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Abstract: In this work, the morphology, anti-corrosion performance and degradation mechanisms of two phosphate chemical conversion coatings containing the AEO (fatty alcohol polyoxyethylene ether) and AES (fatty alcohol polyoxyethylene ether sodium sulfate) on an as-cast Mg-8wt.%Li alloy were explored and compared. Although two coating layers had a petal-shaped structure and were composed of leaf-shaped particles, the coating layer of the AES-coated sample was relatively dense due to the smaller size of the formed petal-shaped structure. Based on the electrochemical data and hydrogen evolution measurements, the corrosion protectability of the coating layer on the AES-coated sample was better than that on the AEO-coated sample. The determined corrosion current densities (i_{corr}) of the AES-coated and AEO-coated samples in the 3.5 wt.% NaCl solution were, respectively, 7.8 mA·cm⁻² and 11.7 mA·cm⁻², whereas the i_{corr} value of the coated sample without a surfactant was 36.2 mA·cm⁻².

Keywords: magnesium-lithium alloy; casting; film layer; performance; surface coating



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1. Introduction

Magnesium (Mg) is one of the most abundant elements in the world, and its density is only 1.74 g/cm^3 . Due to the excellent properties, such as good machining performance, electromagnetic shielding ability, biocompatibility and recyclability, Mg alloys are considered to be the best potential material for replacing steels and aluminum (Al) alloys in the fields of automotive, aerospace and electronics [1-5]. It has been reported that the addition of lithium (Li) could improve the mechanical properties of Mg alloys and further decrease their densities [6]. So far, Mg-Li alloys are the most lightweight metallic structure material. The microstructure of Mg-Li alloys is directly relied on the content of added Li [7]. When the added Li is below a content of 5.7 wt.%, the alloy comprises the close-packed hexagonal (hcp)-structured α -Mg phase [7]. When the content of Li is above 10.3 wt.%, the alloys consist of a body-centered cubic (bcc)-structured β -Li phase [7]. When the Li amount ranges from 5.7 to 10.3 wt.%, two-phase structured Mg-Li alloys are formed [7]. For Mg-Li based alloys with a two-phase structure characteristic, the micro-galvanic corrosion is very prone to occur in the corrosion medium due to the different potential values of α -Mg and β -Li [8]. Thus, it is vital to explore effective approaches for resolving the poor corrosion resistance issue of Mg-Li alloys [9–12].

So far, the main surface protection technologies for Mg alloys embrace organic coating [13], ion implantation technology [14], laser surface treatment [15], anodic oxidation [16], vapor deposition [17], electroplating [18], electrodeposition [19], chemical conversion [20], etc. Among them, the chemical conversion technologies are the most popular because they have the advantages of convenient operation, good protection performance and a low price. The principle for preparation is based on the occurrence of the chemical reaction between the metallic surface and conversion solution to form a layer of a protective passivation film [21]. During the early research on chemical conversion surface films, the excellent corrosion protectability of the chromate conversion technologies was widely used [22,23]. However, the chromate treatment solution contains highly toxic Cr(IV) ions and is carcinogenic and harmful to the environment [8]. Due to this, the preparation of chromium-free conversion coatings has been widely researched. Among them, phosphate conversion coatings possess the potential for replacing the chromate conversion coatings because they have the advantages of good corrosion protectability and simplicity in operation [8]. Generally, for the preparation of chemical conversion surface films, the category of additive in surfactants plays an important role, and their inhibiting effect on corrosion development has been widely studied [8]. Generally, the main functions of additives consist of the following: (1) promoting the formation of a coating film; (2) reducing particle crystallinity; (3) controlling the conversion rate; (4) increasing the hydrophobicity of the metal surface; and (5) enhancing the solubility of the main components of the conversion fluid in water [24–30].

