Transient liquid-phase insert metal bonding of Al$_2$O$_3$ and AISI 304 stainless steel

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Transition liquid-phase insert metal bonding of Al$_2$O$_3$ and AISI 304 stainless steel based materials is investigated. This joining technique allows the continuous replenishment of the active solute which is consumed by the chemical reaction that occurs at the ceramic/filler metal interface. Replenishment is facilitated by employing a sandwich of filler materials comprising tin-based filler metal and amorphous Cu$_{50}$Ti$_{50}$ or NiCrB interlayers. During Al$_2$O$_3$/AISI 304 stainless steel bonding, the highest shear strength properties are produced using a bonding temperature of 500 °C. Thick reaction layers containing defects form at the ceramic/filler material interface when higher bonding temperatures are applied. Bonding at temperatures above 500 °C also increases the tensile residual stress generated at the periphery of Al$_2$O$_3$/AISI 304 stainless steel joints. The shear strength of joints produced using NiCrB interlayers markedly increased following heat treatment at 200 °C for 1.5 h. Heat treatment had little influence on the shear strength of the joint produced using Cu$_{50}$Ti$_{50}$ interlayers.

1. Introduction
Ceramic/metal joining has received much attention in recent years because of the excellent high-temperature strength, corrosion and wear resistance of ceramic substrates. Vacuum brazing is an attractive joining method because it is performed in a single step and the contacting substrates require little preparation prior to the joining operation. However, because brazing is generally carried out at high temperature and the thermal expansion coefficients of ceramic and metal substrates are widely different, residual stresses are generated during cooling to room temperature [1]. High tensile residual stresses generated at the joint periphery may result in cracking or produce joints having low strength. The residual stress, σ, generated due to the difference in thermal expansion coefficients of the ceramic and metal depends on the following relations [2].

When no yielding occurs

$$\sigma = \Delta\alpha\Delta T \, \frac{E_I E_{II}}{E_I + E_{II}} \qquad (1)$$

When yielding occurs

$$\sigma = \sigma_y + \Delta\alpha\Delta T E_w \qquad (2)$$

where σ_y is the yield strength of the metal, $\Delta\alpha$ is the difference in thermal expansion coefficients of the ceramic and metal, ΔT is the difference in temperature between the bonding temperature and room temper-

ature, E_I and E_{II} are the expansion coefficients of the ceramic and the metal, and E_w is the strain-hardening coefficient of the metal. The residual stress will be lowest when low brazing temperatures and soft, ductile interlayers are applied. Also, brazing temperatures as high as 900 °C necessarily limit the application of this technique for ceramic and metal combinations that have been given prescribed heat-treatment cycles at lower temperatures. For example, high-temperature brazing of partially stabilized zirconia (PSZ) to nodular cast iron will severely impair the mechanical properties of the metallic substrates [3].

Based on the above discussion, there is a need for filler materials which permit bonding at lower temperatures than are typical of those when using conventional copper- or silver-based alloys. Although it would be expected that tin-based filler metals would be natural candidates for lower temperature brazing applications, it has been confirmed that bonding temperatures in the range 850–950 °C are required when joining Si$_3$N$_4$ substrates if satisfactory wetting behaviour (low contact angles) is to be achieved [4]. Wetting of ceramics by a liquid metal is promoted by active solutes such as titanium, zirconium and chromium in the filler metal which react chemically with the ceramic substrate [5]. In a non-ideal solution, the chemical potential of the active solute, U_i is given by the relation

$$U_i = U_0 + RT \ln a_i \qquad (3a)$$

where, U_0 is the chemical potential in the standard state, R is the gas constant, T is the absolute temperature and a_i is the activity of the solute in the filler metal. a_i depends on solute content in the filler metal, X_i, and on the activity coefficient, f_i, of the solute, $a_i = f_i X_i$ and therefore

