High-Temperature Viscous Sealing Glasses for Solid Oxide Fuel Cells

DOE SBIR Phase II Contract # DE-SC0002491

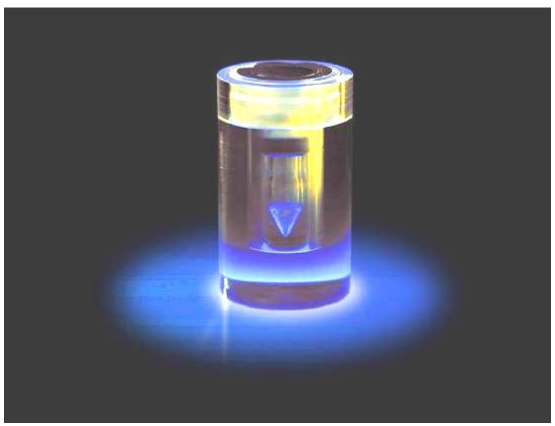
Cheol-Woon (CW) Kim, Joe Szabo, Ray Crouch, and Rob Baird
MO-SCI Corporation, Rolla, MO; ckim@mo-sci.com

Richard K. Brow, Jen Hsien Hsu, and Casey Townsend
Department of Materials Science and Engineering
and the Graduate Center for Materials Research
Missouri University of Science and Technology, Rolla, MO; brow@mst.edu

13th Annual SECA Workshop
Pittsburgh, PA, July 24-25, 2012

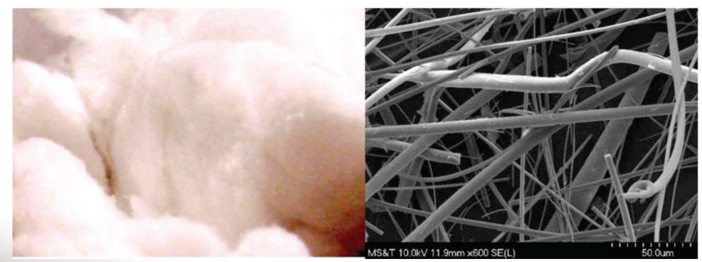
MO-SCI Corp. (www.mo-sci.com)

- Sealing Glasses: SOFCs, Aerospace
- Specialty Glasses for New Applications



RadSpheres

Commercial Blood-Typing Cards



DermaFuse

Why consider a viscous glass seal for an SOFC?

- Potential for lower thermal stresses through viscous relaxation at operational temperatures
  - Less critical that seal has CTE match to dissimilar materials

- Potential for 're-sealing' at operational temperatures through viscous flow

Objectives

- Develop glass compositions that exhibit stable thermomechanical/thermochemical properties, including viscosity, for use as seals for SOFCs

  Requisite Thermal and Physical Properties

  a) Long-term stability in viscosity (650-850°C)

  b) T_g: < 650°C: thermal stress will be relieved

  b) T_{soft}: < 650°C: requisite flow for re-sealing behavior

  c) T_{Liq}: < 800°C (as low as possible): stable, a small volume fraction of crystals

  d) CTE(RT-subT_g): $10\text{-}12.5\times10^{-6}$/°C (YSZ- SS441)

