

# Development of a New Ceramic-to-Metal Brazing Technique for Oxygen Separation/Generation Applications

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## Manuscript

Mixed ionic/electronic conducting (MIEC) oxides, such as  $\text{SrFeCo}_{0.5}\text{O}_x$ ,  $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$ , and  $\text{BaCeO}_3$ , 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, typically at temperatures in excess of  $500^\circ\text{C}$ . Because of their properties, the demand for MIEC oxide-based devices has grown considerably. The value of the present-day market is conservatively estimated to be \$3 billion, with particularly high growth rates in automotive systems, environmental control, and energy generation technology where the devices are employed primarily as amperometric chemical sensors [1]. Solid oxide fuel cells (SOFCs) represent an even larger potential market than that established for chemical sensors. These electrochemical devices convert the chemical energy from fossil fuels into electricity in a highly efficient manner and may find application in a number of energy generation applications, from auxiliary power units in automobiles and trucks to megawatt generators helping to power the electrical grid. MIEC oxides are employed in SOFCs as electrodes, carrying out charge separation and charge transfer at the electrolyte/electrode interface, and as agents to increase the electrocatalytic activity of the electrodes with respect to fuel reformation [2]. If the ionic conductivity of a given MIEC oxide is high enough, it can be employed in electrically driven oxygen-ion transport membranes for oxygen gas separation, partial hydrocarbon oxidation, and waste reduction and recovery [3]. MIEC oxide-based membrane technology offers the potential to separate oxygen from air with far greater efficiency and at one-third lower cost than the cryogenic processing technology used today. And unlike cryo-separation, oxygen transport membranes operate at high temperature, making them ideally suited for direct integration with coal gasification plants [4].

Underlying the excitement over the potential of MIEC oxides is the engineering challenge of how to effectively incorporate these materials into practical devices. Opportunities to fully exploit the unique properties of these advanced ceramics depend in large part on our ability to develop reliable joining techniques. However, because MIEC-based device technology is essentially restricted to high temperature operation, only a limited number of joining technologies are applicable. In a review of ceramic-to-metal joining technology [5], Greenhut discusses a number of joining techniques, of which two, glass joining and active metal brazing, are most suitable for bonding a MIEC oxide to a metallic structural component. Figure 1 illustrates an example of this type of MIEC ceramic-to-metal bond in a portable oxygen generator being developed for medical application. The device operates nominally at  $800^\circ\text{C}$  and is likely to experience numerous thermal cycles over its lifetime, on the order of several thousand hours, during which it must remain hermetically sealed, structurally rugged, and chemically stable.

While glass bonding is potentially a viable joining solution, the maximum operating temperature that a glass joint may be exposed to is limited by the softening point of the glass. At present, high temperature glasses with appropriately matching coefficients of thermal expansion are limited to a narrow range of compositions within the borate-doped aluminosilicate family. These glasses typically display signs of devitrification within the first few hours of exposure at operating temperature [6]. As these glasses begin to crystallize, their carefully engineered thermal expansion properties change significantly, which ultimately limits the number of thermal cycles and the rate of cycling at which the joints are capable of surviving [7].

The second ceramic-to-metal joining technique, active metal brazing, utilizes a filler metal that when heated above its liquidus temperature, will flow and fill the gap between the two joining pieces by capillary action. Unlike metal-to-metal brazes, this particular family of braze alloys contains one or more reactive metals, often titanium, which will chemically reduce the ceramic at the interface with the braze, greatly improving wetting and adherence between the two materials [8,9].

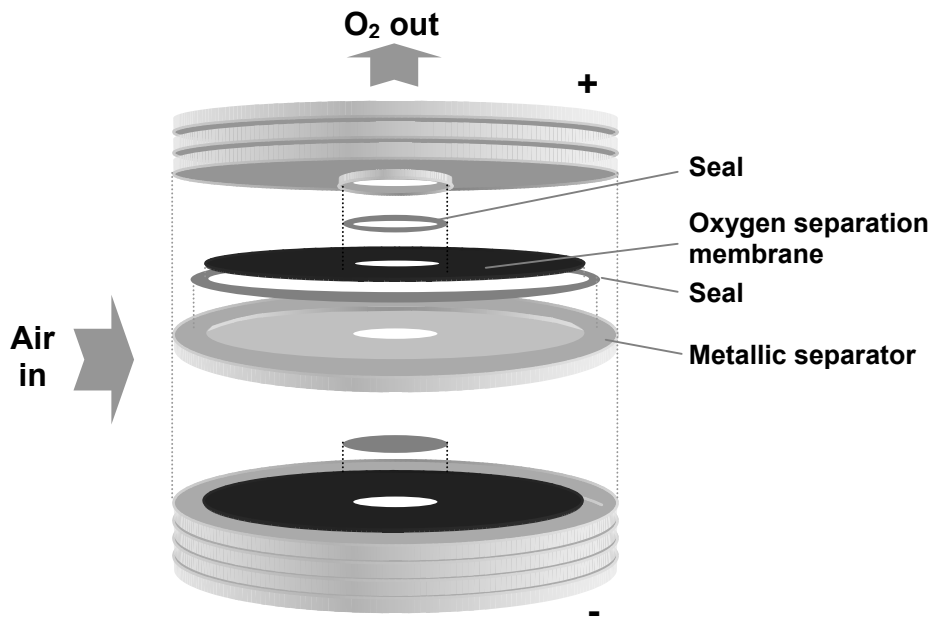


Fig. 1 A schematic drawing of a MIEC oxide based oxygen generator (electrical interconnection not shown).

