NATIONAL ENERGY TECHNOLOGY LABORATORY

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

Presented by:	Gabriel Llausas (student)
Principal Investigator :	Evgeny Shafirovich
Other participants:	Sergio Cordova (student)
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

Project Description and Objectives

- **Purpose of project**
  - To investigate 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
- **Strategic alignment of project to Fossil Energy objectives**
  - MHD direct power extraction has the potential to significantly increase the efficiency of coal-fired power plants.
  - The project focuses on a major hurdle in the MHD development: the lack of suitable electrode materials.
  - The project goal is 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.

Project Description and Objectives

- **Technology benchmarking**
  - Borothermic and carbothermic reduction of oxides are **endothermic** and involve a high-temperature furnace as well as long milling.
  - Magnesiothermic reduction is **exothermic** and can be performed as a combustion process, with no furnace.
  - A major problem in the magnesiothermic reduction route for synthesis of ZrB_2 and HfB_2 is incomplete conversion of oxides to borides.
- **Driving question**
  - What additives and what experimental parameters can improve the conversion in the MASHS of ZrB_2 and HfB_2 from ZrO_2, HfO_2, and B_2O_3?

Project Description and Objectives

- **Current status of project**
  - **Optimal composition:** The addition of 20% excess Mg and 30 wt% NaCl to the stoichiometric $ZrO_2/B_2O_3/Mg$ mixture ensures effective mechanical activation, a steady self-sustained combustion, and a relatively small amount of zirconia in the combustion products. The obtained ZrB_2 powder consists of nanoscale polycrystalline particles.
  - The project goals/objectives have not changed. The last phase of the project focuses on pressureless sintering of the obtained materials.
  - **Industry/input or validation** – This project has not sought feedback or validation from industry.

Project Update

Accomplishments

- **Journal articles**
  - Cordova, S., and Shafirovich, E., "Toward a Better Conversion in Magnesiothermic SHS of Zirconium Diboride," *Journal of Materials Science* 53 (2018) 13600-13616
- **Conferences**
  - Cordova, S., Gutierrez Sierra, L.I., and Shafirovich, E., 10th U.S. National Combustion Meeting, April 23-26, 2017, College Park, MD
  - Cordova, S., and Shafirovich, E., CIMTEC 2018 – 14th International Conference on Modern Materials and Technologies, 14th International Ceramics Congress, June 4-18, 2018, Perugia, Italy
  - Cordova, S., and Shafirovich, E., TMS 2018 147th Annual Meeting & Exhibition, Mar. 11-15, 2018, Phoenix, AZ
  - Cordova, S., and Shafirovich, E., Materials Science and Technology 2017 (MS&T17), Oct. 8-12, 2017, Pittsburgh, PA
  - Cordova, S., and Shafirovich, E., 2017 National Space & Missile Materials Symposium (NSMMS), June 26-29, 2017, Indian Wells, CA
  - Cordova, S., Delgado, A., Esparza, A., and Shafirovich, E., Materials Science and Technology 2016 (MS&T16), Oct. 23-27, 2016, Salt Lake City, UH
- **Awards**
  - Cordova, S., Outstanding Thesis Award, College of Engineering, UTEP, 2017

Project Update

Mechanically activated self-propagating high-temperature synthesis (MASHS)

Mixing

3-D inversion kinematics mixer (Inversina 2L)

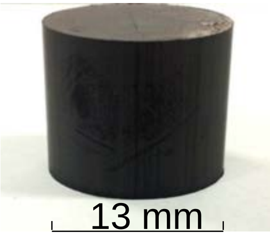
ZrO_2
B_2O_3
Mg
NaCl

Milling

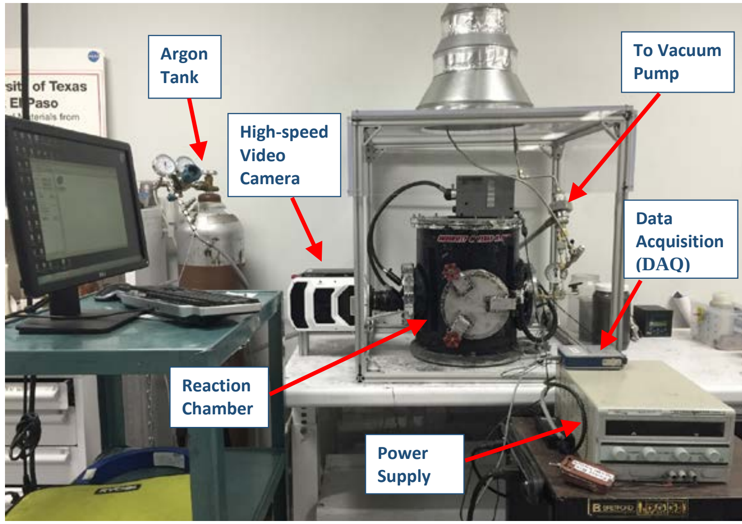
Planetary ball mill (Fritsch Pulverisette 7)

Compacting

Hydraulic press



Combustion synthesis (SHS)