In earlier work, researchers found that adding a small amount of surfactants into the conversion solution can make the structure of formed coatings more uniform and denser, resulting in improved corrosion protectability [8]. Investigating an anti-corrosive dense-structured coating, Yang et al. reported that a cationic surfactant of tetravyl-trimethyl ammonium bromide (TTAB) made the formed chemical conversion film on the surface of AZ31 Mg alloy have a dense structure and higher corrosion resistance [31]. Li et al. reported that the addition of a non-ionic surfactant could obviously improve the corrosion protectability of the vanadate conversion surface film on the AZ31 Mg alloy [32]. In addition, researchers found that the surfactants could also influence the anti-corrosion property of the chemical conversion surface films on Mg alloys [33–42]. Thus, it is important to explore and compare the inherent formation mechanisms of chemical conversion surface films containing different types of surfactants and their induced effect on the corrosion protectability. Although the corrosion behavior of surface films on the Mg-8wt.%Li alloy for calcium phosphate conversion treatment has been investigated [8], we still lack a deep understanding about the effect of the additive types of surfactants on the corrosion behavior of two-phase-structured Mg-Li alloys. Thus, in this work, through investigating the anti-corrosion behavior of calcium phosphate conversion surface films containing the addition of fatty alcohol polyoxyethylene ether (AEO, non-ionic surfactant) and fatty alcohol polyoxyethylene ether sodium sulfate (AES, anionic surfactant) on an as-cast Mg-8wt.%Li alloy, the objective is to compare and clarify the influence of non-ionic and anionic surfactants on the protective performance of chemical conversion surface films.

2. Materials and Methods

2.1. Sample Treatment

The explored material in the current research is an as-cast Mg-8wt.%Li alloy with a twophase structure. By smelting in a vacuum induction furnace, an ingot with a dimensional size of 150 mm \times 150 mm \times 40 mm was cast with argon protection. Then, homogenization treatment at 350 °C for 2 h was performed on the ingot in air furnace. On the basis of the measurement from the inductively coupled plasma atomic emission spectrum, the Li and Mg content of the cast ingot was determined to be 8.2 wt.% and 91.8 wt.%, respectively. Samples with cross-sectional area and thickness values of 10 mm \times 10 mm and 5 mm were cut for the microstructural observation. For the surface coating treatment, the 10 mm \times 10 mm \times 10 mm cubic samples were cut and encapsulated in epoxy resin with one side surface being exposed. Then, the exposed surfaces were sequentially ground with abrasive sandpapers and polished with 1.0 µm diamond grinding powder.

2.2. Preparation of Surface Coatings

The ground sample surfaces were ultrasonically cleaned with 30 mL acetone for 10 min and subsequently immersed in alkaline solution ($50 \text{ g/L NaOH} + 10 \text{ g/L NaNO}_3$) for 5 min at 60 °C to remove the grease and dirt on the surfaces, followed by washing with eight

drops of acid solution (40 wt.% H₃PO₄) to remove the remaining alkaline and increase the active sites on sample surfaces during the conversion process. After the pre-treatment, samples were, respectively, immersed into the AES-containing conversion solution (35 g/L Ca(NO₃)₂·4H₂O + 25 g/L (NH₄)₂HPO₄ + 10 g/L AES) and AEO-containing conversion solution (35 g/L Ca(NO₃)₂·4H₂O + 25 g/L (NH₄)₂HPO₄ + 10 g/L AEO) for 30 min at a temperature of 40 °C and a pH value of 3. For comparison, the reference sample coated without the surfactant was also prepared. After treatments, sample surfaces were washed with deionized water.

2.3. Microstructural Analysis and Characterization of Surface Coatings

For observing the polished microstructure of the Mg-8wt.%Li alloy, a scanning electron microscope (SEM) with the backscatter electron (BSE) imaging mode (SEM, EM Crafts CUBE II, Hanam-si, Republic of Korea) was employed. The analysis of phase components was performed using an X-ray diffractometer (XRD) equipped with monochromatic radiation of Cu Ka. The employed wavelength, step size and scanning rate were, respectively, 0.154056 nm, 0.02° and 4°/min (XRD; D/Max 2400) (Rigaku, Tokyo, Japan). To compare the coating layers of differently coated samples, their surfaces were observed by using SEM. Based on the energy-dispersive spectroscopy (EDS) (SEM, EM Crafts CUBE II, Hanam-si, Republic of Korea), the elemental distributions in the sample surface films of AES-coated and AEO-coated samples were determined. Moreover, their cross-sectional morphologies were observed.

