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Bond strength and interfacial structure of silicon nitride joints brazed with aluminium–silicon and aluminium–magnesium alloys

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From the results of the bending strength and Weibull modulus of the joints of silicon nitride ceramics brazed using aluminium–silicon and aluminium–magnesium alloy filler metals at a temperature of 1073 K for 0.9 ksec in a vacuum of 1.3×10^{-3} Pa, silicon, especially, present in a small amount in the filler metals, was found to be effective in improving the bond strength, while magnesium in the filler metals was harmful to the joining. This can result in the formation of a thick stable alumina layer on the surfaces of the filler metals containing magnesium during brazing which prevented contact of the filler metals with the silicon nitride ceramics.

1. Introduction

Silicon nitride work pieces can be easily brazed using an aluminium filler metal at relative low temperatures such as 1073 K [1]. This joint has attractive application prospect resulting from its high bond strength, although it is limited to service only at temperatures below 573 K [2]. Many studies of brazing had been performed to elucidate the effects of brazing conditions and alloying elements in the filler metals on the bond strength [1, 3, 4]. However, because the interfacial structure, which could result in the fracture behaviour of the joint, has not been examined in detail, the factors influencing the bond strength remain unclear.

Recently, some of the present authors have paid attention to the relationship between the interfacial structure and the bond strength of the joint. When silicon nitride ceramics were brazed with pure aluminium at 1073 K in a vacuum of 10^{-3} Pa, a β′-sialon layer and a silica–alumina non-crystalline layer were known to be formed successively at the interface in order from the silicon nitride side [5]. The latter layer was found to be vital for increasing the bond strength of the joint: the thicker the layer, the higher the bond strength [6, 7]. The layer is considered to be produced by the reaction of aluminium, silicon nitride and oxygen which exists not only in the vacuum system but also in silicon nitride ceramics.

Magnesium and silicon are very important alloying elements for strengthening aluminium. On the other hand, the affinity of the elements for oxygen decreases in the order magnesium, aluminium and silicon. Therefore, the addition of either magnesium or silicon to aluminium filler metal could also change the interfacial chemistry, and hence the bond strength of the joint. In the present study, several kinds of aluminium–magnesium and aluminium–silicon binary alloys were used as filler metals to braze silicon nitride ceramics. The bending strength of the joints was measured and the faying surfaces, fracture surfaces and bond interfaces were examined by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and analytical transmission electron microscopy (AEM) in order to find the factors influencing the bond strength.

2. Experimental procedure

Pressureless sintered silicon nitride ceramics with dimensions 13 mm × 16 mm × 20 mm and with a total amount of 8 wt % Al_2O_3 and Y_2O_3 as densification additives, were supplied by Toshiba Ceramics Co. Ltd. The faying surfaces of the ceramics were ground with a diamond wheel. Six kinds of binary aluminium alloys containing 0.06, 0.33, 1.00 and 10.6 wt % silicon and 0.11 and 0.50 wt % magnesium were used as filler metals and were ground to 0.2 to 0.3 mm thick. The silicon nitride ceramics and the filler metals were cleaned in acetone using an ultrasonic cleaner and then each filler metal was sandwiched between two silicon nitride ceramics before brazing. The sandwich was heated to a temperature of 1073 K in 3.6 ksec, and then held at that temperature for 0.9 ksec under a pressure of 0.5 MPa in a vacuum of 1.3×10^{-3} Pa to braze the ceramics. Bending-test bars with dimensions 3 mm × 4 mm × 40 mm were cut from the joints using a diamond blade and then ground with a diamond wheel. The four-point bending strength was measured with an upper span of 10 mm, a lower span of 30 mm and a cross-head speed of 8.3 μm sec^{-1} (0.5 mm min^{-1}). The fracture surfaces of the test bars were photographed by SEM in order to measure the area fractions of the fracture surface in each of the filler metal, silicon nitride ceramics and at the interfaces. The fracture surface of the joint brazed using an Al–0.50 wt % Mg filler metal was at the bond interfaces and the filler metal side was analysed by XPS. The interfacial structure of the joints brazed with Al–0.50 wt % Mg and Al–0.33 wt % Si filler metals were examined by AEM.

3. Results and discussion

The Weibull plots of the bending strength of the joints are shown in Fig. 1. From the comparison of the plot for the joints brazed with each aluminium alloy with that brazed with pure aluminium, which has been already published [7], it is known that silicon in the filler metal improves the bond strength and the Weibull modulus of the joint. The filler metal with 0.06 wt % silicon, which is of the lowest silicon content, is the best of all the filler metals used in the present work. Magnesium in filler metals is harmful to reliable joining; the greater the amount of magnesium, the lower the bending strength and Weibull modulus of the joints.

