

EFFECTS OF DIFFERENT ELECTROLYTE SYSTEMS ON THE FORMATION OF MICRO-ARC OXIDATION CERAMIC COATINGS OF 6061 ALUMINUM ALLOY

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Abstract: Ceramic coatings on 6061 aluminum alloy were prepared by micro-arc oxidation in Na_2SiO_3 , NaAlO_2 , and $\text{Na}(\text{PO}_3)_6$ electrolyte systems. The breakdown voltage, thickness and hardness of ceramic coatings in different electrolyte systems were comparatively studied. The surface morphology and phase composition of ceramic coatings were analyzed using SEM and XRD techniques. The results show that the breakdown voltage is decreased with increasing of electrolyte concentration, and in Na_2SiO_3 electrolyte system it is the lowest, NaAlO_2 takes the second place and $\text{Na}(\text{PO}_3)_6$ is the highest. In constant-current model, the thickness of ceramic coatings shows linear increase with the increment of oxidation time in electrolyte systems, growth rate remains essentially constant. The ceramic coatings in different electrolyte systems are mainly composed of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$, the relative content of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ in NaAlO_2 electrolyte system is higher than that in the other electrolyte systems. The hardness of dense layer is relatively high, the hardness of loose layer is rather low. The distance from substrate interface is 15 μm , hardness reaches the highest (1270 HV), then it begins to reduce gradually in NaAlO_2 electrolyte system.

1. INTRODUCTION

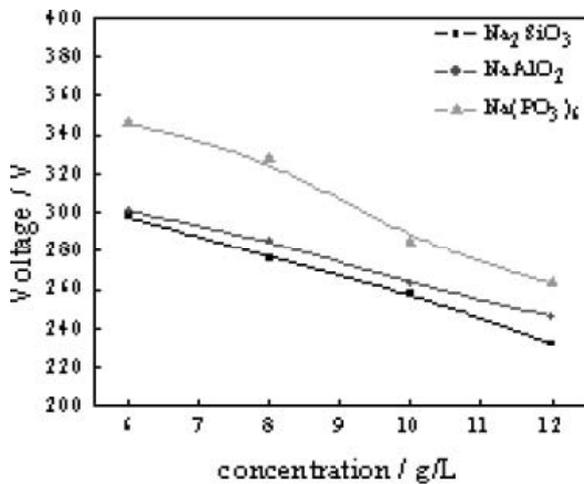
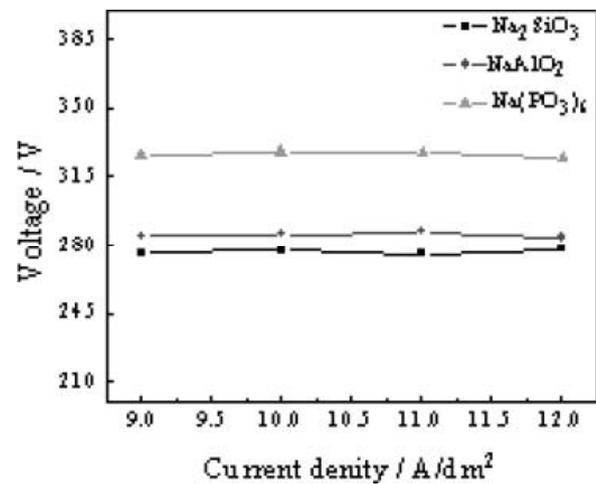
Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO), can in-situ form the ceramic coatings on the surface of valve metal such as Al, Mg, Ti, and their alloys. Ceramic coatings of MAO are much compacter and harder compared with common surface modification technique, which can dramatically improve the wear resistance, corrosion resistance, heat shock resistance, insulation and other properties of the surface of aluminum alloy [1-3]. The main factors affecting MAO process are energy parameters (current density, voltage, pulse frequency and duty cycle), electrolyte, substrate material and working temperature, etc. Electrolyte components are important parameters of MAO process. Acidic and alkaline electrolyte

