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Deposition of Oxide Layer on Aluminium Via Plasma Electrolysis Method in Alkali Solutions by Unipolar Pulsed Current System and Study of its Physical Properties

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Abstract: The principle aim of the present study is to produce Plasma Electrolytic Oxidation (PEO) coating on aluminum via unipolar pulsed current system and to indicate that it is possible to attain the similar bipolar system results reported in the literature. A brief comparison was also made between unipolar deposit properties with those achieved via direct current (duty cycle 100%) system. In the present study, a hard ceramic layer was produced on aluminum by PEO method under unipolar pulsed current system. The results showed that unipolar pulsed current system considerably improves oxide layer properties due to its better deposit growth control as compared with direct current system. The mean hardness value of the PEO coating was found to be 1700 Vickers.

Key words: Plasma electrolysis, unipolar pulsed current system, aluminum

INTRODUCTION

Plasma electrolytic oxide coatings are being interesting subject for researchers due to their special mechanical properties such as hardness, wear resistance, tensile strength, excellent interfacial adhesion and high level of corrosion resistance. In this method a thick oxide layer is formed on aluminum surface by arcing mechanism. The structure of the oxide layer is composed of high temperature α-Al_2O_3 and γ-Al_2O_3 phases.

Unstable γ-Al_2O_3 phase transforms to the stable α-Al_2O_3 phase by annealing during process. This gives rise to an improvement in coating properties. At the beginning, these coatings were produced by using direct current. The resultant deposits exhibited high porosity levels, due to lack of control on current regime. Hence, a controllable current system should be used to improve coating properties (Wang and Nie, 2006).

Curran and Clyne (2005) have produced PEO coatings with different thickness on 6082 aluminum alloy using silicate electrolyte and have investigated their thermo physical properties. Yerokhin *et al.* (2005) have studied the deposition of aluminum oxide layer on an aluminum alloy by bipolar pulsed current. They showed that it is possible to deposit a uniform layer with thickness of 165-190 µm and hardness values of 1800-2300 Vickers by using an electrolyte containing 2-3 g L^{-1} Na_2SiO_3 and 2-3 g L^{-1} KOH. Results of other researchers (Voevodin *et al.*, 1996) indicated that it is possible to produce a 100-200 µm thickness coating with higher wear resistance and 1700 Vickers hardness in 1 g L^{-1} $NaSiO_3$ containing electrolyte. Using an electrolyte containing over 30 g L^{-1} $NaSiO_3$ and 5 g L^{-1} NaOH Tian *et al.* (2002) were able to produce an oxide layer on an Al alloy. They concluded that the γ-Al_2O_3 phase was formed prior to α-Al_2O_3 phase being formed on the substrate surface. They also showed that the γ phase was transformed to a higher wear resistance α phase during deposition process.

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Although the quality of deposits produced in laboratory via bipolar method is excellent but in industrial practice, this is not always feasible since the cost of power supplies and chilling equipment is increased significantly.

The principle aim of the present study is to produce PEO coatings on aluminum via unipolar pulsed current system for various lengths of time, electrolyte concentrations and applied current densities and to indicate that it is possible to attain the similar bipolar system results reported in the literature. An attempt will also be made to compare deposit properties with those of achieved via direct current (duty cycle 100%) system.

MATERIALS AND METHODS

A 5 kW power supply with a maximum rectified voltage of 900 V output and a microprocessor system for producing pulse with controllable current were used. Specimens of 2024 aluminum alloy were ground to 3000 mesh, using SiC emery papers, were degreased by acetone for 3 min and then were activated by 50 Vol%. nitric acid for 20 sec.

The electrolyte consisted of sodium aluminate (5, 10 and 15 g L^{-1}) and potassium hydroxide (0.5 and 1 g L^{-1}) (Shi-Gang *et al.*, 2005). Temperature of the electrolyte was controlled by a temperature controller system over the temperature range of $31\pm1°C$. AISI 304 stainless steel vessel equipped with an agitator which also served as cathode was used as electrolyte bath. Experiments were carried out in various current densities of 5, 10 and 15 A dm^{-2}, frequencies of 50, 150 and 300 Hz and duty cycles of 60, 80 and 100% for 20 min.

Surface morphology of coated samples was studied by a Camscan MV2300 scanning electron microscope. A Brucker D8 Advanced x-ray diffractometer with a Cu K_α radiation source was used to characterize the structure of oxide layers. Bohler microhardness was also used to measure the hardness of the deposits.

