



Influence of alloying elements and microstructure on the formation of hydrotalcite film on Mg alloys



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ABSTRACT

The influence of alloying elements and microstructure of Mg substrates on the formation of hydrotalcite film has been investigated. It is found that the two-step process is also available for the pure Mg and other alloys after modification. A small amount of Zn does not impact the composition of the hydrotalcite film much; whereas the highly active rare earth (RE) affects the constituents of the precursor film as well as the final film on WE54 alloy significantly. The microstructure impacts the initial nucleation and the film morphology depending on the size and chemical activity of the intermetallic particles.

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1. Introduction

Hydrotalcite (HT) film prepared by in situ growth technique has been shown to be a promising alternative for corrosion prevention of Mg alloys [1–6]. Lin et al. have developed the HT film on the Al-rich Mg alloy of AZ91 [1–3]. In our previous work, the HT film has also been in situ grown on the low Al content alloy of AZ31 [4–6]. This conversion film is environmentally friendly and low cost, which can protect Mg alloys for a relatively longer time. However, other kinds of Mg alloys (e.g., Mg–Zn and Mg–RE (rare earth) alloys) also need protection significantly [7–10]. If HT film can be synthesized on different alloy systems, it would be critical for the industrialization applications of the present technology to Mg alloys.

It is well known that the formation of conversion film is an electrochemical process. The film formation kinetics is strongly dependent on the microstructure and constituent of the substrates. The intermetallics (IMCs) in the substrate can act as local anodes or cathodes affecting nucleation, growth and ultimate properties of the conversion films. Many works have been carried out to clarify the role of microstructure in the deposition of chromate conversion coating (CCC) on aluminum alloys [11–14]. Campestrini et al. [11] concluded that all kinds of IMCs acted as preferential nucleation sites. Alternatively, Brown and Kobayashi [12] found that the CCC film started to form as discrete nodules on the Al₆(Cu, Fe, Mn) IMCs

of AA2024 alloy, however halos of film material was first formed on the matrix surrounding the Al₂CuMg IMCs. On the other hand, McGovern et al. [13] found that the CCC formation was suppressed on Al₂CuMg and “depressed” Al₂₀Cu₂FeMn IMCs after long time treatment. Other authors have also reported the limited growth of the CCC at the top of IMCs owing to the absorption of cyanide, which could lead to passivation of the Cu-rich surfaces [11,14].

Generally, Mg alloys are composed of more than two phases, which shows non-homogeneous chemical activity [15]. Recently, there are some definitive works that focused on the formation mechanism of conversion films on Mg alloys, which has already been discussed profoundly [16–19]. It was concluded that the phase structure of Mg alloys has direct impact on the shape of the phosphate precipitation in the initial deposition process. Cui et al. [16] found that the phytic acid coating on β phase (Mg₁₇Al₁₂) (rich in aluminum element) of AZ91D was thinner and more compact than that on α phase (rich in magnesium element). In contrast, Zhou et al. [17] confirmed that the flower-like phosphate particles were preferentially deposited on the β phase and the ball-like phosphate particles were deposited on α phase of AZ91D alloy. Song et al. [18] reported that the calcium phosphate particles were firstly deposited on the electrochemically inhomogeneous β phases of Mg–8.8Li alloy. Furthermore, experiments from Song et al. confirmed the evidence that conversion film technologies for conventional Mg alloys (e.g., Mg–Al, Mg–Zn and Mg–Mn) were not available for Mg–8.8Li alloy. Zeng et al. [19] pointed out that the microstructure (grain size, second phases) and chemical compositions (Al, Mn and Zn) of the AM alloy substrates have a critical

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effect on the formation and corrosion resistance of Zn–Ca–P coatings. Thus, such review assertively confirms the significant influence that alloying elements have on the deposition process of conversion films.

However, compared to these conclusions, further reviewing surfaced anomalies on the results reported on similar phenomenon by different authors. This apparent contradiction may be related either to the differences in the film formation conditions (immersion time, composition, temperature, pH value of the treatment bath, etc.), or to the electrochemical heterogeneity of the alloys caused by the IMCs and alloying elements. However, no apparent reports concerning the roles played by the alloying elements and microstructure of different Mg substrates in the deposition of HT film were found. The aim of the present work is to investigate and clarify whether the novel experimental procedure introduced in this article is applicable and suitable for other Mg alloys (Al-free). Additionally stress is given to identify the distinguishing effect of alloying elements and microstructure features on the nucleation, growth and final properties of HT conversion film on Mg substrates.

