IV.A.14 SOFC Glass Seal Development at PNNL

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Objectives

- To develop and validate devitrifying sealing glasses for intermediate temperature solid oxide fuel cells (SOFCs).
- To study the interfacial chemical compatibility and mechanical integrity of interconnect alloys with candidate sealing glasses.

Accomplishments

- Completed interfacial compatibility and mechanical integrity studies of $(Mn,Co)_3O_4$ spinel-coated Crofer22APU with candidate sealing glasses.
- Completed interfacial compatibility and mechanical integrity studies of aluminized Crofer22APU with candidate sealing glasses.
- Demonstrated the electrical stability of refractory sealing glasses in a simulated SOFC environment under DC loading over 1,200 hours at 850°C. (Due to space limitations, results of electrical testing are not included in this report.)

Introduction

Glasses are considered promising candidates for SOFC seals because of their good wetting behavior, tailorable coefficient of thermal expansion (CTE), electrically insulating behavior, ease of processing, and low cost. Seal development at PNNL is primarily focused on "refractory" devitrifying sealing glasses with relatively high sealing temperatures (e.g., ≥950°C). The major potential advantages of refractory sealing glasses include stable thermal properties (including CTE), reduced interfacial reactivity, and lower volatility. In addition, the higher sealing temperature may enhance sintering and bonding of electrical contact pastes to mating surfaces, and hence, improve mechanical strength and electrical conductance. PNNL has developed "refractory" sealing glasses in the Sr-Ca-Y-B-Si-O system, which exhibit stable CTE in the range of 11.5-12.5 ppm/°C. Microstructural analysis by X-ray diffraction (XRD) and volatility studies confirmed the desired stability in terms of crystallization products and weight loss, but the analysis also revealed the formation of $SrCrO_4$ at alloy interconnect/glass interfaces, near sealing edges. The formation of these chromates at metal interfaces presents a technical challenge that must be dealt with, due to their very high CTE (~22 ppm/°C), which can result in micro-cracking during thermal cycling.

To minimize the formation of undesirable chromate phases, two approaches were evaluated in FY 2007 to prevent direct contact between the Cr-containing interconnect alloy and the sealing glass. The first approach involves aluminization of the alloy, followed by oxidation to form a dense alumina layer. The second approach uses $(Mn,Co)_3O_4$ spinel coatings to prevent the alloy/glass interaction. Use of the spinel coating offers potential advantages over the aluminizing process in that the spinel has a better CTE match, and the metal interconnect would need one coating process, instead of two processes; the same coating could be used for both sealing areas, and active cathode areas. However, reaction of $(Mn,Co)_3O_4$ spinel with the sealing glass, and its limited phase stability in reducing environments are potential challenges for this approach. In FY 2007, the seal (joint) strength of a candidate refractory sealing glass (YSO75) with Crofer22APU coated with either alumina or spinel was evaluated.

Approach

A commercial vendor performed the aluminizing using vapor phase or pack cementation processes, followed by oxidation in air, to form the alumina layer. The $(Mn,Co)_3O_4$ spinel coatings were fabricated in-house using PNNL's slurry-based process. Test samples were prepared by applying glass powder paste between two coated Crofer22APU coupons (1/2"x1/2" squares), followed by sealing at 950°C/2h, and short-term crystallization at 800ºC/4h in air. In some cases, samples were aged for longer periods. For comparison, as-received Crofer22APU was evaluated in seal strength tests. The strength was tested in uni-axial tension, at room temperature. After testing, the samples were examined with optical and scanning electron microscopy, to identify failure origins.

Results

Initially, we evaluated the baseline strength of glass seals with uncoated Crofer22APU. Alloy coupons were pre-oxidized in air, at three conditions (800°C/2h, 1,000°C/2h, and 1,200°C/2h) to promote mild to severe oxidation. The oxide scales were approximately <0.5, 1, and 5-6 microns thick after heat treatment at 800, 1,000, and 1,200°C. Figure 1 shows the seal (joint) strength of samples for as-received and pre-oxidized samples. It is evident that the strength degraded substantially when Crofer22APU was pre-oxidized at 1,000 or 1,200°C. The as-received or 800°C pre-oxidized samples showed seal strength of ~6.3 MPa, while the higher temperature pre-oxidation resulted in strengths of 2.6-2.9 MPa with large standard deviation (0.81 to 0.44 MPa). In post-test analysis, fracture surfaces of the higher pre-oxidation temperature samples (1,000°C/2h and 1,200°C/2h) showed substantial amounts of yellowish color, suggesting fracture through $SrCrO_4$ or at the $SrCrO_4/Cr_2O_3$ interface. Thus, the results supported the assumption that chromate formation negatively affects the strength of the glass seals.

