қатаю бойынша 346,5 МПа, 150^{0}С температурада – 370 МПа, ал 180^{0}С температурада 516 МПа көрсетті. Эпоксид шайырының жоғары температуралы қатаю, оның жоғары сұйықтығында порлардың ішіне кіруімен және көміртекті ровинг бетінің жаксы адгезиялауымен түсіндіруге болады деп түсіндіріге болады

Түйінді сөздер: ғарыш аппараттары, көмірпластик, түтікшелі білекше, орау, орау қондырғысы, ровинг, эпоксид шайыры, беріктік

РЕЗЮМЕ

Углепластиковые трубчатые стержни (УТС) широко используются в силовых конструкциях беспилотных летательных и космических аппаратов. Высокопрочный материал позволяет существенно облегчать массу конструкций. В работе проведено исследование метода получения УТС методом «мокрой» намотки углеродного ровинга, пропитанного эпоксидной смолой. Исследовано влияние на прочность на растяжение/сжатие УТС толщины ровинга, скорости и усилия намотки ровинга, угла намотки ровинга. Максимальная прочность УТС получена при толщине ровинга 24К и параметрах настройки намоточного станка: скорости протяжки ровинга 18 мм/с, усилия протяжки 18,6Н, угла перекрестной намотки 55^0. Получено влияние обработки «сырых» намоток в вакуумном мешке при атмосферном давлении. Вакуумная обработка позволяет снизить пористость изделия и повысить его прочность. Прочность УТС на растяжение/сжатие с использованием эпоксидной смолы с отвердителем, твердеющих при комнатной температуре, составила 346,5 МПа, при температуре 150 ^{0}С – 370 МПа, при температуре 180 ^{0}С – 516 МПа. Сделано предположение, что преимущества горячего твердения эпоксидной матрицы, обусловлены ее высокой текучестью, позволяющей проникать во все поры и хорошо смачивать поверхность углеродного ровинга.

Ключевые слова: космические аппараты, углепластик, трубчатый стержень, намотка, намоточный станок, ровинг, эпоксидная смола, прочность

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OBTAINING CALCIUM-PHOSPHATE COATINGS ON TITANIUM SUBSTRATE UNDER CONDITIONS OF MICRO-ARC OXIDATION

Abstract: The results of experiments on microarc oxidation of a substrate of titanium grade VT 1-0 under conditions of anodic treatment in phosphoric acid electrolytes containing calcium ions at a pH of 1 to 7 and a current voltage of 150 to 250 V are presented. The coatings were investigated by scanning electron microscopy, X-ray phase analysis and optical microscopy. The structure, phase and chemical composition formed as a result of micro-arc treatment of coatings is described. As a result of the studies, optimal regimes and parameters for obtaining calcium-phosphate coatings were established and determined. Processing with the modes found allows one to obtain coatings consisting of a mixture of phases Ca0.5(Ti2P3O12), CaTi4(PO4)6, Ca(PO3)2 and Ca2P2O7, which, according to the literature, are biocompatible compounds. The results of the SEM surface of the obtained coatings showed the presence of three structural components: sponge aggregates in the form of honeycombs, large bubbles having one or more shells, dense lenticular plates. The atomic ratio in the calcium-phosphate coatings varied in the range 0.30-0.62. It is shown that by varying the pH solutions and the magnitude of the stress of the microarc machining process, it is possible to significantly affect the structure, phase composition and thickness of the coatings produced. Promising from the point of view of obtaining biocompatible coatings is microplasma anodic treatment of titanium in phosphate acid electrolytes at pH ~ 3 – 1. A conclusion was made about the prospects of processing endoprostheses from titanium alloys by this method, to improve their coalescence with bone tissue.

Keywords: biocompatible materials, implant, crystallization, microarc oxidation, bioresorption, calcium-phosphate coatings

Introduction. Titanium (Ti) and its alloys are widely used as materials for the manufacture of surgical implants because of their excellent mechanical properties, high resistance to corrosion, low specific gravity and good biocompatibility [1, 2]. However, since the surface of titanium does not contribute to ostiointegration, special biocompatible coatings are used to ensure adhesion to bone tissue [3]. Calcium-phosphate coatings (CF) provide both biological activity and osseointegration. Among them, hydroxyapatite of calcium (GA) ($Ca_{10}(PO_4)_6(OH)_2$) attracts the greatest attention for clinical use due to its close

chemical composition and crystallographic structure with bone tissue. α–TCP ($Ca_3(PO_4)_2$) has a high absorption rate in living media [4] and [5]. Such metal structures with a calcium-phosphate coating not only protect against the corrosive effects of the biomed environment, but also stimulate the processes of bone tissue regeneration. To date, there are various ways to form calcium-phosphate coatings on the surface of metals [6,7].

