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

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Crosscutting Research Portfolio Review

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Goal & Objectives

Goal

Develop nano carbide and boride ceramic solid solution via novel synthesis and processing for hot electrodes for direct powder extraction (e.g., magnetic hydrodynamic, MHD) systems and gain understanding of the fundamental composition-processing-structure-property relationships for the material systems

Specific Objectives (SO)

- ***Synthesize*** *nano composites powders of solid solution for selected carbides and borides via solution-based processing*
- ***Process*** *dense nano-structured carbide and boride solid solutions and related composites via novel flash sintering process*
- ***Test*** *various* ***composition-processing-structure-property relationships*** *for nano carbide and boride solid solutions for their potential as electrodes for direct powder extraction (DPE)*

Outline

Background

- DPE via MHD
- Boride & carbide solid solution for DPE

Methods

- Novel synthesis via solution processing
- Fast densification via flash sintering

Results

- $(Hf\text{-}Zr)B_2$ nano powder synthesis
- Preparation for flash sintering
  - Green body formation
  - Other experimental setup

Summary

Future Work

Acknowledgements

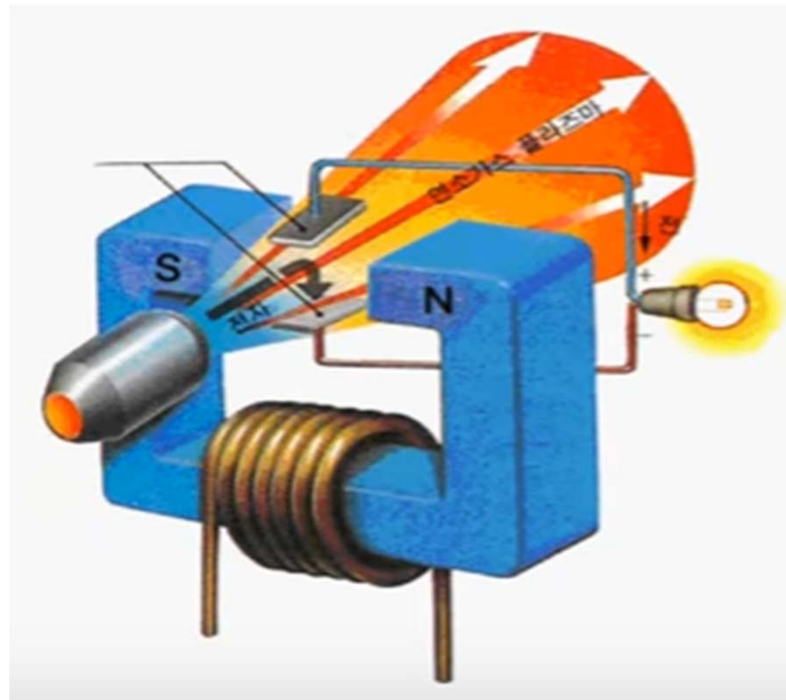
Direct Power Extraction (DPE) via Magnetic Hydrodynamic Power (MHD)

How Does DPE via MHD Work?

- Transform energy of moving 'seeded' (via Na^+ or K^+) plasma into electrical power in a magnetic field

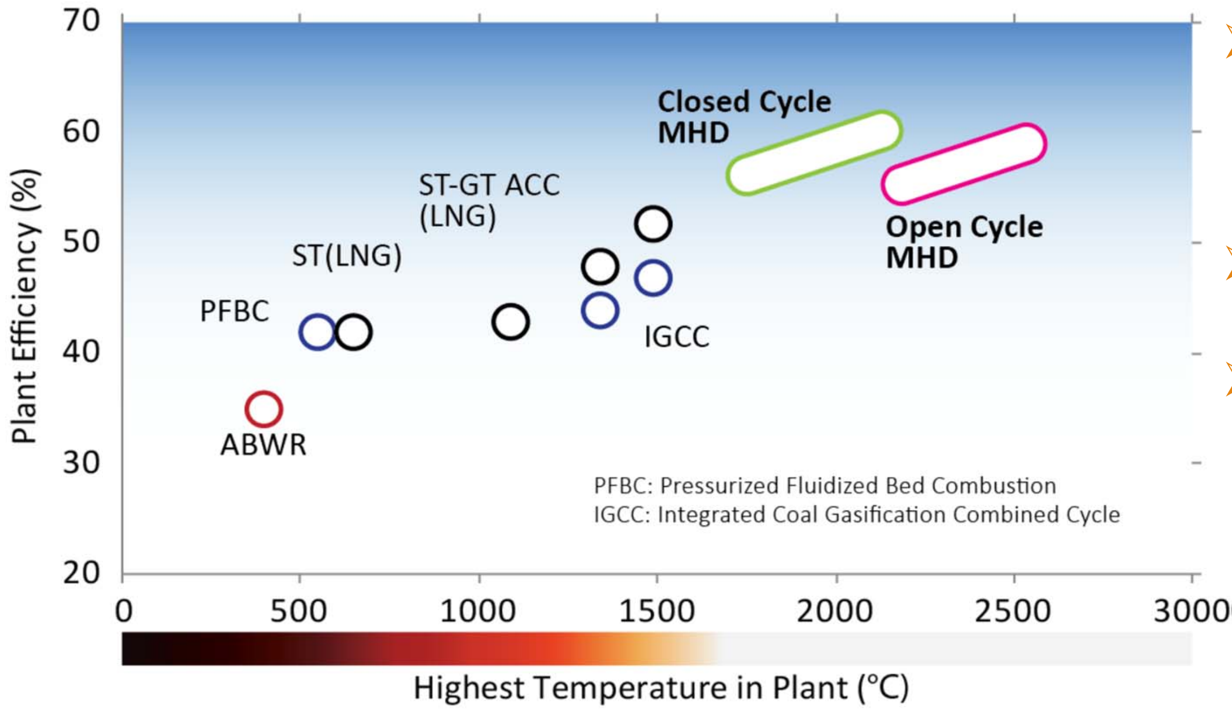
Where Can DPE be Applied?

- Current Implementations:
  Add-on Tech to Current Power Plants
- Future Implementations: Space, Jet, and Rocket Exhaust



https://www.netl.doe.gov/newsroom/news-releases/news-details?id=7e0fa3a4-8bba-4464-9245-de7d94570e11

Advantages of MHD Generation



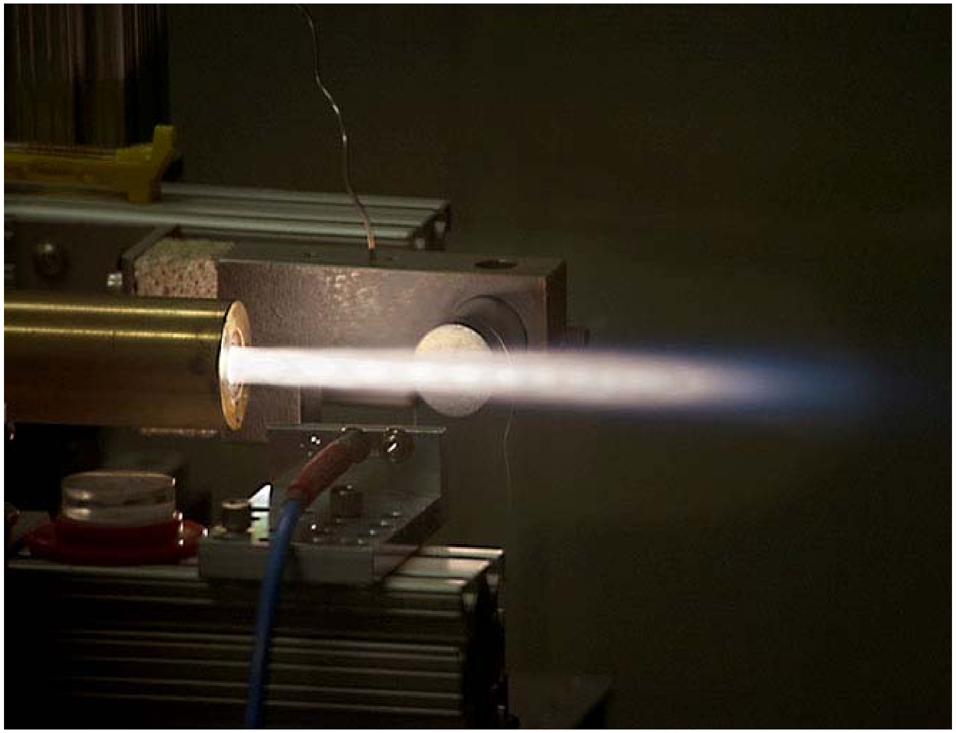
Geo. A. Richards, https://www.netl.doe.gov/File%20Library/events/2013/co2%20capture/G-Richards-NETL-Future-Combustion.pdf

- No moving mechanical parts
  - Reduces mechanical losses
  - More dependable operation
- Reaches full power immediately
- Potentially higher efficiency & lower cost

Why DPE via MHDs Not Widely Used?

- Extreme operational temperature
  - Lack of feasible (electrode) material choices

- Expensive to build
  - Complex materials processing
    - High synthesis temperatures
    - Long processing times



http://solarflower.forumactif.com/t4-hydrodyne-electrical-generator

Challenges with DPE Electrode Materials

Requirements for DPE electrodes

- Good electrical conductivity (>0.01 S/cm) & adequate thermal conductivity
- Resistance to electrochemical corrosion (seed) & erosion
- Resistance to thermal shock & arc attack
- Compatibility with other system materials

Limitations with DPE electrode materials studied

- Low temperature DPE electrode (e.g., Cu): arching that decreases efficiency
- Higher temperature DPE electrodes (~1200-2000 ^oC):
  - **SiC**: low conductivity and significant oxidation above ~1500 ^oC
  - **Doped $LaCrO_3$**: Cr vaporization at high temperature
  - **Doped ZrO_2**: Low electrical conductivity and susceptibility to electrochemical attack

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)

Boride and Carbide Solid Solutions for DPE Electrodes

Boride and Carbides are Attractive DPE Electrode Materials

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

Limitations with Borides and Carbide as DPE Electrodes

- Investigated more than 40 years ago and "lost favor"
- Less than ideal oxidation resistance: e.g., up to ~1000 °C for ZrB_2 and up to ~1500 °C for ZrB_2-SiC composites

New Approach

Borides and Carbide solid solutions for Improved Performance via Novel Processing

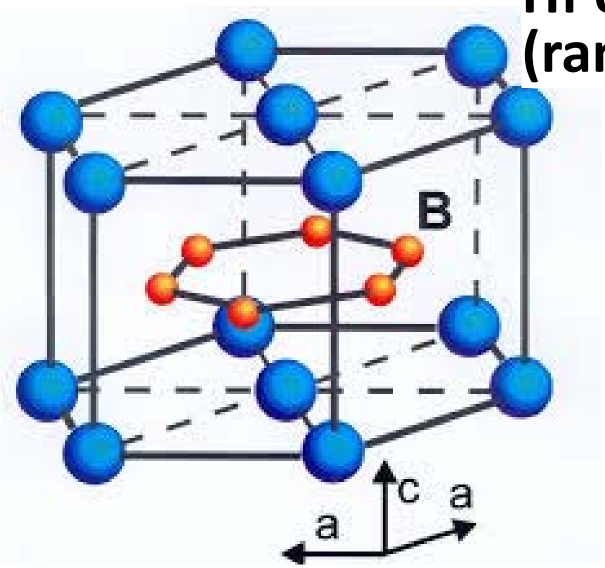
Indrajit Charit and Krishnan Raja, "Boride Based Electrode Materials for MHD Direct Power Extraction" http://www.netl.doe.gov/File%20Library/Research/Coal/cross-cutting%20research/awards-kick-off-2014/2014_UCR-HBCU-Kickoff_UIdaho.pdf

Boride and Carbide Solid Solutions for DPE Electrodes

Solid Solution – an Example

(Hf-Zr)B_2

Hf or Zr (randomly mixed)



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

Three Systems Proposed

- **HfB_2-ZrB_2**
- **HfC-TiC**
- **ZrB_2-CeB_6**

Potential Advantages

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

Experiment Methods Overview

Synthesis of Nano Solid Solution Powders via Solution-based Processing

- Nano powders
- High purity and great uniformity
- Versatility in processing
- Low cost

