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

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DOE HBCU/UCR Kick-Off Meeting
NETL, Morgantown, WV
October 27-28, 2015

Outline

- ❑ **Outline**
- ❑ **Project overview**
- ❑ **Background**
- ❑ **Project description**
  - Objectives
  - Research tasks
  - Team description
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  - Timeline
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- ❑ **Acknowledgements**

Project Overview

- **Grant No: DE-FE0026325**

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

- **FOA information: DE-FOA-0001242**

  Support of Advanced Fossil Resource Utilization Research by Historically Black Colleges and Universities and Other Minority Institutions (HBCUs/OMIs)

  - Topic area A
    "*Functional Materials Development to Support High Temperature Direct Power Extraction Applications*"

- **Institution: Florida International University**

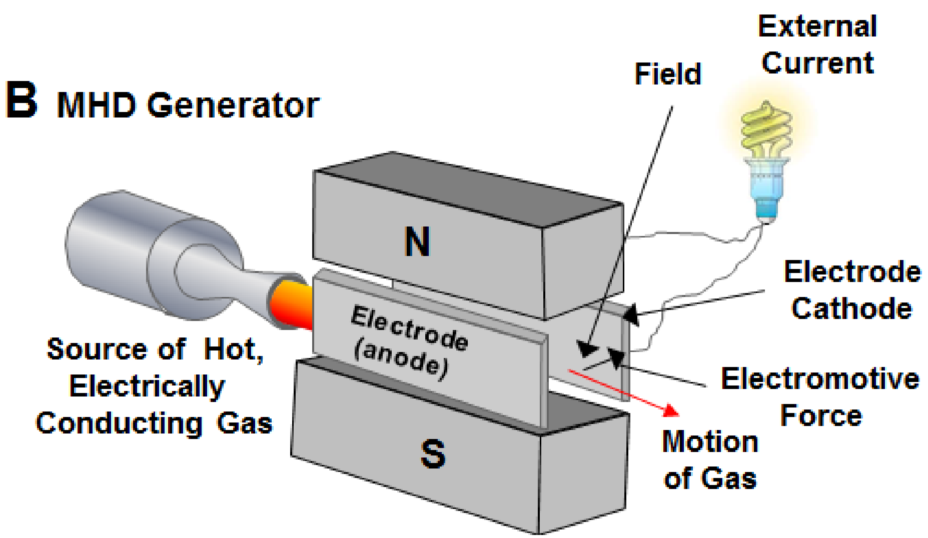
  - PI: Zhe Cheng; Co-PI: Arvind Agarwal

- **Project duration: 10/01/2015 – 09/30/2018**

Direction Power Extraction (DPE) via MHD Generator

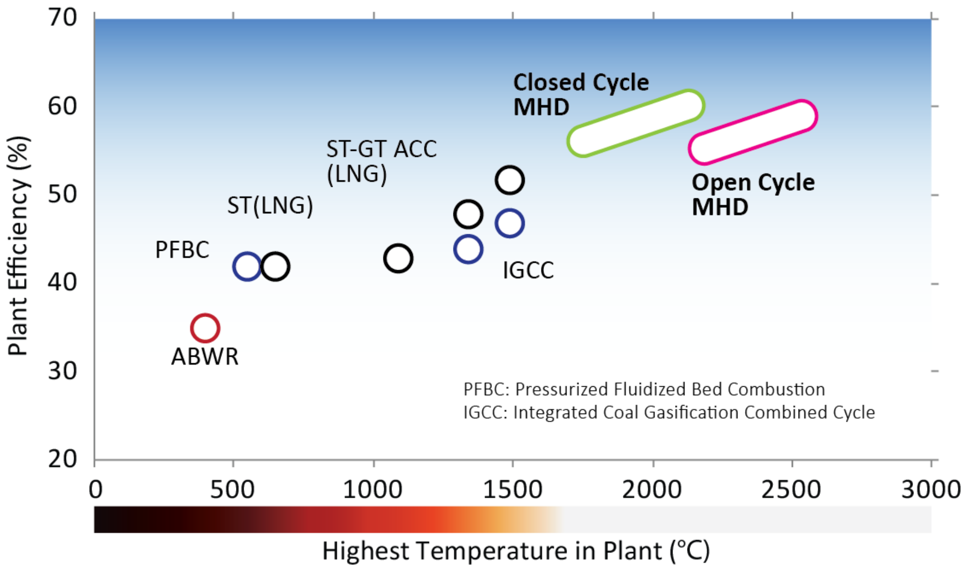
❑DPE

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 seeded with 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 for DPE electrodes

- Good electrical conductivity (>0.01 S/cm)
- Adequate thermal conductivity
- Resistance to electrochemical corrosion (seed/slag)
- Resistance to erosion by high velocity particle laden flow
- Resistance to thermal shock
- Compatibility with other system materials
- Resistance to/minimization of arc 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),

❑Limitations with DPE electrode materials studied

- Low temperature DPE electrode: arching process that decreases efficiency
- Higher temperature DPE electrodes (~1200-2000 ^oC):
  - **SiC**: relatively 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

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
- **Borides and carbide solid solutions for improved performance via novel processing**
  - Possibility to **tune the oxide shell composition for improved oxidation resistance** (and electrical properties)
  - Possibility to **tune microstructure for improved thermal and mechanical properties**
    - Example: TaC-HfC has even higher melting point than TaC and HfC alone
  - Possibility to **simplify processing and reduce cost**

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

Project Objectives

❑Overall objective

Develop nano carbide and boride ceramic solid solution 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 (SO)

