Viscous Silicate SOFC Glass Sealants

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Viscous Sealant Benefits

- Viscous sealants allow flexibility in SOFC stack design
- Fracture is avoided at SOFC operating temperatures providing reliable electricity generation

Target Properties

- Glass transition temperatures below 600 °C
- Sealing below 900 °C
- Thermal stability for 40,000 hrs at operating temperatures between 650 and 850 °C in O_2 and H_2 environments
- Low electrical conductivity

Objectives

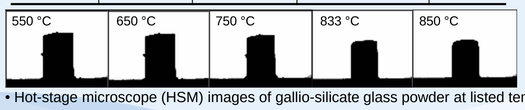
- Develop new glass compositions meeting DOE target properties
- Assess flow behavior of glass powders and frits
- Study interfacial reactions with SOFC stack components to monitor compatibility
- Understand crystallization behavior within SOFC OT range for long times (1500 hrs)

Compositional Modification

- Two main silicate systems are pursued: gallio-silicates & germano-silicates
- Modifications have been toward low or non-alkali compositions
- Desirable flow behavior and Tg have been maintained while lowering alkali content

Gallio-silicates

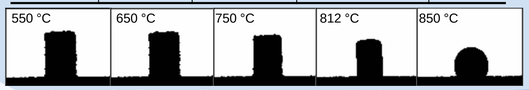
Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)	T_{seal} (°C)
10	0	640 - 650	9 - 10	≈ 900



- Hot-stage microscope (HSM) images of gallio-silicate glass powder at listed temperatures

Gallio-boro-silicates

Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)	T_{seal} (°C)
0	5 - 10	660 - 710	7 - 10	≈ 850



- HSM images of gallio-boro-silicate glass powder at listed temperatures

Gallio-boro-silicates 2

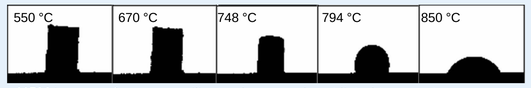
Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)
5	5 - 10	610 - 630	8 - 10

High Temperature Silicates

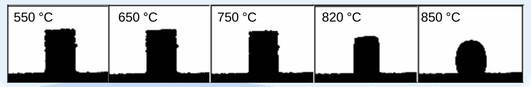
Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)	T_{seal} (°C)
20	0	590 - 770	9 - 12	> 950

Germano-silicates

Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)	T_{seal} (°C)
10	10	540 - 590	7.5 - 10	≈ 650



- HSM images of germano-silicate glass powder at listed temperatures



- HSM images of non-alkali germano-silicate glass powder at listed temperatures

Germano-silicates 2

Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)
5	10	610 - 640	8 -9

Statistical Design Matrix

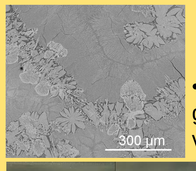
Alkali (mol %)	B_2O_3 (mol %)
0 - 5	5 - 10

Heat Treatment at 850 °C

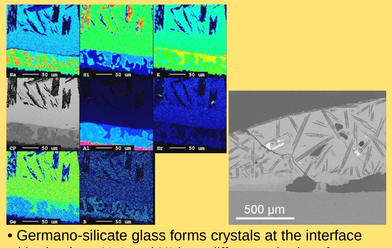
- Glasses on alumina or 8YSZ heat treated for 500, 1000, or 1500 hrs in air

Alumina

- Gallio-silicate glasses crystallize extensively at 850 °C after 504 hrs

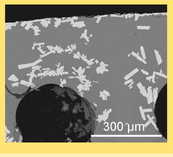


- Little remnant glass phase for viscous flow



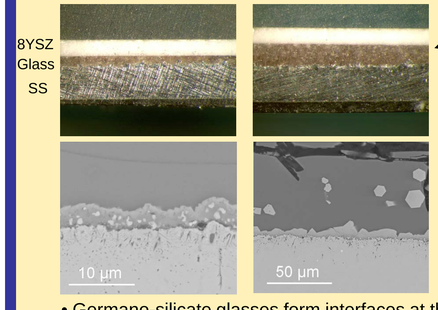
- Germano-silicate glass forms crystals at the interface with alumina. Na^+ and K^+ ions diffuse to the interface.

