Refractory Oxides with Tunable Porosity and Geometry as Versatile Fast-Release Solid Catchers for Rare Isotopes

Nuclear Physics SBIR/STTR Exchange Meeting
August 6-7, 2015

Sponsor: Office of Nuclear Physics, DOE
Program Officer: Dr. Manouchehr Farkhondeh
Phase II Contract Number: DE-SC0007572

Small Business
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Argonne NATIONAL LABORATORY

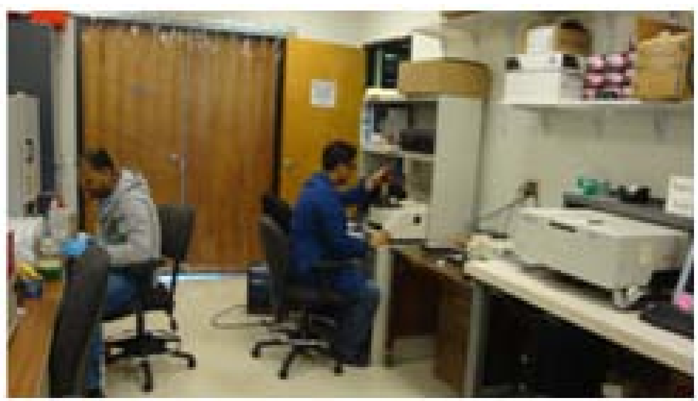
InnoSense LLC

Presentation Overview

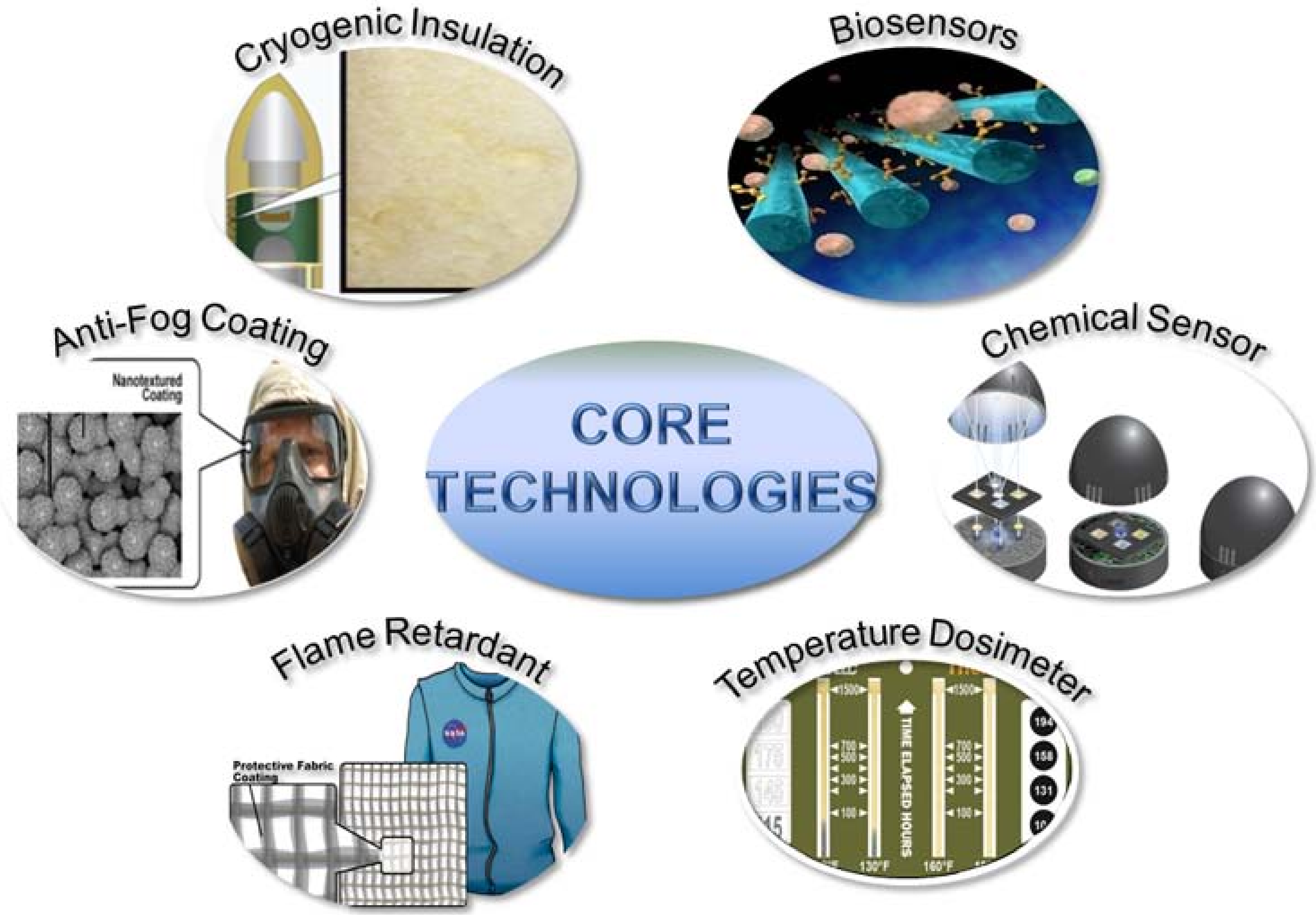
- About InnoSense LLC
- Motivation
- Relevance to Nuclear Physics Programs
- Phase II Accomplishments
  - Fabrication of Refractory Porous Oxides
  - Off-Line Extended Heating Evaluations
  - Simulations
  - In Beam Evaluations
- Summary
- Commercialization Status
- Acknowledgments

