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The effects of metal coating on the diffusion bonding in Al_2O_3/ Inconel 600 and the modulus of rupture strength of alumina

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Alumina with a sputter-deposited metal film was diffusion bonded to Inconel 600. A higher bonding strength and lower joining temperature were obtained with titanium coating compared to that for the non-coated sample. The improved joining behaviour was attributed to an enhanced interface reaction and reduction in the thermal stress. Also, the effect of various coatings of 3 μm thickness on the mechanical property of alumina after heat treatment at 1000 °C for 30 min under 10^{-6} torr vacuum was evaluated in terms of modulus of rupture (MOR) using a Weibull plot. While the Cu coating did not change MOR strength of alumina, the reactive Ti and Zr metal coatings caused a noticeable reduction in averaged MOR strength. The effect of co-sputtering of Ti–Cu, and bilayer coatings of Cu/Ti and Ti/Cu was also investigated.

1. Introduction

A wide variety of techniques have been employed in ceramic-to-metal joining. With active brazing, utilizing filler metals containing active elements, such as Ti and Zr, a strong joint can be achieved associated with the redox reaction at the interface [1]. But the use of brazed joints is limited to low operating temperatures because of their low melting points and poor oxidation resistance of brazing alloys [2]. This barrier has been cleared with the solid-state diffusion bonding process. Diffusion bonding is the only way known to preserve the properties inherent in monolithic materials in both metal-to-metal and ceramic joints. The advantage over brazing is that alloys with comparatively low melting temperatures do not have to be used as fillers, and hence the inherent upper temperature for the use of diffusion-bonded joints in service is relatively high. Numerous applications in high temperatures and corrosive environments, e.g. in engine components and Na–S battery cells, have been reported where diffusion bonding has been used successfully [3]. On the other hand, diffusion bonding requires a substantially longer joining time and higher bonding temperatures. These problems should be overcome by a suitable process method. It has been known that metallization with reactive metal and then brazing with conventional brazing alloys which do not have active elements in their composition permits a strong joint due to the increased wetting and reactivity [4].

Thus it is expected that a reactive metal coating on alumina ceramic part prior to a conventional diffusion bonding can improve the bonding behaviour. Despite the relatively common usage of active metal coating in the brazing process, little has been reported about the active diffusion bonding process using active metal metallization [5]. Therefore, in this paper a reactive metal, such as titanium, was coated onto alumina ceramic to investigate the effect of such a metallization on the solid state diffusion bonding process between Inconel 600 metal and alumina ceramic. For a strong metal/ceramic joint, most work has been concentrated on the joint strength and interface reaction. Little was known about the effect of the coated metal/ceramic interactions on the mechanical properties of ceramic itself. Recently Kang *et al.* [6, 7] demonstrated that strong interactions between coatings and ceramic materials such as Si_3N_4 and Al_2O_3 could reduce the strength of the ceramics themselves. However a general understanding is still lacking in this field. Furthermore, their works were focused on a single coating layer. Many applications of ceramics, nowadays, e.g. packaging in microelectronic devices and composite materials, frequently require multiple coatings with metals [8]. Therefore in the present study bilayer coatings, in addition to a single reactive metal coatings, onto alumina ceramic substrate were also prepared to elucidate the effect of these coatings on the modulus of rupture (MOR) strength of alumina itself.

2. Experimental procedure

The materials used in the diffusion bonding were 99% alumina ceramics (10 mm × 10 mm × 5 mm) and Inconel 600 metal (chemical composition: 73% Ni, 16% Cr, 7% Fe) having a dimension of 10 mm diameter and 5 mm height. Alumina sheet (96 % purity) was also cut and polished into bars of 25 mm ×

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5 mm × 0.6 mm for MOR test specimens. The coatings of Ti and Zr reactive metals and non-reactive Cu metal were conducted on the polished and cleaned alumina faces using a d.c. magnetron sputter coater having two targets. Additionally Ti–Cu co-sputtered coating and bilayer coatings of Ni/Ti, Ti/Cu and Cu/Ti were made. The specimens to be joined were pre-assembled and held in a graphite mould which was heated up to 1100 °C for 30 min in a vacuum of 10^{-5} torr and loaded at 25 MPa. Fracture shear strength of diffusion bonded specimens was measured with a compressive strength testing machine using self-made attachment jigs. The coated MOR bars were exposed to 1000 °C for 30 min under 10^{-6} torr. Then MOR bars were subjected to a three-point bend test at room temperature with the coated side in tension. In order to characterize the fracture surface and interface reaction of coated samples, a scanning electron microscope (SEM) equipped with an energy dispersive X-ray analysis (EDX) facility and Vicker's hardness test were used. Additionally, X-ray diffraction (XRD) analysis was used to examine the reaction products.

