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NANOCOMPOSITE ELECTROLYTIC COATINGS WITH DEFINED FUNCTIONAL PROPERTIES

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Modern electrochemical technologies for surface treatment of titanium alloys to create protective, antifriction, dielectric and catalytically active materials are considered. The physicochemical fundamentals of the processes of plasma-electrolytic formation of conversion and composite electrolytic coatings are highlighted. Separate stages of electrode reactions, regularities of the influence of electrolyte components and electrolysis parameters on the composition, structure and morphology of synthesized materials are examined in detail. Considerable attention is paid for improving the technology for producing nanostructured composite electrolytic coatings based on active dielectrics, fluoropolymer-filled and mixed oxides, including rare and refractory metals. The monograph summarizes the results of the project AR05130069 "Development of nanotechnology for the synthesis of functional galvanic coatings for electrical equipment."

The monograph is designed for specialists in the field of chemical technology, as well as teachers, graduate students and students of higher educational institutions.

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INTRODUCTION

Wide use of titanium and its alloys in aerospace industry, shipping and machinery manufacturing, medicine, electronic engineering and other fields of science and technology is conditioned by the set of such important physicochemical properties as high corrosive resistance, strength-to-weight ratio, hot strength, the technological effectiveness of treatment combined with low density. Nevertheless, there is a range of reasons limiting the use of the materials mentioned above. They include bad anti-friction properties, which lead to problems with the use of titanium alloys in friction couples, high chemical reactivity during welding works and some other properties, whose effective change is possible to reach by coating modification. Bearing that in mind, one of the most efficient approaches here is based on the use of galvanochemical technologies for the deposition of coatings with different content and used for different purposes, among which the most appropriate metals seem to be conversion and composite metals applied together with valve metals. Such scrutiny in their respect is connected not only to an opportunity to add more varied functional properties to products with them in content, but also to the reliability and lifespan increment in the field.

Conversion coatings are protective ones, obtained directly on metal coatings as a result of a chemical reaction. The most widely-used conversion coatings applied in manufacturing may include phosphate, chromate and oxide ones, taking into consideration the wide use of the latter one for many centuries.

Lately, composite electrochemical coatings (CEC) have become commonly used. In their content there are addings increasing hardness and scrub resistance. As a rule, they are carbides, borides, oxides and diamond-like materials.

In most cases CEC are obtained via electrolysis of the electrolyte-suspensions which are aqueous solutions of the metal salts with admixture of high-dispersive powder that gives them specific properties: scrub resistance, hardness, oil retention capacity and a high degree of corrosion resistance in the conditions of the attack by certain types of mechanical stresses.

The way of obtaining CEC is based on the coprecipitation of the dispersive particles of different size and type apart from metals from the electrolyte-suspensions. Joining the coatings, these particles considerably improve their capacities (hardness, scrub resistance, oil retention) and give them new ones (anti-frictional, magnetic, and catalytic). As a result, CEC are widely used in different industries, and the development of new composite coating types and the search for new ways of managing their capacities are an important scientific and technological objective.

The research that gains significant interest is aimed at improving the technologies of oxide coating formation. Still, the most of the existing traditional methods cannot provide the sufficient adhesion characteristics, scrub- and corrosion resistance together with a certain complex of characteristics determining the functional purpose of materials and products. In this regard the method of plasma-electrolytic oxidation (PEO) presents itself as attractive as it allows the formation of oxide coatings firmly attached to the metal surface and having good physico-chemical and mechanical properties (dielectric, protective, anti-frictional etc). PEO-coatings have been successfully used lately as carrier for catalytic materials, yet the potential for creating not only carriers but also catalytically active layers in one fabrication cycle remains unrealized because adding electrolyte components during the coating process may provide conditions for the formation of simple, complex and composite oxides, spinels and other compounds. Biocompatibility and corrosion resistance of CEC-coatings are of special interest in medicine, while high protective and anti-friction properties provide prospects and reasonability of their use in petroleum, chemical and energy-power industries, machinery and environmental technologies.

In the light of the mentioned above description of the formation of coatings with titanium or its alloys in their content, together with metal bases of different nature obtained through plasma-electrolytic oxidation and the research into their functional properties are with no doubt topical. The effective solution of the scientific problems concerning the choice of content and components equivalence ratio in the electrolyte, as well as the optimization of the electrolytic characteristics, pave the way to the development of the technologies to create coatings that have increased lifespan, chemical resistance to impacts of technological environments and abrasive erosion, increased tribological characteristics and catalytic activity in heterogeneous transformations.

These are the functionality of and the demand for the CEC-coatings with titanium alloys in a great many of industries as well as insufficient coating of this topic in scientific and technical literature that predetermined the aim of this work.

CHAPTER 1

SYNTHESIS AND FUNCTIONAL PROPERTIES OF COATINGS FOR TITANIUM ALLOYS

1.1 Current Methods of Producing Functional Coating on Titanium Alloys

A number of unique properties of titanium and its alloys determine its demand and wide usage in medicine, municipal services and many branches of industry. Compared with other constructional materials, titanium has two main advantages: a high specific strength-to-weigth and ratio resistance even in harsh atmospheric conditions as well as in contact with many aggressive chemicals [1]. For some ranges of applications, are important other properties of titanium: it is non-magnetic, has high melting point and low coefficient of bulk etc. [2–5]. The biological inertness regarding to the body, good mechanical properties and corrosion resistance determine its widespread use in medicine. Titanium and its alloys are characterized by high resistance to fatigue wear under alternating loads, which is extremely important in the production of intraosteal locking nails, intra and extra prostheses [6–8].

At present we know a significant number of ways and methods of functional coatings formation for various purposes, including titanium alloys, which can significantly extend the range of physical and medical properties of materials and their field of application [9–13].

An electrochemical method for the synthesis of oxides is one of the most technologically advanced and cost-effective, as it allows obtaining a uniform thickness and compounds with firm adhesion [14–16].

Methods of Formation of Anode Oxide Films

The classic and most common method of forming oxide films is anodizing in aqueous electrolytic solutions. The process is usually carried out at a constant current in the potentio- and galvanostatic modes, i.e., correspondingly, at constant forming of anode current. As electrolytes solutions of acids (sulphuric, chromic, oxalic) are most commonly used, more seldom – salt and alkaline solutions for thin films of special purpose: anti-corrosion, wear-resistant, conductive, electro isolated, protective, and decorative and others [17].

Anodizing in the melted salt allows to obtain considerable thickness oxide films, characterized by a high micro hardness, corrosion resistance, as well as the stability of parameters. During the process of corporation anions of the electrolyte in the anodic oxide films it occurs to a much lesser extend than in aqueous solutions and higher temperature facilitates inter-diffusion, whereby it becomes possible to obtain a dielectric for high precision capacitors, anode oxide films on iron and copper with high electrophysical parameters. For anodizing of melts, its compounds with a low melting point and high conductivity, various eutectic mixtures are used [17].

The formation of oxide films can also be performed by anodization in gas plasma using one of the variants [18]:

- Anodizing in DC (Direct current) glow discharge plasma, which is held in its positive column;
- Anodizing in HF (high-frequency) discharge, which allows to achieve high rates of oxidation and to obtain a uniform film of considerable thickness;
- Anodizing in the arc of low pressure, which is characterized by much higher rate of oxidation and the thickness of the film. However, during this process the extremely rapid destruction of the hot cathodes in an oxygen atmosphere takes place, whereby preference is given to iridium oxide or iridium cathodes coated with thorium.

It should be noted that for all variants of anodizing by the gas plasma it is necessary to distinguish the plasma oxidation, which occurs on the insulated electrode and plasma anodizing, during which the electrode has a positive potential in comprising to the plasma.

The oxide films formed by anodizing in gas plasma on aluminum, silicon and titanium have unipolar volt-ampere characteristics.

Micro arc anodizing – specific method for the synthesis of oxide layers, wherein the anode is partially immersed in an electrolyte, a cathode is positioned over the surface thereof and between them ignite the electric discharge, applying a pulse voltage of 40 – 100 V, and complete a circuit with short contact between the cathode and the electrolyte [19]. Created conditions allow to obtain a dense plasma near the metal while maintaining the low temperature of anode (≤ 80 ºC) due to its contact with the electrolyte solution. The opposite arrangement of the electrodes is also possible, but the productivity of the process of anode oxide coating characteristics is reduced by 15 – 20 %.

The mechanism of micro-arc anodizing contains anodizing elements in aqueous solutions of electrolytes and anodizing in gas plasma, but it also has its own features. Electric discharge during this process takes place in three stages: the formation of the conduction channel; processes supplied by energy liberation; channel gap with its transformation into a gas bubble.

The process of micro-arc anodization is generally carried out in solution, based on sulphuric acid. Plasma-chemical and thermally activated reactions provide high speed coating formation and also allow synthesizing bigger film thickness with a low porosity that can be used as wear-resistant, anti-friction, thermal and electrical insulating materials.

A plasma electrolytic oxidation as well as the anodizing micro arc involves electrical discharges, but it has some significant differences [20]:

- process occurs when an electrolyte of anode and cathode are immersed;
- conduction plasma discharge channels are not formed directly between the anode and the cathode but at a thin boundary layer between the anode surface and the electrode which has a potential of the counter electrode, so-called electrolytic electrode located in randomly moving portions with micro discharges;
- plasma is not aero-stream and it is formed in a mixture of steams of electrolyte and gaseous products of electrolysis;
- discharge is not normal glow, high-frequency, spark or arc but is more complex;
- processing is carried out in alkaline electrolytes with an alternating current and high voltage (up to 1kV).

Here are some main advantages of plasma electrolytic oxidation:

- there is no need in special pre-treatment of the surface;
- there is a possibility of the creation of a considerable thickness of coatings without using refrigeration equipment, which is complex and harmful to the environment;
- electrolytes are environmentally friendly and non-aggressive;
- a number of technological properties of the synthesized coatings, particularly high wear resistance and micro hardness, significant adhesion features and low porosity.

The Essence and Features of the Method of Plasma Electrolytic Oxidation

A plasma electrolytic oxidation (PEO) is one of the most promising methods for the preparation of inorganic coatings on metals. The feature is that the material is synthesized in a single process on a metallic anode which contains compounds of the oxidizing metal and electrolyte. Upon reaching the sparking voltage a sharp increase in the electronic component of the current is observed, it flows through the interface of the metal; the electrolyte, which leads to a substantial increase of temperature in breakdown channels and the rapid growth of the oxide coating and oxide inclusion of the electrolyte components to the oxide compound[21].

According to the scientists who study micro arc plasma electrolytic oxidation [22], the first research on the occurrence of micro-discharges at the electrode were conducted by N. P. Sluginov [23] and R. Colley.

Subsequently, arcing in the anode during the oxidation in the elevated stress was investigated by Gyuntershultse A. and Betz G. [24]. During the experiments they observed that a significant gas evolution on the anode does not obey the Faraday’s law [25], as it was found later due to the thermolysis of the discharge channel. The three characteristic parts (Figure 1.1) were identified during the research on the forming voltage Kinetic chronological relationship:

I – pre-sparking part, where the cell voltage increases linearly;

II – sparking part, determined by visual observation of the appearance of electric discharges on the surface of the electrode during the tradition in which the dependence of U(t) looses linear property;

III – the part of micro arc discharges, characterized by a slight change in voltage, thus there is a consolidation of discharges and their union in micro arcs.

Further process leads to the part IV – arc, accompanied by a reduction of the speed of the growth of the oxide film to practically zero, due to the destruction of the coating and the substrate.

For a long time this phenomena was believed to be a negative one and it lead to the formation of inhomogeneous and porous anode coatings [25, 26–28].

The beginning of the use of PEO as a method for putting functional coatings is considered to be works by W. Neil and L. Grass, published in the 50 – 60s of the last century, which are devoted to the formation of oxide coatings on the surface of aluminum alloys [29, 30]. Scientists managed to use sparking at the anode for the synthesis of complex oxide layer from the substrate components and electrolyte.

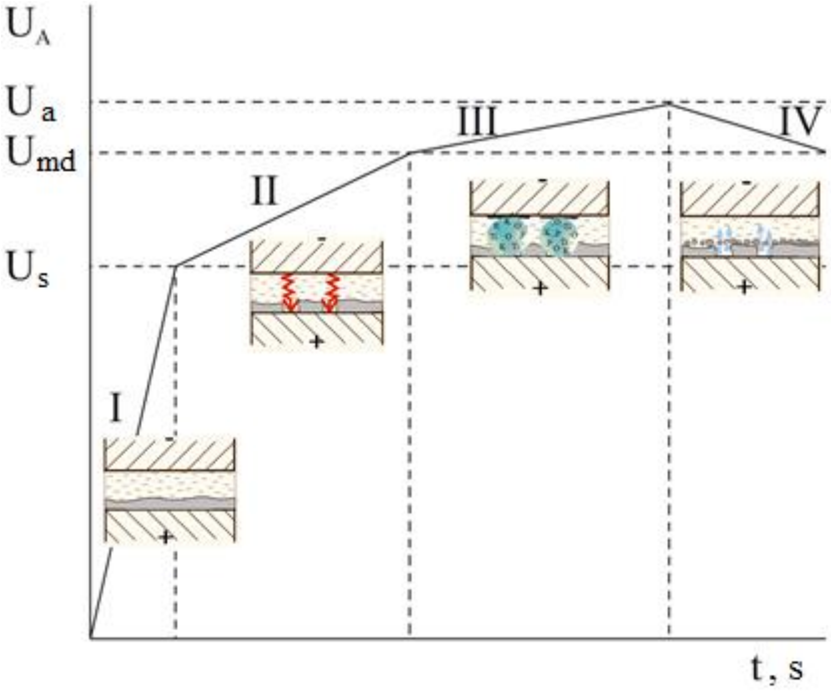


Figure 1.1 – Forming dependence of plasma electrolytic oxidation process

Since 70s, the PEO, conducted with the purpose of obtaining protective coatings on aluminum and alloys on its basis with high functional properties, was widely studied in our country [31, 32], and abroad [33 – 35]. There was a wide range of largely different descriptions of the mechanism of formation micro arc discharges moving through the working electrode surface. However, even at present there is no definitive explanation for the PEO process’s mechanism, to be knowledgeable of which is necessary to control this process and obtain stable coating with the desirable functional properties.

The model, which studies the mechanism of the PEO process on aluminum and titanium, based on the following points became most widely used [36−43]:

- breakdown of the vapor phase formed in the through-pores of the coating;
- removal of the plasma on the surface of micro-discharged channels;
- presence of parallel running processes:

- Exothermic reaction of oxidants with juvenile surface of the bottom micro-discharge channel, which is followed by oxidation of evaporated atoms of the metal substrate components;
- Deposition on the surface of the coating or retraction into the micro-discharges of oxides after plasma and thermo-chemical transformation of the electrolyte components.

