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Corrosion behavior of Al–Si–Cu–(Sn, Zn) brazing filler metals

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Abstract

The corrosion behavior of Al–Si–Cu–(Sn, Zn) filler metals in a 3.5% NaCl aqueous solution were studied using electrochemical tests. The results showed that the addition of Sn or Zn to the Al–Si–Cu filler metal raised its corrosion current density sharply and caused its corrosion potential to become more active. Sn or Zn elements exert harmful effects on such low-melting-point brazing filler metals in that the corrosion resistance is degenerated, and damage is accelerated with an increase in the Sn or Zn content. Scanning electron microscopy (SEM) micrographs of the corroded surfaces of these Al–Si–Cu–(Sn, Zn) filler metals indicate that the Al-rich phase (i.e., Al–Si, Al–Si–Cu, and Al–Si–Cu–Sn eutectic phases) dissolves preferentially, while the Si particles and $CuAl_2(\theta)$ intermetallic compounds remain intact. © 2001 Published by Elsevier Science Inc.

Keywords: Al–Si–Cu–(Sn, Zn) filler; $CuAl_2$; Corrosion behavior

1. Introduction

Aluminum alloys have been widely used in the aerospace, automotive, and construction industries by virtue of their high specific strength, low cost, and superior corrosion resistance. For the applications, brazing has been considered as one of the most important joining methods in the manufacture of aluminum components [1]. Commercially available filler metals for brazing aluminum are usually based on the aluminum–silicon alloy system with compositions predominantly of the Al–12Si eutectic [2,3]. However, in order to obtain stronger joints, the very act of brazing with Al–Si filler metals must be performed in the temperature range of 590–610 °C, which is near, or even above, the melting points of many aluminum alloys. As a result, the aluminum work pieces after brazing must be either fully or partially molten, or their mechanical properties may deteriorate substantially.

There clearly exists a demand for developing newer filler metals with lower melting points for brazing most of the aluminum engineering alloys. Many efforts have been made in this regard over the past 10 years. Kayamoto et al. [4] developed a series of Al–Ge–Si–Mg filler metals with quite low melting points and sufficient joint strengths for brazing 6061 aluminum alloy. However, the manufacture of such filler metals incurs excessively high costs for most applications. Consequently, Humpston et al. [5] and Jacobson et al. [6] both reported on an Al–5Si–20Cu–2Ni filler metal with a melting temperature range between 518 and 538 °C. When this filler metal was used to braze a 3003 Al alloy, a shear strength over 75 MPa was obtained. Earlier, Suzuki et al. [7] studied a series of

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Table 1
Corrosion data of Al–Si–Cu–(Sn, Zn) brazing filler metals in 3.5% NaCl aqueous solution

Filler metals	Φ_{corr} (mV$_{SCE}$)	Φ_{corr}^{d} (mV$_{SCE}$)	Φ_p (mV$_{SCE}$)	$\Delta\Phi$ (mV)	I_{corr} (μA/cm^2)
Al–12Si	−752	−1157	−628	529	5
Al–11.4Si–5Cu	−677	−1016	−633	443	39
Al–10.8Si–10Cu	−674	−1010	−638	372	50
Al–9.6Si–20Cu	−680	−1021	−640	381	61
Al–8.4Si–30Cu	−691	−1041	−645	390	80
Al–7.2Si–40Cu	−705	−1073	−648	416	126
Al–7Si–20Cu–2Sn	−800	−1026	−643	383	63
Al–7Si–20Cu–3Sn	−833	−1027	−678	349	77
Al–9Si–20Cu–5Sn	−892	−1031	−897	134	90
Al–8.4Si–20Cu–10Sn	−940	−1051	−998	53	299
Al–7Si–20Cu–10Zn	−875	−1139	−906	233	248
Al–7Si–15Cu–15Zn	−916	−1169	−918	251	449
Al–7.2Si–20Cu–20Zn	−997	−1190	−1023	167	719
Al–6Si–20Cu–30Zn	−1037	−1207	−1026	181	933

Φ_{corr}: corrosion potential (steady state), Φ_{corr}^{d}: dynamic corrosion potential, Φ_p: pitting potential, $\Delta\Phi$: range of the passive range (=$\Phi_b - \Phi_{corr}^{d}$) I_{corr}: corrosion current density.

ternary eutectic Al–Si–Zn filler metals. They found that by increasing the zinc addition to the Al–12Si filler metal from 0 to 50 wt.%, the eutectic points of such ternary Al–Si–Zn alloys would decrease linearly from 577 to 525 °C. In our laboratory, a series of low-melting-point Al–Si–Cu–(Sn, Zn) filler metals have been developed [8–10]. For the applications of these filler metals, the corrosion issue should be taken into consideration. The efforts of this study are thus concerned with the evaluation of the corrosion behavior of such a series of Al–Si–Cu–(Sn, Zn) filler metals in a 3% NaCl solution.