2.4. Electrochemical Measurements and Hydrogen Evolution

For the differently coated samples, their electrochemical curves in 3.5 wt.% NaCl solution were measured with an electrochemical workstation (CorrTest CS350, Wuhan, China). In a traditional three-electrode system, where (1) the reference electrode is the saturated calomel electrode (SCE), (2) the exposed sample surfaces and the platinum are, respectively, the working and auxiliary electrodes. To measure the electrochemical curves, samples were pre-soaked for 15 min to stabilize the electrode system. For measuring the impedance spectrum, the range of scanning frequency was 100 kHz~10 mHz. To measure the polarization curves, the scanning speed and range were 1 mv/s and $-0.25 ~ +0.25 V_{SCE}$ with respect to OCP. For each condition, the electrochemical curves were measured at least three times from the parallel samples. The measured electrochemical results were fitted with CorrView software (Ametek, San Diego, CA, USA, version 3.30d). For the hydrogen evolution experiment, the AES-coated and AEO-coated samples were soaked for up to 24 h in a 3.5 wt.% NaCl solution, and the volume of evolved hydrogen was recorded every 1 h. The employed hydrogen evolution device can be found in the literature [43].

2.5. Failure Analysis

To clearly reveal the changes in corrosion severity during the soaking process, the surface appearance and the 3D profiles of the AES-coated and AEO-coated samples being soaked for different times were observed by employing an optical stereo microscope (OM; Keyence VHX 2000) (Keyence, Osaka, Japan). To ensure a good comparison, the severely corroded areas of 255 mm \times 300 mm on the surfaces of differently immersed samples were selected as the scanned areas. The key principle for obtaining 3D profiles mainly consists of two steps: (1) automatically in situ focusing and taking photos from the top to the bottom; (2) automatically combining these photos together into one image. Moreover, the cross-sections of the AES-coated and AEO-coated samples being immersed for 24 h were polished and observed by using SEM with the secondary electron (SE) imaging mode (SEM, EM Crafts CUBE II, Hanam-si, Republic of Korea).

3. Results and Discussion

3.1. Microstructural Analysis

Figure 1 shows the microstructure of the investigated as-cast Mg-8wt.%Li alloy. Based on the BSE images of the as-polished surface, it can be seen that the alloy comprises two matrix phases and exhibits a typical two-phase microstructure (Figure 1a). Moreover, the two matrix phases are all irregularly distributed. Our previous work demonstrated that for the as-cast Mg-8wt.%Li alloy, the a-Mg phase was gray, and the β -Li phase was dark in the BSE images [5,7,8]. The XRD phase analysis (Figure 1b) further confirms that the α -Mg and β -Li phases can co-exist in the alloy. By employing the processing software "Image J, version number V1.8.0.112", the volume percentages of α -Mg and β -Li matrix phases are, respectively, calculated to be 60% and 40%.



Figure 1. Microstructural analysis of the as-cast Mg-8wt.%Li alloy: (**a**) SEM observation with the BSE imaging mode and (**b**) XRD pattern.

3.2. Characterization of the Coating Layers

Figure 2 shows the surface morphologies of the coated samples with and without the addition of surfactants. The high-magnification observation reveals that the surface conversion products of differently coated samples are mainly exhibited in a petal-shaped structure. Meanwhile, the size of the petal-shaped structure on the AEO-coated sample surface is relatively bigger than those of the other two coated samples. Additionally, for the AES-coated and AEO-coated samples, their surface coating layers also contain some roundshaped particles, and the volume fraction of round-shaped particles on the AEO-coated sample surface is obviously higher than that of the AES-coated sample. Based on the EDS element scanning analysis, the element distributions on the surfaces of AES-coated and AEO-coated samples are determined, as presented in Figures 3 and 4. This exhibits that two coatings are composed of C, Ca, O, P and Mg. Moreover, the chemical compositions of petal-shaped and round-shaped conversion products are basically the same. Additionally, the contents of P, O and Ca are obviously higher, whilst the contents of C and Mg are relatively lower. As for the presence of Mg in the two coating layers, there are mainly two reasons, i.e., (1) the Mg^{2+} can be generated by anodic dissolution of the a-Mg matrix and then combines with anions in the conversion solution to form Mg-containing compounds on sample surfaces [43]; (2) the coating layers are relatively thin and the chemical composition of the below matrix phases can also be detected.

