Innovative Self-Healing Seals for Solid Oxide Fuel Cells (SOFC)

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Executive Summary

Solid oxide fuel cell (SOFC) technology is critical to several national initiatives. Solid State Energy Conversion Alliance (SECA) addresses the technology needs through its comprehensive programs on SOFC. A reliable and cost-effective seal that works at high temperatures is essential to the long-term performance of the SOFC for 40,000 hours at 800°C. Consequently, seals remain an area of highest priority for the SECA program and its industry teams. An innovative concept based on self-healing glasses was advanced and successfully demonstrated through seal tests for 3000 hours and 300 thermal cycles to minimize internal stresses under both steady state and thermal transients for making reliable seals for the SECA program. The self-healing concept requires glasses with low viscosity at the SOFC operating temperature of 800°C but this requirement may lead to excessive flow of the glass in areas forming the seal. To address this challenge, a modification to glass properties by addition of particulate fillers is pursued in the project. The underlying idea is that a non-reactive ceramic particulate filler is expected to form glass-ceramic composite and increase the seal viscosity thereby increasing the creep resistance of the glass-composite seals under load. The objectives of the program are to select appropriate filler materials for making glass-composite, fabricate glass-composites, measure thermal expansion behaviors, and determine stability of the glass-composites in air and fuel environments of a SOFC. Self-healing glass-YSZ composites are further developed and tested over a longer time periods under conditions typical of the SOFCs to validate the long-term stability up to 2000 hours. The new concepts of glass-composite seals, developed and nurtured in this program, are expected to be cost-effective as these are based on conventional processing approaches and use of the inexpensive materials.

Motivation and Objectives

Solid oxide fuel cell (SOFC) technology is critical to National Energy Security and Energy Independence, and at the same time to protect our environment [1, 2]. SECA (Solid State Energy Conversion Alliance) initiatives address these needs through its comprehensive programs [1, 2]. Among the many fuel cell technologies, the SOFC functions at much higher temperatures of 650-900° C and offers unique advantages of utilization of the more abundant fossil-derived fuels (hydrocarbons) as well as hydrogen. Additionally, much higher efficiencies than the low temperature fuel cell are possible for the SOFC when integrated with the combined cycle utilizing the waste heat. Reliable seals are essential to the long-term performance, cost, and reliability of the SOFC because a leaky seal will degrade cell performance and lead to wastage of fuels in an operating fuel cell stack. Consequently, the SECA program has recognized the Seals for SOFC as an important technology area that requires priority attention.

A variety of seals such as metal-metal, metal-ceramic, and ceramic-ceramic are required for a functioning SOFC as shown in Fig. 1 [3-19]. These seals must function at high

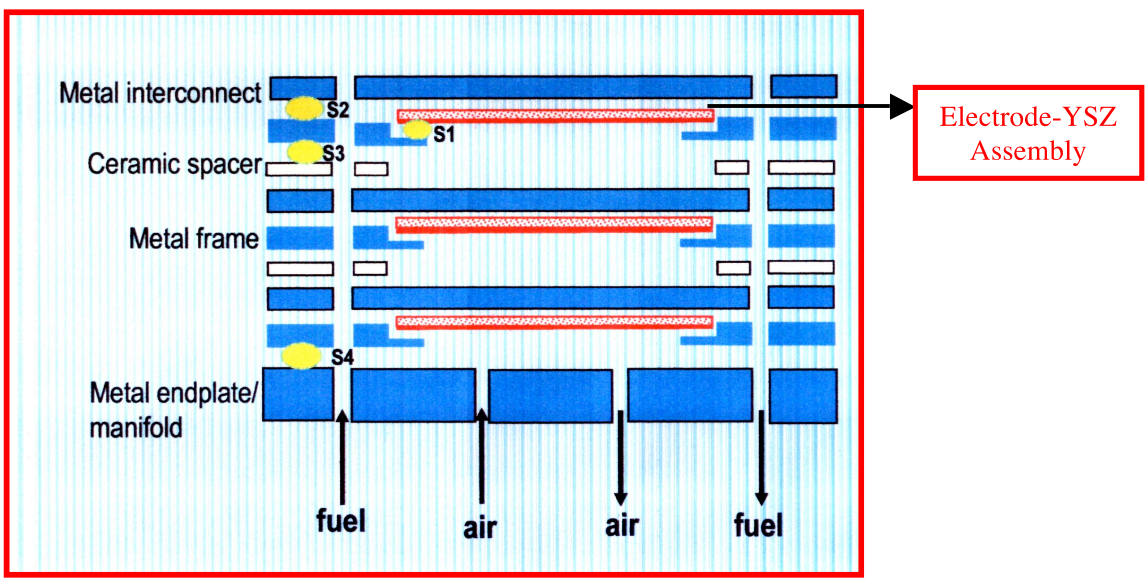

Fig. 1 . Schematic showing a stack of SOFCs and possible seals (S1, S2 etc) and their locations (adapted from Chou and Stevenson (PNNL) [3].

temperatures between 600-900°C and in oxidizing and reducing environments of the fuels and air. Among the different type of seals the metal-metal seals can be readily fabricated using welding, soldering, and brazing techniques. This cannot be said for the metal-ceramic and ceramic-ceramic seals because the brittle nature of ceramics/glasses can lead to fracture and loss of seal functionality. Consequently, any seals involving ceramics/glasses require a significant attention and technology development for reliable SOFC operation. This project was initiated to primarily address the needs for ceramic-metal and ceramic-ceramic seals for SOFC.

