



A SECM study of redox activity on Al-Mg-Si alloy in organic/aqueous solution



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ABSTRACT

SECM (Scanning electrochemical microscopy) coupled with either an organic solution or a neutral aqueous solution was applied to investigate the localized corrosion mechanism of Al-Mg-Si alloy. SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectroscopy) experiments were used to clarify how intermetallic may influence its cathodic activity. In the SECM tests, FcMeOH (Ferrocene methanol) was used as a redox mediator in both two solutions. The SECM results obtained from the organic system reveal some possible sites susceptible to corrosion attack. These sites are composed of large intermetallic particles. Combining with the SECM test conducted in the aqueous system, these sites also show high redox activity. The SECM experiments also reveal that MgSi intermetallic particles after 24-h corrosion show as strong cathodic activity as Al(Fe, Mn)Si.

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1. Introduction

The heat-treatment strengthening Al-Mg-Si alloys have been widely used in automobile vehicles and marine structures due to their desirable combination of high strength and moderate corrosion resistance. The corrosion process of aluminum alloys has been widely studied. For example, it has been proved that the formation of a passive film can effectively hinder the corrosion process of aluminum alloys [1–7]. For Al-Mg-Si alloy, the preferential dissolution of Mg in the MgSi phase will occur [8,9]. Typical electrochemical methods, like Potentiodynamic polarization and EIS (Electrochemical Impedance Spectroscopy), have been applied to investigate the corrosion mechanism of aluminum alloys [4,8–10]. However, none of them is capable of illuminating the microscopic information during a corrosion process where micro-sized electrochemically active sites cannot be distinguished through these common methods.

SECM (Scanning Electrochemical Microscopy) is a powerful tool that has been widely used to investigate local electrochemical activity on a sample surface. This basic idea has been well proved in various disciplines, like biology, enzymes, living cell studies, corrosion, energy, surface modification, kinetics, etc. [9]. It has been well examined that it is of vital importance for scientists to choose a

proper solvent and redox mediator in a SECM experiment. In corrosion studies, SG/TC (substrate generation/tip collection) mode is an effective method to show the active site on the sample surface. Several redox mediators, like $K_3Fe(CN)_6$, KI, FcMeOH (Ferrocene methanol), have been proved that they can work well and give relatively good results with reasonable contrast in a SECM study [11–13]. Fortunately, FcMeOH is a so ideal redox mediator that it can be dissolved in either an organic or aqueous solvent and give well-defined SECM images. For an aqueous system, some investigations were carried out to examine the redox activity at aluminum alloy surface [14,15]. There are, however, several shortcomings for the experiments carried out in an aqueous solution, as the feedback current can always be disturbed by the corrosion product. In this case, neither the cathodic site nor the positive/negative feedback current can be distinguished, and it is impossible to obtain a probe approach curve (PAC) used to figure out a proper distance between the tip and the substrate. No reproducible or reasonable results can be obtained in such a case. Luckily, using an organic solvent and adding different redox mediators according to the requirement was widely applied to investigate the local electrochemical activities on the metal surface during corrosion, like a defect site induced by an oxide breakdown effect [16,17]. It is of great advantage to exploit an organic system since it has a slight influence on the sample surface, and an ultramicroelectrode (UME, a probe tip, a Pt wire with a diameter of 10 μm) used to get the feedback signal is not easily contaminated by the corrosion product. In an SECM study, choosing

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a proper redox mediator is a key factor that determines whether or not a reasonable SECM image can be obtained and whether or not this image can show well-defined contrast for analysis. As mentioned above, a typical redox mediator is FcMeOH, an uncharged redox mediator, ideal for investigating corrosion mechanisms because of its ideal reversibility in both organic solvent and aqueous solution. Its one-electron reversible reaction can be described as Eq. (1):



The ferrocene derivative FcMeOH⁺ can be reduced at the electroactive sites on the metal surface.

However, few studies were carried out to investigate the localized cathodic reactivity of Al-Mg-Si alloy during corrosion. It is widely accepted that the MgSi phase is not always anodic as compared to the Al base due to the preferential dissolution of Mg solutes. Its electrochemical activity was, however, not well discussed. In this study, the electrochemical activity of the micron-sized intermetallic particles, especially MgSi and Al(Fe, Mn)Si was investigated in detail.

2. Experiments

2.1. Materials and sample preparation

A self-designed aluminum alloy (2.30 Mg, 2.30 Si, 0.5 Mn, 0.15 Cr, 0.15 Ti, 0.15 Zr, in wt%) and pure aluminum (99.99 wt%) were used in this research. The alloy was prepared by melting method in a graphite furnace and then homogenized at 520 °C for 24 h. The sample was ground to 2000 grit with silicon carbide papers and polished to 0.5 μm roughness. Finally, it was cleaned with deionized water and dried in flowing air.

