

Study on Preparation, Microstructure and Properties of Micro-Arc Oxidation Ceramic Coating on AZ91 Magnesium Alloy in Phosphate Electrolyte

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Abstract. The micro-arc oxidation behavior of AZ91 magnesium alloy in alkaline phosphate electrolyte was studied. The effect of phosphate on the microstructure and properties of micro-arc oxide film was investigated and characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), scanning electron microscope (SEM), energy dispersive spectrum (EDS) and salt spray test. The results show that phosphate concentration has an important effect on the surface morphology, phase structure, thickness and corrosion resistance of micro-arc oxidation film. With the increase of phosphate concentration from 5g/L to 30g/L, the film quality decreases, the surface roughness increases, the thickness decreases and the corrosion resistance decreases. So in phosphate electrolysis the lower phosphate concentration in the liquid system is helpful to the formation of better film quality.

1. Introduction

AZ91 is the most widely used magnesium alloy, because of its high specific strength and specific stiffness, good damping and shock absorption, good casting performance and easy to be recycled[1-3]. It is widely used in electronic, automotive, aviation and various consumer goods. However, the standard electrode potential of Mg is extremely low ($E_0 = -2.37\text{V}$), so the magnesium alloys are vulnerable to corrosion and oxidation in the process of use[4-5]. In order to improve the corrosion resistance and oxidation resistance, now there are three ways to be used. One is the microalloying of magnesium alloys, the second is to develop various coating treatment techniques, the third is to design more reasonable component connection mode and component matching mode to reduce or avoid chemical corrosion. Micro-arc oxidation is a coating treatment technology, which can produce ceramic coating in situ on the surface of magnesium alloy, greatly improving the corrosion resistance and friction resistance of magnesium alloy. The study of micro arc oxidation technology in America, Japan and Germany began in the 70s of last century, but in China only in 90s of last century began to do this research work. At present, the research on micro-arc oxidation technology of Al, Mg, Ti alloys at home and abroad has been extensive and thorough. The research contents include micro-arc oxidation mechanism, electrolyte formula, electric parameters, oxidation process and so on[6-11]. Although a great deal of work has been done on the micro-arc oxidation technology, there is still a long way to go from the maturity of the technology and the large-scale industrial application. At present, only a few enterprises at home and abroad are popularizing and applying, such as ALGT, Microplasmic Corporation and Keronite, etc[12]. Therefore, it is the only way to promote the development of the technology by continuing to study the process parameters and mechanism. In this paper, AZ91 magnesium alloy was used as substrate to prepare ceramic coating in phosphate electrolyte, and the mechanism of film formation was discussed, and the relationship between microstructure and



properties was established. The aim is to provide theoretical and experimental support for the development of this technology.

2. Materials and Experimental Procedures

The experimental material was AZ91 magnesium alloy, and its chemical composition(wt.%) shows down:Al:8.56,Mn: 0.82, Zn: 0.41, Mg: Bal.. The specimen was rectangular solid(50mm×30mm×4mm). Their treat procedure followed: magnesium ingot→cutting→drilling→rough grinding→fine grinding→polishing→cleaning→degreasing→micro-arc oxidizing→testing. The power supply style of micro-arc oxidizing was MOP-60 which researched by ourselves. Its power was 42KVA. Electrolytic solution was alkaline solution that its major composition was phosphate(Na_3PO_4 :5-30g/L, NaOH :1-5g/L, KF :5-8g/L, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$:0.5-2g/L, EDTA :0.5-2g/L). The whole reaction process was controlled by constant current, current density was $20\text{A}/\text{dm}^2$, the reaction temperature was $20\text{--}40^\circ\text{C}$, the oxidizing time was 30min.

TEM analysis of micro-arc oxide film was carried out at JEM-2010 HRA produced by Hitachi, Japan. To get TEM thin foils, the samples were pre-thinned by electrolysis with single face firstly. The electrolytic double spray apparatus was Tenupol-2, the electrolyte composition was as follow:5.3gLiCl+11.2gMg(ClO_4)₂+100mL $\text{C}_6\text{H}_{14}\text{O}_2$ + 500mL CH_3OH . When spraying the temperature was controlled at about -30°C , the current was 0.12A, the voltage was 40-60V. After double jet thinning, the sample continued to be reduced by ion reducer machine whose style was GL6900, made in China. Thinning working voltage was 5-7KV, the current was 0.15-0.3mA, the incident angle was $15\text{--}20^\circ$.

