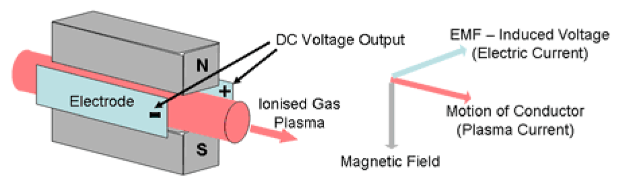
Combustion Synthesis of Boride-Based Electrode Materials for MHD Direct Power Extraction

Sergio Cordova and Evgeny Shafirovich
Department of Mechanical Engineering, The University of Texas at El Paso

Objective

- Use of an open-cycle magnetohydrodynamic (MHD) generator as the topping cycle in combination with Rankine cycle has the potential to increase the efficiency of coal-fired power plants.
  - No moving parts → the maximum temperature is higher



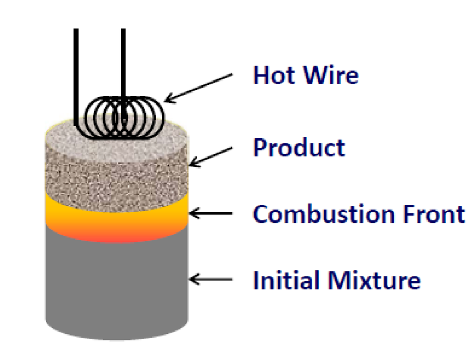
Magnetohydrodynamic Power Generation (Principle)
www.mpoweruk.com/mhd_generator.htm

- Electrodes in MHD generators must withstand extreme temperatures and a thermal shock, possess a high oxidation/erosion resistance, high electrical and thermal conductivities.
- Boride-based ultrahigh-temperature ceramics (UHTCs), such as ZrB_2 and HfB_2, are promising materials for MHD electrodes [1].
- Current processing technologies are complicated and expensive [2].
- This project aims to develop a novel technology for an advanced, low-cost manufacturing of UHTCs that possess all the required properties to function as sustainable MHD electrodes.

Approach

Magnesiothermic combustion synthesis (SHS) of ZrB_2 and HfB_2

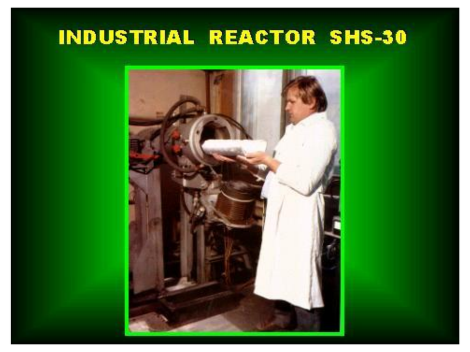
- Advantages
  - Low energy consumption, simple equipment, high purity of products
  - Inexpensive precursors ZrO_2, HfO_2, B_2O_3, and Mg
- Problems and solutions
  - Incomplete conversion when H_3BO_3 was used as the precursor [3]. We plan to use B_2O_3 instead.
  - Low exothermicity. We plan to use mechanical activation.



Self-propagating high-temperature synthesis (SHS)

Pressureless sintering

- Advantages
  - Simple and economic process
  - Near net shape products
- Problems and solutions
  - Insufficient density and need for very high temperatures. We plan to use dopants. SHS products have defects in the microstructure that decrease the sintering temperature.



An industrial SHS reactor
(www.ism.ac.ru/handbook/shsf.htm)

Methodology

Thermodynamic analysis of the combustion process

- Adiabatic flame temperatures and product compositions were calculated with THERMO software at 1 atm for the following systems (**x** was varied):

$ZrO_2 - B_2O_3 - \mathbf{x}Mg$ and $HfO_2 - B_2O_3 - \mathbf{x}Mg$

$ZrO_2 - B_2O_3 - 5Mg - \mathbf{x}NaCl$ and $HfO_2 - B_2O_3 - 5Mg - \mathbf{x}NaCl$

$ZrO_2 - B_2O_3 - 5Mg - \mathbf{x}MgO$ and $HfO_2 - B_2O_3 - 5Mg - \mathbf{x}MgO$

