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Some observations on the wetting and bonding of nitride ceramics

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Several series of experiments have been conducted to gain information about the wettability of AlN, BN, Si_3N_4 and two sialon ceramics by potential braze materials. It was possible to achieve wetting of all five ceramics using aluminium, copper–titanium alloys, and a Ag–28Cu–2Ti alloy. Wetting by aluminium and the Ag–28Cu–2Ti alloy was usually good. Both wetting and non-wetting alloys containing titanium reacted to form TiN and it is argued that the achievement of wettability is associated with a certain degree of hypostoichiometry. While aluminium should also have reacted, no clear evidence was obtained. In supplementary experiments it was found that bonds formed by brazing with aluminium at 1000° C could have shear strengths as great as 60 MPa. Although the experimental work was preliminary in nature, it suggested that good brazing systems could be developed.

1. Introduction

The bonding of ceramic components to metals is a common requirement for their successful application in engineering structures and electronic devices. However, ceramics are generally difficult to bond to metals because of their differing physical and mechanical properties and specialized processes such as the molybdenum–manganese metallization of alumina have had to be developed. For the nitride ceramics, such as Si_3N_4 which is expected to find applications in high performance automobile engines or AlN which could emerge as a favoured heat dissipating electronic substrate, bonding techniques have yet to be fully developed or proven in long run production processes, but the potential importance of these materials has ensured the initiation of many laboratory studies, particularly in the USA and Japan.

In principle, nitride ceramics can be bonded to themselves or to metals by a wide variety of techniques, and recent literature contains many references to successful applications. These include the use of glass frits [1–5] to bond together Si_3N_4 bodies, and of the diffusion bonding of Si_3N_4 and sialon (a Si–Al–O–N ceramic) to metal bodies using ductile metal interlayers [6–9]. Some workers have preheated the nitrides in air or a vacuum to promote beneficial changes in surface chemistry [10, 11], while others have coated the nitrides with brazeable silicide or titanium containing powders [12–15]. Most attention, however, has been paid to active metal brazing of uncoated nitrides. The advantages of the process is that brazing is a well established technique for joining both metals and ceramics and that brazes can usually accommodate some mismatch of the thermal expansion coefficients of the workpieces. Particular attention has been paid to the potential of aluminium and aluminium alloys as brazes for Si_3N_4 [16–22]. Wetting was generally achieved at temperatures of 850–1000° C, and the joints produced had room temperature bend strengths of up to 300 MPa. Some workers have used titanium activated brazes based on copper, silver–copper and nickel for bonding Si_3N_4 [23–29] and a sialon [30], but recent work on other nitride ceramics is sparse.

The study described in this report has been directed to obtaining comparative information for a range of nitride ceramics, rather than optimization of the bonding process for a specific material or application. The technique employed has been brazing, and in order to relate to other work, the initial studies used aluminium as the braze metal and then progressed to copper–titanium and silver–copper–titanium alloys.

2. Materials and techniques

Five ceramics were used in this work: AlN, BN, Si_3N_4 and two sialons. The nitrides, purchased from Elektroschmelzwerk Kempten, (Munich, FRG) and the sialons bought from Lucas-Cookson-Syalon Ltd, (Solihull, UK) had the nominal compositions and properties summarized in Table I. The aluminium used as a braze was obtained from Goodfellows Ltd (Cambridge, UK) as 99.999% pure 1.0 mm diameter wire and 0.5 mm thick sheet. The copper–titanium and silver–copper–titanium alloy brazes were made at Harwell using a vacuum furnace to melt together various proportions of Goodfellows 99.9% pure copper, 99.95% pure silver, and 99.6% pure titanium wire and rod in Al_2O_3 crucibles.

Two vacuum furnaces were employed in the wetting and brazing experiments. Most work was performed in a programmable furnace with a 150 mm diameter

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TABLE I Ceramics used in this work

Ceramic	Source/Grade	Nominal composition (wt %)	Expansion coefficient at room temperature, (K^{-1})	Bend strength at room temperature (MPa)	Density ($g\,cm^{-3}$)	Thermal conductivity ($W\,m^{-1}\,K^{-1}$)
AlN	ESK*, HDALN	Al-64.5/66.5, N_2-32.5/33, $O_2 \sim 2$, C ~ 0.2	4.5×10^{-6}	> 200	3.2	~ 100
BN	ESK, HDBN2	B-43, N_2-53 B_2O_3-< 0.2, total O_2-< 0.8, Ca < 0.15, C < 0.08, Cl < 0.08	4.4×10^{-6}	45	2.2	50
Si_3N_4	ESK, EKasin S	La_2O_3-6, Al_2O_3-4	3.2×10^{-6}	400–700	3.2–3.3	30–40
Sialon	L-C-S†, Sialon 101	Solid solution of Al_2O_3 in Si_3N_4	3.04×10^{-6}	945	3.25	21.3
	L-C-S†, Sialon 201	As 101, but additive of Y and Al		$\geqslant 945$		

*Electroschmelzwerk Kempten, Munich, Federal Republic of Germany.
† Lucas-Cookson-Syalon, Solihull, UK.

200 mm high hot zone supplied by Severn Sciences Ltd (Thornbury, UK). This furnace was evacuated to less than 10^{-5} mbar (1 mPa) after the samples had been loaded, and the vacuum never degenerated to more than 2×10^{-5} mbar at any time during the experimental runs. The partial pressures of the residual gases at the highest experimental temperature used, 1150° C, were 1×10^{-6} mbar of H_2O, CO and CO_2, 6×10^{-7} mbar of N_2, 4×10^{-7} mbar of H_2 and 3×10^{-8} mbar of O_2. The other furnace used was a Harwell constructed facility with a hot zone only 30 mm in diameter and 50 mm high, but with a temperature capability of 1800° C and view ports that permitted close up observation of the samples and a vacuum quality as good as that of the Severn Science facility.

The ceramics used in the work were prepared or supplied as 10 mm square plaques about 3 mm thick. Their surface textures had amplitudes of 0.3–1.1 μm and wavelengths of 49–98 μm as shown in Fig. 1. Before being used, both the ceramics and the braze metals were degreased by ultrasonic agitation for 5 min in acetone and dried in air.

Three types of ceramic–metal sample were used in this work as sketched in Fig. 2. The Type I sessile drop sample yielded data about wetting behaviour, the Type II sandwich sample was used to obtain some information about capillarity and the Type III top hat configuration was used to produce samples that could be strength tested. All three sample types were examined to provide information about microstructures and reactivity.

