Low-Cost Integrated Composite Seal for SOFC: Materials and Design Methodologies

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Outline

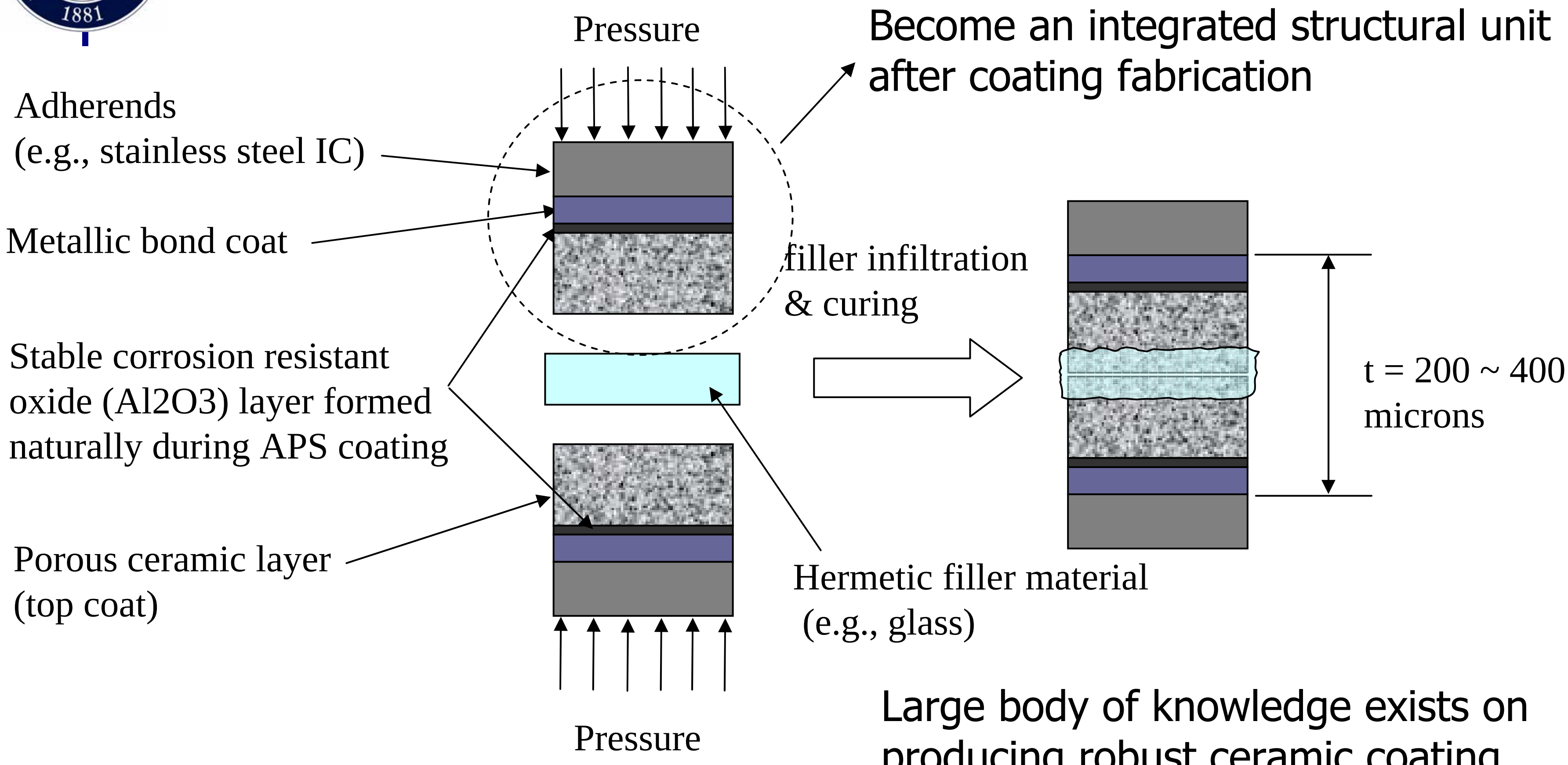
- Concept: integrated multi-layered composite seal
- Coating development: materials selection, fabrication, and screening tests
- Leak testing: methods and initial results
- Summary & future work
- Q & C

General requirements for SOFC seal

Functional Requirements and Materials Selection Parameters [J. Stevenson]	
Mechanical	• Hermetic (or near hermetic) • Minimal CTE mismatch (or ability to yield or deform to mitigate CTE mismatch stresses) • Acceptable bonding strength (or deformation under compressive loading) • Thermal cycle stability • Vibration and shock resistance (for mobile applications)
Chemical	• Long-term chemical stability under simultaneous oxidizing/wet fuel environments • Long-term chemical compatibility with respect to adjacent sealing surface materials • Resistance to hydrogen embrittlement/corrosion
Electrical	• Non-conductive
Fabrication	• Low cost • High reliability with respect to forming a hermetic seal • Sealing conditions compatible with other stack components

Reference: Jeff Stevenson et al, SECA meeting presentation, PNNL

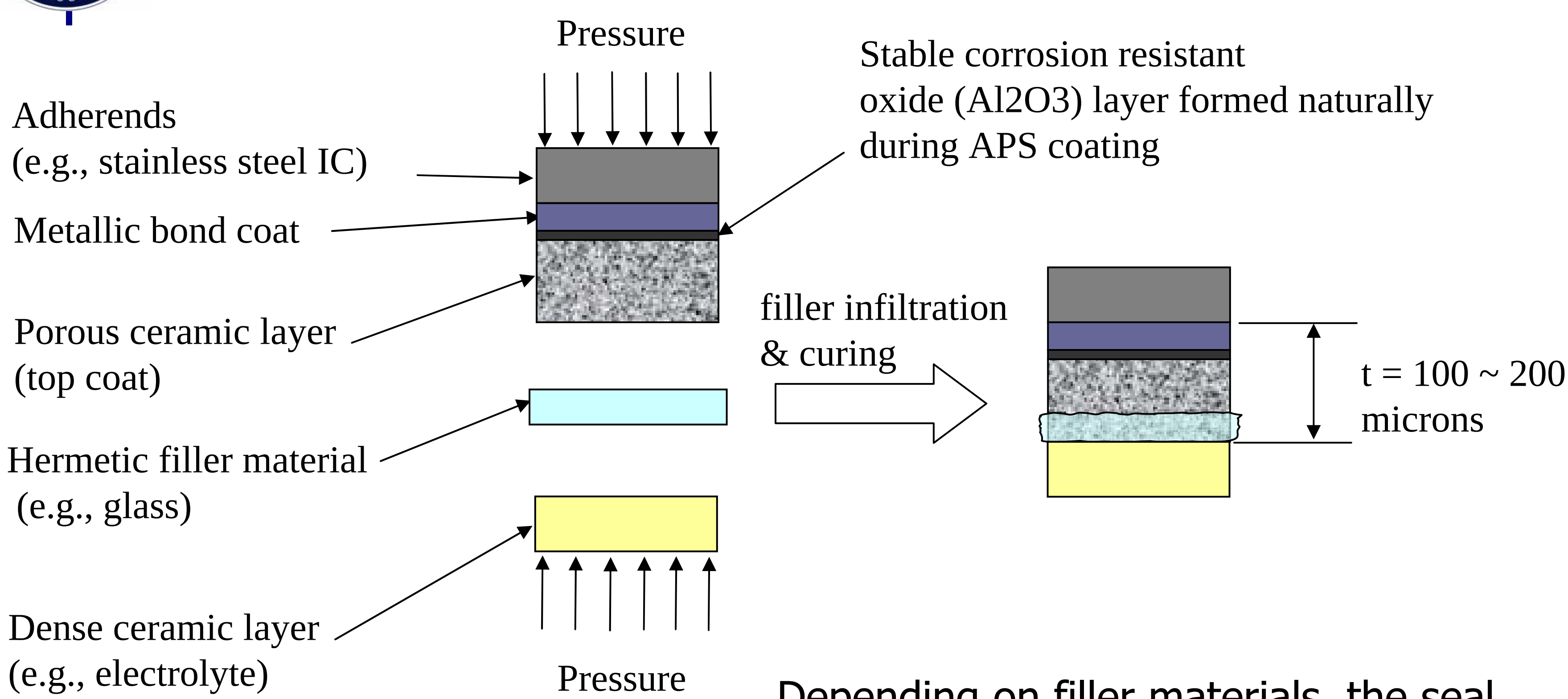
Integrated composite seal concept: IC to IC seal



Become an integrated structural unit after coating fabrication

Large body of knowledge exists on producing robust ceramic coating, particularly thermal barrier coatings (TBC) on metallic substrates

Integrated composite seal concept: IC to ceramic seal



Depending on filler materials, the seal structure can be made either rigid (hard, solid) or compliant (soft, wet)

Potential advantages

- Ceramic coating is expected to have
  - Good compatibility with filler materials (good wetting, long-term chemical stability)
  - Good stability in oxidation and reducing environments
  - Low electric conductivity, high dielectric strength
  - A porous structure that help retaining low-viscosity filler materials
- Relax requirements on filler materials
  - Wetting stainless steel
  - Short-term and long-term chemically stability in contact with stainless steel
  - Low electric conductivity, high dielectric strength
- Multi-layered structure allows gradual transition of thermo-mechanical properties (functional gradients) from substrate → bond coat → top coat → hermetic filler
  - higher resistance to mechanical failure
- Low cost fabrication method available
- Integrated design reduces stack assembly cost

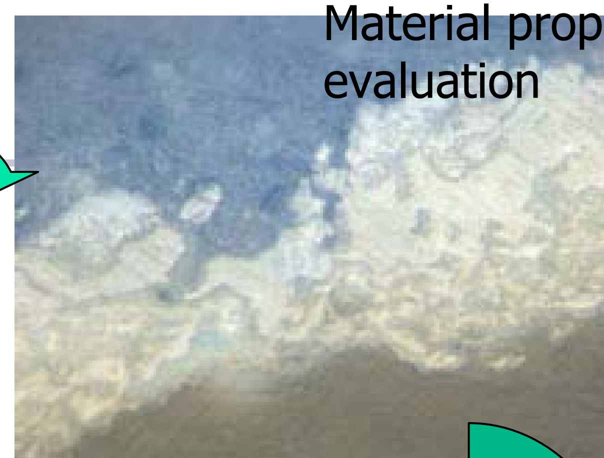
Goal and phase I objectives

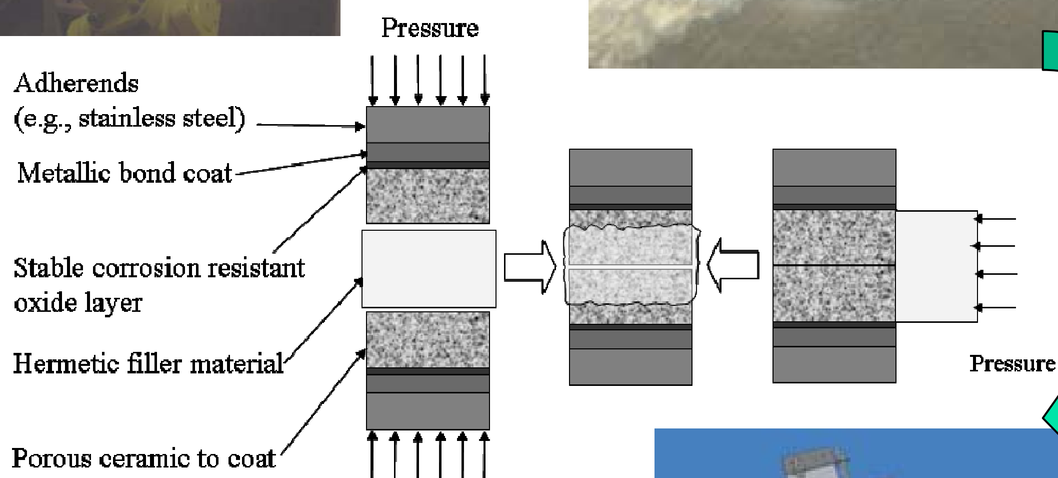
- The goal for this two-phase effort is to create a unique high-temperature composite solid oxide fuel cell (SOFC) seal and the associated design methodologies to support the SECA Industrial Teams in their efforts to design, manufacture, and market reliable SOFC power generation systems.
- The objectives of the Phase I work are <u>to prove a conceived composite structure and to demonstrate a design methodology using subscale samples</u>

