Microstructure of Matrix in UHTC Composites

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Outline

- Issues with UHTCS
- Approaches to improve fracture toughness
  - In-situ reinforcement
    - Preceramic polymer route
    - “Coating” route
  - Fiber reinforcement
    - 2D weaves
    - 3D weaves
Ultra High Temperature Ceramics (UHTCs) : A Family of Materials

- Borides, carbides and nitrides of transition elements such as hafnium, zirconium, tantalum and titanium.
- Some of highest known melting points
- High hardness, good wear resistance, good mechanical strength
  - Good chemical and thermal stability under certain conditions
  - High thermal conductivity (diborides).
    - Good thermal shock resistance

Typical microstructure of a “monolithic” HfB$_2$/SiC material
Where are we going?

- What does a UHTC need to do?
  - Carry engineering load at RT
  - Carry load at high use temperature
  - Respond to thermally generated stresses (coatings)
  - Survive thermochemical environment

- High Melting Temperature is a major criterion, but not the only one
  - Melting temperature of oxide phases formed
  - Potential eutectic formation

- Thermal Stress – \( R' = \sigma k/(\alpha E) \)
  - Increasing strength helps, but only to certain extent

- Applications are not just function of temperature

- Materials needs for long flight time reusable vehicles are different to those for expendable weapons systems
UHTC Challenges: What will make designers use these materials?

1. Fracture toughness: Composite approach is required
   - Integrate understanding gained from monolithic materials
   - Need high temperature fibers
   - Need processing methods/coatings

2. Oxidation resistance in reentry environments
   reduce/replace SiC

3. Modeling is critical to shorten development time, improve properties and reduce testing

4. Joining/integration into a system

5. Test in relevant environment—test data!
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    • “Coating” route
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Preceramic Polymers Can Control Grain Shape

- Conventional source of SiC is powder.
- SiC from a preceramic polymer source:
  - Will affect densification and morphology.
  - May achieve better distribution of SiC source through HfB$_2$.
  - Previous work shows that preceramic polymers can enhance growth of acicular particles (for fracture toughness).
- Potential to improve mechanical properties with reduced amount of SiC and also potentially improve oxidation behavior.
Growth of Elongated SiC Grains

SiC Preceramic Polymer Promotes Growth of Acicular Grains

- Samples processed with 5 to >20 volume % SiC
- Can adjust volume of SiC in the UHTC without losing the high l/d architecture
- Amount of SiC affects number and thickness (but not length) of rods — length constant (~20–30\(\mu\)m)
- Possible to obtain dense samples with high-aspect-ratio phase
- Hardness of high-aspect-ratio materials comparable to baseline material

* Precursor added in amounts sufficient to yield nominal amounts of SiC
In Situ Composite for Improved Fracture Toughness

Evidence of crack growth along HfB$_2$-SiC interface, with possible SiC grain bridging

<table>
<thead>
<tr>
<th>SiC Content</th>
<th>Fracture Toughness (MPa$m^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>3.61</td>
</tr>
<tr>
<td>10%</td>
<td>4.06</td>
</tr>
<tr>
<td>15%</td>
<td>4.47</td>
</tr>
<tr>
<td>Baseline UHTC (20%)</td>
<td>4.33</td>
</tr>
</tbody>
</table>

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When Additives for UHTCs Are Added as Coatings

Fluidized Bed Reactor - Chemical Vapor Deposition Technique (FBR-CVD)

Using coatings, instead of particles, to introduce additives, offers several advantages:

- Uniform distribution and control of coating composition
- Bypasses traditional sources of processing contamination
- May lead to improved oxidation and creep resistance (less O\textsubscript{2} contamination)
- Amount of additive can be controlled
- Reductions in hot-press temperature, pressure, and time
SiC Coating Appearance on Powders

Uncoated Powder

SiC Coated Powder

Gray filamentous material is SiC
Addition of SiC as “Coating”

- Alternative route to growing acicular grains
- HfB$_2$ powders “coated” with Si/C in fluidized bed
- Spark plasma sintered
  - Not fully dense
  - Growth of acicular SiC grains
- Grain boundaries should be very clean, leading to potential improvements in thermal conductivity

HfB$_2$- 5 vol-%SiC (SPS)
Objectives:

- Can we use knowledge gained from controlling microstructures in “monolithic” UHTCs to make matrices for fiber reinforced composites?
- Can both 2D and 3D weaves be infiltrated?

Caveats

- Using available carbon fiber structures
- No fiber coating
Processing of 2D Weave

Composites from 2D weaves
• Carbon fiber cloth (PAN-based)
• Impregnated with preceramic polymer/HfB$_2$ powder mixture—one infiltration per layer
• Layers stacked and hot pressed (~15 layers)
Ultra High Temperature Continuous Fiber Composites

2D Composite microstructure

Dense UHTC matrix with acicular SiC.

Monolithic microstructure

C fibers present after processing.
Woven 3-D Carbon Fabric

- 3D carbon preform
- PAN based fibers
- $V_f \sim 55\%$
- Density $\sim 0.85$ g/cc
3D Woven Composite Infiltration

- Sample infiltrated with milled HfB$_2$ powder followed by repeated infiltrations with preceramic polymer
  - SiC precursor
- Sample heat treated to > 600$^\circ$C between infiltrations to convert the polymer and remove organics
- Final heat treatment to 1650$^\circ$C
- Initial density $\sim$0.9g/cc
- Final density $\sim$2.1g/cc
Fracture Surface of 3D Composite

- Non-uniform infiltration
- Accumulation on surface
- Infiltration throughout the thickness
- Infiltration into fiber bundles
- Brittle fracture

Infiltrated fiber bundle
Polymer-Rich Matrix

- Matrix is generally a mix of HfB$_2$ powder and polymer
- Matrix infiltrates densely in some areas; poorly in others
Infiltration of Powder and Polymer into Fiber Bundles

- Non-uniform
- Both polymer and powder infiltrate between fibers

HfB$_2$ powder
Infiltration of Fiber Bundles

Both powder and polymer infiltrate fiber bundles
Infiltration into 3D weave

Preceramic polymer infiltrates throughout the sample.

Powders infiltrate non-uniformly.
Whiskers Growing on Fibers

SiC whiskers grow in poorly-infiltrated areas.
Edge

Powder and polymer build up on edge of weave
Summary

- Have two approaches to *in-situ* reinforcement of HfB$_2$
  - Preceramic polymers
  - Fluidized bed process for “coating”
- Can infiltrate 2D C fiber weave and achieve desired matrix microstructure
- Can infiltrate 3D C fiber weave
  - Non-uniform infiltration
    - Powder and polymer both penetrate
    - Significant amount of infiltration
    - Growth of SiC whiskers in poorly-infiltrated areas
- Final microstructure unknown
Future Work

- Refine infiltration process
- Complete high temperature treatments of infiltrated composites
- Characterize microstructure