The microarc oxidation (MAO) method is used to produce calcium-phosphate layers. The formation of coatings in the microarc discharge is due to the occurrence of high-temperature chemical reactions, as a result of which local microplasma discharges occur on the surface of the samples under the influence of an external high-voltage source in the region of which the coating is synthesized in the electrolyte. This method is a simple and effective way to produce ceramic layers on metal substrates, such as Ti, Al, Mg, and Zr [8]. The MAO method makes it possible to obtain coatings that have high wear resistance, hardness, chemical and corrosion resistance in corrosive environments, including biological ones [9-11].

The process of formation of the structure of CF coatings on the surface of the TiO_2 layer is associated with several factors, such as the concentration of Ca^{2+} + ions [12], the pH value and the electrolyte temperature [13]. The resulting coatings are characterized by porosity, which is favorable for the ingrowth of bone tissue in them and the formation of a stronger implant-bone connection [14].

Preparation of electrolyte is an important part of the microarc method. Since, the concentration and composition of electrolytes affect the morphological characteristics, porosity, thickness, corrosion resistance and biocompatibility of the MAO coating. Wang et al. [15] made the first report on the synthesis of titanium oxide layers under the action of MAO in simple electrolytes containing NaOH and Na_2SiO_3. K. Venkateswarlu et al. [16] investigated the effect of fluorine-containing electrolytes on the characteristics and electrochemical behavior of coatings obtained by microarc oxidation on commercially pure titanium. The authors of Ref. [17] proposed a method for the formation of calcium-phosphate biocoatings on titanium and its alloys, consisting of conducting MAO in electrolytes based on a 15-20% solution of orthophosphoric acid supplemented with HA and calcium carbonate.

Meanwhile, many aspects of the process of formation of such coatings have not yet been clarified. Particularly problematic is the formation of calcium-phosphate coatings in composition close to GA. Therefore, the search for and the production of new calcium phosphate materials, close to the mineral composition of bone tissue, remain significant and relevant.

The purpose of this work is to study the chemical and phase composition, morphology and microstructure, calcium phosphate coatings formed on titanium VT1-0 under microarc machining in phosphate electrolytes at various pH values and current voltage at the electrodes.

Experimental part. Objects and methods of investigation. To perform this work, a micro-arc installation was assembled, in which an ultrasonic bath of stainless steel with a power of 150 W was used as an electrolysis bath. Installation of MAO allows an anodic treatment of titanium at constant current on various electrolytes. As a source of current, a standard voltage regulator of the RNO-250-10 type was used, powered from the secondary winding of the transformer and connected to a power diode bridge, this allowed the voltage in the bath to vary from 0 to 250 V.

The scheme for implementing the microarc oxidation method for the formation of calcium-phosphate coatings on titanium is shown in Figure 1.

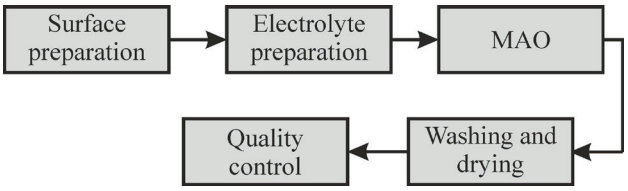


Figure 1 - Scheme of the microarc oxidation experiment

As a substrate for calcium-phosphate coatings, titanium plates of grade VT1-0 with the chemical composition Ti – 99.7, Fe – 0.25, Si – 0.1, O – 0.2 % by weight, dimensions 25x40x5 mm were used. Before oxidation, the samples were machined. The preparation of the surface of titanium for coating included cutting, deburring, grinding, polishing with diamond paste. Then they were degreased with hexane and washed in distilled water, after which the samples were dried at room temperature.

