Development of Brazing Technology for Use in High-Temperature Gas Separation Equipment

K. Scott Weil
Pacific Northwest National Laboratory, 902 Battelle Blvd, P.O. Box 999, Richland, WA 99352
E-mail: scott.weil@pnl.gov; Telephone: (509) 375-6796; Fax: (509) 375-2186

John S. Hardy
Pacific Northwest National Laboratory, 902 Battelle Blvd, P.O. Box 999, Richland, WA 99352
E-mail: john.hardy@pnl.gov; Telephone: (509) 375-2627; Fax: (509) 375-2186

Jin Yong Kim
Pacific Northwest National Laboratory, 902 Battelle Blvd, P.O. Box 999, Richland, WA 99352
E-mail: jin.kim@pnl.gov; Telephone: (509) 376-3372; Fax: (509) 376-2248

Introduction

The development of high-temperature electrochemical devices such as oxygen and hydrogen separators, fuel gas reformers, solid oxide fuel cells, and chemical sensors is part of a rapidly expanding segment of the solid state technology market. These devices employ an ionic conducting ceramic as the active membrane that establishes the electrochemical potential of the device, either under voltage (i.e. to carry out gas separation) or under chemical gradient (to develop an electrical potential and thereby generate electrical power). Because the device operates under an ionic gradient that develops across the electrolyte, hermiticity across this layer is paramount. That is, not only must this thin ceramic membrane be dense with no interconnected porosity, but it must be connected to the rest of the device, typically constructed from a heat resistant alloy, with a high-temperature, gas-tight seal. A significant engineering challenge in fabricating these devices is how to effectively join the thin electrochemically active membrane to the metallic body of the device such that the resulting seal is hermetic, rugged, and stable during continuous high temperature operation.

Active metal brazing is the typical method of joining ceramic and metal engineering components. It employs a braze alloy that contains one or more reactive elements, often titanium, which will chemically reduce the ceramic faying surface and greatly improve its wetting behavior and adherence with the braze. However, recent studies of these brazes for potential use in fabricating high-temperature electrochemical devices revealed problems with interfacial oxidation and subsequent joint failure [1,2]. Specifically, it was found that the introduction of the ceramic electrolyte and/or heat resistant metal substrate dramatically affects the inherent oxidation behavior of the braze, often in a deleterious manner. These conclusions pointed to the need for an oxidation resistant, high-temperature ceramic-to-metal braze and consequently lead to the development of the novel reactive air brazing (RAB) concept.

The goal in RAB is to reactively modify one or both oxide faying surfaces with an oxide compound dissolved in a molten noble metal alloy such that the newly formed surface is readily wetted by the remaining liquid filler material. In many respects, this concept is similar to active metal brazing, except that joining can be conducted in air and the final joint will be resistant to oxidation at high temperature. Potentially, there are a number of metal oxide-noble metal systems that can be considered for RAB, including Ag-CuO, Ag-V_2O_5, and Pt-Nb_2O_5. Our current interest is in determining whether the Ag-CuO system is suitable for air brazing functional ceramic-to-metal joints such as those needed in practical electrochemical devices. In a series of studies, the wetting behavior of the Ag-CuO braze was investigated with respect to a number of potential hydrogen separation, oxygen separation, and fuel cell electrolyte membrane materials and heat resistant metal systems, including: alumina, $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$, $(La_{0.8}Sr_{0.2})FeO_3$, YSZ, fecralloy, and Crofer-22APU. Selected findings from these studies as well as from our work on joint strength and durability during high-temperature exposure testing will be discussed.

Hydrogen Separation

Experimental. There are three classes of hydrogen separation materials currently under investigation in the DOE(FE) program: nanoporous materials, platinum-based alloys, and mixed ionic/electronic conducting oxides such as barum cerate. Thus far, nanoporous alumina appears to be the leading candidate for high temperature separtion of hydrogen from coal gas. As such, Al_2O_3 was chosen for our initial joining studies. High purity, polycrystalline alumina was used as the model substrate in this study and four Ag-CuO compositions were investigated: by molar concentration, 80%CuO/20%Ag, 69.35%CuO/30.65%Ag (the monotectic composition), 60%CuO/40%Ag, and 1.4%CuO/98.6%Ag (the eutectic composition). The brazes were prepared by dry mixing the appropriate amounts of copper powder and silver powder. The copper oxidizes in-situ forming CuO as the braze is heated. For the wetting studies, the mixtures were cold pressed into pellets measuring approximatley 7mm in diameter by 10mm thick. Contact angle experiments were conducted using a standard sessile drop technique, as previously described [3,4]. Four point bend testing was performed at room temperature on alumina bend bars that were joined in the center with the Ag-CuO brazes. The reported joint strength for each braze composition is the average of five idential bars. Microstructural examination of the joints was performed by optical and scanning electron microsopy and by energy dispersive x-ray analysis.

