Sealing Glasses

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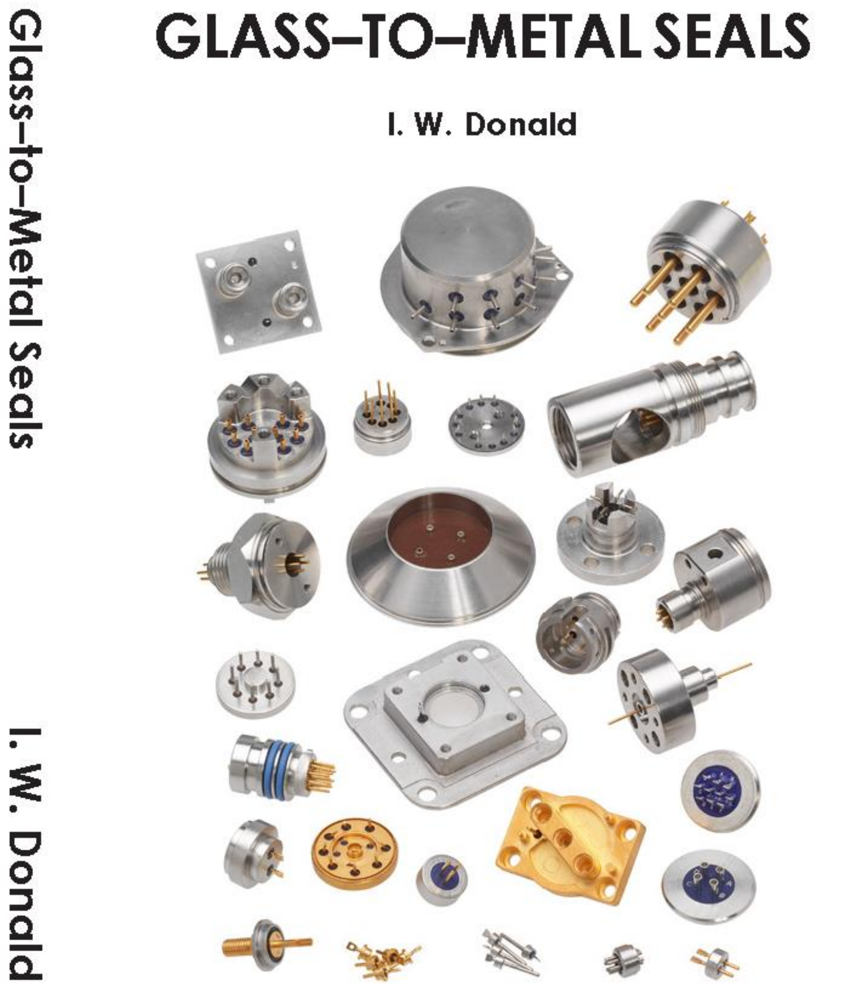
Outline

- Background- and opportunities
  - Low volume, high value technologically enabling glasses
  - Thermal stresses and seal design
  - Interfacial reactions
- A few case studies
  - High strength Ni-based superalloys
  - Stainless steel
  - Reactive metals- titanium, et al.
  - SOFC's
- Some closing thoughts

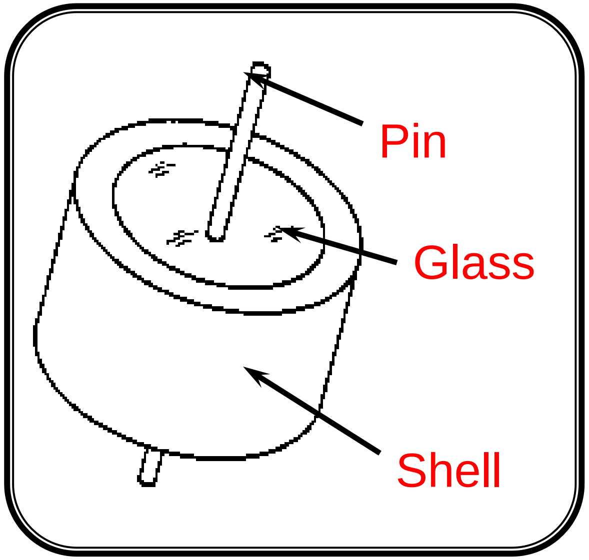
IW Donald, Preparation, properties and chemistry of glass- and glass-ceramic-to-metal seals and coatings, *J. Materials Science*, **28** 2841-2886 (1993).

IW Donald, et al., Recent developments in the preparation, characterization and applications of glass- and glass–ceramic-to-metal seals and coatings, *J. Materials Science*, **46** 1975-2000 (2011).



Function and requirements of hermetic seals

- Isolate components from environment
- Mechanically bond different components
- Electrically insulate one component from another
- Weak link/strong link functions

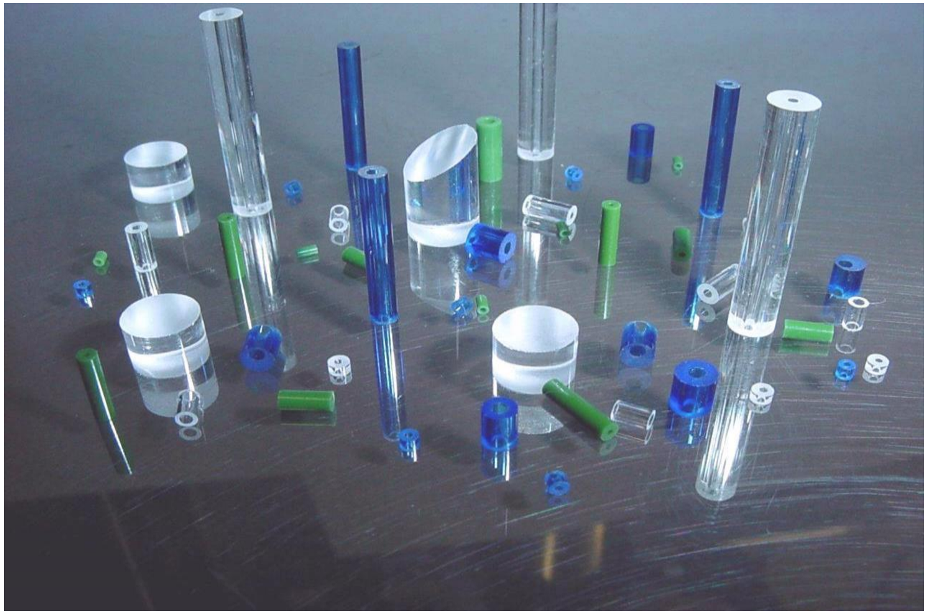


- Thermo-mechanical compatibility
  - CTE requirements (matched vs. compression)
  - Sealing temperature
- Environmental stability (ambient and other component materials)
- Component functionality (dielectric, optical, etc. properties)

Why use glasses for hermetic seals?

- Superior hermeticity
  - $>10^3$ lower permeation rates than polymers
- Compositional flexibility to tailor specific properties
  - E.g., CTE ranges to match fused silica and copper….
- High temperature stability
- Electrically insulating
- Processing flexibility
  - Viscous flow for complex shapes
  - Solid, powder preforms; thin films
  - Glass-ceramic options
- Brittle- CTE mismatches
- Temperature limitations
- Incompatible chemistries

Glass preforms are fabricated from solid and pressed-powders



Electro-glass products

www.elantechnology.com

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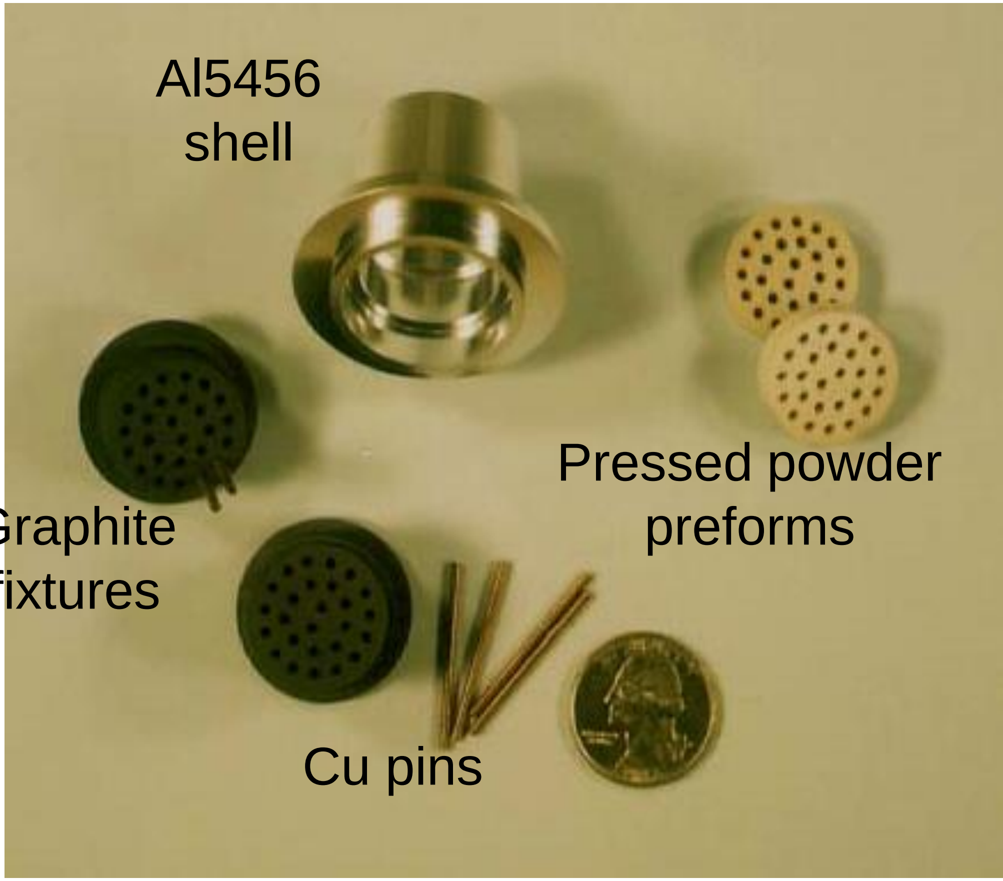
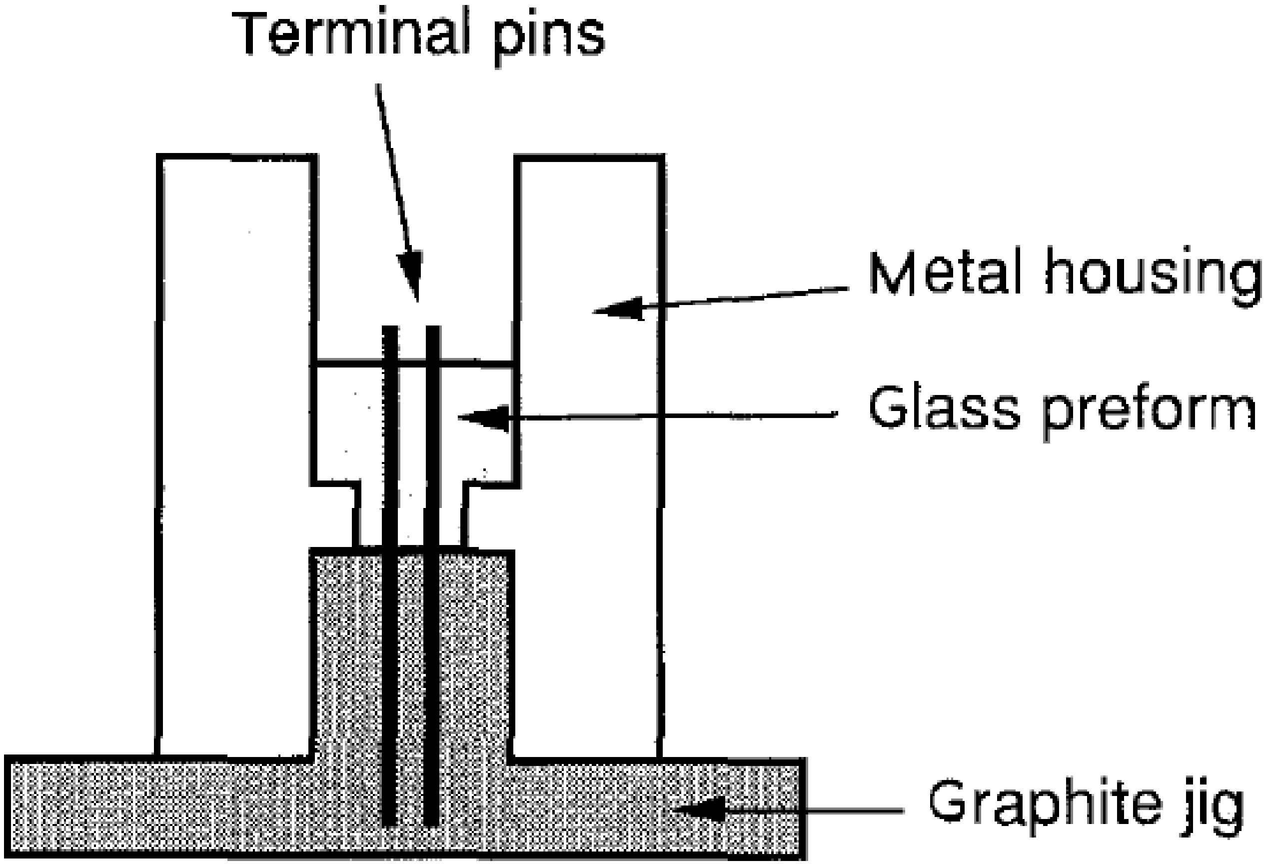
Components for fabricating a glass-metal seal



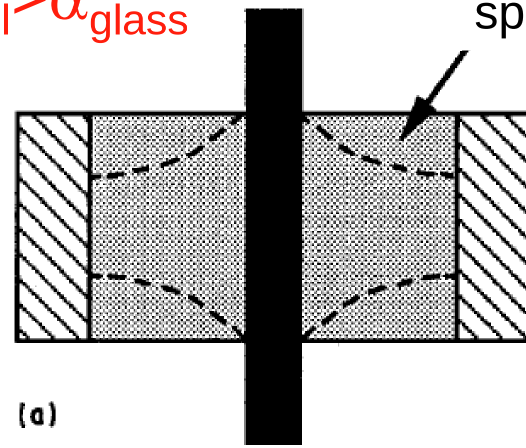


(a)

A few words on thermal expansion and thermal stresses

Two general designs:

Matched seal: $\alpha_{shell}=\alpha_{glass}=\alpha_{pin}$
Compression seal: : $\alpha_{shell}>\alpha_{glass}=\alpha_{pin}$



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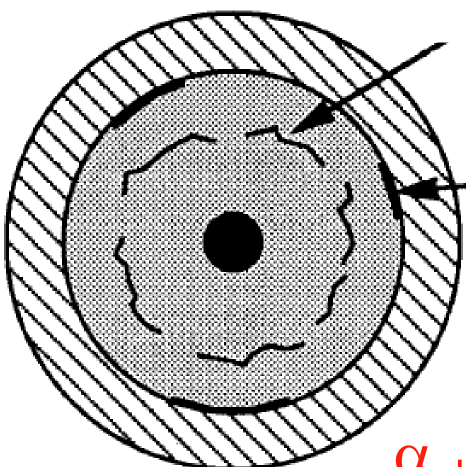
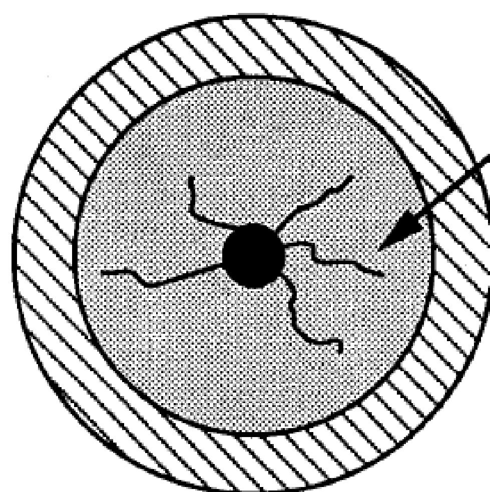
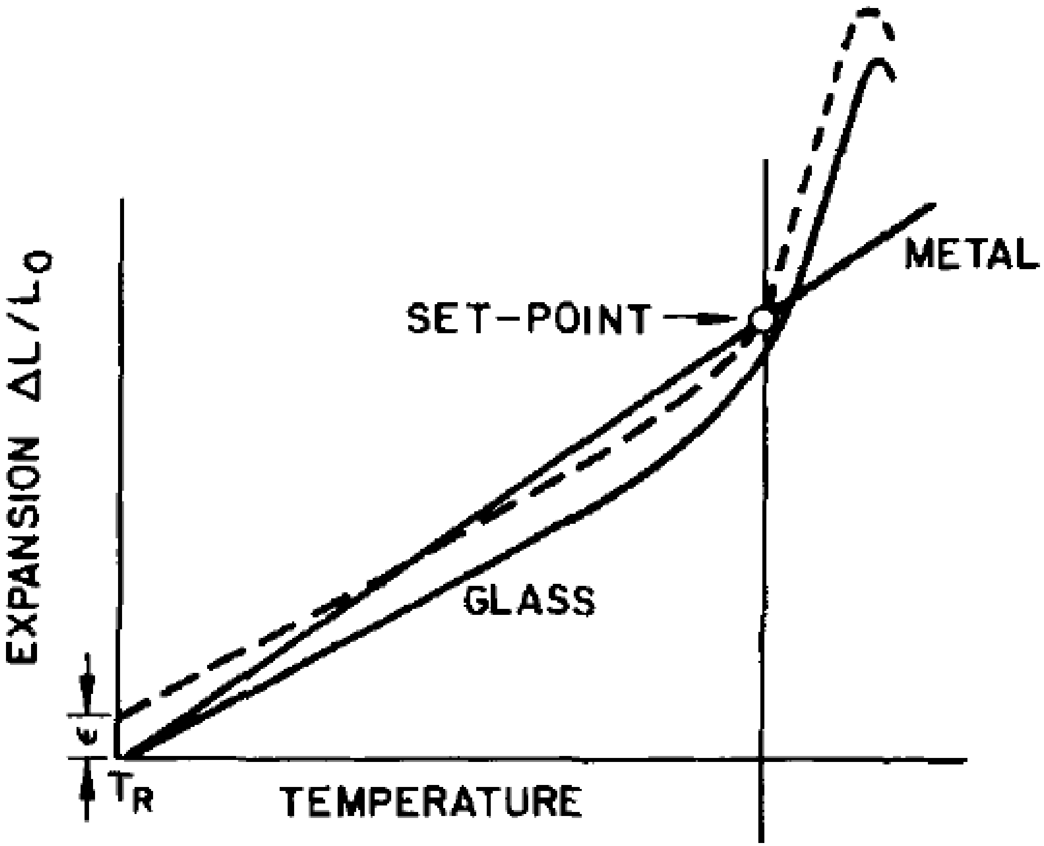


(b)



(c)

AK Varshneya, *The Set Point of Glass in Glass-to-Metal Sealing*, J. Amer. Cer. Soc.,**63**[5-6]311-315 (1980)



$$\varepsilon = \int_{T_Q}^{T_R} \left(\alpha_{glass} - \alpha_{metal}\right) dT$$

$$\sigma_{glass} = \frac{E_{glass}\,\varepsilon}{\left(1 - \nu\right)}$$

Typical design criterion: $\varepsilon < 1\times10^{-4}$ (σ_{glass}<5 MN/m^2, 1000 psi)

How is the set point determined?

- Generally between the strain point ($10^{13.5}$ Pa-s) and the annealing point (10^{12} Pa-s)
- Dependent on thermal history
- Structural relaxation

RS Chambers, FP Gerstle, and SL Monroe, Viscoelastic Effects in a Phosphate Glass-Metal Seal, J. Amer. Ceram. Soc., **72**[6] 929-32 (1989)

Mixed alkali-barium-aluminophosphate glass with a nominal expansion match to stainless steel (pin), sealed to aluminum shell at 500° C.

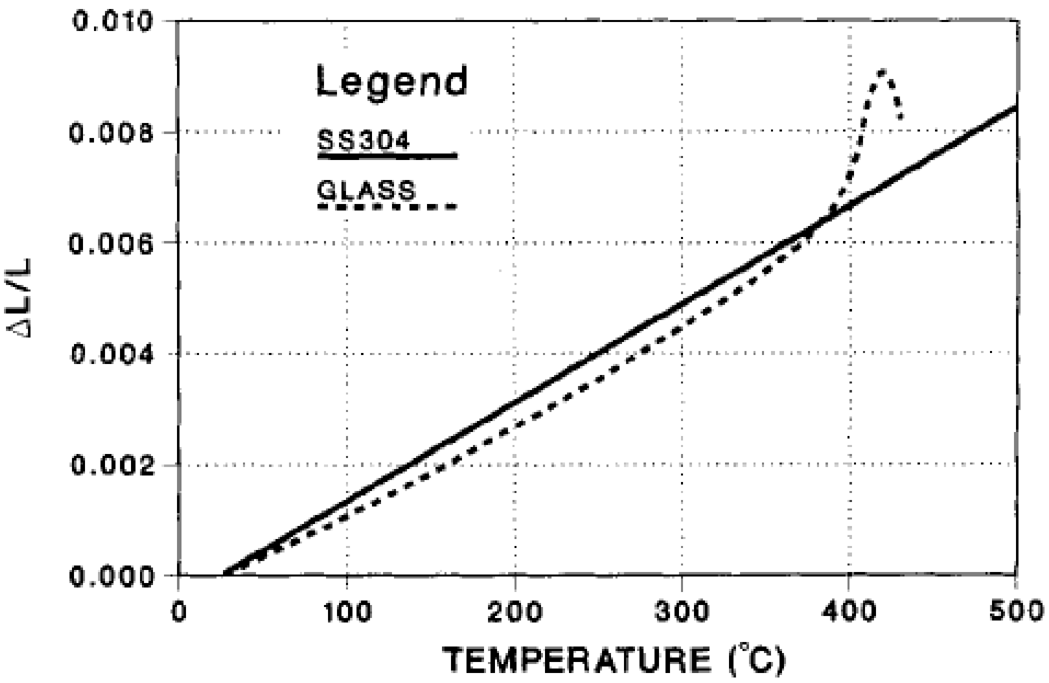
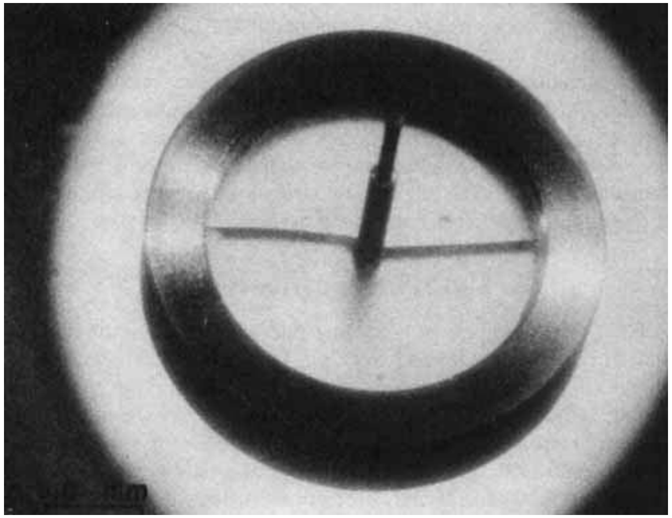


Fig. 1. Comparison of thermally induced expansion exhibited by the phosphate glass and 304 stainless steel.



$$\sigma_{ij}(t) = \delta_{ij}\int_0^t K[\xi(t) - \xi(\tau)]\frac{d}{d\tau}(\varepsilon_{kk} - \Theta)\,d\tau + 2\int_0^t G[\xi(t) - \xi(\tau)]\frac{d}{d\tau}(\varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\,\delta_{ij})\,d\tau$$

Stress tensor (σ_{ij}) depends on strain tensor (ε_{ij}), the bulk (K) and shear (G) moduli, and structural relaxation, defined by a reduced time factor (ξ)

$$\xi(t) = \int_0^t \Phi[T(s), T_f(s)]\,ds$$

$$\ln \Phi[T(s), T_f(s)] = \frac{xH}{R}\left(\frac{1}{T_r} - \frac{1}{T(s)}\right) + \frac{(1-x)H}{R}\left(\frac{1}{T_r} - \frac{1}{T_f(s)}\right)$$

Structural relaxation is described by the fictive temperature (T_f) and an activation energy (H)

$$\Theta = 3\alpha_g(T - T_f) + 3\alpha_l(T_f - T_0)$$

Volume strain (Θ) depends on the expansion characteristics of the glass and liquid, and T_f

$$T_f(t) = T(t) - \int_0^t M[\xi(t) - \xi(\tau)]\frac{dT}{d\tau}\,d\tau$$

Time and temperature dependence of fictive temperature

Chambers, et al.(1989)

Viscoelastic model reveals the development of transient stresses in the glass on cooling

