Glass Seal Development for Tubular Cells in High Temperature Electrolysis Application

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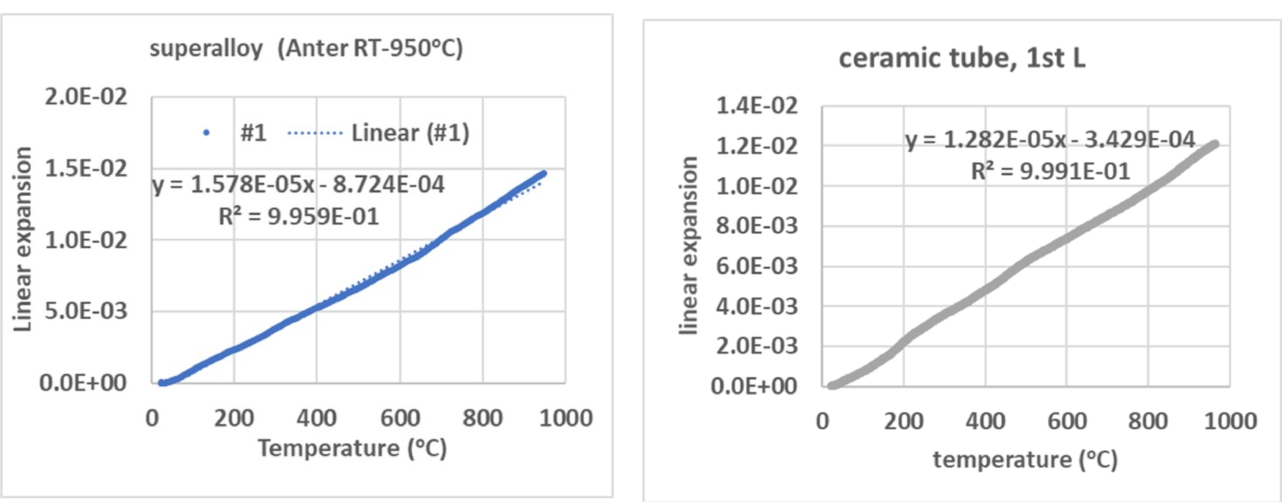
Introduction:

PNNL is working with an industrial partner to develop glass sealants for tubular cells for high temperature electrolysis under the Department of Energy's Technology Commercial Fund (TCF) Program. The objective is to develop suitable glass sealants based on PNNL's SOFC glass seal (Ba-Ca-Al-B-Si) and aluminization coating technologies to advance the partner's SOEC technology to commercialization.

Q1: Glass formulation and thermal property characterization
Q2: Ageing effect on thermal properties and wetting study
Q3: Bonding strength and interfacial reaction study
Q4: Validation test with mini-tube reactor design in dual environment and post-mortem analysis ***in progress***

CTE of Mating Materials for Glass Sealant



Thermal expansion behavior of mating materials for this project: superalloy as the cup seal (left), and ceramic tube (right). Note that the large CTE mismatch between mating materials presents a great challenge for glass seal development.

Target Mating Materials for Glass Seal Development

This photo shows the sizes and shapes of the mating materials for which seals are being developed. The open end of the tube will be sealed inside of a cup-shaped superalloy manifold with the glass sealant.

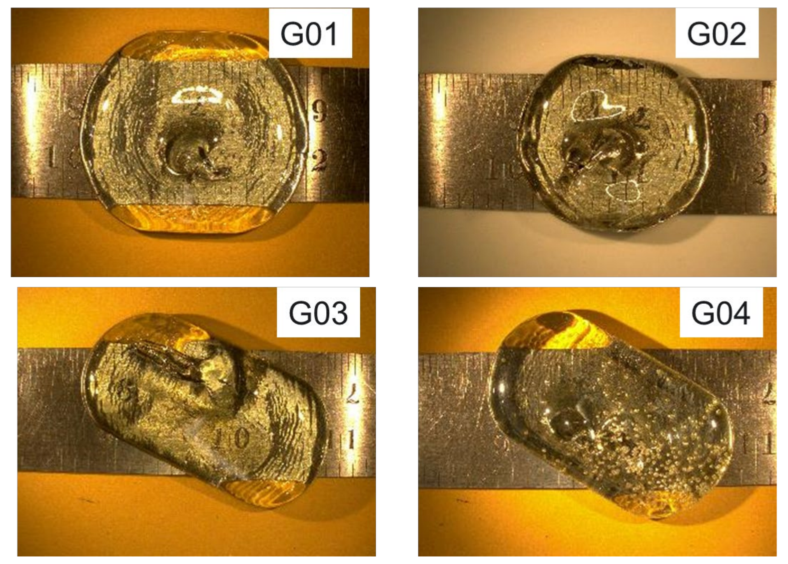
Approaches for Glass Sealant Development