systems are mainly adopted at present. Acidic electrolyte systems mainly include sulfuric acid, phosphoric acid and its salt solution, etc., at present, they are rarely used due to environmental pollution. Alkaline electrolyte systems have almost no pollution on environment. The metal ions of anodic reaction can easily turn into a negatively charged colloidal particles which are re-utilized, the other metal particles in the electrolyte easily convert into negatively charged colloidal particles, then enter into the ceramic coatings to change the phase composition and phase structure of ceramic coatings, thus affect the properties of ceramic coatings. The adsorption degree of ceramic coatings is in sequence of $\text{SiO}_3^{2-} > \text{PO}_4^{3-} > \text{VO}_4^{3-} > \text{MoO}_4^{2-} > \text{WO}_4^{2-} > \text{B}_4\text{O}_7^{2-} > \text{CrO}_4^{2-}$ [4]. The breakdown voltage, surface and cross section morphology,

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Table 1. Chemical composition of 6061 aluminum alloy.

Chemical elements	Si	Mg	Mn	Fe	Zn	Ti	Cr	Cu	Bal
Contents ($\omega\%$)	0.4-0.8	0.8-1.2	0.15	0.7	0.25	0.15	0.04-0.35	0.15-0.4	Al

**Fig. 1.** The changing regularity of breakdown voltage with the variation of electrolytes concentration.**Fig. 2.** The changing regularity of breakdown voltage with the variation of current density.

growth rate, cross-section hardness and phase composition were researched in three different alkaline electrolyte systems in this paper. Effects of different electrolyte systems on the formation of micro-arc oxidation ceramic coatings of 6061 aluminum alloy were analyzed. The electrolyte formulas were further optimized.

2. EXPERIMENTAL METHOD

Experimental samples are 6061 aluminum alloy (15 mm × 15 mm × 3 mm), the chemical composition is shown in Table 1.

Technological process: wire cutting sample - drilling - polishing on abrasive paper (600 #, 800 # and 1500 #) - washing by pure water - drying - micro-arc oxidation - washing by pure water - drying - testing properties of ceramic coatings.

Main components of three electrolyte systems are Na_2SiO_3 , $\text{Na}(\text{PO}_3)_6$, and NaAlO_2 , adding appropriate NaOH , $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2$ and other auxiliary additives to adjust the pH value, stability and electrical conductivity of solutions.

Power supply used in tests was MAO-65D pulse power supply, which could export asymmetric square wave pulse. The thickness of ceramic coatings was measured by TT260 eddy current thickness meter.

The surface morphology of ceramic coatings was characterized by JSM-5610LV scanning electron microscopy (SEM). The phase of ceramic coatings was analyzed by D8 ADVANCE X-ray diffraction (XRD) with diffraction angle 2θ : 20~80°. The hardness of cross section was measured by HV-1000 micro-hardness tester.

3. RESULTS AND DISCUSSION

3.1. Influencing factors of breakdown voltage

The changing regularity of the breakdown voltage with the variation of concentration electrolytes is shown in Fig. 1. The breakdown voltage is decreased with the increase of concentration electrolytes. Electrical conductivity is increased with the increase of concentration of electrolytes, required arcing energy is reduced, so that breakdown voltage is decreased. Different components of electrolyte have different effects on formation of ceramic coatings, the breakdown voltage in Na_2SiO_3 electrolyte system is the lowest, NaAlO_2 takes the second place and $\text{Na}(\text{PO}_3)_6$ is the highest, which was in accordance with Wu [5] researching conclusions. The changing regularity of breakdown voltage with the variation of

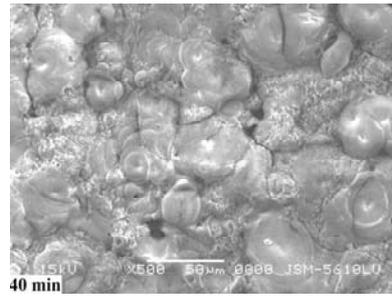
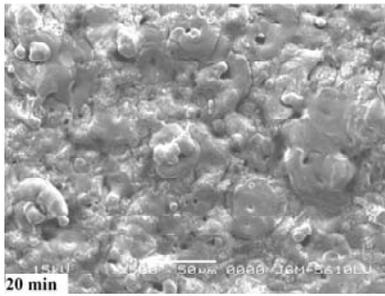


Fig. 3. The surface morphology of ceramic coatings in Na_2SiO_3 electrolyte system.

