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Designing Sealing Glasses for Solid Oxide Fuel Cells

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Thermal and chemical properties of "invert" glasses and glass-ceramics developed for hermetic seals for solid oxide fuel cells are described. The glasses crystallize to form thermally stable pyro- and orthosilicate phases with the requisite thermal expansion match to the Y-stabilized ZrO_2 (YSZ) electrolyte. In addition, the glasses bond to Cr-steel substrates at 800-850 °C without forming extensive interfacial reaction products. The thermal expansion characteristics of the glass-ceramics remain essentially unchanged after 28 days at 750 °C. Compositions with lower (≤2 mol%) B_2O_3 contents exhibit the lowest volatilization rates when exposed to wet forming gas at 750 °C.

Keywords glass-ceramics, hermetic seals, solid oxide fuel cells

1. Introduction

Solid oxide fuel cells (SOFC) convert chemical energy to electricity via an electrochemical reaction. SOFCs are candidates for high-efficiency, low-polluting, alternative energy sources (Ref 1). SOFCs can be classified into two groups by their unit-cell stacking type: planar or tubular (Ref 2). The planar cell designs have a number of advantages over the tubular designs, including simpler manufacturing processes and a relatively short current path that results in higher power density and efficiency (Ref 3, 4). However, for planar SOFCs to operate properly, a suitable sealing material must be available to prevent the fuel gas and air from mixing during operation. Within the fuel-cell stack, the sealant must be compatible with the thermal expansion characteristics of the fuel cell components, must be resistant to chemical interactions with those components, must be stable in the high-temperature, wet oxidizing and reducing operating environments, and must be an electrical insulator. The seal must be able to withstand frequent thermal cycling to room temperature over the operational life time of the cell (>10,000 h) (Ref 5-7). Thus, seal performance not only greatly affects the structural integrity and stability of the SOFC stack, but could also determine the overall stack performance (Ref 1).

Corrosion and volatilization of cell materials and formation of undesirable phases at the sealing interfaces with various cell components are significant concerns for the design of sealing materials. Reducing the cell operational temperature to 700-800 °C mitigates some of these stability problems (Ref 7). The operating temperature of an SOFC can be lowered by reducing the thickness of the electrolyte (Ref 8), by using new electrolytes with greater oxide-ion conductivity (Ref 9, 10), and by using alternative electrode materials (Ref 11). Y_2O_3-stabilized ZrO_2 (YSZ) is the most common electrolyte used in SOFCs. Reducing the operational temperatures also allows designers to replace conducting oxide interconnect materials with oxidation-resistant metal alloys. High-temperature, oxidation-resistant alloys often contain Cr and Al as alloying additives to form a protective oxide scale (Ref 8).

In efforts to develop suitable glass and glass-ceramics seals for SOFCs, many glass-forming systems have been studied, including alkali and alkaline-earth silicates, aluminosilicate, borosilicate, and aluminophosphate glasses (Ref 12-17). The design of a sealing system involves the consideration of a number of potential problems, including thermal-expansion mismatch, poor thermochemical stability, and deleterious interfacial reactions with other fuel-cell components. An example of the latter is the formation of a $BaCrO_4$ reaction product at the interface between BaO-containing sealing glasses and Cr-steel interconnects (Ref 1). Such interfacial reaction products may compromise the long-term mechanical stability of a seal.

The present paper describes the thermal and chemical properties of "invert" glasses and glass-ceramics developed for hermetic seals for solid oxide fuel cells. Invert glasses are those with relatively low concentrations of glass-forming oxides (e.g., <45 mol% $SiO_2 + B_2O_3$), and so they possess molecular-level structures without continuous networks of glass-forming tetrahedra (Ref 18). These glasses crystallize to form thermally stable pyro- and orthosilicate phases with the requisite thermal-expansion match to the Y-stabilized ZrO_2 (YSZ) electrolyte, and the glass-ceramics form strong bonds to a Cr-steel alloy at 850 °C.