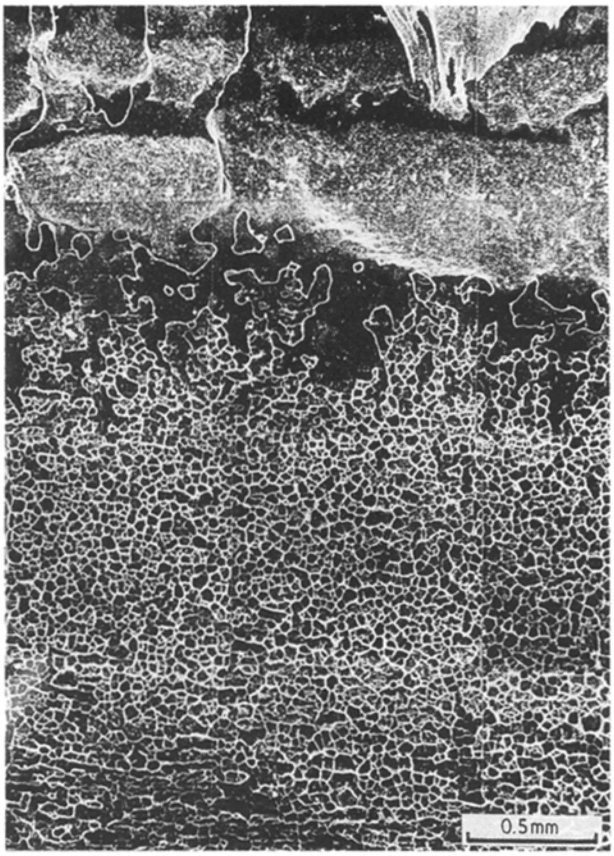

Figure 2 SEM fractograph of the joint brazed using Al–0.06 wt % Si filler metal.

Fig. 2 is a scanning electron micrograph of the fracture surface of the joint brazed using the Al–0.06 wt % Si filler metal. The lower part of the figure was under a tensile stress and the upper part under a compressive stress during the bending test. The fracture of the joint occurs in the filler metal and in the silicon nitride ceramics, but not at the interfaces. In the case of the joint brazed using the Al–0.50 wt % Mg filler metal, the fracture occurs at the interface as

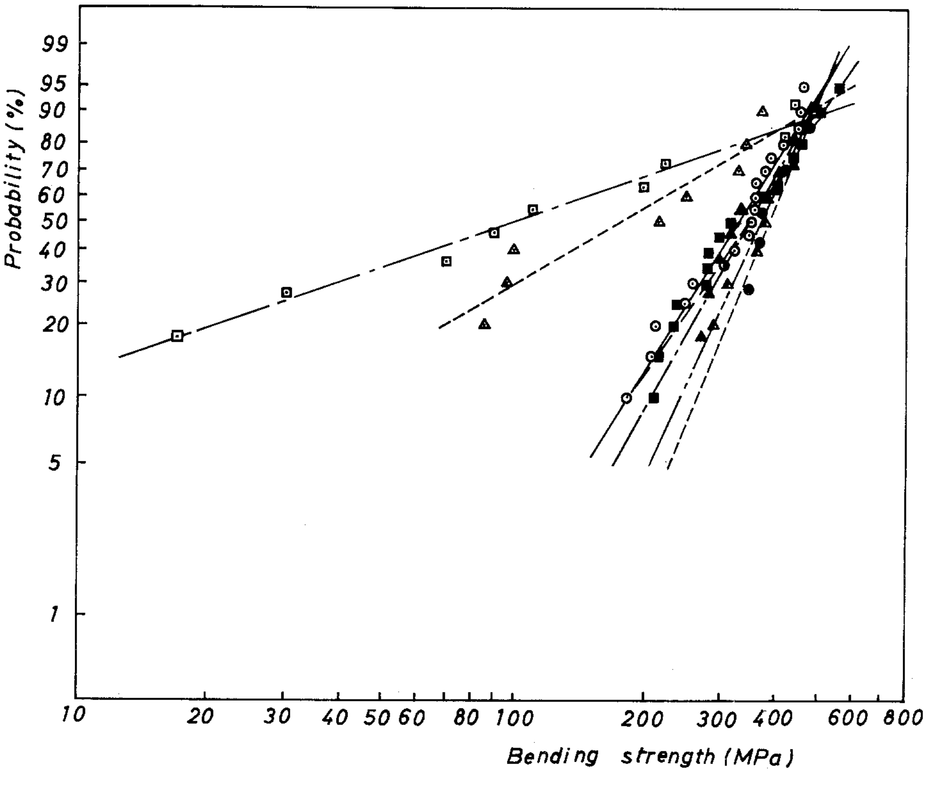

Figure 1 Weibull plots of the four-point bending strength of joints. (—○—) Al (A), (– –△– –) Al–0.11% Mg (M_1), (—□—) Al–0.50% Mg (M_2), (– –●– –) Al–0.06% Si (S_1), (– –■– –) Al–0.33% Si (S_2), (– –▲– –) Al–1.0% Si (S_3), (– – – –) Al–10.6% Si (S_4).

