Boride Based Electrode Materials for MHD Direct Power Extraction

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Outline

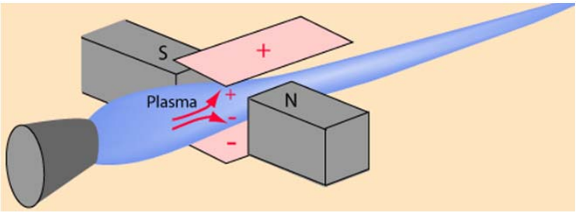
* Introduction and Objectives

* Research Plan –Tasks

* Researchers involved

* Work performed during the last quarter

* Acknowledgment



Courtesy: http://hyperphysics.phy-astr.gsu.edu/hbase/magnetic/maspec.html

Introduction

- Full Project Title: TA [A]: Boride Based Electrode Materials with Enhanced Stability under Extreme Conditions for MHD Direct Power Extraction (Grant #: DE-FE0022988)
- Topic Area A: Materials Development to Support Direct Power Extraction
- PI/PD: Indrajit Charit; co-PI: Krishnan Raja
- Funding Opportunity Number: DE-FOA-00001032
- CFDA Number: 81.057; University Coal Research
- Project Duration: July 1, 2014 to June 30, 2017

Introduction

- MHD direct power extraction – several challenges
- Operative conditions of MHD ducts - very aggressive due to high temperature, high mass flow rate and corrosion
- Electrodes which extract current are subjected to highly arduous conditions.
- Oxide based materials (such as Sr-doped $LaCrO_3$) as electrodes – high electrical resistivity, low thermal conductivity and volatility at high temperatures are issues.
- Development of next generation electrode materials is critical

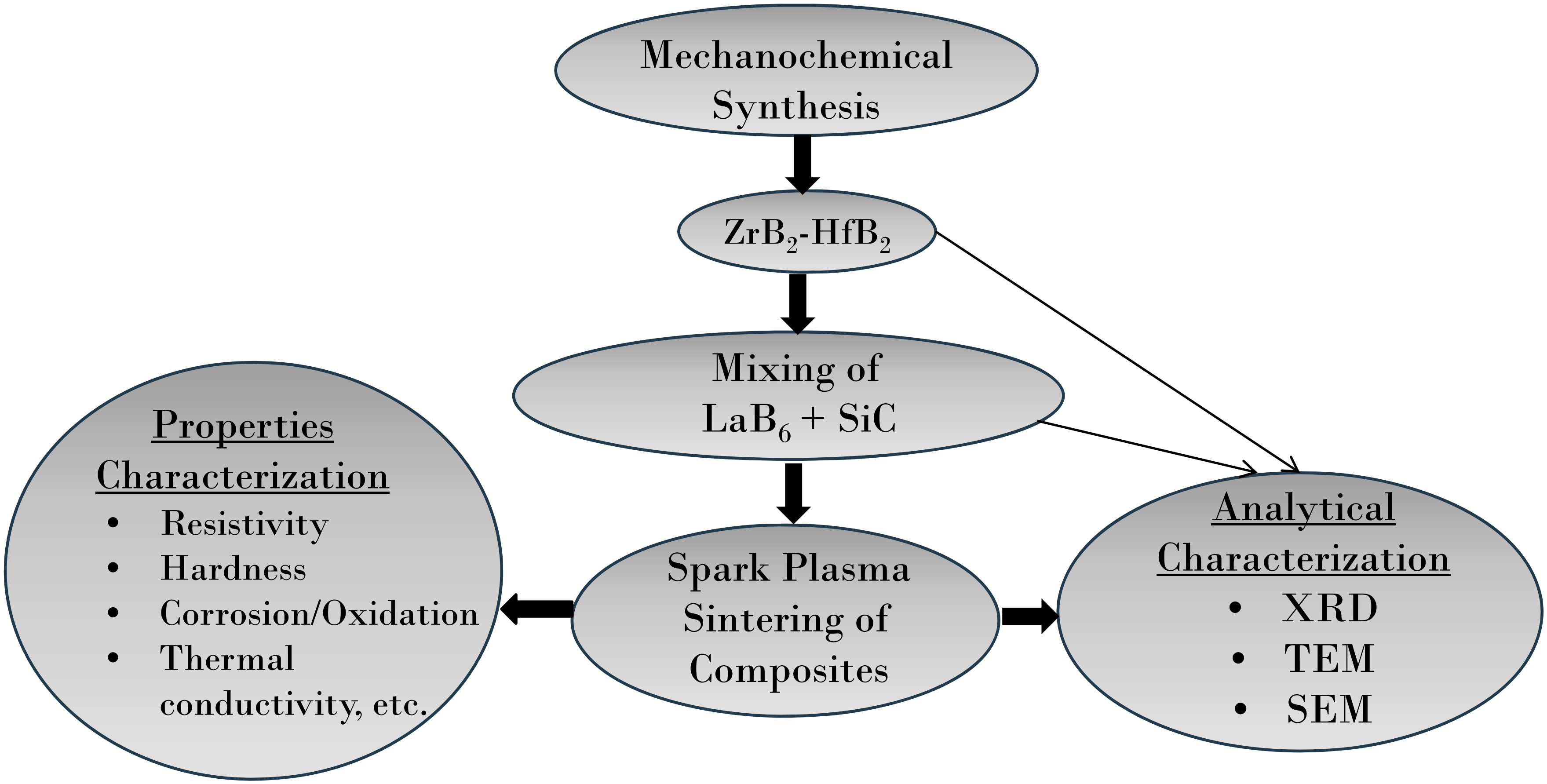
Objectives

- Synthesize ternary solid solutions of transition metal borides containing ZrB_2 and HfB_2 by the mechanically induced self-sustaining reaction process.
- Improve high temperature oxidation resistance (up to 2000 ^oC) of the borides by modifying the boride chemistry.
- Improve the high temperature oxidation resistance of transition metal borides by providing an electrochemical anodic oxide layer
- Evaluate the electrical, mechanical, and thermal stability of the developed materials
- Understand the mechanisms of environmental degradation and phase stability via microstructural characterization
- Develop a unique ultrahigh temperature electrode material that has enhanced stability under the extreme operating conditions of the MHD direct power extraction