When using a Type I sample, a small 0.06 g cylinder of aluminium or 0.20 g tetrahedron of a copper alloy was melted to form a sessile drop. If care had been taken to ensure that the ceramic surface was horizontal, the sessile drop was symmetrical and wetting behaviour could be measured by viewing photographic negatives of the drop profiles with a Nikon CT6 projector. If the contact angle, θ, identified in Fig. 2 was more than 90°, the system was non-wetting, while angles progressively less than 90° denoted increasingly better wetting. To melt the aluminium or copper alloys, the samples were heated at about 5 K min^{-1} to approximately 1150° C in the small Harwell furnace and photographs were taken at frequent intervals once melting had occurred. Some of the samples were subsequently cross sectioned and polished to provide microstructural information.

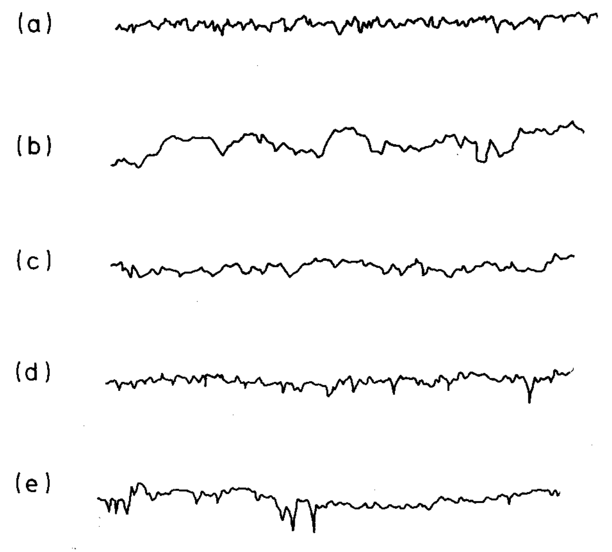

Figure 1 Surface profilometer traces across ceramic samples. Vertical magnification × 1000, horizontal magnification × 40. (a) AlN, $R_a = 0.33\,\mu m$, $\lambda_a = 49.1$; (b) BN, $R_a = 1.08\,\mu m$, $\lambda_a = 82.8$; (c) Si_3N_4, $R_a = 0.35\,\mu m$, $\lambda_a = 56.2$; (d) Sialon 101, $R_a = 0.15\,\mu m$, $\lambda_a = 98.2$; (e) Sialon 201, $R_a = 0.19\,\mu m$, $\lambda_a = 81.7$.

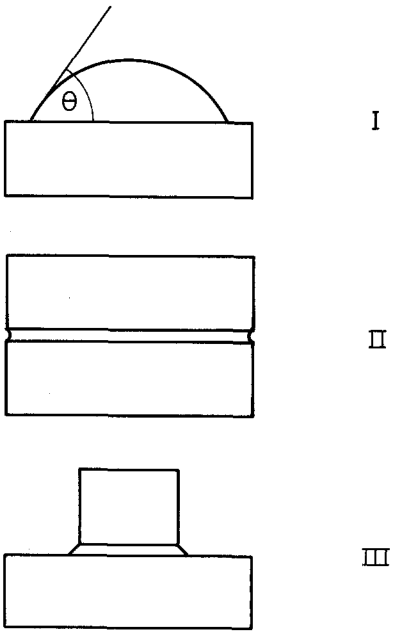

Figure 2 Sample configurations used in this work.

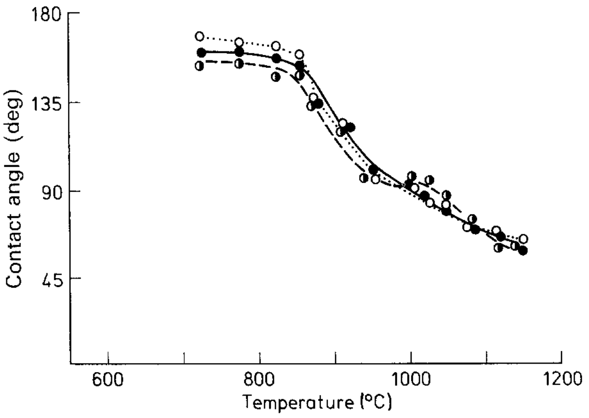

Figure 3 Several sets of contact angle data for aluminium drops on Si_3N_4 plotted as a function of temperature.

Type II and Type III samples were both produced using 0.5 mm thick aluminium sheets as the bonding agents. Small pressures, 1.8 MPa for the Type II and 0.1 MPa for the Type III samples, were used to prevent the workpieces from moving when the aluminium sheets melted. The Type II and Type III samples were formed in the Severn Science furnace by heating at about 8 K min^{-1} and holding at the experimental temperature for 15 min. These samples were subsequently cross sectioned and polished to assess whether the aluminium had retracted on melting and to provide microstructural information. Finally, some of the Type III samples were placed in a shearing jig and stressed to destruction in an Instron 1195 machine operating at a crosshead speed of 1 mm min^{-1}.

3. Results and discussion

3.1. Wetting and bonding by aluminium

Sessile drop experiments were conducted with all five ceramics and many contact angle measurements were made. The precision of any individual contact angle measurement was no worse than ± 2° and as Fig. 3 shows, repeated experimentation with any one ceramic yielded reasonably reproducible wetting data.

Figs 4 and 5 present wetting data for the ceramics used in this study. (Fig. 5 also includes data for 99.5% pure Al_2O_3, obtained in another study using the same experimental equipment, to which reference will be made later.) All the ceramics were wetted during the temperature ramping to 1150° C. The temperatures at which the contact angle of the aluminium drops decreased below 90°, and the ceramics became wetted, ranged from 890° C for sialon 201 to 1025° C for Si_3N_4. The contact angles on the sialon ceramics were lower than those for the pure nitride ceramics at low experimental temperatures, and sialon 201 was marginally better wetted than any of the other ceramics at 1150° C, the highest experimental temperature.

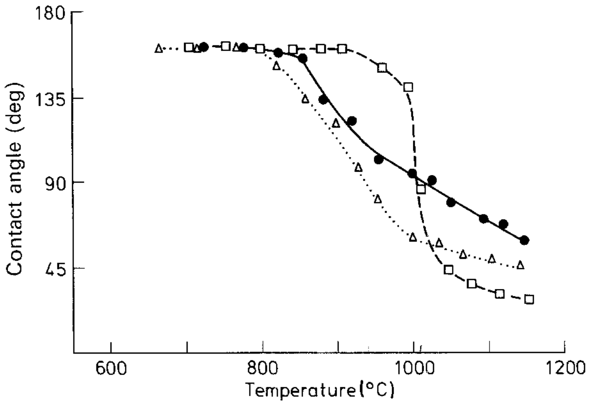

Figure 4 Contact angle data for aluminium drops on several ceramics plotted as a function of temperature. (△) AlN, (□) BN, (●) Si_3N_4.

