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Effect of rare earth Y₂O₃ on the corrosion and friction properties of Al₂O₃ ceramic coatings prepared via microarc oxidation

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Rare earth Y_2O_3/Al_2O_3 ceramic coatings were prepared on 6063 aluminum alloy via micro-arc oxidation. The corrosion and friction properties of the substrates were enhanced. Scanning electron microscopy results showed that the number of "crater" holes increased and decreased, and the diameter of micropores first increased and decreased. X-ray diffraction results indicated that the coatings mainly consisted of α -Al₂O₃, γ -Al₂O₃, and Y₂O₃. The Y₂O₃ contents gradually increased with the increase in Y₂O₃ concentration. The surface roughness of the coatings first increased to 3.231 µm and decreased to 2.404 µm, whereas the thickness increased from 17.8 µm to 22 µm with the increase in Y₂O₃ concentration. Results showed that the surface hardness improved to 596.9 Hv, and the corrosion current decreased to 1.133e⁻⁰⁰⁸ A at Y₂O₃ concentration of 3 g/L. The friction coefficient decreased to 0.42 at Y₂O₃ concentration of 2 g/L.

Keywords: microarc oxidation, yttrium oxide, corrosion property, friction property

1. INTRODUCTION

Aluminum and its alloys are widely used in automation [1], industry [2], and aerospace [3] because of their lightweight and high strength properties [4-6]. However, their poor corrosion and friction performance has hinder their expansion and application. Electrophoretic enhanced microarc oxidation (EEMAO), as a new technique, has been widely used to improve the properties of aluminum alloys. The particles are deposited into the microarc oxidation coatings through spark discharge forming the composite ceramic coating. Nanoparticles, such as MnO₂ [7], Al₂O₃ [8], TiO₂ [9], and Nd₂O₃ [10], are added in the electrolyte to form nano composite coatings. Shokouhfa et al. [11] added SiC, Al₂O₃, and TiO₂ nanoparticles into the electrolyte. The nanoparticles enhanced the corrosion and friction properties of MAO coatings, and TiO₂ nanoparticles exhibited good properties. Zhenwei [12]

added paraffin into the electrolyte. MAO self-lubricating composite coatings exhibited low friction coefficient and wear rates. Yttrium oxide nanoparticles doped on Al₂O₃ ceramic coatings have not been evaluated.

Rare earth elements have important application values and are widely used in various industries [13]. Traces of rare earth elements will obviously improve the comprehensive properties of materials, such as metallurgy [14], welding wire [15], and other applications [16-19]. Rare earth elements are introduced to the surface of coatings through electrophoretic deposition [20-21] and rare earth conversion [22-24] in surface treatment. However, the processing voltage of electrophoretic deposition is low, and the performance of coatings cannot be substantially improved. The thickness of rare earth conversion films is approximately 50 nm, making their performance difficult to improve. As an important component of rare earth oxides, yttrium oxide is rarely reported in the study on MAO. The comprehensive performance of the coatings can be improved by adding a small amount of rare earth yttrium oxide element. In this study, MAO coatings with Y_2O_3 nanoparticles were prepared on 6063 aluminum alloy. The effects of Y_2O_3 nanoparticles on the microhardness, corrosion, and friction properties of the coatings were studied. The relationship between the concentrations of Y_2O_3 nanoparticles and microstructure and the properties of composite coatings was proposed.

2. MATERIALS AND METHOD

2.1. Preparation of MAO coatings

Aluminum specimens had dimensions of 30 mm \times 15 mm \times 2 mm. The elemental chemical composition of the specimens is shown in Table 1. The specimens were gradually polished with #800– #2000 SiC sandpaper, cleaned with alcohol, and dried with air jets. The MAO equipment consisted of a 10-kW power supply, an electrolytic cell, and a cooling system (Disishukong Co., Ltd, Harbin, China).

Table 1. the elemental composition of the aluminum specimens.

Element	Mg	Si	Cu	Fe	Mn	Zn	Cr	Ti	Al
Percentage (%)	0.45-0.9	0.2-0.6	≤0.1	≤0.35	≤0.1	≤0.1	≤0.1	≤0.1	others

The sample was connected to the anode of power supply, and the electrolytic cell was connected to the cathode. The electrolyte solution consisted of Na₂SiO₃, KOH (Sinopharm Chemical Reagent Beijing Co., Ltd, Beijing, China), Y₂O₃ nanoparticles (Nanjing Emperor Nano Material Co., Ltd, Nanjing, China), and deionized water. The processing parameters are shown in Table 2. The average size of Y₂O₃ nanoparticles was 50 nm. Y₂O₃ nanoparticles were stirred into the electrolyte for 30 min to prepare an EEMAO ceramic coating in its suspension fluid. The electrolyte temperature was maintained with a stirring pump at 30 °C–35 °C. The frequency, duty cycle, and time were set to 500 Hz, 50%, and 30 min, respectively, on the basis of preliminary experiment and research results of Hongbin [25]. The MAO power was set to constant current mode, and the current density was set to 30

A/dm^2 .

