Influence of Silicon on Intergranular Corrosion for Aluminum Alloys

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In an effort to improve the tensile strength of aluminum–silicon (Al–Si) alloys used in heat exchangers, we investigated the influence of Si concentration and heat-treatment at 453 K on the susceptibility of Al–Si alloys to intergranular corrosion. It was found that the susceptibility to intergranular corrosion increased with an increase in Si concentration. It also initially increased with heat-treatment at 453 K, but then decreased with long-term heat-treatment at 453 K. The addition of Mg and Mn, which affect the precipitation of Si, promoted precipitation and reduced the susceptibility of the Al–Si alloys to intergranular corrosion. With longer heat-treatment at 453 K, large Si precipitates were observed in the grains and at the grain boundaries, which reduced the susceptibility to intergranular corrosion. Short-term heat-treatment at 453 K formed a continuous Si-depleted layer along the grain boundaries, which increased the susceptibility to intergranular corrosion. It is suggested that the susceptibility to intergranular corrosion was dependent on the addition of Mg and Mn. [doi:10.2320/matertrans.M2013048]

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1. Introduction

Aluminum–manganese (Al–Mn) series aluminum alloys such as 3003, 3103 and 3203 are widely used for heat exchangers because of their high tensile strength and corrosion resistance. Heat exchangers in automobile air conditioners are produced by a brazing process, and CFC-134a (CH₂FCF₃) is used as a refrigerant. The refrigerant may change to carbon dioxide (CO₂), which has lower global warming potential than the alternative fluorocarbon refrigerant.¹⁾ If CO₂ is used as the refrigerant, both the pressure and the temperature in the heat exchanger would increase. Copper (Cu) and Si are often added to Al–Mn alloys in order to increase the tensile strength. However, when the high-strength Al–Mn series aluminum alloys containing Cu and Si are applied to a heat exchanger with CO₂ refrigerant, solute elements precipitate preferentially at the grain boundaries when the operating temperature reaches 453 K.¹⁾ This precipitation induces a concentration difference between the grains and the grain boundaries, possibly leading to intergranular corrosion.

Al–Mn series aluminum alloys have comparatively low susceptibility to intergranular corrosion, although the susceptibility increases as a result of heat-treatment and the addition of alloy elements.^{2–4)} Heat-treatment at more than 673 K causes Al₆Mn and/or Al₆(MnFe) to precipitate preferentially on the grain boundaries, forming a Mn-depleted layer along the boundaries. Subsequent preferential corrosion of the Mn-depleted layer causes intergranular corrosion. In an Al–Mn alloys with Cu as an alloy element, the presence of Fe as an impurity leads to enhanced susceptibility to intergranular corrosion,^{2,3)} while the presence of Si inhibits susceptibility to intergranular corrosion.⁴⁾

The mechanism responsible for intergranular corrosion has been investigated carefully for Al–Cu alloys.⁵⁾ Heat-treatment, by which an Al₂Cu intermetallic compound preferentially precipitates on grain boundaries, forms a Cu-depleted layer along the grain boundaries. This is the reason why the diffusion rate of Cu on the grain boundaries is higher than that in the grains. Because solute Cu makes the pitting

potential (E_{PIT}) of the aluminum alloy noble, the E_{PIT} of the grain boundary is lower than that of the grains. The difference in E_{PIT} between the grains and grain boundaries causes intergranular corrosion, which means that the addition of Cu in aluminum alloys increases intergranular corrosion. However, the tensile strength of aluminum–manganese alloys without Cu is unacceptably low for usage in heat exchangers with CO₂ refrigerant. Thus, the addition of other elements to increase tensile strength is imperative.

Si is typically added to aluminum alloys because it contributes to an increase in tensile strength due to solid-solution and precipitation strengthening. The precipitation of the various intermetallic compounds containing Si is affected by heat-treatment, meaning that susceptibility of the alloy to intergranular corrosion also changes.^{6–11)} Intergranular corrosion was not observed for water-quenched Al–Si⁸⁾ or Al–Si–Mg^{6,7,9)} alloys, but it was observed for air-cooled Al–Si,⁸⁾ Al–Si–Mg^{6,10)} and Al–Si–Mn alloys.¹¹⁾ Heat-treatment increases susceptibility to intergranular corrosion for Al–Si–Mg^{6,7,9)} and Al–Si–Mn.^{10,11)} This intergranular corrosion is caused by dissolution of either Mg₂Si intermetallic compound at the grain boundaries in Al–Si–Mg^{7,9)} or the Si-depleted layer along the grain boundaries in Al–Si and Al–Mn–Si alloys.^{6,8,10,11)} This means that the cause of the intergranular corrosion depends on the type of alloy. However, there are very few reports providing a systematic study of the influence of Si concentration in various alloys and the heat-treatment conditions on the susceptibility to intergranular corrosion. In this study, we investigated how the Si concentration and heat-treatment time at 453 K after brazing affects the susceptibility of various alloys to intergranular corrosion.

