Effect of Iron Content in Brazing Filler Metals on Corrosion of Brazed Aluminum

Tadashi TAKEMOTO* and Ikuo OKAMOTO**

Abstract

Immersion type corrosion tests in aqueous sodium chloride solution have been carried out on brazed aluminum and its alloys to clarify the effect of iron content in Al-10%Si system filler metals. Only 1100 base metal was influenced by the iron content of filler metals. The pit depths of 1100 base metal at brazed interface and bulk were increased with the increase of iron content of filler metals, however, the pit depths were almost constant in the range of 0.5 ~ 1.4%Fe. The pit depths of the other base metals (99.99%Al and 3003) were immune to iron content of filler metals up to 1.4%Fe. The different effect of iron are attributable to the electrochemical characteristics of base metals. Base metals with lower electrode potential than filler metals and with large hysteresis in anodic polarization curves are suggested to be easily influenced by the iron content in filler metals.

KEY WORDS: (Corrosion) (Brazing) (Brazing Filler Metals) (Aluminum) (Pitting Corrosion) (Iron) (Chlorides)

1. Introduction

Many types of aluminum heat exchangers have been produced especially for automobiles. These heat exchangers are required to have high corrosion resistance. The corrosion-perforation due to pitting corrosion of tube materials should be avoided. In aluminum alloys, iron, one of the main impurity elements, forms intermetallic compounds with high electrode potential,[1),2)] the compounds were known to act as effective cathodes for pitting.[3)] A precise work has been performed by Seri *et al.*[4)] Iron is included as an impurity element in the commercial aluminum base metals and filler metals. Minagawa *et al.*[5)] demonstrated the iron segregated at the front of spread filler metal and promoted the pitting corrosion of base metal. But the mechanism of segregation during brazing and the effects of iron content on pitting corrosion of brazed aluminum and base metal composition have not been investigated yet.

The purpose of present work is to clarify the effect of iron content in filler metals on the corrosion behavior of brazed aluminum base metal. The effect of brazed base metal composition on the corrosion was also studied.

2. Materials and Experimental Procedures

2.1 Materials

The base metals are 3003-H14, 1100-H14 commercial alloys and pure aluminum (99.99%Al, 80% cold reduction). The chemical compositions of the base metals are shown in **Table 1**. The surface treatment of base metals was electropolishing or as received condition with ultrasonic degreasing in an aceton bath. Electropolishing was performed in perchloric acid-ethanol solution. The surface of laboratory made pure aluminum plate was not so clean as the commercial ones, therefore the pure aluminum was polished by 600 grade emery paper, followed by 10%NaOH cleaning and 30%HNO_3 neutralization treatment prior to brazing.

The filler metals were melted in graphite crucibles with 99.99%Al and high purity materials. After cast, homogenizing and hot rolling, the filler metals were cold rolled to 1 mm thickness. The chemical compositions of filler metals are listed in **Table 2**.

To investigate the corrosion of brazed specimens, base

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

Base metal	Element						
	Fe	Si	Cu	Mn	Mg	Ti	Al
Pure Al	0.002	0.003	0.002	—	—	—	Bal.
1100	0.23	0.08	0.03	0.02	—	—	Bal.
3003	0.57	0.23	0.14	1.08	0.023	0.021	Bal.

—: <0.01, Zn, Cr: <0.01

Table 2 Nominal chemical compositions of filler metals (wt%).

System of filler metal	Element					
	Si	Fe	Mg	Zn	Sn	Al
Al-10Si-1Mg-Fe	10	—	1	—	—	Bal.
	10	0.15	1	—	—	Bal.
	10	0.3	1	—	—	Bal.
	10	0.5	1	—	—	Bal.
	10	1.4	1	—	—	Bal.

† Received on Nov. 4, 1986
* Research Instructor
** Professor

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

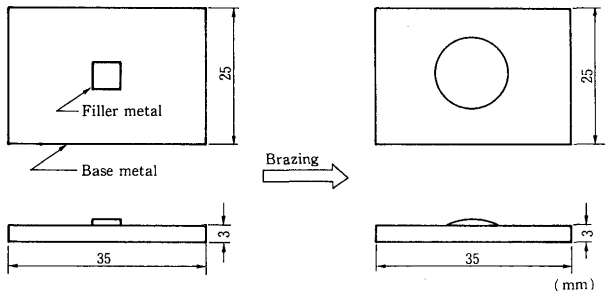

Fig. 1 Shape and size of braze specimen (mm).

materials were cut into rectangular pieces with 35 X 25 X 1 mm along longitudinal direction. Filler metal with 5 X 5 X 1 mm was put at the center of base metal (**Fig. 1**) and then brazed in a vacuum level of 5×10^{-5} torr. Brazing condition was 600°C for 3 min.

2.2 Corrosion test

The brazed specimens were immersed in 0.4 mol/l(M) NaCl + 0.1M H_2O_2 aqueous solution at 30°C for 168 hr. Each specimen was immersed in a glass container respectively (**Fig. 2**). The container contains 300 ml corrosive solution and the specimens were set inclined at 40° to horizontal plane. After immersion test, the corrosion products on the specimen surface were removed by dipping into the HNO_3 aqueous solution. The pit depth were measured by an optical microscope in focusing the surface and bottom of a pit. More than ten deep pits were measured and the mean value of three pits from the maximum was defined as a pit depth. Usually, the triplicate specimens were used under same condition.

