High Temperature Boride and Carbide Ceramics for Direct Power Extraction Electrode Applications

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FIU FLORIDA INTERNATIONAL UNIVERSITY

Goal & Objectives

❑ Goal

- Study the synthesis of boride and carbide solid solutions as potential hot electrodes for direct powder extraction systems (e.g., magnetic hydrodynamic, MHD)

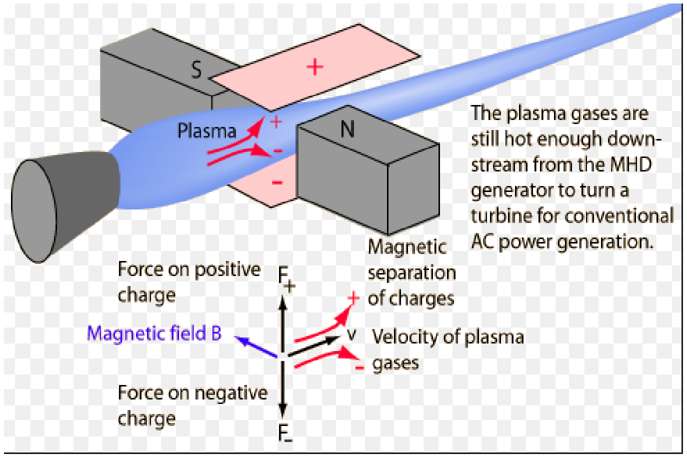
❑ Specific objectives (SO)

- ***SO1*** ***Synthesize*** *nano powders of solid solutions for selected borides and carbides via carbothermal reduction reaction (CTR) from mixed precursors obtained from solution-based processing*
- ***SO2*** *Understand underlying principles between composition, processing and structure relationships for nano boride and carbide solid solutions for applications as electrodes for direct powder extraction (DPE)*
- ***SO3*** ***Process*** *dense nano-structured carbide and boride solid solutions and related composites via novel flash sintering process using the synthesized nano powders*

DPE via MHD Generator

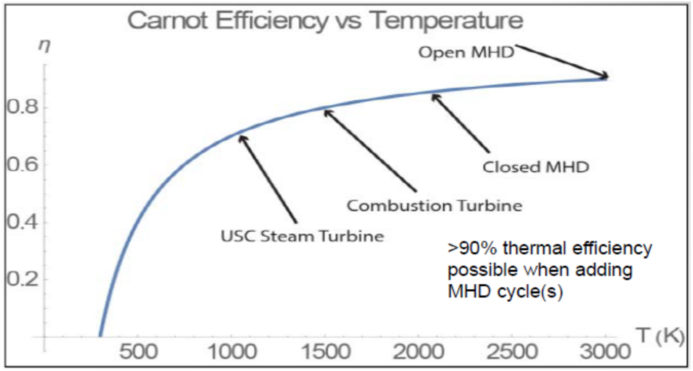
❑Direct Power Extraction (DPE)

- ➢ Electrically conducting gas is produced at high pressure by combustion of a fossil fuel with added seeds (e.g. K+)
- ➢ Ionized gas is then directed through a magnetic field, resulting in an electromotive force



❑Advantages for DPE via MHD

- ➢ No moving parts - can work at higher temp (3000K)
- ➢ High theoretical thermal efficiency >90% and plant efficiency of ~60%



Krishnan A., International Journal of Scientific and Research Publications, Volume 3, Issue 6, June 2013, 1 ISSN 2250-3153

Rigel Woodside, IPT – Direct Power Extraction (2015), http://www.netl.doe.gov/File%20Library/Events/2015/crosscutting/Crosscutting_20150427_1600B_NETL.pdf

DPE Electrodes Materials

❑ Requirements

- ➢ Electrical conductivity (>0.01 S/cm)
- ➢ Good thermal conductivity
- ➢ Resistance to
  - Thermal shock
  - Electrochemical corrosion from seed (e.g., K+)
  - Erosion (e.g. high-velocity gases)
- ➢ Minimization of arc attack

❑ Limitations with DPE electrode materials studied

- ➢ Low temp (~1000 ^{o}C): **arc attack** which decreased efficiency
- ➢ Higher temp (~1200-2000 ^{o}C):
  - **SiC**: Oxidation above 1500 ^{o}C
  - **Doped ZrO_2**: Low conductivity
  - **Doped CeO_2**: Low mechanical properties

Jason Hissam 2015 NETL HBCU/UCR Joint Kickoff Meeting October 27-28, Morgantown, WV. Combustion Synthesis of Boride-Based Electrode Materials for MHD Direct Power Extraction https://www.netl.doe.gov/File%20Library/Research/Coal/cross-cutting%20research/utr-2015/NETL-Kick-off-Meeting-2015-Shafirovich-updated.pdf
Rigel Woodside, IPT – Direct Power Extraction (2015), http://www.netl.doe.gov/File%20Library/Events/2015/crosscutting/Crosscutting_20150427_1600B_NETL.pdf
Yongfei Lu, Vertically Aligned Carbon Nanotubes Embedded in Ceramic Matrices for Hot Electrode Applications (2014),

Borides and Carbides as DPE Electrodes

❑ Borides and carbides are attractive DPE electrode materials

- High melting temp (≥ ~3000 °C)
- Thermal and electrical conductivities comparable to some metals (e.g., ~10^5 S/cm for HfB_2)
- Good thermal shock resistance
- Resistance to plasma sparks and arcs

❑ Limitations with borides and carbides as DPE electrodes

- Investigated 40 years ago - but people lost interest:
  - Still prone to oxidation:
    ~1000°C for ZrB_2 and ~1500°C for ZrB_2-SiC composites

❑ New Approach

Boride and carbide solid solutions for improved performance via novel processing

Indrajit Charit and Krishnan Raja, "Boride Based Electrode Materials for MHD Direct Power Extraction", http://www.netl.doe.gov/File%20Library/Research/Coal/cross-cutting%20research/awards-kick-off-2014/2014_UCR-HBCU-Kickoff_UIdaho.pdf