There are, however, at least two problems with using active metal brazing for the fabrication of solid-state electrochemical devices: 1) the complete oxidation of the active species in the braze during high temperature operation of the device will lead to rapid deterioration of the joint at the ceramic/braze metal interface [10,11] and an eventual loss in hermeticity and 2) exposure of the entire device to a reducing atmosphere at a temperature greater than  $\sim 800^{\circ}\text{C}$ , typical processing conditions for active metal brazing, has been found to be too demanding for many of the oxide materials employed in these devices. MIEC oxides will tend to reduce during the joining operation, which can cause phase separation in the oxide. An example of this is shown in Figure 2, which displays a  $(\text{La}_{0.8}\text{Sr}_{0.2})\text{FeO}_3$  specimen that after vacuum brazing with a commercial active metal gold braze, Nicro ABA, began to exhibit signs of surface spallation and eventually complete braze detachment after only a few hours exposure to ambient room temperature air. Moisture in the air caused the hydration of excess  $\text{La}_2\text{O}_3$  in the sample, which had formed because of reduction and phase separation in the parent oxide during the brazing operation. Regardless of whether or not the braze remains intact, the oxide reduction phenomenon ultimately results in a severe loss in device performance due to the irreversible deterioration of the functional ceramic [12]. To overcome these difficulties, an alternative reactive brazing approach was developed, referred to as reactive air brazing or RAB.

Since joining must be carried out in an oxidizing environment at a temperature greater than the device operating temperature, nominally  $800^{\circ}\text{C}$ , the bond that eventually forms will take place between the functional ceramic component and an oxide scale that grows on the structural metallic forms under these conditions. The objective in RAB is to reactively modify one or both oxide faying surfaces with a compound that has been at least partially dissolved in a noble metal solvent, e.g. silver, gold, or platinum, such that the newly formed surface is readily wetted by the remaining molten filler material. In many respects, this concept is similar to active metal brazing, except that the joining operation can be conducted in air and the final joint should 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-TeO<sub>3</sub>, and Pt-Nb<sub>2</sub>O<sub>5</sub> [13]. Schüler et al. [14] were the first to recognize that the Ag-CuO system could potentially be exploited to bond ceramic components in air, reporting the successful joining of alumina using a 99 mol%Ag-1 mol% CuO braze. Our interest is in investigating whether this system is suitable for air brazing functional ceramic-to-metal joints, such as those needed in practical electrochemical devices. In an effort to begin answering this question, a series of sessile drop measurements were performed to determine the wetting behavior of the different Ag-CuO-based braze compositions on a prototypical materials set for a portable oxygen generating device. Microstructural and chemical analyses of the braze/substrate interfaces within the wetting specimens were also conducted to determine the nature of the wetting in these samples. The results from these studies and from initial RAB joining experiments are reported below.

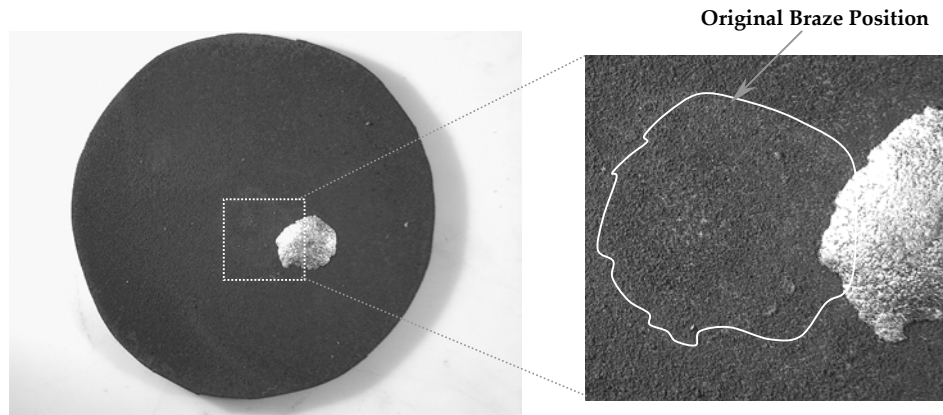


Figure 2 Spallation of a Nioro ABA braze drop from the surface of a  $(\text{La}_{0.6}\text{Sr}_{0.4})\text{FeO}_3$  specimen. The oxide specimen has undergone reduction and phase separation. The resulting  $\text{La}_2\text{O}_3$  at the substrate surface hydrates and swells in ambient air causing separation between the braze and the substrate. As seen at high magnification, the braze is fully detached from its original position on the substrate and is simply lying on the surface for comparison.