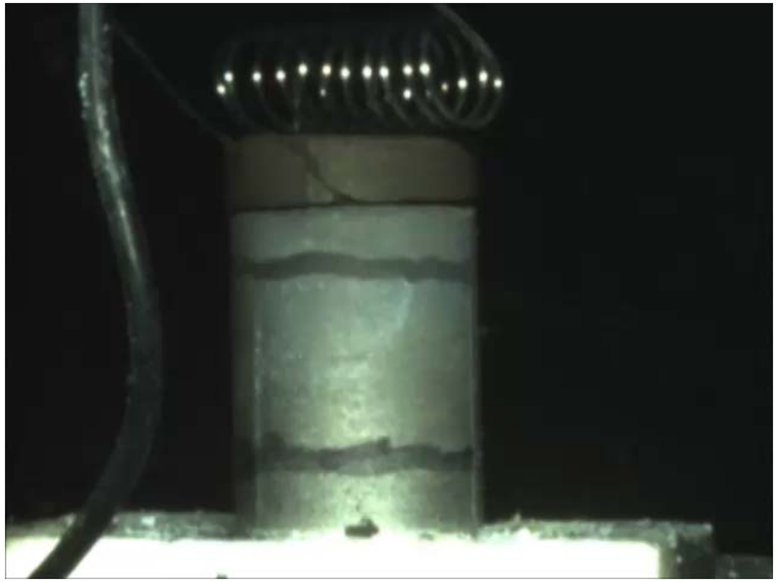
ZrO_2, B_2O_3, MgO, NaCl

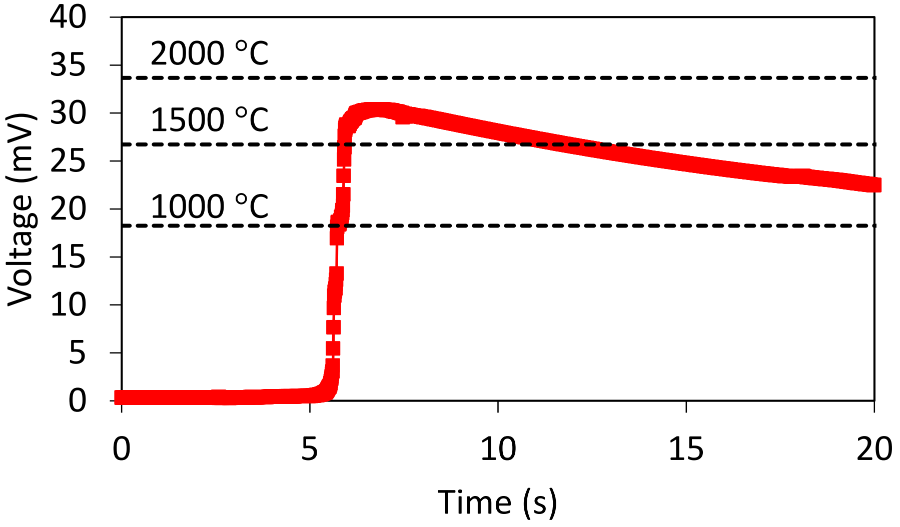
Leaching in diluted HCl

ZrB_2, ZrO_2

Project Update

Combustion of Stoichiometric Mixture (no NaCl)





