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Effect of plasma-electrolytic oxidation on mechanical properties of titanium coatings

The process of plasma electrolytic oxidation (PEO) allows to obtain multifunctional coatings with unique properties, including wear-resistant, corrosion-resistant, heat-resistant, electrical insulating and decorative. Therefore, the field of application of these coatings is quite wide: medicine, aircraft construction, shipbuilding, instrumentation, automotive and other industries. The technology is based on the phenomenon of micro-arc discharges promoting the formation of oxide layers on metal surfaces. In this review the technologies of obtaining coatings by plasma electrolytic oxidation on titanium are considered. The experiment on PEO of VT1-0 titanium substrate under anodic treatment with the addition of TiO_2 nanoparticles to the electrolyte was carried out. Dense, uniform oxide coatings that do not require additional surface grinding were obtained. The coating thickness values were 18.5-62.4 μm. The influence of PEO on the microhardness of calcium-phosphate coatings formed as a result of this treatment was studied. With a satisfactory thickness of the formed layer (62.4 μm), the surface microhardness value (4.04 GPa) was found to be the highest among all the treatment modes compared, simultaneously with a high elastic modulus value (348 GPa) and a small value of the indenter penetration depth on the coating (968.99 nm). These coatings were formed in an electrolyte containing calcium phosphate with the addition of 0.75g of titanium oxide nanoparticles. The increase of microhardness in comparison with the sample without coating is in 2,5 times. As a result of the carried out researches optimum modes and parameters of calcium-phosphate coatings receiving have been established and defined. It is shown that by changing the composition of the electrolyte of the micro-arc treatment process it is possible to influence significantly the structure, thickness and surface properties of the obtained coatings.

Keywords: plasma-electrolytic oxidation (PEO), electrolyte, nanoparticles, coating, structure, microhardness, titanium, titanium oxide.

Introduction

Plasma electrolytic methods of material treatment are a very promising area of research to create new materials with unique properties [1]. Plasma electrolytic oxidation refers to an electrochemical process which has proven effective in altering the surface properties of metals and alloys, offering a number of potential advantages in various applications [2, 3]. This process is carried out at higher voltages, up to 1000 V, with AC and pulsed currents being used more frequently than DC currents. The PEO process is most fully investigated for valve metals and their alloys (aluminium, magnesium, titanium, tantalum, niobium, zirconium, etc.) [4, 5]. The process of PEO allows to receive multifunctional coatings with unique complex of properties, including wear-resistant, corrosion-resistant, heat-resistant, electrical insulating and decorative. Therefore, the field of application of these coatings is quite wide: medicine, aviation, ship, instrumentation, automotive and other industries. One of the applications of electrolytic-plasma treatment is surface modification of medical implants and this process can make them more compatible with the human body, reducing the risk of rejection and improving their overall performance [6-8]. In this paper, technologies for producing coatings on titanium by plasma electrolytic oxidation are discussed. The methods are classified according to the properties of the coatings obtained, but it should be noted that this division is arbitrary, since coatings are often multifunctional. Titanium and its alloys are widely used in medicine, because of their good biocompatibility and high strength, but the improvement of biocompatibility requires the deposition of special coatings on the titanium material. For this purpose, calcium phosphate and hydroxyapatite coatings are applied to the surface using the PEO method. The chemical composition of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is similar to that of bone tissue, so that bone tissue can form a strong chemical bond with the implant and not cause rejection. When titanium oxide nanoparticles are added to the solution, coatings with strong mechanical properties are obtained [9-11].

The aim of this work was to investigate the formation of calcium-phosphate coatings on titanium VT1-0 under anodic PEO in phosphoric acid electrolytes with the addition of TiO_2 nanoparticles, study the cross-sectional microstructure and microhardness of these coatings.

Experimental

Technically pure titanium material VT1-0, often used in medicine, was used as a substrate [12]. Samples of technical titanium VT1-0 for research were cut from rods in the state of delivery in the form of parallelepipeds. The samples were PEO-sanded to remove the oxide film and scratches.

