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INFLUENCE OF REGIMES OF PLASMA-ELECTROLYTIC PROCESS ON POROSITY AND MORPHOLOGY OF OXIDE COATING

Abstract:One of the promising methods of surface treatment to obtain wear-resistant, corrosion-resistant, heat-resistant coatings is the method of plasma electrolytic anodizing. The oxide coatings formed in the microplasma treatment mode have different porosity and developed surface. The reasons for the formation of porosity and the influence of technological regimes on it are in the initial stage of study. In this paper, we investigated the effect of the duration of the anode pulse, the polarizing voltage of the plasma-electrolytic treatment on the surface porosity of the oxide coating. The porosity of the oxide coating obtained under various process conditions varies from 14 to 21 %. Investigation of the morphology of the coating showed that a change in the duration of the anode pulse from 100 to 250 μm leads to an increase in the average pore diameter from 3.3 to 5.4 μm. According to the calculated data, with increasing thickness of the coating, there is a tendency of reduction in the porosity, the number of pores per unit surface. This trend is associated with the formation of oxide, both at the bottom of the pores due to the substrate, and due to the components of the solution inside and around the pores. All this in combination leads to the filling of pores. When studying the effect of polarizing stress on the porosity, it was found that at a value of 100 V, a thin practically non spherical coating forms. At a voltage of 200 V, coatings are formed with small unevenly distributed pores on the surface. Conducting the process with polarizing voltages of 300 V and 400 V leads to an intensive increase in the thickness of the coating with a developed porous surface. Depending on the purpose of the coating, the porosity can be reduced by introducing into the pores various materials - dyes and polymers. Porosity makes it possible to obtain composite multifunctional coatings and serve as a sublayer for metal and paint coatings on aluminum and its alloys.

Key words: plasma-electrolytic anodizing, microarc oxidation, oxide coating, morphology, surface porosity

Introduction. Aluminum and its alloys are widely used as a structural material. Aluminum alloys are easy, pliable, stamping, high thermal conductivity. Aluminum and its alloys are used in many sectors of the national economy: aviation, aerospace, food, construction and others. In this case, products made of aluminum and its alloys should be distinguished by wear resistance, corrosion resistance, heat resistance. There are various ways to modify the surface of products made from aluminum and its alloys. One of the promising methods for obtaining multifunctional coatings on valve metals is electrolyte-plasma oxidation (PEO) in various solutions of electrolytes, mainly in alkaline solutions [1, 2]. During surface treatment with microplasma action, a coating with high adhesion properties is formed on it, which does not collapse when critical mechanical local effects occur [3, 4]. Formed oxide coatings in the microplasma treatment regime have different porosity and developed surface. This property of the coating can be used as a sublayer, as well as creating composite coatings by introducing various materials into the pores [5]. However, the reasons for the formation of porosity and the influence of technological regimes have not been thoroughly studied. In this connection, it is of interest to investigate the effect of the plasma-electrolytic process regimes on the morphology and porosity of the oxide coating.

Experimental part. The samples for applying the oxide coating were made of aluminum grade A0 with a size of 2x2 cm and a thickness of 3 mm, the surface area of the treated surface was 8 cm^2. The samples before mechanical application of the oxide coating were mechanically polished and had a roughness Ra = 0.098 microns.

The formation of the oxide coating was carried out in an electrolyte solution of the following composition, g/dm^3: $Na_2HPO_4 \cdot 12H_2O$ - 40; $Na_2B_4O_7 \cdot 10\ H_2O$- 30; H_3BO_3 - 20, NaF – 10.

The electrolyte was prepared on distilled water from reagents “AR grade”, “CP”. The PEO was carried out in a bath made of stainless steel with a volume of 700 ml, equipped with a water cooling system, the cathode was the body of the bath.

The PEO process was carried out using a pulsed power supply, which makes it possible to obtain voltage pulses of a rectangular trapezoidal shape at a pulse repetition rate of 50 Hz. The current density of the process was 114-130 A/dm^2. Coatings were formed during the anodic polarization of aluminum samples without a cathodic component.

Under these conditions, two batches of samples with an oxide coating were obtained. The first batch of samples with an oxide coating was obtained for various durations of the anode current pulse in solution No. 1, the conditions of the PEO process are given in Table 1.

