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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
List of Poster Presentations

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

Fiber Synthesis/Coating

1) "Atomic Layer Epitaxy"
   R. Aparicio, A. 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 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. Ullman, 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, 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. Somersday, 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. Golkhaled, 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. Chödelka 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 α-Al$_2$O$_3$ Particles at Ultra-Low Temperature"
    S.B. Cho, S. Venigalla, R.E. Chödelka, and J.H. Adair

29) "Monodispersed Nanosize Pt Particles Using Microemulsion Technique"
    V. Nagabushnam and J.H. Adair

* Indicates Presenter
**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.
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
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. Batisch, 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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LIST OF PUBLICATIONS


62. A.D. Cozzi, Z. Fathi, and D.E. Clark, "Nucleation and Crystallization of Li$_2$O • 2SiO$_2$ in a 2.45 GHz Microwave Field," submitted for poster session at the 1993 Conference on Composites and Advanced Ceramics in Cocoa Beach, FL.


64. B.V. Sankar, "A Finite Element for Modeling Delaminations in Composite Beams," accepted for publication in _Journal of Computers and Structures_.


80. Z. Chen and J.J. Mecholsky, Jr., "Toughening by Metallic Lamina in Metal/Alumina Composites," for publication in the Journal of The American Ceramic Society.


Patent Disclosures and Applications


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. Batich and M.D. Sacks

MSE

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.)

Polydimethylsilane

\[ \rightarrow 450-470^\circ C/14 \text{ h} \]

Argon/Autoclave

Polycarbosilane

\[ \rightarrow 280^\circ C \text{ Vacuum} \]

Polycarbosilane \((M_n < 1750)\)

\[ \rightarrow 350^\circ C/N_2 \]

Melt Spun Fibers

\[ \rightarrow 150^\circ C/5 \text{ h/Air} \]

Oxygen-Crosslinked Fibers

\[ \rightarrow 1000-1200^\circ C/\text{Inert Atmosphere} \]

"SiC" Fibers \((8-15 \text{ wt\% Oxygen})\)
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

Lipowtiz 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 ($\geq 25 \mu m$), 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 ($\geq 25 \mu m$), near stoichiometric SiC, good thermal stability, low tensile strength, high elastic modulus

---

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 \(<\text{2 wt\% Oxygen}\)
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
UF Fibers
20°C/min  Argon
I. Increasing Shear Rate

II. Decreasing Shear Rate

---

(A) SHEAR STRESS (Pa) vs. SHEAR RATE (s⁻¹)

(B) VISCOSITY (Pa·s) vs. SHEAR RATE (s⁻¹)
MECHANICAL PROPERTIES OF GREEN AND PARTIALLY-PYROLYZED FIBERS

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Tensile Strength (MPa)</th>
<th>Rupture Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Fibers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green (as-spun)</td>
<td>20</td>
<td>1.0</td>
</tr>
<tr>
<td>(400°C)</td>
<td>44-52</td>
<td>3.5-7.6</td>
</tr>
<tr>
<td>Nicalon-type Fibers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(400°C)</td>
<td>~50</td>
<td>~4</td>
</tr>
</tbody>
</table>

AVERAGE TENSILE STRENGTH (GPa)

AVERAGE FIBER DIAMETER (μm)

Yajima's Data

- UF Fiber Batches (1000°C/N₂)
- As-Received Nicalon (manuf. value)
- As-Received Nicalon (UF value)
- Nicalon (1000°C/N₂)
## ELEMENTAL ANALYSIS

<table>
<thead>
<tr>
<th>Sample</th>
<th>O (wt%)</th>
<th>Si (wt%)</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
<th>H (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Fiber</td>
<td>1.1-2.6</td>
<td>55'</td>
<td>42'</td>
<td>1-2'^</td>
<td>&lt;0.5'</td>
</tr>
<tr>
<td>Nicalon</td>
<td>13.5-15</td>
<td>55'</td>
<td>29'</td>
<td>&lt;0.5'</td>
<td>&lt;0.5'</td>
</tr>
<tr>
<td>Nicalon*</td>
<td>10</td>
<td>58</td>
<td>31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reported by manufacturer  
† Determined by neutron activation analysis  
‡ Determined by atomic absorption  
▲ Determined by LECO combustion method  
▼ Determined by difference
UF Fibers
Argon 10°C/min 1 h at 1550 °C

Nicalon Fibers
Argon 10°C/min 1 h at 1550 °C
Processing Modifications

- Improve Filtration of Spinning Solution
  (2-4 \( \mu m \) glass filter \( \rightarrow \) 0.1-0.2 \( \mu m \) PTFE filter)

- Reduce Oxygen Content in Fibers
  (Lower oxygen partial pressure during pyrolysis)
**OXYGEN ANALYSIS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydimethylsilane</td>
<td>0.3 - 0.4</td>
</tr>
<tr>
<td>Polycarbosilane</td>
<td>0.3 - 1.3</td>
</tr>
<tr>
<td>UF FIBER</td>
<td>1.1 - 2.6</td>
</tr>
</tbody>
</table>