A novel concept of *in situ* crack healing by glasses was advanced, developed, and used to make seals in the previous funding cycle of the SECA program. The fundamental idea underlying this concept is based on the fact that a glass with suitable thermophysical property and viscosity can heal cracks created because of the 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 has been successfully demonstrated and quantified. A number of glasses and glass ceramics were selected for demonstration of the self-healing behavior and potential for making seals that display self-healing response. Glasses were fabricated and characterized to advance this concept and seal testing was done to demonstrate in situ self-repair capability of the glass seals. Seal tests displayed excellent seal performance for 3000 hours and 300 thermal cycles, including in situ self-repair of cracked/leaking seals.

Significant Accomplishments

Introduction:

The self-healing concept requires glasses with low viscosity at the SOFC operating temperature of 800°C but this requirement may lead to excessive flow of the glass in areas forming the seal. To address this challenge, a modification to glass properties such as creep via addition of particulate fillers was pursued in the project. The underlying idea is that non-reactive ceramic particulate filler is expected to form glass-ceramic composite and increase the seal viscosity thereby increasing the creep resistance of the glass-composite seals under load. In addition, the incorporation of an appropriate filler can affect the glass transition and softening temperatures, and coefficient of thermal expansion of the glass-ceramics thereby providing additional flexibility for developing sealing glasses with the optimum expansion mismatch among materials forming the seal thereby reducing mismatch stresses and improving seal reliability. This section summarizes progress made towards advancing this concept and meeting the goals of the program.

The overall program was divided into tasks and subtasks and the results obtained are described and discussed below.

Task 1: Project Management Planning and Reporting

Task 2: Composite Seal Development
 Subtask 2.1: *Materials Selection and Fabrication of Composite Glasses*
 Subtask 2.2: *Properties and Stability of the Composite Glasses*

Task 3: Long-Term Composite Seal Development

The remaining portion of this section describes progress made in achieving the program goals through each of these tasks.

Task 1: Project Management Planning and Reporting

The University of Cincinnati has managed and directed the project in accordance with the Project Management Plan (PMP) to meet all technical, schedule and budget objectives and requirements.

Task 2: Composite Seal Development

As mentioned earlier, the self-healing sealing glass concept requires glasses with low viscosity at the SOFC operating temperature of 800°C but this requirement may lead to excessive flow of the glass in areas forming the seal. To address this challenge, a modification to glass properties such as creep via addition of particulate fillers was pursued in the project because the incorporation of an appropriate filler can affect the glass transition and softening temperatures thereby reducing the flow of glass. In addition, the coefficient of thermal expansion of the glass-ceramics will be affected thereby providing additional flexibility for developing sealing glasses with the optimum expansion mismatch among materials forming the seal thereby reducing mismatch stresses and improving seal reliability. This section summarizes progress made towards advancing this concept.

Subtask 2.1: *Materials Selection and Fabrication of Composite Glasses*

A filler phase is required for sealing glasses as a part of this activity. The filler phase should be oxidation resistant at 800°C, strong, and have expansion behavior close to the sealing glass. Three types of fillers i.e. Al_2O_3, YSZ, and MgO were selected for the initial screening effort for the program because these ceramics have expansion close to or higher than the glass and are electrical insulators. Al_2O_3 and YSZ have expansion slightly smaller than the glass and MgO has higher value than the glass. Samples of glass-composites containing 30% by weight of Al_2O_3, YSZ, or MgO powders were fabricated using tape casting, lamination, and sintering to make dense glass-ceramic composites. The composites were then characterized for density, coefficient of thermal expansion between 25-800°C, stability in air and fuel environments for 2000 hours and crystallization by x-ray diffraction as described in subtask 2.2.

These results suggest that the best filler phase for further studies was YSZ because MgO reacted with the glass and Al_2O_3 produces low CTE. Preliminary data from glass-alumina composite also suggested reaction of alumina with the glass leading to formation of aluminum silicate. From these results YSZ is down-selected for further studies. Composites of glass-YSZ containing 10-30% YSZ were prepared for further characterization and CTE measurements.

Subtask 2.2: *Properties and Stability of the Composite Glasses*

Density of the composite was measured after processing. Glass-30% Al_2O_3 composite was 98% dense, glass-30% MgO composite was 99.5% dense, and glass-30% YSZ composite was 99% dense. Thermophysical (expansion) behavior of each of these composites was measured to determine the role of particulate addition on select properties as described below.

