

## Corrosion mechanism associated with $Mg_2Si$ and Si particles in Al–Mg–Si alloys

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**Abstract:** The electrochemical behaviors and coupling behaviors of the  $Mg_2Si$  and Si phases with  $\alpha(Al)$  were investigated, the corrosion morphologies of Al alloys containing  $Mg_2Si$  and Si particles were observed, and the corrosion mechanism associated with them in Al–Mg–Si alloys was advanced. The results show that Si particle is always cathodic to the alloy base,  $Mg_2Si$  is anodic to the alloy base and corrosion occurs on its surface at the beginning. However, during its corrosion process, the preferential dissolution of Mg and the enrichment of Si make  $Mg_2Si$  transform to cathode from anode, leading to the anodic dissolution and corrosion of the alloy base at its adjacent periphery at a later stage. As the mole ratio of Mg to Si in an Al–Mg–Si alloy is less than 1.73, it contains  $Mg_2Si$  and Si particles simultaneously in the grain boundary area, and corrosion initiates on the  $Mg_2Si$  surface and the precipitate-free zone (PFZ) at the adjacent periphery of Si particle. As corrosion time is extended, Si particle leads to severe anodic dissolution and corrosion of the PFZ at its adjacent periphery, expedites the polarity transformation between  $Mg_2Si$  and the PFZ and accelerates the corrosion of PFZ at the adjacent periphery of  $Mg_2Si$  particle.

**Key words:** Al–Mg–Si alloys; intergranular corrosion; corrosion mechanism; electrochemical behaviors;  $Mg_2Si$ ; Si

### 1 Introduction

6xxx series [AlMgSi(Cu)] Al alloys are generally considered to be corrosion resistant although they can be susceptible to intergranular corrosion, and it was proposed that this could be caused by Si concentration in excess of the  $Mg_2Si$  ratio, precipitation of elemental Si or Cu-containing phases [1], or the anodic dissolution of the intermetallic phase  $Mg_2Si$ , along grain boundaries [2].

Precipitates or particles play an important role in the local distribution and rate of cathodic and anodic reactions. For Al–Mg–Si alloys, aging precipitates and grain boundaries are seen as the main anodic corrosion initiation sites, and most precipitates enhance the corrosion rate due to their cathodic activity [3–5]. It was claimed that intergranular corrosion susceptibility was the result of microgalvanic coupling between AlCu, CuSi or (Al)  $MgSiCu$  grain boundary precipitates and the adjacent precipitate-free zone (PFZ).  $\beta$ -phase ( $Mg_2Si$ )

and pure Si particle may precipitate if the Mg/Si mole ratio is lower than 1.73. Some researchers suggested that grain boundary precipitates of the  $\beta$ -phase are not associated with intergranular corrosion (IGC) susceptibility, unless present as a continuous film [6–8]. There have been many researches concerning the preparation and processing of the Al alloys containing  $Mg_2Si$  particles. However, the exact nature and properties of these precipitates in relation to IGC were not reported [9]. WANG and TIAN [10] presented that Al–Mg–Si alloys with a mole ratio of Mg to Si higher than 1.73 are not sensitive to intergranular corrosion due to little potential difference between  $Mg_2Si$  particle and Al matrix. However, BIRBILIS et al [11] found that the corrosion potential of  $Mg_2Si$  particles was much negative with respect to that of aluminum alloy matrix in 0.1 mol/L NaCl solution. The potential of 6xxx series Al alloy matrix is from about  $-0.72$  V to  $-0.75$  V (vs SCE) and that of  $Mg_2Si$  particles is about  $-1.54$  V in NaCl solution [12]. According to BIRBILIS's result, it can be

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deduced that the Al–Mg–Si alloy with a mole ratio of Mg to Si higher than 1.73 should be sensitive to IGC. This is obviously contradictory to our understanding of the corrosion behavior of 6xxx series Al alloy.

The purpose of the present study is to clarify the corrosion mechanism associated with the grain boundary precipitates of  $\text{Mg}_2\text{Si}$  and Si in Al–Mg–Si alloy. Their electrochemical behavior and coupling behavior with  $\alpha(\text{Al})$  (corresponding to grain boundary PFZ) were investigated, and the corrosion morphologies of the Al alloys containing coarse  $\text{Mg}_2\text{Si}$  and particles were observed. The corresponding corrosion mechanism was advanced.

## 2 Experimental

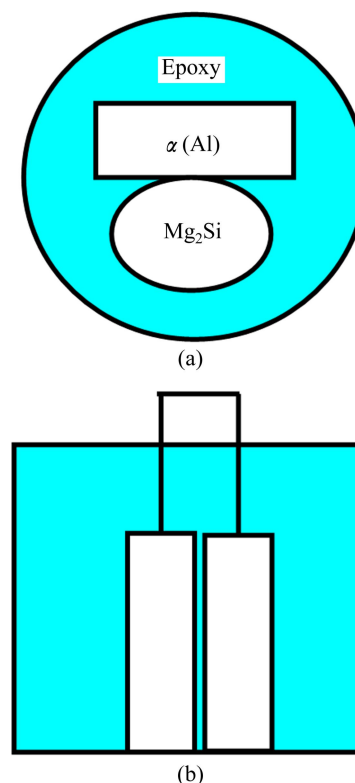
### 2.1 Preparation of simulated $\text{Mg}_2\text{Si}$ phase

The  $\text{Mg}_2\text{Si}$  powder was manufactured through solid state reaction at 450 °C for 40 h according to its chemical proportion. The synthesized powder was identified through X-ray diffraction (XRD). Then, the  $\text{Mg}_2\text{Si}$  powder was sintered through plasma sintering at 900 °C for 10 min under compressive pressure of 30 MPa. In addition, the aluminum alloy matrix or grain boundary precipitation free zone contains low content of alloying elements, which can be replaced by  $\alpha(\text{Al})$  to undergo electrochemical tests.