$$U_i = U_0 + RT \ln \frac{f_i n_i}{n} \tag{3b}$$

because $X_i = n_i/n$ (where n_i is the number of moles of active solute and n is the total number of moles). At constant bonding temperature, the chemical activity of a solute such as titanium in tin-based filler metal is determined by a_{Ti} and X_{Ti}. Both are decreased during low-temperature bonding due to the formation of intermetallic phases (e.g. Sn_5Ti_6) which consumes some of the active solute. Unfortunately, the activity of titanium cannot be increased by increasing its concentration in the tin-based filler metal, because the solidification range of the alloy dramatically increases. For example, increasing the titanium content from 2 at % to 40 at % in tin-based filler metal extend the solidification range from $180\,^{\circ}C$ to $650\,^{\circ}C$ [6]. This increase in the solidification range will have a harmful effect on the spreading characteristics and viscosity of the filler material. With this in mind, some means is required whereby the activity of titanium can be increased without detrimentally affecting the spreading characteristics and viscosity of the tin-based filler metal.

The present paper investigates joining of Al_2O_3 and AISI 304 stainless steel substrates using transient liquid-phase insert metal (TLIM) bonding. During TLIM bonding, the active solute for chemical reaction at the ceramic/metal interface is supplied and continuously replenished without detrimentally affecting the spreading characteristics and viscosity of the filler material. The filler material comprises two tin-based alloy layers which sandwich an amorphous $Cu_{50}Ti_{50}$ or NiCrB interlayer (see Fig. 1). (For the remainder of this paper, the filler material terminology is used to indicate the combination of the two tin-based filler alloy layers with the amorphous $Cu_{50}Ti_{50}$ or NiCrB interlayer materials.) The tin-based alloy layers melt and release active titanium which reacts chemically with the Al_2O_3 ceramic. At the same time, the $Cu_{50}Ti_{50}$ or NiCrB interlayer dissolves in the tin-rich melt and supplies active titanium or chromium. In this way, the active solute is continuously replenished dur-
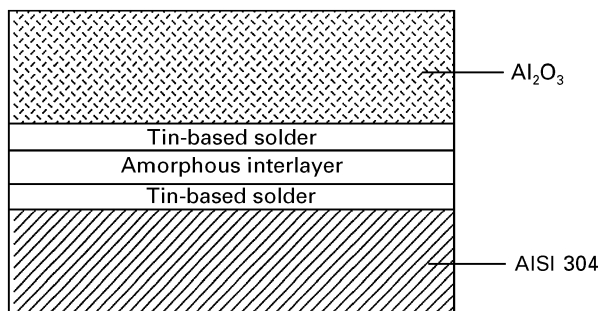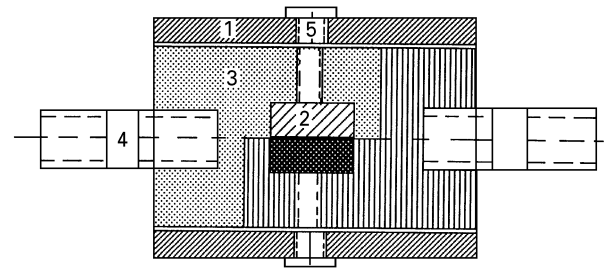

Figure 2 Joint shear testing apparatus. 1, casing pipe; 2, specimen; 3, holder; 4, bolt; 5, screw.

ing the bonding operation. The different stages in TLIM bonding are described and the factors that determine the mechanical properties of Al_2O_3/AISI 304 stainless steel joints are examined in detail.

2. Experimental procedure
2.1. Materials
Cylindrical specimens, 10 mm diameter × 5 mm diameter, of Al_2O_3 and AISI 304 stainless steel were employed throughout. The Al_2O_3 ceramic contained 0.1 wt % MgO and 0.1 wt % CaO as impurities. The chemical composition of the tin-based alloy layers comprised 2 wt % Ag, 1 wt % Cu, 0.05 wt % B, 1 wt % ln, 3 wt % Ti, balance tin. The amorphous interlayer materials comprised $Cu_{50}Ti_{50}$ (containing 50 at % Cu and 50 at % Ti) and NiCrB (containing 15.5 wt % Cr, 3.5 wt % B, balance nickel) alloys. The thicknesses of the tin-based alloy layers and amorphous interlayers were 50 μm, respectively.