Table 1 shows the chemical composition of technically pure titanium VT1-0.

Table 1

Chemical composition of commercially available 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

For the production of calcium-phosphate coatings using the PEO method a pilot plant MAO was used, which consists of a power supply, an electrolytic bath with a cooling system and electrodes.

Pilot plant for PEO is designed and manufactured by scientific-production company “PlasmaScience” (Kazakhstan, Ust-Kamenogorsk) [13]. It is equipped with an AC power unit APS-77300. This equipment enables to apply calcium phosphate coating on medical implants, thus allowing to conduct researches. By controlling the parameters of the MAO, the unit enables several products (total area over 200 cm^2) to be coated simultaneously due to the high power in a single cycle.

APS-77300 power supply with output power: 3000 VA, voltage: up to 600 V, current: up to 25.2 A. Wide range of output voltage settings (amplitude, frequency, start and end phase). Frequency range: 999.9 Hz. Discontinuous adjustment of output parameters in 0.01 V / 0.01 Hz steps. Low harmonic coefficient (0.5 %).

Calcium-phosphate coating was performed in anodic-potentiostatic mode. PEO process parameters 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, electric voltage — 50-100 V. A schematic of the MAO device is shown in Figure 1.

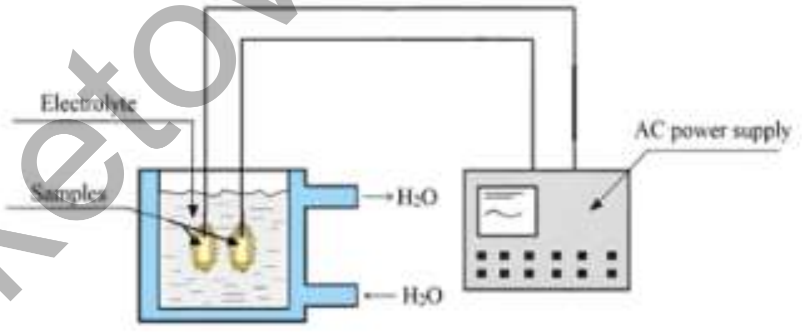

Figure 1. Schematic diagram of the MAO device

Various acid, salt and alkaline electrolytes can be used for the micro-arc treatment of titanium and titanium alloy parts. The most common electrolyte used for MAO titanium is a mixed phosphate-alkaline electrolyte of the KOH-Na_3PO_4 type. In this formulation, KOH is an activator affecting the enrichment capacity, which allows a hardening layer to be formed on the oxidized surface relative to the nominal amount of the part, this results in a significant increase in the adhesion strength of the coatings [9].

The parameters of MAO process in operation include the following limits: pulse duration — 100 μs, pulse frequency — 100 Hz, electric voltage — 100 V, initial current density — 0,15-0,35 A/cm^2, process duration — 10 min. During the calcium-phosphate coating with nanoparticles of titanium oxide the titanium samples attached to suspension were immersed into the electrolyte in the bath. The MAO was carried out in anodic mode at an AC voltage of 100 V for 10 minutes. As a result of the experiment local microplasma discharges appeared on the surface of samples and in their area the coating was synthesized. To obtain calcium-phosphate coating on samples of technical titanium of VT1-0 grade, which underwent PEO process, three different amounts of titanium oxide were added into electrolyte composition.

The thickness and cross-sectional microstructure of calcium-phosphate coatings with the addition of titanium oxide nanoparticles obtained in the MAO process were studied using an ALTAMI-MET-5C optical microscope. To improve the image quality of the microscope, an advanced illumination system with a high-power lamp (12 V, 50 W) is used as the light source. Basic equipment of ALTAMI-MET-5C is equipped with digital USB-camera with 3 MPix resolution and Altami Studio software. To measure the transverse thickness of the calcium-phosphate coatings obtained in the process of MAO, cut to a scale of 1/10 with a preliminary application of glue, epoxy paint and hardener, and a procedure of cryopreservation. The cured specimens were cleaned and wiped with diamond paste, after seating with 100-2000 welding paper.

