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Interfacial Oxide in Diffusion-Bonded Joints of Al-Binary Alloys by Transmission Electron Microscopy†

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Abstract

The effects of alloying elements on the morphology and composition of interfacial oxides in diffusion-bonded joints have been investigated by TEM observations for Al binary alloys containing 0.06-2.0at% Mg, 1.0at% Si, 0.5at% Mn, 1.0at% Zn, and 1.0at% Cu. At the joint interfaces of the Al binary alloys, except for those of the Al-Mg system, continuous amorphous oxide films were observed at all bonding temperatures employed in this investigation. At the joint interfaces of the Al-Mg alloys, as described in a previous paper, the oxide altered gradually from amorphous films to crystalline particles 10-100 nm in size as the bonding temperature was increased. The difference in the behavior of interfacial oxide between the Al-Mg alloys and those of the other alloys can be explained thermodynamically by assuming that crystalline oxides were formed through reductive reactions of the oxide film of Al by Mg. EDS analyses of the amorphous oxide film at joint interfaces of the alloys revealed that Mg atoms were concentrated in the amorphous oxide film of the Al-Mg alloys prior to the formation of the crystalline oxide particles, whereas no concentration of other alloying elements could be detected in the amorphous oxide film of the other alloys.

1. Introduction

In the diffusion bonding of aluminum and its alloys, the stable superficial oxide film is generally accepted as the most important factor which interferes with the formation of metallic bonds across the joint interface and retards the increase in the bond strength[1,2]. Through the TEM observation of the joint interface of commercial aluminum alloys and Al-Mg binary alloys[2-9], we have found that (1) the morphology of oxide at the joint interface is significantly affected by the alloying element, (2) within the commercial Al alloys investigated, the morphology and the crystal structure of interfacial oxides were determined by the Mg content and the bonding temperature, whereas alloying elements of Si, Zn, or Cu had almost no influence on the interfacial oxides, (3) the dependence of the behavior of the interfacial oxides on the Mg content

and the bonding temperature in the Al-Mg binary alloys was nearly equivalent to that observed in the commercial Al alloys, (4) the range of Mg contents and bonding temperatures where the interfacial crystalline oxides of Al_2MgO_4 and MgO formed can be roughly explained thermodynamically by assuming that these crystalline oxides were formed through the reductive reactions of the interfacial amorphous film of aluminum oxide by Mg.

The aim of the present study is to examine the influences of the alloying elements of Si, Mn, Zn, and Cu on the morphology and composition of the interfacial oxide in the Al alloy which does not contain Mg, because the Mg addition has been reported to have significant influences on the oxide formation of other alloying elements in the surface oxidation of the Al alloy[10]. For this, TEM observations of the diffusion-bonded interfaces have been carried out for Al binary alloys containing 0.06-2at% Mg, 1.0at% Si,

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Table 1 Chemical compositions of the base metals(mass%).

Alloy	Mg	Si	Fe	Cu	Mn	Cr	Zn	Ti	Ca	Al
Al-0.06% Mg	0.06	<0.01	<0.01	0.00	0.00	<0.01	0.00	0.00	0.00	Bal.
Al-0.6% Mg	0.56	<0.01	<0.01	0.00	0.00	<0.01	0.00	0.00	0.00	Bal.
Al-1.6% Mg	1.62	<0.01	<0.01	0.00	0.00	<0.01	0.00	0.00	0.00	Bal.
Al-Si (1%)	0.00	0.98	<0.01	0.00	0.00	<0.01	0.00	0.00	0.00	Bal.
Al-Mn (0.5%)	0.00	<0.01	<0.01	0.00	0.51	<0.01	0.00	0.00	0.00	Bal.
Al-Zn (1%)	0.00	<0.01	<0.01	0.00	0.00	<0.01	1.02	0.00	0.00	Bal.
Al-Cu (1%)	0.00	<0.01	<0.01	0.97	0.00	<0.01	0.00	0.00	0.00	Bal.

Table 2 Diffusion-bonding parameters.

Alloy	$T_W(K)$	$t_W(ks)$	$P_W(MPa)$
Al-0.06% Mg	813	1.8	1
Al-0.6% Mg	793-873	1.8	1.2(at T_W=793K)- 1.0(at T_W=873K)
Al-1.6% Mg	713	1.8	3.5
Al-Si (1%)	873-893	1.8	0.75(at T_W=873K)- 0.5(at T_W=893K)
Al-Mn (0.5%)	873-903	1.8	1
Al-Zn (1%)	873	1.8	0.2
Al-Cu (1%)	873-903	1.8	1

1.0at% Mn, 1.0at% Zn, and 1.0at% Cu. It is shown that the observed effects of the alloying elements on the behavior of the interfacial oxide can be explained from a thermodynamic point of view.

2. Experimental Details

The base metals employed were Al-Mg binary alloys with Mg contents from 0.06 to 1.6at% and Al-X binary alloys (X = Si, Mn, Zn, Cu) with chemical compositions as shown in Table 1. The specimen for diffusion bonding was a round bar 17 mm in diameter and 37 mm in length. The faying surface was finished by turning in a lathe followed by electropolishing in an ethanol solution containing 10vol% perchloric acid at 253 K and 18 V. The diffusion bonding was carried out in a vacuum of 10^{-2} Pa using an apparatus similar to that reported in a previous paper[1]. Bonding time t_w was 1.8 ks for all joints bonded in this investigation. Bonding temperature T_w and bonding pressure P_w are listed in Table 2. The bonding temperatures for the joint of the Al-0.6at% Mg alloy ranged from those just below the solidus line to those at which the joint

strength began to lower, and the bonding temperatures for the joints of the Al-0.06at% Mg and Al-0.16at% Mg alloys were those at which the amorphous oxide film remained at the joint interface. The bonding temperatures for the joints of the Al-X binary alloys (X = Si, Mn, Zn, Cu) were not lower than 873 K, since the joint strength of these alloys were supposed to be very low at lower bonding temperatures. The bonding pressure was determined so that the bonding zone was deformed by 1 - 2% (estimated from the increase in the cross-sectional area) during the bonding process.

