Processing, Properties and Arc Jet Testing of HfB$_2$/SiC

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Outline

- Background on UHTCs
- Summary UHTC Processing
  - Powder Processing
  - Scale-up
    - 2" dia. X 2" tall billets
    - 3" dia. x 2" tall billet
- Preliminary Material Properties
  - Mechanical
  - Thermal
- Arc Jet Testing
  - Flat Face Models
  - Cone Models
- Summary
- Future Work
Development of Ultra High Temperature Ceramics

- UHTCs are a family of ceramic materials, including diborides of Hf and Zr, with extremely high melting temperatures
- Previous studies have indicated good oxidation resistance in simulated reentry environments
  - ManLabs 1960’s and 1970’s
  - ARC 1990’s
    - Ground based research: initial materials development by external vendors, Arc Jet testing, computer modeling, etc.
      » Materials provided by external vendors
      » Different vendors used for each flight experiment
      » Focus on flight experiment not on materials development
  - Detailed studies still required to define use environments (Single and Multi-Use Temperatures)

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Motivation for In-House Processing of UHTC Materials

- Until now there has been no consistent effort to develop the UHTC family of materials at NASA.
  - Development work has primarily been part of flight experiment programs.
    - SHARP-B1 and SHARP-B2
- Different vendors supplied materials for the SHARP-B1 and SHARP-B2 flight experiments.
  - NASA did not retain the knowledge on how to process these materials.
    - Therefore, each time the materials development has had to start at the beginning, evaluating material properties, etc...
- Resulted in inconsistent materials
  - Significant differences in microstructure leads to significant variability in material properties.
- Bringing the UHTC processing in-house allows the government to retain the knowledge of how to process the materials and then transfer the technology to industry for production.
  - Precedent has been set at ARC with development of tile coatings.
HfB$_2$-SiC

**HfB$_2$**
- HfB$_2$ has a narrow range of stoichiometry with a melting temperature of 3380°C
- Density = 11.2 g/cc

**SiC**
- aids densification
- limits grain growth
- may enhance oxidation resistance
- Density = 3.2 g/cc
Hot Pressing

- Granulated powders are loaded into grafoil lined graphite dies
- Hot press has a graphite element with graphite insulation.
- Typical hot pressing parameters:
  - Atmosphere
    - Initially vacuum
    - Switch to inert (Ar or He) at 2000°C
      - Extends graphite element life.
  - Temperatures
    - 2000°C to 2200°C
  - Pressures
    - 3 to 4 ksi
- 67 billets pressed to date
  - (8) 2” dia. x 2” tall billets
  - (1) 3” dia. x 2” tall billet
Improved Powder Handling Results
In More Uniform UHTC Microstructures

- Improved powder handling eliminates SiC and HfB₂ agglomeration common in previous materials.
Microstructures of Current HfB$_2$-SiC Materials

- Microstructures show uniform distribution of SiC with a relatively fine grain size.
- XRD and EDS spectra do not reveal the presence of oxide containing phases

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2" Diameter Billet Has a Slightly Larger Density Gradient than the 1" Diameter Billets

- Hot pressing schedule has not been optimized for billet scale-up.

- Densities are typically higher than theoretical due to loss of SiC during hot pressing.

- Die packing currently performed by hand, likely to result in density gradients within the powder during die packing.

- Iso-static pressing of the powder, prior to die packing should increase density uniformity within powder pack increasing final hot pressed density uniformity and we should have this capability soon.

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Previous HfB$_2$/SiC Materials and Ames HfB$_2$/SiC Have Comparable Hardness

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Vickers Hardness (GPa)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames Material</td>
<td>19.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Circa 1999</td>
<td>21.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

- Cracks from indent in Ames material propagate intra-granularly (through the grains) whereas in the heritage materials cracks propagated inter-granularly (between the grains).
Recent Billets Have Consistent Elastic Moduli

<table>
<thead>
<tr>
<th>Billet #</th>
<th>Elastic Modulus (GPa)</th>
<th># of Bars Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>510 ± 9</td>
<td>37</td>
</tr>
<tr>
<td>59</td>
<td>490 ± 17</td>
<td>9</td>
</tr>
<tr>
<td>61</td>
<td>536 ± 10</td>
<td>10</td>
</tr>
<tr>
<td>62</td>
<td>547 ± 4</td>
<td>11</td>
</tr>
<tr>
<td>63</td>
<td>546 ± 6</td>
<td>19</td>
</tr>
<tr>
<td>65</td>
<td>549 ± 9</td>
<td>24</td>
</tr>
</tbody>
</table>

