University of Idaho
College of Engineering

U.S. DEPARTMENT OF ENERGY
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Boride Based Electrode Materials for MHD Direct Power Extraction

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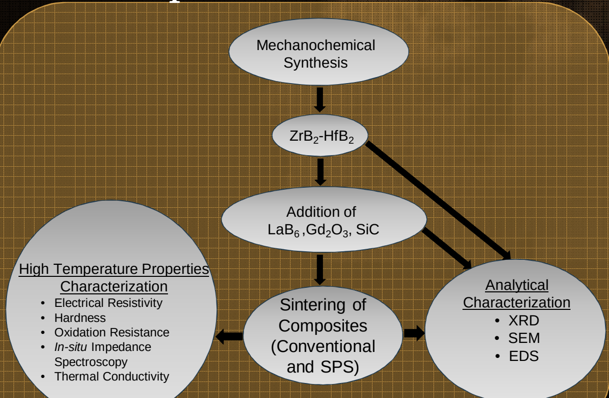
Abstract

In magneto-hydrodynamics (MHD) direct power extraction, a hot conducting combustion flame flows through a transverse magnetic field and current is directly extracted normal to the directions of both the flame flow and the magnetic field. The operative conditions of the MHD ducts are very aggressive due to very high temperatures of the flame (~3000 K), high mass flow rate, and corrosive attack of the potassium salts. The electrodes which extract current are exposed to very arduous conditions. Therefore, development of next generation electrode materials that show high electrical and thermal conductivity infused with better stability in the aggressive high temperature environments is required. In this research, composites containing solid solutions of ZrB_2-HfB_2 with varying additions of SiC and LaB_6 will be prepared. The oxidation resistance of the borides will be improved with the addition of silicon and lanthanum compounds. Furthermore, the LaB_6 additions will help improve electrode kinetics by thermionic emissions.

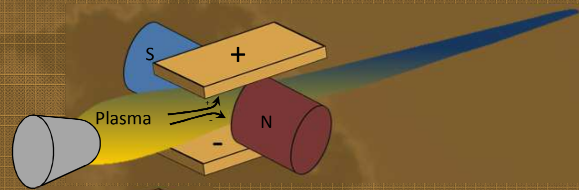
Objectives

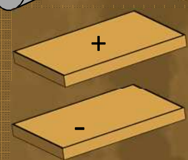
- Synthesize ternary solid solutions of transition metal borides containing ZrB_2 and HfB_2 by the mechanically induced self-sustaining reaction process;
- Improve the high temperature oxidation resistance (up to 2000 °C) of the borides by modifying the chemistry of the borides (metal rich compositions), modifying the cation field strength (replacing some Zr^{4+} and Hf^{4+} with Ta^{5+}), and formation of surface layer of immiscible multicomponent oxide glass by addition of silicon and rare earth (lanthanide series) compounds;
- Evaluate the electrical, mechanical, and thermal stability of the composite materials with different R.E. additions and protective anodic oxide layers at high temperatures under different partial pressures of oxygen and addition of potassium salt.

Experimental Plan



MHD Design Location





These two water cooled copper electrodes are exposed to the extremely corrosive environment of a coal plasma flame and need an electrically conductive and corrosion resistant coating such as Hf-ZrB_2 solid solution.

