The Corrosion Behavior of As-cast Mg–4Al–xEr–0.3Mn Alloys

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ABSTRACT

Magnesium and magnesium alloys are light-weighting candidates as the structure materials. The microstructure and corrosion behavior of Mg–4Al–xEr–0.3Mn (x = 2, 4, 6 all in wt%) alloys were studied. The results showed that the morphology, size and distribution of Mg<sub>17</sub>Al<sub>12</sub> phase were gradually improved with the increasing of Er content, and a large number of Al<sub>2</sub>Er were observed. The Al<sub>2</sub>Er inhibited the hydrogen evolution reaction and promoted the growth of passivation film. Er oxides or hydroxides were found on the surface of the passivation film, and the charge transfer resistance of the film was 4447Ω cm<sup>2</sup>, while the film resistance was 5852Ω cm<sup>2</sup>, which reduced the electron transfer efficiency and improved the density and stability of the passivation film, thus greatly improving the corrosion resistance. As Er content increases 6 wt%, the corrosion rate decreases by nearly 45%.

KEYWORDS: Magnesium Alloys, AE44, Er Element, Corrosion Behavior

Table 1. Nominal compositions of the alloys (in wt%).

| Alloys  | Al  | Er  | Mn  | Mg  |
|---------|-----|-----|-----|-----|
| AE42    | 4   | 2   | 0.3 | Bal.|
| AE44    | 4   | 4   | 0.3 | Bal.|
| AE46    | 4   | 6   | 0.3 | Bal.|

Mg–Al alloy has good casting properties, while its corrosion resistance is poor. According to the previous studies, adding RE elements to the alloy can form the more stable passivation film on the surface. However, there are very few reports about the effect on the corrosion behavior in Mg–Al system alloys (to the knowledge of the authors). Therefore, in this paper the corrosion behavior of the Mg–4Al–xEr–0.3Mn alloys (denoted as AE4x, x represents rare earth element Er, x = 2, 4 and 6) was analyzed and the corrosion mechanism was revealed.

2. Experimental Methods

2.1 Materials preparation

The Mg–4Al–xEr–0.3Mn alloys were prepared from a commercial pure magnesium (>99.99%), pure aluminum (>99.99%), Mg-20 wt% Er intermediate alloy and Mg-5 wt% Mn intermediate alloy, by melting in a crucible resistance furnace under the protection of Ar<sub>2</sub> and SF<sub>6</sub> mixed gas. The molten alloy is cast at 750°C into a steel mold preheated to 300°C and then cooled in air at room temperature. The chemical compositions of the alloys are listed in Table 1.

2.2 Characterization of microstructure and phase

The distribution and morphology of the microstructure were observed by a scanning electron microscope (ZEISS-6035). The phases of the alloys were measured using an X-ray diffractometer (Brook X D8Advance-A25) with a scan rate of 0.02°/s at the range from 15° to 80°. Corrosion products were analyzed using X-ray diffraction (XRD) with Cu Kα radiation at a scan rate of 1°/min.

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photoelectron spectroscopy (XPS Thermo SCIENTIFIC ESCALAB X-\textit{i}+)).

### 2.3 Electrochemical testing

Electrochemical tests were performed using an AutoLab (Metrohm) electrochemical workstation in 3.5 wt% NaCl solution at room temperature. A traditional three-electrode cell was used with platinum as the counter electrode, a saturated calomel electrode (denoted as SCE) as the reference electrode and the sample as the working electrode. The area of the working electrode was 1 cm², and the samples were ground with SiC paper up to 2000 grit size. The samples were immersed in 120 mL 3.5 wt% NaCl solution for 60 minutes in order to achieve a relatively stable open circuit potential (OCP). The potentiodynamic polarization tests were measured with a scan range from -500 mV vs. SCE to +300 mV vs. SCE at a scan rate of 1 mV/s. The corrosion current was obtained by cathode extrapolation. The electrochemical impedance spectroscopy (EIS) measurements were carried out with an amplitude of 10 mV over the frequency range from 100 kHz to 0.01 Hz at an OCP after 60 minutes stabilization.

### 2.4 Immersion experiment

The samples volume of immersion experiment were 8 mm × 8 mm × 5 mm and were ground with SiC paper up to 2000 grit size. The samples were suspended in 250 mL solution with nylon rope and then immersed for 48 h at room temperature. After immersion test, the corrosion products were cleaned using a mixed solution containing 200 g/L CrO₃ and 10 g/L AgNO₃ for 8 minutes in an ultrasonic vibrator. After cleaning, the samples were dried with cold air and then weighed. The corrosion morphology was observed under scanning electron microscope. The weight loss rate \( W_L \) (mg cm⁻² d⁻¹) was calculated using the following formula:

\[
W_L = \frac{W_b - W_w}{At}
\]

where \( W_b \) is the quality (mg) of the sample before the immersion test, \( W_w \) is the quality (mg) of the sample after the removal of corrosion products after the immersion test, \( A \) (cm²) is the surface area of the sample, and \( t \) (day) is the test time.

