Sandia National Laboratories

Glass Composite Seals for Solid Oxide Fuel Cells

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Summary and Conclusions

- Glass composites are a versatile technique for sealing SOFCs
- The method has been demonstrated for a range of glass and filler compositions
- Glass and filler compositions can be optimized independently
- Our borate and borosilicate sealing glasses exhibit long-term stability at 750°C
- They make strong, leak tight seals to ferritic stainless steel alloys and other SOFC materials

Outline

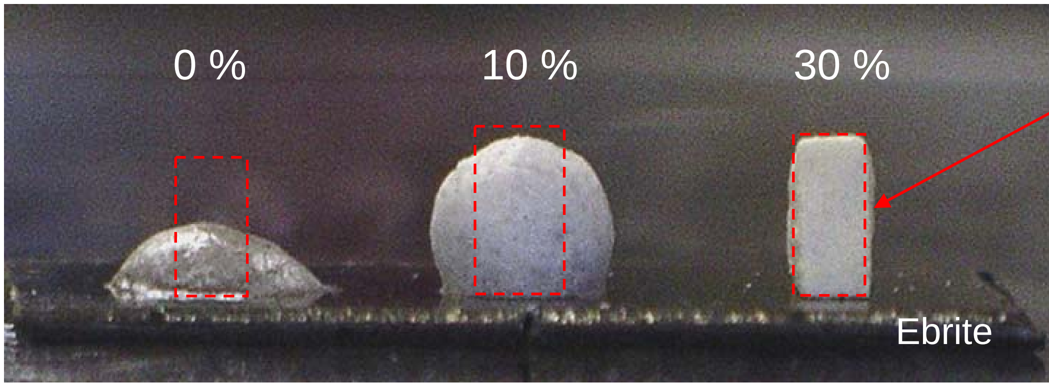
- Introduction to composite seals
- Measurement and control of seal properties
    - Glass composite viscosity and flow
    - Seal material stability
    - Seal strengths
- Conclusions

The SECA goal of 40,000 hr stack lifetimes places extreme demands on SOFC materials

SOFC seals are subject to severe materials constraints

Function	Property
HT stability	decomposition, vaporization
chemically stable	interfacial reactions
mechanically stable	adhesion at temperature
insensitive to thermal cycling	thermal shock resistance
stress tolerant	accommodates CTE mismatch
no gas leaks	hermeticity

Composite seals are attractive because chemical and mechanical properties can be optimized independently



Initial pellet shape

Glass 14A - YSZ powder mixtures heated on Ebrite stainless steel for 10 min at 850°C Percentages indicate the volume of YSZ powder in composite

The Concept

- A deformable seal based on glass flow above its T_g
- Wetting and reaction controlled by glass chemistry
- Control viscosity and CTE with powder additive
- Slight flow to relieve stress, heal cracks
- Composite is rigid enough to remain in joint

We have evaluated a variety of glass and filler compositions for SOFC seals

Glass family: Mg-Ca-Ba-La-Al-Si-B-O

Glass Properties:

T_g from 510 to 735°C

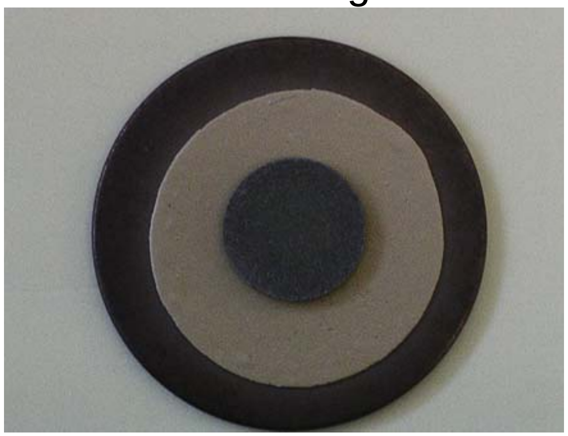
CTEs from 7 to 11.5 x 10^{-6}/°C

η from 45 to 600 MPa•s

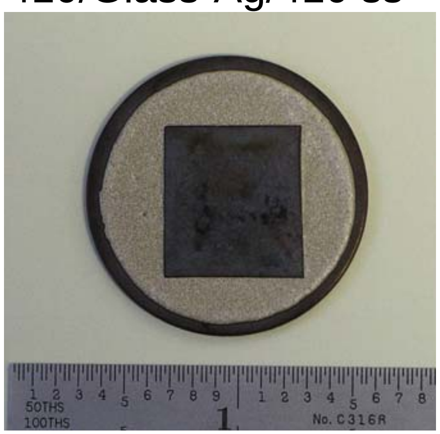
Additives: YSZ, Al_2O_3, Ni, Cr, Ag

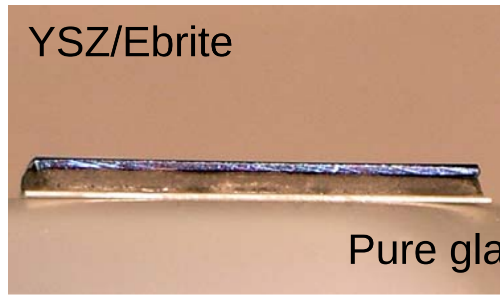
We have sealed different SOFC materials with our glass composites

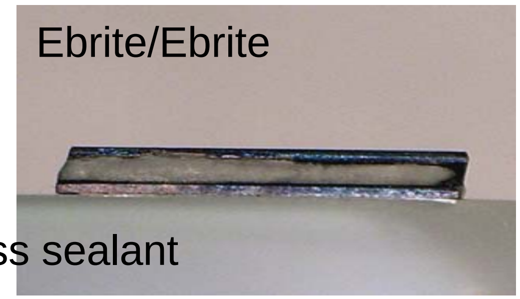
Anode/Glass-Ag/410 ss



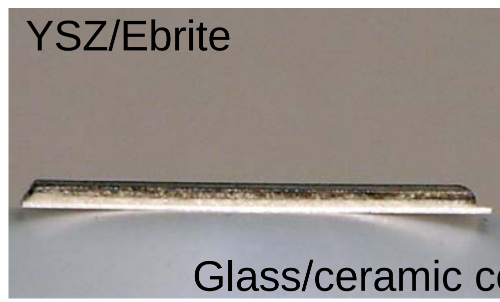
410/Glass-Ag/410 ss

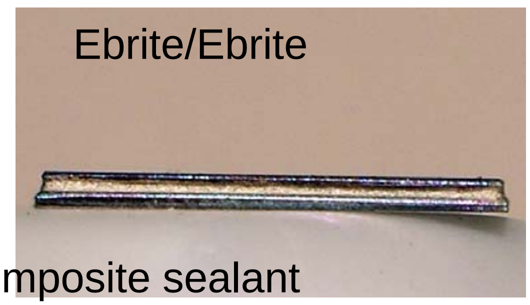






Pure glass sealant



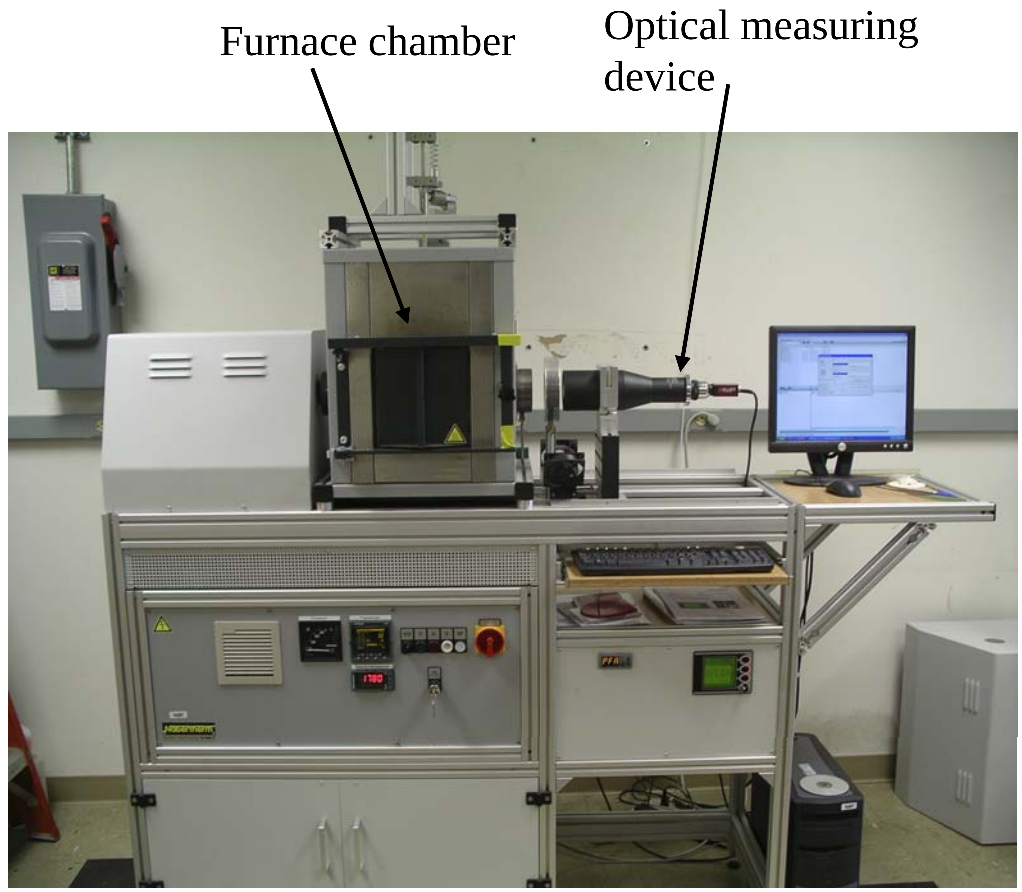


Glass/ceramic composite sealant

We measure and optimize properties of glass-powder composites using a high-temperature furnace with in situ video capabilities

