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The wetting of alumina by copper alloyed with titanium and other elements

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The wettability of alumina by ternary alloys of copper, titanium and aluminium, gallium gold, indium, nickel or silver has been investigated using sessile drop tests conducted in vacuum at 1050–1250° C. Substantial additions of titanium are known to induce copper to wet alumina due to the formation of a titanium rich reaction product at the alloy/ceramic interface, but the present work has shown that the concentration of titanium can be reduced by the addition of ternary alloying elements. Additions of indium are very beneficial, of aluminium, gold or silver are moderately beneficial, and of gallium or nickel are of negligible benefit or detrimental. These observations, and previous work with copper–tin–titanium alloys [1] can be interpreted in terms of effects on the activity of titanium which it is argued will be enhanced if the ternary alloying element has a low surface energy and is readily saturated by titanium. The correlation of the experimental wetting observations with the surface energy and titanium solubility data for the ternary alloying elements provides a basis for the rational development of reactive metal brazes for joining unmetallized ceramics.

1. Introduction

Many ceramics, particularly oxides, are poorly wetted by liquid metals and therefore the development of brazes for fabricating ceramic components is difficult. The basic reason for this tendency is the differeing bonding characteristics of metals and ceramics, and detailed consideration of bonding interactions across metal–ceramic interfaces has led to a better understanding of wetting behaviour for simple systems. Thus Naidich and Kolesnichenko succeeded in predicting the poor wetting behaviour of a number of non-carbide forming metals with carbon, and rather less successfully with silicon carbide, by calculating the Van der Waals interactions across the interfaces [2, 3]. Similarly McDonald and Eberhardt calculated the Van der Waals and ionic interactions at various sites on a model alumina surface and thereby succeeded in ranking the wetting characteristics of a number of metals and a few binary alloys [4]. However, most brazes are not pure metals or even binary alloys but have complex compositions that reflect the many criteria for a satisfactory material. Their development has tended to be semi-emperical at best and as a contribution towards improving our understanding of more complex alloys we have recently studied and attempted to analyse the effects of varying the composition on the wetting behaviour of a ternary alloy system, copper–tin–titanium [1] which has been found to be of use for brazing many ceramics, including alumina and carbon [1, 5].

The good wetting behaviour of copper–tin–titanium alloys is notable for the beneficial effects conferred by tin which does not itself wet many ceramics. Thus we have observed [1] that while additions of about 8% of titanium are needed to induce copper to wet alumina at 1150° C, only 3.5% of titanium is needed if the copper is also alloyed with 11.8% of tin. Similarly the titanium concentration needed to induce wetting of carbon can be reduced from 10% to 1.2% by the addition of 2.8% of tin. The analysis of our wetting data suggested that the addition of the tin was beneficial for two reasons. First, the solubility of titanium is less in tin than copper and hence alloying increased the activity of titanium and led to the formation of more readily wettable hypostoichio-

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TABLE I Some properties of selected elements

Element	Liquid surface energy ($J m^{-2}$) at a temperature (° C) of			Titanium solubility, (at %) at a temperature (° C) of		
	1050	1100	1150	1050	1100	1150
Cu	1.364*	1.353	1.343	67	70.0	73
Sn	0.484	0.482	0.480	13	15.5	17
In	0.448	0.439	0.429	13	17.0	20
Al	0.810	0.804	0.798	2	3.0	5
Ag	0.904	0.897	0.889	4	5.5	8
Au	1.160*	1.070	1.020	10*	7.0	12
Ga	0.614	0.609	0.604	11	19.0	28
Ni	1.965*	1.945*	1.925*	12*	12.5*	13*

*Values extrapolated below melting point of pure element.

metric reaction products. Second, the low surface energy of tin compared to copper causes it to segregate to the alloy surface, thereby increasing its effect on titanium activity at the alloy surface and also enhancing any beneficial changes in wettability.

The objective of the work described in this paper was to assess whether these suggested causes could be used as criteria for the selection of other alloying metals. Six elements were selected for the assessment, aluminium, gallium, gold, indium, nickel and silver. As can be seen from the data in Table 1, [6, 7] their surface energies and abilities to dissolve titanium varied widely, in some cases being greater and in others smaller than those of tin, but all six elements are common components of brazes intended or used for joining ceramics.

