Characterization of glasses for SOFC sealing applications

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Objective: To characterize the microstructure and chemistry changes in candidate glasses for SOFC sealing applications and develop models to predict its evolution as a function of service time and environment.

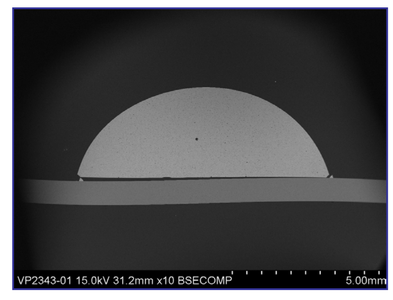
Requirements for SOFC glass seals

- Simultaneous fulfillment of thermal, physical, chemical, mechanical and electrical property requirements.
- Phase stability and chemical compatibility without substantial property degradation for 40,000 hours in oxidizing and wet reducing environments.

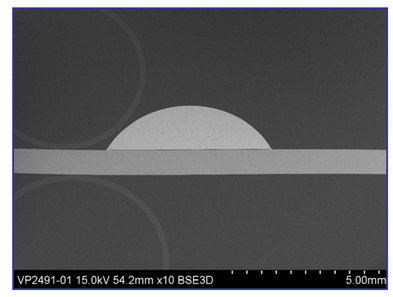
G6 and SCN

Commercially available Alkali Barium Silicate glasses

- Powders are cold pressed into pellets follwed by sintering at 850°C for 2 hours. Specimens exposed at 800°C for 10,000 hours on 8YSZ and Alumina substrates (longer term exposures in progress)
- Exposure in air and steam+H_2+N_2