### 2.2 Electrochemical measurement and coupling behavior of associated phases

The specimens for electrochemical measurement were cut from  $\alpha(\text{Al})$ , the bulk  $\text{Mg}_2\text{Si}$  and Si. They were connected to a copper wire, and mounted in epoxy resin with an exposed surface, respectively. The exposed surface was ground using abrasive papers through 500-grade to 1200-grade, polished with  $\text{Cr}_2\text{O}_3$  powder, rinsed using acetone, degreased with distilled water and then dried in air. After 10 min of immersion in a 3.5% NaCl solution, their potentiodynamic scanning curves were measured with a CHI660 electrochemical workstation at a scanning rate of 1 mV/s. During the measurement, the working electrode was the specimens, a large platinum sheet and a saturated calomel electrode (SCE) with a Luggin capillary served as counter and reference electrodes, respectively.

Meanwhile, the bulk  $\text{Mg}_2\text{Si}$  and Si were coupled separately or simultaneously with  $\alpha(\text{Al})$  in the 3.5% NaCl solution, and the coupling method was shown in our previous paper [13–14], as shown in Fig. 1. During the coupling test, the coupling current was measured. In the coupled system, the area of the  $\text{Mg}_2\text{Si}$ ,  $\alpha(\text{Al})$  and Si were 28.26, 24 and 10.17 mm<sup>2</sup>, respectively. After 312 h, the coupling test was finished, the coupled electrodes were disconnected, and the open circuit potential of



**Fig. 1** Schematic diagram of coupling system: (a) Top view; (b) Lateral view

corresponding electrode was measured with the CHI660 electrochemical workstation.

### 2.3 Potential distribution in Al–Mg–Si alloy with different ratios of Mg to Si

Two Al–Mg–Si alloys with chemical composition of Al–0.63Mg–0.28Si and Al–0.63Mg–0.88Si were prepared, of which the mole ratios of Mg to Si are higher than 1.73 and lower than 1.73, respectively. After solution treatment, the alloy sheet was quenched followed by aging at 175 °C for 1 h. The alloy surface was ground using abrasive papers through 500-grade to 1200-grade, polished with  $\text{Cr}_2\text{O}_3$  powder, rinsed using acetone, degreased with distilled water and then dried in air. Then, the potential distribution associated with the phases in the area of the grain boundary was mapped through a Nano Scope IIIa atomic force microscope (AFM).

### 2.4 Preparation of Al alloys containing corresponding coarse particles and their corrosion morphologies

The corrosion morphologies associated with the aging precipitates in real Al alloys could not be recognized by SEM due to their too small size. To clearly observe the corrosion morphologies associated with the  $\text{Mg}_2\text{Si}$  and Si particles by SEM, two Al alloys containing these particles were made through melting and casting.

One alloy contained  $\text{Mg}_2\text{Si}$  particle, and the other contained  $\text{Mg}_2\text{Si}$  and Si particles simultaneously. In these Al alloys, the Mg content was higher than 5% (mass fraction). After casting, the cast ingot was annealed at 450 °C for 24 h and cooled in the oven. Therefore, the  $\text{Mg}_2\text{Si}$  and Si particles in these alloys were greatly coarsened, then the corrosion morphologies could be distinguished with SEM.

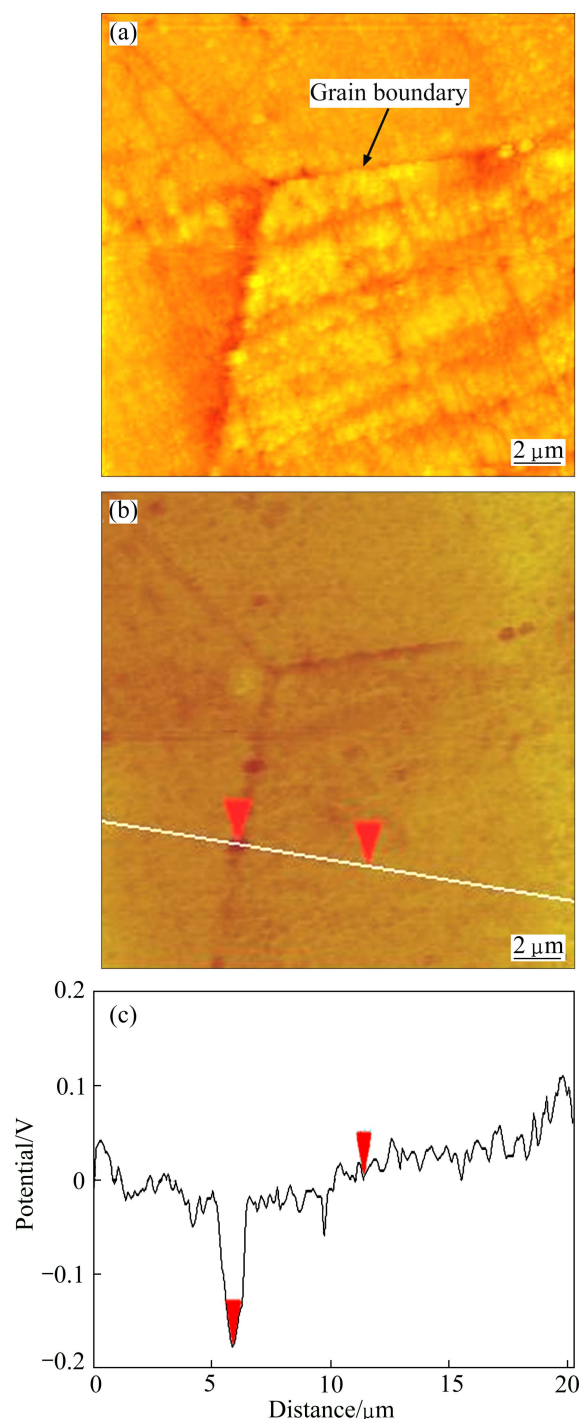
The surfaces of these Al alloys were ground using abrasive papers through 400-grade to 1000-grade, polished with diamond paste, rinsed using acetone, degreased with distilled water and dried in air. Then, they were immersed in the prepared NaCl solution for 12 h. To clearly distinguish the corrosion morphology of the simulated Al alloy, the corrosion product covering on the surface was removed using 2%  $\text{CrO}_3$ +5%  $\text{H}_3\text{PO}_4$  solution at 80 °C, and the corresponding corrosion morphologies were observed with the Sirion200 SEM.