2. Experimental Procedures

Glasses were prepared from mixtures of reagent-grade alkaline-earth carbonates and silica, with concentrations of other oxides to modify the melt and glass properties. The batches were melted in Pt crucibles in air for 4 h, typically at 1550 °C. A typical melt size was approximately 50 g. Melts were quenched on steel plates, and glasses were annealed for 6 h near the appropriate glass-transition temperature. The compositional ranges for the glasses under investigation are (in mol%) (0-30)CaO, (0-30)SrO, (0-30)ZnO, (1-7)B_2O_3, (2-4)Al_2O_3, (0-2)TiO_2, and (35-45)SiO_2.

Glass powders (sieved to 45-75 μm) were used for differential thermal analyses (Perkin-Elmer DTA 7, Norwalk, CT). The powders were heated in air at 10 °C/min to determine the

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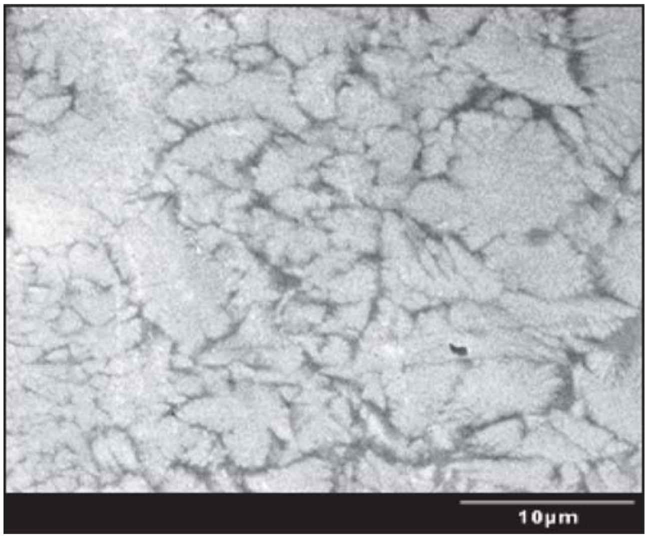

Fig. 1 Scanning electron micrograph of the glass ceramic that forms when glass No. 27 is held at 850 °C for 2 h.

Table 1 Thermal properties of SOFC sealing glasses

Glass ID	Properties				
	T_g, °C	T_d, °C	T_c, °C	CTE/glass (100-600 °C) ($\times 10^{-7}$/°C)	CTE/crystal (RT-700 °C) ($\times 10^{-7}$/°C)
25	682	717	862	93	94
27	700	730	904	95	105
36	745	750	956	109	112
37	649	738	851	68	75
38	660	744	910	84	55
39	649	727	865	92	72

glass-transition temperature, T_g, and crystallization temperature, T_c. The estimated error for T_g and T_c is ±2 °C. Glass powders were crystallized by heat treating at temperatures around T_c for 2 h in an argon atmosphere, and the crystalline phases were identified by x-ray diffraction (XRD, Scintag XDS2000X). The thermal-expansion characteristics of glass and crystallized samples were determined by dilatometric (Orton Dilatometer model 1600D) analyses. Crystallized samples were prepared by first sintering and then crystallizing glass powders in graphite moulds (25 × 10 mm) under argon for the indicated time and temperature. Dilatometric data was collected by heating samples in air at 3 °C/min, to determine the coefficient for thermal expansion (CTE) and dilatometric softening points (T_d).

Sealing tests were performed by reacting glass powders with SOFC component materials, including Y_2O_3 (8 mol%)-stabilized zirconia (YSZ) substrates, prepared by tape-casting, and the oxidation-resistant alloy E-brite (nominally 26.5Cr-1.0Mo-Fe) (Ref 8). The glasses were ground and sieved to separate particles in the size range 45-75 μm, and the powder was mixed with ethanol to form a paste that was then applied to a clean E-brite substrate. The YSZ substrate was set on top of the glass paste, and this "sandwich" assembly was then heated in an alumina muffle furnace in air to 450 °C, to remove organics, and then to the desired sealing temperature under flowing argon. Sealing conditions were determined based on earlier DTA, XRD, and dilatometric analyses.

