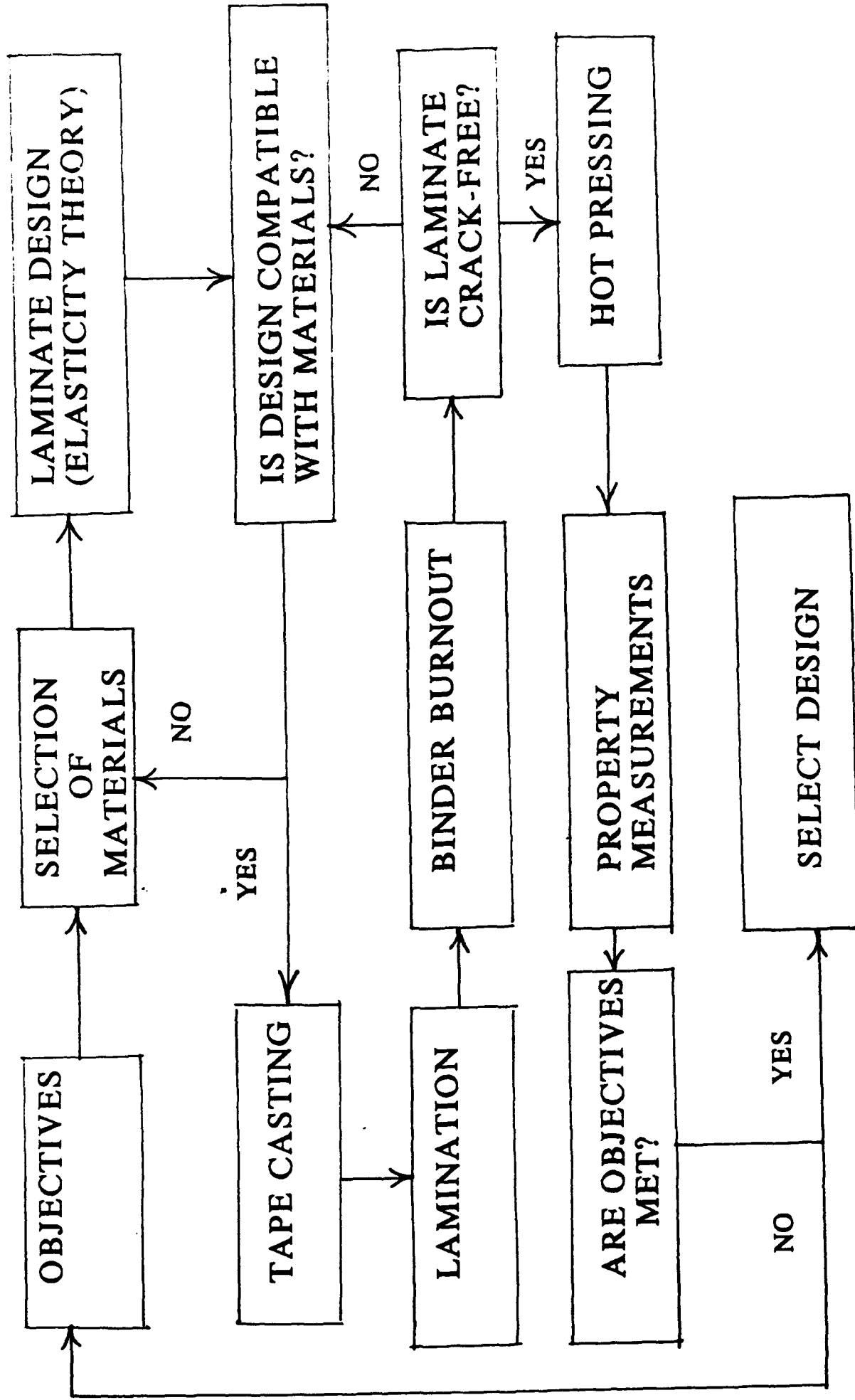
Compressive Residual Stress



Surface Protected



Toughened



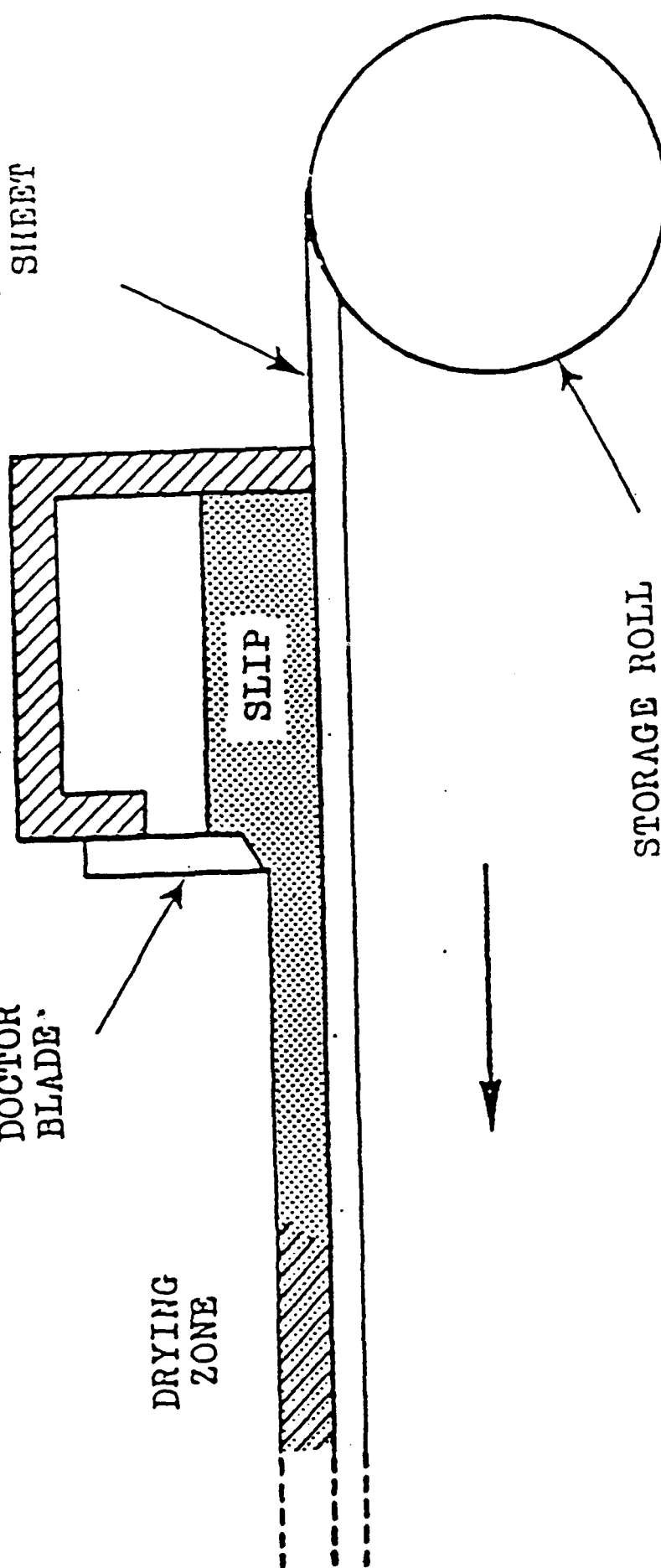
CELLULOSE
ACETATE
SHEET

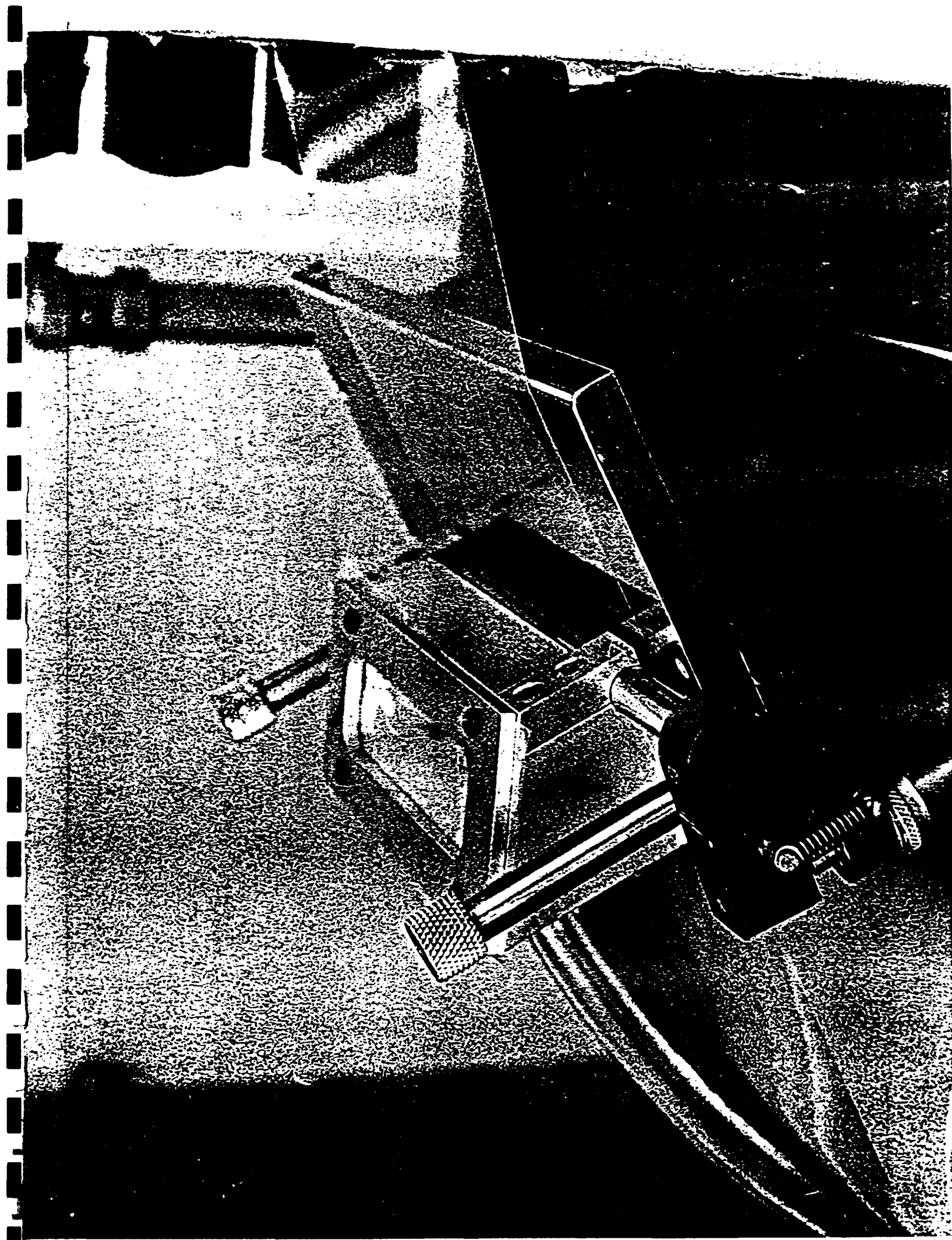
DOCTOR
BLADE

