

# **JOINING OF ADVANCED HIGH-TEMPERATURE MATERIALS**

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## **ABSTRACT**

Various compositions in the Ag-CuO<sub>x</sub> system are being investigated as potential filler metals for use in air brazing high-temperature electrochemical devices such as solid oxide fuel cells and gas concentrators. Prior work has shown that the melting temperature, and therefore the potential operational temperature, of these materials can be increased by alloying with palladium. The current study examines the effects of palladium addition on the joint strength of specimens prepared from yttria stabilized zirconia (YSZ) bars brazed with three different families of filler metals: Ag-CuO, 5Pd-Ag-CuO, and 15Pd-Ag-CuO. In general it was found that palladium leads to a small-to-moderate decrease in joint strength, particularly in low copper oxide compositions filler metals. However the effect is likely acceptable if a higher temperature air braze filler metal is desired. In addition, a composition was found for each filler metal series in which the joint failure mechanism undergoes a transition, typically from ductile to brittle failure. In each case, this composition corresponds approximately to the silver-rich boundary composition of the liquid miscibility gap in each system at the temperature of brazing.

## **INTRODUCTION**

A series of Ag-CuO<sub>x</sub> compositions has been developed for potential use as high-temperature brazing filler metal alloys; specifically for joining and sealing the ceramic and metal components employed in solid-state electrochemical devices such as solid oxide fuel cells (SOFCs), gas concentrators, and sensors [1,2]. These alloys differ from most braze filler metals in that: (1) they readily wet a wide variety of ceramics, (2) brazing can be conducted directly in air without need of an inert cover gas or use of surface reactive fluxes, and (3) the resulting joint is inherently resistant to oxidation at high temperature [3-7]. The latter issue is a particularly significant challenge in high-temperature devices. Recent studies on the oxidation behavior of commercial active metal brazes have shown that they are unreliable at temperatures beyond 500°C, due to oxidation along the interface between the filler metal and ceramic substrate [8,9].

As part of an on-going investigation of these alloys, we examined the effects of palladium on the solidus and liquidus temperatures of this system, as well as on the subsequent wetting characteristics relative to a model set of alumina substrates [10-12]. Two invariant reactions exist in the Ag-CuO<sub>x</sub> system, a eutectic at 942°C and  $x_{Ag} = 0.99$  and a monotectic at 967°C and  $x_{Ag} = 0.36$  [13-15]. Extending between these two points is a two-phase liquid miscibility gap in which a silver-rich (L<sub>1</sub>) and a copper-oxide rich liquid (L<sub>2</sub>) co-exist. Results from differential thermal analysis indicate that the addition of palladium can increase both the liquidus and solidus temperatures, by as much as 350°C in some cases, relative to comparable binary compositions [10-12]. Results from an associated series of sessile drop experiments showed that the added palladium leads to reduced wetting between the resulting filler metal and alumina [11,12]. That is, there is a trade-off in properties for the Pd-Ag-CuO<sub>x</sub> system. On one hand, the increase in liquidus temperature raises the upper temperature limit at which devices joined with these materials can be deployed and also permits two or more brazed seals to be employed in a given device (one “high-temperature” and the other “low-temperature”) without concerns of filler metal re-melting. On the other hand, the reduction in filler metal wettability implies a potential reduction in filler metal adhesion and subsequent joint strength. The present study was undertaken to test the latter correlation by directly studying the effects of palladium content on the mechanical properties of ceramic joints brazed using Pd-Ag-CuO<sub>x</sub> filler metals.

## **EXPERIMENTAL**

As listed in Table 1, three families of filler metal compositions were examined including the Ag-CuO<sub>x</sub> binary, which was added to establish a baseline against which the effects of palladium addition could be compared. The two series of ternary compositions were selected to represent the effects of both a small compositional shift from the original binary phase equilibria (by adding 5mol% Pd) and a larger one (15mol% Pd addition). Prior differential scanning calorimetry (DSC) results indicate that the solidus/liquidus temperatures increase by approximately 25°C/25°C when 5mol% Pd is added and by 40°C/100°C when 15mol% Pd is added [10-12]. Experience has shown that silver volatility limits the long-term use of Pd-Ag-CuO<sub>x</sub> filler metals to temperatures below 1100°C. Therefore from a cost-benefit standpoint, palladium concentrations above 15 – 20mol% in these alloys (where T<sub>liq</sub> is around 1100°C) do not offer a significant operational advantage.

Table 1: Compositions employed in this study.