- Conduct hermetic sealing tests

  SOFC Materials

  a) Aluminized SS441

  b) NiO-YSZ supported YSZ electrolyte bilayers

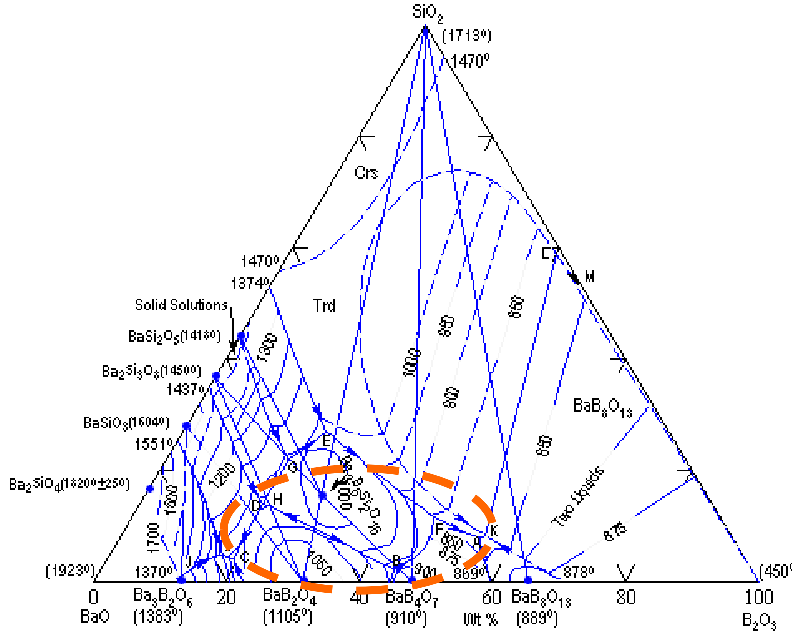
  Supplied by PNNL

- Characterize thermochemical reactions

  a) Volatilization of glass components

  b) Interfacial reactions with SOFC components

Promising compositions were identified

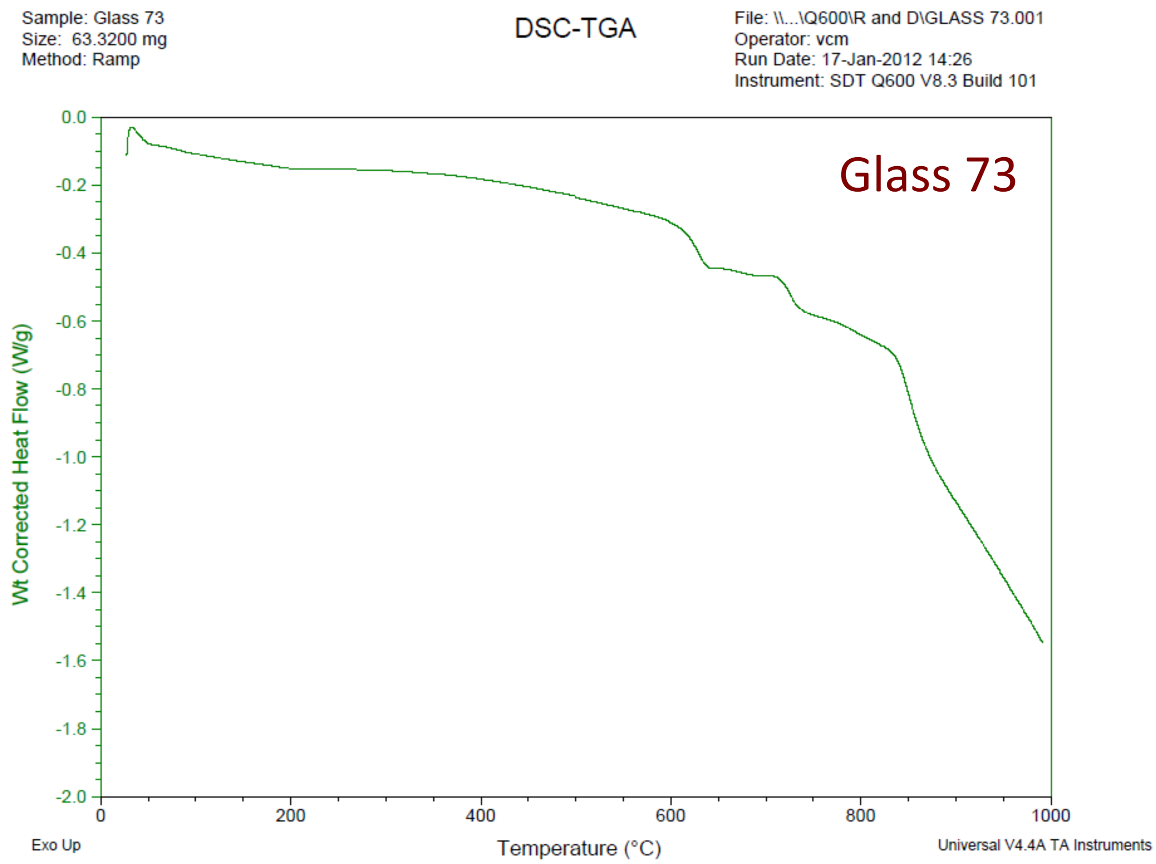


- To date, prepared a total of >90 compositions (including Phase I) and measured properties (T_g, T_s, T_{Liq}, and CTE) of all of the compositions
- Preferred Compositions Exhibit Promising Sealing Behavior

	Phase I			Phase II		
	Glass 2	**Glass 4**	**Glass 28**	**Glass 73**	**Glass 75**	**Glass 77**
Glass system	$BaO-B_2O_3-SiO_2$		$BaO-RO-Al_2O_3-B_2O_3$	$BaO-RO-Al_2O_3-B_2O_3-SiO_2$		
T_g (°C) measured from CTE curve	619	599	581	624	623	625
Dilatometric T_s (°C)	650	632	615	640	650	656
CTE 40-500°C (/°C)	8.19×10^{-6}	7.32×10^{-6}	7.48×10^{-6}	8.48×10^{-6}	8.17×10^{-6}	9.25×10^{-6}
Liquidus T (°C)	805	790	795	800	810	810

DSC Analysis

➢ **Differential Scanning Calorimetry (DSC) Reveals That The Candidate Sealing Glasses Do Not Readily Crystallize**



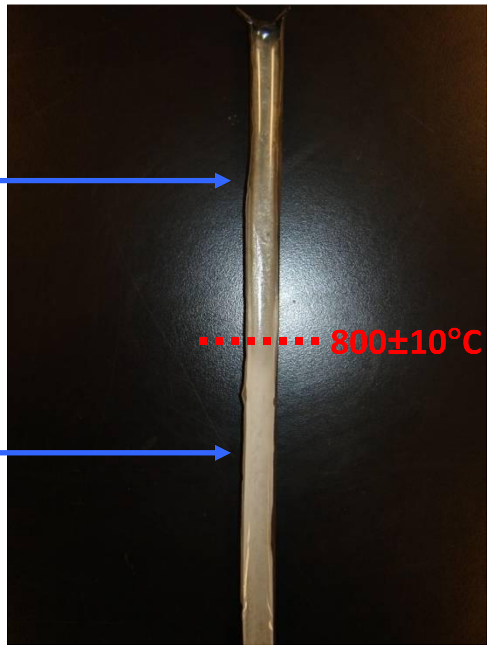
- No Crystallization Peaks Up to 1000°C
- Similar results were found for other candidate compositions

Liquidus Temperature

- Liquidus Temperature (ASTM C829-81), 72 hours in a gradient furnace

Clear Glass

Slightly Cloudy Glass



Glass 73

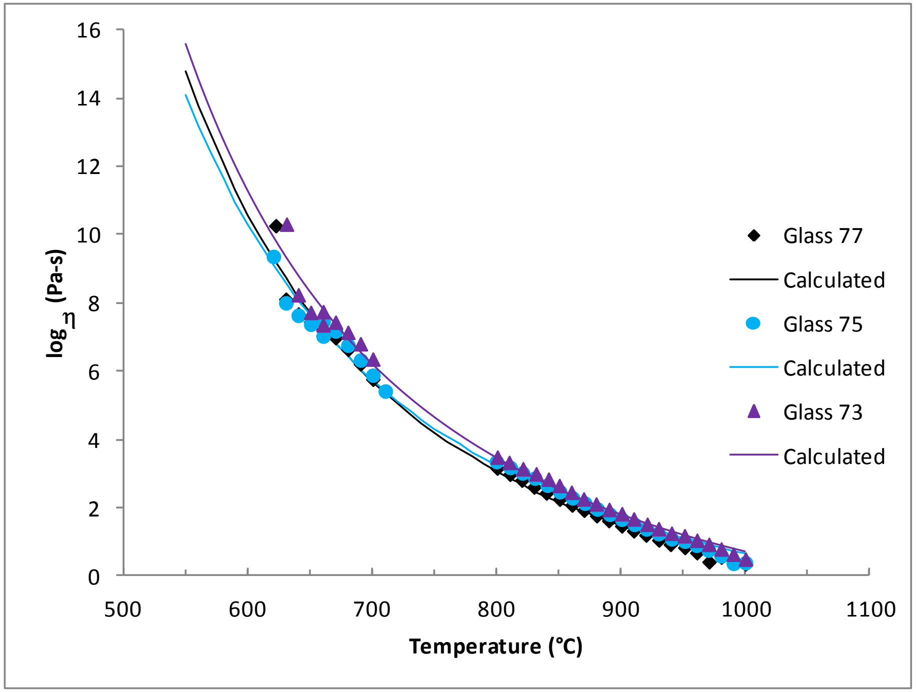
Glass 75

Glass 77

Liquidus Temperature as low as possible

Stable Viscosity

➢ **Viscosity measurements provide valuable performance information**

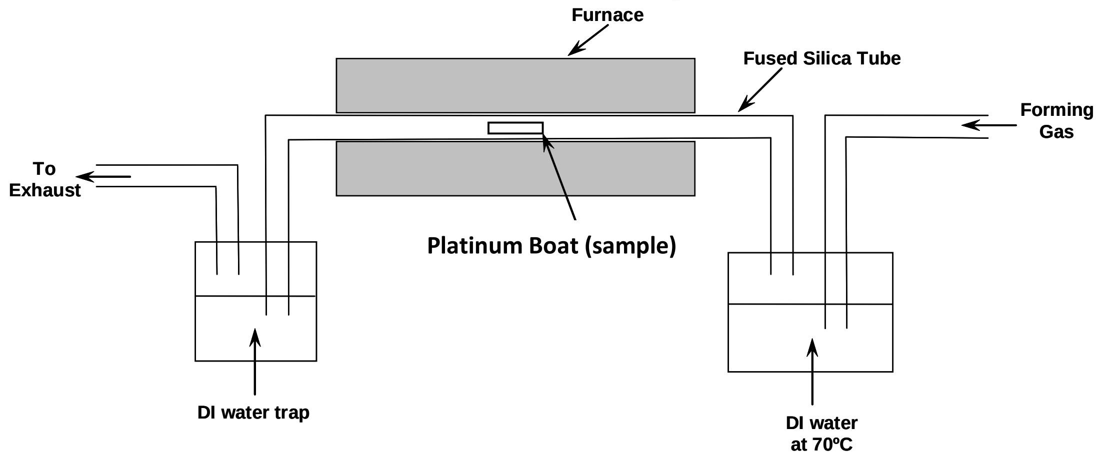


- High temperature measurements (1-10^4 Pa-s) by the rotating spindle technique
- Low temperature measurements (10^5-10^{11} Pa-s) by the parallel plate technique
- Viscosity-temperature curves fit using the Corning viscosity model (JC Mauro, PNAS, 2009)