2. Experimental

A series of Al–Si–Cu–Zn filler metals with various compositions, as shown in Table 1, were prepared

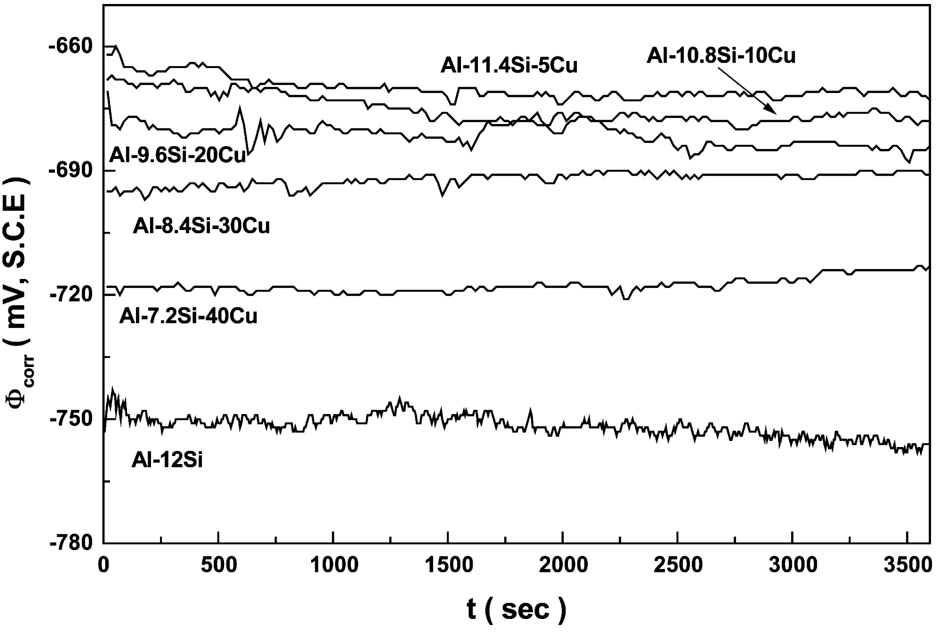

Fig. 1. Corrosion potential (Φ_{corr}) as a function of time (t) for Al–Si–Cu filler metals in 3.5% NaCl aqueous solution.

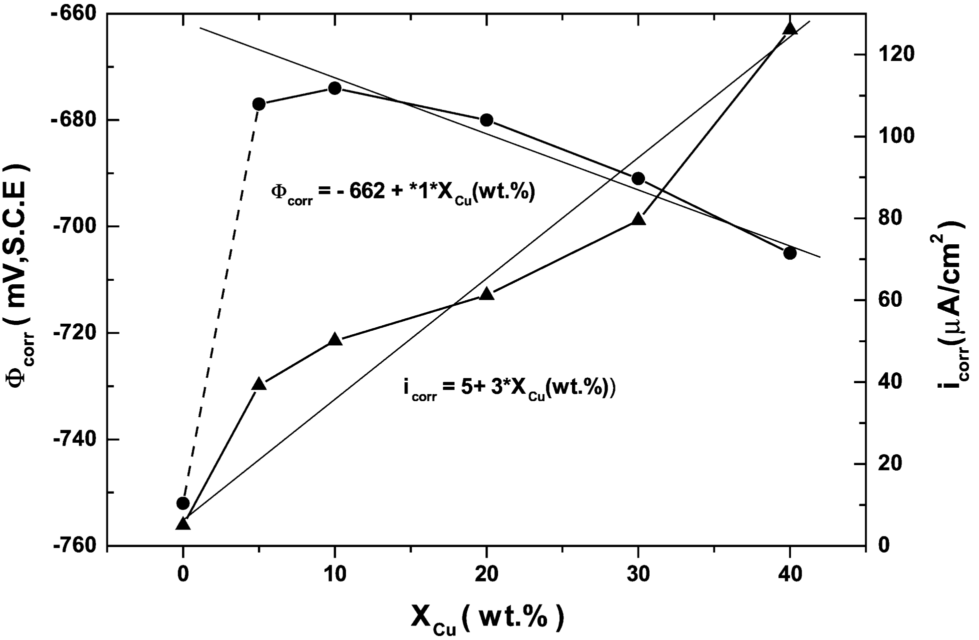

Fig. 2. Corrosion potential (Φ_{corr}) and corrosion current density (I_{corr}) as a function of copper content (X_{Cu}) of Al–Si–Cu filler metals in 3.5% NaCl aqueous solution.

for the study. For this purpose, an Al–12 wt.% Si alloy was melted first at 700 °C in an air furnace, and then the temperature was raised to 1000 °C when various amounts of copper (99.9 wt.%, 2-mm diameter slugs)