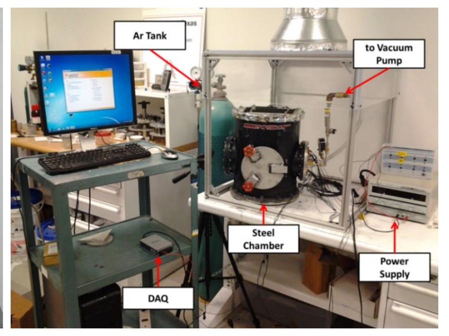
Experimental procedure

- Mixing powders
- Mechanical activation (ball milling at 1000 rpm for 1-10 min)
- Compacting into pellets
- Combustion synthesis
- Leaching of MgO
- X-ray diffraction analysis


Mixer

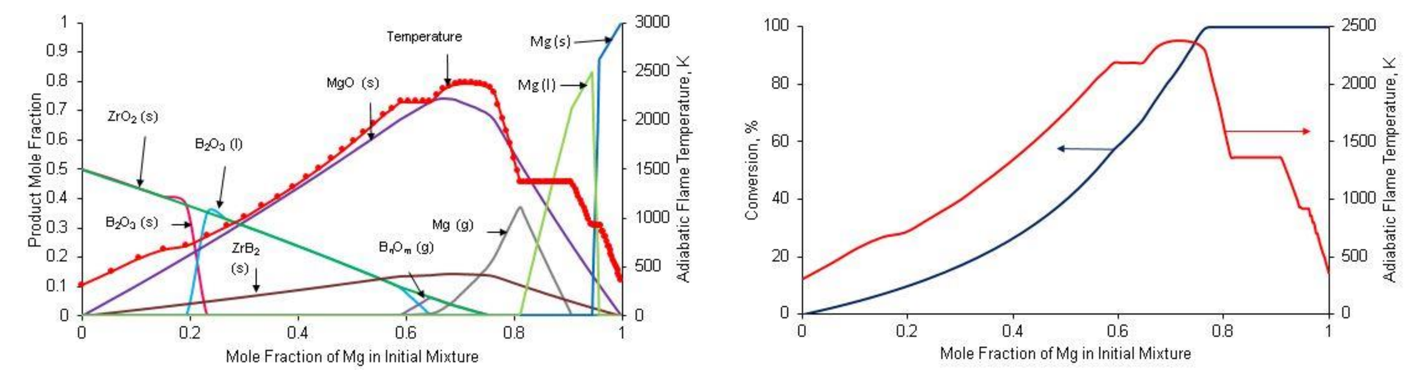

Planetary mill


Press


Combustion synthesis setup

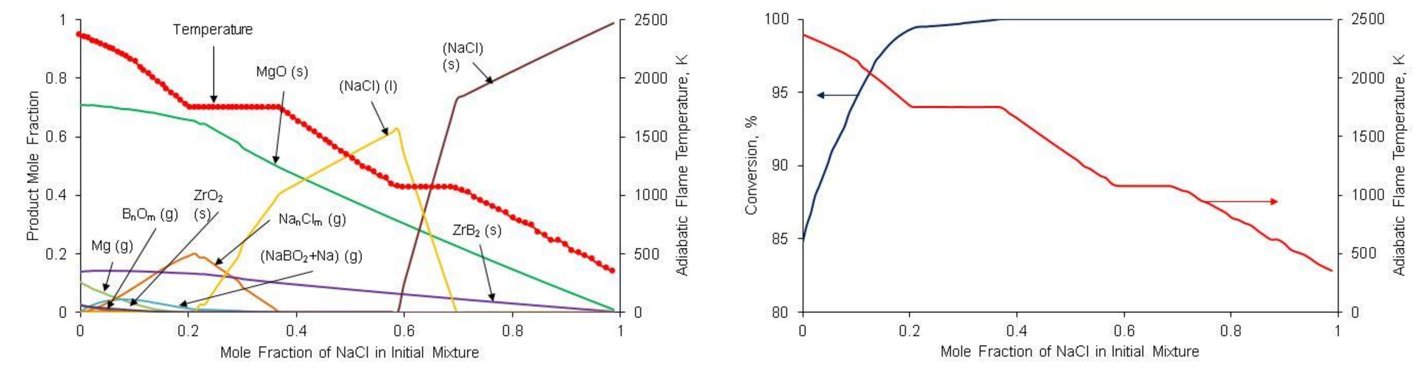
Thermodynamic Analysis

$ZrO_2 - B_2O_3 - xMg$

