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

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Organization:	**The University of Texas at El Paso**
Grant:	**DE-FE-0026333**
Period:	**10/1/2015 – 9/30/2018**
Program Manager:	**Jason Hissam**

Outline

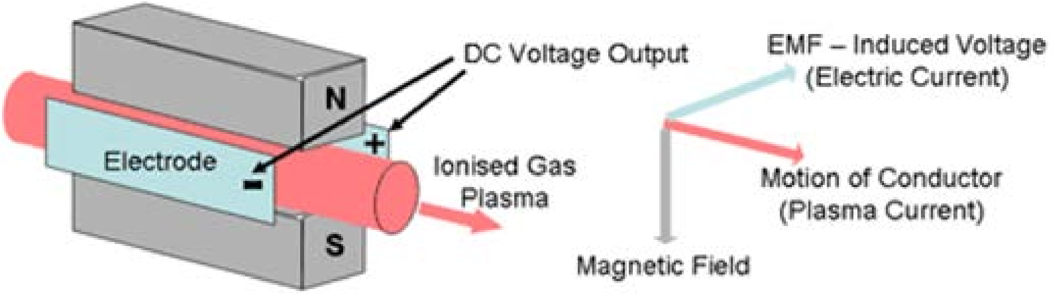
- Project Goal
- Background
- Objectives
- Task Descriptions
- Team Description and Assignments
- Gantt Chart
- Milestones

Project 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 will investigate use of mechanical activation-assisted self-propagating high-temperature synthesis (MASHS) followed by pressureless sintering for the fabrication of fully dense, near-net-shape ceramic materials 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.

Background



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

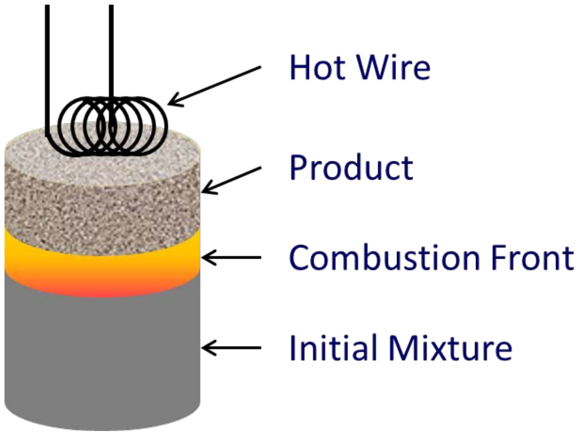
- **Borides of zirconium and hafnium (ZrB_2 and HfB_2) belong to the class of Ultra High Temperature Ceramics (UHTCs)**
  - Extremely high melting temperatures (about 3250 °C)
  - High hardness
  - High electrical and thermal conductivities
  - Chemical stability
  - Good thermal shock and oxidation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



Hot Wire

Product

Combustion Front

Initial Mixture

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

Large-scale ceramic-lined steel pipes produced by SHS

A.G. Merzhanov, *J. Mater. Chem.* 14 (2004) 1779

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

  - Done 40 years ago.
  - 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 will be 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 will be used.

- NaCl will be used as an agent that facilitates ball milling.
  - NaCl diluent also decreases 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 and cooling rates during combustion, SHS products have high defect concentrations in the lattice, which enhances the sinterability of ZrB_2 and HfB_2.
- 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 using standard powder-processing methods, thus reducing processing costs