Consolidation of Nano Powders into DPE Electrodes via Flash Sintering

- New and fast (seconds rather than hours!)
- Low cost (energy & equipment)
- Nanostructure and better (mechanical) properties

Synthesis via Solution-based Processing

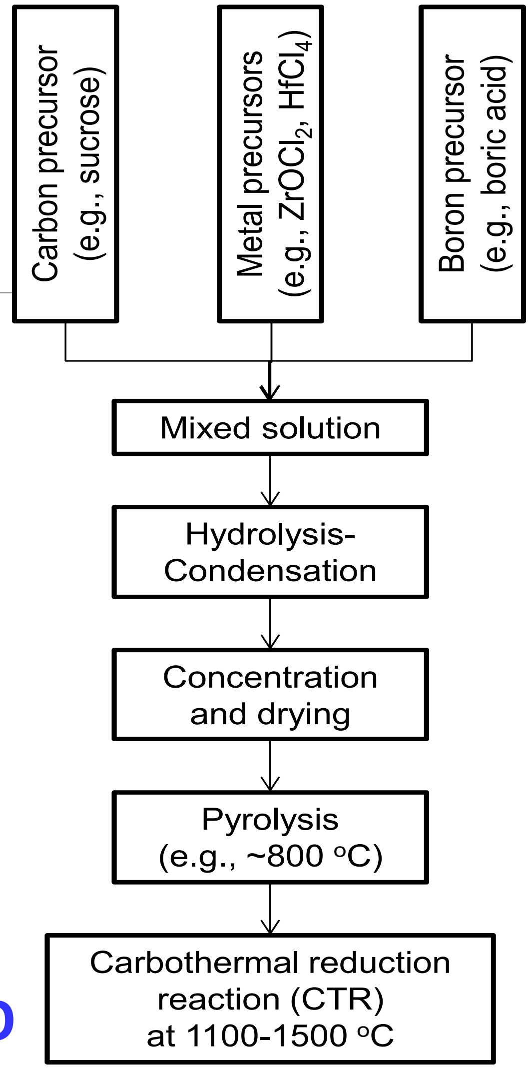
Starting Materials

- Metal precursors
  - Water soluble: $HfCl_4$, $ZrCl_4$, $TiCl_4$
  - Solvent soluble: Ti-Butoxide, Zr-Propoxide
- Carbon precursors
  - Water soluble: Sucrose
  - Solvent soluble: Phenolic Resin
- Boron precursors
  - Water soluble: Boric Acid (H_3BO_3)
  - Solvent soluble: e.g., Tri-Ethyl Borate (TEB)

Procedure using $(Hf\text{-}Zr)B_2$ as an Example

Underlying Carbothermal Reduction (CTR) Reaction:

$$xZrO_2 + (1-x)\, HfO_2 + B_2O_3 + 5C \rightarrow (Hf_{1-x}Zr_x)B_2 + 5CO$$



Solution-based Processing

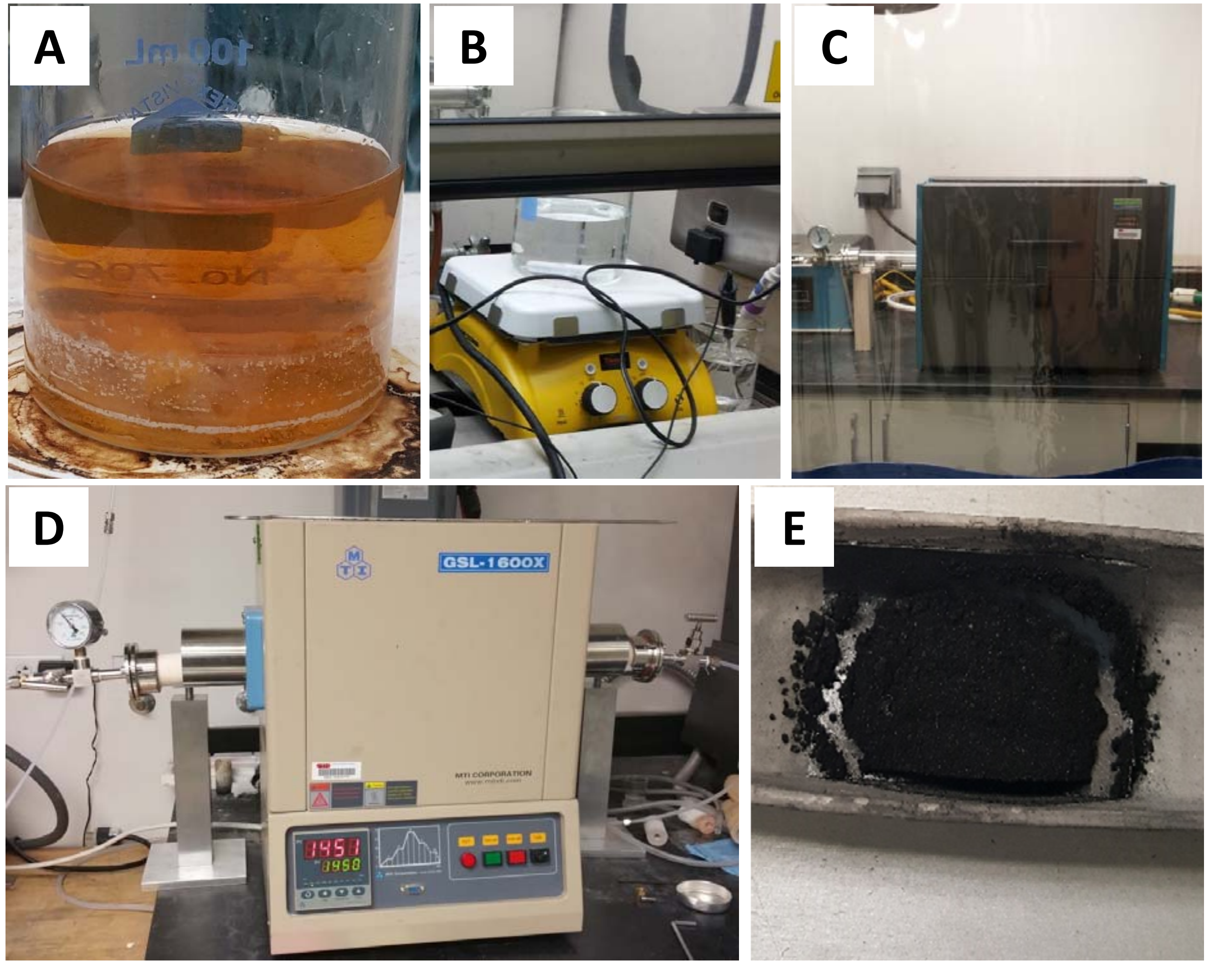
A. (Aqueous) precursor solution mixing

A. Solution drying

B. Pyrolysis heat treatment at 700°C to obtain oxide-carbon mixture

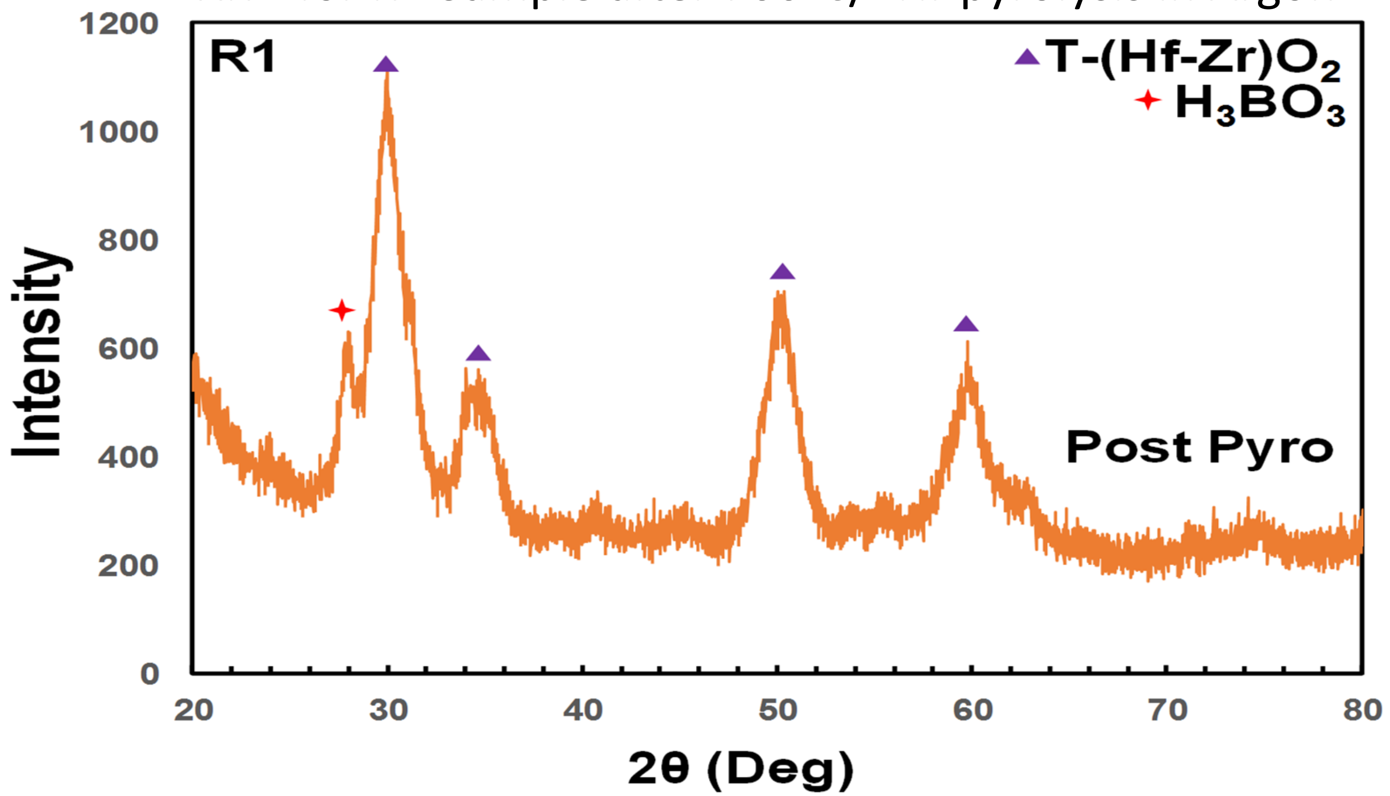
C. CTR heat treatment at >1450°C to obtain nano boride or carbide solid solution powder

D. Final product after CTR



Pyrolyzed Material Composition

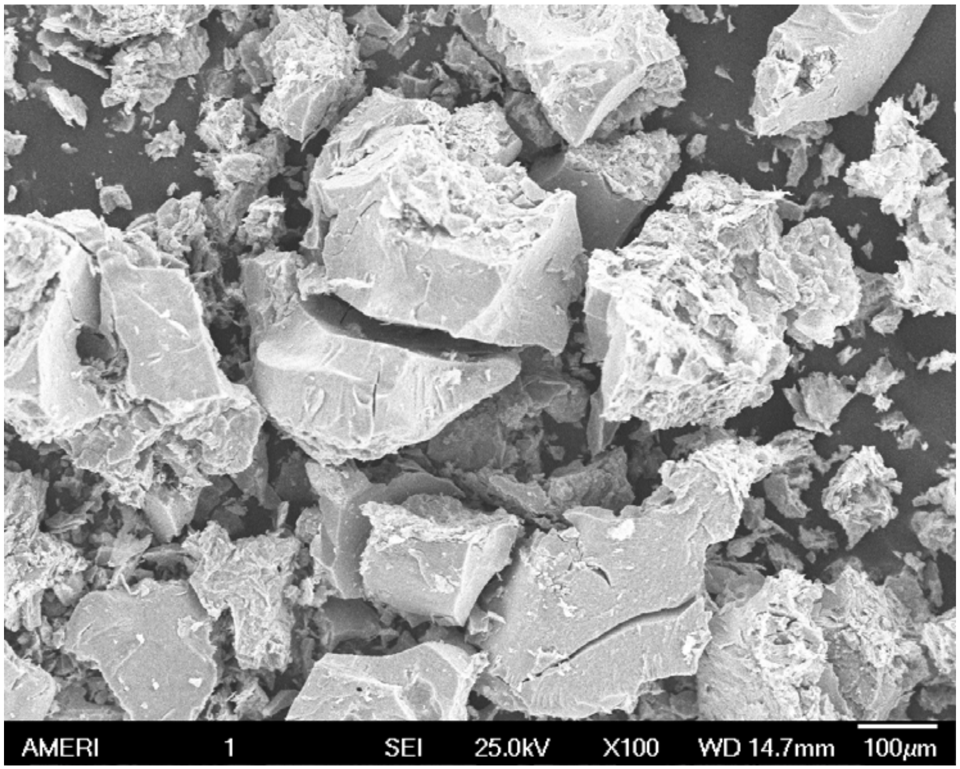
XRD for R1 Sample after 700°C/1Hr pyrolysis in Argon