RESULTS AND DISCUSSION

The voltage between anode and cathode was increased to 250-350 V with applying constant current density on specimens. In above mentioned voltage range sample surface became luminous as a result of micro arcs formation on the surface. By increasing the voltage high density micro arcs were converted to low density macro arcs on the surface. The voltage-time diagram is divided to four regions (Wang and Nie, 2006).

Figure 1 shows the effect of current density on surface morphology of oxide coating. As, can be seen, the surface roughness increases with increasing current density.

With increasing current density, ohmic resistance of oxide layer increases and stronger arcs with much heat pass from coating layer. Consequently, local melting into arc channels increases (Yerokhin *et al.*, 2003) and sprinkle of melted materials on surface leads to high surfaces roughness. Rapid solidification of local melting products gives rise to unstable γ-Al_2O_3 to be formed. With increasing oxide layer thickness, the porosity of its inner parts is recovered by local melting of outer parts of coating. It has been reported that some of the unstable γ-Al_2O_3 in inner parts of oxide layer gradually transforms to the stable α-Al_2O_3 phase due to liberated heat of surface arcs at coating (Khan *et al.*, 2005). It is predicted that with increasing the thickness of oxide layer, inner parts of coating predominated by the stable α-Al_2O_3 phase. On the other hand, due to higher cooling rate of oxide layer adjacent to the electrolyte the unstable γ-Al_2O_3 was the predominated phase at the outer parts of coating.

To better evaluation of α and γ phases, their reference peaks are shown in Fig. 2.

The effect of current density on phase structure of oxide layers is presented in Fig. 3. It shows that an increase in current density gives rise the diffracted picks density of α-Al_2O_3 phase to be
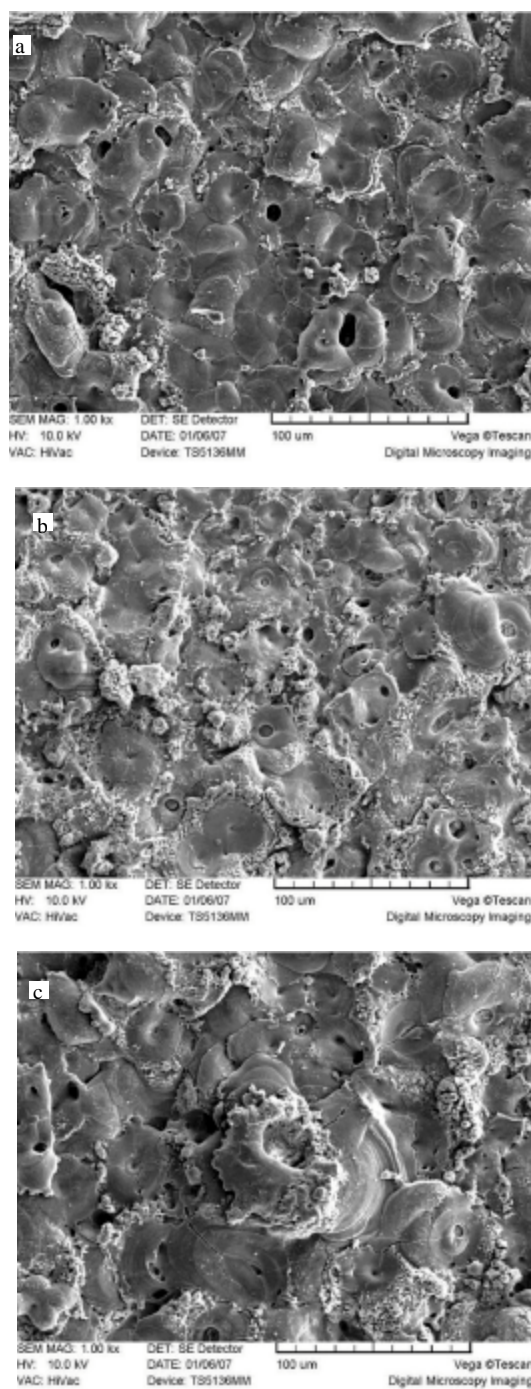
Fig. 1: Effect of current density on surface morphology of oxide coating. Electrolyte containing 10 g L^{-1} $NaAlO_2$ and 1 g L^{-1} KOH, frequency of 50 Hz, duty cycle of 80% and current density of a: 5A dm^{-2}, b: 10A dm^{-2} and c: 15A dm^{-2}
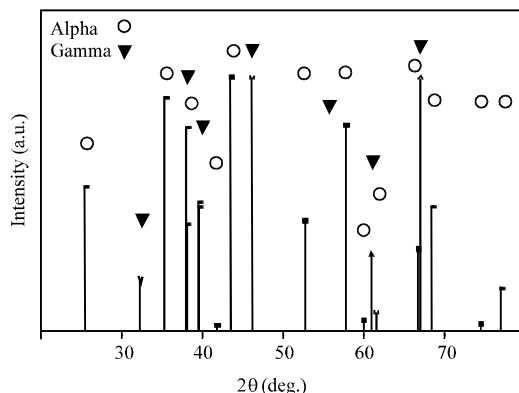
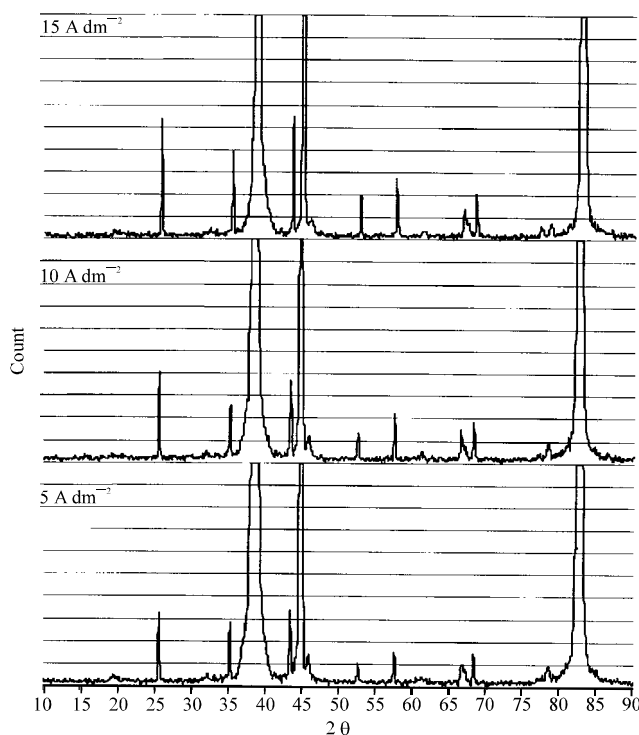Fig. 2: Reference peaks of the α-Al_2O_3 and γ-Al_2O_3 phases (Khan *et al.*, 2005)