Pressureless Sintering

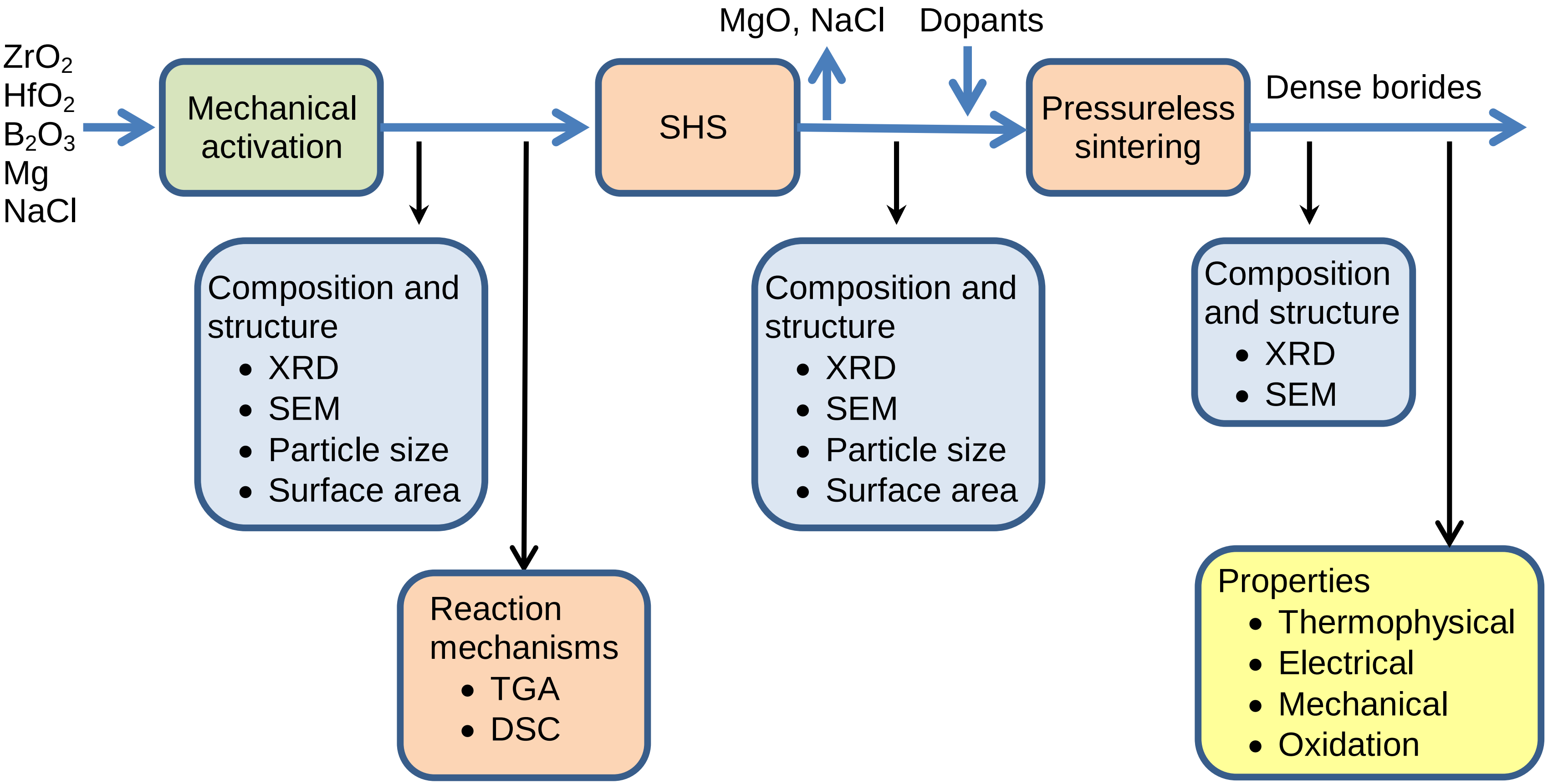
- **Dopants**
  - Carbon containing additives such as C, B_4C, WC, VC or their mixtures
  - Transition metals (Fe, Cr and Ni) and refractory metal silicides ($MoSi_2$, $TiSi_2$ and $HfSi_2$)
- **Nanoscale powders**
  - Nanoscale powders produced by SHS are especially promising because they also have 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
    - densification of 97.5% at 2223 K
    - without NaCl only 81.2% densification

Objectives

- 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.