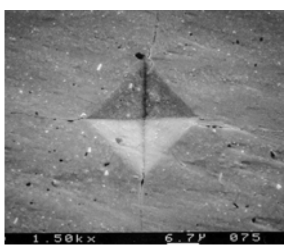
Our approach

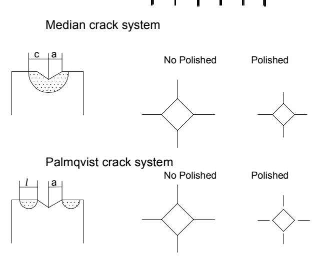
Fabrication

Microstructure &
Material properties
evaluation

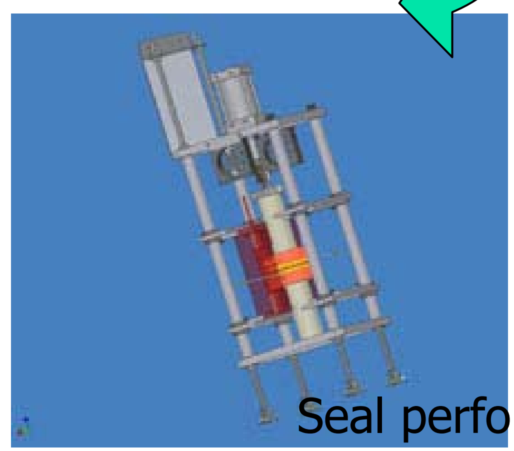








Mechanical robustness



Seal performance

Outline

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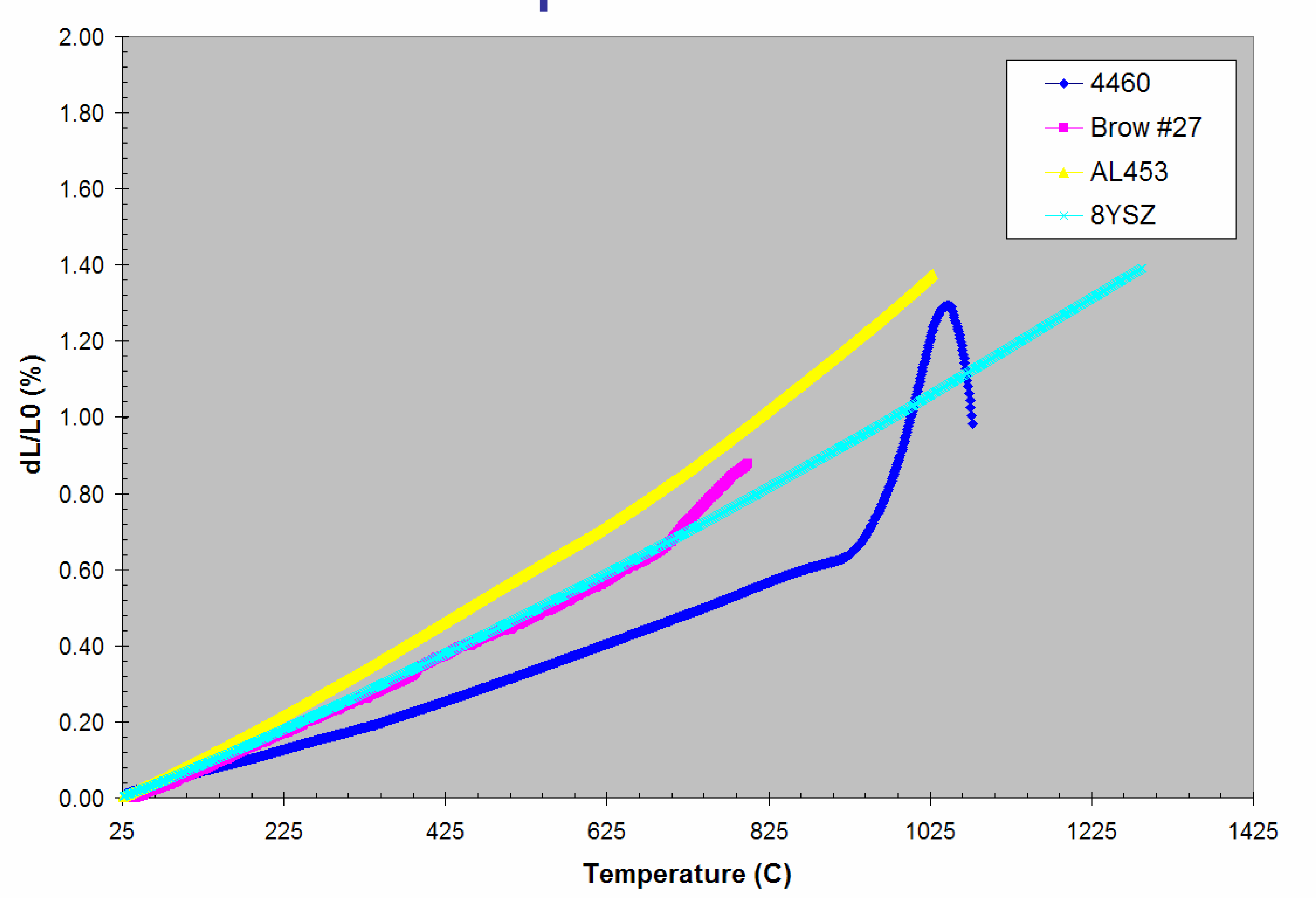
Materials selection

- Stainless steel interconnect and YSZ disks
  - Allegheny Ludlum AL453, Crofer22 APU
  - CoorsTek
- Ceramic coating materials
  - Bond coat (MCrAlY, Ni5Al)
  - Top coat (alpha-Al_2O_3 + partially stabilized ZrO_2)
- Filler glass composition and properties
  - Alkaline earth aluminosilicates
  - Glass property requirements: matching CTE, low softening point, chemically stable, low crystallization rate
  - Coordinates with other CTP efforts on glass formulation: U. Missouri Rolla, U. Cincinnati, and Sandia National Lab.

Thermal expansion curves



Sample size and geometry

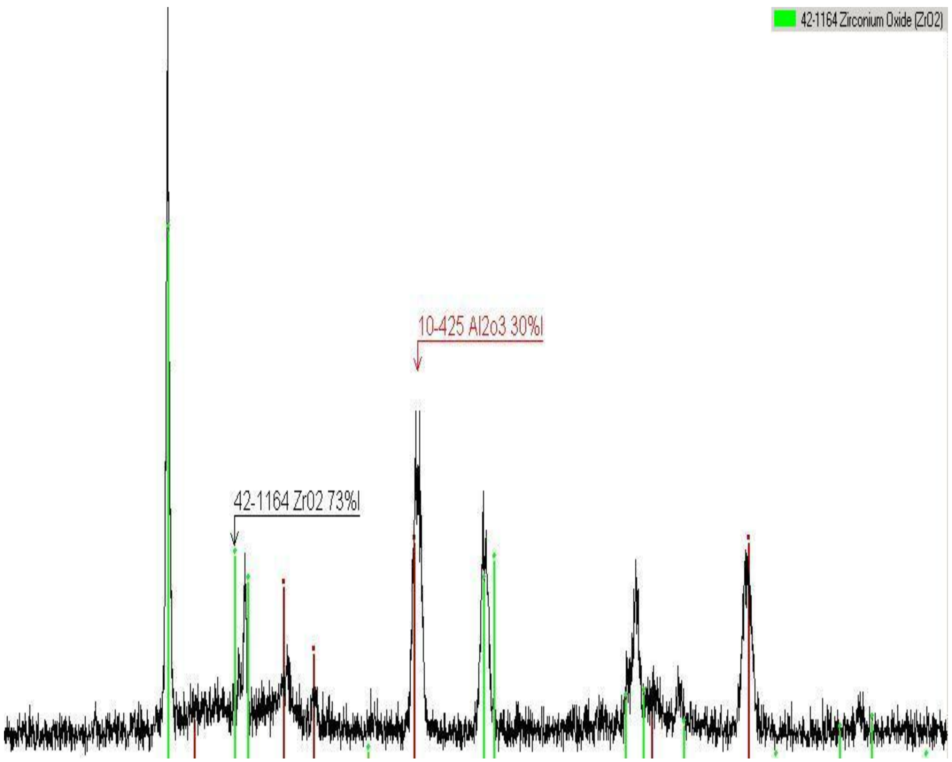
- Use 1"~2" button samples for Phase I work
  - Coated button samples for obtaining basic material properties studies, such as wetability, bond strength, oxidation resistance, etc.
  - Thermal cycling, thermal shock, mid-term aging test
  - Electrical conductivity studies
  - Glass infiltration studies
  - Leak testing
- Avoid complex geometry
  - Circular disks to avoid complexity due to sharp corners

Ceramic coating produced via atmospheric plasma spray (APS)

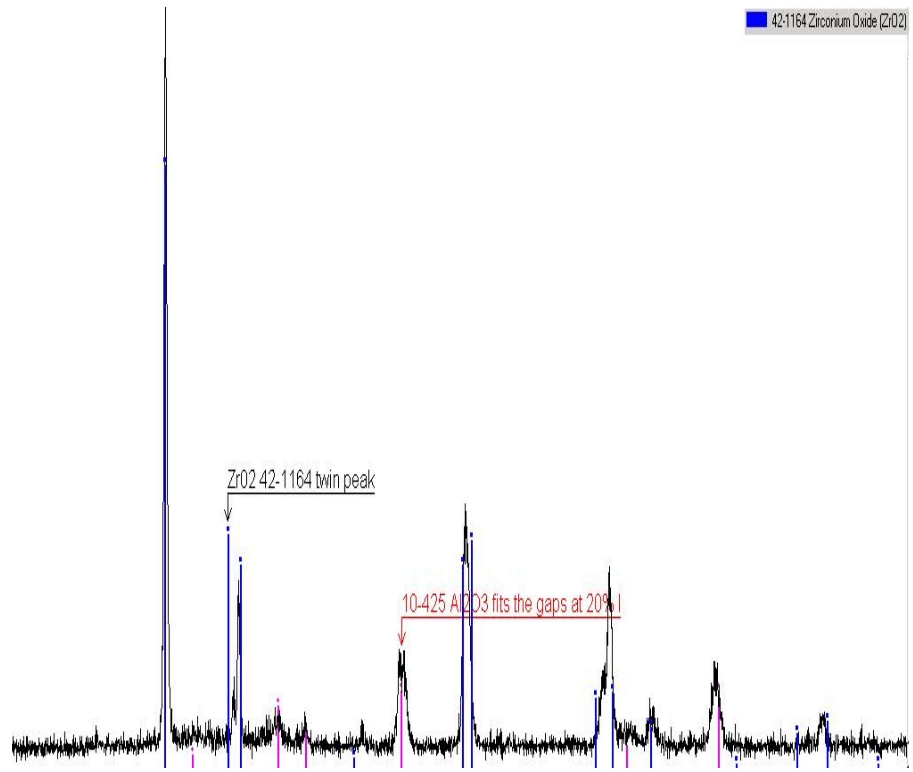
- Relatively low cost (compared to LPPS, VPS, EB-PVD)
- High throughput
- One step fabrication (no additional sintering step required)
- Coating has excellent thermal mechanical robustness
- Amenable to produce functional gradient coating structure

(Picture courtesy of Dr. China Ma, Inframat Corp.)

