

*Проаналізовано технологічні підходи до поверхневої електрохімічної обробки сплавів алюмінію. Показано, що спрямоване модифікування поверхні носія дозволяє розширити функціональні властивості оброблюваного матеріалу. Досліджено механізми обробки сплавів алюмінію різного складу та розроблено технологічні моделі процесів з використанням узагальнених феноменологічних схем. Запропоновано способи поверхневої обробки сплавів алюмінію шляхом формотвірної обробки імпульсним струмом у хлорид-вмісних електролітах та плазмо-електролітного оксидування у лужних розчинах дифосфатів. Показано, що використання імпульсного електролізу сприяє утворенню розвиненої сітчастої та поруватої структури. Узагальнено шляхи керування та фактори впливу на технологічний процес обробки. Одержані системи можуть бути використані як носії каталітичного матеріалу за умови нанесення вторинного каталітично-активного шару. Встановлено, що з використанням плазмо-електролітного оксидування можливо в одному технологічному процесі змінити форму і гомогенізувати поверхневі шари носія та нанести міцно адгезований шар каталітичного матеріалу. Показано, що характеристичні параметри ПЕО залежать від складу оброблювального матеріалу. Встановлено, що морфологія та фазова структура поверхневих оксидних шарів змінюється під час ПЕО. Сформовані оксидні покриття складаються із  $\alpha\text{-Al}_2\text{O}_3$  та мають високий ступінь розвинення поверхні, що є передумовою підвищення їх функціональних властивостей. Запропонований підхід може бути використаний в технології інженерії поверхні та для одержання матеріалів для екотехнологій*

*Ключові слова: поверхнєве модифікування, формотвірна обробка, гомогенізація поверхні, моделювання технологічного процесу, оксидне покриття*

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## 1. Introduction

The use of aluminum alloys is quite common today and has significant prospects for further development. These alloys form the basis of many structures and are used in leading industries – transport and chemical engineering, automotive industry [1, 2], aviation [3], rocket and space and nuclear engineering [4], construction [5], etc. An important direction is the use of aluminum alloys as carriers of catalytic systems and catalysts for neutralizing toxic substances in gas and liquid phases [6, 7].

The wide range of demand for aluminum alloys is due to the peculiarities of their physical, mechanical and chemical properties [8]. The creation of new alloys and development of treatment methods for existing ones are based on the results of solving numerous technical problems. In order to increase

strength characteristics, alloying components (manganese, iron, copper, silicon, magnesium, etc.) are introduced into alloys, which form intermetallic compounds in the alloy structure. This causes the surface heterogeneity of alloyed aluminum alloys, significantly reduces corrosion resistance in aggressive media and complicates the surface treatment of such materials [9].

To give additional functional properties to the surface, surface modification methods are used, when predetermined indicators can be achieved without changing the structure of the base material [10]. Such surface engineering technologies are in demand and promising. Application of thin-film coatings for surface protection and strengthening [11, 12], formation of catalytically active layers [13, 14], electrochemical [15] and plasma-chemical treatment are the most common [16]. Variations and combinations of treatment methods

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# ANALYSIS OF TECHNOLOGICAL APPROACHES TO ELECTROCHEMICAL SURFACE TREATMENT OF ALUMINUM ALLOYS

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allow you to flexibly control the target surface properties of the treated materials.

It should be noted that many developments in this field are mainly experimental and applied in nature and solve only narrow technological problems. Therefore, scientific and applied studies of mechanisms for modifying the surface layers of aluminum alloys and substantiation of technological control models of the treatment process, in particular providing catalytic properties to the treated surface are in demand.

## 2. Literature review and problem statement

A fundamental aspect of the technology of catalytic systems is the nature of the carrier, on the surface of which the catalytically active layer is formed. In most cases, this determines the application, production technology, purpose and performance of the final product. This can be explained by the effect of synthesis conditions on the structure, composition and surface morphology of structural materials [17]. Therefore, researchers assign a separate role to substantiation of effective methods and technologies for the formation of catalytic systems.

One of the most common classes of catalytic materials (catalysts) used in environmentally friendly technologies are metal oxide systems [18]. Such materials are characterized by high catalytic activity due to the surface heterogeneity of the chemical composition and localization of various chemical compounds in the surface layers. In addition, they remain functional for a long time under high temperatures and pressure, which is generally characteristic of the processes of neutralization of toxic components [19].

The use of oxide systems for the organization of catalytic processes primarily involves an increase in the specific surface area of the carrier. Another important parameter is the need for maximum concentration of catalytically active centers with high donor-acceptor capacity [20].

Among the existing approaches, there are two main technological methods to modify the surface of metals and alloys (Fig. 1).

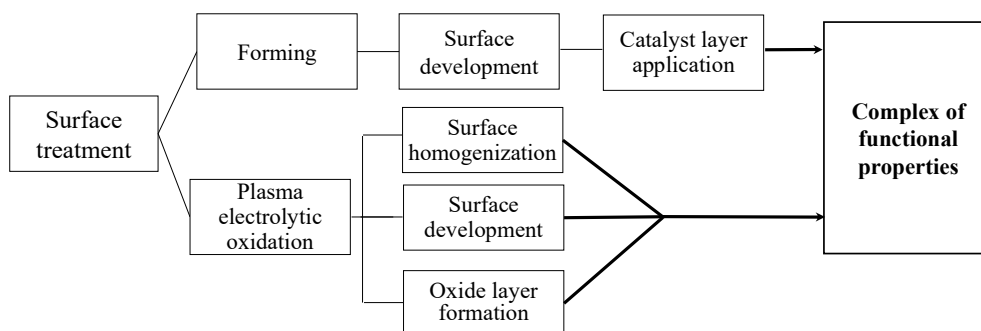


Fig. 1. Classification of approaches to surface treatment of aluminum alloys

The first approach is related to a step-by-step process that involves sequential steps of forming to obtain a porous structure of the carrier (base metal) and subsequent application of a catalytic layer [21]. Various synthesis strategies are used to obtain a highly developed structure of the catalytic bed carrier. The main ones are non-stationary electrochemical treatment, sol-gel method, chemical etching or a combination thereof [22, 23]. The degree of surface development during such treatment characterizes the size of the pores or channels. This parameter is essential for predict-

ing the catalytic properties of materials of this type [24]. For application of catalytic layer on the porous structure of the carrier, impregnation of the obtained materials with compounds of catalytic compositions based on salts of transition metals followed by their subsequent thermal decomposition is most often used [25, 26]. In general, the considered method of forming catalytic material is multi-stage and combines various processes. During the treatment of materials of complex structure, a necessary step to obtain satisfactory performance is preliminary preparation of their surface to remove impurities [27].

