Using plasma electrolytic oxidation technologies in the manufacture of a strengthening surface with better biodesign

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Abstract. A promising method for changing the surface state of metals and influencing product design is plasma electrolytic oxidation (PEO) as one of the innovative surface treatment methods. The PEO method allows for a wide range of surface modifications, either by strengthening it or by changing its structural and morphological state. In the field of biomedical materials science, the creation of new implant materials with biocompatible, bioactive properties and high osseointegration is particularly relevant.

Titanium and zirconium alloys are characterized by an excellent combination of a complex of mechanical and chemical properties with inertness to a living organism, which is ensured by their ability to form a passive film on their surface. Such alloys are used in the field of implantology and for the manufacture of surgical instruments and implants. In order to increase osseointegration, the modification of the surface of such alloys with bioactive substances is positive, as well as the influence in the direction of modifying its design, which includes increasing the roughness and porosity of the surface. In this work, the PEO method was used for surface treatment of titanium and zirconium alloys. Experimental studies have established the correlation of the influence of treatment modes, such as the composition of the electrolyte and the ratio of current densities on the roughness and porosity of plasma electrolytically oxidized coatings at their optimal thickness. The developed alkaline electrolytes were additionally saturated with such biocomponents as diatomite and hydroxyapatite.

Keywords: Coating, Diatomite, Hydroxyapatite, Electrolytic plasma, Biocoating, Biocompatibility, Porosity, Thickness, Roughness, Titanium alloys, Zirconium alloys.

1 Introduction

The development industry needs new ideas that make it possible to produce bioproducts from harmless substrates or that can be dissolved, or that can be produced using harmless technology or equipment [1 – 4]. In modern life, the use of new, promising, innovative and environmentally friendly technologies in the fight for a clean environment is very relevant. Therefore, humanity is trying to develop "green technologies" in production [5]. Thus, "green technologies" have found their application in all areas of human activity and are developing rapidly.

Today, one of the priority areas of research is the production of nanosized metals or coatings of a wide range and different structural organization. There are many ways to coat metal surfaces to better strengthen the surface [6, 7]. An effective solution is to create coatings on the surfaces of these alloys by the plasma electrolytic method. The created coating is characterized by high adhesion to the surface of the alloys. This PEO method gives us the opportunity to independently control the process and create coatings with predetermined properties [8, 9].

One of the most popular and widely studied are titanium and zirconium alloys due to the combination of good mechanical and chemical properties with high antibacterial properties [10 – 12]. The use of nanoparticles to obtain unique properties is very popular for these alloys [13]. The development of new medical materials that must come into contact with the environment of a living organism is a particularly difficult task.

The paper shows a solution to the problem of high biocompatibility and bioactivity of titanium and zirconium alloys by using environmentally friendly technologies.

2 Literature Review

In biomedicine, an important problem is ensuring a strong connection of the coating on the surface to the metal framework of the prosthesis. Often, the strength of the connection between metal and plastic or ceramics created using traditional coating technologies does not meet the requirements [14]. It is known that the half-life of prostheses made of current bioinert materials is about 15 years. This period depends on their clinical use. Bioactive materials, such as titanium and zirconium alloys, allow the use of prostheses for much longer. However, they have mechanical limitations [15]. To solve this problem, it is necessary to optimize the surface, i.e. its depth dimensions. Even such good properties as biological inertness do not allow titanium alloys to osseointegrate with human cells. Thus, the surface of the titanium implant plays a very important role, after which it understands the speed of osseointegration and the success of implantation. Aleh Kurup, Pankaj Dhatrak, Neha Hasnis in their work considered several methods of modifying the surface of titanium alloys. The authors proved that mechanical methods such as acid etching and sandblasting, hydrogen peroxide treatment, acid treatment, nitride coatings, hydroxyapatite coatings, metal oxide coatings and silver coatings significantly increased the osseointegration of the surface of titanium alloys, as well as their biocompatibility, stability and antibacterial properties. An unsolved problem is the interaction of human cells with the surface that was subjected to modification [16]. In [17], the authors demonstrate that surface treatment that increases surface roughness leads to better wettability and biological activity of surfaces. They combined micro- and nanoscale surface modifications with peptides and bioactive compounds, which allowed inducing migration and differentiation of osteogenic cells with subsequent enhancement of mineral matrix formation, which accelerates the osseointegration process. In addition, such treatment made it possible to predict the avoidance of early and late implant failures caused by biofilm accumulation.