Table 1 - Regimes of PEO-1

Polarizing voltage, V	Duration of anode current pulse, microsecond	Electrolyte temperature, °C	Process time, min
300	50	25-27	20
300	100	25-27	20
300	150	25-27	20
300	200	25-27	20

The second batch of samples was obtained at different values of the polarizing voltage, the process conditions are given in Table 2.

Table 2 - Regimes of PEO-2

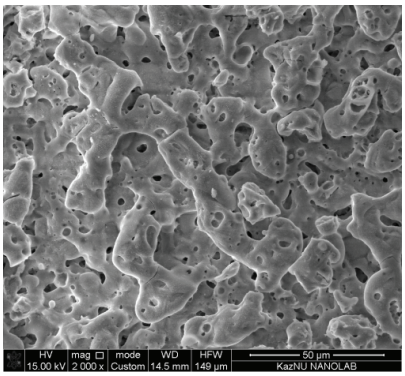
Polarizing voltage, V	Duration of anode current pulse, microseconds	Electrolyte temperature, °C	Process time, min
100	200	25-27	20
200	200	25-27	20
300	200	25-27	20
400	200	25-27	20

The thickness of the coating of the sample was determined on a thickness gauge of QuaNix-1500. The thickness was calculated as the average of 15 measurements, on both sides of the sample. The porosity, shape, pore size distribution were determined by analyzing the photomicrographs of the surface of the test samples obtained by scanning electron microscope Quanta 200i 3D, using planimetry, cross-section and point methods, as the ratio of the pore image area to the total area of the observation site [6].

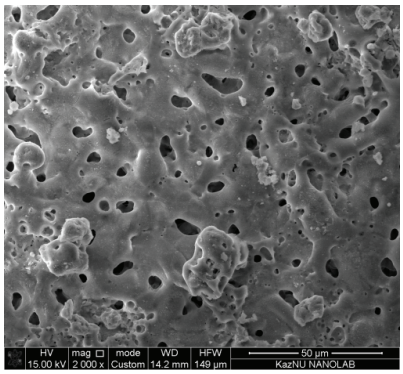
Discussion of results. The porosity of the oxide coatings is dependent on the formation regimes of the coating and the nature of the electrolyte. When plasma electrolytic treatment occurs on the metal surface, local microplasma discharges arise. Under their influence, the structure of the oxide film changes. And, as a rule, in the places of sparking, pores are formed. The shape of the pores can be different. The simplest form of pores is rounded, and it varies depending on various factors of the process of microplasma treatment. With the change in the duration of the anode current pulse (Table 1), the thickness of the coating also changes, so at 50 microseconds it was 7.8 microns; 100 microseconds - 11.1 microns; 150 microseconds - 19.7 microns; 200 microseconds - 26.5 microns.

Figure 1 presents microphotographs of the morphology of the surface of oxide coatings obtained at different durations of the anode current pulse. Electron microscopic images show that with an anode current pulse duration of 50 μs, the formation of the coating is an islet. The average pore diameter is of the order of 3.3 μm, which is lower in comparison with the coatings obtained at higher values of the duration of the anode pulse (Figure 2a). With an increase in both the duration of the anode current pulse and thickness of the oxide layer, a uniform coating is observed, which can be seen in micrographs. The growth of the coating occurs not only due to the transformation of the substrate at the bottom of the pores, but also due to reactions with hydroxide ions and metal ions inside and near the pores where, under the influence of high temperature, the metal hydroxides pass into oxides [7]. The formation of the oxide coating also occurs from the components of the electrolyte solution. As a result of these processes, existing through-holes are filled. It is time to pass from the discharge through to closed, while other pores are formed. On microphotographs small pores are observed inside the large pores, which have mainly a dotted form (Figure 1b, c, d). The increase in the thickness of the coating, which is observed with increasing duration of the anode current pulse, leads to the formation of pores of a larger diameter, but the number of pores per unit area decreases (Figure 2a, c). With increasing thickness of the oxide coating, an increase in its continuity is observed.

