Engineered Glass Composites for Sealing Solid Oxide Fuel Cells

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Albuquerque, NM USA

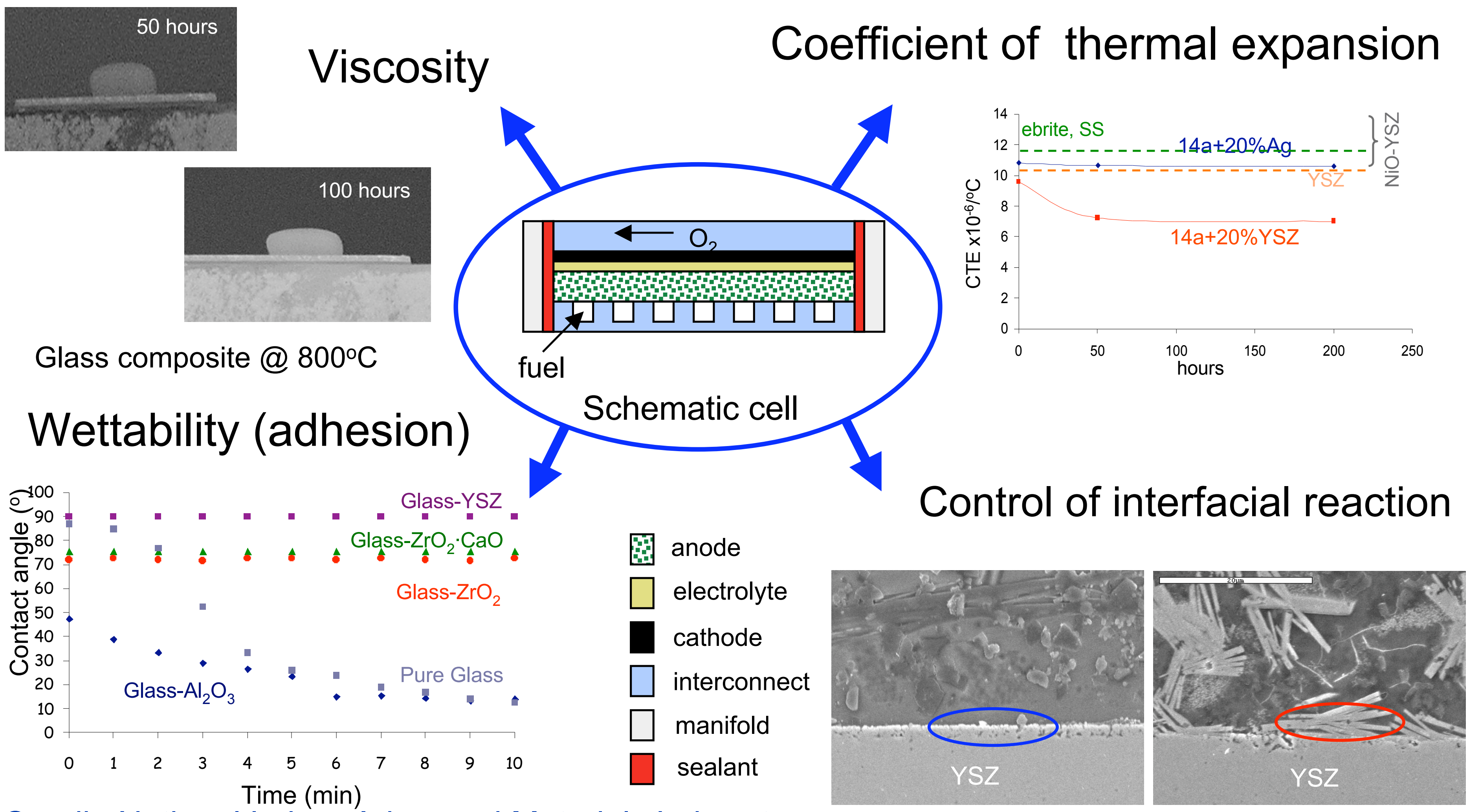
SECA Core Technology Program Review, October 25 - 26, 2005, Lakewood, CO, USA

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Our overall objective is to develop practical joining techniques for SOFCs

- Develop reliable, cost-effective seals based on glass-filled composites
- Determine performance-limiting features of sealing methods
- Optimize seal properties
- Determine seal degradation mechanisms and predict useful seal lifetimes

Glass composites allow us to design for specific seal properties



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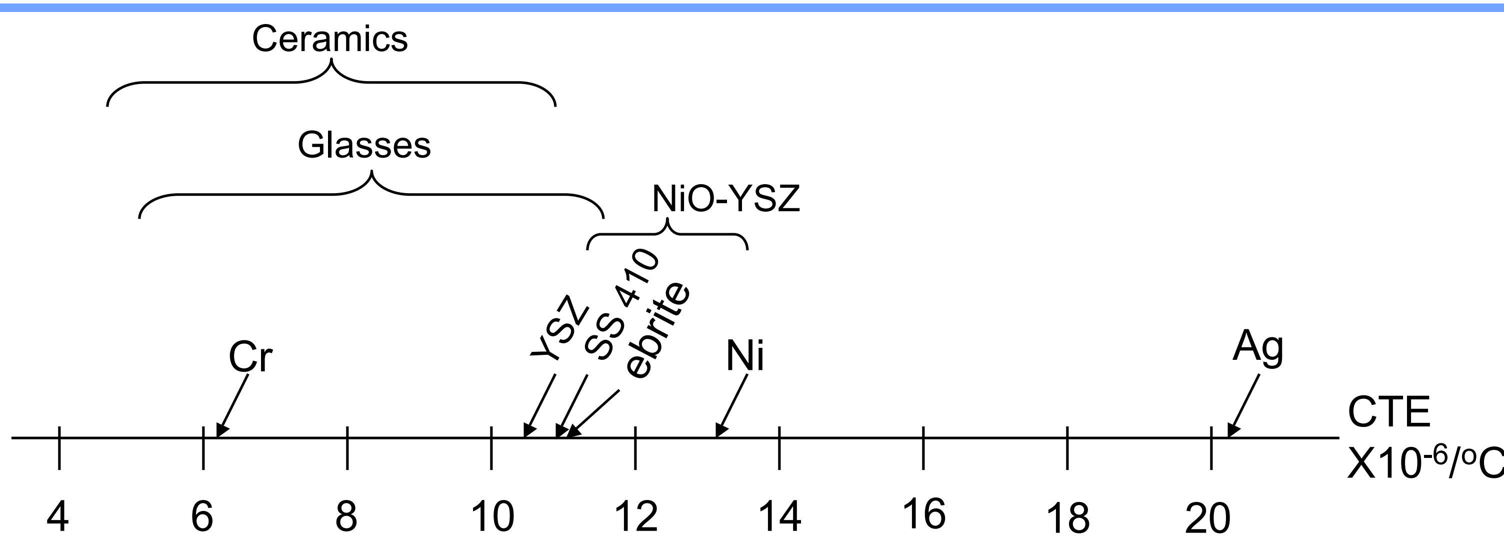
Sealing requires optimization of mutually incompatible material properties



Composites can take advantage of different glass properties

Fluid glasses
- Low Tg, Low Cryst T

Refractory glasses
- High Tg, High Cryst T

Design of glass-ceramic composites optimizes required material properties
- Moderate fluidity for adhesion & self healing
- Reduced crystallization for control of CTE

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Composite seals can be engineered to provide a wide range of chemical and mechanical properties

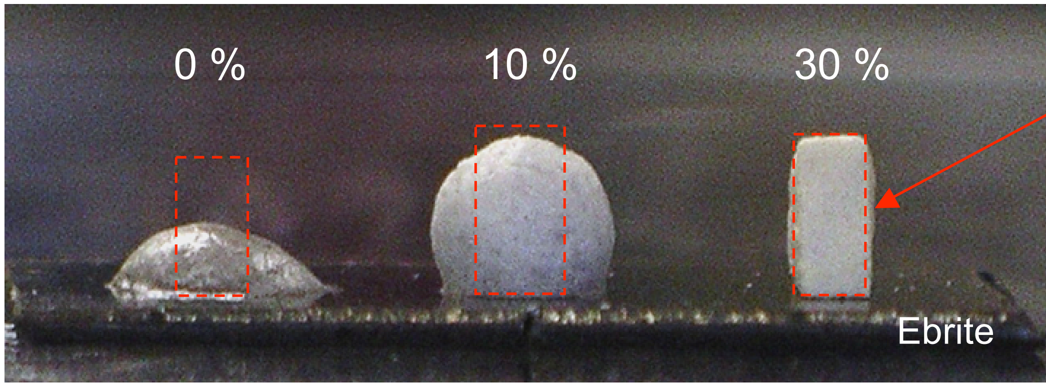
- Composite approach allows glass and filler to be optimized independently
- Glass phase is above its T_g at SOFC operating temperature to reduce thermal and mechanical strains
- Control viscosity, CTE, etc. by adding unreactive powder
- Volume fraction of glass phase can be reduced to minimum for seal

$$\alpha = \frac{\alpha_1 K_1 V_1 + \alpha_2 K_2 V_2}{K_1 V_1 + K_2 V_2}$$

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

Seal wetting and flow properties can be controlled by the composite glass-powder ratio