Glass	Fitting Parameters		T_g(°C)	Isokom T(°C), log(η) (Pa·s)				
	m	T_g(°C)	Dilatometric	11	9	6.6	4	2
Glass 73 as-cast	48.46	610	624	623	655	705	785	886
Glass 73 500hr at 800°C in air	39.54	598	Not Measured	614	652	713	NM	NM

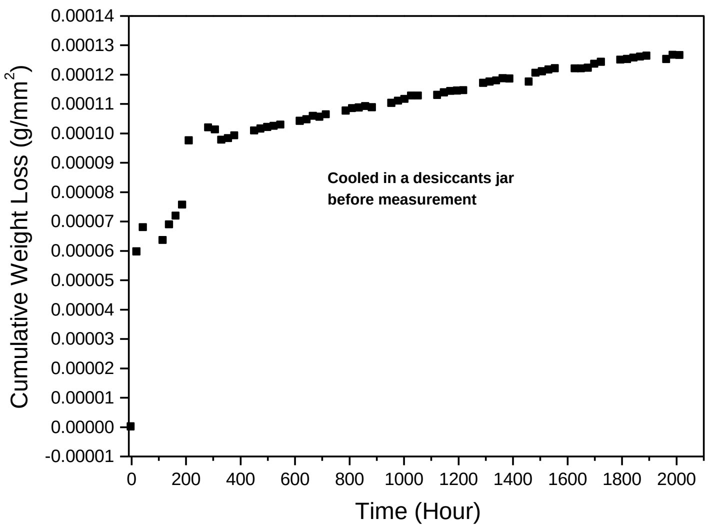
- Long-term viscosity measurements in progress

Volatility



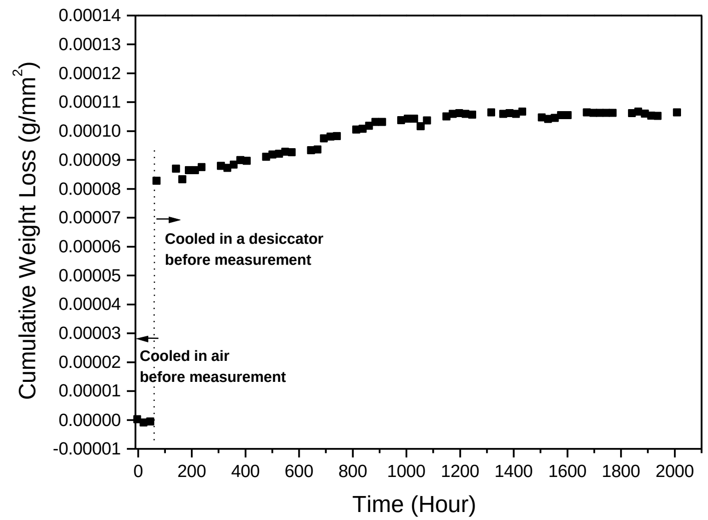
Flowing Wet Forming Gas (5%H_2 95%N_2)

Glass 73 Weight Loss at 750°C in Flowing Wet Forming Gas



Stagnant Dry Air

Glass 73 Weight Loss at 750°C in Stagnant Dry Air



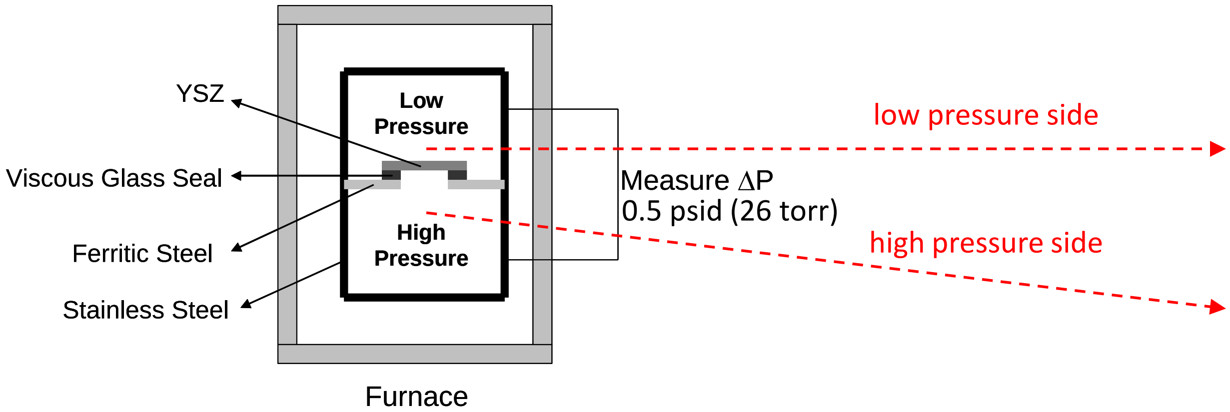
Weight Loss estimated for 40,000 hrs

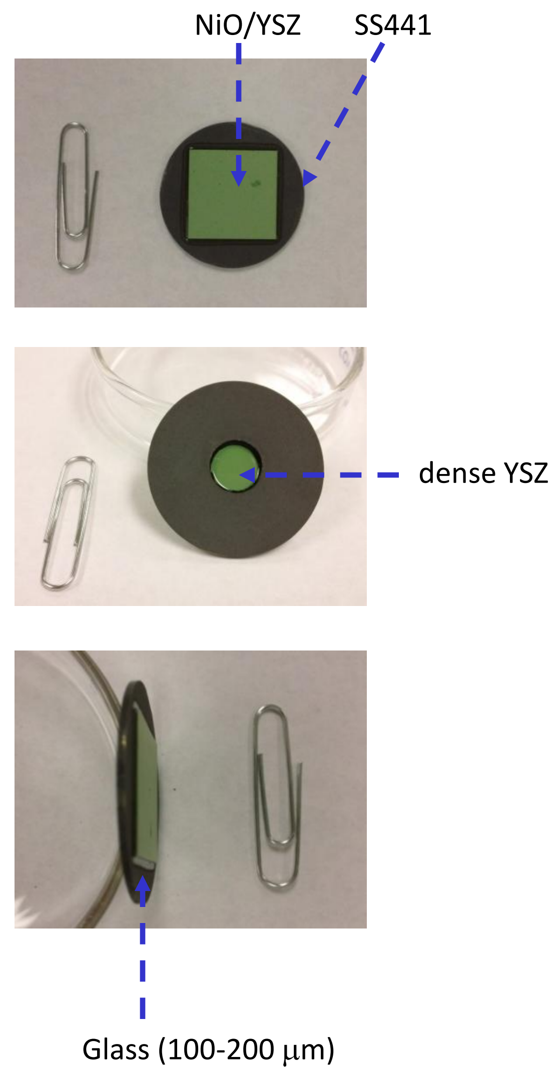
Test Condition at 750°C	Volatility Rate (g/mm²/hr)	Total Weight Loss (%) at 40,000 hrs
Flowing wet forming gas	2.0×10^{-8}	4.5
Stagnant dry air	1.7×10^{-8}	1.9

