

Effects of sodium tungstate on properties of micro-arc coatings on magnesium alloys

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Abstract: Anodic coatings were prepared by micro-arc oxidation on AZ91HP magnesium alloys in a base solution containing 10 g/L NaOH and 12 g/L phytic acid with addition of 0–8 g/L sodium tungstate. The effects of sodium tungstate on the coating thickness, mass gain, surface morphology and corrosion resistance were studied by eddy current instrument, electronic scales, scanning electron microscope and immersion tester. With the addition of sodium tungstate, the electrolytic conductivity increases and the final voltage decreases. The sodium tungstate has a minor effect on the coating thickness, but lightens the coating color. With increasing sodium tungstate concentration, the size of micropores on the coatings is enlarged and the corrosion resistance of the anodized samples decreases.

Key words: magnesium alloy; micro-arc oxidation; electrolyte; sodium tungstate

1 Introduction

Micro-arc oxidation (MAO), developed under the traditional oxidation, is an effective method to improve the corrosion and wear resistance of magnesium alloys. The coating properties are mainly determined by the concentrations and compositions of the electrolytes[1]. Due to the health and environmental pressure, some environmentally friendly processes have been developed in alkaline solutions containing some inorganic additives such as silicate[1–4], borate[5] and aluminate[5–6]. Among the oxysalts, sodium silicate is a favorable additive of electrolyte[3] and widely used in MAO. Recently, sodium tungstate (Na_2WO_4) has been used as an electrolyte in MAO on magnesium alloys[4, 7–8]. DING et al[4] systematically studied the effects of sodium tungstate on the microstructure, compositions and mechanical tribological characteristics of the oxide coatings. The results show that with increasing concentration of Na_2WO_4 in the solution, the microhardness of the oxide coatings increases, while the wear rates decrease. However, the effect of Na_2WO_4 on

the corrosion resistance, one of the important coating properties, is not evaluated.

Phytic acid ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$), first known as the storage form of phosphorus in seeds[9], is a naturally occurring acid and innocuous, biocompatible and green to the environment. A variety of benefits of phytic acid on human health have been reported, including anti-cancer agent, inhibitor for renal stone development and antioxidant agent. Phytic acid can also be used in treating metals to prevent rust as a replacement for cyanide[10]. Recently, $\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$ was used as a main electrolyte in MAO on magnesium alloys[11–12]. The result showed that the corrosion resistance of anodic coatings formed in the $\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$ solution was better than that in sodium silicate solution[12]. However, to the best of the author's knowledge, there is no report about the effects of Na_2WO_4 on coating properties formed in an alkaline solution containing $\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$.

In this work, the influence of Na_2WO_4 on coating thickness, surface morphology, mass gain and corrosion resistance were studied with an eddy current instrument, scanning electron microscope, electronic scales and immersion tester.

2 Experimental

An ingot of AZ91HP magnesium alloy was employed and its chemical compositions were as follows (mass fraction, %): Al 8.93, Zn 0.47, Mn 0.22, Si 0.03, Cu 0.002, Ni 0.001, Fe 0.001 and Mg balance.

Samples for MAO treatment were cut into 5 cm×7 cm×1 cm and were anodized after being ground, washed, degreased and dried. The base solution was 10 g/L NaOH and 12 g/L phytic acid. 0–8 g/L Na₂WO₄ was separately added into the base solution to form different solutions as listed in Table 1.

Table 1 Compositions and concentrations of different anodizing processes

Process No.	Composition of electrolyte
1	10 g/L NaOH, 12 g/L C ₆ H ₁₈ O ₂₄ P ₆
2	10 g/L NaOH, 12 g/L C ₆ H ₁₈ O ₂₄ P ₆ , 2 g/L Na ₂ WO ₄
3	10 g/L NaOH, 12 g/L C ₆ H ₁₈ O ₂₄ P ₆ , 4 g/L Na ₂ WO ₄
4	10 g/L NaOH, 12 g/L C ₆ H ₁₈ O ₂₄ P ₆ , 6 g/L Na ₂ WO ₄
5	10 g/L NaOH, 12 g/L C ₆ H ₁₈ O ₂₄ P ₆ , 8 g/L Na ₂ WO ₄

The equipment for MAO consisted of a MAOI-50C power supply, a stainless steel barrel and a stirring and cooling system that controlled the solution temperature below 30 °C. The treatment was performed by the unipolar (positive) pulse under a constant current control mode. The electrical parameters were fixed as follows: current density of 40 mA/cm², frequency of 2 000 Hz, duty cycle of 20% and treatment time of 3 min. The solution conductivity was measured by a DDS-307W microprocessor conductivity meter. The coating thickness was measured by a TT230 current instrument, which was calibrated with the same base metal. The morphologies of the treated samples were observed by a scanning electron microscope (SEM QUANTA 200) after being washed, dried and coated with gold. The compositions of anodic films were determined by EDX analysis. The anodized samples were tested under immersion conditions in a 3.5% (mass fraction) NaCl solution for 24 h to evaluate the corrosion performance.