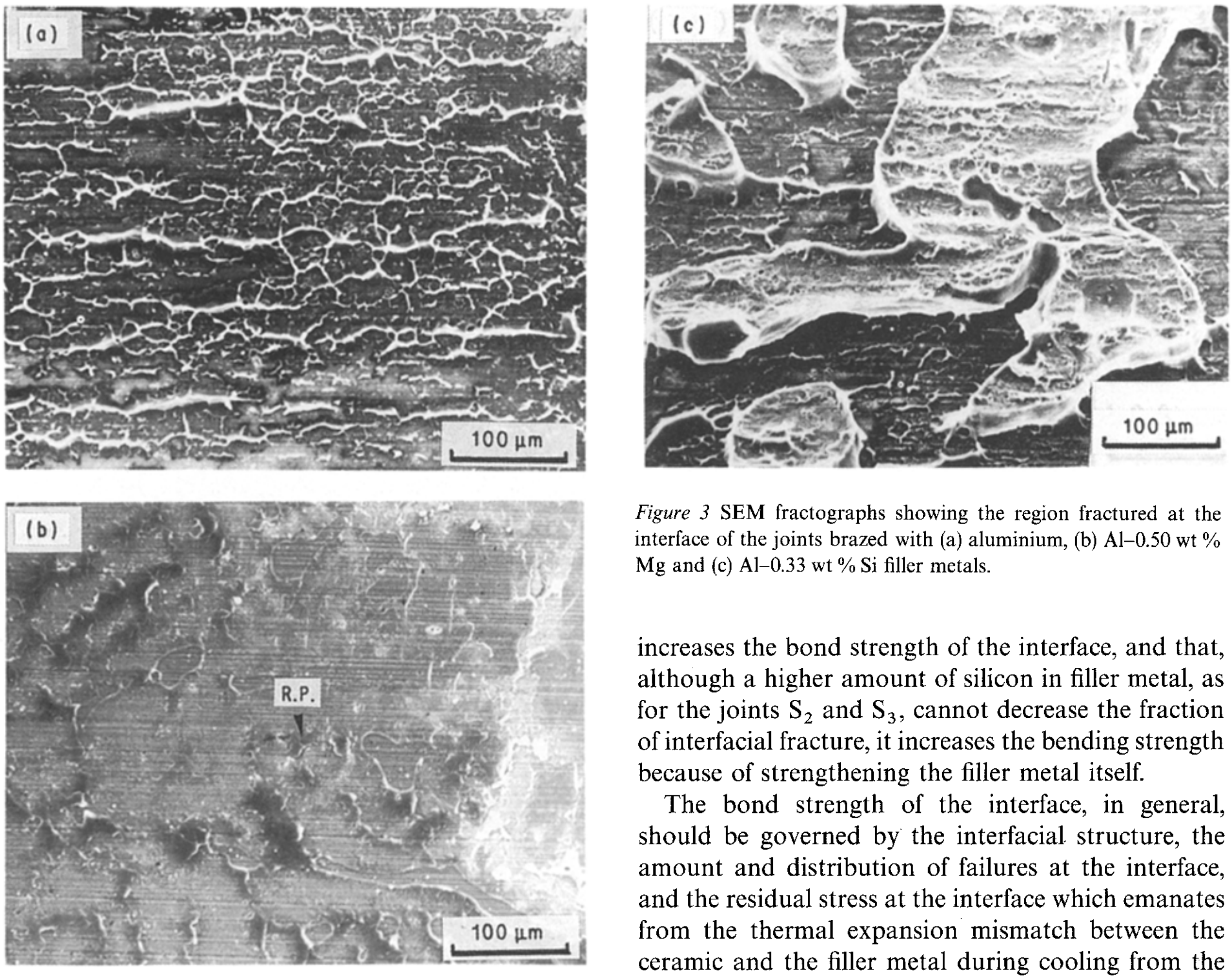

Figure 3 SEM fractographs showing the region fractured at the interface of the joints brazed with (a) aluminium, (b) Al–0.50 wt % Mg and (c) Al–0.33 wt % Si filler metals.

shown in Fig. 3b. The fracture of the other joints occurs partly at interfaces (Fig. 3) and partly in silicon nitride ceramics and filler metals.

Fig. 4 shows the relationships of the area fraction of the fracture surface at interfaces, to the Weibull modulus and mean bending strength of the joints. The Weibull modulus and the bending strength decrease linearly as the fraction of interfacial fracture increases. This evidence implies that the bending strength and Weibull modulus of the joints depend on the bond strength of the interface. From the results it is also known that a small amount of silicon in filler metal increases the bond strength of the interface, and that, although a higher amount of silicon in filler metal, as for the joints S_2 and S_3, cannot decrease the fraction of interfacial fracture, it increases the bending strength because of strengthening the filler metal itself.

The bond strength of the interface, in general, should be governed by the interfacial structure, the amount and distribution of failures at the interface, and the residual stress at the interface which emanates from the thermal expansion mismatch between the ceramic and the filler metal during cooling from the brazing temperature, and can be made to decrease by the plastic deformation of the filler metal, if the filler metal is soft.

In practical brazing, a chemical reaction occurs between the ceramic and filler metal. A proper degree of chemical reaction is usually necessary in order to obtain strong joints. In Fig. 3b, some black scars can be observed on the silicon nitride ceramic at the fracture surface of the joints brazed with aluminium–magnesium filler metals. These scars are neither silicon nitride nor aluminium from SEM observation and are considered to be some reaction products (RP). However, they were not observed at other fracture surfaces

