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Behavior of Oxide Film in Diffusion Bonding of Aluminum†

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Abstract

The microstructure of bond interface in the diffusion-bonded joint of aluminum has been investigated with transmission electron microscope (TEM) in order to obtain a direct evidence for the existence of aluminum oxide which originates from oxide films on faying surfaces. The effect of the state of faying surface on the morphology of the oxide has also been examined using faying surfaces subjected to the following three treatments: (i) wire brushing, (ii) electropolishing subsequent to grinding on 1200 grade emery paper, and (iii) electropolishing subsequent to wire brushing. Results obtained are summarized as follows:

The oxide was found at the bond interface for all the surface treatments (i), (ii) and (iii). However, the morphology and distribution of the oxide were strongly influenced by the surface treatments. When the faying surface subjected to the treatment (i) was used, a number of oxide particles were distributed within a zone about 1 to 3μm in thickness along the bond interface. The zone was found to consist of many small grains less than 1μm in diameter. The formation of this zone is ascribed to a surface layer into which a significant degree of cold working and a lot of oxides are introduced during the wire brushing. The zone involving the oxide had harmful effects on the bond strength, because the surface treatment (i) led to a much lower bond strength than the treatment (ii) and (iii). On the other hand, when faying surfaces subjected to the treatments (ii) and (iii) were used, the oxide was observed only along the bond interface as a thin film about 30 to 40nm in thickness. The proportion of the bond interface where the oxide was broken up was larger when faying surfaces were subjected to the treatment (iii) than the treatment (ii), and so a higher bond strength was obtained by using the treatment (iii) than the treatment (ii).

KEY WORDS: (Aluminum) (Oxide Film) (Diffusion Bonding) (Surface Treatment) (Transmission Electron Microscope)

1. Introduction

The superficial oxide film of aluminum is generally accepted as one of the most important factors which interfere with the formation of metallic bonds across the bond interface in the diffusion bonding of aluminum(1-3); for the aluminum oxide film, which is very stable and tenacious, is considered to remain at the bond interface even at temperatures near the melting point of the base metal. The oxide remaining at the bond interface, however, can hardly be observed with conventional optical microscope or scanning electron microscope, because its thickness is less than 10nm. On the other hand, it is rather difficult to prepare a thin foil specimen for TEM (transmission electron microscope) observation from a bond interface, because the bond interface is attacked preferentially by conventional electropolishing. For these reasons, no direct observation of the oxide at the bond interface has been made, though the importance of the oxide has been suggested by several authors(1-3).

The present investigation aims at obtaining a direct evidence for the existence of the oxide by the observation with TEM. Since the morphology and kind of the oxide film are expected to be influenced by the surface treatment, surfaces to be bonded are finished by mechanical and chemical treatments.

2. Experimental Details

Specimens for the diffusion bonding were prepared from a cold drawn bar (20 mm in diameter) of commercially pure aluminum A1050 with chemical composition as shown in **Table 1**. The specimen was a rod 20mm in diameter and 37mm in length, and the face to be bonded (faying surface) was the end surface of the rod. In

Table 1 Chemical composition of the base metal used (mass %).

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
0.05	0.11	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	Bal.

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order to investigate the effect of the surface treatment on the morphology and distribution of the oxide, the faying surface was finished by the following three treatments: (i) wire brushing (stainless steel wire 0.1mm thick), (ii) electropolishing subsequent to grinding on metallographic paper of 1200 grade, (iii) electropolishing subsequent to wire brushing. The mechanical surface treatment (i) has been reported to lead to a bond strength considerably higher than other mechanical treatments such as machining with lathe and grinding on metallographic paper$^{(4)}$. The surface treatments (ii) and (iii) are chemical, but the faying surface finished by (iii) is rougher than that finished by (ii). As shown in **Fig. 1**, the faying surface finished by the treatment (i) was most rough, and the mean height of microasperities R_M was about 10 μm. The mean height R_M on the faying surface finished by the treatment (ii) was less than 1 μm, and that finished by the treatment (iii) about 5 μm. The electropolishing in the surface treatments (ii) and (iii) was made in a solution cooled to 253K for 0.6ks at 12V. The electrolyte used was constituted of 80% ethanol and 20% hyperchloric acid. The thickness of surface layer removed by this electropolishing was 50 ~ 60 μm. Faying surfaces finished by these treatments were degreased by washing in acetone just before the bonding.

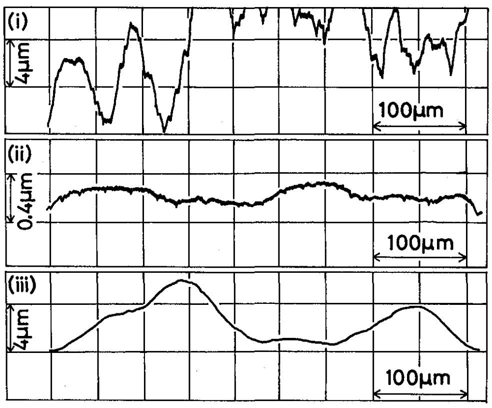

Fig. 1 Profiles of microasperities on faying surfaces finished by wire brushing (i), electropolishing subsequent to grinding on metallographic paper of 1200 grade (ii), and electropolishing subsequent to wire brushing (iii).