- **SO1** ***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 sol-gel processing*
- **SO2** ***Process*** *dense nano-structured carbide and boride solid solutions and related composites via novel flash sintering process using the synthesized nano powders*
- **SO3** *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)*

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

Task 1 - Project Management & Planning

❑ Meetings

- **Monthly FIU team meeting among PI, co-PI, and students**

  To plan for research and communicate progress against milestones, technical achievements, and barriers, and update the project management plan

- **Conference call with DOE program manager**

  To update program manager about project progress and pose questions and request clarification

❑ Technical reports

- **Quarterly, annual and final technical reports**

  To summarize the progress, major discoveries, observations, and barriers met or anticipated, and plans for overcoming them as prepared by the PI with help from team members

❑ Technical and administrative issues

- **Consultation with DOE program manager**

  To address issues such as technical re-directions, budget assignment, and intellectual properties

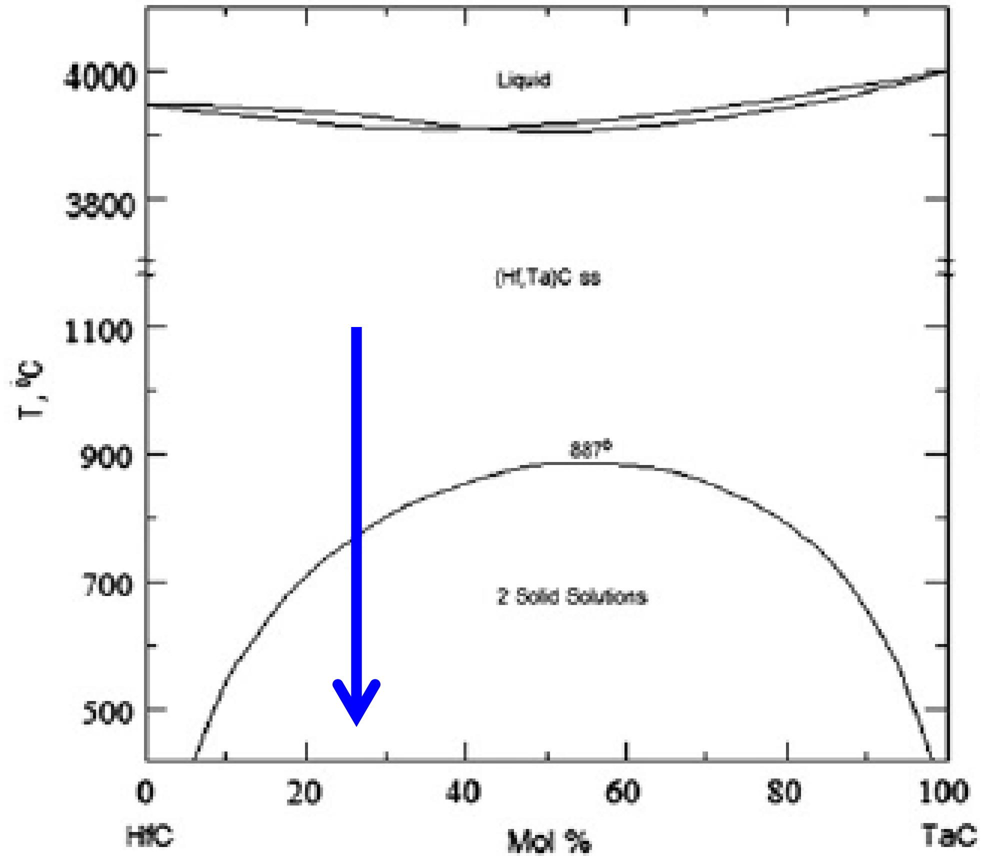
Task 2 - Synthesis of Nano powders of Carbide and Boride Solid Solutions

❑Research hypothesis

H1: *Nano carbide and boride solid solutions will form under fast cooling rate while nano composite powders will form under slower cooling rate after a CTR reaction*

❑Rationale for hypothesis

- Phase diagram for systems such as HfC-TiC or HfC-TaC have miscibility gap, leading to phase separation, which would prevent obtaining uniform solid solution powder at room temperature:
  - During synthesis, the system form uniform solid solution, which have the tendency to phase separate
  - Fast cooling may limit diffusion and prevent phase separation