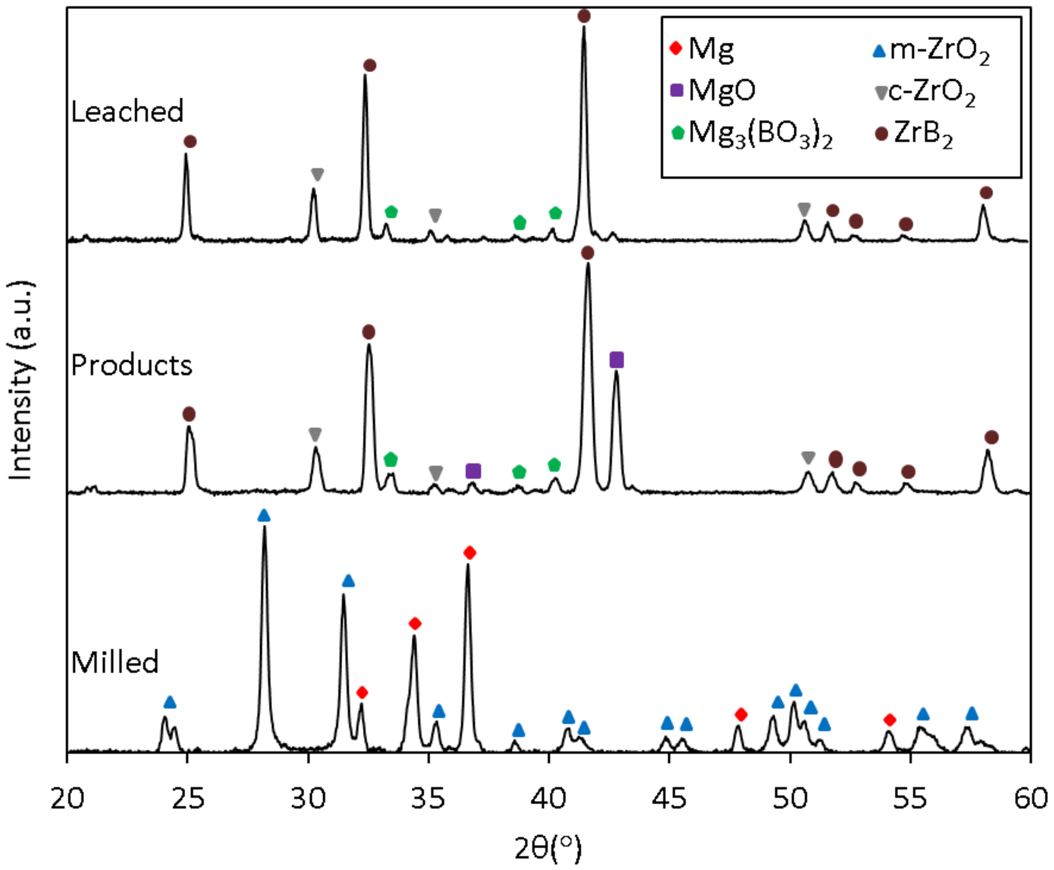
Thermocouple recording

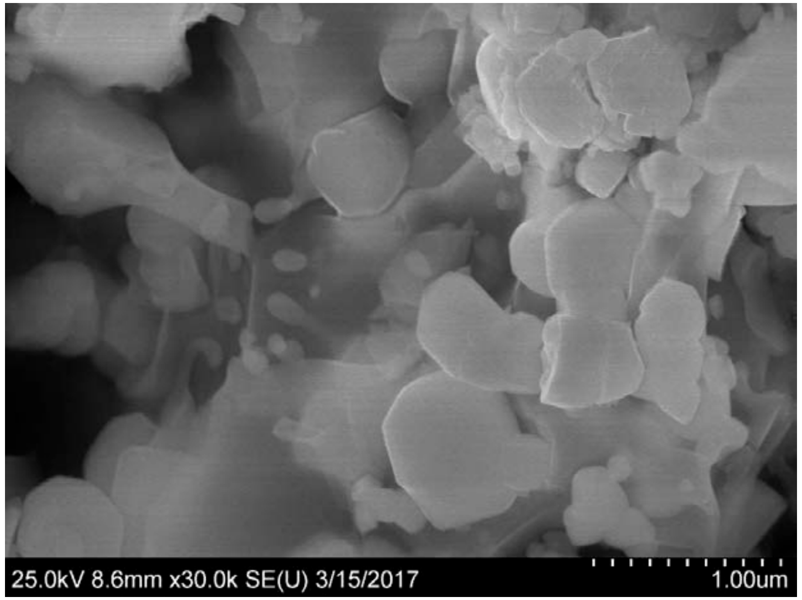
- Pellet dimensions
  - Diameter: 13 mm
  - Height: 18 mm

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

Project Update

XRD and SEM Characterization



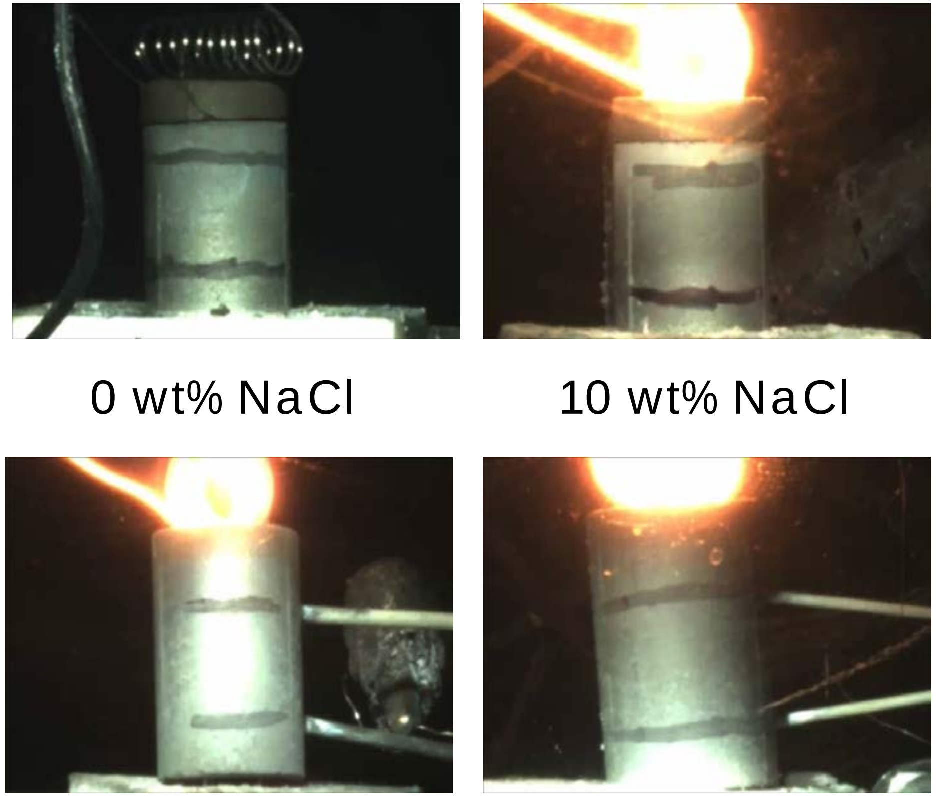


- Mg reduces most of ZrO_2.
- Formed MgO stabilizes cubic ZrO_2.
- Leaching removes MgO.
- Product: micron-size particles