About InnoSense LLC

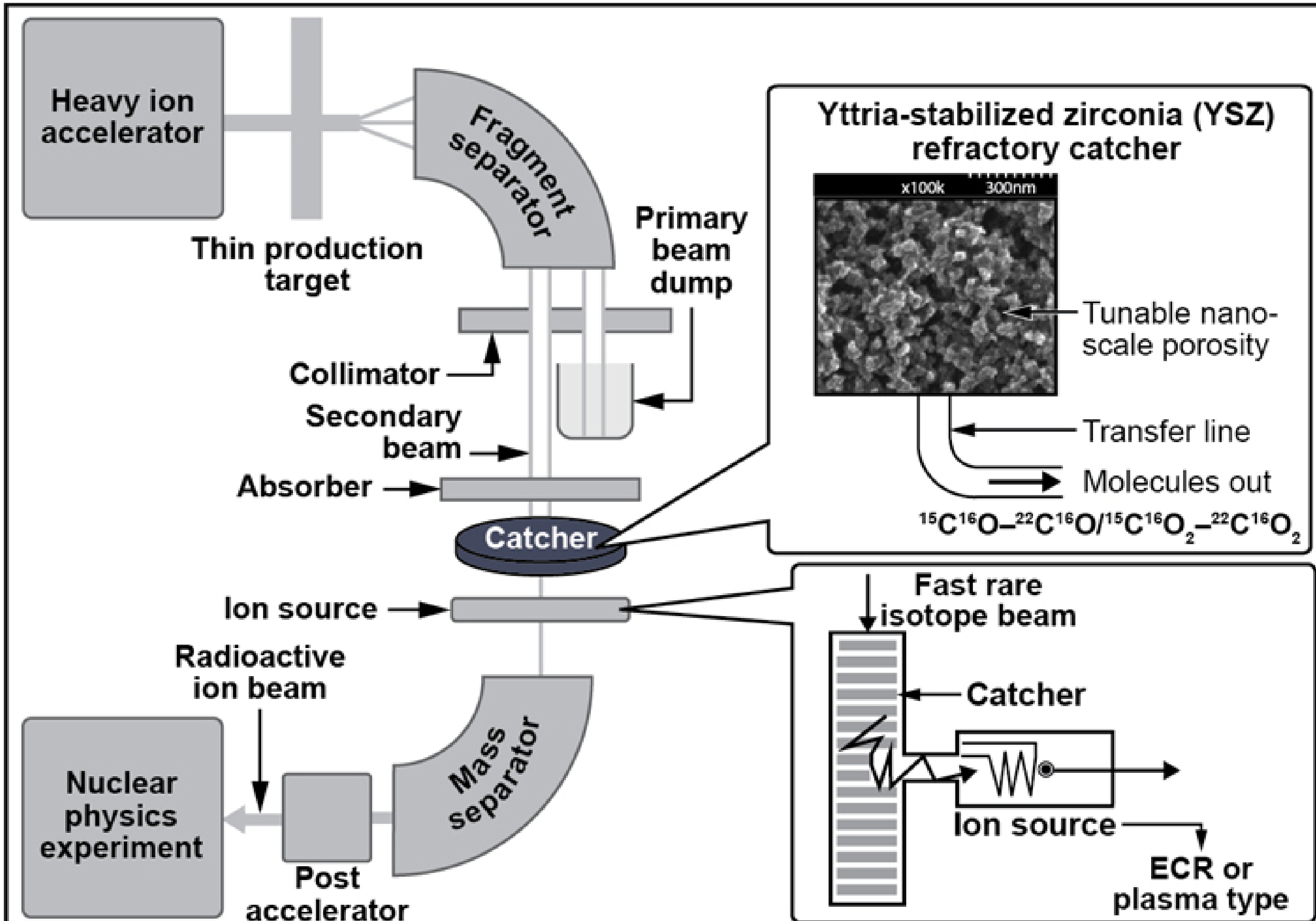
- Established in 2002 by private investment, R&D operations in 2004, housed in a recently expanded 9,000 square feet laboratory facility located in Torrance, California.
- Key laboratories include five “wet” chemical facilities equipped with fume hoods, a clean room, a spectroscopy facility, optics and testing laboratory, and two machine shops.
- 18 employees, including 4 PhD, 3 MS and 3 MBA degree holders.



InnoSense LLC – Core Technologies



Refractory Hot Catchers for Rare Isotopes



Features

- Refractory YSZ of tunable porosity and geometry
- Stable in energetic radioactive beams
- Supplementary to the gas catcher

Advantages

- Higher stopping power (~100 times) over gas catchers
- Allows diffusion/effusion of short-lived isotopes as atoms or molecules
- Enable understanding of the formation of the cosmos

Collaborators

Argonne National Laboratory

National Superconducting Cyclotron Laboratory at Michigan State University

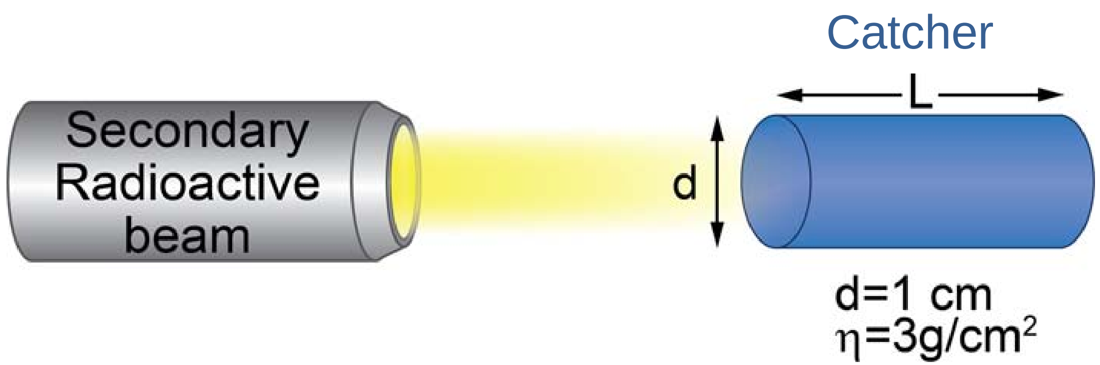
- *Design heater and ion source*
- *Beam-line studies*

Primary purpose of porous oxide monolith is to catch ^{9}C–^{22}C isotopes and convert them to $^{9}C^{16}O$– $^{22}C^{16}O$ expected to be released almost as a noble gas.

Catcher Materials Under Investigation

Refractory Catcher	Beam	Expected Isotope
Tungsten-coated SiO_2 Aerogel	^{18}O (typical)	$^{8\text{-}11}Li$ $^{6,8}He$
Carbon Aerogel	^{16}O, ^{48}Ca, etc.	$^{12}C^{14}O$–$^{12}C^{24}O$ $^{12}C^{14}O_2$–$^{12}C^{24}O_2$
Yttria-Stabilized Zirconia and Hafnia Porous Monolith	^{12}C, ^{48}Ca, etc.	$^{9}C^{16}O$–$^{22}C^{16}O$ $^{9}C^{16}O_2$–$^{22}C^{16}O_2$
Sintering-inhibited Tungsten, Tungsten + Hafnia Tungsten Carbide	^{4}He, ^{7}Li ^{4}He, ^{7}Li, ^{13}C, ^{120}Sn ^{18}O	$^{8\text{-}11}Li$ $^{6,8}He$, ^{120}Sn, ^{120}SnS $^{12}C^{18}O$, $^{12}C^{18}O_2$

Catcher Thickness Considerations



- Desired area density (η) for efficient isotope capture is ~ 3 g/cm^2 or more
- Area density can be related to the volumetric apparent density (ρ) measured by:
    - $\eta = \rho L$
- Meter(s) long gas catcher is replaced by a relatively small (cm-long) catcher

Background on ISOL Target Materials

Isotope Separation On-Line (ISOL) used to generate radionuclides

- Targets are used with high power beams
- Isotopes are produced by reactions of the beam with target material
- Target must be dense enough to stop energetic beam, yet porous enough to allow rapid diffusion of radionuclides to the accelerator source
- Must be thermally conductive to withstand beam power
- Targets are heated to > 2000 °C to increase diffusion rates of radioactive nuclides

Benefits When Used in Catcher Mode

- Catchers used to stop high energy radioactive isotopes created in a separate production target up stream
- In the catcher mode, thermal conductivity is less relevant since the beam power is deposited in the thermally separated production target irradiated with heavy ion beams
- No radiation damage when used in catcher mode since only secondary radioisotope beams impinge on it
- Selection of materials is open to new approaches that cannot work with ISOL targets, e.g. aerogels with low thermal conductivity
- The porous refractory materials will theoretically offer more stopping power and fast-release for the generation of intense rare isotopes
- The refractory nature potentially allows them to be used as:
  - Compact isotope catcher/ion source placed in the first focal plane of the fragment separator with the capability of selective harvesting for isotopes for different applications

Technical Objectives and Milestones Accomplished

Objective 1. Refine formulations and processing conditions to reproducibly fabricate porous, solid catchers of yttria-stabilized zirconia and hafnia.

Milestone 1: *Exceeded targets by achieving open porosities ranging from 50–75% after 30 minutes at 1500 °C compared to the 800 °C planned for (**Month 9 of Year 1)***

Objective 2. Evaluate porous monoliths off-line in long duration heating at temperatures ranging from 1000–1500 °C.

Milestone 2: *Achieved higher open porosities of 41–51% (targeted 30–50%) after long-term heating at 1500 °C, simulating a production run (**Month 4 of Year 2**).*

Objective 3. Develop a new method for in-beam evaluation of solid catchers for rare isotopes using accelerated stable beams and a very sensitive residual gas analyzer (RGA).