Seven series of experiments on the MAO of the surface of titanium samples were performed at different pH values of the electrolyte. Suspension of the phosphate electrolyte was prepared from a mixture of orthophosphoric acid with a concentration of 7.5 % (0.8 mol/dm^3) and a different amount of CaO, adjusting the pH solution to 1, 2, 3, 4, 5, 6, 7 units. The acidity of the electrolyte was measured with a pH

meter of pH-150. The electrolyte was poured into an ultrasonic bath, where the solution was further stirred by an electric stirrer.

When coatings were applied to a bath containing an electrolyte, titanium samples anchored on the "suspension" were immersed. MAO was carried out in the anode mode at potentials of direct current on a sample of 150, 175, 200, 225, 250 V, the duration of exposure was 5 minutes. As a result, local microplasma discharges appeared on the surface of the samples, in the region of which the coating was synthesized. The temperature of the electrolyte in all the experiments was maintained at 20 °C.

Samples of titanium plates after MAO were studied by X-ray phase analysis (XRD), scanning electron microscopy (SEM), and optical microscopy.

The study of surface morphology and microanalysis was carried out on a microprobe analyzer JXA-8230 (JEOL) with an accelerating voltage of 20 kV and an electron beam current of up to 7 nA at various magnifications.

Micrographs of the surface of coatings were obtained with the help of an optical microscope "Neophot 32" with magnifications x250, x500, x1000 and a camera Canon 40D combined with it.

The phase composition analysis of the obtained samples was carried out with a diffractometer D8 Advance (BRUKER) with α - Cu radiation (λ≈1.54 Å); U = 40 kV, I = 40 mA; The shooting speed was 0.1-1 deg/min; Angular interval 2Θ 4-90º with scanning step 0.01º. X-ray photography was carried out with Bragg-Brentano focusing. For the phase analysis, the PDF 2 database was used.

Table 1 - Percentage fractions of phases of calcium-phosphate coatings obtained in electrolytes from pH 1 to pH 7

