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OBTAINING OF CALCIUM-PHOSPHATE COATINGS ON THE TITANIUM SURFACE BY MICRO-ARC OXIDATION

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The results of experiments on obtaining calcium-phosphate coatings on substrates of titanium grade VT1-0 by micro-arc oxidation (MAO) are presented. The coatings were obtained by adding different amounts of titanium oxide nanoparticles to the electrolyte. The microstructure and tribological properties of calcium phosphate coatings were investigated. In conducted research results have been established and determined optimal modes and parameters for obtaining calcium phosphate coatings. It is shown that the addition of titanium oxide nanoparticles to the electrolyte can affect the structure also the strength of the obtained coatings. The research results led to conclude that such treatment of MAO from titanium alloys is promising to improve their splices with bone tissue.

Keywords: micro-arc oxidation (MAO), plasma electrolytic oxidation (PEO), nanoparticles, coatings, wear, titanium.

Introduction

For the date a wide range of developed and tested methods are used to create calcium phosphate (CF) coatings on metal implants: plasma spraying process, micro-arc oxidation, methods based on crystallization of coatings from various solutions, detonation-gas spraying method, electrochemical deposition, sol-gel processes, etc. Each of these methods has its advantages and disadvantages. Among the disadvantages, the following can be noted: poor adhesion of coatings to the substrate, the inability to regulate their elemental composition, restrictions in the choice of substrate material for coating formation. Studies have shown that the use of the micro-arc oxidation (MAO) method, namely the plasma electrolytic oxidation (PEO) method, provides high adhesion strength between the substrate and the coating [1-3].

The MAO method in aqueous solutions of electrolytes has become widespread in the last decade as a method of applying bioactive CF coatings to the surface of titanium [4]. The coating formation in a micro-arc discharge is associated with the course of high-temperature chemical processes in the zone of local micro-plasma and micro-arc discharges under the influence of an external high voltage source and is associated with the oxidation of the base material, as well as the transition of the ultrafine phase in the electrolyte into the coating. The coatings obtained by this method have a good complex of physicochemical properties: high corrosion resistance, wear resistance, hardness and chemical resistance in aggressive environments [5].

If evaluate the current state of the scientific or scientific-technological problem being solved, then in the last decade in the field of biomaterial development there have been directions for creating materials that ensure the formation of a transition zone between bone and implant [6]. Such area should have a strong connection with the implant material, also macro- and microstructure suitable for the body, as well as bioavailability. Structural materials such as stainless steel, cobalt- and titanium-based alloys are widely used to create artificial implants due to their excellent mechanical properties, however, in some cases they cause allergic reactions and, as a result, out of order. In addition, a violation of the splices of the surface of the endoprosthesis with bone tissue leads to its gradual loosening, which requires repeated operations to replace or strengthen the implant. To increase the bioavailability of these materials, additional coatings are applied to their surface. Recently, there has been an increased interest in coatings made of CF and hydroxyapatite

$Ca_{10}(PO_4)_6(OH)_2$ (HA), which significantly increase the adhesion of implants to bone tissue [7]. The solution of the problem of increasing the bioavailability and osseointegration of implants in orthopedics and surgery is of very important social importance, since at present the rejection of implants in the postoperative period, cases requiring repeated implantation operations, the development of allergic reactions, a high probability of relaxation can lead to a long recovery of the patient. Coating the implant surface close to HA with titanium oxide nanoparticles provides not only high bioavailability, also develops osseointegration [6].

The purpose of this work is to study the effect of PEO on the microstructure, roughness, tribological characteristics of calcium phosphate coatings with the addition of titanium oxide nanoparticles.

1. Materials and research methods

Technically pure titanium material VT1-0 which often used in medicine, was used as a substrate. Samples of technical titanium VT1-0 for research were cut from rods in the state of delivery in the form of parallelepipeds. Previously, the samples were grinded to remove the oxide film and scratches. Table 1 shows the chemical composition of technically pure titanium VT1- 0. In comparison with other metals used as implants, pure titanium has a number of advantages: good corrosion resistance due to the formation of a passive oxide layer on the surface; high bioavailability; bio-inertia; practically non-toxic; low thermal conductivity; low coefficient of linear expansion; relatively low density compared to steel [8].

