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

The University of Texas at El Paso
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2017 Project Review Meeting for Crosscutting Research, Gasification Systems, and Rare Earth Elements Research Portfolios

March 23, 2017

DOE Award Number: **DE-FE-0026333**

Period of Performance: **10/1/2015 – 9/30/2018**

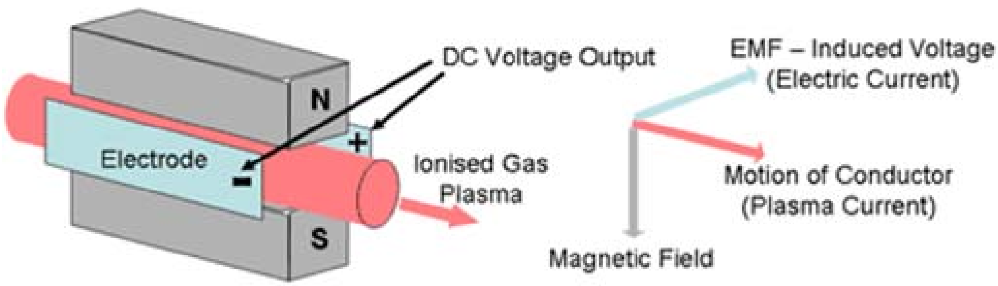
Project Goals and Objectives

- 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_2O_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 Power Generation (Principle)

- 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

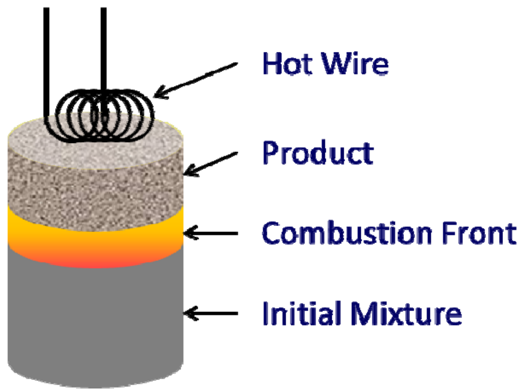
- **Borides of zirconium and hafnium (ZrB_2 and HfB_2) belong to the class of Ultra-High-Temperature Ceramics (UHTCs)**
  - Extremely high melting temperatures (about 3250 °C)
  - High hardness
  - High electrical and thermal conductivities
  - Chemical stability
  - Good thermal shock and oxidation 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 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 will investigate 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

Image: www.ism.ac.ru/handbook/shsf.htm

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**

  $ZrO_2 + B_2O_3 + 5Mg \rightarrow ZrB_2 + 5MgO$; $\Delta H^o_{rxn} = -959$ 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.

  – ZrO_2, HfO_2, B_2O_3, and H_3BO_3 are cheap.

  – Mg is much less expensive than Zr and Hf.

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.

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

- Inert powders such as 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

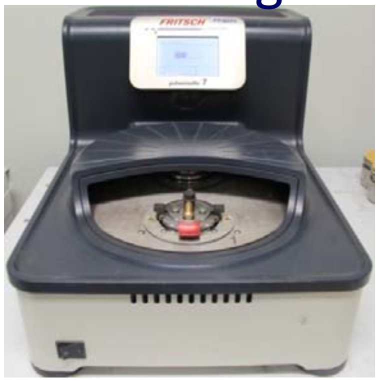
- **Dopants**
  - Carbon containing additives (C, B_4C, WC, and VC)
  - Transition metals (Fe, Cr, and Ni)
  - Refractory metal silicides ($MoSi_2$, $TiSi_2$, and $HfSi_2$)
- **Nanoscale powders**
  - Nanoscale powders produced by SHS are especially promising because they also have high defect concentrations.
  - To decrease the particle size, NaCl is used as an inert diluent.
  - NaCl is removed from the products by dissolution in water.
  - Nanoscale ZrB_2 powder produced with adding NaCl showed excellent sinterability

Mechanical Activation

Mixing

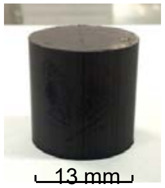
3-D inversion kinematics mixer (Inversina 2L)

Milling



Planetary ball mill (Fritsch Pulverisette 7)

