BORIDE BASED ELECTRODE MATERIALS UNDER EXTREME CONDITIONS FOR MHD DIRECT POWER EXTRACTION

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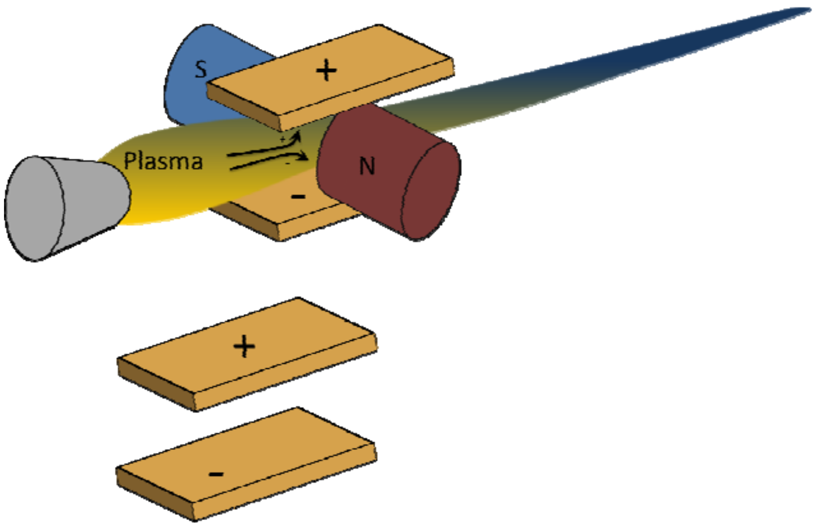
INTRODUCTION

Magnetohydrodynamic (MHD) Direct Power Extraction



Flame temperature: > 3000 K

Atmosphere:
Oxidizing with possible atomic oxygen present in the plasma

Potassium salt for conductivity leading to hot corrosion at 1700 – 2200 K

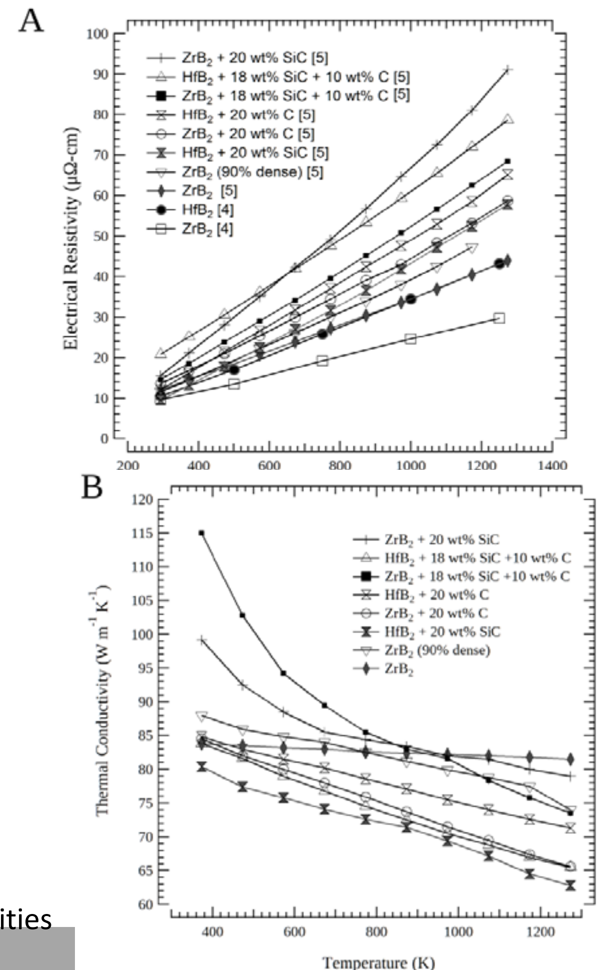
Electrode materials should have high electrical conductivity, good thermal shock resistance, and durability in aggressive environments.

INTRODUCTION

Hafnium and Zirconium Diborides

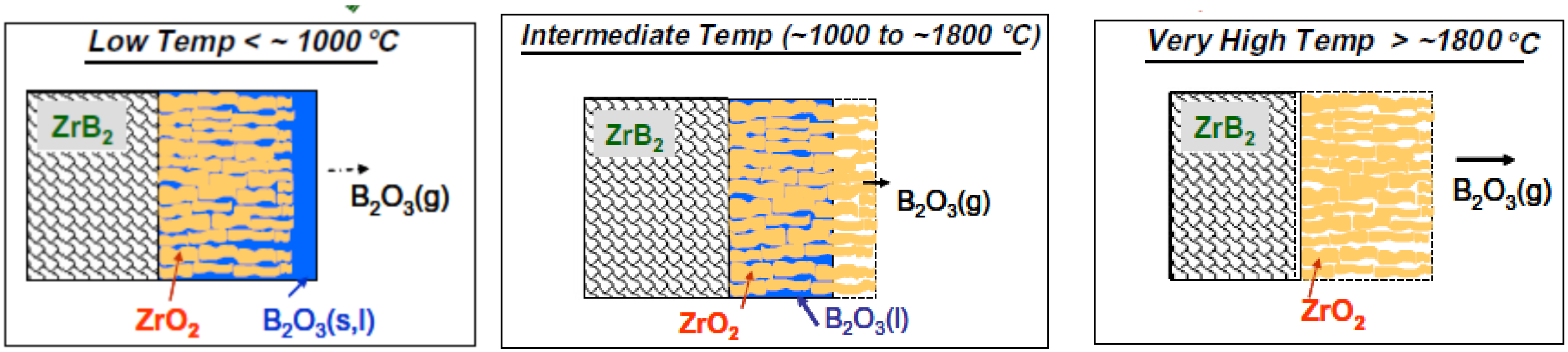
- HfB_2-ZrB_2 solid solution
  - Superior electrical conductivity
  - Oxidation resistance
  - Extremely high melting point

Currently investigated for thermal protection systems of re-entry space craft vehicles, electrodes for EDM, and protective coatings for micro-electronics.



Tye, R. P., Clougherty, E. V. (1970). The Thermal and Electrical Conductivities of Some Electrically Conducting Compounds. Proceedings of the Fifth Symposium on Thermophysical Properties, Newton, Massachusetts, 396-401

High Temperature Oxidation of ZrB_2:



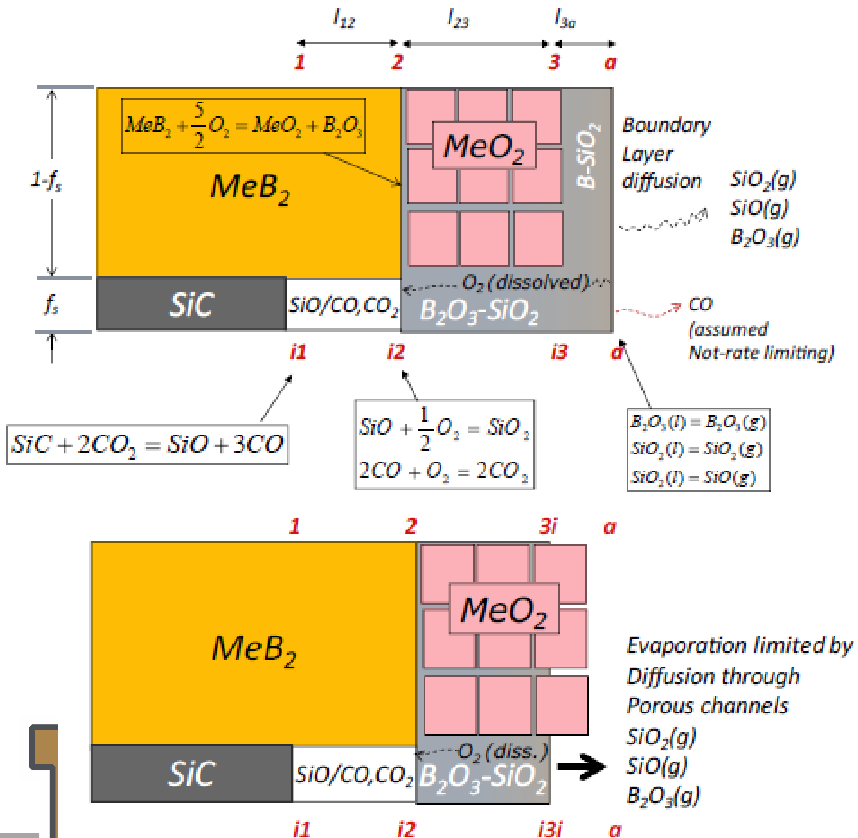
From: T.A. Parthasarathy et al., Acta Materialia, 55 (2007) 5999.

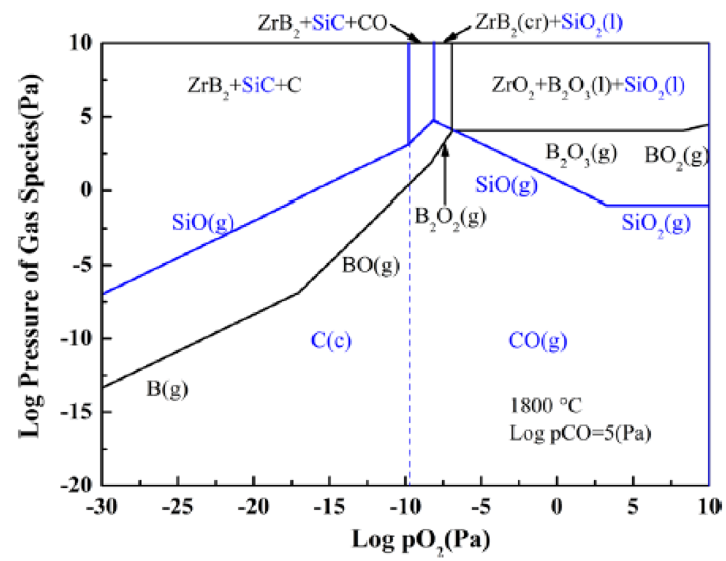
$$ZrB_2 + 5/2\ O_2 \rightarrow ZrO_2 + B_2O_3$$

