Reactive Air Brazing: A Novel Method of Sealing SOFCs and Other Solid-State Electrochemical Devices

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High-temperature electrochemical devices operate via an ion gradient that develops across a solid electrolyte. Consequently, hermeticity across this membrane is paramount. Not only must the electrolyte contain no interconnected porosity, but it must be connected to device chassis with a gas-tight seal. Here we report a new method of brazing developed specifically for solid-state electrochemical applications. We demonstrate that the seal is hermetic and resistant to thermal aging, can be thermally cycled under rapid heating rates with no measurable loss in seal strength, and has shown promise in sealing full-size planar solid oxide fuel cell (pSOFC) components.
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One of the critical issues in designing and fabricating high-temperature electrochemical devices such as planar solid oxide fuel cell (pSOFC) stacks is the ability to hermetically seal adjacent metal and ceramic components. Depending on the specific application, the seal may be exposed to an oxidizing and/or reducing atmosphere at an operating temperature of 500-850°C and experience numerous thermal cycles, but must still retain its hermeticity, mechanical ruggedness, and chemical stability over the lifetime of the device; typically on the order of several thousand hours. With regard to pSOFCs, there are currently only a few accepted methods of sealing the stack components, none of which fully meet the design requirements of stack builders. By far the most popular of these is glass joining, which is a relatively simple, cost-effective technique.[1-4] However the final seal is brittle, nonyielding, and particularly susceptible to fracture when exposed to tensile stresses; for example, the type encountered during nonequilibrium thermal events such as rapid stack heating or cooling or due to thermal expansion mismatches between the glass and the joining substrates.[5-7] An alternative method of ceramic-to-metal joining is active metal brazing, which employs a reactive element such as titanium to facilitate wetting between the braze filler and the ceramic faying surface.[8] There are however at least two problems with using this technique for sealing solid-state electrochemical devices: (*i*) complete oxidation of the active species in the braze during high temperature operation of the device in air may lead to rapid deterioration of the joint at the ceramic/braze metal interface,[9] and an eventual loss of hermeticity, and (*ii*) exposure of the entire device to a reducing atmosphere at a temperature greater than ~800°C, typical processing conditions required in active metal brazing, is deleterious to many of the complex oxide materials employed in these devices.

The brazing technique we have developed is conducted directly in air without the use of fluxing agents to remove surface scale during joining. In fact, the strength of the reactive air brazing (RAB) bond is largely dependent upon a thin, adherent oxide scale that forms on the metal component during heating. RAB utilizes a molten oxide that is at least partially soluble in a noble metal solvent to prewet the oxide faying surfaces, thereby forming a new surface that is more readily wetted by the remaining molten filler material. Potentially, there are a number of metal oxide-noble metal systems that can be considered, including Ag-CuO, Ag-V_2O_5, and Pt-Nb_2O_5.[10-12] In the study discussed below, we examined the Ag-CuO system for use in sealing pSOFC stack components; specifically, the cell-to-frame seal. A common method of stack fabrication is to seal the electrolyte of a cell directly to a metal frame and join this sub-unit to a separator plate, thus forming the repeat unit in the stack. To demonstrate the feasbility of the RAB technique for these types of cell-to-frame seals, we carried out our joining studies on

yttria stabilized zirconia (YSZ) and FeCrAlY, two of the more commonly used electrolyte and frame materials in pSOFC stacks.

Experimental

Anode-supported bilayers, consisting of NiO-5YSZ as the anode and 5YSZ as the electrolyte, and thin gauge FeCrAlY (Fe, 22% Cr, 5% Al, 0.2% Y) stainless steel were employed as the model SOFC ceramic cell/structural metal system in this study. Bilayer coupons were fabricated by traditional tape casting and co-sintering techniques[13] and measured nominally 28 mm in diam by 600 μm thick, with an average electrolyte thickness of ~8 μm. Prior to their use in the wetting and joining experiments, the samples were cleaned with acetone and ethanol and dried in air at 300°C for 1 h. As-received 12 mil thick FeCrAlY sheet was sheared into 2 cm square pieces for the wetting experiments, polished lightly on both sides with 1200 grit SiC paper, and ultrasonically cleaned in acetone for 10 min. For the joining experiments, flat washer-shaped specimens measuring 4.4 cm in diam with a concentric 1.5 cm diam hole were punched from the 12 mil sheet, then polished and cleaned in the same manner.