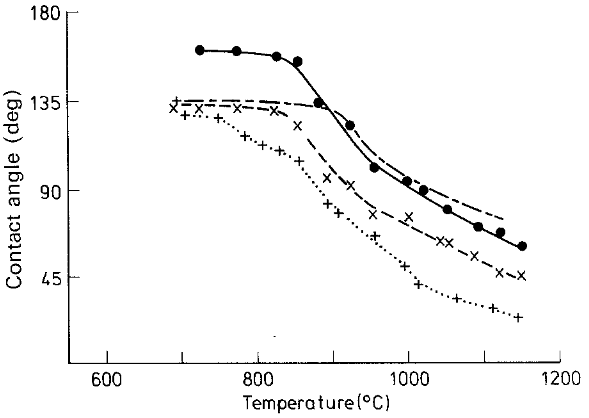

Figure 5 Contact angle data for aluminium drops on several ceramics plotted as a function of temperature. (●) Si_3N_4, (×) 101, (+) 201, (- - -) Al_2O_3.

Some characteristics of these experiments, such as the initial insensitivity of wetting to increasing temperature, have been observed also for aluminium drops on other types of ceramic and attributed to the inhibiting effects of a continuous film of Al_2O_3 on the surface of the molten metal [31]. Thus the general behaviour of the nitrides used in this work was not unexpected, but nevertheless the differences between the individual ceramics are worthy of comment.

In attempting to understand the wetting behaviour of the various nitrides it is possible to produce various rankings depending on the criteria employed. In this work, attention has been paid particularly to the temperature at which wetting is initiated and to the final contact angle achieved at 1150° C. These criteria therefore identify Si_3N_4 as being particularly difficult, and sialon 201 as being rather easy to wet with aluminium. The relatively good wetting behaviour of the sialon ceramics is noteworthy since they are essentially a solid solution of Al_2O_3 in Si_3N_4 and yet are more easy to wet than either, Fig. 5. Also of interest is the behaviour of BN in that it requires a high temperature for wetting to be initiated despite being the least stable ceramic used, but thereafter is well wetted.

In view of the sometimes apparently curious wetting behaviour observed in this work, it is interesting to compare our data with those reported recently by other workers. Such a comparison for Si_3N_4 is shown in Fig. 6. The agreement between the high temperature data is quite good, with the lower contact angles reported by Naka *et al.* [32] possibly reflecting their long, 60 min, dwell times. In the low temperature region, our ceramic was clearly less wettable than that of Ljungberg and Warren [20], but the reason for this discrepancy is not immediately obvious. Thus, Ljungberg and Warren had taken steps to improve the wettability of their material by grinding away the surface layer which had a high Si_2N_2O content, but

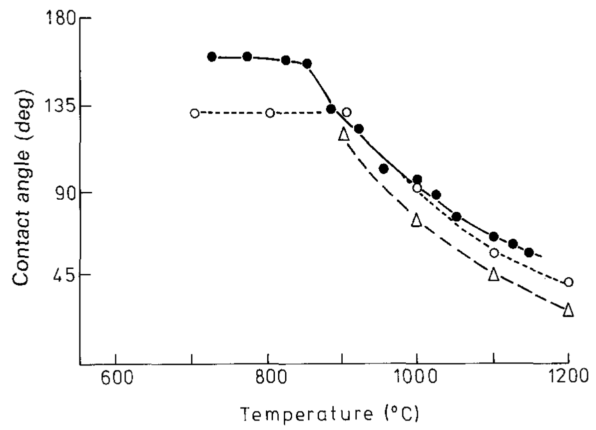

Figure 6 The effect of temperature on the wetting of Si_3N_4 by aluminium. (○) [20], (△) [32].

XPS studies of our ceramic revealed no evidence of oxynitride. For the other ceramics, detailed comparisons are not possible, but it is noteworthy that Rhee [33] reported aluminium to wet AlN at 1150° C, but not at 970° C, and Meaders and Carithers [34] commented on the excellent wetting of BN achieved by aluminium heated to 1000° C.

Despite the sometimes confusing nature of the wetting data, molten aluminium can be used to bond ceramics over a range of temperatures. Thus in this work, Type II sandwich samples of the ceramics were produced at 800 and 1000° C. Increasing the fabrication temperature affected the structure of the sandwiches, the aluminium sheets forming bonding layers with thicknesses of about 40 or 20 μm for samples fabricated at 800 or 1000° C. Excess aluminium was exuded as droplets during the fabrication of samples. The joints formed at both these temperatures were well filled and the metal–ceramic interfaces appeared to be in good contact.

Other workers have bonded Si_3N_4 to metals using aluminium interlayers at 700–950° C [17, 18], and sialon to metals using a molten aluminium–silicon–magnesium alloy at 610° C [7, 8] to produce joints with four-point bend strengths of up to 320 MPa [7] and tensile strengths of up to 60 MPa [8]. Thus the evidence is clear that high integrity interfaces can be formed. In our work, an assessment of joint strengths was made by testing Type III samples bonded at 1000° C for 15 min. The BN and Si_3N_4 samples failed at their metal–ceramic interfaces, but the other samples fractured at least partially within the ceramics. Measurable shear strengths were obtained for all the ceramics. The most strongly bonded were the sialon 201 and sialon 101 samples having shear strengths of 61.3 ± 14.9 and 52.5 ± 5.5 MPa, respectively. The AlN and Si_3N_4 samples had similar strengths, 34.6 ± 11.5 and 39.7 ± 6.2 MPa, while the BN samples were the weakest, failing at shear stresses of 6.1 ± 2.0 MPa. These strengths were compared with other system properties, and a correlation was observed with the bulk ceramic strengths listed in Table I, as shown in Fig. 7. Similar workpiece/bond strength correlations have been observed before, but usually with the strengths of a series of metals bonded to a single ceramic such as Al_2O_3 [35–37].

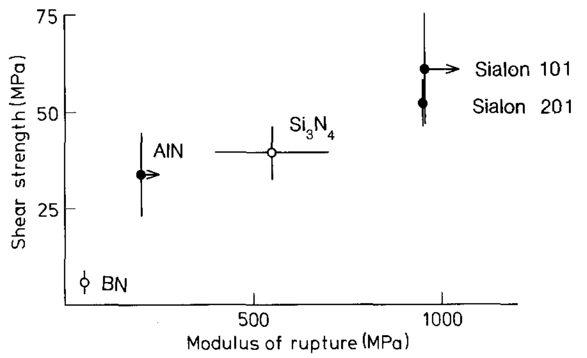

Figure 7 Comparison of ceramic bulk strengths with those of bonds formed with aluminium.