Cross-section microhardness of coatings on VT1-0 alloy was investigated with nanosensor “NanoScan-4D Compact”. NanoScan-4D Compact uses a diamond pyramid of Berkovich type as an indenter. The Berkowitz-type indenter is a triangular pyramid with an angle of 65.3° between the pyramid's axis and the surface. The equivalent angle of the cone is 70.32°. The radius of curvature of the indenter tip is less than 100 nm. Ten measurements of the micro-hardness values of the coatings for each sample were made. The arithmetic mean values are used in this work.

The values of microhardness and modulus of elasticity of the material were automatically calculated using a special programme “NanoScan Viewer” in the form of a table. The results were obtained in the form of a graph showing the depth of penetration of the indenter into the sample as a function of the applied force.

Results and Discussion

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

Table 2

MDO process limits for each electrolyte

Electrolyte	No.1 0.5 g TiO_2 + 500 g dist.water + 10 g H_3PO_4 + 5 g HA: No. 1	No.2 0.75 g TiO_2 + 500 g dist.water + 10 g H_3PO_4 + 5 g HA: No. 2	No.3 1 g TiO_2 + 500 g dist.water + 10 g H_3PO_4 + 5 g HA: #3
Frequency (Hz)	100 Hz	100 Hz	100 Hz
Voltage (V)	100 V	100 V	100 V
Pulse (μs)	100 μs	100 μs	100 μs
Time (min)	10 min	10 min	10 min

The process of surface modification of titanium alloy VT1-0 by plasma electrolytic oxidation was investigated. PEO allows to obtain dense, uniform, not requiring additional surface grinding oxide coatings. The coating thickness values were 18.5-62.4 μm.

Figure 2 shows the cross-sectional thickness of calcium-phosphate-coated titanium VT1-0 when 0.5 g titanium oxide is added to the electrolyte.

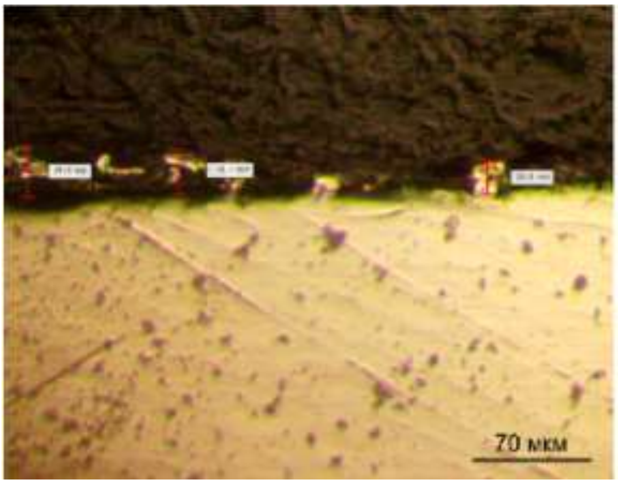

Figure 2.Cross-sectional thickness of calcium-phosphate-coated titanium VT1-0 when 0.5 g titanium oxide is added to the electrolyte composition

In most cases, the main quality parameter for a coating that meets technical and economic requirements is its thickness. In addition, the determination of coating thickness is the basis for quality assurance.

Studies of the cross-sectional structure of MAO coatings have shown that they have a three-layer structure regardless of the base material. The elements contained in the electrolyte must reside mainly in the porous outer layer of the MAO coatings (Fig. 1), which for different alloys is 20 % or more of the total coating thickness (Fig. 2). Thin barrier (transitional layer between the MAO coating and the substrate) layer located in close proximity to the base material must contain polycrystalline titanium oxide [14, 15]. In between is an intermediate layer (Fig. 2-4) consisting mainly of the TiO_2 phase. In this case the total thickness of MAO-coatings exceeds the thickness of the pro-oxidized titanium layer by about 20 %.

The cross-sectional thicknesses of VT1-0 titanium obtained by the MAO method when 0.5 g of titanium oxide nanoparticles were added to the electrolyte were 29.3 µm, 25.4 µm, 18.5 µm.

