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

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Institution: Florida International University
Project Duration: 10/01/2015 – 09/30/2018

FIU | FLORIDA INTERNATIONAL UNIVERSITY

Goal & Objectives

❑Goal

Develop nano carbide and boride ceramic solid solutions and related composites via novel synthesis and processing and understand the fundamental composition-processing-structure-property relationships for such materials as potential hot electrodes for direct powder extraction (e.g., magnetic hydrodynamic, MHD) systems

❑Specific objectives (<u>SO</u>)

- **<u>SO1</u>** ***Synthesize*** *nano powders of solid solution and related nano composites for selected carbides and borides via carbothermal reduction reaction from intimately mixed precursors obtained from solution-based processing*
- **<u>SO2</u>** ***Process*** *dense nano-structured carbide and boride solid solutions and related composites via novel flash sintering process using the synthesized nano powders*
- **<u>SO3</u>** *Reveal fundamental* ***composition-processing-structure-property relationships*** *for nano carbide and boride solid solutions and related composite materials for potential applications as electrodes for direct powder extraction (DPE)*

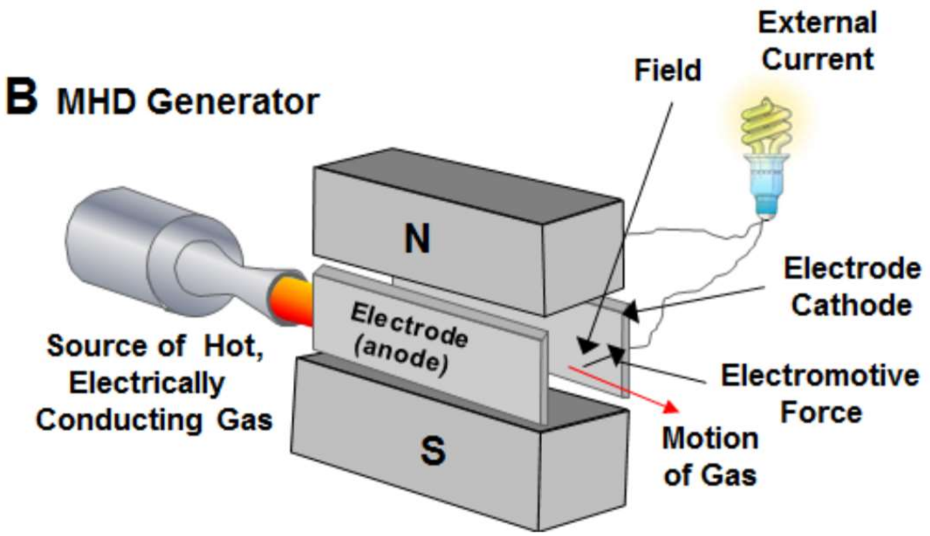
Outline

- ❑**Background**
  - DPE via MHD
  - Boride & carbide solid solutions for DPE
- ❑**Methods**
  - Synthesis via solution-based processing/CTR for solid solution nanopowders
  - Fast densification via flash sintering
- ❑**Results**
  - $(Hf\text{-}Zr)B_2$ solid solution nano powder synthesis
  - Preliminary flash sintering experiments
- ❑**Future Work**
- ❑**Summary**
- ❑**Acknowledgements**

Direction Power Extraction (DPE) via MHD Generator

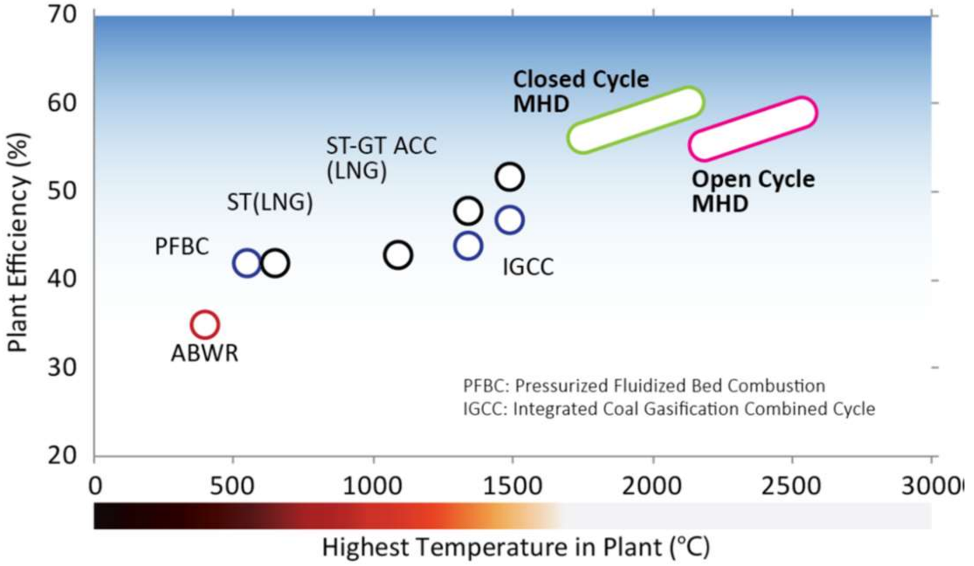
❑DPE

DPE via magnetic hydrodynamic (MHD) power generator is an attractive technique for generating power from fossil fuels such as coal: fuel is burned with help of added oxygen and salts seeds(e.g. K_2CO_3) to become ionized, which in magnetic field, provide electromotive force



❑Advantages for DPE via MHD

- Conceptually simple due to no moving mechanical parts
- Very high theoretical efficiency



Geo. A. Richards, https://www.netl.doe.gov/File%20Library/events/2013/co2%20capture/G-Richards-NETL-Future-Combustion.pdf

Challenges with DPE Electrode Materials

❑Requirements

- Electrical conductivity >>0.01 S/cm
- Adequate thermal conductivity
- Resistance to
  - Corrosion
  - Erosion (e.g., slug)
  - Thermal shock
- Compatibility
- Minimization of arc attack

❑Limitations with DPE electrode materials studied

- Low temp (~1000 ^{o}C): **arching!** → decreased efficiency!
- Higher temp (~1200-2000 ^{o}C):
  - **SiC**: Low conductivity, Oxidation above 1500 ^{o}C
  - **Doped $LaCrO_3$**: Cr vaporization
  - **Doped ZrO_2**: Low conductivity and susceptibility to corrosion
  - **Doped CeO_2**: Low mechanical properties

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?

❑ **Boride and carbides appear attractive as DPE electrode materials**

- High melting points (e.g., ~3245 °C for ZrB_2)
- Electrical and thermal conductivity close to some metals
  - e.g., ~10^5 S/cm for ZrB_2

❑ **Limitations with borides and carbide as DPE electrodes**

- Investigated in 1960-1970s → **"lost favor"**
- Less than ideal oxidation resistance:
  - 1000 °C for ZrB_2
  - 1500 °C for ZrB_2-SiC composite

❑ **New Approach**

- Borides 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

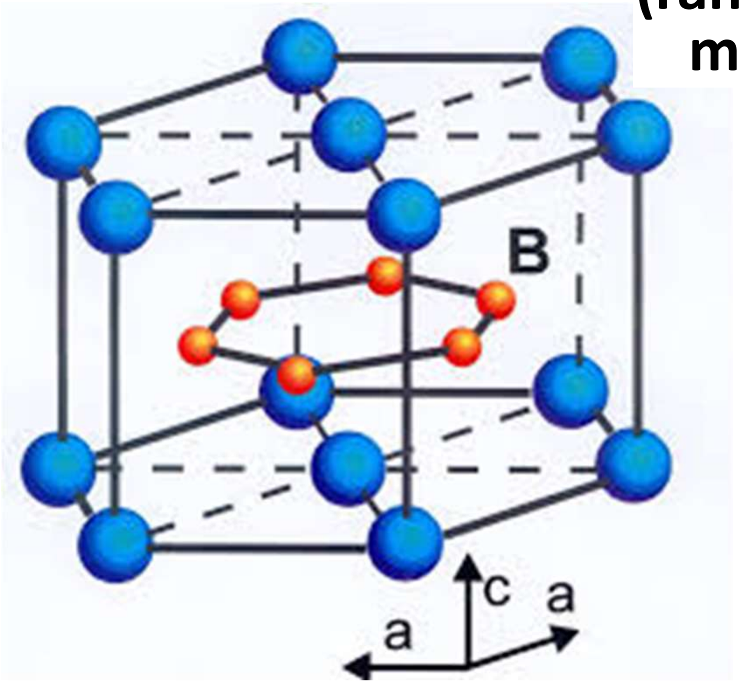
Boride and Carbide Solid Solutions for DPE

❑**Potential advantages**

- Tune oxide shell composition for improved oxidation resistance and electrical properties
- Tune microstructure for improved thermal and mechanical properties
- Simplify processing and reduce cost

Solid Solution – an Example

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



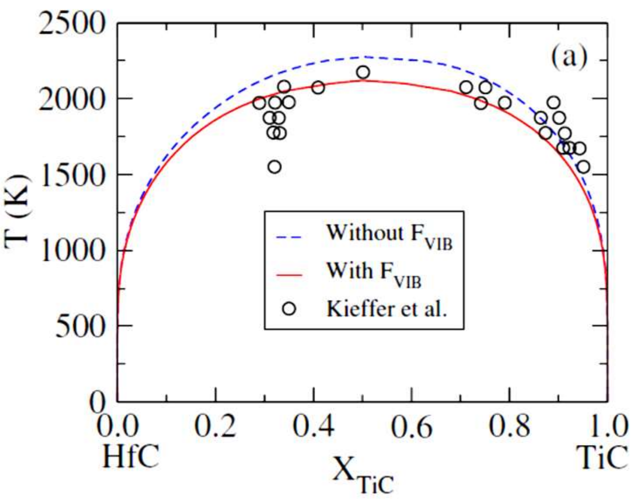
http://physics.aalto.fi/groups/nanospin/facilities/pulsed-laser-deposition/