The diffusion bonding was carried out in a vacuum of 10^{-2}Pa using an apparatus similar to that reported in a previous paper$^{5)}$; the bonding zone was heated with a radiant resistance heater of molybdenum foil (0.1 μm thick), and the bonding pressure to the bond interface was exerted with a hydraulic press. Bonding temperature adopted ranged from 893K to 923K. Bonding time and pressure were 1.8ks and 2MPa, respectively. In the diffusion bonding, specimens were so arranged that grooves on two faying surfaces caused by the wire brushing or grinding crossed almost perpendicularly to one another.

Specimens for TEM observation were prepared from a joint in the following manner. As shown in **Fig. 2**, several plates (1mm thick) including a bond interface were cut from a joint, and ground to a thickness about 100 μm on metallographic papers. Then the plate was subjected to electropolishing and subsequently to Ar ion beam thinning, to make the vicinity of the bond interface as thin as observable with TEM. The electropolishing was carried out using a twin jet polishing apparatus operated at 18V. A methanol solution containing 5% hyperchloric acid cooled to 253K was used for the electrolyte. The acceleration voltage of Ar ion beam thinning was 4 ~ 5kV. The Ar ion beam thinning was applied because the metallic aluminum was thinned much more rapidly than the aluminum oxide by the electropolishing; accordingly the aluminum oxide was preferentially left at the bond interface by the electropolishing, and so the observation of a specimen made only by the electropolishing resulted in overestimation of the size and volume of the oxide. TEM observation was carried out at an acceleration voltage of 125kV.

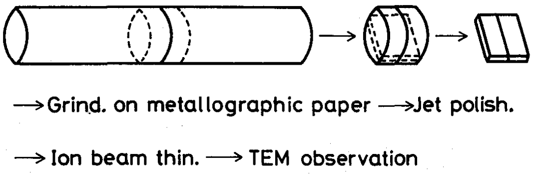

Fig. 2 Preparation of the specimen for TEM observation from a diffusion-bonded joint.

3. Experimental Results

3.1 Effect of faying surface treatment on the bond strength and microstructure

Prior to the observation with TEM, a tensile test of joints was carried out to investigate the effect of the faying surface treatment on the bonding process. The tensile strength of joints was influenced strongly by the surface treatments (i), (ii) and (iii) as shown in **Fig. 3**. The broken line in this figure indicates that almost all joints having strength higher than this level were fractured at the base metal (all except for a joint bonded at 893K with faying surfaces finished by the treatment (iii)). As shown in Fig. 3, when the faying surface was finished by the treatment (iii) (electropolishing subsequent to wire brushing), bond strength comparable to the tensile strength of the base metal was obtained at a bonding temperature of 893K. In contrast to this, the bonding temperature at which the bond strength started to be comparable to the tensile strength of the base metal was 903K for the

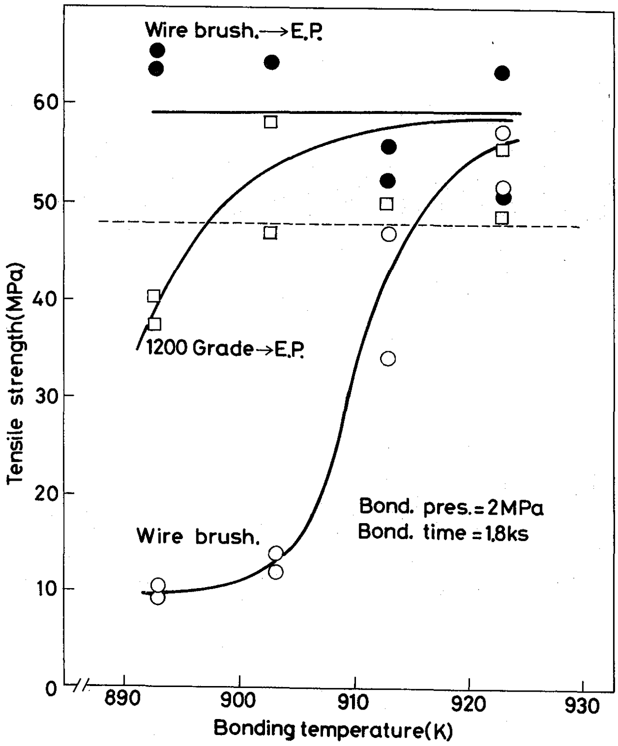

Fig. 3 Tensile strength of joint vs. bonding temperature for diffusion bonding of aluminum with faying surfaces finished by the treatments (i), (ii) and (iii).

surface treatment (ii) and 923K for the surface treatment (i). Thus the bond strength increased with the rise of bonding temperature depending strongly on the surface treatments (i), (ii) and (iii).

