Effect on Corrosion Property of Si in Mg-Al-RE Magnesium Alloy

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Abstract. Magnesium and magnesium alloys’ corrosion property is very terrible, Which limits the use of Magnesium and magnesium alloys. Thus, study the corrosion behavior and mechanism is important to improve the development of magnesium alloys’ industry. The study of Mg-Al-RE alloy(AE44, AE44-0.3Si) in simulating seawater with SEM, XRD, weight loss method, hydrogen evolution method, EIS, polarization curve and so on. We can know the microstructure, component and behavior of corrosion electrochemistry. Based on these data discuss corrosion mechanism. The results show as follows: AE44 alloy has terrible corrosion property in simulating seawater; AE44-0.3Si alloy by adding Si in AE44 alloy, Si eutectic react with Mg generates the second phase--Mg2Si phase. Mg2Si phase clustered at grain boundary or around grain boundary, which has mutual effect with dislocation, improve the corrosion property of Mg-Al-RE Alloy.

Keywords: Die-casting Alloy, Mg-Al-RE Alloy, Microstructure, Corrosion Property

1. Introduction
Resource reserve of Magnesium and rare earth element is abundant in China [1-3]. Thus, it’s meaningful to develop heat-resistant magnesium alloys containing rare earth [4, 5]. In the near future, the key of magnesium industrial development is costing down automotive heat-resistant magnesium alloy [6]. Poor high temperature strength and corrosion resistance of magnesium alloys, so, improving magnesium alloys’ performance become key task in magnesium alloys’ development and research [7-9]. In these paper, research on the microstructure and corrosion resistance in simulating seawater of Mg-Al-RE alloy then discover the relationship between them [10,11]. From the base, we can research heat-resistant magnesium alloys further.
2. Material and Method

2.1. Experiment Material
In these paper, experiment material is Mg-4Al-4RE(AE44) compared with Mg-4Al-4RE-0.3Si(AE44-0.3Si).RE is mixture (La: Ce: Pr: Nd=23:55:6:16). All the samples were cut by wire cutting machine from the center of Magnesium Alloy Casting. The size of AE44 alloy is 10mm 10mm 4mm, the size of AE44-0.3Si alloy is 10mm 4mm. In order to carry out the corrosion test, holes are punched in the sample for easy hanging. The samples were polished with 320 #, 500 #, 800 #, 1200 # and 2000 # sandpaper, then cleaned with acetone, and finally cleaned with distilled water.

2.2. Method
The corrosion property test of specimen includes weight loss method, hydrogen evolution method, EIS, polarization curve. Using Versastat3 electrochemical station, the scanning frequency range of the sample under the same condition is 10kHz-10mHZ, the amplitude of the disturbance is 10mV, and the scanning range of the polarization curve is -250mv+ 125mV, the scanning speed is 1 mv/S, the initial potential is-0.35 v, the ending potential is 0.5 v, the effective area is 1cm², the corrosion medium is the corrosion solution of simulated seawater concentration, the device is connected and then kept at room temperature for 5 min, and the open circuit potential is stabilized before measuring. The composition, relative content and surface morphology of the corrosion products formed on the surface of the samples were further analyzed by X-ray diffraction, XRD and scanning microscope. The corrosion products were examined by x-ray photoelectron spectroscopy and XPS. Finally, the main components of the magnesium alloy surface film and the corresponding proportional relationship are obtained. The scanning angle is 20-80 and the scanning rate is 10/min.

3. Result and Discussion
Figure1 is corrosion property test of AE44 alloy and AE44-0.3Si alloy.

![Figure 1. Corrosion Property test of AE44 alloy and AE44-0.3Si alloy](image-url)
(a) speed of corrosion  (b) hydrogen evolution test  (c) Tafel plot  (d) EIS

The open-circuit potential of AE44-0.3Si alloy is -1.58 V, and the open-circuit potential of AE44 alloy is -1.60 V. The experimental results show that the initial corrosion potential of AE44 alloy increases rapidly, and then the initial corrosion potential of AE44 alloy is stable at a relatively fixed value until the value is constant in a certain time range. In this process, there are some relatively obvious signs of corrosion on the working surface of the magnesium alloy, and there are some bubbles on the local surface of the working surface, which is the hydrogen produced in the corrosion process. There are some fluctuations in the early stages of open-circuit potential stabilization, but these fluctuations are generally around 1.6 V.

