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Synthesis and Static Oxidation Testing of Doped HfB$_2$ Powders

Pengxiang Zheng, Jon Binner* and Bala Vaidhyanathan

Loughborough University
*University of Birmingham
UK
Problems with HfB$_2$ Ceramic Oxidation

HfB$_2$ oxidises to HfO$_2$ readily; whilst not a problem in itself, like ZrO$_2$, HfO$_2$ undergoes a phase transformation with an associated volume change that opens up porosity.

Phase transformation of the oxide product of HfB$_2$

One solution is to dope the HfB$_2$ so that on oxidation it forms stabilised, tetragonal HfO$_2$
Dopant Selection

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point /°C</th>
<th>Crystal structure</th>
<th>Covalent radius of the metal atom / pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfB₂</td>
<td>3250</td>
<td>Hexagonal</td>
<td>175±10</td>
</tr>
<tr>
<td>YB₄</td>
<td>2150</td>
<td>Tetragonal</td>
<td>190±7</td>
</tr>
<tr>
<td>TaB₂</td>
<td>2850</td>
<td>Hexagonal</td>
<td>170±8</td>
</tr>
<tr>
<td>LaB₆</td>
<td>2250</td>
<td>Cubic</td>
<td>207±8</td>
</tr>
<tr>
<td>MgB₂</td>
<td>830</td>
<td>Hexagonal</td>
<td>141±7</td>
</tr>
</tbody>
</table>

TaB₂ was chosen because of its similar crystal structure and atomic radius to that of HfB₂
Addition of Ta-Dopant

\[ \text{TaCl}_5 \text{ dispersed in ethanol, HfCl}_4 \text{ in de-ionised water. Ammonia used to form hydroxides & remove Cl}^- \text{ions.} \]

\[ \Delta G < 0 \text{ at } >1350^\circ \text{C} \]

\[ \text{Phenolic resin} \]

\[ \text{Dissolved in ethanol} \]

\[ \text{Co-precipitates} \]

\[ \text{Ta}_2\text{O}_5 + 2\text{B}_2\text{O}_3 + 11\text{C} \rightarrow 2\text{TaB}_2 + 11\text{CO}^\uparrow \]

\[ \Delta G < 0 \text{ at } >1327^\circ \text{C} \]
Ta-Doped HfB$_2$ Powder

10 wt% Ta-doped HfB$_2$ powder

EDX mapping shows the Ta distributed homogeneously. The particle size was $\sim$0.5 µm, but the final product contained hard agglomerates.
All the peaks correspond to HfB$_2$ confirming the formation of (Ta,Hf)B$_2$ solid solution
Lattice Parameter of Pure and Doped HfB$_2$

Peak of HfB$_2$ (101) plane shifts to right with addition of more TaB$_2$ dopant

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>HfB$_2$ (literature)</th>
<th>HfB$_2$ (this study)</th>
<th>5% TaB$_2$-doped HfB$_2$</th>
<th>10% TaB$_2$-doped HfB$_2$</th>
<th>15% TaB$_2$-doped HfB$_2$</th>
<th>TaB$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a / nm</td>
<td>0.3141</td>
<td>0.3142</td>
<td>0.3140</td>
<td>0.3139</td>
<td>0.3138</td>
<td>0.3088</td>
</tr>
<tr>
<td>c / nm</td>
<td>0.3470</td>
<td>0.3470</td>
<td>0.3468</td>
<td>0.3466</td>
<td>0.3464</td>
<td>0.3241</td>
</tr>
</tbody>
</table>
After 1600°C oxidation, pure HfB$_2$ yielded entirely monoclinic HfO$_2$ whilst the 10%TaB$_2$-doped HfB$_2$ gave almost phase pure tetragonal HfO$_2$. 
After 1600°C oxidation, pure HfB$_2$ yielded entirely monoclinic HfO$_2$ whilst the 10%TaB$_2$-doped HfB$_2$ gave almost phase pure tetragonal HfO$_2$. 

XRD Results after 1600°C Oxidation of Powder
Modelling

*Low Temp < ~ 1000°C*

- ZrB$_2$
- B$_2$O$_3$(s,l)
- ZrO$_2$
- B$_2$O$_3$(g)

Porous ZrO$_2$ – Wetted by B$_2$O$_3$

*Intermediate Temp (~1000 to ~1800°C)*

- ZrB$_2$
- ZrO$_2$
- B$_2$O$_3$(l)
- B$_2$O$_3$(g)

Porous ZrO$_2$ – partially filled

*Very High Temp > ~1800°C*

- ZrB$_2$
- B$_2$O$_3$(g)
- ZrO$_2$
- ZrO$_2$(g)

Porous ZrO$_2$ – Enhanced Oxidation

**Predicted:** recession rates, scale thicknesses, weight gain (all validated against expts)

Phase transformation of ZrO$_2$ and HfO$_2$ plays a significant role (increases pore volume)

TA Parthasarathy

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Loughborough University

UNIVERSITY OF BIRMINGHAM

XMat
Materials Systems for Extreme Environments
Modelling

Predicted: recession rates, scale thicknesses, weight gain (all validated against experiments).

Phase transformation of ZrO₂ and HfO₂ plays a significant role (increases pore volume).
<table>
<thead>
<tr>
<th>Ta-Doped Samples after SPS at 2100°C, 50 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treibacher HfB$_2$</td>
</tr>
</tbody>
</table>

20 mm
Ta-Doped Samples after SPS at 2100\(^\circ\)C, 50 MPa

- Peak shifts show that Ta atoms remain in solid solution.
- No residual TaB\(_2\) in the 15 wt% Ta-doped HfB\(_2\) sample.
# Ta-Doped Samples after SPS at 2100°C, 50 MPa

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density / g cm⁻³</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treibacher HfB₂</td>
<td>9.83</td>
<td>93.62%</td>
</tr>
<tr>
<td>0 wt% Ta-doped HfB₂</td>
<td>8.93</td>
<td>85.04%</td>
</tr>
<tr>
<td>5 wt% Ta-doped HfB₂</td>
<td>9.24</td>
<td>87.73%</td>
</tr>
<tr>
<td>10 wt% Ta-doped HfB₂</td>
<td>9.36</td>
<td>88.59%</td>
</tr>
<tr>
<td>15 wt% Ta-doped HfB₂</td>
<td>9.55</td>
<td>90.12%</td>
</tr>
</tbody>
</table>

*Theoretical value for HfB₂ 10.50*

*Theoretical value for TaB₂  11.15*

*The addition of Ta improves the sinterability of HfB₂*
The addition of Ta improves the sinterability of HfB₂
10 wt% Ta-doped HfB$_2$

Ta homogeneously distributed.

Carbon was found in all the samples (including the commercial HfB$_2$). It is probably from the protective graphite sheet used for SPS.
Ta-Doping of HfB$_2$ – Summary & Future Work

- High purity, sub-micron ($\sim$0.5 µm) Ta-doped HfB$_2$ has been synthesized.
- The 10 wt% Ta-doped HfB$_2$ was able to almost fully stabilize HfO$_2$ in the tetragonal phase after oxidation of the powder at 1600°C.
- The addition of Ta-dopants improve the sinterability of HfB$_2$.

- In order to achieve higher density, the 10 wt% Ta-doped HfB$_2$ powders will be SPSed at 2400°C and 500 MPa at QML.
- Samples with satisfactory density (>98%) will be oxidized to investigate TAPs’ model.
Thank You