Robust UHTC for Passive Sharp Leading Edge Applications

Stanley R. Levine, Mrityunjay (Jay) Singh, and Elizabeth J. Opila

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Ultrahigh temperature ceramics have performed unreliably due to material flaws and attachment design. These deficiencies are brought to the fore by the low fracture toughness and thermal shock resistance of UHTCs. If these deficiencies are overcome, we are still faced with poor oxidation resistance as a limitation on UHTC applicability to reusable launch vehicles. We have been addressing the deficiencies of UHTCs for the past year via a small task at GRC that is part of the 3rd Gen TPS effort. Our focus is on composite constructions and functional grading to address the mechanical issues and on composition modification to address the oxidation issue. The approaches and progress will be reported.

a: QSS, Inc.
b: Cleveland State University

Outline

- Introduction
  - UHTC Background
  - Performance Issues for Leading Edges
- Robust UHTC: Objective and Approaches
- Oxidation Resistance Improvement
- Functional Gradient and Composite Materials
- Summary and Conclusions
Ultra High Temperature Ceramics

- Materials consisting of refractory metal borides, refractory metal carbides, silicon carbide, and carbon which have potential use temperatures limited by the melting point of the oxide scale.
  - $\text{HfO}_2$ Melting point 5073°F (2801°C)
  - $\text{ZrO}_2$ Melting points 4904°F (2707°C)
  - $\text{SiO}_2$ 3142°F (1728°C), cristobalite
- $\text{ZrO}_2$ is not a highly protective oxide. Lifetimes based on $\text{ZrB}_2$ recession will be relatively short. 20 volume % SiC additions have been found to give lowest oxidation rates.
- Current Fabrication Approaches: hot pressing or chemical vapor infiltration

Potential Applications

- Inlets, nose tips, leading edges
- Satellite on-board propulsion system components
- Nozzle throats for divert and attitude control thrusters
- High performance short-life turbines
UHTC Lack Robustness

- UHTC have performed unreliably in ARC tunnels and flight due to material and attachment design flaws.
- Oxidation resistance is unacceptable for reusable TPS leading edge applications.
- Current UHTC materials are not reproducible and reliable:
  - Partially intrinsic: low fracture toughness and strength
  - Partially extrinsic: process derived flaws
  - Thermal shock an area of concern

ZrB$_2$/ 20 v/o SiC UHTC Oxidized in Air
10 Minute Cycles

<table>
<thead>
<tr>
<th># cycles</th>
<th>1327°C</th>
<th>1627°C</th>
<th>1927°C</th>
</tr>
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<td>10</td>
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Robust UHTC

- **Objectives**
  - Increase toughness and reliability
  - Improve oxidation resistance

- **Approach**
  - Alloying to improve oxidation resistance
  - Composites and functionally graded material (FGM)
  - Combine oxidation improvements with composite and FGM approaches
Oxidation Resistance

- Pure, dense ZrO₂ or HfO₂ scale impossible
  - Off stoichiometry
  - Porosity, cracking and spalling due to gaseous oxidation products and CTE mismatch
- Doped ZrO₂ or HfO₂
  - Limit oxygen transport via lattice vacancies
  - Still must deal with porosity, cracking, and spalling
  - Ta₂O₅ is the most practical based on melting point and formation of an intermediate ternary oxide with ZrO₂ and HfO₂
  - Potential sources of tantalum are:
    - TaB₂ or TaB : introduces B
    - TaC : introduces additional C
    - TaSi₂ or Ta₂Si₃ : introduces more Si + relatively low melting TaSi₂ (~2400 °C)
- Just beginning to think about Re₂ZrO₇ or Re₂HfO₇

Properties of Relevant Compounds

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<tr>
<th>Compound</th>
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<td>BN</td>
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<td>2810</td>
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<tr>
<td>Nb₂O₅</td>
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<td>1460</td>
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<td>≥2900(d)</td>
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<td>5.8</td>
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Additives selected to replace diboride
History for Ta Additions