Glass-Alumina Composites:

The data for the glass and glass-30% Al_2O_3 composite is shown in Fig. 2. It shows that the coefficient of thermal expansion decreased to 8.8-9.8 ppm/°C because of the addition of 30% alumina. In addition, the glass transition and softening temperatures increased for the composite. Both of these responses are as expected because the coefficient of thermal expansion of alumina is lower than the glass and addition of particulate to the glass is expected to increase viscosity and consequently the glass transition and softening temperatures. X-ray diffraction from glass-alumina composite is shown in Fig. 3 and clearly indicated reaction of glass with alumina and formation of the orthoclase phase. Therefore, alumina based glass composites are not expected to remain stable with the self-healing glass as a function of time leading to progressive crystallization. This behavior in affect will diminish self-healing ability of the glass. As a consequence glass-alumina composites were not down-selected and pursued any further in this program.

Glass-Magnesia Composites:

Thermophysical (expansion) behaviors of the glass and glass-30% MgO composite are measured and shown in Fig. 4. It shows that the coefficient of thermal expansion increased as a result of the MgO addition, which is expected behavior because CTE of MgO is much higher than the

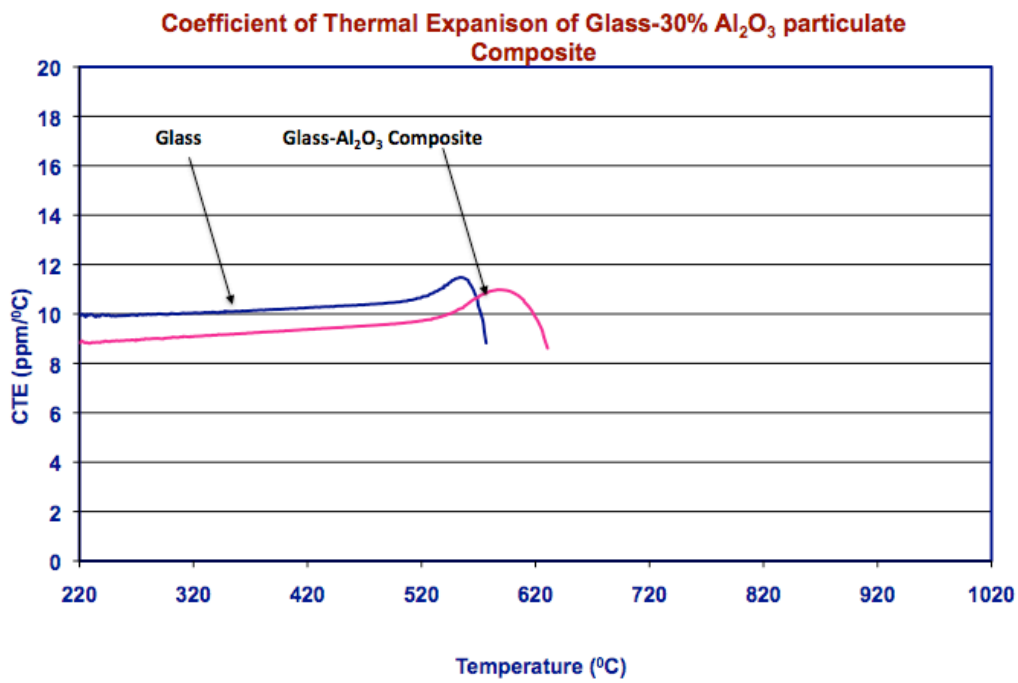

Fig. 2. Coefficient of thermal expansion of a glass and glass-30% Al_2O_3 composite in the as fabricated state.

glass. However, the glass transition and softening behaviors show a significant change. In fact the data in Fig. 5 shows two humps in the CTE behavior. One around 600°C and another around 850° C. This behavior is as a result of reaction of MgO with glass and the x-ray diffraction data indicated formation of the enstatite ($MgSiO_3$) and fosterite (Mg_2SiO_4) phases as shown in Fig. 5. A significant amount of these crystalline phases are not desirable for self-healing behavior. As a result no further studies on glass-MgO composite in this program was performed and glass-MgO composite was not down-selected as a consequence.

Glass-YSZ Composites:

The results for glass-30% YSZ composite are shown in Fig. 6. The CTE of glass-YSZ composite is lower than the glass, as expected, and the glass transition and softening temperatures increased with YSZ addition. The glass softening temperature for the glass-30%YSZ composite is ~700° C, which is significantly higher than the value of 570°C for the glass alone. In addition there was no crystallization of glass as shown later, which is desirable for self-healing behavior.

