

Study of the growth kinetics, microhardness and morphology of PEO coatings formed on Al 2024 alloy in alkaline-silicate electrolytes using different current waveforms

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Plasma Electrolytic Oxidation (PEO) is currently widely used technique of Al-alloys surface treatment providing the obtaining of composite anticorrosive and wear resistant coatings. The microhardness of these coatings can be almost equal to the theoretical corundum microhardness thanks to the formation of high temperature α -modification of alumina in the inner part of coating. However the conditions of intensive formation of this phase of alumina in the coating have not been defined explicitly, and therefore the ways of obtaining of relatively thin ($< 40 \mu\text{m}$) and hard coatings are not established.

The purpose of the present work is to investigate the ways to intensify $\alpha\text{-Al}_2\text{O}_3$ formation in the PEO-coating making vary different parameters such as current waveform and substrate temperature using a widely used commercial alloy Al 2024.

The PEO coatings were obtained using inverter based PC controlled power supply which allows to provide 50 Hz sinusoidal AC with adjustable DC offset, in an alkaline silicate electrolytes (3g/L NaOH ; 7 g/L $\text{Na}_2\text{O} \cdot 2,9\text{SiO}_2 \cdot 8\text{H}_2\text{O}$). We took as varying parameter the ratio R between positive (Q_p) and negative (Q_n) charges such as

$$R = \frac{Q_p}{Q_n}.$$

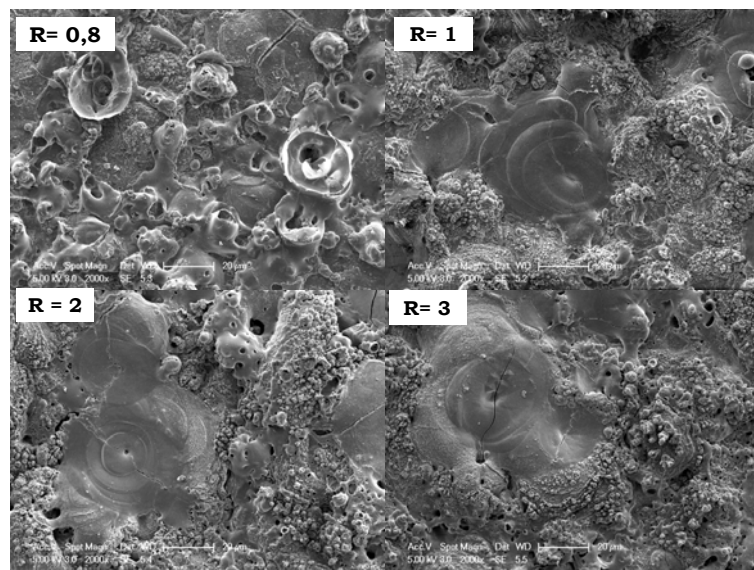


Figure 1. SEM-micrography of coatings' surfaces

The experimental results presented in figure 1 show that increasing value of R leads to the increase of dimensions of "pancakes" as well as the diameter of pore and the presence of Si-rich phase (probably SiO_2). These facts lead to increase of coating roughness as shown in figure 2. The precipitation of Si has been revealed only in the outer layer of coating. During PEO in alkaline-silicate solutions the deposition of SiO_2 on the coating surface is a result of thermo-chemical transformations of polyanions such as $n[\text{Si}_x\text{O}_y]^{2-}$ into SiO_2 , and also evaporation of solvent of electrolyte in contact with plasma micro-discharges.