## Experimental

### Copper Oxide-Silver Based Brazing

Past investigations of the Ag-CuO system [15] have determined that there two invariant points in the Ag-CuO phase diagram from which new braze compositions could be developed: a monotectic reaction at  $964\pm 3^\circ\text{C}$ , where CuO and a liquid  $L_2$  coexist with a second liquid phase  $L_1$  at a composition of 30.65 mol.% Ag and 2) a eutectic reaction at  $932\pm 3^\circ\text{C}$ , where Ag and CuO 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. Although Schüler et al. [14] did not conduct contact angle measurements in their experiments with the Ag-CuO braze, Meier et al. [16] demonstrated in a previously series of sessile drop experiments, conducted in inert atmosphere, that the contact angle between silver and alumina is greatly reduced by small additions of CuO. The improvement in wetting apparently results because of an increase in the oxygen activity of the melt and the formation of an interfacial compound,  $\text{CuAlO}_2$  [17-19]. Furthermore, a recent phase study on the CuO-TiO<sub>2</sub> system demonstrates that this binary exhibits a eutectic reaction at  $919^\circ\text{C}$  with a wide compositional range centered on the eutectic composition of  $X_{\text{TiO}_2} = 16.7\text{mol}\%$  [20], suggesting to us that the addition of titania to a Ag-CuO braze may improve its wetting characteristics by modifying the CuO phase as the braze is heated to its molten state. Consequently, the use of TiO<sub>2</sub> as a wetting agent was also explored in this investigation.

### Materials

$(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$  (LSCoF) and feralloy were selected as the model joining system on which to carry out the initial RAB development effort. LSCoF was chosen because it is a well-known MIEC with excellent ionic and electronic transport properties, making it a strong candidate for use in commercial oxygen generators [21]. In addition, it has been demonstrated that this oxide will undergo phase separation and cracking under typical active metal brazing conditions [22], making RAB essentially the only alternative to glass sealing. LSCoF pellets were fabricated by uniaxially compacting the oxide powder (99.9% purity; Praxair Specialty Ceramics, Inc.) in a carbon steel die under 7ksi of pressure. The cold pressed pellets were further densified by cold isostatic pressing at 20ksi, followed by sintering in air at  $1250^\circ\text{C}$  for four hours. The final pellets measured approximately  $1\frac{1}{4}$ " in diameter by  $\frac{1}{8}$ " thick, with an average density of 96% of theoretical. The pellets were polished on one face to a  $10\mu\text{m}$  finish using successively finer grit diamond paste, cleaned with acetone and rinsed with propanol, air dried, and finally heated in static air to  $600^\circ\text{C}$  for four hours to burn off any residual organic contamination.

Feralloy (22% Cr, 4.8% Al, 0.3%Si, 0.3%Y, bal. Fe) was chosen as the metal component for joining because it is a low-cost, commercially available ferritic stainless steel of the type that is being strongly considered for use in SOFCs and other solid state electrochemical devices. Additionally, this alloy forms a protective aluminum oxide scale, which gives it excellent oxidation resistance properties at  $800^\circ\text{C}$  and which is also one of the reactants required for the RAB concept described above.

As-received 20 mil thick fecralloy sheet was sheared into 1" square coupons, which were polished on one side to a 10 $\mu$ m finish. The samples were flushed with de-ionized water to remove the polishing grit and ultrasonically cleaned in acetone for 10 minutes, then rinsed with propanol and dried in a stream of warm air. To form the reactive alumina layer, the samples were pre-oxidized at 1050°C for 2hrs in static air. The average thickness of the alumina scale formed on the fecralloy in this manner was ~0.6 $\mu$ m.

As listed in Table I, eight different braze compositions were formulated by dry mixing the appropriate amounts of silver (99.9%, 0.75 $\mu$ m average particle diameter; Alfa Aesar), copper (99%, 2.5 $\mu$ m average particle diameter; Alfa Aesar), and titanium hydride powders (-325 mesh, Alfa Aesar). The copper and TiH<sub>2</sub> oxidize in-situ as the braze is heated, respectively forming CuO and TiO<sub>2</sub>. For the wetting studies, the mixtures were cold pressed into pellets measuring approximately 7mm in diameter by 10mm thick. To prepare braze pastes for the joining experiments, a liquid binder (BX-18, Ferro Corp.) was added to the dry powder mixture in a 1:5 weight ratio and the resulting blend was thoroughly mixed on a three-roll mill. As formed, the paste was found to have acceptable thixotropic properties for the joining experiments.

Table I. Target compositions of the brazes investigated in this study

Braze I.D.	Ag Content (in mole%)	CuO Content (in mole%)	TiO <sub>2</sub> Content (in mole%)
Ag	100	0	0
Ag-½Ti	99.5	0	0.5
Ag-1Cu	99	1	0
Ag-1Cu-½Ti	98.5	1	0.5
Ag-2Cu	98	2	0
Ag-2Cu-½Ti	97.5	2	0.5
Ag-4Cu	96	4	0
Ag-4Cu-½Ti	95.5	4	0.5

### Testing and Characterization

Wetting experiments were performed in a static air box furnace furnished with a large quartz window on the front door through which the heated specimen could be observed. A high speed video camera equipped with a zoom lens was used to record the wetting specimen during an entire heating cycle. Each braze pellet was placed on the polished side of the LSCoF pellet or pre-oxidized fecralloy substrates and heated at 30°C/min to 900°C, at which point the heating rate was reduced to 10°C/min. The furnace continued heating until it reached the first set point, 950°C, where the temperature remained for fifteen minutes, then resumed heating. In this way, the contact angle between the braze and substrate was allowed to stabilize for measurement at several different soak temperatures, 950°C, 1000°C, 1050°C, and 1100°C, during one heating cycle. Using Videum™ software (Winnov, Inc.), select frames from the videotape were converted to computer images, from which the wetting angle between the braze and substrate could be measured and correlated with the temperature log for the heating run.