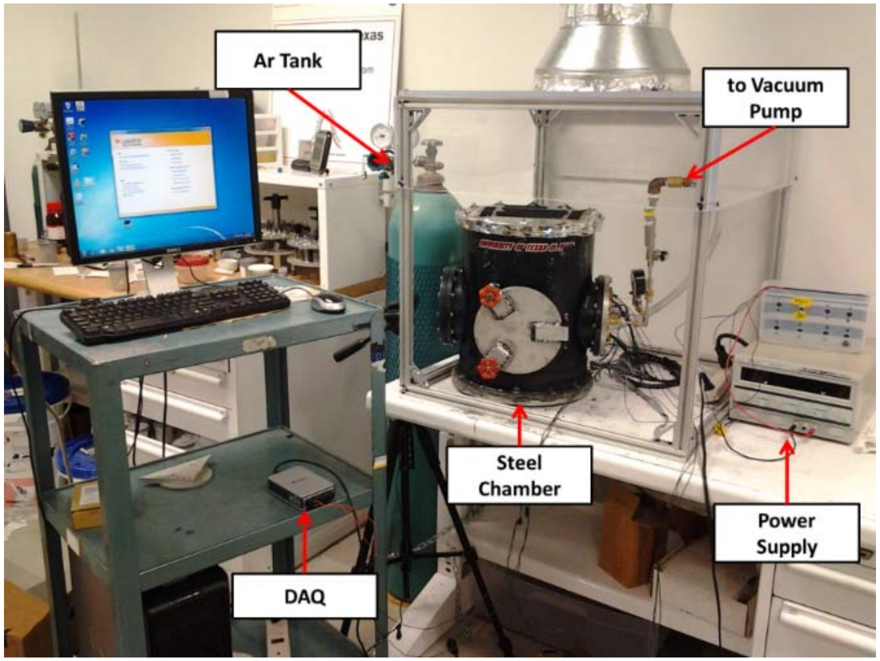
Pressing



- Activated $ZrO_2/B_2O_3/Mg$ and $HfO_2/B_2O_3/Mg$ mixtures are prepared with NaCl or MgO as inert diluents.
- ZrO_2/B_2O_3 and HfO_2/B_2O_3 mole ratios are 1:1.
- Mg/B_2O_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



Hot-wire ignition facility

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

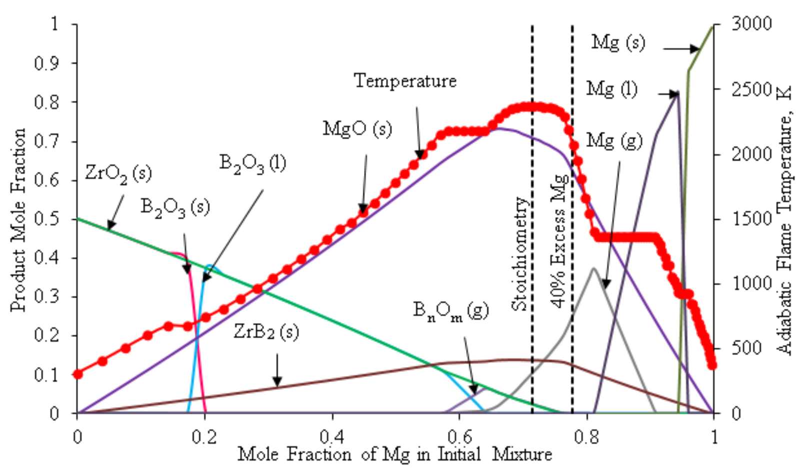
3-D inversion kinematics mixer (Inversina 2L)

Pressing

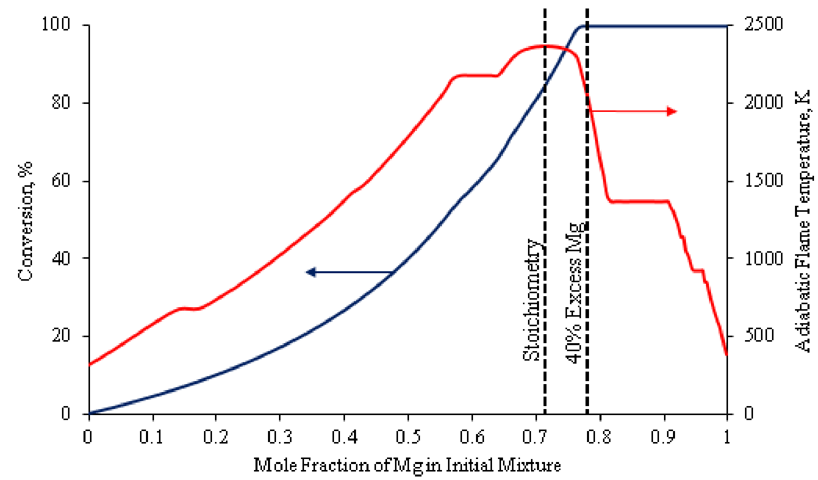
Sintering

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

Thermodynamic Analysis



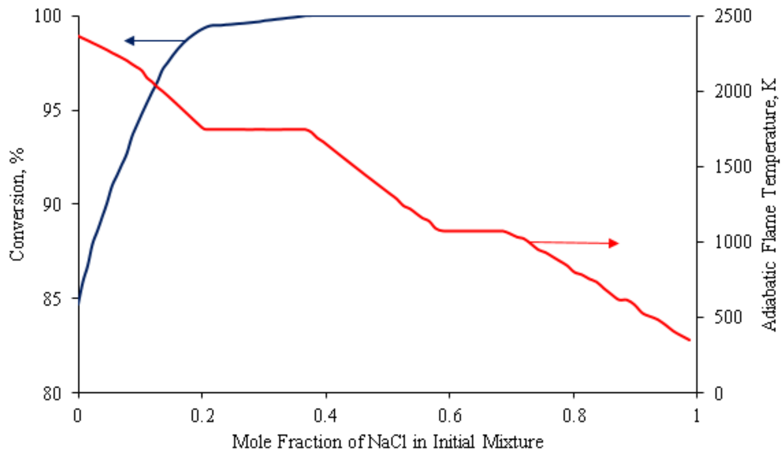
Adiabatic flame temperature and product composition *vs* Mg concentration in $ZrO_2/B_2O_3/Mg$ system



