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Microstructure and corrosion resistance of micro arc oxidation plus electrostatic powder spraying composite coating on magnesium alloy

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ABSTRACT

Based on the morphological characteristics of the microporous micro arc oxidation (MAO) ceramic coating, a double layer composite coating system was applied on the surface of AZ31 magnesium alloy by MAO plus electrostatic powder spraying (EPS) technique. The Mg sample coated with MAO plus EPS (MAO + EPS) was compared with Mg sample coated by MAO coating or EPS monolayer. The results indicated that the corrosion resistance of AZ31 Mg alloy was significantly improved by MAO + EPS composite coating with the exellent binding force. Furthermore, the corrosion mechanism of three coated Mg alloy was discussed.

1. Introduction

Weight reduction is of great significance to transportation, aerospace, military and other fields [1]. Magnesium alloys are very promising structural materials due to their low density, high specific strength, high modulus, electromagnetic shielding and excellent casting, cutting performance and easier recycle and so on [2–4], regarded as green engineering materials in 21 st century. However, the standard potential of pure magnesium is only −2.37 eV, indicating that Mg is prone to corrosion in a humid environment. This restricts its wide spread applications [5,6]. As a result, magnesium alloys can only be used after appropriate surface treatment. Various surface modification methods, such as chemical conversion coatings [7,8], physical vapor deposition (PVD) films [9,10], micro arc oxidation (MAO) [11–13], polymeric coatings [14,15] and cold spraying [16,17], were tried to prepare suitable coatings for protecting Mg and its alloys. Especially, cold spray has been used successfully for improving properties of Mg alloys, which is economical and environmentally friendly [17].

Among all of the surface treatments available for Mg alloys, MAO is a recent technique for protecting Mg, which can provide an adherent, hard, scratch-resistant, wear-resistant, and corrosion-resistant coating [18]. The growth of MgO coating is mainly dependent on the conversion of matrix magnesium atoms to magnesium oxide [19,20], especially in a single sodium silicate electrolyte, which is environmentally friendly. The MAO ceramic coating is in good combination with the substrate and the growth of the coating is relatively uniform, which is affected by the MAO growth mechanism [21]. However, the corrosive medium could penetrate into the interface between MAO coating and magnesium matrix, resulting in the corrosion of magnesium due to the porous surface structure of the MAO coating [22]. In particular, the MAO ceramic coating as an alkaline oxide, exposed to acid rain, sun and sand and other adverse weather in the application of magnesium alloy auto parts, is prone to pitting corrosion. Researchers developed the organic sealing process on the porous structure of the MAO ceramic coating. For example, the MAO and electrophoretic coat (E-coat) technique were combined to provide a two-layer coating system for improving corrosion resistance of Mg alloys [22,23]. However, the electrochemical environment of micro arc oxidation (pH = 14) and electrophoresis (pH = 5) of two processes for Mg surface treatment is different, which leads to a necessary washing process between these two processes.

The electrostatic powder spraying (EPS) technique is a process for depositing organic coatings on samples. Its principle is that the coating material, dispersed into uniform and fine droplets by a kind of gun or nebulizer, is applied to the sample surface, which is a "dry" processing technique. In this paper, MAO and EPS composite technique were combined to provide a double-layer (MAO + EPS) coating system, expecting to integrate the advantages of both MAO and EPS technology. After the MAO treatment on bare AZ31 magnesium alloy, an EPS coating was applied on top of MAO coating to seal the porous and provide extra protection for the substrate. So, the composite process avoided the demand for water washing between the two processes of MAO and E-coat. Furthermore, this new MAO + EPS coating and substrate system might have an improved binding force by the mechanical interlocking between the porous MAO ceramic coating and top EPS coating layer. Finally, Mg samples coated by three types of coating schemes, MAO process only (MAO), EPS process only (EPS) and MAO plus EPS process (MAO + EPS), were prepared, analyzed and compared

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in terms of microstructure, adhesion and corrosion resistance. The results could provide support for the surface protection technology of magnesium alloy.

2. Experimental

2.1. Materials

The material used in the experiment is AZ31 magnesium alloy (3.10% Al, 0. 50% Mn, 1.18% Zn, 0.04% Ca, 0.05% Si, 0.01% Cu and balance Mg, mass fraction). The specimens (Φ30 mm × 6 mm) were mechanically polished with 1200# abrasive papers, respectively, cleaned with a detergent and rinsed with distilled water prior to treatment.

2.2. Coating preparation

The MAO coatings were prepared on Mg alloy using JHMAO-60 micro arc oxidation equipment (made by Xi'an University of Technology, China). Electrolyte was prepared from the solution of 30 g/L sodium silicate (Na_2SiO_3) in a 2000 mL glass vessel at room temperature, and pH value was 14. A constant voltage was 400 V in the experiment following a rectangular DC wave with frequency 400 Hz and duty cycle 10%. The oxidation time was 3 min, 5 min and 8 min, respectively. After that, the EPS coatings were deposited on the bare Mg substrate and MAO coated samples, and the process parameters were shown in Table 1.