NO.	Electrolytic				
	Na ₂ SiO ₃	KOH	Y_2O_3		
	(g/L)	(g/L)	(g/L)		
А	4	3	0		
В	4	3	1		
С	4	3	2		
D	4	3	3		
Е	4	3	4		

Table 2. the chemical composition of the electrolyte

2.2. Analysis of structure and composition of the coatings

The microstructure of the specimens was observed through scanning electron microscopy (SEM, JSM-6480A). The phase of the specimens was analyzed through X-ray diffraction (XRD, D/max-r BX-ray diffraction, Cu K α radiation). Scattering angle 20 was set from 10° to 90° with a step of 0.041, acquisition time of 1 s/step, and energy of 40 kV, 40 mA. Surface roughness was measured using a TR200 roughness tester (cut off length of 0.8 mm), and thickness was measured using a TT260 coating thickness gauge. The surface hardness of the coatings was evaluated using a digital microhardness tester (HVS-1000) in HV mode at a load of 4.900 N for 5 s. The corrosion property was measured using an electrochemical workstation (CHI604C), and tafel testing was evaluated using a polarization curve at 3.5% NaCl aqueous solution from the initial potential (-2 V) to the final potential (+1 V), with time of 100 s and scan rate of 1 mV/s. The friction coefficient was determined using a HIT-II friction and wear test machine at a load of 10 N and speed of 300 r/min.

3. RESULTS AND DISCUSSION

3.1 Response of voltage vs. time

The voltage versus time responses under different Y_2O_3 concentrations are shown in Fig. 1. The MAO process included general anodization, sparking anodization, and MAO [26]. The Y_2O_3 particles did not obviously affect the oxidation behavior in the general anodization stage. After the general anodization stage, the voltage improved at the same MAO process time, and the MAO reaction intensified with the increase in Y_2O_3 concentration, as shown in electrolytes A to E. The addition of nanoparticles promoted the growth of MAO coatings [27]. Electrolyte resistance decreased with the increase in nanoparticle concentration from electrolytes B to E. The nanoparticles were involved in the MAO process, and the thickness of the coatings increased. A high voltage was required to maintain the breakdown discharge at the constant current mode and same process time. Thus, the voltage increased with the same MAO process time.



Figure 1. Voltage versus time response under different Y₂O₃ concentrations (a) A: Y₂O₃, 0 g/L, (b) B: Y₂O₃, 1 g/L, (c) C: Y₂O₃, 2 g/L, (d) D: Y₂O₃, 3 g/L, (e) E: Y₂O₃, 4 g/L.

3.2 SEM

SEM morphologies of the coatings under different Y₂O₃ concentrations are presented in Fig. 2. The MAO coatings exhibited the general morphology in electrolyte A, as shown in Fig. 2a, and the micropores were distributed on the coatings. The electrolyte concentration, the number of holes, and the diameter of micro pores increased, as shown in Fig. 2b. The Y₂O₃ concentration improved the process voltage at the same time in electrolyte B, whereas it did not affect the morphology of the coatings, thereby increasing the diameter of micropores. The number of holes decreased with the increase in Y₂O₃ concentration, as shown in Fig. 2c. Nano-Y₂O₃ particles deposited near the "crater" during the microarc discharge, thereby decreasing the diameter of micropores. The diameter of micropores decreased with the increase in Y₂O₃ concentration, as shown in Fig. 2d. The holes became small and shallow when the concentration reached 4 g/L (electrolyte E). "Stack" accumulation occurred, indicating that the Y₂O₃ concentration was extremely high, which may affect the performance of the coatings. The deposition of Y₂O₃ blocked the pores during arc discharge, thereby decreasing the number of holes. The Y₂O₃ nanoparticles were involved in the MAO discharge process under the action of electric and mechanical forces [28], and the morphology of the coatings remained constant under low concentration. Many nanoparticles entered the coatings, and the number of micropores on the surface of the coatings decreased with the increase in Y₂O₃ concentration. The pore diameter of the coatings increased, and the number of pores decreased with the blocking of the nanoparticles. The SEM results indicated that the Y₂O₃ nanoparticles were involved in the MAO process under mechanical mixing and electric field forces.



Figure 2. SEM of the Y_2O_3/Al_2O_3 composite coatings under different Y_2O_3 concentration (a) $Y_2O_3,0g/L$, (b) $Y_2O_3,1g/L$, (c) $Y_2O_3,2g/L$,(d) $Y_2O_3,3g/L$, (e) $Y_2O_3,4g/L$.