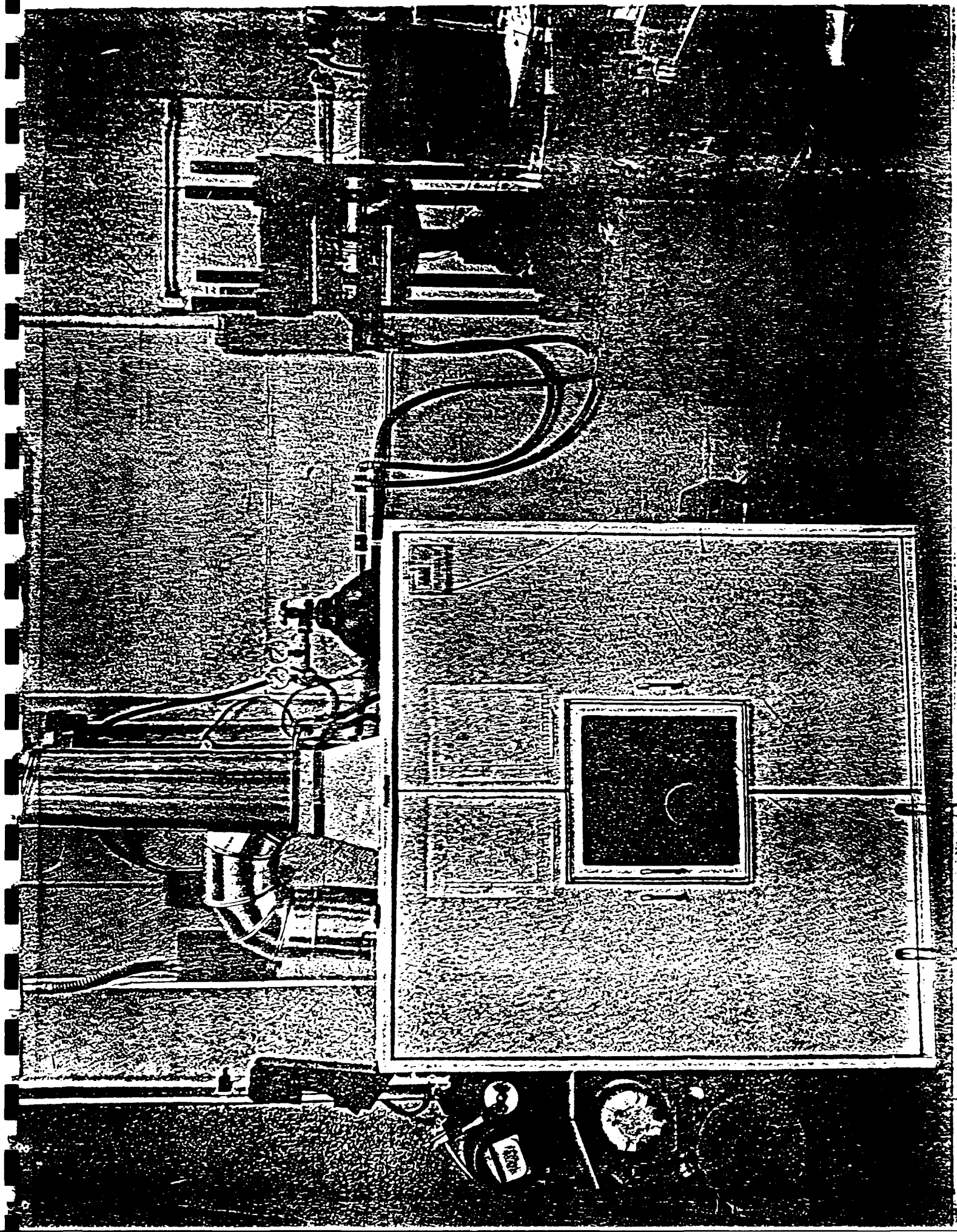
DRYING
ZONE

SLIP

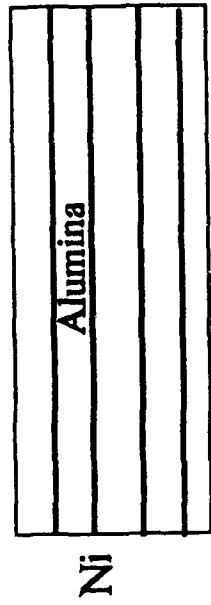
STORAGE ROLL
FOR CELLULOSE
ACETATE SHEET



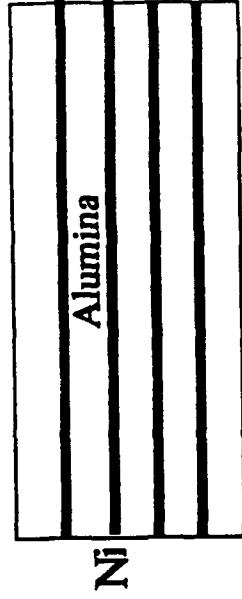




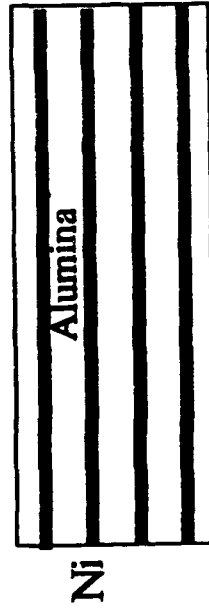
SAMPLE DESIGNATION