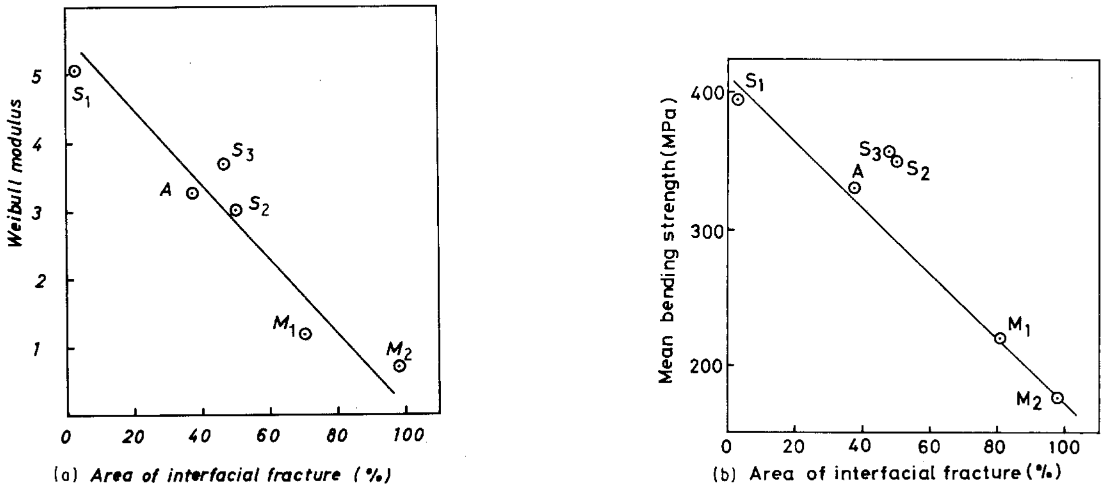

Figure 4 Relationships of the area fraction of fracture surface at the interface to (a) the Weibull modulus and (b) the mean bending strength of joints.

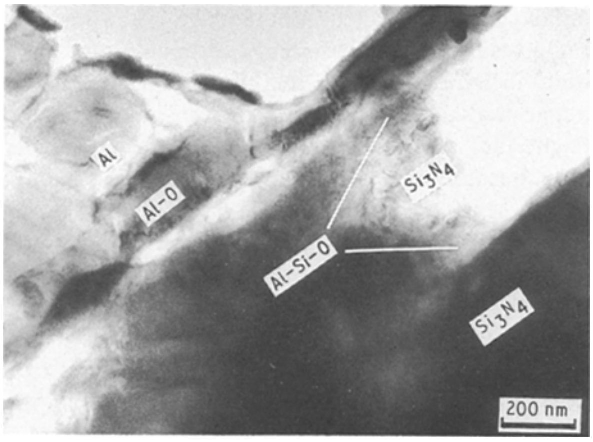

Figure 5 Transmission electron micrograph showing an interfacial area of the joint brazed with Al–0.50 wt % Mg filler metal, where two oxide reaction product layers are found at the interface.

of the joints brazed with aluminium or aluminium–silicon alloy filler metals (Fig. 3a, c).

In the previous work [7], a silica–alumina non-crystalline layer was found to be formed between pure aluminium and silicon nitride ceramic. The same oxide layer was also observed in the joint brazed with the Al–0.33 wt% Si alloy. However, it was shown that the joint brazed with the Al–0.50 wt % Mg alloy has different interfacial structures from that brazed with the aluminium–silicon alloy. From the AEM, two oxide reaction products, Al–O and Al–Si–O systems were found at the interface, as shown in Figs 5 and 6. The energy dispersive spectra (EDS), electron energy loss spectra (EELS) and the electron diffraction patterns (ED) show clearly that the reaction product of the Al–O system in contact with the filler metal is α-Al_2O_3, and another reaction product, in the Al–Si–O system, is an Al–Si spinel which has recently been found by Low and McPherson [8], both products containing a small amount of magnesium. Fig. 7 is another transmission electron micrograph showing the interface of the same joint; the EDS and ED of points A and D near the interface are shown in Fig. 8. Point A has the structure of aluminium and point D has the same structure as silicon nitride. No oxide layer, therefore, is observed at the interface, though such regions are a very few, and only the diffusion of aluminium and magnesium into the silicon nitride and of silicon into the filler metal occurs at the interface. Comparing the EDS of the interface with that of the filler metal containing 0.50 wt % Mg (Fig. 6c), it is found that magnesium concentrates at the interface.

The fracture of the same joint occurs along the interface. Fig. 9 shows the XPS spectra of the fracture surface at the filler metal side of the joint and of the centre of the filler metal in the binding energy range 40 to 100 eV. The elements of magnesium, aluminium

