IV.A.22 Resilient Sealing Materials for Solid Oxide Fuel Cells

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Objectives

- Develop silicate-based glasses with requisite properties to be used for hermetic seals for solid oxide fuel cells (SOFCs).
- Evaluate thermo-mechanical and thermo-chemical properties of the glass-ceramics under SOFC operational conditions.
- Demonstrate hermeticity and materials compatibility of SOFC seals.

Accomplishments

- Formulated new alkaline earth silicate glass-ceramic compositions with requisite thermal properties, including sealing temperatures at or below 900ºC and coefficients of thermal expansion (CTE) in the range 11-12 ppm/ºC.
- Produced hermetic seals between interconnect alloys and SOFC components, including Y-stabilized zirconia (YSZ) electrolytes and Ni-YSZ anodes, that pass He-leak tests after at least 55 thermal cycles between 800ºC and room temperature.

Introduction

Reliable hermetic sealing technologies must be developed to achieve the high power densities possible for SOFC stacks. For the past decade, considerable effort has gone into the development of glasses and glass-ceramics that are suitable for these seals [1]. Compositions with the requisite thermal properties for seals have been developed (see, for example, reference [2] for a recent survey), but questions about long-term property stability, deleterious interfacial reactivity, and component volatility make the development of new, reliable sealing materials a priority.

Approach

The glasses developed at University of Missouri-Rolla (UMR) have relatively low silica contents (<45 mole%) with molecular-level structures that are much less connected than conventional silicate glasses, allowing the melts to readily flow at relatively low temperatures before crystallizing to form glass-ceramic phases with the desired thermal properties. Some compositions were designed to fully-crystallize to form rigid glass-ceramic seals, and others were designed to retain a significant fraction of a glassy phase after crystallization to allow viscous relaxation of thermal stresses.

Results

Nearly eighty glass compositions have been prepared and evaluated. Many of the compositions have the requisite thermal properties required for SOFC seals (e.g., CTE match to SOFC components and sealing temperatures at or below 900ºC) and have received closer examination for their suitability as potential sealing materials. Figure 1 shows how one compositional variation affects the CTE of crystallized sealing glasses. In this case, increasing the relative ZnO-content of the base glass decreases the CTE of the crystallized material, through the formation of lower expansion Zn-silicate phases, including Zn_2SiO_4.

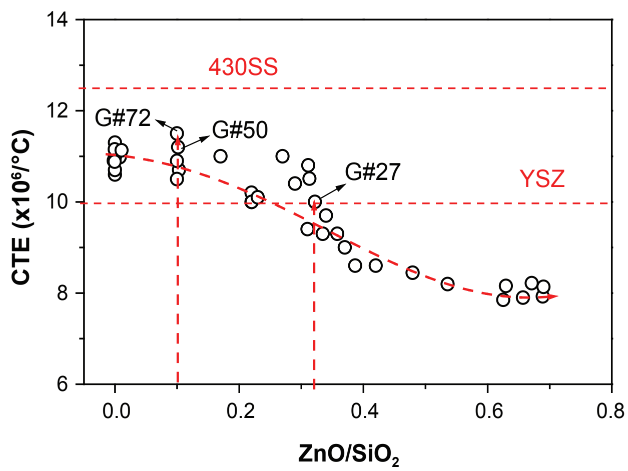

FIGURE 1. The effect of the ZnO/SiO_2 molar ratio on the CTE of crystallized "invert" silicate glass-ceramics. The CTE values for YSZ and 430SS are shown for comparison.

Compositions with relatively large ZnO contents, like G#27, produce glass-ceramics that have thermal expansion coefficients that are good matches to YSZ (~10ppm/°C), whereas compositions like G#50 or G#72, with a lower ZnO-content, have CTE values that are closer matches to 430SS.

