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РЕЖИМИ СИНТЕЗУ КОНВЕРСІЙНИХ ПЛАЗМОЕЛЕКТРОЛІТНИХ ПОКРИТТІВ НА ЦИРКОНІЄВІЙ ОСНОВІ ТА ЇХ КОРОЗИЙНІ ВЛАСТИВОСТІ

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Метою роботи було проведення спектрального аналізу електролітичної плазми. Було встановлено, що температура плазми, в якій утворюється високотемпературний оксид, становить 8000-500 К. Досліджено вплив складу електроліту та співвідношення густин струму на електрофізичні параметри плазмоелектролітного окислення.

Під час дослідження було досліджено корозійну стійкість в такому агресивному середовищі, як 10% HCl. В результаті експериментів було встановлено, що отримані оксидокерамічні покриття характеризуються високою мікротвердістю та корозійною стійкістю.

Ключові слова: плазмоелектролітне окиснення, оксидокерамічні покриття, захисні покриття, мікроструктура, корозійні властивості, обробка поверхні.

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SYNTHESIS MODES OF CONVERSION PLASMA-ELECTROLYTIC COATINGS ON ZIRCONIUM BASIS AND THEIR CORROSION PROPERTIES

The aim of the work was to conduct a spectral analysis of electrolytic plasma. It was established that the plasma temperature in which the high-temperature oxide is formed is 8000 500 K. The influence of the electrolyte composition and the ratio of current densities on the electrophysical parameters of plasma-electrolytic oxidation was investigated.

During the research, a study of corrosion resistance in such an aggressive environment as 10% HCl was conducted. As a result of the experiments, it was found that the obtained oxide-ceramic coatings are characterized by high microhardness and corrosion resistance.

Key words: plasma electrolytic oxidation, oxide ceramic coatings, protective coatings, microstructure, corrosion properties, surface treatment.

Statement of the problem. Due to its properties, zirconium and alloys based on it are widely used in various industries. For example, zirconium alloys have found their application in nuclear power engineering for the manufacture of shells of heat-generating elements with an increased operating temperature, channel pipes, etc. Such use is due to the ability of zirconium to have a low thermal neutron capture and high corrosion resistance [1]. Of course, the use of zirconium is not limited to the nuclear power industry. Alloys based on it are also attractive for chemical engineering, as a structural material with high anti-corrosion properties in acids and aqueous environments. Zirconium is an inert material in biological environments, and therefore promising in the medical industry. Due to this property, implants in dentistry and traumatology, as well as surgical instruments, are made from zirconium alloys [2, 3].

Protective coatings on alloy products, as is known, must meet many requirements, the most important of which are: sufficient adhesion of coatings to the substrate (base), uniformity in thickness, low porosity and, accordingly, high corrosion resistance, satisfactory mechanical properties (hardness, wear resistance). These and other characteristics depend on the method of coating application, the technological conditions of its formation, the nature and composition of the alloy.

In modern mechanical engineering, metals with low specific gravity and high corrosion resistance are widely used, for example, aluminum and titanium alloys, but their characteristics are often limited by low wear resistance and strength, the thickness of the protective film to various types of damage.

Most methods for protecting metal from corrosion are aimed at weakening or preventing the appearance of corrosion. Plasma electrolytic oxidation (PEO) has recently been considered a promising method for surface protection of light alloys against corrosion and mechanical damage [4].

The PEO method makes it possible to obtain coatings on metal surfaces that are identical in physicochemical properties (hardness, heat, wear, and corrosion resistance) to refractory ceramic materials [5]. The combination of functional properties with the decorative appearance of products obtained by this method makes it possible to use them in rocketry, shipbuilding, aviation, as well as in building decoration, etc.

Analysis of recent research and publications. Plasma-electrolytic oxidation (other names: microplasma, anodic spark, microarc) is one of the most promising methods of surface treatment of materials. The essence of the method is that when a high-density current passes through the metal-

electrolyte interface, conditions are created when the tension at the interface becomes higher than its dielectric strength and micro-plasma discharges with high local temperatures and pressures appear on the electrode surface. The result of the action of micro-plasma discharges is the formation of a coating layer consisting of oxidized forms of the elements of the base metal and components of the electrolyte. Depending on the modes of plasma-electrolytic oxidation (PEO) and the composition of the electrolyte, ceramic coatings with unique characteristics and a very wide range of applications can be obtained [6].