The specimen for the TEM observation was prepared as follows. Firstly a thin plate about 1 mm in thickness including the joint interface was cut at an angle of 90° with the joint interface, and then ground on 1500 grade emery paper to a thickness of about 100 μm. The plate was further thinned by electropolishing using a twin jet polishing apparatus. The electrolyte used was a solution of 5vol% perchloric acid in methanol. The electropolishing temperature and voltage were 253 K and 18 V, respectively. The plate was finally thinned by Ar ion thinning. TEM observations and EDS analyses were carried out at an acceleration
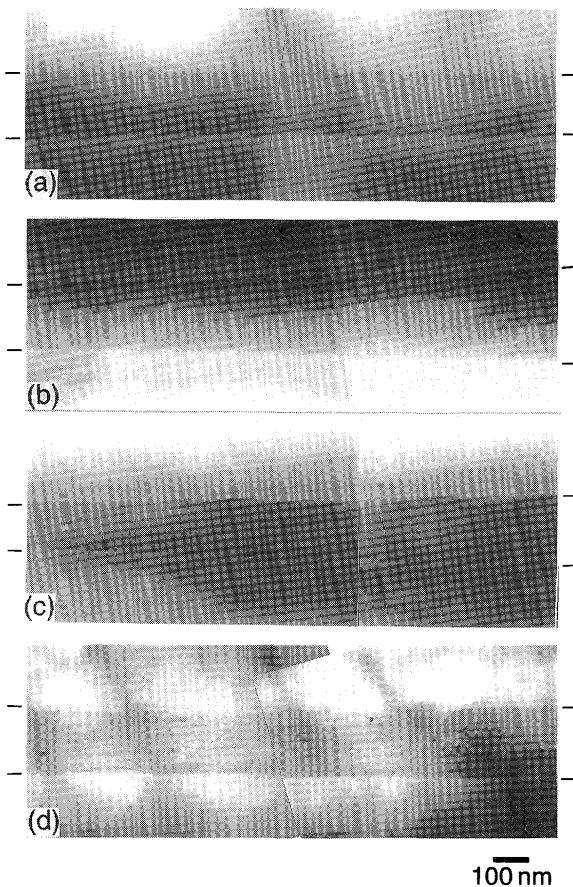
Fig.1 Electron micrographs of joint interfaces of Al-X alloys (T_w = bonding temperature, P_w = bonding pressure, and t_w = bonding time (= 1.8 ks)) : (a) Al-1at% Si (T_w = 893 K, P_w = 0.5 MPa), (b) Al-0.5at% Mn (T_w = 903 K, P_w = 1 MPa) , (c) Al-1at% Zn (T_w = 873 K, P_w = 0.2 MPa), and (d) Al-1at% Cu (T_w = 903 K, P_w = 0.5 MPa). The joint interfaces are tilted by 35° to the incident beam in (a), (c), and (d), and by 20° in (b).

Fig.2 Electron micrographs of joint interfaces of Al-0.6at% Mg alloy tilted by 35° to the incident beam (P_w = 1 MPa, t_w = 1.ks): (a)T_w = 813 K,(b)T_w = 833 K, (c)T_w = 853 K, and (d) T_w = 873 K.

voltage of 200 kV. The diameter of the electron beam for the EDS analysis was about 3 nm at the surface of the specimen.

3. Experimental Results

3.1 TEM observation of joint interfaces of Al-X binary alloys (X = Mg, Si, Mn, Zn, and Cu)

The bright field images of the joint interfaces of the Al-X binary alloys (X = Si, Mn, Zn, Cu) are shown in **Fig. 1**. As shown in Figs. 1(a) - 1(d), continuous amorphous films less than 10 nm thick were observed at the joint interfaces of the Al-Si, Al-Mn, Al-Zn, and Al-Cu alloys, respectively. The slight fluctuation in contrast observed in the images of the amorphous film
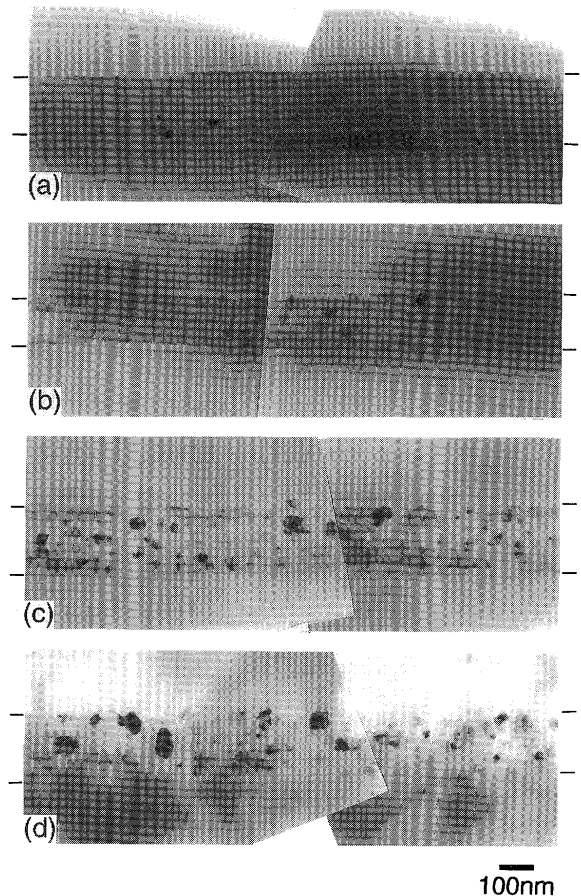
suggests that the thickness of the film is not homogeneous. As reported[8] previously, interfacial amorphous oxide films showing similar appearances were also observed in the joint of 4N pure Al. The amorphous film that occupied almost the whole area of the joint interface of the Al-X binary alloys (X = Si, Mn, Zn, Cu) can also be considered to be composed of an amorphous oxide film originating from the superficial oxide film that had existed on the alloy surfaces.