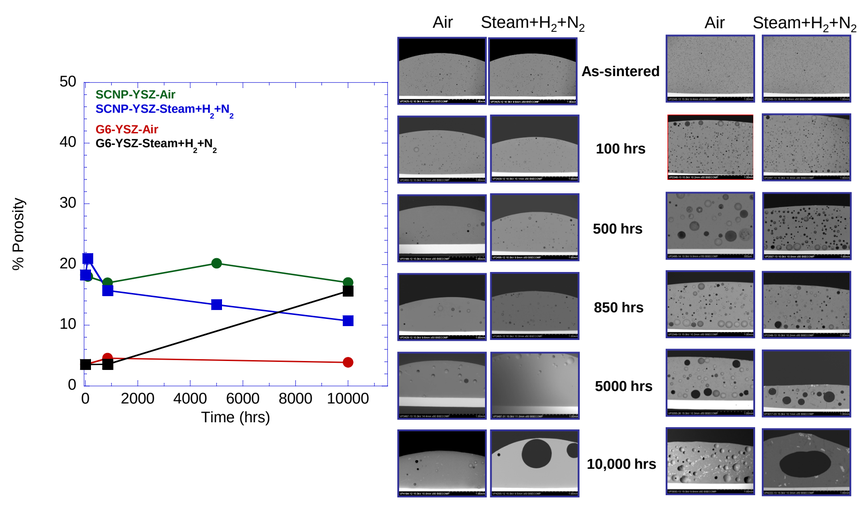


SCN



G6

Evolution of Porosity with Time of Exposure

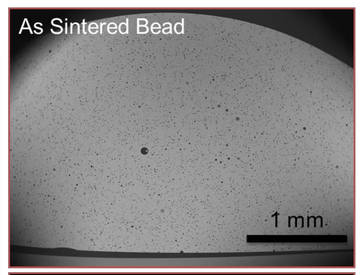


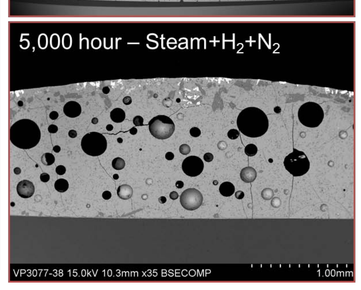
Microstructural changes in SCN glass

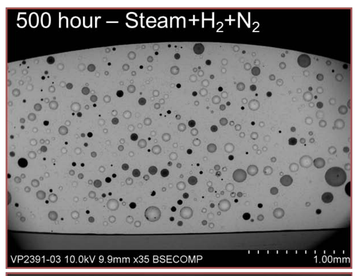
Table/images for alumina substrate

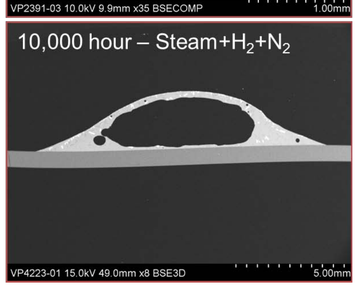
Exposure Condition	Glass	$KAlSi_3O_8$	Barium type oxide	Ca-rich silicate	SiO_2	Bead Attached
SCN Glass – As sintered	✓	x	x	x	x	x
100 hours – Air	✓	✓	x	x	x	x
100 hours – Steam+H_2+N_2	✓	✓	✓(s)	x	x	x
500 hours – Air	✓	✓	x	x	x	x
500 hours – Steam+H_2+N_2	✓	✓	✓(s)	x	x	x
865 hours – Air	✓	✓	✓(s)	x	x	✓(r)
850 hours – Steam+H_2+N_2	✓	✓	✓(s)	✓(s)	x	x
5,000 hours – Air	✓	✓	✓(s)	✓	✓(s)	✓(r)
5,000 hours – Steam+H_2+N_2	✓	✓	✓(s)	✓(s)	x	✓(r)
10,000 hours – Air	✓	✓	✓	✓	✓(s)	✓(r)
10,000 hours – Steam+H_2+N_2	✓	✓	✓(s)	✓(s)	x	✓(r)

✓(s) – Phase forms only on the surface of the bead
✓(r) – Bead remains attached due to formation of reaction layer