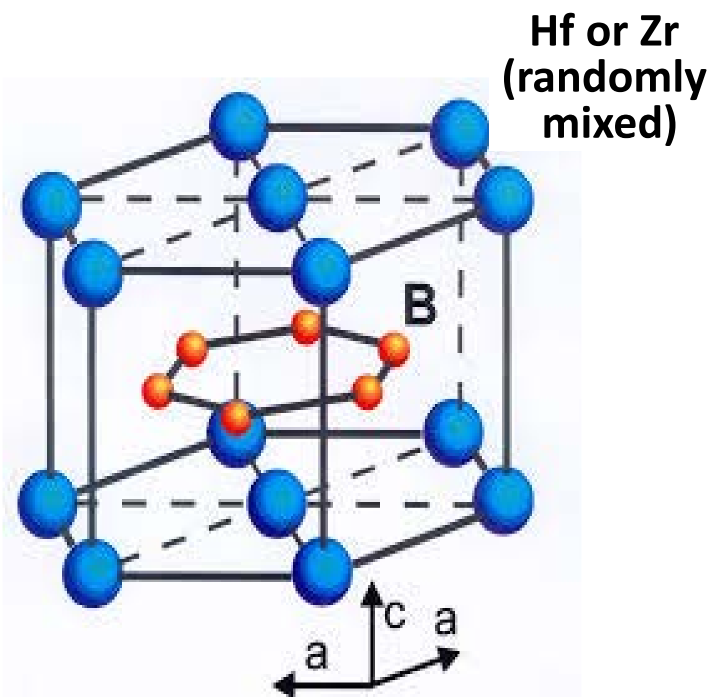
Boride and Carbide Solid Solutions for DPE

❑Potential advantages

- ➢ Tunable oxide shell composition for improved oxidation resistance & electrical properties
- ➢ Tunable microstructure for improved thermal & mechanical properties
- ➢ Novel processing for reduced cost

Solid Solution – an Example

$(Hf\text{-}Zr)B_2$

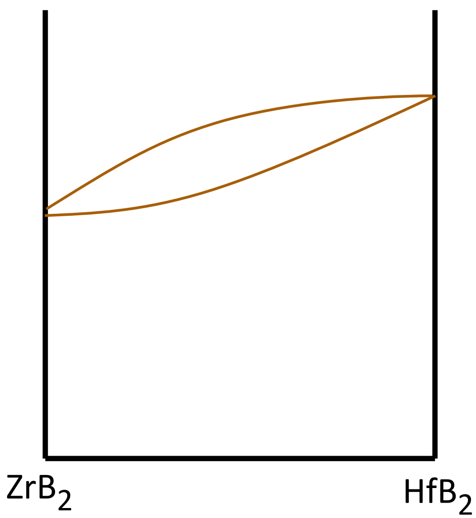


http://physics.aalto.fi/groups/nanospin/facilities/pulsed-laser-deposition/

Materials Systems

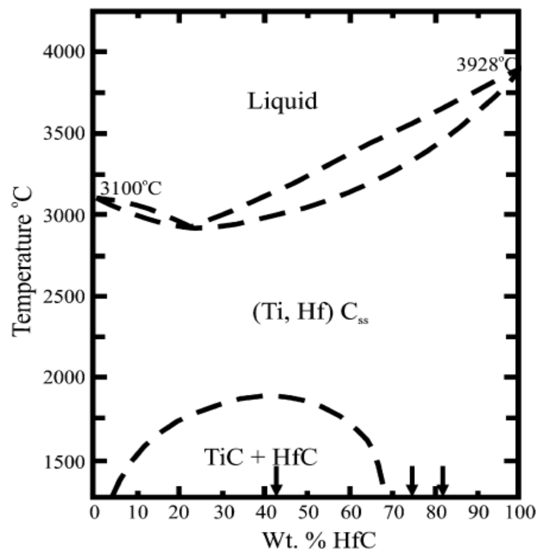
❑Materials systems of choice

ZrB_2-HfB_2
Continuous solid solution



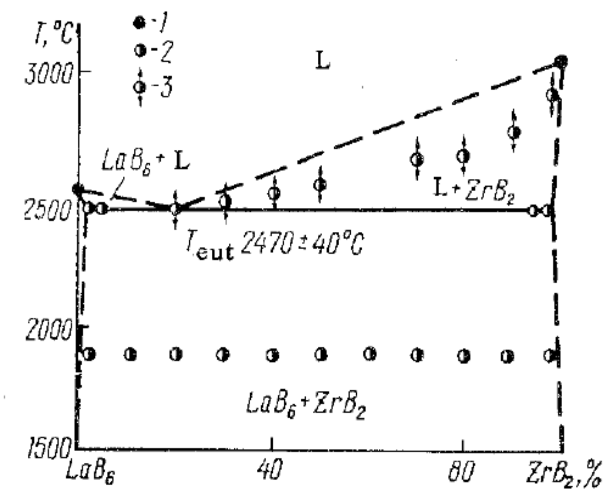
Fahrenholtz J. Am. Ceram. Soc., (2007) 1347

