

Characteristic of Oxide Coatings Produced on Aluminium by PEO Process at Different Frequency of Pulsed Current

Wojciech Gebarowski¹ and Stanislaw Pietrzyk²

^{1,2}*Department of Physical Chemistry and Metallurgy of Non-ferrous Metals,
AGH University of Science and Technology, Kraków, Poland
E-mail: ¹wojciech.gebarowski@agh.edu.pl*

Abstract—The Plasma Electrolytic Oxidation (PEO) is a surface modification process that allows producing protective oxide coatings on light metal alloys. These coatings are characterized by high microhardness and wear resistance. Changes of electrical conditions of alternate current during process, such as duration and frequency of anodic and cathodic pulses, influence on layer growth rate, its microstructure and final properties. In this study aluminium samples were oxidized at different electrical parameters in sodium silicate electrolyte. The growth rates of oxide layers were determined by mass change and thickness measurements. The microstructure of the obtained coatings was investigated by using scanning electron microscope. Additionally phase composition of coatings was determined by X-ray diffraction on top surfaces of layers. Generally shorter duration and higher frequency of anodic pulses provides more uniform structure at lower growth rate. Nevertheless there are certain ranges of electrical parameters that provide decent uniformity of oxide coatings.

Keywords: Plasma Electrolytic Oxidation, Aluminium Oxide, Coatings, Microstructure, X-ray Diffraction

INTRODUCTION

Plasma Electrolytic Oxidation (PEO) is a process of producing oxide layers on Al, Ti and Mg alloys. It is based on the anodic oxidation in aqueous solutions at voltages exceeding the breakdown voltage of the developing oxide layer on the surface of metal [1-3]. This results in an occurrence of short-living electrical microdischarges, uniform on the whole surface of the electrode, which promotes growth of oxide layer. Due to the low magnitude of an individual discharge, very high temperature gradient causes rapid solidifying of melted material and its depositing on and within oxide layer. These processes are mainly responsible for the characteristic structure and morphology of oxide layers obtained in PEO which have high microhardness [4], wear and corrosion resistance [5].

The PEO process can be carried out using different current waveform such as: direct current, pulsed current and alternate current [6]. Most of recent works using alternate current which as the most effective current parameters. In the literature there are a small number reports about benefit of pulsed current in respect of direct current [7]. The aim of this work is to compare pulsed current mode at different frequencies to direct current with preserving the same current densities. Also to study how significant is the influence of interrupting flow of current on growth rate, composition and structure of coating structure.

EXPERIMENTATIONS

The samples of size 10 x 30 x 1.5 mm were cut from of 1050 aluminium alloy sheet. Before the PEO process, the samples were prepared in few steps: degreasing in acetone, etching in 0.25 mol·dm⁻³ NaOH solution, brightening in 7 mol·dm⁻³ HNO₃ solution and rinsing in distilled water. Oxidation of samples was conducted in 4

dm³ stainless steel tank which acted as counter electrode. Composition of electrolyte was: 0.04 mol·dm⁻³ KOH, 0.08 mol·dm⁻³ Na₂SiO₃ and its temperature was maintained at 20±1°C. Bath was agitated by mechanical stirrer. PEO process was conducted using pulsed current at different frequency with maintaining constant average current densities at 7.5 A·dm⁻². A different period time of oxidation: 15, 30, 45 and 60 minutes were used. As a voltage source the programmable DC power supply Chroma 62012P was used. Pulsed were generated by custom switch unit controlled by real-time platform with LabVIEW-RT. Duty cycle of all waveforms were 50%. Anode and cathode were short-circuited between pulses. After the PEO process, the samples were rinsed in distilled water in ultrasonic cleaner in order to remove residual electrolyte from pores of oxide layers. The samples were weight before and after oxidation process in order to specify mass gain. Additionally the thickness of oxide layers was determinate by eddy-current method. Phase composition was determined by X-ray diffraction on top surfaces of layers (RigakuMiniFlex, CuKα). Structure observations of the top surfaces of layers were conducted on SEM (Hitachi SU-70).

RESULTS AND DISCUSSION

The graph presented in figure 1 shows voltage changes during oxidation process. There are only substantial differences between plots for individual frequencies. For all of plots, in first period rapid increase of voltage up to about 400 V is visible. This is breakdown voltage of oxide layer and after reaching this value microdischarges appear on the surface of electrode. Then slower voltage increase to about 500V is observed during rest time of 60 minutes of process. For frequency of 100 Hz voltage changes are almost identical like for direct current up about 38 minute.