2.2. SEM & SECM

A SEM (Scanning Electron Microscopy, Zeiss Sigma 300 FEG SEM) equipped with an EDX (Energy Dispersive X-ray) detector was used in this study to observe the surface morphology of the alloy and analyze the element distribution in the alloy. The accelerated voltage of the EDX detector used in this paper were set as 20 kV.

According to an organic solvent (CH₃CN, acetonitrile) used in the test, a reference electrode Ag/AgNO₃ (silver wire immersed in 0.01 M AgNO₃ in acetonitrile connected to the cell via a 0.1 M TBAPF₆ (Tetrabutylammonium hexafluorophosphate) in acetonitrile salt bridge) was used in the experiment, as shown in Fig. 1a. For the aqueous system, a normal Ag/AgCl/KCl (3.0 M) electrode was used as a reference electrode. A four-electrode SECM system (CHI920D, Shanghai Chenhua Instrument, China) was applied in this study. A

schematic representation of the SECM setup applied in this investigation is shown in Fig. 1b. A 10 diam Pt UME was the working electrode, Pt wire the counter electrode, Al/Al-Mg-Si alloy another working electrode, and Ag/AgCl or Ag/AgNO₃ the reference electrode according to the electrolyte. The redox mediator used in the experiment was FcMeOH present in either acetonitrile or deionized water. The organic system was composed of 0.5 mM FcMeOH and 0.1 M TBAPF₆ in acetonitrile. The aqueous system was 1 mM FcMeOH and 0.1 M KCl in deionized water. PAC was obtained by moving the probe tip to the substrate. The tip was biased at a proper potential to make the oxidation rate of FcMeOH under diffusion control. When the tip was held far from the substrate, the *I*_{ss} (steady-state current) measured at the tip can be described as:

$$I_{ss} = 4NFDC^*a \quad (2)$$

Where *C*^{*} and *D* is the bulk concentration and the diffusion coefficient of the redox mediator, respectively. *N* is the number of electrons involved in the redox reaction *N* = 1 for FcMeOH according to Eq. (1). *a* is the Pt UME radius and *F* the Faraday constant. For the SECM imaging procedure, the increment time for each *x*, *y* location is 0.02 s *x* axis was set as the long direction in the procedure. An increment of 5 μm was used in the *y* direction after each scanning process along the *x* direction was finished.

3. Results and discussions

3.1. SG/TC mode

Fig. 2 shows typical CV results of FcMeOH in either the organic or aqueous solution using a 10 μm diam Pt UME as the working electrode. A clear sigmoidal shape and plateau-limiting current (~2.3 nA in the organic system; ~1.4 nA in the aqueous solution) can be observed. Thanks to the wide potential window of acetonitrile, a substrate can be biased at a very negative potential, like -0.7 V, without disturbing by any other side reaction. In this scenario, the tip was biased at +0.25 V (vs. Ag/AgNO₃ in organic solution) or +0.45 V (vs. Ag/AgCl in aqueous solution), so that FcMeOH can be oxidized to FcMeOH⁺ at a diffusion-limited rate at the tip. If the tip is held closely to the substrate and a proper potential is biased on the substrate, those FcMeOH⁺ that produced on the Pt tip can diffuse to the substrate and be reduced back to FcMeOH at the electrochemically active sites. Therefore, those reduced FcMeOH can be in turn oxidized on the tip (positive feedback). On the other hand, when the tip is held closely above an insulated site, due to the blocking effect, those FcMeOH in the bulk solution cannot diffuse to the tip and be oxidized there so easily as the case that the tip is held far away from the substrate. Therefore, one can expect a lower

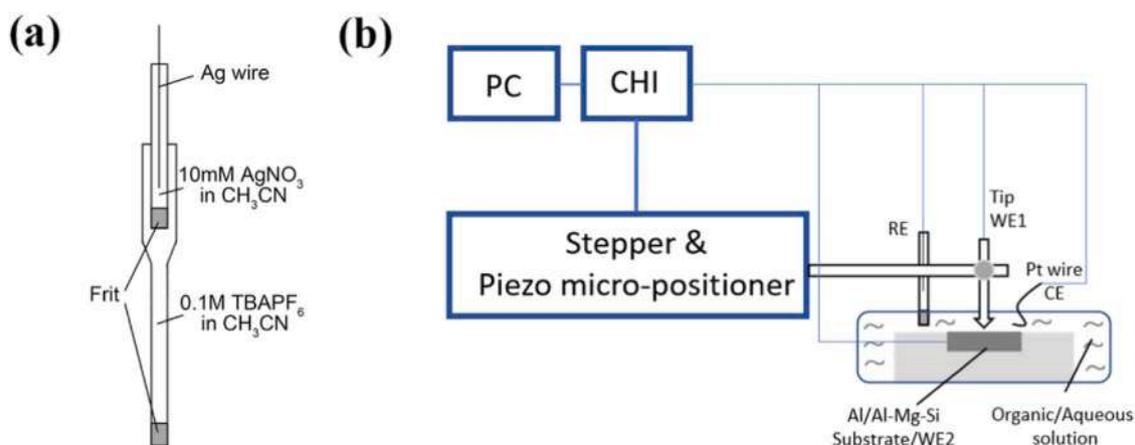


Fig. 1. SECM device: (a) non-aqueous Ag/AgNO₃ reference electrode; (b) schematic diagram of a typical SECM device.

