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Study of the corrosion product films formed on the surface of Mg–*x*Zn alloys in NaCl solution

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ABSTRACT

The corrosion product films formed on the surface of Mg–2Zn and Mg–5Zn alloys in NaCl solution were investigated by electrochemical measurement, scanning electron microscopy (SEM) observation and X-ray photoelectron spectroscopy (XPS) analysis. It is found that a compact corrosion product film is formed in the initial stage of immersion, and then the film gradually degrades due to dissolution reaction. The product film formed on Mg–2Zn alloy presents better protection property than that on Mg–5Zn alloy, which can be attributed to the different chemical composition and microstructure of the both alloys.

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1. Introduction

Mg is a very active metal. The naturally formed oxide film in air mainly consists of MgO whose P/B ratio is below 1, which is not as compact as that formed on the metals of Al and Ti. Also, the oxide films formed in aqueous electrolytes mainly consist of $Mg(OH)_2$ whose P/B ratio is beyond 1 [1], and they cannot still provide effective protection to the Mg substrate, which can be attributed to the following reasons: (1) the formation of $Mg(OH)_2$ film accompanies the intense hydrogen evaluation reaction [2,3], which can degrade the compactness of the film; (2) the $Mg(OH)_2$ film is not chemically stable and susceptible to dissolution in corrosive electrolytes [4]. Thus, the oxide films regardless of formed in air or electrolytes cannot effectively retard the corrosion of Mg substrate.

Plenty of studies are carried out to adjust the chemical composition and microstructure of the oxide films by addition of alloying elements. It is found that the naturally formed oxide films on the surface of Mg alloys play a key role in the corrosion process [5–9]. Wang et al. [10] reported that the presence of Al in AZ31 and AZ91 Mg alloys can form $Al_2O_3/Al(OH)_3$-containing oxide films in NaCl solution, together with the carbonate products to provide a better passivation and retard the chloride-induced corrosion. Zhao et al. [11] found that the surface films formed in corrosive mediums can be more or less effective in hindering the corrosion of AZ91. Liu et al. [12] analyzed the surface film formed in ultrapure water on pure Mg and two Mg–Al intermetallic compounds and found that the film composition on Al_3Mg_2 was $AlMg_{1.4}O_{0.2}(OH)_{5.4}$ whilst on $Mg_{17}Al_{12}$ the composition was $AlMg_{2.5}(OH)_8$. These studies indicate that the alloying element of Al is available to improve the protection performance of the surface films in aqueous solution to some extent.

Rare Earths (RE) are also very beneficial alloying elements to enhance the surface films of Mg alloys [13–15]. Pinto et al. [16,17] studied the passive behavior of RE-containing Mg alloys in borate and alkaline solutions. It is found that an amorphous yttrium oxide/hydroxide thick film is formed, which possesses higher stability when compared to magnesium oxide/hydroxide. Liu et al. [18] also found that Y in the Mg–Y binary alloys can improve the protection property of the surface films.

Zn is another very popular alloying element [19–21]. There are some studies about the effect of Zn-containing second phases on the corrosion behavior of Mg alloys. Bi et al. [22] researched the corrosion property of Mg–2Dy–*x*Zn ($x = 0$, 0.1, 0.5 and 1 at.%) alloys and found that the corrosion resistance first decreases and then greatly increases with Zn addition. However, the effect of Zn element on the formation of natural oxide films is paid little attention. Only Ha et al. [23] mentioned that the solid solution of Zn enhanced the protectiveness of the passive film, but the detailed characteristic of the passive film was not reported. In our previous work [24] the microstructure and protection performance of the naturally formed oxide films in air on the surface of the Mg–*x*Zn alloys have been investigated. The results indicate that the oxide films on the Mg–2Zn and Mg–5Zn alloys present a similar chemical

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composition, consisting of surface layer of basic magnesium carbonate and MgO following with MgO and ZnO, but the oxide film on the Mg–5Zn is thicker and has more defects than that on the Mg–2Zn. Moreover, it is found that there are visible surface product films naturally formed on Mg–*x*Zn alloys in NaCl solution. However, the microstructure and protection property of the films are still not clear. Thus, the aim of this paper is to investigate the naturally formed corrosion product films on the Mg–2Zn and Mg–5Zn alloys in NaCl solution, and then clarify their protection ability to the Mg substrate.

2. Experimental

The experimental materials used for this investigation were the extrusion Mg–2Zn and Mg–5Zn plates which were provided by Korea Institute of Materials Science (KIMS) as reported in the previous paper [24–26]. The samples were successively ground to 3000 grit paper, cleaned in alcohol, and then dried in cool air. The samples for metallographic observation were further ground to 5000 grit paper, finely polished using 1 μm diamond paste and then etched by the solution consisting of 1 g oxalic acid, 1 mL nitric acid, 1 mL acetic acid and 150 mL distilled water.

The samples were immersed in 0.1 M NaCl solution for various times and then the surface morphologies were observed using a Phillips XL30 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX).