* Determined by neutron activation analysis
Oxygen Contamination During Fiber Fabrication

- Spinning (ambient air atmosphere)

- Pyrolysis (ungettered furnace, nitrogen)
Nicalon™  1600°C in Argon
AVERAGE TENSILE STRENGTH (GPa)

AGING TEMPERATURE (°C)

- UF - Highest Strength
- UF - 127
- UF - 80
UF fibers were prepared by dry spinning of concentrated solutions of high molecular weight (~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 μm), round cross-sections, and relatively smooth surfaces
- Average tensile strengths as high as ~3.3 GPa for as-pyrolyzed fibers
- Average rupture strain ~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
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
High Performance Fibers Now Are Solution Spun

Kevlar (DuPont)
Spectra (Allied-Signal)
Extendable (continued)

- Same solutions can be used for coatings (original goal)
- Synthesis modification has potential for infiltration
- Same benefits for BN precursors and others
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 Al controlled spinning of high-strength mullite and composite mullite fibers with improved high temperature (>1200°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 Al-based fiber spinning and processing operations.

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SIO₂ - Al₂O₃ PHASE DIAGRAM

MOLE % Al₂O₃

LIQUID

MULLITE + LIQUID

SIO₂ + MULLITE

MULLITE

AL₂O₃ + MULLITE

TEmPERATURE (°C)

WEIGHT % Al₂O₃


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

Precursor Solution Preparation → Precursor Sol Ageing → Spinning Process

Precursor decomposition 
Solvent evaporation 
Organic burnout

High Temperature Heat-treatment for Mullite formation and Sintering

High temperature Strength Tests

Green Fiber Formation

Blanket Weaving
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 Al 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

- Silica alumina colloid

Highly branched polymeric clusters of silica alumina

Method #1: Centrifugal Spinning
Method #2: Pulled by Hand

Continuous Spinning
SOL-GEI 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**

- Aluminum Chlorohydroxide Solution
- Colloidal Silica
- Nitric Acid
- Filtration
- Concentration
- Fiber Drawing
- Drying
- Sintering

**METHOD #2**

- Aluminum Formoacetate Solution
- Lactic Acid
- Colloidal Silica
- Nitric Acid
- Polymer
- Filtration
- Concentration
- Fiber Drawing
- Drying
- Sintering
100 Mullite Fibers (Method #1)

0 200 400 600 800 1000 1200 1400 1600
TEMPERATURE (°C)

Mullite Fibers (Method #2)

0 200 400 600 800 1000 1200 1400 1600
TEMPERATURE (°C)
Mullite Fibers (Method #1)

Mullite Fibers (Method #2)

Specific Surface Area $\text{(m}^2\text{g)}$

Temperature $\text{(°C)}$

![Graph A](image)

![Graph B](image)
Mullite Fiber (Method #1)
MULLITE BASED FIBERS (SOL-GEL PROCESS)

AI-CHLOROHYDROXIDE-SILICA SOL PRECURSOR, 1500°C

3M NEXTEL 480
AFTER 2hr. AT 1500°C
Mullite Fiber (Method #2)
Silica Sol Methods

Method #3

1. **Tri sec butoxy Aluminum**
2. **2 Butanol**
   - **Triethylamine**
   - **2 Butanol**
   - **Deionized water**
   - **2 Butanol**
   - **TEOS**
   - **2 Butanol**
   - **Silica Sol**
   - **Alumina Sol**
   - **Fiber Drawing**
   - **Drying**
   - **Sintering at 1200 C**

Method #4

1. **Tri sec butoxy Aluminum**
2. **2-Butanol**
   - **Triethylamine**
   - **2 Butanol**
   - **Deionized water**
   - **Acetic Acid**
   - **TEOS**
   - **2 Butanol**
   - **Ethylamine**
   - **Highly branched silica sol**
   - **Silica Alumina Sol**
   - **Fiber Drawing**
   - **Drying**
   - **Sintering at 1300 C**
SILICA SOL METHODS

METHOD # 3

Sample: S1
Size: 53.60 mg
Rate: 10°C/MIN
Program: TGA Analy/1s V2.0

Date: 8-May-92   Time: 23:14:41
Operator: SAA
TGA
Place: 9-May-92   3:25:32

Residual:
39.18 %
(21.00 mg)
SILICA SOL METHODS
METHOD # 3

Sample: S2
Size: .1037
Rate: 10

Date: 18-May-92  Time: 10:04:53
File: SAADTA.02 ZACKTA41
Operator: SAA

Temperature Difference (°C)

Temperature (°C)

DuPont 109
SILICA SOL METHODS
METHOD # 3

Surface Area Change with Temperature for Mullite Fibers
SILICA SOL METHODS
METHOD # 3