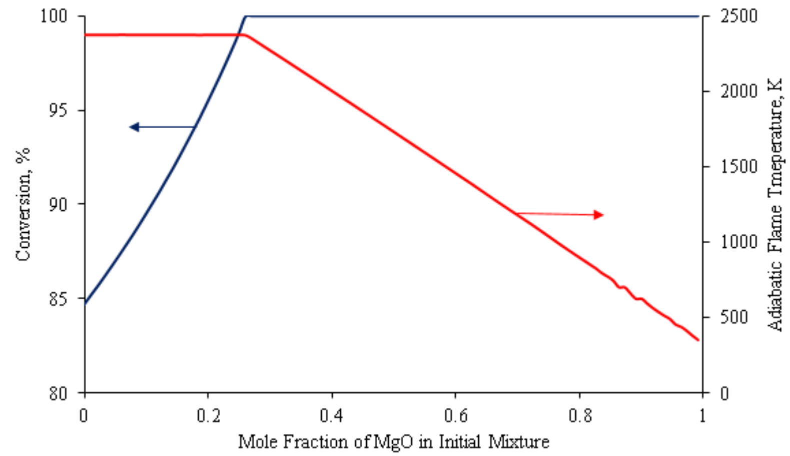
Adiabatic flame temperature and conversion % of ZrO_2 to ZrB_2 *vs* Mg concentration in $ZrO_2/B_2O_3/Mg$ system

- **Complete conversion of oxides to ZrB_2 (or HfB_2) 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



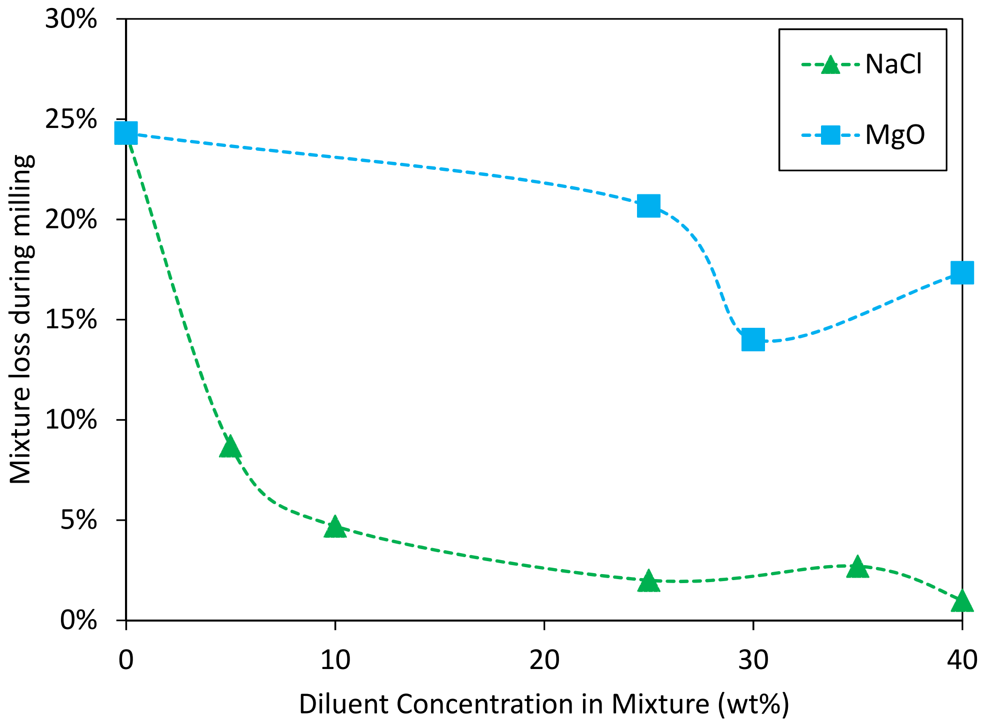
Adiabatic flame temperature and conversion % of ZrO_2 to ZrB_2 *vs* NaCl concentration in $ZrO_2/B_2O_3/Mg/NaCl$ system



Adiabatic flame temperature and conversion % of ZrO_2 to ZrB_2 *vs* MgO concentration in $ZrO_2/B_2O_3/Mg/NaCl$ system

- **Complete conversion of oxides to ZrB_2 (or HfB_2) is achieved at 44 wt% NaCl or 25 wt% MgO.**
  - **No gaseous products**

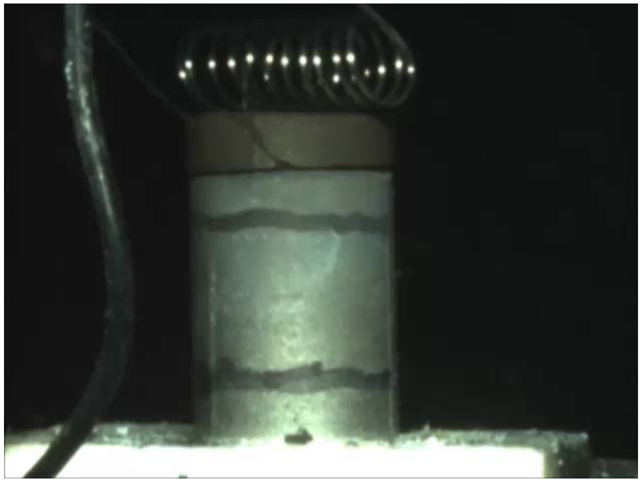
Effect of Inert Diluents on Milling

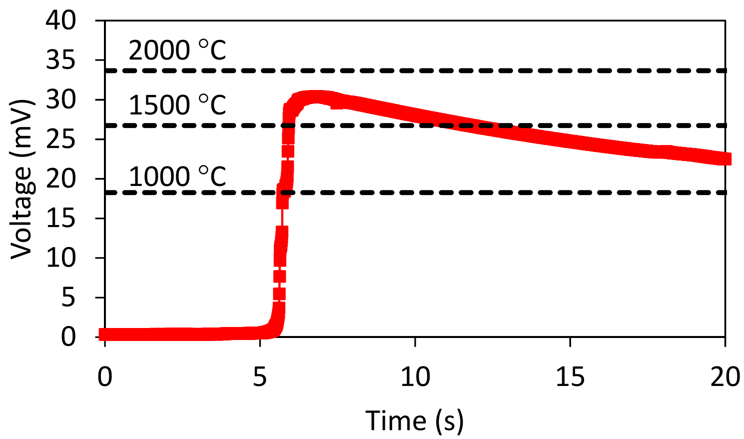


Mixture lost during milling *vs.* inert diluent concentration

- **High-energy ball milling of $Mg/ZrO_2/B_2O_3$ 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 $ZrO_2/B_2O_3/Mg$ Mixture



