IV.A.21 Innovative Seals for Solid Oxide Fuel Cells

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Objectives

- Further develop the self-healing glasses with long-term durability through compositional modifications and seal testing.
- Develop toughened glasses by fiber and filler reinforcements for enhancing toughness.
- Characterize long-term stability of the self-healing and toughened glasses through ex-situ and *in situ* seal testing. Work with the Solid State Energy Conversion Alliance (SECA) industry teams to help transition some of the technologies developed in Phase II through collaborative efforts.

Accomplishments

- Self-healing glasses were developed for making seals for solid oxide fuel cells (SOFCs). The seals were tested for leakage at 800°C and demonstrated self-healing ability for tests performed for 3,000 hours and 300 thermal cycles in a variety of test environments typical of a SOFC.
- Self-healing glasses have shown stability against crystallization in seal tests for 3,000 hours, and in thermal annealing tests in moist fuel and air at 800°C for 1,500 and 2,500 hours, respectively.
- *In situ* X-ray diffraction of glasses at temperatures from 25°C to 800°C displayed no crystal phases in tests performed at the National Energy Technology Laboratory.
- The weight loss experiments performed in moist fuel environment at 800°C for 500 hours yielded insignificant weight loss. A weight loss of 0.53% over 40,000 hours is calculated from the extrapolated data.
- These results show great promise towards meeting SECA goals for seals for SOFCs.

Introduction

A functioning SOFC requires seals that prevent electrode leakage and internal gas manifold leakage if internal gas manifolds are utilized. The seals must prevent the mixing of fuel and oxidant streams as well as prevent reactant escape to the surrounding environment. The seal material must be electrically isolating as well as mechanically and chemically stable in contact with interfacing cell components in humid duel reducing and oxidizing conditions. Particularly important is the ability to seal between metallic and ceramic components with differing coefficients of thermal expansion (CTE), and to do so while exposed to temperature transients over a range from room temperature up to SOFC operating temperature (800ºC). This project is developing innovative sealing concepts for both short- and long-term functionality of SOFCs, addressing the aforementioned issues.

Approach

A novel concept of *in situ* crack healing by glasses was pursued in Phase I of the project and is continued in Phase II of the project. The fundamental idea underlying this concept is based on the fact that a glass with suitable low viscosity can heal cracks created by thermal expansion mismatch between materials that are being joined by a glass seal in a SOFC. The functionality of this innovative sealing approach based on *in situ* crack healing by a glass was demonstrated and quantified. Toughening and strengthening of the glass by fibers/particulates was pursued to minimize or eliminate bulk cracking of the seals. These concepts are pursued further in Phase II to address sealing capabilities and durability issues related to a functioning seal for a SOFC. In particular, exposure of the self-healing glasses over an extended time period is being pursued to determine long-term stability of the self-healing and reinforced glasses when exposed to environments simulating fuel and air at 800°C. These results are expected to provide inputs towards meeting SECA goals of 40,000 hours of seal life for a SOFC.

Results

The object of work performed for this project is to select glasses that show self-healing behavior and long-term stability in SOFC environments. Some of the glasses from Phase I are being used and modified by changes to their composition to achieve stability over long times in SOFC conditions. The purpose of the compositional modifications is also to achieve optimum expansion behavior in contact with Crofer and Ni-YSZ (nickel-yttria-stabilized zirconia), glass transition and softening temperatures over a range of temperatures between 600 and 800°C without adversely affecting stability. Fillers are being used to modify glass properties to achieve some of these goals as well. The stability of the glasses selected above is determined by annealing glass samples in air and simulated fuel (Ar-4%H_2-6%H_2O) environments at 800°C; the glasses have accumulated >1,500 hours in these tests. The weight change is monitored to observe any loss, which will be related to changes in the composition of the glass by techniques such as energy-dispersive X-ray (EDAX), secondary ion mass spectrometry (SIMS), or electron spectroscopy for chemical analysis (ESCA). Species being lost will be identified by mass spectroscopy and other analytical approaches.

The weight loss for a self-healing glass annealed at 800°C in humid fuel environment consisting of Ar-4%H_2-6%H_2O over a time period of 500 hours was measured. From the preliminary data on weight loss, a total loss in weight of the glass of 0.53% in 40,000 hours is estimated, which is insignificant. A new set of samples was prepared, and weight loss measurements are continuing for up to 500 hours. Subsequent to this, the samples will be characterized by EDAX, SIMS, and X-ray photoelectron spectroscopy (XPS) for surface and depth profiles in order to identify species responsible for the small weight loss observed.

Glass samples alone and those containing 5-10% (wt) YSZ powder were annealed in air and Ar-4%H_2-6%H_2O atmospheres at 800°C over a range of times up to 1,500 hours to determine long-term stability, crystallization behavior, and weight loss. Figure 1 shows

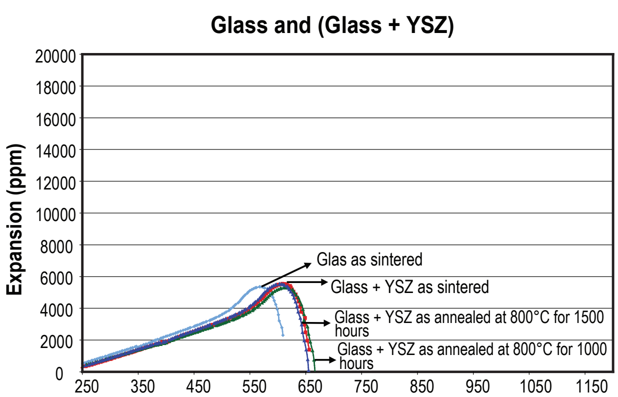

FIGURE 1. Effect of Annealing at 800°C in Ar-4%H_2-6% H_2O Moist Fuel Environment on the Thermal Expansion Behavior of the Glass Containing 5% YSZ Filler Annealed for 1500 Hours

