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# Effect of Oxide Film on the Early Process of Diffusion Welding†

— Study of the Early Process of Diffusion Welding by Means of Electric Resistance Measurement (Report I) —

Toshio ENJO\*, Kenji IKEUCHI\*\* and Naofumi AKIKAWA \*\*\*

## Abstract

The early bonding process of diffusion welding of metals has been investigated by means of electric resistance measurement of bonding zone with particular reference to the behavior of oxide film on faying surfaces; a couple of base metals were placed in a vacuum with their faying surfaces in contact, and the electric resistance across bonding interface was measured in a process of heating the bonding zone from room temperature to a temperature below melting point at a constant rate. The base metals used were commercially pure aluminum, titanium, iron, copper and silver.

The electric resistance across bonding interface  $\rho$  for each metal was higher than the resistivity  $\rho_M$  of base metal at room temperature before heating and approached  $\rho_M$  as the bonding zone was heated. The initial values of the electric resistance  $\rho$  (at room temperature before heating) except for silver were considerably higher than that estimated using the constriction resistance theory on the assumption that the faying surfaces were perfectly clean metallic surface. In particular, those of aluminum and titanium bonding zone were extremely higher.

As the thickness of these oxide films of aluminum, titanium and copper was increased by oxidation treatment in air at a high temperature before welding, the electric resistance  $\rho$  increased evidently in its initial value, and approached the resistivity of the base metal at considerably higher temperature. These results indicate that the oxide film on the faying surface except for silver is one of the most important factor which prevents the attainment of true metal-to-metal contact at the bonding interface.

**KEY WORDS:** (Diffusion Welding) (Oxide) (Contact Resistance)

## 1. Introduction

The diffusion welding is a process by which metals are joined in solid state without remarkable deformation of base metal. It has been pointed out by several authors<sup>1)-5)</sup> that such process of diffusion welding is much influenced by the microscopic state of faying surface. The real surface of metals is in general rough in a microscopic sense and covered with oxide film, chemically reacted and adherent layer, or contaminations (oil, grease, dirt, etc.)<sup>1)</sup>. Among these, the oxide film on the faying surface is regarded as one of the most important factor which makes the contact between metallic surfaces difficult and prevents the formation of metallic bond between the faying surfaces<sup>1),2),3)</sup>. As to the roughness of faying surface which is regarded as another important factor for the bonding process, the joint efficiency decreases in many cases as the faying surface becomes rougher<sup>4),5)</sup>. However, inversely, some investigators<sup>2)</sup>

have reported that a better joint efficiency is obtained by using faying surface with proper roughness.

Bartle<sup>3)</sup> has suggested that in order to attain metallic bond between faying surfaces it is necessary to eliminate the oxide film and microasperities by taking advantage of the diffusion of atoms and deformation in the vicinity of bonding interface. Thus oxide film and microasperities, even though less than 1  $\mu\text{m}$  in thickness or height, can exert significant effects on the bonding process. However it is very difficult to observe the behavior of these microscopic factors with conventional optical microscope or scanning electron microscope. The electric resistance measurement is well known as a method to detect sensitively various changes in microstructure of metals. Therefore the electric resistance measurement is considered to be successfully applied to examine the behavior of the oxide film and microasperities. But little attempt has been made to apply the electric resistance measurement

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to an investigation concerning the bonding process<sup>6)</sup>.

In the present investigation, the electric resistance measurement across bonding interface has been applied to examine the behavior of oxide film in the early process of diffusion welding; a couple of base metals were set in a vacuum with their faying surfaces in contact at a constant welding pressure and the electric resistance across the bonding interface was measured in a process of heating the bonding zone from room temperature to a temperature below melting point. The obtained electric resistance across the bonding interface are analyzed on the basis of the constriction resistance theory. The effect of the faying surface roughness on the bonding process will be reported in a subsequent report.

## 2. Constriction Resistance

In the early process of diffusion welding, true contact between the faying surfaces is considered to be restricted within very narrow area. In such a case, the electric resistance across the bonding interface can be described by the constriction resistance theory<sup>7)</sup>, assuming that the faying surfaces are perfectly clean metallic surfaces. As schematically shown in Fig. 1, the constriction resistance is the consequence of the current flow being constricted through a small conduction spot. When a couple of semi-infinite dimensional metals are in contact with each other at a small spot (radius:  $a$ ) and the electric properties at the

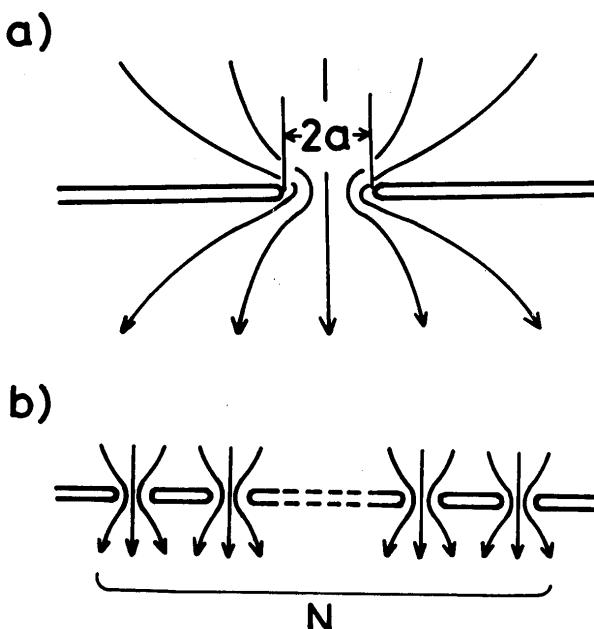


Fig. 1 Schematic diagram showing lines of current flow in cases where  
 (a) true metal-to-metal contact occurs over a circle of radius  $a$ , and  
 (b) true metal-to-metal contact occurs over a number of circles.