Sample: SAF1  File: DUO: [300, i]SAF1.RD  01-JUN-92  15:28

A16S12013 MULLITE, SYN
15-776
SOL-GEL PROCESSING OF CONTINUOUS MULLITE-BASED FIBERS

SOL-GEL APPROACHES FOR PRODUCING MULLITE

<table>
<thead>
<tr>
<th></th>
<th>Results:</th>
<th>Problems:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal Sols</td>
<td>Mullite phase formed (1200C)</td>
<td>Spinnability difficult to achieve</td>
</tr>
<tr>
<td></td>
<td>Full densification</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No intergranular glass phase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fine grain structure</td>
<td></td>
</tr>
<tr>
<td>Polymer Sols</td>
<td>Mullite phase formed (1000C)</td>
<td>Full density</td>
</tr>
<tr>
<td></td>
<td>Fine grain structure</td>
<td>difficult to achieve</td>
</tr>
<tr>
<td></td>
<td>Spinnability excellent</td>
<td></td>
</tr>
<tr>
<td>Seeded Sols</td>
<td>Promise:</td>
<td>Process control</td>
</tr>
<tr>
<td></td>
<td>Full density</td>
<td>has many variables</td>
</tr>
<tr>
<td></td>
<td>No glass phase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spinnability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fine grain structure</td>
<td></td>
</tr>
<tr>
<td>Glass Leaching</td>
<td>Starts with woven blanket</td>
<td>Borate glass phase</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Process control</td>
</tr>
</tbody>
</table>
Seeded Sol Methods

Method #5

- Colloidal Silica
  - Deionized water

- Boehmite powder
  - Deionized water

- Tri sec butoxy Aluminum
  - 2 Butanol
  - Triethylamine
  - 2 Butanol
  - Deionized water
  - TEOS
  - 2 Butanol
  - Silica Sol

- Hydrolysis

Alumina Silica Sol

- Fiber Drawing

Drying

Sintering at 1500 C
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 presursors 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 Al₂O₃ · 1 SiO₂ 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

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.
CHEMICAL VAPOR DEPOSITION APPROACHES TO IMPROVED COMPOSITE STRUCTURES

Tim Anderson
Chemical Engineering Department
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 polishibility

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

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## System Features
- Four Independent Gaseous Sources (Currently BCl₃, SiH₂Cl₂, CH₄, and NH₃ or HCl)
- Three Independent Liquid Sources (Currently TiCl₄, SiCl₄, and PCl₅)
- 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

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REACTION LIMITED DEPOSITION OF TiCₙ

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

Microstructure of TiCₙ on Alumina, clockwise from upper left-hand side corner, T=1300 °C and CH₄/TiCl₄=0.5, T=1300°C and CH₄/TiCl₄=1.0, T=1300°C and CH₄/TiCl₄=3, T=1300°C and CH₄/TiCl₄=4.0.
COMPARISON OF ACTIVATION ENERGY AND ORIENTATION FOR DEPOSITION OF TiCₙ

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>130</td>
</tr>
<tr>
<td>Graphite</td>
<td>109</td>
</tr>
<tr>
<td>Nicalon</td>
<td>210</td>
</tr>
</tbody>
</table>

Preferred Orientations of TiC grown on different substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>T(°C)</th>
<th>(HKL)</th>
<th>T(°C)</th>
<th>(HKL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1050</td>
<td>(200)</td>
<td>1200</td>
<td>(220)</td>
</tr>
<tr>
<td>Nicalon</td>
<td>1050</td>
<td>(200)</td>
<td>1200</td>
<td>(200)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1050</td>
<td>(111)</td>
<td>1200</td>
<td>(111)</td>
</tr>
<tr>
<td>Mo</td>
<td>1050</td>
<td>(220)</td>
<td>1200</td>
<td>(200)</td>
</tr>
<tr>
<td>Ta</td>
<td>1050</td>
<td>(200)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Deposition Temperatures of > 1100°C. Increased cracking is observed at fracture toughness of the TiC matrix. Increasing the hardness and decreases the increasing the deposition temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H K (MPa·m(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>27 2.1 26 2.1</td>
</tr>
<tr>
<td>1050</td>
<td>21 3.5 22 2.6</td>
</tr>
<tr>
<td></td>
<td>(GPa) (MPa·m(^{1/2}))</td>
</tr>
</tbody>
</table>

**Deposition Graphite**

Toughness of CVD TiC

Microhardness and Fracture
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

CVI WITH THERMAL GRADIENT AND HCL FLOW CONTROL

COLD 1 2 3 HOT 1: ETCHING ZONE 2: DEPOSITION ZONE

DEPOSITION ZONE

1300°C

DEPOSITION-ETCHING BOUNDARY AT $P_{\text{HCl}}$

ETCHING ZONE

800°C

POSITION

800°C

ETCHING ZONE

1300°C

DEPOSITION-ETCHING BOUNDARY AT $P_{\text{HCl}}$

POSITION

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

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TiC YIELD vs DEPOSITION TEMPERATURE and HCl CONCENTRATION

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ULTRA-HIGH TEMPERATURE APPLICATIONS

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

Gas Injector

Gases

Grafoil Gasket

Sample Holder

Fiber Preform

Hot Zone

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

Top Layer (1000°C)  Middle Layer  Bottom Layer (1300°C)