Braze pellets employed in the wetting experiments were fabricated by mixing and cold pressing copper (10 μm average particle diam; Alfa Aesar) and silver (5.5 μm average particle diam; Alfa Aesar) powders in ratios required to meet a series of target compositions. Using the standard sessile drop technique,[14] the melting and wetting behaviors of the various Ag-CuO braze compositions on the ceramic and metal substrates were video recorded through the quartz viewing window of the air muffle furnace in which they were heated. The samples were heated at a rate of 30°C/min up to 900°C then subsequently heated at 10°C/min to 1050°C, where they were held for 15 min to allow the bead of molten braze to reach its equilibrium shape. Conversion of the analog video data to digital form for image analysis was performed using VideoStudio6 (Ulead Systems, Inc.) frame capturing and video editing software. The digitalized images were subsequently imported into Canvas graphic software (V 8.0.5, Deneba Systems, Inc.) for droplet shape measurement. The outline of the droplet was circumscribed with a circle of best fit, which was used to determine the droplet's radius. The contact angle was then calculated from the radius and the diameter of contact between the droplet and the substrate.

For the joining studies, braze pastes were formulated by mixing the appropriate ratio of copper and silver powders with a standard screen printing binder. Joining was conducted by applying a concentric 24 mm ring of braze paste to the FeCrAlY washer using an automated pressure-driven dispenser. After allowing the paste to dry, the bilayer was placed YSZ-side down onto the washer and dead-loaded with 100 g of weight. The assembly was heated in air at 10°C/min to 1050°C and held at temperature for 30 min before furnace cooling to room temperature. The hermeticity and ultimate strength of the seal were measured using a rupture test rig of the
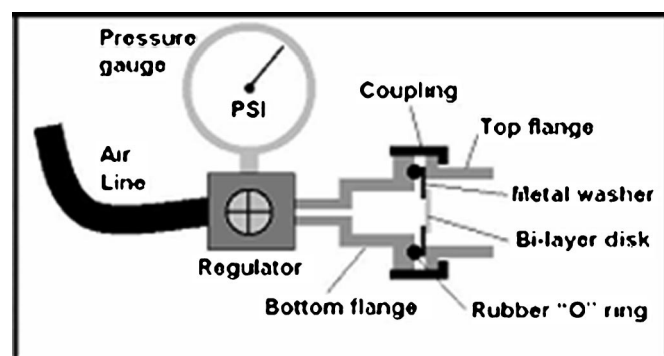
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Figure 1. A schematic of the rupture test apparatus.

Figure 3. Joining samples after rupture testing: (a) specimen joined using a 50 mol % CuO composition and (b) specimen joined with a 1 mol % CuO braze.

type shown schematically in Fig. 1, the details of which have been reported previously.[15] Hermeticity was determined by pressurizing the sample to a value less than that required for failure and measuring whether the pressure subsequently decays as a function of time. Seal strength was determined by slowly pressurizing the sample to the point of failure.

Rupture strength testing was conducted on as-brazed specimens to determine the nascent strength of the joint and on specimens that were thermally cycled or exposure tested in high-temperature hydrogen or air. Thermal cycle testing was conducted by heating the specimens in air at a rate of 75°C/min to 750°C, holding at temperature for 10 min, and cooling to ≤70°C within ~40 min before reheating under the same conditions. Exposure testing was conducted by aging rupture test specimens for varying lengths of time at 750°C in either wet hydrogen, humidified by bubbling the gas through room temperature water, or ambient air. In all cases, a minimum of six specimens was tested for each test condition. Microstructural analysis 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.