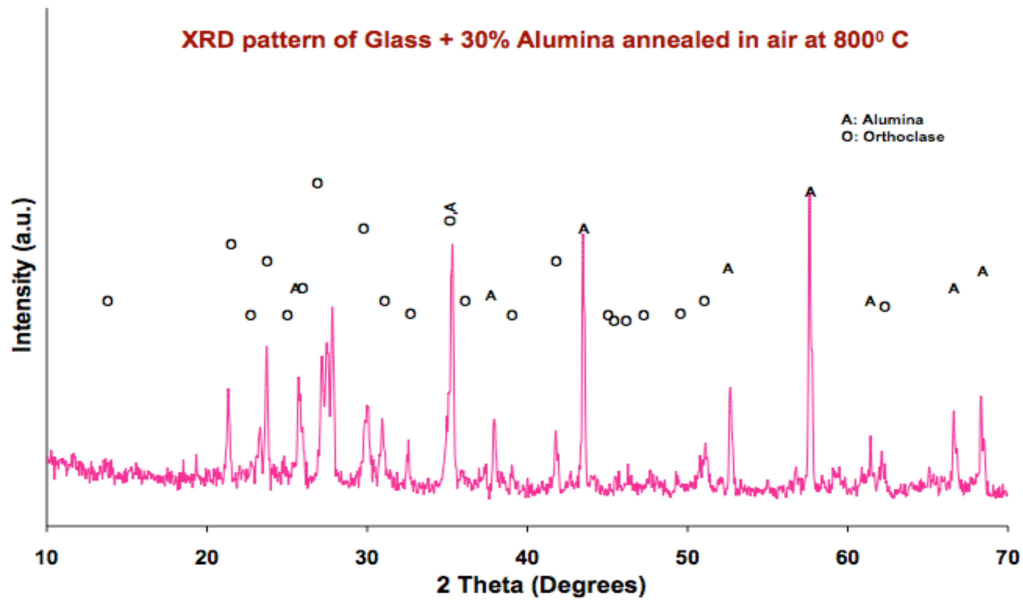

Fig. 3. X-ray diffraction from glass-30% Al_2O_3 composite after annealing at 800°C showing formation of orthosilicate.

These results suggest that the best filler phase for further studies is YSZ because MgO and Al_2O_3 fillers reacted with the glass and Al_2O_3 also produced low CTE. From these results YSZ was down-selected for further studies as described below.

Processing of Glass-YSZ Composites and Thermal Stability in SOFC Environments:

Composites of glass-YSZ containing 10, 20, and 30% YSZ were prepared for further characterization and CTE measurements. These composites were placed on YSZ plate and annealed in air and in moist fuel environments for up to 2000 hours at 800°C to demonstrate coefficient of thermal expansion and stability as a function of time. In addition, crystallization behavior upon annealing was evaluated by x-ray diffraction.

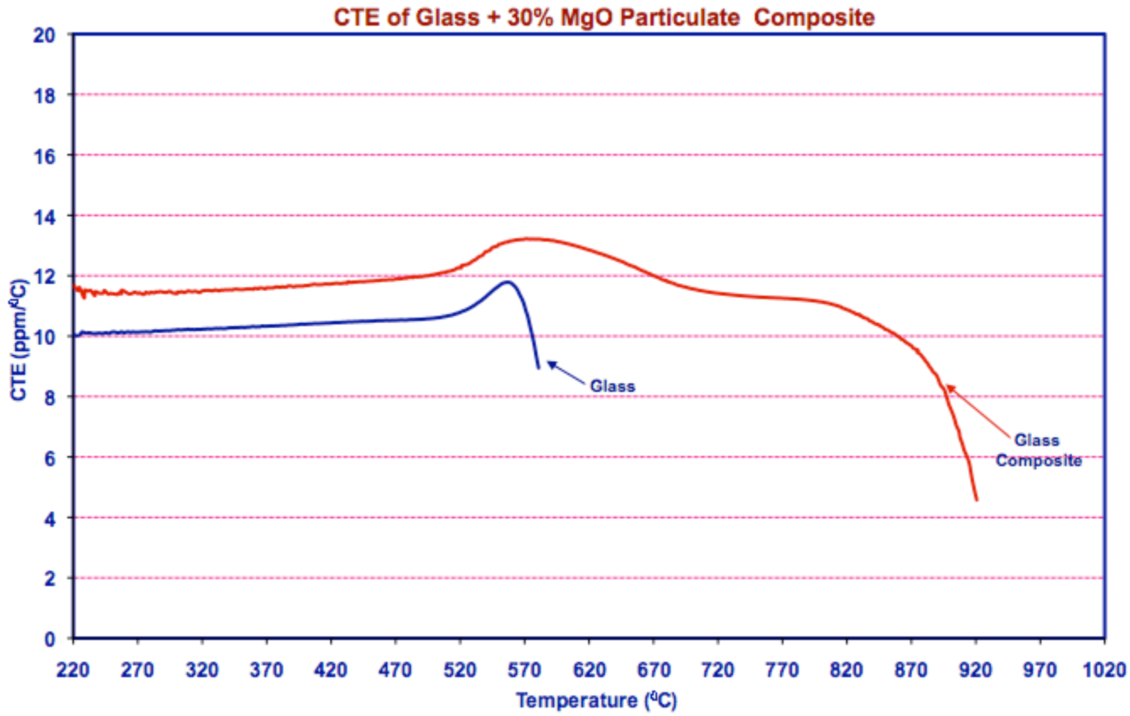

Fig. 4. Coefficient of thermal expansion of a glass and glass-30% MgO composite in the as fabricated state.

