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Wetting and reaction between β′-sialon, stainless steel and Cu–Ag brazing alloys containing Ti

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Abstract

Joining of sialon to austenitic stainless steel has been carried out using active brazing alloys. Copper–silver eutectic alloys do not react with sialon at 900°C and no wetting or chemical bonding occurs, however, it was shown that copper–silver with addition of Ti to form active braze alloys, reacted chemically to cause wetting and chemical bonding. The surface active effect of indium in Cu–Ag based braze alloys results in different effects at the ceramic–braze and the steel/braze interfaces. The effect of indium in increasing the activity of titanium in Cu–Ag alloys results in enhanced reaction at the ceramic–braze interface, while at the steel–braze interface the solubility and diffusion of metallic elements from the steel into the braze alloy is limited and so the extent of reaction is smaller when indium is present. The samples which were brazed at 950°C gave good bending strength, and fracture occurred in the sialon indicating that the brazing process had produced an excellent interfacial bond. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Brazing; Cu–Ag alloy; Joining; Sialons; Steel; Wetting

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1. Introduction

Brazing is a process in which two or more closely fitting parts are joined via an intermediate metallic material (a brazing metal or alloy) which melts, then wets the surfaces being joined, reacts and finally solidifies. The first requirement of a braze is that it wets both components and the ability to do so can be measured by the contact angle (θ) between the surface of the liquid front and the solid substrate. The angle is less than 90° for a wetting system and is zero for complete wetting when the liquid spreads over the surface. The contact angle can be related to the surface energies between solid/vapour (γ_{sv}), liquid/vapour (γ_{lv}) and solid/liquid (γ_{sl}). The interfacial energies may be manipulated to promote wetting and composition of the alloy, atmosphere and temperature all play critical roles and small variations can influence the interfacial energies. The commonly used sessile drop method of wetting measurements requires equilibrium but it should be noted that the contact angle in fact changes with time as the liquid, solid and vapour interact (see, for example, Fig. 1).

Two basic mechanisms are involved in bond formation, wetting of the surfaces by the braze alloy and interface reaction. Brazing systems are chosen to satisfy the wetting requirements discussed above and in addition normally show reaction layers of some micrometers thickness at the interfaces. If these reaction layers increase in thickness the bond strength of the joints may be degraded, promoting premature failure by interfacial stresses due to thermal expansion mismatch.

Brazing is well known in metallic bonding but is also one of the most promising methods of ceramic–ceramic and ceramic–metal joining because of its relatively non-stringent joint tolerance requirements and because ductile brazes are able to accommodate the thermal expansion mismatch which occurs in dissimilar joining systems. In brazed glass–metal joins it is common to preoxidize the metal and the resulting oxide layer, by providing a more compatible structure may lower the solid–liquid interfacial energy, γ_{sl}, and thereby promote wetting.[1] In the case of ceramic–metal seals, compositional transition from oxide ceramic to metal promotes effective bonding on the metal surface layer. In these cases the ceramics are oxide-based and although many of the

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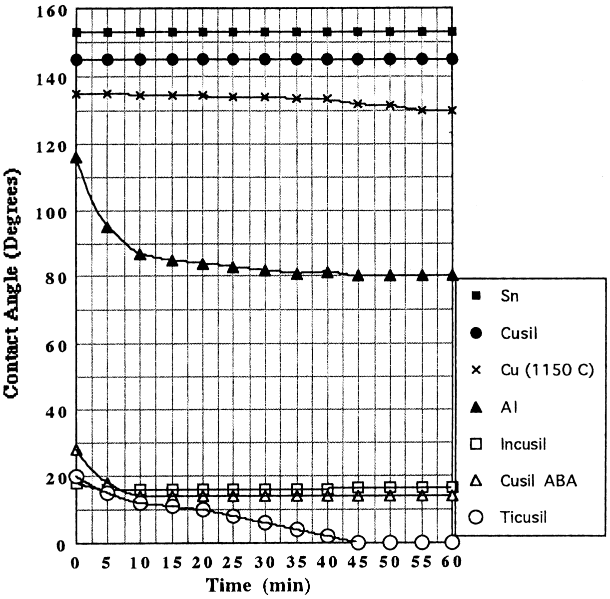

Fig. 1. Variation of contact angle with time for a range of braze alloys (after Tomsia and Pask[5]).

same arguments apply for non-oxide ceramics, reactivity to form carbides, nitrides and other compounds will have a profound effect on the simple concepts of wetability.[2–6]