XRD of APS top coat

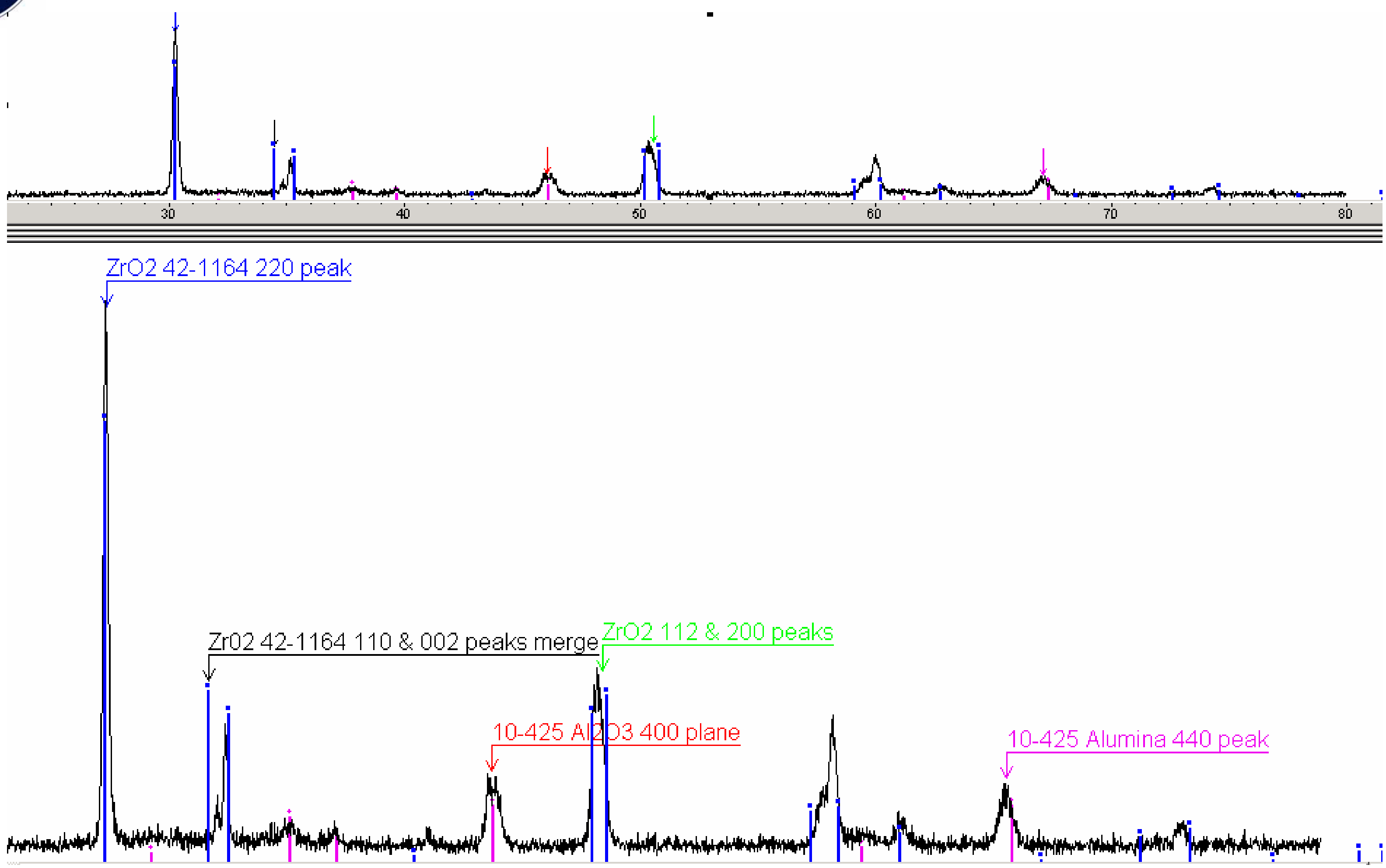


SECA coating type 3
(higher Al2O3 contents)



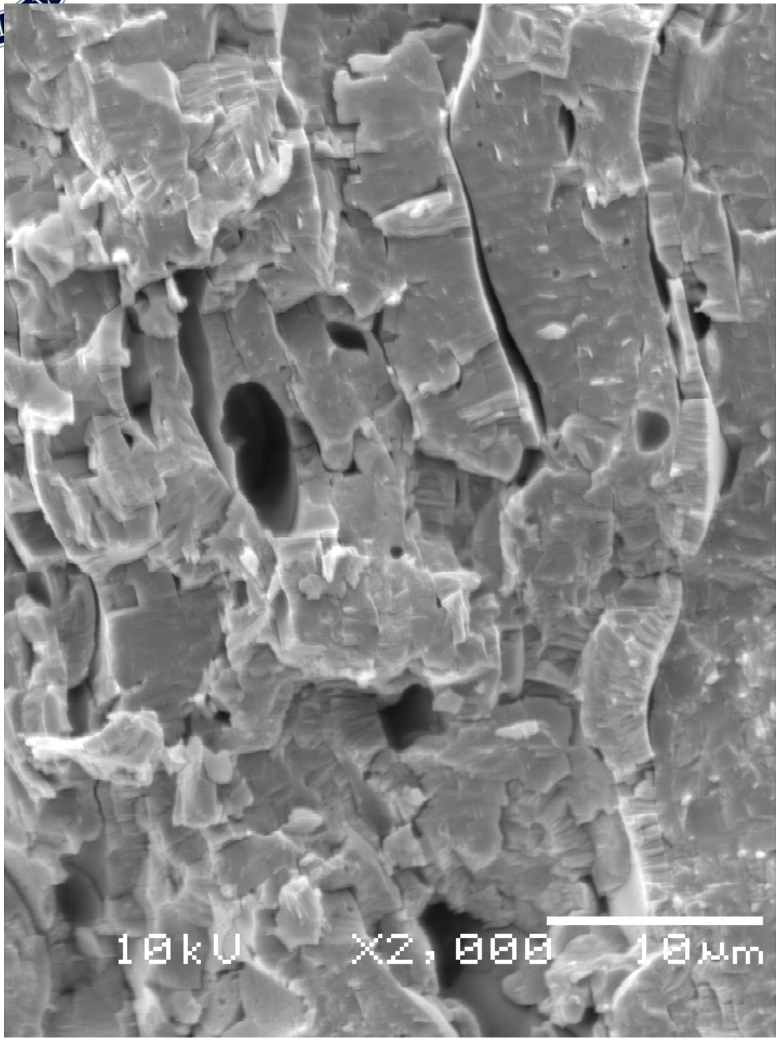
SECA coating type 4

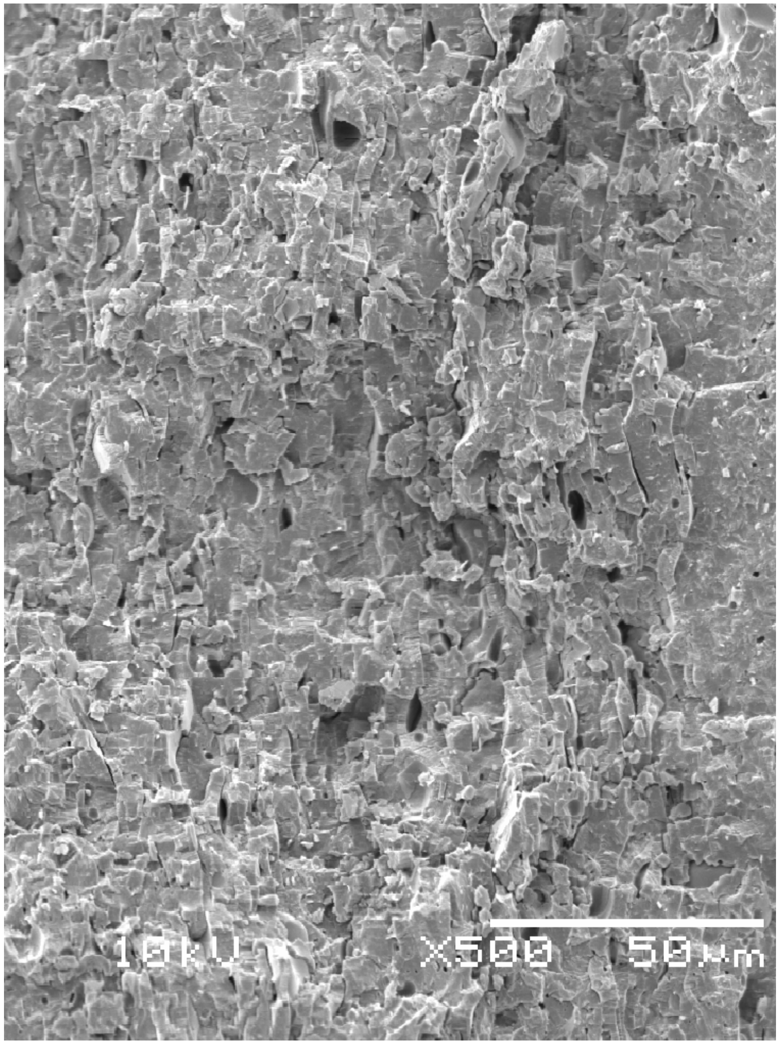
XRD peak identification



Microstructure of APS top coat

Particle flying direction





Mercury intrusion porosimetry (Quantachrome Poremaster 6000)

- Measures distribution of pore volume over a range of pore sizes (0.003-200 microns)
- Based on Washburn equation

