Ultrahigh temperature ceramics for thermal protection systems, propulsion and energy

Diletta Sciti
National Research Council of Italy (CNR)
Institute of Science and Technology for Ceramics
Via Granarolo 64, 48018 Faenza (RA)
Acknowledgements

• Ing. Cantoni, Ing. A. Del Vecchio, CIRA.

• AFOSR research grant FA8655-12-1-3004 (Contract monitor Dr. Sayir) for short fiber-UHTCs composites.

• MoD for cofunding activity on UHTCs for propulsion applications (SMARP – Sviluppo di MMateriali ceramici ultraResistenti all’ablazione per applicazioni nella Propulsione) through PNRM.

• ISTEC staff: L. Zoli, L. Silvestroni, A. Natali Murri, V. Medri...

• Prof. Savino, Department of Industrial Engineering (DII) – Aerospace section, University of Naples “Federico II”, for tests on TPS and rocket nozzles.
Outline

• Introduction
• Short fibers- ZrB$_2$ composites for TPS
• SiC/C long fibers ZrB$_2$ composites for TPS
• Development of ultra-ablation resistant ceramics for application in the propulsion - SMARP
• Conclusions
Ultra High Temperature Ceramics

Potential materials for use in extreme environments such as:

- scramjet engine components, leading edges, nosecones for hypersonic vehicles;
- Rockets nozzles
- cladding materials in generation IV nuclear reactors;

Critical challenges:

- thermal shock resistance
- damage tolerance
- ...

<table>
<thead>
<tr>
<th>Tm (°C)</th>
<th>ρ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3890</td>
<td>TaC 13.9</td>
</tr>
<tr>
<td>3880</td>
<td>HfC 12.7</td>
</tr>
<tr>
<td>3540</td>
<td>ZrC 6.7</td>
</tr>
<tr>
<td>3380</td>
<td>HfB₂ 11.2</td>
</tr>
<tr>
<td>3305</td>
<td>HfN 13.8</td>
</tr>
<tr>
<td>3245</td>
<td>ZrB₂ 6.1</td>
</tr>
<tr>
<td>2950</td>
<td>ZrN 7.1</td>
</tr>
</tbody>
</table>
ISTEC – CIRA long term collaboration

Sharp Hot Structures (CIRA)- 2000

UHTC massive tip

C/ SiC

H = 90 mm
D = 120 mm

UHTC Winglet in EXPERT (ESA Programme) (2006-on hold)

SHARK ESA project (2010)

Most of test articles in monolithic UHTC suffered from a dramatic failure!
Short fibers-reinforced UHTCs

- Easy approach to increase the fracture toughness (SiC particles $\rightarrow$ SiC fibers)
- Same processing as conventional powders

SiC fibers:
- Hi-Nicalon, Tyranno SA3....

C fibers

- Highest values: 20% Hi Nicalon uncoated fiber, densification 1600°C
- Tyranno lower than Hi nicalon
- Type S < Hi Nicalon, Tyranno

- Strength: decreases almost linearly
- Highest values for Tyranno
- Type S (coated/uncoated) similar to Tyranno
### Boride –SiC<sub>fiber</sub> vs Boride –SiC<sub>particle</sub>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Temperature, °C</th>
<th>Density g/cm³</th>
<th>$K_{IC}$ MPam&lt;sup&gt;1/2&lt;/sup&gt;</th>
<th>$\sigma_{RT}$ MPa</th>
<th>$\sigma_{1200}$ MPa</th>
<th>$\sigma_{1500}$ MPa</th>
<th>TSR K</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB&lt;sub&gt;2&lt;/sub&gt;-20SiCf</td>
<td>1700</td>
<td>5.3</td>
<td>5.5-6.5</td>
<td>400-500</td>
<td>300-400</td>
<td>200-300</td>
<td>450</td>
</tr>
<tr>
<td>ZrB&lt;sub&gt;2&lt;/sub&gt;-20SiCp</td>
<td>1900</td>
<td>5.3</td>
<td>~3.5</td>
<td>700-1000</td>
<td>-</td>
<td>200-500</td>
<td>385</td>
</tr>
</tbody>
</table>

ZrB<sub>2</sub>-SiC particles have very high strength even at 1500°C

**BUT**

Low damage tolerance causes failure before high temperature regimes are reached
Arc Jet Tests (in collaboration with DII)