2. Experimental materials and techniques

The ceramic substrates used in this work were 99.5% pure, silica free AL23 alumina and was obtained from Degussa, Frankfurt am Main. They were in the form of 20 mm diameter, 2 mm thick discs with an average surface roughness of 0.8 μm. All the metals used were spectroscopically pure and obtained from Johnson Matthey Ltd, London. The various alloys identified in Table II were produced *in situ* by machining a cylinder of copper 3 mm in diameter and about 6 mm high with a deep hole in the top face in which the required amounts of alloying elements were placed, the total weight of the sample being 0.300 g.

The wetting behaviour between the alloy cylinders and the ceramic discs was investigated by sessile drop tests and defined in terms of the contact angle, as illustrated in Fig. 1. Liquids with contact angles of more than 90° are non-wetting and will not freely spread over surfaces or penetrate capillaries as required for a braze. Similarly, liquids with contact angles of less than 90° wet and penetrate capillaries, and their spreading over surfaces becomes particularly marked when the contact angles are less than about 25°.

The metal and ceramic samples were cleaned before use in the sessile drop tests by ultrasonic agitation in acetone. They were then placed on a platform in a vacuum furnace and positioned so that they could be viewed through observation ports. The furnace chamber was evacuated to a pressure of about 10^{-3} Pa and the samples were heated slowly to 800° C and outgassed for 30 minutes. The samples were then heated rapidly to a temperature of 1000° C, then 1050, 1100 and 1150° C, and held at each temperature for 20 minutes to establish equilibrium. Samples containing nickel, additions of which increase the melting temperature of copper, were further heated to 1250° C. Profiles of the molten sessile drops were photographed at each temperature using an Asahi 35 mm camera and contact angles were measured from the negatives using a Nikon CT6 projector.

Selected samples were sectioned and polished to a ¼ μm finish using diamond impregnated pads for subsequent metallographic and electron probe microanalyser examination.

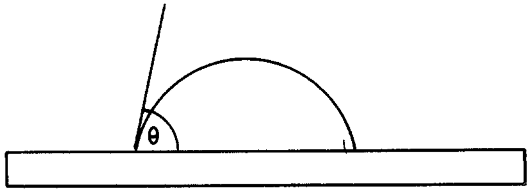

Figure 1 Sketch of a sessile drop of liquid with a contact angle θ resisting on a horizontal solid substrate.

TABLE II Nominal alloy compositions (at %)

Cu					
with Ag and Ti	with Al and Ti	with Au and Ti	with Ga and Ti	with In and Ti	with Ni and Ti
Cu/5–34 Ag	Cu/2–40 Al/5 Ti	Cu/20–34 Au	Cu/2–30 Ga/5 Ti	Cu/25–30 In/2.5 Ti	Cu/20–30 Ni
Cu/10–12.5 Ag/2.5 Ti		Cu/25–30 Au/2.5 Ti		Cu/2–34 In/5 Ti	Cu/25–30 Ni/2.5 Ti
Cu/2.5–15 Ag/5 Ti		Cu/15–20 Au/5 Ti		Cu/10–28 In/10 Ti	Cu/5–34 Ni/5 Ti
Cu/2.5–5 Ag/10 Ti		Cu/5–15 Au/10 Ti		Cu/5–15 In/15 Ti	Cu/5–20 Ni/10 Ti
		Cu/2–5 Au/20 Ti		Cu/2.5–8 In/20 Ti	Cu/5 Ni/15 Ti
		Cu/2 [illegible] Au/25 Ti		Cu/2.5–5 In/25 Ti	Cu/2.5–5 Ni/25 Ti

3. Results

Most alloys became completely molten and formed symmetrical drops within one or two minutes at 900–1000° C and remained quiescent as they were further heated to the experimental temperatures. The only samples that had higher melting points were the few containing high nickel and low titanium concentration which did not become completely liquid until 1100–1150° C. The contact angles assumed by the sessile drops became constant after two or three minutes at the experimental temperatures and measurements taken after fifteen minutes were used to characterise the equilibrium behaviour of the alloys.* This behaviour was little dependent on the experimental temperature within the range used in this work as illustrated in Fig. 2 for a series of copper–gallium–titanium and copper–indium–titanium alloys.

