Characterization of an Ultra-High Temperature Ceramic Composite

Stanley R. Levine, Elizabeth J. Opila, Raymond C. Robinson\textsuperscript{a}, and Jonathan A. Lorincz\textsuperscript{b}

NASA Glenn Research Center
Cleveland, Ohio 44135

Ultra-high temperature ceramics (UHTC) are of interest for hypersonic vehicle leading edge applications. Monolithic UHTCs are of concern because of their low fracture toughness and brittle behavior. UHTC composites (UHTCC) are being investigated as a possible approach to overcome these deficiencies. In this study a small sample of a UHTCC was evaluated by limited mechanical property tests, furnace oxidation exposures, and oxidation exposures in a flowing environment. The composite was prepared from a carbon fiber perform using ceramic particulates and a preceramic polymer.

The as-received composite plate was non-uniform from front to back surface. Plate dimensions were 150 x 150 x 6 mm. The back surface had a fibrous, uniform appearance; XRD analysis revealed the presence of SiC and C. The front surface was smooth and non-uniform in appearance with evidence of a coarse grain structure produced by a liquid phase; XRD analysis revealed the presence of HfB\textsubscript{2}. Microcracks were present throughout the thickness as one might expect from a carbon fiber reinforced composite with attendant large thermal expansion mismatch between the matrix phases and the fibers. The HfB\textsubscript{2} phase on the front surface was comparable in thickness to a fiber ply or about 0.6 mm, and surface microcracks were evident. Limited four point flexural tests were carried out at span to depth ratios of approximately 14 and 16 with markedly different results. Tests were run with the front or the back surface in tension. At the shorter span to depth failures occurred under a loading pin for both orientations. At a span to depth of 16 failures occurred in the center of the span with fracture clearly initiating from a tensile failure. Ultimate flexural strength, strain at ultimate stress, stress and strain at deviation from linear elastic behavior are reported. Strains at ultimate stress ranged from about 0.6 to 0.7\% for the back surface in tension, and 0.4 to 0.6 for the front surface in tension. At constant span to depth the strain at ultimate stress was about 0.2\% greater for the back surface in tension and the ultimate strength was also higher. Strengths were in line with predictions from theory.

Furnace oxidation studies were carried out at 1627 and 1927°C in a static furnace environment using ten minute cycles and one, five, and ten cycles. Limited oxidation studies were also carried out in a flowing oxyacetylene torch environment. Specimens were photographed, and weight and dimensional changes were determined. XRD and SEM characterizations were performed. Weight losses were attributed primarily to carbon fiber oxidation. The composite survived the torch test with little visible distress. Further details will be determined once metallographic studies are completed.

\textsuperscript{a} QSS Group Inc.
\textsuperscript{b} Ohio University
Characterization of an Ultra-High Temperature Ceramic Composite

Stanley R. Levine, Elizabeth J. Opila, Raymond C. Robinson, and Jonathan A. Lorincz
NASA Glenn Research Center
Cleveland, Ohio 44135

October 19, 2003
Characterization of an Ultra-High Temperature Ceramic Composite

Outline

• Background
• Objectives
• UHTCC Description
• Results
  – Flexural tests
  – Furnace oxidation
  – Torch tests
• Concluding Remarks
Ultra High Temperature Ceramic Composite (UHTCC) Leading Edge

Key Issues
- Thermal stress resistance
- Oxidation resistance
- Temperature capability
- Architecture optimization

<table>
<thead>
<tr>
<th>Oxidation Resistant Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionally Graded Transition</td>
</tr>
<tr>
<td>UHTC Composite Core</td>
</tr>
</tbody>
</table>
Characterization of an Ultra-High Temperature Ceramic Composite

• Objectives
  – Characterize a UHTC composite plate fabricated by Starfire
    • CAVEAT: Recognize that little or no development effort went into fabrication of this material. It was a best effort fabrication for NASA LaRC
  – Reveal some of the issues associated with the UHTCC concept
UHTCC Processing by Starfire

Constituents
- Zoltek Panex® 30 Carbon Fabric PW06
- Starfire Systems’ SP-Matrix Polymer (Allylhydridopolycarbosilane (AHPCS))
- HfB₂ Powder
- SiC Powder

Processing of Part Number 000928-6-64

• Initial Cycle:
  • Zoltek cloth is cut into ~6”x6” pieces. 11 plies used
  • For the initial lay up the **bottom 6 layers of cloth are coated with a SiC/AHPCS slurry and the top 5 layers are coated with a HfB₂/AHPCS slurry.**
  • The cloth is put into an Al mold and pressed to ~1800lbs. The mold is clamped and cured under inert gas to 400°C.
  • The plate is removed from the mold and clamped between graphite plates and fired to 850°C under inert gas to pyrolyze.