3. Results

Fig. 1 shows the bonding force versus temperature for diffusion bonded samples. The direct diffusion bonding of Al_2O_3 to Inconel 600 was not achieved at 1050 °C. At a slightly higher temperature of 1100 °C, bonding occurred for the uncoated sample but it had a very small bonding force of 16 kg. Sputter coating of Ti onto Al_2O_3 was used to modify the ceramic surface and then a conventional diffusion bonding process was employed. With a Ti-metallization of 3 μm thickness, bonding occurred at the lower temperature of 1000 °C which was 100 °C below that for the non-coated conventional diffusion bonding temperature of 1100 °C. In addition to this, the Ti-coated samples gave higher bonding forces compared to that of the non-coated one. Furthermore a diffusion bonded sample, subjected to 20 thermal cycles between 400 and 25 °C holding at each temperature for 10 min, did not fail during the thermal shock test. Although the bonding force was decreased to 17 kg after this thermal cycle, compared to 58 kg bonding force for the as-bonded specimen, the diffusion bond after Ti-metallization had a good resistance to thermal shock. It has been recognized that active brazing materials containing active metals, such as Ti or Zr elements, enhance the wetting and bonding strength. Also metallization of oxide ceramics followed by brazing with non-active brazing filler metals has been established for several decades [4]. These known facts are well correlated to the results of higher bonding force and lower bonding temperature with the Ti-metallized active diffusion bonding process employed in this experiment. The bonding strength initially increased with temperature and then decreased at a higher temperature. Although it had a maximum bonding force at 1050 °C with Ti-metallization, its bonding force of 6 MPa is still too low a value for some applications. It is noteworthy that a bilayer coating of Ti followed by Ni onto Al_2O_3 does not give bonding to Inconel 600 metal at 1000 °C. This suggests that the second layer of Ni-coating reduced the interfacial reaction between Ti and Inconel 600 at this temperature.

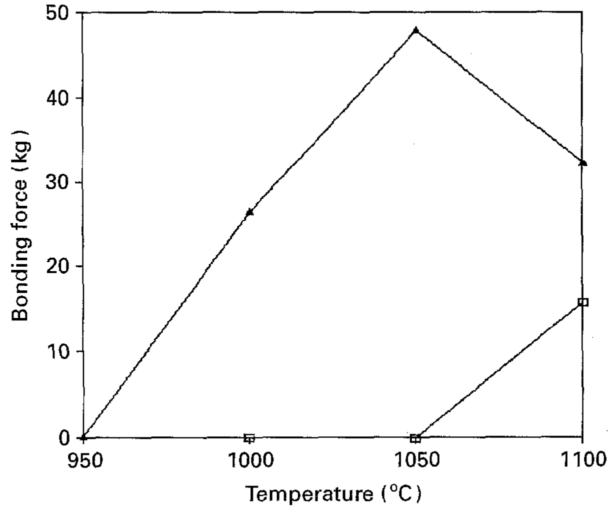

Figure 1 The change of bonding force with joining temperature for alumina/Inconel 600 (△: Ti-coated diffusion bonded, □: uncoated direct diffusion bonded).

The micrograph and titanium-line profile across the interface are shown in Fig. 2 for a sample, diffusion-bonded with 3 μm thick Ti-metallization at 1000 °C for 30 min at 10^{-5} torr. This photograph shows a tightly bonded interface and the growth of two continuous distinct layers at the Ti/Inconel interface. The titanium-line scan shows the Ti level on the Inconel metal side is slightly higher than that in alumina. This illustrates that the metallized Ti element diffuses

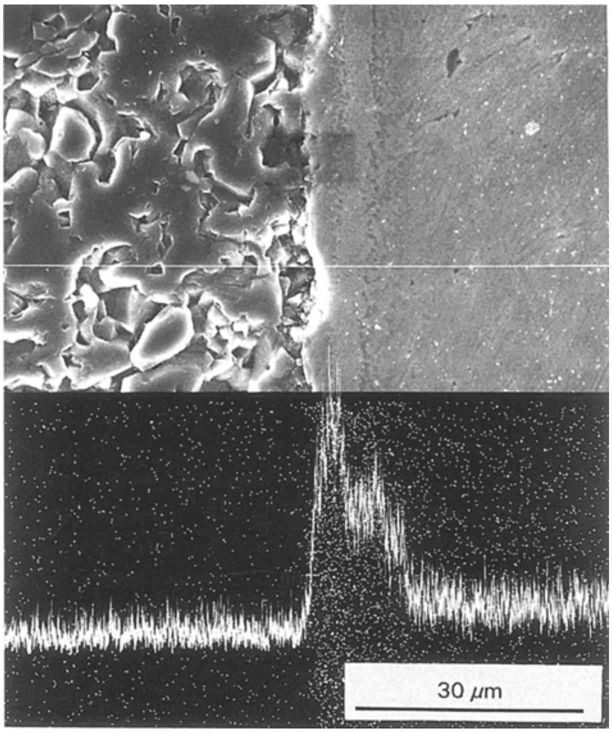

Figure 2 The SEM micrograph and titanium line profile at the interface for diffusion bonded specimen with Ti-coating. Left side is alumina, right part is Inconel 600 metal.