HfC-TiC
Complete solid solution
w/ a **miscibility gap**



C. Heiligers International Journal of Refractory Metals & Hard Materials 25 (2007) 300–309

ZrB_2-CeB_6
Eutectic system with very limited solubility in solid



***Ordan'yan**, Soviet Powder Metallurgy and Metal Ceramics (1983) 946*

Solid Solution Powders Synthesis Method

❑ Solution-based processing followed by CTR heat treatment

- **Step 1: Solution-based processing**

  Nano-scale mixing of metal and carbon precursors in solution

  - Product uniformity
  - Low cost
  - Microstructure control

- **Step 2: Carbothermal reduction (CTR) reaction**

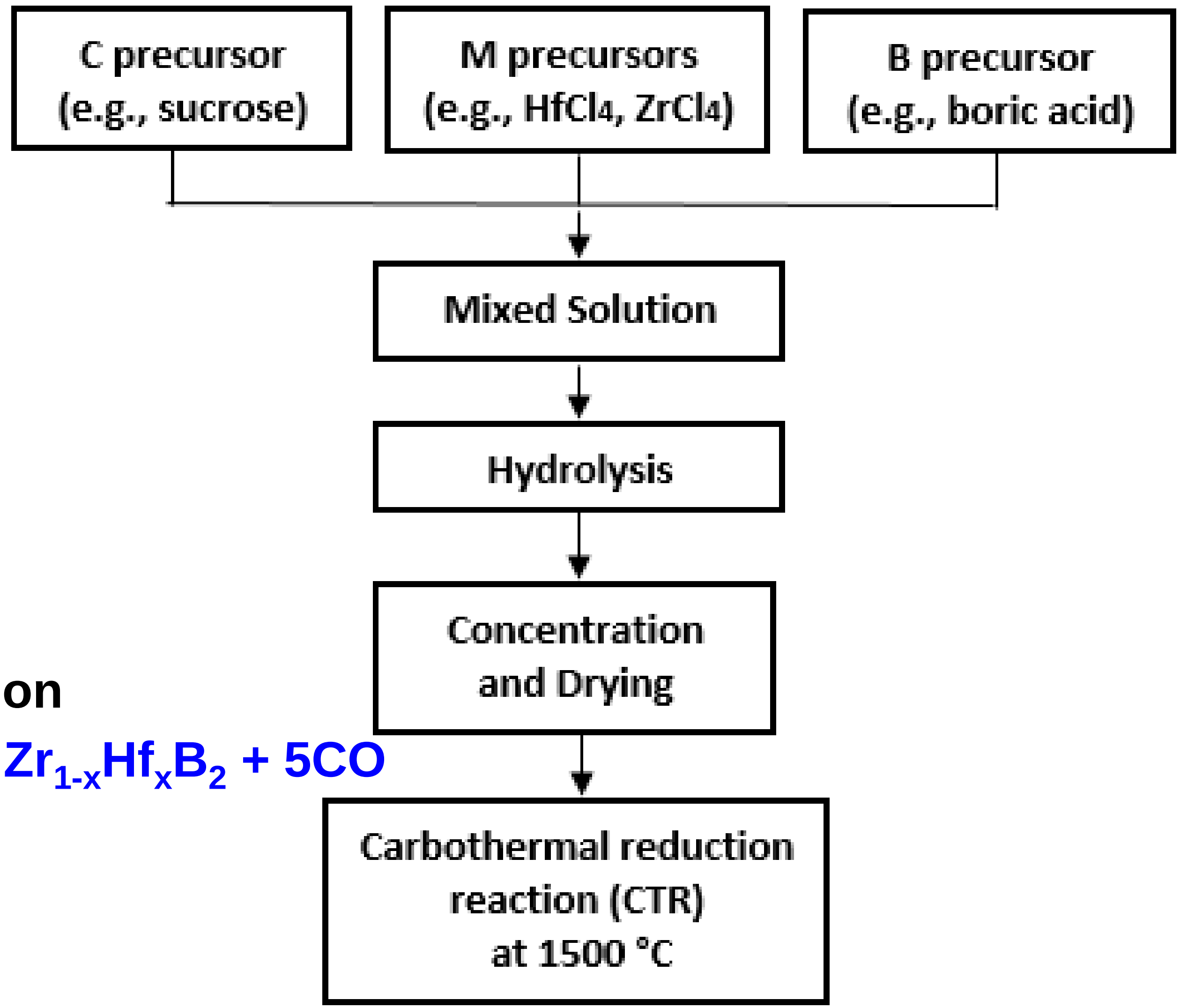
  Carbides $MO_x + 1.5x\,C = MC_{x/2} + x\,CO$

  Borides $MO_x + B_2O_3 + (3+x)\,C = MB_2 + (3+x)\,CO$

  - Many choices of precursors
  - Low cost
  - Scalable

Starting Materials & Underlying Reaction

- ❑ 1^{st} system: HfB_2-ZrB_2



- ❑ Underlying CTR reaction

$$Zr_{1-x}Hf_xO_2 + B_2O_3 + 5C = Zr_{1-x}Hf_xB_2 + 5CO$$

Starting Materials & Underlying Reaction

❑ 2nd system chosen: HfC-TiC

- Starting materials
  - M precursors: $HfCl_4$ and Titanium isopropoxide (Ti[OCH(CH₃)2]4)
  - C precursor: Sucrose ($C_{12}H_{22}O_{11}$)
- Soluble oxide/carbon precursors → finely mixed oxides + carbon → CTR reaction → Carbide solid solution

