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MORPHOLOGY OF COATINGS ON TITANIUM ALLOY WITH THE ADDITION OF BIOCOMPONENTS

In this work, the method of plasma electrolytic oxidation on a titanium alloy with the introduction of calcium-containing components and bioadditives in the form of diatomite into the coating is widespread. In order to increase the biocompatibility of the synthesized surface, working environments and coating application modes were developed. The study of the stage nature of PEO in such electrolytes allowed predicting the properties of coatings in the future depending on the requirements for their roughness.
Key words: *plasma electrolytic oxidation, anodic, cathodic, alkaline, hydroxylapatite, diatomite, roughness, porosity.*

Formulation of the problem. Attractive properties of titanium alloys make them widely used in many branches of modern industry. Titanium and its alloys are characterized by their high inert properties, making them indispensable for the manufacture of implants, and the advantageous combination of specific strength and density makes them particularly attractive for aircraft [1–4]. However, difficult operating conditions, increased requirements for high quality require the search for new methods of processing such alloys.

Promising methods are the application of coatings with high corrosion and mechanical properties. An important condition for such coatings may be the possibility of additional creation of a widely developed surface (highly porous surface with high roughness) [5-7]. Such a solution makes it possible to make titanium implants indispensable in orthopedic surgery.

The plasma electrolytic oxidation method refers to electrochemical methods of coating application. The advantages of the method are control of the composition, structure and properties of coatings. The synthesized coatings are characterized by high adhesive intermolecular bonds between the base and the coating, which makes this method particularly attractive. The environmental friendliness of the PEO method allows it to compete with known coating application methods, such as vacuum arc spraying, surface ion bombardment, the SHS process, etc.

Analysis of recent research and publications. Wouter Habraken, Pamela Habibovic, Matthias Epple and Marc Bohner raise the issue of implant placement worldwide. The authors describe the bleak prognosis for treatment of patients with osteoporosis-related injuries, with as many as 20% of such patients not surviving the first year after surgery. Some experts predict that less than 30% of hospital beds will be occupied by patients with osteoporosis [8]. Bone replacement surgery is already second only to the most widespread blood transfusion procedure. Scientists such as Carayon M.T., Lacout J.L., have analyzed the relevance of bone segment implantation in the world. In their work [9] they note that there are about 2 million bone transplants in the world, of which 0,5 million were performed in the USA. In 2010, global sales of bone tissue substitutes reached 1,3 billion US dollars with a forecast of 10% annual growth and a volume of 2,7 billion dollars [9].

Such data provide an understanding of the great need for biomaterials in the world. Therefore, the problems of our time require the search for new ideas for the production of new technologies for the creation of innovative biomaterials that would be characterized by biocompatibility, bioactivity, osteoinductivity, bioresorption [10]. The surface chemistry of biomaterials plays an important role in determining the organism's response and biocompatibility [11, 12].

Two main approaches to solving this issue have emerged: the search for bioenvironments [13-16] and technologies for creating biomaterials [17-20].

Setting objectives. The main objective of this work was to develop a technology for plasma electrolytic oxidation (PEO) of titanium alloys in an environment with hydroxylapatite and diatomite. To determine the impact of this technology on the change in biocompatible properties, a necessary condition is to establish the porosity and roughness of the synthesized coatings. High indicators of such properties indicate high biocompatibility of the coatings.

To explain the nature of the formation of biocoatings by the PEO method, a necessary condition is the synthesized stages, at which it is possible to study the dependence of the change in voltage at the anode on the synthesis time.

Knowing the impact of adding biocomponents to the working environment on changing regimes allows us to predict coating properties in the future.

Presenting main material. PEO coatings were applied to various metal substrates with different electrolytes in alternating current mode. The work investigated a biocompatible ceramic layer of TiO_2 composition with the content of hydroxylapatite (HAp) and diatomite, applied to the titanium alloy Ti-6Al-4V. For the synthesis of the coating, a titanium sample was used as the anode, and a stainless steel (electrolytic bath) was used as the cathode. In order to determine the gradation of the synthesis process of oxide ceramic coatings, the change in voltage at the anode during the entire coating build-up process was investigated. In order to analyze the influence of individual electrolyte components on the PEO phases, the operating synthesis parameters were experimentally selected.