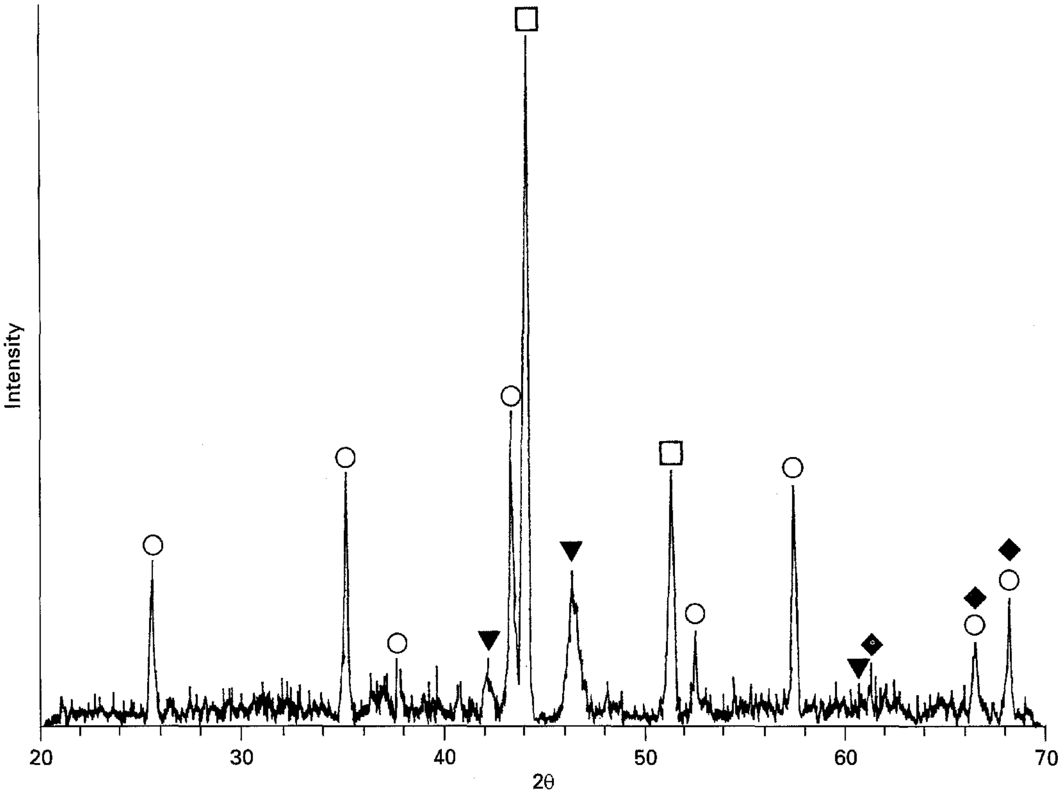

Figure 3 XRD spectrum at the reaction layer for Inconel/Ti-coated alumina. Diffusion bonded at 1000 °C for 30 min in 10^{-5} torr. Key: ○ Al_2O_3; □ Inconel 600; ▼ Ni_3Ti; ◆ Ti_2Ni.

into the Inconel during the bonding process. The step of Ti-line scan and Ni-line scan (not shown here) at the interface clearly indicates that these distinct layers are reaction products between Ti and Inconel 600. The chemical analysis on the first layer with EDX is found to be 58% Ti, 29% Al, 4% Cr, 2% Si in atomic per cent. Excluding the other elements, the atomic concentration ratio of Ti/Ni is 2, which corresponds to the intermetallic compound of Ti_2Ni. The chemical composition for the second layer is 68 % Ni, 28% Ti, 2% Al, 1% Si. The atomic concentration ratio of Ni/Ti is found to be 2.4 which may correspond to $TiNi_3$ intermetallic compound.

To identify these phases glancing angle XRD was used after removing the Inconel metal part by cutting and chemical etching from the bonded specimen. Fig. 3 shows the XRD pattern for this sample. The reaction products of Ni_3Ti and Ti_2Ni were found. In contrast Hinotani and Ohmori [9] found three intermetallic compounds shown in the Ti–Ni binary phase diagram from the Ti/Ni diffusion couple bonded at 850 °C for 60 min. The absence of one of the three phases is probably due to its being too thin. The decrease in bonding strength at a high bonding temperature greater than 1050 °C shown in Fig. 1 might be associated with the formation of thick intermetallic compounds at this higher temperature.

Fig. 4 shows the Vickers hardness as a function of distance from the interface under the experimental condition of 100 g for 12 s. The hardness decreases rapidly to the normal value for Inconel metal with distance, which again shows the presence of intermetallic compound reaction layers. In addition to this, a higher tensile residual stress within the Ti-film and/or Inconel part may give such a high hardness value in this region.

