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Effect of microstructure on the zinc phosphate conversion coatings on magnesium alloy AZ91

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ABSTRACT

The effect of the microstructure, particularly of β-$Mg_{17}Al_{12}$ phase, on the formation and growth of zinc phosphate conversion coatings on magnesium alloy AZ91 (AZ91) was studied. The zinc phosphate coatings were formed on AZ91 with different microstructures produced by heat treatment. The effect of the microstructure on the zinc phosphate coatings were examined using optical microscope (OM), X-ray diffraction (XRD), coatings weight and etching weight balances, scanning electron microscopy (SEM) and salt immersion test. Results showed that as-cast AZ91 contained a high volume fraction of the β-$Mg_{17}Al_{12}$ phase and it was dissolved into α-Mg phase during heat treatment at 400 °C. The β-phase became center for hydrogen evolution during phosphating reaction (cathodic sites). The decreased volume fraction of the β-phase caused decreasing both coatings weight and etching weight of the phosphating process. However, it increased the crystal size of the coatings and improved corrosion resistance of AZ91 by immersing in 0.5 M NaCl solution. Results also showed that the structure of the zinc phosphate conversion on AZ91 consisted of two layers: an outer crystal $Zn_3(PO_4)_2{\cdot}4H_2O$ (hopeite) and an inner which was mainly composed of $MgZn_2(PO_4)_2$ and $Mg_3(PO_4)_2$. A mechanism for the formation of two layers of the coatings was also proposed in this study.

1. Introduction

In recent years magnesium and its alloys (Mg alloys) have been interested for many applications such as the automobile industry, computer parts, aerospace components, mobile phones, sporting goods, handheld tools and household equipment. Although magnesium alloys have many advantages such as low density, high strength/weight ratio, good machinability, high damping capacity, great castability and excellent recyclability, applications of Mg alloys are limited due to their poor corrosion resistance [1–4]. Surface treatments, such as chemical conversion coatings, anodizing, plating and metal coatings, are commonly applied to magnesium alloys in order to increase the corrosion resistance. Among them, chemical conversion coatings are regarded as one of the most effective and cheapest ways to prevent corrosion resistance. Chemical conversion coatings can protect a substrate by providing a barrier between the metal and its environment through the presence of corrosion inhibiting chemicals in them [2].

Zinc phosphate conversion coatings have been successfully used as a primer coating on steels and aluminum alloys in automotive industries for many years because they increase the corrosion resistance and also enhance good adhesion of the paint and substrates [5,6]. Zinc phosphate conversion coatings are one of the most promising methods for Mg alloys anticorrosion and pretreatment process before painting. It is being explored as an alternative to conventional chromate conversion coatings, and recently, it has been intensively studied [7–17].

At present, however, there is lack of understanding of the mechanism and also effects of base materials such as phases, structure on the zinc phosphate conversion coatings process. Hence, results have been reported inconsistent and it has been limited in expanding applied scales. For example, Kouisni et al. [10,11] found that the zinc phosphate coatings formed on Mg alloy AM60 are mainly consists of large hopeite crystals ($Zn_3(PO_4)_2{\cdot}4H_2O$). Zeng et al. [12] reported that the zinc phosphate coatings consists of very small hopeite particles and randomly distributed on a network film with micro-cracks, which is mainly composed of MgF_2. They explained that the formation of MgF_2 due to reaction of F^- ions with $Mg(OH)_2$ is formed by the reaction of Mg alloy with H_2O molecules in phosphating solution. By fitting electrochemical impedance spectroscopy (EIS) data with equivalent electrical circuits, Li et al. [16] suggested that the zinc phosphate coatings include two layers: inner flat amorphous layer and outer porous crystal layer. The outer