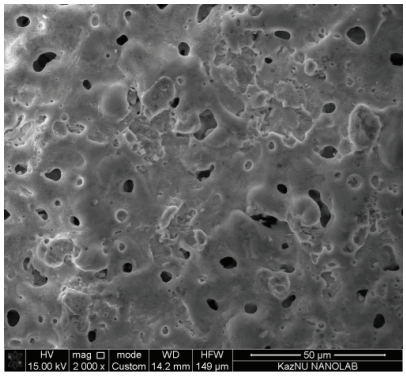
Microphotographs of the surface of the oxide coating at different polarizing voltages are shown in Figure 3. The thickness of the coating depends on the polarizing voltage, and at 100 V, the thickness of the layer is 1.2 μm, 200 V - 3.0 μm, 300 V - 26.5 μm, 400 V - 36.9 μm. As can be seen on electron-microscopic images at a voltage of 100 V, a non-porous thin coating is formed (Figure 3a). At a given polarizing voltage in the process of plasma-electrolytic treatment, spark processes are observed occasionally. At a voltage of 200 V, the microarc discharges that occur in the PEO process lead to the formation of fine pores, the thickness of the coating remains insignificant (Figure 3b). At a voltage of 300 V, micro-arc discharges occur practically from the first seconds of the process. The rate of coating formation increases, which leads to a sharp increase in its thickness and porosity. At a voltage of 400 V, the dimensions of the microarc discharges increase.



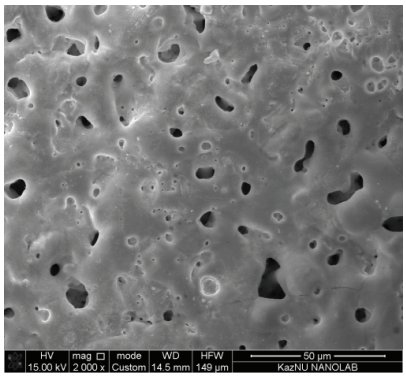
a



b



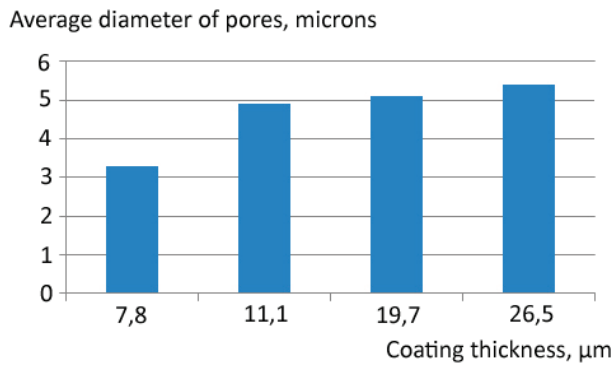
c



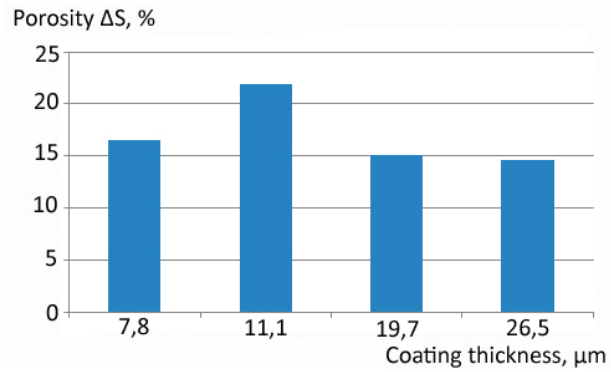
d

Increase in all cases: x 2000
The duration of the anode current pulse, µs:
a - 50; b - 100; c - 150; d - 200

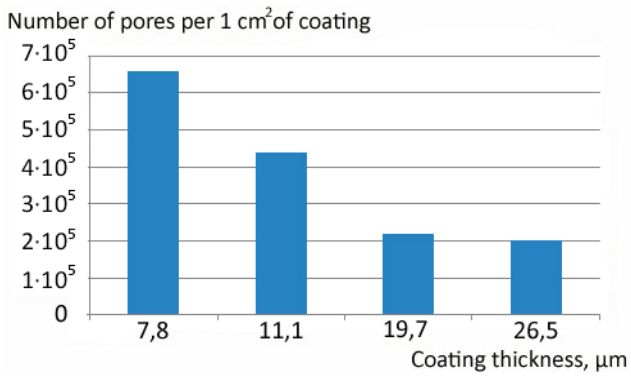
Figure 1 - Morphology of oxide coating surface



a



b



c

Dependence on coating thickness of: a – average pore diameter; b – porosity; c – number of pores per unit area