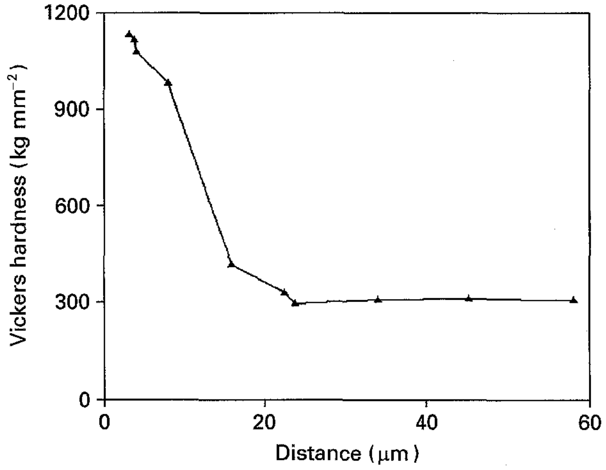

Figure 4 The change of Vickers hardness with distance from alumina. Diffusion bonding at 1000 °C for 30 min in 10^{-5} torr after 3 μm Ti-coating.

All the diffusion bonded samples failed in Al_2O_3 ceramic part after a shear test at room temperature. This result indicated that a large residual stress had developed in the joint. Fig. 5 shows the fracture surface of a broken specimen. The bright (lower) block is Inconel 600 metal, the upper (dark) block is Al_2O_3 ceramic. The bonding strength of the ceramic/metal joint is well known to have decreased with the residual stresses that were generated during cooling after joining due to thermal contraction mismatch between both materials. The thermal stress can be simply

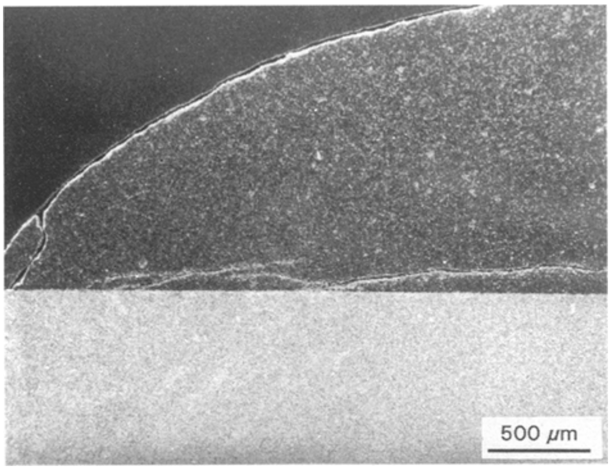

Figure 5 SEM micrograph for the cross-section of diffusion bonded sample after shear test. Upper dark part is alumina and lower white part is Inconel 600.

evaluated from the mismatch in coefficient of thermal expansion by [10]

$$\sigma_i = -\sigma_j = \frac{E_i E_j}{E_i + E_j}(\alpha_i - \alpha_j)\Delta T$$

where E is elastic modulus, α is the thermal expansion coefficient, and i and j represent the materials being bonded. Substituting the suitable values [11] $E(Al_2O_3) = 330$ GPa, E(Inconel) = 214 GPa, $\alpha(Al_2O_3) = 7.8 \times 10^{-6}$, α(Inconel 600) = 12.1×10^{-6} and $\Delta T = 1000\,^{\circ}C$ into this equation gave a compressive stress around 560 MPa in alumina at the central contact area. This thermal stress may exceed the strength of alumina and thus produced cracks as seen in Fig. 5. But this compressive stress suppresses crack opening in the ceramic part. However at the edge of the joint, high tensile stress was present in the ceramic [12]. In this case, crack formation and detrimental crack growths are likely to start at the edge of Al_2O_3 ceramic part. Therefore the fracture path should develop as shown in Fig. 5. With the titanium metallization ($E = 106$ GPa, $\alpha = 8.9 \times 10^{-6}$), the thermal stress in the central alumina is calculated to be 90 MPa, which is much lower than the 560 MPa obtained for the non-coated diffusion bonded sample. Thus, it resulted in a higher bonding strength for the Ti-coated diffusion bonded samples as shown in Fig. 1. This illustrates that titanium metallization is an important step in diffusion bonding of Al_2O_3 and Inconel 600.

The influence of Ti-coating thickness on bonding strength is shown in Fig. 6 for diffusion bonding performed at 1000 °C for 30 min. The bonding force decreases with increasing Ti-thickness except for a very thin film of 0.7 μm, in which case the whole alumina surface was not covered by the Ti-coating layer because of the surface roughness of the alumina. Thus a direct contact was made between Al_2O_3 and Inconel instead of Ti and Inconel, producing no bonding at the interface, which was similar to that of the non-coated diffusion bonded sample. In an adhesive joint prepared using alumina adherend and glass adhesive, it was reported that the magnitude of stress increased with increasing adhesive thickness and the stresses were concentrated at the perimeter [13]. Thus the reduction in joint forces with Ti-coating thickness of more than 3 μm can be interpreted in terms of this increased residual stress and higher stress concentration at the perimeter that caused a joint failure in the alumina as shown in Fig. 5. Another possible interpretation could be made on the basis of the interaction at the Ti/Al_2O_3 interface. It will be shown later that the fracture strength of alumina with a reactive metal coating is decreased. Also it had been claimed that the MOR strength was decreased with increasing coating thickness [6]. Therefore the detrimental effect of interaction at the Ti/Al_2O_3 interface was thought to be the other reason for the reduction in bonding force with increasing Ti-coating thickness.