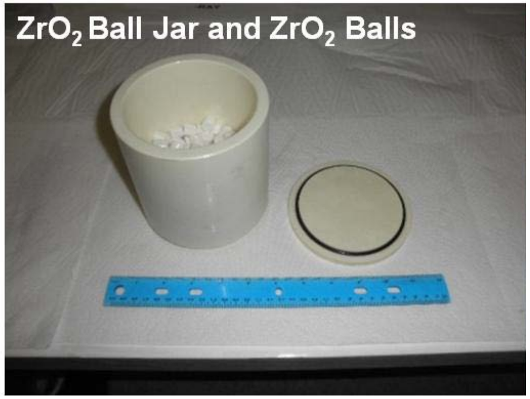
Milestone 3: *The first demonstration of CO release was accomplished using the off-line RGA apparatus commissioned at Argonne (**Month 4 of Year 2**).*

Objective 4: Evaluate candidate porous oxide (YSZ and HfO_2) monoliths with in-beam studies using new apparatus.

Milestone 4: *The first predictions of the preliminary simulations on oxide systems were completed and verified by experimental observations of CO release at temperatures below 1000 °C **(Month 6 of Year 2).***

Milestone 5: *The RGA apparatus was moved to FSU and used for the first on-line validation of its sensitivity by measuring the release of ^{4}He atoms implanted in an alumina nanopowder sample (**Month 12 of Year 2**.*

Tape Casting Process to Fabricate Porous Oxides


ZrO_2 Ball Jar and ZrO_2 Balls

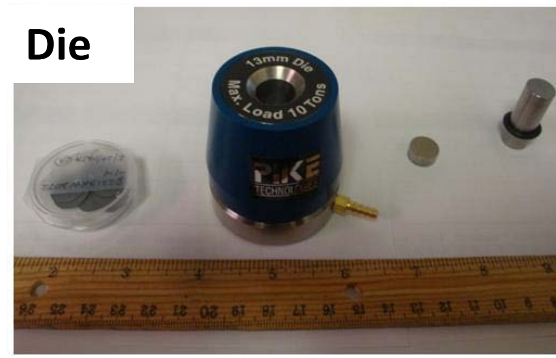

½” Die Punch

Pressed Green Disk

Ball Mill

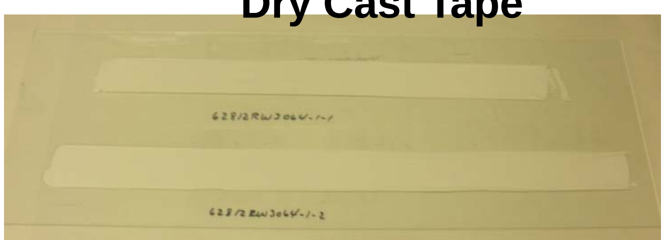
Carver Hydraulic Press

Die



Die in Press

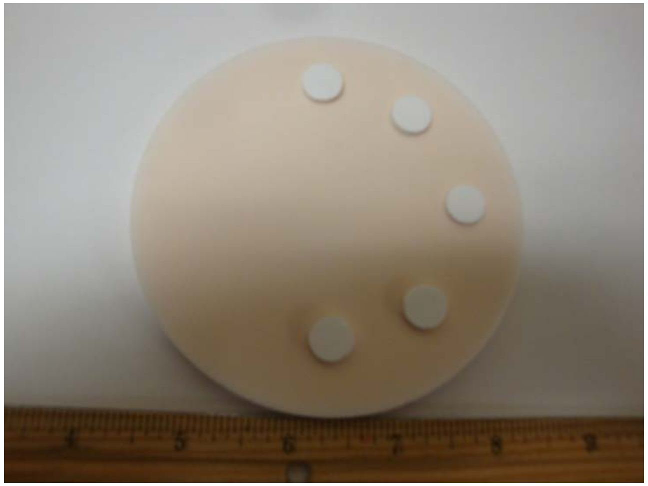
Dry Cast Tape



Tape Cast Porous Oxide Monoliths

Diced Stacked Hot Pressed Tape

Disks After 1500 °C firing



Dye Penetrant Test

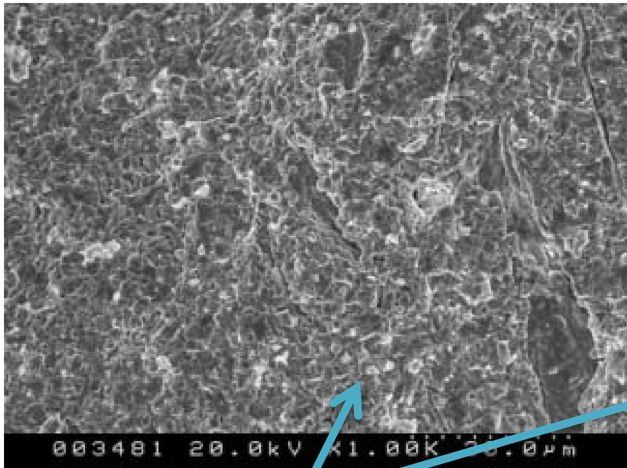
Top

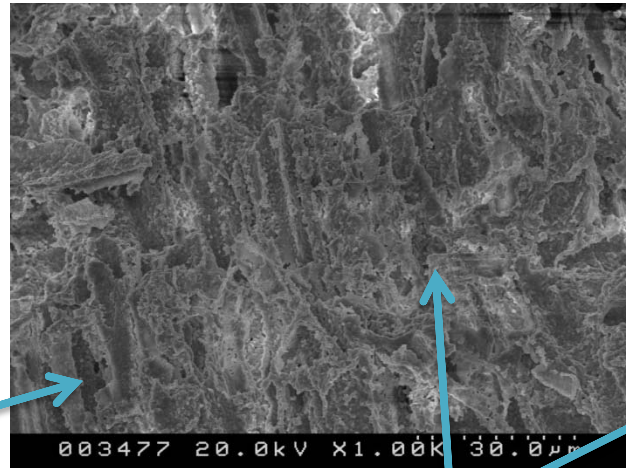
Bottom

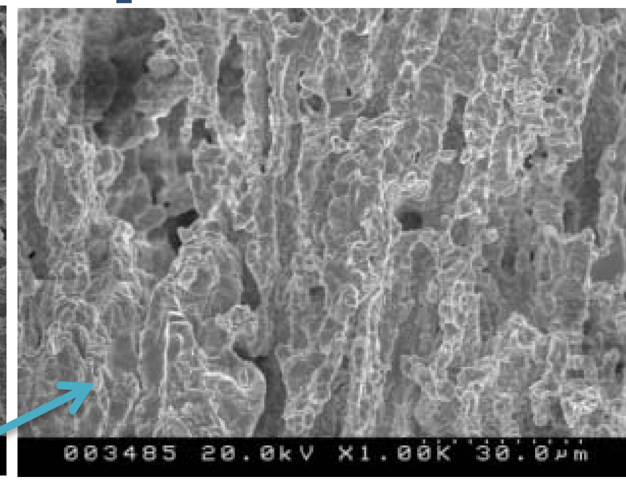
Originally white disk turns red upon wetting by dye

Grain Growth Inhibition Demonstrated

HfO_2 after 24 h@1500 °C | **HfO_2 + carbon wires** | **HfO_2 + carbon wires + GGI**