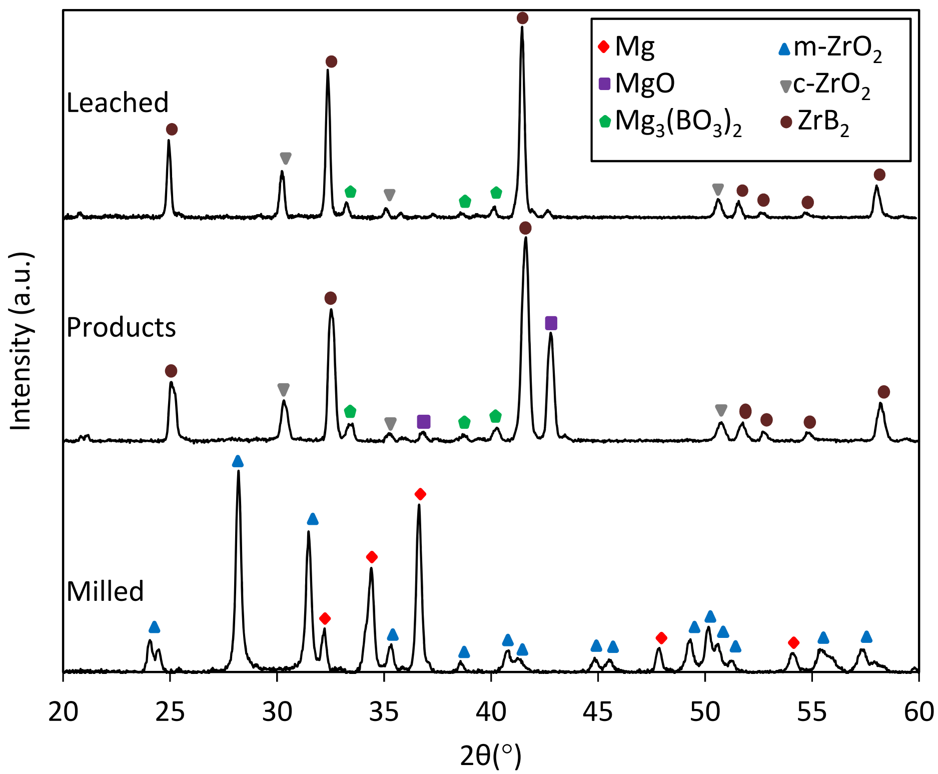


Thermocouple recording

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

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

XRD

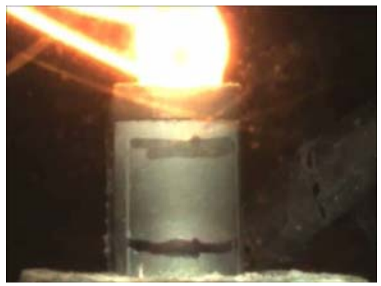


- **There are no reactions during milling.**
- **Mg reduces most of ZrO_2.**
- **MgO stabilizes the cubic phase of ZrO_2.**
- **The undesired compound $Mg_3(BO_3)_2$ is present in the combustion products and after leaching.**
- **Leaching removes NaCl and MgO.**