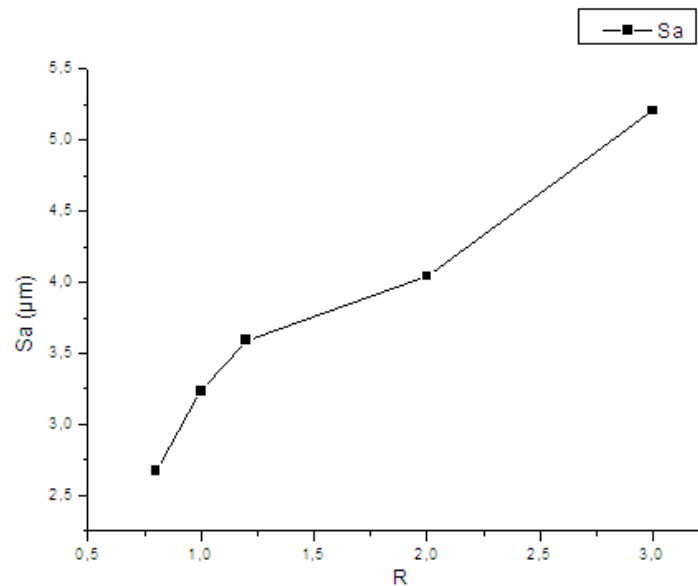


Figure 2. Influence of ratio R on coating roughness (Sa)

According to EDX analysis, the pancakes are mainly composed by Aluminium and Oxygen (obviously of Alumina) without any trace of Si (figure 3a) in contrast to the “sponge” phase that is mainly composed of Si (figure 3b).

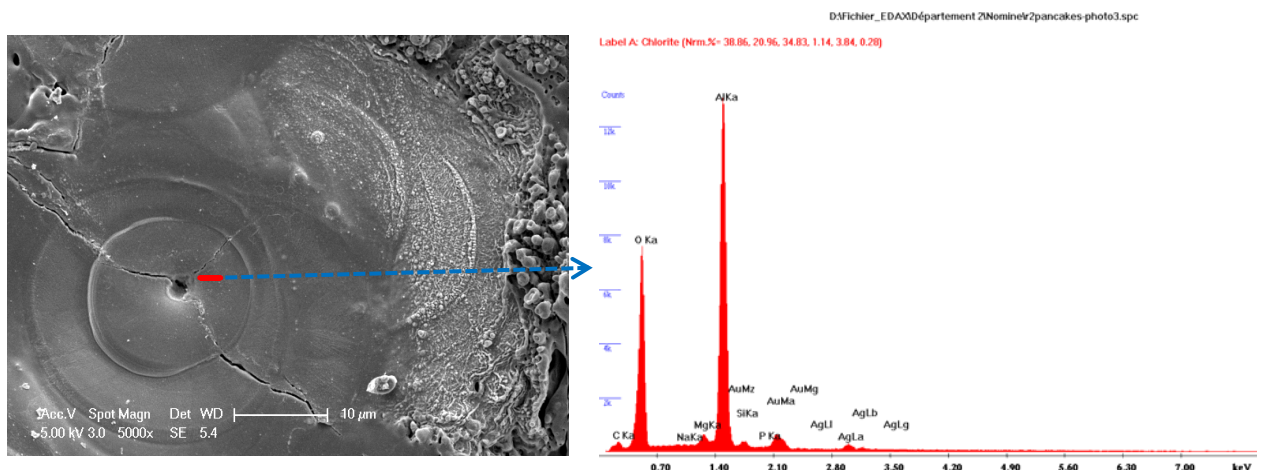


Figure 3a. EDX qualitative analysis on “pancake”