Project Update

Effect of NaCl on combustion

$ZrO_2/B_2O_3/5Mg + NaCl$

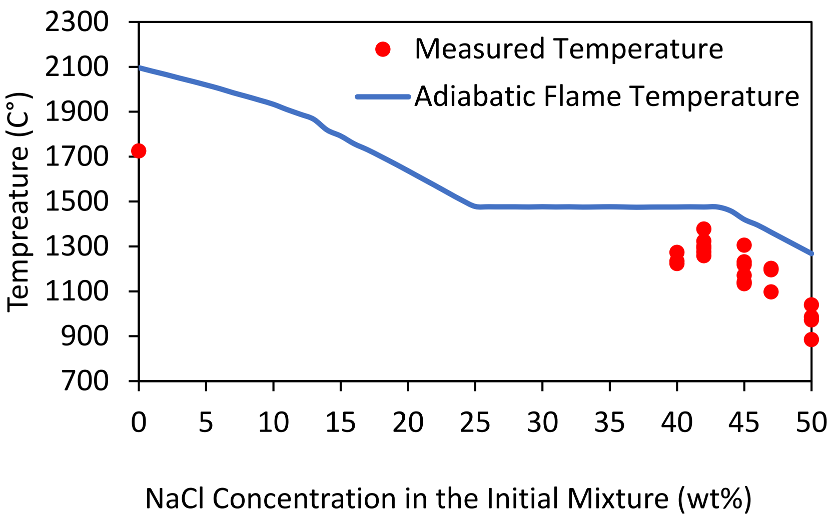


0 wt% NaCl

10 wt% NaCl

40 wt% NaCl

50 wt% NaCl

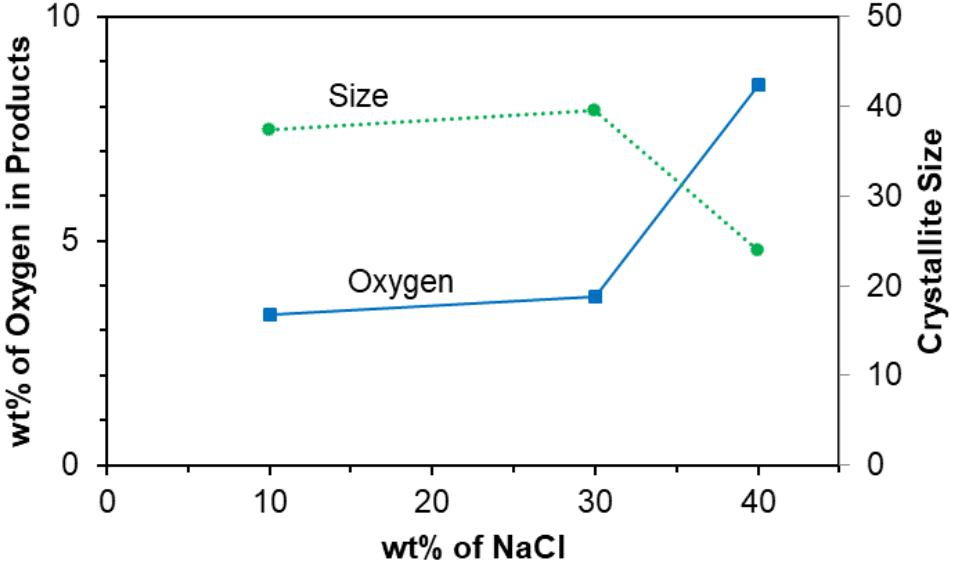


Combustion temperature *vs.* NaCl concentration

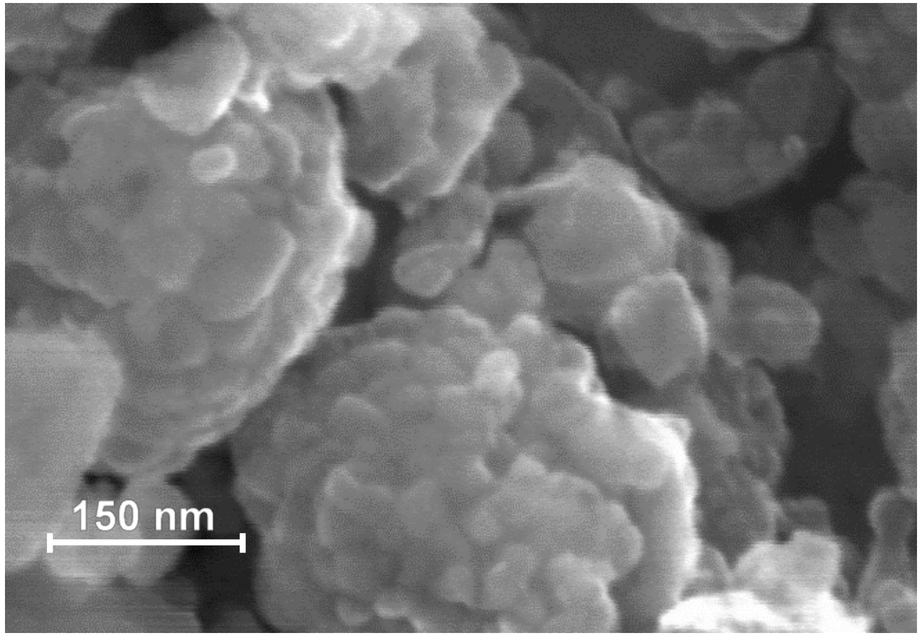
- NaCl decreases combustion temperature and decelerates propagation.

