Combustion Synthesis of Boride-Based Electrode Materials for MHD Direct Power Extraction

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Project Goals and Objectives

• Goal: To develop an advanced, low-cost manufacturing technique for fabrication of boride-based ultrahigh-temperature ceramics (UHTCs) that possess all the required properties to function as sustainable electrodes in MHD direct power extraction applications.

• Specifically, the project investigates use of mechanical activation-assisted self-propagating high-temperature synthesis (MASHS) followed by pressureless sintering for the fabrication of UHTCs based on ZrB$_2$ and HfB$_2$ from inexpensive raw materials ZrO$_2$, HfO$_2$, and B$_2$O$_3$, with Mg as a reactant.
  – Determine optimal conditions of mechanical activation, SHS, and pressureless sintering for fabrication of doped ZrB$_2$ and HfB$_2$ for DPE applications.
  – Determine thermophysical, electrical, mechanical, and oxidation properties of borides obtained by MASHS followed by pressureless sintering.
Outline

• Background
• Methods
• Results
• Summary
• Future Work
MHD Generator

- Magnetohydrodynamic (MHD) generator is thermodynamically advantageous over gas turbines.
  - No moving parts → the maximum working temperature is higher.

- Use of an open-cycle MHD generator as the topping cycle in combination with Rankine cycle has the potential to increase the efficiency of fossil-fuel burning power plants.
Requirements to MHD Electrodes

- To withstand temperatures up to 800 K in the case of a slagging generator and from 1800 K to 2400 K in the case of a clean generator.
- To possess sufficient electrical conductivity and provide smooth transfer of electric current to and from the plasma.
- To have an adequate thermal conductivity and be thermally stable at operating conditions.
- To withstand a thermal shock.
- To be resistive to erosion from high-velocity gases and to electrochemical attack resulting from interactions with slag and/or seed (e.g., potassium) in an electromagnetic field.

The development of such materials and of low-cost techniques for their fabrication is a great challenge.
Borides of Zirconium and Hafnium

- Borides of zirconium and hafnium (ZrB$_2$ and HfB$_2$) belong to the class of Ultra-High-Temperature Ceramics (UHTCs)
  - Extremely high melting temperatures (about 3250 °C)
  - High hardness
  - High electrical and thermal conductivities
  - Chemical stability
  - Good thermal shock and oxidation resistance
  - Resistance to molten metals and slags
  - Resistance to plasma sparks and arcs
  - With dopants (e.g., SiC), high resistance to ablation in oxidizing environments
Fabrication of Zr\textsubscript{2}B\textsubscript{2} and HfB\textsubscript{2}

- The available methods for fabrication of doped ZrB\textsubscript{2} and HfB\textsubscript{2} are complex, energy-consuming, and expensive.

- The project will investigate the feasibility of fabricating doped ZrB\textsubscript{2} and HfB\textsubscript{2}, using an advanced, low-cost manufacturing technique based on combustion synthesis and pressureless sintering.
Self-propagating High-temperature Synthesis (SHS)

- **Advantages of SHS:**
  - Short processing time
  - Low energy consumption
  - Simple equipment
  - Tailored microstructure and properties
  - High purity of the products

Schematic of SHS process

Image: www.ism.ac.ru/handbook/shsf.htm
SHS of ZrB\textsubscript{2} and HfB\textsubscript{2}: Pathways

• SHS from elements

\[ \text{Zr} + \text{B} \rightarrow \text{ZrB}_2; \quad \Delta H^{\circ}_{\text{rxn}} = -323 \text{ kJ} \]
\[ \text{Hf} + \text{B} \rightarrow \text{HfB}_2; \quad \Delta H^{\circ}_{\text{rxn}} = -328 \text{ kJ} \]

– Zr, Hf, and B are very expensive!