The wetting characteristics of the alloys were markedly influenced by their titanium contents and some, but not all of the ternary alloying additions also exerted an influence, thus Figs. 3 and 4 show that gold, indium and silver additions enhance wetting behaviour while Fig. 5 shows that additions of gallium cause no significant benefit at 1150° C and additions of nickel are similarly ineffective even at 1250° C. The effect of aluminium was slight, some enhancement being produced but only by additions of more than 30 at % (Fig. 6). For reasons that will be discussed later, it was expected that the beneficial effect of aluminium would be more marked than was observed. In case this had been inhibited by the relatively poor vacuum used in this work, a second series of experiments was conducted in a better vacuum, 10^{-5} Pa, at 1150° C with alloys containing 5 at % titanium but no improvement in wetting behaviour was found as illustrated in Fig. 6.

The co-operative interaction of titanium and some alloying elements was revealed further when the experimental results were plotted on ternary composition diagrams. Fig. 7 presents such a plot of the wetting data obtained at 1150° C for copper–indium–titanium alloys and it is noteworthy that both the 90° and, particularly, the 25° isoclines defining marginal and excellent wetting behaviour are concave towards the copper rich corner of the diagram. Similar concavities were observed in the 90° and 25° isoclines for copper–tin–titanium alloys in a previous study [1] and alloys containing gold and silver in this study, as summarized in Fig. 8. However, aluminium additions produced only a slight concavity of the 90° isocline, gallium additions of up to 30 at% produced no discernible concavity, and nickel additions caused the isocline to become convex, suggesting an inhibition of the beneficial effect produced by titanium additions.

The decrease in contact angles observed in this work when copper–titanium alloys were further alloyed with aluminium, gold, indium or silver can be interpreted as evidence of changes produced at the alloy/alumina interfaces and optical microscopy and electron probe microanalysis provided some support for this. Examination of cross-

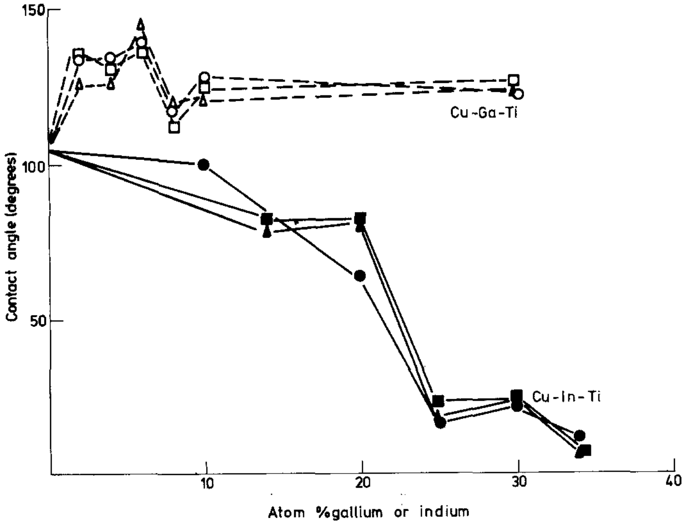

Figure 2 The effects of ternary element additions on the wetting of alumina by copper–5 at % titanium alloys at 1050° C, □■ 1100° C, △▲, and 1150° C, ○●.

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*A complete listing of these angular measurements is presented elswhere for reference purposes [8]

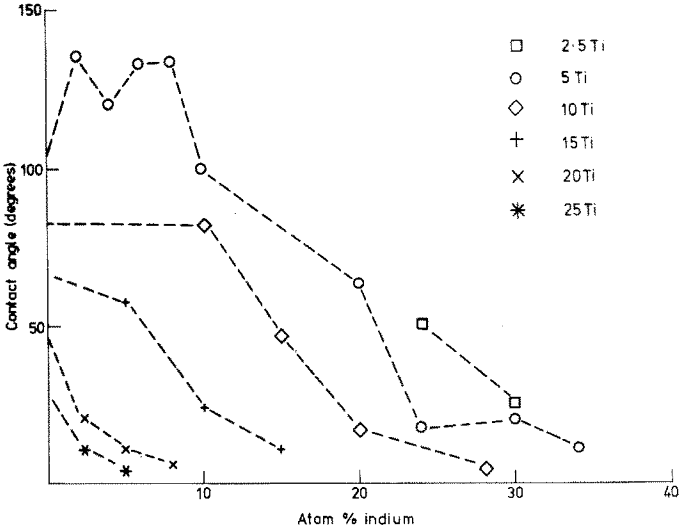

Figure 3 The effects of additions of indium on the wetting of lumina by copper titanium alloys at 1150° C.