For many brazing systems, active gas rather than inert or vacuum atmospheres may be used to affect wetting by altering the interfacial energies with the vapour and modifying the liquid or solid by oxidising, reducing or diffusing particular components. It should be noted, however, that the various approaches used to produce or significantly improve wetting may also have an affect on the chemical reactions which occur in the brazing system. By careful process control the presence of transition or reaction layers at the braze interfaces can promote both improved wetting and bonding and both are required for a strong bond. However, it is difficult to assess the relative contribution of each in many joining applications.[7]

Intimate contact between the workpieces to be bonded is a prerequisite of successful joining. The contacting surfaces must be converted into an atomically bonded interface and finally this interface and its adjacent material must be able to accommodate stresses due to thermal expansion mismatch which are generated between the materials during cooling after bonding. In the case of dissimilar materials, such as metals and ceramics, molten brazes fulfil the condition of intimate contact providing they will wet and penetrate into irregularities of the surfaces. Ceramics are seen to have poor wetability due to the ionic or covalent nature of their lattices by which electron movement is restricted but if the braze alloy contains an element capable of changing the chemistry of the ceramic surface (the definition of an active braze) its ability to spread and wet will be drastically improved. The most commonly used active metal additive in brazing is titanium, Ti[2,3,8] although elements such as V, Nb, Ta, Zr, Hf and La were recommended more than 20 years ago in the patent literature.[9] Generally, Ag–Cu eutectic alloys containing only a small percentage of the active metal are used.

In this investigation, joining of sialon to austenitic stainless steel of grade AISI 316L was carried out using active brazing alloys. Silver–copper eutectic alloys were used with titanium additions to give the active component, while the surface energies were altered by addition of indium which is known to be surface active in these systems.[10] Copper–silver eutectic does not react with nitride ceramics at 900°C and thus no wetting or chemical bonding occurs.[4] The result of the wetting of pure metals such as Ag, Cu, Al and In on silicon nitride are summarised in Table 1 from the work of Jungberg and Arren.[4] In wetting the as-received silicon nitride surface, it was found in that work that certain of the molten metals did not flow out symmetrically. This phenomenon was first noticed with pure aluminium but it was also noticed that pure copper had a reddish brown tarnished surface after the wetting experiments. A higher oxygen level on the drops of all the pure metals taken from the as-received silicon nitride surface was confirmed by scanning Auger microscopy analysis.

Fig. 1 represents the wetting behaviour of several Cu–Ag alloys, with and without Ti addition, on as-polished Si_3N_4-8 wt.% Y_2O_3 at 900°C (Tomsia and Pask[5]). (The range of brazing alloys are known by the commercial generic name Cusil with variations such as Incusil and Ticusil to describe additions to the basic composition.) The figure shows that Cusil Cu–Ag alloy did not wet sialon, as indicated by a large obtuse contact angle, but that additions of Ti (Ticusil) or In (Incusil) or other compositional modifications resulted in much lower contact angles and significant wetting. The figure also shows how the contact angle changes with time as reaction takes place at the ceramic–braze interface. From the results in Fig. 1, it can also be seen that the kinetics of wetting and spreading are faster for alloys containing Ti.

These observations provide the basis for the present work in which Cusil-type copper–silver, with addition of

Table 1
Wetting of silicon nitride with pure metals (contact angle after 5 min at 1100°C) — after Jungberg and Arren[4]

Metals	Contact angle (as-received surface)	Contact angle (ground to 30 μm)
Ag	Non-wetting	155
Al	Non-wetting	58
Cu	144	131
In	–	Non-wetting 600°C

Ti to form active braze alloys, reacted chemically with the nitride ceramic to cause wetting and chemical bonding. The reaction products were sufficiently extensive to form complex microstructures in the interfacial zone and these were studied to show how changes in processing conditions have an effect on the ultimate strength of the joint assembly.

2. Experimental

Materials used in this study are Syalon 201 [β′-sialon $z=0.75$ (Vesuvius Zyalon Ltd)], stainless steel grade AISI 316L and three different brazing alloys; Cusil ABA, Incusil and an experimental Cusil alloy. The composition of these materials is listed in Tables 2 and 3. The sialon is comprised of silicon nitride densified by 4%Y_2O_3 and 4%Al_2O_3 to give a β′ structure of $z=0.75$ with an amorphous intergranular phase. The ceramic and steel were supplied in the form of plates. Technical specification sheets (Wesgo Inc, Belmont, California) show that Cusil-ABA provides increased wetability, is available in various forms for ease of application (50 μm foil was used in this case) and is designed to produce ductile brazed joints. The alloy has been shown to wet and bond to ceramics including nitrides. Incusil is also a commercial alloy equivalent to Cusil-ABA but has addition of 12% In to lower the metal surface tension, while the third alloy used is an experimental active brazing alloy with increased titanium content.