Results and Discussion

Plotted in Fig. 2 are the contact angles that each braze forms on 5YSZ and FeCrAlY in air at 1050°C and the rupture strength of the corresponding joint. Although braze wetting improves significantly with increasing CuO content, rupture strength is maximized in the range of 4-8 mol % CuO in silver, then degrades significantly with increasing oxide concentration. Accordingly, the mode of failure also appears to change with CuO content. Above ~20 mol % CuO, the rupture specimens fail at the seal, predominantly along the interface between the braze and metal substrate as shown in Fig. 3a. Conversely, joining specimens prepared with the lower CuO content
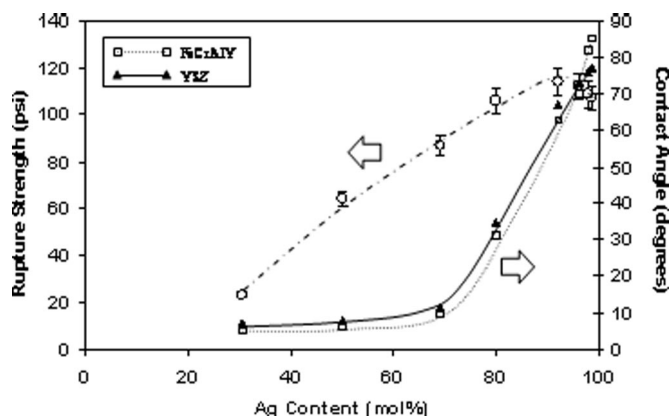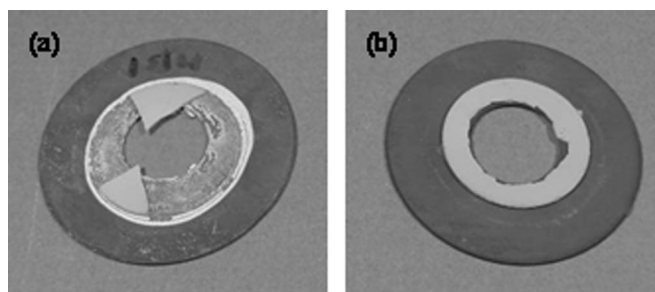
brazes do not rupture at the joint, but instead fail within the center of the ceramic substrate as seen in Fig. 3b. This type of inverse relationship between braze wettability and joint strength is not commonly observed in ceramic-to-metal brazing; typically, improvements in wetting lead to increased strength. However, metallographic examination of the joining specimens reveals significant differences in their interfacial microstructures that likely account for the observed dependences of wetting behavior, rupture strength, and mode of specimen failure on CuO content in the RAB joints.

In SEM images of a typical high CuO-containing braze joint, shown in Fig. 4a and b, the braze/substrate interfaces are encapsulated with a thick, continuous layer of copper oxide. Whereas the YSZ/braze interface appears to be free of reaction products, a reaction zone forms along the FeCrAlY faying surface, apparently due to interaction between the copper oxide in the braze and the iron/chromium oxide-doped alumina scale on the metal. EDX results suggest that the primary product phase in this interfacial region is a continuous band of $CuO-Al_2O_3$, in mixed solid solution, decorated by an occasional 1-3 µm size crystallite of $CuAlO_2$. Although diffraction analysis is needed for confirmation, this result is consistent with the $CuO-Al_2O_3$ phase diagram[16] and has been reported previously in studies of high temperature reaction between copper oxide and high purity alumina.[17] Only a small amount of silver is observed along either interface and is found as discrete, fine-scale particles trapped underneath the copper oxide or within the reaction zone. It is the continuous interfacial oxide phases that appear to account for the excellent wetting characteristics of these brazes. Likewise, it is these brittle phases, which exhibit poor coefficient of thermal
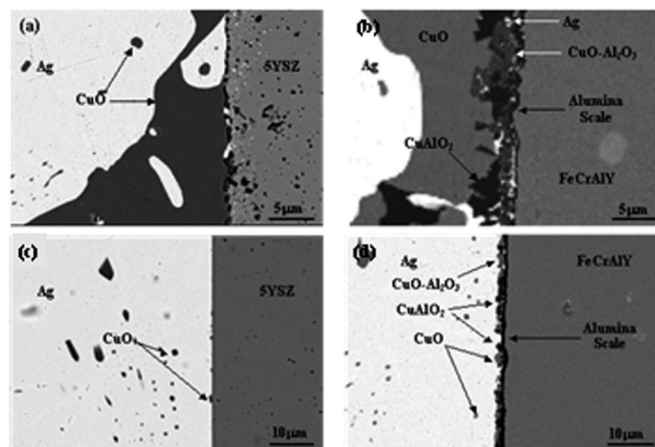

Figure 2. Room-temperature rupture strength and wetting angle data of the Ag-CuO brazes on FeCrAlY and YSZ as a function of braze composition.