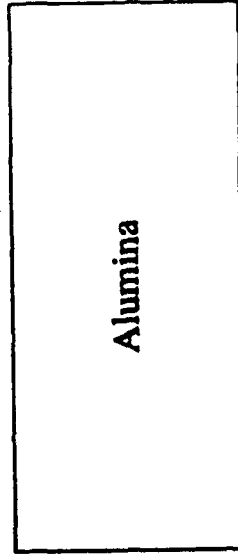
Ni(.125)



Ni (.180)



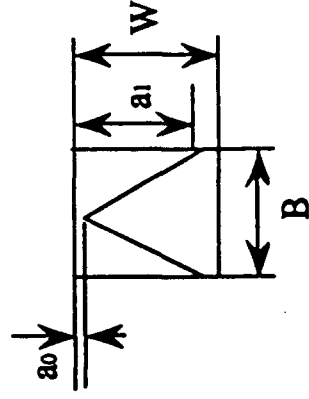
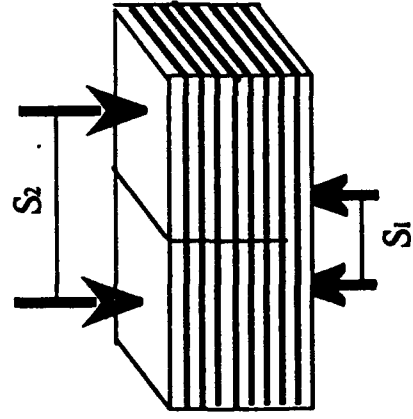
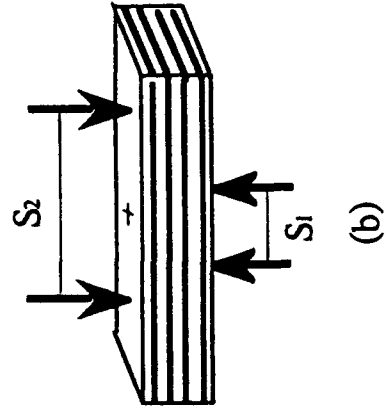
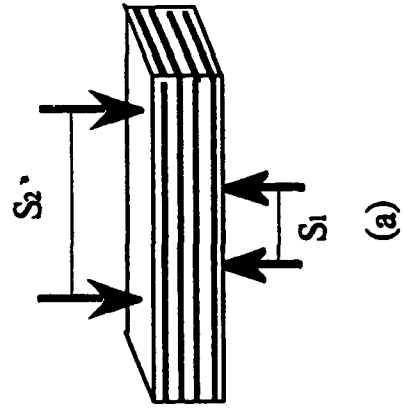
Ni (.240)