Fig. 3: Effect of current density on phase structure of aluminum oxide layer. Electrolyte containing 10 g L^{-1} $NaAlO_2$ and 1 g L^{-1} KOH, frequency of 50 Hz and duty cycle of 80%

increased. It is believed that increasing current density give rise to more heat in oxide layer. This has led to much unstable γ phase to be transformed to stable α phase, especially in inner layer. Since the hardness of α phase is higher than γ phase (Yerokhin *et al.*, 1999), the hardness values at inner layer is more than that of outer layer (Table 1).

As indicated in Table 1, by increasing current density from 5 to 10 A dm^{-2}, hardness values have been increased in inner parts of the coating. But this has been reduced again with additional increase in current density from 10 to 15 A dm^{-2}.
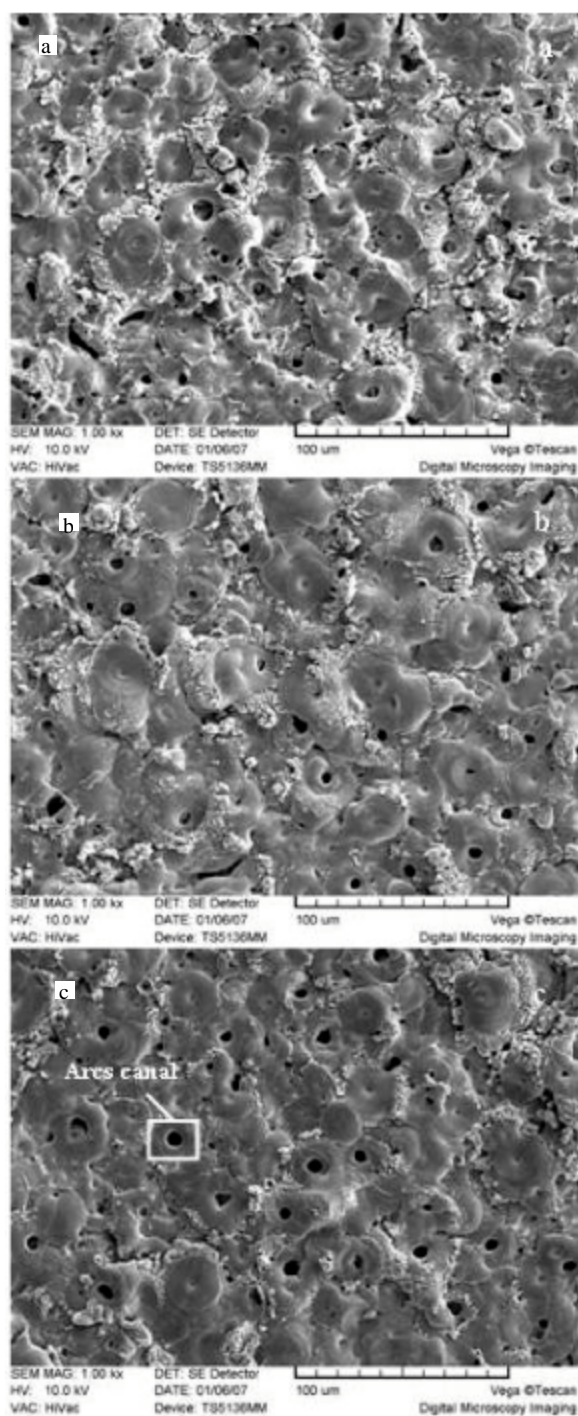
Fig. 4: Effect of frequency on surface morphology. Electrolyte containing 10 g L^{-1} $NaAlO_2$ and 1 g L^{-1} KOH, current density of 5A dm^{-2}, duty cycle of 80% and frequency of a: 50Hz, b: 150Hz and c: 300Hz

The reason for this is believed to be due to more heat liberation at surface arcs of coating when current density rises to 15 A dm^{-2}. At this condition, depths of arc affected zones increases. This gives rise to local melting and subsequently higher amount of porosity is formed at inner parts of oxide layer. Outer parts of coating which contain more arc channels are more porous and therefore show lower hardness values than inner parts. The presence of more γ phase at outer parts of coating is also another parameter in reducing their hardness values. This result is similar to that of Yerokhim *et al.