Effect of NaCl on Combustion

$ZrO_2/B_2O_3/5Mg$ + NaCl

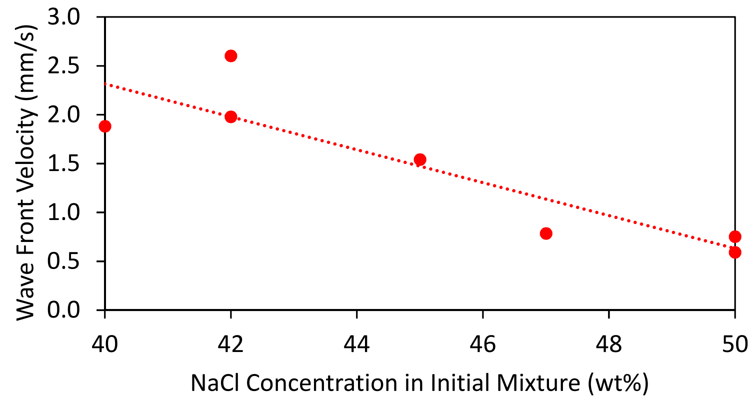
0 wt%



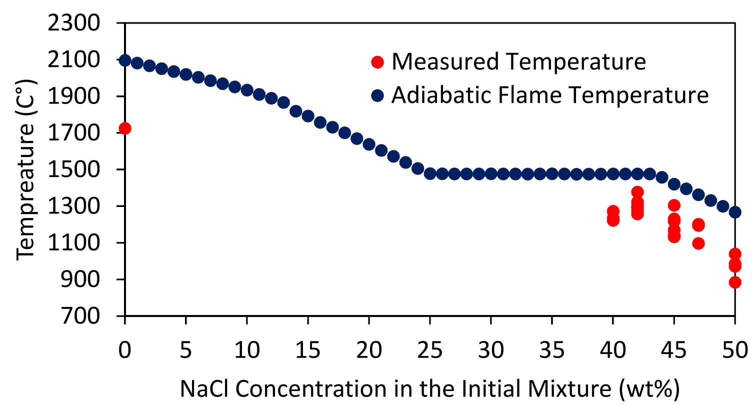
10 wt%

40 wt%

50 wt%

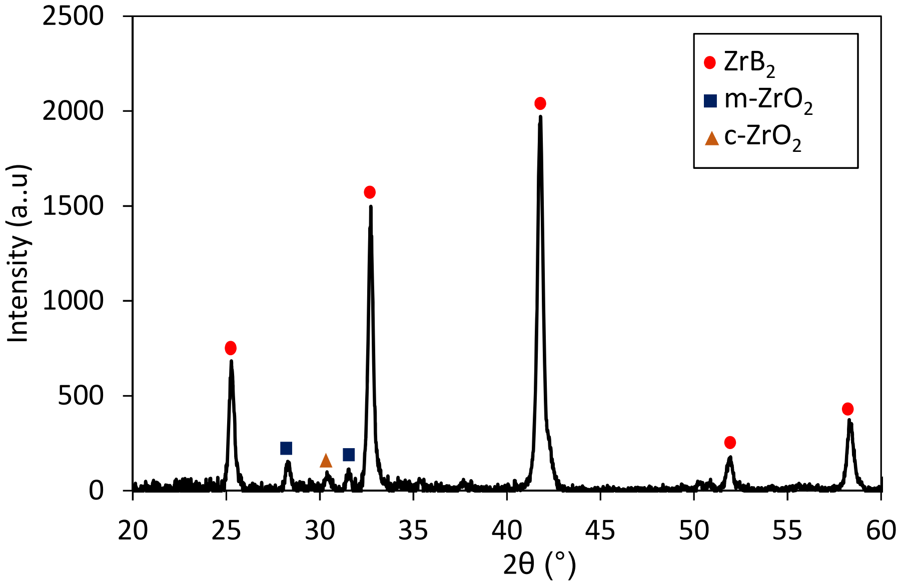


Wave front velocity *vs.* NaCl concentration

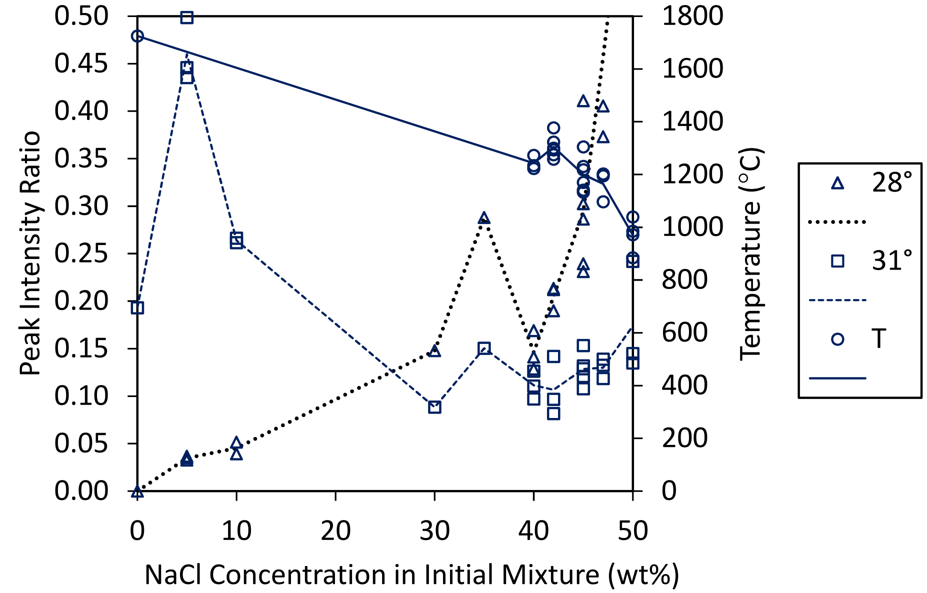


Measured temperatures and adiabatic flame temperatures vs. NaCl concentration

Effect of NaCl on Combustion Products



XRD pattern of Combustion Products after Leaching



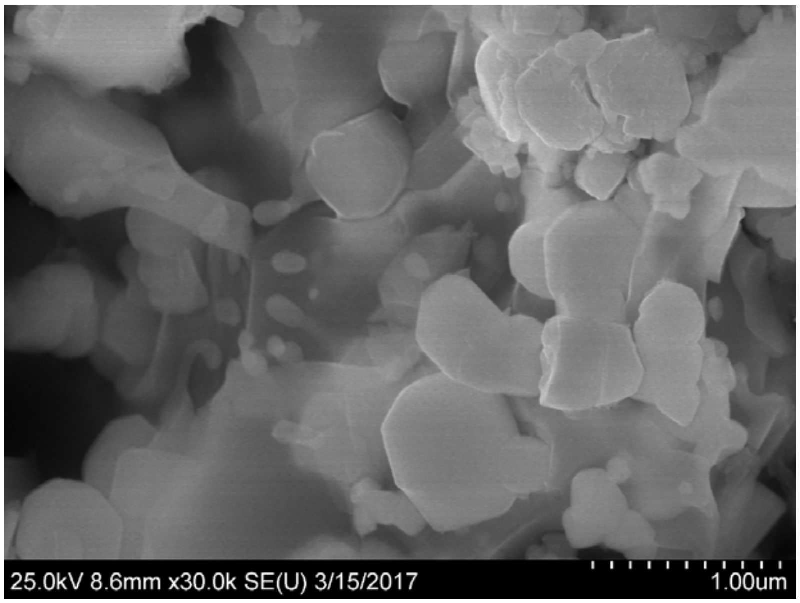
Peak Intensity Ratios *vs.* NaCl Concentration

