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# Structure and corrosion resistance of ZrO<sub>2</sub> ceramic coatings on AZ91D Mg alloys by plasma electrolytic oxidation

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#### ABSTRACT

The aim of this work is to study the structure and the corrosion resistance of the plasma electrolytic oxidation  $ZrO_2$  ceramic coatings on Mg alloys. The ceramic coatings were prepared on AZ91D Mg alloy in  $Na_5P_3O_{10}$  and  $K_2ZrF_6$  solution by pulsed single-polar plasma electrolytic oxidation (PEO). The phase composition, morphology and element distribution in the coating were investigated by X-ray diffractometry, scanning electron microscopy and energy distribution spectroscopy, respectively. The results show that the coating thickness and surface roughness were increased with the increase of the reaction time. The ceramic coatings were of double-layer structure with the loose and porous outer layer and the compact inner layer. And the coating existed in the form of amorphous state, while Zr crystallized in the form of *t*-ZrO<sub>2</sub> and a little *c*-ZrO<sub>2</sub> in the coating. Electrochemical impedance spectra (EIS) and the polarizing curve tests of the coatings were measured through CHI604 electrochemical analyzer in 3.5% NaCl solution to evaluate the corrosion resistance. The polarizing curves tests.

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#### 1. Introduction

Magnesium and its alloys have been applied in many fields like aerospace, automobile, computer, etc., due to the excellent low density, high strength to-weight ratio and mechanical castability [1-3]. Unfortunately, the high susceptibility to corrosion of magnesium alloys greatly restricts their further application. Therefore, some kinds of techniques like surface oxidation, PVD/CVD coating or ion implanting are studied by many researchers [4–7] to improve the corrosion resistance of magnesium alloys. Among these methods, plasma electrolytic oxidation (PEO) is considered as one of the most promising surface treatment techniques of the Mg alloys [8-10]. At present, much research on PEO technique is being focused on the preparation of the ceramic coatings on magnesium alloys in widely adopted alkaline electrolytes such as phosphate, silicate, or sodium hydroxide solutions and so on. And meantime the growth characteristics of the coating on magnesium alloy in these electrolyte systems were also studied by some researchers [11-16].

Besides, ZrO<sub>2</sub> ceramic coatings on Al, Ti or Mg alloys by PEO method have been attracted much attention recently since Schukin

et al. for the first time reported the preparation of  $ZrO_2$  coatings on Al alloys in  $K_2ZrF_6$  solution in 1996 [17–21]. Except adding dispersed  $ZrO_2$  or  $Zr(OH)_4$  particles in the other electrolytes [22–24] or adopting  $Zr(SO_4)_2$  electrolyte directly [19], fluorozirconate electrolyte is the most often adopted one to prepare  $ZrO_2$  ceramic coating up to now [25–29]. In most cases of PEO process, such additives as  $H_3PO_4$  and  $NaH_2PO_4$  was used fluorozirconate electrolyte system to keep the PEO process carrying out under an acid environment. In this work the sodium tripolyphosphate ( $Na_5P_3O_{10}$ ) was used to make the pH of the electrolyte solution nearly equals to 7 because of the pollution of the acid electrolyte to the environment. Meantime, the phase composition, structure and corrosion resistance of the  $ZrO_2$  ceramic coatings on an AZ91D Mg alloy were investigated.

#### 2. Experimental details

#### 2.1. Preparation of ceramic coatings by plasma electrolytic oxidation technique

Plate samples of AZ91D Mg alloy with a reaction dimension of  $15 \,\mathrm{mm} \times 20 \,\mathrm{mm} \times 0.6 \,\mathrm{mm}$  were used as working electrode and the electrolyser made of stainless steel served as the counter electrode. The electrolyte used in the experiment was Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> with the concentration of 3 g/L and K<sub>2</sub>ZrF<sub>6</sub> with the concentration of 1 g/L. A home-made high power pulsed single-polar electrical source with power of 5 kW was used for plasma electrolytic oxidation under the pulsed current density of 10A/dm<sup>2</sup> for different time. The duty ratio was 50% and the working frequency was 500 Hz. The reaction temperature was controlled to be

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Fig. 1. Thickness of the coatings prepared for different time.

below 30  $^{\circ}$ C by adjusting the cooling water flow. After the treatment, the coated samples were flushed with water and dried in air.