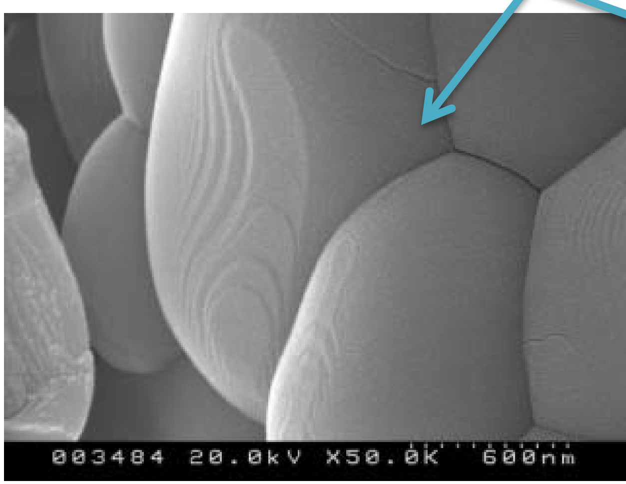


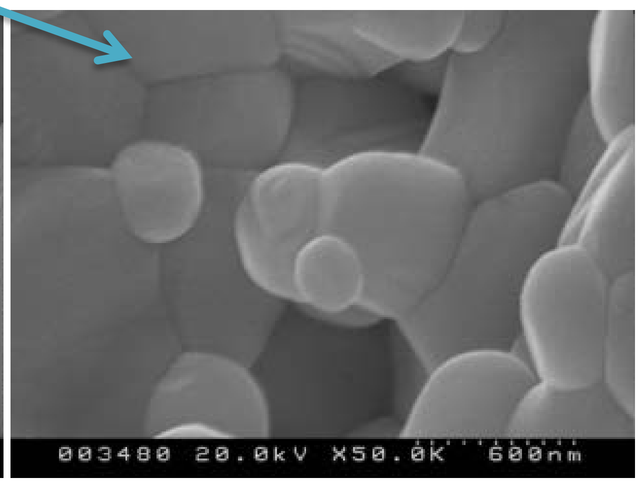


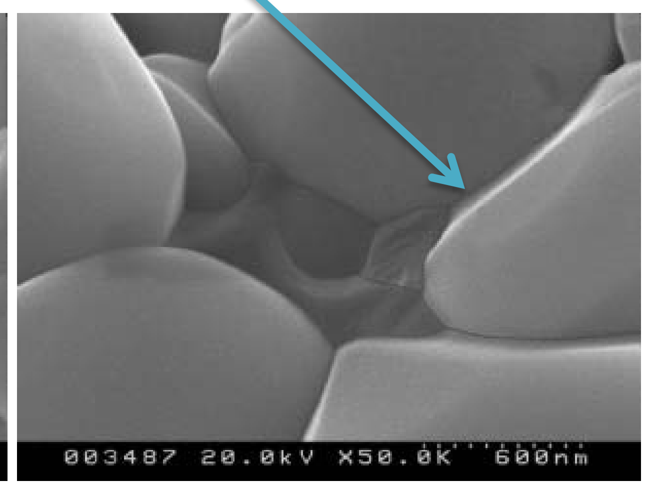
Imaged at x1k and x50k

Needle like pores

Grain boundary phase



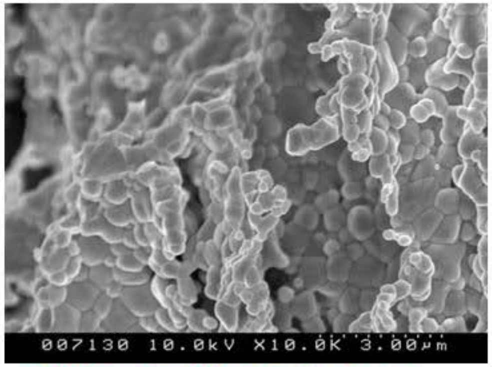




Fracture Surfaces of Hafnia Formulations

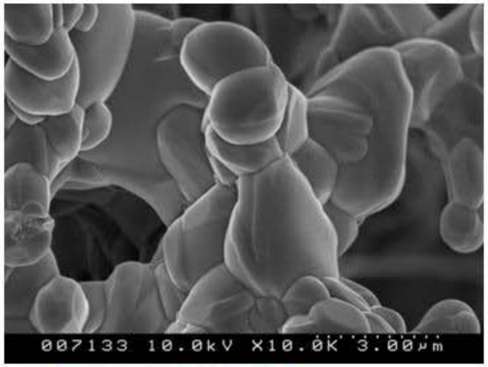
24 h

HfO_2 + C wire



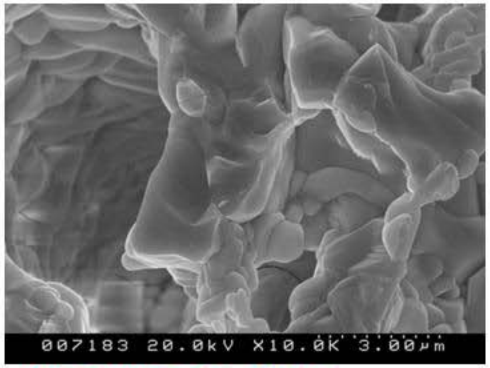
Grain size ~0.25–1.5 µm
App. Porosity ~ 58%
Intrusion Porosity ~49.1%*

HfO_2 + C wire + CaO



Grain size ~1–6 µm
App. Porosity ~59%
Intrusion Porosity ~48.7%*

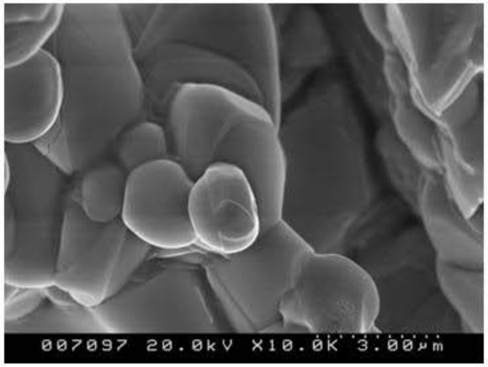
HfO_2 + C wire + Ce_2O_3



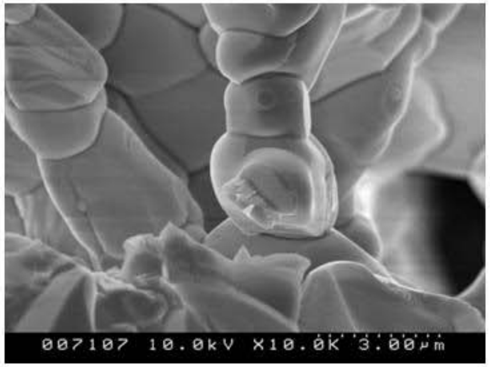
Grain size ~2–9 µm
App. Porosity ~60%
Intrusion Porosity ~NM

