Glass Sealing of Solid Oxide Fuel Cells

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Introduction

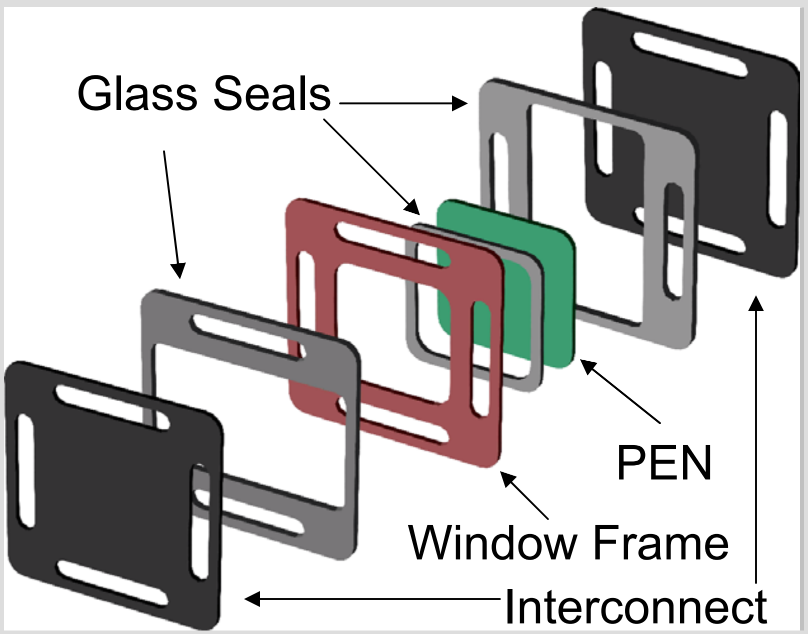
- SOFC Sealing requirements
- Current PNNL seal properties
- Current Sealing Issues
- Future Improvements

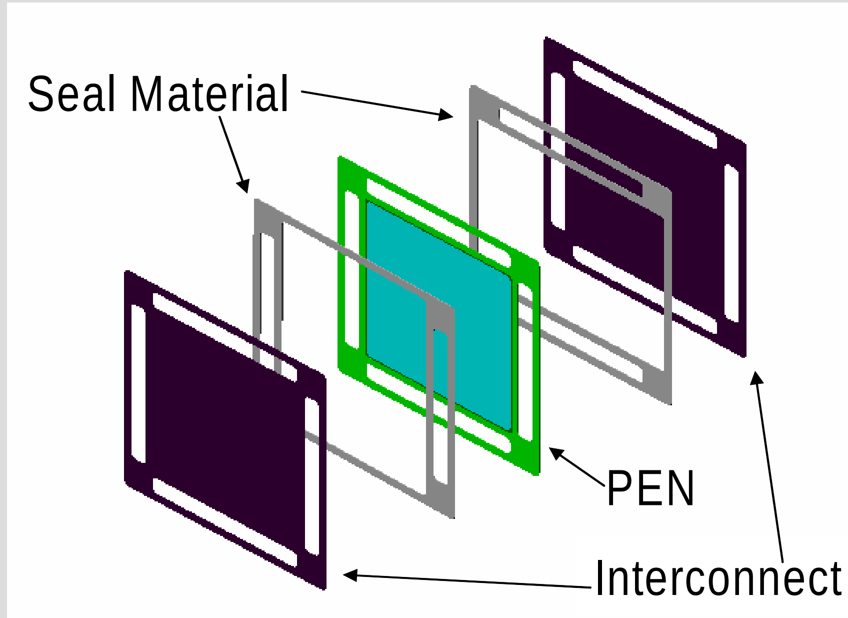
SOFC Sealing Requirements

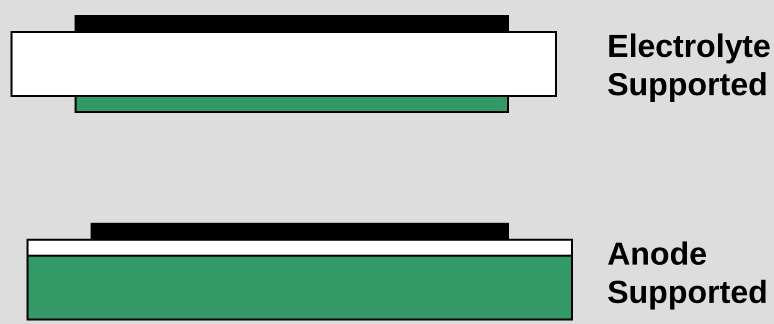
- Close TEC match
  - 12.5×10^{-6} /°C
- Stability in both Air and Reducing Environments
  - Po_2 range from 0.2 to 1×10^{-21}
- Minimal Chemical Interactions with other cell components
  - Zirconia, Ferritic Stainless
  - Good bond strength
- Electrically Insulating (for most applications)
- Thermal Cycle
- Long term stability
  - Operating temperature is above Tg
- Seal at an appropriate temperature
  - Above 750°C and Lower than 950°C
- Ability to reheat to the sealing temperature without remelting the seal
  - May not be critical, but allows greater flexibility in assembly

Planar SOFC Seal Areas

- Cell to Cell seal
  - Keeps the reactant gasses separated
  - Electrically Isolates
- PEN to window frame seal





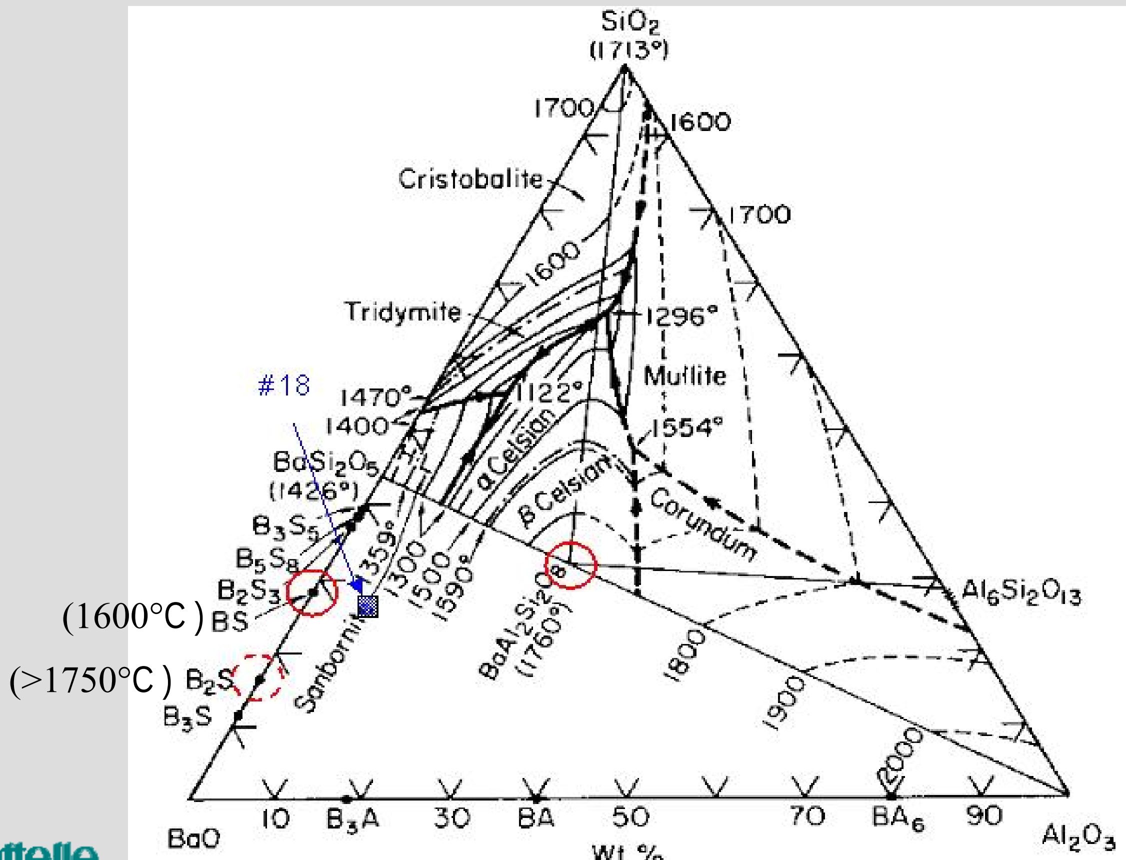


Glass Selection

- Potential Glass Systems
  - P_2O_5 Based Glasses
    - Volatility and reaction with the anode
  - B_2O_3 Based Glasses
    - Volatility in Wet Fuel Gas
  - SiO_2 Based Glasses
    - Best Possible Candidate
- Alkaline earth (barium) aluminosilicate glasses
  - High Electrical Resistively,
  - High Thermal Expansion,
  - High Glass Transition Temperature
  - Glass - Ceramic.

PNNL G-18 Glass

- G-18 Composition
  - Patents
    - US 6,430,966
    - US 6,532,769



Mol%

BaO	35
CaO	15
Al_2O_3	5
SiO_2	35
B_2O_3	10

- $BaSiO_3$
- (1.5Ba,0.5Ca)SiO_4 ss
- ($BaAl_2Si_2O_8$)
  - Hexa-celsian
  - Mono-celsian