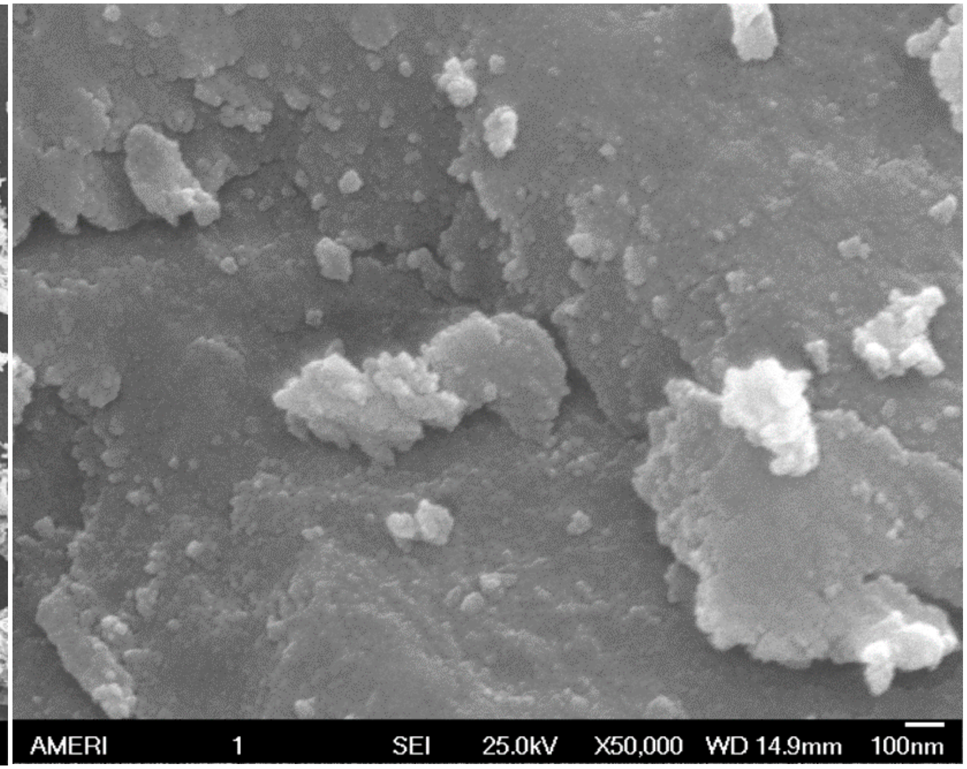


➢ Solution processing and subsequent pyrolysis yields an oxide and (amorphous) carbon mixture

Pyrolyzed Material - Morphology

SEM images for R1 Sample after 700^{o}C/1Hr pyrolysis in Argon

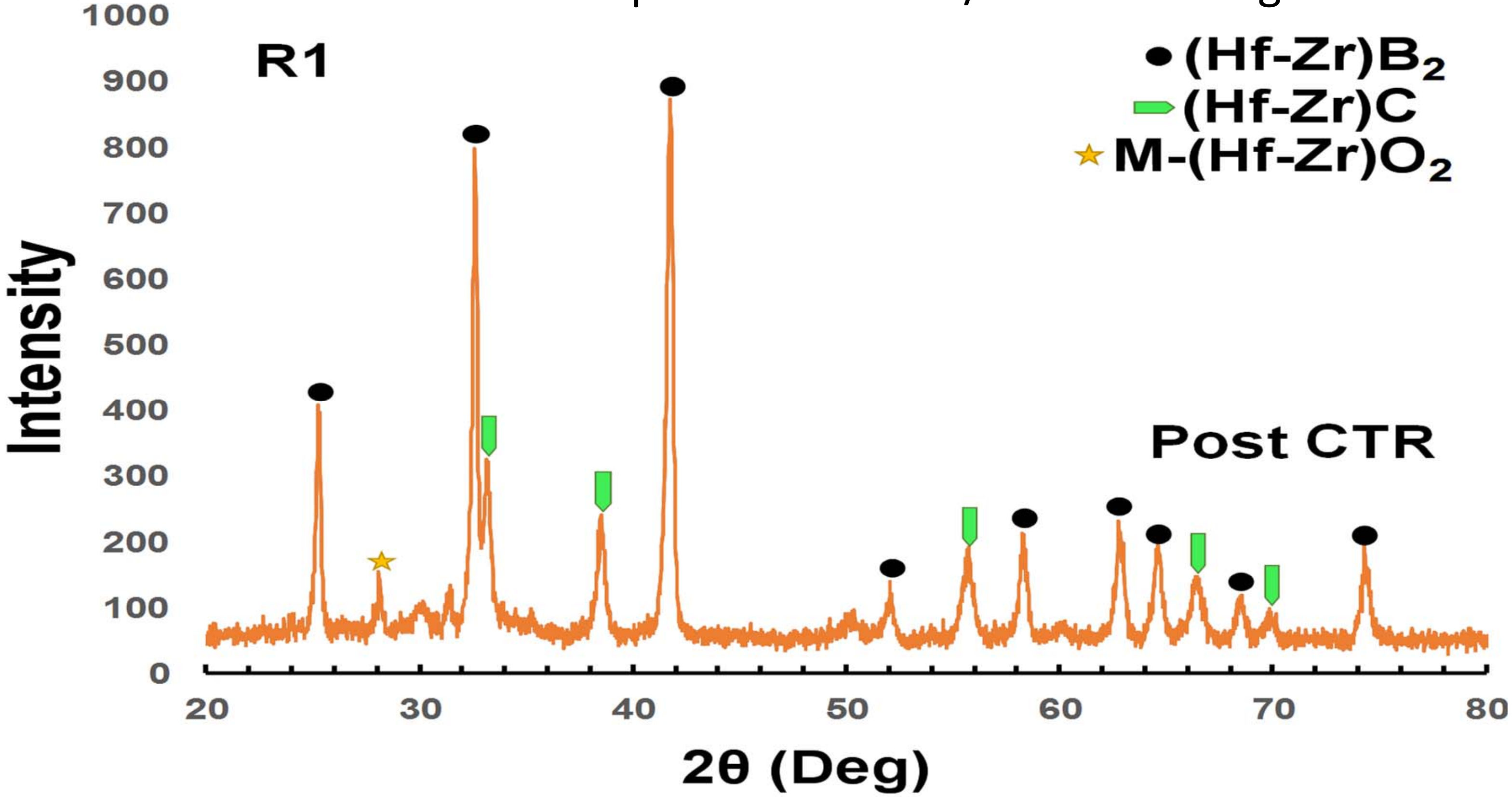




- Sample appears dense and uniform after pyrolysis

Post CTR Material - Composition

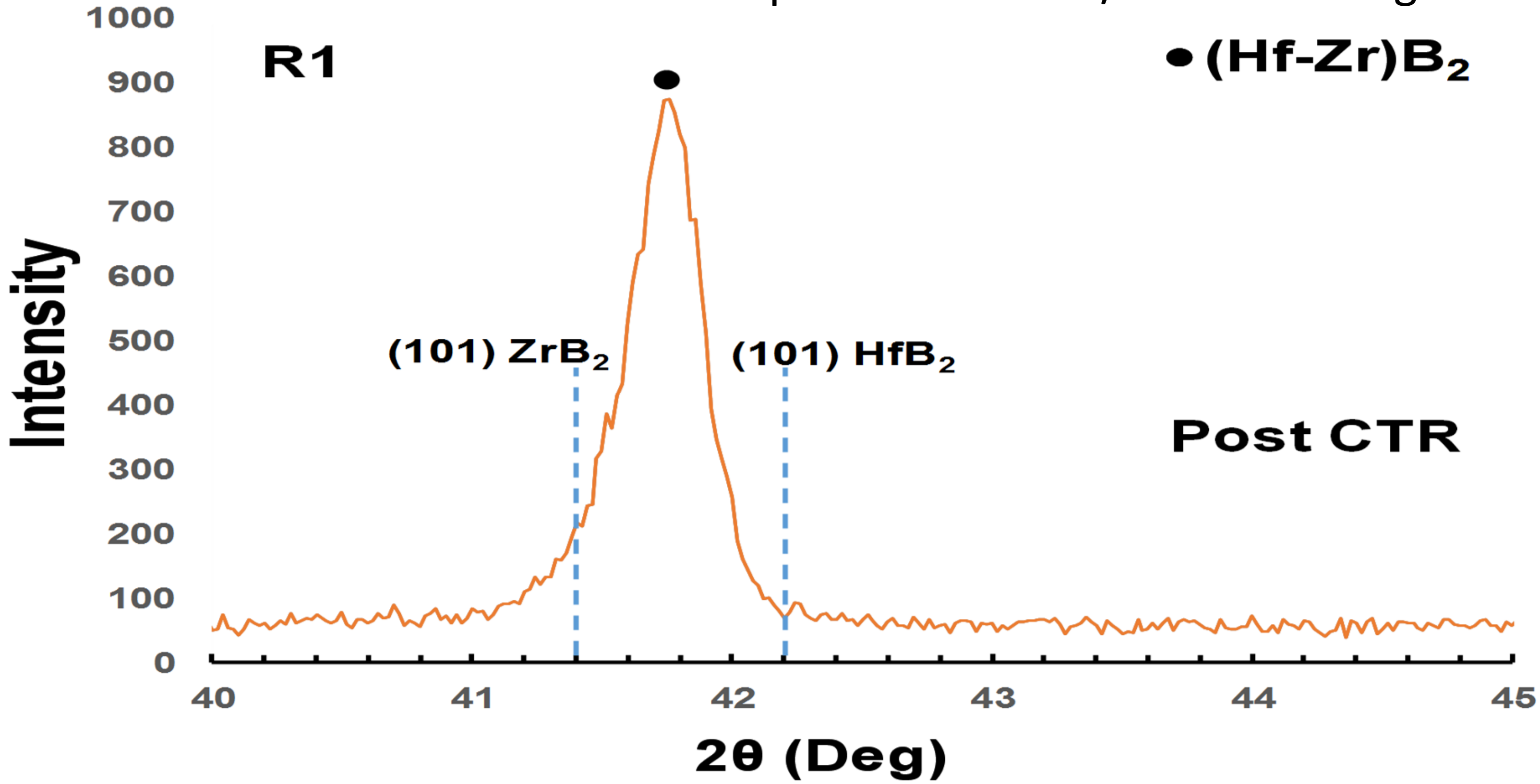
XRD for R1 Sample after 1500^{o}C/1Hr CTR in Argon



- Solid solution for $(Hf\text{-}Zr)B_2$ obtained
- Trace carbide and oxide impurities remain