$$B_2O_3\ (l) \rightarrow B_2O_3\ (g)\ \ (> 1100\ ^oC)$$

Vapor pressure of boria at 1800 ^oC : 1.3×10^4 Pa

High Temperature Oxidation of ZrB_2 with addition of SiC



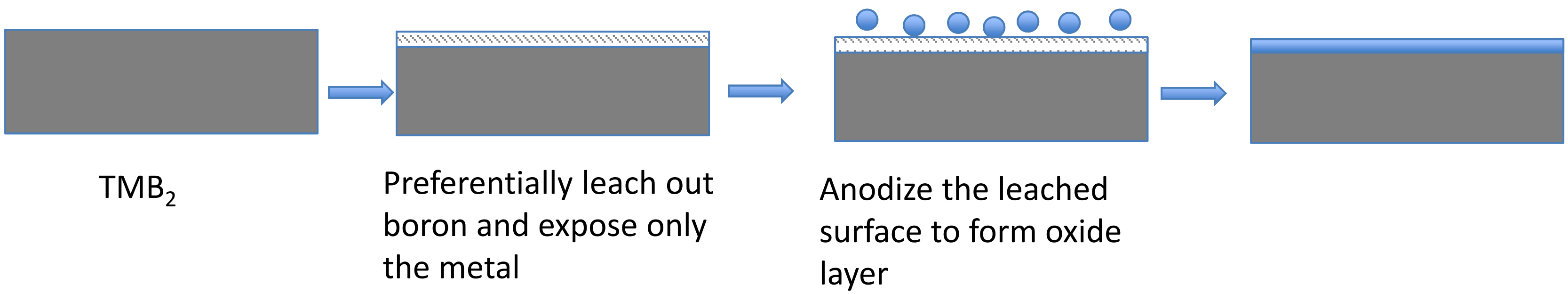


Combined volatility diagram of ZrB_2, SiC, and graphite (H. Jin et al., *Ceramic Int*. 42 (2016) 6480)

From: T.A. Parthasarathy et al., J. Am.Cer. Soc., 95 (2012) 338.

Research Approach

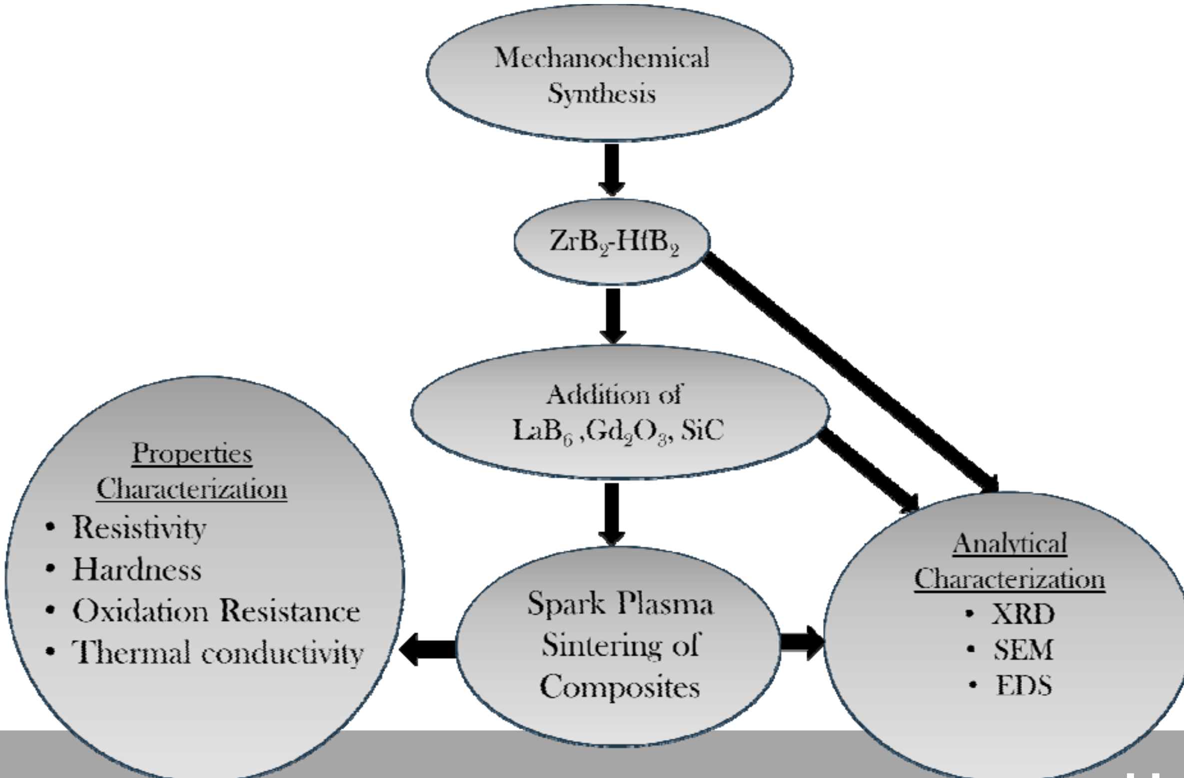
1) Provide a thin, continuous, and impervious oxide layer to improve the oxidation resistance without significantly losing the electrical conductivity



2) Incorporate RE oxides La_2O_3 and Gd_2O_3 to improve the oxidation resistance by forming cubic pyrochlore phases

3) Forming metal rich borides with addition of higher valent elements to hinder diffusion of oxygen in the oxide layer

PROJECT FLOW CHART



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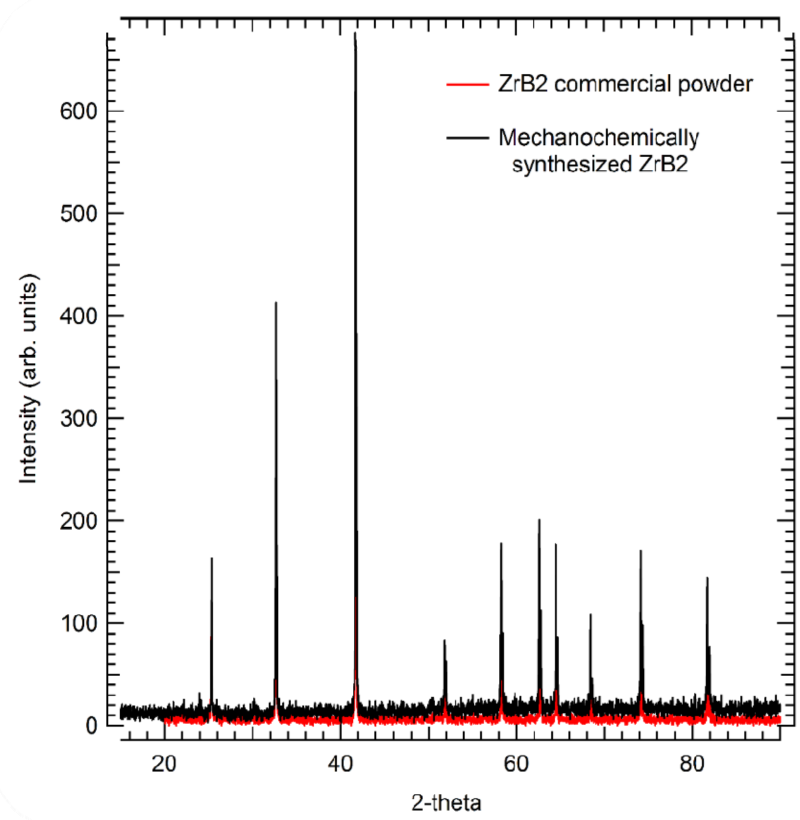
PROCESSING

Hafnium and Zirconium Diborides

- Commercially available HfB_2 and ZrB_2
- Elemental mechanochemical synthesis
- No difference was found



PROCESSING

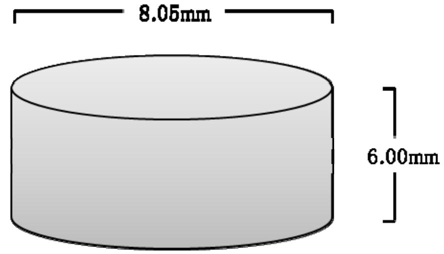
Mechanochemical synthesis

- Achieved through ball milling
  - SPEX 8000M Mixer/mill
- Steel milling media caused contamination
- 3 mol% Yttria stabilized zirconia grinding media and vial were used
  - 1:10 powder to ball ratio
  - 3 hour milling time
  - 6.5 mm diameter

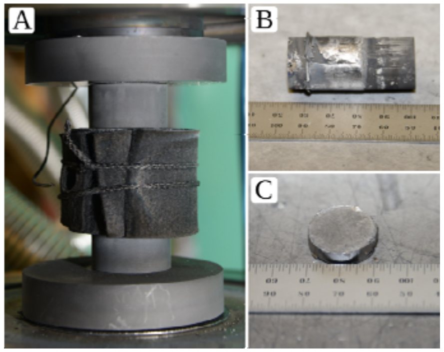
PROCESSING

Sintering

- Conventional Sintering
  - Compacted pellets at ~1.0 kN
  - Sintered in argon at 1700 ^{0}C



- Spark Plasma Sintering
  - 5 kN force
  - 10^{-3} torr vacuum
  - 1700 ^{0}C



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PROCESSING

Sample Identifier	Composition	SPS Hold Time (s)
A	HfB_2	180
B	ZrB_2	600
AB	1:1 HfB_2 - ZrB_2	600
A4B	1:4 HfB_2 - ZrB_2	600
4AB	4:1 HfB_2 - ZrB_2	600
ABT	1:1 HfB_2 - ZrB_2 + Ta (B/Me = 1.86)	180
ABZ	1:1 HfB_2 - ZrB_2 + Zr (B/Me = 1.86)	180
ABH	1:1 HfB_2 - ZrB_2 + Hf (B/Me = 1.86)	180
ABL	1:1 HfB_2 - ZrB_2 + 1.8 mol % LaB_6	300
ABG	1:1 HfB_2 - ZrB_2 + 1.8 mol % Gd_2O_3	300