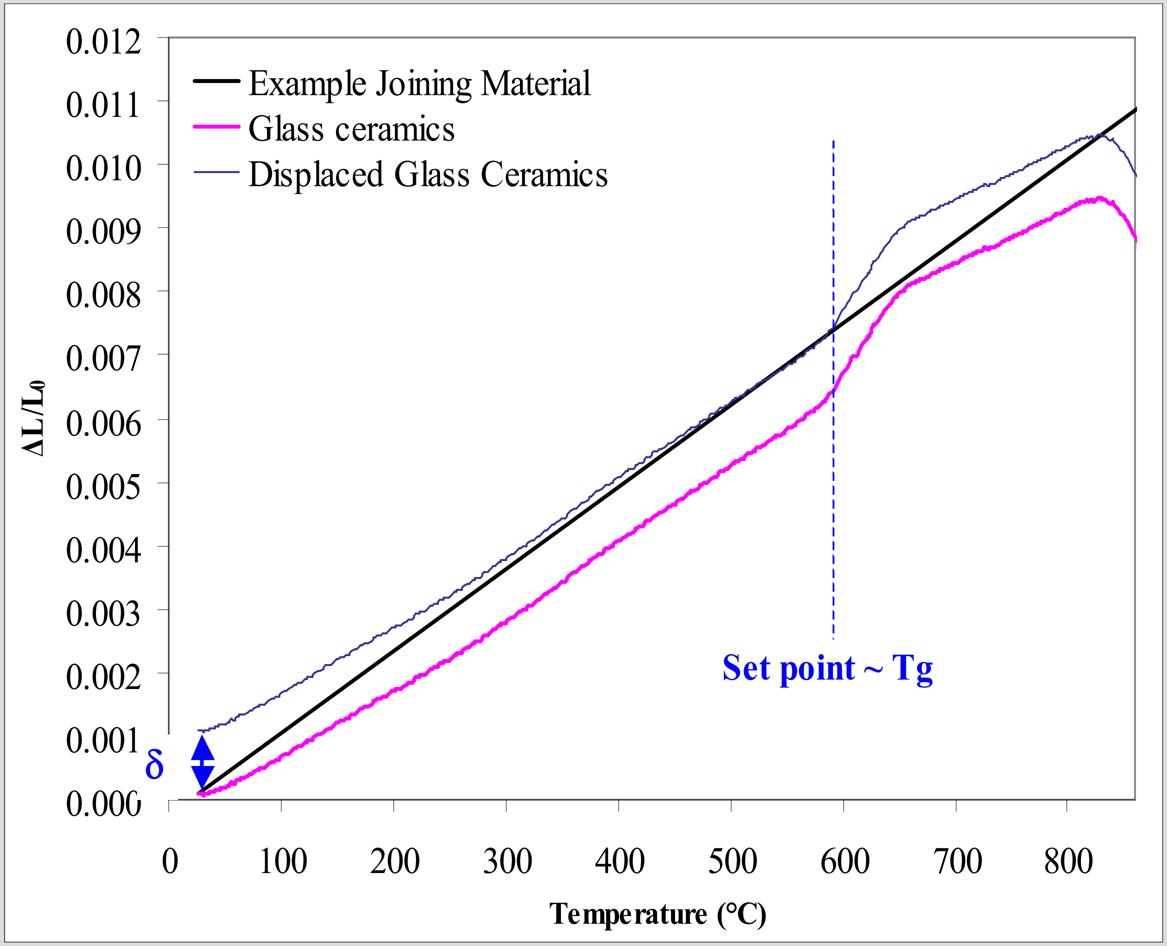
Thermal Expansion of Crystal Products

Name	Composition	TEC	T range (°C)	Reference
Quartz	SiO_2	**11.2** **13.2** **23.3**	20-100 20-300 20-600	Donald 1993
Enstatite	$MgSiO_3$	**9** **12**	20-400 300-700	Donald 1993
Clinoenstatite	$MgSiO_3$	**7.8** **13.5**	100-200 300-700	Donald 1993
Protoenstatite	$MgSiO_3$	**9.8**	300-700	Donald 1993
Forsterite	Mg_2SiO_4	**9.4**	100-200	Donald 1993
Wollastonite	$CaSiO_3$	**9.4**	100-200	Donald 1993
Calcium orthosilicat	Ca_2SiO_4	**10.8-14.4**		Donald 1993
Barium silicate	$BaSiO_3$	**~12.5** **~10.5**	20-550 20-1000	PNNL measured PNNL measured
Hexa-celsian*	$BaAl_2Si_2O_8$	**~8**	20-1000	Bansal and Hyatt 1989
Mono-celsian	$BaAl_2Si_2O_8$	**~2.3**	20-1000	Bansal and Hyatt 1989

*Metastable at <1590°C

Thermal Expansion

- **Illustration of Stress Formation by Thermal Expansion Mismatch**



For thin glass layer stress in glass is

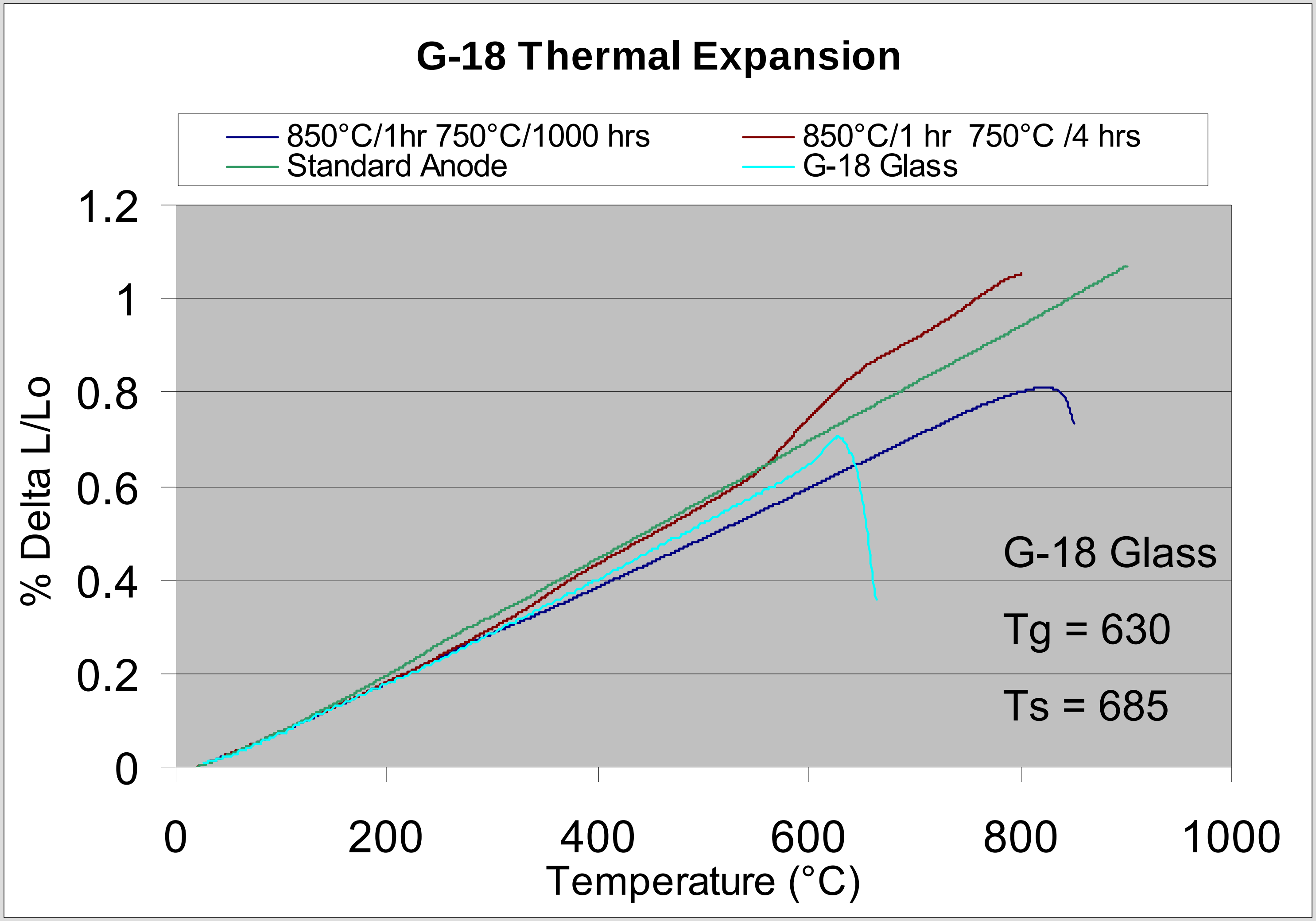
$$\sigma_g \sim -E_g\delta/(1 - \nu)$$

E_g: Young's modulus
ν: Poisson ratio

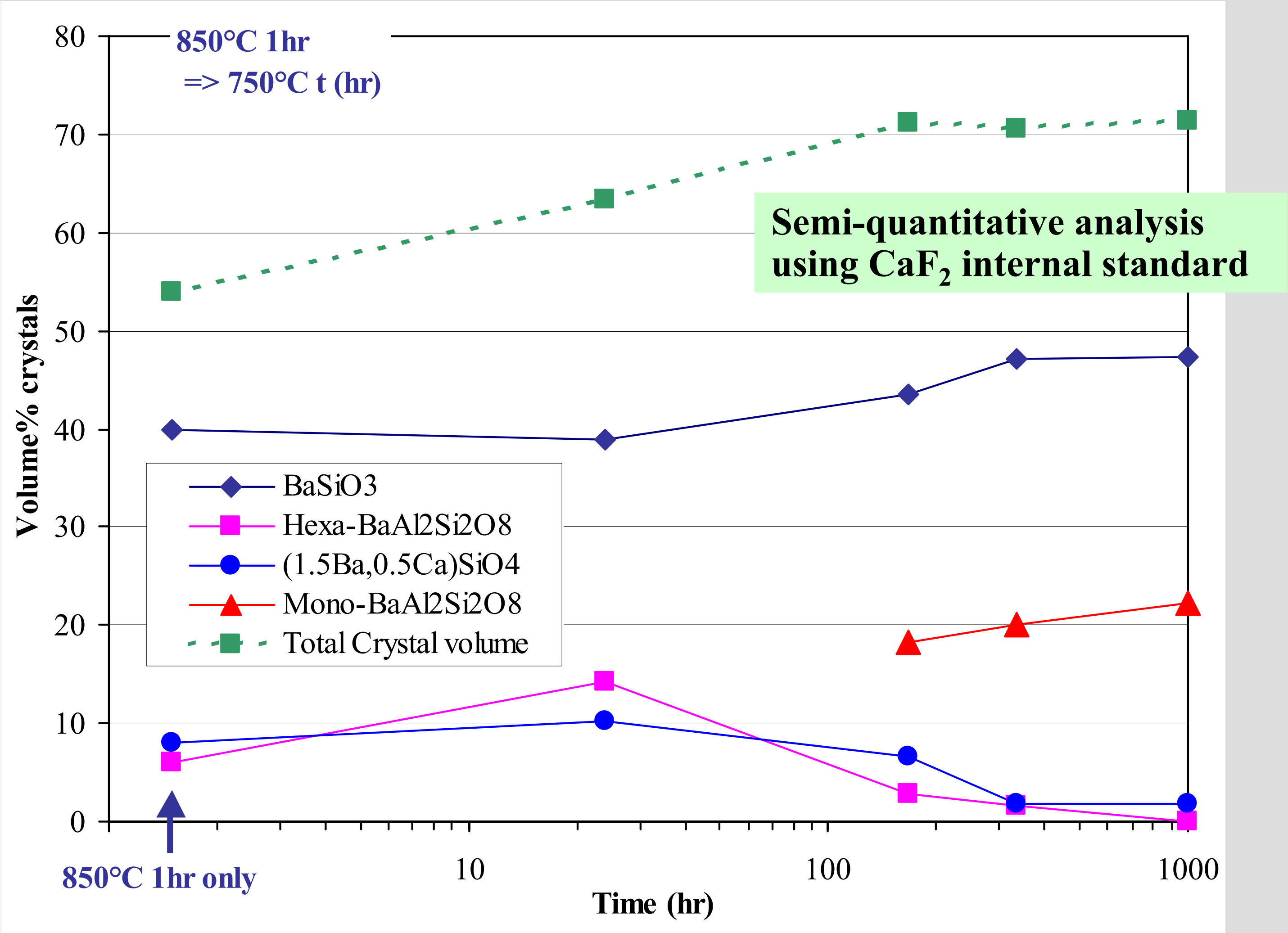
Rule of thumb
$\Delta\alpha/\alpha < 5\%$

