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The Influence of Oxygen on Wetting and Bonding in the Copper-Tungsten System

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The influence of the oxygen content of copper on its wetting of, and bonding to, tungsten has been investigated in detail using sessile-drop and pull-out strength tests. As little as 41 ppm of oxygen has been found to inhibit wetting and to result in bond strengths of less than 2 ton/in.^{2} (3.2 kg/mm^2).

1. Introduction

The authors have recently reported [1] the results of preliminary experiments which showed that the purity of a copper has a marked influence on its ability to wet and bond to tungsten. Thus, spectroscopically pure copper readily wetted tungsten, even at 1088° C, and produced bonds with room-temperature shear strengths of 12.5 ton/in.^{2} (1.0 ton/in.^{2} = 1.6 kg/mm^2); while high-conductivity copper did not wet at temperatures below 1125° C and produced bonds with strengths of only 1.85 ton/in^2. This difference in behaviour was thought to be related to the oxygen content of the copper, because metallographic examination showed wetted samples to have clean interfaces, and non-wetted samples to have a purple-brown layer at the interface.

The present paper is an account of the studies that followed these preliminary experiments. Particular attention was paid to possible correlations between wetting and bonding behaviour and the oxygen contents of the various coppers employed.

2. Experimental Techniques

The two prime grades of copper used were oxygen-free spectroscopically pure copper (JM30, ex Johnson Matthey Ltd) and high-conductivity copper (BSS 1433, ex Enfield Rolling Mills Ltd) containing 251 ppm oxygen. Other intermediate grades were produced by arc-melting together varying proportions of the prime grades. The oxygen contents of these "alloys", presented in table I, were assessed by estimating the area of oxide present in metallographic sections. This technique depends upon correct identification of the Cu_2O inclusions and the validity of the assumption of complete insolubility of oxygen in copper at room temperature. The sky-blue colour of Cu_2O helped in the identification of the inclusions, and, while oxygen has an appreciable solubility in copper at high temperatures (solubilities of about 45 and 15 ppm at approximately 1000 and 550° C having been reported [2]), it is effectively insoluble at room temperature [3]. It should be noted that the oxygen content of the "alloys" was not directly proportional to the high-conductivity copper content; it is presumed that some oxygen was lost during the arc-melting process. Another grade of copper was produced from the high-conductivity material by bringing it into contact with tungsten for 5 min at 1300° C in a vacuum. Table I shows that this "treated" copper was oxygen-free. The thermodynamics of the process are not known; but experimental data, to be presented later in this paper, suggest that a WO_3 layer is formed at the copper/tungsten interface. The tungsten used in the treatment and in the wetting and bonding tests was 99.9% pure.

The wetting behaviour of the various coppers was observed by measurement of sessile-drop contact angles. The tungsten plaque surfaces were metallographically prepared and finished on a $\frac{1}{4}$ μm diamond pad, and both the 0.200 g copper cylinders and the plaques were ultrasonically cleaned in methyl alcohol for 5 min before insertion in the tantalum-strip vacuum

TABLE I The metallographically determined oxygen contents of the various qualities of copper used.

Alloy	Composition	Oxygen content (ppm)
1	HC	251 ± 15
2	HC - 10 wt % JM30	209 ± 8
3	HC - 20 wt % JM30	170 ± 6
4	HC - 30 wt % JM30	106 ± 13
5	HC - 40 wt % JM30	41 ± 10
6	HC - 50 wt % JM30	0
7	HC - 60 wt % JM30	0
8	HC - 70 wt % JM30	0
9	HC - 80 wt % JM30	0
10	HC - 90 wt % JM30	0
11	JM30	0
12	Treated HC	0