* (2005) which they have achieved in bipolar pulsed system.

Figure 4 shows the effect of frequency on oxide layer morphology. In unipolar pulsed current system, it is possible to control arc life time. Controlling arc life time itself, results in liberated heat and depths of arcs to be controlled. By decreasing arc life time as a result of increasing frequency, it is possible to reduce liberated heat and the amount of local melting in arc channels. This lowers the surface relative roughness. Of course, high amount of open arc channels is the secondary effect of increasing frequency. This issue is obvious in Fig. 4C when the amount of frequency is 300 Hz. Reduction in hardness values as a result of increasing frequency is shown in Table 1. This is believed to be due to impossibility of recovering inner layers of coating by surface arcs. As mentioned earlier, high frequency leads to heat reduction in coating and consequently less transformation of γ phase to α phase Fig. 5.

The effect of duty cycle on oxide layer morphology is almost similar to frequency effects as mentioned above. Therefore to avoid repetition, the related XRD patterns and morphology of the oxide layer have not been presented.
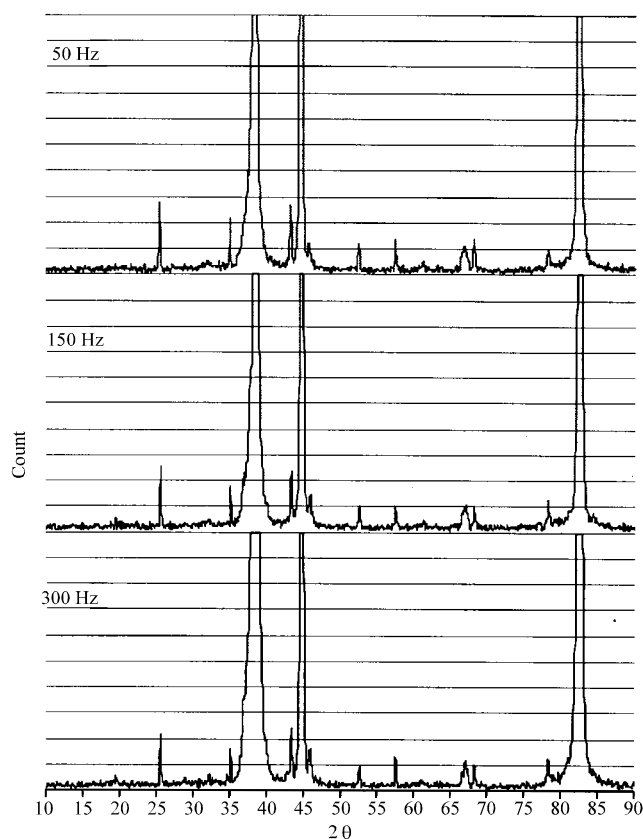

