Ultra High Temperature Ceramics for Space Propulsion

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2nd Intern. Symposium: “Hypersonic Flight: from 100,000 to 400,000 ft”
Rome, Italy 30th June - 1st July 2016

01/07/16
2° Hypersonic International Symposium - Roma, 30 June - 1 July 2016
**Ultra High-Temperature Ceramics (UHTCs)**

UHTCs are based on metal refractory borides and carbides such as ZrB$_2$ ($T_m=3323$ K), ZrC ($T_m=3805$ K), HfB$_2$ ($T_m=3523$ K), HfC ($T_m=4103$ K), TaB$_2$ ($T_m=3373$ K), TaC ($T_m=3500$ K) which make them suitable for high temperature applications in harsh environments such as Thermal Protection Systems (TPS) and Components for Solid Propellant Engines.

Addition of silicon carbide (SiC) to these materials strongly improves their oxidation resistance at high temperature as well as room temperature strength.

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**AIM OF THIS WORK**

Development and Testing of Innovative UHTCs for Nozzle Components in Small Scale Solid Propellant Engines

**General requirements**

Suitable combination of: density, thermal expansion coefficient, thermal diffusivity, specific heat, thermal conductivity, mechanical strength and capability to withstand severe environment (CO$_2$, N$_2$, H$_2$, CO, etc.) and temperatures (up to 3000 K)
DEVELOPED STRATEGY

- Fabrication of fully dense small size samples of various UHTC systems
- Screening of UHTC candidates by means of TGA under different conditions (CO₂, N₂, air)
- Fabrication of relatively large size samples for standard testing
- Performing ablation test
- Evaluation of thermophysical properties (Thermal diffusivity and conductivity, heat capacity, etc.)
- Thermo-mechanical properties
- Fabrication of Small Scale Nozzle Components (Prototype)
- Prototype validation under operating conditions of Solid Propellant Engines

Fabrication of dense UHTC materials

Critical features

Consolidation methods
- Pressure-Less Sintering (PLS) or classical Hot Pressing (HP)
- Severe sintering conditions:
  - Temperature (> 2000°C)
  - Processing times (hours)
- Coarse microstructure
- High production costs

Sintering stages
Fabrication of dense UHTC materials

Use of efficient synthesis/sintering methods

SHS (Self-propagating High-temperature Synthesis) for highly sinterable powders

SPS (Spark Plasma Sintering) for nearly full dense materials

Self-propagating High-temperature Synthesis

SHS refers to a solid-solid process where an highly exothermic reaction occurs between reactants in powder form (ex. Zr+2B → ZrB\(_2\), (\(\Delta H\))= 323 kJ/mol)

**ADVANTAGES**
- Extremely rapid process
- High quality of products
- No use of solvents
- Extremely simple process
- Energy saving
- Good sinterability
**Spark Plasma Sintering Technology**

Simultaneous application of a pulsed electric current and a mechanical load (Joule effect)

**Advantages**
- Relatively short times (< 1 h)
- Lower temperatures
- Energy efficient with respect to traditional hot sintering technologies (Hot Pressing)

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**SPS equipments**

- **SPS 515S** Sumitomo
  - Small samples
- **SPS-FCT HP D 25**
  - Large samples
### UHTC Systems Investigated

<table>
<thead>
<tr>
<th>Monolithic</th>
<th>Binary Composites</th>
<th>Ternary Composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borides Carbides</td>
<td>ZrB₂ ZrC ZrB₂ - SiC ZrB₂ - ZrC - SiC</td>
<td>TaB₂ TaC TaB₂ - SiC TaB₂- TaC - SiC</td>
</tr>
<tr>
<td></td>
<td>HfB₂ HfC HfB₂ - SiC (1) HfB₂- HfC - SiC</td>
<td>HfB₂ - SiC (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HfB₂ - SiC (3)</td>
</tr>
</tbody>
</table>

### UHTC Samples Produced

- **TGA and Thermophysical Properties**
- **Thermo-mechanical Characterization**
- **Ablation test**

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**TGA**

1) Operating gas: \(N_2\)

- Maximum operating Temperature: 1450°C
- Heating schedule: \(50°C/min\)
- Step under isothermal conditions: 15 min
- Free cooling

2) Operating gas: \(CO_2\)

- Maximum operating Temperature: 800°C
- (Degradation of thermocouples at higher T)
- Heating schedule: \(50°C/min\)
- Step under isothermal conditions: 30 min
- Free cooling

3) Operating gas: \(Air\)

- Maximum operating Temperature: 1450°C
- Heating schedule: \(2°C/min\)
- Free cooling

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*TGA in \(N_2\)_Results (1)*
**TGA in CO₂ Results (2)**

![Graphs showing mass change vs. time for Borides and Binary Composites](#)

**TGA in Air Results (3)**

![Graphs showing mass change vs. temperature for Borides and Binary Composites](#)

Curves relative to monolithic carbides are not included as they oxidize markedly when exposed to air at high T.

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Ablation Test

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Ablation Test

Beginning of the test

During the test

Heat Flux 1 (HF1) = 450 W/cm² for 120 s, A/O ratio 1:3
Heat Flux 2 (HF2) = 1050 W/cm² for 80 s, A/O ratio 1:1.3
Heat Flux 3 (HF3) = 1250 W/cm² for 100 s, A/O ratio 1:1.7

Weight losses of samples during ablation tests are negligible

<table>
<thead>
<tr>
<th></th>
<th>Virgin (g)</th>
<th>HF1 (g)</th>
<th>Delta W1 (%)</th>
<th>HF2 (g)</th>
<th>Delta W2 (%)</th>
<th>HF3 (g)</th>
<th>Delta W3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfB₂-SiC (2)</td>
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<td>HfB₂-SiC (3)</td>
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<tr>
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<td>29.38484</td>
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<td>-0.00050</td>
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</table>

Weight losses of samples during ablation tests are negligible.
Thermo-physical characterization

Thermal Diffusivity and Conductivity decrease up to 1900°C with the typical dependence for phonon conductors.

<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>
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<tbody>
<tr>
<td>18</td>
<td>38.448</td>
<td>0.256</td>
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<td>1500</td>
<td>14.653</td>
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<tr>
<td>1898</td>
<td>13.278</td>
<td>0.504</td>
<td>60.603</td>
</tr>
</tbody>
</table>

Conclusions

- UHTCs formulations identified and obtained in this work as fully dense products are very promising for High Temperature applications in aggressive environments.
- In particular, based on the results obtained with TGA tests conducted with different gaseous environments, the HfB₂-SiC system was selected for the fabrication of small size nozzle components.
- The capability of HfB₂-SiC system to withstand harsh conditions was confirmed by the additional characterizations carried out:
  - Ablation tests conducted under different heat fluxes
  - Evaluation of thermophysical properties at high T
Work in progress and future plans

- Thermo-mechanical characterization at high T
- Fabrication of Small Scale Nozzle Components
- Prototype validation under actual operating conditions of Solid Propellant Engines
- Future work: Process scale-up for the fabrication of larger sized components