BORIDE BASED ELECTRODE MATERIALS UNDER EXTREME CONDITIONS FOR MHD DIRECT POWER EXTRACTION

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Award Administrator: Amanda Lopez
INTRODUCTION
Magnetohydrodynamic (MHD) Direct Power Extraction

Flame temperature: > 3000 K

Atmosphere:
Oxidizing with possible atomic oxygen present in the plasma

Potassium salt for conductivity leading to hot corrosion at 1700 – 2200 K

Electrode materials should have high electrical conductivity, good thermal shock resistance, and durability in aggressive environments.
INTRODUCTION
Hafnium and Zirconium Diborides

- \( \text{HfB}_2-\text{ZrB}_2 \) solid solution
  - Superior electrical conductivity
  - Oxidation resistance
  - Extremely high melting point

Currently investigated for thermal protection systems of re-entry space craft vehicles, electrodes for EDM, and protective coatings for micro-electronics.

High Temperature Oxidation of ZrB$_2$:

\[
\text{ZrB}_2 + \frac{5}{2} \text{O}_2 \rightarrow \text{ZrO}_2 + \text{B}_2\text{O}_3
\]

\[
\text{B}_2\text{O}_3 (\text{l}) \rightarrow \text{B}_2\text{O}_3 (\text{g}) (> 1100 \degree \text{C})
\]

Vapor pressure of boria at 1800 $\degree$C : $1.3 \times 10^4$ Pa
High Temperature Oxidation of ZrB$_2$ with addition of SiC

Combined volatility diagram of ZrB$_2$, SiC, and graphite (H. Jin et al., Ceramic Int. 42 (2016) 6480)

Research Approach

1) Provide a thin, continuous, and impervious oxide layer to improve the oxidation resistance without significantly losing the electrical conductivity.

- TMB$_2$
- Preferentially leach out boron and expose only the metal
- Anodize the leached surface to form oxide layer

2) Incorporate RE oxides La$_2$O$_3$ and Gd$_2$O$_3$ to improve the oxidation resistance by forming cubic pyrochlore phases.

3) Forming metal rich borides with addition of higher valent elements to hinder diffusion of oxygen in the oxide layer.
PROJECT FLOW CHART

Mechanochemical Synthesis

ZrB$_2$-HfB$_2$

Addition of LaB$_6$, Gd$_2$O$_3$, SiC

Properties Characterization
- Resistivity
- Hardness
- Oxidation Resistance
- Thermal conductivity

Spark Plasma Sintering of Composites

Analytical Characterization
- XRD
- SEM
- EDS

University of Idaho
College of Engineering
PROCESSING

Hafnium and Zirconium Diborides

- Commercially available HfB$_2$ and ZrB$_2$
- Elemental mechanochemical synthesis
- No difference was found
PROCESSING

Mechanochemical synthesis

- Achieved through ball milling
  - SPEX 8000M Mixer/mill
  - Steel milling media caused contamination
- 3 mol\% Yttria stabilized zirconia grinding media and vial were used
- 1:10 powder to ball ratio
- 3 hour milling time
- 6.5 mm diameter
PROCESSING

Sintering

- Conventional Sintering
  - Compacted pellets at ~1.0 kN
  - Sintered in argon at 1700 °C

