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Modification of the surface of titanium alloys by the synthesis of coatings by the PEO method in alkaline electrolytes saturated with diatomite

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Abstract. One of the most promising directions of modern materials science is the search for methods of improving the biocompatibility properties of metals used in implantology, which will allow to reduce the percentage of rejection of implants by the living organism. Therefore, it is promising to use processing methods to change the state of the surface of metals due to surface modification, which includes the method of plasma electrolytic oxidation. The main goal of this work was to develop a technological process for obtaining coatings with higher biocompatibility compared to the base metal due to the introduction of natural components into the coating. The presence of elements in biocoatings and their quantity was determined using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS), which allowed for targeted analysis of the surface of the samples. The elemental composition of coatings synthesised on the basis of titanium alloy in alkaline electrolytes based on KOH, liquid glass of calcium hydroxide, sodium polyphosphate and sodium pyrophosphate with the addition of hydroxyapatite and diatomite was researched in the work. A direct relationship between the composition of the electrolyte and the Ca/P ratio was established. It has been proven that biocoatings synthesised in alkaline solutions by the PEO method satisfy the conditions of biocompatibility. It has been established that in an environment containing alkalis and phosphates, coatings are synthesised for which Ca/P = 1.21. The introduction of hydroxyapatite into the electrolyte leads to an increase in the Ca/P ratio to a value of 1.28, and an increase in the concentration of the electrolyte and the addition of diatomite increases this ratio to a value of 1.57. The obtained results establish the possibility of a wide range of regulation of the Ca/P ratio in the biocoating

Keywords: elemental analysis; biocompatibility; chemical properties; synthesis modes; coating composition

Introduction

Titanium alloys are utilised for fracture fusion and splicing, as well as for knee, hip, and shoulder prosthesis. J. Jakubowicz (2020) described that high biocompatibility is due to the ability of titanium to form a protective oxide layer on its surface in a fraction of a second, thanks to which it does not corrode and does not release free metal ions that can cause pathological processes around the implant, and the tissues surrounding the prosthesis remain free of metal ions. T. Hanawa (2022) note that the PEO coating on titanium alloys is characterised by high bioactivity and biocompatibility. They developed a new graphical method for evaluating the porosity of PEO oxide films, which helps predict their bioactivity. O. Povstyanoy *et al.* (2024) describe in his works the effective use of coatings with a wide range of porosity. Y. Gu *et al.* (2018) point out that the main disadvantages of titanium alloys are poor machinability, high coefficient of friction, relatively low modulus of elasticity, and for implantology, resistance to marginal corrosion, low chemical activity and low adhesion. These

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facts can lead to bone resorption around them. M. Fazel *et al.* (2019) pay attention to the prospect of using compositions with antimicrobial properties of the surface of materials in implantology. An effective method of preventing this effect is the preliminary application of a bactericidal layer to the surface of the material.

J. Zhou *et al.* (2019) pointing on possible solution to this problem is superficial surface modifications that improve osseointegration of implants or reduce bacterial infection. Considering the above the use of compositions with antimicrobial properties in bone plastic is promising. N.Y. Imbirovych *et al.* (2023) examine the plasma-electrolytic oxidation (PEO) technique as a possible means of improving light alloy's surface characteristics. They found that as a result of a 4-fold increase in the concentration of electrolyte components and the addition of diatomite (20g/l), the coating synthesis process is stabilised and coatings with higher roughness (3-4 times) and porosity (1.9 times) are formed compared to coatings synthesised in an electrolyte without diatomite. T. Li *et al.* (2022) investigated PEO coatings corrosion properties synthesised on titanium alloys. The authors established that the change in the corrosion state is influenced by the coatings structural flaws and porosity caused by the peculiarities of the technological process. F. Malekmohammadi *et al.* (2020) determined the influence of nanoparticles on the thickness of PEO coatings. They observed that, in contrast to the coating that was synthesised in PEO electrolyte containing cerium (III) chloride, the nanostructured cerium dioxide/titanium composite formed from functions as a barrier to porosity growth from nitrate salt during the PEO process. It also shows improved corrosion resistance in 0.1 M HCl solution at ambient temperature and stronger impedance resistance at lower frequency.