α: thermal expansion coefficient

Thermal Expansion

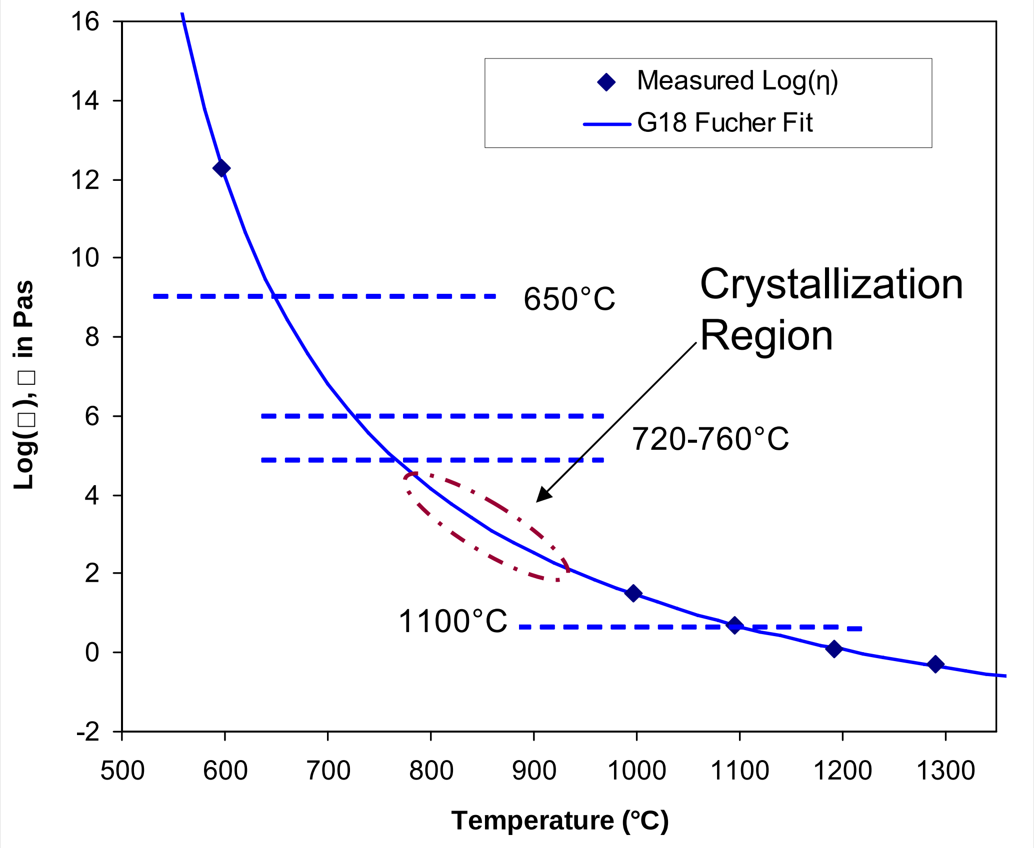


Phase Development vs. Time



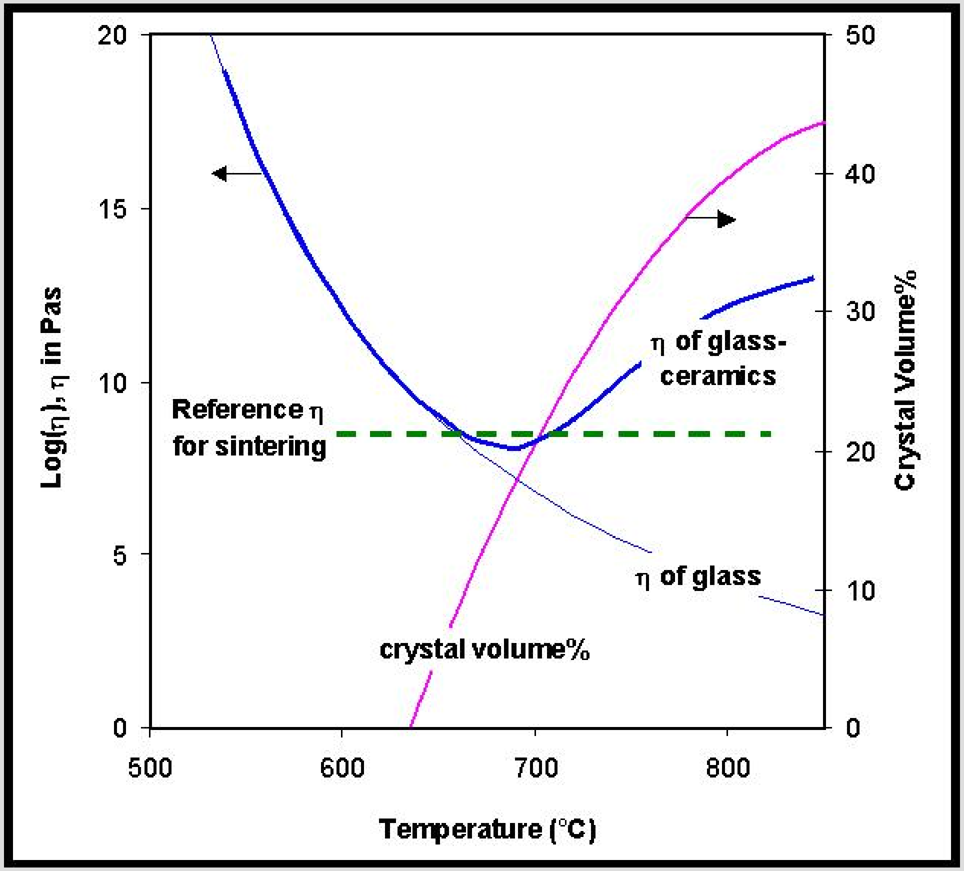
Glass Properties

- Viscosity
  - Can only be measured at the high and low end of the viscosity range.
  - The values in between are estimated with a Fucher fit.



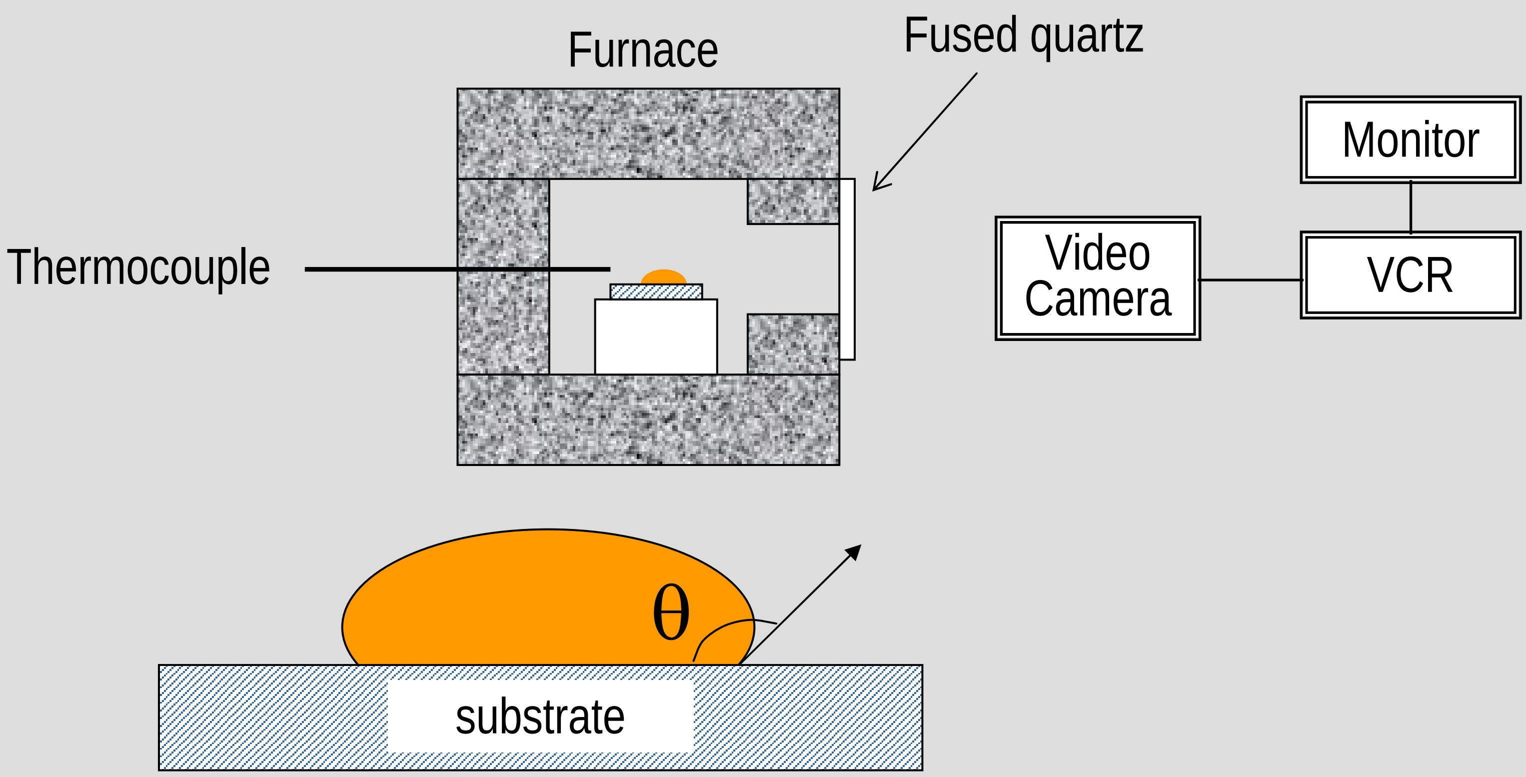
Glass-Ceramic Sealing Issue

- Viscosity affected by Crystallization
  - If the rate of crystallization is high, viscosity will increase too quickly and the seal will not bond well.
  - If the rate of crystallization is to low, the glass viscosity will be too low making seal very sensitive to load and temperature. Also long hold times will be required to crystallize the seal.