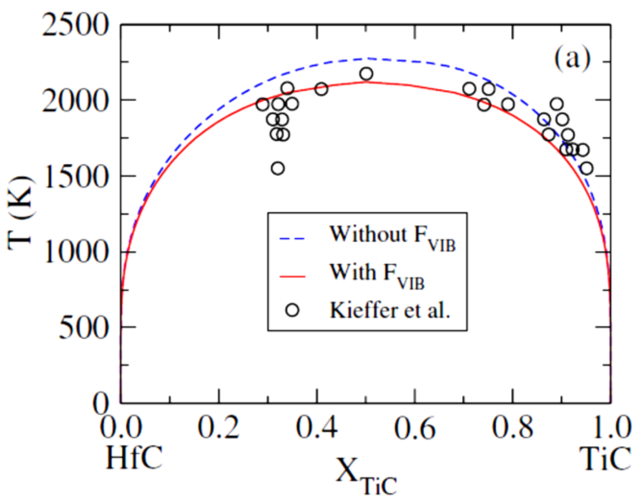


Materials System & Subtasks

❑ Materials systems of choice

i) HfC-TiC

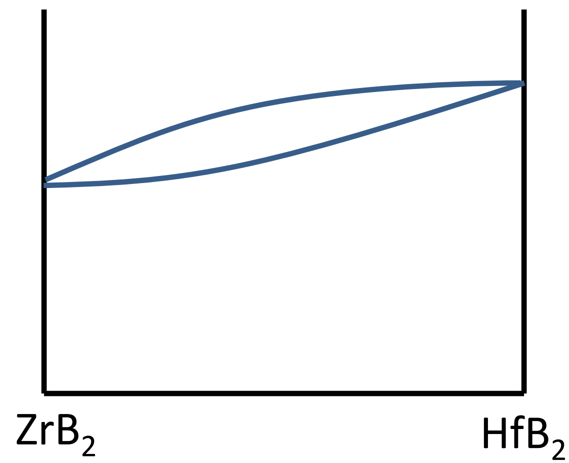
Complete solid solution w/ a **<u>miscibility gap</u>**



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

ii) ZrB_2-HfB_2

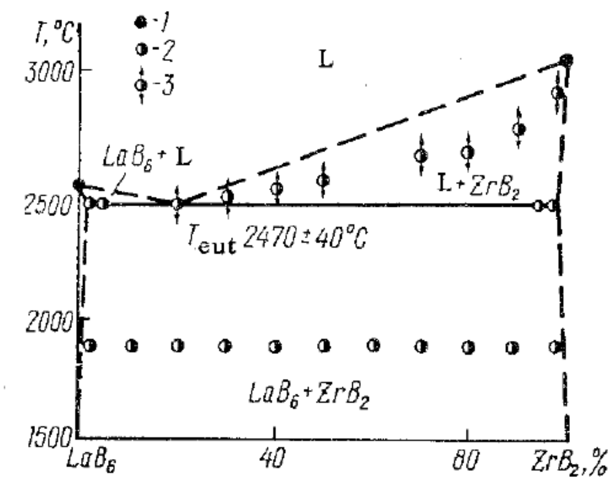
Continuous solid solution



***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

Materials Synthesis Method

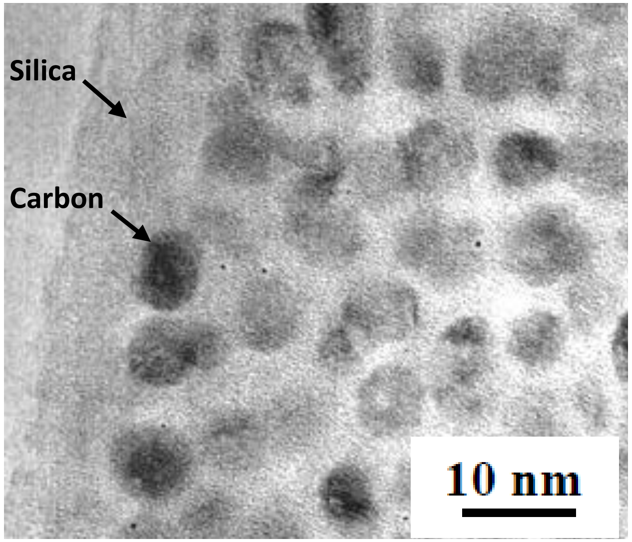
❑Sol-gel followed by carbothermal reduction (Sol-gel/CTR method)

Using sol-gel processing to deliver intimate mixing for oxides and carbon precursors, which, in subsequent heat treatments, go through carbothermal reduction (CTR) reaction (i.e., reduction of oxides by carbon) to form carbides or borides, e.g.,

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

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

- Advantages for **CTR reaction** for boride and carbide solid solution synthesis
  - Low cost processing
  - Great selection of (low cost) starting materials
  - Commercially adopted for carbide and boride powder production
- Advantages for **Sol-Gel processing**
  - Intimate mixing of starting materials, which yield nano-scale mixing of precursor materials
  - Low reaction temperature and better control of microstructures
  - Example: nano SiO_2-carbon mixture obtained from sol-gel processing followed by pyrolysis



Cheng, MS Thesis (2004)

Starting Materials and Synthesis Procedure

❑ Starting materials

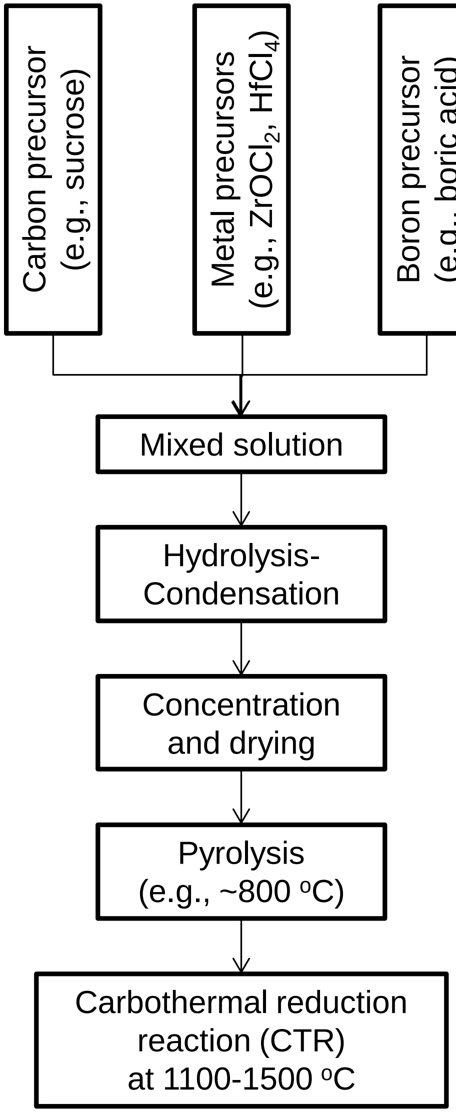
- Metal precursors
  - Water soluble: e.g.,
    - Hf source: $HfCl_4$
    - Zr source: $ZrOCl_2$
    - Ti source: $TiCl_4$
  - Solvent soluble: e.g., titanium butoxide
- Carbon precursors
  - Water soluble: sucrose
  - Solvent soluble: phenolic resin
- Boron precursors
  - Water soluble: boric acid (H_3BO_3)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