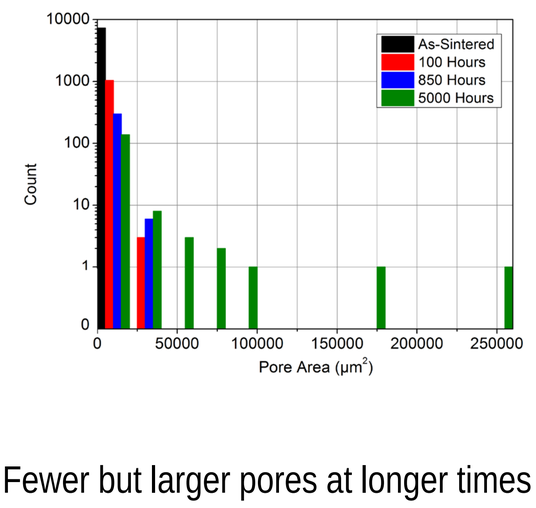


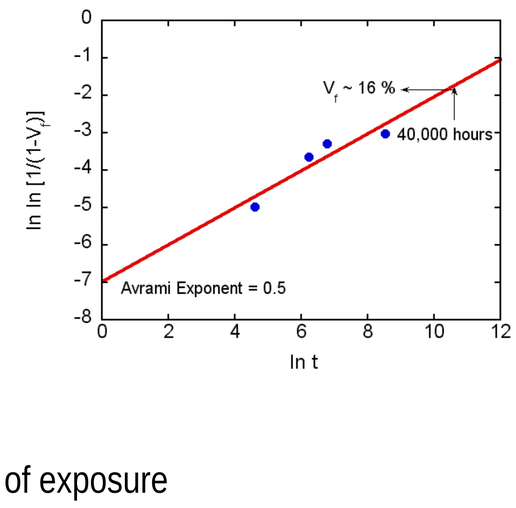


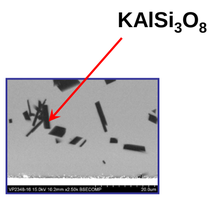




SCN Glass on Substrate: 8YSZ; environment: steam+H_2+N_2



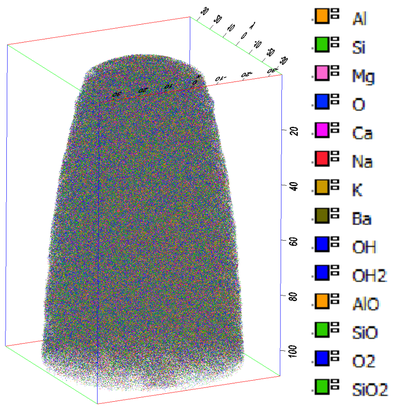




Chemical Analysis

	ICPMS (ORNL)	ICPAES (ORNL)	APT Tip 1 R06_15869		APT Tip 2 R06_15853	
	at.%	at.%	at.%	statistical error (at.%)	at.%	statistical error (at.%)
O*	66.67	66.67	57.13	0.07	57.25	0.04
Si	27.38	27.96	25.64	0.04	26.65	0.03
K	1.90	1.64	2.85	0.01	2.73	0.01
Ba	0.50	0.45	2.00	0.01	2.16	0.01
Na	2.11	1.72	3.48	0.01	3.54	0.01
Ca	0.48	0.60	2.32	0.01	2.35	0.01
Al	0.62	0.60	2.64	0.01	2.78	0.01
Mg	0.24	0.26	1.21	0.01	1.23	0.00
Ti	0.05	0.06	ND		ND	
B	0.05	0.04	ND		ND	
Zn	0.01	0.01	ND		ND	
Zn	0.00	0.00	ND		ND	
Fe	0.00	0.00	ND		ND	
Zr	0.00	0.00	ND		ND	
Li	0.00	0.00	ND		ND	
H**	ND	ND	2.71	0.01	1.32	0.01
Total	100	100	100		100	

ND = not detected
* Oxygen normalized to SiO_2 stoichiometry for ICPMS and ICPAES
** Hydrogen from OH and OH_2 molecular ion peaks



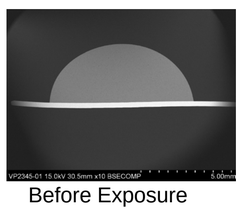
70 x 70 x 109 nm³

- Fewer but larger pores at longer times of exposure
- Heterogeneous microstructure
- At present rate ~15% of glass would crystallize after 40,000 hours

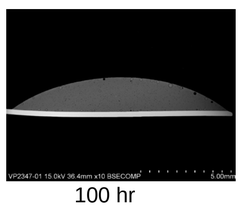
- Atom probe-based technique developed for measurement of glass chemistry at nanoscale

Effect of time of exposure on dimensional stability / Tg

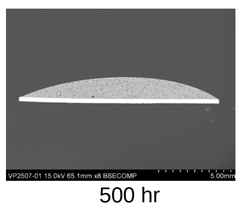
SCN Glass on Substrate: 8YSZ; environment: steam+H_2+N_2



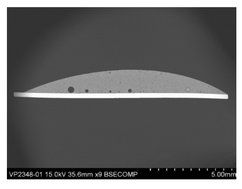
Before Exposure



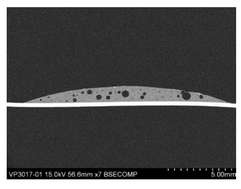
100 hr



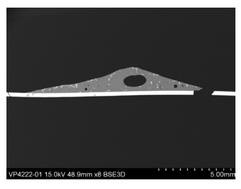
500 hr



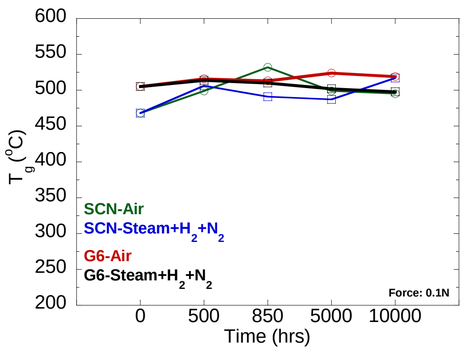
865 hr



5000 hr



10,000 hr



- Glass transition temperature remains nearly constant after 10,000 hours of exposure demonstrating long term self-healing behavior

Summary

- The effect of time of exposure in air and steam+H_2+N_2 at 800°C on the microstructural, chemical and dimensional stability of two commercially available alkali barium silicate glasses is being investigated
- The kinetics of devitrification, porosity and pore size distribution were characterized. Models are being developed to predict microstructural changes for long periods of service time.
- Long-term exposure of SCN and G6 glasses (20,000 hours+) is in progress.

Acknowledgements

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