The experiments were carried out under argon gas at 1 atm (101 kPa) or vacuum (0.13 Pa) in a die designed to provide a small compressive stress on the joint during brazing experiments. This was based on the known expansion of the metal and ceramic test pieces held rigidly in a graphite die. By securing the assembly at room temperature the pressure on the specimen during brazing can be controlled over a known range of temperature change. The die is usually coated with boron nitride to prevent the formation of carbides (which may affect the strength of the joint) which can be formed by reaction between carbon and the active element, such as titanium. The brazing pressure can be calculated from the difference in length ($\delta L=L-L_0$) between the initial length of the metal and ceramic, L_0, and that at brazing temperature, L. From this value of expansion strain the resultant compressive stress can be calculated and in the present experiments was typically about 15 MPa.

Table 2
Composition of the stainless steel used in this study (AISI 316L)

Fe%	C%	Ni%	Cr%	Mo%	Mu%	P%	S%	Si%
Balance	0.03	17.8	13	3.5	1.2	0.05	0.03	0.4

Table 3
Composition of the brazing alloys

Brazing alloy	Ag%	Cu%	Ti%	In%
Cusil ABA	Balance	35.25	1.75	0
Incusil	Balance	27	1.25	12
Experimental Alloy	Balance	38	2	0

Pressureless-sintered sialon and stainless steel were cut into slabs approximately 10×5×5 mm for use as substrates and the brazing alloy cut into 5×5 mm pieces of 50 μm foil. The sialon surface was ground to 1 μm diamond finish and the same procedure was followed for the stainless steel. Both sialon and stainless steel were washed in acetone using ultrasonic agitation. As a final treatment the sialon was heated at 600°C in air to provide some thermal etching of grain boundaries and improve bonding, then the joint pieces were fixed in the graphite die and inserted inside the furnace. The experiments were carried out at different temperatures ranging between 850 and 1000°C using an argon atmosphere or vacuum for 30 min.

3. Results and discussion

3.1. Interfacial reactions

Preliminary experiments over the range of temperatures given above showed that optimum effective joining for these systems occurred at 950°C; examples of the microstructures formed are shown in Figs. 2(a), 3(a) and 4(a). These photographs show an integral bond between the sialon and braze alloy with a sharp interface while the steel/braze interface is characterised by a line of dark/light contrast in the electron image corresponding to intermetallic layers as identified by chemical analysis (see below). Reactions between both stainless steel and sialon and the Ti-containing braze alloys at 950°C were observed to be extensive and energy-dispersive X-ray analysis (EDS) results shown in Figs. 2(b)–4(b) show titanium concentration peaks at both braze–stainless steel and braze–ceramic interfaces. The spacing between the two titanium peaks corresponds to the braze thickness. Titanium was found only at the braze interfaces, with none observed in the stainless steel or ceramic and only background levels in the bulk braze as shown in the line scans of Figs. 2(b), 3(b) and 4(b).

The polished cross sections and EDS traces of the reaction interface between β′, Cusil braze alloys and stainless steel after 30 min at 950°C show that adjacent to the β′-sialon an approximately 10–20 μm thick layer is formed depending on the braze alloy composition, while that of the stainless steel interface is 12 μm for the Incusil alloy but 25 μm for the others. The bulk composition of the braze alloy is altered by the reaction and separation of the eutectic composition occurs on cooling