Finally, solidified sessile drop, sandwich, and top-hat samples were cross sectioned and examined using optical microscopy. No voidage along the aluminium–ceramic interfaces was detected, even for sandwich samples fabricated at temperatures at which sessile drops did not wet. Further, there was no cracking of the ceramics at the edges of the sessile drops where contractional stresses generated by cooling of the solidified drops would be concentrated. The only cracks observed were a few produced by grinding near the centre of a sialon 201 sample and it was noteworthy that these had been penetrated by the Al during brazing at 800° C. Although wetting of ceramics by metals is usually associated with chemical reactions, neither optical metallography or EPMA surveys revealed any evidence of interdiffusion except for that of silicon into aluminium to depths of about 5 μm from interfaces formed with Si_3N_4 and the sialon ceramics, Fig. 8. (The aluminium signal shown in the figure to be generated within the bulk by the sialon can be attributed to that pre-existing in solid solution rather than evidence of interdiffusion.) EPMA surveys, however, revealed no evidence suggesting migration of B from BN, or of course of aluminium from AlN, into the aluminium interlayers. Similarly, our optical microscopy and EPMA surveys did not reveal any reaction product layers, but very thin layers may have formed. Thus Naka *et al.* [38] and Ning *et al.* [39] had to use TEM techniques to reveal the presence of sialon type material formed at Si_3N_4–aluminium interfaces. This

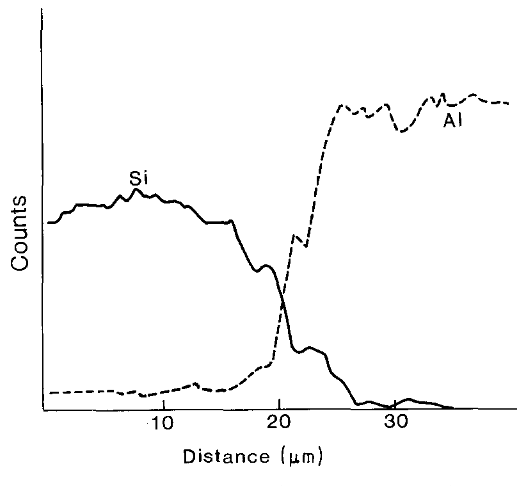

Figure 8 EPMA traces across a sialon 101/aluminium interface formed at 1000° C.

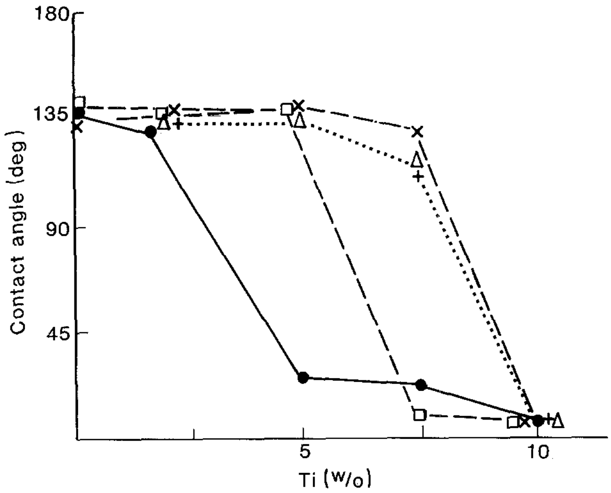

Figure 9 Contact angle data for copper–titanium drops on various ceramics at 1150° C. (△) AlN, (□) BN, (●) Si_3N_4, (×) 101, (+) 201.

behaviour therefore is in marked contrast with that of interfaces formed by titanium containing alloys.

3.3. Wetting by copper alloys containing titanium

Sessile drop experiments were performed using copper, Cu-5 Ti, Cu-7.5 Ti and Cu-10 Ti alloys heated to 1150° C and held for 15 min. Copper did not wet any of the ceramics, but the Cu-10 Ti alloy wetted all of them, as shown in Fig. 9. The sialon ceramics and AlN required more than 7.5 Ti to be in the alloy before they were wetted, but BN was very well wetted by a Cu-7.5 Ti alloy and Si_3N_4 was wetted even by a Cu-5 Ti alloy. When wetting occurred, it was always good with measured contact angles of less than 30°. For these sessile drops, liquid spreading across the ceramic surfaces was initiated as the alloys became partially molten at temperatures above their solidus of 885° C [42] and good wetting by well formed sessile drops was achieved once the alloy melting points had been exceeded, as indicated by the data for Si_3N_4 plotted in Fig. 10. Thus the behaviour of these alloys was more complex than that of aluminium, although once more fragmentary literature evidence provides general support for the reported observations. Our finding that additions of 5% titanium were sufficient to induce wetting of Si_3N_4, but not of the other ceramics in accord with recent work of Ljungberg and Warren with Si_3N_4 [20] and that of Rhee [40] with AlN and Naidich [41] with BN.

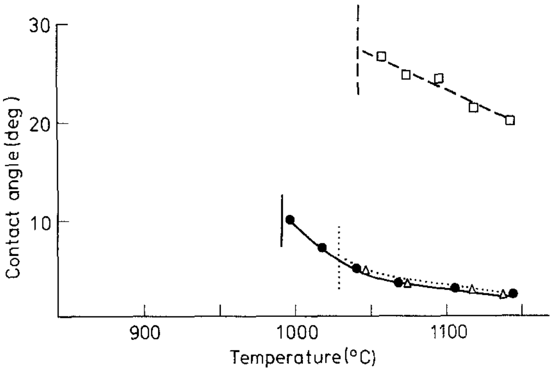

Figure 10 Contact angle data for wetting copper–titanium alloys on Si_3N_4 at various temperatures. (□) Cu-5Ti, (△) Cu-7.5Ti. (●) Cu-10Ti.

Solidification and shrinkage stresses caused several of the sessile drops to separate from their ceramic substrates, plucking out material as fragments or occasionally as complete lenses. As illustrated in Fig. 11, subsequent microstructural studies showed that even the intact samples could be cracked within the ceramics at the drop peripheries. Titanium has a high affinity for nitrogen, and the microstructural studies also revealed that reaction product layers had been formed at the alloy–ceramic interfaces. The product layers varied in thickness from about 10 to 30 μm and the thicker ones were cracked. In a few cases, these cracks extended into the ceramic substrates, and in no case had the cracks been deflected to the reaction product–ceramic interface. In one cross section, Fig. 12, of a Cu-10 Ti–sialon 201 interface, there was evidence that this cracking had occurred while the braze alloy was molten since metal was present in a flaw within the ceramic.