- Wuchina et al (NSWC) looked at TaB and TaC additions to pure HfC, HfN and HfB₂
  - Limited reporting of results
  - Denser oxide scale at 1500°C and 25% additive reported for HfB₂
- Talmy et al (NSWC) looked at up to 20% TaB₂ additions to ZrB₂ + 20%SiC
  - Only looked at furnace oxidation temperatures up to 1400°C
  - Significant improvements in oxidation resistance attributed to phase separation in the glass
  - Other mechanisms are possible

Mechanisms for ZrO₂ Protective Scale Enhancement via Ta₂O₅ Additions

- Ta₂O₅ as a glass modifier
  - Talmy et al
- Ta⁺⁵ as a dopant in ZrO₂ lattice
  - Fill O⁻² vacancies
  - Decrease O⁻² transport
- Ta₂O₅ as a major oxide scale constituent
  - Phase V
  - Low melting point
ZrO$_2$-Ta$_2$O$_5$ Diffusion Couple
1450°C, 1 h

Intermediate phase formation and Ta solubility are evident

Processing

- **Baseline ZrB$_2$**
  - Plates hot pressed to > 95% average density at 2000°C, 10ksi, up to 2h, vac
- **Ball milling of mixed powders identified as preferred powder processing procedure**
  - One composition processed to 100% density at 1900°C, 10ksi, 2h, vac
  - Segregation observed in some early batches suggested addition of spray drying to the procedure, especially for HfB$_2$ based system
  - Later batches prepared by the milling of mixed powders appeared to be satisfactory
- **Compositions prepared from mixture of ball milled individual powders were unacceptable**
  - Non-homogeneous with large agglomerates and cracks
  - Further milling as mixed powders solved the problem in the one case tried.
**ZrB\textsubscript{2} – 20\% SiC**

**Effect of Sintering Time**

1h, 2000°C, 10 ksi  
2h, 2000°C, 10 ksi

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**Flexural Strength Results for ZrB\textsubscript{2}-based Compositions**

<table>
<thead>
<tr>
<th>Run</th>
<th>Composition</th>
<th>Powder Process</th>
<th>Processing</th>
<th>UTS, Mpa</th>
<th>% strain</th>
<th>E, GPA</th>
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<tr>
<td>877-1</td>
<td>ZrB\textsubscript{2}-20vloSC</td>
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<td>377.4</td>
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<td></td>
<td>722.6</td>
<td>0.171</td>
<td>405.5</td>
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<tr>
<td>877-3</td>
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<td></td>
<td></td>
<td>749.0</td>
<td>0.181</td>
<td>394.5</td>
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<td>877-avg</td>
<td></td>
<td></td>
<td></td>
<td>618.6</td>
<td>0.161</td>
<td>361.8</td>
</tr>
</tbody>
</table>

| 878-1 | ZrB\textsubscript{2}-20vloSC   | batch 2, milled | 2000°C, 10ksi, 2h, vac | 505.2 | 0.120 | 265.5 |
| 878-2 |                             |                |            | 505.2 | 0.120 | 265.5 |
| 878-3 |                             |                |            | 505.2 | 0.120 | 265.5 |
| 878-avg |                           |                |            | 505.2 | 0.120 | 265.5 |

| 882-1 | ZrB\textsubscript{2}-20vloSC   | mixed milled | 1800°C, 10ksi, 1h, vac | 547.2 | 0.127 | 402.9 |
| 882-2 |                             |                |            | 580.2 | 0.133 | 378.9 |
| 882-3 |                             |                |            | 580.2 | 0.133 | 378.9 |
| 882-avg |                           |                |            | 580.2 | 0.133 | 378.9 |