2. Experimental Procedure

2.1 Process and materials

The chemical composition of the specimens is shown in Table 1. All specimens were cast in a rectangular parallelepiped mold, homogenized at 873 K for 1.08×10^4 s, hot rolled at 793 K to a 3.5 mm thickness, and then cold rolled to a 1 mm thickness. The sheets were annealed at 673 K for

Table 1 Chemical composition of specimens.

Specimen	Composition (mass%)					
	Si	Fe	Cu	Mn	Mg	Al
0.4Si	0.4	0.4	0.0	0.0	0.0	Bal.
0.8Si	0.8	0.4	0.0	0.0	0.0	Bal.
1.2Si	1.2	0.4	0.0	0.0	0.0	Bal.
1.4Si	1.4	0.4	0.0	0.0	0.0	Bal.
0.2Mg–0.9Si	0.9	0.4	0.0	0.0	0.2	Bal.
0.2Mg–1.3Si	1.3	0.4	0.0	0.0	0.2	Bal.
1.1Mn–0.4Si	0.4	0.4	0.0	1.1	0.0	Bal.
1.1Mn–0.8Si	0.8	0.4	0.0	1.1	0.0	Bal.
1.1Mn–1.2Si	1.2	0.4	0.0	1.1	0.0	Bal.
1.1Mn–1.4Si	1.4	0.4	0.0	1.1	0.0	Bal.
1.1Mn–0.2Mg–0.6Si	0.6	0.4	0.0	1.1	0.2	Bal.
1.1Mn–0.2Mg–0.8Si	0.8	0.4	0.0	1.1	0.2	Bal.
1.1Mn–0.2Mg–1.2Si	1.2	0.4	0.0	1.1	0.2	Bal.
1.1Mn–0.2Mg–1.4Si	1.4	0.4	0.0	1.1	0.2	Bal.

7.2×10^3 s. The annealed sheets were heat-treated at 873 K for 180 s, which corresponds to a brazing process. Finally, the sheets were reheated at 453 K, which is the maximum working temperature for CO₂ air conditioners, for $0-7.20 \times 10^6$ s. The heat-treatment time at 453 K after the heat-treatment simulating the brazing process is denoted as HTT in this paper.

2.2 TEM observation

The distribution of precipitated intermetallic compounds near the grain boundaries of the specimens heat-treated at 453 K was observed by transmission electron microscopy (TEM, JEOL Ltd., JEM-3100FEF, accelerating voltage: 300 kV).

2.3 Evaluation of susceptibility to intergranular corrosion

The susceptibility of the alloys to intergranular corrosion was evaluated by anodic dissolution. A Pt plate was used as a counter electrode. The test solution was 5 mass% NaCl adjusted to a pH of 3 by acetic acid. As a pretreatment, the specimens were immersed in 5 mass% NaOH at 333 K for 30 s, rinsed with distilled water, immersed in 30 mass% HNO₃ at 298 K for 60 s, and then rinsed with distilled water. The applied anodic current density was 10 A m^{-2} , at which point the specimens were polarized to a potential that was higher than E_{PT} . The polarization time was 2.16×10^4 s. After the anodic dissolution, a cross section of the center of each specimen was observed with an optical microscope to identify the corrosion morphology and measure the corrosion depth. In this paper, the corrosion depth is defined as the maximum depth from the surface to the bottom of the corrosion in 30 observed views.

