

The effect of TiO₂ on the wetting behavior of silver–copper oxide braze filler metals

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Abstract

A series of silver–copper oxide ceramic brazing alloys was compositionally modified by doping with small amounts of titania. Subsequent contact angle measurements indicate that concentrations as low as 0.5 mol.% TiO₂ can significantly enhance wettability over a wide range of binary silver–copper oxide compositions.

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1. Introduction

Over the past several years, a new method of ceramic–ceramic and ceramic–metal joining has been developed for applications ranging from power semiconductor packaging to the seals employed in planar solid oxide fuel cells and oxygen concentrators [1–3]. Referred to as air brazing, the technique forms a predominantly metallic joint directly in air without need of an inert cover gas or the use of surface reactive fluxes. The resulting bond has been shown to be hermetic under a range of high-temperature operating conditions, offers excellent strength, and is inherently resistant to oxidation during application [3–5]. The key in developing a successful filler metal composition for air brazing is to identify a metal oxide that is mutually soluble in a molten noble metal solvent. It is the metal oxide that serves as a wetting agent with ceramic substrates. One particular oxide–metal combination that is readily suited for this purpose is Ag–CuO_x, a system originally of interest in developing cuprate-based superconductors. Results from equilibrium phase studies performed by Nishiura et al. [6]

indicate that there are two invariant points in the pseudobinary Ag–CuO_x phase diagram, respectively corresponding to a eutectic and a monotectic reaction, around which new braze compositions could be developed.

In recent studies, we have investigated the wetting behavior of silver–copper oxide filler metals on various ceramic substrates including yttria-stabilized zirconia, alumina, and lanthanum strontium cobalt ferrite [3–5]. Here we report on our recent effort to modify braze wettability by adding a ternary constituent, TiO₂. Titania was originally selected as a potential melting point depressant for Ag–CuO_x based on a prior study of a low-temperature eutectic reaction in the CuO–TiO₂ system [7]. While this phase equilibrium effect was found to be minimal, it was observed that small additions of titania display a dramatic effect on the wetting behavior of alloys containing less than ~34 mol.% copper oxide.

2. Experimental methods

Four series of filler metal compositions were investigated in this study, ranging in CuO content from 0 to 80 mol.% and containing either 0, 0.5, 1, or 2 mol.% TiO₂. These were formulated by dry mixing silver powder

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(99.9%, 0.75 μm average particle size, Alpha Aesar), copper powder (99%, 1.25 μm average particle size, Alpha Aesar) and titanium dioxide powder (99.9+%, submicron average particles size, Aldrich) using a mortar and pestle. It has been previously shown that the copper readily oxidizes to become CuO under typical air brazing conditions [8], which was accounted for in calculating the appropriate powder weights for each filler metal composition. Pellets measuring 2 mm in diameter by 2 mm thick were prepared from the powders by cold pressing. Polycrystalline alumina was chosen as a model substrate in the wetting experiments. High purity disks measuring 50 mm in diameter by 6 mm thick were obtained from Alfa Aesar (Al-23, 99.7% pure, 98% dense). The discs were polished on one face to a 10 μm finish, then cleaned with acetone, rinsed with propanol, air dried, and finally heated in static air to 600 °C for 4 h to burn off any residual organic contamination.

To examine the effect of TiO₂ on the monotectic and eutectic temperatures in the Ag–CuO_x system, thermal analysis was conducted from room temperature to 1050 °C using a combined differential scanning calorimetry/thermogravimetric analysis system (DSC/TGA; Netzsch, STA 449C Jupiter). The sample pellets employed in these experiments contained approximately 5–10 mg of a given powder mixture. The DSC runs were performed in yttria-stabilized zirconia crucibles at a heating rate of 10 °C/min under dry flowing air (10 ml/min). A minimum of three heating and cooling curves were recorded for each sample to ensure good reproducibility. The Pt/Pt–10%Rh thermocouples employed in the DSC instrument were calibrated using indium, tin, CsCl, and gold standards.