contact spot are the same as those of the base metal, the constriction resistance  $R$  is given as<sup>7)</sup>

$$R_C = \rho_M / 2a, \dots \dots \dots \quad (1)$$

where  $\rho_M$  is the electric resistance of base metal.

When plane surfaces such as the faying surface of diffusion welding are brought into contact with each other, a number of contact spots form as shown in Fig. 1 (b). In such a case, the contact resistance is given by considering that resistances which correspond to each contact spot are connected in parallel at the bonding interface. Therefore, if the distance between the contact spots is much larger than the radius of contact spot, the contact resistance across the bonding interface  $R_C$  is given by<sup>7)</sup>

$$R_C = \frac{\rho_M}{2Na} = \frac{\sqrt{\pi} \rho_M}{2\sqrt{NS_M}}, \dots \dots \dots \quad (2)$$

where  $N$  and  $S_M$  are the number of contact spots and the total contact area ( $= \pi Na^2$ ), respectively. Though eqs. (1) and (2) are derived for the contact between semi-infinite dimensional base metals, these equations can be applied to a contact between finite dimensional metals if the area of true contact spots is much smaller than the apparent contact area. In this investigation, the contact resistance per a unit area was adopted in order to compensate the error in the dimensions of base metals. The constriction resistance per a unit area  $\rho_C$  is derived from eq. (2) as

$$\rho_C = R_C S = \frac{\sqrt{\pi} S}{2\sqrt{NS_M}} \cdot \rho_M, \dots \dots \dots \quad (3)$$

where  $S$  is the apparent contact area ( $\simeq$  the area of bonding interface).

As shown in eq. (3), the constriction resistance  $\rho_C$  is inversely proportional to the square root of the area  $S_M$  and number  $N$  of true contact spots. Eq. (3) is derived on the assumption that the faying surfaces are perfectly clean metallic surfaces. However, as described later, the conventional metal surface can not be regarded as clean metallic surface because of the existence of superficial oxide film. Nevertheless, eq. (3) is considered as sufficient to describe the qualitative tendency if the contact spot between metallic surfaces where oxide film is removed is taken as the true contact spot. For instance, if the oxide film is an insulator, eq. (3) can describe approximately the contact resistance across the bonding interface. On the other hand, if the oxide film can not be regarded as an insulator, the electric current flows not only through

the true contact spots but also through the contact spots with oxide film. Consequently, in such a case the electric resistance across the bonding interface is smaller than that given by eq. (3). In other words, the values of  $S_M$  and  $N$  estimated from eq. (3) give their upper limits. Thus the decrease in the electric resistance across the bonding interface is caused by the increase in the area and/or number of the true contact spots and contact spots through the oxide film. However, considering that the oxide film is generally a semiconductor and has rather high resistance, the decrease in the electric resistance across the bonding interface is caused chiefly by the increase in the area and/or number of true contact spots, as pointed out by Kimura et al<sup>6</sup>).

### 3. Experimental Details

Base metals used are commercially pure aluminum, titanium, iron, copper and silver. The aluminum and titanium have very stable and tenacious oxide film on their surfaces. The oxide film of iron is not so stable as those of aluminum and titanium but more stable than those of copper and silver. Table 1 shows the compositions of aluminum, titanium, iron and copper. The base metal of silver was made from a silver plate of 99.99% nominal purity. Figure 2 shows the dimensions of base metals. The faying surface was finished by polishing with emery paper of 1500 grade, and degreased in acetone just before the welding. The faying surfaces were brought into contact with each other in such a way that grooves on the faying surfaces caused by polishing with emery paper crossed at nearly right angle. The mean height  $\bar{h}$  of microasperities on the finished faying surface was estimated from the profile of microasperities obtained with profilometry. The mean height  $\bar{h}$  were 0.7  $\mu\text{m}$  for aluminum, 0.2  $\mu\text{m}$  for silver, 0.15  $\mu\text{m}$  for copper, and 0.1  $\mu\text{m}$  for titanium and iron. In order to investigate the effect of the oxide film on diffusion welding, the thickness of oxide film was increased by oxidation treatment in air at high temperatures after the degreasing in acetone. The oxidation temperatures were 600°C for aluminum and

titanium, and 200°C for copper. After holding at high temperatures, the base metals were cooled in furnace.

The measurement of the electric resistance across the bonding interface was carried out by using a high temperature optical microscope equipped with a compressing device. After the degree of vacuum in welding chamber was of the order of  $10^{-5}$  mmHg, the welding pressure was applied onto the bonding interface, and the contacted base metals were heated at the constant rate of 15°C/min. The bonding zones of the base metals were heated within 1 hr after the finishing with emery paper except for those of the base metals subjected to the oxidation treatment.