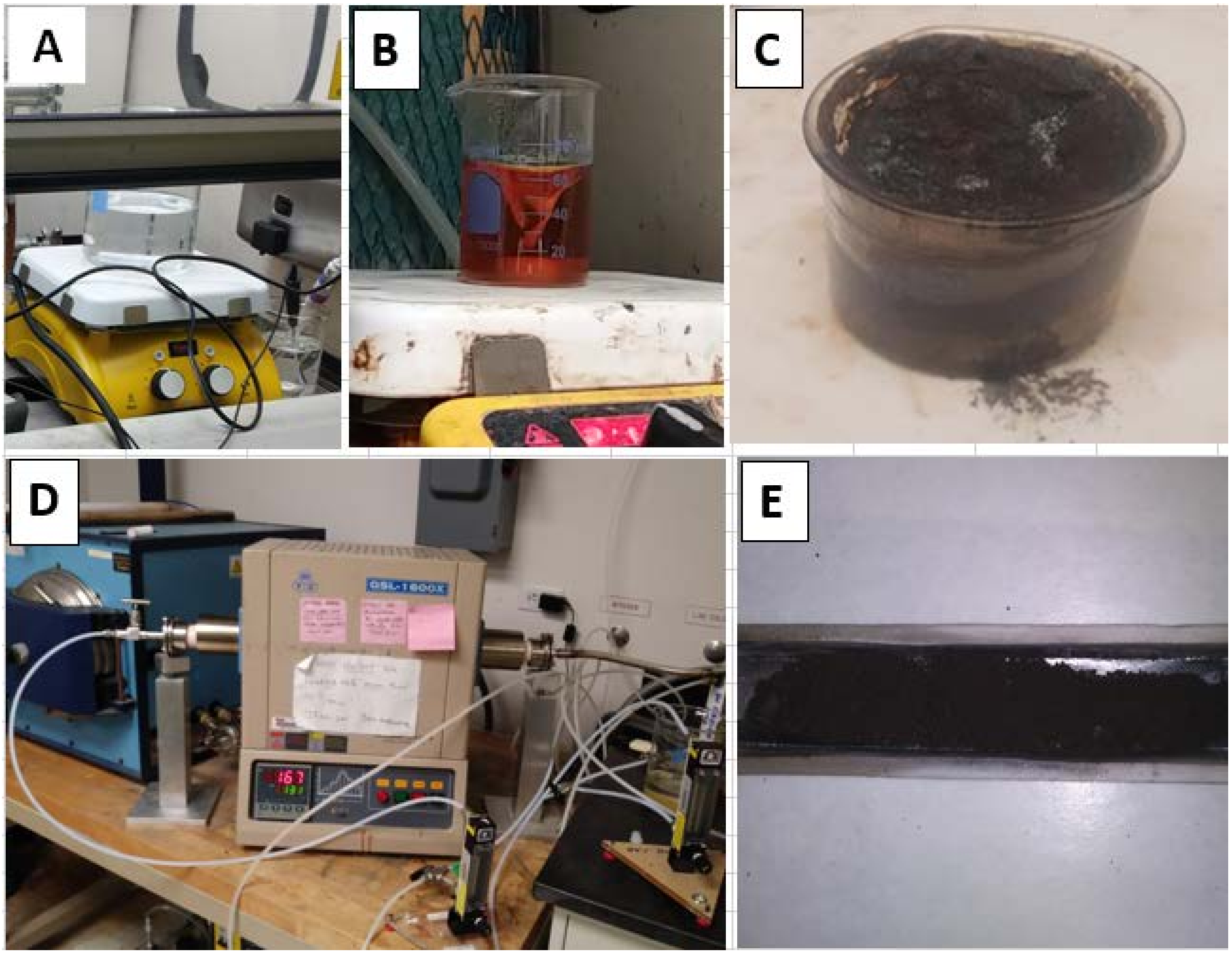
❑ Underlying CTR reaction

$$Hf_{1-x}Ti_xO_2 + 6C = 2(Hf_{1-x}Ti_x)C + 4CO$$

Synthesis Procedure

(Aqueous) precursor solution mixing

CTR heat treatment (~1500-1650 ^{o}C in Argon)