Materials System & Subtasks

❑Materials systems of choice

HfC-TiC

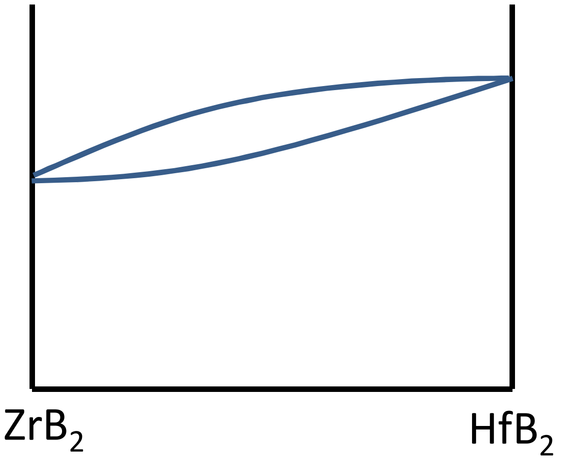
Complete solid solution
w/ a **miscibility gap**



***Adjaoud**, PHYS REV B (2009) 134112*

ZrB_2-HfB_2

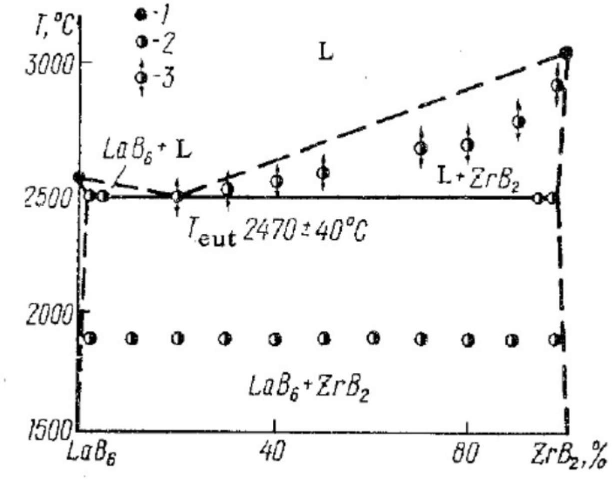
Continuous solid solution



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

ZrB_2-CeB_6

Eutectic system with very
limited solubility in solid



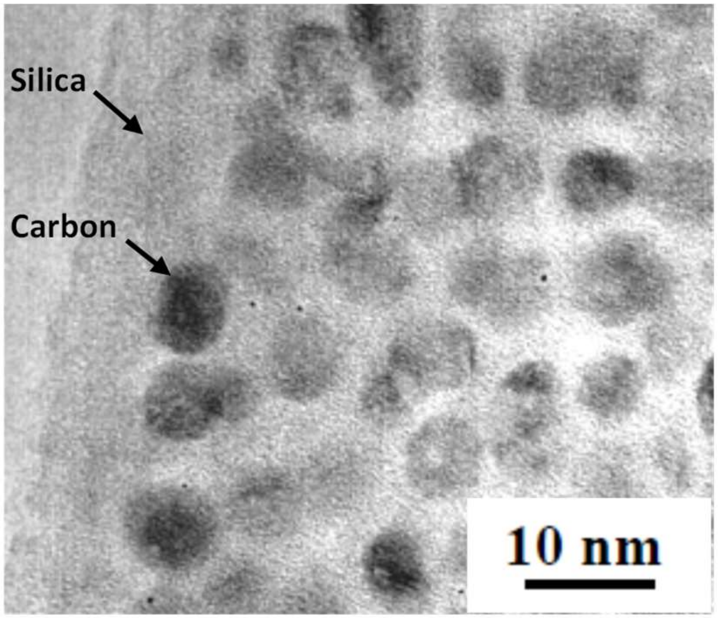
***Ordan'yan**, Soviet Powder Metallurgy and Metal Ceramics (1983) 946*

Solid Solution Powders Synthesis Method

❑Solution-based processing w/ CTR Heat Treatment

- **<u>Solution-based processing</u>**
  - Nano-scale mixing of metal and C precursors
  - Lower T heat treatments
  - Product uniformity
  - Microstructure control
- **<u>Carbothermal reduction (CTR) reaction</u>**
  - Many choices of precursors
  - Low cost
  - Scalable

nano SiO_2-C mixture from solution processing followed by pyrolysis



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

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

Cheng, MS Thesis (2004)

Starting Materials & Underlying Reaction

❑Starting (precursor) materials

- Metal
  - Water soluble: e.g., $HfCl_4$, $ZrOCl_2$, $TiCl_4$
  - Solvent soluble: e.g., titanium butoxide
- C
  - Water soluble: sucrose
  - Solvent soluble: phenolic resin
- Boron
  - Water soluble: boric acid (H_3BO_3)
  - Solvent soluble: e.g., triethyl borate (TEB)

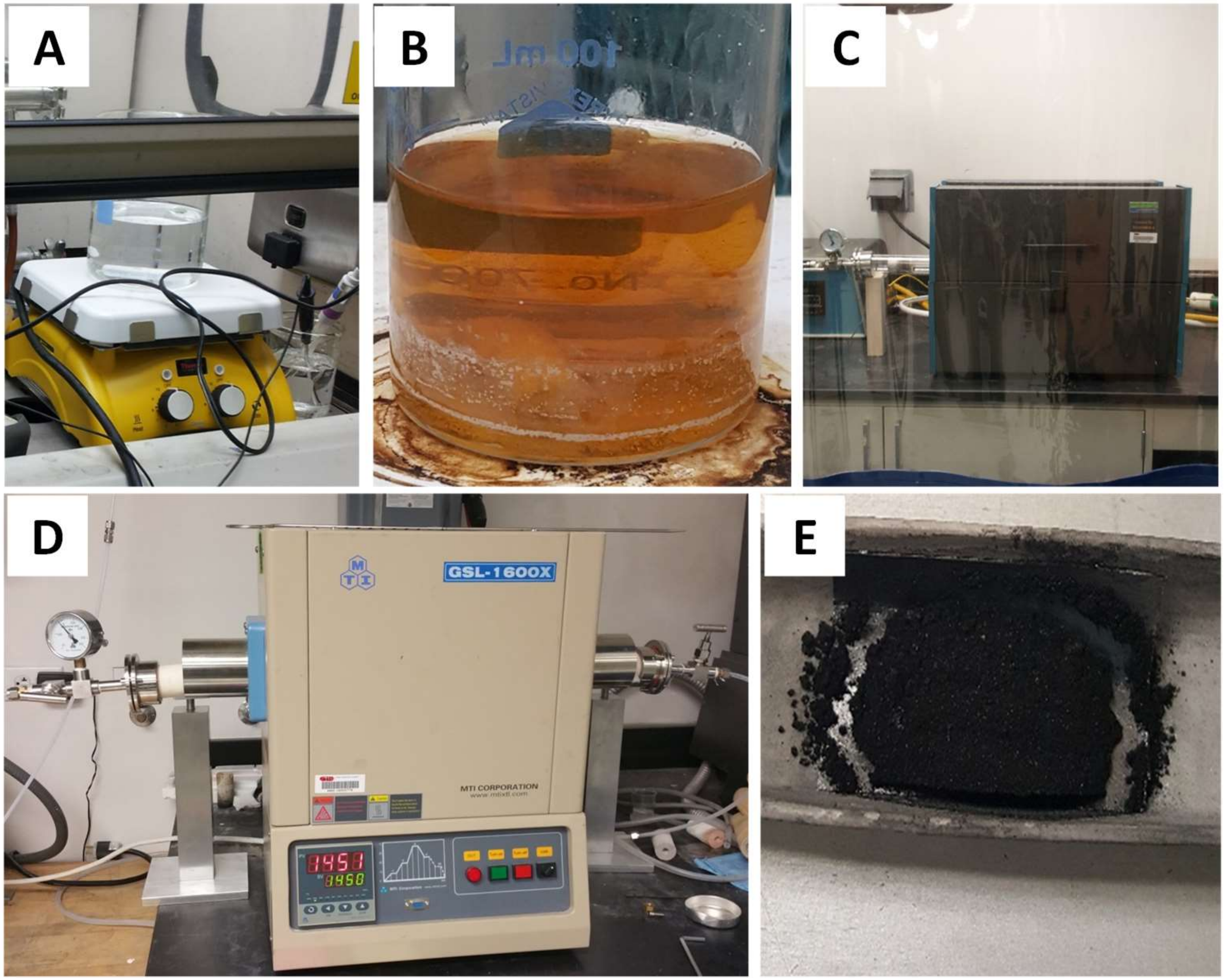
❑Underlying CTR reaction

e.g., for (Hf-Zr)B_2 solid solution: $Zr_{1-x}Hf_xO_2 + B_2O_3 + 5C = Zr_{1-x}Hf_xB_2 + 5CO$