In contrast, TEM observations of the joint interface of the Al-Mg binary alloys indicated that (1) at Mg contents not less than 0.06 at%, the interfacial oxide altered gradually from amorphous films to crystalline particles, as the bonding temperature was increased, (2) the crystalline oxide particles at the joint interface were

Al_2MgO_4 at Mg contents from 0.06 to 0.6at% and MgO at Mg contents from 1.3 to 2.0at%, irrespective of the bonding temperature, and (3) at Mg contents from 0.9 to 1.1at%, the crystalline oxide particles changed from MgO to Al_2MgO_4, passing through a range where MgO and Al_2MgO_4 coexisted, as the bonding temperature was increased[9].

As an example, the joint interfaces of the Al-0.6at% Mg alloy bonded at temperatures from 813 to 873 K are shown in Fig.2. At a bonding temperature of 813 K, continuous amorphous oxide films remained over almost the whole area of the joint interface and crystalline particles were observed only in a small area, as shown in Fig. 2(a). At a bonding temperature of 833 K, the area occupied by the amorphous oxide film decreased, and the number and volume of the crystalline oxide particles increased as can be seen from Fig. 2(b). As indicated in Fig. 2(c), at a bonding temperature of 853 K, the crystalline particles predominated over the amorphous oxide film, which was annihilated completely at a bonding temperature of 873 K (see Fig. 2(d)).

3.2 EDS analysis of interfacial amorphous oxide of Al-X binary alloys (X = Mg, Si, Mn, Zn, and Cu)

As mentioned in §3.1, amorphous oxide films were observed over almost the whole area of the joint interfaces of the Al-X binary alloys (X = Si, Mn, Zn, Cu) even at bonding temperatures high enough to annihilate them in the Al-Mg alloys joints. As reported in a previous paper[9], Auger electron spectroscopy analyses suggested that the amorphous oxide film at the joint interface of the Al-0.6at% Mg alloy was highly enriched in Mg prior to altering to the crystalline particle.

In order to investigate whether the amorphous oxide film at the joint interface of the other alloys undergoes a similar compositional change, the interfacial amorphous oxide film was analyzed with EDS. The EDS spectra obtained from the interfacial amorphous oxide film of the Al-X binary alloys (X = Si, Mn, Zn, Cu) are shown in Fig.3. As shown in Fig. 3(a), only a small peak of Si was detected in the amorphous oxide film at the Al-Si alloy joint interface, although the peaks of Al and O were clearly observed.

Similar results were also obtained for the Al-Mn, Al-Zn, and Al-Cu alloys (see Figs. 3(b)-3(d)). An EDS spectrum from the Al-Mn alloy matrix adjacent to the joint interface is shown in Fig.4. The intensity of the characteristic X-ray of Mn detected from the matrix was comparable to that detected from the amorphous oxide
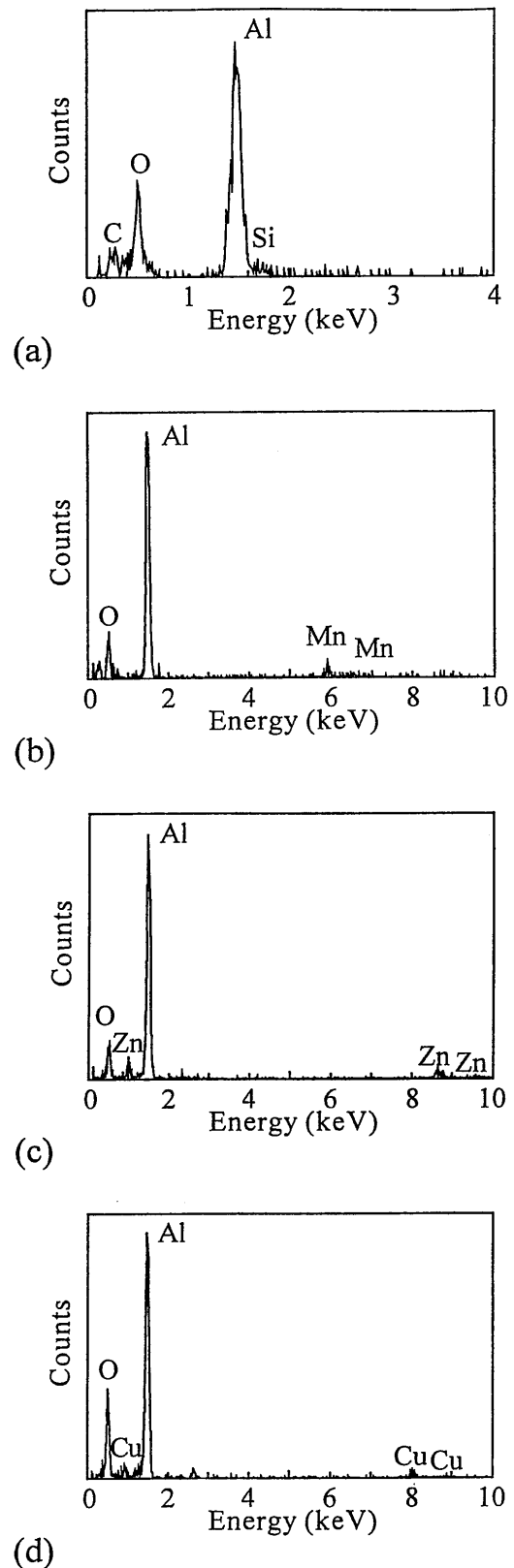