- Spark Plasma Sintering
  - 5 kN force
  - $10^{-3}$ torr vacuum
  - 1700 °C
<table>
<thead>
<tr>
<th>Sample Identifier</th>
<th>Composition</th>
<th>SPS Hold Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HfB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>180</td>
</tr>
<tr>
<td>B</td>
<td>ZrB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>600</td>
</tr>
<tr>
<td>AB</td>
<td>1:1 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>600</td>
</tr>
<tr>
<td>A4B</td>
<td>1:4 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>600</td>
</tr>
<tr>
<td>4AB</td>
<td>4:1 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>600</td>
</tr>
<tr>
<td>ABT</td>
<td>1:1 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt; + Ta (B/Me = 1.86)</td>
<td>180</td>
</tr>
<tr>
<td>ABZ</td>
<td>1:1 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt; + Zr (B/Me = 1.86)</td>
<td>180</td>
</tr>
<tr>
<td>ABH</td>
<td>1:1 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt; + Hf (B/Me = 1.86)</td>
<td>180</td>
</tr>
<tr>
<td>ABL</td>
<td>1:1 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt; + 1.8 mol % LaB&lt;sub&gt;6&lt;/sub&gt;</td>
<td>300</td>
</tr>
<tr>
<td>ABG</td>
<td>1:1 HfB&lt;sub&gt;2&lt;/sub&gt; - ZrB&lt;sub&gt;2&lt;/sub&gt; + 1.8 mol % Gd&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
</tr>
</tbody>
</table>
CHARACTERIZATION

Electrical resistivity
- Polarization Resistance
- Gamry Interface 1000
- $\rho = \frac{AR}{L}$

Hardness
- Vickers microhardness
- LECO LM1000

Density
- Archimedes principle
- Ohaus Explorer Pro
- $\rho = \frac{M_{\text{air}}}{M_{\text{air}} - M_{\text{water}}} (\rho_{\text{water}} - \rho_{\text{air}}) + \rho_{\text{air}}$
Microstructure Analysis:

Grain size by back scattered SEM

BSE FESEM micrograph of SPSed Hf0.5Zr0.5B2
**LATTICE PARAMETERS**

Vegard’s Law for SPSed Hf\(_{(1-x)}\)Zr\(_{x}\)B\(_2\)

\[ \alpha_{BxA(1-x)} = x\alpha_B + (1 - x)\alpha_A \]
# CHARACTERIZATION

<table>
<thead>
<tr>
<th>Sample Identifier</th>
<th>Density (g/cm³)</th>
<th>Relative Density (%)</th>
<th>Hardness (GPa)</th>
<th>Electrical Resistivity (µΩ-cm)</th>
<th>Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfB₂</td>
<td>9.594</td>
<td>91.4</td>
<td>20.07</td>
<td>9.2</td>
<td>3.6 ± 1.6</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>5.308</td>
<td>87.2</td>
<td>12.86</td>
<td>6.79</td>
<td>3.1 ± 1.8</td>
</tr>
<tr>
<td>Hf₀.₅Zr₀.₅B₂</td>
<td>6.346</td>
<td>76.2</td>
<td>-</td>
<td>5.4</td>
<td>3.3 ± 2.1</td>
</tr>
<tr>
<td>Hf₀.₂Zr₀.₈B₂</td>
<td>5.796</td>
<td>82.9</td>
<td>3.13</td>
<td>6.0</td>
<td>2.3 ± 1.4</td>
</tr>
<tr>
<td>Hf₀.₈Zr₀.₂B₂</td>
<td>7.377</td>
<td>76.5</td>
<td>8.32</td>
<td>9.3</td>
<td>3.7 ± 1.6</td>
</tr>
<tr>
<td>Hf₀.₅Zr₀.₅B₂ +Ta</td>
<td>8.215</td>
<td>94.6</td>
<td>-</td>
<td>17.3</td>
<td>-</td>
</tr>
<tr>
<td>Hf₀.₄Zr₀.₆B₁.₈₆</td>
<td>7.801</td>
<td>94.8</td>
<td>5.82</td>
<td>8.4</td>
<td>-</td>
</tr>
<tr>
<td>Hf₀.₆Zr₀.₄B₁.₈₆</td>
<td>8.250</td>
<td>96.2</td>
<td>12.04</td>
<td>11.6</td>
<td>-</td>
</tr>
<tr>
<td>Hf₀.₅Zr₀.₅B₂ +LaB₆</td>
<td>7.957</td>
<td>97.2</td>
<td>-</td>
<td>12.2</td>
<td>-</td>
</tr>
<tr>
<td>Hf₀.₅Zr₀.₅B₂ +Gd₂O₃</td>
<td>7.418</td>
<td>89.5</td>
<td>-</td>
<td>12.4</td>
<td>-</td>
</tr>
</tbody>
</table>
Electrochemical corrosion studies in aqueous solutions