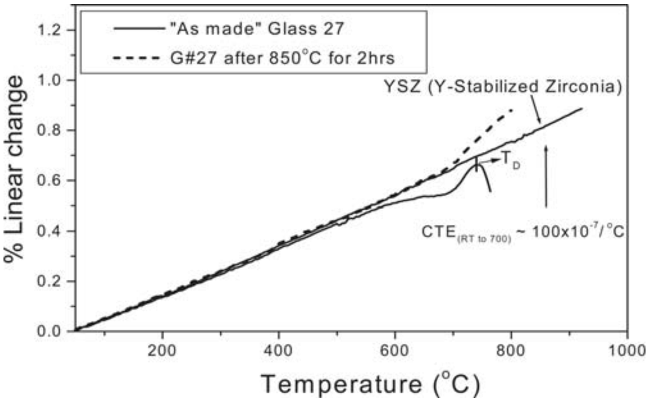

Fig. 2 Dilatometric curves for glass No. 27 before and after crystallization at 850 °C for 2 h. Also shown is the dilatometric curve for YSZ. Note the softening point in the CTE curves near T_g for the crystallized glass.

In general, the glass melts, spreads, and bonds to both substrates and then crystallizes to form the desired "glass-ceramic" phases. Some reaction couples were further subjected to long-term heating at 750 °C in air. Reaction couples were prepared for microscopic evaluation. Samples were cross-sectioned with a diamond saw, polished to a submicron finish, and then evaluated by analytical scanning electron microscopy (Hitachi 4700 SEM with the Phoenix EDAX system).

Chemical stability of crystallized glass samples in reducing environments was evaluated by measuring the mass loss from bulk samples held in wet, flowing forming gas (10% H_2, 90% N_2) at 750 °C for up to 10 days. The samples were polished to a 600 grit finish with SiC paper, cleaned with acetone, and supported by a Ni-Cr wire in the furnace. Measurements were made for each crystallized glass sample, and the average mass loss, normalized to the glass surface area, was determined.

3. Results and Discussion

The thermal properties of several invert glasses and resulting glass-ceramics are summarized in Table 1. In general, increasing the ZnO content and/or the B_2O_3 content of the glass reduces T_g and T_d, and so reduces the expected sealing temperature. Glasses with greater ZnO contents have lower thermal-expansion coefficients. Several compositions, like glasses No. 25 and No. 27, produce glass-ceramics that have thermal-expansion coefficients that are good matches for YSZ (~100 × 10^{-7}/°C). Figure 1 compares CTE curves for glass No. 27, before and after crystallization, with the dilatometric curve for YSZ. The crystallized sample exhibits an inflection in the expansion curve the T_g of the "as-made" glass.

Glass-ceramics were produced by crystallizing each glass at 850 °C for 2 h in air. Figure 2 shows a scanning electron micrograph of a glass-ceramic formed after crystallization of glass No. 27. The crystal morphology is typical of the glass-ceramics formed from these systems. A residual glassy phase is evident between the crystals shown in the micrograph. Figure 3 (top) shows an XRD pattern from glass No. 27 after the initial crystallization treatment. Two crystalline phases can be identified in this sample: $CaSrAl_2SiO_7$ and $Ca_2ZnSi_2O_7$. Other samples yield crystalline orthosilicates, such as Sr_2SiO_4 and Zn_2SiO_4. These crystalline phases are consistent with the "low-

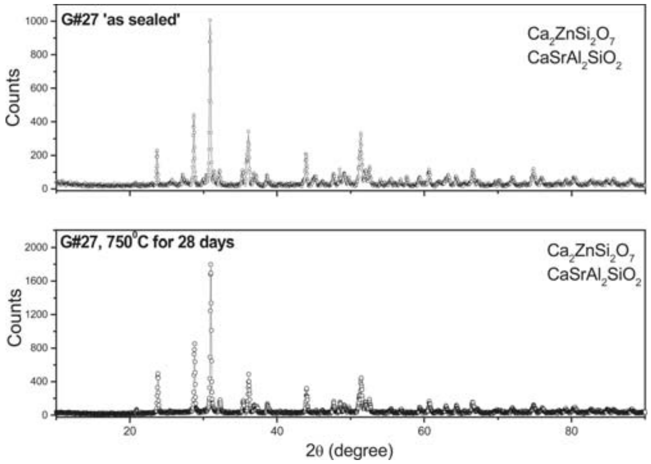

Fig. 3 XRD patterns for glass No. 27 (top) after crystallization at 850 °C for 2 h and (bottom) after being held for 28 days at 750 °C

