

Composition, morphology and tribological properties of PEO-coatings formed on an aluminum alloy D16 at different duty cycles of the polarizing signal

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The paper presents the results of a study of the chemical composition, morphology, and tribological properties of coatings produced on an aluminum alloy D16 in a tartrate-containing electrolyte by plasma electrolytic oxidation (PEO). In order to form the coatings, a transistor power supply was used, providing a 5 μ s square-wave voltage pulses to the treated sample. The power supply is capable to control the pauses between pulses to achieve the required duty cycle values D . The influence of the parameters of the polarizing signal and the time of oxidation on the properties of the obtained PEO coatings is studied. It is established that the change in the duty cycle of the polarizing signal affects the chemical composition, thickness and properties of the formed oxide coatings. The results of X-ray diffraction data indicate that the main component of the PEO layers under investigation is a cubic modification of aluminum oxide (γ -Al₂O₃). In addition to cubic, the β -alumina (β -Al₂O₃), aluminum phosphate (AlPO₄) and molybdenum and aluminum carbide (Al₂Mo₃C), which are formed as a result of plasma-chemical reactions involving the processed alloy and electrolyte components, are also present in the PEO layers. The analysis of the dependence of the friction coefficient μ on the number of cycles shows that the PEO coatings formed at larger values of the duty cycle and oxidation time can withstand substantially more abrasion cycles. With the increase in the amount of electricity consumed to create the coating, thicker PEO layers are formed, which contributes to the improvement of tribological properties. It is established that an increase in the duty cycle of the polarizing signal leads to the reduction of the apparent porosity of the formed PEO layers, formation of more aluminum and molybdenum carbides in their composition, which leads to an increase in the wear resistance and hardness of the coatings.

Key words: plasma electrolytic oxidation, microsecond pulses, aluminum, protective coatings, microhardness, duty cycle, friction coefficient.

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Introduction

Aluminum is commonly used as constructional and functional material in aviation, architecture, shipbuilding etc. However, it requires additional protection being exposed to aggressive media. One of the most effective surface treatment methods for the production of the multifunctional coatings providing protection of metals and alloys against mechanical damage and aggressive media is plasma electrolytic oxidation (PEO). PEO-layers have a high adhesion to the substrate, low thermal conductivity, high hardness, good abrasion and excellent corrosion resistance. This type of coating is successfully used for the protection of not only such valve metals as aluminum [1–5], magnesium [6–12], titanium

[13–18] alloys, but also steel [19]. These works confirm that oxidized forms of elements of the processed alloy and electrolyte components are included in the chemical composition of the formed coatings.

Analysis of the literature [1, 3, 5, 6, 10, 12, 15] and our experimental data [13, 20] demonstrates that parameters of the polarizing signal have a significant effect on formation conditions and the quality of resulting coatings. In [10, 12, 15], a significant effect of duty cycle D on morphology, chemical and elemental composition and the features of the distribution of chemical elements over the treated surface of the formed oxide coatings was found. It is shown [13] that the rectangular shape of polarizing signal in the oxidation of commercially pure titanium provides, along with a decrease in the total energy consumption of

the PEO process, also an increase in the barrier properties of the formed coatings up to 2 times in comparison with the nonrectangular shape.

In this manuscript, the influence of the polarization signal duty cycle during plasma electrolytic oxidation on the composition, morphology, and tribological performances of coatings formed on an aluminum alloy D16 in a tartrate-containing electrolyte are investigated.

Experimental part

The rectangular plates (30×20×1.5 mm) of the wrought D16 (2024T3) aluminum alloy belonging to Al – Cu – Mg system (% (wt.): Cu 3.8–4.9; Mg 1.2–1.8; Mn 0.3–0.9; Si 0.5; Fe 0.5; Zn 0.25; Cr 0.10; Ti 0.15; Al – balance) were used as a samples. For the standardization, plates were ground with the sandpapers with different grit sizes (320–400, 600, 800, 1000) until the roughness parameter $R_a = 0.12 \mu\text{m}$. After mechanical treatment samples were thoroughly washed with deionized water and dried in the airflow.