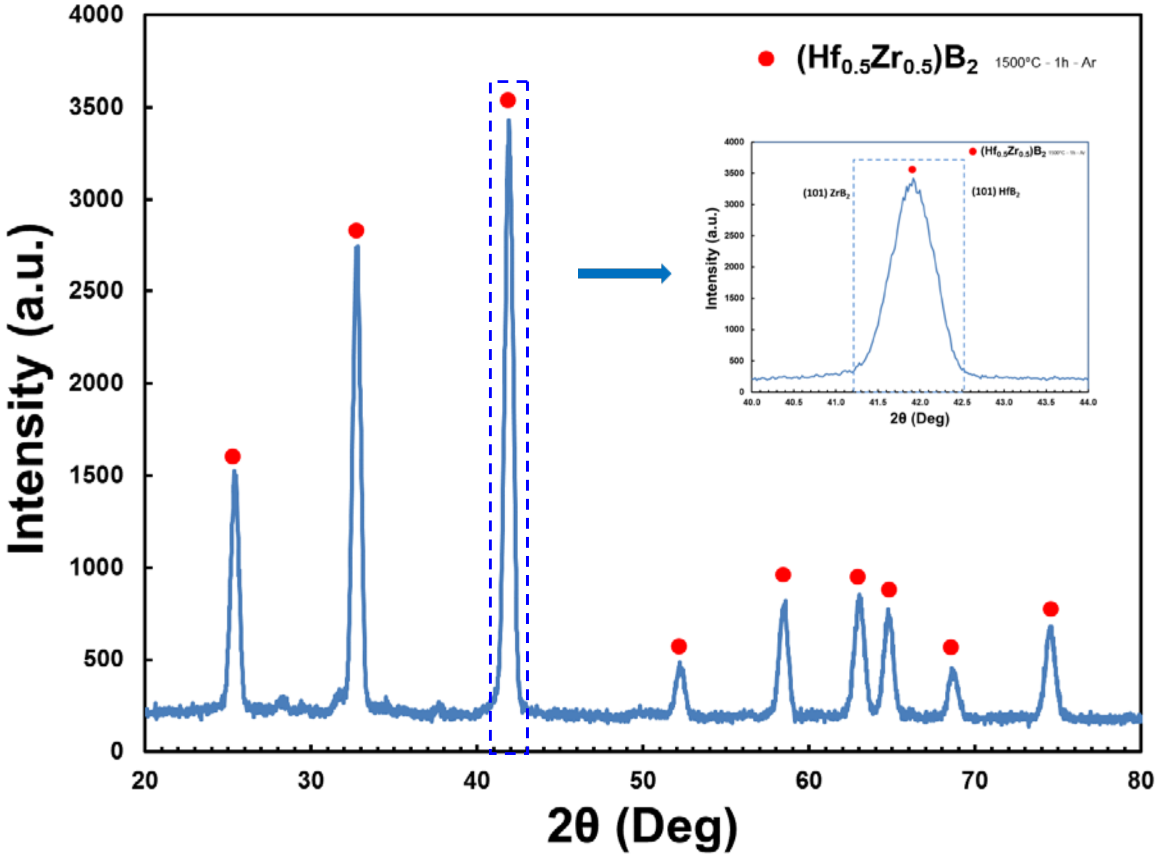


Dried precursor from solution-based processing

Solid solution powders

$(Hf\text{-}Zr)B_2$ Synthesis

- **High purity $(Hf\text{-}Zr)B_2$ solid solution powder synthesized**



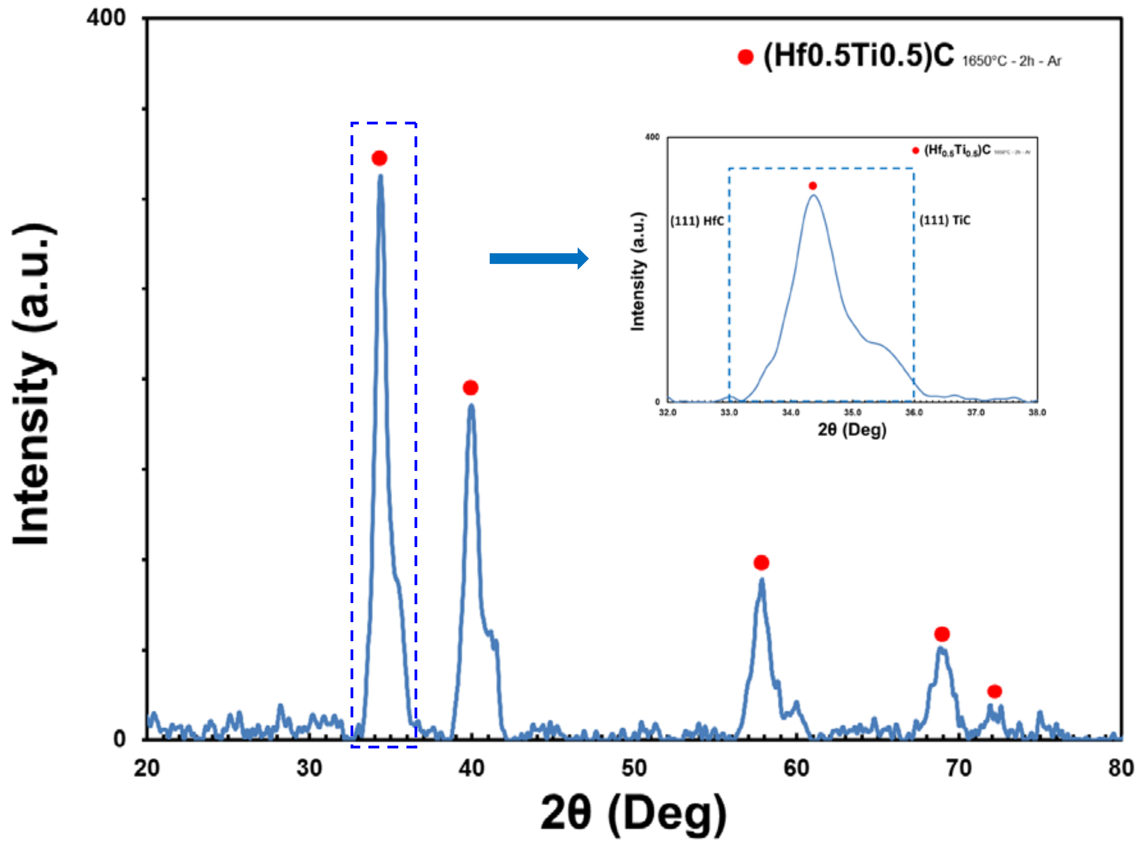
XRD pattern

$(Hf\text{-}Zr)B_2$ Powder Microstructures

- ❑ **Submicron to nano powders with some <u>non-uniformity</u>**

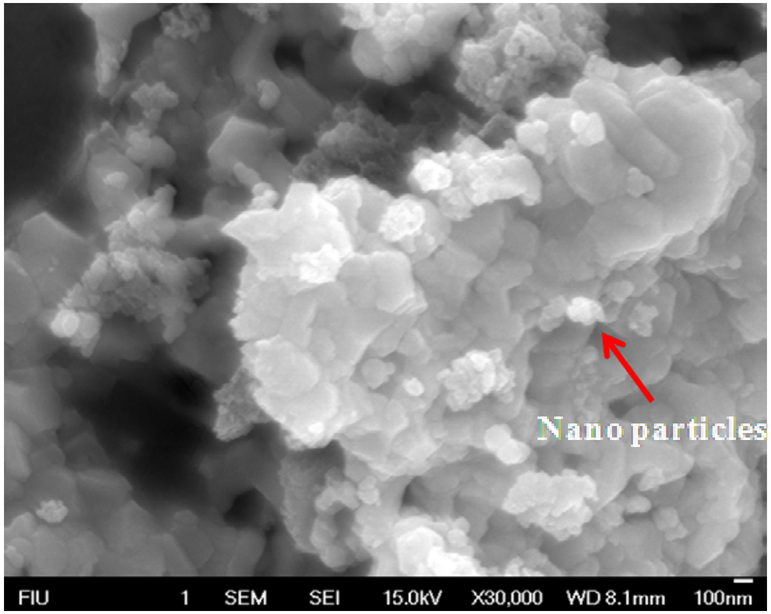
(Hf-Ti)C Synthesis

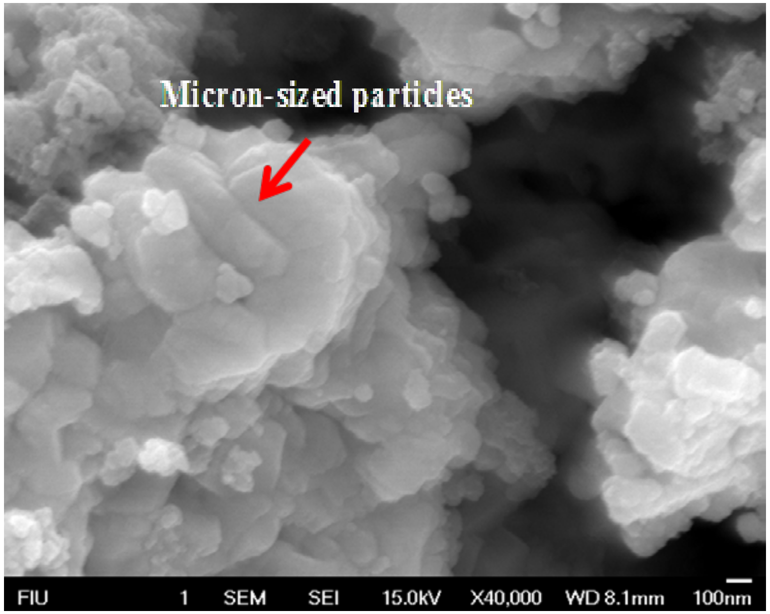
- ❑ **High purity almost complete (Hf-Ti)C solid solution powder synthesized**