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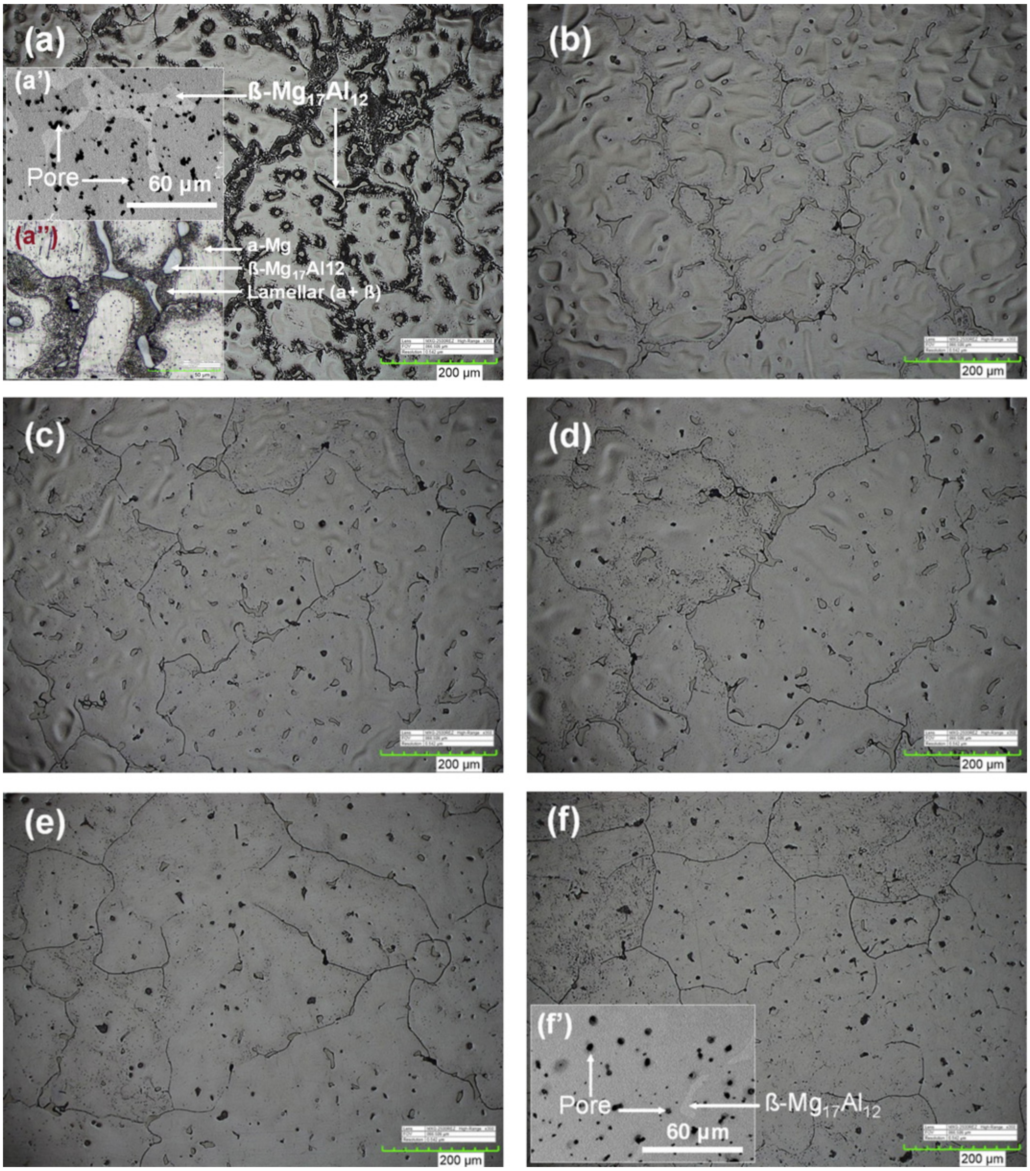

Fig. 1. Optical microstructures of AZ91 for various heat treatment times of 0 h (a, a''), 2 h (b), 4 h (c), 8 h (d), 12 h (e), 24 h (f) and inserted (a', f'): SEM backscattered electron of samples (a, f), respectively. Heat treatment temperature: 400 °C.

layer was composed of crystal clusters of hopeite ($Zn_3(PO_4)_2{\cdot}4H_2O$) but compositions of inner layer were not mentioned. In our experimental results, compositions and structures of Mg alloys played important roles in the formation and growth of phosphate coatings through zinc phosphating process. The differences of the coatings could be formed on AZ91 at the same phosphating solution, which depends on properties of samples.

In general, Mg–Al alloy has typically a primary α-Mg phase and β-$Mg_{17}Al_{12}$ phase [1–3,18]. During phosphating process, the α-Mg and the β-$Mg_{17}Al_{12}$ phases act as anodic and cathodic sites, respectively [10,19]. The presence of the β-phase can act as a galvanic cathode to accelerate phosphating reactions and also can act as a barrier to hinder phosphating reactions. During heat treatment, the β-phase can dissolve into the α-phase, so it can be changed properties of Mg alloy [20–22].

In this study, the zinc phosphate conversion coatings were studied on AZ91 with the different microstructures produced by heat treatment to elucidate the effect of microstructure, particularly of the β-$Mg_{17}Al_{12}$ phase, on the formation of the coatings. Various studies such as in situ micrographs of phosphating process, balances of coatings weight and etching weight, observed the formation and growth of the coatings, and corrosion test are used for investigation the effect of microstructure on the zinc phosphate conversion coatings.

2. Experimental

Magnesium alloy AZ91 with a nominal composition of 9 wt.% Al, 1 wt.% Zn and Mg balance was used in this study. The samples were cut from an as-cast ingot with a size of 35 mm × 45 mm × 2 mm. The samples were heat treated at 400 °C for 0 h, 2 h, 4 h, 8 h, 12 h and 24 h, followed by water quenching.

The microstructure was observed using an optical microscopy (OM) (Hirox, Japan) after metallographic preparation by mechanical grinding successively to 2000 grit abrasive paper, followed by finishing with 1 μm diamond paste, etched in a solution containing of 19 mL water, 60 mL ethylene glycol, 20 mL acetic acid and 1 mL nitric acid for 2 min. Phase structures of samples were analyzed by using the X-ray diffraction (XRD) (Rigaku, Japan) with a diffractometer operating at 40 kV, 30 mA, using Cu K_α target. The