• Cycle 2:
  • Coat the HfB₂ side of the plate with more HfB₂/AHPCS slurry.
  • Clamp and fire directly to 850°C under inert gas.

• Cycle 3: Repeat cycle 2

• Cycle 4 - 10:
  • Vacuum infiltrate with AHPCS only.
  • Pyrolyze directly to 850°C under inert gas, no clamping necessary.
As-Received UHTCC Plate

C/SiC Side

UHTC Side

150 mm
As-Received UHTCC

C/SiC Side

UHTC Side

STARC_AR 6.0kV 12.2mm x30 SE(M) 100μm

STARC_AR 6.0kV 12.0mm x1.00k SE(M) 50.0μm

STARH_AR 6.0kV 19.4mm x1.00k SE(L) 07/17/2003 50.0μm

STAR_ARH 6.0kV 12.4mm x5.00k SE(L) 07/17/2003 10.0μm

spot 1

spot 2
UHTCC Cross-section

SiC

C

Phases Detected by XRD

HfB₂
HfB$_2$-rich Side of UHTCC
Constituents in As-Received UHTCC

HfB₂ Coating Layer

Matrix on C/SiC Side

HfB₂

SiC

Uncommon Tramp

Si-O-C

SiC

Starfire 6.0kV 12.2mm x6.00k SE(L) 5.00µm

Starfire 6.0kV 11.9mm x2.50k SE(L) 20.0µm
# Flexural Strength Tests

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Test Fixture</th>
<th>Orientation</th>
<th>Ultimate Load</th>
<th>Calculated Load Based on Beam Theory*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>width thickness</td>
<td>inner span outer span span/depth fracture side down</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>A</td>
<td>12.7 mm 5.79 mm</td>
<td>40 mm 80 mm 13.8 mm</td>
<td>under pin C/SiC</td>
<td>972</td>
</tr>
<tr>
<td>B</td>
<td>12.7 mm 5.92 mm</td>
<td>40 mm 80 mm 13.5 mm</td>
<td>under pin UHTC</td>
<td>757</td>
</tr>
<tr>
<td>C</td>
<td>12.7 mm 6.04 mm</td>
<td>48 mm 96 mm 15.9 mm</td>
<td>center C/SiC</td>
<td>1025</td>
</tr>
<tr>
<td>D</td>
<td>12.7 mm 6.06 mm</td>
<td>48 mm 96 mm 15.8 mm</td>
<td>center UHTC</td>
<td>811</td>
</tr>
<tr>
<td>E</td>
<td>12.7 mm 6.07 mm</td>
<td>48 mm 96 mm 15.8 mm</td>
<td>center UHTC</td>
<td>855</td>
</tr>
</tbody>
</table>

- Sample B remained intact. All other samples fractured into 2 pieces.
- Samples B, D, and E retained an obvious permanent set.

*Calculated load at 0.7% strain
- Panex 30 minimum property: $E = 193 \text{ GPa}$
- Rule of mixtures with no matrix contribution
<table>
<thead>
<tr>
<th>Test</th>
<th>Tensile</th>
<th>Ultimate flexural strength (crosshd)</th>
<th>Deviation from linearity</th>
<th>Strain at deflectometer</th>
<th>MPa</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C/SiC</td>
<td>137.0</td>
<td>26.4</td>
<td>0.105</td>
<td>23.0</td>
<td>0.058</td>
</tr>
<tr>
<td>B</td>
<td>UHTC</td>
<td>102.3</td>
<td>31.4</td>
<td>0.113</td>
<td>26.0</td>
<td>0.059</td>
</tr>
<tr>
<td>C</td>
<td>C/SiC</td>
<td>161.8</td>
<td>28.2</td>
<td>0.078</td>
<td>23.0</td>
<td>0.063</td>
</tr>
<tr>
<td>D</td>
<td>UHTC</td>
<td>136.7</td>
<td>24.7</td>
<td>0.056</td>
<td>26.1</td>
<td>0.063</td>
</tr>
<tr>
<td>E</td>
<td>UHTC</td>
<td>131.8</td>
<td>26.1</td>
<td>0.090</td>
<td>26.1</td>
<td>0.063</td>
</tr>
</tbody>
</table>
UHTCC Flexural Strength Results