Braze I.D.	$x_{Pd}/(x_{Pd} + x_{Ag} + x_{Cu})$	$x_{Ag}/(x_{Pd} + x_{Ag} + x_{Cu})$	$x_{Cu}/(x_{Pd} + x_{Ag} + x_{Cu})$	$x_{Ag}/(x_{Ag} + x_{Cu})$
Ag-1CuO	0	0.990	0.010	0.99
Ag-2CuO	0	0.980	0.020	0.98
Ag-4CuO	0	0.960	0.040	0.96
Ag-8CuO	0	0.920	0.080	0.92
Ag-16CuO	0	0.840	0.160	0.84
Ag-32CuO	0	0.680	0.320	0.68
Ag-64CuO	0	0.360	0.640	0.36
5Pd-Ag1CuO	0.05	0.941	0.010	0.99
5Pd-Ag2CuO	0.05	0.931	0.019	0.98
5Pd-Ag4CuO	0.05	0.912	0.038	0.96
5Pd-Ag8CuO	0.05	0.874	0.076	0.92
5Pd-Ag16CuO	0.05	0.798	0.152	0.84
5Pd-Ag32CuO	0.05	0.646	0.304	0.68
5Pd-Ag64CuO	0.05	0.342	0.608	0.36
15Pd-Ag1CuO	0.15	0.842	0.009	0.99
15Pd-Ag2CuO	0.15	0.833	0.017	0.98
15Pd-Ag4CuO	0.15	0.816	0.034	0.96
15Pd-Ag8CuO	0.15	0.782	0.068	0.92
15Pd-Ag16CuO	0.15	0.714	0.136	0.84
15Pd-Ag32CuO	0.15	0.578	0.272	0.68
15Pd-Ag64CuO	0.15	0.306	0.544	0.36

The four-point bend specimens were prepared and tested according to the AWS C3.2M/C3.2:2001 test procedure [16]. Each series of four-point bend bar specimens was machined out of a pair of two-piece yttria stabilized zirconia plates (YSZ; 8mol%  $Y_2O_3$ ; Tosoh Corporation, Tokyo Japan) that were brazed using one of the filler metal compositions listed in Table 1. Originally measuring 100mm long by 50mm wide by 4mm thick, the plates were quartered into 25mm long by 50mm wide by 4mm sections with a fine cut diamond blade saw, leaving an approximately  $9\mu m$  finish. The edges to be joined (the 50mm cut edge) were further polished in a series of steps: first using a 45 and then a  $15\mu m$  diamond wheel, followed by polishing using 9, 3, and  $1\mu m$  diamond suspensions on the appropriate polishing pads (Allied High Tech). Prior to joining, the YSZ plates were cleaned with acetone and rinsed with isopropanol and heated in static air to  $600^\circ C$  to burn off any remaining organic residue.

The filler metal compositions investigated in this study were prepared by dry ball-milling the appropriate ratios of constituent metal powders, silver (99.9%,  $0.75\mu m$  average particle size, Alpha Aesar Company), copper (99%,  $1.25\mu m$  average particle size, Alpha Aesar Company) and palladium (99.9+%, submicron average particles size, Aldrich Chemical Company) for 12 hours. The powders were then blended with a polymer binder (Heraeus V-006, Heraeus Inc., Conshohocken PA) in a 85:15 weight ratio. To establish a uniform application thickness, the paste was stencil printed on each faying surface. After drying at  $70^\circ C$  for 60 minutes, the final thickness of the filler metal layer between two given YSZ plates measured  $\sim 200\mu m$ . Each pair of plates was assembled and held in place using a set of steel clips. The assemblies were placed vertically in an air muffle furnace separated by a slotted alumina support plate. An 850g ceramic dead load was placed on the support plate to ensure that the assemblies were under constant compression during the entire brazing cycle, which was conducted by heating in static air at  $3^\circ C/min$  to  $1000^\circ C$ , holding at  $1000^\circ C$  for 1 h, and cooling to room temperature at  $3^\circ C/min$ . Once joined each assembly was cut into a series of rectangular bend bar specimens using a low speed reciprocating diamond saw. Each specimen measured 4 mm x 3 mm x 50 mm with the joint located midway along the length. The edges to be placed under tension during bending were chamfered to remove machining flaws that could cause premature failure. The final sample width and height were carefully measured at the joint using dial calipers (accurate to 1mil or 0.0254mm) prior to testing.