Temperature to 1750°C in air

- Non-contact, optical measurements
- CTE measurement
- Contact angle measurement
- Viscosity determination
- Loaded sintering
- Thermogravimetric analysis
- Oxidation studies

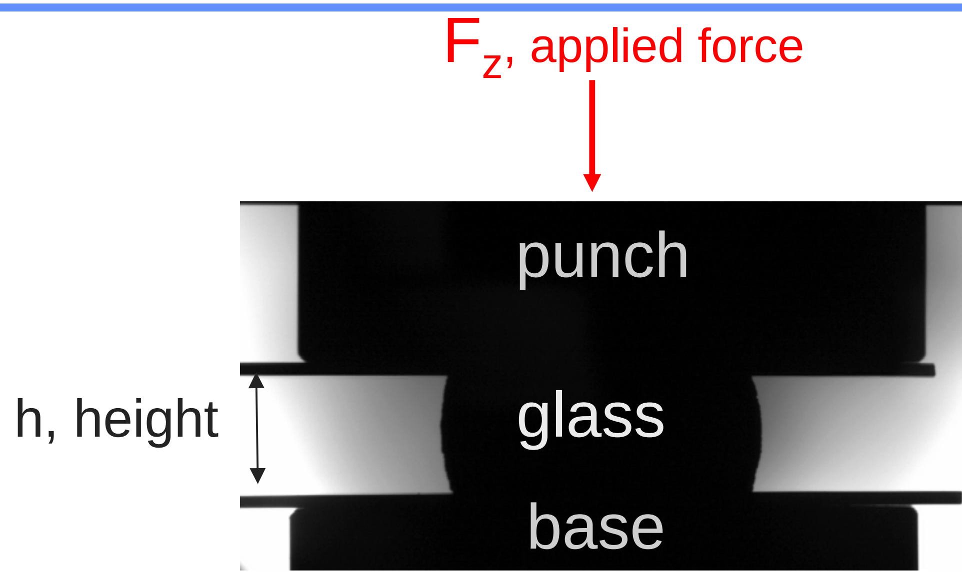


Strain rate measurements give uniaxial viscosity, which is necessary for SOFC design and modeling

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{F_z}{A} \times \frac{1}{\dot{\varepsilon}_z}$$

η=viscosity
σ=stress
A=area
$\dot{\varepsilon}$=strain rate

Assumptions:
1) Newtonian flow
2) Constant shear rate throughout specimen



$$\dot{\varepsilon}_z = \frac{\Delta \varepsilon_{\varepsilon}}{\Delta t}$$

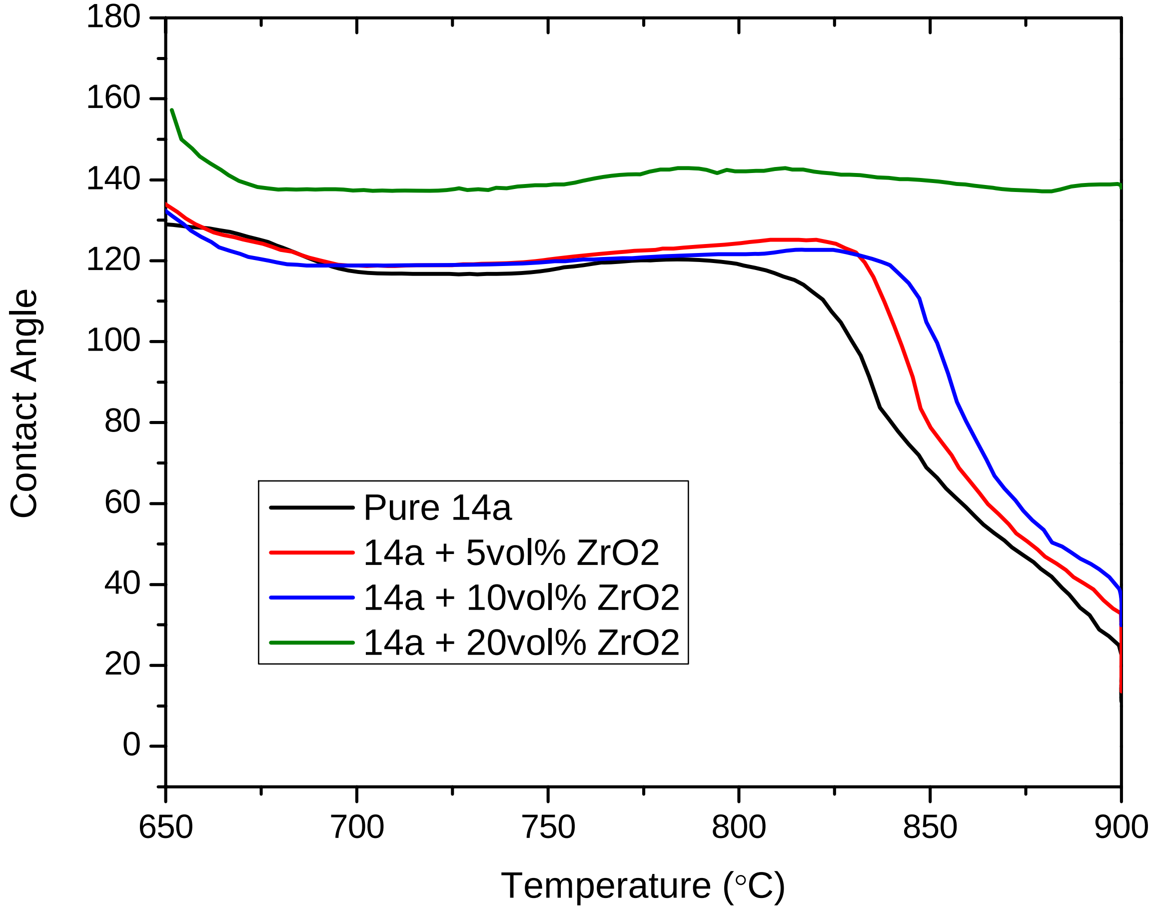
$$\varepsilon = \ln\left(\frac{h_i}{h_o}\right)$$

$\dot{\varepsilon}$=strain rate
$\Delta\varepsilon$=change in strain
Δt=change in time

ε=strain
h_i=instantaneous height
h_o=oringinal height

Glass wetting and spreading behavior can be controlled by addition of filler powder

Wetting and spreading data are needed to design sealing cycle



Fillers increase viscosity and apparent contact angles.