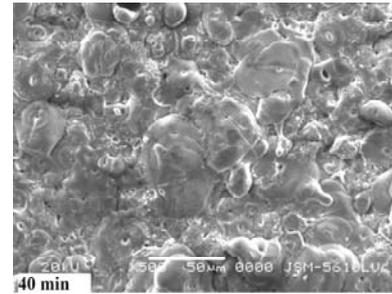
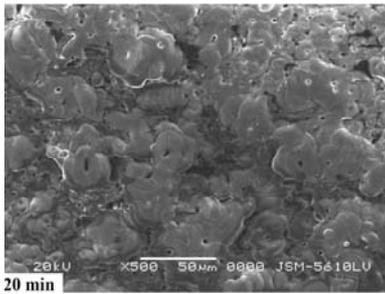


Fig. 4. The surface morphology of ceramic coatings in $(\text{NaPO}_3)_6$ electrolyte system.

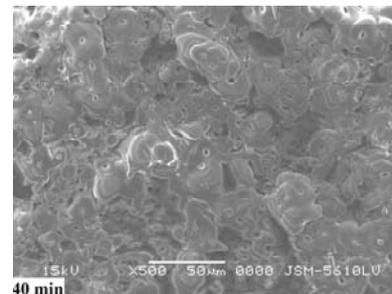
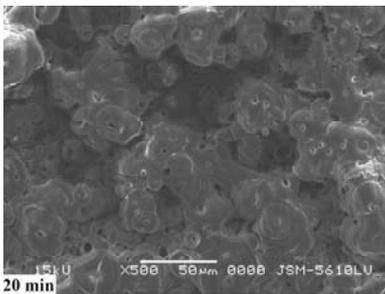


Fig. 5. The surface morphology of ceramic coatings in NaAlO_2 electrolyte system.

current density is shown in Fig. 2. The breakdown voltage of three kinds of electrolyte systems is almost invariant, in the case of certain electrolyte concentration, there is no significant relationship between breakdown voltage and current density. Yerokhin et al. [6,7] further researches show that breakdown voltage is related to distance between anode and cathode, electrode material and electrode polarity, in addition, no relationship is found out with electrolyte temperature.

3.2. Analysis of the surface morphology of ceramic coatings with different electrolyte systems

Samples are treated with three different electrolyte systems by constant current (8 A/dm^2) for 20 and 40 minutes. The changing regularity of surface morphology of ceramic coatings is shown in Fig. 3. From the macro point of view, ceramic coatings in three electrolyte systems are all offwhite. From the microscopic point of view, dark spots cover with on

the surface sample, this phenomenon shows that the discharge channel exists at that location. Many melting particles appear on the surface of ceramic coatings in Na_2SiO_3 electrolyte system (as shown in Fig. 3). There are no significant melting particles on the surface of ceramic coatings in the other two electrolyte systems, but show more regular round pie structure (as shown in Figs. 4 and 5). With increase of oxidation time, the microporous aperture of surface largens, the size of discharge channels are significantly increased, their number is decreased, there is molten material with rapid cooling and solidification around the discharge channels.

3.3. The growth of ceramic coatings in different electrolyte systems

The main concentration of electrolytes is all 8 g/L , samples are treated with constant current density (8 A/dm^2). The changing regularity of thickness of ceramic coatings with variation of oxidation time is