2.2. Procedure
The contacting surfaces of the Al_2O_3 and AISI 304 stainless steel substrates were polished using 1200 grade emery paper and, prior to bonding, the samples were cleaned using acetone. Bonding was carried out at temperatures ranging from 320–600 $^{\circ}C$ in the 10^{-5} torr (1 torr = 133.322 Pa) vacuum furnace. The heating rate between room temperature and the bonding temperature was $5\,^{\circ}C\,s^{-1}$ and, following given holding times, the joints were furnace-cooled.

Joint shear strength was evaluated using a specially designed fixture which placed the joint interface region in shear (see Fig. 2). Mechanical testing was carried out using a 100 kN Instron machine and all tests were carried out at room temperature. The shear strength results indicated in this paper are the average of three tests at each condition.

3. Results and discussion
The TLIM bonding process can be considered to comprise five distinct stages.

3.1. Stage 1
During this stage the joint is heated from room temperature to the melting point of the tin-based alloy

Figure 1 Filler material applied during TLIM bonding.

layers. When the tin-based alloy layers melt at temperature T_m, the chemical reaction between the ceramic substrate and active titanium in the filler metal initiates and the rate of diffusion of the active solute to the ceramic/filler metal interface (dM/dt) is determined by the relation

$$\frac{dM}{dt} = D_i(C_0 - C_1) \qquad (4)$$

where C_0 is the concentration of active solute in the tin-rich liquid, C_1 is the concentration of active solute at the ceramic/metal interface and D_i is the diffusion coefficient of the active solute in the tin-rich liquid. Because C_1 is zero at temperature T_m, dM/dt is high and equals $(D_i C_0)$.

3.2. State 2
When the joint is heated between T_m and the brazing temperature, T_b, the chemical reaction between the ceramic substrate and the active titanium continues at the ceramic/filler metal interface and the amorphous interlayer begins to dissolve in the tin-rich liquid. The width of the reaction layer, δ, formed at the ceramic/metal interface is determined by the relation

$$\frac{dM}{dt} = \frac{D_i}{\delta}(C_0 - C_1) \qquad (5)$$

When the width of the reaction layer increases, dM/dt decreases and intermetallic phases are formed.

The amount of amorphous interlayer, M_s, dissolved in the tin-rich liquid is determined by the relation [7]

$$M_s = \rho_L C_L \frac{V_L}{S}\left(1 - \exp = \left(\frac{-a_0 t S}{V_L}\right)\right) \qquad (6)$$

where ρ_L is the density of the tin-rich liquid, C_L is the maximum solubility of the active element in the tin-rich liquid, V_L is the volume of the tin-rich liquid, S is the contact area at the solid–liquid interface, a_0 is the dissolution coefficient of the amorphous interlayers material in the tin-based melt, and t is the contact time. The dissolution rate of the amorphous interlayer is therefore

$$\frac{dM_s}{dt} = \rho_L C_L a_0 \exp - \frac{a_0 t S}{V_L} \qquad (7)$$

When the temperature rises from T_m to the bonding temperature, C_L, a_0 and dM_s/dt are increased. Because dM/dt is high, dM/dt exceeds dM_s/dt at temperatures immediately above T_m. However, the value of dM_s/dt increases when the temperature rises from T_m to the bonding temperature, T_b.

3.3. Stage 3
When the bonding temperature is attained, a dynamic situation is established involving (i) consumption of active titanium due to the chemical reaction at the ceramic/filler metal interface, and (ii) continuous replenishment of titanium as a result of dissolution of the amorphous interlayer in the tin-rich melt. Because the thickness of the reaction layer increases with hold-
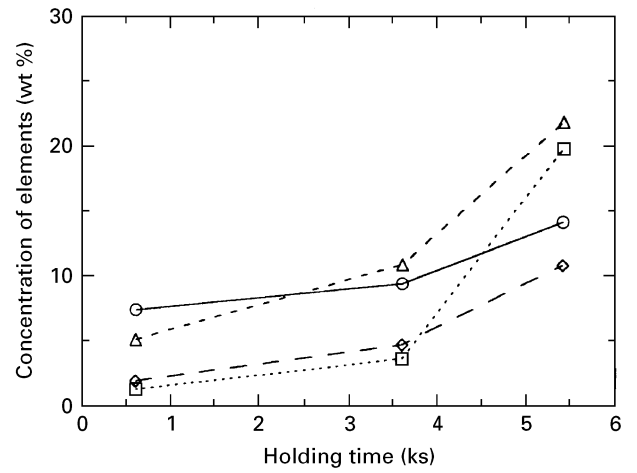

Figure 3 Variation with holding time of the ($\bigcirc$) titanium, ($\diamondsuit$) chromium, ($\triangle$) copper and ($\square$) nickel concentrations in the tin-rich layer.

ing time at T_b, dM/dt will decrease (see Equation 5). In contrast, the dissolution rate of the amorphous interlayer is constant at T_b and because dM/dt decreases with holding time, dM_s/dt will eventually become equal to dM/dt.

