Influence of Si/Mg, Cu Content and Aging Condition on the Electrochemical Behaviors of Al-Mg-Si Alloy

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Measurements of potentiodynamic polarization curves (PDS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were utilized to investigate the effects of Si/Mg, Cu content, and aging condition on the corrosion and electrochemical behavior of Al-Mg-Si alloy in H_2SO_4 or NaCl aqueous solution. The results of electrochemical tests showed that Al-Mg-Si alloy was more susceptible to corrosion with longer aging time due to the growth of the precipitates and a decrease in corrosion potential. However, it was more resistant to corrosion with higher Si/Mg and Cu content due to an increase in corrosion potential and smaller corrosion current. With Cu addition, the growth of precipitate during aging can be significantly inhibited, resulting in better corrosion resistance. During the corrosion process, the initial corrosion attack took place on interfaces with potential drop, such as interfaces between matrix and Mg-Si or Al-Fe-(Mn)-Si particles.

Keywords: Al-Mg-Si Al alloy, Si/Mg, Cu content, aging, Corrosion behavior, Polarization curve

1. INTRODUCTION

Aluminum alloy has the advantages of light weight, high specific strength, good electrical conductivity, easy recycling, good corrosion resistance and formability. It is widely used in aerospace, 3C/IT, and transportation industries[1-2]. In the application of portable electronic products, such as laptops, tablets, mobile phones, and wearable products, etc., the pursuit of energy saving, lightness and how to increase the strength of materials to reduce the thickness and weight of the case is the main trend nowadays. Generally speaking, the strength of precipitation-hardening Al-Mg-Si alloys is higher than existing widely used strain-hardening Al-Mg alloys and has been gradually applied to the 3C/IT products. Following a solution heat treatment, by controlling aging temperature and time, the strength of 6xxx series Al-Mg-Si alloys can be increased via the formation of precipitates[3]. The presence of precipitates is a favorable microstructural heterogeneity for strength development and is also simultaneously an unfavorable electrochemical heterogeneity for corrosion resistance[4]. Hence, the alloying elements and aging conditions which control the precipitation behavior, also affect the material strength and electrochemical behavior. Furthermore, the subsequent anodizing treatment for 3C/IT products will also be affected.

However, there are few studies on the effects of element addition on the electrochemical behavior incorporating microstructure characterization in Al-Mg-Si alloy. In this study, microstructures and electrochemical behaviors of Al-Mg-Si alloy with different Si to Mg ratio and Cu content were investigated. The effect of aging conditions on the corrosion of Al-Mg-Si alloy will also be considered. Potentiodynamic polarization curves were utilized to investigate the effects on the corrosion and electrochemical behavior. The microstructure characterization was conducted by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was used to study the size and number density of precipitates formed in the alloys during aging.

2. EXPERIMENTAL METHOD

2.1 Materials

Chemical compositions of custom made Al-Mg-Si Al alloy sheets are given in Table 1, where it can be seen that Cu contents and Si to Mg ratio are varied respectively. The alloy sheets were prepared by casting from commercial purity materials. Alloying element contents were analyzed by using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.2 Heat treatment

Solution heat treatment of the as received samples

Table 1 The chemical compositions of custom made Al-Mg-Si Al alloy under study (wt%).

Alloy	Mg	Si	Cu	Fe	Mn	Al
Cu=0	1.0	0.6	0.0	0.1	0.06	Bal.
Cu=0.2	1.0	0.6	0.2	0.1	0.06	Bal.
Cu=0.9	1.0	0.6	0.9	0.1	0.06	Bal.
Si/Mg=2.6	0.5	1.3	0.0	0.1	0.06	Bal.
Si/Mg=1.5	0.7	1.1	0.0	0.1	0.06	Bal.
Si/Mg=0.5	1.1	0.6	0.0	0.1	0.06	Bal.

was carried out at 550°C for 1h, followed by quenching immediately in ice-water. The specimens were kept at -5°C to prevent or minimize the effect of natural aging before any artificial aging treatment. Some of these specimens were tested in natural aging condition and the other specimens were artificially aged at 165°C for 1~10 hours. After any aging treatment, the alloy specimens were also quenched in ice-water and kept at -5°C until they were taken for corrosion test.