Results. The wetting angles of each braze on alumina and the four-point bend strengths of each corresponding joint are plotted as a function of braze composition in Figure 1. All four braze compositions displayed measurable wetting on the polished polycrystalline alumina substrates; in all cases the contact angle reached its stable value within five minutes. Between the monotectic and eutectic compositions, the contact angle displays a monotonic increase with increasing silver content. The bend strength results reveal that joint strength improves significantly with increasing silver content, i.e. a trend that is in direct contrast to that found with wetting angle. Thus, the specimen joined using the braze containing 80 mol% of CuO displays a bending strength of 84±20 MPa while the specimen brazed with the eutectic composition, 1.4 mol% of CuO, exhibits a two-fold improvement in bending strength of 181±20 MPa. The reasons for this dramatic difference are apparent from the four joint microstructures.

Back scattered electron images of the as-joined RAB specimens are shown in Figure 2. As seen in Figure 2(a), the sample that was joined using the CA8020 braze, which is hypermonotectic with respect to CuO composition, exhibits an extensive and continuous copper alumunium oxide, $CuAlO_2$, reaction zone adjacent to the braze/alumina interface. The composition of this reaction product is consistent with that predicted by the copper oxide (Cu_2O and CuO)-alumina phase diagrams [5]. Extending from the reaction zones toward the center of the braze is a region which consists of two blocky phases which compositionally are nearly pure CuO and nearly pure silver.

The microstructure of the monotectic braze, seen in Figure 2(b), contains a random mixture of two phases, one which is nearly pure silver and the other nearly pure CuO. This microstructure is typical for a monotectic reaction. At the monotectic temperature, solid CuO and a silver-rich liquid nucleate simultaneously from the silver-poor monotectic liquid. Proportionally, CuO is the major product. As it forms and grows during the invariant recation, the oxide precipitates will eventually impinge with each other trapping the still molten silver-rich phase within. The 60%CuO/40%Ag braze joint, shown in Figure 2(c) also displays two phases, CuO and silver, but the morphologies of each are quite different from that of the monotectic braze. Most of the CuO in the 60/40 braze is found in a nearly continuous layer along each interface with the alumina.

The joint formed using the braze with the smallest CuO content, a eutectic composition of 1.4 mol% CuO and 98.6 mol% Ag, displays discrete CuO particles both within a nearly pure silver central region and along the interface with alumina. At 1000°C, the CA0199 braze will form a single silver-rich liquid phase between the two alumina faying surfaces. Upon cooling to the eutectic

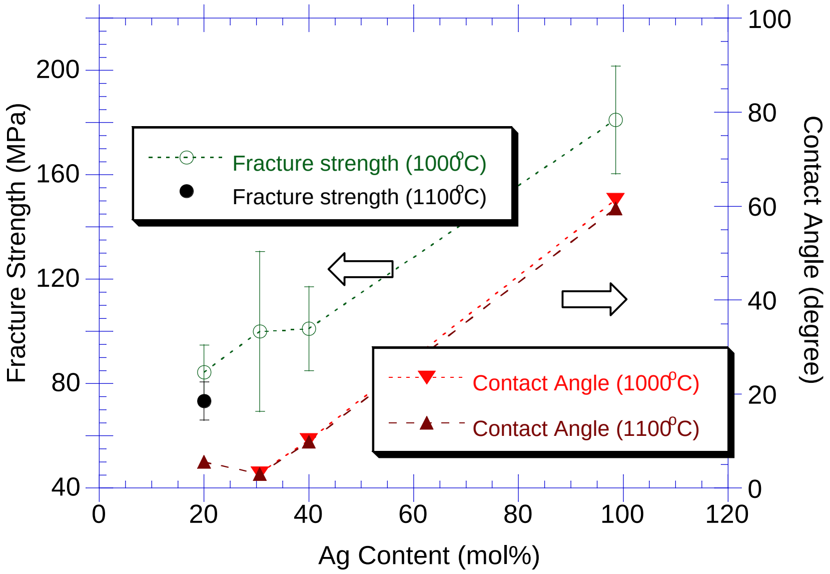

Figure 1 Room temperature four-point bend strength and contact angle as a function of Ag content.

temperature, solid silver and CuO form simultaneously from the eutectic liquid. However, because the CuO concentration of the molten phase is very low, the CuO nucleates as fine, discrete particulate decorating the interface with alumina and the interior of the braze. The joints were exposure tested in flowing wet hydrogen (10cc/min) at 750°C for 500hrs. SEM examination of these specimens indicated that the joints essentially retain their original microstructural condition with only a small amount of coarsening apparent in the copper oxide phases.