First, PEO coatings were applied to titanium alloy samples in the presence of electrolytes containing KOH alkali, liquid glass, sodium pyro- and polyphosphate based on distilled water without the addition of additives. Later, HAp and diatomite nanoparticles were added to the electrolyte. Table 1 shows the synthesis modes of coatings on Ti alloy by the PEO method in different electrolytes.

Table 1 – Modes of synthesis of PEO coatings on Ti alloy

№ sample	Components electrolyte, g/l							Processing time τ, min	Current density, Ia/Ic, A/dm^2
	KOH	$(Na_2O(SiO_2)_n$	$Ca(OH)_2$	$Na_4P_2O_7$	$Na_6P_6O_{18}$	HAp	diatomite		
1	5	5	-	-	-	-	-	60	1,25
2	10	10	0,5	-	-	-	-	120	1
3	0,5	0,5	0,5	0,5	0,5	-	-	100	1
4	5	5	5	5	5	1	-	60	1
5	20	20	20	20	20	-	20	60	1

According to the obtained values of the synthesis voltage, its decrease is observed in electrolytes with a larger number of components (Fig. 1).

The exception is the synthesis of the coating in the electrolyte with the addition of only calcium hydroxide (Fig. 1, curve № 2). This effect is explained by the high energy consumption of the system.

When the concentration of KOH and liquid glass components is increased by half, the initial voltage at the anode decreases by only 8 V, but increasing the concentration of these same components by 1,5 times by introducing $Ca(OH)_2$ into the system reduces the initial voltage. This fact also indicates a decrease in the conductivity of electrolytes when calcium hydroxide is included in their composition.