Wetting experiments were conducted by the classical sessile drop technique [9]. Each filler metal pellet was placed on a polished alumina substrate and heated through a series of temperatures above the point at which the pellet becomes molten. Changes in the braze droplet's base diameter, height, and angle of contact with the substrate were monitored via high speed video camera. The specimens were heated at 30 °C/min to a sub-liquidus temperature of 900 °C, at which point the heating rate was reduced to 10 °C/min for the rest of the cycle. Once stable at 900 °C, the furnace temperature was raised to 1000 °C, where it remained for 15 min. It was then increased again to a second isothermal hold at 1050 °C for 15 min, followed by a final 15 min soak at 1100 °C. In this way, the shape of the sessile drop was allowed to stabilize for measurement at each temperature. Once the wetting experiment concluded, each sample was quenched at 10 °C/min to 550 °C, then furnace cooled to room temperature.

The analog video data was converted into digital form using VideoStudio6™ (Ulead Systems, Inc.) for subsequent image analysis using Canvas™ graphic software (version 8.0.5, Deneba Systems, Inc.). 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 this radius and the diameter of contact between the droplet and the substrate. Micro-

structural analysis was conducted on polished cross-sectioned samples by scanning electron microscopy (SEM; JEOL, JSM-5900LV) and energy dispersive X-ray analysis (EDX; Oxford Systems).

3. Results

Reported in Table 1 are the results of DSC studies conducted on four series of Ag–CuO_x–TiO₂. Listed for each composition are the corresponding temperatures at which a given endotherm could be identified. With the addition of TiO₂, it was expected that a small but measurable depression in both the eutectic and monotectic temperatures of the Ag–CuO_x system, 942 °C and 969 °C respectively [6], would be observed given that titania forms a low melting eutectic with CuO at 919 °C ($x_{\text{eut}} \sim 16.7$ mol.% TiO₂) [7]. The anticipated effect was first predicted by Gaye and Lupis [10] and has been experimentally observed previously in a number of systems, including Ag–Cu–Au, Ag–Cu–Sn, and Ag–Cu–Zn [11]. In our own studies, we have demonstrated a proportional elevation in the invariant reaction temperatures of the Ag–CuO_x system with small additions of palladium. However as seen from the data in Table 1, no such effect was observed in the present work. The temperatures of the original eutectic and monotectic reactions both remain essentially constant as TiO₂ is added to the binary silver–copper oxide system. The reasons for this are not yet fully understood, although it is suspected that the TiO₂ may partition the copper oxide during liquefaction, drawing a portion of it out of solubility with the silver to form a separate liquid phase as seen in the microstructural results for these specimens. A more detailed

Table 1
Results of the DSC experiments on the Ag–CuO–TiO₂ system

x_{TiO_2}	$x_{\text{Ag}} + x_{\text{CuO}} + x_{\text{TiO}_2}$	Onset temperature (°C)	
		Endothermic peak 1	Endothermic peak 2
0	0.000	953	
0	0.010	940	948
0	0.020	940	967
0	0.040	941	966
0	0.100	942	967
0.005	0.000	954	
0.005	0.010	939	948
0.005	0.020	941	966
0.005	0.040	942	966
0.005	0.100	941	967
0.010	0.000	955	
0.010	0.010	940	947
0.010	0.020	941	965
0.010	0.040	940	965
0.010	0.100	942	967
0.020	0.000	953	
0.020	0.010	938	946
0.020	0.020	939	966
0.020	0.040	937	964
0.020	0.100	940	965

phase equilibrium investigation is underway to test this hypothesis.