X. Yang *et al.* (2019) imply that one aspect of the PEO technique is the ability to modify the electrolyte and working substance composition to regulate the mechanical and physical characteristics of coatings. To increase the biocompatibility of implants, it is important to form porous coatings with increased roughness on the surface. V. Subha *et al.* (2023) modified the surface of titanium alloys with diatomaceous earth. They showed that the introduction of diatomaceous earth particles leads to an increase in the mechanical and thermal properties of titanium alloys. Diatoms are naturally occurring silica and could be a potential source of silicon for the electrolyte used in the PEO method. That is why there is great interest in introducing such a natural component into the structure of oxide coatings on a titanium alloy.

The purpose of this work is to modify the surface of titanium alloys by applying coatings with high porosity and antimicrobial properties to their surface.

Materials and methods

In this work, a combination of SEM and EDS was used to investigate the elemental composition of the coatings produced on the surface of titanium alloys. With the help of SEM analysis, was got a qualitative image of the coatings. Under a microscope, specimens of Grade 5 titanium alloy were shaped like cylinders, measuring 25 mm in diameter and up to 10 mm in thickness. The goal used EDS was research composition of coatings that are synthesised into various electrolytes such as: 20 g/l KOH+20 /l liquid glass+20 g/l sodium pyrophosphate+20 g/l sodium polyphosphate+20 g/l diatomite, 5 g/l KOH+5 g/l liquid glass+5 g/l sodium pyrophosphate+5 g/l sodium polyphosphate+5 g/l hydroxyapatite and 5 g/l KOH+5 g/l liquid glass+5 g/l sodium pyrophosphate+5 g/l sodium polyphosphate. The current density from the anode to the cathode (Ia/Ic) was equal to 5/5 A dm^2. The time of the PEO process was 10 min.

Titanium alloys of Grade 2 and Grade 5 were used in the work. The coating was synthesised by the PEO method in the anode-cathode mode, where the sample was the anode and the bath with the electrolyte was the cathode. The IMPELOM installation, which works in alternating anode-cathode mode, was used as a power source. The current is applied alternately to the anode and cathode. Spark discharges that result from the current flowing through the sample in the electrolyte solution guarantee a high temperature in the surrounding area. Temperature influences the introduction of electrons into the oxide layer at the spark plug locations. J. Jovović *et al.* (2012) studied the temperature of the plasma channel and noted that it varies from 4000 K to 33000 K. These thermodynamic circumstances cause electrons to be injected into the oxide layer from the electrolyte.

The synthesis of coatings on titanium alloys was carried out in three environments: 5 g/l KOH+5 g/l liquid water (l.g.)+5$Ca(OH)_2$+5 g/l $Na_4P_2O_7$+5 g/l $Na_6P_6O_{18}$, 5 g/l KOH+5 g/l l.g.+5$Ca(OH)_2$+5 g/l $Na_4P_2O_7$+5 g/l $Na_6P_6O_{18}$+1 g/l HPA and 20 g/l KOH+20 g/l l.g.+20 g/l $Ca(OH)_2$+20 g/l $Na_4P_2O_7$+20 g/l $Na_6P_6O_{18}$+20 g/l diatomite. The ratio of current densities and processing time for all the studied systems were the same, respectively: Ia/Ic = 5/5 A/dm^2, t = 10 min. A Phenom XL scanning electron microscope (SEM) with automatic measurement, equipped with a backscattered electron detector (BSED) and 3D roughness reconstruction, was used to analyse the coatings that were manufactured in various modes. Additional Elemental Mapping and Line Scan software allows for further elemental distribution analysis. The technique of energy dispersive spectroscopy (EDS) analyses the X-ray radiation produced by electrons from an electron beam interacting with a sample. Combination of SEM and EDS makes it possible to assess the surface of the studied samples in detail and determine their elemental composition. Samples of Grade 5 titanium alloy, which were viewed under a microscope were cylindrical in shape, measuring 25 mm in diameter and up to 10 mm in thickness.