3 Results and discussion

3.1 Final voltage and coating thickness

The solution conductivity, final voltage, coating thickness and color obtained in different processes are listed in Table 2.

With the increase of Na₂WO₄ concentration, the number of ions in the solution increases and therefore the solution conductivity (*k*) increases (see Table 2). As the reciprocal of the electrolyte conductivity, the electrolyte

Table 2 MAO parameters, coating thickness and color obtained by different processes

Process No.	Conductivity/(mS·cm ⁻¹)	Final voltage/V	Coating thickness/μm	Coating color
1	24.1	374	4.9	Dark grey
2	24.5	369	4.9	Grey
3	25.0	365	5.5	Grey
4	25.6	317	5.2	White
5	26.2	269	4.6	White

resistivity (ρ) is correlated with the breakdown voltage according to the empirical equation[13]:

$$U_B = a_B + b_B]g\rho \quad (1)$$

where a_B and b_B are the constants for a given metal and electrolyte composition, ρ is electrolyte conductivity.

According to Eq.(1), the breakdown voltage increases with increasing electrolyte resistivity or decreasing solution conductivity. Under the condition of the same electric parameters, with the increase of Na₂WO₄ concentration, the solution conductivity increases, which results in the decrease of breakdown voltage as well as the final voltage.

In the base solution, the coating thickness is 4.9 μm. After different concentrations of Na₂WO₄ are added, the coating thickness changes between 4.6 μm and 5.5 μm, which indicates that Na₂WO₄ has a minor effect on the coating thickness.

The color of the anodized sample obtained in the base solution is dark grey. The samples obtained in the solution with 2 g/L and 6 g/L Na₂WO₄ are grey and white, respectively, which indicates that Na₂WO₄ can change the coating color.

3.2 Surface morphology and chemical compositions of anodic coatings

The surface morphologies of the anodic coatings obtained by different processes are shown in Fig.1. It can be seen that, all the coatings, whether obtained with or without Na₂WO₄ addition, show typically porous structure, but they are slightly different in pore size and uniformity. In Na₂WO₄-free base solution, the pore size and the distances between two adjacent pores of the coatings are 1.0 μm and 0.6–2.0 μm, respectively (see Fig.1(a)). After adding 2 g/L Na₂WO₄, the micropores become larger. In addition, the coating surface becomes rougher (see Fig.1(b)). With increasing Na₂WO₄ concentration, the coatings become rougher and rougher (see Figs.1(c) and 1(d)). The coatings formed in the solution containing 8 g/L Na₂WO₄ are very irregular (see Fig.1(e)).

The EDX spectra of anodic coatings obtained in the base solution with and without Na_2WO_4 addition are shown in Fig.2. In Na_2WO_4 -free solution, the anodic coatings contain C, O, Mg, Al and P, indicating the presence of species derived from both the substrate and electrolyte. After adding Na_2WO_4 (for example 2 g/L Na_2WO_4), additional W element is found in the coatings (see Fig.2) and it is attributed to Na_2WO_4 in the solution.

The chemical compositions of anodic coatings formed in the solution with different concentrations of Na_2WO_4 are listed in Table 3. With increasing Na_2WO_4 , the W content of the coatings increases.

3.3 Mass gain of anodized sample

The mass gain per unit area of each sample treated by different processes is shown in Fig.3.