furnace. This furnace, which has been described in detail elsewhere [4], was a water-cooled brass chamber containing a vertical, tantalum, split cylinder element surrounded by a pack of tantalum radiation shields. Power was supplied by a constant-wattage control unit built by Hirst Electronic Ltd. Temperature was not controlled directly and could be reproduced to only 5 to 10° C, but was constant to within ±3° C during any one run. A molybdenum pillar topped by a horizontal platform was situated in the centre of the furnace. The tungsten plaques were placed on the platform and the copper cylinders were located in the centre of the plaques. Viewing ports were provided in the water-cooled chamber to enable the specimens to be observed in both the horizontal and vertical planes. The specimens were inserted, the chamber was pumped down to 1×10^{-5} mm of mercury, and the specimens were then degassed by heating at 900° C for 30 min. The vacuum at the wetting temperature was always better than 4×10^{-5} mm of mercury and, unless otherwise stated, the time at temperature was 15 min.

The contact angles of some of the drops were measured directly from photographs taken at temperature, but most values were derived from the drop diameters and volumes calculated from the cylinder weights and the density of liquid copper at the appropriate temperature [5]. It was assumed in the derivation that no vaporisation losses occurred, and that the drops were so small that gravitational effects were negligible and they had the form of spherical caps. No retraction of the drops on cooling and solidification was observed, and the diameters were measured at room temperature with a vermier travelling microscope. Because of its experimental ease, this technique was adopted as standard, after a number of checks had shown the contact angles computed from the room-temperature measurements to be within ±3° of those shown on photographs taken at temperature.

The bond strengths of the copper/tungsten interfaces were measured in shear, by determining the load needed to pull a 0.237 in. diameter tungsten rod out of a 0.500 in. diameter copper block that had been melted around it (1.0 in. = 25.4 mm). The testing technique was chosen because it closely resembled the interfacial stressing conditions that may be encountered in a fibre-composite [6]. The specimens were prepared by melting the copper under a vacuum of better than 4×10^{-5} mm of mercury, and holding for 15 min at the particular wetting temperature selected. The tungsten surfaces were abraded with 400 silicon carbide paper and, with the copper to be used, were ultrasonically cleaned in methyl alcohol for 5 min before being placed in the furnace.

The specimens selected for metallographic examination were prepared with diamond impregnated pads, the final pad holding $\frac{1}{4}$ μm diamond paste. The specimens were normally examined in the unetched condition, but a few were etched with Murakami's reagent. When photomicrographs were taken, a red filter was used to emphasise the colour contrast between the two metals.

3. Experimental Results

3.1. Wetting Behaviour

The contact angles of the different types of copper employed are plotted as functions of the wetting temperature and composition in fig. 1. All the oxygen-free coppers wetted tungsten over the entire temperature range investigated, even though there were differences in the contact angles assumed by the various grades. Wetting behaviour of the oxygen-containing coppers was much more complex. In the case of high-conductivity copper, tungsten was not wetted at the lower temperatures employed, but a dramatic fall through 90° occurred in the contact-angle values as the temperature was raised from 1125 to 1140° C. At even higher temperatures, the copper wetted tungsten and assumed contact angles very similar to those of the oxygen-free, treated, high-conductivity copper. The wetting of tungsten by the other oxygen-containing coppers was not examined in such detail, but the few contact angles measured indicate a similar change from non-wetting to wetting as the temperature is raised.

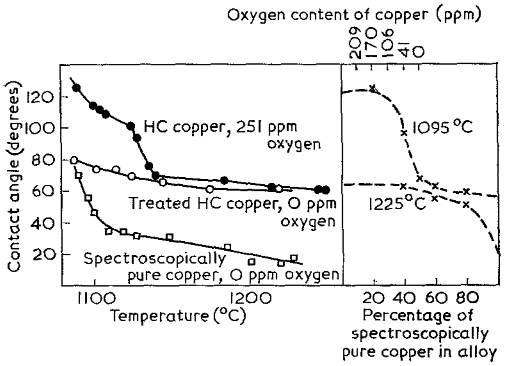


Figure 1 The contact angles of various qualities of copper on tungsten plotted as a function of wetting temperature and composition.