2.3 Electrochemical measurement

Electrochemical behavior of filler metals and base metals were investigated by the measurement of anodic and cathodic polarization curves. Poralization curves were obtained by step sweep method. The polarization rate is 10 mV/min if not mentioned. After brazing heat cycle the specimens were polished by emery paper and immersed in 10%NaOH and then neutralized in HNO_3. The surface was covered with silicone resin except the measuring area of 1 cm^2. Polarization tests were carried out in 0.4M NaCl aqueous solution at 30°C in an open air atmospher. Some tests were conducted in 0.4M NaCl solution with pH 10.0 adjusted by additionof 10%NaOH aqueous solution. Electrode potential was measured using saturated calomel electrode (SCE).

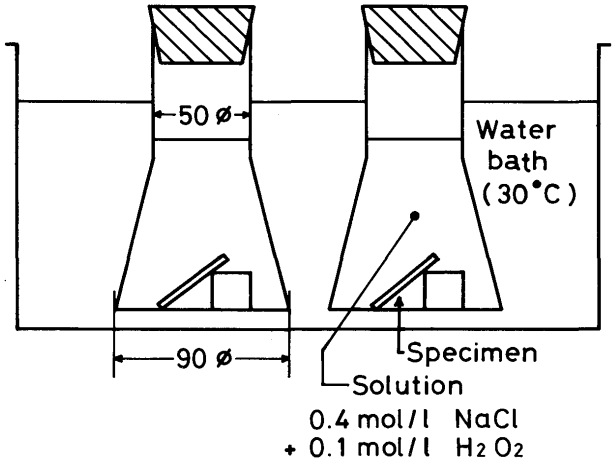

Fig. 2 Schematic of immersion type corrosion test.

Contact current between base metal and filler metal was measured by the zero shunt ammeter. Contact polarization curves were measured by decreasing the resistance of variable resistor between dissimilar materials. The potential of each electrodes was plotted against the contact current between them. Electrometer with input impedance of more than $10^{11}\ \Omega$ was used for the measurement of electrode potential.

Scanning electron microscopy, X-ray diffraction analysis (CuKα, Ni filter, 35 kV, 15 mA) and EPMA analysis were also conducted.

3. Experimental Results

3.1 Effect of iron content in filler metals

The cross section of brazed specimen after corrosion test is shown in **Fig. 3**. The corrosion of base metal was classified into two types. One is the corrosion at the front of spread filler metal (corrosion at interface), and the other is the pitting corrosion of base metal which occurred far from the filler metal (bulk corrosion, Fig. 3). The appearance of cross section differed depending on the base metal composition. The corrosion of 1100 and 3003 base metals were pitting corrosion. The corrosion at interface of 1100 base metal was pitting, but in 3003 base metal the corrosion at interface was not typical pitting but continuous local corrosion along the front of spread filler metal. In pure aluminum, neither sever loccal corrosion nor pitting corrosion was observed both at bulk and interface.

Figure 4 shows the effect of iron content of filler metals on the corrosion of brazed base metals with as received surface. In pure aluminum base metal, the corrosion depths of both interface and bulk were extremely small and were not influenced by the iron content of filler metals. In 3003 base metal, the corrosion depths at bulk plate were larger than the ones at interface, but the corrosion at bulk plate seems to be slightly increased with increasing the iron content. On the other hand, in 1100 base metal, both corrosion depths at interface and bulk were increased with the iron content of filler metals up to 0.5%Fe. Further addition of iron have little influence on the corrosion depth up to 1.4%Fe. The