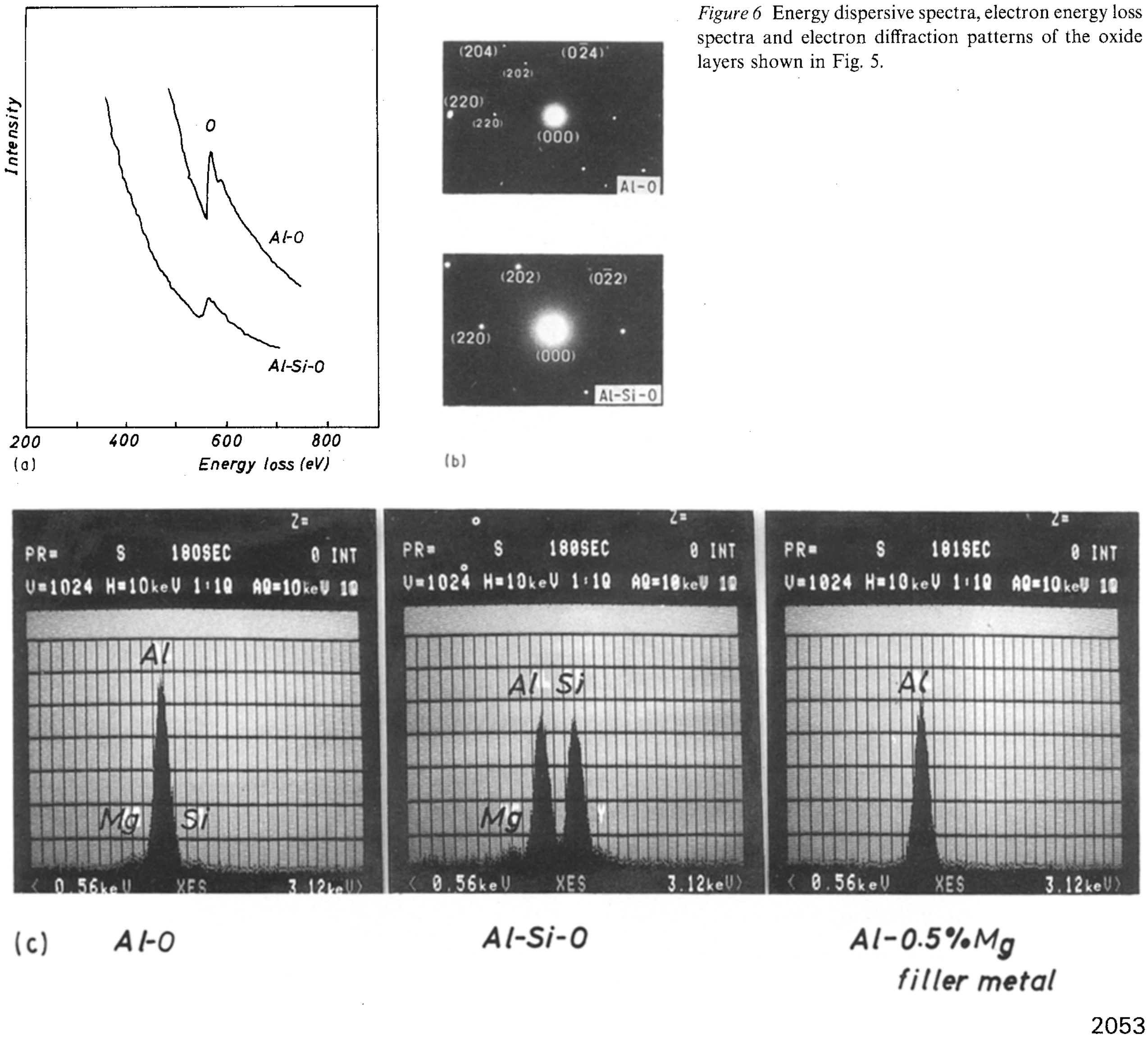

Figure 6 Energy dispersive spectra, electron energy loss spectra and electron diffraction patterns of the oxide layers shown in Fig. 5.

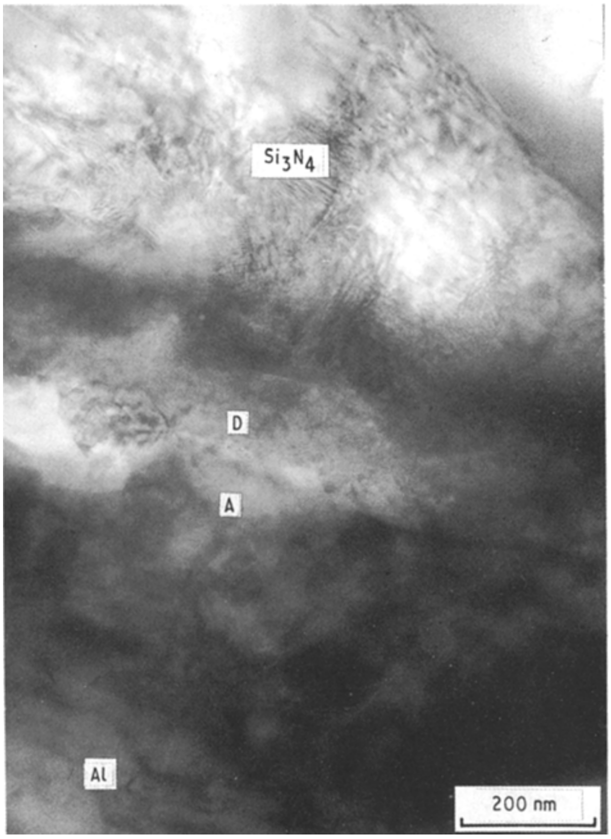

Figure 7 Transmission electron micrograph showing another interfacial area of the same joint as shown in Fig. 5.

and oxygen are detected from the XPS spectrum of the fracture surface, while the peak of magnesium is not found in the spectrum of the filler metal, because the magnesium content is low. This result confirms that magnesium concentrates at the interface. Furthermore, because no silicon is detected from the fracture surface, it is concluded that the fracture path mainly runs in the α-Al_2O_3 layer or between the reaction products of the α-Al_2O_3 and the Al–Si spinel.