mo-sci CORPORATION

MISSOURI S&T University of Science & Technology

Hermetic Sealing Tests

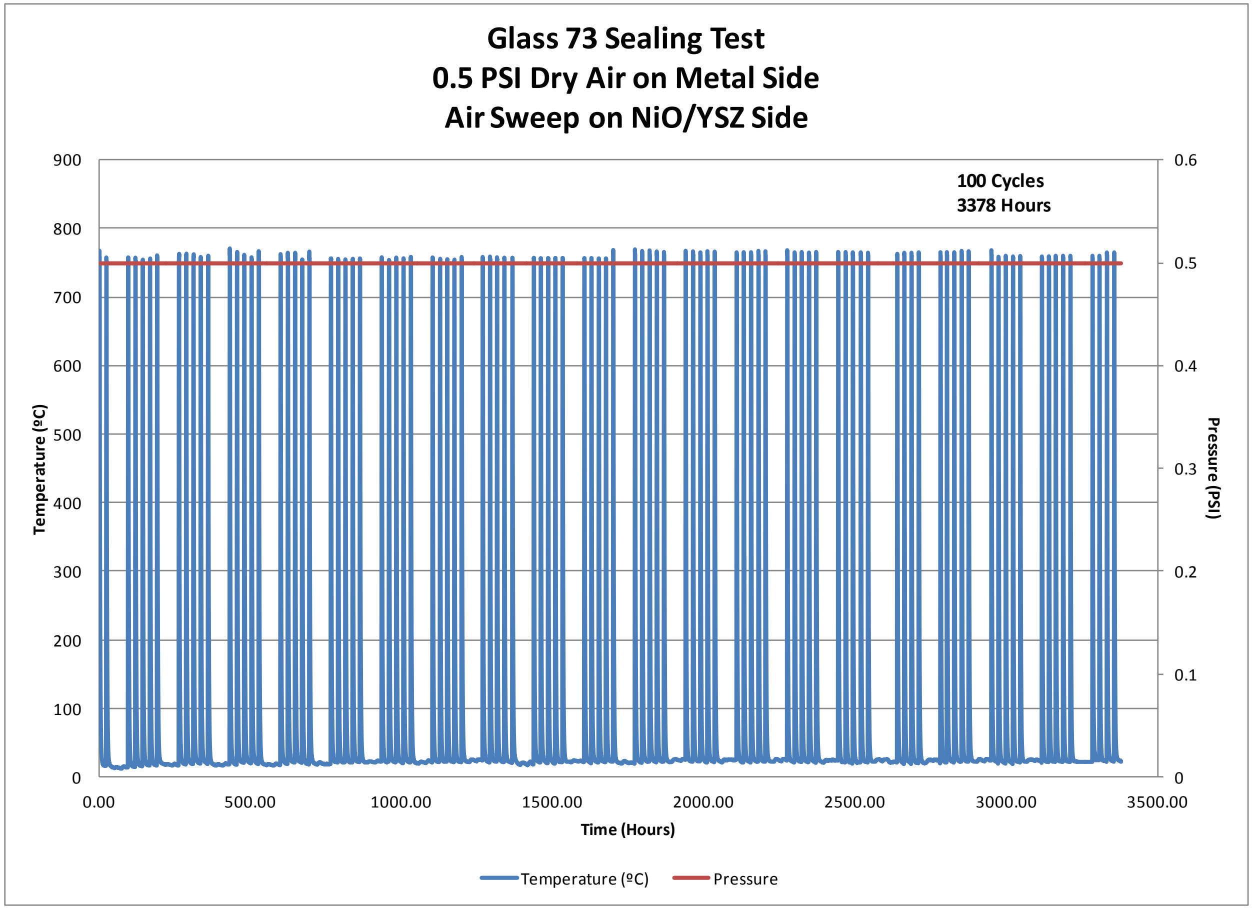




Schematic seal performance test system

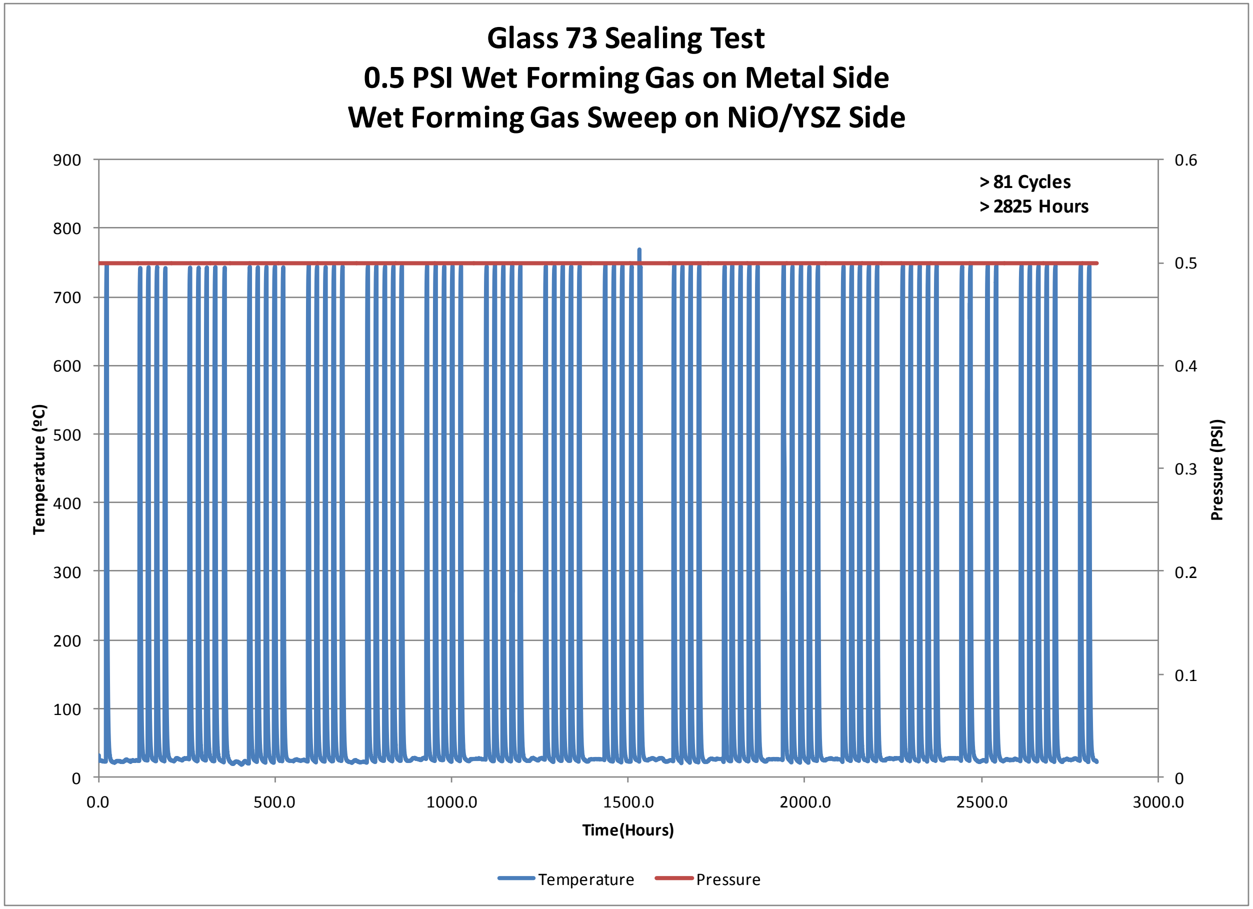
- **Sandwich sample:**
  - Glass pastes were made from powders (-45 µm) mixed with a solution of PVB binder and acetone, and used to bond NiO/YSZ bi-layer to aluminized steel (SS441) substrate (materials from PNNL)
  - Sandwich seals fired in air at 850°C for 8 hours