Zirconium metal is widely used in the chemical industry due to its high resistance to corrosion in aggressive environments. Zirconium is inert in biological environments, and this property allows it to be used in medicine as implants, in dentistry and traumatology, as well as for the manufacture of surgical instruments [18]. This is mainly due to the ability of zirconium alloys to form highly resistant and inert ceramics on their surface. Such properties make it widely demanded. The ability to modify zirconium oxide with ideal additives makes it very popular in various industries [19]. The promising application of zirconium alloys in medicine is also explained by their low modulus of elasticity, which allows reducing stress in joints using implants made of such alloys [20]. E. Rosado, E. Cañas, P. Recio, E. Sánchez, R. Moreno investigated the thermal insulation properties of zirconium coatings created by plasma spraying. They developed suspensions for the plasma spraying method [21]. In paper [22], the authors investigated the effect of induction heat treatment on the composition and mechanical properties, in particular the hardness and elastic modulus, of zirconium with oxide coatings. J. Musil, P. Karvánková and J. Kasl in their work [23] sputtered a zirconium-based Ni-Zr-N nanocomposite film onto a steel substrate. The authors found a high correlation between the film structure, the Ni content in the nanocomposite and the film properties. Therefore, modification of zirconium coatings with various components can lead to a strong interaction of zirconium elements with the introduced bioactive components, which opens up new possibilities in the direction of surface modification of zirconium alloys [23]. It is distinguished by particularly valuable properties in the field of implantology. M.M. Pylypenko, A.O. Drobyshevska and others in their work [24] investigated the properties of thermally oxidized zirconium in air. The authors found that this method allows to increase the surface roughness to a value of 0.1 μm. They found that prolonged oxidation with zirconium allows to increase the thickness of the coatings, but the integrity of the coating itself may be violated. Bannunah A.M. in his work [25] proves that ZrO_2-based nanomaterials demonstrate high antibacterial activity against various strains of bacteria, as well as excellent antioxidant activity. Such statements of the authors make it possible to establish that the improvement of the surface state of titanium and zirconium alloys has high prospects in the field of implantology. The choice of technology for morphological influence on the surface of light alloys is important.

The authors [8, 9, 11, 13, 26] point out the advantages of the plasma electrolytic oxidation method (PEO), as one that allows for wide regulation of coating application modes, and also stands out among others [6, 7, 21, 24] for its ability to create coatings with high adhesive bonds to the alloy surface, as well as acceptable mechanical properties.

3 Research Methodology

The growing demand for bioactive materials, which include titanium and zirconium alloys, is accompanied by a change in surface characteristics [27]. Studies of the surface of PEO coatings were associated with the determination of the thickness, porosity and roughness of the coatings, with special attention paid to the geometry of the surface in the corners, which are stress concentrators. Fractographic studies of the synthesized coatings were also carried out. The process of PEO synthesis happened in three stages. In the process of PEO synthesis, plasma electrolytic reactions occur between the electrolyte components and the sample. The development of the technology of plasma electrolytic oxidation and the study of biocoating were carried out on plate and round samples of titanium and zirconium alloys of grades ASTM B265 and Zr-2,5%Nb, respectively, with a total working area of 1 dm^2 (**Fig. 1**).

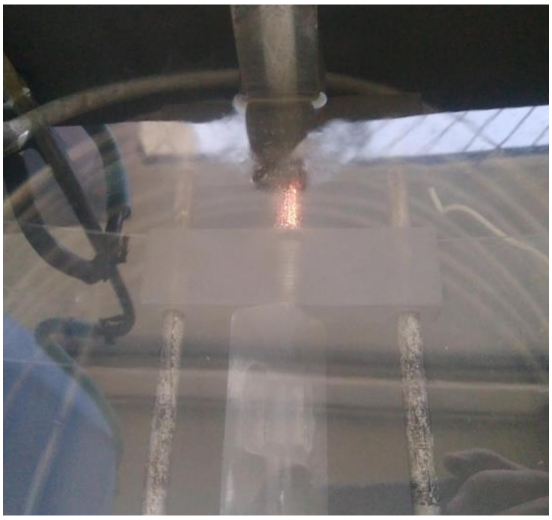


Fig. 1. Synthesis of oxide ceramic coating in spark discharge plasma on a titanium alloy sample