The specimens were tested in a silicon carbide four-point bend fixture (20/40 mm spans) that permitted full-articulation, as recommended by the test guidelines. The specimens were loaded at a constant displacement rate of 0.5mm/min in an MTS Bionix 400 (MTS Systems Corp., Eden Prairie, MN) mechanical screw load frame equipped with a 2kN load cell. Load data was collected using TestWorks v3.10 software (MTS Systems Corp., Eden Prairie, MN) and the stress at failure ( $\sigma_F$ ) was calculated from the following equation [16]:

$$\sigma_F = \frac{3P \cdot L}{4b \cdot d^2}$$

where P is the applied load, L the span between the bottom rollers (40mm), and b and d are the width and height of the specimen bar. To obtain statistically significant data, a minimum of five specimens were tested for each filler metal composition, each machined from the same brazed plate assembly. Microstructural analysis was performed on representative specimens prior to and after four-point bend testing using a scanning electron microscope (SEM, JEOL, JSM-5900 LV) equipped with an Oxford windowless energy dispersive X-ray (EDX) detector for chemical microanalysis. Backscattered electron (BSE) imaging was employed to identify phases of differing composition via visual contrast. Cross-sectional samples were cut and polished using the same techniques described above and coated with carbon to prevent charging in the SEM.

## RESULTS

Shown in Figures 1 – 3 are representative cross-sectional BSE micrographs of the joining specimens in the as-brazed condition, prior to bend testing. Specimens brazed using the binary filler metals are shown in Figures 1(a) – (d), those joined with the 5Pd filler metal alloys are shown in Figures 2(a) – (d), and those prepared using the 15Pd alloys are shown in Figure 3(a) – (d). The filler metal/substrate interfaces of specimens joined using the lowest copper containing filler metal in each series, respectively Figures 1(a), 2(a), and 3(a), all exhibit the same microstructural features: little to no interfacial porosity, the presence of small interfacial copper oxide precipitates, and a small amount of copper oxide, also in precipitate form, within the bulk of the joint. The lack of interfacial porosity indicates wetting between the filler metal and YSZ substrate, a phenomenon previously reported with Ag-CuO filler metals [2]. Note that specimens brazed with filler metals containing 2mol% CuO, Figures 1(b), 2(b), and 3(b), exhibit a similar joint microstructure, i.e. evidence of good wetting the filler metal/substrate interfaces that are decorated with discrete copper oxide particles.

The filler metal compositions used to prepare the specimens shown in Figures 1(c) and (d) both lie well within the miscibility gap of the Ag-CuO<sub>x</sub> phase diagram at 1000°C [14,15]; i.e. at the braze temperature, each molten filler metal is composed of two liquids, one rich in copper oxide and the second rich in silver. As has been observed previously, the copper oxide-rich liquid preferentially wets the YSZ substrate and in doing so encapsulates the silver-rich liquid [2]. Even though the copper-oxide liquid is of lower density than the silver-rich liquid, it forms an intruding liquid layer and prevents the heavier liquid from wetting the lower substrate in the joint. This is an example of perfect wetting, a phenomenon that was originally described by J. W. Cahn [16]. While it has been observed experimentally in a number of organic liquid and low-temperature metal systems [17,18], the recent work on the Ag-CuO system is the first published example of perfect wetting at high temperature [2]. Upon cooling through the monotectic temperature, the copper oxide-rich liquid solidifies forming a copper oxide matrix that entraps the remaining silver-rich liquid as a series of fine-scale droplets. With further cooling, these droplets and the same silver-rich liquid found in the center of the joint undergo a eutectic transformation, yielding micron-sized copper oxide precipitates within a silver matrix.

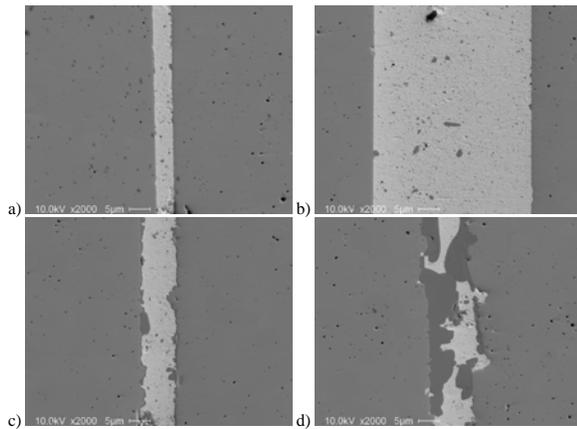


Figure 1: Cross-sectional scanning electron microscopy images of YSZ joining specimens brazed using: (a) Ag-1CuO, (b) Ag-2CuO, (c) Ag-4CuO, and (d) Ag-32CuO.

