Microstructure of Matrix in UHTC Composites

Sylvia M. Johnson, NASA -ARC
Margaret Stackpoole, Michael Gusman, Jose Chavez-Garcia
ERC
Evan Doxtad, NASA EA Program
Sylvia.m.johnson@nasa.gov
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 – \( R' = \frac{\sigma k}{\alpha E} \)
  - 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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    - 3D weaves
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

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 μm)
Possible to obtain dense samples with high-aspect-ratio phase
Hardness of high-aspect-ratio materials comparable to baseline material

SiC Preceramic Polymer Promotes Growth of Acicular Grains

- 5%* SiC
- 10%* SiC — Rod diameter ~2μm
- 15%* SiC — Rod diameter ~5μm

* 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
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 $O_2$ contamination)
- Amount of additive can be controlled
- Reductions in hot-press temperature, pressure, and time

Quartz Frit

450 kHz Copper Induction Coil

Reactant Gases

e.g.: $H_2 + CH_4$ or $TiCl_4$ or $SiCl_4$

Fluidizing Gas

(Ar)

UHTC Fluidized Powder Bed

$HfB_2 + HfH_2$
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

Monolithic microstructure

Dense UHTC matrix with acicular SiC.

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 HfB₂ powder followed by repeated infiltrations with preceramic polymer
  - SiC precursor
- Sample heat treated to > 600°C between infiltrations to convert the polymer and remove organics
- Final heat treatment to 1650°C
- Initial density ~0.9g/cc
- Final density ~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