

COMPOSITE COATINGS COMBINING PEO LAYER AND EPD LAYER ON MAGNESIUM ALLOY

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Abstract

Protective composite coatings were prepared combining plasma electrolytic oxidation (PEO) treatment and cathodic electrophoretic deposition on magnesium alloy AZ91D. The corrosion protection of composite coatings were evaluated using potentiodynamic polarization measurements in 3.5% NaCl solution, copper accelerated acetate salt spray (CASS) test and immersion test in acid solution. The adhesion of composite coatings was evaluated using cross-cut test and pull-off test. It is indicated that the corrosion resistance of magnesium alloy AZ91D with the composite coatings is improved obviously compared to it merely with PEO coating and it is also shown that pitting corrosion of PEO coating on magnesium alloy is decreased with EPD post-treatment. The adhesion of composite coatings could be up to 11.3 N/mm² in quantitative method due to the interlocking effect of organic layer in pores of PEO layer.

Introduction

Magnesium and its alloys are considered to be the most promising material in the field of structural materials for its advantageous properties including low density, high strength-to-weight ratio, good electromagnetic shielding and easy recycled. Therefore it is available in applications including automobile, aerospace components and computers [1-3]. Unfortunately, magnesium and its alloys are susceptible to galvanic corrosion, which greatly limits its use in harsh environments.

It is one of the effective ways to prepare coating on magnesium alloy to improve corrosion prevention. Thus a number of coating techniques appears, including electrochemical plating, conversion coating, gas-phase deposition, plasma electrolytic oxidation (PEO), cathodic electrophoretic deposition [4-6]. Among them, PEO is a new and effective way to magnesium alloy and the hard PEO coating containing outer layer and inner layer can be formed on magnesium alloy. Unfortunately, pores can be run through the PEO coating formed during continual and intense sparking discharges and gas bubbles on surface [7]. Furthermore, low Pilling-Bedworth (PB) ratio of magnesium oxide to metal substrate make PEO coating much loose. Therefore a number of posttreatment were developed to protect the magnesium alloy from corrosion ions more effectively. Duan Hongping [8] combined PEO and multi-immersion technique to improve corrosion resistance of magnesium alloy AZ91D. Zeng Liyun reported a composite coating produced by PEO and electroless plating on magnesium alloy AZ91D [9].

However, there are restrictions for previous technologies in severe environment. Thus it is necessary to develop new methods. At present EPD technology is one of best promising method to corrosion protection on the magnesium alloy. However, it is difficult to directly apply EPD to magnesium alloys due to the following reasons: (1) The magnesium alloys are severely corroded in aqueous electrolytes; (2) The loose MgO formed on

surface of magnesium alloy rapidly inhibit successive electrodeposition and reduce the adhesion of the EPD coating; and (3) Magnesium alloys are easily dissolved in cathodic electrophoretic solutions below pH 7 [6]. A combination of the PEO and EPD to prepare composite coating on magnesium alloys is promising to improve corrosion prevention.

Therefore, a composite coating on magnesium alloy AZ91D prepared combining PEO and EPD has been developed in this paper. The surface and cross-section morphological of the composite coating on magnesium alloy AZ91D was investigated using SEM. The corrosion protection of composite coatings on magnesium alloy AZ91D was evaluated using potentiodynamic polarization, copper accelerated acetate salt spray and immersion test in acid solution. The adhesion of composite coatings was determined using cross-cut test and pull-off test.

Experimental

Rectangular samples in dimension of 50mm×50mm×1mm cut from die-cast magnesium alloy AZ91D (Al 8.5-9.5%, Zn 0.50-0.90%, Mn 0.17-0.27%, Mg balance) were used as working electrode and stainless steel were used as counter electrodes. The samples were polished with SiC paper (grade 400, 800, and 1200) and degreased with acetone followed by rinsing with distilled water before PEO process. Then PEO coating on magnesium alloy were prepared in 8 g/L Na₂SiO₄, 10 g/L KF and 2 g/L NaOH solution under pulsed DC mode, the current density was controlled constant at 0-10 A/dm².

Then the PEO samples were cleaned using ultrasonic cleaning machine. Organic coating was deposited at 100-200V voltage in 30-240 seconds on the PEO coating in cell as shown in Figure 1. the samples with PEO was used as the cathode, the stainless steel as the anode. Then the coated samples were rinsed with distilled water and baked in infrared oven at 160-170 °C for 20-30min.

The surface and cross-section morphologies of PEO coating and composite coatings were investigated in JSM-6360IA scanning electron microscopy (SEM). Thickness and roughness of PEO coating were evaluated using TR200 roughometer.