3.3 XRD

XRD was used to study the valence and chemical composition of the composite coatings. The XRD diffraction patterns of the composite coatings obtained at different concentrations are depicted in Fig. 3, which present the formation of α -Al₂O₃, γ - Al₂O₃, and Y₂O₃. Y₂O₃ appeared on the coatings at 29.157°, 48.539°, and 57.629°. This phenomenon illustrated that the Y₂O₃ particles were doped on the coatings during the MAO process. The Y₂O₃ particles were drawn toward the anode through the mechanical shearing force during the MAO process. They deposited on the discharge areas and generated the Y₂O₃/Al₂O₃ composite coatings. The coatings were composed of γ -Al₂O₃ and α -Al₂O₃ at

electrolyte A, and the peak of α -Al₂O₃ was weak. The coatings were extremely thin to be detected by XRD, whereas the peak of Al was strong. The peaks of α -Al₂O₃ enhanced in electrolyte B, indicating that Y₂O₃ promoted the γ -Al₂O₃ transformation to α -Al₂O₃. On the one hand, Y₂O₃ increased the conductivity of the solution. Considerable amount of energy was used to increase the growth of the coatings at the same power supply. On the other hand, voltage was high at the same process time, as shown in the voltage versus time response. Voltage is an important factor in phase transformation and growth of the coatings. γ -Al₂O₃ transformed to the stable phase as α -Al₂O₃ [29], and the temperature of γ -Al₂O₃ transformation was 750 °C-1200 °C with the considerable amount of heat generated by high voltage [30]. Under the same treatment parameters, the greater the thickness of the coatings made it difficult for XRD rays to penetrate them. The comparison of electrolytes D and E indicated that the Y₂O₃ peak increased with the increase in Y₂O₃ concentration. This condition illustrated that Y₂O₃ was involved in the MAO process and comprised the composite coatings. The peak of α -Al₂O₃ was caused by the increase in voltage, as shown in Fig. 1.



Figure 3. XRD of the Y₂O₃/Al₂O₃ nano-composite coatings under different Y₂O₃ concentration (a) A: Y₂O₃, 0g/L, (b) B: Y₂O₃, 1g/L, (c) C: Y₂O₃, 2g/L, (d) D: Y₂O₃, 3g/L, (e) E: Y₂O₃, 4g/L.

3.4 Roughness and thickness

The surface roughness and thickness results under different conditions are shown in Fig. 4. The surface roughness results are shown in Fig. 4a. The roughness of the coatings first increased from $3.231 \,\mu\text{m}$ to $3.416 \,\mu\text{m}$ and decreased to $2.404 \,\mu\text{m}$ with the increase in Y_2O_3 concentration. Roughness increased with the increase in the diameter of micropores, as shown in Fig. 2b. Voltage increased, whereas the content of Y_2O_3 was insufficient to change the structure of the coatings at electrolyte B. Roughness decreased with the increase in Y_2O_3 content and decrease in the number of micropores. The deposited Y_2O_3 did not enter the coatings when the Y_2O_3 concentration was extremely high, as shown in the "stack" of Fig. 2e. The thickness of the coatings increased from 17.8 μm to 22 μm with the increase in Y_2O_3 concentration. On the one hand, this condition illustrated that the thickness of the coatings increased with the increase in Y_2O_3 concentration [31]. On the other hand, the process voltage gradually increased, the reaction intensified, and the thickness of the coatings gradually increased at the same process time.



a) Roughness of the coatings b) Thickness of the coatings

Figure 4. Roughness and thickness of the Y₂O₃/Al₂O₃ nano composite coatings under different Y₂O₃ concentration (a) A: Y₂O₃, 0 g/L, (b) B: Y₂O₃, 1 g/L, (c) C: Y₂O₃, 2 g/L, (d) D: Y₂O₃, 3 g/L, (e) E: Y₂O₃, 4 g/L.

3.5 Micro-hardness

The hardness of the coatings increased with the increase in Y_2O_3 concentration. On the one hand, this phenomenon indicated that the Y_2O_3 content increased on the surface and inside the coatings. The hardness of the composite coatings was effectively improved by the Y_2O_3 nanoparticles because of their high hardness [32]. On the other hand, this phenomenon occurred because Y_2O_3 promoted the transformation from γ -Al₂O₃ to α -Al₂O₃. The results indicated that the composite coatings with Y_2O_3 -doped α -Al₂O₃ had a high hardness. However, the hardness decreased in electrolyte E (4 g/L). This phenomenon was because some of Y_2O_3 particles deposited on the coatings, whereas some of them did not enter the coatings and formed a "stack" microstructure, as shown in the SEM results (Fig. 2e). The deposition quality is poorer than that of the deposition of the MAO composite coatings. Therefore, the hardness is lower than that of the composite coatings.