Transition to non-spreading behavior at higher powder volume fractions

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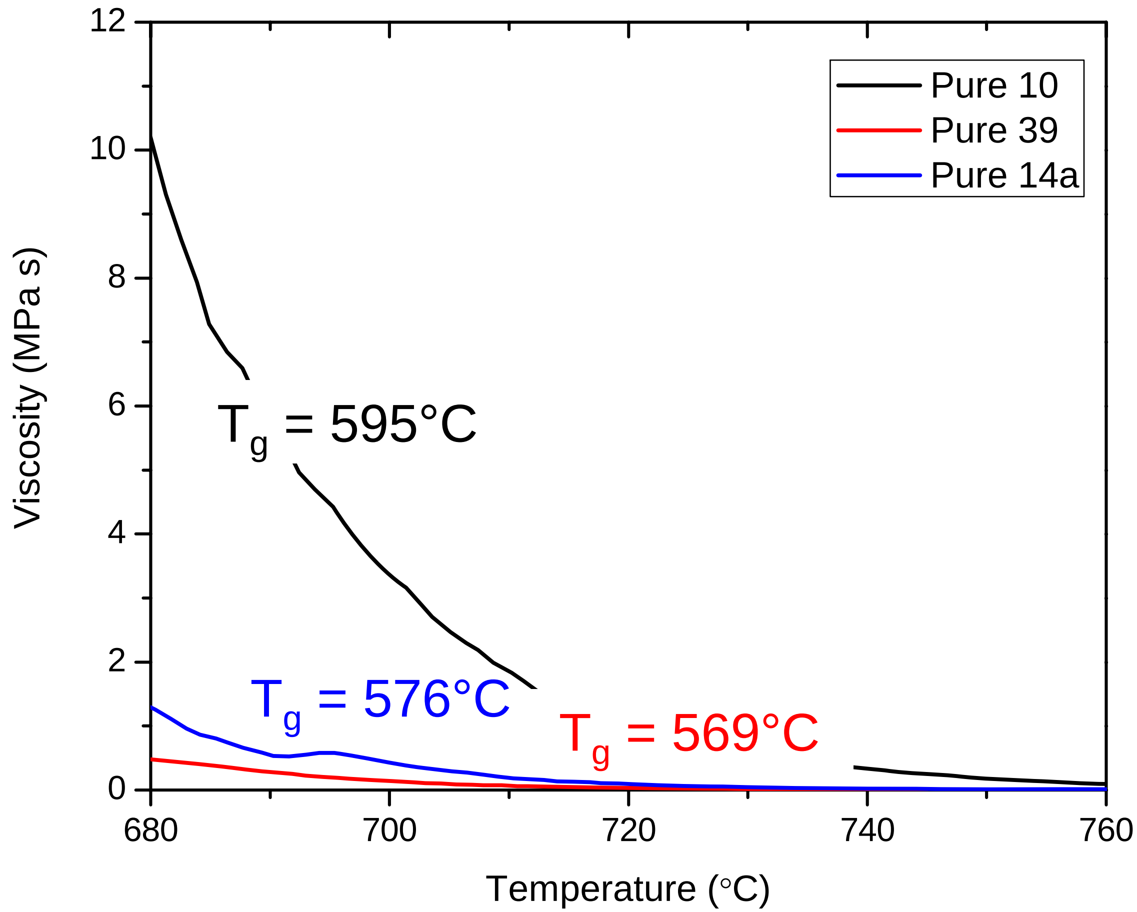
Temperature variation of glass viscosities show expected dependence on T_g

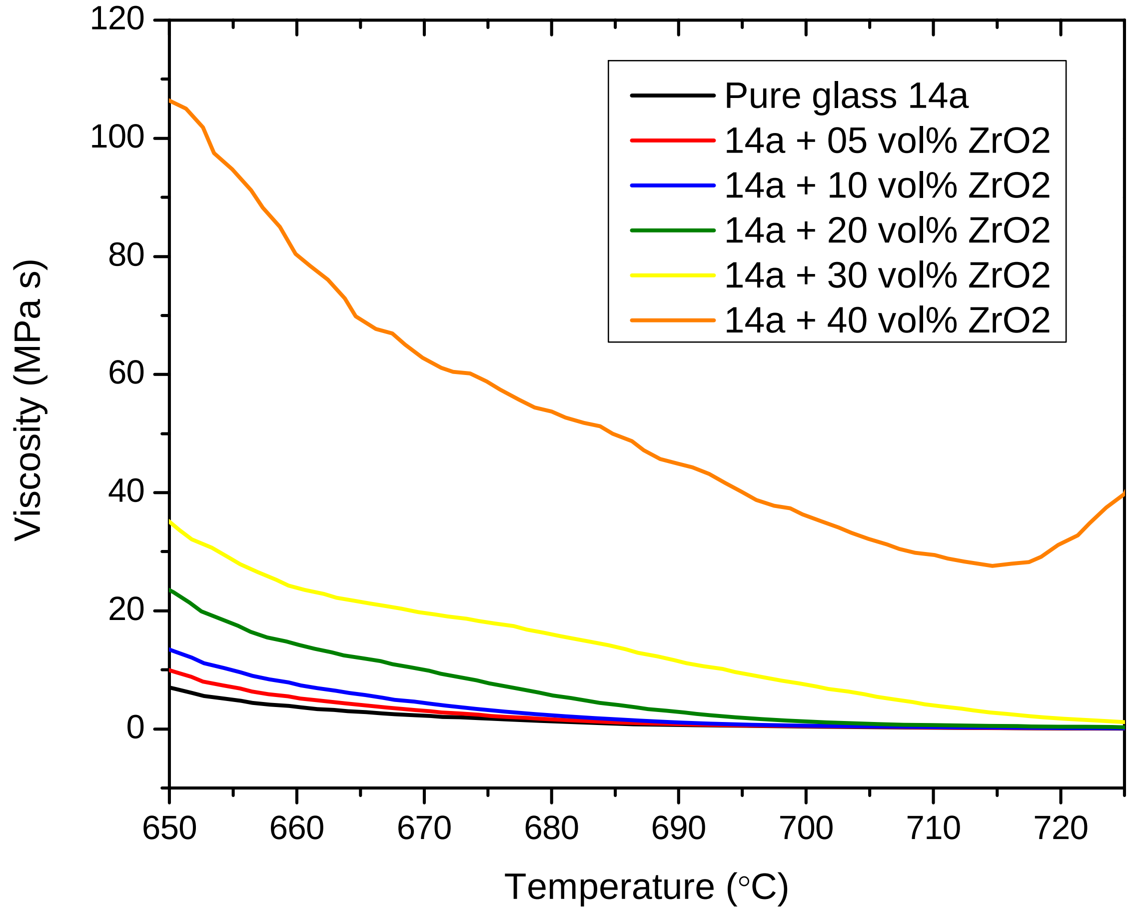


Addition of ZrO_2 powder systematically increases composite viscosity

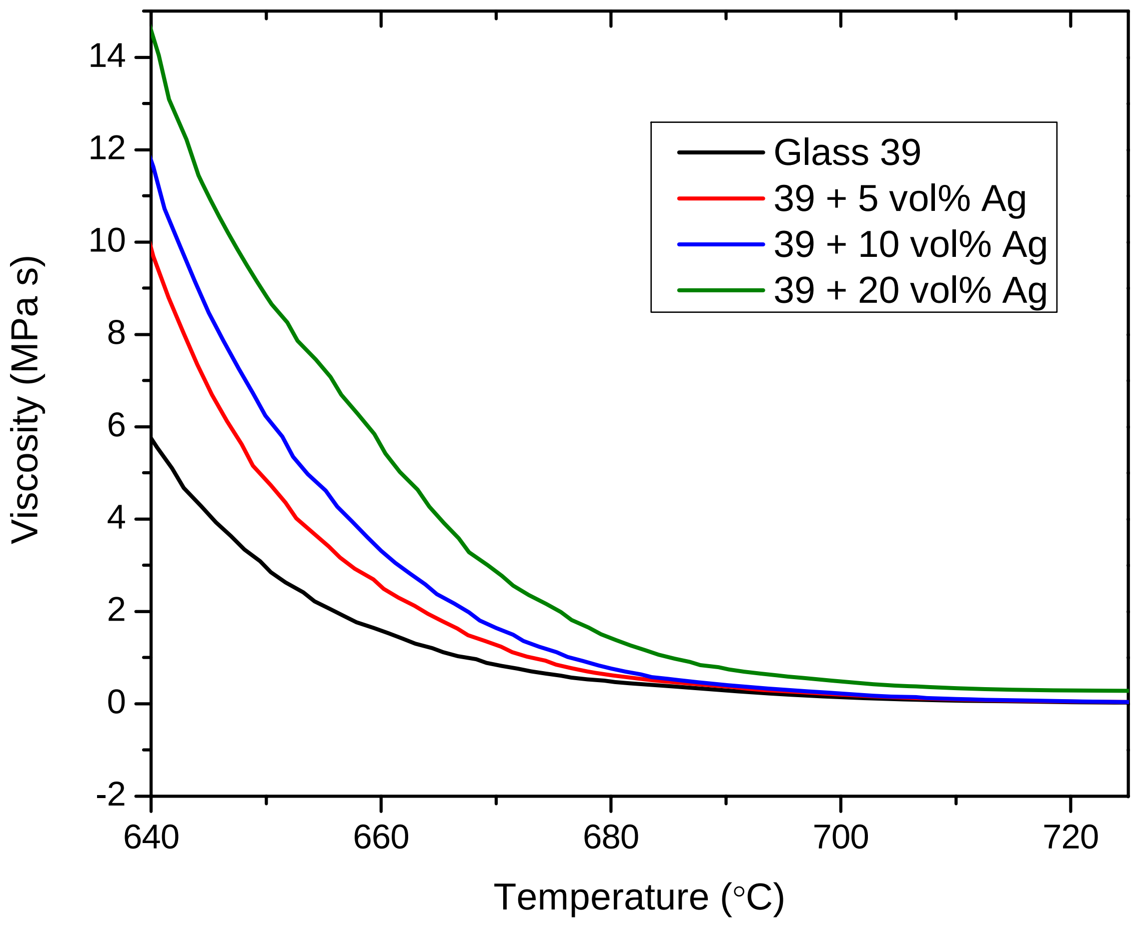
Such data allow rational design of composite seal compositions

$$\eta = \left(1 + \frac{\kappa\phi}{1 - \left(\phi / \phi_{max}\right)}\right)^2$$

