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Fabrication and characterization of Mg-M layered double hydroxide films on anodized magnesium alloy AZ31

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ABSTRACT

Highly oriented Mg-M layered double hydroxide (LDH) films were firstly fabricated by a facile in-situ growth method on anodized magnesium alloy AZ31. It is proved to be an effective method to seal the porous anodic oxide film. M presents metal cations, such as Al^{3+}, Cr^{3+} and Fe^{3+}. The characteristic structure, morphology and composition of the LDH films were investigated via field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), fourier transform infrared spectrometer (FT-IR) and energy dispersive spectrometer (EDS) respectively. Besides, the corrosion resistance of the LDH films on magnesium alloy was investigated by using potentiodynamic polarization and electrochemical impedance spectroscopy. The result demonstrates that anodic oxide film can be sealed by the formation of LDHs with nano-container structures. The corrosion resistance of anodized magnesium alloy is remarkably improved by Mg-M LDHs, especially by Mg-Al LDHs. Finally, the protection mechanism of Mg-M LDHs was proposed.

1. Introduction

The poor corrosion resistance of the magnesium alloy limits the viability of the increasing magnesium widespread application [1,3–7]. Whereas, magnesium alloys are of particular demand for the automobile, transport applications [4], mobile phones, aerospace and biomedicine [2,3] because of their low density, adequate mechanical properties [8–17]. At present, the main effective approach of enhancing the corrosion resistance of magnesium alloys is the surface treatment technology, among which the anodic oxidation is widely used [11,12], because of mature and facile process relatively. Nevertheless, on account of loose and porous structures of anodic films [18], the magnesium alloy substrate cannot be protected effectively once the film has contact with corrosion solutions. However, commercial application of Mg anodization to improve the corrosion resistance is still not well documented [19]. Thus, it is extremely urgent to find an effective sealing method of the anodic oxide film [20].

Layered double hydroxides (LDHs) is considered to be an active corrosion system. LDHs is a promising class of typical two-dimensional laminar nanomaterial [1,21], the general formula of which is $[M^{2+}_{1-x}M^{3+}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where the cations M^{2+} and M^{3+} occupy the octahedral holes in a brucite-like layer, and the metal anion A^{n-} is located in the hydrated interlayer galleries [22]. Such inorganic nano-container is widely used in the study of corrosion protection due to the advantage of small size, high loadings and easy modification. Moreover, the distinct characteristic of ion-exchange, that is, releasing the interlayer anion and adsorb Cl^- at the same time when it comes to corrosive ions perceived in the environment. Consequently, the LDHs film growing on the anodized magnesium surface cannot only enhance the thickness of the protective film but also seal the porous anodic oxide layer effectively. Therefore, such structure possesses a synergistic effect to improve the corrosion resistance of the Mg alloy.

Up to now, a two-step method is widely used, firstly, the LDH power precursor is synthesized by the co-precipitation method and then the film is obtained using a certain process. In recent studies, Zeng [23] adopted such method to prepare Zn-Al LDHs film on the surface of AZ31 by controlling the pH and temperature of the reaction solution, and demonstrated that the resulting film had the excellent adhesion with the magnesium substrate. In

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addition, the similar method was employed in manufacturing Zn-Al LDH film on the AZ91 substrate [24]. As a result, the magnesium alloy was endowed with a better corrosion resistance according to the electrochemical test. However, it cannot be ignored that the co-precipitation method is rather cumbersome as well as uncontrollable. The in-situ growth LDH film can be obtained easily, and only one kind of metallic ion is needed. So it proves significant potential.

Besides, Fuente [25] synthesized the Al-Zn-vanadate hydrotalcite on aluminum alloys using the co-precipitation and air-spraying method. Chen et al. [26–28] developed a new two-step technique to fabricate Mg-Al LDH on magnesium alloy AZ31. A precursor film with network cracks is first formed in the pretreatment solution and then this film is transformed into Mg-Al LDH after the post treatment. Furthermore, they optimized the experimental conditions and studied the growth mechanism. Moreover, Li [29,30] adopted the in-situ growth method to prepare LDH film on the anodic alumina substrate. In his study, the anodic alumina substrate was sealed by boiling water before and after respectively, and then the Zn-Al LDH film added vanadate corrosion inhibitor ions was fabricated. It was concluded that the LDH film with the corrosion inhibitor enhanced the corrosion resistance of the aluminum alloy. Kuznetsov [31] also adopted this similar novel approach to fabricated Zn-Al LDH on anodized aluminum alloy successfully. The anodized aluminum alloy was sealed by the formation of LDHs. Conceptually, the sealing of anodic layer using in situ growth LDH looks promising to provide an enhanced combined passive/active corrosion protection. A LDH treatment may seal the pores in the anodized layer (barrier effect), imparting at the same time active corrosion protection via release of corrosion inhibitor when aggressive species reach the pores [31]. By that analogy, the magnesium alloy, having the similar property with the aluminum alloy, also can be treated by such method to enhance the corrosion resistance and expand the usable range. However, there are few publications reporting on the formation of LDHs on anodized magnesium alloys.