On the other hand, **Fig. 4** presents the effect of the surface treatments (i), (ii) and (iii) on the optical microstructure of the bond interface. All the bond interfaces appeared as a black band or line, and so no difference could be observed, except that the bond interface for the surface treatment (i) was a little wider than those for the surface treatments (ii) and (iii). These results shown in Figs. 3 and 4 suggest that the bond strength of the diffusion-bonded aluminum is affected strongly by the difference in the bonding state which can not be distinguished with optical microscope. Consequently, more microscopic observation with TEM is necessary for better understanding of an important factor for the bond strength.

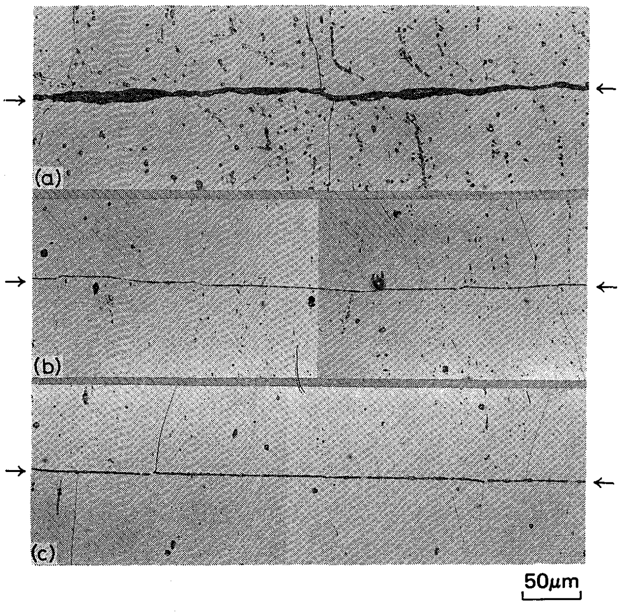

Fig. 4 Optical micrographs of bond interfaces. For the bond interfaces shown in (a), (b) and (c), faying surfaces were finished by the treatments (i), (ii) and (iii), respectively. The arrows on both sides of the micrographs indicate the bond interfaces.

3.2 Observation of bond interface with TEM

When faying surfaces were finished by the wire brushing (treatment (i)), the bond interface observed with TEM is shown in **Figs. 5(a)** and **(b)**. Along the bond interface shown in Fig. 5(a), a number of accicular inclusions about 0.5 μm in length and granular inclusions less than 0.1 μm in diameter were distributed within a zone about 1 to 3 μm in thickness. As described in §4.1, these small inclusions can be regarded as aluminum oxides. This zone probably corresponds to the black band in the optical micrograph shown in Fig. 4(a), since the thickness of the zone is of the same order as that of the black band.

On the other hand, at the bond interface shown in Fig. 5(b), the amount of aluminum oxides became much smaller than at the bond interface shown in (a), and oxides were aligned only along the bond interface. At a bonding temperature of 893K, the zone shown in Fig. 5(a) was found at all the bond interface observed. And the proportion of the part as shown in Fig. 5(b) increased with the rise of bonding temperature, that is, with the rise of bond strength. This indicates that the zone as shown in Fig. 5(a) exerts a harmful effect to the increase in the bond strength when faying surfaces are finished by wire brushing.

A result of closer examination to this zone including a number of oxides is shown in **Fig. 6**. A bright field image of the zone observed at a higher magnification is shown in Fig. 6(a). A selected area diffraction pattern taken from the area shown in (a) consisted of diffraction spots distributed on several concentric circles as shown in Fig. 6(c). Almost all the diffraction spots were on the diffraction rings corresponding to the interplanar spacings of aluminum as schematically shown in Fig. 6(d). This indicates that in the area shown in (a) there are many small grains of aluminum. A dark field image of the area (a) imaged with 111 diffracted beam (marked with a broken circle in (d)), in fact, shows that a grain as small as 0.5 μm in diameter exists in the observed area, as seen in