An important consideration for long-term SOFC applications is the thermal stability of the CTE of the sealing material. Figure 2 shows the average CTE (between 200 and 700°C) for four crystallized sealing glasses as a function of time at 800ºC. Three of the compositions, G#27, G#50, and G#72 have relatively stable values of CTE, whereas G#36 shows significant decreases in CTE, particularly after the first two weeks on test. X-ray diffraction (XRD) analyses, shown elsewhere [1], indicate that glasses with stable CTEs exhibit no significant changes with time in their crystalline phase assemblages, whereas those materials with decreasing CTEs have crystalline compositions that change with time. For example, the decrease in CTE for G#36 results from the formation of a low expansion phase ($CaSiO_3$) with heat-treatment time. G#50 retains a relatively high CTE (11.4×10^{-6}/°C) after 112 days at 800°C (Figure 2). The XRD patterns collected from these samples reveal no discernible changes in the distributions of the crystalline phases, $(Ca,Sr)SiO_3$, $Sr_2Al_2SiO_7$ and $CaSrSiO_4$, over the course of the long-term heat treatments.

A series of simple seals have been fabricated using G#50 and 430 stainless steel, a possible SOFC interconnect material, and with either YSZ electrolytes or Ni/YSZ anode substrates. The seals were fabricated using glass tapes (PVB binder, 2.3 μm glass particles) fired in air to 850-900°C. These test samples were heated to 800°C at 2°C/minute in different atmospheres, held for 24 hours, then cooled to room temperature (-2°C/minute) where they were tested for hermeticity using helium gas at 2 psig. Samples that did not leak (hold 2 psig pressure for four hours) were reheated for another 800°C/24 hour heat treatment, and cycled back to room temperature for another hermeticity measurement. Table 1 summarizes the results of some of these tests. Post-mortem analyses of these test samples reveal good chemical compatibilities between the glasses and the various SOFC materials.

TABLE 1. Summary of thermal cycling/hermeticity tests on sealed components. All tests were done using helium at room temperature, following the thermal treatment indicated.

Sealing Materials	Test Conditions	Number of Cycles	Notes
430SS/ glass 50/YSZ	800°C, 24 hours, wet forming gas	31	Failed after 31 cycles due to the break of YSZ
430SS/glass 50/YSZ	800°C, 24 hours, air	60	Failed after 60 cycles due to the break of YSZ
430SS/glass 50/Ni-YSZ	800°C, 24 hours, air	30	Failed after 30 cycles due to the break of Ni-YSZ
430SS/glass 50/Ni-YSZ	800°C, 24 hours, wet forming gas	36	Failed after 60 cycles due to the break of Ni-YSZ

The seal failures after 30+ thermal cycles may be related to defects in the glass seals related to the rapid crystallization of the glass powders used to fabricate the tapes. The effects of glass particle size on the crystallization kinetics have been studied using differential thermal analytical techniques developed at UMR [3]. Figure 3 summarizes those effects. Particles that have diameters of ~10 μm fully crystallize in less

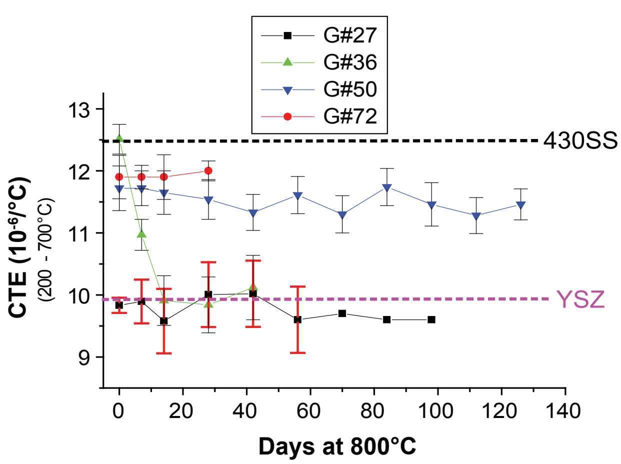

FIGURE 2. CTE data for crystallized glasses #27, and #50 held at 800°C in air for up to 120 days. The 'as received' CTE values for YSZ and 430SS are shown for comparison.