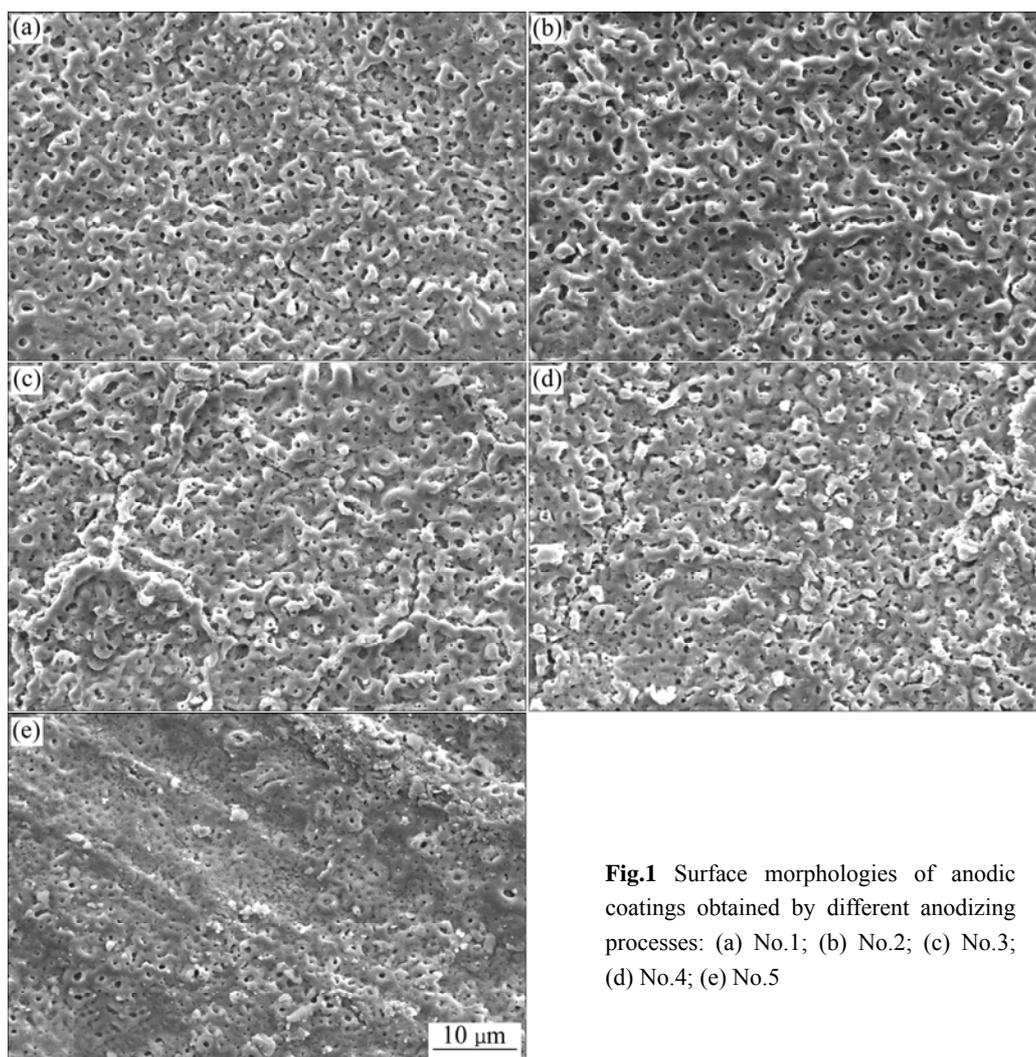


Fig.1 Surface morphologies of anodic coatings obtained by different anodizing processes: (a) No.1; (b) No.2; (c) No.3; (d) No.4; (e) No.5

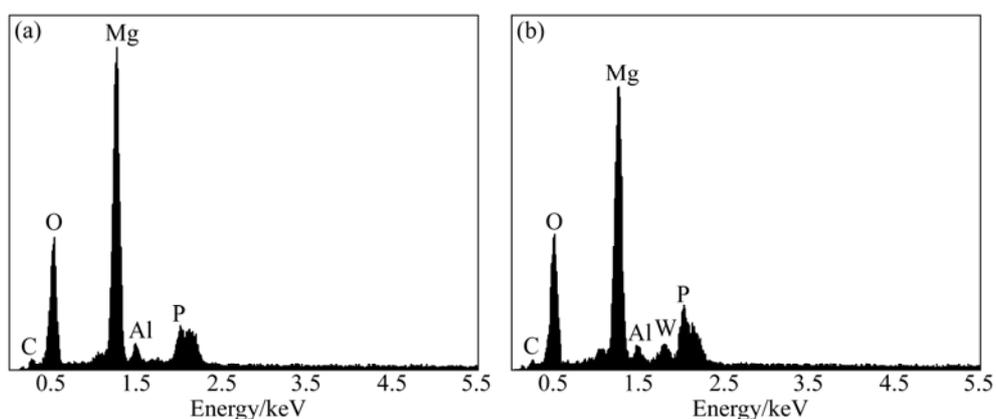
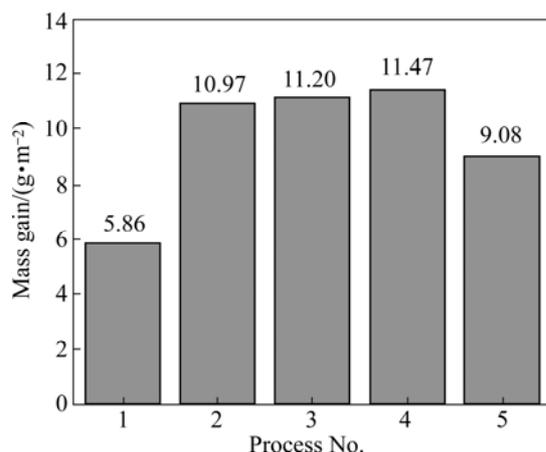


