Ultra high temperature ceramics (UHTCs) including HfB$_2$ + SiC (20% by volume), ZrB$_2$ + SiC (20% by volume) and ZrB$_2$ + SiC (14% by volume) + C (30% by volume) have historically been evaluated as reusable thermal protection systems for hypersonic vehicles [1]. This study investigates UHTCs for use as potential combustion and aeropropulsion engine materials. These materials were oxidized in water vapor (90%) using a cyclic vertical furnace at 1 atm. The total exposure time was 10 hours at temperatures of 1200, 1300, and 1400°C. CVD SiC was also evaluated as a baseline comparison. Weight change measurements, X-ray diffraction analyses, surface and cross-sectional SEM and EDS were performed. These results will be compared with tests ran in static air at temperatures of 1327, 1627, and 1927°C [2]. Oxidation comparisons will also be made to the study by Tripp [3]. A small number of high pressure burner rig (HPBR) results at 1100 and 1300°C will also be discussed.

Specific weight changes at all three temperatures along with the SiC results are shown in Figure 1. SiC weight change is negligible at such short duration times. HfB$_2$ + SiC (HS) performed the best out of all the tested UHTCs for all exposure temperatures. ZrB$_2$ + SiC (ZS) results indicate a slightly lower oxidation rate than that of ZrB$_2$ + SiC + C (ZCS) at 1200 and 1400°C, but a clear distinction cannot be made based on the limited number of tested samples.

Scanning electron micrographs of the cross-sections of all the UHTCs were evaluated. Figure 2 is a representative area for HS at 1400°C for 26 hours, which was the composition with the least amount of oxidation. A continuous SiO$_2$ scale is present in the outermost edge of the surface. Figure 3 is an image of ZCS at 1400°C for 10 hours, which shows the most degradation of all the compositions studied. Here, the oxide surface is a mixture of ZrSiO$_4$, ZrO$_2$ and SiO$_2$.

References
Oxidation of Ultra-High Temperature Ceramics in Water Vapor

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Outline

- Background and Objective
- Materials and Testing Conditions
- Parabolic Oxidation Rates & X-ray Diffraction Results
- Macro, Micrographs, and Energy Dispersive Spectroscopy (EDS)
- Results of Box Furnace Test (Air) and Parabolic Rate Constants
- Results of High Pressure Burner Rig (HPBR) Results for Weight Changes and Recession Measurements
- Summary/Conclusions
Background

Ultra-High Temperature Ceramics (UHTCs)

- Refractory Metal Borides and Carbides – limited by the Melting Point of the Oxide Scale

- High Melting Points (°C)
  \[
  \begin{align*}
  \text{HfB}_2 & : 3100 \\
  \text{ZrB}_2 & : 3040 \\
  \text{SiC} & : 2100
  \end{align*}
  \]

- Oxide Melting Points (°C)
  \[
  \begin{align*}
  \text{HfO}_2 & : 2800 \\
  \text{ZrO}_2 & : 2700 \\
  \text{SiO}_2 & : 1730
  \end{align*}
  \]
Possible Applications for UHTCs

- Thermal Protection Systems for Hypersonic Vehicles
  
  Re-entry Conditions:  
  - high temperature (to 1727°C) and velocity  
  - low pressures (.005 - .010 atm)  
  - short times (~15 minutes/re-entry)  
  - O₂ and N₂, (shock leads to O, N, ions)

- Structural Components or Coatings for Aeropropulsion Applications
  
  Combustion Conditions:  
  - high temperature (900 – 1500°C) and velocity  
  - high pressures (10 – 100 atm)  
  - long times (1000s hours)  
  - hydrocarbon fuels, exhaust (N₂, O₂, COₓ and H₂O)
SiC Containing UHTCs Rely on the Formation of a Protective SiO₂ Layer to Increase Oxidation Resistance.

