JOURNAL OF MATERIALS SCIENCE 13 (1978) 1509–1514

The wetting of alumina and vitreous carbon by copper-tin-titanium alloys

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The wetting behaviour of copper-rich copper–tin–titanium alloys on alumina and vitreous carbon substrates at 1050 to 1150° C has been determined using the sessile drop technique. Substantial additions of titanium induce copper to wet, but tin has no significant effect. However, the simultaneous addition of tin and titanium is markedly beneficial, particularly with vitreous carbon. Metallographic and EPMA studies showed that titanium-rich reaction products were formed at the interfaces. The wetting and reactivity data are interpreted in terms of surface enrichment of the alloys by tin and of a disproportionately greater activity of titanium in tin.

1. Introduction

Brazing is used extensively in the fabrication of metallic components, but its usefulness with ceramics is limited by the inability of the many conventional alloys based on copper, silver and tin to wet industrially important oxides, carbides or carbon [1]. The most widely adopted solution to this problem is to coat the ceramic surface before brazing with a metal layer by physical or chemical techniques, vapour deposition or the molybdenum–manganese oxide process for instance, before brazing. However, this approach suffers from technical and economic disadvantages that have led to the development of brazes that can be used with unmetallized ceramics. These have been produced by adding a reactive element, particularly titanium, to a conventional braze material in the hope that it will change the chemistry and enhance the wettability of the ceramic surface. Thus the addition of about 10% of titanium induces copper to wet carbon [2] due to the formation of a titanium carbide reaction product, and copper alloyed with 49 to 57% titanium has been recommended as a braze for alumina and graphite [3, 4]. In practice, ternary rather than binary alloy brazes are commonly used, particularly the copper–50.9% silver–15.2% titanium alloy developed from the copper–72% silver eutectic braze. There has also been significant exploitation of a copper 10.3% tin 12.8% titanium braze [5] which is cheaper and less volatile.

The work described in this paper was conducted as part of a programme attempting to develop a wider and better characterized range of brazes. Attention has concentrated so far on copper–tin–titanium alloys with the specific objective of systematically determining the effect of composition on the wetting behaviour between the alloys and alumina or vitreous carbon. From this it was hoped that some understanding would be gained of why the addition of tin, which is itself non-wetting, should be beneficial, and that a more rational basis for the development of other reactive metal brazes would result.

2. Materials and techniques

The vitreous carbon and alumina substrates were in the form of 15 to 20 mm diameter disks approximately 2 mm thick. The vitreous carbon obtained from Vitreous Carbon Ltd. of Bishop Auckland, was polished to give a surface finish of better than 0.1 μm C.L.A.* The 99.5% pure silica free AL 23 alumina was obtained from Degussa, Frankfurt am Main and was used, in the as-received condition with a surface finish of 0.8 μm C.L.A. All the metals employed were spectro-

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*Centre line average roughness.

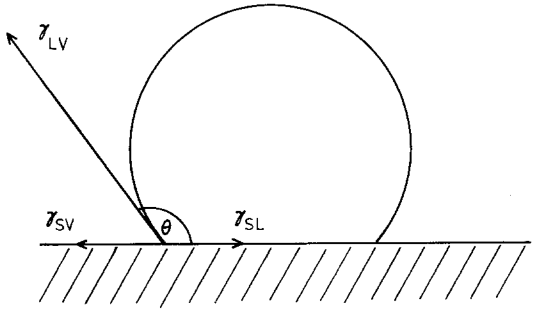

Figure 1 Schematic appearance of a non-wetting sessile drop defining the contact angle and indicating the interplay of surface and interfacial energies at the drop periphery.

scopically pure material obtained from Johnson Matthey Ltd., London.

The wetting behaviour between these ceramics and the various alloys were measured in terms of the contact angle subtended between the peripheral surface of a small sessile drop of molten alloy and the horizontal surface of the ceramic substrate as indicated in Fig. 1. This angle, θ, is related to the solid and liquid surface energies, γ_{SV} and γ_{LV} and the solid–liquid interfacial energy, γ_{SL}, by the Young–Dupre equation

$$\gamma_{SV} = \gamma_{LV} \cos\theta + \gamma_{SL} \qquad (1)$$

The alloys used in the sessile drop experiments were produced *in situ* by machining a cylinder of copper 3 mm in diameter and about 6 mm high with a hole in the top face into which the required amounts of alloying element were placed, the total weight of the cylinder plus alloying additions being 0.300 g. The metal samples and ceramic disks were then ultrasonically cleaned in methylated spirits before being placed in a vacuum furnace in a position from which they could be viewed through observation ports. After loading, the furnace was evacuated to less than 5×10^{-5} mm of mercury and the temperature raised slowly to 800° C. After being outgassed for 30 min at that temperature, the samples were heated rapidly to 1050° C, then 1100° C and finally 1150° C and held for 20 min at each temperature to establish equilibrium conditions. Profiles of the molten sessile drops were photographed using an Asahi 35 mm camera and contact angles were measured from the negatives using a Nikon CT6 projector.