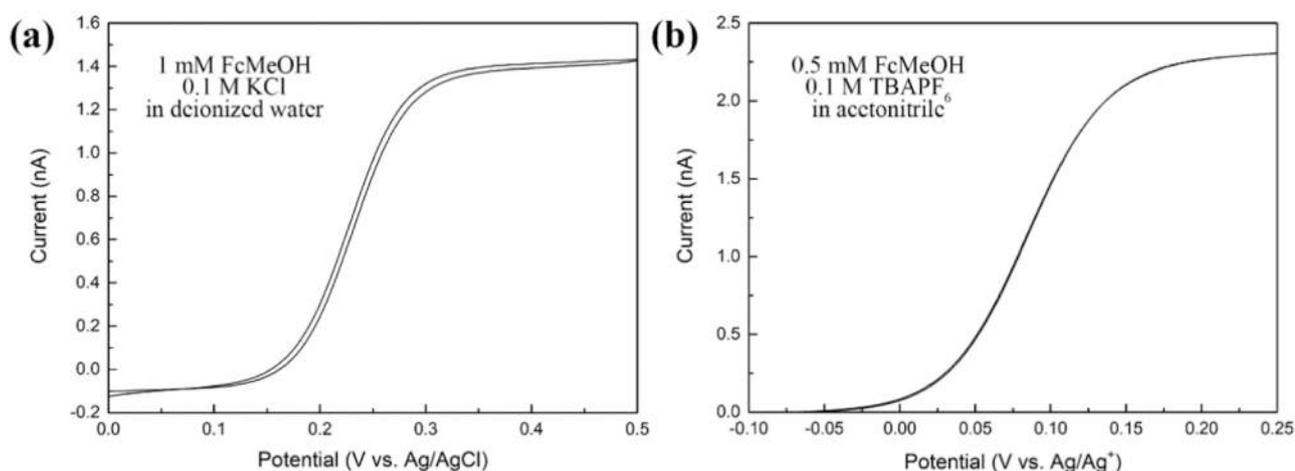


Fig. 2. Typical CV results of FcMeOH in two different solutions using a 10 μm Pt probe: (a) 1 mM FcMeOH and 0.1 M KCl in deionized water; (b) 0.5 mM FcMeOH and 0.1 M TBAPF₆ in acetonitrile.

feedback current than the diffuse-limited current (negative feedback). In summary, the positive/negative feedback current can reveal the electrochemically active site on the sample surface, and finally, a SECM image can be obtained according to this different electroactive contrast.

3.2. Pure aluminum

Pure Al was used as a contrast sample to rule out the possibility that positive/negative feedback was only due to the aluminum itself but not the intermetallic in the alloy. In this experiment, the organic system was used to investigate the electrochemically active sites on the sample surface. All the potential in this organic system is with reference to an Ag/AgNO₃ electrode as mentioned in "Section 2". In such a system, I_{ss} is approximately equal to 2.3 nA, according to which, a feedback current lower than this value can be considered as a negative feedback current, while a positive feedback current is higher than this value.

Before the SECM test, A scratch was put on the sample surface in advance. When the tip was scanned over the scratch, the feedback current would be higher than the other place, because the distance between the concave groove and the probe tip is bigger than the other even place. Therefore, the diffusion of FcMeOH was not so strongly hindered, that the blocking effect was not so strong as the even place. Thus, a higher feedback current can be expected and it was not due to any possible positive feedback, but the larger distance between the tip and the substrate. In the PAC test, the tip was biased at +0.25 V (vs. Ag/AgNO₃), the Al substrate was biased at -0.7 V (vs. Ag/AgNO₃). Fig. 3a shows the PAC result in which negative feedback was observed. 75% I_{ss} was set as the cut-off value, and the tip stopped approaching immediately this negative feedback signal was detected. The tip was then retracted 3 μm from its final position before carrying out the SECM test for avoiding unwanted contact between the probe tip and the substrate. The SECM image, as shown in Fig. 3b, indicates that only negative feedback occurs. Besides, higher feedback current (Brilliant blue contrast) caused by the scratch can also be detected by the tip. This result suggests that this Al sample is electrochemically insulated even though it just went through the sample preparation process. Such nature may be largely due to the oxide film on the Al surface which formed during the sample preparation. This result indicates that pure Al with high purity shows good anti-corrosion ability because of the formation of the oxide film so that it can insulate the metal base from the corrosion electrolyte.