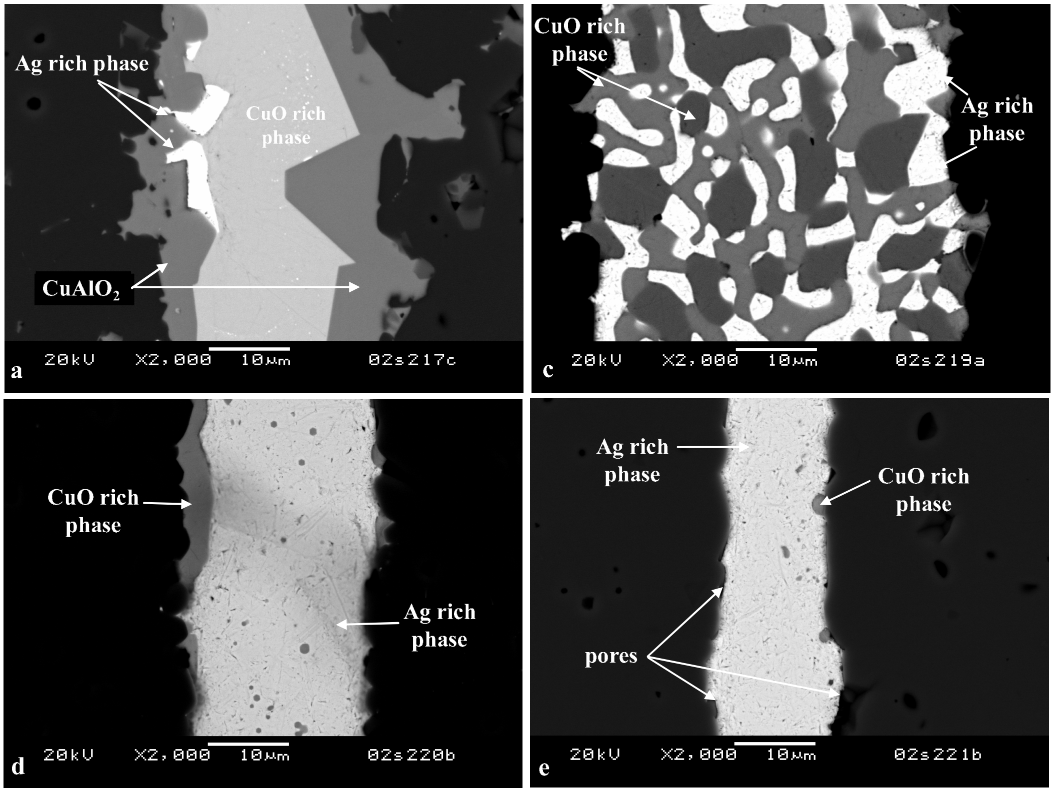

Figure 2 Cross-sectional SEM micrographs of braze/alumina interfaces: (a) CA8020, (b) CA6931, (c) CA6040, and (d) CA0199.

Conclusions. Although wetting is greatly meliorated by the addition of CuO to silver, it appears that the presence of a continuous phase of CuO either within the interior of the braze, as in the cases of CA8020 and CA6931, or along the braze/alumina interface (CA6040) is deleterious to the strength of the joint. Only when the CuO nucleates and grows as a discrete phase at the interface with the substrate are wetting behavior and joint strength enhanced simultaneously and the strength of the RAB joint approaches that of monolithic alumina. Means of further improving the CuO-Ag RAB braze might include: (1) increasing the wettability of silver on the discrete interfacial CuO phase that was found to form in the CA0199 specimen, (2) modifying the braze composition or processing conditions such that a finer size, more closely spaced dispersion of CuO particles nucleates on the surface of the alumina, and (3) investigating whether a $CuO-Al_2O_3$ diffusion zone is established in eutectic or near-eutectic braze compositions and what effect this might have on wetting behavior and bond strength.

