2018 Project Review Meeting for Crosscutting Research, April 10-12, Pittsburgh, PA

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

Principal Investigator :	Evgeny Shafirovich
Organization:	The University of Texas at El Paso
DOE Award Number:	DE-FE-0026333
Period of Performance:	10/1/2015 – 8/31/2019
Program Manager:	Jason C. Hissam

Outline

- Project Goal and Objectives
- Background
- Experimental Procedures
- Results
- Conclusions and Future Work
- Students, Publications, and Presentations

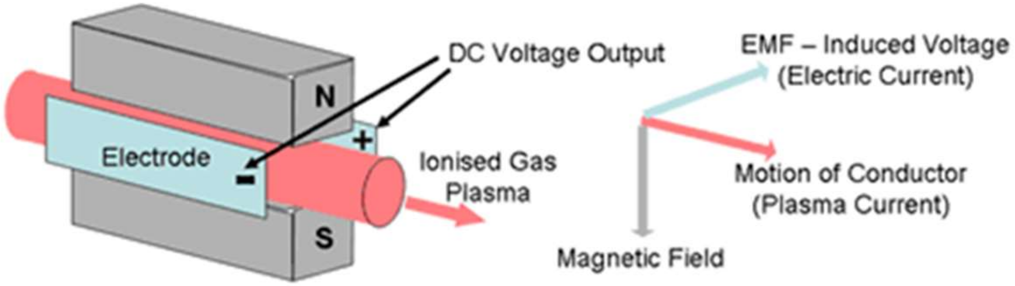
Project Goal and Objectives

- 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_2O_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 Power Generation (Principle)

- 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

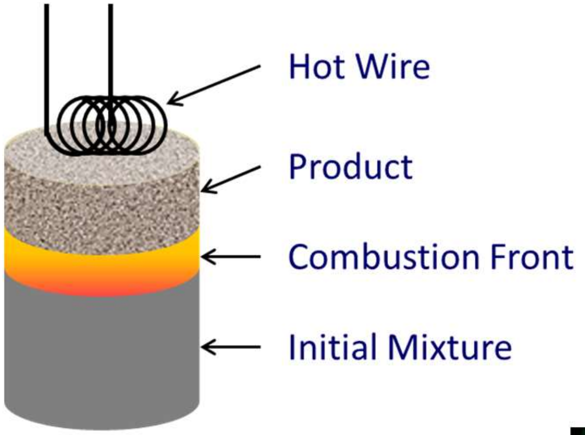
- **Borides of zirconium and hafnium (ZrB_2 and HfB_2) belong to the class of ultra-high-temperature ceramics (UHTCs)**
  - Extremely high melting point (about 3250 °C)
  - High hardness
  - High electrical and thermal conductivities
  - Chemical stability
  - Good thermal shock and oxidation resistance
  - 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.

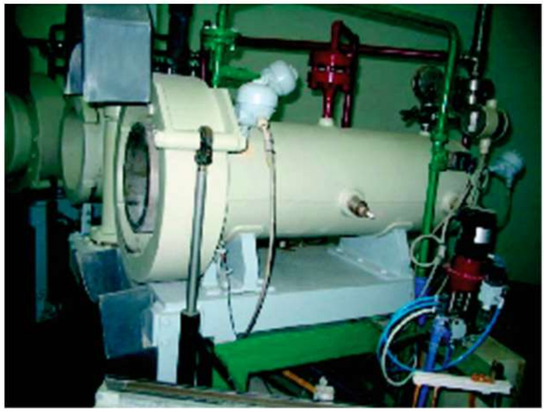
- The project investigates the feasibility of fabricating doped ZrB_2 and HfB_2, using an advanced, low-cost manufacturing technique based on **combustion synthesis** and **pressureless sintering**.

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.
Levashov et al., Int. Mater. Rev. 62 (2017) 203.

SHS of ZrB_2 and HfB_2: Pathways

- **SHS from elements**

  $Zr + B \rightarrow ZrB_2$; $\Delta H^o_{rxn} = -323$ kJ

  $Hf + B \rightarrow HfB_2$; $\Delta H^o_{rxn} = -328$ kJ

  - Zr, Hf, and B are very expensive.

- **Magnesiothermic SHS from oxides**

  $ZrO_2 + B_2O_3 + 5Mg \rightarrow ZrB_2 + 5MgO$; $\Delta H^o_{rxn} = -989$ kJ

  $ZrO_2 + 2H_3BO_3 + 5Mg \rightarrow ZrB_2 + 5MgO + 3H_2O$; $\Delta H^o_{rxn} = -769$ kJ

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

Mechanical Activation

- Ignition of $ZrO_2/B_2O_3/Mg$ and $HfO_2/B_2O_3/Mg$ 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.

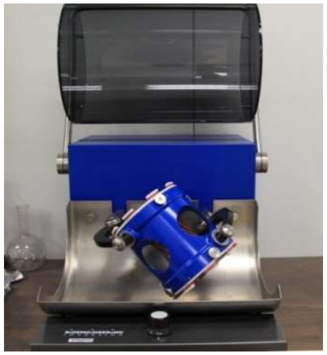
Sintering of SHS-produced ZrB_2 and HfB_2

- 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)