  $D = 4 \gamma \cos\theta / P$ where

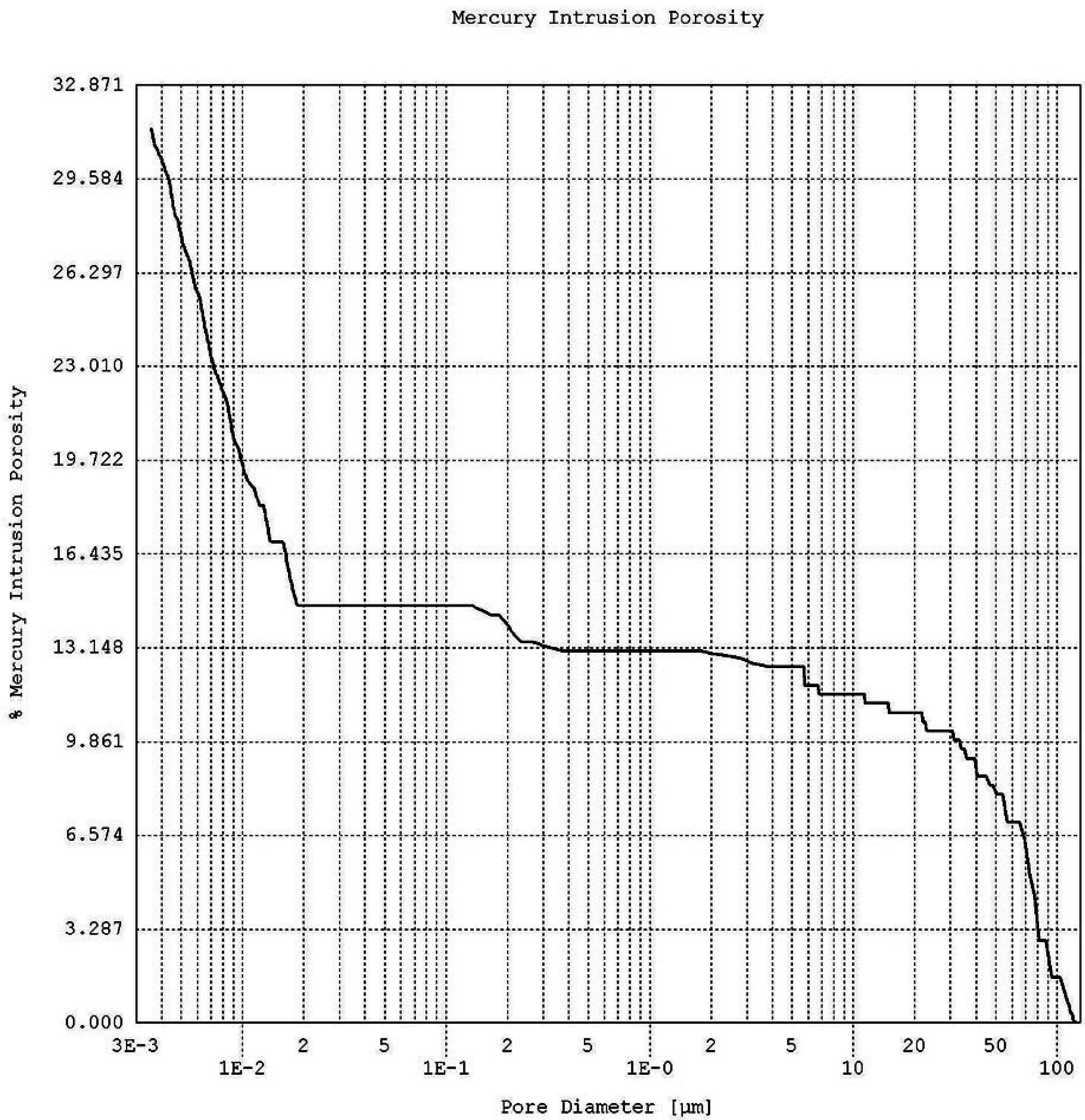
  D = pore diameter

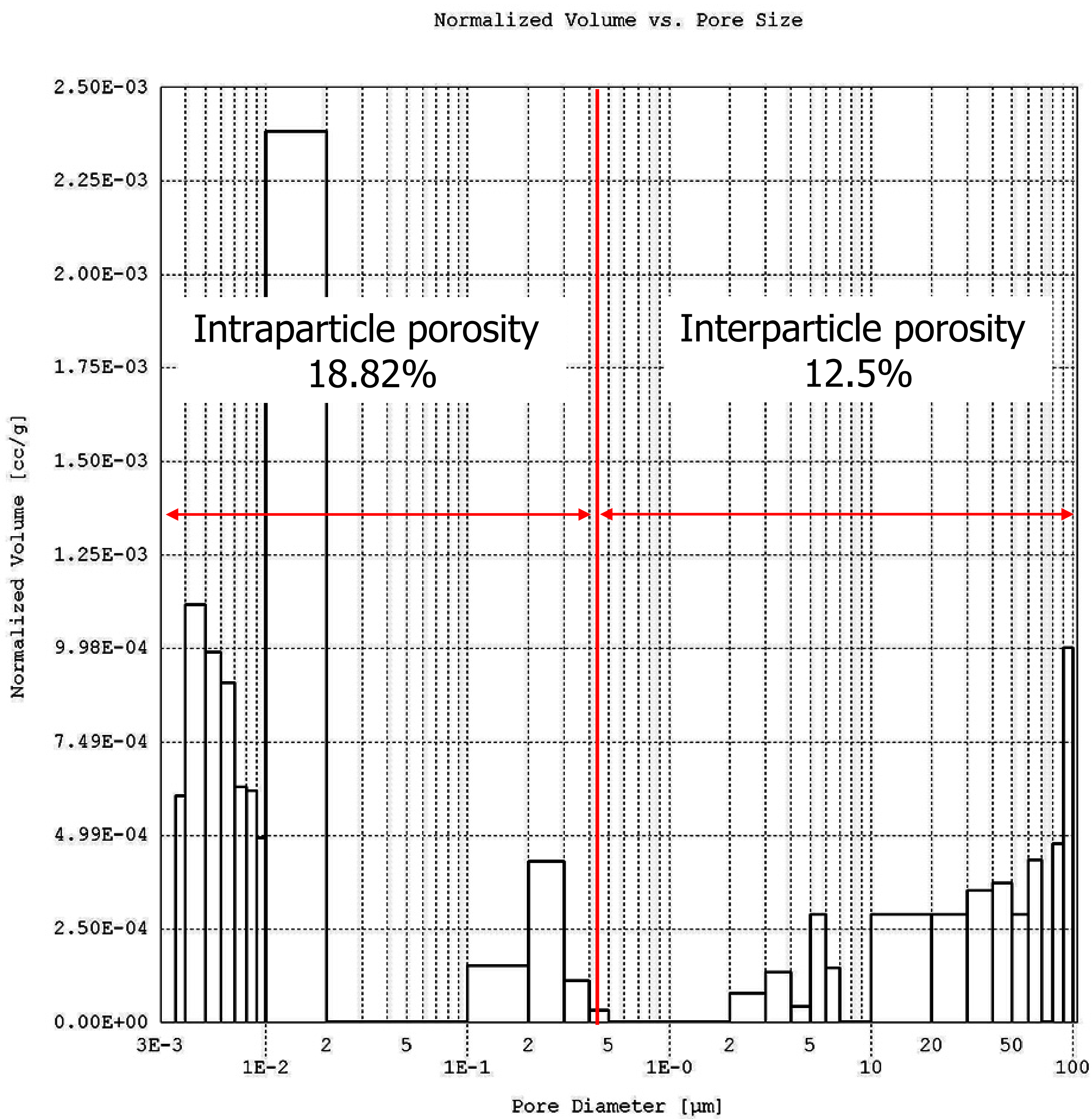
  γ = surface tension of wetting fluid

  Θ = contact angle

  P = applied pressure
- Sample is exposed to mercury at increasing pressure up to 60,000 psi
- Volume of mercury that goes into pores in sample measured

Dense substrate attached

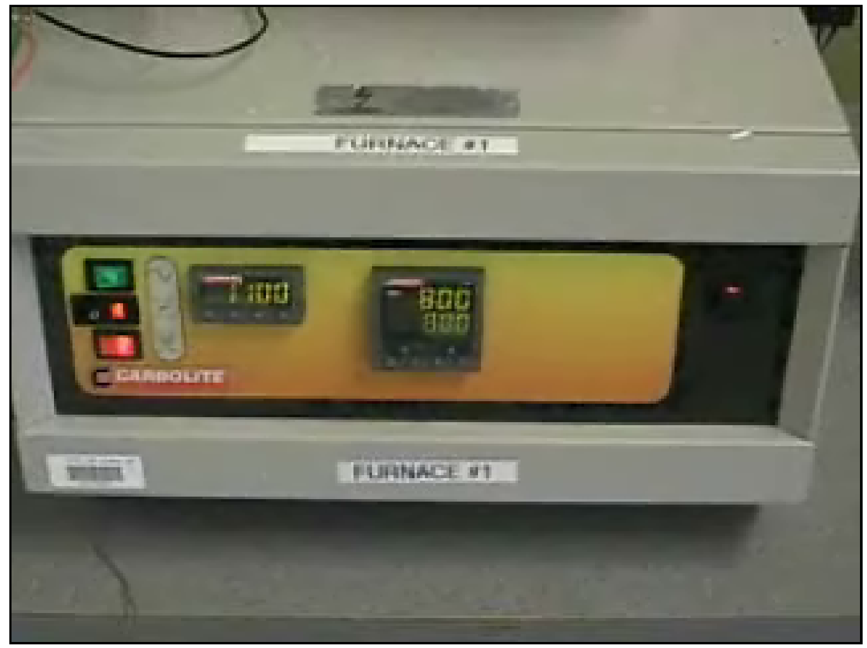




Normalized Volume vs. Pore Size
Normalized Volume [cc/g]
2.50E-03
2.25E-03
2.00E-03
1.75E-03
1.50E-03
1.25E-03
9.98E-04
7.49E-04
4.99E-04
2.50E-04
0.00E+00
3E-3
1E-2
2
5
1E-1
2
5
1E-0
2
5
10
20
50
100
Pore Diameter [µm]
Intraparticle porosity 18.82%
Interparticle porosity 12.5%

Material screening test

- Basic thermal cycle resistance & high temp aging test to evaluate thermo-mechanical robustness of coating
- Electric resistance of coating/Pt/coating structure using DC or AC method
- Wetting behavior of selected glass and ceramic compositions