2.3. Characterization of the coating

Thickness of three MAO coatings was measured using the TT240 eddy current thickness meter with an accuracy of 0.1 μm. Six measurements were carried out evenly on the whole sample surface. Field emission scanning electron microscope (FESEM) was performed to characterize the surface morphologies of the obtained coatings. Energy dispersive X-ray spectrometer (EDS) was used to test the element distribution of the coatings after friction tests. The adhesion of the coatings on the Mg alloy substrates was assessed by a scratch tester performed on a Rockwell diamond indenter with a conical tip of 0.2 mm in radius. The normal load of the indenter was linearly amped from the minimum (1 N) to the maximum (80 N) during scratching. During the test, the scratch length was 3.00 mm and the scratch speed was 5 mm/min. The loads corresponding to the coatings peeled to the substrates were used to evaluate the binding strength. Each binding experiment of the coated sample was repeated 3 times. Finally, corrosion property of the coated AZ31 magnesium alloy was evaluated by the acid corrosion test following GB1763 and electrochemical potentiodynamic polarization in 5 wt.% NaCl solution. During the process of electrochemical test, a three electrode cell with the coated specimens as working electrode, the platinum sheet as auxiliary electrode, the saturated calomel electrode as the reference electrode was used, and the samples with an exposed area of 0.785 cm^2 were immersed in the corrosion medium. The scanning speed is 5 mV/s. During the electrochemical test, the scratches with 3 mm length were completely exposed to the corrosive media. In the acid corrosion test, 9.800 g sulphuric acid was accurately weighed using electronic analytical balance with a precision of 0.001 g, and then it was added into 1000 mL pure water to obtain the corrosion solution. The bottom of MAO + EPS coated sample was immersed in this sulfuric acid corrosion solution at 24–26 °C with corroded area 28 cm^2. The corroded samples were weighed in every two hours. The corrosion speed of the coated sample was calculated according to the following relationship.

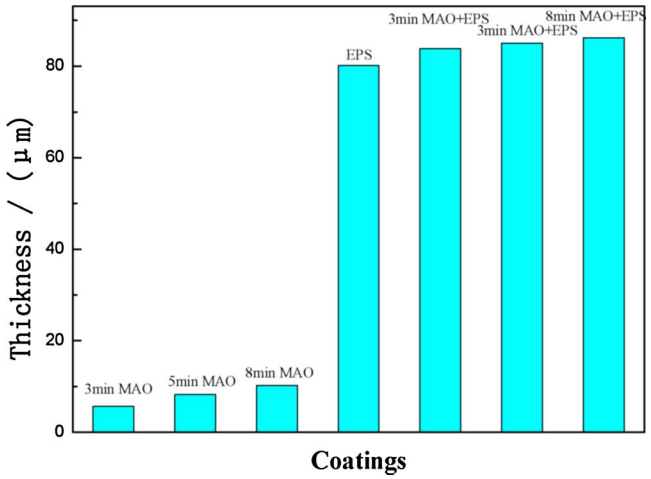

Fig. 1. Thickness of different coatings on magnesium alloy.

$$\nu = (m_0 - m_1)/S \quad (1)$$

Where m_0 is the original weight (g), m_1 is the weight (g) after corrosion, S is the surface area (m^2) exposed in the acid solution.

3. Results

Fig. 1 shows the thickness of the coatings on magnesium alloy, 3 min MAO, 5 min MAO, 8 min MAO, EPS, 3 min MAO + EPS, 5 min MAO + EPS, and 8 min MAO + EPS. It could be seen that the thickness of 3 min MAO, 5 min MAO, and 8 min MAO was 5.72 μm, 8.24 μm, and 10.22 μm, respectively. The thickness of EPS monolayer was 80.10 μm. Theoretically, the thickness of 3 min MAO + EPS, 5 min MAO + EPS, 8 min MAO + EPS coatings should be 85.82 μm, 88.34 μm, 90.32 μm, which was higher than the actual values of the three composite coatings. Furthermore, a decreasing trend of the overall thickness of three composite coatings had been shown with the increase of the thickness of MAO coatings. This was due to the distribution of a large number of micropores on the MAO coatings, resulting in the epoxy resin particles filling into the pores after the EPS treatment [20].

Different from a typical porous morphology with micropores and micro cracks of the as-prepared MAO coating, the surface morphology of MAO + EPS composite coating as shown in Fig. 2a was smooth and free of micropores. The MAO coating was covered by EPS coating, mainly consist of epoxy resin, and the coating surface was smooth and compact without any defects. Fig. 2b showed the cross-section morphology of MAO + EPS coated Mg samples. It was found that about 85 μm thick of uniform organic EPS coating reached the bottom of the pores in MAO coating with 10 μm thick and was locked into the discharge channels, which demonstrated a relatively dense and more uniform structure, implying that the top EPS coating layer completely sealed the micro pores and cracks of MAO coating. The open pores on the surface of MAO coating were fully filled with the EPS material to enhance the bonding strength of the organic coating.

Fig. 3 shows the cross-section magnified SEM images and EDS result of MAO + EPS composite coating. It could be seen that the MAO

Table 1
Parameters of EPS process.

Powder	Carrier gas	Flour output	Voltage	Current	Curing time	Curing temperature
Epoxy resin	N_2	20%	80 KV	25 μA	15 min	185 °C