Verification of Solid Solution Formation

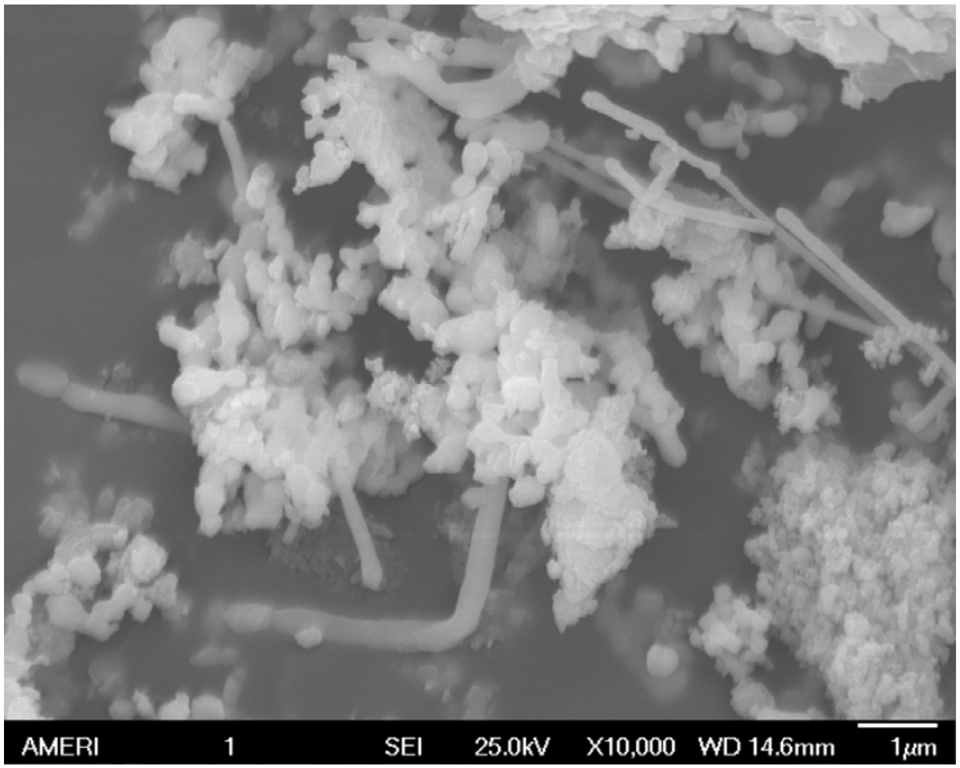
Zoom-in of XRD for R1 Sample after 1500°C/1Hr CTR in Argon

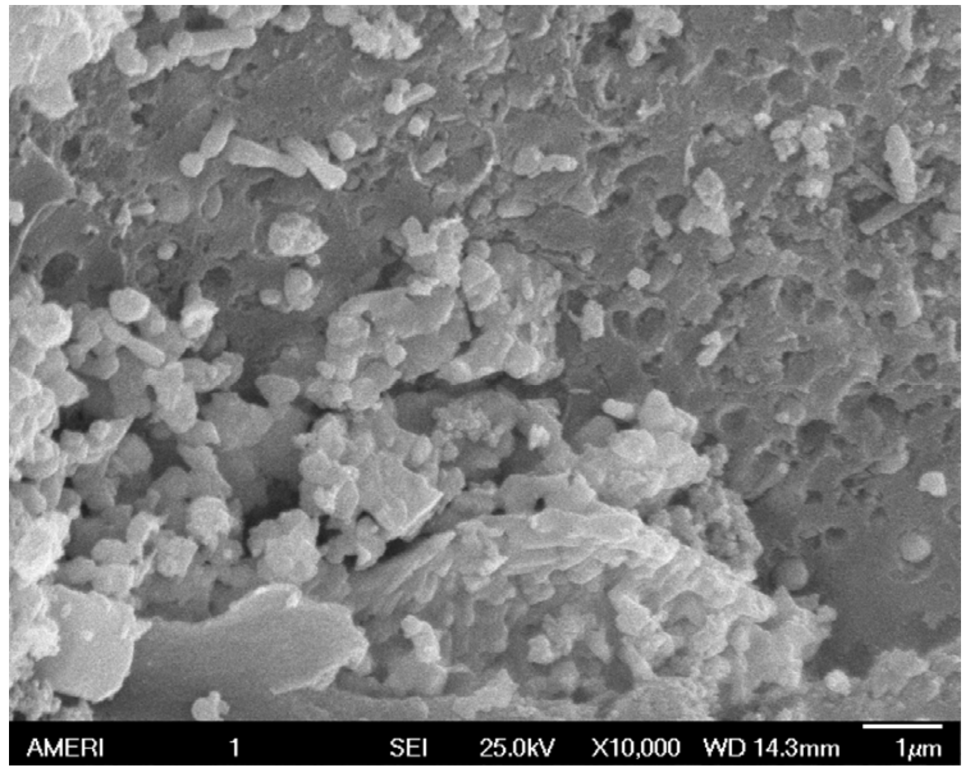


- (Hf-Zr)B_2 XRD peaks rest in-between those of pure HfB_2 and ZrB_2 confirming solid solution formation

Post CTR Material - Morphology

SEM images for R1 sample after 1500^{o}C/1Hr CTR in Argon





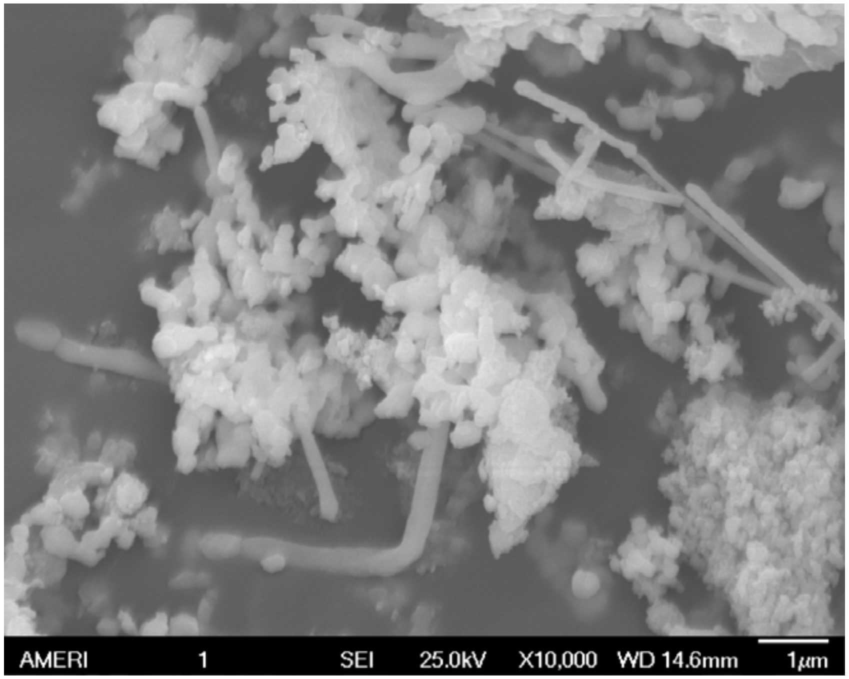
- Nano-grained powder with agglomeration
- Variations in morphology typical of borides

Recap on Synthesis

- **Solution-based processing advantages**
  - Nano powders
  - Simple processing
  - Low Cost

- **Nano $(Hf\text{-}Zr)B_2$ solid solution powder obtained**

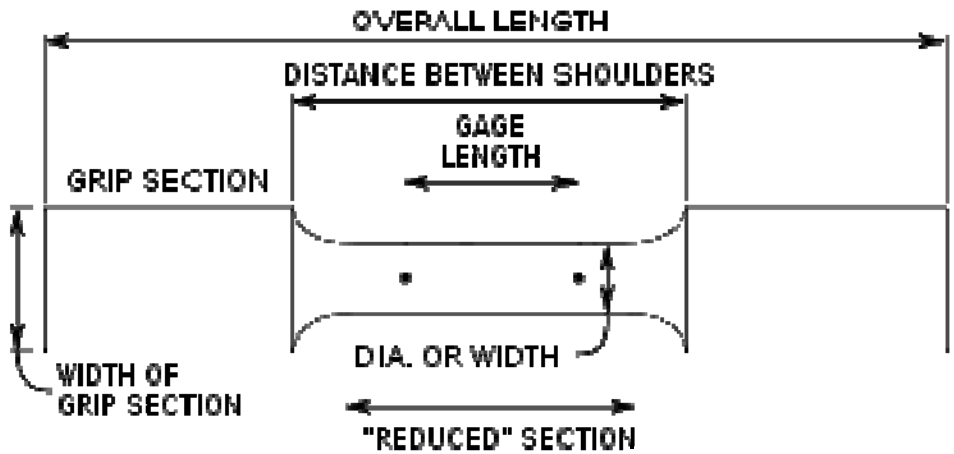
- **Optimization needed**
  - Trace carbide & oxide impurities
  - Variations In product morphology



SEM for R1 sample after 1500°C/1Hr CTR in Argon

Green Body Formation

- 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

Slip casting

- A green body formation process of ceramics via pouring ceramic slip into a mold and allowing it to solidify

Features

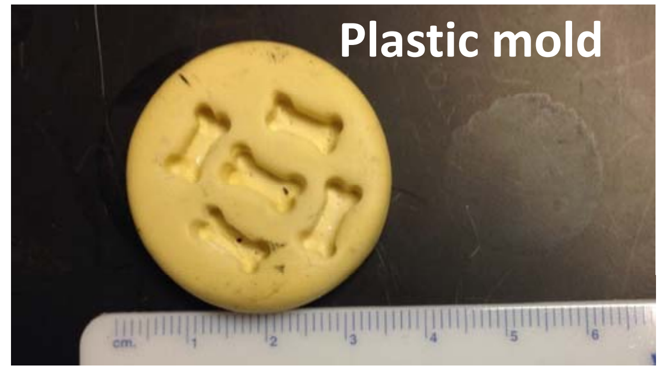
- Suitable for complex shape
- Low cost
- Mass-production ready

Green Body Formation via Slip Casting

Recipe	YSZ Content	Binder Content	Solvent(s) Content
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.%

Two recipes give good results

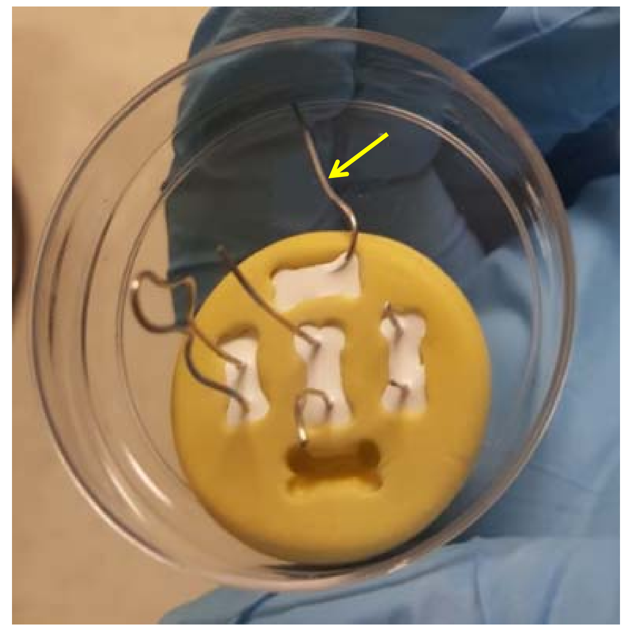
- Dense, non-porous structure
- No chipping or cracks
- Respectable mechanical strength – sustaining a fall from the workbench (~4ft)