CHARACTERIZATION

Electrical resistivity

- Polarization Resistance
- Gamry Interface 1000
- $\rho = \frac{AR}{L}$

Hardness

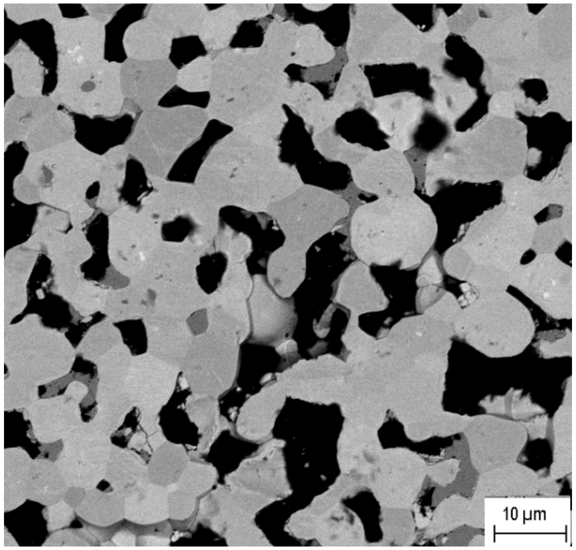
- Vickers microhardness
- LECO LM1000

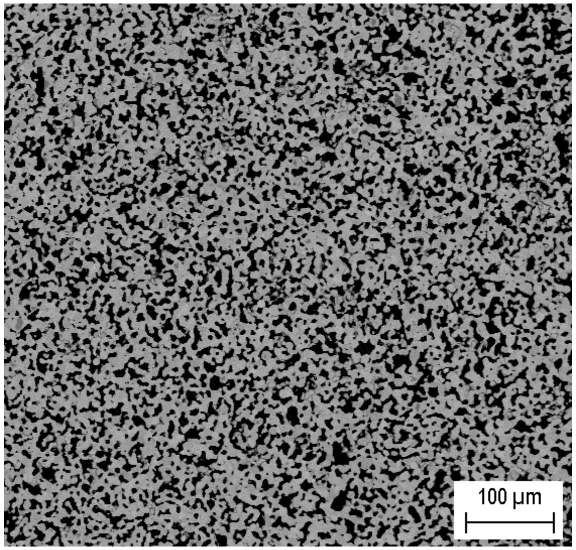
Density

- Archimedes principle
- Ohaus Explorer Pro
- $\rho = \frac{M_{air}}{M_{air}-M_{water}}(\rho_{water} - \rho_{air}) + \rho_{air}$

Microstructure Analysis:

Grain size by back scattered SEM



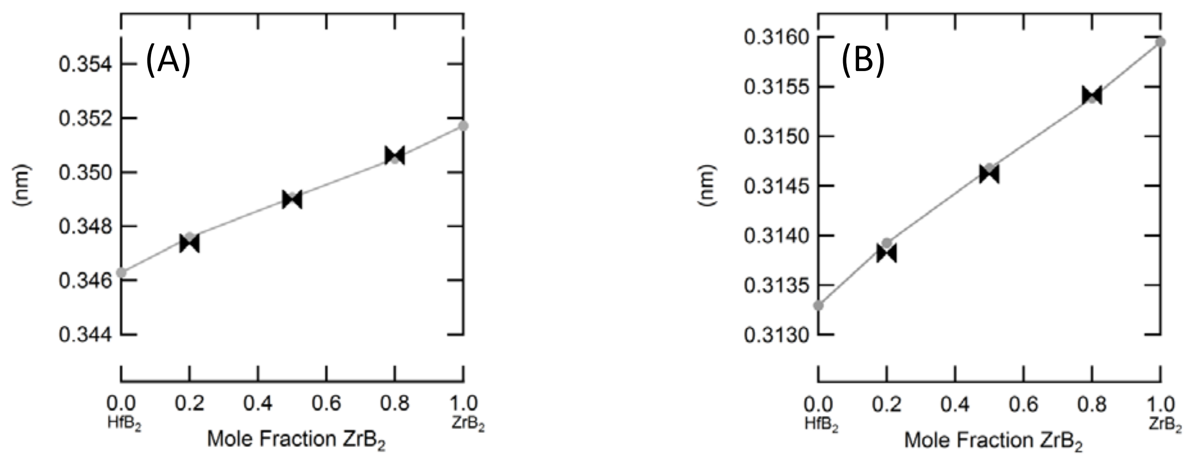


BSE FESEM micrograph of SPSed Hf0.5Zr0.5B2

LATTICE PARAMETERS

Vegard's Law for SPSed $Hf_{(1-x)}Zr_{(x)}B_2$

$$\alpha_{B_x A_{(1-x)}} = x\alpha_B + (1-x)\alpha_A$$



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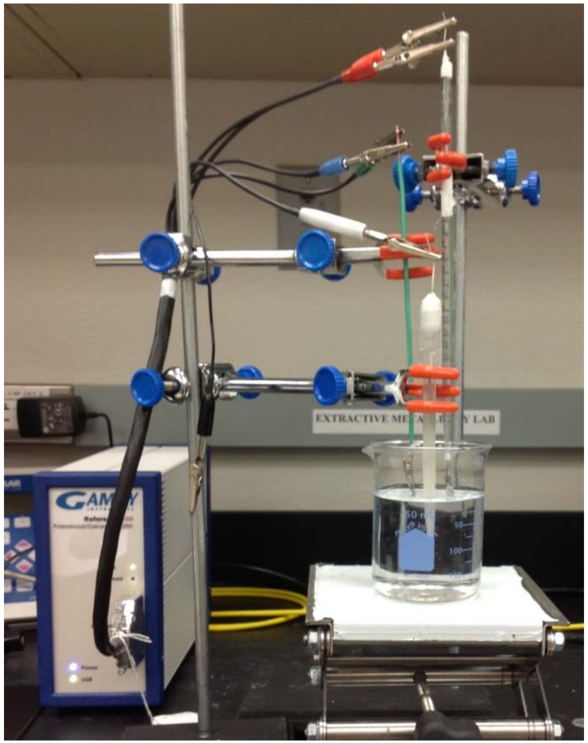
CHARACTERIZATION

Sample Identifier	Density (g/cm^3)	Relative Density (%)	Hardness (GPa)	Electrical Resistivity (μΩ-cm)	Grain Size (μm)
HfB_2	9.594	91.4	20.07	9.2	3.6 ± 1.6
ZrB_2	5.308	87.2	12.86	6.79	3.1 ± 1.8
$Hf_{0.5}Zr_{0.5}B_2$	6.346	76.2	-	5.4	3.3 ± 2.1
$Hf_{0.2}Zr_{0.8}B_2$	5.796	82.9	3.13	6.0	2.3 ± 1.4
$Hf_{0.8}Zr_{0.2}B_2$	7.377	76.5	8.32	9.3	3.7 ± 1.6
$Hf_{0.5}Zr_{0.5}B_2$ +Ta	8.215	94.6	-	17.3	-
$Hf_{0.4}Zr_{0.6}B_{1.86}$	7.801	94.8	5.82	8.4	-
$Hf_{0.6}Zr_{0.4}B_{1.86}$	8.250	96.2	12.04	11.6	-
$Hf_{0.5}Zr_{0.5}B_2$ +LaB_6	7.957	97.2	-	12.2	-
$Hf_{0.5}Zr_{0.5}B_2$ +Gd_2O_3	7.418	89.5	-	12.4	-

Electrochemical corrosion studies in aqueous solutions



Purpose: To rank the compositions for testing in hot corrosion environments

Resistance to room temperature aqueous corrosion can be translated to high temperature corrosion resistance in the presence of relevant species

Potentiodynamic polarization studies using three-electrode configuration

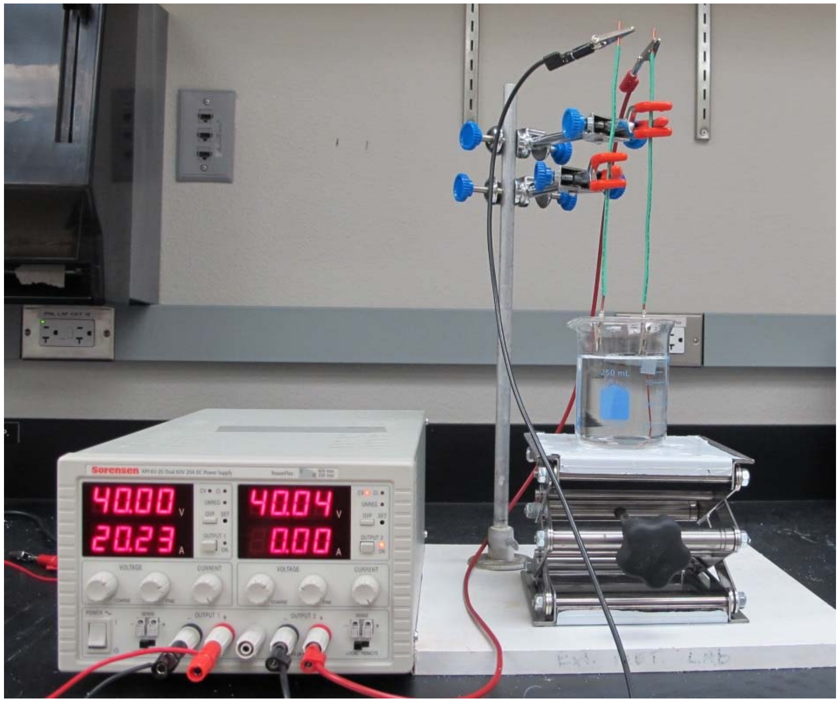
- 0.1 M H_2SO_4
- 0.1 M NaCl
- 0.1 M NaOH
- 0.1 M NaOH + 0.1 M NaCl

Reference electrode: Ag/AgCl in saturated KCl

Counter electrode: Platinum foil

ANODIZATION

- Anodized $HfB_2 + ZrB_2$
  - Ethylene Glycol
    - 4% H_2O
    - 0.14 M NH_4F
  - Potassium Hydroxide
  - H_3PO_4 + NaF
  - Potential: 10 – 60 V
  - Time: 30 – 60 minutes
  - Counter electrode: Ti foil