3.3. Al-Mg-Si alloy

For convenience and to clarify the role of the intermetallic (Mg₂Si, Al(Fe, Mn)Si) that plays in the corrosion process, a crosshair was processed on the sample surface. As shown in Fig. 4, the SEM image clearly shows the trench-like topography caused by the crosshair on the alloy surface and several kinds of contrasts induced by the intermetallic in the alloy. EDX results were used to show the element aggregation and shed light on how these elements may influence the feedback signals during the SECM tests. The phase with black contrast is Mg₂Si and the phase with white contrast is Al(Fe, Mn)Si (see Fig. 4c–f).

For the SECM test, no matter how the test was carried out in an organic or an aqueous system, the procedure applied to set a proper distance between the tip and the substrate was the same as the case in pure Al (the special case will be specified).

In the organic system, both the positive and negative feedback currents occur on the as-prepared sample surface as shown in Fig. 5a and b. Besides, the feedback current induced by the crosshair used to locate the scanning area was also detected by the probe tip. Like the case shown in pure Al, the convex trench (the crosshair) can be regarded as a place with a distance between the tip and the substrate larger than the other even area. Therefore, the feedback current from scanning through the crosshair will be equal to I_{ss} (~2.3 nA). Another important thing is that one can contribute strong positive feedback on the place other than the crosshair to the positive feedback effect since these places are much more even than the scratches. Thus, it is appropriate to ascribe the positive feedback current to the cathodic activity, but not a possible corrosion pit or trench on the active sites. One should keep in mind that this kind of cathodic electroactivity can only prove that there are several electroconductive places where FcMeOH⁺ can be reduced to FcMeOH in the organic system.

By comparing the SECM (Fig. 5) and the SEM images (Fig. 4), it is interesting to find that, cathodic activities occur on both the place where the intermetallic is present (indicated by A, B, and C in Fig. 5) and Site D with no obvious element aggregation. The sites marked by a series of Circle D (D1, D2 in Fig. 5) show a strong positive feedback signal in the SECM image. However, according to the EDX mapping results, no obvious element aggregation occurs at this site, and no intermetallic particles as large as those present in Site B and C can be detected from the SEM observation. It seems that the feedback current at this site is stronger than other places. This will be discussed later. Considering that only negative feedback can be detected when the substrate was set as the pure aluminum, for those areas containing intermetallic particles, it seems that protective film

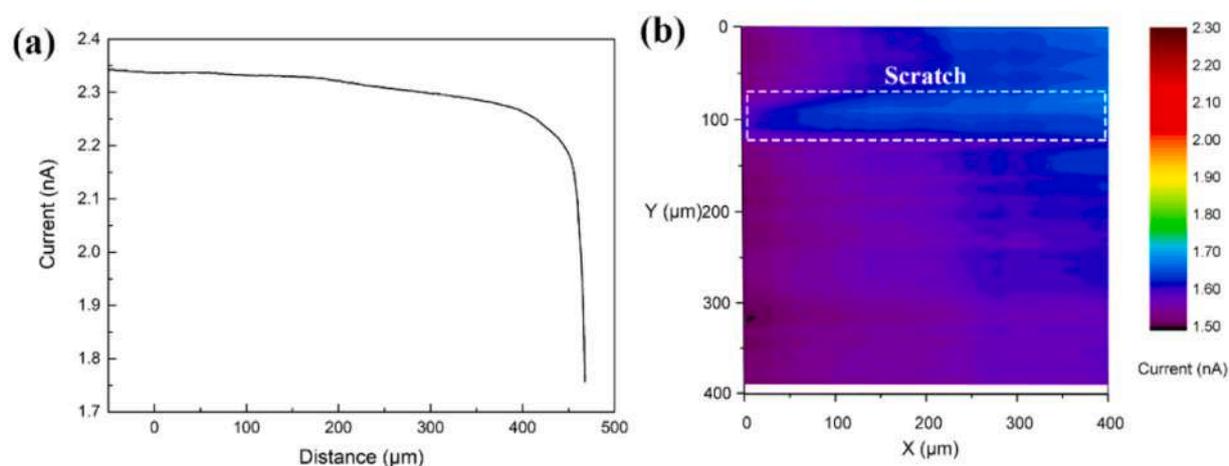


Fig. 3. SECM results of pure aluminum in 1 mM TBAF₆ in acetonitrile solution containing 0.5 mM FcMeOH as a redox mediator: (a) probe approach curve; (b) SECM image with a scanning area of 400 × 400 μm.