Plasma electrolytic oxidation is a complicated process of forming a coating surface of an electrically conductive material in the high voltage mode; ensure the availability of local micro-discharges, which are moving along the surface of the electrode in the anodic polarization. The PEO has a number of advantages in comparison to other methods, which are used in industry: anodizing, chemical oxidation, electrophoresis, plasma and flame splaying etc. The main advantages of the PEO method are:

- the possibility of anti-corrosion coatings with higher mechanical properties (hardness, wear resistance, adhesion to a metal substrate, fatigue resistance);
- minimization of production areas and reduction in the duration of technological processes does not require careful pre-treatment of the surface of details and constructions, what is required in other methods of putting protective coatings;
- High environmental friendliness.

The authors of a considerable number of works, dedicated to the theoretical grounding of the electrical breakdown of anodic oxide films nature came to a conclusion about the avalanche mechanism. The specified hypotheses have quite persuasive experimental justifications, however, there are premises letting us think that under certain conditions the phenomenon of a breakdown is of thermal nature [45-46]. Avalanche development depends significantly on electron injection into the conduction band method, on agility of holes, formed in the valence band in the ionization process, etc. Thus, it is reasonable to consider the breakdown mechanisms, not being related to thermal instability of dielectrics.

In particular, to explain the properties of aluminum oxide films in metal-oxide electrolyte system the ideas of ion-induced breakdown were used. According to them it was assumed that the metal transfer from the anode to the cathode occurs in the film as well as the formation of the projections penetrating into oxide on a metal surface of the latter. The growth of these projections decreases dielectric thickness between the anode and the cathode, and at the same time increases the field density, which in its turn causes even greater increase of protrusions. The resulting positive feedback leads to the unlimited growth of the current and the origination of a local breakdown. However, the described mechanism is purely qualitative in nature, although the attempts to use it in order to explain aluminum, tantalum, niobium [47] breakdown were made.

The majority of theories concerning electrical breakdown of solid dielectrics are based on the notions of impact ionization [48-50], according to which the charge carriers in the pre-breakdown stage are electrons as ions are at very low energy levels.

Injected from the cathode into the insulator, electrons having enough energy to form in the collision with the atoms pair electron-hole. Since the mobility of holes in dielectrics is very small, they create a positive charge, contributing to an increase in field strength at the cathode and thus an increase of the injection current.

It should be noted that the current uncontrolled growth is inhibited by drift and recombination of holes with electrons, so the current instability is possible only by achieving the critical field strength.

When considering the breakdown mechanism of amorphous thin films, specifically, the anodic oxide films, many authors ignore characteristics of the electrical properties of disordered dielectrics and develop their own ideas based on classical notions of impact ionization in the crystals. However, the development of impact ionization in an amorphous dielectric prevents low carrier mobility and consideration of the process from the perspective of general representations classical theories is only possible within the framework of the electronic model phase transition - the conductivity type changes from dielectric to metal. Depending on the nature of the phenomena that hinder impact ionization process, distinguish ionization-drift (ID) and ionization-recombination (IR) model.

The relations for determining the critical stress of field and the breakdown development time can be obtained by solving the system of equations [50]:

$$i = AE_{\text{к}}\exp(-\frac{B}{E_{\text{к}}}) \tag{1.1}$$

$$\frac{\partial E}{\partial x} = ep/(\tilde{\mathrm{E}}_0\tilde{\mathrm{E}}) \tag{1.2}$$

$$\frac{\partial p}{\partial t} = \frac{i}{q}(\alpha - \sigma) \tag{1.3}$$

$$\alpha = \alpha_0\exp(-\frac{H}{E}) \tag{1.4}$$

where A and B are constants; Ec is field gradient at the cathode;

p - density of holes; α - coefficient of collision ionization;

σ – hole capture cross-section;

H = Ei / (z • le); Ei - the energy needed for collision ionization;

le - mean free path for electrons before scattering their energy in phonons.

A quantitative description of the IR model based on the above-mentioned equations assumes that the electron injection occurs through their tunneling through the interface between the cathode-insulator (mechanism of Fowler-Nordheim equation (1.1)). Relation (1.2) is a Poisson equation (1.3) – the speed of hole occurrence (1.4) - the dependence of the ionization coefficient on the field density. Similar expressions can be obtained for ID models, both in case of small and large ionizations. For ID models the mobility of holes, which depends on the field density should also be taken into account. Choice preference of IR or ID model is ultimately determined by the hole mobility.

The appearance of the breakdown on reaching the critical point is of probabilistic nature, while the solution of the equation system (1.1) - (1.4) gives rigidly defined critical values. This is the drawback of the considered theory, however, the calculations made on the basis of collision ionization models agree with the experimental data.

The mechanism of anodic oxide films formation by PEO

Anodic oxide films formation during plasma electrolytic oxidation is a complex process, comprising the stages of metal passivation, the formation of the barrier oxide layer, its breakdown and its processing by electrical discharges.

Passive state is achieved by the formation of monoatomic layers of adsorbed oxygen, hydroxide ions, monomolecular oxide layers or three-dimensional oxide films on the metal surface. The behavior of metal passivation stage depends sufficiently on the nature and composition of the anionic electrolyte. Passive state occurs especially easily in solutions containing corrosion inhibitors which can be divided into three groups: anions - strong oxidizing agents; anions that form sparingly soluble compounds with metal; anions - weak oxidants.

The possibility of obtaining the anodic oxide films on the metal surface is determined by the chemical composition of the passive layer and its conductivity type. In most cases there is a change in oxide composition for the thickness (even within the barrier layer), the degree of oxidation of metal is decreasing in the direction from the electrolyte to the surface of a substrate. Conductivity type of the passive film is determined by the presence of non-stoichiometric oxides and may vary widely depending on its thickness and composition of the electrolyte.

Classical studies by Gyuntershultse and Betz [51] ascertained that the oxide film growth occurs due to mass transfer and the ion charge of metal and oxygen. Connection of Ii ion current with the E field density in the oxide can be characterized by the following relation:

$$I_i = Aexp(BE), \tag{1.5}$$

where A and B are constants.

The exponential connection between the current density and the field density makes it clear that there is a potential barrier to the oxidation reaction. The concept of it are taken as a basis of the first theories of the ionic conductivity of oxide films. The differences between them reduce themselves to the localization of the barrier. Verwey [52] suggested that the leading part is played by the energy barrier between the two minima of the potential ion energy moving in the crystalline oxide.

According to Cabrera-Mott theory [53], the leading part is played by the energy barrier at the metal-oxide interface. According to this theory, charge carriers in the film are only metal cations which interact with the electrolyte to form an oxide when reaching the interface. The immutability of the field density through the film thickness is an important feature of this theory.

In spite of an enormous amount of researches aiming to confirm the validity of the set out theories, it fails to make a choice in favor of one or another ion transport mechanism in the film. However, the half-width of the barrier, calculated from the constant B, is the same for both the Verwey Theory and the Cabrera-Mott Theory. At the same time, the experimental verification of the Cabrera-Mott Theory revealed a significant discrepancy between the calculated and experimental values, as well as the distortion of the linear dependence of the Tafel slope from the temperature. The discrepancies between theory and experiment are easily eliminated, taking into account the presence of the space charge generated by ions, situated in the interstices in the film. Only at very low concentrations of the latter the space-charge effect can be neglected and the Verwey Theory will be effective. The space charge does not consider the Cabrera-Mott Theory, since it is assumed that the speed of the film formation is determined by the rate of ions transfer through metal-oxide.

Thus, the field density at any point of oxide has two components connected with the contribution of the surface and spatial charges. The latter occurs when the total charge of ions moving in the interstices happens to be uncompensated net charge of the electrons which is removed from the film under the condition of a strong field.

In accordance with Dewald's ideas [54], current density of a moulder at a distance x from the metal border - the solution is determined by the equation:

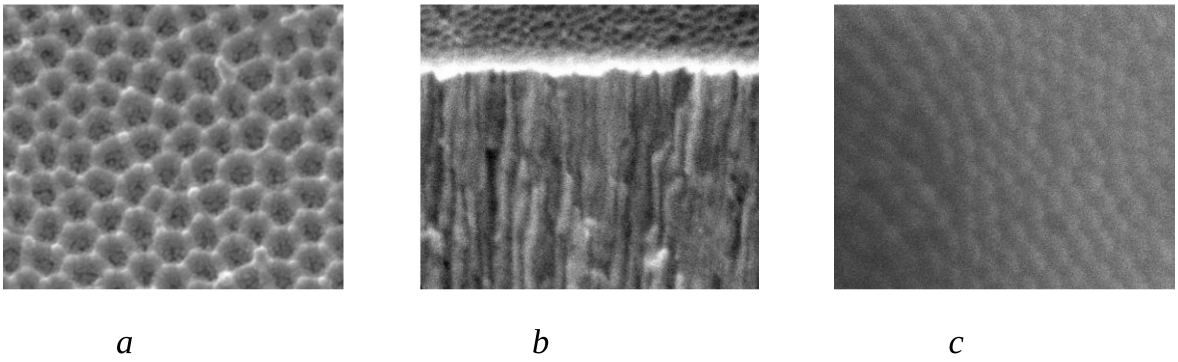
$$i(x) = 2avn(x)sh[Eaz/(kT)]exp[-W_0/(kT)], \qquad (1.6)$$

where W_0 is the height of the energy barrier between adjacent positions of minimum potential energy, located at a distance equal to half the lattice constant.

According to the equation for weak fields, a linear dependence of the current density on the field is characteristic. At quite high field densities the entrance barrier may be lower than the height of the diffusion barrier (barriers inside the film) even when the field was absent inverse relationship between them was observed. Consequently, the charge transfer mechanism may change with field density.

Fromhold and Cook [55] calculated the diffusion current in the crystal lattice, which occurs under the influence of a strong electric field, taking into account the space charge and concentration changes in the film. The theoretical ratio were compared to experimental data of L. Young, who confirmed the forecast by the theory of the electric current rectification on the metal film.

These ionic conductivity models imply oxide layers of the crystalline structure. Besides, it is well-known that they are generally amorphous. However, despite this disparity, there is a fairly good qualitative agreement between the theory and the experiment. The most significant drawback of the classical anodic oxide film growth theory is its inability to explain the experimental results about the ion transport numbers determination. At the same time many different authors have shown by tracer method that the numbers of the cations and anions transfer for some oxides are approximately equal. This means that the film formation process takes place throughout oxide rather than on the boundary of the electrolyte-oxide section, as it was traditionally considered (Fig. 1.2).



a- surface, b – the chip, c - side of the barrier layer.

Figure. 1.2 - Photomicrographs of porous anodic aluminum oxide synthesized at 60 in a 0.5M $(COOH)_2$ solution x100000.

This work [56] describes a method of determining transport numbers using the tracers, the principle of which is as follows: a small amount of radioactive tracer is applied by ion bombardment on the surface of the metal sample. Upon further oxidation of the sample in the electrolyte, energy of radioactive particles will depend on the thickness of the oxide grown on the metal surface. If the oxide film is formed only due to the migration of cations to the oxide electrolyte border, the indicator will remain on the metal surface, and the energy of radioactive particles will progressively decrease when the film thickness increases. In case when only the migration of anions takes place, the oxide film growth will occur on the metal oxide-section, and radioactive tracer atoms will take their places at the oxide electrolyte boundary. If both types of ions are involved in the charge transfer, a layer of a radioactive tracer will move into oxide.

Dighnam made an attempt to take into account the differences in the numbers of cations and anions transfer within the cooperative particle transport theory [56]. According to him, the numbers of transfer are to a large extend determined by the proportion of the charge, which some molecular entities share by anions and cations. Dighnam’s Theory predicts a quadratic dependence of activation energy on the field density and operates with the concepts of the dipole moments of molecular entities that are capable of rapid and slow changes in polarization.

Ion transfer theories can not explain the dependence of kinetics of growth of the film on the electrolyte composition, because they do not consider the processes occurring at the solution-oxide boundary, usually coated by a layer of chemisorbed OH - groups, resulting from the interaction of not fully coordinated metal and oxygen ions with water molecules.

Plasma colloid theory is developed in the works by A. F. Bogoyavlenskiy [57, 58]. Unlike the ion transport theory it helps to explain such a complex process as galvanoluminescence. The theory is based on the idea of the existence of almost two-dimensional plasma growing directly under the oxide film which consists of electrons, the electrolyte anions, oxygen ions with different charge, protons, hydroxyl groups and water. Aluminum and oxygen ions form clusters, which are the nuclei of colloidal particles of anodic oxide – mononen. Mononen aggregates form micelles of hydrated aluminum, oriented along the field. The double electric layer occurring on the surface of the micelles as a result of anions adsorption and prevents their merger and leads to the growth of rod-like structures. In cases where the electrolyte anions adsorbate weakly, the double layer is not being formed and the solid barrier-type film is growing on the oxide surface, as it is observed in the borate solution.

The most difficult thing to explain is the inclusion of the anodic oxide films of electrolyte components. In the case of the barrier films, the formation of chemical compounds nonstoichiometric composition can be assumed.

The authors of the report [59] carried out a detailed study of the incorporation of anions of different nature in the barrier film on the aluminum layer by layer via spectral, X-ray analysis methods as well as by the use of radioactive tracers. The most intensely moving in the barrier oxide arsenate, borate and phosphate anions are usually transferred from the electrolyte border - oxide into a film or remain stationary. The resulting distribution of the direction of the anions impurity depends on the relative velocity of their movement and the film growth rate. In general, the content included in the oxide anions determined by their ability to adsorb onto the surface of precipitate or form nonstoichiometric compounds.

The authors of the report [60] also consider that the growth mechanism of the coating does not depend on the physical nature of breakdowns and places of their localization, and electrolyte affects the dielectric strength of the coating and the vapor phase composition. The appearance and the movement of micro plasmic discharges occurs at an electrode surface areas with a sufficiently high current density.

Formation of PEO coatings with required properties and parameters may be carried out only with the proper choice of metal-electrolyte pair. Based on experimental data, electrolytes of plasma electrolytic oxidation of titanium are divided into 6 groups [61]. The first one is salt solutions, in which rapid dissolution of substrate occurs (NaCl, NaOH, $NaNO_3$, HCl). The second group includes electrolytes which promote achieving passive state of the metal, particularly it's boric, citric and tartaric acids and their salts, and salts of carbonic and phosphoric acids. Succinic, lactic, adipic, and acetic acid, which belong to the third group of electrolytes for plasma electrolytic oxidation, have less effective passivating properties and, consequently, worse ability to create conditions for spark discharge. Substances of the fourth group – sulphuric acid, ammonium thiosulfate, sodium sulphate – are characterized by weak dissolution of metal. In oxalic acid and its sodium salt, sodium acetate, and phosphoric acid (the fifth group), the voltage range, in which spark discharge is achieved, is quite narrow. The sixth group includes solutions of NaF, KF, sodium phosphate dehydrate and sodium sulfite.

