NEW PLANAR SOFC SEALING TECHNIQUES
FOR POTENTIAL TRANSPORTATION APPLICATIONS

K. S. Weil, C. A. Coyle, J. S. Hardy, G-G. Xia, and J. Y. Kim
Pacific Northwest National Laboratory
Richland, WA 99352, USA

ABSTRACT

Among the various SOFC stack designs under development worldwide, the planar configuration has received growing attention because of its compact nature and associated high volumetric power density – design features which are essential in transportation applications. With the advent of anode-supported cells that employ thin YSZ electrolytes, these devices can be operated at reduced temperatures (700 - 800°C) and still achieve the same current densities exhibited by their high-temperature, thick electrolyte-supported counterparts. The lower operating temperature not only makes it possible to consider inexpensive, commercially available high temperature alloys for use in the stack and balance of plant, but also expands the list of materials/techniques that could be employed in device sealing. Here we discuss two such methods that may have potential application in pSOFCs.

INTRODUCTION

Because SOFCs function under an oxygen ion gradient that develops across the electrolyte, hermeticity across this membrane is paramount. In a planar design, this means that the YSZ layer of the cell must be dense, must not contain interconnected porosity, and must be connected to the rest of the device with a high temperature, gas-tight seal. One of the fundamental challenges in fabricating pSOFCs is how to effectively seal the thin electrochemically active YSZ membrane against the metallic body of the device such that the resulting stack is hermetic and rugged and performs in a stable fashion. In the present work, we use the following operating/exposure conditions as guidelines in our seal designs: 1) an average operating temperature of 750°C; 2) continuous exposure to an oxidizing atmosphere on the cathode side and a wet reducing gas on the anode side; and 3) an anticipated device lifetime of 10,000+ hours.

We have recently developed an alternative method of ceramic-to-metal brazing specifically for fabricating high temperature solid-state devices such as oxygen and hydrogen generators (1,2). Referred to as air brazing, the technique differs from traditional active metal brazing in two important ways: 1) it utilizes a liquid-phase oxide-noble metal melt as the basis for joining, and thereby exhibits high-temperature oxidation resistance, and 2) the process is conducted directly in air without the use of fluxes and/or inert cover gases. In fact, the strength of the bond formed during air brazing relies on the formation of a thin, adherent oxide scale on the metal substrate. The technique employs a molten oxide that is at least partially soluble in a noble metal solvent to pre-wet the oxide
facing surfaces, creating a new surface that the remaining molten filler material easily wets. One system that has shown particular promise in the development of air brazing is Ag-CuO. Prior work has shown that the addition of 1.4 to 8 mol% CuO to silver results in excellent wetting on a variety of oxide surfaces, while producing filler metal and interfacial microstructures that lead to good joint strength (3,4). Here the effects of thermal aging, under prototypical pSOFC fuel and oxidant atmospheres, and of aggressive thermal cycling on the subsequent rupture strength and microstructure of air brazed seals are considered.

A second sealing concept under development utilizes a thin stamped metal foil that is bonded to both sealing surfaces. Like the mica-based compressive gaskets currently employed in several stack designs, this seal is geometrically compliant and can accommodate mismatches in thermal expansion between the adjoining substrates. However compliance does not take place via sliding, as observed with mica seals. Instead the foil-based seal is designed to readily yield or deform under modest thermo-mechanical loading in order to mitigate the transfer of these stresses to the adjacent ceramic and metal components while at the same time providing a hermetic joint. One of the advantages that this sealing concept potentially offers is that a more expansive array of alloys could be considered for use in the pSOFC interconnect. At present the candidate list is limited to those that display good CTE matching with the ceramic cell, namely the chromia scale-forming ferritic stainless steels. If high CTE nickel-based alloys could be used, the mechanical, oxidation, and through-scale electrical properties of the interconnect would be significantly improved (5).