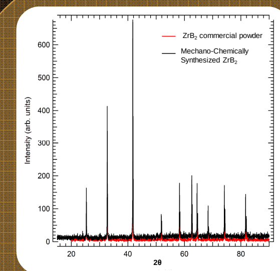
Materials Matrix

Using Commercial Compounds	Starting with Elemental Powders
1:1 HfB_2 - ZrB_2	1:1 $HfB_{1.75}$ - $ZrB_{1.75}$
1:4 HfB_2 - ZrB_2	1:4 $HfB_{1.75}$ - $ZrB_{1.75}$
4:1 HfB_2 - ZrB_2	4:1 $HfB_{1.75}$ - $ZrB_{1.75}$
1:1 HfB_2 - ZrB_2 + 20vol% SiC	1:1 $HfB_{1.75}$ - $ZrB_{1.75}$ + 20vol% SiC
1:1 HfB_2 - ZrB_2 + 20vol% SiC + 10_{vol}% LaB_6	1:1 $HfB_{1.75}$ - $ZrB_{1.75}$ + 20vol% SiC + 10vol% LaB_6
1:1 HfB_2 - ZrB_2 + 20vol% SiC + 10_{vol}% Gd_2O_3	1:1 $HfB_{1.75}$ - $ZrB_{1.75}$ + 20vol% SiC + 10vol% Gd_2O_3
1:1 HfB_2 - ZrB_2 + 20vol% SiC + 10_{vol}% Ta	1:1 $HfB_{1.75}$ - $ZrB_{1.75}$ + 20vol% SiC + 10vol% Ta

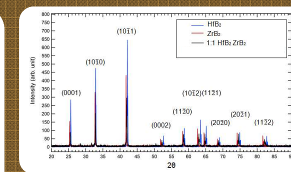
Why These Materials?

- HfB_2-ZrB_2 solid solution base material was chosen due to the superior electrical conductivity, oxidation resistance, and extremely high melting point of the individual borides.
- SiC is added to aid in densification though sintering and to help with oxidation resistance.
- LaB_6 is added to help improve the plasma ionization and oxidation resistance of the transition metal borides at high temperatures.
- Gd_2O_3 is chosen as a rare earth addition to further improve the oxidation resistance.
- Ta is added to modify the cation field strength, and electronic structure that will enhance the oxidation resistance.
- Metal-rich mixtures of the borides were chosen to help improve the electrical conductivity and the oxidation resistance.

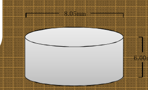
Experimental Results



↑ XRD analysis comparing commercially available ZrB_2 and mechano-chemically synthesized ZrB_2 from elemental Zr and B. Shows that the readily available commercial borides are identical to elemental borides.

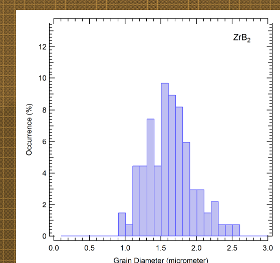


↑ XRD analysis showing solid solution formation after mechanical alloying commercially available ZrB_2 and HfB_2.

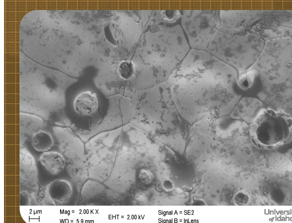


← Dimensions of average green pellet made from compacted powder prior to sintering.

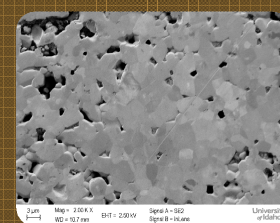
Typically, pellets are compacted up to 53kN in one minute with a two minute hold at 53 kN. The force on the pellets is relieved steadily over one minute. Typically no binder are used in compaction.



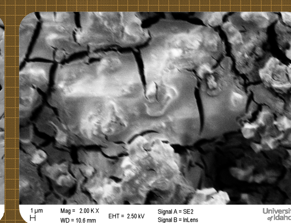
↑ Grain size distribution for elemental mechano-chemically synthesized ZrB_2. 45 minute mill time with a 1:10 pbr. Sintered at 1700ºC for 1 hour.



↑ 1:1 HfB_2 - ZrB_2 + 20vol% SiC. 5 hour mill time with a 1:10 pbr, Sintered at 1700ºC for 45 minutes. Sample oxidized during sintering stage. An oxygen pre-filter has been added to the system to prevent this occurrence in the future.



↑ 1:1 HfB_2 - ZrB_2 + 20vol% SiC. 3 hour mill time with a 1:10 pbr, Sintered at 1700ºC for 1 hour. Polished to 1 micron.



↑ 1:1 HfB_2 - ZrB_2 + 20vol% SiC. 5 hours mill time with a 1:10 pbr, Sintered at 1700ºC for 45 minutes. Same sample as above. Anodized at 40 V for 1 hour.

DOE Award #: DE-FE0022988; Dr. Jason Hissam (Program Manager)

Team Members (Students)
Cody Hill
Steven Sitler