2. Experimental

2.1. Fabrication of the HT film

The materials used in this study were extruded AZ31 alloy, as-cast pure Mg and Al-free Mg alloys (extruded Mg2Zn and as-cast WE54). The reasons for the choice of these Mg and its alloys are as follows: (1) there are no alloying elements in pure Mg as it only exist in single α phase. Hence it can be used for comparing both roles of alloying elements and microstructure features in the film formation with other Mg alloys. (2) Mg2Zn is an Al-free alloy possessing a very fine second phase, with a small amount of other alloying elements [20]. This can be used to clarify whether the novel process introduced is suitable for the Al-free Mg alloys. In addition, it can also be used for comparison with WE54 alloy which has relatively more alloying elements and larger-scale second phases. The chemical composition of Mg and its alloys is listed in Table 1. The samples were ground to 2000 grit SiC paper, ultrasonically cleaned in ethyl alcohol, and then dried in the cold air. The films were prepared by a two-step method. The samples were first treated by the first step (Step 1) to obtain the precursor films, and then consequently treated by the second step (Step 2) to obtain the final HT films. The details of different treatments are listed in Table 2.

Table 1
Chemical composition of Mg and its alloys (wt.%).

Alloys	Al	Zn	Mn	Gd	Y	Nd	Si	Ca	Cu	Zr	Mg
AZ31	8.93	0.47	0.22				0.03		0.002		Bal.
Pure Mg		0.05	0.018						0.013		Bal.
Mg2Zn		1.96					0.007	0.004			Bal.
WE54				2.13	5.02	1.92				0.45	Bal.

Table 2
Technological parameters for different treatments.

Step	Films	Solution	Treatment time/temperature
Step 1	Precursor film 1	Carbonic acid solution at pH 8	30 min/60 °C
	Precursor film 2	Carbonic acid solution at pH 8.5	50 min/60 °C
Step 1 + Step 2	Final film 1	Carbonic acid solution at pH 8 (Step 1) + carbonic acid solution at pH 8 adjusted to pH 10.5 by NaOH (Step 2)	30 min/60 °C + 1.5 h/80 °C
	Final film 2	Carbonic acid solution at pH 8.5 (Step 1) + carbonic acid solution at pH 8.5 adjusted to pH 11.5 by NaOH (Step 2)	50 min/60 °C + 1.5 h/80 °C

Pre step

Before going to Step 1, carbonic acid solution with pH value of approximately 4.0 was prepared by bubbling CO₂ gas through 200 ml of distilled water at room temperature (20 ± 2 °C) for 10 min. After dissolving pure Al plate in 0.5 M Na₂CO₃ solution, the resultant Al solution was then added drop wise to carbonic acid solution to obtain two base solutions with pH value 8 and 8.5 respectively.

Step 1. Mg substrates were dipped in the base solutions of pH 8 and 8.5 for 30 and 50 min at 60 °C to obtain precursor film 1 and precursor film 2, respectively. For investigating the growth process of precursor films, the samples were dipped in the base solutions for 5 and 30 s respectively to obtain the initial precursor films. Continuous bubbling of CO₂ gas was carried out during the preparation of precursor films.

Step 2. In Step 2, the solutions were prepared by dropwise addition of 2 M NaOH solution to the Step 1 solution (pH of 8 and 8.5 initially) until the pH rises to 10.5 and 11.5 respectively. This was followed by the immersion of precursor film 1 and precursor film 2 (obtained by Step 1) in the solutions with pH of 10.5 and 11.5 respectively for 1.5 h at 80 °C to obtain the final film 1 and final film 2.

2.2. Characterization

Electrochemical test was carried out using a ParStat 4000 potentiostat. A classical three-electrode system was applied. The samples, a saturated calomel electrode (SCE) and a platinum plate were used as working electrode, reference electrode and auxiliary electrode respectively. The polarization curves were obtained on exposed area of 1 cm² at a constant voltage scan rate of 0.5 mV s^{−1} after an initial delay of 300 s. The curves were fitted using the Corr-View software in the mode of Tafel (traditional) by intersecting the cathodic Tafel line and the level line at corrosion potential (E_{corr}).

The morphologies of the films were observed using a Philips XL30 environmental scanning electronic microscope (ESEM) equipped with an energy dispersive X-ray spectroscopy (EDS). The chemical compositions of the film formed on different substrates were analyzed by EDS, X-ray photoelectron spectroscopy (XPS) and X-ray diffractometry (XRD). The XPS analysis was probed using an ESCALAB 250 X-ray photoelectron spectroscopy with Al K α radiation (1486.6 eV). The power was 150 W, with pass energy of 50.0 eV and a step size of 0.1 eV. All energy values were cor-

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