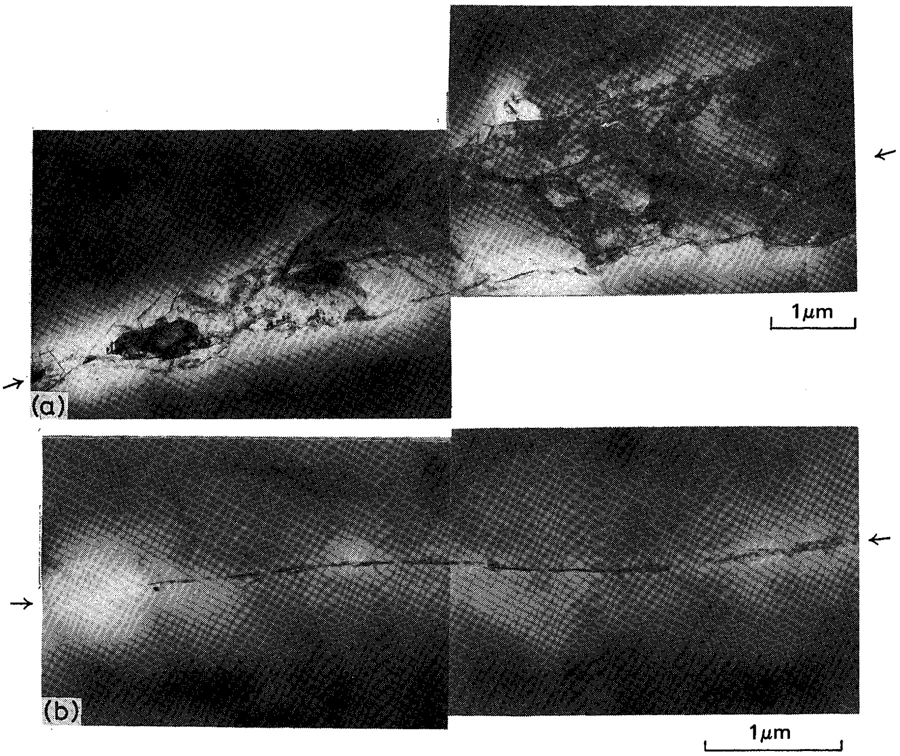

Fig. 5 TEM micrographs of a bond interface for the surface treatment (i). The bonding temperature (T_B) was 923K, bonding pressure (P_B) 2MPa and bonding time (t_B) 1.8ks.

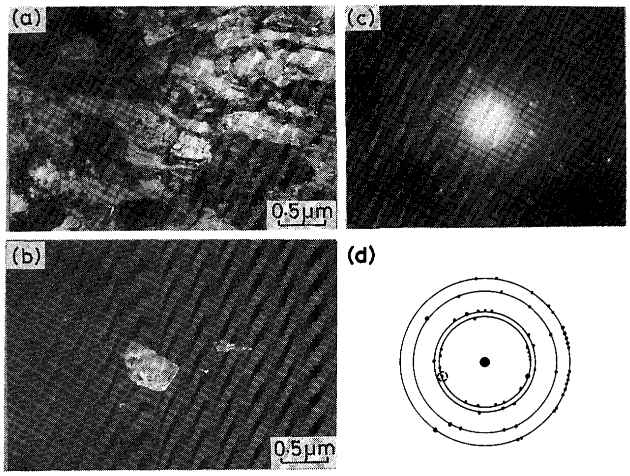

Fig. 6 (a) Bright field image of a bond interface for the surface treatment (i) (T_B = 893K, P_B = 2MPa, t_B = 1.8ks). (b) Dark field image of the same area as (a) using a 111Al diffracted beam (marked with a broken circle in (d)). (c) Selected area diffraction pattern taken from the area shown in (a). (d) Schematic diagram illustrating the diffraction spots shown in (c) and diffraction rings corresponding to the interplanar spacings of aluminum.

Fig. 6(b). The size of these fine grains seemed to increase with the rise of bonding temperature.

On the other hand, the zone including a number of oxides could not be found, when faying surfaces were finished by the chemical treatments (ii) and (iii). The bond interface for the surface treatment (ii) (electropolishing subsequent to grinding on metallographic paper of 1200 grade) is shown in **Fig. 7**. The bond interface was nearly parallel to the direction of the electron beam (direction of observation) in Fig. 7(a), and the same area was tilted so that the bond interface made an angle of 30° with the electron beam in (b). In Figs. 7(a) and (b), the dark thin films along the bond interface can be regarded as the oxide. The oxide was partially broken up as shown in Figs. 7(a) and (b).

When faying surfaces were finished by the treatment (iii) (electropolishing subsequent to wire brushing), the oxide also appeared as thin films aligned on the bond interface as shown in **Fig. 8**. In this case, the oxide was broken up at more places than in the case of the surface treatment (ii). In a previous paper$^{6)}$, we (E.T. and K.I.) have suggested that breaking-up of the oxide at the bond interface is promoted by roughening the faying surface. The faying surface finished by the treatment (iii) is more rough than that finished by (ii) (see Fig. 1). Thus, the results shown in Figs. 7 and 8 agree quite well with our previous suggestion. The difference in the breaking-up of the oxide between the surface treatment (ii) and (iii) can be considered to cause the difference in the bond strength shown in Fig. 3. As to the effect of bonding temperature on the behavior of oxide, the oxide was broken up at more places with the rise of temperature both in the case