Side view



Initial pellet shape

Top view

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

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Specific FY05 project milestones

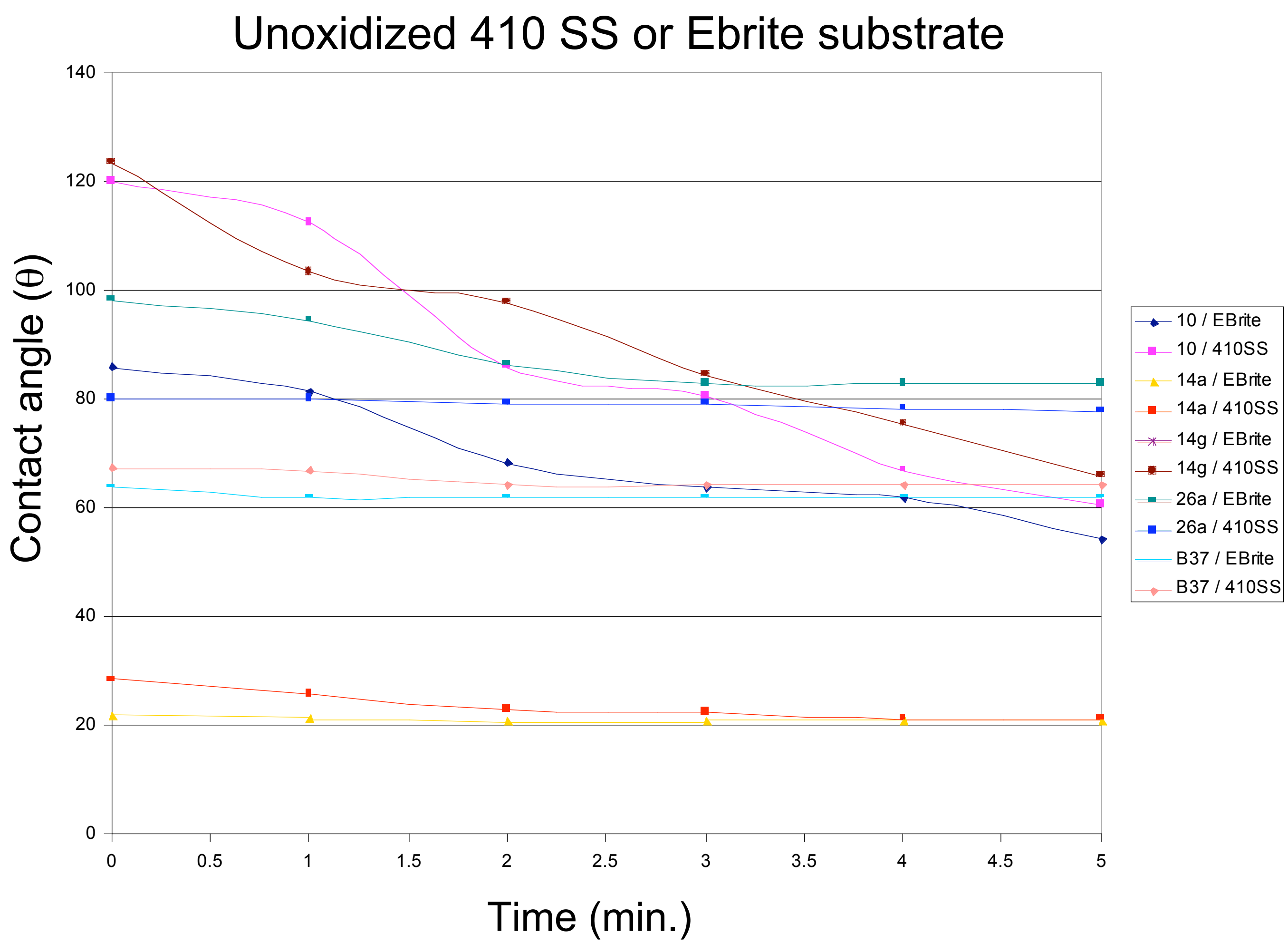
Q1: Test glasses for reactivity with anode materials

Q2: Test glasses and glass composites for reactivity with interconnect; identify any Cr dissolution and migration

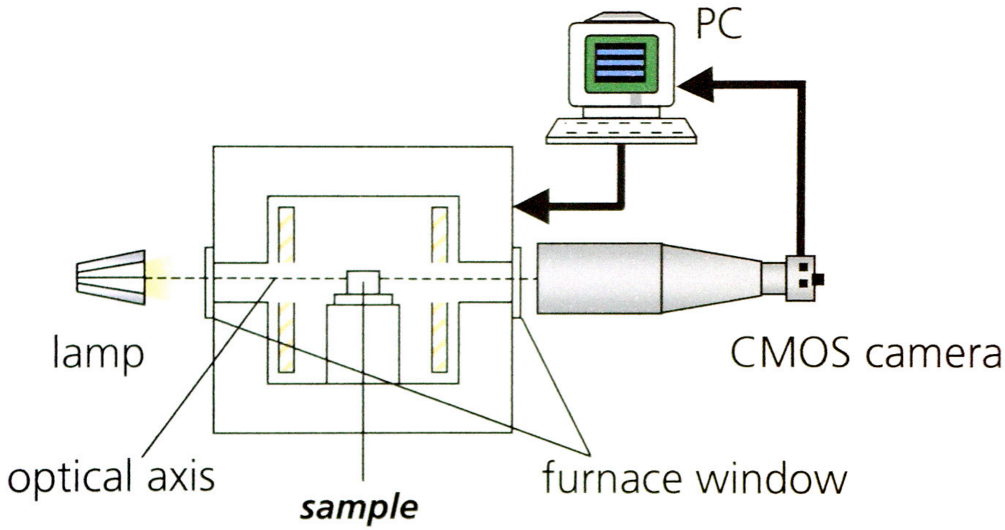
Q3: Determine effect of interconnect preoxidization on wetting and adhesion

Q4: Determine glass-composite stability at operating temperature for interconnect-anode seals

Varied glass compositions provide a wide range of flow properties on stainless steel alloys



Properties of glass-powder composites were measured using a high-temperature furnace with in situ video capabilities (TOMMI)



schematic diagram of TOMMI

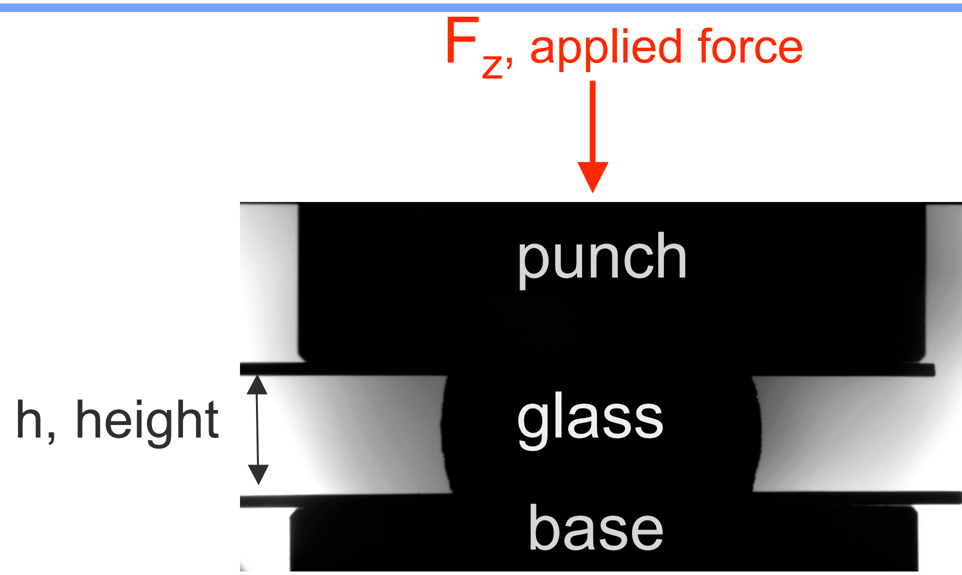
- Non-contact, optical measurements
- CTE measurement
- Contact angle measurement
- Viscosity determination
- Loaded sintering
- Thermogravimetric analysis
- Oxidation studies