The coefficient of thermal expansion of glass-YSZ composites were measured after processing as shown in Fig. 7. It shows that the coefficient of thermal expansion decreased as a result of the YSZ addition, which is expected behavior because CTE of YSZ is lower than the glass. The glass transition and softening temperatures show a significant change because of the addition of YSZ. Both increased upon YSZ addition. In particular the softening temperature increased from ~560°C to 750°C with 30% YSZ addition. This is very promising because YSZ addition should provide superior load-carrying capability for the glass-composite seal. The coefficient of thermal expansion decreased from 10.4 to 9.3 ppm/°C upon addition of 30% YSZ to the glass. An optimum level of YSZ in a glass can be determined from sealing ability and the overall requirement of resistance to deformation of composite seal under load.

The glass-YSZ (30%) composites was placed on YSZ plate and annealed in flowing air and in moist fuel (Ar-4% H_2-6% H_2O) environments for up to 2000 hours at 800°C to demonstrate stability. In addition, crystallization behavior upon annealing was evaluated by x-ray diffraction along with the CTE data.

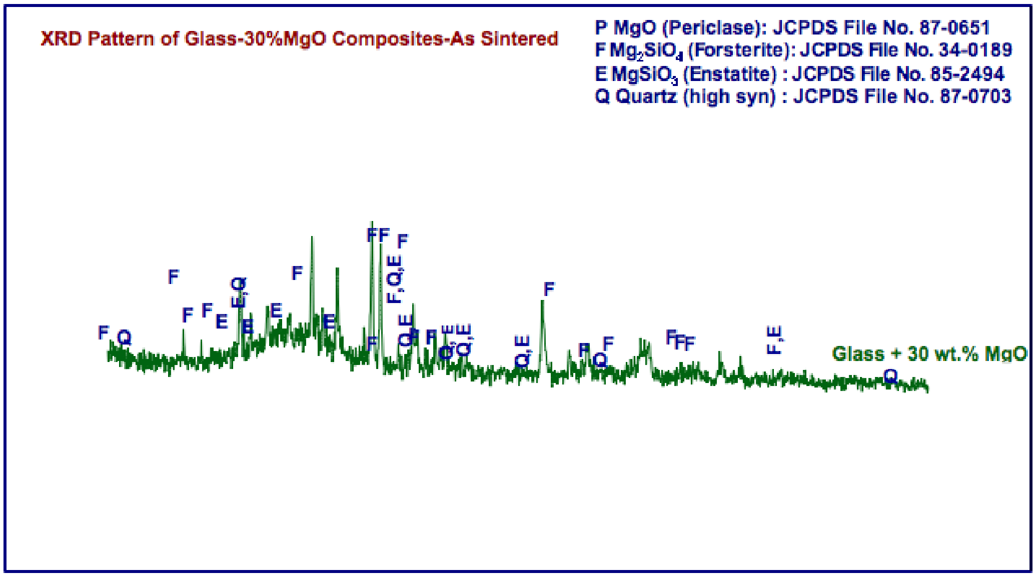

Fig. 5. X-ray diffraction from glass-30% MgO composite showing formation of magnesium silicate phases (enstatite and forsterite).

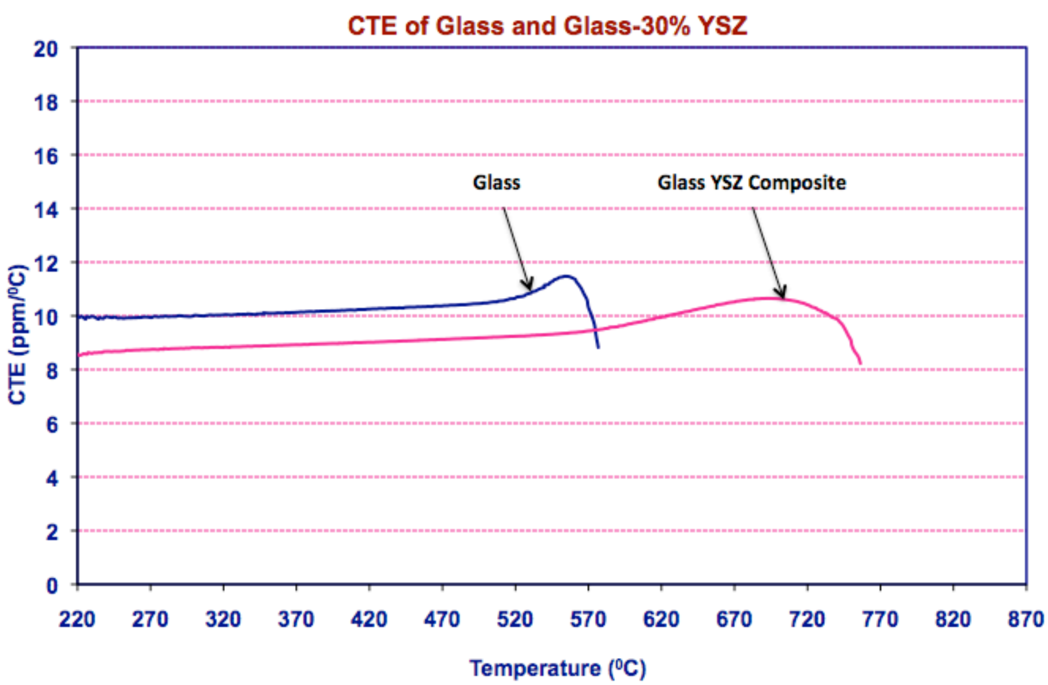

Fig. 6. Coefficient of thermal expansion of a glass and glass-30% YSZ composite in the as fabricated state.