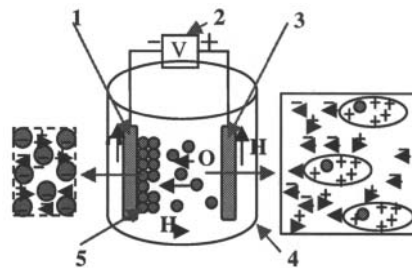


Figure 1. Schematic diagram of apparatus for EPD on PEO coating: 1. sample with PEO coating, 2. power supply unit, 3. stainless steel 4. cell, 5. electrochromic paint.

The corrosion protection of PEO coating and composite coatings was investigated using PS-268A at scan rate of 1 mV/s. Copper accelerated acetate salt spray (CASS) was carried out up to 320 h on composite coatings. The corrosion solution, containing 50g/L NaCl, 0.26g/L $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, was used, which pH was adjusted among 3.0-3.1 with glacial acetic acid. The test was operated in continuous spray conditions at temperature of 50 °C. Samples were inspected for every 24 h.

The corrosion rate of composite coatings with different parameters is evaluated using immersion test in acid solution. The test is operated at 24-26 °C in 0.1 mol/L H_2SO_4 solution. The weight loss of samples was evaluated to the FS-1006 electronic balance every 3-5h.

The adhesion of composite coatings was determined by qualitative method called cross-cut test according to GB/T 9286-1998 and quantitative method called pull-off test equipped with Elcometer F106 adhesive tester.

Results and Discussion

Microstructure

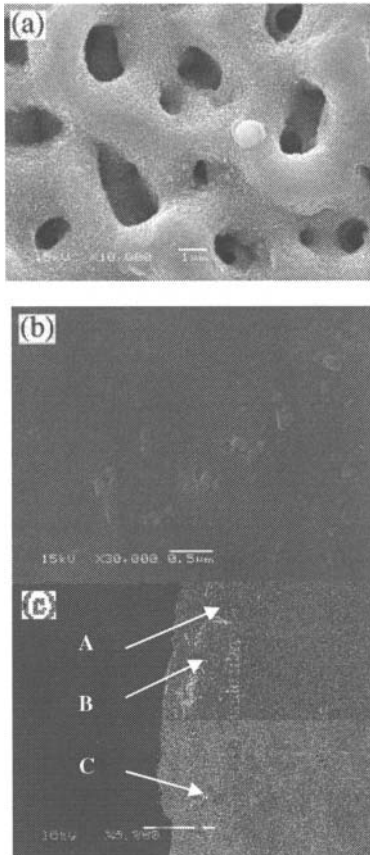


Figure 2. (a) surface morphology of PEO coating (b) surface morphology of composite coating (c) cross-section of composite coating.

Figure 2a shows surface of PEO coating. It is presented that micro-pores are randomly distributed on the PEO coating due to impact or tunneling ionization during PEO process. Figure 2b and Figure 2c shows the surface and cross-section morphologies of composite coatings. It is shown in Figure 2b that there are few micro-pores on composite coatings, whereas the formation of mechanical interlocking between PEO layer and EPD layer as in location of A, B and C is presented through the penetration of organic resin into PEO micropores as shown in Figure 2c.

Potentiodynamic Polarization

The corrosion protection of the PEO coating and the composite coatings are evaluated using potentiodynamic polarization in 3.5% NaCl solutions. Figure 3 presents the potentiodynamic polarization curves of the substrate, the PEO coating and composite coatings in different parameters. Table I is a summary of the potentiodynamic polarization parameters. It is indicated that the corrosion current (i_{corr}) of samples with PEO coating are very lower than that of magnesium alloy substrate, but the corrosion current (i_{corr}) of samples with PEO coating are higher than all that of composite coatings, the corrosion current of composite coatings was decreased by three orders of magnitude in comparison to magnesium alloy substrate and was decreased by two orders of magnitude in comparison to the sample with PEO coating, whereas the polarization resistance (R_p) of the composite coatings is higher than the sample with PEO coating by one order of magnitude. It is demonstrated that the corrosion resistance of magnesium alloy has been obviously improved with composite coating.

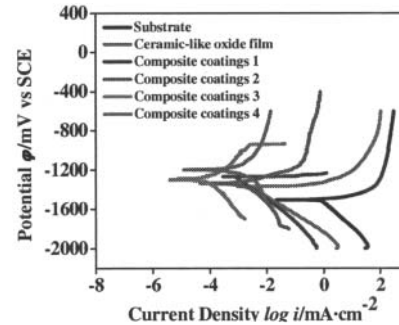


Figure 3. Potentiodynamic polarization curves of the substrate, the PEO coating and the composite coatings.

Table I. Results of the potentiodynamic corrosion tests in 3.5 % NaCl solution.