Table 1. Chemical composition of technically pure titanium VT1-0 (wt.).

Fe	C	Si	N	Ti	O	H
0. 25	0. 07	0. 1	0. 04	99. 7	0. 2	0. 01

To obtain calcium-phosphate coatings by the PEO method, an experimental-industrial MAO installation was used, which consists of a power source, an electrolytic bath with a cooling system and electrodes. The pilot-industrial installation for PEO was developed and manufactured in the research and production company PlasmaScience LLP (Kazakhstan, Ust-Kamenogorsk). Equipped with APS-77300 AC power supply. This equipment makes it possible to apply calcium phosphate coatings to medical implants, changing the coating modes on a large scale and thereby allowing for research. By controlling the parameters of the MAO, the installation allows to simultaneously cover several products (with a total area of more than 200 cm^2) due to high power in one cycle.

APS-77300 power supply unit output power: 3000 VA, voltage: up to 600 V, current: up to 25.2 A. Wide range of output voltage settings (amplitude, frequency, initial and final phases). Frequency range: 999.9 Hz. Discrete setting of output parameters in increments of 0.01 V / 0.01 Hz. Low harmonic coefficient (0.5%).

Calcium-phosphate coating was carried out in the anode-potentiostatic mode. The parameters of the PEO process included the following limits: pulse duration - 100-500 μs, pulse frequency - 50-100 Hz, initial current density - 0.13-0.35 A/cm^2, process duration - 5-20 min, electrical voltage - 50-100 V. The scheme of the MAO device is shown in Figure 1.

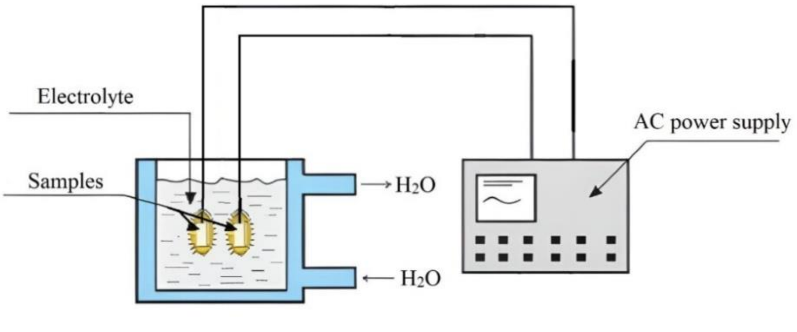


Fig. 1 - Scheme of the MAO device.

Various acid, salt and alkaline electrolytes can be used for micro-arc machining of titanium and titanium alloys parts. The most common electrolyte for MAO-titanium is a mixed phosphate-alkaline electrolyte of the KOH-Na_3PO_4 type. In this composition, KOH is an activator that affects the enrichment capacity, which makes it possible to form a strengthening layer on the oxidized surface in relation to the nominal amount of the part; this leads to a significant increase in the adhesive strength of the coatings [9].

Three different electrolytes were obtained by adding 500 g of distilled water, 10g of phosphoric acid H_3PO_4, 5g of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, 0.5g/0.75g/1g of titanium oxide TiO_2. The parameters of the MAO process during exploitation include the following limits: pulse duration - 100 μs, pulse frequency - 100 Hz, electrical voltage - 100V, initial current density - 0.15-0.35 A/cm^2, process duration - 10min. When applying a calcium-phosphate coating with titanium oxide nanoparticles, titanium samples attached to the suspension were immersed in an electrolyte in a bath. The MAO was carried out in the anode mode at AC voltage of 100V for 10 minutes. As a result of the experiment, local micro-plasma discharges appeared on the surface of the samples, and a coating was synthesized in their area. To obtain a calcium-phosphate coating on samples of technical titanium grade VT1- 0, which underwent the PEO process, three different amounts of titanium oxide were introduced into the electrolyte.

Microstructural analysis was performed on an ALTAMI-MET-5Smicroscope. To improve the image quality in the microscope, an advanced lighting system with a powerful lamp (12V, 50W) is used as a light source. The basic equipment of ALTAMI -MET-5S is equipped with a digital USB camera with a resolution of 3 MP and Altami Studio software.

