

Characteristics of Oxide Layers on 2021 Al Alloys by Plasma Electrolytic Oxidation in Aluminate Fluorosilicate Electrolyte

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Abstract: Oxide layers were prepared on 2021 Al alloys substrate under a hybrid voltage of AC 200V (60Hz) combined with DC 260V value at room temperature within 5~60min by plasma electrolytic oxidation (PEO). An optimized aluminate-fluorosilicate solution was used as the electrolytes. The surface morphology, thickness and composition of layers on 2021 Al alloys within different reaction times were studied. The results showed that it is possible to generate good property oxide layers on 2021 Al alloys in aluminate-fluorosilicate electrolytes. Analysis show that the double-layer structure oxide layers consist of different states of Al₂O₃ such as α -Al₂O₃ and γ -Al₂O₃. For short treatment times, the formation process of oxide layers follows a linear kinetics, while for longer times the formation process slows down and becomes a steady stage. During the PEO processes, the average size of the discharged channels increase gradually as the treatment time increased.

Keywords: Plasma Electrolytic Oxidation, 2021 Al Alloy, Aluminate Fluorosilicate, Oxide Layer

1. INTRODUCTION

High strength aluminum alloys are widely used in automotive and aircraft industries, which allow reducing significantly the weight of the engineering constructions. In these fields, very often the main requirements for the components include high fatigue, corrosion and wear resistance. The first requirement is achieved usually by a proper material selection. For example, 2021 is an aluminum alloy, with copper and magnesium as the alloying elements, which is used in applications requiring high strength to weight ratio, as well as good fatigue

resistance. Due to poor corrosion resistance, it is often clad with Zn for protection, although this will reduce the fatigue strength. Traditional anodizing process is another classical approach to increase the tribological properties of aluminum alloys. The process running at low temperature allows formation of a thick and strongly adherent oxide layer with high hardness [1]. However, the coating brittleness and the cracks induced during the anodizing process also will reduce the fatigue strength of the hard-anodized components [2].

The novel electro-chemical surface treatment process, plasma electrolytic

oxidation (PEO), has been proved an effective surface protection technique to produce oxide layers on Al alloys with high tribological properties. It is reported [3,4] that the PEO layer may cause no more than 10% reduction in fatigue limit of magnesium and aluminum alloys, which is substantially lower than the effect of anodizing. One of the most important factors affecting the fatigue strength of PEO layers is the residual internal stress. It is recognized that the compressive residual stresses retard the fatigue crack initiation in the layer and therefore the fatigue life of the coated components increases [5]. Further researches showed that the PEO oxide layers offered attractive combination of wear resistance, corrosion resistance, mechanical strength, interfacial adhesion and thermal property [6-8].

According to previous researches [3], aluminate solution has been proved that it is able to form smooth oxide layers on Al alloys as no introduction of impurities. Besides, the addition of fluorite and silicate elements can also effectively enhance the property of the oxide layers [9]. In the present work, the PEO processes were carried out to produce oxide layers on 2021 Al alloy in alkaline aluminate fluorosilicate electrolytes. An optimized hybrid voltage of 200V AC amplitude combined with 260V DC value was applied from the power supply. The surface morphology, microstructures, elements distribution and microhardness of oxide layers were investigated.

2. EXPERIMENTAL

2021 Al alloy (Cu, 5.8-6.8 wt.%; Mg, 1.2-1.8 wt.%; Si, 0.5 wt.%; Fe, 0.5 wt.%, Zn, 0.1 wt.%; Mn, 0.2-0.4 wt.%; Ti, 0.15 wt.% and Al, balance) with dimension of D 30 mm $\times$ H 16 mm and surface roughness of $Ra \leq 0.1 \mu\text{m}$ were fabricated. Prior to PEO treatment, samples were pretreated (degreased and ultrasonically cleaned in the acetone medium and thoroughly dried), and then immersed in electrolyte for PEO treatment. During the treatment, the PEO

process was carried out at the room temperature for 5~60min in a 2-litre water-cooled stainless steel tank, which also served as a counter electrode, and the metallic samples immersed in the electrolyte served as an anode. The electrolytes contain Na_2AlO_2 , Na_2SiF_6 and NaOH of 8g/l, 0.5g/l and 2g/l separately. According to previous researches, a hybrid voltage of 200V AC (60-Hz) with 260V DC was applied from the PEO power supply. After the treatment, the specimens were thoroughly rinsed in running demineralized water and dried with compressed air.