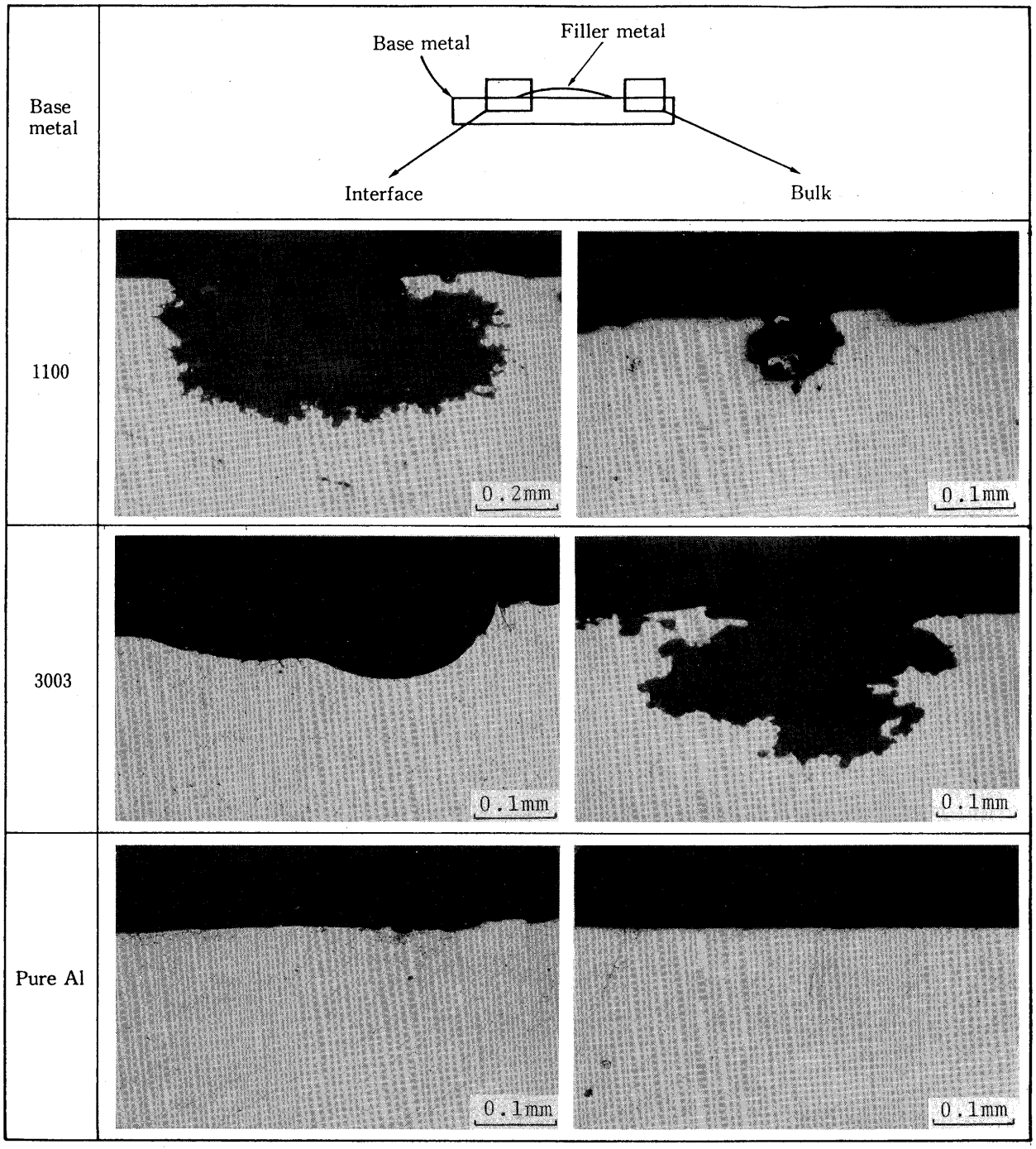

Fig. 3 Cross section of brazed specimen after corrosion test.

pits at interface were deeper than at bulk plate in iron bearing filler metals.

The corrosion depths of electropolished base metals are shown in **Fig. 5**. The results are similar to the profiles in Fig. 4. In 1100 base metal, the pit depths at interface remarkably increased with iron content up to 0.5%. In the range of 0.5~1.4%, the depths were almost the same. The pit depths at interface were larger than the ones at bulk plate. Similarly in as received material, the corrosion depths of 3003 and pure aluminum were not influenced by the iron content.

When comparing the Fig. 4 with Fig. 5, the corrosion depth of base plate is slightly small in electropolished ones. This may be due to the thin and uniform oxide film with less defects on electropolished surface, as pits are known to initiate easily at the surface defects.

Figure 6 represents the top view of the corrosion at spread front of filler metal *i.e.* corrosion at interface of electropolished specimen. In 1100 base metal, large facet pits were linked along spread front of filler metal. In 3003 base metal, facet pits were not observed, the corrosion at interface was relatively smooth and uniform along the

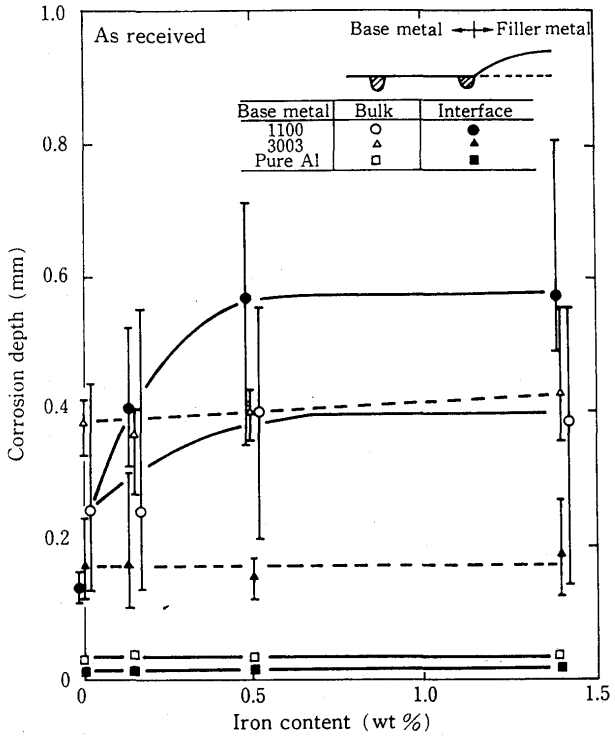

Fig. 4 Effect of iron content in Al-10Si-1Mg filler metals on corrosion depth of brazed base metals with as received surface.

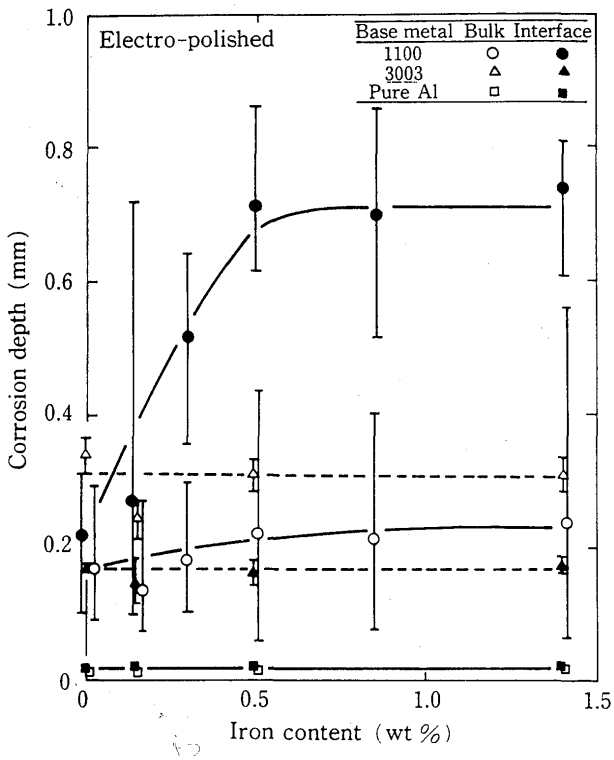

Fig. 5 Effect of iron content in Al-10Si-1Mg filler metals on corrosion depth of brazed base metals with electropolished surface.