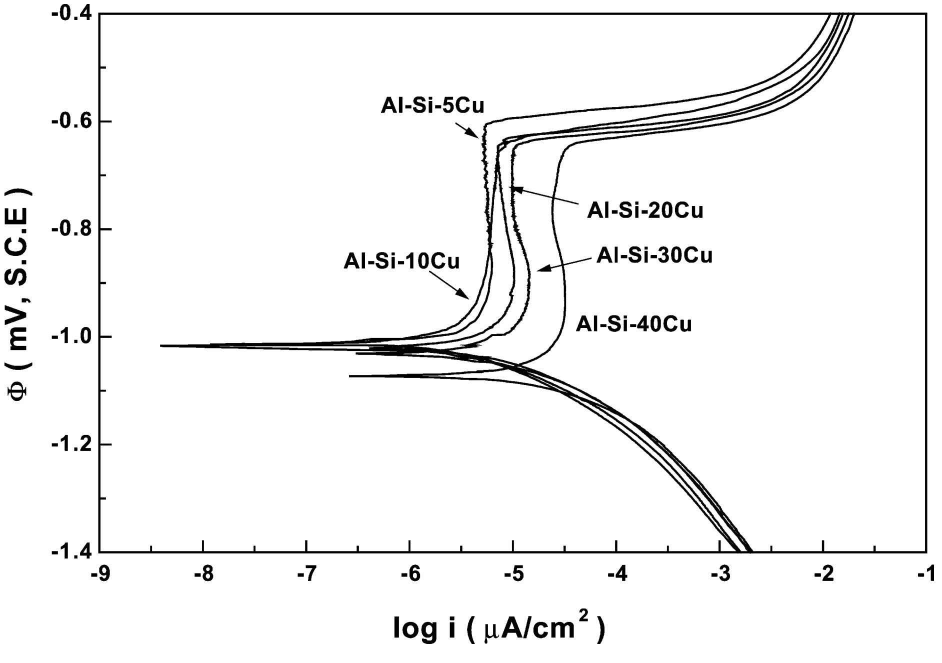

Fig. 3. Polarization curves of Al–Si–Cu filler metals in 3.5% NaCl aqueous solution.

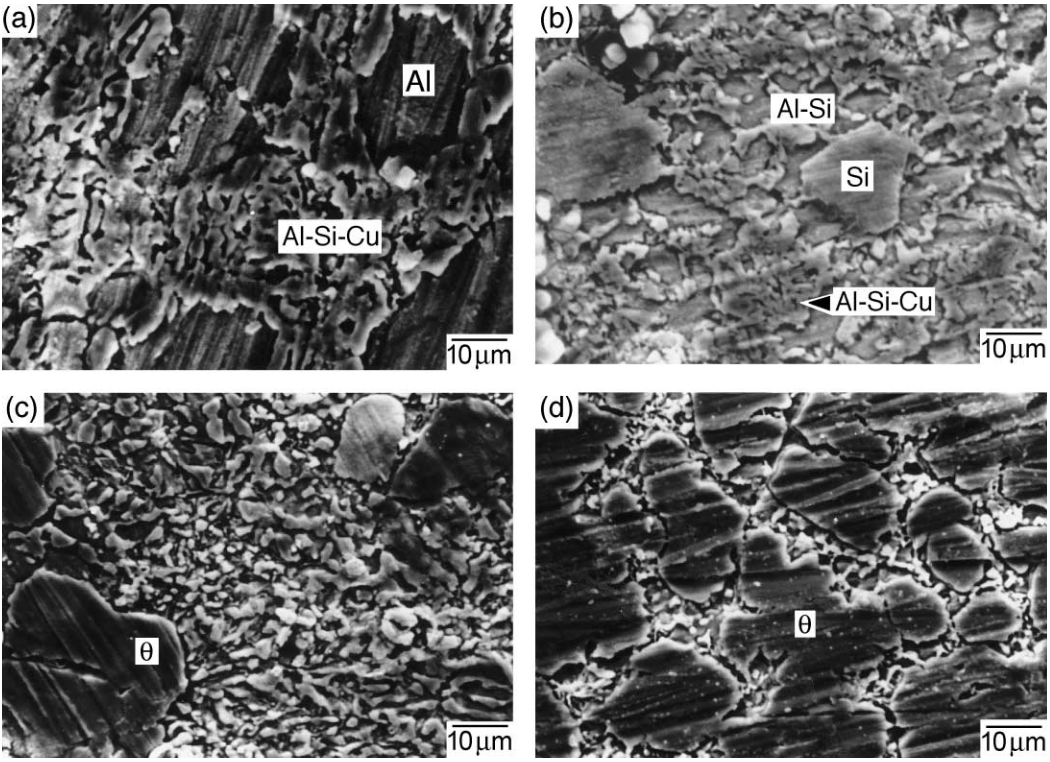

Fig. 4. Corroded surfaces of Al–Si–Cu filler metals after polarization tests in 3.5% NaCl aqueous solution: (a) Al–10.8Si–10Cu, (b) Al–9.6Si–20Cu, (c) Al–8.4Si–30Cu, (d) Al–7.2Si–40Cu.

