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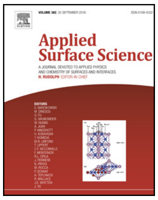

Characterization of AZ31 magnesium alloy by duplex process combining laser surface melting and plasma electrolytic oxidation

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ABSTRACT

Top ceramic coatings were fabricated on the laser surface melting (LSM) modified AZ31 alloy by plasma electrolytic oxidation (PEO) in a phosphate electrolyte. The effect of LSM treatment on the microstructure and corrosion behavior of the bare and PEO treated AZ31 alloy was evaluated. Results showed that LSM treatment produced a homogeneous modified layer with redistributed intermetallic compounds, resulting in enhanced corrosion resistance of AZ31 alloy. The LSM treatment had no obvious influence on the surface and cross-sectional microstructures of the PEO coatings on AZ31 alloy. Besides, MgO was the main constituent for PEO coatings, regardless of LSM pretreatment. However, the long-term corrosion properties of the PEO coated AZ31 alloy with LSM pretreatment revealed large enhancement. Based on the analysis of microstructure and corrosion property, the corrosion mechanisms of the PEO and LSM-PEO coated AZ31 alloy were proposed.

1. Introduction

In recent years, magnesium (Mg) alloys are attractive for the automotive, electronics and aerospace industries due to their low density and adequate strength to weight ratio [1–3]. However, the practical application of Mg alloys is often limited by their high susceptibility to corrosion, which is primarily attributed to the high chemical activity of Mg and to the unstable imperfect natural oxide film on its surface [4–6]. Thus, various surface treatments are applied to protect Mg alloys from corrosion, such as conversion coating, laser surface melting, gas phase deposition and electrochemical plating [7]. Of these techniques, laser surface melting (LSM) is effective technique that offers significant potential for improvement in near-surface properties, because it can homogenize and refine the microstructure, and dissolve the second phases [8–16]. It has been proved [11–16] that the LSM treatment had a positive effect on corrosion resistance of Mg alloys.

Plasma electrolytic oxidation (PEO) is one of the most common methods for corrosion protection of Mg alloys, because it can produce a relatively thick, dense and well adherent ceramic-like coating [17–29]. Many works have proved that the PEO coatings can significantly enhance the corrosion resistance of Mg alloys in short term [17–20]. Unfortunately, there exist many inherent defects including micro-pores and micro-cracks in the PEO coating [21–29]. The inherent defects of PEO coating would facilitate the infiltration of corrosive medium into the alloy substrate and thus make PEO locally failed after long-term exposure to the corrosive environments [21–29].

Studies indicated that the corrosion properties of PEO coated Mg alloys depended not only on the microstructure and composition of PEO coating, but also on microstructure characteristics of the substrate [28–31]. As mentioned above, LSM treatment can greatly change the microstructure of Mg alloys, and its subsequent effect on long-term corrosion performance of PEO coating is of great concern. Wang et al. [25] analyzed the effect of LSM treatment on the PEO coated AZ91 Mg alloy and concluded that the LSM-PEO coating could provide better long-term corrosion protection to AZ91 alloy than the PEO coating alone. In this work, AZ31 alloy was treated using duplex techniques of LSM and PEO. The effects of LSM treatment on microstructure and corrosion behavior of the bare and PEO coated AZ31 alloys were evaluated. Especially, the relationship between the LSM modified layers and the corrosion resistance of the LSM-PEO coated Mg alloy was analyzed.

2. Material and methods

2.1. Laser surface melting process

AZ31 Mg alloy was used as the substrate in this investigation. Nominal composition of the AZ31 alloy is listed in Table 1. Before LSM treatment, the specimens, 50 mm × 50 mm × 10 mm in dimen-

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Table 1
EDS elemental analysis of the as-received, LSM treated AZ31 alloy and appointed phase in Fig. 2.

Alloys	Content of elements (wt.%)			
	Mg	Al	Mn	Zn
AZ31	96.17	2.59	0.31	0.93
1	13.27	29.20	57.25	0.28
AZ31 LSM	94.89	3.49	0.38	1.24

sion, were ground with nos. 2000 SiC abrasive paper and then sand blasted. The LSM process was carried out in argon shielding gas at a pressure of 0.2 MPa, using a 10 kW transverse-flow continuous-wave CO_2 laser. The beam diameter of laser process was 3 mm and the overlapped track was 50%. The laser energy densities were set as 76 J/mm^2. Subsequently, the specimens were cut into rectangular plates of 30 mm × 20 mm × 10 mm, ground with SiC abrasive paper to 2000 grit and polished with Al_2O_3 paste to get a smooth surface for the following PEO treatment.

2.2. Preparation of PEO coatings

The PEO process was carried out using a pulsed bi-polar power source. The electrolyte was prepared from the solution of 10.0 g/L $Na_3PO_4 \cdot 12H_2O$ (AR, Alfa Aesar) and 1.0 g/L KOH (AR, Yantai Shuangshuang Chemical Reagents Company) in distilled water. During the PEO process, the samples and the wall of the stainless steel container were used as the anode and the cathode, respectively. The electrical parameters were fixed as follows: frequency 150 Hz, the positive pulse 1.0 ms, the negative pulse 1.5 ms, and duty cycle 37.5%. A constant current density was maintained at 5.0 A/dm^2 by modulating the positive and negative voltages and all samples were treated for 30 min. The temperature of the electrolyte solution was always kept at $20 \pm 2\,^\circ$C by a water cooling system. After the PEO treatment, each sample was washed thoroughly in distilled water and dried in air immediately.