| 908-1 | HEB\textsubscript{2}-20vloSC   | milled | 2000°C, 10ksi, 2h, vac | 549.6 | 0.133 | 398.0 |
| 908-2 |                             |                |            | 549.6 | 0.133 | 398.0 |
| 908-3 |                             |                |            | 549.6 | 0.133 | 398.0 |
| 908-avg |                           |                |            | 549.6 | 0.133 | 398.0 |

| 911-1 | HEB\textsubscript{2}-20vloSC   | milled | 2000°C, 10ksi, 2h, vac | 549.6 | 0.133 | 398.0 |
| 911-2 |                             |                |            | 549.6 | 0.133 | 398.0 |
| 911-3 |                             |                |            | 549.6 | 0.133 | 398.0 |
| 911-avg |                           |                |            | 549.6 | 0.133 | 398.0 |
ZrB$_2$ + 20 $\%$ SiC (ZS) After Furnace Oxidation at 1627°C

Side A

1 Cycle* 5 Cycles 10 Cycles

*1 cycle = 10 minutes hot & 10 minutes cool

ZrB$_2$ + 20 $\%$ SiC + Mixed Ta Compounds (RB) After Oxidation at 1627°C

Side A

1 Cycle 5 Cycles 10 Cycles
ZrB₂ + 20% SiC + 20% TaSi₂ (ZSTS) Oxidized at 1627°C Side A

1 Cycle 5 Cycles 10 Cycles

UHTC Oxidation at 1627°C in Zirconia Furnace

Specific weight change (mg/cm²)

0 1 2 3 4 5 6 7 8
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8

Time (hrs)

- ZS 882
- ZSTS 889
- RB 878
- Poly. (ZS 882)
- Poly. (RB 878)
- Poly. (ZSTS 889)
UHTC Oxidation at 1627°C in Zirconia Furnace

- ZS 882
- ZSTS 889
- RB 878
- Linear (RB 878)
- Linear (ZS 882)
- Linear (ZSTS 889)

20 %TaSi₂ Modified ZrB₂ + 20% SiC
After Furnace Oxidation at 1627°C in Air

1x10 min cycle, at 1000x
10x10 min cycles, at 2000x
10x10 minute cycles, air, 1627°C

TaSi$_2$ Modified ZrB$_2$-20 V/o SiC

>10 X improvement in oxidation resistance relative to industry baseline based on weight change and oxidation damage

UHTCMC Hybrid System

Coated or Improved Oxidation Performance ZrB$_2$+SiC or HfB$_2$+SiC Ceramics

Ceramic Composites (C/ZrB$_2$+SiC or C/HfB$_2$+SiC)

Advantages of UHTCMC hybrids

- Thickness and composition of UHTC layers can be changed to suit the application requirements
- Improved toughness
- Improved environmental durability
  - Tailored surface coatings
  - Crack healing matrices
  - Control of residual stresses
- Smooth composite surfaces
  - Low drag
  - Machinable without fiber damage
  - Easier to bond and attach sensors and other devices
  - Critical to good attachments/seals

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UHTCMC Hybrid System Processing

- Carbon Fiber Preforms
  - Made into Net Shapes

- Infiltration of RB₂+SiC+C Mixtures
  - Curing and Pyrolysis

- Surface Treatment
  - (RB₂+SiC+C)

- Melt Infiltration
  - (Rare Earth Alloys)

- Ultra-High Temperature Ceramic Matrix Composites
  - (UHTCMCs)

Microstructure of UHTCMC Hybrid System

- ZrB₂+SiC+TaSi₂+Si Coating
  - ZrB₂ + SiC slurry infiltrant in C/SiC preform
  - Similar microstructures in silicon and Si-Ta alloy melt infiltrated systems
  - Cracked coatings and matrix due to thermal expansion mismatch
  - Process optimization and property characterization underway
CMCs by Prepregging and Melt Infiltration (PREMI)

- Coated Fibers (C, SiC, Oxides)
  - Prepregging in Resin Mixture
- Lay-up (2-D Prepregs)
- Resin Transfer Molding (2-D Prepregs)
- Filament Winding (Tow-pregs)
- Curing and Pyrolysis