The fall in the sessile-drop contact angles of high-conductivity copper between 1125 and 1140° C was accompanied by marked drop-oscillation and a bodily movement away from the original locations, leaving behind circular, brown patches. Similar behaviour was noticed with the 40 wt %, spectroscopically pure copper specimens (containing 41 ppm oxygen) during the heat-up periods for the 1225° C wetting tests. Fig. 2 shows that the times for which oxygen-containing drops remained sessile and non-wetting were found to be influenced by several experimental variables, such as the wetting temperature, the drop mass and its oxygen content.

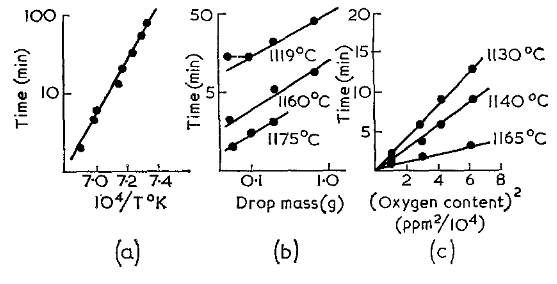
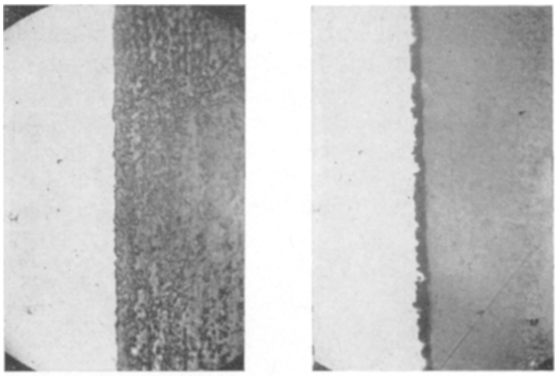


Figure 2 The influence of temperature, drop mass, and oxygen content on the times for which copper drops remain non-wetting on tungsten: (a) high-conductivity copper, 0.2 g drop mass; (b) high-conductivity copper; (c) high-conductivity/spectroscopically pure copper alloys 1, 2, 3, and 4, 0.2 g drop mass.

The metallography of the sessile-drop specimens revealed a correlation between the wetting behaviour and interfacial structure. The oxygen-free coppers formed metallographically clean interfaces with tungsten (fig. 3a). The interfaces formed between high-conductivity copper and tungsten at temperatures above 1140° C (i.e specimens for which the contact angle was less than 90° and in which bodily movement away from the original location had occurred) were also metallographically clean. At temperatures below 1125° C however, high-conductivity copper reacted with tungsten to form purple-brown layers (fig. 3b). Electron microprobe analysis of these layers gave tungsten and copper contents of 78.4 and 0.5 wt % respectively. As a blue fluorescence was noted during the analysis, the layers were tentatively identified as WO_3 (79.3 wt % tungsten and 20.7 wt % oxygen).



(a) (b)

Figure 3 The metallographic appearance of various copper/tungsten interfaces (×450): (a) treated, high-conductivity copper, 1104° C, etched; (b) high-conductivity copper, 1108° C, unetched.

These results suggested that non-wetting was associated with the presence of WO_3 at the interface. The deleterious effect of WO_3 was confirmed by the 140° angle, measured at 1145° C, for oxygen-free, spectroscopically pure copper in contact with tungsten sheet pre-oxidised in air for 10 min at 750° C.

3.2. Bond Strengths

As an attempt to correlate wetting and bonding behaviour was one of the objectives of the work, a check was made on whether the different tungsten surface finishes employed for the pull-out and sessile-drop specimens (400 silicon carbide paper and $\frac{1}{4}$ μm diamond pad) had a significant effect on copper contact angles. Table II presents the results of the four checking experiments and demonstrates that the wetting behaviour was not significantly affected by the surface-finish difference.