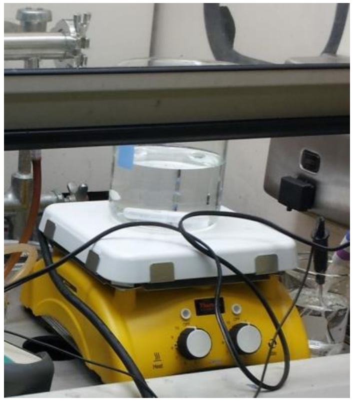
❑ Synthesis procedure

Example: for (Hf-Zr)B_2 solid solution

Overall CTR reaction:

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



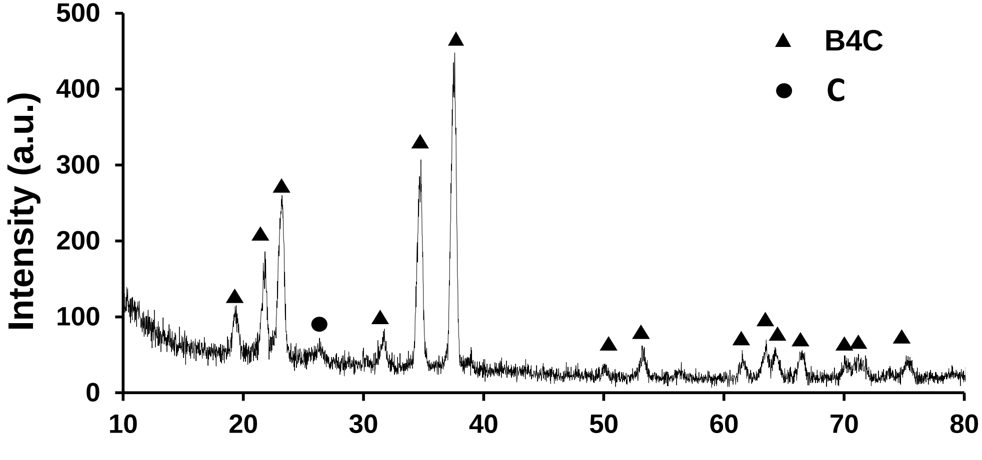


Unpublished results

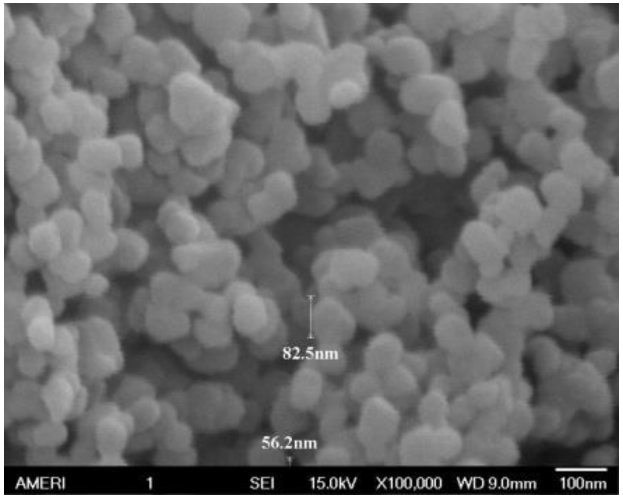
Demonstration of Feasibility (1)