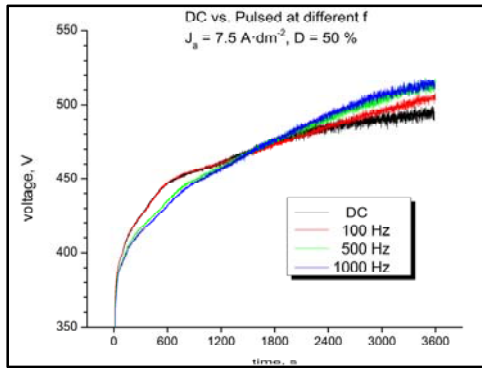


Fig. 1: Voltage Changes during PEO Process at different Frequency of Pulses

For higher frequencies of pulses lower voltages are visible in earlier stages and higher in later stages of process than for lower frequency and DC.

The growth rate of oxide coatings are shown on plots in figure 2. It is visible nearly linear character of curves, especially for higher frequencies. Generally the higher frequency of pulses the lower growth rate of oxide layer.

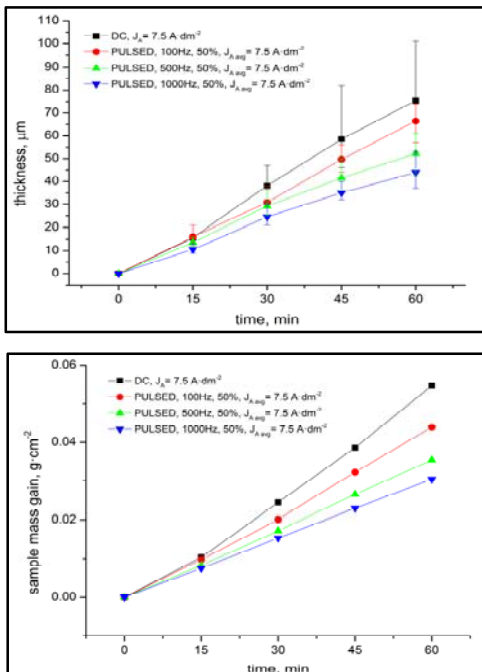


Fig. 2: Growth Rates of Oxide Coatings by Thickness Measurement (Above) and Changes Mass of Samples (Below)

This tendency is even more highlighted after taking into account voltage and calculating energy consumptions for producing certain volume of oxide coating (figure 3). Higher frequencies cause higher amount of electrical energy required for producing the same thickness layer. For example, 1000 Hz consumes 7.2 and 7.9 kWh per μm^2 in 15th and 60th minute of process respectively.

This is 44 % and 51% more than for 100 Hz and 51 % and 72 % than for direct current.

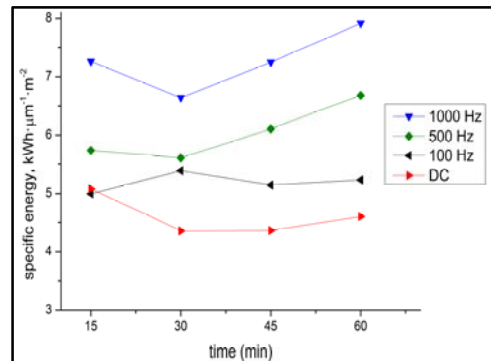


Fig. 3: Specific Energy of Oxide Coatings Creation during Process

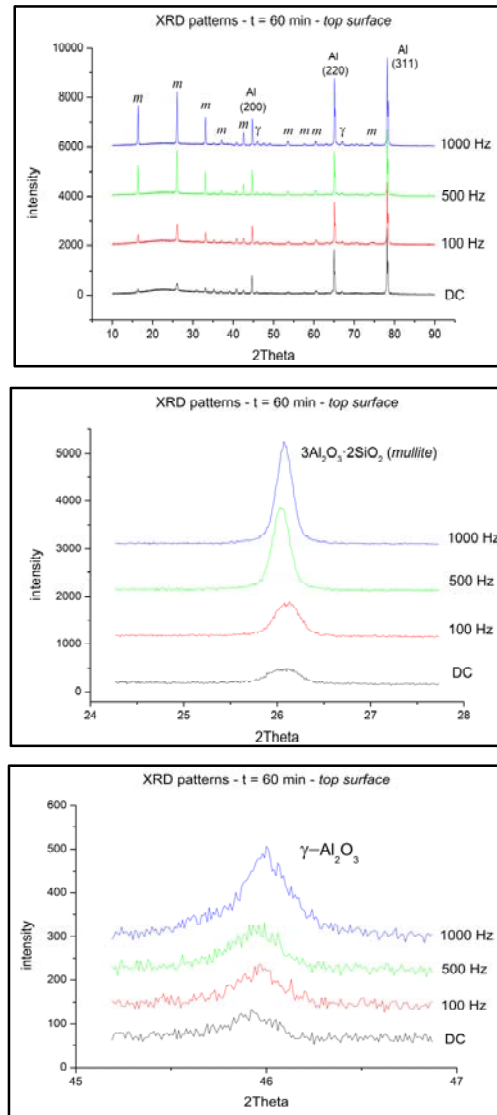


Fig. 4: XRD Patterns of Samples Surfaces

Oxide layers containing only two crystalline phases: mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and $\gamma\text{-Al}_2\text{O}_3$ instead of aluminium which originate from substrate. Mullite phase predominate in oxide over alumina phase for all cases. It is clearly visible that with increase of frequency, the higher content of crystalline phases is observed in case both mullite and gamma alumina. There is also higher concentration of amorphous phase on samples oxidized at lower frequencies, and the highest amount in case of direct current.