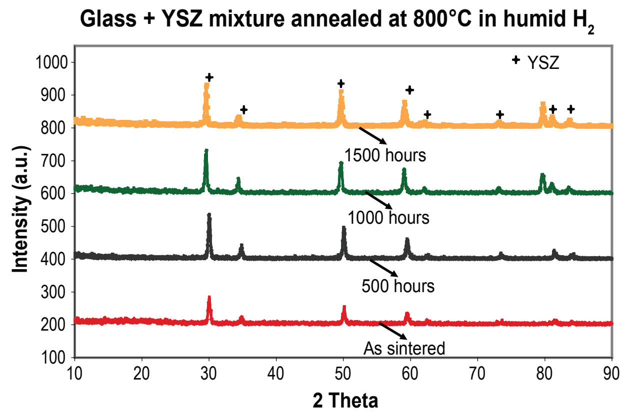

FIGURE 2. Effect of annealing at 800°C in Ar-4%H_2-6% H_2O moist fuel environment on the X-ray diffraction behavior of the glass containing 5% YSZ filler annealed for 1,500 hours. Note a lack of crystallization of the glass-5%YSZ upon annealing for 1,500 hours.

an example of the effect of annealing in Ar-4%H_2-6%H_2O atmosphere on the expansion behavior of a glass containing 5% (by weight) YSZ powder as a filler. The data on the pure glass is also shown. The addition of 5% YSZ in the glass increased the glass transition and softening temperatures. However, annealing of the glass-YSZ mixture for 1,500 hours in moist fuel did not change the expansion behavior. The X-ray diffraction patterns from the glass-5% YSZ taken at different times of annealing are shown in Figure 2, which indicates that the glass did not show any evidence of crystallization due to the 5% YSZ over the annealing time of 1,500 hours at 800°C in moist air. This test is being continued to accumulate more annealing time to assess long-term stability of the glass and glass with YSZ filler. Towards this goal, glass and glass containing YSZ as fillers were also prepared and annealed in air to assess any changes in crystallization behavior over a longer period of time because of the annealing in air. In addition, electrical resistivity of the glass under direct current applied electric field is being measured between 25 and 800°C.

A sample of the glass was also prepared for high-temperature X-ray diffraction studies at the National Energy Technology Laboratory in collaboration with Dr. Chris Johnson. The glass sample was run at 400, 500, 600, 700, and 800°C in a high temperature diffractometer. It was heated in air between 25 and 800°C in steps and held at 400, 600, 700, and 800°C for 1 hour each, and the X-ray pattern was taken at each temperature. The X-ray patterns were also collected while cooling from 800°C to 25°C by holding for 1 hour each at 700, 600, 400, and 25°C. The results show no evidence of crystalline phases in the high temperature X-ray patterns. These results confirm stability of the glass at high temperature against crystallization.

These results on stability of the self-healing glass with and without fillers show excellent stability over extended time periods of annealing and are quite promising for developing seals to meet the SECA goals for SOFCs.

Conclusions and Future Directions

- Seals incorporating self-healing glasses were fabricated. The effect of up to ~300 thermal cycles between 25 and 800°C and ~3,000 hours at 800°C on hermeticity of the seals was demonstrated. Self-healing behaviors of the leaking seals were also demonstrated. These results are important for achieving SECA goals for SOFC sealing systems.
- Long-term stability of the self-healing glasses with and without fillers was studied. The glasses demonstrated stability against crystallization in annealing tests performed over 1,500 hours in fuel and air environments at 800°C.
- Insignificant weight loss of 0.53% over 40,000 hours was estimated for self-healing glasses when annealed in moist fuel at 800°C over 500 hours.
- High temperature X-ray diffraction runs on self-healing glasses to 800°C showed no evidence of crystallization.
- Plans are to further pursue long-term stability of the self-healing glasses, reinforced glasses, and seals made thereof to further demonstrate long-term performance, stability, and applicability of the self-healing glass seals to SOFCs.

FY 2007 Publications/Presentations

1. Program Quarterly Reports Between July 2006 and June 2007.

2. Phase-I Annual Report (July, 2006).

3. R.N. Singh, "High-Temperature Seals for Solid Oxide Fuel Cells (SOFC)," J. Mater. Eng. Per. 15[4] 422-426 (2006).

4. R.N. Singh and S.S. Parihar, "Performance of Self-Healing Seals for Solid Oxide Fuel Cells," Ceram Eng. Sci. Proc. 27(2-8), (2006).

5. R.N. Singh and S.S. Parihar, "Performance of Self-Healing Seals for Solid Oxide Fuel Cells," 30th Annual Cocoa Beach Conference and Exposition on Composites, Advanced Ceramic Materials, and Structures, January 23–26, Cocoa Beach, FL (2006).

6. R.N. Singh, "Approaches to High Temperature Seals for Solid Oxide Fuel Cells," **Invited Presentation**, MS&T Conference, October 15-19, Cincinnati, OH (2006).

7. S.S. Parihar and R.N. Singh, "Crack Healing Behavior of Glasses for Solid Oxide Fuel Cell," **Invited Presentation**, MS&T Conference, October 15–19, Cincinnati, OH (2006).