Hermetic Sealing Tests-cont.



- Glass 73 seal has survived 100 thermal cycles (750°C to RT) in dry air at a differential pressure of 0.5 psi (26 torr) over the course of > 3,300 hours without failure and the test was deliberately terminated for analysis

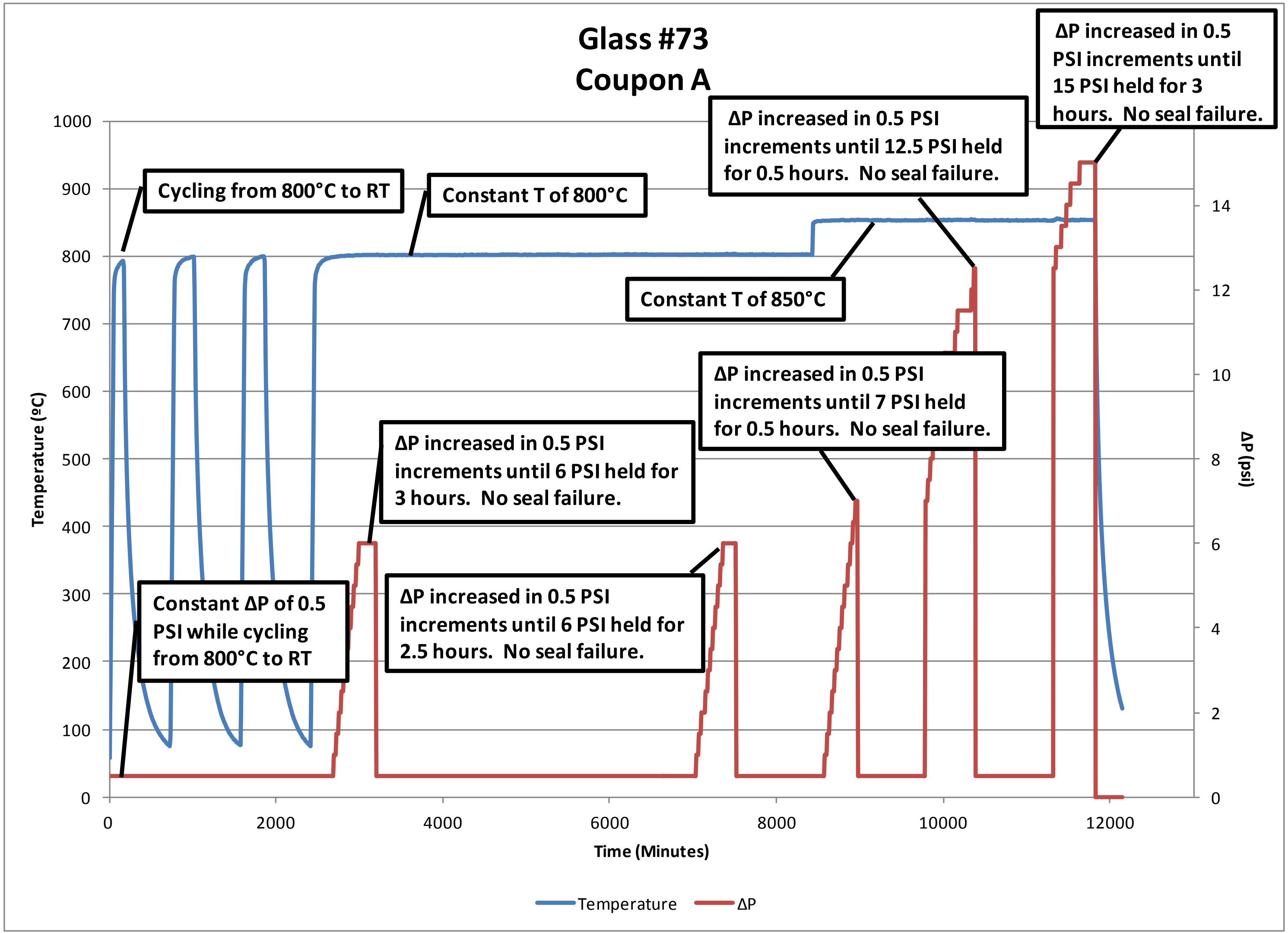
Hermetic Sealing Tests-cont.