The corrosion rate \( P_w \) (mm y⁻¹) can be calculated by the formula:

\[
P_w = 2.10 \times W_L
\]

The mosaic approach was used during the sample hydrogen evolution test so that only surface area (1 cm²) was exposed. The samples were immersed in the solution with a volume of 250 mL at room temperature for 48 h and hydrogen was collected with burette. Each alloy is tested at least three times under the same conditions to ensure the accuracy of the tests.

### 3. Results

#### 3.1 The phase analysis and microstructure observing

Figure 1 shows the XRD patterns of the as-cast Mg–4Al–xEr–0.3Mn alloys. There are diffraction peaks of \( \alpha\)-Mg, \( \text{Mg}_{17}\text{Al}_{12} \) and \( \text{Al}_2\text{Er} \) in the all three alloys. In addition, the diffraction peak of \( \text{Al}_2\text{ErMn}_5 \) is also found in the XRD patterns of the AE42 alloy. With the increase of Er content, the diffraction peaks intensity of \( \text{Al}_2\text{Er} \) also increase and the peaks intensities of \( \text{Al}_2\text{Er} \) reached the maximum in the AE46 alloy.

Figure 2 shows the microstructures of as-cast Mg–4Al–xEr–0.3Mn alloys. The lamellar-like \( \text{Mg}_{17}\text{Al}_{12} \) precipitated with \( \alpha\)-Mg eutectic is very fine and dispersion distribution as shown in Fig. 2a.

![Figure 1. XRD patterns of the as-cast Mg–4Al–xEr–0.3Mn alloys.](image)

![Figure 2. SEM images of (a) AE42 alloy, (b) AE44 alloy and (c) AE46 alloy.](image)
The clump-like Al2ErMn5 and bar-like Al2Er were also found in AE42 alloy (see Fig. 2a), while the particle-like Al2Er in AE44 and AE46 alloys (as shown in Figs. 2b and 2c). This is consistent with the results in previous literatures.17,18 Since the solidification temperature of Al2Er is much higher than that of the Mg17Al12 and thus the Al atoms and Er atoms are preferred to form intermetallic compound Al2Er first during the solidification, which is as nucleation sites of the α-Mg and Mg17Al12 and further modifies the morphology, size and distribution of the Mg17Al12 owing to Er as active element inhibiting the growth of the Mg17Al12.19 With the increasing of Er content, the volume fraction of the Mg17Al12 decreased, while the volume fraction Al2Er increased.

Figure 3 are SEM images and energy spectrum of EDX element surface distribution of the three alloys. The bar-like Al2Er precipitate and the lamellar-like Mg17Al12 precipitate are shown in Fig. 3a. With the increasing of Er content, the sizes of the Mg17Al12 are fined, while the sizes of Al2Er are coarsen. A few of Al2ErMn5 particles are also found in Fig. 3a, while the Al2ErMn5 can hardly be seen in Figs. 3b and 3c, which are consistent with XRD results.

3.2 Corrosion behavior

Figure 4 shows the potentiodynamic polarization curve of the alloy after 60 minutes of open circuit potential measurement. The breakdown potentials are marked with arrows. The cathodic polarization curves indicate hydrogen evolution at the cathode and the anodic polarization curve indicates the dissolution of magnesium ions. It is obvious that the current densities of the cathode and anode decrease with the increasing of the Er content. Furthermore, there is an obvious passivation tendency on the anode branches of AE42 and AE46 alloys. It is implied that there is a protective oxide film on the surface of the alloy. The corrosion potentials of AE42 and AE46 alloys are lower than the breakdown potential, while the corrosion potential of AE42 is higher than the breakdown potential.

The cathode hydrogen evolution rate and anode dissolution rate of AE46 alloy are the slowest among the three alloys. When the potential reaches the breakdown potential, the corrosion current increases rapidly, indicating that the ruptured surface film at this critical point is no longer protective and local corrosion occurs. The Tafel fitting15,20,21 was used to fit the experimental results as listed in Table 2. $E_{\text{corr}}$, $I_{\text{corr}}$ and $E_{\text{bp}}$ represent the corrosion potential, corrosion current density and breakdown potential, respectively.