Melt Infiltration (Silicon or Silicon-Alloy)

Large and Complex Shape CMC Components

Microstructure of UHTCMCs by Prepregging and Melt Infiltration (PREMI)

- 12 layers of T-300, 5-HS cloth prepreged with ZrB$_2$+SiC or ZrB$_2$+TaSi$_2$ mixture
- Warm pressed, pyrolyzed, and melt
- Infiltrated with Si or Si-Ta alloy

Cracket

Microscl et al
not WSA

ZrB$_2$+SiC matrix
- 75 um

Carbon Fibers
- 30 um

300 um
Summary

- Current UHTCs lack robustness (low fracture toughness, reliability and oxidation resistance)
- Alloy and functionally graded materials approaches have been identified to improve oxidation resistance
  - Ta addition appears to be promising with oxidation rate reduced by > 10X @ 1627°C
  - FGM approaches in processing
- Several composites approaches have been identified to increase mechanical robustness
  - Infiltration processing and prepregging have produced materials with interesting microstructures
  - Further characterization of microstructures, and mechanical property and environmental durability is needed to guide the next processing cycle

Conclusions

- Alloying can yield a large improvement in oxidation resistance in a static environment
  - Need to demonstrate in a flowing environment representative of the application
- Several approaches to fabrication of UHTC composites appear to be promising in so far as microstructural appearance
  - Mechanical property and environmental durability evaluations will guide future directions
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  - SiO₂

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    - TaC: introduces additional C
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  - Fill O⁻² vacancies
  - Decrease O⁻² transport
- Ta₂O₅ as a major oxide scale constituent
  - Phase V
  - Low melting point
**ZrO$_2$-Ta$_2$O$_5$ Diffusion Couple**

1450°C, 1 h

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- **Ball milling of mixed powders identified as preferred powder processing procedure**
  - One composition processed to 100% density at 1900°C, 10ksi, 2h, vac
  - Segregation observed in some early batches suggested addition of spray drying to the procedure, especially for HfB$_2$ based system
  - Later batches prepared by the milling of mixed powders appeared to be satisfactory
- **Compositions prepared from mixture of ball milled individual powders were unacceptable**
  - Non-homogeneous with large agglomerates and cracks
  - Further milling as mixed powders solved the problem in the one case tried.
### Effect of Sintering Time