The AC amplitude was slowly increased to 200 V to maintain the current density at 3~4 dA/cm^2 throughout the experimentation, afterwards the DC value was increased gradually till 260V so as to maintain the reset current density even as the layer thickness gradually increased. The plasmas initiated to discharge throughout the surface at DC 140 V based on AC 200 V. During the PEO process, plenty amount of water vapor was generated by the exothermal PEO reaction.

The phases of the oxide layers were investigated with Philips-X'Pert system X-ray diffractometer (XRD) (Cu K_α radiation) and the scans were performed with 0.02° θ step size in the 2θ range of $30-90^\circ$. The microstructures of surfaces and cross-sectional morphologies of treated samples were examined by a JSM 5610 scanning electron microscopy (SEM). The microhardness of the oxide layers at each 10 different places were measured by VLPK2000 Mitutoyo Hardness Test Machine using 0.1 N loading energy in 30s dwell time, and then the average microhardness was calculated.

3. RESULTS AND DISCUSSION

The XRD patterns of PEO layers prepared in 5, 10, 15 and 60min separately are presented in Fig. 1. Strong diffraction peaks of the Al substrate were detected because the layers are so thin that X-rays could penetrate the layers easily. From Fig. 1, it is concluded

that typical phase composition of PEO layers represented by α - Al_2O_3 and γ - Al_2O_3 are the main phases. The γ - Al_2O_3 phase dominated the layers during the short time treatment. With the increasing treatment time, γ - Al_2O_3 phase gradually transformed into α - Al_2O_3 phase. It is well known that α - Al_2O_3 is a stable alumina phase, which has trigonal structure with a high melting point of 2050 °C. Moreover, γ - Al_2O_3 is a meta-stable phase, which can transform into α - Al_2O_3 phase by heating up to the temperature interval between 800 and 1200 °C [10, 11].

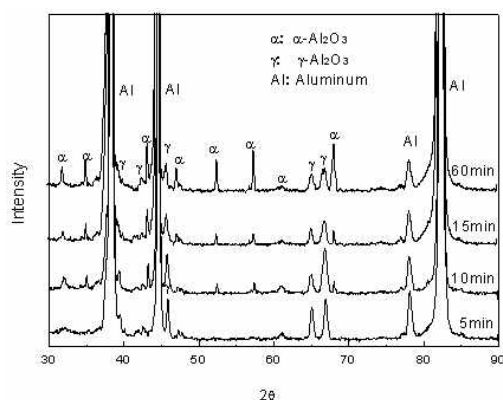


Figure 1: XRD patterns of the oxide layers prepared in 5, 10, 15 and 60min.

Fig. 2 illustrates the surface features of the PEO-treated samples in different reaction times. It is clearly indicated that the presence of discharge channels in all electrolytes appeared as the same dark circular spots, with pancakes like microstructures, which distributed all over the surface of the layers. As the existence of the brittle phase of α - Al_2O_3 , surface defects of cracks unavoidable appeared on the layer surfaces. From the figures, it is concluded that the average size of the discharged channels increase gradually as the treatment time increased. Besides, there were some porous phases on the layer surfaces. Sodium fluorosilicate was easily decomposed at high temperatures in the discharging channels to release silicon and fluorite ions. Silicon was prove to be an immigrate element [12], which would combine with aluminum ions to form the Al-Si-O phase. Afterwards, the

Al-Si-O phase would then be ejected out of the discharging channels and pushed around the discharging channels, finally cooled down and solidified as the porous phase around the channels.

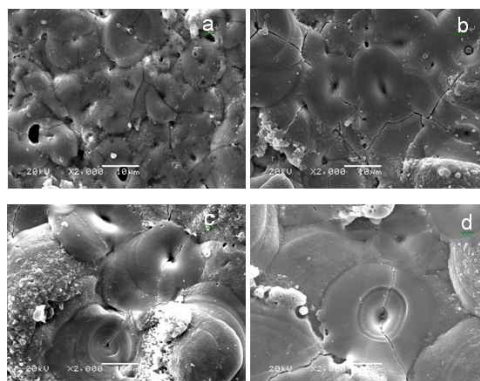


Figure 2: SEM surface morphologies of PEO treated samples prepared in different times of a) 5min; b) 15min; c) 30min and d) 60min.