### 3 Results and discussion

The AFM images of grain boundary in the Al–0.63Mg–0.28Si ( $n(\text{Mg})/n(\text{Si}) > 1.73$ ) alloy are shown in Fig. 2. The  $\text{Mg}_2\text{Si}$  particles distributed on the boundary are distant from each other (Fig. 2(a)). The dark regions in the potential distribution map (Fig. 2(b)) are related to  $\text{Mg}_2\text{Si}$  particles with more negative potential and there exists a potential difference as high as 180 mV (Fig. 2) between the grain boundary  $\text{Mg}_2\text{Si}$  particles and Al base. AFM images of grain boundary in the Al–0.63Mg–0.88Si ( $n(\text{Mg})/n(\text{Si}) < 1.73$ ) alloy are shown in Fig. 3. Si particles (whiter dots) and  $\text{Mg}_2\text{Si}$  particles (darker dots) at the grain boundary can be distinguished (Fig. 3(a)). As can be seen in the potential distribution curve (Fig. 3(b)), Si has the most positive potential, followed by Al base, while  $\text{Mg}_2\text{Si}$  comes the last (Fig. 3(c)). The potential difference between Si and Al base is 180 mV. While, the potential difference between Si and the  $\text{Mg}_2\text{Si}$  is up to 269 mV. The potential measurement result through AFM is consistent with that measured through electrochemical method.

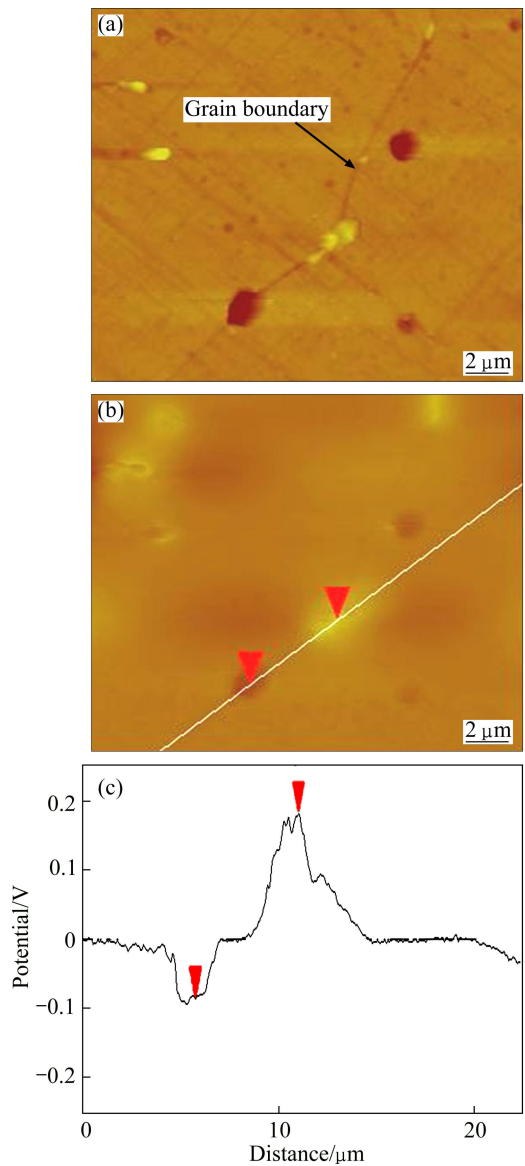
Figure 4 shows the XRD pattern of the synthesized  $\text{Mg}_2\text{Si}$  powder. It shows that the powder almost consists of single-phased  $\text{Mg}_2\text{Si}$ . The sintered bulk  $\text{Mg}_2\text{Si}$  could substitute for the real aging precipitate of  $\text{Mg}_2\text{Si}$  in Al–Mg–Si alloy to undergo electrochemical measurement. Meanwhile,  $\alpha(\text{Al})$  could substitute for the precipitate-free zone or the alloy base, due to its extremely little alloying element.

The potentiodynamic scanning curves and the corresponding corrosion parameters of individual  $\alpha(\text{Al})$ ,  $\text{Mg}_2\text{Si}$  and Si are presented in Fig. 5 and Table 1, respectively. It is clearly seen that the corrosion potential ( $\phi_{\text{corr}}$ ) of  $\text{Mg}_2\text{Si}$  is the most negative, while that of Si is

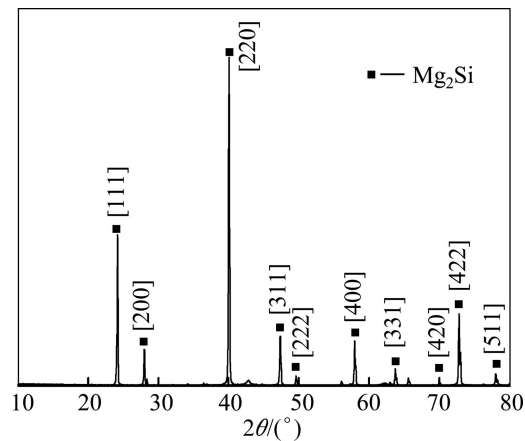


**Fig. 2** AFM observation of grain boundary in Al–0.63Mg–0.28Si alloy: (a) AFM morphology; (b) Potential distribution; (c) Potential distribution curve along straight line in Fig. 2(b)