Tribological friction tests were carried out according to the standard "ball-disc" technique on the Anton Paar TRB^3 tribometer (international standards ASTM G 133-95 and ASTM G 99). As a counter wire, a ball with a diameter of 3.0 mm was used, certified material - Al_2O_3. The tests were carried out at a load of 1N and a linear velocity of 2cm/s, a wear curve radius of 3mm, a friction path of 40m. The tribological characteristics of the modified layer were characterized by the intensity of wear and friction coefficient.

The surface roughness was measured with a model 130 profilometer. The action of the profilometer is based on the principle of perception of the roughness of the measured surface by the probe of an inductive sensor - in the process of control by a diamond needle (moving the sensor along the measured surface at a constant speed), which converts the translation of the sensor into an analog-digital signal and further digital signal processing.

2. Research results

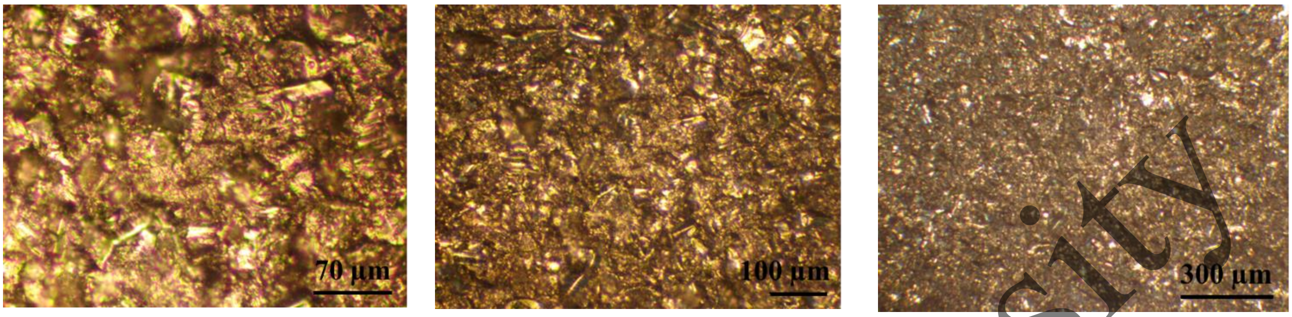
To find out the effect of electrolytes on the calcium-phosphate coating with titanium oxide nanoparticles from the MAO process, an electrolyte of three different compositions was prepared (Table 2). The calcium phosphate coating with titanium oxide nanoparticles was obtained using distilled water, orthophosphoric acid, hydroxyapatite and three different grams of titanium oxide.

Table 2. Limits of the MAO process for each electrolyte.

Electrolyte	0.5g TiO_2 + 500g dist.water + 10g H_3PO_4 + 5g HA: No1	0.75g TiO_2 + 500 500g dist.water + 10g H_3PO_4 + 5g HA: No2	1g TiO_2 + 500g dist.water + 10g H_3PO_4 + 5g HA:No3
Frequency (Hz)	100 Hz	100 Hz	100 Hz
Voltage (V)	100 V	100 V	100 V
Impulse (μs)	100 μs	100 μs	100 μs
Time (min)	10 min	10 min	10 min

The MAO process affects the structural characteristics and mechanical properties of titanium VT1-0 not only surface, but also deeply located structural elements. The nature of structural changes and changes in mechanical characteristics depends on the chemical composition of the alloy [9]. The microstructure, roughness, and tribological characteristics of VT1-0 titanium with a calcium phosphate coating with the addition of titanium oxide nanoparticles after the MAO process were studied. Figure 2 shows the initial microstructure of titanium VT1-0. The initial dimensions of the VT1-0 titanium microstructure were assumed to be 70μm, 100μm and 300μm.

In the initial state (in the state of delivery), titanium grade VT1-0 has a partially recrystallized structure (Fig. 2), with an average size of the elements of the grain-subgrain mixture d = 4.7µm, while the size of the recrystallized grains in such a material is ~ 10µm. As a result of local high-energy exposure, layers were formed on the surface of the samples, including both matrix elements (oxidized metal) and electrolyte elements [8]. When the anode current lasts 100 µs, dense uniform oxide coatings are formed in all electrolyte solutions. The thickness of the oxide coatings was 30-60 µm.



a) b) c)

Fig.2. Microstructure of VT1-0 titanium in its initial state.