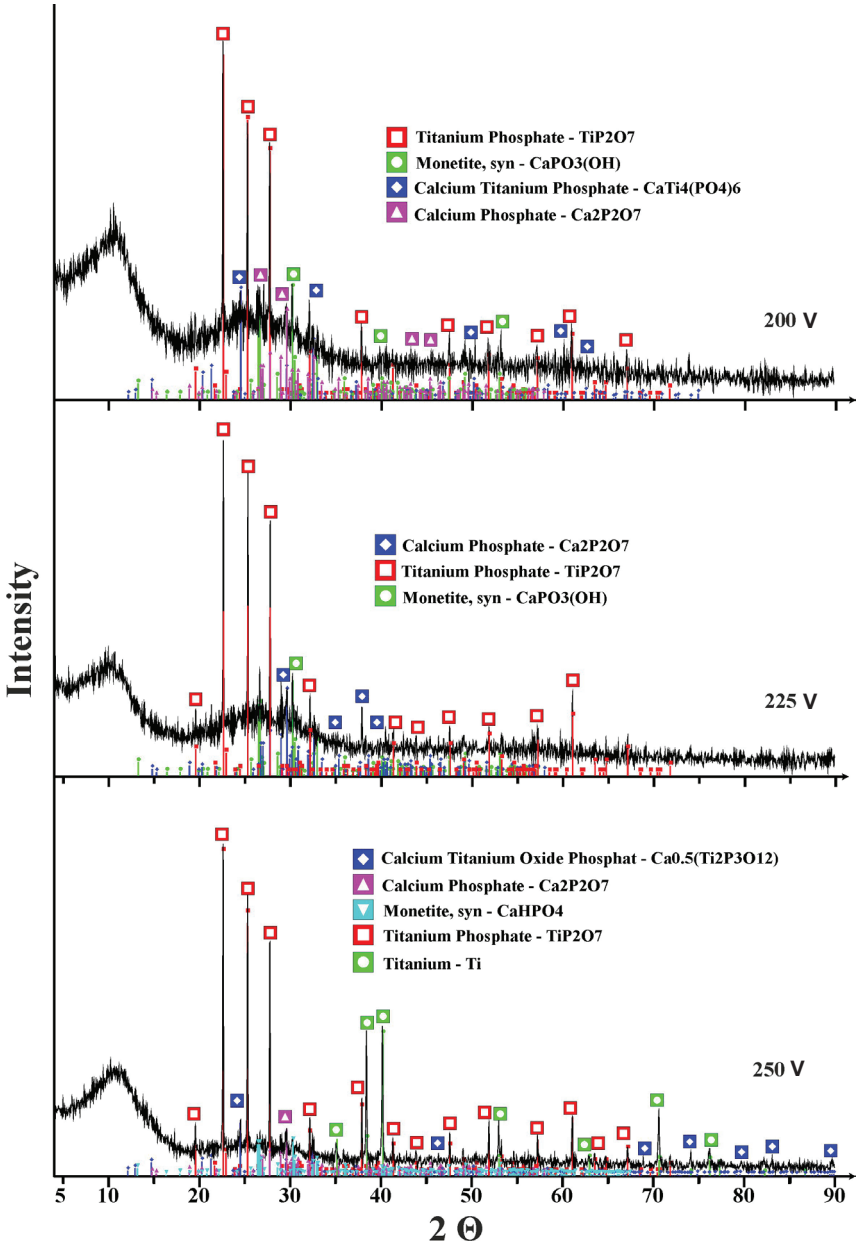
pH1					
Voltage, V	Percentages of phases,%				
	TiP_2O_7	$CaTi_4(PO_4)_6$	$Ca_{0.5}(Ti_2P_3O_{12})$	$Ca_2P_2O_7$	$CaHPO_4$
200	Amorphous subs.	Amorphous subs.	Amorphous subs.	Amorphous subs.	Amorphous subs.
225	62.7	20.9	–	–	16.5
250	62.5	–	19.8	17.8	–
pH2					
Voltage, V	Percentages of phases,%				
	TiP_2O_7	$CaTi_4(PO_4)_6$	$Ca_{0.5}(Ti_2P_3O_{12})$	$Ca_2P_2O_7$	$CaHPO_4$
200	52.8	16.7	–	13.4	17.1
225	64.5	–	–	16.7	18.8
250	54.2	–	8.8	7.7	5.7
pH3					
Voltage, V	Percentages of phases,%				
	TiP_2O_7	$CaTi_4(PO_4)_6$	$Ca_{0.5}(Ti_2P_3O_{12})$	TiO	Ti
200	81.4	14.7	–	–	3.9
225	63	27.7	–	9.3	–
250	72.4	–	27.6	–	
pH4					
Voltage, V	Percentages of phases,%				
	$Ca(H_2PO_2)_2$	Ti	Ti_3O	Ti_6O	
200	<0.1	96.5	2.1	1.4	
225	<0.1	96.5	1.4	2.1	
250	<0.1	96.5	1.4	2.1	
pH5					
Voltage, V	Percentages of phases,%				
	$Ca(H_2PO_2)_2$	Ti	Ti_3O	Ti_6O	
200	<0.1	95.8	1.2	3	
225	<0.1	95.9	2.1	2	
250	<0.1	96.5	1.4	2.1	
pH6					
Voltage, V	Percentages of phases,%				
	TiP_2O_7	Ti_3O_5	Ti	$Ca(PO_3)_2$	
200	–	6.4	76.2	17.4	
225	15.9	5.7	57.2	21.2	
250	11.5	5.5	67.5	15.4	
pH7					
Voltage, V	Percentages of phases,%				
	Ti				
200	100				
225	100				
250	100				

Results and discussion. As a result of X-ray phase analysis, it was found that the formation of calcium phosphate coatings in phosphoric acid electrolytes occurs in a narrow pH-electrolyte interval at voltages greater than 175 V.

Table 1 shows data on the phase composition of coatings obtained on the surface of titanium in phosphoric acid electrolytes with a pH from 1 to 7 at different strains of the microarc oxidation process. As follows from the data obtained under these conditions, a large spectrum of titanium, calcium, and titanium oxide phosphates can be formed: TiP_2O_7, $CaTi_4(PO_4)_6$, $Ca_{0.5}(Ti_2P_3O_{12})$, $Ca_2P_2O_7$, $Ca(PO_3)_2$, $CaHPO_4$, $Ca(H_2PO_2)_2$, Ti_6O, Ti_3O, Ti_3O_5, Ti. The main phase that forms coatings with MAO in the range pH 1-3 and voltages from 200 to 250 V is titanium phosphate TiP_2O_7. Its maximum content is found in the coating formed in the electrolyte with pH 3.