Purpose: To rank the compositions for testing in hot corrosion environments

Resistance to room temperature aqueous corrosion can be translated to high temperature corrosion resistance in the presence of relevant species

Potentiodynamic polarization studies using three-electrode configuration

- 0.1 M H$_2$SO$_4$
- 0.1 M NaCl
- 0.1 M NaOH
- 0.1 M NaOH + 0.1 M NaCl

Reference electrode: Ag/AgCl in saturated KCl

Counter electrode: Platinum foil
ANODIZATION

- Anodized HfB$_2$ + ZrB$_2$
- Ethylene Glycol
  - 4% H$_2$O
  - 0.14 M NH$_4$F
- Potassium Hydroxide
- H$_3$PO$_4$ + NaF

- Potential: 10 – 60 V
- Time: 30 – 60 minutes
- Counter electrode: Ti foil
THERMOGRAVIMETRIC ANALYSIS

- Netzsch STA 409 PC Luxx
  - 3 °C/min ramp rate
  - 1500 °C for 2 hours
  - Argon > pO₂ = 0.1 Pa
  - Oxygen > pO₂ = 0.3 x 10⁵ Pa
  - CO/CO₂: > PO₂ = 1 x 10⁻⁸ Pa
RESULTS & DISCUSSION
SOLID SOLUTION

XRD analysis of mechanochemically synthesized HfB$_2$ + ZrB$_2$ showed a successful solid solution mixture.
ANODIZATION

EG + 0.14 M NH₄F, 30 V, 30 min.

0.1 KOH, 40 V, 30 min.

0.1 KOH, 40 V, 120 min.

Double anodized EG + 0.14 M NH₄F, 20 V, 30 min. + 0.01 M F, 30 V, 30 min.

Leached in H₃PO₄ + NaF and anodized in EG + 0.01 M F⁻, 30 min. + 0.01 M F, 40 V, 30 min.
AQUEOUS CORROSION - 0.1 M $\text{H}_2\text{SO}_4$
AQUEOUS CORROSION – 0.1 M SODIUM HYDROXIDE
AQUEOUS CORROSION – CHLORIDE IN BASIC SOLUTION

0.1 M NaOH + 0.1 M NaCl

0.1 M NaOH + NaCl

Protection potential

Potential (V vs Ag/AgCl)

Current (A/cm²)

Potential (V vs Ag/AgCl)

Current (A/cm²)
TGA Results: Argon + Oxygen (0.1 Pa), and 0.3 bar $O_2$.

TGA Results of ZrB$_2$+HfB$_2$+LaB$_6$ in Mixture of CO + CO$_2$

TGA Results: Argon + Oxygen (0.1 Pa), and 0.3 bar O₂.

---

TGA Results of ZrB$_2$+HfB$_2$+LaB$_6$ in Mixture of CO + CO$_2$

<table>
<thead>
<tr>
<th>CO:CO$_2$</th>
<th>mg$^2$/cm$^4$.h</th>
<th>kg$^2$/m$^4$.s</th>
<th>log $k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5</td>
<td>10.596</td>
<td>2.9E-07</td>
<td>-6.531</td>
</tr>
<tr>
<td>1:15</td>
<td>12.294</td>
<td>3.4E-07</td>
<td>-6.467</td>
</tr>
<tr>
<td>1:30</td>
<td>9.096</td>
<td>2.5E-07</td>
<td>-6.597</td>
</tr>
</tbody>
</table>
## PARABOLIC RATE CONSTANTS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate constant (k_p), (\text{mg}^2/\text{cm}^4\ \text{h})</th>
<th>Log (k_p), (\text{kg}^2/\text{m}^4\ \text{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABL as-sintered</td>
<td>1174.2</td>
<td>-4.49</td>
</tr>
<tr>
<td>ABL anodized</td>
<td>1053.0</td>
<td>-4.53</td>
</tr>
<tr>
<td>AB as-sintered</td>
<td>1682.4</td>
<td>-4.33</td>
</tr>
<tr>
<td>AB anodized</td>
<td>692.4</td>
<td>-4.72</td>
</tr>
</tbody>
</table>
ZrB₂+HfB₂ Oxidized in different conditions