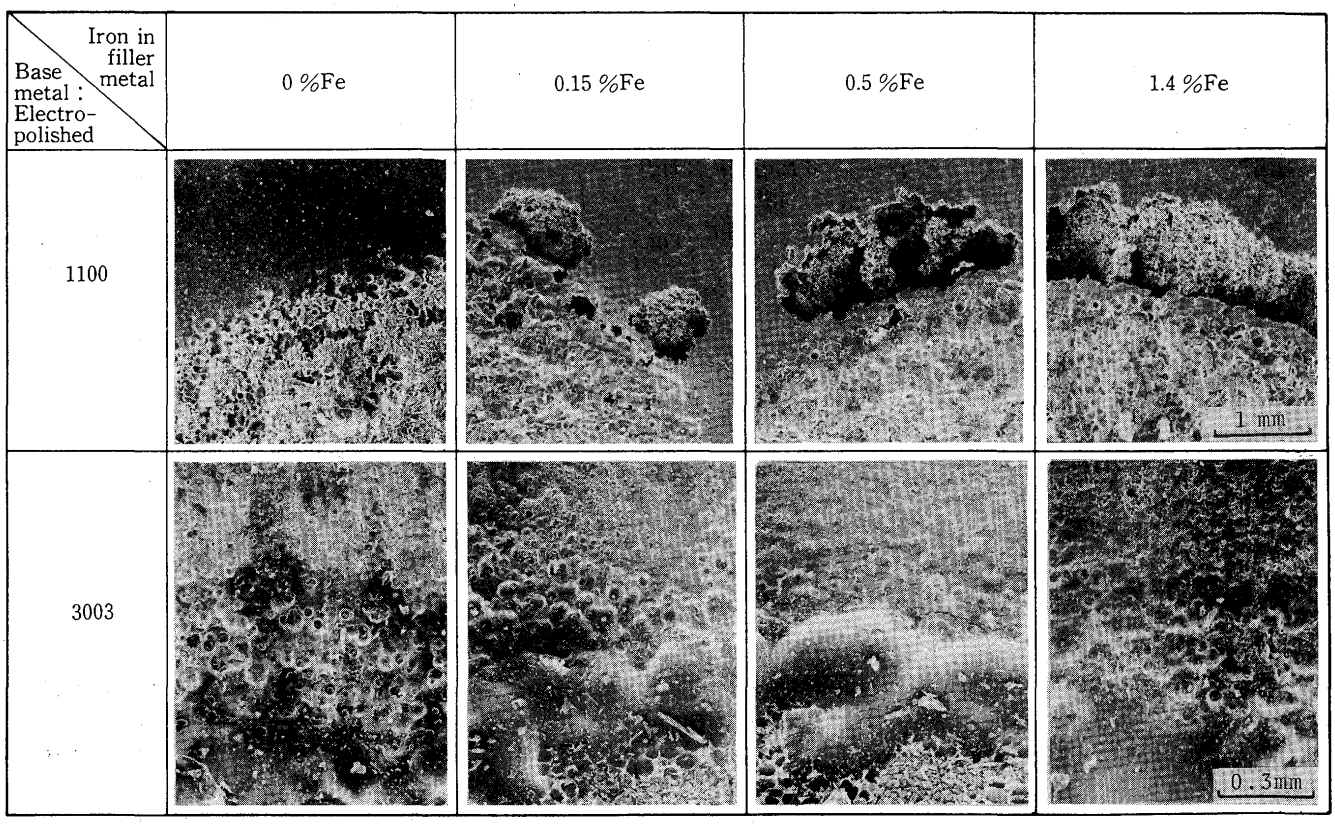

Fig. 6 Scanning electron micrographs of local corrosion at spread front of filler metal (corrosion at brazed interface), base metals were electropolished, top view.

spread front of filler metal.

3.2 Iron in filler metals

The secondary electron image and characteristic X-ray profiles of iron, aluminum and silicon are shown in **Fig. 7**. Iron beyond the solubility limit forms intermetallic compounds with acicular shape. In 1.4%Fe filler metals, block shape compounds were also found. The quantitative analysis by EPMA on block shape intermetallic compounds revealed the following composition, Al: 56%, Fe: 29%, Si: 15%, in wt%, by converting into atomic %, the composition becomes $Al_{66.3}Fe_{16.6}Si_{17.1}$, namely the compound is expressed as Al_4FeSi.

Figure 8 shows the diffraction lines of filler metals with 0%Fe and 1.4%Fe. Filler metals without iron is composed of aluminum solid solution and eutectic silicon. In filler metals with 1.4%Fe, β-(Al, Fe, Si) was found. The composition is reported to be: Al: 59.3%, Fe: 27.2%, Si: 13.3%, in wt%, the values are coincided well with the observed values. Thus the iron in filler metal was existed as β-(Al, Fe, Si). As the color of β-(Al, Fe, Si) and silicon particle is different, they are easily distinguished under optical microscope.