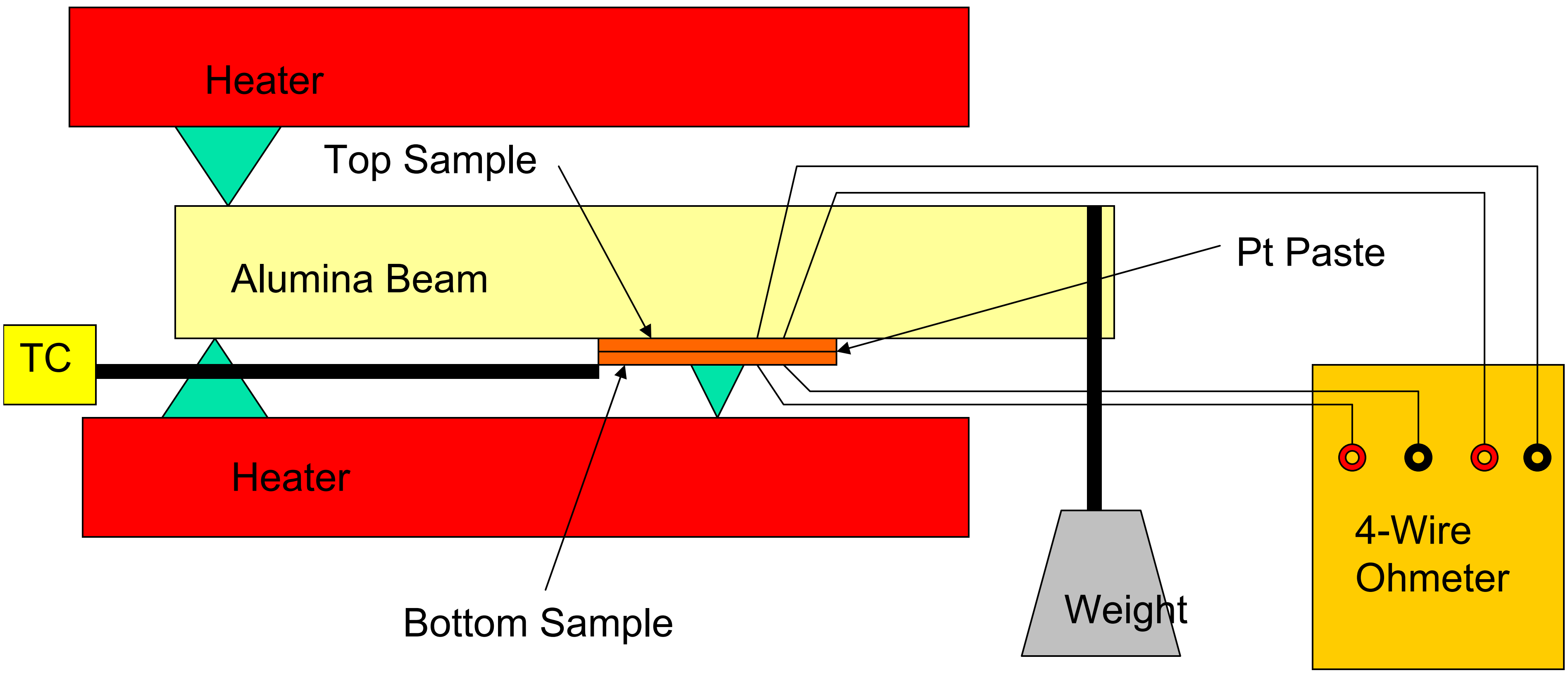


Water quench test from 800 °C

High temperature electric conductivity: ceramic coating

800 C in air, ASR=9.25~320.7 kΩ·cm[2]
920 C in air, ASR=2.61~189.1 kΩ·cm[2]

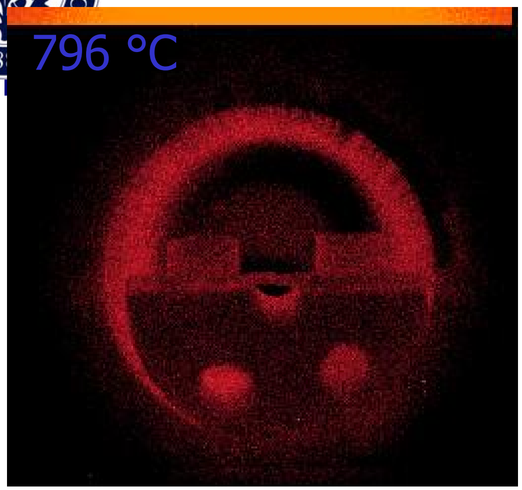
← increasing YSZ contents

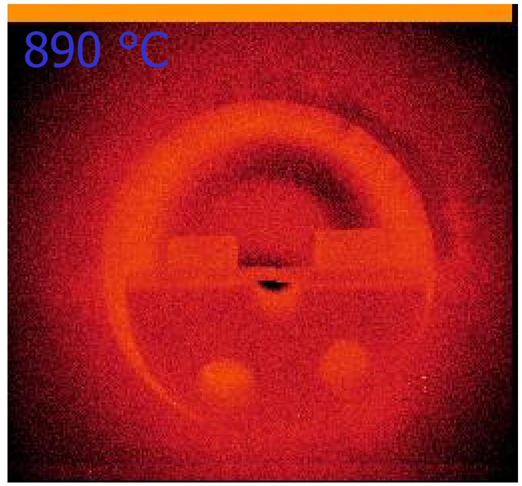


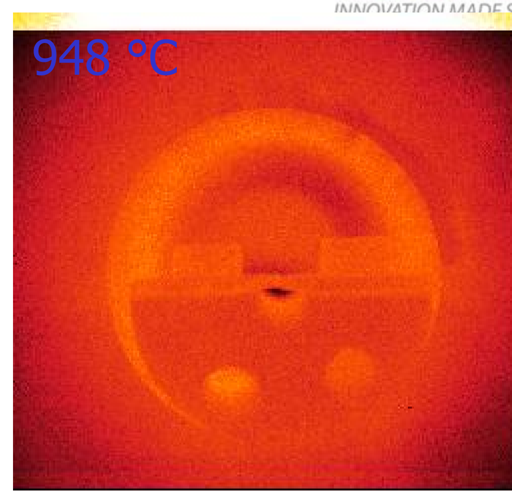
Glass infiltration and curing

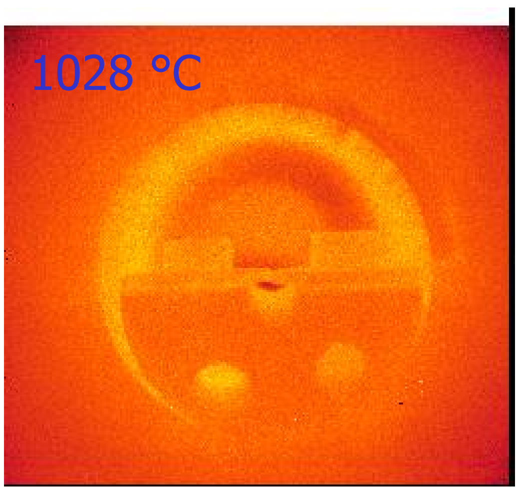
- Natural wicking or vacuum/pressure assisted infiltration
  - Porosity before and after glass infiltration
  - Interface morphology
- Curing schedule
  - Maximum temperature limited by furnace and substrate materials
  - Adjust heating/cooling rate and high temperature dwell to suite particular glass: maximize viscosity and avoid excessive crystallization
  - Apply pressure