#### Flexural Strength Results for ZrB₂-based Compositions

<table>
<thead>
<tr>
<th>Run</th>
<th>Composition</th>
<th>Powder Process</th>
<th>Processing</th>
<th>UTS, Mpa</th>
<th>% strain</th>
<th>E, GPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>877-1</td>
<td>ZrB₂-20% SiC</td>
<td>batch 1, milled</td>
<td>2000°C, 10Ksi, 1h, vac</td>
<td>377.4</td>
<td>0.131</td>
<td>289.5</td>
</tr>
<tr>
<td>877-2</td>
<td>ZrB₂-20% SiC</td>
<td>batch 1, milled</td>
<td>2000°C, 10Ksi, 1h, vac</td>
<td>722.6</td>
<td>0.171</td>
<td>401.5</td>
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<tr>
<td>877-3</td>
<td>ZrB₂-20% SiC</td>
<td>batch 1, milled</td>
<td>2000°C, 10Ksi, 1h, vac</td>
<td>749.9</td>
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<td>394.5</td>
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<td>877-avg</td>
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<td>676.0</td>
<td>0.161</td>
<td>361.8</td>
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<tr>
<td>882-1</td>
<td>ZrB₂-20% SiC</td>
<td>batch 1, milled</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>581.4</td>
<td>0.088</td>
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<td>882-2</td>
<td>ZrB₂-20% SiC</td>
<td>batch 1, milled</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>568.8</td>
<td>0.106</td>
<td>531.2</td>
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<tr>
<td>882-3</td>
<td>ZrB₂-20% SiC</td>
<td>batch 1, milled</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>489.9</td>
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<td>472.3</td>
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<td>882-avg</td>
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<td></td>
<td>549.7</td>
<td>0.107</td>
<td>471.4</td>
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<tr>
<td>897-1</td>
<td>ZrB₂-20% SiC</td>
<td>batch 2, milled</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>576.3</td>
<td>0.129</td>
<td>434.3</td>
</tr>
<tr>
<td>897-2</td>
<td>ZrB₂-20% SiC</td>
<td>batch 2, milled</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>580.2</td>
<td>0.123</td>
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<td>897-3</td>
<td>ZrB₂-20% SiC</td>
<td>batch 2, milled</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>560.2</td>
<td>0.120</td>
<td>395.8</td>
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<td>897-avg</td>
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<td></td>
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<td>574.9</td>
<td>0.127</td>
<td>402.9</td>
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<td>897-1</td>
<td>ZrB₂-20% SiC</td>
<td>milled mix</td>
<td>1900°C, 10Ksi, 2h, vac</td>
<td>638.7</td>
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<td>897-2</td>
<td>ZrB₂-20% SiC</td>
<td>milled mix</td>
<td>1900°C, 10Ksi, 2h, vac</td>
<td>634.3</td>
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<td>473.7</td>
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<tr>
<td>897-3</td>
<td>ZrB₂-20% SiC</td>
<td>milled mix</td>
<td>1900°C, 10Ksi, 2h, vac</td>
<td>729.3</td>
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<td>690.0</td>
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<tr>
<td>897-1</td>
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<td>milled mix</td>
<td>1600°C, 10Ksi, 2h, vac</td>
<td>549.9</td>
<td>0.133</td>
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<td>ZrB₂-20% SiC</td>
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<td>1600°C, 10Ksi, 2h, vac</td>
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<td>0.165</td>
<td>414.7</td>
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<tr>
<td>897-3</td>
<td>ZrB₂-20% SiC</td>
<td>milled mix</td>
<td>1600°C, 10Ksi, 2h, vac</td>
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<td>730.9</td>
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<td>412.8</td>
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<tr>
<td>908-1</td>
<td>HfB₂-20% SiC</td>
<td>milled mix</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>563.8</td>
<td>0.116</td>
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<tr>
<td>908-2</td>
<td>HfB₂-20% SiC</td>
<td>milled mix</td>
<td>2000°C, 10Ksi, 2h, vac</td>
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<tr>
<td>908-3</td>
<td>HfB₂-20% SiC</td>
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<td>2000°C, 10Ksi, 2h, vac</td>
<td>518.5</td>
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<td>908-avg</td>
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<td>485.9</td>
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<tr>
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<td>HfB₂-20% SiC</td>
<td>milled mix</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>549.5</td>
<td>0.118</td>
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<tr>
<td>911-2</td>
<td>HfB₂-20% SiC</td>
<td>milled mix</td>
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<td>559.0</td>
<td>0.117</td>
<td>453.4</td>
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<tr>
<td>911-3</td>
<td>HfB₂-20% SiC</td>
<td>milled mix</td>
<td>2000°C, 10Ksi, 2h, vac</td>
<td>534.6</td>
<td>0.117</td>
<td>423.4</td>
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<td>911-avg</td>
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<td>546.7</td>
<td>0.117</td>
<td>441.8</td>
</tr>
</tbody>
</table>
ZrB₂ + 20% SiC (ZS) After Furnace Oxidation at 1627°C

1 Cycle* 5 Cycles 10 Cycles

*1 cycle = 10 minutes hot & 10 minutes cool

ZrB₂ + 20% SiC + Mixed Ta Compounds (RB) After Oxidation at 1627°C

1 Cycle 5 Cycles 10 Cycles
ZrB$_2$ + 20 \% SiC + 20 \% TaSi$_2$ (ZSTS)

Oxidized at 1627°C

Side A

1 Cycle 5 Cycles 10 Cycles

UHTC Oxidation at 1627°C in Zirconia Furnace

![Graph showing specific weight change vs. time for different materials](image-url)
UHTC Oxidation at 1627°C in Zirconia Furnace

![Graph showing specific weight change squared against time (hrs) for different materials.]