• Magnesiothermic SHS from oxides

\[ \text{ZrO}_2 + \text{B}_2\text{O}_3 + 5\text{Mg} \rightarrow \text{ZrB}_2 + 5\text{MgO}; \quad \Delta H^{\circ}_{\text{rxn}} = -959 \text{ kJ} \]
\[ \text{ZrO}_2 + 2\text{H}_3\text{BO}_3 + 5\text{Mg} \rightarrow \text{ZrB}_2 + 5\text{MgO} + 3\text{H}_2\text{O}; \quad \Delta H^{\circ}_{\text{rxn}} = -769 \text{ kJ} \]

– MgO is separated by mild acid (HCl) leaching.
– ZrO\textsubscript{2}, HfO\textsubscript{2}, B\textsubscript{2}O\textsubscript{3}, and H\textsubscript{3}BO\textsubscript{3} are cheap.
– Mg is much less expensive than Zr and Hf.
Mechanical Activation

• Ignition of $\text{ZrO}_2$–$\text{B}_2\text{O}_3$–$\text{Mg}$ and $\text{HfO}_2$–$\text{B}_2\text{O}_3$–$\text{Mg}$ mixtures is more difficult than that of $\text{Zr/B}$ and $\text{Hf/B}$ mixtures because of lower exothermicities.

• To improve ignition, mechanical activation (short-time, high-energy ball milling) of mixtures before SHS is used.

• Inert powders such as $\text{NaCl}$ are used sometimes to facilitate ball milling.
  – Inert diluents also decrease the combustion temperature, the reaction propagation velocity, and the product particle size, thus leading to a finer product with improved sinterability.
Sintering of SHS-produced ZrB$_2$ and HfB$_2$

• SHS products can be densified by:
  – Hot pressing (HP)
  – Spark plasma sintering (SPS)
  – Pressureless sintering (PS)

• Because of high heating rates, SHS products have high defect concentrations in the lattice, which enhances the sinterability.

• Pressureless sintering (PS) offers several advantages over HP and SPS.
  – Inexpensive equipment (furnaces) that can be scaled up readily
  – Near-net-shape processing of ceramic parts with complex geometries
Pressureless Sintering

• Dopants
  – Carbon containing additives (C, B₄C, WC, and VC)
  – Transition metals (Fe, Cr, and Ni)
  – Refractory metal silicides (MoSi₂, TiSi₂, and HfSi₂)

• Nanoscale powders
  – Nanoscale powders produced by SHS are especially promising because they also have high defect concentrations.
  – To decrease the particle size, NaCl is used as an inert diluent.
  – NaCl is removed from the products by dissolution in water.
  – Nanoscale ZrB₂ powder produced with adding NaCl showed excellent sinterability
Activated ZrO$_2$/B$_2$O$_3$/Mg and HfO$_2$/B$_2$O$_3$/Mg mixtures are prepared with NaCl or MgO as inert diluents.

ZrO$_2$/B$_2$O$_3$ and HfO$_2$/B$_2$O$_3$ mole ratios are 1:1.

Mg/B$_2$O$_3$ / ZrO$_2$ mole ratio is varied to find the optimal Mg concentration.

The amount of inert diluent (NaCl or MgO) is also varied.
Combustion Synthesis

• Combustion characteristics (the maximum temperature and the front propagation velocity) are determined.
  – Ar environment
  – The pellet is ignited at the top.
  – High-speed video recording
  – Thermocouples
Acid Leaching

- To remove MgO and NaCl, the SHS products are leached in diluted hydrochloric acid (10% HCl).
- The dissolution process is carried out in a Erlenmeyer flask with a mechanical stirrer at atmospheric pressure and room temperature for 2 hours.
- ZrB$_2$ is separated using a paper filter.
- The products are washed in water and dried for 24 hours.
Sintering

Mixing with dopants

3-D inversion kinematics mixer (Inversina 2L)

Pressing

Sintering

2000ºC Temperature-Controlled 30KW Induction Heating System (MTI Corp., EQ-SP-50KTC)
Thermodynamic Analysis

- Complete conversion of oxides to ZrB₂ (or HfB₂) is achieved at 40% excess Mg.
- High concentration of Mg vapor and hence undesired pressure increase.
- Temperatures lower than 2370 K are needed to achieve full conversion.
Thermodynamic Analysis with Inert Diluents

Complete conversion of oxides to ZrB$_2$ (or HfB$_2$) is achieved at 44 wt% NaCl or 25 wt% MgO.
- No gaseous products
Effect of Inert Diluents on Milling

- High-energy ball milling of Mg/ZrO$_2$/B$_2$O$_3$ mixtures is accompanied by a significant loss of materials due to sticking to the grinding media.