While the addition of TiO_2 appears to have little influence on the eutectic and monotectic reactions in the Ag-CuO_x system, it does substantially modify the wetting behavior, as indicated by the plot of wetting angle versus composition in Fig. 1(a) for each family of filler materials. When the data is re-plotted as the differential wetting angle ($\Delta\theta$) between each ternary composition and its corresponding binary counterpart as a function of composition, Fig. 1(b), it is apparent that the effect of TiO_2 on silver-copper oxide wetting behavior strongly depends on copper oxide content. For each curve, three regions of behavior can be identified. For example in all three filler metal series at copper oxide concentrations below 1% (Region I), a detrimental effect is observed. Above this threshold wetting is synergistically enhanced, which defines the behavior in Region II. The copper oxide concentration at which the phenomenon is maximized occurs at ~ 4 mol.% CuO. After reaching this maximum, the degree of wetting enhancement declines and eventually disappears at copper oxide concentrations above ~ 34 mol.%, defining the trend observed in

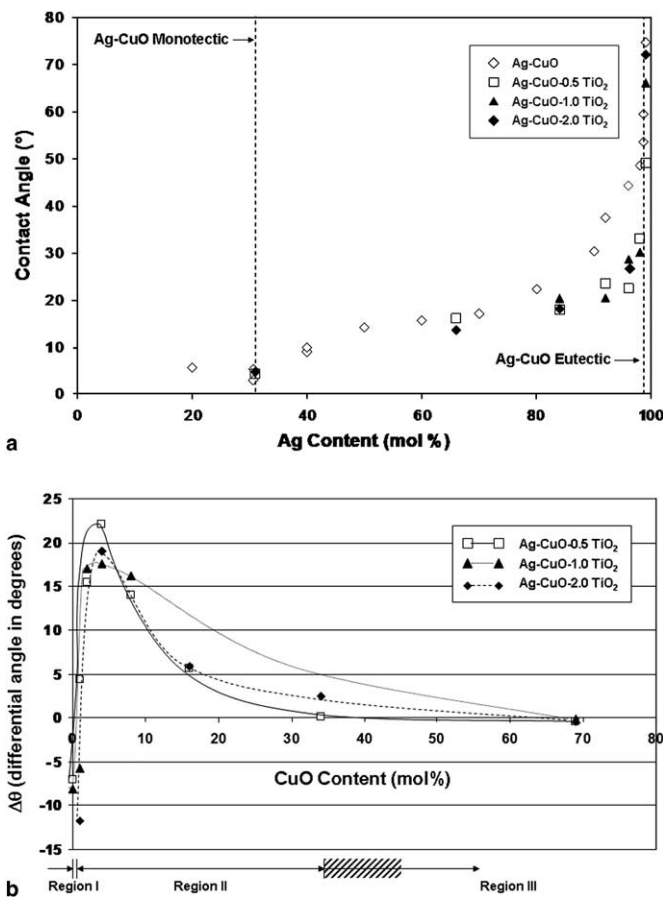


Fig. 1. (a) Contact angle as a function of silver content for Ag–CuO filler metals with additions of 0.5, 1.0, and 2.0 mol.% TiO_2 . (b) Differential contact angle between each ternary filler metal composition and its corresponding binary counterpart as a function of copper oxide content. Measurements were recorded after holding at 1100 °C for 15 min.

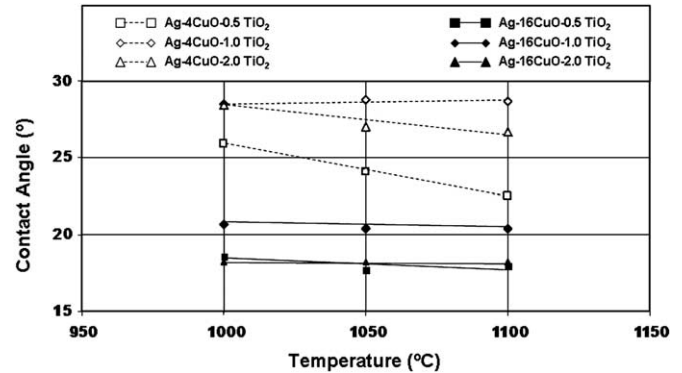


Fig. 2. Contact angle as a function of temperature for sessile drop specimens containing 4 and 16 mol % CuO with additions of 0.5, 1.0, and 2.0 mol % TiO_2 . Samples were isothermally held for 15 min at each measurement temperature.