Green Body Formation via Slip Casting

Demonstration of Scalability

Pre-embedding of Lead Wires



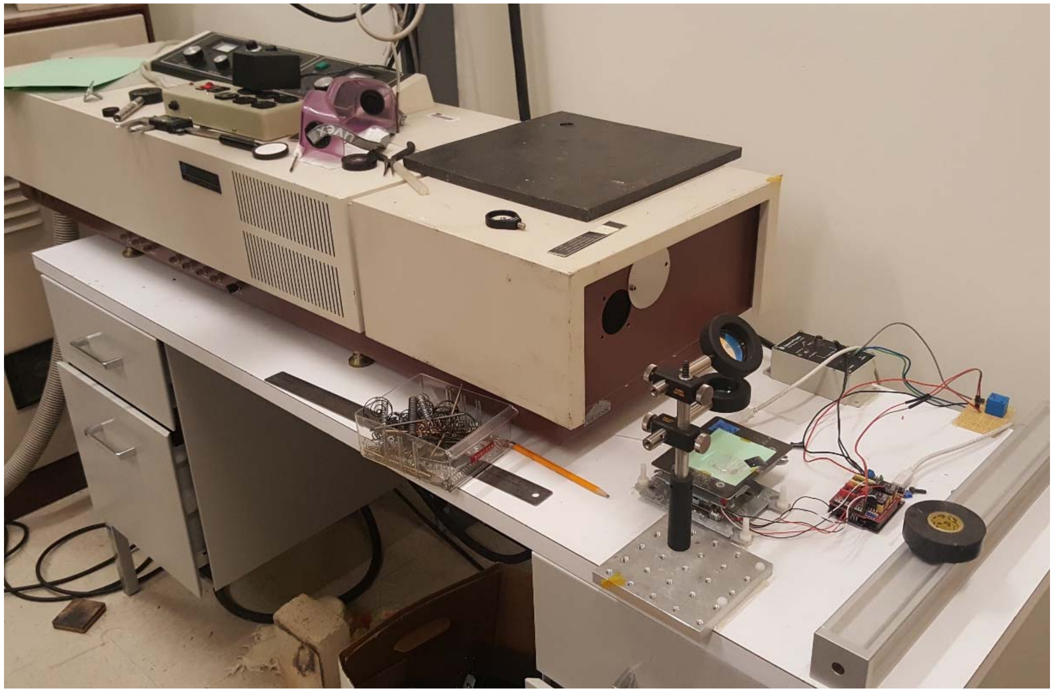
Green Body Formation via Laser Cutting

Laser cutting

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

Features

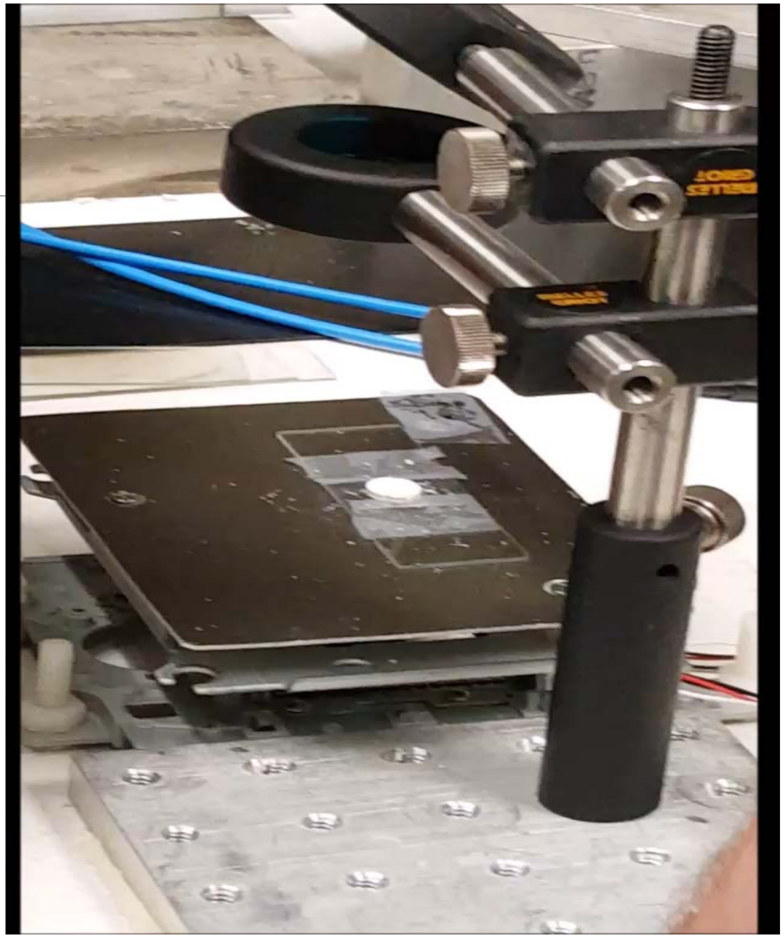
- Simple and fast
- Adaptable to intricate shapes
- Limited to low thickness



Green Body Formation via Laser Cutting

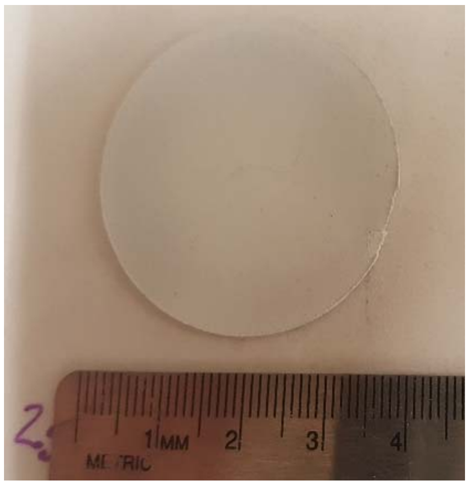
Laser cutting at FIU CeSMEC

- Quanta Ray Nd: YAG Laser
  - Max Output: 50 J/Pulse
  - Q-Switch capability
- Automated mechanical stage
  - X, Y and Z functionality
- Interfaced with computer/LabVIEW control

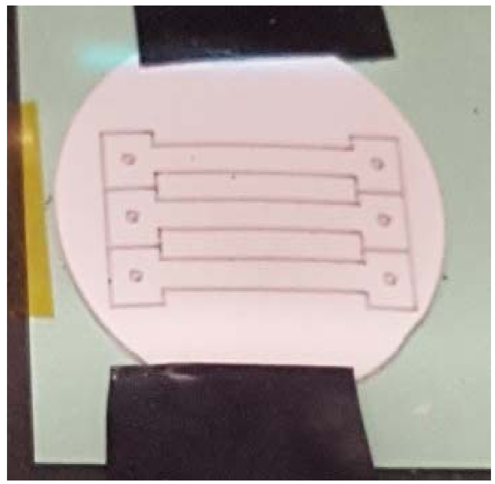


Green Body Formation via Laser Cutting

Dry-pressed Pellet



Post-cut Pellet



Isolated Dog-bone Shaped Sample

- ➢ Successful sample preparation via laser cutting
  - ❑ 5 laps at ~3 min/lap for clean cut
  - ❑ Simple and good flexibility
- ➢ Limitation: sample thickness only 0.250 mm

Recap on Green Body Formation

Slip Casting

- Successful sample preparation using optimized recipe

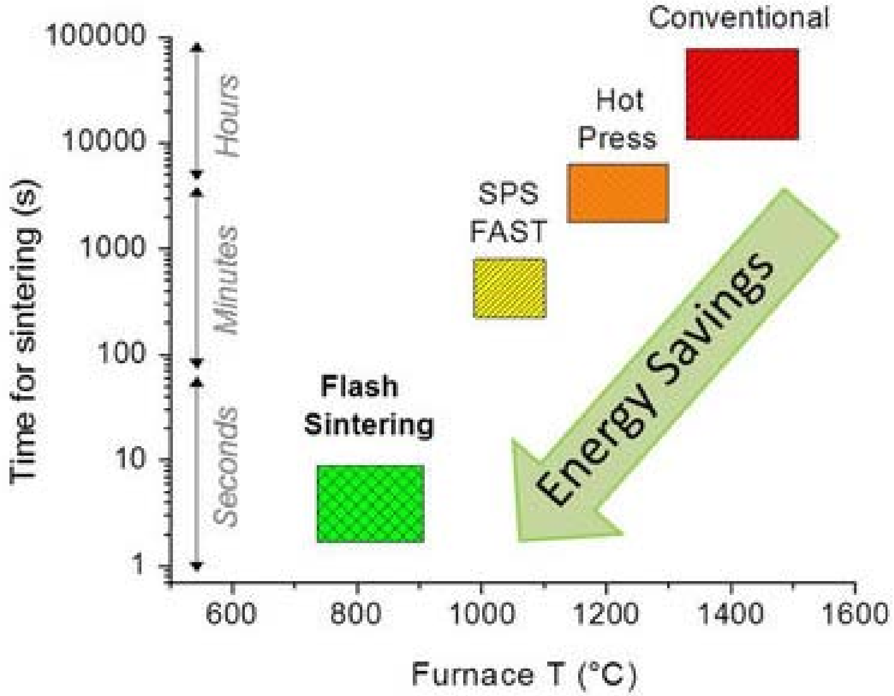
Laser Cutting

- Successful sample preparation with reasonable speed and flexibility
- Concern with sample thickness

Optimization expected for BOTH when using in-house synthesized nano carbide or boride solid solution materials

Flash Sintering for Ceramics Densification

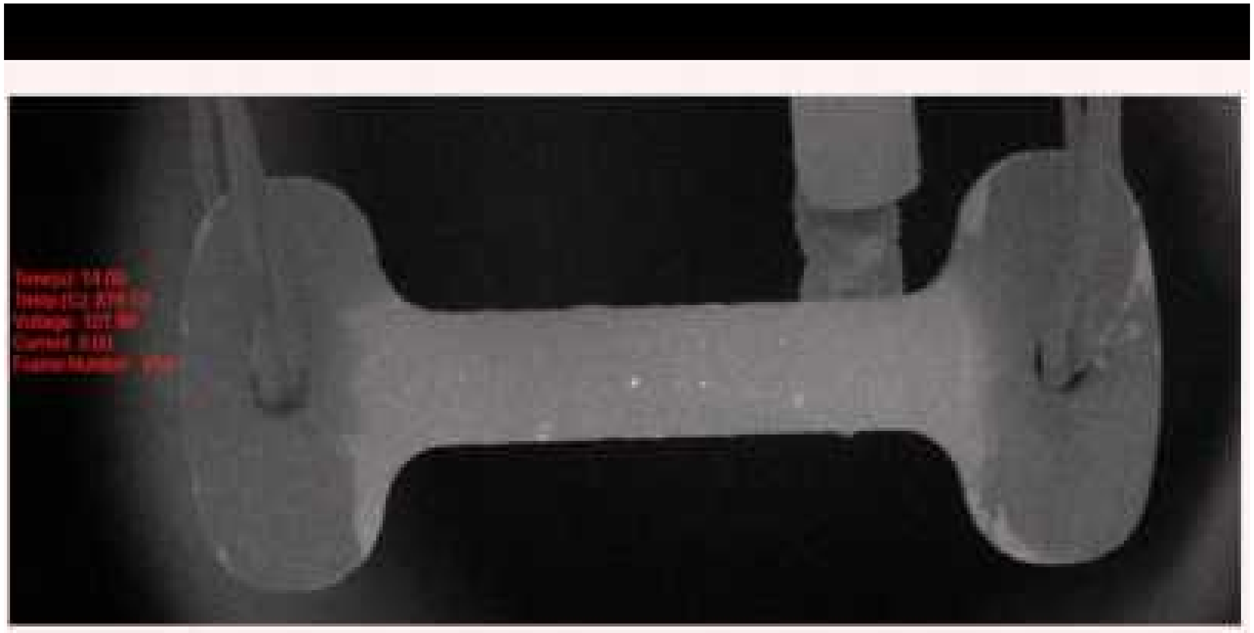
- Ceramics often need sintering/densification
- Traditional approaches to sintering
  - Long processing times
  - High energy consumption
- **Flash Sintering**
  - Pioneered by Dr. Rishi Raj of U Colorado – Boulder
  - Rapid densification (in seconds!)
  - Driven by applied (DC) electrical field
  - Saves time & energy
  - Carbides and borides not extensively studied