Results

The chemical composition of the coating created by plasma-chemical reactions is crucial for guaranteeing the coating's biocompatibility. This depends on the base on which the coating is synthesised, alloy grade, and electrolyte components. For the development of coatings characterised by high biocompatibility, a necessary condition is that the composition of the coatings is as close as possible to bone. Bone consists of minerals, organic substances and water (Fig. 1). Therefore, the working electrolytes were saturated with phosphates and calcium salts. Thus, polyphosphate is an inorganic polymer, which, due to its biocompatibility and low toxicity, is a biomedical compound of hydroxyapatite, the main component of bone tissue. To saturate the electrolyte with calcium components, calcium hydroxide was introduced into the working environment, which is soluble in water and loses moisture at temperatures above 580°C, turning into calcium oxide.

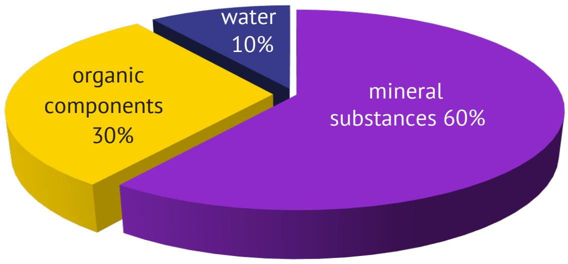


Figure 1. *The components that make up a bone*

Source: *developed by the author*

Diatomite is a non-metallic clay mineral, the main chemical composition of which is amorphous silica (80-95%), which consist small amounts of montmorillonite, kaolinite, quartz and other clay impurities and organic substances. In an aqueous solution (electrolyte) in the presence of alkalis KOH or $Ca(OH)_2$, a neutralisation reaction occurs:

$$SiO_2 + 2KOH \rightarrow K_2O(SiO_2) + H_2O; \quad (1)$$

$$SiO_2 + CaOH_2 \rightarrow CaSiO_3 + H_2O. \quad (2)$$

As a result, potassium and/or calcium silicates are formed. Due to its high porosity, diatomite has good absorption. In addition, diatomite has antibacterial properties.

To establish the biocompatibility of coatings, the Ca/P ratio is used, which in hydroxyapatite $Ca_5[OH(PO_4)_3]$ (the main component) is 1.67. M. Tzaphlidou (2005) shows that there is a small variation in the Ca/P ratio between the bones of men and women between the ages of 15 and 55. In adults (from 21 to 120 years old), the Ca/P ratio in bones is 0.79...1.65%. For children, this ratio slightly increases. In general, the difference varies within 0.34...2.14%. So, elemental analysis of bio-coatings makes it possible to establish the interaction of the sample surface with the components of the electrolyte and understand the reactivity under thermodynamic conditions. Therefore, the amount of phosphorus and calcium in the electrolytes used in this work was first determined.

Electrolyte composition 5 g/l KOH+5 g/l r.s.+5 $Ca(OH)_2$+ +5 g/l $Na_4P_2O_7$+5 g/l $Na_6P_6O_{18}$ contains phosphorus:

$$n = \frac{m}{M}. \quad (3)$$

The content of phosphorus in sodium polyphosphate, which is contained in this electrolyte, was calculated in the amount of 5 g/l. The volume of distilled water in the bath is 20 liters, therefore, sodium polyphosphate is contained in the electrolyte 100 g.

$$n(P) = \frac{100\,g}{102\frac{g}{mol}} = 0.9804\,mol. \quad (4)$$

The amount of phosphorus in sodium pyrophosphate is equal to:

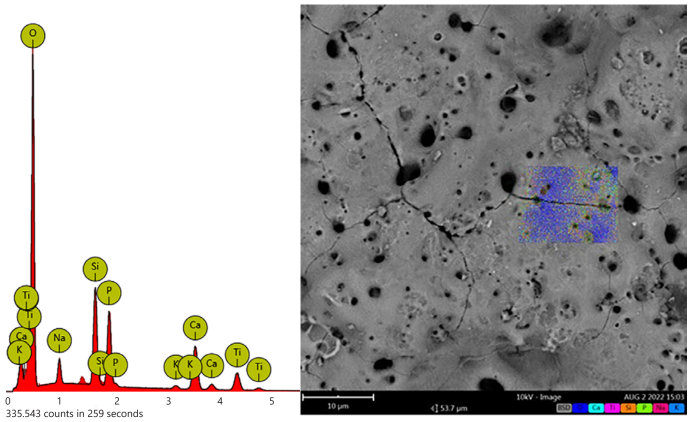
$$n(P) = 2n(Na_4P_2O_7); \quad (5)$$

$$\frac{m(P)}{266\frac{g}{mol}} = \frac{200\,g}{266\frac{g}{mol}} = 0.7519\,mol. \quad (6)$$