Images from scanning electron microscope show characteristic structure of oxide coatings surfaces with large roughness and micropores remained after microdischarges (Fig. 5).

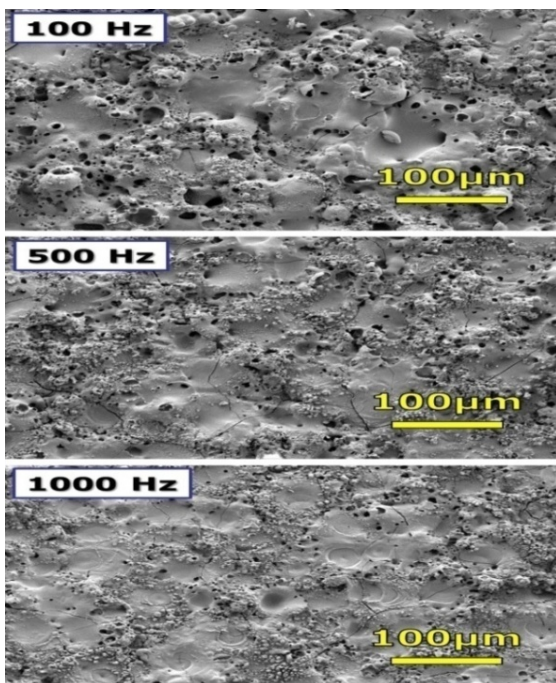


Fig. 5: SEM Images of Oxide Layers Surfaces

For lower frequencies surface is rougher and have higher amount of defects. With increasing frequency surface become more uniform, less-defective and have lower number of micropores. It is also seen for samples oxidized at 1000 Hz that there are many spots where

discharge channels were encapsulated by molten material of layer and lesser open pores are remained.

CONCLUSION

- PEO conducted at higher frequency cause decreasing growth rate of oxide coating and increasing energy-consuming of process.
- The higher frequency of pulses the higher amount crystalline phases content in layer.
- Oxide coatings obtained at higher frequencies have more uniform structure, less roughness and lower number of pores.
- PEO process carried out using the pulse current, as in the case of DC, has some limitations, due to occurrence of a large discharge at certain stage of process.

REFERENCES

- [1] Jiang, B.L. and Wang, Y.M. (2010), "Plasma Electrolytic Oxidation Treatment of Aluminium and Titanium Alloys", in: Hanshan Dong (Ed.), *Surface Engineering of light alloys*, Woodhead.
- [2] Yerokhin, A., Nie, X., Leyland, A., Matthews, A., Dowe, S.J. (1999), "Plasma Electrolysis for Surface Engineering", *Surface and Coatings Technology*, Vol. 122, pp. 73–93.
- [3] Krishna, L.R., Purnima, A.S., Wasekar, N.P. and Sundararajan, G. (2007), "Kinetics and Properties of Micro arc Oxidation Coatings Deposited on Commercial Al Alloys", *Metallurgical and Materials Transactions A*, Vol. 38, pp. 370–378.
- [4] Voevodin, A.A., Yerokhin, A.L., Lyubimov, V.V., Donley, M.S., Zabinski, J.S. (1996), "Characterization of Wear Protective Al-Si-O Coatings Formed on Al-based Alloys by Micro-arc Discharge Treatment", *Surface. Coatings Technology*, Vol. 86–87, pp. 516–521.
- [5] Wen, L., Wang, Y., Zhou, Y., Ouyang, J.-H., Guo, L., and Jia, D., "Corrosion Evaluation of Microarc Oxidation Coatings Formed on 2024 Aluminium Alloy", *Corrosion Science*, 2010, Vol. 52, pp. 2687–2696.
- [6] Xin, S., Song, L., Zhao, R., and Hu, X. (2006), "Influence of Cathodic Current on Composition, Structure and Properties of Al_2O_3 Coatings on Aluminum Alloy Prepared by Micro-arc Oxidation Process", *Thin Solid Films*, Vol. 515, pp. 326–332.
- [7] Godja, N., Kiss, N., Löcker, C., Schindel, A., Gavrilovic, A., Wosik, J., Mann, R., Wendrinsky, J., Merstallinger, A. and Nauer, G., "Preparation and Characterization of Spark-anodized Al-alloys: Physical, Chemical and Tribological Properties", *Tribology International*, 2010, Vol. 43, pp. 1253–1261.