Al₂O₃

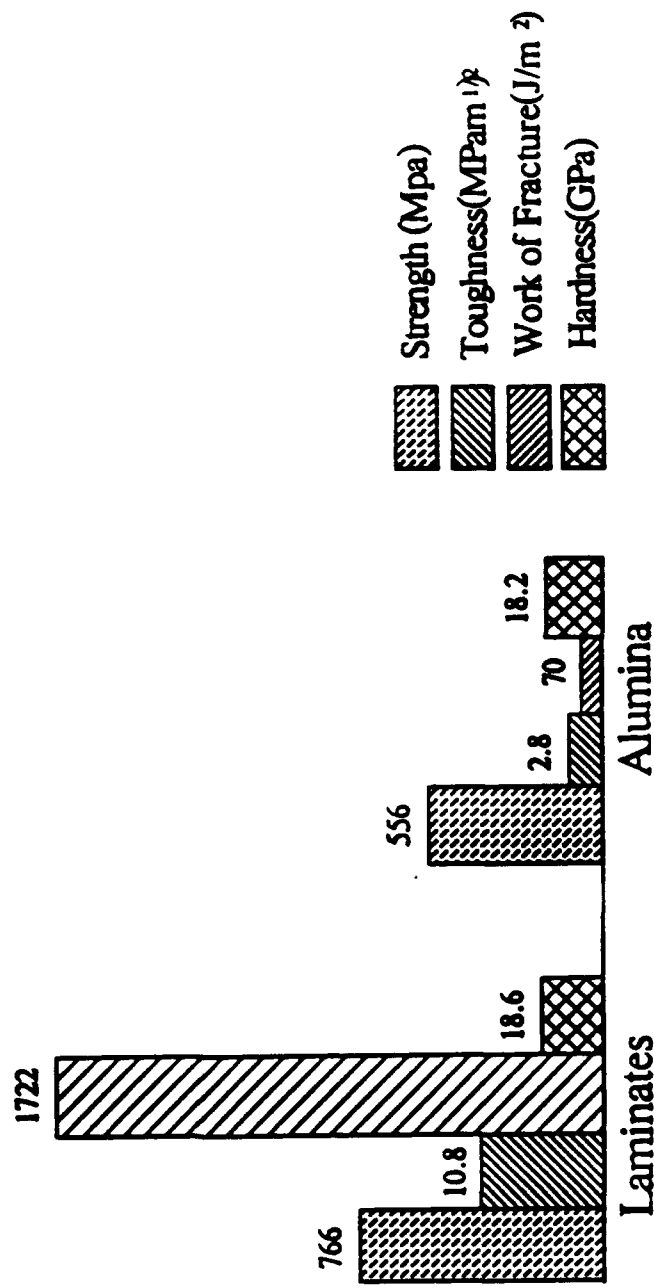
All external layers are .22 mm and internal layers are .30 mm for alumina

DIFFERENT TESTS ARE REQUIRED TO EVALUATE COMPOSITES

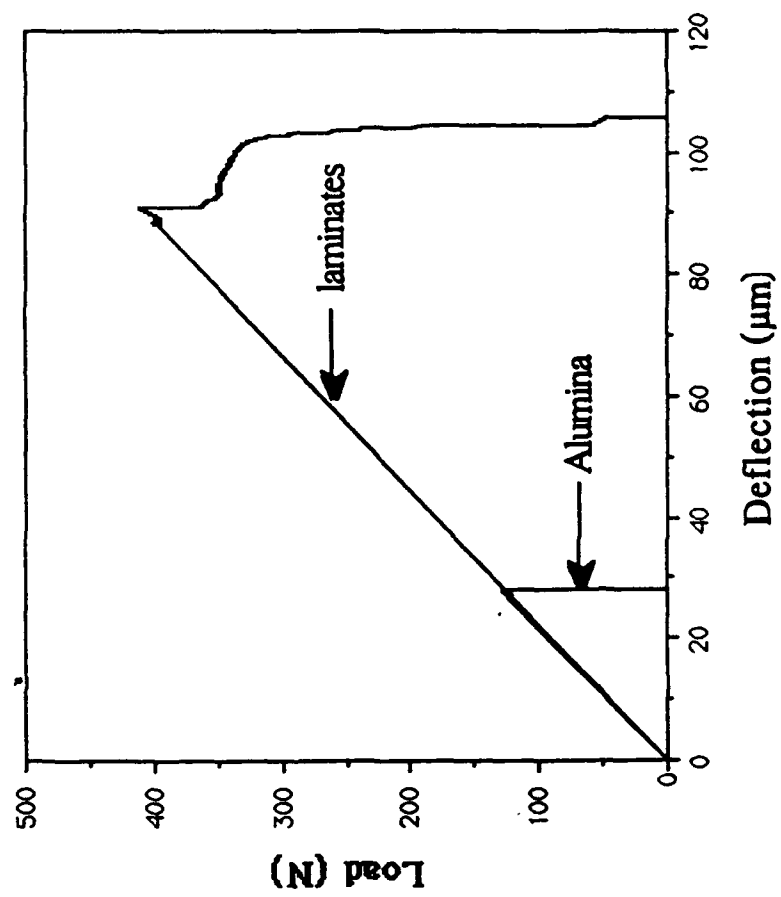


(c)