Selected solidified drops were sectioned and polished to a $\frac{1}{4}$ μm finish using diamond impregnated pads, for subsequent metallographic and electron probe microanalyser examination.

3. Results

Tables I and II present the contact angle values measured during the present study or previous work employing the same experimental techniques, equipment and ceramic substrates. The data show that the addition of substantial amounts of titanium, 6 to 10 at %, induces copper to wet both alumina and vitreous carbon. In contrast the addition of tin has little effect on the wetting behaviour of copper, additions of up to about 50 at % in fact producing a slight increase in the contact angle values. The simultaneous addition of tin and titanium has a markedly beneficial effect on wetting behaviour, increasing amounts of tin reducing the titanium content needed to produce wetting. Thus the combined effect of 11.8 at % of tin and only 3.5 at % of titanium is

TABLE I Contact angles of copper–tin–titanium alloys on alumina

Composition (at %)			Contact angle (deg)		
Cu	Sn	Ti	1150° C	1100° C	1050° C
97.2	0	2.8	138	142	-
93.6	0	6.4	91	92	143
92.2	0	7.8	91	91	94
75.1	0	24.4	28	57	77
69.5	0	30.7	13	15	19
62.5	0	37.5	< 10	< 10	< 10
95	5	0	-	-	141 [6]
90	10	0	-	-	149 [6]
80	20	0	-	-	148 [6]
70	30	0	-	-	148 [6]
0	100	0	-	-	145 [6]
87.9	8.6	3.5	113	121	-
84.7	11.8	3.5	86.5	112	129
73.9	22.5	3.6	60.5	72.5	75.5
90.7	2.7	6.6	92	93	97
87.7	5.6	6.7	89	98	100
84.5	8.5	7.0	73	80	82
81.2	11.6	7.2	74	115	123
77.8	14.9	7.3	65	70	76
74.1	18.4	7.5	56	65	70
64.7	27.6	7.7	39	42	45
79.5	9.9	10.6	< 10	< 10	13
81.8	7.8	19,4	12	17	21
82.7	4.0	13.3	14	20	25
81.2	5.5	13.3	< 10	< 10	< 10
74.5	11.4	14.1	< 10	< 10	< 10
76.5	1.3	22.2	44.5	61.5	62.5
78.0	2.6	19.4	29	40	47

TABLE II Contact angles of copper–tin–titanium alloys on vitreous carbon

Composition (at %)			Contact angle (deg)		
Cu	Sn	Ti	1150° C	1100° C	1050° C
100	0	0	145	-	-
98.7	0	1.3	142		-
98.0	0	2.0	144	-	-
95.2	0	4.8	146 (2)	-	
90.0	0	10.0	90 (2)	-	-
88.9	0	11.1	79 (2)	-	-
88.0	0	12.0	69 (2)	-	
86.8	0	13.2	24 (2)	-	-
85.0	0	15.0	15 (2)	-	-
78.5	0	21.5	5		
94.4	5	0	161		
88.2	11.8	0	153		
81 4	18.6	0	158		
73.7	26.7	0	161		
65.1	34.9	0	161		
55.5	44.5	0	148		
44.5	55.5	0	137		
31.8	68.2	0	137		
17.2	82.8	0	141		
0	100	0	132		
96	2.8	1.2	78		
00.0	8.7	1.3	< 10		
83.8	14.8	1.4	< 10		
79.9	18.6	1.5	< 10		
72.2	26,3	1.5	< 10		
63.6	34.8	1.6	< 10		
94.4	1.6	4.0	132	135	137
92.5	4.1	3.4	32	37	45
91 0	5.6	3.4	< 10	22	53
84.7	11.8	3.5	< 10	16	32.5
92.4	1.0	6.6	100	120	132
90.7	2.7	6.6	84	95	102
89.2	4.1	6.7	< 10	15	43
87.7	5.6	6.7	< 10	< 10	28
84.5	8.5	7.0	< 10	< 10	11
88.9	1.4	9.7	62	64	67
87.4	2.7	9.9	37	42	49
85.4	2.6	11.9	15	33	43
85.9	4.1	10.0	< 10	< 10	34
84.4	5.5	10.1	< 10	< 10	20
85.7	1.4	12.9	51	60	7
74 5	11.4	14.1	< 10	< 10	< 10
82.6	1.3	16.1	12	49	73