Another approach is to form catalytic materials by plasma electrolytic oxidation (PEO). Peculiarities of PEO processes allow combining homogenization and development of surface layer and formation of oxide coating in one technological process of surface treatment. The introduction of additional components to working electrolytes promotes the formation of heteroxide composite layers with a wide range of functional properties [28]. PEO coatings have found application in many industries, especially catalysis and catalytic materials [29]. Variation of treatment conditions provides flexible control of the specified processes and formation of materials with specified characteristics.

The processes of obtaining catalytic materials are mainly multi-stage and lengthy procedures, involving numerous technological operations [30]. The most common process of applying a catalytic material by impregnation of the primary or secondary carrier followed by calcination does not provide a strong adhesion of the active layer to the carrier and does not meet the requirements of energy saving and environmental safety. In addition, it remains quite difficult to control the composition of the catalytic material in the synthesis process, especially during the treatment of multicomponent alloys. The use of metal carriers almost always requires the development of measures to increase their specific surface area and application of secondary layers to ensure sufficient adhesion of the catalytic material.

## 3. The aim and objectives of the study

The aim of the study is to substantiate the optimal method of surface electrochemical treatment of aluminum alloys. This will allow choosing optimal treatment parameters and expand the scope of aluminum alloys in the field of catalysis.

To achieve the aim, the following objectives were set:

- to develop a method of surface forming of aluminum alloys by the pitting mechanism;
- to investigate the mechanism of plasma electrolytic oxidation of aluminum alloys, to work out the method of their treatment to optimize the synthesis of catalytic material with a given level of properties;
- to substantiate structural and technological schemes of surface electrochemical treatment of aluminum alloys of different composition.

#### 4. Methods of surface electrochemical treatment of aluminum alloys, study of process parameters and surface layer characteristics

##### 4.1. Methods of surface electrochemical treatment

Aluminum alloys belonging to different systems were selected for the study (Table 1).

Table 1

Characteristics of aluminum alloys selected for studies

Alloy grade	Classification	System
A99	primary aluminum	Al
D16	wrought aluminum alloy	Al-Cu-Mg
AMn		Al-Mn
AL25	cast aluminum alloy	Al-Si-Cu

The chemical composition of the studied materials is given in Table 2.

Chemical composition of aluminum alloys used for studies

Alloy grade	Al	Cu	Mg	Mn	Fe	Si	Zn	Ti	Impurities
A99	min 99.99	to 0.002	to 0.001	to 0.002	to 0.003	to 0.003	to 0.003	to 0.002	Ga to 0.003
D16	90.9–94.7	3.8–4.9	1.2–1.8	0.3–0.9	≤0.5	≤0.5	≤0.3	≤0.1	Ni≤0.1
AMn	96.35–99.0	≤0.2	≤0.5	1.0–1.6	≤0.7	≤0.6	≤0.1	–	–
AL25	79.5–85.55	1.5–3.0	0.8–1.3	0.3–0.6	≤0.8	11.0–13.0	≤0.5	≤0.1	Ni 0.8–1.3; Pb≤0.1; Sn≤0.02; Cr≤0.2

Surface forming was performed by pulse current in 0.2 mol/dm<sup>3</sup> NaCl solution with the addition of 0.04 NaNO<sub>3</sub> mol/dm<sup>3</sup> and 0.1 mol/dm<sup>3</sup> NaClO<sub>4</sub> at a current density of 20–30 A/dm<sup>2</sup>. The duration of the anode current pulses (on time) and pauses (off time) was  $t_{on}$  0.5–5 ms,  $t_{off}$  1–10 ms respectively, PEO was performed in 1 mol/dm<sup>3</sup> K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution in the DC mode at an anodic polarization current density of 5 A/dm<sup>2</sup>. The temperature of the working electrolytes was maintained within 20–25 °C.

Preparation of the samples surface for electrochemical treatment included machining, degreasing, etching and washing with water after each procedure of the technological operation, as described in [31].

An experimental laboratory system consisting of a PI-50-1.1 potentiostat with a PR-8 programmer, an electrolytic cell, and working electrodes was used to form the samples in the pulse mode. The laboratory installation for PEO treatment of experimental samples consisted of a B5-50 industrial stabilized DC source (Ukraine), forced-cooling electrolytic cell, working electrodes, temperature sensor, MTech ADC-UI18 recorder for online recording of oxidation process parameters.

##### 4.2. Methods of research of the modified surface

A ZEISS EVO 40XVP scanning electron microscope (Germany) was used to analyze the morphology of the modified surface. The degree of surface development ( $k_d$ ) was determined by measuring the capacitive component of the sample impedance before ( $C_0$ ) and after ( $C$ ) anodic treatment  $k_d=C/C_0$ . The chemical composition of the surface layers was investigated using an Oxford INCA Energy 350 energy-dis-

persive spectrometer (UK) with the integrated SmartSEM software environment. The topography of the surface layers was studied by the contact method using an NT-206 atomic force microscope (Belarus). X-ray phase analysis was performed on a DRON-2 diffractometer (Russian Federation) in monochromatized Co-K $\alpha$  radiation ( $\alpha=1.7902$  Å). The compounds were identified by comparing the characteristics of the obtained experimental dependencies with the data of the PCPDFWIN electronic file cabinet.

#### 5. Results of electrochemical surface treatment of aluminum alloys

##### 5.1. Surface forming of aluminum alloys

Surface forming electrochemical treatment of aluminum alloys consisted in controlled “growing” of a branched network (grid) of pits on the surface of the treated material by applying pulse electrolysis (Fig. 2).

Table 2

It is found that the following scheme of aluminum surface etching is implemented in the pulse mode. During the period of the anode current pulse, the metal potential is shifted to the pit formation area, and the generation and development

of pits occur. During the pause period, the metal potential decreases and conditions for pit repassivation are created [32].

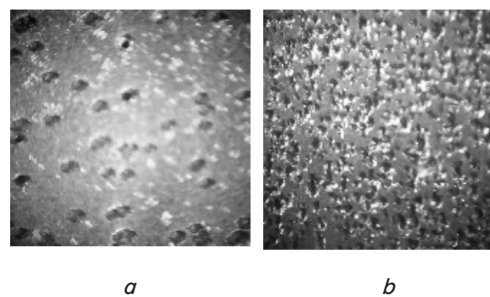


Fig. 2. Surface morphology of the aluminum alloy after treatment with a pulse current of  $j=30$  A/dm<sup>2</sup>:  
a –  $t_{on} = 5$  ms,  $t_{off} = 10$  ms; b –  $t_{on} = 0.5$  ms,  $t_{off} = 10$  ms

The main characteristics of surface forming of aluminum alloys by the pitting mechanism are the pit formation  $E_{pf}$ , pit repassivation  $E_{pr}$  potentials and steady potential  $E_s$ . According to the results of the studies, the dependencies of the potentials of the carrier samples on the composition of the working electrolyte were obtained (Fig. 3).

It was found that with an increasing concentration ratio of activator ions ( $Cl^-$ ) and inhibitors ( $ClO_4^-$ ) of pitting, there is a decrease in the steady potential of aluminum  $E_s$ , while a decrease in the pit formation  $E_{pf}$  and repassivation  $E_{pr}$  potentials is not so significant.