**Ultimate Flexural Strength**

- **Tension Side**
  - C/SiC
  - UHTC

**Ultimate Strain**

(based on crosshead)

<table>
<thead>
<tr>
<th></th>
<th>Longer S/D</th>
<th>Shorter S/D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MPa</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Longer S/D</th>
<th>Shorter S/D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>%</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
UHTCC After 1627°C Furnace Oxidation

C/SiC Side

HfB$_2$ Side

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.167</td>
</tr>
<tr>
<td>5</td>
<td>0.833</td>
</tr>
<tr>
<td>10</td>
<td>1.667</td>
</tr>
</tbody>
</table>
Furnace Oxidation of UHTCC at 1627°C
UHTCC After 10 Ten-minute Cycles in Air at 1627°C
UHTCC Oxy-Acetylene Torch Test

- **Sample O**: One 4 min. cycle to 1805°C
  - Photos on cool down
  - Temps with Irccon 2 color pyrometer, 980-1760°C range
  - Weight change
    - Initial weight 41.66 g
    - Final weight 40.87 g
    - Weight loss 0.79 g, or 1.9%

- **Sample N**: Three ~4 min. cycles
  - Cycle 1 max temp 1815°C
  - Cycle 2 max temp 1915°C
  - Cycle 3 max temp 2015°C
    - Photos on heat up
  - Weight change
    - Initial weight 41.99
    - Final weight 40.04
    - Weight loss 1.95 g, or 4.6%

### Sample O

<table>
<thead>
<tr>
<th>Time, min.</th>
<th>Temp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1720</td>
</tr>
<tr>
<td>1.0</td>
<td>1750</td>
</tr>
<tr>
<td>1.5</td>
<td>1750</td>
</tr>
<tr>
<td>2.0</td>
<td>1755</td>
</tr>
<tr>
<td>2.5</td>
<td>1765</td>
</tr>
<tr>
<td>3.0</td>
<td>1775</td>
</tr>
<tr>
<td>3.5</td>
<td>1790</td>
</tr>
<tr>
<td>4.0</td>
<td>1805</td>
</tr>
</tbody>
</table>
UHTCC Torch Test Video
UHTCC Torch Test Cool Down

0 sec

10 sec

20 sec

30 sec
UHTC Surface After Three 4-Minute Torch Cycles to 1815 to 2025°C
SEM of Center of UHTC Surface After Three Torch Cycles
SEM of UHTC Surface, Three Torch Cycles
Conclusions

• **Processing**
  – Uniform and through thickness graded microstructure achieved
  – Matrix cracking due to thermal expansion mismatch between C fibers and matrix constituents is a concern

• **Mechanical Properties**
  – Flexural strength was close to expected values based on rule of mixtures with no matrix contribution
  – Some evidence of composite behavior

• **Furnace Oxidation**
  – Based on weight loss, carbon fiber oxidation occurred rapidly

• **Torch Test**
  – Material withstood ~2000°C (~3600°F), severe heat-up and thermal gradients with no major visible distress
  – Based on observed temperature spikes during test, adherence of the HfO₂-rich scale is an area of concern
Recommendations

• The thermal stress response of this early UHTCC makes the concept worthy of further study
• Fiber coatings need to be incorporated to address fiber oxidation issues
• Advanced SiC fibers need to be evaluated to address oxidation and thermal expansion mismatch issues
Future Work

- Continue UHTCC development
- Complete metallography on Starfire specimens
- Evaluate other NASA and industry developed materials
Acknowledgements

• Thanks to Terry R. McCue for scanning electron microscopy support and Ronald E. Phillips for assistance with testing.
• Thanks to David Glass of NASA Langley for providing the Starfire UHTCC plate.
• Thanks to Walt Sherwood of Starfire Inc. for providing processing details and for permission to present this study.