3.4. Stage 4
Because dM/dt decreases when the holding time increases, dM_s/dt will exceed dM/dt at a particular holding time and the concentration of active solute in the tin-rich melt will rise. Fig. 3 shows the changes in titanium, nickel, chromium and copper concentration in the tin-rich alloy layer for holding times up to 1.5 h at T_b. The largest change in content of these elements occurs when the holding time exceeded 3.6 ks (1 h). Diffusion of titanium into the tin-rich layer increases its viscosity and melting point and finally isothermal solidification occurs at temperature T_b.

3.5. Stage 5
Joint homogenization occurs during this stage of the TLIM bonding process. The rate of homogenization will be determined by the holding temperature and on the diffusion rate of solutes in the filler material and in the AISI 304 stainless steel substrate. The processes that occur during this stage in TLIM bonding are similar to those in conventional transient liquid-phase bonding and have been discussed at length elsewhere [8].

3.6. Factors affecting joint strength
3.6.1. Effect of bonding temperature
Figs 4 and 5 show the relations between the bonding temperature and average shear strength, and the reaction layer width and bonding temperature. The highest shear strength properties were produced using a bonding temperature of 500 °C. It has already been confirmed that the optimum tensile strength of Al_2O_3/Al_2O_3 joints brazed using Ag–Cu–Ti filler material [9] and Si_3N_4/Mo joints brazed using
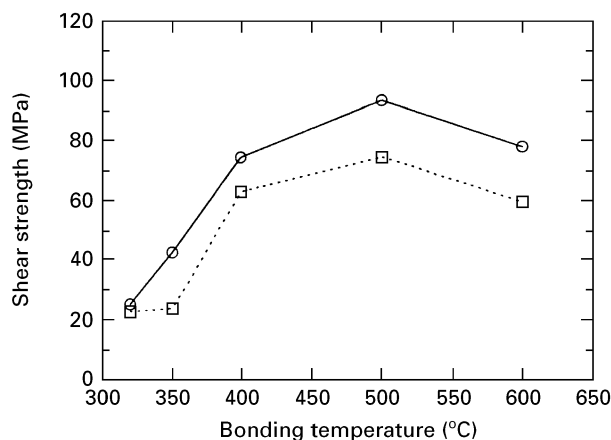
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Figure 4 Relation between the average joint shear strength and the bonding temperature (for (○) amorphous $Cu_{50}Ti_{50}$ and (□) NiCrB interlayer materials).

Figure 6 Reaction layer produced using a bonding temperature of 600 °C showing cracking (using amorphous $Cu_{50}Ti_{50}$ interlayer material).
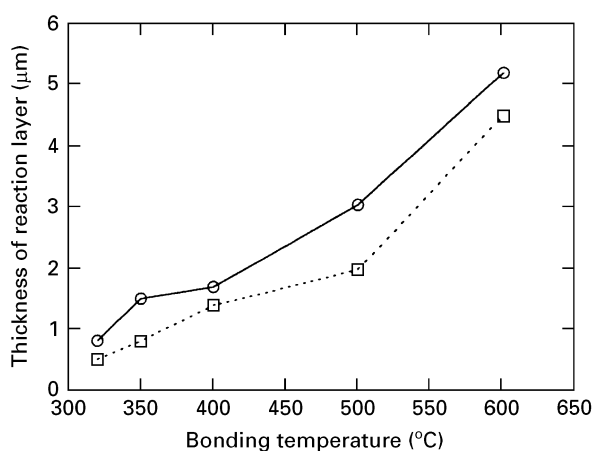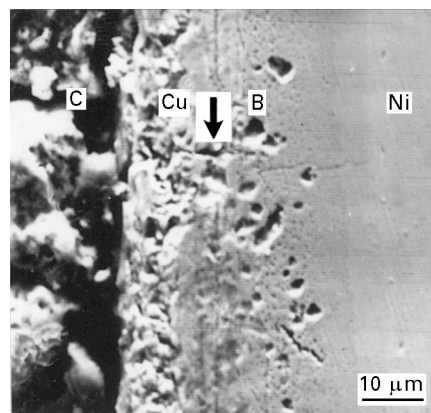