Microstructural analysis of the wetting specimens was performed on polished cross-sectioned samples, by optical microscopy and by examination with a JEOL JSM-5900LV scanning electron microscope (SEM). The SEM is equipped with an Oxford energy dispersive X-ray analysis (EDX) system, which employs a windowless detector for quantitative detection of both light and heavy elements. To avoid electrical charging of the samples in the SEM, they were carbon coated and grounded. Elemental profiles were recorded across joint interfaces in the line-scan mode.

## **Results and Discussion**

Contact angle measurements of the molten Ag-CuO-TiO<sub>2</sub> brazes on polished LSCoF are shown as a function of temperature in Figure 3. Within a 10 - 20°C difference, melting of the binary silver-copper oxide braze compositions initiated at the temperature predicted by the Ag-CuO phase diagram, indicating that the CuO and Ag are not impeded from reaching equilibrium by diffusion or solid state reaction kinetics. The fifteen minute hold time used in taking the sessile drop measurements appeared to be long enough for interfacial equilibrium to be established; in all cases the contact angle reached

its stable value within five minutes. With the exception of the Ag-4 mol% CuO composition, the contact angles between the different brazes and the LSCoF surface are essentially invariant with respect to temperature over the 950 – 1100°C range. The wetting angle curves appear to fall into two distinct categories, those which exhibit little or no wetting and those which wet quite well, suggesting that a minimum concentration of CuO is required for wetting and that this minimum can be reduced by the introduction of TiO<sub>2</sub> to the braze. The two control compositions, Ag and Ag-0.5 mol% TiO<sub>2</sub>, display no wetting with the ceramic. It is not until at least 4 mol% CuO is added to the binary Ag-CuO braze that sufficient wetting takes place, and this only occurs at 1100°C. However, when 0.5 mol% TiO<sub>2</sub> is added, the 2 mol% CuO braze wets the LSCoF at essentially the same contact angle as the best binary braze and does so at a temperature which is at least 150°C lower. No additional improvement in wetting occurs when the CuO content of this ternary braze is doubled.

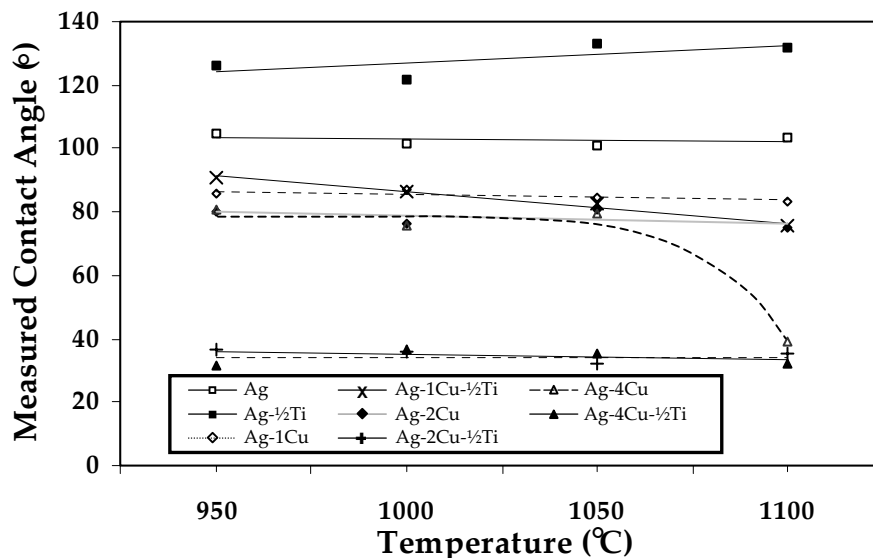


Figure 3 Contact angle of Ag-CuO-TiO<sub>2</sub> brazes on (La<sub>0.6</sub>Sr<sub>0.4</sub>)(Co<sub>0.2</sub>Fe<sub>0.8</sub>)O<sub>3</sub> in air as a function of temperature. The hold time at each soak temperature was fifteen minutes.