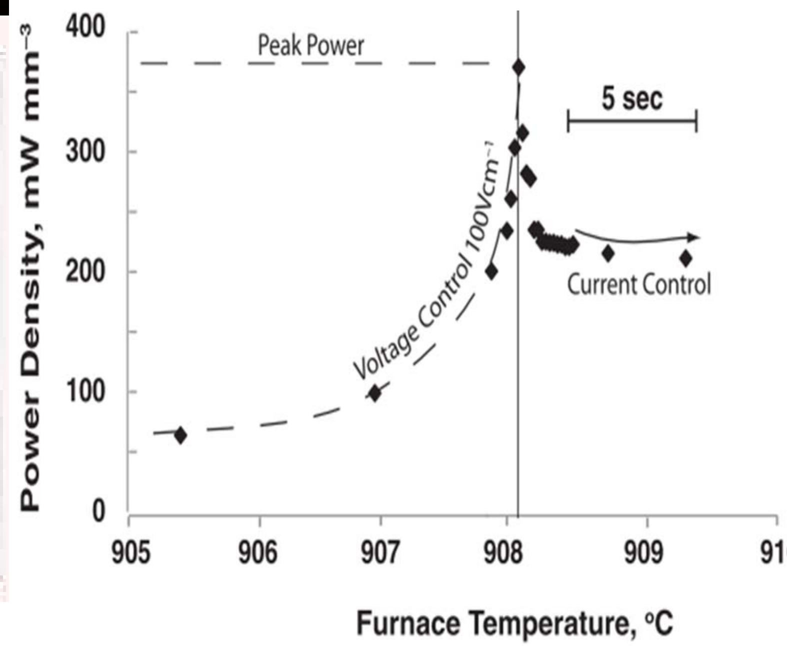
Cologna and Raj, Univ Colorado

In situ Flash Sintering

Dr. Raj Group's Video Showing Flash Sintering

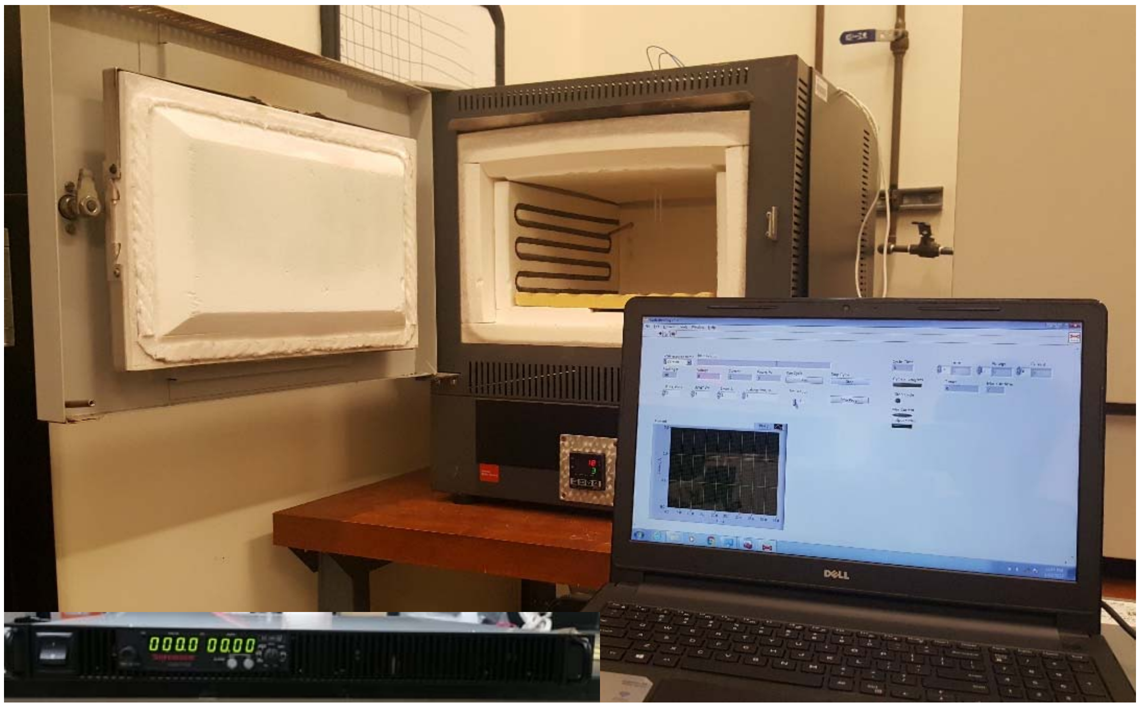


Change in Electrical Power Consumption in Flash Sintering



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



- Furnace
- Electrical power supply
- Metal wires (Ag) fed into furnace for conduction & power
- Software/Computer for control

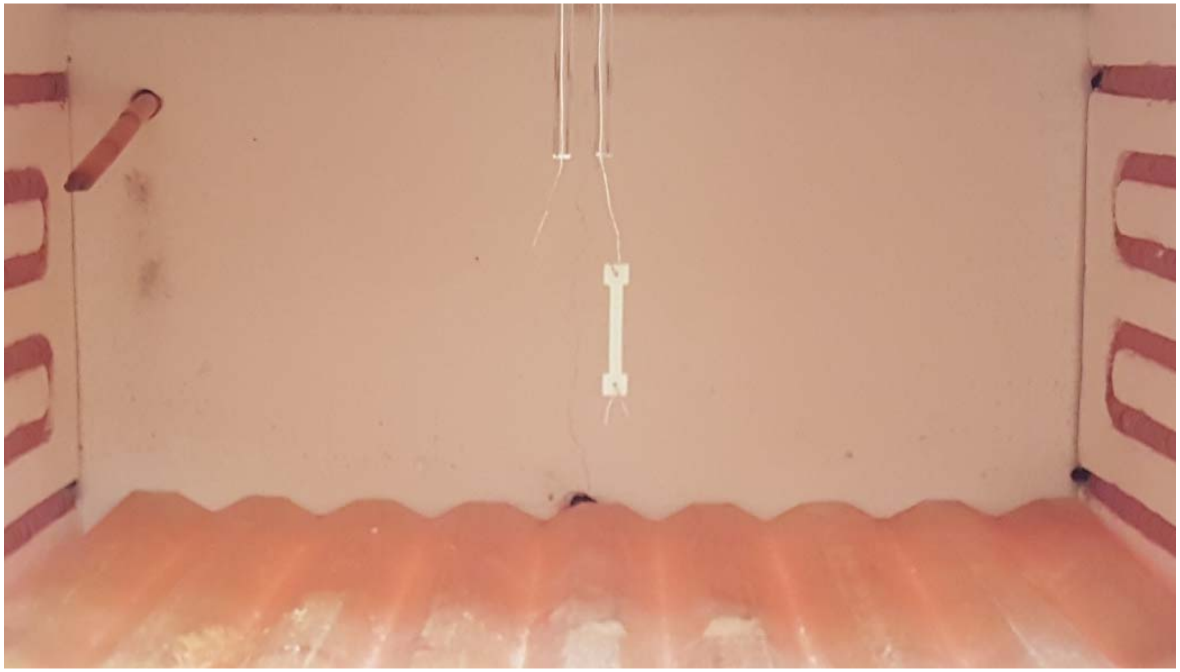
Flash Sintering Preliminary Trial

Parameters Attempted:

- Voltage:
  - 1V, 5V 25V, 50V and 100V
- Current:
  - 1A, 2A, 5A, 15A
- Temperature:
  - 850, 900, 950ºC

Flash Sintering Preliminary Trial

- Applied electrical field
- Ramped up T & monitored if power surge would occur
- Ag wire failed before flash due to creep



Summary

Nano Solid Solution Powder Synthesis

- Nano crystalline (Hf-Zr)B_2 solid solution obtained via solution-based synthesis
- Optimization needed due to trace carbide and oxide impurities & variations morphology

Preparation for Flash Sintering

- Green bodies prepared successfully using both slip casting and laser cutting methods
- In house flash Sintering set up implemented, but prelimary trial not yet successful due to Ag electrical wires used

Future Work

Nano Solid Solution Powder Synthesis

- Fine tune recipe and processing
  - Oxide impurities → Increase Carbon precursor or alternative pyrolysis condition
  - Carbide impurities → Increase Boron precursor
  - Morphological non-uniformity → Optimize thermal processing
- Work on the other two systems

Densification of Nano Solid Solution Powders via Flash Sintering

- Switch to Pt wire
- Optimization of flash sintering process
  - Modeling
  - Experimental screening (Voltage, Ampere, Flash On Set Temperature)

Composition-Processing-Structure-Property Relationships

Acknowledgements

DOE NETL Program Manager: Maria Reidpath

Co-PI: Dr. Arvind Agarwal

Research Engineer: Dr. Andriy Durygin

Other Students: Driany Alfonso, Jose Fernandez Urdaneta

FIU Advanced Materials Research Engineering Institute (AMERI)

FIU Center for the Study of Matters Under Extreme Conditions (CeSMEC)

¿Questions?


thank you
danke
рахмат
謝謝
ngiyabonga
شكراً جزيلاً
teşekkür ederim
Баярлалаа
спасибо
faafetai lava
mersi
barka
welalin
tack
dank je
misaotra
matondo
paldies
grazzi
gracias
tapadh leat
vinaka
blagodaram
kiitos
dankie
nanni
nandri
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Participants

PI: Dr. Zhe Cheng

- Ph.D. Georgia Tech (2008)
- Assistant Professor in Mechanical & Materials Engineering of FIU
- Group website: https://ac.fiu.edu

Minority Ph.D. Student: Andrés Behrens

- B.S Rutgers University (2014)
- Joined FIU Materials Science & Engineering Program in 2016 Summer

Timeline

Timeline for the project

Tasks \ Year & Quarter	Year 1				Year 2				Year 3			
	1	2	3	4	1	2	3	4	1	2	3	4
T1 *Synthesis of nano carbide and boride solid solution and related composites*												
T1.1 *Synthesis*												
T1.2 *Characterization*												
T2 *Flash sintering of nano carbide and boride solid solution and composites*												
T2.1 *Sintering*												
T2.2 *Characterization*												
T3 *Evaluating oxidation resistance and electrical properties*												
T3.1 Oxidation resistance												
T3.2 Electrical properties												

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

PRESENTATION INSTRUCTIONS

- Please refer to the agenda for the time of your presentation and confirm when you arrive at the conference in case of last-minute changes.
- A laptop and LCD projector will be available for your presentation, which must be in PowerPoint format (.ppt or .pptx) uploaded to the conference website.
- Presentation files are to be named in the following filename format:

PresentationDate_TimeSession_AgreementNumber_OrganizationAbbreviation.ppt
(i.e., 20170320_0930A_FE0000xxxx_NETL.ppt)

- Projectors will be set to 16:9 widescreen format.
- Department of Energy and National Energy Technology Laboratory logos are attached for your use.
- Presentations are to follow the outline below:

Proposed Presentation Format
Projector Format: 16:9 widescreen

Slides 4 – N: Expand on Project on Each Project Outline Topic

- Should address each topic in the outline

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- Fill out release form, sign, and scan. Submit electronically in PDF format to Crosscutting-Technology-Research@netl.doe.gov by **February 15, 2017**.
- Please use the following format for the filename:

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- Copy the completed **PROJECT METADATA** table and paste in the body of the email with scanned PDF form.

INSTRUCTIONS REMOVE!!!!

Slide 2: Project Goals and Objectives

- **Include brief description of project goals and objectives**
- **Milestones**

INSTRUCTIONS REMOVE!!!!

Slide 3: Presentation Outline

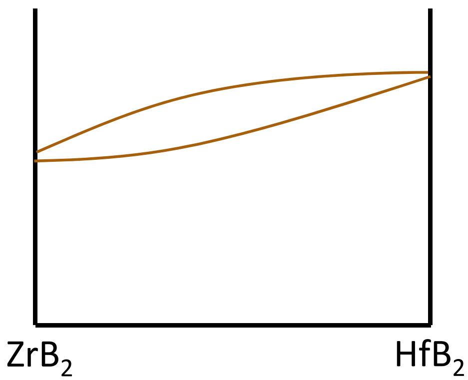
- **List topics to be covered in presentation**

background,
methods,
results,
accomplishments,
summaries,
Status (?)
future work

Materials Systems to be Studied

(A) HfB_2-ZrB_2

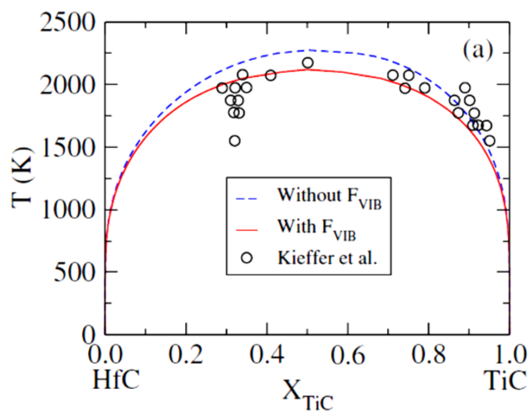
<u>Continuous</u> solid solution



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

(B) HfC-TiC

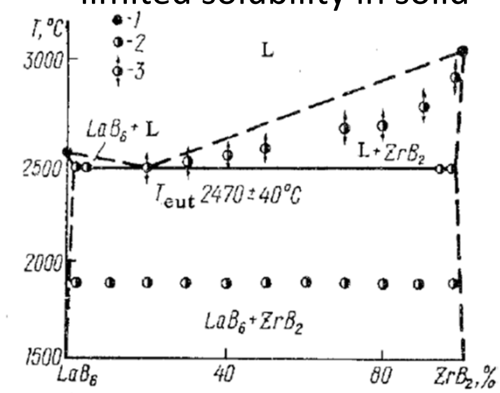
Complete solid solution w/ a **<u>miscibility gap</u>**