The surface morphology of the micro-arc oxide film was observed on Leo 1530V with EDS analysis. The phase structures of the film determined with a X-ray diffractometer(XRD, X-pert MPD.Pro, Philips company, made in Holland). The film thickness was measured with an eddy current coating thickness meter(phynix, made in Germany). The corrosion resistance of the film was evaluated by neutral salt spray test. The test was carried out according to the national standard (GB/T10125-1997, artificial atmosphere corrosion Test—Salt spray Test), the machine style was FQYO/0A(produced by Shanghai Experimental instrument General Factory in China), the corrosion time was 36 hours. The surface roughness of the micro-arc oxidizing film was measured using surface profilometer(BMT expert3D, BMT Company, made in Germany).

3. Results and Discussion

3.1. Effect of Phosphate Concentration on the Process of Micro-Arc Oxidation

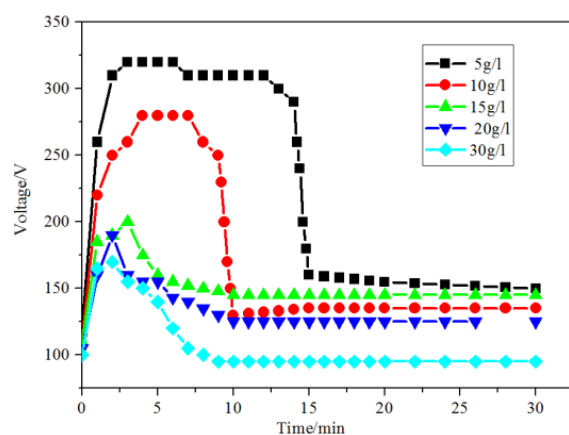


Figure 1. Effect of phosphate concentration on tank voltage in constant current mode

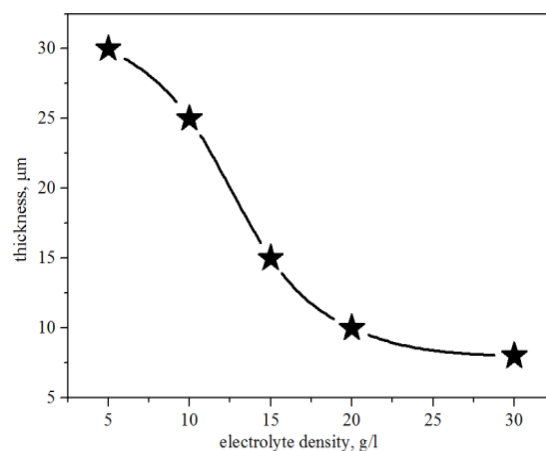


Figure 2. Effect of phosphate concentration on film thickness

Figure 1 studies the effect of phosphate concentration on tank voltage during micro-arc oxidation. According to the curve of the relationship between voltage and treatment time, the micro-arc oxidation process of AZ91 magnesium alloy can be divided into four stages.

The first stage corresponds to the rapid rising phase of the curve, which ranges from a few seconds to a few hundred seconds, which is related to the composition of the electrolyte. There were no arcs on the surface of the samples at this stage, but a large number of bubbles appeared, corresponding to the anodizing stage of the sample, the passivation layer was formed by anodic oxidation, which was a prerequisite for the appearance of micro-arc oxidation. The second stage of the curve is the peak platform stage, when the sample enters the micro-arc oxidation, a large number of small flicker and fast moving arc spots appear on the surface of the sample, accompanied by the explosion sound and a large number of bubbles. The length of the peak platform is determined by the process parameters. The third stage of the curve is the rapid drop in voltage. The duration of this phase is also determined by process parameters, ranging from tens of seconds to hundreds of seconds. At this time, the small arcs on the surface of the samples are less and less, accompanied by the appearance of some larger arcs, which move slowly or even gather in one place. The voltage of the fourth stage of the curve decreases to a certain value basically no change. At this time the surface of the sample basically can not see the arc spot, but there are bubbles coming out, this stage is the phase of extinguishing the arc.