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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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FORCED-FLOW CVI COUPLED WITH HCL ETCHING

Top Layer (1000°C)  Middle Layer  Bottom Layer (1300°C)

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FIBER PULL-OUT AFTER POLISHING INFILTRATED NICALON PREFORM

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COMPARISON OF CVI PROCESSES

Conventional Forced-flow CVI of a Nicalon Preform with TiC$_x$

Forced-flow CVI coupled with HCl injection

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**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+ μm
- 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 μm
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Interface Without Carburization

Interface With Carburization

1 μm

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WITH CARBURIZATION

Sample: EA77  File: DUO: [300,1]EA77.RD  29-APR-92  14:09

SIC
29-1129

SI SILICON, SYN
5-565
Void Formation During Carburization

CH$_4$ + H$_2$ → Si + SiC

Substrate Coverage: Silicon provided only through grain boundaries via surface diffusion.

Nucleation and 3D Growth: Uncovered areas provide silicon at growth interface.

2D Growth: Continued silicon diffusion through grain boundary results in pitting.
Equilibrium Deposition Diagram
ATOMIC LAYER DEPOSITION (ALD)

Step 1: Ti Adsorption

Step 2: Desorption of Physically Adsorbed TiCl₄

Step 3: C Adsorption

Step 4: Desorption of Physically Adsorbed CH₄

Repeat Steps 1-4
Cubic Boron Nitride Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>$4.7 \times 10^9$</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>10 W/cm</td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>B-N Bond Strength</td>
<td>152 kcal/mol</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>3.61 Å</td>
</tr>
<tr>
<td></td>
<td>3.57 Å (diamond)</td>
</tr>
</tbody>
</table>
CVD BN on Si(100) via BCl$_3$/NH$_3$ System

Surface (200 torr, 1000°C)  Cross-section
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

CVD BN on Diamond via BCl₃/NH₃ System

Surface (200 torr, 1000°C)
B-KVV CVD BN on Diamond(110)
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N-KVV CVD BN on Diamond(110)

KINETIC ENERGY, eV

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B-KVV ALE BN on Diamond(110)

KINETIC ENERGY, eV

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TiN FILM GROWN BY ALE ON Nb

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Nb SUBSTRATE PRIOR TO ALE

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XPS SPECTRA OF TiN FILM GROWN BY ALE

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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

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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
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
\[ \Delta G \text{ vs Temperature for the Reaction} \]

\[
\text{BP(s).} + \text{NH}_3(g) \rightarrow \text{c-BN(s)} + \text{PH}_3(g)
\]
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

Nb₃Al
- 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

Ta₂TiAl₃
- 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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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

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)
Characteristics of NiAl*

Advantages

- Density ~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 (~300°C) than current superalloys
- Wider solubility range than many other compounds (MoSi₂, NbAl₃)

Disadvantages

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

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

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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
**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)
RHC of Aluminides

- Intermetallic formed from elemental powders
- Highly exothermic reaction
- Slow controlled heating $\rightarrow$ Al melts first
- Reaction rate depends on rate at which $\Delta H_{\text{form}}$ 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
Reaction Initiated

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 < 37 µm
Al 6 µm (average)

Nb₃ Al

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The Nb-Al System

Processing Cycle

RHC Processed NbAl₃
Volume Fraction of Porosity < 2%
Green Compact Compositions

1605 °C

42.2

1660 °C

NbAl₃

Atomic % Nb

Volume Fraction

Mean Spacing

1

6.9%

25 μm

383.8 μm

2

14.6%

25 μm

142.4 μm

3

27.68%

25 μm

75.1 μm
Effect of Heating Rate

DTA profile of Nb and Al powder samples (NbAl\textsubscript{3} composition) performed at four heating rates
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

T < 600 C

T = 600 C

O Al □ Ni □ Liquid □ NiAl

Temperature/Rem Pressure

50 MPa

900 C

1250 C

0 30 60 90 120
Time (minutes)

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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
Matrix-Reinforcement Considerations

- Mechanical Properties of Matrix and Potential Reinforcements
- Microstructural Stability (Anticipated Reactions)
- Mechanical Stablility (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.

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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

**Fiber Selection**

- **Best Available Fibers for NiAl**
- **Needed Fibers for NiAl**

**Diagram Details:**
- Elastic Modulus at Room Temperature, GPa
- Coefficient of Thermal Expansion (10^-6 /°K)

**Materials:**
- Al₂O₃
- Ta
- Nb
- ZrO₂
- Al₃Nb
- TiAl
- Y₂O₃
- ZrO₂ (CaO)
- SiC
- Mo
- AlN
- MoSi₂

**Institution:**
- MSE
- University of Florida
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

- **Pre-treated Reinforcement**
  - $R_2O_y$ + Matrix Powders $\rightarrow$ Protected Reinforcement

- **Un-treated Reinforcement**
  - $R$ + Matrix Powders $\rightarrow$ Protected Reinforcement