2.3 Electrochemical characterization

Corrosion tests were performed in H_2SO_4 or NaCl aqueous solution at 25°C prepared with analytical reagents. The electrochemical technique was employed by linear potentiodynamic polarization curves. The electrochemical tests were performed using a Princeton Applied Research VersaSTAT3 potentiostat, along with a three electrode glass cell incorporating a Pt counter electrode and a silver chloride electrode (Ag/AgCl) as a reference electrode. Prior to testing, all the specimens were ground to 2000 grit SiC paper finish, and all the electrochemical tests were initiated after 30 min. at the open circuit potential (OCP) of each specimen. Polarization curves were recorded at a constant sweep rate of 1 mV/s at the interval from -200 to +600 mV with respect to the open circuit potential, E_{corr}. Each sample was tested at least 3 times.

2.4 Microstructural characterization

The samples of custom made Al-Mg-Si alloy were examined using a JEOL JSM-6510 SEM incorporating energy dispersive X-ray spectroscopy (EDS) before and after potentiodynamic polarization tests. Transmission electron microscopy was performed on various aging treatment specimens to analyze the precipitate size by a JEOL-2010 TEM operated at 200 kV. The specimen preparation for TEM involved mechanical thinning of the alloy sheets to 100-150 mm, followed by punching of 3 mm discs, which were subsequently electropolished in methanol-nitric acid solution.

3. RESULTS AND DISCUSSION

3.1 Microstructural characterization

In order to identify the intermetallic compounds present in the custom made Al-Mg-Si alloy, samples polished to mirror quality were studied by the SEM with EDS analysis. The results obtained indicate that intermetallic compounds such as those shown in Fig.1.(a) & (c) can mainly be divided into two categories: white-grey Al-Fe-(Mn)-Si and dark colored Mg-Si particles. Fig.1.(a) & (c) shows the intensity of dark colored Mg-Si particles is higher in the Al alloy with lower Si to Mg ratio. That may be because of less Mg content. As for the Al alloy with Cu addition, as shown in Fig.1.(b) & (d), it has finer both white-grey Al-Fe-(Mn)-Si and dark-colored Mg-Si intermetallic particles. It indicates that Cu addition may inhibit the growth of intermetallic particles. Hence, with different Si/Mg and Cu addition, the microstructure of Al-Mg-Si alloy was changed. Table 2 [5] shows the corrosion potentials of common intermetallic compounds in Al-Mg-Si alloy, it can be seen that Al-Fe-(Mn)-Si has higher corrosion potential than that of the Mg-Si particle, which indicates that intermetallic particles may affect the corrosion behavior of the Al alloy.