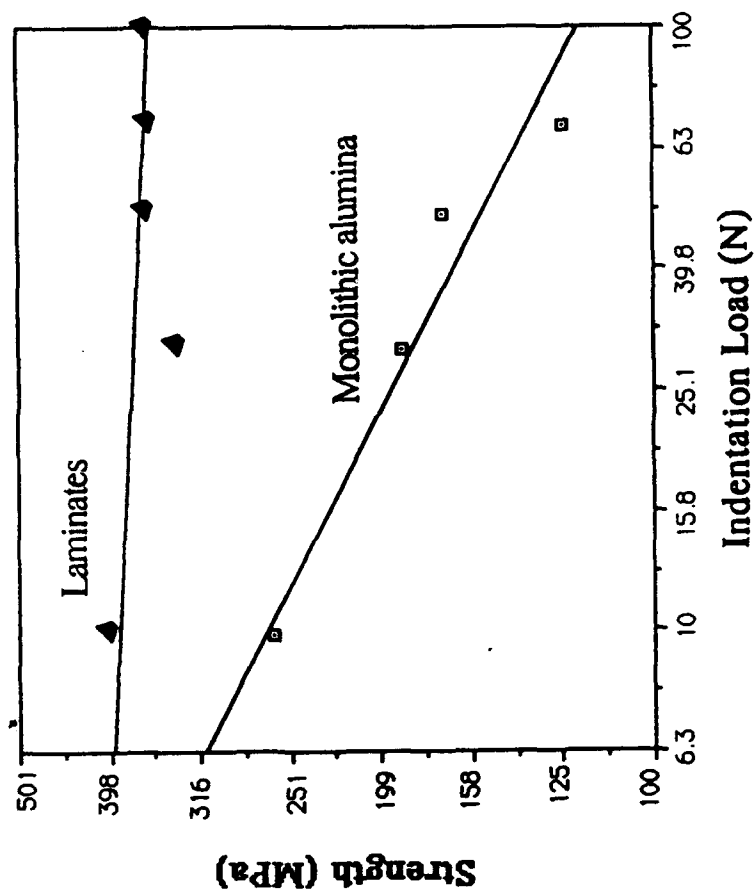
Improved Mechanical Properties



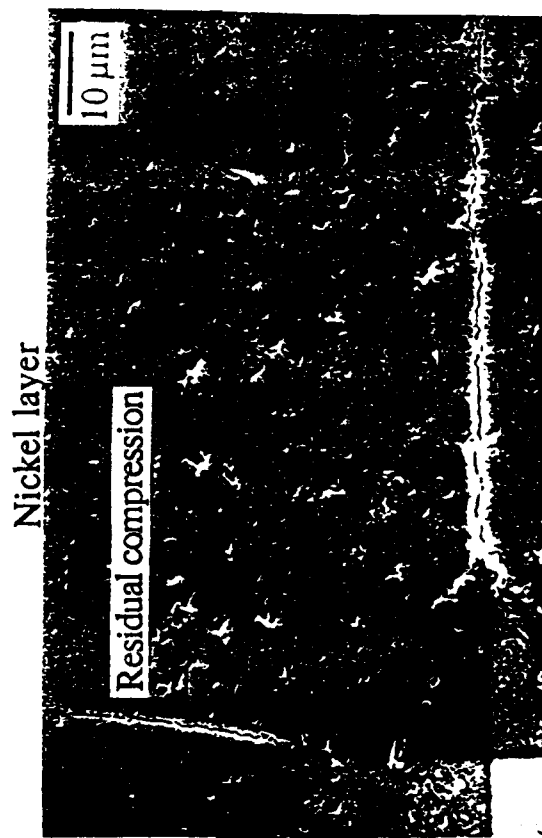
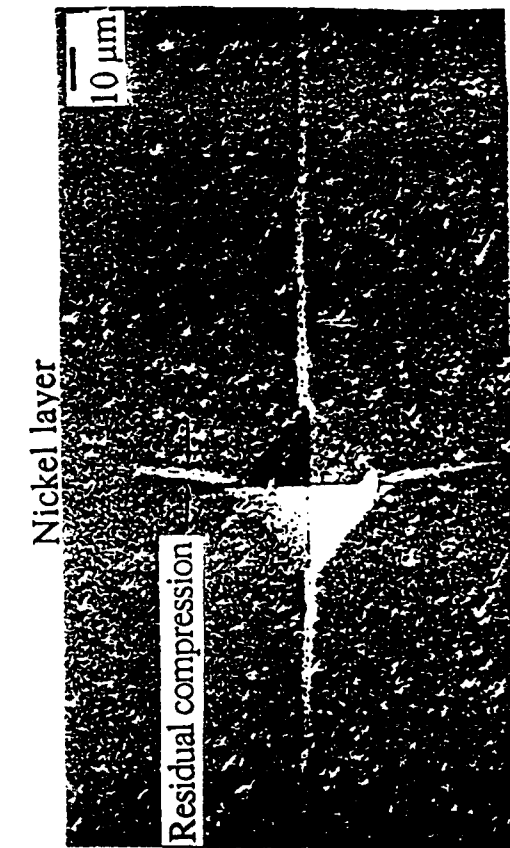
LAMINATES SHOW INCREASED TOUGHNESS OVER MONOLITHICS