- M \approx 3 \text{ (supersonic regime)}
- 1 \text{ g/s of } 80\%\text{N}_2 + 20\% \text{O}_2
- static pressure in the chamber \approx 200 \text{ Pa}
- specific total enthalpy 8-16.4 \text{ MJ/kg}
- maximum stagnation point pressure 6-12 \text{ kPa}
- 2 colour pyrometer + IR camera

<table>
<thead>
<tr>
<th>Test</th>
<th>$H_{\text{0 max}}$ (MJ/kg)</th>
<th>time (sec)</th>
<th>$T_{\text{max}}$ ($^\circ$C)</th>
<th>$\varepsilon_1$ \mu m</th>
<th>Tot. time</th>
</tr>
</thead>
<tbody>
<tr>
<td>f1</td>
<td>13.8</td>
<td>285</td>
<td>1380</td>
<td>0.88</td>
<td>16' 45''</td>
</tr>
<tr>
<td>f2</td>
<td>17.0</td>
<td>330</td>
<td>1590</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>f3</td>
<td>12.3</td>
<td>120</td>
<td>1395</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>f4</td>
<td>17.0</td>
<td>270</td>
<td>1680</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>

The wedge survived the 4 tests!
ISTEC/CIRA 2010-2013 collaboration

Extensive characterization campaign of short fibers-ZrB₂ composites

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Thermal Diffusivity mm²/s</th>
<th>Specific Heat J/(gK)</th>
<th>Thermal Conductivity W/(mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>28.624</td>
<td>0.426</td>
<td>65.657</td>
</tr>
<tr>
<td>599</td>
<td>15.950</td>
<td>0.692</td>
<td>59.391</td>
</tr>
<tr>
<td>900</td>
<td>14.493</td>
<td>0.701</td>
<td>54.644</td>
</tr>
<tr>
<td>1198</td>
<td>13.403</td>
<td>0.745</td>
<td>53.773</td>
</tr>
<tr>
<td>1500</td>
<td>12.544</td>
<td>0.748*</td>
<td>50.515</td>
</tr>
</tbody>
</table>

Oxidation tests

SCRAMSPACE project 2013

Fiber-reinforced UHTC

Winglet
Long fiber reinforced UHTCs (ZrB$_2$)

- Simple preforms: tows or 1D preforms
- SiC or C fibers
- Slurry infiltration & sintering

GOALS
- Increase the fiber volumetric amount >40%
- Non-brittle behaviour
ZrB$_2$ – SiC 1D textiles

Overall: fiber vol. amount is 40%
Maximum density is 60-70%
Fracture: fiber surface is very smooth
Matrix fully dense
Problems: cracks
ZrB$_2$ - 1D carbon textiles

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>$\sim 2.3 \text{ g/cm}^3$</td>
</tr>
<tr>
<td>Fiber</td>
<td>$\sim 75 \text{ vol}%$</td>
</tr>
<tr>
<td>Relative Density</td>
<td>80-85%</td>
</tr>
</tbody>
</table>
Load - Displacement behaviour

Load [N]

Displacement [mm]
Development of ultra-ablation resistant ceramics for application in the propulsion - SMARP

Combustion flame of oxygen and hydrocarbon gases (butane-propane)

<table>
<thead>
<tr>
<th></th>
<th>Max Temp. (°C)</th>
<th>ΔW/W₀ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1600</td>
<td>-26.2</td>
</tr>
<tr>
<td>HfC</td>
<td>1900</td>
<td>+0.2</td>
</tr>
<tr>
<td>TaC</td>
<td>1700</td>
<td>+0.5</td>
</tr>
</tbody>
</table>

Tests at DII- Univ. of Naples

Figure 2. Experimental setup: 1) test sample, 2) alumina support, 3) ceramic support, 4) burner, 5) FLIR ThermaCAM P40 thermal camera, 6) MikronImpac ISQ5 pyrometer, 7) CCD camera.
Rocket nozzles tests

Temperature profiles

1 s

60 s

P=10 bar, rapporto di miscelamento pari a 3.

Ceramic rocket nozzle (monolithic or reinforced)

Comparison with graphite nozzles

Rocket engine test at DII- prop lab
Conclusions

• ISTEC research is focused on reinforced UHTC systems (UHTC-CMCs)

• Addition of short fibers (up to 30 vol%) is a simple process, BUT brittle behaviour, density $\sim 5 \text{ g/cm}^3$

• Long fibers: volumetric amount increased from 40-70%, non brittle behavior, density $\sim 2.5 \text{ g/cm}^3$
Thank you for your kind attention