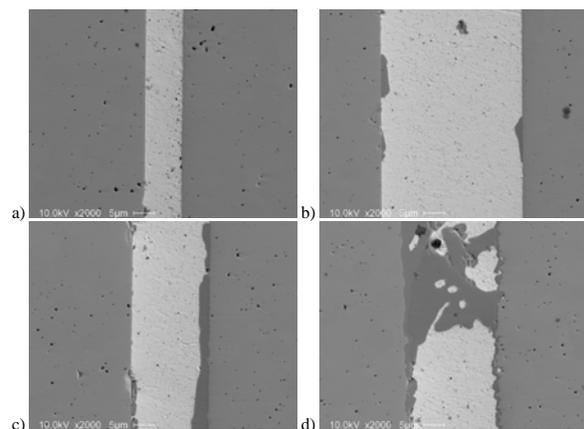


Figure 2: Cross-sectional scanning electron microscopy images of YSZ joining specimens brazed using: (a) 5Pd-Ag1CuO, (b) 5Pd-Ag2CuO, (c) 5Pd-Ag4CuO, and (d) 5Pd-Ag32CuO.

The analogous “high copper oxide content” filler metal specimens of the 5Pd and 15Pd series are shown respectively in Figures 2(c) and (d) and 3(c) and (d). In all four figures there is evidence of liquid phase separation during brazing, with a copper oxide-rich liquid phase preferentially wetting the two ceramic substrates in the joint and correspondingly forming a thin copper oxide interfacial layer upon cooling. Again, this microstructure is due to liquid-liquid immiscibility that takes place at 1000°C. While the phase diagram for the pseudoternary Ag-Pd-CuO<sub>x</sub> system has yet to be completely defined, it is known that the 4 and 32 mol% CuO compositions lie within a liquid miscibility gap region for the 5Pd-Ag-CuO<sub>x</sub> system [10-12]. Apparently this is true as well for the 5Pd-Ag-CuO<sub>x</sub> system, based on the evidence of liquid-liquid phase separation. Note that in all four cases, palladium is found solely in the  $\alpha$  phase (metal phase); i.e. no palladium was measured in the copper oxide rich phases via EDX.

Shown in Figure 4 are plots of ambient temperature bend strength for all three filler metal series as a function of copper oxide content. Each data point represents the average of five samples and the error bars illustrate the corresponding standard deviation. The bend strength of the YSZ used in preparing the bend specimens in this study was determined to be 193±19MPa. For the binary filler metal system, the bend strength is lowest for joints brazed with the 1mol% CuO filler metal composition. As the copper oxide content is increased to Ag-2CuO the average joint strength increases over 200% to an average of 148MPa, which is ~77% of that measured in the monolithic YSZ. The average bend strength of these specimens is also significantly higher than those brazed with the Ag-4CuO filler metal. To determine if experimental variability or sample preparation was responsible for this difference, the 4-point bend tests for the Ag-2CuO and Ag-4CuO compositions were repeated. New specimens were prepared using a second set alloy powders and YSZ substrates. The first and second set of tests yielded bend strengths of 148±24 and 157±24MPa for the Ag-2CuO brazed joining specimens and 109±14 and 109±21MPa for those brazed with the Ag-4CuO filler metal. Given the degree of consistency between each pair of measurements, it is clear that joint strength is optimized for binary filler metal compositions close to 2mol% CuO in silver.

As the copper oxide content is increased from Ag-4CuO to Ag-64CuO, the average bend strength decreases from ~100MPa to ~80MPa. However given the wide scatter in the data, the differences in joint strength across this series of compositions are not considered to be statistically significant; i.e. bend strength remains approximately constant for joints brazed with filler metal compositions ranging from 4 to 64mol% CuO in silver. Thus there are three regions of joint strength behavior that can be identified for the specimens joined using the binary filler metals: (1) a sharp increase in bend strength as CuO is added to pure silver up to (2) a critical composition at which bend strength is maximized (corresponding to Ag-2CuO), followed by (3) a sharp decline in bend strength to a value that remains constant over a wide compositional range.

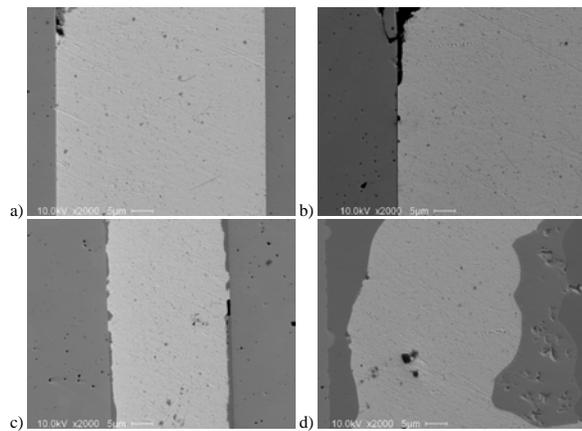


Figure 3: Cross-sectional scanning electron microscopy images of YSZ joining specimens brazed using: (a) 15Pd-Ag1CuO, (b) 15Pd-Ag2CuO, (c) 15Pd-Ag4CuO, and (d) 15Pd-Ag32CuO.