Measured uniaxial viscosity is related to the composite shear viscosity

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

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

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



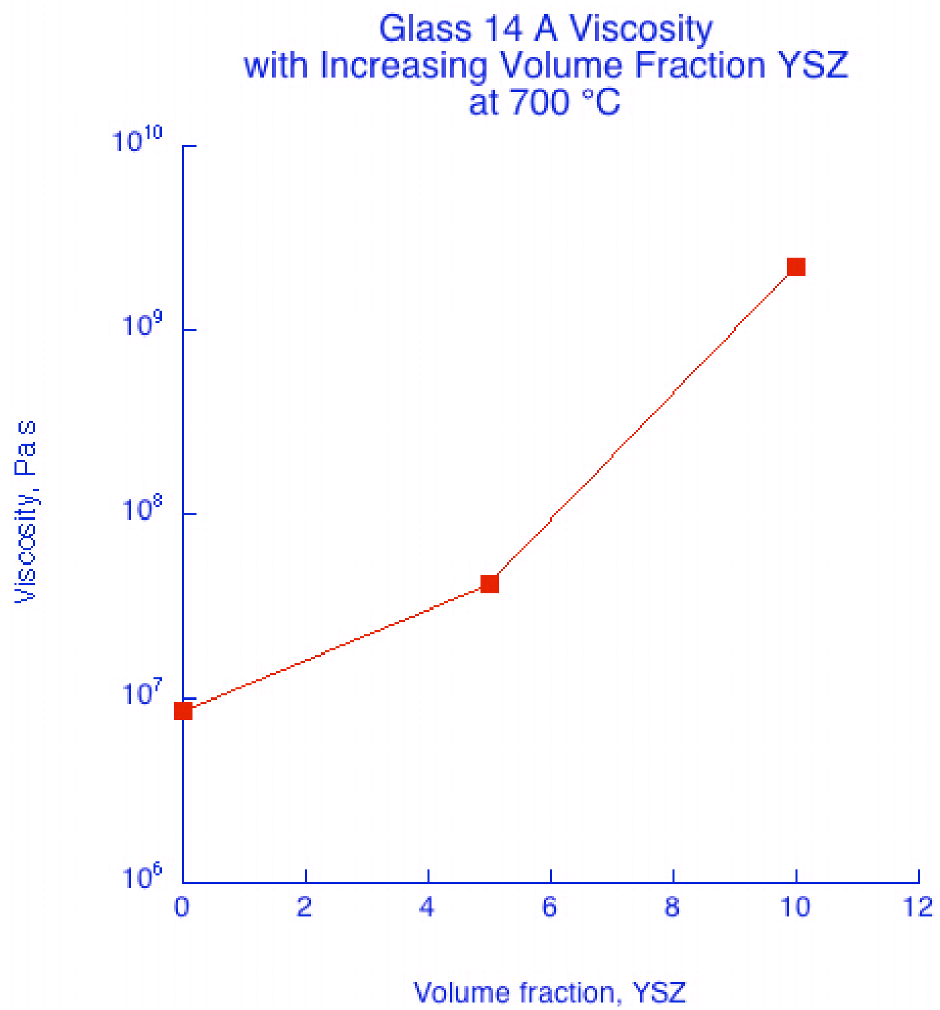
$$\dot{\varepsilon}_z = \frac{\Delta \varepsilon_{\varepsilon}}{\Delta t}$$

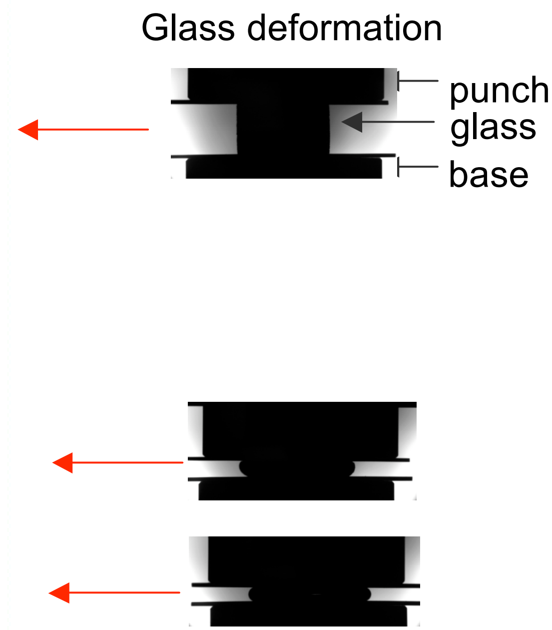
$$\varepsilon = \ln\left(\frac{h_i}{h_o}\right)$$

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

ε=strain
h_i=instantaneous height
h_o=oringinal height

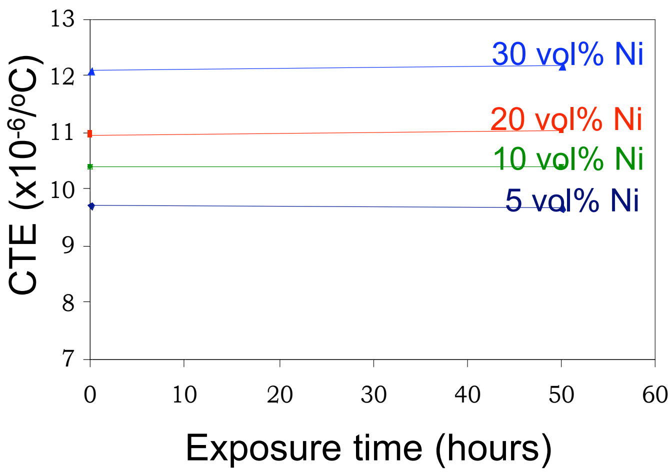
As predicted, composite viscosity increases with increasing volume fraction of powder filler



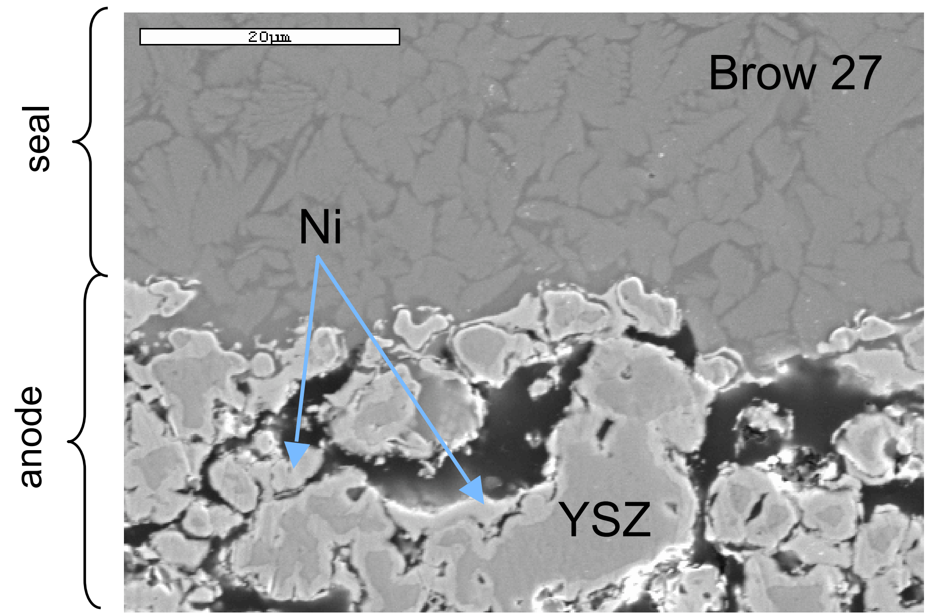


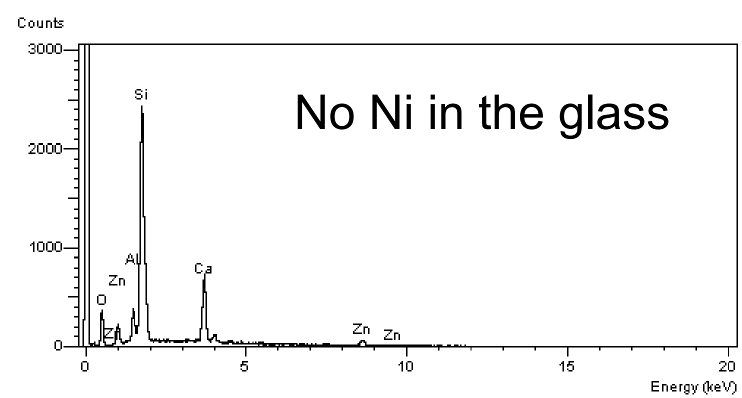
Studies of glass/anode reactivity show that glass is compatible with pure Ni and with anode compositions