3. Results

3.1 Al–Si alloys

3.1.1 Susceptibility to intergranular corrosion

Figure 1 shows optical micrographs of the cross section for Al–0.4Si, –0.8Si and –1.2Si alloys at HTT = 0, 8.64×10^4

and 2.59×10^4 s after anodic dissolution tests. At HTT = 0 s, the corrosion morphology depends on the Si concentration. Pitting corrosion was observed for Al–0.4Si and –0.8Si alloys and intergranular corrosion was observed for Al–1.2Si alloy. At HTT = 8.64×10^4 s, pitting corrosion was observed for Al–0.4Si alloy, whereas intergranular corrosion was observed for Al–0.8Si and –1.2Si alloys. The corrosion depth at HTT = 8.64×10^4 s was deeper than that at HTT = 0 s. However, the corrosion morphology was independent of Si concentration, showing pitting corrosion at HTT = 2.59×10^6 s.

Figure 2 shows variations of corrosion depth with HTT for Al–0.4Si, –0.8Si, –1.2Si and –1.4Si alloys after anodic dissolution tests. The open and solid symbols show pitting corrosion and intergranular corrosion, respectively. If the current efficiency is constant in anodic dissolution regardless of corrosion morphology and the volume of dissolved aluminum is constant with a constant current density, the corrosion depth would show degree of intergranular corrosion susceptibility.

The corrosion depth of Al–0.4Si alloy is independent of HTT, approximately 50 μm , and the corrosion morphology is pitting corrosion. The corrosion depth and morphology of Al–0.8Si, –1.2Si and –1.4Si alloys depend on HTT.

For Al–0.8Si alloy, the corrosion morphology is pitting corrosion at HTT = 0 s. The corrosion depth increases at $0 \leq \text{HTT} \leq 8.64 \times 10^4$ s, although intergranular corrosion is observed at $7.2 \times 10^3 \leq \text{HTT} \leq 6.05 \times 10^5$ s. Furthermore, the corrosion morphology is pitting corrosion again at HTT = 2.59×10^6 s.

For Al–1.2Si and –1.4Si alloys, intergranular corrosion is observed at HTT = $0-6.05 \times 10^5$ s and pitting corrosion is observed at HTT = 2.59×10^6 s. The corrosion depth is the deepest at HTT = 8.64×10^4 or 1.73×10^5 s, and then it decreases rapidly with an increase in HTT. That is, susceptibility to intergranular corrosion shows a peak at HTT = 8.64×10^4 for Al–0.8Si and –1.2Si alloys and at HTT = 1.73×10^5 s for Al–1.4Si alloy.

3.1.2 TEM observation

Figure 3 shows bright-field TEM images of precipitates on grain boundaries for Al–1.2Si alloy at HTT = 0 and 2.59×10^6 s. At HTT = 0 s, Si precipitates with diameters of about 0.1 μm are observed on the grain boundaries, but they are not observed in the grains. On the other hand, Si precipitates with diameters of about 10 μm are observed in the grains and on the grain boundaries at HTT = 2.59×10^6 s. This indicates that precipitation and growth of Si precipitates occur by the heat-treatment at 453 K.

3.2 Al–0.2 mass% Mg–Si alloys

3.2.1 Susceptibility to intergranular corrosion

Figure 4 shows optical micrographs of the cross section for Al–0.2Mg–0.9Si and –0.2Mg–1.3Si alloys at HTT = 0, 8.64×10^4 and 2.59×10^6 s after anodic dissolution tests. The corrosion morphology depends on Si concentration at HTT = 0 s. Pitting corrosion is observed for Al–0.2Mg–0.9Si alloy and intergranular corrosion is observed for Al–0.2Mg–1.3Si alloy. At HTT = 8.64×10^4 s, obvious intergranular corrosion is observed for Al–0.2Mg–0.9Si alloy and the corrosion morphology is pitting corrosion for Al–0.2Mg–

Fig. 1 Optical micrographs of the cross section for Al-0.4Si, -0.8Si and -1.2Si alloys at HTT = 0, 8.64×10^4 and 2.59×10^6 s after anodic dissolution tests.

Fig. 2 Variations of corrosion depth with HTT for Al-0.4Si, -0.8Si, -1.2Si and -1.4Si alloys after anodic dissolution tests. Pitting corrosion and intergranular corrosion is denoted as PC and IGC, respectively.

1.3Si alloy. At $\text{HTT} = 2.59 \times 10^6$ s, the corrosion morphology is pitting corrosion for each Si concentration.

Figure 5 shows variations of corrosion depth with HTT for Al-0.2Mg-0.9Si and -0.2Mg-1.3Si alloys after anodic dissolution tests. The open and solid symbols show pitting corrosion and intergranular corrosion, respectively. Both the corrosion depth and corrosion morphology depend on HTT.