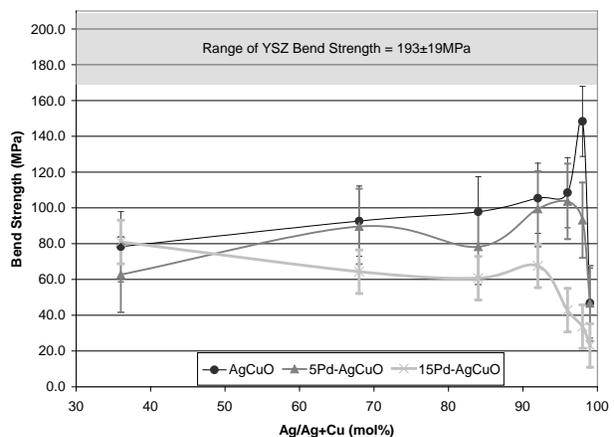


Figure 4: Bend strength versus CuO content for YSZ joining specimens brazed with the Ag-CuO, 5Pd-Ag-CuO, and 15Pd-Ag-CuO series of braze filler metals.

In the case of the 5Pd-Ag-CuO filler metal series, again an initial increase in bend strength is observed as copper-oxide content is increased. The maximum strength appears to have shifted to ~4mol% CuO relative to the binary filler metal series, beyond which there is a modest decline in average strength with increasing copper oxide content.

Again based on the size of the error bars, it can be argued that the composition-strength curve essentially levels off over this compositional range. Thus like the binary filler metal specimens, the bend strength data for the 5Pd-Ag-CuO specimens exhibits three general regions of behavior: (1) between 0-4mol% CuO, increasing joint strength with increasing copper oxide content, (2) a maximum in joint strength at ~4mol% CuO addition, followed by short decline in strength with increasing addition, and (3) compositional invariance over the range of ~16 to 64mol% CuO.

The data set for the 15Pd-Ag-CuO filler metal specimens is slightly different in that no local maximum is observed. The average bend strength values for YSZ joints brazed with this series of filler metals appear to increase with increasing copper oxide up to the end composition of 64mol% CuO. However based on the error bars associated with each data point, the greatest increase in joint strength with CuO addition occurs up to ~8mol% CuO; again indicating a steady shift in this inflection point relative to the binary and 5Pd ternary filler metals. Beyond this point, the slope of the curve very gradually increases. That is, two regions of behavior can be identified in the plot: (1) an increase in joint strength with increasing CuO content over the range of 0 – 8mol% CuO and (2) near compositional invariance for filler metal compositions higher than 8mol% CuO.

Shown in Figures 5 – 7 are images of the fracture surfaces in a series of joining specimens tested to failure. In figures that display only one of the two fracture halves for a given bend bar specimen, the fracture front progressed from left to right in the image (or bottom to top in the specimen during bend testing). In the figures where both fracture halves are shown together, the direction of fracture is from the center to the outer edges of the image. During metallographic examination, distinct differences in surface appearance were observed that could be traced back to both the internal microstructure and mechanical behavior of each joint. For example in the binary series shown in Figures 5(a) – (e), those specimens brazed with the lowest CuO-containing filler metals [e.g. Ag1CuO in Figure 5(a)] exhibit signs of localized or “patchy” wetting between the YSZ and filler metal, which correlates with the prior report on the compositional dependence of wetting properties in these filler metals [1,2]. Only small patches of the silver-rich filler metal remain adhered to the YSZ surface. Failure appears to have occurred by ductile peeling between the filler metal and YSZ substrate, indicating not only insufficient wetting, but also the lack of adhesion (weak bonding) across the filler metal/YSZ interface.

Shown in Figure 5(b) is one of the fracture halves from a specimen brazed using the Ag-2CuO filler metal. The surface displays several features that indicate how failure likely took place. Marked on the left side of image is a region where the YSZ substrate is missing a large divot of material, which was found attached to the opposing fracture surface. Similarly, a piece of the opposing YSZ substrate is observed on the surface shown in the micrograph. The portion of exposed filler metal found in the center of this image exhibits signs of ductile failure; notably cup and cone dimpling. Failure in this specimen appears to have originated within one of the YSZ substrates along the edge placed in tension during bending (on the left hand side of the micrograph), and propagated through the thickness of the filler metal and into the second YSZ substrate. The increase in the strength of this joint relative to that formed by brazing with the Ag1CuO filler metal appears to be due to not only to the improved level of wetting, but also to a high degree of adhesion across the filler metal/YSZ interface. Unlike the Ag-1CuO specimen, no evidence of peeling between the filler metal and YSZ was observed in this specimen.