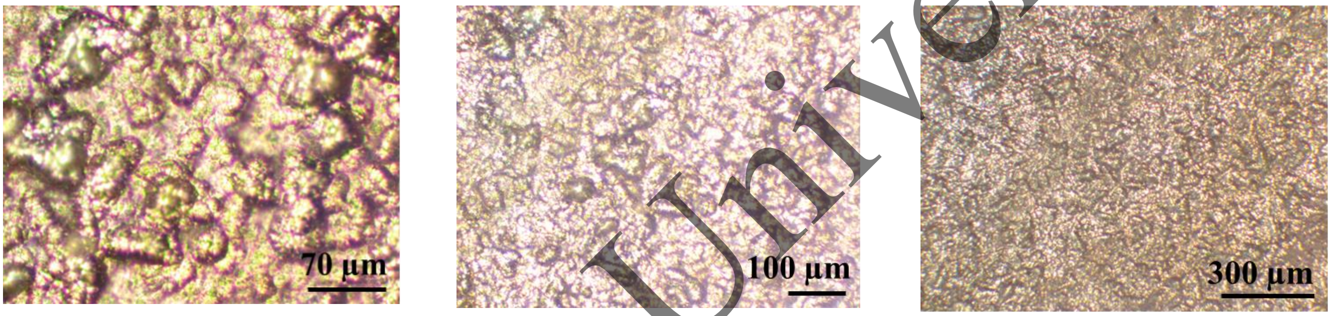


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Fig. 3. Microstructure of titanium VT1-0 in a calcium phosphate coating with 0.5g of titanium oxide.

The microstructure of the calcium phosphate coating obtained in the presence of 0.75 nanoparticles of titanium oxide, orthophosphoric acid and hydroxyapatite in the electrolyte is shown in Fig. 4. The study of the structure of coatings formed during PEO on the surface of titanium with different electrolyte compositions shows that they have a common nature. In particular, when treated in such electrolytes, a coating with a developed porous structure and glassy bubbles is formed in the voltage range (Fig. 4.).

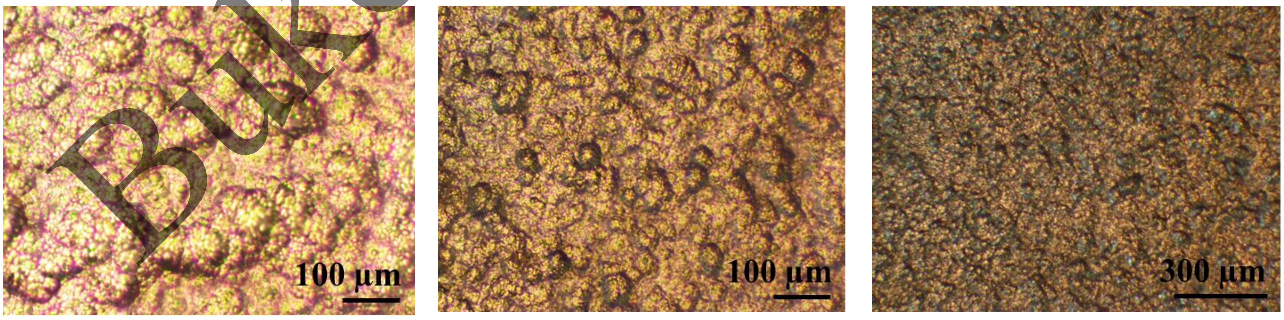

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Fig. 4. Microstructure of titanium VT1-0 in a calcium phosphate coating with 0.75 g of titanium oxide.

The microstructure of the calcium phosphate coating obtained in the presence of nanoparticles of titanium oxide 1, orthophosphoric acid and hydroxyapatite in the electrolyte is shown in Fig.5.

Microstructural analysis showed that with this electrolyte composition and the corresponding PEO treatment mode, titanium dioxide is intensively formed on the surface of titanium samples, forming a sufficiently dense layer. The results of optical microscopy of calcium-phosphate coatings formed in the electrolytes, the composition of which is given above, indicate that at these oxidation stresses they have small aggregates with a discontinuous loose structure.