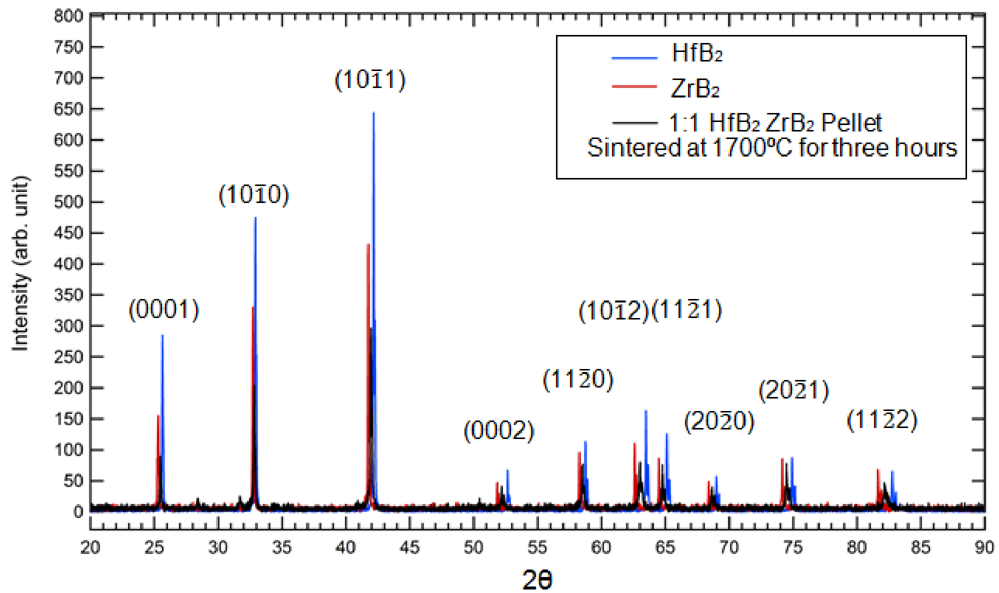
THERMOGRAVIMETRIC ANALYSIS

- Netzsch STA 409 PC Luxx
  - 3 ^{o}C/min ramp rate
  - 1500 ^{o}C for 2 hours
  - Argon > pO_2 = 0.1 Pa
  - Oxygen > $pO_2 = 0.3 \times 10^5$ Pa
  - CO/CO_2: > $PO_2 = 1 \times 10^{-8}$ Pa

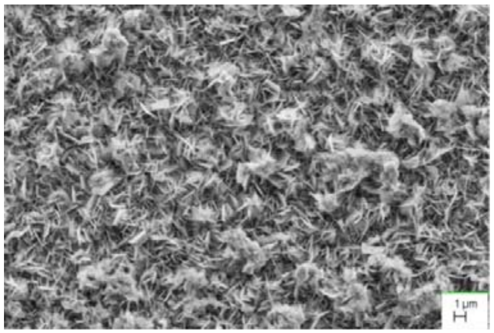
RESULTS & DISCUSSION

SOLID SOLUTION

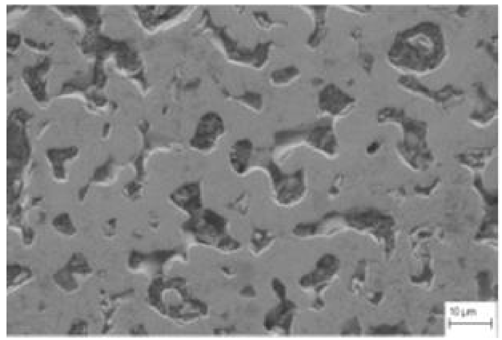
XRD analysis of mechanochemically synthesized HfB_2 + ZrB_2 showed a successful solid solution mixture



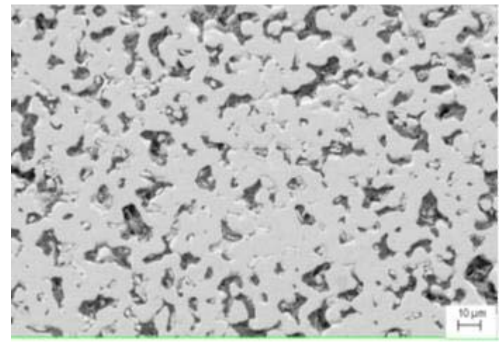
ANODIZATION



EG + 0.14 M NH_4F, 30 V, 30 min.

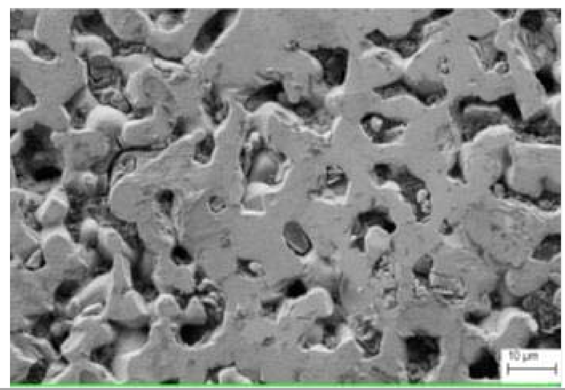


0.1 KOH, 40 V, 30 min.



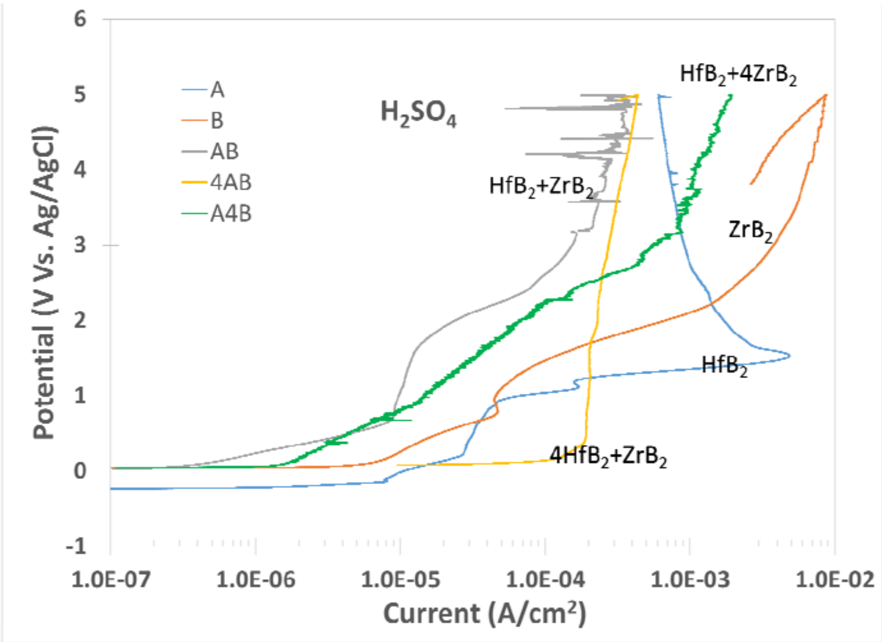
0.1 KOH, 40 V, 120 min.

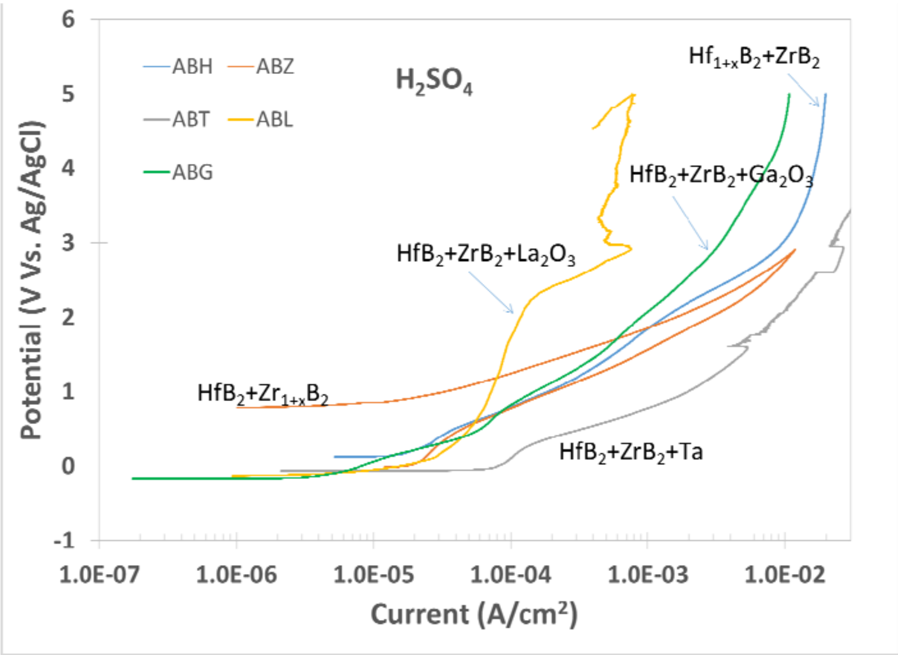
Double anodized EG + 0.14 M NH_4F, 20 V, 30 min. + 0.01 M F, 30 V, 30 min.



Leached in H_3PO_4 + NaF and anodized in EG + 0.01 M F^-, 30 min. + 0.01 M F, 40 V, 30 min.