1200 – 1400°C

\[
\begin{align*}
\text{SiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{g}) & \rightarrow \text{Si(OH)}_4(\text{g}) \\
\text{B}_2\text{O}_3(\text{l}) + \text{H}_2\text{O}(\text{g}) & \rightarrow 2 \text{BO}_2\text{H}(\text{g})
\end{align*}
\]
Objective

Evaluate UHTCs (containing 13-20%v SiC) in Model Combustion Environment and see if Water Vapor has a Major Role/Difference in Oxidation as Compared to Stagnant Air
Materials and Test Conditions

- Materials Compositions:
  - HS (HfB$_2$ + 20%v SiC)
  - ZS (ZrB$_2$ + 20%v SiC)
  - ZCS (ZrB$_2$ + 30%v C + 14%v SiC)


- Sample Size: 2.54 x 1.28 x 0.32 cm & (0.32 cm hole)

- Testing Conditions: Cyclic Furnace
  - vertical furnace tube
  - 90% H$_2$O and 10% O$_2$
  - 1 atm
  - 1200, 1300, and 1400°C.
  - 10 hrs (26 hr max)

- CVD SiC was used in each test as a control
Furnace Schematic

- 90% H₂O and 10% O₂ Cyclic Furnace Test (1-hr cycles), 1 atm
- Total Linear Gas Flow Velocity = 128cm/min
- Alumina Furnace Tube, MoSi₂ Elements, Platinum Hanger
- Hot Zone = 5 cm
Typical Specific Weight Change in 90% Water Vapor at 1200°C
Complete Specific Weight Change in 90% Water Vapor, 10 hrs

\[ K_p = (\text{mg}^2/\text{cm}^4\text{h}) \]

SiC not to scale

- SiC
- HS
- ZS
- ZCS

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Specific Weight Change (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200°C</td>
<td>7.7x10^-1</td>
</tr>
<tr>
<td></td>
<td>1.5x10^-1</td>
</tr>
<tr>
<td></td>
<td>2.6x10^-3</td>
</tr>
<tr>
<td></td>
<td>3.2x10^-1</td>
</tr>
<tr>
<td></td>
<td>3.3x10^-3</td>
</tr>
<tr>
<td></td>
<td>6.8x10^-1</td>
</tr>
<tr>
<td></td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>50.4</td>
</tr>
</tbody>
</table>
X-Ray Diffraction Results at 10hrs in 90% Water Vapor

90% H₂O and 10% O₂, Cyclic Furnace (1-hr cycles)

<table>
<thead>
<tr>
<th>1200°C</th>
<th>HfB₂/SiC</th>
<th>ZrB₂/SiC</th>
<th>ZrB₂/C/SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Major</td>
<td>Minor</td>
<td>Major</td>
</tr>
<tr>
<td>HfO₂</td>
<td>HfSiO₄</td>
<td>ZrO₂</td>
<td>ZrSiO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ZrO₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1300°C</th>
<th>HfB₂/SiC</th>
<th>ZrB₂/SiC</th>
<th>ZrB₂/C/SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Major</td>
<td>Minor</td>
<td>Major</td>
</tr>
<tr>
<td>HfO₂</td>
<td>HfSiO₄</td>
<td>ZrO₂</td>
<td>ZrSiO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ZrO₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1400°C</th>
<th>HfB₂/SiC</th>
<th>ZrB₂/SiC</th>
<th>ZrB₂/C/SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Major</td>
<td>Minor</td>
<td>Major</td>
</tr>
<tr>
<td>HfSiO₄</td>
<td>HfO₂</td>
<td>ZrO₂</td>
<td>ZrSiO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ZrO₂</td>
</tr>
</tbody>
</table>
HS Macrographs in 90% Water Vapor

A: As Received
B: 1200°C, 10 hr
C: 1300°C, 10 hr
D: 1400°C, 26 hr
HS SEM Cross-Section in 90% Water Vapor

As Received

1200°C
10 hrs
10 µm

1300°C
10 hrs
10 µm

1400°C
24 hrs
20 µm
HS EDS Cross-Section at 1300°C in 90% Water Vapor at Edge

O, Si, trace impurity Al, B?

Hf, O, Si?

Hf, O
ZS Macrographs in 90% Water Vapor

A: As Received
B: 1200°C, 10 hr
C: 1300°C, 10 hr
D: 1400°C, 10 hr
ZS SEM Cross-Section in 90% Water Vapor after 10 hrs

As Received

ZS-ASR 6.0kV 12.5mm x200k SE(L) 12/17/2001
20.0μm

1300°C
40 μm

ZS-1300C 6.0kV 12.4mm x250 SE(L) 12/17/2001
200μm

1400°C
40 μm

1200°C
40 μm

SiO₂

ZS-1200C 6.0kV 12.0mm x250 SE(L) 12/17/2001
200μm

ZS-1400C 6.0kV 12.0mm x300 SE(L) 11/29/2001
100μm
ZS Cross-Section at 1300°C in 90% Water Vapor
ZCS Macrographs in 90% Water Vapor