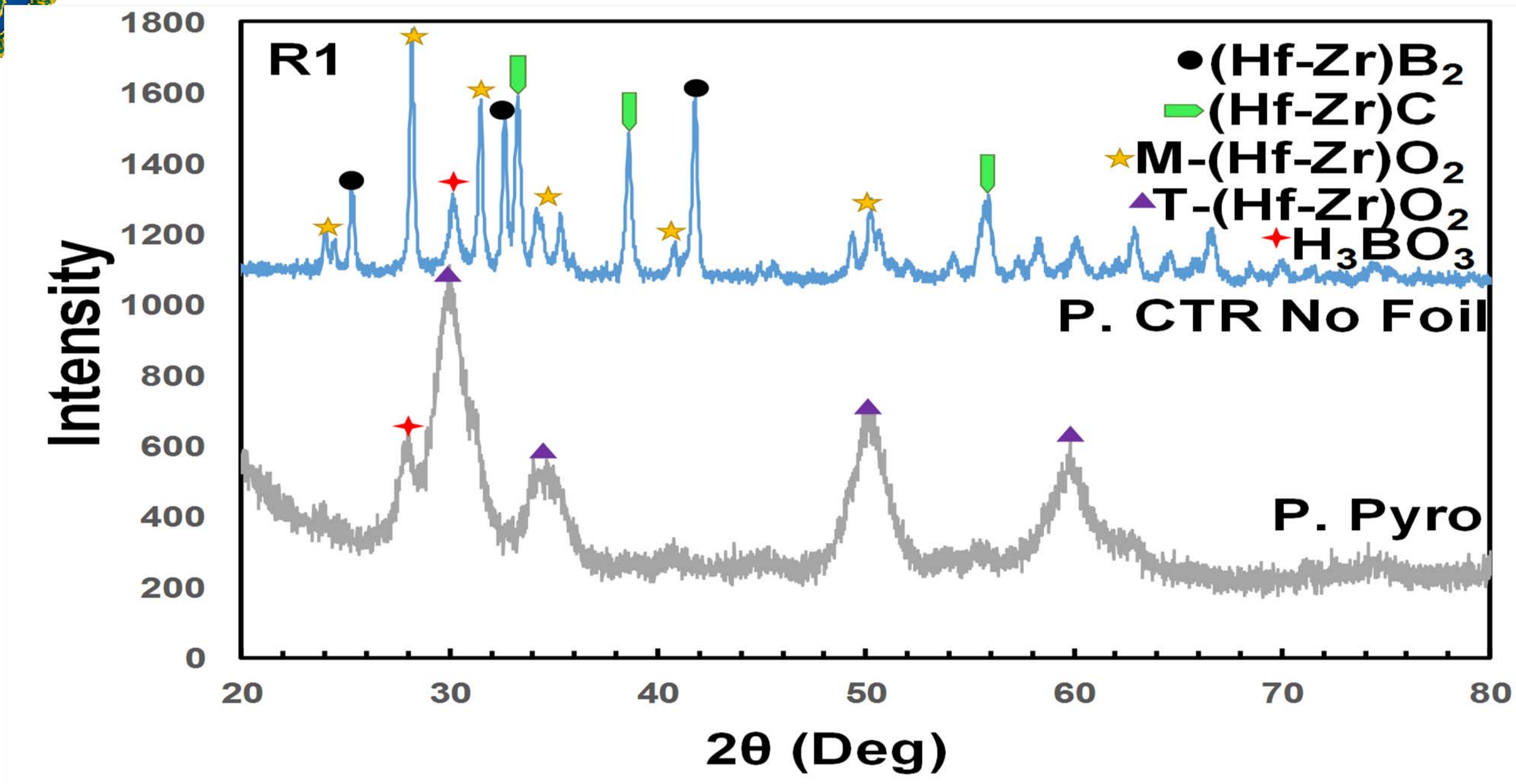
Adjaoud*, PHYS REV B (2009) 134112*

(C) ZrB_2-CeB_6

<u>Eutectic</u> system with very limited solubility in solid



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



Evolution of Oxide, Boride and Carbide after CTR

Results: Sy

P. PYRO AND P. CTR NO FOIL

After Pyrolysis

- B_2O_3 Remains
  - Maybe be caused from reformation due to the absorption of moisture.

Upon undergoing Carbon Thermal Reduction (CTR)

- Production of Monoclinic Oxide phase
- Production of both
  - (Hf-Zr)C
  - (Hf-Zr)B_2

P. CTR NO FOIL AND P.CTR G. FOIL

Addition of graphite foil helped reduce oxidation.

- Maybe help reduce any impurities in inert gas source (Ar) or leaks
- Should be noted that foil will reduce the diffusion of CO_2 away from sample
- Processing parameters for all samples were as follows:
  - 1500^{o}C for 1Hr for CTR
  - 700^{o}C for 1Hr for pyrolysis.

Green Body Formation via Slip Casting (1)

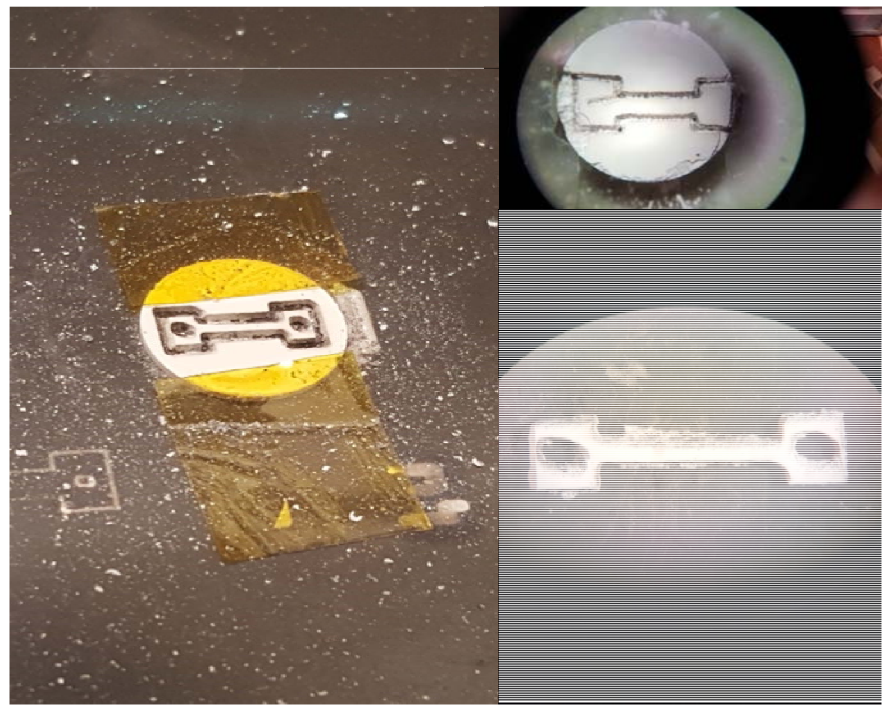
Green Body Formation via Laser Cutting (3)

Initial Attempt Parameters:

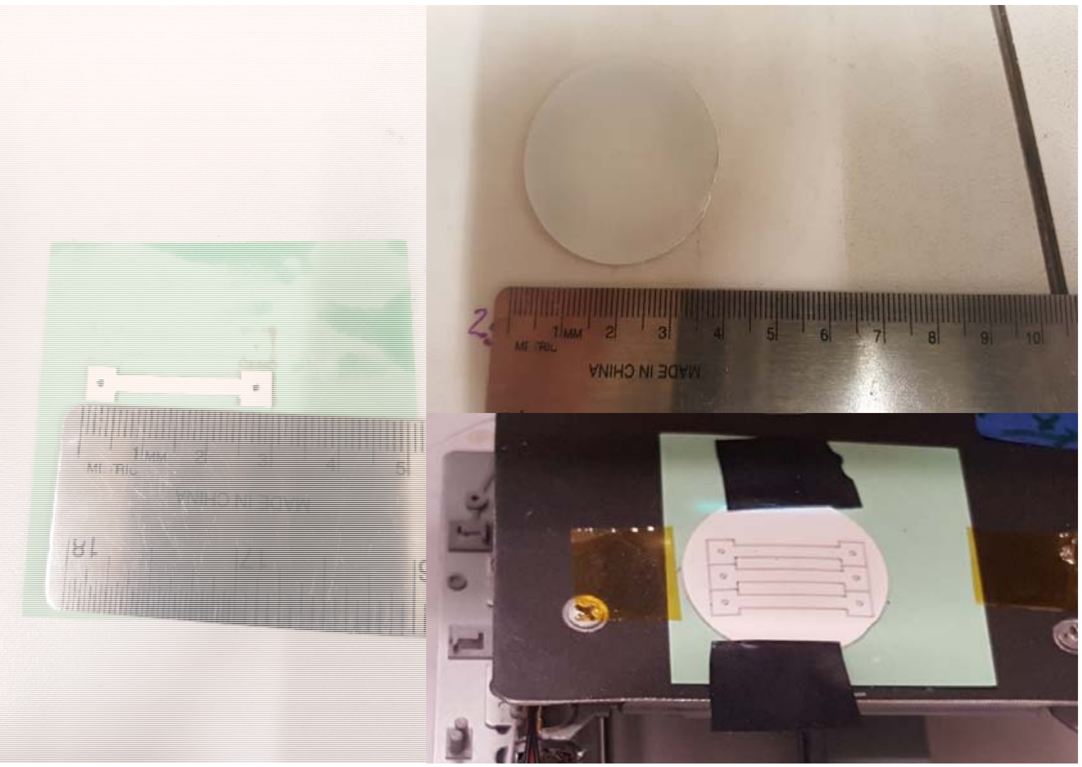
- Pellet Diameter: 10mm *Better Photos, Ruler*
- Thickness: .250mm
- Dog Bone Size: 8mm
- Power Setting- 50J/Pulse
- Backing: Steel Plate
- 5 laps at ~2 Min Per laps
- 10 Mins Per Sample.
- With and Without Q-switch

Problems & Findings

- ❑ Too Small Sample To handle
- ❑ Tape damaged sample
- ❑ Q-switch did not help too powerful



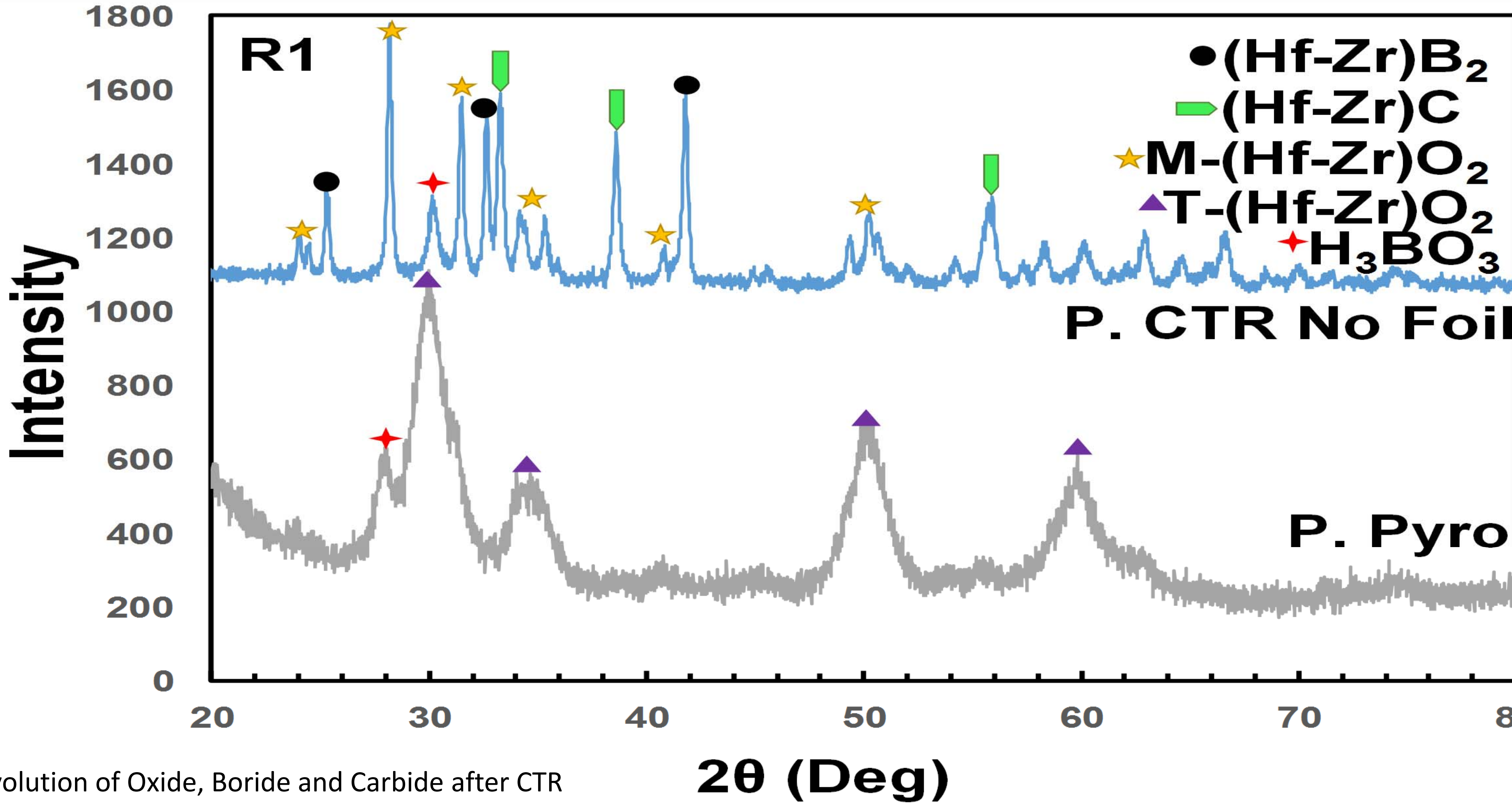
Green Body Formation via Laser Cutting (3)