Figure 5 Effect of bonding temperature on the width of the reaction layer formed at the ceramic/filler metal interface (for (○) amorphous $Cu_{50}Ti_{50}$ and (□) NiCrB interlayer materials).

Cu–1 wt % Nb, Cu–5 wt % Cr and Cu–3 wt % V filler materials [5] occurred when a critical reaction layer width formed at the ceramic/filler metal interface. For example, when the critical reaction layer width was exceeded in Si_3N_4/Mo joints, the reaction layer contained voids and cracks [5]. During TLIM bonding of Al_2O_3 to AISI 30-4 stainless steel base material, the highest shear strength occurred when the reaction layer widths were 3 μm (using a $Cu_{50}Ti_{50}$ interlayer) and 2 μm (using a NiCrB interlayer). When the TLIM bonding temperature exceeded 500 °C, the reaction layer formed at the ceramic/metal interface also contained large numbers of cracks (see Fig. 6). This readily explains the lower shear strength of these joints.

As pointed out earlier, the mechanical properties of dissimilar Al_2O_3/AISI 304 stainless steel joints are markedly affected by the residual stress distribution generated during cooling from the bonding temperature. The magnitude of the tensile residual stress acting at the periphery of Al_2O_3/AISI 304 stainless steel joints markedly increases when the bonding temperature increases (see Equation 1). Consequently, the

lower shear strength of Al_2O_3/AISI 304 stainless steel joints produced at temperatures exceeding 600 °C may be *in part* attributed to higher tensile residual stresses acting at the joint periphery.

The average shear strength/temperature and reaction layer/temperature relations in Figs 4 and 5 involve a holding time of 30 min. Because reaction layer growth is determined by the bonding temperature and the time at temperature, the optimum bonding temperature (500 °C in Fig. 4) only applies for a holding time of 30 min. Also, the heating rate between room temperature and the bonding temperature will influence reaction layer growth. For example, for a given holding time at T_b, very slow heating rates from room temperature to the bonding temperature will favour growth of thicker reaction layers at the ceramic/filler metal interface. The influence of the joint processing cycle (heating rate, holding time at the bonding temperature and cooling time following the joining operation) and of filler metal chemistry on reaction layer growth during ceramic bonding has recently been investigated by Torvund *et al.* [10]. These investigators have developed process models which take into account the different factors determining reaction layer growth at the ceramic/filler metal interface and explain the observed differences between measured and calculated reaction layer widths, particularly the deviation from the expected parabolic growth rate relation.

3.6.2. Effect of interlayer selection
The highest joint shear strength properties were produced using amorphous $Cu_{50}Ti_{50}$ interlayer material (see Fig. 4). The reaction layers formed in joints containing NiCrB interlayers comprise mainly chromium oxide (because the titanium content in the tin-based filler metal is low). It has been shown that the strength of joints between alumina and nickel substrates increases when the chemical affinity of the active metal for oxygen increases [11]. Consequently, the higher strength of joints made using $Ti_{50}Cu_{50}$ interlayers may be due to titanium's higher chemical affinity for

TABLE I Hardness at the centreline of joints produced using NiCrB and $Ti_{50}Cu_{50}$ interlayers