In coatings obtained under these conditions, similar phases of calcium-phosphate compounds are identified. At 200-225 V, calcium pyrophosphate $Ca_2P_2O_7$ and calcium-titanum phosphate $CaTi_4(PO_4)_6$ are formed. At 250 V instead of the phase $CaTi_4(PO_4)_6$ compound $Ca_{0.5}(Ti_2P_3O_{12})$ is formed.

Analysis of the X-ray diffraction patterns (Figure 2) of coatings obtained with MAO in the pH range 1-3 shows the presence of an amorphous component in the structure, as evidenced by the halo. Processing at voltages above 225 V leads to the formation of well-crystallized films.



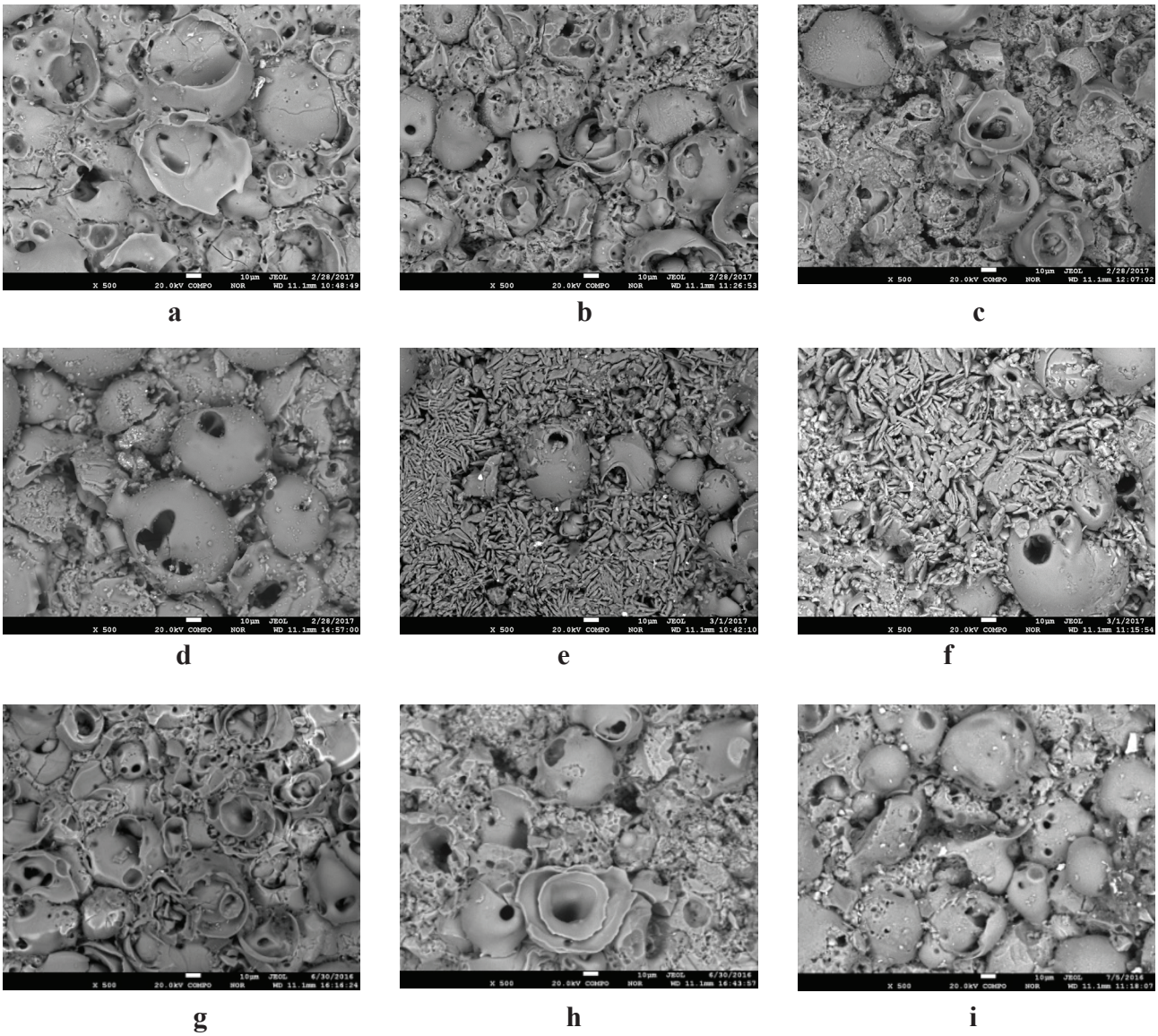
Voltage, V: 200, 225, 250; pH 2

Figure 2 - X-ray diffraction patterns of coatings obtained as a result of MAO of titanium in phosphoric acid electrolyte

In the case of using electrolytes with pH 4 and 5, titanium oxides in the form of Ti_6O, Ti_3O, Ti_3O_5 and an insignificant amount of $Ca(H_2PO_2)_2$ are predominantly formed. At pH 6, at a stress of 200, 225, 250 V, the layer formed on the titanium surface mainly contains calcium-phosphate $Ca(PO_3)_2$ (up to 21 %) and titanium pyrophosphate TiP_2O_7 (up to 16 %), small amounts (up to 6.4 %) of titanium oxide Ti_3O_5. The main reflections on the X-ray patterns give