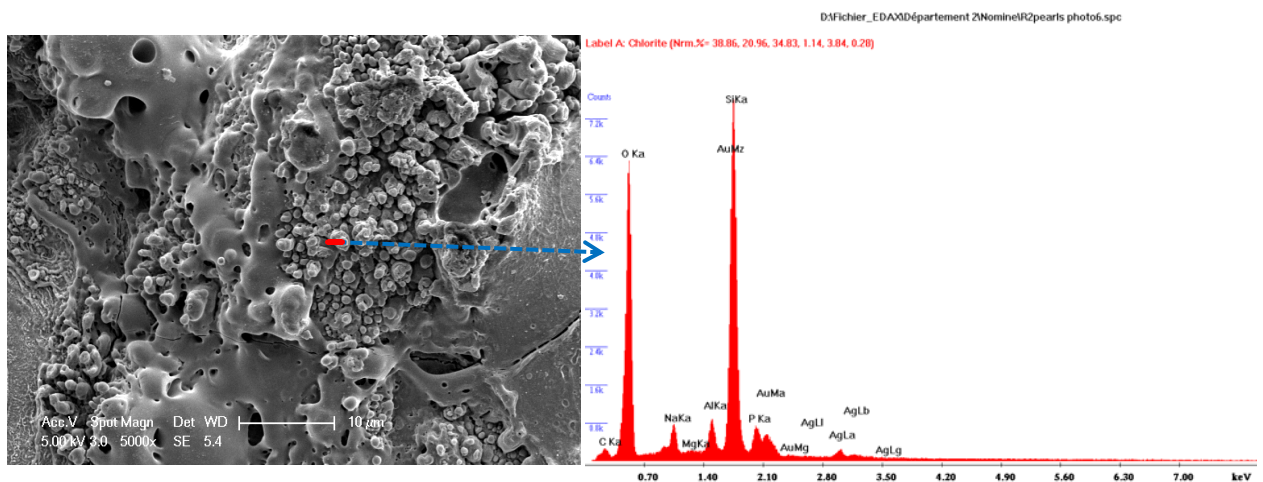


Figure 3b. EDX qualitative analysis on “sponge”

The XR analysis revealed the presence of slight amount of corundum phase in coating obtained with a current density of 15 A/dm² with R varying from 0,8 till 3. Nevertheless the increasing R value provides higher amount of α -phase in the coating (figure 4). The high temperature modification of alumina is mainly concentrated in the inner layer of coating.