The electric resistance measurement was carried out using a conventional potentiometric method as shown in Fig. 3; a constant direct current flew between the terminal

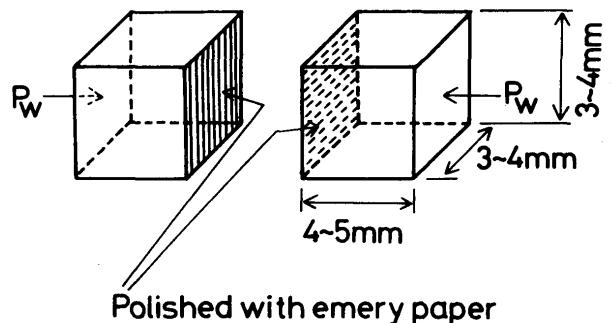


Fig. 2 Dimensions of the base metals used and their configuration for the electric resistance measurement of bond.  $P_W$  denotes welding pressure.

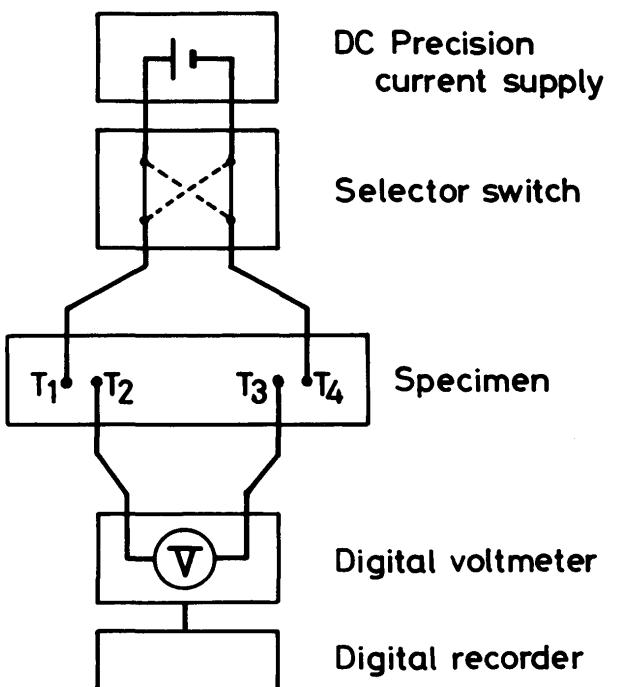


Fig. 3 Schematic diagram showing the circuit for electric resistance measurement.

Table 1 Chemical compositions of base metals used (wt%).

	Cu	Fe	Si	Mg	Mn	Zn	Cr	Ti	Al
Aluminum	0.01	0.24	0.01	0.01	0.01	0.04	0.01	0.01	Bal.
<hr/>									
	C	Fe	N	O	H	Ti			
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Titanium	0.018	0.036	0.0057	0.083	0.0026	Bal.			
<hr/>									
	C	Si	Mn	P	S	Fe			
<hr/>									
Iron	0.019	0.012	0.29	0.010	0.013	Bal.			
<hr/>									
	Pb	Fe	Ni	S	Ag	O	P	Cu	
<hr/>									
Copper	0.0004	0.0007	0.0005	0.0019	0.0011	0.415	-	Bal.	

$T_1$  and  $T_4$ , and the potential difference between the terminal  $T_2$  and  $T_3$  was measured. Then the electric resistance  $R$  between the terminal  $T_2$  and  $T_3$  was evaluated by using Ohm's law. The obtained electric resistance  $R$  consists not only of the resistance across bonding interface, but also of the resistance of the matrix between  $T_2$  and  $T_3$ ; i.e., the electric resistance  $R$  between  $T_2$  and  $T_3$  can be expressed as

$$R = \rho_S/S + (l/S) \cdot \rho_M, \dots \quad (4)$$

where  $l$  is the distance between  $T_2$  and  $T_3$  and  $\rho_S$  the electric resistance across the bonding interface per a unit area. The value of  $S$  and  $l$  in eq. (4) were measured after the electric resistance measurement. In the present investigation,  $\rho$  which is given as the following equation was employed to express the variation of the electric resistance across the bonding interface for comparison with the resistivity of base metal.

$$\rho = \rho_S + \rho_M \dots \quad (5)$$

The electric resistance  $\rho$  corresponds to the resistance of a cubic base metal  $1 \times 1 \times 1$  cm with a square bonding interface  $1 \times 1$  cm.

In order to compensate the effect of thermo-electric power generated in the circuit on the electric resistance measurement, wires of the same metal as the base metal was used as lead wires, and the direction of the current between  $T_1$  and  $T_4$  was reversed. The mean value of the potential difference (between  $T_2$  and  $T_3$ ) for each current direction was adopted for the evaluation of the electric resistance  $R$ . The current flowing between  $T_1$  and  $T_4$  was  $100.00 \pm 0.01$  mA and the smallest detectable change in the potential difference by the digital volt meter was 10 nV.