In light of the large CTE mismatch of the mating materials we have assessed two approaches:

1. **Plain glass where a (Ba,Sr) (Al, Y, La) B silicate glass was formulated and made**
2. **Composite glass where a typical SOFC glass sealant (G18: Ba-Ca-Al-B-Si) was mixed with a high CTE ceramic phase to tailor the composite's CTE**

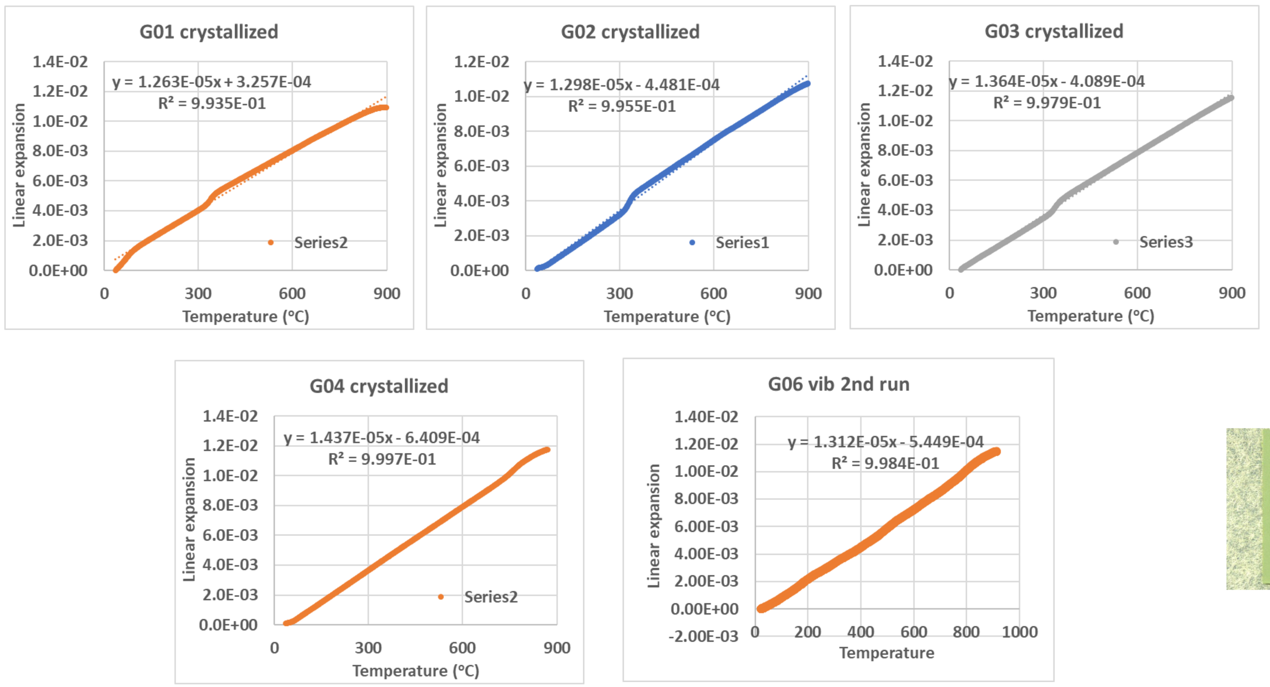
1. Plain glass formulation and thermal properties

mole%	SiO2	B2O3	Al2O3	BaCO3	SrCO3	Y2O3	La2O3	as-made
G01	39.0	10.0	9.0	33.0	9.0	0.0	0.0	transparent
G02	39.0	10.0	9.0	36.0	6.0	0.0	0.0	transparent
G03	39.0	10.0	9.0	39.0	3.0	0.0	0.0	transparent
G04	39.0	10.0	9.0	42.0	0.0	0.0	0.0	transparent
G05	39.0	10.0	0.0	33.0	9.0	9.0	0.0	opaque
G06	39.0	10.0	0.0	33.0	9.0	0.0	9.0	transparent