- Nano B_4C and HfB_2 synthesized in PI's lab via the sol-gel/CTR method

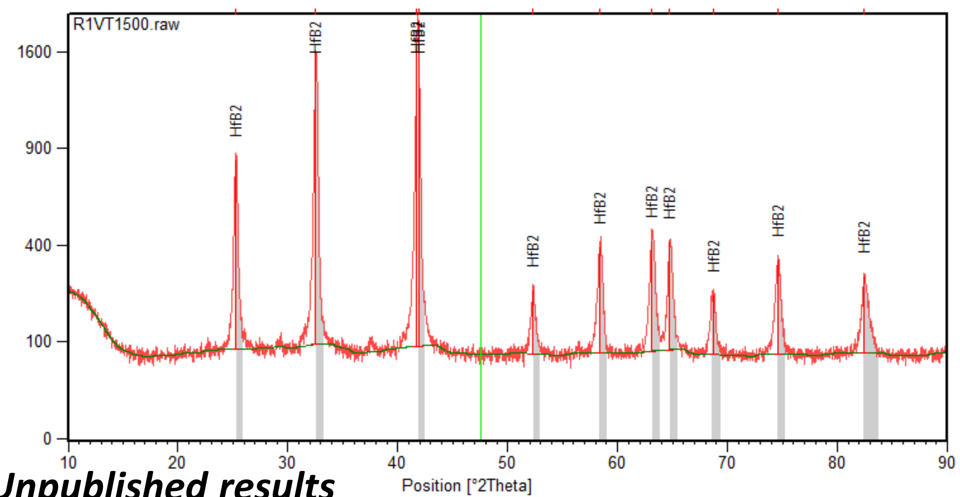
B_4C



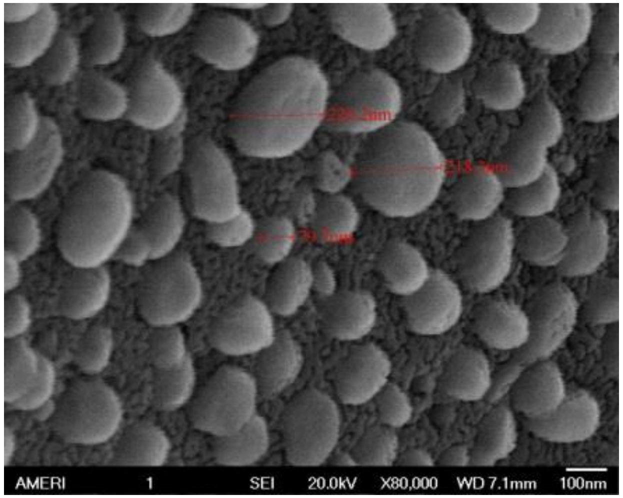
Unpublished results



HfB_2



Unpublished results

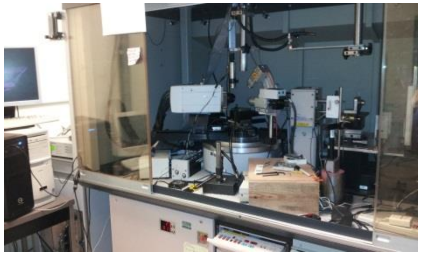


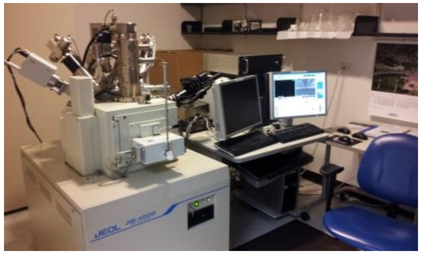
Characterization of Synthesized Materials

❑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

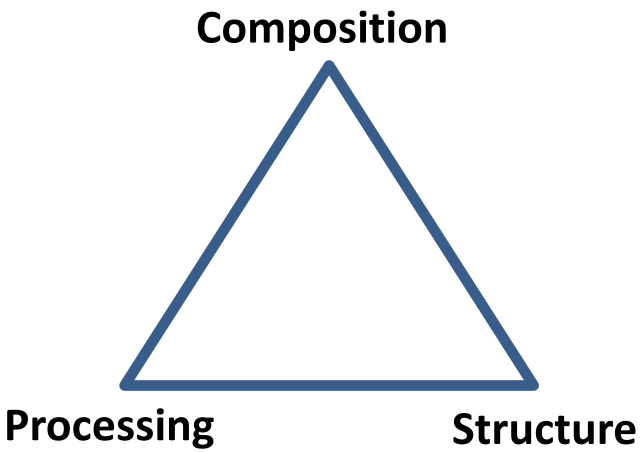
XRD, SEM/EDS/FIB, and TEM at FIU





❑Critical research questions

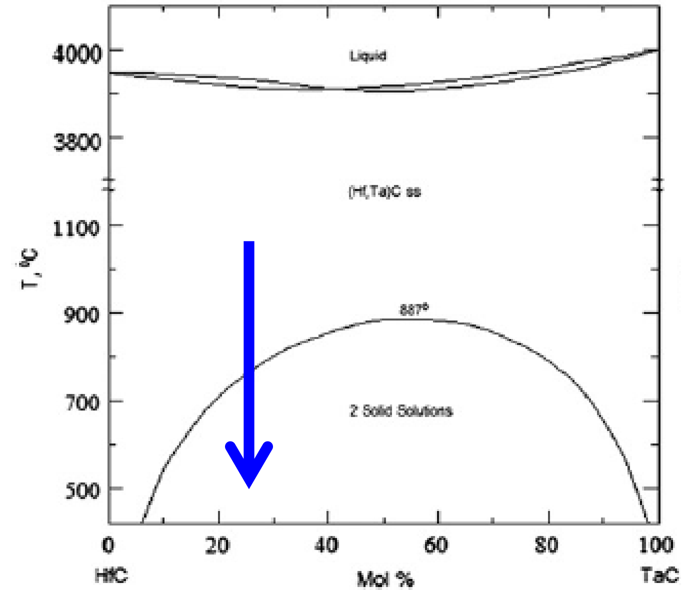
- How do nano carbide and boride solid solution phase form and transform?
  - In CTR reaction and in subsequent transformation process
- How does composition and processing condition (e.g., temperature, time) influence resulting material microstructure (e.g., grain size, morphology, interface structures)?