$$\text{Peak Intensity Ratio}=\frac{I_{m-ZrO_2(\bar{1}11)}}{I_{ZrB_2(101)}}$$

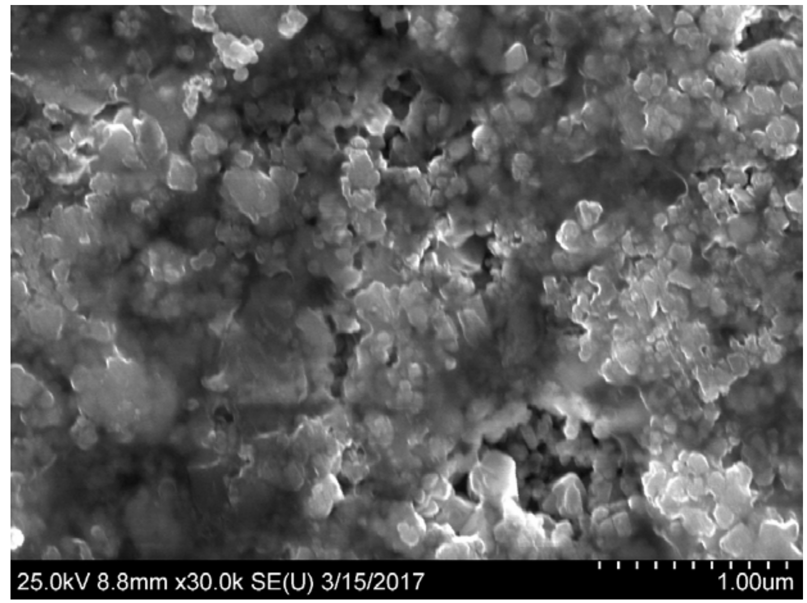
$$\text{Peak Intensity Ratio}=\frac{I_{c-ZrO_2(111)}}{I_{ZrB_2(101)}}$$

- **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



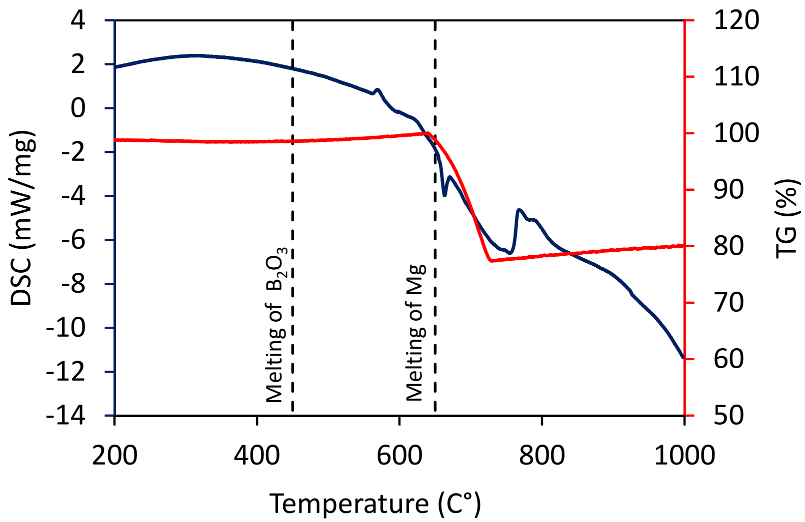
SEM Image of ZrB_2 obtained from a mixture without NaCl



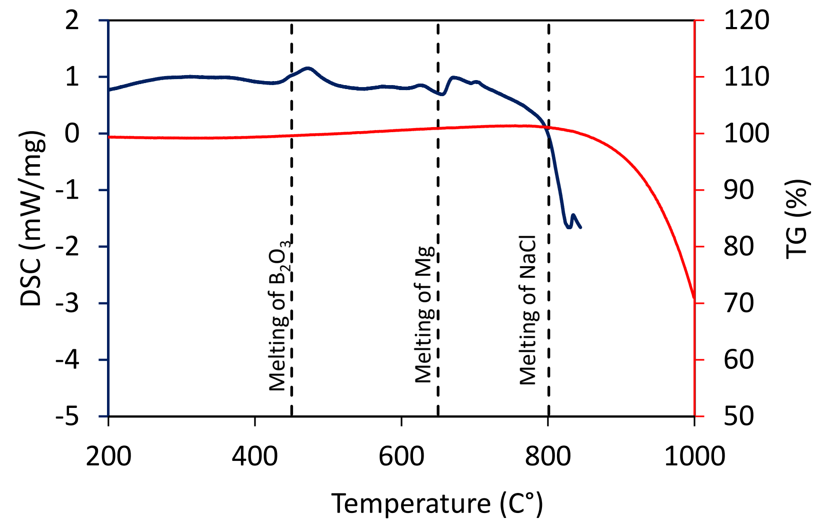
SEM Image of ZrB_2 obtained from a mixture with 30 wt% NaCl