Therefore, 1.7323 mol of all phosphorus is contained in this electrolyte. The amount of calcium in $Ca(OH)_2$ is:

$$n(Ca) = \frac{100\,g}{74\frac{g}{mol}} = 1.3514\,mol. \quad (7)$$

Therefore, the Ca/P ratio in the electrolyte is 0.5 g/l KOH+0.5 g/l r.s.+0.5 $Ca(OH)_2$+0.5 g/l $Na_4P_2O_7$+0.5 g/l $Na_6P_6O_{18}$ according to calculations is 1.3514/1.7323 = 0.7801. Based on the ratio of current densities Ia/Ik=5/5 A/dm^2, Figure 2 presents the elemental analysis results of the coatings produced in the electrolyte of 5 g/l KOH+5 g/l r.s.+5Ca(OH)2+5 g/l $Na_4P_2O_7$+5 g/l $Na_6P_6O_{18}$. The results were obtained using a scanning electron microscope. According to the presented elemental analysis, coatings were obtained that contain the largest amount of oxygen (69.72 at.%), which is released from water, which in turn is ionised in the place of intense spark formation (or arc discharge plasma) (Table 1).



a *b*

Figure 2. *Elements in the coating synthesised on a titanium alloy (a); arrangement of elements present on the surface of the coating synthesised (b)*

Note: *synthesis mode: 5 g/l KOH+5g/l l.g.+5Ca(OH)$_2$+5 g/l Na$_4$P$_2$O$_7$+5 g/l Na$_6$P$_6$O$_{18}$, Ia/Ic = 5/5 A/dm^2, t = 10 min*

Source: *developed by the author*

Table 1. *Quantitative content of elements in the coating synthesized in the electrolyte 5 g/l KOH+5 g/l l.g.+5Ca(OH)$_2$+5 g/l Na$_4$P$_2$O$_7$+5 g/l Na$_6$P$_6$O$_{18}$, Ia/Ic = 5/5 A/dm^2, t = 10 min*

Element Symbol	Atomic Conc.	Weight Conc.
O	69.72	51.28
Ca	8.18	15.07
Ti	4.97	10.94
Si	7.50	9.69
P	6.74	9.60
Na	2.38	2.51
K	0.51	0.91

Source: *developed by the author*

It should also be noted that in a sufficient electrolyte, the potassium content becomes:

$$n = \frac{100\ g}{39\frac{g}{mol}} = 2.57\ mol. \qquad (8)$$

Comparing the amount of calcium in the electrolyte with the amount of potassium, a value of 1.9 was determined, which represents a larger proportion of potassium ions. However, elemental analysis showed that the coating contains 16 times more calcium ions than potassium, which is explained by the higher water solubility of KOH. In turn, Ca ions are heavier and less soluble in water, and therefore, being in the boundary region, they are introduced into the surface, thereby modifying it. Studies of the phasing of the PEO process have established that the system, which does not contain calcium hydroxide, but only consists of KOH and liquid glass in the weight equivalent of 5 g/l each, requires a voltage of approximately 40 V to ensure the process of stable synthesis of the titanium alloy's surface oxide layer, while to ensure the synthesis of a bio-coating in an electrolyte containing KOH, sodium silicate (liquid glass) and Ca(OH)$_2$, respectively, 5 g/l, the system requires an increase in the operating voltage, which ensures uniform growth of the oxide on the surface to a value of 140 V, which on 100 times more than the coating synthesis in an electrolyte with a lower concentration.