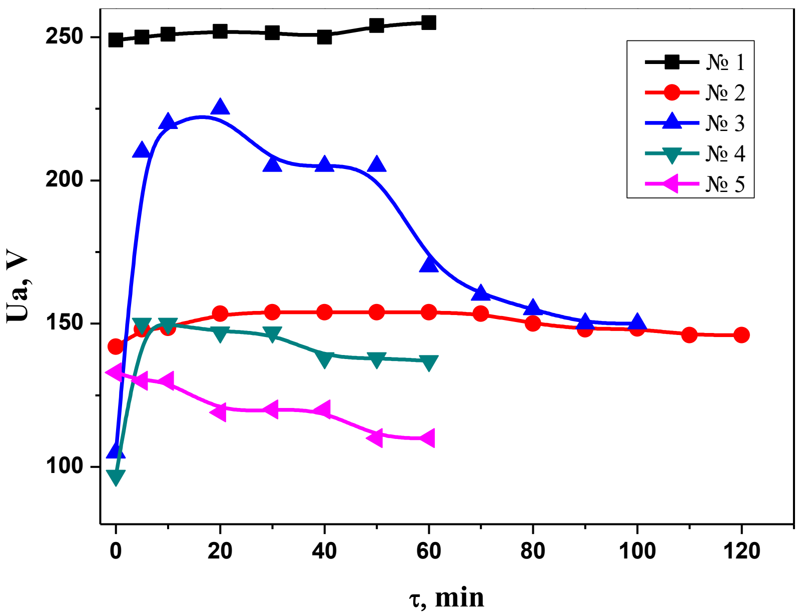


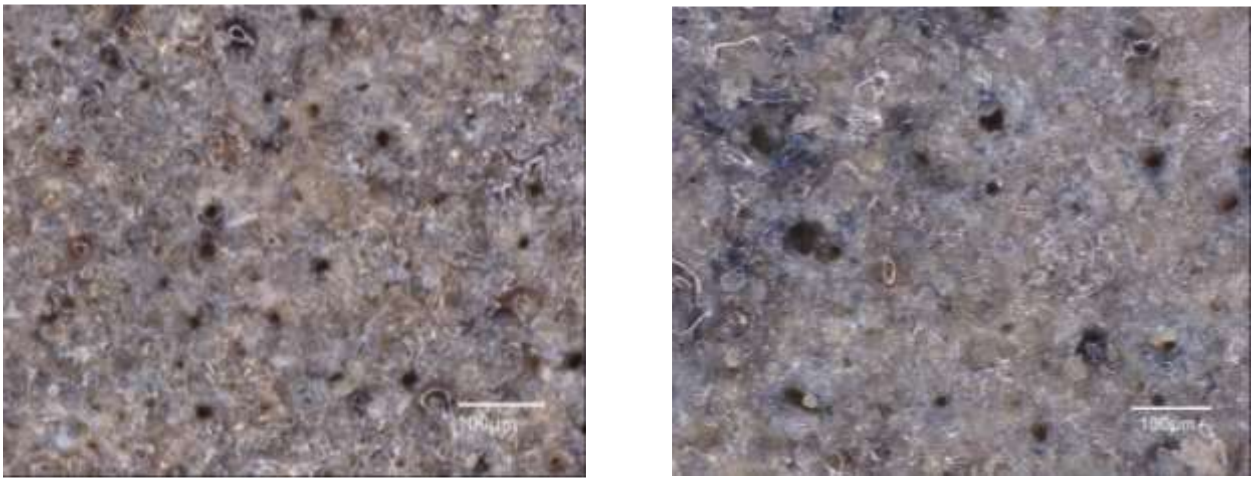
Figure 1 – The course of coating synthesis in electrolytes № 1, 2, 3, 4, 5 (see Table 1)

It should also be noted that the synthesis of the coating in the electrolyte with slaked lime occurs evenly, that is, in this case, areas of rapid increase and decrease in voltage at the anode are eliminated. Hydroxyapatite has the greatest structural similarity to bone, so the content of this component in the coating makes it a highly biocompatible material. The addition of diatomite (natural silica) to the electrolyte helps increase the porosity and roughness of the surface, increasing antibacterial properties. Fig. 2 shows samples of Ti alloy with coatings containing HAp and diatomite.

a b c

Figure 2 – Titanium alloy before surface treatment (a) and after synthesis in an electrolyte with HAp (b) and diatomite (c) (sample diameter 10 mm)

In this work, the surface morphology of the synthesized coatings was investigated. The study data indicate the presence of pores in all coatings (Fig. 3).



a b

Figure 3 – Pores on the surface of PEO coatings: a – режим № 4, b – режим № 5 (see Table 1)

Studies of surface roughness make it possible to establish the biocompatibility of this type of coating, because it was described above that implants with high roughness take root faster and thereby help reduce the time for the rehabilitation period after surgery. Fig. 4 shows the results of a study of the roughness of PEO coatings synthesized on a titanium alloy in a diatomaceous earth environment.

The results obtained established a high surface roughness of the synthesized coatings on titanium alloy by the PEO method. The established values of the coating roughness exceed approximately twice the roughness of the coatings synthesized in an electrolyte with hydroxylapatite.

In the electrolyte containing alkali and phosphates, coatings with an average roughness Rz=51 µm, Ra=8,7 µm are formed. By increasing the current density to 4/4 A/dm^2, the surface roughness increases slightly. The introduction of 20 g/l of diatomite into the electrolyte and an increase in the current density by another 1 A/dm^2 at the anode and cathode reduces the surface roughness to the values Ra=6,6 µm, Rz=40,1 µm.

Thus, the obtained results allow us to establish the dependence of the diatomite content on the roughness of the synthesized coatings. It was found that adding diatomite to the electrolyte in an amount of 20 g/l allows us to obtain a surface with a widely developed morphology. This effect has a positive effect on the biocompatibility and osseointegration of PEO coatings.