- Z8 882
- ZSTS 889
- RB 878

Linear (RB 878)
- Linear (Z8 882)
- Linear (ZSTS 889)

20 %TaSii Modified ZrB2 + 20% SiC
After Furnace Oxidation at 1627°C in Air

![Images showing microstructure after oxidation.]

1x10 min cycle, at 1000x
10x10 min cycles, at 2000x
10X Improvement in Oxidation Resistance of TaSi₂ Modified 20% SiC

10x10 minute cycles, air, 1627°C

TaSi₂ Modified ZrB₂-20% SiC

>10 X improvement in oxidation resistance relative to industry baseline based on weight change and oxidation damage

UHTCMC Hybrid System

Coated or Improved Oxidation Performance ZrB₂+SiC or HfB₂+SiC Ceramics

Ceramic Composites (C/ZrB₂+SiC or C/HfB₂+SiC)

Advantages of UHTCMC hybrids

- Thickness and composition of UHTC layers can be changed to suit the application requirements
- Improved toughness
- Improved environmental durability
  - Tailored surface coatings
  - Crack healing matrices
  - Control of residual stresses
- Smooth composite surfaces
  - Low drag
  - Machinable without fiber damage
  - Easier to bond and attach sensors and other devices
  - Critical to good attachments/seals
UHTCMC Hybrid System Processing

1. Carbon Fiber Preforms Made into Net Shapes
2. Infiltration of RB₂⁺SiC+C Mixtures
3. Curing and Pyrolysis
4. Surface Treatment (RB₂⁺SiC+C)
5. Melt Infiltration (R or R-Si alloys)
6. Ultra High Temperature Ceramic Matrix Composites (UHTCMCs)

Microstructure of UHTCMC Hybrid System

• ZrB₂ + SiC slurry infiltrant in C/SiC preform
• Similar microstructures in silicon and Si-Ta alloy melt infiltrated systems
• Cracked coatings and matrix due to thermal expansion mismatch
• Process optimization and property characterization underway
Microstructure of UHTCMCs by Prepregging and Melt Infiltration (PREMI)

- 12 layers of T-300, 5-HS cloth prepregged with ZrB₂+SiC or ZrB₂+TaSi₁₃ mixture
- Warm pressed, pyrolyzed, and melt
- Infiltrated with Si or Si-Ta alloy

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CMCs by Prepregging and Melt Infiltration (PREMI)

- Lay-up (2-D Prepregs)
- Resin Transfer Molding (2-D Prepregs)
- Filament Winding (Tow-prep)
- Curing and Pyrolysis
- Melt Infiltration (Silicon or Silicon-Alloy)
- Large and Complex Shape CMC Components
Summary

- Current UHTCs lack robustness (low fracture toughness, reliability and oxidation resistance)
- Alloy and functionally graded materials approaches have been identified to improve oxidation resistance
  - Ta addition appears to be promising with oxidation rate reduced by > 10X @ 1627°C
  - FGM approaches in processing
- Several composites approaches have been identified to increase mechanical robustness
  - Infiltration processing and prepregging have produced materials with interesting microstructures
  - Further characterization of microstructures, and mechanical property and environmental durability is needed to guide the next processing cycle

Conclusions

- Alloying can yield a large improvement in oxidation resistance in a static environment
  - Need to demonstrate in a flowing environment representative of the application
- Several approaches to fabrication of UHTC composites appear to be promising in so far as microstructural appearance
  - Mechanical property and environmental durability evaluations will guide future directions