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Magnesium hydroxide/magnesium phosphate compounds composite coating for corrosion protection of magnesium alloy by a combination process of chemical conversion and steam curing

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ABSTRACT

Anticorrosive composite films composed of amorphous or crystalline magnesium phosphate compounds and crystalline magnesium hydroxide were successfully prepared on magnesium alloy by a combination process of chemical conversion and steam-curing for the first time. The films had film thicknesses of ca. 30 μm and were composed of outer and inner layers. The corrosion resistances of the films coated magnesium alloy were investigated by electrochemical and gravimetric measurements. The films showed a much higher corrosive resistance than the uncoated one in corrosion tests.

1. Introduction

Magnesium and its alloys have excellent physical and mechanical properties such as low density, good electromagnetic shielding, and high strength/weight ratio [1,2]. They are, thus, expected to be applied to aerospace, automobile, railway industries. Their poor corrosion resistance, however, hinders their use on a larger scale. Therefore, various surface treatments such as physical vapor depositions, anodic oxidations, and chemical conversions [3–12] have been developed to improve corrosion resistance. Among these, the chemical conversion is a simple and low cost process for magnesium alloys [13–15]. Thus, various chemical conversions have been used as surface treatments of magnesium alloys. Among various chemical conversions, chromate systems show excellent corrosion-inhibition property [16]. However, the chromate treatment is being eliminated due to its high toxicity and carcinogenicity [17]. Phosphate chemical conversion is a promising coating method for corrosion protection films of magnesium alloys [18–20], because metal phosphates are insolubility in water and have high temperature resistance and chemical stability [21]. In addition, they do not include ecologically harmful element at all. However, the corrosion resistance is much lower than that of chromate system film. To improve the corrosion resistance of the phosphate chemical conversions, it is necessary to advance the existing phosphate chemical conversion methods.

In this paper, we report preparation of an anticorrosive composite film composed of magnesium hydroxide/magnesium phosphate compounds on AZ31 magnesium alloy by a combination process of chemical conversion and steam-curing for the first time. In addition, the corrosion resistance of the composite film coated AZ31 was also investigated in 5 wt.% NaCl solution by electrochemical measurements and immersion test.

2. Experimental procedures

2.1. Film preparation

Magnesium alloy AZ31 (composition: 2.98% Al, 0.88% Zn, 0.38% Mn, 0.0135% Si, 0.001% Cu, 0.002% Ni, 0.0027% Fe, and the rest is Mg) with a size of 10 × 10 × 1.5, or 20 × 20 × 1.5 mm was used as the substrate. The substrates were ultrasonically cleaned in absolute ethanol for 10 min. The cleaned AZ31 was immersed for 3 min in an aqueous solution containing 5 wt.% or 20 wt.% $(NH_4)_2HPO_4$ to form a precursor of the anticorrosive composite film. The solution pH was measured to be c.a. 8. The temperature of the solution was kept at 323 K during the immersion. After the immersion, the AZ31 was extracted from the solution and dried with inert Ar gas. As next

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step, the steam curing of the sample was performed using a vertical type autoclave made of stainless steel with a volume of 19 L. 3 L of distilled water was introduced into the bottom of the autoclave to produce steam. The chemically treated AZ31 was set at substrate stage in the autoclave. The autoclave was heated to a temperature of 423 K and then held at this temperature for 3 h. The steam pressure was kept at ca. 0.9 MPa. The autoclave was then cooled naturally to room temperature. Hereafter, we referred the samples obtained from the aqueous solution containing 5 wt.% or 20 wt.% $(NH_4)_2HPO_4$ for 3 min at 323 K, followed by steam curing for 3 h at 423 K to sample 5 or sample 20, respectively.

2.2. Film characterizations

The surface morphologies of anticorrosive composite films were observed with a FE-SEM (Hitachi High-Technologies Corp., S-4300) at 10 to15 keV. The surface roughness of the samples was estimated using profilometer (Mitutoyo Corp., SURFTEST SJ-500). The microstructure, high resolution TEM (HRTEM) and electron diffraction were observed by TEM using JEOL (JEM-2010) at 200 kV. The composition of the samples was quantitatively determined using energy dispersive X-ray analysis (TEM–EDAX). The crystal structure of the samples was examined by XRD (Rigaku, RINT2200V) within the range of 9° and 90° at an incident angle of 3° and scanning rate of $2\theta = 4°$ (min^{-1}).

2.3. Corrosion tests

All electrochemical measurements were performed in a 5.0 wt.% NaCl aqueous solution at room temperature using a computer-controlled potentiostat (Princeton Applied Research, VersaSTAT^3). Potentiodynamic polarization curves were measured at a scanning rate of 0.5 mV/s from −400 to +800 mV with respect to the OCP after the immersing the film coated AZ31 into the NaCl solution for 30 min. The composite film coated on the AZ31 magnesium alloy and a platinum plate were employed as the working and counter electrodes, respectively. A saturated calomel electrode (SCE) was used as a reference. Immersion test was also used to evaluate the corrosion resistance of the coated samples. The samples for corrosion test were prepared using adhesive tape with a square-shaped window of 1 cm^2. The sample surface was exposed to the electrolyte through the window. They were immersed into the 5.0 wt.% NaCl solution at 308 K. Mass loss was measured using the film coated AZ31 before and after immersion in 5.0 wt.% NaCl aqueous solution at 308 K as a function of immersion time.