The film breakdown potential of AE42, AE44 and AE46 alloys are $-1.55$ V vs. SCE, $-1.48$ V vs. SCE and $-1.43$ V vs. SCE, respectively. The results showed that the breakdown potentials increased with the increasing of Er content in the alloys and the passivation films of the samples with higher Er content were more protective. Therefore, the adding of the Er enhances the electrochemical stability of the passivation film, which is consistent with the results in literature.22

The results of electrochemical measurement are given in Fig. 5. According to the Nyquist curve in Fig. 5a, the Nyquist plots of all alloys consist of three loops including a high-frequency capacitive loop, a medium-frequency capacitive loop, and a low-frequency
The tendency of pitting corrosion is. The sample surface. The higher the induction resistance, the less at lower frequency is attributed to local corrosion on the surfaces of the alloys immersed in 3.5 wt% NaCl electrolyte.

Figure 5. The electrochemical measurement of tested specimens in a 3.5 wt% NaCl electrolyte: (a) Nyquist plots, (b) Bode plots, (c) equivalent circuit used to fit the EIS spectra.

Table 3. The fitted EIS data.

| Alloys  | \( R_s \) (Ω cm\(^2\)) | \( R_t \) (Ω cm\(^2\)) | \( Y_{dl} \) (Ω\(^{-1}\) cm\(^2\) g\(^{-2}\)) | \( n_{dl} \) | \( Y_f \) (Ω\(^{-1}\) cm\(^2\) g\(^{-2}\)) | \( n_f \) | \( R_L \) (Ω cm\(^2\)) | \( R_L \) (Ω cm\(^2\)) | \( L \) (H cm\(^{-2}\)) |
|---------|-------------------|-------------------|-----------------|------|-----------------|------|-----------------|-----------------|-----------------|
| AE42    | 10.33             | 463               | 1.58 \times 10^{-5} | 0.93 | 29.5 \times 10^{-4} | 0.05 | 4396            | 294             | 267             |
| AE44    | 12.34             | 2055              | 9.78 \times 10^{-6} | 0.57 | 11.45 \times 10^{-4} | 0.50 | 4820            | 3581            | 84800           |
| AE46    | 5.68              | 4447              | 9.27 \times 10^{-6} | 0.85 | 6.83 \times 10^{-4} | 0.79 | 5852            | 4617            | 89619           |

After 12 h, more and more hydrogen are collected, and the hydrogen evolution rate is obviously accelerated. This indicates that the passivation film formed during the initial immersion process has been damaged with the continuous erosion of Cl\(^-\), resulting in an accelerated corrosion rate. Although EIS results show that there is a tendency to pitting corrosion on the surface. It is surprising to find that AE46 alloy has much less hydrogen evolution from 0 to 48 h than those of the other alloys. This indicates that the passivation film is produced on the surface of the AE46 alloy, thus the corrosion resistance of the alloy is greatly improved.

Figure 6b shows the weight loss corrosion rates calculated according to Eqs. 1 and 2 for the three alloys after being immersed in 3.5 wt% NaCl solution for 48 h. It is found that the adding Er to the Mg alloys has an obviously protective effect on the magnesium alloys in 3.5 wt% NaCl solution. The corrosion rate is only 0.7 mm y\(^{-1}\) when the addition of the Er reaches 6 wt%. The corrosion rates of the three alloys are as follows: AE42 > AE44 > AE46.

Figure 7 shows the morphologies of corrosion products on the surfaces of the three alloys immersed in NaCl solution after 48 h (without chromic acid cleaning). It is observed that there is a passivation film of corrosion products on the surface of the sample and it is accompanied by the generation of microcracks. In Fig. 7a, the passivation film are not compact and some deeper corrosion pits can be seen on the surface of the passivation film as shown in inset of the Fig. 7a. The corrosion products are not stable and thus easily

3.3 Corrosion rate

Figure 6a shows the hydrogen evolution rates curves of the three alloys immersed in 3.5 wt% NaCl solution for 48 h. In the first 12 h, the hydrogen evolution rates of the three alloys are relatively slow.
fall off from the surface. Figure 7b shows that although the passivation film morphology of the AE44 alloy is similar to that of the AE42 alloy, there are no deeper corrosion pits and the corrosion products are more compact than those of the AE42 alloy. No deep corrosion pits are found on the passivation film of the AE46 as shown in Fig. 7c. It is observed that the passivation film are the most compact among the three alloys and thus it can effectively prevent the alloy from being further corroded. The results in literature showed that the initially formed Mg(OH)₂ films did not have microcracks. However, in the high vacuum environment of electron microscopy, Mg(OH)₂ was transformed into MgO, which resulted in microcracks due to changing in molar volume of the passivation film.

