High-Temperature Viscous Sealing Glasses for Solid Oxide Fuel Cells

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Phase I Technical Objectives

1. Develop viscous sealing glass compositions that can be used at 650-850°C
   * Requisite Thermal and Physical Properties
     a) Long-term stability in viscosity (650-850°C)
     b) T_g, T_s: < 650°C
     c) T_{Liq}: < 800°C
        Stable, slow crystallization kinetics
     d) Viscosity: 10^6 Pa-s (10^7 Poise) - 10^{12} Pa-s (10^{13} Poise) in sealing temperature range
     e) CTE(40-500°C): 10-12.5×10^{-6}/°C (YSZ-SS441)
2. Conduct hermetic sealing tests
   SOFC Materials: Aluminized SS441
   NiO-YSZ supported YSZ electrolyte bilayers supplied by PNNL
3. Characterize thermochemical reactions
   a) volatilization of glass components
   b) interfacial reaction

Compositions Exhibit Promising Sealing Behavior

➢ Prepared a total of 45 compositions and measured properties (T_{Liq}, T_g, T_s, and CTE) of all of the 45 compositions

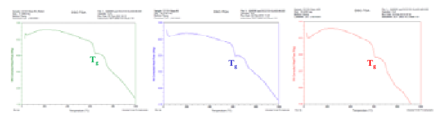
$BaO-B_2O_3-SiO_2$ or $BaO-B_2O_3-Al_2O_3$-RO systems

	Glass 2	Glass 4	Glass 28
Melting temp (°C)	1150	1150	1100
T_g (°C) measured from CTE curve	619	599	581
Dilatometric T_s (°C)	650	632	615
CTE (40-500°C)	8.19x10^{-6}	7.32x10^{-6}	7.48x10^{-6}

DSC Analysis

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

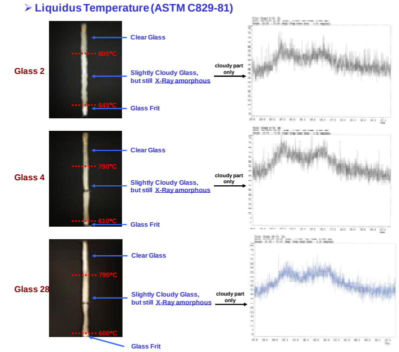
Glass 2 | Glass 4 | Glass 28



No Crystallization Peaks Up to 1000ºC

Liquidus Temperature

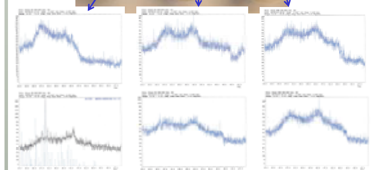
➢ Liquidus Temperature (ASTM C829-81)



500 hr Crystallization and Volatilization in Air

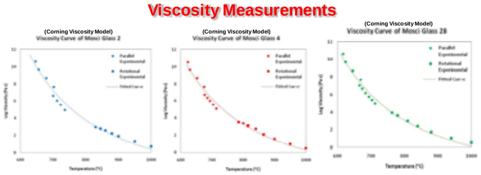
Glasses exhibit negligible weight loss in air

	650 °C / 500 hrs	850 °C / 500 hrs
	% Weight Loss	
Glass #2	0.04018	0.06622
Glass #4	0.03188	0.08111
Glass #28	0.03898	0.09027



No Obvious Crystallized Phases After 500 Hours at 650ºC/850ºC

Viscosity Measurements



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

$$\log \eta(T) = \log \eta_\infty + (12 - \log \eta_\infty)\frac{T_g}{T}\exp\left[\left(\frac{m}{12-\log \eta_\infty} - 1\right)\left(\frac{T_g}{T} - 1\right)\right]$$

Viscosity-cont.

Glass	Fitting Parameters: $\log \eta_\infty$	m	T_g(°C) fit	T_g(°C) CTE	Isokom T(°C), log(η/Pa·s)= 11	9	6.6	4	2
Glass 2	-3.5	68.7	620	619	643	668	708	779	887
Glass 4	-3.5	65.2	594	599	615	643	685	762	868
Glass 28	-3.5	66.1	589	581	610	637	680	753	859

1 ↑ 2

1. Very Good Agreement Between the T_g Predicted by the Viscosity Model and That Measured by Dilatometry
2. Littleton Softening Point Within the SOFC Operational Temperature (650-850°C)
3. Singh* reports 'self-healing' behavior for an SOFC sealing glass with a viscosity of 10^5 Pa-s at 800ºC. Similar behavior would be expected for the MO-SCI glasses at temperatures in the range of 725-750ºC. This temperature range is below the liquidus temperatures for these compositions.