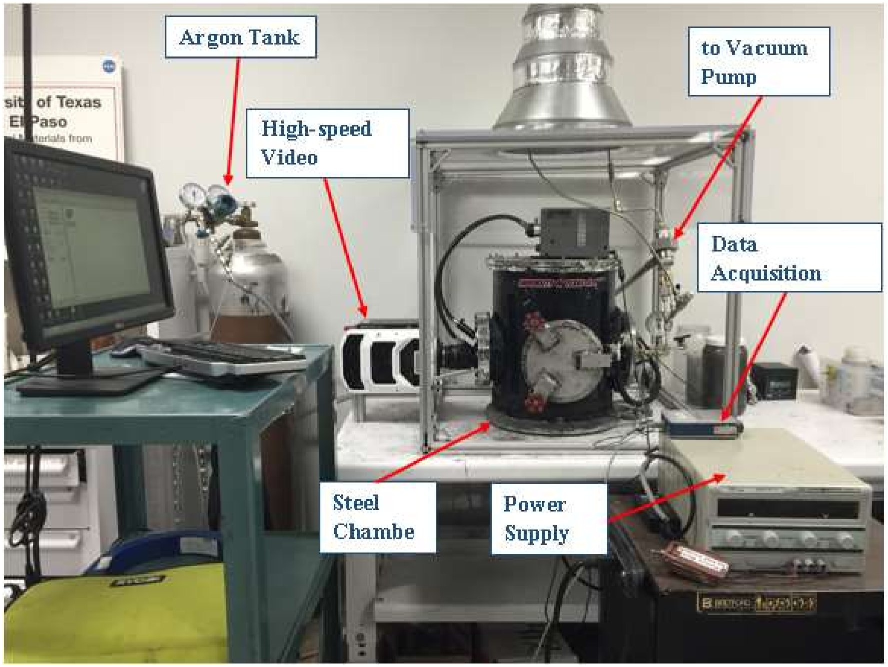
Milling

Planetary ball mill (Fritsch Pulverisette 7)

Pressing

- Activated Mixtures of:
  - $ZrO_2/B_2O_3/Mg/MgO$
  - $ZrO_2/B_2O_3/Mg/NaCl$
  - $ZrO_2/HfO_2/B_2O_3/Mg$
- ZrO_2/B_2O_3 and HfO_2/B_2O_3 mole ratios are 1:1.
- Varied amounts of MgO, NaCl, and excess Mg

Combustion Synthesis



Reaction chamber

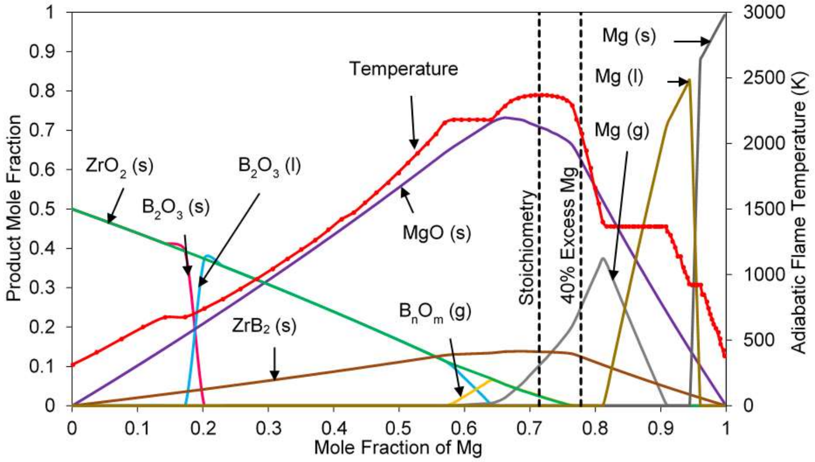
- Ar environment
- The pellet is ignited at the top.
- Video recording
- Thermocouple measurements
  - Maximum temperature
  - Front propagation velocity

Leaching

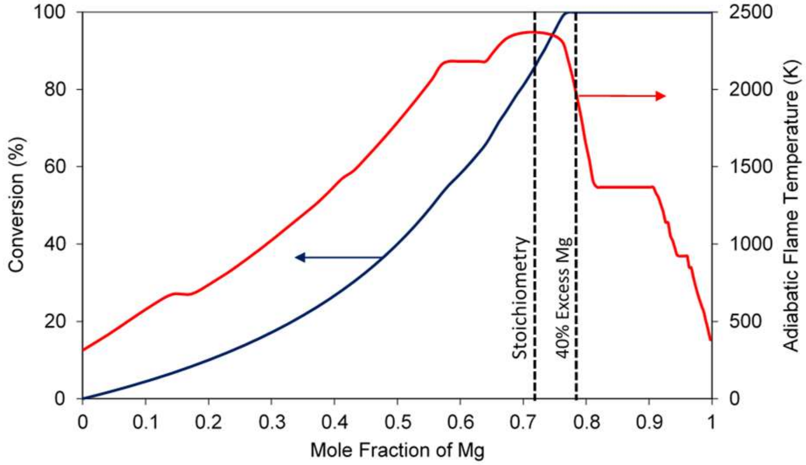
- To remove MgO and NaCl, the SHS products are leached in 200 mL of diluted (1M) HCl acid.
- Stirring at room temperature for 2 hours
- Solid products are separated using a paper filter, washed in water, and dried for 24 hours.

RESULTS

Thermodynamic Analysis



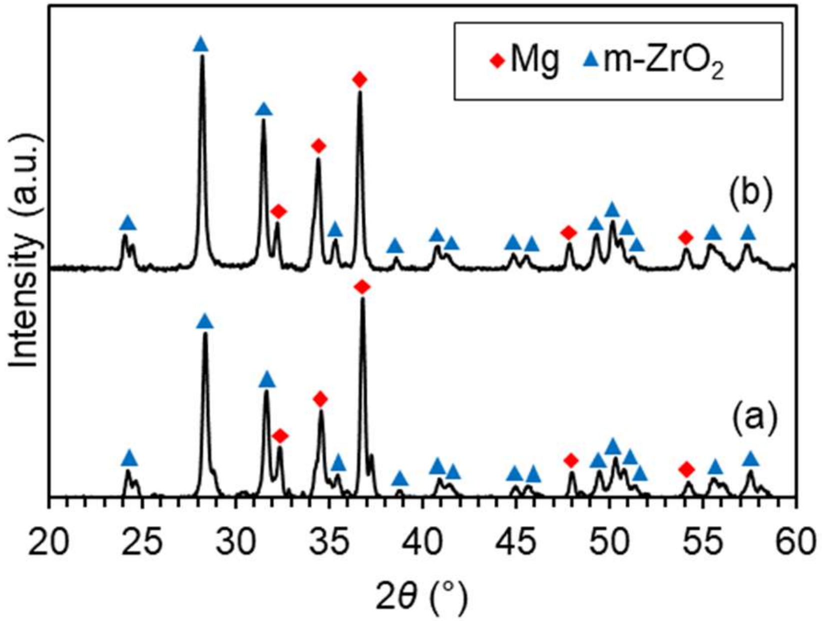
Adiabatic flame temperature and product composition in $ZrO_2/B_2O_3/Mg$ System



