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

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Project Goal 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 mechanically activated 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 and NaCl or MgO as an inert diluent.
  – 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.
BACKGROUND
MHD Generator

- Magnetohydrodynamic (MHD) generator is thermodynamically advantageous over gas turbines.
  - No moving parts → Higher temperature

- Use of an 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 (ZrB₂ and HfB₂) belong to the class of ultra-high-temperature ceramics (UHTCs)
  – Extremely high melting point (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 ZrB$_2$ and HfB$_2$

• The available methods for fabrication of doped ZrB$_2$ and HfB$_2$ are complex, energy-consuming, and expensive.

• The project investigates the feasibility of fabricating doped ZrB$_2$ and HfB$_2$, using an advanced, low-cost manufacturing technique based on combustion synthesis and pressureless sintering.
Self-propagating High-temperature Synthesis (SHS)

Schematic of SHS process

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

SHS reactor for industrial production of powders.
SHS of ZrB$_2$ and HfB$_2$: Pathways

- **SHS from elements**

  $\text{Zr} + \text{B} \rightarrow \text{ZrB}_2$; $\Delta H^\circ_{\text{rxn}} = -323 \text{ kJ}$

  $\text{Hf} + \text{B} \rightarrow \text{HfB}_2$; $\Delta H^\circ_{\text{rxn}} = -328 \text{ kJ}$

  - Zr, Hf, and B are very expensive.

- **Magnesiothermic SHS from oxides**

  $\text{ZrO}_2 + \text{B}_2\text{O}_3 + 5\text{Mg} \rightarrow \text{ZrB}_2 + 5\text{MgO}$; $\Delta H^\circ_{\text{rxn}} = -989 \text{ kJ}$

  $\text{ZrO}_2 + 2\text{H}_3\text{BO}_3 + 5\text{Mg} \rightarrow \text{ZrB}_2 + 5\text{MgO} + 3\text{H}_2\text{O}$; $\Delta H^\circ_{\text{rxn}} = -769 \text{ kJ}$

  - MgO is separated by mild acid (HCl) leaching.
  - Materials are relatively inexpensive.
Mechanical Activation

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

• Ignition can be improved by mechanical activation (short-time, high-energy ball milling) of mixtures.

• Inert diluents (e.g., MgO and NaCl) could be used to improve milling and SHS, leading to better properties of the products.
Sintering of SHS-produced ZrB$_2$ and HfB$_2$

• SHS products can be densified by:
  – Hot pressing
  – Spark plasma sintering
  – Pressureless sintering

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

• Advantages of pressureless sintering
  – Inexpensive equipment (furnaces) that can be scaled up readily
  – Near-net-shape processing of ceramic parts with complex geometries
EXPERIMENTAL PROCEDURES
Mechanical Activation

Mixing

3-D inversion kinematics mixer (Inversina 2L)

Milling

Planetary ball mill (Fritsch Pulverisette 7)

Pressing

• Activated Mixtures of:
  – ZrO$_2$/B$_2$O$_3$/Mg/MgO
  – ZrO$_2$/B$_2$O$_3$/Mg/NaCl
  – ZrO$_2$/HfO$_2$/B$_2$O$_3$/Mg

• ZrO$_2$/B$_2$O$_3$ and HfO$_2$/B$_2$O$_3$ mole ratios are 1:1.
• Varied amounts of MgO, NaCl, and excess Mg
Combustion Synthesis

- Ar environment
- The pellet is ignited at the top.
- Video recording
- Thermocouple measurements
  - Maximum temperature
  - Front propagation velocity

Reaction chamber
Leaching

• To remove MgO and NaCl, the SHS products are leached in 200 mL of diluted (1M) HCl acid.
• Stirring at room temperature for 2 hours
• Solid products are separated using a paper filter, washed in water, and dried for 24 hours.
RESULTS
Thermodynamic Analysis

- Excess Mg decreases temperature and improves conversion.
- In experiment, excess Mg compensates for the loss of Mg (boiling point: 1093°C at 1 atm).
- The decrease in temperature and the increase in conversion can also be achieved with inert diluents.
Products after Milling

- No reaction during milling

XRD Pattern of stoichiometric ZrO$_2$/B$_2$O$_3$/Mg mixture (a) before and (b) after milling
Effect of Inert Diluents on Milling

• During high-energy ball milling of Mg/ZrO$_2$/B$_2$O$_3$ mixtures, part of materials sticks to the grinding media.

• Adding MgO does not prevent sticking.

• 5-10 wt% NaCl effectively decreases the amount of stuck materials.
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

Thermocouple recording
Products after Combustion and after Leaching

- Mg reduces most of ZrO$_2$.
- MgO stabilizes cubic ZrO$_2$.
- Undesired Mg$_3$(BO$_3$)$_2$ phase is present.

- Leaching removes NaCl and MgO.
Effect of MgO on Combustion Products

- MgO decreases conversion.

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\text{Peak Intensity Ratio} = \frac{I_{m-Zr_2(\bar{1}11)}}{I_{ZrB_2(101)}}
\]

\[
\text{Peak Intensity Ratio} = \frac{I_{c-ZrO_2(111)}}{I_{ZrB_2(101)}}
\]
Effect of NaCl on Combustion

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

10 wt% NaCl  40 wt% NaCl  47 wt% NaCl
Effect of NaCl on Products

- Traces of Mg$_3$(BO$_3$)$_2$ phase remained.