#### 4. Experimental Results and Discussion

##### 4.1. Electric resistance of bonding zone for various metals.

In the present investigation, the variation of electric resistance  $\rho$  (given by eq. (5)) across bonding interface was investigated in a process where the bonding zone was heated at the constant rate of  $15^\circ\text{C}/\text{min}$ . Figure 4 shows the variation of electric resistance  $\rho$  in the heating process up to  $640^\circ\text{C}$  for aluminum base metal. The variation of electric resistance  $\rho$  in the cooling process subsequent to the heating process is also shown in the figure. The value of  $\rho$  in the cooling process is regarded as nearly equal to the resistivity of the aluminum base metal within experimental error of the magnitude of about 10%. The experimental error was mainly due to the error in the

measurement of the distance  $l$  between  $T_2$  and  $T_3$ . As shown in Fig. 4, the initial value of the electric resistance  $\rho$  was much higher than the resistivity  $\rho_M$  of the base metal, about  $5 \times 10^3$  times as large as  $\rho_M$ . In the heating process from room temperature to  $200^\circ\text{C}$ , the electric resistance of the bonding zone increased with the rise of temperature in the similar manner as the resistivity of the base metal. In the temperature range from  $200^\circ\text{C}$  to  $480^\circ\text{C}$ , the value of  $\rho$  fluctuated largely in many cases as shown in Fig. 4. The amplitude of the fluctuation was different among specimens. A large decrease in  $\rho$  with the rise of temperature was observed in the temperature range from  $480^\circ\text{C}$  to  $630^\circ\text{C}$ . This large decrease in  $\rho$  was accompanied with a deformation of the base metal. At  $630^\circ\text{C}$  just below the melting point of aluminum, the value of  $\rho$  was regarded as nearly equal to the resistivity of the base metal. As described above, the magnitude of the error in the measurement of  $\rho$  was about 10%. Considering this experimental error, the electric resistance  $\rho$  less

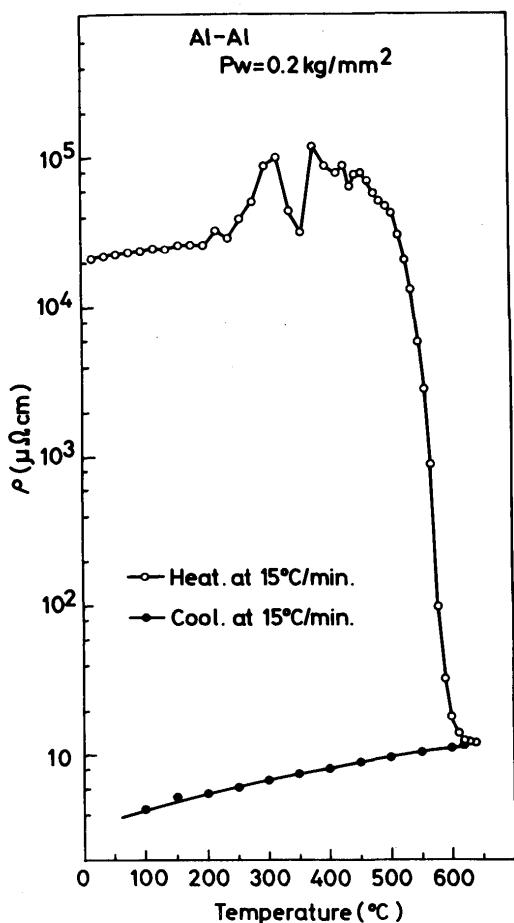


Fig. 4 Variation of electric resistance across bonding interface  $\rho$  with temperature for aluminum in a process of heating (—○—) a couple of base metals which were placed in a vacuum with their faying surfaces in contact, and the variation of  $\rho$  in cooling process (—●—) after the heating up to  $640^\circ\text{C}$ . The heating and cooling rates were  $15^\circ\text{C}/\text{min}$  and welding pressure  $P_W$  was  $0.2 \text{ kg/mm}^2$ .

than  $1.1 \rho_M$  was regarded as nearly equal to the resistivity  $\rho_M$  of the base metal. The upper limit of  $(S_M N/S)$  for  $\rho = 1.1 \rho_M$  is estimated to be about  $10^{-1}$  from eqs. (3) and (5). As to the electric resistance  $\rho$  of titanium, iron, copper and silver, the experimental error in the measurement of  $\rho$  is the same as that described for aluminum.

Figure 5 shows the variation of electric resistance  $\rho$  with temperature for a titanium bonding zone in a heating process up to  $1000^\circ\text{C}$  and subsequent cooling process. The value of electric resistance  $\rho$  in the cooling process is regarded as nearly equal to the resistivity of the base metal within experimental error similarly to that of the aluminum bonding zone. As shown in Fig. 5, the initial value of the electric resistance was much higher than the resistivity  $\rho_M$  of the base metal, about 300 times as large as  $\rho_M$ . The variation of the electric resistance in the heating process can be divided into three stages: stage 1 from room temperature to  $320^\circ\text{C}$  where  $\rho$  decreased markedly with the rise of temperature, stage 2 from  $320^\circ\text{C}$  to  $500^\circ\text{C}$  where  $\rho$  changed slightly and stage 3 from  $500^\circ\text{C}$  to  $870^\circ\text{C}$  where  $\rho$  decreased gradually with the rise of temperature. The upper limit of  $(S_M N/S)$  at the final temperature of stage 1 where  $\rho$  decreased most largely is estimated to be 0.02 from eqs. (3) and (5). The decrease in the resistance  $\rho$  observed from  $870^\circ\text{C}$  to  $910^\circ\text{C}$  is considered to be related to the  $\alpha \rightarrow \beta$  phase transformation of titanium. As shown in Fig. 5, the electric resistance  $\rho$  approached quickly to the resistivity of the base metal as the  $\alpha \rightarrow \beta$  phase transformation was undertaken. This fact indicates that the bonding process is accelerated by undertaking the  $\alpha \rightarrow \beta$  phase transformation. This result is consistent with that reported by authors<sup>8)</sup> in a previous paper about the effect of  $\alpha \rightleftharpoons \beta$  phase transformation on the bonding process of titanium.

