Effect of the graphene oxide additive on the corrosion resistance of the plasma electrolytic oxidation coating of the AZ31 magnesium alloy

Jingmao Zhao [a,b,*], Xiong Xie [a], Chen Zhang [a]

[a] College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[b] Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing 100029, China

ABSTRACT

Graphene oxide (GO) was added into the electrolyte during the preparation of the plasma electrolytic oxidation (PEO) coating on AZ31 magnesium alloy. The effects of the GO additive on the microstructure, phase composition, and corrosion resistance of the PEO coating were studied. The results demonstrated that GO successfully incorporated into the PEO coating and it was partially reduced to rGO during the PEO process. As a result, the number of micropores on the PEO coating was significantly decreased. Moreover, the electrochemical test revealed that the corrosion resistance of the PEO coating was markedly improved upon the incorporation of 2 g/L GO.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Plasma electrolytic oxidation (PEO) treatment can effectively improve the corrosion resistance of magnesium and its alloys [1–6]. Over the past few decades, this technique has received considerable attention and becomes more and more popular [7,8]. The performance of PEO coatings is mainly determined by their microstructures and phase compositions [9,10]. However, it cannot provide high-barrier long-term protection due to its high porosity [11].

To further improve the physical and mechanical properties of PEO coatings, researchers incorporated some oxide particles (e.g., ZrO_2, TiO_2, CeO_2, SiO_2 and Al_2O_3) or other materials (e.g., CNTs and graphite) into the electrolytes [12–19]. During the electrochemical oxidation process, these additives can be incorporated into the PEO coatings, resulted in obtaining a less defect and crack coating, and in this way the corrosion resistance of PEO coating was enhanced greatly. Sun et al. [20] added the Halloysite nanotubes (HNT) and benzotriazole (BTA) loaded HNT to a silicate-based electrolyte to produce PEO coatings on AM50 alloy. The HNT increased coating scratch resistance greater than BTA-HNT, although the latter enhanced corrosion resistance due to a self-healing effect.

Graphene, including graphene oxide (GO) and reduced graphene oxide (rGO), has shown its potential use in anti-corrosion coating for metal substrates. Kirkland et al. [21] employed graphene as a corrosion protection barrier for nickel and copper. Singh et al. [22] reported the fabrication of a robust graphene-reinforced composite coating with excellent corrosion resistance by aqueous cathodic electrophoretic deposition. Ramezanzadeh et al. [23] developed a sol-gel based silane film filled with functionalized GO nanosheets to enhance the epoxy coating resistance against corrosion and cathodic delamination over the steel substrate. Qi et al. [24] synthesized a new type of solution-processable graphene coating by grafting polymethyl-methacrylate (PMMA) brushes on GO. They found that the PMMA-grafted GO coating can effectively block the charge transfer at the metal–electrolyte interface and prevent corrosion of the copper substrate under aggressive saline conditions. Ramezanzadeh et al. [25] synthesized an amino functionalized graphene oxide (FGO) and demonstrated that incorporation of 0.1 wt.% of FGO nanosheets into the epoxy coating significantly enhanced the corrosion resistance by improving its ionic resistance as well as barrier properties. Yang et al. [26] showed that the incorporation of fluorographene into polyvinyl butyral coating noticeably enhanced its corrosion resistance performance through insulating the conductive graphene sheets and obtaining coating with high degree of barrier action.

Thus far, there is no report on applying GO to PEO coatings for magnesium and its alloys. In this study, the PEO coating on the AZ31 magnesium alloy was formed in electrolytes supplemented

Table 1
Chemical compositions of the AZ31 magnesium alloy.

Element	Al	Zn	Mn	Si	Fe	Cu	Mg
Content (wt%)	2.95	0.97	0.23	0.014	0.16	0.01	Balance

Table 2
The chemical compositions of the base electrolyte used in PEO process.

Na$_2$HPO$_4$ (g/L)	NaF (g/L)	Sodium citrate (g/L)	Glycerol (ml/L)	Sodium dodecyl sulfate (g/L)
15	5	5	15	0.3

Table 3
The electrolytes used for fabrication of the coated samples.

Sample	Electrolyte
E0	base electrolyte
E1	base electrolyte +1 g/L GO
E2	base electrolyte +2 g/L GO
E3	base electrolyte +3 g/L GO

with varying concentrations of GO. The microstructure and phase composition of the PEO coating were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). In addition, the effect of the GO additive on the corrosion resistance of the PEO coating was examined using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve measurements.