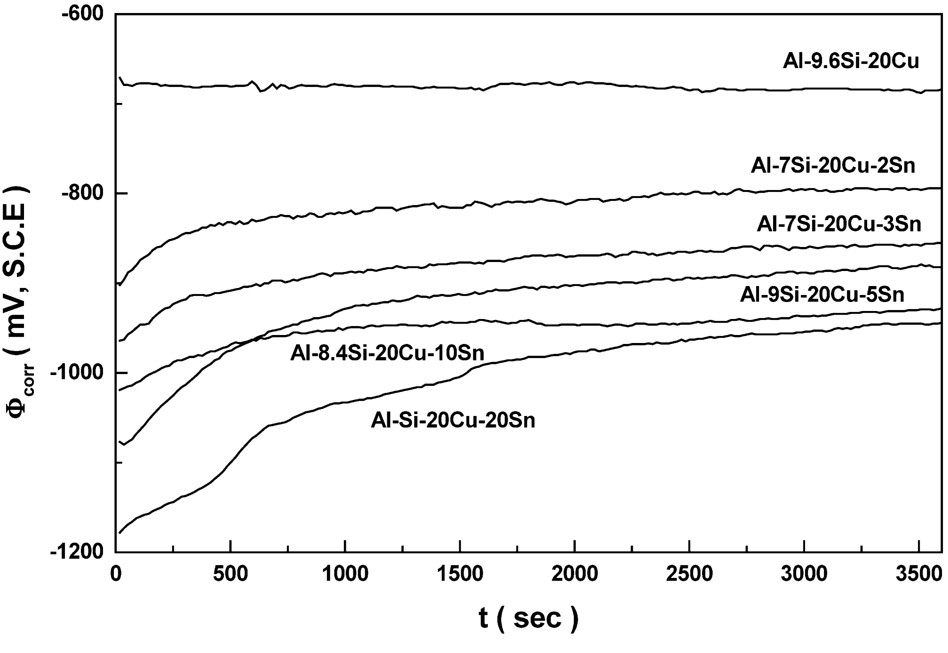

Fig. 5. Corrosion potential (Φ_{corr}) as a function of time (t) for Al–Si–Cu–Sn filler metals in 3.5% NaCl aqueous solution.

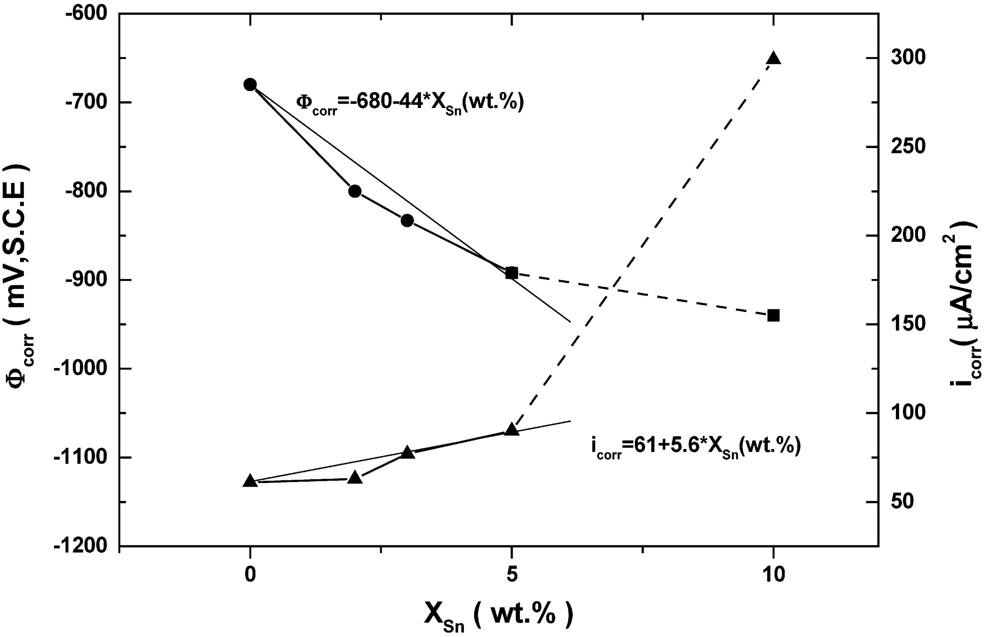

Fig. 6. Corrosion potential (Φ_{corr}) and corrosion current density (I_{corr}) as a function of copper content (X_{Sn}) of Al–Si–Cu–Sn filler metals in 3.5% NaCl aqueous solution.

were added into the molten Al–12Si alloy. After the mixture was stirred for 30 min for homogenization, various amounts of tin or zinc were added to the Al–Si–Cu alloys. Then, they were cast in a stainless steel