Typical appearance of as-made plain glass that was melted in a Pt crucible at ~1450-1500°C and casted. Note that glasses G01 to G04 were transparent as shown above, while G05 were opaque indicating undesirable crystallization. Glass G06 was also transparent (not shown here). The observed transparency and absence of surface crystallization suggests good homogeneous glass formulations.

2. Thermal expansion behavior of crystallized plain glass

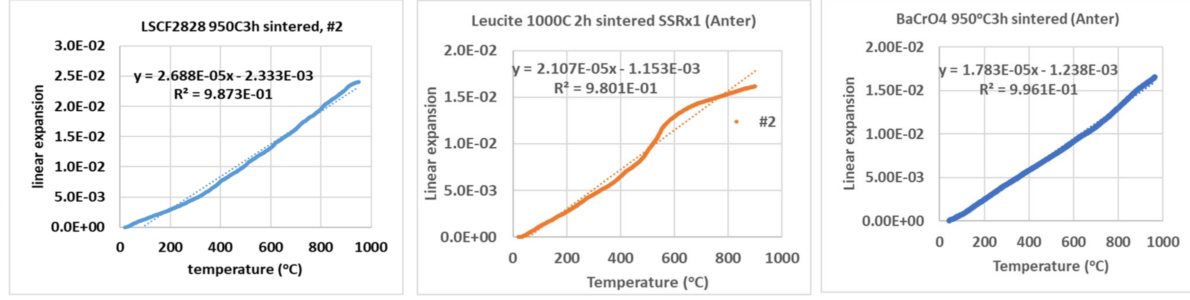


Vibratory milled glass powers were pressed into bars and fired at 900-950°C. The linear thermal expansion indicates substantial crystallization. Glass G04 has the most desirable CTE with values between those of the mating materials. However, the rapid and substantial crystallization resulted in poor wetting and sealing, therefore the plain glass approach was not further pursued.

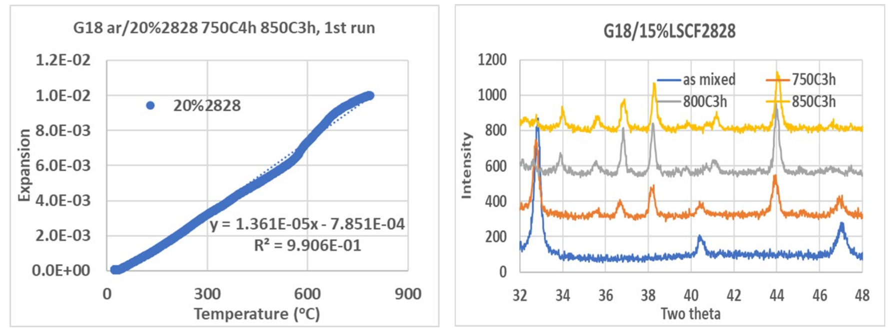
3. Composite glass approach with high CTE phases and fibers

$$\alpha_{comp} = (\alpha_1 K_1 F_1/\rho_1 + \alpha_2 K_2 F_2/\rho_2)/(K_1 F_1/\rho_1 + K_2 F_2/\rho_2)$$

(Turner, hydrostatic tension and compression only)



