Role of Microstructure on the Performance of UHTCs

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Sharp Leading Edge Technology

- Sharp leading edge technology
  - Enhances vehicle performance
  - Leads to improvements in safety
    - Increased vehicle cross range
    - Greater launch window with safe abort to ground
- Sharp leading edges place significantly higher temperature requirements on the materials:
  - Current shuttle RCC leading edge materials: T~1650 °C
  - Sharp leading edged vehicles will require: T>2000 °C

_Ultra High Temperature Ceramics are candidates for use in sharp leading edge applications._
UHTC Material Property Considerations

• Emittance determines amount of re-radiated energy.
  – *Emittance should be as high as possible*
  – Surface oxidation can reduce emittance

• Thermal diffusivity determines amount of energy conducted within the material.
  – High thermal conductivity is desirable in sharp leading edge applications.
    – Enhances vehicle performance
    – Increases thermal shock resistance

• Catalycity determines amount of chemical energy released near the surface due to recombination of dissociated species.
  – Surface catalycity should be low
  – Catalycity estimated from temperature measurements during arcjet experiment
  – If facility conditions are known and material properties (such as emittance and thermal diffusivity) are known, then the heating from catalycity can be estimated.

\[ q_{\text{re-rad.}} = \varepsilon_w \sigma T_w^4, \text{ where } \varepsilon_w = \text{emissivity} \]
• Experimental approach
• Results
  – Strength/fracture toughness
  – Thermal conductivity
  – Oxidation resistance
• Computational approach

Outline

HfB$_2$/20v%SiC
Hot Pressed (Baseline)
UHTC Research at NASA Ames

• Controlling microstructure and composition to improve properties
  – Strength
  – Fracture toughness
  – Thermal conductivity
  – Oxidation resistance in re-entry

• Focus has been on monolithic materials and in situ composites

• Goal is to incorporate our research into both monolithic and composite materials
UHTC Suitability for TPS

- UHTCs are only for specialized TPS applications for which other material systems are not as capable or straightforward or their capabilities are required when active cooling is not feasible.

- Choice of materials driven by design, environment, and material properties.
  - Feasible simple nose-cone and passive-leading-edge designs have been developed. (UHTC leading edge designs use small volumes of material.)
  - UHTCs have high temperature capabilities (> 2000 °C / 3600 °F)

- Material selection should be based on appropriate testing of matured material in relevant environment.

- Concerns about monolithic UHTC properties are being addressed by processing and engineering improvements (ceramic matrix composites [CMCs])
Controlling Microstructure & Composition

• Control grain size
  – Additives (Ir additions)
  – Processing by field-assisted sintering (FAS)

• Control grain shape
  – Addition of preceramic polymers
  – Particle coatings (Fluidized Bed CVD)

• Control purity (grain boundaries)
  – Addition of preceramic polymers
  – Processing (FB CVD)
  – Self-propagating reactions

• Control oxide formation
  – Increase oxide stability / emissivity (additives)
  – Reduce amount of SiC
Controlling Grain Size

- Additives (Ir additions) — improve microstructures of hot-pressed materials to match that of FAS materials (very refined)
- Processing (FAS) — refined microstructure
Physical Characterization: Microstructure

Hot Pressed

HfB$_2$-SiC Baseline

Grain Size 7.7µm

HfB$_2$-SiC-TaSi$_2$

Grain Size 8.5µm

HfB$_2$-SiC-TaSi$_2$-Ir

Grain Size 5.1µm

Field-Assist Sintered (FAS)

Grain Size 4.1µm

Grain Size 2.3µm

Grain Size 1.6µm

Grain Size 5 µm
In Situ Composite for Improved Fracture Toughness

Evidence of crack growth along HfB₂-SiC interface, with possible SiC grain bridging

<table>
<thead>
<tr>
<th>SiC Content</th>
<th>Fracture Toughness (MPam₁/²)</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>

Oak Ridge National Laboratory
What About Active Oxidation?

- Silicon-containing materials will actively oxidize under high temperature, low pressure conditions, forming SiO as gas
- Most problematic during re-entry (not during cruise)
- Mitigation approaches:
  - Reduce volume of SiC
    - Reduce overall oxidation
    - Below percolation threshold
  - Reduce scale of SiC particles
    - Allows formation of protective oxide sooner
    - Increase tortuosity of diffusion path
    - Balance between control of grain size and limit of oxidation
  - Additives
    - To change viscosity of the oxide
      - Change emissivity (lower surface temperature)
      - Change diffusivity of species through the oxide
    - To form a physical barrier
    - To change sintering behavior of UHTC with consequent reduction in SiC
Controlling the Composition of Oxides

• High temperature use of UHTCs will form surface oxides
  – Composition of resultant surface oxide is an important factor when considering:
    • Protective characteristics of newly formed surface may be dependent on its viscosity and CTE
    • Emissivity characteristics of oxides
    • Temperature capability (mp) of the oxide
    • Oxidation resistance

• Investigating the effects of additives to address these goals

• Using FBR-CVD and reactive pressing to add:
  – Rare earths
  – Transition metals
Additives as CVD Coatings and Reactive Powders

- Using CVD coatings applied in a Fluidized Bed Reactor, instead of particles, it is possible to:
  - Distribute a uniform and controlled coating
  - Bypass traditional sources of processing contamination
  - Improve oxidation and creep resistance (less O\textsubscript{2} contamination)
  - Control amount of additive