Synthesis Procedure

Solution Drying

(Aqueous) precursor solution mixing



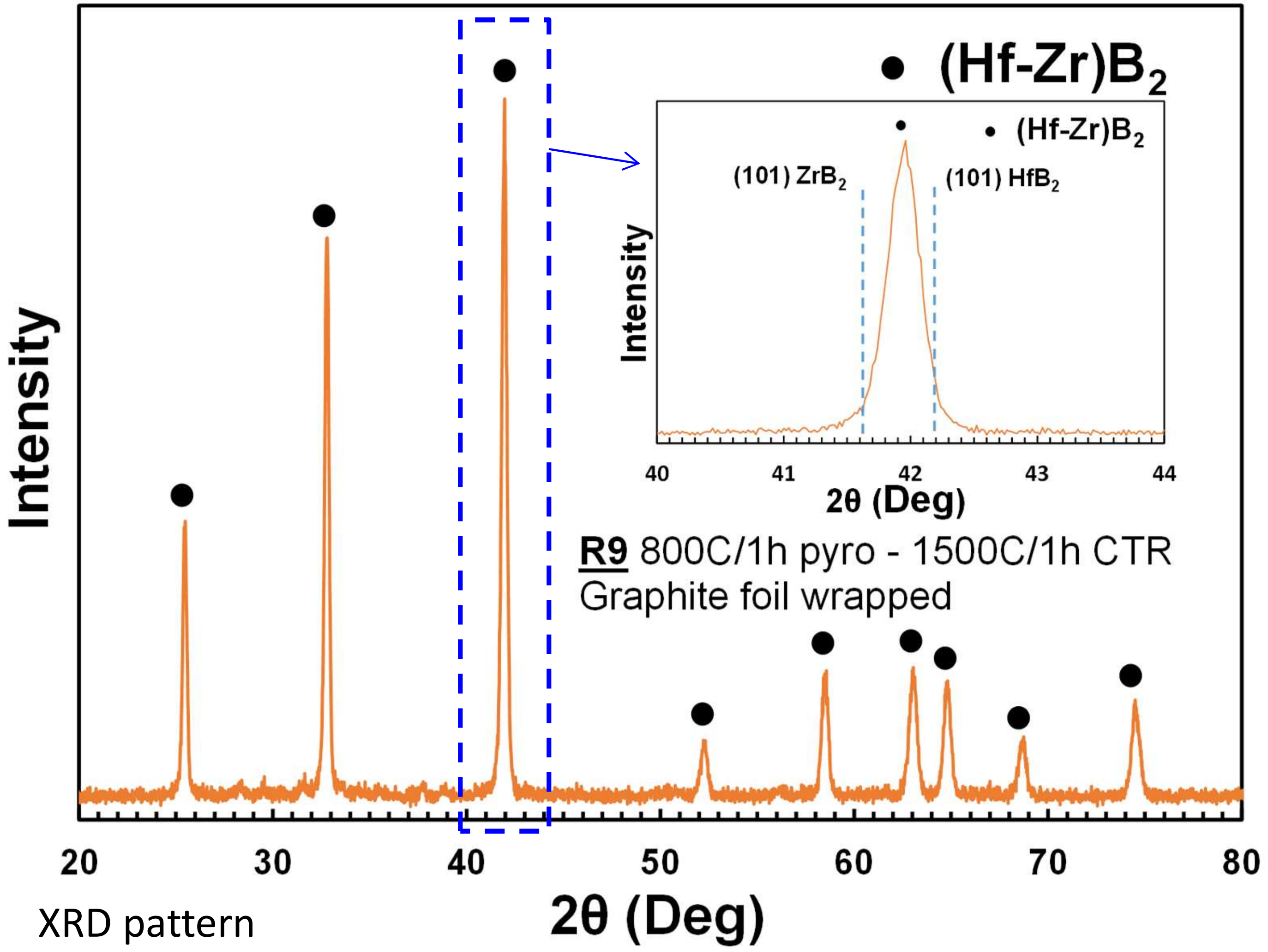
Pyrolysis, e.g. 700^{o}C/Ar, to obtain oxides-C mixture

CTR, e.g., 1500^{o}C/Ar, to obtain nano boride solid solution

Solid solution powders

Synthesis Results

❑High purity (Hf-Zr)B_2 solid solution powder obtained!



XRD pattern

Critical Parameters in Synthesis

❑**Secure low pO_2** (e.g., protection via use of graphite boat with cover)

❑**Adjust for B_2O_3 loss** (via evaporation)

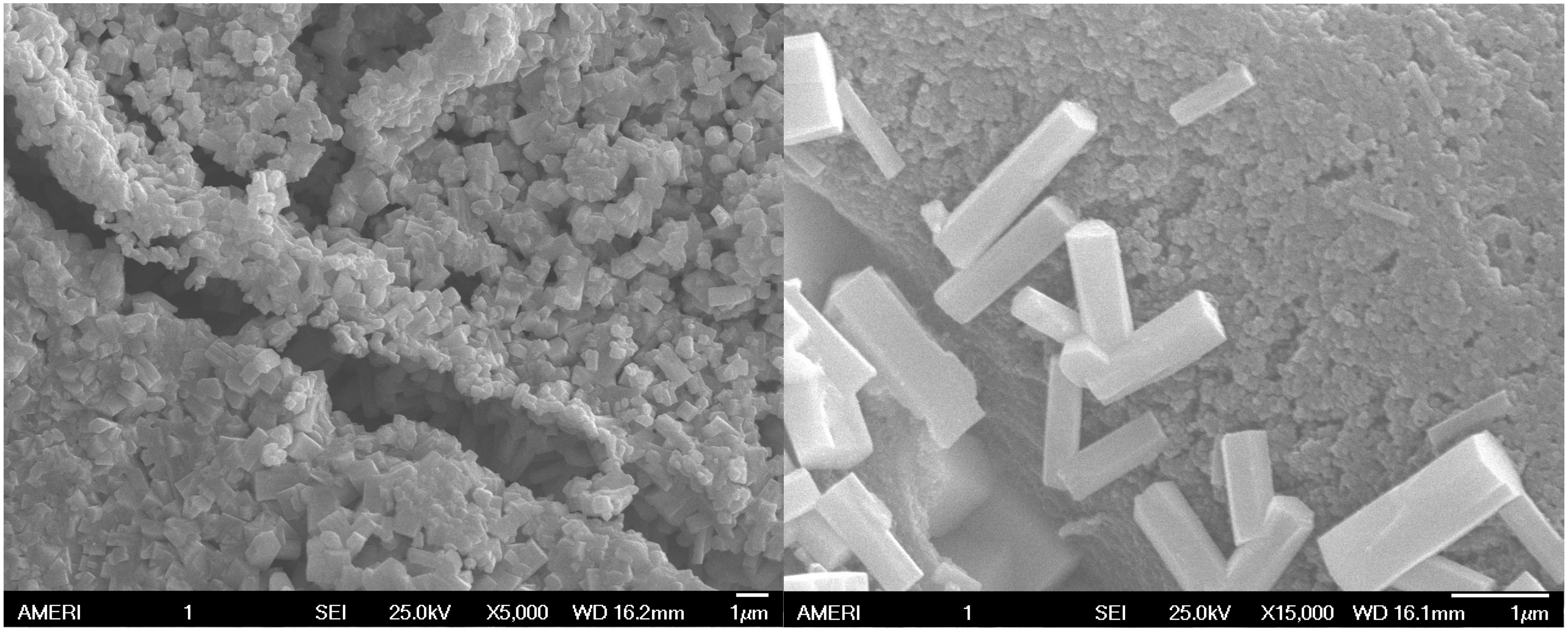
Zr : Hf : B : C mol. ratio	0.5 : 0.5 : $\underline{2}$: 5	0.5 : 0.5 : $\underline{3}$: 5
Oxide & carbide **impurities**	~20%	<2%

❑**Ensure adequate temperature and time**

CTR condition	1300°C/24 h	1500°C/5 min	1500°C/1 h
Oxide **impurities**	~90%	~5%	<~2%
$(Zr\text{-}Hf)B_2$	~10%	~95%	>~98%

Powder Microstructures

❑**Submicron powders w/ non-uniformity**



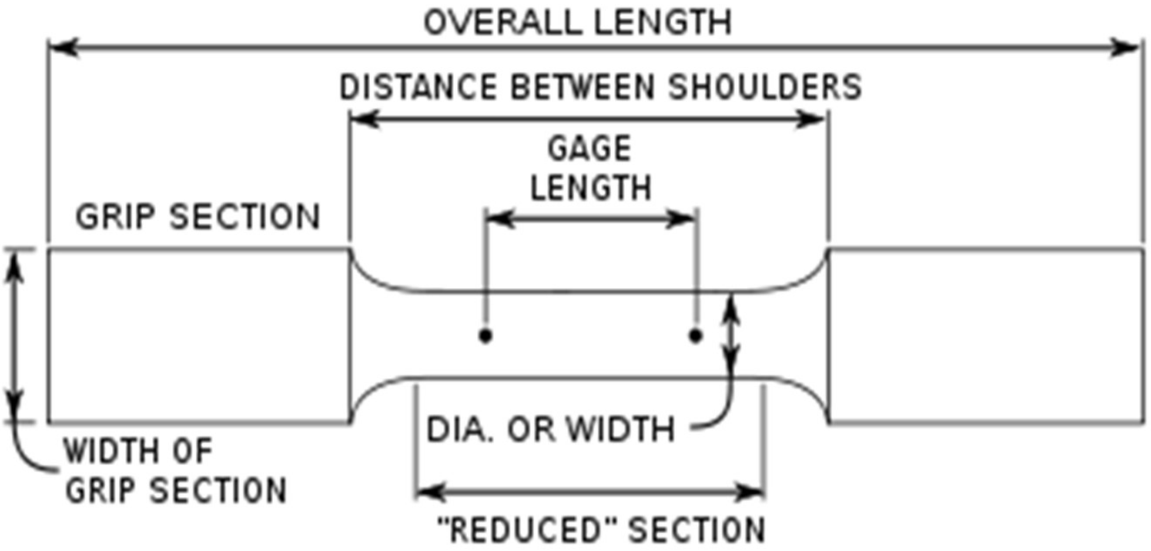
❑**Optimization needed to obtain nano powders**