Figure 3 shows the cross-sectional thickness of calcium-phosphate-coated titanium VT1-0 when 0.75 g titanium oxide is added to the electrolyte.

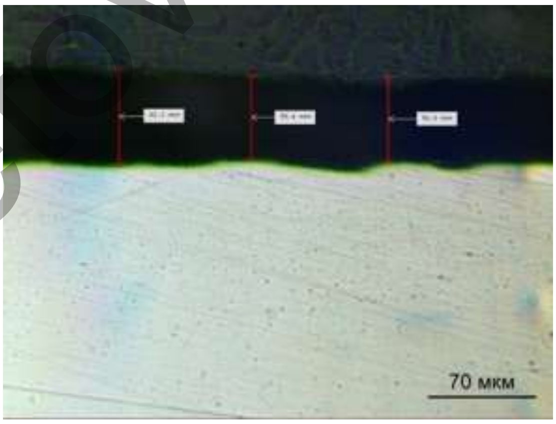

Figure 3. Cross-sectional thickness of calcium-phosphate-coated titanium VT1-0 when 0.75 g titanium oxide is added to the electrolyte composition

The cross-sectional thicknesses of VT1-0 titanium obtained by the MAO method with the addition of 0.75 g of titanium oxide nanoparticles to the electrolyte were 62.4 µm, 55.6 µm, 56.6 µm.

Thus, three different layers can be distinguished in the coating structure: an agglomerated layer (at the coating surface), an intermediate layer and a barrier layer (at the interface with the titanium substrate).

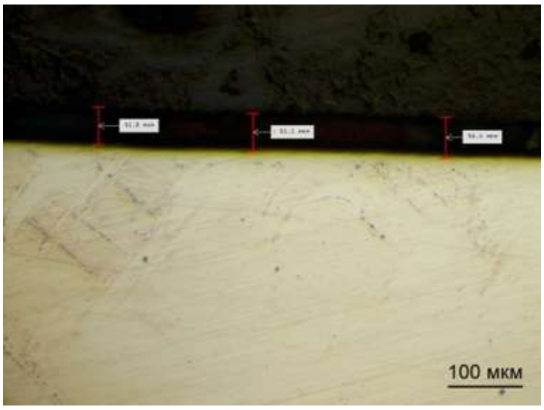

Figure 4.Cross-sectional thickness of calcium-phosphate-coated titanium VT1-0 when 1 g of titanium oxide is added to the electrolyte

The cross-sectional thicknesses of VT1-0 titanium obtained by MAO with calcium-phosphate coating when 1 g of titanium oxide nanoparticles were added to the electrolyte were 51.8 µm, 51.1 µm, 56.4 µm.

The process of oxide coating formation in plasma electrolytic oxidation or micro-arc oxidation is presented in several successive stages: Salt dissociation into ions; ion delivery to the electrode surface; electrochemical reaction and accompanying microplasma process; oxide or ceramic coating formation; subsequent chemical reaction, removal of gaseous reaction products [8]. As a result of local high-energy impact on the surface of the products layers are formed which include both elements of the matrix (oxidized metal) and elements of the electrolyte [9]. With a PEO treatment duration of 10 min, dense uniform oxide coatings are formed in all electrolyte solutions.

The highest micro-hardness of the coating was obtained in electrolyte No. 2 and is 2.84 GPa (Table 4), and the increase compared to the uncoated sample is 2.5 times.

The results of microhardness measurements of all calcium-phosphate coatings of VT1-0 titanium with titanium oxide nanoparticles, showed significant increases compared to the microhardness of pure uncoated titanium (1.7 GPa).

Figure 5 shows a graph of the depth of penetration of an indenter into the sample as a function of the applied force for calcium-phosphate-coated titanium VT1-0 obtained by adding 0.5 g of titanium oxide to the electrolyte.

