Glass-Ceramic Seals for Solid Oxide Fuel Cells

Teng Zhang, Signo T. Reis and Richard K. Brow

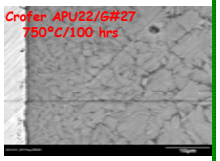
7th Annual SECA Workshop
September 12-14, 2006
Philadelphia, PA

Materials Science & Engineering Department
University of Missouri-Rolla
Rolla, MO 65409

UMR

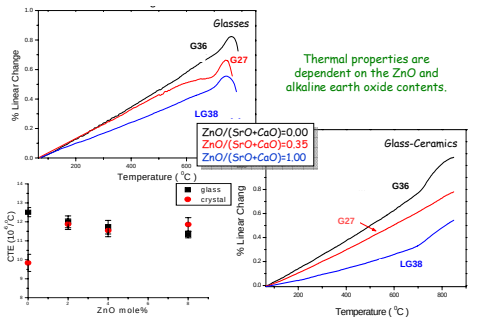
Goal: Develop stable sealing materials for SOFCs

- ZnO-modified alkaline earth invert silicates
  - Mixed CaO, SrO, ZnO (45-55 mole%)
    - BaO-free
- [O]/[Si]>3.3, SiO_2<45 mole%
- Minor oxides include Al_2O_3, B_2O_3, TiO_2



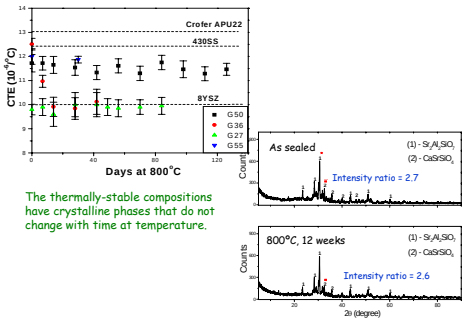
Property design targets:
- Seal/crystallized <900°C
- CTE-match to SOFC components
- Thermomechanically stable at >750°C
- Thermochemically stable in oxidizing and reducing conditions

Glass properties depend on composition



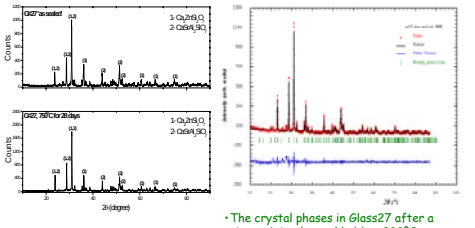
Thermal properties are dependent on the ZnO and alkaline earth oxide contents.

Certain glasses have good thermal stability



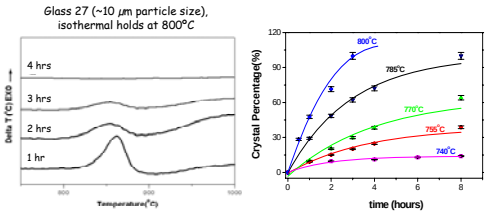
The thermally-stable compositions have crystalline phases that do not change with time at temperature.

We study the crystal phase distributions using Rietveld refinement



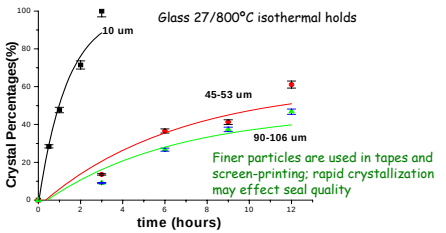
- The crystal phases in Glass27 after a six week isothermal hold at 800°C are:
  - $CaSrAl_2Si_2O_7$ (7.2 mole%)
  - $Ca_2ZnSi_2O_7$ (92.8 mole%)