The effects of aging in different environments were also studied. Sealed coupons were tested at 850°C, either in air for 500 hours, or in 30% H_2O / 70% dilute hydrogen (2.7%H_2/Ar) for 250 hours. The joint strengths are plotted in Figure 2 along with those of the as-sealed samples. Aging in air degraded the strength from an initial value of ~6.3 MPa to ~0.5 MPa. The yellowish color observed on the fracture surfaces indicated the formation of $SrCrO_4$. Overall, these tests suggest that a protective coating is required to prevent chromate formation on the airside of interconnect seals. Aging in the wet reducing environment did not result in degradation of strength. This is not surprising, since chromate formation is thermodynamically unfavorable under reducing conditions typical of the SOFC fuel environment.

Results of strength tests for seals to aluminized Crofer22APU are plotted in Figure 3. Two pre-oxidation conditions (in air) for the aluminized alloy were evaluated: 1,000°C/2h and 1,200°C/2h. Overall, the seal strength for the aluminized Crofer22APU was similar to that of the uncoated alloy. For the aluminized samples, the fracture mode was primary through the glass, rather than the alumina/glass interface. This is consistent with the CTE of the constituents; alumina has the lowest CTE and, therefore is likely to be in compression after cooling

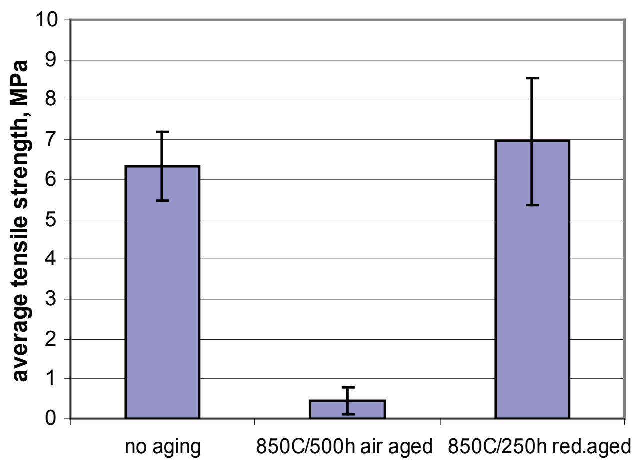

FIGURE 2. Room Temperature Seal (Joint) Strength of As-Received Crofer22APU with Refractory Sealing Glass (YSO75) after Aging in Different Atmospheres

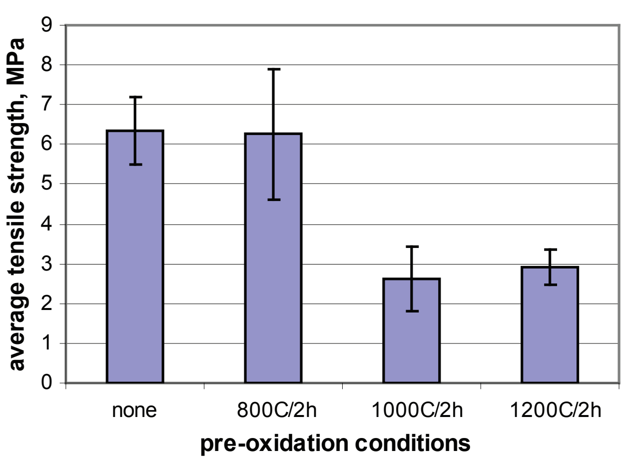

FIGURE 1. Room Temperature Seal (Joint) Strength of Uncoated Crofer22APU and Refractory Glass (YSO75) as a Function of Pre-Oxidation Temperature

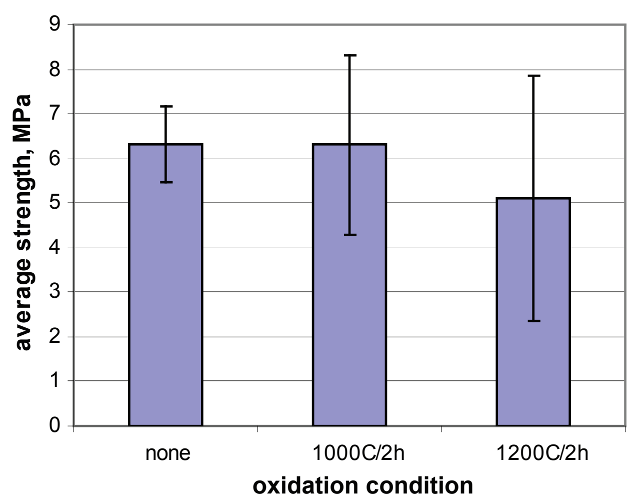

FIGURE 3. Room Temperature Seal (Joint) Strength of Aluminized Crofer22APU with Refractory Sealing Glass (YSO75)

while the glass was in tension. As a result, the fracture propagated through the glass. Earlier reports showed that a dense alumina layer was effective in suppressing the chromate formation (at least in the short term) and therefore, one might expect to have seen improvement in joint strength, since no high CTE chromate should have been present along the interfaces. The reason for the observed similar strength of aluminized Crofer22APU to the uncoated Crofer22APU (either as-received or 800°C oxidized) is not clear. One possible cause is that the edge defects were larger for the aluminized alloy (which had a relatively rough surface) than the uncoated alloy (with a smoother surface). Another possible cause could be residual tensile stress induced by the low CTE alumina layer (CTE ~8.8). The tests will be repeated using a second batch of aluminized Crofer22APU, which has a smoother surface due to improvements in the aluminization process.