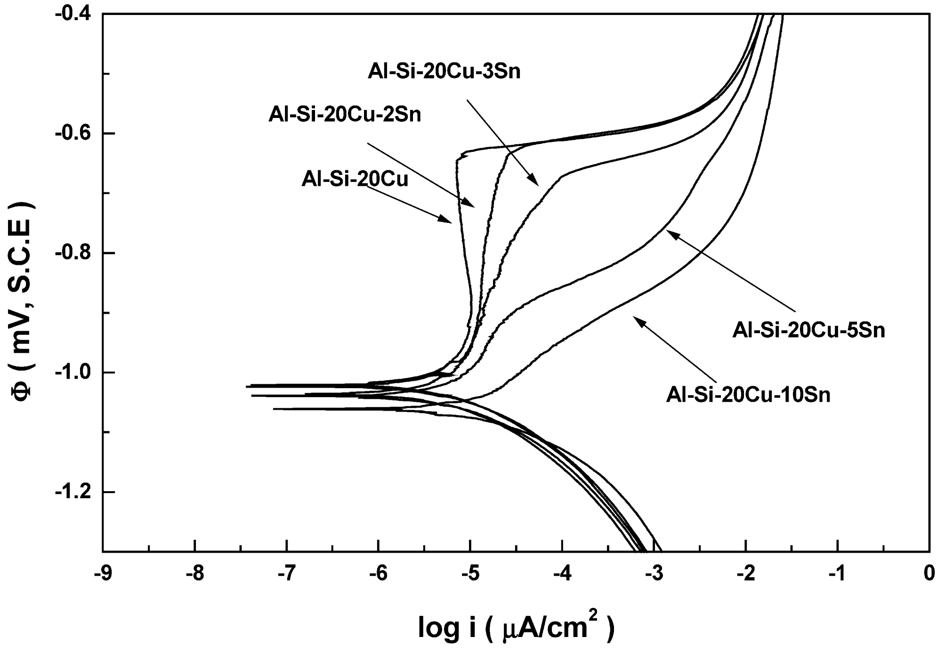

Fig. 7. Polarization curves of Al–Si–Cu–Sn filler metals in 3.5% NaCl aqueous solution.

mold. The microstructures and melting temperatures of these Al–Si–Cu–(Sn, Zn) filler metals were given in the authors' previous works [8–10]. The specimens were heated from room temperature to 600 °C at a heating rate of 10 °C/min under argon atmosphere. Corrosion specimens were cut from the filler metal ingots, ground with 600-grit SiC paper, and cleaned with acetone. All corrosion tests were conducted at room temperature in a 3.5% NaCl aqueous solution (pH=7.2) using an EG&G Mode 273A Potentiostat. At the outset of the dynamic potentiostatic polarization tests, the potential was first held at -1.5 V_{SCE} for 5 min to remove any oxide film formed prior to polarization testing, and then polarized in the direction from active to noble at a scanning rate of 1 mV/s. The corroded specimens after polarization tests were observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Al–Si–Cu filler metals

The corrosion potentials as a function of time for Al–Si–Cu filler metals with various Cu contents remain more or less constant as shown in Fig. 1. The results listed in Table 1 indicate that the corrosion potential of Al–12Si increases 75 mV with the addition of 5 wt.% Cu, which is attributable to the noble characteristic of the element copper. By further increasing the Cu content of the Al–Si–Cu filler metals to 40 wt.%, their corrosion potentials decline in a roughly linear relation as shown in Fig. 2: $\Phi_{corr}=-662-1*X_{Cu}$ (wt.%). Because the noble Si content of these Al–Si–Cu filler metals decreases from 11.4 to 7.2 wt.% accompanied by an increase in Cu content, the results imply that the effect of Si addition on corrosion potential in driving it toward the noble direction is stronger than the case of Cu addition to Al–Si–Cu filler metals. The polarization curves of various Al–Si–Cu filler metals are shown in Fig. 3.

Corrosion data obtained from these polarization curves are listed in Table 1. It can be seen that the corrosion current density of various Al–Si–Cu filler metals increases with the increase in the Cu content of the alloys. The results are plotted in Fig. 2, which shows a quasi-linear relation between corrosion current density and Cu content: $I_{corr}=4.7+3*X_{Cu}$ (wt.%). As Table 1 also indicates, the Al–Si–Cu filler metals with copper content possess a higher pitting tendency (smaller $\Delta\Phi$ value) than the traditional Al–12Si filler metals. The higher pitting tendency of Al–Si–Cu filler metals can be attributed to the existence of $CuAl_2(\theta)$ intermetallic compounds in these alloys, which causes localized galvanic corrosion between $CuAl_2(\theta)$ phases and their matrix.

The corroded surfaces of the Al–Si–Cu filler metals after polarization tests are shown in Fig. 4. It can be observed that the preferentially corroded spots consist of an α-Al solid solution as well as Al–Si and Al–Si–Cu eutectic phases [11,12], while the $CuAl_2(\theta)$ intermetallic compounds and Si particles remain immune from corrosion due to attributes nobler than those corroded phases.

