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Corrosion resistance of calcium-modified zinc phosphate conversion coatings on magnesium–aluminium alloys

Rong-Chang Zeng [a],*, Fen Zhang [a], Zi-Dong Lan [c], Hong-Zhi Cui [a],*, En-Hou Han [b]

[a] *School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266510, China*
[b] *Environmental Corrosion Center, Institute of Metals Research, Chinese Academy of Sciences, Shenyang 110016, China*
[c] *School of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400050, China*

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ABSTRACT

The influence of the microstructure of the calcium-modified zinc phosphate (Zn–Ca–P) conversion coatings of Mg–Al alloys on corrosion resistance was investigated using OM and SEM and hydrogen evolution tests. The results demonstrated that the Zn–Ca–P coatings markedly enhanced the corrosion resistance of the alloys. The microstructure and chemical compositions of the alloys exerted a significant influence on the corrosion resistance of their coatings. A model was proposed to elucidate the formation mechanism of the porous Zn–Ca–P coating on the AM30 alloy.

1. Introduction

Magnesium alloys are prime candidates for applications in the automotive, electronics and biomedical fields [1–3]. Magnesium alloys are usually divided into two types: cast and the wrought. The latter attracts much more attention due to its superior mechanical properties and corrosion resistance. Deformation processes can fabricate a variety of magnesium alloy extrusions, such as plates and pipes.

Unfortunately, magnesium alloys possess lower corrosion resistance, especially in chloride-containing environments, which restricts their use on a larger scale. Therefore, it is critical to enhance the corrosion performance of magnesium alloys. Chemical conversion [4–7], polymer [8,9], metal [10,11], sol–gel [12,13] and plasma electrolyte oxidation (PEO) or microarc oxidation (MAO) [14–17] coatings on magnesium alloys have been investigated to this end.

Among these surface treatments, chemical conversion coatings have such advantages as lower cost and simplicity in operation. Many chemical conversion coatings have been applied to magnesium alloys, including chromate [18], phytic acid [19,20], phosphate–permanganate [21–23], phosphate–calcium [24], stannate [25–27], vanadium [28], stearic acid [29], dawsonite [6], rare earth [30–33], fluoride [34] and silane [10,11] as well as hydrotalcite [35–38] coatings. Nevertheless, some of these conversion coatings, e.g., chromate, vanadate and fluoride-based coatings, present an environmental hazard. For example, stannate, silane and hydrotalcite are not applicable for practical use on a large scale at this stage.

Conversely, phosphate conversion coatings are more environmentally friendly and have been successfully exploited to protect magnesium alloys against corrosion. At present, phosphate conversion coatings for magnesium alloys can be classified into four categories: (1) manganese-phosphate conversion coatings [39], (2) zinc phosphate conversion coatings [5,40,41], (3) barium phosphate [42] and molybdate phosphate fluorinate (Mo-P-F) [43] and (4) Zn–Ca phosphate conversion coatings (Zn–Ca–P coating) [44–46], the latter of which was invented by our group. Our previous studies have revealed that the addition of Ca^{2+} ions in the phosphating baths results in fine-grained Zn–Ca–P coatings on AZ31 alloys, significantly improving the corrosion resistance [44,46].

The influence of the surface finish of the substrates on coating quality is a major concern during practical applications. Indeed, the surface roughness of a magnesium alloy workpiece has a critical influence on its corrosion behaviour [47]. It has been found that an increase in surface roughness degrades the corrosion resistance of magnesium alloys [48–50]. Moreover, it is found that increasing surface roughness of AZ91 magnesium alloy gives rise to the pitting tendency of the alloy [51].

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* Corresponding authors. Tel.: +86 532 80681226; fax: +86 532 86057920.
E-mail addresses: rczeng@foxmail.com (R.-C. Zeng), cuihongzhi1965@163.com (H.-Z. Cui).

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Furthermore, it is demonstrated that the corrosion resistance of magnesium alloys is influenced by their microstructural and metallurgical properties and chemical compositions [47,52–56]. Samaniego et al. [47] reported that the corrosion of the polished surface and AZ61 surfaces is slower than that of the respective as-received and AZ31 surfaces. In addition, these tendencies vary with the exposure time. Thus, the microstructural characteristics and chemical compositions of the substrates may have an important influence on the surface roughness of the coatings and thereby their corrosion resistance. Yoo et al. [57] found that the corrosion resistance of the PEO-coated AZ91 alloy decreases as the surface roughness of the PEO coating increases due to the increase in the area exposed to the medium. However, the number of corrosion pits is not affected by the surface roughness.

Nevertheless, to the best of the authors' knowledge, the influence of the microstructure (e.g., grain size) and chemical composition of the magnesium alloy extrusions on the surface roughness and corrosion behaviour of the phosphate conversion coatings has not yet been reported [55].