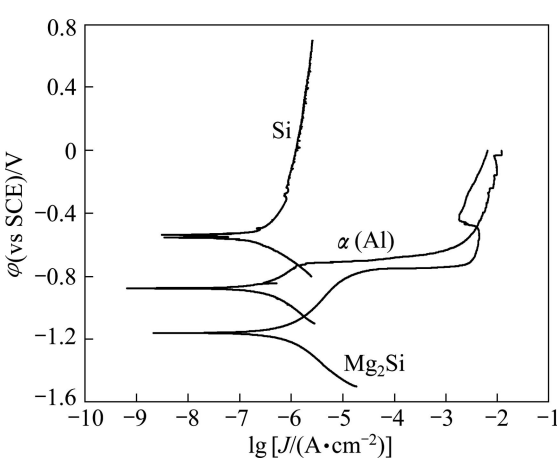
the most positive. This is consistent with the AFM measurement result. The polarization resistance ( $R_p$ ) of  $\alpha(\text{Al})$  or  $\text{Mg}_2\text{Si}$  is less than that of Si. Meanwhile, the corrosion current density ( $J$ ) of  $\text{Mg}_2\text{Si}$  is much greater than that of  $\alpha(\text{Al})$  or Si. These results indicate that  $\text{Mg}_2\text{Si}$  particles are more susceptible to corrosion than  $\alpha(\text{Al})$  or Si particles at the beginning.



**Fig. 3** AFM observation of grain boundary in Al-0.63Mg-0.88Si alloy: (a) AFM morphology; (b) Potential distribution; (c) Potential distribution curve along straight line in Fig. 3(b)



**Fig. 4** XRD pattern of synthesized  $Mg_2Si$  powder



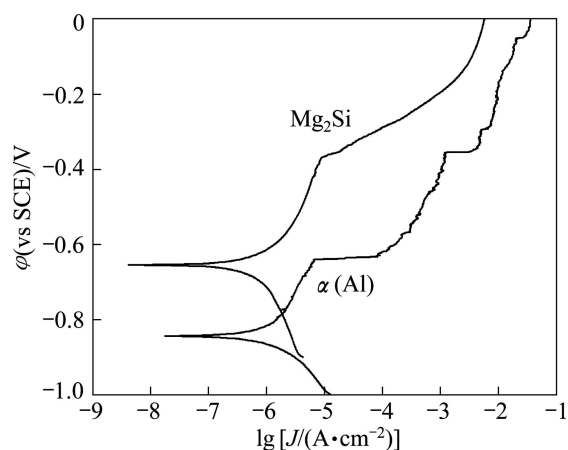
**Fig. 5** Potentiodynamic scanning curves of individual  $\alpha(Al)$ , Si and  $Mg_2Si$  in 3.5% NaCl solution at the beginning

**Table 1** Corrosion parameters of  $\alpha(Al)$ , Si and  $Mg_2Si$  in 3.5% NaCl solution at the beginning

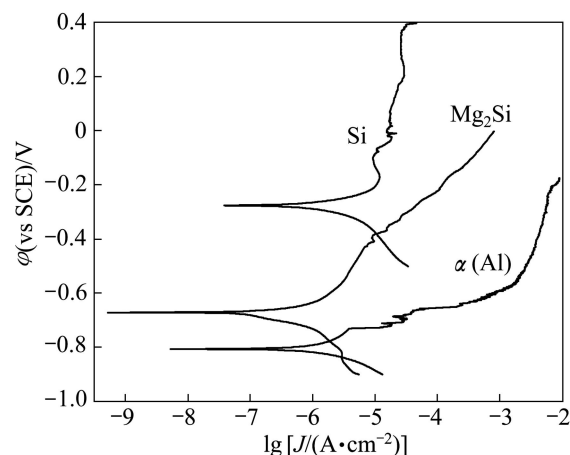
| Phase        | $\phi_{corr}(vs\ SCE)/V$ | $J/(A \cdot cm^{-2})$  | $R_p/(\Omega \cdot cm^2)$ |
|--------------|--------------------------|------------------------|---------------------------|
| $\alpha(Al)$ | -0.8761                  | $7.674 \times 10^{-7}$ | $3.399\ 4 \times 10^4$    |
| $Mg_2Si$     | -1.1598                  | $1.282 \times 10^{-6}$ | $2.034\ 2 \times 10^4$    |
| Si           | -0.5470                  | $1.912 \times 10^{-7}$ | $1.364\ 4 \times 10^5$    |

For the  $Mg_2Si$ - $\alpha(Al)$  coupling system, after coupling for 312 h in NaCl solution, the potentiodynamic scanning curves of  $\alpha(Al)$  and  $Mg_2Si$  are shown in Fig. 6. It is found that the open circuit potential of  $Mg_2Si$  moves towards a positive direction to about -0.62 V(vs SCE) from the initial about -1.16 V, resulting in the potential order variation of  $Mg_2Si$  and  $\alpha(Al)$ , and a polarity transformation is generated. The potential of  $Mg_2Si$  electrode moves to a positive direction, which is due to the preferential dissolution of active Mg elements and the enrichment of Si. Energy spectrum of  $Mg_2Si$  phase after coupling for 312 h showed that Mg content was decreased, while Si content was increased. The preferential dissolution phenomenon was also found in  $S(Al_2CuMg)$  particle in 2024 Al alloy. BUCHHEIT et al [15], SHAO et al [16], and LI et al [17] found that as 2xxx series Al alloy containing  $S(Al_2CuMg)$  particle was immersed in NaCl solution, active Mg element in the S particle was preferentially dissolved, resulting in Cu-rich remnants.

