Formation of coatings on the basis of titanium by the method of plasma electrolytic oxidation, saturated with biocomponents

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Abstract. In the work, the influence of the composition of the electrolyte on the electrophysical parameters of the synthesis of coatings with increased biocompatible properties was studied. It was established that under conditions of increased electrolyte concentration, the voltage at which the coating is synthesized decreases. This effect can be explained by the thermodynamic Gibbs conditions. According to these conditions, the system needs more energy when the medium contains more elements, which must also consume a certain amount of energy. The authors found that sodium salts increase the conductivity of the working environment. This effect affects the speed of the synthesis process and can reduce the cost of the energy reserve of the system as a whole.
Spectral analysis established that during the synthesis of a titanium alloy in an alkaline electrolyte, an equilibrium non-degenerate quasi-ideal plasma is realized in the discharge channel with a temperature of $(1...1,1)\times10^4$ K and an electron density of $(3,2...3,4)\times10^{22}$ m^{-3}. It is under these conditions that molecules dissociate into ions and interact with the components of the electrolyte, which leads to oxidation of the surface of valve metals and the formation of stable compounds with high biocompatible properties.

Keywords: Akaline electrolyte, Datomite, Hydroxyapatite, Anode voltages, Current density ratio, Titanium alloys, Electrolytic plasma.

1 Introduction

One of the most promising approaches in modern materials science is surface modification of functional materials in order to give them a new set of physical-mechanical, physical-chemical and operational properties. In the field of biomedical materials science, the creation of new implant materials with bioactive properties is particularly relevant. In recent years, significant progress has been made in the development of new approaches in implantology, but there are also significant problems related to the biocompatibility of the surface of implants, as this directly affects their compatibility with the living organism. In this regard, one of the important problems of modern implantology is the creation of new-generation implants with increased biocompatibility, which ensures a decrease in the probability of rejection. PEO coatings are formed as a result of electron injection, which is provided by the appropriate energy conditions of the system. Therefore, it is relevant

to study the stage of the plasma-electrolyte oxidation process, which is determined by the voltage on the working electrode (anode).

2 Literature Review

Titanium and its alloys are widely used as materials for biomedical applications such as dental and orthopedic implants due to their non-toxicity, high specific strength and good biocompatibility [1]. Increasing the operational properties of metals is essential [2, 3]. However, titanium and its alloys are bioinert and cannot induce bone growth [4]. To overcome this drawback, researchers tried to change the composition and topography of implant surfaces [5 – 7]. The formation and vital activity of bone tissue at the border with non-biological structures depends to a large extent on the micro-structure of the surface of the material. Previously, it was proposed to synthesize a coating on the surface of titanium alloys in an alkaline environment with diatomite [8]. The authors found that the positive effect of adding diatomite to the electrolyte is its antimicrobial properties, as well as the possibility of synthesizing coatings with a roughness of Rz = 137,498 μm, which is many times higher than the roughness of coatings synthesized in an environment without diatomite. Modern scientific progress makes it possible to increase the compatibility of the surfaces of parts by using synthesized oxide ceramic coatings. Currently, many methods of surface strengthening of materials have been developed [9]. However, they are characterized by the following disadvantages: high cost or long duration of the process, small thickness of the reinforced layer and insufficient adhesion, surface distortion, etc. Plasma electrolytic oxidation (PEO) is a relatively new type of surface treatment. and strengthening of valve metals, which originates from traditional anodizing and refers to electrochemical processes. Such spraying reduces the coefficient of friction and improves the corrosion properties of parts with valve metals. This method of surface treatment allows to obtain multifunctional metal-ceramic coatings with a unique set of properties. Technologies for creating conversion oxide-ceramic coatings on valve metals are mainly used for surface strengthening of aluminum, zirconium, titanium, and magnesium alloys [10-13].

In [10], the properties of the coatings synthesized on titanium samples were studied, and the authors established that the surface porosity affects the biocompatibility properties. It was also found that surface porosity favors HA nucleation and thus improves bioactivity. In [11], the authors described the influence of the concentration of electrolyte components and the anode current density at the Ia/Ic cathode on the morphological features of the surface coatings synthesized on the basis of zirconium by the PEO method. S. L. Aktug, S. Durdu, I. Cudbay and M.Usta investigated the phase structure, morphology, hardness, adhesive strength, surface roughness, and wear resistance of PEO coatings in solution of potassium hydroxide (KOH) and different concentration of sodium metasilicate pentahydrate ($Na_2SiO_3 \cdot 5H_2O$) electrolytes. It was seen that the wear rate, hardness and surface roughness of the coatings were increased when the concentration of $Na_2SiO_3 \cdot 5H_2O$ electrolyte was increased [12]. In article [13] researched the rate of wear of OCC, which was formed in the alkaline electrolyte Na_2SiO_3+KOH. Found that oxideceramic cover with dry friction increases wear resistance investigated alloys 10 ... 15 times. Wenbin Hue,

