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**Characterization of ultra-high temperature materials produced by rapid-laser chemical vapor deposition (R-LCVD)**

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Laser-driven Chemical Vapor Deposition

-SiC fiber performance in composite materials

-Novel Fiber developments
The Possibilities From A Novel Process

- Laser Chemical Vapor Deposition (LCVD) allows stoichiometric purity
- >15 patents issued, and dozens pending, worldwide
- Numerous successful SBIR contracts with DoD, DoE sponsors
The Possibilities From A Novel Process
Background

• Company founded in 2006
• Significant SBIR/government funded support across an array of agencies
• Material solution formats: ‘long’ and ‘short’ fiber, powder
• LCVD is not chip fabrication in the microelectronics industry
• No clean room requirements
• LCVD production tool <<< micro fab tool
Representative Projects

• DOE Accident Tolerant Fuels
• 3-D Ceramic Composite Cladding
• Homogenous Joining of SiC/SiC

• DOD
• High Temperature, Low Dielectric Constant Fiber
• Thermal Shock Resistant Apertures

• Semiconductor
Why Ceramic Fibers and Ceramic Composites?
20 Year old application chart:

Application for CMCs in Gas Turbine Engines

- Combustor liners
- Vanes
- Shrouds
- Blades
- Turbine Frame Flowpath
- Flaps & Seals

Courtesy of GE Aircraft Engines
Silicon Carbide Background

- Acheson Process over 100 years old for Silicon Carbide raw materials for powders
- Silicon Carbide Fiber commercial for over 50 years
- Coarse, monofilament produce by CVD on conductive core
- Spinning of pre-ceramic polymer fibers before pyrolysis: Oxygen issue
- SiC fibers state of the market
  - 2400 F Maximum CMC service temperature with current SiC fibers
  - GE Aviation: > 100,000 SiC/SiC parts flying
20 Year old application chart:

Reality!
Stoichiometric = High Purity

- Silicon Carbide
- Silicon Nitride
- Novel Oxides: Hf, Ta, Zr
- Borides
- Refractory Carbides: Hf, Zr, et al
- Novel Nuclear Compositions
• Parallelization through laser beam multiplexing
• Material agnostic process
• Concentrated energy delivery yields conditions for high volume manufacturing
Deposition Process (Video)
SiC Fiber Manufacturing (Video)

- ‘Hairbrush’ formation of SiC fiber parallel arrays
- Single reactor head
- Scale up of manufacturing by replication of heads
- Not a batch chemical mixing process
LCVD SiC-Composition and Crystallinity

X-ray Diffraction
LCVD SiC-Composition and Crystallinity

<table>
<thead>
<tr>
<th>Crystalline Phase Analysis (wt. %)</th>
<th>6 SiC 7129 71621</th>
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</thead>
<tbody>
<tr>
<td>SiC (3C)</td>
<td>91.3 (78 Å)</td>
</tr>
<tr>
<td>Si</td>
<td>3.5 (193 Å)</td>
</tr>
<tr>
<td>SiC (6H)</td>
<td>5.1</td>
</tr>
<tr>
<td>SiO₂ (Quartz)</td>
<td>0.1</td>
</tr>
<tr>
<td>Amorphous</td>
<td>?</td>
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</tbody>
</table>

X-ray Diffraction
High Purity Materials

Fundamentals of CVD

• No oxygen present

• Energy dispersive x-ray spectroscopy, Auger electron spectroscopy, LECO oxygen analyzer, transmission electron microscopy-energy electron loss spectroscopy

• Precision control of composition

• SiC: by weight percent ratios, Si:C from 70:30 to 80:20
High Temperature Performance

• Single fiber creep
  • Based on single fiber tensile
  • 1500°C, Argon & air environments, 250-750 MPa
• Oxy-acetylene torch exposure
  • Estimated 1625°C
• Comparison of Hi Nicalon-Type S, Sylramic, and FFF 71:29 SiC fiber
High Temperature Performance (Video)

Temperature: 1550-1600°C
Date: December 17, 2018
Si3N4 IRAD Status

- Internal R&D led to the production of initial batch of silicon nitride Fibers
- Developed ~ 50-to-60-micron diameter fibers
- Transition to funded R&D
- Working to optimize fiber diameter, surface morphology, and microstructure
Si3N4 Purity

<table>
<thead>
<tr>
<th>Crystalline Phase Analysis (wt. %)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Si$_3$N$_4$ (Nierite)</td>
<td>84.0</td>
</tr>
<tr>
<td>β-Si$_3$N$_4$</td>
<td>13.4</td>
</tr>
<tr>
<td>Si</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Si3N4 IRAD

• Highly elongated fibrils in the center, evolving to teardrop beads at the edge
Si3N4 IRAD

• Sinters to Full Density
Silicon Nitride Fiber

• Internal R&D
• Navy SBIR (data restrictions)
• Papers at USACA, EM Windows
• Optimization ongoing to achieve full density
• Production scale focus
• Characterization work ongoing: electrical (dielectric), mechanical (tensile, creep)
Refractory Oxide Fibers

• Follows work on Si3N4 Fibers

• Identified precursor materials from multiple sources
• Commercially available gases, other materials to achieve purity
• Varying laser types, process parameters, explored
• Hafnium, Tantalum, Zirconium and others
Refractory Carbides

- HfC Coating
  - Applied under a range of conditions
  - Hafnium tetrakis (ethylmethylamide)—\(\text{C}_{12}\text{H}_{32}\text{HfN}_{4}\)
  - Dimethylbis (cyclopentadienyl) hafnium—\(\text{C}_{12}\text{H}_{16}\text{Hf}\)
Refractory Carbides