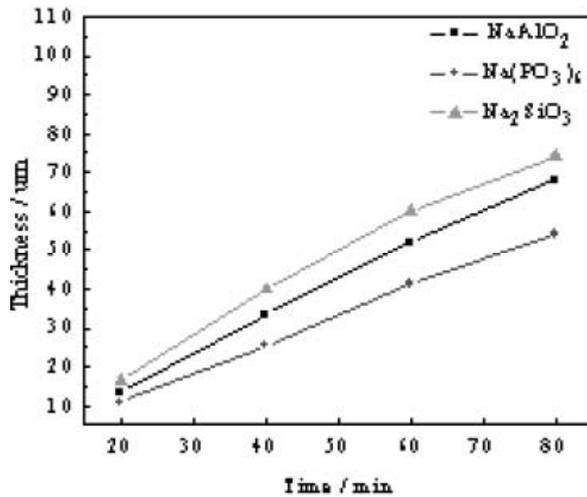


Fig. 6. The changing regularity of thickness of ceramic coatings with variation of oxidation time.

shown in Fig. 6. In the same oxidation time (<80 min), the thickness in Na₂SiO₃ electrolyte system is the thickest, NaAlO₂ takes the second place, Na(PO₃)₆ is the thinnest. Under conditions of certain current density and electrolyte concentration, the thickness of ceramic coatings in three electrolyte systems all basically appears linear growth trend with time increasing. Calculation of growth rate is used by the ratio of thickness and oxidation time, as can be seen from Fig. 6, the slope of the line is basically invariant. In the constant current model, the working voltage increases with the thickness ceramic coatings increasing, and the total current density is invariant to generate micro-arc discharge, so that the average growth rate of ceramic coatings is basically invariant in some oxidation time.

3.4. The changing regularity of hardness of ceramic coatings in different electrolyte systems

The load of micro hardness is 0.98 N, the pressure is kept for 10 seconds to the hardness of dense layer. The changing regularity of hardness of dense layer in different electrolyte systems is shown in Fig. 7. With the increase of oxidation time, the thickness of coatings is increased, the hardness of dense layer is improved gradually. The hardness of dense layer is the highest in NaAlO₂ electrolyte system, Na₂SiO₃ takes the second place, Na(PO₃)₆ is the lowest. The hardness distribution of cross section coatings is shown in Figure 8. The thickness of ceramic coatings obtained in NaAlO₂ electrolyte system is 60 μm. As can be seen from Fig. 8, the hardness of dense layer is relatively high, the

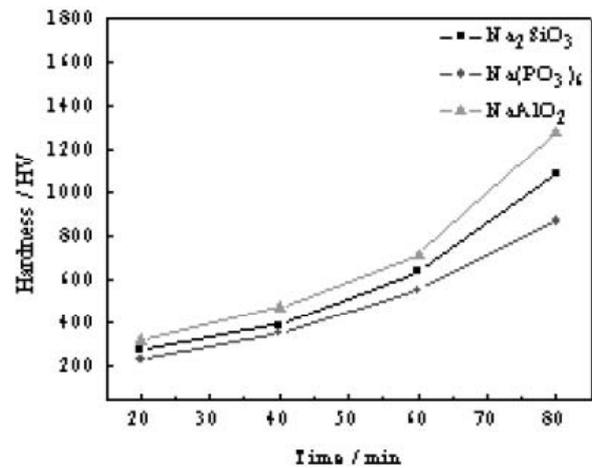


Fig. 7. The changing regularity of hardness of dense layer in different electrolyte systems.

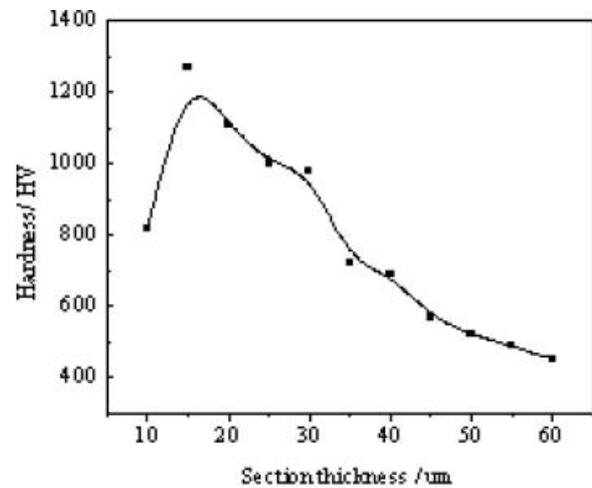


Fig. 8. The hardness distribution of cross section coatings in NaAlO₂ electrolyte system.

hardness of loose layer is rather low. When the distance from substrate interface is 15 μm, the hardness reaches the highest (1270 HV), then it begins to reduce gradually. There is a transition zone between the coatings and near the substrate interface with its own substrate material and ceramic coatings material, therefore the hardness is rather low in this region, which further promotes metallurgical bonding between ceramic coatings and substrate [8].