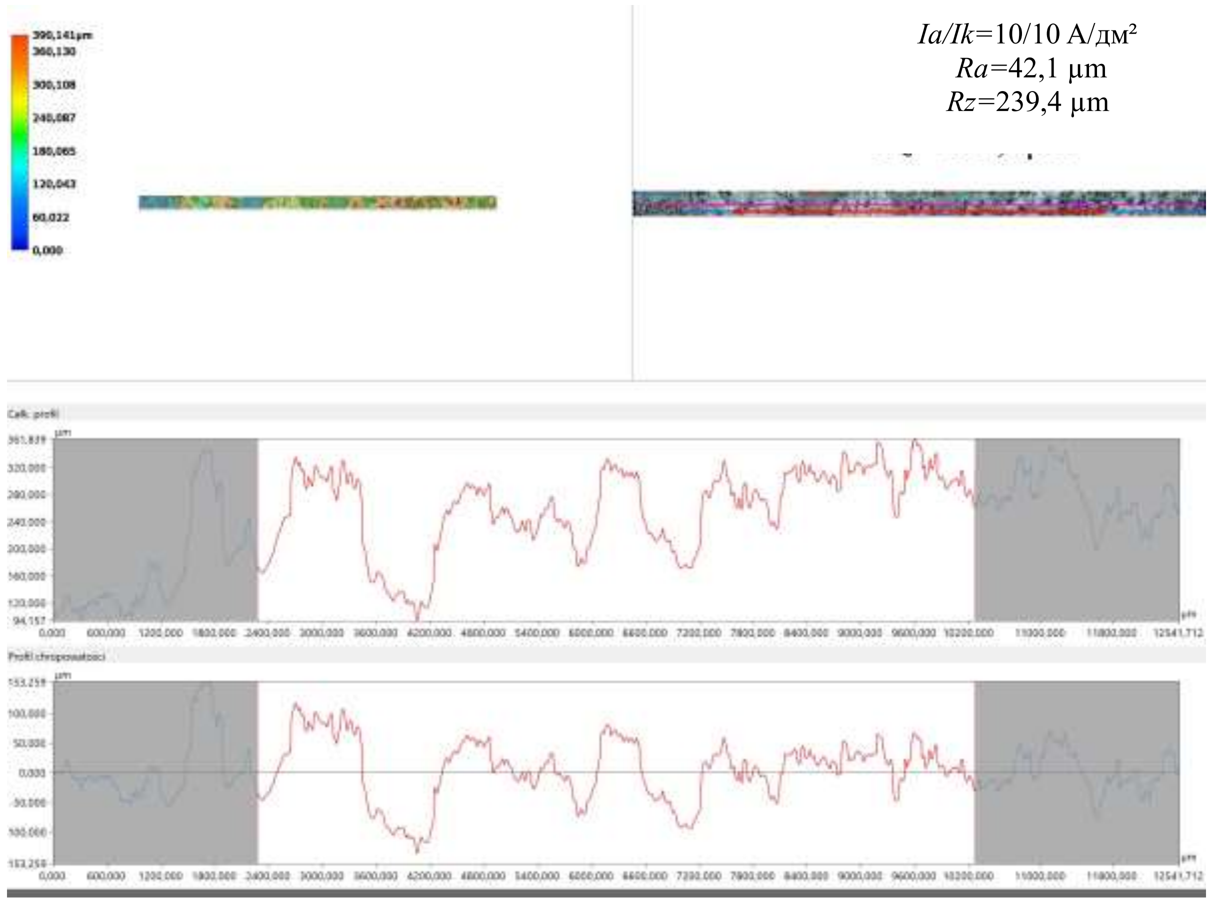


Figure 4 – Profilogramme of the coating synthesized according to mode № 5

Conclusions. As a result of the experiments, it can be noted that titanium-based coatings formed in alkaline electrolytes with hydroxylapatite and diatomite are porous. In addition, high surface roughness was established when forming it in an electrolyte with diatomite. It was found that adding diatomite to the electrolyte makes it possible to increase the roughness of the coatings to the value Rz=119,7 μm. A longer oxidation time of the titanium alloy in the electrolyte with diatomite leads to an increase in the roughness of the coatings. Thus, in 30 minutes of synthesis, coatings with Rz=119,7 μm are formed, and when applying surface treatment for 1 hour, the roughness of the coatings doubles.

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МОРФОЛОГІЯ ПОКРИТТІВ НА ТИТАНОВОМУ СПЛАВІ З ДОДАВАННЯМ БІОКОМПОНЕНТІВ

У даній роботі поширений метод плазмового електролітичного оксидування на титановому сплаві з введенням в покриття кальційвмісних компонентів і біодобавок у вигляді діатоміту. З метою підвищення біосумісності синтезованої поверхні розроблено робочі середовища та режими нанесення покриття. Дослідження стадійної природи ПЕО в таких електролітах дозволило прогнозувати властивості покриттів у майбутньому в залежності від вимог до їх шорсткості.

Ключові слова: *плазмове електролітичне окислення, анодне, катодне, лужне, гідроксилапатит, діатоміт, шорсткість, пористість.*