The advantages of the method are the ability to create ultra-strong coatings with unique characteristics, obtaining several protective characteristics in a complex, practically infinite service life of the electrolyte, the ability to process complex profile parts, high dispersion ability of the electrolyte (the coating is applied into holes and planes without difficulties), there is no need for special surface preparation before applying the coating and mechanical treatment after applying the coating, obtaining different coatings on the same material.

Setting tasks. The aim of the study was to investigate the corrosion resistance of oxide-ceramic coatings synthesized on a zirconium alloy Zr-2,5%Nb in an alkaline electrolyte of the composition 10 g/l KOH + 15 g/l liquid glass (the electrolyte base is distilled water).

Presentation of the main material. In general, the production line for PEO coatings consists of: power equipment (specialized power supplies); baths in which surface preparation, processing and washing are carried out; a manipulator for moving the suspension with parts (in the case of serial production); metal structures for placing baths and a manipulator; auxiliary equipment - a distiller, a pump-filter for cleaning and pumping solutions; reserve tanks, devices for controlling the quality of the coating and the state of the electrolyte.

The process of coating formation takes place in an electric field, which is a source of energy for plasma-chemical reactions on the working electrode. At a certain voltage, a sharp heating of the thin channel in the oxide layer occurs, and the current there is interrupted due to the formation of a vapor-gas bubble, due to the evaporation and electrolysis of the electrolyte. With a further increase in voltage, an electric spark breakdown of this bubble occurs, which is accompanied by a sharp thermal increase in its volume, and, accordingly, the interelectrode distance in the discharge channel - the voltage to maintain it begins to be insufficient, and the spark discharge is extinguished. After the discharge is extinguished, the bubble cools sharply and contracts, which is accompanied by a crackling characteristic of anodizing in a spark discharge. Galvanoluminescence, the valve effect, spark discharge at the anode, and electric breakdown of oxide films continue to be studied today [7]. In the breakdown channel, the temperature increases sharply, dissociation and ionization of the electrolyte occur, and a plasma clot is formed, in which plasma-chemical reactions of oxide synthesis take place.

In this work, the zirconium alloy Zr-2.5%Nb was investigated. The experiments were carried out in alkaline electrolytes based on distilled water of the following composition: 3 g/l KOH + 2 g/l liquid glass, 10 g/l KOH + 15 g/l liquid glass, 10 g/l KOH + 15 g/l liquid glass + 0,1 g/l GrO₃, 10 g/l KOH + 15 g/l liquid glass + 0,1 g/l GrO₃ + 10 g/l glycerin, 10 g/l KOH + 15 g/l liquid glass + 0.1 g/l GrO₃ + 10 g/l glycerin + 10 g/l H₂O₂, 10 g/l KOH + 15 g/l liquid glass + 0.1 g/l GrO₃ + 18 g/l glycerin + 10 g/l H₂O₂. To achieve homogeneity of the electrolyte concentration throughout the volume, it was constantly stirred with air. Chromium oxide GrO₃ (VI), which is a strong oxidizer, is obtained by the action of excess concentrated H₂SO₄ on a saturated aqueous solution of potassium dichromate. Acidic chromium oxide, reacting with alkalis, forms chromates CrO₄²⁻. The synthesis of oxide ceramics was carried out at different ratios of the anode current to the cathode current (I_a / I_c): 20/20 A / dm², 10/15 A / dm², 10/10 A / dm², 20/30 A / dm². Synthesis time from 20 to 60 min.

To solve this problem, the dependences of voltage change over time at a constant current density in the process of synthesis of a coating on titanium and zirconium alloys were constructed. The Faraday region is an integral part of the process at the pre-spark stage, and its duration depends on the method of implementing the process and the rate of voltage growth to the sparking potential.