Region III. When the contact angle data is plotted as a function of temperature, as in Fig. 2, the wetting aid effect attributed to TiO_2 is found to be essentially invariant of temperature with the exception of a small decline with increasing temperature for the Ag–4CuO–0.5 TiO_2 composition. In general, this suggests that the titania wetting aid phenomenon is likely not dependent on an interfacial reaction between the substrate and filler material. Detailed microstructural analysis confirms this conclusion.

Shown in Figs. 3 and 5 are two pairs of back-scattered electron images that typify the joint microstructures found in comparable binary and ternary filler metal wetting specimens of low and high copper oxide content, respectively. Note that in each case, the specimen was heated to a final temperature of 1100 °C and allowed to equilibrate for 15 min before cooling at 10 °C/min. In the binary filler metal specimen of low CuO content (4 mol.%), shown in Fig. 3(a), discrete CuO precipitates approximately 10 μm in size are found along the filler metal/substrate interface. A small amount of a secondary oxide phase containing Al_2O_3 and CuO in solid solution is observed within the interfacial copper oxide, generally a short distance from direct contact with the prior alumina facing surface. Traces of copper are also found within the alumina substrate along grain boundaries, indicating possible diffusional migration of copper cations into the alumina. The appearance of the mixed oxide phase in both the CuO precipitates and the alumina grain boundaries is not surprising given the large degree of mutual solubility displayed Al_2O_3 and CuO [12]. However it is interesting to note no CuAlO_2 was observed between the interfacial copper oxide and alumina, as was previously reported in an earlier study [4]. The rest of the solidified sessile drop lying above the filler metal/substrate interface consists of a silver-rich matrix containing copper oxide precipitates that measure ~ 1 –3 μm in size on average.

In the comparable ternary filler metal specimen, containing 0.5 mol.% TiO_2 and shown in Fig. 3(b), far less CuO is found along the original surface of the substrate.

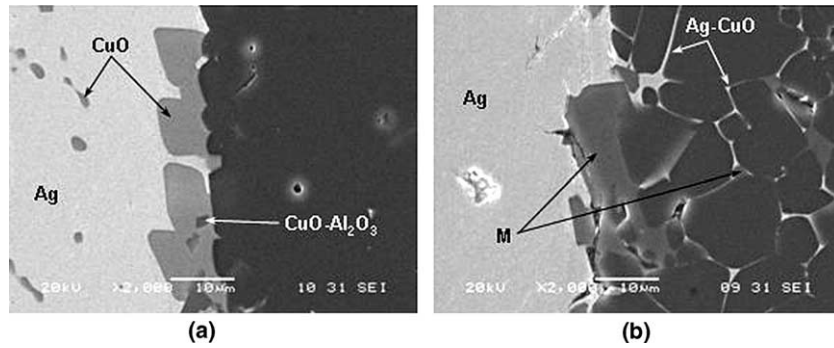


Fig. 3. Back scattered electron images of the filler metal/alumina interface in specimens of the following filler metal compositions: (a) Ag-4CuO and (b) Ag-4CuO-2TiO₂. Both samples were held at 1100 °C for 15 min prior to cooling.

Instead, a substantial amount of filler metal appears to have infiltrated the sub-faying surface region along the grain boundaries of the substrate. As seen in Fig. 4 the degree of filler metal penetration is extensive, up to 200–300 µm into the substrate. EDX analysis indicates that at the furthest extent of filler metal penetration, the intergranular phase contains Al, Cu, Ti, and O. Behind this leading edge, significant amounts of silver are found within the grain boundaries. A metal oxide phase, referred to as M in Fig. 3(b), which consists of Al, Cu, and Ti in varying ratios is found along the original faying surface and throughout the infiltrated region. Comparing the two microstructures in Fig. 3, it appears that the addition of TiO₂ leads to intergranular melting of the alumina. While the cause of this remains unclear, two potential explanations are offered. For this particular filler metal composition, the liquid sessile drop is expected to be diphasic [6], consisting of a small amount of a CuO-rich and a larger portion of a silver-rich liquid. Prior work has shown that