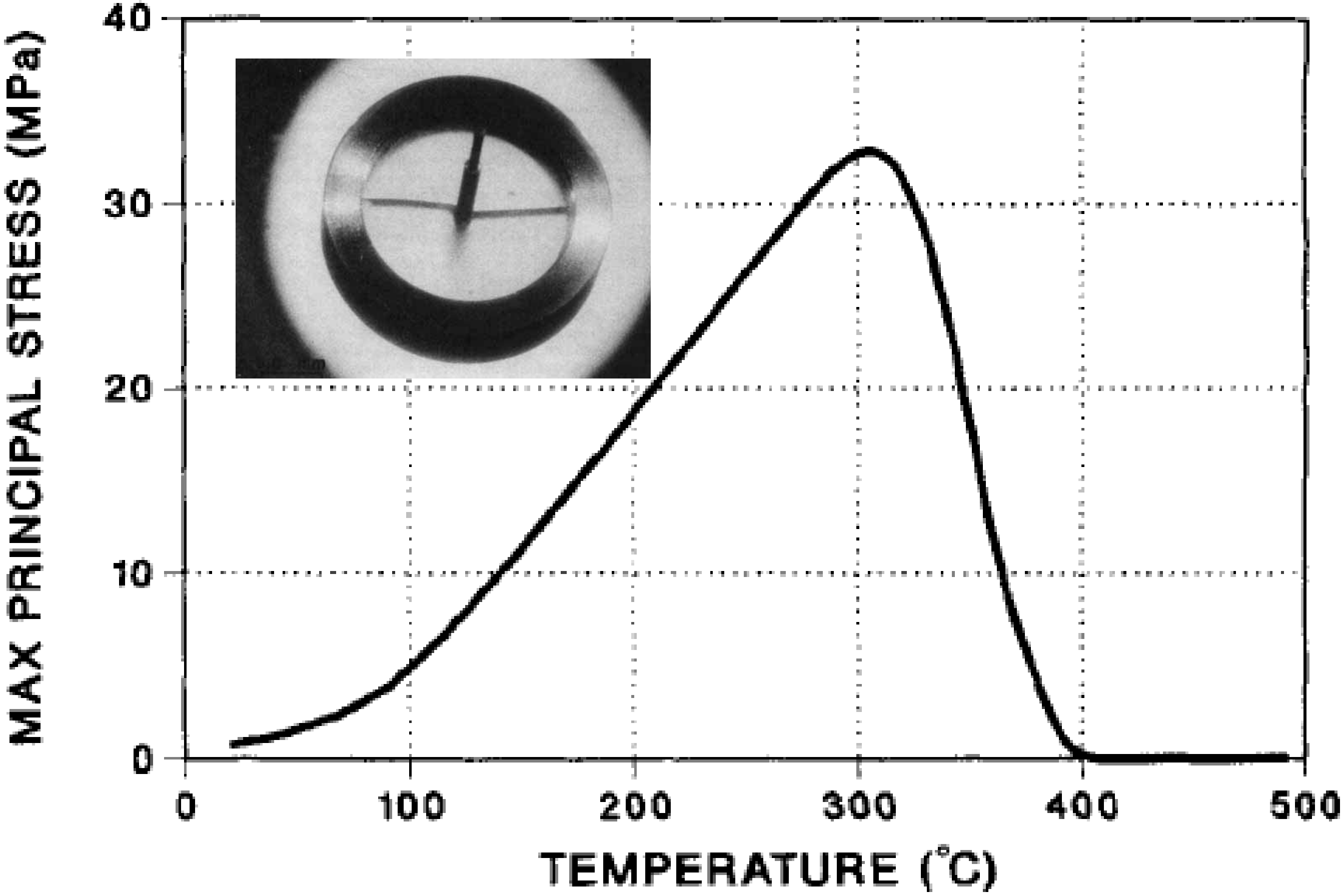
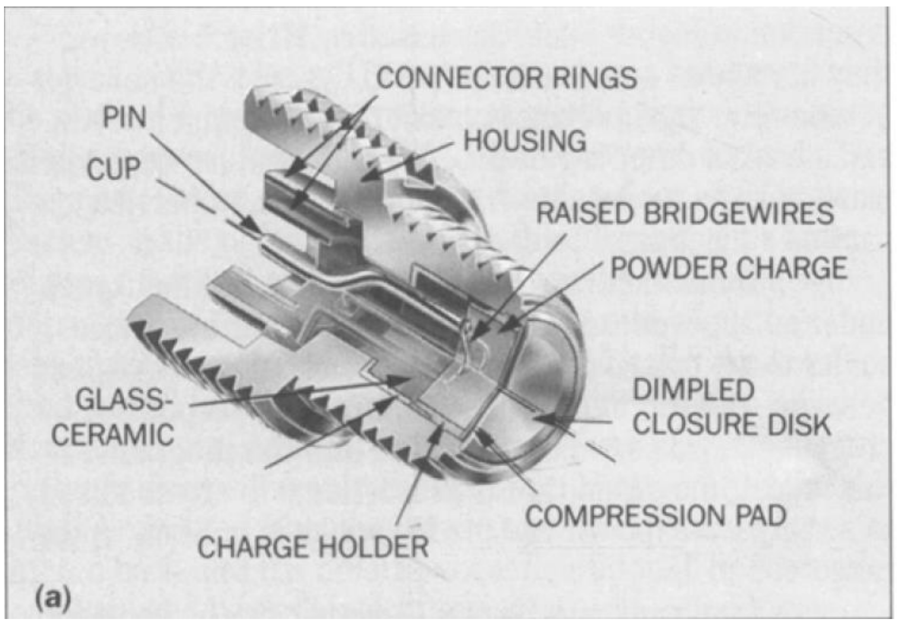
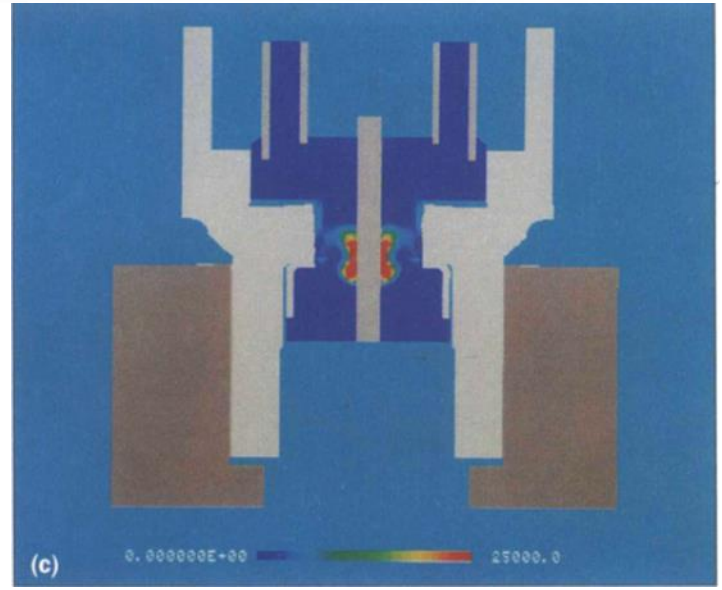


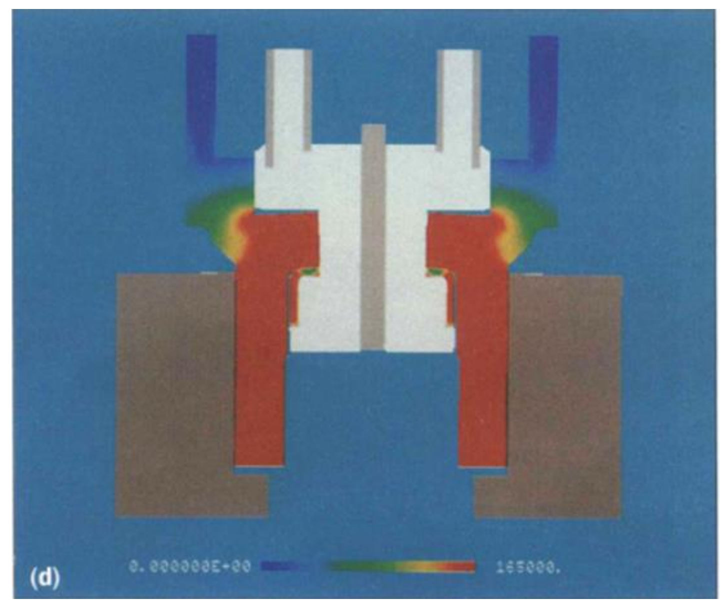
Fig. 5. Maximum principal stress in the glass at the pin interface plotted as a function of temperature during cooling.

Chambers, et al.(1989)

Viscoelastic models are critical to the accurate predictions of the thermal stresses associated with slight CTE mismatches

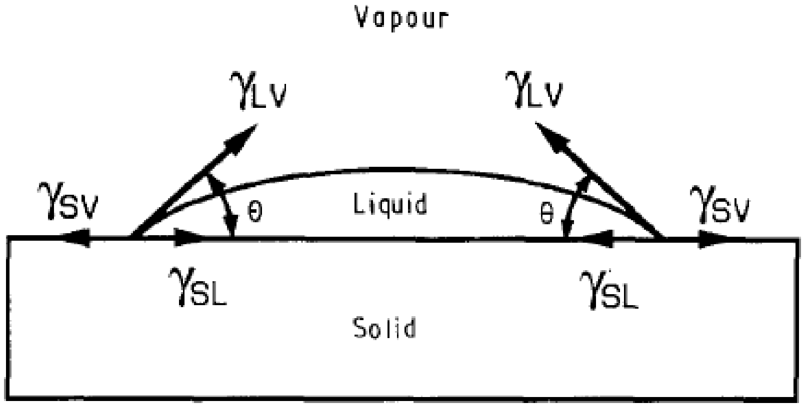




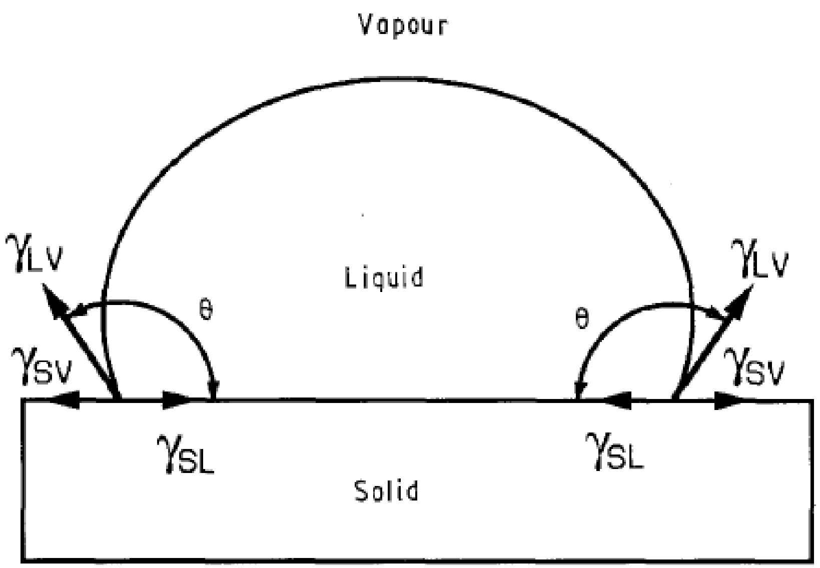


JH Biffle, SN Burchett, AT&T Technical Journal, 66[6] 51 (1987)

A few words about glass-metal interfaces…



(a)



(b)

Wetting: molten glass on metal substrate is a balance of interfacial energies. Small contact angles are associated with a greater work of adhesion (W_A):

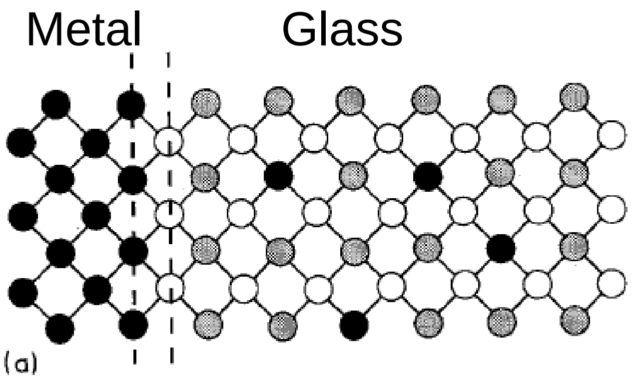
$$W_A=\gamma_{LV}(1+\cos\theta)$$

Chemical reactions at the glass-metal interface can also contribute to improved wetting and the work of adhesion:

$$W_A=\gamma_{LV}(1+\cos\theta)+\gamma_{Ri}+C\Delta G^0_{rxn}$$

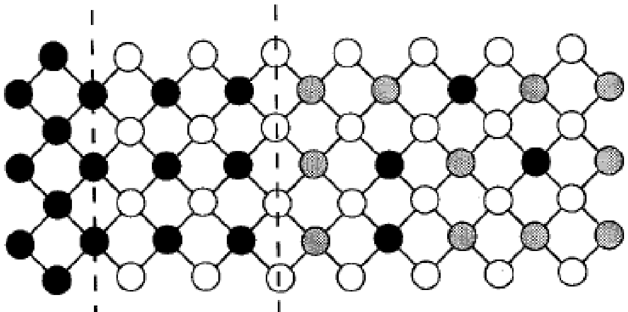
γ_{Ri} is the interfacial energy between the reaction product and substrate, and ΔG^0_{rxn} is the free energy of the interfacial reaction (C is a constant)

A few words about glass-metal interfaces…



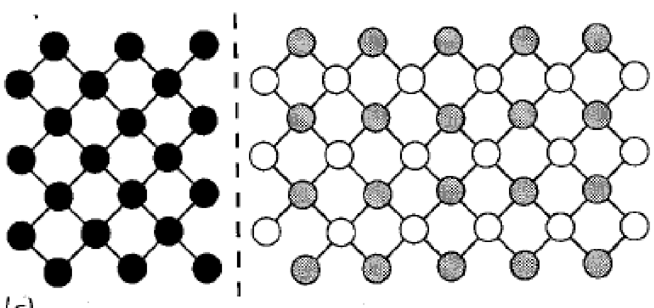
(a)

Glass saturated with metal ions, strong chemical bond through an interfacial metal oxide “monolayer



(b)

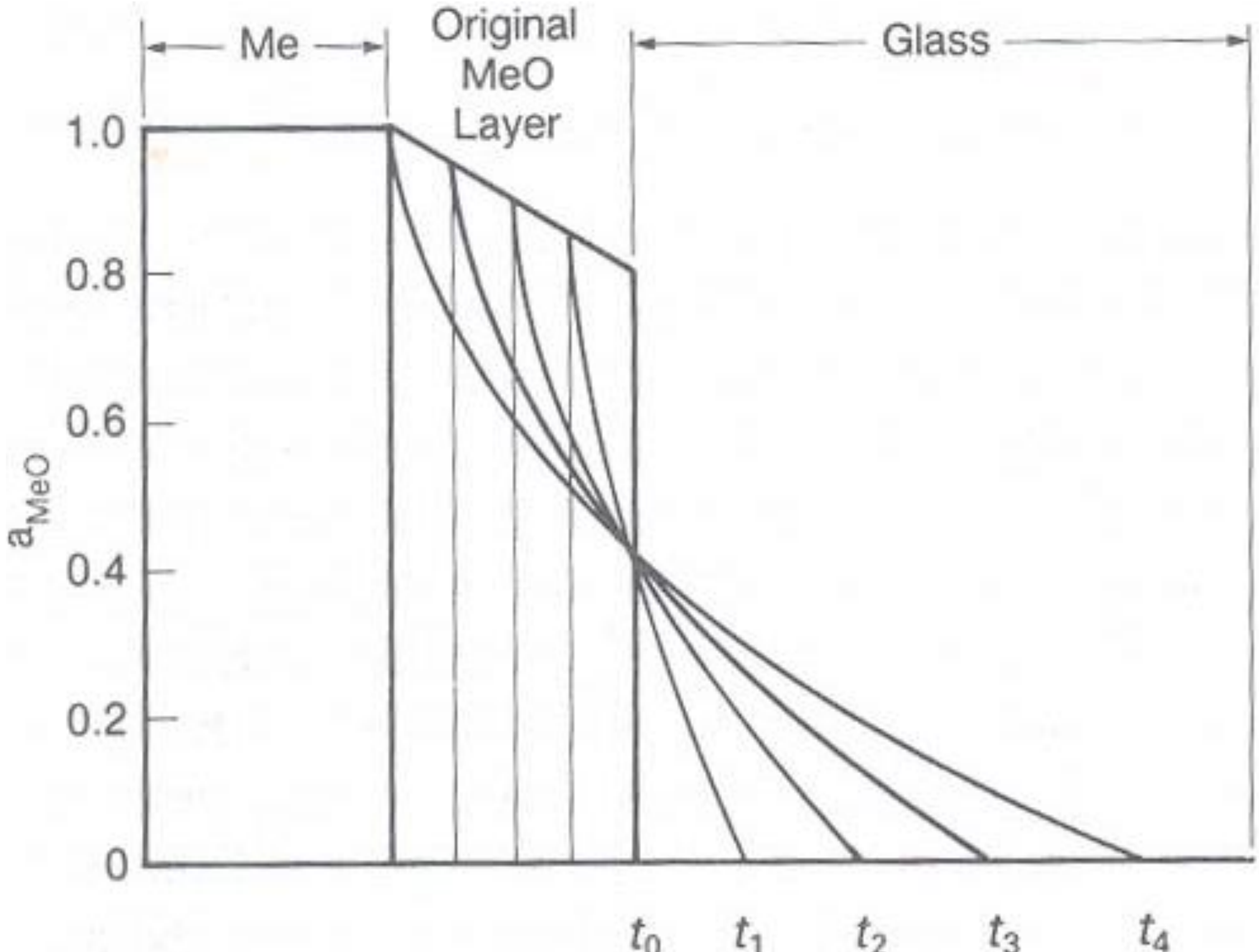
Glass saturated with metal ions, thick interfacial metal oxide; seal properties dependent on interfacial oxide



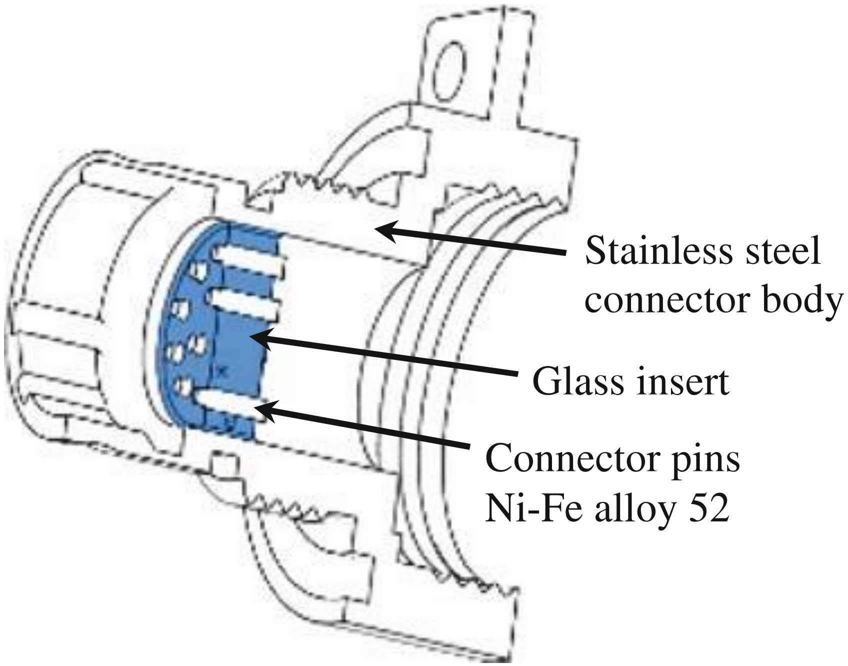
(c)

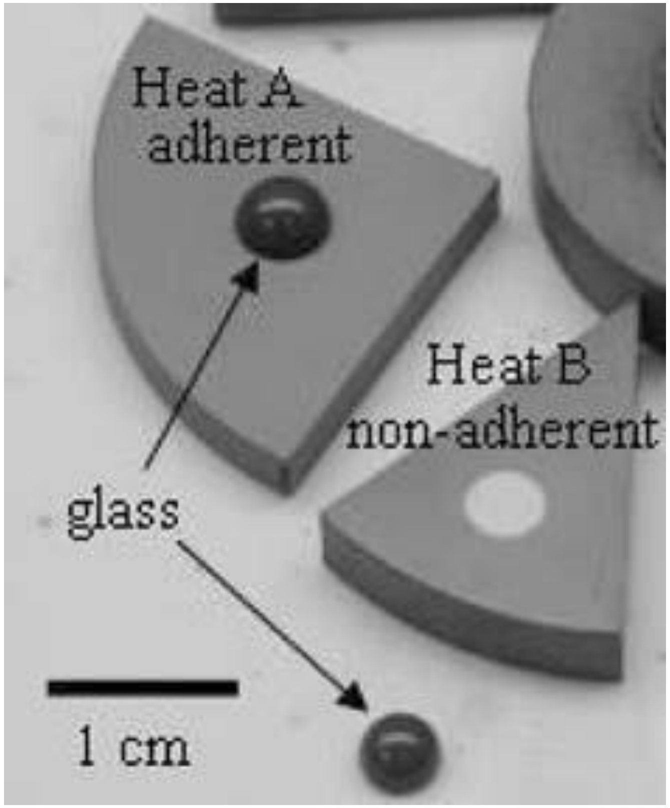
No metal ions in glass, weak bonding through an van der Waals interactions

Pre-oxidation can contribute to the compositional/electronic interfacial gradients necessary for a successful glass-metal seal (Pask)



DF Susan, et al., The Effects of Pre-Oxidation and Alloy Chemistry of Austenitic Stainless Steels on Glass/Metal Sealing, Oxid Met (2010) 73:311–335





Adherent seals result when $MnCr_2O_4$ spinel forms an interfacial oxide

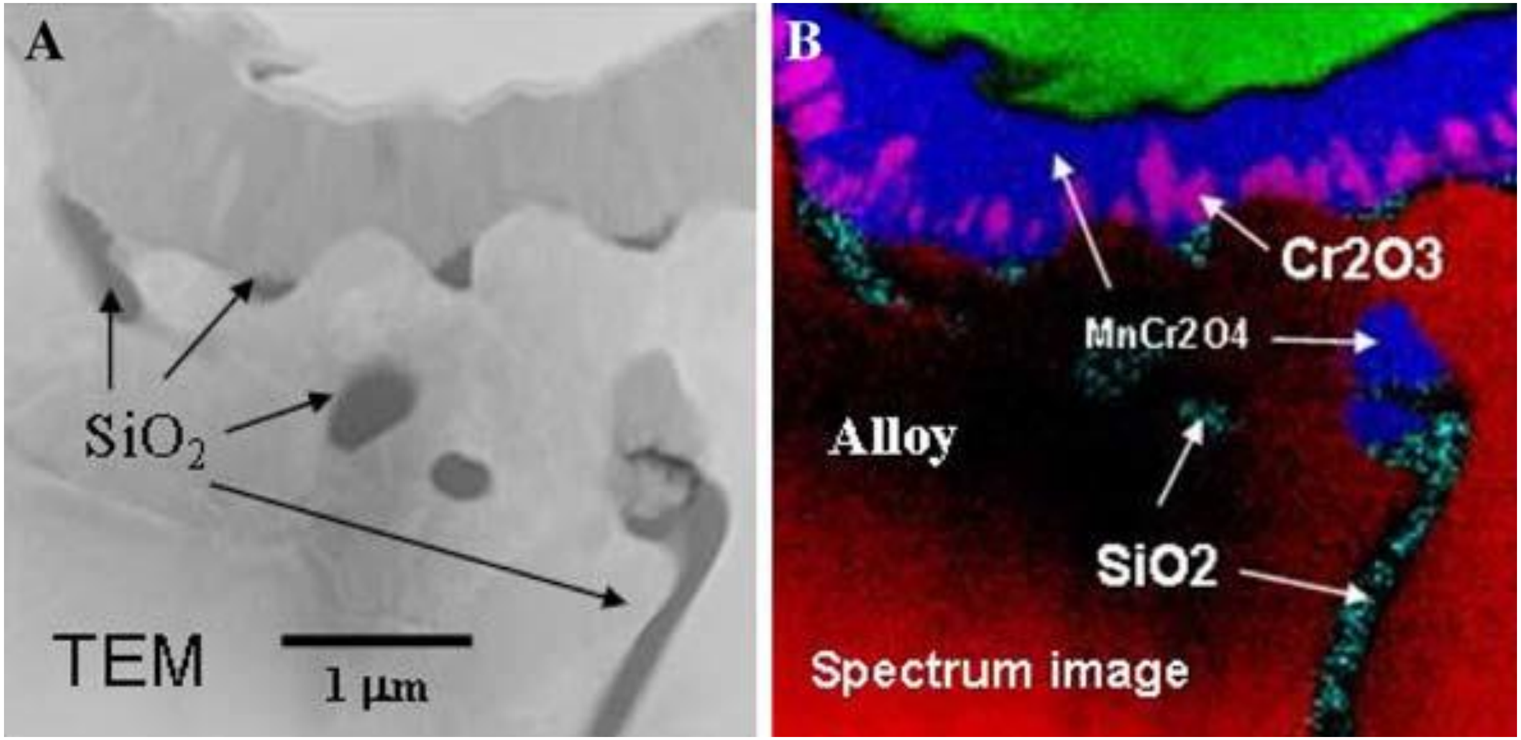
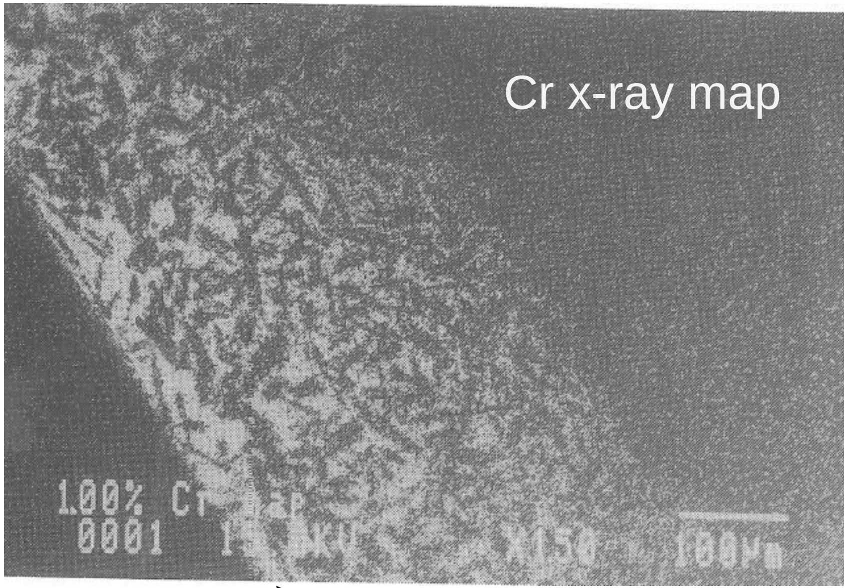


Fig. 5 **a** TEM image and **b** corresponding spectrum image of heat 304L-A oxide (sample pre-oxidized 1050 °C, 30 min)

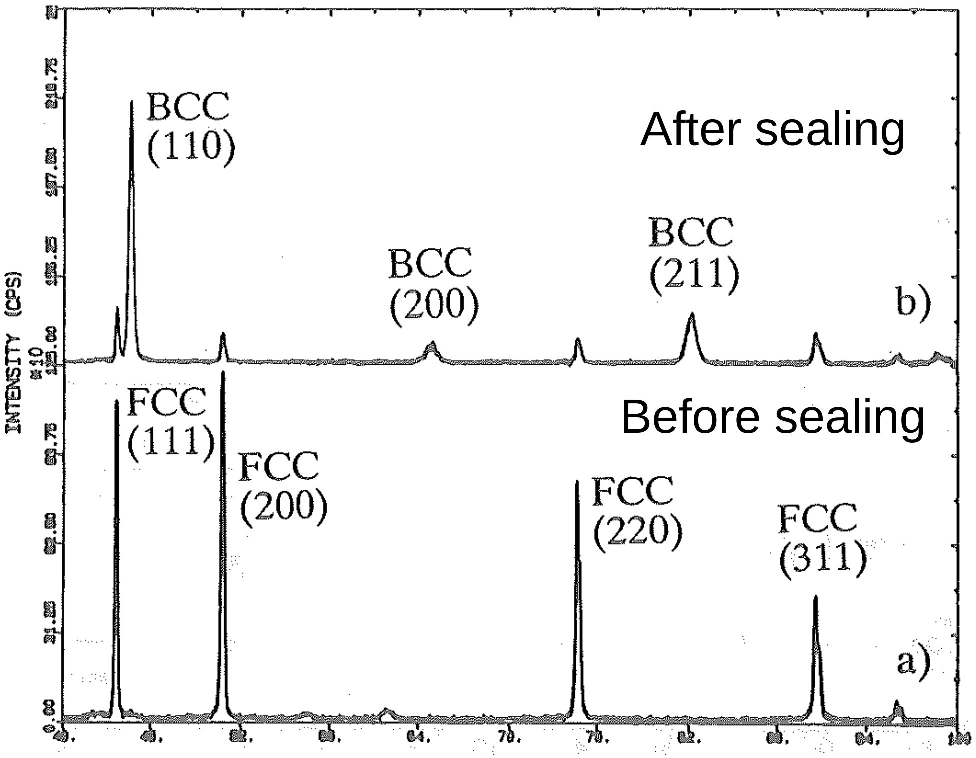
Deleterious reactions can occur at the glass-stainless steel interface- Example: 304 stainless steel/lithium silicate GC