CTE of seal made with Brow 27 can be adjusted by Ni additions



No change of CTE over first 50 hours of exposure at 800°C

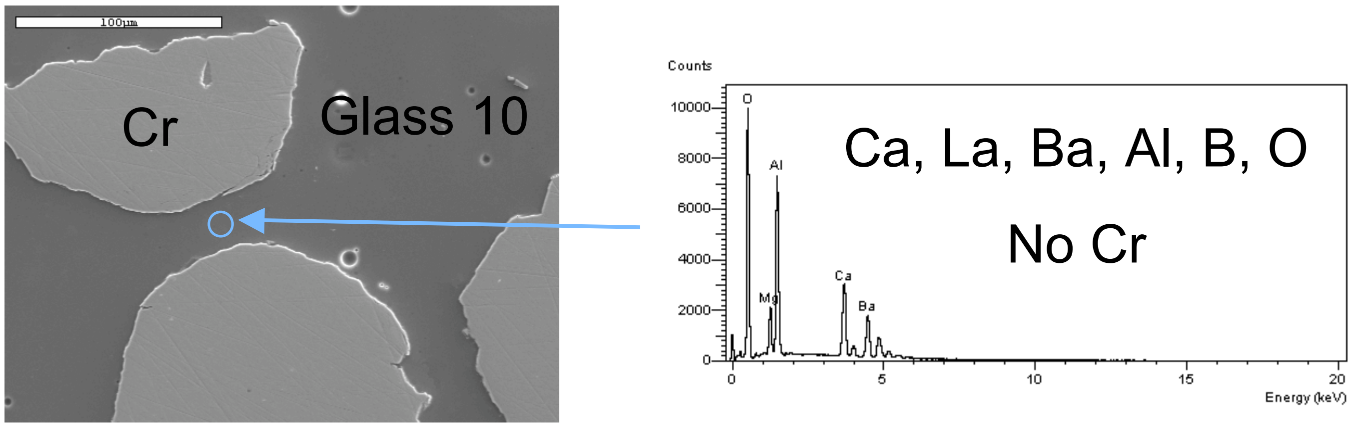


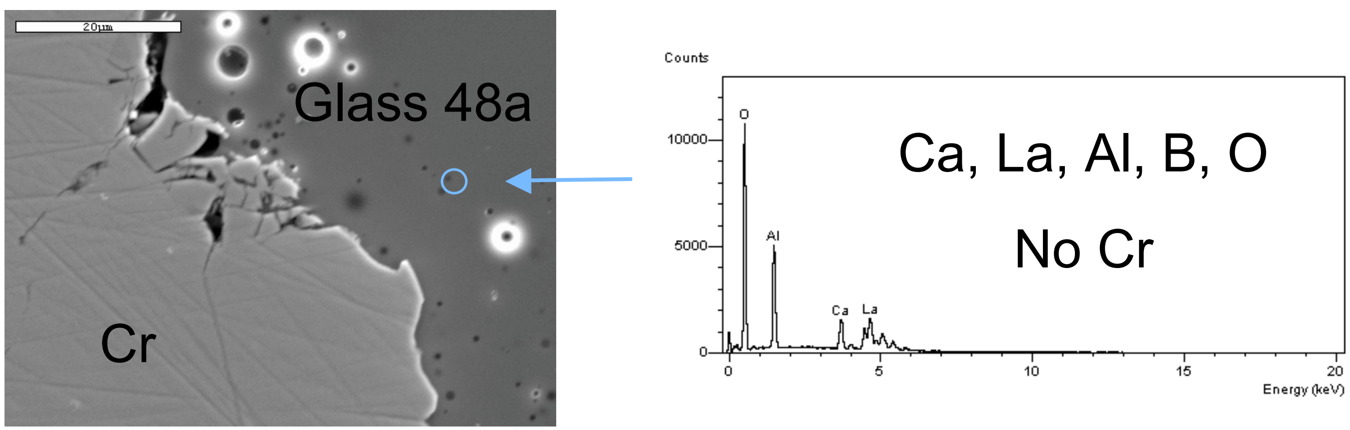


Cr is the most reactive species in interconnect materials

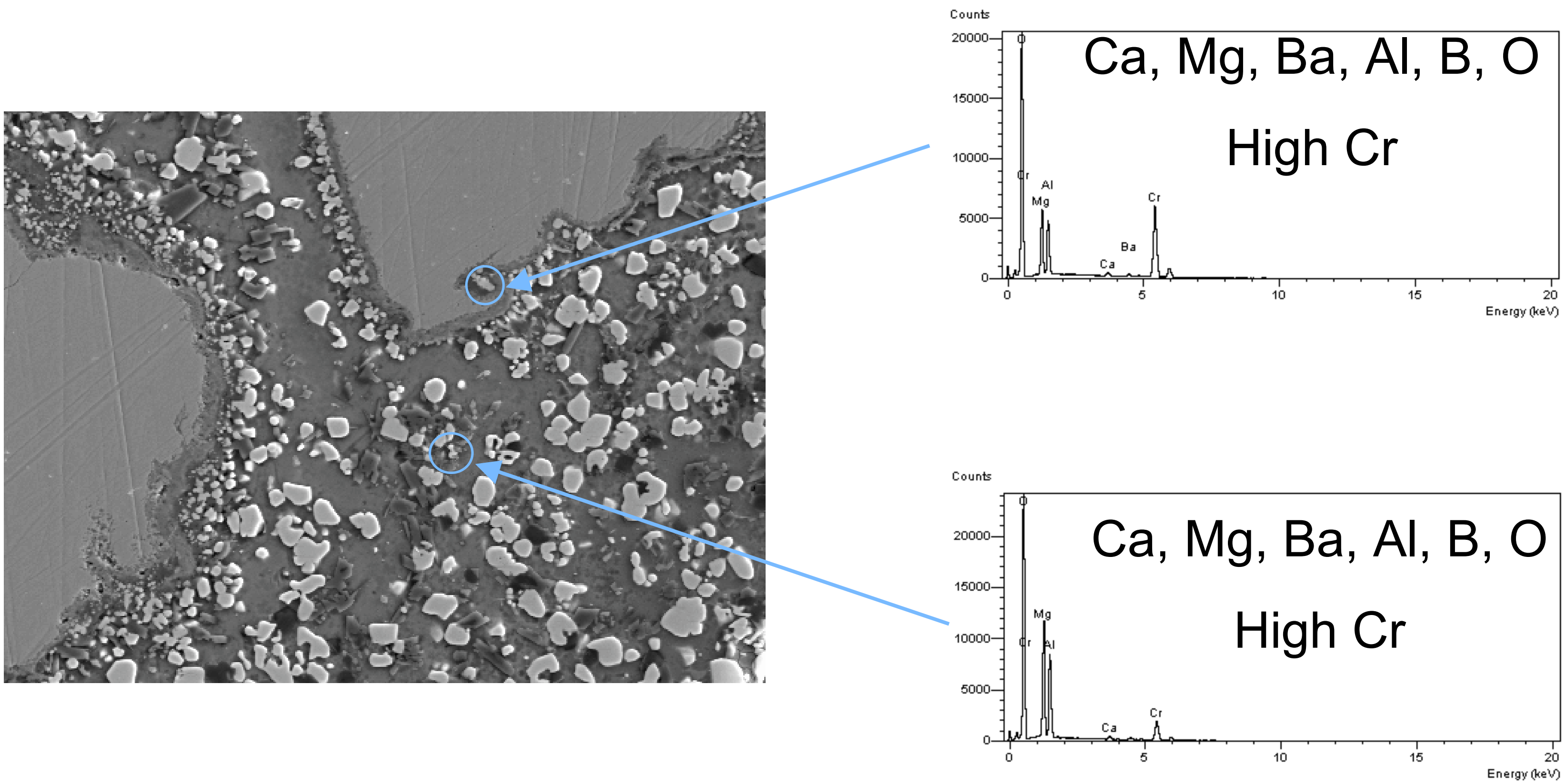
- Several glass compositions were blended with Cr powder and heated to 750°C and 850°C for 3 hours
- Large Cr surface area enhances potential for Cr dissolution in molten glass
- Pure Cr instead of bulk stainless steel alloy increases Cr concentration available for dissolution
- Thus, an accelerated test for Cr dissolution into glass from interconnect