Of these, the most effective substances for the formation of oxide coatings on titanium are electrolytes based on phosphate compounds, alkalis, silicates, borates, carbonates and citrates. Data on the formation of oxide coatings with a wide range of functional properties in electrolytes based on polyphosphate compounds is presented in [62-65].

One electrolyte is known for production of oxide layers, which have high hardness and wear resistance, during spark discharge on the surface of the titanium [66]. This electrolyte contains a number of inorganic compounds, including sulphates, borates or mixtures thereof. For filling of the oxide layer, the electrolyte is injected with aluminates, silicates, molybdates, etc., as well as dispersions of titanium, tungsten carbides, titanium, aluminum oxides, or boron suspensions. The process is carried out in spark mode at a current density of over 100 A/dm^2. On the surface, an oxide film is formed with composition TiOx (x = 1-2) and microhardness of 3,600 MPa.

One electrolyte [65] contains caustic potash, sodium calgon, magnesium or aluminum sulphate, sodium aluminate, sodium silicate, with a calgon to aluminum ratio of 3-4 : 1. The high content of alkali components (pH 13) leads to etching of coating during PEO, carried out at high anodic current density. On titanium and aluminum, thin layers (up to 5 μm) are formed, which include TiO_2 (anatase) and X-ray amorphous phase on titanium. According to X-ray phase analysis, only substrate lines (Al) are shown on aluminum. These coatings have substantial hardness, but cannot be used as wear resistant.

One electrolyte produces protective coatings on titanium and its alloys [67] and contains, g/dm3: sodium aluminate 3-10, alkali-metal sulphate 5-15, magnesium sulphate 10-25 or hydrazine sulphate 10-15, ammonium persulfate 0.5-0.8. Oxidation is carried out in plasma electrolytic mode. Voltage applied to anode is 150-300 V, current density is 15-40 A/dm^2, oxidation time is 5-10 min. Synthesized coatings consist of TiO_2 (rutile) and spinel Al_2TiO_5.

The composition of an electrolyte for the formation of coatings with high microhardness and wear resistance [68], containing aluminate and sodium sulphate, is further supplemented by sodium tetraborate and aluminum borate (2 $Al_2O_3 \cdot B_2O_{3x} \cdot 5H_2O$) with a following content of components, g/l: sodium sulphate 5-12, sodium aluminate 3-8, sodium tetraborate 2-10, aluminum borate 0.25-0.5.

Treatment of products made of aluminum, titanium, zirconium or their alloys in an electrolyte [69], which has such components as sodium silicate (80-120 g/l), sodium phosphate (5-10 g/l), and sodium hydroxide (5-15 g/l), on an alternating current (50 Hz) with a density of 5-30 A/dm^2 and a voltage of 120-220 V for 5-80 minutes provides coatings on the products of aluminum, titanium, zirconium and their alloys with high physical, mechanical, and operational characteristics. By controlling the parameters of the plasma electrolytic oxidation in an alternating current, it is possible to widely adjust growth rate of an oxide layer, porosity and surface microhardness of coatings due to changes of the components in the coating – oxides of aluminum, titanium, and zirconium (Al_3O_3, TiO_2, ZrO_2).

Chemical and phase composition of coatings in plasma electrolytic oxidation of titanium is largely dependent on the composition and concentration of electrolyte; in particular, in solutions based on salts of carbonic, sulphuric, and phosphoric acids titanium dioxide films are formed in the form of rutile and anatase modifications [70]. The relationship between these phases can be changed within wide limits by varying the content of electrolyte components. For example, with an increase of concentration of sulphate ions in the solution, the basis of the formed coating is rutile, while high phosphate electrolytes can increase the proportion of anatase.

Typically, the phase composition of coatings varies along the thickness of the oxide layer. It is found that high-temperature oxide modifications are located within its internal layers, while the number of low-temperature modifications increases towards the outer surface of the film [71]. In close vicinity to the metal substrate, density, and sometimes composition, of micro-arc coatings differ from the rest of the coating. The thickness of dense layer may be 20-30% of the total thickness of sediment.

The morphology of films and their dispersion may vary widely depending on the choice of electrolyte components and the mode of oxidation [72]. However, it should be noted that there are no general principles of selection of electrolysis conditions that would provide desired coating structure. Electrolysis conditions for each specific electrolyte and processed metal should be determined experimentally.

The mode of coating formation determines the temperature in the path of spark breakdown and consequently the cooling rate of this path after the discharge process. In any case, the coating surface in contact with the electrolyte has clear melting traces. Coating defects include unwelded breakdown paths, so called craters. Degree of fusion of micro-arc coatings is the greater, the higher the end voltage of the process, therefore, high density deposits can be received at high voltages.

Dispersibility of the coating material is eventually determined by the cooling rate of breakdown paths, so the thin deposits are finely divided.

Plasma electrolytic oxidation in electrolytes containing polymer anions (silicate, phosphate, tungstate, etc.), leads to the formation of complex chemical composition of coatings [73].

The nature of compounds, which appear in the transition layer "metal – oxide layer" providing adhesion of coatings to metallic substrate, is very important from a practical standpoint. Assuming that the processes in breakdown paths are similar to solid phase synthesis of materials by thermal diffusion welding, there is a possibility of using thermodynamic analysis of probability of interaction of oxide coatings with a number of structural metals. Metastable grain structure and random orientation of oxide compounds appear as a result of rapid release of heat through walls of pores. Observations made with an electron microscope [74] show similarity in structures of sediments formed by micro-arc oxidation and other methods of rapid surface melting.

Modes of plasma electrolytic oxidation process are much more diverse than in the case of classical anodizing. Among the possible classification principles, core can be identified, which allows to classify them according to the following criteria:

- type of current (DC, AC, and their imposition);
- polarity of the applied voltage (anode, cathode, anode-cathode, and "cycling" – cyclic change of polarity of modes with possible dead time);
- change in electrical parameters (current-controlled, electrotype-dinamic, controlled potential, potentiodynamic, constant power mode, reducing power mode, etc.);
- nature of discharge (spark, micro-arc, arc, arc electrophoresis);
- degree of management (manual, semiautomatic, automatic);
- method of discharge formation (soft, soft-hard, hard-soft, hard) [75-77].

While analyzing possible differences in the nature of the formed coatings, we will note only the basic features. For instance, the process of plasma electrolytic oxidation is carried out by both direct and alternating current. In the case of superimposition of alternating current on the electrode with valve properties, it is separated into faradaic and capacitive components. The first results in faradaic conversions and the second causes the formation of electrical double layer.

Reducing power mode is performed when a cell is supplied with current density, which provides the formation on anode surface of a solid anodic film, the growth of which leads to a gradual increase in anode potential and striking of spark. From that moment formation of coating begins with thickness determined by the time of holding the anode in the electrolyte. However, when a certain thickness is reached, the forming current is reduced so that a further increase in the mass does not take place [77].

Formation of anodic oxide film in controlled potential mode is determined by the residual current and dielectric parameters of oxide film. The said properties of oxide films depend on current density, final forming voltage, electrolyte composition, its temperature and initial state of the substrate surface [78].

One of the common modes of oxidation, removing diffusion restrictions – multi-stage formation of the oxide film. The main feature of such oxidation is to stabilize voltage in time in current-controlled mode of the formation of oxide layer. Multi-stage oxidation is most efficient in case of porous electrodes, because it reduces the differences in acidity of electrolyte and in its temperature [79-81]. Two stages of current-controlled oxidation with a voltage delay of ten minutes is enough to reduce the temperature inside the porous anode at the end of the formation from 40 to 30 ºC. Such temperature reduction improves dielectric characteristics of oxide films by 15-20% [82].

During oxidation of smooth anodes in mixed mode (current-controlled and voltstatic) [83], optimal densities of the oxide layer forming current are about 5.1 $mA\cdot cm^{-2}$. Oxide layers produced under these conditions have highest dielectric properties. Increasing the current density leads to deterioration of dielectric characteristics of both chemically activated and non-activated substrates.

The formation of oxide layers on porous substrates [77, 84] is similar to the formation of those layers on smooth electrodes. The main feature of a porous electrode with valve properties, is highly developed surface, enclosed in a small geometric volume. Formation of the oxide film on the outer surface of the porous electrode is carried out similarly to the formation of such film on non-porous electrodes. Oxidation of the internal layers is limited by the volume of electrolyte in pores, dimensions of which are comparable with the thickness of diffusion layer. Mass transfer in the bulk-porous anodes, as in most electrochemical systems, is performed by diffusion, migration, and convection. The discharge of water molecules and low rate of diffusion of the reaction products contribute to a significant increase in concentration of the electrolyte within the porous electrodes, and the growth in concentration and temperature of the electrolyte have an adverse effect on dielectric properties of oxide films. In order to minimize the contribution of these factors, methods that accelerate the diffusion processes are applied – prior vacuum impregnation of electrodes and a.c. modes of oxidation.

During electrochemical oxidation of titanium, generally a film is formed having anatase structure containing small amounts of rutile. Such films are transparent, non-porous, durable, and have high chemical stability in neutral, mildly acidic, mildly alkaline salt solutions and oxidizing environments. Thin phase films on the surface of passivated titanium are semiconducting in nature, have free electron and limited ionic conductivity. In the process of anodic oxidation of titanium and its alloys within the potential range of 6-18 V the thickness of the oxide film increases with the growth of potential. This changes the color of the film from a bright yellow to blue or sky blue. Oxide layers of substantial thickness are formed during the passivation of titanium in more severe conditions: oxidation in air at high temperatures, in oxidizing environments at boiling temperature, anodic oxidation at high potentials.

During anodic polarization of titanium in sulphuric acid solution with a mass fraction of 40% in the potential range of 0.7-1.4 V with a potential increase to the value of 0.7 V, 1.0 V, and 1.4 V a decrease of the oxide layer thickness is shown to $4 \cdot 10^{-9}$, $3 \cdot 10^{-9}$ and $2 \cdot 10^{-9}$ m respectively. Electrochemical behavior of passive titanium is determined mainly by thickness and properties of the barrier layer. The outer layer has rutile structure, and the barrier layer at elevated temperature consists of anatase. The formation of the barrier layer at potentials of 0.14-1.4 V leads to a significant increase of its protective properties [85].

Anodic oxide films on valve metals are achieved also by imposing pulses of current of various shapes (rectangular, triangular, etc.). In particular, such process was studied on the tantalum and aluminum electrodes during their polarization by sinusoidal pulses of power current [86]. High quality films obtained via oxidation by rectangular and sinusoidal pulses is explained by more uniform distribution of charged particles in the oxide, which provides consistency of electric field intensity.

Severity of discharge influences the time for electrochemical and micro-arc material processing, operating current values, which determine the temperature in the discharge path, and characteristics of coatings such as porosity, hardness, breakdown voltage, etc. Modes of plasma electrolytic oxidation are classified according to the method of discharge formation, which is predetermined by output parameters of the current supply. This expressly affects the beginning and the end of the plasma electrolytic discharge in each half-cycle [83].

The soft mode means natural start of the breakdown of the coating already formed at the time when the electric field intensity at the metal-oxide-electrolyte boundary smoothly, in accordance with the shape of sinusoidal input voltage, reaches its critical value. In hard mode, the initial difference of potentials is admittedly larger than critical, which provides compulsory start of the breakdown. The end of the discharge for soft mode is determined by the capacitance of the condensing power supply and is classified as natural, and for hard mode – by the form of voltage in high power network and is classified as compulsory. In accordance with the terminology, the soft mode provides a natural start and natural end of the discharge, soft-hard – a natural start and compulsory end, hard-soft – compulsory start and natural end, and hard – compulsory start and compulsory end of the discharge.

Therefore, a significant effect on the properties of oxide films, primarily dielectric, is caused by oxidation mode and type of polarizing voltage. Oxidation by alternating current, pulse and step modes intensifies the process and allows you to automate it [87], however, this involves the use of special, rather complicated equipment.

1.2 Synthesis of doped coatings in micro-arc mode

As of today, a fairly large number of methods were suggested for the formation of functional coatings doped with various components, such as transition metal oxides [88, 89], but the vast majority is characterized by high labor intensity and multistage process. A significant problem is also to ensure uniformity of sediments and sufficient adhesion, whereas the plasma electrolytic oxidation method allows for the formation of the oxide matrix substrate and its filling with transition metal oxides in a single stage, which results in achieving high content of dopant, uniformity in composition and thickness, as well as considerable adhesion strength of the coatings [90].

Titanium, as well as other valve metals, is oxidized to produce coatings for various purposes, e.g. for use as catalytically-active layers, corrosion resistant and anti-friction coatings, etc. Directed synthesis of films of a given composition and structure is required to create an effective protective coatings and new materials [91]. Coatings formed in the micro-plasma mode [92] are characterized by biological inertness, radiolucency, corrosion resistance, developed globular structure. It is known that metal oxides are used as catalysts in many industrial processes in gas and liquid media, as electrode materials in electrosynthesis and chemical current supplies, etc. The oxides of non-stoichiometric composition are of particular interest, since the rates of electrochemical and chemical processes rise with an increase in degree of deviation from stoichiometry [93]. In this regard, we will note that the PEO method allows to improve physical and chemical properties of products and to create versatile polyfunctional bio-compatible composite materials while giving them a range of necessary properties: anticorrosive, tribological, bioinert, etc. [94-96], as well as to receive the contact surface of implanted structures with desired structure and thickness. Oxide coatings with a controlled degree of porosity provide a tight connection of the surface of an implant with the superstructure and, as a result, good condition of soft tissues, no gaps between the components [97]. On the other hand, using anode-spark method in aqueous electrolytes with polyphosphates and acetates Zn(II), Mg(II), Ni(II) and Mn(II) on titanium, coatings with biocidal properties were obtained [98], which can be used both in equipment, for protection of products from microflora, and in medicine.

Development of approaches for the formation on metals and alloys of surface structures containing compounds of di-, tri-, multivalent metals, including noble, in a specific ratio is of significant interest for the development of new functional materials used in catalysis, e.g. for processes requiring high thermal conductivity [99].

Using electrochemical treatment in galvanostatic mode of titanium alloys in aqueous solutions based on salts $Zr(SO_4)^2$, $K_2[ZrF_6]$ [100] films comprising zirconium oxide were synthesized, which can be used in the production of catalysts, sorbents, semiconductor devices, sensors, and protective coatings.