- Adjusting Temp/time
- Reducing excess B_2O_3
- Others

Green Body Formation before Sintering

- ❑Dog-bone shaped samples often used for flash sintering (Rishi Raj and co-workers)

- ❑Two approaches explored for dog-bone shaped green body formation
  - Slip Casting
  - Laser Cutting



Green Body Formation via Slip Casting (1)

☐Slip casting

Pouring ceramic powder suspension in a solvent (slip) into a mold and solidify

☐Features

- Complex shape suitable
- Low cost
- Mass-production ready

Green Body Formation via Slip Casting (2)

❑ **Two recipes give good results**

Recipe	YSZ%	Binder%	Solvent(s)%
5.2	21.1 wt.%	1.4 wt. % Arabic Gum (AG)	Water: 54.6 wt. % Ethanol: 22.9 wt.%
6.2	49.9 wt.%	1.76% PVA	Water: 48.3wt.%

- Dense, non-porous structure w/o chipping or cracks
- Respectable mechanical strength (~4ft drop)

Dog-bone shaped sample from slip casting

Pre-embedding of lead wires

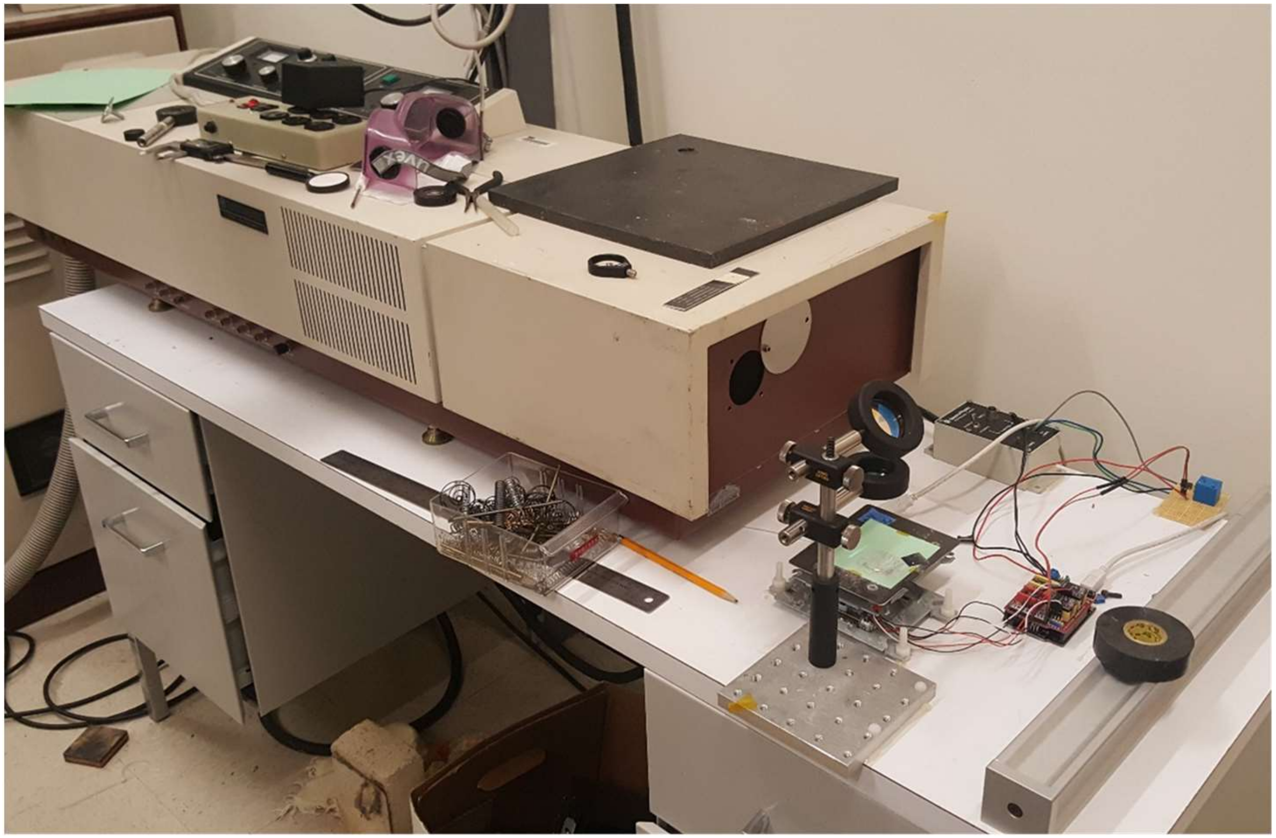
Green Body Formation via Laser Cutting (1)

❑**Laser cutting**

Use of high power pulsed laser to cut dry-pressed samples

❑**Features**

- Simple
- Fast adaption to different shapes
- Limited to low thickness



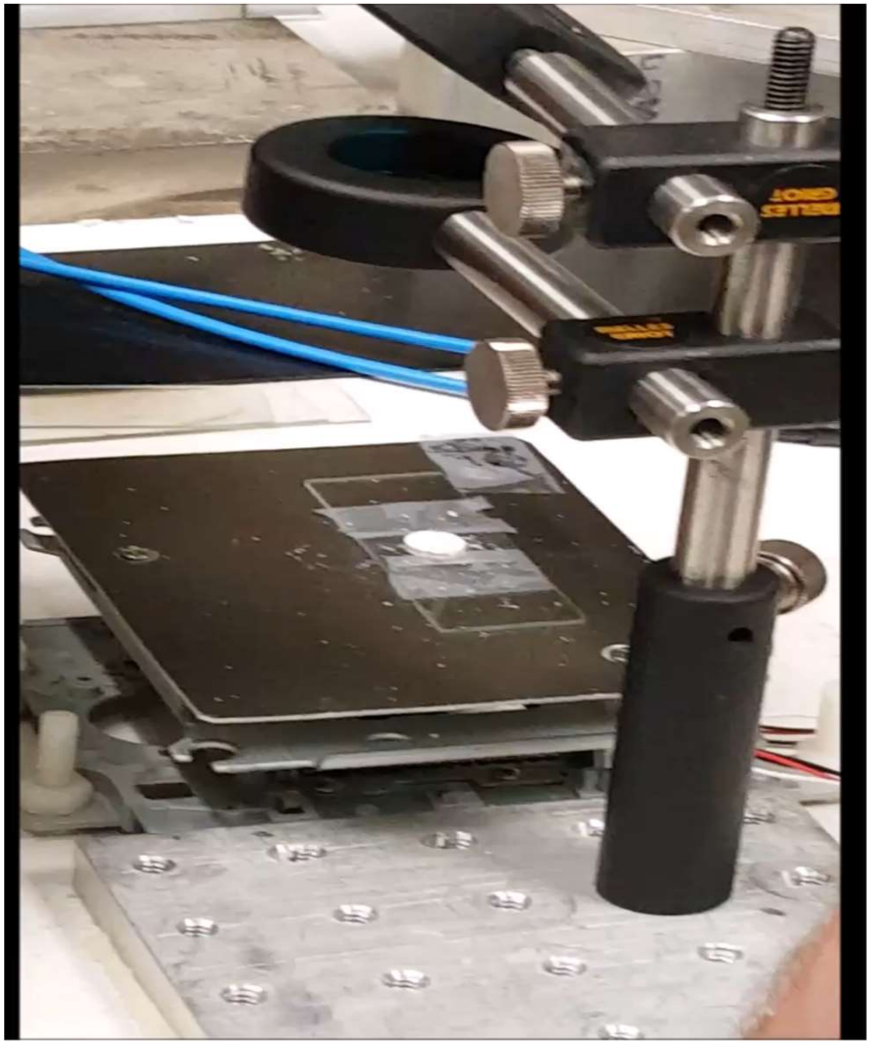
Green Body Formation via Laser Cutting (2)

❑Laser cutting at FIU CeSMEC

- Quanta Ray Nd: YAG Laser
- Max Output: 50 J/Pulse
- Q-Switch capability

❑Automated mechanical stage

- X, Y and Z functionality
- Interfaced with LabVIEW control

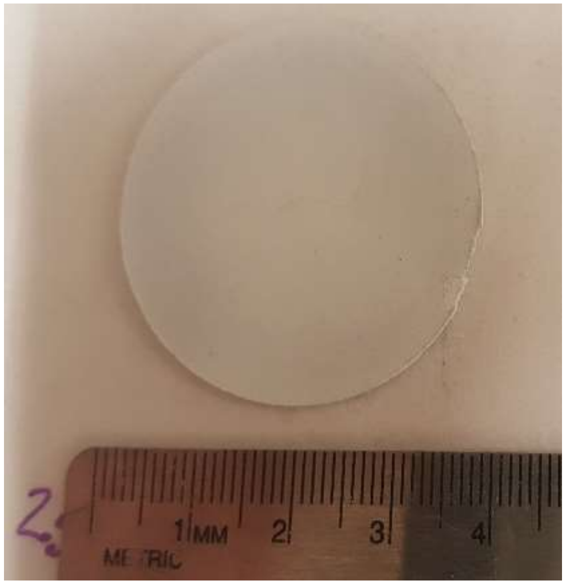


Green Body Formation via Laser Cutting (3)