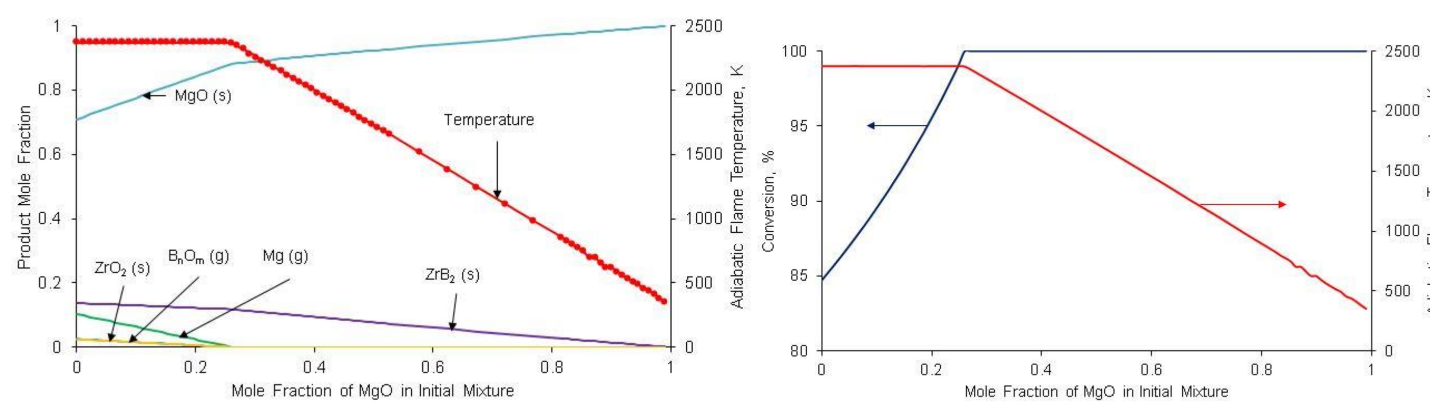


- Complete conversion of oxides to ZrB_2 (or HfB_2) is achieved at 40 % excess Mg.
- Excess Mg leads to high concentration of Mg vapor and undesired pressure increase.

$ZrO_2 - B_2O_3 - 5Mg - xNaCl$



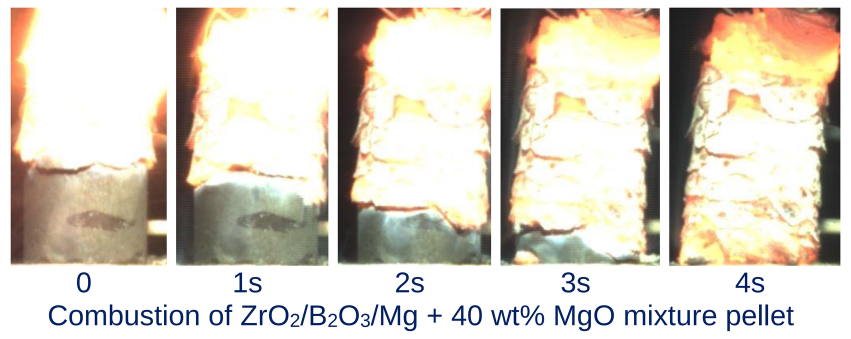
$ZrO_2 - B_2O_3 - 5Mg - xMgO$



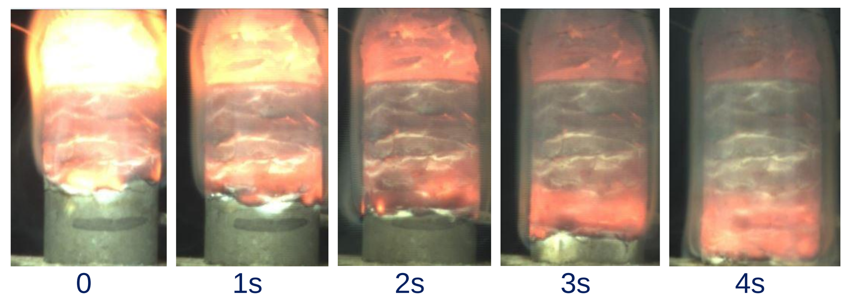
- Complete conversion of oxides to ZrB_2 (or HfB_2) is achieved at 44 wt% NaCl or 25 % MgO.
- No gaseous products