- Modulus decreases with decrease in density
- Decreased moduli probably due to a combination of porosity and change in SiC content (↑ SiC)
- Modulus measured using a pulse echo technique
Improved Processing Reduces Strength Distribution in Later Billets

- Grafoil flakes introduced into billets during hand packing
- Flakes are responsible for low strengths in billet #59
- Improved die packing will eliminate this source of extrinsic defects

ASTM C1161

Strength measured in 4-pt bending
Bar Size: 3 x 4 x 45 mm
Bi-axial testing
Disc Size: 25mm dia. x 1mm thick
As ground surfaces
Weibull Modulus of ARC HfB$_2$/SiC Improved Compared to Previous Materials

- Strength distributions are improving with time, as experience is gained.

Weibull Modulus of previous materials (1999 era) ~4.
## Summary of Strengths

<table>
<thead>
<tr>
<th>Billet #</th>
<th>Strength (MPa)</th>
<th># of Bars Tested</th>
<th>Strength Less Extrinsic Defects (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>440 ± 114</td>
<td>7</td>
<td>473 ± 89 (6)</td>
</tr>
<tr>
<td>59</td>
<td>157 ± 43</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>407 ± 57</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>411</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>415 ± 81</td>
<td>5</td>
<td>451 ± 22 (4)</td>
</tr>
<tr>
<td>65</td>
<td>454 ± 46</td>
<td>14</td>
<td>460 ± 41 (13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>470 ± 23 (12)*</td>
</tr>
<tr>
<td>SHARP B2</td>
<td>356 ± 91</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>ManLabs</td>
<td>312 ± 26</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

- For this average and standard deviation assumed that both low strength bars in billet 65 had an extrinsic defect such as grafoil, fractography has confirmed this for one bar, continuing examination of other bars.

- All strengths measured in 4-pt bending on 3 x 4 x 45 mm bars

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Fracture Surfaces of ARC Materials Do Not Show Evidence of SiC Agglomeration

Circa 1999 HfB$_2$/SiC  
Ames Processed HfB$_2$/SiC

- Red circles highlight SiC agglomerates found in SHARP B2 material as a result of un-optimized powder processing
- Fracture surfaces of ARC materials do not reveal SiC agglomeration
- Some ARC bars show Grafoil flakes in the material introduced during die packing
  - Grafoil defects can be eliminated via improved die packing procedures
SiC Particulate Does Not Appear to Affect the Materials Fracture Toughness

- Fracture toughness measured according to ASTM C1421
- Used Chevron Notched Specimens
- Bar Size: 3 x 4 x 45 mm
- Need stable crack growth during test

<table>
<thead>
<tr>
<th>Material</th>
<th>$K_{IVB}$ (MPam$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Si}_3\text{N}_4$</td>
<td>3 - 7</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>3 - 4</td>
</tr>
<tr>
<td>SiC</td>
<td>3 - 4</td>
</tr>
<tr>
<td>Porcelain</td>
<td>~1</td>
</tr>
<tr>
<td>Si</td>
<td>~1</td>
</tr>
<tr>
<td>HfB$_2$/20% SiC</td>
<td>4.1 ± 0.2</td>
</tr>
</tbody>
</table>

Notch Tip

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CTE of ARC HfB$_2$/SiC is the Same as SHARP B2 Material

- CTE measured using high temperature dilatometry
- Pushrod dilatometer used
- T = -130°C to 1500°C
Conductivity of ARC Materials
Lower than Heritage Materials

![Graph showing conductivity of different materials](image-url)

- ● ARC 2" Dia. Billet (HSp-58)
- ○ ARC 1" Dia. Billet (HSp-47)
- □ SHARP B2
- ▲ ManLabs 1970's
- ⧿ SiC NIST Property Database

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Summary: Processing and Properties