AQUEOUS CORROSION- 0.1 M H_2SO_4





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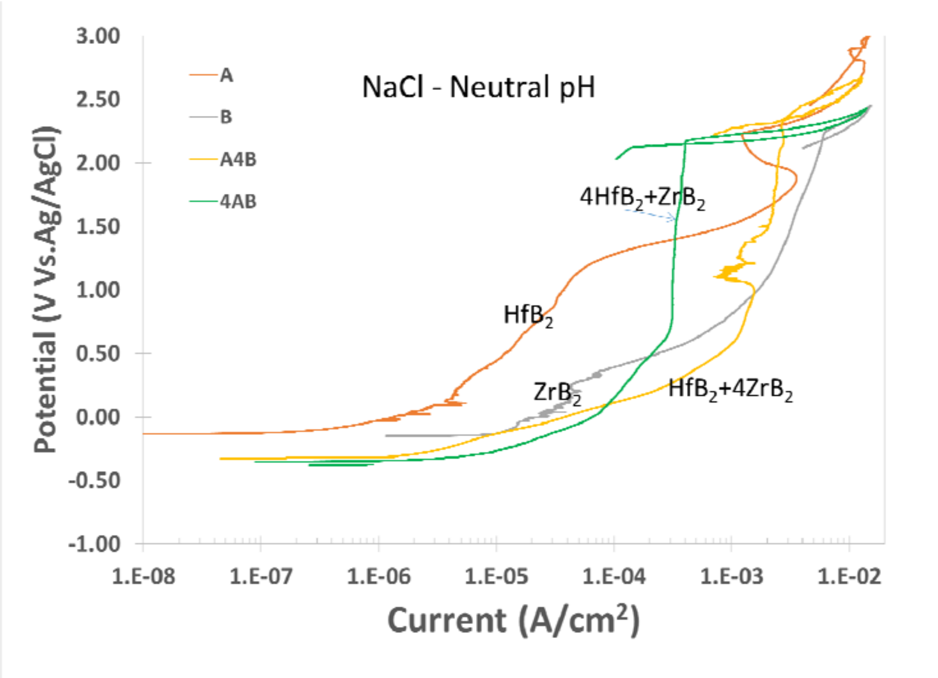
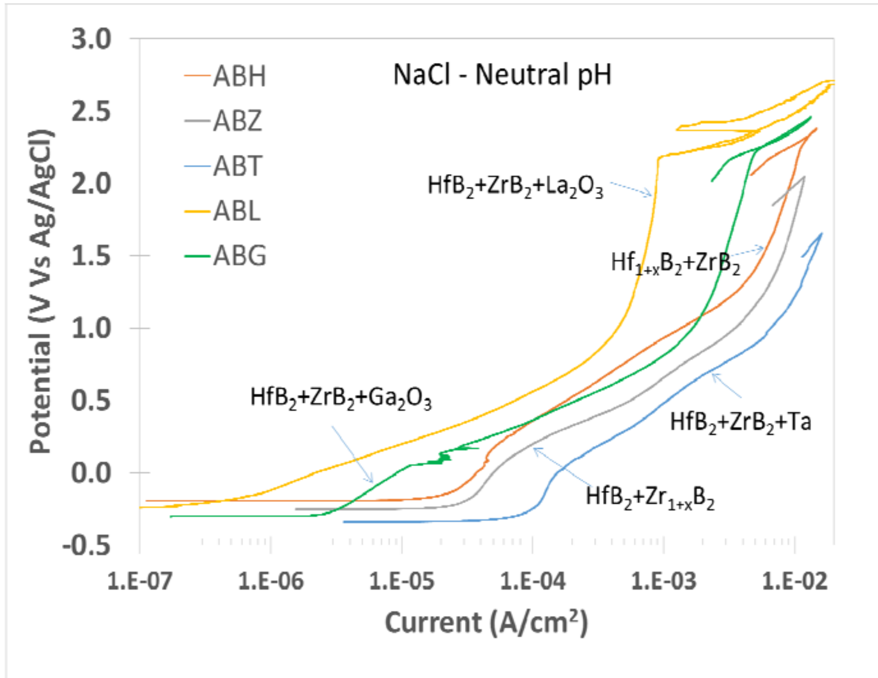
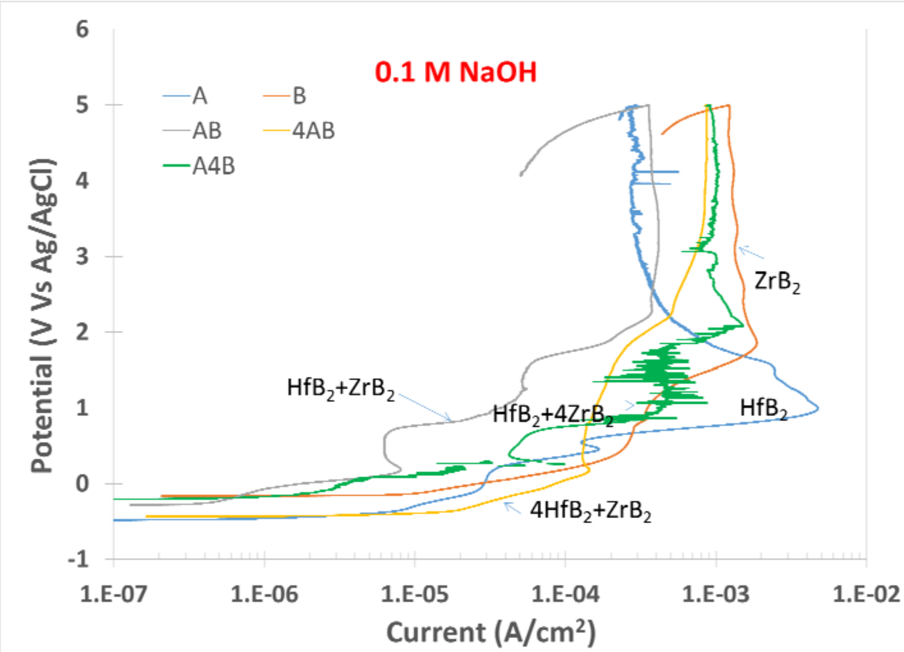
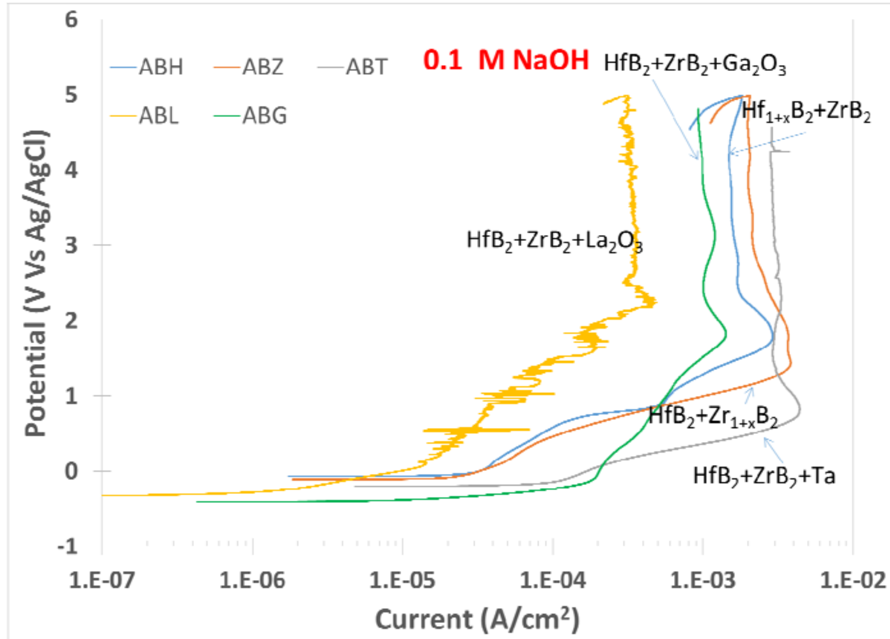
AQUEOUS CORROSION - 0.1 M SODIUM CHLORIDE





AQUEOUS CORROSION – 0.1 M SODIUM HYDROXIDE





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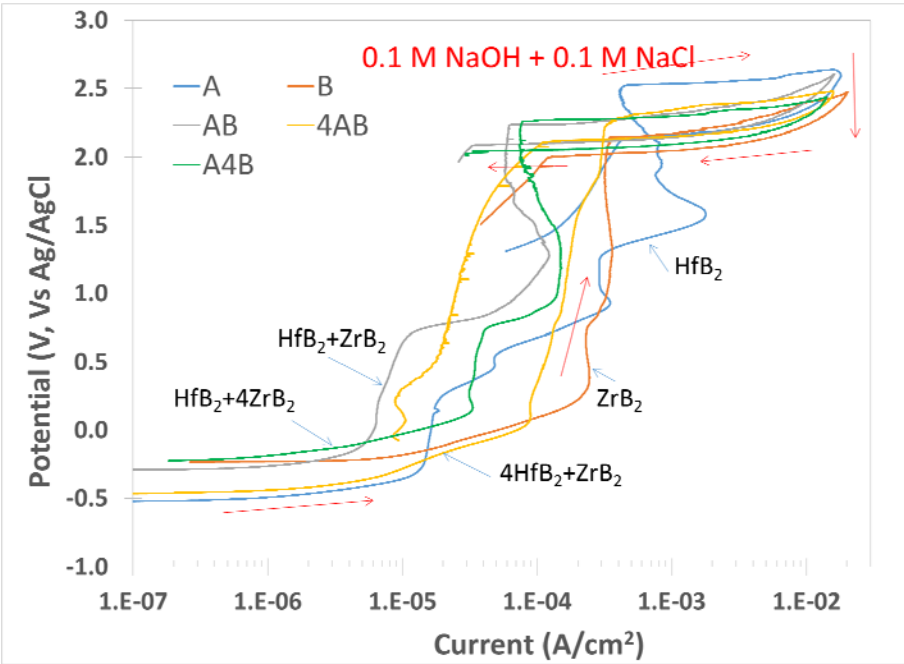
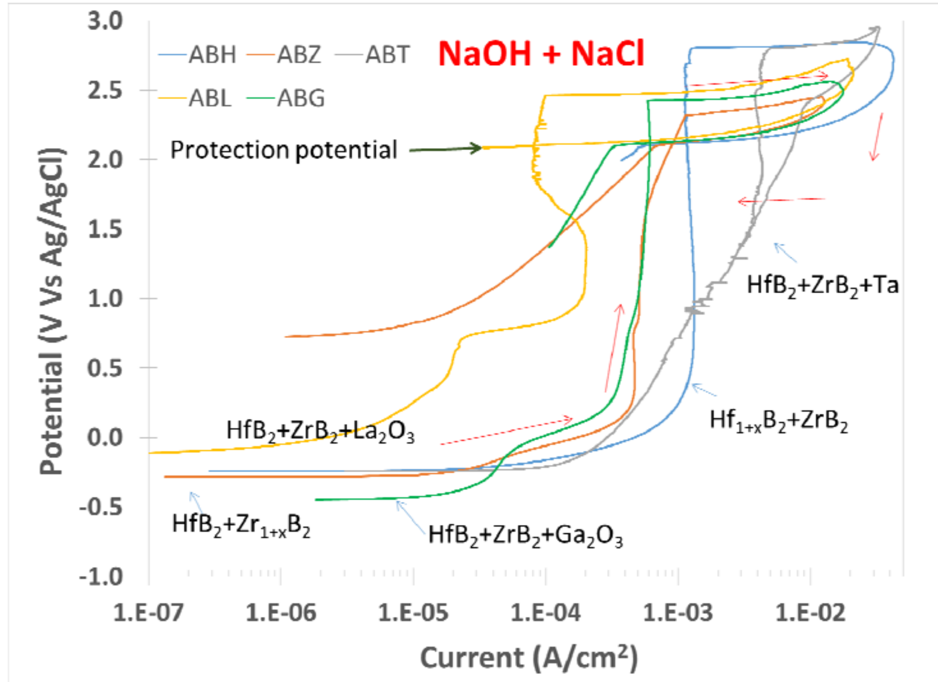
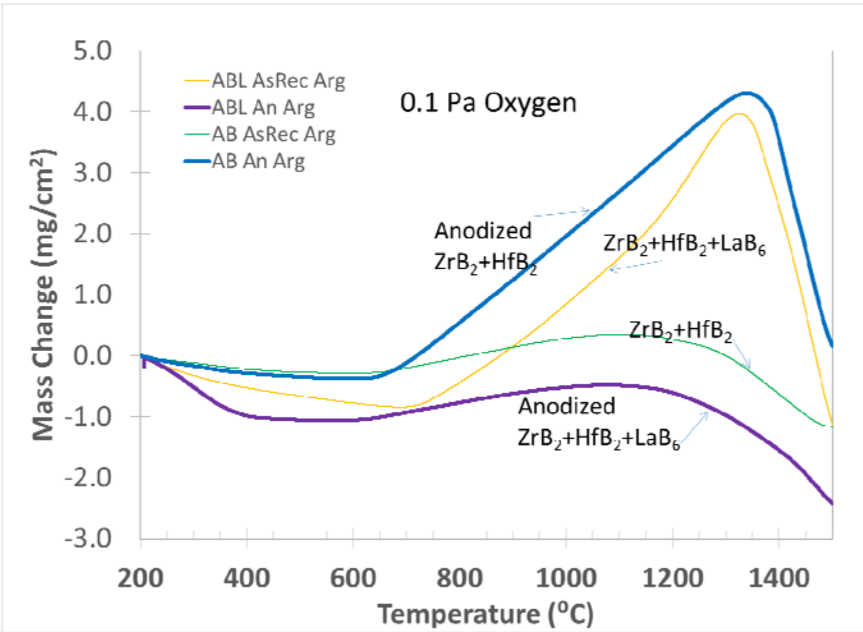
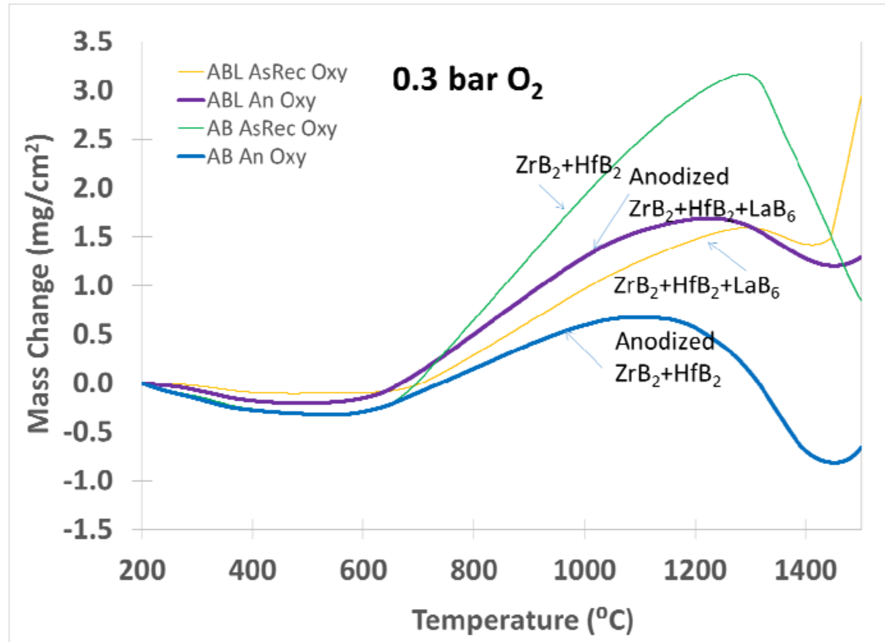
AQUEOUS CORROSION – CHLORIDE IN BASIC SOLUTION