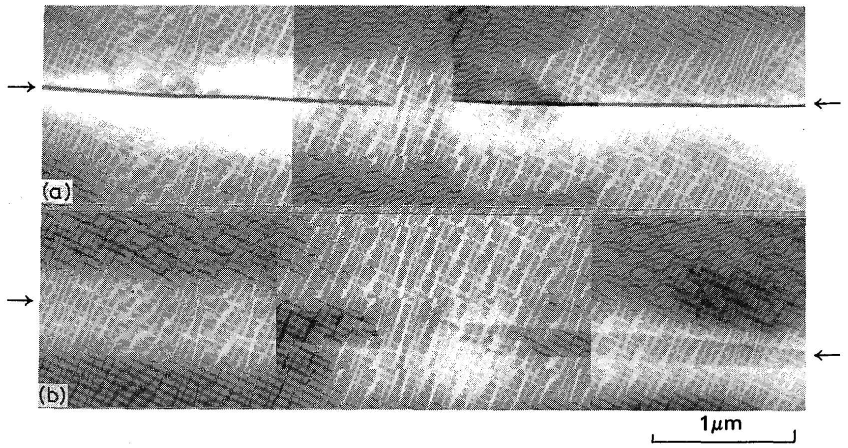

Fig. 7 TEM micrographs of a bond interface for the surface treatment (ii) (T_B = 893K, P_B = 2MPa, t_B = 1.8ks).

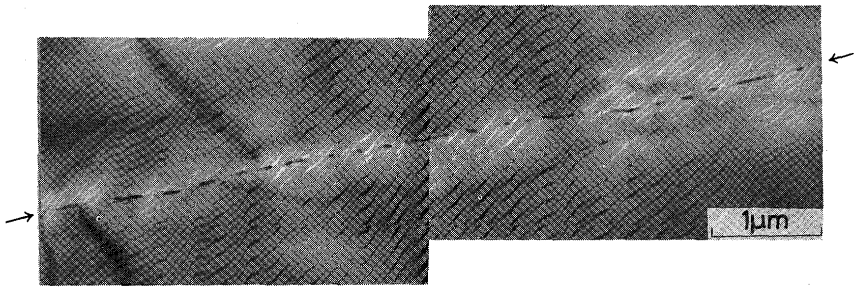

Fig. 8 TEM micrographs of a bond interface for the surface treatment (iii) (T_B = 923K, P_B = 2MPa, t_B = 1.8ks).

of the surface treatment (ii) and in the case of the surface treatment (iii).

Among the surface treatments (i), (ii) and (iii), the zone including a number of oxides was found only in the case of wire brushing (treatment (i)). A zone similar to that shown in Fig. 5(a) was also found when faying surfaces were finished by turning in a lathe to JIS3-S (mean height of microasperities $R_M \simeq 1$ μm). This height R_M of microasperities was smaller than that on faying surfaces finished by the chemical treatment (iii). Thus, the zone as shown in Fig. 5(a) was formed irrespective of the roughness of faying surface, when faying surfaces were finished by mechanical treatments such as wire brushing and turning. Therefore, it can not be accounted for by the difference in the roughness of faying surfaces that the zone as shown in Fig. 5(a) is not formed in the case of the chemical treatments (ii) and (iii). The formation of this zone can be rather interpreted as follows: The mechanical treatment such as wire brushing and turning forms a cold-worked surface layer which includes a lot of oxides, and the surface layer remains after the diffusion bonding to form the zone as shown in Figs. 5(a) and 6(a). The fact that the surface treatment (i) led to a bond strength considerably lower than the treatments (ii) and (iii) indicates that the cold-worked surface layer interferes with the increase in the bond strength.

Thus the oxide was found at the bond interface for all the surface treatments (i), (ii) and (iii). **Figure 9** shows an

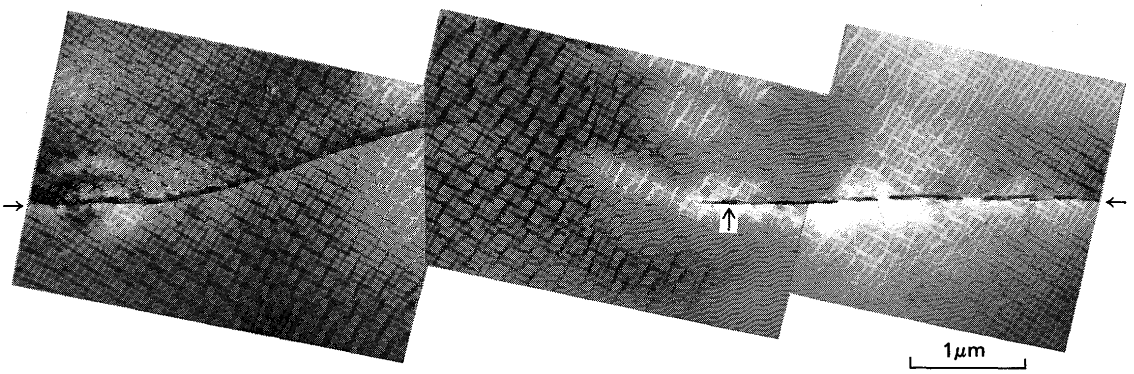

Fig. 9 TEM micrograph of a bond interface showing that the oxide suppresses the migration of bond interface at a point where a grain boundary meets the bond interface (faying surface finish: treatment (iii), T_B = 923K, P_B = 2MPa, t_B = 1.8ks).

example of the effect of the oxide on the migration of bond interface (surface treatment (iii)). At a place where a grain boundary met the bond interface, the bond interface started bending in the direction to reduce the energy of grain boundary. However, further migration of the bond interface was suppressed by a oxide indicated by the arrow; accordingly the oxide has an effect of pinning the bond interface. Because of this pinning effect, the bond interface in the diffusion bonding of aluminum was not eliminated even at a bonding temperature of 923K just below the melting point, and remained a straight line as shown in Fig. 4.