- Modified hot pressing schedule has significantly improved UHTC billet processing
  - Density and microstructure uniformity have improved
- 2" dia. x 2" tall UHTC billets have been successfully hot pressed
  - Scaled up billets have slightly higher density gradients axially than 1" billets
    - Need to evaluate radial density uniformity
  - Hot press schedule has not been optimized for scaled up billets
  - Hot pressed (1) 3" dia. x 2" tall billet
- Strengths and strength distributions are improving with experience
  - Need to evaluate strength uniformity in the center of the billets
    - Most bars cut from outside of billet around wedge models
- CTE or ARC materials compares favorably with heritage materials.
- Thermal conductivity of ARC materials considerably different than that of heritage materials.
Behavior of HfB$_2$-SiC Materials in Simulated Re-Entry Environments
Arc Jet Testing Objectives/Goals

- Investigate the oxidation/ablation behavior of HfB$_2$/SiC materials in simulated re-entry environments
- Use the arc jet test results to define appropriate use environments for these materials for use in vehicle design
  - Use environments will be vehicle dependent
    - Application will drive desired performance
  - Parameters to be investigated include:
    - Surface Temperature
    - Stagnation Pressure
    - Duration
    - # of Cycles
    - Thermal Stresses
Surface Energy Balance

Blunt Nose

\[ \dot{q}_{\text{conv}} \approx \dot{q}_{\text{rad}} \]

\[ q_{\text{cond}} \approx 0 \]

SiC Coated C/C

Sharp Nose

\[ \dot{q}_{\text{conv}} = \dot{q}_{\text{rad}} + \dot{q}_{\text{cond}} \]

Low Thermal Conductivity

High Thermal Conductivity

- Insulators and UHTCs manage energy in different ways:
  - Insulators store energy until it can be eliminated the same way it came in
  - UHTCs conduct energy through the material and reradiate it through cooler surfaces
Needs for Arc Jet Testing

- Arc jet testing is the best ground based method of evaluating a materials oxidation/ablation response in re-entry environments.
- A materials oxidation behavior when heated in static or flowing air at ambient pressures is likely to be significantly different than in a re-entry environment.
- In a re-entry environment:
  - Oxygen and nitrogen may be dissociated
    - Catalycity of the material plays an important role
    - Recombination of O and N atoms adds to surface heating
  - Stagnation pressures may be less than 1 atm.
    - Influence of active to passive transitions in oxidation behavior of materials
      - SiC materials show such a transition when the protective SiO$_2$ layer is removed as SiO
Arc Jet Testing

- Ground based simulation of re-entry environment.

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Example of Model
During Arc Jet Testing
Use-Temperature (Flat Face) Model Assembly

- Aluminum outer sleeve
- Aluminum inner sleeve
- Tungsten adapter
- Graphite model holder
- UHTC sample
- Back face instrumentation
- Water-cooled sting
Specimen Geometry

2.54 cm
Specimen mounted in coated graphite holder
Design 1
Held by graphite pins (ends protected)

Water Cooled Sting

Coated Graphite Model Holder
Design 1

Arc Jet Flow

Ames UHTC model

Specimen on Sting Arm

Original Specimen
## Arc Jet Test Conditions

<table>
<thead>
<tr>
<th>Model #</th>
<th>Density (g/cc)</th>
<th>Heat Flux (W/cm²)*</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF-61-1</td>
<td>9.59</td>
<td>285</td>
<td>0.05</td>
</tr>
<tr>
<td>FF-61-2</td>
<td>9.57</td>
<td>350</td>
<td>0.07</td>
</tr>
<tr>
<td>FF-62-1</td>
<td>9.64</td>
<td>430</td>
<td>0.08</td>
</tr>
<tr>
<td>FF-62-2</td>
<td>9.47</td>
<td>530</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*Heat flux is referenced to a 3" Cu hemisphere

- Each model was run twice
- Run durations were 10 min. each
- Flat face models machined from 2" dia. Billets
- Surface temperatures are measured using 1-color and 2-color optical pyrometers.
Summary of Flat Face Models

1st Run
- $q_{stag} = 285 \text{ W/cm}^2$
- $P_{stag} = 0.05 \text{ atm}$
- $\% \Delta wt = -0.0$

2nd Run
- $q_{stag} = 350 \text{ W/cm}^2$
- $P_{stag} = 0.07 \text{ atm}$
- $\% \Delta wt = -0.5$

- $T_{ss} = 1691^\circ C$
- $T_{ss} = 2362^\circ C$

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FF 61-1: \( q_{stag} = 285 \text{ W/cm}^2 \)