The fracture surfaces of joining specimens brazed with filler metals containing 8 and 32 mol% CuO are shown in Figures 5(d) and (e), respectively. In both cases, signs of cleavage fracture are clearly evident. This coupled with the general lack of silver present on each of the surfaces, indicates brittle failure of the joints; ostensibly through a nearly continuous layer of copper oxide that forms due to the liquid-liquid immiscibility phenomenon previously described. Thus, the strengths of joints prepared using filler metal compositions found well within the Ag-CuO miscibility gap are dominated by the mechanical behavior characteristics of CuO, which accounts for the statistically flat region of the corresponding bend strength curve in Figure 4.

Shown in Figures 6(a) – (e) are the fracture surfaces of failed bend bar specimens brazed using 5Pd-AgCuO series of filler metals. Note that nearly 50% of the fracture surface in the 5Pd-Ag1CuO specimen shown in Figure 7(a) is uncovered; that is, not properly wetted by the filler metal. Where the braze filler metal did wet the substrate, there is evidence of strong adhesion with the YSZ surface, with fracture occurring into the YSZ substrate as opposed to peeling along the YSZ/filler metal interface. As the copper oxide content of the filler metal is increased, there appears to be greater material wetting and spreading as seen in the respective micrographs for the 5Pd-Ag2CuO and 5Pd-Ag4CuO specimens [Figures 6(b) and (c)].

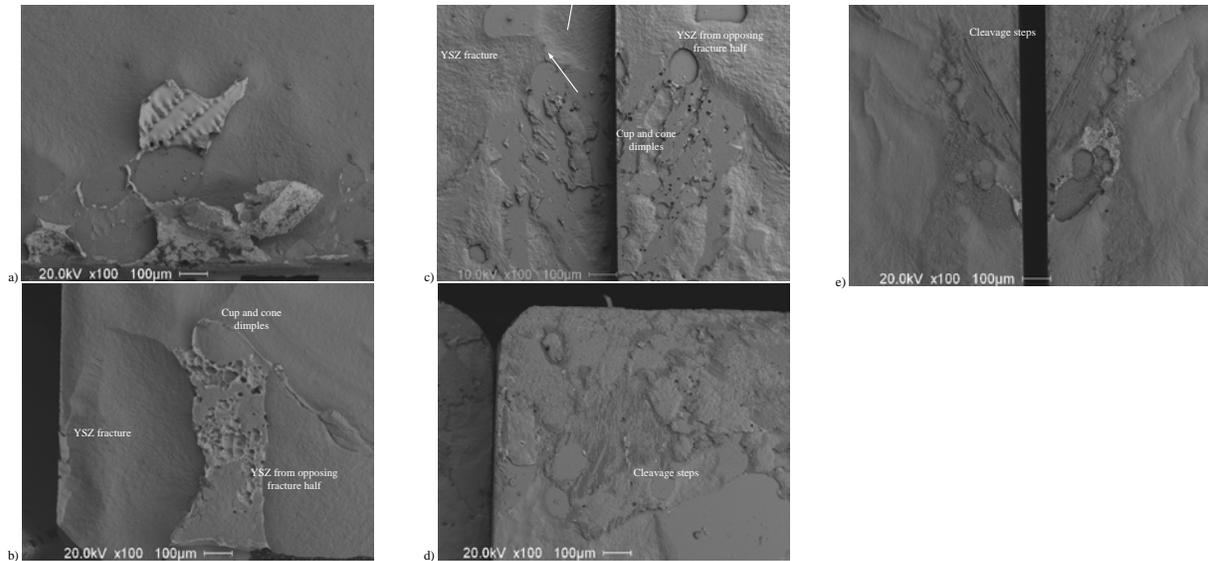


Figure 5: Backscattered electron images of the fracture surfaces of four-point bend specimens brazed with: (a) Ag1CuO, (b) Ag2CuO, (c) Ag4CuO, (d) Ag8CuO, and (e) Ag32CuO.

