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Refractory Glass Seals for SOFC

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Introduction

One of the critical challenges facing planar solid oxide fuel cell (SOFC) technology is the need for reliable sealing technology. Seals must exhibit long-term stability and mechanical integrity in the high temperature SOFC environment during normal and transient operation. Several different approaches for sealing SOFC stacks are under development, including glass or glass-ceramic seals, metallic brazes, and compressive seals. Among glass seals, rigid glass-ceramics, self-healing glass, and composite glass approaches have been investigated under the SECA Core Technology Program. The U.S. Department of Energy's Pacific Northwest National Laboratory (PNNL) has developed the "refractory" glass approach in light of the fact that higher sealing temperatures (e.g., 930-1000^oC) may enhance the ultimate in-service bulk strength and electrical conductivity of contact materials, as well as the bonding strength between contact materials and adjacent SOFC components, such as interconnect coatings and electrodes. This report summarizes the thermal, chemical, mechanical, and electrical properties of the refractory sealing glass.

Materials and fabrication

The PNNL refractory glasses are alkaline-earth based silicate glasses fabricated by conventional glass melting processes using commercially available raw materials such as oxide and carbonate powders. The glasses contain alkaline earths (Ba, Sr, Ca, and/or Mg), Y or Al modifiers, and Si and B glass formers. After evaluating a number of formulations which exhibited a wide range of thermal properties, several preferred compositions have been selected which offer sealing temperatures in the range of 930-1000ºC, and CTE in the 11.5 – 12.5 ppm/ºC range.

Crystal structure and thermal stability

As noted above, the refractory sealing glasses are designed to seal at higher temperatures than conventional SOFC sealing glasses (e.g., PNNL's G18, sealing T ~830^oC). Table I shows the thermal expansion of a refractory sealing glass (YSO1, sealing T ~1000^oC) before and after an accelerated isothermal aging test at 900^oC in air or a wet reducing environment. For comparison, the CTE behavior of G18 in air is also listed. It is apparent that the refractory sealing glass exhibited improved CTE stability compared to G18. The aged refractory glass was also characterized with x-ray diffraction. Figure 1 shows the diffraction patterns for refractory glass after 4, 1000, and 2000 hrs of aging (green, blue, and red plots, respectively). It is apparent that the refractory sealing glass was very stable in terms of crystalline phase formation, as no new phases or significant changes in relative amounts of phases were observed after the initial 4 hr heat treatment. The major phase was $SrSiO_3$ with lesser amounts of Ca_3SiO_5, Ca_2SiO_4, and Y_2SiO_5 also present. The observed stability in the XRD patterns is consistent with the stability observed in the CTE measurements.

Electrical stability

Results of an electrical stability test on a representative refractory glass (YSO75, sealing T ~975^oC) are shown in Figure 2. The test was performed under 0.7V DC loading in dual environments at 850^oC; 850^oC was chosen to accelerate any potential reactions. The test was run with dilute fuel (2.7 H_2/Ar + 30% H_2O) for the first 432 hrs and then with pure H_2 + 30% H_2O for the rest of the test. The glass exhibited an electrical resistivity greater than 10^4 ohm-m, about 5 orders of magnitude higher than YSZ (~2.5x10^{-1} ohm-m @ 800^oC) and 9 orders higher than cathode (LSM ~$6x10^{-5}$ ohm-m @ 800^oC) or anode materials (Ni/YSZ ~$1x10^{-5}$ ohm-m @ 800^oC). The high electrical resistivity clearly indicates that no significant electrical loss through the sealing glass would be expected.

Volatility

Since most of the refractory glasses contain ~7-10 mol% of B_2O_3 and an appreciable amount of SiO_2 as the glass former, the potential weight loss, especially in reducing environments, needs to be addressed. The volatility of glass may have two impacts. First, electrochemical performance may be degraded if the volatile species deposit onto active electrochemical sites. In addition, excessive evaporation of sealing material could weaken the seal and cause leakage. Volatility of two refractory sealing glasses was evaluated in a wet reducing environment at 800^oC for ~1600 hrs; weight loss results are shown in Figure 3. Following an initial period (~600 hrs) of rapid weight loss, the volatility decreased significantly. The second stage volatility rates (3.2-3.6 x 10^{-8} g/cm^2-hr were similar to estimated values for SiO_2 (4.3-14 x $10^{-8}g/cm^2$-hr) based on published activation energies. Using the measured volatility and assuming a typical seal geometry, it is estimated that the total material loss for 40,000 hr operation at 800^oC would be less than 0.1 wt%.