TGA Results: Argon + Oxygen (0.1 Pa), and 0.3 bar O_2.





S.J. Sitler, C. Hill, K.S. Raja, I. Charit, HT Oxidation of ZrB_2+HfB_2 Solid Solution with LaB_6 Addition, *Metall. Mater. Trans. E*, in press, doi: 10.1007/s40553-016-0072-2

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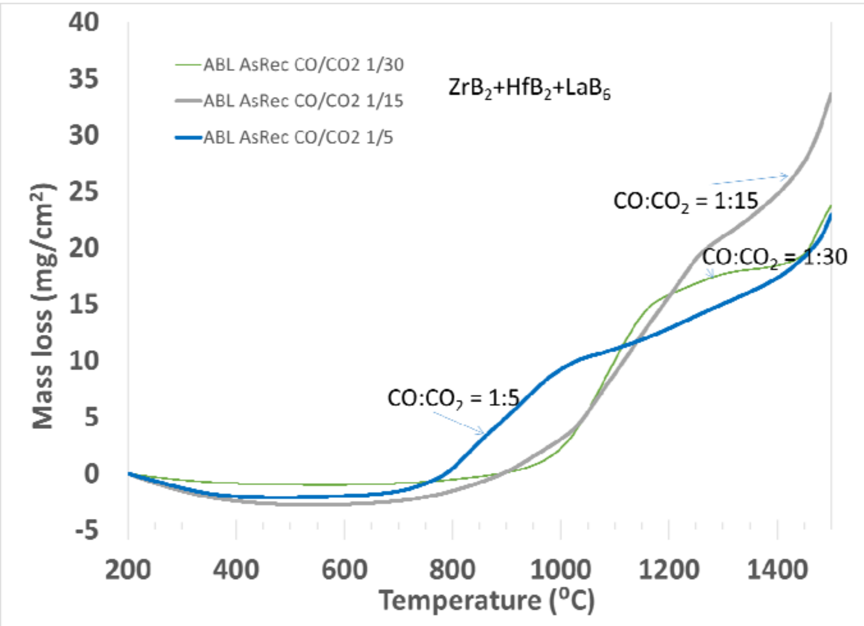
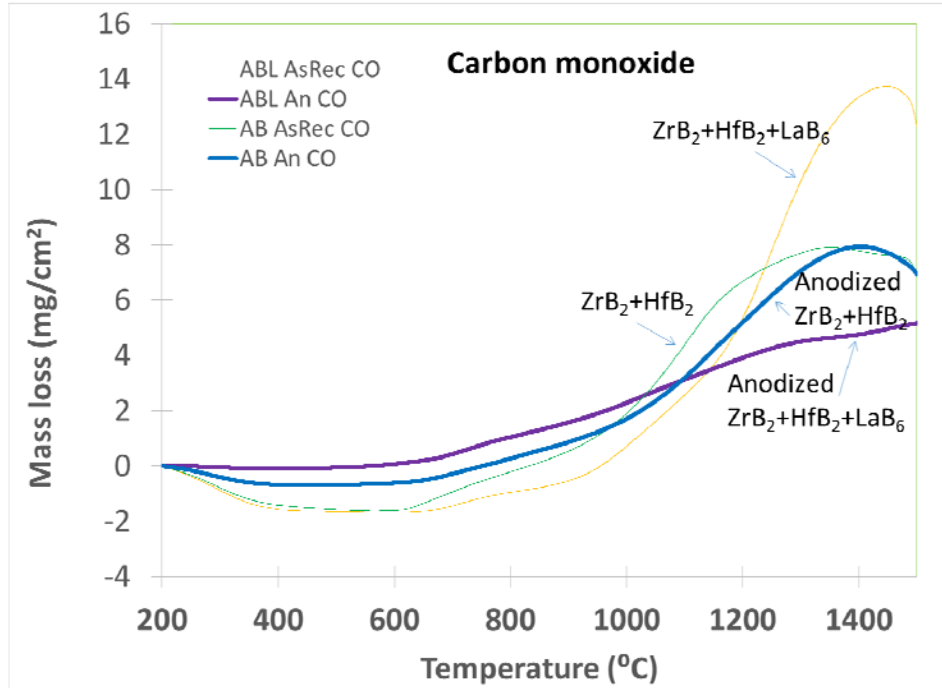
TGA Results of ZrB_2+HfB_2+LaB_6 in Mixture of CO + CO_2





S.J. Sitler, K.S. Raja, I. Charit, High Temperature Oxidation Study of Hafnium & Zirconium Diborides: MHD Electrode Coatings, to be presented in MS&T 2016

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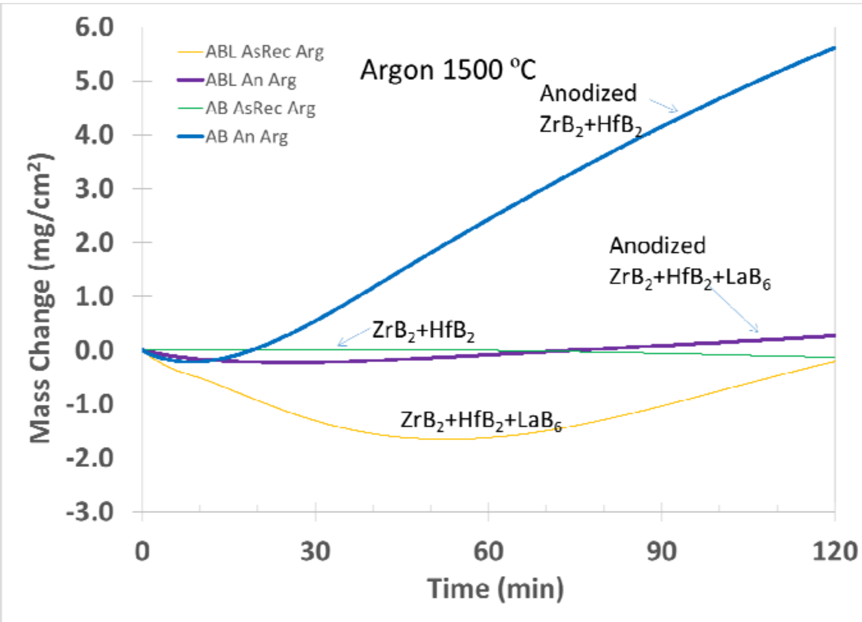