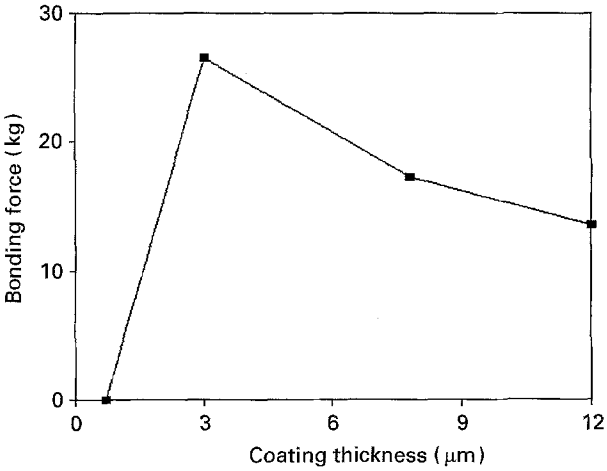

Figure 6 The change of bonding force with Ti-coating thickness.

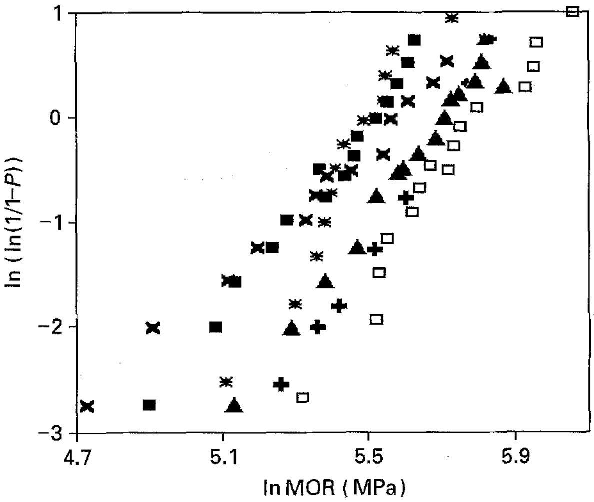

Figure 7 Weibull plots of MOR strength of alumina with various coatings. Key: ■ Ti; * Zr; × Ti–Cu; ▲ Cu/Ti; + Ti/Cu; □ uncoated.

In order to investigate the effect of active metal coatings on the fracture strength of alumina, the MOR strength of alumina was measured by a three-point bend test. Fig. 7 shows the Weibull plot of alumina MOR bars with various coatings of 3 μm thickness after heat treatments at 1000 °C for 30 min in 10^{-6} torr. The strength of uncoated alumina bars which were heat treated under the same conditions as the coated bar was also included for the comparison. The active metal coatings of Ti and Zr caused a noticeable reduction in MOR strength of the bars, while the inactive Cu-metal coating did not change the MOR strength of alumina (not plotted in this figure for clarity). The average in MOR strength was decreased to 220 MPa (29% reduction) for Ti-coating and 233 MPa (25% reduction) for Zr-coating compared with 310 MPa for uncoated alumina bars. This indicates the reduction in MOR strength was directly related to the interaction between reactive coating materials and the ceramic substrate. Also MOR tests for a single layer of co-sputtered Ti–Cu, and bilayers of Cu/Ti and Ti/Cu coatings with a total 3 μm thickness were conducted with the same heat treatment. The average in MOR strength was found to be 243, 276 and 286 MPa for co-sputtered Ti–Cu, Cu/Ti/Al_2O_3 and Ti/Cu/Al_2O_3, respectively. The fracture surface of the Ti-coated bar shown in Fig. 8 illustrates that the titanium-coating adhered very well to the alumina. However, it shows a large number of surface cracks present on the top surface of the coating after a bending test. Also fine microcracks were observed within the Ti-coating film.

Fig. 9 shows X-ray diffraction profiles for Ti-coated alumina bars before and after heat treatment at 1000°C for 30 min in 10^{-6} torr vacuum. The profile of the as-coated alumina specimen shows only their diffraction peaks. But the spectra of the heat-treated sample show the diffraction peaks of reaction products corresponding to TiO and Ti_3Al. This result coincided with the studies of Tressler *et al.* [14]. Also