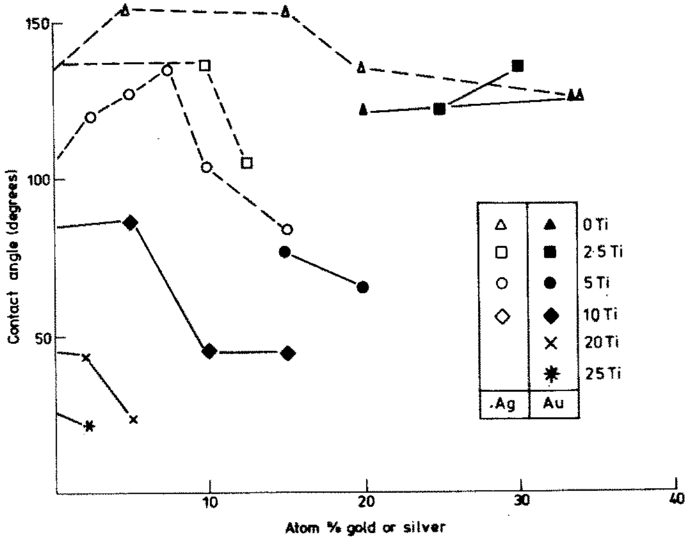

Figure 4 The effects of additions of gold or silver on the wetting of alumina by copper titanium alloys at 1150° C.

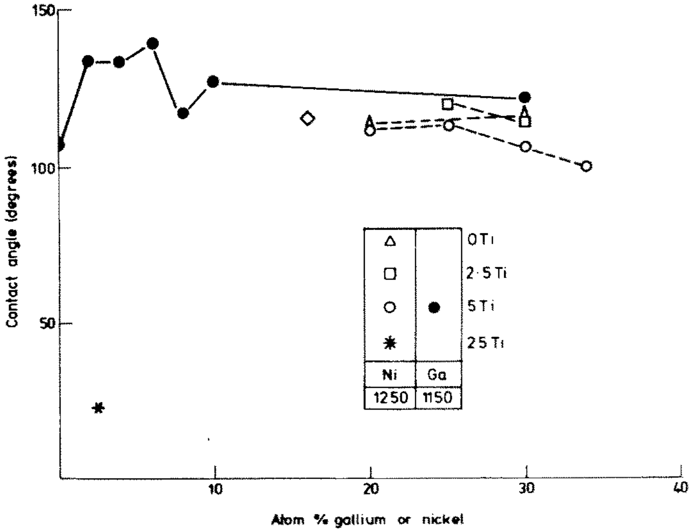

Figure 5 The effects of additions of gallium or nickel on the wetting of alumina by copper titanium alloys.

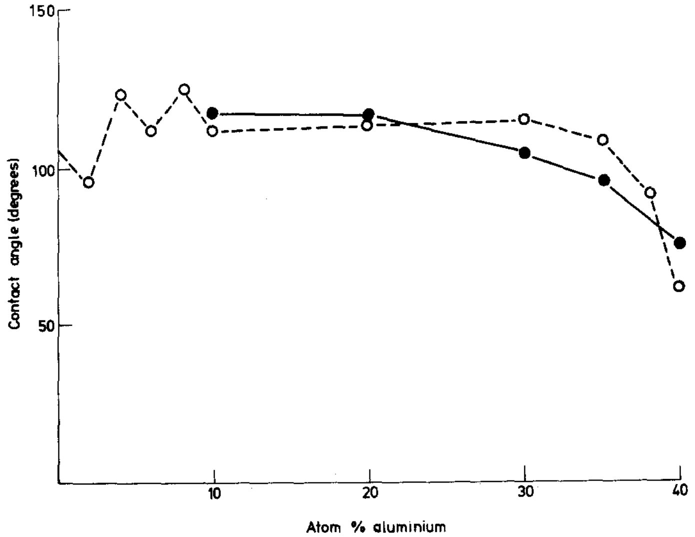

Figure 6 The effects of aluminium on the weeting of alumina by copper–titanium alloys at 1150° C in a vacuum of 10^{-3} Pa, hollow circles, or 10^{-5} Pa, full circles.