Task Descriptions



ZrO_2
HfO_2
B_2O_3
Mg
NaCl

Mechanical activation

SHS

MgO, NaCl

Dopants

Pressureless sintering

Dense borides

Composition and structure
- XRD
- SEM
- Particle size
- Surface area

Reaction mechanisms
- TGA
- DSC

Composition and structure
- XRD
- SEM
- Particle size
- Surface area

Composition and structure
- XRD
- SEM

Properties
- Thermophysical
- Electrical
- Mechanical
- Oxidation

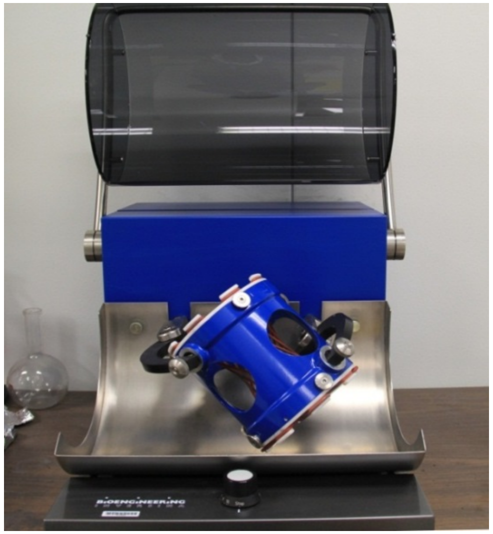
Work Flowchart

Mechanical Activation

- Activated $ZrO_2/B_2O_3/Mg/NaCl$ and $HfO_2/B_2O_3/Mg/NaCl$ mixtures will be prepared.
- ZrO_2/B_2O_3 and HfO_2/B_2O_3 mole ratios will be 1:1.
- Mg/B_2O_3 mole ratio will be varied to find the optimal Mg concentration:
  - The conversion of metal oxides to borides is close to 100%.
  - The amount of unreacted Mg is minimal.
- The amount of NaCl will also be varied.

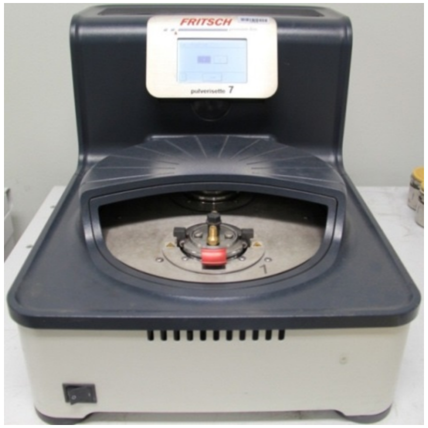
Mechanical Activation, cnt'd

Mixing



3-D inversion kinematics mixer (Inversina 2L)

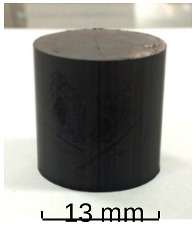
Milling



Planetary ball mill (Fritsch Pulverisette 7)

Shaker mill (SPEX SamplePrep 8000D)

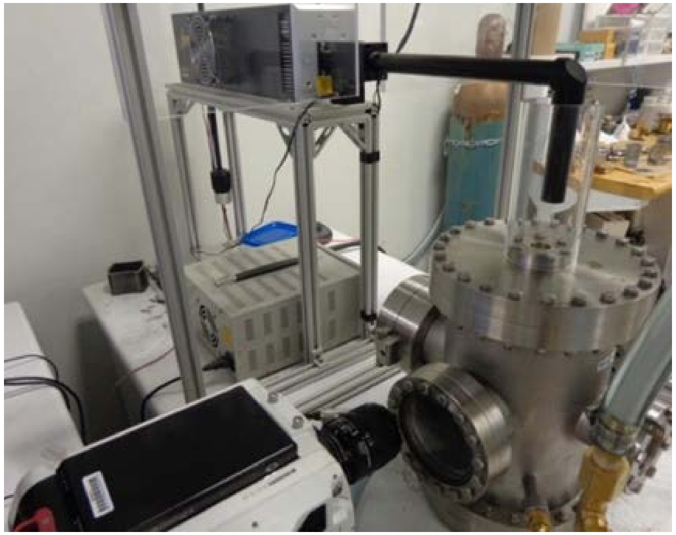
Pressing



SHS

- Combustion characteristics (the maximum temperature and the front propagation velocity) will be determined.
    - Ar environment
    - The pellet is ignited at the top.
    - High-speed video recording
    - Thermocouples
- To remove MgO and Mg, the SHS products will be submerged in HCl.
- To remove NaCl, the solution will be filtered and a solid residue will be washed in water.