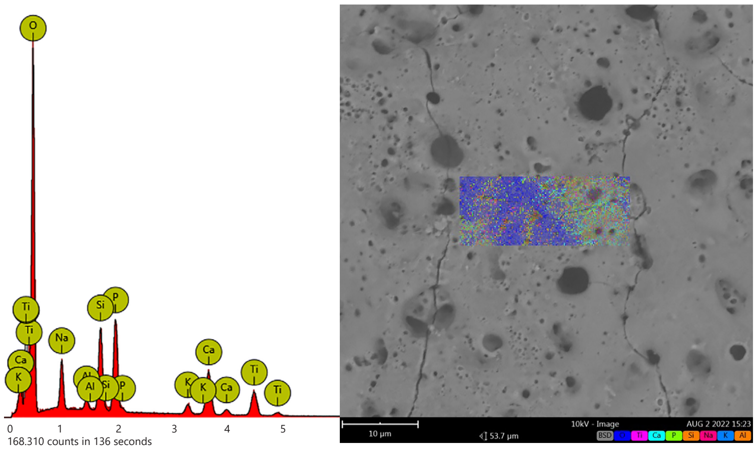
Thus, this fact indicates that the system needs a larger reserve of energy to ensure the state to which the system tends according to the principle of Le Chatelier-Brown (Gibbs, 1878), who proved that every system tends to balance. A slightly different effect was obtained when analysing the content of sodium ions in the electrolyte and in the coating synthesised in it. According to calculations of the amount of sodium ions in the electrolyte, the following was found: sodium ions are contained in liquid glass, which is sodium silicate Na$_2$O(SiO$_2$)n, sodium pyrophosphate, and sodium polyphosphate. Therefore, n(Na) (liquid glass) = 4.35 mol, n(Na) (Na$_4$P$_2$O$_7$) = 1.07 mol, n(Na) (Na$_6$P$_6$O$_{18}$) = 1.45 mol. Its total amount in the working electrolyte is 6.87 mol. While the coating of sodium ions contains only 2.38 at.%. Sodium dissolves quite well in water. However, comparing the obtained values of the amount of such components in the electrolyte and in the coating as potassium and sodium, it can be noted that the potassium in the coating is 5 times less than in the electrolyte, and the amount of sodium deposited on the modified surface by the PEO method is almost three times smaller.

The amount of silicon is related in the following way. The number of silicon ions in the electrolyte is:

$$n = \frac{100\ g}{28\ \frac{g}{mol}} = 3.57\ mol. \quad (9)$$

According to the carried out elemental analysis, its amount in the coating is 7.50 at.%. Unlike sodium and potassium ions, silicon is present in the base of the produced metal, which is why its abundance in the coating has increased. From the obtained result, it was established that the coating mainly contains oxides, which upon interaction with the titanium matrix form TiO_2 in various crystal modifications. The resulting titanium-based ceramics also contain a sufficient amount of calcium and phosphorus, the ratio of which in the coating is Ca/P = 1.21.

The results of research into the elemental composition of coatings in hydroxyapatite environments are shown in Figure 3.



a *b*

Figure 3. *Elements in the coating synthesised on a titanium alloy (a); distribution of elements on the surface of the coating synthesised (b)*

Note: *synthesis mode: 5 g/l KOH+5 g/l l.g.+5Ca(OH)$_2$+ 5 g/l Na$_4$P$_2$O$_7$+5 g/l Na$_6$P$_6$O$_{18}$+1 g/l HPA, Ia/Ic = 5/5 A/dm^2, t= 10 min.*

Source: *developed by the author*

Already from the obtained spectrogram, an increase in the number of potassium elements. Following a quantitative examination of the calcium and phosphorus contents in the hydroxyapatite working electrolyte, it was discovered that in the salt $Ca(OH)_2$:

$$n(CaOH_2) = \frac{100\ g}{40+16\cdot2+1\cdot2\left(\frac{g}{mol}\right)} = 1.3514\ mol. \quad (10)$$