Research Plan

- Task 1: Project Management, Planning and Reporting
- Task 2: Synthesis of ZrB_2-HfB_2 Solid Solution
- Task 3: Spark Plasma Sintering of ZrB_2-HfB_2-SiC-LaB_6 composite
- Task 4: Electrochemical Coating for Oxidation Resistance
- Task 5: Characterization of Microstructure and Material Properties
- Task 6: High Temperature Oxidation Study
- Task 7: Hot Corrosion Study of the Composite Material

Work Flowchart



Task 2: Solid Solution Synthesis

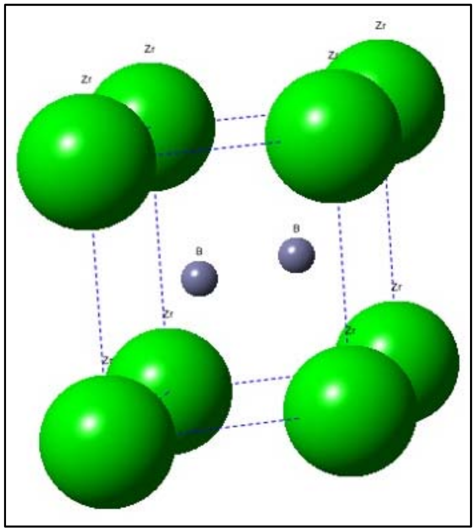
- Solid solutions of ZrB_2-HfB_2 will be synthesized using mechano-chemical approach.

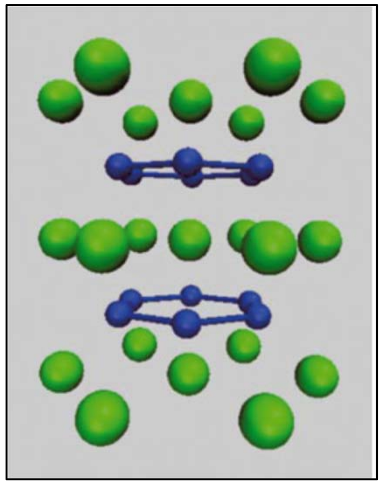
- Investigate borides enriched with metal such as $(Zr,Hf)B_{2-x}$ with x varying from 0.1 – 0.3.

- ΔH_{298} = -79.06 and -77.84 kcal/mol for HfB_2 and ZrB_2 respectively.*

* M. Binnewies and E. Milke, Thermochemical Data of Elements and Compounds, Wiley-VCH, Weinheim, Germany, 1999

Task 2: Solid Solution Synthesis (contd.)





Hexagonal crystal structure of ZrB_2 and HfB_2 with a symmetry group P6/mmm (left)

Layered atomic arrangement of the diboride structures illustration (right)

Material	Crystal structure / Space group	a (nm)	c (nm)	Density (g/cm^3)	Melting Point, °C
ZrB_2	Hexagonal (D_{6h}), P6/mmm	0.317	0.353	6.08	~3246
HfB_2	Hexagonal(D_{6h}), P6/mmm	0.314	0.348	10.5	~3250

J.W. Lawson, C.W. Bauschlicher Jr., and M.S. Daw, Ab Initio Computations of Electronic, Mechanical, and Thermal Properties of ZrB_2 and HfB_2, J. Am. Ceram. Soc., (2011) 94:3494–3499.

Task 2: Solid Solution Synthesis (contd.)

- Mechano-chemical synthesis by high-energy ball milling
    - Zr, Hf, and B in their pure elemental form
    - Argon atmosphere
- Powder handling in a glove box controlled atmosphere
    - Oxygen and moisture below 2 ppm
- Milling variables: Milling time, ball to powder ratio (BPR) and ball size