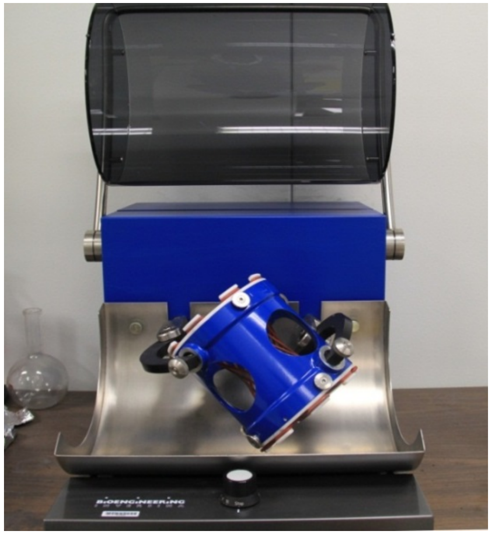
Hot-wire ignition facility



Laser ignition facility

Sintering

Mixing with dopants



3-D inversion kinematics mixer (Inversina 2L)

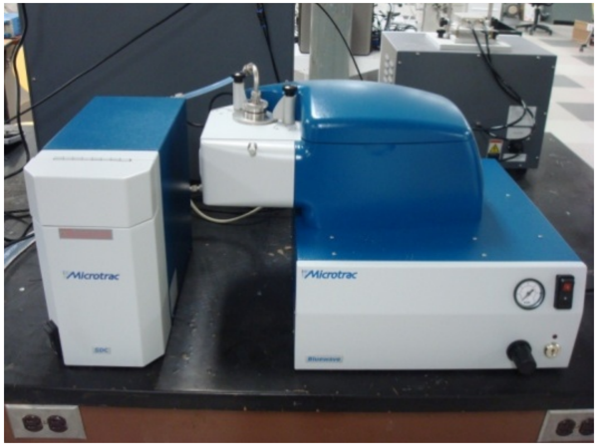
Pressing

Sintering

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

Composition and Structure

- X-ray diffraction analysis (Bruker D8 Discover XRD)
- Scanning electron microscopy (SEM, Hitachi S-4800)
- Particle size distribution
- Specific surface area

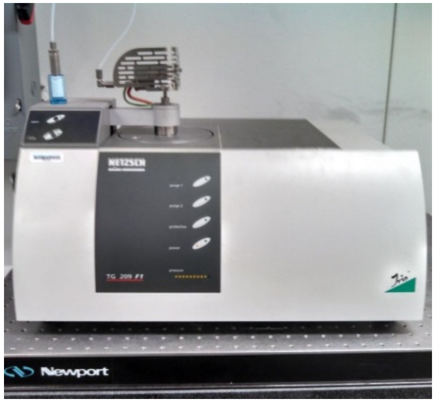


Particle size analyzer (Microtrac Bluewave)

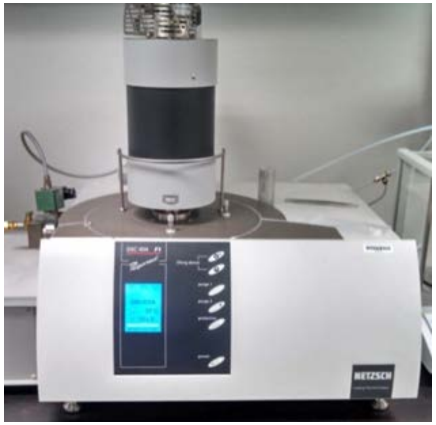
Surface area analyzer (Microtrac SAA)

Reaction Mechanisms

- Thermogravimetric analysis (TGA)
- Differential scanning calorimetry (DSC)
  - The characteristic temperatures of different processes will help understand the reaction mechanisms occurring during the SHS process.
  - To determine the kinetics of the involved reactions, TGA and DSC tests will be conducted at different heating rates.