The working environment was a weakly concentrated alkaline solution of KOH and liquid glass based on distilled water. The concentration of alkaline components of the solution ranged from 3 g/l to 10 g/l of KOH and from 2 g/l to 10 g/l of liquid glass. The developed electrolytes were saturated with phosphates in the form of $Na_4P_2O_7$ and $Na_6P_6O_{18}$ (from 0,5 to 20 g/l).To improve the biological and antibacterial properties of the surface of titanium alloys, the synthesis of PEO coatings was carried out in alkaline electrolytes with the addition of hydroxyapatite and diatomite. Hydroxyapatite and diatomite components were added to the developed electrolytes at concentrations of 5 and 20 g/l, respectively. The electrolytes were constantly stirred by air supplied to the electrolytic bath by a compressor. After the synthesis process, the samples were immediately washed with distilled water and dried.

Metallographic studies were performed on microsections made using standard technology. Microanalysis was performed on a Microtech MMP-14C and MIM-10 microscope at different magnifications (×50…×400). The surface after PEO was examined using a Tagarno Prestige FHD controller XPlus microscope. Using the automatic measurement function, repeated measurements were performed on samples of the same shape. The magnification and illumination parameters, as well as three-dimensional coordinates, were reproduced automatically.

The surface morphology and its roughness were studied using profilograms obtained on a Keyence VHX 7000 three-dimensional laser scanning microscope; it was analyzed in accordance with DSTU ISO 4287:2012 by the following roughness parameters: Ra – arithmetic mean deviation of the profile and Rz – height of profile irregularities at 10 points.

The porosity of the coatings was determined by the hydrostatic method and also analyzed using surface photographs taken on a Tagarno Prestige FHD controller XPlus microscope.

4 Results and Discussion

Mann [28] proves the relevance of the use of functional biomaterials, discussing in detail the chemical principles and concepts of biomineralization and their properties. He identifies five main points of influence on the mechanism of biomineralization, including chemical, spatial, structural, morphological and constructive. Therefore, control of the thickness of the synthesized coatings becomes of particular importance.

PEO coatings were synthesized on titanium alloy according to the conditions presented in **Table 1**.

In an alkaline medium of 0,5 g/l KOH+0,5 g/l aqueous solution+0,5 g/l $Ca(OH)_2$+0,5 g/l $Na_4P_2O_7$+0,5 g/l $Na_6P_6O_{18}$, a coating was synthesized on a titanium alloy (**Table 1**, modes 3 – 6) at current ratios Ia/Ic from 10/10 A/dm^2 to 20/20 A dm^2. To saturate the electrolyte with phosphates, sodium pyrophosphate and polyphosphate were added to the working environment (**Table 1**, modes 1-2). The ratio of current densities was set 10/10 A/dm^2 and 20/20 A dm^2.

Table 1. Synthesis modes of titanium alloy

№ sample	t, min	Ia/Ic, A/dm^2	Electrolyte composition, g/l				
			KOH	liquid glass	$Ca(OH)_2$	$Na_4P_4O_7$	$Na_6P_6O_{18}$
1	60	20/20	0,5	0,5	0,5	0,5	0,5
2	60	10/10				0,5	0,5
3	30	10/10				-	-
4	20	10/10					
5	25	10/15					
6	25	20/20					

Sodium phosphate crystals are quickly dissolution in water. The molar mass of sodium polyphosphate is approximately twice that of sodium pyrophosphate, therefore, it requires more time and energy to introduce them into the coating. Thus, the synthesis time for coatings synthesized in such environments was determined to be longer compared to the synthesis of PEO-coatings on titanium alloy in environments that did not contain phosphates. The results of the values of coatings synthesized on titanium alloys are presented in **Fig. 2**.

Coatings formed on the basis of titanium for 25 min are characterized by a thickness of 12…13 μm. In addition, this characteristic of the coatings is affected by the current density. An increase in Ia/Ic led to the formation of coatings of greater thickness. This dependence is manifested in coatings synthesized by modes 1, 2, 5 and 6.