Electrical parameters for the synthesis of oxide-ceramic coating (OCC) are selected mainly experimentally, without proper theoretical justification. However, it is the ratio of the anodic current to the cathodic current (I_a/I_c) and the voltage that determine the nature and intensity of the discharges, and also affect the temperature conditions on the alloy surface. These parameters also affect the functional characteristics of the formed coating, such as hardness, wear resistance, and corrosion resistance. When synthesizing OCC, the stage of spark discharge formation on the sample surface is important. Studies of voltage changes during the synthesis of oxide-ceramic coating on zirconium alloy Zr-2.5%Nb have shown that with the growth of the coating, the voltage on the anode smoothly decreases. An increase in the anodic

potential outside the Faraday region leads to a breakdown of the dielectric or semiconductor film of the anode, which is formed when passing the Faraday region (Fig. 1a). The breakdown occurs due to the injection of electrons from the valence band to the conduction band.

The formation of the OCP on the zirconium alloy occurs in two stages: in the first seconds, the anode voltage U_a increases by about 5...10 V (Fig. 1a, stage I), here the formation of the primary oxide film occurs by the electrochemical mechanism. The only reaction on the anode at a voltage of up to 100 V is the anodic growth of the oxide. In this case, the overvoltage of oxide formation is less than the voltage of electrolyte decomposition. At the second stage of the formation of the spark discharge channel in the “metal – oxide – electrolyte” system, with a further increase in voltage during the synthesis of the coating, a breakdown of this channel by electrons occurs.

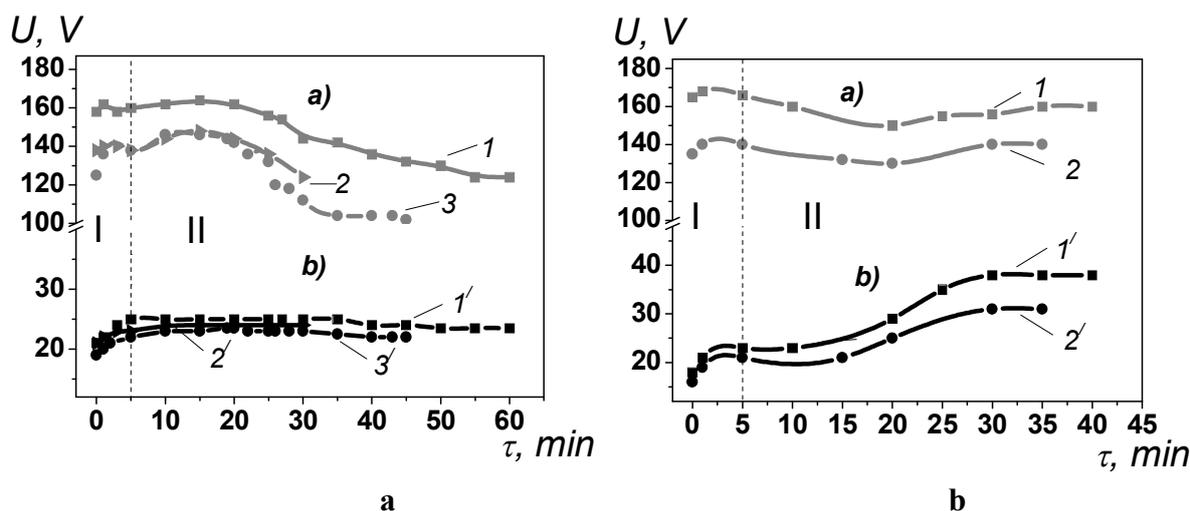


Fig. 1. Dependence of the anodic a) and cathodic b) voltages on the time of synthesis on zirconium alloy electrodes in electrolyte (a): 3 g/l KOH+2 g/l liquid glass with different current densities I_a/I_c : 1, 1/ - 20/20 A/dm², 2, 2/ - 10/15 A/dm², 3, 3/ - 10/10 A/dm²; (b): 10 g/l KOH+15 g/l liquid glass with different current densities I_a/I_c : 1.1/ - 20/20 A/dm², 2, 2/ - 10/10 A/dm²

During the synthesis of the anodic spark coating on the zirconium alloy, a slight increase in the anodic U_a and cathodic U_c voltages is observed with an increase in the concentration of KOH and liquid glass in the electrolyte (Fig. 1a, b). With an increase in the concentration of KOH and liquid glass (Fig. 1b, stage II) the process of coating formation stabilizes and occurs uniformly. Only with the addition of 10 g/l H₂O₂ at the stage of coating formation does the voltage begin to gradually decrease (Fig. 2, field II).