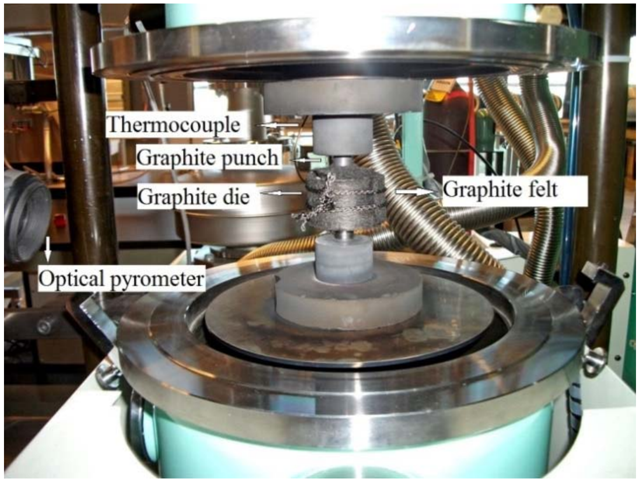
Glove Box

Mixer/Mill

Vial/Steel Balls

Task 3: Spark Plasma Sintering

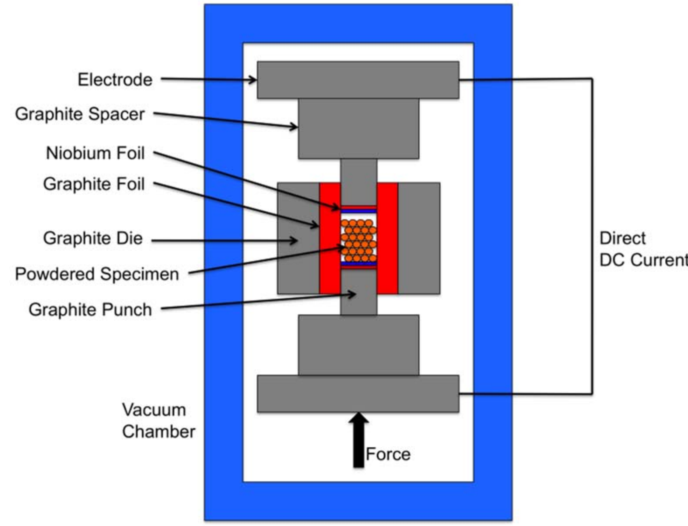
- Spark plasma sintering
  - Higher than 95% of the theoretical density
  - Density to be measured by Archimedes method
- SiC and LaB_6 added as sintering aids
  - Increase in the oxidation resistance
  - Aid in thermionic emission control
  - Prepared by mixing the boride solid solutions with:
    - Up to 20 vol% SiC
    - Up to 10 mol% LaB_6
    - Mixing will be carried out by ball milling for different durations

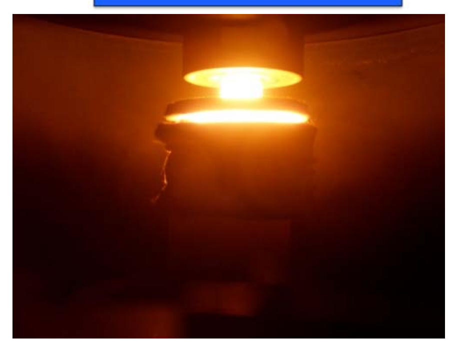


Dr. Sinter 515S machine available at CAES, Idaho Falls

Task 3: Spark Plasma Sintering (contd.)

- Sintering at lower temperatures, shorter dwell times and rapid heating
- Simultaneous uniaxial pressing and passing of pulsed dc
- Heating due to Joule effect
- Local melting, evaporation of oxide layers, surface and volume diffusion enhance the neck formation





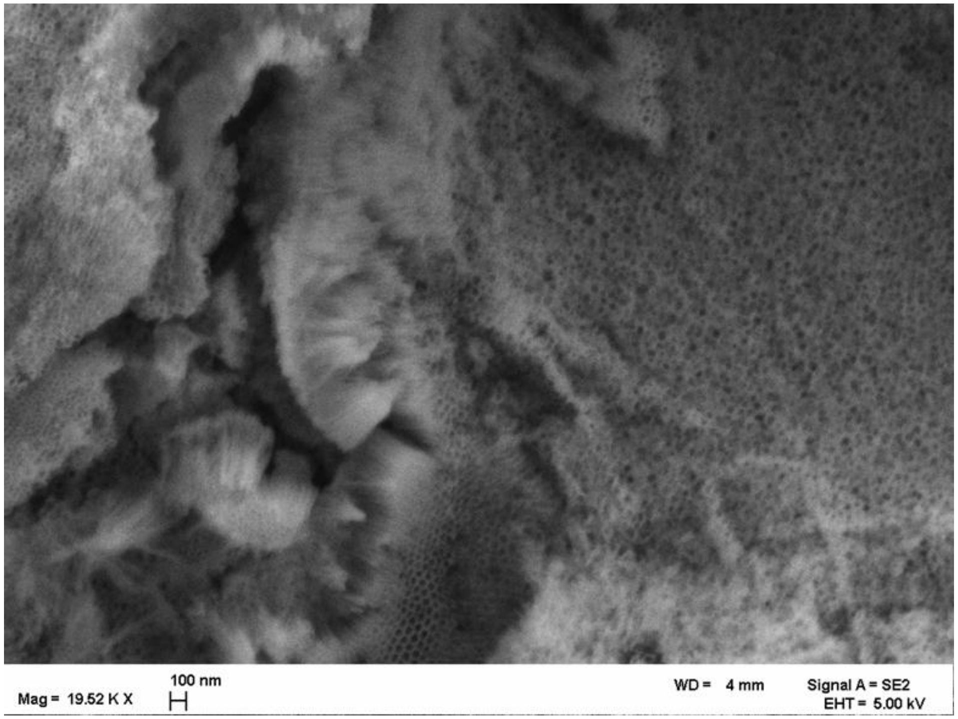
Courtesy: J. Webb, Ph.D. Dissertation, University of Idaho)