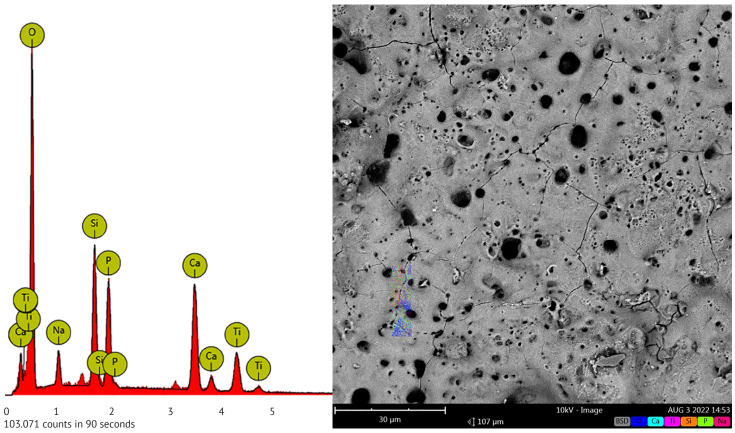
The calcium content in the electrolyte with hydroxyapatite is 1.5506 mol. In the coating, its content is 7.06 at.% and 12.87 wt.% (Table 2). Furthermore, by comparing the calcium and phosphorus contents of the coating that formed in the electrolyte with and without hydroxyapatite, it was found that the phosphorus content increased to 7.17 at.% against 6.74 at.% in the electrolyte that has 0.2 mol more calcium due to the introduction of hydroxyapatite, while the calcium content in the coating decreased by approximately 1 at.%. At the same time, the phosphorus content in the electrolyte without hydroxyapatite is 5.37 mol, and in the electrolyte containing HPA is 5.97 mol. Calculations showed that the Ca/P ratio in these coatings is 1.28.

Table 2. *Quantitative content of elements in the coating synthesised in the electrolyte 5 g/l KOH+5 g/l l.g.+5Ca(OH)$_2$+5 g/l Na$_4$P$_2$O$_7$+5 g/l Na$_6$P$_6$O$_{18}$+1 g/l HPA, Ia/Ic = 5/5 A/dm^2, t = 10 min*

Element Symbol	Atomic Conc.	Weight Conc.
O	68.12	49.53
Ti	5.95	12.95
Ca	7.06	12.87
P	7.17	10.09
Si	5.62	7.17
Na	4.05	4.23
K	1.24	2.21

Source: *developed by the author*

Analysis of the elemental composition of coatings that were synthesised in the composition electrolyte 20 g/l KOH+20 g/l l.g.+20g/l $Ca(OH)_2$+20g/l $Na_4P_2O_7$+20g/l $Na_6P_6O_{18}$+ 20g/l diatomite for 10 minutes is presented in Figure 4. The presence of oxygen ions under this regime is 61.61 at.%, while a slight decrease in oxygen ions in the coating is observed (Table 3).



a *b*

Figure 4. *Elements in the coating synthesised on a titanium alloy (a); distribution of elements on the surface of the coating synthesised (b)*

Note: *synthesis mode: 20 g/l KOH+20 g/l l.g.+20Ca(OH)$_2$+20 g/l Na$_4$P$_2$O$_7$+20 g/l Na$_6$P$_6$O$_{18}$+20 g/l diatomite, Ia/Ic = 5/5 A/dm^2, t = 10 min.*
Source: *developed by the author*

Table 3. *Quantitative composition of the coating's components made in the electrolyte 20 g/l KOH+20 g/l l.g.+20Ca(OH)$_2$+20 g/l Na$_4$P$_2$O$_7$+20 g/l Na$_6$P$_6$O$_{18}$+20 g/l diatomite, Ia/Ic = 5/5 A/dm^2, t = 10 min*

Element Symbol	Atomic Conc.	Weight Conc.
O	61.61	41.9
Ca	13.95	23.36
Ti	7.82	15.64
Si	7.65	8.98
P	6.62	8.57
Na	2.35	2.26

Source: *developed by the author*

It is also worth noting that the coating synthesised in these modes consists of almost twice as much calcium with an almost unchanged amount of phosphorus. This effect confirms the fact of higher absorption of coatings synthesised in an electrolyte with diatomite.