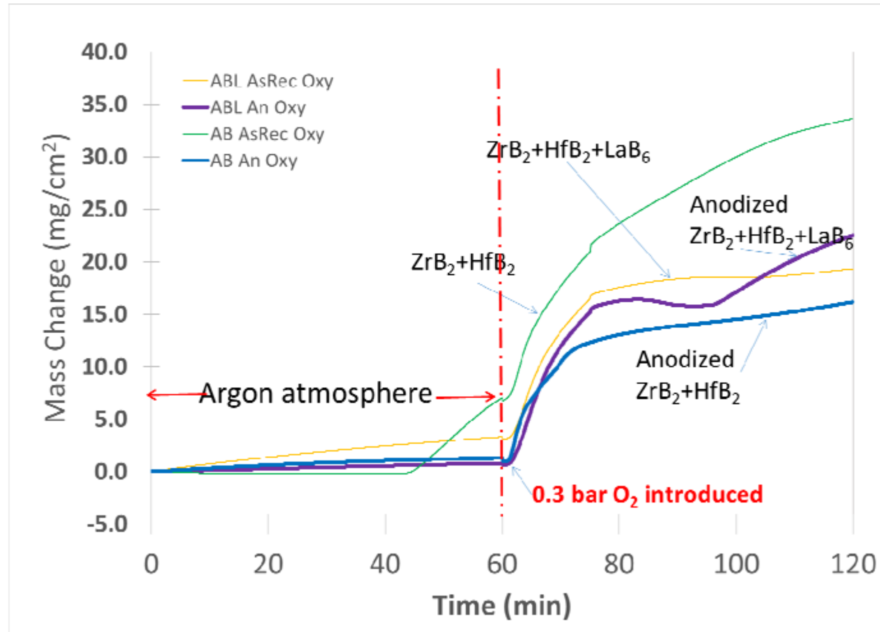

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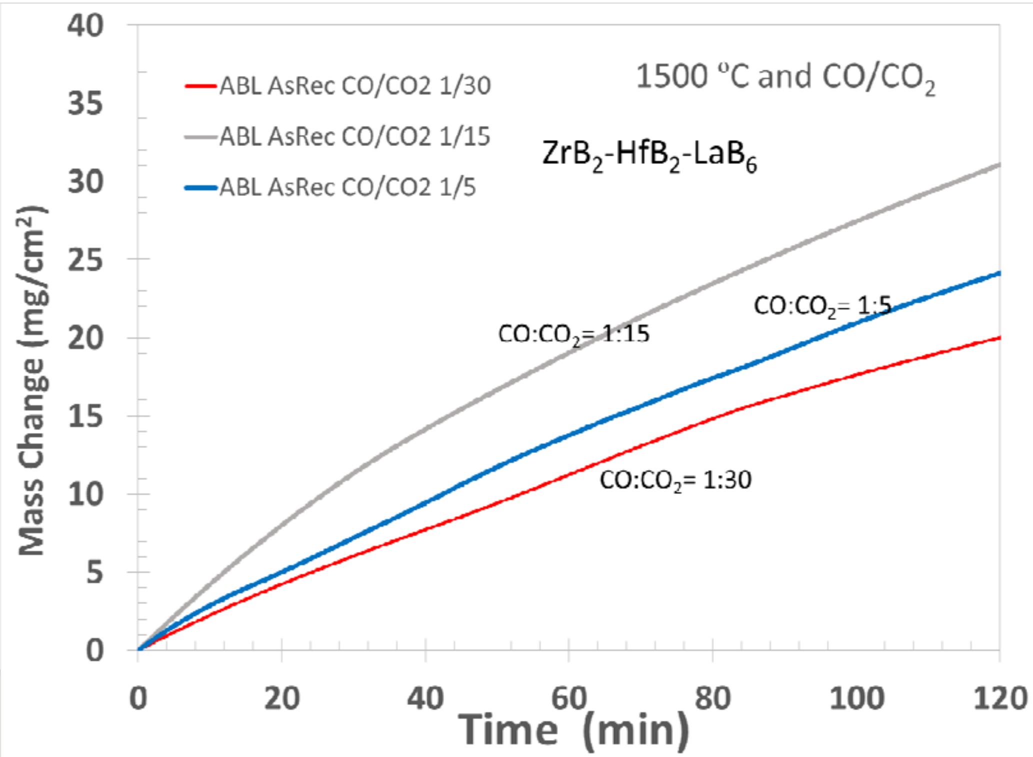

$CO:CO_2$	$mg^2/cm^4.h$	$kg^2/m^4.s$	log k_p
1:5	10.596	2.9E-07	-6.531
1:15	12.294	3.4E-07	-6.467
1:30	9.096	2.5E-07	-6.597

S.J. Sitler, K.S. Raja, I. Charit, High Temperature Oxidation Study of Hafnium & Zirconium Diborides: MHD Electrode Coatings, to be presented in MS&T 2016

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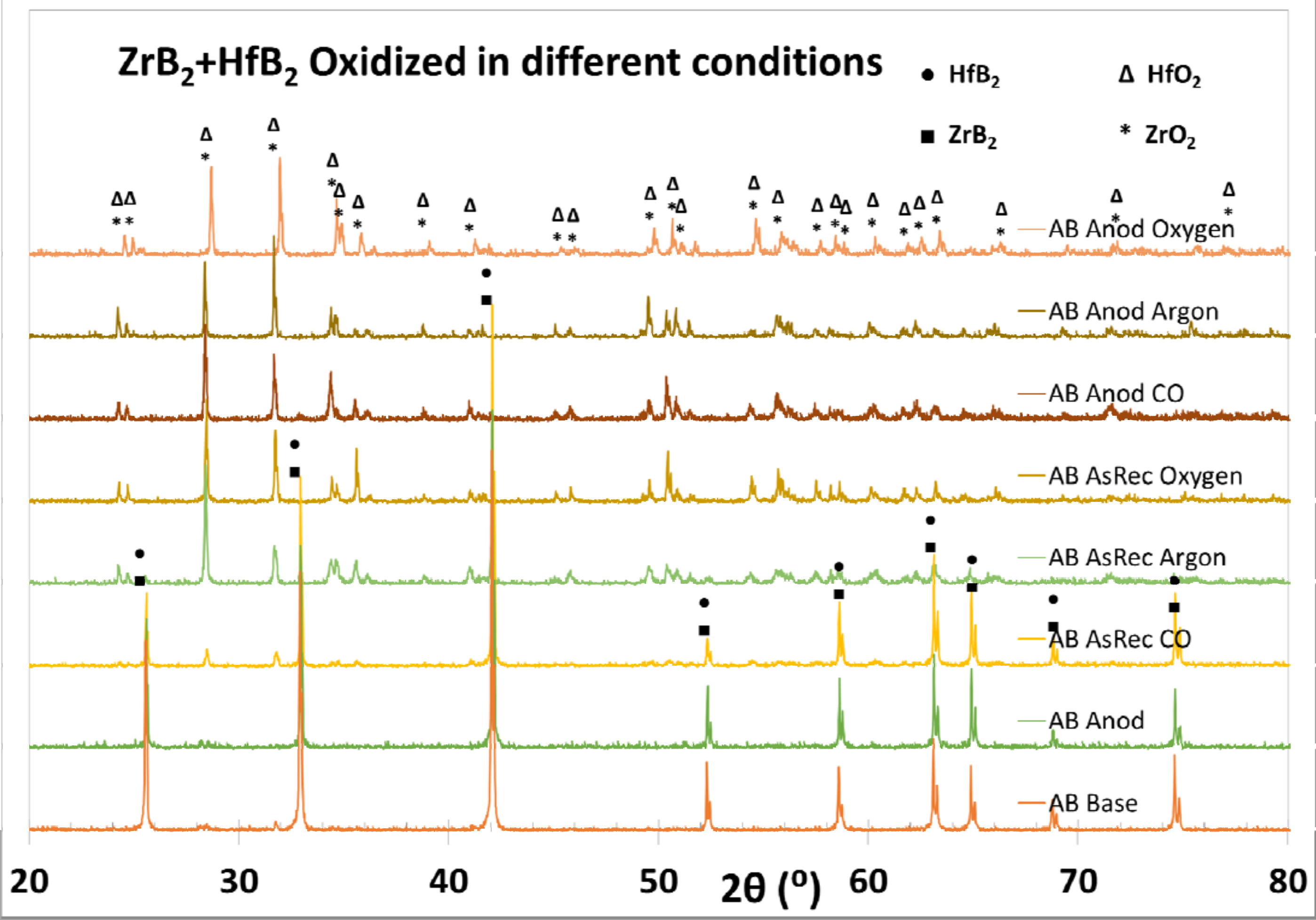
PARABOLIC RATE CONSTANTS

Sample	Rate constant (k_p), $mg^2/cm^4\ h$	Log (k_p, $kg^2/m^4\ s$)
ABL as-sintered	1174.2	-4.49
ABL anodized	1053.0	-4.53
AB as-sintered	1682.4	-4.33
AB anodized	692.4	-4.72