(a)

(b)

(c)

(d)

Fig.3 EDS analyses of the interfacial amorphous oxide films of Al-X alloy joints (t_w = 1.8 ks): (a) Al-1at% Si (T_w = 893 K, P_w = 0.5 MPa), (b) Al-0.5at% Mn (T_w = 903 K, P_w = 1 MPa) , (c)Al-1at% Zn (Tw = 873 K, P_w = 0.2 MPa), and (d) Al-1at% Cu (T_w = 903 K, P_w = 0.5 MPa).

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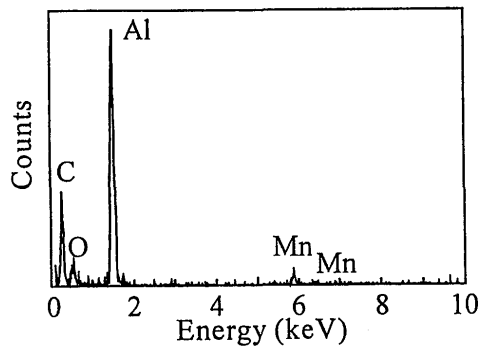
Fig. 4 EDS analysis of the matrix of Al-0.5at% Mn alloy ($T_w = 903$ K, $P_w = 1$ MPa, $t_w = 1.8$ ks).
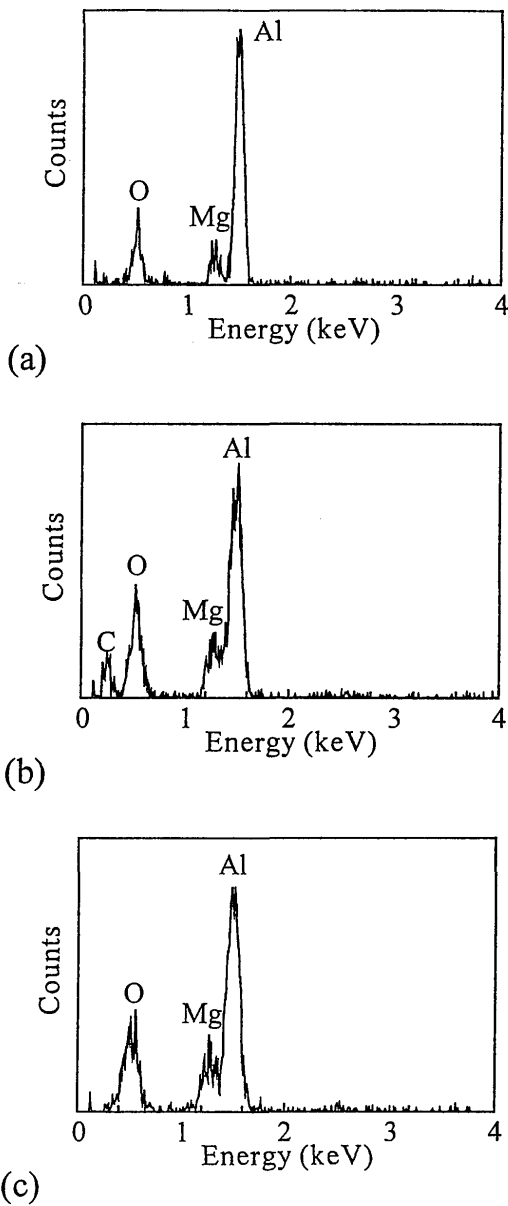

(a)

(b)

(c)

Fig. 5 EDS analyses of the interfacial amorphous oxide films of Al-Mg alloy joints ($t_w = 1.8$ ks) : (a) Al-0.06at% Mg alloy ($T_w = 813$ K, $P_w = 1$ MPa), (b) Al-0.6at% Mg alloy ($T_w = 823$ K, $P_w = 1$ MPa), and (c) Al-1.6at% Mg alloy ($T_w = 713$ K, $P_w = 3.5$ MPa).
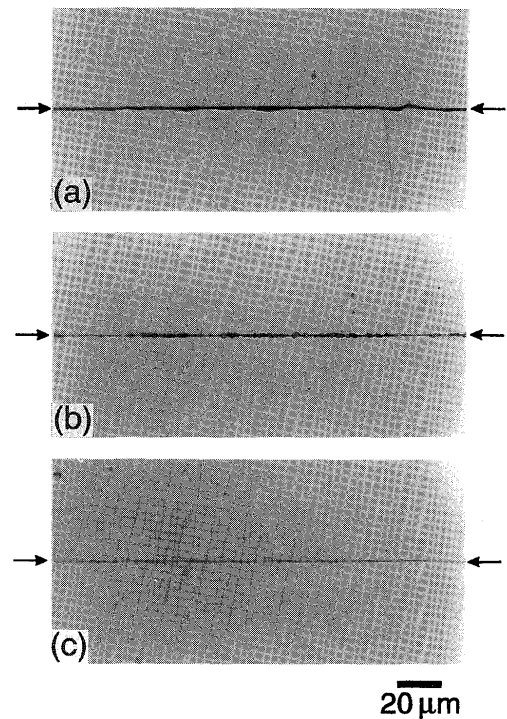