For Al-0.2Mg-0.9Si alloy, the corrosion morphology is pitting corrosion at $\text{HTT} = 0$ and 7.20×10^3 s. The corrosion morphology is intergranular corrosion at $\text{HTT} = 1.44 \times 10^4$ – 3.46×10^5 s. The corrosion depth increases with an increase in HTT and reaches a maximum at $\text{HTT} = 8.64 \times 10^4$ s. However, the intergranular corrosion is observed until $\text{HTT} = 3.46 \times 10^5$ s, at which point the corrosion depth decreases. The corrosion morphology is pitting corrosion again at $\text{HTT} = 4.61 \times 10^5$ s.

For Al-0.2Mg-1.3Si alloy, the intergranular corrosion is observed at $\text{HTT} = 0$ – 2.88×10^4 s. The corrosion depth increases with HTT. The corrosion morphology is pitting corrosion at $\text{HTT} = 8.64 \times 10^4$ s and the corrosion depth decreases rapidly with HTT. That is, the susceptibility to intergranular corrosion of Al-0.2Mg-0.9Si and -0.2Mg-1.3Si alloys shows a peak at $\text{HTT} = 8.64 \times 10^4$ and 2.28×10^4 s, respectively.

3.2.2 TEM observation

Figure 6 shows bright-field TEM images of precipitates on grain boundaries for Al-0.2Mg-1.3Si alloy at $\text{HTT} = 2.88 \times 10^4$ and 8.64×10^4 s. At $\text{HTT} = 2.88 \times 10^4$ s, Si precipitates with diameters of approximately $0.04 \mu\text{m}$ are observed on the grain boundaries but they cannot be observed in the grains. A precipitate-free zone (PFZ) along the grain boundary is observed. At $\text{HTT} = 8.64 \times 10^4$ s, large Si precipitates with

Fig. 3 Bright-field TEM images of precipitates on grain boundaries for Al-1.2Si alloy at HTT = 0 and 2.59×10^6 s.

Fig. 4 Optical micrographs of the cross section for Al-0.2Mg-0.9Si and -0.2Mg-1.3Si alloys at HTT = 0, 8.64×10^4 and 2.59×10^6 s after anodic dissolution tests.

diameters of approximately 0.1 μ m on the grain boundaries and small ones with diameters of approximately 0.01 μ m in the grains are observed. This indicates that Si precipitates and

Fig. 5 Variations of corrosion depth with HTT for Al-0.2Mg-0.9Si and -0.2Mg-1.3Si alloys after anodic dissolution tests. Pitting corrosion and intergranular corrosion is denoted as PC and IGC, respectively.

grows by the heat-treatment at 453 K. PFZ is also observed at 8.64×10^4 s.

3.3 Al-1.1 mass% Mn-Si alloys

3.3.1 Susceptibility to intergranular corrosion

Figure 7 shows optical micrographs of the cross section for Al-1.1Mn-0.4Si, -1.1Mn-0.8Si and -1.1Mn-1.4Si alloys at HTT = 0, 8.64×10^4 and 2.59×10^6 s after anodic dissolution tests. The corrosion morphology depends on Si concentration at HTT = 0 s. Pitting corrosion is observed for Al-1.1Mn-0.4Si and -1.1Mn-0.8Si alloys and intergranular corrosion is observed for Al-1.1Mn-1.4Si alloy. At HTT of 8.64×10^4 s, pitting corrosion is observed for Al-1.1Mn-0.4Si alloy and intergranular corrosion is observed for Al-1.1Mn-0.8Si and -1.1Mn-1.4Si alloys. At HTT = 2.59×10^6 s, the corrosion morphology is pitting corrosion for each Si concentration.

Figure 8 shows variations of corrosion depth with HTT for Al-1.1Mn-0.4Si, -1.1Mn-0.8Si, -1.1Mn-1.2Si and -1.1Mn-1.4Si alloys after anodic dissolution tests. The open and solid symbols show pitting corrosion and intergranular

Fig. 6 Bright-field TEM images of precipitates on grain boundaries for Al-0.2Mg-1.3Si alloy at $\text{HTT} = 2.88 \times 10^4$ and 8.64×10^4 s.