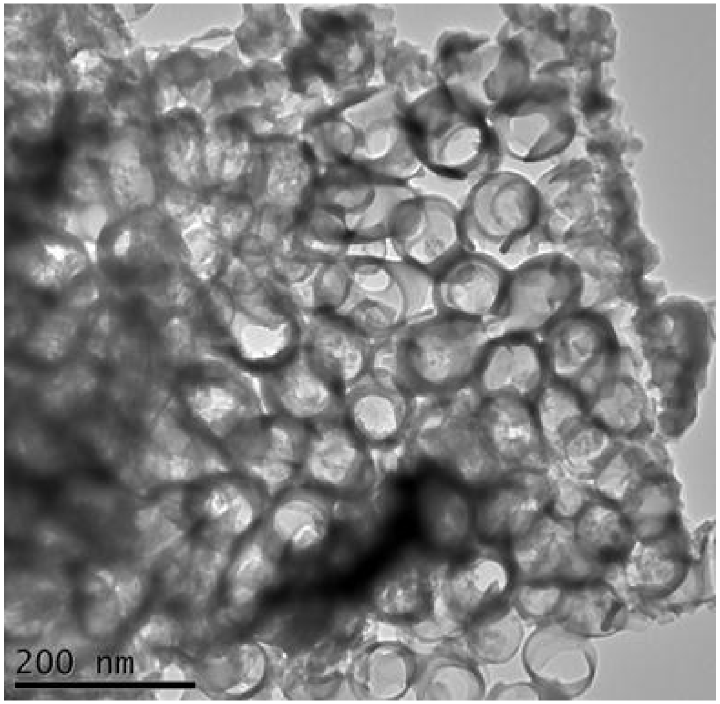
Task 4: Oxidation Resistant Coating

- Addition of SiC
  - Silica-rich borosilicate liquid layer wets crystalline oxide layer of HfO_2 and ZrO_2
  - $ZrB_2\ (c) + 2.5O_2 \rightarrow ZrO_2\ (c) + B_2O_3\ (l,g)$ (1)
  - $SiC + 1.5\ O_2 \rightarrow SiO_2\ (l) + CO_2\ (g)$ (2)
  - $2SiO_2\ (l) \rightarrow 2SiO\ (g) + O_2$ (3)
- Electrochemical Anodization
  - Nanoporous oxide layer onto boride-SiC
  - Creates Pillars of ZrO_2/HfO_2 with a liquid roof of borosilicate glass
  - Oxygen diffusion barrier created

J.B. Berkowitz-Mattuck, "High-Temperature Oxidation. 3. Zirconoum and Hafnium Diborides," J. Electrochem. Soc., 113 [9] 908-914 (1966)

Task 4: Oxidation Resistant Coating (contd.)





Morphology of the oxide layer formed on Zr-20wt%W alloy by anodization in 0.2M NH_4F + 5 vol% water + ethylene glycol solution at 40 V for 1 h.

Ju Li, Thomas J. Lenosky, Clemens J. Forst and Sidney Yip, Thermochemical and Mechanical Stabilities of the Oxide Scale of ZrB_2-SiC and Oxygen Transport Mechanisms, J. Am. Ceram. Soc., 91 [5] 1475–1480 (2008)

Task 5: Characterization

- Microstructural Characterization
  - HRTEM, SEM, XRD
- Electrical Characterization
  - EIS
- Mechanical Characterization
  - Hardness testing
- Thermal analysis
  - Differential scanning calorimetry
  - Thermal conductivity up to 1700 ^{o}C

Leco Vickers microhardness tester

Netzsch STA 409PC

Analytical Characterization Facilities

Siemens D5000 Diffractometer

Zeiss Leo Supra 35 VP SEM

JEOL 2010 HRTEM

Task 6: High Temp. Oxidation Study

- Oxidation kinetics up to 1800 °C
  - SEM, EDAX, XRD, HRTEM
  - Change O_2/Ar ratio of the purge gas
- Oxidation studies higher than 1800 °C
  - Oxy-acetylene torch at 2000 °C and 2200 °C
  - EIS, Mass Change
- Electrical conductivity up to 2200 °C
  - Four point probe method, EIS

Task 7: Hot Corrosion Resistance

- Samples coated with 0.2 to 4.0 mg/cm^2 Na_2SO_4
- Salt coated samples
  - Three temperatures between 1600 – 2200 °C
  - Maximum exposure time of 100 h
- Weight loss/gain will be recorded as a function of salt coating mass, temperature and time.
- Electrical conductivity and electrochemical impedance of tested samples will be measured.
- Microstructural examination will be carried out to understand the corrosion attack mechanism.

Project Milestones

- Procurement of all raw materials (end of Quarter 2)
- Optimization of mechanical milling process (end of Quarter 5)
- Optimized parameters for spark plasma sintering (end of Quarter 6)
- Optimization of anodization parameters (end of Quarter 7)
- Completion of high temperature oxidation studies under steady state conditions (end of Quarter 8)
- Graduation of the MS student (end of Quarter 8)
- Graduation of the PhD student (end of Quarter 12)

Team Member (PI/PD)

Indrajit Charit, Ph.D., P.E.
Associate Professor of Materials
Science & Engineering
Chemical and Materials Engineering
University of Idaho

Research interests:
High Temperature Materials;
Mechanical Behavior of Materials;
Advanced Materials Processing
Techniques

Team Member (Co-PI)

Krishnan S. Raja, PhD
Assistant Professor of Materials
Science & Engineering
Chemical and Materials Engineering
University of Idaho

Research Interests:
Energy Conversion Materials; Energy Storage Materials; Electrochemical Synthesis of Nanomaterials

Team Member (Graduate Student)

Steven Sitler

University of Idaho

- BS Chemical Engineering
- MS Materials Science & Engineering
- Pursuing PhD in Materials Science & Engineering

Steven Sitler preparing samples in glovebox

Team Member (Graduate Student)