Minagawa *et al.*[5] reported that iron in filler metal segregated at spread front and initiated the pitting corrosion of base metal, however, in the present work remarkable segregation of iron at spread front was not observed by optical and SEM observation. One example is the surface analysis of brazed 1100 shown in **Fig. 9**. Tendency of iron segregation at spread front was not found. The results were same in electropolished surface. Of course, at particular area iron was found at the spread front of filler metal, however, the probability was very

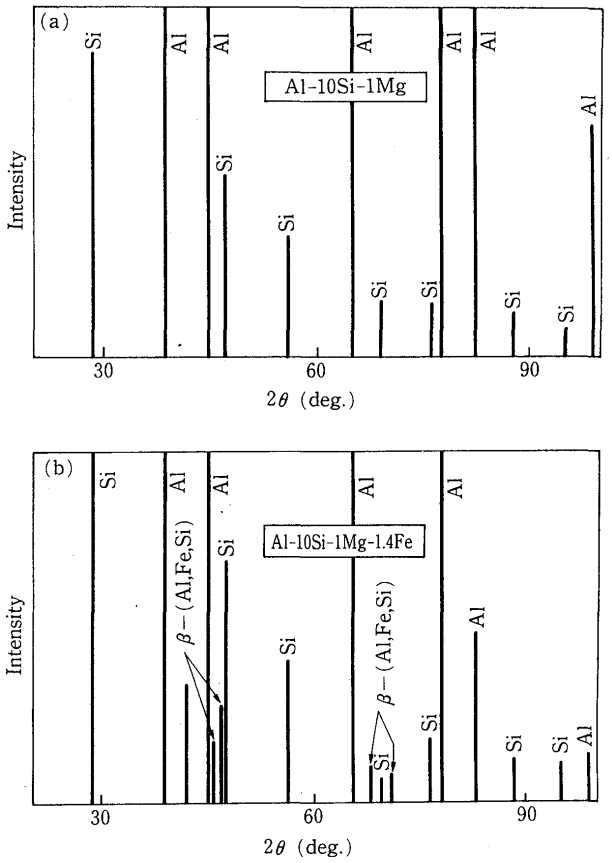

Fig. 8 X-ray diffraction lines of filler metals with 0%Fe (a) and 1.4%Fe (b).

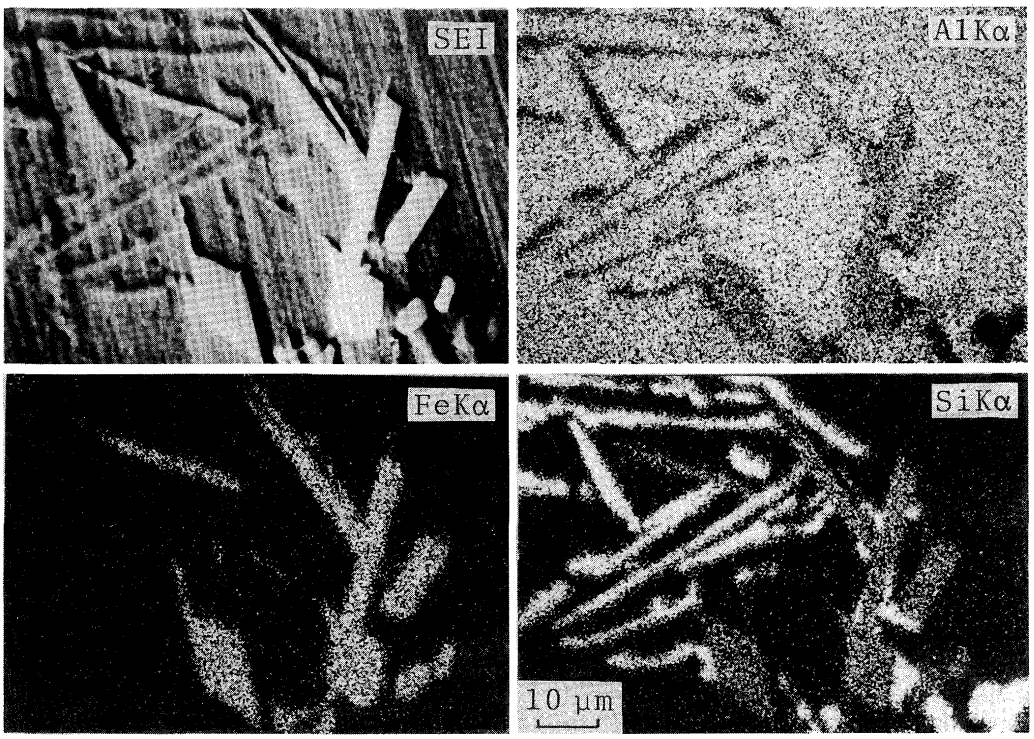

Fig. 7 Scanning electron micrographs of filler metals with 1.4%Fe.