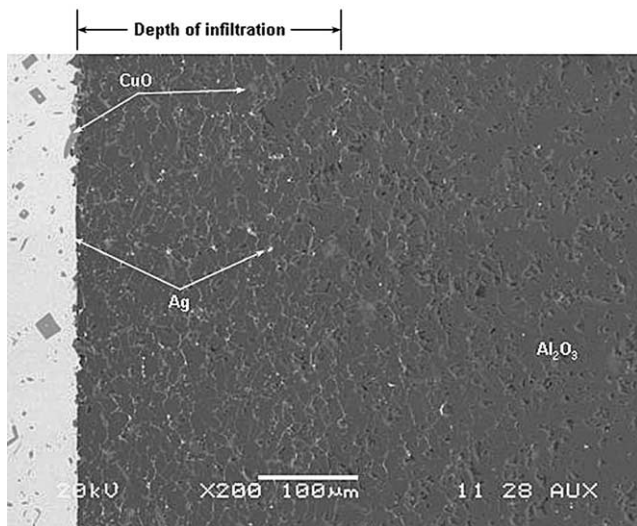


Fig. 4. Low magnification back scattered electron image of the filler metal/alumina interface for the Ag-4CuO-2TiO₂ specimen, which displays filler metal infiltration to a depth of 200–300 µm into the alumina substrate.

the CuO-rich liquid preferentially wets the ceramic substrate [4,5]. In doing so, it is possible that the addition of TiO₂ lowers the eutectic temperature of the CuO-Al₂O₃ system, allowing local melting to take place along regions of highest energy, namely in grain boundaries. Alternatively, although the substrates employed are of high purity, they contain a small amount of silicate, presumably added to facilitate densification via liquid phase sintering [13]. Thus, it is possible that the resulting silicate enriched grain boundaries are more susceptible to dissolution by the liquid CuO-TiO₂ phase. However, no trace of silicon was found in multiple EDX analyses of the intergranular regions in these specimens.

In wetting samples containing greater CuO concentrations in the filler metal, i.e. selected to represent Region III in Fig. 1(b), the interfacial microstructures of comparable binary and ternary compositions are quite similar, as seen in Fig. 5(a) and (b). In the binary sample shown in Fig. 5(a), a band of copper oxide of varying thickness and containing a series of small silver precipitates is observed in contact with the alumina substrate. The appearance of this continuous interfacial layer is not surprising given that this filler metal composition lies within the miscibility gap of the Ag-CuO_x phase diagram [6]. Thus as the filler metal melts and undergoes phase separation into two liquid phases, one rich in copper oxide and the other in silver, the oxide-rich liquid preferentially wets the alumina substrate. Upon cooling below the monotectic temperature, CuO precipitates along the interface with the substrate. With further cooling below the eutectic point, both silver and copper oxide precipitate out onto this proeutectic layer leading to the microstructure observed in Fig. 5(a).

The addition of TiO₂ in this case does not lead to significant infiltration of the filler metal, although a small amount of grain boundary melting is apparent from the isolated Al₂O₃ grains that are found separated from the new filler metal/substrate interface. The dissolution phenomenon that was observed extensively along grain boundaries in the lower CuO-containing filler metal specimen is limited primarily to the faying surface in the higher CuO content specimen. As with the corresponding binary filler

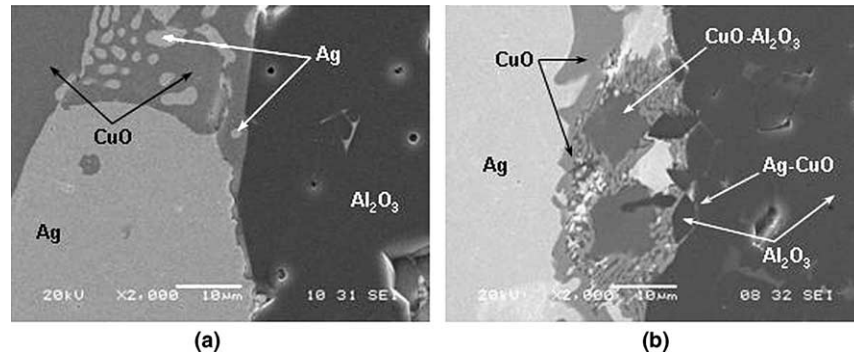


Fig. 5. Back scattered electron images of the filler metal/alumina interface in specimens of the following filler metal compositions: (a) Ag–30CuO and (b) Ag–34CuO–2TiO₂. Both samples were held at 1100 °C for 15 min prior to cooling.