The thickness of the reaction product layers depended on both the ceramics and the alloys used as illustrated in Fig. 13, the thickest layers being observed for the sialon ceramics wetted by the Cu-10 Ti alloy while the

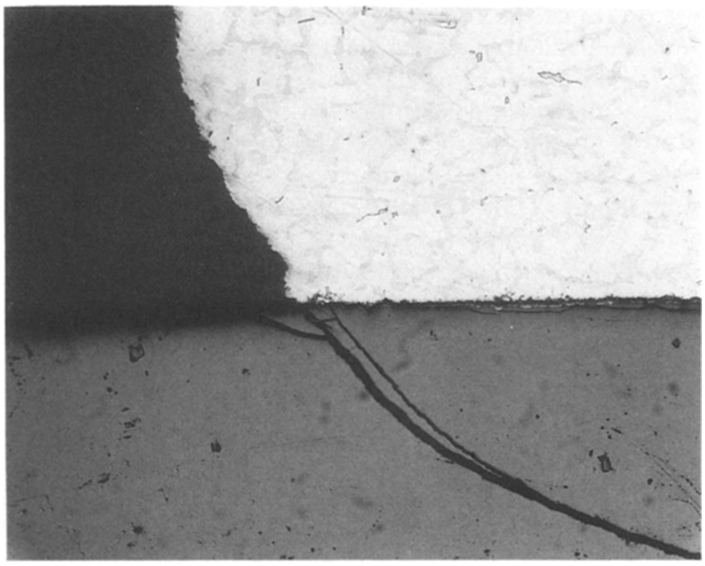

Figure 11 Peripheral crack observed in a cross-sectioned Cu-7.5Ti/sialon 201 sample × 96.

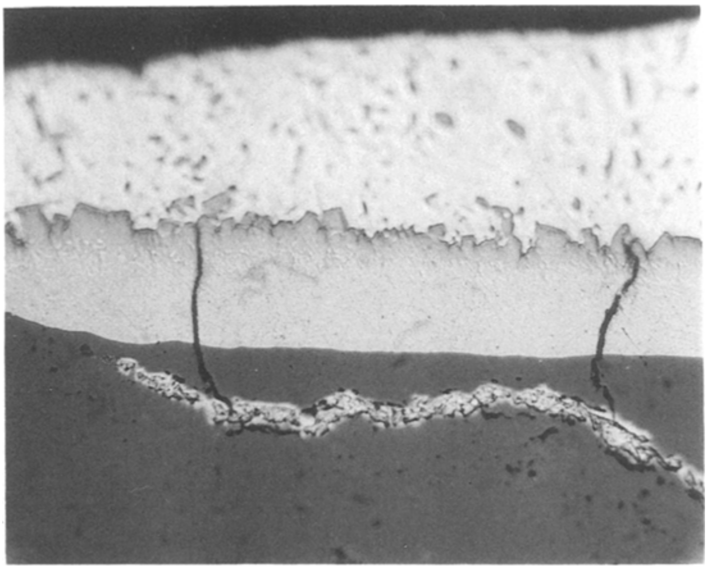

Figure 12 Cross section of a Cu–10Ti–sialon 201 sample near the drop periphery × 480.

thinnest were exhibited by the AlN ceramics that had been in contact with more dilute alloys. Some of the reaction product layers appeared to be single phase when viewed optically, but most had a more complex structure with nodular growths or fine particulate zones adjacent to the alloy. EPMA surveys across the alloy–ceramic interfaces revealed a variety of chemistries as shown by the traces in Figs 14 to 16. In every case the reaction product revealed by the optical microscopy was found to be titanium-rich. This enriched layer was thickened when the titanium content of the alloy in contact with Si_3N_4 was increased from 5 to 10%, Fig. 15. In that figure and also in Fig. 16, silicon peaks are shown to occur within the titanium-rich zones adjacent to the copper. Within the copper itself there were also a few small associated peaks for silicon and titanium when the ceramic substrate had been Si_3N_4 or sialon 101, Figs 15 and 16. In contrast there was no evidence of aluminium from AlN in the reaction layer formed by that ceramic or in the attached metal, Fig. 14. Traces for the BN samples were difficult to obtain, possibly due to surface smearing of the soft ceramic during the metallographic preparation, but the titanium peak shown in Fig. 14 indicates a concentration variation across the reaction zone.

These observations that reaction products are formed at both wetting and non-wetting interfaces demonstrate that their detailed chemistry can be of importance. Small changes could affect the energy of the braze–ceramic interface and hence the basic requirement for wetting. The EPMA traces shown in Figs 14 to 16 demonstrate that the copper–titanium alloys formed titanium-rich reaction products, and thermodynamic calculations predict that these will be principally TiN. However, the predicted conditions in which the stoichiometric product is formed are not associated with wetting. Thus, the free energy of formation of stoichiometric TiN, $200\,\mathrm{kJ^{-1}\,g\,mol^{-1}}$, suggests that it should be formed by contact of the ceramics with copper melts containing no more than a 0.001 wt % titanium, but several per cent of titanium are needed to induce wetting. These more concentrated alloys could have reacted to form a titanium-rich hypostoichiometric product since the stability range at 1150° C extends from TiN to $TiN_{0.43}$ [42]. Copper does not wet bulk TiN but these hypostoichiometric variants can be expected to be more wettable by virtue of their greater metallic nature, as is the case for carbides and oxides [41]. Therefore the requirement for the wetting of the ceramics used in the present study is that the concentration, or rather activity, of titanium in the copper should be sufficient to cause a wettable hypostoichiometric TiN to form. Fig. 9 indicates the threshold concentration is 2–9%, equivalent to an activity of 0.02–0.09 [43] for a copper solvent, but the free energy of formation data needed to associate these activities with particular degrees of hypostoichiometry are lacking.