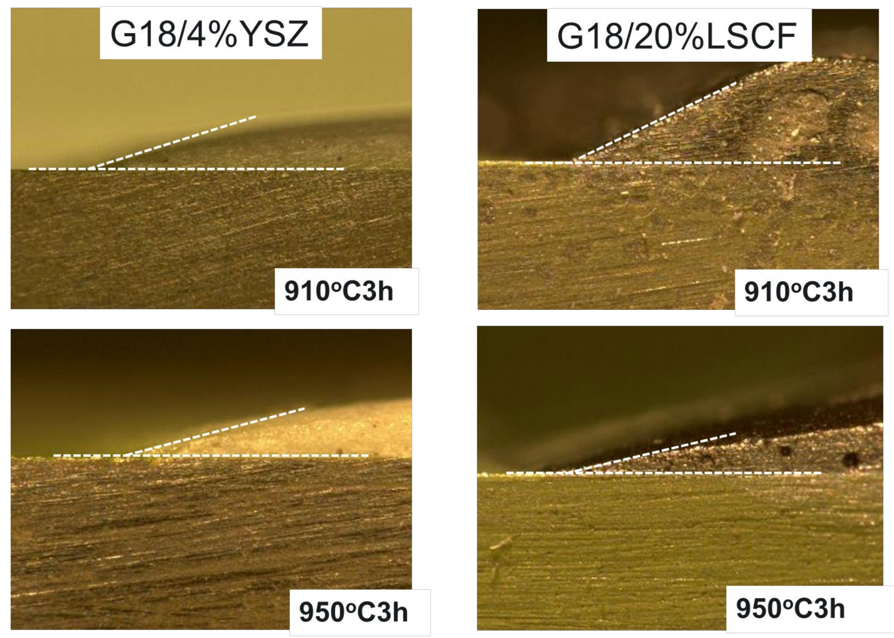
4. Thermal properties of composite glass



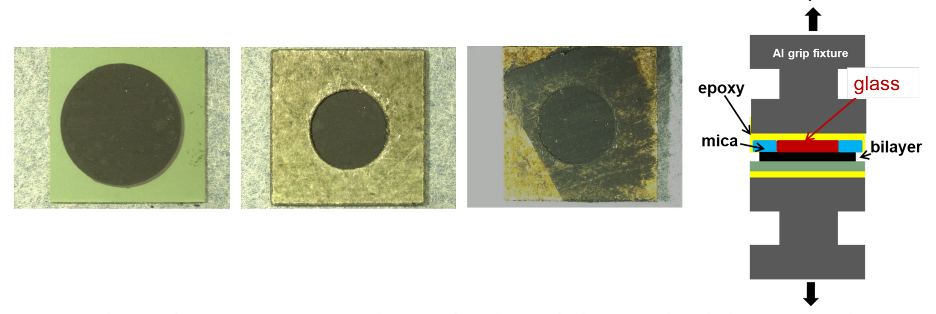
Vf	CTE (G18/2828)	CTE (G18/leucite)	CTE (G18/BaCrO4)
0.00	12.5	12.5	12.5
0.05	14.2	13.0	12.7
0.10	15.6	13.4	12.8
0.15	16.9	13.9	13.0
0.20	18.0	14.4	13.2
0.25	19.0	14.8	13.4
0.30	19.9	15.2	13.6

Linear thermal expansion of fired composite glasses as a function of ceramic phase concentration. CTE values differ greatly from model predictions. The cause was attributed to reaction between ceramics and the parent glass. Only BaCrO4 showed minute reaction with the G18 glass matrix; however, thermodynamic calculations predicted gas evolution when exposed to reducing environments. Therefore, only G18/LSCF and G18/YSZ(fiber) were further pursued.

5. Good wetting behavior over a wide temperature range



6. Glass bonding strength with YSZ layer (as-fired, aged in air, and aged in reducing)



Pictures show the preparation of samples from left to right: bilayer, mask on bilayer, glass paste applied, and uniaxial tensile testing