Glass Properties

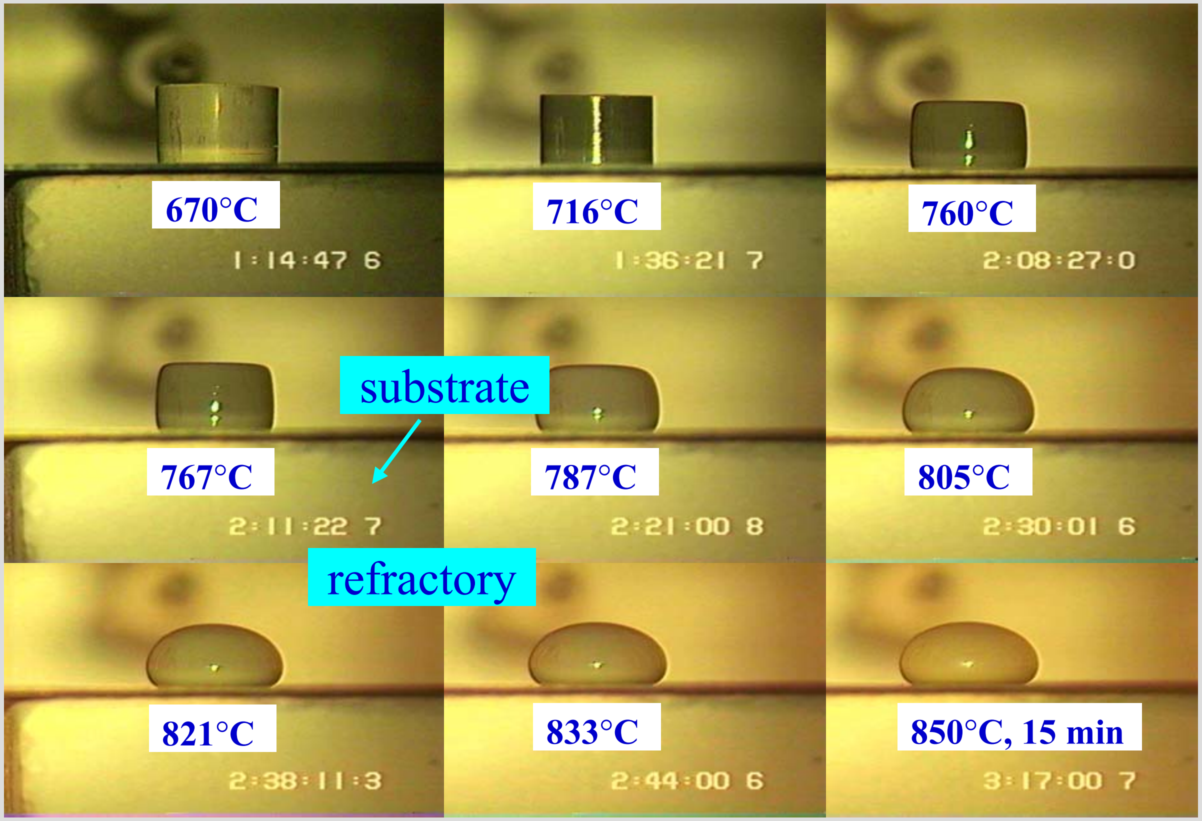
- Contact Angle - Schematic



$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$

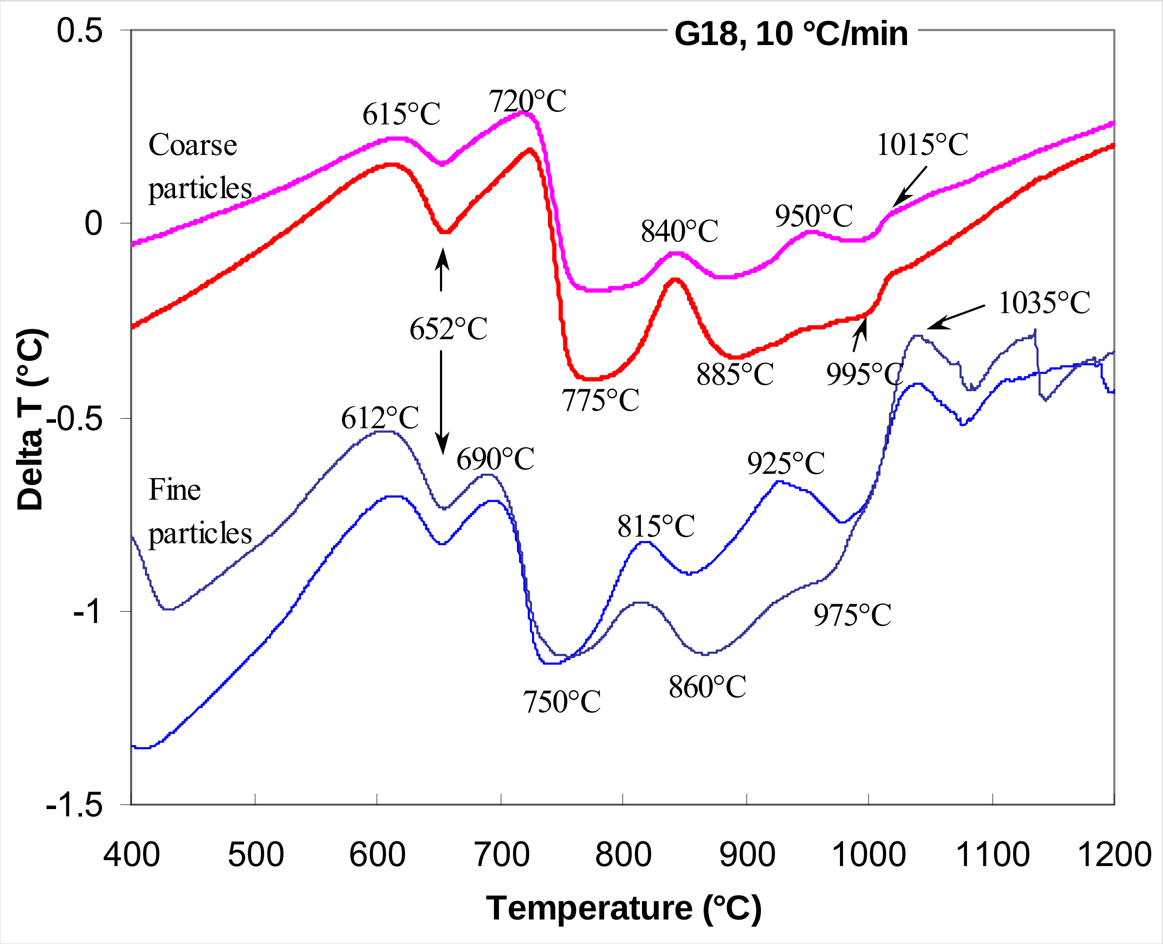
Glass Properties

- Contact Angle
  - Glass Powder pressed into a pellet d~10mm by h~10mm
  - Heated to 850°C at 5°C/min
  - Crystallization increases viscosity
  - Temperature required to achieve < 90°C angle ~ 1000°C
  - Contact angle is > 90° at 850°C. Therefore pressure is required to produce a good bond.



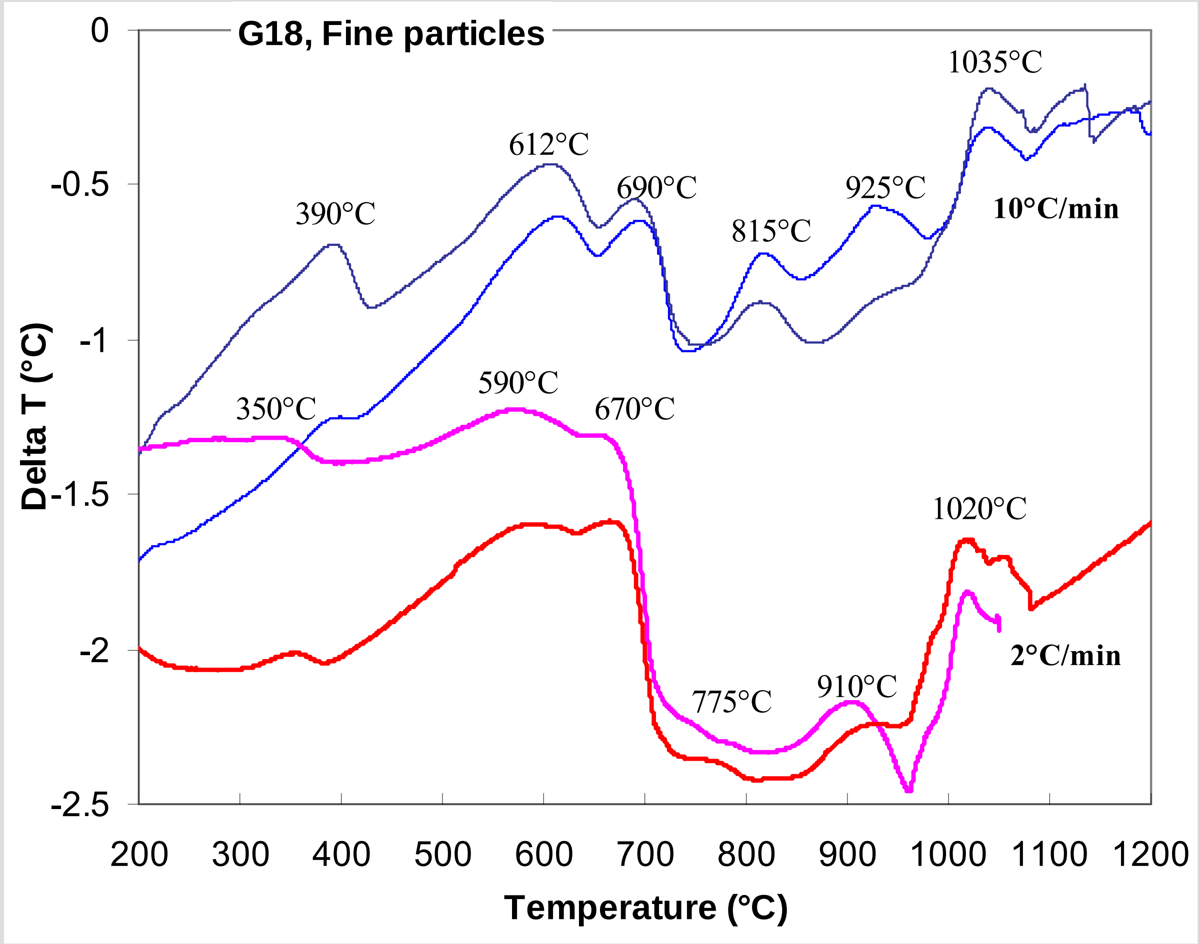
Crystallization Studies by DTA

- Effect of Glass Particle Size
  - Coarse: D_{50} ~ 8 µm
  - Fine: D_{50} ~ 1 µm



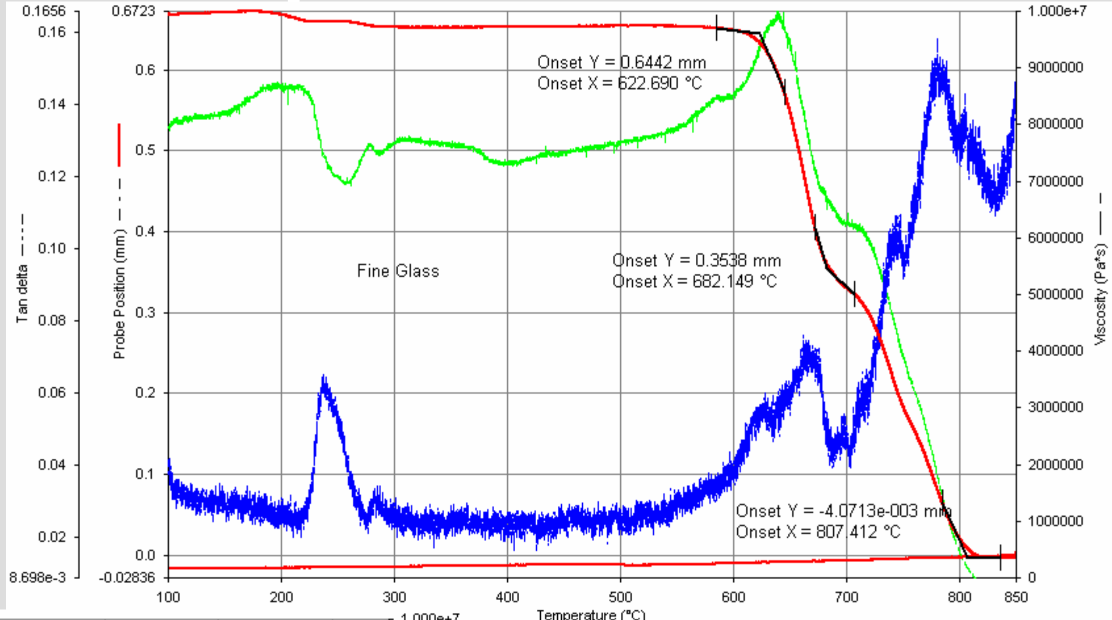
Crystallization Studies by DTA

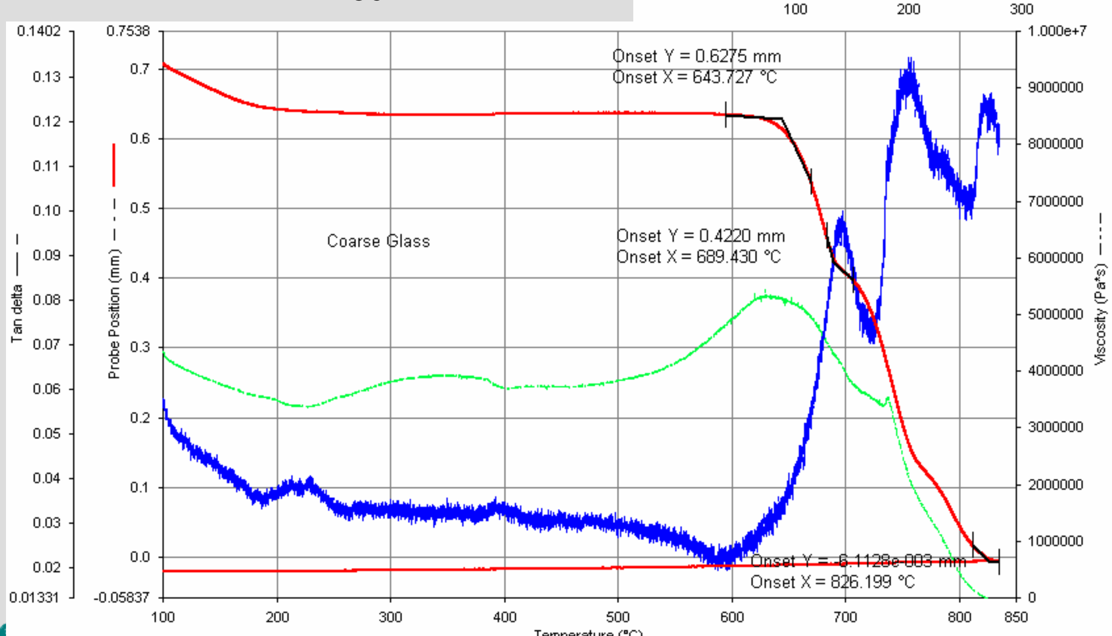
- Effect of Heating Rate
  - Fine Particle size $D_{50} \sim 1\ \mu m$
  - 10 °C / min
  - 2 °C / min