At the same time, within the ratios  $c_{Cl^-} / c_{ClO_4^-}$  from 1:10 to 1:1, the range of potentials corresponding to the optimal

etching mode is 0.09...0.07 V, and with increasing  $c_{Cl^-} / c_{ClO_4^-}$  it decreases to 0.05 V.

It is known that during the polarization pulse, aluminum dissolution is activated by the pitting mechanism, i.e. generation of pits, and during the pause, conditions on the inner pit surface are created for its repassivation and subsequent activation [33].

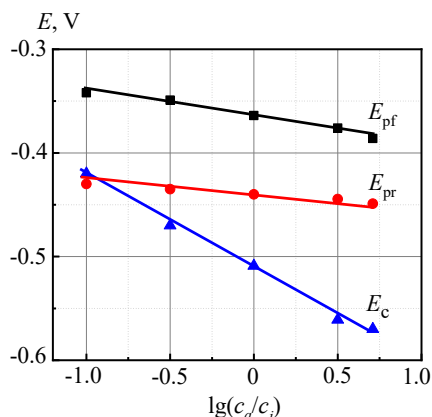


Fig. 3. Dependency of the steady potential of aluminum  $E_s$ , pit formation  $E_{pf}$  and repassivation  $E_{pr}$  potentials on the concentration ratio of activator ions ( $Cl^-$ ) and inhibitors ( $ClO_4^-$ ) in solution

Based on the study of the effect of variation of pulse duration and ratio  $t_{on}/t_{off}$  on the course of the material etching process, it is shown that reducing the duration of the anode pulse leads to an increase in the number of pits on the treated surface (Fig. 4).

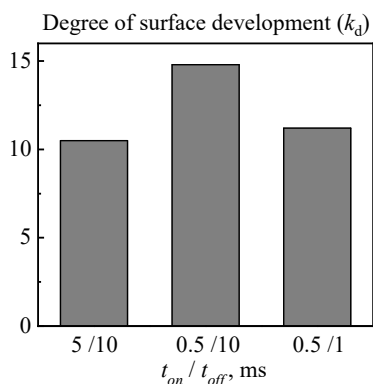


Fig. 4. Effect of time parameters of pulse electrolysis on specific characteristics of aluminum surface at  $j=20 A/dm^2$

With a constant ratio of electrolyte components, reducing  $t_{on}$  from 5 to 0.5 ms promotes pit nucleation and reduces the likelihood of deep pits and sample perforation. This causes the formation of not one deep pit, but many small ones on the surface of the existing one, which leads to a more uniform etching of the aluminum surface.

It was found that a pause of 10 ms is sufficient to prevent significant surface etching, while an increase in  $t_{off}$  leads to a decrease in the number of pits, and a decrease

in  $t_{off}$  causes the formation of deep large pits, deteriorating the mechanical properties of the carrier.

As a result of the proposed forming, a highly developed surface of the carrier material is formed, which can be used for subsequent application of a layer of catalytically active substance [34, 35]. Thus, the process of pit formation can be controlled by maintaining the technological parameters within the appropriate limits. The regularities formed the basis for the development of a model of the surface formation process of aluminum alloys.

5. 2. Plasma electrolytic oxidation of aluminum alloys

PEO of aluminum alloys was performed in a 1 mol/dm<sup>3</sup>  $K_4P_2O_7$  solution with recording voltage changes during oxidation (Fig. 5). It is found that the voltage chronograms of the studied materials in general have a classical form with division into characteristic areas: pre-spark, spark, microarc and arc discharge, as noted earlier [36]. The sparking intensity during the oxidation process is quite high for all the treated materials.

At the same time, PEO of each alloy has certain features, which affects the shape and slope of the characteristic sections of the voltage dependencies on the formation time  $U-t$  (voltage chronograms). It should be noted that the slope of the voltage chronograms depends on the resistivity of oxides formed on the metal surface. Therefore, the higher resistivity of the corresponding oxide causes a rapid voltage increase over time ( $dU/dt$ ), i.e. the slope of the  $U-t$  dependencies. At the same time, the quantitative parameters of the PEO process, namely the sparking voltage  $U_s$  and the final formation voltage  $U_f$  will be maximum. Thus, the slope of the  $U-t$  dependencies reflects the nature and characteristics of the oxide or other compound formed on the surface. It is quite natural that the slope of individual sections of voltage chronograms can be used to study the kinetics and determine the mechanism of the processes that occur during the PEO of aluminum alloys [37].

The  $U-t$  dependency of A99 aluminum is the closest to the classical one (Fig. 5, curve 1).

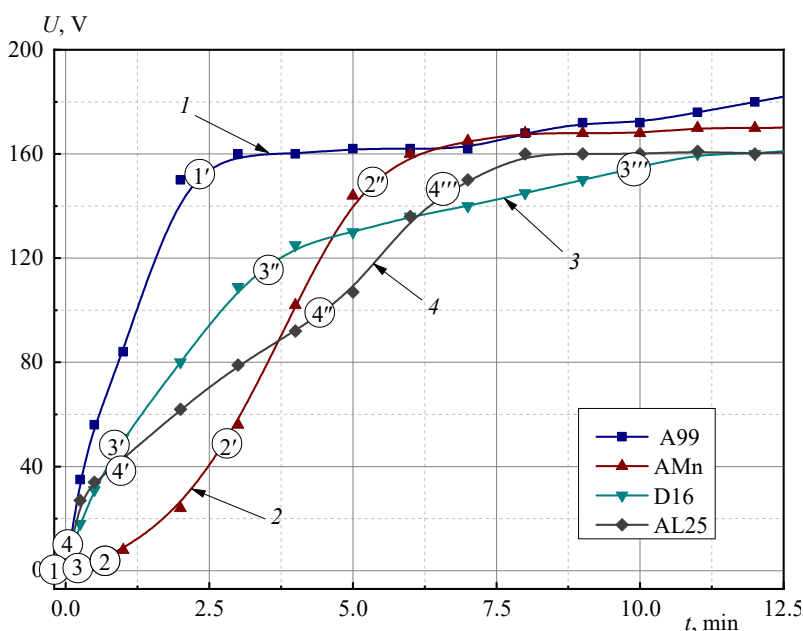
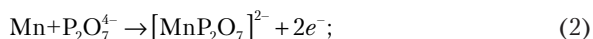
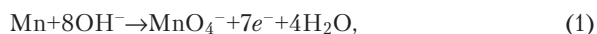


Fig. 5. Voltage chronograms during PEO of aluminum alloys in 1 mol/dm<sup>3</sup>  $K_4P_2O_7$  solution: 1 – A99, 2 – AMn, 3 – D16, 4 – AL25

This is due to the small amount (up to 0.01 wt %) of impurity elements in the alloy. At the initial stage (section 1–1'), the process of alloy surface anodizing with the formation of barrier (phase) alumina with high resistivity takes place within 2.5 min. At a voltage of 150 V, a breakdown of the oxide film is initiated, which propagates mainly by the surface, and the process goes into the sparking mode. This is visualized by the appearance of many sparks that move stochastically on the electrode surface. A gradual voltage increase to 160–170 V indicates the healing of defects in the breakdown zones and the inclusion of the electrolyte remelt in the coating. Due to this, PEO goes into the microarc discharge mode, which is optimal for surface treatment and formation of a composite oxide layer of adjustable thickness. Voltage oscillations within 160–180 V are the operating voltage range for PEO treatment of A99 alloy.