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

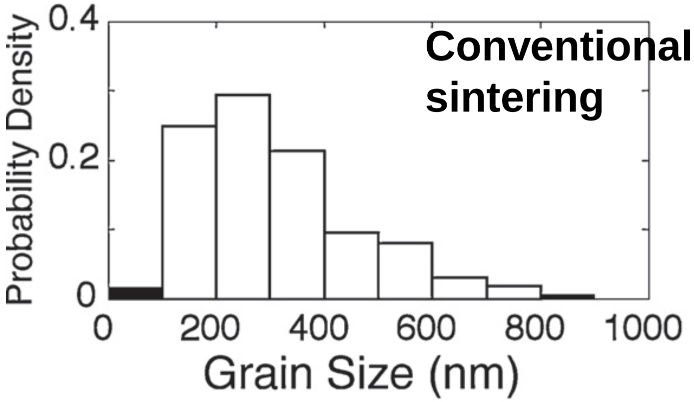
❑Research hypothesis

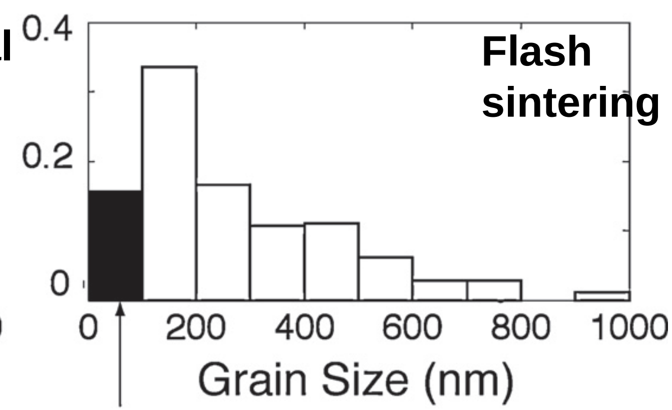
H2: *Densification via flash sintering will enable precise control of the final phases (uniform solid solution versus composites) and microstructure for the carbides and borides*



❑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*

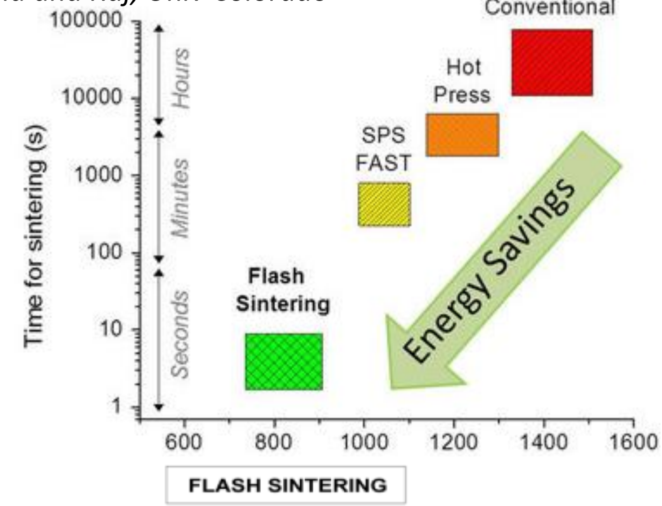
Materials Densification via Flash Sintering

❑Flash sintering

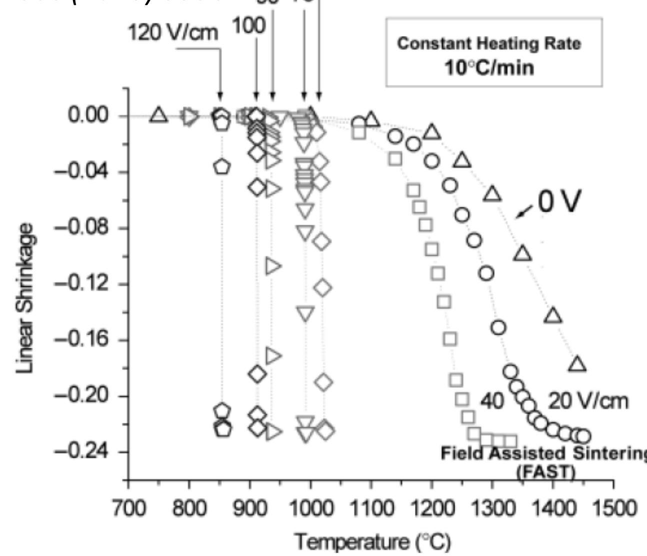
Rapid sintering process (sometimes within a few seconds) for materials under electrical field (in most cases DC) exceeding certain critical level, which yields densification at furnace temperatures dramatically lower than in conventional sintering or even SPS sintering

- Advantages
  - Significantly reduced temperature, time, and energy for densification
  - Maintenance of fine microstructure
- Demonstrated systems
  - 3 mol.% Y_2O_3-doped ZrO_2 (3YSZ), Co_2MnO_4 SiC…
- Features
  - Onset voltage/temperature gets lower with smaller particle size
  - Not yet carried out for high temperature ceramic solid solutions

Cologna and Raj, Univ Colorado



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



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

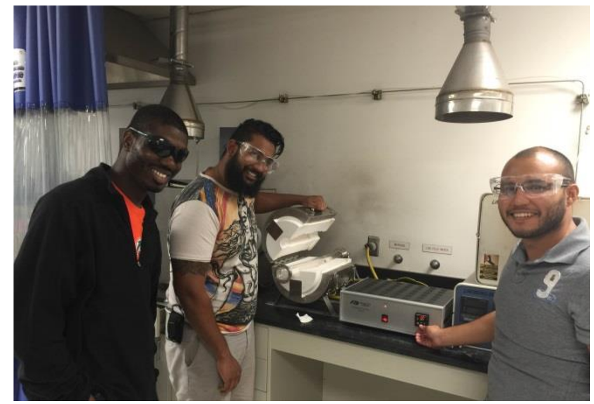
AMTEK 1500W power supply

❑Critical questions to answer

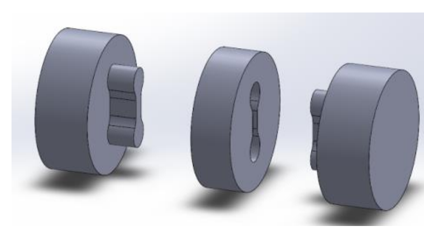
- How do applied power and temperature impact the flash sintering including on-set temperature?
- How do phase and microstructure evolve in flash sintering for nano solid solution?