Adiabatic flame temperature and conversion of ZrO_2 to ZrB_2 in $ZrO_2/B_2O_3/Mg$ system

- 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.

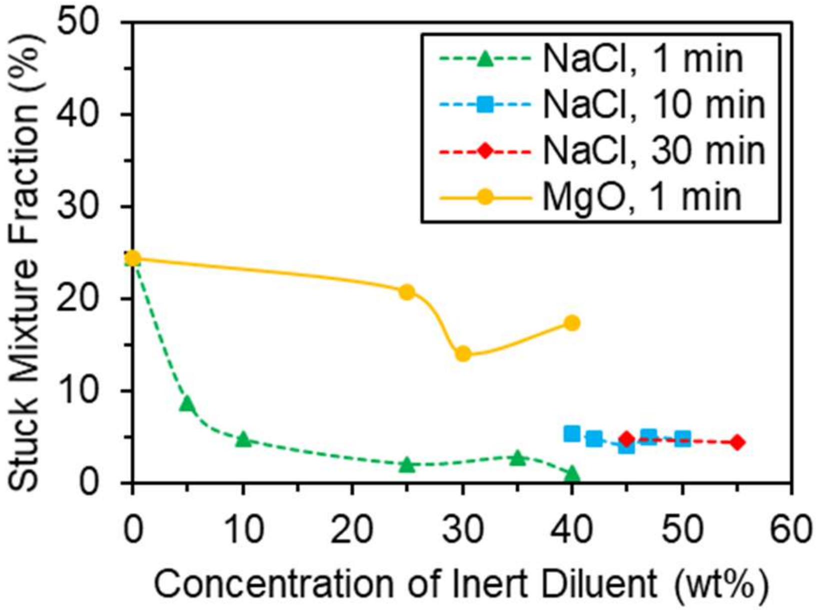
Products after Milling



XRD Pattern of stoichiometric ZrO_2/B_2O_3/Mg mixture (a) before and (b) after milling

- No reaction during milling

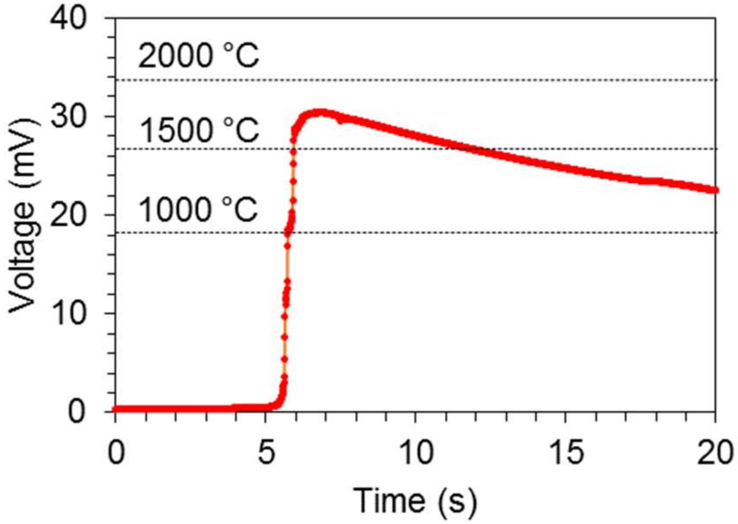
Effect of Inert Diluents on Milling



- During high-energy ball milling of $Mg/ZrO_2/B_2O_3$ 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 $ZrO_2/B_2O_3/Mg$ Mixture

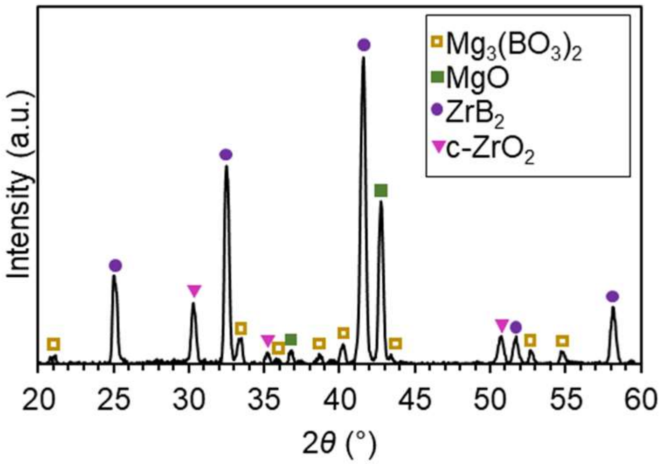
- Pellet dimensions
  - Diameter: 13 mm
  - Height: 18 mm



