Technical Note: A High Corrosion-Resistant Al₂O₃/MgO Composite Coating on Magnesium Alloy AZ33 by **Chemical Conversion**

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An Al₂O₃/MgO composite coating was synthesized on magnesium alloy AZ33 using a chemical conversion process for the first time. EDTA-2Na was introduced in the AI conversion solution to chelate AI^{3+} , and involved AI^{3+} in the cogrowth reaction. Inductively coupled plasma mass spectrometry and x-ray diffraction results showed that the coating consisted of Al₂O₃ and MgO with the ratio of 1:6. Visual and crosssectional analysis revealed that the coating was compact and flat after heat-treatment. The polarization resistance (R_p) of the coated alloy was about three orders of magnitude higher than that of the untreated alloy in 3.5 wt% aqueous NaCl solution. The coated alloy still maintained high corrosion resistance after 72 h immersion in the solution. It is believed that this effective and low-cost method can provide a new coating for the protection of magnesium alloys.

KEY WORDS: chemical conversion coating, corrosion resistance, magnesium

INTRODUCTION

he fabrication of composite oxide coatings is an efficient method for providing corrosion protection of magnesium alloys.¹ Anodization process and micro arc oxidation (MAO) are generally used for their fabrication,²⁻⁹ but the coatings obtained contain pores and cracks and require further treatment.¹⁰⁻¹¹ In contrast, the chemical conversion process is simple to operate and inexpensive.¹²⁻¹³ To date, several types of chemical conversion coatings, such as phosphate coatings,¹⁴⁻¹⁵ sol-gel coatings,¹⁶⁻¹⁷ hydrothermal coatings,¹⁸⁻¹⁹ and rare earth elementcoatings²⁰⁻²¹ have been developed. Coatings containing aluminum compounds are commonly fabricated using a hydrothermal process at high-temperature and high-pressure. The coating obtained using a such method is called Mg-Al Layered Double Hydroxide, and the corrosion resistance is limited.²²⁻²³ No aluminum conversion coating on magnesium alloys fabricated by conventional chemical conversion has been reported to date in the literature. One of the main reasons is the high activity of Mg²⁺ in solution, leading to the formation of large amounts of Mg(OH)₂ on the substrate, thereby hindering coating formation.

A new conversion solution developed for magnesium alloy AZ33 is described here. During the conversion process, cogrowth of Al(OH)₃ and Mg(OH)₂ occurs on the surface of the alloy due to the addition of EDTA-2Na. The coating is subsequently heat treated at 673 K to obtain a stable composite oxide layer consisting of Al₂O₃ and MgO. The resulting coating is compact and exhibits superior corrosion resistance when compared to coatings using other chemical conversion

methods.^{20,24-27} Moreover, the coating using the new process also could be obtained on other Al-containing magnesium alloys, such as AZ31B (UNS number: M11311) and AZ91D (UNS number: M11916).

MATERIALS AND METHODS

Plates of AZ33 magnesium alloy (2.92 wt% Al, 3.12 wt% Zn, 0.002 wt% Fe, 0.001% Cu, 0.005 wt% Ni, 0.005 wt% Mn, and Mg balance) were used in this study. To obtain uniform and active surface, the plate was ground to a 5000-grit finish and immersed in a pretreatment solution composing of 90 vol% ethyl alcohol and 10 vol% hydrochloric acid for 30 s at room temperature. Subsequently, the pretreated sample was transferred directly into the Al-based conversion solution at a temperature of 370 K for 4 h to form an Al conversion coating. The Al-based conversion solution used in this study was prepared using 0.13 M Al(NO₃)₃, 1.2 M NaOH, and 0.18 M EDTA-2Na in deionized water. Finally, the sample was transferred into a muffle furnace, and was heated in air at 673 K for 1 h to obtain Al₂O₃/MgO composite coating.

The morphologies of as-prepared samples were observed using a field-emission scanning electron microscope (SEM) operated at 15 kV. An x-ray diffractometer was used to analyze phase structure. Elemental analysis of the Al₂O₃/MgO composite coating was performed using an Inductively Coupled Plasma Mass Spectrometer. An electrochemical test was performed by a classical three-electrode configuration with an Ag/AgCl reference electrode. The exposed surface area was 1 cm². Following immersion for 2 h (to reach steady state) in

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Submitted for publication: April 27, 2018. Revised and accepted: December 13, 2018. Preprint available online: December 13, 2018, https://doi.org/10.5006/2861. [‡] Corresponding author. E-mail: zhougs@mail.xjtu.edu.cn.

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