- **Matrix Powders With Ternary Element**
  - $AB+C$ $\rightarrow$ In-Situ Formed Reinforcement
  - $AB(+O)+C$ $\rightarrow$ Clean Matrix AB

Combinations of the Above

Materials Science & Engineering
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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.)
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

\[ \text{NbAl}_3 \text{ Composites} \]

**Ductile phase toughening**
- RHC studies
- \textit{In-situ} interface coatings
- Mechanical properties

**Matrix development**
- Alloying to effect the \( \text{DO}_{22} \rightarrow \text{L}_1 \) transformation
- Alloying to enhance slip and/or twinning
- Second phase effects
- Combination of enhanced matrices with \textit{in-situ} coating scheme

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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 compation of mixture of Nb, Al powder and the oxidized Nb filaments

Final product of in-situ coated Nb/NbAl3 composite

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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
THERMAL STABILITY AT 1200°C: ANNEALED FOR 100 HOURS

"In-Situ" Coated Nb Filament

Uncoated Nb Filament
INOVATIVE 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:
- NbAl₃
- Nb₂Al
- α-Al₂O₃
- Nb
Toughening Effect of Nb Filament Reinforcements With Alumina Diffusion Barrier Produced "In-Situ"

**FRACTURE TOUGHNESS TEST**

- **Nb/NbAl<sub>4</sub> Composite (with alumina coating)**
- **NbAl<sub>3</sub>**

**K<sub>c</sub> MPa·m<sup>0.5</sup>**

- **9.6**
- **3.5**
- **2.5**
- **1.6**

Monolithic: 13.4 Vol.% Second Phase Reinforced: 20 Vol.% Nb Filament Reinforced

Toughening Due to Interfacial Debonding

Toughening Due to Filament Pull-Out

[Scale: 200 µm, 50 µm]
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**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 DO₂₂→L₁₂ transformation is not possible for this compound.

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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

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Reaction Schemes for NiAl Matrix Composites

Extension of Nb/NbAl₃ Work

\[ \text{NiAl} + \text{Nb}/\text{Nb}_2\text{O}_5 \rightarrow \text{NiAl}/\text{Al}_2\text{O}_3/\text{Nb} \]

Related Approaches for Molybdenum & Tungsten Reinforcements

\[ \text{NiAl(C)} + \text{Mo or W} \rightarrow \text{NiAl}/\text{Mo}_2\text{C} /\text{Mo} \text{ or } \text{NiAl}/\text{W}_2\text{C}/\text{W} \]

\[ \text{NiAl} + \text{Mo}/\text{Mo}_2\text{C} \text{ or } \text{W}/\text{W}_2\text{C} \rightarrow \text{NiAl}/\text{Mo}_2\text{C} /\text{Mo} \text{ or } \text{NiAl}/\text{W}_2\text{C}/\text{W} \]

Related Approaches for Sapphire Reinforcements

\[ \text{NiAl(Si)} + \text{Sapphire} \rightarrow \text{NiAl}/\text{Mullite}/\text{Sapphire} \]
 Nb-NiAl Diffusion Couple
4 Hours at 1200 °C

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

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$K_{lc}$ (MPa$\sqrt{m}$)</th>
<th>FRACTURE ENERGY (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00-000</td>
<td>11.03 ± 1.09</td>
<td>1253.6 ± 289.6</td>
</tr>
<tr>
<td>00-125</td>
<td>7.15 ± 1.21</td>
<td>1481.5 ± 183.0</td>
</tr>
<tr>
<td>00-250</td>
<td>12.75 ± 1.62</td>
<td>6794.8 ± 2157.9</td>
</tr>
</tbody>
</table>
NiAl / Mo diffusion couple

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Precarburized molybdenum

NiAl/Mo₂C / Mo diffusion couple

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NiAl(+C) / Mo diffusion couple

A: Mo
B: Mo_2C

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INTERMETALLIC MATRIX COMPOSITES

NiAl(+)C / W diffusion couple

A: W
B: W2C

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MoSi$_2$ Studies

**Ductile phase toughening studies**
- Niobium/MoSi$_2$ laminates
- Coating studies
- Modeling

**Matrix development**
- Tape casting of MoSi$_2$ 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
Physical Properties of MoSi₂

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-m¹/²

(From Brewer and Lamoreaux, 1980)
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Toughness and Interfacial Fracture Energy of MoSi$_2$
Composites with 20 vol.% of Nb Laminae

<table>
<thead>
<tr>
<th>Materials</th>
<th>MoSi$_2$</th>
<th>uncoated Nb reinforced</th>
<th>Al$_2$O$_3$ coated Nb reinforced</th>
<th>ZrO$_2$ coated Nb reinforced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial fracture energy (J/m$^2$)</td>
<td>-</td>
<td>&gt; 33.7 ± 1.4</td>
<td>16.1 ± 1.3</td>
<td>12.8 ± 1.0</td>
</tr>
<tr>
<td>Damage tolerance (MPa.m$^{1/2}$)</td>
<td>3.3 ± 0.3</td>
<td>15.2 ± 1.3</td>
<td>14.0 ± 1.5</td>
<td>12.8 ± 1.5</td>
</tr>
<tr>
<td>Work of fracture (J/m$^2$)</td>
<td>690 ± 30</td>
<td>21,600 ± 3,000</td>
<td>28,700 ± 1,900</td>
<td>28,700 ± 4,600</td>
</tr>
</tbody>
</table>