Fig.2 EDX spectra of anodic coatings formed in base solution (a) and with addition of 2 g/L Na_2WO_4 (b)

Table 3 Chemical compositions of anodic coatings obtained by different processes (mass fraction, %)

Process No.	O	Mg	Al	W	P	C
1	26.36	50.25	3.75	–	10.75	8.89
2	26.04	40.43	3.01	11.03	13.25	6.25
3	25.37	37.64	1.40	16.90	12.39	6.30
4	22.42	31.64	2.06	23.06	11.91	8.91
5	22.45	29.31	1.82	30.28	10.31	5.84

**Fig.3** Mass gain of each anodized sample by different processes

In the base solution, the mass gain per unit area of the sample treated by MAO is 5.86 g/m². After addition of 2 g/L Na₂WO₄, the value increases evidently and reaches 10.97 g/m².

In the solution, Na₂WO₄ took part in the coating formation and entered into the coatings, existing as WO₃/Na₂WO₄ or W element[4]. Because the density of these tungstate-containing compounds is large, the mass gain per area of the coatings increases quickly. With increasing Na₂WO₄ concentration, on one hand, the sparks on the sample surface become large resulting in the accelerated dissolution speed of anodic coatings in the solution. Meanwhile, the pore size of the anodic coatings become large. The conditions as above result in the decrease of the coating mass. On the other hand, the increase of W content in the coatings causes the increase of the coating mass. Under the conjunct effects, the mass gain of the sample treated in the solution of 8 g/L Na₂WO₄ is the minimum.

3.4 Corrosion resistance of anodized sample

After being immersed in 3.5% NaCl for 24 h, the samples treated by different processes were taken out from the solution, washed with distilled water, dried by hot wind and observed by the naked eye. The results of the corrosion resistance are listed in Table 4.

According to Table 4, with the increase of Na₂WO₄ concentration, the corrosion resistance of the anodized samples decreases.

Table 4 Results of immersion experiment for anodized samples by different processes

Process No.	Number and size of corrosion pits
1	One small corrosion pit
2	One small corrosion pit
3	Two corrosion pits, with size of 4 mm×4 mm and 4 mm×3 mm, respectively
4	Three corrosion pits, with largest pit of 6 mm×4 mm
5	Four corrosion pits, with largest pit of 8 mm×6 mm

The corrosion resistance of anodic coatings depends on a lot of factors such as the substrate alloy[14], coating composition[15], thickness[16] and porosity[14]. The results showed that anodic coatings with higher chemical stability compounds offered an opportunity to produce layers with better corrosion resistance[15]. In addition, the corrosion resistance of anodized samples improves with the coating thickening under the constant coating porosity[16], but decreases with the increase of coating porosity[14]. In the experiment, after addition of Na₂WO₄, the tungstate-containing compounds such as WO₃/Na₂WO₄ or W form and they are not stable in water. For example, Na₂WO₄ is soluble in water, while WO₃ can react with OH⁻ ions to produce soluble WO₄²⁻ according to



Meanwhile, the coating thickness does not increase greatly, but the diameter of micropores on the coatings increases. Therefore, in the corrosive environment, the corrosive medium can easily penetrate the pores and reaches the substrate, which decreases the corrosion resistance of the anodized samples.

4 Conclusions

- 1) In the base solution containing phytic acid, sodium tungstate can change the coating color but has a minor effect on the coating thickness.
- 2) Sodium tungstate takes part in coating formation, which results in the increase of the mass gain per area and the microarc pores of anodic coatings.
- 3) The immersion test shows that sodium tungstate decreases the corrosion resistance of the anodized samples.

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