#### 2.2. Analysis of phase composition and structure of the coatings

Phase composition of the coatings was examined with XRD (D/max-rB, RICOH, Japan) with a Cu K $\alpha$  source. Surface images of the produced coatings were studied with SEM (S-570, Hitachi, Japan). The elemental distribution was investigated by energy-dispersive spectroscopy (EDS; US PN5502). The coatings' thickness was measured, using an eddy current based thickness gauge (CTG-10, Time Company, China). In this experiment, the average thickness of each of the triplicate samples was obtained from 10 measurements at different positions.

#### 2.3. EIS of the ceramic coatings

EIS spectra of the coatings were measured in a three-electrode cell (a Pt plate was used as a counter electrode, a calomel electrode as an auxiliary electrode, and the coated sample as a working electrode with the reaction area of 1 cm<sup>2</sup>) through CHI604 electrochemical analyzer (Shanghai, China) in 3.5% NaCl solution. A sinusoidal AC perturbation of 5 mV was applied to the electrode at the open circuit potential of the coated samples over the frequency range 0.1 Hz-100 kHz.

#### 2.4. The corrosion resistance of the coatings

The corrosion resistance of the coatings was evaluated by the polarizing curves in 3.5% NaCl solution, using the same three-electrode cell as in 2.3. The polarization curve's scanning rate was 1 mV/s, with a scanning range from -0.25 V of open circuit potential to +0.25 V of open circuit potential.

#### 3. Results and discussion

#### 3.1. The thickness of the coatings

At the initial stage of the PEO process, the anode pulse voltage was increased quickly and reached the breakdown voltage of the oxide film within 2 min. From this moment the reaction time was recorded. The voltage was increased gradually to the designed reaction time under the fixed current density. Fig. 1 is the thickness of the coating prepared for different time. Clearly, the coating thickness was increased linearly with the reaction time. Through the line fitting of the thickness *vs.* time, with the result shown in formula (1):

Thickness 
$$(\mu m) = 6.476 + 1.537 \times \text{Time (min)}$$
 (1)

The growth rate of the coating was  $1.537 \,\mu$ m/min or so under the experimental conditions. Actually, it can be found from Fig. 1 that in the initial 2 min stage of PEO process, the coating with the thickness of about 6.476  $\mu$ m already generated on the substrate. Table 1

The relative contents of main elements on the surface of the coating by EDS analysis (atom%).

| Time/min | Zr   | Mg   | Al  | Р    | K   |
|----------|------|------|-----|------|-----|
| 5        | 8.9  | 14.9 | 2.2 | 73.0 | 1.0 |
| 10       | 10.4 | 12.9 | 0.1 | 75.3 | 1.3 |
| 20       | 37.5 | 7.8  | 0   | 51.8 | 2.9 |
| 30       | 32.5 | 9.6  | 0   | 54.3 | 3.6 |

## 3.2. The morphologies and the element distribution of the coatings

Fig. 2 is the surface images of the coatings for different time. There were some residual discharging channels and many microholes on the coating surface. Meantime, there were some cracks and bumps. Increasing the PEO time, the cracks and the bumps were enlarged and the coating became rough and uneven. The relative contents of the main elements on the surface of the coating was analyzed by EDS under the spatial resolution of 200s, with the results shown in Table 1, it can be noted that the coating was composed of P, Zr, Mg and K, of which P and Zr were the main elements in the coating. At the initial stage of the PEO reaction, much P from the electrolyte joined the PEO reaction. But increasing the reaction time, the amount of P in the coating surface was gradually decreased so that the amount of Zr was more than that of P for in the coating. The amount of Mg in the coating surface was decreased with the reaction time in general, which illustrated that the amount of Mg joining PEO process was reduced with the reaction time. Meantime, a little Al from the substrate was also checked on the surface of the coating of the short time.

Fig. 3 is the section morphologies of the coatings for different time. There were many micro-sized cracks and pores in the coating. The coating for 10 min was comparatively compact and its thickness was generally uniform. Increasing the reaction time, the coating thickness was increased, but the coating thickness was much less than the measured results by CTG-10. This is because the coating surface was so loose and coarse that it was easily embedded or destroyed by the mounting resin. Besides, the coating was of double layer structure: the outer layer was much loose and porous whereas the inner layer was comparatively compact.