**AIR BRAZING**

**Experimental**

The filler material used in brazing was formulated by ball-milling in methanol the appropriate amounts of copper (99%, Alfa Aesar) and silver powder (99.9%, Alfa Aesar) required to achieve an as-oxidized target composition of 4 mol% CuO in silver. Previous results from X-ray diffraction indicate that the copper powder will fully oxidize in-situ during a typical air brazing heating schedule to form CuO, the wetting agent employed in this method of air brazing (2). The milled powder was dried, then mixed with a polymer binder (B75717, Ferro Corp.) in a 1:1 weight ratio to form a paste that could be dispensed onto the substrate surfaces using an automated syringe dispenser at a uniform rate of 0.1 g/linear cm. Anode-supported bilayers, consisting of NiO-5YSZ as the anode and 5YSZ as the electrolyte, and thin gage stainless steel (FeCrAlY and Crofer-22 APU) were employed as the model substrates in our study. Disc-shaped bilayer coupons were fabricated by traditional tape casting and co-sintering techniques and measured 25mm in diameter by 600 µm in thickness, with an average electrolyte thickness of ~8µm. As-received 300 µm thick FeCrAlY and Crofer-22 APU sheets were cut into washer-shaped specimens measuring 4.4cm in diameter with a concentric 1.5cm diameter hole and cleaned with acetone prior to joining. The filler metal paste was dispensed onto the YSZ side of each bilayer disc. The discs were concentrically positioned one at a time onto a corresponding metal washer, loaded with a dead-weight, and heated in air under the following brazing schedule: heat from room temperature to melting (~1000°C - 1050°C), hold at temperature for 15min, and cool to room temperature. Afterward, the degree of
hermeticity and strength in the resulting joining specimens were tested by pressurizing the backside of the bilayer disc (rupture testing) while keeping the adjoining metal ring clamped in a hermetically sealed fixture. Specific details concerning the design of the test apparatus and the testing procedure are reported in Reference (6).

It is important to recognize that the differential pressure expected to arise across each individual cell in an actual operating stack is quite small. Thus except for an accidental transient condition, the rupture strength test places the cell, seal, and metal frame under a highly exaggerated stress condition relative to prototypic steady-state operation. However by doing so, the test makes it possible to identify the weakest constituent in the sealing system, i.e. the ceramic substrate, the braze material, the metal substrate and associated oxide scale, or any of the interfaces in between, so that the seal can potentially be improved in the next round of development. Ideally for the purposes of quantitative comparison, one would like the stress in the seal to be either pure shear or pure tension at failure. Unfortunately, the stress state in the rupture test specimen is mixed-mode. Although the test does not yield a strict quantitative measure of failure stress in the seal, it does provide a figure of merit, rupture stress, which as we will show can be used to compare various batches of specimens that have been joined or tested under different sets of conditions.

Aging tests were conducted by exposing sets of six specimens at 750°C to either 20cc/min of flowing dry air for 200, 400, or 800 hrs. Upon cooling, the specimens were rupture tested as described above. Thermal cycle testing was conducted in a pancake-shaped infrared furnace containing a horizontal 3” thick x 15” diameter chamber into which a series of high-intensity quartz lamps could radiate and thereby induce rapid rates of heating with great reproducibility. The specimens were heated to 750°C at 75°C/min and held at temperature for 10 min followed by cooling at 75°C/min to 400°C, after which the samples were cooled to 70°C in approximately 25 min. Testing was conducted in 20 cc/min dry flowing air out to a total of 5, 10, 20 or 50 cycles, after which the samples were tested for hermeticity and rupture strength. Microstructural analysis of the joints after rupture testing was conducted on polished cross-sectioned samples using a JEOL JSM-5900LV scanning electron microscope (SEM) equipped with an Oxford energy dispersive X-ray analysis (EDX) system. In order to avoid electrical charging on the samples, they were carbon coated and grounded. Elemental profiles were determined across the joint interfaces in the line-scan mode.