This paper aims to deposit a novel Zn–Ca–P coating on a variety of magnesium aluminium alloy substrates, determine the relationship between the surface roughness and corrosion resistance of the substrates and their respective coatings and clarify the effect of the microstructure on the corrosion of the Zn–Ca–P coatings on magnesium alloys.

2. Experimental

2.1. Materials

All chemicals were reagent grade and were used without pretreatment. Three magnesium alloys were used as the substrates for the coatings: as-extruded AZ31 plate (2 mm thick), AZ31 pipe (Φ35 mm × 1.2 mm) and AM30 pipe (Φ70 mm × 4.5 mm). Their chemical compositions are shown in Table 1.

For the metallographic observation, the samples were mechanically ground to 1200 grit SiC paper and then polished. The AZ31 alloy samples were etched in 5% nitric acid alcohol solution, and the AM30 alloys were etched in a solution containing 10 ml of acetic acid, 4.2 g of picric acid, 70 ml of ethanol and 10 ml of distilled water. The grain size was measured by scanning electron microscopy (SEM) using the linear intercept method based on the standard ASTM E122-88 [58].

2.2. Coating preparation

The substrates were mechanically ground to 1500-grit SiC paper and then sequentially subjected to alkaline degreasing, acid activation and surface activation. The conversion processing was in pH 2.5 phosphate solution, including 70.0 mmol/L Na_2HPO_4, 31.7 mmol/L $Zn(NO_3)_2$, 12.2 mmol/L $Ca(NO_3)_2$ and 58.0 mmol/L $NaNO_2$ as well as 47.6 mmol/L NaF.

2.3. Corrosion characterization

Electrochemical measurements could not be used in this study due to the shape and dimensions of the samples. Therefore, the hydrogen evolution was used to evaluate the corrosion rate, according to the following chemical reaction:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \uparrow \tag{1}$$

All of the hydrogen evolution tests were conducted in 3.5 wt% NaCl solution at ambient temperature. The setup for the collection of hydrogen gas is the same as that in the literature [2]. The tests were performed in triplicate in 3.5 wt% NaCl solution with a volume of 500 ml; the data were recorded once per hour. The hydrogen evolution rate (HER), v_H, is defined as [54]

$$v_H = \frac{V}{st} \tag{2}$$

where V is the volume of hydrogen gas, ml; s is the sample area exposed to the solution, cm^2; and t is the immersion time, h.

Table 1
Chemical compositions of the magnesium alloy extrusions (wt%).

Mg alloys	Al	Mn	Zn	Mg	Al/Mn ratio
AZ31 pipe	3.06	0.47	1.18	Bal	6.51
AZ31 plate	3.13	0.25	0.87	Bal	12.53
AM30 pipe	2.90	0.40	0.18	Bal	7.25

2.4. Surface roughness measurement

The surface profile was measured after tracing the actual surface profile using a probe. In addition, the measured values were filtered through the effect of the stylus tip radius. The surface roughness was measured by a roughness tester (TR-200) with a range of −80 μm to 80 μm and a sliding distance of 0.8 mm. The arithmetic mean surface roughness (Ra) was calculated after three repeated measurements.

2.5. Surface analysis

The microstructure of the magnesium alloys was observed using an optical microscope (OM). In addition, SEM (JSM-6460LV) was utilized to discern the surface morphologies of the coatings. The phases and composition of the coatings were examined via X-ray diffraction (XRD, Riguta D/max-RC) and energy dispersive spectroscopy (EDS, Oxford 742), respectively.

3. Results

3.1. Microstructure of the alloys

The microstructures of the AZ31 alloy and the AM30 alloy are characterised by α-Mg and the dispersed AlMnSi or AlMn particles, as shown in Fig. 1. The intermetallic compounds AlMnSi in AZ31 alloy have been identified in our previous literature [34]. Compared to the AZ31 plate, the AZ31 pipe has a relatively smaller grained and more homogeneous microstructure (Fig. 1b). However, the microstructure of the AM30 pipe is characterized by coarse and elongated grains along the extrusion orientation and fibrous texture (Fig. 1c). Additionally, the secondary phase AlMn particles are found in the microstructure of the extruded AM60 alloy [59].

3.2. Surface morphologies of the Zn–Ca coatings

Fig. 2 presents the SEM morphologies of the Zn–Ca–P coatings on the three extruded magnesium alloys after preparation via the same phosphating processes. It can be seen that the compactness of the coatings on the AZ31 plate (Fig. 2a) and the AZ31 pipe (Fig. 2b) is better than that of the AM30 pipe (Fig. 2c). The Zn–Ca–P coating prepared might not be optimal but was wholly deposited on the surface of the AM30 pipe under this processing condition, producing a relatively rough microstructure. The morphological features are related to the microstructural properties, such as the grain size, the distribution and size of the intermetallic compounds AlMnSi or AlMn and chemical factors, such as the content and species of chemical elements in the substrates. The details are elucidated in the subsequent discussion.