At these voltages, developed loose aggregates are formed, similar to a spongy structure, formed by randomly arranged glassy bubbles. High porosity is observed in all samples. The presence of pores is favorable for the ingrowth of bone tissue in them and the formation of a stronger connection of the implant with the bone [4]. In order to confirm and coordinate the obtained optical microscopy data, it is necessary to additionally conduct scanning electron microscopy studies and X-ray spectral analysis, the results of which are planned to be published by the authors in the following papers.

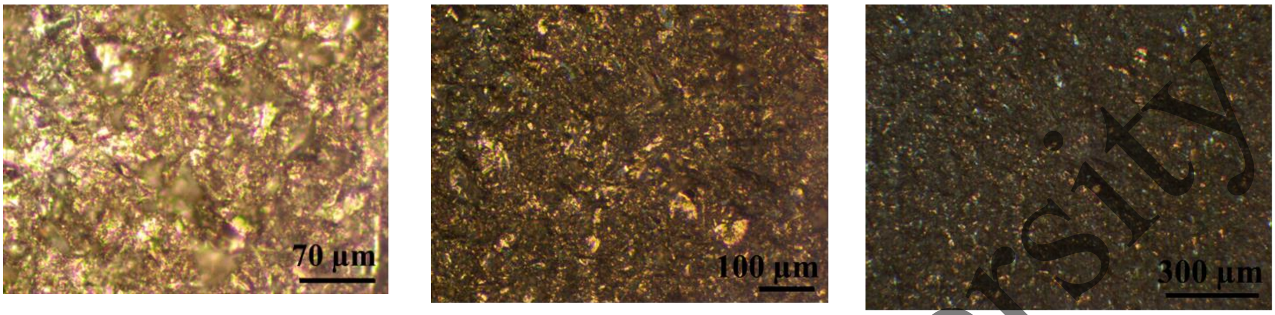

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Fig. 5. Microstructure of titanium VT1-0 in a calcium phosphate coating with 1g of titanium oxide.

Thus, titanium PEO with the addition of titanium oxide nanoparticles is promising from the point of view of obtaining biocompatible coatings, the coatings obtained in this case have a developed surface, which will serve their improved fusion with bone tissue. A positive feature of this processing method is the high rate of film formation and, accordingly, the low energy intensity of the process [10]. The roughness of the investigated surface of titanium VT1-0 was measured at small permissible areas, so the baseline lines were selected considering the parameter of reducing the influence of the undulating state of the surface on the change in altitude parameters. The contours of the profile were obtained during control using a diamond needle, and the trace was recorded on a profilogram. Figure 6 shows the roughness of the surface of titanium VT1-0 in its initial state.

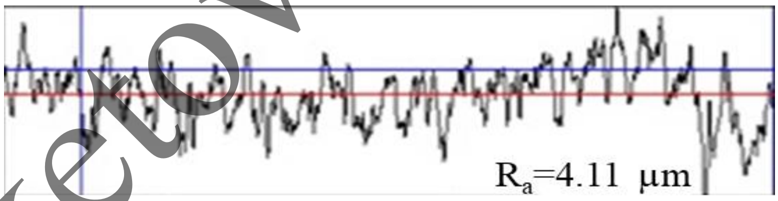


Fig. 6. Indicators for measuring the roughness of titanium VT1-0 in the initial state.

The surface roughness of the PEO coating is created by pores and irregularities in the form of meltdowns, which are formed during micro-plasma breakdown, as shown above (Fig.3-5). As the results of the study of surface roughness before and after processing have shown, the surface roughness of PEO coatings changing. Figure 7 shows the roughness of titanium VT1-0 with a calcium phosphate coating after the MAO process with the addition of 0.5g of titanium oxide nanoparticles to the electrolyte.