Samples	E_{corr} (V vs SCE)	i_{corr} (A/cm ²)	R_p (Ω)
Substrate	-1.501	3.0281×10^{-4}	7.1791×10^1
PEO coating	-1.367	1.3120×10^{-5}	1.6570×10^3
Composite coatings 1(EPD in100 V)	-1.267	8.8534×10^{-6}	2.4554×10^3
Composite coatings 2(EPD in130 V)	-1.334	1.5906×10^{-6}	1.3667×10^4
Composite coatings 3(EPD in160 V)	-1.298	2.5482×10^{-7}	8.5310×10^4
Composite coatings 4(EPD in200 V)	-1.198	8.7604×10^{-7}	2.4815×10^4

Copper Accelerated Acetate Salt Spray (CASS)

Copper accelerated acetate salt spray was carried out to investigate corrosion protection of PEO coating and composite coating. The surface morphology of PEO coating for 72 h and composite coatings for 320 h after copper accelerated acetate salt spray is shown in Figure 4. It is indicated that the noticeable corrosion pitting was presented on magnesium alloy with PEO coating after 72 h testing as shown in Figure 4a. There is no noticeable corrosion on magnesium alloy with composite coatings with exception the edge regions until 320 h copper accelerated acetate salt spray testing (Figure 4b).

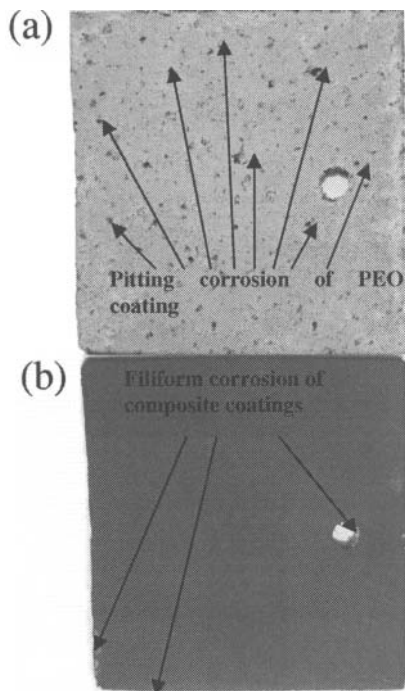
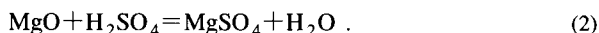
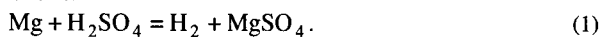


Figure 4. Surface morphology of CASS test for (a) PEO coating after 72 h; (b) composite coatings after 320h.

Weight Loss of Magnesium Alloy with Composite Coatings in Acid Corrosion

The immersion tests were performed in acid solution to evaluate corrosion rate of magnesium alloy with composite coatings. Sample with PEO coating is liberated gas in acid solutions in 25 s, whereas corroded completely in 80 s. The reaction is possible as follows:



The corrosion rate of magnesium alloy with composite coatings combining PEO layer about 17.2 μm in thicknesses for PEO 200s and EPD layer at 28.6 μm 42.3 μm and 48.6 μm in thicknesses for corresponding to EPD for 120V, 160V and 200V, respectively, is shown in Figure 5a. The corrosion rate of the sample with posttreatment EPD for 120V is lower than the sample with posttreatment EPD for 160V, it may be attributed to that water and sulfate radicals can permeate into the thinner PEO coating in

a short time. However, the sample with posttreatment EPD for 200V with the high corrosion rate may be due to the high voltage in posttreatment EPD process.

The samples combining PEO time at 50s, 300s and 900s and EPD for 160V, respectively, have different corrosion rate. Sample 4 with PEO layer 21.6 μm in thickness and with EPD layer 40.7 μm in thickness has the higher corrosion rate than that of sample 5 with PEO layer 33.5 μm in thickness and with EPD layer 57.6 μm in thickness may because that the sample 4 has the thicker organic coating but also has the thinner PEO coating, the corrosion rate increased when the sulfate radical ions permeate into the PEO coating as shown in Figure 5b. However, sample 6 with PEO layer 40.6 μm in thickness and with EPD layer 71.3 μm in thickness has the high corrosion rate may due to the reason which is same as the sample 3. Therefore, good corrosion resistance of composite coatings was prepared combining PEO and EPD in the suitable parameters process. The corrosion rate of samples in 0.1 mol/L H_2SO_4 solutions with composite coatings in different parameters from 1 to 6 at 10h, 48h was also in Table II. It is indicated that the corrosion products mainly contain oxidation of substrate.