Mechanical integrity

Butt joint testing was performed to study the mechanical integrity of the refractory sealing glass. Stainless steel squares (1/2"x1/2") were joined with the sealing glass at elevated temperatures (e.g., 950^oC) in air. After joining, the couples were tested in uni-axial tension at room temperature. Some samples were aged in air or a wet reducing environment to study environmental effects. In addition to the as-received steel, aluminized steel coupons were also tested. The strengths are shown in Figure 4. It is evident that the seal strength degraded greatly when aged in air, while no degradation resulted from aging in a reducing environment. The loss of strength resulted from tensile residual stresses due to CTE mismatch between an interfacial reaction product ($SrCrO_4$, CTE ~22 ppm/^oC) and the other materials (CTE ~11.5-12.5 ppm/^oC). Aluminization was effective in preventing this loss of strength during air aging.

Glass validation in a single-cell stack assembly

To further evaluate the performance of the refractory sealing glass in a realistic manner, the glass (YSO77 sealing, T ~950^oC) was tested in a single-cell stack assembly. A commercial 50mm x 50mm anode-supported cell with LSM/YSZ cathode was tested for thermal cycle stability and baseline performance stability using 97% H_2 + 3%H_2O vs. air at 800^oC. The cell was first sealed onto an aluminized SS441 cell frame at 950^oC 2h in air. The sealed couple was then assembled with SS441 anode and cathode plates, contact pastes, perimeter seals, and fuel and air heat-exchangers. Figure 5 shows the open circuit voltage (OCV) versus thermal cycles. For each cycle the sample was heated from room temperature to 750^oC in 3 hrs, held for 3 hrs, then cooled to near room temperature. The total time for each cycle was 24 hr. Throughout the thermal cycle testing, the measured OCV was very close to the theoretical Nernst potential, suggesting no fracture of the refractory sealing glass. The structural integrity of the seal was further verified during post-test analysis. Results from an electrochemical performance stack fixture test are shown in Fig. 6. This test again used refractory sealing glass for the cell-to-frame frame. Overall, the ~1400 hr test showed very good stability in electrochemical performance, with degradation (calculated from observed power density after 300 hr) about 1.3%/1000 hr. The final

OCV before terminating the test was 1.089V (@800°C), suggesting that good sealing was achieved for the entire test.

Post-test interfacial analysis

Figure 7 shows the sealing glass/YSZ interfacial region of a cell tested in the stack test fixture. Clearly there are reactions between the sealing glass and YSZ electrolyte as demonstrated by "needle" formation along the interface. Thermodynamic calculations indicated the formation of $BaZrO_3$ or $SrZrO_3$, which was consistent with EDS chemical analysis. The presence of the needles is not expected to be an issue, since the CTEs of the zirconates are very close to YSZ. At the interface between the glass and the aluminized AIS 441 (Fig. 8), no chromate phase was identified. An aluminum-rich band was observed at the glass/metal interface due to substantial dissolution of the alumina surface layer, but no distinct evidence of crystalline phase formation was observed.

Acknowledgements

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Contacts

PNNL currently has several candidate refractory sealing glasses with sealing temperature ranging from ~930-1000°C. For more information, please contact:

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Table I. CTE of sealing glass before and after aging.

glass	temperature	environment	before	1000hr	2000 hr
YSO1	900	air	11.73	11.51	11.62
YSO1	900	wet+red.	11.73	11.62	N/A
G18	750	air	12.50	11.10	N/A