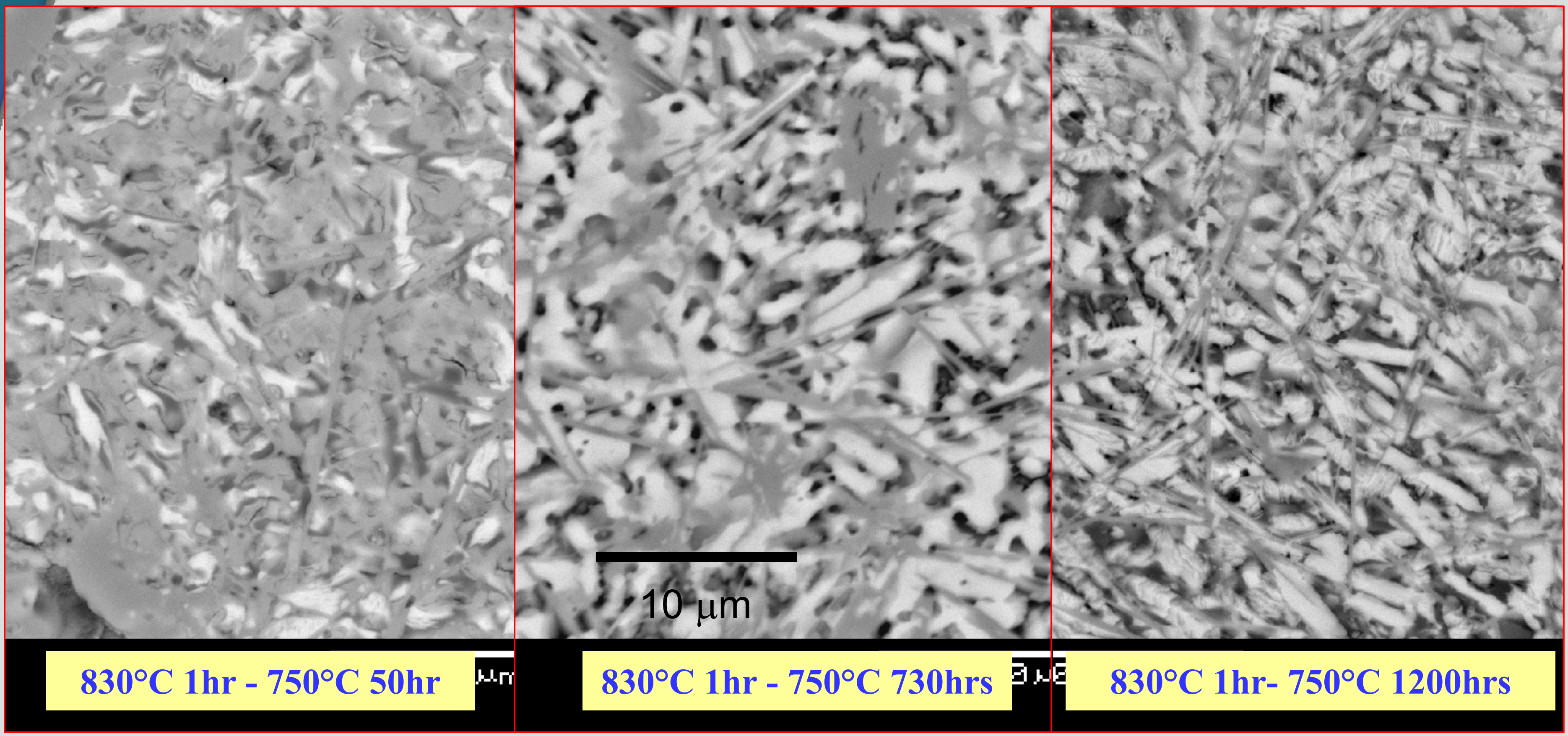
Glass Properties

- Thermal Mechanical Analyzer (TMA)
  - Effect of Particle Size
    - Tape cast glass
    - 1°C/min heating rate
    - Coarse: D_{50} ~ 8 μm
    - Fine: D_{50} ~ 1 μm





Microstructure evolution – G18

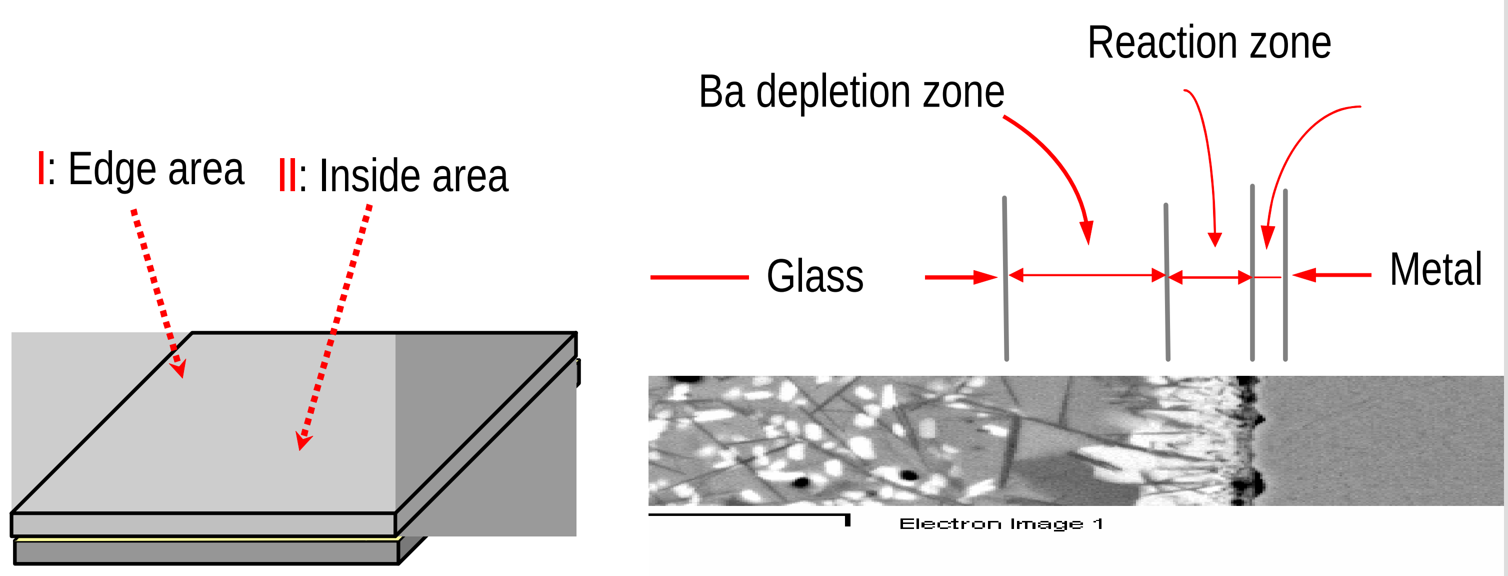


Sealing Issues

- Chemical Interactions
  - Reactions with Interconnect materials
  - Reactions with the Electrolyte
- Strength of the G-18
  - Strength as a function Temperature
  - Strength as a function Crystallization Time
- Bond Strength
  - To the interconnect material
- Application Method
  - Tape cast
  - Dispense

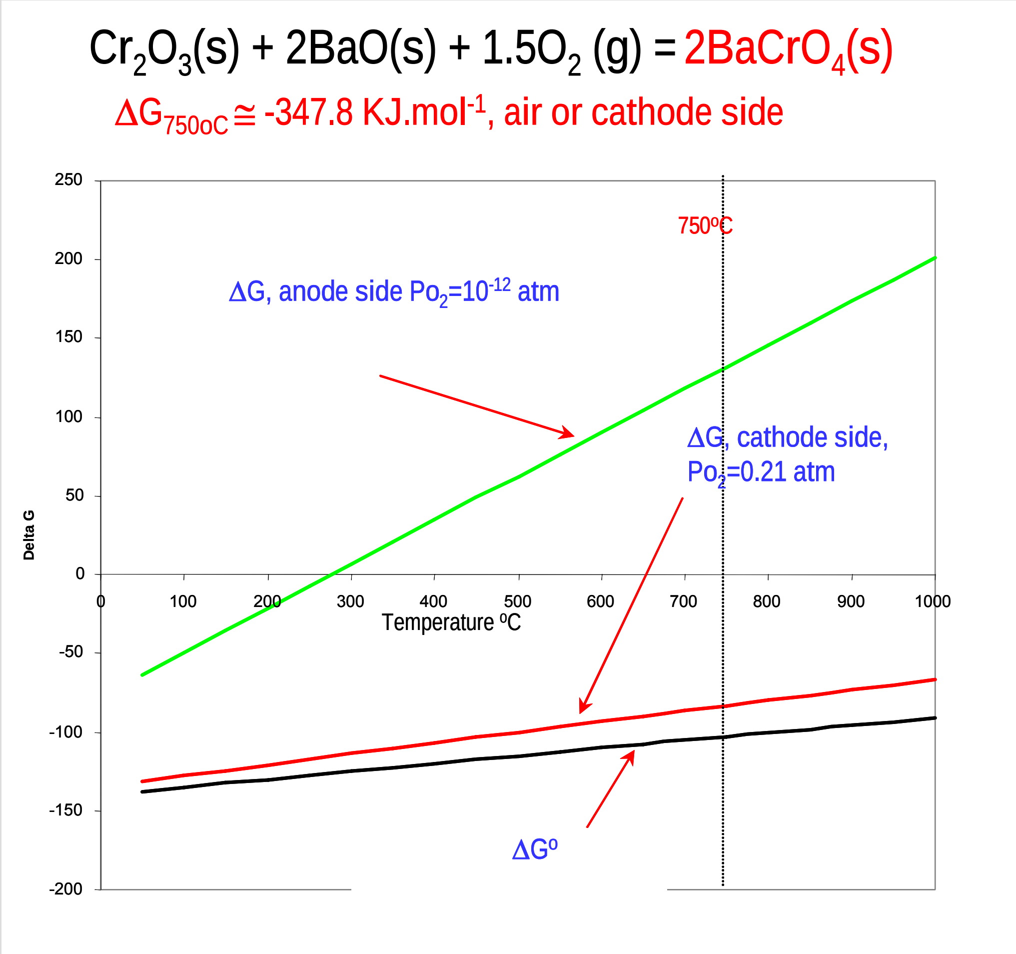
Reaction with Interconnect Materials

- Chrome Formers
  - $BaCrO_4$ Formation
    - Occurs only were Air is present
    - Weak interface
    - Forms in the edge area of the seal
    - Ba Depletion near the reaction zone