- Surface temp. does not change during 2nd exposure
- For the 1-color pyrometers assuming an \( \varepsilon = 0.65 \) based on ManLabs results
FF 61-2: \( q_{stag} = 350 \text{ W/cm}^2 \)

- Surface temp. begins to rise toward end of 1\textsuperscript{st} exposure
- During the 2\textsuperscript{nd} exposure surface temp rises to same point where temp. peaked during the 1\textsuperscript{st} exposure

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Porous Oxide Layer Forms During Arc Jet Testing

Surface of Model

Cross Section

$ q_{stag} = 350 \text{ W/cm}^2, \quad P_{stag} = 0.07 \text{ atm} $
Summary: Flat Face Arc Jet Testing

- Completed testing of 4 UHTC models
  - Two 10 min. exposures each
- Surface temperatures in excess of 2300°C have been observed with some oxidation and spalling of the oxide layer, but no apparent large scale melting.
- During arc jet testing 2 zones in the material develop:
  - A surface oxide layer, primarily composed of HfO₂
  - And a porous HfB₂ region between the surface HfO₂ layer and the base HfB₂/SiC material.
- Active oxidation of the SiC results in the porous HfB₂ layer below the surface oxide layer.
- At ~20 vol. % the SiC particulate phase is above the percolation threshold and results in an interconnected SiC phase which is oxidized away and results in the depletion zone.
- The surface temperatures during the 2nd exposures at heat fluxes between 350 and 530 W/cm² are similar.
Future Work

- Perform additional arc jet testing to adequately define multi-use temperature/environment, includes evaluation of:
  - Multiple Exposures
  - Long Durations
  - Different Stagnation Pressures
- Use experimental results to develop models to describe the oxidation mechanisms and use for predictions
- Investigate alternative compositions
  - Different SiC contents
  - Different additives
  - ZrB$_2$
Recent Studies on the Sintering Behavior of Diboride Based Materials
Hot Pressed - Pure Diborides

- Raw powders sinter poorly with extensive porosity when sintered at the same conditions as those materials sintered with SiC (2000-2200°C)

**ZrB₂**

Hot Pressed  
$T_1\,^\circ$C - 1 hour

**HfB₂**

Hot Pressed  
$T_1+200\,^\circ$C - 1 hour

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Alternatively Processed Pure HfB$_2$

- Hot pressed materials were porous
- SPS materials sintered with minimal porosity, reduced grain size

![HfB$_2$](image)

Hot Pressed
T$_2$°C - 1 hour

![HfB$_2$ SPS](image)

Spark Plasma Sintered
T$_2$-300°C - 10 minutes
Hot Pressed - Pure Diborides

- Attempts to remove porosity by hot pressing HfB₂ and ZrB₂ at a higher temperature failed when raw powders became molten and leaked from the die.
Raw Material Processing

\[ \text{MOxide} + \text{B} + \text{Boron Carbide} + \text{C} \rightarrow \text{MBoride} + \text{Side Products} \]

- Typical Metal Boride reaction used is capable of yielding large quantities of powder but can contain side products (borates) or a product with off target stoichiometry

\[ \text{M} + \text{B} \rightarrow \text{MBoride} \]

- Elemental reaction (under investigation) can yield a more stoichiometric product free from most side products
- Currently yields small quantities of powder but scalability is under investigation by our vendor, Cerac, Inc.

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Other Free Sintered Borides and Carbides

- HfB₂ formed from an elemental reaction did not melt, neither did the carbides of Hf and Zr

All samples Free Sintered @ 2350°C - 30 minutes
Boride / Carbide Mixtures

- Free Sintered Boride/Carbide mixtures show varied results, still under investigation

Free Sintered
2350°C - 30 minutes
Alternatively Processed Boride / Carbide Mixtures

- Elemental reaction of Hf-B-C sinters to near full density yielding a microstructure with a even distribution of fine grains.

- Compound reaction of Hf-B & ZrC does not sinter well, yielding phase separation and a porous microstructure.

Spark Plasma Sintered
T₂-300°C - 10 minutes
Conclusions

- Raw materials do not hot press well but can be consolidated with alternate methods such as Spark Plasma Sintering.
- Increased hot press temperatures revealed that as received hafnium and zirconium diboride were found to liquefy well below their theorized melting point.
- Improvements in raw material processing and powder mixing show promising results.