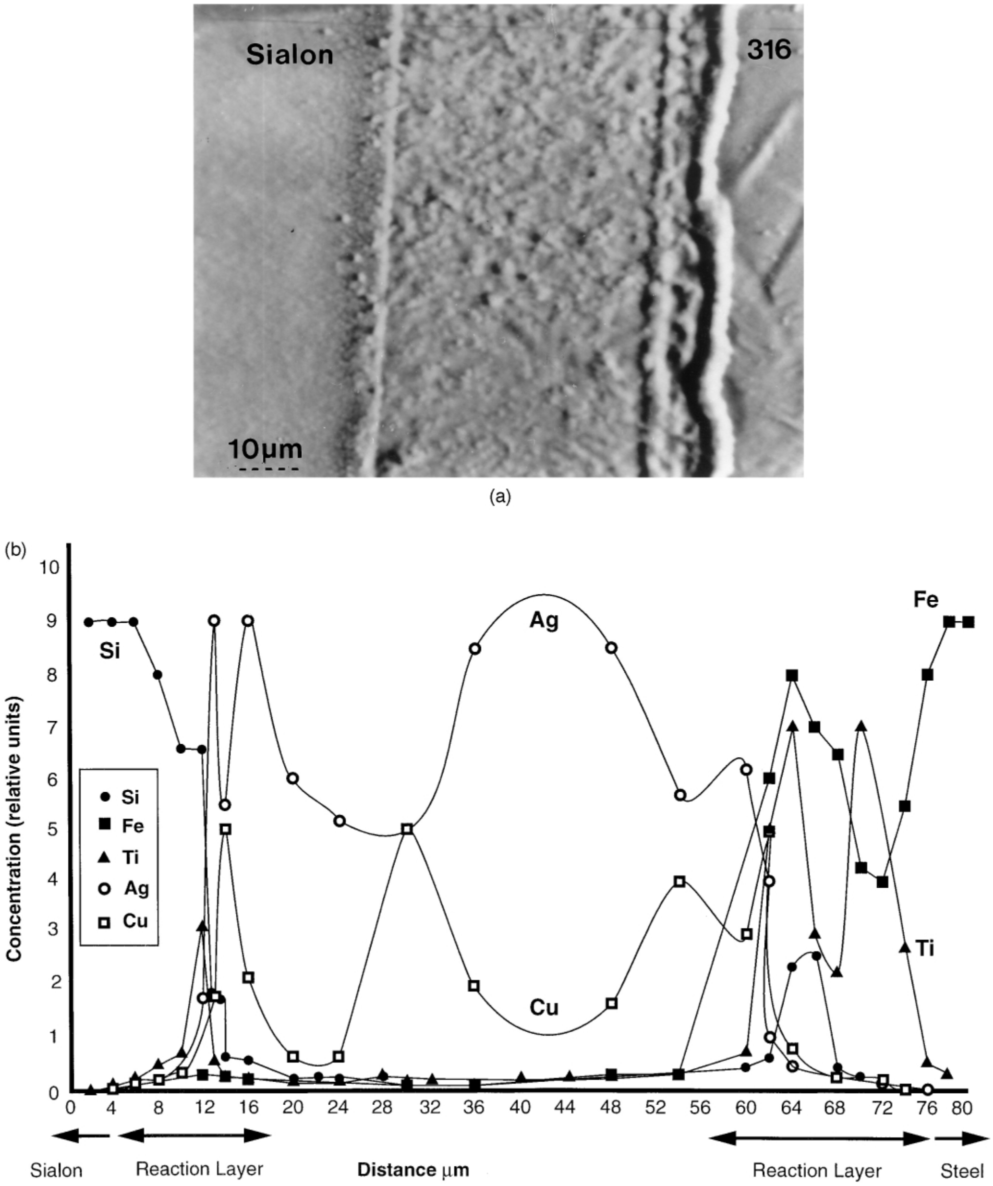

Fig. 2. (a) Scanning electron micrograph of sialon and AISI 316 with Cusil braze; (b) concentration profiles across the join shown in (a).

giving regions of primary (Ag–Cu) solid solution and primary (Cu–Ag) solid solution. This is evident in the figures where the wide variation in Ag/Cu concentrations arises due to random point analysis in the coarse eutectic structure.

4. Analysis of the interlayers

4.1. Ceramic/braze

Active brazing depends on the decomposition and change of the ceramic surface due to reaction between the active component in the filler metal and the ceramic, and equilibrium thermodynamics offer some important indications on possible reactions. The feasibility of different Ti-sialon reactions can be estimated using the criterion of a negative Gibbs free energy and some possible reactions at 950°C (considering sialon as an impure silicon nitride) are:

$$\mathrm{Si_3N_4} + 4\mathrm{Ti} = 4\mathrm{TiN} + 3\mathrm{Si}$$

$$\Delta G = -135\ \mathrm{kJ/mol}$$

$$\mathrm{Si_3N_4} + 3\mathrm{Ti} = 3\mathrm{TiSi} + 2\mathrm{N_2}$$

$$\Delta G = 10\ \mathrm{kJ/mol}$$

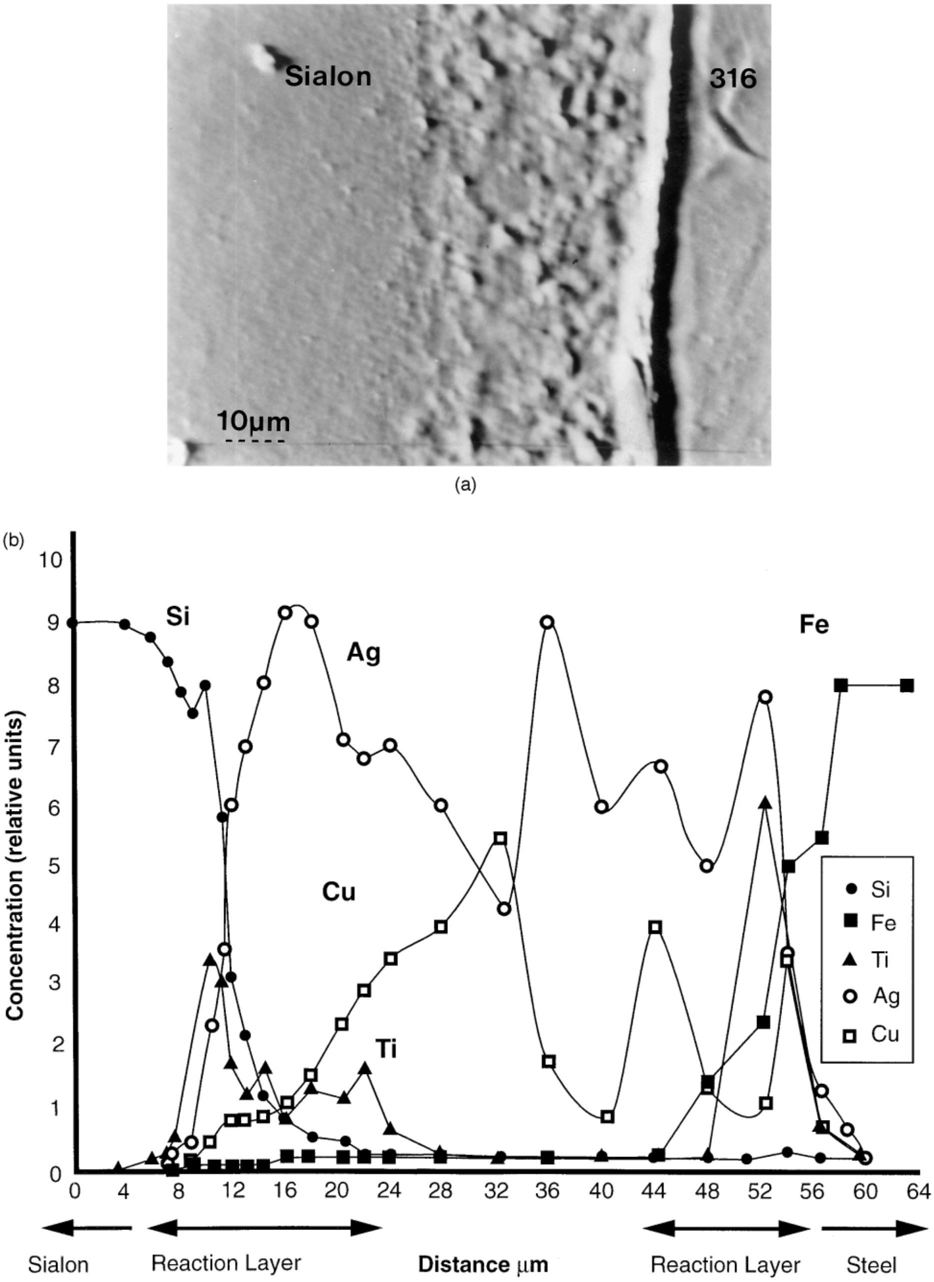

Fig. 3. (a) Scanning electron micrograph of sialon and AISI 316 with Incusil braze; (b) concentration profiles across the join shown in (a).

$$2Si_3N_4 + 3Ti = 3TiSi_2 + 4N_2$$

$$\Delta G = 100 \ \text{kJ/mol}$$

$$Si_3N_4 + 5Ti = Ti_5Si_3 + 2N_2$$

$$\Delta G = -40 \ \text{kJ/mol}$$

These energy data were taken from Kubaschewski et al.[11] It is obvious that the reaction leading to the formation of TiN is favoured over the corresponding silicide reactions in the range of temperature and leads to the conclusion that TiN will be the dominant reaction product. The presence of TiN could not be confirmed experimentally however as the EDS system used could not detect nitrogen (which would in any case be dominated by the adjacent sialon) and the layer was too thin to yield meaningful X-ray diffraction reflections.

