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Properties of Zr_2ON_2 film deposited on Mg-Gd-Zn alloy with Mg-Al hydrotalcite film by arc ion plating

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ABSTRACT

A Mg-Al hydrotalcite/Zr_2ON_2 composite film was deposited on Mg-Gd-Zn alloy by arc ion plating in order to improve the corrosion resistance and mechanical properties. The corrosion current density of the composite film sample immersed in a simulated body fluid is approximately 2.725×10^{-6} A cm^{-2}, which is approximately two orders of magnitude less than that of the substrate. During 120 h immersion tests, results have shown that samples coated with the composite film have low hydrogen evolution rate. Moreover, scratch tests and nano-indentation measurements show that the composite film samples have superior mechanical properties. Such results demonstrate that coating Mg-Al hydrotalcite/Zr_2ON_2 composite film on Mg-Gd-Zn alloy can provide not only good protection efficiency but also stable protection.

1. Introduction

Magnesium and its alloys are lightweight materials, attributed to their fascinating properties, such as low density, high strength-to-weight ratio, high thermal conductivity, and favorable electromagnetic shielding characteristics [1]. Rare-earth magnesium alloys [2] have been developed for the purpose of gaining additional advantages such as good mechanical properties and biocompatibility, which have attracted the attention of material science researchers. In recent years, there has been a growing interest in Mg-Gd-Zn(-Zr) alloy [3,4]. Zhang et al. [4] have reported that Mg-Gd-Zn-Zr alloy can be used as a promising biomaterial due to its mild cytotoxicity which has been proven by the methylthiazolyldiphenyl-tetrazolium bromide method. However, some key problems, such as large corrosion rate and localized corrosion mode, remain to be solved before Mg alloys turn into the new paradigm for biomaterials. The addition of Zr has also been reported for refining grains. Problem arises when the existence of a Zr-rich phase as the cathode aggravates the localized corrosion of the Mg alloy [5]. Although the Mg-Gd-Zn alloy has been prepared without the addition of Zr, large corrosion rate is still observed, and mechanical properties cannot meet the demands of clinical applications.

In an attempt to improve the corrosion resistance of Mg alloys, surface modification technologies have been developed, including electroless plating [6,7], electroplating [8], chemical conversion [9–12], anodic oxidation [13], and micro-arc oxidation [14]. Chemical conversion coatings [9–12], as protective films for Mg alloys, exhibit a number of outstanding features such as low cost and simple preparation; hence, they are worthy of promotion and development. Recently, Mg-Al hydrotalcite (HT) which is prepared using carbonated water [15–18], has become a chromate-free and environment-friendly film for improving the corrosion resistance of Mg alloys. As a typical anion-exchange material, Mg-Al HT has been used for the separation of corrosive anions (such as Cl^-) and water molecules from the Mg alloy matrix [18]. However, there are several problems in the current technology: (1) Mg-Al HT film has been mostly grown in situ on Al-containing AZ series Mg alloys [15–20], which results in mental numbness, hindering the applications of Mg-Al HT film in medical treatment. (2) Several micro-cracks [17,21] in the Mg-Al HT film limit the improvement of corrosion resistance as conductive pathways for corrosive electrolytes. Hence, the development of preparation technology of Mg-Al HT film on Mg alloys without Al and protection systems with sealing ability for Mg-Al HT film is a crucial and challenging issue.

Arc ion plating produces intense ionization by its arc, and these ions can gain sufficient energy by substrate bias, which contributes to the preparation of surface films [22]. Currently, arc ion plating technology has been developed owing to rapid deposition speed and good throwing power [23]. Because of the good throwing power, it is promising to seal the micro-cracks of Mg-Al HT film. Zirconium oxynitride (Zr_xON_y) [24] has been used as a film material, exhibiting good mechanical property, for meeting the demands of medical applications; it exhibits high

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corrosion resistance, cell adhesion and cell proliferation, as evaluated by corrosion test and biocompatibility response. However, cohesion strength between the film and substrate, as well as density of the film, is related to substrate materials, which decide film quality [25]. Hence, appropriate substrate materials have been widely investigated for improving film quality. A Mg-Al HT film with good adhesion strength may be a promising substrate material as a transition layer, the micro-cracks of which exhibit good effects on mechanical pinning for the purpose of improving film-substrate cohesion strength.

This study aims at the two-step preparation of a composite film (Mg-Al HT/Zr_xON_y) on Mg-Gd-Zn alloy for the further improvement in corrosion resistance and mechanical properties, which combines two surface modification technologies. First, the Mg-Gd-Zn alloy is immersed in treatment solutions to form the Mg-Al HT film, and then the HT film sample is treated by arc ion plating for preparing the Zr_xON_y film on the HT film surface.

2. Experimental

2.1. Sample preparation

Mg-6Gd-2Zn alloy materials with dimensions of Φ 14 mm × 4 mm were used. Sample surfaces were ground to 1500 grit SiC sandpaper and polished. Then, the samples were cleaned with anhydrous ethanol by ultrasonic for 10 min, washed with deionized water, and dried in cold air. Firstly, samples were immersed in a 0.01 mol/L $Al_2(SO_4)_3$ solution with the continuous bubbling of CO_2 gas at room temperature for 1 h; secondly, they were treated in a 0.5 mol/L Na_2CO_3 solution at 60 °C for 1 h to obtain the Mg-Al HT film. After immersion, the samples were cleaned with deionized water and dried in cold air. The Mg-Al HT film were prepared on the Mg alloys.