Live Deng, Ruhi Chen and others [14] established that the OCC on aluminum alloy consists of two layers – a loose layer and a compact layer. They revealed that The Hμ and E in the compact layer are about 18–32 GPa, 280–390 GPa, respectively. The Hμ and E profiles are similar, and both of them exhibit a maximum value at a same depth of the coatings. They found that the nanohardness Hμ and the modulus of elasticity E in the compact layer are approximately 18–32 GPa and 280–390 GPa, respectively. The profiles of Hμ and E are similar, and both show a maximum value at the same coating depth. They investigated that changes in the content of α-Al_2O_3 and γ-Al_2O_3 are the result of different cooling rates of molten aluminum oxide in the micro-arc discharge channel at different coating depths.

The polarization behavior of technically pure titanium during plasma electrolytic oxidation was investigated in a KOH solution [15]. It was established that the behavior of the discharge depends on the concentration of the solution [16, 17]. The authors determined that for all concentrations, when the voltage increases in the first stage, anodization occurs and oxygen bubbles are formed. For intermediate concentrations of KOH, when the voltage passes the critical value, the current density increases and sparks appear on the surface. A further increase in voltage leads to the formation of large arcs and a sharp increase in the current density, which is accompanied by an intensive release of gas (oxygen) due to the oxidation of water. All three oxidation stages are also present in electrolytes containing three sodium orthophosphate (Na_3PO_4), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), sodium nitrite ($NaNO_2$) and urea $CO(NH_2)_2$ [18].

The main goal of this work was to establish the dependence of the effect of adding phosphates, hydroxyapatite and diatomite to the alkaline electrolyte on the electrophysical parameters of PEO.

3 Researches Methodology

The main electrophysical parameters of PEO are the voltages at the anode Ua and cathode Uk, the synthesis time, as well as the current density at the anode, cathode Ia, and Ik, respectively, which are used to calculate the current density ratio Ia/Ik.

First, the area of the surface to be oxidized was determined, which was used to calculate the current that must be applied to the sample. By setting a constant current on the anode and cathode at the beginning of the synthesis, Ua and Uk were recorded every 1-2 seconds. After approximately 5 minutes of the oxidation process, voltmeter readings were taken every 5 minutes. On the basis of the obtained values, curves of voltage dependence on time were constructed, according to which the stages of the PEO process were determined.

The physical parameters of the electrolytic plasma, in which oxides are synthesized on a metal substrate, were studied on a special low-power installation for oxide-ceramic oxidation (**Fig. 1**) [19], equipped with a C-115 spectrophotometer.

Under the action of the current on the sample located in the electrolyte bath, spark discharges are produced, in which the plasma state is realized and the radiation through the output window made of US-88 glass is fed to the input window of the spectrophotometer. The emission spectra of electrolytic plasma of the system zirconi-

um alloy - aqueous solution were studied. No radiation was observed in the short-wavelength region (190...290 nm), after which it is absorbed by the electrolyte.

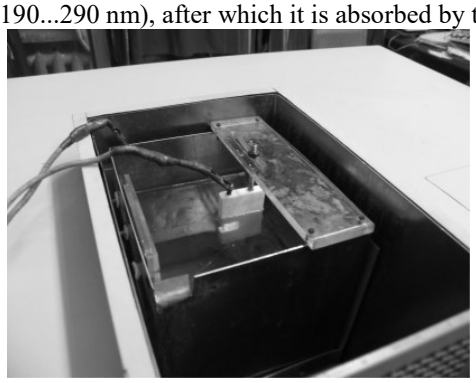

Fig. 1. Electrolytic bath for plasma oxidation with determination of physical parameters of plasma

The electrolytic plasma of the titanium alloy – electrolyte system was studied according to the method outlined in [19]. An aqueous solution of 1 g/l KOH+1 g/l Na_2SiO_3 (with a current density of 1,38 g/cm^3) served as the electrolyte. The synthesis of the oxide ceramic coating was carried out on the titanium alloy. The IMPELOM installation was used as a power source. The current density is 3 kA/m^2, the ratio of cathodic to anodic current densities Ia/Ic=1, pulse frequency 50 Hz. The radiation spectrum entered the spectrophotometer using an optical fiber cable, which made it possible to observe titanium radiation in the region up to 300 nm.