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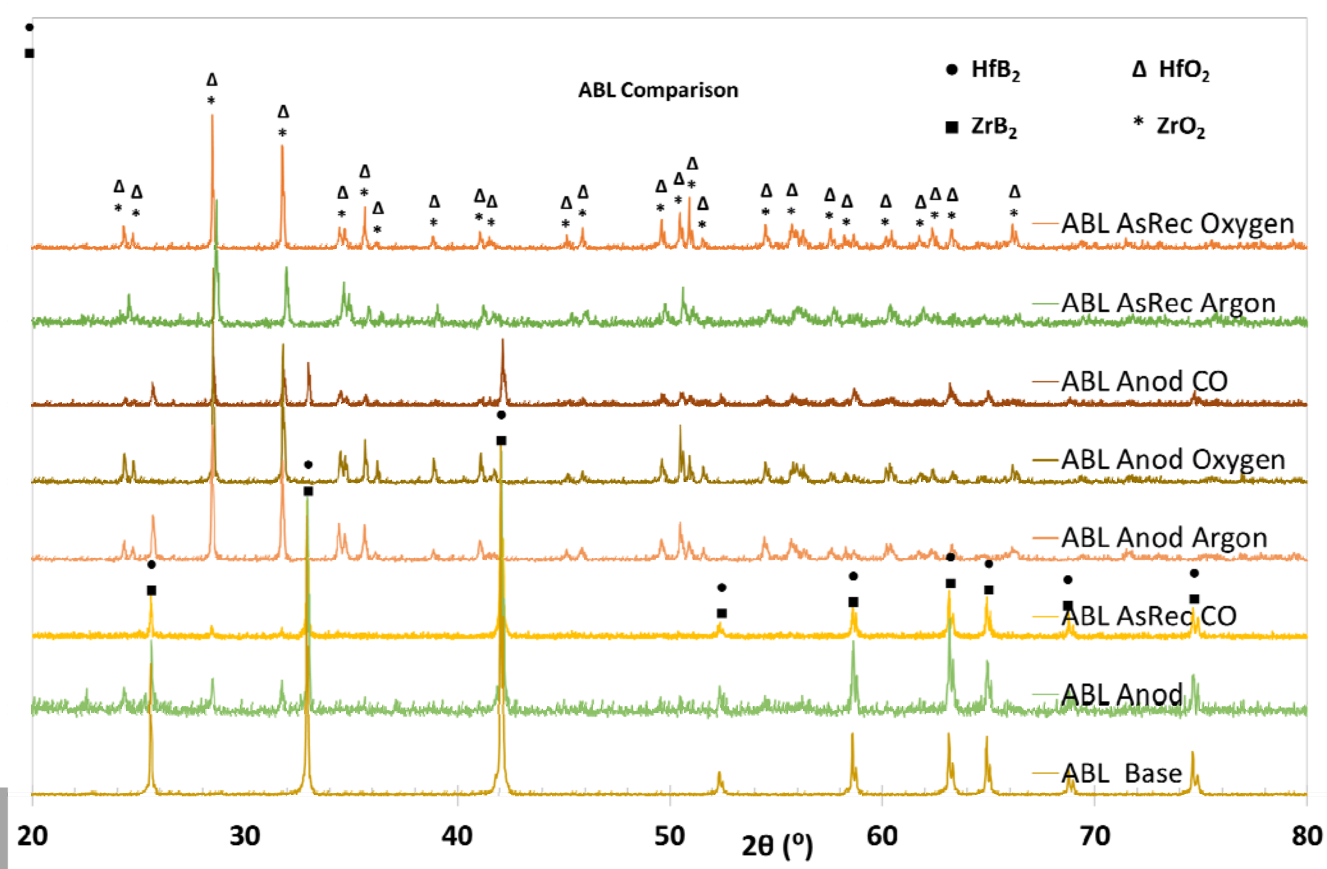
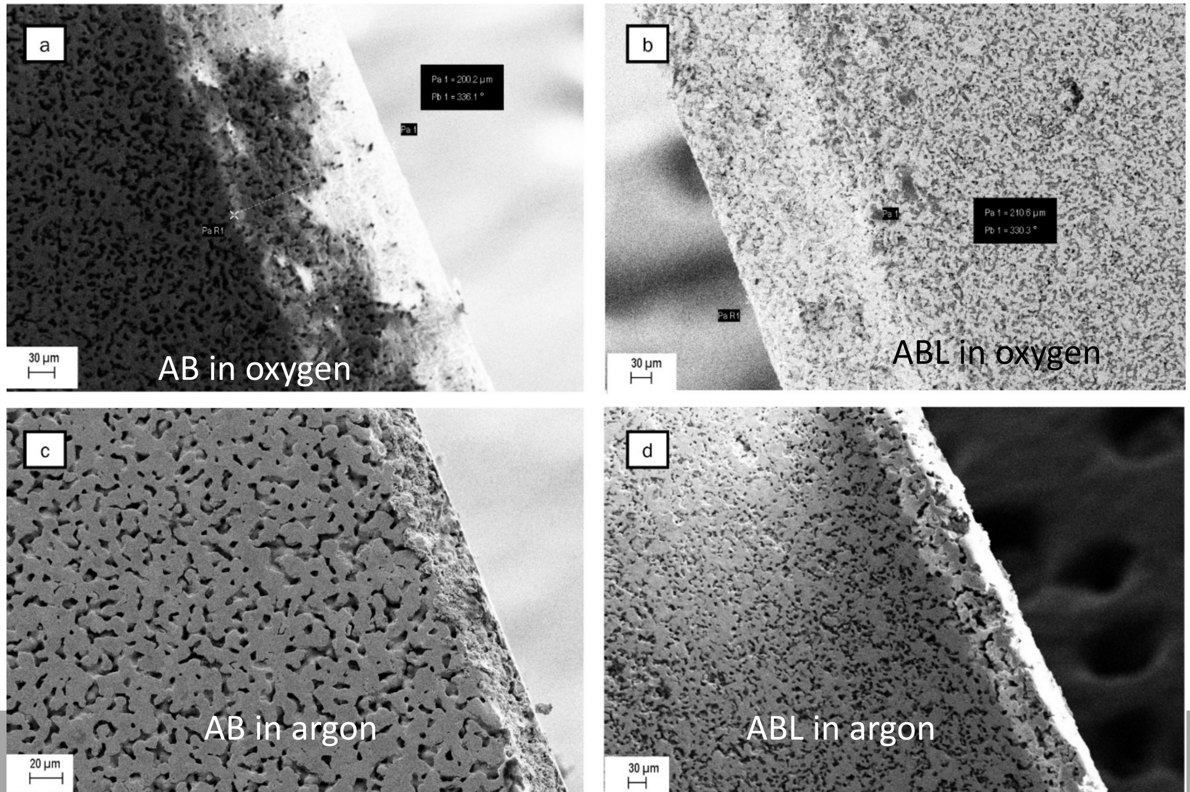
LaB_6 containing ZrB_2+HfB_2 Oxidized in different conditions



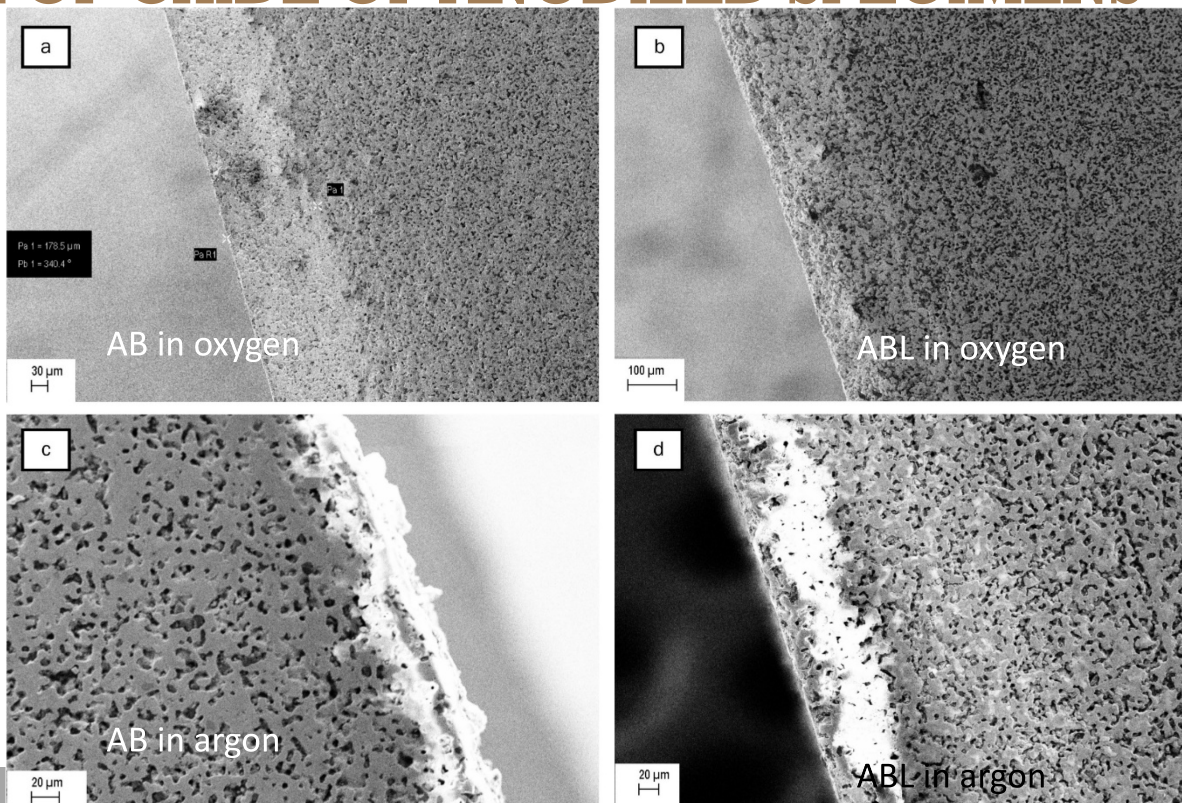
AVERAGE COMPOSITION BY EDS

Element	ABL Anodized (mole %)			
	Base	As-Anodized	Oxidized in argon	Oxidized in oxygen
Zr		46.7	-	57.0
La		1.4	-	0.1
Hf		52.0	-	42.9
	AB Anodized (mole %)			
	Base	As-anodized	Oxidized in argon	Oxidized in oxygen
Zr		39.1	65.2	53.1
Hf		60.9	34.8	46.9
	ABL As-sintered (mole %)			
	Base		Oxidized in argon	Oxidized in oxygen
Zr	48.9		48.9	-
La	02.0		0.6	-
Hf	49.1		50.1	-
	AB As -sintered (mole %)			
	Base		Oxidized in argon	Oxidized in oxygen
Zr	54.5		55.0	55.4
Hf	45.5		45.0	44.6

SEM OF OXIDE OF AS-SINTERED SPECIMENS



SEM OF OXIDE OF ANODIZED SPECIMENS



OXIDE THICKNESS COMPARISON

Oxide Layer Thickness Measurements			
Sample	**Anodized samples (µm)**		
	Initial thickness of anodic oxide	Oxidized in argon	Oxidized in oxygen
ABL	20	70	180
AB	20	30	160
	As-sintered samples (µm)		
		Oxidized in argon	Oxidized in oxygen
ABL		80	210
AB		20	200

CONCLUSIONS

- Elemental and commercial powders of both HfB_2 and ZrB_2 are confirmed to be essentially equivalent.
- The mechanochemical synthesis has been confirmed by XRD to produce a solid solution.
- Electrical resistivity measurements of the base materials shows that a 1:1 mixture of HfB_2 and ZrB_2 has been conductivity than either of the individual borides.
- Anodization does aid in reducing oxidation.
- LaB_6 additive appears to give the highest increase in densification of all the additives tested and increase in the oxidation resistance

Outcomes:

A masters student has graduated with M.S degree

Three presentations have been made in the international conferences

One manuscript has been accepted for publication in Metallurgical and Materials Transactions-E.

Three manuscripts are in preparation and will be submitted by June 2016 for peer review

THANK YOU!

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LATTICE PARAMETERS

To calculate lattice parameter, *a*, take XRD reflections of *hk*0 type.

$$a = \frac{\lambda}{\sqrt{3} sin\theta}\sqrt{h^2 + hk + k^2} \qquad \text{Eq. 1}$$

To calculate lattice parameter, *c*, take XRD reflections of 00*l* type.

$$c = \frac{\lambda}{2\, sin\theta} l \qquad \text{Eq. 2}$$