The difference of the interfacial structure between the joints brazed with aluminium–silicon and aluminium–magnesium filler metals may result from the difference of the oxidation behaviour of the filler metals. In order to make this clear, small pieces of three filler metals used in the present work, Al–0.33 wt % Si, Al–1.0 wt % Si, and Al–0.50 wt % Mg, and aluminium, were heated, held and then cooled together in a graphite holder under the same condition as the brazing operation. Fig. 10a schematically shows the surface shape of the specimens after cooling in the holder and Fig. 10b shows photographs of the top views of the specimens. The top surface of each of the aluminium–silicon alloys is hemispherical and smooth, although dendrite structure is observed, while that of Al–0.50 wt % Mg alloy is irregular and rough. In the case of pure aluminium, some scars still exist on the surface, although the top surface becomes hemispherical. Because the change in the surface tension of aluminium liquid on the addition of 0.8 wt %

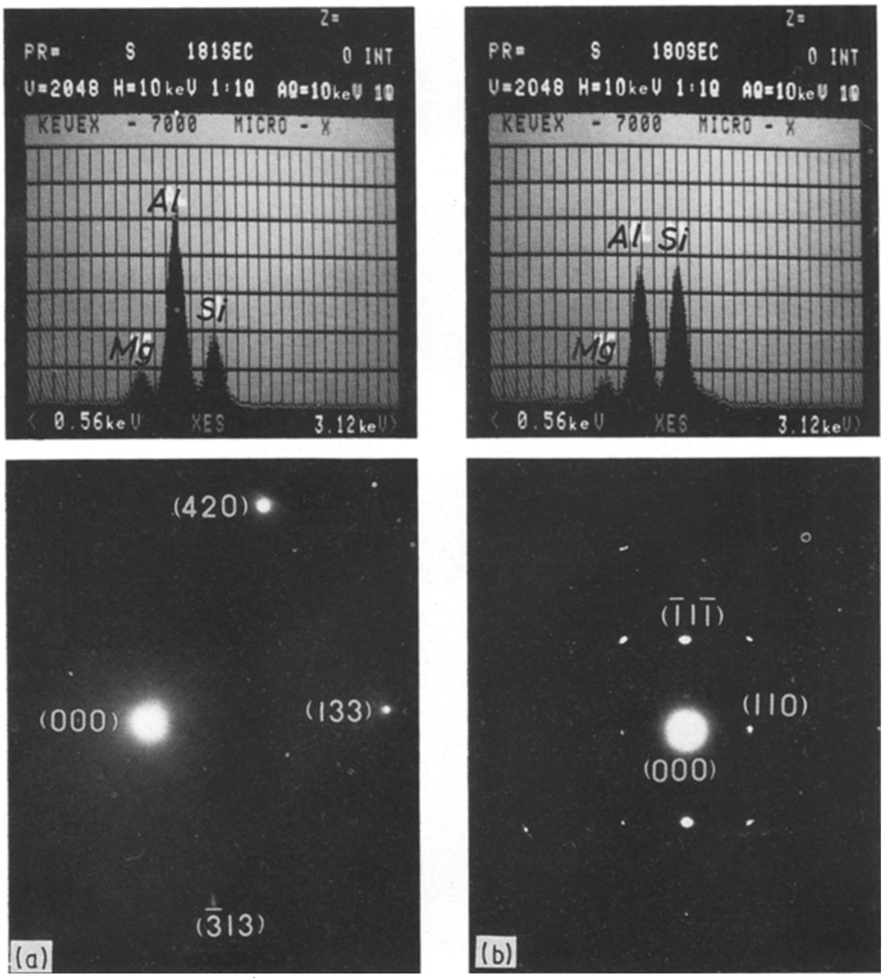

Figure 8 Energy dispersive spectra and electron diffraction patterns of points (a) A and (b) D in Fig. 7.

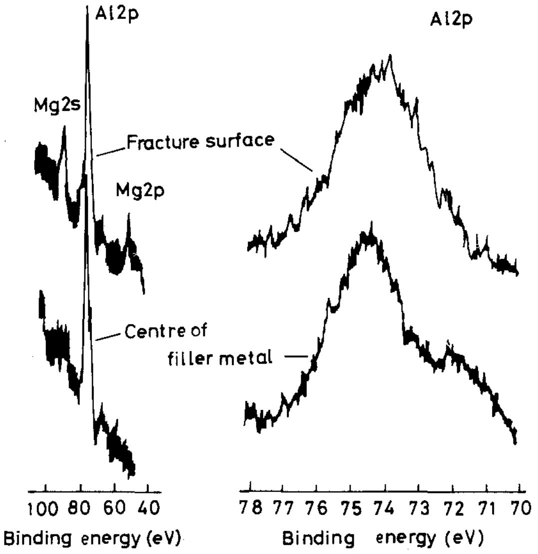

Figure 9 XPS spectra of the fracture surface at the filler metal side of the joint brazed with Al–0.5 wt % Mg filler metal, and the centre of the filler metal.