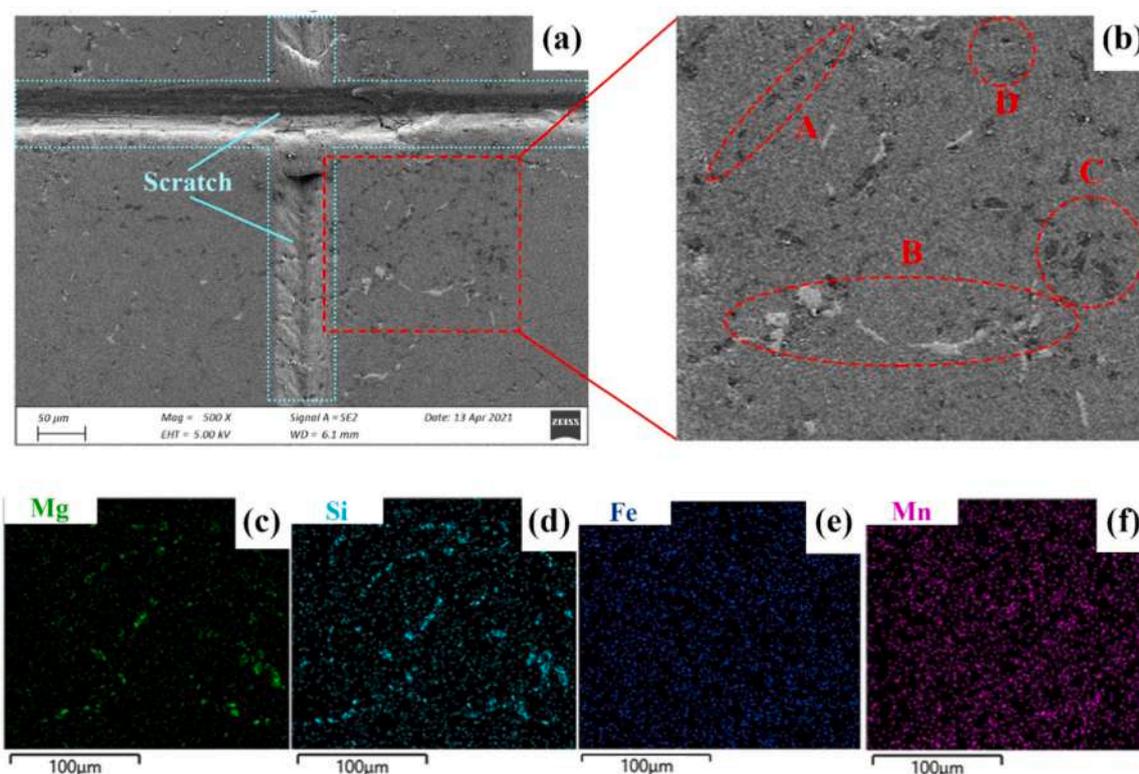


Fig. 4. SEM and EDX results of Al-Mg-Si alloy: (a) SEM image of the alloy with a crosshair on the surface; (b) enlarged area indicated by a red rectangle in (a); (c–f) EDX scanning map of an area shown in (b).

cannot easily form on those places so that FcMeOH⁺ can be reduced there without too much blocking effect induced by the oxide film. The sites marked by Letter B and C are the typical areas where Al(Fe, Mn)Si and MgSi are present there respectively (corroborated by the EDX results shown in Fig. 4c–f). However, not all of these intermetallic show the electroconductive nature in the SECM test. The site marked by Letter A is another typical place where MgSi particles are present there. This may be caused by the weak feedback current not being distinguishable from the other insulated area.

After the SECM test, the sample was cleaned by an aqueous solution with 75% alcohol and deionized water consecutively. It was then immersed in 0.1 M NaCl aqueous solution for 6 h. Then, deionized water was used to gently remove the NaCl solution and 75% alcohol aqueous solution was used to clean the sample surface

gently. The sample was dried in flowing air before another SECM test. According to the second SECM results (see Fig. 5c and d), one can find that the contrast and the configuration caused by the crosshair are not so clear as the case in Fig. 5a and b. This result is largely due to the growth of the oxide film during the corrosion process. (The evidence will be shown later). The corrosion product may accumulate in the groove and therefore make it become less rough. In this case, the distance between the tip and the groove would be smaller because of this accumulative effect. The sites marked by B2, C2, and D2 still show high positive feedback signals in the test. This result indicates that the areas occupied by the intermetallic can be easily exposed to the corrosion solution and serve as electrochemically active sites. Besides, Area A2 also shows visible contrast (yellow) compared to the substrate (pale green). This is