The reactions forming wettable titanium-rich hypostoichiometric TiN liberate aluminium, boron, oxygen or silicon and these elements can either become solutes in the copper or themselves react to form products with the titanium as suggested by the nodular growths or particulate zones of a slightly different shade adjacent to the metal drops, Fig. 13. More relevant information about these nodular and particulate zones was derived from the EPMA surveys. Thus the metal side peaking of silicon within the titanium enriched zones formed by contact with Si_3N_4 and the sialons and the varying titanium content of the enriched zone formed with BN, Figs 14, 15 and 16, provide specific support for the formation of silicides and borides. Titanium forms several silicides and borides, Ti_5Si_3, TiSi, $TiSi_2$ and TiB, Ti_3B_4, TiB_2, at our experimental temperatures and their specific chemistry will determine wetting behaviour if they are formed as continuous layers. Thus while it may be expected that silicides would be wettable because of their metallic nature, literature data [41] indicate that at least TiB_2 is not and hence its formation may account for the poor wettability of BN relative to Si_3N_4 at low titanium concentrations. In the case of the sialon ceramics, there is a possibility that an oxide product could be formed as well, but only TiO appears to be wettable and in practice this requires about 10% of titanium in

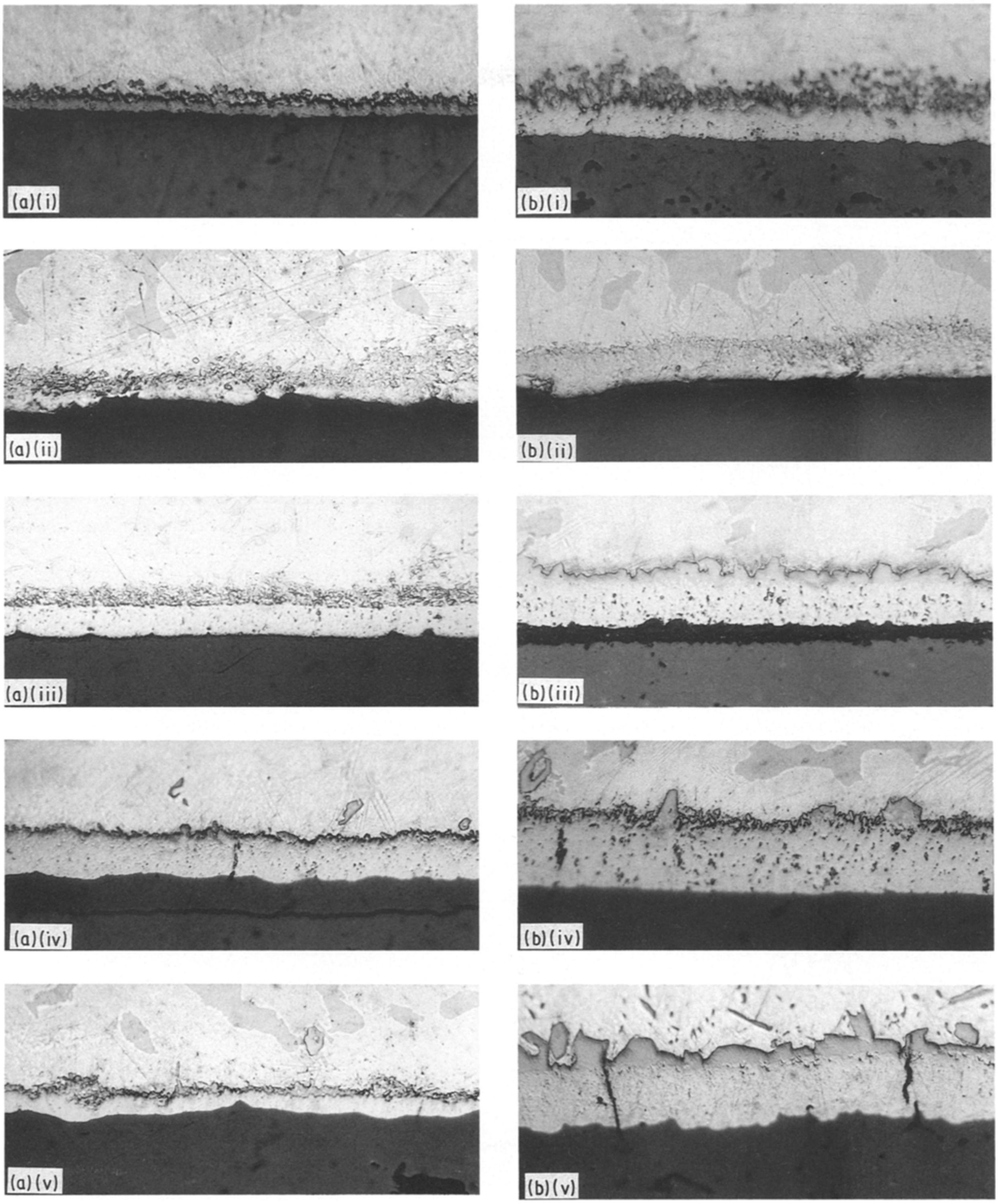

Figure 13 Structures of alloy–ceramic interfaces. × 480 (i) AlN, (ii) BN, (iii) Si_3N_4, (iv) sialon 101, (v) sialon 201, (a) Cu–5Ti. (b) Cu–10Ti.

copper to form it so there is no beneficial effect on the ceramic behaviour.

3.4. Wetting by the Ag–28Cu–2Ti alloy

A final series of experiments used the Ag–28Cu–2Ti alloy as sessile drops. In every case, excellent wetting was achieved by heating to the maximum temperature of 950° C, Fig. 17. The best wetting immediately after the alloy had melted, at about 780° C, was that of AlN. BN remained unwetted until the temperature was above 900° C, but at 950° C the alloy had spread to the edges of the BN plaques. The excellent wetting by this alloy, and in particular its spreading over the ceramic surface as soon as it melted, is consistent with its use as a braze at 820° C by Mizuhara and Mally [23]. Literature reports relevant to the other ceramics are lacking, but the spreading of the alloy over their surfaces as it melted, except for BN, and the excellent wetting achieved in every case at 950° C can be compared to the behaviour of the titanium-rich Cu–10Ti alloy at higher temperatures.

When samples were cross sectioned, polished and examined microscopically, reaction product layers were observed to have been formed. Their structures closely resembled those shown in Fig. 13, but the layers were somewhat thinner than those of the copper–titanium alloys. From the analysis of the copper-titanium behaviour, the product formed by the

