



Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Corrosion mechanism and evaluation of anodized magnesium alloys

Guang-Ling Song^{a,b,*}, Zhiming Shi^b^a College of Materials, Xiamen University, 422 S Siming Rd, Siming District, Xiamen, Fujian 361005, China^b The University of Queensland, Materials Engineering, St. Lucia, Brisbane, Qld 4072, Australia

ARTICLE INFO

Article history:

Received 15 October 2013

Accepted 7 April 2014

Available online xxx

Keywords:

A. Magnesium

B. EIS

B. Polarization

C. Anodic film

ABSTRACT

The corrosion of anodized Mg alloys is investigated by means of immersion, salt spray, polarization curve, AC electrochemical impedance spectroscopy (EIS), SEM and optical microscopy analyses. Based on the blocking, retarding and passivating effects of an anodized coating on corrosion of Mg alloys, a corrosion model is proposed to illustrate the corrosion reaction at the coating/substrate interface in coating through-pores. It is found that EIS can sensitively respond to the occurrence of corrosion in anodized Mg alloys and reflect the protection performance of anodized coatings, which may be used as an in situ method of monitoring corrosion for anodized Mg alloys.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Magnesium alloys as structural materials are attractive to the automotive, aerospace and electronic industries for their low density, high ratio of strength to weight, excellent castability and good electromagnetic interference shielding property [1–3]. Mg alloys are also great functional materials and could be used as battery electrodes, sacrificial anodes, hydrogen storage materials and even biodegradable implants [1–7]. Unfortunately, these fascinating properties are offset by their highly reactive nature or low corrosion resistance [8–12]. Currently, Mg alloys in the automotive industry are simply being considered for uses in mild service environments [13–15]. Significantly improving the corrosion resistance of Mg alloys is a challenging task.

A variety of surface treatments have been proposed to protect Mg alloys from corrosion. Anodizing is one of the most popular processes [16]. Mg anodizing in many cases is also known as a micro-arc process due to the eye-catching sparking phenomenon in the bath. However, in nature it is still an anodizing reaction between Mg substrate and the bath electrolyte. Several commercial coatings have been developed for Mg alloys, such as Tagnite [17], Anomag [18], Magoxid [19], Keronite [20], HAE [21] and Dow 17 [22], and numerous new anodizing techniques are being proposed [23–25]. Current anodizing studies range from coating formation mechanisms to post-treatments [26–30]. Having realized some limitations of existing anodizing techniques, researchers recently have started to explore composited coating systems that

include an anodized layer as the base and another film as its top [31]. For example, Song et al. [32–34] developed a rapid dipping electroless E-coating process which can be applied to anodized Mg alloys to significantly improve their corrosion performance [35–37].

Normally, anodized coatings on Mg alloys are porous [16,38,39]. The core technique of anodizing includes control of baths and optimization of operation conditions in order to form a uniform, stable and less porous oxide layer on Mg alloys. The thickness, stability and porosity of an anodized coating can influence the protection performance of an anodized coating, and these coating parameters are also functions of substrate phase constituent and microstructure, electrolyte composition and concentration, anodizing current density and voltage. Therefore, the corrosion resistance of an anodized Mg alloy is eventually determined by the substrate, bath and operation parameters, all of which should be carefully selected and controlled in practice [40–45].

Almost all the developed anodized coatings are claimed by their inventors to be able to satisfactorily protect Mg alloy components from corrosion attack. It is important to know which anodizing process is really suitable for a given Mg alloy component in the service environment. A normal way of assessing and comparing anodized Mg alloys is the well-known salt spray test [34,46]. However, this method is time-consuming and does not provide detailed information on corrosion mechanism. There is a need for a rapid informative method to evaluate anodized Mg alloys in the auto industry, particularly when there are a large number of anodized samples. Such a method is also essential for gaining a deep insight into the corrosion mechanism of anodized Mg alloys and understanding the corrosion behavior of anodized coatings. Establishment of such

* Corresponding author. Current address: Materials Science and Technology Division, ORNL National Lab, 1 Bethel Valley Rd, Oak Ridge, TN 37831, USA.

E-mail address: guangling.song@gmail.com (G.-L. Song).

a technique may provide a solid foundation for developing more robust coatings for Mg alloys.

Since electrochemical reactions are responsible for corrosion damage, electrochemical techniques should be capable of revealing the corrosion mechanism and evaluating the corrosion performance of anodized Mg alloys. There are hundreds of publications using EIS in Mg corrosion studies, but most of them are on bare Mg alloys [47,48], and some on conversion and organic coatings [49–52]. Not many EIS studies are on anodized Mg alloys. In the limited number of EIS investigations of anodized Mg alloys, the AC impedance features, such as capacitive and inductive loops, are mainly employed to characterize the overall corrosion resistance of anodized coatings [53–55]; their physical meanings are not very clear or have not been convincingly interpreted [56]. Some researchers employed existing equivalent circuits from other systems to explain the corrosion of anodized coatings [57] or proposed new equivalent circuits with clear physical meanings for all the circuit components to analyze their EIS results [58]. However, they failed to justify theoretical foundations for the selected or proposed EIS models. For example, it is unclear why the equivalent components must be in series not parallel, or why the circuit should evolve or change with time in that way [59–61]. Although in the equivalent circuits used by Yagi et al. [58], elements representing coating pores have been included, the electrochemical processes in these pores have not been explored further. In fact, defects, like pores and micro-cracks, are critical sites that determine the protection performance of an anodized coating. The electrochemical processes in these defects contain a wealth of useful information on coating degradation. A detailed EIS model that can illustrate the corrosion reaction inside the defects of an anodized coating will undoubtedly be helpful in understanding the corrosion mechanism and evaluating the corrosion performance of anodized Mg alloys. Unfortunately, pertinent studies on so detailed corrosion mechanism of anodized coatings on Mg alloys are still relatively rare currently.