Thermogravimetric analyzer (Netzsch TGA 209 F1 Iris)



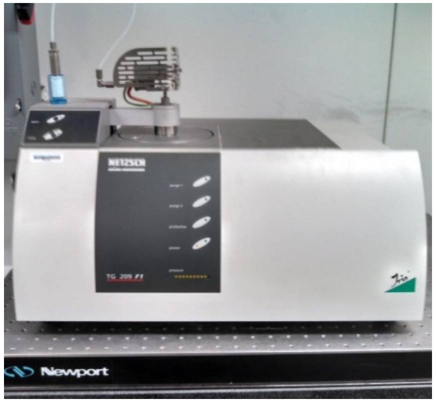
Differential scanning calorimeter (Netzsch DSC 404 F1 Pegasus)

Thermophysical Properties

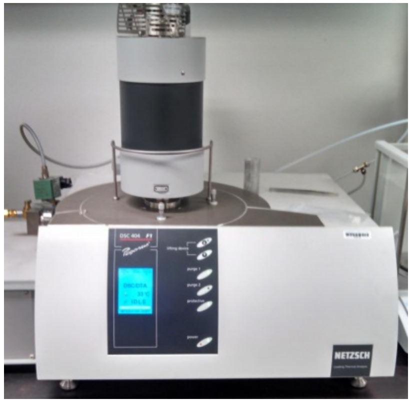
- Specific heats of the obtained ZrB_2 and HfB_2 based materials will be measured by DSC
  - From 25 to 1550°C
- Thermal diffusivities will be determined by laser flash analysis
  - From 25 to 1100°C
- Thermal conductivities will be calculated based on thermal diffusivity, specific heat, and density

Laser flash apparatus (Netzsch LFA-457 MicroFlash)

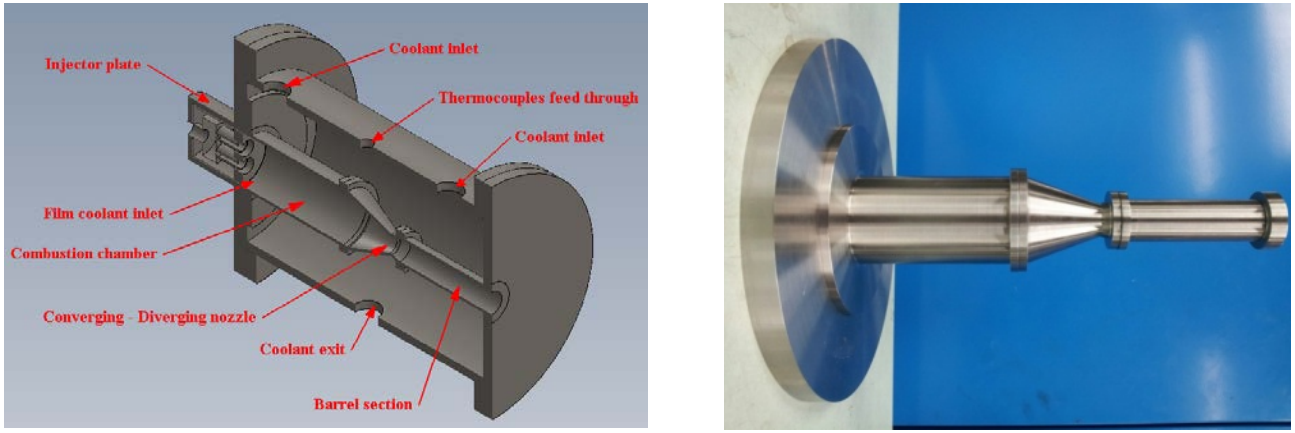
Oxidation Properties



Thermogravimetric analyzer
(Netzsch TGA 209 F1 Iris)



Differential scanning calorimeter
(Netzsch DSC 404 F1 Pegasus)



High-temperature, high-velocity flow facility

Electrical Properties

- The electrical resistance and impedance of the obtained ZrB_2 and HfB_2 materials will be measured in a temperature range from 25 to 900°C using a facility that includes:
  - HP LCR meter
  - Sample loading assembly
  - Custom-made temperature-controlled furnace
  - Data acquisition system