- HfC Coating

![Graph showing XPS spectra with binding energies and atomic percentages]

- Atomic %
  - Hf4d: 50.6
  - C1s: 49.4

- Atomic %
  - C1s: 66.6
  - Hf4f: 33.4
Refractory Carbides

• HfC Coating
  • XPS analysis using PHI 5000 VersaProbe performed at Rensselaer Polytechnic Institute
  • Data collected after 2 minute argon ion sputter of sample surface
  • Hf d-peak and f-peak differences
  • Oxygen presence believed to be from microprobe spot diameter mismatch to fiber sample diameter
UHT Materials

• SiC/ZrB2-SiC Matrix
• 4.12 g/cc
Capacity Expansion
Capacity Expansion

• Transition from R&D Operations and Culture
• Nearly Doubling of Footprint with ability to add more
• Multiple Production Cells
• Moved from Proof of Concept (grams) to Small Scale Commercial (kilograms)
• Commercial Production in Metric Tons/year outlined
Capacity Expansion
Operational Growth

• Quality Systems Being Implemented
• Locking Down Product Specifications
• Process Flow Diagrams
• Disaster Recovery Plan
• Consistent, Reliable, Products and Processes, Not R&D
Product Forms

- Fibers
- Powders
  - Size Reduction Techniques
  - Purity continuity
- Preforms
  - Non-woven
  - Composites-specific
Product Forms
Product Specifications

• Pricing and Capacity is highly dependent on product mix
• Fiber Diameter Ranges
  • 15 – 250 microns
• Fiber Lengths
  • mm to meters
• Fiber Composition
• Fiber Purity

<table>
<thead>
<tr>
<th>Variables</th>
<th>Affected Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser selection</td>
<td>Fiber Density</td>
</tr>
<tr>
<td>Precursors</td>
<td>Fiber Composition</td>
</tr>
<tr>
<td>Gas ratios</td>
<td>Fiber Composition</td>
</tr>
<tr>
<td>Laser power</td>
<td>Fiber Diameter</td>
</tr>
<tr>
<td>Pressure</td>
<td>Fiber Diameter</td>
</tr>
</tbody>
</table>
Ceramic Matrix Composites
Technical Plan: Fiber Processing

• Veil Conversion
  • Wet laid process
  • 180-200 grams/meter$^2$ veil
  • Southeast Nonwovens
    • September 2021
Technical Plan: SiC/Si$_3$N$_4$ Composite

- Preform
  - Powder Infiltration/Impregnation with Ube SN E-10 Si$_3$N$_4$ powder
  - $D_{50}$ nominally 0.65 micron
  - Free Form Fibers (November 2021)

- Composite Formation
  - Press and Sintered
  - 1 hour at 1750 C, 2 ksi pressure
  - 1 Atmosphere of N$_2$
  - Exothermics (December 2021)
  - Nominal 12-15% Fiber Volume Fraction
Technical Plan: Room Temperature and Elevated Temperature Testing

• Testing
  • At room temperature and 2700°F
  • 4 Point Flex testing
    • ASTM C-1341-13(2018)
  • CMC Coupons
  • Monolithic Coupons (made in parallel with CMCs at Exothermics)
    • 0.050 in/min test speed

• Cincinnati Test Labs (January 2022)
Test Results

- CMC Coupons 92% dense, < 15% fiber volume
- Monolithic 99% dense
- Room Temp Flexural Strength:
  - CMC 87% of monolithic sample (290MPa)
- 2700°F Flexural Strength:
  - CMC 46% of monolithic sample (70MPa)
- CMC coefficient of variance for strength and strain to failure smaller and failure behavior more consistent at 2700°F than monolithic samples
Evaluation of Fracture Samples

- Small number of coupons and data points
- Veil layers in reinforced samples
Room Temperature Sample-500X Magnification

- One of the denser fiber concentration areas
- Low level of fiber reinforcement did not strengthen composite
- General indications of brittle failure
  - Smooth fast fracture surface
Room Temperature Sample-1000X Magnification

- Cleavage of fiber
- Mechanical bond between fiber and matrix
- SiC vs. Si$_3$N$_4$ modulus difference did not yield fiber pullout behavior
- Further investigation of fiber-matrix bond pending
2700°F Sample-1000X Magnification

- Fracture surface as tested
- Surface roughness apparent
  - Evidence of mild toughening?
- Fiber-matrix interface
  - Any chemical interaction?
2700°F Sample-2500X Magnification

- As-fractured surface image
  - Close up of fiber in matrix
- Fiber survival during processing and elevated temperature testing
Takeaways

• SiC veil/Si$_3$N$_4$ composites successfully demonstrated
  • >90% density
  • Low fiber volume <15%
• Elevated temperature fiber performance confirmed
• More consistent mechanical behavior at elevated temperature
• Processing time = cost
  • 1/2 day veil forming
  • 2 days preform fab
  • 2+ days high temp fab
Future Work

• Higher fiber volume fraction specimens (veil gsm loading)
• Refine composite processing to produce higher density samples
• Expand testing
  • More flexural
  • Add tension, creep, and 3 point bend for shear response
• Perform analytical analysis (EDS) of SiC fiber/Si$_3$N$_4$ matrix interface
  • Room temperature coupons
  • Elevated temperature testing
• Expand the statistical data set
ABOUT FREE FORM FIBERS

Free Form Fibers employs advanced laser-driven chemical vapor deposition (LCVD) technology to manufacture high performance ceramic fibers. If you would like to explore the development of a new fiber material, or if you are looking for a new source of pure, dimensionally controlled silicon carbide, boron, or boron carbide fiber, please contact us.
Contact Information

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Market and Product Focus

- Aerospace and Hypersonic
- Semiconductor
- Nuclear

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