Shown in Figures 4(a) – (d) are back scattered electron images of the four braze compositions which exhibit the best wetting on the LSCoF substrate: Ag-2Cu, Ag-2Cu-½ Ti, Ag-4Cu, and Ag-4Cu-½ Ti. Each of these wetting specimens was heat treated under the conditions described for the in-situ wetting experiments, ultimately reaching a final soak temperature of 1100°C. It is apparent from all of the micrographs that the majority phase in the bulk of the braze is pure silver. Fine precipitates of CuO on the order of 1 – 5µm in size are typically found in the silver matrix away from the interface with the LSCoF. If the micrographs are paired, Figures 4(a) and (c) and Figures 4(b) and (d), the effect of the TiO<sub>2</sub> addition is readily seen. In the two cases where no titania was added, Ag-2Cu and Ag-4Cu, there is a thin interfacial zone where the CuO appears to preferentially wet the LSCoF. In Figure 4(a), which displays the Ag-2Cu braze, the CuO decorates the interface with the MIEC substrate, forming discrete, ~1µm half lens-shaped precipitates. An occasional silicate particle on this interface can also be found and is presumed to be an impurity introduced into the LSCoF powder during milling. The Ag-4Cu braze in Figure 4(c) exhibits a nearly continuous CuO phase along the braze/LSCoF interface which is occasionally disrupted by a short band of pure silver. Note in both figures signs of braze infiltration into the substrate, presumably via interconnected porosity, up to a depth of ~2µm.

Referring to Figure 3, our results suggest that the formation of a continuous layer of interfacial CuO improves the wetting of a Ag-CuO braze with LSCoF. It is possible that the two different CuO morphologies observed in Figure 4 are the direct result of the miscibility gap in the Ag-CuO phase diagram [15]. At 1100°C both brazes will form a single phase liquid. However, according to the Ag-CuO phase diagram, as the Ag-4Cu braze is cooled to ~1025°C, the system enters a miscibility gap. Below 1025°C, two liquids are formed, a minority phase which is rich in CuO and a majority phase which is CuO-poor. Because the phases are immiscible, it is expected they will segregate, with the CuO-rich liquid preferentially migrating to and wetting the LSCoF because of its higher oxide content and therefore lower expected interfacial energy with the MIEC oxide

substrate. Upon further cooling to the monotectic temperature, 964°C, CuO will begin to precipitate from this liquid, nucleating at the interface with LSCoF. As it does so, the silver-rich liquid becomes further enriched with silver. At the eutectic temperature, solid CuO and Ag will simultaneously nucleate from the remaining liquid, presumably heterogeneously on the surface of the previously formed CuO layer which coats the boundary with LSCoF. The Ag-2Cu braze, on the other hand, does not enter a miscibility gap when cooled. Just below 964°C, a small amount of proeutectic CuO precipitates out of solution, nucleating heterogeneously at the interface with LSCoF. Upon cooling to the eutectic temperature, solid Ag and CuO form simultaneously from the eutectic liquid.

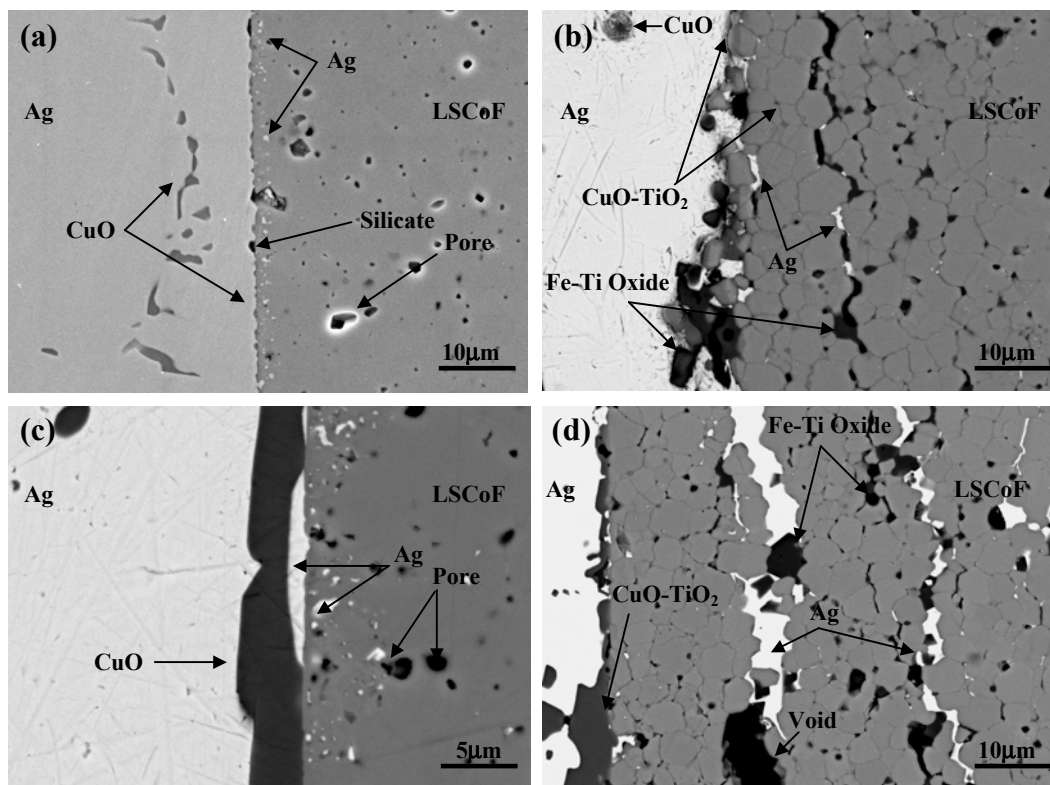


Figure 4 Cross-sectional SEM micrographs of braze/LSCoF interfaces: (a) Ag-2Cu, (b) Ag-Cu- $\frac{1}{2}$ Ti, (c) Ag-4Cu, and (d) Ag-4Cu- $\frac{1}{2}$ Ti. Each wetting specimen was heated in air at a final soak temperature of 1100°C.