- To date, Glass 73 seal has survived 81 thermal cycles (750°C to RT) under wet forming gas at a differential pressure of 0.5 psi (26 torr) over the course of > 2,800 hours without failure and the test continues

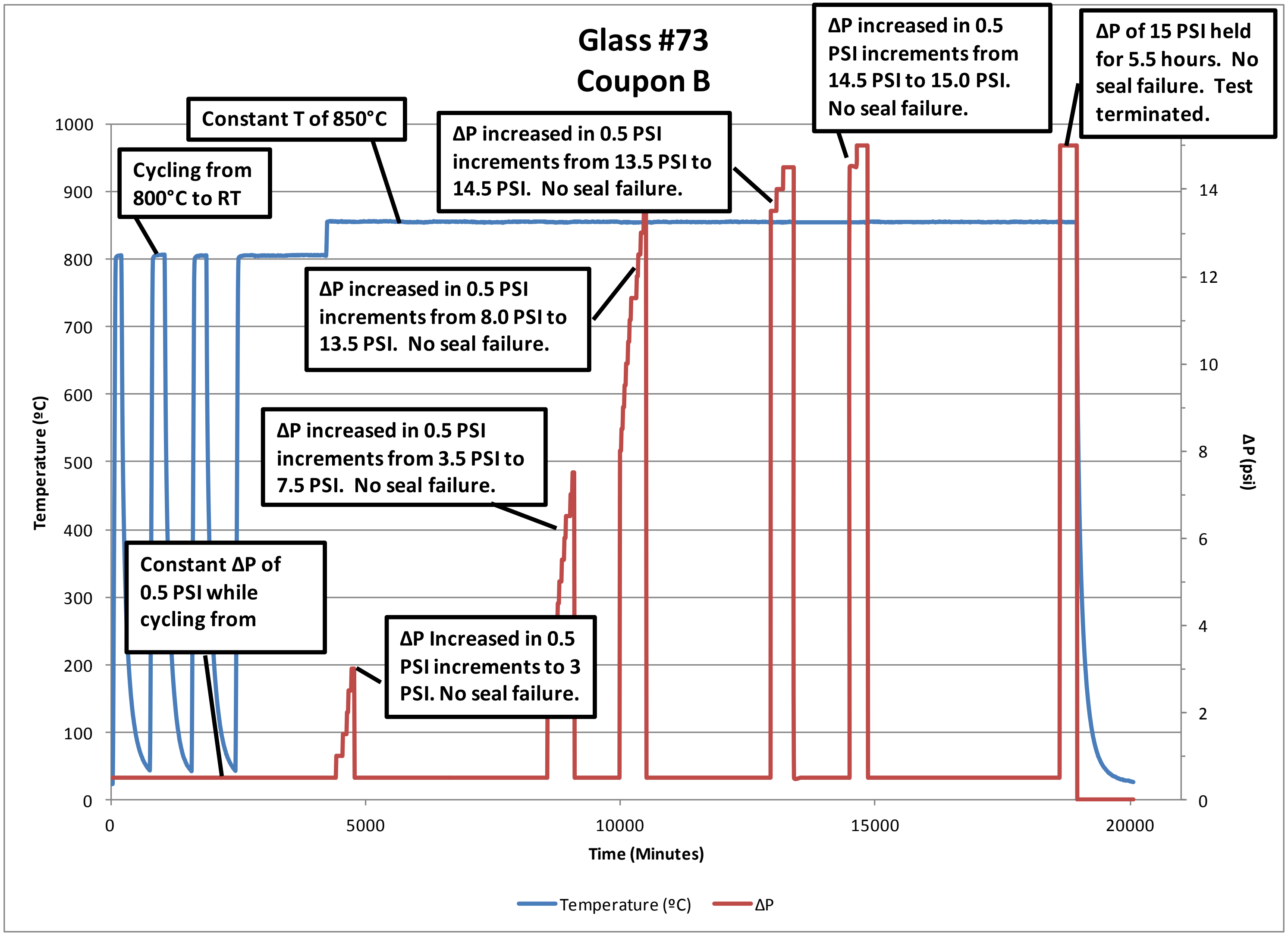
Re-Sealing Tests

- Tried to break a seal by fast cooling as possible in the furnace, but no seal failure
- Glass 73-Coupon A: No seal failure up to 15 psi, 850°C



Re-Sealing Tests-cont.

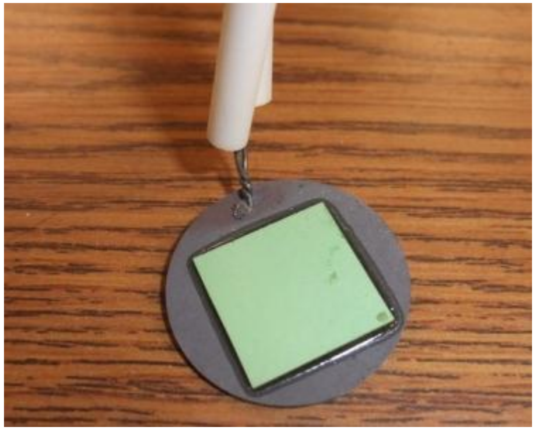
- Glass 73-Coupon B: No seal failure up to 15 psi, 850°C



Re-Sealing Tests-cont. (ex-situ)

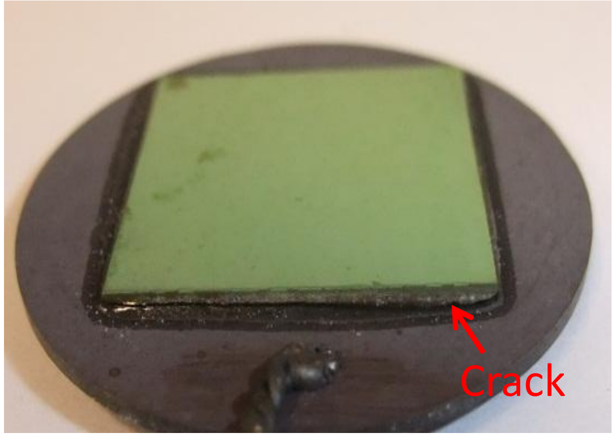
- **Glass 73-Coupon C: Thermally cracked and healed**

Seal originally found to be hermetic



↓

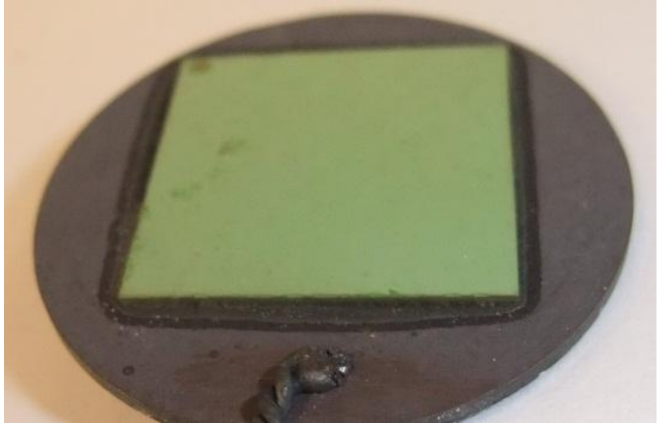
Glass seal deliberately cracked by high cooling rate quench (> 25°C/s)



↓

Foaming in soapy water

Crack healed after re-heating to 725°C for 2 hrs



↓

No foaming in soapy water

MO-SCI CORPORATION

MISSOURI S&T University of Science & Technology

Re-Sealing Tests-cont. (ex-situ)