3.2 Effect of aging condition on corrosion

The main temper grades for Al-Mg-Si alloy used for 3C/IT products are T4 and T6. T4 means natural aging after solution treatment, and T6 means artificial aging after solution treatment. Al-Mg-Si alloy with T6 aging treatment can significantly improve mechanical strength. The potentiodynamic polarization curve is a helpful tool in determining the instantaneous corrosion rate of a substrate. In a typical polarization curve, a lower corrosion current density (I_{corr}) or a higher corrosion potential (E_{corr}) corresponds to a lower corrosion rate and a better corrosion resistance[6]. Figure 2 shows that the alloy with T4 temper has higher E_{corr} and lower I_{corr} than with T6 temper. It indicates that the sample with T4 temper has
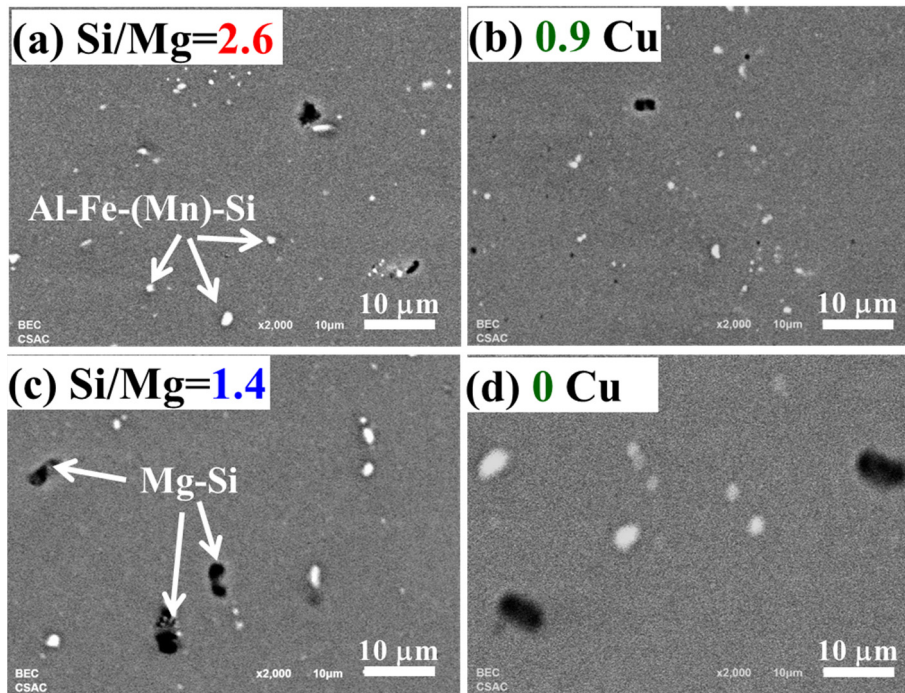
Fig.1. SEM observation of custom made Al-Mg-Si alloys under study. (a) Si/Mg=2.6, (b) with 0.9wt% Cu content, (c) Si/Mg=1.4, and (d) without Cu addition.

Table 2 Corrosion potentials of intermetallic compounds in Al-Mg-Si Al alloy (ASTM G 69) [5].

Intermetallic phases	Corrosion potential, V_{SCE} (Ref. 5)
Si	-0.17
Al_3Fe	-0.47
Al-Fe-(Mn)-Si	-0.58
Al-4%Cu	-0.61
Al_6(Fe, Mn)	-0.76
Al-3wt%Mg	-0.78
Mg_2Si	-1.19
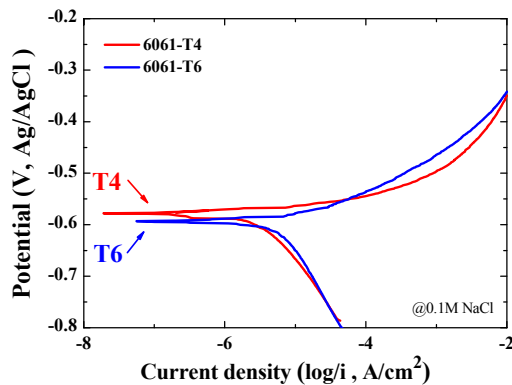
Fig.2. Potentiodynamic polarization curves for 6061 Al alloy with T4 and T6 aging condition in NaCl solution.

better corrosion resistance. In order to clarify the relation between precipitate morphology and electrochemical behavior under different aging conditions, the polarization curves of 6061 Al alloys with artificial aging at 165°C for 2~10 hours were measured. As shown in Figure 3, it can be observed that E_{corr} decreases with increasing aging time, and the I_{corr} is also increasing.

Figure 4 shows the transmission electron microscopic observation of T4 natural aging and artificial aging for 2hrs and 10hrs. Under the same magnification, the T4 natural aging can be clearly observed as the Mg_2Si precipitates are very fine and not obvious. After artificial aging at 165°C for 2 hours, the precipitates begin to appear, but the size is still small. However, the

precipitates become obvious after artificial aging for 10 hours, and the size and the amount are larger than the previous two. That is, the precipitate size and the amount both increase with the increase of the artificial aging time. The sequence of precipitate sizes is as followed: artificial aging for 10hrs> artificial aging for 2hrs> T4 natural aging. In addition, the Mg_2Si precipitates have lower E_{corr} than Al matrix, therefore, it promotes the corrosion to occur more easily when the precipitates grow larger and with a higher amount. Thereby, the aging condition of the Al-Mg-Si aluminum alloy affects the electrochemical behavior and its corrosion properties.
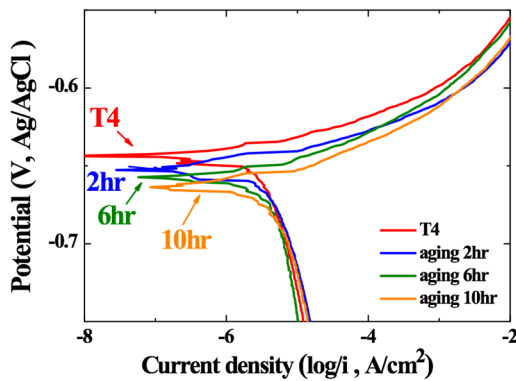