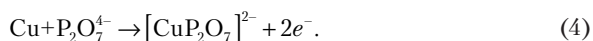
For doped alloys containing a significant amount (more than 3 wt %) of impurity elements, there is a natural change in the shape of each of the characteristic sections of the PEO voltage chronograms.

The peculiarity of the anode behavior of the AMn alloy in alkaline diphosphate-based electrolytes (Fig. 5, curve 2) is associated, in our opinion, with manganese oxidation in the surface layers by known reactions, given the alkaline nature of the electrolyte:



In fact, the formation of phase alumina begins after the removal of manganese from the surface layer when the voltage reaches 50–60 V (section 2–2'). The voltage decrease compared to A99 is explained by the lower resistivity of manganese oxides. After homogenization of the composition of the surface layers, PEO occurs according to the classical mechanism described above. Therefore, the spark voltage for AMn is almost the same as for A99 and is 145–150 V, and the operating voltage of PEO treatment is also within 160–180 V.

The D16 alloy differs from those previously considered by significant copper content (5.0 wt %) and presence of intermetallides [38], the potentials of which are much more positive compared to aluminum. Therefore, the processes of PEO treatment and formation of a uniform oxide layer are significantly complicated. This is due to the probability of formation of copper oxides of different valence ( $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ) and variable resistivity during anodic oxidation [39]. However, due to the presence of diphosphates in the working electrolyte, copper is removed from the surface layer and bound into soluble complexes by the reaction:



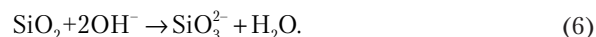
Given the heterogeneity of the D16 alloy, the initial section (3–3') of the voltage chronogram (Fig. 5, curve 3) looks quite predictable, where phase alumina is formed and oxidation of magnesium occurs (1.2–1.8 wt %), the resistivity of which oxide is less than alumina. The slope of the section (3'–3'') is flatter compared to A99, because it is associated with the oxidation of copper and intermetallides by the reaction (4). The specific bending of the dependency at the point 3'' is due to the intensification (in section 3''–3''')

of manganese oxidation by the above mechanism. Thus, the beginning of sparking for D16 occurs at a voltage of 125–135 V, and the transition to the microarc mode – after homogenization of the surface layer at 160–180 V.

On the voltage chronogram in the PEO of the AL25 alloy (Fig. 5, curve 4), the number of characteristic areas is determined by its chemical composition. Substantial silicon content (up to 13 wt %) and lower content of other alloying elements compared to D16 cause the formation of a mixture of phase alumina and silicon oxide with almost the same resistivity in the first section of the  $U-t$  dependency (section 4–4'). This conclusion is supported by an almost identical slope of the voltage chronograms in this section. After reaching a voltage of 30–40 V, section 4'–4'' begins, at which  $dU/dt$  decreases, i. e. the nature of the anode process changes. Based on the fact that the slope of this section differs from all previously considered cases, we can assume that there are processes involving silicon. Probably, the acidic nature of silicon oxide and its thermal instability initiate the process of its dissolution from the surface layers, especially in local heating areas, by the known reactions:



or



The slope of the third section (4''–4''') of the  $U-t$  dependency of the AL25 alloy is identical to  $dU/dt$  of the D16 alloy on the section (3'–3''). This indicates the course of reactions of copper removal from the surface layers by the above mechanism. And only after surface homogenization, the process of alumina formation on silumin begins to dominate. So, the spark initiation voltage is the lowest in the series of investigated alloys and is 115–120 V. The forming voltage corresponding to the microarc mode is also slightly reduced to 16–165 V.

Clarification of the characteristic process parameters ( $U_s$  and  $U_j$ ) was performed using the analysis of the differential dependencies  $dU/dt-U$  (Fig. 6).

We consider this approach more informative and accurate, as it takes into account the peculiarities of the processes during plasma electrolytic treatment [37] in contrast to the common study of changes in the thickness of the oxide layer from oxidation time [40, 41]. Such an analysis becomes especially relevant for heterogeneous alloys, the oxidation of which produces oxides of different nature and resistivity.

Different slope angles of the  $dU/dt-U$  dependencies in the initial sections up to 30–40 V (Fig. 6, region I) testify in favor of the formation of oxides of different nature on the surface. The dominance of dissolution reactions of the alloy components from the surface layers and in the breakdown zones over oxidation reactions with high resistivity, in particular aluminum oxides, is manifested in the independence of the rate of formation voltage change of voltage, so there is a plateau on  $dU/dt-U$  dependencies (Fig. 6, region II). The end of the plateau corresponds to the acceleration of the alumina formation process, which is reflected in the beginning of sparking at a voltage  $U_s$ , when there is a breakdown and healing of defects and the inclusion of electrolyte remelts in the oxide layer.

The increase in the oxide thickness provides the transition of the process to the microarc mode, which is identified by an increase in the formation voltage to 160–170 V (Fig. 6, region III). In the microarc discharge mode, the

dominant process is the formation of the oxide layer, which mainly consists of the oxide of the treated metal and may contain remnants of electrolyte components. A characteristic feature of the process is a low rate of voltage change (up to 10 V/min).

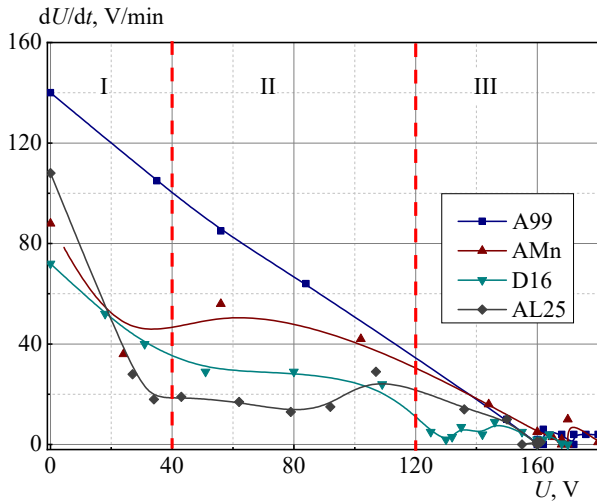


Fig. 6. Rate of voltage change in PEO of aluminum alloys in 1 mol/dm<sup>3</sup> K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution

Taking into account the obtained results, it can be assumed that at the initial stage of treatment, the surface layer of the treated material is homogenized by removing the alloying components from the surface layers [42]. This assumption is supported by the analysis of the chemical composition and morphology of the studied samples before and after PEO in potassium diphosphate solution (Fig. 7).