Based on the thermodynamically stable phase diagram for the PO_4^{3-} and Ca^{2+} containing solutions [44], the elements of Ca, P and O in the surface coating are mainly present in the highly stable $Ca_3(PO_4)_2$ and $CaHPO_4 \cdot 2H_2O$. Their formation ensures that the formed coating films have good corrosion protectability for the substrate [8,43]. It has been reported that the dissolution of a-Mg and b-Li phases of two-phase-structured Mg-Li alloys can increase the concentration of OH^- ions at the interface of the substrate and phosphate solution [45,46], which will cause an increase in the pH value at the metal bath solution

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interface. Thus, the change in the pH value, associated with the dissolution equilibrium, leads to the formation of HPO_4^{2-} and PO_4^{3-} according to Reactions (1) and (2) [32]:

$$\mathrm{H}_{2}\mathrm{PO}_{4}^{-} + \mathrm{OH}^{-} \to \mathrm{HPO}_{4}^{2-} + \mathrm{H}_{2}\mathrm{O} \tag{1}$$

$$HPO_4^{2-} + OH^- \to PO_4^{3-} + H_2O$$
 (2)



Figure 2. SEM observations for the surface films of: (a) AES-coated sample, (b) AEO-coated sample and (c) reference sample coated without the surfactant; (**d**–**f**) high-magnification observations of the labelled areas in images (**a**–**c**).

Then, the formed HPO_4^{2-} will combine with a Ca^{2+} ion to form insoluble $CaHPO_4 \cdot 2H_2O$ according to Reaction (3):

$$Ca^{2+} + HPO_4^{2-} + 2H_2O \rightarrow CaHPO_4 \cdot 2H_2O$$
(3)

Moreover, Mg^{2+} and Ca^{2+} can, respectively, combine with the PO_4^{3-} to form $Mg_3(PO_4)_2$ and $Ca_3(PO_4)_2$ at the metal solution interface [27]. Thus, for the AES-coated and AEOcoated samples, their surface coatings should be composed of $CaHPO_4 \cdot 2H_2O$, $Mg_3(PO_4)_2$ and $Ca_3(PO_4)_2$. The morphology observations for the cross-sections of two types of AES-coated and AEO-coated samples are shown in Figure 5. This reveals that the thickness values of the coating layers of AES-coated and AEO-coated samples are 13 μ m and 17 μ m, respectively. Moreover, the coating layer on the AES-coated sample is much more compact than that of the AEO-coated sample.



Figure 3. EDS mappings of the elements in the AES-coated sample surface film: (**a**) the microstructure and morphology of the film, (**b**) Mg, (**c**) C, (**d**) Ca, (**e**) P and (**f**) O element distribution.

Since the Cl⁻ ions can easily penetrate the existing gaps [8,21], the corrosion protectiveness of the coating layer on the substrate of the AEO-coated sample will be reduced. In addition, for the AES-coated sample, the added surfactant is anionic and has the advantages of emulsification, wetting and cleaning effects [47], resulting in the formation of a uniform coating layer. However, for the AEO-coated sample, the added surfactant is non-ionic and mainly plays a foaming and cleaning role in the formation of the coating layer. Therefore, the types of surfactant could influence the corrosion resistance of the chemical conversion films on the Mg-8wt.%Li alloy.



Figure 4. EDS mappings of the elements in the AEO-coated sample surface film: (**a**) the microstructure and morphology of the film, (**b**) Mg, (**c**) C, (**d**) Ca, (**e**) P and (**f**) O element distribution.

3.3. Electrochemical Testing

Figure 6 shows the electrochemical curves of the coated samples with and without the addition of surfactants. It can be seen that the potentiodynamic polarization curves of the two differently coated samples have basically identical cathode branches (Figure 6a). Generally, for the Mg alloys, the cathodic branch corresponded to the occurrence of hydrogen evolution, whereas the anodic branch was associated with the anodic dissolution of the α -Mg matrix [48]. Since the negative difference effect (NDE) and pitting could occur during the potentiodynamic polarization tests, the anodic branch was not suitable for fitting [48]. Therefore, the electrochemical corrosion parameters of the coated samples were fitted from the cathodic branches using Tafel extrapolation and are listed in Table 1.