Fig. 7 Optical micrographs of the cross section for Al-1.1Mn-0.4Si, -1.1Mn-0.8Si and -1.1Mn-1.4Si alloys at $\text{HTT} = 0$, 8.64×10^4 and 2.59×10^6 s after anodic dissolution tests.

corrosion, respectively. The corrosion depth and morphology of Al-1.1Mn-0.4Si alloy are independent of HTT, whereas the corrosion depth and morphology of Al-1.1Mn-0.8Si, -1.1Mn-1.2Si and -1.1Mn-1.4Si alloys depend on HTT.

For Al-1.1Mn-0.8Si alloy, corrosion morphology is pitting corrosion at $\text{HTT} = 0$ and 7.2×10^3 s and intergranular corrosion at $\text{HTT} = 1.44 \times 10^4$ s. Corrosion morphology is pitting corrosion again at $\text{HTT} = 6.05 \times 10^5$ s.

For Al-1.1Mn-1.2Si alloy, the corrosion morphology is pitting corrosion at $\text{HTT} = 0$ s and intergranular corrosion at $\text{HTT} = 7.2 \times 10^3$ – 3.45×10^5 s. The corrosion morphology is pitting corrosion again at $\text{HTT} = 6.05 \times 10^5$ s. The corrosion depth increases with increasing HT, reaches a maximum at $\text{HTT} = 3.64 \times 10^5$ s and then decreases with a further increase in HTT.

For Al-1.1Mn-1.4Si alloy, intergranular corrosion is observed at $\text{HTT} = 0$ – 3.46×10^5 s and corrosion morphology is pitting corrosion at $\text{HTT} = 6.05 \times 10^5$ s. Corrosion depth is the deepest at $\text{HTT} = 8.64 \times 10^4$ s and then decreases rapidly with an increase in HTT. That is, the susceptibility to intergranular corrosion of Al-1.1Mn-1.2Si and -1.1Mn-1.4Si alloys shows a peak at $\text{HTT} = 3.46 \times 10^5$ and 8.64×10^4 s.

3.3.2 TEM observation

Figure 9 shows bright-field TEM images of precipitates on grain boundaries for Al-1.1Mn-1.2Si alloy at $\text{HTT} = 0$ and 7.2×10^6 s. Intermetallic compounds observed at $\text{HTT} = 0$ s are Al-Mn series intermetallic compounds with gray

Fig. 8 Variations of corrosion depth with HTT for Al-1.1Mn-0.4Si, -1.1Mn-0.8Si, -1.1Mn-1.2Si and -1.1Mn-1.4Si alloys after anodic dissolution tests. Pitting corrosion and intergranular corrosion is denoted as PC and IGC, respectively.

spherical or elliptical shapes. The distribution of Al-Mn series intermetallic compounds at $\text{HTT} = 7.2 \times 10^6$ s is the almost same as that at $\text{HTT} = 0$ s. Dark black compounds are also observed on Al-Mn series intermetallic compounds, which are Si precipitates as identified by elemental analysis. It is suggested that Si precipitates and grows by the heat-treatment at 453 K.

3.4 Al-1.1 mass% Mn-0.2 mass% Mg-Si alloys

3.4.1 Susceptibility to intergranular corrosion

Figure 10 shows optical micrographs of the cross section for Al-1.1Mn-0.2Mg-0.6Si, -1.1Mn-0.2Mg-0.8Si and -1.1Mn-0.2Mg-1.4Si alloys at $\text{HTT} = 0$, 8.64×10^4 and 2.59×10^6 s after anodic dissolution tests. Corrosion morphology depends on Si concentration at $\text{HTT} = 0$ s. Pitting corrosion is observed for Al-1.1Mn-0.2Mg-0.6Si and -1.1Mn-0.2Mg-0.8Si alloys and intergranular corrosion is observed for Al-1.1Mn-0.2Mg-1.4Si alloy. The pitting corrosion is observed for Al-1.1Mn-0.2Mg-0.6Si alloy and intergranular corrosion for Al-1.1Mn-0.2Mg-0.8Si and -1.1Mn-0.2Mg-1.4Si alloys at $\text{HTT} = 8.64 \times 10^4$ s. At $\text{HTT} = 2.59 \times 10^6$ s, the corrosion morphology is pitting corrosion in each Si concentration.