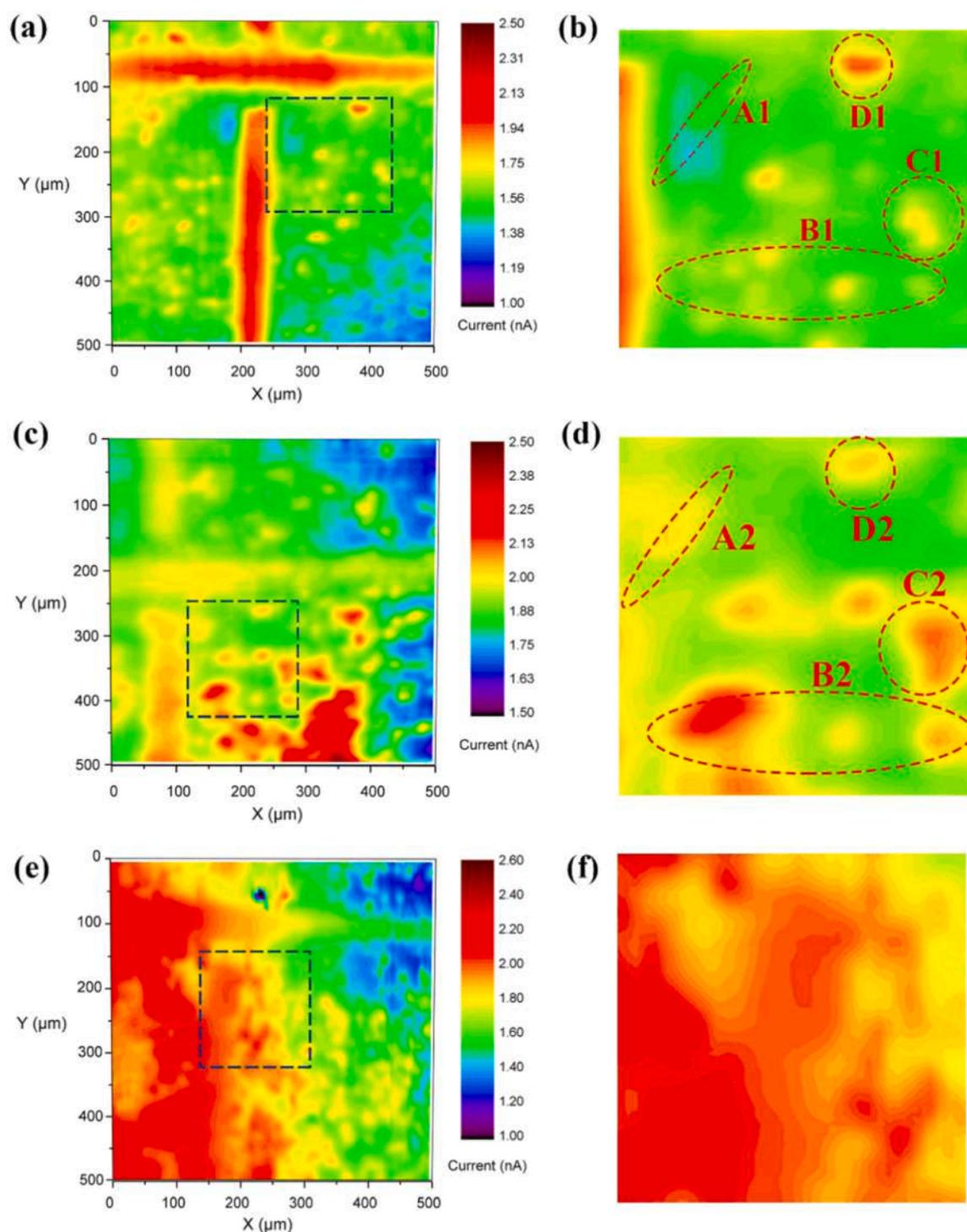


Fig. 5. SECM images, obtained from an organic system, of Al-Mg-Si alloy after corrosion for different hours: (a–b) 0 h; (c–d) 3 h; (e–f) 24 h; image (b), (d), (f) are the enlarged area indicated by the rectangles shown in (a), (c), (e) respectively.

because the probe is closer to the substrate than the case in the first SECM test. Specifically speaking, Site B2 and C2 show higher feedback signals as opposed to B1 and C1. More FcMeOH^+ can be reduced on the electroactive sites and then diffused back to the probe tip. The positive feedback current would increase in this way. The reason why the distance (the gap between the probe and the substrate) cannot keep the same in each SECM test is that the probe approach process could be always disturbed by either the corrosion product or the intermetallic on the alloy surface. So, when 75% I_{SS} was detected

in the probe approach procedure, this distance may be largely influenced by the nature and the topography of the sample surface.

After the second SECM imaging process, the sample was cleaned again by using the treatment after the first SECM test. Another 18-h corrosion in 0.1 M NaCl aqueous solution was carried out on the sample. The third SECM test was performed after this corrosion process (see Fig. 5e and f). It is not easy to distinguish the contrast induced by the crosshair in Fig. 5e. It is also difficult to separate the feedback current from each site, as shown in Fig. 5f. These results are largely due to the thick and uneven corrosion product which may