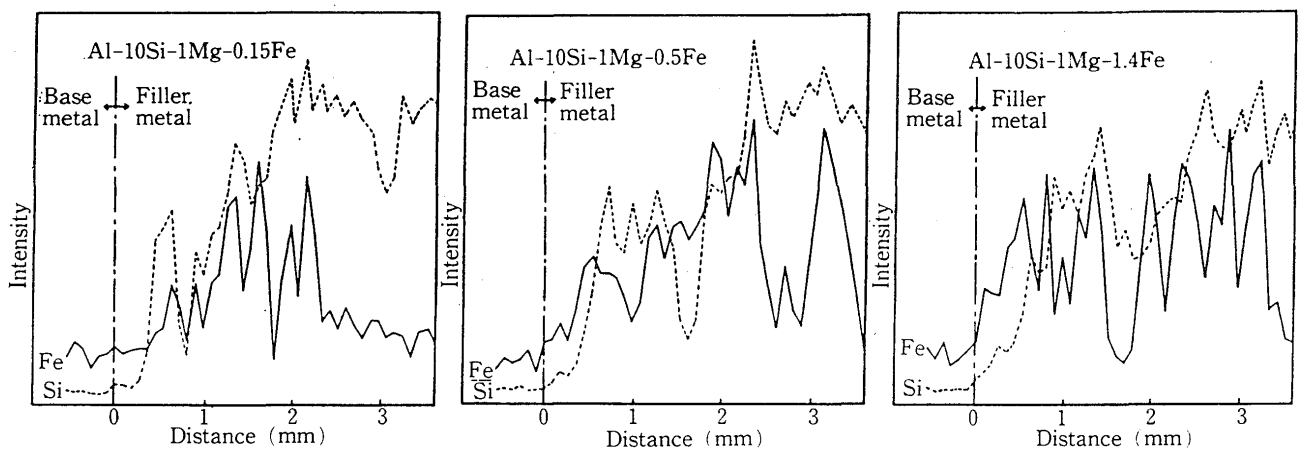

Fig. 9 Characteristic X-ray intensity of brazed specimen surface, 1100 base metal, as received surface.

small. As the reason of segregation at spread front, they mentioned the viscosity of Al-Fe-Si might be lower and spread easily than Al-Si because the eutectic point of Al-Fe-Si (574.5°C) is lower than that of Al-Si (577°C).[5] However, the filler metal contains magnesium, the melting occurrs at lower temperature, Al-Si-Mg ternary eutectic (555 ~ 559°C).[6),7)] A report mentioned the melting occurs at 551°C.[8)] McGurran[6)] reported the exudation of liquid filler metal occurred at 555°C. These differences might be caused by the difference of iron content in filler metals, however, the temperature difference is only 4 ~ 8°C similar to Al-Si-(Fe) system. The liquid appeared in these temperature range during heating stage should be only a little amount because the iron content is very small. Accordingly even if the iron rich liquid flew preferentially, the major part of liquid flows subsequently according to the temperature rise. Therefore there is no necessity of segregation of iron at the spread front of filler metal.

4. Discussion

The effect of iron in filler metals is dominant only on 1100 base metals. In the other base metals such as 3003 and pure aluminum, the corrosion at interface and bulk plate were not influenced by the iron content of filler metal. Iron in filler metals existed as an intermetallic compound, β-(Al, Fe, Si) phase with composition of Al_4FeSi. The electrode potentials of various alloys and β-(Al, Fe, Si) phase were measured in 0.4M NaCl aqueous solution. The β-(Al, Fe, Si) phase was melted according to its chemical fraction (Al_4FeSi) and the formation was confirmed by X-ray diffraction. The β-(Al, Fe, Si) phase showed the highest potential and the potential becomes low in the following order, β-(Al, Fe, Si) > Al-10Si-1Mg-0 ~ 1.4Fe ≒ 3003 > 1100 >> Pure Al. The β-(Al, Fe, Si) phase showed the highest potential, thus by contact with base metals, β-(Al, Fe, Si) phase becomes local cathode.

Figure 10 shows the cathodic polarization curves of β-(Al, Fe, Si) phase and filler metals. The β-(Al, Fe, Si) phase gave larger cathodic current than filler metals. The range of polarization curves of filler metals are also indicated in the figure, no distinct difference depending on the iron content was found. But the curves of iron less filler metal (0%Fe) are limited within the hatched area, slightly smaller than the iron bearing filler metals.

Figure 11 shows the change of contact current between 1100 base metal and filler metals. In this combination, all filler metals were acted as cathodes, and 1100 was an

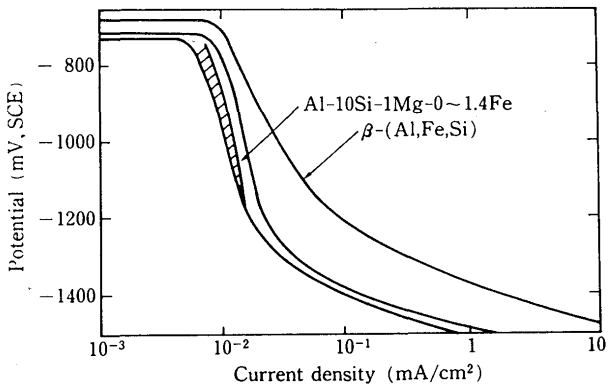

Fig. 10 Cathodic polarization curves of β-(Al, Fe, Si) and filler metals in 0.4 M NaCl.

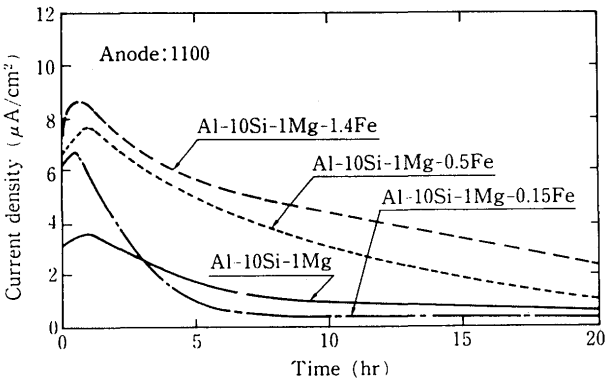

Fig. 11 Contact current between 1100 and filler metals with different iron content.

anode. The iron bearing filler metals showed large current just after immersion. The contact current lowered gradually, but current was larger in filler metals with 0.5 and 1.4%Fe than iron less filler metal. The tendency coincides with the results of immersion test on brazed 1100 base metal (Fig. 4 and 5). But after 20 hr, the current became small and the difference was not so large. From the results, the existence of β-(Al, Fe, Si) phase might enhance the pitting corrosion of 1100 base metal because its large cathodic reaction accelerates the anodic dissolution of adjacent base metal, especially the effect of β-(Al, Fe, Si) phase in filler metal might be highly exerted at the initiation stage of pitting (Fig. 11).