Fig.3.　Potentiodynamic polarization curves for 6061 Al-Mg-Si alloy in NaCl solution with different aging conditions.

3.3 Influence of Si/Mg on corrosion behavior

Figure 5 shows the corrosion polarization curve of 6000 series Al-Mg-Si alloy with Si to Mg ratio from low to high (0.5, 1.5, 2.6) in 0.6M NaCl electrolyte. It shows that the alloy with Si/Mg=2.6 has the highest corrosion potential Value (E_{corr}=-0.649V), on the contrary, the alloy with Si/Mg=0.5 has the lowest corrosion potential value (E_{corr}=-0.68V), showing a tendency that the corrosion potential of Al-Mg-Si alloy increases with the

increase of Si/Mg ratio, that is, the alloy with high Si/Mg has better corrosion resistance. In addition, Fig.5 also shows that the alloys with a lower Si/Mg ratio have a larger corrosion current density, which is consistent with the tendency of the corrosion potential. Hence, the corrosion resistance sequence of Al-Mg-Si alloys with different Si/Mg is as followed：2.6> 1.5> 0.5.
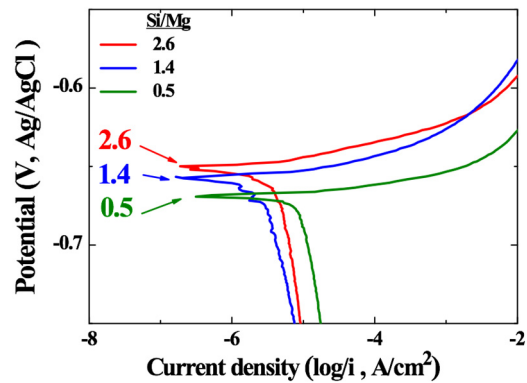

Fig.5.　Potentiodynamic polarization curves for Al-Mg-Si alloy in NaCl solution with different Si to Mg ratio.

3.4 Influence of Cu content on corrosion behavior

Figure 6 shows the polarization curves of Al-Mg-Si alloys with different Cu content in the solution of 0.6M NaCl. It can be seen that the alloy with 0wt% Cu content has the lowest corrosion potential (E_{corr}=-0.67V), and with a Cu content increase of 0.2wt%, the potential rises to (E_{corr}=-0.64V), and finally at 0.9wt% Cu has the highest potential (E_{corr}=-0.61V), which shows that the corrosion potential of the Al-Mg-Si alloy moves to a higher potential with the increase of Cu content. Figure 7 shows the potentiodynamic polarization curves for Al-Mg-Si alloy with 0wt% and 0.9wt% Cu content aged at 165°C for 6 and 22 hours. It can be observed that corrosion potential decreased with increasing aging time.
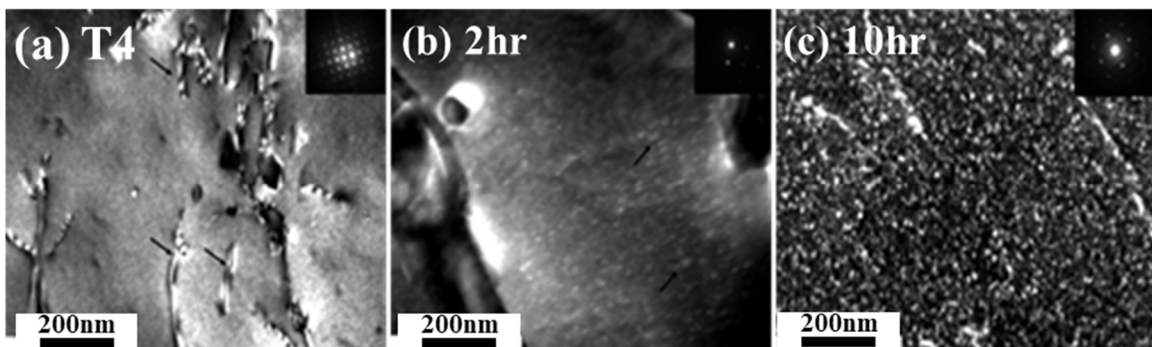