#### 3.3. Phase analysis of the coatings for different time

Fig. 4 is the XRD patterns of the coatings prepared for different time. From which it follows that the coating was composed of t-ZrO<sub>2</sub> and a little c-ZrO<sub>2</sub>. According to the intensities of the diffraction peaks, the amount of ZrO<sub>2</sub> can be approximately compared for the coatings of different time. Increasing the reaction time, the amount of ZrO<sub>2</sub> was increased in general. However, when the reaction time was 20 min, the intensity of diffraction peaks corresponding to the ZrO<sub>2</sub> was lower than that when reaction time was 10 min, which seemed that the amount of ZrO<sub>2</sub> was reduced. This conflict may be related to the penetration depth of X-rays. The extending of the reaction time increased the coating thickness, and correspondingly decreased the penetration depth of X-rays, which maybe led to the decrease of the detected amount of ZrO<sub>2</sub>. However, P and K in the coating were not crystallized, whether its amount was more or less; and Mg and Al from the substrate were not in the form of the crystalline in the coating yet. This may be related to the quick cooling speed by the electrolyte during the PEO process. A large amount of Zr and P from the electrolyte solution joined the PEO reaction and formed the coating. Therefore, the coating thickness was mainly determined



Fig. 2. The surface morphologies of the coatings for different time (a): 5 min; (b): 10 min; (c) 20 min; (d): 30 min.

by the contents of Zr and P. Besides, the diffraction peaks corresponding to the substrate can also exist in the patterns, but their intensity was generally decreased with the increasing time. But, there also existed the exceptions, which may be related to the pores and the cracks induced in the coatings discussed in Section 3.2.

#### 3.4. EIS analysis of the coatings

Fig. 5 is EIS (Bode plot) of PEO ceramic coatings for different time in 3.5% NaCl solution, which clearly shows that the impedance values and phase angles look greatly different as the reaction time was increased. The impedance values were increased with the decrease of the frequency to different extents. It can be noted from the phase angle extremum in panel (b) that there was only one time constant for the Mg alloy substrate, which was obviously corresponding to the capacitance of the double layer of the electrode interface ( $C_{dl}$ ). But, there were two differentiated time constants for the coatings of 1 min and 5 min, which should also be corresponding to the capacitance elements of the equivalent circuit. Increasing the reaction time, the coating electrode became porous and rough, the relaxation effect of the electrode surface was strengthened, by which the two time constants may be overlapped and seemed to become one.

Based on the above analyses and the porous double-layer structure of the coatings in Fig. 3, the EIS equivalent circuit for the PEO coatings on magnesium alloy AZ91D is presented in Fig. 6 with the fitted results shown in Table 2.  $R_s$  was the solution resistance, which was determined by the conductance of the NaCl solution, therefore, all the  $R_s$  were almost the same.  $R_1$  and  $C_1$  were corresponding to





Fig. 3. The section morphologies of the coatings for different time. (a): 10 min; (b): 20 min.



Fig. 4. XRD patterns of the coatings and the AZ91D substrate.

| Table 2  |
|--|
| Impedance fitting values of the coatings prepared for different time |



Fig. 5. EIS (Bode plot) of PEO ceramic coatings for different reaction time and the AZ91D substrate.

the outer layer of the PEO coating.  $R_2$  and  $C_2$  were corresponding to the inner layer of the PEO coating.

With the increase of the reaction time, the value of  $C_1$  was decreased gradually. Because  $C_1$  was in series with  $C_2$  and much less than  $C_2$ , therefore, the whole capacitance of the coating was determined by the  $C_1$ . The phase angle extremums in panel (b) were decreased and moved to the low frequency area with the increasing reaction time, which meant that the capacitance interface was weakened. This just complied with the changing regularity of the value of  $C_1$ . The value of the  $C_2$  in Table 2 changed little, which showed the inner layers of all the coatings had the similar capacitance features. Besides, the values of  $R_1$  and  $R_2$  were decreased first and then increased, which was related to the density and the thickness of the coatings.  $R_2$  was much larger than  $R_1$ , which showed