In this work, we developed a LDH-based sealing method for the anodized magnesium alloy AZ31. Three kinds of LDH films were fabricated directly using the magnesia of anodic films, and only one type of the M^{3+} cation(Al^{3+}, Cr^{3+} or Fe^{3+}) was added in the reaction solution. Such one-step in-situ method is quite simple as well as convenient, also the technology proves stable. Besides, the characteristic of structure, morphology and composition of the LDH layers were investigated via FE-SEM, XRD, FT-IR and EDS. Also potentiodynamic polarization and EIS were used to study the corrosion resistance of the LDH layers on magnesium alloys.

2. Experimental

2.1. Materials

The substrate material used in this study is AZ31 magnesium alloys (the nominal compositions in wt.%: Al 2.5–3.5, Zn 0.6–1.3, Mn 0.2–1, Ca 0.04, Si 0.1, Cu 0.05, and balanced Mg). Before the preparation of the LDH films, the samples were mechanically ground with SiC paper up to 2000 grit to ensure the same surface roughness, ultrasonically cleaned in ethyl alcohol, and then dried in cold air. After that above, the samples were anodized in an electrolyte containing 7.14 g/L NaOH and 4 g/L $NaAlO_2$ for 30 min with applied voltage of 20 V to form anodic films.

2.2. Synthesis of Mg-M LDH

The Mg-M LDH films were prepared by immersing the anodized samples in 0.05 M $M(NO_3)_3$ (M = Al, Cr and Fe) and 0.3 M NH_4NO_3 mixture solution with a pH value among the alkaline range by adding the diluted ammonia. And the synthesis was carried out at 125 °C for 12 h with the reaction solutions putting into the Teflon-lined autoclave. After that, the filmed samples were rinsed with deionized water, ultrasonically cleaned in ethyl alcohol and dried under ambient conditions.

2.3. Characterization

The surface microstructure, chemical composition as well as thickness of the films were observed via a field-emission scanning electronic microscope (FE-SEM, JSM-7800F, JEOL, Japan)equipped with an energy dispersive X-ray spectrometer (EDS). The accelerating voltage of SEM is 10 Kv. The whole samples used for the SEM observation were sputtered with platinum to guarantee excellent conductivity. In addition, crystallographic structures of the films were determined by an X-ray diffractometer(XRD, Rigaku D/Max 2500X, Rigaku, Japan) with a Cu target ($\lambda = 0.154$ nm). The accelerating voltage of 40Kv and the current of 150 mA, and the patterns gained at a glancing angle of 2°. Fourier transform infrared (FT-IR, iS5 FT-IR, Nicolet, American) spectra were obtained in the range of 4000–400 cm^{-1}.

Moreover, the corrosion resistance was investigated in 3.5 wt.% NaCl solution by potentiodynamic polarization curves and electrochemical impedance spectra (CIMPS-2 Zahner, Germany). A conventional three-electrode system was applied, and it is consisted of a saturated calomel reference electrode (SCE), a platinum foil as counter electrode and the samples as working electrode with tested area of 1 cm^2. Meanwhile, the samples ought to be immerged in the solution for 20 min before the electrochemical tests. And the amplitude of the sinusoidal perturbation was 5 mV(vs.E_{ocp}), the polarization curves were recorded with a sweep rate of 2 mV/s. EIS measurements were acquired at the frequency range of 100 KHz to 10 mHz. Besides, three parallel samples were tested at any rate for each kind of condition to ensure the repeatability of results.

Gravimetric measurements were performed by immersing in 3.5 wt.% NaCl solution at room temperature, and the size of the samples were 2 cm × 2 cm. Prior to the immersion tests, specimens were measured and weighed. After soaking in the solution for 336 h, the samples were extracted, rinsed with ethyl alcohol, dried in the air, and then weighed again in order to calculate the mass loss per unit surface area.

3. Results and discussion

3.1. Characterization of Mg-M LDH films

Fig. 1 shows scanning electron microscope (SEM) images at lower and higher magnifications of the LDH film, where M presents the metal cations of Fe^{3+}, $Cr^{3+}$and Al^{3+}, from which the blade-like surface can be seen obviously [32,33], and it proves the result of the combination between metal hydroxide and the inner ions. At the same time, the SEM images indicate that the types of metal cations have greatly influence on the morphology of the samples. Mg-Al LDH "blade" is flat relatively, while Mg-Fe LDH and Mg-Cr LDH are rather close to curly petals. Besides, the Mg-Cr LDH nanosheet is small, which shows that the crystallinity of Mg-Al LDH is higher than that of Mg-Cr LDH. Furthermore, compared with the images at lower and higher magnification, the porous structures of anodic oxide films were sealed effectively by the formation of LDH layer as shown in Fig. 1. And the energy dispersive spectrometer (EDS) results shown in Fig. 2 demonstrate that the metal cations Fe^{3+}, $Cr^{3+}$and Al^{3+} take part in the formation of the film indeed. Also, Fig. 3 shows the cross-sectional view of the films, and the thickness of the anodic oxide film is almost 14 μm. After the growth

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