- Adding MgO does not prevent loss of material.

- 5-10 wt% NaCl effectively decreases the mixture loss.
Combustion of ZrO$_2$/B$_2$O$_3$/Mg Mixture

- Pellet dimensions
  - Diameter: 13 mm
  - Height: 18 mm

- Measured max. temperature: 1725 °C
- Adiabatic flame temperature: 2097 °C
There are no reactions during milling.

Mg reduces most of ZrO₂.

MgO stabilizes the cubic phase of ZrO₂.

The undesired compound Mg₃(BO₃)₂ is present in the combustion products and after leaching.

Leaching removes NaCl and MgO.
Effect of NaCl on Combustion

\[ \text{ZrO}_2/\text{B}_2\text{O}_3/5\text{Mg} + \text{NaCl} \]

0 wt% 10 wt% 40 wt% 50 wt%

Measured temperatures and adiabatic flame temperatures vs. NaCl concentration

Wave front velocity vs. NaCl concentration
Effect of NaCl on Combustion Products

- ZrO$_2$ is partially stabilized by MgO in mixtures with NaCl.
- The amount of cubic ZrO$_2$ that is stabilized by MgO decreases at lower temperatures.
- Leaching removes Mg$_3$(BO$_3$)$_2$
Effect of NaCl on Microstructure

- NaCl decreases the particle size of ZrB₂.
Effect of Milling and NaCl on the Reaction Mechanisms

- The mass loss in the unmilled and milled mixtures is caused by Mg and NaCl, respectively.
- Milling decreases the ignition temperature of the reaction and prevents Mg loss.
- Melting of B₂O₃ and melting of Mg play important roles.
The reaction between $\text{B}_2\text{O}_3$ and $\text{Mg}$ is initiated by melting of $\text{B}_2\text{O}_3$ and is intensified by melting of $\text{Mg}$.

The reaction between $\text{ZrO}_2$ and $\text{Mg}$ needs temperatures greater than 750 °C.

The content of NaCl decreases due to vaporization after melting (801 °C).
Effect of MgO on Combustion Products

- Adding MgO to the mixture partially stabilizes ZrO$_2$.
- Unfortunately, MgO decreases the conversion of ZrO$_2$ to ZrB$_2$.
Effect of Excess Mg on Combustion Products

- 20% excess Mg was added to the mixture to compensate for Mg loss during combustion.
- Excess Mg increases the conversion of oxides to borides.
Microstructure of ZrB₂

- **Nanoscale Particles**
  - Lower sintering temperature
  - Finer grain size

- **Polycrystalline particles**
  - Sinter better than single-crystal particles

SEM Image of ZrB₂ obtained from a mixture with 30 wt% NaCl and 20% excess Mg
Summary

😊 Adding NaCl to ZrO₂/B₂O₃/Mg effectively decreases the loss of materials during milling.

😊 Mechanical activation has enabled magnesiothermic SHS of ZrB₂.
  – The products also contain undesired phases ZrO₂ and Mg₃(BO₃)₂.

😊 Excess Mg increases the conversion of oxides to borides.

😢 MgO has an adverse effect on conversion of ZrO₂ to ZrB₂.

😊 Increasing NaCl content decreases the particle size of ZrB₂.
  – The obtained particles are polycrystalline and nanoscale, which may enhance sintering.
Future Work

- Optimization of the mixtures for fabricating HfB$_2$
- Further investigation of the product microstructure
- Use of EDS and quantitative XRD methods for measurements of oxygen content in the powders
- Sintering of the obtained powder, with and without dopants
- Measurements of electrical, mechanical, oxidation and thermophysical properties
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