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

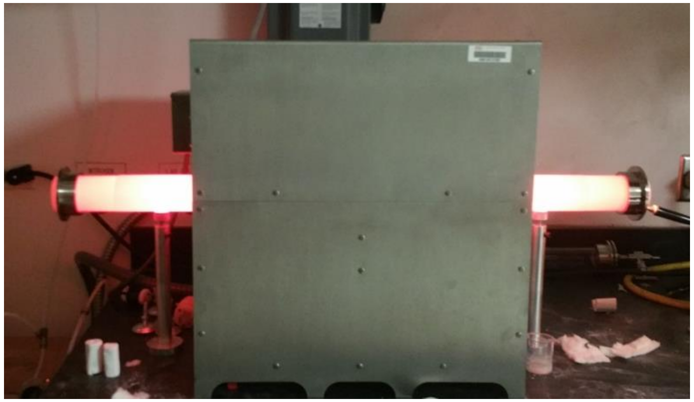
❑Subtasks

- **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 ºC



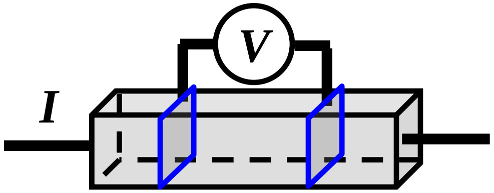
Task 4 - Characterization of Oxidation Resistance and Electrical Properties (2)

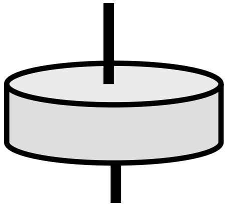
❑ Subtasks

- **Subtask 4.2**

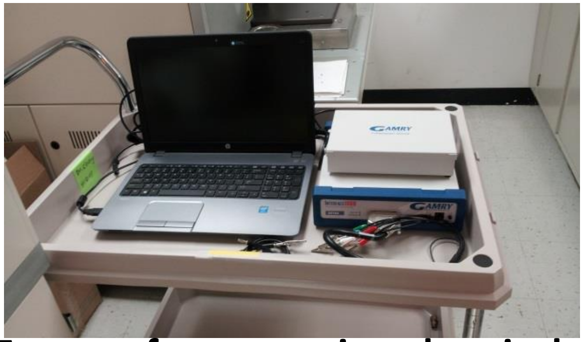
Evaluation of electrical properties

- Electrical conductivity/resistivity and contact resistance

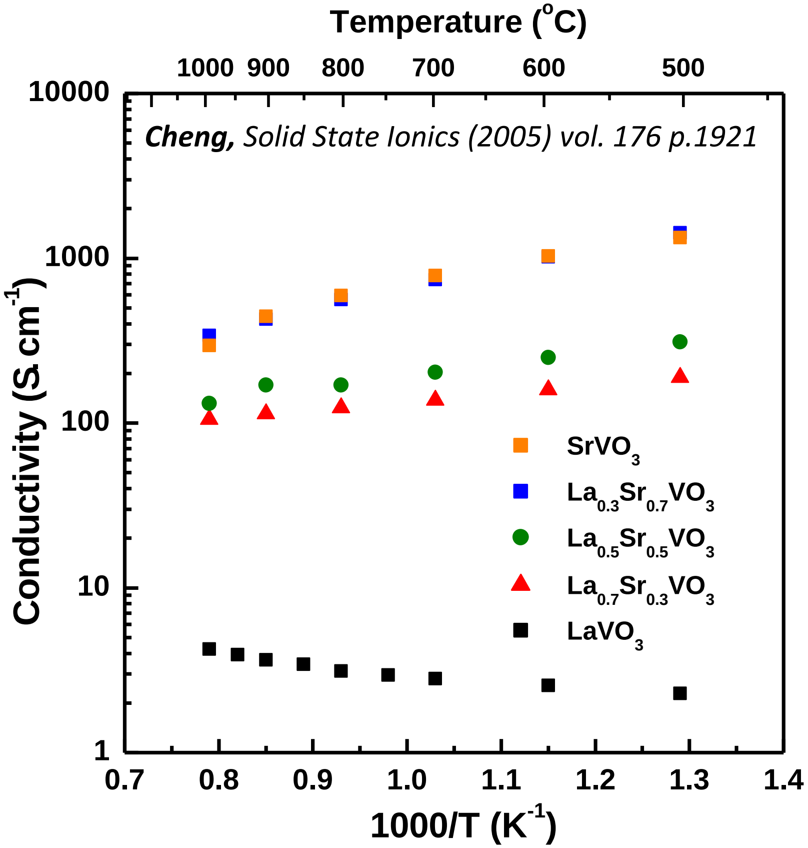




Potentiostat w/ impedance capability for evaluting electrical properties



Furnace for measuring electrical properties up to 1500 ºC

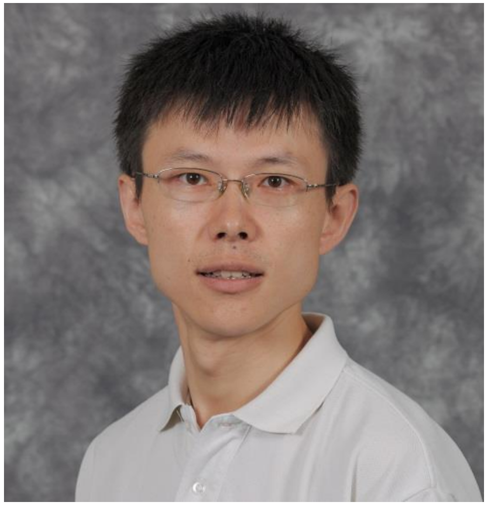


Team Description - PI

❑Dr. Zhe Cheng

Assistant professor (2013/08-)
Department of Mechanical & Materials Engineering
Florida International University (FIU)