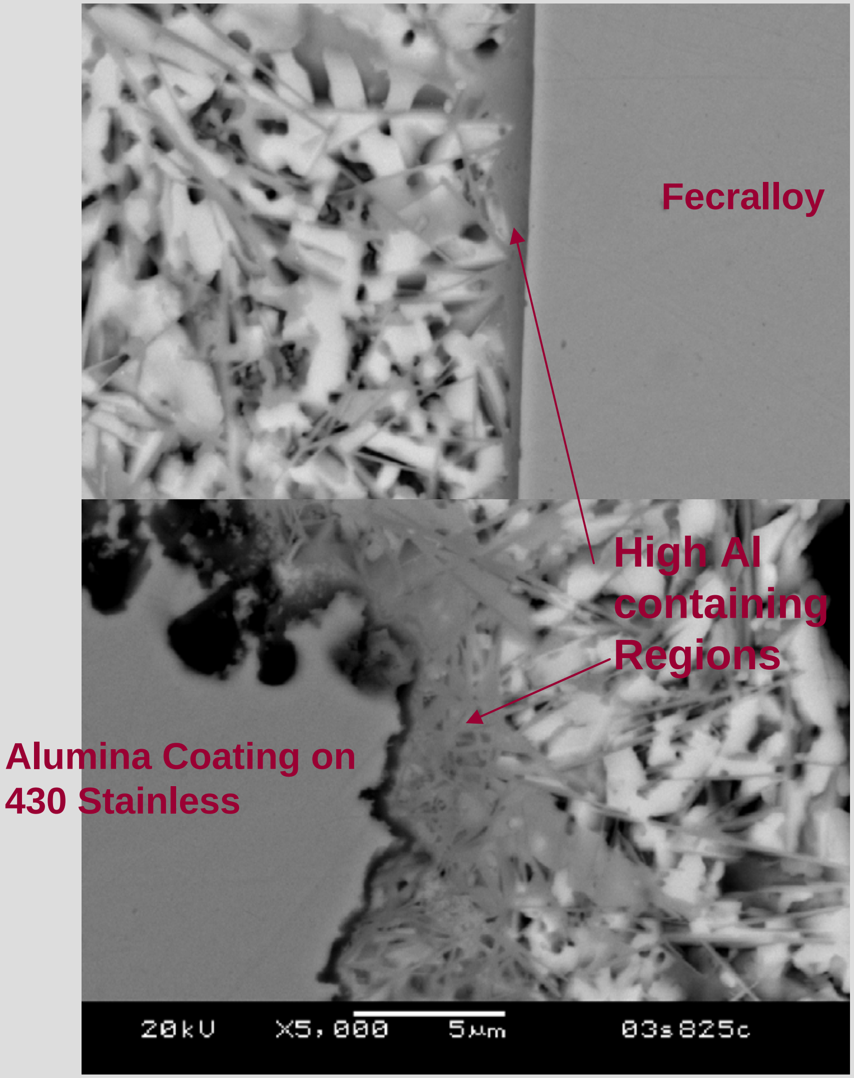
Reaction with Interconnect Materials

- **Chrome Interaction**
  - Solid Chrome interaction
    - **$Cr_2O_3(s) + 2BaO(s) + 1.5O_2(g) = 2BaCrO_4(s)$**
    - **$\Delta G_{750^oC} \cong -347.8$ KJ.mol^{-1}**
  - Chrome Vapor interaction
    - **$CrO_2(OH)_2(g) + BaO(s) = BaCrO_4(s) + H_2O(g)$**
    - **$\Delta G_{750^oC} \cong -476$ KJ.mol^{-1}**



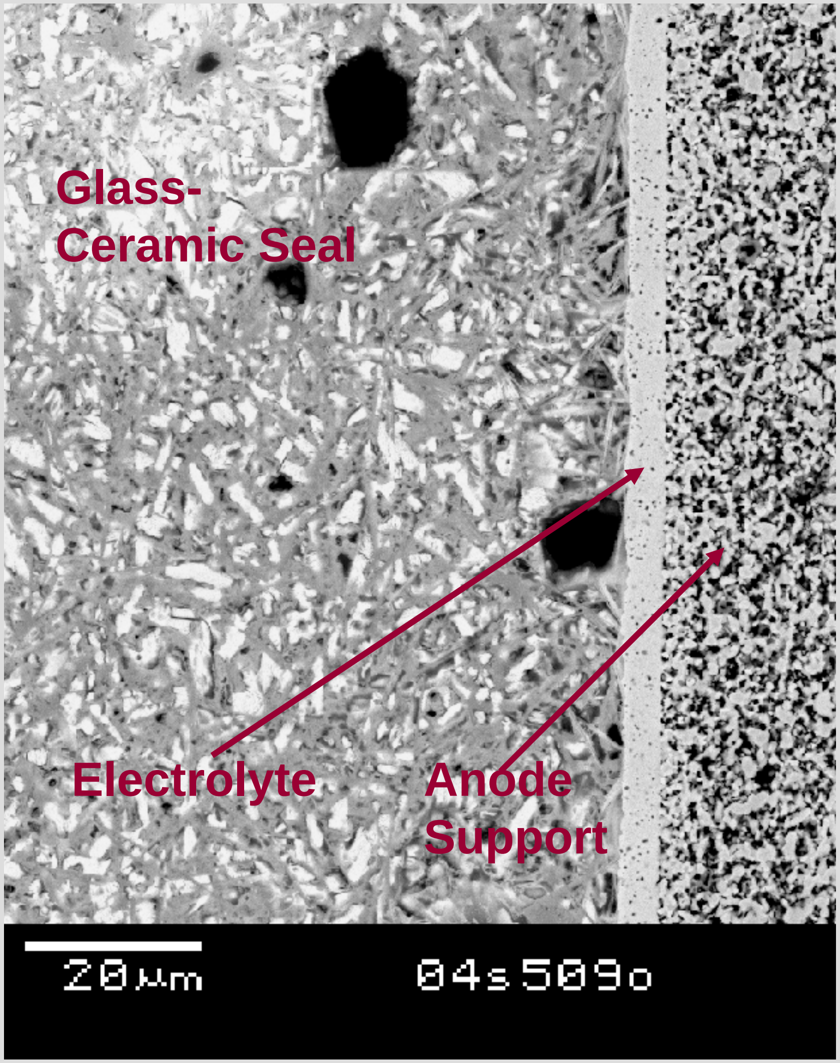
Reaction with Interconnect Materials

- Alumina Formers
  - Fecralloy, or alumina coated 400 series stainless (700 hrs)
    - Scale is Alumina
    - Chrome Volatility is minimized
    - $BaCrO_4$ does not form
    - Al diffusion into the glass seal promotes the formation of $BaAl_2Si_2O_8$ at the interface
    - If the $BaAl_2Si_2O_8$ transforms to or forms as mono-celsian the interface will fracture on cooling



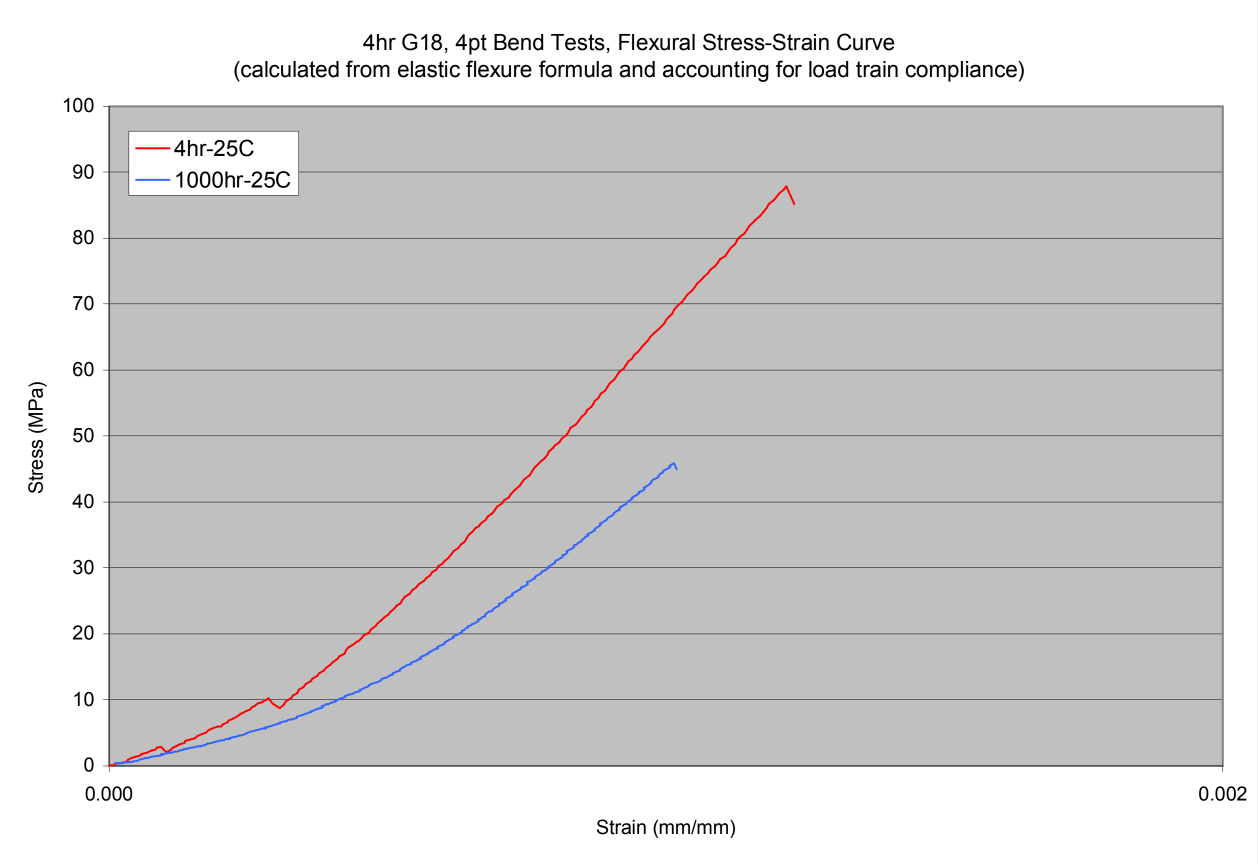
Interaction with the Electrolyte

- Glass – Yttria Stabilized Zirconia (YSZ) Interface
  - Sample shown has operated at 750°C for 1200 hours
  - Minimal Interaction
    - Very small amounts of potentially $BaZrO_3$ at the surface of the YSZ