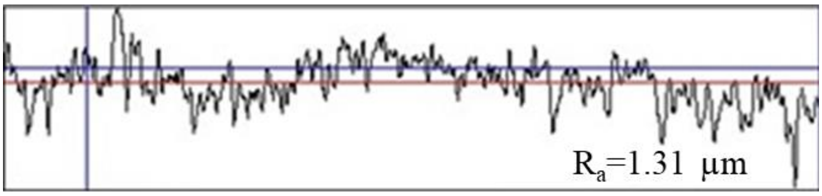


Fig. 7. Indicators for measuring the roughness of titanium VT1-0 in a calcium-phosphate coating with 0.5g of titanium oxide.

The roughness of titanium VT1-0 with a calcium phosphate coating obtained by the MAO method with the addition of 0.75g of titanium oxide nanoparticles to the electrolyte is shown in Figure 8. There is a direct relationship that determines the characteristics of the treated surface, the higher the class index, the lower the height of the measured surface and the better the quality of processing.

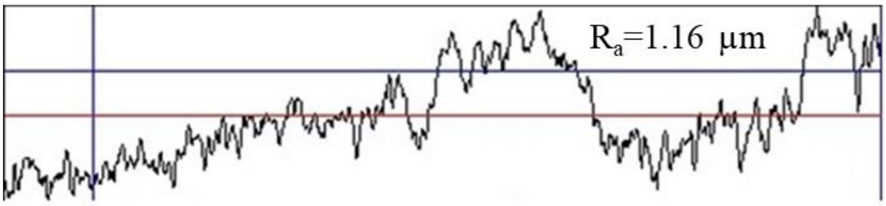


Fig. 8. Indicators for measuring the roughness of titanium VT1-0 in a calcium-phosphate coating with 0.75g of titanium oxide.

Figure 9 shows the roughness of titanium VT1-0 with a calcium phosphate coating after the MAO process with the addition of 1g of titanium oxide nanoparticles to the electrolyte.

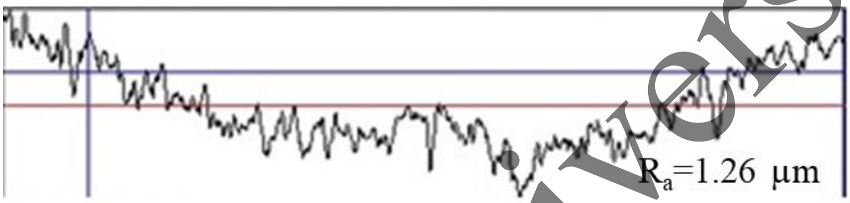
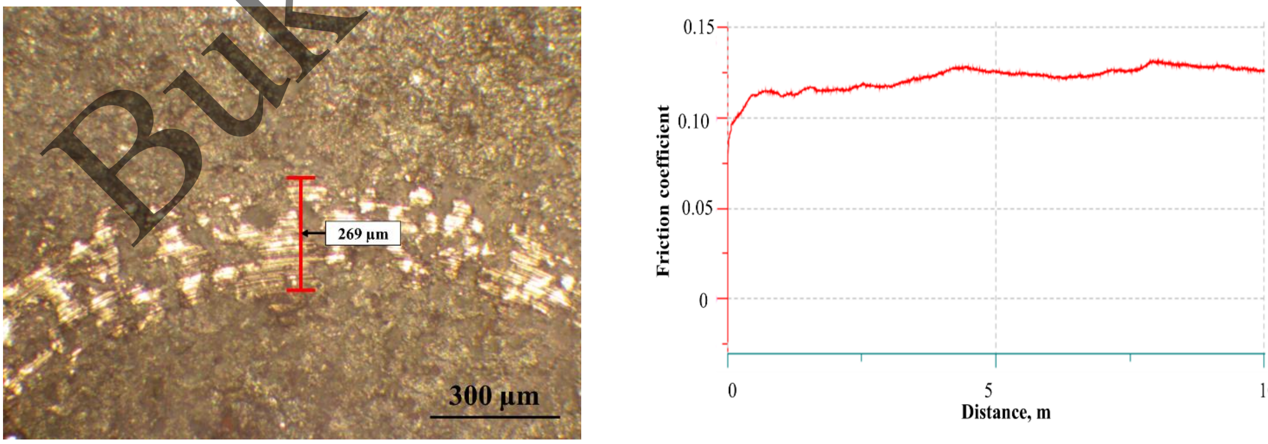


Fig. 9. Measurement values of titanium roughness VT1-0 on a calcium phosphate coating with 1g of titanium oxide.