For all three braze alloys the compositional distribution shown in the EDS data [Figs. 2(b), 3(b) and 4(b)] are similar. At the interface with the ceramic there is a pronounced peak in the concentration of titanium

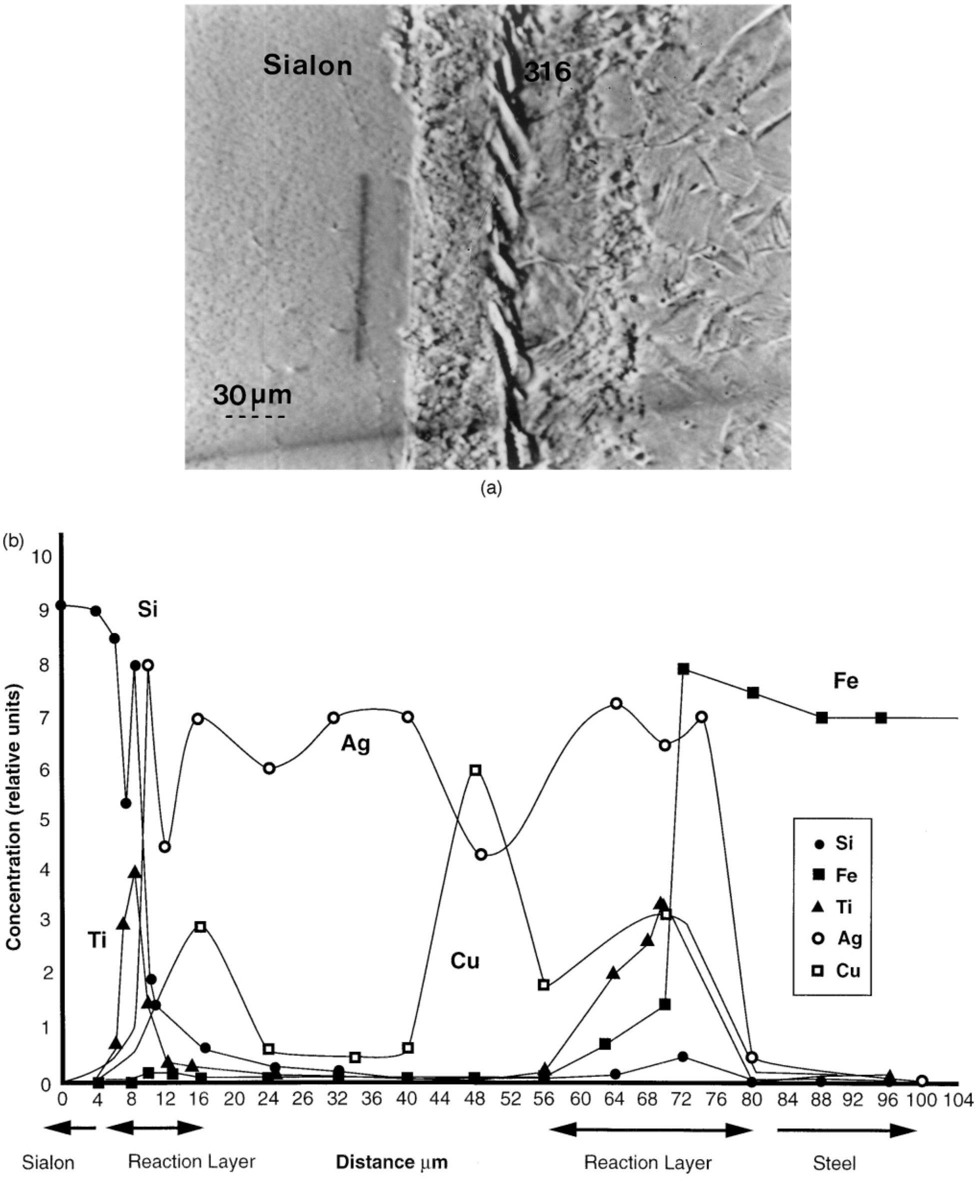

Fig. 4. (a) Scanning electron micrograph of sialon and AISI 316 with experimental alloy braze; (b) concentration profiles across the join shown in (a).