Interface between a failed 304SS/LSGC seal

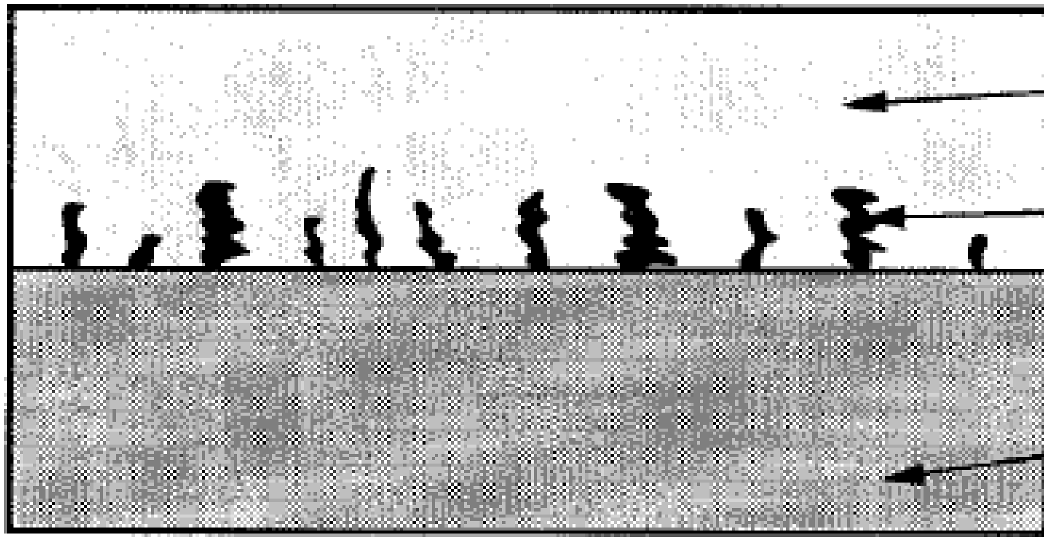
Knorovsky and Brow, Ceram. Trans. 20 (1990)

X-ray diffraction patterns of 304SS



Cr-depletion from the 304SS into the sealing glass transforms steel from austenitic to ferritic structures; volume change caused seal to fail

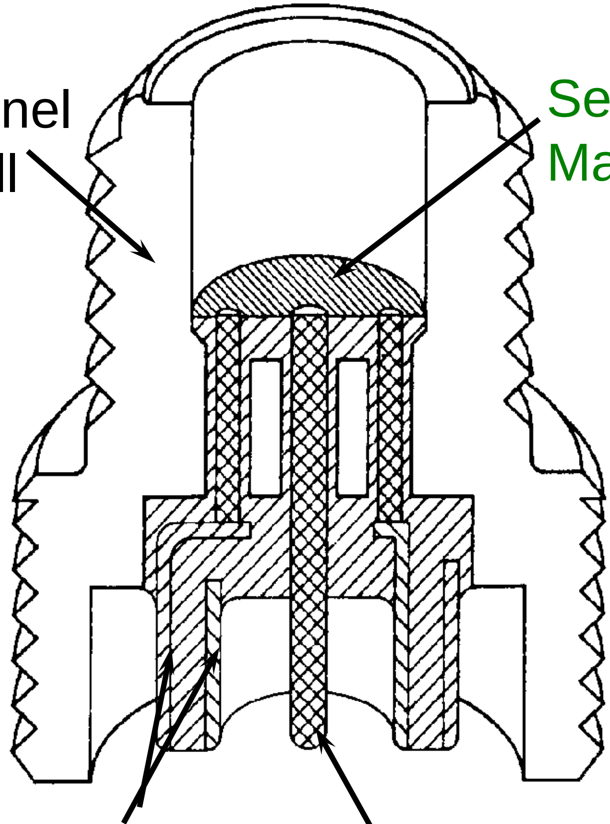
Interfacial reactions can promote good glass-metal bonding; e.g., mechanical adherence through the formation of interfacial dendrites- sealing glasses doped with CoO



(a)

$$CoO_{glass} + Fe_{metal} = Co_{dendrites} + FeO_{glass}$$

Sometimes deleterious interfacial reactions can occur
Example: high-strength seals for pyrotechnics

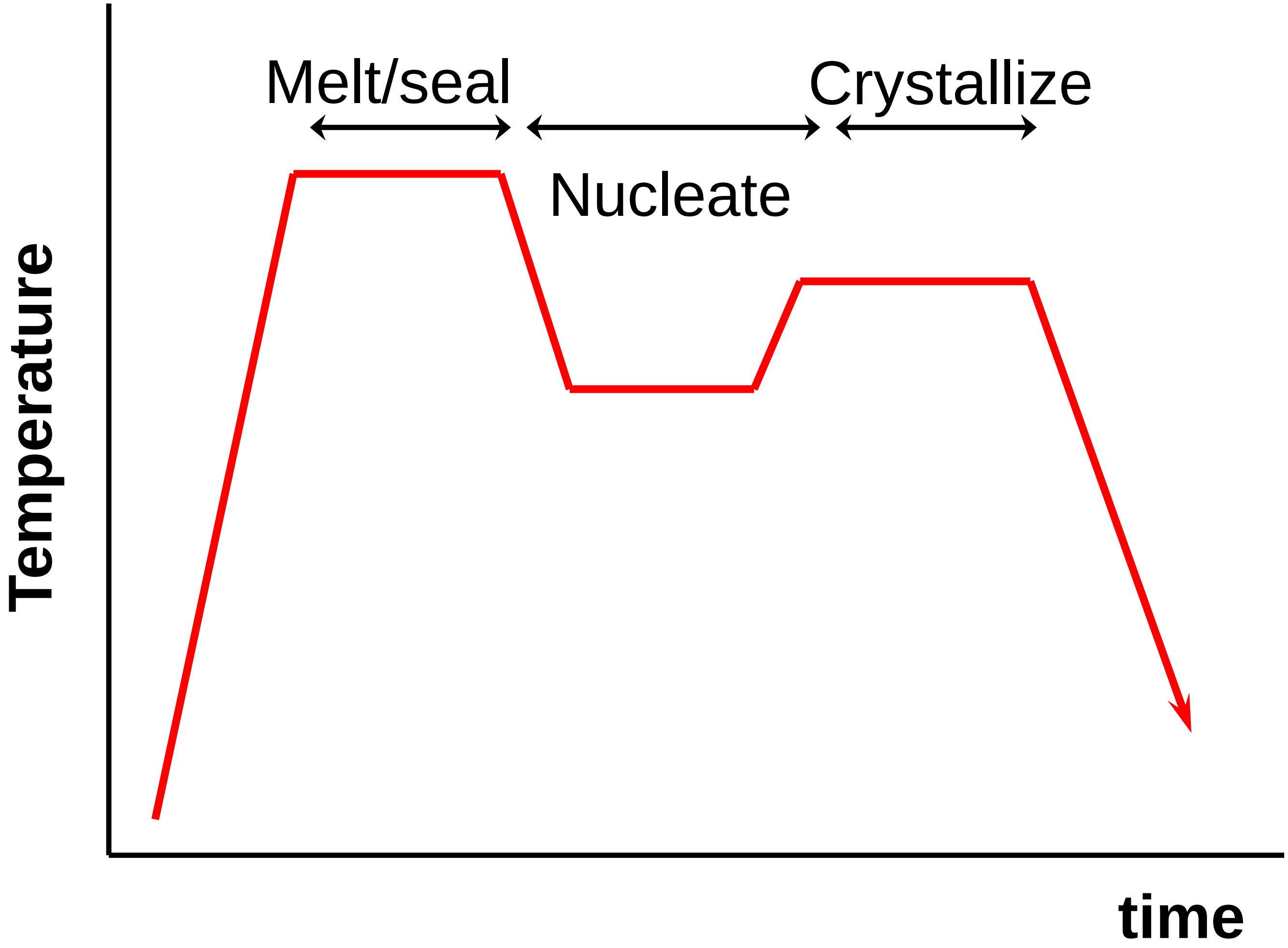


- High yield strengths
  - >100 kpsi
- good fracture toughness
- excellent corrosion resistance

Problem:
Hermetic seals are required to isolate air-sensitive materials.

- Glass-ceramics are the solution
  - good mechanical properties
  - CTE-matches to many alloys
  - good chemical properties
  - convenient manufacturing

Conventional glass-ceramic process profile



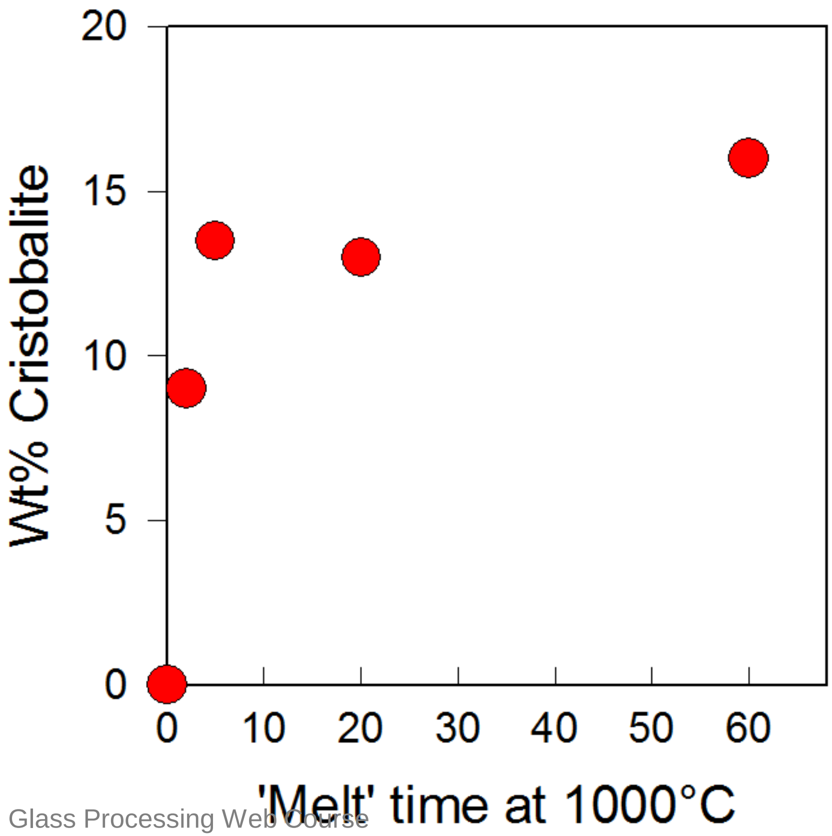
Li-silicate glass ceramics have the requisite CTEs for super-alloy seals

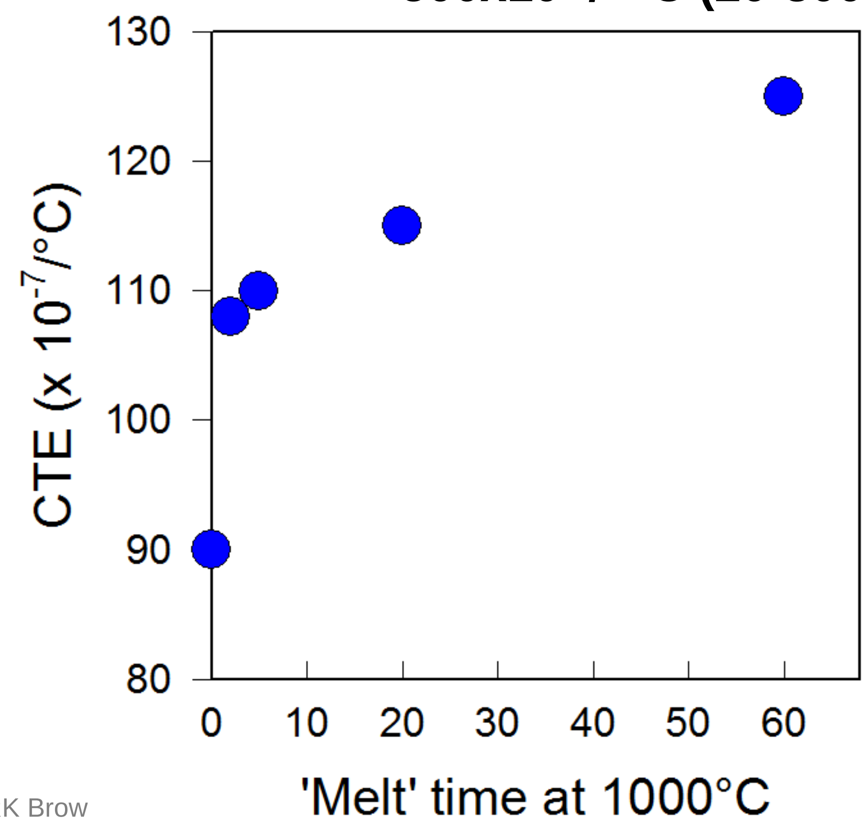
'S-glass' (mole%)

23.7 Li_2O 2.8 K_2O 2.6 Al_2O_3 2.6 B_2O_3 1.0 P_2O_5 67.1 SiO_2

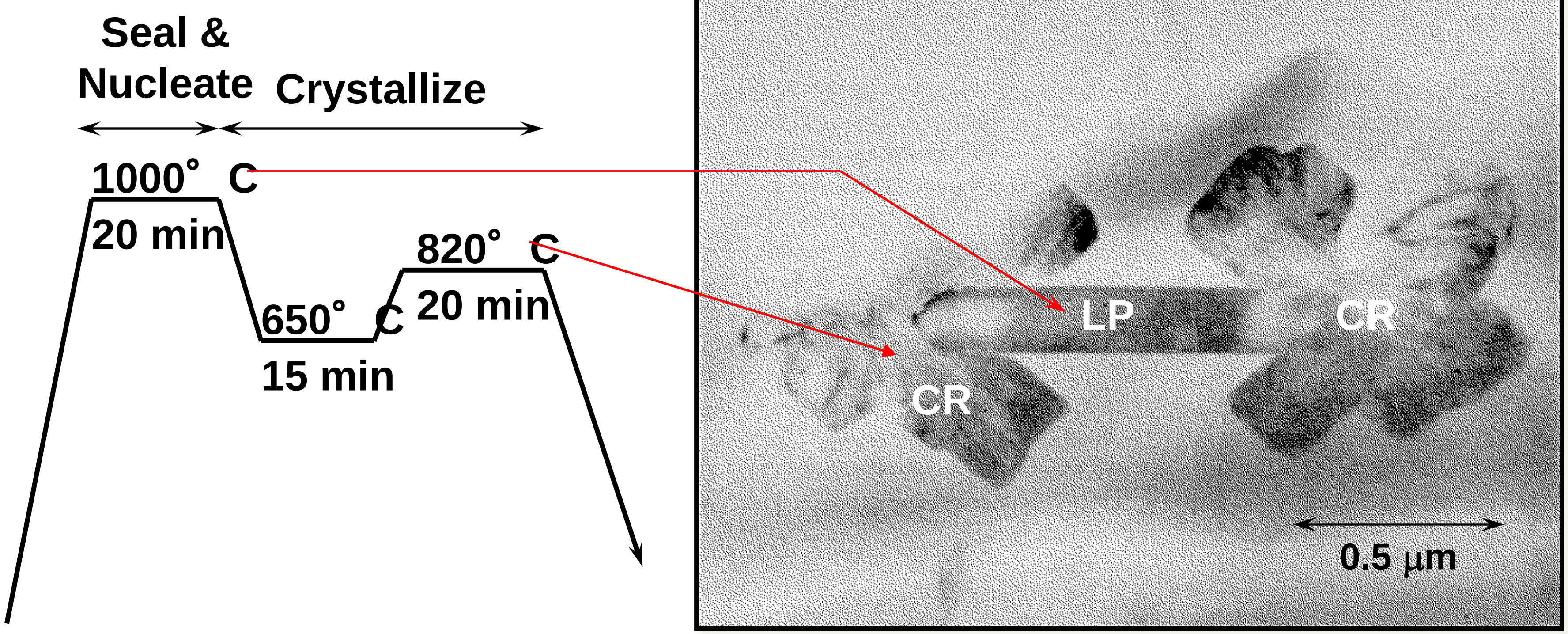
CTE depends on crystalline phases:

Li-disilicate,	**CTE**	**~110x10^{-7}/° C**
cristobalite,	**CTE**	**~125x10^{-7}/° C (20-100° C)**
		~500x10^{-7}/° C (20-300° C)





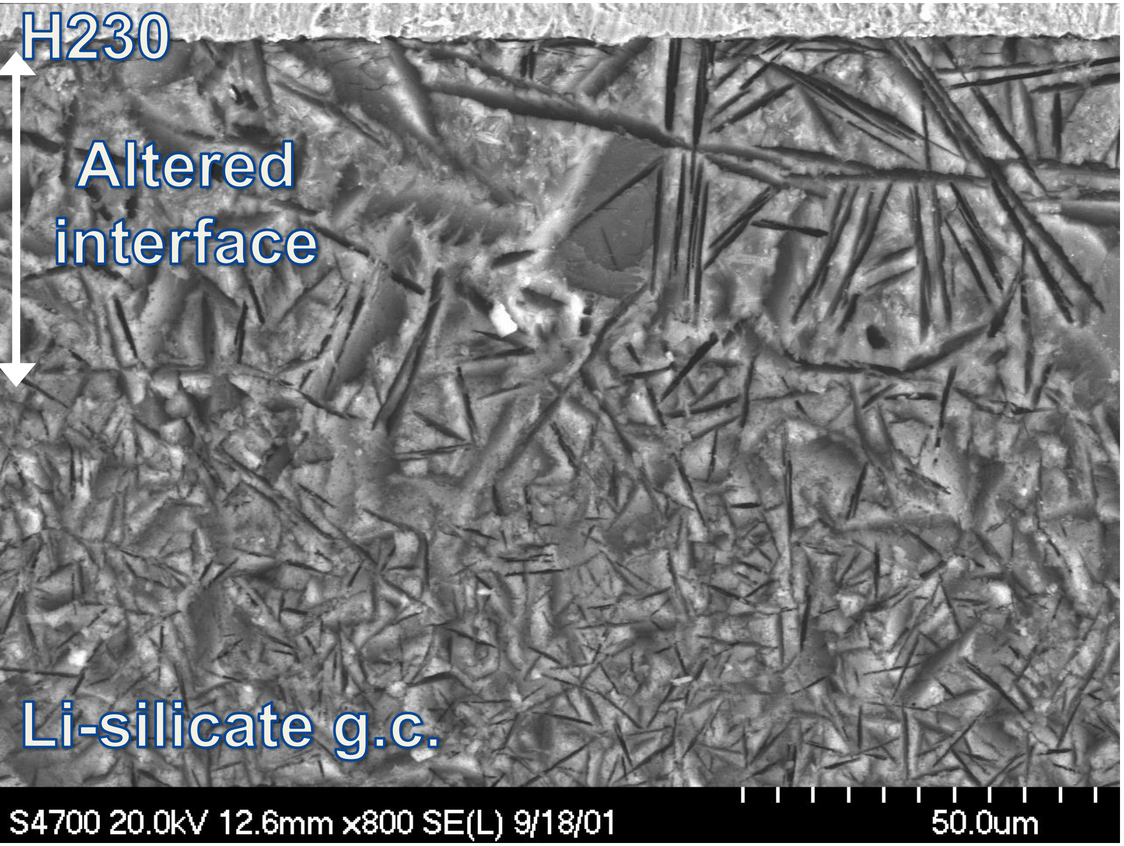
High temperature heterogeneous nucleation leads to desirable glass-ceramics



- Li_3PO_4 nuclei form at 1000° C
- Epitaxial growth of cristobalite at 820° C
    - no nuclei: low CTE Li-disilicate

(Headley and Loehman, J. Am. Ceram. Soc., 1984)

The heterogeneous nucleation mechanism has important application ramifications



- poorly crystallized interface
- Cr-phosphide crystallites

$Cr_{(metal)} + Li_3PO_4 \rightarrow Cr_xP_y + Li_2O_{(gl)}$

- 25% lower CTE

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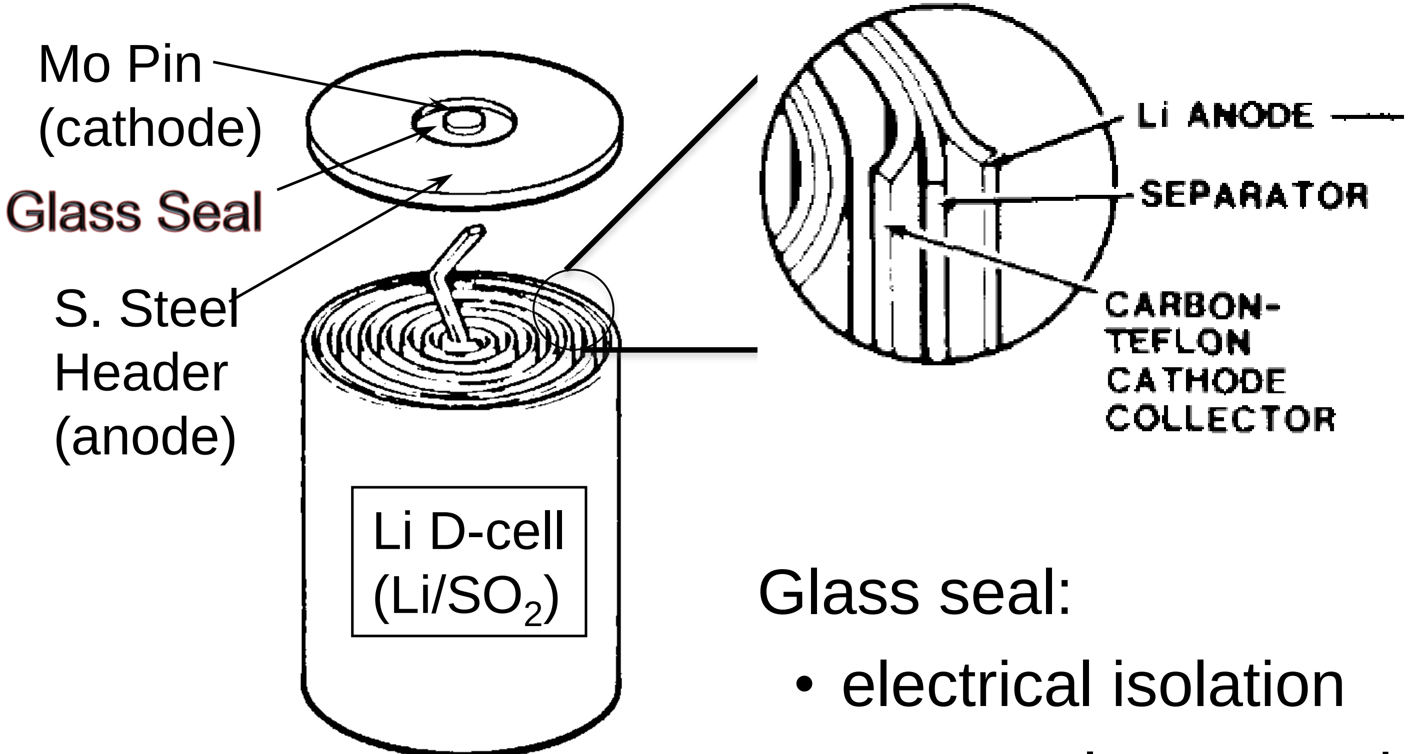
A Few Sealing Glass Case Studies

Example: Lithium D-cell



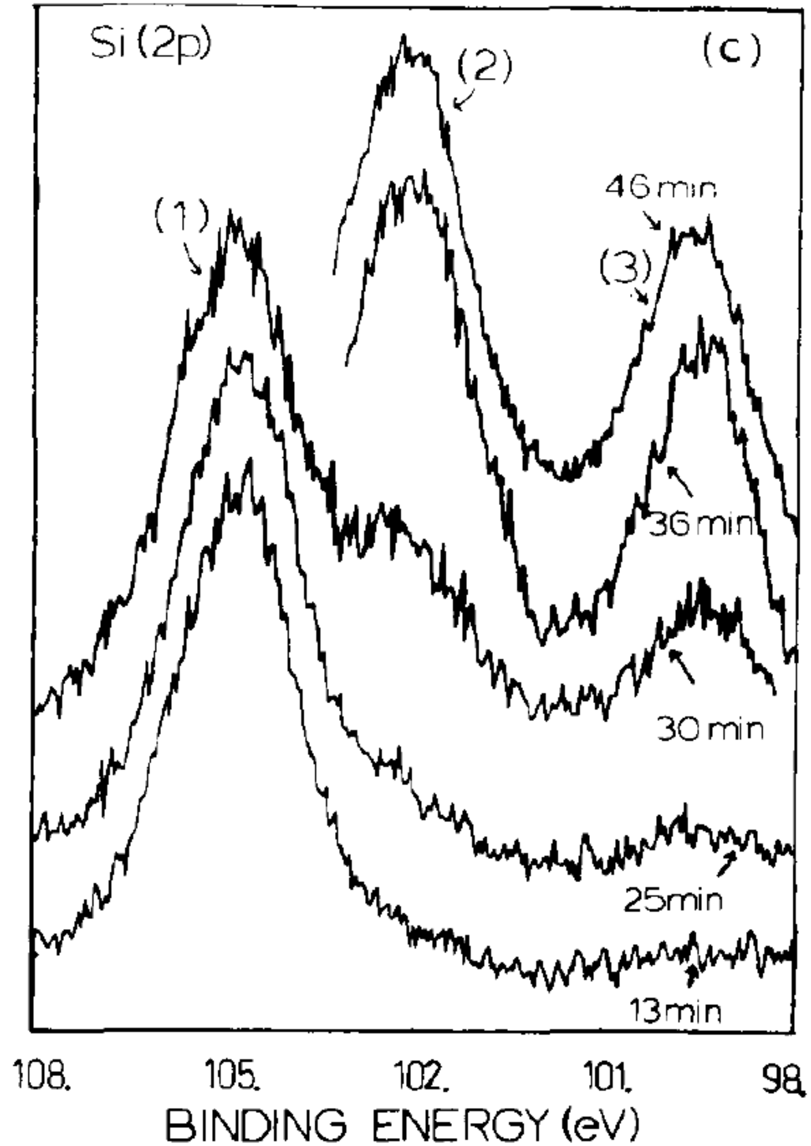
Glass seal:

- electrical isolation
- encapsulates reactive electrolyte

Lithium and other alkali metals react with silicate glasses

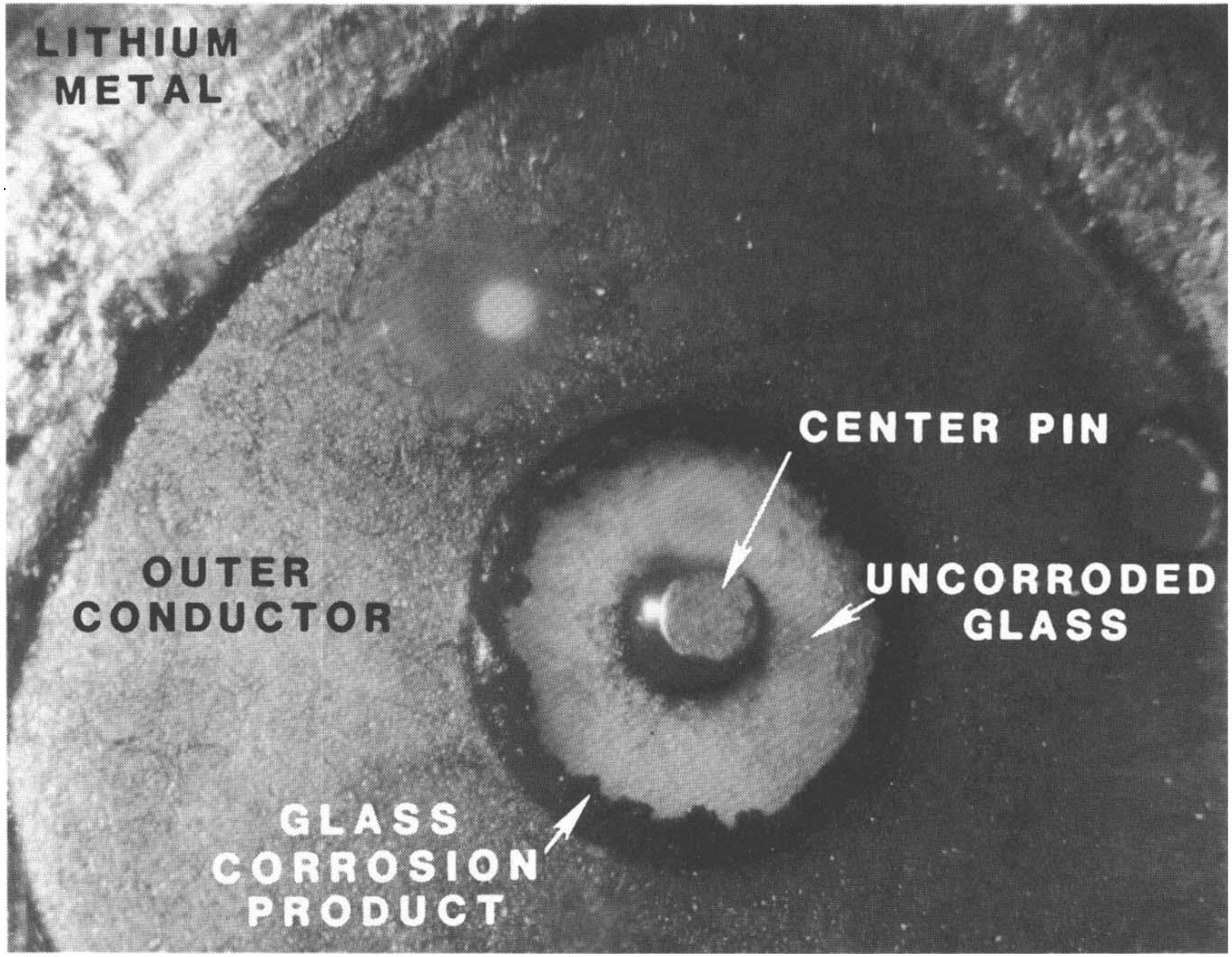
Li thin film on silica at 75° C

$$4Li + SiO_2 \rightarrow 2Li_2O + Si$$



Maschoff, et al., Appl. Surf. Sci. 27 (1986)

Silicate glass seals are attacked by lithium

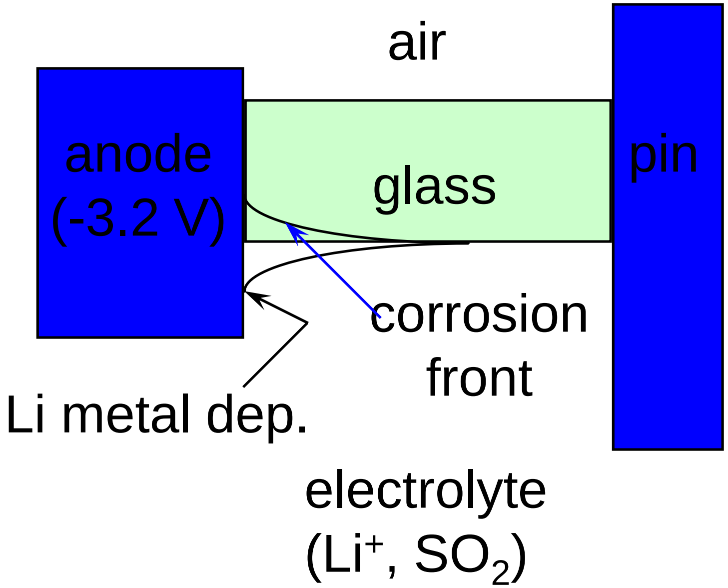


Conventional silicate sealing glass after three months at 70° C, Li/$SOCl_2$ electrolyte-

Bunker et al., J. Mat. Res. 2 (1987)

A mechanism for glass corrosion has been established

Underpotential Deposition



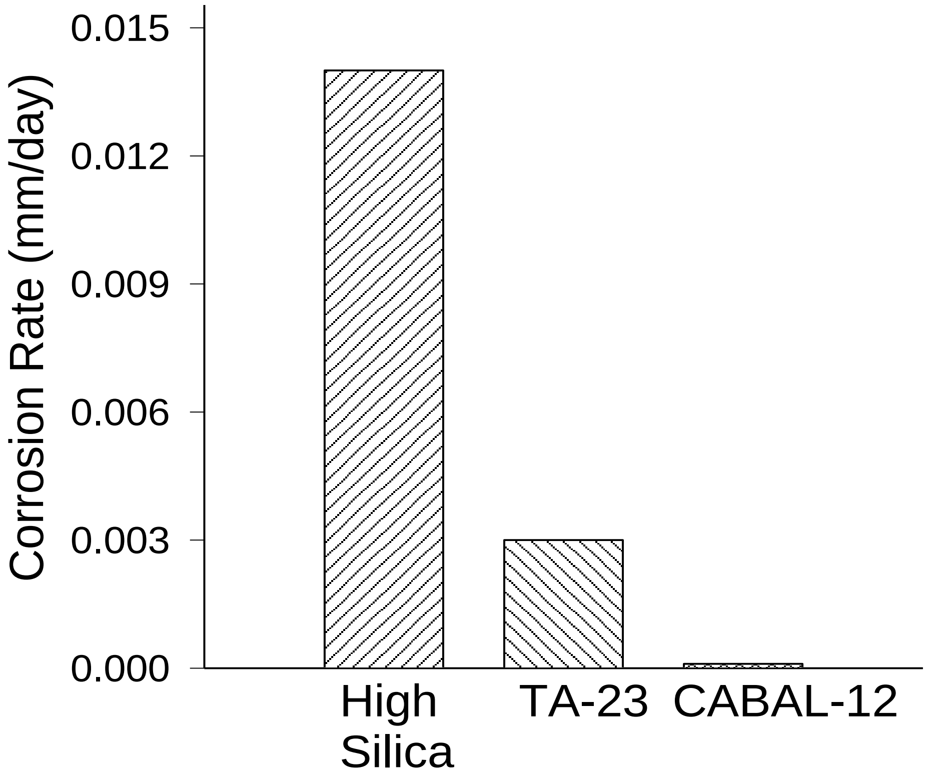
Reaction limits the shelf-life of Li liquid electrolyte cells

$$4Li + SiO_2 \rightarrow 2Li_2O + Si$$

(Bunker *et al.*, *J. Mater. Res.*, 1987.)

Corrosion resistant glasses have been developed

1. **Low silica compositions**
   - **TA-23** (45 wt% SiO_2)
     - shelf-life > 5 years
2. **Aluminoborate compositions**
   - **CABAL-12** (silica-free)
     - $20MgO \bullet 20CaO \bullet 20Al_2O_3 \bullet 40B_2O_3$
     - shelf-life > 20 years
     - lower sealing temperature
     - less prone to crystallization



Applications include Li-batteries for cameras, computers, and biomedical components.

These glasses are used in designs for long-life Li cells

United States Patent (10) **Patent No.: US 7,803,481 B2**
Howard et al. (45) **Date of Patent: Sep. 28, 2010**

LITHIUM-ION BATTERY

United States Patent (10) **Patent No.: US 7,641,992 B2**
Howard et al. (45) **Date of Patent: Jan. 5, 2010**

MEDICAL DEVICE HAVING LITHIUM-ION BATTERY

4,446,212	A	5/1984	Kaun
4,464,447	A	8/1984	Lazzari et al.

United States Patent (10) **Patent No.: US 6,498,951 B1**
Larson et al. (45) **Date of Patent: Dec. 24, 2002**

IMPLANTABLE MEDICAL DEVICE EMPLOYING INTEGRAL HOUSING FOR A FORMABLE FLAT BATTERY

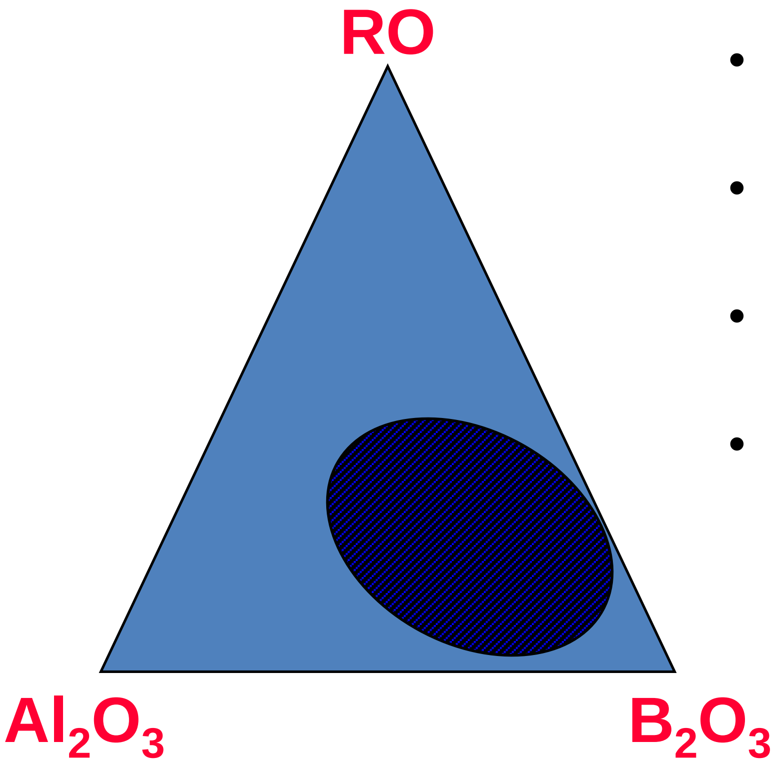
5,199,428	A	4/1993	Obel et al.	128/419 C
5,207,218	A	5/1993	Carpentier et al. ...	128/419 PG
5,312,453	A	5/1994	Shelton et al.	607/19

United States Patent Application Publication (10) **Pub. No.: US 2005/0255380 A1**
Lasater et al. (43) **Pub. Date: Nov. 17, 2005**

LITHIUM-ION BATTERY SEAL

(60) Provisional application No. 60/346,031, filed on Nov. 9, 2001.

Alkaline earth aluminoborate glasses have the requisite properties for lithium battery seals

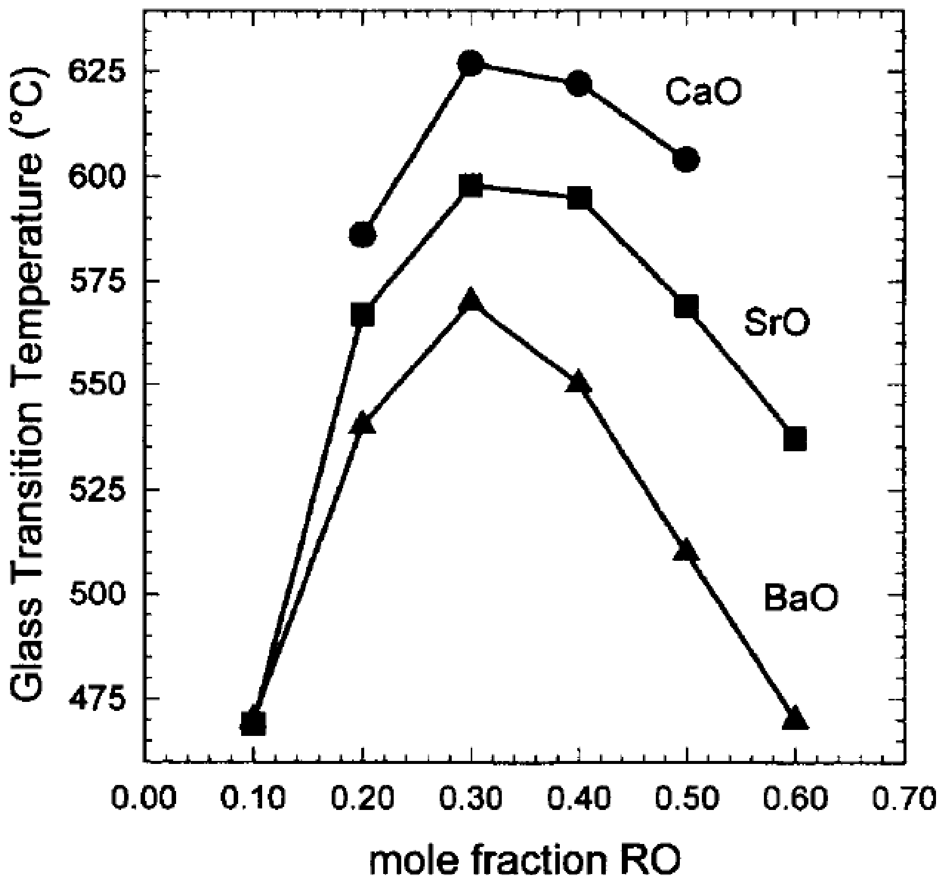


- Range of CTEs for variety of pin materials
- Relatively low sealing temperatures (<800° C)
- CABAL glasses are used in Na-vapor lamps
- Resist attack by lithium
  - kinetic stability (Li reduces B_2O_3 to boride)
  - >20 year projected battery lifetime

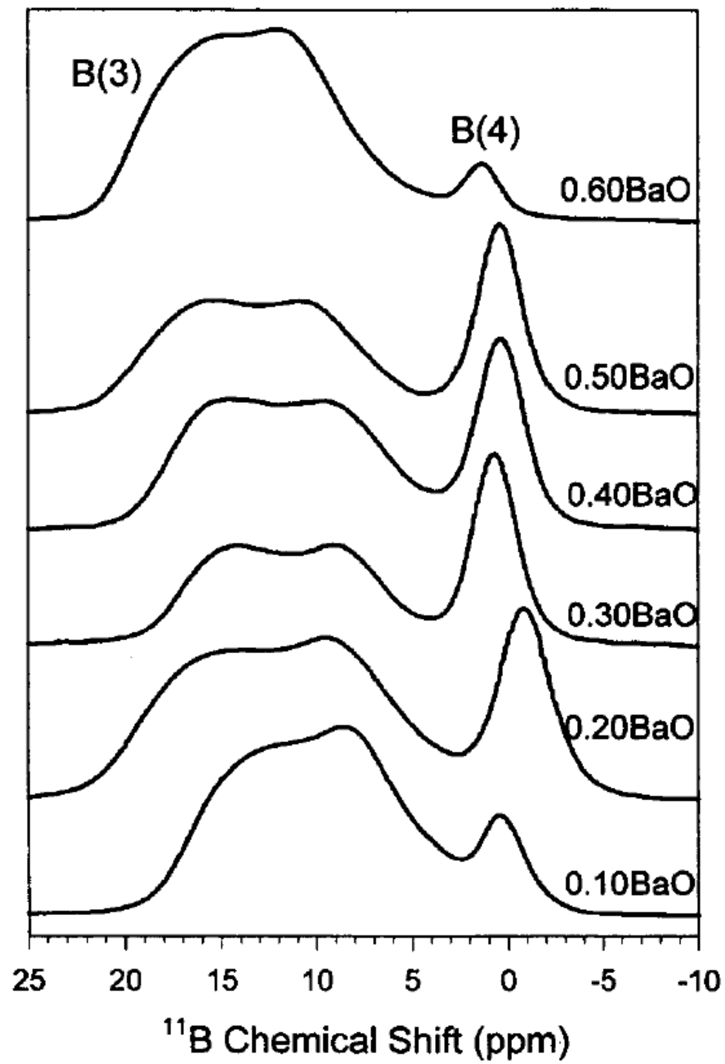
How does structure affect useful properties?

Glass properties depend structure

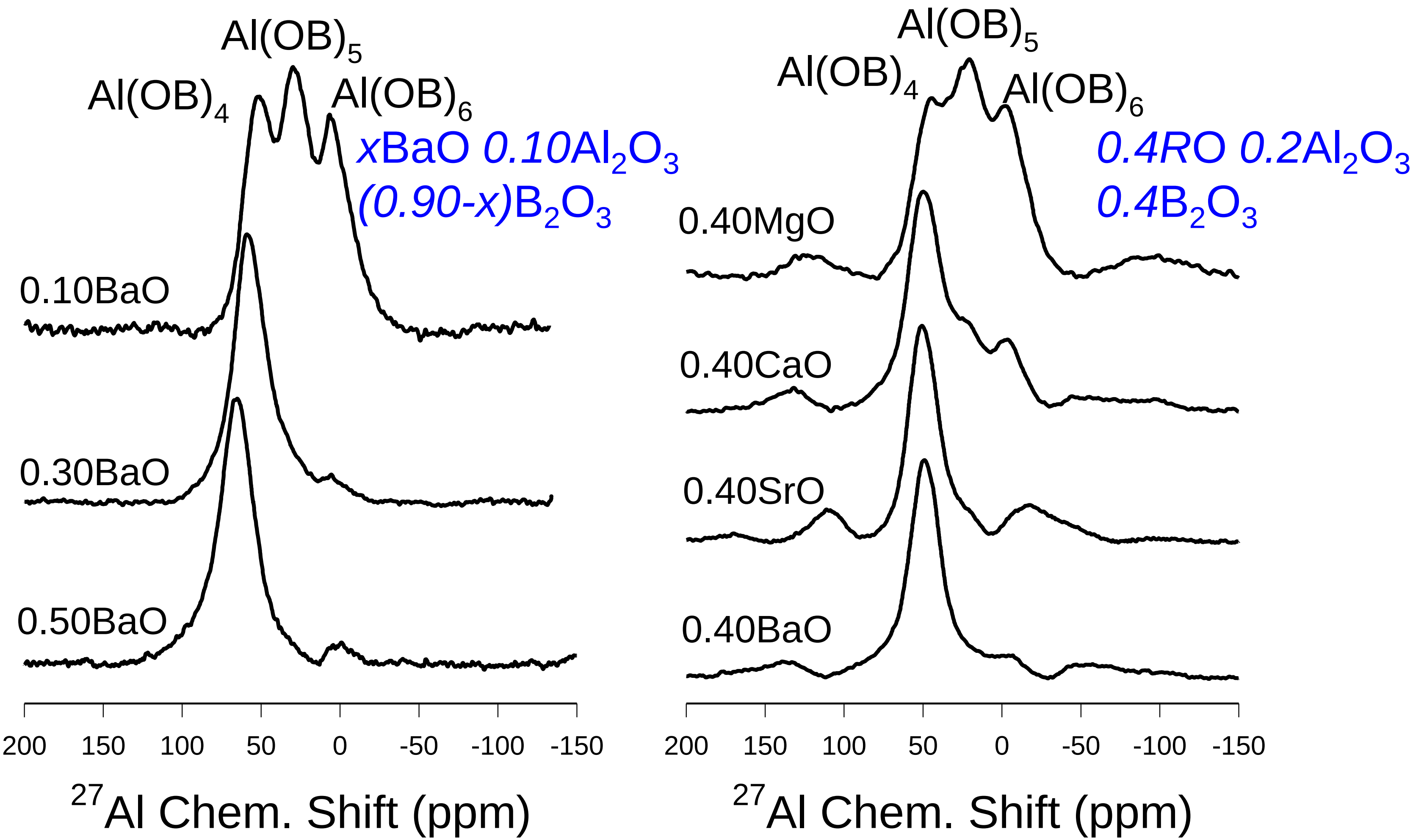
xRO $0.10Al_2O_3$ $(0.90-x)B_2O_3$



Brow and Tallant, JNCS (1997)

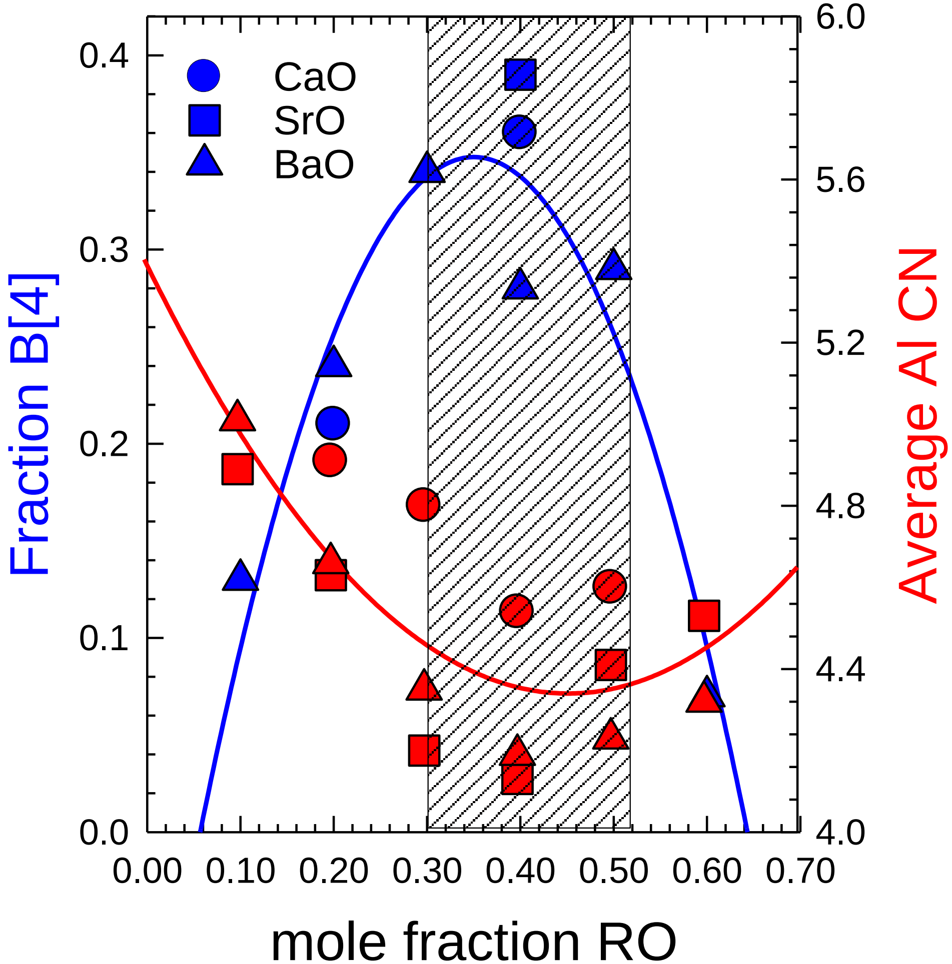


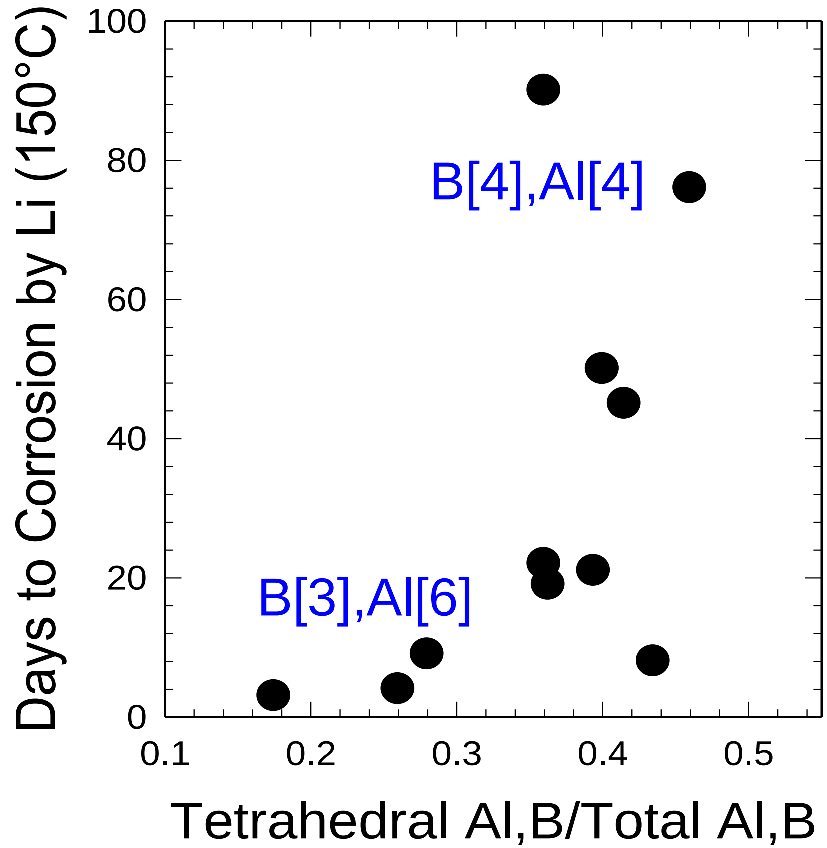
Alumina coordination also depends on composition