sufficient to ensure the wetting of alumina at 1150° C or even more remarkably the addition of 2.8 at % of tin and 1.3 at % of titanium induces copper to wet vitreous carbon at 1150° C. The contact angles assumed by titanium containing alloys were always lower on vitreous carbon than alumina substrates. These compositional effects are illustrated graphically in Figs. 2 and 3 in which the 90° and 10° isoclines defining marginal and excellent wetting at 1150° C are plotted on ternary diagrams. Contact angles were measured also at 1100 and 1050° C but the compositional effects were very similar to those shown in Figs. 2 and 3.

Metallographic examination showed reaction products to be present at the interfaces formed by titanium containing alloys with both alumina and vitreous carbon but none were observed at those formed by copper or copper–tin alloys. There was no clear difference between the reaction products formed by wetting and non-wetting alloys. Thus Fig. 4 shows that alloys assuming contact angles on vitreous carbon at 1150° C of 142° and 10°, produced similar duplex interfacial structures consisting of an attached 1 to 2 μm-thick reaction product layer and detached particles or flakes. The reaction products formed at the interfaces with alumina by both non-wetting and wetting alloys were continuous. Electron probe microanalysis showed that the reaction product layers formed with both vitreous carbon and alumina were titanium-rich, but quantitative analysis was not possible because of their thinness and the difficulty of measuring carbon and oxygen.

4. Discussion

The data presented in Tables I and II enable compositional effects on the wetting behaviour of copper-rich copper–tin–titanium alloys to be described with some confidence. They demonstrate that the addition of tin to copper does not enhance its ability to wet ceramics, but the addition of titanium does, and the simultaneous addition of tin and titanium is particularly beneficial, in general agreement with the few relevant data reported in the literature [5, 7–9]. It is particularly noteworthy that the commercially developed copper–10.3 at % tin–12.8 at % titanium brazing alloy falls well within the compositional regions that produced excellent wetting of both alumina and vitreous carbon.

A complete understanding of the effects of alloy composition on the wetting behaviour of the copper–tin–titanium system is not yet possible, but a partial interpretation can be attempted. The Young–Dupre equation (Equation 1) shows that a change from non-wetting to wetting behaviour must be due to a decrease in the energy of the alloy–ceramic interface from more than to less

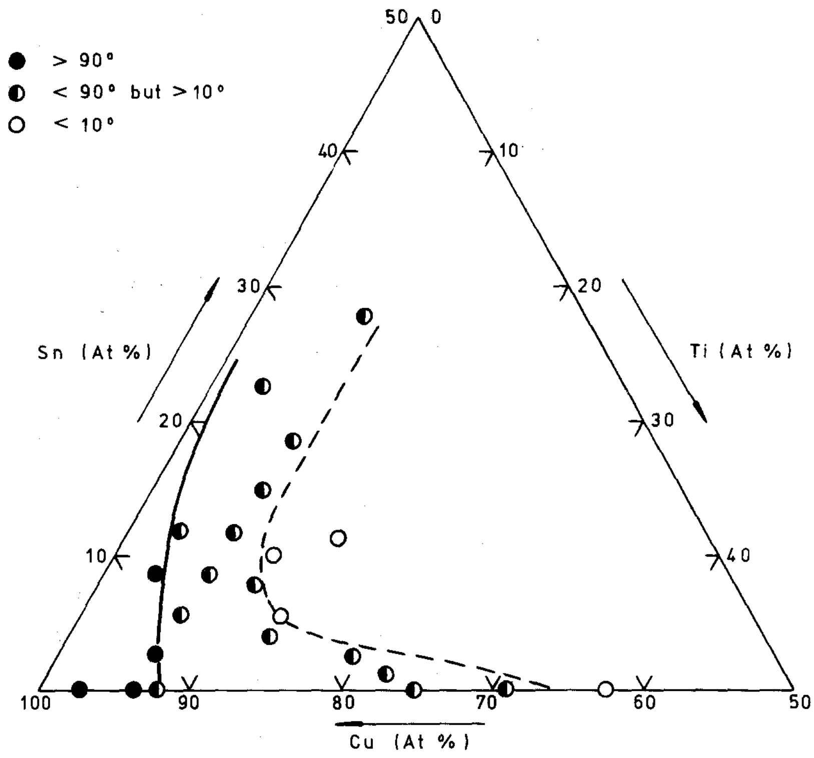

Figure 2 Wetting behaviour between alumina and copper–tin–titanium alloys at 1150° C.