It can be seen from the relationship curve that the concentration of phosphate has a significant effect on the oxidation tank voltage. First, it affects the striking voltage of micro-arc oxidation and the rising speed and duration of the first stage. With the increase of phosphate concentration, the starting arc voltage decreases from 310-320V with the concentration of phosphate is 5g/L to about 180-190V with the concentration of phosphate is 30g/L. One of the explanations is that the increase of ion concentration increases the conductivity of electrolyte, and the increase of conductivity is favorable to the decrease of starting voltage[13-14]. Second, the concentration of phosphate affects the peak platform survival time of micro-arc oxidation. With the increase of phosphate concentration, the peak platform survival time shortens. At 5g/L and 10g/L, the peak platform lasts longer, and the peak platform's duration is shorter than that of 15g/L. The peak platform stage is the normal growth stage of the micro-arc oxide film, and the longer the time is, the more favorable the growth of the film is. Third, the concentration of phosphate affects the voltage drop rate in the third stage of micro-arc oxidation, and decreases with the increase of the concentration. The high falling rate is beneficial to the quality of the oxide film and can reduce the damage caused by the large arc spot on the surface of the film. Fourth, the concentration of phosphate also affects the termination voltage of micro-arc oxidation, the general trend is that the termination voltage decreases as the concentration increases.

Fig.2 shows the relationship between phosphate concentration and film thickness. It can be seen that with the increase of phosphate concentration, the thickness of the film decreases. The thickest film is formed at 5g/L. It is in agreement with the results of the above voltage analysis that at 5g/L the peak platform survival time is longest, which is most favorable to the growth of the oxide film. Therefore, when phosphate is used as main film forming salt, low salt concentration should be selected for micro-arc oxidation.

3.2. Morphologies of MAO Coating

Figure 3 studies the effect of phosphate concentration on the morphology of the surface during micro-arc oxidation with current density 20A/dm^2 in constant current mode. It can be seen from the results that when phosphate concentration is low, the surface of the film is smooth, even and compact when the phosphate concentration is 5g/L and 10g/L(Fig.3a, Fig.3b), and when the concentration is relatively high(15g/L, 20g/L and 30g/L), the surface of the film is relatively rough, uneven and loose(Fig.3c, Fig.3d and Fig.3e).

Fig.4 shows the relationship between the roughness and the phosphate concentration. The surface roughness of the film increases with the increase of phosphate concentration, which is consistent with the observation by SEM. The results of the analysis in figure 1 show that the phosphate concentrations of 5g/L and 10g/L allow the sample to have a longer time of micro-arc oxidation at the peak platform stage, which corresponds to small and dense arcs. As a result, the surface of the film is smooth and compact, and the time of rapid voltage drop is very short, the corresponding larger arc spot appears in

a shorter time, and the damage to the surface of the film is also relatively slight. Therefore, The higher the mass of the film formed in the micro-arc oxidation stage, the more favorable to reduce the destruction of the large arc spot. However, the peak platform duration of phosphate concentration of 15g/L, 20g/L and 30g/L is shorter, which is not conducive to the growth of the film, and the time of falling stage is longer, the duration of large arc-spot is longer, and the damage effect of the film is greater[15-17]. The region marked by A, B, and C (Fig. 3c, Fig. 3d, Fig. 3e) should be the result of a large arc spot effect. Therefore, in order to obtain smooth, compact and high quality coatings in phosphate electrolyte, the micro-arc oxidation should be carried out at lower concentration.