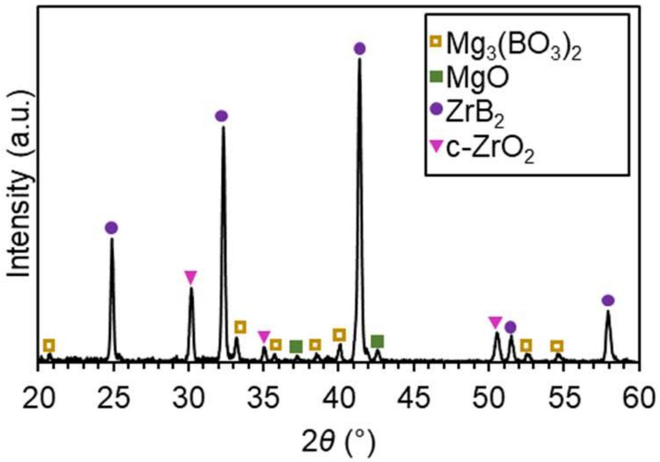
Thermocouple recording

- Measured max. temperature: 1725 °C
- Adiabatic flame temperature: 2097 °C

Products after Combustion and after Leaching



After combustion

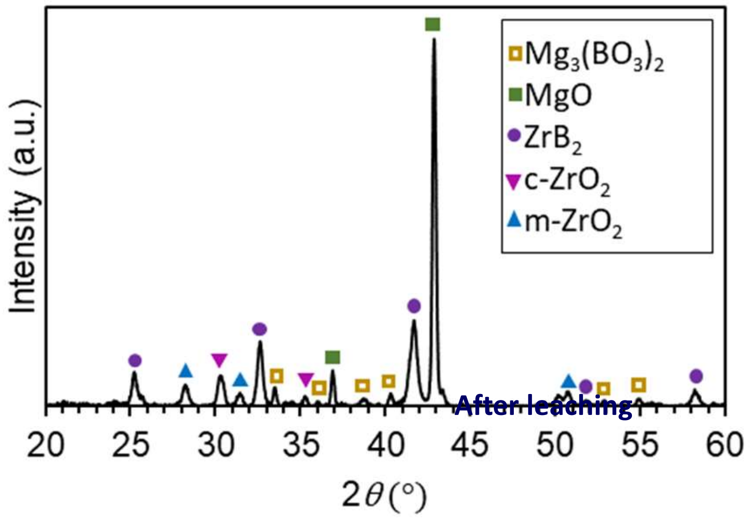


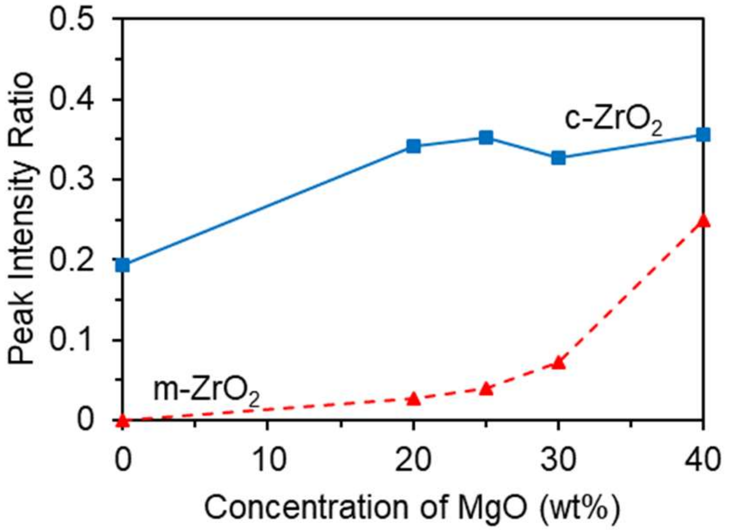
After leaching

- 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





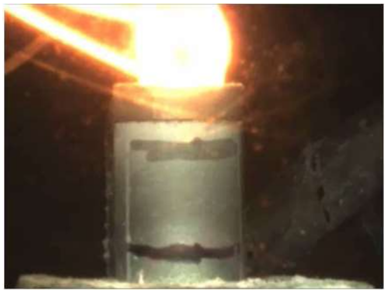
Peak Intensity Ratio=$\frac{I_{m-Zr\ \ 2(\bar{1}11}}{I_{ZrB_2(101)}}$

Peak Intensity Ratio=$\frac{I_{c-ZrO_2(111)}}{I_{ZrB_2(101)}}$

- MgO decreases conversion.