Fig.4.　Dark field TEM of selected alloys with: (a) natural aging, (b) artificial aging at 165°C for 2 hr, (c) artificial aging at 165°C for 10 hr.
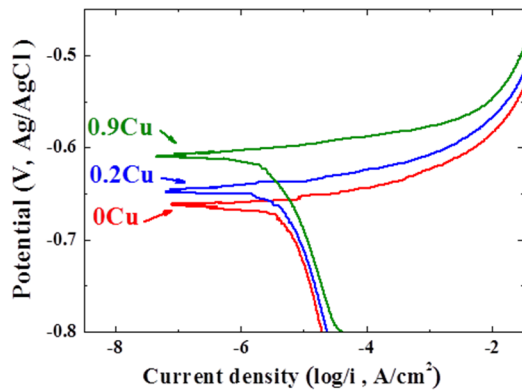
Fig.6. Potentiodynamic polarization curves for Al-Mg-Si alloy in NaCl solution with different Cu content.
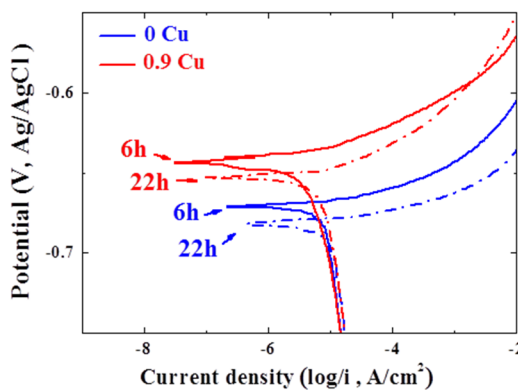

Fig.7. Potentiodynamic polarization curves for Al-Mg-Si alloy with 0wt% and 0.9wt% Cu content aged at 165°C for 6 and 22 hours.

In addition, the 0.9wt% Cu alloy has higher corrosion potential and lower corrosion current density than the 0wt% Cu alloy after aging for both 6 and 22 hours, which indicated the addition of Cu can also improve the corrosion resistance of Al-Mg-Si alloy after aging treatment. Therefore, from the results presented above, the corrosion resistance of 6xxx series Al-Mg-Si alloys was improved with an increase in Cu content, and with a decrease in aging time.

Results of microstructural analysis using TEM for selected alloys are shown in Fig.8. All specimens were imaged in the <001> direction. It was found that the precipitates had obviously grown and coarsened as the aging time increases. However, the precipitates in 0wt% Cu alloys, as shown in Fig.8.(a) & (c), were coarser and lower in number density when compared to the precipitates in 0.9wt% Cu alloys, as shown in Fig.8.(b) & (d). The precipitate coarsening was suppressed with Cu addition. The results indicated that the presence of Cu can prevent the Mg$_2$Si precipitates from growing excessively and coarsening during the aging treatment, and remained as finer particles, thereby reducing the potential drop of the interface between Al-matrix and precipitates, then the corrosion resistance is enhanced. The role of Cu was suggested to be segregated to the interfaces of precipitates and Al-matrix, which would inhibit the growth of precipitates during aging[7-9], hence the finer particles could be kept.