- **NaCl decreases the particle size of ZrB_2.**

Effect of Milling and NaCl on the Reaction Mechanisms



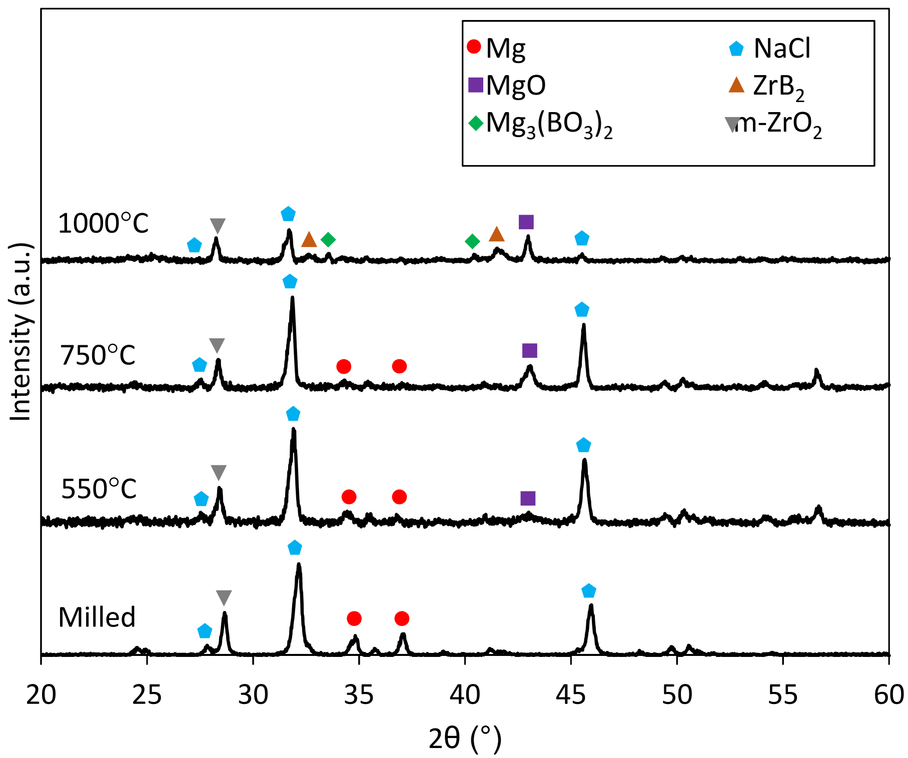
DSC and TG curves of unmilled stoichiometric mixture



DSC and TG curves of milled mixture with 45wt% NaCl

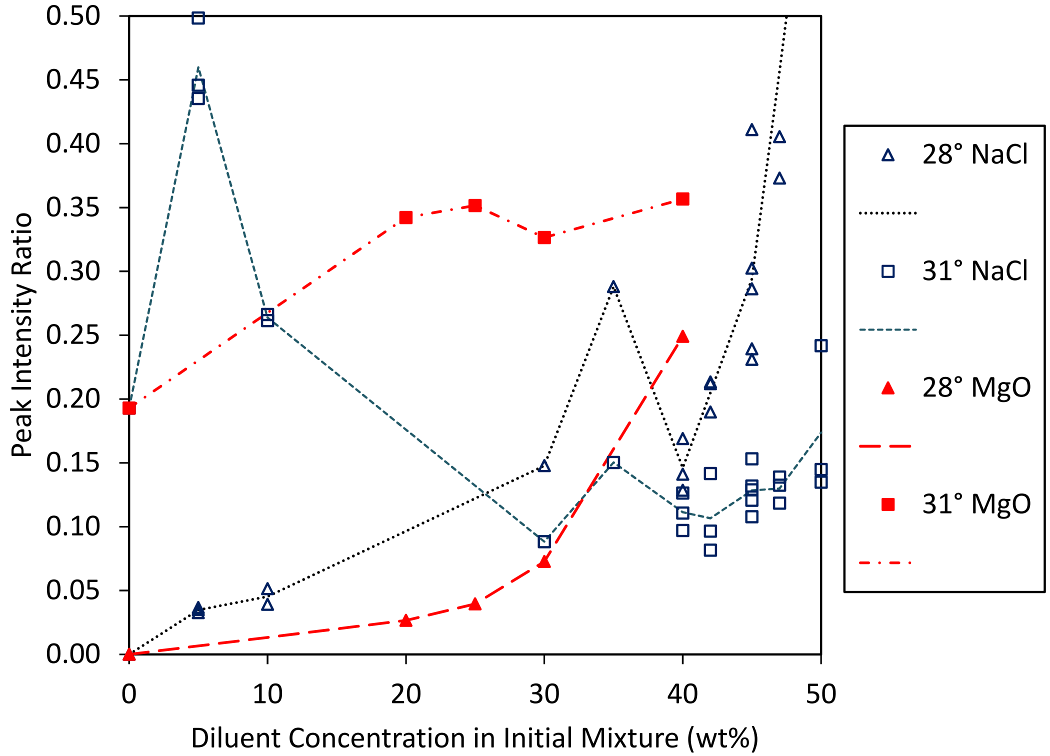
- **The mass loss in the unmilled and milled mixtures is caused by Mg and NaCl, respectively.**
- **Milling decreases the ignition temperature of the reaction and prevents Mg loss.**
- **Melting of B_2O_3 and melting of Mg play important roles.**

XRD of Samples Quenched during DSC



- **The reaction between B_2O_3 and Mg is initiated by melting of B_2O_3 and is intensified by melting of Mg.**
- **The reaction between ZrO_2 and Mg needs temperatures greater than 750 °C.**
- **The content of NaCl decreases due to vaporization after melting (801 °C).**