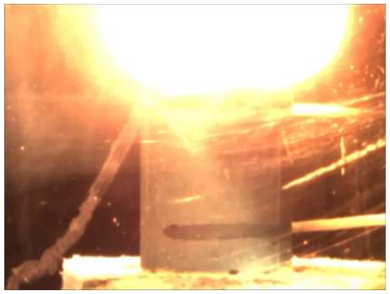
Effect of NaCl on Combustion

$ZrO_2/B_2O_3/5Mg + NaCl$

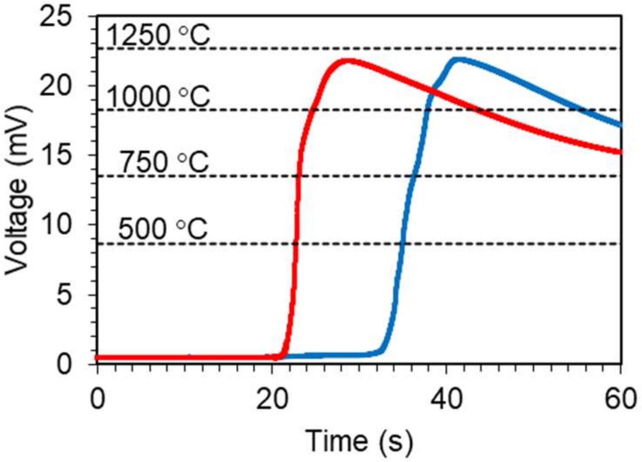


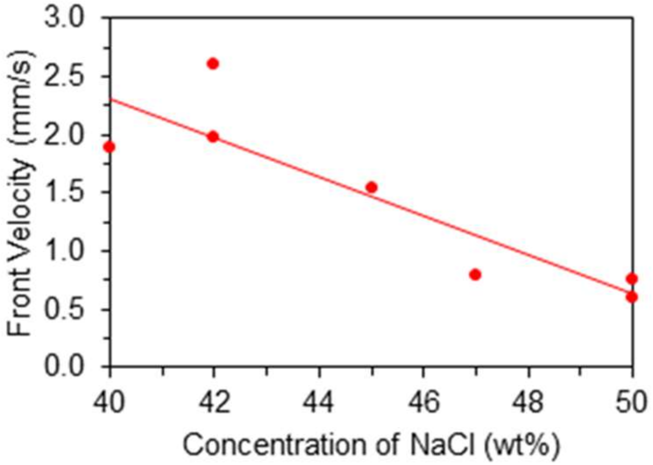
10 wt% NaCl

40 wt% NaCl

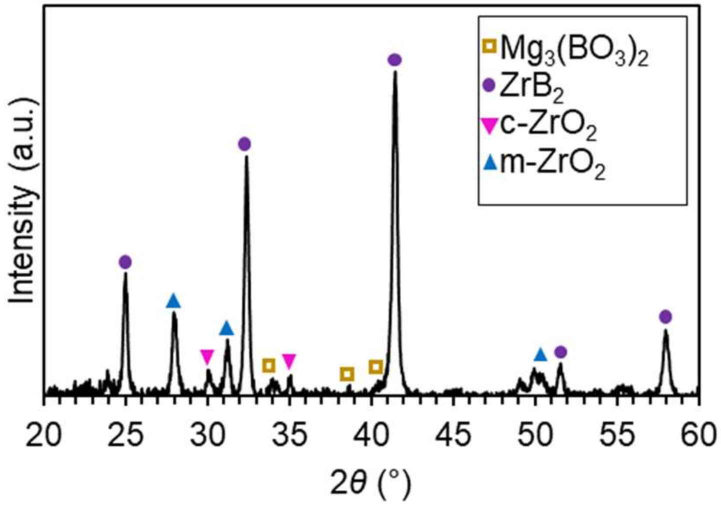


47 wt% NaCl

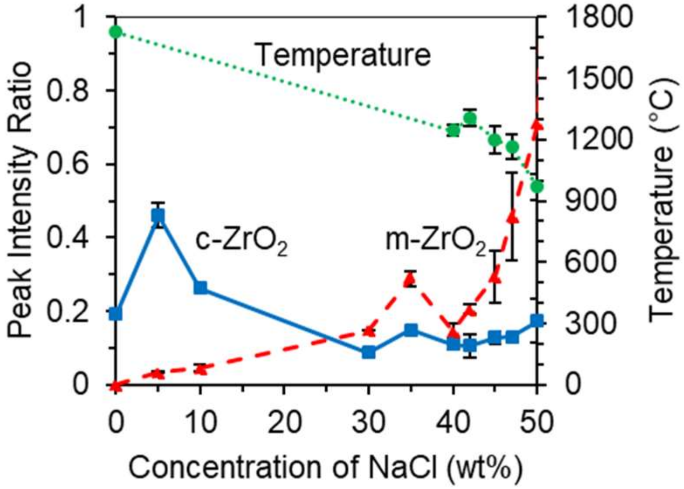




Effect of NaCl on Products