sections of drops of these alloys still attached to their alumina substrates revealed the presence of thin, 3 to 5 μm, but continuous, reaction product layers at alloy–alumina interfaces as illustrated in Fig. 9. However, there was no clear relationship between the structures or thicknesses of the layers and the alloy compositions or wetting temperatures. No such layers were observed to be formed by alloys containing gallium or nickel, but this evidence is inconclusive because the samples had separated from the alumina substrates after solidification. Electron probe microanalysis showed the layers to be rich in titanium. Quantitative measurement was not possible because of the thinness of the layers, but it was noted that the strength of the titanium signals increased as the titanium or ternary element contents of the alloys increased; for example, the signal increased from 2.0 to 5.6 times that for copper when the indium content of a 5 at % titanium alloy was increased from 20 to 30 at %.

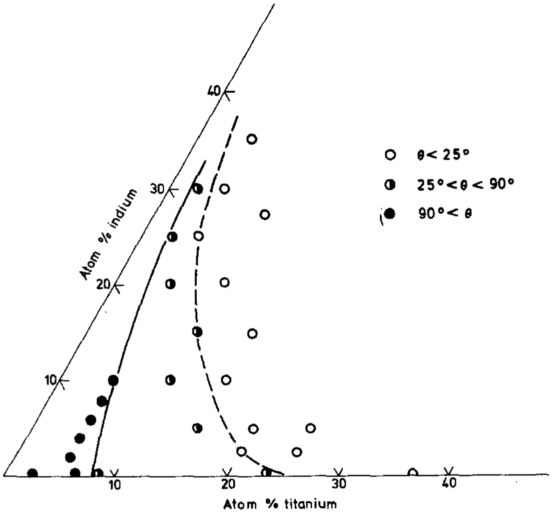

Figure 7 The effect of composition on the wetting of alumina by copper–indium–titanium alloys at 1150° C.

4. Discussion

This work has shown that small additions of some, but not all, ternary alloying elements can enhance the wetting of alumina by copper–titanium alloys, decreasing the titanium concentration needed to induce marginal or good wetting. Thus the effect of tin reported previously [1] is neither unique nor universal, similar, albeit less, effects being produced by gold, indium and silver, and to a small extent by aluminium. The characteristic of these beneficial additions is their co-operative interaction with titanium to produce concave isoclines when wettability data are plotted on a ternary composition diagram as shown in Figs. 7 and 8. In contrast, the data for gallium containing alloys do not permit the drawing of an isocline while those for nickel containing alloys define a convex isocline.

Indium was the most effective of the ternary alloying elements used in this work and comparisons of Figs. 1, 4, 5 and 6 with previously reported data [1] enables the other elements to be ranked in terms of declining effectiveness as follows; tin, indium, gold or silver, aluminium, gallium or nickel. The ternary alloying elements used in this programme were selected on the basis of their titanium solubility and liquid surface energy data and it was expected that the most