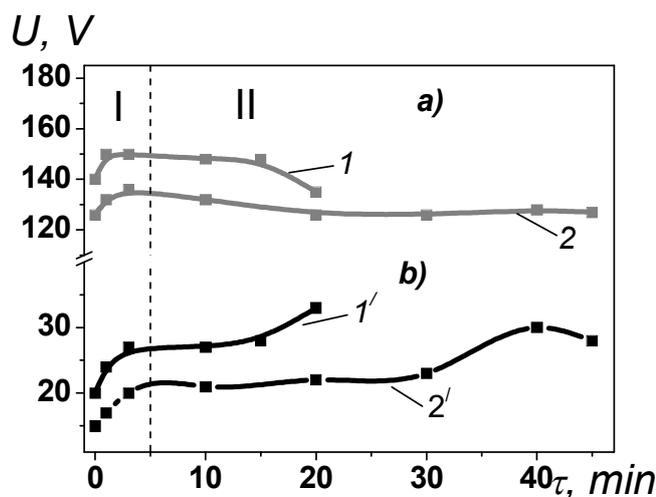


Fig. 2. Dependence of anodic (a) and cathodic (b) voltage on the synthesis time on zirconium alloy electrodes in an electrolyte 10 g/l KOH + 15 g/l liquid glass + 0.1 g/l GrO₃ + 18 g/l glycerol + 10 H₂O₂ with different current densities: 1, 1/ -20/30A/dm², 2, 2/ -10/15 A/dm².

A single reaction on the anode at a voltage of up to 100 V results in anode growth of the oxide. In this case, the overvoltage is created by the mensch oxide due to the voltage of the electrolyte.

Thus, the electrophysical parameters of the process of synthesis of OKP on zirconium alloy depend on the composition of the electrolyte and the ratio of the density of the anodic current to the cathodic current. Thus, in the least concentrated electrolyte, which contains alkali and liquid glass, the synthesis is uneven, which affects the quality of the coating. Such a coating does not completely cover the surface of the metal, forming islands of synthesized oxide on the surface (Fig. 3) and, therefore, is not of high quality.

Plasma electrolyte coating is inert. One of the explanations in them is that there are various options for compounds that can lead to the destruction of metal or alloy. All this reduces the functionality of the power and will soon end the use of the alloy. Due to the fact that the corrosion chemistry of plasma-electrochemical coatings on zircon and titanium alloys in various corrosive-aggressive environments is revealed and it is important for their corrosion jets, for these they judged the speed of corrosion alloys.

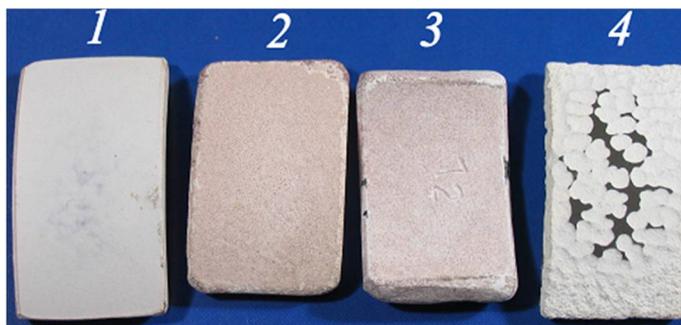


Fig. 3. Oxide-ceramic coatings on zirconium alloy (processing modes are given in Table 1)

Table 1

Processing modes of oxide-ceramic coatings on zirconium alloy

№	Electrolyte composition, g/l			I_a/I_c , A/dm ²	τ , min	H_{μ} , GPa	Thickness, mm
	KOH	Liquid glass	GrO ₃				
1	5	5	—	14/20	30	9	70...100
2	10	15	—	20/20	40	16	70...130
3	10	15	0,1	20/20	30	10	90...160
4	3	2	—	20/20	30	14	20...50

After the formation of the OCC, corrosion processes are essentially galvanized. In hydrochloric acid environments, corrosion flows, which are reduced in a curve against the matrix in the order.