The electrolyte (pH = 9.5) was prepared in deionized water by adding the following components, g/L: 0.6 of NaF; 5 of $\text{C}_4\text{H}_4\text{O}_6\text{K}_2 \cdot 0.5\text{H}_2\text{O}$; 10 of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; 10 of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; 10 of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. The temperature of the electrolyte was maintained in the range of 8–10 °C. During the oxidation process the temperature of the electrolyte was maintained by means of ChillerSmart H150-3000 (LabTech Group, UK).

Plasma electrolytic oxidation was performed using a transistor power supply equipped with an automated control system with appropriate software [13, 20]. The duration of polarizing pulses was equal to 5 μs . The amplitude values of the current and voltage detected by the electronic sensors were recorded, and the parameters of the individual pulses were determined with an interval of 0.5 μs using the software of the PEO automated control system. To analyze the shape and duration of the pulses, the PowerGraph software (DISOFT, Russia) was used, which allows calculating the energy consumption of PEO-coatings formation.

Samples were treated in the bipolar mode for 30 and 60 min. In the anodic period the voltage increases from 30 to 360 V at a rate of 65 V/min. Next, the rate of the voltage increase was sequentially reduced down to 2.5 and 1.1 V/min for a total oxidation time of 30 and 60 min, respectively. Thus, the final voltage was equal to 420 V. In the cathodic period, the galvanostatic mode with a current density of 0.12 A/cm² was maintained in both cases.

Morphology of the PEO-coatings was examined by scanning electron microscopy (SEM) on a Zeiss EVO 40 (Carl Zeiss Group, Germany). SEM-images of the surface and cross-sections of the PEO-coatings were obtained at an accelerating voltage of 20 kV. The nanoscale Cr layers were deposited on the surfaces of the samples under test in order to reduce image distortion associated with

charging of the non-conductive coating. During analysis of the EDX (Energy Dispersive X-Ray Analysis) data, the chromium peak was excluded.

The coating phase composition was studied using a D8 ADVANCE X-ray diffractometer (Bruker), with a source of $\text{CuK}\alpha$ radiation operated at 30 mA and 30 kV, scan range $2\theta = 5\text{--}80^\circ$, step size of 0.028/s, exposure time – 2 s.

The elemental composition of the alloy was confirmed by Energy Dispersive X-Ray Analysis (EDX) with using EDX-800HS (Shimadzu, Japan). Coatings composition was evaluated using Zeiss EVO 40 equipped with EDX microanalysis system at an accelerating voltage of 20 kV.

Results and discussion

The formation parameters and thickness of PEO-layers on the samples of D16 aluminum alloy are presented in Table 1. From the analysis of the presented data, it follows that with an increase of the duty cycle from 0.06 to 0.12, the quantity of electricity (Q) spent during the oxidation procedure for 30 min increased by 1.23 times, and with an increase in D to 0.21 by 1.54 times. During oxidation for 60 min, an increase in D up to 0.12 caused Q to increase by 1.43 times, and up to 0.21 by 1.81 times.

In addition, as the value of D increased, the thickness of the coatings formed in the bipolar mode was increased (see Table 1). The increase in the duration of the oxidation process by a factor of 2 (60 min) led to a corresponding twofold increase of the coatings thickness (see Table 1). It can be noted that the quantity of electricity consumed to form an oxide layer and the thickness of the oxide layers formed on D16 are very close to the corresponding values obtained for coatings on Al – Mg – Mn – Si system aluminum alloy [20].

SEM images show that the most pores in oxide coatings formed for 30 and 60 min have a diameter of 0.5–1 μm (Fig. 1). Analysis of SEM micrographs indicates a uniform distribution of pores over the surface. As a result of oxidation, coatings with the largest number of pores with a diameter of 2–5 μm and an apparent porosity of 2.88% are formed for 30 min at a duty cycle $D = 0.06$ (Fig. 1, a). The increase of the oxidation time up to 60 min

Table 1

Formation parameters and thickness of PEO coatings on aluminum alloy*

Treatment time, min	Sample #	D	Q , C	Thickness, μm
30	1	0.06	110±3	3±1
	2	0.12	136±4	4±1
	3	0.21	170±3	5±1
60	4	0.06	193±5	6±1
	5	0.12	277±4	7±1
	6	0.21	350±5	9±1

* Anodic voltage $U_a = 30\text{--}420$ V; cathodic current density $j_c = 0.12$ A/cm².