4 Results

To establish the stagedness of the process of synthesis of oxide-ceramic coatings, the change in voltage on the anode (sample) from the beginning of the process to its end was investigated. In order to analyze the influence of individual components of the electrolyte on the phasing of PEO, the operating parameters of the synthesis were selected experimentally. The modes by which the stages of the process of synthesis of titanium alloy Ti-6Al-4V by the PEO method were studied are presented in the **Table. 1.**

The synthesis of the coating in the electrolyte with a higher weight content of potassium hydroxide and liquid glass slightly lowers the synthesis voltage (**Fig. 2**).

The obtained results indicate the influence of the concentration of components and the density of the currents on the stages of the PEO process. Thus, it follows from the dependences that an increase in the current density by 10 A/dm^2 both at the anode and at the cathode leads to an increase in the initial voltage by 30 V for all the specified systems.

Table 1. The environment in which the titanium alloy coating was synthesized

№ sample	Electrolyte components, g/l						
	KOH	$(Na_2O(SiO_2)_n$	$Ca(OH)_2$	$Na_4P_2O_7$	$Na_6P_6O_{18}$	HPA	Diatomite
1	3	2	-	-	-	-	-
2	5	5	-	-	-	-	-
3	10	10	0,5	-	-	-	-
4	0,5	0,5	0,5	0,5	0,5	-	-
5	5	5	5	5	5	1	-
6	20	20	20	20	20	-	20

The breakdown of the natural oxide film, that is, the voltage at which sparks are formed on the surface of the sample, also occurs at a higher voltage when the current density increases by 10 A/dm^2. However, in another way, this process takes place with a change in the concentration of the electrolyte. In a less concentrated electrolyte, the system needs to spend more energy and time on the breakdown of the natural protective film on the surface of the titanium alloy, and therefore the voltage for such systems increases rapidly by approximately 20 V from the beginning of synthesis.

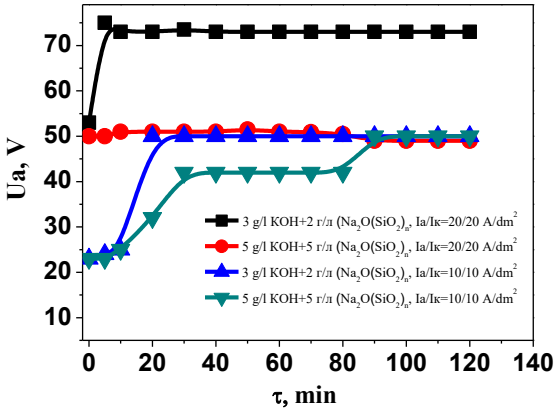

Fig. 2. Electrophysical parameters of PEO titanium alloy in electrolytes № 2 and № 3 during synthesis 120 min at Ia/Ic=10/10 A/dm^2 and 20/20 A/dm^2

For systems with a higher concentration of components in the electrolyte, less energy is spent on the breakdown of the protective barrier on the surface of the same alloys, and when twice as much current is applied to the system, the oxide film breaks through at almost the initial voltage (the increase occurred only by 1 V in 10 min of synthesis time). This effect can be explained by the higher conductivity of the electrolyte, which is given by liquid glass.

As a result of the interaction of $Ca(OH)_2$ with CO_2, which is supplied to the electrolyte bath for its mixing, a reaction is formed:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O \quad (1)$$

As a result of this interaction, insoluble calcium carbonate is formed, which gives the solution turbidity.

In an electrolyte of 10 g/l KOH + 10 g/l $Na_2O(SiO_2)n$ +0,5 g/l $Ca(OH)_2$, the synthesis of an oxide ceramic coating on a titanium alloy occurs according to a similar mechanism as under the previous regimes (**Fig. 3**). However, according to the results of the experimental dependences, it can be seen that the adding of a small amount of calcium hydroxide (0,5 g/l) into the electrolyte requires more energy from the system.