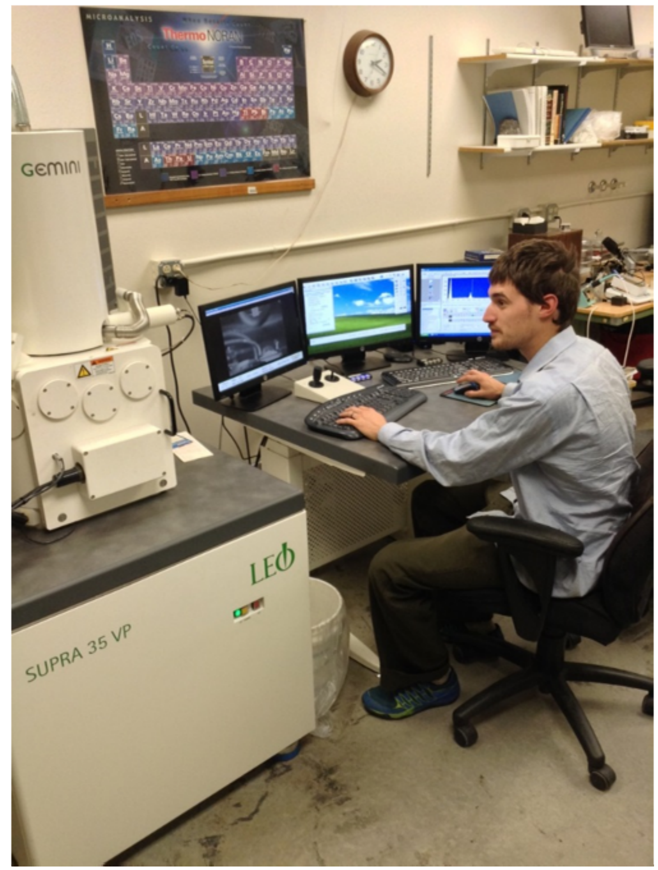
Cody Hill

Humboldt State University.

- BS in Chemistry and Physics

University of Idaho

- Pursuing MS in Materials Science & Engineering



Cody Hill analyzing samples on SEM

Team Member (Undergraduate Student)

Adam Grebil

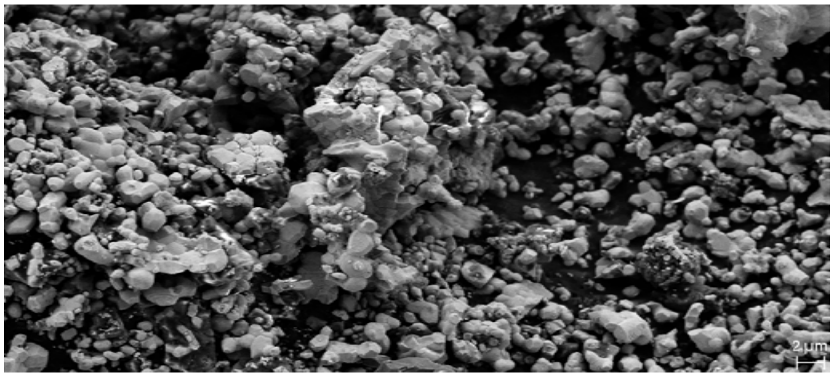
University of Idaho

- Pursuing BS in Materials Science & Engineering

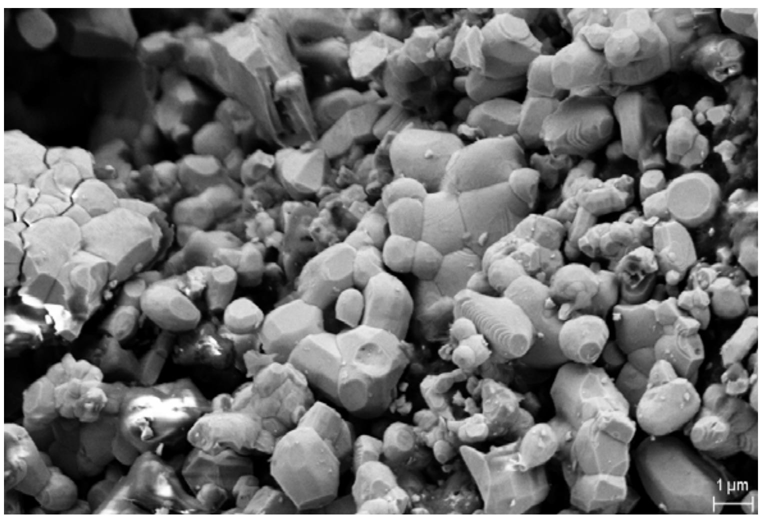
Adam Grebil checking the fit of a SPEX milling vial

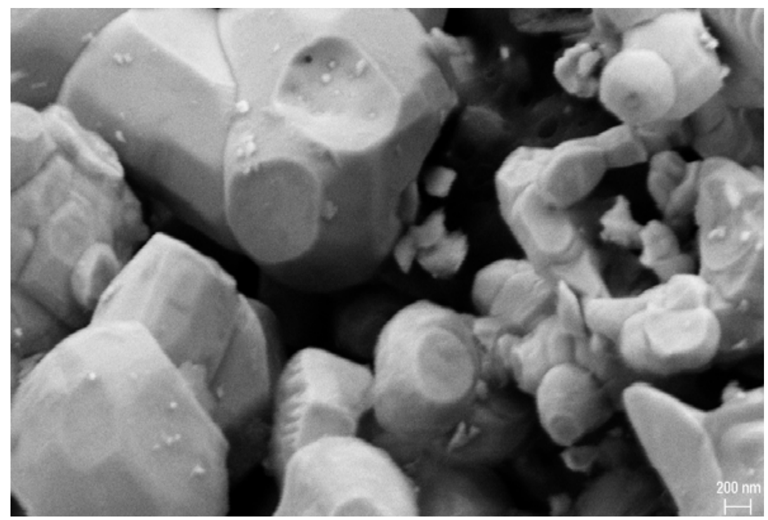
SEM Analysis:

As Received HfB_2 Powder

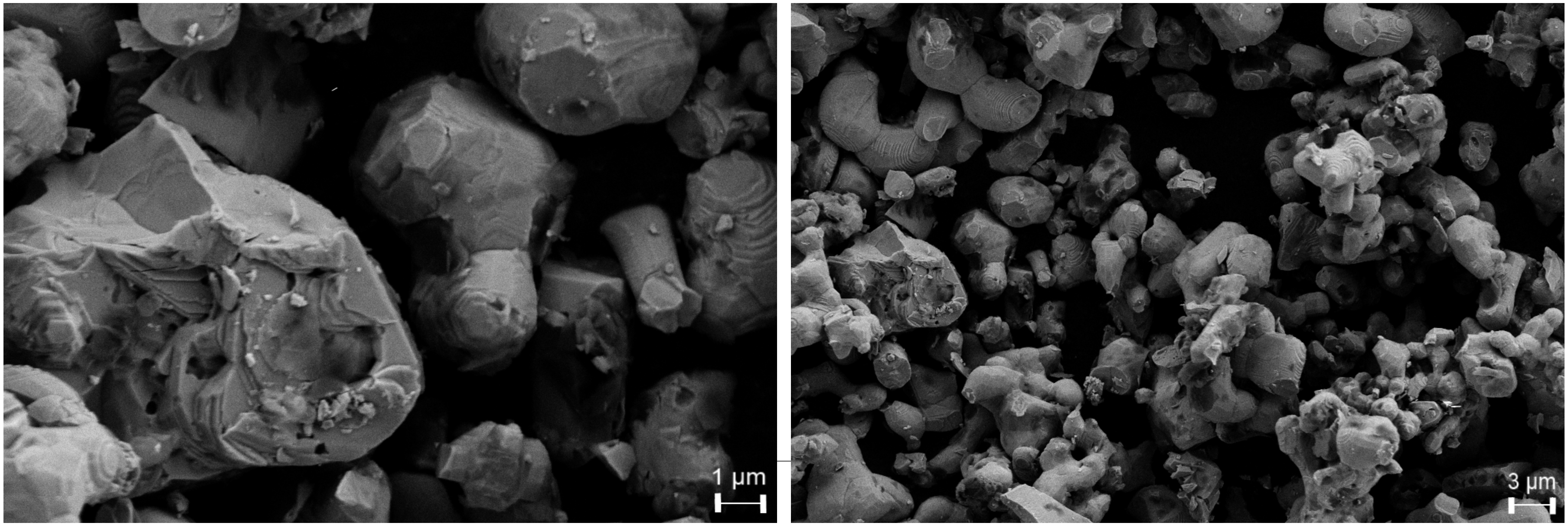


Hafnium Di-Boride (99.5% purity); -325 mesh size



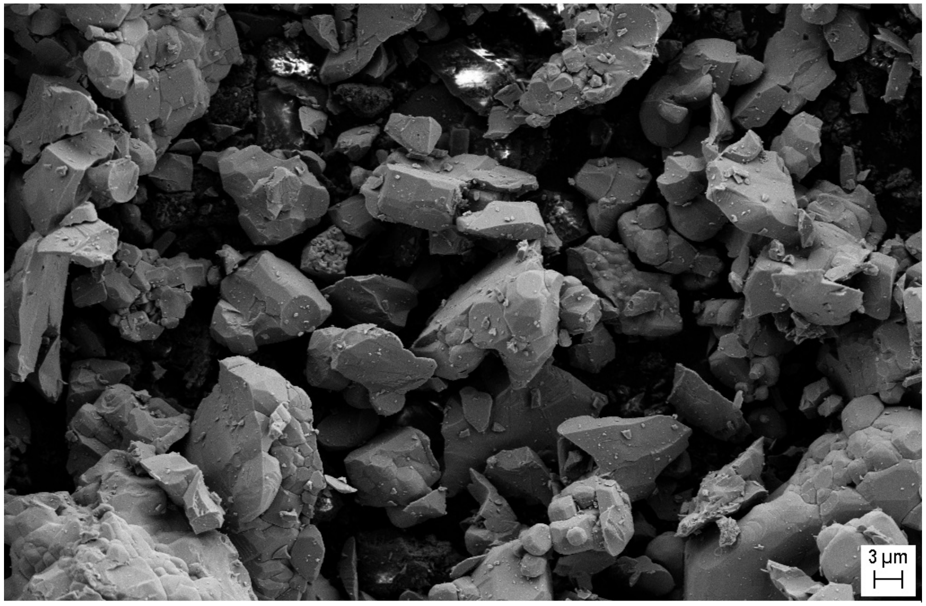


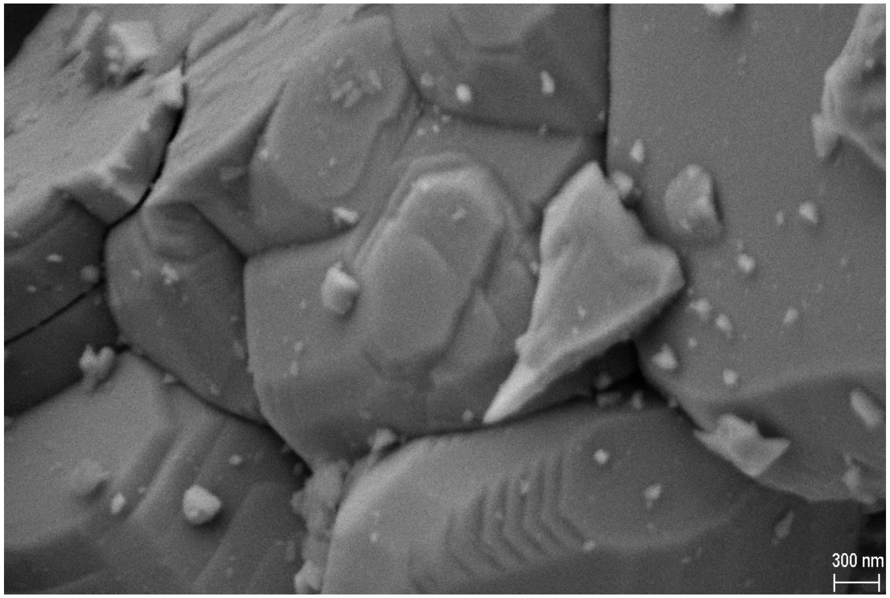
SEM Analysis: As Received ZrB_2 Powder



