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Corrosion protection of AZ31 magnesium alloy by a TiO_2 coating prepared by LPD method

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ABSTRACT

TiO_2 layer was prepared as a protective coating for AZ31 magnesium alloy by the liquid phase deposition (LPD) method followed by an annealing treatment. The structural evolution and crystallization of coating brought by annealing were investigated by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD), respectively. The corrosion protection performance was evaluated in a three-electrode electrochemical examination system. The anatase TiO_2 layer shows evident corrosion resistance. With the increase of the annealing temperature and prolongation of annealing time, the anticorrosion property was improved. The improvements of the anticorrosion properties were related with the structural evolution of the coating brought by the annealing treatment.

1. Introduction

In recent years, magnesium alloys have been widely applied in the fields of automotive, aerospace and electronic industry due to its low density, high specific strength, good thermal conductivity, excellent damping characteristics and well machinability [1]. Recently, magnesium alloy is also proposed as a promising biomaterial for the human body implant because of its close mechanical property and good compatibility with human bone [2,3]. However, magnesium and its alloys have high chemical activity and low electrode potential (−2.37 V, versus standard hydrogen electrode (SHE)) [4]. In addition, the oxide layer on the surface of magnesium alloys is too loose to protect the substrate from corrosion and oxidation effectively [5]. These disadvantages limit the expansion of application of magnesium alloys.

Although magnesium alloys are usually alloyed with aluminum, manganese and zinc to improve corrosion resistance, further surface treatment is also required to physically prevent contact with the environment. The coating technologies, including the electrochemical plating, conversion coatings, hydride coating, anodizing and thermal spray coatings, were used to achieve the corrosion resistance [6–8]. Recently, TiO_2 layers were used as protective layers on the substrate of 316 L stainless steel and other metals [9–11]. It should be pointed that it is not easy to grow TiO_2 layer on Mg alloy substrate because the corrosive and oxidizing growth atmosphere in some preparation method of TiO_2 always leads to poor adhesion and inhomogeneity of the layer. In our previous work [12], a modified liquid phase deposition (LPD) method was used to prepare the TiO_2 layer on AZ31 magnesium alloy substrate. Special emphases were put on the hydrolysis process and its influence on the weight loss rate in sodium chloride solution. In present paper, the structural evolution after annealing treatment is investigated. Further measurement of corrosion resistance is carried out by electrochemical method and an attempt is made to relate the anticorrosion property with the structural evolution and compare with our former results.

1.1. Experiments

In this method, TiO_2 layer was prepared by hydrolysis of ammonium hexafluorotitanate $[NH_4]_2TiF_6$. The chemically pure $[NH_4]_2TiF_6$ was dissolved in the deionized water with concentration of 0.2 mol/L as the mother solution. At the same time, boric acid, as F^-scavenger, was dissolved in the solution with concentration of 0.075 mol/L and anatase TiO_2 powder with the size of a few tens of nanometers were added into the mother solution (2 g/l) and the mixture was ultrasonically mixed for 30 min. The reaction and hydrolysis process was described in detail in reference [12–14].

Wrought magnesium alloy AZ31 pieces (20×8×3 mm) were used as the substrates. The substrates were ground by emery paper with the No. from 100 to 1000 and polished by alumina powder of 0.05 μm size; after that the substrate was washed ultrasonically in the acetone (chemically pure) and ethanol (chemically pure) for 10 min, respectively, and finally flushed with distilled water.

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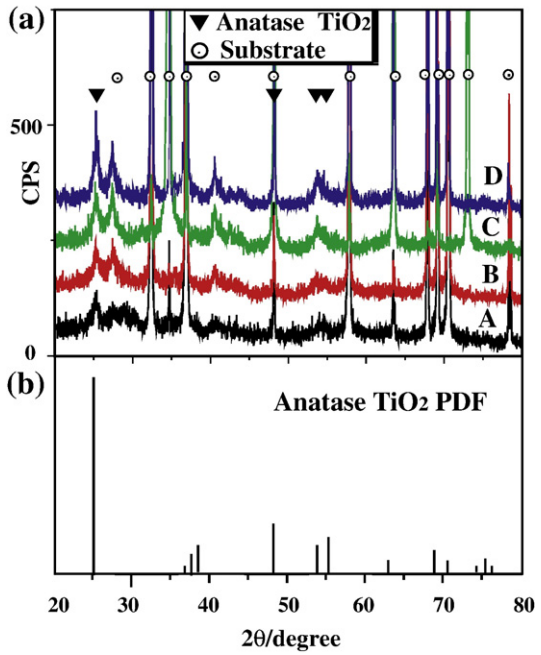

Fig. 1. (a) XRD patterns of TiO_2/AZ31 prepared at the annealing temperature of (A)250 °C, (B)300 °C, (C)350 °C and (D)380 °C. The diffraction peaks of anatase TiO_2 and AZ31 were shown by the mark of triangle and circle, respectively. (b) a standard powder diffraction profile (PDF) of anatase TiO_2 [15].