Combustion Synthesis

- $ZrO_2/B_2O_3/Mg/MgO$ and $ZrO_2/B_2O_3/Mg/NaCl$ (20-40 wt% inert diluent)
  - Mechanically activation is necessary.
  - Increasing the milling time from 1 min to 10 min facilitates ignition and accelerates combustion.
  - Adding more MgO or NaCl decreases the combustion front velocity.
  - The differences in combustion behavior of mixtures with NaCl and MgO may be associated with the low melting point of NaCl (801 °C).

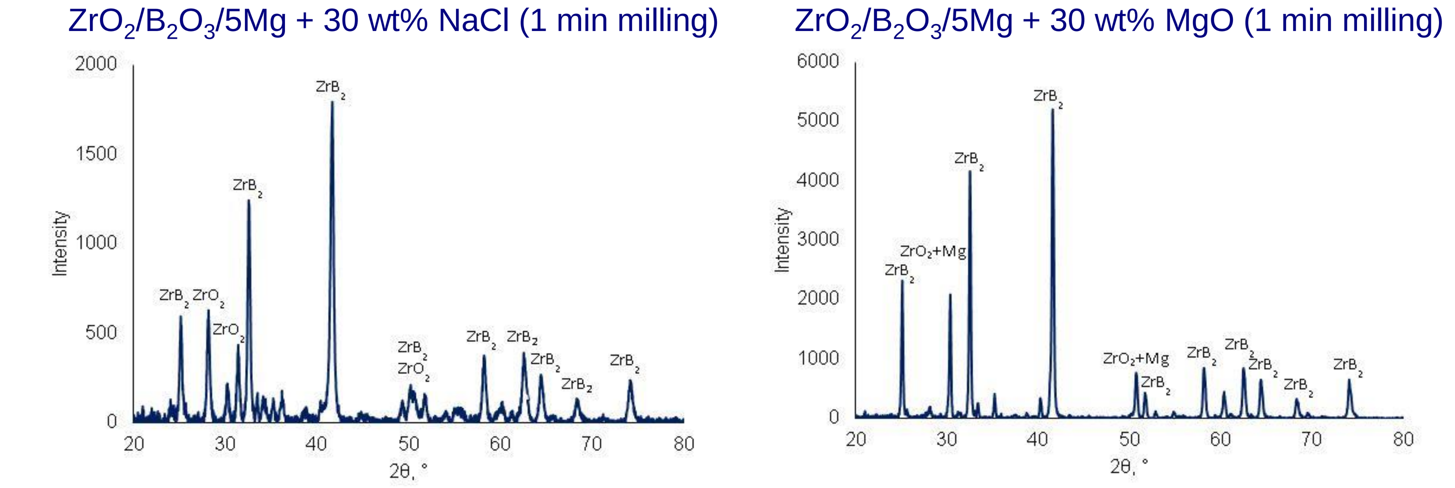


Combustion of $ZrO_2/B_2O_3/Mg$ + 40 wt% MgO mixture pellet



Combustion of $ZrO_2/B_2O_3/Mg$ + 40 wt% NaCl mixture pellet

XRD Analysis of Products



- ZrB_2 is the dominant phase, but ZrO_2 is still present in the products.
- Leaching completely removed MgO and NaCl from the products.

Conclusions

- Thermodynamic calculations have shown that full conversion can be achieved by the addition of NaCl, MgO, or excess Mg.
- Mechanical activation has improved magnesiothermic SHS of ZrB_2 from mixtures with inert diluents NaCl and MgO.

Future Work

- Experimentally investigate the effect of additive concentration on the conversion degree.
- Determine the optimal mixture composition and milling parameters.
- Experimentally investigate magnesiothermic SHS of HfB_2.
- Determine the reaction mechanisms of the used SHS process.
- Investigate pressureless sintering of the obtained ZrB_2 and HfB_2.
- Determine thermophysical, oxidation, mechanical, and electrical properties.
- Investigate the effects of dopants on sintering and properties of the obtained materials.

Acknowledgment

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References

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