4. Discussion

4.1 Existence of the oxide at the bond interface

As described in §3.2, inclusions which can be regarded as aluminum oxides are observed at the bond interface for all the surface treatments (i), (ii) and (iii). However, no diffraction pattern to be assigned to the aluminum oxide could be obtained by selected area diffraction of the bond interface as shown in Fig. 6, and so a definitive evidence that identifies these inclusions as oxides has not been obtained yet.

In order to confirm the existence of the oxide at the bond interface, analysis of oxygen with electron probe microanalysis(EPMA) was made across the bond interface. A secondary electron image of the bond interface for the surface treatment (i) is shown in **Fig. 10**, together with a result of line analysis of oxygen along the line A-A′. A significant increase in the oxygen concentration was observed in a zone along the bond interface which involved a lot of inclusions similarly to those shown in Fig. 5(a). This increase in the oxygen concentration indicates that the oxide exists in the zone along the bond interface.

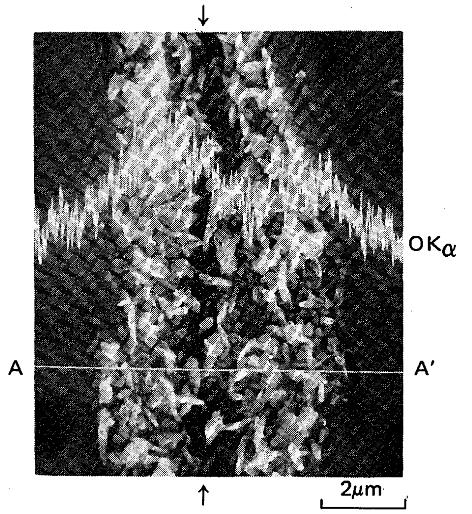

Fig. 10 Scanning electron micrograph of a bond interface for the surface treatment (i) and distribution of oxygen along the line A-A′ analyzed with EPMA (T_B = 923K, P_B = 2MPa, t_B = 1.8ks).

The existence of the oxide is also supported by the fact that the zones shown in Figs. 5(a) and 6(a) consist of fine grains as small as less than 1 μm in diameter. That is, such fine grains exist after the diffusion bonding made at a temperature of 893K and 923K much higher than the recrystallization temperature of aluminum. If such fine grains are to exist after the diffusion bonding, something to suppress the grain growth must be present in the vicinity of the bond interface at temperatures above 893K. In the commercially pure aluminum used, only the aluminum oxide can be considered to exist abundantly in the vicinity of the bond interface and to have a strong effect of suppressing the grain growth at temperatures above 893K. From these results, it may be concluded that the oxide exists at the bond interface in the case of the surface treatment (i). And it is only the accicular and granular inclusions that can be assigned to the oxide at the bond interface shown in Fig. 5(a).

On the other hand, in the case of the surface treatments (ii) and (iii), the inclusion which can be regarded as the oxide is aligned at the bond interface as a thin film less than 30 ~ 40nm thick. The EPMA used in Fig. 10 can not detect the increase in oxygen concentration due to such a thin film, because its smallest analyzing volume is more than 2 ~ 3 μm in diameter. For this reason, in the case of the surface treatment (iii), analysis of oxygen was made by investigating the electron energy loss spectroscopy(EELS) transmitted through the bond interface by the use of scanning transmission electron microscope (STEM) (Hitachi H-800, acceleration voltage: 200keV). **Figure 11** shows a result of EELS together with a STEM image of the bond interface. Since the resolution of the STEM image was not so high as that of TEM, it was impossible to distinguish the oxide, but the position of the bond interface could be distinguished. The relative intensity of electron beam transmitted through the bond interface is shown as a function of energy loss in Fig. 11; the zero point of the horizontal axis corresponds to the energy (200keV) of incident beam, and the sensitivity to electron intensity, the scale of the vertical axis, was increased successively by a factor of ten, since the electron intensity decreased rapidly with the increase in energy loss. As shown in Fig. 11, a peak was observed at an energy corresponding to the absorption energy of oxygen K-shell. Such absorption peak of oxygen could not be found in EELS made at a place other than the bond interface. Consequently, the content of oxygen at the bond interface was higher than that at other places. This