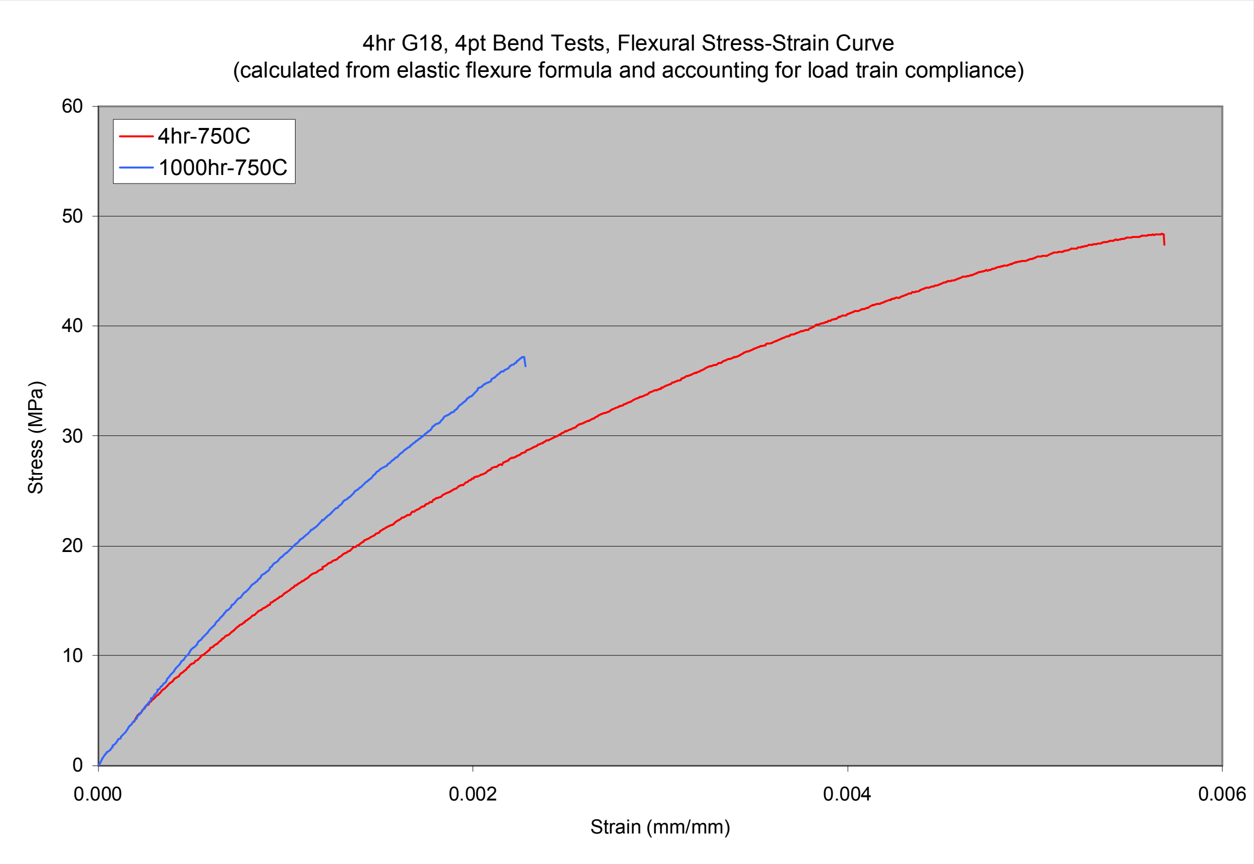
Mechanical Properties

- Low temperature Strength (25°C)
  - Mean Strength
    - Initial Material (at 750°C 4 hrs) 79 MPa
    - Aged (at 750°C 1000 hrs) 43 MPa
      - Samples had some internal porosity



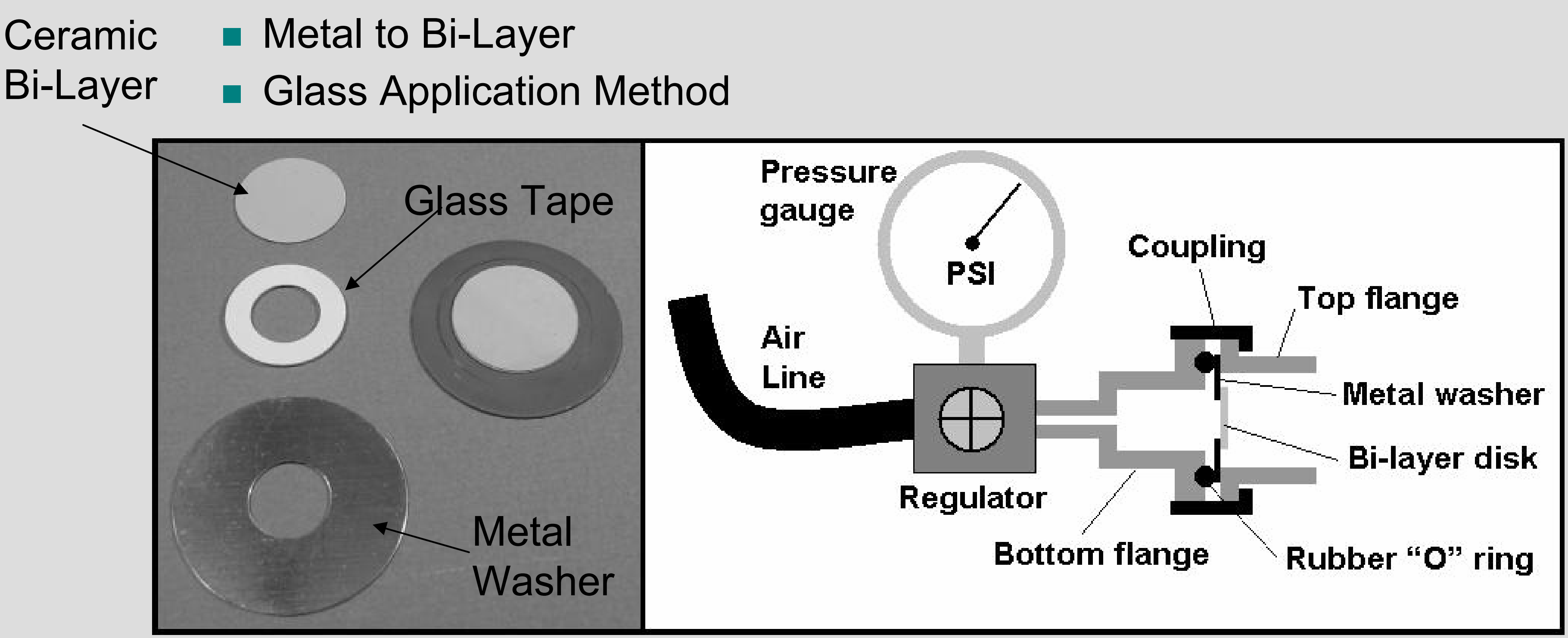
Mechanical Properties

- High Temperature Strength (750°C)
  - Mean Strength
    - Initial Material (at 750°C 4 hrs) 48 MPa
    - Aged (at 750°C 1000 hrs) 39 MPa

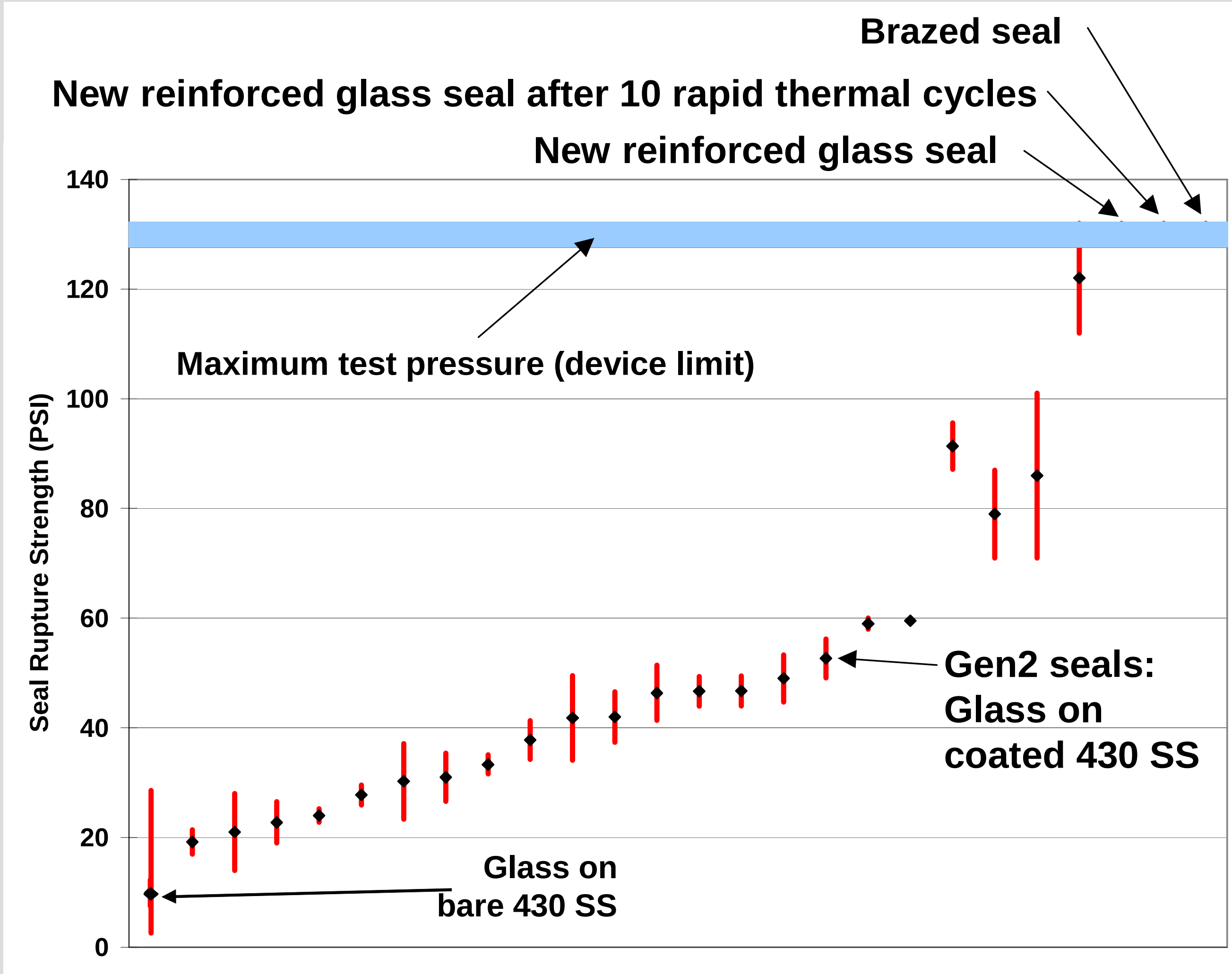


Bond Strength

- "Pop-Gun" Testing
  - Relative test of the bond strength of the seal material
    - Metal to Metal
    - Metal to Bi-Layer
    - Glass Application Method