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

Interfacial microstructures

Uncoated  Al$_2$O$_3$ coated  ZrO$_2$ coated

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Effects of Size of Ductile Phases on Toughness of MoSi$_2$ Composites with 20 vol.% of Nb Laminae

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

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

Orientation Dependence of the Toughness of the Composites

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

Fracture Surfaces of the Composite Laminates

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

Crack propagates transverse to the lamina plane (T-orientation)
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Interfacial Microstructures in MoSi$_2$/Nb Composites

- Uncased
- Al$_2$O$_3$ coated via sol gel technique
- Al$_2$O$_3$ coated via aluminum anodizing

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load-displacement curves of the Chevron notched samples

Fracture Toughness of MoSi$_2$/Nb Composites

- Uncoated Nb filament, 1.0 mm
- Al$_2$O$_3$ coated Nb filament, 1.0 mm
- Al$_2$O$_3$ coated Nb filament, 0.25 mm
- ZrO$_2$ coated Nb foil, 0.25 mm
- Uncrusted Nb filament, 0.25 mm
- Uncrusted Nb foil, 0.25 mm

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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.
Typical microstructures (SEM) of MoSi$_2$ - 30 vol.% SiC$_6$ 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 (SiO$_2$ and/or porosity) in MoSi$_2$ made from commercial powder — MoSi$_2$ can be synthesized at room temperature by mechanical alloying. Carbon can be added to both reduce SiO$_2$ and form SiC.

- High temperature strength of MoSi$_2$ decreases rapidly at temperatures approaching 1200$^\circ$C — can use MA to introduce dispersoids into MoSi$_2$.

- 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 MoSi$_2$ — can consolidate MA'd powders at relatively low temperatures (e.g., 1200$^\circ$C)
X-ray diffractogram of a typical powder sample attritted for 40 hours showing the presence of $\alpha$-MoSi$_2$ (labelled T), $\beta$-MoSi$_2$ (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 $\alpha$-MoSi$_2$.

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Reaction Schemes for MoSi$_2$ Studies

Multi-step Reactions

SiO$_2$ $\rightarrow$ SiO + [O]
C + O $\rightarrow$ CO
SiO + 2C $\rightarrow$ SiC + CO$_2$

SiO + 2C $\rightarrow$ Si (silicide) + CO

Overall Reaction

SiO$_2$ + 3C $\rightarrow$ Si C + 2CO
SiO$_2$ + 2C $\rightarrow$ Si (silicide) + 2CO
Phase relations in the Mo/Si/C System

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

1200°C Isotherm by F. J. J. van Loo et al.

N = Mo₅Si₃C
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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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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
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 $\alpha$- and $\beta$ forms are present.
Bright Field TEM of $\beta$-SiC particle formed in-situ in a typical ternary (C-modified) MA MoSi2 sample.

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Bright Field Transmission Electron Micrograph of a typical ternary (C-modified) MA MoSi2 showing the clean silica-free grain boundaries
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(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
Figure 1 Mo-Si phase diagram (Brewer 1982). Schematic Free energy vs. Composition curves for this system, illustrating the range of silicon activities in MoSi$_2$. 

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Figure 2. Equilibrium silicon vapor pressure over MoSi$_2$.

Figure 6. Mechanical alloyed Mo-Si-C vacuum hot pressed at > 1600°C. 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: MoSi$_2$, Light phase: Mo$_5$Si$_3$C)
Highlights of MoSi$_2$ Studies

- Under optimized conditions, refractory metal toughening (Nb) leads to damage tolerances approaching 17 MPa.m$^{1/2}$.
- Reliable coating schemes (sol-gel and PVD) have been developed.
- SiC whisker reinforced MoSi$_2$ composites have been produced via tape casting and are being evaluated from the standpoint of high temperature properties.
- Carbon additions to MoSi$_2$ 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 MoSi$_2$/SiC alloys with much less of the higher Mo phases (e.g., Mo$_5$Si$_3$ & Mo$_5$Si$_3$C).
- 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.