Oxygen Separation

Experimental. Mixed ionic/electronic conducting (MIEC) oxides, such as $SrFeCo_{0.5}O_x$, $BaCeO_3$, and $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$, are a class of ceramics that contain ionic and electronic carriers in high enough concentration that both forms of charge conduction are exhibited at high level and can form the basis of an ion transport membrane for use in oxygen gas separation, partial hydrocarbon oxidation, and waste reduction and recovery [6]. As an example, this type of technology offers the potential to separate oxygen from air with far greater efficiency and at one-third lower cost than present-day cryogenic processing. And unlike cryo-separation, oxygen transport membranes operate at high temperature, making them ideally suited for direct integration with coal gasification plants [7]. For our studies, lanthanum strontium cobalt ferrite, $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ (LSCoF), was selected as the model MIEC oxide on which to carry out the initial RAB joining experiments. LSCoF pellets were fabricated by sintering an isostatically compressed compact of the oxide in air at 1250°C for two hours. Braze pellets were again fabricated by mixing copper and silver powders in the appropriate ratios to yield the following five target compositions: 100%Ag, 1%CuO/99%Ag, 2%CuO/98%Ag, 4%CuO/96%Ag, and 8%CuO/92%Ag (respectively labelled: A100, CA0199, CA0298, CA0496, and CA 0892).

Results. Contact angle measurements of the molten Ag-CuO brazes on polished LSCoF are shown as a function of temperature in Figure 3. As predicted by the Ag-CuO phase diagram [8], all of the brazes melt above 900°C. With the exception of pure silver, all of the brazes displayed wetting with the LSCoF. As indicated in the figure, the wetting behavior of this series of brazes on LSCoF appears to be invariant of temperature, but quite sensitive to CuO content, improving dramatically with increasing amounts of the oxide.

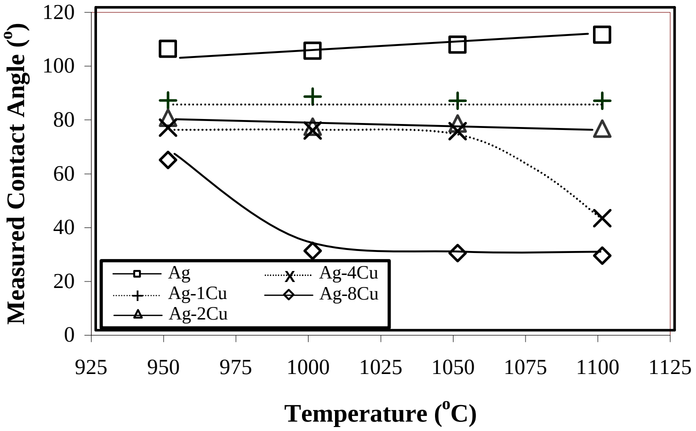

Figure 3 Contact angle of Ag-CuO brazes on $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ in air as a function of temperature. The hold time at each soak temperature was fifteen minutes.

Back scattered electron images of the four Ag-CuO wetting specimens, shown on the next page in Figures 4(a) – (d), suggest that this compositional dependence is related to the concentration and morphology of CuO along the braze/LSCoF interface. The bulk region of the braze in each sample consists of small ~1 – 5μm diameter particles of CuO surrounded by a matrix of pure silver, which is not surprising considering the high silver content of the brazes and the fact that CuO is not soluble in silver at room temperature. Along the braze/LSCoF interface in each specimen, CuO appears to preferentially wet the substrate, forming a thin but distinct zone within the braze that exhibits one of two microstructural patterns. In the case of the two brazes that contain 2% CuO or less, the interface is decorated with discrete, ~1μm half lens-shaped precipitates of CuO. The distance separating these precipitates appears to be greater in CA0199 than in CA0298. In the higher CuO content specimens, a nearly continuous band of CuO is found in contact with the former LSCoF surface, occasionally disrupted by a small islands of pure silver. The oxide band is thickest in the CA0892 specimen, which contains the highest CuO concentration of the five brazes investigated in this study. Note that in all of the samples in Figure 4, evidence of Ag and CuO infiltration into the substrate can be observed, which occurs presumably via interconnected surface porosity. When correlated with the results of the wetting experiments in Figure 3, these micrographs indicate that a higher coverage of CuO on the LSCoF surface improves the wetting of the Ag-CuO braze. It is likely that the two different CuO morphologies observed in Figures 4(a) – (d) are the direct result of the miscibility gap in the Ag-CuO phase diagram [8].