A: As Received
B: 1200°C, 10 hr
C: 1300°C, 10 hr
D: 1400°C, 10 hr
Cross-Section SEM ZCS in 90% Water Vapor after 10 hrs

As Received

1200°C
100 μm

1300°C
40 μm

1400°C
200 μm
ZCS Cross-Section at 1400°C in 90% Water Vapor
## Recession and Weight Change Table for 90% Water Vapor

<table>
<thead>
<tr>
<th></th>
<th>Total Recession 90% H₂O Vapor</th>
<th>Specific Weight Change 90% H₂O Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1400°C 10h (μm per side)</td>
<td>1400°C 10h (mg/cm²)</td>
</tr>
<tr>
<td><strong>HS</strong></td>
<td>35.0 ± 0.01 (26 hrs)</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>ZS</strong></td>
<td>86.5 ± 0.03</td>
<td>11.0</td>
</tr>
<tr>
<td><strong>ZCS</strong></td>
<td>535.0 ± 0.10</td>
<td>22.8</td>
</tr>
</tbody>
</table>
**Oxidation Rate Comparison for 90% Water Vapor vs. Air**

<table>
<thead>
<tr>
<th></th>
<th>1300°C in 90% H₂O (mg²cm⁴/h)</th>
<th>1327°C in Air (mg²cm⁴/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>0.35</td>
<td>0.48 *</td>
</tr>
<tr>
<td>HS</td>
<td>0.29</td>
<td>----</td>
</tr>
<tr>
<td>ZS</td>
<td>16.56</td>
<td>4.94[^3]</td>
</tr>
<tr>
<td>ZS</td>
<td>10.19</td>
<td>6.29[^3]</td>
</tr>
<tr>
<td>ZCS</td>
<td>15.40</td>
<td>17.2[^3]</td>
</tr>
<tr>
<td>ZCS</td>
<td>11.03</td>
<td>----</td>
</tr>
</tbody>
</table>

No Significant Difference between Oxidation Rates in Low Velocity Water Vapor and Stagnant Air

[^3]: Indicates data is in the third decimal place.

*Opila – unpublished
Levine et al. (2002)
High Pressure Burner Rig (HPBR) Macrographs

50 hour exposure at 1300°C

HPBR Test Conditions:

• 6 atm
• 18 meters/sec
• f/a = 0.060

Sample Size:

1.3 x 7.6 x 0.3 cm

Wt loss = HS (3%) ZS (36%) ZCS (48%)
Specific Weight Change in HPBR

ECS 2003 25
### HPBR Weight Change and Recession Measurements

<table>
<thead>
<tr>
<th></th>
<th>HPBR Specific Weight Change (mg/cm²)</th>
<th>HPBR Total Recession (µm per side)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100°C 48h</td>
<td>1100°C 48h</td>
</tr>
<tr>
<td></td>
<td>1100°C 50h</td>
<td>1300°C 50h</td>
</tr>
<tr>
<td>HS</td>
<td>+2.2</td>
<td>----</td>
</tr>
<tr>
<td>ZS</td>
<td>-6.1</td>
<td>178 ± 14</td>
</tr>
<tr>
<td>ZCS</td>
<td>-79.3</td>
<td>469 ± 8</td>
</tr>
</tbody>
</table>

Paralinear Weight Loss and High Recession Rates due to Volatility and Spallation Effect
Summary

- 3 Compositions (HS, ZS, ZCS) of UHTCs were Evaluated in a 90% Water Vapor Cyclic Furnace for Ten Hours.
- High Oxide Growth were Observed for all UHTCs Compared to that of SiC Control. The Most Oxidation Resistant UHTC in this Study is HS.
- Results were Compared to that of Stagnant Air and HPBR (6atm)

Factors to Take into Account:

vs. Stagnant Air: → Similar Oxidation Rates

vs. HPBR: → High Velocity causes Volatility and Scale Spallation  
→ Accelerated Recession
Conclusions

- Low Velocity Water Vapor Does Not Have a Significant Effect on the Oxidation Rates as Compared to Stagnant Air
- Gas Velocity is an Important Contributor to Volatility, Spallation and Accelerated Recession
- UHTC Materials are Inappropriate for Long Term Aeropropulsion Applications
References