Brow and Tallant, 1997

The most durable glasses have tetrahedral networks

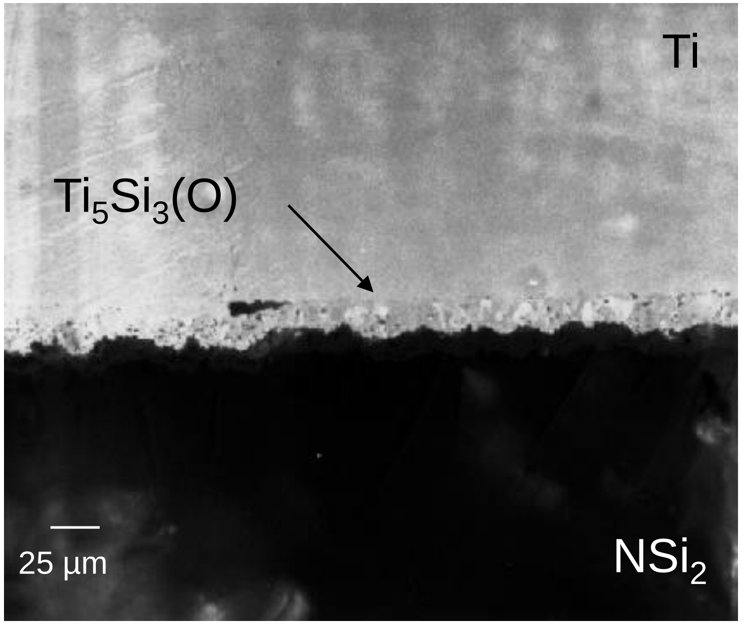




Aqueous durability exhibits similar structural dependencies

Spin-Off Development: Titanium Sealing Glasses

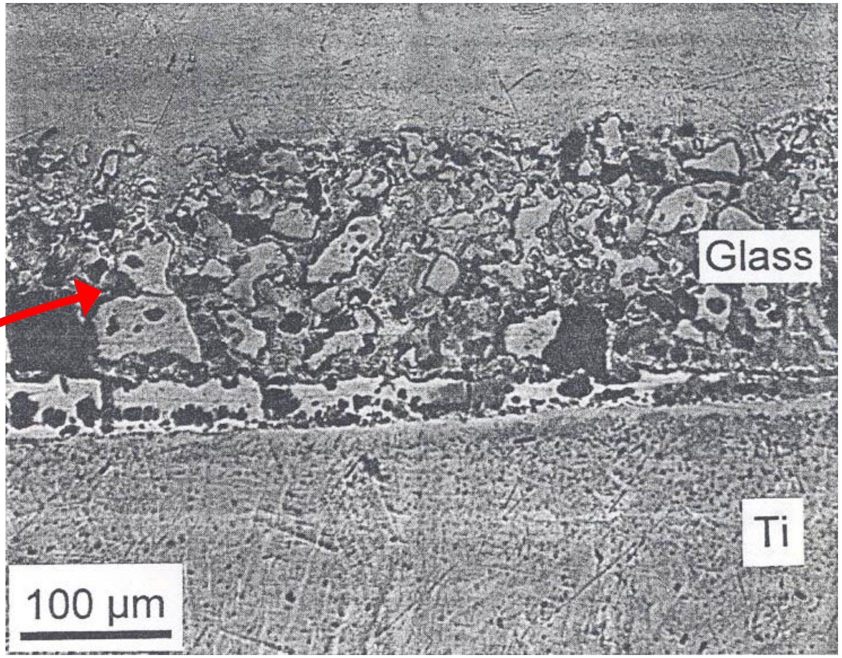
- Titanium alloys have a variety of useful properties
  - High strength-to-weight ratio
  - Superior corrosion resistance
  - Reasonable weldability
- Potential Sealing Applications:
  - Satellite connectors, actuators
  - Implanted biomedical components (pacemakers, insulin pumps, etc.)
  - Biocompatible coatings on prosthetic alloys

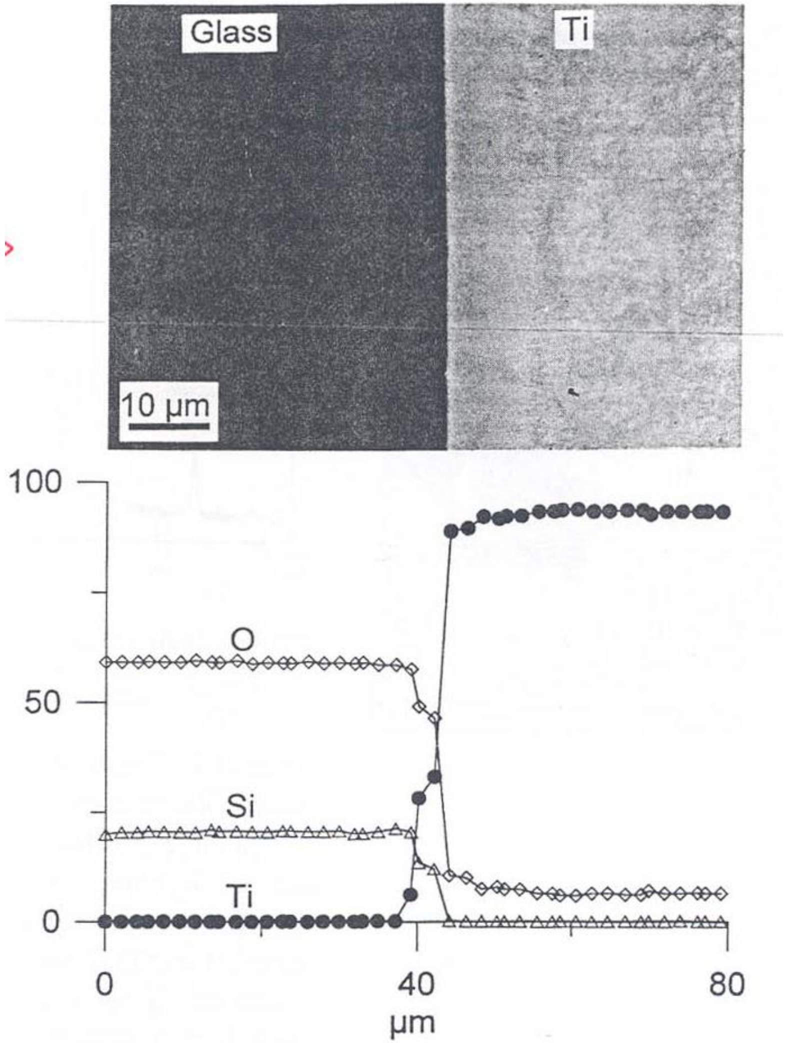


Limitation: Reliable, commercial hermetic sealing technology
- conventional silicate sealing glasses are reduced by titanium
  - silicide formation leads to weak glass/Ti interfaces

Silicate bio-glass coatings for titanium require very short processing times

800°C/1 minute: no deleterious reactions between silicate glass and Ti.

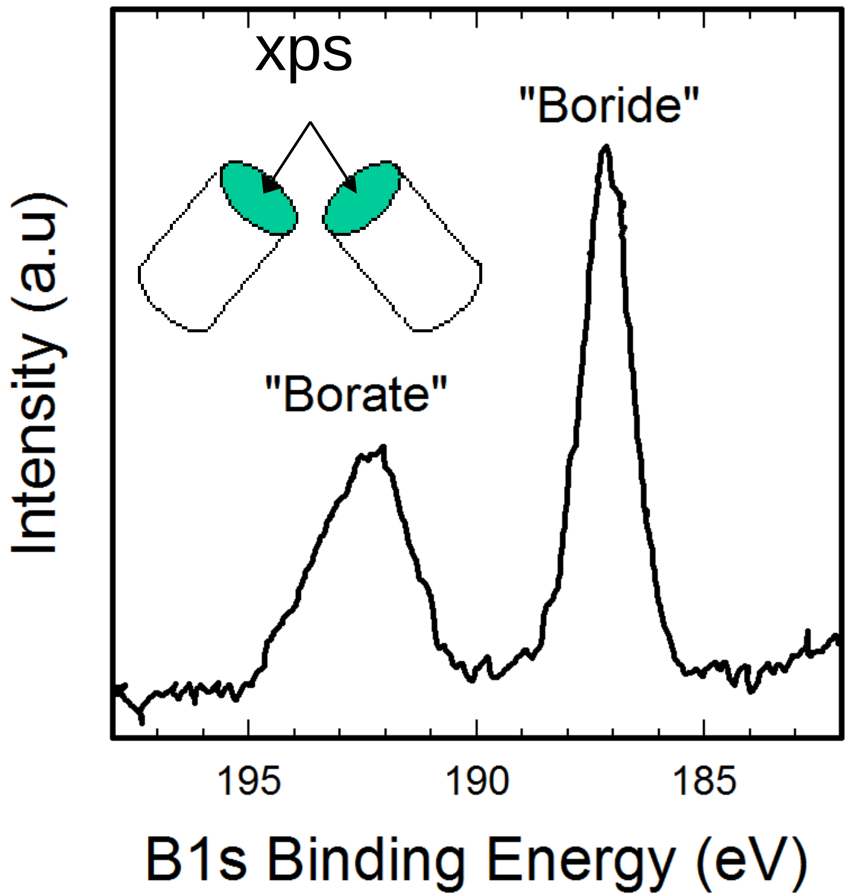




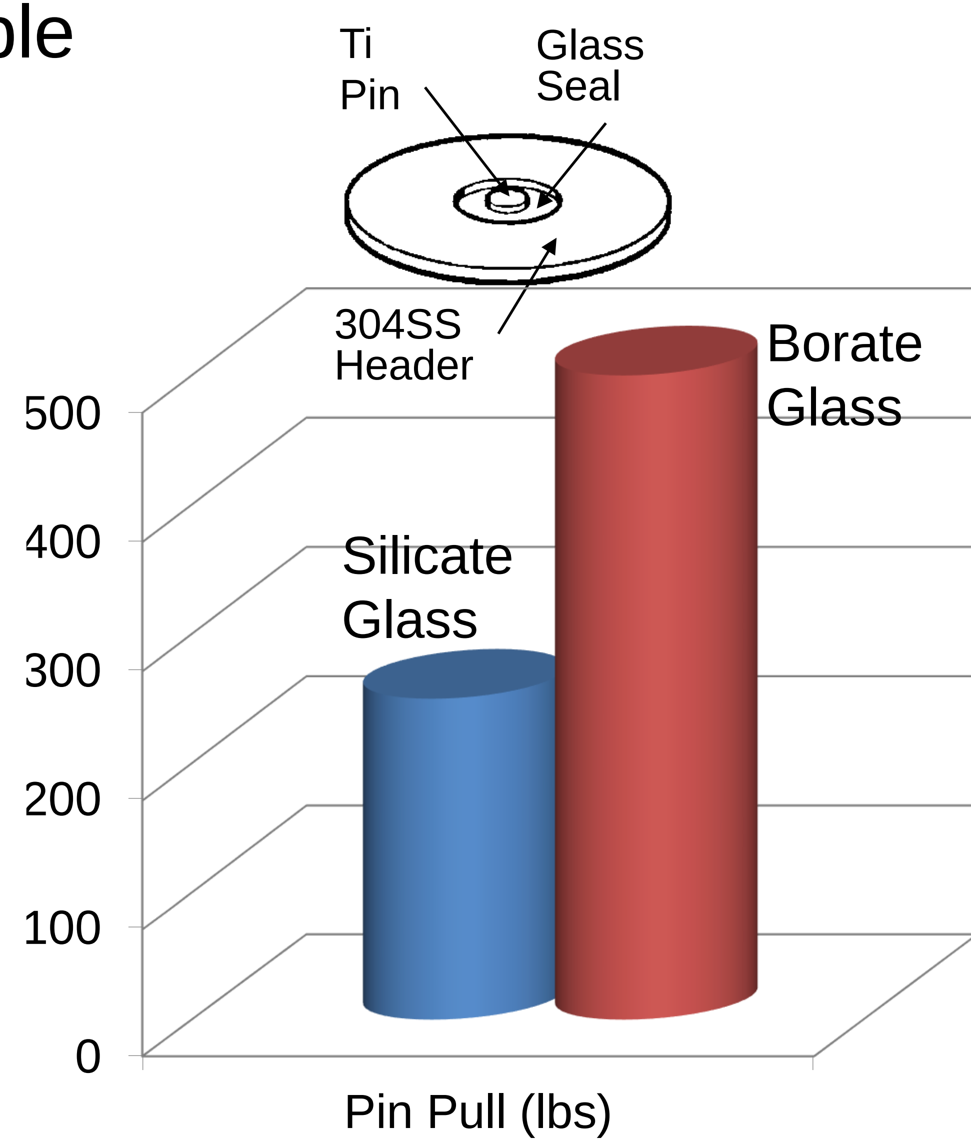
900°C/1 minute: excessive interfacial reactivity between Bioglass and Ti.

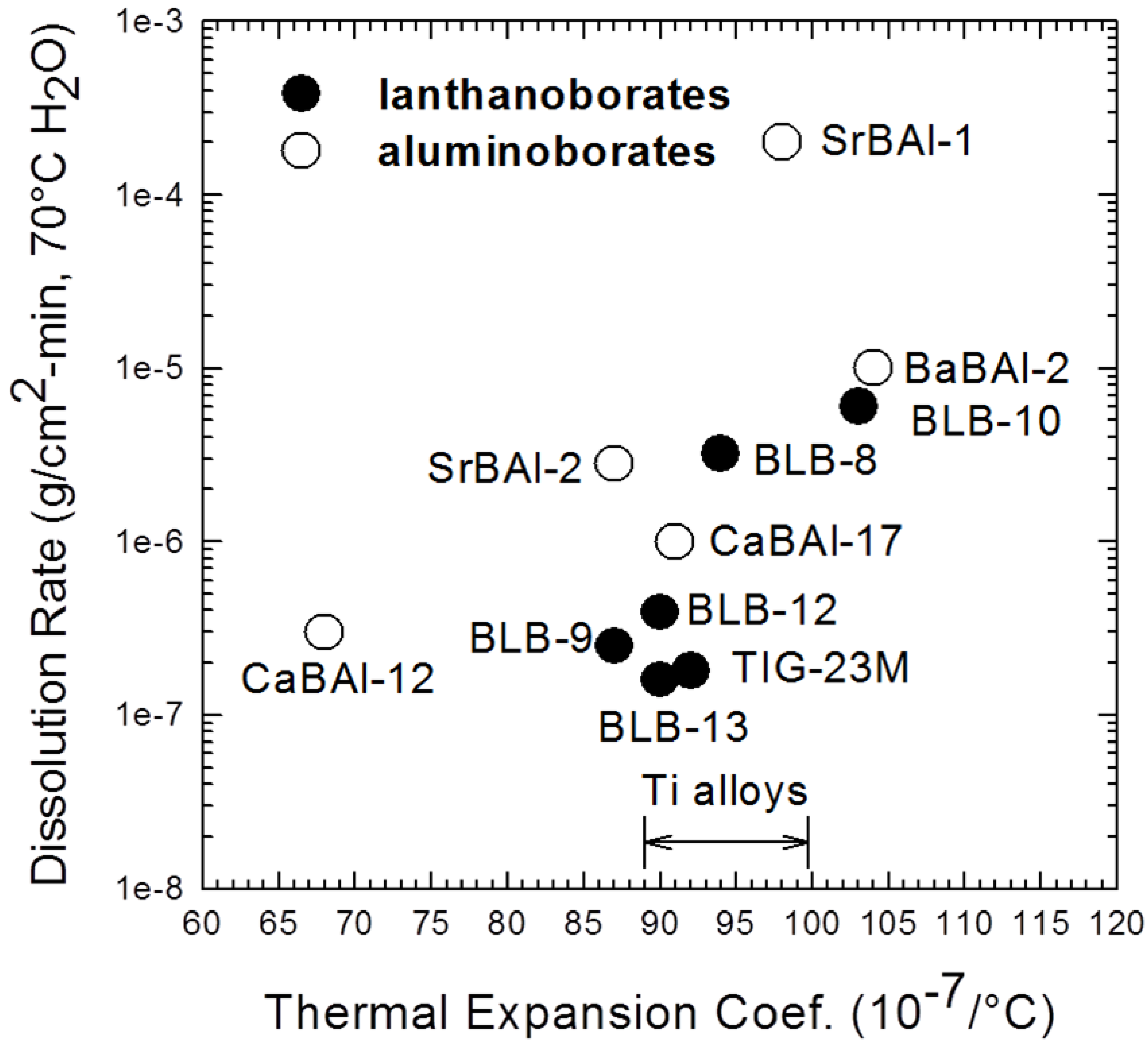
Pazo et al (1998)

Borate glasses are compatible with titanium alloys



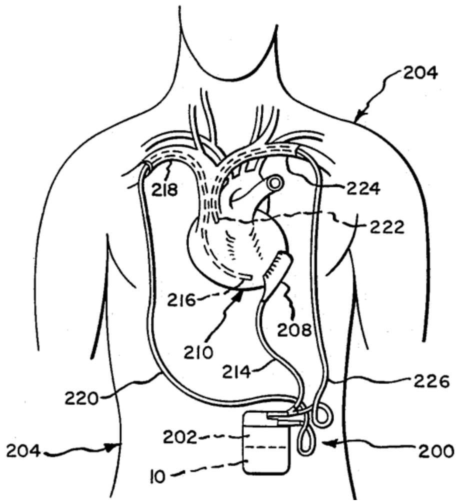
$$Ti + B_2O_3 \rightarrow TiB_x + TiO_y$$



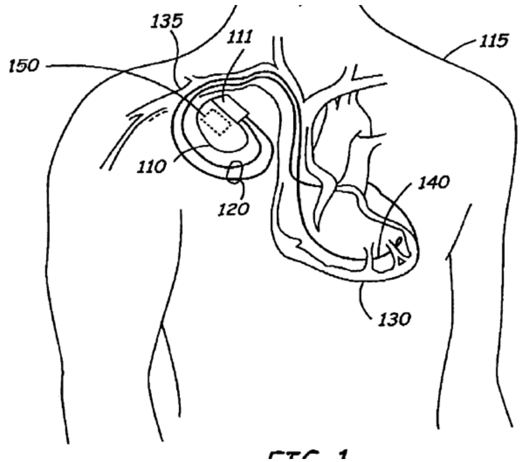


lanthanoborates
aluminoborates
SrBAl-1
BaBAl-2
BLB-10
BLB-8
SrBAl-2
CaBAl-17
BLB-12
BLB-9
TIG-23M
CaBAl-12
BLB-13
Ti alloys
1e-3
1e-4
1e-5
1e-6
1e-7
1e-8
60
65
70
75
80
85
90
95
100
105
110
115
120
Dissolution Rate (g/cm2-min, 70°C H2O)
Thermal Expansion Coef. (10-7/°C)

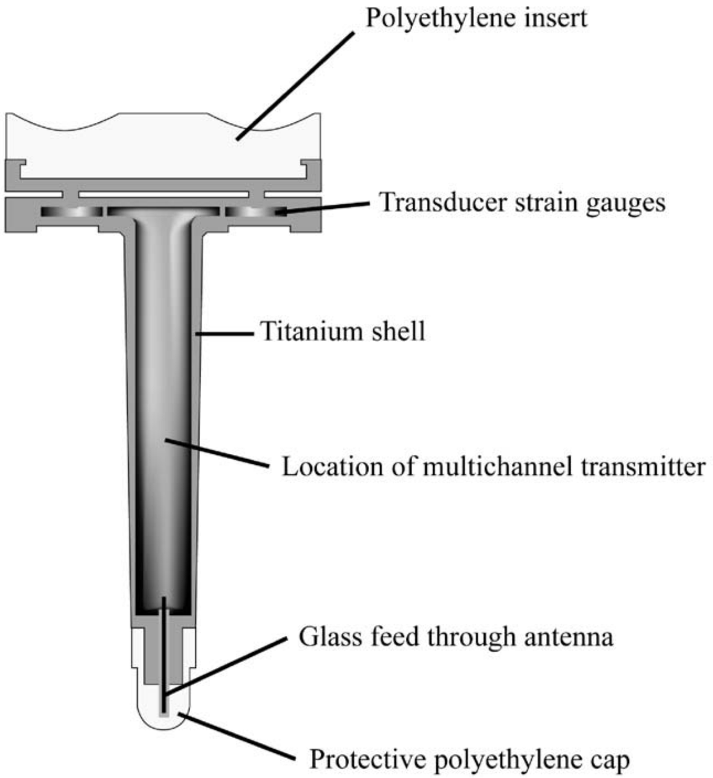
Borate glasses are now being used in a variety of titanium biomedical applications



Pacemakers and defibrillators

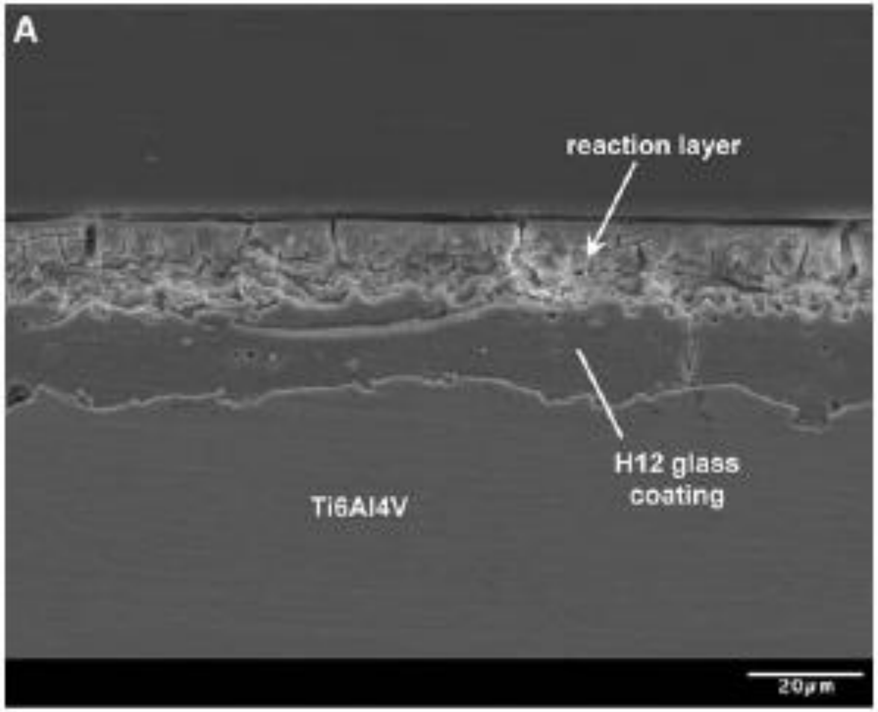


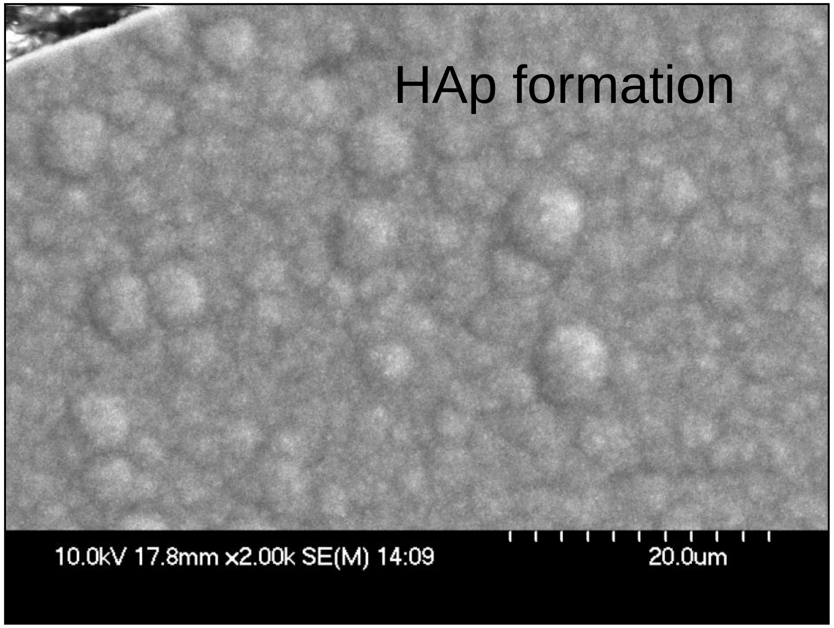
Insulin pumps



Orthopedic pressure sensors

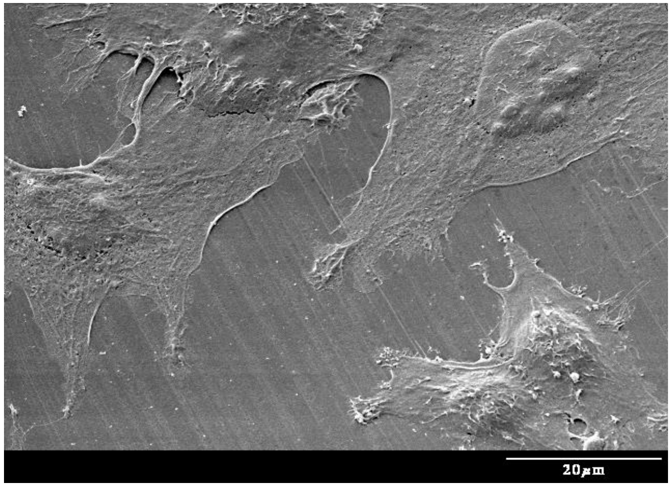
Bioactive borate glass coatings have been developed for titanium

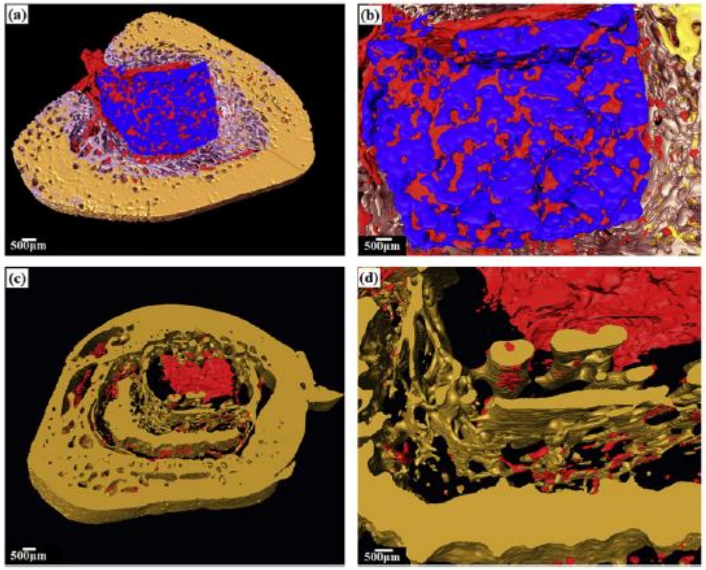




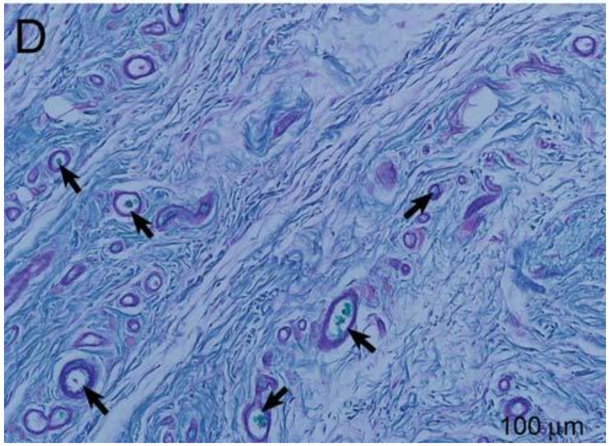
L. Peddi, RK Brow and RF Brown, J. Mater. Sci. Mater Med (2008) 19, 3145

Saos-2 cell compatibility





MN Rahaman et al., Acta Biomatl., 7, 2355 (2011)



Yinan Lin, RF Brown, SB Jung, DE Day, Angiogenic effects of borate glass microfibers in a rodent model, J. Biomedical Mat. Res. A, 102A [12], 4491 (2014).