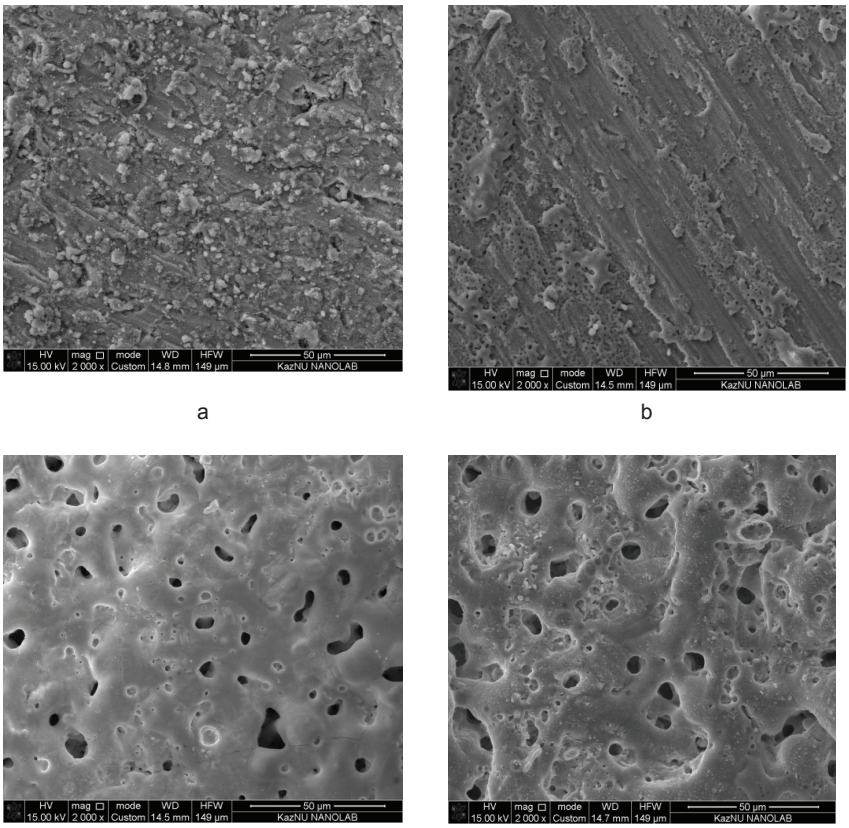
Figure 2 - Surface porosity of oxide coating

The intensity of microplasma discharges leads to a strong heating of the electrolyte to 40 °C. The high temperature of the electrolyte is an undesirable factor that affects the quality of the coating. The functional outer layer is formed more roughened and friable. The porosity of the coating increases (Figure 3 g). The realization of the process at 400 V for obtaining a better coating requires additional systems for cooling the electrolyte.

It is impossible to obtain coating without pores during oxidation which is due to the nature of the process. In some cases, the porosity of the coating is a positive factor.

To obtain a coating with antifriction properties, the pores can be filled with various materials. Fluoroplastic, graphite, and metallic copper can be used as antifriction materials for pore filling. Filling of pores can be carried out by dipping, rubbing, metal deposition by chemical or electrochemical methods.

Thin porous oxide coatings can serve as a subcoat for paint and metal coatings. Since the coatings applied to aluminum and its alloys without preliminary, preparation can easily peel off under the influence of atmospheric or other factors. This process is associated with a number of problems caused by a negative value of the substrate potential, which leads to a contact separation of metals having a more negative potential and, accordingly, to a low adhesion value of the coating with the substrate [8]. Improving the adhesion of coatings to the metal is achieved mainly by applying a porous oxide coating.



Polarizing voltage, V: a-100; b - 200; c - 300; d - 400

Figure 3 – Morphology of oxide coating surface

Conclusions. The influence of the plasma-electrolytic treatment regimes on the morphology and porosity of the oxide coating was studied. It is shown that under the anodic regime without the cathode component, as the both duration of the anode current pulse and increase, there is a tendency of reduction in the porosity, the number of pores per unit surface.

The nature of the pores depends on the thickness of the coating, the duration of the pulse and the voltage of the current, from which it can be concluded that the technological regimes have a significant effect on porosity. It is established that the average pore diameter increases with increasing coating thickness, this is due to the increase in the duration of the anode current pulse and the polarizing voltage. At the same time, it can be said that the number of through-pores decreases, due to the flow of the process along the bottom and walls of the pores.

The porosity of the oxide coating can play a positive role in the creation of composite antifriction, electrically conductive coatings. The porosity of the coating prevents the development and destruction of the material when the coated sample is loaded due to the relaxation of normal stresses at the vertices of the mesotrains.