Conclusions. Contact angle experiments conducted on LSCoF substrates demonstrate that the wetting behavior of the braze improves significantly with increasing amounts of copper oxide. Microstructural analysis indicates that this phenomenon is associated with the formation of a nearly continuous CuO layer that wets and covers the braze/LSCoF interface. In high electrical current testing conducted in air at 750°C (not discussed here), a junction between the 4% CuO braze and LSCoF displayed a very low initial value of area specific resistance, which remained stable during the duration of the initial 100 hr, 1.5A d.c. current age test. Metallographic comparison between the electrically tested junction and one in the as-brazed condition indicated no significant microstructural differences, suggesting the potential use of the braze as a high temperature electrical contact material.

Solid Oxide Fuel Cells

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) were employed as the model SOFC electrolyte membrane/structural metal system in this study. Bilayer coupons were fabricated by traditional tape casting and co-sintering techniques and measured nominally 600μm in thickness, with an average electrolyte thickness of ~8μm. As-received 12mil thick FeCrAlY sheet was sheared into 2cm square pieces for the wetting experiments, polished lightly on both sides with 1200 grit SiC paper, and ultrasonically cleaned in acetone for 10 minutes. Flat washer-shaped specimens measuring 4.4cm in diameter with a concentric 1.5cm diameter hole were punched from the 12mil sheet and the surfaces of these were polished and cleaned in the same manner prior to use in the joining experiments. The braze pellets employed in the wetting experiments were again fabricated by mixing and cold pressing copper and silver powders in the appropriate ratios to yield the same target compositions used in the LSCoF experiments. Wetting angles were again measured at several different temperatures in air using the sessile drop technique.

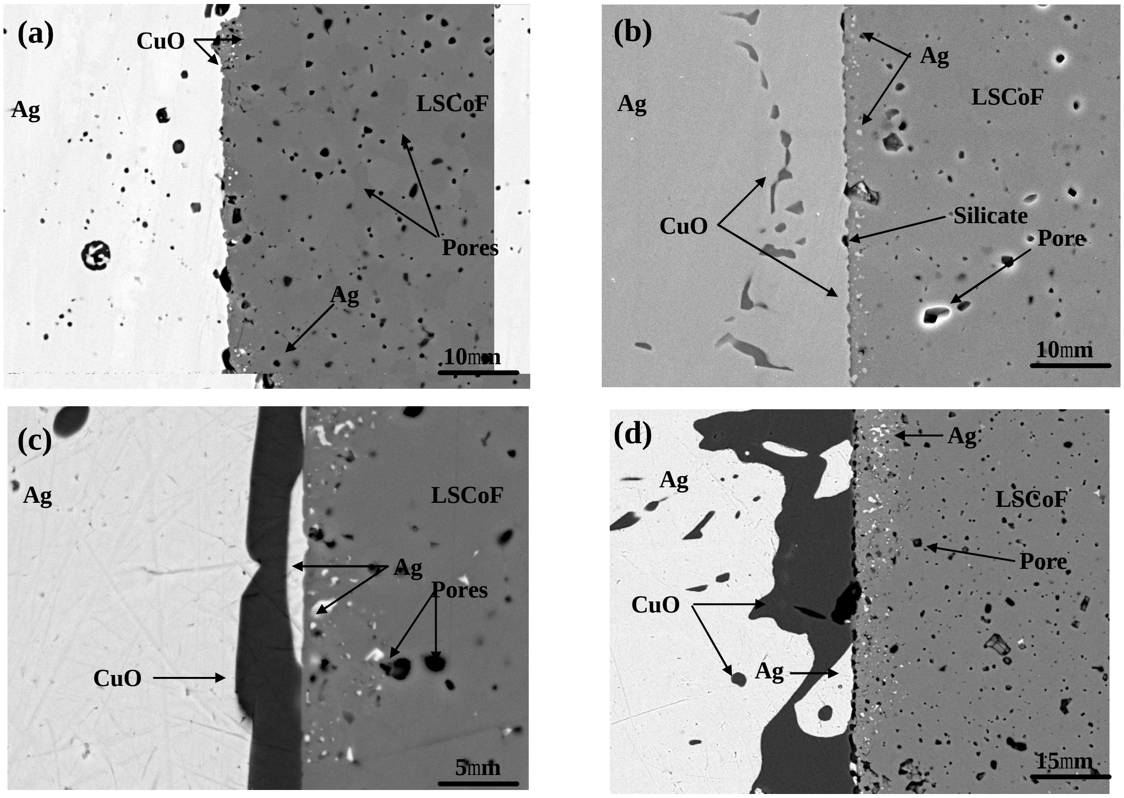

Figure 4 Cross-sectional SEM micrographs of braze/LSCoF interfaces: (a) CA0199, (b) CA0298, (c) CA0496, and (d) CA0892. Each wetting specimen was heated in air at a final soak temperature of 1100°C.