As is shown in figure1-(a)(b), loss method and hydrogen evolution method come to the same conclusion that the corrosion speed of AE44-0.3Si alloy is lower than AE44 alloy. Figure1-(c) (d), in order, Tafel plot and EIS. The corrosion self electric potential of AE44 alloy and AE44-0.3Si alloy are -1.525V, -1.504V in order. The current density of AE44-0.3Si alloy is lower than AE44 alloy in interval between corrosion self electric potential and 0V, Pitting potential of AE44 alloy and AE44-0.3Si alloy are slightly lower than the corrosion self electric potential, thus, partial corrosion occur in AE44 alloy and AE44-0.3Si alloy spontaneously. The EIS of AE44 alloy and AE44-0.3Si alloy in corrosive liquid presents two different circular radius arc, because capacitive reactance arc in high frequency region which from the process of double-layer capacitor’s charge-discharge, and presents corrosion reaction product is hydroxide on the surface of AE44 alloy and AE44-0.3Si alloy. While corrosive intermediate’s extension products capacitive reactance in low frequency region. The ARC radius of AE44-0.3Si alloy is larger than that of AE44 alloy, so the corrosion resistance of AE44-0.3Si alloy is better than that of AE44 alloy. When the ARC size decreases, the corrosion rate increases and the protective effect of the protective film weakens. Compared with AE44 alloy, corrosion resistance of AE44-0.3Si alloy is better, because of Si.

Figure2 is XRD test result of AE44 and AE44-0.3Si alloys’ corrosion reaction film. It turns out that main corrosion reaction product is Mg(OH)₂.

![XRD test result of AE44 and AE44-0.3Si alloys’ corrosion reaction film](image)

**Figure 2.** XRD test result of AE44 and AE44-0.3Si alloys’ corrosion reaction film

Figure3 is the microstructure of AE44 alloy and AE44-0.3Si alloy, which are cleaned by chromic acid lotion after staying in corrosive liquid for 24 hours.
Figure 3. Microstructure of AE44 alloy and AE44-0.3Si alloy after corrosive reaction
(a)AE44 (b)AE44-0.3Si

In figure 3(a) AE44 alloy close-set corrosion etch pits are punctate, and corrosion reaction film can’t protect basis material from corrosive liquid, thus lead to serious corrosion on base material. In figure 3b, AE44-0.3Si alloy presents less corrosion etch pits in same enlargement factor, and corrosion reaction film still tightly linked. Because Si can improve Die-casting Alloys’ character, and Si eutectic react with Mg generates the second phase--Mg2Si phase. Mg2Si phase clustered at grain boundary or around grain boundary, and Mg2Si phase and dislocation have mutual effect, which limits dislocation movement. On the other hand, Mg17Al12 can impede further corrosion happen when alloy in corrosive liquid, thus improve corrosion resistance of alloy.

As shown in figures 4(a) and 4(b), the corrosion film of AE44-0.3Si alloy is still closely connected without obvious fracture under the same condition. The corrosion film of AE44 alloy has been broken obviously, and the corrosion hole is obvious. Compared with 4(c) figure and d figure, the grain boundary of AE44-0.3Si alloy in c figure is intact and smooth, while the grain boundary of AE44 alloy in d figure appears obvious fracture. For all these reasons, in same corrosion condition, AE44-0.3Si alloy presents better corrosion resistance than AE44 alloy.

Figure 4. Microstructure analysis of alloy corrosion film
4. Conclusion

(1) The corrosion resistance of die-cast AE44 magnesium alloy in 3.5% NaCl solution is poor. The corrosion begins locally and pitting is the main feature. The surface of Mg(OH)$_2$ alloy was damaged seriously in a short time because the corrosion products, such as Mg(OH)$_2$, had more cracks and holes and were not distributed evenly.

(2) The corrosion resistance of AE44-0.3Si alloy with proper amount of Si is better than that of AE44 alloy by weight loss method, hydrogen evolution method and electrochemical method. Xrd analysis shows that the main composition of the corrosion film is Mg(OH)$_2$. Sem Analysis shows that the eutectic reaction of Si element with magnesium in AE44-0.3 Si alloy results in the second phase Mg$_2$Si phase, which distributes at or near the grain boundary, the corrosion resistance of the alloy is improved by effectively preventing the corrosion of the Matrix by the corrosion solution.

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