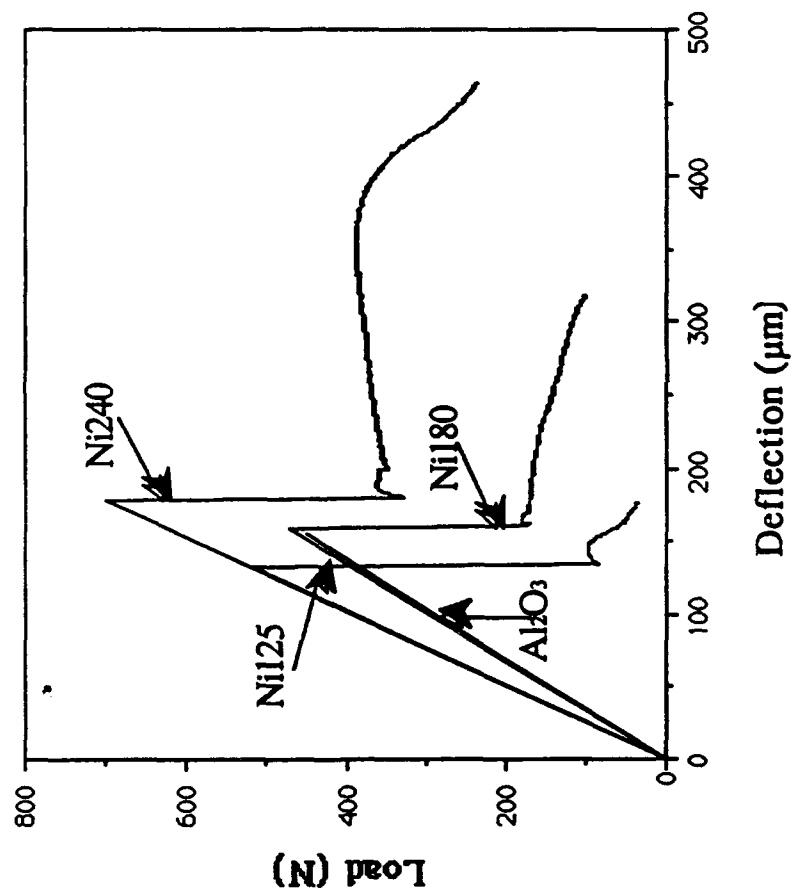
STRENGTH NEARLY INDEPENDENT OF CRACK SIZE FOR LAMINATES



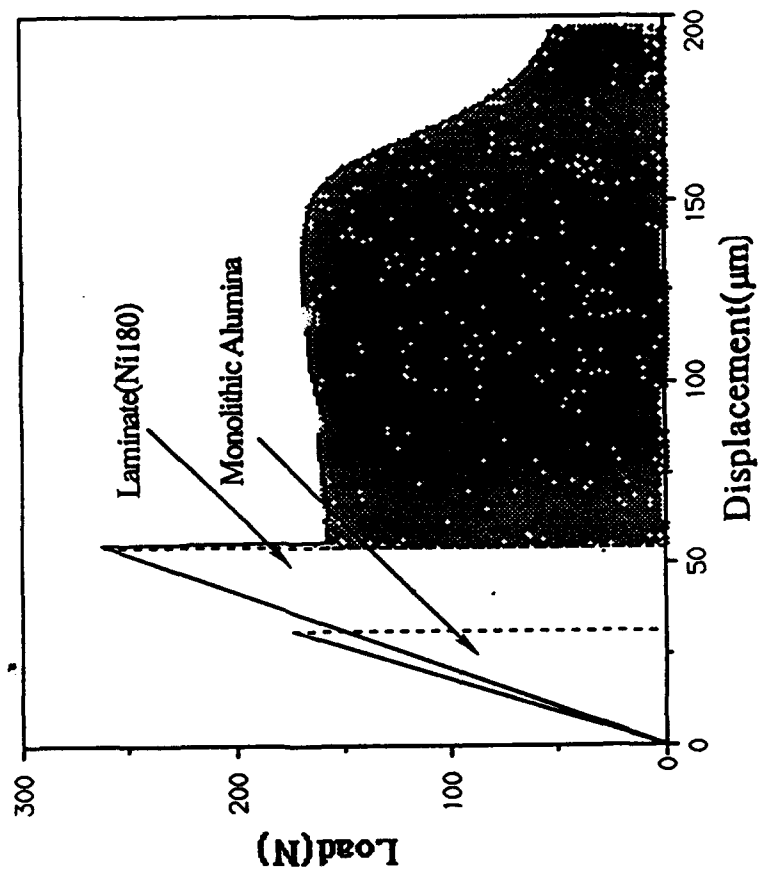
RESIDUAL COMPRESSIVE STRESSES IMPEDE CRACK DEVELOPMENT



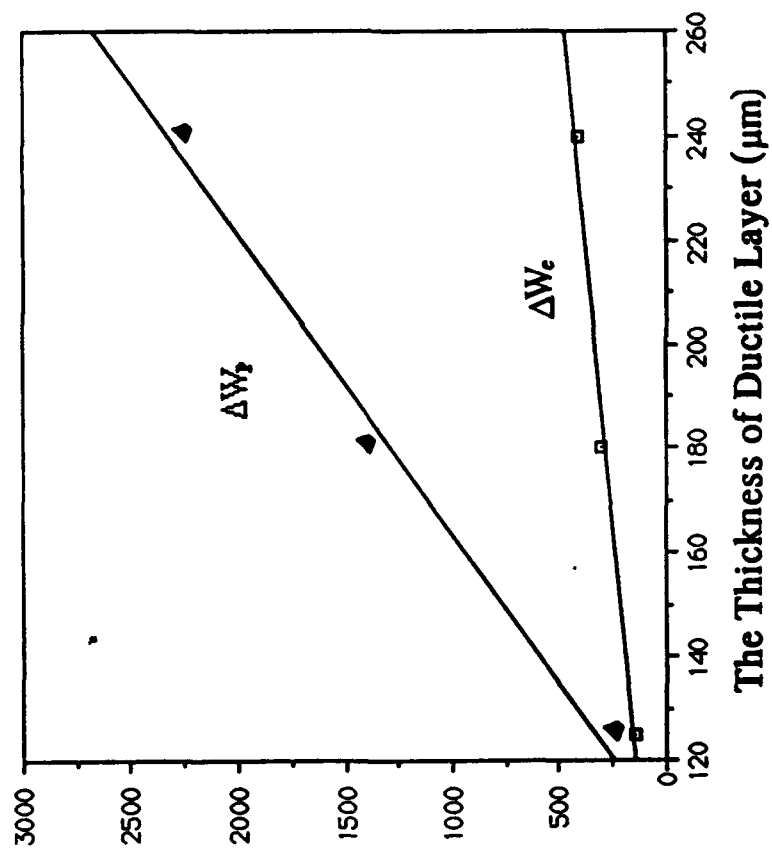
DUCTILITY INCREASES WITH INCREASING THICKNESS OF METAL LAYER



APPARENT TOUGHNESS INCREASES DUE TO ELASTIC AND PLASTIC PROCESSES

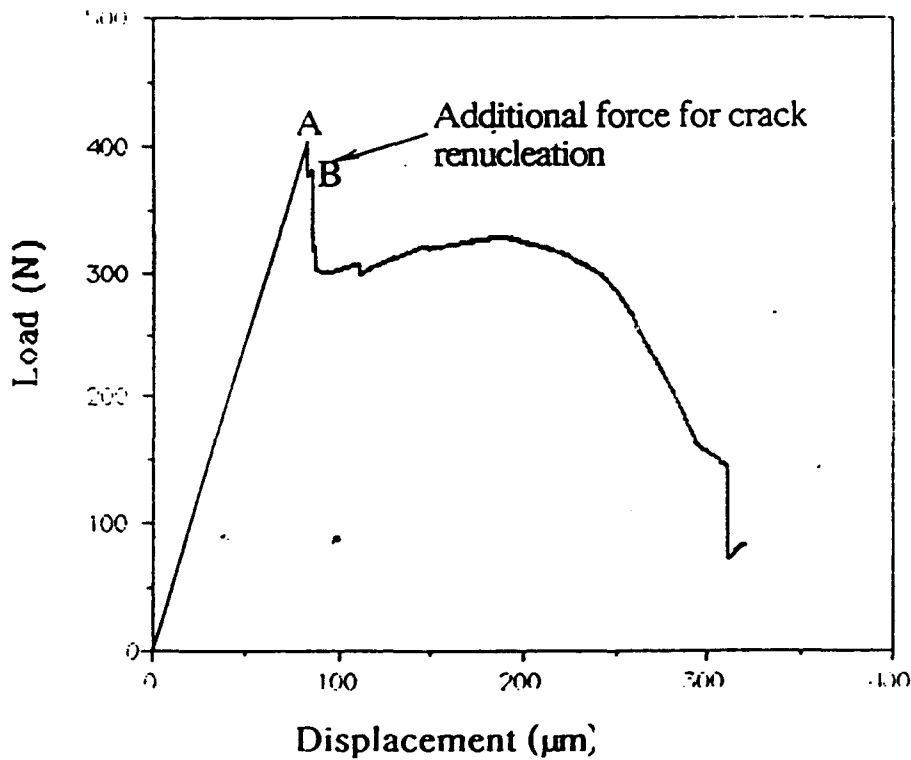


WORK OF FRACTURE INCREASES WITH INCREASE IN THICKNESS





a. Scanning electron micrograph of the fracture surface of a laminate illustrates the crack renucleation created beneath the ductile layer at B, after fracture started at A.



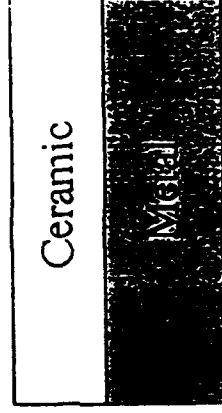
b. Load-displacement curve shows an interruption at B due to crack renucleation during load drop.

Figure 13. Scanning electron micrograph and graph illustrate crack renucleation in a laminate.