Mechanical Properties

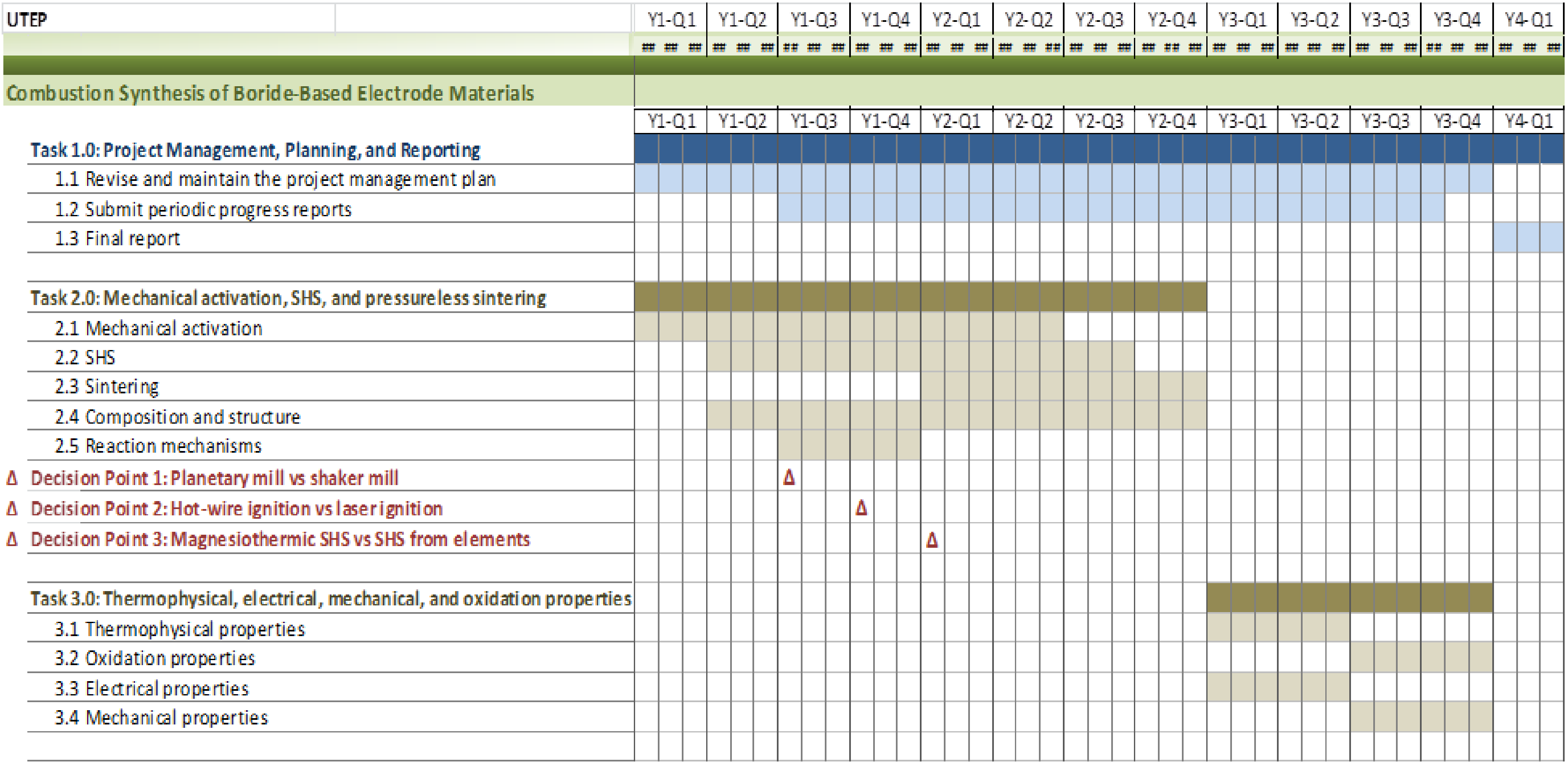
- The mechanical strength and hardness of the obtained ZrB_2 and HfB_2 materials will be determined using load-controlled nano-indentation tests.