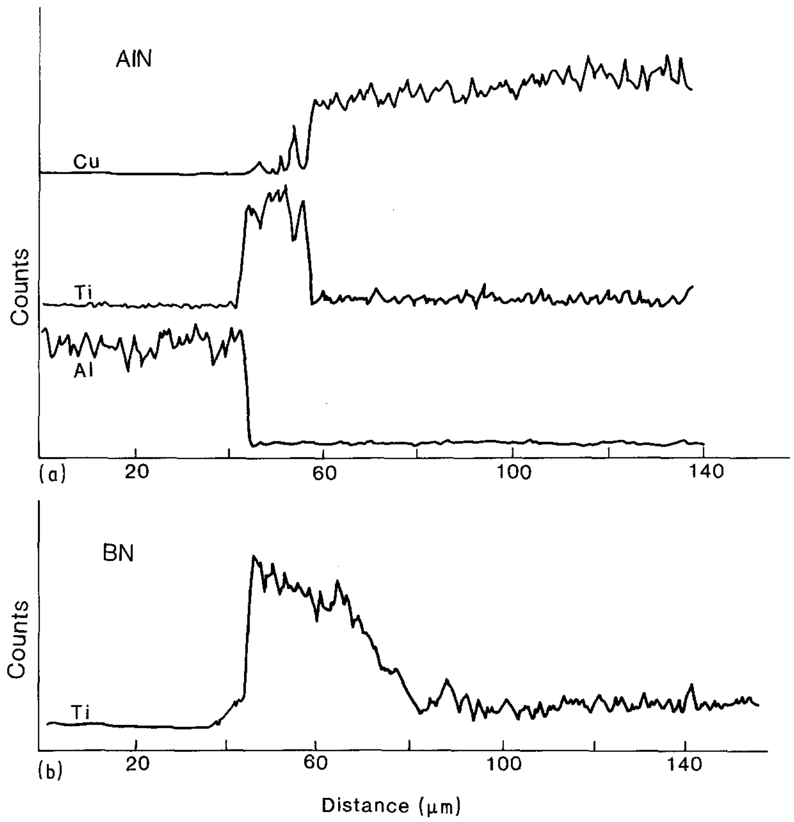

Figure 14 EPMA traces across interfaces with Cu–10Ti and AlN or BN.

wetting alloys should be hypostoichiometric TiN and if it is assumed that the same product is formed by the wetting, Ag–28Cu–2Ti alloys, it can be argued that the titanium activity in that alloy and in Cu–10Ti must be similar.

The activity coefficient of titanium in copper is approximately one [43] but there is some evidence to suggest that the activity in silver should be larger. Phase diagram studies of the silver–copper–titanium system by Chang *et al.* [44] have revealed a region of

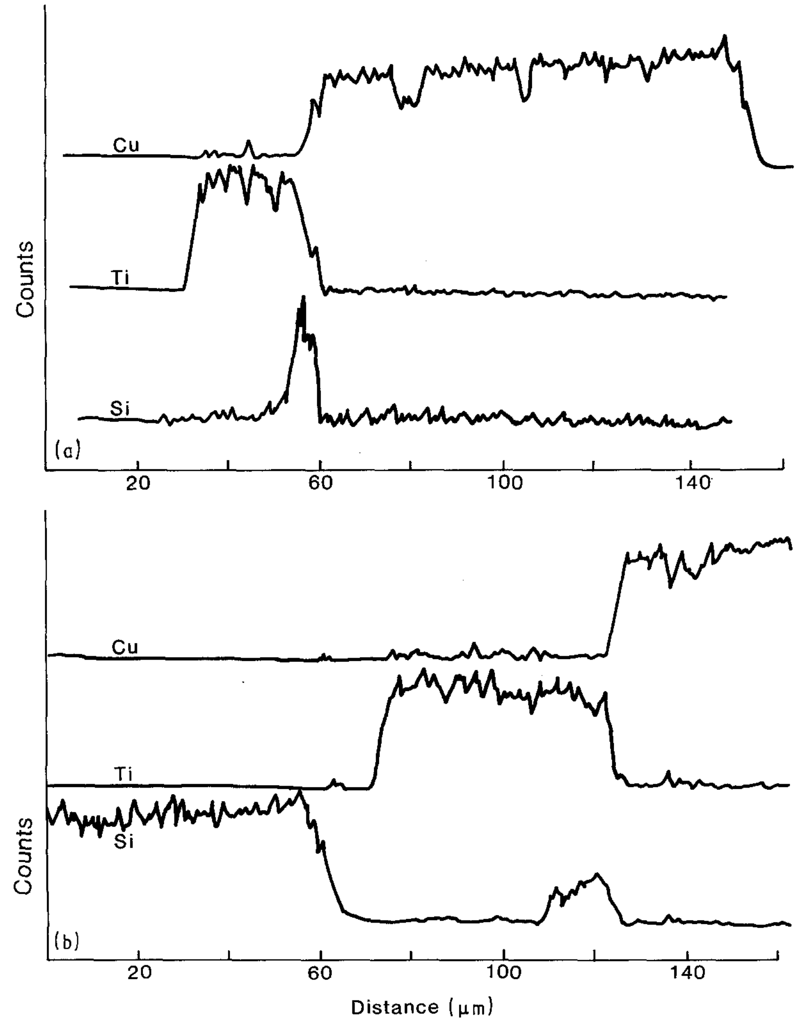

Figure 15 EPMA traces across, (a) a Cu–5Ti drop separated from a Si_3N_4 substrate and, (b) a Cu–10Ti/Si_3N_4 interface.

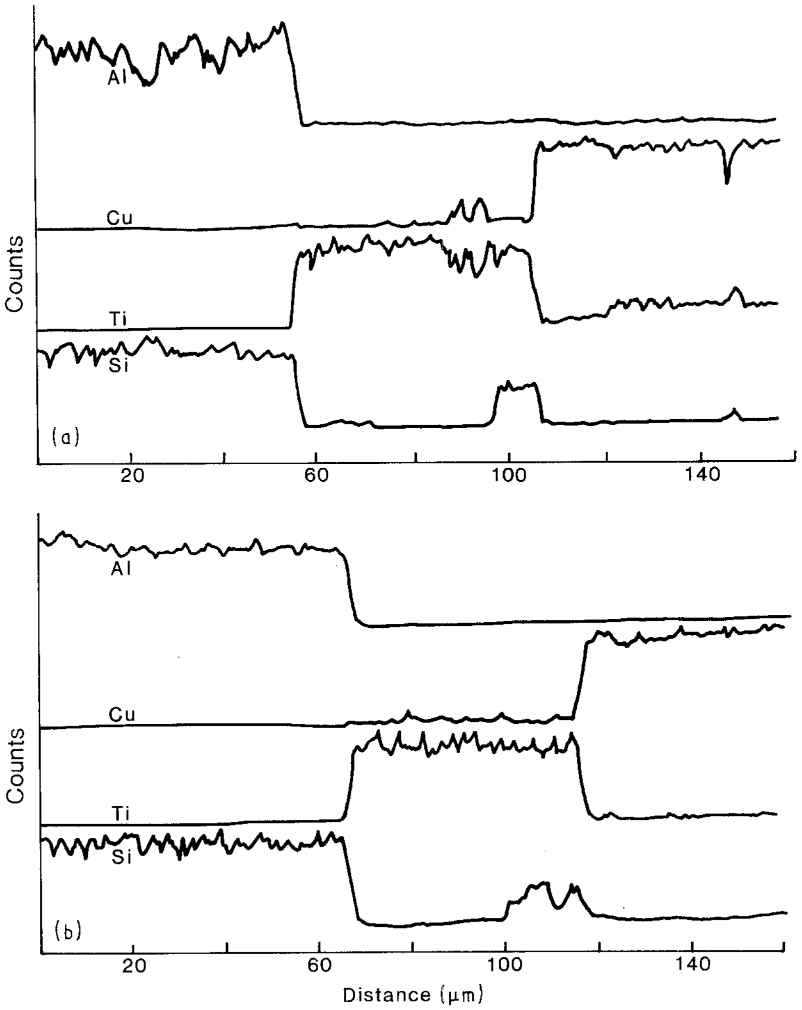

Figure 16 EPMA traces across interfaces formed by Cu–10Ti and (a) sialon 101 and (b) sialon 201.