Fig. 5: Effect of frequency on phase structure of aluminum oxide layer. Electrolyte containing 10 g L^{-1} $NaAlO_2$ and 1 g L^{-1} KOH, current density of 10 A dm^{-2} and duty cycle of 80%
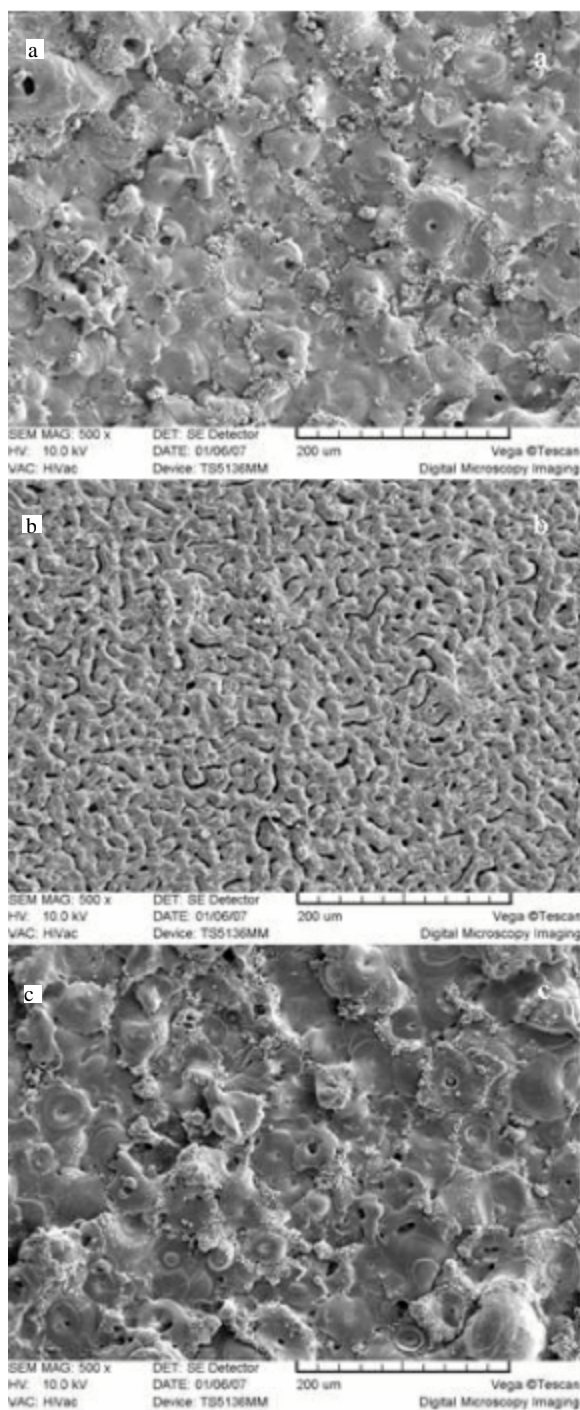
Fig. 6: Effect of electrolyte concentration on surface morphology of aluminum oxide layer. Current density of 10A dm^{-2}, frequency of 50 Hz, duty cycle of 80% and electrolyte containing a: 5 g L^{-1} NaAlO$_2$, 1 g L^{-1} KOH, b: 5 g L^{-1} NaAlO$_2$, 0.5 g L^{-1} KOH and c: 15 g L^{-1} NaAlO$_2$, 1 g L^{-1} KOH

At constant current density and frequency, higher duty cycle results in higher arc life time, local melting, depths of arc channels and surface relative roughness. The effect of duty cycle on oxide phase structure of coating is the same as frequency effect. When duty cycle equals to 1, unipolar pulsed current regime convert to direct current regime. The generated heat at arc channels and amount of γ to α phase transformation increases with increasing duty cycles. But it seems when duty cycle increases from 80 to 100%, the arc channels extended into inner layers of coating. This gives rise to more porosity and γ to be formed again and consequently hardness values to be reduced (Table 1).