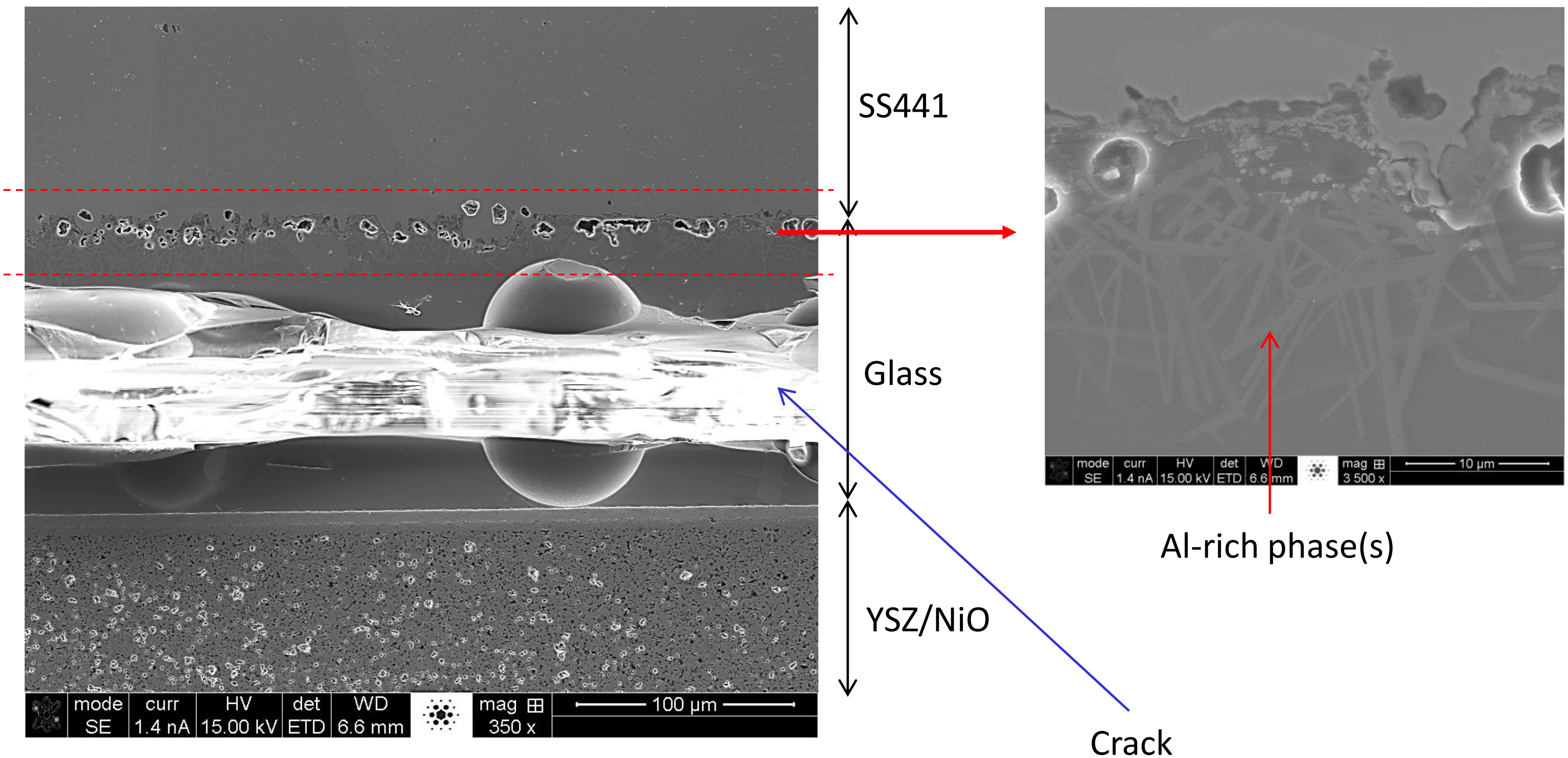
Temperature (°C)	Time (hr)	Observation	Viscosity log(η) (Pa-s)
800	2	Healed	3.4
750	2	Healed	5
725	2	Healed	5.7
700	2	Healed once, but not healed second time; more tests in progress at 700°C or below	6.4

Glass	Fitting Parameters		T_g(°C)	Isokom T(°C), log(η) (Pa·s)				
	m	T_g(°C)	Dilatometric	11	9	6.6	4	2
Glass 73 as-cast	48.46	610	624	623	655	705	785	886