Electrochemical tests were performed in 0.1 M NaCl solution using an EG&G potentiostat model 273 (Princeton Applied Research, USA) and a model 5210 lock-in amplifier. A classical three–electrode cell was used, with a platinum plate as counter electrode, a saturated calomel electrode as reference electrode and the sample with an exposed area of 1 cm^2 as working electrode. The samples were immersed in 0.1 M NaCl solution for 0, 1, 2, 5, 9 and 24 h, respectively, and then electrochemical impedance spectroscopy (EIS) measurements were carried out under open circuit potential after an initial delay of 300 s. The sample named "0 h" represented that immersion treatment was not carried out before EIS measurement expect for the initial delay of 300 s. The scan frequency ranged from 100 kHz to 10 mHz with a sine perturbation amplitude of 5 mV (peak to zero). The data were fitted by a ZSimpWin 3.20 software. The samples immersed in 0.1 M NaCl solution for 1, 2 and 5 h, respectively, were used for potentiodynamic measurements. The measurements started from −200 mV below open circuit potential at a constant scan rate of 0.5 mV s^{-1} and were terminated until a final current density of approximately 10 mA cm^{-2} after an initial delay of 300 s. At least three electrochemical measurements were performed under the same testing conditions for ensuring the reproducibility.

The chemical composition of the corrosion product films formed in 0.1 M NaCl solution for 2 h was probed using an ESCALAB 250 X-ray photoelectron spectroscopy (XPS). Depth profiling was carried out from surface to inner layer. The sputtering rate was 0.1 nm s^{-1}. The data were analyzed using a Xpspeak 4.1 software.

3. Results

3.1. Microstructure of Mg–2Zn and Mg–5Zn alloys

The microstructures of Mg–2Zn and Mg–5Zn alloys have been reported in our previous papers [24–26]. To facilitate understanding, the surface morphologies of the both alloys are shown in Fig. 1 again. In the case of Mg–2Zn alloy, the alloying element of Zn is completely dissolved into Mg matrix and there are no precipitation phases observed. In the case of Mg–5Zn alloy, some of Zn is dissolved into Mg matrix and the rest is precipitated on the grain boundaries. The precipitation phases were identified by the XRD in our previous work [26]. However, there were no precipitation phases detected probable due to their low volume fractions. Thus, these white precipitation phases are named as Mg_xZn_y according to EDX analysis.

3.2. Electrochemical investigation of corrosion product films

The corrosion characteristics of the Mg–2Zn and Mg–5Zn alloys immersed in NaCl solution for various times are investigated by EIS measurements as shown in Figs. 2 and 3. The Nyquist plot of the Mg–2Zn alloy with 0 h immersion consists of two well–defined capacitance loops, which describe the features of double electric layer and surface film [27], respectively. At the immersion time of 1 h, the plot still consists of two capacitance loops, but the dimension of the plot increases in comparison with 0 h immersion, indicating that the corrosion resistance of the Mg–2Zn alloy is improved. When the immersion time is 2 h, the dimension of the plot reaches the maximum value. However, the shape of the plot take place great change after the immersion time of 5 h. The second capacitance loop disappears and a large inductance loop is observed. The existence of inductance loop indicates that the Mg substrate suffers attack [28]. With increasing immersion time to 9 h, the shape of the plot keeps constant, namely, a high frequency capacitance loop and a low frequency inductance, but the diameters of the plot decrease. After a longer immersion time of 24 h, the plot nearly coincides with that of 9 h immersion.

In view of the Bode plot of frequency vs. impedance, the impedance values first increase and then decrease, and finally tend to be stable with increasing immersion time. It is worth to note that the impedance values of 1 and 2 h immersion are larger than that of 0 h immersion. This case can be attributed to the formation of compact product film in the NaCl solution. As for the Bode plot of frequency vs. degree, two wave crests are observed at the immersion times of 0, 1 and 2 h, implying the existence of two capacitance

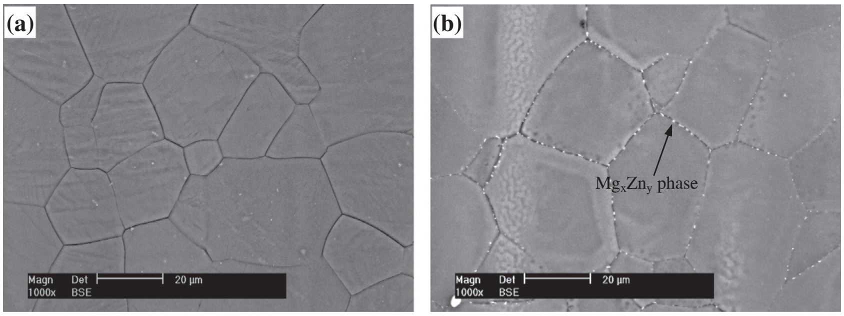

Fig. 1. Microstructure of the Mg–2Zn and Mg–5Zn alloys (a) Mg–2Zn; (b) Mg–5Zn.

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