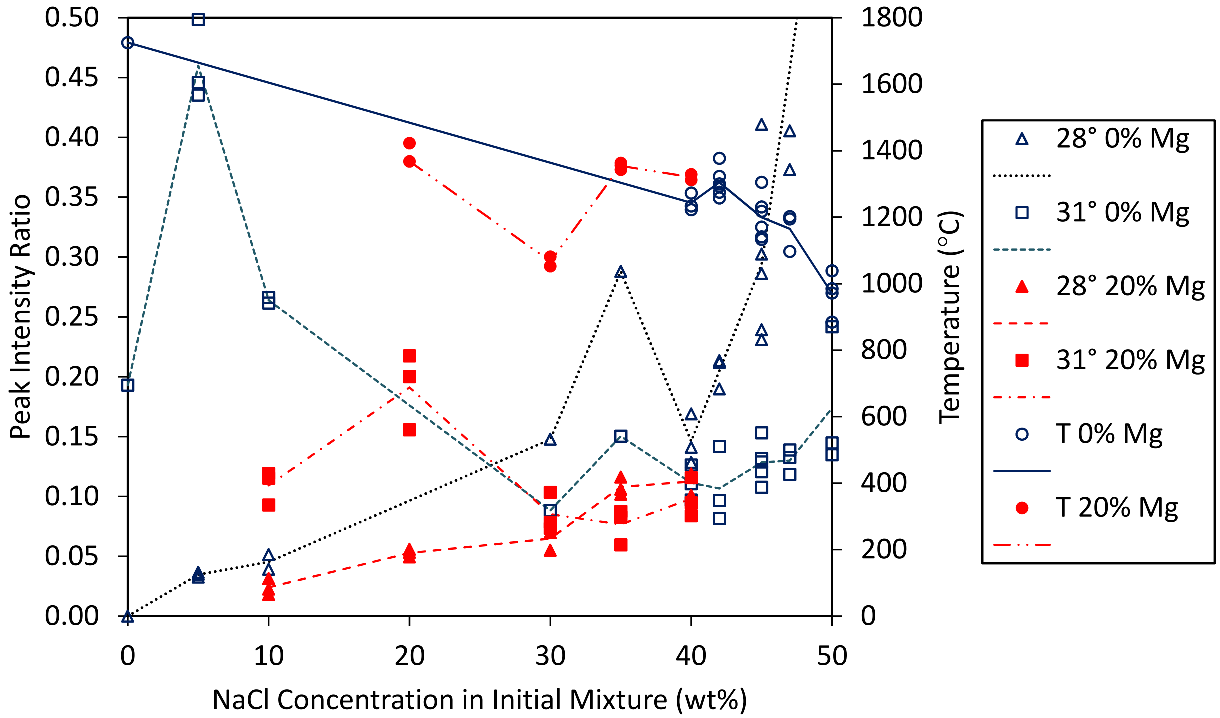
Effect of MgO on Combustion Products



Peak intensity Ratios *vs.* inert diluent concentration

- **Adding MgO to the mixture partially stabilizes ZrO_2.**
- **Unfortunately, MgO decreases the conversion of ZrO_2 to ZrB_2.**

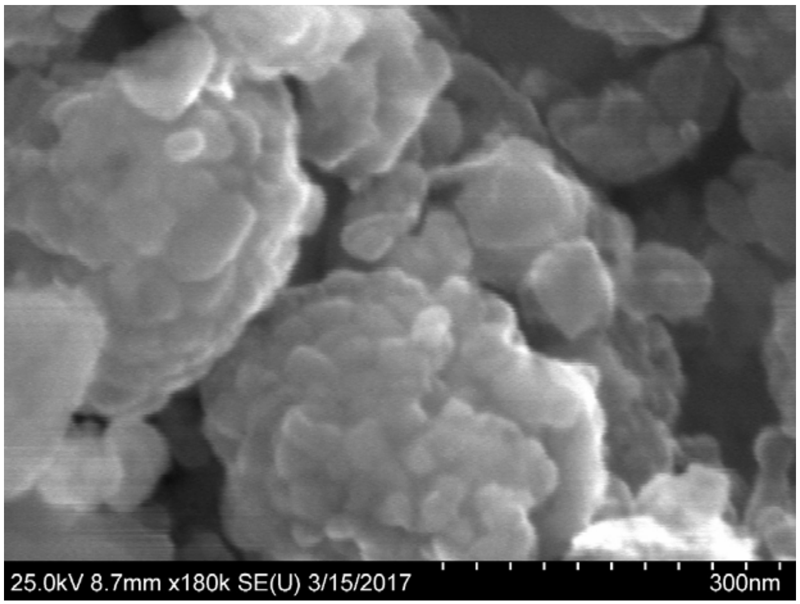
Effect of Excess Mg on Combustion Products



Peak intensity ratios *vs.* NaCl concentration

- **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 ZrB_2



SEM Image of ZrB_2 obtained from a mixture with 30 wt% NaCl and 20% excess Mg

- **Nanoscale Particles**
  - **Lower sintering temperature**
  - **Finer grain size**
- **Polycrystalline particles**
  - **Sinter better than single-crystal particles**

Summary

☺ Adding NaCl to $ZrO_2/B_2O_3/Mg$ effectively decreases the loss of materials during milling.

☺ Mechanical activation has enabled magnesiothermic SHS of ZrB_2.

– The products also contain undesired phases ZrO_2 and $Mg_3(BO_3)_2$.

☺ Excess Mg increases the conversion of oxides to borides.

☹ MgO has an adverse effect on conversion of ZrO_2 to ZrB_2.

☺ Increasing NaCl content decreases the particle size of ZrB_2.

– 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

Acknowledgments

- DOE NETL Program for Crosscutting Research
- Program Manager: Jason Hissam
- Graduate Student: Sergio Cordova
- Undergraduate Students: Leonardo Gutierrez Sierra

Thanks!