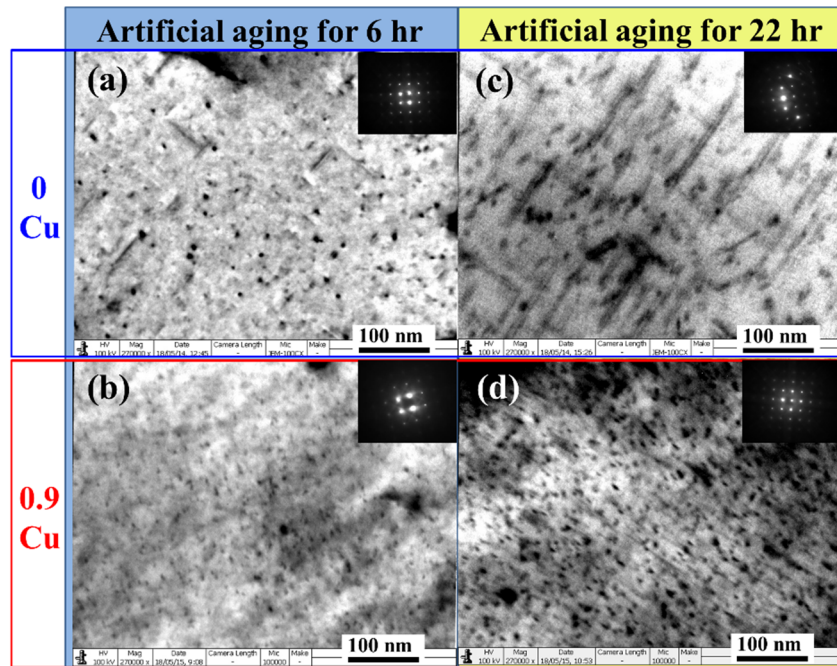### 3.5 Morphology of corrosion attack

Fig.8. Bright field TEM of selected Al-Mg-Si alloys with (a) 0wt% Cu aged for 6 hr, (b) 0.9wt% Cu aged for 6 hr, (c) 0wt% Cu aged for 22 hr and (d) 0.9wt% Cu aged for 22 hr.

Figure 9 shows the SEM micrographs of the corroded surfaces of the samples after the potentiodynamic polarization in 0.05M H_2SO_4 or 0.6M NaCl solution. It can be observed that pitting corrosion has occurred in all samples. As the Si/Mg ratio decreases, the pits become deeper and larger. However, as the amount of Cu addition increases, the degree of surface pitting corrosion becomes less severe, indicating that higher Si/Mg ratio and Cu addition are beneficial to enhance corrosion resistance. This microscopic observation is consistent with the electrochemical analysis described previously.

In order to investigate the corrosion evolution of Al-Mg-Si alloy, the potentiodynamic polarization test was cutoff at different potentials which is utilized to control the surface corrosion stages. Fig.10.(a) shows the interface of white-grey Al-Fe-(Mn)-Si intermetallic particles with higher corrosion potential (more noble) and relatively lower corrosion potential Al matrix (less noble).
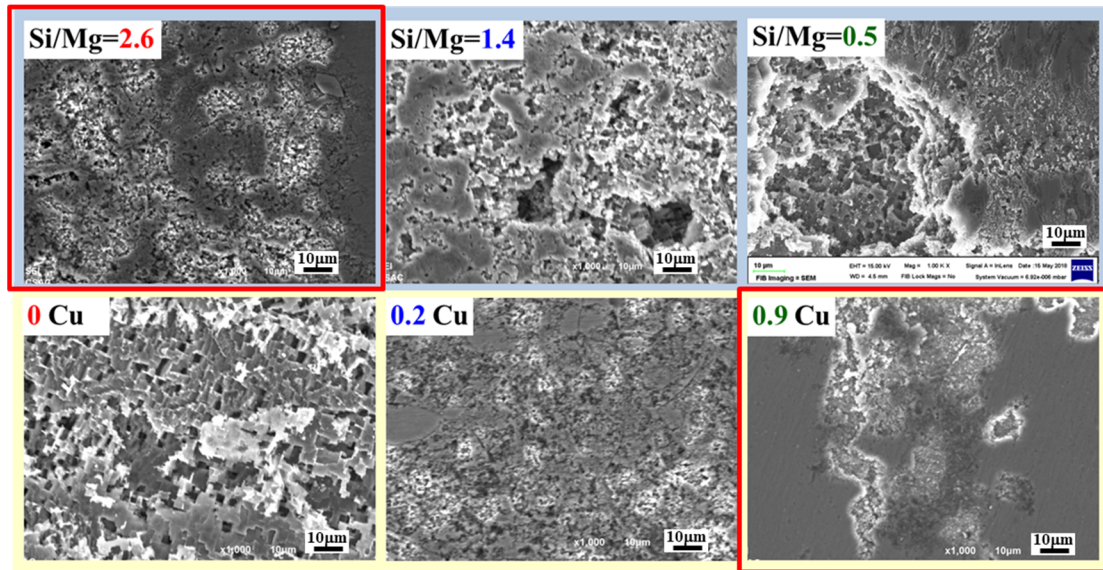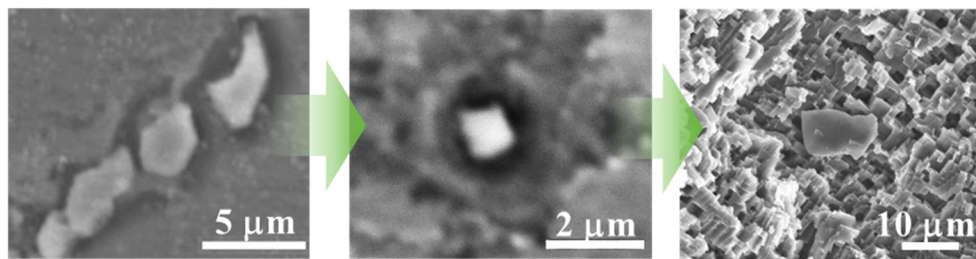