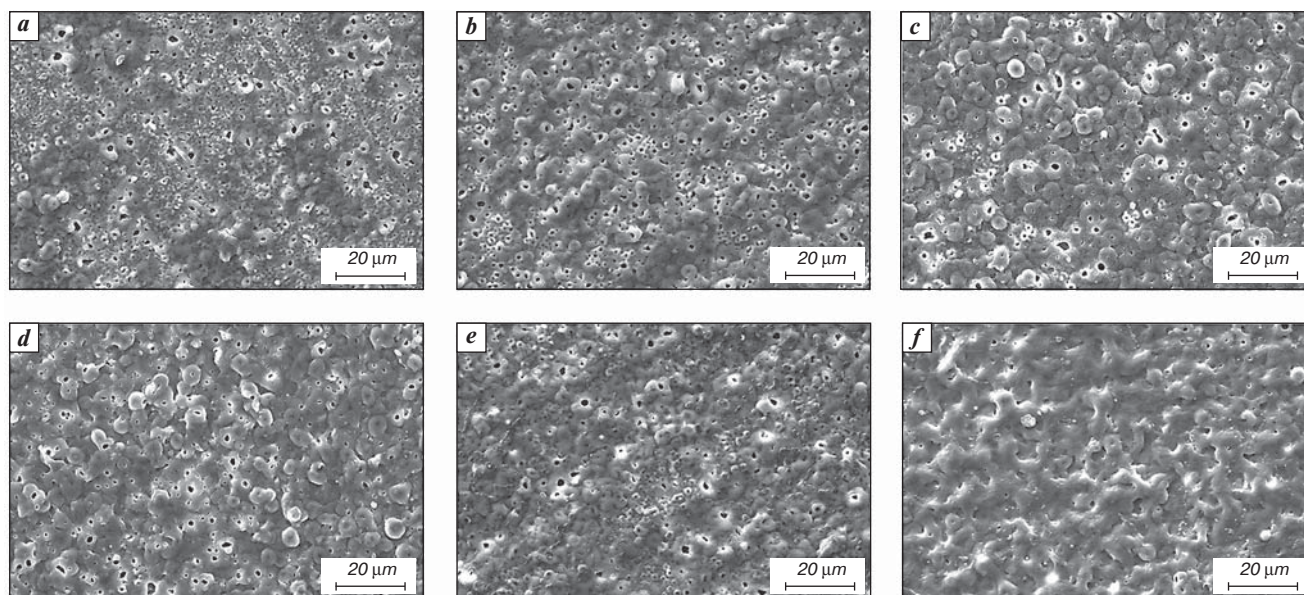


Fig. 1. SEM images of PEO-coatings formed by D16 alloy for 30 min (*a, b, c*) and 60 min (*d, e, f*) at duty cycle (*D*) of 0.06 (*a, d*); 0.12 (*b, e*); 0.21 (*c, f*)

at $D = 0.06$ (Fig. 1, *d*) contributes a decrease in porosity in two fold (down to 1.49%). When D is increased up to 0.21, the porosity of the films formed during 30 and 60 min of oxidation decreases down to 0.85 and 0.79%, respectively (Fig. 1, *c, e*).

According to the results of the elemental composition of PEO-coatings, the main elements are oxygen (50.1–59.3 % (at.)), aluminum (20.5–26.5 % (at.)) and carbon (13.9–23.2 % (at.)). In smaller quantities, compounds containing magnesium (up to 0.7 % (at.)), phosphorus (up to 0.6 % (at.)), sodium (up to 0.3 % (at.)) and potassium (up to 0.15 % (at.)) are introduced into the coating composition. Despite the significant amount of copper in the alloy, its content in the coating is small – (0.1–0.3) % (at.). The concentration of molybdenum

in the coatings formed at $D = 0.21$ for 30 min does not exceed 0.4 % (at.), and for the formed ones for 60 min it reaches 1.2 % (at.). A twofold increase should be noted in the concentration of carbon in the composition of PEO-coating formed at $D = 0.21$ for 60 min as compared to the one formed for 30 min.