Figure 11 shows variations of corrosion depth with HTT for Al-1.1Mn-0.2Mg-0.6Si, -1.1Mn-0.2Mg-0.8Si, -1.1Mn-0.2Mg-1.2Si and -1.1Mn-0.2Mg-1.4Si alloys after anodic dissolution tests. The open and solid symbols show pitting corrosion and intergranular corrosion, respectively. For Al-1.1Mn-0.2Mg-0.6Si alloy, the corrosion depth is independent of HTT and the morphology is pitting corrosion in spite of HTT.

The corrosion depth and morphology of Al-1.1Mn-0.2Mg-0.8Si, -1.1Mn-0.2Mg-1.2Si and -1.1Mn-0.2Mg-1.4Si alloys depend on HTT.

For Al-1.1Mn-0.2Mg-0.8Si alloy, corrosion morphology is pitting corrosion at $\text{HTT} = 0$ s and intergranular corrosion at $\text{HTT} = 7.20 \times 10^3$ s. Corrosion morphology is pitting corrosion again at $\text{HTT} = 6.05 \times 10^5$ s. The corrosion depth at $\text{HTT} = 2.88 \times 10^4$ s is the deepest within HTT.

Fig. 9 Bright-field TEM images of precipitates on grain boundaries for Al-1.1Mn-1.2Si alloy at $\text{HTT} = 0$ and 7.2×10^6 s.

Fig. 10 Optical micrographs of the cross section for Al-1.1Mn-0.2Mg-0.6Si, -1.1Mn-0.2Mg-0.8Si and -1.1Mn-0.2Mg-1.4Si alloys at $\text{HTT} = 0, 8.64 \times 10^4$ and 2.59×10^6 s after anodic dissolution tests.

Fig. 11 Variations of corrosion depth with HTT for Al-1.1Mn-0.2Mg-0.6Si, -1.1Mn-0.2Mg-0.8Si, -1.1Mn-0.2Mg-1.2Si and -1.1Mn-0.2Mg-1.4Si alloys after anodic dissolution tests. Pitting corrosion and intergranular corrosion is denoted as PC and IGC, respectively.

For Al-1.1Mn-0.2Mg-1.2Si alloy, intergranular corrosion is observed at $\text{HTT} = 0\text{--}3.45 \times 10^5$ s. The corrosion morphology is pitting corrosion at $\text{HTT} = 6.05 \times 10^5$ s. The corrosion depth at $\text{HTT} = 2.88 \times 10^4$ s is the deepest.

For Al-1.1Mn-0.2Mg-1.4Si alloy, intergranular corrosion is observed at $\text{HTT} = 0\text{--}1.73 \times 10^5$ s and the corrosion morphology is pitting corrosion at $\text{HTT} = 3.46 \times 10^5$ s. The corrosion depth at $\text{HTT} = 3.46 \times 10^4$ s is the deepest and then the corrosion depth decreases rapidly. That is, the susceptibility to intergranular corrosion of Al-1.1Mn-0.2Mg-0.8Si, -1.1Mn-0.2Mg-1.2Si and -1.1Mn-0.2Mg-1.4Si alloys becomes a maximum at $\text{HTT} = 2.88 \times 10^4$ s.

4. Discussion

As shown in Figs. 1 and 2, Al-Si alloys containing less than 0.4 mass% Si show no intergranular corrosion regardless of HTT. Those containing more than 0.4 mass% Si show intergranular corrosion at $\text{HTT} \geq 0$ or 8.64×10^4 s. It is clear that the susceptibility to intergranular corrosion increases with an increase in Si concentration. Therefore, the intergranular corrosion that occurs at $\text{HTT} = 0\text{--}2.59 \times 10^6$ s is caused by Si. Because solute Si makes the E_{PIT} of aluminum noble, as does solute Cu,¹²⁾ it is thought that a mechanism for the susceptibility to the intergranular corrosion caused by Si is the same as that caused by Cu. According to the mechanism of the intergranular corrosion in Al-Cu alloys, the intergranular

corrosion is preferential corrosion on the grain boundaries caused by the difference of E_{PIT} between the grains and the Cu-depleted layer along the grain boundaries.⁵⁾ Thus, it is suggested that the intergranular corrosion in Al–Si alloys is generated by the Si-depleted layer along the grain boundaries because diffusion coefficient of Si on the grain boundaries is higher than in the grains. It is expected that the depth of intergranular corrosion will increase with increasing Si concentration because of the formation of a continuous Si-depleted layer caused by increase driving force of both Si precipitation and Si diffusion with increasing Si concentration and an increase in the difference of E_{PIT} between the grains and the Si-depleted layers along the grain boundaries leading to preferential dissolution of the grain boundaries. This tendency is found in Fig. 2.