- The amount of cubic ZrO$_2$ that is stabilized by MgO decreases at lower temperatures.
Effect of NaCl on Products

- At 10 – 40 wt% NaCl: 5 wt% residual oxygen

- NaCl significantly decreases the particle size of ZrB₂.
Effect of Excess Mg on Products

- Increasing excess Mg to 20% significantly increases the conversion.

10% NaCl, after combustion
Effect of NaCl in Mixtures with 20% Excess Mg

After combustion

After leaching
Effect of NaCl in Mixtures with 20% Excess Mg

- At 10 – 30 wt% NaCl: 3 – 4 wt% residual oxygen
- Nanoscale polycrystalline particles obtained.
  - Nanoscale: Lower sintering temperature
  - Polycrystalline: Sinter better than single-crystal particles

ZrB$_2$ obtained from a mixture with 30 wt% NaCl and 20% excess Mg

After leaching
MASHS of HfB$_2$

- Stoichiometric HfO$_2$/B$_2$O$_3$/Mg mixture (1:1:5 mole ratio)
- Dominant phase: HfB$_2$
- Significant amount of cubic HfO$_2$
- MgO can be removed by acid leaching.

XRD pattern of combustion products
MASHS of ZrB$_2$-HfB$_2$

- ZrO$_2$/HfO$_2$/B$_2$O$_3$/Mg mixture (1:1:2:10 mole ratio)

- The composition of the boride phase was determined based on the angle between the most intensive peak of boride and the neighboring peak of MgO.

- The diboride phase is **solid solution** of ZrO$_2$ and HfO$_2$.
  - May be approximated by Zr$_{0.5}$Hf$_{0.5}$B$_2$.
  - May possess promising properties.
CONCLUSIONS AND FUTURE WORK
Conclusions

• Mechanical activation has enabled magnesiothermic SHS of ZrB$_2$, HfB$_2$, and ZrB$_2$–HfB$_2$ solid solution.

• MgO is not a good diluent.
  – Cannot decrease sticking of mixture during milling.
  – Increases the amount of ZrO$_2$ (both monoclinic and cubic) in the products.

• NaCl is a promising additive.
  – Decreases the amount of mixture stuck during mechanical activation.
  – Decreases the amount of cubic ZrO$_2$ in the products.
  – Decreases the particle size of ZrB$_2$.

• Mixture with 20% excess Mg and 10 – 30 wt% NaCl
  – Effective mechanical activation
  – Steady self-sustained combustion
  – Relatively small amount of zirconia in the combustion products
  – Nanoscale polycrystalline product particles
Future Work

• Sintering of the obtained powders, with and without dopants

• Measurements of electrical, thermophysical, oxidation resistance, and mechanical properties
Pressureless Sintering

• **Nanoscale polycrystalline powders**
  – The obtained nanoscale polycrystalline powders are promising for sintering.

• **Dopants**
  – Improve sinterability
  – May reduce remaining oxide phases
  – May improve properties
  – Previously tested: C, B_4C, WC, VC, Fe, Cr, Ni, MoSi_2, TiSi_2, and HfSi_2

ZrB_2 obtained from a mixture with 30 wt% NaCl and 20% excess Mg
Sintering Procedure

1. Mixing with dopants
   - 3-D inversion kinematics mixer (Inversina 2L)

2. Pressing

3. Sintering
   - 2000°C Temperature-Controlled 30KW Induction Heating System (MTI Corp., EQ-SP-50KTC)
The electrical conductivity will be measured with an electric property analyzer (Netzsch SBA 458 Nemesis).

- 25°C – 1100°C
Thermophysical Properties

• **Specific heats** will be measured using a differential scanning calorimeter (Netzsch DSC 404 F1 Pegasus)
  - 25°C – 1550°C

• **Thermal diffusivities** will be measured by laser flash analysis (Netzsch LFA-457 MicroFlash)
  - 25°C – 1100°C

• **Thermal conductivities** will be calculated based on thermal diffusivity, specific heat, and density
Oxidation Resistance

2000°C Temperature-Controlled 30KW Induction Heating System (MTI Corp., EQ-SP-50KTC)

Differential scanning calorimeter (Netzsch DSC 404 F1 Pegasus)

Thermogravimetric analyzer (Netzsch TGA 209 F1 Iris)
Mechanical Properties

• The **mechanical strength** and **hardness** will be determined using load-controlled nano-indentation tests with a nanomechanical test instrument (Hysitron TI 750H Ubi).
Students Involved

• Graduate students
  – Sergio Cordova (M.S. May 2017, Outstanding Thesis Award from UTEP’s College of Engineering, currently PhD student and NASA Space Technology Research Fellow)

  – Gabriel Llausas (M.S. studies in progress, expected graduation: 2019)

• Undergraduate students
  – Leonardo Gutierrez Sierra
Publications and Presentations

• **Peer-reviewed Journal Articles**

• **Conferences**
  – Cordova, S., and Shafirovich, E., Materials Science and Technology 2017 (MS&T17), Pittsburgh, PA, Oct. 8-12, 2017.
  – Cordova, S., and Shafirovich, E., Southwest Emerging Technology Symposium, El Paso, TX, Apr. 9, 2016.
Thank you!