2. Experimental

2.1. Preparation of the magnesium alloy samples

The AZ31 magnesium alloy samples used as the substrate for the PEO experiments were thin square sheets with a size of 35 mm × 35 mm × 2 mm. The chemical compositions of the AZ31 magnesium alloy were listed in Table 1. Before oxidation, the alloy samples were abraded with silicon carbide abrasive paper (up to 1000 grit), degreased in acetone, rinsed with ethanol, and dried with a hot air stream.

2.2. Preparation and characterization of GO

Compared to rGO, GO can be easily dispersed in aqueous solutions due to the existence of oxygen-containing functional groups [27–29]. Thus we selected GO as the additive in the PEO coating process. GO was prepared using the method developed by Hummers [30] and the obtained GO sample was characterized using XRD (D/Max 2500 v/pc, Rigaku) and UV–vis spectroscopy (UV-2450, Shimadzu). The particle size and zeta potential of GO were measured using a Malvern Nano ZS90 Zetasizer.

2.3. PEO treatment on the AZ31 magnesium alloy samples

The PEO treatment was performed using a 10-kW DC pulse power supply. The AZ31 samples and the wall of stainless steel container were used as the anode and cathode, respectively. The temperature of the electrolyte was maintained at 20–30 °C during the PEO treatment using a cooling bath under constant stirring.

GO is prone to aggregate in strong acidic or strong alkaline electrolytes [31,32], so a slightly acidic electrolyte (pH 5.73) was used as base electrolyte in this study and its chemical compositions were shown in Table 2. Despite many trials at different conditions, including constant-voltage oxidation and constant-current oxidation, our preliminary experiments showed that PEO coating of the magnesium alloy samples cannot be achieved in this electrolyte. Thus, a two-step PEO coating process was developed. In the first step, the alloy samples were oxidized under a constant current (100 mA/cm^2) for 1 min in a phosphate-based electrolyte containing 12 g/L Na$_3$PO$_4$·12H$_2$O and 2 g/L KOH, pH = 13.13. In the second step, the obtained samples were oxidized under a constant voltage (400 V) for 9 min in the base electrolyte containing 0, 1, 2 and 3 g/L GO, respectively. The coated samples were denoted as E0, E1, E2

and E3 accordingly as shown in Table 3. The duty cycle was maintained at 10% and the frequency was maintained at 500 Hz for both steps. Finally the coated samples were rinsed with deionized water and dried under a flow of warm air.

2.4. Characterization of the PEO coatings

The thickness of the PEO coatings was measured using a digital thickness gauge (TT230, Time). The measurement was performed at twenty random points across each sample. The average thickness value was calculated and used to represent the coating thickness of the sample. The surface and cross section morphologies of the coatings were characterized by SEM (Quanta 200F, FEI). The elemental compositions of the PEO coatings were analyzed by energy-dispersive X-ray spectroscopy (EDS) using an EDS spectrometer coupled to the microscope. The analyzed area of each sample was about 100 μm^2 and the reported values calculated from the average of three measurements. The phase composition of the PEO coatings was measured by XRD (D/Max 2500 v/pc, Rigaku). In the XRD measurement, the range of 2θ was from 20° to 80° and the scan rate was 0.02°/min. The chemical state of GO in the PEO coatings was determined by X-ray photoelectron spectroscopy (XPS) using a ThermoFisher Scientific Escalab 250 spectrometer.

2.5. Electrochemical measurements

Corrosion resistance of the PEO coatings was evaluated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve measurements using a Gamry Instrument Interface 1000 potentiostat in a conventional three-electrode cell: a platinum electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the AZ31 alloy sample as the working electrode. The test solution was 3.5 wt% NaCl.

EIS experiments were conducted at open circuit potential (OCP) with an AC amplitude of 10 mV (peak-to-peak) in the frequency range from 100 kHz to 0.01 Hz. Before each test, the working electrode was immersed in the test solution for 30 min to reach a stable state (i.e., the OCP fluctuation was less than ±5 mV, as shown in Fig. 1). Zsimpwin software was utilized to simulate the experimental data. At the end of each EIS measurement, potentiodynamic polarization was conducted over a potential range from −0.2 to +0.5 V vs. OCP at a scan rate of 1 mV/s. The corrosion current density and other electrochemical parameters were determined by fitting the curves in the weak polarization zone using the Gauss-Newton method [33,34]. All electrochemical tests were conducted at room temperature. Three independent measurements were performed under each experimental condition and the mean values of the three measurements were reported.

3. Results and discussion

3.1. Chemical properties of GO

The particle size of GO synthesized by the Hummers method was 1.02 μm. Fig. 2 shows the UV–vis spectrum of the GO sample. The maximum absorption peak was located at ca. 230 nm, which corresponding to the $\pi \rightarrow \pi^*$ transition of aromatic C—C bonds [35,36]. A