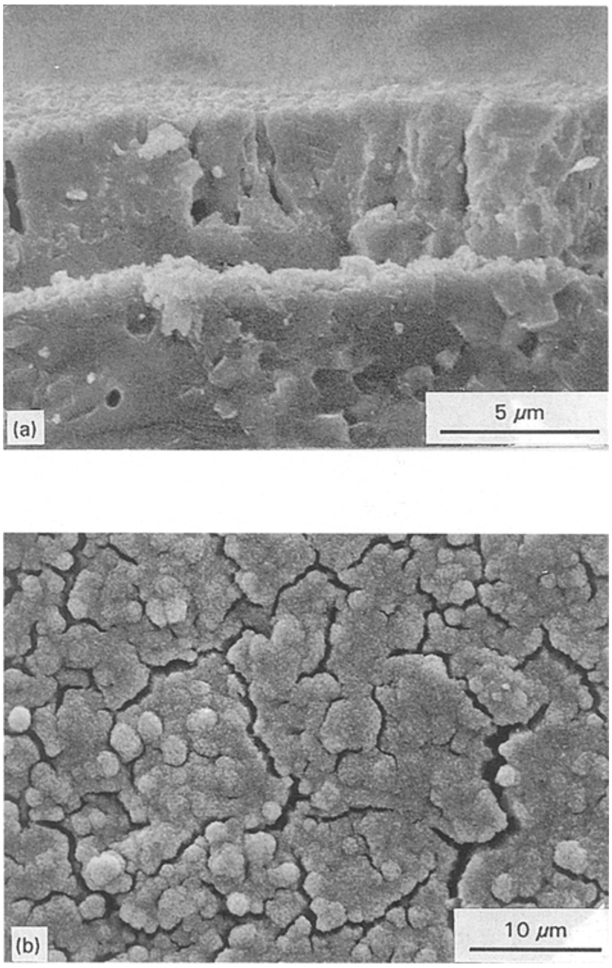

Figure 8 SEM micrographs of Ti-coated MOR bar for (a) cross-section and (b) top surface of coating.

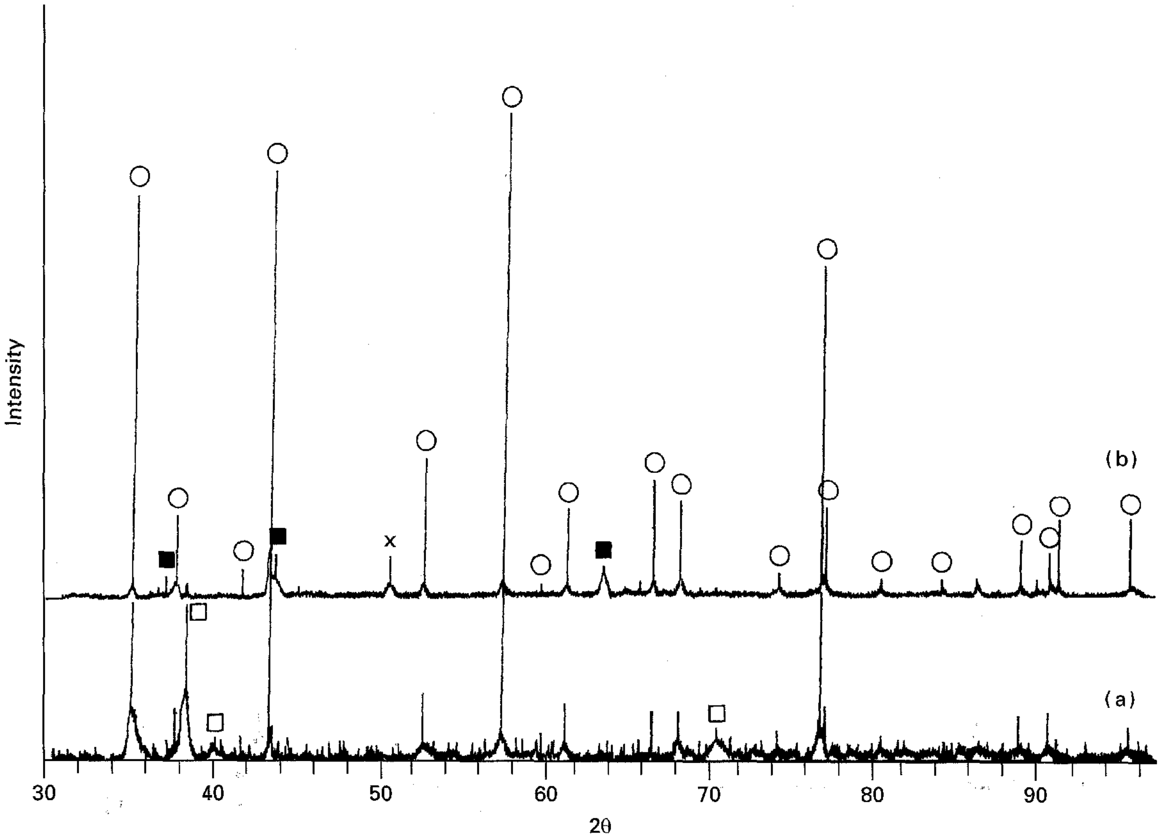

Figure 9 XRD spectra of Ti-coated alumina for (a) as-coated and (b) after vacuum heat treatment. Key: ● Al_2O_3; □ Ti; ■ TiO; × Ti_3Al.