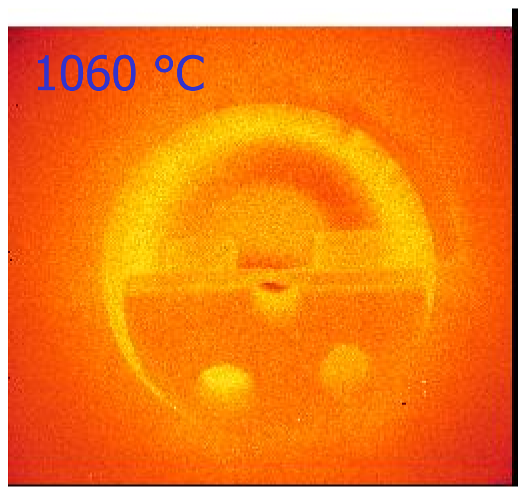
Glass pellets on coated button sample

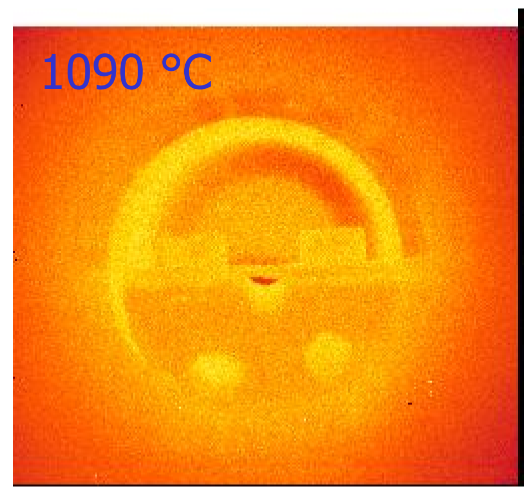




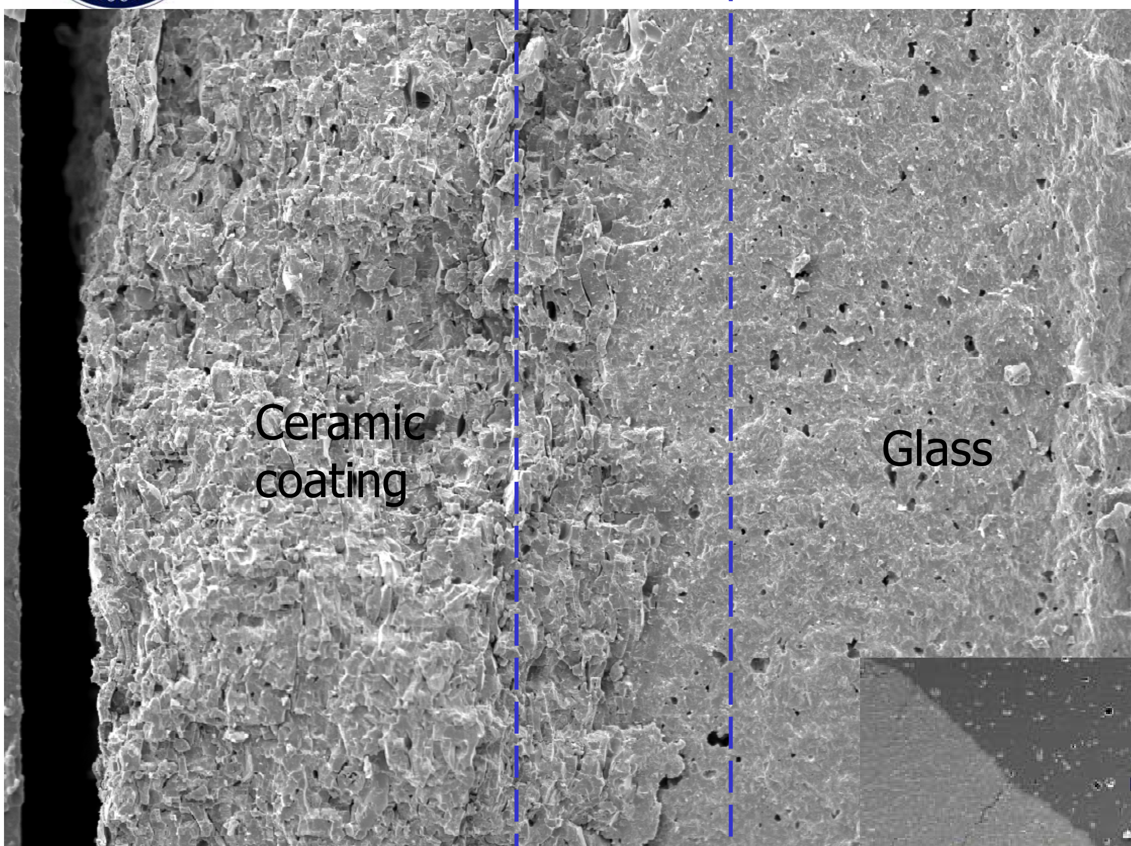




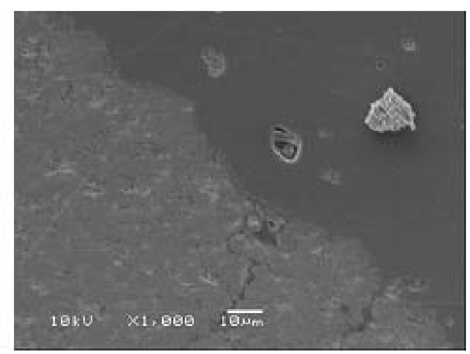




Glass ceramic interface



Pictures of glass/ceramic interface shows good wetting



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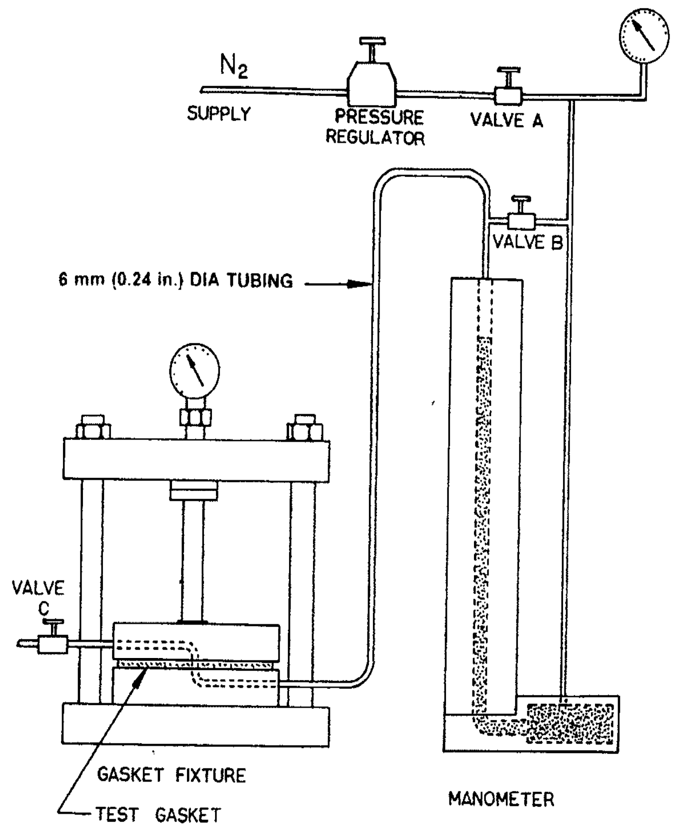
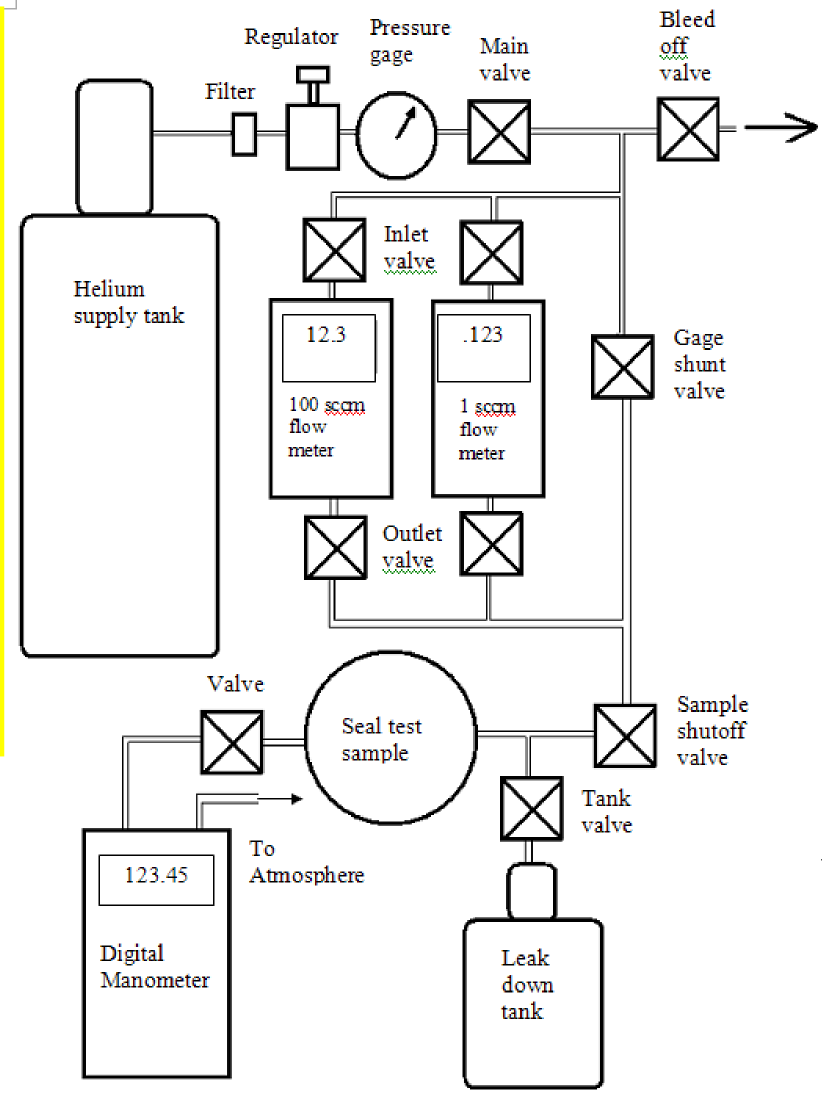
Sealing performance: leak rate testing

- Objective: measure gas leak rate (sccm) per bond line length (cm) per unit pressure difference (psig)
- Facilitate the study of aging and thermal cycle effect on seal performance:
  - Leak rates v.s. # of thermal cycles
  - Leak rates v.s. hrs of aging time
- Reference: ASTM F 37-00 with controlled temperature and gas environment



Leak rate testing method

- Direct leak flow rate measurement
  - Measure flow rate of gas supply into sealed chamber
  - Allow continuous monitoring of leak rate
- Pressure leak-down test
  - Sealed chamber initially pressurized, pressure decay recorded
  - Effective in ultra-low leak rate regime
- Helium leak detector (mass-spec)
- Electrochemical method
  - monitoring OCV



UConn SOFC seal leak test stand

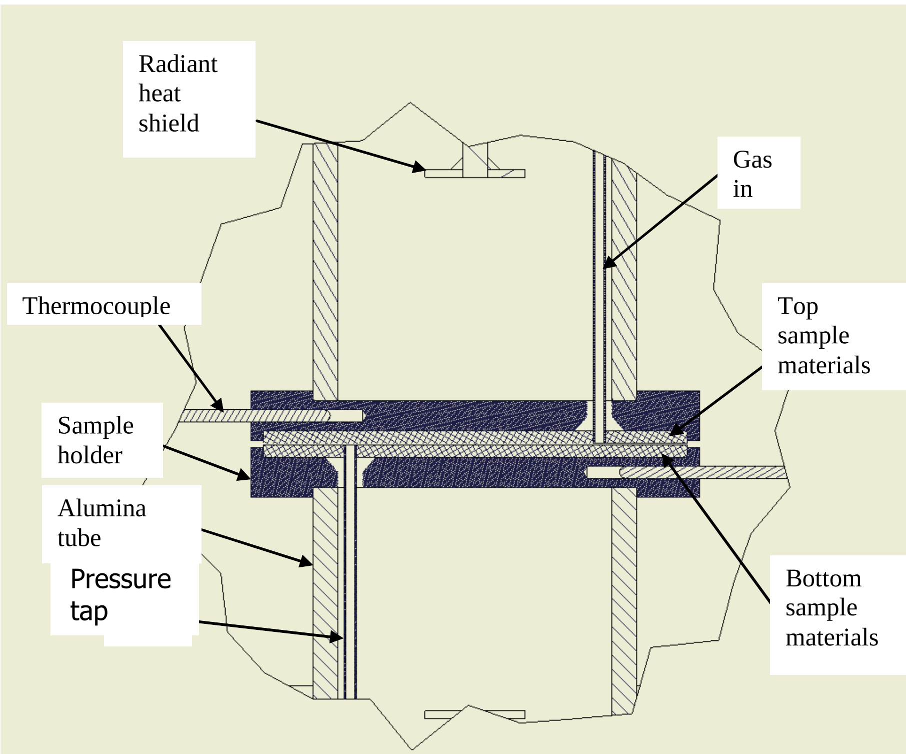


Figure 3 – Seal Area Cross-Sectional View

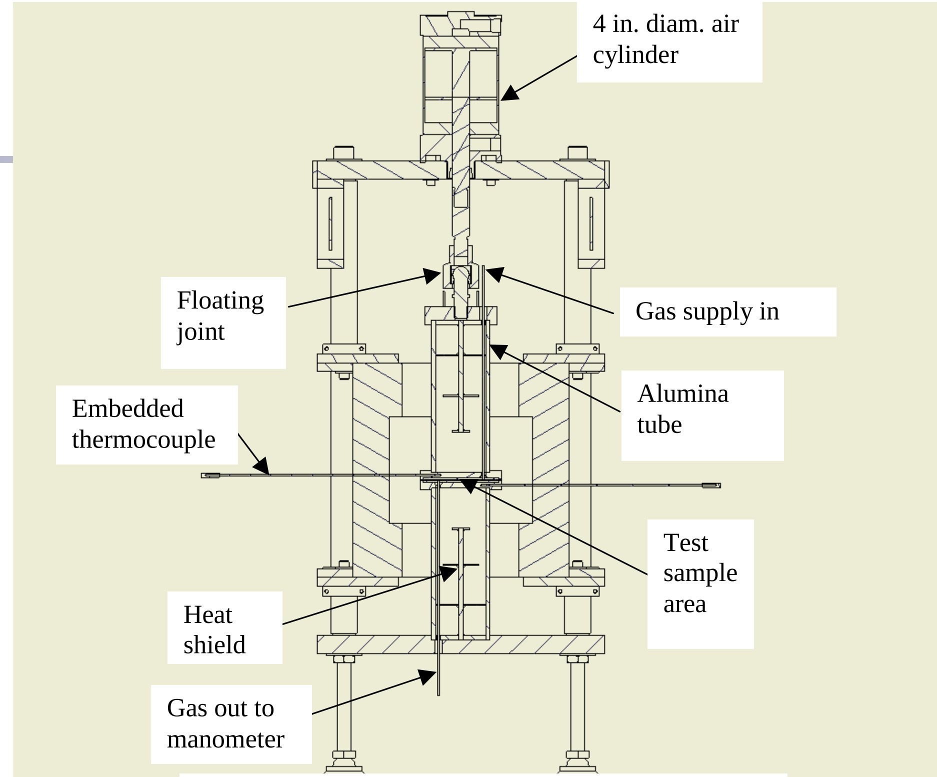
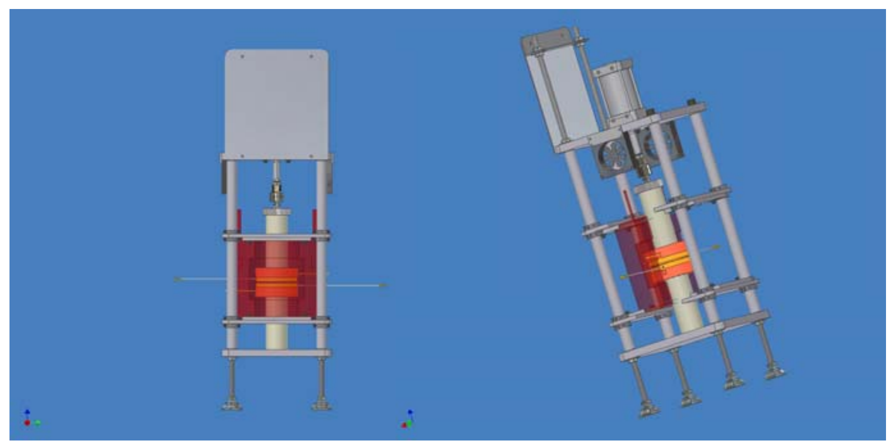
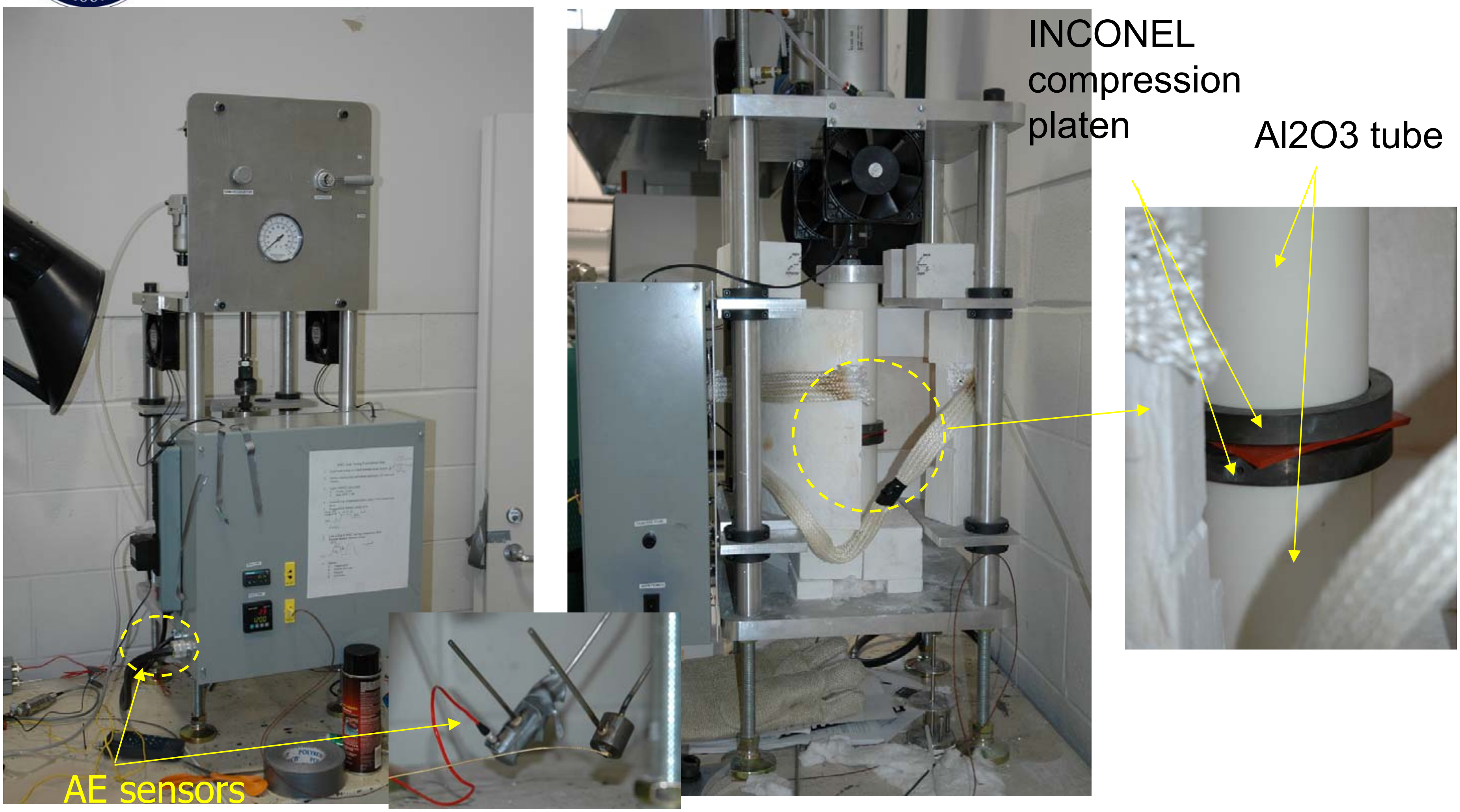