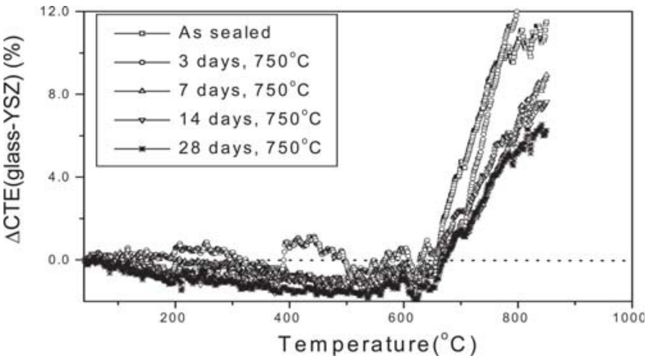

Fig. 4 CTE difference curves between YSZ and glass No. 27, held at 750 °C for up to 28 days. Breaks in the ΔCTE curves near 650 °C are likely caused by the expansion characteristics of the residual glassy phases.

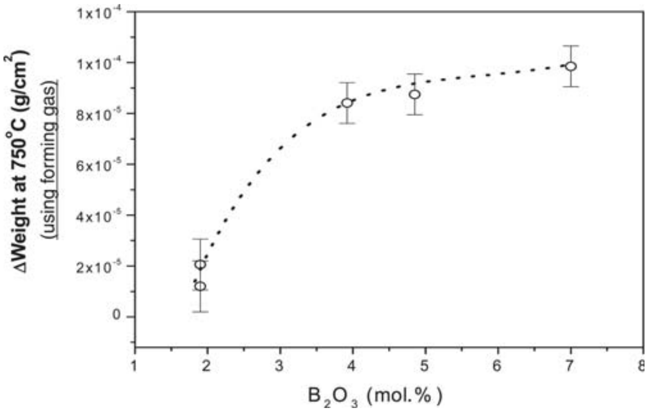

Fig. 5 Sample mass losses after 10 days at 750 °C in forming gas

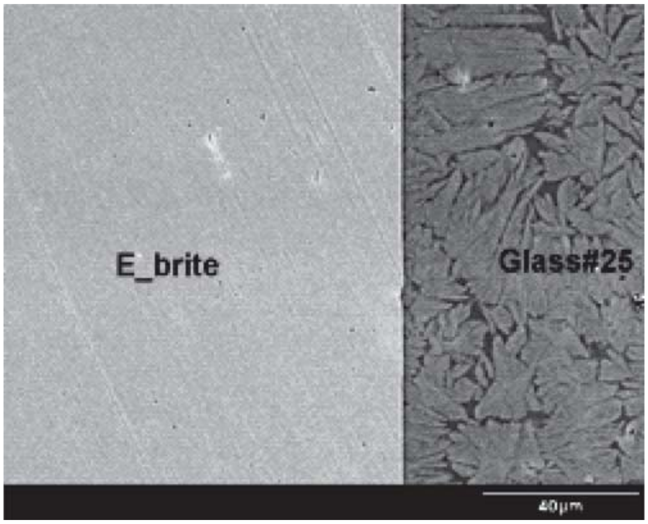

Fig. 6 Scanning electron micrograph of the bonding interface between E-brite and glass No. 25 after 4 h at 850 °C

connectivity" structures of the parent invert glasses. Glasses with greater silica contents crystallize to form more well-connected phases, particularly the metasilicates (Ref 13, 14, 9).