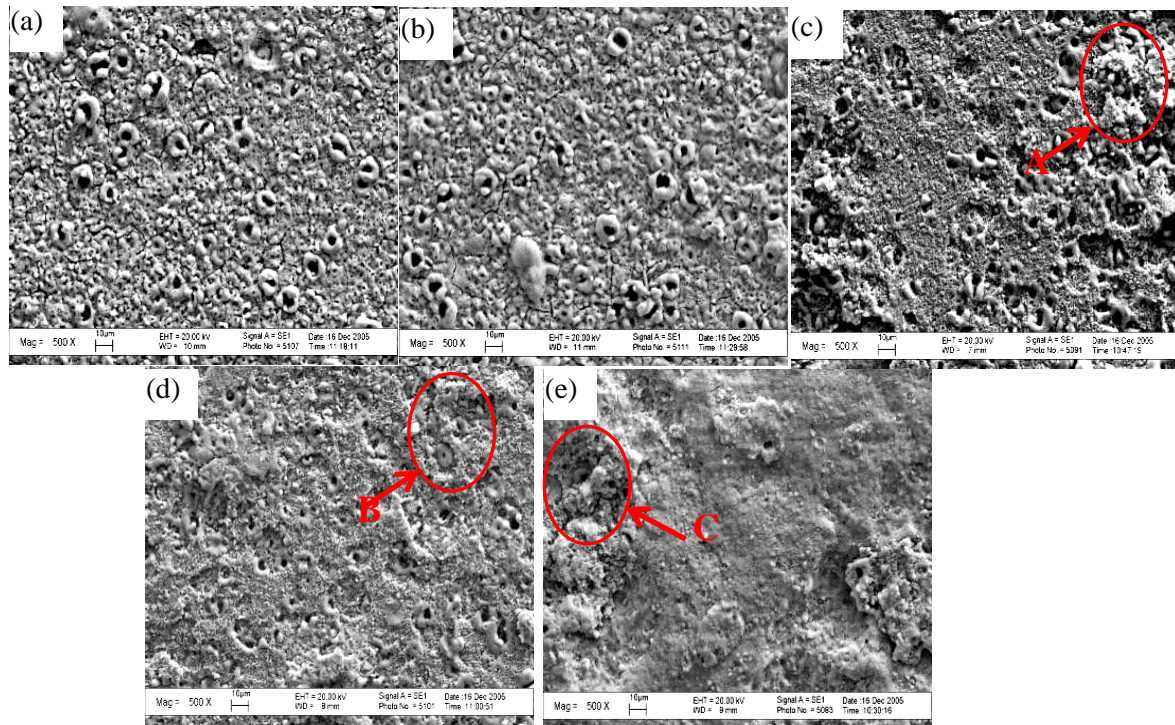


Figure 3. Effect of phosphate concentration on surface morphologies of MAO film
(a)5g/L; (b)10g/L;(c)15g/L;(d)20g/L;(e)30g/L

3.3. Phase Structure Analysis of MAO Film

Figure 5 is the result of EDS analysis on the surface of the film. It is shown that the surface of the film is mainly composed of Mg, O, P, Al and a small amount of K, Na elements (the specific content is shown in Table 1). Among them, Mg and Al come from the matrix of the AZ91 magnesium alloy, P, K and Na come from the electrolyte.

XRD patterns of MAO films with different phosphate concentrations are shown in Fig.6. The micro-arc oxide films consist mainly of MgO, $\text{Mg}_3(\text{PO}_4)_2$, MgAl_2O_4 and Mg. The diffraction peak of MgO and $\text{Mg}_3(\text{PO}_4)_2$ intensity is strongest, combining the results of EDS, the two phases are the most abundant in the MAO coatings. However, the K and Na appeared in EDS analysis did not show the corresponding phase in XRD analysis. These two elements should be distributed in the surface layer of the film as the adsorbed form, but the amount of K and Na should be relatively small compared with the whole film layer, so there is no corresponding diffraction peaks.

3.4. TEM Analysis of MAO Coating

Figure 7 shows the TEM observation of the micro-arc oxidation film. Fig.7a is a bright field image, Fig.7.b is a dark field image ($g=(200)$), and Fig.7c is a selective diffraction ring and an amorphous diffraction disk. Through the standardization to the diffraction pattern, it is found that there are MgO and MgAl_2O_4 of crystalline and amorphous states in the region. The crystalline substance mainly exists in nanocrystalline and microcrystalline form in the film (Fig.7a and Fig.7b).