- Pellet Diameter: 38 mm
- Thickness: 0.250 mm
- Dog Bone Gauge Length: 20mm
- Power Setting- 50J/Pulse
- Backing: Construction Paper
- 5 laps at ~3 Min Per laps
- 15 Mins for 3 Samples. (5 mins per Sample)

Improvements

- Construction Paper Backing
  - Protected stage from damage
  - Easier to transport samples to work station
- Increased pellet size Increased product yield
  - Easier to remove and handle sample
- Decreased sample time by half
  - 1 sample was 10 mins
  - 3 sample are 15 mins



Evolution of Oxide, Boride and Carbide after CTR

Ultra High Temperature Ceramics (UHTC)

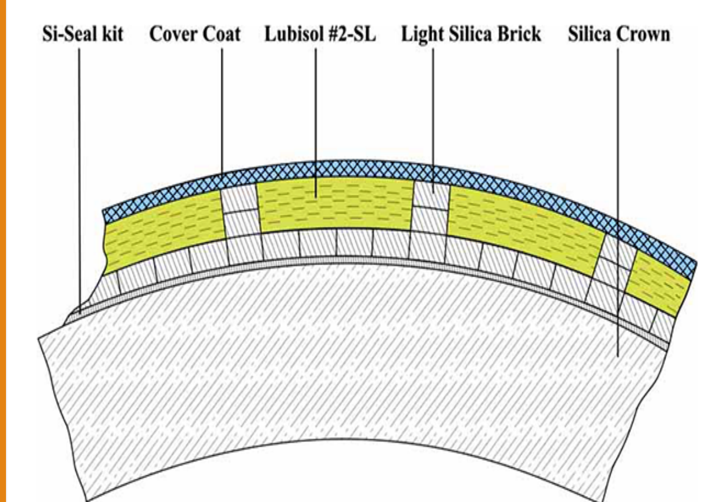
- **A Class Of Ceramics - Inorganic, and Non-metallic Solid (Compounds)**
- **UHTC Characteristics…**
  - High Melting Temperature (T_m)
  - High Ultimate Usage Temperature
- **UHTC Chemical Composition**
  - Borides
  - Nitrides
  - Carbides

Where Are UHTCs Used

- **Leading Edge (Wing) Technology**
- **Molten Metal Confinement**
- **Furnace Insulation**
- **Wear Resistant Surfaces**
- **High Temperature Electrodes (HTEs)**

http://www.raytheon.com/news/feature/hypersonics_01.html

https://c1.staticflickr.com/7/6073/6026390438_fe32e2371a_b.jpg



http://www.lubisol.com/furnace-crown-insulation.html


http://p.globalsources.com/IMAGES/PDT/BIG/396/B1054545396.jpg

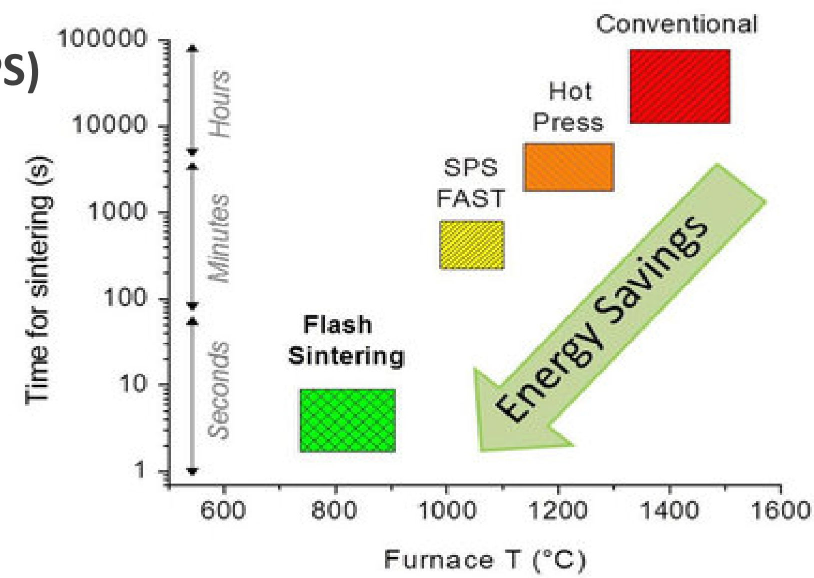
Flash Sintering for Ceramics Densification

Techniques Used to Improve Material Properties:

1. Rapid Solidification (RS)
- **Field Assisted Sintering Techniques (F.A.S.T)** → **Flash Sintering (FS)**
- **Spark Plasma Sintering (SPS)**
- **Hot Pressing (HP)**

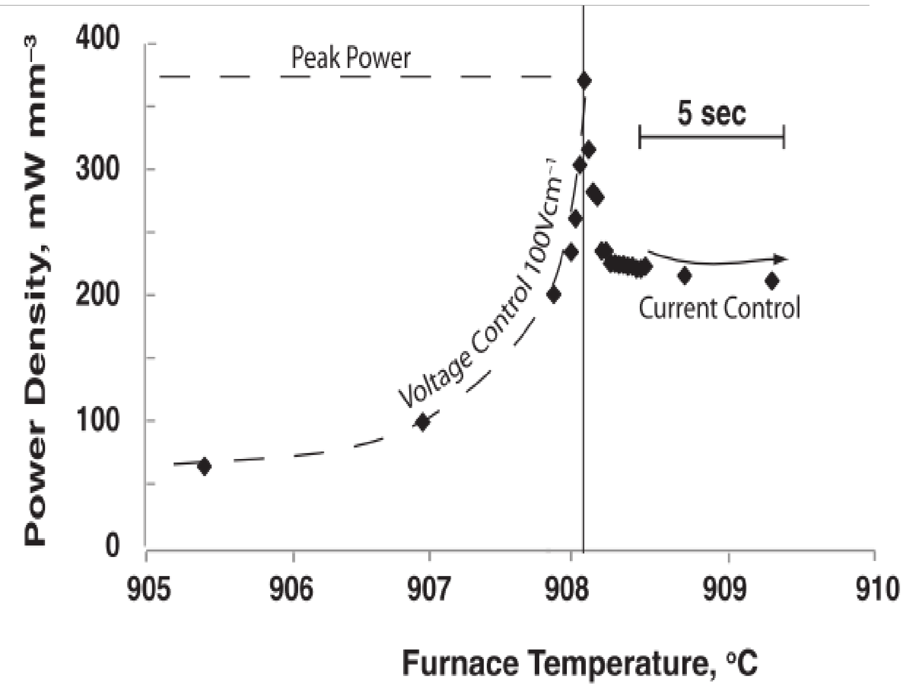
2. Vapor Deposition (VP)

3. Mechanical Alloying & Chemical Doping



Flash Sintering

- **Flash sintering is that the sudden onset of sintering which is accompanied by an equally abrupt increase in the conductivity of the specimen.**
- **The power supply must be switched to current control to prevent electrical runaway.**
- **For current control mode, power into the specimen declines, since the resistance continues to fall**
  - Negative Feedback Loop
- **Specimen temperature rises gradually during the power-spike towards a quasi-steady state value in current controlled mode**

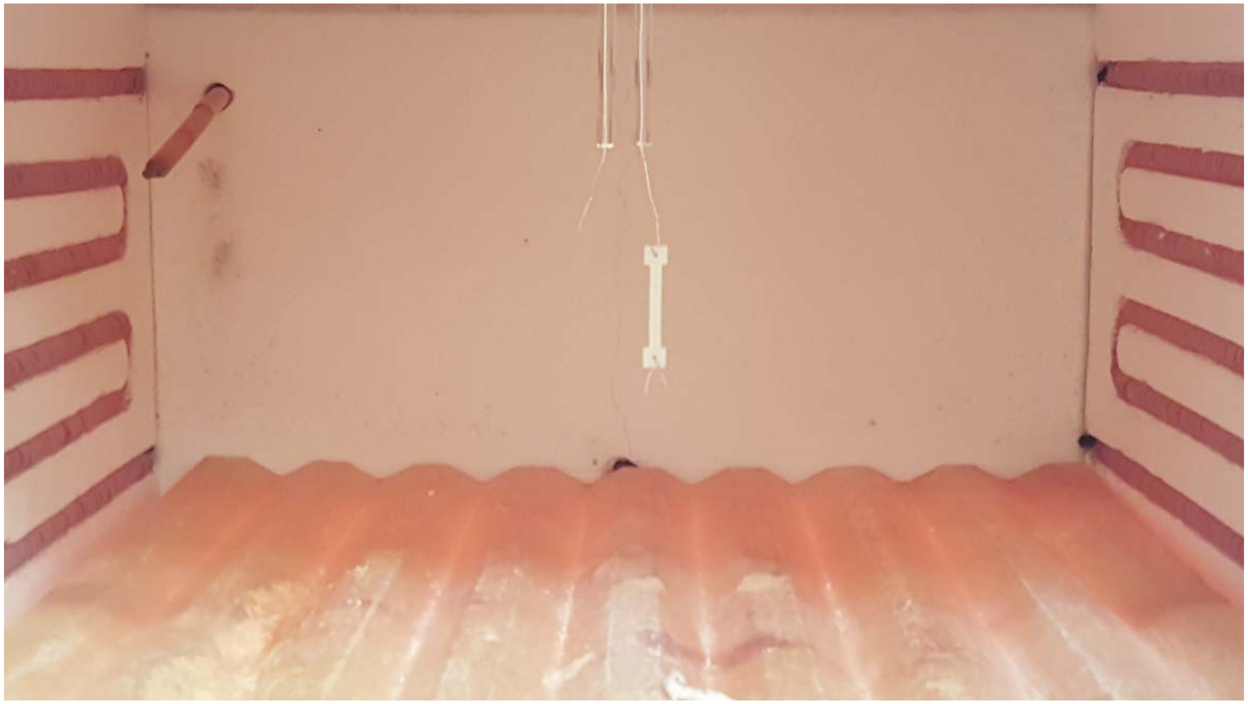


Raj, Rishi. "Joule Heating during Flash-sintering." *Journal of the European Ceramic Society*32.10 (2012): 2293-301. Web.

Improvements To Be Made

Improvements To Make

- Platinum Wires
- Platinum Paint
- Primary Power Supply limits
  - Voltage: 100 V
  - Ampere: 15.75 Ω
- Secondary Power Supply limits
  - Voltage: 20 V
  - Ampere: 20 Ω



Summary

Synthesis

- Nano crystalline (Hf-Zr)B_2 solid solution obtained via solution-based synthesis
- Optimization needed due to trace carbide and oxide impurities & variations morphology.

Green body formation

- Green body prepared successfully using both slip casting and laser cutting

Flash Sintering

Due to the usage of silver wires the maximum temperature we where able to reach in the furnace was ~950°C

- After holding at 950°C the wire mechanical reliability gave out and sample became detached (Previous photo)
- According to the literature (R.Raj) 3YSZ has a flash on set temperature as low as 850°C for an applied field of 120 V/cm