Bonding Strength of Ceramic/Metal Depends on Total Contact Area of the Interface

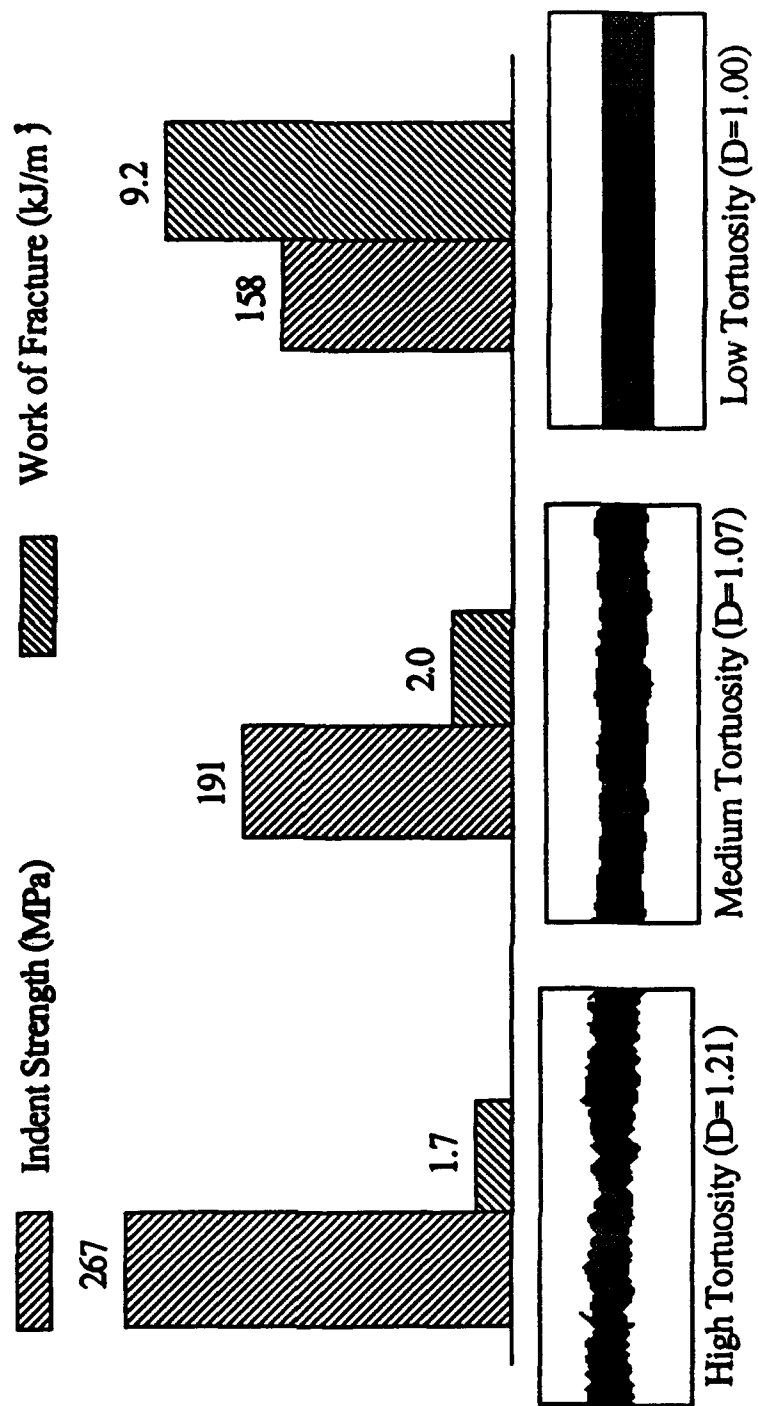


Larger Total Contact Area
(High Tortuosity)

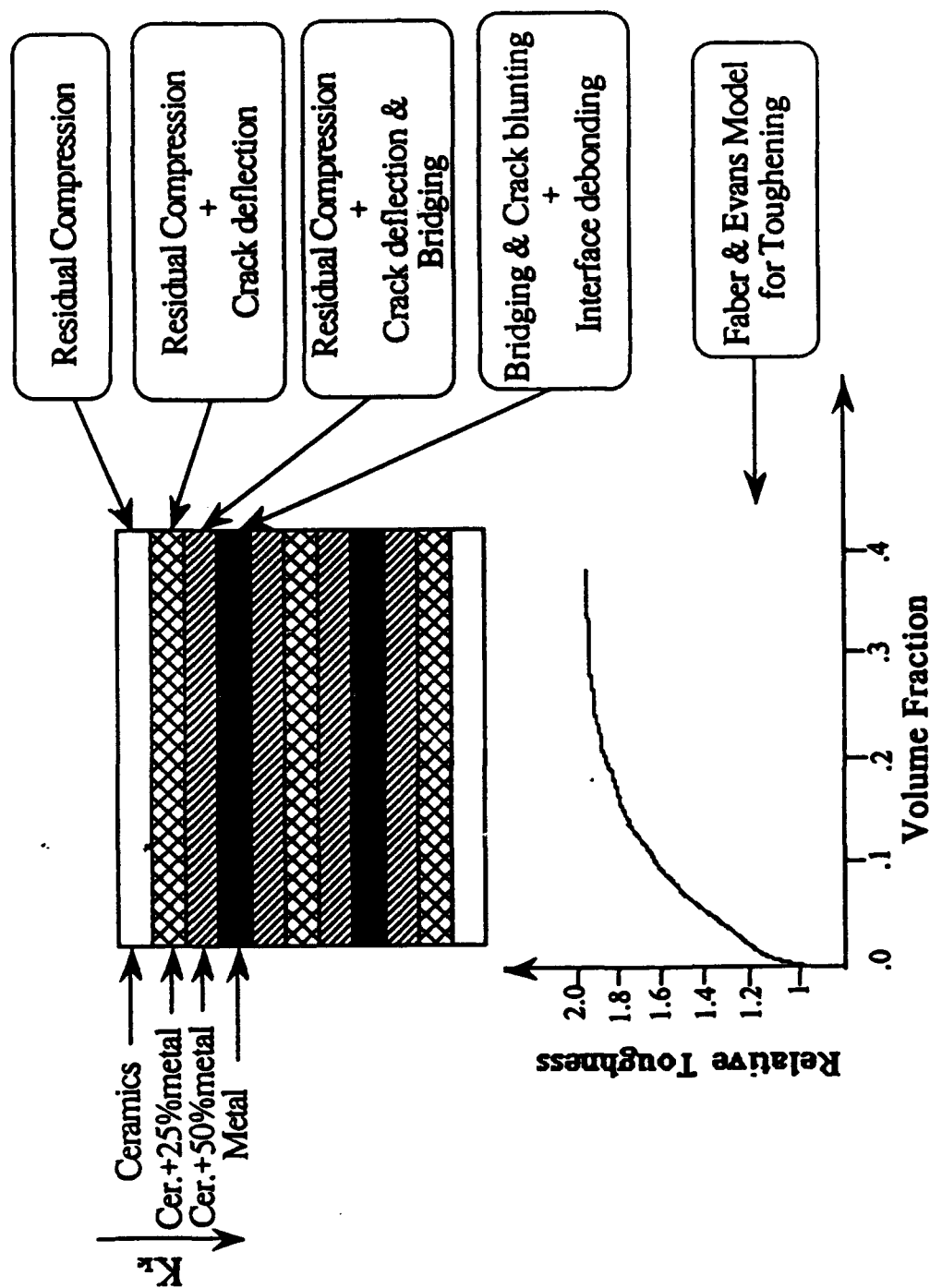


Small Total Contact Area
(Low Tortuosity)