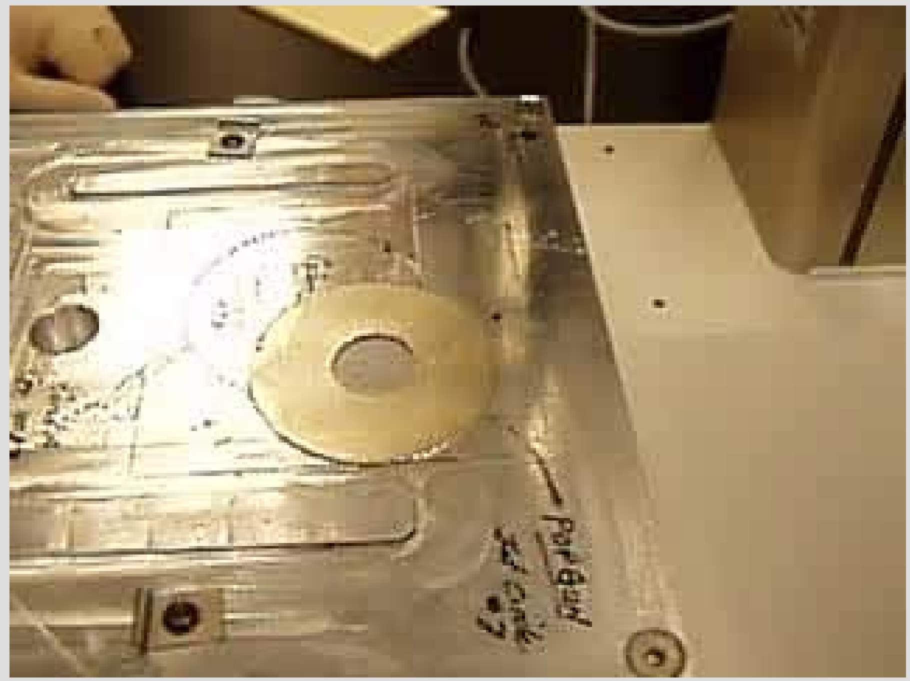


Pop-Gun Results



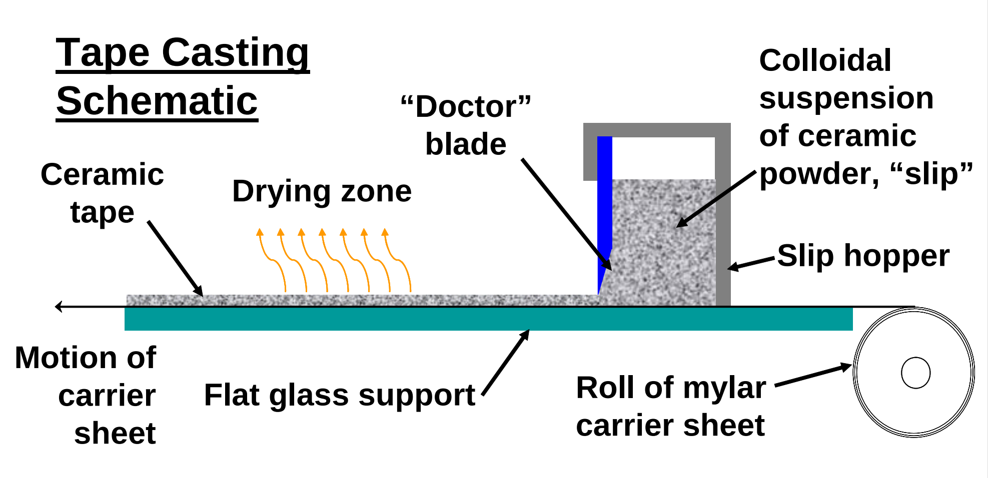
Application Methods

- Dispensing
  - Glass frit is dispersed in a binder-solvent system to form a high viscosity paste.
  - The paste is put in a pneumatic syringe and dispensed on the parts of choice with a robotic dispenser
- Pros:
  - Less Waste
  - Fewer handing steps
  - Conforms to the sealing surface
  - Lower Binder content, faster sealing heating rate
- Cons:
  - Drying shrinkage may cause gaps in the seal
  - Uneven dried surface makes assemble more problematic.
  - Some thickness variation
  - Dried paste can be broken off during handling



Application Methods

- Tape Casting
  - Glass frit is dispersed in a binder-solvent system to form a tape-cast slip
  - Slip is cast to the desired tape thickness with a doctor blade
  - Tape is dried
  - Multiple Tapes are laminated to achieve the desired thickness
  - Laminated tape is cut out to the desired shape (Gasket)
- Pros:
  - Easy to Assemble
  - Uniform thickness
- Cons:
  - Large amount of scrap (may be able to reclaim)
  - Not very good for very narrow seals (difficult to handle)
  - Large amount of binder
    - Slow heating rate is required to remove the binder
    - Large amount of shrinkage



Modifications to the G-18 Glass

- Needed improvements
  - Higher Crystallized TEC
    - Crystallized TEC that doesn't change with time
    - Crystallized Phase Stability
  - Improved Bonding
    - Minimize Chemical interaction with interconnect materials
      - Alumina formers
      - Chrome formers
    - Better Contact Angle
      - Slower Crystallization ?

Modifications to the G-18 Glass

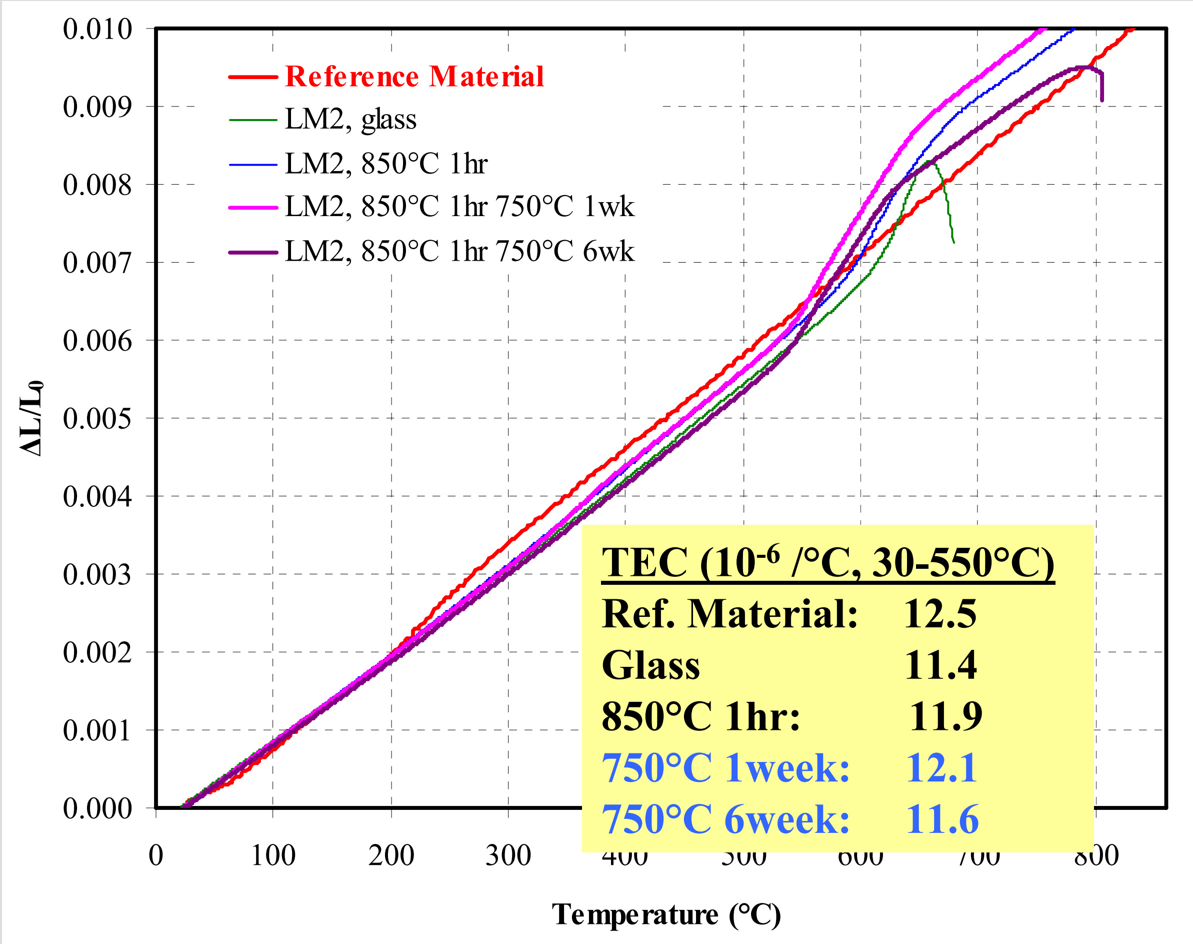
- Effect of additive components on glass properties
  - **By <u>Schwickert et al. 2002</u> (BaO-CaO-Al2O3-SiO2 glass system)**

La_2O_3, Nd_2O_3, Y_2O_3	increase TEC, T_g, T_M
B_2O_3	improves flux; reduces TEC, surface tension, and stability of the glass
ZnO, PbO	improves flux, reducing agent
Al_2O_3	improves flux
Cr_2O_3, V_2O_5	reduces surface tension
NiO, CuO, CoO, MnO	improves adhesion
TiO_2, ZrO_2, SrO	stimulates crystallization
Sb_2O_3	oxidizing agents

Above are expected to be valid for a certain range of base compositions within a limited concentration range

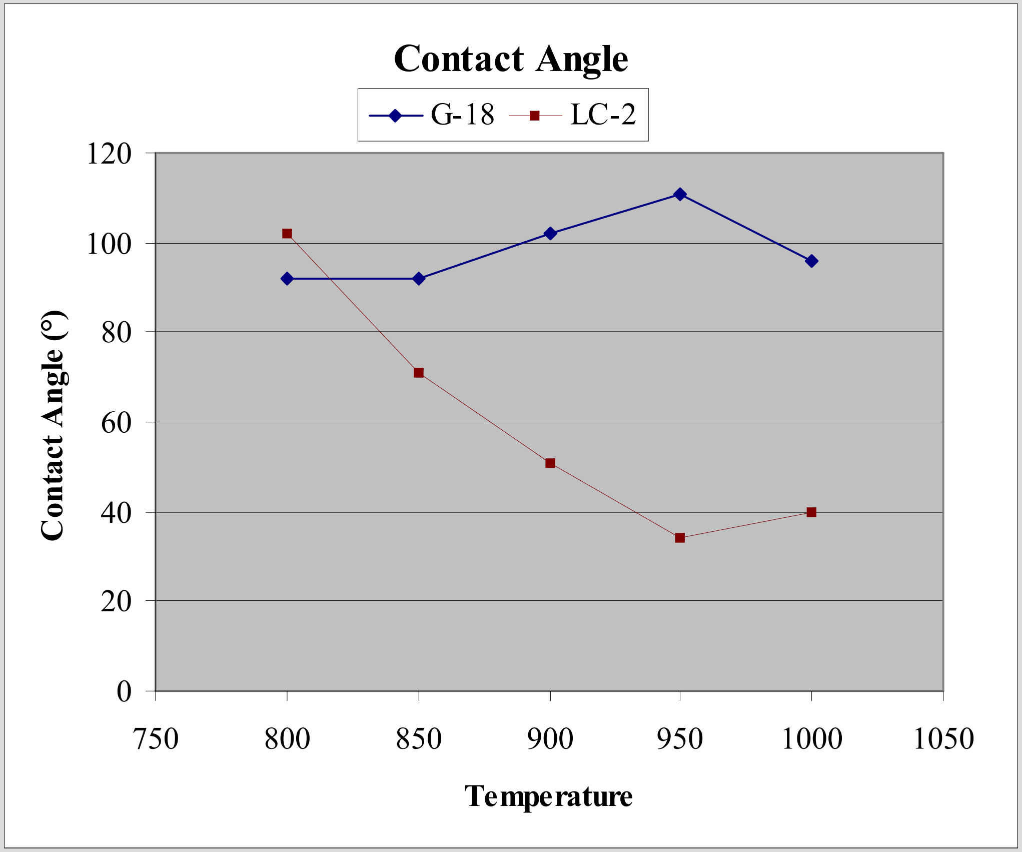
Improved Thermal Expansion

- Example with La_2O_3 and MnO
  - La_2O_3 ties the Al_2O_3 up.
  - Prevents the formation of Celsian
  - Poor Bonding
  - $La(OH)_3$?



Improved Contact Angle

- Example with La_2O_3 and CuO additions
  - Contact angle measured on cylinders cut from pre-melted glass
    - Rapid heating to each temperature starting from 500°C
    - Average heating rate: >30°C/min
  - Modified glass has better contact angle due to slower crystallization?



Summary

- Criteria for a SOFC Glass-Ceramic Seal
  - TEC match (initially and over time)
  - Stability over time and in the environment.
  - Good Bond Strength
  - Seals at an appropriate temperature
  - Minimal Chemical interactions
- Doubtful that any seal will meet all requirements
  - 90% solution and engineer around the remaining issues
    - Example: G-18 Bond strength

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