Possible Healing as low as 700-725°C

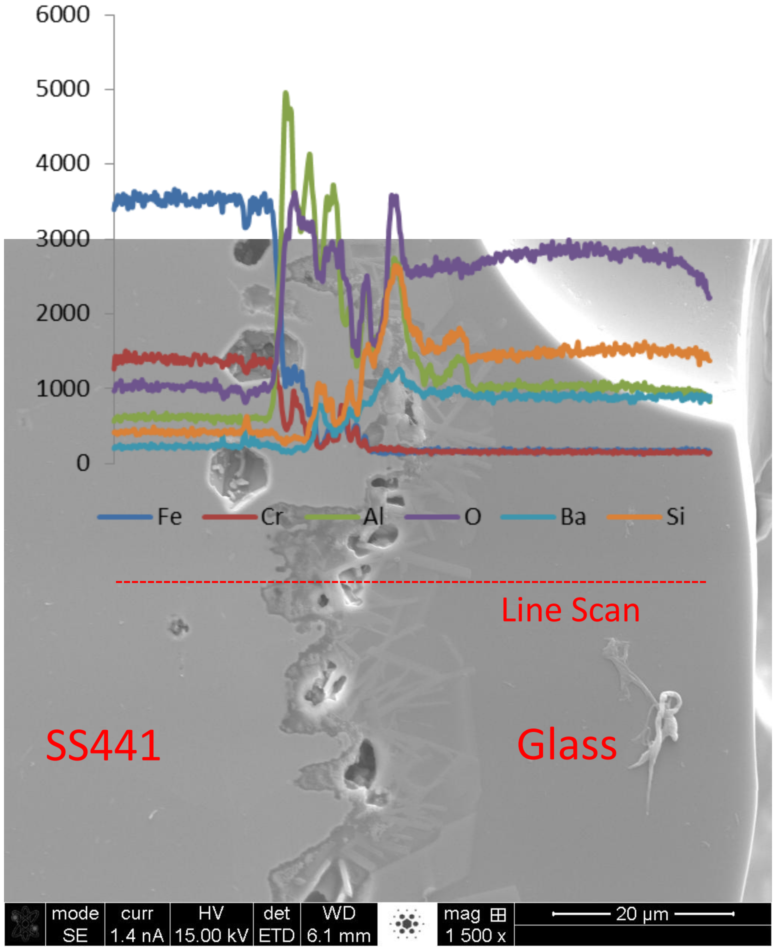
Reactivity Characterization
Glass 73

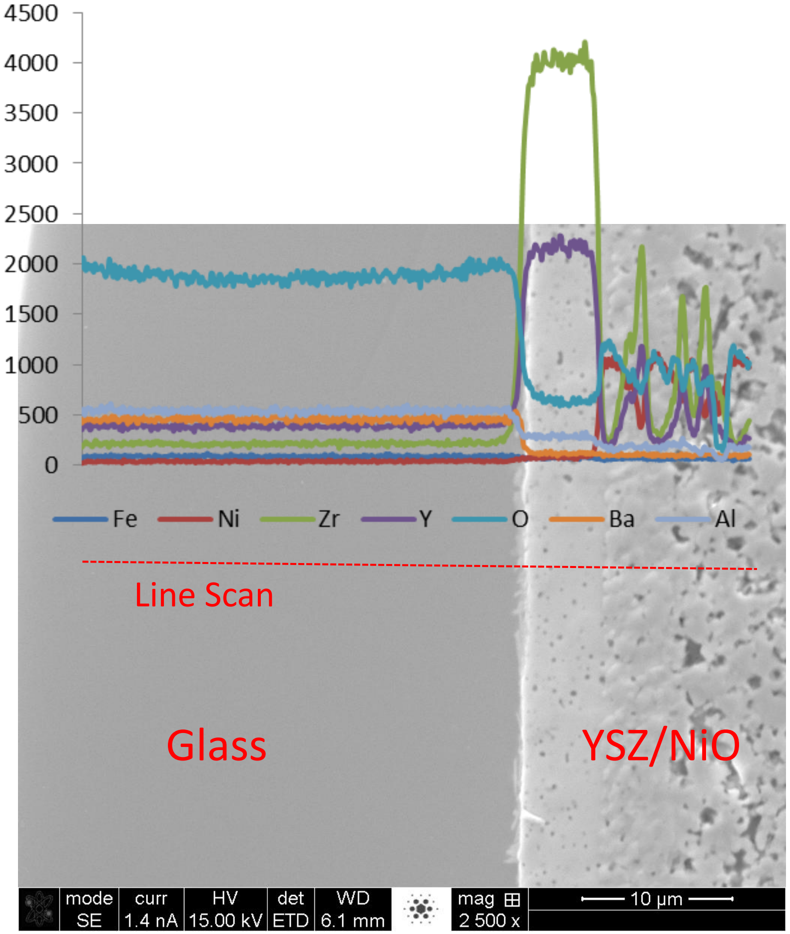
800°C for 168 hours in air



- **Excellent wetting and bonding to both aluminized metal and YSZ**
- **Some interfacial reactions between glass and metal, long-term characterization will be required**
- **No major interfacial reactions between glass and ceramic substrate**

Reactivity Characterization
Glass 73-cont.





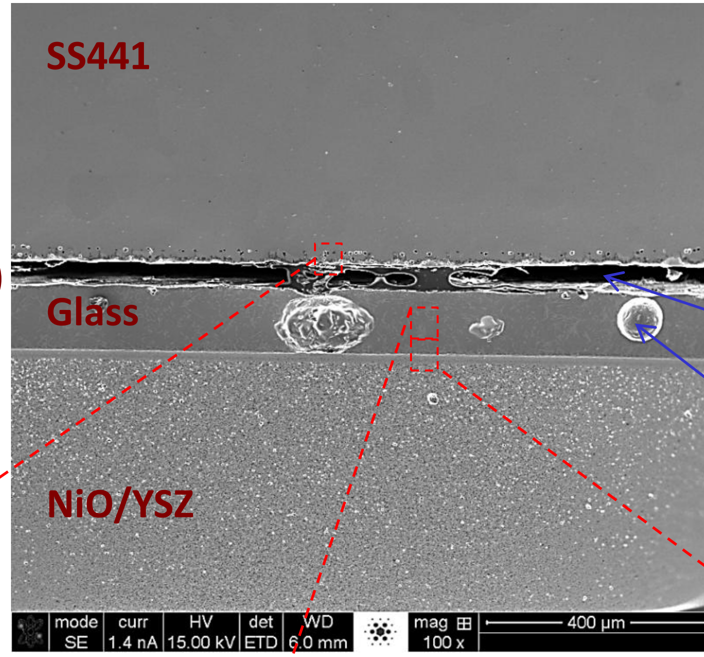
- **No major Cr or Fe migration to glass seal**
- **Some Al migration to the interface of glass seal**

- **No elemental migration to glass seal or to ceramic substrate**

Long-Term Reactivity Characterization

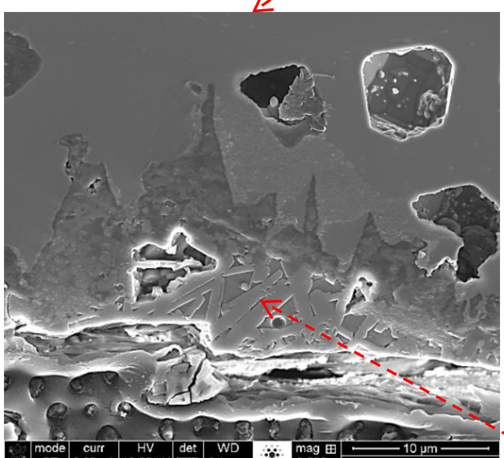
- **Glass 73 reaction couple:**
  100 Thermal cycles (750°C to RT)
  > 3,300 hours, dry air

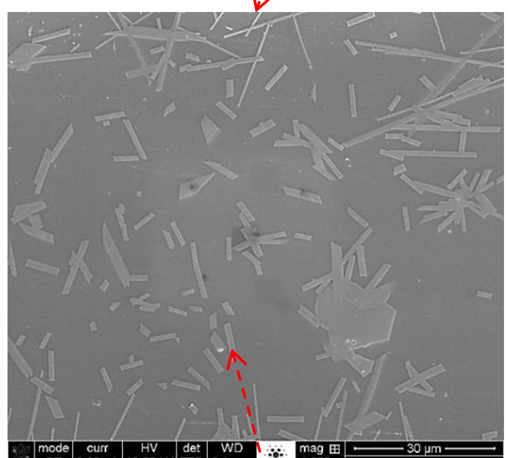
- **More analysis in progress**

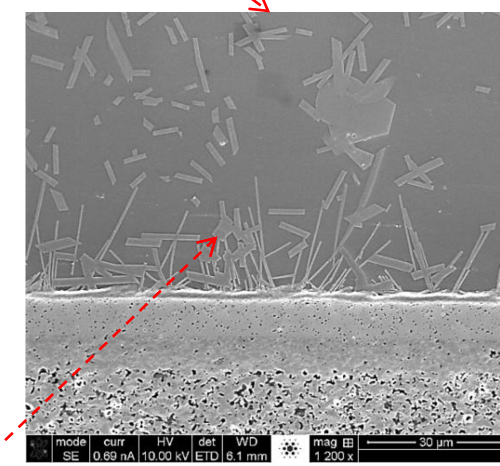


Crack

Bubble: a few large bubbles







Al- or Si-rich phase(s)

On-going & Planned Work

- Refine and optimize glass compositions
- Study long-term viscous behavior
- Characterize long-term thermochemical reactions
- Hermeticity and 're-sealing' behavior
- Characterize porosity
- Stack tests (PNNL)

Acknowledgements

- SECA
- DOE SBIR Phase II Contract # DE-SC0002491
- DOE Project Officer: Joseph Stoffa, NETL
- Yeong-Shyung Matt Chou/Jeff Stevenson, PNNL