κ = 1/particle size,
ϕ/ϕ_m = particle packing density



Addition of Ag powder also systematically increases composite viscosity



Long-term and functional tests show seal stability

- Glass and composite stability and reactivity

  vaporization with time at temperature

  crystallization

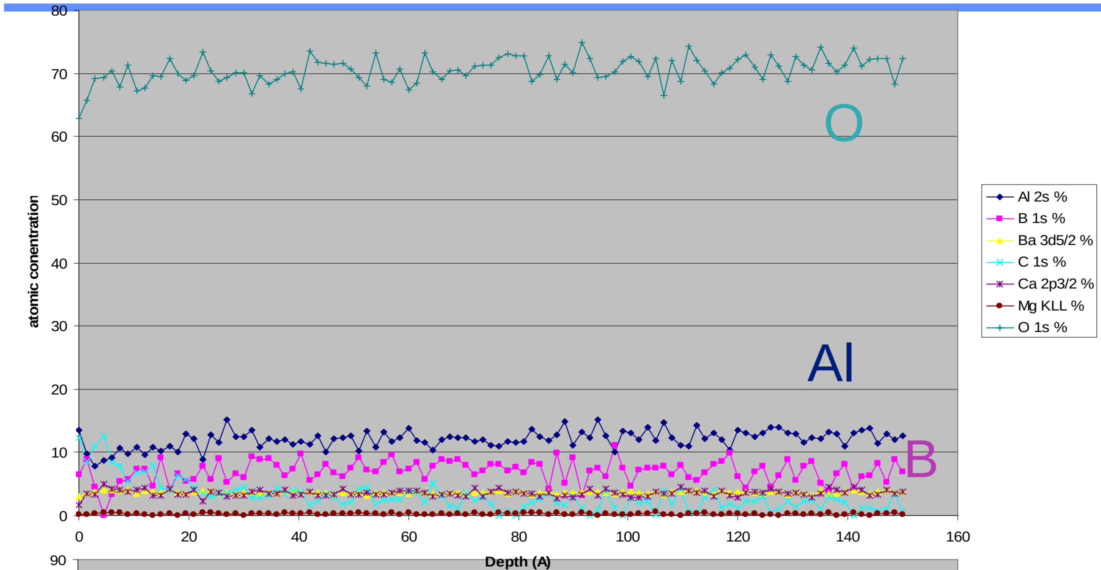
  reaction at joined interfaces

- Seal strengths

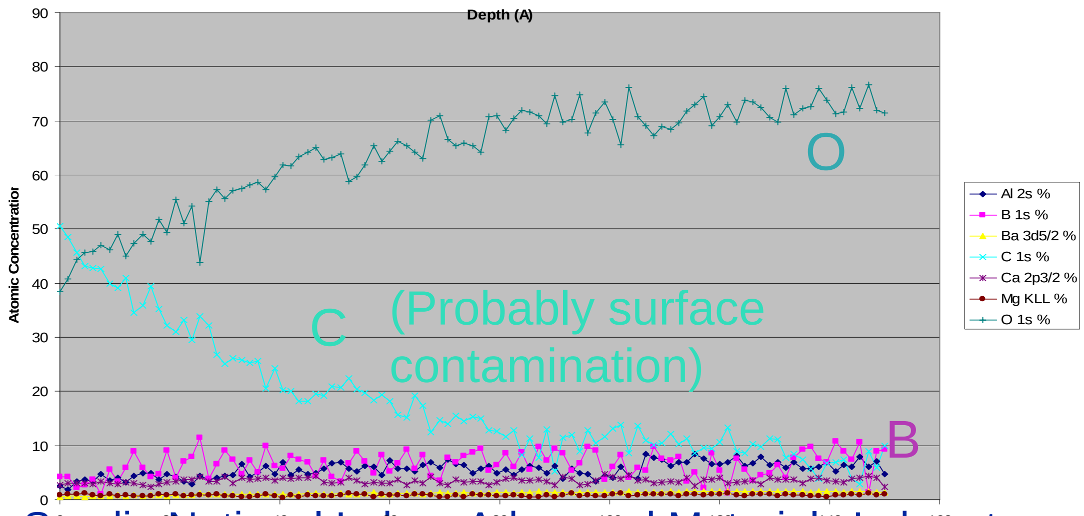
  at room temperature after thermal cycling

  at 750°C

XPS depth profiles show near surface compositions unchanged after 2000 hr at 750°C



Glass14a after 2000hr anneal

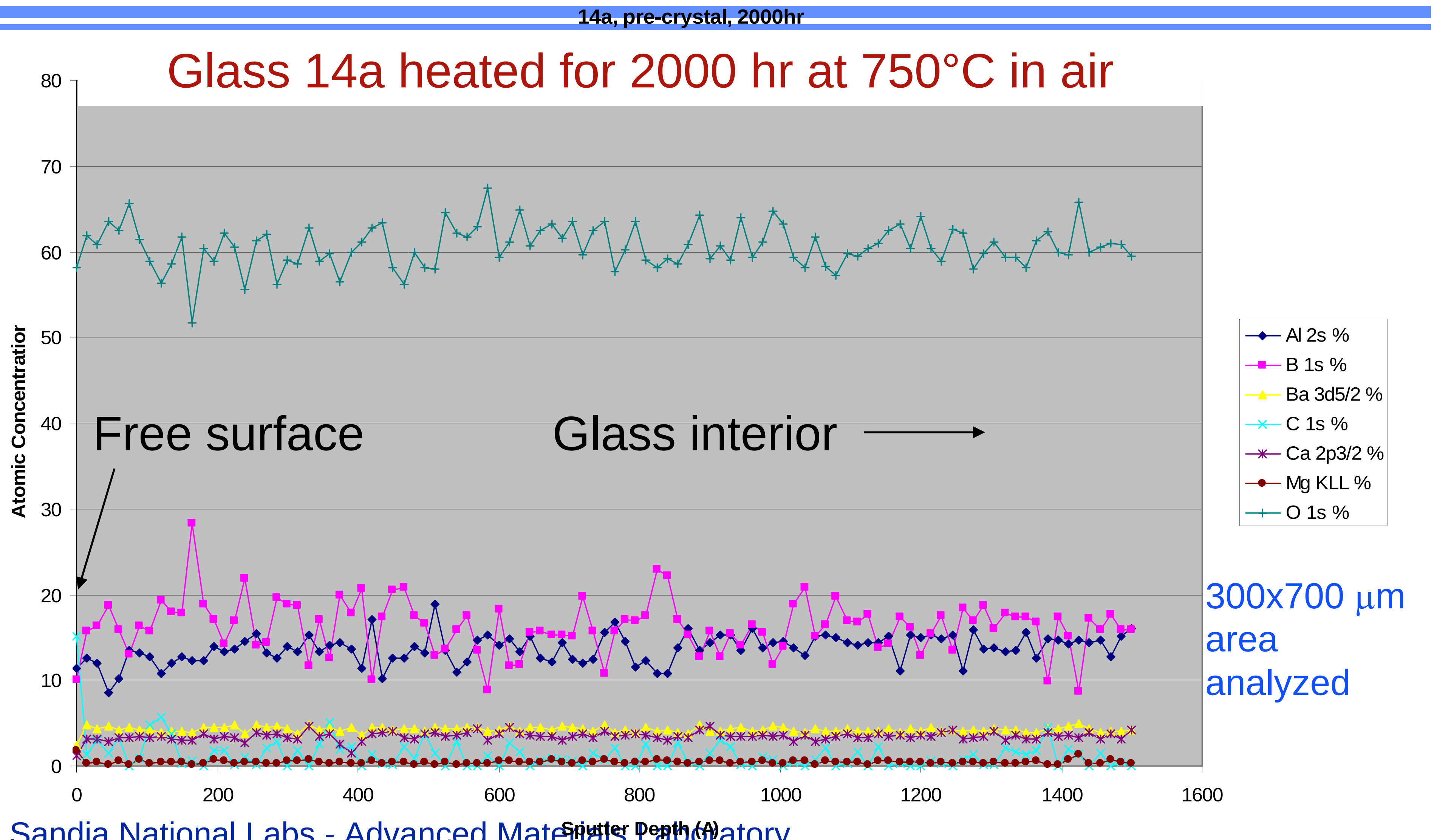


Glass14a, as-cast

Heated in air at 750°C

300x700 μm area analyzed

XPS sputter depth profiles show borate glass compositional stability at temperature