Ti, which is caused by the reflection of X-rays from the crystal lattice of the substrate itself. Therefore, the actual phase composition of coatings is represented to a greater degree by calcium-phosphate compounds and titanium oxides.

MAO in an electrolyte with a pH 7 throughout the current voltage range, according to X-ray phase analysis, did not lead to any crystalline phases, although at 200-225 V thick layers of milky color are visually observed on the surface of the samples.

The results of optical and raster electron microscopy of coatings formed with MAO on the surface of titanium in phosphoric



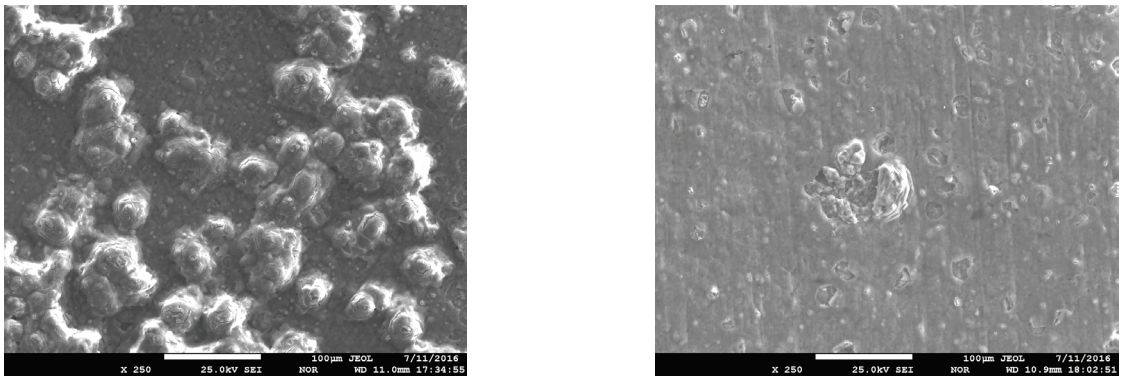
PH 1, voltage, V: a - 200, b - 225, c - 250; PH 2, voltage, V: d - 200, e - 225, f - 250; PH 3, voltage, V: g - 200, h-225, and - 250

Figure 3 - SEM image of CF coatings obtained in phosphoric acid electrolytes

acid electrolytes at pH 1-3 under different conditions show that they have a common nature. The structure analysis makes it possible to distinguish three structural components: sponge aggregates having thin walls in the honeycomb form with an open fine-pored structure; Large single transparent bubbles for the transmitted light, having one or more shells; Dense lenticular plates (Figure 3).