XRD pattern

(Hf-Ti)C Powder Microstructures



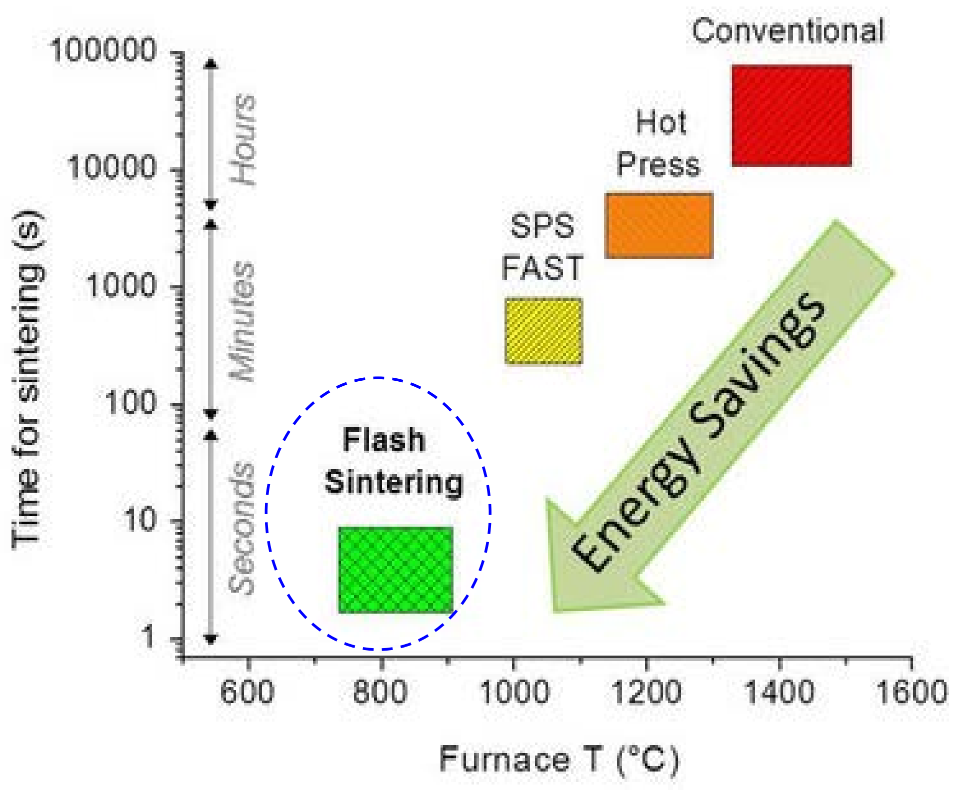


❑**Mostly submicron to nano-sized agglomerated powders**

Materials Densification via Flash Sintering

- ❑ **Ceramics need sintering**
- ❑ **Flash sintering**
  - ➢ Rapid densification (in seconds) of powders under (DC) electrical field exceeding certain critical level
- ❑ **Advantages**
  - ➢ Reduced Temp, Time, & Energy
  - ➢ Finer microstructure
- ❑ **Demonstrated systems**
  - ➢ 3 mol.% Y2O3-doped ZrO2 (3YSZ)
  - ➢ Co2MnO4
  - ➢ Many more…