Solid Oxide Fuel Cells

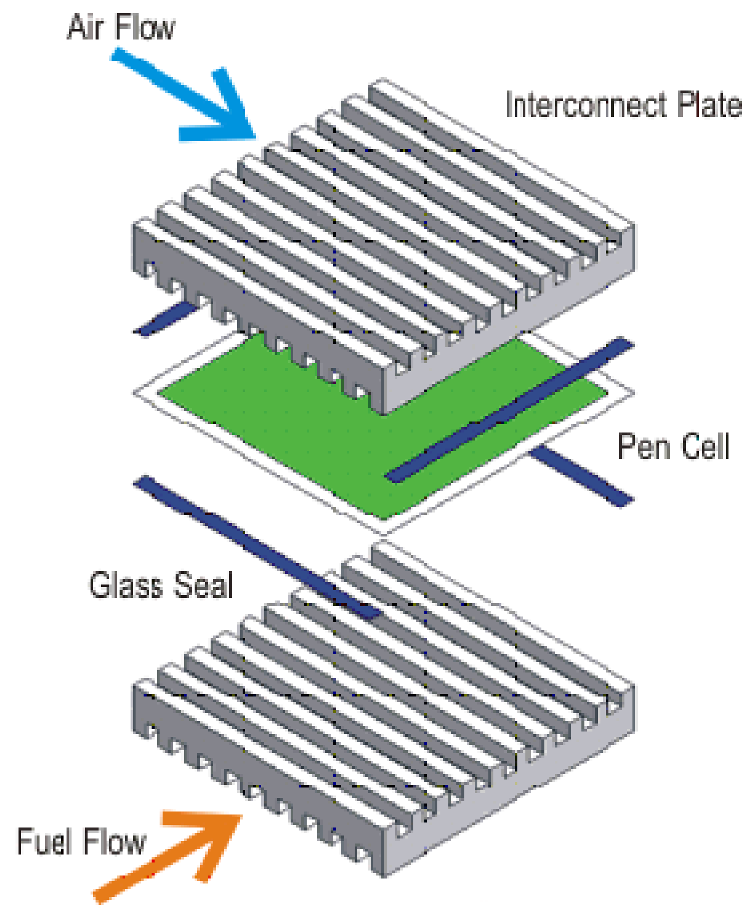
From I. Donald, et al., J Mater Sci (2011) 46:1975–2000

Fig. 6 SOFCs. Experimental unit. Julich Research Centre 13.3 kW

Designing glasses for SOFC seals is a significant challenge

Function:
- Prevent mixing of fuel/oxidant within stack
- Prevent leaking of fuel/oxidant from stack
- Electrically isolate cells in stack
- Provide mechanical bonding of components

Challenges:
- Thermal expansion matches to a variety of materials
- Relatively high operational temperatures (>700ºC)
  - Long lifetimes (>10000's hrs)
  - Maintain stability over range of P_{O2}, P_{H2O}
- Relatively low sealing temperatures (<900ºC)
  - Avoid altering other SOFC materials



For some designs, glass-ceramics may be suitable, others may require viscous seals

There have been a number of recent reviews of SOFC sealing glasses

J Mater Sci (2007) 42:3465–3476
DOI 10.1007/s10853-006-0409-9

J. Mat. Sci. (2007)

A review of sealing technologies applicable to solid oxide electrolysis cells

Journal of Power Sources 147 (2005) 46–57

J. Power Sources, (2005)

Review

Sealants for solid oxide fuel cells

Jeffrey W. Fergus *

Contents lists available at ScienceDirect

Materials Science and Engineering R

journal homepage: www.elsevier.com/locate/mser

Glass-based seals for solid oxide fuel and electrolyzer cells – A reviev

M.K. Mahapatra, K. Lu *

Mat Sci Eng B (2010)

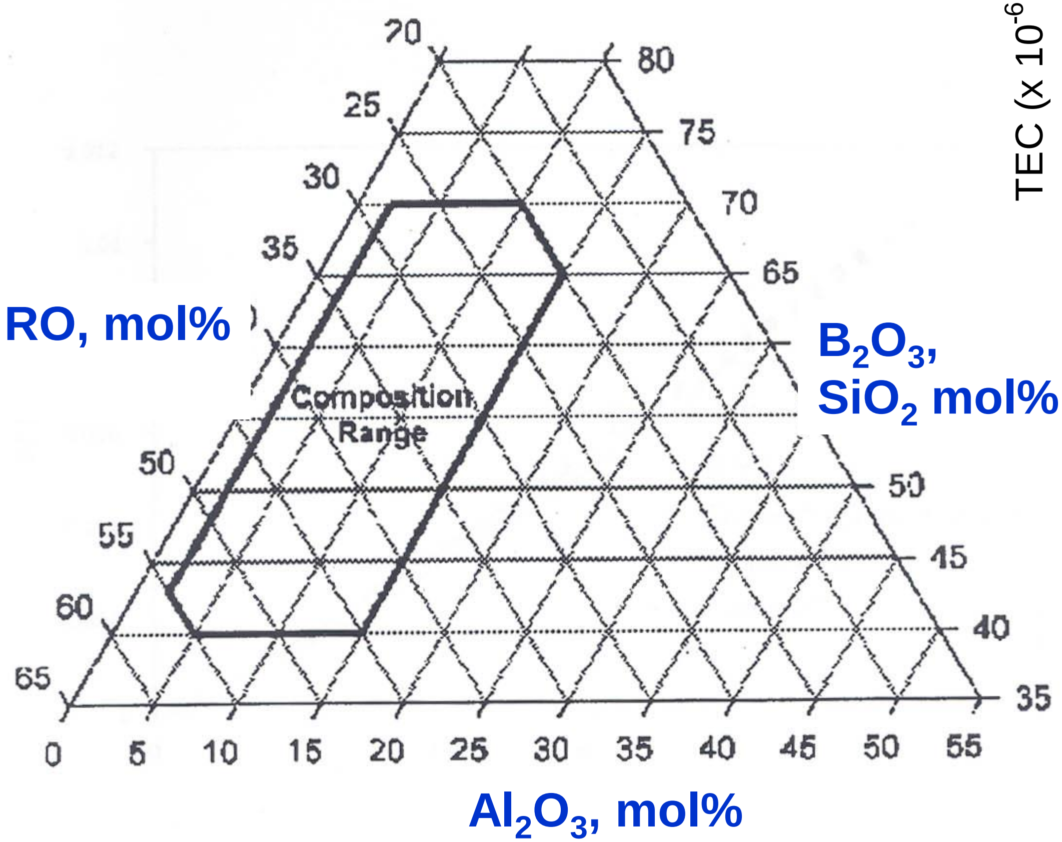
The State-of-the-Art in Sealing Technology for Solid Oxide Fuel Cells

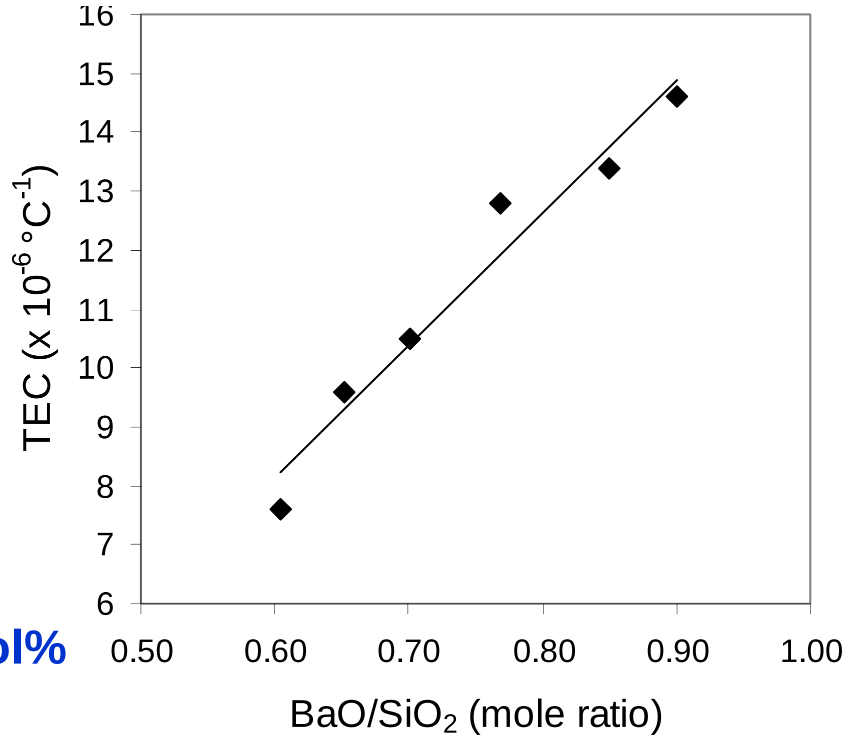
K. Scott Weil

JOM, August 2006

Ba-silicate glass-ceramics have shown promise

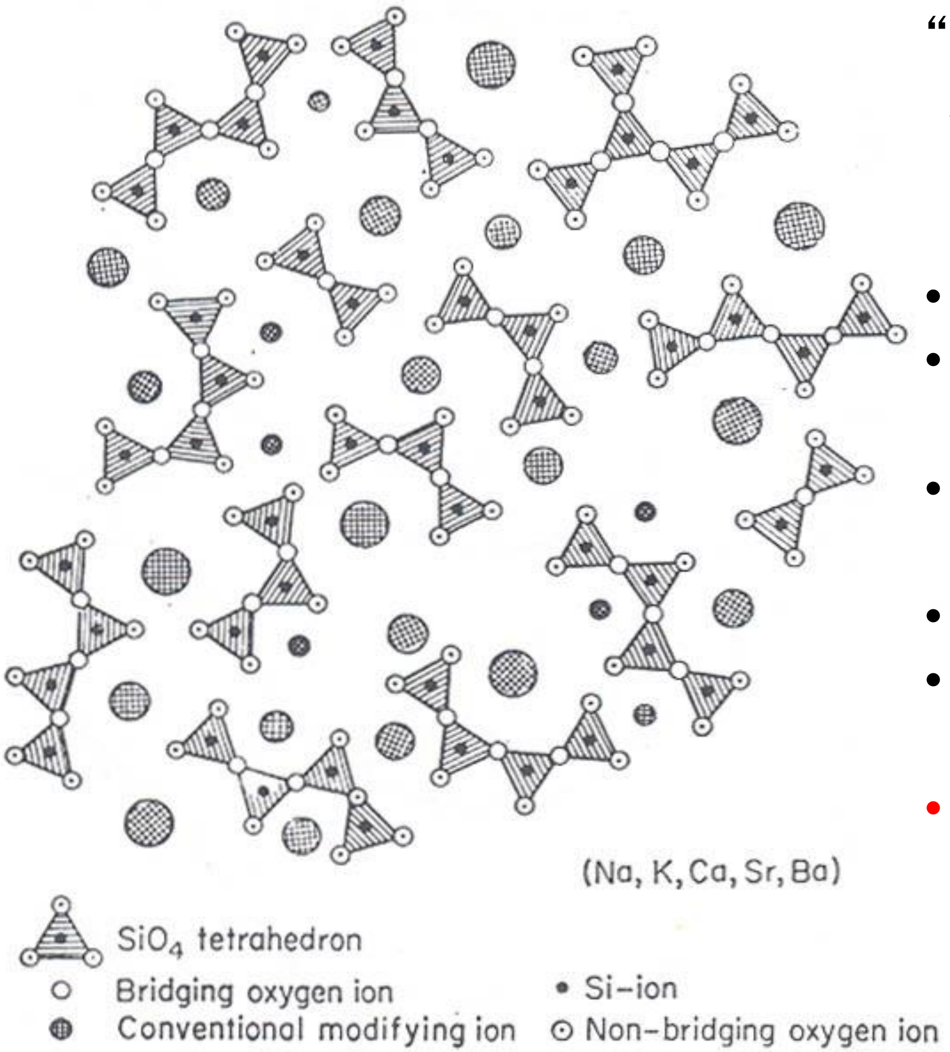
Meinhardt, et al., USP 6,532,769
Mar. 18, 2003





Sealed, crystallized to form high CTE Ba-silicate & Ba-alumino-silicate phases; e.g., $BaO{\cdot}2SiO_2$, $2BaO{\cdot}3SiO_2$

Candidate sealing glasses have 'invert' structures

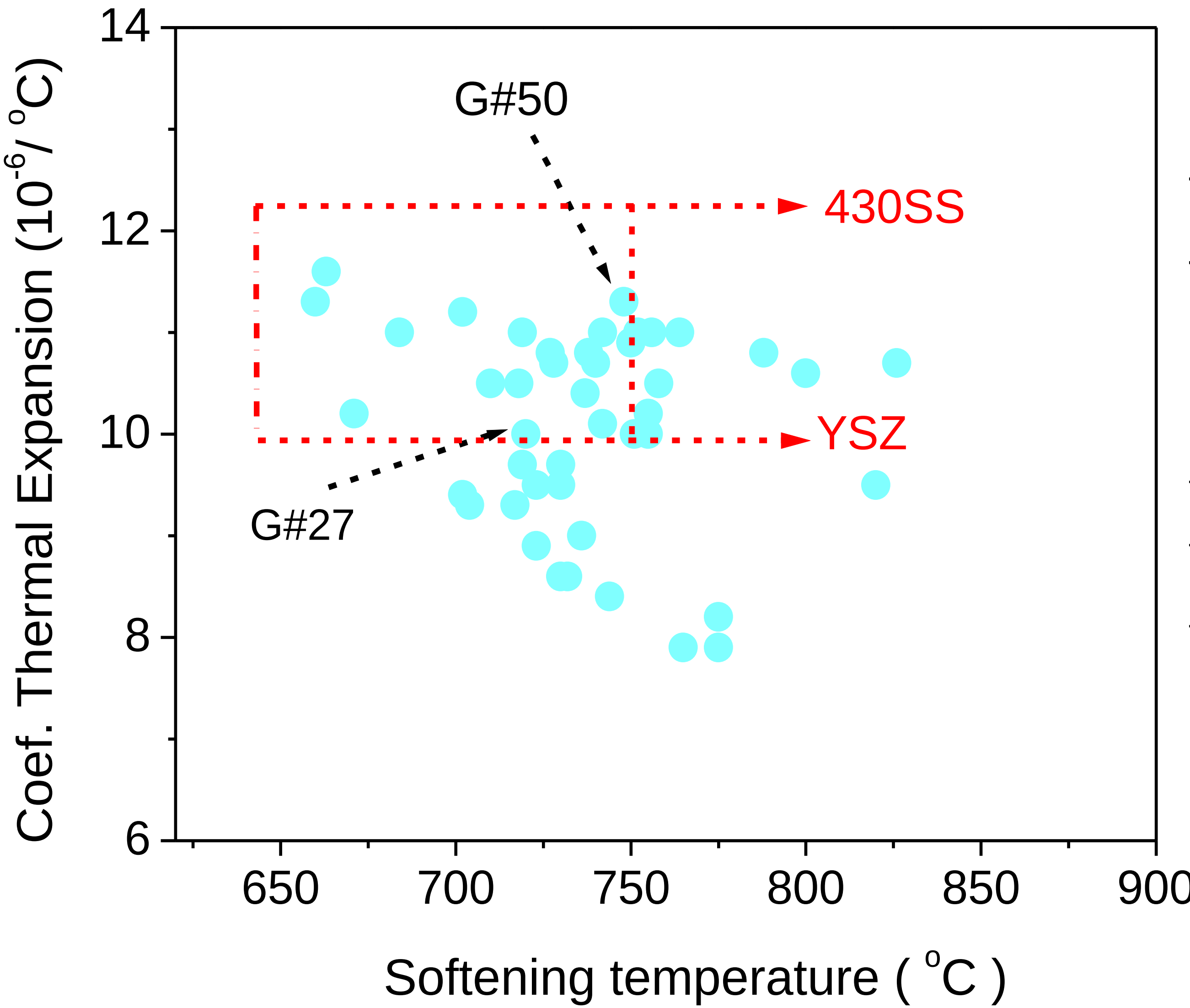


"**Invert Glasses**": discontinuous silicate anions tied-together through modifying cations.

- Greater CTE's
- More fragile viscosity behavior
  - 'shorter' glasses
- More 'basic' reaction chemistries

- Metasilicates (chains): [O]/[Si]~3.0
- Polysilicates (short chains): [O]/[Si]>3.0

- Greater CTEs from polysilicate crystalline phases



"Invert" silicate:

Glasses with

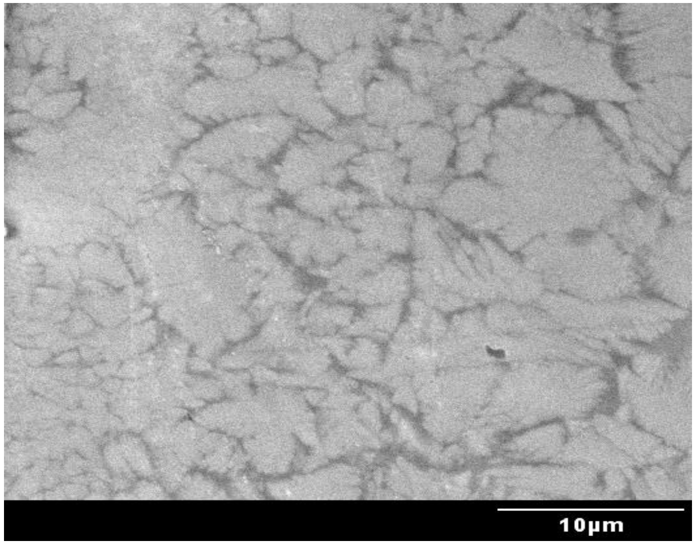
SiO_2<45 mole%

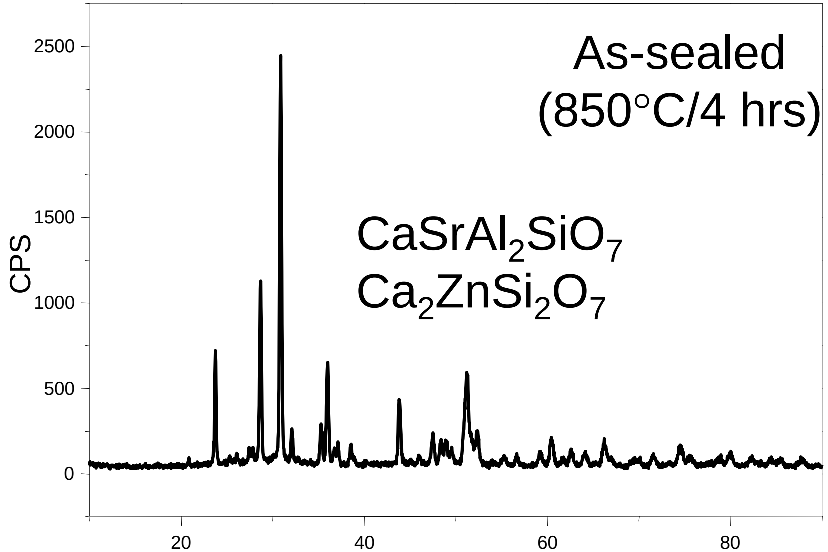
Compositions based on:

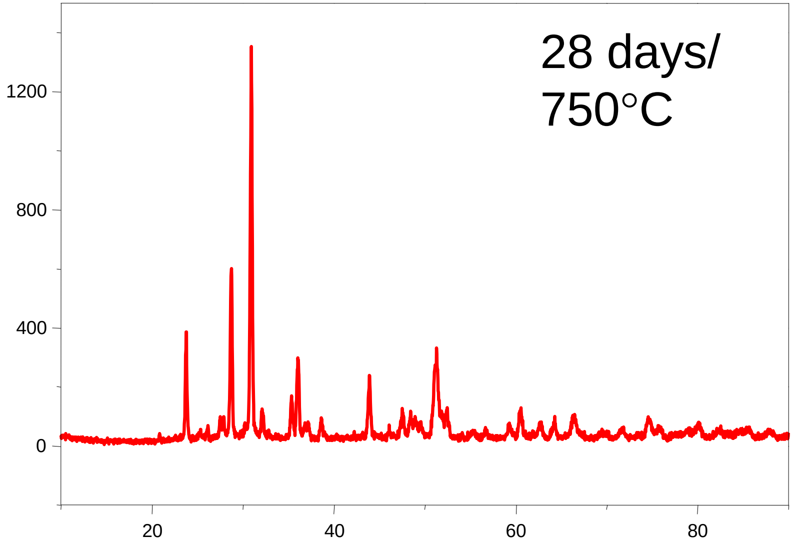
Pyrosilicate and

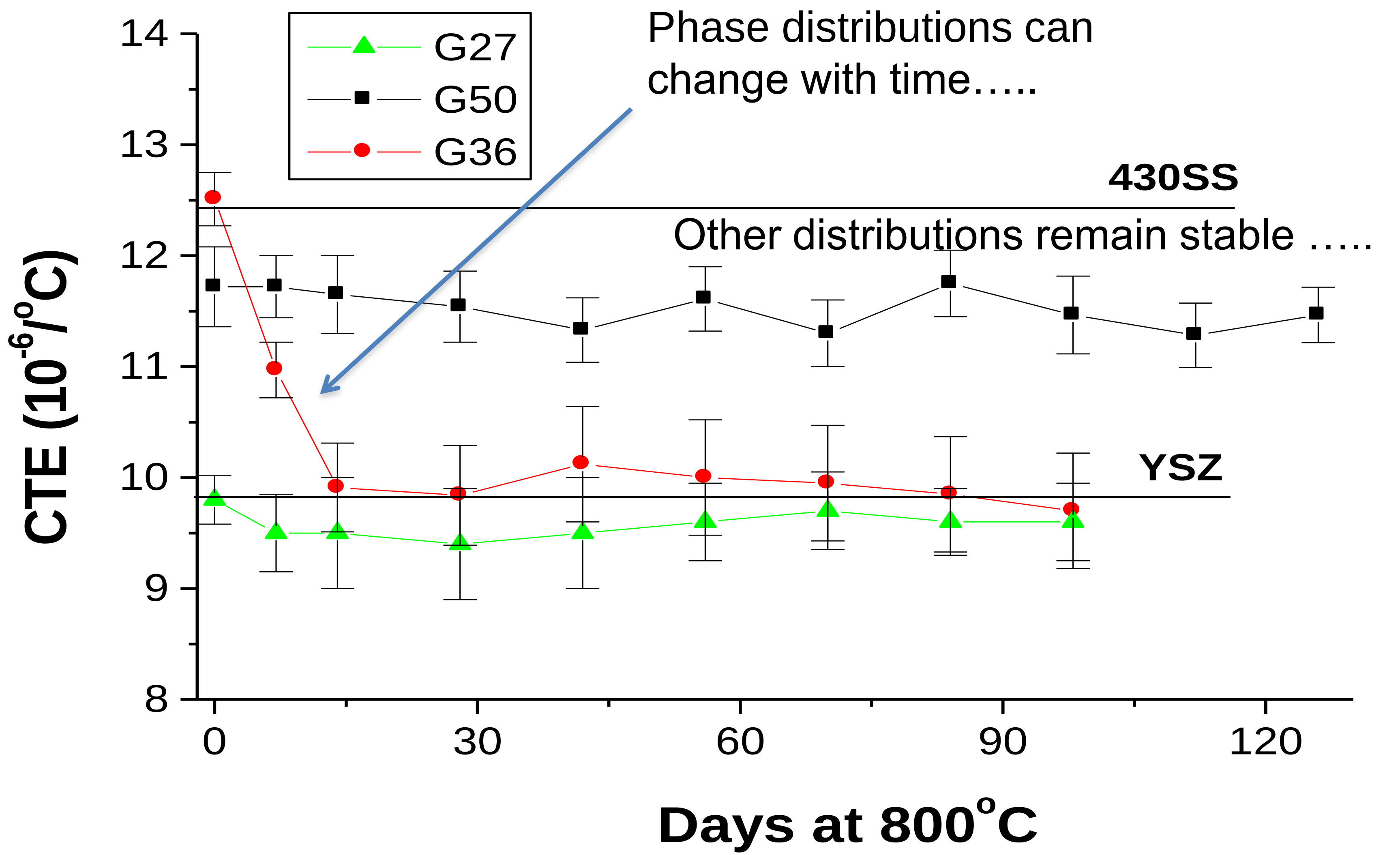
Orthosilicate phases

- **Pyrosilicates**
  - $CaSrAl_2SiO_7$, $Ca_2ZnSi_2O_7$
- **Orthosilicates**
  - Sr_2SiO_4, Zn_2SiO_4
- The crystalline phases appear to be thermally stable.