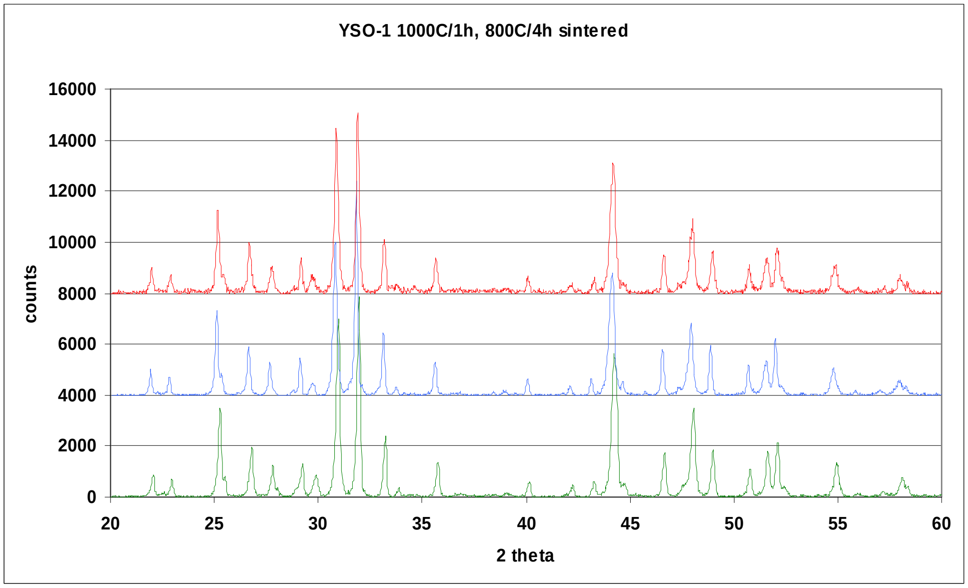

Figure 1. XRD patterns of refractory glass (YSO1) before and after accelerated aging at 900°C.

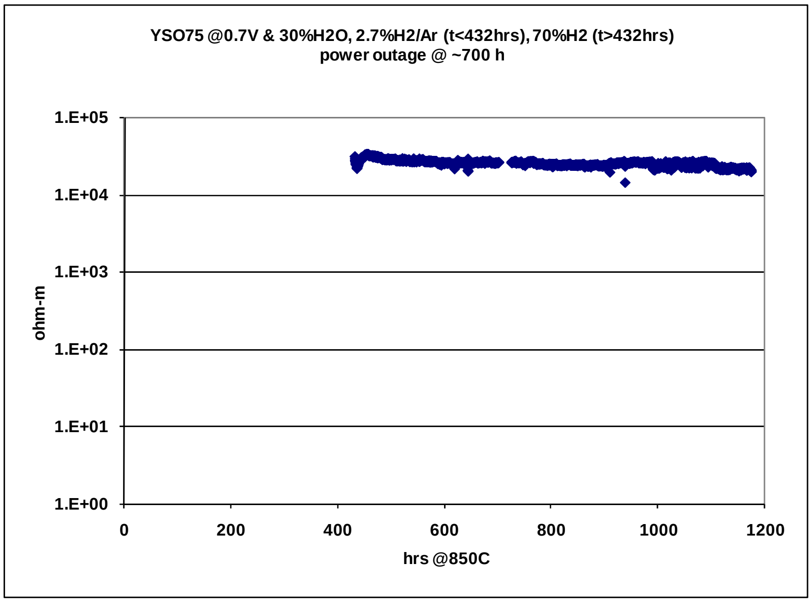

Figure 2. Electrical stability of refractory glass (YSO75) during isothermal aging under a 0.7 V DC loading and dual environments (pure H_2+30%H_2O vs. air) at 850°C. Resistivity data were not recorded during the first ~400 hrs of the test.