Zirconium Di-Boride Powder, 99.5% purity; -325 mesh size

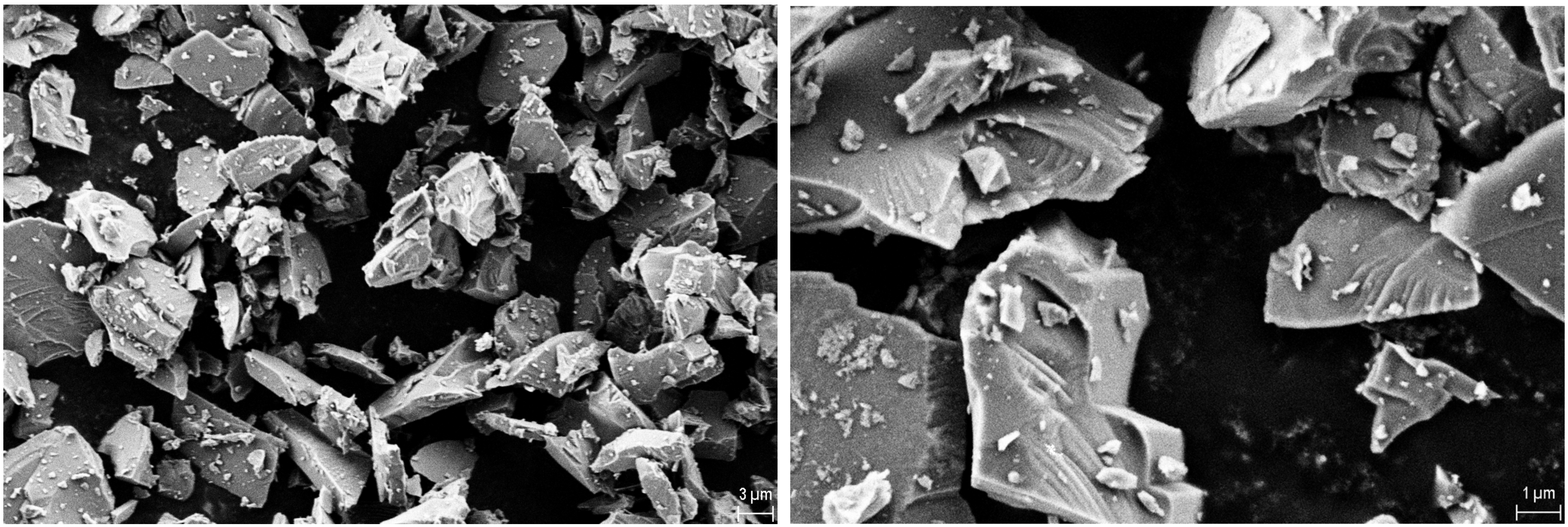
SEM Analysis:
As Received LaB_6 Powder





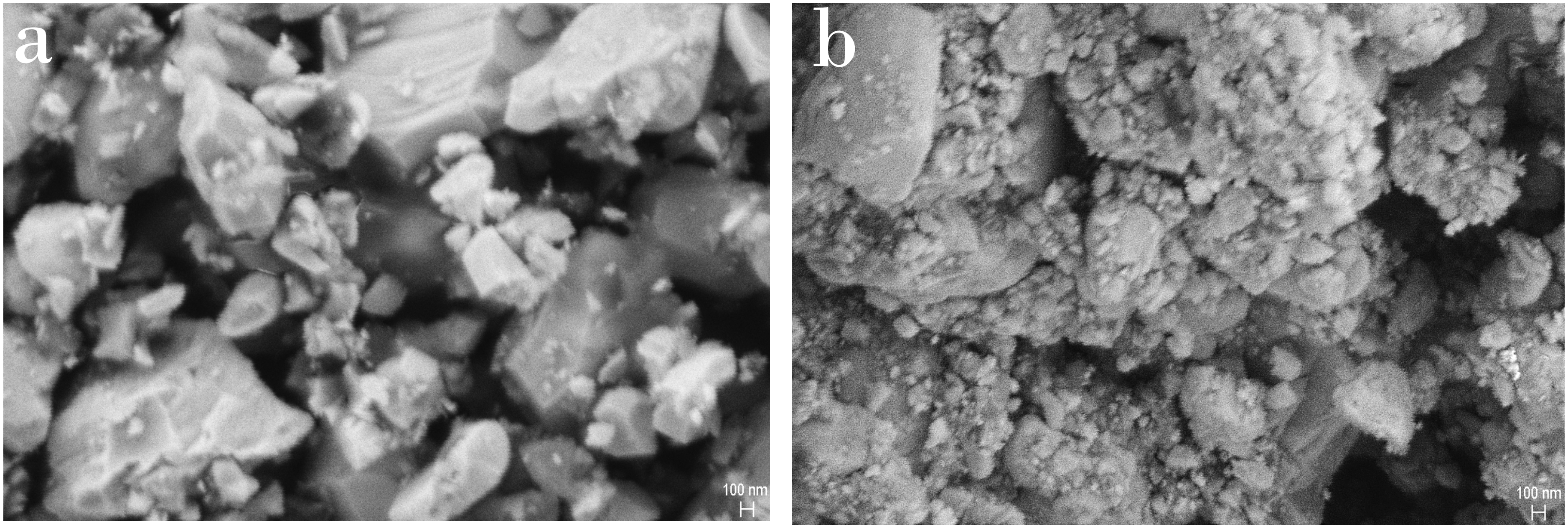
Lanthanum Hexaboride (99.5% purity); -325 mesh size