Micro-arc oxidation of magnesium alloys is a plasma discharge process, and the instantaneous temperature in the plasma region can reach 8000K[18]. The matter in this region will be melted and sintered by plasma discharge, which will be condensed to form sintered oxide in the electrolyte system. The temperature difference between the plasma region and the electrolyte is very large, so the cooling rate of the material formed in the plasma discharge region is very high, up to 10^8K/s [19]. At such a high cooling rate, the grain nucleation and growth time of the micro-arc oxide film is very short, according to nucleation and growth kinetics, the grains formed under such conditions are very small. Therefore, the grains formed in the process of micro-arc oxidation mainly exist in nanocrystalline and microcrystalline morphology.

According to TEM observation, there are some amorphous substances in the micro-arc oxide film. The formation condition of amorphous phase is also due to the high cooling rate. When the cooling rate reaches 10^6K/s , amorphous phase can be formed[20-22]. However, the cooling rate in the process of micro-arc oxidation can reach 10^8K/s , so there are some amorphous substances in the ceramic coating.

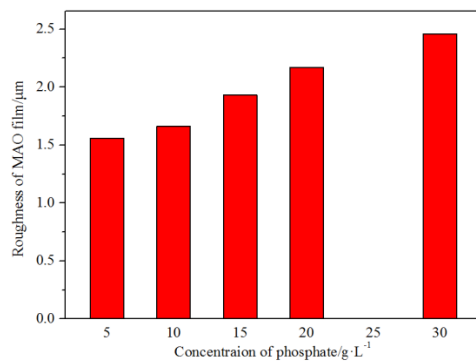


Figure 4. Effect of phosphate concentration on surface roughness of MAO film

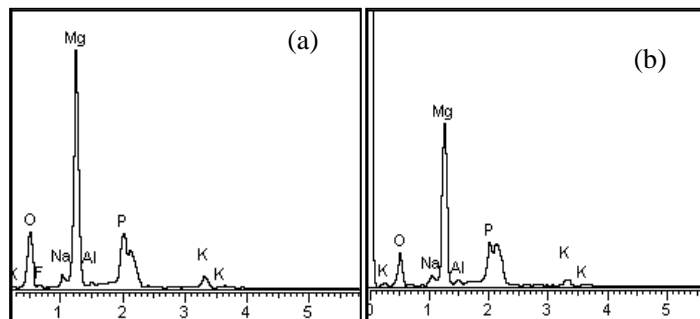


Figure 5. EDS spectra of MAO film (a) Na_3PO_4 : 5g/L; (b) Na_3PO_4 : 30g/L

Table 1. Content of related elements in EDS spectra

P(g/L)	Composition (wt.%)					
	Mg	O	P	Al	Na	K
5	46.12	34.21	11.07	2.43	2.72	3.45
30	47.23	34.26	9.88	2.65	2.75	3.23

3.5. Effect of Phosphate Concentration on Corrosion Performance

Figure 8 studies the effect of phosphate concentration on corrosion rate. The film was prepared by micro-arc oxidation of 30min with current density 20A/dm^2 in constant current mode. It can be seen from the diagram that the corrosion rate increases with the increase of phosphate concentration, lowest at 5g/L, highest at 30g/L. From the previous discussion, we know that the quality of the film is the best when phosphate concentration is 5g/L, so the corrosion resistance is also the best. The quality of the film formed at 30g/L is the worst, so the corrosion resistance is also the worst. Therefore, in order to obtain a high corrosion resistance film, a lower phosphate concentration should be selected.