As is obvious from Figures 4(b) and (d), the addition of 0.5 mol% TiO<sub>2</sub> significantly changes the interfacial microstructure of the braze/LSCoF couple. In both cases, Ag-2Cu- $\frac{1}{2}$ Ti and Ag-4Cu- $\frac{1}{2}$ Ti, virtually no titanium was found in the bulk braze, even within the CuO precipitates. However, the samples exhibit a large affected zone, approximately 35µm and 50µm respectively, which contain a number of titanium-based reaction products. As expected, the CuO and TiO<sub>2</sub> form a low-melting eutectic (~919°C). This liquid segregates to the interface with the LSCoF, reacting with substrate to form an iron-cobalt-titanium oxide phase and a copper oxide-rich phase that contains significant levels of lanthanum and strontium. Unexpectedly, however, the CuO-TiO<sub>2</sub> liquid attacks the LSCoF intergranularly, forming a low-melting complex oxide phase between grains, which displays high concentrations of copper, titanium, iron, and cobalt. Approximately 15 µm into the oxide substrate of the Ag-2Cu- $\frac{1}{2}$ Ti sample is a nearly continuous band of oxide running parallel to the braze/LSCoF interface. This oxide band contains Co, Fe, Cu, and Ti in roughly a 2:2:1:1 molar ratio. The EDS data suggests that the LSCoF grains adjacent to this band have become enriched in lanthanum and strontium, although the mechanism by which this occurs is not known, e.g. by dissolution or by micro-scale phase separation. The oxide band, which spans from one layer of LSCoF grains to the next, is occasionally disrupted by a short band of silver. The formation of reaction zones within the Ag-4Cu- $\frac{1}{2}$ Ti sample is even more extreme. Two continuous bands form which are wider than the one observed in the lower CuO-content

braze. In addition, a significant amount of silver has infiltrated these gaps that again appear to form via grain boundary melting and separation. Evidence of grain separation is apparent from the number of large voids that populate the two bands.

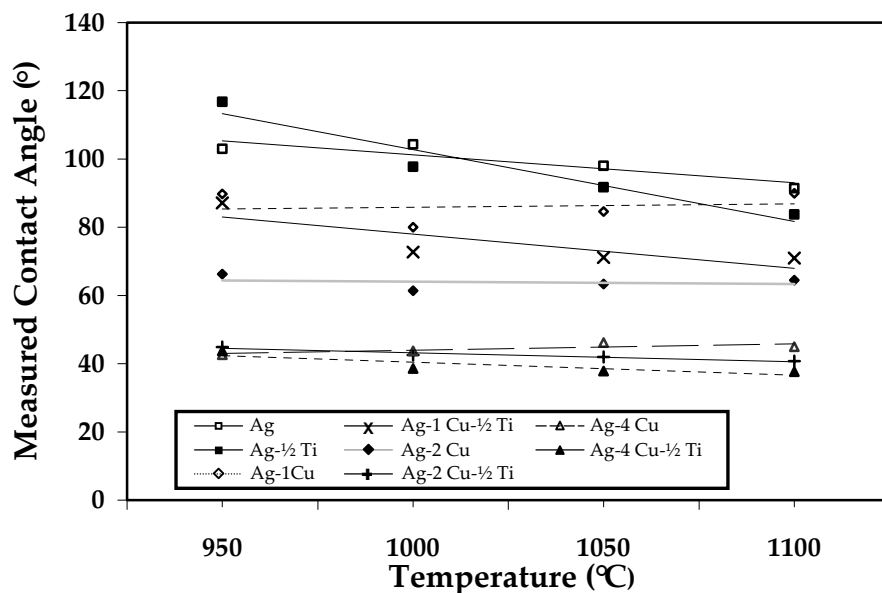


Figure 5 Contact angle of Ag-CuO-TiO<sub>2</sub> brazes on the alumina scale of pre-oxidized fccalloy in air as a function of temperature. The hold time at each soak temperature was fifteen minutes.

Figure 5 shows the effect of composition and temperature on the contact angle between the Ag-CuO-TiO<sub>2</sub> brazes and the alumina scale surface of pre-oxidized fccalloy. The brazes appeared to melt in the same manner observed in the LSCoF experiments and again reached interfacial equilibrium quickly, as a stable wetting angle was rapidly attained in each case. Again a number of the wetting angle curves are invariant with temperature. However, two braze compositions display a measurable dependence on temperature, both containing 0.5 mol% TiO<sub>2</sub> and less than 2 mol% CuO. If the braze has at least 2 mol% CuO, the temperature dependence due to TiO<sub>2</sub> is mitigated, indicating that the nature of wetting has changed for these braze compositions. With the pre-oxidized fccalloy surface, increasing the CuO content of the braze makes a continuous improvement in the wettability of the braze, although the effect is strongest for the binary Ag-CuO compositions. Only a small reduction in contact angle is observed for the ternary brazes beyond a CuO content of 1 mol%.