The study of the topography of the surface oxide layers by atomic force microscopy confirms the assumption of increasing specific surface area of the samples (Fig. 8).

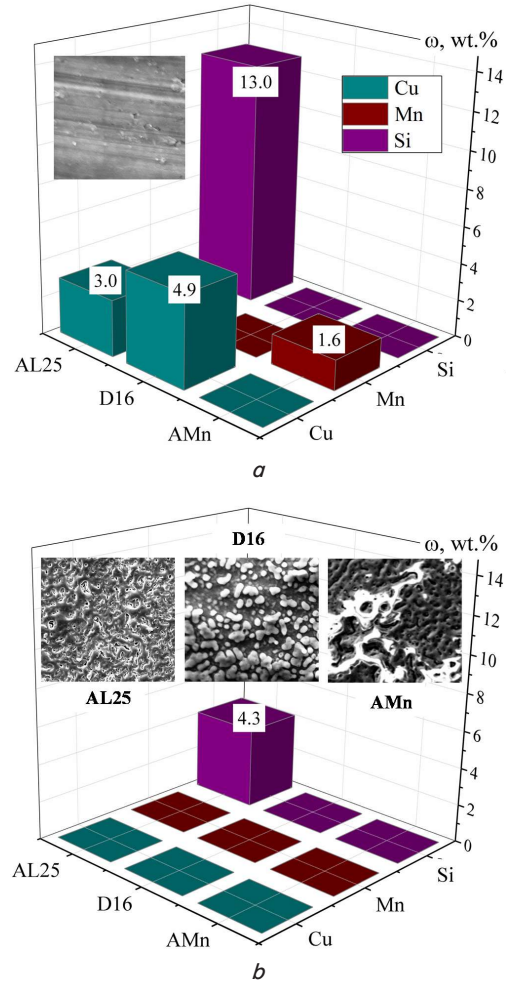


Fig. 7. Composition and morphology of surface layers of aluminum alloys: *a* – before treatment, *b* – after PEO with 1 mol/dm<sup>3</sup> K<sub>4</sub>P<sub>2</sub>O<sub>7</sub>

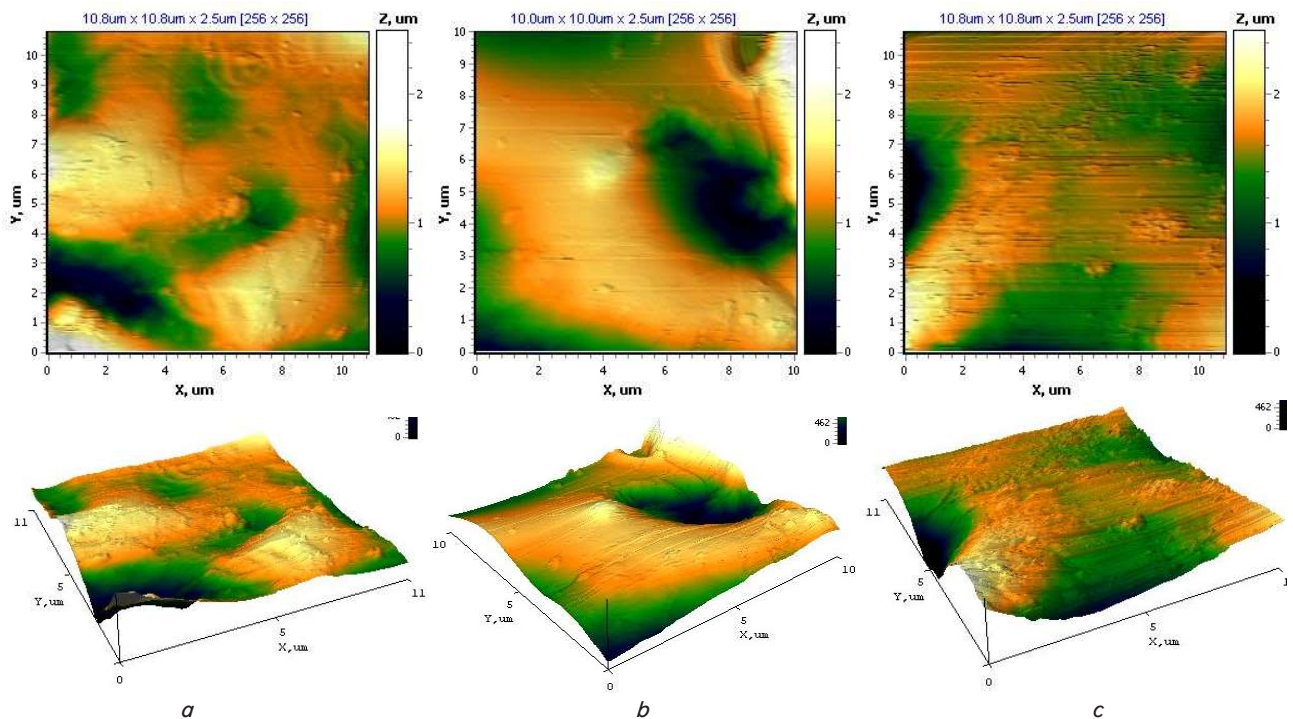


Fig. 8. 2D- and 3D-maps of the surface of Al|Al<sub>2</sub>O<sub>3</sub> coatings formed in 1 mol/dm<sup>3</sup> K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> on alloys: *a* – A99; *b* – D16; *c* – AL25

Analysis of the topography of the surface layers confirmed that the most developed surface is formed on the AL25 silumin. On the surface there are crater-like melted depressions formed during the burning of spark and microarc discharges. Such depressions are probably the outer part of the burning channel – closed (dead-end) pore [43]. Taking into account the curvature radius of the probe, it can be found that the size of such pores varies from several tens of nanometers to micrometers and more and increases in the series of alloys A99<D16<AL25.

Confirmation of structural changes during plasma electrolytic oxidation is the results of X-ray structural analysis of the studied systems (on the example of AL25 alloy) (Fig. 9).