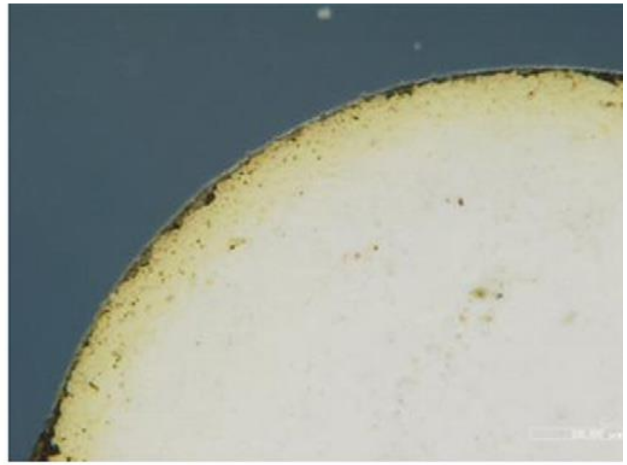




Phase distributions can change with time…..
Other distributions remain stable …..
G27
G50
G36
430SS
YSZ
CTE (10^{-6}/°C)
Days at 800°C
14
13
12
11
10
9
8
0
30
60
90
120

One potential problem is deleterious reactions with chromia

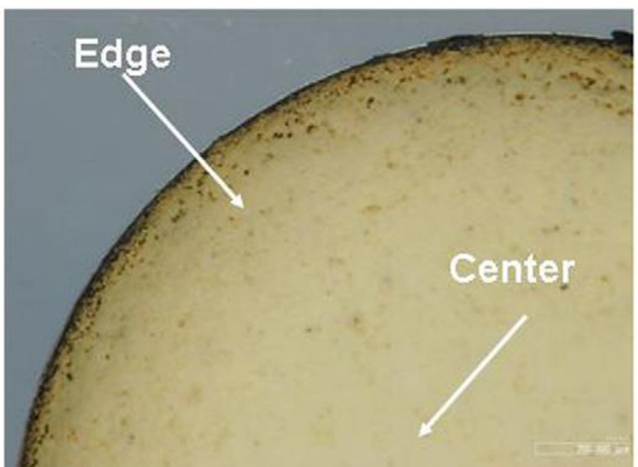
As sealed



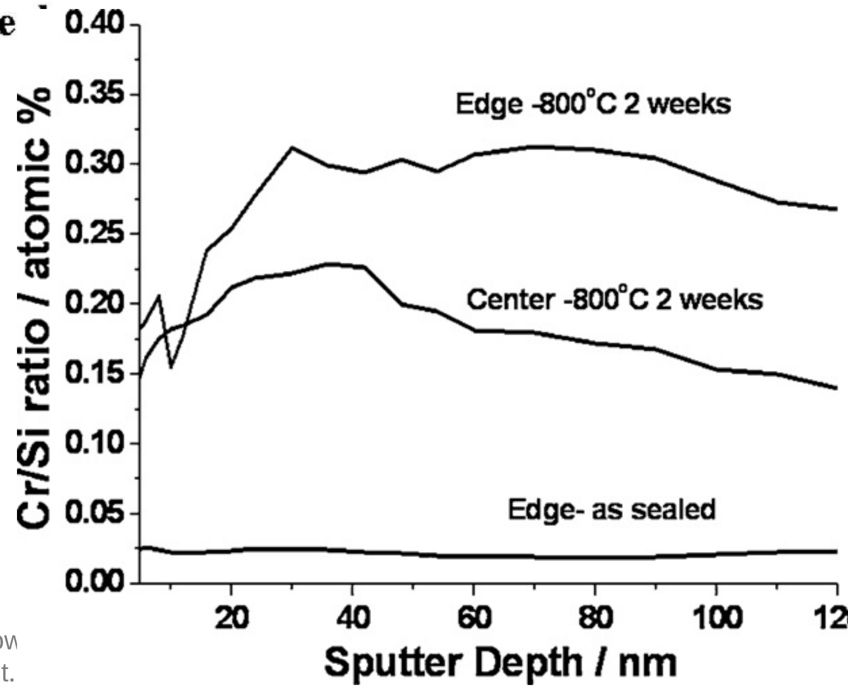
800°C for 1 we

CTE mismatches occur at the glass-metal interface:

$BaCrO_4$: 18 ppm/K
Steel/Glass: 12ppm/K



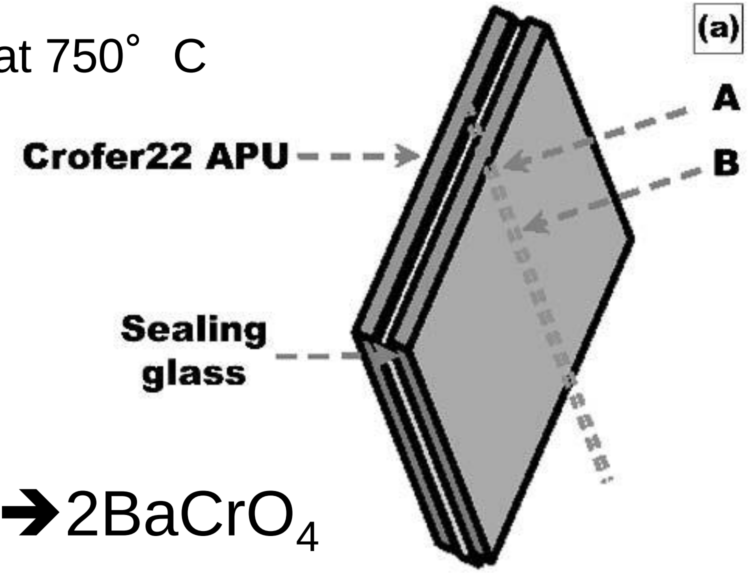
800°C for 2 weeks



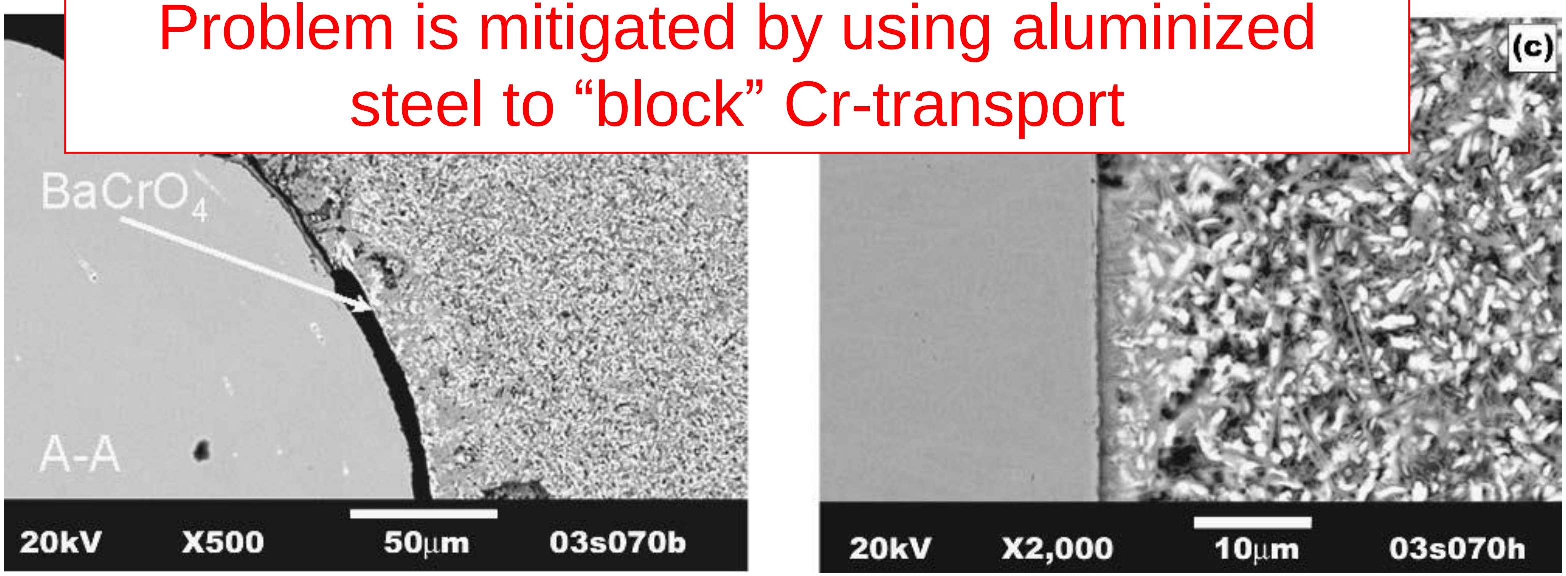
Zhang, et al, JACerS (2010)

RK Brow
brow@mst.

G18/Crofer after 1 week at 750° C



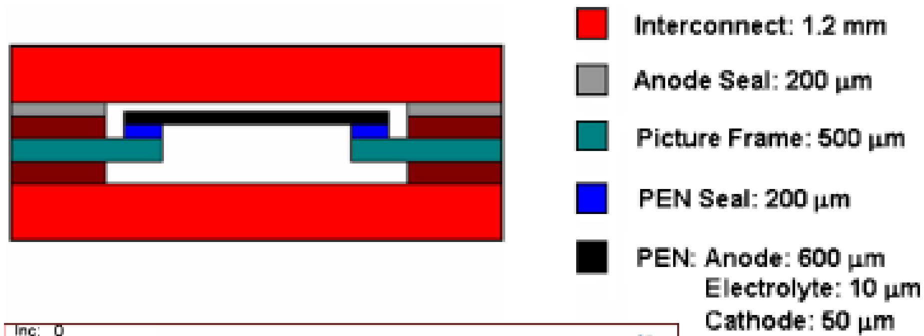
$$2BaO+Cr_2O_3+\frac{1}{2}O_2 \rightarrow 2BaCrO_4$$

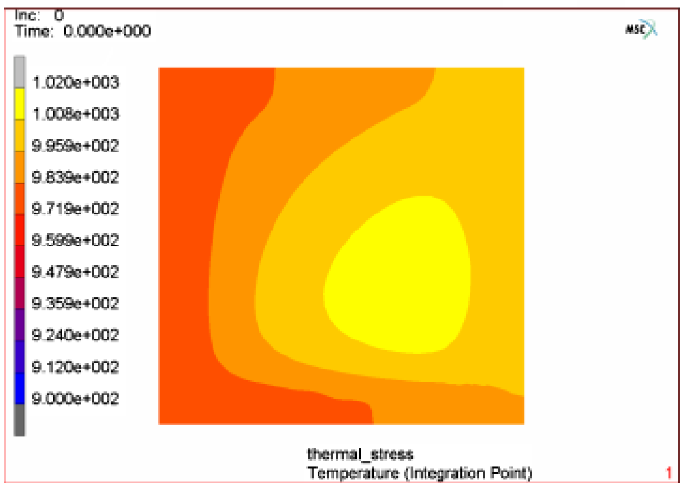


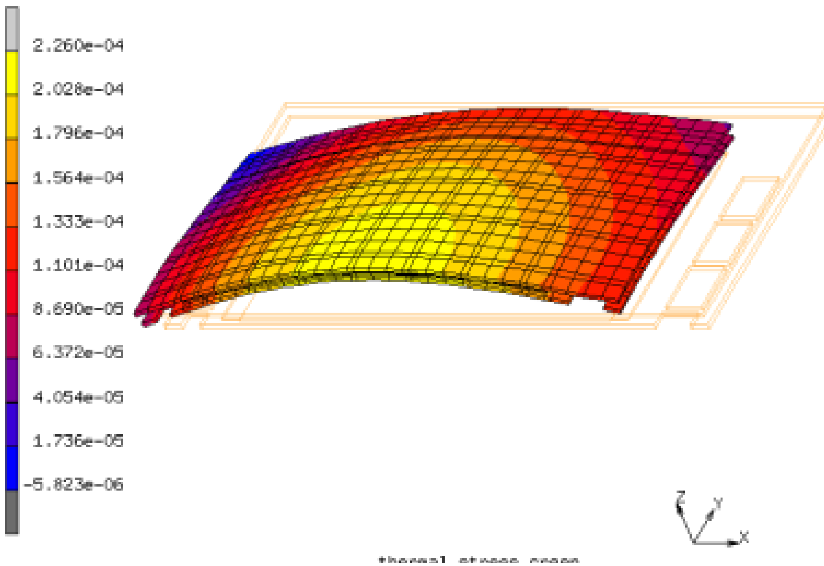
Problem is mitigated by using aluminized steel to "block" Cr-transport

Yang et al., JMEPEG 13, 327 (2004)

A second problem with ‘rigid’ glass-ceramic seals involves the thermal stresses associated with slight CTE mismatches



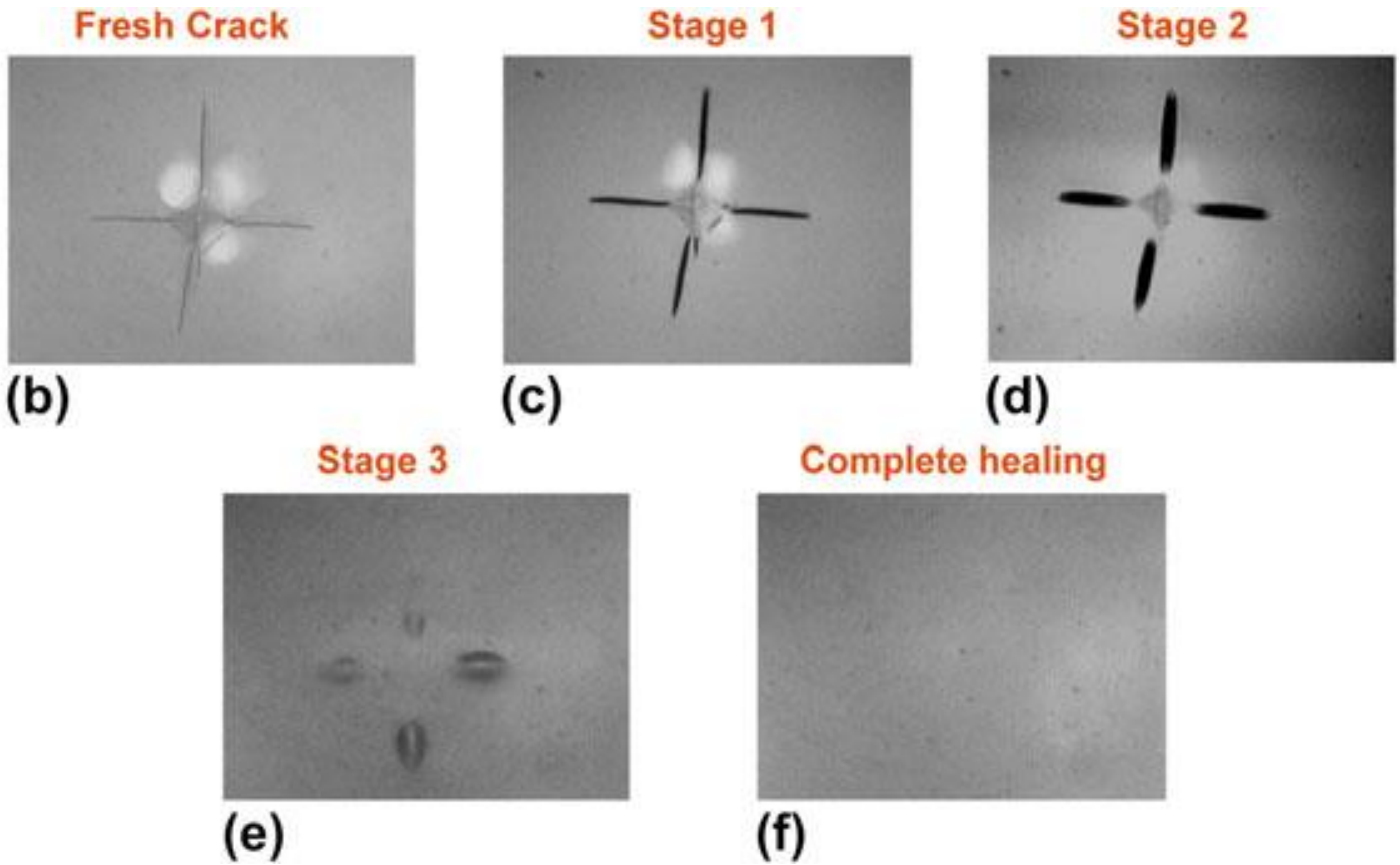




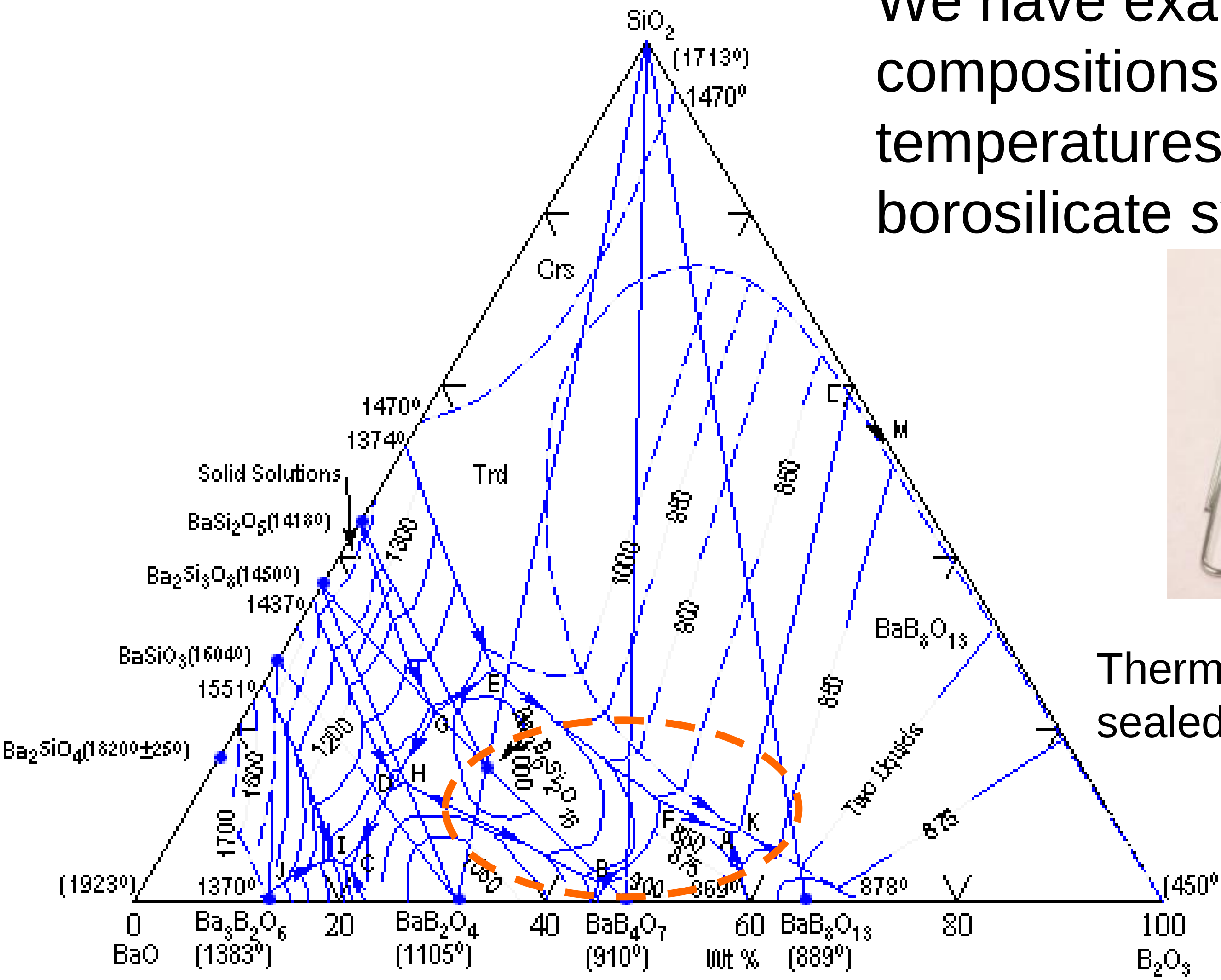
Liu, et al., Int. J. Appl. Cer. Tech., 8[1], 49 (2011)

One solution may be to use a ‘viscous’ seal that will ‘re-heal’ on heating

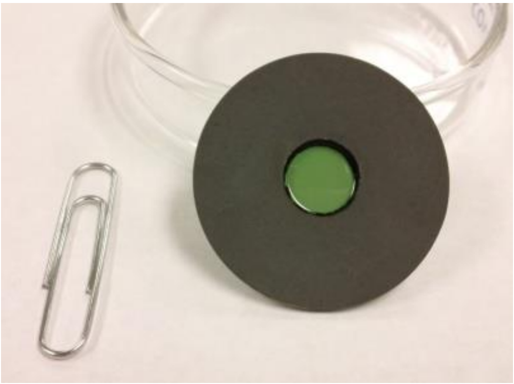
Viscous sealing glasses- self-repairable?



Singh, J. Mater. Res., 27[15] 2055 (2012)



We have examined compositions with low liquidus temperatures in the Ba-borosilicate system



Thermally shocked glass re-sealed by reheating to ≈10^5 Pa-s

JH Hsu, et al., An alkali-free barium borosilicate viscous sealing glass for solid oxide fuel cells, J. Power Sources, 270 14-20 (2014).

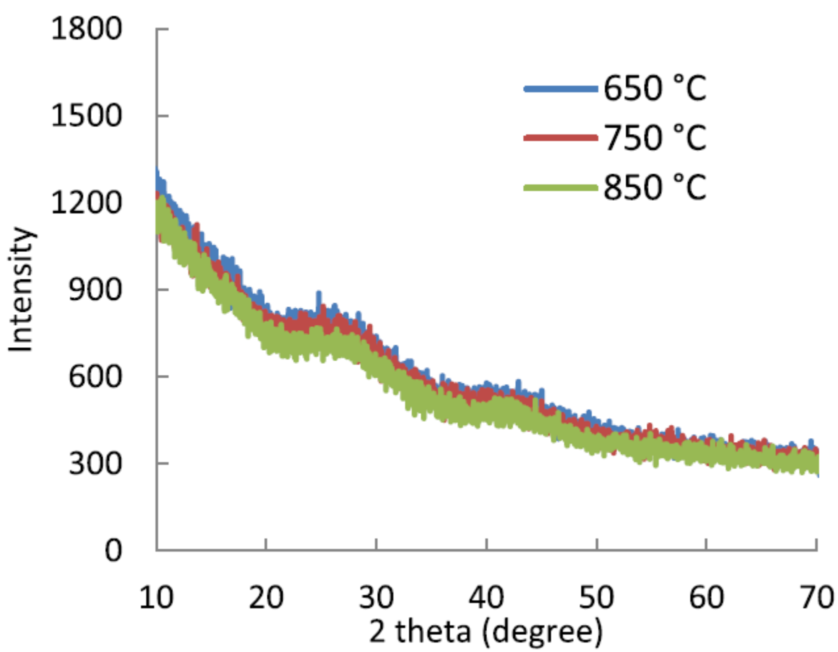
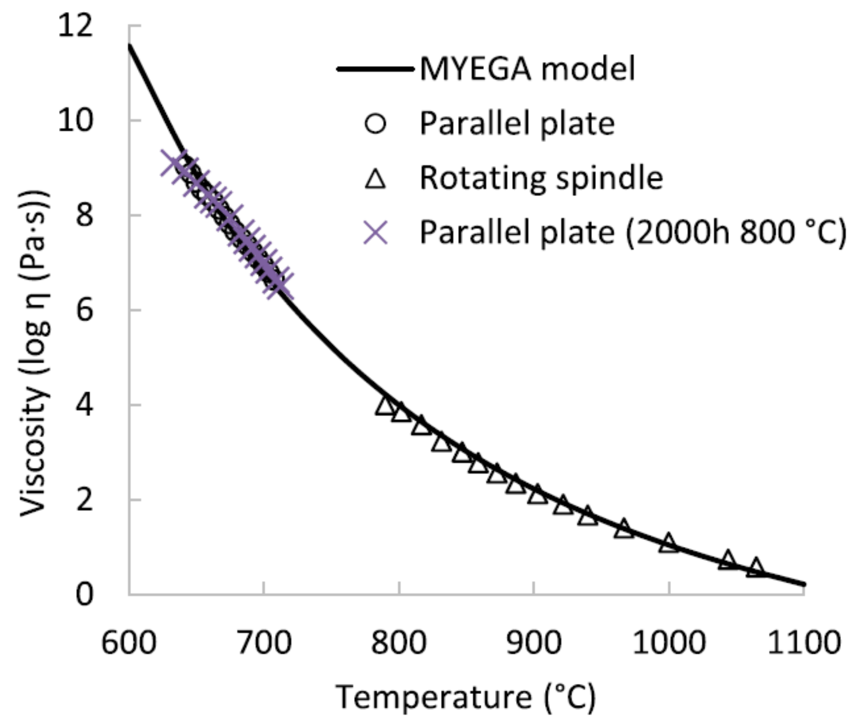


Fig. 1. XRD patterns of G102 after 2184 h at 650 °C, 750 °C and 850 °C.



JH Hsu, et al., An alkali-free barium borosilicate viscous sealing glass for solid oxide fuel cells, J. Power Sources, 270 14-20 (2014).

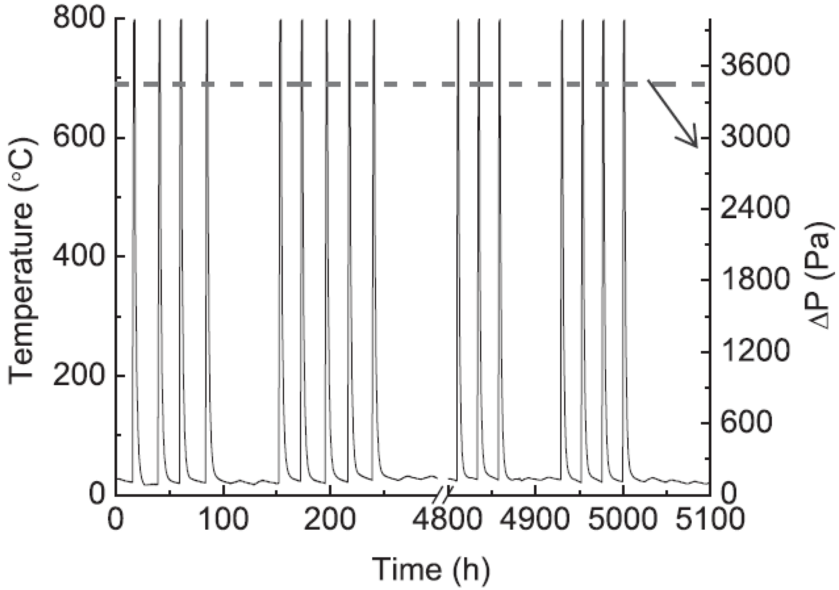


Fig. 8. Demonstration of the hermeticity of the sandwich seal assembly. This seal has survived 148 thermal cycles (800 °C to RT) in dry air at a differential pressure of ~3.4 kPa (dash line) over the course of more than 5000 h.