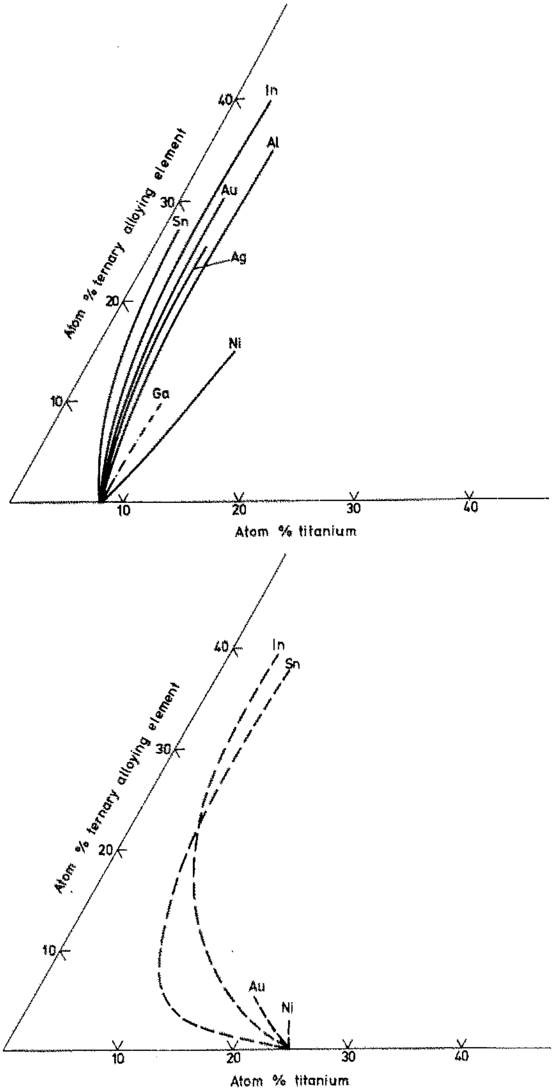

Figure 8 The effect of composition on the 90°, top and 25° bottom isoclines defining the wetting of alumina at 1150° C by copper–titanium alloyed with the indicated ternary elements.

effective additions would be those with low values of both these parameters. With one possible exception, the ranking of the elements revealed by the experimental wetting data is in accord with these expectations. Thus, comparison of the values cited in Table 1 for the selected elements with those for tin reveals three groupings of elements which should have decreasing beneficial effects on wetting behaviour; (a) indium which has a similar titanium solubility and surface energy to tin, (b) aluminium, gold and silver which have lower titanium solubilities but higher surface energies, and (c) gallium which has a higher titanium solubility, and nickel which has a much higher surface energy.

The data cited above demonstrate that the ranking of ternary alloying elements in terms of their wettability data and their titanium solubility and surface energy parameters are in broad accord. However, a closer comparison for aluminium, gold and silver reveals that while the parametric data suggest that aluminium should be the most effective additive, wettability data show it to be the least. This apparently anomalous behaviour was noticed when the experiments were in progress and tentatively ascribed to surface oxidation effects although no supporting evidence was obtained when additional experiments were conducted in a vacuum of 10^{-5} rather than 10^{-3} Pa. There is, therefore, an uncertainty at present about why aluminium is a less effective additive than gold or silver.

This confusion about the effect of aluminium additions reflects our imprecise understanding of the mechanisms by which ternary alloying elements influence wetting behaviour. It was argued during analysis of the effect of tin additions on the wetting of carbon by copper–titanium alloys that this was due to the effects of tin on the solubility of titanium and the surface energy of the alloy [1]. The solubility of titanium is less in tin than copper and hence additions of tin reduce the concentration of titanium needed to saturate copper. In the case of binary copper–titanium alloys, the saturated liquid solution at 1150° C is in equilibrium with a 90 at% titanium solid phase and thus the activity of titanium in the liquid will be high, about 0.9. Similarly, titanium saturated liquid tin will be in equilibrium with a titanium rich intermetallic at 1150° C. Non-saturated

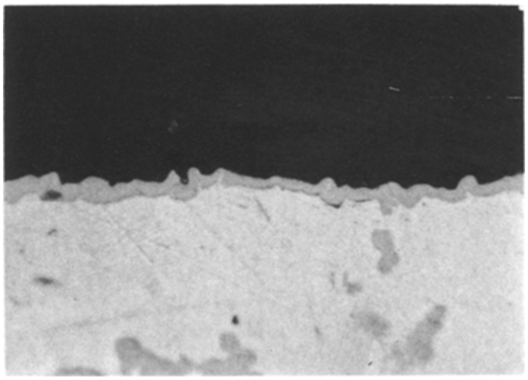

Figure 9 Cross-section through the interface formed with alumina by copper–5% titanium–20% indium, x1560.

copper or tin alloys will have activities that increase monotonically with concentration. If the activities of the titanium rich solids in equilibrium with the saturated liquids are similar, the lower solubility in tin will result in a given concentration of titanium having a higher activity than in copper, as illustrated in Fig. 10 for two hypothetical binary alloys. The activity of titanium in the two phase liquid–solid region of a ternary alloy may not be invariant [9], but nevertheless the reduced solubility of titanium in copper alloyed with tin should be associated with an enhanced activity. The effect will be greater at the alloy surface because the low surface energy of tin causes it to segregate. Analysis of the data of Kwai *et al.* [10] plotted in Fig. 11 using equations derived from the Gibbs adsorption isotherm assuming the alloys to be Raoultian solutions suggests that a surface concentration of 90 at% tin could be produced by a bulk addition of only 15 to 20 at%. Replacing nine tenths of the copper atoms at the surface by tin will reduce the solubility of titanium at 1150° C from about 75 to 25 at% and thus substantially increase the activity of a given titanium concentration.