Fig.9.   SEM micrographs of corroded surface of samples after polarization tests in H_2SO_4 or NaCl solution
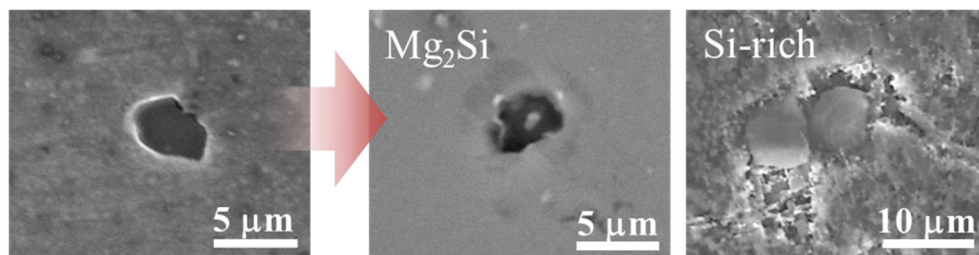

Fig.10.   The micrographs of interface between matrix and (a) higher potential Al-Fe-(Mn)-Si intermetallic particles, (b) lower potential Mg-Si intermetallic particles during corrosion process, show initial corrosion attack takes place on interface with potential drop

It can be observed that corrosion starts from Al matrix and continues to the dissolution of Al matrix, which is served as local anode. Finally, the etching hole is enlarged gradually and only the high corrosion potential Al-Fe-(Mn)-Si particles, serving as local cathode, are left. Fig.10.(b) shows the interface of dark-colored Mg-Si intermetallic particles and Al matrix. Oppositely, the Mg-Si particle with lower corrosion potential is served as a local anode and itself undergoes dissolution (independent of the matrix). The damage accumulation takes the form of incongruent dissolution. According to the above results, it is evident that the initial corrosion takes place from the interface with the corrosion potential drop.

4. CONCLUSIONS

Electrochemical measurements combined with microstructural characterizations of custom made 6xxx Al-Mg-Si alloy with different Si/Mg, Cu content, and aging condition were studied in this study. The composition and aging condition of 6xxx series Al-Mg-Si alloys played an important role in influencing the nanostructure development and hence the electrochemical behavior. The presence of Cu and higher Si to Mg ratio in Al-Mg-Si alloys increased the E_{corr} and made the alloys more resistant to corrosion. In addition, a decrease in the E_{corr} occurred with an increase in artificial aging time due to the growth of the precipitates. With Cu addition, the growth of precipitate during aging can be significantly inhibited, resulting in better corrosion resistance. Therefore, element composition and aging condition changed precipitation behavior in the Al-Mg-Si alloys and then affected its electrochemical behavior and corrosion resistance.

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