Since the electrode potential of 3003 alloy is almost the same to filler metals, the alloy is not suffered the contact corrosion with filler metal. This is the reason that the corrosion of 3003 alloy was not influenced by the iron content of filler metals. But the reason that the pure aluminum with the lowest potential was not affected by iron content is not expressed by the enhanced cathodic reaction of β-(Al, Fe, Si) phase. The high corrosion resistance of pure aluminum base metal would be due to the electrochemical characteristics of base metal. Then the pitting potential of each base metal was measured in 0.4M NaCl aqueous solution with pH10.0. In alkaline solutions, the pitting potential is easily distinguished. **Figure 12** shows the current density-time curves of base metals obtained by step sweep method with sweep rate of 10 mV/min. In horizontal axis, the corresponding potentials are indicated. The current remained a constant value up to a certain potential, but beyond it, small fluctuation of current was observed and sudden increase of current initiated by further rise of potential. The potential is so called pitting potential, beyond this potential the surface film is shifted from stable state to unsuitable state.

The pitting potentials of base metals were as follows, 3003: −700 ~ −680, 1100: −740 ~ −730, pure Al: −740 ~ −730 (mV, SCE). The pit depth of base metals and the corrosion depth at brazed interface decreased in the following order respectively: 3003 > 1100 > Pure Al for base metals; 1100 > 3003 > pure Al for interface. There is no relation between the pitting potential and the corrosion of brazed specimens.

Figure 13 shows the anodic polarization curves. The polarization direction was converted at current density of 6 mA/cm^2. In pure aluminum, there is little hysteresis in high current density, but 3003 alloy showed large hysteresis, the current is still high after the polarization direction was turned downward. The 1100 base metal shows the intermediate properties between pure aluminum and 3003 alloy. The degree of hysteresis coincided well with the pit depth of base metal. In pure aluminum with little hysteresis, even if the pit initiated above pitting potential, the pit is not stable and the growth will stop when the potential is lowered under the pitting potential. On the other hand, in 3003 alloy once initiated pit is stable under the pitting potential, because of its high hysteresis. The growth of pits will not easily stop and the pits will not be extinguished. The surface observation of base metals after polarization test revealed the pit depth was shallow in pure aluminum, but in 3003 alloy observed pits were large and deep (**Fig. 14**). In 1100, the shape was similar to 3003 but the depth was shallow.

From the above mentioned results, in pure aluminum the growth of pit is not easy even the pit initiated. This would be the main reason that the corrosion depth of pure aluminum is shallow and the corrosion is not influenced by the iron content in filler metals. Consequently the base metals having following characteristics might be influenced by the iron content in filler metals, the electrode potential of base metal is lower than the

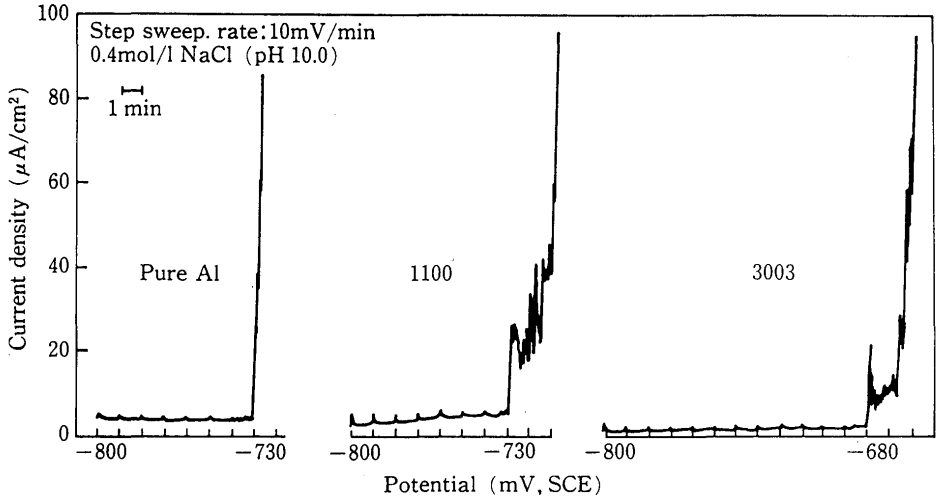

Fig. 12 Current-time curves during step sweep anodic polarization of base metals in 0.4 M NaCl with pH 10.0.