Figure 2 – SOFC Seal Test Stand Cross-sectional

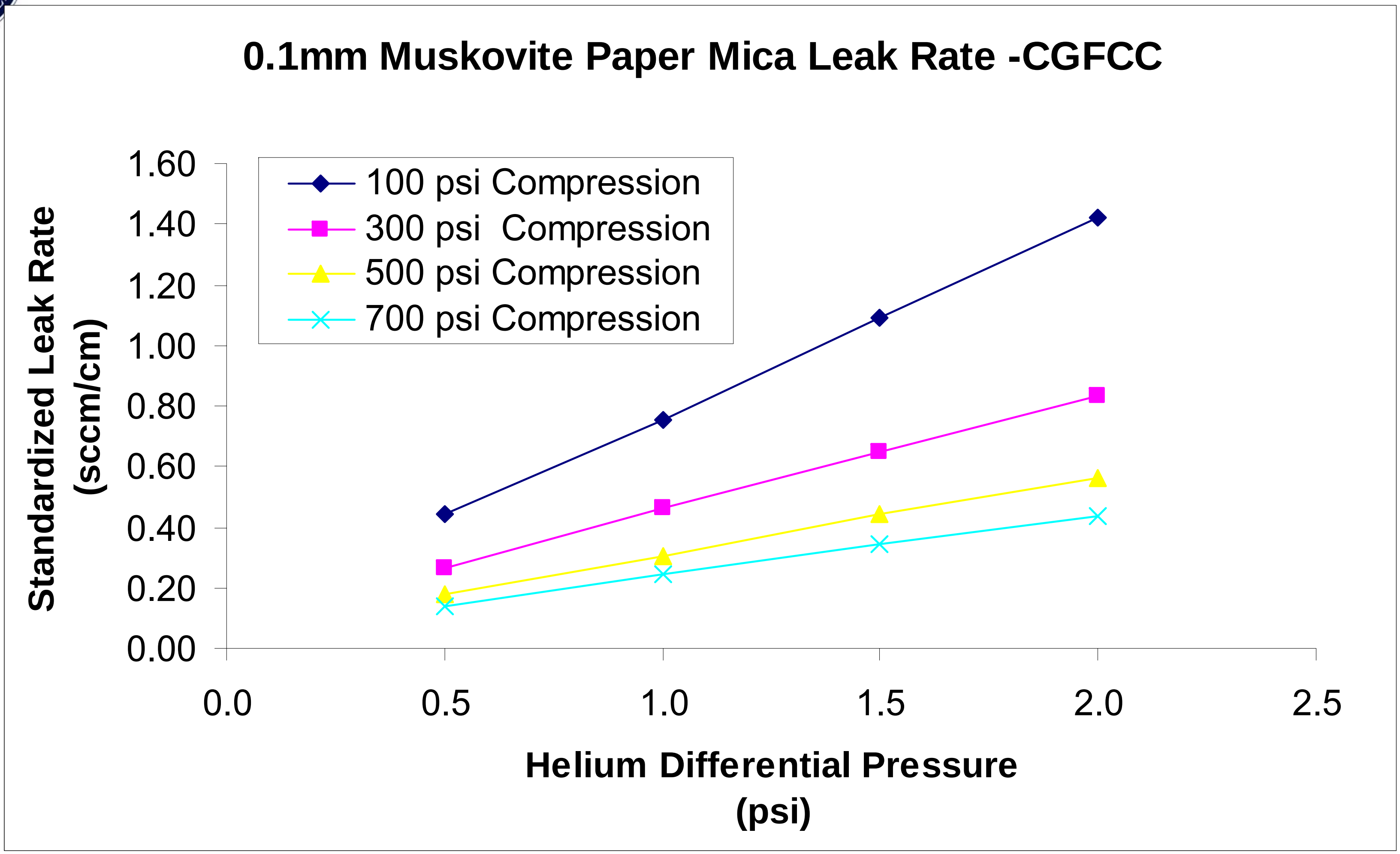


UConn SOFC seal test stand

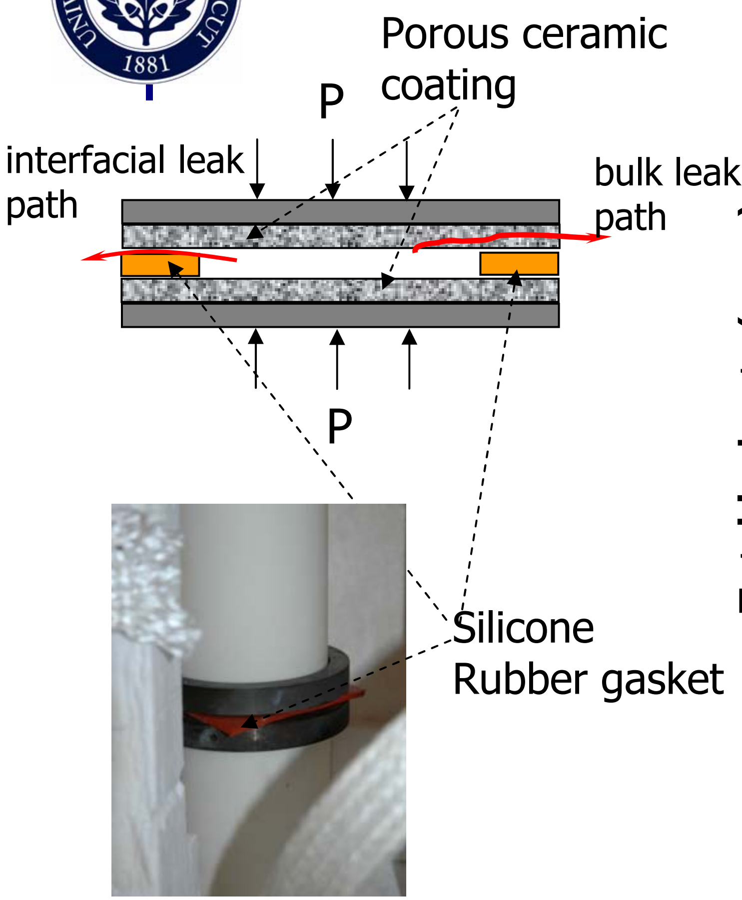
Temperature range: RT to 1100°C
Sample size: up to 5" in dia
Dynamic range (direct flow): 0.01~125 sccm