Figure 6 shows the variation of electric resistance  $\rho$  with temperature for an iron bonding zone in the heating process up to  $1000^\circ\text{C}$  and subsequent cooling process. The value of electric resistance  $\rho$  in the cooling process is regarded as nearly equal to the resistivity of the base metal within experimental error. As shown in Fig. 6, the variation of electric resistance  $\rho$  can be divided into three stages similarly to that of the titanium bonding process: stage 1 from room temperature to  $370^\circ\text{C}$ , stage 2 from  $370^\circ\text{C}$  to  $760^\circ\text{C}$  and stage 3 from  $760^\circ\text{C}$  to  $850^\circ\text{C}$ . The upper limit of  $(S_M N/S)$  at the final temperature of stage 1 is estimated to be 0.15 from eqs. (3) and (5). In the bonding process of iron, the decrease in electric resistance  $\rho$  which could be related to  $\alpha \rightarrow \gamma$  phase transformation was not observed in contrast to the  $\alpha \rightarrow \beta$  phase transformation of titanium.

Figure 7 shows the variation of electric resistance  $\rho$  with temperature for a copper bonding zone in the heat-

ing process up to  $1000^\circ\text{C}$  and subsequent cooling process. The value of  $\rho$  in the cooling process is regarded as nearly equal to the resistivity of the base metal within experimental error. The initial value of  $\rho$  of the copper bonding zone was about 6 times as large as the resistivity of the

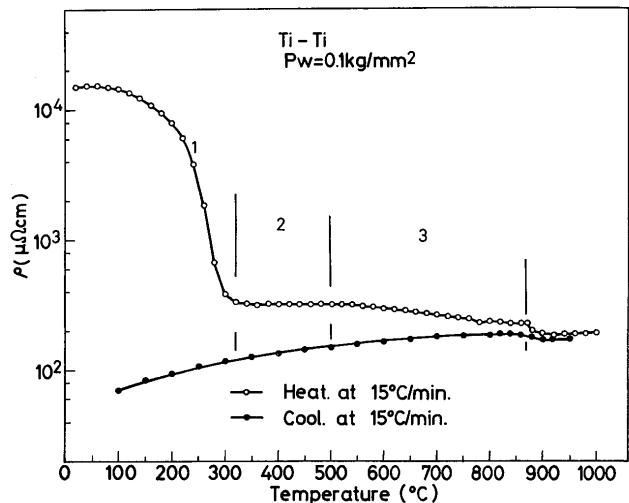


Fig. 5 Variation of electric resistance  $\rho$  with temperature for titanium in a heating process ( $\circ$ ) of the bonding interface up to  $1000^\circ\text{C}$  and cooling process ( $\bullet$ ) after the heating.

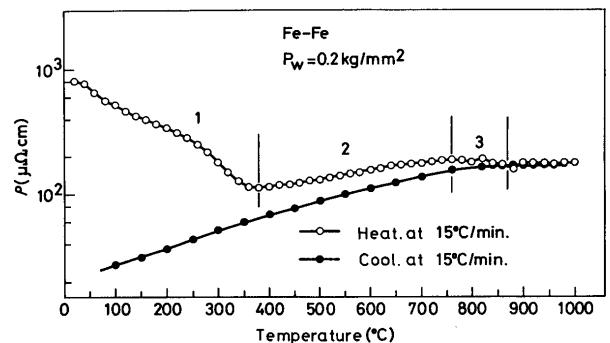


Fig. 6 Variation of electric resistance  $\rho$  with temperature for iron in a heating process ( $\circ$ ) of the bonding interface up to  $1000^\circ\text{C}$  and cooling process ( $\bullet$ ) after the heating.

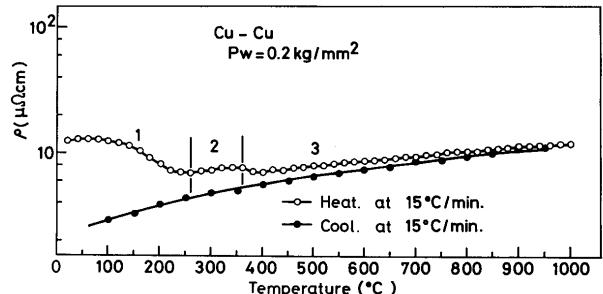


Fig. 7 Variation of electric resistance  $\rho$  with temperature for copper in a heating process ( $\circ$ ) of the bonding interface up to  $1000^\circ\text{C}$  and cooling process ( $\bullet$ ) after the heating.

base metal, much smaller than those of the aluminum and titanium bonding zone. The variation of electric resistance  $\rho$  can be divided into three stages as shown in Fig. 7. The electric resistance  $\rho$  in the heating process is regarded as nearly equal to the resistivity of the base metal at about 600°C. The upper limit of  $(S_M N/S)$  at the final temperature of stage 1 is estimated to be 0.2 from eqs. (3) and (5).