After 3 hours at 750°C no dissolution from Cr particles is observed in sealing glasses

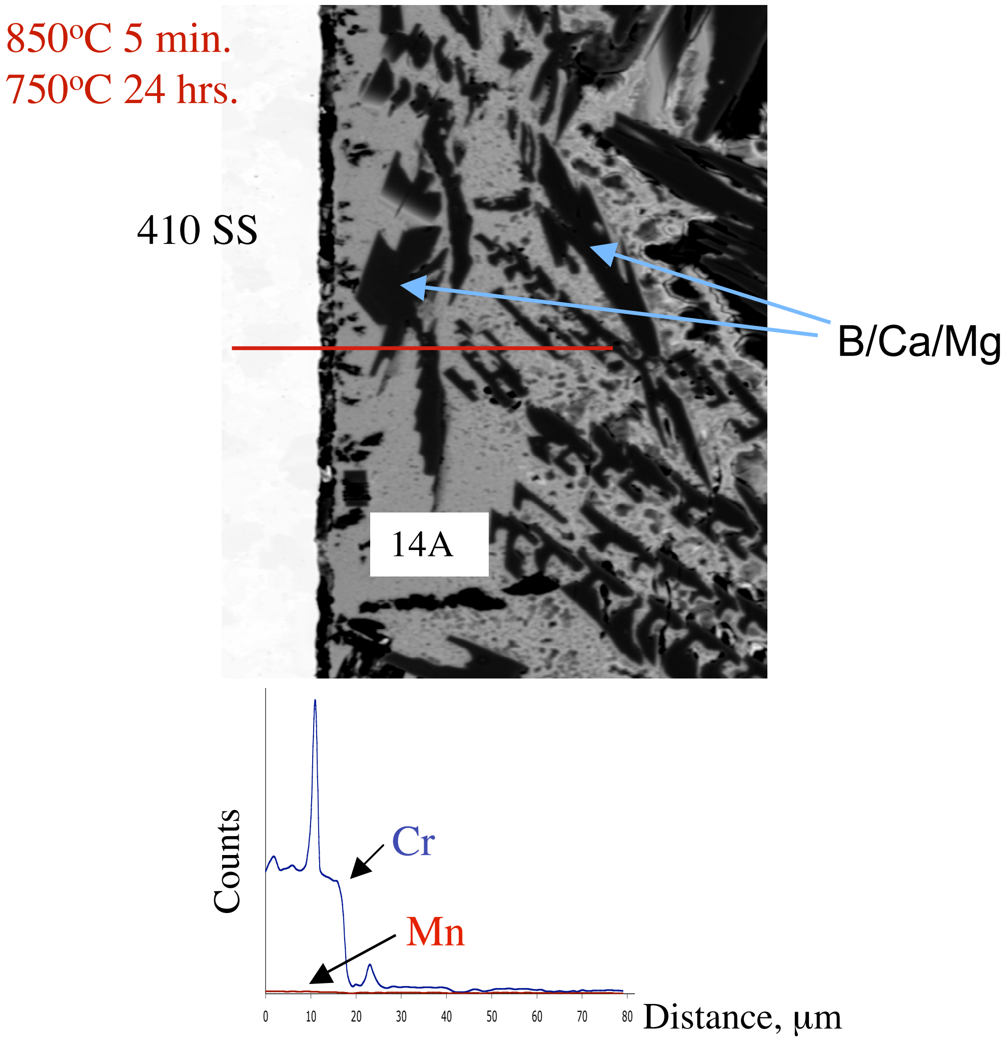


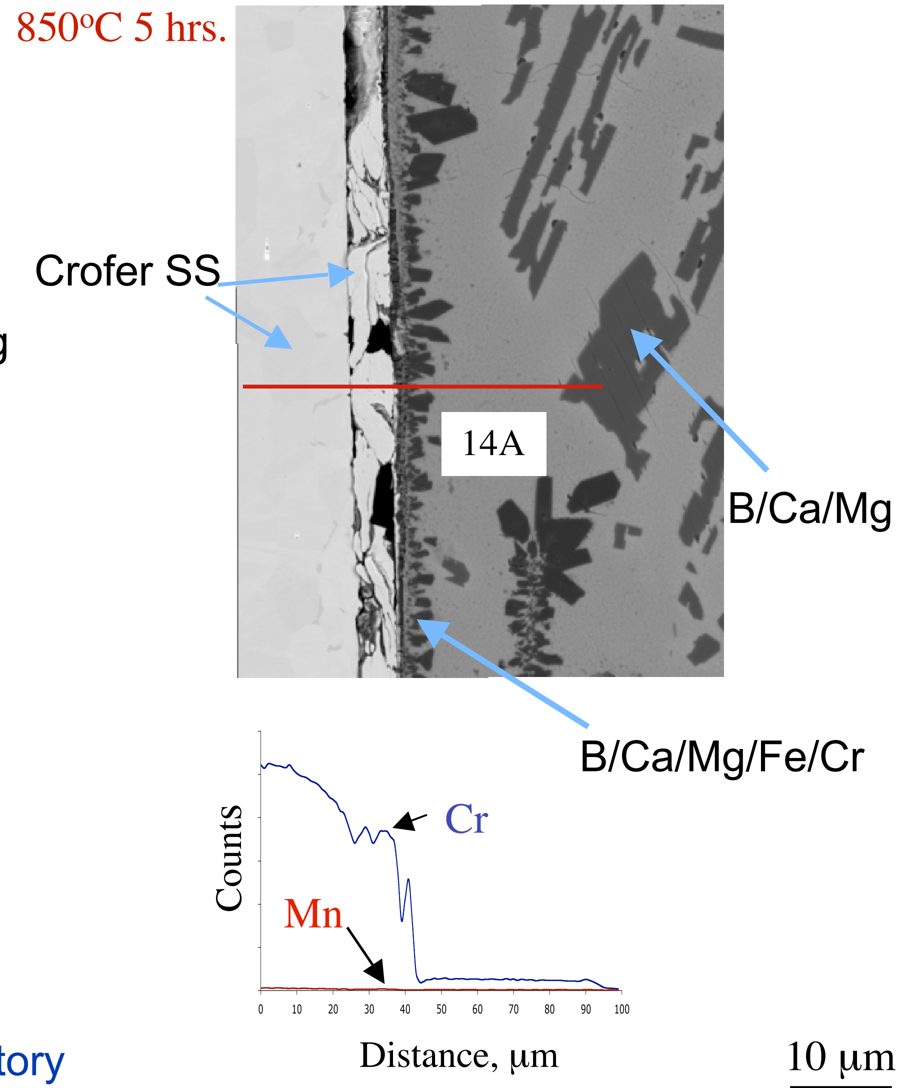


At 850°C a Cr/O layer forms around the Cr, and Cr can be found in the glass



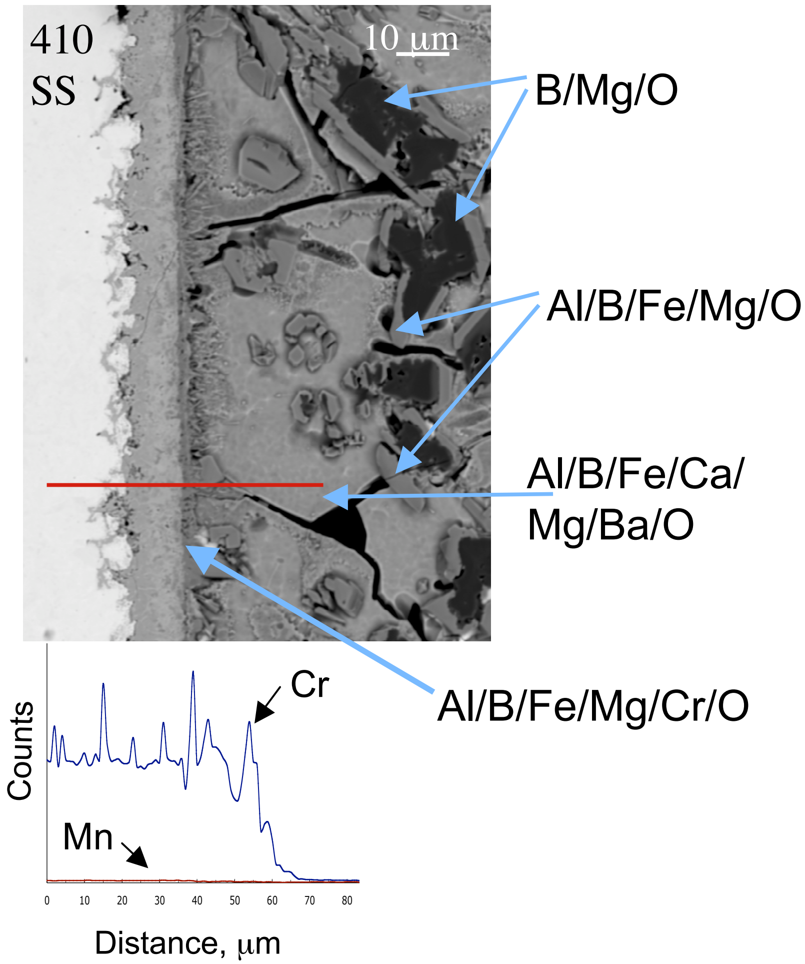
Electron microprobe analysis shows formation of Cr_2O_3 layer at glass-metal interface





Electron microprobe analysis shows that exposure to higher temperatures promotes Fe migration into glass and segregation of B/Mg phases

850°C
5 hrs.