The effect of aluminate and potass concentration on coating surface morphology is shown in Fig. 6. At constant concentration of aluminate, the surface morphology changes from wormicular form at 0.5 g L^{-1} potass to a rougher one at 1 g L^{-1} potass as a result of discharge channels and local melting around them. The wormicular morphology might be resulted from preferred growth of coating on Al surface (Wang and Nie, 2006). By increasing potass amount to 1 g L^{-1}, conductivity of the electrolyte is improved and growth mode changes from preferred to a uniform one and oxide layer extended uniformly on Al surface. Increasing the potass amount raises dissolution of oxide layer; however, this negative effect is negligible up to 1 g L^{-1} due to passivating role of aluminate. At constant potass concentration, an increase in aluminate concentration which plays as a passive role of oxide layer

Table 1: Hardness mean values of the oxide layer obtained at different conditions

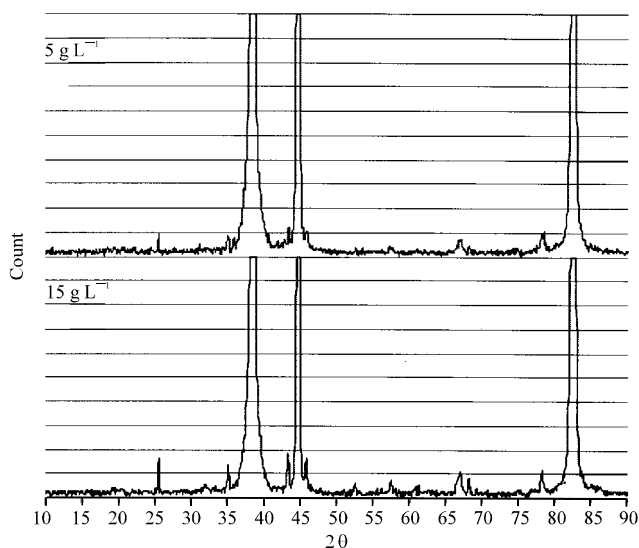| Parameters		Hardness of oxide layer (VHN)	
		Middle parts	Outer parts
Current density (A dm 2)	5	1720	1460
	10	1850	1500
	15	1760	1600
Frequency (Hz)	50	1850	1540
	300	1700	1440
Duty cycle (%)	60	1760	1590
	80	1850	1510
	100	1700	1440
NaAlO2 concentration (g L 1)	5	1680	1330
	15	1850	1440

Fig. 7: Effect of aluminate concentration on phase structure of aluminum oxide layer. Current density of 5A dm^{-2}, frequency of 50 Hz, duty cycle of 60% and KOH concentration of 0.5 g L^{-1}

prevents it from dissolution. The presence of aluminate in electrolyte also acts as a source for Al and O ions and increases the growth rate of coating. Increasing coating growth rate growth rate also affects the phase structure of coating. Acquired voltage for passing current increases with increasing coating growth rate due to raising dielectric resistance of oxide layer. Increasing voltage give rise to more heat liberation in arc channels in inner parts of coating and much transformation of γ to α phase (Fig. 7) and higher hardness coating (Table 1).

CONCLUSION

PEO coatings on aluminum consist of two high temperature α-Al$_2$O$_3$ and γ-Al$_2$O$_3$ phases. Unstable γ-Al$_2$O$_3$ phase transforms to stable α-Al$_2$O$_3$ phase during annealing. Numerous factors such as electrolyte concentration, current density, duty cycle and frequency influence morphology, phase structure and hardness of PEO coatings. There are optimum conditions for the amounts of current density (10 A dm^{-2}), aluminate (10 g L^{-1}) and potass concentration (1 g L^{-1}). Higher current densities or aluminate concentrations give rise to reduction in coating hardness values. The quality and hardness values of outer layers of PEO coatings are lower than inner layers due to the existence of higher porosity and lower α phase. The usage of unipolar pulsed current regime allows control arc life time, consequently generated heat in coating reduces and quality of coating improves. The quality of deposited layer via pulsed unipolar is better than that of simple DC current (duty time 100%) system and is approximately similar to the deposited oxide layer by pulse bipolar system.

ACKNOWLEDGMENT

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