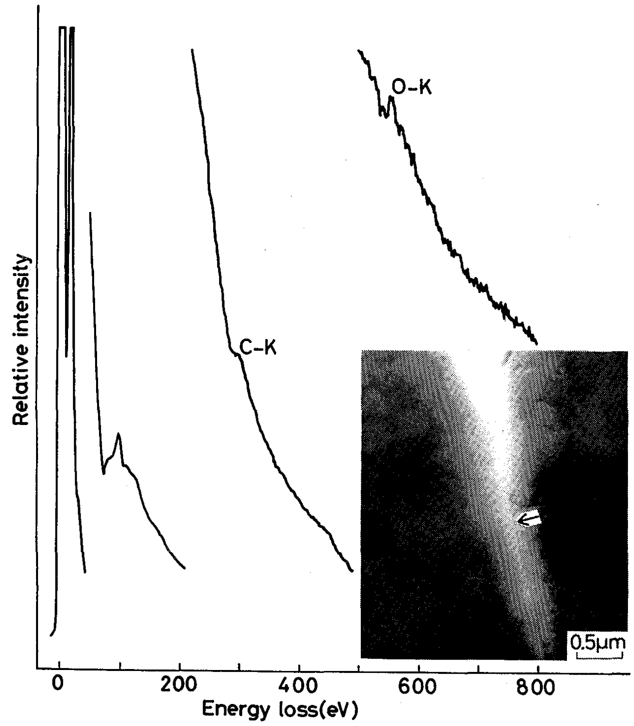

Fig. 11 Energy loss spectroscopy of electrons transmitted through the bond interface indicated by the arrow in the image of STEM (faying surface finish: treatment (ii), T_B = 923K, P_B = 2MPa, t_B = 1.8ks). Absorption peaks for exciting the K-shells of carbon and oxygen are indicated by C-K and O-K.

indicates the existence of the oxide at the bond interface. It is only the thin film inclusion that can be regarded as the oxide at the bond interface shown in Figs. 7 and 8.

4.2 Oxide at the bond interface and bond strength

The bonding conditions of the bond interface shown in Figs. 5, 8 and 9 were those under which a bond strength not less than the base metal was obtained as shown in Fig. 3. However, a considerable amount of oxides were still observed at these bond interfaces; in spite of the existence of oxides at the bond interface, the joint was fractured in the base metal on tensile test. In order to make clear the reason for this, specimens for TEM observation were prepared from a joint fractured in the base metal on tensile test, and the bond interface subjected to the tensile test was observed for comparison with that before the test.

As shown in **Fig. 12**, no crack or void could be observed at the bond interface even after the tensile test, but the bond interface deformed to form steps. The step formed at places where the oxide still existed as well as at places where the oxide was eliminated already, as shown in **Figs. 13(a)** and **(b)**. The oxide at the bond interface originates from superficial oxide films which exist separately on two faying surfaces. Therefore, it should be impossible for the bond interface where the oxide exists to bear the stress and strain on tensile test, unless a bond strength between the superficial oxide films becomes comparable to the strength of the base metal. In other words, the joint was fractured in the base metal inspite of the existence of oxides at the bond interface, because the bond strength between the superficial oxide films is high enough to bear the stress and strain in tensile test. Thus, the results shown in Figs. 12 and 13 indicate that the bonding between the superficial oxide films is attained under bonding conditions adopted in the present investigation (see Fig. 3).

On the other hand, it is well known that the bulk aluminum oxide has a melting point as high as 2320K, and can not be bonded at bonding temperatures adopted in this investigation. Therefore, it seems that the superficial oxide film of aluminum behaves quite differently from the bulk oxide in the diffusion bonding. This suggestion is supported by an observation of the oxide at a higher magnification as shown in **Fig. 14**. The thickness of oxides observed at the bond interface is more than 20nm in some places. On the other hand, the thickness of the superficial oxide film was estimated to be 4 ~ 6nm by using ellipsometry. Consequently, the thickness of oxides at the bond interface is partly larger than twice the thickness of the superficial oxide film. This increase in the thickness of oxide can not be attributed to the growth of the oxide, since it is very difficult for the oxide to grow in the diffusion bonding; i.e., the atmosphere of diffusion

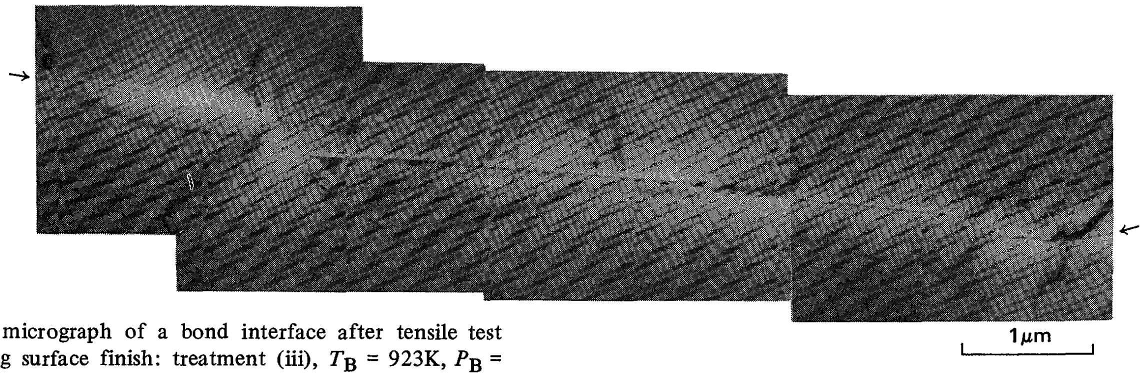

Fig. 12 TEM micrograph of a bond interface after tensile test (faying surface finish: treatment (iii), T_B = 923K, P_B = 2MPa, t_B = 1.8ks).