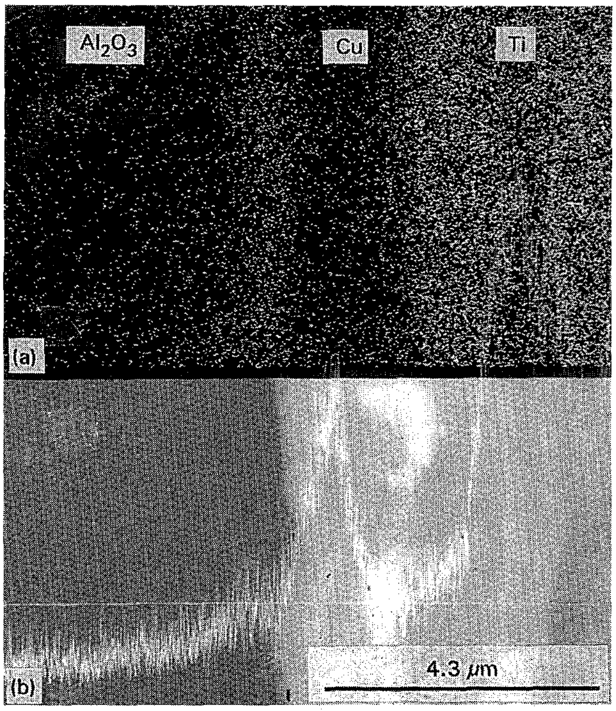

Figure 10 (a) Ti-mapping and (b) Ti-line profile showing Ti-segregation into Al_2O_3 with heating for a bilayer coating of $Ti/Cu/Al_2O_3$.

thermodynamic calculations showed that the Ti reaction with alumina produces TiO and Ti_3Al [15, 16]. The TiO phase was known to be electrically conductive and metallic in nature, and thereby serves as a transition layer between the nonconductive ceramic and the conductive metal of the brazing filler metals [17]. That is, the TiO layer serves as a wettable surface that promotes bonding in the brazing process. Taking account of this fact, the higher bonding force and lower bonding temperature with diffusion bonding after Ti-coating shown in Fig. 1 could be easily understood. This implies that TiO is also an important intermediate phase in the solid-state diffusion bonding between metal and alumina ceramic. For the Zr-coated alumina bar sample after the same heat treatment, the reaction products of ZrO_2 and Zr_3Al_2 were found from the glancing angle XRD study. This indicated that alumina was dissociated by zirconium, and the liberated aluminium atoms reacted with Zr atoms and became stabilized as Zr–Al intermetallic compound.

In spite of the beneficial effect of the titanium coating on the diffusion bonding, MOR strength of alumina with a Ti-coating decreased as shown in Fig. 7. Recently Sung and Ostreicher [18] reported that the reaction of titanium with an amorphous grain boundary phase and an alumina substrate produced Ti_3Al at the interface. Kang and Selverian [7] claimed that the reduction in MOR strength of alumina coated with Ti was attributed to strain due to the thermal expansion mismatch and brittle nature of Ti_3Al. They showed that the Ti_3Al layer cracked at room temperature. This can explain the presence of surface cracks shown in Fig. 8b. Considering the strong adhesion at the Ti/Al_2O_3 interface associated with the TiO phase, these cracks can easily propagate into the alumina substrate which in turn caused the reduction in MOR strength with Ti coating as shown in Fig. 7.

In the case of co-sputtering of Ti and Cu, the titanium element had a good bonding character onto alumina substrate while the areas contacting with elemental copper were expected to debond with an