As a result of studies, the authors of [101] proposed a method of formation on titanium alloys of molybdenum-containing antifriction layers in the phosphate electrolyte with addition of chlorides. It was shown that the anti-friction properties of the coating are caused by the presence of X-ray amorphous phase consisting of finely divided titanium dioxide modified with molybdenum-, aluminum-, phosphorus-, and hydroxy-containing compounds. The tests of the coatings showed a decrease of the friction coefficient to 0.06-0.16.

During anodic-spark deposition of coatings in molybdate-phosphate electrolytes, coatings are formed with high content of phosphorus and molybdenum, and for treatment of commercial titanium BT1-0 at current density of 0.05 A/cm^2 [102] the use of electrolyte solutions on the basis of $NaH_2PO_4\cdot 2H_2O$, $Na_2HPO_4\cdot 12H_2O$, $Na_2H[PW_{12}O_{42}]\cdot 9H_2O$, $Na_2WO_4\cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ was proposed. Concurrently there is a joint insertion of phosphorus and tungsten into oxide layers. The atomic ratio P/W in the coatings is 1.2-1.6.

The [103] discusses the use of the plasma electrolytic oxidation method to form catalytically-active layers on valve metals. The data [104] was given on the synthesis of manganese, tungsten- and nickel-containing layers on titanium, their composition and catalytic activity in oxidation reaction of carbon oxide (II). During the study of catalytic activity of electrochemically synthesized oxide-hydroxide compounds, in particular manganese, in the reaction of hydrogen peroxide decomposition, it was established that from a number of factors: the composition of compounds, the total electrical conductivity, the proportion of ionic and electronic conductivity, namely the ionic component of conduction, which characterizes deficiency of the compound structure, is a quantitative measure of its catalytic activity.

Using plasma electrolytic oxidation in aqueous electrolytes with polyphosphate complexes Ni(II) and Cu(II), oxide-phosphate layers were formed on titanium [105]. The resulting composition film/Ti show catalytic activity in the oxidation of CO to CO_2.

Using micro-plasma oxidation of aluminum and titanium alloys in aqueous solutions with polyphosphate complexes Ni(II) and Fe(II), oxide-phosphate layers with a thickness of 5-50 μm were synthesized [106]. Studies of elemental and phase compositions found that films on aluminum are composed of $AlPO_4$, $NiAl_2O_4$ and Fe_2O_3, while coatings formed on the titanium are a mixture of the following compounds: $Ni_2P_2O_7$, $Ni_{0,5}TiOPO_4$, $NaTi_2(PO_4)_3$, $M(II)M(III)Ti(PO_4)_3$, $FePO_4$ $Fe_2Fe\ (P_2O_7)_2$.

The introduction to the electrolyte based on sodium tetra-borate of one of admixtures: $KMnO_4$, $Mn(CH_3COO)_2$, $Pb(CH_3COO)_2$, $Pb(NO_3)_2$, $Co_3(PO_4)_2$ and $K_4[Fe(CN)_6]$ makes it possible in power breakdown conditions to form on titanium anode coatings containing, in addition to titanium oxide, compounds of manganese, lead, cobalt or iron [107-109]. Phase and element composition of coatings depends both on the concentration of salt, and on their nature.

For the formation of mixed coatings based on oxides of cobalt, manganese and nickel [110], treatment of titanium electrodes by asymmetrical alternating current is used in aqueous solutions of boric acid and salts of co-deposited metals.

Manganese and its compounds occupy a special place among the catalysts; manganese dioxide is of particularly high interest due to its large number of its varieties, differing in chemical and electrochemical properties and wide use in many industrial processes.

Manganese dioxide has several modifications with different physical properties and oxidation potential, depending on the production method (αMnO_2-cryptomelane, β-MnO_2-pyrolusite, γ-MnO_2- ramsdellite), with the most active being the γ-modification. The structure of manganese dioxide may be layered, spinel-type, amorphous, and tunnel with different channels sizes [111]. Octahedra of MnO_6 are basic structural units of the manganese dioxide of one or the other modification, but oxygen deficit is observed in most types of manganese dioxides (MnO_x where $1.7 < x < 2$) [112]. Furthermore, the total water content in manganese dioxide can vary in a fairly wide range from near zero in high-quality β-MnO_2 to 20-30% in amorphous structures. The most attractive in terms of deficiency and non-stoichiometry is bound water, i.e. groups of OH [113].

One of the most efficient ways of production of manganese oxides on the surface of metal carriers, according to the analysis of scientific and technical information, should be considered an electrochemical oxidation in solutions containing manganese compounds of different oxidation states, which will promote the formation of coatings with strong adhesion to the substrate by mixed non-stoichiometric oxides. For instance, using the anode-spark oxidation in electrolytes with polyphosphate manganese complexes [114], manganese-containing layers of complex chemical composition were synthesized. The results of studies of thermal properties and phase composition of the coatings correspond to representations of incorporation into the oxide layer of electrolyte components due to thermolysis of the sediment, which contains hydrated metal polyphosphates, in near-breakdown areas.

Therefore, the scientific and technical developments in the field of creation of new and improvement of existing technologies of formation of anode-spark layers with predictable properties, especially oxide-mixed coatings, are promising and certainly relevant.

Detailed analysis of processes, which take place during plasma electrolytic oxidation, allows to identify possible ways of optimizing conditions of formation of functional coatings on titanium alloys using kinetics of anodic reactions and test results of functional properties of coatings. The above circumstances determined the purpose of the research – development of technology of coatings with catalytic, anticorrosion, dielectric and anti-friction properties for titanium alloys using a hypothesis about the possibility of the formation of mixed oxide systems in high-energy fields not only by incorporating electrolyte components in the coating composition, but also as a result of thermochemical and intramolecular reactions.

Chapter 2

FORMATION OF COATINGS IN DIPHOSPHATE SOLUTIONS

2.1 Anodic behavior of titanium alloys in diphosphate solutions

The study of the anode behavior of titanium alloys in diphosphate solutions creates the prerequisites for substantiating the composition of electrolytes and plasma-electrolytic oxidation modes during the formation of coatings with the necessary set of properties.

The kinetics of anode processes was studied by linear voltammetry (LVA) method on specially made electrodes of VT1-0 and OT4-1 titanium alloys (Table 2.1) with a working surface of 0.2 - 0.3 cm^2

Table 2.1 – The chemical composition of titanium alloys, mas.%

Alloy	Ti	Fe	C	Si	N	O	Mn	Zr	Impurities
VT1-0	99,2–99,7	<0,25	<0,07	<0,1	<0,04	<0,2	–	–	0,3
OT4-1	94,3–97,5	<0,3	<0,1	<0,12	<0,05	<0,15	0,7–2,0	<0,3	0,3

Analysis of linear voltammetry data is based on the use of the general equation of electrochemical kinetics [115]. Based on it, the instantaneous current of a one-stage electrode process, controlled by the rate of semi-infinite linear diffusion of the reagent to a flat electrode with a constant surface, is determined by the Randles-Shevchik equation [116]

$$I = PzFAcD^{1/2}\left(\frac{zFs}{RT}\right)^{1/2}, \tag{2.1}$$

where ,

P – function $zFst/2RT$,

A – electrode area, sm^2;

c – concentration of electroactive substance, mol/dm^3;

D – diffusion coefficient of electroactive substance, sm^2/s;

s – speed of potential sweep, V/s.

At the peak potential E_p, the function P acquires the maximum value, and the equation of the peak current I_p of the reversible process has the form:

$$I_п = 0{,}446\,\frac{(zF)^{3/2}}{(RT)^{1/2}}\,AD_o^{1/2}s^{1/2}c_o\,. \tag{2.2}$$

The logarithm of equation (2.2) gives the diagnostic criterion of Semerano

$$X_s = \left(\frac{\Delta\lg I_п}{\Delta\lg s}\right)_c, \tag{2.3}$$

its value for reversible processes is close to 0.5, and the ratio $I_p{\cdot}s^{-½}$ does not depend on s. The criterion was calculated from the dependence of the peak current on the concentration:

$$X_c = \left(\frac{\Delta\lg I_п}{\Delta\lg c}\right)_s, \tag{2.4}$$

which for reversible diffusion processes is close to 1, and the ratio I_p/c does not depend on c.

The peak potential E_p for reversible electrochemical reactions does not depend on the potential sweep speed, while the peak and half-peak potentials $E_{1/2}$ are related by ratio:

$$E_п = E_{1/2} - 1{,}11\,\frac{RT}{zF}\,. \tag{2.5}$$

When analyzing the results, it was taken into account that the reversibility of the electrode process is determined by the following criteria:

- E_p does not depend on s;
- the peak of current linearly increases with $s^{½}$, the ratio $I_p{\cdot}s^{-½}$ also does not depend on s, and $X_s = 0{,}5$;
- peak width $E_w = E_{p/2} - E_p$, where $E_{p/2}$ – potential at $I_p/2$, $E_{p/2} = 2{,}218\cdot[RT/(zF)]$;
- the ratio I_p/c does not depend on c in a wide range of concentration, and Xc = 1.

The current of an irreversible process is described by the equation [117]:

$$I = P'z(\alpha z)^{1/2}AD^{1/2}s^{1/2}c\,, \tag{2.7}$$

where P' is the function for the irreversible process, similar to the function P in (2.2), and the peak current and peak potential are found as:

$$I_п = 0{,}496\ zFAc_o D^{1/2}\left(\frac{\alpha zFs}{RT}\right)^{1/2}, \tag{2.8}$$

$$E_п = -1{,}14\frac{RT}{\alpha zF} + \frac{RT}{\alpha zF}\ln\frac{k_s}{D^{1/2}} - \frac{RT}{2\alpha zF}\ln \alpha zs\ . \tag{2.9}$$

The heterogeneous rate constant of the charge transfer stage k_f is related to the peak current and peak potential by the Hochstein equation [118]:

$$k_f = 4{,}35\frac{I_п}{zFcA}\exp\left(\frac{\alpha zF}{RT}E_п\right). \tag{2.10}$$

As for reversible processes, I_p is proportional to $s^{½}$ ($\sqrt{s}$), since $X_s = 0{,}5$.

The product of the transfer coefficient and the number of electrons αz of the irreversible stage can be determined in several ways:
from incline in coordinates E_p–lgI_p, which is $\alpha zF\ /\ 2{,}303\ RT$;

- by the angular coefficient in coordinates E_p– lg$s$

$$\frac{\Delta E_п}{\Delta \lg s} = -\frac{2{,}303\ RT}{\alpha zF}; \tag{2.11}$$

The following criteria were considered grounds for concluding that the electrode process is irreversible (inhibition of the charge transfer stage):

- E_p depends on s, where $E_{p/2} - E_p = 0{,}048/\alpha z$;
- peak potential difference $\Delta E_p = E_{pa} - E_{pк}= 0{,}0295/\alpha z$, increases by 30 mV with increasing s by an order of magnitude;
- other criteria match with characteristics of reversible processes.

Irreversibility of electrode processes, in addition to the inhibition of the charge transfer stage, also determines the preceding, parallel or subsequent chemical reactions. For such cases, the dependence of I_p on $s^{½}$ is nonlinear, the ratio of $I{\cdot}s^{-½}$ decreases with increasing s, and $Xs = 0.5$

The presence of adsorption complications of electrode reactions is detected by characteristic signs:

- adsorption waves are predominantly symmetrical with respect to the peak potential E_p;
- $I_p{\cdot}s^{-½}$ increases with increasing s, and for adsorption of the reagent, the Semerano criterion $X_s = 0{,}5 - 1$;
- at adsorption, the $I_p/cs^{-½}$ ratio rapidly increases with increasing speed of potential sweep, but I_p/cs can remain almost constant;
- the value of the I_p/c ratio increases with decreasing reagent concentration, and at low concentration this value becomes constant;

- at adsorption of the reagent $X_c = 0,5 - 1$; I_p does not depend on c, and I_p/c increases at low concentration;
- at product adsorption, I_p does not depend on c at high concentration.

At low concentration and high potential sweep rates, the contribution of adsorption to the response of the system prevails, while at high concentration and low speeds, the influence of the kinetic factor dominates. An analysis of the totality of the kinetic parameters listed and characteristic diagnostic dependencies is the basis for determining the mechanism of processes in the formation of oxide systems.

Electrochemical studies were carried out by linear voltammetry [119] using a laboratory complex including a PI-50-1.1 potentiostat, a PR-8 programmer and a PC equipped with a board for automatic on-line data recording with a specially developed program for digitizing measurement results. The complex includes a three-electrode cell YaSE-2, a platinum electrode was used as an auxiliary, the potential value was monitored by a silver chloride reference electrode EVL-1M1, which was connected with an electrolytic key filled with thickened agar-agar which is saturated with the solution of potassium chloride. Polarization measurements were carried out on VT1-0 and OT4-1 titanium alloys in the potentiodynamic mode of 1 mol / dm^3 Na_2SO_4 in aqueous solutions of potassium diphosphate of varying concentration (Table 2.2) with a change in the speed of potential sweep in the range of $s = 5\cdot10^{-3} - 10^{-1}$ V/s.

Table 2.2 – Composition of solutions

№ of solution	1	2	3	4
Potassium diphosphate concentration, mol /dm^3	0,001	0,003	0,005	0,01

The anodic polarization dependences (APZ) of VT1-0 and OT 4-1 alloys in a 1 mol/dm^3 Na_2SO_4 solution and with the addition of diphosphate (Fig. 2.1, 2.2) are characterized by an increase in current density with a shift of the potential from a stationary value to a positive region to 0,5 V, which corresponds to the ionization of titanium by:

$$Ti = Ti^{4+} + 4e^{-}. \qquad (2.12)$$

The maximum of polarization dependency corresponds to the beginning of the process of passivation of the titanium surface due to the formation of a phase oxide film, as it is observed for aluminum [120]. Under ordinary conditions, during anodic polarization in oxidizing media (neutral, weakly acidic, slightly alkaline), titanium oxidizes mainly to TiO:

$$Ti + H_2O \rightarrow TiO + 2H^{+} + 2e^{-}. \qquad (2.13)$$

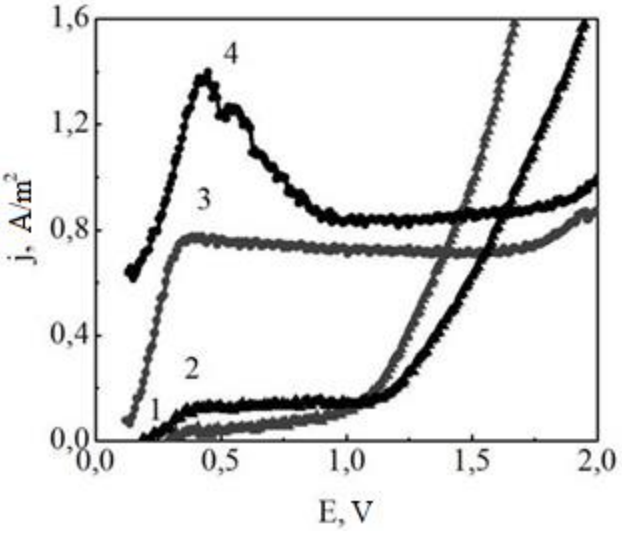


Figure 2.1 – Anodepolarization dependencies of alloys VT1-0 (1, 2) and OT4-1 (3, 4) in a background solution of 1 M Na_2SO_4 (1, 3) and with addition of 0,001 M $K_4P_2O_7$ (2, 4).
Potential sweep speeds $s = 1 \cdot 10^{-2}$ B/c.