Figure 5. The morphologies of cross-sections observed by using SEM with the secondary electron imaging mode: (a) AES-coated and (b) AEO-coated samples.



Figure 6. Electrochemical results of AES-coated, AEO-coated and reference samples: (**a**) potentiodynamic polarization curves and (**b**) electrochemical impedance spectra. The proposed equivalent circuit for fitting EIS curves is placed in image (**b**).

Sample Conditions	i_{corr} (mA·cm ⁻²)	E_{corr} (V _{SCE})
AES-coated	7.8 ± 1.3	-1.56 ± 0.01
AEO-coated	11.7 ± 1.5	-1.58 ± 0.01
Coated without surfactant	36.2 ± 1.8	-1.58 ± 0.01

Table 1. Fitted parameters from the polarization curves of the coated samples with and without the addition of surfactants.

After phosphate chemical conversion treatment, the corrosion current densities (i_{corr}) of the AES-coated and AEO-coated samples are, respectively, 7.8 mA·cm⁻² and 11.7 mA·cm⁻². For comparison, regarding the reference sample coated without the surfactant, its i_{corr} value is 36.2 mA·cm⁻². Generally, a lower current value indicates that the sample has higher corrosion resistance. Therefore, it demonstrates that the addition of surfactants can effectively enhance the corrosion resistance of phosphate conversion coatings on the as-cast Mg-8wt.%Li alloy. Moreover, the corrosion resistance of the AES-coated sample is much better than that of the AES-coated sample. Moreover, the corrosion potentials (E_{corr}) of the AES-coated, AEO-coated and reference samples are $-1.56 V_{SCE}$, $-1.58 V_{SCE}$ and $-1.58 V_{SCE}$, respectively.

From the EIS curves of differently coated samples, only one capacitive loop can be observed (Figure 6b). Based on the proposed equivalent circuit, the EIS curves of the AES-coated, AEO-coated and reference samples are fitted, and the determined data are listed in Table 2. Among them, R_s and Q_{dl} are, respectively, the solution resistance and the double electric layer between the solution and films, which is determined by the parameters of Y_{dl} and n. R_{ct} is the charge transfer resistance and related to the corrosion resistance of the sample. It can be seen that the determined R_{ct} values of AES-coated, AEO-coated and reference samples are 5751 $\Omega \cdot \text{cm}^2$, 4575 $\Omega \cdot \text{cm}^2$ and 2412 $\Omega \cdot \text{cm}^2$, which further demonstrates that the sequence ranking of corrosion resistance is as follows: AES-coated sample > AEO-coated sample > reference sample coated without surfactant.

Table 2. The fitted EIS parameters of the coated samples with and without the addition of surfactants.

Sample Conditions	$R_{\rm s}~(\Omega~{ m cm}^2)$	Y_{dl} (µF)	n _{dl}	$R_{\rm ct}$ ($\Omega \ {\rm cm}^2$)
AES-coated	17.1 ± 0.7	29.9 ± 1.6	0.68 ± 0.12	5751 ± 250
AEO-coated	18.1 ± 0.8	33.4 ± 1.8	0.69 ± 0.13	4575 ± 235
Coated without surfactant	15.3 ± 0.6	35.0 ± 1.4	0.70 ± 0.15	2412 ± 185

Figure 7 shows the hydrogen evolution curves of AES-coated and AEO-coated samples. Based on their slopes, we can calculate out the hydrogen-evolved speeds of the two coated samples. When Mg alloys undergo electrochemical corrosion, a synergistic process of the evolved hydrogen at the cathode and Mg dissolution at the anode will happen. For the differently coated samples with the same exposed area, the larger volume of evolved hydrogen means a faster rate of anodic dissolution. After 24 h immersion in 3.5 wt.% NaCl solution, the evolved hydrogen volumes of AES-coated and AEO-coated samples were, respectively, 1.45 mL/cm² and 2.14 mL/cm², indicating that the AES-coated sample had better corrosion resistance. Moreover, the AES-coated and AEO-coated samples exhibit similar hydrogen evolution characteristics, and their hydrogen evolution curves can comprise two periods: (1) when immersed for less than 6 h, the volumes of evolved hydrogen of the two coated samples are quite small, indicating the good corrosion protectability of the coating layers; (2) when immersed 6~24 h, their hydrogen evolution rates are gradually increased, indicating the destruction and degradation of the coating layers. Moreover, it reveals that the evolved hydrogen rate of the AEO-coated sample is obviously quicker than that of the AES-coated sample.