The beneficial effects on wetting behaviour of such changes can be understood reasonably well for carbon substrates. Thus, Storms [11] has shown that increasing titanium activity causes the titanium carbide with which it is in equilibrium to become more hypostoichiometric, and several workers have observed the wettability of titanium carbide by copper to increase with hypostoichiometry [12–14]. The effect of increased titanium activity on the wettability of alumina is not easy to assess since the free energy of titanium–alumina redox reaction is small and hence the chemistry of the ceramic surface uncertain. However, it can be argued that the titanium : oxygen ratio of the ceramic surface must increase with titanium activity. It is noteworthy, therefore, that Naidich *et al.* [15, 16] found titanium rich oxides to be formed on alumina surfaces by interaction with copper–titanium and gold–titanium alloys, and that the contact angles of copper at 1150° C on Al_2O_3, Ti_2O_3, and $TiO_{1.14}$, and $TiO_{0.86}$ are 138, 113, 82 and 72° [16, 17]. Such changes from non-wetting to wetting behaviour could be more marked for copper–tin alloys than copper because of their lower surface energies.

In the case of alloys containing ternary elements other than tin, even fewer data are available with

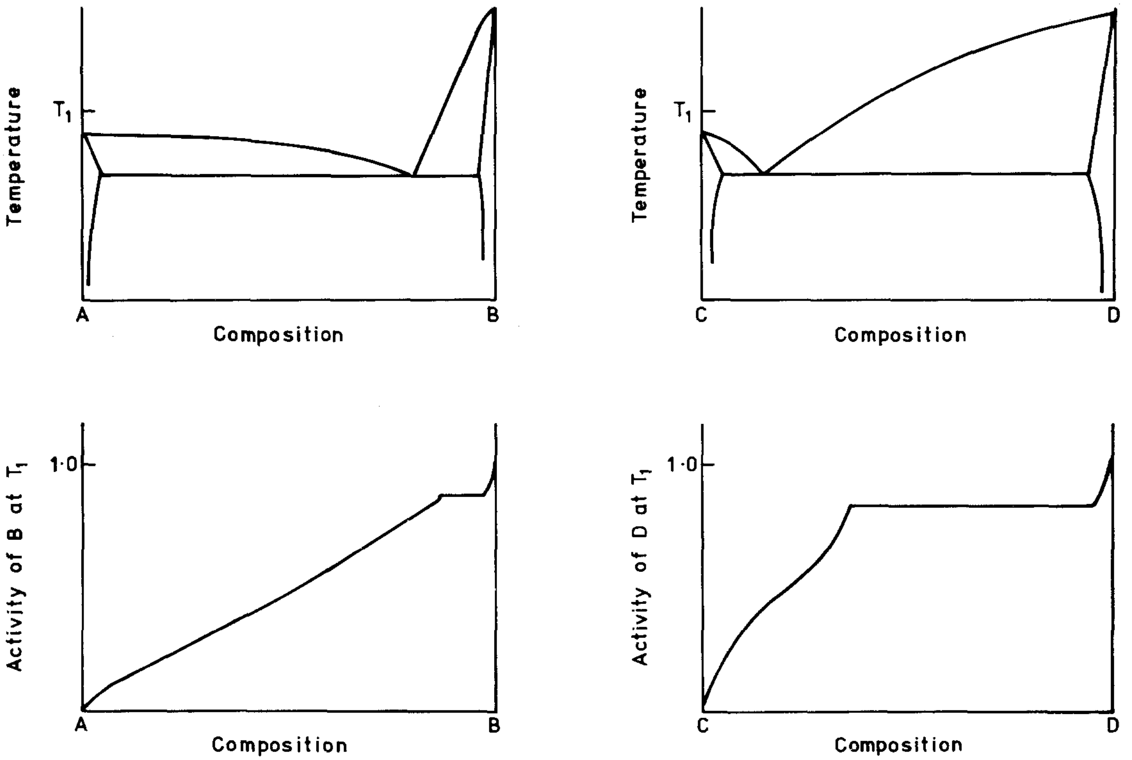

Figure 10 Schematic illustration of the effect of alloying solubilities on the activity of a solute in non-saturated liquid.