7 days

Grain size ~0.3–9 µm
App. Porosity ~58%
Intrusion Porosity ~48.3%



Grain size ~1–12 µm
App. Porosity ~64%
Intrusion Porosity ~51.6%

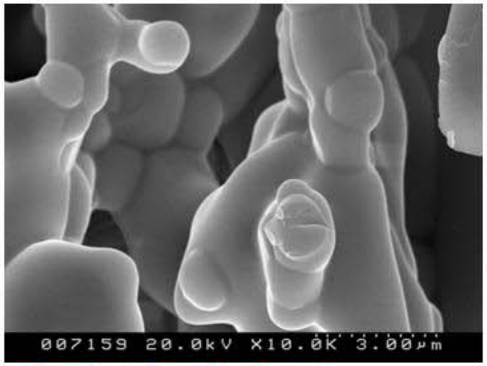


Grain size ~1–9 µm
App. Porosity ~55%
Intrusion Porosity ~47%

Fracture Surfaces of YSZ Formulations

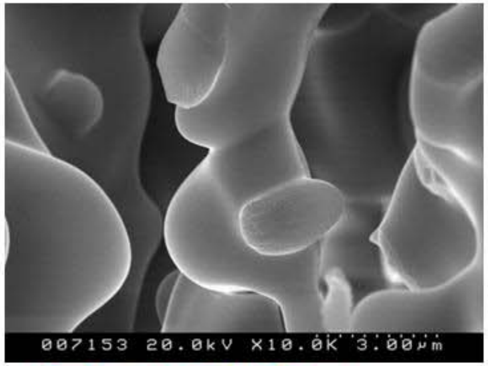
24 h

YSZ+ C wire



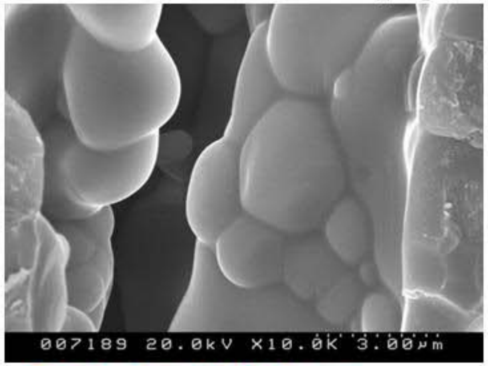
Grain size ~1–6 µm
App. Porosity ~52%
Intrusion Porosity ~NM*

YSZ+ C wire + CaO



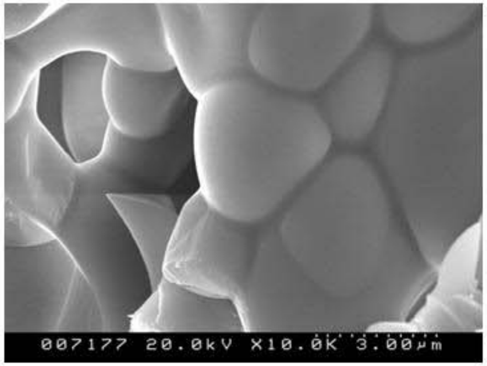
Grain size ~1–12 µm
App. Porosity ~65%
Intrusion Porosity ~NM*

