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Composite coatings on a Mg–Li alloy prepared by combined plasma electrolytic oxidation and sol–gel techniques

Zhijun Li, Xiaoyan Jing, Yi Yuan *, Milin Zhang

Key Laboratory of Superlight Materials & Surface Technology, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

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ABSTRACT

We present a facile procedure by combining plasma electrolytic oxidation (PEO) technique with sol–gel method to improve the corrosion resistance of magnesium–lithium alloy. A further deposition of a titanium sol–gel layer on the PEO film improves the compactness and anti-corrosion properties. X-ray photoelectron spectroscopy and X-ray diffraction measurements reveal that the PEO coating is composed of MgO and Mg_2SiO_4, while after sol–gel treatment, the coating contains titania and some low valence titanium compounds. Long-term immersion testing show that the PEO/sol–gel composite coating with better compactness and fewer defects exhibits a superior anti-corrosion property in comparison with PEO alone.

1. Introduction

Due to its unique physical and mechanical properties of high strength-to-weight ratio, high dimensional stability, high specific stiffness, good machining property, excellent magnetic screen and shock resistance ability, superlight magnesium–lithium (Mg–Li) alloys are attractive materials and expected to have great potential use in transportation vehicles and light-weight enclosures for computer, communication and consumer electronic products [1–7]. Unfortunately, Mg–Li alloys exhibit poor corrosion resistance in aggressive environments that results from the high chemical reactivity of magnesium and lithium and external protection is therefore imperative. In this regard, a mass of endeavors have been focused on the development of different methods for improving corrosion resistance of Mg alloys, such as chemical conversion [8], electroless deposition [9], self-assembled monolayers (SAMs) [10], immersion [11], epoxy coating [12] anodic oxidation [13]. However, there are relatively few publications on corrosion resistance of Mg–Li alloys [14–17]. Hence, it is especially essential to develop a simple and highly effective approach to delay the onset of corrosion on Mg–Li alloys. Plasma electrolytic oxidation (PEO) is a novel process which produces stable oxide coatings *in vivo* on valve metals such as Al, Mg and Ti [18–21], and the results show that the corrosion resistance of alloy substrate has been improved by the formation of PEO coating. However, the inherent defects, including numerous micropores and microcracks, would let the penetration of aggressive species proceed and lower the corrosion resistance of PEO coatings [22,23].

Sol–gel method is quite promising for prepare protective coatings with high corrosion resistance and good adhesion to both metallic substrates and top coatings, which can offer ways to preparation of functional coatings with different properties [24–26]. Hexavalent chromium-containing compounds are a traditional kind of corrosion inhibitor which exhibits much better corrosion resistance due to strong oxidation properties of Cr^{6+}. In spite of good corrosion protection, the properties of the chromates make them environmentally unfriendly. Thus, the need for the development of non-chromate and environmental-friendly surface treatments is urgent. To pursue further improvement, the development of a combined process based on PEO is highly desirable to solve these inherent defects of PEO coatings. However, to the best of our knowledge, composite coatings based on PEO have rarely reported. Liang et al. report a combined process of PEO and filtered cathode arc deposition, and the duplex PEO/DLC coating exhibits a better tribological property than the DLC or PEO monolayer on Mg alloy substrate [27]. Duan et al. demonstrate that the corrosion resistance of composite coatings prepared on AZ91D by PEO treatment plus a top coating with sealing agent using multi-immersion technique under low-pressure conditions is superior evidently to that of PEO coating [28]. Shi et al. fabricate composite coatings on magnesium by two steps: (i) PEO and (ii) a top TiO_2 sealing layer formed by sol–gel dip coating followed by hydrothermal treatment [29], which exhibits improved corrosion resistance. In our previous work, we have successfully fabricated the duplex plasma electrolytic oxidation/molybdate conversion (PEO/MoC) coatings with highly improved anti-corrosion properties on Mg–Li alloy [30], which

* Corresponding author. Tel./fax: +86 451 82533026.
E-mail address: yi.yuan@hrbeu.edu.cn (Y. Yuan).

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motivates us to design novel composite coatings on Mg–Li alloys that imparts excellent anti-corrosion resistance by using a combined PEO technique with sol–gel method.

Herein, we report a general and technically feasible approach to prepare PEO/sol–gel composite coatings on the surface of Mg–Li alloy using a combination of PEO and sol–gel method. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) are employed to elaborately characterize the microstructure, chemical and phase compositions and functional groups of PEO and PEO/sol–gel composite coatings. Additionally, the anti-corrosion properties of PEO and PEO/sol–gel composite coatings are investigated by potentiodynamic polarization and electrochemical impedance spectroscopy.

2. Experimental section

2.1. Materials and specimen preparation

Mg–Li alloy (5% Li, 3% Al, 2% Zn, 0.5% Sn and Mg balance) with a size of ϕ = 15 mm, H = 16 mm was used as substrate material. The specimen preparation was according to the method reported in our previous work [31]. Titanium sol was prepared by slowly adding water to the mixture of tetraethyl titanate, ethanol and triethanolamine, under vigorous stirring. The final volume ratio of starting materials in the titanium sol was $Ti(OC_4H_9)_4$:ethanol:triethanolamine:H_2O = 3:12:1:1 and pH was adjusted to 7–8. The solution was stirred magnetically for 1 h and aged for 24 h at room temperature [32].