| 1 0    |                                    |                              |                           |                              |                         |
|--------|------------------------------------|------------------------------|---------------------------|------------------------------|-------------------------|
|        | $R_{\rm S}$ (ohm cm <sup>2</sup> ) | $R_1$ (ohm cm <sup>2</sup> ) | $C_1 ({\rm F}{\rm cm}^2)$ | $R_2$ (ohm cm <sup>2</sup> ) | $C_2 ({ m F}{ m cm}^2)$ |
| 1 min  | 24.10                              | 260.3                        | $2.017\times10^{-7}$      | 8260                         | $2.187\times10^{-6}$    |
| 5 min  | 25.34                              | 256.1                        | $1.793 	imes 10^{-7}$     | 7517                         | $3.306 \times 10^{-6}$  |
| 10 min | 28.22                              | 105.8                        | $1.616 \times 10^{-7}$    | 4151                         | $2.733\times10^{-6}$    |
| 20 min | 26.80                              | 401.8                        | $6.241 	imes 10^{-8}$     | 5594                         | $4.749\times10^{-6}$    |
| 30 min | 24.65                              | 896.1                        | $2.947\times10^{-8}$      | 5902                         | $8.208\times10^{-6}$    |
|        |                                    |                              |                           |                              |                         |



**Fig. 6.** Equivalent circuit used for PEO coatings on AZ91D magnesium alloy in 3.5% NaCl solution.  $R_5$  is the solution resistance,  $R_1$  and  $C_1$  are corresponding to the outer layer of the PEO coating,  $R_2$  and  $C_2$  are corresponding to the inner layer of the PEO coating.

that the density of the inner layer was much more than that of the outer layer although the thickness of the inner layer was less than that of the outer layer. The values of  $R_1$  and  $R_2$  of the coatings for short PEO time were comparatively large; this was mainly due to the high density of the formed coatings at the initiate stage. Increasing the reaction time, the decrease of the values of  $R_1$  and  $R_2$  was due to the increase of the porosity and the cracks of the coatings. However, increasing the reaction time further, the values of  $R_1$  and  $R_2$  were increased again, which was mainly attributable to the increase of the coating thickness. Therefore, the EIS of the coatings reflected the structure of the coating with the increasing PEO time.

#### 3.5. The corrosion resistance of the coatings for different time

Generally, it is considered that the impedance values measured at the low frequency area in the EIS spectra can reflect the corrosion resistance of the coatings. Considering the established EIS equivalent circuit in Fig. 6, the polarization resistance  $R_p$  of the coatings should approximately equal to the sum of the  $R_1$  and  $R_2$ , which was completely corresponding to the impedance values measured at the low frequency area in the EIS spectra. The corrosion resistance of all the coatings was much better than that of the Mg alloy substrate, and the coating prepared for the 1 min was the best, and then increasing the reaction time, the corrosion resistance of the coating was decreased first and then increased again. In order to assess the corrosion resistance of the coating samples, the polarizing curve method was used to calculate the corrosion current density of the coating samples for different time and the substrate in 3.5% NaCl solution with the results shown in Fig. 7, which also presented the same regularity as the results of R<sub>p</sub> obtained from EIS analyses. According to the above analyses, the general corrosion resistance of the coatings was mainly



**Fig. 7.** The corrosion current density of the coatings and AZ91D substrate in 3.5% NaCl solution by polarizing curve method.

determined by the density of the coatings, not the coating thickness. And the extending of the PEO time was not liable to improve the density of the coatings although increasing the coating thickness.

#### 4. Conclusions

Ceramic coatings on AZ91D Mg alloy were prepared by plasma electrolytic oxidation in tripolyphosphate-potassium fluorozirconate solution, the research on the composition, structure and corrosion resistance of coatings allowed the following conclusions to be drawn:

- (1) The PEO ceramic coatings on AZ91D Mg alloy were composed of t-ZrO<sub>2</sub> and a little c-ZrO<sub>2</sub>. With the increase of the reaction time, the coating thickness was increased linearly and the coating turned rough. And the coating was of double-layer structure and the out layer was loose while the inner layer was comparatively dense. EDS analysis showed that the coating was composed of P, Zr, Mg and K, of which P and Zr were the main elements in the coating.
- (2) EIS and the established equivalent circuit were corresponding to the double-layer structure of the coatings. Besides, the polarization resistance  $R_p$  (the sum of the  $R_1$  and  $R_2$  in the equivalent circuit) can reflect the corrosion resistance of the coatings for different time, which was consistent with the corrosion current density of the samples obtained through the polarizing curves. The corrosion resistance of the coatings was much better than that of the Mg alloy substrate. And the coating prepared for 1 min had the best corrosion resistance mainly due to its better density.

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