3.2. Al–Si–Cu–Sn filler metals

With the addition of 2–10 wt.% Sn to the Al–Si–20Cu filler metal, the melting point of the filler metal

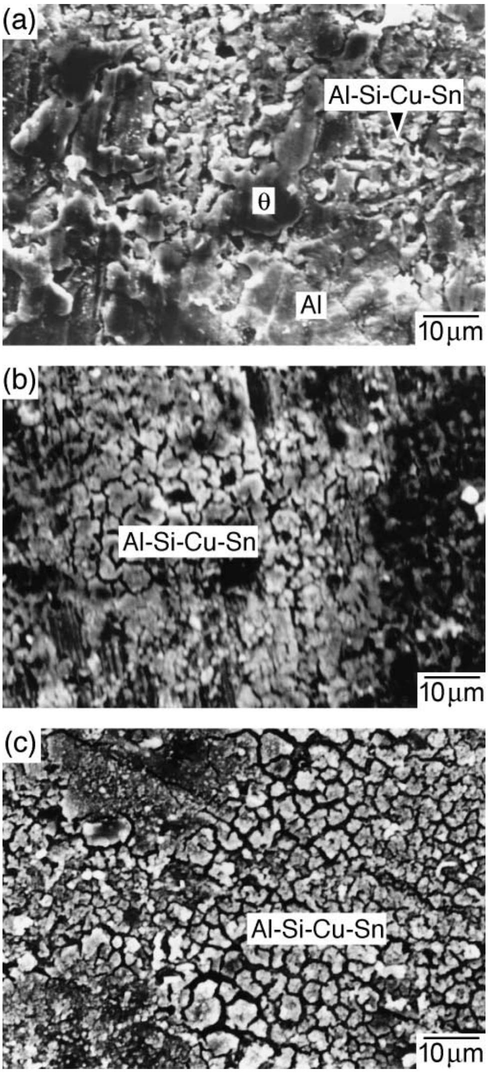

Fig. 8. Corroded surfaces of Al–Si–Cu–Sn filler metals after polarization tests in 3.5% NaCl aqueous solution: (a) Al–7Si–20Cu–2Sn, (b) Al–9Si–20Cu–5Sn, (c) Al–8.4Si–20Cu–10Sn.

drops about 17–23% [8]. In contrast to the Al–Si–Cu filler metals, the corrosion potentials of various Al–Si–Cu–Sn filler metals exhibit a more active value at the initial stage, then move onward to a nobler value and remain constant after immersion in a 3.5% NaCl solution for about 10 min (Fig. 5).

For all Al–Si–20Cu–Sn filler metals, the corrosion potentials are more active than those of Al–Si–20Cu filler metals. In fact, the corrosion potentials of various Al–Si–Cu filler metals in this study are nobler than those of the Al–Si–Cu–Sn filler metals as evinced in Table 1. Fig. 6 shows that the corrosion potentials of Al–Si–Cu–Sn filler metals decline with increasing Sn content in a roughly linear relation: $\Phi_{corr}=-680-44*X_{Sn}$ (wt.%).

Fig. 6 also shows that the corrosion current density obtained from the polarization curves in Fig. 7 increases with increasing Sn content in a quasi-linear relation: $I_{corr}=61+5.6*X_{Sn}$ (wt.%). From Table 1, it can also be seen that both corrosion current density and pitting tendency of various Al–Si–20Cu–Sn filler metals are higher than those of the Al–9.6Si–20Cu filler metals. As the Sn Content increases, the pitting tendency increases. In summary of the corrosion data in Table 1, it is obvious that the addition of the element Sn into the Al–Si–Cu filler metal degrades its corrosion resistance.

SEM micrographs of the corroded surfaces of various Al–Si–Cu–Sn filler metals after polarization tests are shown in Fig. 8. Similar to observations on the corroded surfaces of Al–Si–Cu filler metals, the preferentially corroded regions for Al–Si–Cu–Sn filler metals also consist of an α–Al solid solution and Al–Si, Al–Si–Cu, and Al–Si–Cu–Sn eutectic phases.

3.3. Al–Si–Cu–Zn filler metals

The addition of 10–30 wt.% Zn to the Al–Si–20Cu filler metal causes the melting temperature to drop about 23–61 °C [10]. However, its corrosion potential becomes very active in comparison with that of Al–9.6Si–20Cu filler metal (Fig. 9). The result is attributed to the active element Zn, which has dissolved at a high solubility in the Al–Si–Cu alloys. Fig. 10 shows that the corrosion potentials of these Al–Si–Cu–Zn filler metals decline with increasing Zn content in a roughly linear relation: $\Phi_{corr}=-680+13*X_{Zn}$ (wt.%). Their polarization curves in Fig. 11 also move in the direction of larger current density corresponding to that of Al–9.6Si–20Cu filler metal. As evidenced by Table 1, the corrosion current density of various Al–Si–Cu–Zn filler metals obtained from these polarization curves is raised to relatively high values due to the addition of the element Zn. Fig. 10 shows that the Zn content of Al–Si–Cu–Zn filler metals causes their corrosion current densities to raise in a roughly linear relation: $I_{corr}=61+28*X_{Zn}$ (wt.%). After polarization tests, the surfaces of the Al–Si–Cu–Zn filler metals suffer