A better comparison of the thermal-expansion characteristics of crystallized glass No. 27 and YSZ is shown in Fig. 4, where the CTE *differences* between the materials are plotted. Shown are dilatometric data collected from crystallized samples held at 750 °C for up to 28 days. The differences in CTE between glass No. 27 and YSZ are minimal up to 650 °C, and the difference remains stable for glass No. 27 samples held at 750 °C for up to 28 days. Above 650 °C, the CTE of glass No. 27 increases relative to YSZ, likely a reflection of the expansion characteristics of the residual glass in the glass-ceramic. Figure 4 shows some small, but systematic changes in the ΔCTE behavior of glass No. 27 above 650 °C, indicating some change in the nature of the residual glass with time at 750 °C; however, these changes do not appear to have a significant effect on the expansion characteristics of the glass-ceramic below 650 °C. X-ray diffraction analysis of a crystallized glass No. 27 after 28 days at 750 °C (Fig. 3, bottom) indicates no discernible changes in the material from that formed immediately after initial crystallization (Fig. 3, top). This phase stability is consistent with the stability of the ΔCTE behavior shown in Fig. 4.

The mass losses recorded from several different glass-ceramics with a range of B_2O_3 contents after 10 days at 750 °C in wet forming gas are shown in Fig. 5. In general, glasses with greater concentrations of B_2O_3 exhibit greater volatilization rates under these conditions. In addition, materials with a greater fraction of residual glass tend to exhibit greater volatilization rates (not shown). These volatilization experiments provide clues about the long-term stability of a proposed sealing system and so place constraints on compositional design. Based on this constraint, the most promising sealing glasses have low B_2O_3 contents.

Figure 6 shows a scanning electron micrograph of the interface of a bond between crystallized glass No. 25 and E-brite, after 4 h at 850 °C. The bonding interface appears to be uniform, with no obvious heterogeneities.

Microscopic characterization of the glass/YSZ interface (not shown) indicates no apparent formation of sealing heterogeneities. Sandwich seals between YSZ and E-brite have survived 10 thermal quenches from 750 °C to room temperature without separating.

Figure 7 shows a high-magnification electron micrograph of an E-brite/glass No. 25 interface after 14 days at 750 °C. Energy-dispersive x-ray spectroscopy indicates the presence of a Cr-rich layer at this interface, but this layer is far less apparent than the extensive interfacial reaction zones reported for BaO-

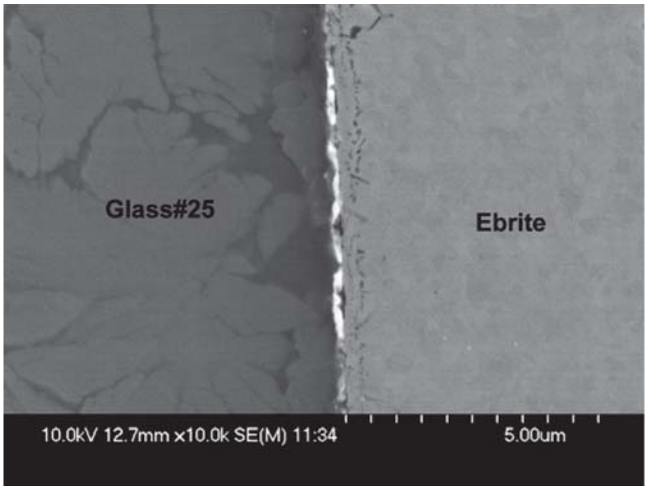

Fig. 7 High-resolution SEM micrograph of E-brite/glass No. 25 interface after 14 days at 750 °C. The bright phase at the interface is Cr-rich.

containing glasses bonded to Cr-containing interconnect materials (Ref 19). Other glass/E-brite reaction couples have been held at 750 °C for up to 60 days without formation of significant interfacial reaction products.

4. Conclusions

The thermal properties and thermochemical stability of invert silicate glasses that crystallize to form stable pyro- and orthosilicate phases make them attractive candidates for SOFC applications. Promising compositions possess desirable thermal-expansion characteristics that are compatible with YSZ substrates and that remain stable under SOFC operational conditions. The glass-ceramics bond to YSZ and Cr-steel alloys, like E-brite, proposed for interconnects, without forming the extensive interfacial reaction products that are observed in other sealing systems.

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