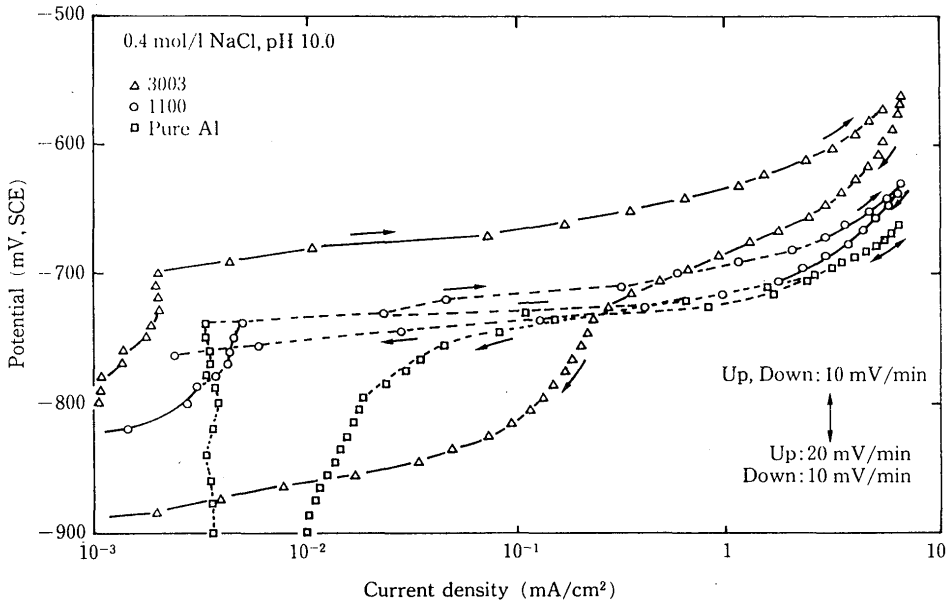

Fig. 13 Anodic polarization curves of base metals, sweep direction was inverted at current density of 6 mA/cm².

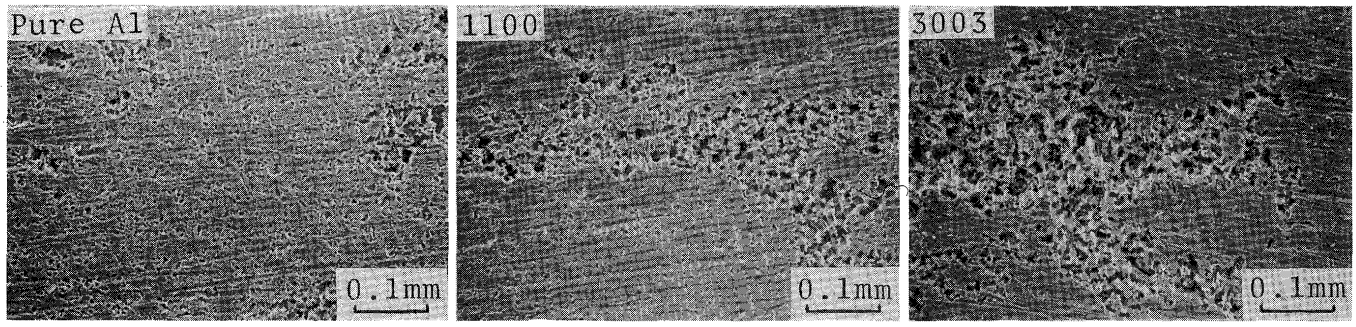

Fig. 14 Scanning electron micrographs of base metals after anodic polarization in 0.4 M NaCl with pH 10.0.

filler metal, and large hysteresis in anodic polarization curve that means once the pit initiates the pit grows easily (large hysteresis in anodic polarization curve).

5. Conclusions

The effects of iron content in brazing filler metals on the corrosion behavior of brazed aluminum were investigated. The obtained results are summarized as follows.

(1) The pit depth of base metal became larger in the following order, pure aluminum, 1100, 3003. The corrosion depth of brazed base metal was not influenced by the iron content in filler metal except 1100. In 1100 base metal, the pit depth slightly increased in filler metals with more than 0.5%Fe.

(2) Iron in filler metal formed β-(Al, Fe, Si) with composition of Al_4FeSi, the electrode potential was higher than base metals.

(3) The corrosion at brazed interface was influenced by the iron content of filler metals only in 1100 base metal. The corrosion depth increased with the iron content up to 0.5%Fe and were almost constant by further addition of iron. On the other hand, in 3003 and pure aluminum, the corrosion at interface was not influenced by the iron content in filler metals.

(4) The conditions that the corrosion of base metal is influenced by the iron content in filler metals are suggested to be as follows; the electrode potential of base metal is lower than the filler metal, and more over, base metal exhibits large hysteresis in anodic polarization curve.

Acknowledgement

The studies were conducted with the financial support of the Grant-in-Aid for Scientific Research (B), The Ministry of Education, Science and Culture, in 1983 and 1984. The authors would also thank to Mr. K. Kuroshima for experimental works. Thanks are also to Mr. H. Ohi and K. Harada at Elionics Corporation for their helpful works on the observation of EPMA.

References

1) Aluminum, Vol. 1, ASM (ed. by K. R. Horn), Ohio, (1971), 212.
2) L. F. Mondolfo: Light Met. Age, Vol. 37 (1979), 20.
3) W. K. Johnson: Br. Corros. J., Vol. 6 (1971), 200.
4) O. Seri and N. Masuko: J. Japan Inst. Light Metals, Vol. 32 (1982), No. 6, 303 (in Japanese).
5) K. Minagawa, M. Izu and E. Sato: ibid., Vol. 33 (1983), No. 2, 96 (in Japanese).
6) B. McGurran and M. G. Nicholas: Weld J., Vol. 63 (1984), No. 10, 295-s.
7) For example, H. Watanabe and E. Sato: J. Japan Inst. Light Metals, Vol. 19 (1969), No. 11, 499 (in Japanese).
8) W. L. Winterbottom and G. A. Gilmour: J. Vac. Sci. Technol., Vol. 13 (1976), No. 2, 634.