Back scattered electron images of the four braze compositions that display the best wetting behavior on the alumina scale surface of the pre-oxidized fccalloy are shown in Figures 6(a) – (d). By again pairing the micrographs for the brazes which contain no TiO<sub>2</sub> wetting aid, Ag-2Cu [Figure 6(a)] and Ag-4Cu [Figure 6(c)], and those which do, Ag-4Cu and Ag-4Cu-1/2 Ti shown in Figures 6(b) and 6(d) respectively, we observe microstructural similarities within each pair. The brazes containing no wetting aid display a continuous, 1/2 - 1µm thick alumina scale that contains a small amount of iron and chromium, ~5 mol% and 3 mol% respectively. Both specimens also show the formation of a thin reaction zone which contains a mixture of discrete phases, including CuAlO<sub>2</sub>, silver, and a mixed copper-aluminum oxide, assumed to be CuO-Al<sub>2</sub>O<sub>3</sub> since CuO and Al<sub>2</sub>O<sub>3</sub> exhibit complete solubility with each other [23]. EDX results indicate ~5 – 8 mol% each of iron and chromium is dissolved in this mixed oxide phase. Note that in the Ag-2Cu brazed sample the reaction zone is approximately 1µm thick, whereas in the Ag-4Cu sample the reaction zone is nearly seven times wider. However, the most significant difference is the thickness and continuity of the CuO phase adjacent to the reaction zone. In the case of the 2 mol% CuO braze, the copper oxide phase is about 2µm thick and has not yet become a continuous layer, having been penetrated at numerous points by one or more of the phases that populate the reaction zone. In the higher CuO-content braze however, the CuO layer is approximately 20 – 30µm thick and forms a continuous band that completely covers the reaction zone. The contact angle data for these brazes, Figure 5, again bears out the wetting advantage that a continuous layer of CuO offers relative to the more discontinuous microstructure. As with the case of wetting on LSCoF, we assume that the difference in morphology between the two binary brazes results at least partially because of the miscibility gap in the Ag-CuO phase diagram.

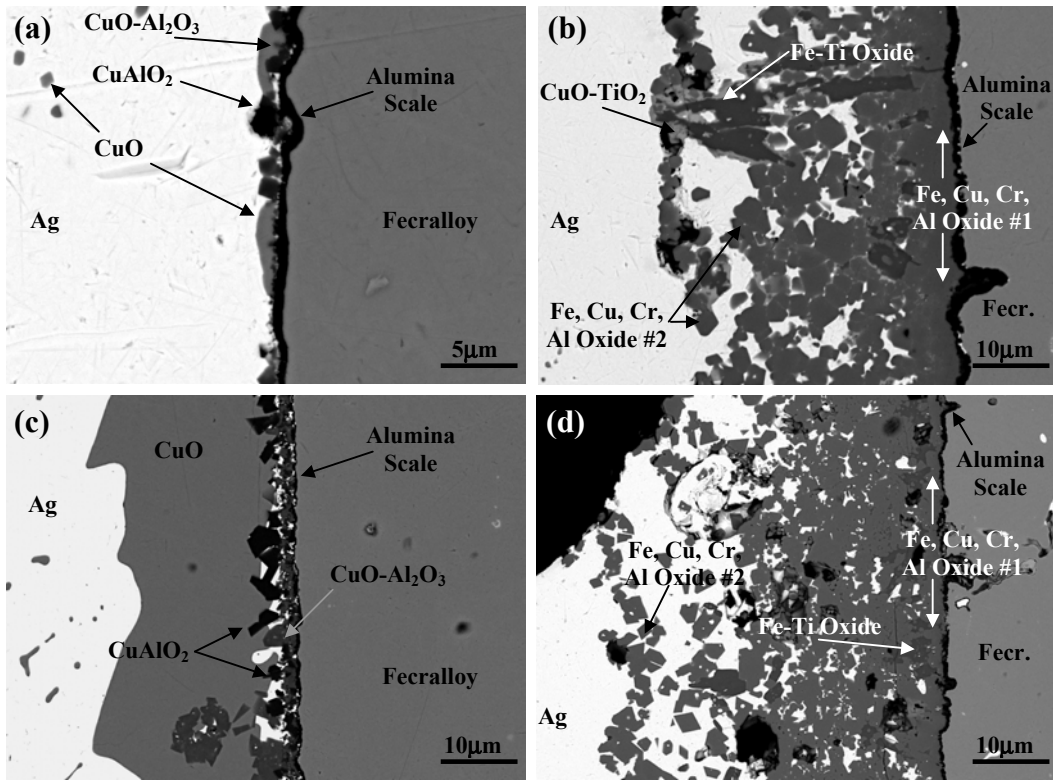


Figure 6 Cross-sectional SEM micrographs of braze/pre-oxidized fecralloy interfaces: (a) Ag-2Cu, (b) Ag-Cu- $\frac{1}{2}$ Ti, (c) Ag-4Cu, and (d) Ag-4Cu- $\frac{1}{2}$ Ti. Each wetting specimen was heated in air at a final soak temperature of 1100°C. Fe, Cu, Cr, Al oxides #1 and #2 are described in the text.