2.3. Microstructure characterization

AZ31 alloy was etched using an acetic-picral solution (10 ml acetic acid glacial+ 4.2 g picric acid + 10 ml H_2O + 70 ml ethanol absolute). The metallurgical microstructures of the as-received, LSM, PEO and LSM-PEO treated specimens were observed by a Zeiss Axio Imager.A2 m microscope. The microstructural features and elemental composition of the specimens were analyzed using a scanning electron microscope (SEM, JSM-5600LV, JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS, KEVER). The phase compositions of the specimens were determined by a D/Max-2400 X-ray diffractometer (XRD, Cu Kα radiation) at a grazing angle of 5°. The thickness of the PEO coatings was measured with a Minitest 1100 micro-processor coating thickness gauge (Elektro-Physik Koln, Germany), which utilized eddy currents induced in the substrate to measure coating thickness with an accuracy of about ±1 μm.

2.4. Electrochemical and immersion tests

The corrosion resistance of the specimens was evaluated from electrochemical impedance spectroscopy (EIS) on an Autolab PGSTAT302 N electrochemical workstation. All electrochemical measurements were conducted using a typical three-electrode cell system with the samples as the working electrode, a platinum plate as the counter electrode and an Ag/AgCl (saturated with KCl) electrode as the reference electrode. The samples with an exposed area of 0.5 cm^2 were immersed into 3.5 wt.% NaCl solution. EIS tests were operated after certain immersion periods at the open circuit potential with an AC amplitude of 10 mV over a frequency range from 30000 to 0.01 Hz. The degradation phenomena of the coatings can be revealed by analyzing the change features in the impedance spectra. All the electrochemical tests were carried out at room temperature and were performed in duplicate to ensure the reproducibility.

Prior to immersion test, the samples were sealed by polyurethane with the working surface exposed only. The immersion tests were performed by exposing the samples to a solution of 3.5 wt.% NaCl at room temperature. The surface appearances of samples were taken by a digital camera after certain immersion periods. After immersion test, the specimens were gently washed in clean running water to remove salt deposits from their surface, and then immediately dried in warm air. Subsequently, the surface and cross-sectional corrosion morphologies of the specimens were characterized by SEM. To observe the degradation process of MgO itself, the MgO power (AR, Xilong Chemical CO., Ltd.) was also immersed in 3.5 wt.% NaCl solution at room temperature. After immersion for different durations, a small amount of turbid liquid was taken out and filtered under vacuum. The chemical components composition of percolation residue was examined by means of XRD.

3. Results

3.1. Microstructure of LSM modified layer

Fig. 1a presents the microstructure of the as-received AZ31 Mg alloy after etching. The AZ31 alloy was characterized by polyhedral α-Mg grains with some Al_8Mn_5 phases (denoted by arrows). The presence of Al_8Mn_5 phase was further confirmed by EDS elemental analysis in Fig. 2a and Table 1. The grain labeled as 1 in Fig. 2a including 29.20 wt.% Al and 57.25 wt.% Mn, was referred to Al_8Mn_5 phase. Fig. 1b-c illustrates the cross-sectional and surface microstructures of the LSM treated AZ31 alloy. The LSM treatment produced a uniform modified layer with an average depth of 0.9 mm on top of the alloy. Compared to the as-received alloy, many of the α-Mg grains changed from polyhedron into long strips after LSM treatment. This phenomenon was caused by temperature gradient and strain rate during the LSM process. In addition, Al_8Mn_5 phases were dramatically refined and uniformly distributed in the α-Mg matrix.

Fig. 2 exhibits the element distribution characteristics in the as-received and LSM treated AZ31 alloy. The EDS maps clearly indicated that the Al and Mn elements distributed more uniformly after LSM treatment, which was attributed to the dissolution and redistribution of Al_8Mn_5 phase. In addition, the Al content on the surface of the LSM treated AZ31 alloy was slightly higher than that of the as-received one (Table 1), which was mainly attributed to the evaporation of Mg and dissolution of Al_8Mn_5 phases. In summary, the LSM treatment of the AZ31 alloy resulted in the elongation of α-Mg grains, refinement of Al_8Mn_5 phase and improvement of Al content in α-Mg matrix.

3.2. Coating analysis

Fig. 3 gives XRD patterns of the PEO coatings on the as-received and LSM treated AZ31 alloy. MgO was found to be the main constituent for both coatings, regardless of LSM pre-treatment. There were no diffraction peaks of $Mg_3(PO_4)_2$ or $MgAl_2O_4$ as reported by others [18,23], which may be attributed to their very low content in coating under the preparation parameters used in this work.

Fig. 4 shows the surface morphologies of PEO coatings on the as-received and LSM treated AZ31 alloy. Two coatings were similar porous structure. Further, some micro-cracks could also be detected on the surface of the coatings. The micro-pores were