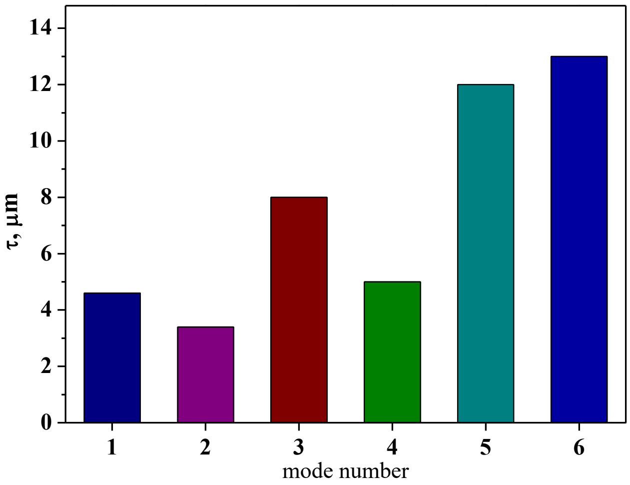


Fig. 2. Thickness of coatings on titanium alloy synthesized according to the modes in Table 1.

Coatings synthesized on a titanium surface in an electrolyte with diatomite are presented in **Fig. 3**. Coatings synthesized in electrolytes with diatomite are characterized by a significantly higher thickness compared to coatings synthesized without such a bioadditive. The possibility of the electrolyte medium influencing the coating thickness is obvious, as proven by experimental studies. Adding 20 g/l of diatomite to a weakly concentrated alkaline solution allows to increase the thickness of the PEO-coating to an average value of 87 μm, which is more than 10 times higher compared to coatings synthesized without diatomite (**Fig. 3 *a***).

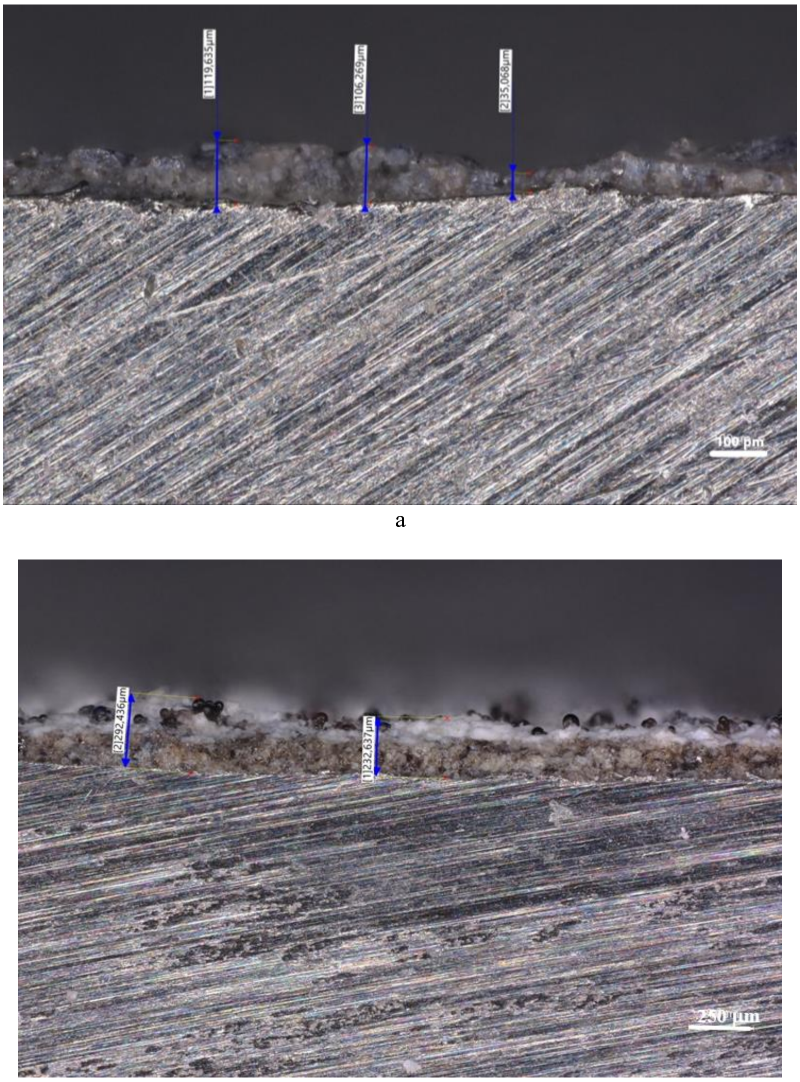
The influence of the current density ratio Ia/Ic is very noticeable when synthesizing coatings in a environment with diatomite, since it was found that the thickness of coatings that were synthesized in the same time, namely 30 min, for Ia/Ic= 20/20 A/dm^2 was 263 μm. (**Fig. 3 *b***). The main component of diatomite is silica SiO_2 (80 – 95%). In an aqueous solution in the presence of alkalis KOH or $Ca(OH)_2$, a neutralization reaction occurs:

$$SiO_2 + 2KOH = K_2O(SiO_2) + H_2O$$

$$SiO_2 + Ca(OH)_2 \rightarrow CaSiO_3 + H_2O$$

As a result, potassium and / or calcium silicates are formed. The alkaline solution also includes liquid glass, which consists of an aqueous-alkaline solution of sodium silicates $Na_2O(SiO_2)_n$ and / or potassium $K_2O(SiO_2)_n$.