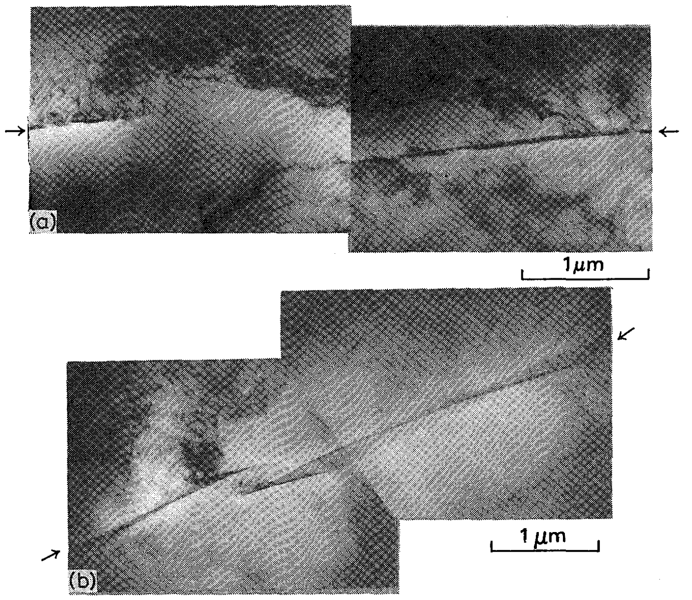

Fig. 13 TEM micrograph of a bond interface after tensile test showing that steps are formed at a place where the oxide is not broken up (b) as well as at a place where oxide is broken up (a) (faying surface finish: treatment (iii), T_B = 923K, P_B = 2MPa, t_B = 1.8ks).

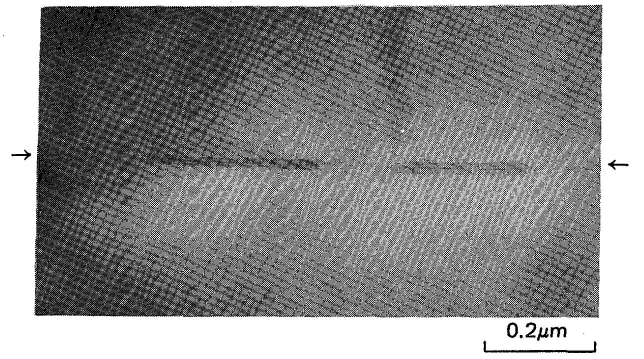

Fig. 14 Oxides at the bond interface for the surface treatment (ii) (T_B = 923K, P_B = 2MPa, t_B = 1.8ks).

bonding was a vacuum of 10^{-2}Pa, and moreover the supply of oxygen was suppressed by the intimate contact between faying surfaces. Consequently, the fact that the oxide more than 20nm thick was observed suggests that the oxide deformed so as to decrease the surface energy (to decrease the area of surface with its volume constant). This deformation to decrease the surface energy may not be related directly to the formation of bond between the superficial oxide films, but is enough to indicate that the superficial oxide film has a characteristic quite different from the bulk aluminum oxide.

5. Conclusion

The aim of present investigation is to prove the existence of oxides at the bond interface of aluminum by a direct observation with TEM. Since the oxide originates from the superficial oxide film on faying surfaces, its morphology and distribution are expected to be influenced strongly by the treatment of the faying surface. For this reason, the faying surface was finished by the following three treatments: (i) wire brushing, (ii) electropolishing subsequent to grinding on metallographic paper of 1200 grade and (iii) electropolishing subsequent to wire brushing. Results obtained are summarized as follows:

(1) The oxide was found at the bond interface for all the surface treatments (i), (ii) and (iii). The morphology and distribution of the oxide were strongly influenced by the surface treatments.

(2) When the faying surface was finished by the treatment (i), a number of oxides were distributed within a zone about 1 to 3 μm thick along the bond interface. The zone was found to consist of a lot of fine grains less than 1 μm in diameter. The formation of this zone is ascribed to a superficial layer into which a number of oxide and a significant degree of cold working are introduced by the wire brushing. The superficial layer had a harmful effect on the increase in the bond strength, since the surface treatment (i) led to a much lower bond strength than (ii) and (iii).

(3) When the faying surface was finished by the treatments (ii) and (iii), the oxide was aligned along the bond interface as thin films less than 40nm in thickness. In the case of the surface treatment (iii), the oxide was broken up at more places than in the case of the surface treatment (ii). For this reason, a higher bond strength was obtained by the use of the surface treatment (iii) than by the surface treatment (ii).

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