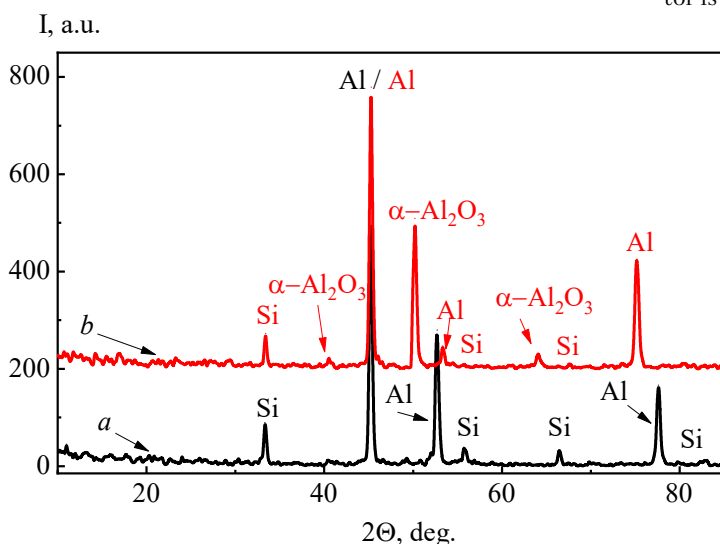


Fig. 9. Diffraction patterns of AL25 aluminum alloy surface: *a* – untreated surface, *b* – after PEO treatment in 1 mol/dm<sup>3</sup> K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution

Peaks belonging to the main alloy components are visualized on the untreated surface. After PEO, the number and intensity of aluminum and silicon peaks decrease, but α-Al<sub>2</sub>O<sub>3</sub> (corundum) peaks appear. This is evidence of the course of high-temperature processes during PEO and homogenization of the surface layer [44].

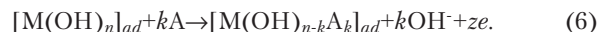
Thus, the use of electrochemical methods of surface treatment of aluminum alloys in alkaline electrolytes allows obtaining a set of functional characteristics. The formed coatings have a high degree of surface development, which is a prerequisite for high catalytic activity and corrosion resistance of the obtained oxide systems [45].

## 6. Discussion of the results of surface electrochemical treatment of aluminum alloys using generalized technological schemes

### 6.1. Surface forming by the pitting mechanism

Physico-chemical features of the process of surface electrochemical treatment of aluminum alloys are due to the fact that a passive film is present on the metal surface. For surface forming, at least two types of particles that are not indifferent to the electrode reaction must be introduced into the working solution – activator ions and passivators or inhibitors. Initiation of the initial stages of surface development (pit formation) is a consequence of replacement of

passivating particles of the surface complex with electrolyte nucleophiles, usually anions (A), according to the scheme:



If the resulting surface compounds are well-soluble or unstable, easily hydrolyzed, a series of successive acts of nucleophilic substitution and transition of the products of this reaction to the electrolyte will lead to pit formation due to perforation of the passive film in the most electrophilic reactive areas.

The tool for controlling the process rate (number and depth of pits) is the current density amplitude, which directly affects the values of the system potentials [46]. Another factor is the parameters of pulse electrolysis (pulse/pause duration ratio) (Fig. 3). As the polarization time (pulse duration) increases, deep, sometimes through pits are formed, which leads to a decrease in the mechanical strength of the samples. The short pulse duration does not allow achieving the appropriate level of surface development and treatment efficiency. The duration of the pause also significantly affects the process intensity and the end result. A short pause is insufficient for repassivation, and too long significantly reduces the rate and efficiency of treatment. In the optimal mode, etching zones are the same in size and shape (hemispherical) and evenly distributed on the metal surface [27].

Thus, the result of surface forming depends on the electrolyte composition (the concentration ratio of activator ions and inhibitors of pitting), treatment modes (amplitude of anode current density), duration of pulses and pauses and their ratio.

The generalized technological scheme of treatment of aluminum alloys by the pitting mechanism can be represented by a set of parameter vectors A1–A4 (Fig. 10). The surface treatment of the material (S<sub>0</sub>) can be carried out by controlled chemical interaction of the material with the components of electrolyte solutions μ(t) under conditions of spontaneous dissolution (ΔG<0) or under the influence of external polarization j(t) in working solutions (ΔG>0).

The variability of the technology is provided by vectors A1...A4 reflecting the contribution of various factors:

- vector A1 – composition and ratio of solution components;
- vector A2 – electrical and time parameters of external polarization;
- vector A3 – parameters, the control of which will allow forming pits with specified characteristics (number, size, shape);
- vector A4 – chemical nature of the treated metal or alloy.

The patterns of aluminum behavior in such solutions formed the basis for the development of a model of the surface formation process. The algorithm for constructing a controlled process is complex and requires a steady state for effective surface treatment. However, the presence of impurities and intermetallides significantly limits the outlined approach to the treatment of high-alloy aluminum alloys due to the multi-factor nature of such parameters as pit formation and repassivation potentials [27].

To construct a generalized topological model, the principles of general systems theory were used. The topology of local (pitting) surface development is represented by the

structural graph  $G(S, t)$ . Such a graph (Fig. 11) is a set of individual states  $S_i$ , the transition intensities of which correspond to the rates of direct ( $\lambda_{ij}$ ) and inverse reactions ( $\mu_{ji}$ ).

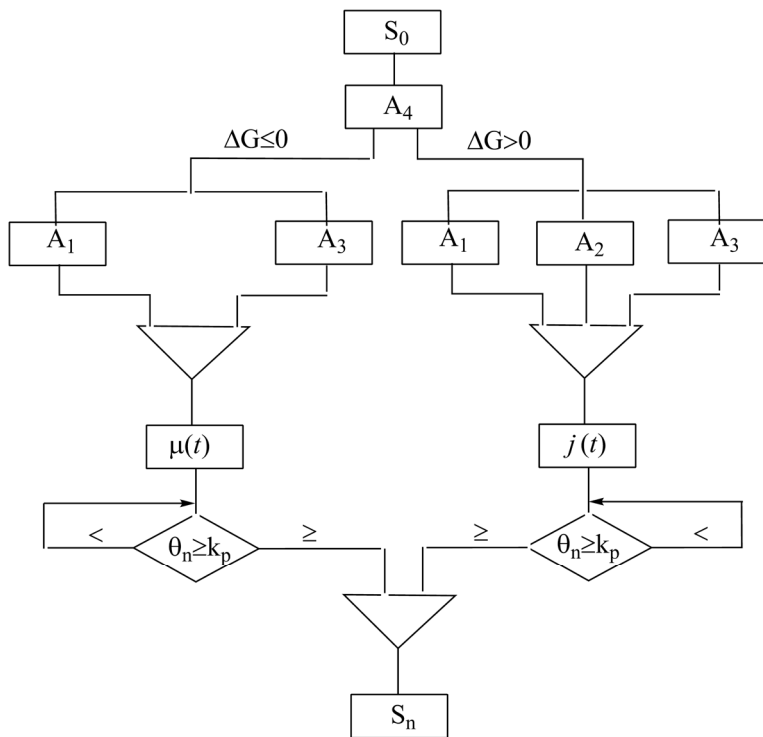


Fig. 10. Block diagram of surface forming of aluminum alloys by the pitting mechanism