which on the basis of the above discussion is taken to be due to formation of titanium nitride at the interface by reaction of titanium in the alloy with nitrogen from the sialon. As the solubility of nitrogen in liquid Cu–Ag alloy is negligible, this reaction is confined to the immediate ceramic–braze interface and cannot develop by titanium diffusion in the liquid phase to the interface as the reaction layer forms a barrier to further reaction. Careful examination of Figs. 2(b)–4(b) shows, however, that the peak in titanium concentration is relatively broad and is coincident with a significant silicon concentration. This second effect is due to the release of silicon from sialon by the titanium nitride reaction and the high solubility of silicon in liquid copper alloys which results in diffusion of silicon in the liquid braze toward the counter diffusing flow of titanium resulting in titanium silicide formation. Thus, although the stability of titanium silicide is less than that of titanium nitride, the relative concentrations result in formation of titanium silicides in a layer adjacent to the titanium nitride layer but further from the interface. This is shown schematically in Fig. 5. The integral nature of this metal–intermetallic–ceramic bond is clear from the micrographs of Figs. 2(a)–4(a).

In summary, it is proposed that a nitride layer is nucleated at the interface by reaction of titanium with the β′ grains of the ceramic, silicon is released simultaneously and dissolves in the liquid metal. Once the layer is continuous, the reaction is dependant on diffusion of titanium to the reaction interface and diffusion of silicon

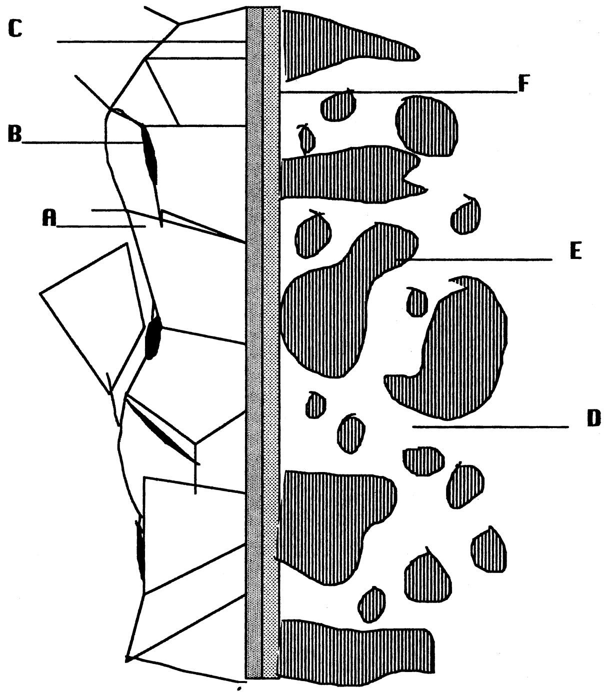

Fig. 5. Schematic of the sialon/braze alloy interface (A, sialon grains; B, glassy phase; C, TiN layer; D/E, copper–silver eutectic; F, titanium silicide layer).

through the layer to the braze. The amount of titanium initially present might be expected to increase both the rate of the reaction and the extent of formation of silicide but no significant difference in the thickness of the interfacial layer was measured between Cusil [Fig. 2(b); 1.75%Ti] and the experimental alloy [Fig. 4(b); 2%Ti].

4.2. *Steel/braze*

EDS data from the reaction between Ti and stainless steel shown in Figs. 2–4 indicate the presence of an enhanced Ti concentration at the stainless steel-braze interface. Similar to the case for the ceramic, there are many intermetallic compounds which may form by reaction at the interface between the brazing alloy and the stainless steel. The reaction between stainless steel and Cusil braze alloy, adjacent to the stainless steel can be given by reactions such as:

$$Ti + 2Fe = TiFe_2$$

$$2Ti + Ni = Ti_2Ni$$

$$Ti + Cr = TiCr$$

There is, however, insufficient published data to allow thermodynamic calculation for these compounds. [In Figs. 2(b)–4(b) the concentration of iron is shown for clarity: the profiles for chromium and nickel are similar.]

The mechanism by which this interlayer forms is by reaction of the metallic elements in the steel with titanium in the braze thereby setting up a concentration gradient which causes further diffusion of titanium in the liquid phase. As there is a considerable excess of steel alloy element concentration over that of titanium and because the steel remains solid during brazing, the rate-limiting step is dissolution of the steel in the liquid braze. No effect of increased titanium content on the thickness of the interfacial layer (25 μm: Cusil and experimental alloy) was detected.