As shown in Fig. 2, the corrosion depth initially increases and then decreases with HTT. This mechanism, in which corrosion depth has such HTT dependence, is thought to occur as follows. Si precipitates on the grain boundaries during the cooling process after brazing and heat-treatment process at 453 K, and a Si-depleted layer is formed continuously along the grain boundaries. The continuous Si-depleted layer causes intergranular corrosion. However, an extended heat-treatment not only causes Si to precipitate but also decreases the solute Si concentration in the grains. The Si concentration in the grains continues to decrease until the compensation of the Si concentration at the grain boundaries is completed. This means that the pitting potentials in the grains and grain boundaries become identical. Thus, corrosion progresses in both the grains and the grain boundaries, which indicates that the corrosion depth decreases and the susceptibility to intergranular corrosion is reduced. To confirm this mechanism, Fig. 12 shows EDS line analysis for Si-depleted zones on grain boundaries for 1.4Si at $\text{HTT} = 0$ and 2.59×10^6 s. At $\text{HTT} = 0$ s, Si intensity decreases around the grain boundaries. The decrease in Si intensity corresponds to the Si-depleted layer along the grain boundaries. At $\text{HTT} = 2.59 \times 10^6$ s, the difference in Si intensity between the grains and the grain boundaries is not observed.

As shown in Figs. 6 and 9, regardless of the alloy elements, precipitation and growth of Si precipitates occur by the heat-treatment at 453 K. It is thought that the generation and disappearance of the intergranular corrosion are caused by the Si-depleted layer along the grain boundaries for Al–0.2 mass% Mg–Si alloys, as mentioned in section 3.2, Al–1.1 mass% Mn–Si alloys in 3.3, and Al–1.1 mass% Mn–0.2 mass% Mg–Si alloys in 3.4 in the same manner as with the Al–Si alloys. Figure 13 shows influences of Si content on HTT leading to the maximum corrosion depth (A) and the transition from intergranular corrosion to pitting corrosion (B). These characteristic HTT values depend little on Si concentration when the corrosion depth is the deepest or the corrosion morphology changes from intergranular corrosion to pitting corrosion. These HTT values are the longest for Al–Si alloys and are shortened by the use of other alloy elements. This is why the addition of Mn and Mg induces precipitation of some kinds of intermetallic compounds as shown Figs. 6 and 9. These intermetallic compounds promote precipitation of Si because these intermetallic compounds become nucleation sites.

Fig. 12 EDS line analysis for Si-depleted zones on grain boundaries for Al–1.4Si alloy at $\text{HTT} = 0$ and 2.59×10^6 s.

Fig. 13 Influences of Si content on HTT leading to the maximum corrosion depth (A) and the transition from intergranular corrosion to pitting corrosion (B).

5. Conclusion

We investigated that susceptibility to intergranular corrosion of Al–Si, Al–0.2 mass% Mg–Si, Al–1.1 mass% Mn–Si and Al–1.1 mass% Mn–0.2 mass% Mg–Si alloys heat-treated at 453 K after the heat-treatment simulating the brazing process. In terms of increasing and decreasing the susceptibility of these alloys to intergranular corrosion the following conclusions can be drawn:

- (1) The addition of Si increased susceptibility to intergranular corrosion for each alloy series. Susceptibility to intergranular corrosion was observed for the as-brazed specimens containing more than 1.2 mass% Si.
- (2) Susceptibility to intergranular corrosion initially increased with an increase in the heat-treatment time at 453 K and then decreased.
- (3) Short-term heat-treatment at 453 K caused precipitation and growth of Si precipitates on grain boundaries, and then, a continuous Si-depleted layer was formed along the grain boundaries. Si also precipitated in grains with long-term heat-treatment at 453 K and the solute Si concentration in the grains decreased to that on the grain boundaries. This is the reason why the susceptibility to intergranular corrosion was time-dependent.

- (4) The addition of Mg and Mn increased susceptibility to intergranular corrosion because Mg_2Si intermetallic compounds and Al–Mn series intermetallic compounds promote precipitation of Si.
- (5) The addition of Mg and Mn decreased the susceptibility to intergranular corrosion, in the same manner as the increase in susceptibility.

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