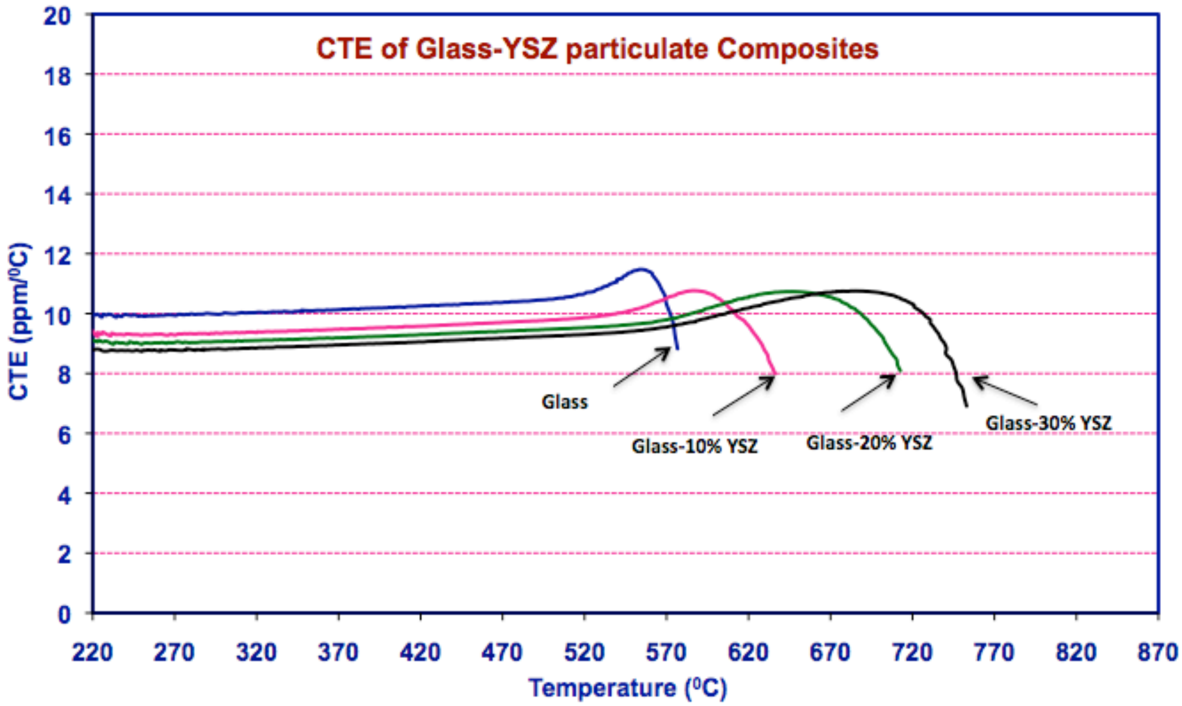

Fig. 7. Coefficient of thermal expansion of glass-YSZ composites in the as fabricated state.

Figure 8 shows the effect of annealing on the stability of glass-YSZ (30%) composite after annealing in air at 800°C for 2000 hours. There is an insignificant change in the coefficient of thermal expansion from the as-sintered state indicating excellent stability of the glass-YSZ composite in maintaining the thermophysical properties. There are also no changes in either the glass transition or the softening temperature for the glass-YSZ composite. Figure 9 shows similar data for glass-30% YSZ composite sample annealed in a fuel environment of a SOFC at 800°C over 2000 hours. There is also an insignificant change in the CTE values from the as-sintered state indicating stability of the glass-YSZ composites in fuel environment as well. In order to further confirm stability of the glass-YSZ composite against crystallization, x-ray diffraction data were collected in the as-sintered state and after annealing at 800°C for 2000 hours as sown in Fig. 10. The glass shows amorphous nature and all other crystalline peaks in the as-sintered state and after annealing are from YSZ filler phase. These x-ray results further confirm that the glass-YSZ composite is stable against crystallization for 2000 hours of exposure at 800°C.