300x700 μm area analyzed

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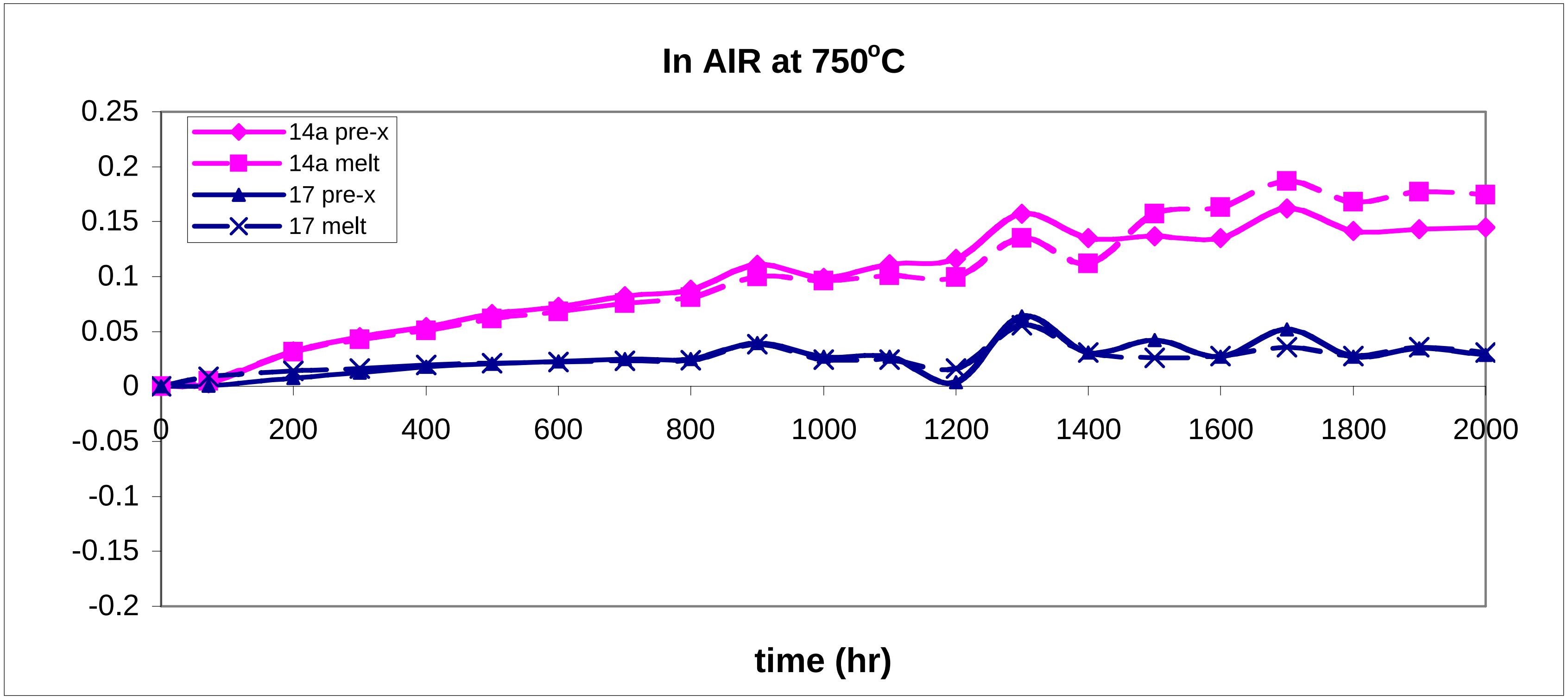
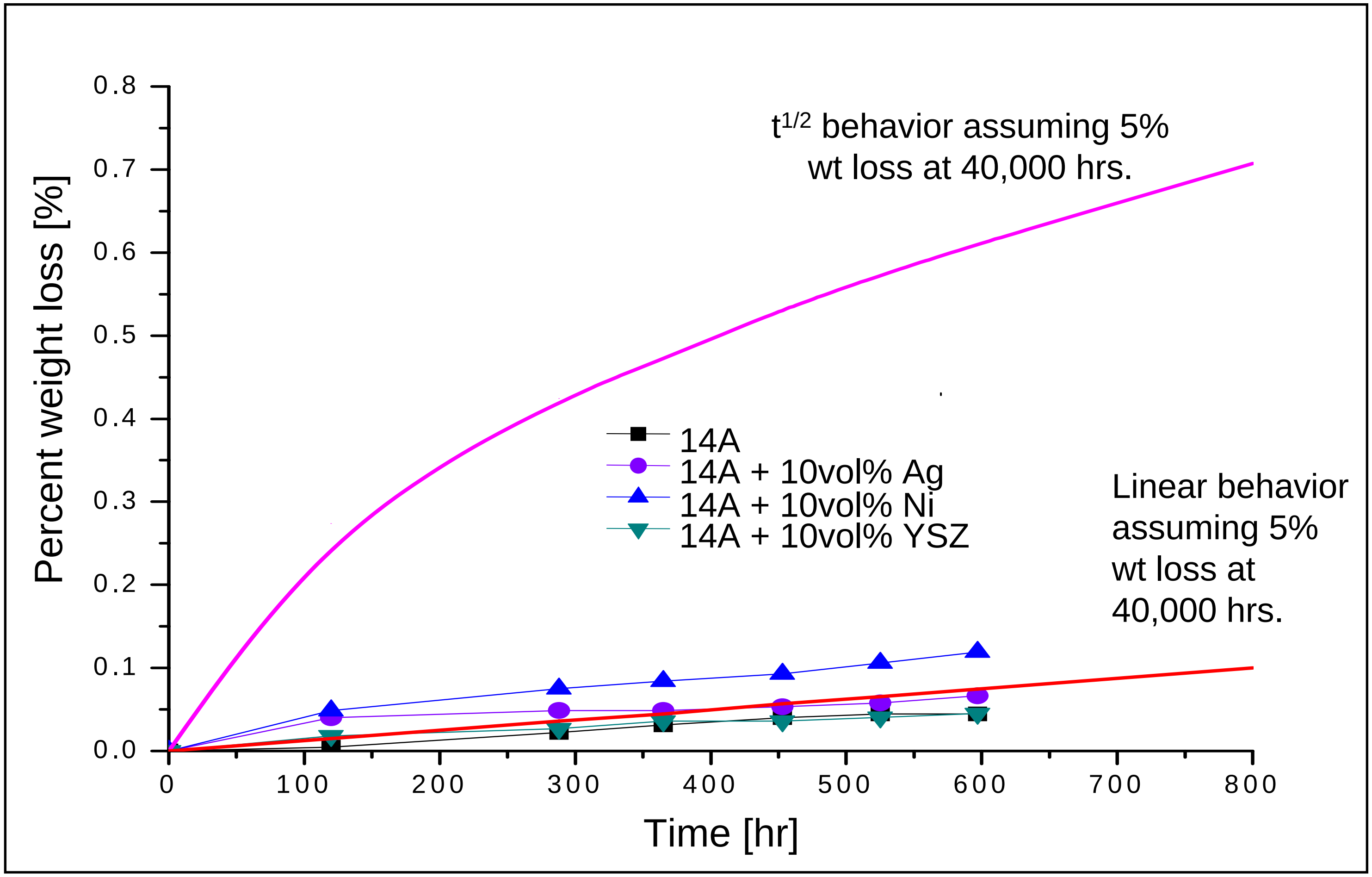
Low weight losses show sealing glasses are stable in long-term heating in air at 750°C

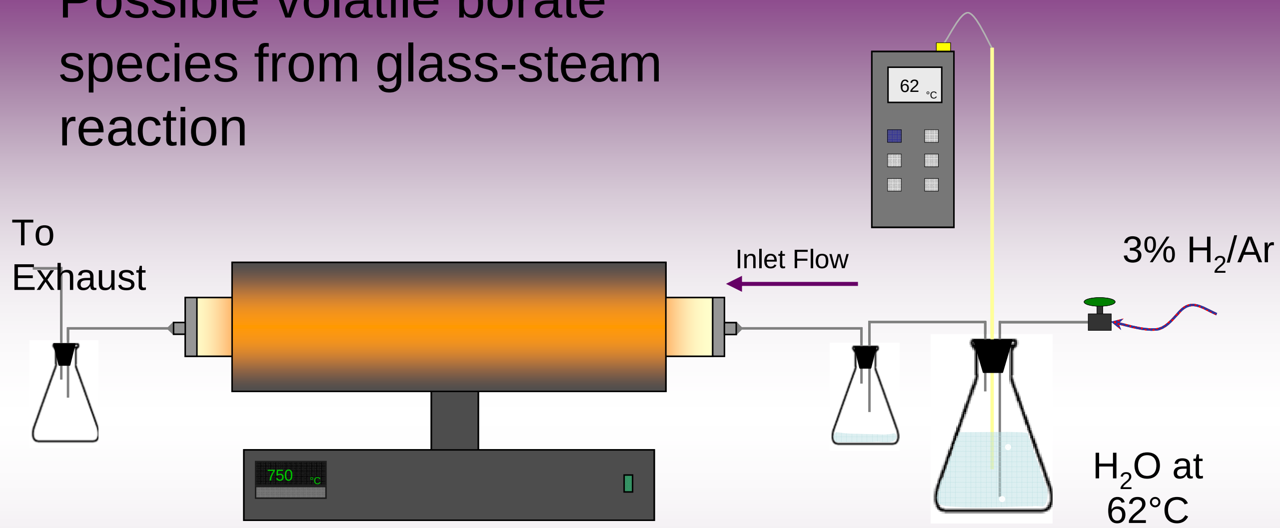


Extrapolated weight losses show stability of composite sealants after 40,000 hr operation