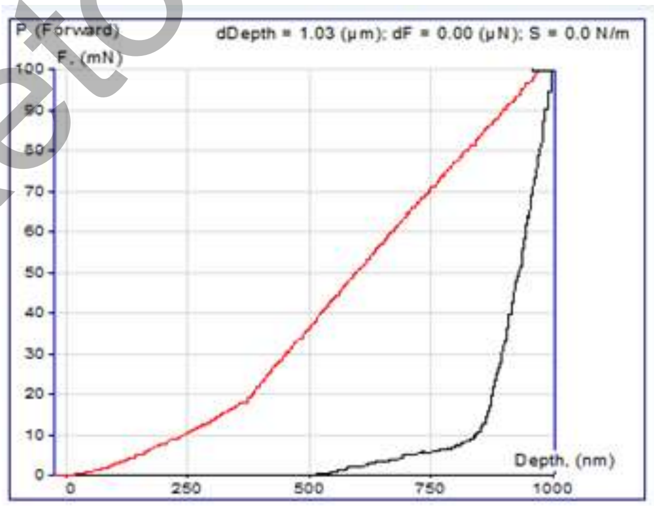

Figure 5. Dependence plot of indenter penetration depth on applied force in calcium-phosphate-coated titanium VT1-0 sample when 0.5 g titanium oxide is added to the electrolyte

Nano-hardness tester data for calcium-phosphate-coated titanium VT1-0 obtained by adding 0.5 g of oxide to the electrolyte is shown in Table 3.

Table 3

Values measured on a calcium phosphate nanohardness tester for calcium phosphate coatings obtained by adding 0.5 g titanium oxide to the electrolyte

	h_{max}, нм	h_c, нм	Force, mN	H, GPa	E, GPa	r,%	W_p	W_e
Average value	1382.77	1266.21	99.59	2.84	128.92	45.93	41.55	14.41
Standard deviation	311.10	263.10	0.29	1.18	114.11	33.23	8.06	8.02

Figure 6 shows a plot of the indenter penetration depth versus applied force in a calcium-phosphate-coated VT1-0 titanium sample when 0.75 g of titanium oxide is added to the electrolyte.

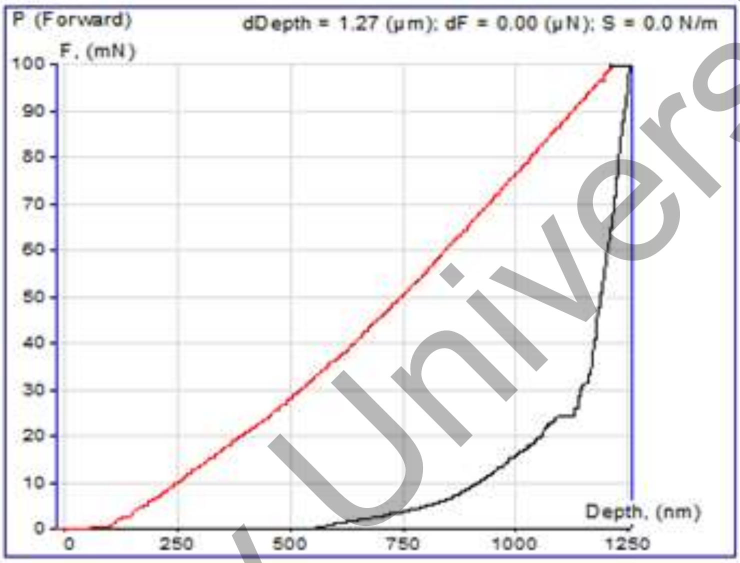

Figure 6. Dependence plot of indenter penetration depth on applied force in calcium-phosphate-coated titanium VT1-0 sample when 0.75 g titanium oxide is added to the electrolyte

The values obtained on the nanohardness tester for the electrolyte composition with the addition of 0.75 g of titanium oxide are shown in Table 4.