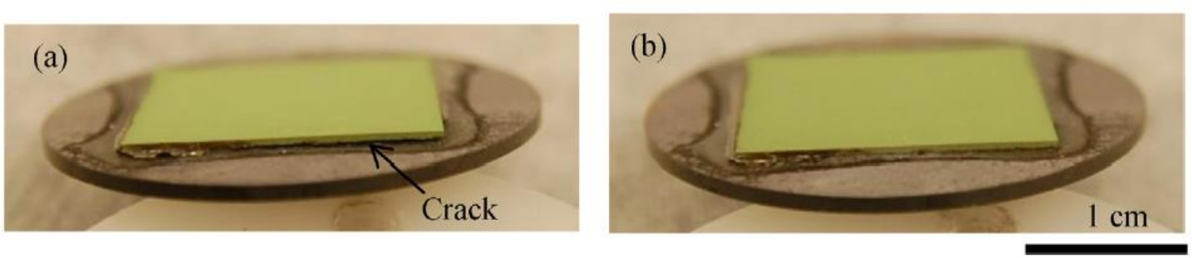
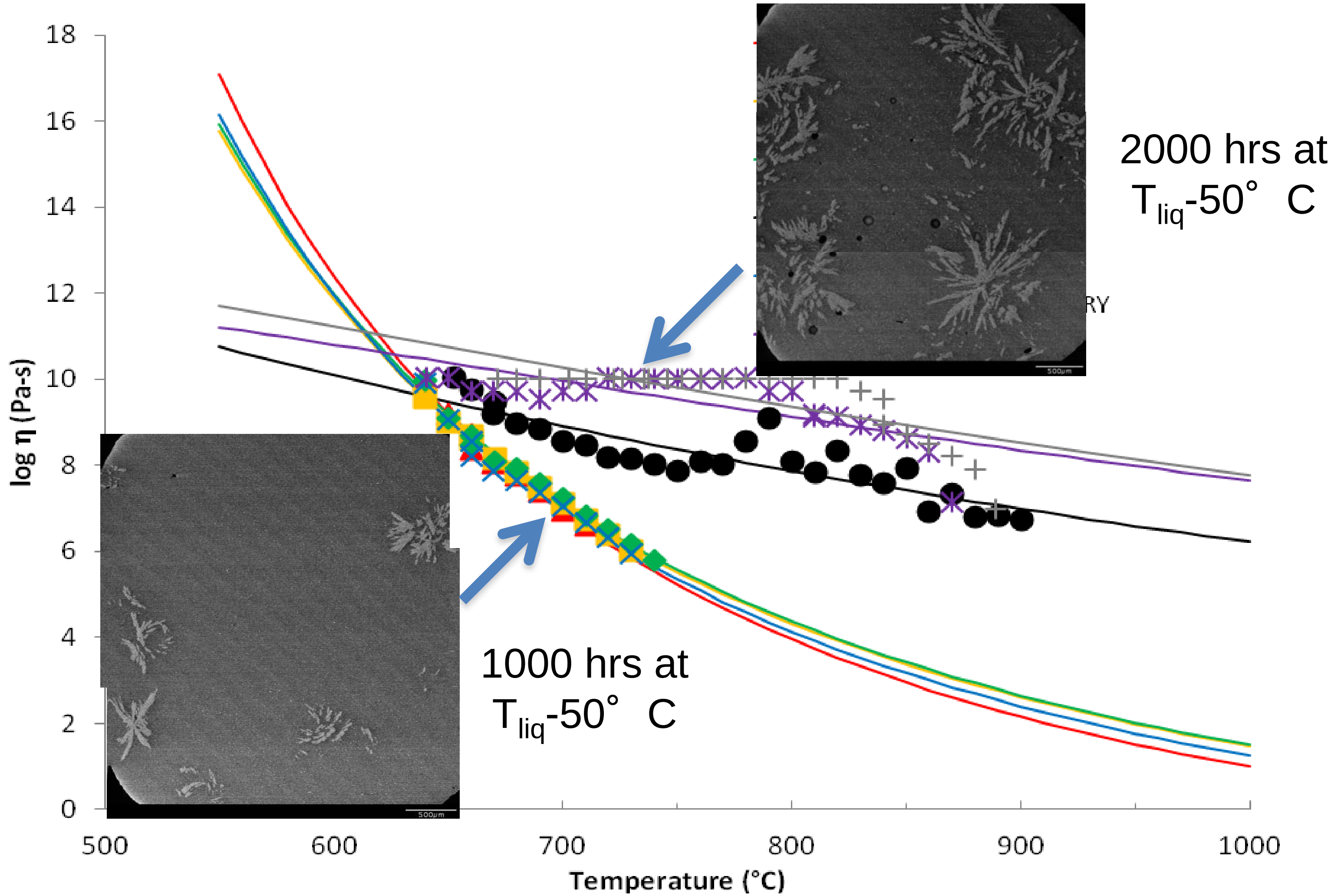
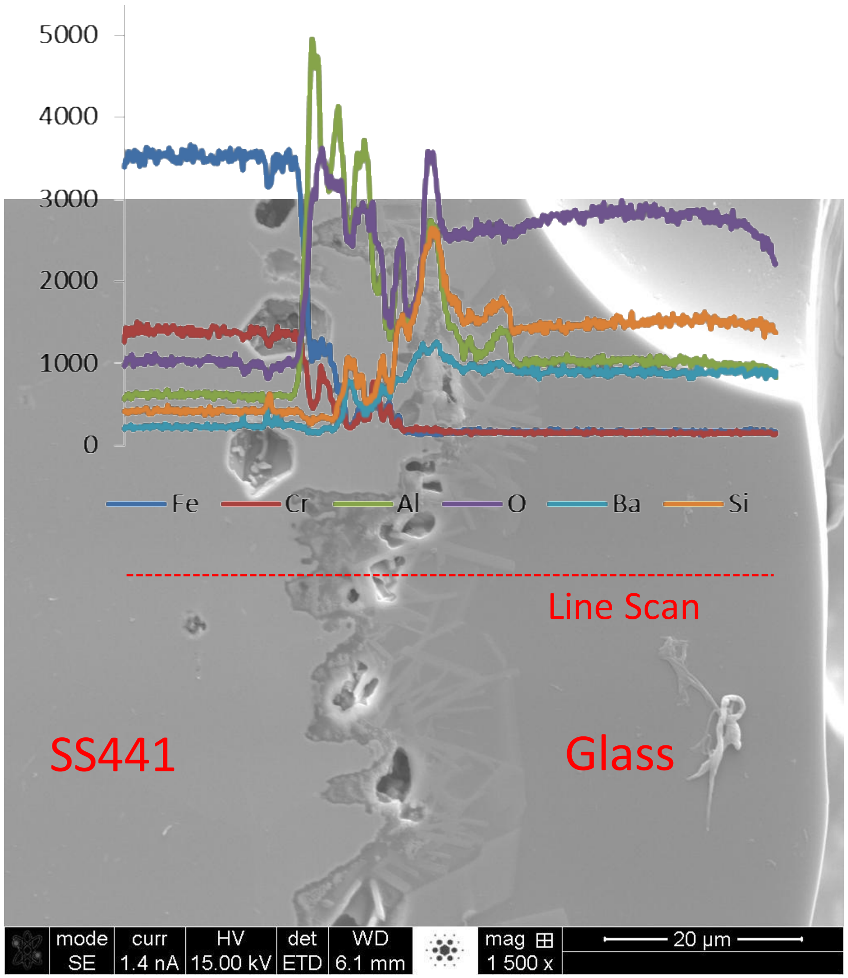


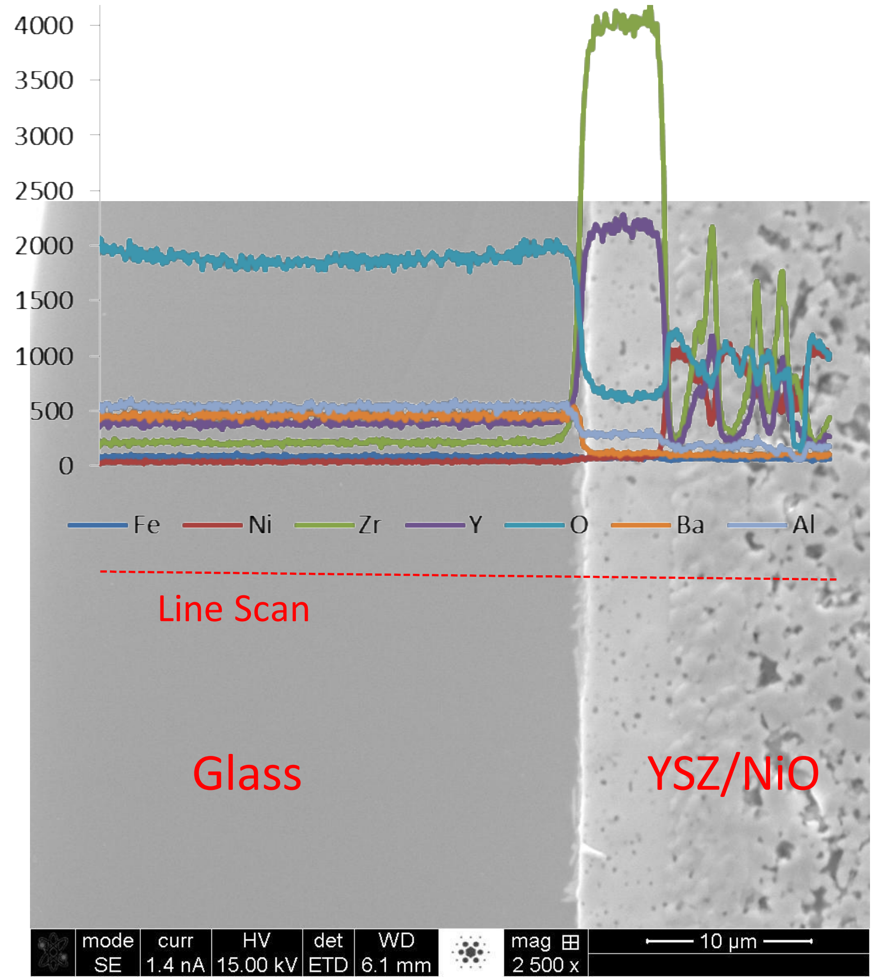
Fig. 10. Sandwich seal made with G102; (a) crack caused by thermal shock (b) crack healed and the seal was again hermetic, holding a 13.8 kPa different pressure, after re-heating at 800 °C for 2 h.

Long-term crystallization will affect glass viscosity- and so the self-sealing properties



Viscous seals may be more reactive that the glass-ceramics- dissolution of aluminized layer





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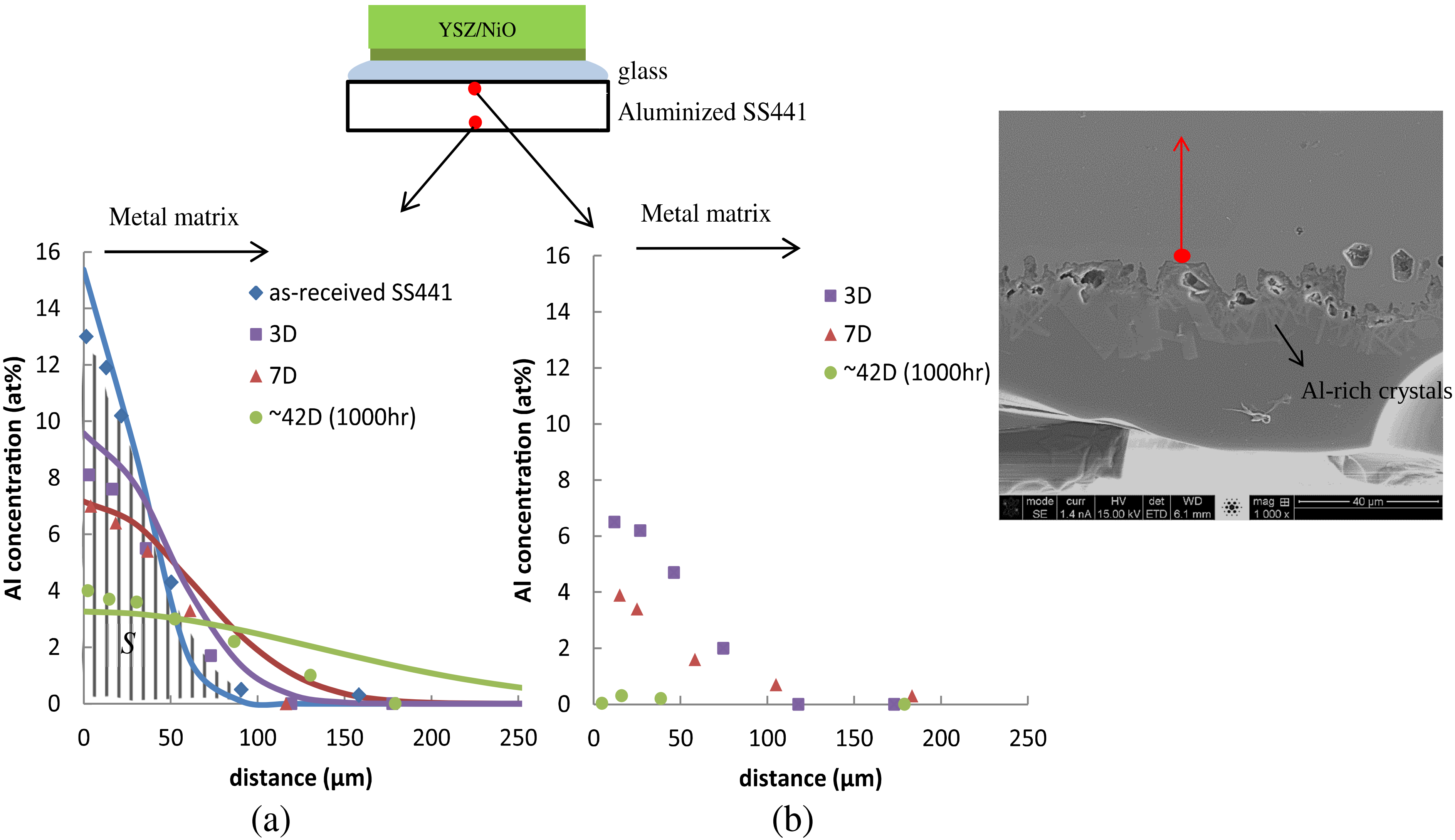
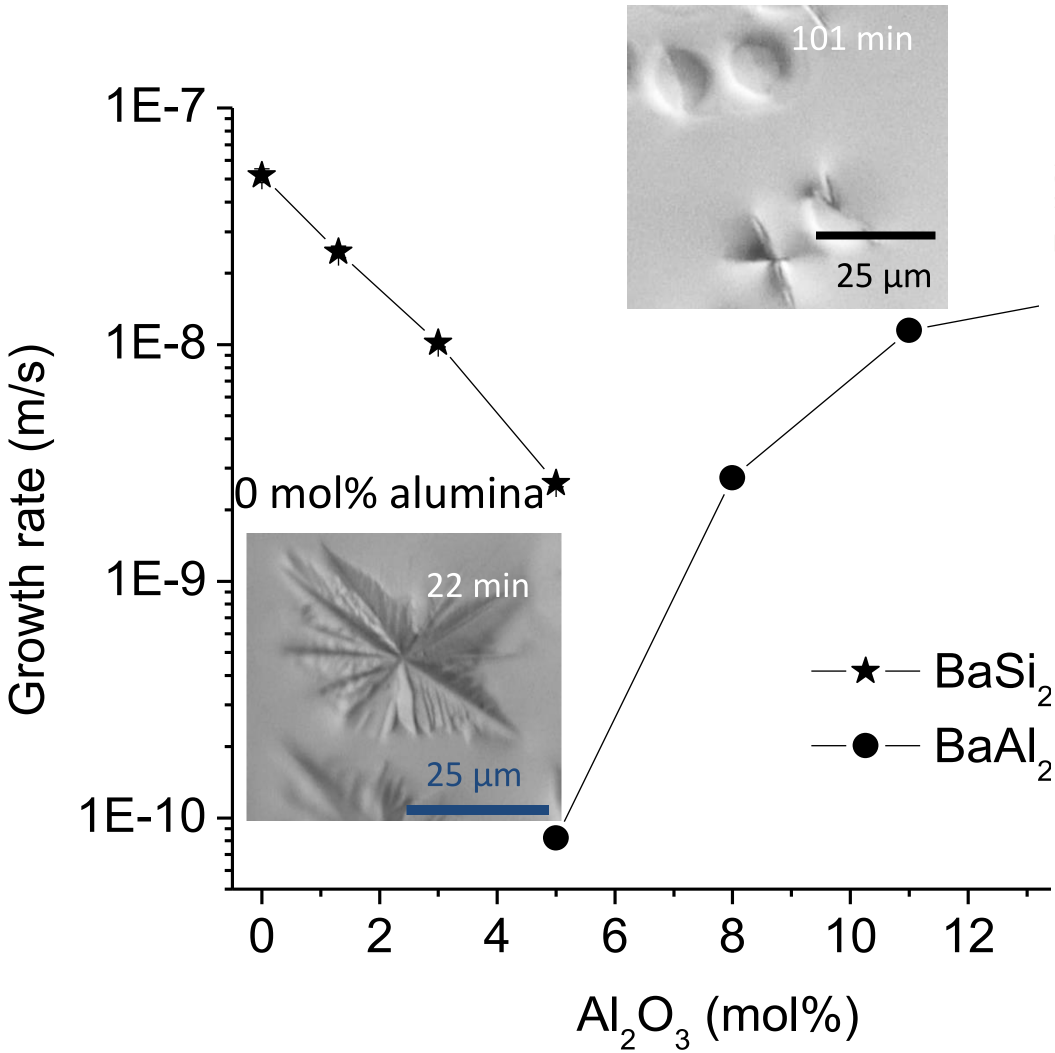
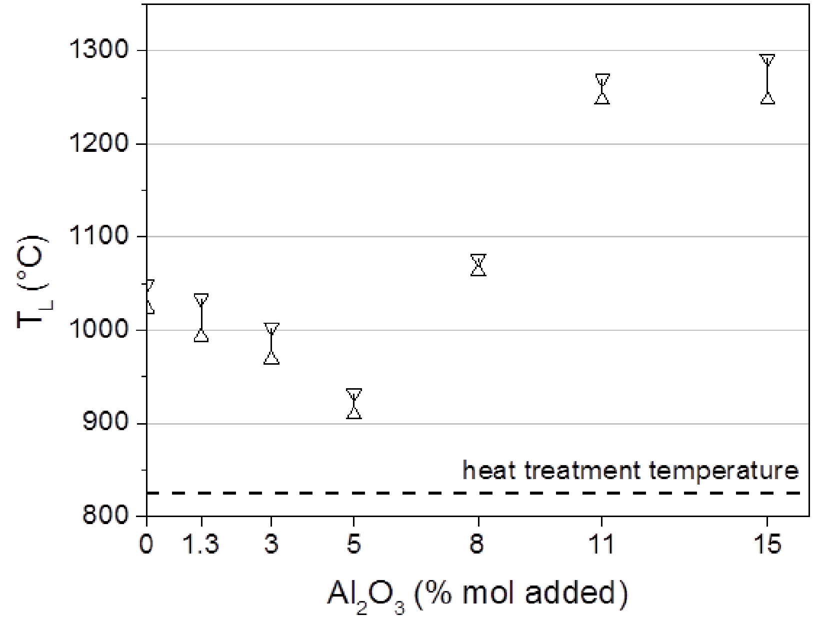


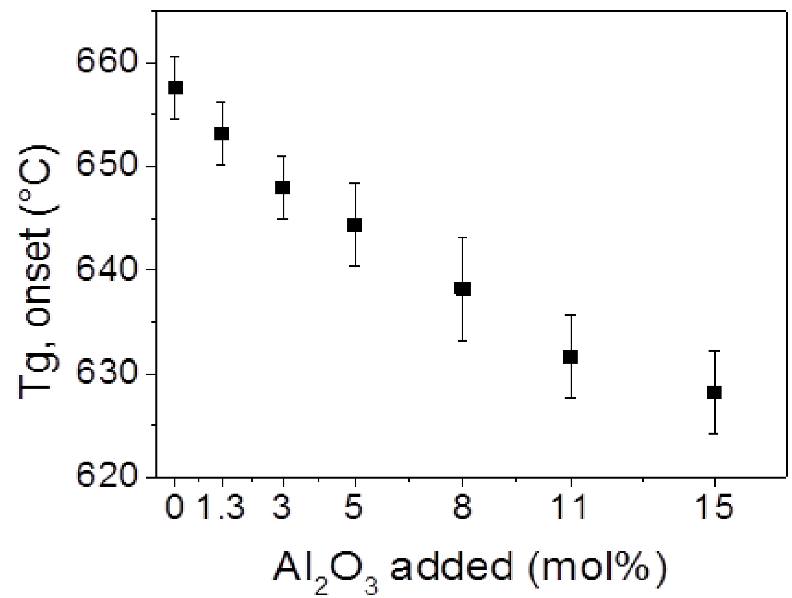
Hsu et al., “Interfacial interactions between an alkali-free borosilicate viscous sealing glass and aluminized ferritic stainess steel”, *Journal of Power Sources* 250 (2014) 236-241

Ba-borosilicate base glass

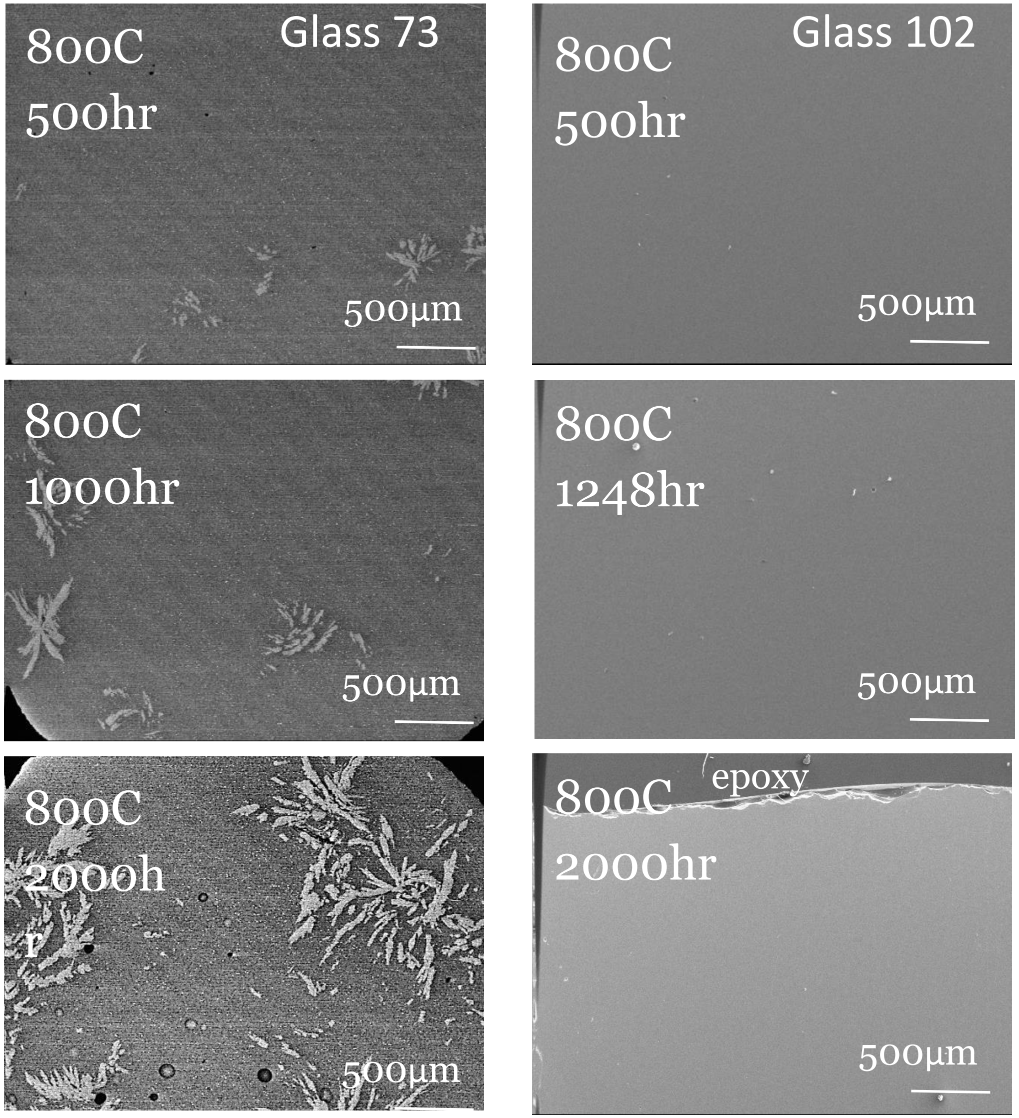


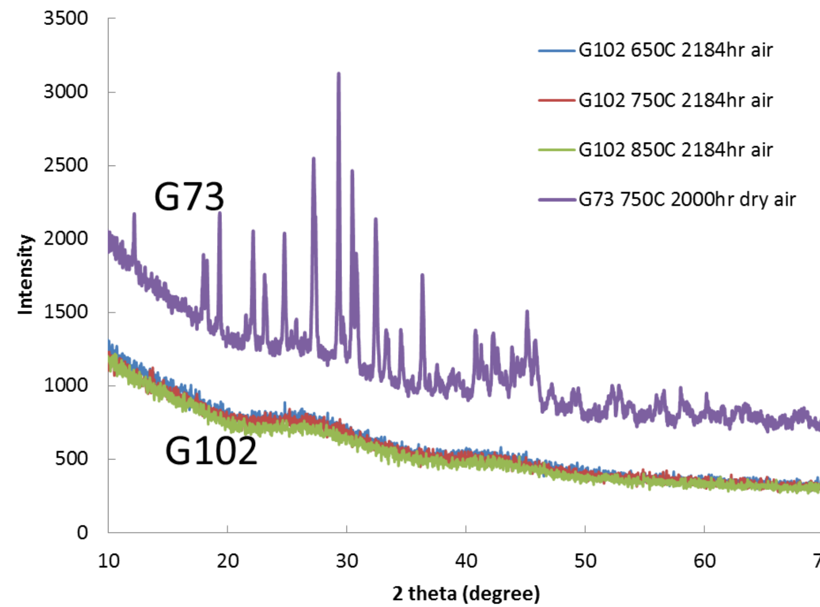
Crystal growth rates at 850° C





"Non-crystallizing" compositions have been developed





How do you measure the liquidus temperature of a glass that resists crystallization?

Summary

- As a materials science platform, sealing glasses offer opportunities to explore new compositions and to study glass phenomena
  - Chemically stable non-silicate compositions
  - Crystallization around the liquidus temperature
  - High temperature compatibility with metals

- Glass seals are enabling materials for many technologies
  - Reliable Li-batteries➔biomedical devices
  - Optimization still required for SOFC systems

- The ability to model sealing processes may be the key to ’scaling up’ technologies to useful products
  - Accurate viscoelastic properties
  - Well-controlled manufacturing process parameters
  - Well-understood ‘application’ conditions

Acknowledgments

- Department of Energy/SECA
  - Mo-Sci Corp. (Rolla)- CW Kim
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  - Laxikanth Peddi, Heather Teitlebaum, Roger Brown
- Sandia National Labs