At potentials up to 2 V, films of mixed $Ti_2O_3{\cdot}nTiO_2$ oxides are formed on the surface of titanium alloys, where $n = 3 – 4$, with the predominance of Ti_5O_9 and Ti_6O_{11} oxides. At more positive potentials, the composition and structure of oxide films changes due to the formation of higher titanium oxide:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-. \tag{2.14}$$

Addition of diphosphate leads to the appearance of a peak in the polarization dependence of the OT4-1 alloy and a twofold increase in the peak current, however, it practically does not change the anode polarization dependencies (APD) shape of the VT1-0 alloy. This behavior of the OT4-1 titanium alloy can be explained by the presence of alloying components in its composition, in particular manganese, which oxidizes in dilute diphosphate solutions to form oxoanions. As a result of hydrolysis of a weak anion of a polybasic acid $P_2O_7^{4-}$:

$$P_2O_7^{4-} + H_2O \leftrightarrow HP_2O_7^{3-} + OH^-,$$

alkalization of the electrolyte occurs, which facilitates the oxidation of manganese, the content of which in the OT4-1 alloy is significantly higher compared to VT1-0. Reactions with its participation proceed stepwise in solutions of different acidity, but when the medium is alkalized, the values of redox potentials decrease, and the oxidation rate increases, respectively:

$$\begin{aligned}
&\mathrm{Mn} + 2\mathrm{OH}^- \rightarrow \mathrm{Mn(OH)}_2 + 2e, \quad E^0 = -1{,}55 \quad \mathrm{B};\\
&\mathrm{Mn} \rightarrow \mathrm{Mn}^{2+} + 2e, \quad E^0 = -1{,}18 \quad \mathrm{B};\\
&\mathrm{Mn(OH)}_2 + 6\mathrm{OH}^- \rightarrow \mathrm{MnO}_4^- + 4\mathrm{H}_2\mathrm{O} + 5e, \quad E^0 = 0{,}34 \quad \mathrm{B};\\
&\mathrm{Mn}^{2+} + 4\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{MnO}_4^- + 8\mathrm{H}^+ + 5e, \quad E^0 = 1{,}51 \quad \mathrm{B}.
\end{aligned} \tag{2.15}$$

With an increase in the diphosphate concentration to 0.01 mol/dm^3 (Fig. 2.2), the oxidation current density of the VT1-0 alloy increases, while the APD of the OT4-1 alloy is characterized by a decrease in current and the degeneracy of the peak in the wave. This behavior of the alloys can be explained by two reasons: firstly, with an increase in the diphosphate concentration by an order of magnitude, the degree of hydrolysis decreases by at least three times and, accordingly, the pH of the electrolyte decreases, as a result of which the rate of formation of soluble manganate (VII) ions decreases

The second reason is the competition between oxidation reactions to oxo compounds of different solubilities (2.13 - 2.15) and cations of alloying elements M^{2+} (M = Fe, Mn). The latter, with a local excess of the solubility product at higher concentration of diphosphate in the near-electrode layer, can form $M_2P_2O_7$ precipitates. These processes lead to the passivation of the manganese-containing alloy OT4-1 [121], while the oxidation rate of VT1-0 increases. To establish the kinetics of electrode processes during anodic polarization of titanium in the studied electrolytes (Table 2.2), it is advisable to use an algorithm for the analysis of polarization dependences, which is based on determining the characteristic parameters of electrochemical reactions.

The transfer coefficient and the effective number of electrons in the limiting stage of the anodic process αz are determined by the results of one measurement from the equation of S. Matsuda and I. Ayabe:

$$E_{\text{п}} - E_{1/2} = -1{,}85\,\frac{RT}{\alpha z F}\,. \qquad (2.15)$$

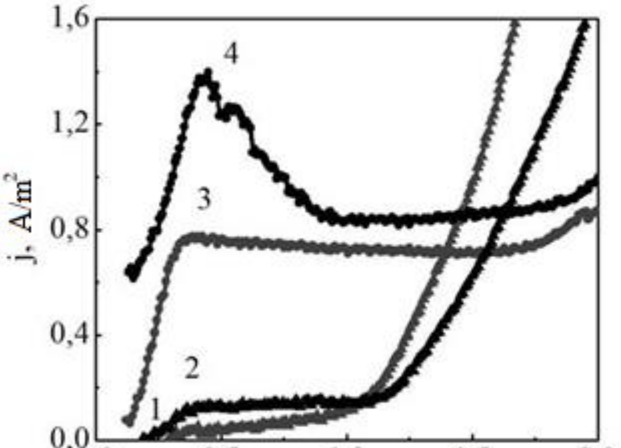


Figure 2.2 - Anodepolarization dependenciesalloys VT1-0 (1, 2) and OT4-1 (4, 3) at background of 1 M Na_2SO_4 at concentration $K_4P_2O_7$, M: 0,001 (1, 4) и 0,01 (2, 3). Potential sweep speed $s = 1 \cdot 10^{-2}$ V/s.

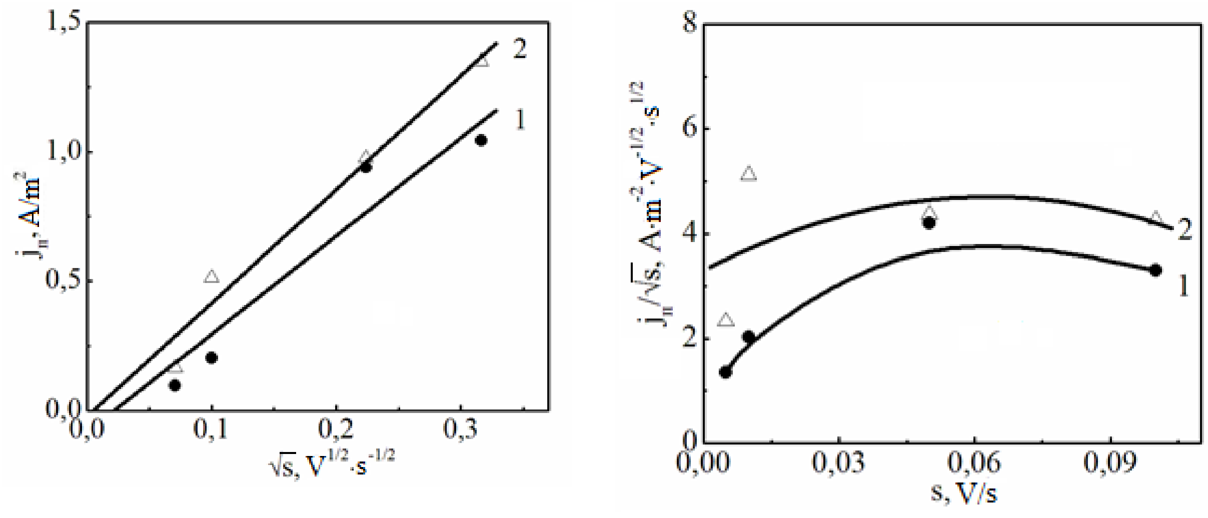
The speed constants calculated by the Y. Gokhshtein equation (2.10) for the heterogeneous oxidation reaction of VT1-0 and OT4-1 alloys in an electrolyte with a potassium diphosphate concentration of 0.01 mol/dm^3 at a potential sweep speed of 10^{-1} V / s do not differ significantly (Table 2.3) The order of their values, according to the classification of processes proposed by I. Ayabe and S. Matsuda, taking into account the dependence of k_s on s, characterizes the process under consideration as irreversible with a limiting stage of electron transfer.

Table 2.3 - Reaction speed constants k_s (cm/s) of the anodeoxidation of titanium alloys in solutions of 1M Na_2SO_4 and diphosphateat various s (V / s)

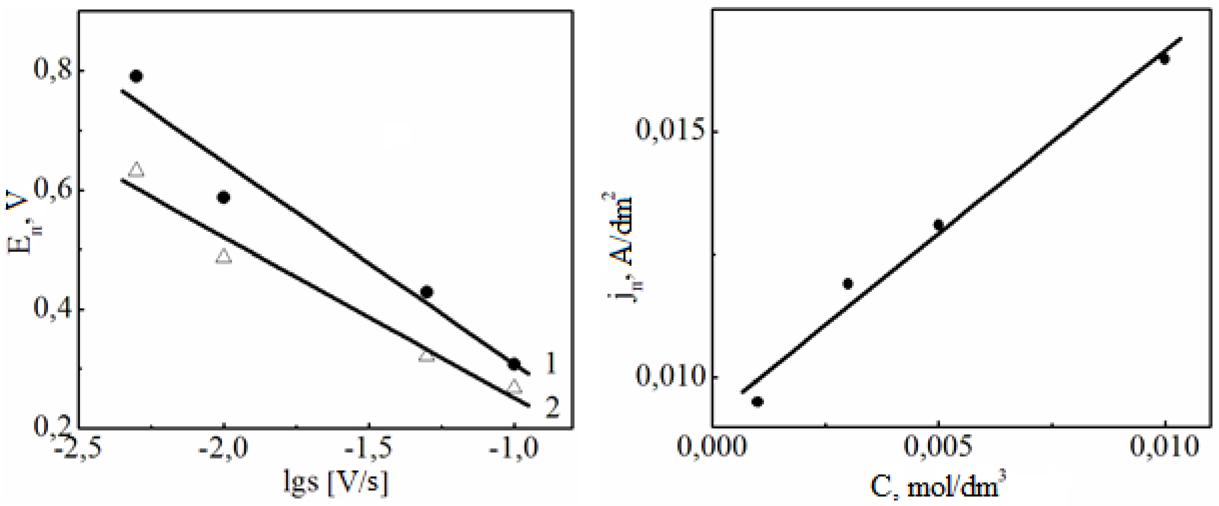
Material of electrode	Concentration of $K_4P_2O_7$, mol/dm^3			
	0,01		0,001	
	s=10^{-1}	s=5·10^{-3}	s=10^{-1} V/s	s=5·10^{-3} V/s
VT1-0	$5{,}39\cdot10^{-9}$	$1{,}40\cdot10^{-6}$	$3{,}32\cdot10^{-6}$	$1{,}04\cdot10^{-7}$
OT4-1	$5{,}61\cdot10^{-9}$	$1{,}65\cdot10^{-6}$	$5{,}98\cdot10^{-6}$	$4{,}33\cdot10^{-7}$

At a low potential sweep speed of 5×10^{-3} V / s, the value of k_s for both alloys increases by almost three orders of magnitude (Table 2.3), which indicates an increase in the oxidation rate, but does not change the characteristics of the process as irreversible with a limiting charge transfer stage. At a low potassium diphosphate concentration of 0.001 mol/dm^3, an inversion of the dependence of k_s on the potential sweep speed is observed. It should be noted that for s=10^{-1} V/s in a dilute diphosphate solution, the oxidation speed constants of both alloys increase by three orders of magnitude compared to the more concentrated, while at s = 5 · 10^{-3}, the value of k_s is practically independent of diphosphate concentration (Table 2.3). This character of the dependences of ks on s and c ($K_4P_2O_7$)) indicates a significant contribution of diphosphate adsorption to the electrode process and confirms the passivation of the metal.

The concentration criterion X_c for VT1-0 alloy in electrolyte solutions 1 and 4 (Table 2.2) are 0.4 and 0.63, respectively, and for OT4-1 X_c alloy it is slightly higher and amounts to 0.46 and 0.65, which confirms the irreversible nature of the anodic oxidation of titanium and the enhanced contribution of adsorption at a higher concentration of potassium diphosphate. Based on the data obtained, it can be assumed that in concentrated solutions the probability of incorporation of phosphorus compounds in the oxide coating increases.