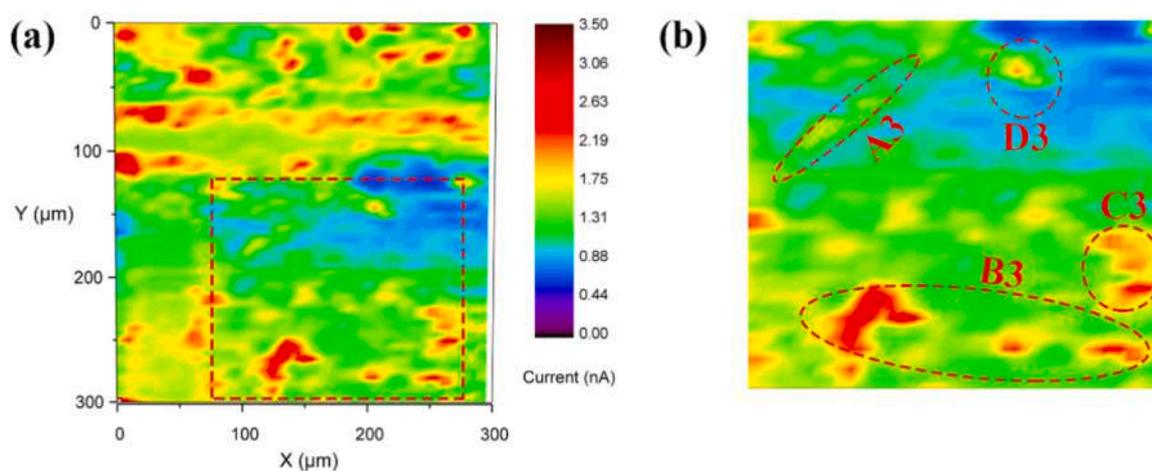


Fig. 6. SECM images, obtained from an aqueous system, of Al-Mg-Si alloy after corrosion for 24 h: (a) a 300 × 300 μm scanning area; (b) enlarged area indicated by a red rectangle in (a).

disturb the scanning process. In this case, it was hard to conduct a PAC procedure in this condition, so that it was a challenge to establish a proper distance between the tip and the substrate. Besides, due to a large scanning area (500 μm × 500 μm), even a small tilt can result in an unwanted contact between the tip and the corrosion product. Too much withdrawal distance applied on the probe after the PAC procedure could not guarantee a clear SECM result in this organic system. The reason why a good SECM cannot be obtained in the organic solution is still unclear. To sum up, in the organic system, the SECM results clearly show that during the corrosion process, the micron-sized intermetallic is easily exposed to the corrosion electrolyte.

Luckily, a withdrawal distance of 4 μm can be applied in the aqueous system. An illustrative SECM image was obtained by this method (see Fig. 6). Although it is impossible to obtain a clear SECM image for the as-prepared sample in the aqueous system due to the probe contamination, it is worthwhile to investigate what will happen in the long-term corrosion process of Al-Mg-Si alloy. After the alloy suffered a 24-h corrosion attack, the nature of the oxide film or the corrosion product on the alloy surface can be regarded as being a stable state. Therefore, it is possible that the aqueous system mentioned in the “Section 2” can be applied in this scenario. The aqueous solution containing 1 mM FcMeOH and 0.1 M KCl was used as the electrolyte in the SECM test. The probe tip was biased at +0.45 V (vs. Ag/AgCl) and the Al-Mg-Si substrate was biased at -0.7 V (vs. Ag/AgCl), a typical OCP value of Al-Mg-Si alloy during the corrosion process. In this aqueous system, as compared to the organic system, those cathodically active sites can be viewed as the real sites on which not only FcMeOH⁺ can be reduced, but cathodic reactions during the corrosion process in an aqueous solution can occur. One can observe that the feedback contrast produced by the crosshair is not so clear as the as-prepared sample in the organic solution as shown in Fig. 5a. In order to verify the assumption mentioned above that the corrosion product can have a strong influence on the SECM imaging process, a SEM experiment was performed to observe the corrosion morphology of the alloy after the 24-h corrosion treatment (see Fig. 7). Fig. 7a clearly shows that the groove was filled with the corrosion product. The contour of the crosshair is not well-defined in the image. This is the very reason why the feedback signal caused by the crosshair in the SECM tests (in the organic system) becomes weaker and weaker along with the corrosion time.

Site D3 also shows high cathodic reactivity (also occurs in the organic system like D1 and D2). This may result from the weak or less intact oxide film on that site so that it is easier for FcMeOH⁺ to contact the metal substrate and be reduced there. A corrosion hole in this site was found in the SEM experiment (see Fig. 7b). The

accelerated voltage in the EDX experiment was 20 kV, which was high enough to detect the element distribution beneath the surface to an extent as deep as several micrometers. Since no obvious intermetallic particles as large as that in Site B and Site C can be observed in the SEM image, it is highly possible that there was a void defect present there rather than some possible intermetallic particles buried beneath the surface. Even though there is some corrosion product inside the hole, it is still not sufficient enough for it to cover the whole void. Therefore, this kind of defect provides an effective site where cathodic reactions can occur and this is the reason why the strong positive feedback signal can be detected around this defect in the SECM tests even without the presence of obvious element aggregation (see Fig. 5). However, further study is still needed to clarify this phenomenon due to the lack of solid evidence.