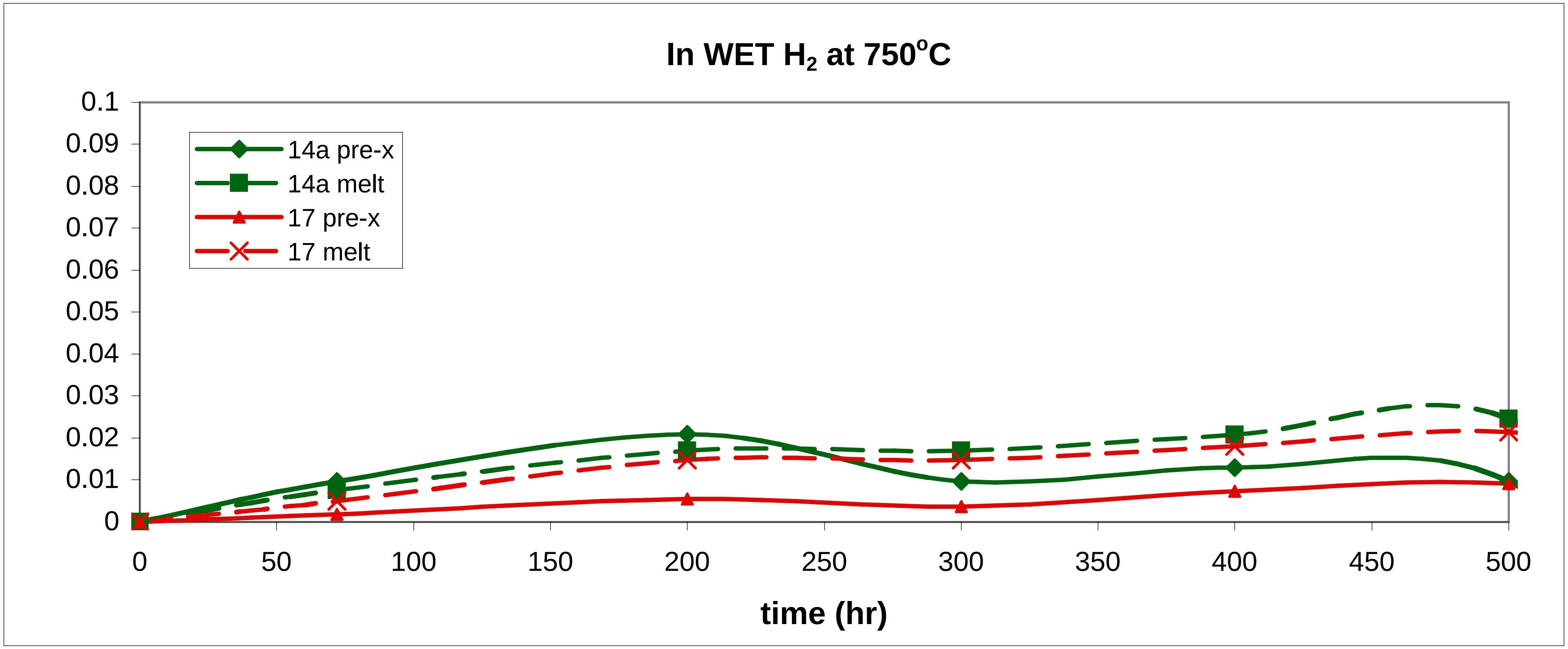
We are conducting long-term tests of composite seal material stability in a simulated steam atmosphere

Possible volatile borate species from glass-steam reaction

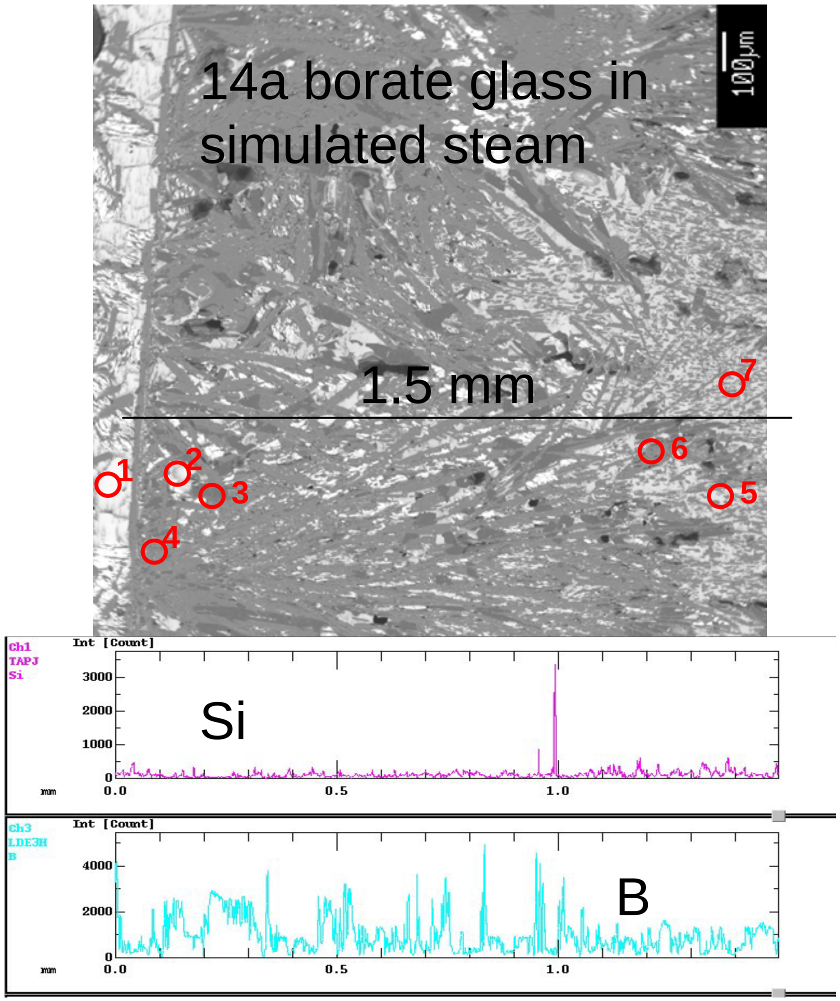


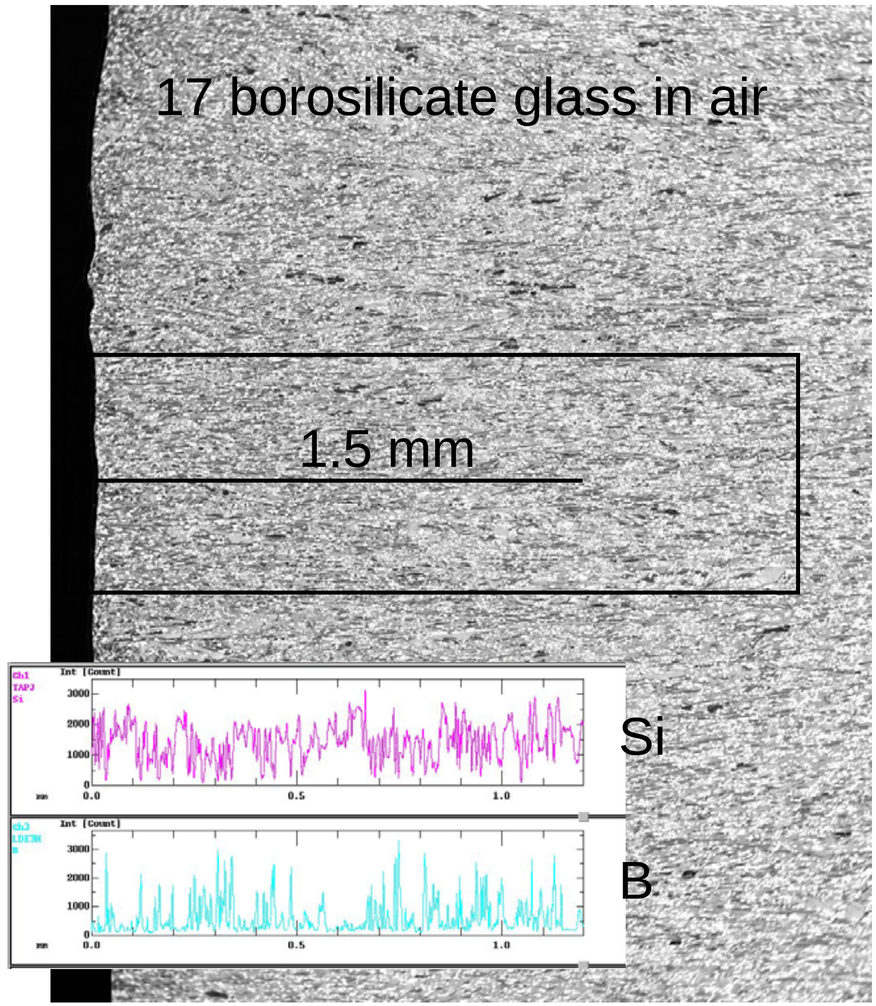
- 3% H_2/Ar bubbled through a 62°C water bath corresponds to 30% steam atmosphere
- Periodically remove samples to measure weight change
- Use measured data to estimate weight loss at 40,000 hour design lifetimes.