The X-ray diffraction method allowed establishing that the layers under study have a multiphase chemical composition (Fig. 2). The spectra of the samples with coatings after formation revealed the presence of gibbsite – $\text{Al}(\text{OH})_3$ and multiple low-intensity peaks, which are difficult to relate to any particular crystalline form of the compounds presented in the coatings. In connection with this, the samples were heat treated at 450 °C for 1 h, followed by the X-ray spectra was recorded. It allows receiving a more detailed information on the phase composition of the coatings. It should be noted that the differences between the spectra shown in Fig. 2 for coatings formed during 30 and 60 min are insufficient. Aluminum on X-ray diffraction patterns is represented by the peaks $2\theta = 38.5^\circ, 44.8^\circ, 65.0^\circ$ and 77.9° . Its presence in the spectra of the analyzed samples is related to the alloy (substrate), and it is due to the low absorbing capacity of the PEO-layers. Most of the peaks found in the spectra ($19.6^\circ, 32.1^\circ, 37.8^\circ, 42.9^\circ, 44.6^\circ, 46.0^\circ, 60.9^\circ, 67.0^\circ, 74.1^\circ$) indicate the presence of a cubic modification of aluminum oxide $\gamma\text{-Al}_2\text{O}_3$, which is a main component of the investigated PEO-layers (see Fig. 2).

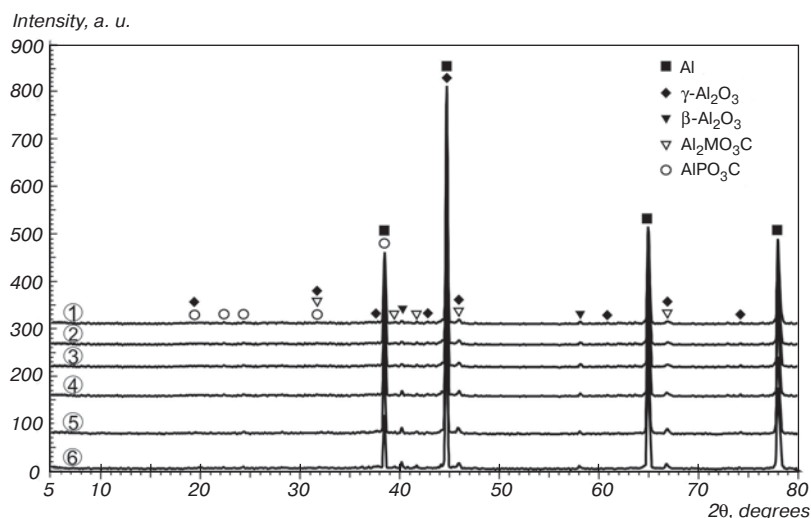


Fig. 2. X-ray diffraction patterns of PEO-coatings formed on D16 alloy for 30 min (1–3) and 60 min (4–6) at duty cycle (D) of 0.06 (1, 4); 0.12 (2, 5); 0.21 (3, 6). Samples after heat treatment at 450 °C for 1 h

In addition to the cubic modification of aluminum oxide — the β - Al_2O_3 ($2\theta = 40.1^\circ$ and 58.1°), AlPO_4 — aluminum phosphate ($2\theta = 19.6^\circ$, 22.3° , 24.2° , 32.1° , 38.5°) and molybdenum and aluminum carbide — $\text{Al}_2\text{Mo}_3\text{C}$ ($2\theta = 32.1^\circ$, 39.5° , 41.9° , 46.0° , 74.2°) formed as a result of plasma-chemical reactions involving the elements of the processed alloy and electrolyte components are presented in the chemical composition of the PEO-layers. Thus, the phase composition of coatings formed on a copper-containing aluminum alloy does not differ from the surface layers formed on Al — Mg — Mn — Si system aluminum alloy [20].