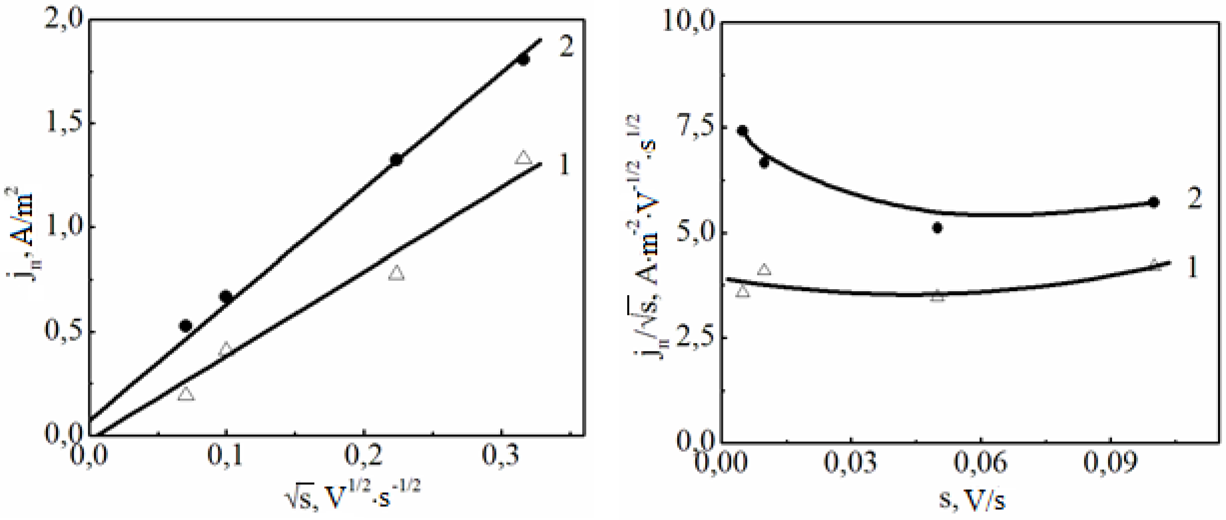


a *b*

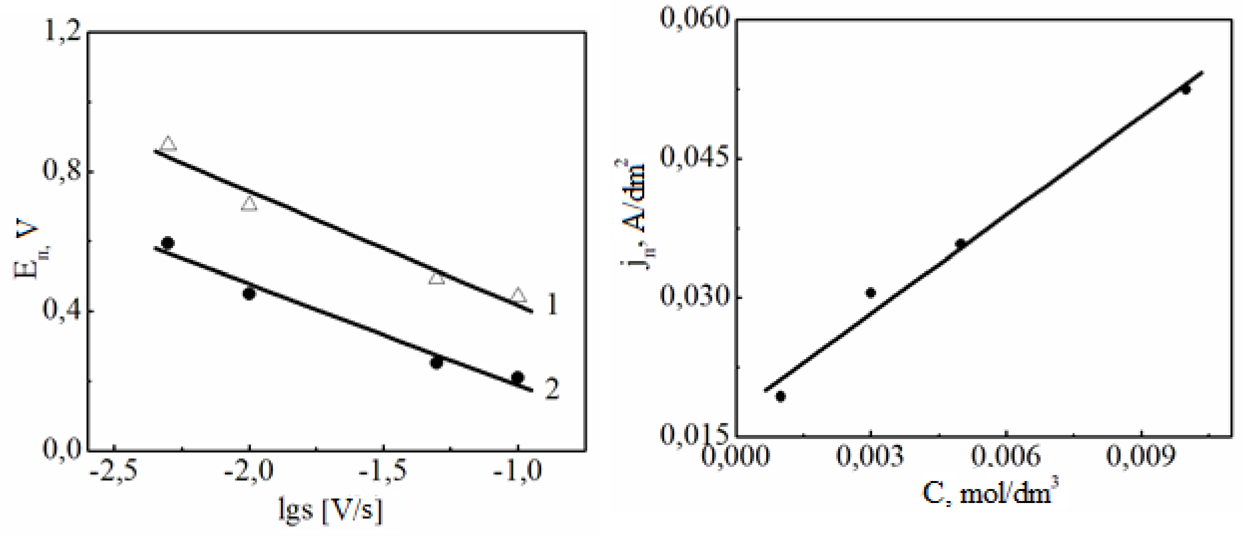


c *d*

Figure 2.3 - Dependence of peak current density j_p (*a*), characteristic criterion $j_p/\sqrt{s}$ (b), peak potential E_p (c) of VT1-0 alloy on speed potential scans at the background of 1 mol/dm^3 Na_2SO_4 at a concentration of $K_4P_2O_7$, mol / dm^3: 0.001 (1); 0.01 (2); j_p on the concentration of $K_4P_2O_7$ (d) at s = $5 \cdot 10^{-3}$ V/s



a *b*



c *d*

Figure 2.4 - Dependences of the peak current density j_p (*a*), the characteristic criterion $j_p/\sqrt{s}$ (b), the peak potential E_p (*в*) of the OT4-1 titanium alloy on the potential sweep speed at the background of 1 mol/dm^3 Na_2SO_4 at a concentration of $K_4P_2O_7$, mol/dm^3: 0.001 (1); 0.01 (2); dependence of j_p on the concentration of $K_4P_2O_7$ (d) at s =$5 \cdot 10^{-3}$ V/s

Additional information on the mechanism of the anodic oxidation of titanium alloys in solutions with a variable concentration of diphosphates was obtained from the analysis of the characteristic dependences (Fig. 2.3, 2.4) of the change in current density (j_p) and peak potential (E_p) on the potential sweep speed (s) and concentration $K_4P_2O_7$ (c). An increase in jp with increasing s, the nature of the dependences $j_p/\sqrt{s}$ - s and E_p – lg$s$, confirm that the anode process is limited by the stage of charge transfer. Dependences j_p - s for both VT1-0 and OT4-1 alloys are linear and go from the origin, which indicates the occurrence of irreversible redox processes. The linearization of the dependence of the peak potential on the potential sweep speed in the coordinates E_p – lg$s$ for both alloys indicates the formation of a phase oxide on the electrode surface.

Thus, the analysis of the APZ of titanium alloys allows us to conclude that the OT4-1 oxidation rate is higher than that of VT1-0 in dilute diphosphate solutions, which is associated with the presence of manganese in the OT4-1 composition and greater alloy heterogeneity. An increase in the concentration of diphosphate in the electrolyte leads to the passivation of the OT4-1 alloy, while the anodic behavior of the VT1-0 alloy remains virtually unchanged, especially at low polarization rates.

2.2 Plasma electrolytic oxidation

Oxide coatings were formed on rectangular plates of various sizes and thicknesses, which were pretreated according to the standard procedure [122], including mechanical cleaning of technological impurities, degreasing, etching and washing with distilled water.

Solutions for preliminary surface preparation, working electrolytes for the oxidation and synthesis of coatings with mixed oxides were prepared from certified reagents of the “KhCh” and “ChDA” brands (Table 2.4) in distilled water. The pH control of electrolytes was carried out using a pH meter of pH-150 M grade. The pH values of working solutions of potassium diphosphate with concentration of 0.5 - 1.0 mol/dm^3 are in the range of 9.0 - 9.2.

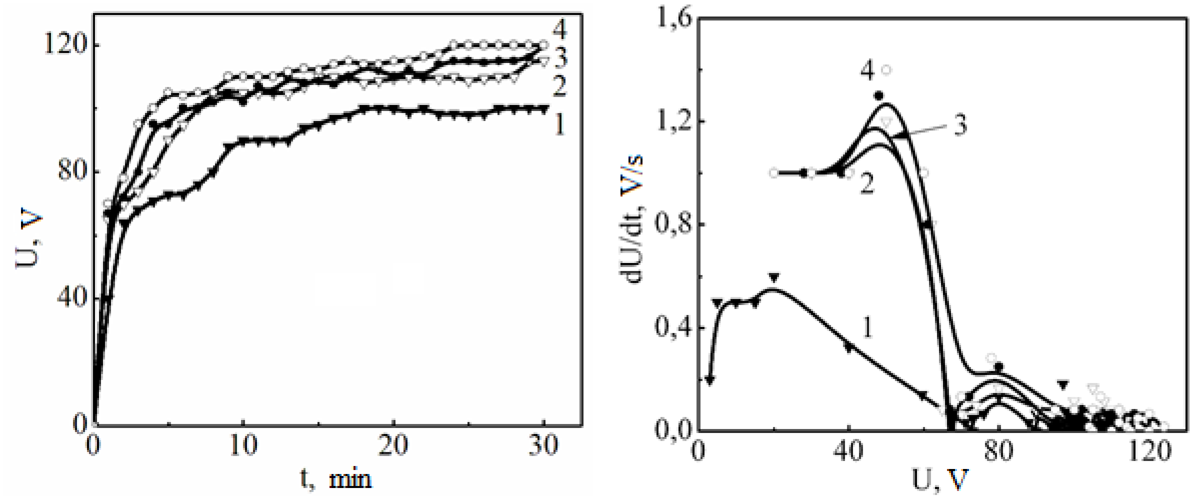
Table 2.4 – The composition of solutions for processing titanium alloys

The purpose of the solution	Reagent	Concentration ranges, mol/dm^3	Remark
Degreasing	NaOH or $Na_2CO_3 \cdot 7H_2O$	0,2 – 0,3 0,1 – 0,3	Electrode pretreatment
Etching	HF HNO_3	0,1 – 0,3 0,3 – 0,9	Electrode pretreatment
Oxidation	$K_4P_2O_7$	0,1 – 1,0	PEO coating formation

Plasma-electrolytic oxidation of titanium alloys was carried out in the galvanostatic mode using a stabilized DC source B5-50. The current density varied between 1 - 5 A/dm^2, the processing time was 30-60 minutes. To mix solutions and ensure their constant temperature (electrolyte temperature should not exceed 25 °C), an MM-5 magnetic stirrer was used.

Chronograms of voltage during the plasma-electrolytic oxidation of titanium alloys (Fig. 2.5) for all studied electrolytes have a classic look with the division into three characteristic areas: pre-spark, sparking zone and microarc discharges. Dependencies corresponding to the pre-spark region of coating formation are almost linear, which is explained by an increase in the film thickness and, accordingly, an increase in its resistance. The time before sparking in all the studied electrolytes is 1–2 minutes in the range of current densities of 2.5–5.0 A/dm^2, and with an increase in the density of the oxidation current, the rate of change of voltage dU/dt, the sparking voltage U_s and and the final voltage U_f of the molding process.

The oxide films formed in the electrolyte based on potassium diphosphate in the pre-spark region have a light gray color which is characteristic of titanium (IV) oxide. This assumption does not contradict the data of [123], according to which TiO_2 modifications of rutile are formed in the pre-spark region in phosphate-containing electrolytes on titanium [124].



a *b*

Figure 2.5 - Chronograms of the molding voltage of the VT1-0 alloy in 1 M $K_4P_2O_7$ (a) and voltage’s rate of change d*U*/d*t* (b) at current densities *j*, A/dm^2: 1 (1), 2.5 (2), 4 (3), 5 (4)

An analysis of the phase composition and structure of the synthesized oxide coatings was carried out using a DRON-2.0 X-ray diffractometer in the radiation of an iron anode. X-ray diffraction patterns were recorded in discrete mode with an interval of 0.1 ° with an exposure at each point of 15–20 s. According to the results of the analysis, it was found that the coatings include a mixture of titanium oxides: Ti_3O TiO_2, TiO, Ti_3O_5, and also the inclusion of the $Ti(HPO_4)_2$ phase.

The dependence in voltage's rate of change (Fig. 2.5 b) on the voltage d*U*/d*t* – *U* has a classical character. In the pre-spark region, d*U*/d*t* is constant, but increases with increasing current density. In the sparking region, voltage’s rate of change increases, and higher the current density, greater the increase in d*U*/d*t*. Since sparking is accompanied by a local increase in temperature in the breakdown zone of phase oxide according to [124] to 700–2000 ºC, it becomes possible for thermolysis of water to occur with evolution of oxygen, the bubbles of which shield the surface. In addition, thermal decomposition of the electrolyte components occurs and their inclusion in the conversion layer, as well as “healing” of coating defects due to remelting of the mineral phase of the electrolyte, which leads to an increase in dU / dt. Upon reaching a voltage of U = 60 V, its rate of change decreases, then it again increases and a second maximum is observed at U = 80 V. This nature of the dependence is explained by the randomization of the formation and dissolution of oxides. The transition to the microarc region is characterized by a sharp decrease in dU / dt and its further fluctuations, which may be due to the contribution of the following factors:

- the nature and mechanism of the reactions occurring on the anode changes;
- gas evolution and surface heating in the zones of sparking reduces the current efficiency of the process;
- under microarc discharges, the fraction of ionic decreases and the fraction of electron current increases;

- the parameters of the oxide coating are changed due to the inclusion of electrolyte components in its composition.

All of the above factors indicate the instability of the oxidation process in the microarc region, as a result of which, obviously, fluctuations in the value of dU/dt arise.

In the pre-spark region, the increase in the thickness of the oxide layer and the rate of change in the voltage of the plasma electrolytic oxidation process in the galvanostatic mode can be determined from the equations [125]:

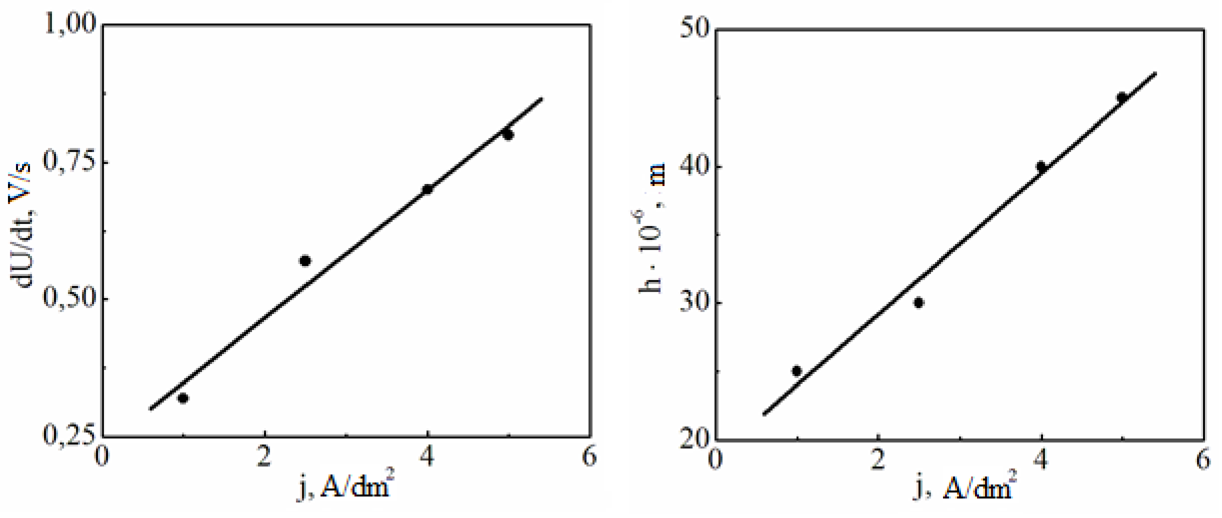
$$\frac{dh}{dt} = \lambda \frac{M}{z\rho F} j, \tag{2.16}$$

$$\frac{dU}{dt} = \lambda \frac{M}{z\rho F} E_g j, \tag{2.17}$$

where λ is the molding efficiency, which is defined as the ratio of the ion current to the total current passing through the system;

M – molar massof oxide, kg/mol;
ρ – oxide density, kg/m^3;
z – the number of electrons involved in the reaction;
F – Faraday number;
E_g – field strength in the coating, V/m;
j – molding current density A/m^2.

The dependence of the thickness of oxide coatings and voltage's rate of change linearly depends on the current density (Fig. 2.6) in full accordance with (2.16, 2.17).



a *b*

Figure 2.6 - Dependence of voltage's rate of change (a) and thickness (b) on the current density of the formation of oxide coatings on VT1-0 alloy in a 1M $K_4P_2O_7$ solution

The angular coefficient $1/j\cdot dU/dt$ reflects the mechanism of the formation of a new phase under changing electrolysis conditions and can be defined as the slope $dU/dt, j$ - dependence. Taking into account the parameter values $z = 4$, $M = 84\cdot10^{-3}$ kg/mol; $\rho = 4{,}26\cdot10^{3}$ kg/m^3, coefficient $1/j \cdot dU/dt = 3{,}50\cdot10^{-3}$ V·s^{-1}·A^{-1}·m^2, assuming that the molding efficiency λ is close to 100% since the electrolyte practically does not dissolve the oxide layer, the field strength in oxide films in the pre-spark region $E_g = 6{,}85\cdot10^{7}$ V / m was calculated by equation (2.17). It turned out that for oxide coatings on titanium this value is approximately an order of magnitude lower than for alumina ($E_g = 2{,}4\cdot10^{8}$ V/m [126]), which indicates the formation of titanium (IV) oxide in the pre-spark region, whose resistance , according to [127], is an order of magnitude lower than aluminum oxide.