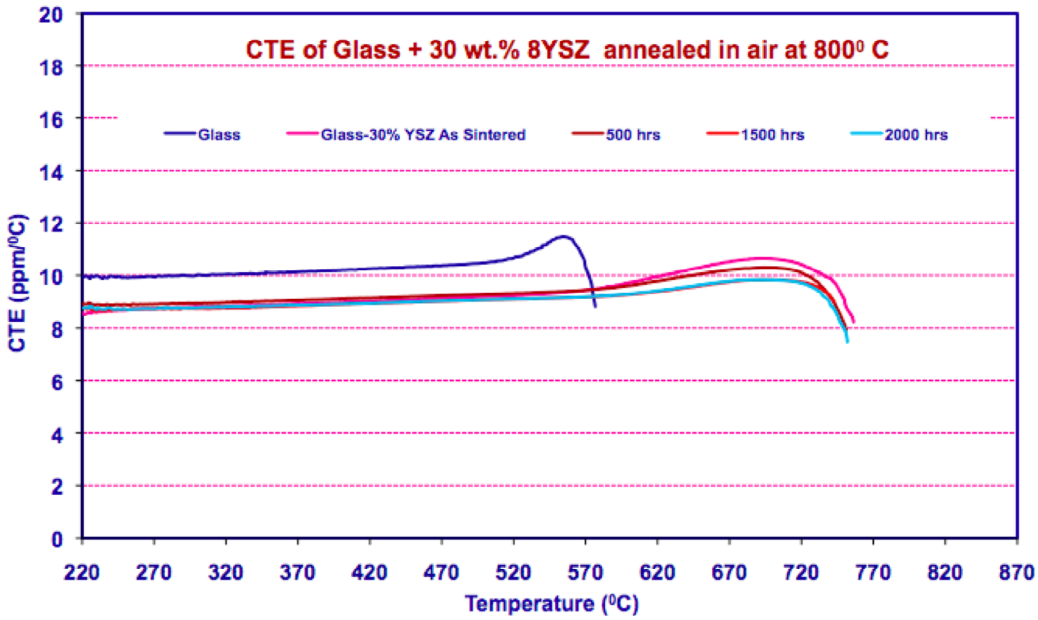

Fig. 8. Effect of annealing in air at 800°C on the coefficient of thermal expansion of glass-30%YSZ composites.

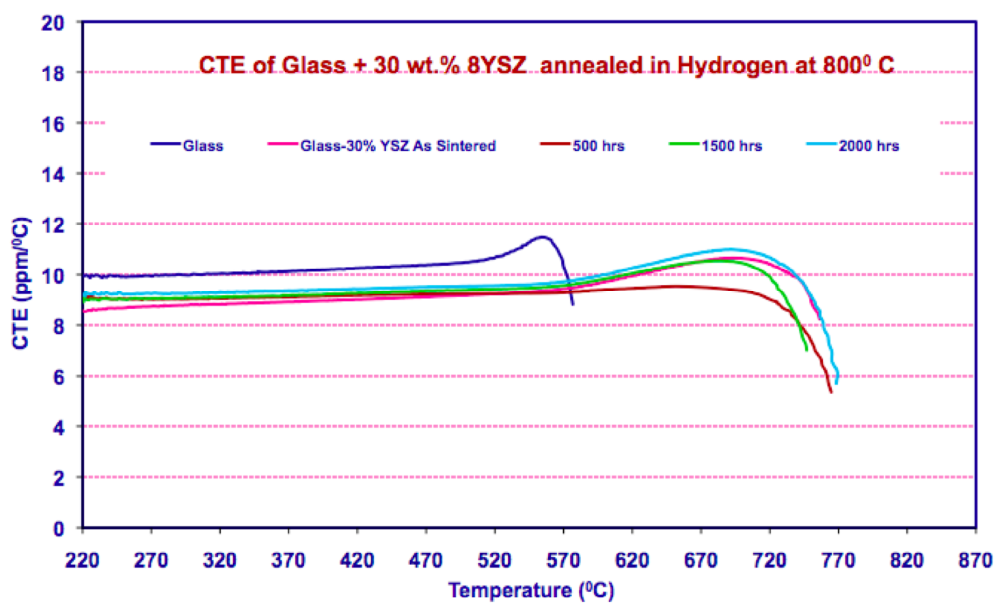

Fig. 9. Effect of annealing in fuel (Ar-4% H_2-6% H_2O) environment at 800°C on the coefficient of thermal expansion of glass-30%YSZ composites.

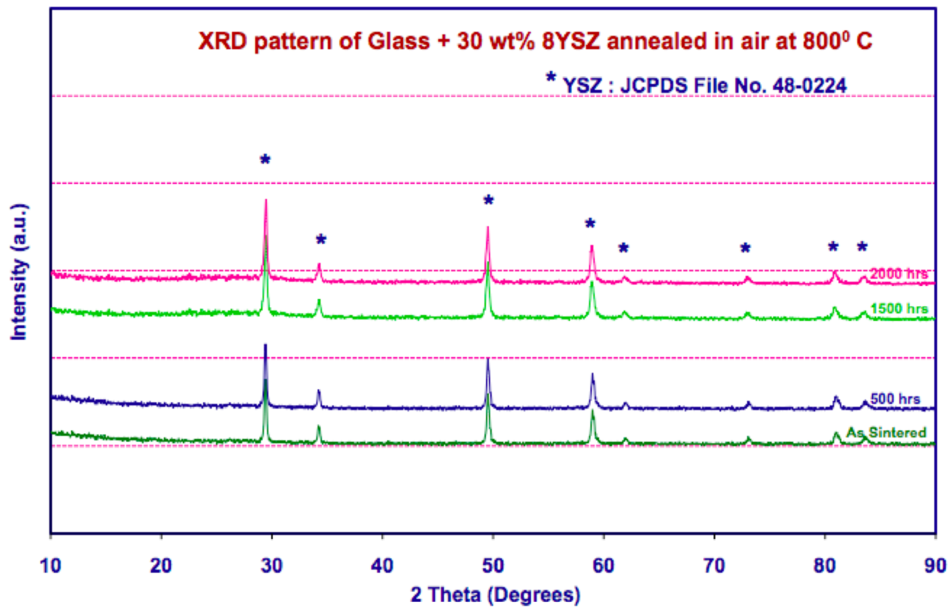

Fig. 10. X-ray diffraction from glass-30% YSZ composite showing no new phase formation upon annealing at 800°C for 2000 hours.