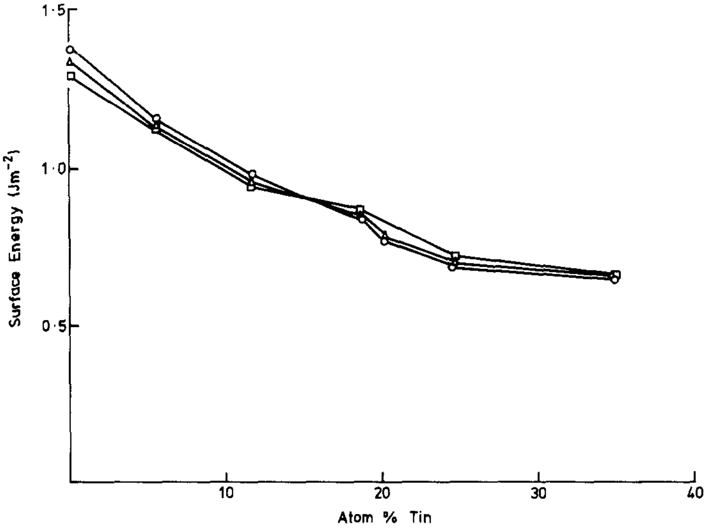

Figure 11 The effect of composition on the surface energy of copper tin alloys at 1100° C (○) 1150° C (△) and 1200° C (□).

which to assess the reasonableness of the model. Nevertheless it is clear that in most cases the addition of a ternary alloying element with a low surface energy and solubility for titanium has a beneficial effect on the wetting of alumina by copper–titanium alloys. It is noteworthy, therefore, that the data for gallium presented in Table 1, suggest that it should be a beneficial additive, albeit less so that any of the other elements evaluated in the programme except nickel. No beneficial effect of gallium on the wetting of alumina was observed, but the limited nature of the data do not exclude the possibility. Support for this qualified conclusion is provided by the wetting behaviour between copper–gallium–titanium alloys and vitreous carbon, which work with copper–tin–titanium alloys showed to be more sensitive to compositional effects than alumina. Data for these substrates show gallium additions to be beneficial as illustrated in Fig. 12, but much less so than tin [8].

This work has demonstrated that the beneficial effects of some ternary elements on the wetting behaviour of copper–titanium alloys can be rationalized in terms of their possible effects on titanium activities and interfacial chemistries. Progress has been made, therefore, in providing bases for selecting the compositions of brazes to be used with unmetallized ceramics, and *ad hoc* work on other programmes has shown that these bases can also be useful in the selection of copper free solder alloys. An ability to wet well is the prime criterion that must be satisfied by a braze, but many others such as the formation of a strong interface between the ceramic and the solidified braze must also be satisfied by a technically useful material. Changes in interfacial chemistry affecting wetting behaviour can also influence bond strength, as

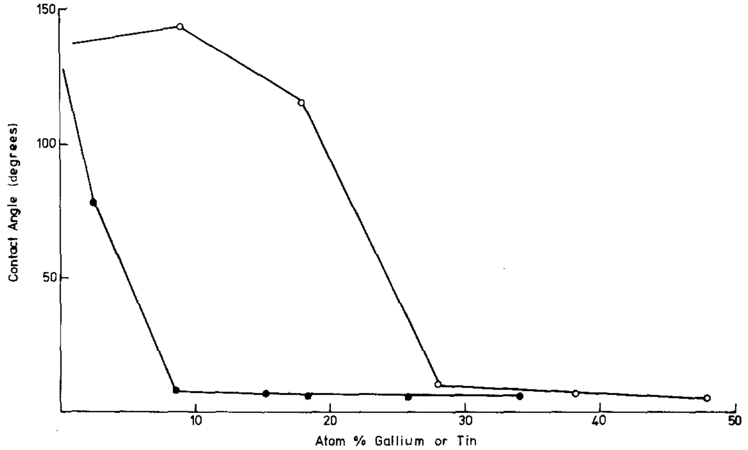

Figure 12 The effect of additions of gallium (○) or tin (●) on the wetting of vitreous carbon at 1150° C by copper–1.3 at % titanium alloys.

demonstrated by some of our data for the brazing of diamonds by copper–tin–titanium [18]. and a systematic study of this could represent a useful next step in the development of a rational basis for designing brazes.

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