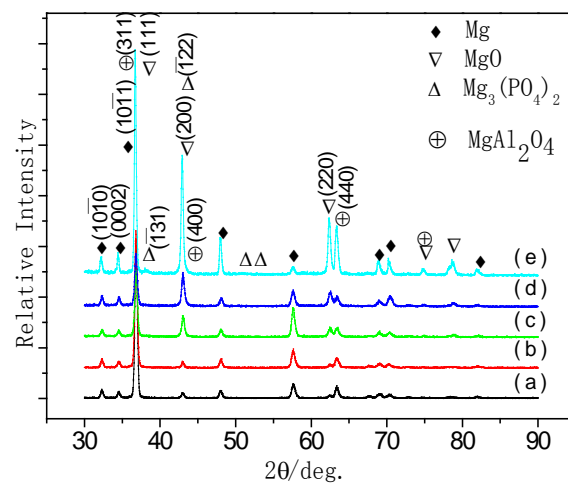


Figure 6. XRD patterns of MAO film (a)30g/L; (b)20g/L;(c)15g/L;(d)10g/L;(e)5g/L

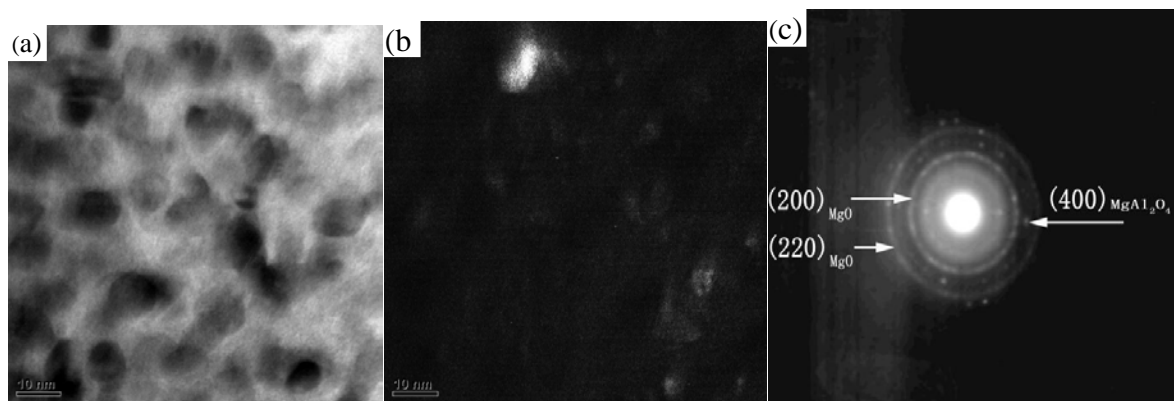


Figure 7. TEM image of MAO coatings(5g/L)

(a)TEM image of the mixed micro-crystalline and amorphous MgO(BF); (b)DF, $g=(200)$; (c) a selective diffraction ring and an amorphous diffraction disk

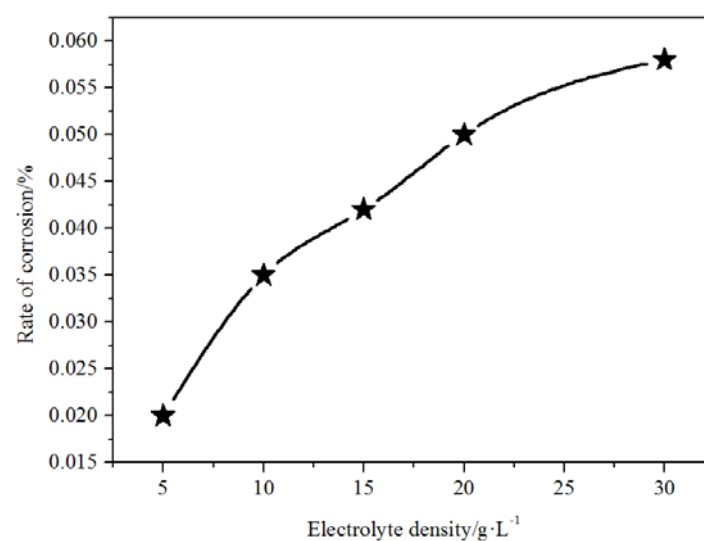


Figure 8. Effect of phosphate concentration on corrosion performance

4. Conclusions

(1) The process of micro-arc oxidation in constant current mode can be divided into four stages, which are fast rising stage, peak platform stage, fast descending stage and arc extinguishing stage. The survival time of the peak platform has an important effect on the quality and performance of the film.

(2) When micro-arc oxidation is carried out in phosphate system, the film formed with lower phosphate concentration had better quality, lower surface roughness and higher corrosion resistance.

(3) The MAO films prepared in phosphate electrolyte contains most crystalline substances and a small amount of amorphous substances, the crystalline substances exists in nanocrystalline and microcrystalline.

5. Acknowledgments

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6. References

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