Sealing glasses show low weight loss after heating in simulated steam



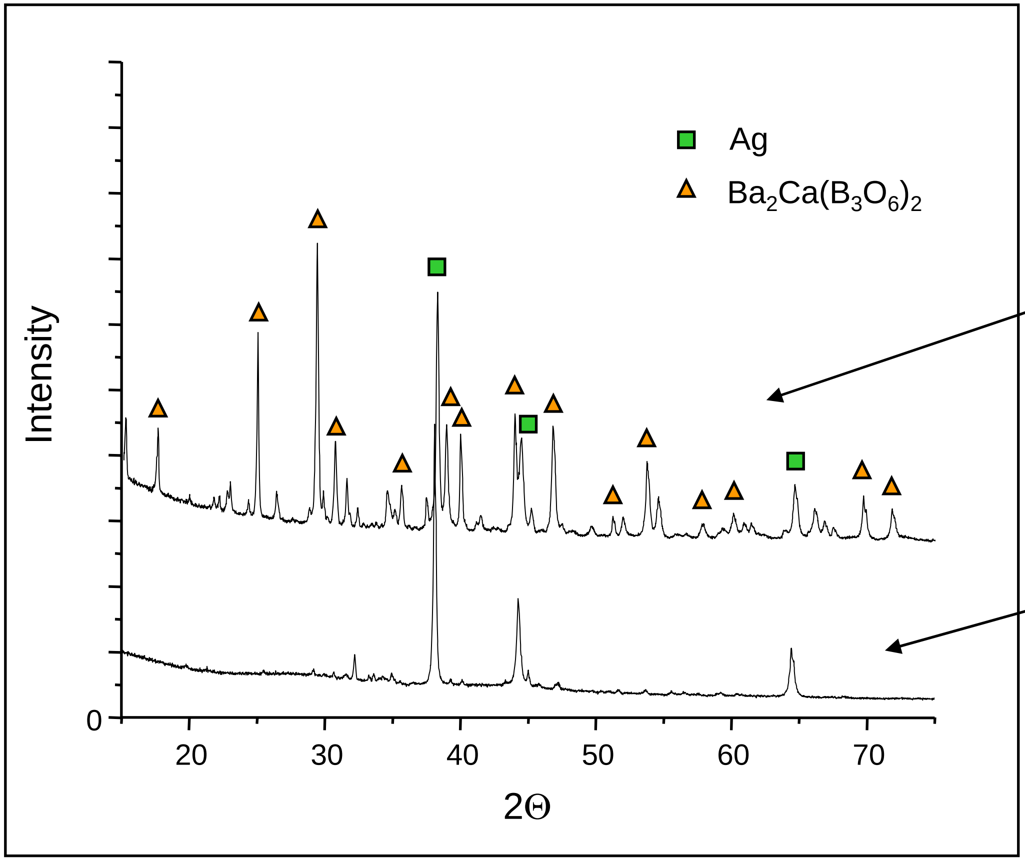
Microprobe scans show glass compositional stability after 500 hr at 750°C





XRD shows formation of $Ba_2Ca(B_3O_6)_2$ phase in 2000 hr samples

However, DTA experiments suggest crystallization occurs during the brief 900°C seal cycle and not subsequently at 750°C

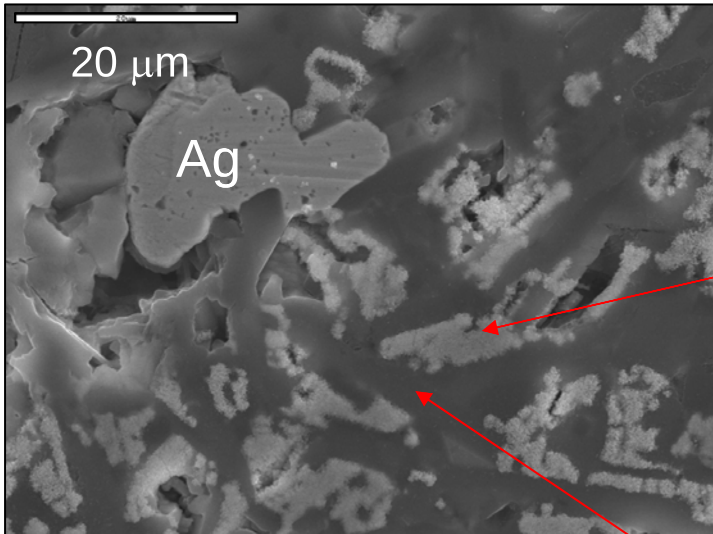


Glass 14a + Ag sealed at 900°C and heated at 750°C for 2000 hr

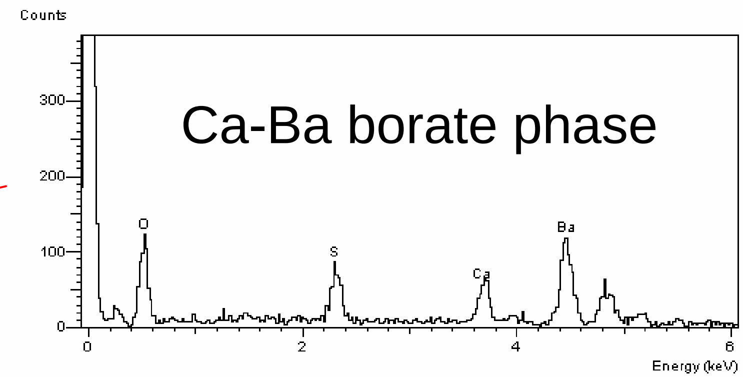
Glass 14a + Ag heated to 750°C for 20 min and cooled to RT

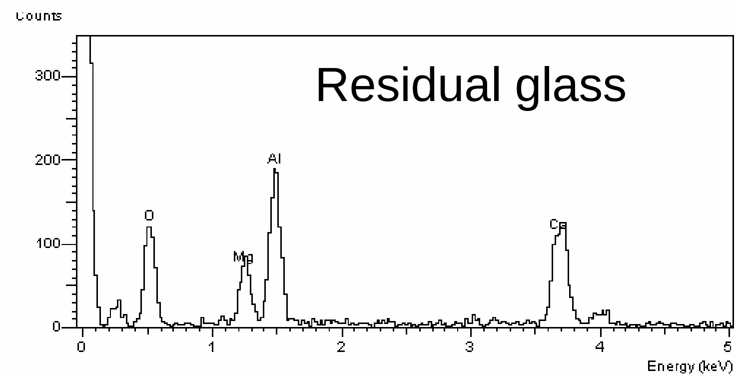
Crystallization accounted for by adjusting amount of added filler

After 2000 hrs at 750°C, glass 14a contains the same Ca-Ba borate phase as when initially sealed