The biocompatibility of coatings generated in an electrolyte of 20 g/l KOH+ 20 g/l l.g.+20Ca(OH)$_2$+ + 20 g/l $Na_4P_2O_7$+ 20 g/l $Na_6P_6O_{18}$+ 20 g/l diatomite is evaluated by analysing the ratio of Ca/P elements, which is 1.57.

a *b* *c*

Figure 5. *The coating synthesised in the electrolyte 20g/l KOH+20g/l l.g.+20g/l Ca(OH)$_2$+20g/l Na$_6$P$_6$O$_{18}$+20g/l Na$_4$P$_2$O$_7$+20g/l diatomite*
Source: *developed by the author*

This result is the most acceptable for the conditions of biocompatibility. As Figure 5 illustrates, the addition of diatomite to the electrolyte causes coatings with increased porosity and roughness to form on the titanium alloy's surface.

Discussion

The properties of the surface of materials have a decisive influence on the working properties of the product. L. Markashova *et al.* (2019) indicate the modification of the metal surface with metal-ceramic coatings by spraying. Studies were conducted into the structural-phase state of cumulative-detonation sprayed coatings. The dislocation density of these coatings is found to be uniformly distributed in their matrix, the substructures are significantly dispersed, and a nano-sized strengthening phase is formed. V. Korzhyk *et al.* (2024) determined the regularities in the interrelation between the strength and crack resistance characteristics of functional metal-ceramic coatings on metal parts and their structural and phase properties, taking into consideration the structural requirements that provide the necessary combination of strength and crack resistance properties. Is relevant to study the factors and reasons behind how technological modes of the processing method (PEO) affect specific product attributes, specifically the material's surface layer under study. The authors researched the mechanism of formation of hydroxyapatite coating on Grade 5 titanium alloy under combined treatment. It is noted that this treatment aids in the expansion of the hydroxyapatite phase, which leads to an increase in the biocompatibility of the surface of the titanium alloy.

A. Azmat *et al.* (2023) believe that modification of the titanium alloy surface can significantly affect the process and quality of osseointegration. P. Pesode & S. Barve (2021) note that the biological aspect of the interaction of the vitality of the organism's tissue with the non-biological environment depends on the modification of its surface, for example, extending the oxide film's thickness, giving the surface of the material roughness and texture. X. Li *et al.* (2018) found that coatings obtained under potentiostatic conditions show better wear resistance. They found that the wear rate of such coatings is approximately 10 times lower than that of galvanostatic coatings due to the formation of low porosity coatings, because when the size of the microdischarges can be controlled in the potentiostatic mode. Ł. Maj *et al.* (2024) determined the electrolyte's influence, electrical modes on the microstructures and composition of the resulting layers. In their work, the authors discussed in detail the properties of the obtained coatings and gave examples of their applications.

M. Molaei *et al.* (2021) highlight the importance of figuring out why specific coating qualities are impacted by PEO technology modes. The authors discovered that enhancing solutions with specific sized particles can help PEO coatings perform better. The addition of ZrO_2 particles to the electrolyte was found by the researchers to have a good influence on mechanical and chemical properties, including resistance to oxidation of PEO oxide coatings formed on titanium and its alloys, biological processes, wear and corrosion.

G. Montes-Hernandez & F. Renard (2020) note that integration with bone tissue can be improved and enhanced by the presence of bioactive materials on the surface, which also include calcium phosphate-containing materials. The authors research identifies unique chemical pathways to help better explain the creation of amorphous calcium phosphate phases and their subsequent transition into brushite or hydroxyapatite nanocrystals under abiotic circumstances. These paths have relevance in both natural settings and a wide range of technology applications. I. Zglobicka *et al.* (2019) think that diatom frustules are ideal model systems for manufacturing materials and gadgets using biomimicry. They used nano-X-ray computed tomography (XCT) to non-destructively visualise the diatom *Didymosphenia geminata's* frustule structure. The authors' biomimetic strategy serves as a proof of concept for upcoming advancements in production scaling based on the unique characteristics of microorganisms. The research of M. Ghobara *et al.* (2024), showed that diatom frustules are characterised by a high ability to absorb the environment due to a highly porous structure. They determined through a combined theoretical and experimental approach their mechanical properties, such as Young's modulus, which was estimated at 31.8 GPa. Research results obtained by L. Li *et al.* (2019) indicate the promotion of early osteogenesis and osseointegration of porous surfaces. They point out that this kind of structure might promote early in vivo bone integration and strengthen the link between implants and bone. V. Subbotina *et al.* (2022) research of a synthesised coating on an aluminium alloy makes it possible to determine the impact of adding hexametaphosphate to an alkaline silicate electrolyte on coating thickness. The thickness formation rate, according to the authors, is 0.9 μm/min when hexametaphosphate is present and 0.7 μm/min when it is not. Regarding the phase composition, no discernible impact was found. It was discovered that adding aluminium sodium aluminate-silicate electrolytes up to 13 g/l had an impact on the phase composition of the coating but had no discernible effect on the coating's thickness.