| Sample condition	Hardness
As-received NiCrB sheet	772–882 HV10
Hardness at joint centreline using NiCrB interlayer	824–946 HV100
Hardness at joint centreline using $Ti_{50}Cu_{50}$ interlayer	24–46 HV10
Hardness following heat treatment at 200 °C for 5.4 ks using a NiCrB interlayer	960–970 HV100
Hardness following heat treatment at 200 °C for 5.4 ks using a $Ti_{50}Cu_{50}$ interlayer	34–54 HV10
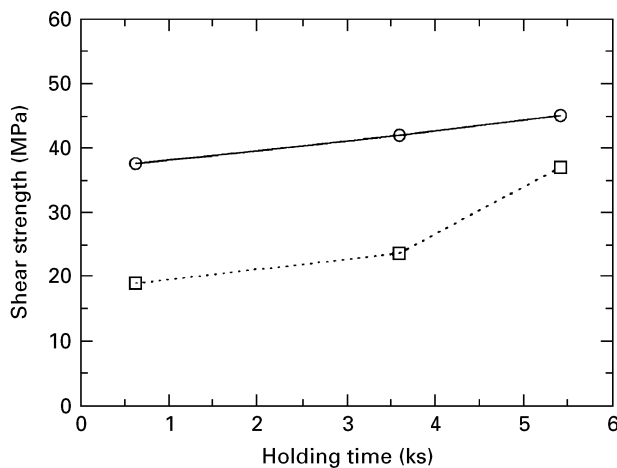
Figure 7 Effect of holding time at 200 °C on the average shear strength of joints TLIM bonded at 350 °C. (○) $Cu_{50}Ti_{50}$ interlayer, (□) NiCrB interlayer.

oxygen. However, Equation 1 confirms that the yield strength of material at the joint centreline has a strong influence on the tensile residual stress acting at the periphery of ceramic/metal joints. The highest joint centreline hardness occurred in NiCrB-containing joints (see Table I). Assuming a general relation between the hardness and strength of material at the joint centreline, the magnitude of the tensile residual stresses acting at the periphery of Al_2O_3/AISI 304 stainless steel joints will be much higher when NiCrB interlayers are applied. Consequently, the lower strength of Al_2O_3/AISI 304 stainless steel joints produced using NiCrB interlayers may be partly explained by this factor.

3.6.3. Effect of heat treatment

Fig. 7 shows the influence of holding time at 200 °C on the shear strength of Al_2O_3/AISI 304 stainless steel joints TLIM bonded at 350 °C using $Cu_{50}Ti_{50}$ and NiCrB interlayers. Heat treatment markedly increased the shear strength of joints produced using NiCrB interlayers. However, there was only a small effect of heat treatment on the shear strength of joints made using $Cu_{50}Ti_{50}$ interlayer material.

When an NiCrB interlayer was employed, heat treatment almost doubled the width of the reaction layer

formed at the ceramic/filler metal interface (from 0.8 μm to 1.5 μm). In contrast, when a $Cu_{50}Ti_{50}$ interlayer was applied, the reaction layer width was only marginally altered (it increased from 1.5 μm to 1.7 μm). Also, heat treatment had no observable effect on the hardness (strength) of material at the joint centreline (see Table I). With this in mind, the substantial strength improvement in the NiCrB-containing joints may be associated with the marked increase in reaction layer width and with improved chemical bonding between the Al_2O_3 ceramic and the chromium oxide-rich reaction layer. Because the reaction layer width was not markedly altered in $Cu_{50}Ti_{50}$-containing joints, this may account for the limited improvement in joint shear strength properties following heat-treatment.

4. Conclusions

TLIM bonding allows the continuous replenishment of the active solute which is consumed by the chemical reaction at the ceramic/filler metal interface. This is achieved by applying a sandwich of filler materials comprising tin-based filler metal and amorphous $Cu_{50}Ti_{50}$ or NiCrB interlayers at the joint interface. An investigation of Al_2O_3/AISI 304 stainless steel joints produced using TLIM bonding produced the following results.

1. The highest joint shear strength properties were produced during TLIM bonding at 500 °C. Bonding at higher temperatures produced lower strength joints because thick reaction layers containing voids and cracks were formed at the ceramic/filler metal interface. Also, higher bonding temperatures increased the tensile residual stress generated at the periphery of Al_2O_3/AISI 304 stainless steel joints.

2. TLIM-bonded joints made using amorphous $Cu_{50}Ti_{50}$ interlayers had the highest shear strength properties. The shear strength of joints produced containing NiCrB interlayers markedly increased following heat treatment at 200 °C for 1.5 h. However, heat treatment had little influence on the shear strength of joints produced using $Cu_{50}Ti_{50}$ interlayers.

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