Joining samples were prepared by placing a piece of previously fabricated Ag-Cu braze foil between a FeCrAlY washer specimen and the YSZ side of a 2.5cm diameter bilayer coupon, heating the combination in air to 1050°C, and holding at this temperature for 30min. The braze foil was synthesized by diffusion bonding copper and silver foils of the same areal dimension, but with thicknesses appropriate to achieve the target braze compositions discussed above. Diffusion bonding was conducted in an Ar/4% H_2 cover gas at 720°C for 10hrs under a static load of ~½ psi after which the foil was rolled to a thickness of 0.07mm and cut into 2mm wide strips for use in joining.A rupture strength test was developed to facilitate quantitative comparison of the RAB seal joint strengths. On the next page in Figure 5 is a photo of the test specimens, prior to and after joining, and a schematic of the rupture test equipment. The joining sample is clamped into the test fixture and the air pressure behind the joined bi-layer disk is slowly increased until the seal or the disk breaks. A series of six specimens was tested for each joining condition.

Results. Plotted in Figure 6 are the contact angles that each braze forms on 5YSZ and fecralloy in air at 1050°C and the rupture strength of the corresponding joint. The results show that rupture strength improves significantly with increasing Ag content, whereas wettability, which is the inverse of contact angle, moves in the opposite direction. Thus, the specimen joined using the braze containing the highest level of CuO (CA6931) displays excellent wetting on 5YSZ and fecralloy, but has an average rupture strength of only 23 psi while the specimen brazed with the lowest CuO-containing alloy (CA0199) exhibits moderate-to-poor wetting on the two substrates but displays greater than a four-fold increase in rupture strength of 109 psi. In fact, the CA0199 seal does not fail during testing but instead the bilayer disc ruptures leaving behind a ring of ceramic still joined to the metal washer as shown in Figure 6. The CA6931 braze specimen on the other hand fails along the interface between the FeCrAlY and the braze. This 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. Upon examination of the joining specimens by SEM, it was apparent that significant differences in their interfacial microstructures likely account for the observed dependences of wetting behavior, rupture strength, and mode of specimen failure on CuO content in the braze.

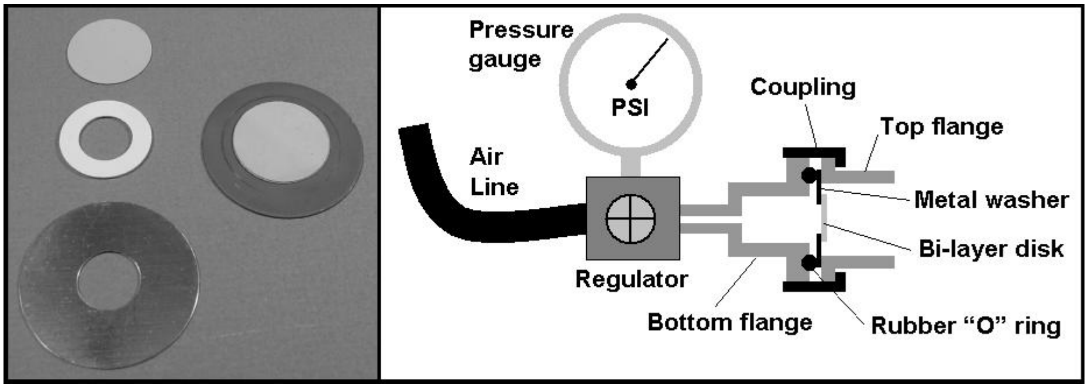

Figure 5 Far left: Components of rupture strength test specimen; from bottom, FeCrAlY washer, braze foil ring, bi-layer disk. Middle: Assembled test specimen. Right: Rupture strength test schematic.