Thus, when diatomite is added, the alkaline electrolyte is highly saturated with silica, the atoms and molecules of which are introduced into the coating in the plasma environment of spark discharges.



a

b

Fig. 3. Thickness of coating synthesized based on ASTM B265 alloy in an environment 20 g/l KOH+20 g/l l.g.+20 g/l $Na_4P_2O_7$+20 g/l $Na_6P_6O_{18}$+ 20 g/l diatomite with the ratio of current densities: a – Ia/Ic=5/5 A/dm^2 and synthesis time t=30 min; b – Ia/Ic=10/10 A/dm^2 and synthesis time t=30 min

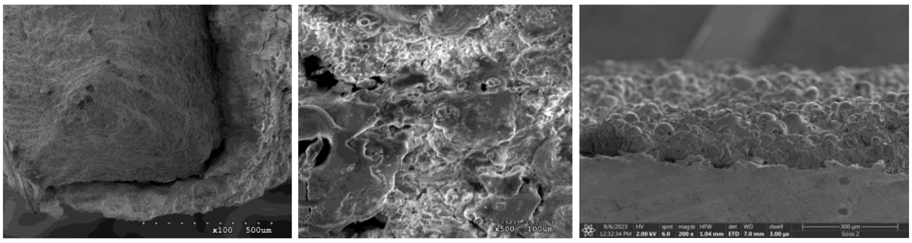
The synthesis of coatings on zirconium alloy showed that their thickness in environments containing alkali (KOH), liquid glass and CrO$_3$ reaches values from 60 to 160 µm (**Table 2**). The synthesis of PEO coatings on zirconium alloy in an electrolyte of 10 g/l KOH and 15 g/l liquid glass at a ratio of Ia/Is = 20/20 A/dm^2 ensures the formation of coatings with a sufficiently high microhardness (16 GPa).

Table 2. Treatment modes for coatings on zirconium alloy

№ sample	Electrolyte composition, g/l			I_a/I_c, A/dm^2	t, min	t, мкм
	KOH	liquid glass	GrO$_3$			
1	5	5	-	14/20	30	70 … 100
2	10	15	-	20/20	40	70 … 130
3	10	15	0,1	20/20	30	60 … 160
4	3	2	-	20/20	30	20 … 50

The introduction of 0,1 g/l of chromium oxide CrO$_3$ into the electrolyte makes it possible to synthesize a coating on a zirconium alloy of greater thickness (90...160 µm), however, the microhardness of such a coating decreases to 10 GPa.

Coatings synthesized by the plasma electrolytic oxidation method have low through-hole porosity. This is explained by the fact that the coating is synthesized at high temperatures, as a result of which the pores are melted. **Fig. 4** shows the fracture fractographs of the synthesized zirconium alloy.



a b c

Fig. 4. PEO-coating on zirconium alloy: zirconium alloy with coating (a); PEO-coating (b); PEO-coating on titanium alloy (c)

Analysis of the cross-section of the coating showed good repeatability of the shape of the base metal (**Fig. 5**). In addition, these photographs show that the coatings are rough. It should be noted that highly rough surfaces contribute to its rapid interaction with the muscle tissues of a living organism and the absence of capsule formation, the presence of which increases the percentage of rejection. Therefore, in implantology, a highly developed implant surface has a positive value.

The corners are stress concentrators, as a result of which a larger breakdown of the semiconductor region occurs in these areas and in these places there may be thinning or, conversely, thickening of the coatings. Having studied such a section of the samples, it was found that the thickness of the biocoating at the corners of the sample, which was treated in an electrolyte of 20 g/l KOH + 20 g/l l.g. + 20 g/l

$Na_4P_2O_7$ + 20 g/l $Na_6P_6O_{18}$ + 20 g/l diatomite by the PEO method at Ia/Ik = 5/5 A/dm^2 for 30 min, was on average 119,7 µm. The largest thickness was 148,476 µm, and the smallest was 89,422 µm.