Figure 8 shows the variation of electric resistance  $\rho$  with temperature for a silver bonding zone in the heating process up to 900°C and subsequent cooling process. The value of  $\rho$  in the cooling process is regarded as nearly equal to the resistivity of the base metal within experimental error. The initial value of electric resistance  $\rho$  for the silver bonding zone was lowest in the metals used in the present investigation. No remarkable decrease in the electric resistance  $\rho$  was observed and  $\rho$  approached gradually the resistivity  $\rho_M$  of the base metal. And the  $\rho$  became nearly equal to  $\rho_M$  at about 600°C.

Table 2 lists the ratios  $(\rho_I/\rho_M)$  of the initial value of electric resistance  $\rho_I$  ( $\rho$  at room temperature before the heating) to the resistivity of the base metal  $\rho_M$ . As shown in the table, the values of  $(\rho_I/\rho_M)$  for aluminum and titanium are very large. In order to examine the cause for such high value of  $(\rho_I/\rho_M)$ , the electric resistance across bonding interface is analyzed on the basis of the constriction resistance theory.

If the faying surface was a perfectly clean metallic surface, the contact area  $S_A$  to bear the welding pressure  $P_A$  at bonding interface would correspond to the area  $S_M$  where true metal-to-metal contact was attained. The area  $S_A$  is given approximately by

$$S_A = \frac{P_A}{\alpha P_M} \cdot S, \quad \dots \dots \dots \quad (6)$$

where  $P_M$  is the yield stress of the base metal and  $\alpha$  is a constant  $\simeq 1.5^9$  as far as the deformation of microasperities is small. In this case, as described in § 2, the electric resistance across bonding interface  $\rho_S$  corresponds to the constriction resistance  $\rho_C$ . Consequently, when eqs. (3) and (6) are substituted into eq. (5),  $(\rho_I/\rho_M)$  is expressed as

$$\frac{\rho_I}{\rho_M} = \frac{\sqrt{\pi}}{2} \sqrt{\frac{\alpha S P_M}{N P_A}} + 1. \quad \dots \dots \dots \quad (7)$$

The number of contact spots  $N$  required for plane surfaces to be in stable contact with each other is not less than 3. Within experimental condition of this investigation, the value of  $(P_M/P_A)$  is less than 400 and  $S \simeq 0.16 \text{ cm}^2$ . When these values of  $N$ ,  $(P_M/P_A)$  and  $S$  are substituted into eq. (7), the maximum value of  $(\rho_I/\rho_M)$  is estimated

to be 6, which is smaller compared with those of metals except for silver. This fact indicates that the faying surfaces of metals except for silver are not clean metallic surface.

As shown in Table 2, the values of  $(\rho_I/\rho_M)$  are remarkably large for aluminum and titanium having stable and tenacious oxide film. From this result, it is suggested that the oxide film is an important factor which prevents true metal-to-metal contact at bonding interface.

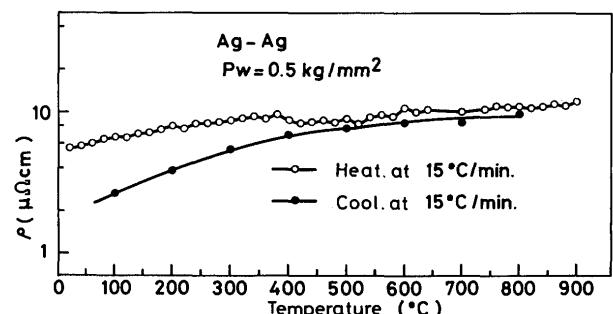


Fig. 8 Variation of electric resistance  $\rho$  with temperature for silver in a heating process (—○—) of the bonding interface up to 900°C and cooling process (—●—) after the heating.

Table 2 Ratio of initial electric resistance across bonding interface  $\rho_I$  to resistivity of base metal  $\rho_M$  for various base metals.

Metals	$\rho_I/\rho_M$
Al	800 ~ 8000
Ti	100 ~ 2000
Fe	8 ~ 70
Cu	5 ~ 20
Ag	2 ~ 3

#### 4.2. Effect of superficial oxide film on the electric resistance across bonding interface

In order to investigate the effect of superficial oxide film on the bonding process, the thickness of oxide film of aluminum, titanium and copper base metals was increased by oxidation treatment in air at high temperatures before the welding.

Figure 9 shows the variation of electric resistance  $\rho$  with temperature for the aluminum bonding process using base metals subjected to the oxidation treatment at 600°C for 2 hr and 4 hr. As shown in the figure, in case where the thickness of oxide film was increased, the initial value of electric resistance  $\rho$  increased remarkably and the temperature range where  $\rho$  largely decreased shifted to a higher temperature range compared with those for bonding process using the as-polished base metals (not subjected to the oxidation treatment). From these results it can

be concluded that the oxide film on the faying surfaces is an important factor which causes the electric resistance of the bonding zone larger than the resistivity of the base metal even at a temperature higher than 600°C. Thus the disruption of the oxide film is not sufficient for the electric resistance of the bonding zone to be equal to the resistivity of base metal unless the heating temperature became just below the melting point.