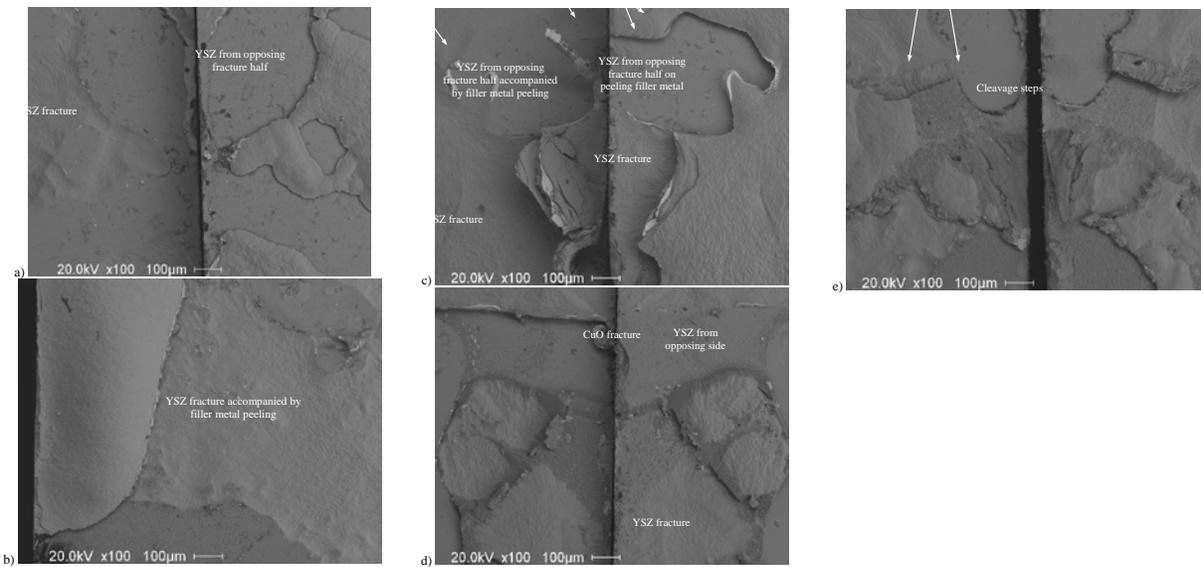


Figure 6: Backscattered electron images of the fracture surfaces of four-point bend specimens brazed with: (a) 5Pd-Ag1CuO, (b) 5Pd-Ag2CuO, (c) 5Pd-Ag4CuO, (d) 5Pd-Ag8CuO, and (e) 5Pd-Ag32CuO.

Based on the phase equilibrium data for the Pd-Ag-CuO system [10-12], the 5Pd-Ag4CuO composition lies just inside a liquid phase miscibility gap at 1100°C. As such, a small amount of a copper oxide-rich liquid should form and preferentially wet the YSZ substrates during brazing, leaving behind a CuO-rich layer along these interfaces upon cooling. This appears to be consistent with fracture mode observed in Figure 6(c). Note the evidence of fracture through both the YSZ and various CuO-rich (darker contrast) regions on these surfaces. As the copper oxide content is increased to 8 and 32mol% CuO, more CuO is found on the fracture surfaces, as seen respectively in Figures 6(d) and (e). As was found in the series of binary filler metal specimens, this phase dominates the fracture mechanics of joints brazed with “miscibility gap” filler metals; in this case, those that lie within the miscibility gap for the 5Pd-Ag-CuO system. Again, the corresponding flexural strength curve flattens for compositions containing greater than ~4mol% CuO and the mechanical behavior of these joints correlate with their microstructure, which in turn can be approximately predicted by the phase diagram for the system.

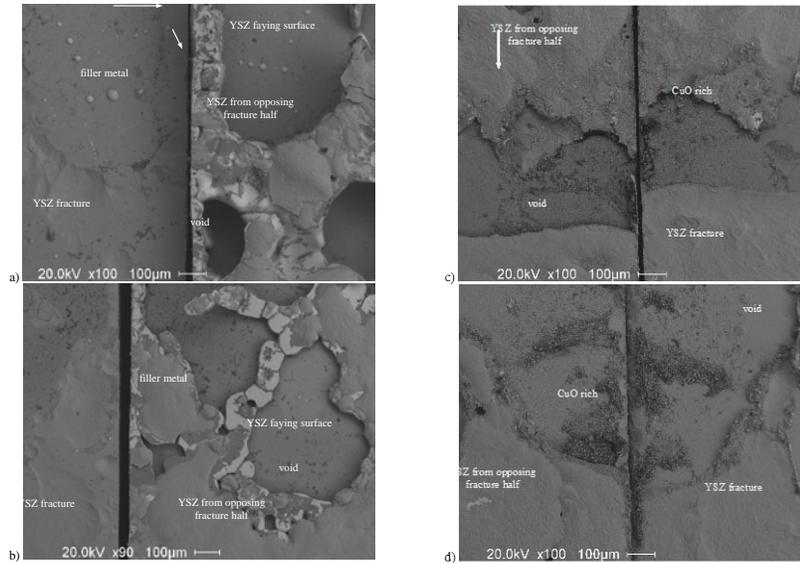


Figure 7: Backscattered electron images of the fracture surfaces of four-point bend specimens brazed with: (a), 15Pd-Ag2CuO, (b), 15Pd-Ag4CuO, (c) 15Pd-Ag8CuO, and (d) 15Pd-Ag32CuO.