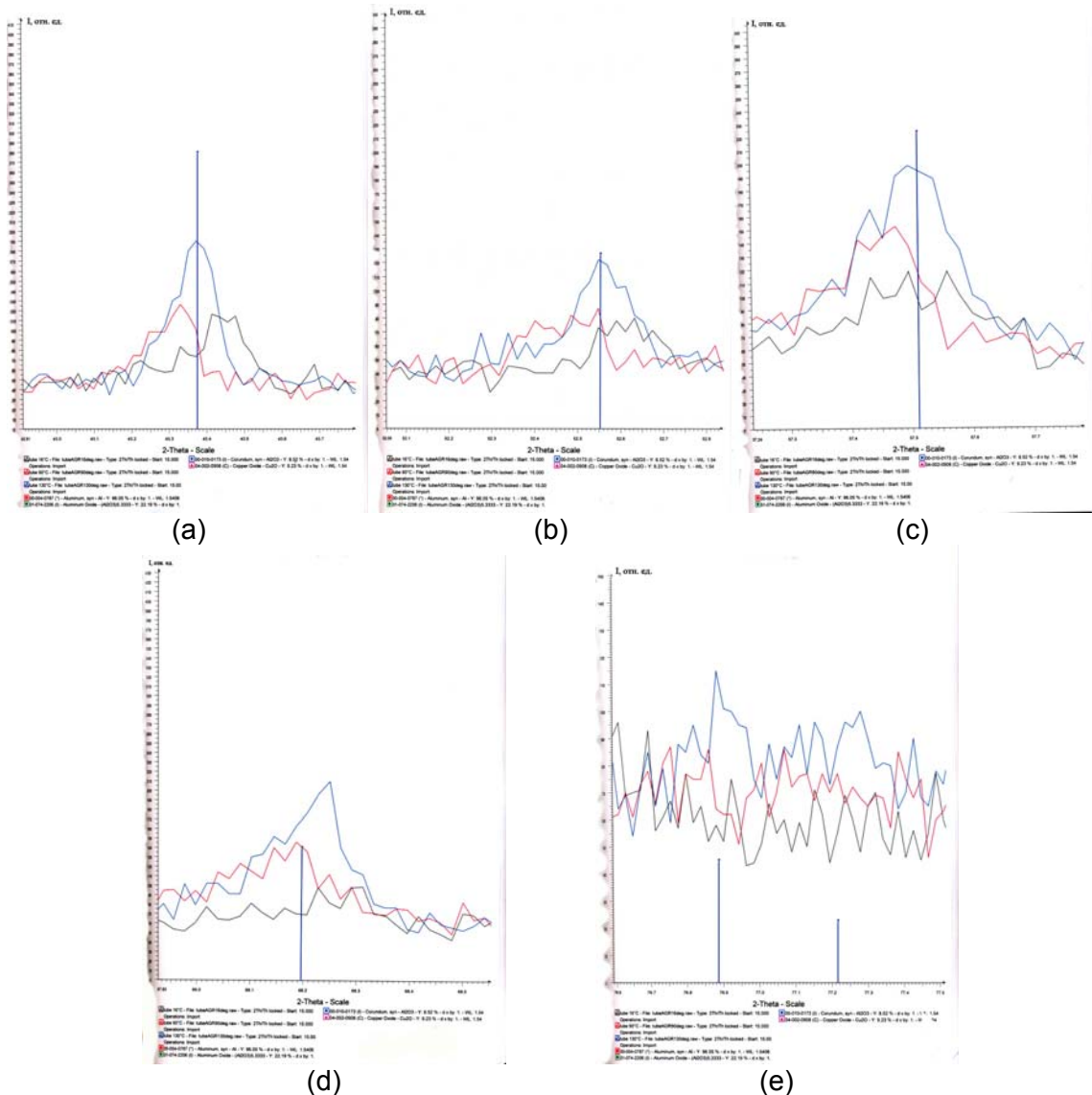


Figure 4. Relative intensity of the XR-peaks given by α -Al₂O₃ of the coatings obtained under different substrate temperature: 130 °C (blue line), 90 °C (red line), 16 °C (black line). The values of 2 Θ angle are 43,7° (a); 52,55° (b); 57,51° (c); 68,19° (d); 76,88° and 77,21° (e)

We put forward a working hypothesis according to which the concentration of α -phase of alumina depends on a time-temperature couple: the parts of coating which are close to the microdischarges should be heated up to the temperatures more than 1200 °C and stay at this temperature for a certain time. The joint action of these factors should provide the high rates of α -alumina formation.

In witness of our working hypothesis the following experiments have been carried-out. The outer surface of the metallic tubes made out of Al 2024 and Al 6063 alloys was oxidized with an additional independent heating of substrate by means of oil ($T \approx 16...150$ °C) circulating through the tubular samples and thermostat.

According to XR-data the increasing temperature of substrate leads to the higher amount of α -alumina in the PEO coating formed on the Al tubular samples. As a result the microhardness of inner coating layer increases with increasing temperature of substrate. For instance, the external additional heating of tube made out of Al 2024 up to the temperature about 150 °C allows to obtain relatively thin coating (≈ 40 μ m) with microhardness (1620 ± 280

HV) almost equal to microhardness (1680 ± 250 HV) of relatively thick coating ($\approx 80 \mu\text{m}$) obtained under the same conditions but without additional external heating of a substrate. However the increasing temperature of oil circulating through the tubular samples causes the same effects of the PEO coating formed on the outer surface of tubes as the increasing value of parameter R. Obviously the increase of substrate temperature as well as the increase of R value lead to the heating of inner part of coating that results in higher amount of high-temperature modification of alumina, particularly of corundum (α -alumina). We have proposed that a coating heating is mainly contributed by 1) Joule heat and 2) low porosity of coating.

Beyond all doubt the research of temperature of microdischarges occurred on the sample surface during PEO process is of the highest scientific interest. However if the temperature of discharges overtops the melting temperature of alumina the further increase of it does not significantly accelerate α -alumina formation in the PEO coating. According to the literature data the temperature of the discharge area lies in a range from 2500 till 20000 °C, i.e. depending on time during which the parts of coating are heated up to these temperatures different amount of α -alumina can be revealed in the coating.

On the basis of our research we have suggested that in case of details the obtaining of relatively thin ($< 40 \mu\text{m}$) and hard (> 1600 HV) PEO coatings can be achieved by using of high-frequency current.