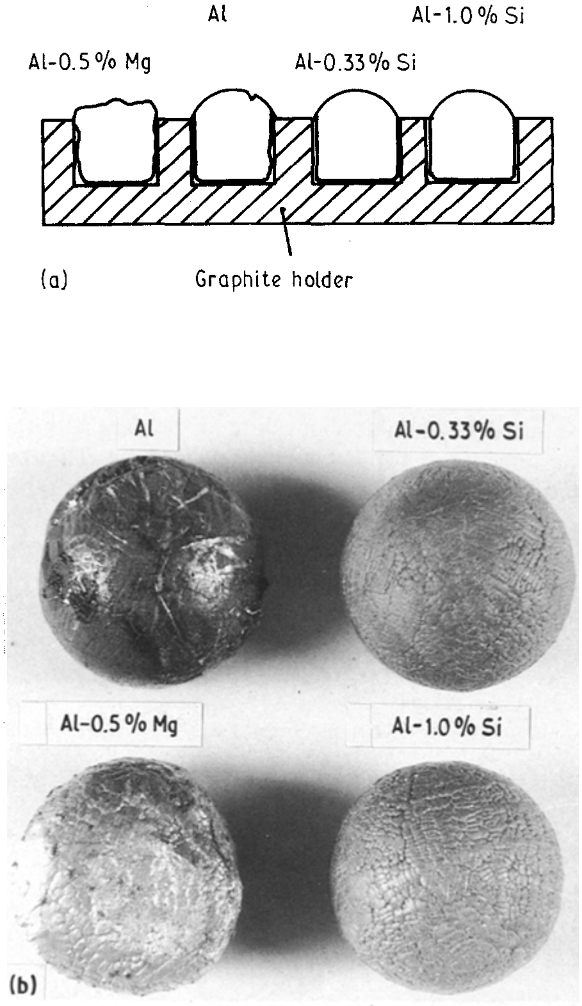

Figure 10 Appearance of some filler metal specimens after thermal treatment under the same conditions as on brazing in a graphite holder. (a) Schematic appearance, and (b) top view.

magnesium at 1073 K is less than 1%, such a difference in the surface appearance might be due to the difference in the affinities of silicon, aluminium and magnesium for oxygen and hence the difference in the thickness and stability of an aluminium oxide layer formed during heating. Fig. 11 shows scanning electron micrographs of the top surfaces of the specimens. Part of the surface of the aluminium specimen (Fig. 11a) is covered with a thick oxide layer (A) and the other part is covered with a thin one (B), where the porosity formed during solidification can be seen clearly. Meanwhile all the surfaces of aluminium–silicon alloys are covered with a thin oxide (Fig. 11b). But the surface of Al–0.50 wt % Mg alloy is covered with a very thick oxide layer (Fig. 11c). Rod-like crystals about 10 μm long and less than 1 μm diameter can be seen in the oxide layer (Fig. 11d). These crystals are considered to be the α-Al_2O_3 which was detected by AEM at the bond interface. Hehn and Fromm [9] found that the oxide layer formed at 993 K in a vacuum of 10^{-4} Pa is an amorphous one. Thus magnesium in the filler metal promotes the oxidation of aluminium and the crystallization of the oxide, but silicon prevents the oxidation of aluminium.

Low and McPherson have studied the phase transformation of Al_2O_3–SiO_2 gel during heating and found that an Al–Si spinel forms during continuous heating of the sample to the temperature range 1173 to 1243 K [8]. Thus the Al–Si spinel detected at the interface of the joint brazed with aluminium–magnesium alloy may be a more stable phase of the non-crystalline silica–alumina which was detected at the interface of the joints brazed with aluminium and aluminium–silicon alloy. Magnesium in the filler metal which concentrates at the interface during brazing may also promote the crystallization of the non-crystalline silica–alumina.

In addition to the interfacial structure, the elements in the filler metal also influence the plasticity of the filler metal. Silicon in aluminium decreases the elongation of aluminium tremendously, especially in the range up to 0.3 wt % and increases the hardness of aluminium. As a result, residual stress in the joint increases with increasing silicon content. From the fracture surface of the joint brazed with the Al–0.33 wt % Si filler metal (Fig. 3c), it is observed that the filler metal attached to silicon nitride is island-like, which means that the stress in the filler metal is high enough for secondary cracks perpendicular to the bond interface to be formed in the filler metal in addition to the main crack along the bond interface. The higher level of stress in the joint decreases the bond strength of the interface, which may be the reason why the bending strength and Weibull modulus of the joints brazed using the filler metals with higher silicon content are lower than those of the joint brazed using the filler metal of low silicon content of 0.06 wt %.

4. Conclusion

In brazing with aluminium–magnesium filler metals, magnesium concentrates on the surface of the filler metal and promotes the surface oxidation of the metal. A thick alumina layer is formed on the surface of the filler metal. This layer obstructs the reaction of alumi-