After pre-treatment, the substrates were immersed into the mother solution and suspended therein vertically for 20 h at the room temperature. Then, the substrates were withdrawn from the solution, sufficiently rinsed in the deionized water and dried at ambient temperature. After deposition, the annealing process was carried out in the vacuum furnace with the vacuum degree of 2×10^{-4} Pa. The annealing temperature was from 250 °C to 380 °C and the annealing time was 1.5 h. At the temperature of 250 °C, the annealing time were prolonged to 3 h.

The crystal structure of the resultant layer was investigated by X-ray diffraction (XRD) instrument (Philips, PW-1700X) with Cu Kα (λ=0.15406 nm) in the scanning angles from 20° to 80°. The surface and cross-section morphology were observed using field emission scanning microscopy (FE-SEM, JEOL-6700F). Energy dispersive spectroscopy (EDS) was employed to determine the elements composition of the layers. Electrochemical measurements were carried out in a three-electrode cell using a computer-controlled EG&G (M352) electrochemical corrosion system, employing a carbon auxiliary electrode and a saturated calomel reference electrode (SCE). The working electrode is testing materials and the testing solution is 3.5 wt.% NaCl solution at the temperature of 25±1 °C.

2. Result and discussion

Fig. 1(a) shows the XRD patterns of TiO_2/AZ31 prepared at different annealing temperatures for 1.5 h. As comparison, a standard powder diffraction profile (PDF) of anatase TiO_2 is shown in Fig. 1(b) [15]. In Fig. 1(a), diffraction peaks corresponding to anatase TiO_2 are observed, and the spectra agree with that of PDF file. It should be noted that one peak of the anatase, at position of 2θ=48.0°, is coincident with that of substrate. The peak intensity of anatase TiO_2 increases with the annealing temperature, which proves that crystallization of anatase can be improved by the increase of annealing temperature.

The influence of annealing temperature on the morphology of the TiO_2 layers is shown by some FE-SEM images in the Fig. 2. These layers were deposited for 20 h and annealed at different temperatures for 1.5 h in vacuum furnace. From Fig. 2(a), which shows the image of an as-deposited TiO_2 layer, the loosely deposited particles on the

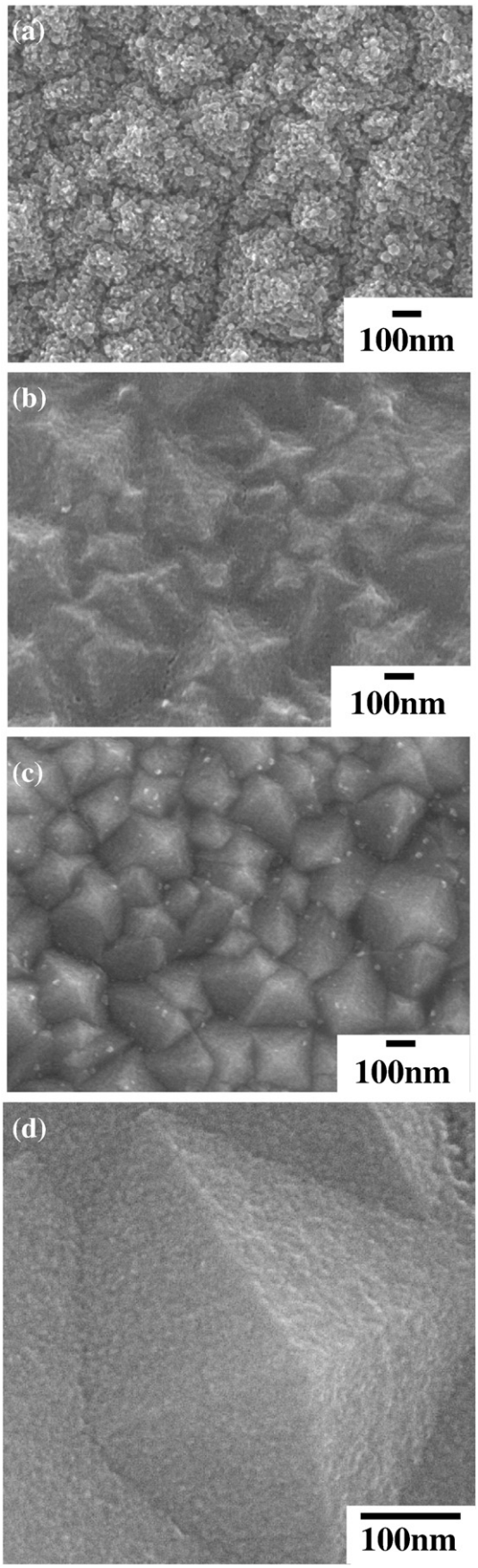

Fig. 2. FE-SEM images of surface morphology of TiO_2 layer. Here, the layers were deposited for 20 h and annealed at different temperatures for 1.5 h in vacuum furnace. (a) as-deposited TiO_2 layer; (b) annealed at 250 °C; (c) annealed at 350 °C; (d) enlarged image of the particles on the surface shown in Fig. 2 (c).