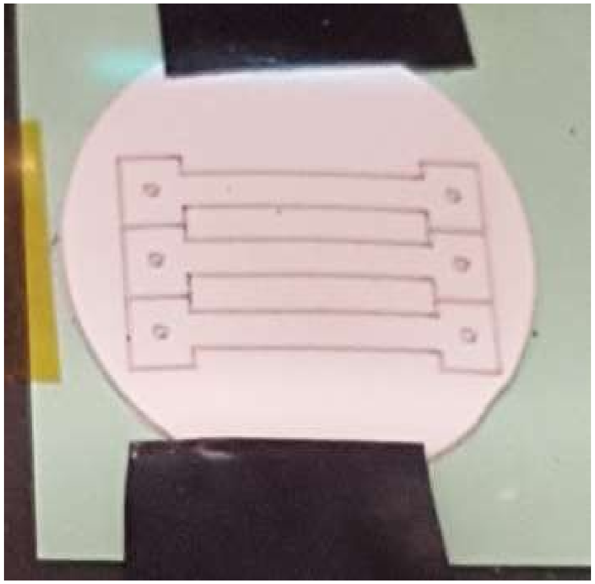
❑**Successful sample preparation**

- 5 laps at ~3 min/lap for clean cut

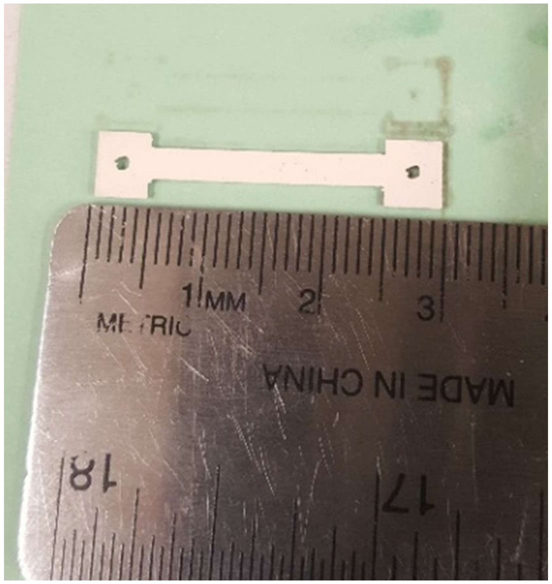
Dry-pressed pellet



Post-cut pellet



Isolated sample



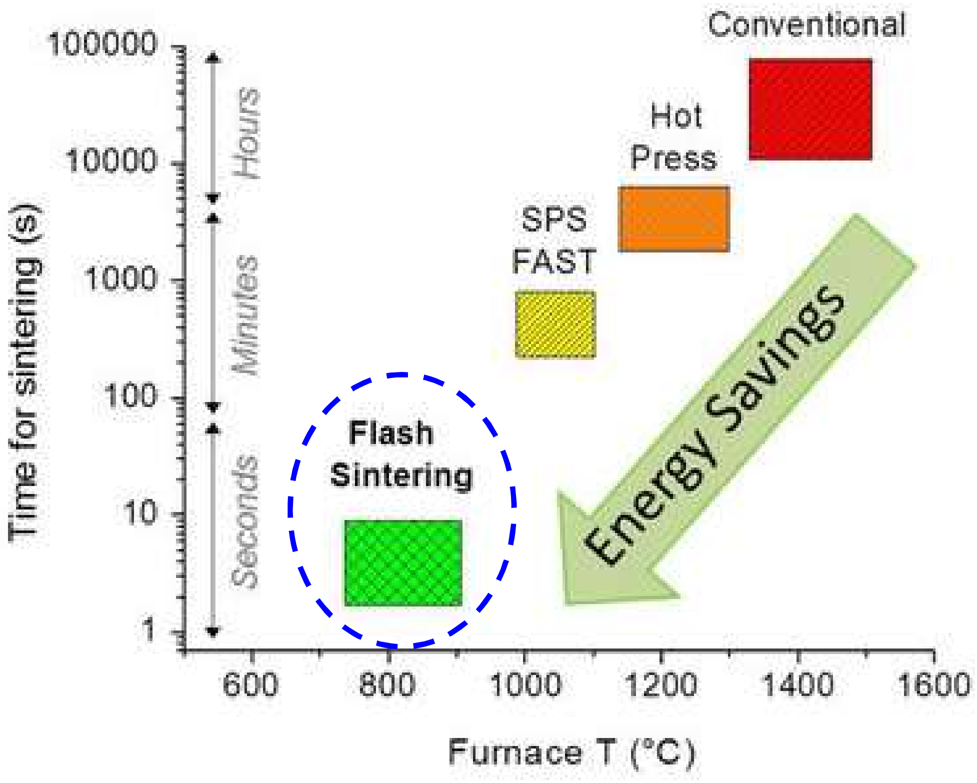
❑**Limitation: low sample thickness ~0.25 mm**

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.% Y_2O_3-doped ZrO_2 (3YSZ)
  - Co_2MnO_4
  - …
- ❑**Features**
  - Onset V/T lowers w/ smaller particles
  - Few studies on carbides or borides

Cologna and Raj, Univ Colorado

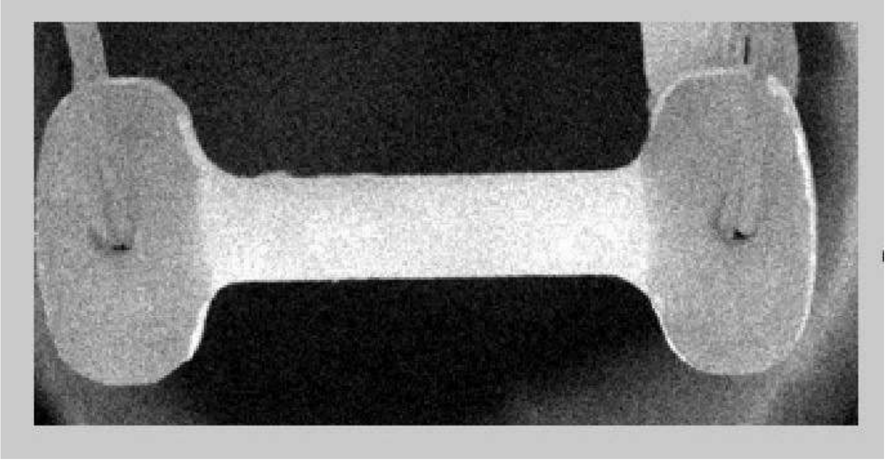


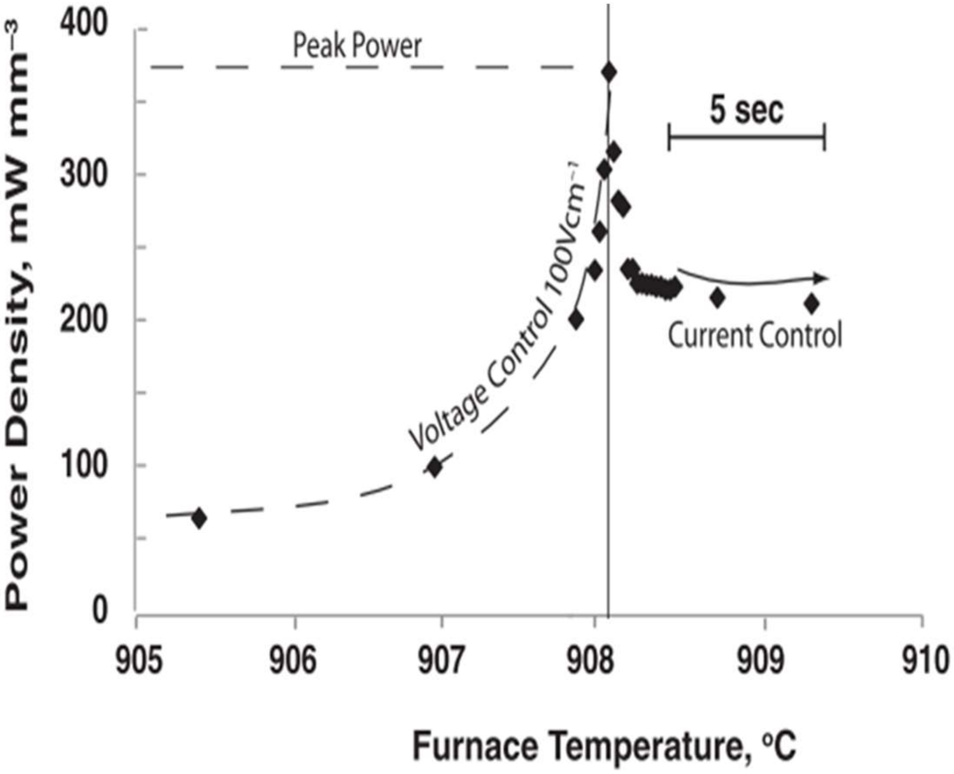
Cologna and Raj, J Am. Ceram. Soc (2010) 3556