TABLE II The contact angles of two grades of copper on tungsten sheet finished on 400 silicon carbide paper and $\frac{1}{4}$ μm diamond pads.

Copper quality	Temperature (°C)	Contact angle (degrees)	
		400 silicon carbide finish	$\frac{1}{4}$ μm diamond finish
HC	1110	110	108
	1245	62	60
Spectroscopically pure	1089	75	70*
	1220	15	14

*extrapolated value

Fig. 4 shows that copper quality had a marked effect upon the pull-out bond strength, strong bonds being formed by oxygen-free coppers and weak bonds by the oxygen-containing coppers. The temperature at which the bonds were formed, however, did not have a significant influence on their (room-temperature) strengths.

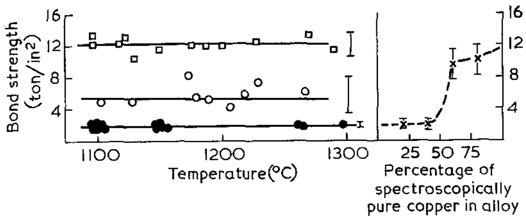


Figure 4 Room-temperature shear strengths of the bonds formed between various qualities of copper and tungsten plotted as a function of specimen preparation temperature and copper composition: □ – spectroscopically pure copper, 0 ppm oxygen; ○ – treated, high-conductivity copper, 0 ppm oxygen; ● – high-conductivity copper, 251 ppm oxygen; X – high-conductivity/spectroscopically pure copper alloys 3, 5, 7, and 9, various oxygen contents. (*Note* 1.0 ton/in.^{2} = 1.6 kg/mm^2)

The metallography of the specimen interfaces correlated reasonably well with their strengths. The interfaces formed by tungsten with oxygen-free coppers were metallographically clean and indistinguishable from each other (even though the bond strengths varied between 5.3 ± 2.3 and 12.35 ± 1.60 ton/in.^{2}). The interfaces formed with oxygen-containing coppers exhibited purple-brown layers of considerable thickness regardless of the specimen preparation temperature (as could be expected, since the geometry of the specimen prevents movement of copper away from its original location).

4. Discussion

The experimental results demonstrate that the prime reason for the variable wetting and bonding behaviour of copper-tungsten is the presence or absence of an interfacial oxide layer. When the copper/tungsten interfaces are metallographically clean, their bond strengths are high and the sessile-drop contact angles are less than 90°. When an oxide layer is present, however, the bond strength is low and wetting does not take place.

The oxide layer has not been identified positively, but it is believed to be WO_3. Since this layer is only present at the interfaces of tungsten with oxygen-containing coppers, it can be concluded that it is formed *in situ*. Thus the composition of the oxygen-containing coppers will change with time, as the WO_3 layer thickens, and, ultimately, complete deoxidation of the copper will occur. The drop configuration is then unstable, since the total energy of the system will decrease if the drop moves off its oxide raft. There is, therefore, a driving force for drop movement away from the original, oxidised location, and chance extensions of the drop outside the original contact area, due, perhaps, to small temperature fluctuations and gradients, will be permanent. The contact-angle measurements plotted in fig. 1 show that, after the movement is completed, the drop is equivalent to treated, high-conductivity copper in contact with a clean tungsten surface.

This approach provides a reasonable qualitative explanation for the instability and physical movement of oxygen-containing sessile drops. Quantitatively, the time for which the drops remain non-wetting (i.e. oxygen-containing) can be calculated by assuming that the WO_3 layer grows parabolically and that the sessile-drop contact angle, and hence the contact area, does not change with time prior to the drop movement. If these assumptions are made, the relationship between t_n, the time for which the drop remains non-wetting, at temperature T, the drop mass, m, and the oxygen content of the copper, C, can be expressed in terms of the equation

$$(Cm/10^6A)^2 = K_0 t_n \exp(-H/RT) \qquad (1)$$

where A is the contact area, H a temperature coefficient, and K_0 and R are constants.