The field strength in the formed films at the end of the oxidation process $E_{gк}$ is calculated as:

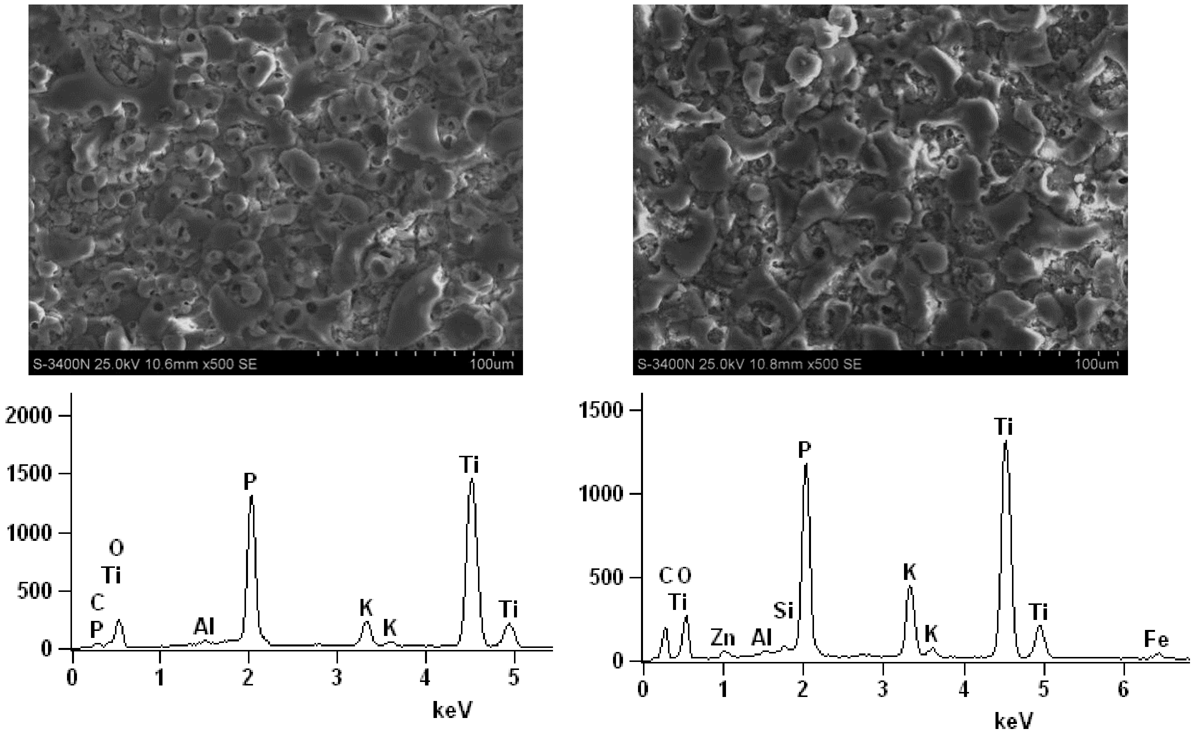
$$E_{gк(K)} = \frac{U_к}{h}, \tag{2.18}$$

where $U_к$ is the final voltage of the formation, V; h - coating thickness.

The field strength in PEO coatings with a thickness of 45 μm, the final molding voltage of which is 120 V, turned out to be $2.67 \cdot 10^{6}$ V/m, and a decrease in the indicated value of $E_{gк}$ is observed with increasing thickness of the oxide coating. This behavior is due to the coating formation mechanism (polarization features, the appearance of space charges, regions with different types of conductivity, etc.), as well as the heating of the oxide film, as a result of which the conditions for the appearance and occurrence of discharge phenomena change.

The elemental composition of the coatings was determined by the X-ray fluorescence method using the Sprutt portable X-ray universal technical spectrometer with a relative standard deviation of 10^{-3}–10^{-2}. To study the surface of the samples, a ZEISS EVO 40XVP scanning electron microscope was used. The surface image of the samples was obtained by recording secondary electrons by scanning the surface with an electron beam, which made it possible to study the surface topography with high resolution and contrast [128]. Photographs of the surface were obtained at magnifications of 100-10,000 times. For image processing, the SmartSEM software environment was used. The chemical composition of the surface was determined by analyzing the characteristic X-ray spectrum, which was recorded using an INCA Energy 350 energy-dispersive spectrometer (Fig. 2.7).

X-ray radiation was excited by irradiating the samples with an electron beam with an energy of 15 kV. Visual analysis of the surface of the coatings was carried out using an optical microscope brand MBS-9 at a 15-times magnifications. X-ray microanalysis and scanning electron microscopy data indicate that, in addition to TiO_2, electrolyte component melts are included in the coating composition. The coatings are characterized by a globular structure, with titanium oxide predominating in the pores, and phosphorus and potassium oxides prevailing on toroidal structures. Particular attention should be paid to the fact that the coating on the OT4-1 alloy has a more pronounced relief structure, lower porosity and contains trace amounts of alloying components.



The content of elements excluding oxygen, at.%:

Ti – 56,15; P – 34,0; K – 9,35; Al – 0,5

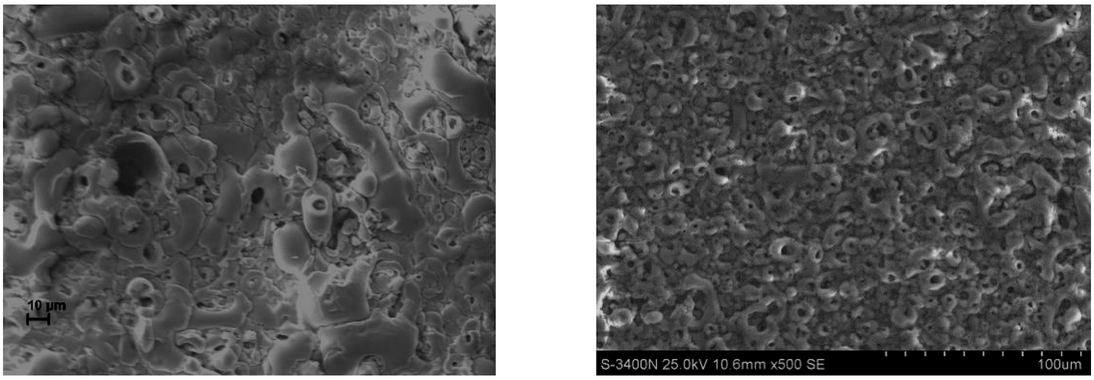
Ti – 50,72; P – 33,76; K – 11,37;
Al – 0,24; Si – 0,83; Fe – 2,06; Zn – 1,02

а *б*

Figure 2.7 - Morphology and composition of coatings on VT1-0 (a) and OT4-1 (b) alloys obtained by PEO in a 1 M $K_4P_2O_7$ solution at j = 4 A/dm^2. x1500 magnification

Taking into account the amount of oxygen, we can assume that coatings containing TiO_2, P_2O_5 и K_2O oxides in the ratio 6: 2: 1 are formed on the surface of the VT1-0 alloy. A sufficiently high content of phosphorus oxide in the coatings creates the prerequisites for their use as a protective layer of implants [129].

Thermal treatment of samples with coatings at 450 ºC for 6 hours promotes crystallization and revealing the anatase structure, while the ratio of components in the coating remains almost unchanged (Fig. 2.8 *a*). A decrease in the oxidation current density to 1 A/dm^2 promotes the formation of a more uniform microglobular structure (Fig. 2.8 *b*), which includes a mixture of fine needle grains, an increase in the content of titanium oxide in the surface layer and a decrease in potassium inclusions, while the phosphorus concentration remains unchanged. When diluting the potassium diphosphate solution, the final oxidation stress and the thickness of the coatings formed over the same period of time naturally increase (Table 2.5). Naturally, the coating thickness depends on the molding current density and increases linearly with the growth of the latter (Fig. 2.6).



a *б*

Ti – 55,68; P – 34,85; K – 9,37; Al – 0,1 Ti – 61,39; P – 34,86; K – 3,75

a – *j* = 4 A/dm^2 followed byannealing; *b* - *j* = 1 A/dm^2. X1500 magnification

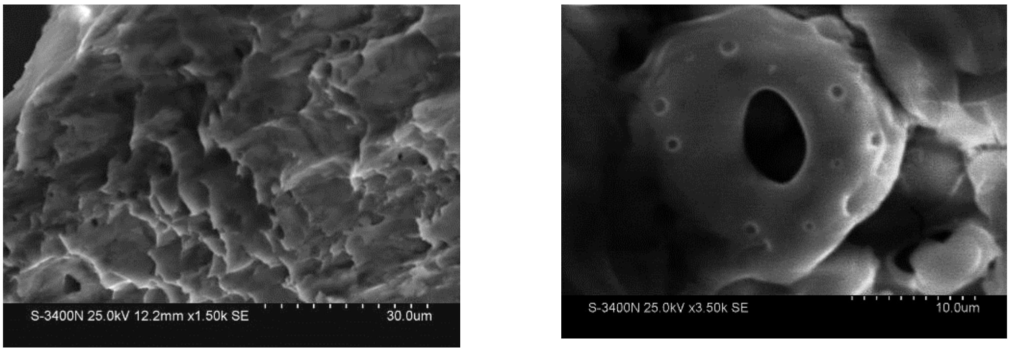
Figure 2.8 - Morphology and composition of coatings on VT1-0 alloy obtained by PEO in a solution of 1 M $K_4P_2O_7$:

Table 2.5 -The influence of the concentration of diphosphate on indicators of PEO of titanium alloys (current density 2 A/dm^2, time 30 minutes)

№	Diphosphate concentration, mol / dm^3	Final voltage molding, V	Coating thickness, μm
1	1,0	110	20
2	0,5	140	40
3	0,1	170	55

Thus, by varying the concentration of potassium diphosphate in the electrolyte, the current density and the time of PEO, oxide coatings of a given composition, morphology, and thickness can be obtained on titanium alloys.

Particular interest in plasma-electrolytic coatings on titanium is due to the prospects of their use for implants, which puts forward serious requirements for biocompatibility, non-toxicity of the surface layers, and adhesive stability. In addition, it is necessary to create such a surface relief that would ensure minimal friction and damage to bone tissue at a maximum rate of growth of biological tissues [129]. The electrolyte compositions and electrolysis modes tested in this work allow the formation of coatings that satisfy all of the above criteria. High adhesion of the oxide layer to the titanium surface, provided by the synthesis modes, is confirmed by the results of fingerprint analysis of sections. The viscous failure observed along the shear line (Fig. 2.9 a) indicates strong adhesion of the oxide layer to the base and stability of the Ti | Ti_nO_m, which will prevent fragmentation of the implant.



a *b*

Figure 2.9 - Micrographs of the cross-section (a) and grain (b) of Ti_nO_m PEO coatings

The microstructure of the formed layer is a collection of large rounded grains with evenly distributed pores, sometimes filled with small grains or a mixture of needle grains (Fig. 2.9 b). It is the rounded grains that provide good glide on the surface, which is extremely important, in particular, for hip joint implants, and appear to be such a relief that provides maximum compatibility with biostructures.

2.3 Functional properties of metal oxide systems Ti | Ti_nO_m

The mechanical strength and wear resistance of parts made of titanium alloys can be significantly improved by applying oxide coatings that are resistant to abrasion. Strength properties depend not only on the composition of the substrate, but are mainly determined by the thickness, composition and structure of the coating.

The abrasion rate of materials $\Delta l/\Delta t$ was determined by the *Callotte* method [130] by the depth of coating damage l for a period t during which an imprint, the so-called *Callotte* ring, remains on the surface of the samples. The testing technique consists in the continuous rolling of a spherical steel ball with a diameter of d 30 mm with a constant force on the surface of the sample (Fig. 2.10). For testing hard and superhard materials, the steel ball is additionally coated with abrasive diamond paste. The damage depth is determined by the geometric dimensions a and b of the ring::

$$l = (a \cdot b)/d. \tag{2.19}$$

The assessment of the microhardness of coatings with complex oxides is methodologically difficult due to the features of their relief and uneven surface. Naturally, high mechanical characteristics are determined by the significant thickness of the coatings, which depends on the density of the anode current (Fig. 2.6) and is proportional to the final molding voltage.

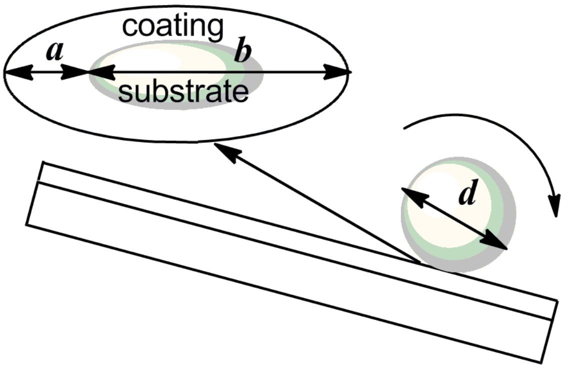


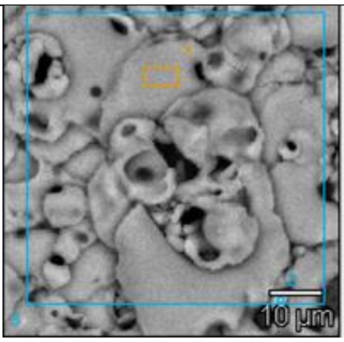
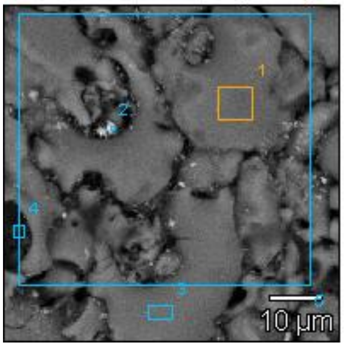
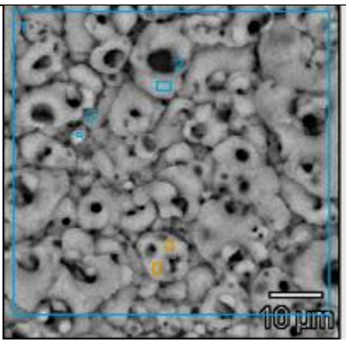
Figure 2.10 - The scheme for determining the speed of abrasive wear according to the *Callotte* method

However, to a greater extent, wear resistance is ensured by the composition of the coatings, namely, the presence of oxide layers on the surface. As a result of this, as follows from Table 2.6, with an increase in the content of titanium oxides in the composition of coatings with mixed oxides, the rate $\Delta l/\Delta t$ decreases. In addition, PEO coatings may contain remelted electrolyte components that form a glassy structure. As the analysis of the distribution of the main components over the coating thickness (Fig. 2.11) showed, the surface is enriched with oxygen and phosphorus, and when moving deeper into the coating to the oxide - metal interface, the titanium atomic fraction increases. Naturally, the composition of titanium oxides TiO_x also changes in the direction of decreasing stoichiometric index x.