Flash Sintering of YSZ

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

Flash - spike in electrical power dissipation

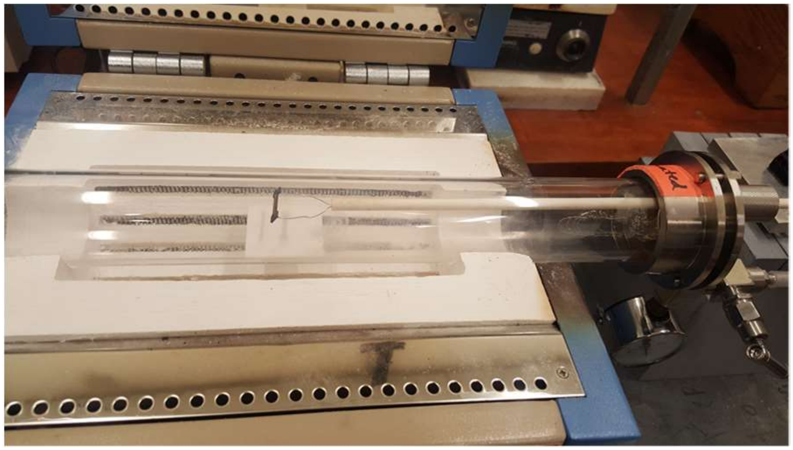




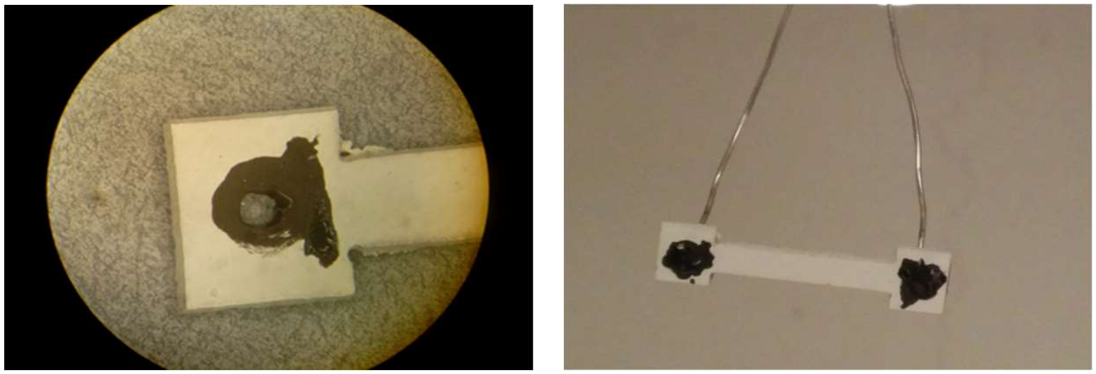
Raj, Rishi. "Joule Heating during Flash-sintering." *Journal of the European Ceramic Society*32.10 (2012): 2293-301. Web.

In House Flash Sintering Set-up

- Tube furnace for heating w/ atmosphere control



- Pt wires with Pt paste for electrical connection & power delivery

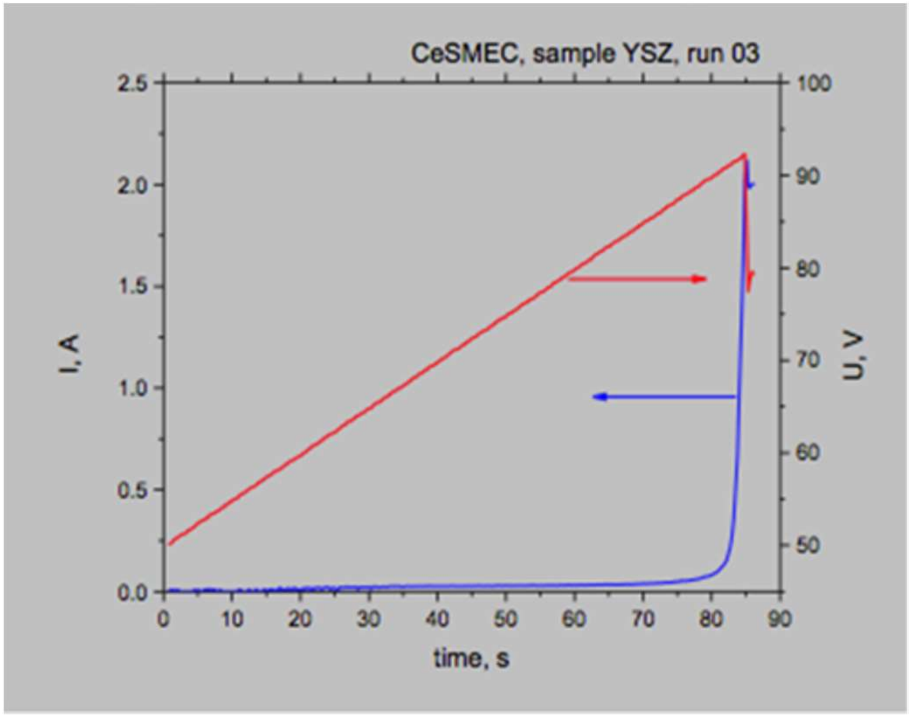


- DC power supply & LabVIEW control

Reproducing Flash Sintering on YSZ

❑Experimental

- Temperature: 940 °C
- Limit current: 2 A
- Initial voltage: 50 V
- Final voltage: 90 V
- Voltage ramp rate: 0.5 V/s

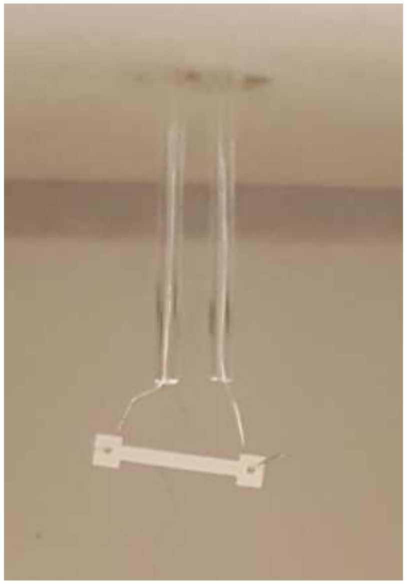


❑Flash occurred upon ramp of voltage

❑Sample sintered but not very uniform

Adjustments & Continued Work

- **Low resistivity for carbides and borides → Higher current**
- **Change in configuration**



Current Status & Path Forward

❑ **Graduate student Andres Behrens graduate with MS; In the process of recruiting another graduate student**

❑ **Request for no cost extension (NCE) to 09/2019 submitted**

❑ **Remaining research tasks and timeline**

Dec 2018	Synthesize <100 nm powders of HfC-TiC and ZrB_2 – CeB_6 solid solutions
Jun 2019	Demonstrate flash sintering of nano carbide and boride powder
Sep 2019	Oxidation resistance/electrical measurements for flash sintered solid solution/composites

Characterization of Oxidation Resistance

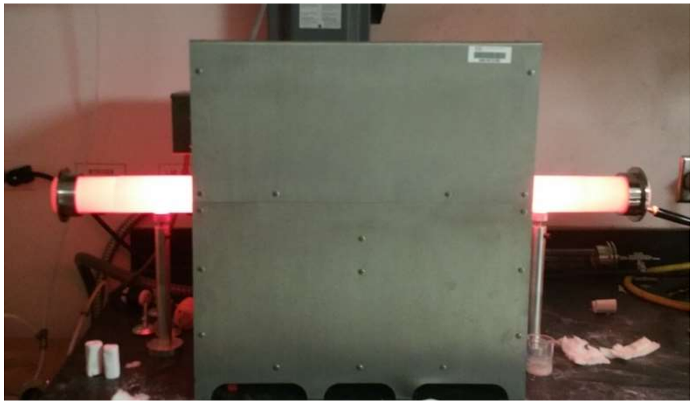
❑Hypothesis

Carbide and boride solid solution composite enables enhanced oxidation resistance

❑Evaluation of oxidation resistance

- Weight change
- Phase change
- Microstructure
  - oxide shell integrity
  - Porosity
  - flow characteristics

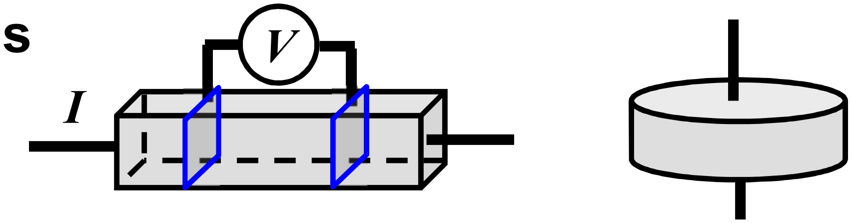
Furnace for static oxidation of sintered ceramic solid-solution in static or flowing air or oxygen up to 1800 °C



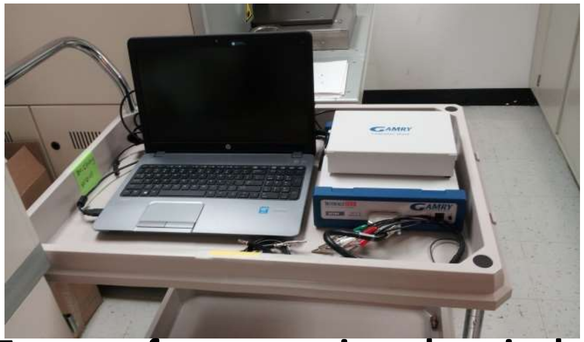
Characterization of Electrical Properties