4.3. *Effect of indium*

Additions of about 8% of titanium are needed to induce copper to wet alumina at 1150°C but only 3.5% of titanium is needed if the copper is also alloyed with 11.8% indium.[10] The analysis of wetting data suggests that addition of indium was beneficial for two reasons. The solubility of titanium is lower in indium–copper and hence alloying increases the activity of titanium and leads to the formation of more readily wettable surfaces, and secondly the low surface energy of indium, compared to copper, causes segregation to the alloy surface, thereby increasing its effect on titanium activity at the alloy surface and also enhancing any beneficial changes in wetability.[10]

The results of the joining experiments with Cusil and Incusil are shown in Figs. 2 and 3. The reaction zone between the ceramic and braze alloy was about 12 μm in the case of Cusil and 20 μm for Incusil alloy and the reaction at the steel surfaces are 20 μm and 12 μm respectively. Thus the presence of indium appears to have different effects at the ceramic/braze and steel/braze interfaces. In the first case, the increased titanium activity combined with diffusion of silicon from the ceramic into the liquid braze results in a wider reaction zone when indium is present. This is primarily due to silicide formation as the titanium nitride layer is immediately adjacent to the sialon surface and no nitrogen diffusion occurs into the braze. This is confirmed by the relatively high titanium and silicon concentration profiles [Fig. 3(b)] extending into the braze layer. It should also be noted that the ceramic bond appearance in this case is much more coherent than with the other braze alloys [compare Figs. 2(a) and 4(a) with 3(a)].

In the case of the steel/braze interface it is the segregation and surface activity effect of titanium which dominates. The presence of surface segregated indium at the liquid braze/solid steel interface restricts the transfer of metallic alloy elements across the interface and diffusion in the braze. The extent of reaction to form intermetallics is, therefore, reduced and the thickness of the interface layer is smaller [compare Fig. 3(b) with Figs. 2(b) and 4(b)].

[It should be noted that in EDS analysis, peaks for Ag ($L_{\alpha,\beta}$) and In ($L_{\alpha,\beta}$) are immediately adjacent and overlap. Therefore, the higher Ag peak dominates and quantitative analysis for In is not possible.]

By examining all three braze alloys which allow comparison of different titanium concentrations and the effect of indium, it is clear that the latter is the dominant factor and that increasing the Ti alloy content within the levels studied has no noticeable effect.

4.4. Bond integrity

The strength and integrity of the composite brazed joint was assessed by carrying out standard four-point bond tests on the sample geometry (20×5×5 mm) described above in the Experimental section. The samples brazed at 950°C showed the highest bending strength and the alloys can be ranked as Cusil (600 MPa) > Incusil (500 MPa) > experimental alloy (450 MPa). However, of greater importance is the observation that in all cases the failure occurred in the sialon ceramic (manufacturers reported fracture strength 825 MPa) away from, but parallel to the interface with the braze alloy. Thus the limiting factor is that of stress concentration at intrinsic defects in the pressureless sintered ceramic and not the structure of the interfaces or braze alloy which can accommodate (ductile) deformation. It should be noted that comparison of the bond strengths with the failure strength of the parent sialon is not appropriate as the latter value is for a stress-free material while the sialon in the bonded structure has some unknown level of residual thermal stress after cooling from joining temperature. Other work in the authors' laboratory[12] shows that a tensile stress of up to 400 MPa perpendicular to the interface is possible.

5. Conclusions

Copper–silver eutectic brazing alloy does not react with sialon and no wetting or chemical bonding occurs. However, copper–silver, with addition of Ti to form active braze alloys, reacted chemically to cause wetting and bonding.

Titanium was found to be segregated to the braze interfaces with both steel and sialon and a negligible amount was detected in the braze alloy, ceramic or stainless steel.

The thermodynamic calculations for reactions between Ti and Si_3N_4 show that the reaction leading to the formation of TiN is more favourable than the corresponding suicide reactions. It is proposed that the nitride layer is nucleated at the interface by reaction of titanium with the β' grains but that the silicon released by the reaction reacts further with titanium in the liquid braze alloy to form suicides as a second interfacial layer. The solubility of titanium is decreased by indium additions to copper alloys and hence the activity of titanium is increased, while the low surface energy of indium causes it to segregate to the interfaces thereby increasing its effect on titanium activity. The thickness of the ceramic bond layer and coherence of the join are greater when indium is present.

At the braze–steel interface the alloy elements in the stainless steel dissolve in the braze during joining to react with titanium and form an interfacial intermetallic layer. The surface active effect of indium is also effective at the steel–braze interface. The solubility and diffusion of metallic elements from the steel is limited and so the reaction layer is smaller when indium is present.

The samples which were brazed at 950°C gave good bending strength, and the fracture occurs in the sialon indicating that the brazing process had produced an excellent interfacial bond.

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