* Singh, R. (2008), "Innovative seals for solid oxide fuel cells (SOFC)," Final Progress Report, DOE Award DE-FC26—04NT42227.

Viscosity-cont.

Isokom Temperatures (ºC) at viscosity of $10^{6.6}$ Pa·s

Glass	As-cast	650 ºC 500 hrs	750 ºC 500 hrs	850 ºC 500 hrs
Glass 2	713 ± 18	714 ± 4	715	733
Glass 4	689 ± 13	692 ± 2	-nm-	689 ± 1
Glass 28	682 ± 11	684 ± 3	681	683

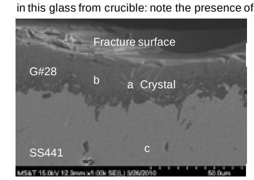
Isokom Temperatures (ºC) at viscosity of 10^8 Pa·s

Glass	As-cast	650 ºC 500 hrs	750 ºC 500 hrs	850 ºC 500 hrs
Glass 2	679 ± 23	685 ± 1	679	700
Glass 4	660 ± 13	661 ± 1	-nm-	656 ± 3
Glass 28	653 ± 13	653 ± 5	647	649

Reactivity Characterization

- Pastes were made from glass powders (45-60 μm) and acetone, and used to bond Ni/YSZ bi-layer to aluminized steel (SS441) substrate (materials from PNNL)
- Sandwich seals held in air at 800°C for 500 hours
- Seals were cross-sectioned, polished, then analyzed by analytical SEM

General observations
- Glass cracked down the center of the seal
- Glass wets and may react with SS441
- Some evidence for crystals in the glass
  - EDS indicates that the crystal (point 'a') is a Ba-aluminosilicate- silica contamination in this glass from crucible: note the presence of Si in point 'b'

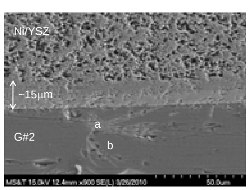


Relative atomic concentrations (EDS):

a.8Ba·1Ca·20Al·17Si·57O
b.6Ba·2Ca·22Al·3Si·0.3Zr·1Fe·66O
c.9Al·1Si·17Cr·73Fe

Reactivity Characterization-cont.

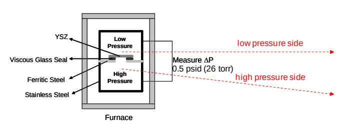
General observations (continued)
- Glasses wet/bond well to the ceramic substrate
  - Crystal in glass #2 (pt. 'a') appears to be a Ba-silicate (EDS) or a Ba-borate (XRD)
  - Some Al-contamination in 'base glass' (pt. 'b') – from crucible?
  - No significant degradation of the glass/zirconia interface



Relative atomic concentrations (EDS):

a.17Ba·1Na·0.5Al·16Si·66O
b.10Ba·1Na·7Al·16Si·66O

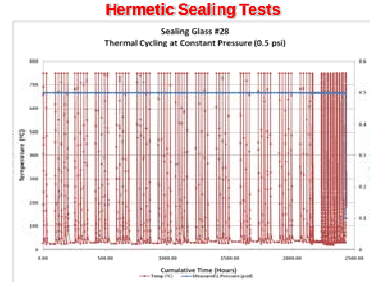
Hermetic Sealing Tests



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 Ni/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



Glass 28: Survived 75 thermal cycles (room T - 750ºC) at constant pressure of 0.5 psid

Phase I Conclusions

1. Glass compositions from the Ba-borosilicate (or Ba-borate) system have been identified that possess the properties desired for 'self-sealing' behavior:
   - Liquidus temperatures as low as possible (< 800°C)
   - Softening-range viscosities within the operational temperatures (650-850°C)
   - Stable viscosities at operational temperatures (500 hours)
     - Need to understand the role of limited crystallization when operating near, but below, the liquidus temperatures
   - Wet/bond to Ni/YSZ and SS441
     - Need to determine if 'molten glass' is more reactive than 'solid glass-ceramics', particularly for the metal substrates
   - Low volatilization rates in air
2. Hermetic seals have been made between Ni/YSZ and SS441
   - Survive 75 thermal cycles between 750°C and room T
   - Need to increase the glass (sub-T_g) CTE for better match to other SOFC components
   - Need to re-design hermeticity testing rig to evaluate 'self-sealing' behavior
3. Provided foundation for Phase II

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