❑Evaluation of electrical properties

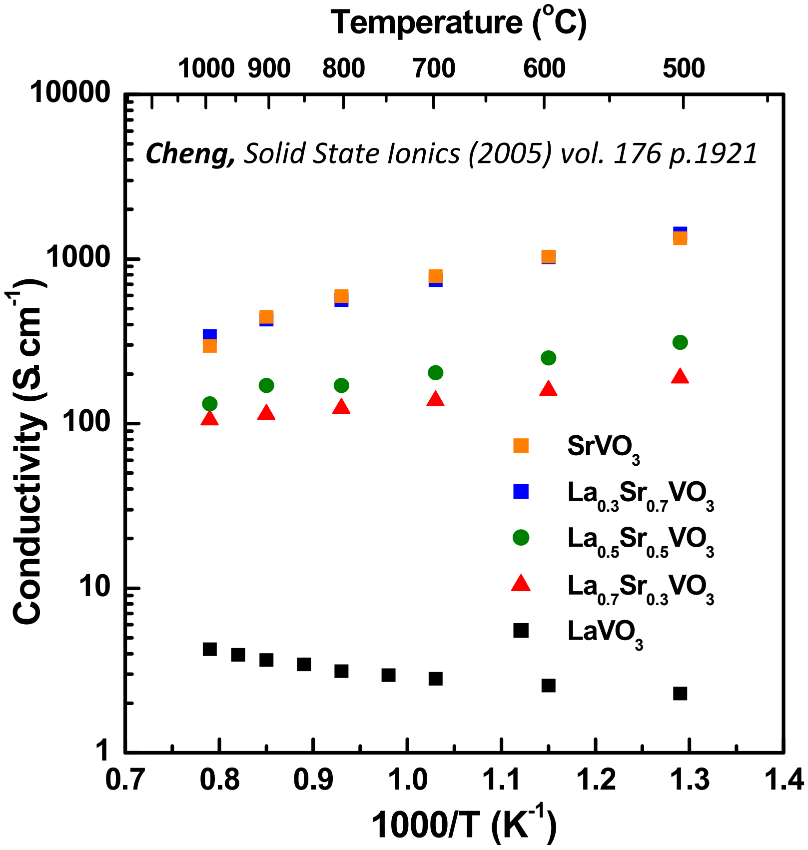
- Electrical conductivity/resistivity and contact resistance



Potentiostat w/ impedance capability for evaluting electrical properties



Furnace for measuring electrical properties up to 1500 ºC



Summary

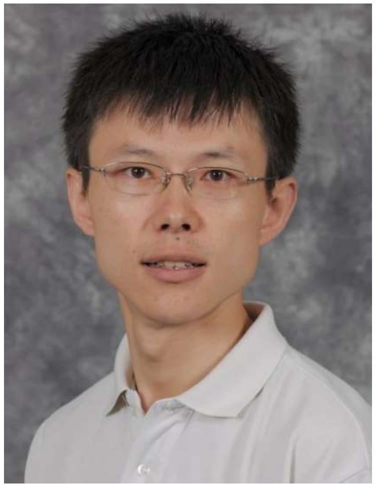
- ❑High purity (Zr-Hf)B_2 solid solution powder synthesized, but still needs optimization for reduced grain size.

- ❑Flash sintering demonstrated for conventional YSZ materials but needs to be modified for carbide/borides

Team Members

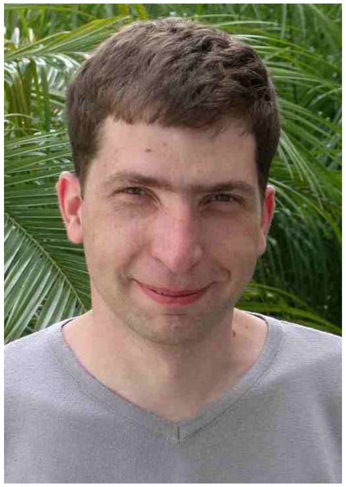
- **Current and Past Members**

Dr. Z Cheng
(PI)



Dr. A Agarwal
(co-PI)

Dr. A Durygin
(engineer)



A Behrens
(minority
MS student)

D Alfonso
(minority
BS student)

- **In the process of recruiting another graduate student**

Acknowledgements

❑ **DOE National Energy Technology Laboratory (NETL) Crosscutting Research Technology Program**

- Grant Number: DE-FE0026325

❑ **Federal Project Manager (FPM): Maria M Reidpath**

❑ **Florida International University**

- College of Engineering & Computing New faculty startup support
- Advanced Materials Engineering Research Institute (AMERI)

Research Tasks & Deliverables

❑Research tasks

- Task 1.0 Project Management, Planning, and Reporting
- Task 2.0 Synthesis of nano powders of carbide and boride solid solution and related composites via sol-gel/CTR method
- Task 3.0 Processing of nano carbide and boride solid solution/composites via novel flash sintering
- Task 4.0 Characterization of oxidation resistance and electrical properties for nano carbide and boride solid solution and related composites

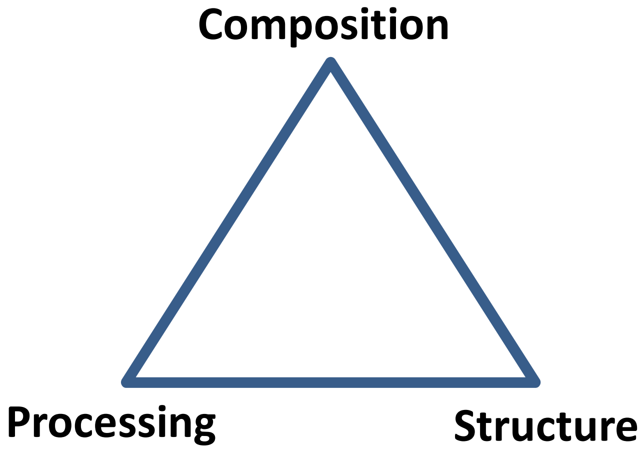
❑Deliverables

- Quarterly, annual and final technical reports to DOE NETL HBCU/UCR program
- Research publications in peer reviewed journals
- The composition and processing conditions for new nano carbide and boride solid solutions and composites that show dramatically improved oxidation resistance and electrical properties at high temperature for potential DPE electrode applications

Characterization of Synthesized Materials

- ❑ **Materials characterization tools to be used**
  - **XRD**: for phase, lattice parameter, and solubility analysis
  - **SEM, TEM, FIB, EDS**: for crystallite size, shape, micro-defects and micro-chemical analysis
- ❑ **Critical research questions**
  - How do nano carbide and boride solid solution phase form and transform?
    - In CTR reaction and in subsequent transformation process
  - How does composition and processing condition (e.g., temperature, time) influence resulting material microstructure (e.g., grain size, morphology, interface structures)?

XRD, SEM/EDS/FIB, and TEM at FIU



Composition

Processing

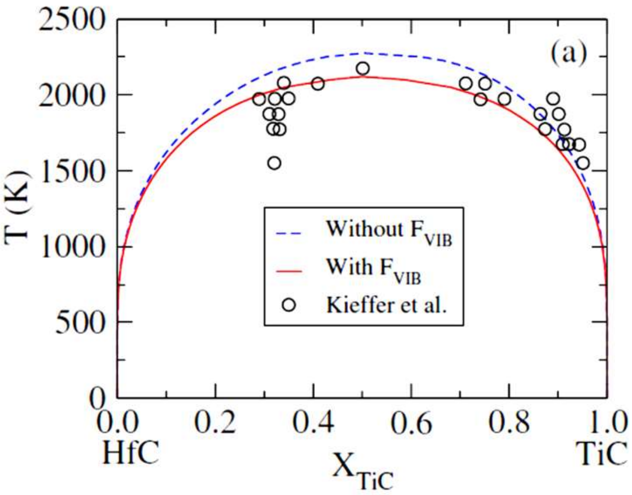
Structure

Materials System & Subtasks

❑ Materials systems of choice

i) HfC-TiC

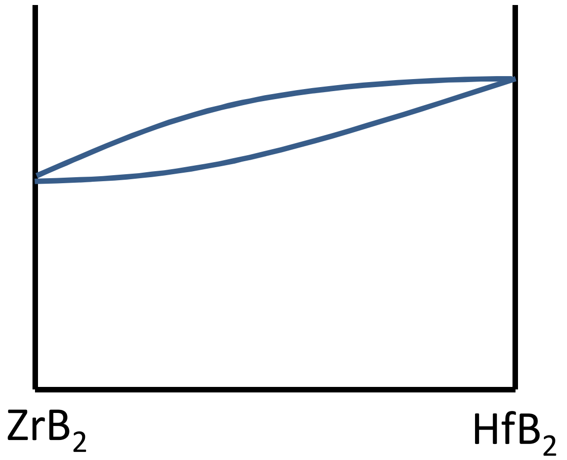
Complete solid solution
w/ a **miscibility gap**



***Adjaoud**, PHYS REV B (2009) 134112*

ii) ZrB_2-HfB_2

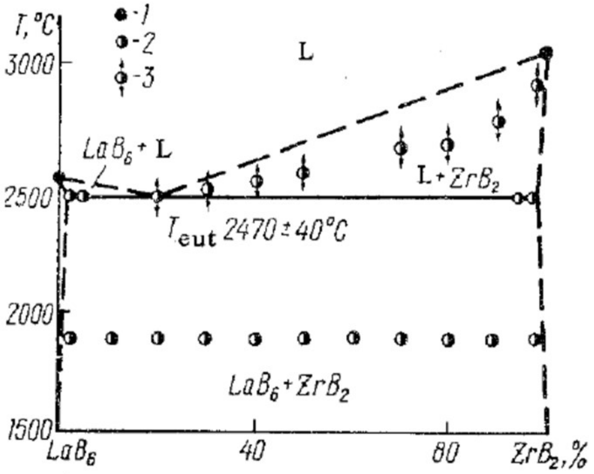
Continuous solid solution



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

iii) ZrB_2-CeB_6

Eutectic system with very limited solubility in solid



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

❑ Subtasks

- **Subtask 2.1**
  Synthesis of nano carbide and boride solid solutions and composite powders
- **Subtask 2.2**
  Characterization of nano carbide and boride solid solution and composite powders