Project Update

Optimal composition: 20% excess Mg and 10 – 30 wt% NaCl



- 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



SEM image of ZrB_2 obtained with 30 wt% NaCl

Project Update

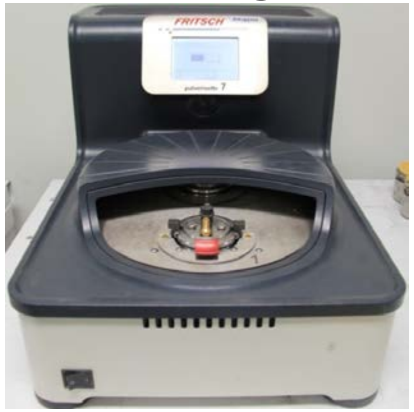
Pressureless sintering

- ZrB_2
  - Commercial
  - Produced by MASHS
- Sintering additives
  - $MoSi_2$
  - B_4C

Mixing

3-D inversion kinematics mixer (Inversina 2L)

Milling



Planetary ball mill (Fritsch Pulverisette 7)

Compacting

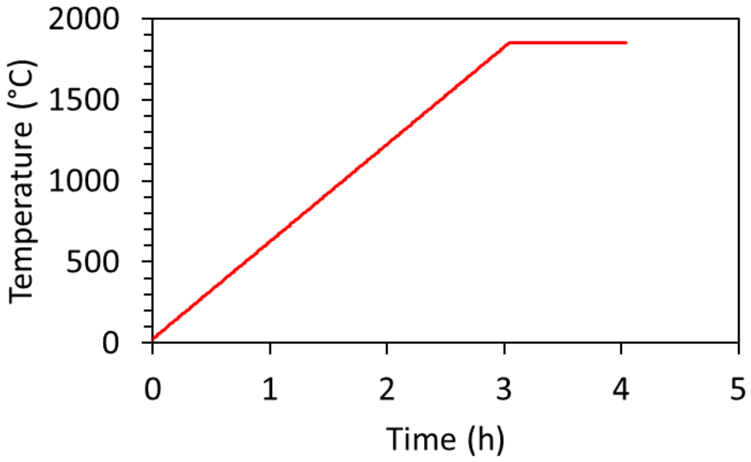
Hydraulic press

- Pellet size
  - 6 mm
  - 13 mm

Project Update

Induction Heating System (MTI Corp., EQ-SP-50KTC)

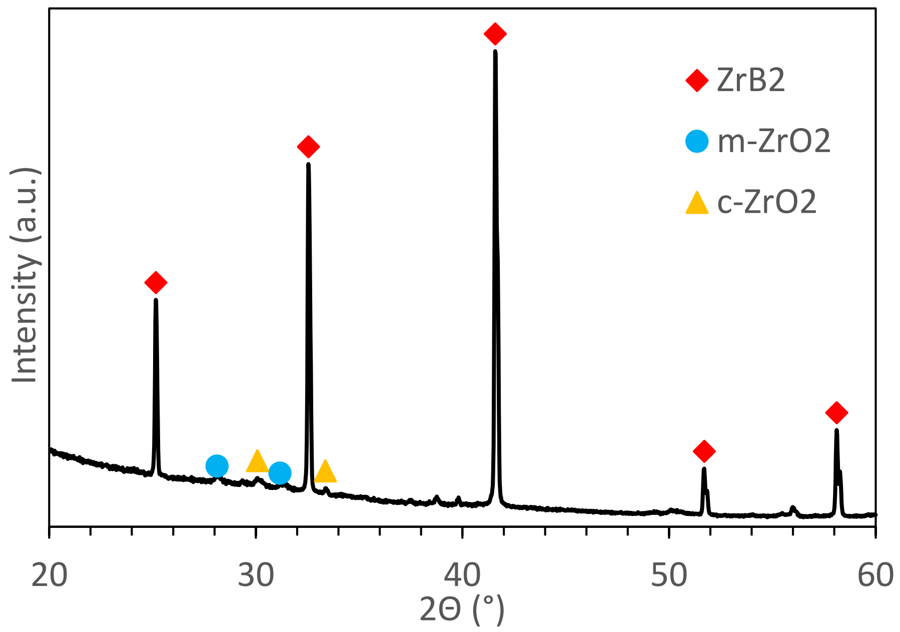
- Induction furnace
  - Graphite crucible
  - Insulation: graphite felt and ceramics
- Power supply (30 kW)
- Cooling system
  - Water chiller
- Operating environment
  - Argon feeding system (200 mL/min)
  - Vacuum pump (1 Torr)
- Programmable temperature controller
  - Thermocouple (up to 2000 °C)