YSZ+ C wire + Ce_2O_3

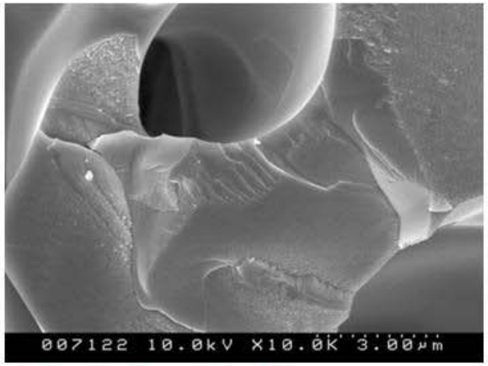


Grain size ~0.6–9 µm
App. Porosity ~51%
Intrusion Porosity ~NM*

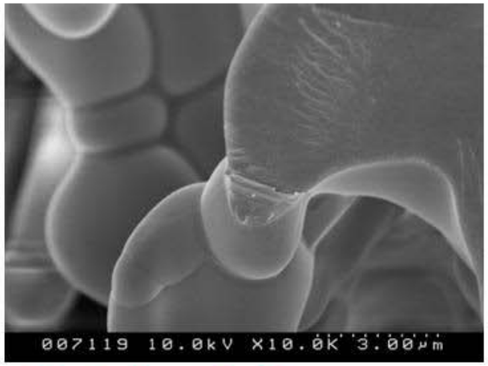
7 days



Grain size ~1–9 µm
App. Porosity ~49%
Intrusion Porosity ~42.2%

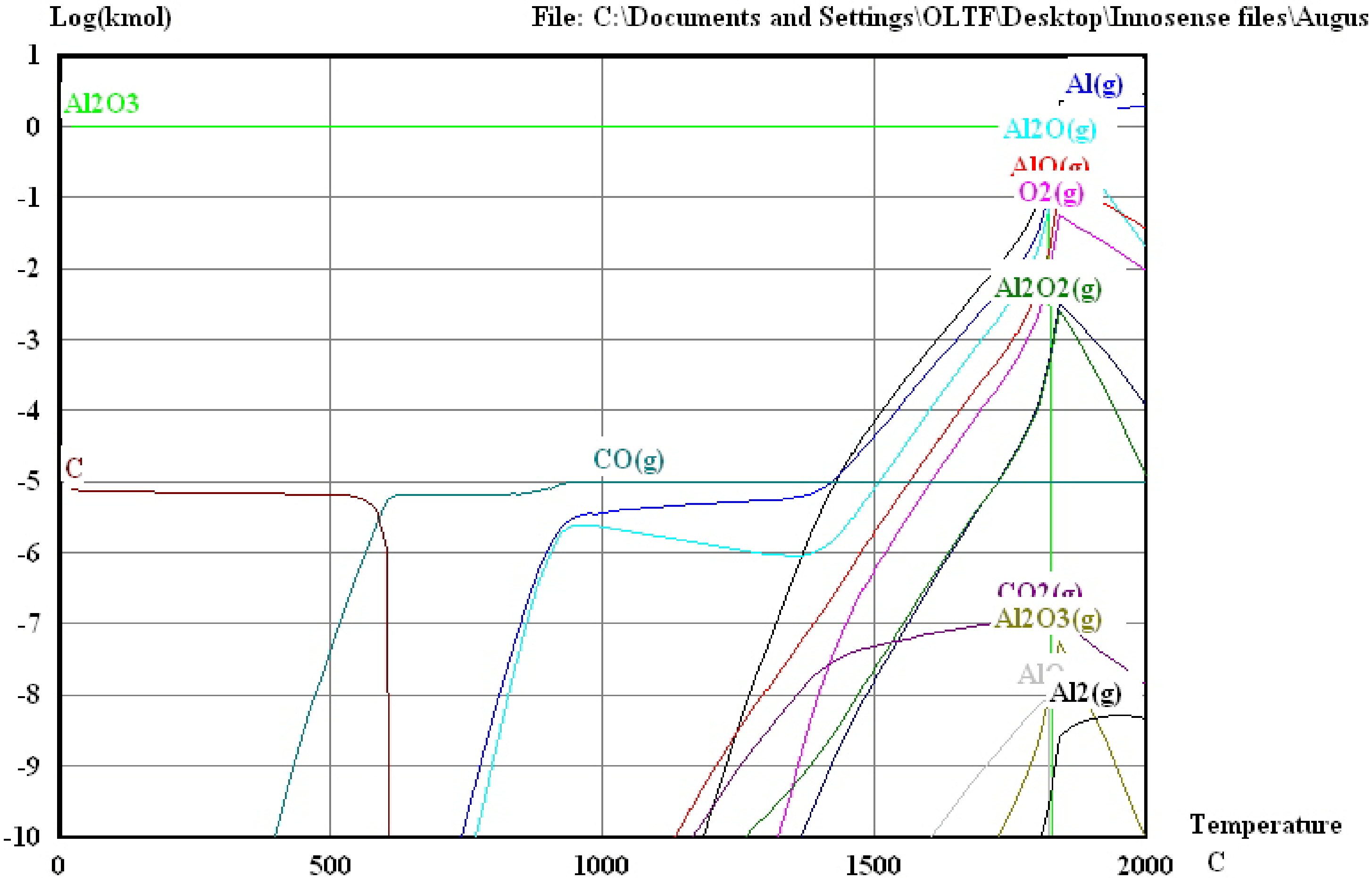


Grain size ~2–17 µm
App. Porosity ~55%
Intrusion Porosity ~47.2%



Grain size ~1–12 µm
App. Porosity ~41%
Intrusion Porosity ~41.9%

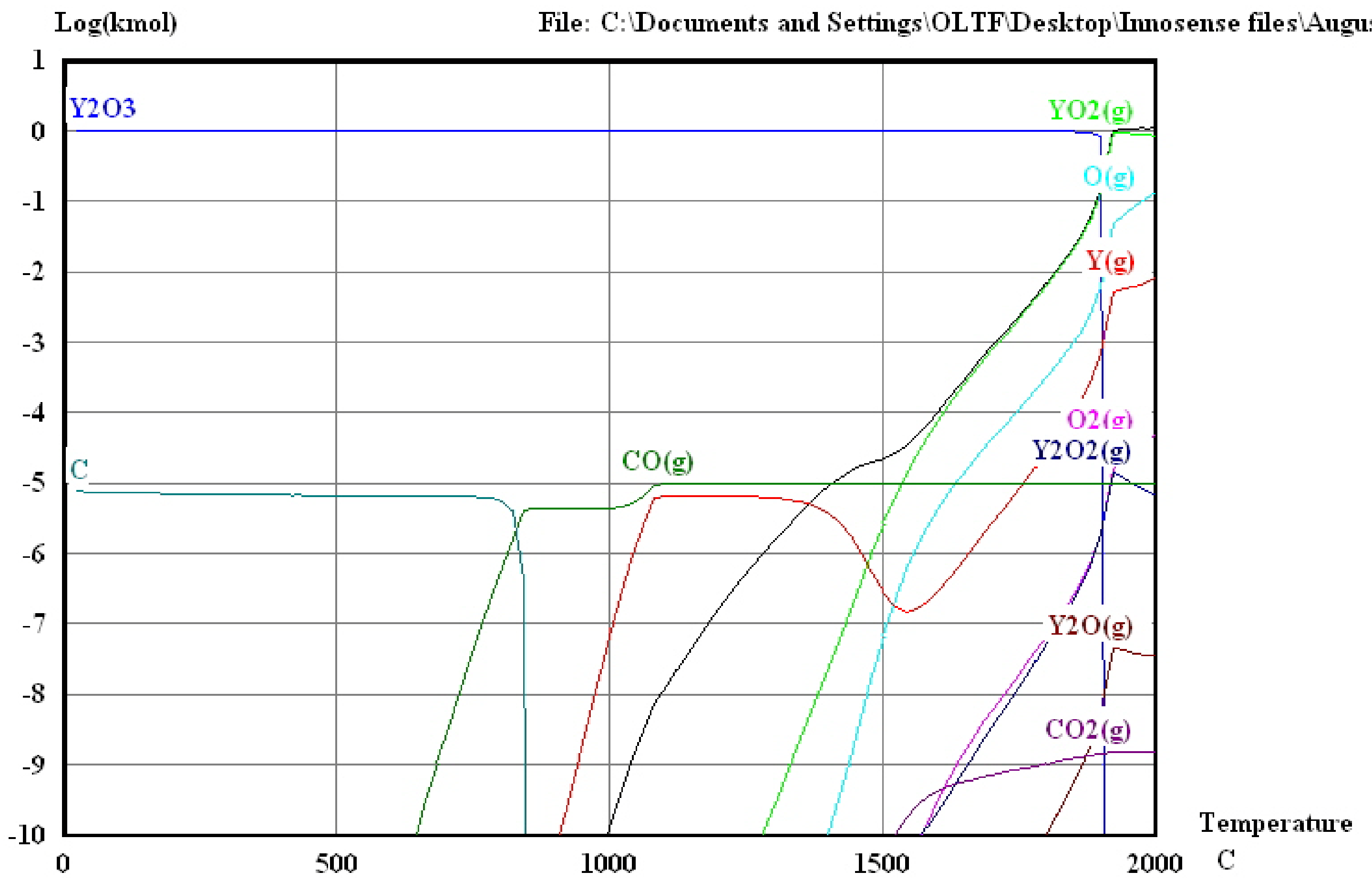
Thermo-Chemical Simulation Using the HSC Program for CO Release from Al_2O_3 + Trace C



Significant conversion of elemental C to volatile CO molecule at 700 °C.

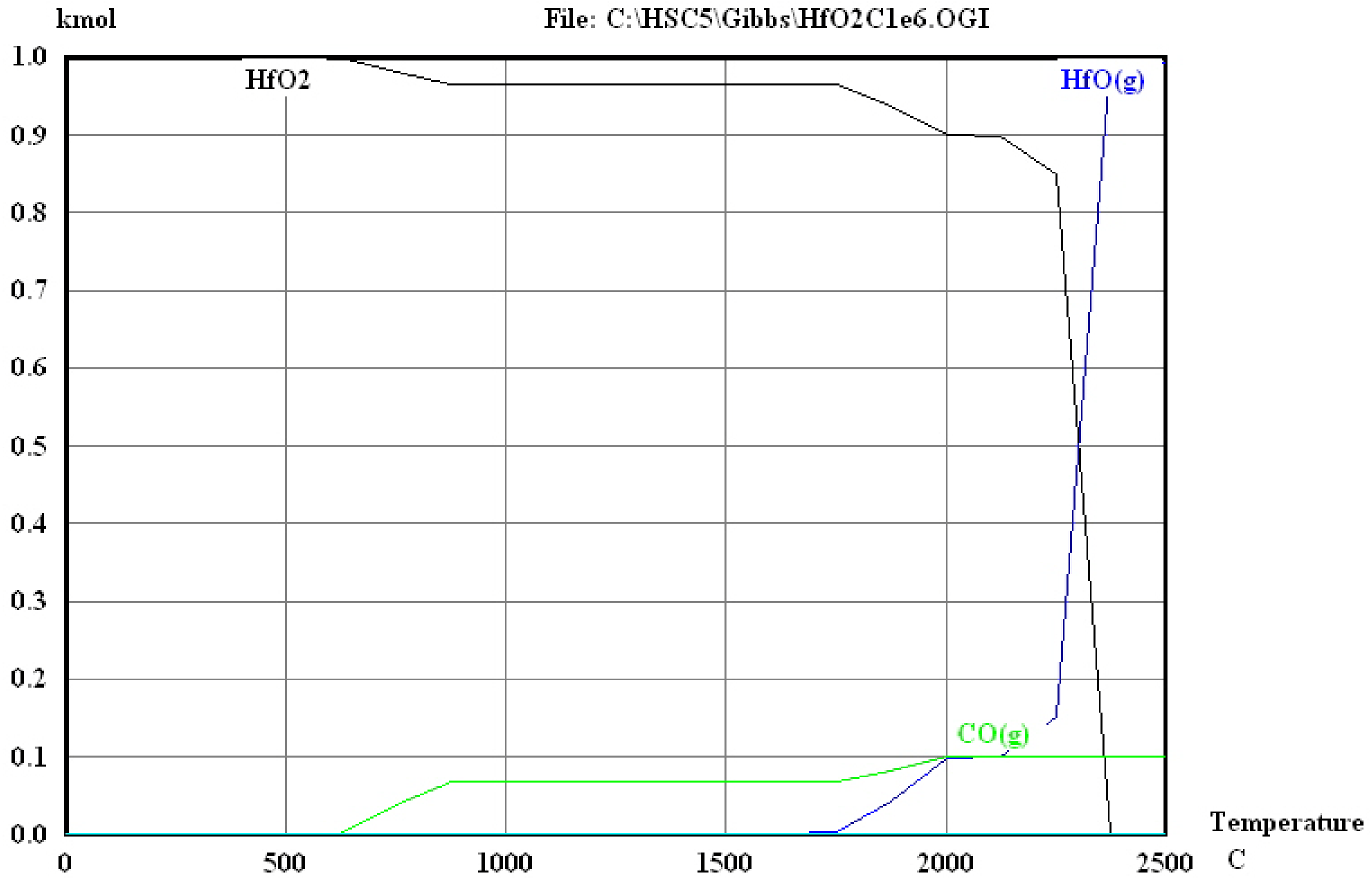
Al_2O_3 breaks down at <800 °C – Not a practical catcher material when higher temperatures are used to enhance diffusion rates from solid catcher.