- HfB₂
- HfO₂
- ZrB₂
- ZrO₂

- AB Anod Oxygen
- AB Anod Argon
- AB Anod CO
- AB AsRec Oxygen
- AB AsRec Argon
- AB AsRec CO
- AB Anod
- AB Base
LaB$_6$ containing ZrB$_2$+HfB$_2$ Oxidized in different conditions

![X-ray diffraction patterns of LaB$_6$ containing ZrB$_2$+HfB$_2$ oxidized in different conditions.](image)

- **ABL AsRec Oxygen**
- **ABL AsRec Argon**
- **ABL Anod CO**
- **ABL Anod Oxygen**
- **ABL Anod Argon**
- **ABL Anod CO**
- **ABL Base**
# AVERAGE COMPOSITION BY EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>ABL Anodized (mole %)</th>
<th>AB Anodized (mole %)</th>
<th>ABL As-sintered (mole %)</th>
<th>AB As -sintered (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base As-Anodized</td>
<td>Oxidized in argon</td>
<td>Oxidized in oxygen</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>46.7</td>
<td>-</td>
<td>57.0</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>1.4</td>
<td>-</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>52.0</td>
<td>-</td>
<td>42.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Base As-anodized</td>
<td>Oxidized in argon</td>
<td>Oxidized in oxygen</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>39.1</td>
<td>65.2</td>
<td>53.1</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>60.9</td>
<td>34.8</td>
<td>46.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Base Oxidized in argon</td>
<td>Oxidized in oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>48.9</td>
<td>48.9</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>02.0</td>
<td>0.6</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>49.1</td>
<td>50.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Base Oxidized in argon</td>
<td>Oxidized in oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>54.5</td>
<td>55.0</td>
<td>55.4</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>45.5</td>
<td>45.0</td>
<td>44.6</td>
<td></td>
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</tbody>
</table>
SEM OF OXIDE OF AS-SINTERED SPECIMENS

AB in oxygen

ABL in oxygen

AB in argon

ABL in argon
SEM OF OXIDE OF ANODIZED SPECIMENS

AB in oxygen

ABL in oxygen

AB in argon

ABL in argon
# Oxide Thickness Comparison

## Oxide Layer Thickness Measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anodized samples (μm)</th>
<th>As-sintered samples (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial thickness of anodic oxide</td>
<td>Oxidized in argon</td>
</tr>
<tr>
<td>ABL</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>AB</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>
CONCLUSIONS

• Elemental and commercial powders of both HfB₂ and ZrB₂ are confirmed to be essentially equivalent.
• The mechanochemical synthesis has been confirmed by XRD to produce a solid solution.
• Electrical resistivity measurements of the base materials shows that a 1:1 mixture of HfB₂ and ZrB₂ has been conductivity than either of the individual borides.
• Anodization does aid in reducing oxidation.
• LaB₆ additive appears to give the highest increase in densification of all the additives tested and increase in the oxidation resistance
Outcomes:

A masters student has graduated with M.S degree

Three presentations have been made in the international conferences

One manuscript has been accepted for publication in Metallurgical and Materials Transactions-E.

Three manuscripts are in preparation and will be submitted by June 2016 for peer review
THANK YOU!
LATTICE PARAMETERS

To calculate lattice parameter, $a$, take XRD reflections of $hk0$ type.

$$a = \frac{\lambda}{\sqrt{3} \sin \theta} \sqrt{h^2 + hk + k^2} \quad \text{Eq. 1}$$

To calculate lattice parameter, $c$, take XRD reflections of $00l$ type.

$$c = \frac{\lambda}{2 \sin \theta} l \quad \text{Eq. 2}$$