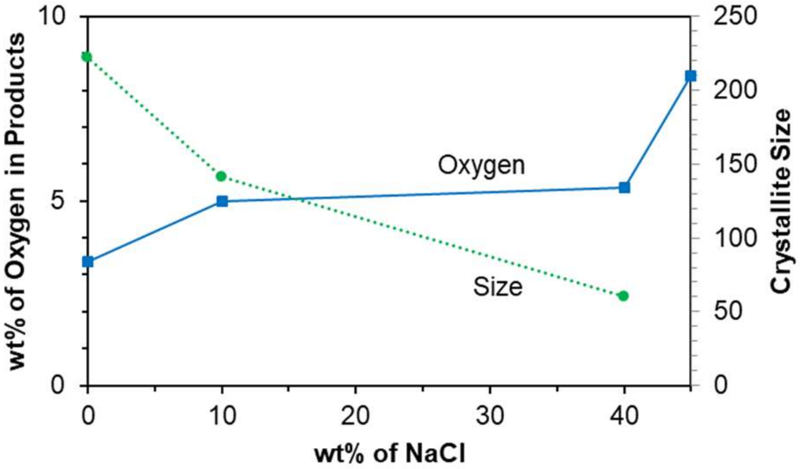
After leaching

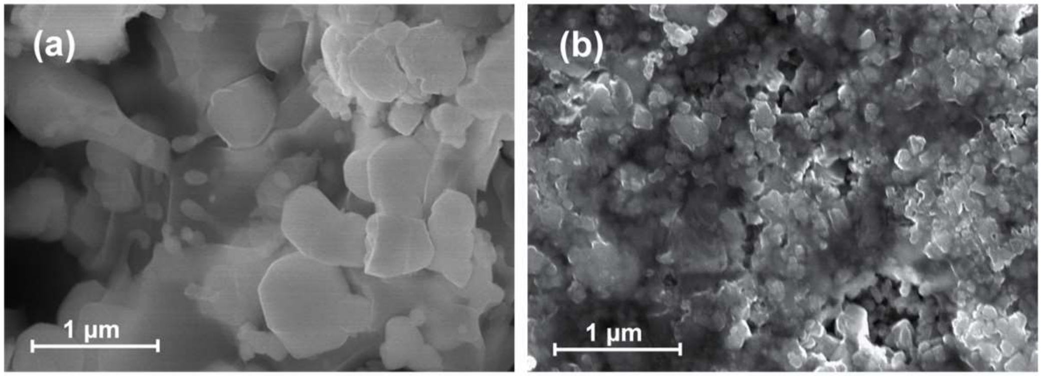


Peak intensity ratios *vs.* NaCl concentration

- 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



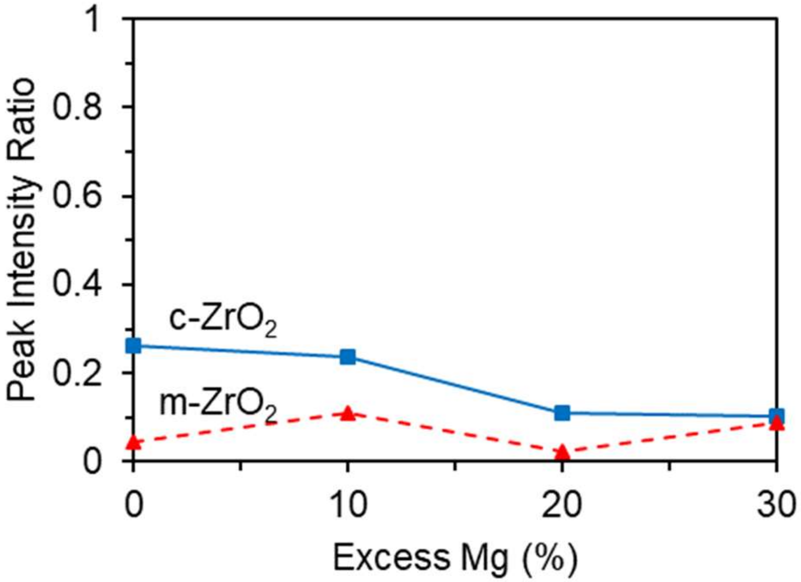


No NaCl

30 wt% NaCl

- At 10 – 40 wt% NaCl: 5 wt% residual oxygen
- NaCl significantly decreases the particle size of ZrB_2.