Simulation of CO Release from Y_2O_3 + Trace C



Y_2O_3 + trace C mixture indicating significant conversion of elemental C to the volatile CO molecule at 800 °C.

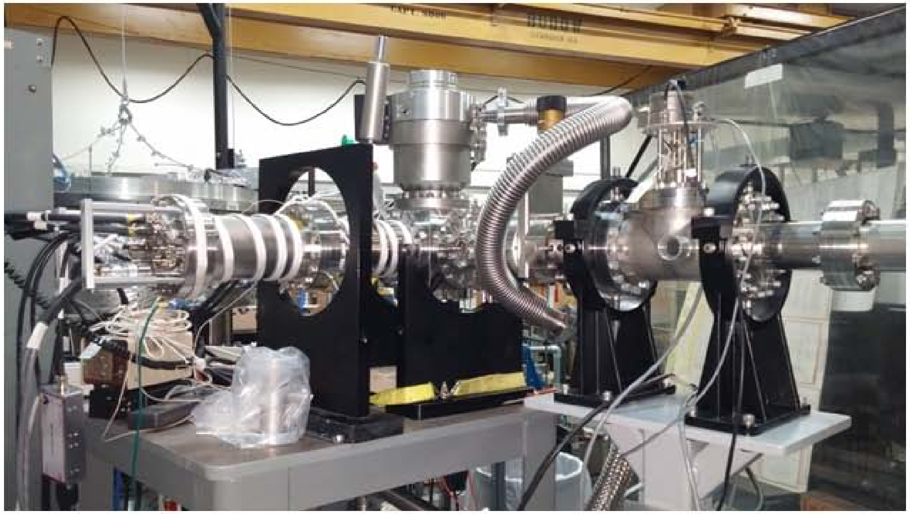
Simulation of CO Release from Hafnia + Trace C



HfO_2+ trace C mixture indicating significant conversion of elemental C to the volatile CO molecule over a wide range from ~750 °C to ~1700 °C.

RGA Installed in the FSU Tandem Accelerator

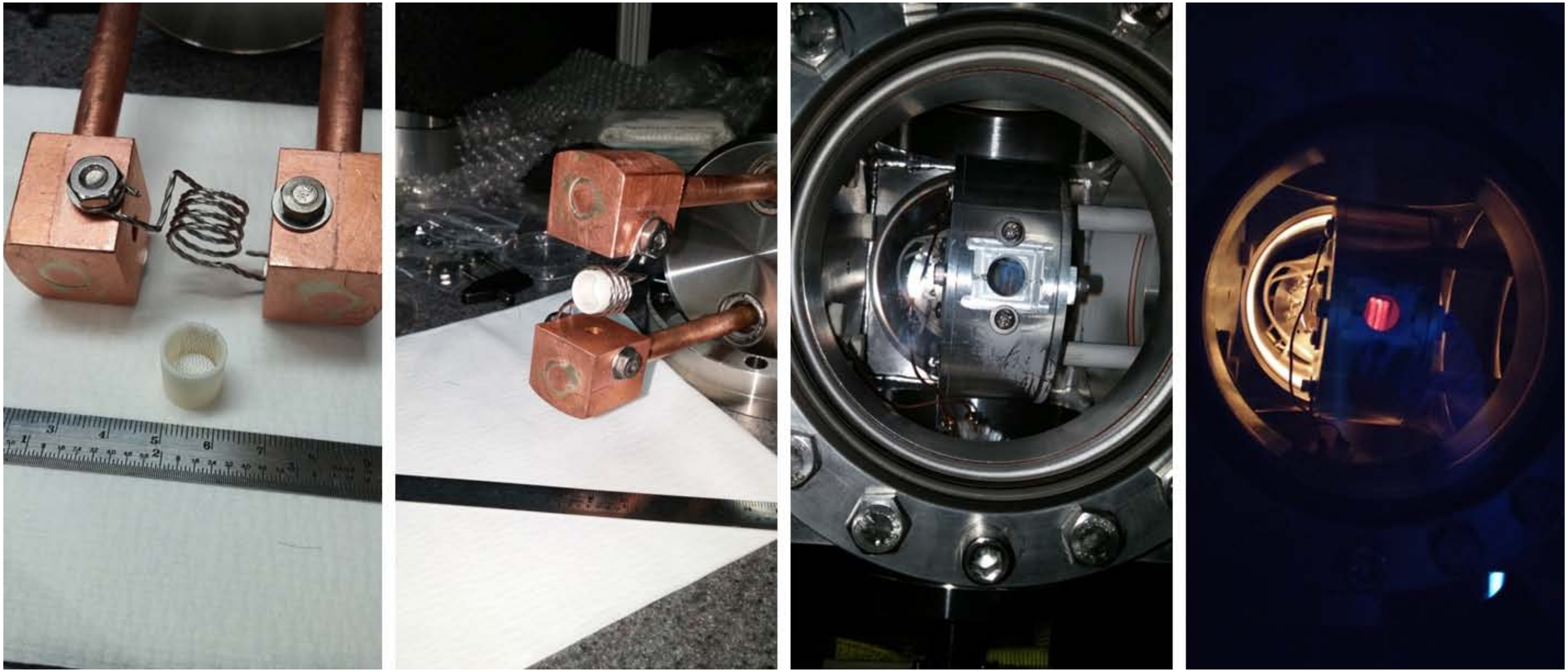
Beam comes from the right, the RGA is on the left, and the sample chamber is in the center below the turbo pump.