Figure 5. Micro-hardness of the Y_2O_3/Al_2O_3 nano-composite coatings under different Y_2O_3 concentration (a) A: Y_2O_3 , 0 g/L, (b) B: Y_2O_3 , 1 g/L, (c) C: Y_2O_3 , 2 g/L, (d) D: Y_2O_3 , 3 g/L, (e) E: Y_2O_3 , 4 g/L.

3.6 Corrosion property

The corrosion resistant properties under different conditions are shown in Fig. 6. The corrosion voltage and current are presented in Table 3. The coatings' corrosion voltage increased, whereas the corrosion current decreased with the increase in Y_2O_3 concentration. The corrosion voltage increased to -0.153 V, and the corrosion current decreased to $1.133e^{-008}A$ at Y_2O_3 concentration of 3 g/L (electrolyte D). The addition of Y_2O_3 improved the corrosion resistance of the coatings. First, the Y_2O_3 nanoparticles exhibited superior corrosion resistance, and the corrosion resistance of the composite coating composed of Y_2O_3 nanoparticles improved [33]. Second, the increasing α -Al₂O₃ content improved the corrosion voltage decreased at the Y_2O_3 concentration of 4 g/L (electrolyte E). Y_2O_3 loose attachment on the surface of the coatings, and the coatings exhibited a stacking morphology, as shown in Fig. 2e. This condition may have caused the decrease in corrosion property.



Figure 6. Corrosion property of the Y₂O₃/Al₂O₃ nano composite coatings under different Y₂O₃ concentration (a) A: Y₂O₃, 0 g/L, (b) B: Y₂O₃, 1 g/L, (c) C: Y₂O₃, 2 g/L, (d) D: Y₂O₃, 3 g/L, (e) E: Y₂O₃, 4 g/L.

Table 3. Corrosion potential, current and resistance of the coatings

	Potential	Current	Resistance
	V	А	Ω
base	-0.942	4.215e-007	98942.6
А	-0.671	1.068e-007	449253.6
В	-0.626	2.560e-008	1866592.6
С	-0.545	2.173e-008	1956925.3
D	-0.153	1.133e-008	3965926.5
Е	-0.297	2.347e-008	2016198.1

3.7 Friction coefficient

7690

The friction coefficients under different Y_2O_3 concentrations are shown in Fig. 7. The friction coefficient of the coatings decreased with the increase in Y_2O_3 concentration. The friction coefficient decreased after the MAO treatment, accompanied with slight fluctuation. The friction coefficients decreased to 0.42 at electrolytes C and D with the increase in Y_2O_3 concentration. The friction coefficient of the coatings remained at 0.42 at 4 g/L concentration (electrolyte E) and was slightly higher than electrolyte C. This condition indicated that the continuous increase in Y_2O_3 content had small effect on the friction coefficient of the coefficient of the coatings. The Y_2O_3 attached to the composite coatings did not contribute to the decrease in friction coefficient, as shown in the SEM at 4 g/L (Fig. 2e). The addition of Y_2O_3 improved the wear-resistant property of the coatings. On the one hand, the roughness of the coatings decreased and the hardness increased with the increase in Y_2O_3 concentration, thereby decreasing the friction coefficient [34]. On the other hand, the XRD and EDS results indicated that the Y_2O_3 nanoparticles comprised the composite coatings and improved their performance because of their superior hardness.



Figure 7. Friction coefficient of the Y₂O₃/Al₂O₃ composite coatings under different Y₂O₃ concentration (a) A: Y₂O₃, 0 g/L, (b) B: Y₂O₃, 1 g/L, (c) C: Y₂O₃, 2 g/L, (d) D: Y₂O₃, 3 g/L, (e) E: Y₂O₃, 4 g/L.

4. CONCLUSIONS

Rare earth Y_2O_3/Al_2O_3 ceramic coatings were prepared on 6063 aluminum alloy using the MAO technique, and the effects of Y_2O_3 concentration were clarified. The coatings had a porous morphology, where the number of holes increased and decreased, and the diameter of the micropores first increased and decreased with the increase in Y_2O_3 concentration. γ -Al₂O₃, α -Al₂O₃, and Y_2O_3 were the main phases under varying fabrication conditions, and the content increased with the increase in Y_2O_3 concentration. The surface roughness of the coatings first increased to 3.231 µm and gradually decreased to 2.404 µm, whereas the thickness increased from 17.8 µm to 22 µm with the increase in Y_2O_3 concentration. The surface hardness and corrosion current of the coatings successfully improved

to 596.9 Hv and $1.133e^{-008}$ A, respectively, whereas the friction coefficient decreased to 0.42.

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