3. Results and discussions

3.1. Crystal structures and surface observation of the films

Fig. 1(a) shows XRD patterns of (i) the untreated AZ31, (ii) sample 5, and (iii) sample 20. The sample 5 had seven peaks. The seven peaks at around $2\theta = 18$, 33, 38, 51, 58, 62, and 72° were assigned to the 001, 100, 101, 102, 110, 111, and 201 diffraction peaks of brucite type $Mg(OH)_2$. The sample 20 had many peaks related to the brucite type $Mg(OH)_2$ and $NH_4Mg(PO_4)$ H_2O. In addition to these peaks, some peaks at around $2\theta = 23$, 31, and, 33 were assigned to the 120, 122, and, 033 diffraction peaks of $Mg_2PO_4OH \cdot 3H_2O$ (JCPDS No. 45-1380), indicating that the film was composed of crystalline $NH_4MgPO_4 \cdot H_2O$, $Mg_2PO_4OH \cdot 3H_2O$ and $Mg(OH)_2$. The precursors of these hydrated compounds were considered to be formed during the chemical conversion process using phosphate solution at high concentration because no peak originating from phosphate compounds can be detected in the XRD pattern for the sample 5. Fig. 1(b) and (c) shows FE-SEM images of the samples 5 and 20, respectively. The surface of the sample 5 was relatively smooth and had some minute pores. On the other hand, rough and large particles were found on the surface of the sample 20. The surface roughnesses of the samples 5 and 20 were 0.39 and 4.60 μm, respectively. The differences in the surface morphologies could be related to the precursors formed during chemical immersion treatments. Each inset in Fig. 1(b) and (c) revealed that the film thicknesses of the samples 5 and 20 were estimated to be ca. 29 and 31 μm, respectively.

Fig. 2 shows elemental mapping results of the cross-sectional images of the samples 5 and 20, respectively. For both samples, the elemental phosphorous was concentrated at outer layer, whereas the elemental magnesium and oxygen were presented at the whole of the films. Both films were found to be compact and continuous and composed of at least two layers. The outer layers include magnesium, oxygen, and phosphorous, and the inner layers were comprised of magnesium and oxygen. As shown in Fig. 1(a), no peak originating from phosphate compounds can be observed on the XRD pattern for the sample 5. Thus, amorphous phosphate compounds and crystalline $Mg(OH)_2$ were mainly formed as composite film in the film. On the other hand, the sample 20 was composed of crystalline

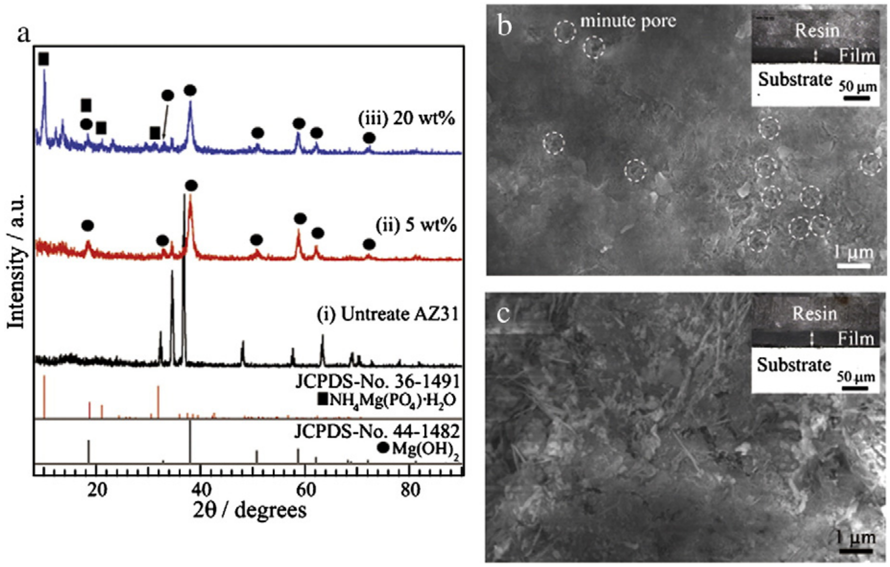

Fig. 1. (a) XRD patterns of (i) bare AZ31, (ii) sample 5, and (iii) sample 20. (b) FE-SEM image of the samples 5. The inset shows the cross-sectional optical microscopic image of the sample 5. (c) FE-SEM image of the sample 20. The inset shows the cross-sectional optical microscopic image of the sample 20. White dotted lines show minute pores.