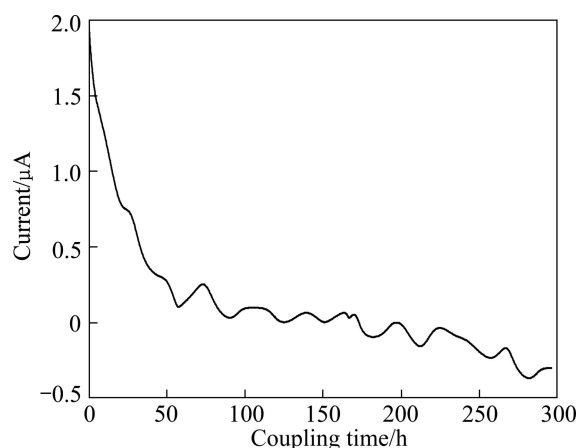
The open circuit potential order change of the  $Mg_2Si$ - $\alpha(Al)$  coupled system will cause the coupling current variation, as shown in Fig. 7. At the beginning of the coupling process, the potential of  $Mg_2Si$  electrode is negative to that of  $\alpha(Al)$  electrode, indicating that  $Mg_2Si$  electrode acts as anode and endures anodic current. During the coupling process, its potential moves to a positive direction with increasing immersion time. As a



**Fig. 6** Potentiodynamic scanning curves of  $\alpha(\text{Al})$  and  $\text{Mg}_2\text{Si}$  in  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$  coupling system after coupling for 312 h in NaCl solution



**Fig. 8** Potentiodynamic scanning curves of individual  $\alpha(\text{Al})$ , Si and  $\text{Mg}_2\text{Si}$  in  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si coupling system after coupling for 312 h in NaCl solution

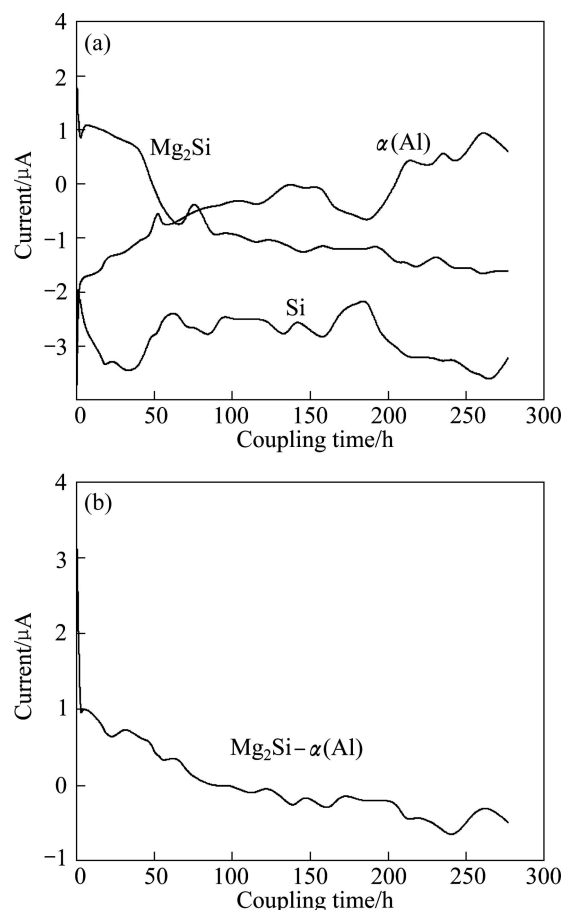


**Fig. 7** Coupling current of  $\text{Mg}_2\text{Si}$  with  $\alpha(\text{Al})$  in 3.5% NaCl solution

result, the corroded  $\text{Mg}_2\text{Si}$  becomes cathodic to the  $\alpha(\text{Al})$  electrode at a later stage, and the anodic current of  $\text{Mg}_2\text{Si}$  electrode changes to cathodic current and increases.

For the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si coupling system, the potentiodynamic scanning curves of individual  $\alpha(\text{Al})$ , Si and  $\text{Mg}_2\text{Si}$  after coupling for 312 h in the NaCl solution are shown in Fig. 8. The open circuit potential order change of  $\text{Mg}_2\text{Si}$ ,  $\alpha(\text{Al})$  and Si in the three-electrode coupling system is also observed. The electrode potential of  $\alpha(\text{Al})$  and  $\text{Mg}_2\text{Si}$  is still negative with respect to that of Si. However, the potential of  $\text{Mg}_2\text{Si}$  electrode moves to a positive direction, resulting in the potential of  $\alpha(\text{Al})$  being negative to that of  $\text{Mg}_2\text{Si}$  phase and Si phase. Energy spectrum also showed the preferential dissolution of Mg and the enrichment of Si in  $\text{Mg}_2\text{Si}$  electrode.

The open circuit potential order change of the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si coupling system also causes the coupling current variation, as shown in Fig. 9(a). During all the coupling process, Si electrode always acts as



**Fig. 9** Coupling current of  $\text{Mg}_2\text{Si}$ , Si and  $\alpha(\text{Al})$  in  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si coupling system: (a) Coupling current of  $\text{Mg}_2\text{Si}$ , Si and  $\alpha(\text{Al})$ ; (b) Coupling current of  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$

cathode and endures cathodic current. At the beginning,  $\text{Mg}_2\text{Si}$  electrode acts as the only anode and endures anodic current. With increasing the coupling time, its potential moves to a positive direction, as a result, the corroded  $\text{Mg}_2\text{Si}$  electrode becomes cathodic to  $\alpha(\text{Al})$