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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
**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

![Graph showing R.T. Fracture Toughness Values of TaTiAl2 Composites](image-url)
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Matrix/Reinforcement

Thermochemical Compatibility

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Interaction</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>No Reaction</td>
<td>A</td>
</tr>
<tr>
<td>Y2O3</td>
<td>No Reaction</td>
<td>A</td>
</tr>
<tr>
<td>ZrO2</td>
<td>Moderate</td>
<td>B</td>
</tr>
<tr>
<td>ZrN</td>
<td>Extensive</td>
<td>C</td>
</tr>
<tr>
<td>ZrC</td>
<td>Extensive</td>
<td>C</td>
</tr>
<tr>
<td>SiC</td>
<td>Extensive</td>
<td>C</td>
</tr>
<tr>
<td>TiB2</td>
<td>Extensive</td>
<td>C</td>
</tr>
<tr>
<td>Nb</td>
<td>Extensive</td>
<td>D</td>
</tr>
<tr>
<td>Nb (alumina coated)</td>
<td>No Reaction</td>
<td>A</td>
</tr>
</tbody>
</table>

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
Coated Nb Filament
Microhardness Profiles
Short Fiber Alignment Process

1. Mix Fibers/Matrix Powder/Polymer Solution
2. Gelation in acid bath
3. Wash, Dry, and Cut
4. Characterization and Testing
5. P, T, t
Flexural Yield Strengths and Elastic Moduli of Composites at High Temperatures
Matrix Development in the Ta-Ti-Al System

Highlights

- Heavy segregation occurs upon solidification
- Large $\alpha$ & $\beta$ phase fields at 1450°C
- Complex decomposition sequences -- corresponding large variation in microstructures and properties
- $\gamma$ forms massively from $\alpha$ upon water quenching
- Phase boundary positions vary considerably with temperature -- undesirable from an applications standpoint
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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 MoSi₂
  2. Form dispersoid phases -- SiC in MoSi₂
  3. Form interface coatings
     * Alumina in Al₃Nb/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.

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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.
A Combination of RHC, In-Situ Coating and Fiber Alignment
(Schematic)
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
MICROWAVE PROCESSES INVESTIGATED

Sintering
Annealing (superconductors)
Self-Propogating 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
YBa$_2$Cu$_3$O$_{7-x}$ Superconductors - Sintering and Annealing

- TiC
- Al$_2$O$_3$/TiC
- Others

Microwave SHS

Na$_2$O·Al$_2$O$_3$·SiO$_2$ - Surface Modification
- Li$_2$O·2SiO$_2$
- BaO·Al$_2$O$_3$·2SiO$_2$

Crystallization

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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Ultra-rapid Sintering of A-16 Alumina at 1800°F for 30 minutes
NW Zeolite Heating vs. Conventional Fast Firing
MICROHARDNESS OF 99.5%–94% ALUMINA JOINT WITH AND WITHOUT GEL

T = 1350°C, t = 80 min

99.5% ALUMINA

94% ALUMINA

NO GEL

GEL

DISTANCE FROM JOINT (MICROMETERS)
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

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

* 99.5%-GEL-94% ALUMINA
  $T=1350^\circ C$, $t=60$ min
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

![Graph showing bending strength vs. joining temperature]

**BENDING STRENGTH (MPa)**

**JOINING TEMPERATURE (°C)**

- □ Original Material
- ● Joined Sample
- ○ No Joining

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MICROWAVE CONTROLLED COMBUSTION SYNTHESIS (MICROCOM)

PROCESSING TIME:

0:00 min.   6:00 min.   8:00 min.   12:00 min.

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

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LOW EXPANSION MATRIX DEVELOPMENT

PROJECT GOALS

To evaluate BaO·Al₂O₃·2SiO₂ 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.
WHY CELSIAN?

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

- CTE $2.3 \times 10^{-6}/\text{°C}$
- 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

Melt raw materials >2100°C

Frit glass

Forming/Shaping

Heat treat to simultaneously density and crystallize 1200-1350°C

SOL-GEL PROCESS

Produce sol 60°C

add second phase (SiC)

Gelation

Crush to powder

Forming/Shaping

Controlled Gelation

add second phase (SiC)

Forming/Shaping

Controlled Drying

Microwave

Heat treat to density 1000°C

Microwave

Heat treat to crystallize - 1300°C
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

Barium Aluminosilicate + 10 wt% CuO
dried at 850°C

Delta-T (°C)
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17

Temperature (°C)
900 950 1000 1050 1100 1150 1200 1250

- densification without crystallization
- crystallization occurs
- hexagonal
- monoclinic
INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

BaO–Al₂O₃–2SiO₂ + 10 wt.% CuO

most peaks correspond to the monoclinic phase
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.
ACCOMPLISHMENTS cont.

Produced amorphous BaO·Al₂O₃·2SiO₂ 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.
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
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

\[ 3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \text{ (Mullite)} \]
FABRICATION OF MULLITE/SILICON CARBIDE COMPOSITES

Chemical Reaction

Densification

3Al₂O₃ + 2SiO₂ + xSiC

3Al₂O₃·2SiO₂·xMullite + xSiC
TRANSIENT VISCOS SINTERING

\[
\begin{align*}
SiO_2 + Si_3N_4 + Al_2O_3 + AlN &\rightarrow SiO_2 + Si_3N_4 + Al_2O_3 + AlN \\
&\rightarrow SIALON
\end{align*}
\]
-1750°

3(SiO₂)  3Al₂O₃·SiO₂  2(Al₂O₃)

3Al₂O₃·AlN  Al₂O₃·AlN

Si₂N₂O  20  40  60  80  Mol %

Si₃N₄  20  40  60  80  4(AlN)
CERAMICS AND COMPOSITES PREPARED BY VISCIOUS AND
TRANSIENT VISCIOUS 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)
74 wt% Al₂O₃/ 26 wt% SiO₂
10 vol% SIC Fibers