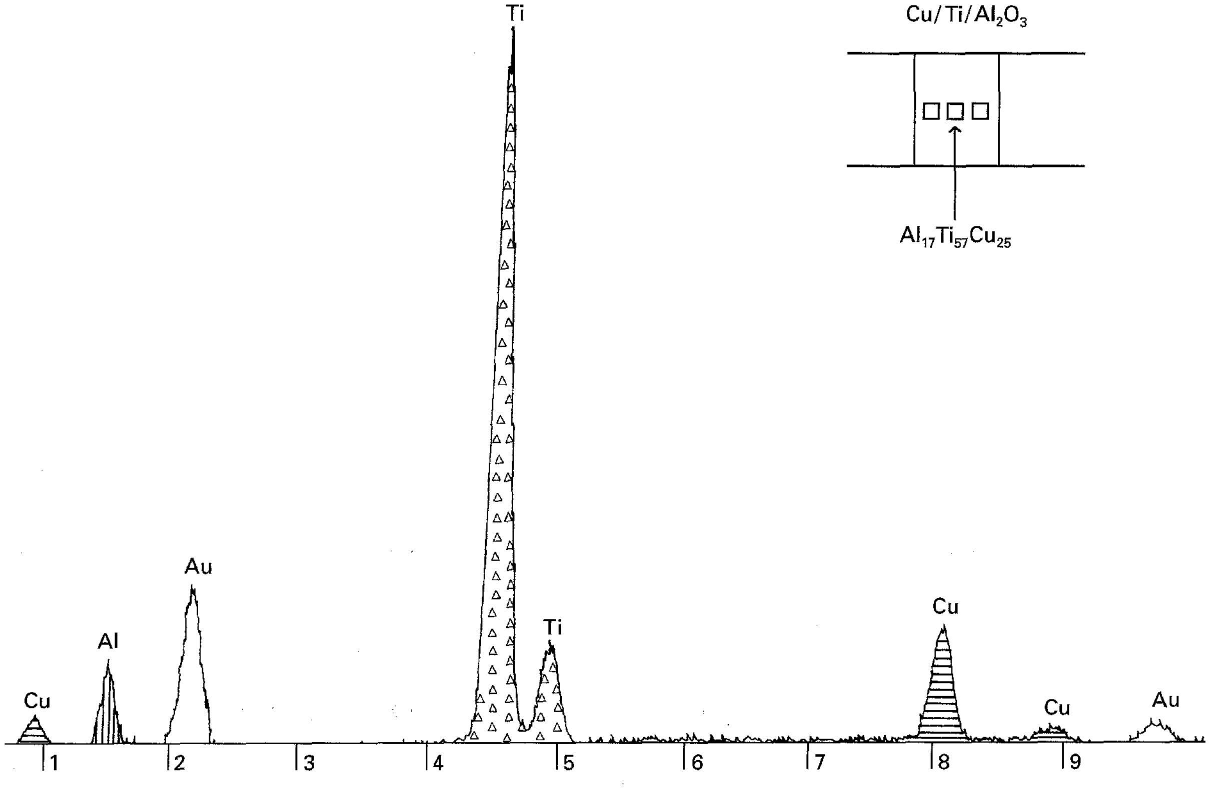

Figure 11 EDX spectrum at the centre of titanium coating layer for $Cu/Ti/Al_2O_3$.

associated high wetting angle [19]. In other words, the non-uniformities of reaction and bonding at the interface caused the reduction in MOR strength and Weibull modulus as shown in Fig. 7. It is interesting to find that the bilayer coated specimens of $Ti/Cu/Al_2O_3$ also decreased the MOR strength of alumina even when the non-reacting copper coating was adjacent to alumina as in this case. To clarify this behaviour, X-ray dot mapping and line scans of titanium across the interface after heat treatment were performed and are shown in Fig. 10. The titanium enriched region is adjacent to the alumina. This titanium segregation at the interface is very similar to the finding in the brazing process with Ti-containing active brazing filler metals [20]. The segregated titanium might have reacted with the alumina substrate and then caused a decrease in MOR strength of alumina just as the single Ti-coating did, as mentioned above.

Fig. 11 is a EDX spectrum at the centre of Ti-coating film for the double coated specimen of $Cu/Ti/Al_2O_3$ after heat treatment. Aluminium and copper diffused into this titanium layer. The chemical composition at this point was found to be 58% Ti, 25% Cu, 17% Al in atomic per cent excluding the Au peak which arises from Au coating for SEM observation. It was apparent that Cu atoms diffused from the Cu-coating layer during heat treatment. It has been reported that alumina is reduced by the titanium [16]. The ratio of Ti/Al is 3.4 which nearly corresponds to Ti_3Al compound. This finding is in agreement with the earlier XRD observation (Fig. 9).

4. Conclusions

1. In diffusion bonding between alumina and Inconel 600, a higher bonding strength and a lower joining temperature was obtained with a Ti-metallization of 3 μm thickness compared to that of non-coated samples. All the diffusion bonded samples failed in alumina after shear test. The improved bonding behaviour was attributed to the decrease in the thermal stress by employing Ti-coating. The formation of reaction products Ti_2Ni and Ni_3Ti at the Ti/Inconel interface led to a higher Vickers hardness.

2. The reactive Ti and Zr metal coating with 3 μm thickness caused a noticeable decrease in the average MOR strength of alumina after heat treatment due to the formation of TiO and Ti_3Al phases at the Ti/Al_2O_3 interface. While the single Cu-coating did not change MOR strength, the bilayer coating of $Ti/Cu/Al_2O_3$ reduced the MOR strength of alumina which was associated with the titanium segregation onto the alumina side. It was found that single coatings of Ti, Zr and Ti–Cu co-sputtering, and bilayer coatings of $Cu/Ti/Al_2O_3$ and $Ti/Cu/Al_2O_3$ reduced MOR strength of alumina in the order listed.

From these experimental results it was found that the role of Ti-coating on alumina is controversial. In this case, diffusion bonding using metallization with Ti gave a beneficial effect in the bonding character. However, the reactive metal coating decreased the mechanical property of alumina. Therefore a compromise should be considered for employing metal coatings on ceramics.

Acknowledgements

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