The arithmetic mean deviation of roughness in the initial state was 0.0589 μm. The arithmetic mean deviation of titanium VT1-0 in a calcium phosphate coating with the addition of 0.5g of titanium oxide nanoparticles to the electrolyte after MAO is 1.456 μm, with 0.75g of titanium oxide nanoparticles is 1.223 μm, with 1g of titanium oxide nanoparticles is 1.253μm.

After the experiment, the value of the arithmetic mean deviation of roughness increased. The correct use of the method for determining the roughness of surfaces allows to achieve high processing accuracy, and the particle size allows to significantly improve the quality of the finished product. The smaller the roughness, the less corrosion and the higher the accuracy of the installation of parts during assembly [11].

During tribological tests, curves of change in the friction coefficient, data on the widths of the wear tracks were obtained. Coated samples were tested. Fig. 10-12 shows images of the type of wear strip with measurements of its width of the surfaces of samples with a track and shows the corresponding curves of the friction coefficients for the VT1-0 alloy with a coating obtained in solutions of electrolytes No.1, 2, 3.



a) b)

Fig. 10. Microstructural image of wear marks (a) and profilogram of titanium VT1-0 (b) on a calcium phosphate coating with 0.5g of titanium oxide as an electrolyte.

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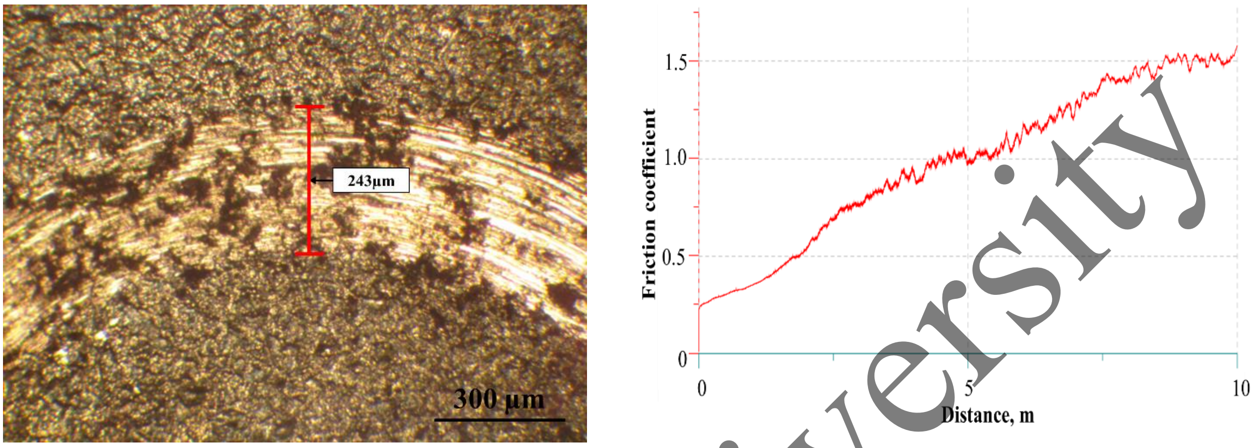
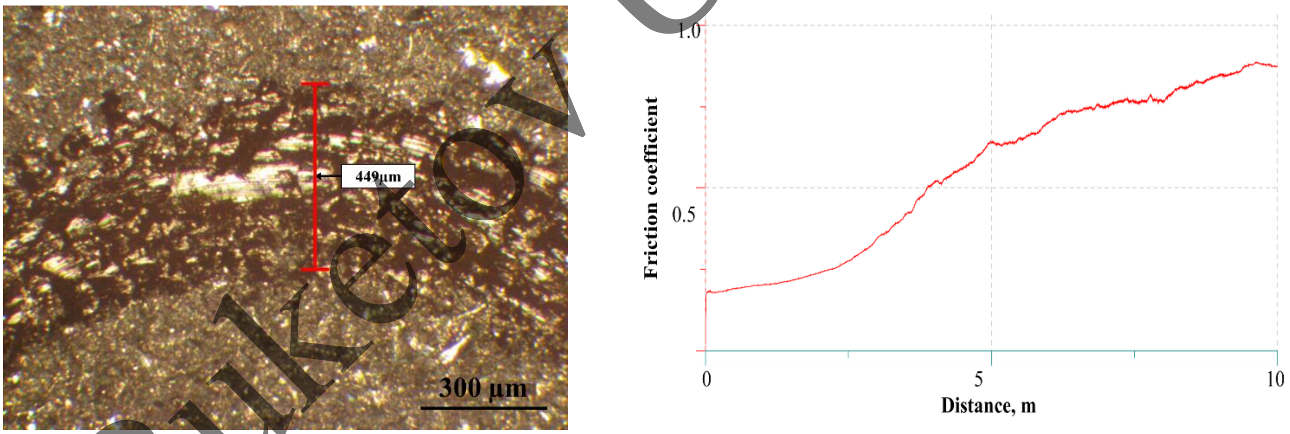
On the curves of the coefficient of friction of coatings, there are zones of tribosystem run-ins, where the rubbing surfaces adapt to each other and are accompanied by a high degree of wear. The stages are also visible, which are characterized by stable friction conditions and almost constant and relatively low wear intensity. There is no sharp change in the coefficient of friction characteristic of the destruction of the coating. Oxide coatings do not break down and do not wear down to the base. The length of the wear trace of titanium VT1-0 on a calcium phosphate coating containing 0.5g of titanium oxide nanoparticles in an electrolyte obtained by the MAO method is 269 μm.