Results

Plotted respectively in Figures 1(a) and (b) are the rupture strengths of the brazed Crofer and FeCrAlY sealing specimens as a function of time in 750°C air. The results indicate that thermal aging in air has no significant effect on joint strength out to 800hrs for either metal substrate. Regardless of the composition of the stainless steel substrate employed, all of the specimens appeared to fail in the same manner, due to fracture initiating within the cell. Examples of this are shown in Figure 2. In each case, the brazed seal region remains entirely intact. The average strength of the bilayers is 187±39 MPa, as measured at room temperature using ball-on-ring biaxial flexure testing (ASTM F 394-78). The corresponding range of rupture strength values, indicated by the shaded regions in Figures 1(a) and (b), are the effective pressures at which failure is expected to occur in the cell; i.e. the type of failure observed in Figure 2. To verify this, additional testing was
conducted using 1200 µm thick bilayer discs (which display a correspondingly higher strength). Crofer-based specimens in the as-joined and the 200 and 800 hr air-aged conditions displayed no leaking or failure through either the seal or cell out to the maximum rupture test pressure of 130 psi.

As a point of comparison, rupture strength data obtained on barium aluminosilicate (BAS)-based glass sealed specimens [from Reference (6)] are also included in Figure 1(a). Note that the thermal aging of glass seals in air leads to a degradation in seal strength. Two reasons for this phenomenon were offered: 1) the microstructure and composition of the glass-ceramic in the bulk portion of the sealing glass changes with time at temperature and 2) the reaction zone that forms at the glass/metal interface during initial sealing also evolves during soaking at high temperature. In both cases, the coefficient of thermal expansion (CTE) of the resulting material that forms in the bulk of the seal and at the interfaces decreases relative to the original as-joined state. Thus upon cooling to room temperature, large thermally induced mismatch stresses are generated in the sealing material and the substrates, which subsequently causes a reduction in the measured rupture strength. In contrast, although the brazed seals also experience substantial CTE mismatch upon cooling (α_{brazier} \sim 10.6 \mu m/m^\circ K, \alpha_{Crofer} \sim 12.5 \mu m/m^\circ K, and \alpha_{silver} \sim 22.8 \mu m/m^\circ K), the ductile sealing material yields and plastically deforms, thereby mitigating the transfer of significant stresses to the adjacent substrates. It is likely that the mechanical properties of the silver, i.e. low yield strength and high elongation, are instrumental in allowing the brazed seals to remain intact.

Shown in Figure 3 are typical cross-sectional micrographs of the two different types of specimens in the as-brazed condition. As seen in Figures 3(a) and (c), the silver-based braze wets the YSZ substrate quite well, infiltrating into the submicron roughness along the interface. EDX analysis gave no indication of a reaction zone at the YSZ/braze interface, although a dispersion of half-lens shaped CuO crystallites along this interface were readily observed, with essentially pure silver in between. More equiaxed CuO precipitates are found in the bulk portion of the filler metal. The composition of the surrounding matrix is again elemental silver. On the stainless steel side of the specimens, shown in Figures 3(b) and (c) respectively for Crofer and FeCrAlY, the interface between the braze and the underlying metal substrate displays a distinct reaction zone. In the case of Crofer, this zone assumes an undulating morphology. Dark patches of chromia scale doped with iron and manganese oxide form directly on the Crofer. Some of the chromia reacts with the copper oxide in the braze, giving rise to a \sim 10 \mu m thick region between the scale and braze. EDX analysis indicates that in addition to copper oxide, two newly formed phases are found: 1) copper chromate, with a composition that approximates CuCr_{2}O_{4}, and 2) a mixed oxide containing both CuO and Cr_{2}O_{3} in apparent solid solution.