Fig. 6 Optical micrographs of bond interfaces of Al-0.6at% Mg alloy ($t_w = 1.8$ ks): (a) $T_w = 793$ K, $P_w = 1.2$ MPa , (b) $T_w = 833$ K, $P_w = 1$ MPa, and (c) $T_w = 873$ K, $P_w = 1$ MPa.

film (see Fig. 3(b)). The characteristic X-ray of O observed in Fig. 4 was presumably due to the superficial oxide film of the TEM specimen.

In contrast, as can be seen from **Fig. 5**(a), a peak of Mg was clearly observed as well as those of Al and O in the amorphous oxide film at the interface of the Al-0.06% Mg alloy bonded at 813 K. The intensity of the characteristic X-ray of Mg shown in Fig. 5(a) was much higher than that detected in the adjacent matrix. Similar results were also obtained for the joints of the Al-0.6% Mg and Al-1.6% Mg alloys (see Figs. 5(b) and 5(c)).

Thus, while Mg atoms concentrated in the interfacial amorphous oxide film prior to its alteration to the crystalline particles, no concentration of Si, Mn, Zn, or Cu was observed, even when their contents in the matrix were much higher. That is, the interfacial amorphous oxide film underwent a marked compositional change depending on the alloying elements, even if no distinct morphological effect can be detected.

3.3 Optical microstructure of joint interfaces of Al-Mg binary alloys

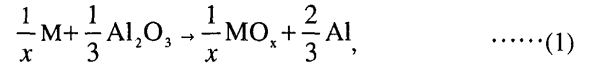In order to investigate the influence of the morphological changes of the interfacial oxide on the

optical microstructure, joint interfaces of the Al-0.6at% Mg alloy bonded at various temperatures were observed with an optical microscope. As shown in **Fig. 6**(a), the joint interface appeared as a rather continuous black band several μm in width at a bonding temperature of 793 K, viz. when the continuous amorphous oxide film remained over almost whole area of the joint interface. As can be seen in Figs. 6(b) and 6(c), with the increase in the bonding temperature, the black band became narrower and discontinuous. These results suggest a plausible correspondence between the annihilation of the interfacial amorphous oxide film and the disappearance of the black band. The optical microstructure of the joint interface, however, is quite sensitive to the polishing and etching conditions, which made it difficult to establish the morphology of the interfacial oxide from the optical microstructure.
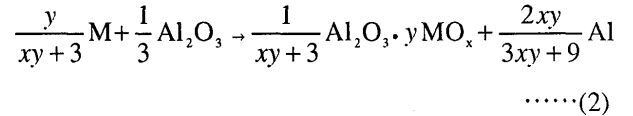
4. Discussion

In previous papers[6-9], it has been found that Mg in the Al alloy can alter the morphology of the interfacial oxide from amorphous film to crystalline particles at Mg contents not less than 0.06at%, whereas Si, Zn, and Cu in commercial Al alloys containing Mg have almost no influence on the morphology of interfacial oxide. From these observations and the results described in §3.1, it follows that alloying elements of Si, Mn, Zn, and Cu of about 1at% have almost no influence on the morphology and composition of interfacial oxide irrespective of the addition of Mg. However, significant influences of these alloying elements on the behavior of the superficial oxide film of Al alloys have been reported in papers concerning surface oxidation; e.g., by in-situ TEM observations in a vacuum of 1.3 x 10^{-2} Pa at temperatures between 673 K and 793 K, Scamans et al.[10] found the formation of crystalline particles of Al-Zn spinel oxide on the surface of the Al-7mass% Zn alloy. In addition, they have reported that only MgO was formed on the surface of Al-6mass% Zn-3mass% Mg under the same conditions, suggesting that the addition of Mg might have a significant influence on the oxide formation of other alloying elements in contrast to our results mentioned at the beginning of this chapter. Therefore, in order to explain the effects of the alloying elements on the interfacial oxide of a diffusion-bonded joint, the formation reactions of the crystalline oxides are examined from the thermodynamic point of view.

There are two types of possible reactions through which the observed crystalline oxides can be formed from the alloying elements and the superficial oxide
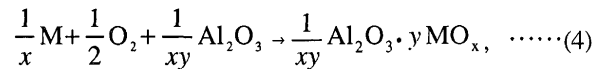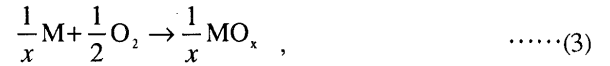
film of aluminum. One of them is the reductive reaction of the oxide film by the alloying element. The reductive reactions to form a simple oxide of MO_x and a complex oxide of $Al_2O_3 \cdot y(MO_x)$ can be expressed by following equations:

$$\frac{1}{x}M + \frac{1}{3}Al_2O_3 \rightarrow \frac{1}{x}MO_x + \frac{2}{3}Al, \quad \cdots\cdots(1)$$