Table 4

Values measured on a calcium phosphate nanohardness tester for calcium phosphate coatings obtained by adding 0.75 g titanium oxide to the electrolyte

	h_{max}, nm	h_c, nm	Force, mN	H, GPa	E, GPa	r,%	W_p	W_e
Average value	1019.17	968.99	99.29	4.04	348.52	19.55	30.23	5.39
Standard deviation	58.94	61.38	0.92	0.41	82.05	15.26	3.48	0.96

Figure 7 shows a plot of the indenter penetration depth versus applied force in a calcium-phosphate-coated VT1-0 titanium sample when 1 g of titanium oxide is added to the electrolyte.

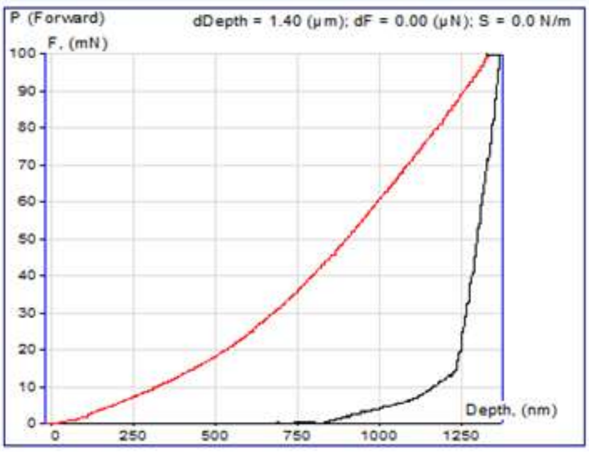

Figure 7.Dependence of indenter penetration depth on applied force in calcium-phosphate-coated titanium VT1-0 sample when 1 g titanium oxide is added to the electrolyte

The values obtained on the nanohardness tester for the composition of the electrolyte with the addition of 1g of titanium oxide are shown in Table 5.

Table 5

Values measured on a calcium phosphate nanohardness tester for calcium phosphate coatings obtained by adding 1 g of titanium oxide to the electrolyte

	h_{max}, nm	h_c, nm	Force, mN	H, GPa	E, Gpa	r,%	W_p	W_e
Average value	1147.75	1083.53	99.75	3.44	235.06	13.03	36.79	6.71
Standard deviation	114.66	115.25	0.17	0.57	25.96	1.46	3.89	1.18

Tables 3-5 show that the mechanical properties of the samples as well as the thickness of the MAO layer depend on the concentration of titanium oxide nanoparticles. When evaluating all the considered parameters of the obtained layer, the best performance was and obtained with the composition of electrolyte No. 2 (see Table 2). With a satisfactory thickness of the formed MAO layer (62.4 μm), the surface microhardness value (4.04 GPa) was found to be the highest among all compared processing modes, simultaneously with a high modulus of elasticity (348 GPa) and a low indentation depth (Fig. 5-7) in the coating (968.99 nm).

Conclusions

The process of plasma electrolytic oxidation of VT1-0 titanium with different composition of electrolyte was investigated. PEO allows to obtain dense, uniform, not requiring additional surface grinding oxide coatings. Three different layers can be distinguished in the coating structure: agglomerated (at the coating surface), intermediate and barrier (at the boundary with the titanium base). The coating thickness values were 18.5-62.4 μm. The obtained coatings are distinguished by high surface microhardness. The oxide coating microhardness of which is 4,04 GPa at covering thickness of 62,4 microns is received. These coatings were formed in an electrolyte containing calcium phosphate with the addition of titanium oxide nanoparticles. The increase compared to the uncoated sample is 2.5 times.

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Титан жабындарының механикалық қасиеттеріне плазма-электролиттік тотығудың әсері