Examination of the corresponding interface in the FeCrAlY specimen, Figure 3(c), shows that the braze-substrate reaction zone is much thinner, \sim 2 \mu m thick. EDX analysis indicates that this region is a mixture of two phases, CuAlO_{2} and CuO-Al_{2}O_{3}. Adjacent to the reaction zone is a \sim 0.5 \mu m thick alumina scale that forms on the FeCrAlY during brazing. We found that if a non-optimized braze composition is employed in joining (typically when the CuO content is too low), porosity can develop along the joint interfaces due to regions of non-wetting. Shown in Figure 4 are typical cross-sections of the two different aging specimens. A comparison of the corresponding YSZ-braze and
braze-metal substrate interfaces in each indicates that the respective exposure conditions have little effect on the bulk or interfacial microstructures of the brazed seal. For example as shown in Figures 4(a) and (c), the microstructure along the YSZ-braze interface remains essentially constant upon aging. A similar observation can be made by examining the braze-stainless steel interfaces in Figures 4(b) and (d).

Results from rupture tests conducted on thermally cycled specimens are shown in Figures 5(a) and (b). All of the tested specimens were found to be hermetic out to the maximum number of thermal cycles considered in each case, respectively 50 and 40 cycles for Crofer and FeCrAlY. As was seen with the aging specimens, failure occurs within the ceramic disc, not within the seal, indicating that the cell material is the weakest component in the rupture specimen configuration. By comparison, conventional BAS glass sealed specimens displayed an average initial strength of 12.3 psi, which degraded to nearly zero after twenty thermal cycles. Failure in these glass sealed specimens appears to initiate at the interface between the sealing glass and the scale on the stainless steel. Based on the above results, we have begun brazing full-size planar stack components. Initial studies indicate that the air brazing process is readily scalable and that leak-tight seals can be formed in parts as large as 15 m x 10 cm. We intend to continue thermal cycle testing of these components, as well as conducting long-term exposure testing and full-scale stack studies.

**BONDED COMPLIANT SEAL**

**Experimental**

A number of high temperature alloys can be considered for use as the foil membrane in the bonded compliant seal concept. As part of a proof-of-concept study, our initial materials screening analysis focused on four key properties: high oxidation resistance, low stiffness, high ductility, and low cost. Based on these factors, we chose a commercial alumina-forming ferritic steel as the foil membrane: DuraFoil (22% Cr, 7% Al, 0.1% La+Ce, bal. Fe, manufactured by Engineered Materials Solutions, Inc.). Supplied as 50 μm thick sheet, the DuraFoil was sheared into 3cm x 3cm samples, annealed in vacuum at 900°C for 2 hrs, and stamped into cap-shaped washers using a die designed specifically for this purpose. The stamped foils were ultrasonically cleaned in soap and water, and then flushed with acetone to remove the lubricant from the stamping operation.

Each foil washer was bonded to a 6.2 mm thick Haynes 214 washer, with an outside diameter of 4.4 cm and an inside diameter of 1.5 cm, using BNi-2 braze tape (Wall Colmonoy, Inc.). As an alumina-scale forming nickel-based superalloy, Haynes 214 displays excellent oxidation resistance at temperatures in excess of 1000°C, but also exhibits an average CTE of 15.7 μm/m·K, which is almost 50% higher than that of the anode-supported bilayer (CTE = 10.6 μm/m·K). Fabrication of the specimen was completed by air brazing the top side of the stamped foil to the YSZ side of a 25 mm diameter bilayer disc using a Ag-4 mol% CuO paste at the conditions described previously. The specimens were characterized via rupture and thermal cycle testing and subsequently analyzed by SEM and EDS.
Results