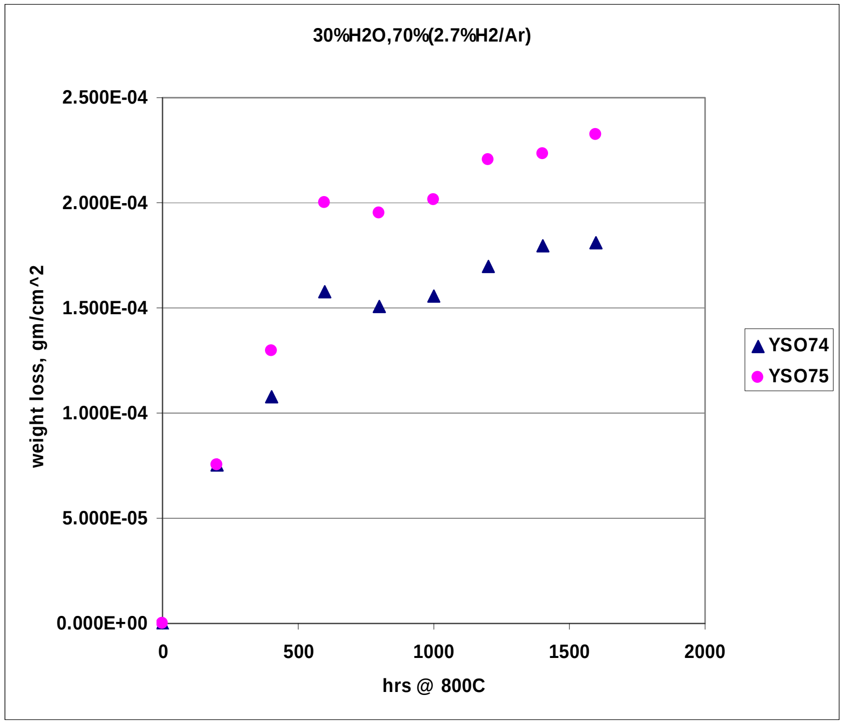

Figure 3. Weight loss versus aging time at 800°C in flowing wet and reducing gas (30% H_2O+70%(2.7%H_2/Ar)) for 2 refractory sealing glasses.

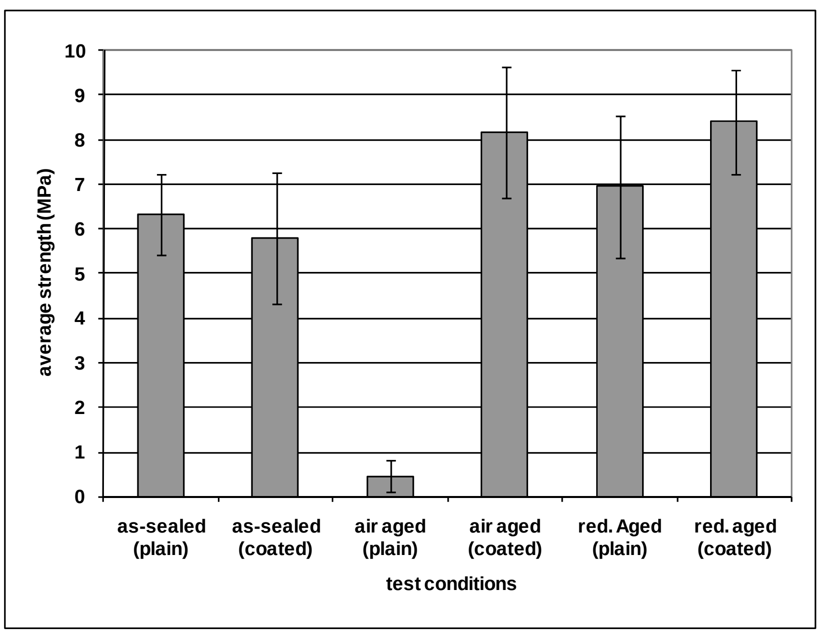

Figure 4. Effect of environmental aging on the tensile strength of joined steel/glass/steel coupons. The glass used for this test was YSO75 with sealing T ~975°C.