It is difficult to reveal an unambiguous relationship between the content of electrolyte components in the coatings and their mechanical properties, since coatings of a similar composition have different wear rates $\Delta l/\Delta t$. It can be assumed that one of the main factors ensuring a high level of mechanical properties of coatings, in addition to their composition and structure, is the surface morphology (Table 2.6).

The nature of the surface, of course, depends on the composition of the electrolyte and the molding conditions. The decrease in grain size and the formation of the microglobular structure of oxide systems contributes to an increase in abrasion resistance, as is observed for coating 3 (Table 2.6). It is also obvious that a decrease in the potassium content in the coating at a higher concentration of titanium and phosphorus oxides leads to a decrease in the rate of abrasive wear. Oxide systems of more advanced morphology also have higher mechanical characteristics.

Table 2.6 - the Resistance of oxide coatings to abrasive wear. Electrolyte 1 M $K_4P_2O_7$, PEO time 30 minutes

№	Surface morphology and molding modes	The composition of the coating on various surface areas, at.% (excluding oxygen)	Abrasive wear rate $\Delta l/\Delta t$, μm/h
1	 j = 5 А/дм^2; $U_\text{к}$ = 115 V	**1** Ti – 56,71; P – 37,04; K – 6,25	2,50
		2 Ti – 54,44; P – 32,01; K – 13,55	
		3 Ti – 58,34; P – 33,09; K – 8,57	
2	 j = 2,5; $U_\text{к}$ = 110 V	**1** Ti – 53,21; P – 32,71; K – 14,08	1,05
		3 Ti – 48,16; P – 35,81; K – 16,03	
		5 Ti – 52,17; P – 33,76; K – 14,07	
3	 j = 1,5 A/dm^2; $U_\text{к}$ = 95 V	**1** Ti – 60,72; P – 34,28; K – 5,0	0,45
		2 Ti – 53,48; P – 38,55; K – 7,98	
		3 Ti – 63,74; P – 33,96; K – 2,30	

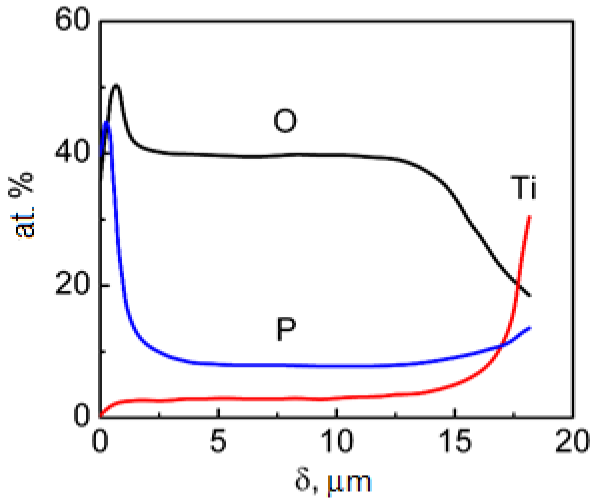


Figure 2.11 - Distribution of the main components by coating thickness (Fig. 2.8 b).Mark 0 corresponds to coating surfaces

Corrosion of titanium in the presence of Cl⁻-ions proceeds with mixed depolarization and is characterized by staged anodic and cathodic reactions. The anode process includes the adsorption and sequential oxidation of titanium to Ti^{3+}:

$$Ti + H_2O \leftrightarrow (TiOH)_{адс} + H^+ + e,\ (TiOH)_{адс} \leftrightarrow (TiOH)_{адс}^{\ +} + e,$$
$$(TiOH)_{адс}^{\ +} \leftrightarrow (TiOH)_{адс}^{\ 2+} + e,\ (TiOH)_{адс}^{\ 2+} + H^+ \leftrightarrow Ti^{3+} + H_2O,$$

moreover, the role of Cl^--ions is led to the depassivation of the anode sites.

Oxygen depolarization prevails in neutral and alkaline environments:

$$O_2 + 2H_2O + 4e \leftrightarrow 4OH^-,$$

however, there is a non-zero probability of a hydrogen recovery reaction:

$$2H_2O + 2e \rightarrow H_2 + 2OH^-.$$

With local alkalization of the cathode sections on the metal surface, there is a danger of chemical destruction of oxide coatings, the protective ability of which decreases in the presence of activator ions.

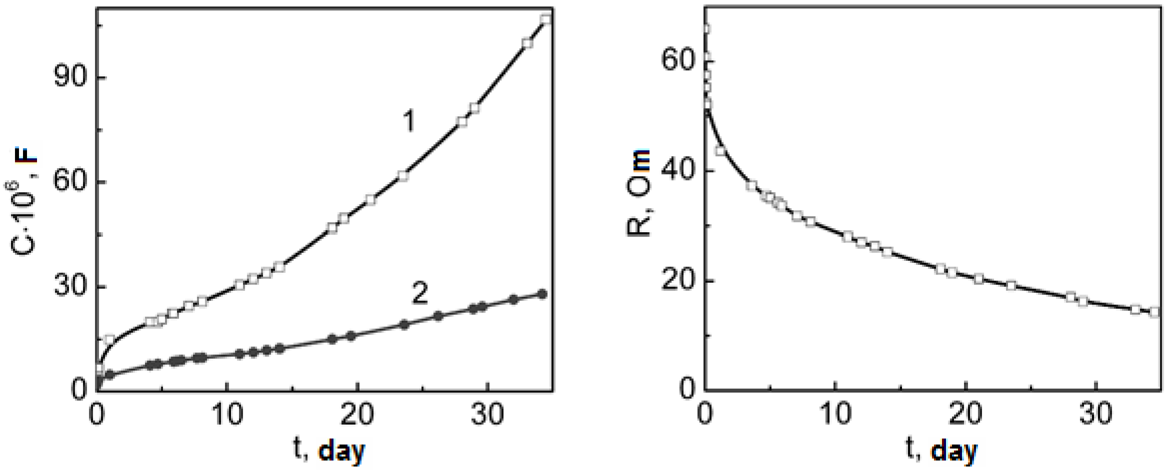
The corrosion behavior of alloys with oxide coatings was studied by the method of impedance spectroscopy using an R-5083 automatic alternating current bridge at two frequencies of 1 and 10 kHz and in the frequency range $20–1{\cdot}10^5$ Hz [131]. Measurements according to the serial scheme were carried out using auxiliary electrodes — a coaxially located platinum grid or coplanar plates made of X18H10T stainless steel. The dynamics of the corrosion potentials of PEO coatings in Ringer's solution (0,15 M NaCl; 0,004 M KCl; 0,004 M $CaCl_2$) [130], simulating biological media, as well as a 2M NaOH solution was determined using a B7-35 high-resistance digital voltmeter.

Potentiometric measurements (Table 2.7) indicate a high corrosion resistance of materials in alkaline media and in the presence of activator ions. Positive values of corrosion potentials indicate a passive state of the system, which is especially important if we take into account that traditional titanium oxides are chemically unstable in alkalis and chloride-containing environments. It is obvious that coatings formed from diluted electrolytes are characterized by higher anticorrosion properties, due to a decrease in porosity as a result of an increase in molding stress and coating thickness (see Table 2.5).

Table 2.7 – Corrosion potential of PEO coatings Ti_nO_m

The concentration of $K_4P_2O_7$ in the molding electrolyte, mol/dm^3	Corrosion potential, V	
	2M NaOH	Ringer's solution
0,1	0,43	0,12
0,5	0,41	0,07
1	0,39	0,06

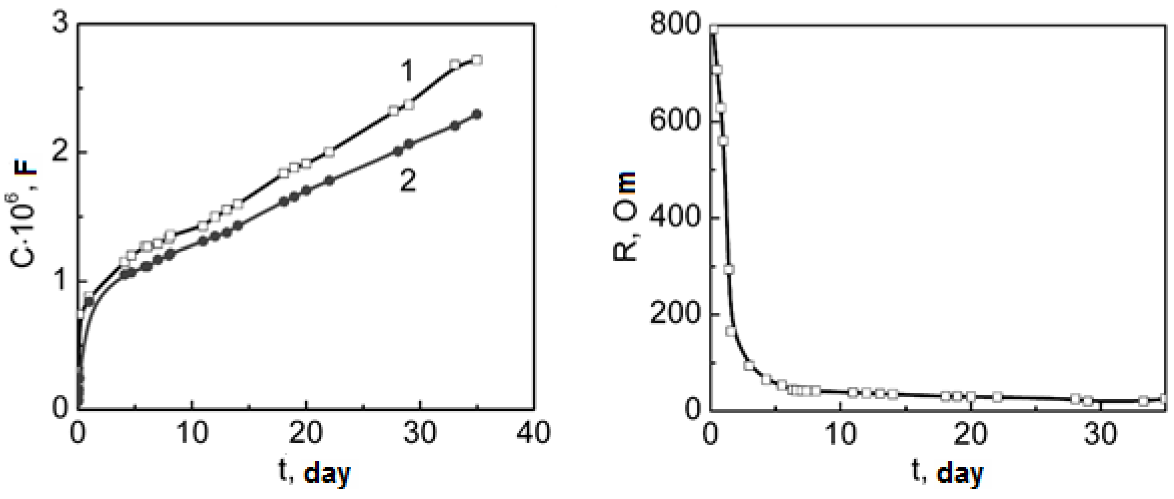
A comparison of the chronograms of the capacitance and resistance of samples with coatings obtained by traditional oxidation (Fig. 2.12) and PEO systems (Fig. 2.13) unambiguously indicates a higher corrosion resistance of the latter.



a *б*

Figure 2.12 - Chronograms of capacitance (*a* - at frequencies *f*, kHz: 1 - 1; 2 - 10) and resistance (*b* - *f* = 1 kHz) of samples with oxide coatings,formed in sulfuric acid. Medium – 0.1 M H_2SO_4

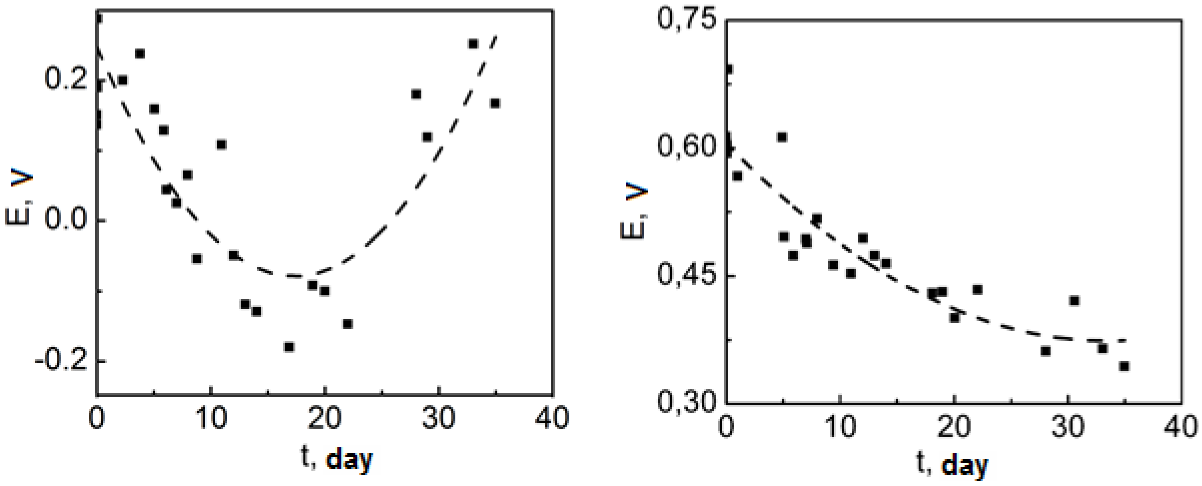
The resistance *R* of samples with a traditional oxide coating is lower than that of PEO coatings, and the capacitance *C* is correspondingly higher, the latter increasing by 30 times during the 0.1 M H_2SO_4 tests, which is a sign of an increase in the porosity of the coatings and a decrease in their thickness. The capacity of PEO systems is also growing, but after 35 days the exposure remains an order of magnitude less.



a b

Figure 2.13 - Chronograms of capacitance (a - at frequencies *f*, kHz: 1 - 1; 2 - 10) and resistance (*b* - *f* = 1 kHz) of samples with PEO coatings. Medium - 0.1 M H_2SO_4

The resistance of the samples decreases, and the corrosion potentials shift to the negative region (Fig. 2.14), which is explained by an increase in the porosity of the coatings. Chronograms are distinguished by a large number of oscillations, since there is a chemical dissolution of the components of the oxide coatings under the action of sulfuric acid, which leads to the development of a corrosion process. At the same time, the resulting corrosion products slow down the process of destruction of the films. Despite a negative shift, the potentials of samples with PEO systems are nobler than with traditional oxide coatings, which indicates high protective properties of PEO coatings [132].



a b

Figure 2.14 - Chronograms of electrodes’ potentials with oxide coating:traditional (a) and PEO (b). Medium - 0.1 M H_2SO_4

According to the results of corrosion tests, it was found that during exposure in solutions of sodium chloride and sulfuric acid, coatings formed in the PEO mode exceed the corrosion resistance obtained by classical anodization (Table 2.8).

Table 2.8 - Indicators of the corrosion rate of oxide systems

Corrosive environment	Coating	Corrosion Rate	
		$j_{\text{кор}} \cdot 10^6$, A/sm^2	$k_h \cdot 10^3$, mm/year
0,1M NaCl	TiO_2^*	4,28	5,66
	$TiO_{x\,(PEO)}$	0,30	0,40
0,1M H_2SO_4	TiO_2^*	10,36	13,56
	$TiO_{x\,(PEO)}$	0,43	0,56

* oxide films formed in a solution of sulfuric acid in a spark mode. The above results indicate that, using the PEO method, depending on the treatment time, oxide coatings 30–100 µm thick can be obtained on titanium alloys. The chemical and phase composition, surface topography, grain size, and abrasion resistance can be varied by changing the electrolyte concentration and molding current density. The formed oxide layer significantly increases the corrosion resistance of titanium in an alkaline medium and Ringer's solutions. The resulting coatings with good adhesion are promising for bio-applications for various purposes.