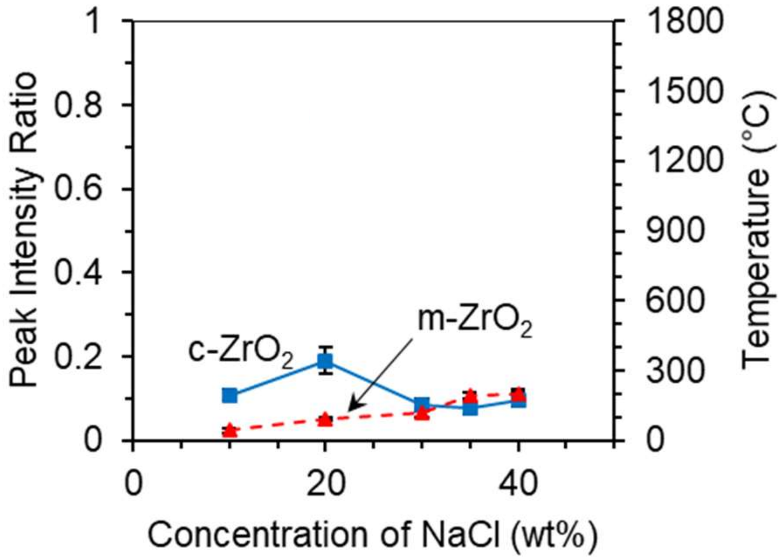
Effect of Excess Mg on Products



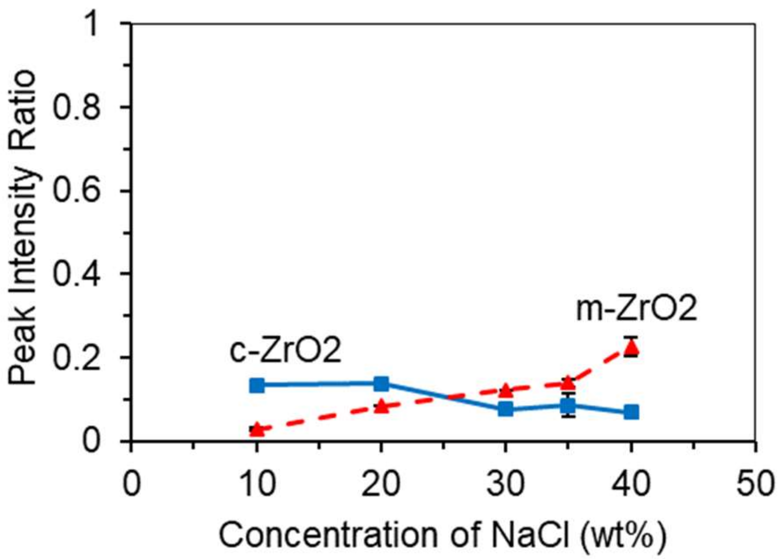
10% NaCl, after combustion

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

Effect of NaCl in Mixtures with 20% Excess Mg

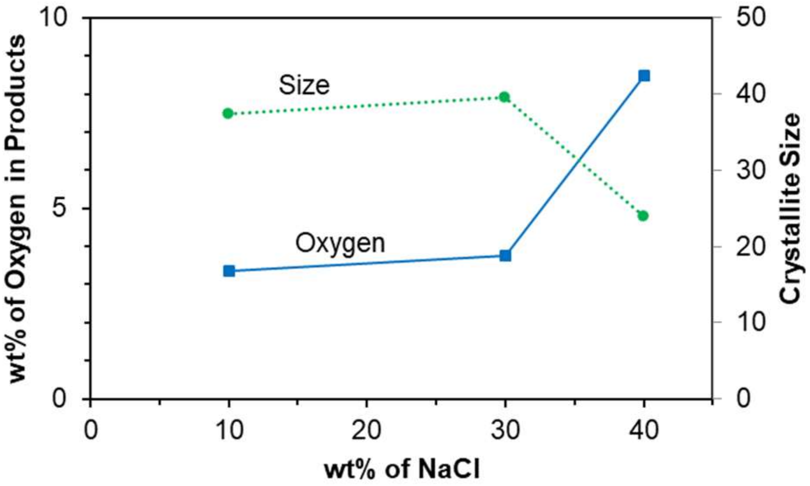


After combustion

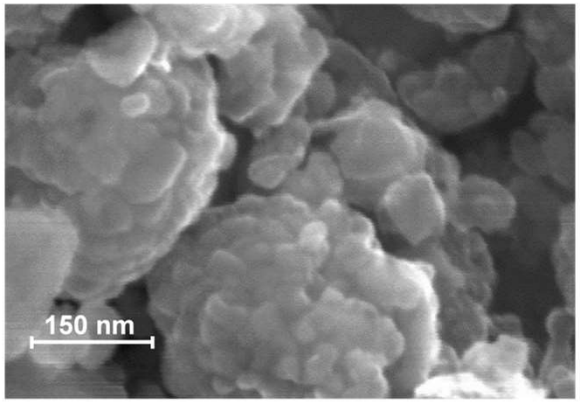


After leaching

Effect of NaCl in Mixtures with 20% Excess Mg



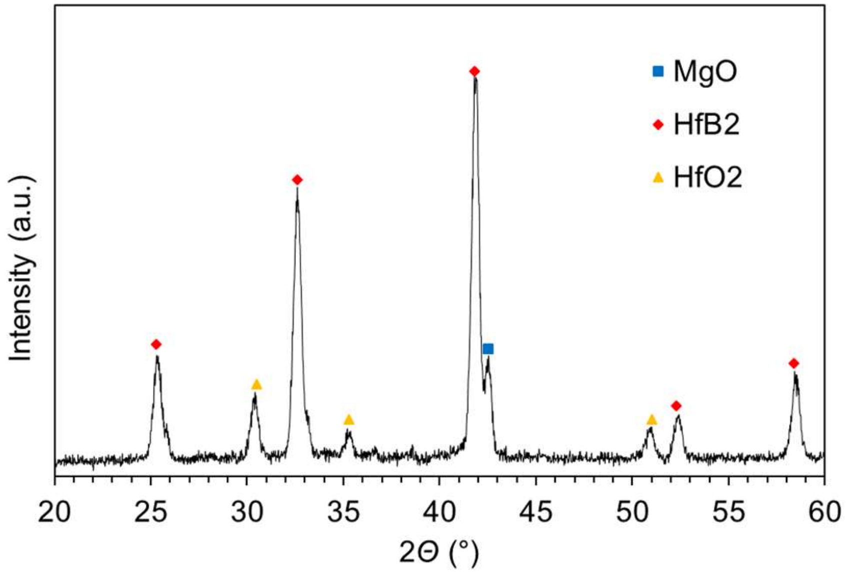
After leaching



ZrB_2 obtained from a mixture with 30 wt% NaCl and 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

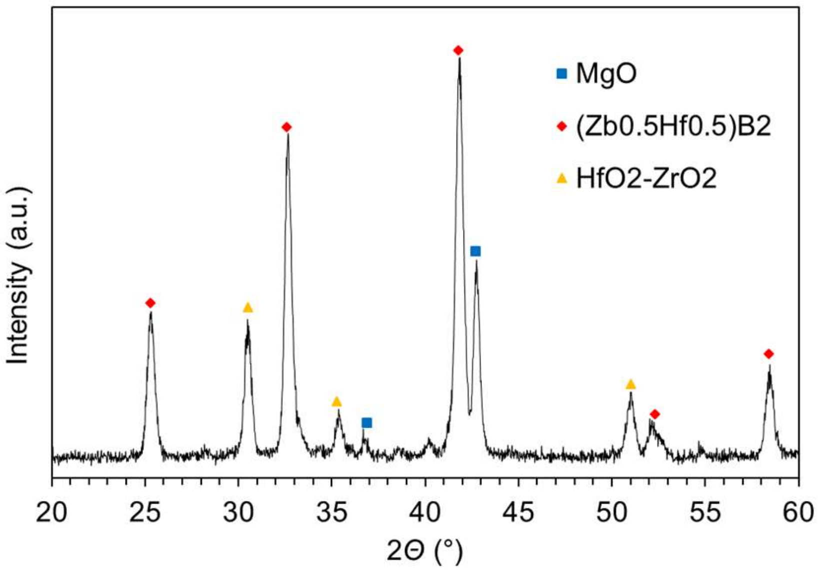
MASHS of HfB_2



XRD pattern of combustion products

- Stoichiometric $HfO_2/B_2O_3/Mg$ mixture (1:1:5 mole ratio)
- Dominant phase: HfB_2
- Significant amount of cubic HfO_2
- MgO can be removed by acid leaching.