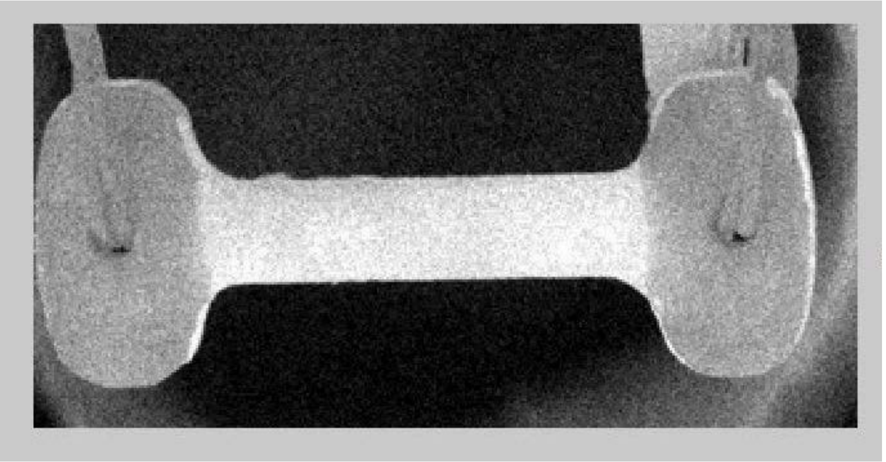
Cologna and Raj, Univ Colorado



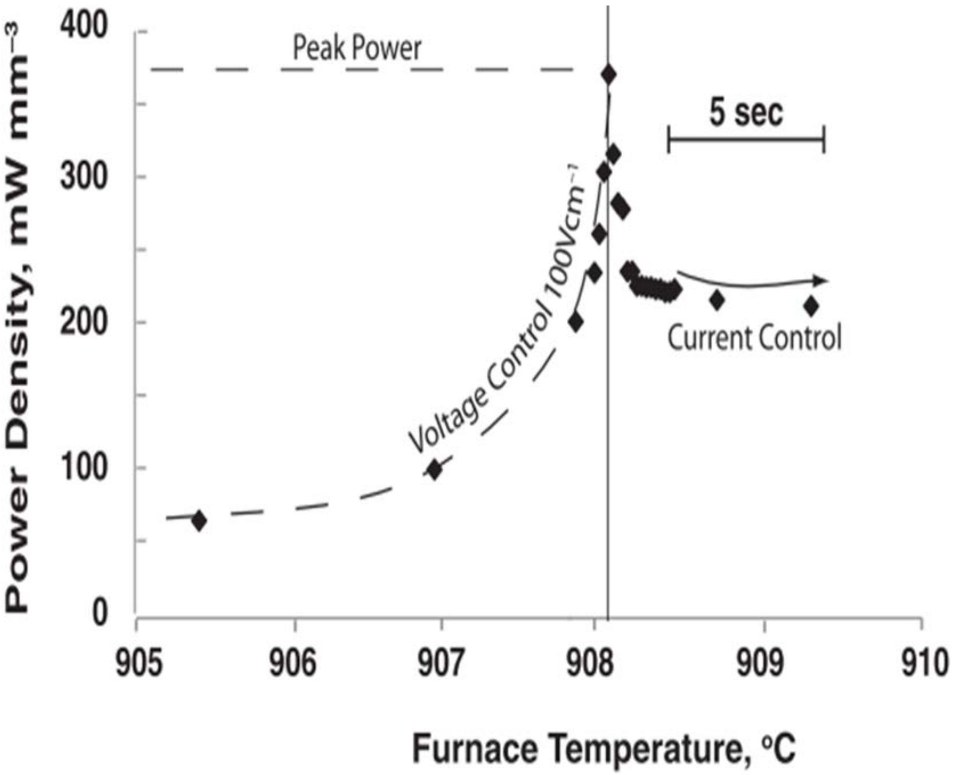
Cologna and Raj, J Am. Ceram. Soc (2010) 3556

Flash Sintering of YSZ

- Flash sintering by Rishi Raj and co-workers at U Colorado



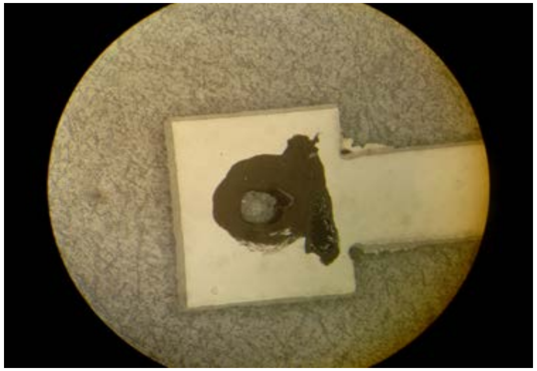
Flash - spike in electrical power dissipation



Raj, Rishi. "Joule Heating during Flash-sintering." *Journal of the European Ceramic Society*32.10 (2012): 2293-301. Web.

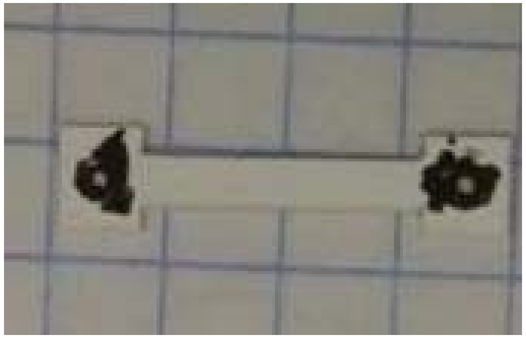
Initial In-house Flash Sintering

- ❑ Similar dog-bone shaped samples
- ❑ Pt wires with Pt paste for electrical connection & power delivery