1300°C Hot Press

ENGINEERING STRESS (MPa)

TIME (min)

0 5 10 15 20 25 30 35 40 45 50

0 10 20 30 40 50 60 70 80 90

74 wt% Al₂O₃/ 26 wt% SiO₂
10 vol% SIC Fibers

1300°C Hot Press

DISPLACEMENT (mm)

TIME (min)

0 5 10 15 20 25 30 35 40 45 50

0 1 2 3 4 5 6 7 8 9
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)
\textbf{\~{}10 wt\% B}_2\text{O}_3

\textbf{\~{}17 wt\% B}_2\text{O}_3
**BULK DENSITY (g/cm³)**

- ▼ SiO₂/Al₂O₃
- □ Borosilicate (-10 wt% B₂O₃)/Al₂O₃
- ○ Borosilicate (-18 wt% B₂O₃)/Al₂O₃

**OPEN POROSITY (%)**

- ▼ SiO₂/Al₂O₃
- □ Borosilicate (-10 wt% B₂O₃)/Al₂O₃
- ○ Borosilicate (-18 wt% B₂O₃)/Al₂O₃

**TEMPERATURE (°C)**

- X 400 600 800 1000 1200 1400 1600
Borosilicate (-23 wt% $\text{B}_2\text{O}_3$) / Silicon Nitride
Silica / Silicon Nitride

**Bulk Density (g/cm$^3$)**

**Open Porosity (%)**

**Temperature (°C)**
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.
Infiltrated with Silicon

Infiltrated with Carbon Precursor and Silicon
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

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N. Bozkurt
I.Y. Park
R. Raghunathan
K. Wang
Y.J. Lin
A.E. Bagwell
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INNOVATIVE PROCESSING OF COMPOSITES FOR ULTRA-HIGH TEMPERATURE APPLICATIONS

TAPECAST LAMINATED COMPOSITES

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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 LAMINAЕ INTERFACES.

- IMPROVED LAMINATE TOUGHNESS TO >10MPam^{1/2} USING FUNCTIONALLY GRADED DESIGN.

- IMPROVED THERMAL SHOCK RESISTANCE OF ALUMINA UP TO ΔT = 1200°C.

- ACHIEVED LAMINATE STRENGTHS > 700 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

- Hard Surface (e.g., Aluminize)
- Core (Lightweight)
- Ductile

α Increases

Compressive Residual Stress

High Toughness Lamina

Toughened

- Porous
- Substrate

High Specific Strength

Surface Protected
SAMPLE DESIGNATION

Ni
Alumina

Ni (.125)

Ni
Alumina

Ni (.180)

Ni
Alumina

Ni (.240)

Al2O3

All external layers are .22 mm and internal layers are .30 mm for alumina
DIFFERENT TESTS ARE REQUIRED TO EVALUATE COMPOSITES
Improved Mechanical Properties

- Laminates:
  - Strength (MPa): 766
  - Toughness (MPam\(^1\))
  - Work of Fracture (J/m\(^2\))
  - Hardness (GPa)

- Alumina:
  - Strength (MPa): 10.8
  - Toughness (MPam\(^1\))
  - Work of Fracture (J/m\(^2\))
  - Hardness (GPa)

Values:
- Laminates: 1722
- Alumina: 556
LAMINATES SHOW INCREASED TOUGHNESS OVER MONOLITHICS
STRENGTH NEARLY INDEPENDENT OF CRACK SIZE FOR LAMINATES

![Graph showing strength nearly independent of crack size for laminates.](image)
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.

![Micrograph](image)

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

![Graph](image)

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

- Indent Strength (MPa)
  - High Tortuosity (D=1.21)
    - 267
  - Medium Tortuosity (D=1.07)
    - 191
  - Low Tortuosity (D=1.00)
    - 158

- Work of Fracture (kJ/m)
  - 9.2
Graded Composites Are Designed To Improve Toughness

- Residual Compression
- Residual Compression + Crack deflection
- Residual Compression + Crack deflection & Bridging
- Bridging & Crack blunting + Interface debonding
- Faber & Evans Model for Toughening

Volume Fraction

Relative Toughness

Ceramics
Cer.+25%metal
Cer.+50%metal
Metal
R-Curve Behavior Improved By Designing Laminates

New Laminates
\[ y = -6.4 + 7.2 \cdot \log(x) \quad R^2 = 0.88 \]

Laminates
\[ y = -5.0 + 5.6 \cdot \log(x) \quad R^2 = 0.94 \]

Alumina

Crack Resistance (MPa.m^0.5)

Crack Length (μm)
LAMINATES SHOW DAMAGE TOLERANCE

![Graph showing thermal shock temperature difference (°C) vs. indentation strength (MPa) for various materials.](image)

- Laminates
- Alumina

* All samples were quenched into room temperature water
** All samples with a 12 Kg load indentation
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.