At low oxidation voltages of 150-175 V, in the indicated pH range 1-3, the coatings are predominantly of type I and have small aggregates with a non-continuous loose structure. At 150 V, the coating is formed in the form of islands, and at 175 V a uniform layer is formed, the thickness of the cell walls is at the level of 0.3-1 μm. An increase in the voltage of MDO to 200 V leads to the appearance of large up to 150 μm chaotically located bubbles with a wall thickness of 1.5 μm or more, while in electrolytes with pH 2 the main structural component is platelet discharge, and at pH 1 and 3 - honeycomb (Figure 3), The sizes of which increase with an increase in the voltage of MAO. Microstructural analysis showed that at a pH of electrolyte corresponding to 7 in the voltage range 200-225 V, a layer is formed on the surface of titanium, characterized by high density and not significant porosity. The maximum uniformity, thickness and adhesion it has at 225 V (Figure 4). At the same time, according to the microprobe analysis, these films contain mainly oxygen atoms ~ 66 atom% and titanium ~ 33 atom%

Coatings formed with MAO on the surface of titanium in phosphoric acid electrolytes with a pH of



a **b**

Voltage, V: a - 200; b - 225

Figure 4 - Microstructure of the coating obtained by microarc oxidation of titanium in phosphoric acid electrolyte with pH 7

4-6 in the voltage range from 150 to 250 V and at pH 7 in the range 150-175 and 250 V have a very small thickness, as can be judged from the color ripples on the surface titanium after treatment.

As follows from the data on the elemental composition of the coatings obtained in electrolytes with pH 1 and 2 at 250 V shown in Figure 5, they have a different ratio of Ca and P. It should be noted that the concentrations of Ca and P and the ratio of Ca to P in the coatings were increased with a change in the pH value of the phosphate electrolyte (Figure 5, pH 2). The atomic ratio of Ca/P coatings ranges from 0.30-0.62.

Analysis of literature data indicates that the compound $Ca_{0.5}(Ti_2P_3O_{12})$ and $Ca_2P_2O_7$ are biocompatible. One way to increase the bioresorbability of phosphate materials is to create highly disperse structures that circulate biological fluids. The chemical composition of the coating, in turn, determines the degree of biodegradation of the coating. As resorbable phases, calcium-phosphates with a lower Ca/P ratio (Ca/P = 1.67) compared with hydroxyapatite (HA) should be considered. Such phases are calcium pyrophosphates ($Ca_2P_2O_7$, Ca/P=1) [18].

Thus, promising from the point of view of obtaining biocompatible coatings, is microplasma anodic treatment of titanium in phosphate electrolytes at pH ~ 3 and 1, the resulting coatings have a developed surface that will serve to improve their adhesion to bone tissue. A positive feature of this processing method is the high speed of film formation and, accordingly, low energy intensity and cost of the process, it is possible to form films on complex surfaces.

Conclusions. A comparative study of the effect of the voltage of microarc oxidation and pH of a phosphate electrolyte containing calcium ions on the morphology, microstructure, phase and elemental composition of coatings formed on the surface of titanium is performed. Optimum regimes and parameters of obtaining calcium-phosphate coatings are revealed. Treatment with the regimes found allows one to ob-