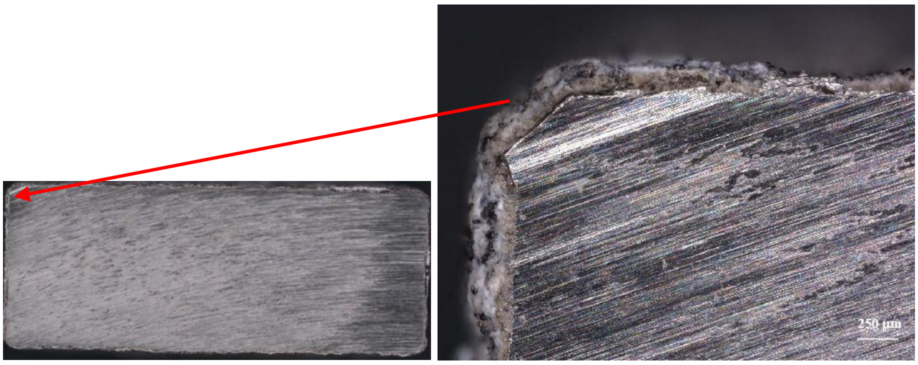


Fig. 5. Cross-sectional image of a coating synthesized in an electrolyte: corner view of the sample

Comparing the thicknesses of coatings synthesized with the same regime on a flat surface, we found that the difference in thickness values is small, which is positive.

The surface of the coatings obtained as a result of PEO is covered with craters and pores and is characterized by a rather high roughness. This is explained by the peculiarities of the synthesis process, which is characterized by the constant formation of breakdown channels and their disappearance throughout the entire PEO time. Studies of surface morphology and its roughness made it possible to establish that coatings synthesized in an electrolyte with diatomite (electrolyte 20 g/l KOH+20 g/l l.g. +20 g/l $Na_6P_6O_{18}$+20 g/l $Na_4P_2O_7$ + 20 g/l diatomite) have a higher surface roughness (from 40 to 239 µm), while coatings synthesized in an electrolyte of the composition 20 g/l KOH+20 g/l rs+20 g/l $Na_6P_6O_{18}$+20 g/l $Na_4P_2O_7$ have a roughness within 28…100 µm. To promote the osseointegration process, the surface of ceramic coatings must be highly porous.

Coatings synthesized in electrolytes of different composition differ in their external characteristics. With longer treatment, the surface porosity increases significantly. Thus, coatings synthesized in an electrolyte without the addition of hydroxyapatite are characterized by the formation of larger but smaller craters on the surface. Coatings synthesized in an electrolyte to which hydroxyapatite was added formed with a larger number of craters, but the size of their opening is somewhat smaller.

5 Conclusions

The study of the thickness of PEO coatings makes it possible to establish the influence of current densities on the thickness. In an electrolyte of higher concentration, a coating of smaller thickness is formed due to the greater value of energy spent on reserving the system for plasma-chemical reactions. Synthesis in an electrolyte consisting of KOH, liquid glass and $Ca(OH)_2$ requires a smaller energy reserve of the system, so the coating in this case is obtained of greater thickness.

It was established that at the lowest optimal current density of 10/10 A/dm^2 and the shortest oxidation time, coatings with a minimum thickness of 5 μm are formed on a titanium alloy. If the PEO process is continued for another 10 min, coatings with a thickness of 8 μm are obtained. The introduction of sodium pyrophosphate and polyphosphate into the electrolyte significantly reduces the thickness of the coating.

So, according to the results of the conducted research, it was found that adding diatomite to the electrolyte makes it possible to increase it by 5 times.

In this work, it was found that the duration of treatment affects the surface roughness. Thus, coatings that were treated twice as long (60 min versus 30 min) have a surface roughness 5 times greater.

It was found that the highest value of open porosity of 0,75% is characteristic of coatings synthesized in the electrolyte 0,5 g/l KOH + 0,5 g/l l.g. + 0,5 $Ca(OH)_2$ + 0,5 g/l $Na_4P_2O_7$ + 0,5 g/l $Na_6P_6O_{18}$ and the highest water absorption is characteristic of coatings formed in the electrolyte with diatomite. In addition, the advantage of using diatomite is also its antibacterial properties.

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