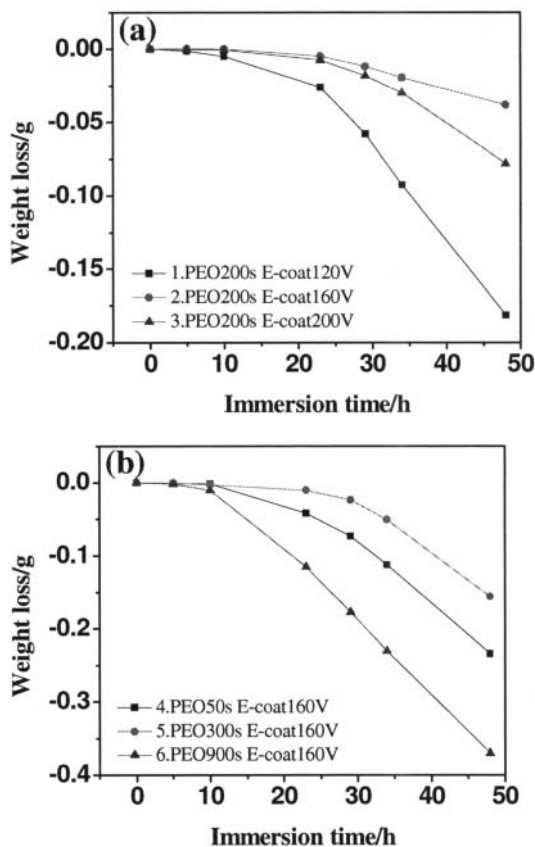


Figure 5. Dependence of weight loss of magnesium alloy with composite coatings on different parameters in acid solution: (a) PEO 200s, different EPD voltage; (b) different PEO time, EPD voltage 160V.

Table II. Corrosion rate of composite coatings in 0.1 mol/L H₂SO₄ solutions.

Samples	1	2	3	4	5	6
After 10h(mg/h)	0.0005	0.0003	0.0001	0.0002	0.0001	0.0010
After 48h(mg/h)	0.0038	0.0008	0.0016	0.0049	0.0032	0.0077

Adhesion of Composite Coatings

The formation of the mechanical interlocking between PEO layer and EPD layer occurs due to the organic layer permeate into the pores of PEO layer. Therefore, the adhesion of composite coatings is related to roughness of PEO coating resulting from the increase of the diameter of pores caused increase of roughness. The variation of roughness for PEO coating with the PEO time is presented as shown in Figure 6 (a). It was apparent that the roughness increased with prolong of the PEO treat time. Figure 6 (b) shows that adhesion of composite coatings was not increasing with increasing of roughness of PEO coating. The value of adhesion for composite coatings is up to 4 N/mm² when roughness of PEO coating is at 0.2245 μm in 3 specimens. However, wettability of electrophoresis paint on PEO coating decrease with increase of roughness of PEO coating, thus electrophoresis paint cannot completely run into the pores of PEO coating.

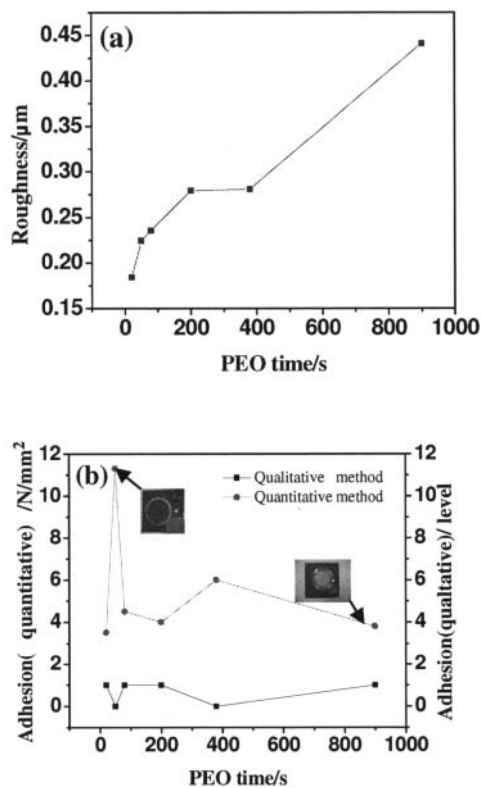


Figure 6. Adhesion (qualitative and quantitative method) variation of composite coatings with the roughness of PEO coating.

Conclusions

The composite coatings prepared combining PEO and EPD have good corrosion resistance in comparison to that with merely PEO coating on magnesium alloy AZ91D. The corrosion protection of composite coatings was superior to the PEO coating by three orders magnitudes. The principle of composite coatings was filiform corrosion rather than the pitting corrosion of PEO coating due to the copper accelerated acetate salt spray. The adhesion composite coatings is up to 4 N/mm² in quantitative method when roughness of PEO coating is 0.2245 μm because of good mechanical interlocking between organic layer and PEO layer.

Acknowledgements

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