Figure 10 shows the effect of the thickness of superficial oxide film on the bonding process of titanium. The thickness of the oxide film was increased by the oxidation treatment in air at 600°C for 20 and 60 min. According to Peshkov<sup>10)</sup>, the thickness is about 600 Å after the oxidation for 20 min and 860 Å after the oxidation for 60 min. As shown in Fig. 10, the initial value of the

electric resistance  $\rho$  increased and the temperature range where  $\rho$  largely decreased in the heating process shifted to higher temperature as the thickness of oxide film was increased. These facts indicate that for the bonding process of titanium the oxide film on the faying surface is an important factor which prevents the attainment of true metal-to-metal contact at the bonding interface. However, in contrast to the aluminum bonding process, even in case using the oxidized base metals, the electric resistance  $\rho$  of titanium bonding zone approached the resistivity  $\rho_M$  of the base metal at a temperature about 800°C much lower than the melting point. And  $\rho$  became nearly equal to  $\rho_M$  as the  $\alpha \rightarrow \beta$  phase transformation was undertaken.

Figure 11 shows the effect of the thickness of oxide film on the bonding process of copper. The thickness of oxide film was increased by the oxidation treatment in air at 200°C for 20, 60 and 180 min. As shown in Fig. 11, the electric resistance  $\rho$  increased largely in its initial value and approached the resistivity of the base metal at higher temperatures as the thickness of oxide film was increased. Consequently in the bonding process of copper the oxide film is considered as an important factor which prevents the attainment of true metal-to-metal contact at the bonding interface.

According to an equilibrium phase diagram<sup>11)</sup>, there are two kinds of copper oxide (CuO and Cu<sub>2</sub>O), and the oxide Cu<sub>2</sub>O decomposes into CuO and Cu at temperatures below 375°C by eutectoid reaction. However, it has been said<sup>12), 13), 14)</sup> that the oxide film formed by oxidation in air at a temperature about 200°C consists of both Cu<sub>2</sub>O and CuO and the amount of Cu<sub>2</sub>O formed is

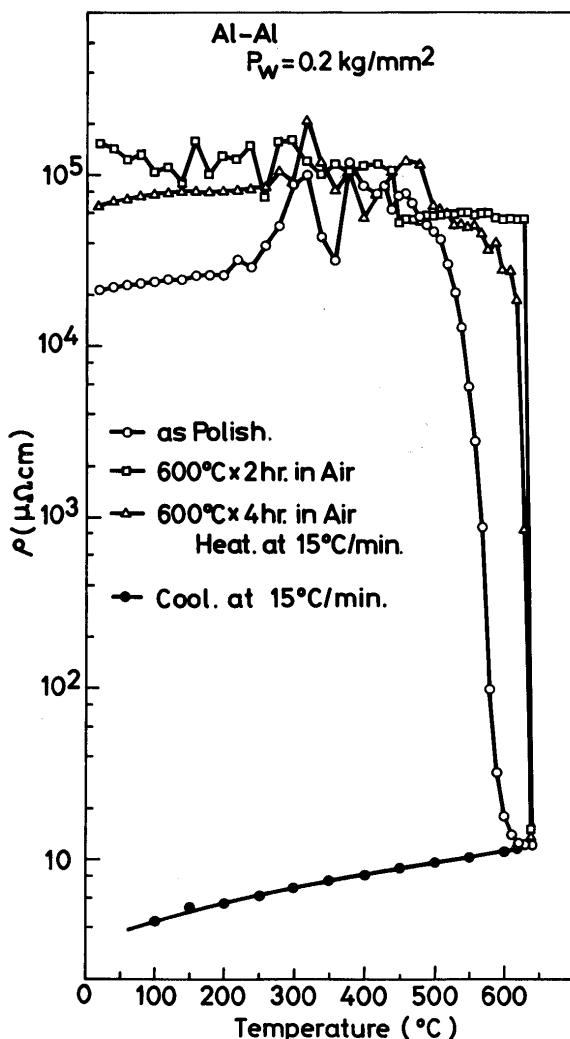


Fig. 9 Effect of increase in the thickness of superficial oxide film on the variation of the electric resistance  $\rho$  with temperature for aluminum in a heating process of the bonding interface. The faying surfaces were oxidized in air at 600°C for 2 hr (—□—) and 4 hr (—△—) before the welding.