If A is assumed to be proportional to $m^{2/3}$, the equation can be rewritten as

$$t_n = BC^2m^{2/3}/\exp(-H/RT) \qquad (2)$$

where B is an arbitrary constant.

The usefulness of this approach is confirmed by fig. 2, which demonstrates that t_n is indeed proportional to $m^{2/3}$ C^2, and $[\exp(-H/RT)]^{-1}$; where H is 176 kcal/mole.

While oxygen has a marked effect on wetting and bonding behaviour in the copper-tungsten system, other impurities also produce measurable effects. Thus, there was a difference in the contact-angle values and bond strengths of oxygen-free, spectroscopically pure copper and oxygen-free, treated, high-conductivity copper. Similarly, a 20 wt % addition of high-conductivity copper, which did not introduce any oxygen, nevertheless raised the contact angle of spectroscopically pure copper at 1225° C from 14 to 51°, and decreased the bond strength from 12.35 to 10.1 ton/in.^{2} (1 ton/in.^{2} = 1.6 kg/mm^2).

While composition changes caused alterations in both the contact-angle and bond-strength values, changes in the specimen preparation temperature did not affect the bond-strength values, presumably because the liquid atomic configurations were not retained. Thus the only contact angles of possible relevance to the room-temperature bond strengths are those at the melting point. The Young-Dupré equation, $W_A = \gamma_L(1 + \cos\theta)$, predicts a simple relationship between the work of adhesion, W_A, of a solid/liquid interface and the contact angle of the system. Fig. 5, however, demonstrates that the relationship between the room-temperature bond strengths (which might be expected to be directly proportional to W_A) and cos θ, near the melting point, is complex though monotonic.

The influence of tungsten surface preparation on the resultant bond strength was not investigated; but, since the contact angles were the same for the two preparation techniques employed in this work, it is expected that the bond strengths also would be unaffected by surface finish variations.

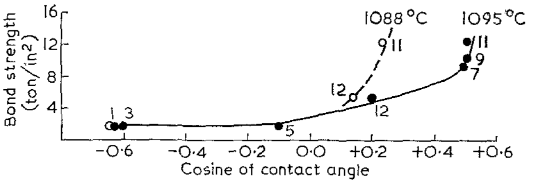


Figure 5 The room-temperature bond strength of interfaces formed between tungsten and various copper alloys plotted as a function of the contact angle. The numbers indicate the alloy identity.

The only conclusions it seems safe to draw from a comparison of the bond-strength and contact-angle data are: (i) the wetting temperature is not a significant factor influencing the bond strength even though it may cause marked contact-angle changes; (ii) the bond strengths of oxygen-containing coppers are low and insensitive to contact-angle changes caused by composition variations; (iii) the bond strengths of oxygen-free coppers are high, and sensitive to compositional variations that have only slight effects on the contact angles at temperatures near the melting point.

Since this study was prompted by the current technological interest in copper-tungsten fibre structures, it is worthwhile considering whether the new data acquired have any technological significance. The study has provided an explanation, in terms of oxygen contamination, of why difficulties are sometimes encountered in the infiltration of tungsten structures with copper [1]. Thus, the use of low-quality copper can be a false economy unless steps are taken to reduce the oxygen concentration, since any bonds formed will be weak (as was found by Tylecote [7] who used copper with an oxygen content of 140 ppm to braze tungsten to tungsten). The oxygen content of copper is normally decreased by melting in a reducing atmosphere; but this work has shown that infiltration (requiring a contact angle of less than 90°) and a marked improvement in bond strength could be achieved merely by allowing the copper to react with scrap tungsten prior to the actual fabrication process.

Even if the copper is rendered oxygen-free by some technique, small compositional variations may affect the bonding behaviour and hence the product quality. The identities of these other harmful impurities are not known, but the work of Petrasek [8] suggests that nickel may be one of them. Finally, the experimental data suggest that the use of a high superheat temperature during infiltration will not result in the production of stronger composites.

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