Spectra of XRD of ceramic coatings formed in three different electrolyte systems is shown in Fig. 9. There is mainly Al substrate and Al₂O₃ diffraction peaks, ceramic coatings mainly consist of the phases of α-Al₂O₃ and γ-Al₂O₃. γ-Al₂O₃ phase increases gradually from inside to outside, α-Al₂O₃ shows a contrary tendency. α-Al₂O₃ phase is thermodynamically stable phase, γ-Al₂O₃ for the thermodynamics of non-stable phase, and can be

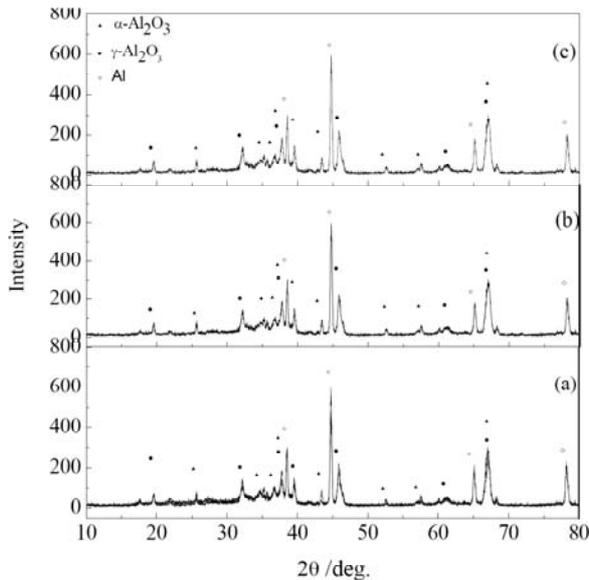


Fig. 9. Spectra of XRD of ceramic coatings formed in three different electrolyte systems.

transformed into α - Al_2O_3 phase within the temperature range of 1000 °C to 1200 °C [9]. According to the relatively strong diffraction characteristics of a and g phase, if the distance is nearest between the diffraction peaks, and there is no overlap with other diffraction peak, then the relative content of α - Al_2O_3 and γ - Al_2O_3 can be calculated by the ratio intensity of these diffraction peaks [10]. The relative content of α - Al_2O_3 and γ - Al_2O_3 is 56.3% in Na_2SiO_3 electrolyte system, 43.6% in $\text{Na}(\text{PO}_3)_6$ electrolyte system and 62.8% in NaAlO_2 electrolyte system. The hardness of ceramic coatings obtained in NaAlO_2 electrolyte system is higher than that in the other electrolyte systems.

4. CONCLUSIONS

(1) The breakdown voltage is decreased with increasing of electrolyte concentration, there is no significant relationship between breakdown voltage and current density in three kind of electrolyte systems. Breakdown voltage is closely related to the type and concentration of electrolyte systems, it is the lowest in Na_2SiO_3 electrolyte system.

(2) In constant current model, the thickness of ceramic coatings shows linear increase with the increment of oxidation time in three kinds of electrolyte systems, growth rate remains essentially

constant. In the same oxidation time (<80 min), the thickness in Na_2SiO_3 electrolyte system is the thickest, NaAlO_2 takes the second place, $\text{Na}(\text{PO}_3)_6$ is the thinnest.

(3) The ceramic coatings in different electrolyte systems are mainly composed of α - Al_2O_3 and γ - Al_2O_3 , the relative content of α - Al_2O_3 and γ - Al_2O_3 in NaAlO_2 electrolyte system is higher than that in the other electrolyte systems. The hardness of dense layer is relatively high, the hardness of loose layer is rather low. When the distance from substrate interface is 15 μm , the hardness reaches the highest (1270 HV), then it begins to reduce gradually.

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