liquid immiscibility, Fig. 18, with a tie-line between the Ag–28Cu–2Ti and Cu–12Ag–22Ti compositions. Thus the activities of the components of these two alloys are equal and the activity coefficient of titanium in Cu–28Ag must be about 10. The smaller titanium content of the silver–copper–titanium alloy, however, means that the reactive components will be rapidly depleted by TiN formation and hence only thin reaction product layers can be formed.

4. Concluding remarks

The work conducted in this study was preliminary in nature and having discussed the several experimental series separately, it is appropriate to finish by considering what general observations can be made.

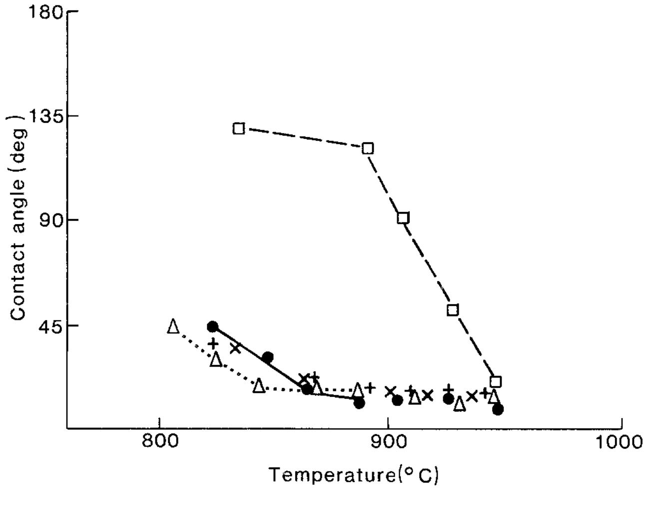

Figure 17 Contact angle data for Ag–28Cu–2Ti drops on various ceramics. (△) AlN, (□) BN, (●) Si_3N_4, (×) 101, (+) 201.

The main conclusions that can be drawn from the work is that a number of braze materials can be identified that wet well both nitride and sialon ceramics. For Si_3N_4, there are data in the published literature that concur with our observations and hence lend credence to our unsubstantiated observations for the other ceramics. Each type of braze employed in this work was capable of wetting well all five ceramics used in this work. However, while it has already been pointed out that the wettability of the ceramics by a particular braze can be ranked, that ranking was not the same for the different brazes. Thus the sialon 201 ceramic was that most easily wetted by aluminium, whereas the copper-titanium and silver–copper–titanium alloys wetted Si_3N_4 more readily.

Interest in wetting behaviour arises from the desire to braze nitrides, but once wetting has been achieved the next most important attribute of a braze is that it bonds. In this work, bonding achieved by aluminium has been found to be good and hence consistent with the technological interest in aluminium as a braze [16–22]. Similarly the work has indicated that bonding by the reactive copper-titanium alloys was good. Although no strength values were obtained for copper-titanium bonded nitrides, the microstructural studies showed that intimate contact was achieved and fracture paths seldom propagated along the alloy–ceramic interfaces. These fractures were initiated by stresses

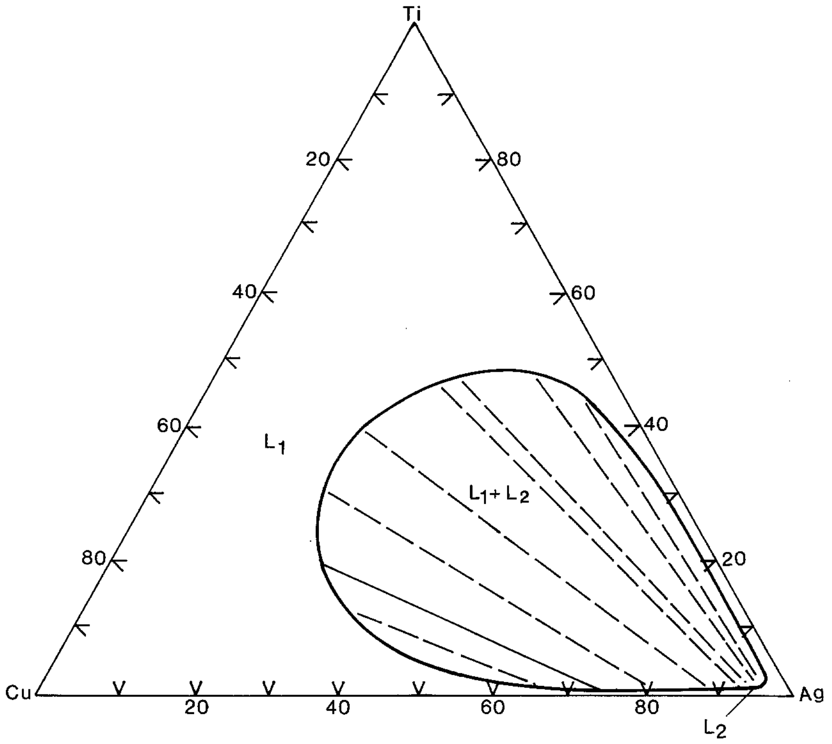

Figure 18 Phase diagram for the silver–copper–titanium system at 1300° C showing activity tie-lines across the liquid immiscibility gap, after Chang *et al.* [44].

generated by the growth of reaction products and by the mismatched contractions of the ceramics and the relatively rigid copper–titanium alloys. The crack free microstructures of the aluminium bonded samples, therefore, can be related to both the extreme thinness of any reaction product layers formed at their interfaces and the low yield strength of the metal.

More work is needed to improve our understanding of metal–nitride systems and to optimize fabrication processes, but the prospects for the technological development of satisfactory braze systems look good.

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