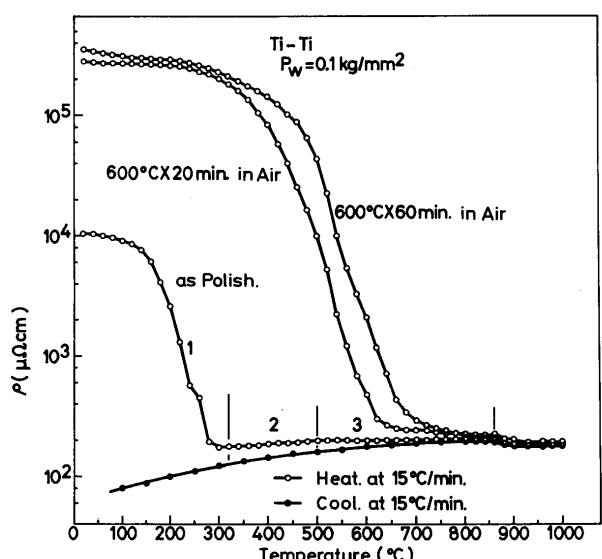


Fig. 10 Effect of increase in the thickness of superficial oxide film on the variation of electric resistance  $\rho$  with temperature for titanium in a heating process of the bonding interface. The faying surfaces were oxidized in air at 600°C for 20 min and 60 min before the welding.

considerably larger than that of CuO. The resistivity of the oxide  $\text{Cu}_2\text{O}$  (semi-conductor) decreases with the rise of temperature<sup>1,5)</sup> and the resistivity of the oxide has been reported to decrease at much higher rate with the rise of temperature above 350°C than that below 350°C, which is nearly equal to the starting temperature of stage 3<sup>1,5)</sup>. On the other hand, according to the equilibrium phase diagram, CuO forms  $\text{Cu}_2\text{O}$  by reaction with Cu above 375°C. The oxide CuO is in general a dielectric or an insulator and so the resistivity of CuO is considered to be higher than that of  $\text{Cu}_2\text{O}$  which is a semi-conductor. Consequently the reaction  $\text{CuO} + \text{Cu} \rightarrow \text{Cu}_2\text{O}$  leads to a decrease in the electric resistance of the oxide film. In addition, the volume change caused by this reaction is considered to promote the disruption of the oxide film. All of these changes in the electric resistance and reaction of the oxide film have a possibility to promote the decrease in the electric resistance across the bonding interface in the temperature range above about 350°C. Therefore it seems that these changes in the resistivity and reaction of the oxide film are related to the initiation of stage 3.

## 5. Summary

The early process of diffusion welding for several kinds of commercially pure metals (aluminum, titanium, iron, copper and silver) was investigated by means of electric resistance measurement with particular reference to oxide film on faying surface. A couple of base metals were placed in a vacuum with their faying surfaces in contact at a constant welding pressure and the couple was heated at

a constant rate from room temperature to a temperature below melting point. The electric resistance across bonding interface  $\rho$  was measured during the heating process and the result was analyzed on the basis of the theory of constriction resistance. Results obtained are summarized as follows;

- (1) The electric resistance across bonding interface  $\rho$  for each metal was higher than that of the base metal at the beginning of heating and approached that of the base metal as the bonding interface was heated. The temperature at which the value of  $\rho$  became to be nearly equal to the resistivity of the base metal was different among the base metals; the temperature was 630°C for aluminum, 900°C for titanium, 850°C for iron, 600°C for copper and 500°C for silver.
- (2) The ratios of the initial electric resistance across bonding interface (before heating) to the resistivity of the base metals except for silver were rather higher than the value ( $\approx 6$ ) estimated from constriction resistance theory on the assumption that the faying surfaces were perfectly clean metallic surfaces. In particular those of the aluminum and titanium which had stable and tenacious oxide film on the faying surface were much higher ( $10^2 \sim 10^5$ ). This fact suggests that the faying surfaces of metals except for silver are not clean metallic surfaces but have factors which prevent true metal-to-metal contact at the bonding interface.
- (3) The electric resistance across bonding interface of aluminum, titanium and copper increased largely, as the thickness of oxide film on the faying surfaces increased (the faying surfaces were subjected to oxidation treatment in air at a high temperature before welding). And the temperature at which the value of  $\rho$  approached the resistivity of the base metal became higher with increasing the thickness of oxide film.

These results described above indicate that the oxide film is an important factor which prevents true metal-to-metal contact at the bonding interface.

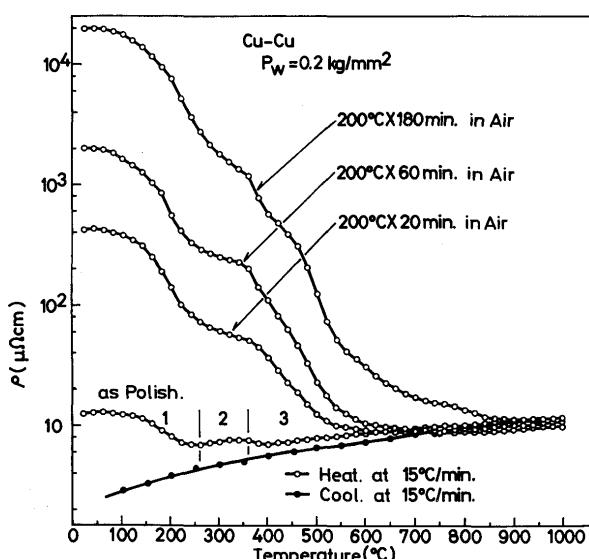


Fig. 11 Effect of increase in the thickness of superficial oxide film on the variation of electric resistance  $\rho$  with temperature for copper in a heating process of the bonding interface. The faying surfaces were oxidized in air at 200°C for 20 min, 60 min and 180 min.

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