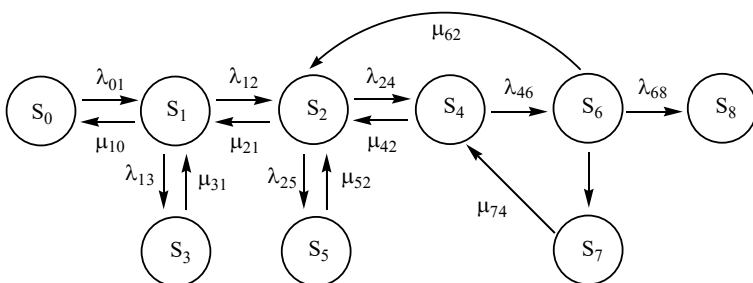


Fig. 11. Graph of metal states, reflecting surface development due to local dissolution by the pitting mechanism:  $S_0$  – initial state;  $S_1$  – passivity state;  $S_2$  – local dissolution;  $S_3$  – uniform dissolution;  $S_4$  – pit generation;  $S_5$  – pit formation;  $S_6$  – stable pit;  $S_7$  – steady pit;  $S_8$  – final surface state

The oriented graph includes: states  $S_0$  and  $S_1$ , the transition intensities of which reflect the processes of formation and dissolution of the passivating film under the action of the medium;  $\lambda_{13}$  – intensity of uniform dissolution of the electrode surface, in particular from the transpassivity state;  $S_2$  – initial state of local anodic dissolution or in the form of pits – state  $S_5$  with the transition intensity  $\lambda_{25}$ , or pit –  $S_4$ ,  $S_6...S_8$  chain.

The individual states of this chain correspond to pit generation  $S_4$  and development  $S_6$ , formation of steady pits  $S_7$  and the final state of the electrode with a developed surface  $S_8$ .

The intensities  $\lambda_{46}$ ,  $\lambda_{67}$ ,  $\lambda_{68}$  reflect the kinetics of the process,  $\mu_{62}$  and  $\mu_{74}$  – repassivation, taking into account that the state  $S_7$  corresponds to the destruction or perforation of the metal.

The recovery intensities  $\mu_{62}$  and, especially,  $\mu_{74}$  will have a non-zero value only due to external control effects. The graph  $G(S, t)$  also contains two cycles  $S_2-S_4-S_6$  and  $S_4-S_6-S_7$ .

As noted in previous studies [27], an electrochemical system of this type (Fig. 10) will not have a steady state. This confirms the need for non-stationary mode of electrochemical surface treatment.

The variability and versatility of the considered model reflect the fact that active-passive transitions and repeated reproduction of the “pit activation – development – repassivation” cycle to achieve the final state are inherent not only in aluminum alloys. The proposed model can be extrapolated and used to model the treatment of passivation-prone metals for optimal shaping of their surface.

### 6. 2. Plasma electrolytic oxidation of aluminum alloys

A feature of PEO in comparison with surface etching by pulse electrolysis is the possibility of synthesizing a material, which may include components of the treated alloy and electrolyte remelts in a single process [47]. The process proceeds without complications for pure metals (Fig. 5, curve 1). PEO of doped alloys occurs in stages, as evidenced by a more complex form of voltage chronograms (Fig. 5, curve 2–4).

For PEO implementation, it is important to select the type and composition of the working electrolyte [48]. Given the heterogeneity of the studied aluminum alloys due to the presence of intermetallic compounds and hardening phases, an alkaline solution of diphosphate was chosen for PEO treatment. This approach allowed the formation of the oxide layer of pure metal A99 and homogenization of the surface layers of doped alloys by oxidation of impurity components and binding them into soluble complexes. The alkaline medium also allowed partial processes of manganese oxidation in AMn and D16 alloys.

Factors affecting the course of PEO processes are a set of technological parameters, among which the main ones are treatment current density, PEO time and process voltage. Their variation allows controlling the process of surface homogenization and formation of oxide layers [49].

The study of the mechanism of PEO treatment of aluminum alloys by analyzing the differential dependencies  $dU/dt-U$  (Fig. 6) allowed minimizing the influence of the oxidation time parameter during PEO treatment. It is found that the sparking voltage  $U_s$  for the studied systems increases in the AL25<D16<AMn<A99 series and is within 115–150 V. The operating voltage of the oxide layer formation in the microarc mode ( $U_j$ ) for all systems is 160–170 V. An increase in the process voltage over 170 V leads to the transition of PEO in the arc mode, deterioration of the properties of the synthesized oxide layer and its detachment.

In general, the process of changing the state of surface layers of the studied alloys can be provided by a set of the following schemes:



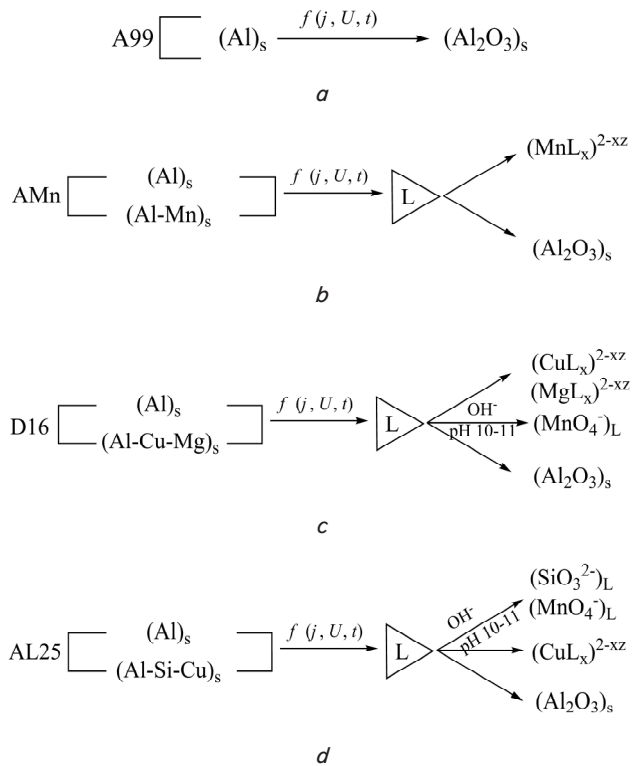


Fig. 12. Scheme of transformations of surface layers of aluminum alloys during PEO: a – A99; b – AMn; c – D16; d – AL25

The schemes reflect the partial processes occurring during the PEO treatment of aluminum alloys with current density  $j$  during time  $t$  under the influence of voltage  $U$  in a solution containing ligand L. The course of reactions corresponds to the characteristic sections of the voltage chronograms (Fig. 5). It is assumed that the process of surface homogenization and oxide layer formation can be controlled by changing the electrolyte composition and PEO treatment mode (current density, oxidation time), as noted in studies of the formation of mixed oxide systems on aluminum and titanium alloys [50, 51].