- Standard composition starts with “as received” HfB\textsubscript{2}
  - Powder coated with B, Si, & C, after pretreatment with H\textsubscript{2}
  - Forms filamentous SiC (amorphous)
Increasing Oxide Emissivity

HfB$_2$-SiC

HfB$_2$-SiC-TaSi$_2$

• Arcjet test: Performance of HfB$_2$/SiC/TaSi$_2$ **comparable** to HfB$_2$/SiC after testing for 5 minutes at $Q_{cw} \sim 300$ W/cm$^2$

• HfB$_2$/SiC/TaSi$_2$ clearly has a higher post-test emissivity than HfB$_2$/SiC and demonstrated lower surface temperatures

Arcjet Characterization: Surface

HfB$_2$-SiC Baseline

- Hot Pressed: Emittance = 0.65
- Field Assist Sintered: Emittance = 0.87

HfB$_2$-SiC-TaSi$_2$

- Emittance = 0.89

HfB$_2$-SiC-TaSi$_2$-Ir

- Emittance = 0.87

Did not arcjet test. Sample cracked during fabrication.
Close up of arcjet model with iridium, showing surface accumulation of Ir and corresponding SEM cross section
Arcjet Characterization: Additives & Influence of Microstructure

Both oxide scale and depletion zone can be reduced.
Additions of TaSi$_2$ seem to improve oxidation resistance of coupons fabricated with either HP or FAS. However, the sample fabricated by HP has a large SiC depletion zone, similar to the baseline material.

Samples processed with iridium showed improved oxidation resistance and much smaller SiC depletion zones, in comparison to the baseline.

<table>
<thead>
<tr>
<th>Model ID</th>
<th>Sinter Method</th>
<th>Heat Flux (W/cm$^2$)</th>
<th>Pstag (atm)</th>
<th>Duration (sec)</th>
<th>Oxide Layer (µm)</th>
<th>SiC Depletion (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfB$_2$-SiC (Baseline)</td>
<td>Hot Press</td>
<td>300</td>
<td>0.19</td>
<td>600</td>
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<td>24</td>
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<td>HfB$_2$-SiC</td>
<td>FAS</td>
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<td>0.10</td>
<td>600</td>
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<tr>
<td>HfB$_2$-SiC-TaSi$_2$</td>
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<td>HfB$_2$-SiC-TaSi$_2$</td>
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<td>0.10</td>
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<td>6</td>
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<tr>
<td>HfB$_2$-SiC-TaSi$_2$-Ir</td>
<td>Hot Press</td>
<td>250</td>
<td>0.10</td>
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<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>
Some Recent Work

• Experimental effort
  – Initially focused on optimizing matrix — UHTC or other high-temperature fibers not available
  – Presently includes investigation of UHTC fiber composites — currently NASA has SBIRs with companies to develop UHTC fibers

• Computational effort — modeling to better optimize microstructure / properties
• Image at top right shows dense UHTC matrix with indications of high aspect ratio SiC.
• Image at bottom right shows the presence of C fibers after processing.
Modeling of UHTCs Will Enhance Development

Goals
- Reduce materials development time
- Optimize material properties/tailor materials
- Guide processing of materials
- Develop design approaches

Approach
- Develop models integrated across various length scales
- Correlate models with experiment whenever possible
Multiscale Modeling of Materials

• **Ab initio calculations** — intrinsic material properties
  - *Enables*: structure, bonding, optical and vibrational spectra, chemical reactions, etc
  - *Challenges*: computationally very demanding (very small systems only — $10^2$ atoms)

• **Atomistic simulations** — localized interfaces, defects, transport, and so forth
  - *Enables*: thermal transport, mechanical properties, interface (for example, grain boundary) adhesion, impurities effects
  - *Challenges*: requires difficult interatomic potential development (except for C, Si, and so forth) (small systems and short time scales — $10^8$ atoms and $10^{-9}$ sec)

• **Image-based FEM** — microstructural modeling
  - *Enables*: thermal, mechanical, fracture analysis based on microstructure
  - *Challenges*: requires large database of materials parameters (from experiment or modeling). Nonlinear problems (fracture, plasticity) are very challenging. Macroscopic limit may be difficult.
Modeling UHTCs – What’s Next?

• Accomplishments
  – *Ab initio* calculations of lattice structure, bonding characteristics, elastic constants, phonon spectra and thermal properties of ZrB$_2$ and HfB$_2$
  – *Ab initio* calculations of formation and migration energies for simple defects (vacancies)
  – Development of interatomic potentials for ZrB$_2$ and HfB$_2$ for atomistic simulations

• Opportunities
  – *Ab initio* calculations of simple/ideal grain boundary structures with and without chemical impurities
  – *No UHTC atomistic simulations exist in the literature.* New potentials mean the field is wide open!
  – FEM modeling of microstructure to relate processing and properties
Summary

• Have investigated number of methods to control microstructure. We have routes to form:
  – *in situ* “composites”
  – Very fine microstructures

• Arcjet testing and other characterization of monolithic materials

• Control oxidation through microstructure and composition

• Beginning to incorporate these materials as matrices for composites

• Modeling effort to facilitate material design and characterization