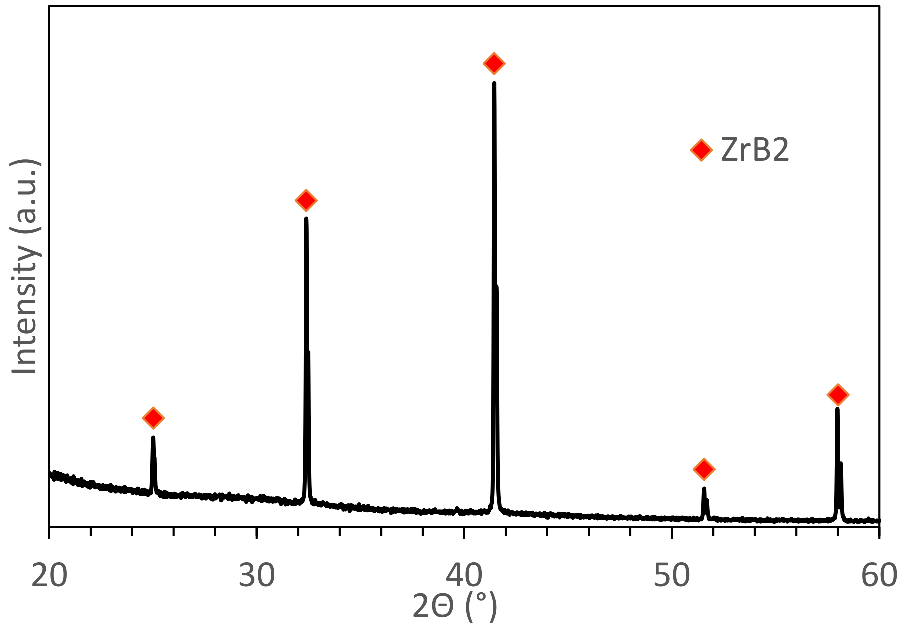
Heating profile

Project Update

Removal of ZrO_2 with no additives



After heating at 1800 °C

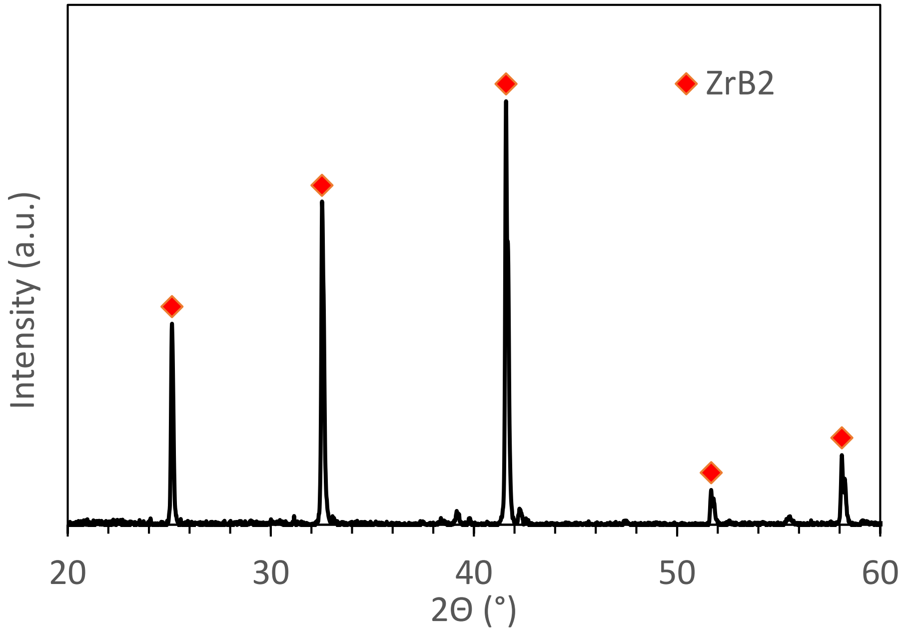


After heating at 2000 °C

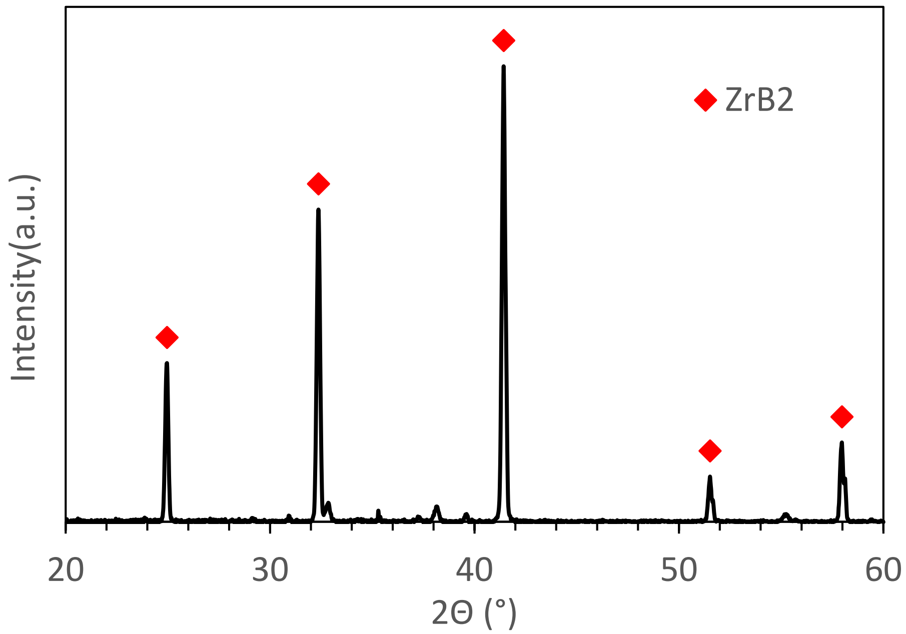
- ZrO_2 disappeared with increasing temperature up to 2000 °C.

Project Update

Reduction of ZrO_2 by additives



After heating at 1850°C with $MoSi_2$



After heating at 1850°C with B_4C

- With each additive, ZrO_2 disappeared (was reduced) at 1850 °C.