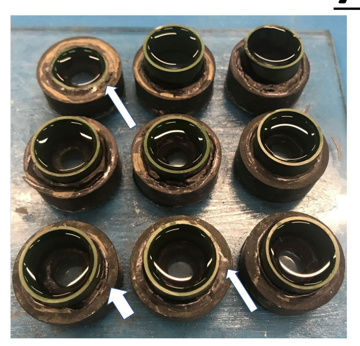
	MPa		MPa	
as-fired	20%2828	Note	4%YSZ	Note
1	9.68	epoxy/Al	9.64	epoxy/Al
2	9.59	epoxy/Al	10.82	epoxy/Al
4	9.65	epoxy/Al	7.87	epoxy/Al
5	8.72	epoxy/Al	10.52	epoxy/Al
6	8.17	epoxy/Al	8.93	epoxy/Al
7	9.96	epoxy/Al	11.01	epoxy/Al
8	8.02	epoxy/Al,	9.84	epoxy/Al
3	2.80	bilayer	6.15	bilayer
avg	9.29	avg	9.80	
std	0.69	std	1.12	

	MPa		MPa	
air aged	20%2828	Note	4%YSZ	Note
1	4.97	epoxy/Al	7.08	epoxy/glass
2	3.30	epoxy/Al	6.18	epoxy/Al
5	7.28	epoxy/Al	7.58	epoxy/Al
6	6.05	epoxy/Al	6.58	epoxt/glass
8	8.53	in bilayer	9.46	glass/ysz
7	3.73	in bilayer	4.43	bilayer
3	3.06	in bilayer	5.83	bilayer
4	3.31	in bilayer	5.09	mixed
avg	6.02	avg	7.37	
std	2.03	std	1.28	

	MPa		MPa	
red. aged	20%2828	Note	4%YSZ	Note
1	8.17	epoxy/Al	7.65	epoxy/glass
2	7.37	epoxy/glas	8.01	mixed bil/epo
5	9.18	mixed	10.21	epoxy/Al
6	5.92	epoxy/Al	11.29	epoxt/Al
8	7.37	mixed	7.14	epoxt/Al
4	8.00	in bilayer	7.78	mixed bil/epo
7	4.06	in bilayer	5.11	epoxy/Al
3	4.71	in bilayer	9.18	bilayer
avg	7.67	avg	8.30	
std	1.08	std	1.92	

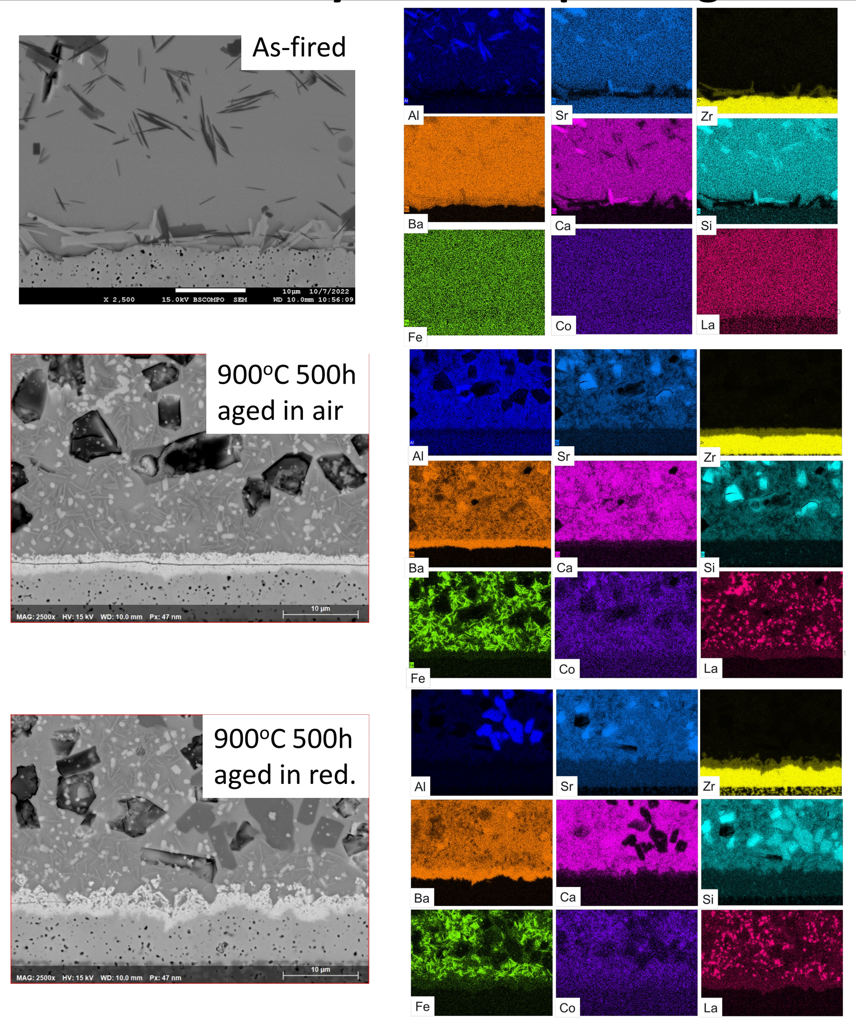
- **G18/YSZ showed slightly higher strength, likely due to strong fiber reinforcement.**
- **Small reduction in bond strength after ageing is likely attributed to crystallized microstructure.**