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ТҮЙІНДЕМЕ

Тозуға төзімді, коррозияға төзімді, ыстыққа төзімді жабынды алу мақсатында плазмалы электролитті анодтау әдісі қолданылады, бетті өңдеу перспективалы әдісінің бірі болып табылады. Қалыптасқан оксидті беттер микроплазмалық өңдеу режимінде түрлі кеуектілік және дамыған беті бар. Кеуектіліктің қалыптасуының себептері және технологиялық режимдердің әсері зерделеудің бастапқы сатысында. Осы жұмыста анодты импульстің ұзақтығы, кернеуді поляризациялайтын плазмалы- электролитті өңдеу әдісін оксидті жабын бетті кеуектілік зерттелген. Процесстің түрлі режимдерінің көмегімен алынған оксидті жабынның кеуектілігі 14- 21% аралығында. Анодты импульстің ұзақтығының өзгеруі 100- 250 мкм, орташа диаметрдің 3,3-тен 5,4 мкм әкеліп соқтыратының, жабынның морфологиясының зерттеуі көрсетті. Есептік мәліметтер бойынша жабынның қалыңдығы ұлғайған сайын, кеуектіліктің төмендеу үрдісі байқалады, кеуектілік саны беттің бірлігіне қарағанда. Осы үрдіс оксидтің пайда болуымен байланысқан, кеуектіліктің түбіндегі төсем арқылы және де ерітіндінің ішіндегі және кеуектілік маныңдағы компоненттер арқасында. Осының барлығы кеуектілік толып қалуына әкеліп соқтырады. Зерттеу кезінде поляризацияланған кернеудің кеуектілікке әсерінен мәні 100 В деп шешілген, іс жүзінде жұқа және де әлсін білінетін кеуектілігі бар жабын пайда болады. Кернеу 200 В болған кезде бетіне кеуектілік кішкене біркелкі емес орналасқан жабын пайда болады. Процесстің жүзеге асуы поляризацияланған кернеудің мәні поляризацияланған кернеудің мәні 300- 400 В болған кезде озықты кеуек бетімен қоса, жабынның қалындығының интенсивті өсуіне әкеліп соғады. Жабынның мақсатына қарай бояғыш немесе полимерлердің көмегімен кеуектілікті төмендетуге болады. Кеуектіліктің көмегімен көпфункционалды композитті жабынды алуға болады, сондай-ақ алюминий және оның қорытпаларына, металл және лак бояуы бар жабындарға қабатша ретінде қызмет етеді.

Түйін сөздер: плазмалық электролиттік анодтау, микродоғалы қышқылдандыру, оксидті жабын, морфология, бет кеуектілігі

РЕЗЮМЕ

Одним из перспективных методов обработки поверхности с целью получения износостойких, коррозионностойких, термостойких покрытий является метод плазменного электролитического анодирования. Сформированные в режиме микроплазменной обработки оксидные покрытия имеют различную пористость и развитую поверхность. Причины образования пористости и влияние на нее технологических режимов находятся в начальной стадии изучения. В данной работе исследованы влияние длительности анодного импульса, поляризующего напряжения плазменно-электролитической обработки на поверхностную пористость оксидного покрытия. Пористость оксидного покрытия, полученная при различных режимах процесса, варьируется в интервале от 14 до 21 %. Исследование морфологии покрытия показало, что изменение длительности анодного импульса от 100 до 250 мкм приводит к увеличению среднего диаметра пор от 3,3 до 5,4 мкм. По расчетным данным с увеличением толщины покрытия наблюдается тенденция снижения пористости, количества пор на единицу поверхности. Данная тенденция связана с образованием оксида, как на дне пор за счет подложки, так и за счет компонентов раствора внутри и около пор. Все это в совокупности приводит к заполнению пор. При исследовании влияния поляризующего напряжения на пористость было установлено, что при значении 100 В образуется тонкое практически беспористое покрытие. При напряжении 200 В образуются покрытия с мелкими неравномерно распределенными по поверхности порами. Ведение процесса при поляризующих напряжениях 300 и 400 В приводит к интенсивному росту толщины покрытия с развитой пористой поверхностью. В зависимости от назначения покрытия пористость может быть снижена путем введения в поры различных материалов – красителей и полимеров. Пористость позволяет получить композиционные многофункциональные покрытия, а также служить в качестве подслоя для металлических и лакокрасочных покрытий на алюминии и его сплавах.

Ключевые слова: плазменно-электролитическое анодирование, микродуговое оксидирование, оксидное покрытие, морфология, поверхностная пористость

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