metal, a predominantly CuO-rich phase is found along the interface with the substrate. In addition, a significant amount of a second mixed oxide phase, composed primarily of Al, Cu, and O is observed as a series of slightly darker contrast precipitates within the interfacial band of copper oxide.

The results obtained on the ternary filler metal systems suggest that wetting takes place via a mechanism that is different than that observed in the binary materials. Whereas evidence of diffusion, but not substrate dissolution, is observed in the Ag–CuO sessile drop specimens, the addition of titanium dioxide appears to cause partial dissolution of the alumina. This is readily observed at regions of easiest attack (i.e. grain boundaries), and leads to the formation of an oxide solid solution. Judging from the degree of infiltration of the Ag–CuO–TiO₂ filler metals into the alumina substrate, this effect appears to be greater at a higher TiO₂/CuO ratio, for example for Ag–4CuO–2TiO₂ in Figs. 3(b) and 4, than at a lower ratio, e.g. Ag–34CuO–2TiO₂ in Fig. 5(b). As noted in Fig. 1(b), the Ag–4CuO–2TiO₂ composition corresponds to the maximum $\Delta\theta$ measured in this series of filler metals indicating a positive correlation between the infiltration and wetting aid effects.

4. Summary

The addition of TiO₂ to the Ag–CuO braze system was studied by observing its effects on phase equilibria, wettability, and resulting filler metal/substrate interfacial microstructure. Although the phase equilibria effect is minimal, it was found that TiO₂ concentrations as small as 0.5 mol.% can significantly decrease the contact angle of Ag–CuO on alumina over a compositional range of 1–34 mol.% CuO. The effect appears to maximize at a copper oxide concen-

tration of ~4 mol.% CuO regardless of the titania content, above 0.5 mol.% TiO₂. Metallography indicates that the addition of TiO₂ causes partial dissolution of the alumina substrate, presumably due to the presence of a TiO₂–CuO liquid at the faying surface. At the optimal TiO₂/CuO ratio, dissolution is intergranular and takes place well into the sub-surface of the substrate. At lower TiO₂/CuO ratios, i.e. higher CuO content for a given TiO₂ concentration, dissolution takes place predominantly near the faying surface of the substrate.

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References

- [1] Shüler CC, Stuck A, Beck N, Keser H, Täck U. *J Mater Sci: Mater Electron* 2000;11:389.
- [2] Erskine KM, Meier AM, Pilgrim SM. *J Mater Sci* 2002;37:1705.
- [3] Weil KS, Kim JY, Hardy JS. *Electrochem Solid State Lett* 2005;8:A133.
- [4] Kim JY, Hardy JS, Weil KS. *J Am Ceram Soc* 2005;88:2521.
- [5] Hardy JS, Kim JY, Weil KS. *J Electrochem Soc* 2004;151:J43.
- [6] Nishiura H, Suzuki RO, Ono K, Gauckler LJ. *J Am Ceram Soc* 1998;81:2181.
- [7] Lu F-H, Fang F-X, Chen Y-S. *J Eur Ceram Soc* 2001;21:1093.
- [8] Darsell JT, Weil KS. *J Phase Equil Diff*, in press.
- [9] Mortimer DA, Nicholas MG. *J Mater Sci* 1973;8:640.
- [10] Gaye H, Lupis CHP. *Metall Trans* 1975;6:1057.
- [11] Lupis CHP. *Metall Trans B* 1978;9B:231.
- [12] Misra SK, Chaklader ACD. *J Am Ceram Soc* 1963;46:509.
- [13] Bettinelli A, Guille J, Bernier JC. *Ceram Int* 1988;14:31.