and

$$\frac{y}{xy+3}M + \frac{1}{3}Al_2O_3 \rightarrow \frac{1}{xy+3}Al_2O_3 \cdot yMO_x + \frac{2xy}{3xy+9}Al \quad \cdots\cdots(2)$$

where M represents the alloying element and the superficial oxide film is assumed to be α-Al_2O_3. The other type of reactions are oxidation reactions due to the oxygen supplied from the atmosphere, and expressed by the following equations:

$$\frac{1}{x}M + \frac{1}{2}O_2 \rightarrow \frac{1}{x}MO_x \quad , \quad \cdots\cdots(3)$$

$$\frac{1}{x}M + \frac{1}{2}O_2 + \frac{1}{xy}Al_2O_3 \rightarrow \frac{1}{xy}Al_2O_3 \cdot yMO_x, \quad \cdots\cdots(4)$$

The values of x and y in eqs. (1) - (4) are determined from those of the most stable oxides in the respective systems at the bonding temperatures employed. That is, $x = 1$ for the oxides of Mg, Mn, Zn, and Cu, and $x = 2$ for the Si oxide. For the complex oxides of Mg, Mn, Zn, and Cu, y is assumed to be 1, and for the complex oxide of Si, y is assumed to be 2/3 (mullite)[12,13]. Free energy change $\Delta G_f(1)$ - $\Delta G_f(4)$ caused by reaction (1) - (4) can be described by the following equations:

$$\Delta G_f(1) = \frac{1}{x}\Delta G^0_{f,MO_x} - \frac{1}{3}\Delta G^0_{f,Al_2O_3} + R T \cdot \ln\frac{a_{Al}^{\frac{2}{3}}}{a_M^{\frac{1}{x}}} \quad \cdots\cdots(5)$$

$$\Delta G_f(2) = \frac{1}{xy+3}\Delta G^0_{f,Al_2O_3 \cdot yMO_x} - \frac{1}{3}\Delta G^0_{f,Al_2O_3} + RT \cdot \ln\frac{a_{Al}^{\frac{2xy}{3xy+9}}}{a_M^{\frac{y}{xy+3}}} , \quad \cdots\cdots(6)$$

$$\Delta G_f(3) = \frac{1}{x}\Delta G^0_{f,MO_x} + RT \cdot \ln\frac{1}{a_M^{\frac{1}{x}} \cdot Po_2^{\frac{1}{x}}} , \quad \cdots\cdots(7)$$

$$\Delta G_f(4) = \frac{1}{xy}\Delta G^0_{f,Al_2O_3 \cdot yMO_x} - \frac{1}{xy}\Delta G^0_{f,Al_2O_3} + RT \cdot \ln\frac{1}{a_M^{\frac{1}{x}} \cdot Po_2^{\frac{1}{x}}} , \quad \cdots\cdots(8)$$

where $\Delta G^0_{f,Al_2O_3}$, $\Delta G^0_{f,MO_x}$, and $\Delta G^0_{f,Al_2O_3 \cdot yMO_x}$ are the standard free energies of formation of Al_2O_3, MO_x, and
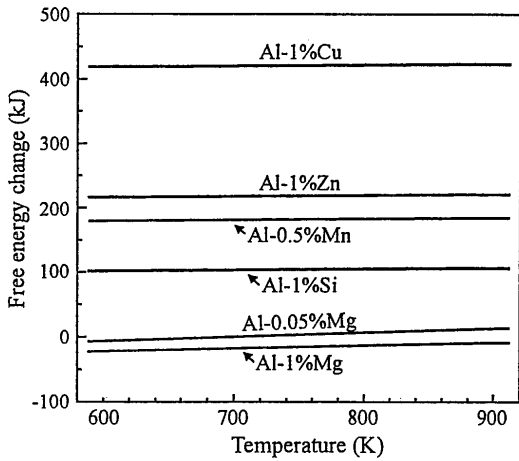
F i g. 7 Free energy changes by reaction (1) in Al-X alloys (X = 0.05at% Mg, 1.0at% Mg, 1.0at% Si, 0.5at% Mn, 1.0at% Zn, and 1.0at% Cu).
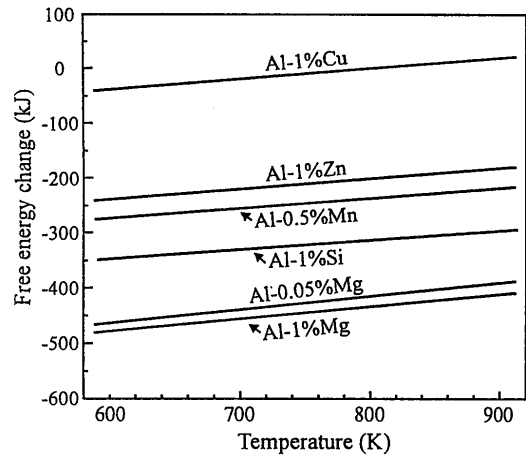

F i g. 9 Free energy changes by reaction (3) in Al-X alloys (X = 0.05at% Mg, 1.0at% Mg, 1.0at% Si, 0.5at% Mn, 1.0at% Zn, and 1.0at% Cu) at partial oxygen pressure = 5x10^{-3} Pa.
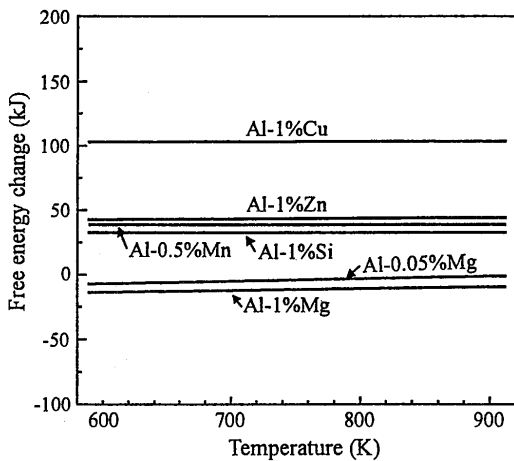