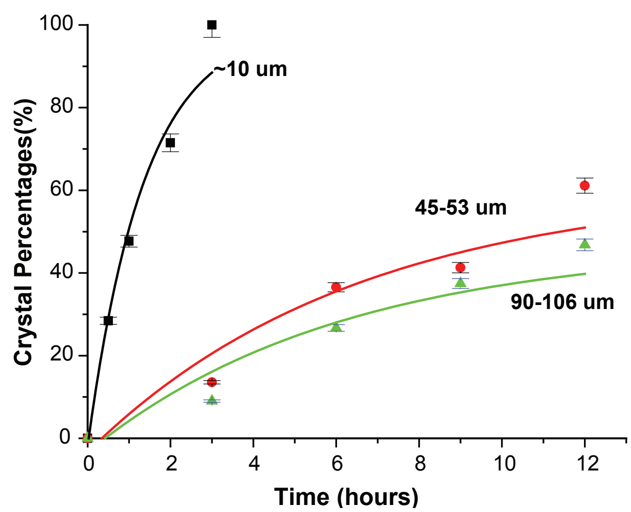

FIGURE 3. Crystallization Kinetics for Glass#27 with Different Particle Sizes at 800°C in Air, as Determined by Differential Thermal Analysis

than two hours, whereas larger particles crystallize much more slowly. These results are typical for glasses that crystallize predominantly from their surfaces, and this indicates that care must be taken in developing sealing cycles that account for this behavior.

Conclusions and Future Directions

- Promising sealing glass compositions have been developed and evaluated.
- Hermetic seals have been fabricated and tested at room temperature after thermal treatments at 750-800°C, in oxidizing and reducing environments.
- The effects of ZnO on the thermo-mechanical and thermo-chemical stability of new glass systems under SOFC operational conditions are under investigation. In particular, we wish to understand what effect (if any) ZnO has on the formation of deleterious interfacial chromate phases.
- The influence of the B_2O_3 content on the residual glass of glass-ceramic under SOFC conditions is under investigation. The presence of residual glass could be potentially positive since the glass relaxation would help relieve some stresses that would otherwise develop because of CTE-mismatches among the cell materials.

Special Recognitions & Awards/Patents Issued

1. R.K. Brow, S. T. Reis, G. M. Benson, "Glass and glass-ceramics for solid oxide fuel cell hermetic seals," US Patent Application, UM Disclosure No. 04UMR023 entitled "Glass and Glass-Ceramic Sealant Compositions," filed January 2005.

FY 2007 Publications/Presentations

1. C. S. Ray, T. Zhang, S. T. Reis, and R. K. Brow, "Determining Kinetic Parameters for Isothermal Crystallization of Glasses," *Journal of the American Ceramic Society*, **90**[3], 769 – 773 (2007).

2. S. T. Reis*, Teng Zhang, and R. K. Brow, "Development of thermochemically stable sealing glasses for solid oxide fuel cells" 4th International Symposium on Solid Oxide Fuel Cells: Materials and Technology, Daytona Beach, Florida, January 22–27, 2007.

3. S.T. Reis, R.K. Brow, "Designing Sealing Glasses for Solid Oxide Fuel Cells," Journal of Materials Engineering and Performance, **15** 410 – 413 (2006).

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1. S.T. Reis, R.K. Brow, "Designing Sealing Glasses for Solid Oxide Fuel Cells," Journal of Materials Engineering and Performance, **15** 410 – 413 (2006).

2. N. Q. Minh, "Ceramic fuel cells", *J. Am. Ceram. Soc.*, **76,** 563 – 588 (1993).

3. T. Zhang, C.S. Ray, S.T.Reis, and R.K. Brow, "Isothermal Crystallization of Solid Oxide Fuel Cell Sealing glass by Differential Thermal Analysis," J. Amer. Ceram. Soc. (in preparation).