a) b)

Fig. 11. Microstructural image of wear marks (a) and profilogram of titanium VT1- 0 (b) on a calcium phosphate coating with 0.75g of titanium oxide as an electrolyte

The length of the wear trace of titanium VT1-0 on a calcium phosphate coating containing 0.75 g of titanium oxide nanoparticles in an electrolyte obtained by the MAO method is 343 μm.



a) b)

Fig. 12. Microstructural image of wear marks (a) and profilogram of titanium VT1- 0 (a) on a calcium phosphate coating with 1g of titanium oxide as an electrolyte

The length of the wear trace of titanium VT1-0 on a calcium-phosphate coating containing 1g of titanium oxide nanoparticles in an electrolyte obtained by the MAO method is 449μm. When the length of the wear marks is longer, the wear resistance becomes worse. After testing, it was found that titanium VT1-0 in a calcium-phosphate coating obtained by adding 0.5g of titanium oxide to the electrolyte has increased wear resistance. During tribological tests, the process of running in the product/counter body pair occurs, the rubbing surfaces adapt to each other. Then comes the stage of steady wear, which has the longest duration. It is characterized by stable friction conditions and almost constant and relatively low wear intensity [12]. During its development, wear gradually increases, which is accompanied by damage to the surface.

Conclusion

The study of the structure of coatings formed during PEO on the surface of titanium with different electrolyte compositions showed that they have a common nature. As a result of this MAO mode, a coating with a developed porous structure and glassy bubbles is formed. The presence of pores is favorable for the ingrowth of bone tissue in them and the formation of a stronger connection of the implant with the bone.

As the results of the study of surface roughness before and after processing have shown, the surface roughness of PEO coatings changing. After the experiment, the value of the arithmetic mean deviation of roughness decreased by 4 times compared to the initial state. After the conducted studies, it was found that the use of the addition of TiO_2 nanoparticles to the electrolyte can significantly improve the tribological characteristics of the oxide layers formed during the MAO of titanium alloys.

Studies of the wear resistance of oxide coatings have shown a significant increase in it compared to the uncoated sample. The oxide coating obtained in different electrolyte compositions increases wear resistance compared to the uncoated sample. It is shown that the introduction of titanium oxide nanoparticles into the electrolyte makes it possible to obtain wear-resistant coatings. This is probably due to the introduction of titanium oxide into the coating, which is formed under the influence of high temperatures during micro-arc discharge.

Thus, titanium PEO with the addition of titanium oxide nanoparticles is promising from the point of view of obtaining biocompatible coatings, the coatings obtained in this case have a developed surface, which will serve their improved fusion with bone tissue. A positive feature of this processing method is the high rate of film formation and, accordingly, the low energy intensity of the process.

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