SEM Analysis:
As Received SiC Powder



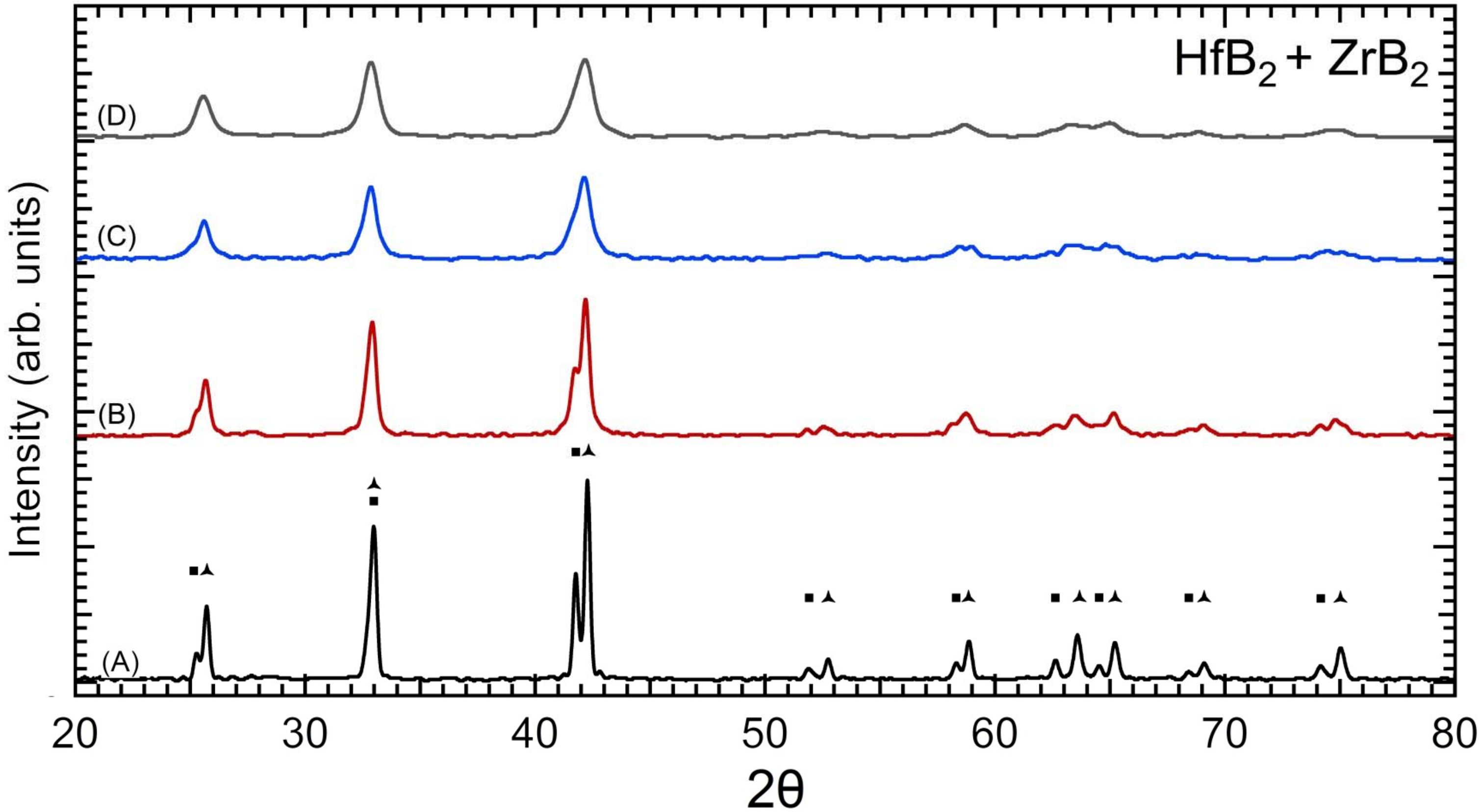
Silicon Carbide (99.5% purity), ~7 Micron Size

SEM Analysis:
Boride Solid Solution Synthesis



HfB_2 and ZrB_2 in 1:1 molar ratio was milled in a SS vial (20:1 ball to powder ratio) in a SPEX 8000M Mixer/Mill for (a) 5 min and (b) 60 min

Hf-Zr Boride Synthesis: XRD analysis



X-ray powder diffraction patterns of the products after milling a (1:1) mixture of $HfB_2 + ZrB_2$, powder to ball ratio (1:20): (A) 5 minutes mill time, (B) 60 minutes mill time, (C) 180 minutes mill time, (D) 270 minutes mill time, (■) ZrB_2, (▲) HfB_2.

Acknowledgment

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Award Administrator: Amanda Lopez

Kickoff Meeting Coordinator: Jessica Mullen

Thank You!

Questions?