Seal strength tests were also performed using spinel-coated Crofer22APU. The measured strengths of the as-sealed, air-aged, and reducing environment-aged samples are shown in Figure 4. The as-sealed tensile strength was 5.5 ± 0.7 MPa, slightly lower than the strength of the uncoated Crofer22APU (6.3 ± 0.8 MPa). The air-aged spinel-coated samples, however, were much stronger than the air-aged uncoated samples (4.6 ± 1.1 MPa vs. 0.5 ± 0.3 MPa). The reducing environment-aged samples had similar strengths to the as-sealed samples (5.4 ± 0.8 MPa). Overall, the current tests indicated that the initial seal (joint) strength was relatively independent of the presence/absence or type of coating. However, while the seal strength of uncoated samples degraded substantially during aging in air, the spinel-coated samples retained much of their initial strength after aging in either air or a wet, reducing environment.

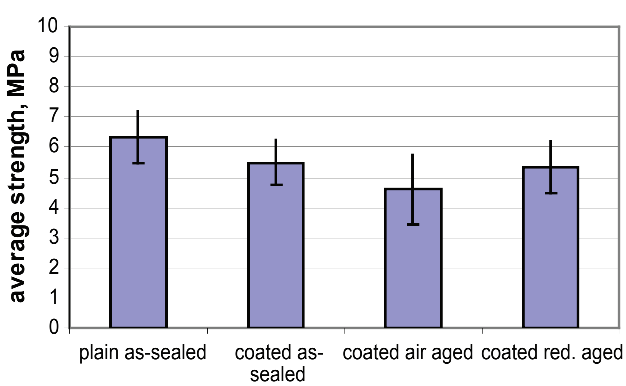

FIGURE 4. Room Temperature Seal (Joint) Strength of Spinel-coated Crofer22APU before and after Aging with Refractory Sealing Glass (YSO75)

Conclusions and Future Directions

Room temperature strength testing of sealed Crofer22APU/glass/Crofer22APU coupons showed similar strengths for samples in the as-sealed state, with or without protective coatings. Without the coatings, the strength degraded substantially, after aging in air for 500 hours at 850°C. With the coatings however, strength showed significantly less degradation during aging in air. During aging in a wet, reducing environment, no strength degradation was observed. Future directions of glass seal development will include continued electrical stability testing of coated Crofer22APU (aluminized and spinel coating) in SOFC environments, and interfacial microstructure analysis after the DC loading tests. Strength and short-term thermal cycling tests will also be performed on these electrically aged samples. In addition, optimization of coating microstructure (thickness and porosity) will be performed for several refractory sealing glasses covering a sealing temperature range of ~950 to ~1,050°C in air. Concerning glass microstructure development, a study of glass, particle size effects, as well as fine-tuning of glass compositions will be performed to yield better wetting (sealing) and dense microstructure. In addition to the current Crofer22APU, a low-cost interconnect candidate stainless steel (441) will be evaluated in terms of chemical compatibility, seal strength, and coating adhesion. Finally, the performance of candidate refractory seals glasses will be tested in a 2" x 2" single cell stack.

FY 2007 Publications/Presentations

1. Y-S Chou, J. W. Stevenson, R. N. Gow, "Novel alkaline earth silicate sealing glass for SOFC, Part I: the effect of nickel oxide on the thermal and mechanical properties," J. Power Sources, 168, 426 (2007).

2. Y-S Chou, J. W. Stevenson, P. Singh, "Novel refractory alkaline earth silicate sealing glasses for planar solid oxide fuel cells," J. Electrochemical Society, 154, B644 (2007).

3. Y-S Chou, J. W. Stevenson, and P. Singh, "Effect of pre-oxidation of a metallic interconnect on the bonding strength of a SOFC sealing glass," Presented at 31st International Conference on Advanced Ceramics & Composites, January 21–26, 2007, Daytona Beach, FL.

4. Y-S Chou, J. W. Stevenson, and P. Singh, "Effect of ageing on the thermal and electrical properties of a novel SOFC sealing glass," Presented at 31st International Conference on Advanced Ceramics & Composites, January 21 – 26, 2007, Daytona Beach, FL.

5. Y-S Chou, J. W. Stevenson, and P. Singh, "Glass seal development at PNNL," presented at Glass & Optical Materials Meting and 18th University Conference on Glass, The American Ceramic Society, May 20–23, 2007, Rochester, NY.

6. Y-S Chou, J. W. Stevenson, and P. Singh, "SOFC seal development at PNNL," presented at TMS 2007 Annual Meeting and Exhibition: Materials in Clean Power System: Fuel Cells, Solar and Hydrogen Based Technologies, February 25 – March 1, 2007, Orlando, FL.