Figure 4. Cross-sectional SEMs of a joint specimen brazed with 69 mol % CuO/31 mol % Ag: (a) the 5YSZ/braze interface and (b) the braze/FeCrAlY interface and of a joint specimen brazed with 1 mol %CuO/99 mol % Ag: (c) the 5YSZ/braze interface and (d) the braze/FeCrAlY interface.

expansion matching with the 5YSZ and FeCrAlY, that likely lead to the low rupture strengths observed in the corresponding joining specimens.

The copper oxide segregation observed in these micrographs can be explained in terms of the Ag-CuO phase diagram[10] and critical point wetting theory, originally forwarded by Cahn.[18] At equilibrium, the Ag-CuO system displays two invariant points: a monotectic reaction at $964 \pm 3°C$, where CuO and a liquid L_2 coexist with a second liquid phase L_1 at a composition of 30.65 mol % Ag, and a eutectic reaction at $932 \pm 3°C$, where CuO and Ag coexist with the liquid phase L_2 at a composition of 98.6 mol % Ag. Extending between these three-phase reaction points is a two-phase liquid miscibility gap. At 1050°C, this gap spans from ~6 to ~70 mol % CuO. Critical point wetting theory predicts a transition in the wetting behavior of a multicomponent liquid below a critical temperature at which the liquid-liquid immiscibility occurs. That is, upon cooling to this temperature, the previously homogeneous liquid separates into two immiscible liquids, only one of which will wet the adjacent solid substrate. In doing so, this liquid encapsulates the second liquid phase and thereby excludes it from contact with the solid. When cooled to monotectic temperature, copper oxide precipitates from L_1, forming a thick layer along the interface with the YSZ substrate, *i.e.*, of the type observed in Fig. 4a and b. This should hold true only for those compositions that exhibit high temperature immiscibility, of which the 69 mol % CuO/31 mol % Ag braze depicted in Fig. 4a and b is one example.

At the other extreme of braze composition, Fig. 4c and d indicate that the faying surfaces in joints brazed with low CuO-containing brazes are wetted by significantly more silver. At the interface with the 5YSZ, a nearly continuous layer of silver is found decorated by discrete micron-size islands of CuO along the faying surface. The Ag-CuO phase diagram[10] indicates for this composition that a homogeneous single phase liquid forms at 1050°C. Upon cooling to the eutectic temperature, solid Ag and CuO nucleate heterogeneously from the eutectic liquid, forming an interspersion Ag and CuO along the braze substrate interface of the type observed in Fig. 4c. Ideally, under a long isothermal hold, the resulting solid should consist of a lath-type morphology commonly observed in slow cooling eutectic alloys.[19] However, the rapid cooling rate appears to have suppressed the formation of this characteristic eutectic microstructure. On the other side of the joint, contiguous to the micrometer-thin alumina scale on the FeCrAlY component, an interfacial reaction again occurs. This time however, the resulting $CuO-Al_2O_3$ product is thin and patchy and frequently interrupted by fingers of silver and CuO that extend back into the bulk of the braze. It is the lack of a thick, continuous interfacial oxide layer in this specimen that appears to confer higher strength relative to those joints made using high CuO content brazes.

Based on the initial joint strength results, a braze composition of 4 mol% CuO in Ag was selected for additional exposure and thermal cycle testing. As reported in Table I, neither thermal treatment was found to have a significant effect on the rupture strength of these specimens, at least under the conditions tested. The mode of failure remained the same as before, *i.e.*, the type displayed in Fig. 3b, with the rupture strength entirely dependent on the strength of the ceramic component. Encouraged by these findings, we initiated a demonstration study aimed at incorporating this method of joining into a full-scale test stack. The first such stack consisted of three 144 × 98 mm cells.[20] The 4 mol % CuO braze paste was dispensed onto the YSZ side of each cell and the cell was fixtured against a corresponding Crofer-22 APU frame. Brazing was conducted in ambient air at 1050°C for 15 min, forming a peripheral seal that measured on average ~3 mm wide by ~100 μm thick. The brazed frames were then sealed together using a conventional barium aluminosilicate based glass to prevent shorting between adjacent cells. In a fully brazed stack, an electrical insulator (possibly a coating over the sealing surfaces of the separator plates) would need to be incorporated into the brazed seals between each repeat unit to avoid shorting. After final assembly and initial start-up, the stack was op-

Table I. Average rupture strength of bilayer/FeCrAlY specimens brazed with 4 mol % CuO as a function of thermal test condition.