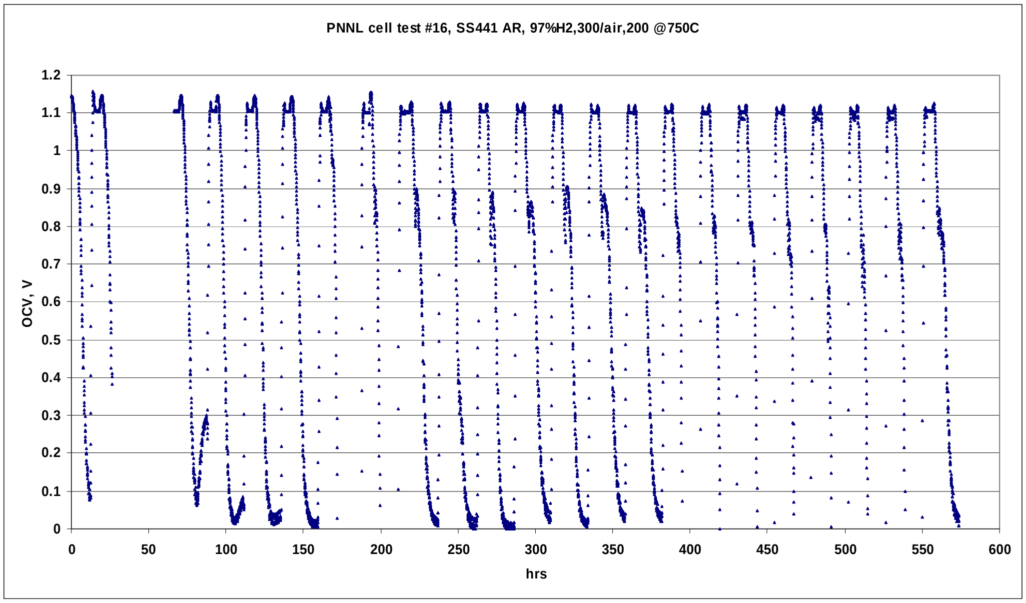

Figure 5. Thermal cycle stability test of refractory sealing glass (YSO77).

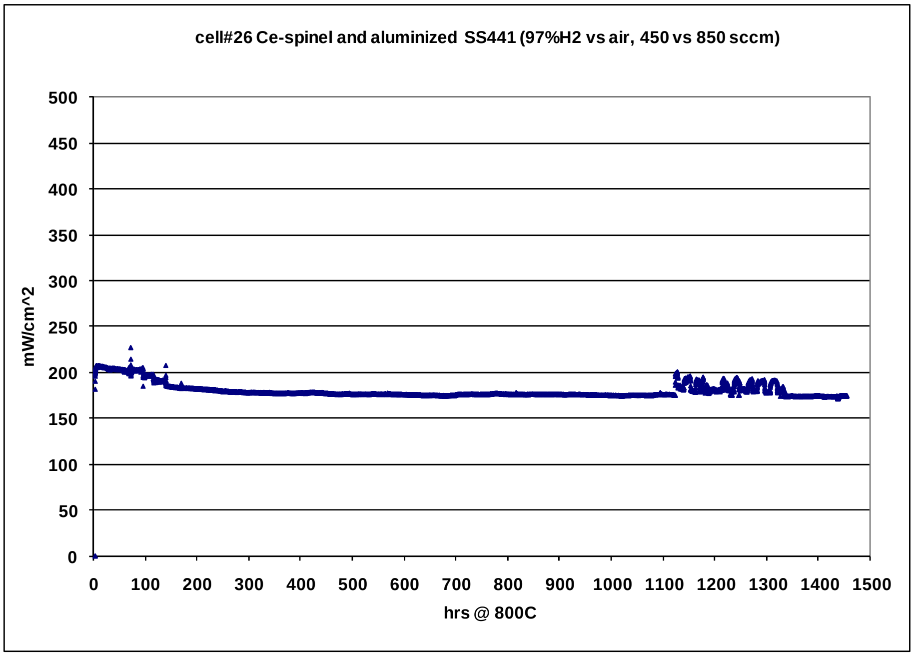

Figure 6. Electrochemical performance of anode-supported cell tested at 800°C and 0.7 V using 97% H_2+3%H_2O vs. air.