- 14A/410 SS
- Heat treatment: 850°C 5 hrs.
- Complex microstructure with various phases
- Cr detected throughout the interfacial area and in nearby glass
- Phase segregation with Fe-rich boundaries

Time at temperature of 850°C and above should be limited for seals of La-Al borate glasses to interconnects

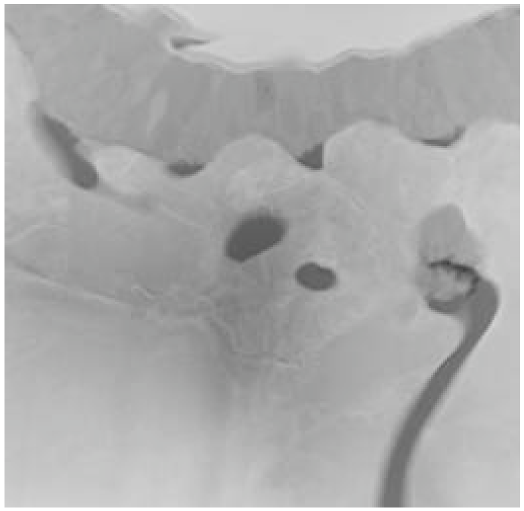
- Cr dissolution appears not to be an issue at 750°C
- Cr can be observed in the glass matrix after long times at 850°C, but not at 750°C
- Extended time at 850°C can cause Cr_2O_3 formation

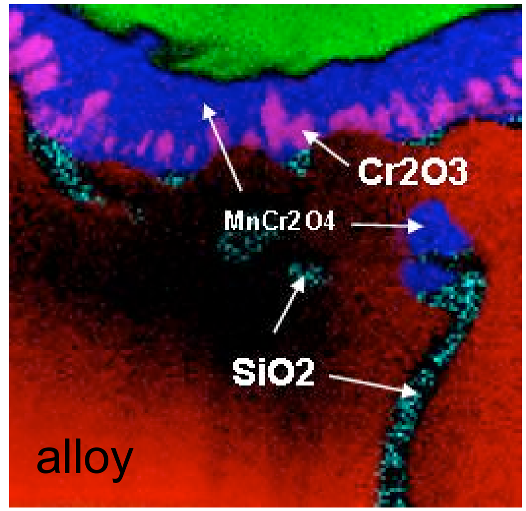
Preoxidation is commonly used for 304 SS-glass interconnect seals. Might it also be useful for processing SOFC seals?

- Oxidation reaction is very well understood in 300 series stainless steels
- Preoxidation of 304 stainless steel improves wetting and adhesion

TEM/Spectrum imaging of pre-oxidized samples shows differences in interface structure for different heats of 304 stainless steels