F i g. 8 Free energy changes by reaction (2) in Al-X alloys (X = 0.05at% Mg, 1.0at% Mg, 1.0at% Si, 0.5at% Mn, 1.0at% Zn, and 1.0at% Cu).
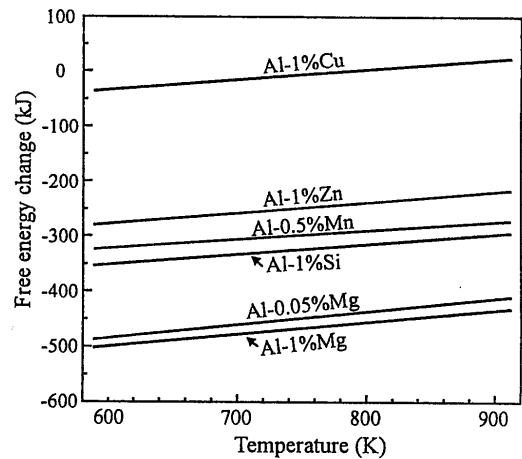

F i g. 1 0 Free energy changes by reaction (4) in Al-X alloys (X = 0.05at% Mg, 1.0at% Mg, 1.0at% Si, 0.5at% Mn, 1.0at% Zn, and 1.0at% Cu) at Po$_2$ = 5×10^{-3} Pa.

$Al_2O_3 \cdot yMO_x$, respectively. The activities of Al and Mg are denoted by a_{Mg} and a_{Al}, and the partial pressure of O_2 in the atmosphere is denoted by Po_2.

Free energy changes, ΔG_f (1) - ΔG_f (4) , calculated using eqs. (5) - (8) are shown as a function of temperature in **Figs. 7 to 1 0**, respectively. In these calculations, the content of the alloying elements nearly equal to that of the base metal are employed: 0.05at% and 1at% for Mg, 1at% for Si, Zn, and Cu, and 0.5at% for Mn. The reported values are employed for the standard free energies of formation of the oxides[14-24]. The activity of Mg is extrapolated from the data reported by Brown et al. for Al-5at% Mg alloy at 660 and 710 K[25]. The activity of Zn is based on the data reported by Takahashi et al. for Al-Zn alloy at 653 K[26].

The activities of Al, Si, Mn, and Cu are assumed to be equal to their atomic fractions. The partial pressure of O_2 was assumed to be $5 \cdot 10^{-3}$ Pa ~ the partial pressure of O_2 in the bonding chamber.

As can be seen from Figs. 7 to 10, the free energy changes caused by reactions (1) - (4) increased in the order of 1at% Mg, 0.05at% Mg, Si, Mn, Zn, and Cu at all bonding temperatures employed. As can be seen from Figs. 7 and 8, ΔG_f (1) and ΔG_f (2) take positive values over a temperature range from 600 to 900 K except for those in the Al-1at% Mg and Al-0.05at% Mg alloys. In Al-1at% Mg alloy both ΔG_f (1) and ΔG_f (2) take negative values at all temperatures between 600 and 900 K, while in Al-0.05at% Mg alloy ΔG_f (1) takes

positive values at temperatures above 800 K. On the other hand, as can be seen from Figs. 9 and 10, ΔG_f (3) and ΔG_f (4) take negative values over a temperature range from 600 to 900 K except for the Al-Cu alloy, and in the Al-Cu alloy ΔG_f (3) and ΔG_f (4) take positive values at temperatures above about 800 K. These calculated results suggest that the reductive reactions of the interfacial oxide film by alloying elements Si, Zn, Mn, and Cu can not proceed, while the progresses of oxidation reactions (3) and (4) are thermodynamically permissible. However, the oxygen supply from the atmosphere to the joint interface is a prerequisite to the oxidation reactions (3) and (4).

As described in §3.1, no crystalline oxides which involve Si, Mn, Zn, or Cu as a major constituent were observed at the joint interface of the Al-X binary alloys(X = Si, Mn, Zn, Cu). This result implies that reactions (3) and (4) could not proceed during the diffusion bonding probably because of the lack of the oxygen supply from the atmosphere. This assumption is supported by the result reported in a previous paper[9] that the ranges of Mg contents and bonding temperatures where the crystalline oxides of Al_2MgO_4 and MgO formed at the joint interface of Al-Mg binary alloys agreed quite well with those estimated from the free energy changes caused by the reactions (1) and (2). From these results, it follows that the crystalline oxides observed at the joint interface of the Al-Mg binary alloys were formed via the reductive reactions of the interfacial amorphous film by Mg. Consequently, it can be concluded that the formation free energy of the oxide of the alloying element and its activity in the matrix (see eqs. (5) and (6)) are thermodynamic factors that control the morphological change of the interfacial oxide which results from the reductive reaction of the amorphous oxide film by the alloying element.