4. Discussion

It is well known that the Mg(OH)₂ prevent the magnesium from the corrosion is very limited. It is attributed to the layered structure of Mg(OH)₂ in the alloy attacked easily by Cl⁻, which destroys the integrity of the passivation film and thus the corrosion occurs further. The magnesium atoms dissolve into not only divalent magnesium ions but also monovalent magnesium ions. Namely, magnesium atoms first lose electrons and become monovalent magnesium ions and subsequently monovalent magnesium ions react with water to form more stable divalent magnesium ions and thus release hydrogen (anodic hydrogen evolution). As shown in Figs. 7a and 7b, because of the incompleteness of the passivation film and the Cl⁻ reacts with the magnesium further. Therefore, AE42 and AE44 alloys have more hydrogen evolution. The compact passivation film of the AE46 (see Fig. 7c) is more protective to the magnesium matrix and the hydrogen evolution rate of the AE46 is the lowest one among the three alloys. This is consistent with the results in Fig. 6a. However, the rare earth elements as alloying elements of magnesium are believed to increase the stability of the passivation film. The incorporation of Er in the Mg(OH)₂ lattice reduced the corrosion sensitivity of Mg(OH)₂, hence improving the
cathodes weaken the tendency of local corrosion and turn into passivation film. It may be consist of Al$_2$O$_3$ and Er$_2$O$_3$ or Er(OH)$_3$ exist in the passivation film. This is consistent with previous electrochemical results as shown in Figs. 4 and 5.

With increasing the content of the Er element, the volume fraction of the Mg$_{17}$Al$_{12}$ precipitates change from coarser discontinuous precipitation to finer continuous precipitation. However, it is inevitable to introduce a large amount of Al-RE intermetallic compounds in the alloy, which lead to micro-galvanic corrosion. The cathode current density, charge transfer resistance and surface oxide film resistance of the Mg alloys.

Figure 8 is the XPS spectrums of the AE46 alloy immersed in 3.5 wt% NaCl solution for 48 h. It is shown in Fig. 8a that the spectrums of Mg 1s have a peak of Mg(OH)$_2$ at 1303.67 eV and a peak of MgO at 1304.67 eV. There is a sharp peak at 74.36 eV as shown in Fig. 8c, which indicates that Al element is enriched in the passivation film of the AE46 alloy and hence the passivation film may be consist of Al$_2$O$_3$ and/or Al(OH)$_3$. The compact passivation film of the Al$_2$O$_3$ formed on the AE46 alloy can provide a better protective effectiveness of the alloy. The Er$^{3+}$ peaks also appear in the spectrum of Er 4d as observed in Fig. 8d, which indicates that the Er$_2$O$_3$ and/or Er(OH)$_3$ exist in the passivation film. This is consistent with previous electrochemical results as shown in Figs. 4 and 5.

5. Conclusion

Based on the experimental investigation of the corrosion resistance and corrosion mechanism of as-cast Mg–4Al–xEr–0.3Mn alloy, the following results are obtained:

(1) With the increasing of Er content, the volume fraction of the effective cathode Mg$_{17}$Al$_{12}$ decreases and the grains of Mg$_{17}$Al$_{12}$ are fined, while the volume fraction of the Al$_2$Er increases and the grains of Al$_2$Er are coarsen.

(2) AE46 alloy has the best corrosion resistance in 3.5 wt% NaCl solution. The hydrogen evolution rate of cathode and dissolution rate of anode of the AE46 alloy are lowest in all of the three alloys. And the corrosion current density, the charge transfer resistance, the film resistance and the corrosion rate are 6.02 µA cm$^{-2}$, 4447 Ω cm$^2$, 5852 Ω cm$^2$, and 0.7 mm·y$^{-1}$, respectively.

(3) The high corrosion resistance of AE46 alloy is attributed to the compact passivation film produced on the surface during corrosion. Besides Mg(OH)$_2$, there may also exist Al$_2$O$_3$, and/or Al(OH)$_3$, and Er$_2$O$_3$ and/or Er(OH)$_3$ in the passivation film, which improve the corrosion resistance of AE46 alloy.

(4) Although there is a large amount of Al$_2$Er phase in AE46 alloy, the hydrogen evolution rate is reduced compared with those of the AE42 and AE44 alloys. It is found that the numerous micro-cells are formed on the surface of the alloy to cause overall corrosion and thus accelerate the formation of passivation film.

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CRediT Authorship Contribution Statement

Yanzhuo Liu: Writing – original draft (Lead)
Yongfeng Li: Software (Supporting)
Honggang Zhang: Software (Supporting)
Jinhui Wang: Project administration (Lead)
Peipeng Jin: Writing – review & editing (Lead)

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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