The Zr_xON_y film was deposited on the Mg-Al HT film using a TGP-800 multi-arc ion plating machine. Fig. 1 shows the schematic for the process of film deposition. Zr target (99.98%) was provided by Alluter Technology (Shenzhen) Co., Ltd.

The samples were fixed on a workbench in a vacuum chamber, and then the chamber was evacuated to a base pressure of approximately 5×10^{-3} Pa using a vacuum pump and then heated up to a desired temperature. The mixture gas (Ar, N_2, and O_2) was then introduced. The working pressure was 0.5 Pa. For obtaining uniform film, the samples were continuously rotated during deposition. Relevant parameters for the deposition process are shown in Table 1.

Table 1
Parameters for the deposition of Zr_xON_y film by arc ion plating.

Parameters	Value
Ar flux rate/(cm^3 min^{-1})	50
Electric current for deposition/A	80
Deposition temperature/°C	200
N_2 flux rate/(cm^3 min^{-1})	60
O_2 flux rate/(cm^3 min^{-1})	15
Treatment time/min	10

In this study, four specimens were prepared: Mg alloy substrate, Mg-Al HT-coated Mg alloy, Zr_xON_y-coated Mg alloy, and composite-film-coated Mg alloy (Mg-Al HT and Zr_xON_y).

2.2. Characterization

The phase composition of the specimens was determined by X-ray diffraction (XRD; Rigaku Ultima IV) using the CuKα_1 line at 1.5405 Å as the diffraction source. XRD patterns were analyzed by MDI Jade 6.0 software. Film morphologies were observed by scanning electron microscope (SEM; JSM-6360LV; JEOL Ltd.) equipped with energy dispersive X-ray spectroscopy (EDS).

Electrochemical tests were conducted using an Ametek Parstat 2273 potentiostat with PowerSuite software. A classical three-electrode system was applied, in which the samples, a saturated calomel electrode (SCE), and a platinum plate were used as the working electrode, reference electrode, and auxiliary electrode, respectively. The area of samples exposed to the solution was 1 cm^2. All tests were performed in a simulated body fluid (SBF) [26] solution at 37 °C. Electrochemical impedance spectroscopy (EIS) measurements started after an initial delay of 600 s. EIS data were collected at frequencies ranging from 100 mHz to 100 kHz with an ac amplitude of 5 mV. The Zsimpwin software was used to control and fit collected data. When polarization curves were obtained, the potential was scanned from −400 to +400 mV vs the open current potential at a scanning rate of 3 mV/s.

Immersion tests were conducted according to ASTM G31-72 in the SBF at 37 °C for 120 h. The ratio of the specimen surface area to the solution volume was 1 cm^2:60 mL, and the SBF was renewed every 24 h.

The adhesion strength of the film was measured by an automatic scratch tester (WS-2005; Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences) with a 0.2 mm tip radius Rockwell diamond indenter. The diamond tip was drawn across the films with a loading

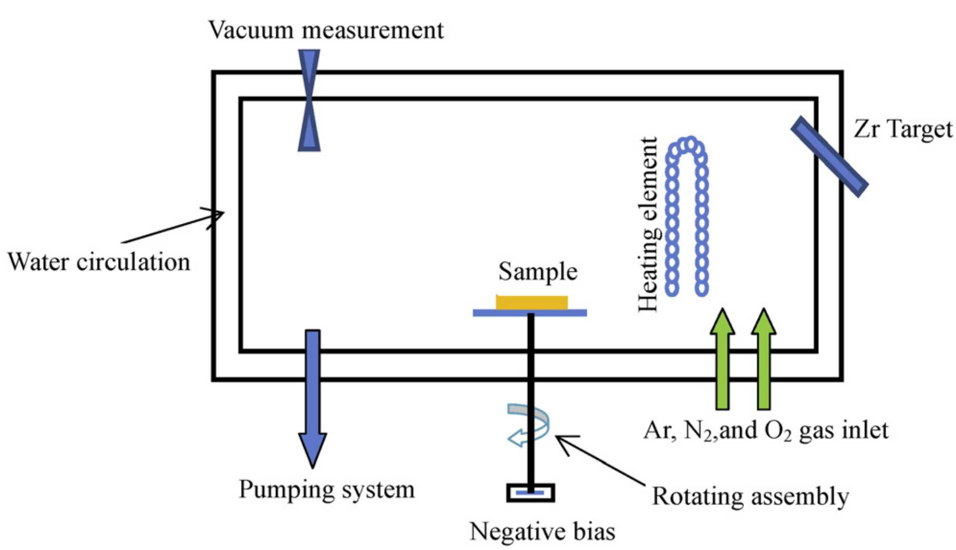

Fig. 1. Schematic for the process of Zr_xON_y film deposition.