Subtasks & Research Questions

❑Subtasks

- **Subtask 3.1**

  Flash sintering of nano carbide and boride solid solution/composite powders
  - Flash sintering of small-size sample (~mm^2 cross-section area) using AMTEK 1500 W power supply
  - Flash SPS sintering of larger-size sample (cm^2 cross-section area) using SPS with higher power capability
- **Subtask 3.2**

  Characterization of the flash-sintered carbide and boride solid solution/composites

Conventional furnace for normal flash sintering

SPS furnace by co-PI Dr. Agarwal in FIU AMERI

AMTEK 1500W power supply

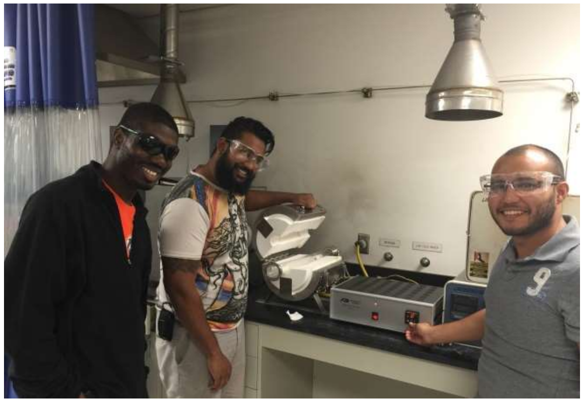
❑Critical questions to answer

- How do applied power and temperature impact the flash sintering including on-set temperature?
- How do phase and microstructure evolve in flash sintering for nano solid solution?

Current Status

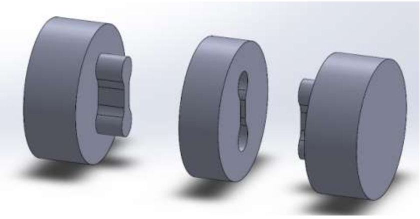
❑ **PI is advising and sponsoring an FIU 2015 senior design project by Mechanical Engineering undergraduate students**

- Project title:
  Field Assisted Sintering of Advanced Ceramic Materials
- Team members
  - Nikhil Mohip
  - Seth Mongbeh
  - Alejandro Vera (all minority student)



❑ **Status**

- Defined and purchased power supply
- Designed and machined unique sample die for green body formation
- Will test set up first with YSZ and SiC powders in Nov 2015 and then will continue with the synthesized carbide and boride solid solution powders



***Nikhil Mohip, Seth Mongbeh, Alejandro Vera**, EML 4905 Senior Design Project, 75% report, 2015-10-19*

Task 4 - Characterization of Oxidation Resistance and Electrical Properties (1)

❑Research hypothesis

H3: *Nano carbide and boride solid solution and related composite will enable enhanced oxidation resistance while delivering excellent electrical properties*

❑Rationale for hypothesis

- Appropriate metal doping may help formation of a multi-component viscous oxide shell, which offers better oxidation resistance while helping to improve conductivity of the oxide shell thus enabling better conductivity

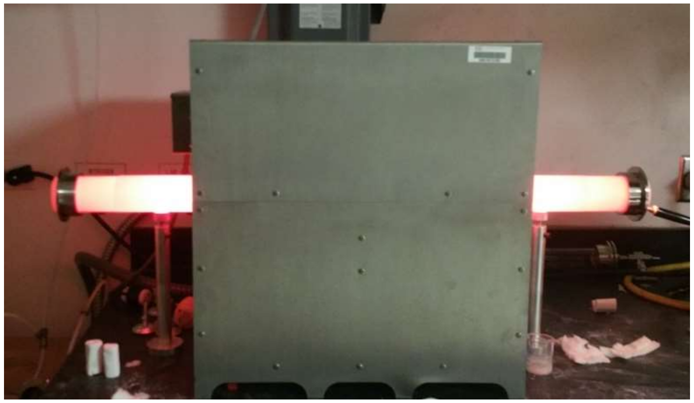
❑Subtasks

- **Subtask 4.1**

Evaluation of oxidation resistance

  - Weight change (gain/loss)
  - Phase change
  - Microstructure for ceramics in oxidation including oxide shell integrity, porosity, and flow characteristics

Furnace for static oxidation of sintered ceramic solid-solution in static or flowing air or oxygen up to 1800 °C



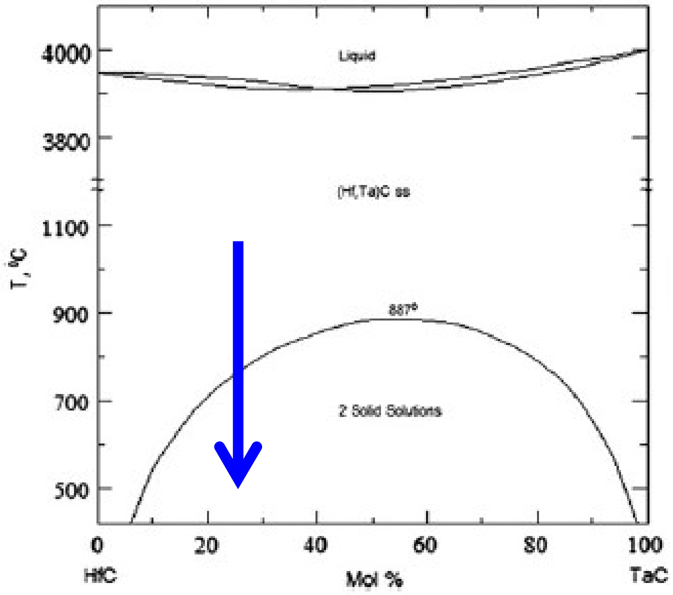
Task 3 - Novel Flash Sintering of Nano Carbide and Boride Solid Solutions

❑Research hypothesis

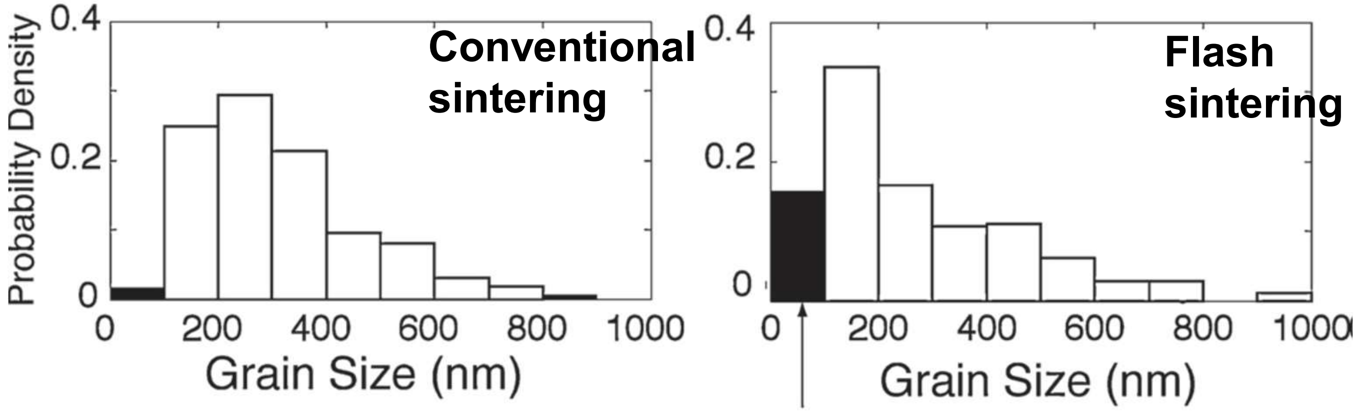
H2: *Densification via flash sintering will enable precise control of the final phases (uniform solid solution versus composites) and microstructure for the carbides and borides*

❑Rationale for hypothesis

- Flash sintering results in extreme rapid heating and cooling and enable better preservation of uniform solid solution phase



- Flash sintering, due to inherent rapid processing, will be able to better preserve fine microstructures down to submicron scale



Grain size distribution for ZrO_2-3 mol.% Y_2O_3 (3YSZ)

***Francis**, J Europe Ceram Soc (2012) 3129*

Milestones

❑**Budget period 1 Oct 2015 to Sep 2016**

Sep 2016	Achieve <100 nm powders of HfC-TiC and ZrB_2 – HfB_2 solid solution and/or related composites

❑**Budget period 2 Oct 2016 to Sep 2017**

Dec 2016	Achieve <100 nm powders of ZrB_2 – CeB_6 solid solution and/or related composites
Jun 2017	Demonstrate flash sintered ceramics with >90% relative density

❑**Budget period 3 Oct 2017 to Sep 2018**

Mar 2018	Achieve flash sintered HfC-TiC, ZrB_2 – HfB_2 and ZrB_2 – CeB_6 solid solution/composites with >90% relative density
Jun 2018	Finish oxidation resistance evaluation for flash sintered solid solution/composites
Sep 2018	Finish electrical measurement for flash sintered solid solution/composites