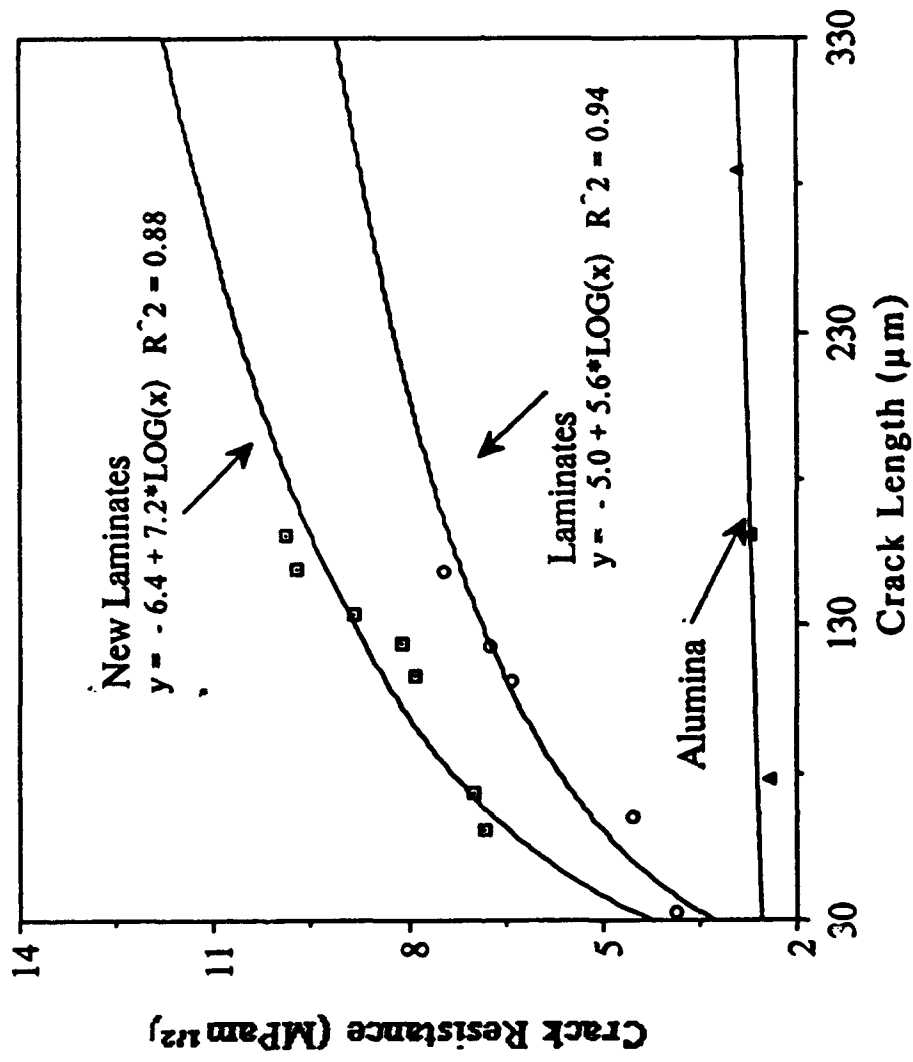
Interface Tortuosity Controls Strength And Toughness



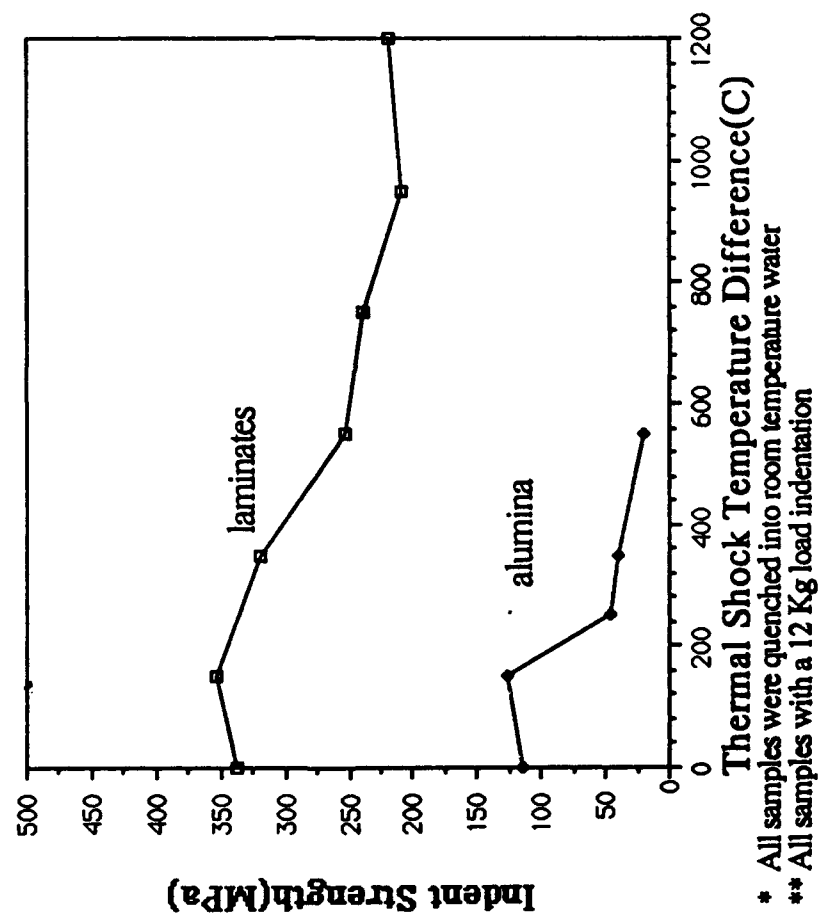
Graded Composites Are Designed To Improve Toughness



R-Curve Behavior Improved By Designing Laminates



LAMINATES SHOW DAMAGE TOLERANCE



CONCLUSIONS - Multilayered Design Offers New Potential

- I. Multilayer Laminate Design Offers the Potential of New Materials.
- II. Tapecasting Offers the Potential Of Commercial Production.
- III. Ceramic/Metal Composites Offer the Potential of Crack Size Independent Strength and Damage Tolerant Design.