This paper will employ polarization curve and AC impedance techniques together with Scanning Electron Microscope (SEM) to investigate the corrosion behavior of anodized Mg alloys, aiming to establish a comprehensive EIS model to understand their corrosion mechanisms and also to obtain a rapid non-destructive method for evaluating and monitoring the protection performance of anodized coatings on Mg alloys.

2. Experimental details

If not specified, all the tests were conducted at ambient temperature and the solutions used in the study were prepared using analytical purity chemicals and demineralized water. All the potentials are relative to an Ag/AgCl reference electrode if not specified in the following text or denoted in figures.

2.1. Alloys, specimens and testing solutions

Magnesium alloys AZ91D (8.3–9.7 wt.% Al, 0.35–1 wt.% Zn, 0.15–0.50 wt.% Mn), ZE41 (3.5–5 wt.% Zn, 0.4–1.0 wt.% Zr, 0.75–1.75 wt.% rare earth elements) and pure Mg (99.96 wt.%) were cut from ingots, machined into coupons (2 cm × 2 cm × 0.5 cm), abraded to P#1200 with SiC paper, degreased with ethanol and then dried in air. These specimens were stored in a desiccator in the lab before experiments.

Various amounts of NaCl were mixed with Mg(OH)₂ in demineralized water to make up Mg(OH)₂-saturated NaCl solutions, which contained 0.1 wt.% NaCl, 0.5 wt.% NaCl and 5 wt.% NaCl, respectively. Their pH values were ~11 because of saturated Mg(OH)₂. They were used in AC impedance and polarization measurements

as electrochemical test solutions in this study. Another solution, 5 wt.% NaCl (pH ~7) without Mg(OH)₂, was also prepared and used as a corrosion test solution in immersion and salt spray experiments.

2.2. Anodizing

The samples were anodized using a KSP process that has been reported in literature [38]. The samples were immersed in an alkaline solution containing borate and silicate (12 wt.% NaOH + 12 wt.% Na₄B₂O₇·10H₂O + 9 wt.% Na₂SiO₃) at 75–95 °C to remove surface oil and contaminants. After being washed with demineralized water and dried, they were anodized in an alkaline electrolyte containing silicate and potassium hydroxide (1.6 wt.% K₂SiO₃ + 1 wt.% KOH) at ambient temperature. The anodizing current density was controlled at 20 mA/cm² for 10 min, then 10 mA/cm² for 10 min and finally 5 mA/cm² for 10 min. The anodized specimens were then washed with demineralized water and dried in air.

For comparison purposes, some ZE41 specimens were anodized using a commercial anodizing process Tagnite™. A few Anomag™ anodized AZ91D die-casting plates (8 cm × 12 cm × 0.3 cm) that had been exposed to 5 wt.% NaCl salt spray for 21 days were also used in this study.

2.3. Potentiodynamic polarization and AC electrochemical impedance

Polarization curve and AC electrochemical impedance spectroscopy (EIS) measurements were conducted using a three-electrode flat electrolyte cell system (Princeton Applied Research, K0235) which has a 1 cm² open window for a working electrode to expose its flat surface to the electrolyte in the cell. The working electrode specimen in a slot holder outside the cell was attached tightly to the window by a steel screw bolt through the holder. The bolt pushed the specimen firmly against the window, and also acted as an electrical conductor to connect the working electrode specimen to an electrochemical measurement system (Solatron 1260). Anodized and unanodized coupons in normal size (2 cm × 2 cm × 0.5 cm) were directly placed in the electrode holder and attached to the cell open window. Those larger samples, like Anomag and Tagnite anodized die-casting plates (8 cm × 12 cm × 0.3 cm), were cut into smaller coupons (3 cm × 3 cm × 0.3 cm) before being attached to the window. A KCl saturated (4.2 mol/L KCl) Ag/AgCl electrode, which is 0.197 V more positive than the standard hydrogen electrode in equilibrium potential, was used as reference in the cell, and the auxiliary electrode was a platinum mesh. The electrolyte cell contained 450 mL of Mg(OH)₂ saturated 0.1 wt.% NaCl solution. The specimen was immersed in the solution for 0.5 h to allow its corrosion potential or corrosion potential (E_{corr}) to reach a relatively stable value. As EIS measurement does not significantly alter the corrosion status of an electrode system, it was carried out first on the specimen at its corrosion potential E_{corr} . A 10 mV peak-to-peak amplitude of AC potential signal was selected. Frequency range was from 100 kHz to 10 mHz. On completion of EIS measurement, polarization curve measurement was carried out immediately. Potentiodynamic scanning rate was set at 0.167 mV/s. Under each testing condition, AC impedance and polarization curve measurements were repeated 3–7 times, depending on experiment reproducibility. If an experiment had good reproducibility, it was simply repeated 3 times. In case of bad reproducibility, 7 repetitions were required for the same measurement.

2.4. Immersion and salt spray

Anodized specimens were immersed in 5 wt.% NaCl solution in beakers, and their corrosion morphologies after immersion were

Download English Version:

<https://daneshyari.com/en/article/7895744>

Download Persian Version:

<https://daneshyari.com/article/7895744>

[Daneshyari.com](https://daneshyari.com)