- Research group website: https://ac.fiu.edu
- Education: Ph.D. Georgia Institute of Technology
- Prior work experience: Research scientist, DuPont



❑Research expertise

- Advanced nanomaterials for high temperature and ultra-high temperature ceramics
- Ceramic electrolyte and electrode materials for solid oxide fuel cell (SOFC) and solid oxide electrolysis cells (SOEC)
- Ceramic materials for thin film solar cells
- Fundamental mechanism study of ceramic materials using advanced *in situ* characterization tools

Team Description - Co-PI

- **Dr. Arvind Agarwal**

  Professor

  Director, Advanced Materials Engineering Research Institute (AMERI)

  Associate Dean for Research

  Department of Mechanical & Materials Engineering

  College of Engineering & Computing

  Florida International University (FIU)

  - Research group website: http://web.eng.fiu.edu/agarwala/
  - Education: Ph.D. University of Tennessee

- **Research expertise**
  - Plasma spray and other coating technology for aerospace, defense, energy, and biomedical applications
  - Synthesis and processing of nano composites containing carbon nanotubes and graphene's
  - Nano mechanics and nano tribology
  - Electrical field assisted sintering including spark plasma sintering (SPS) for advanced ceramics and composites

Team Description – Ph.D. Student

❑Ms. Paniz Foroughi

Ph.D. candidate (graduation expected in 2018)
Department of Mechanical & Materials Engineering
College of Engineering & Computing
Florida International University

❑Research expertise

- Nano high temperature and ultra high temperature ceramics synthesis and processing
- Fundamental reaction mechanism and kinetics research for high temperature ceramics
- Advanced materials characterization techniques

Team Description - Undergraduate Students

- **PI is currently advising and sponsoring two FIU Mechanical Engineering (ME) senior design teams consisting of all minority and underrepresented students**

- **2015 Fall ME Senior design team**
  - Team members: Mr. Nikhil Mohip, Mr. Seth Mongbeh, Mr. Alejandro Vera
  - Topic: **Field Assisted Sintering of Advanced Ceramic Materials**
  - Status: team has defined and purchased all necessary equipment and supplies and in the process of setting flash sintering system up

- **2016 Spring ME Senior Design team**
  - Team members: Ms. Iti Mehta. Ms. Laura Reyes, and Mr. Juan Estepa
  - Topic: **Spray pyrolysis for continuous production of nano high temperature and ultra-high temperature ceramic powders**
  - Status: team is in the process of defining the process and the equipment including atomizers and pumps to be used for spray pyrolysis synthesis

Team Responsibility Assignment

❑ PI

- Lead the entire project and collaboration between different team members
- Lead research involving
  - Design, synthesis, and characterization new nano carbide and boride solid solution and related composite powders
  - Flash sintering for synthesized nano carbide and boride solid solution and related composites
  - Evaluation of the electrical property and oxidation resistance for sintered carbide and boride ceramic solid solution and related composites

❑ Co-PI

- Provide support in flash sintering for nano carbide and boride materials
- Lead research involving
  - Flash SPS sintering for nano carbide and boride materials for samples with larger dimension that request higher current

❑ Graduate student

- Carrying out detailed research including instrument setup, experiments, and data analysis
- Drafting of technical reports and research papers

❑ Undergraduate students

- Help graduate students carrying out experiments and setup/operation/maintenance of equipment

Risk Management Plan

Perceived risks or uncertainties	Proposed approach to resolve the uncertainties or mitigate the risks
The systems identified for study did NOT show improved oxidation resistance or improved high temperature electrical property	• Based on the discovery about oxidation rate and oxidation product formation, identify and explore alternative metal doping elements to form solid solution and/or composites
The cooling rate for achieved through "quick pulling" type of set up may not be fast enough to obtain uniform solid solution and always yield a composite	• Alternative cooling mechanism mimicking "quenching" type experiment will be carried out, especially for powder samples • On the other hand, even if the sintered sample are composites at room temperature, when heated up to actual MHD usage temperature (e.g., >1500 ^oC), the materials may be in solid solution region due to change in solubility
Due to low resistivity for the carbide and boride samples, flash sintering may request too high a current	• Instead of using low power rating power supply, SPS furnace (available through co-PI Dr. Agarwal) with modification will be used so that high current will pass through the sample instead of the pressing die to achieve flash SPS type sintering, which has been shown in 2014 in a UK research group (J Am Cera Soc 2014, p.2405).

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

Summary

- Nano carbides and boride solid solution ceramics hold promises as potential high temperature electrodes for DPE applications due to flexibility in tuning its composition and chemical/electrical properties

- New nano carbide and boride solid solution powders will be synthesized using sol-gel/CTR method from low cost water-soluble precursors and the impacts of composition and processing condition on phase formation and microstructure development will be studied

- The nano carbide and boride solid solution powders will be consolidated into dense ceramic body via flash sintering process and the oxidation resistance and electrical properties for the sintered ceramics will be evaluated for potential DPE electrode applications

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