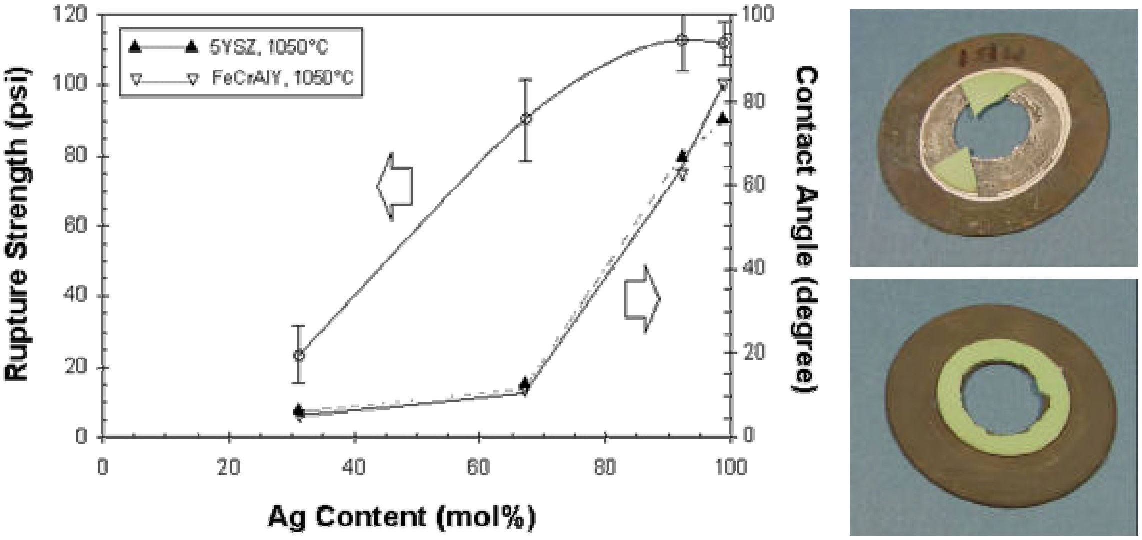

Figure 6. Left: Room temperature rupture strength and contact angle as a function of Ag content. Right: The CA6931 (top) and CA0199 (bottom) joining samples after rupture testing.

SEM images of the as-joined RAB specimens are shown in Figure 7. As seen in Figure 7(a), the sample that was joined using the CA6931 braze exhibits an extensive CuO phase that covers the 5YSZ faying surface of the joint and a thick copper alumunium oxide reaction zone along the braze/FeCrAlY interface. This zone results from an interaction between the CuO in the braze and the alumina scale that forms on the surface of the metal and gives rise to two product phases: a continuous mixed-oxide solid solution $CuO-Al_2O_3$ region that is decorated with $CuAlO_2$ crystallites. Very little silver is observed along either interface with the braze. Instead it is found trapped as discrete particles in the bulk of the braze. It is the continuous interfacial oxide phases that account for the excellent wetting characteristics of the CA6931 braze on both faying surfaces. These results are similar to those observed inthe $Ag-CuO/Al_2O_3$ and $Ag-CuO/(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ braze/substrate systems. Likewise, it is these brittle phases, which exhibit poor coefficient of thermal expansion matching with the 5YSZ and FeCrAlY, that contribute to the low rupture strengths observed in the corresponding joining specimens.

At the other extreme, the braze/5YSZ interface in the CA0199 specimen shown in Figure 7(d) is covered by a nearly continuous layer of pure silver, with discrete micron-size CuO particles occasionally found on the 5YSZ faying surface. The silver acts essentially as a matrix for the CuO particulate found in the bulk of the braze as well. Along the FeCrAlY interface in this joining specimen is a continuous ½ - 1µm thick alumina scale, as was observed in the CA6931 specimen, that includes a small amount of