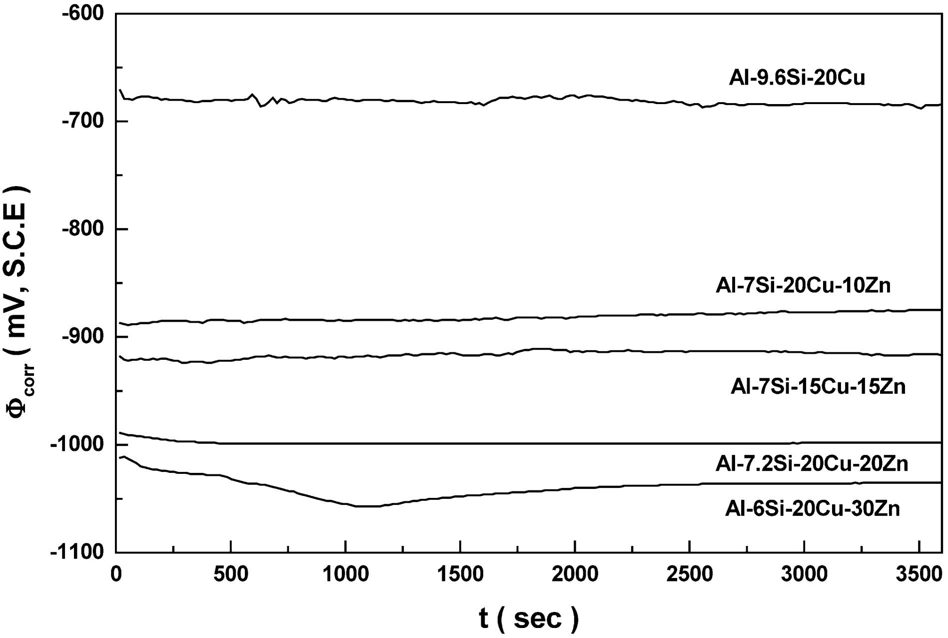

Fig. 9. Corrosion potential (Φ_{corr}) as a function of time (t) for Al–Si–Cu–Zn filler metals in 3.5% NaCl aqueous solution.

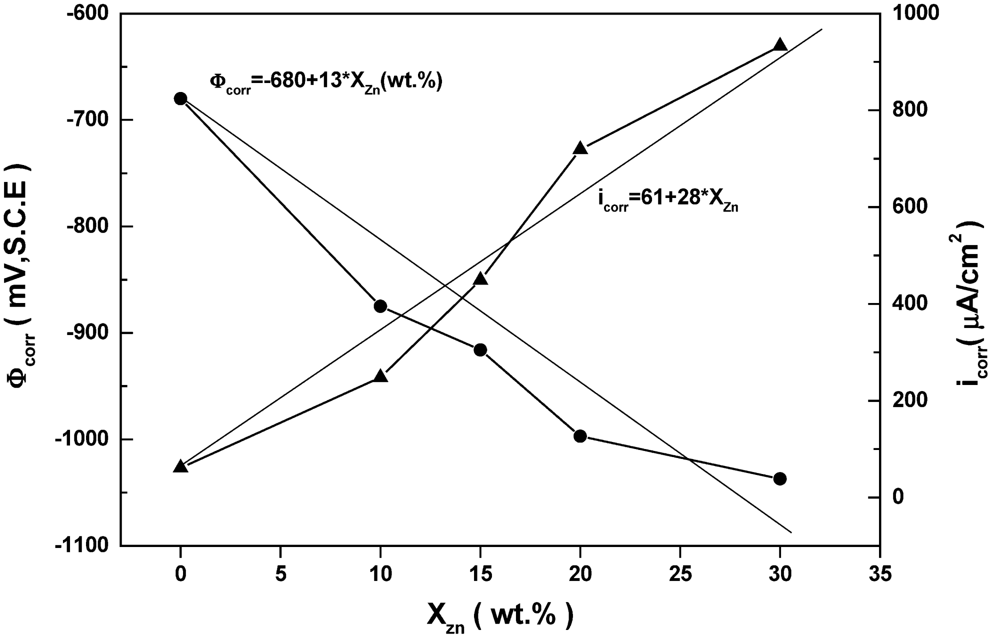

Fig. 10. Corrosion potential (Φ_{corr}) and corrosion current density (I_{corr}) as a function of copper content (X_{Zn}) of Al–Si–Cu–Sn filler metals in 3.5% NaCl aqueous solution.

from severe corrosion as shown in Fig. 12. Only small regions of the $CuAl_2(\theta)$ phases survive and the Al-rich matrix that contains Zn has been preferentially dissolved. The preferential corrosion of the Al-rich matrix is aggravated due to the existence of the active element Zn in the matrix, which forms a