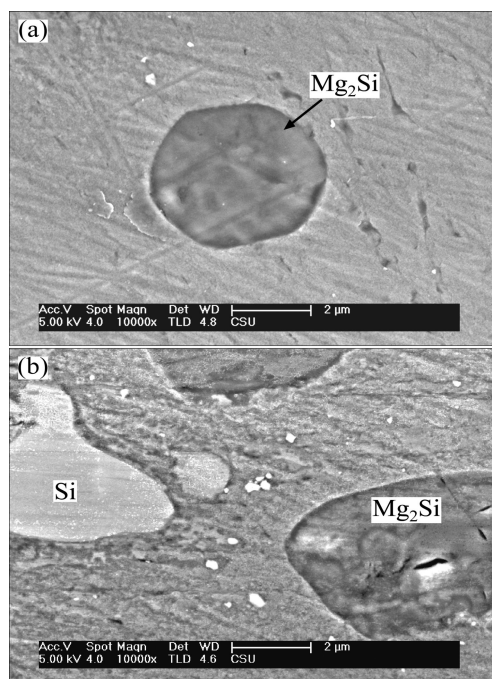
electrode at a later stage, leading to the anodic current of  $\text{Mg}_2\text{Si}$  electrode changing to cathodic current and increasing. While the  $\alpha(\text{Al})$  electrode acts as cathode and endures cathodic current at the beginning, its cathodic current is changed to anodic current and increases with increasing the coupling time. At a later stage, the  $\alpha(\text{Al})$  electrode acts as the only anode and endures all anodic current. Due to the potential order change, during the coupling intervals of the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si coupling system, as only  $\text{Mg}_2\text{Si}$  and  $\alpha(\text{Al})$  are coupled, the anodic current of  $\text{Mg}_2\text{Si}$  electrode changes to cathodic current and increases, as shown in Fig. 9(b).

For both the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$  two-electrode coupling system and the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si three-electrode coupling system, there exists an electrochemical polarity transformation process between  $\text{Mg}_2\text{Si}$  electrode and  $\alpha(\text{Al})$  electrode. However, the beginning time of electrochemical polarity transformation is different. In the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$  coupling system, after coupling for about 100 h, the cathodic current of  $\alpha(\text{Al})$  electrode changes to anodic current (Fig. 7). While, in the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si coupling system, the beginning time when the cathodic current of  $\alpha(\text{Al})$  electrode changes to anodic current is decreased to about 50 h (Fig. 9). In addition, compared with that in  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$  coupling system,  $\alpha(\text{Al})$  electrode endures higher anodic current in the  $\text{Mg}_2\text{Si}$ – $\alpha(\text{Al})$ –Si at the later stage.

Figure 10 shows the corrosion morphologies of Al alloys containing coarse  $\text{Mg}_2\text{Si}$  particles and  $\text{Mg}_2\text{Si}$ +Si particles immersed in 3.5% NaCl solution for 0.5 h. It is seen that the corrosion occurs on  $\text{Mg}_2\text{Si}$  particle surface of these two alloys. No corrosion occurs on Si particle surface, but corrosion occurs on the Al base at the adjacent periphery of Si particle.

The corrosion morphologies of these two Al alloys immersed in 3.5% NaCl solution for 2 h are shown in Fig. 11. In the Al alloy only containing coarse  $\text{Mg}_2\text{Si}$  particle, corrosion occurs on the  $\text{Mg}_2\text{Si}$  particle surface. It is also observed that corrosion occurs on the Al base at its adjacent periphery (Fig. 11(a)). The EDS spectrum (Fig. 11(b)) shows that the Mg content is decreased, while the Si content in the corroded  $\text{Mg}_2\text{Si}$  particle is increased to 52.13%, which is higher than the original Si content of the  $\text{Mg}_2\text{Si}$  particle. In the Al alloy containing coarse  $\text{Mg}_2\text{Si}$  and Si particles, severe corrosion occurs on the Al base at the adjacent periphery of Si particle (Fig. 11(c)). Meanwhile, corrosion is observed on the  $\text{Mg}_2\text{Si}$  particle surface and also on the Al base at its adjacent periphery. Correspondingly, EDS spectrum (Fig. 11(d)) shows that the Si content in the  $\text{Mg}_2\text{Si}$  particle is greatly increased to about 79%.

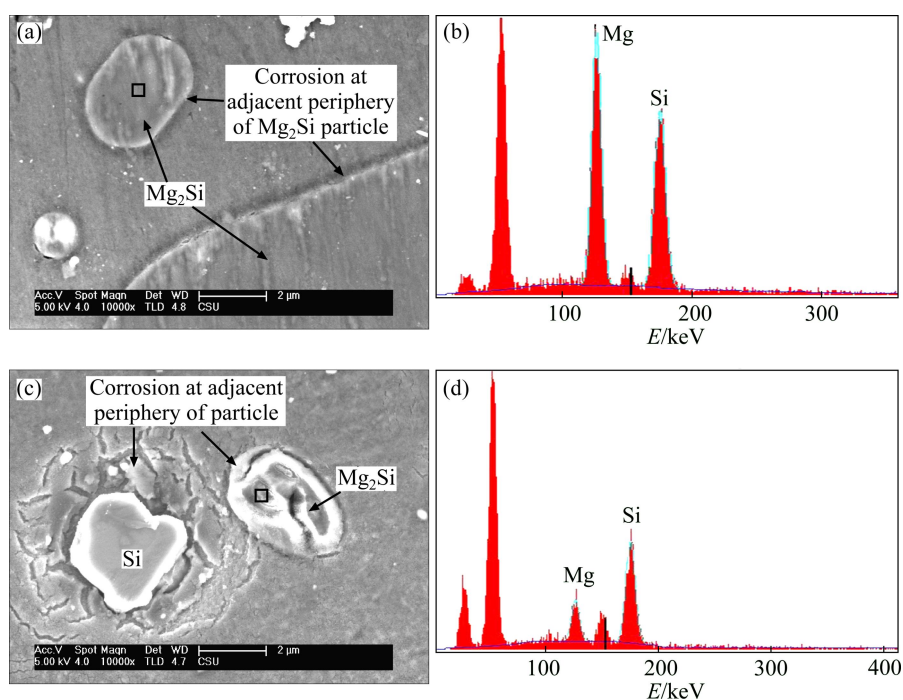
As the immersion time is extended, the corrosion on Al base at the adjacent periphery of the  $\text{Mg}_2\text{Si}$  particle is due to the preferential dissolution of Mg in the  $\text{Mg}_2\text{Si}$



**Fig. 10** Corrosion morphologies of Al alloys containing coarse particles immersed in 3.5% NaCl solution for 0.5 h: (a)  $\text{Mg}_2\text{Si}$  particle; (b)  $\text{Mg}_2\text{Si}$ +Si particles

particle and the electrochemical polarity transfer, which is consistent with the above coupling test. That is to say, there exists a dynamic conversion corrosion mechanism associated with the  $\text{Mg}_2\text{Si}$  particle. At the beginning, the  $\text{Mg}_2\text{Si}$  particle is anodic to the Al base and corrosion occurs on its surface. However, during its corrosion process, its potential moves to a positive direction with increasing immersion time, due to the preferential dissolution of Mg and the enrichment of Si. As a result, the corroded  $\text{Mg}_2\text{Si}$  particle becomes cathodic to the Al base at a later stage, leading to the anodic dissolution and corrosion of the Al base at its adjacent periphery.