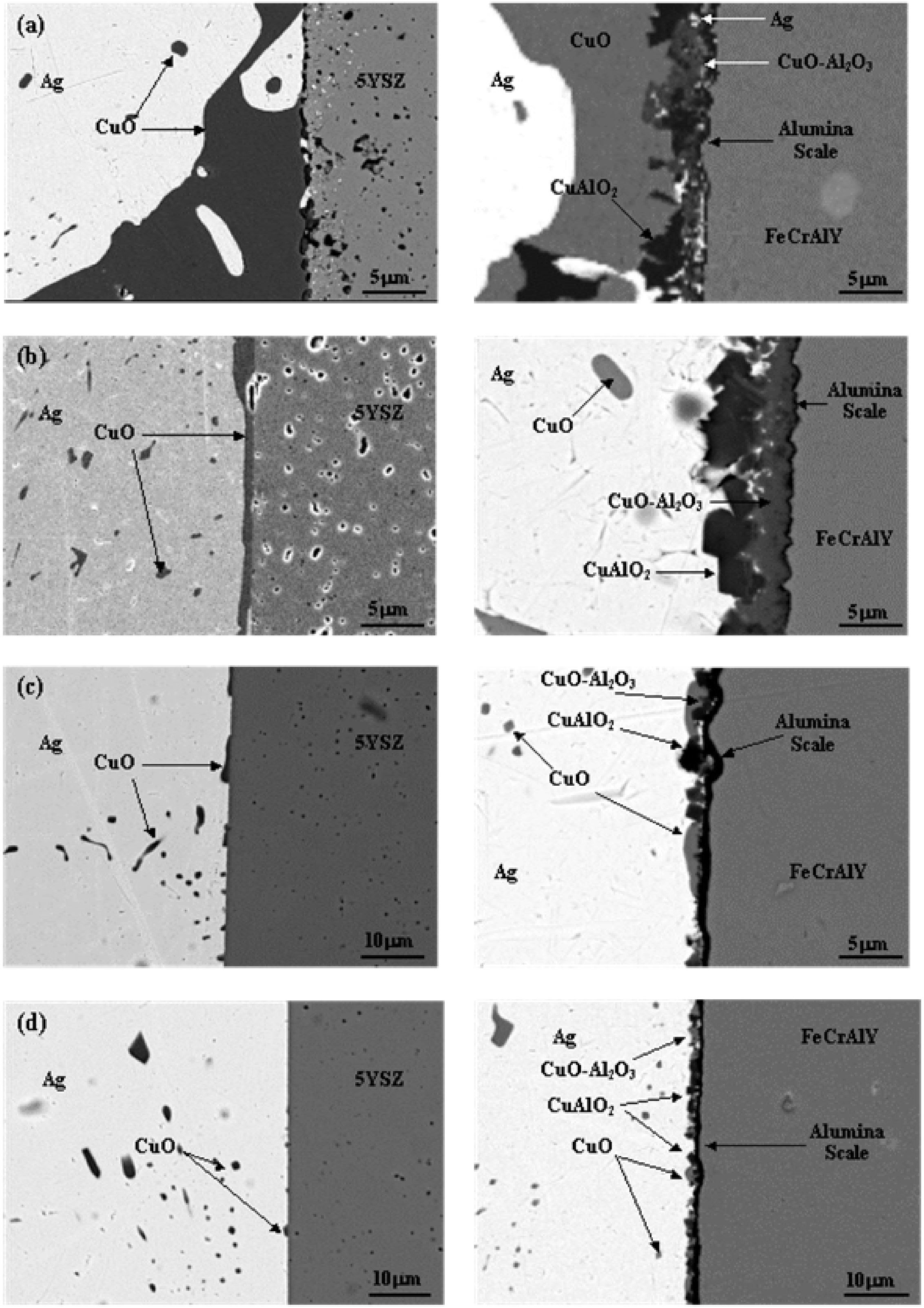

Figure 7 Cross-sectional SEM micrographs of braze/5YSZ interfaces (on the left) and braze/FeCrAlY interface (on the right) of: (a) CA6931, (b) CA3169, (c) CA0298, and (d) CA0199.

iron and chromium, ~5 mol% and 3 mol% respectively. Again, an apparent alloying reaction takes place forming regions of CuO-Al_2O_3 contiguous to the metal scale. In this case however, the reaction zone is thin and patchy and is frequently interrupted by discrete islands of silver and CuO and occasional $CuAlO_2$ crystallites measuring roughly 1 - 3µm in diameter. Because a continuous CuO or mixed-oxide reaction phase does not form on either interface in this specimen, the wetting angle of the braze is larger than was observed in the high CuO content braze. Conversely however, the lack of a thick, continuous interfacial oxide phase leads to a much higher average joint strength. As seen in Figures 7(b) and (c), the two intermediate braze compositions display interfacial microstructures with characteristics that lie between the two extremes, i.e. thinner or discrete interfacial oxide phases, and subsequently exhibit more moderate wetting and joint strength behaviors.

Conclusions. Reaction air brazing is a promising method of sealing the active ceramic membranes and metallic structural components used in solid oxide fuel cells. Wetting experiments conducted on protoypical faying surfaces for these devices, 5YSZ and FeCrAlY, indicate that increasing amounts of copper oxide in the braze significantly improve its wetting behavior on both substrates. In general, the observed decrease in contact angle is related to increasing coverage of the faying surface by CuO, in the case of 5YSZ, or by a CuO-Al_2O_3 reaction zone along the braze/FeCrAlY scale interface. Despite the improvement in wetting due to the addition of CuO, the resulting rupture strengths of these brazed joining specimens is significantly poorer than those of their low-CuO counterparts. Our microstructural results suggest that the presence of a thick, continuous oxide phase along the interface between the braze and the 5YSZ or the FeCrAlY degrades joint strength. Only when the CuO or mixed-oxide forms as a discrete phase along these respective interfaces does the strength of the RAB joint increase substantially.

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