K674

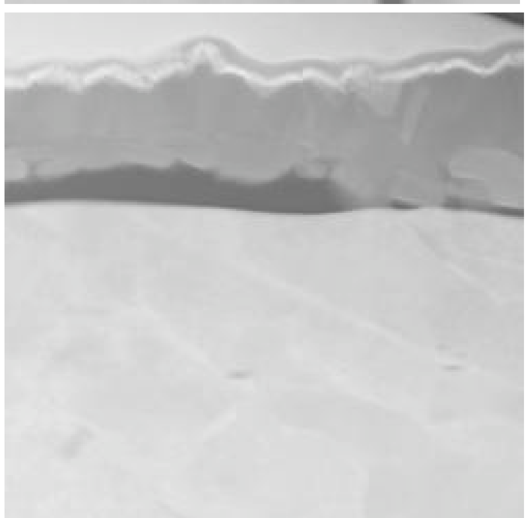


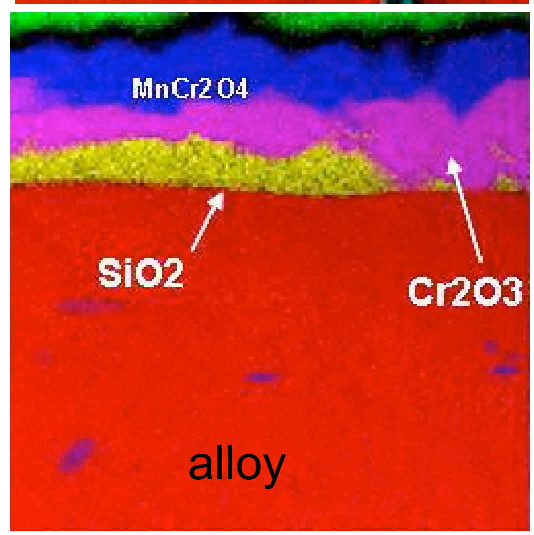


Good glass-sealing behavior

This system used for electrical interconnects

K398





Poor glass-sealing behavior

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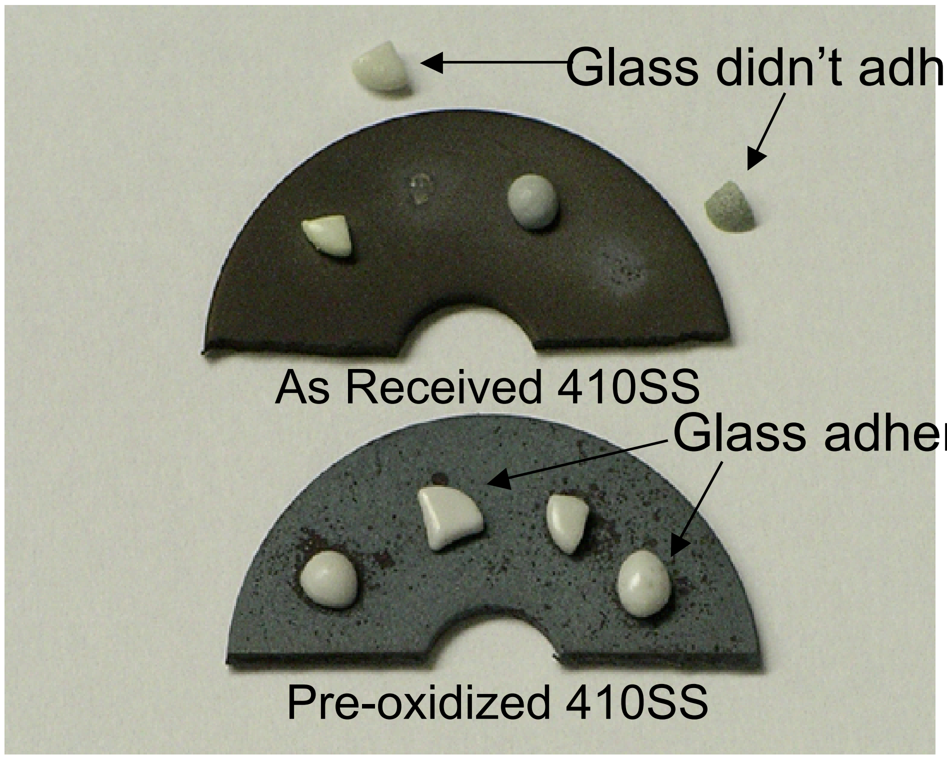
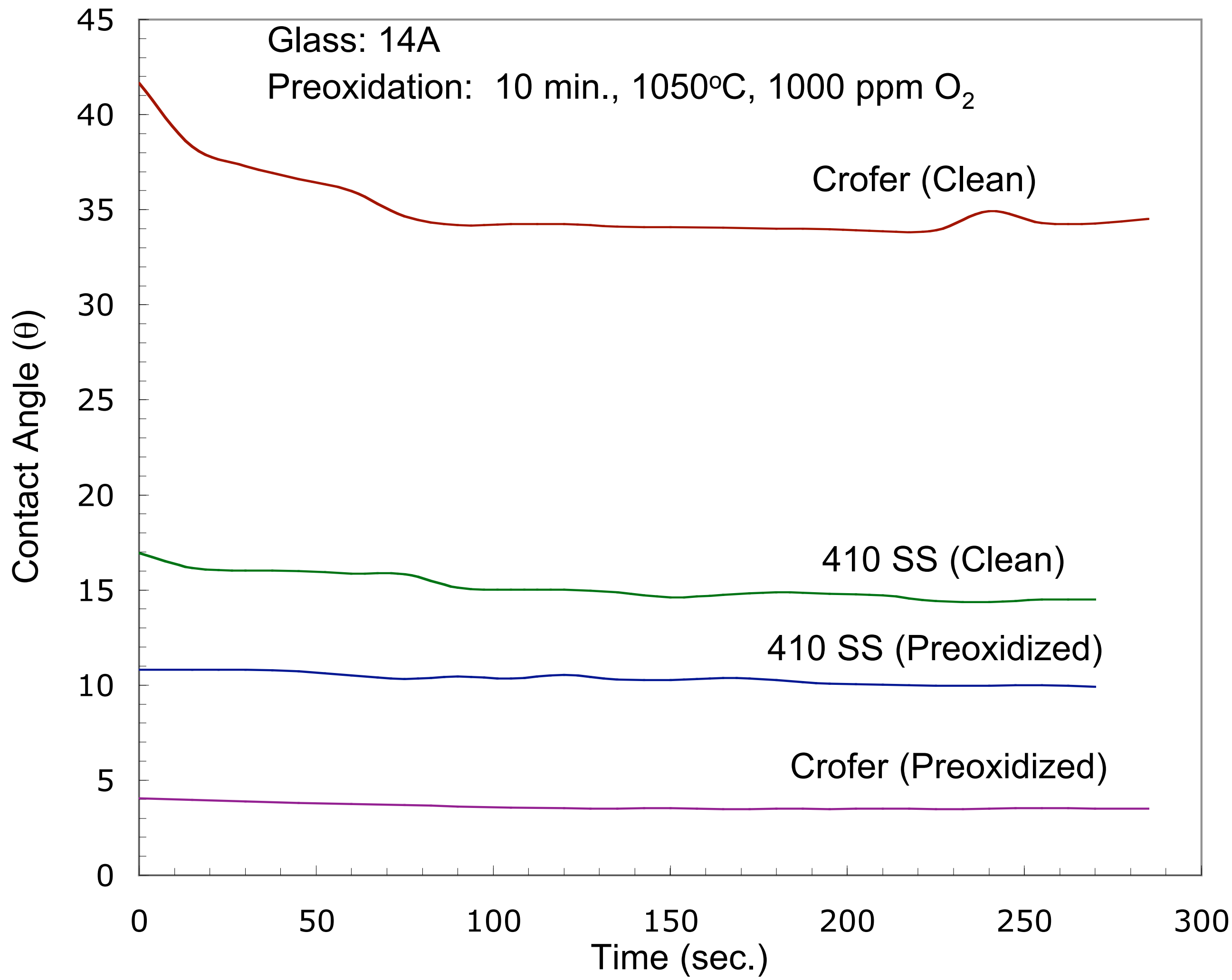
Glass sealed at 850°C in air adhered better to preoxidized 410 SS than to the as-received form

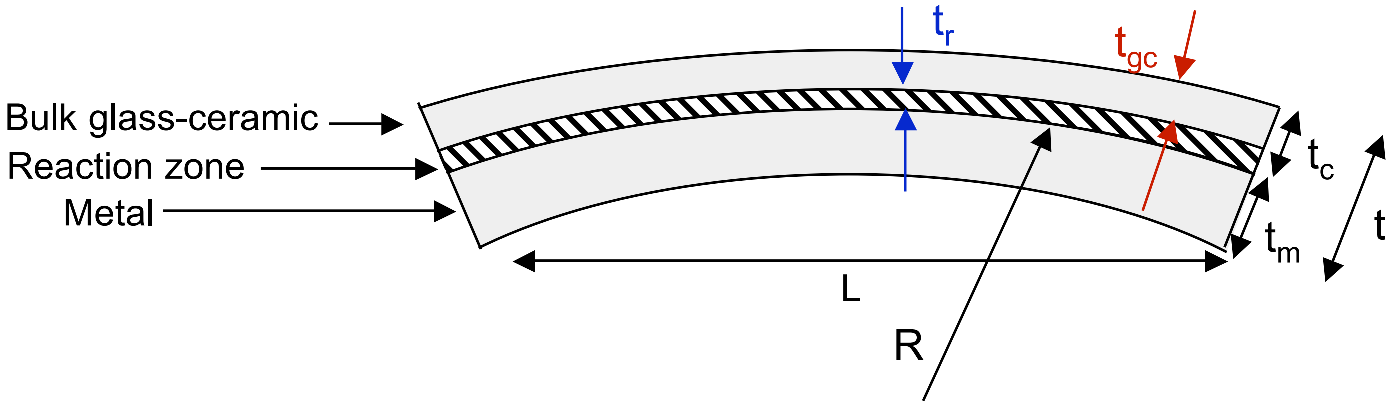


Preoxidation at 1050°C in Ar/1000 ppm O_2

Experiments from TOMMI furnace show effect of preoxidation of Crofer and 410 SS on wetting by sealing glasses



Interface stresses can be calculated using Tomishenko's elastic analysis equations



•The compressive stress in the reaction zone (σ_r) and the tensile stress in the metal (σ_m) can be calculated using the radius of curvature (R), Young's modulus (E), and the seal thickness (t).

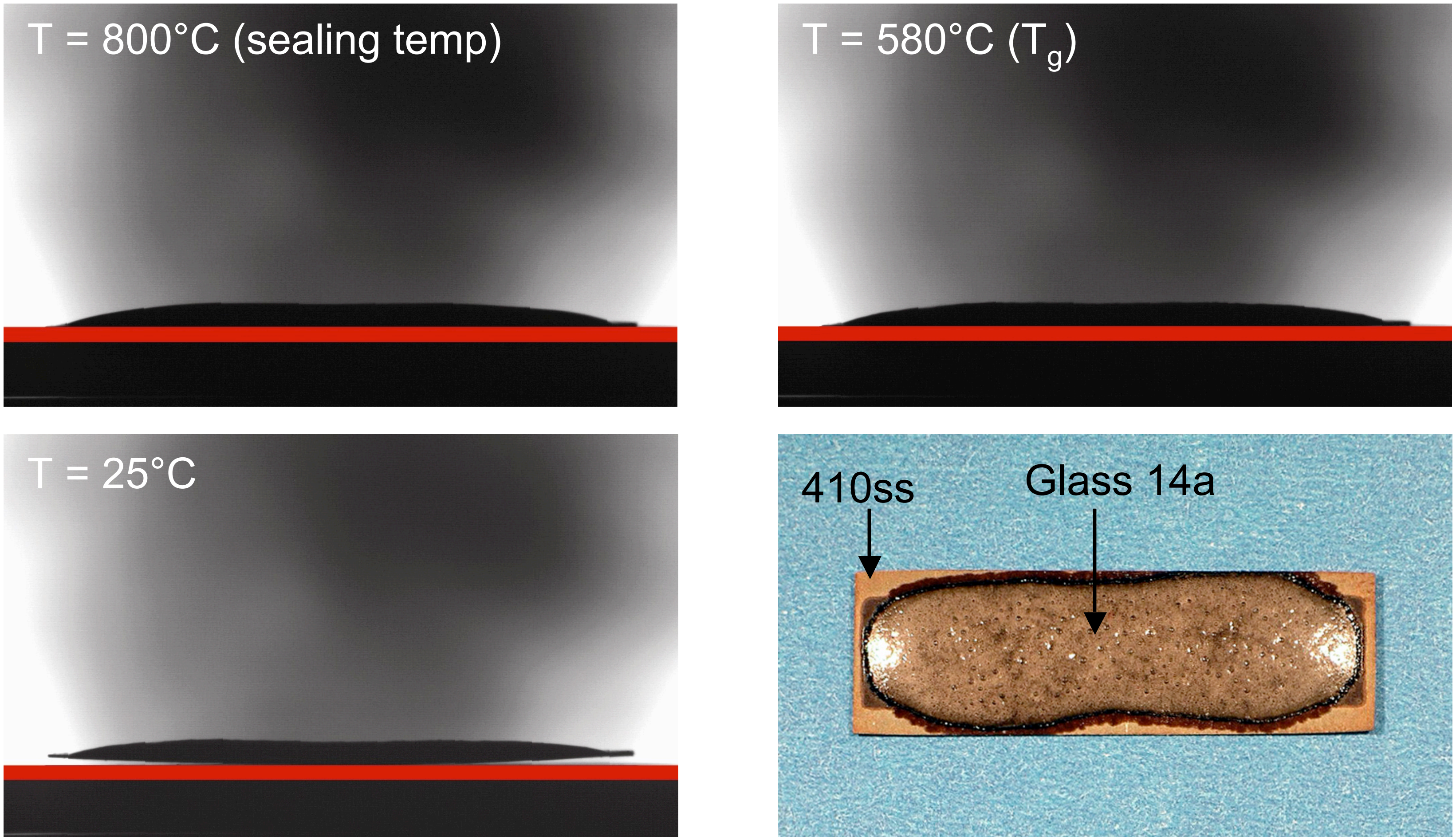
•Combined mechanical and thermal strains in the reaction zone equal those in the metal:

$$\varepsilon_r + \alpha_r \Delta T = \varepsilon_m + \alpha_m \Delta T$$

•CTE of reaction zone producing curvature of the strip seal

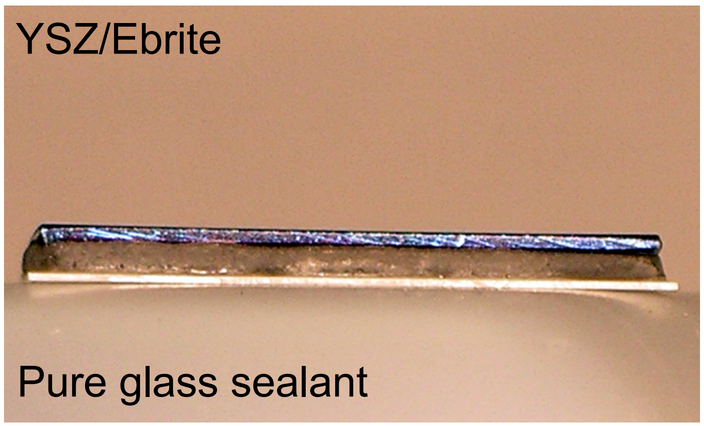
$$(\alpha_m - \alpha_r)\Delta T = \varepsilon_r - \varepsilon_m$$

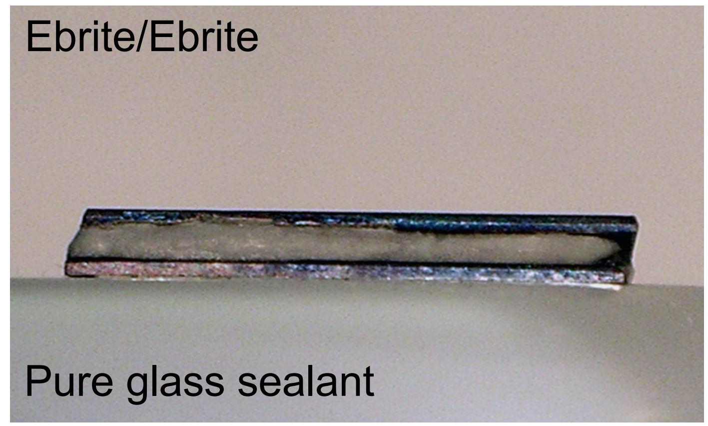
Strip seal experiments show real time strains from glass-stainless steel CTE mismatch

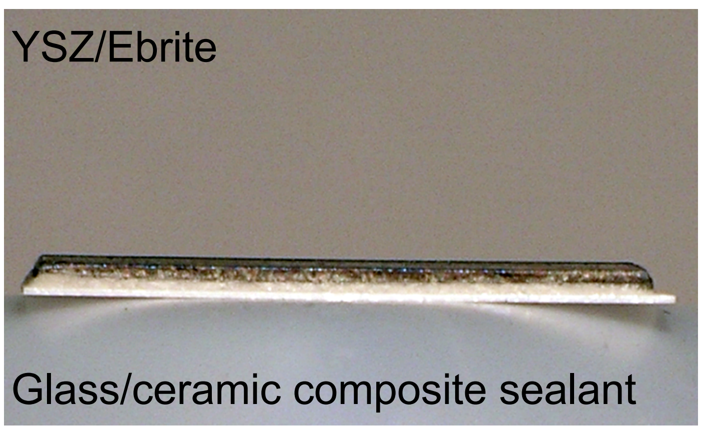


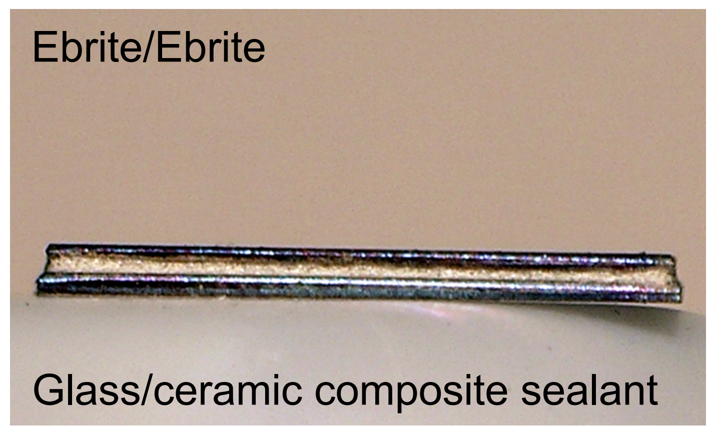
Glass 14a on 410 stainless steel, cooled at 20°C/min

Sample seals have been made with both pure glass and glass/ceramic composites





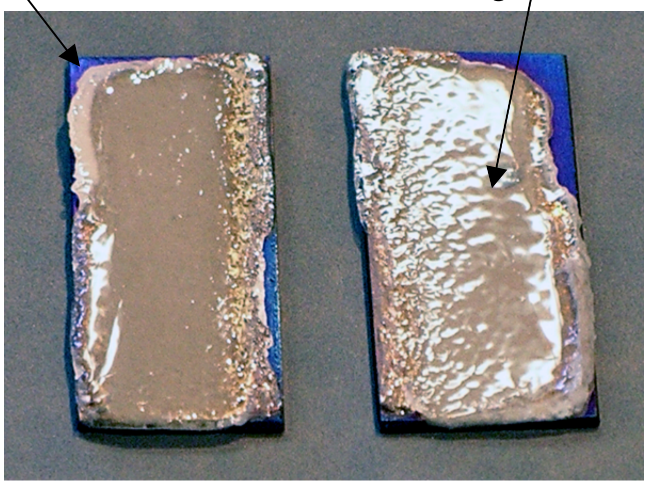




Cracked glass and composite seals can be bonded on reheating

Ebrite

Sealing glass

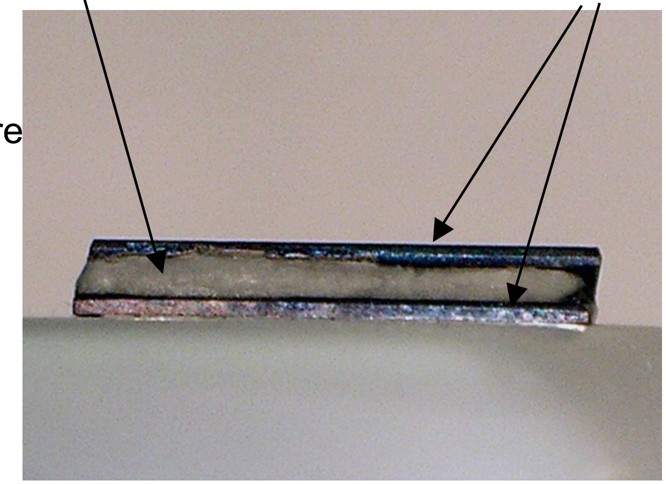


Reheated to sealing temperature

850°C for 10 min.

Sealing glass

Ebrite



FY06 Objectives

- Analyzing interfacial reactions
- Thermal cycling and long time exposure at service temperature (environmental exposure)
- Mechanical testing of composite seal materials
- Mechanical testing of seal adhesion on YSZ substrates
- Development of seals on alloys such as E-brite

Summary and Conclusions

- Glass and crystalline compositions can be optimized independently
- Glass composites allow a wide range of properties and seal designs
- Composite approach seems very promising for sealing SOFCs
- We are ready to adapt this approach to specific vertical team needs