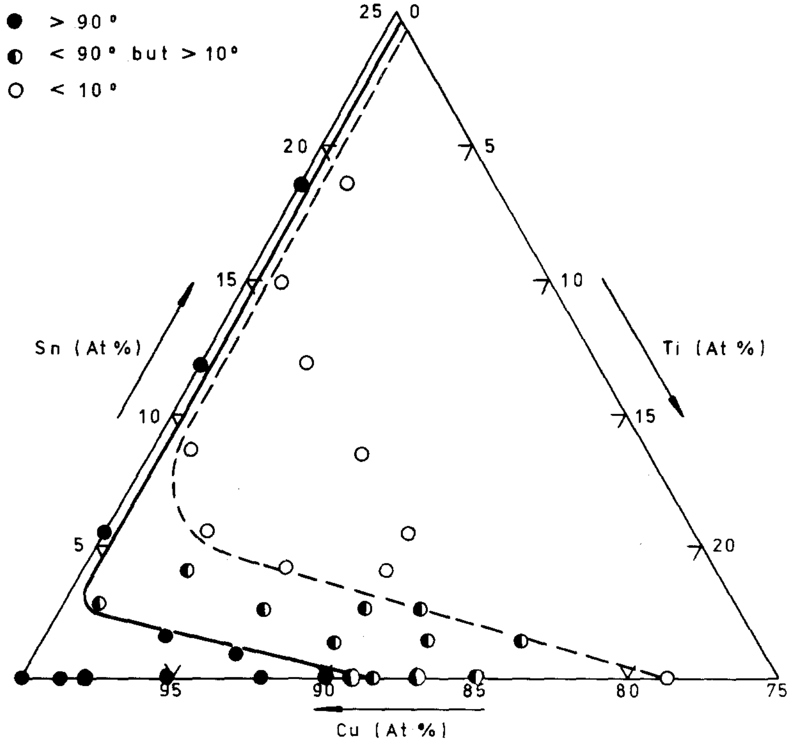

Figure 3 Wetting behaviour between vitreous carbon and copper–tin–titanium alloys at 1150° C.

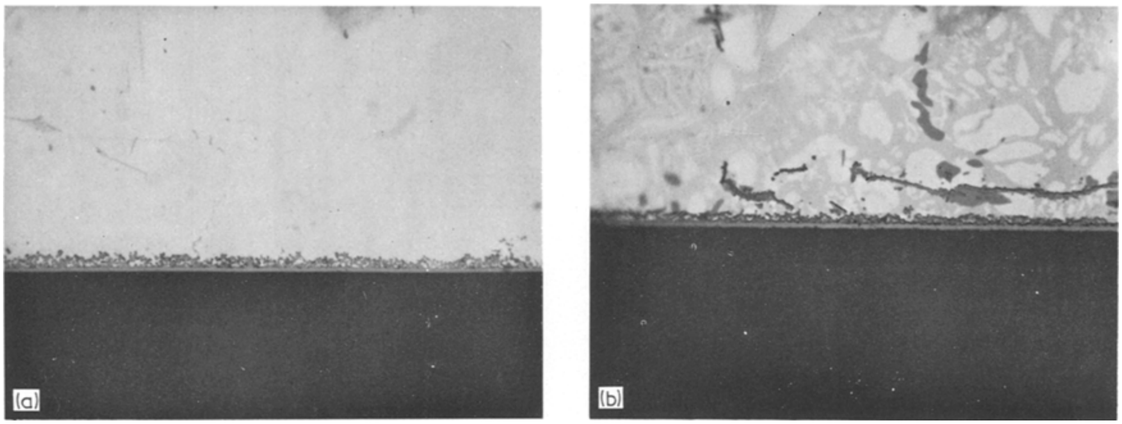

Figure 4 Microstructure of alloy–vitreous carbon interfaces formed at 1150° C by (a) a Cu–1.3 Ti alloy with a contact angle of 142°, and (b) a Cu–14.8 Sn–1.4 Ti alloy with a contact angle of less than 10° (X 600).