As found with the LSCoF wetting specimens,  $\text{TiO}_2$  has a significant effect on the composition and microstructure of the braze/pre-oxidized fecralloy interface. Both samples exhibit a wide affected zone,  $\sim 40\mu\text{m}$  in the case of the Ag-2Cu- $\frac{1}{2}$ Ti sample and over  $50\mu\text{m}$  for Ag-4Cu- $\frac{1}{2}$ Ti. Near the interface with the  $1\mu\text{m}$  alumina scale, a  $10\mu\text{m}$  thick zone can be found in both specimens which consists primarily of two distinct but complex phases, one with a Fe, Cu, Cr, Al molar ratio of 1:1:1:1 and the second which appears to be primarily an iron-titanium oxide phase (possibly  $\text{FeTiO}_3$ ) with a small fraction of Al and Cu. In general, this interfacial zone is relatively free of silver, although an occasionally precipitate can be found. Further into the bulk of the braze, roughly  $15\mu\text{m}$  away from the alumina scale in the case of the Ag-2Cu- $\frac{1}{2}$ Ti braze and  $25\mu\text{m}$  for the higher CuO-content material, a second zone starts. Within this region, significantly more silver is found, forming a matrix that encapsulates two faceted oxide phases: (1) an iron-titanium oxide of the same Fe:Ti molar ratio and impurity composition as the interfacial product and (2) crystallites with an Fe, Cu, Cr, Al compositional ratio of 2:2:1:1. In addition, voids can be found in this zone, although the Ag-4Cu- $\frac{1}{2}$ Ti specimen exhibits a far greater number than does Ag-2Cu- $\frac{1}{2}$ Ti.

Based on the results of the wetting experiments and subsequent microstructural analyses, a joining study has been initiated using the Ag-2Cu and Ag-4Cu brazes. Joint samples have been prepared by placing a small, 6.5mm diameter x 1mm cold pressed braze pellet onto the pre-oxidized surface of the fecralloy. The LSCoF pellet was then placed polished side down on the braze pellet. In this way, the joint was kept under compression by the weight of the LSCoF. Thus far, joining has been conducted under the following heat treatment conditions: heat in static air at  $5^\circ\text{C}/\text{min}$  to  $1100^\circ\text{C}$ , hold at  $1100^\circ\text{C}$  for  $\frac{1}{2}$  hour, and cool to room temperature at  $5^\circ\text{C}/\text{min}$ . An example of a brazed joint prior to and after tensile testing is shown in Figures 7(a) and (b). The mechanical strength of the joints is currently under investigation and will be reported in the future.



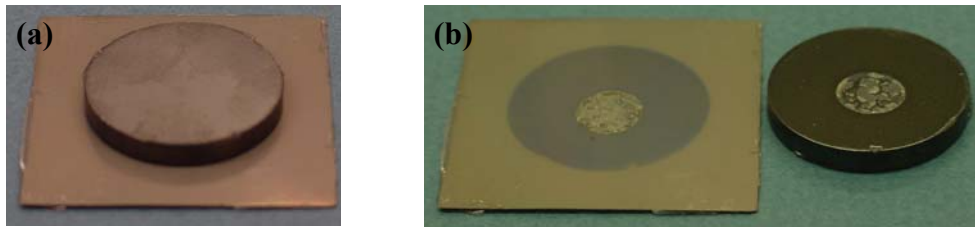


Figure 7 Examples of a Ag-CuO braze LSCoF/Fecralloy joint (a) prior to and (b) after tensile testing. The specimen was prepared using the Ag-4Cu braze and was heated at 5°C/min to 1100°C, soaked at 1100°C for ½ hr, and cooled at 5°C/min to room temperature.

### Conclusions

Reaction air brazing using Ag-CuO and Ag-CuO-TiO<sub>2</sub> brazes was investigated as an alternative means of joining a mixed ionic/electronic conducting oxide, (La<sub>0.6</sub>Sr<sub>0.4</sub>)(Co<sub>0.2</sub>Fe<sub>0.8</sub>)O<sub>3</sub>, to a structural alloy candidate, fecralloy, for an oxygen generator application. Wetting experiments demonstrated that copper oxide significantly improves the wetting behavior of silver on both the LSCoF and pre-oxidized fecralloy substrates, but that a minimum concentration is required. This minimum level of CuO can be reduced by adding a small amount of TiO<sub>2</sub> to the braze, but microstructural analysis indicates that a deleterious reaction zone may be formed at the substrate surface, particularly in the case of LSCoF, where evidence of grain boundary melting was observed. In general, it was found in the Ag-CuO brazes that the formation of a nearly continuous CuO layer along the interface with either substrate greatly improves the wetting characteristics of the braze. Based on the promising results obtained in the wetting experiments, a series of joining experiments have been initiated using the binary RAB brazes.

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