Hysitron TI 750 Ubi

Team Description and Assignments

- **PI: Dr. Shafirovich; leads the project; responsible for:**
  - Mechanical activation
  - Combustion characteristics
  - Pressureless sintering
  - Particle size and surface area
  - Thermoanalytical experiments
  - Thermophysical and oxidation properties
- **Co-PI: Dr. Ramana; responsible for:**
  - Composition and microstructure (XRD and SEM)
  - Mechanical and electrical properties
- **Graduate student: Sergio Cordova**
- **Undergraduate student: Arturo Catalan**

Gantt Chart



UTEP	Y1-Q1	Y1-Q2	Y1-Q3	Y1-Q4	Y2-Q1	Y2-Q2	Y2-Q3	Y2-Q4	Y3-Q1	Y3-Q2	Y3-Q3	Y3-Q4	Y4-Q1
	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##	## ## ##
Combustion Synthesis of Boride-Based Electrode Materials													
	Y1-Q1	Y1-Q2	Y1-Q3	Y1-Q4	Y2-Q1	Y2-Q2	Y2-Q3	Y2-Q4	Y3-Q1	Y3-Q2	Y3-Q3	Y3-Q4	Y4-Q1
Task 1.0: Project Management, Planning, and Reporting	■	■	■	■	■	■	■	■	■	■	■	■	■
1.1 Revise and maintain the project management plan	■	■	■	■	■	■	■	■	■	■	■	■	
1.2 Submit periodic progress reports			■	■	■	■	■	■	■	■	■	■	
1.3 Final report													■
Task 2.0: Mechanical activation, SHS, and pressureless sintering	■	■	■	■	■	■	■	■					
2.1 Mechanical activation	■	■	■	■	■	■							
2.2 SHS		■	■	■	■	■	■						
2.3 Sintering					■	■	■	■					
2.4 Composition and structure		■	■	■	■	■	■	■					
2.5 Reaction mechanisms			■	■									
Δ Decision Point 1: Planetary mill vs shaker mill			Δ										
Δ Decision Point 2: Hot-wire ignition vs laser ignition				Δ									
Δ Decision Point 3: Magnesiothermic SHS vs SHS from elements					Δ								
Task 3.0: Thermophysical, electrical, mechanical, and oxidation properties									■	■	■	■	
3.1 Thermophysical properties									■	■			
3.2 Oxidation properties											■	■	
3.3 Electrical properties									■	■			
3.4 Mechanical properties											■	■	

Milestones

Budget Period	Quarter	Milestone Description	Planned Completion
1	Q1	Updated Project Management Plan	10/31/2015
1	Q2	Preliminary results on MASHS of ZrB_2 and HfB_2 obtained.	3/31/2016
1	Q3	Preliminary results on the reaction mechanisms (TGA and DSC) obtained.	6/30/2016
1	Q4	The reaction mechanism studies using TGA and DSC are complete.	9/30/2016
2	Q1	Preliminary results on pressureless sintering obtained.	12/31/2016
2	Q2	Mechanical activation task is complete.	3/31/2017
2	Q3	SHS experiments are complete.	6/30/2017
2	Q4	Pressureless sintering experiments are complete.	9/30/2017
3	Q1	Preliminary results on thermophysical and electric properties obtained.	12/31/2017
3	Q2	Study of thermophysical and electric properties is complete.	3/31/2018
3	Q3	Preliminary results on oxidation and mechanical properties obtained.	6/30/2018
3	Q4	Study of oxidation and mechanical properties is complete. The optimal operating parameters and dopants for the fabrication of ZrB_2 and HfB_2 based materials for MHD electrodes by mechanically-assisted SHS followed by pressureless sintering are reported. The data on thermophysical, electrical, mechanical, and oxidation properties of the obtained materials are reported. Conclusions on the feasibility of the tested methods for the fabrication of ZrB_2 and HfB_2 based materials are made.	9/30/2018