Therefore, the experimental studies of the above-mentioned authors made it possible to reasonably develop new bioenvironments for the synthesis of coatings characterised by high biocompatibility.

Conclusions

It was feasible to determine from the analysis of the content of PEO coatings synthesised in three different electrolytes that the addition of diatomite to the electrolyte produces a highly developed surface and positively affects the composition of the produced coating. Taking into account the conditions of surface compatibility, the Ca/P ratio was calculated in all synthesised coatings. The obtained results show that the introduction of hydroxyapatite into the composition of the electrolyte makes it possible to increase such a ratio from the value of 1.21, which is set for the coating synthesised in the electrolyte without hydroxyapatite, to the value of 1.28. Increasing the electrolyte concentration and adding diatomite instead of hydroxyapatite leads to an increase in the Ca/P ratio to 1.57. The broad development of coatings formed on a titanium base by plasma-electrolytic oxidation was established with the aid of scanning electron microscopy. As a result, a significant number of pores of various sizes were discovered on the coatings final surfaces.

Therefore, in further research, it is important to determine the size of these pores and identify their presence in the coating layer, as well as their type. The obtained results will make it possible to predict the time of osseointegration of the synthesised coatings by PEO method in vivo, and the combination of the results obtained in this work will open the possibility of regulating a wider range of predicted properties of biocoatings on titanium alloys.

Conflict of interest

None.

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Модифікація поверхні титанових сплавів синтезом покриттів методом ПЕО в лужних електролітах, насичених діатомітом

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Анотація. Одним із перспективних напрямків сучасного матеріалознавства є пошук методів покращення властивостей біосумісності металів, які використовуються в імплантології, що дозволить зменшити відсоток відторгнення імплантатів живим організмом. Тому перспективним є використання методів обробки для зміни стану поверхні металів за рахунок поверхневої модифікації, до яких належить метод плазмового електролітичного оксидування. Основною метою даної роботи була розробка технологічного процесу отримання покриттів з підвищеною біосумісністю порівняно з основним металом за рахунок введення до складу покриття природних компонентів. Наявність елементів у біопокриттях та їх кількість визначено за допомогою растрового електронного мікроскопа (SEM) та енергодисперсійної рентгенівської спектроскопії (EDS), що дозволило провести прицільний аналіз поверхні зразків. У роботі досліджено елементний склад покриттів, синтезованих на основі титанового сплаву в лужних електролітах на основі KOH, рідкого скла гідроксиду кальцію, поліфосфату натрію та пірофосфату натрію з додаванням гідроксиапатиту та діатоміту. Встановлено пряму залежність між складом електроліту та співвідношенням Ca/P. Доведено, що біопокриття, синтезовані в лужних розчинах методом ПЕО, задовольняють умови біосумісності. Встановлено, що в середовищі, яке містить луги та фосфати, синтезуються покриття, для яких Ca/P = 1,21. Введення в електроліт гідроксиапатиту призводить до збільшення співвідношення Ca/P до значення 1,28, а підвищення концентрації електроліту та додавання діатоміту збільшує це співвідношення до значення 1,57. Одержані результати свідчать про можливість широкого діапазону регулювання співвідношення Ca/P у біопокриття

Ключові слова: елементний аналіз; біосумісність; хімічні властивості; режими синтезу; склад покриття