The cross-sectional SEM micrographs of the layers processed in 5, 15, 30 and 60min are shown in Fig. 3. Fig. 4 reports the measurements of the average layer thickness as a function of the treatment time. From these figures, it is clear that the average layer thickness increases linearly as the reaction times increase at the initial state, and then the growth rate slowed down, and finally it came to a limitation after 30min reaction. Such increasing growth kinetics for the formation of the oxide layers was studied by other researchers [13]. According to these researchers, the oxide layers growth results from molten aluminum that was oxidized when flowing outwards through the discharging channels. By this way, alumina was formed and transformed to form different phases, and contributed to the growth of the layers when being ejected from the channels and rapidly quenched at the interface between electrolyte and substrates. In the initial linear growth stage, the transformation of γ - Al_2O_3 to α - Al_2O_3 was the main reason that led the growth of the outer oxide layer. By observing the PEO treatment with eyes, the discharge phenomenon presented violet, tiny and fast moving features. When the outer oxide layer grew

thick enough that the alumina phase transformation slowed down, and the γ - Al_2O_3 phase gradually increase and form the inner layer. Finally, when both the outer and inner oxide layer grew thick, they were hard to be broken down. So the growth rate decreased rapidly, and finally became zero. In this stage, the discharge phenomenon became yellow, larger and slower moving. Above all, the double-layer structure oxide layer finally formed, consisted of hard α - Al_2O_3 phase distributing upon γ - Al_2O_3 phase, which could behavior as a buffer zone and resulted in good shock absorption ability.

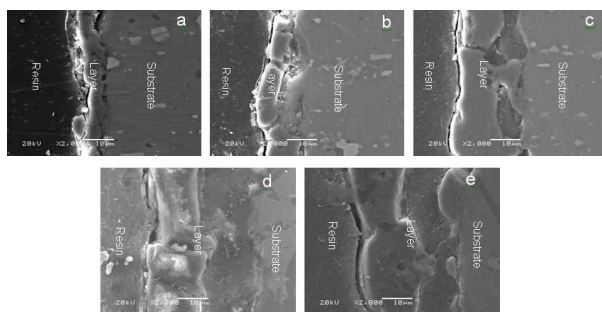


Figure 3: Cross sectional SEM micrographs of the oxide layers prepared in different times of a) 5min; b) 10min; c) 15min, d) 30min and e) 60min.

It is found that it is hard to break down the oxide layers when they became thicker and thicker with the treatment time increasing. So at the last stage of the PEO process, only few weak area continue to discharge, which could effectively heal the defects such as crack and bubbles generated in the initial stage.

Fig. 4 reports the measurements of the outer layer microhardness and the total layer thickness as a function of the treatment time. The outer layer microhardness presents a similar growth trend as the total layer thickness. It is expected that the proportion of α - Al_2O_3 phase gradually increased with the reaction time. Such a phase gradient is responsible for the observed microhardness variation accounted with the reaction time. While the inner layer microhardness is about 400Hv as it is consisted of soft γ - Al_2O_3 phase.

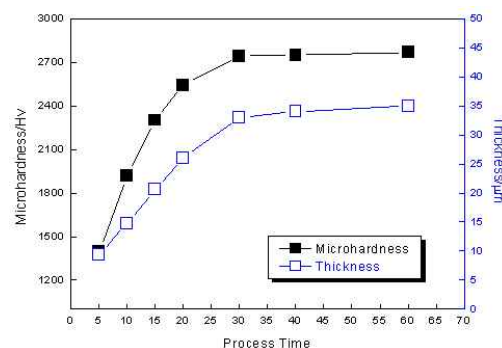


Figure 4: Microhardness and thickness of the oxide layers prepared in 5~60min.

4. CONCLUSIONS

The PEO processes were carried out in alkaline aluminate fluorosilicate electrolytes on 2021 Al alloys substrate within 5~60min under a hybrid voltage. The PEO oxide layers present smooth surfaces, with pancake structures surrounded by small amounts of Al-Si-O porous phases. During the PEO process, the size of the discharge channels increase gradually as the treatment time increased. The oxide layers mainly consist of γ - Al_2O_3 and α - Al_2O_3 . The transformation of γ - Al_2O_3 into α - Al_2O_3 results in the linear growth of the oxide layer in the initial stage, and then the growth of γ - Al_2O_3 took the place of transformation to accelerate the growth of the oxide layer, finally the growth rate became zero and a double-layer structure oxide layer formed. The content of different alumina phases is dependent of the oxide layer thickness and microhardness.

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