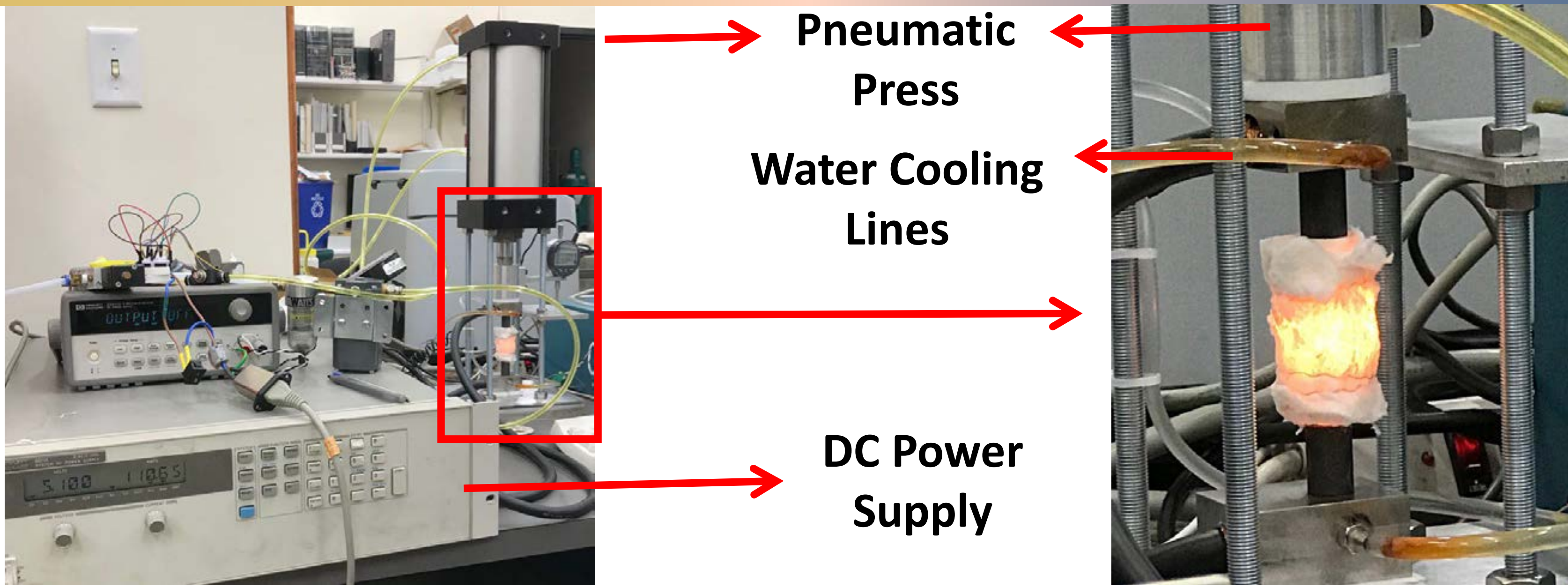


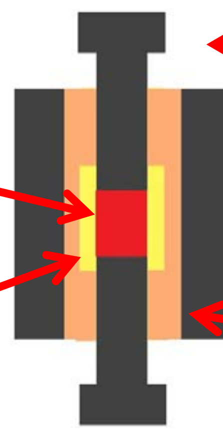
- ❑ DC power supply & LabVIEW control

- ❑ Sample sintered but not uniform



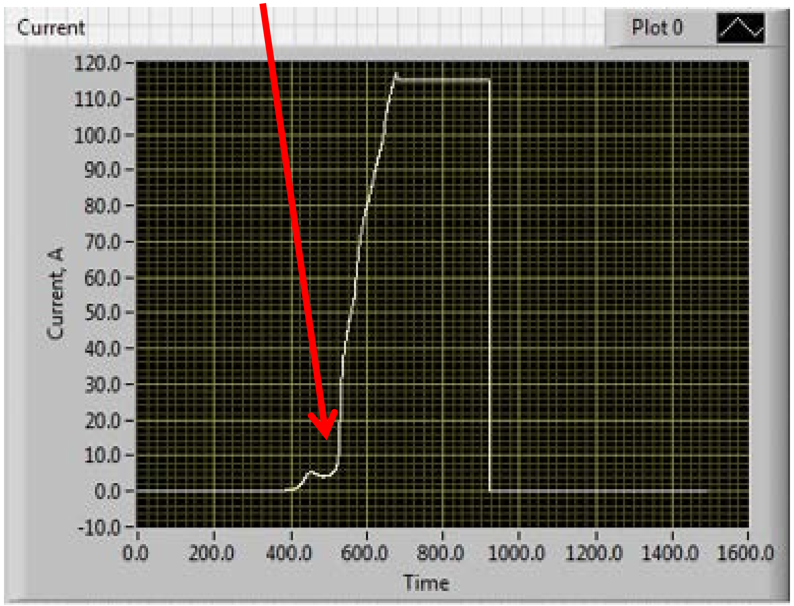
Modified Flash Sintering Set-up





Experimental Set-up

Current Spike/"Flash"



Rapid Shrinkage

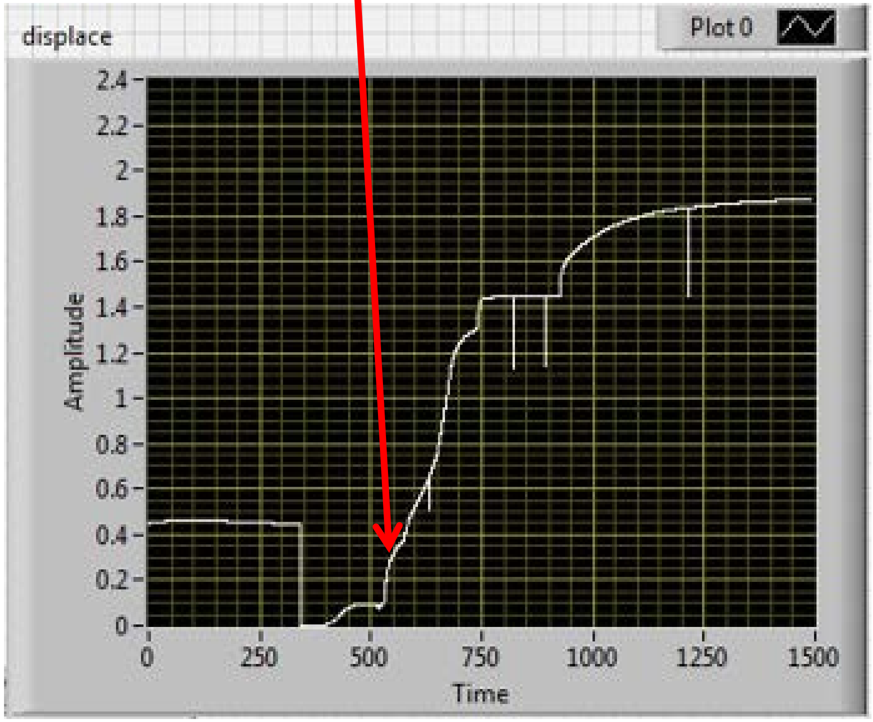


Photo of sample assembly

Ceramic sample after flash sintering

Summary and Future Work

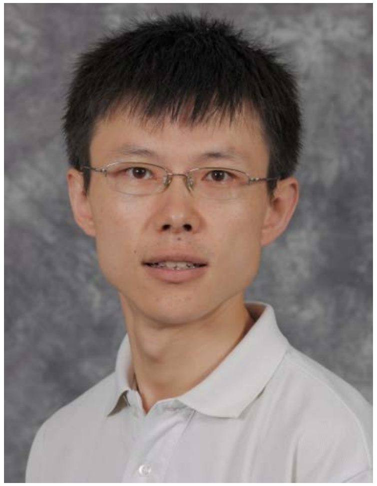
- **High purity, submicron (Hf-Zr)B_2 and (Hf-Ti)C solid solution powders synthesized**
- **Modified flash sintering setup demonstrated on similar high temperature ceramics**

- **Synthesis of ZrB_2-CeB_6 nano solid solutions powders**
- **Optimization still needed to obtain uniform nano powders**
  - Adjusting temperature/time
  - Reducing excess B_2O_3 (liquid) to reduce diffusion rates for borides
  - Reducing carbon (e.g. sucrose) content for carbides
  - Others
- **Carry out flash sintering on new synthesized carbide/borides and characterize their physical/chemical properties**

Team Members

❑Current Members

Dr. Z Cheng (PI)



Dr. A Agarwal (co-PI)

Dr. A Durygin (engineer at FIU CeSMEC)

J Belisario (minority PhD student)

❑Past Members

- A Behrens (minority MS student)
- D Alfonso (minority BS student)

Acknowledgements

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  - Advanced Materials Engineering Research Institute (AMERI)
  - Center for Study of Matter under Extreme Conditions (CeSMEC)