Shown in the images in Figures 7(a) – (d) are the fracture surfaces of joining specimens prepared using the 15Pd-AgCuO series of filler metals. The fracture surfaces of the low CuO content filler metal specimens, such as those of the 15Pd-Ag2CuO sample shown in Figure 7(a), exhibit evidence of poor wetting. This is not surprising; recent findings indicate that for a constant copper oxide composition, the wettability of Pd-Ag-CuO filler metals decreases substantially with increasing palladium content. However it is also observed that the filler metal exhibits good adhesion with the YSZ substrate, which is apparent from patches of YSZ that remain attached to the filler metal after fracture. A similar phenomenon is found with the 15Pd-Ag4CuO specimen shown in Figure 7(b). Note that there appears to be a higher percentage of detached YSZ on one of the fracture halves of this specimen. Both of these filler metal compositions lie outside of the miscibility gap for the 15Pd-Ag-CuO system [11,12]; i.e. they form a single phase liquid upon melting.

On the other hand, the filler metals employed in brazing the bend bar specimens in Figures 7(c) and (d) lie within the miscibility gap at 1100°C and therefore separate into two immiscible liquid phases. As reasoned before, the one rich in CuO preferentially wets the YSZ faying surfaces and upon solidification leaves behind a copper oxide interfacial layer. This layer is apparent in the fracture surfaces of the 15Pd-Ag8CuO and 15Pd-Ag32CuO specimens, shown respectively in Figures 7(c) and (d). Note that the degree of wetting in both samples appears to be higher than that found with the lower CuO-content filler metals. Thus the amount of uncovered faying surface (i.e. void area) is also significantly lower, which likely accounts for the somewhat higher joint strengths observed in Figure 4.

## CONCLUSIONS

In general the addition of palladium lowers the joint strength, particularly when low copper oxide containing filler metals are employed. Note that each series displays an increase in average bend strength with copper oxide content up to a transition composition, beyond which the bend strength either drops slightly or approximately maintains a constant value. The threshold composition is different for each of the compositional families tested. The transition occurs around 2mol% CuO for the binary system, at ~4mol% CuO for the 5Pd system, and at ~8mol% CuO and for the 15Pd system. Fractographic analysis confirms the existence of these transition compositions, indicating a distinct change in failure mechanism at each. In the binary system, for example, the following regions of failure behavior occur: (1) over a compositional range of 0 – 2mol% CuO, peeling along the filler metal/YSZ interface and a dramatic increase in bend strength with increasing CuO content due to improved filler metal coverage and greater interfacial adherence; (2) at ~2mol% CuO, optimal bend strength with mixed cone-cup type ductile fracture and brittle YSZ fracture; and (3) beyond 2mol% CuO, a modest decrease in bend strength followed by compositional invariance which is accompanied by fracture predominantly an interfacial copper oxide-rich phase. Failure behavior in joints prepared from the 5Pd-AgCuO filler metals can be summarized as follows: (1) over a compositional range of 0 – 4mol% CuO, an increase in bend strength due to improved filler metal wetting and greater interfacial

adherence; (2) at ~4mol% CuO, maximum bend strength is observed; and (3) beyond ~4mol% CuO, bend strength gradual declines with copper oxide additions due to brittle failure through a greater fraction of interfacial copper oxide. The 15Pd-AgCuO filler metals are characterized by: (1) an increase in bend strength with copper oxide composition over a compositional range of 0 – 8mol% CuO, primarily due to improved wetting with copper oxide addition and (2) a near constant bend strength over the compositional range of 8 – 64mol% CuO, with failure attributable predominantly to fracture through both the interfacial copper oxide-rich and substrate phases. For each system, the composition at which the transition in failure behavior takes place corresponds to the silver-rich boundary composition of the liquid miscibility gap at 1000°C, indicating that the phenomenon of two-phase wetting is the key factor in defining the joint strengths of these air braze filler metals.

#### ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Program. Thermal analysis equipment used was provided by Office of Basic Energy Sciences, Division of Materials and Engineering Physics. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the United States Department of Energy (U.S. DOE) under Contract DE-AC06-76RLO 1830.

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