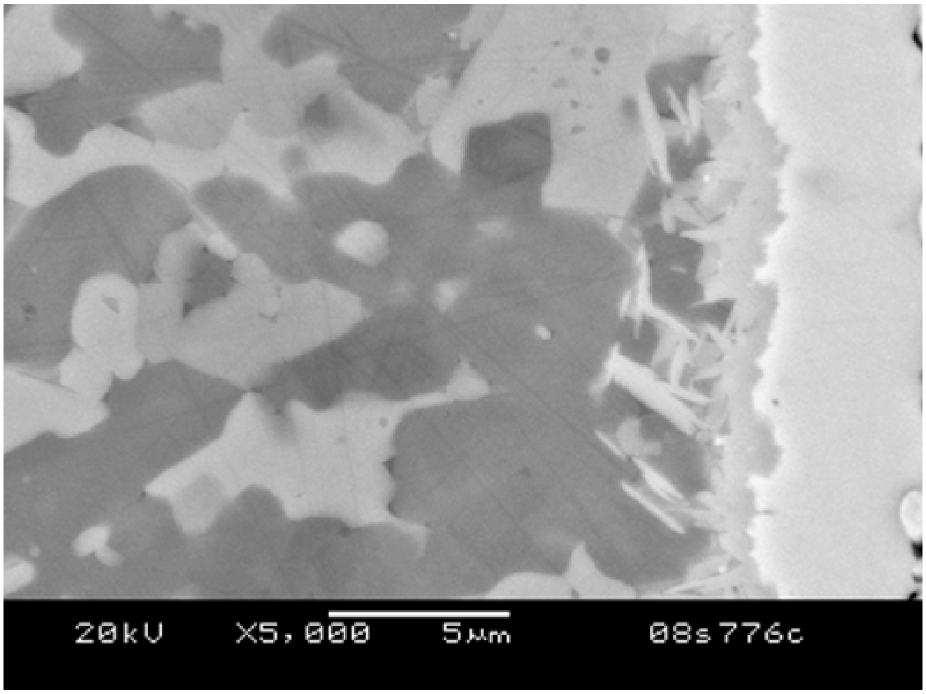

Figure 7. Interfacial microstructure along the glass/YSZ interface after 2325 hr test at 800^oC and 0.7V; YSZ is on the right.

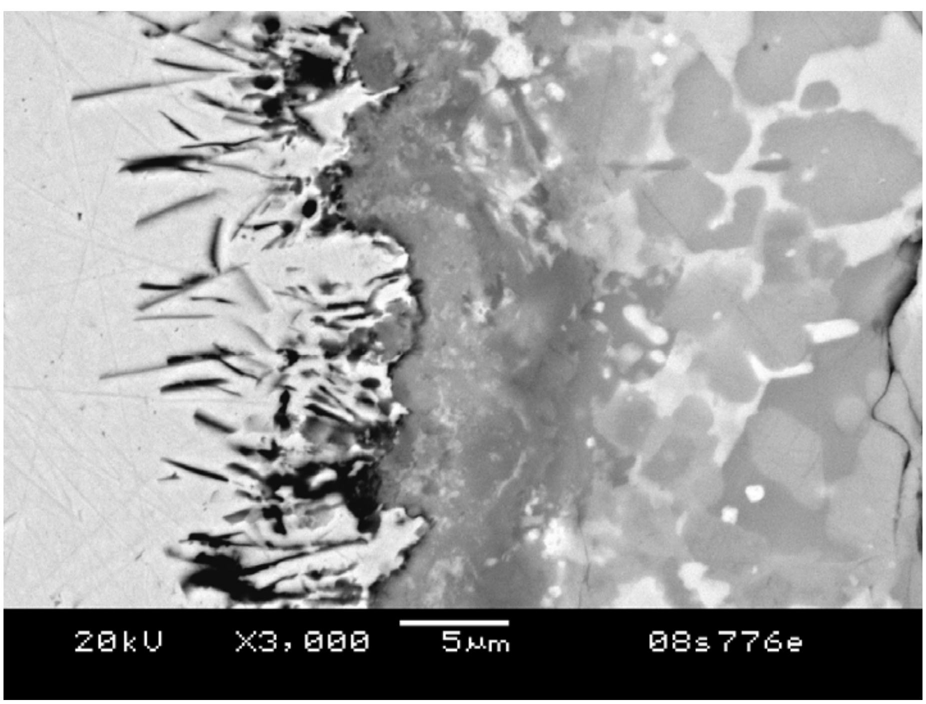

Figure 8. Interfacial microstructure along the glass/aluminized AISI 441 interface after 2325 hr test at 800^oC and 0.7V; the aluminized AISI 441 is on the left.