MASHS of ZrB_2-HfB_2



XRD pattern of combustion products

- ZrO_2/HfO_2/B_2O_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

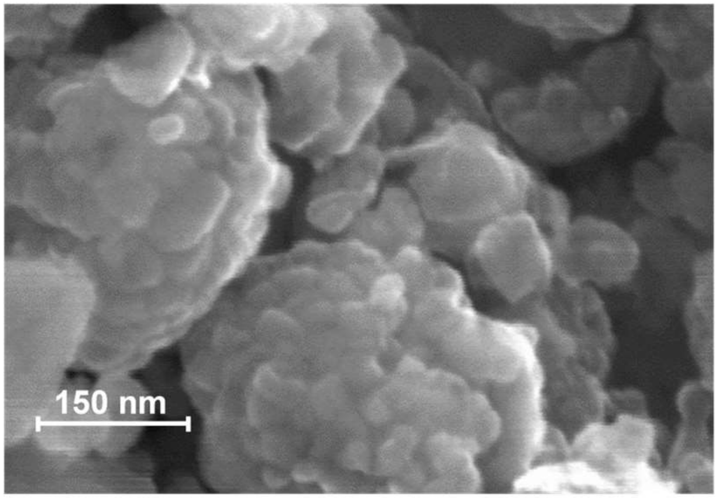
- **Mechanical activation has enabled magnesiothermic SHS of ZrB_2, HfB_2, and ZrB_2–HfB_2 solid solution.**
- **MgO is not a good diluent.**
  - Cannot decrease sticking of mixture during milling.
  - Increases the amount of ZrO_2 (both monoclinic and cubic) in the products.
- **NaCl is a promising 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

Mixing with dopants

3-D inversion kinematics mixer (Inversina 2L)

→

Pressing

→

Sintering

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

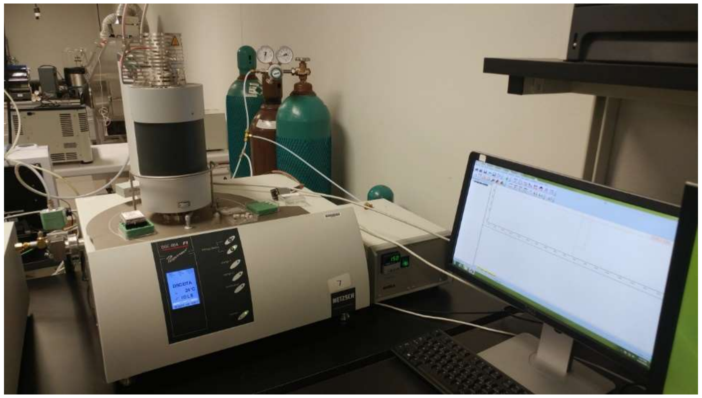
Electrical Properties

- The **electrical conductivity** will be measured with an electric property analyzer (Netzsch SBA 458 Nemesis).
  - 25°C – 1100°C

Electric property analyzer (Netzsch SBA 458 Nemesis)

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

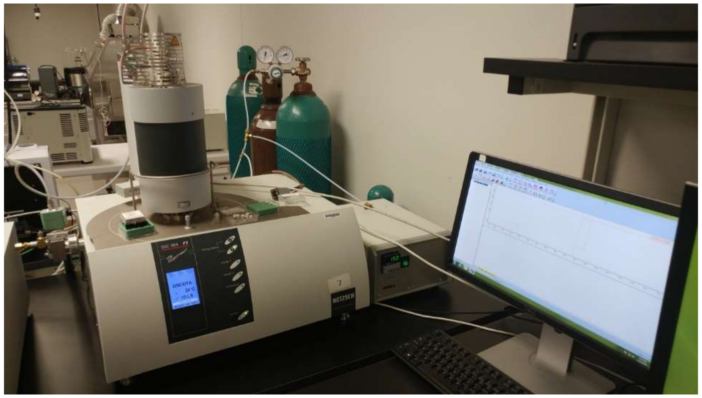


Differential scanning calorimeter (Netzsch DSC 404 F1 Pegasus)

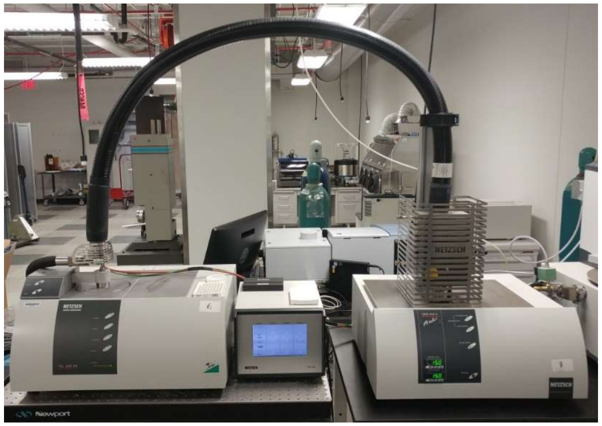
Laser flash apparatus (Netzsch LFA-457 MicroFlash)

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).

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**
  - Cordova, S., and Shafirovich, E., "Toward a Better Conversion in Magnesiothermic Synthesis of Zirconium Diboride," *Journal of Materials Science*, in review.
- **Conferences**
  - Cordova, S., and Shafirovich, E., TMS 2018 147th Annual Meeting & Exhibition, Phoenix, AZ, March 11-15, 2018.
  - Cordova, S., and Shafirovich, E., Materials Science and Technology 2017 (MS&T17), Pittsburgh, PA, Oct. 8-12, 2017.
  - Cordova, S., and Shafirovich, E., 2017 National Space & Missile Materials Symposium (NSMMS), Indian Wells, CA, June 26-29, 2017.
  - Cordova, S., Gutierrez Sierra, L.I., and Shafirovich, E., 10th U.S. National Combustion Meeting, College Park, MD, April 23-26, 2017.
  - Cordova, S., and Shafirovich, E., Southwest Emerging Technology Symposium, El Paso, TX, Apr. 1, 2017.
  - Cordova, S., Delgado, A., Esparza, A., and Shafirovich, E., "Materials Science and Technology 2016 (MS&T16), Salt Lake City, UH, Oct. 23-27, 2016.
  - Cordova, S., and Shafirovich, E., 2016 National Space & Missile Materials Symposium (NSMMS), Westminster, CO, June 20-23, 2016.
  - Cordova, S., and Shafirovich, E., Southwest Emerging Technology Symposium, El Paso, TX, Apr. 9, 2016.

Thank you!