2.2. PEO/sol–gel composite coatings preparation

The alkaline silicate electrolyte was prepared from a solution of Na_2SiO_3 (10.0 g/L) in distilled water with an addition of NaOH (3.0 g/L) and triethanolamine (10 ml/L). For PEO process, a DC pulsed electrical source was employed to control the voltage, current density and other electrical parameters such as frequency and duty cycle. The sample of Mg–Li alloy and a stainless steel container were used as anode and cathode, respectively. A cooling system was used to keep the temperature of electrolyte at room temperature. The appropriate electrical parameters were as following: frequency: 2000 Hz, duty cycle: 15%, current density: 5 A/dm^2. The coated sample was rinsed thoroughly with distilled water and dried in cool air after a PEO treatment of 10 min. Subsequently, the coated sample was submersed vertically in the titanium sol for 5 min, then the sol–gel coating was fabricated by a withdrawing method at a speed of 6 cm min^{-1}. This procedure was repeated four times to make sure the titanium sol covered the micropores and microcracks of the PEO coating. Finally, the sample was dried in an oven at 170 °C for 3 h. After the above treatment, the PEO/sol–gel composite coatings were successfully fabricated onto the surface of Mg–Li alloy. Three samples were made under each condition to ensure the reliability of the experiments.

2.3. Characterization of PEO/sol–gel composite coatings

The surface, cross-sectional morphologies and elemental compositions of PEO and PEO/sol–gel coatings were examined by JSM-6480A scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). The microstructure of Mg–Li alloy was studied by optical microscope (OM). The thickness of samples was measured with an eddy current coating thickness measurement gauge (TT 230, Time Group Inc., China). The thickness data given were the average of 10 measurements made at different locations. The phase composition of coatings was analyzed by thin-film X-ray diffraction (TF-XRD, Philip X'Pert, Holland), using a Cu $K\alpha$ radiation as the excitation source at a grazing angle of 1° and a powder X-ray diffraction system (Rigaku D/max-TTR-III) using Cu $K\alpha$ radiation (k = 0.15405 nm) at 40 kV and 150 mA with a continuous scanning mode at a rate of 3° min^{-1} was used to analyze the sol–gel powder calcined at different temperatures. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a ESCALAB-MKII X-ray photoelectron spectrometer (VG Instruments, UK) using monochromatized Al K_α radiation (photon energy 1486.6 eV) as the excitation source and the binding energy of C 1s (284.6 eV) as the reference. Xpspeak 4.1 software was used to analyze the data. Fourier-transform infrared (FT-IR) spectrum was recorded with an AVATAR 360 FT-IR spectrophotometer using a standard KBr pellets.

For corrosion resistance evaluation of samples, potentiodynamic polarization and EIS measurements were performed on Im6ex electrochemical workstation (Zahner Co. Ltd.) with THALES 3.08 software package. All electrochemical measurements were conducted in 3.5 wt.% NaCl solution at room temperature using a conventional three-electrode cell with Mg–Li alloy or coated alloy as the working electrode with an exposed area of 1 cm^2, a saturated calomel electrode (SCE) as the reference electrode and a platinum plate as the counter electrode. For the potentiodynamic polarization test, scanning at a rate of 2.5 mV/s was from −1.8 to −1.0 V after an initial 10 min delay. For EIS test, the frequency ranged from 100 kHz to 100 mHz with an AC amplitude of 10 mV over the open circuit potential after 10 min immersion in the electrolyte. ZsimpWin 3.2 software was used for the data fitting of impedance spectra. Immersion tests were performed at open circuit potential with AC amplitude of 10 mV over the open circuit potential in the frequency range from 100 kHz to 100 mHz after immersion periods of 10, 50, 150, 300, 450, 600, 800, 1000, 1200 and 1500 h, respectively. All electrochemical tests were conducted in triplicate in order to ensure the reproducibility of results.

3. Results and discussion

3.1. Surface morphology characteristics of PEO coating and PEO/sol–gel composite coatings

Surface morphologies and the microstructure details of PEO coating and PEO/sol–gel composite coatings are presented in Fig. 1. We observe that the surface of PEO coating prepared in an alkaline silicate electrolyte has porous microstructures and some volcano top-like micropores and microcracks distribute disorderly on the surface, as shown in Fig. 1a. The micropores ranges from 1 to 11 μm are formed by molten oxide and gas bubbles thrown out of discharge channels during the PEO process, and microcracks result from the thermal stress attribute to the rapid solidification of molten oxide in the cooling electrolyte, which permit the penetration of corrosive ions to the substrate of Mg–Li alloy and corrosion proceed. As for PEO/sol–gel composite coatings shown in Fig. 1b, we notice that all the micropores and microcracks that existed on the surface of PEO coating have almost disappeared after the sol–gel treatment, instead a relatively smooth and uniform surface with less cracks is obtained and the cracks are the result of thermal stress after the coating was dried in an oven at 170 °C for 3 h.

Table 1 lists the EDX analysis results of PEO coating and PEO/sol–gel composite coatings. The composition of PEO coating is mainly composed of Mg, Si and O. Mg originating from the substrate is presumed to have entered the dispersed discharge channels and existed in the coating. The presence of Si and O suggests that the components of electrolyte are intensively incorporated into the plasma chemical oxidation reaction to form PEO coating as well. After sol–gel treatment, PEO/sol–gel composite coatings