Figure 7. Evolved hydrogen volume versus soaking time curves of AES-coated and AEO-coated samples.

3.4. Corrosion Morphology

To characterize the difference in corrosion resistance, the AES-coated and AEO-coated samples were, respectively, soaked for 2, 6, 16 and 24 h. Then, their surface morphologies and corresponding 3D profiles were observed, as shown in Figures 8 and 9. These figures reveal that when the soaking time is less than 6 h, the corrosion severity of the two coated sample surfaces is weak, and only a few areas are corroded, indicating that the film layers have better corrosion protectability on the substrate at this stage. Based on the height difference measured by 3D profiles, the depths of these corroded areas on the surfaces of AES-coated and AEO-coated samples are, respectively, 34.56 µm and 34.43 µm. With an increasing soaking time, the corrosion severity of the coated surfaces intensifies gradually, indicating that the corrosion protectability of the two types of film layers is degraded. When the immersion time is 24 h, the AES-coated and AEO-coated sample surfaces are almost completely corroded. Based on the height difference measured by 3D profiles, the thickness values of formed corrosion product layers on the surfaces of AES-coated and AEO-coated samples can reach 80.19 µm and 90.08 µm, respectively. Meanwhile, the remaining uncorroded area on the AES-coated sample surface is more than that of the AEO-coated sample surface, indicating that the corrosion severity of the AES-coated sample is relatively weaker than that of the AEO-coated sample.

For a comparison between the corrosion performance of the AES-coated and AEOcoated samples, their cross-sectional morphologies after being immersed for 24 h were examined, as shown in Figure 10. It reveals that the AES-coated sample has a lower thickness for the corroded product layer than the AEO-coated sample. Moreover, it can be seen that for two samples, the preferential corrosion attack mainly takes place in the region of the α -Mg phase. The main reason is that, although the lower potential of the β -Li phase in Mg-8wt.%Li alloys can induce preferential corrosion, the formed Li₂CO₃ dense film in the β -Li phase could offer effective protection for the substrate β -Li phase [38,39].



Figure 8. Surface morphologies and 3D profiles of AES-coated samples after being soaked in 3.5 wt.% NaCl solution for: (**a**) 2, (**b**) 6, (**c**) 16 and (**d**) 24 h. The locations of 3D profiles are squared by red frames in images (**a**–**d**).



Figure 9. Surface morphologies and 3D profiles of AEO-coated samples after being soaked in 3.5 wt.% NaCl solution for: (a) 2, (b) 6, (c) 16 and (d) 24 h. The locations of 3D profiles are squared by red frames in images (**a**–**d**).



Figure 10. Morphological observations for the cross-sections: (**a**) AES-coated and (**b**) AEO-coated samples after being soaked for 24 h.

4. Conclusions

Through characterizing and researching the corrosion performance of a Mg-8wt.%Li alloy coated with chemical conversion films containing AES and AEO, respectively, three conclusions are obtained:

- (1) The corrosion resistance of the AES-coated and AEO-coated samples is clearly higher than that of the reference sample coated without a surfactant.
- (2) For the AES-coated and AEO-coated samples, the coating layers have a petal-shaped structure and are composed of leaf-like particles, whilst the coating layer of the AEScoated sample is relatively dense due to the smaller size of the petal-shaped structure.
- (3) The measurements of electrochemical data and hydrogen evolution demonstrate that the corrosion resistance of the AES-coated sample is better than that of the AEO-coated sample.
- (4) For the AES-coated and AEO-coated samples, the film layers have better corrosion protectability on the substrate when immersed for less than 6 h. When the soaking time increases, the corrosion protectability of the two types of coating layers will be gradually degraded.

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