Comparison of data obtained by the methods of energy-dispersive X -ray analysis and X -ray diffraction allows one conclude, that when the duty cycle of the polarizing signal and the oxidation time are increased, the molybdenum and carbon concentrations in the coating increase (Table 2), and the intensity of the $\text{Al}_2\text{Mo}_3\text{C}$ peaks increases significantly (see Fig. 2).

According to the literature during the PEO process the temperature in the discharge channels can reach 10,000–20,000 K [14]. Thermolysis of water, leading to the formation of a predominantly reducing atmosphere ($2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$), is intensified at temperatures exceeding 3,000 K [21].

In addition to thermolysis, electrolysis realized during PEO plays an important role in the decomposition of water. In the cathode phase at the bipolar (anodic-cathodic) mode hydrogen is formed near electrode according to the electrochemical reaction: $2\text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + 2\text{OH}^-$. In the reducing atmosphere the formation of molybdenum carbides is possible. Since the carbon in the coating composition is presented in significant amounts, it is impossible to exclude the possibility of formation of Mo_2C and MoC as an amorphous phase. The absence of the carbide phase peaks in the diffractograms of the coatings under investigation can be explained by the low sensitivity of the X -ray method and the small content of molybdenum in the coating. According to EDX data Mo concentration in the surface layer does not exceed 2%.

Tribological tests indicate that during the friction of the corundum ball on the surface of the studied samples, the coating material is wear gradually, accompanied by the appearance of a wear track. At the end of the process, a dense, nonporous inner sublayer of the coating collapses, and the corundum ball comes into contact with the Al alloy substrate, which causes a sharp increase of friction coefficient μ .

Analysis of the dependence of μ on the number of revolutions required to achieve the substrate by the counterbody shows that PEO-coatings formed at a higher duty cycle and oxidation time can withstand significantly more abrasion cycles than coatings formed at a lower D value and a shorter oxidation time (see Table 2). With the increase of electricity quantity consumed to create the coating, PEO-layers with a greater thickness are formed,

Table 2

Wear and roughness parameters for oxide layers

Sample #	D	Wear, $\text{mm}^3/(\text{N}\cdot\text{m})$	R_a , μm	Number of cycles*
1	0.06	$3.56 \cdot 10^{-3}$	0.33	130
2	0.12	$3.52 \cdot 10^{-3}$	0.36	168
3	0.21	$3.44 \cdot 10^{-3}$	0.34	188
4	0.06	$3.30 \cdot 10^{-3}$	0.34	205
5	0.12	$3.27 \cdot 10^{-3}$	0.37	217
6	0.21	$3.08 \cdot 10^{-3}$	0.39	248

*At the moment of the counterbody contact with substrate.

which contributes to the improvement of tribological properties. This conclusion is confirmed by data on the wear of coatings (see Table 2). It should be noted that the roughness parameter R_a of the formed coatings does not exceed $0.39 \mu\text{m}$, which indicates a fairly flat surface and indirectly indicates a low porosity.

Conclusions

The protective coatings on an aluminum alloy D16 (2024T3) have been formed in the bipolar mode of plasma electrolytic oxidation using the polarizing signal with a microsecond pulses with a different duty cycle D . These coatings possess wear resistance higher than that for the substrate material.

It is established that an increase of the D up to 0.21 contributes a reduction in porosity (down to 0.79%) with a significant increase of the thickness of the formed PEO-layers (up to $9 \pm 1 \mu\text{m}$).

The chemical composition of the surface layers formed on D16 is represented by γ - and β -modifications of Al_2O_3 , AlPO_4 , molybdenum and aluminum carbide — $\text{Al}_2\text{Mo}_3\text{C}$ obtained as a result of plasma chemical reactions involving both the components of the processed alloy and the electrolyte. According to elemental and X -ray analysis at increasing D and oxidation time, the concentration of molybdenum and carbon in the coating is increased, and the intensity of the $\text{Al}_2\text{Mo}_3\text{C}$ peaks is increased significantly.

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