Плазма-электролиттік тотығу процесі (ПЭТ) тозуғатөзімді, коррозияғатөзімді, ыстыққатөзімді, электр оқшаулағыш және сәндік қасиеттерін қоса алғанда, бірегей қасиеттері бар көп функционалды жабындарды алуға мүмкіндік береді. Сондықтан бұл жабындардың қолданылу аясы айтарлықтай кең. Атап айтсақ: медицина, авиация, кеме жасау, аспап жасау, автомобиль жасау және басқа салалар. Технология металдардың бетінде оксид қабаттарының пайда болуына ықпал ететін микродоғалық разрядтарының құбылысына негізделген. Бұл жұмыста титанға плазмалық электролиттік тотығу арқылы жабындарды алу технологиялары қарастырылған. TiO_2 нанобөлшектерін электролитке қоса отырып, анодты өңдеу жағдайында ВТ1-0 маркалы титаннан жасалған субстратқа плазмалық-электролиттік тотықтыру (ПЭТ) бойынша эксперимент жүргізілді. Бетті қосымша тегістеуді қажет етпейтін тығыз, біркелкі оксидті жабындар алынды. Жабынның қалыңдығы 18,5–62,4 мкм болды. Осы өңдеу нәтижесінде алынған кальций-фосфат жабындарының микроқаттылығына ПЭТ-дың әсері зерттелді. Түзілген қабаттың орташа қалыңдығымен (62,4 мкм) барлық салыстырылған өңдеу режимдерінің ішінде бетінің микроқаттылығының ең үлкен мәні (4,04 ГПа) жоғары серпімділік модулімен (348 ГПа) және индентордың жабынға (968,99 нм) ену тереңдігінің аз мәнімен анықталды.

Бұл жабындар кальций фосфаты бар электролитке 0,75г титан оксиді нанобөлшектерін қосу арқылы түзілді. Жабынның микроқаттылығы жабынсыз үлгінің микроқаттылығымен салыстырғанда 2,5 есе жоғары болды. Жүргізілген зерттеулер нәтижесінде кальций-фосфат жабындарын алудың оңтайлы режимдері мен параметрлері анықталып, дәлелденді. Алынған жабындардың құрылымына, қалыңдығына және беткі қасиеттеріне микродоғалық өңдеу процесінің электролит құрамын өзгерту арқылы айтарлықтай әсер етуге болатындығы көрсетілген.

Кілт сөздер: плазма-электролиттік тотығу (ПЭТ), электролит, нанобөлшектер, жабын, құрылым, микроқаттылық, титан, титан оксиді.

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Влияние плазменно-электролитического оксидирования на механические свойства титановых покрытий

Процесс плазменно-электролитического оксидирования (ПЭО) позволяет получать многофункциональные покрытия с уникальным комплексом свойств, в том числе износостойкие, коррозионностойкие, теплостойкие, электроизоляционные и декоративные. Поэтому область применения данных покрытий достаточно широка: медицина, авиа-, судо-, приборо-, автомобилестроение и другие отрасли промышленности. В основу технологии положено явление микродуговых разрядов, способствующих образованию оксидных слоев на поверхности металлов. В данной работе был проведен эксперимент по плазменно-электролитическому оксидированию подложки из титана марки ВТ1–0 в условиях анодной обработки с добавлением в электролит наночастиц TiO_2. Были получены плотные, равномерные, не требующие дополнительной шлифовки поверхности оксидные покрытия. Значения толщины покрытий составили 18,5–62,4 мкм. Исследовано влияние ПЭО на микротвердость кальций-фосфатных покрытий, образующихся в результате данной обработки. При удовлетворительной толщине сформированного слоя (62,4 мкм) было выявлено наибольшее среди всех сравниваемых режимов обработки значение микротвердости поверхности (4,04 ГПа) одновременно с высоким показателем модуля упругости (348 ГПа) и малым значением глубины проникновения индентора на покрытие (968,99 нм). Данные покрытия сформированы в электролите, содержащем кальций-фосфат, с добавлением 0,75 г наночастиц оксида титана. Увеличение микротвердости по сравнению с образцом без покрытия происходит в 2,5 раза. В результате проведенных исследований установлены и определены оптимальные режимы и параметры получения кальций-фосфатных покрытий. Показано, что, меняя состав электролита, возможно существенно воздействовать на структуру, толщину и поверхностные свойства получаемых покрытий.

Ключевые слова: плазменно-электролитическое оксидирование, электролит, наночастицы, покрытие, структура, микротвердость, титан, оксид титана.

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