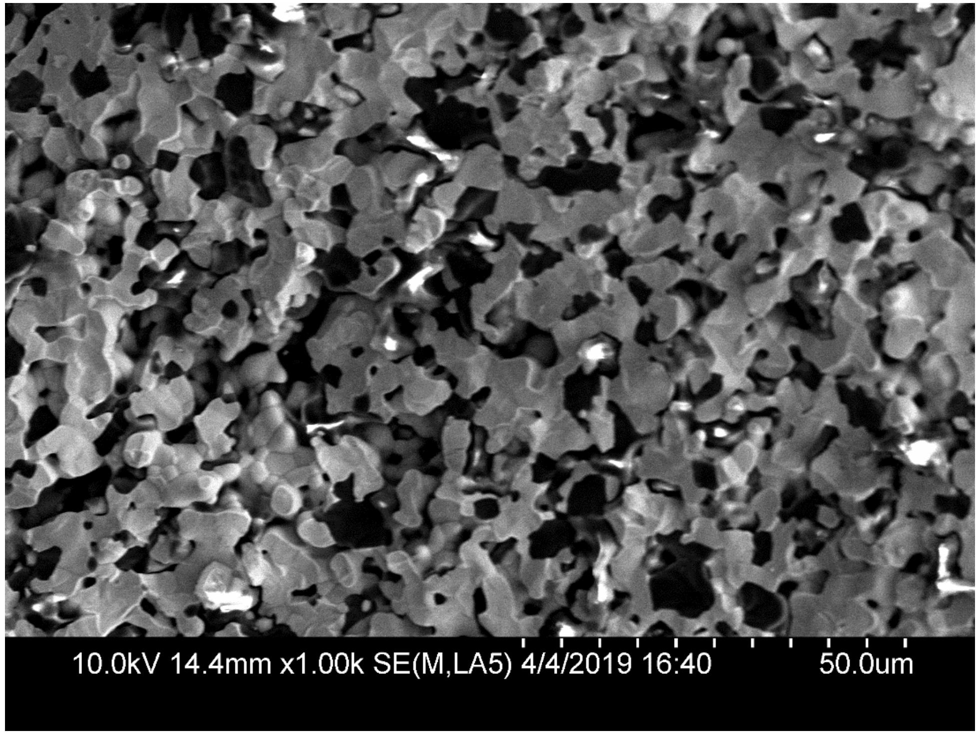
Project Update

Effect of milling on relative density

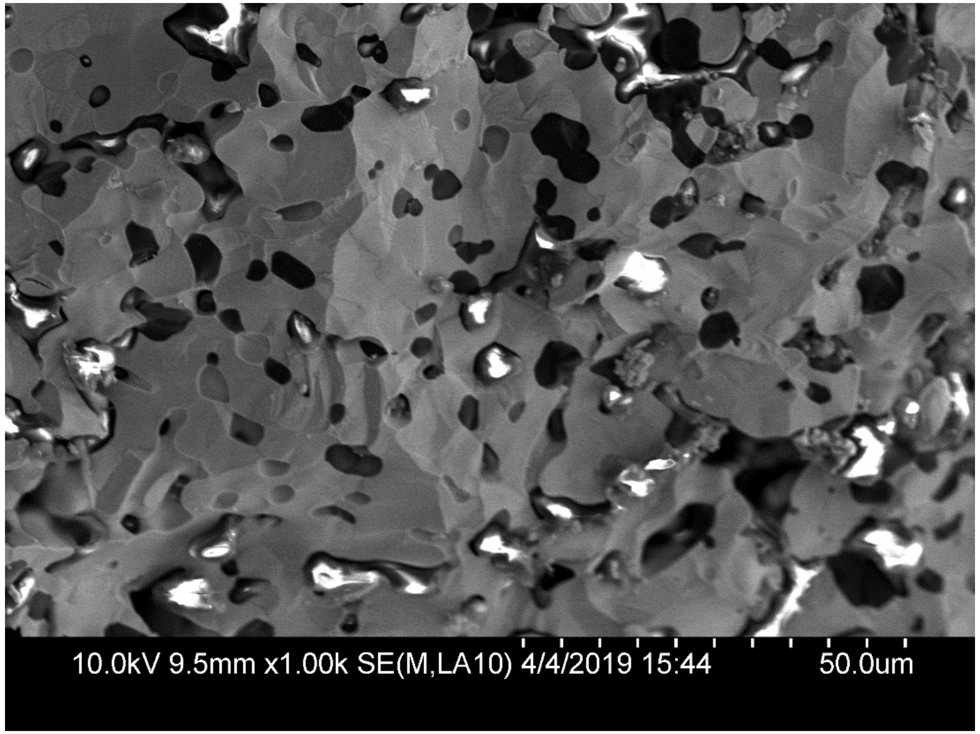
- No milling
  - After pressing: 60%
  - After heating: 38%
- Milling for 1 min
  - After pressing: 60%
  - After heating: 60%
- Milling for 5 min
  - After pressing: 70%
  - After heating: 70%
- Conclusion: Milling is critical for sintering.