The above corrosion morphologies also indicate that the corrosion occurs firstly on the  $\text{Mg}_2\text{Si}$  particle surface and develops on the Al base at its adjacent periphery in the Al alloy containing only  $\text{Mg}_2\text{Si}$  particle. However, in the Al alloy containing  $\text{Mg}_2\text{Si}$  and Si particles, the corrosion begins on the  $\text{Mg}_2\text{Si}$  particles surface and the Al base at the adjacent periphery of Si particle. Then, the corrosion develops on the Al base at the adjacent periphery of Si particle, and also develops on the Al base at the adjacent periphery of  $\text{Mg}_2\text{Si}$  particle. Compared with that at  $\text{Mg}_2\text{Si}$  adjacent periphery, the corrosion degree of Al base at Si adjacent periphery is much higher. In addition, the Si enrichment of the corroded  $\text{Mg}_2\text{Si}$  particles in the Al alloy containing coarse  $\text{Mg}_2\text{Si}$  and Si particles is more server than that in the Al alloy containing only  $\text{Mg}_2\text{Si}$  particle. It indicates that existence of Si particles enhances the preferential dissolution of

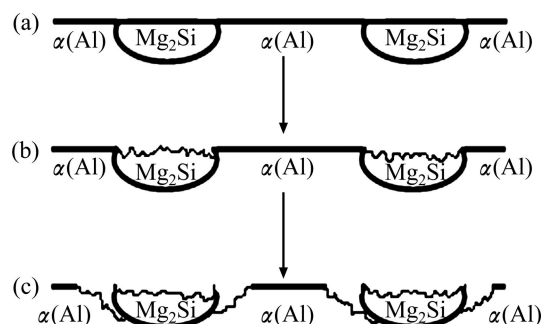


**Fig. 11** Corrosion morphologies and corresponding EDS spectra of Al alloys containing coarse particles immersed in 3.5% NaCl solution for 2 h: (a), (b)  $\text{Mg}_2\text{Si}$  particle; (c), (d)  $\text{Mg}_2\text{Si}+\text{Si}$  particles

Mg and the enrichment of Si during the corrosion process of  $\text{Mg}_2\text{Si}$  particle.

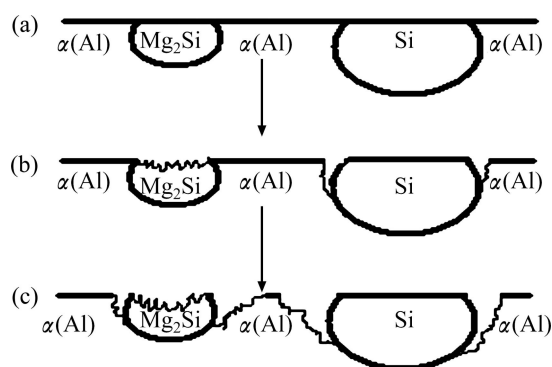
According to the above results and discussion, the intergranular corrosion mechanism of Al–Mg–Si alloys with different mole ratios of Mg to Si was advanced, as shown in Figs. 12 and 13. In the Al–Mg–Si alloys with a mole ratio of Mg to Si higher than 1.73, only  $\text{Mg}_2\text{Si}$  is precipitated at the grain boundary. There exists a dynamic conversion corrosion mechanism associated with the precipitate of  $\text{Mg}_2\text{Si}$ . At the beginning, the precipitate of  $\text{Mg}_2\text{Si}$  is anodic to the alloy base (or precipitate-free zone, PFZ) and corrosion occurs on its surface (Fig. 12(b)). However, during its corrosion process, its potential moves to a positive direction with increasing corrosion time, due to the preferential dissolution of Mg and the enrichment of Si in  $\text{Mg}_2\text{Si}$  precipitate. As a result, the corroded  $\text{Mg}_2\text{Si}$  phase becomes cathodic to the PFZ at the grain boundary at a later stage, leading to the anodic dissolution and corrosion of the PFZ at its adjacent periphery (Fig. 12(c)). That is to say, the corrosion develops along the PFZ at the adjacent periphery of  $\text{Mg}_2\text{Si}$  precipitate. Because the  $\text{Mg}_2\text{Si}$  precipitates at the grain boundary are distributed discontinuously, there is no continuous corrosion channel at the grain boundary. Therefore, the Al–Mg–Si alloy with the mole ratio of Mg to Si higher than 1.73 is not susceptible to intergranular corrosion.