7. Leak testing of cup seals with iso-propanol



composite glass	seal T/hr	as-sealed	after 10 TC (50-900C/1h)	bonding	900C500h air
G18 vib/20%LSCF2828	950C/3h	hermetic	hermetic	strong	hermetic
15T vib/20%LSCF2828	950C/3h	hermetic	hermetic	strong	hermetic
G18 vib/30%leucite	950C/3h	hermetic	hermetic	strong	hermetic
15T vib/30%leucite	950C/3h	hermetic	hermetic	strong	hermetic
UGG04 vib/20%leucite	950C/3h	hermetic	hermetic	strong	hermetic
YSO78 vib/15%LSCF2828	950C/3h	hermetic	leaked, small	strong	cracked

8. Interfacial EDS analysis of composite glass G18/LSCF2828 with YSZ layer



- **Some discrete crystals formed along interface: Sr-Ca-silicate, $BaZrO_3$.**
- **Al-Ca-silicate and Sr-Ca-silicate in matrix.**
- **LSCF appeared well dissolved in the glass matrix, no crystalline phases identified along interface.**

- **~3 µm dense $BaZrO_3$ layer formed at interface.**
- **$BaZrO_3$ cracks due to machining.**
- **Uniformly distributed La- or Fe-enriched precipitates.**
- **Microstructure evolution resulted in some irregular voids, likely due to redissolution.**

- **~2 µm dense $BaZrO_3$ layer formed at interface.**
- **Uniformly distributed La- or Fe-enriched precipitates.**
- **Microstructure evolution resulted in some irregular voids, likely due to redissolution.**
- **No significant difference from ageing in air.**

9. Validation of composite glass in dual environment

Summary and Conclusions

- **Formulated 6 glasses - 5 showed good glass behavior, one crystallized upon casting.**
- **CTE of as-made plain glasses were lower than targeted values - crystallized glass G04 had the closest match; however, sealing behavior was undesirable due to rapid crystallization.**
- **3 high CTE ceramic phases were identified as candidates for composite glass sealants using G18 glass as the matrix material.**
- **Chemical compatibility was studied for the high CTE ceramic + G18 composites. $BaCrO_4$ was the least reactive, while leucite and LSCF reacted readily with G18 glass melt.**
- **Composite G18/20%LSCF2828 and G18/4%YSZ(f) were selected for further study. Both showed good wetting on YSZ over a wide temperature range for sealing.**
- **Interfacial EDS analysis of G18/LSCF on YSZ showed BaZrO3 formation which grows over time at 900°C to form a dense and continuous layer. No distinct microstructural difference was observed after ageing in air or reducing/humid environment.**
- **Tensile testing showed strong bonding of candidate composite glasses with YSZ, while glass with YSZ fibers showed a slightly greater strength, due to higher elasticity and toughness. Bond strength showed a small decrease after ageing for 900°C/500h in air or reducing environment.**
- **Composite glass validation in a mini-tube reactor in dual environment is underway. Preliminary mini-tube cup sealing often exhibited shear fracture due to microstructural inhomogeneities in the ceramic tubes coupled with large intrinsic stresses caused by the CTE mismatch between the superalloy and tube.**

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