than that of the ceramic surface. Such changes can be attributed often to a chemical reaction between the alloy and the ceramic to form a product with a low liquid–solid interfacial energy. However, metallographic studies showed similar reaction products to be present at the interfaces formed by both wetting and non-wetting alloys. It appears therefore that the detailed chemistry of the reaction products may have a marked effect on wetting behaviour and there is evidence that this is so for the binary alloys. For example, several workers have found that titanium carbide with C/Ti ratios of less than 0.65 are wetted by copper [10–12] as shown in Fig. 5. The thermodynamic calculations of Storms [13] summarized in Table III demonstrate that such carbides will be produced by the reaction of carbon with copper alloys that have a titanium activity larger than 0.1. The activity coefficient of titanium in copper is probably close to one at 1150° C since its solubility is high, 73 at % [14], and hence the data in Fig. 5 are consistent with the observation that about 10 at % of titanium is needed to induce copper to wet vitreous carbon. In contrast, the solubility of titanium in tin is only 17 at% at 1150° C [14] and hence its activity coefficient is probably significantly greater than unity. It is noteworthy, therefore, that a low concentration, less than 1 at%, of titanium is needed to induce tin to wet vitreous carbon, even though there is no supplementary information on wetting behaviour between tin and titanium-rich carbides.

TABLE III Activity of titanium in equilibrium with TiC_{1-x}

Carbide composition	Titanium activity at 1127° C
$TiC_{0.95}$	6×10^{-7}
$TiC_{0.91}$	7×10^{-5}
$TiC_{0.80}$	2×10^{-3}
$TiC_{0.70}$	2×10^{-2}
$TiC_{0.60}$	0.22
$TiC_{0.48}$	1.0

Similar thermodynamic calculations can be made for titanium oxides and there is experimental evidence that wettability and metallicness are related. Thus the contact angles of copper on Ti_2O_3 and $TiO_{0.86}$ are 115° and 70°, and X-ray diffraction studies have shown that titanium-rich oxides are formed on alumina surfaces wetted by copper–titanium alloys and tin–titanium alloys [9–15]. Furthermore, less titanium is needed to induce wetting by tin than copper [15].

The behaviour of the ternary copper–tin–titanium alloys is more complex than that of the binary systems because of segregation effects.

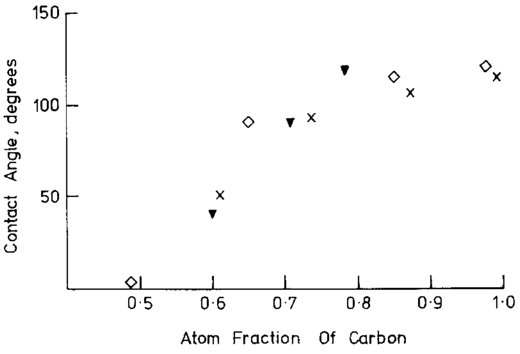

Figure 5 The influence of stoichiometry on the wetting behaviour of copper, X –[10], ▼ –[12], ◇ –[11].

Thus the liquid surface energy of tin is so much less than that of copper, 0.48 as compared to 1.28 J m^{-2} at 1100° C [16], that it will segregate and enrich the surfaces of the alloys. Similarly, segregation to interfaces formed with alumina and vitreous carbon is likely since contact angle and surface energy data indicate that the replacement of copper by tin will reduce their energies by 10 to 30%. Because of this enrichment, the surface and interfacial properties of copper–tin–titanium alloys will approach those of tin–titanium alloys at low bulk concentrations of tin. This simple description is consistent with the better wetting of vitreous carbon than alumina by tin–titanium and copper–tin–titanium alloys but not by copper–titanium alloys [7, 15]. The limited reactivity of the wetting ternary alloys with vitreous carbon is noteworthy since the reaction zones of wetting tin–titanium alloys are also continuous and less than a micron thick [17], while those of wetting copper–titanium alloys are particulate and tens of microns thick [2].

The present study implies that the wetting behaviour of copper–titanium alloys may be improved by the addition of a third element that has a lower surface energy than copper and in which titanium has a more restricted solubility. Several metals besides tin satisfy these criteria as shown by the data assembled in Table IV and it is significant that indium, lead and silver have been suggested in the patent literature as having beneficial effects on the behaviour of copper–titanium alloys. Magnesium and zinc satisfy the criteria but they were not included in the table because of their high volatilities and neither are they known to have been recommended in the UK patent literature. The most frequent patent references are to the commercially developed copper–50.9% silver–15.2% titanium alloy, and it is noteworthy that the high silver content is consistent with a relatively low segregation tendency due to its high surface energy. Thus the criteria identified in this study provide some guidance for the development of other brazes.

TABLE IV Some properties of selected metals at 1150° C

Element	Liquid surface energy (J m^{-2}) [16]	Titanium solubility (at%) [14]
Cu	1.28	73
Sn	0.48	17
Ag	0.87	8
Ga	0.61	28
In	0.47	20
Pb	0.36	-

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Received 19 September and accepted 4 November 1977.