We use DTA to characterize crystallization kinetics



Longer heat treatments leave less residual glass to crystallize on reheating

Crystallization kinetics are enhanced for finer particle sizes

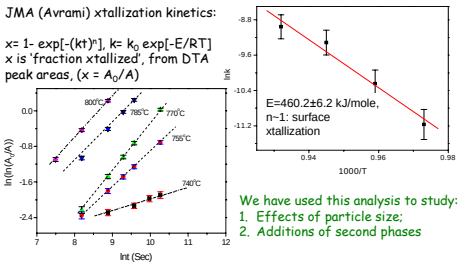


Finer particles are used in tapes and screen-printing; rapid crystallization may effect seal quality

DTA provides quantitative crystallization information

JMA (Avrami) xtallization kinetics:

x= 1- exp[-(kt)^n], k= k_0 exp[-E/RT]
x is 'fraction xtallized', from DTA peak areas, (x = A_0/A)



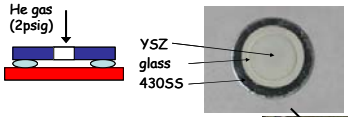
We have used this analysis to study:
1. Effects of particle size;
2. Additions of second phases

Crystallization kinetics are changed by either particle sizes or 'filler'

Glass sample	E (kJ/mole)	k_0(s^{-1})	n
~ 10μm	460.2±6.2	$3.8x10^{18}$	0.81±0.31
45-53μm	519.7±10.7	$3.7x10^{19}$	1.38±0.56
90-106μm	553.9±3.9	$1.6\ x10^{22}$	1.45±0.17
45-53μm with 10 vol % Ni	599.0±20.7	$3.1x10^{25}$	0.99±0.17
45-53μm with 10 vol % YSZ	597.4±46.0	$1.0x10^{25}$	0.74±0.14

Surface crystallization is the dominant mechanism.

Seal performance is being evaluated



- Glass tapes, 200 μm thick (PVB binder, 10 μm glass particles)
- Binder burn-out at 450°C (air)
- Sealed at 850-900°C (1-2 hours)
- Thermal cycle from 800°C
  - Hold 24 hours (forming gas or air)
  - -2°C/min to room temperature
  - Test for He-leak (2 hour pressure hold)

Summary of thermal cycling experiments

Sealing materials	Test Conditions	Number of Cycles	Notes
430SS/G50UMR/YSZ	800°C, 24 hours, air	31	Failed; glass prepared at UMR
430SS/G50MOSci /YSZ	800°C C, 24 hours, air	21	Failed; glass prepared by Commercial vendor
430SS/G50UMR/Nickel-YSZ	800°C, 24 hours, air	36	Broke during test; glass prepared at UMR
430SS/G50MOSci/Nickel-YSZ	800°C, 24 hours, air	35	Still on test; glass prepared by Commercial vendor
430SS/G50MoSci-Ag/Nickel-YSZ	800°C, 24 hours, air	2	Still on test; glass prepared by Commercial vendor
430SS/G50UMR/YSZ	800°C, 24 hours, wet forming gas	19	Still on test; glass prepared at UMR
430SS/G50UMR/Nickel-YSZ	800°C, 24 hours, wet forming gas	9	Still on test; glass prepared at UMR
430SS/G50MOSci/Nickel-YSZ	800°C, 24 hours, wet forming gas	12	Still on test; glass prepared by Commercial vendor

Current Research Efforts

- Hermetic tests at temperature
  - Inconel test manifold under construction;
- Scale-up studies of promising compositions
  - kilogram melts;
  - 'commercial' tape casting/ screen printing;
  - 100 mm x 100 mm cells
- Interfacial reactions under SOFC conditions;
  - With ferritic steels and Ni/YSZ anodes
- Glass property optimization
  - Viscosity characteristics

Acknowledgements

Many colleagues have contributed their expertise and advice to this project, including
- Xiao Dong Zhou, Harlan Anderson, Clarissa Vierrether, Chandra Ray and Jinbo Yang (UMR)
- Ron Loehman (Sandia National Labs),
- Matt Chou (PNNL)

*The financial support of the Department of Energy (grant number DE-FC26-04NT4221) is gratefully acknowledged- **Ayyakkannu Manivannan**, Program Manager.*