As mentioned in §3.2, only in the case of the Al-Mg binary alloys, was high concentration of the alloying element in the interfacial amorphous oxide film observed prior to the formation of the crystalline oxides. According to the equilibrium phase diagram, the solid solubility of Mg in the crystalline aluminum oxide α-Al_2O_3 is very small, similar to the other alloying elements at the bonding temperatures employed in this investigation. Therefore, it can be suggested that the amorphous oxide film of aluminum has much higher solubility for elements with strong affinity for oxygen than the crystalline oxide.

5. Conclusions

The effects of the alloying element on the morphology and composition of interfacial oxides in the diffusion-bonded joint have been investigated by TEM observations for Al binary alloys containing 0.06-2.0at% Mg, 1.0at% Si, 0.5at% Mn, 1.0at% Zn, and 1.0at% Cu, and discussed from the thermodynamic point of view. Results obtained are summarized as follows :

(1) At bonding temperatures around 873 K, the continuous amorphous oxide film remained at the joint interfaces of Al-X binary alloys (X = Si, Mn, Zn, Cu), which indicated that the alloying elements of approximately 1at% of Si, Mn, Zn, and Cu have no significant influences on the morphology of the interfacial amorphous oxide film. On the other hand, as reported in a previous paper[9], Mg could alter the morphology of the interfacial oxide from amorphous films to crystalline particles of MgO and Al_2MgO_4 at Mg contents not less than 0.06at%.

(2) Marked concentration of Mg in the interfacial amorphous oxide film occurred prior to the alteration from the amorphous film to the crystalline particle, whereas no concentration of the other alloying elements could be detected.

(3) The difference in the effects of the alloying elements between Mg and the other elements on the morphology of the interfacial oxide could be explained in terms of the free energy changes caused by the reductive reactions of the interfacial amorphous oxide film by the alloying elements. That is, under the diffusion-bonding conditions employed, the free energy changes in Al-Mg binary alloys take negative values, and so the progress of the reductive reactions is permissible. In contrast, since those in the other alloys take positive values, the reductive reaction cannot proceed. From thermodynamic calculation, it can be concluded that the free energy of the oxide formation and activity of the alloying element are major thermodynamic factors which control the progress of the reductive reactions and resulting morphological change of the interfacial oxide from the amorphous film to the crystalline particle.

References

1) T. Enjo, K. Ikeuchi, and N. Akikawa : Trans. JWRI, **10** (1981), 45.

2) T. Enjo, K. Ikeuchi, and K. Furukawa : Trans. JWRI, **14** (1985), 115.

3) T. Enjo, K. Ikeuchi, and H. Fujita : Trans. JWRI, 1 5 (1986), 117.

4) T. Enjo, K. Ikeuchi, and H. Yoshikawa : IIW Doc. No.

IX-1561-89, (1998).

5) K. Kotani, K. Ikeuchi, and F. Matsuda : IIW. Doc. No. IX-1797-95, (1995).

6) K. Ikeuchi, K. Kotani, and F. Matsuda : Quart. J. Japan Weld. Soc., 1 4(1996), 122.

7) K. Kotani, K. Ikeuchi, and F. Matsuda : Quart. J. Japan Weld. Soc., 1 4(1996), 382.

8) K. Kotani, K. Ikeuchi, and F. Matsuda : Quart. J. Japan Weld. Soc., 1 4(1996), 389.

9) K. Kotani, K. Ikeuchi, and F. Matsuda : Quart. J. Japan Weld. Soc., 1 4(1996), 551.

10) G.M. Scamans and E.P. Butler: Metall. Trans. A, 6(1975), 2055.

11) T. Enjo, K. Ikeuchi, and T. Horinouchi : Trans. JWRI, 1 5(1986), 61.

12) S. Aramaki and R. Roy: J. Am. Ceram. Soc., 4 5(1962), 229.

13) F.J. Klug and S. Prochazka: J. Am. Ceram. Soc., 7 0(1987), 750.

14) (for Al_2O_3) I. Barin: Thermochemical Data of Pure Substances, VCH (1989), p.48.

15) (for MgO) ibid., p.868 .

16) (for SiO_2) ibid., p.1359.

17) (for MnO) ibid., p.900.

18) (for ZnO) ibid., p.1690.

19) (for CuO) ibid., p.483.

20) (for Al_2MgO_4) ibid., p.869.

21) (for $Al_6Si_2O_{13}$) ibid., p.61.

22) (for Al_2MnO_4) ibid., p.903.

23) (for Al_2ZnO_4) I. Barin: Thermochemical Data of Pure Substances, VCH (1989), p.17, p.1681, M.Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frutip, R.A. McDonald, and A.N. Syverud: JANAF Thermochemical Tables, Third Edition, American Institute of Physics(1985), p.1667, O. Knacke, O. Kubaschewski, and K. Hesselmann :Thermochemical Properties of Inorganic Substances I, Second Edition, Springer-Verlag (1991), p.2369.

24) (for Al_2CuO_4) I. Barin: Thermochemical Data of Pure Substances, VCH (1989), p.17, p.465, M. Chase, Jr., C.A. Davies, J.R. Downey,Jr., D.J. Frutip, R.A. McDonald, and A.N. Syverud: JANAF Thermochemical Tables, Third Edition, AmericanPhysi (1985),p.1667, O. Knacke, O. Kubaschewski, and K. Hesselmann : Thermochemical Properties of Inorganic Substances I, Second Edition, Springer-Verlag (1991), p.626.

25) J.A. Brown and J.N. Pratt : Metall. Trans., 1(1970), 2743.

26) T. Takahashi and N. Asano: The memoir of the Niihama Technical College, 18(1982), 78.