In the Al–Mg–Si alloys with a mole ratio of Mg to Si less than 1.73,  $\text{Mg}_2\text{Si}$  and Si precipitate at the grain boundary simultaneously. At the initial corrosion stage,



**Fig. 12** Schematic diagram of function mechanism of  $\text{Mg}_2\text{Si}$  precipitate in intergranular corrosion of Al–Mg–Si alloys with  $n(\text{Mg})/n(\text{Si}) > 1.73$ : (a)  $\text{Mg}_2\text{Si}$  particles along grain boundary; (b) Corrosion initiation on  $\text{Mg}_2\text{Si}$  surface at the beginning; (c) Corrosion of PFZ at adjacent periphery of corroded  $\text{Mg}_2\text{Si}$  particles at a later stage

the corrosion potential of  $\text{Mg}_2\text{Si}$  is negative with respect to that of  $\alpha(\text{Al})$  or Si, so the corrosion mainly occurs on the  $\text{Mg}_2\text{Si}$  particles surface firstly. Meanwhile, the cathodic Si particle also leads to the anodic dissolution and corrosion of the PFZ at its adjacent periphery. That is to say, the corrosion initiates at grain boundary  $\text{Mg}_2\text{Si}$  particle and also at the grain boundary PFZ at Si particle adjacent periphery, as shown in Fig. 13(b). During the corrosion process, the Si phase always acts as cathodic zone. The anodic dissolution and corrosion of the grain boundary PFZ at its adjacent periphery are increased with increasing immersion time (Fig. 13(c)). Meanwhile, the cathodic Si particles accelerate the preferential



**Fig. 13** Schematic diagram of function mechanism of  $\text{Mg}_2\text{Si}$  and  $\text{Si}$  precipitates in intergranular corrosion of Al-Mg-Si alloys with  $n(\text{Mg})/n(\text{Si}) < 1.73$ ; (a)  $\text{Mg}_2\text{Si}$  and  $\text{Si}$  particles along grain boundary; (b) Corrosion initiation on  $\text{Mg}_2\text{Si}$  surface and on PFZ at adjacent periphery of  $\text{Si}$  particle at the beginning; (c) Corrosion of PFZ at adjacent periphery of corroded  $\text{Mg}_2\text{Si}$  and  $\text{Si}$  particles at a later stage

dissolution of Mg and the enrichment of Si in  $\text{Mg}_2\text{Si}$  precipitates, and expedite the polarity transformation between  $\text{Mg}_2\text{Si}$  and the grain boundary PFZ. Therefore, the electrochemical driving force for anodic dissolution of the PFZ at the adjacent periphery of  $\text{Mg}_2\text{Si}$  precipitate is increased, and the corrosion of the PFZ at the adjacent periphery of  $\text{Mg}_2\text{Si}$  precipitate is enhanced. That is to say, the corrosion develops along the grain boundary PFZ at the adjacent periphery of both the  $\text{Si}$  particles and the corroded  $\text{Mg}_2\text{Si}$  precipitates, as shown in Fig. 13(c). The  $\text{Si}$  particles lead to the sever-corrosion development of the PFZ at its adjacent periphery, which accelerates the corrosion of the PFZ at the adjacent periphery of  $\text{Mg}_2\text{Si}$  precipitates. Even though the  $\text{Mg}_2\text{Si}$  precipitates are distributed discontinuously at the grain boundary, there also can form a continuous corrosion channel.

## 4 Conclusions

1) At the beginning of corrosion process, the precipitate of  $\text{Mg}_2\text{Si}$  is anodic to the Al base, and the anodic dissolution and corrosion occur on its surface. However, during its corrosion process, active Mg is preferentially dissolved, resulting in the enrichment of Si, which makes  $\text{Mg}_2\text{Si}$  potential move to a positive direction. As a result, the corroded  $\text{Mg}_2\text{Si}$  becomes cathodic to  $\alpha(\text{Al})$ , leading to the anodic dissolution and corrosion of the Al base at its adjacent periphery at a later stage.

2) At the grain boundary of Al-Mg-Si alloys with a mole ratio of Mg to Si higher than 1.73, the  $\text{Mg}_2\text{Si}$  precipitates are distributed discontinuously, and there is no continuous corrosion channel, showing that the alloy is not sensitive to intergranular corrosion.

3) There exist  $\text{Mg}_2\text{Si}$  precipitates and coarse Si particles at the grain boundary of Al-Mg-Si alloys with a mole ratio of Mg to Si less than 1.73. Corrosion initiates on the  $\text{Mg}_2\text{Si}$  surface and at the PFZ at the adjacent periphery of Si particle. As corrosion time is extended, Si particle leads to severe anodic dissolution and corrosion of the PFZ at its adjacent periphery. Meanwhile, the Si particle also accelerates the preferential dissolution of Mg in  $\text{Mg}_2\text{Si}$  precipitate, expedites the polarity transformation between  $\text{Mg}_2\text{Si}$  and the PFZ, therefore the corrosion of the PFZ at the adjacent periphery of  $\text{Mg}_2\text{Si}$  precipitate is enhanced.

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## Al–Mg–Si 合金中 $Mg_2Si$ 和 Si 粒子 在晶间腐蚀过程中的作用机理

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**摘 要:** 研究 Al–Mg–Si 合金晶界组成相( $Al-Mg_2Si$  及  $Al-Mg_2Si-Si$ )间的电化学反应和动态电化学反应耦合行为, 提出 Al–Mg–Si 合金的晶间腐蚀机理。研究表明, 晶界 Si 的电位比其边缘 Al 基体的正, 在整个腐蚀过程中作为阴极导致其边缘 Al 基体的阳极溶解; 晶界  $Mg_2Si$  的电位比其边缘 Al 基体的负, 在腐蚀初期作为阳极发生阳极溶解, 然而由于  $Mg_2Si$  中活性较高的元素 Mg 的优先溶解, 不活泼元素 Si 的富集, 致使  $Mg_2Si$  电位正移, 甚至与其边缘 Al 基体发生极性转换, 导致其边缘 Al 基体的阳极溶解。当  $n(Mg)/n(Si) < 1.73$  时, 随着腐蚀的进行, 合金晶界同时会有  $Mg_2Si$  析出相和 Si 粒子, 腐蚀首先萌生于  $Mg_2Si$  相和 Si 边缘的无沉淀带, 而后, Si 粒子一方面导致其边缘无沉淀带严重的阳极溶解, 另一方面加速  $Mg_2Si$  和晶界无沉淀带的极性转换, 从而促使腐蚀沿晶界 Si 粒子及  $Mg_2Si$  粒子边缘向无沉淀带发展。

**关键词:** Al–Mg–Si 合金; 晶间腐蚀; 腐蚀机理; 电化学反应;  $Mg_2Si$ ; Si

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