Results from rupture testing are shown in Figure 6. Each specimen was found to be hermetic up to the maximum pressure (60psi) tested during initial leak testing. More extensive pressure testing up to the point of rupture indicated no failure in any of the seals, even in the specimens that underwent as many as twenty rapid thermal cycles. As with the air brazed specimens above, failure occurred in the ceramic disc. Shown in Figure 7 is a composite cross-sectional micrograph of a bonded compliant seal specimen. The sample was hermetic, as determined by leak testing conducted prior to metallographic analysis. The entire seal is approximately 1.1mm thick, although it is expected that this can be readily reduced simply by altering the geometry of the DuraFoil stamping. In the particular sample shown in Figure 7, the BNi-2 braze has caused the outer periphery of the foil to curl due to a mismatch in CTE between the two materials. While this does not degrade the strength of the rupture specimen, it could potentially affect the performance of the seal in an actual stack; an issue that will need to be addressed. On the ceramic side of the seal, the CuO-Ag braze appears to form a robust joint between the YSZ and the alumina scale of the DuraFoil. Note that the braze is thicker toward the center of the specimen. No reaction zone is observed at the YSZ/braze interface. However as described earlier, a reaction zone forms on the DuraFoil due to reaction between the Al2O3 scale and the CuO in the braze. Efforts are currently underway to develop a torsion testing technique that will yield quantitative shear strength data for both the air brazing and compliant sealing concepts. These data, as well as that obtained on BAS glass seals, will be used to refine models that we are developing for future stack design.

CONCLUSIONS

Planar SOFCs continue to hold much promise for efficient, high density power generation. To fulfill this promise, robust sealing technologies must be developed that can meet the functional requirements of both stack designers and manufacturers. There are a number of techniques currently under development including glass bonding, compressive sealing, and reactive joining. At Pacific Northwest National Laboratory, we are developing two alternative methods of sealing planar stacks: air brazing and bonded compliant sealing. Results from recent studies demonstrate hermetic YSZ-to-stainless steel joints can be formed in both cases, and these joints remain leak-free and well bonded after aggressive thermal cycle testing. Continuing work will investigate the long-term durability of the seals, as well as the potential for scale-up and prototypic use in demonstration stacks.

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REFERENCES

1. J. S. Hardy, J. Y. Kim, and K. S. Weil, *J. Electrochem. Soc.*, **151**, J43 (2004).
2. J. Y. Kim, J. S. Hardy, and K. S. Weil, *J. Mater. Res.*, **19**, 1717 (2004).
3. A.M. Meier, P. R. Chidambaram, G.R. Edwards, *J. Mater. Sci.*, **30**, 4781 (1995).
4. K. S. Weil, J. Y. Kim, and J. S. Hardy, *Electrochem. and Sol. St. Lett.*, in press.
5. Z. G. Yang, K. S. Weil, D. M. Paxton, and J. W. Stevenson, *J. Electrochem. Soc.*, **150**, 1188 (2003).
6. K. S. Weil, J. E. Deibler, J. S. Hardy, D. S. Kim, G-G Xia, L. A. Chick, and C. A. Coyle, *J. Mater. Eng. Perf.*, **13**, 316 (2004).

Figure 1. Rupture strength of the bilayer/Ag4CuO/stainless steel specimens as a function of exposure time in 750°C air using: (a) Crofer-22 and (b) FeCrAlY.
Figure 2. Examples of specimen failure upon rupture testing.

Figure 3. Cross-sectional SEM micrographs of as-joined rupture specimen employing a Crofer substrate: (a) along the YSZ-braze interface and (b) along the braze-Crofer interface. (c) Cross-sectional SEM micrograph of an as-joined couple employing a FeCrAlY substrate.
Figure 4. Cross-sectional SEM micrographs of a Crofer based specimen that was exposed at 750°C to air (20 cc/min) for 400 hrs: (a) along the YSZ-braze interface and (b) along the braze-Crofer interface. Cross-sectional SEM micrographs of a FeCrAlY based specimen that was exposed at 750°C to air (20 cc/min) for 500 hrs: (a) along the YSZ-braze interface and (b) along the braze-Crofer interface.

Figure 5(a). Rupture strength of the bilayer/Ag4CuO/Crofer-22 specimens as a function of thermal cycling in 750°C air.
Figure 5(b). Rupture strength of the bilayer/Ag4CuO/FeCrAlY specimens as a function of thermal cycling in 750°C air.

Figure 6. Rupture strength of the bonded compliant seal specimens in the as-joined and as-cycled conditions.

Figure 7. A composite cross-sectional micrograph of an as-joined bonded compliant seal rupture test specimen.