According to the EDX maps (see Fig. 4c–f) and Fig. 6b, it is no surprise to find that the place (typically indicated by B3) occupied by Al(Fe, Mn)Si phase shows a strong positive feedback signal. It is well accepted that Al(Fe, Mn)Si is the electrochemically active site where it is easier for the cathodic reactions, like oxygen reduction, to take place [8,18]. It is interesting to find that those MgSi particles, typically marked by A3 and C3, also show positive feedback signals. The feedback current produced in area C3 is as intense as that of area B3. This SECM result can shed light on the idea that, during the corrosion process, MgSi remnants can serve as an active site where cathodic reactions can take place. One may propose that the topography fluctuation caused by the corrosion products may somehow disturb the information in the SECM experiments. The CV result of the aqueous system clearly indicates that the current under diffusion-limited control is approximately equal to 1.4 nA. If the substrate is insulated, under no circumstances can the feedback current be higher than 1.4 nA. However, in the SECM result carried out in the aqueous solution, the positive feedback current (1.75–3.0 nA) is much higher than this value. That is to say, both MgSi and Al(Fe, Mn)Si show strong cathodic activity. In this case, it is unnecessary to establish a correction factor to eliminate the influence induced by the corrosion product. Recently, it is also proved that the MgSi particle is not always anodic in the corrosion process [19]. Also, the MgSi phase has been proved that it becomes cathodic-active after the dealloying process caused by corrosion [8,20]. The weaker signal in area A3 as compared with C3 can be ascribed to its less area of exposure, so that corrosion product may partly cover its surface and thus less FcMeOH⁺ can be reduced at this place. This can be also corroborated by the SEM image shown in Fig. 7a that the intermetallic cannot be observed. Besides, one can notice that, although there are many small element aggregations in the alloy, as corroborated by the EDX map shown in Fig. 4, a clear positive feedback

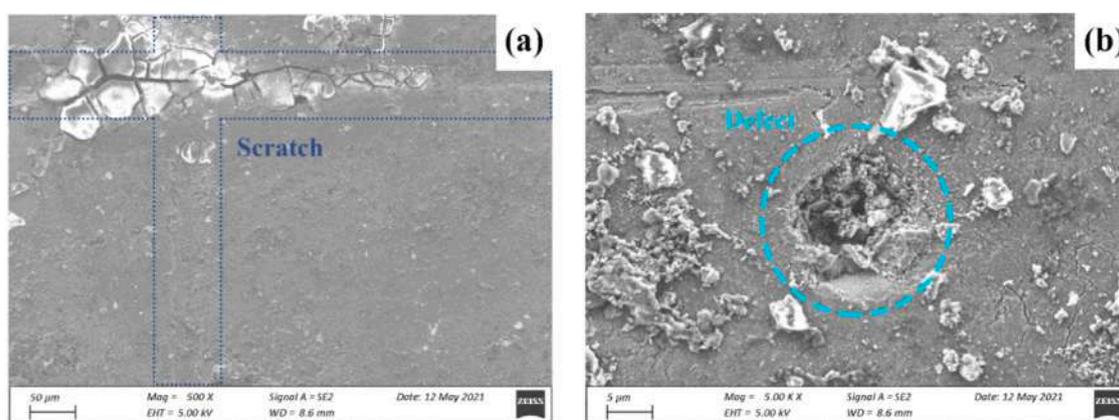


Fig. 7. SEM images of Al-Mg-Si alloy after corrosion in 0.1 M NaCl aqueous solution for 24 h: (a) a scanning area corresponding to Fig. 4a; (b) a defect site associated with the positive feedback signal in the SECM test.

signal in the SECM result can only be observed from the micron-sized intermetallic. The nano-sized dispersoid may not be able to be served as a detectable site in the SECM test, either because its weak feedback current is negligible or the corrosion product may cover its surface to form a quasi-insulated site.

Although the experiment in this paper can only prove that the MgSi phase is the electroconductive site in organic solution and it shows as strong electrochemical reactivity as Al(Fe, Mn)Si phase in aqueous solution after 24-h corrosion, it is still impossible to investigate whether MgSi phase can serve as a possible site for cathodic reactions when it is not under serious corrosion stage (a stage that Mg is preferentially dissolved and a Si-rich site remains).

4. Conclusions

SECM shows a powerful ability to reveal the nature of the alloy surface during corrosion. It is of great advantage to apply SECM combined with an organic solution to investigate the electroactive site on the alloy surface. Although probe contamination may disturb the test in an aqueous solution, a good SECM image can be also obtained when a stable oxide film forms on the alloy surface. By applying both the organic and aqueous system to investigate the corrosion mechanism of Al-Mg-Si alloy, the main conclusions are summarized as follows:

- I. Micron-sized intermetallic particles can be easily attacked by a corrosion electrolyte since an intact and protective oxide film cannot form on their surface.
- II. MgSi intermetallic in Al-Mg-Si alloy can serve as an electroactive site for the cathodic reactions during corrosion in an aqueous solution. After 24-h corrosion, MgSi remnant has comparable cathodic activity as compared to Al(Fe, Mn)Si.

CRedit authorship contribution statement

Chuan He: Conceptualization, Methodology, Software, Writing – review & editing, Formal analysis. **WenFeng Mo:** Resources, Investigation. **YaYa Zheng:** Resources, Investigation. **S.P. Feng:** Supervision, Validation. **BingHui Luo:** Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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