Stability Against Interface Reaction of Glass-YSZ Composites:

The results on the stability of the self healing glass-YSZ composite based on CTE and x-ray diffraction suggested that the glass-YSZ composite should also be stable against reaction with YSZ electrolyte membrane at 800°C over an extended time period. In this study, stability of the glass-YSZ composite was also investigated by placing a glass-30% YSZ composite on a dense YSZ membrane and then fabricating a glass-composite/YSZ seal by sintering the sample at 800°C for 2 hours. Then the sample was cooled to room temperature, annealed in air and fuel environments for 2000 hours, sectioned, and polished to reveal the glass-composite/YSZ interface for examination by SEM. The results in Fig. 11 shows an interface between glass-YSZ composite and YSZ substrate indicating a total lack of reaction between the glass-composite and YSZ substrate indicating stability in contact with a dense YSZ membrane.

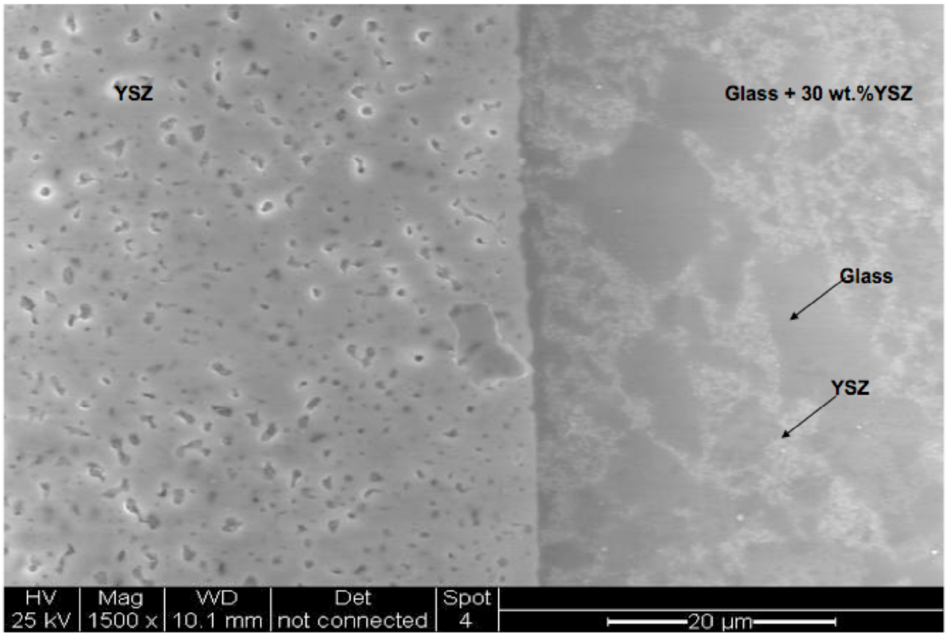

Fig. 11. SEM micrograph from annealed glass-30% YSZ composite/YSZ substrate indicating no reaction of the glass with the substrate material.

Conclusions:

- A self-healing sealing concept is further advanced for SOFC to satisfy significant thermo chemical and thermomechanical incompatibilities among materials requiring hermetic seals. In particular, emphasis of the current program was to find suitable filler materials that can be used to modify glass properties to avoid excessive flow of the self-healing sealant glass.

- Glass-composites with Al_2O_3, MgO, and YSZ fillers were fabricated to assess their role on thermomechanical behavior. Stability of the reinforced glasses were measured by x-situ experiments at 800°C to demonstrate stability.

- Alumina and MgO fillers reacted with the glass and found to be unsuitable as fillers. YSZ was stable and a more promising filler material. Stability of the glass-YSZ filler composites was determined by annealing samples up to 2000 hours in fuel and air environments. Stability of glass-YSZ composite was demonstrated for 2000 hours.

- Long-term stability demonstrated promise of the self-healing glass-YSZ composite seals for potential applications in SOFC.

- All the objectives of the program were accomplished.

Publications and Presentations Resulting from Project:

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2. S. K. Singh and R. N. Singh, "Viscous Glass Composite Seal for Solid Oxide Fuel Cell", Materials and Energy Conference: The Ohio innovation summit, *UCEAO*, Columbus, OH, E 32, April 20 (2010).
3. S. K. Singh and R. N. Singh, "Viscous Glass Composite Seal for Solid Oxide Fuel Cell", *University of Cincinnati*, Poster Forum, p 34, March 5 (2010).

Acknowledgments

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