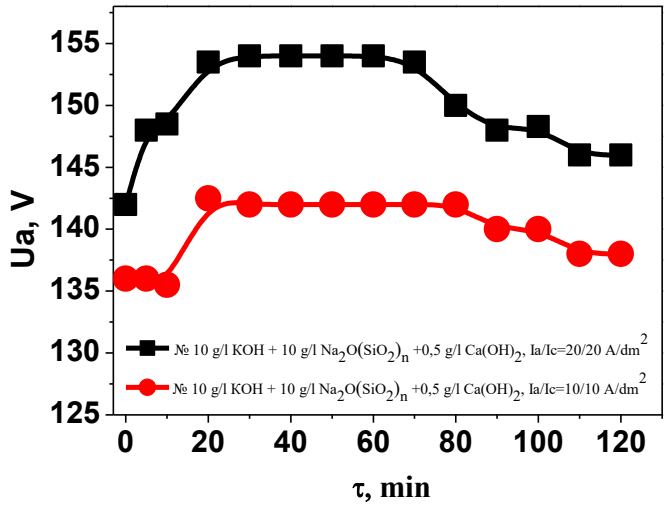

Fig.3. Electrophysical parameters of PEO titanium alloy in electrolyte № 3 at Ia/Ic=20/20 A/dm^2 and 10/10 A/dm^2, synthesis time 120 min

After synthesizing titanium alloy samples with different ratios of current densities, it was found that they were formed under regimes Ia/Ic = 1,5; 2 and 1,25 coatings were of poor quality already from a visual inspection (**Fig. 4**).

a b c d

Fig. 4. PEO-coatings synthesized according to the following modes:
a) 0,5 g/l KOH + 0,5 g/l $Na_2O(SiO_2)n$ +0,5 g/l $Ca(OH)_2$ + 0,5 g/l bone glue at Ia/Ic =1;
b) 0,5 g/l KOH + 0,5 g/l $Na_2O(SiO_2)_n$ +0,5 g/l $Ca(OH)_2$ at Ia/Ic=2;
c) 0,5 g/l KOH + 0,5 g/l $Na_2O(SiO_2)_n$ +0,5 g/l $Ca(OH)_2$ at Ia/Ic=2,3;
d) 10 g/l KOH + 10 g/l $Na_2O(SiO_2)_n$ +0,5 g/l $Ca(OH)_2$ at Ia/Ic=1,25.

Therefore, in the future, it was not advisable to investigate such coatings, and the regimes under which low-quality coatings were formed were indicated as ineffective for such alloys.

To realize the synthesis of coatings on titanium alloys with increased biocompatibility, electrolytes of a separate composition have been developed.
To increase the biocompatibility of the coatings and obtain their chemical composition, as close as possible to the composition of bones, phosphate salts, such as sodium pyrophosphate $Na_4P_2O_7$, sodium hexaphosphate $Na_6P_6O_{18}$, as well as calcium hydroxide, hydroxyapatite and diatomite, were added to the working electrolytes. This made it possible to control the chemical composition of the formed PEO-coating. As in previous studies, the stages of the PEO process were the stages of synthesis (**Fig. 5**).
The conducted research made it possible to establish the effect of calcium hydroxide on the staged process of the titanium-based coating synthesis. The established dependencies made it possible to determine a voltage drop of approximately 5 V at the anode due to the addition of 0,5 g/l of $Ca(OH)_2$ to the electrolyte. Such an effect is obviously associated with an increase in the viscosity of the electrolyte, which requires more energy consumption at the anode. By increasing the concentration of calcium hydroxide in the electrolyte by two times and reducing the current density by two times, we achieved the same voltage at the anode in the third stage of synthesis, which is characterized by the growth of oxide on the surface of the sample. However, it should be noted that in this case the initial voltage is lower by 6 V, and also that the breakdown voltage was not recorded in this mode.

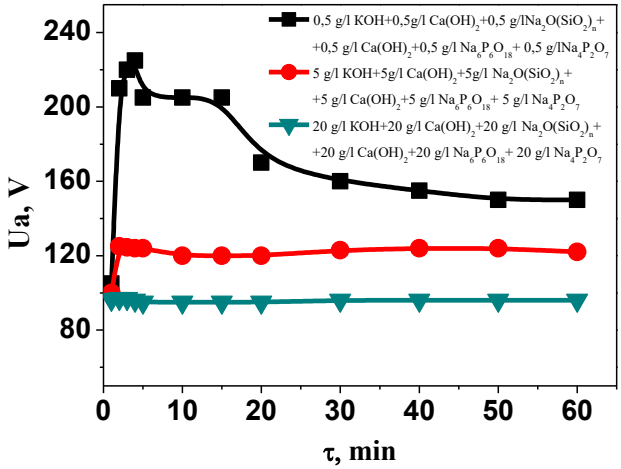

Fig. 5. Electrophysical parameters of PEO titanium alloy in electrolyte № 4, № 5 and №6 at Ia/Ic=20/20 A/dm^2, synthesis time 60 min

Dependencies of the stages of the synthesis process on a titanium alloy in an electrolyte № 4 made it possible to establish that breakdown of the oxide film occurs much faster than during biocoating synthesis in an electrolyte without sodium salts. Thus, under mode № 4, the second stage (breakthrough of the natural oxide film) occurs at the fourth minute of PEO of the titanium alloy. At lower current densities, namely with ratios Ia/Ic=1,5 and Ia/Ic=1, the breakdown of the film takes a little longer. So, it should be noted that for the ratio Ia/Ic=15/10 A/dm^2, the breakdown voltage is 147 V, and in this case, the third stage of synthesis occurs after 10 min of oxidation. When

Ia/Ic=10/10 A/dm^2, stable sparking on the sample occurs only after 20 minutes of oxidation.