It is seen that high corrosion power of zirconium is allowed into a thin-walled acidified liquid of oxides partially ZrO₂ (Table 2). However, respected minds, engaged and declaring personally aggressive middle peasants (including in the case of robots) chickens, within the limits of small thickness and low rigidity, do not exclude high anti-corrosion powers.

Corrosion jets covered this, which judged the speed of corrosion of the material, reducing all the systems used.

The corrosion potential of the corrosion-German zirconium alloy when diluted with 10% HCl has a negative value of -370 mV (Fig. 4 a), the corrosion jet is 80 mA / m².

When forming this alloy, OCC produces softening by 1...2 serial places in the electrolyte warehouse, where the tires were synthesized. Since it is synthesized in a low-concentration electrolyte, which is the case with alkali and glass, it is possible to find lower corrosion activity because of this, which were synthesized in more concentrated electrolytes and have a value of $1,2 \cdot 10^{-3}$ A/m² (Fig. 4 a, curve 4). With an additional increase in the concentration of electrolyte on the streams of corrosion and cor OCC are reduced.

The coating obtained in an electrolyte of 10 g/l KOH + 15 g/l rs has a corrosion current value of $1,39 \cdot 10^{-4} \text{ A/m}^2$, and when 10 g/l H_2O_2 is introduced into the electrolyte, the i_{cor} decreases to a value of $1,21 \cdot 10^{-4} \text{ A/m}^2$.

This result is obviously associated with the combination of high hardness and thickness of the coating.

Conclusions. Plasma is formed within 3...5 min (initial section of the curve), the voltage in this section increases. Further increase in the electrolyte concentration by increasing the content of the main composition of KOH and liquid glass and by introducing additional chromium stabilizes the synthesis process. The current ratio does not change the nature of the voltage dependences on time, i.e. does not affect the stability of the synthesis process. A decrease in currents reduces the anodic and cathodic components of voltage, and this in turn affects the properties of the coatings. The most favorable conditions for the formation of oxide are formed at a current density ratio of $I_a/I_c=1,5$ and at a relatively low electrolyte concentration of 10 g/l KOH+15 g/l liquid glass. Studies of the corrosion properties of plasma-electrolytic coatings showed that the corrosion currents of the OCC for all studied systems are reduced by 2...3 orders of magnitude.

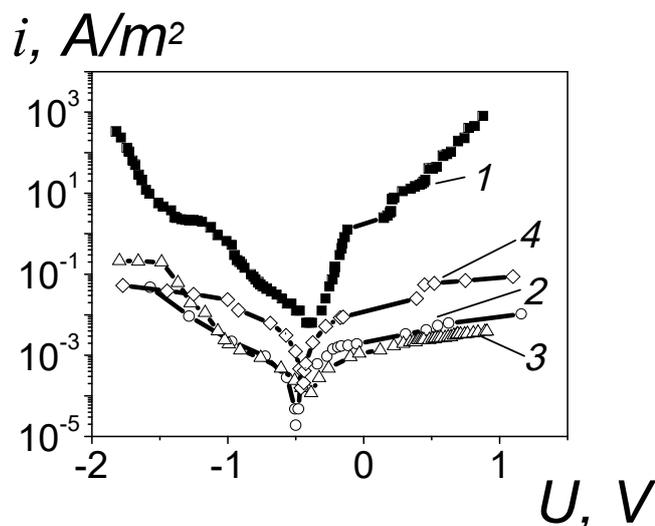


Fig. 4. Polarization curves: a – zirconium alloy (1) and its OCC (2, 3, 4) in a 10% HCl solution (modes are presents in Table 1)

Table 2

Corrosion potential and current of Zr - 2,5%Nb alloy and coating on it under different oxidation regimes

№	Corrosive environment	Electrolyte composition, g/l				I_a/I_c A/dm ²	τ , min	U_{cor} , B	i_{cor} , A/m ²
		KOH	l.g.	CrO ₃	H ₂ O ₂				
1	10%HCl	—	—	—	—	—	—	0,37	$8,07 \cdot 10^{-2}$
2		10	15	—	10	20/20	30	0,41	$0,21 \cdot 10^{-4}$
3		10	15	—	—	20/20	30	0,50	$1,39 \cdot 10^{-4}$
4		3	2	—	—	20/20	20	0,45	$12,07 \cdot 10^{-4}$

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