Project Update

SEM images of ZrB_2 after heating at 1850 °C



Heating with no additive



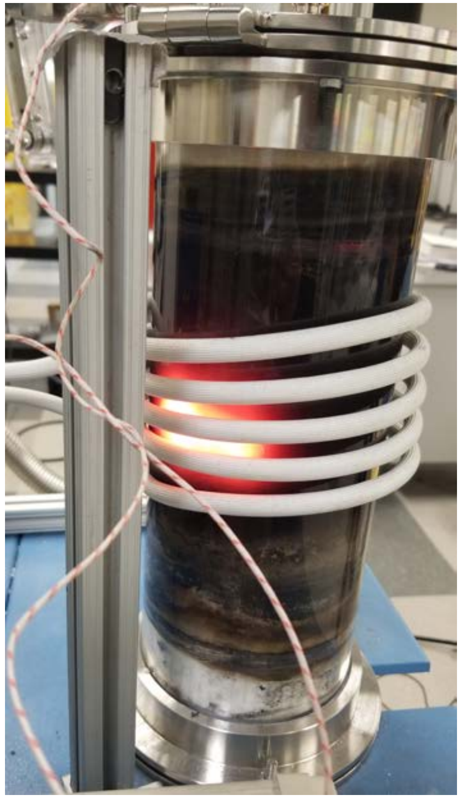
Heating with B_4C

- B_4C promotes sintering and decreases porosity.

Project Update

Technological and/or collaborative challenges

- Damage of refractory liner
  - Needs frequent replacement.
- Damage of thermocouple shell
  - Tungsten coating has prolonged the thermocouple lifetime.
  - O_2 impurity was removed from Ar using heated titanium sponge.



Hot spot on the furnace surface

Damaged tip of thermocouple

Preparing Project for Next Steps

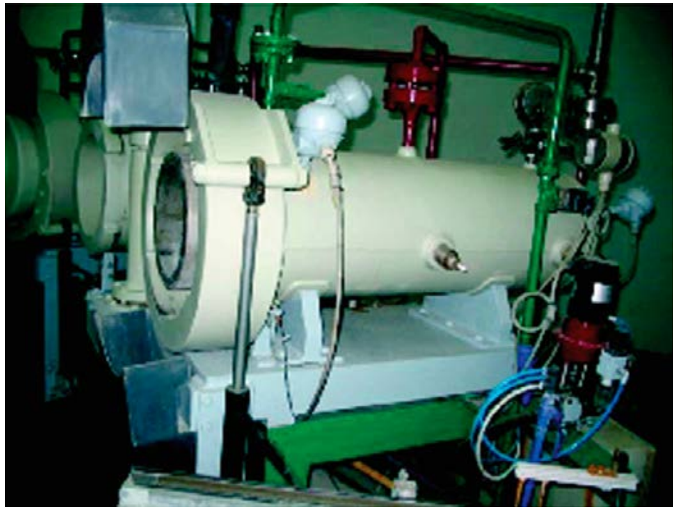
Market Benefits/Assessment

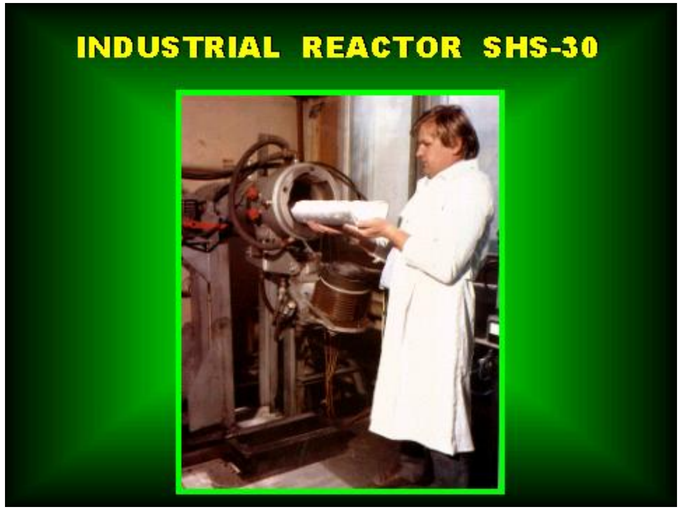
- This project addresses the lack of low-cost methods for fabrication of ZrB_2 and HfB_2, promising materials for MHD electrodes and for hypersonics as well.
- This program aims to develop a low-cost, low-energy-consuming technique for the fabrication of UHTCs based on ZrB_2 and HfB_2 from inexpensive raw materials ZrO_2, HfO_2, and B_2O_3, with Mg as a reactant and NaCl as an inert diluent.
- Optimal composition and process parameters for a high conversion of oxides to borides have been determined.

Preparing Project for Next Steps

Technology-to-Market Path

- How the end result of this project can be transferred to market or integrated into existing industry solutions to achieve FE objectives:
  - The mechanical activation and combustion synthesis steps have to be scaled up.
  - An effective method for densification should be used.





Industrial SHS reactors

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

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

Preparing Project for Next Steps

NATIONAL ENERGY TECHNOLOGY LABORATORY

Technology-to-Market Path

- Remaining technology challenges in achieving the objective
  - Scale-up of mechanical activation and combustion synthesis
- Potential new research
  - Explore densification using hot pressing or spark plasma sintering
- Needed industry collaborators
  - Companies that possess or can develop an industrial SHS reactor
  - Companies that possess hot pressing or spark plasma sintering

Concluding Remarks

Applicability of technology to Fossil Energy and alignment to strategic goals

- The technology addresses one of the key challenges for Fossil Energy – insufficient efficiency of new and existing coal-fired power plants
- MHD direct power extraction has the potential to significantly increase the efficiency of coal-fired power plants.
- The project focuses on a major hurdle in the MHD development: the lack of suitable electrode materials.
- The project aims 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.

Project's next steps and current technical challenges

- Scaling up the mechanical activation and combustion synthesis steps
- Robust methods for densification of products