According to the experimentally established data of voltage changes over time, it becomes obvious that a system with a higher concentration of components requires more energy to carry out reactions between the metal and the electrolyte. Therefore, comparing modes № 4 and № 3, it turns out that the voltage increase at the anode in the process of synthesis by 85 V is higher for mode № 4. So, it was found that the electrolyte with a higher content of components has a higher conductivity and thus a higher voltage at a constant current acts on the sample according to modes № 3 and № 4, respectively.

Synthesizing an oxide biocoating on a titanium alloy in electrolytes № 5 and № 6, the stages of the synthesis process remain the same, i.e. the initial (I area, which is characterized by the release of hydrogen on the surface of the anode), breakdown voltages (II area, which is characterized by the formation of the first sparks on the anode) and the growth region of the coating (III area, which is characterized by the stable growth of oxide on the anode) were revealed (**Fig. 5**).

The characteristic spectrum of electrolytic plasma radiation is shown in **Fig. 6**.

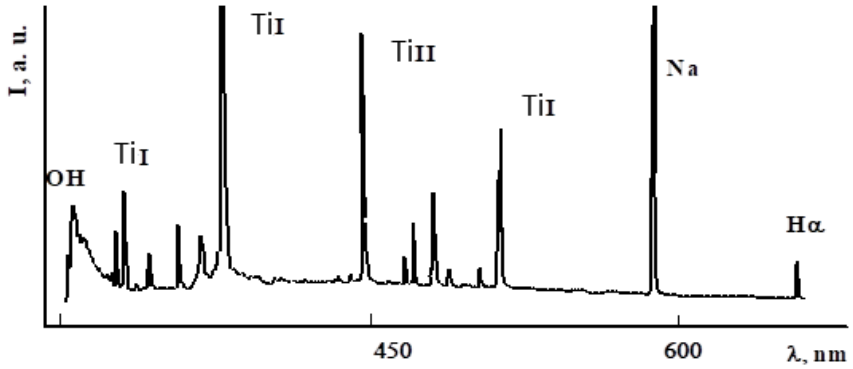

Fig. 6. Emission spectra of electrolytic plasma during the synthesis of oxide ceramic coatings on titanium alloys

Titanium oxide is a dielectric with a large band gap. The breakdown of the film formed in a weakly concentrated electrolyte occurs at a higher electric field intensity, which correlates with the emission of a larger number of lines observed in the spectrum (**Fig. 6**). Based on the broadening of the H_α hydrogen line based on the Stark effect and the relative intensities of the emission lines of magnesium ions and atoms and the methods described in [101], it was established that in the discharge channels during the synthesis of titanium-based oxide ceramics, a plasma with an electron density $n_e = (3{,}2...3{,}4)\times10^{22}$ m^{-3} and the electron temperature $T_e = (1...1{,}1)\times10^4$ K [18].

5 Conclusions

It can be noted that in conditions of increased concentration of the working medium (electrolyte), the voltage at which the coating is synthesized decreases.
It was experimentally confirmed that the synthesis of the coating in an electrolyte with a higher weight content of potassium hydroxide and liquid glass, namely 5 g/l KOH + 5 g/l $Na_2O(SiO_2)_n$ versus 3 g/l KOH + 2 g/l $Na_2O(SiO_2)_n$ slightly lowers the synthesis voltage. Using the time dependences of the voltage on the anode in the PEO process, it was found that a more uniform formation of oxide on the surface of titanium alloys is formed at the ratio Ia/Ic = 10/10 A/dm^2 and 20/20 A/dm^2. The presented results indicate that sodium salts increase the conductivity of the working medium, which proves the result of the supply of smaller currents to the anode and cathode, but with a different ratio, which is not 1, but 1,5.
Studies of the physical properties of plasma established that during the synthesis of oxide ceramic coatings in an electrolytic plasma at a temperature of (1...1.1)×10^4 K with an electron density of (3,2...3,4)×10^{22} m^{-3} and a degree of ionization (0,02...0,10) on a titanium base, an equilibrium, non-degenerate, quasi-ideal plasma is realized in the discharge channel.

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