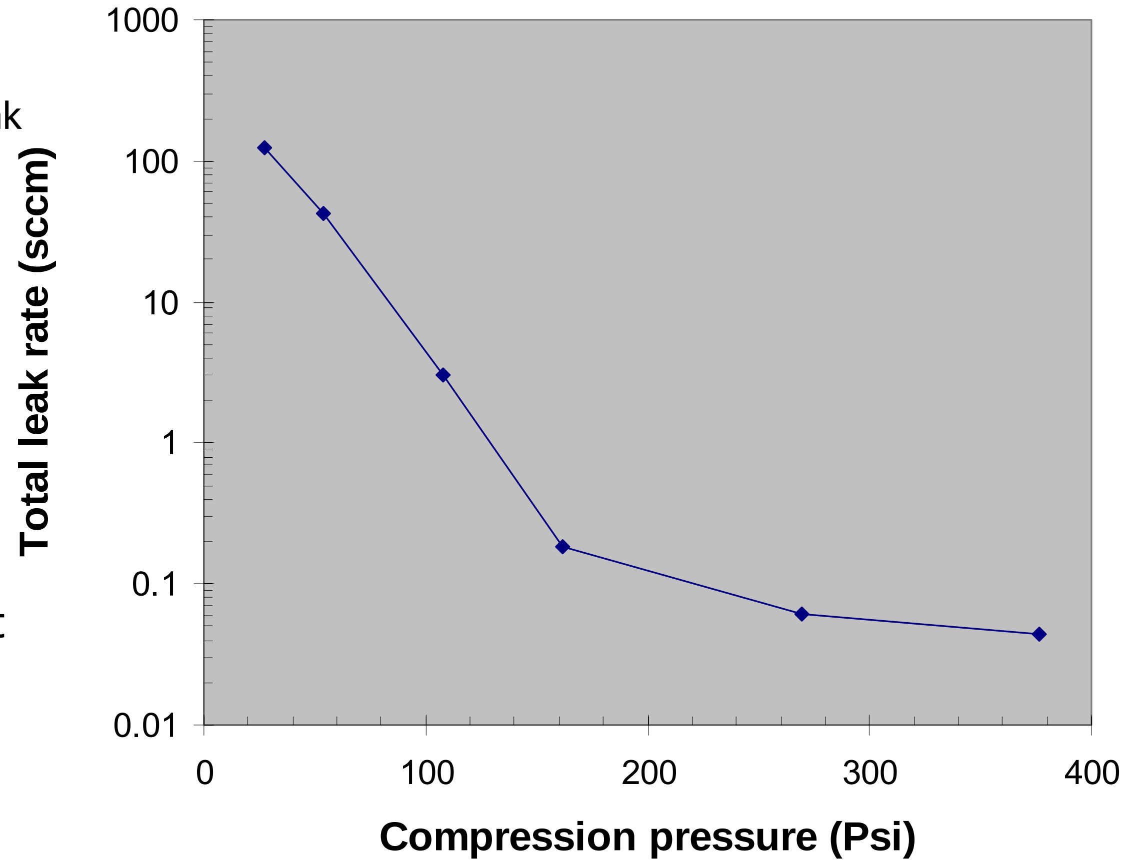


Mica leak rates generated with UConn SOFC seal test rig

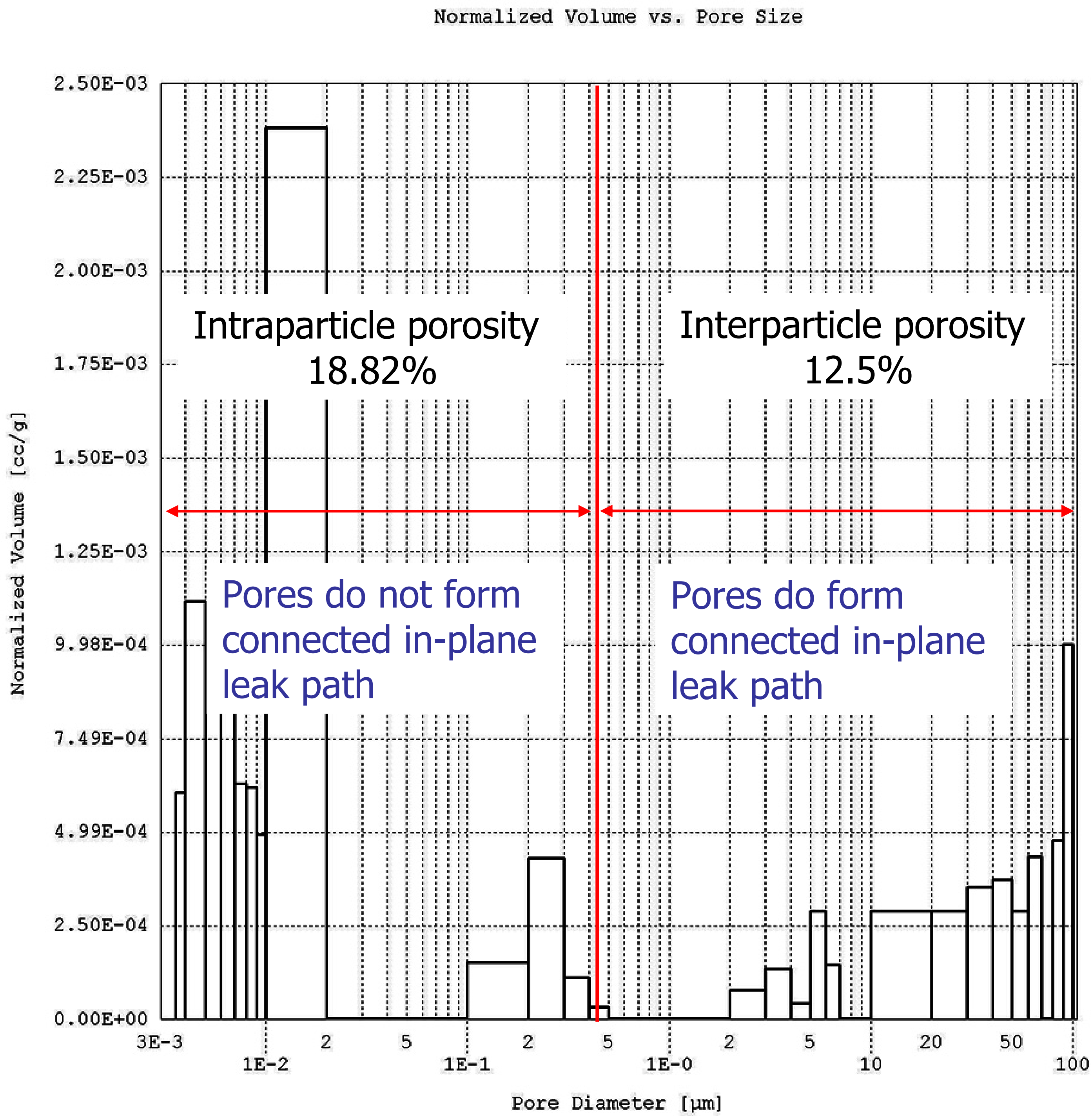


Room temperature leak test results





Gas leaks primarily through the interfacial path; leak rate through the bulk is about 4 order of magnitudes lower !!



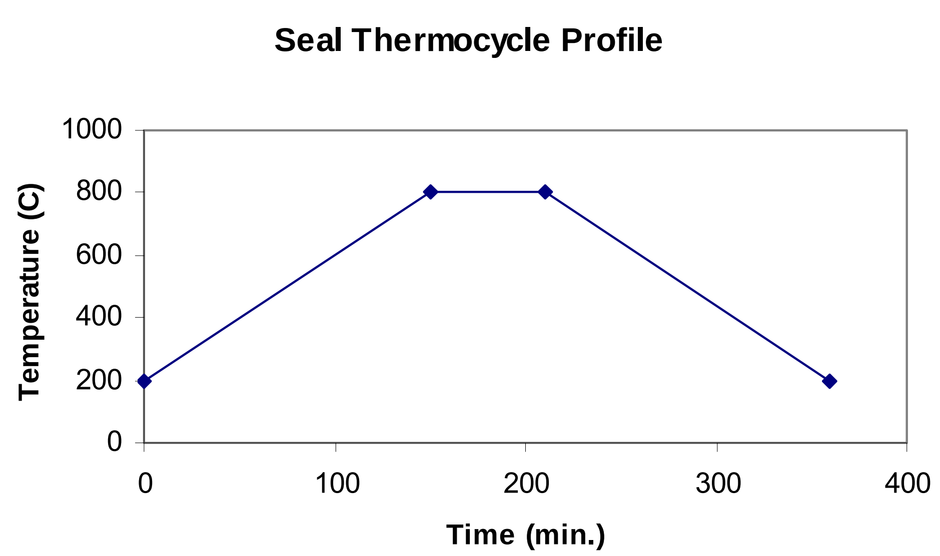
May not need to infiltrate hermetic fillers into the bulk !

High tem leak test : 1” sample, hard glass (4460), matched CTE

Initial Leak Rate Data		
Temperature	800	°C
Gas Pressure	2	psig
Cylinder Pressure	5	psi
Intial Leak Rate	1.8	sccm
Intial Leak Rate	6.147E-07	$^{g}/_{cm\text{-}s}$
Est. Leak Rate @ .1 psig	3.07E-08	$^{g}/_{cm\text{-}s}$
SECA goal @ .1 psig	1.00E-06	$^{g}/_{cm\text{-}s}$
Leak Rate after 38 hr.	1.6	sccm
Cylinder Pressure	0	psi
Leak at low cyl. pressure	2.3	sccm

Thermocycle Leak Rate Data		
Gas Pressure	2	psig
Cyl. Press 5 Thermocycles	0	psi
L.R. after 5 Thermocycles	2.0	sccm
Est. Leak Rate @ .1 psig	3.41E-08	$^{g}/_{cm\text{-}s}$
SECA goal after 10 cycles	2.00E-06	$^{g}/_{cm\text{-}s}$

Leak found to be insensitive to Compression !

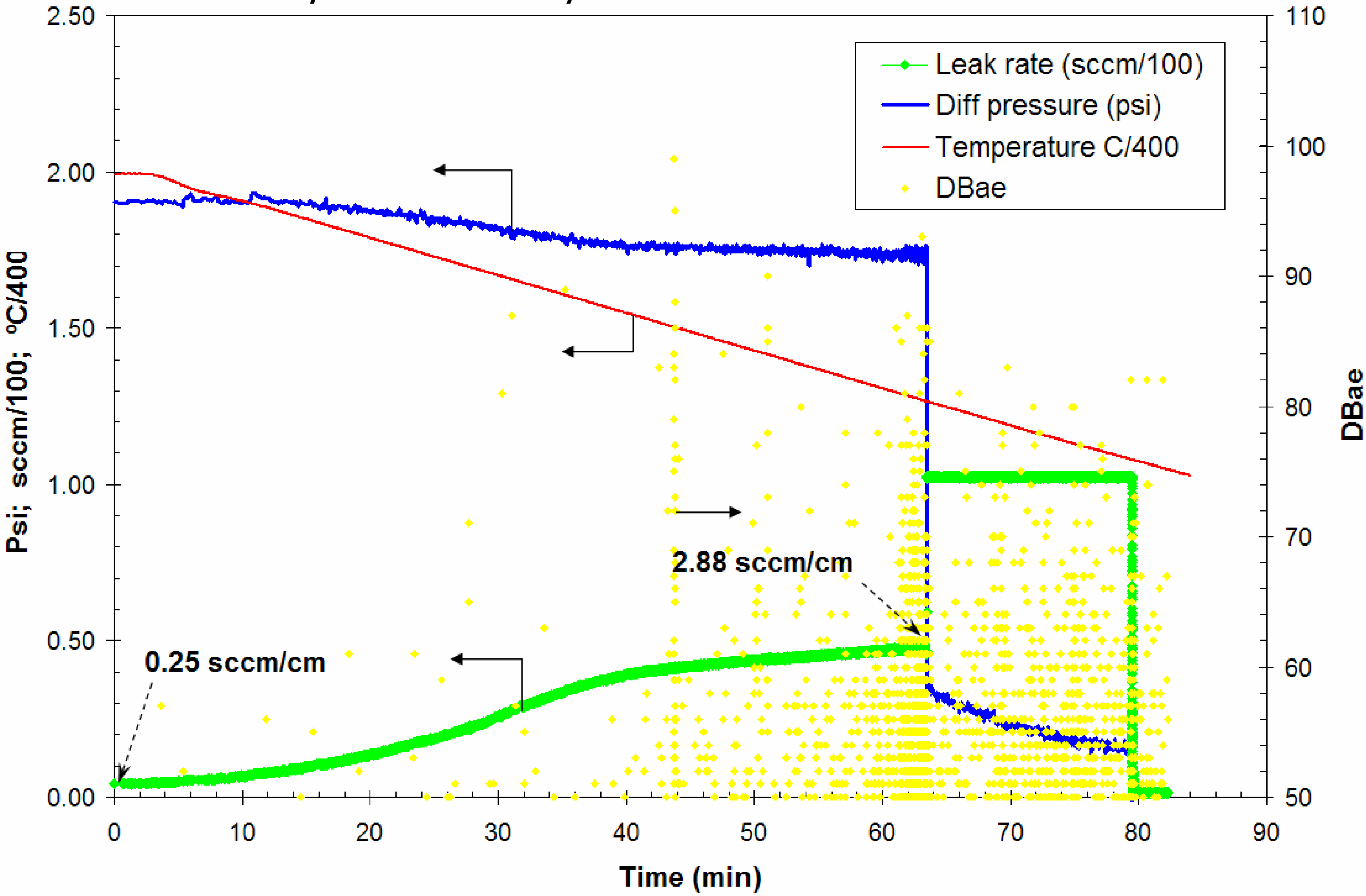


High temp leak test : 2" sample, hard glass (Brow#27), mismatched CTE

Glass may have over crystallized

INCONEL
16~17 ppm/C

Coated AL453
12~13 ppm/C

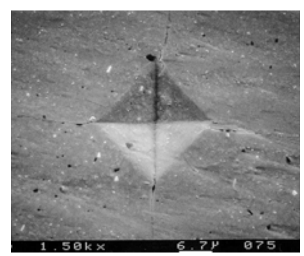


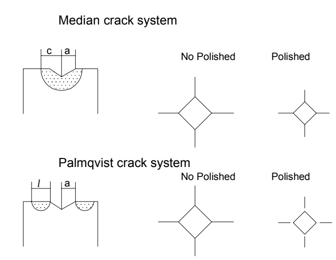
Summary & future work

- As one of the layers in the proposed composite seal structure, a tough APS coating on Fe-Cr stainless steel based low-cost raw materials has been developed and tested
  - The unique micro-cracking pattern/pore structure in the top coat seems to contribute to the superiors thermal shock resistance without forming leak paths
- A flexible SOFC seal testing system has been designed, manufactured, and applied to evaluate composite seal leak performance.
  - Composite seal made with hard glass show brittle failure during thermal cycling
  - Composite seal made of soft filler glass is being evaluated
  - Future work: try other oxides and compounds with low melting points
- At room temperature, the interface is the major leak path

Summary & future work

- Further mechanical testing and modeling work are being planed
  - Crack initiation and propagation resistance: strength and toughness
    - Pull-out test @ RT
    - Three/Four point bend test on a composite beam @ RT
  - Localized material properties
    - Vicker's indentation test
  - FEM modeling of simple seal geometry





Ke An, PhD Dissertation, ESM Dept, Va Tech 2002

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Questions and comments ?