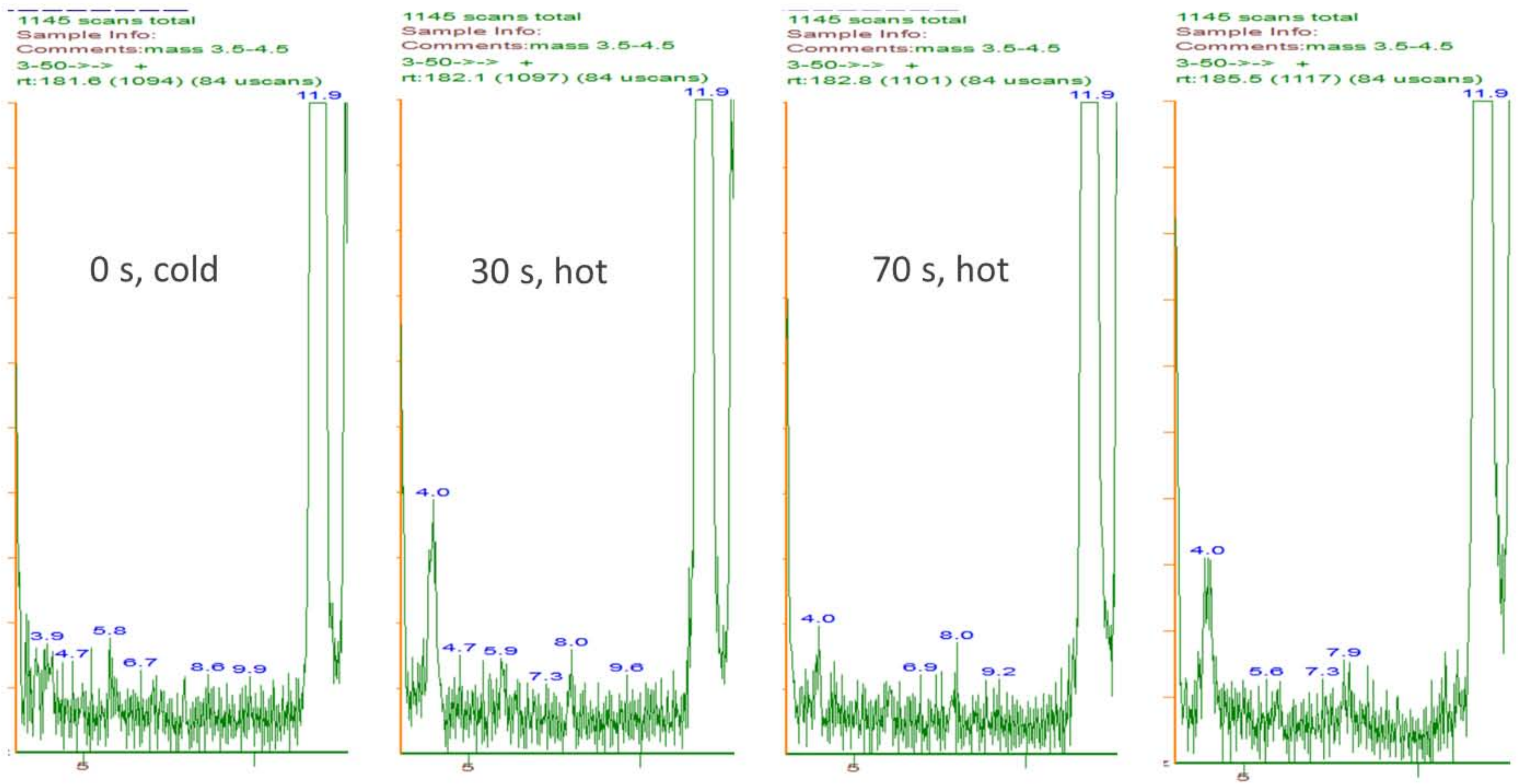
Close-up of the sample chamber with the sample holder visible through the window. Beam enters from the left. A beam diagnostics cross is upstream of the sample chamber.

Sample Holder and Heater in RGA

Left and left-center: Alumina crucible, tungsten heater, and current feed-throughs. ***Right-center:*** View through the chamber window of the sample holder and its heat shield. ***Right:*** View of the sample with the heater on.



RGA Spectra of ^{4}He from Calibrated Leak and from Alumina Stopper Implanted with ^{4}He



Implanted cold | Peak release | After release | Cal. Leak = beam

RGA spectra between masses 3 and 12. ***Left–*** *After ^{4}He implantation with sample at room temperature;* ***Left-center*** *– Same region after heating to ~1000 ℃ in 30 s showing release of He gas;* ***Right-center*** *– Same region 40 s later showing He depletion from sample;* ***Right*** *– Same region with cold and calibrated He leak open to chamber (leak rate is 6E10 atoms/s equivalent to 10 particle nanoamps of beam current.*

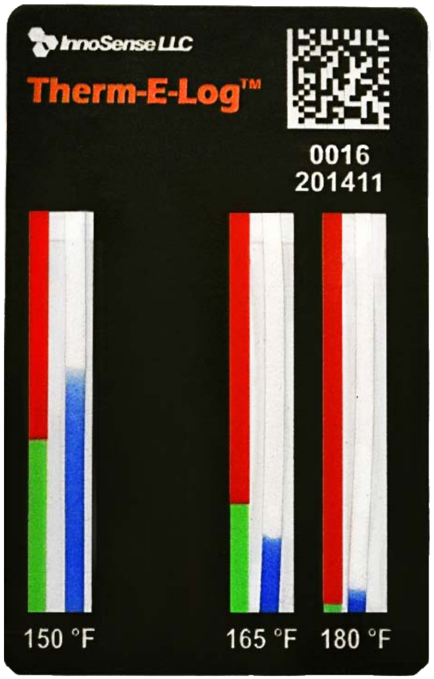
Summary

- YSZ porous solid catchers 1–2 mm thick
  - Density ranging from 2.74–3.04g/cm^3
  - Intrusion or open porosity ranged from 42–47%
- Hafnia porous solid catchers 1–2 mm thick
  - Density ranging from 3.93–4.28 g/cm^3
  - Intrusion or open porosity ranged from 47–51%.
- Grain growth inhibition is demonstrated with porogens, calcium oxide and cerium oxide.
- New RGA method for release characteristics of stable isotopes developed and demonstrated mass 29 (^{13}CO release)
- New heater design completed for in-beam studies
- Beam line tests demonstrated molecular ^{13}CO release from nanoalumina powder with trace C additive and calibrated ^{4}He leak
- First beamline studies of hafnia monoliths demonstrated trace ^{13}CO release. More runs planned at FSU in a dedicated beam line starting in September 2015.

Commercialization Status

Army: W15QKN-09-C-0153

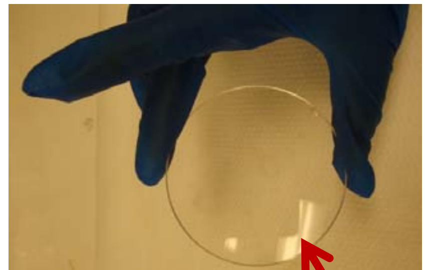
Passive Temperature Dosimeter



- **Phase IIE Funding**
- **Correlation Testing at Yuma Proving grounds Sep 2015.**
- **Anticipate production of ~ 44,000 units in March 2016 for one type of ammunition**

Army: W911NF-11-C-0056

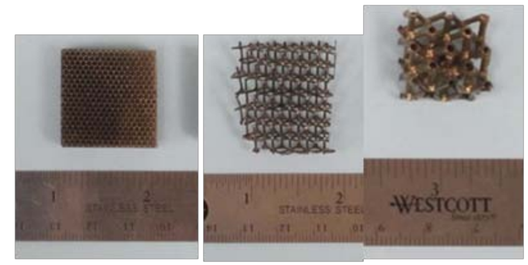
Permanent anti-fog coating

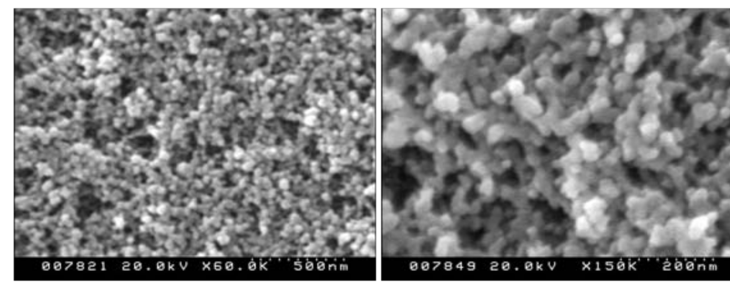


PC lens and PU visor

- **DOD RIF award from DTRA - 2015**
- **Partnered with eyewear safety products manufacturer for scale up and marketing**
- **Automotive headlamps – Evaluations**

PO for silica aerogel coatings on metal lattices - Invoiced 7/4/15





Prior DOE ONP funding enabled us to develop the technology for monoliths and build capabilities

Acknowledgments

DOE and the Office of Nuclear Physics to support these efforts through the following grants DE-SC0007572 and DE-SC0011346

Program Officer – Dr. Manouchehr Farkhondeh

Dr. Georg Bollen for technical discussions and sustained interest to evaluate the catcher materials at FRIB

Dr. Dan Stracener for the ThermoCalc simulations of release studies

Dr. Elizabeth Bartosz - suggestion to approach FSU for beam time.

Dr. Ingo Weidenhover at FSU for beam-line studies at the FN Tandem accelerator