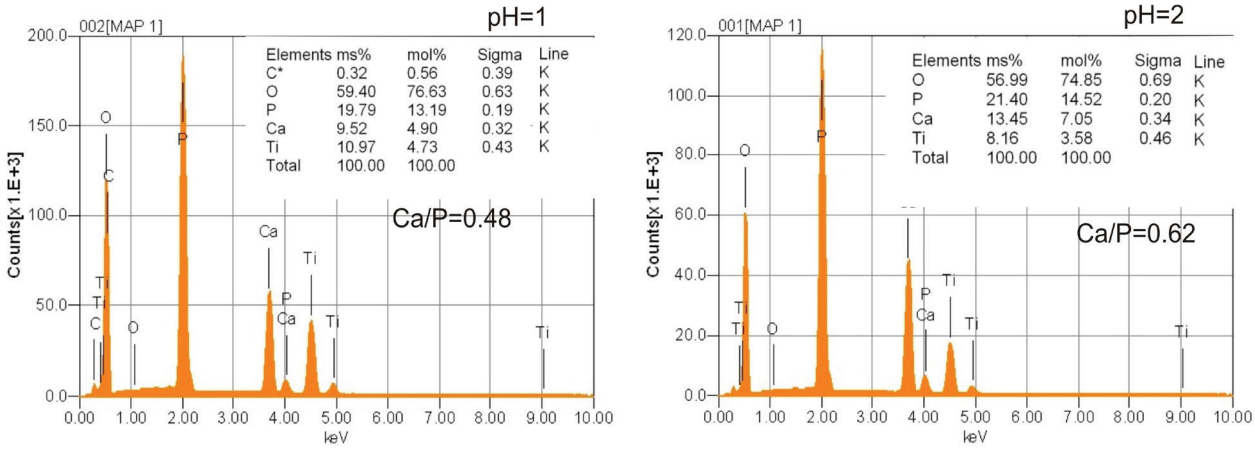


Figure 5 - Micro-X-ray spectral analysis of coatings formed at 250 V, pH 1 and 2

tain coatings consisting of a mixture of the phases $Ca_{0.5}(Ti_2P_3O_{12})$, $CaTi_4(PO_4)_6$, $Ca(PO_3)_2$ and $Ca_2P_2O_7$, which, according to the literature, are biocompatible compounds. The resulting coatings have a developed surface, which will serve to improve their adhesion to bone tissue

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ТҮЙІНДЕМЕ

Кальций йондары бар фосфорлы қышқыл электролитте pH мөлшері 1ден 7ге дейінгі және тоқ кернеуі 150 ден 250В шамасында маркасы ВТ 1-0 титанды төсенішті анодтық өңдеу шарасында микродоғалық оксидтеу тәжірибелерінің нәтижелері келтірілген. Жабындылар РФА, РЭМ және оптикалық микроскопия әдістерімен зерттелді. Микродоғалық оксидтеудің нәтижесінде пайда болған жабындылардың құрылымы, фазалық және химиялық құрамы сипатталды. Жасалған зерттеулердің нәтижесінде оптималды режимдер және кальций-фосфатты жабындыларды алу параметрлері орнатылды және айқындалды. Микродоғалық өңдеу процессіндегі ерітіндінің pH мөлшерін және тоқ кернеуін түрлендіру арқылы алынатын жабындылардың құрылымына, фазалық құрамына және оның қалыңдығына едәуір әсерін тигізуі мүмкіндік бар. Берілген әдіс бойынша титанды қорытпалардан жасалған эндопротездерді өңдеудің сүйекпен біту қасиетін жетілдіру маңыздылығы айқындалды.

Кілттік сөздер: Биоүйлесімді материалдар, имплanттар, микродоғалық оксидтеу, кальций-фосфаттық жабындылар, гидроксиапатит.

РЕЗЮМЕ

Приведены результаты экспериментов по микродуговому оксидированию подложки из титана марки ВТ 1-0 в условиях анодной обработки в фосфорнокислых электролитах, содержащих ионы кальция, при pH от 1 до 7 и напряжении тока от 150 до 250 В. Покрытия исследованы методами растровой электронной микроскопией, рентгенофазового анализа и оптической микроскопией. Описана структура, фазовый и химический состав образующихся в результате микродуговой обработки покрытий. В результате проведенных исследований установлены и определены оптимальные режимы и параметры получения кальций-фосфатных покрытий. Обработка при найденных режимах позволяет получать покрытия, состоящие из смеси фаз $Ca_{0.5}(Ti_2P_3O_{12})$, $CaTi_4(PO_4)_6$, $Ca(PO_3)_2$ и $Ca_2P_2O_7$, которые, согласно литературным данным, являются биосовместимыми соединениями. Результаты РЭМ поверхности получаемых покрытий показали наличие трех структурных составляющих: губчатые агрегаты в форме сот, крупные пузыри, имеющие одну или более оболочек, плотные пластины линзообразной формы. Атомное соотношение в кальций-фосфатных покрытиях варьировалась в интервале 0,30–0,62. Показано, что варьируя pH-растворов и величину напряжения процесса микродуговой обработки возможно существенно воздействовать на структуру, фазовый состав и толщину получаемых покрытий. Перспективной с точки зрения получения биосовместимых покрытий, является микроплазменная анодная обработка титана в фосфорнокислых электролитах при pH ~ 3 - 1. Сделано заключение о перспективности обработки эндопротезов из титановых сплавов этим методом для улучшения их сращивания с костной тканью.

Ключевые слова: биосовместимые материалы, имплантат, кристаллизация, микродуговое оксидирование, биорезорбция, кальций-фосфатные покрытия

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