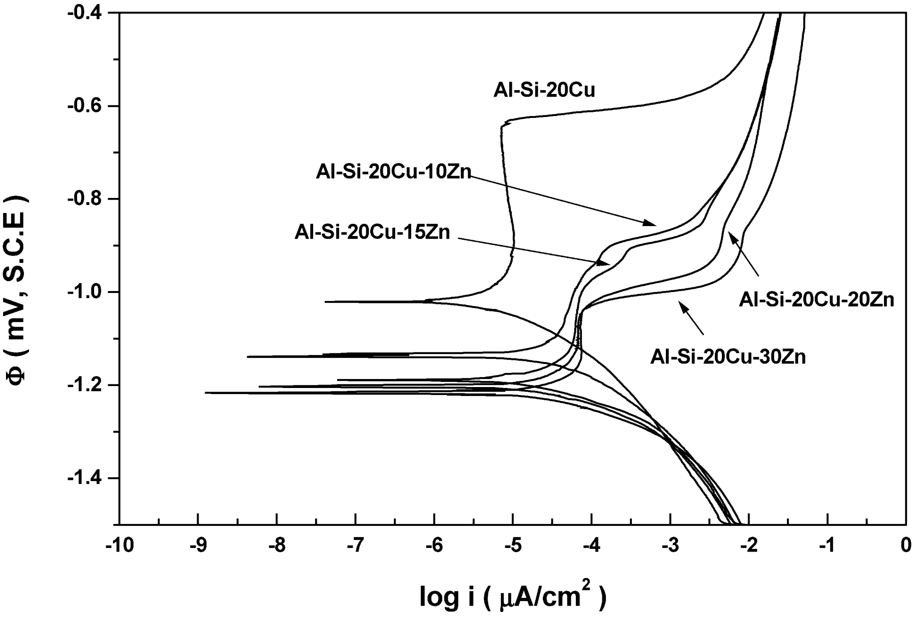

Fig. 11. Polarization curves of Al–Si–Cu–Sn–Zn filler metals in 3.5% NaCl aqueous solution.

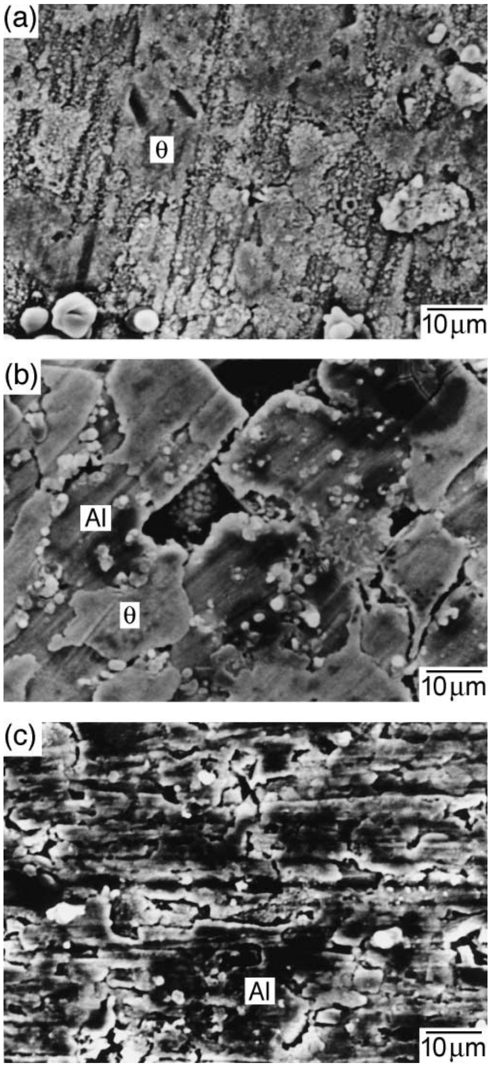

Fig. 12. Corroded surfaces of Al–Si–Cu–Zn filler metals after polarization tests in 3.5% NaCl aqueous solution: (a) Al–7Si–20Cu–10Zn, (b) Al–7.2Si–20Cu–20Zn, (c) Al–6Si–20Cu–30Sn.

galvanic cell filled with the noble $CuAl_2(\theta)$ intermetallic compounds.

4. Conclusions

With 5 wt.% Cu added to the Al–12Si filler metal, the corrosion potential of the filler metal raises from −752 to −677 mV. With further increases of the Cu content of the Al–Si–Cu filler metals, their corrosion potentials decline gradually. However, the corrosion current densities of various Al–Si–Cu filler metals increases with the increase in their Cu content. For Al–Si–Cu–Sn and Al–Si–Cu–Zn filler metals, their corrosion potentials decrease linearly with increasing Sn or Zn content. In contrast, their corrosion current density increases with increasing Sn or Zn content. On the whole, the Al–Si–Cu–Sn filler metals possess a lower corrosion resistance than the Al–Si–Cu filler metals. In fact, Al–Si–Cu–Zn filler metals exhibit the poorest corrosion behaviors among these Al–Si–Cu–(Sn, Zn) filler metals.

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