Changes in the morphology and composition of the surface layers of doped alloys (Fig. 7) confirm the course of processes of their surface homogenization during PEO. Plasma electrolytic oxidation of AMn and D16 alloys in diphosphate solution allows complete removal of impurity elements (Mn, Cu) from the surface of the treated samples. For the AL25 alloy, complete removal of copper and reduction of silicon content by 3 times compared to untreated material were revealed. The obtained results confirm the efficiency of using diphosphate solutions for surface homogenization of aluminum alloys during PEO [52].

The oxidized surface of aluminum alloys contains  $\alpha\text{-Al}_2\text{O}_3$  (Fig. 9). This indicates the peculiarity of the PEO course in the microarc mode (Fig. 6, region III), namely the ultra-high temperatures in the discharge channels and remelting of the base metal components. This approach is used in the formation of heteroxide composite coatings by introducing additional components into the working electrolytes.

The formed oxide coatings have a layered and porous structure. It is found that with increasing the number of al-

loying components in the alloy, an oxide layer with a greater degree of development and porosity is formed (Fig. 7). This pattern is fully consistent with the study of surface morphology according to SEM analysis and is evidence of the peculiarities of the formation of composite coatings and oxide structures on alloys of different composition [50].

The obtained results allow determining the ways of controlling the processes of surface treatment and formation of oxide layers in diphosphate electrolytes. Modeling of the PEO process can be performed according to the generalized structural-technological scheme (Fig. 13), containing a set of parameter vectors **A1–A4**, as well as during forming (Fig. 10). The feature of the PEO process is that the surface treatment of the material ( $S_0$ ) can be carried out only under the action of external polarization  $j(t)$  in an electrolyte solution containing ligand L.

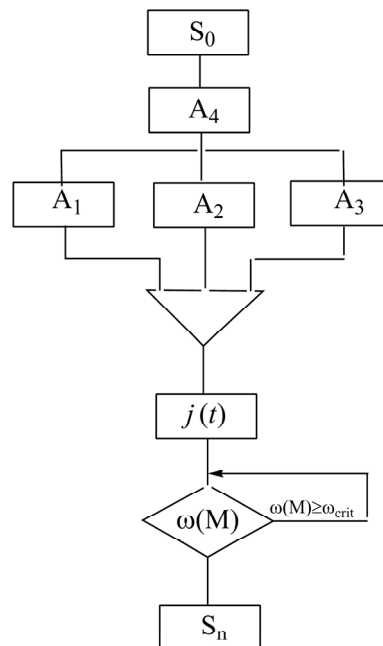


Fig. 13. Structural technological scheme of plasma electrolytic treatment of aluminum alloys

The variability of the technology can be represented by vectors **A1...A4**, which also reflect the contribution of various factors: vector **A1** – composition and component ratio of the working electrolyte; vector **A2** – current density and time parameters of PEO; vector **A3** – voltage parameters ( $U_s, U_f$ ); vector **A4** – chemical nature of the treated material. The parameter that controls the course of the process is the content of impurity components ( $\omega$ ) in the surface layer of the oxide coating until it reaches a predetermined content  $\omega_{crit}$ . If necessary, additional control parameters characterizing the level of functional properties of the obtained oxide layer can be introduced into the scheme.

This approach can be used to design the technological scheme of heteroxide composite coatings on aluminum alloys and other valve metals.

The process of PEO of aluminum alloys, as well as their forming, can be represented by the structural graph  $G(S, t)$  (Fig. 14). Symbols and terminology are provided in accordance with (Fig. 11).

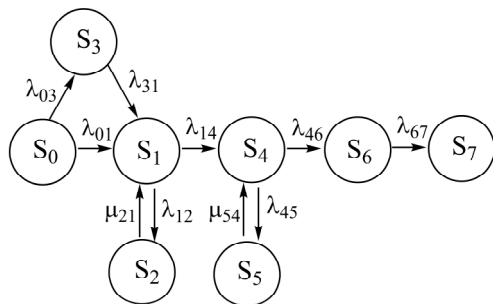


Fig. 14. Surface state graph, reflecting the PEO process of the alloy:  $S_0$  – initial state;  $S_1$  – formation of phase alumina;  $S_2$  – dissolution of phase alumina;  $S_3$  – surface homogenization;  $S_4$  – healing of defects in breakdown zones;  $S_5$  – inclusion of remelts of electrolyte components in the coating;  $S_6$  – oxide layer formation;  $S_7$  – final surface state

The oriented graph includes: states  $S_0$  and  $S_7$ , the transition intensities of which reflect the processes of formation and dissolution of the phase oxide; surface homogenization, healing of defects in the breakdown zone and formation of the oxide layer. The intensities of transitions during PEO  $\lambda_{01}$ ,  $\lambda_{02}$ ,  $\lambda_{14}$ ,  $\lambda_{21}$ ,  $\lambda_{46}$ ,  $\lambda_{67}$  reflect the process kinetics according to Fig. 5 and Fig. 6.

The proposed approaches facilitate the implementation of transitions between individual links of the “process parameters – composition and structure of material – properties – functions – field of use” chain, as well as provide a basis for controlling the flow of transformations during surface treatment of aluminum alloys [31].

The practical significance of the work lies in the possibility of using the proposed approaches and generalized models in the technologies of surface treatment of aluminum alloys.

Limitations on the use of the proposed technological approaches are related to the need to maintain and control the operating parameters of the process. Deviations from the recommended values may be the reason for the low quality of surface treatment of these structural materials. Given the peculiarities of the processes of forming and plasma electrolytic oxidation, it is advisable to apply certain safety

measures by workers during the organization of the technological process. The reproducibility of the results will be affected by the quality of equipment and working materials. Preference should be given to multifunctional automated systems. The costs of implementing the proposed technical solutions may be associated with the purchase of certified equipment and materials, modernization of existing areas of electrochemical treatment and training of staff.

The direction of further research is aimed at expanding the range of working electrolytes and adapting the developed models for surface treatment of other types of structural materials.

## 7. Conclusions

1. The method for surface forming of aluminum alloys by pulse current treatment in chloride-containing electrolytes is developed. The presence of impurities and intermetallics significantly limits the application of this approach to the treatment of high alloys.

2. The method of plasma electrolytic oxidation of aluminum alloys of different chemical composition in alkaline solutions of diphosphates is developed. It is shown that PEO allows combining homogenization of the surface layer, its development and formation of the oxide coating in one technological process. The mechanism of the process of plasma electrolytic oxidation of alloys of different chemical composition is investigated by the analysis of differential dependencies  $dU/dt-U$ . The analysis of morphology, chemical composition, topography and structure of the formed oxide layers is carried out. It is shown that the formed coatings have a high degree of surface development, which is a prerequisite for high catalytic activity and corrosion resistance of the obtained materials.

3. Structural-technological models of the surface forming process by the pitting mechanism and plasma electrolytic oxidation of aluminum alloys are substantiated. The proposed models can be used to model the surface treatment of other structural materials and form the basis for controlling the flow of transformations during surface treatment of aluminum alloys of different chemical composition.

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