- Germano-silicate glasses retain ~70% amorphous phase after 1500 hrs at 850 °C to sustain viscous sealant behavior



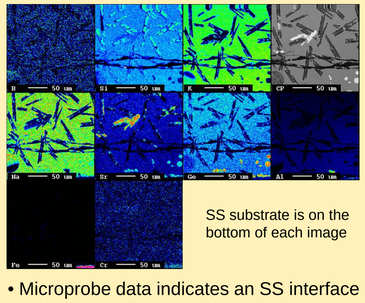
Test Seal with Aluminized SS & 8YSZ

- Germano-silicate glasses between 8YSZ and aluminized stainless steel (SS) heat treated for 500 hrs in air



No fractures in seal before polishing

- Germano-silicate glasses form interfaces at the SS surface. Fracture is not observed at the interface suggesting these glasses are compatible with SOFC stack components.

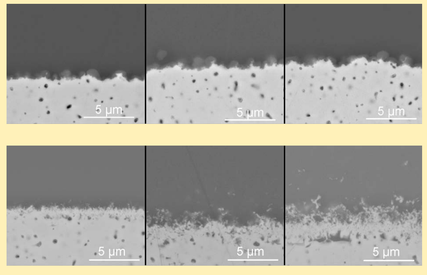


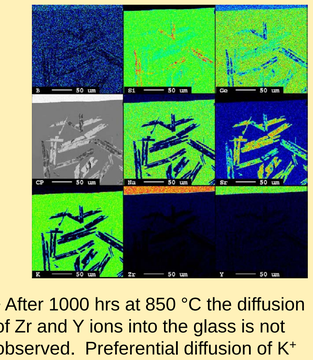
SS substrate is on the bottom of each image

- Microprobe data indicates an SS interface rich in Ge and Sr ions. Al ions appear to diffuse into the glass while Fe and Cr ions are mostly immobile.

8YSZ

- Germano-silicate glass pellets on 8YSZ substrates at 850 °C for 500, 1000, and 1500 hrs. Interaction with 8YSZ is minimal for some glasses, while some continuously dissolve the substrate

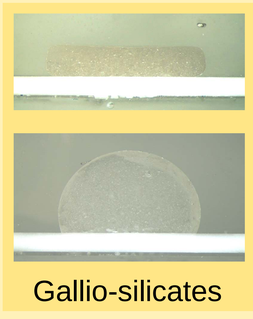




- After 1000 hrs at 850 °C the diffusion of Zr and Y ions into the glass is not observed. Preferential diffusion of K^+ and Na^+ ions is not observed. Some germano-silicate glasses appear stable with 8YSZ.

Heat Treatment at 650 °C

- Glasses were heat treated at 850 °C for 30 min, cooled to 650 °C, then held for 500 hrs.
- Gallio-silicate glasses do not exhibit extreme crystallization at 650 °C. This compositional series appears promising for viscous sealants at the low end of the OT range.
- Germano-silicate glasses partially crystallize, yet retain a high amorphous content. It appears this compositional series may be used within the entire OT range



Gallio-silicates

Germano-silicates

Conclusions

- Amorphous content of Germano-silicate glass powders remains high after heat treatment at 650 °C and 850 °C.
  - These glasses appear to be excellent candidates for viscous sealants at any temperatures within the SOFC OT range
  - Some glasses exhibit minimal interaction with 8YSZ substrates
  - These glasses may provide excellent composite sealants with 8YSZ powders
  - Test seals suggest excellent compatibility with SOFC stack components
- Gallio-silicate glass powders crystallize extensively at 850 °C, yet may be used as viscous sealants with SOFC stacks operating at the low end of the OT range.
- Modified gallio-silicate and germano-silicate glasses approach the DOE target properties. New compositions may exhibit desirable crystallization behavior.
- The compositions within the statistical compositional design should offer more glasses for viscous sealing.

Future Work

- Crystallization behavior will be studied at intermediate temperatures within the SOFC OT range.
- Extensive testing in wet H_2 environments will be performed.
- Newly formulated glasses will be tested for compatibility with SOFC stack components.