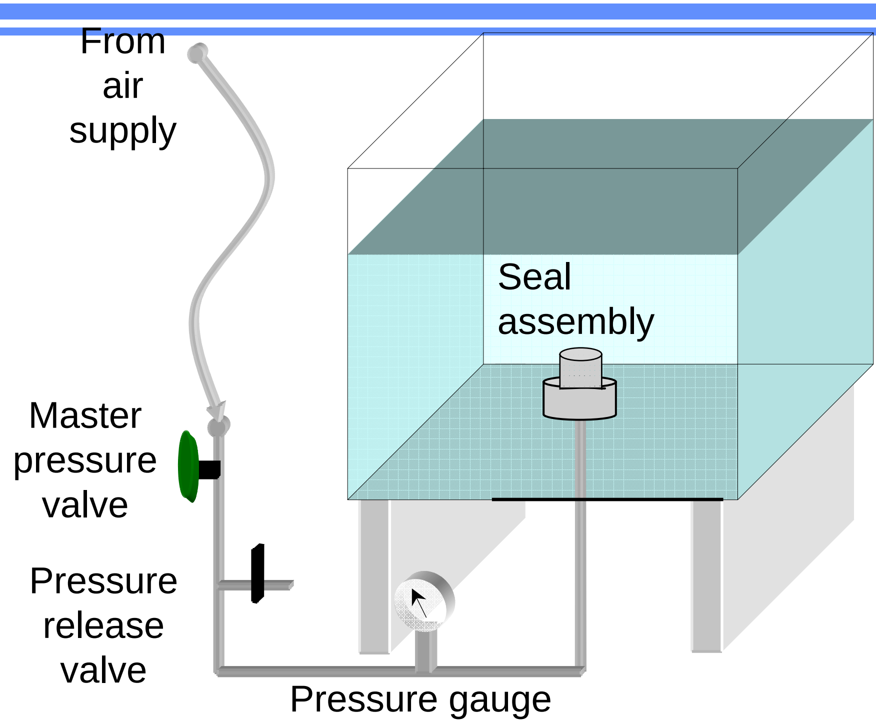


14a+Ag (4-7μm)
after 2000hr in air at 750°C



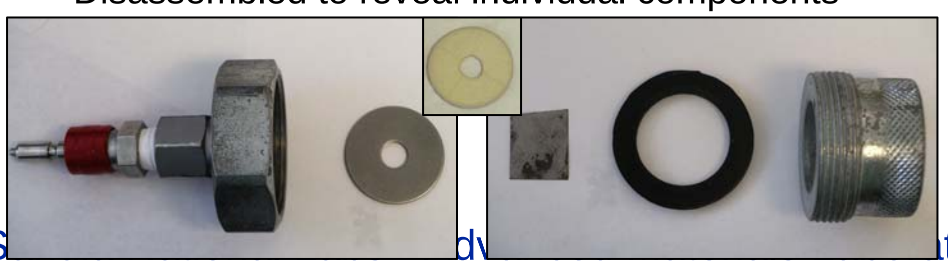


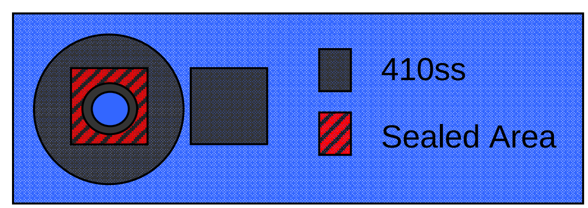
Gas pressure test is used to detect leaks and measure seal strengths



- Room temperature test assumes that flaws at operating temperature will likely persist at RT.
- To test for leaks as well as strength.
- Test to failure (i.e. air bubble leakage), up to 4 atm (60psi).
- Determine stress per unit bond (sealed) area at failure.

Seal assembly
Disassembled to reveal individual components





Glass-Ag composite seals are strong after repeated thermal cycles

SS410 - SS410 seals taken to 750°C and tested at room temperature

No. of samples	Bond thickness	Avg Pressure kPa (psi)	No. heat cycles ea.	Avg Strength# N/mm^2 (psi)
2*	0.22 mm	>413.7 (60)	10	0.084 (12.2)
5*	0.22	>413.7 (60)	9	0.126 (18.3)
1*	0.22	>413.7 (60)	3	0.129 (18.8)
1*	0.53	>413.7 (60)	3	0.126 (18.8)
1*	1.02	>413.7 (60)	3	0.124 (18.0)
3	0.46	39.3 (5.7)	1	0.010 (1.5)
3	0.22	34.9 (5.1)	1	0.0088 (1.3)

* Metal etched before sealing

failure stress/bond area

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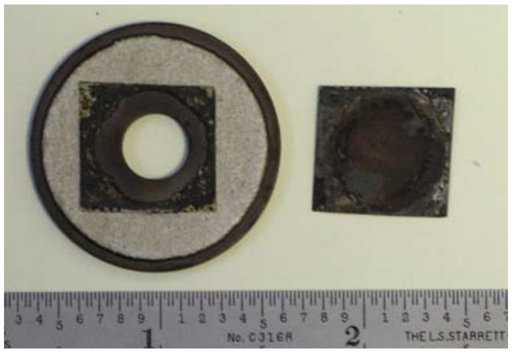
Glass composite seals are inherently self healing

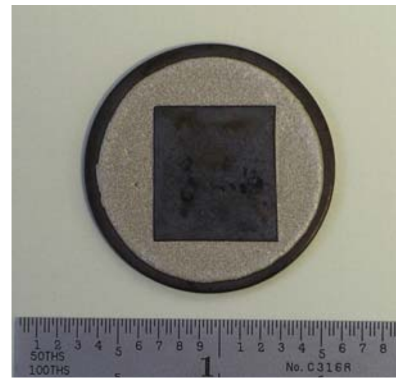
410/Glass-Ag/410 ss

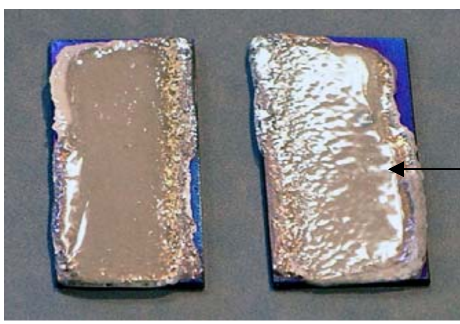


Reheated to sealing temperature

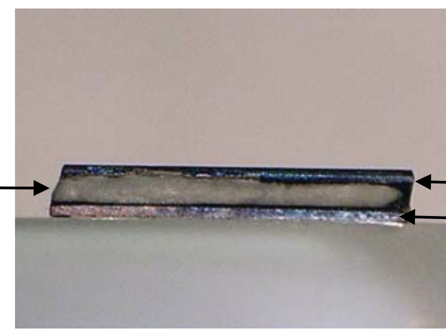
850°C for 10 min.

410/Glass-Ag/410 ss





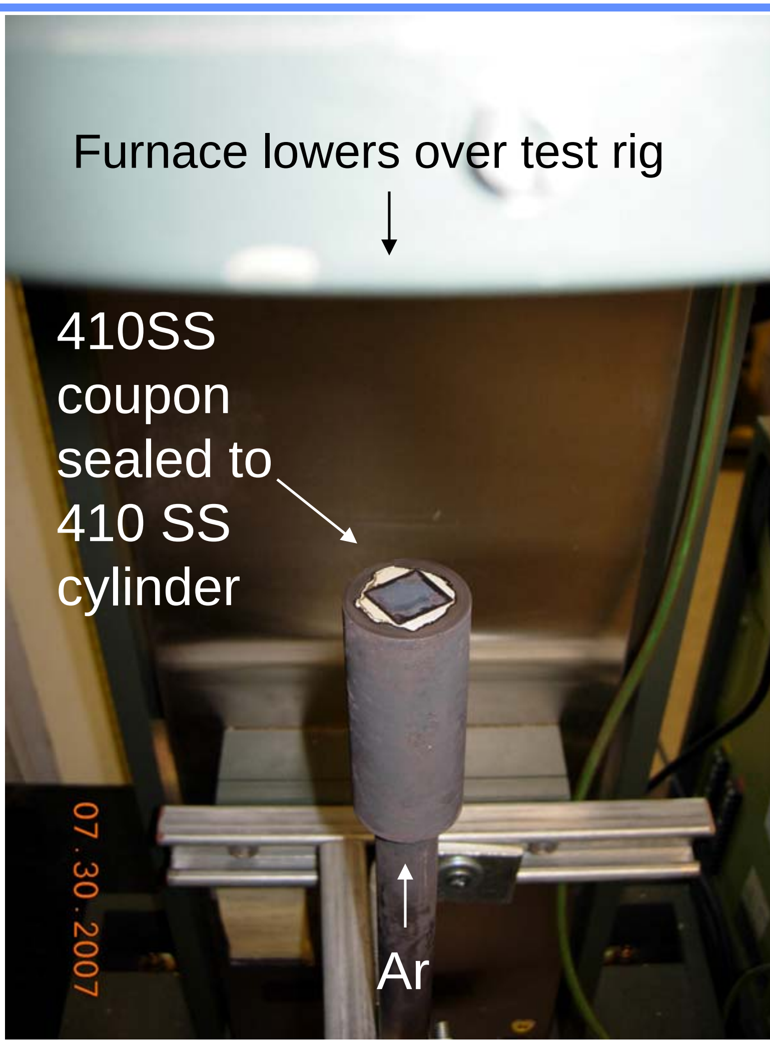
Sealing glass



Ebrite

Essential requirement is a continuous glass network with a T_g ~ 100 to 200 °C below the desired sealing temperature

Pressure tests at 750°C show strength of composite seals



Test surface after at-temperature debond

No. of samples	Avg failure pressure	Avg failure strength[@] 750°C
2	52.4±2.9 kPa, 7.6±.85 psi	.012 N/mm^2 1.8 psi
3*	97.2±10.6 kPa 14.1±1.5 psi	.020 N/mm^2 2.9 psi
3*	Held 3 psi for 30 min at 750°C	

* Etched 410ss

[@] stress/bond area

Summary and Conclusions

- Glass composites are a versatile technique for sealing SOFCs
- The method has been demonstrated for a range of glass and filler compositions
- Glass and filler compositions can be optimized independently
- Our borate and borosilicate sealing glasses exhibit long-term stability at 750°C
- They make strong, leak tight seals to ferritic stainless steel alloys

Future Work

- make seals to 441 alloy
- continue evaluating long-term stability
- obtain more strength data, particularly at temperature
- evaluate seals using PNNL test bed