Age testing at 750°C			Thermal cycle testing[a]	
Aging Time (hrs)	Avg. rupture strength[b] upon aging in wet H_2 (psi)	Avg. rupture strength[b] upon aging in air (psi)	Number of thermal cylces	Avg. rupture strength[b] (psi)
50	112 + 6	110 + 7	5	113 + 4
100	114 + 6	113 + 6	10	111 + 7
500	111 + 4	112 + 5	20	111 + 5
800	112 + 6	114 + 7	40	112 + 4

[a] Each thermal cycle was conducted in air as follows: heat the specimens from room temperature to 750°C in 10 min, hold at 750°C for 10 min, and cool to <70°C in ~40 min.

[b] All of the samples failed through the center of the ceramic bilayer disk and not through the seal.

erated at 750°C for 120 h on 2 lpm of 48.5% H_2, 48.5% N_2, 3% H_2O fuel gas flow on the anode side and 4 lpm of air flow on the cathode side. Both gases were preheated to ~550°C prior to entering the stack.

While the stack exhibited a steady decline in current output over this period of operation, from an intial value of 253.5 to 231.7 Å at 21% fuel utilization and a control voltage of 0.7 V average per cell, a near theoretical open circuit voltage was realized throughout, 3.23 V on average, implying that the seals remained hermetic during the entire operation. Experience based on in-house single cell testing, combined with the post-test analysis results of the stack suggest that the power degradation observed in this test is attributable to chromia volatilization. SEM analysis of the seals, an example of which is shown in Fig. 5, indicates little change in the braze microstruture due to stack operation. Note, however, that the interface formed between the braze and Crofer differs significantly from that observed in the FeCrAlY specimens, for example in Fig. 4d. The interfacial zone is measureably thicker, on the order of 10-15 μm, displays an undulating morphology, and consists primarily of CuO precipitates and two reaction products, $CuO·Cr_2O_3$ and $CuCr_2O_4$, neither of which appears as a continuous phase. Both exposure and thermal cycle testing of rupture specimens and *in situ* stack testing of full-size components are continuing to determine the high-temperature stability of the RAB seal over longer periods of time.
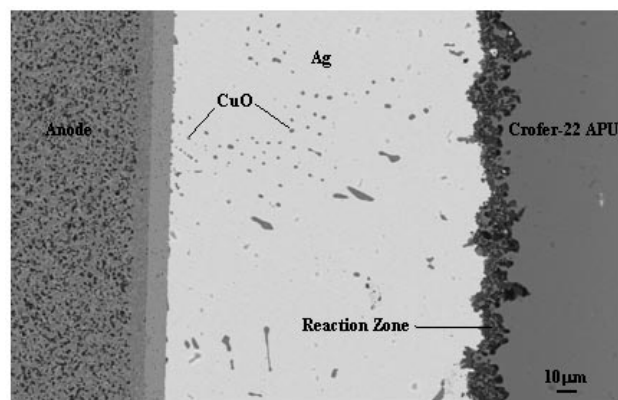

Figure 5. Cross-sectional SEMs of a brazed joint in a full-scale stack that underwent 120 h of operation at 750°C. The composition of the braze is 4 mol % CuO in Ag.

Conclusions

A novel method of ceramic-to-metal joining has been shown to have promise in sealing the components of high-temperature electrochemical devices, specifically in SOFCs. Initial contact angle and rupture strength experiments were valuable in identifying a braze composition, 4 mol % CuO in Ag, that exhibits optimized strength and adequate wettability on the YSZ and stainless steel substrates of interest. Thermal cycling and exposure testing, followed by rupture strength measurements indicate that, under the conditions tested, the braze remains quite durable. Reactive air brazing was implemented as a means of sealing full-scale ceramic cells to metallic frames in a three cell stack that subsequently underwent 120 h of testing at 750°C, using diluted hydrogen as fuel. Open-circuit voltage measurements conducted periodically throughout operation indicated that the seals remained hermetic over the entire test and post-test SEM analysis revealed no significant changes in the microstructures of the brazed seals due to stack operation.

Acknowledgments

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