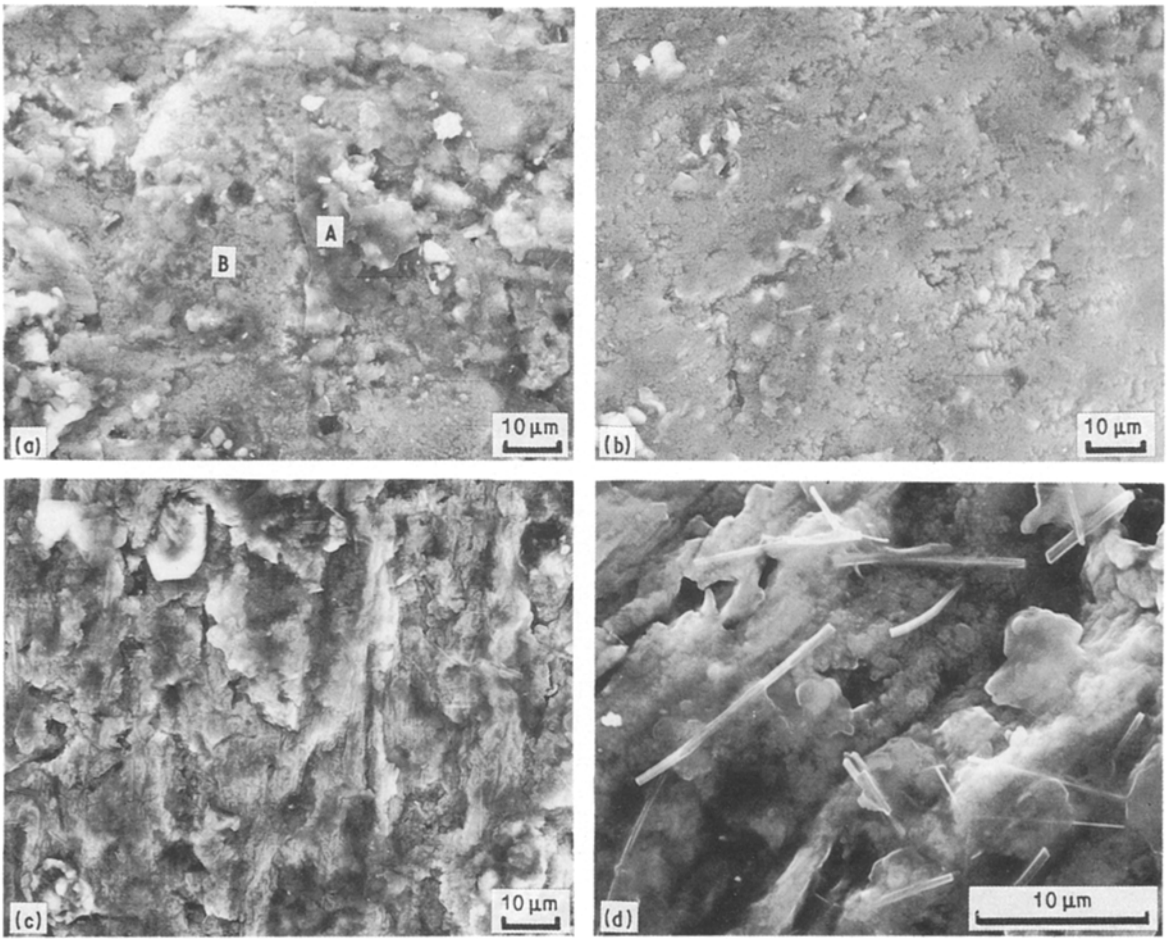

Figure 11 Scanning electron micrographs of the top surface of some of the specimens shown in Fig. 10. (a) Aluminium, (b) Al–0.33 wt % Si, (c, d) Al–0.50 wt % Mg.

nium to silicon nitride and remains stable at the interface between the filler metal and the silicon nitride after brazing. In addition to this, an Al–Si spinel reaction product layer also exists at the interface. The fracture occurs easily in the alumina layer or along the interface between the alumina and the Al–Si spinel layers, and hence aluminium–magnesium filler metals make the strength of the joints small.

In the case of aluminium–silicon filler metals, because the oxide formed on the surface of the filler metals is very thin, a silica–alumina non-crystalline layer is formed easily at the interface during brazing. This layer strengthens the bond interface, and hence aluminium–silicon filler metals increase the strength of the joints. The condition of the oxide layer formed on the surface of the filler metals is an important factor influencing the bond strength of the joints. On the other hand, silicon in aluminium influences the plasticity of aluminium greatly and should reduce the ability of the filler metal to relax the thermal stress which occurs from the expansion mismatch between the filler metal and the silicon nitride ceramic. This may be the reason why a small amount of silicon in aluminium is the most effective.

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References

1. K. SUGANUMA, T. OKAMOTO, K. KOIZUMI and M. SHIMADA, *J. Mater. Sci.* **22** (1987) 1359.
2. A. KOHNO, T. YAMADA and K. YOKOI, *Nippon Kinzoku-Gakkaishi* **49** (1985) 876.
3. M. NAKA, M. KUBO and I. OKAMOTO, *J. Mater. Sci.* **22** (1987) 4417.
4. M. MORITA, K. SUGANUMA and T. OKAMOTO, *J. Mater. Sci. Lett.* **6** (1987) 474.
5. X. S. NING, K. SUGANUMA, M. MORITA and T. OKAMOTO, *Phil. Mag. Lett.* **55** (1987) 93.
6. X. S. NING, K. SUGANUMA, T. OKAMOTO, A. KOREEDA and Y. MIYAMOTO, *J. Mater. Sci.*, **24** (1989) 2879.
7. X. S. NING, T. OKAMOTO, Y. MIYAMOTO, A. KOREEDA and K. SUGANUMA, *ibid.*, **24** (1989) 2865.
8. I. M. LOW and R. McPHERSON, *ibid.* **24** (1989) 926.
9. W. HEHN and E. FROMM, *Aluminium* **64** (1988) 180.

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