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Research of regimes of applying coats by the method of plasma electrolytic oxidation on Ti-6Al-4V

In this work, ceramic coatings were formed on Ti6Al4V titanium alloy using a technique of plasma electrolytic oxidation. Plasma electrolytic oxidation was carried out in electrolytes with different chemical compositions and the effect of the electrolyte on the macro-and microstructure, pore size, phase composition and wear resistance of coatings was estimated. Three types of electrolytes based on sodium compounds were used, including phosphate, hydroxide, and silicate. The composition of the electrolyte affects the intensity and size of microcharges and the volume of gas release of various electrolytes. The plasma electrolytic oxidation processes were carried out at a fixed voltage (270 V) for 5 minutes. The results showed that the coating was mainly composed of rutile- and anatase TiO_2, but a homogeneous structure with lower porosity and a large number of crystalline anatase phases was obtained in the coating prepared in the silicate-based electrolyte. The diffractogram electrolytes did not reveal the peaks of the crystalline phases associated with the PO_4^{3-} and SiO_3^{2-} anions. This means that these anions included only oxygen in the coatings. The morphology and phase composition of the samples were studied using a scanning electron microscope and an X-ray diffractometer, respectively. Wear resistance was evaluated by the "ball-disc" method on the TRB^3 tribometer. The wear resistance of various coatings formed on Ti6Al4V titanium alloys showed completely different wear resistance. The lowest coefficient of friction ($\mu = 0.3$) was demonstrated by the coating obtained based on phosphate. This may be due to a large number of crystal phases of rutile. The sample prepared in a hydroxide-based electrolyte showed a high wear coefficient (μ=0.52). This effect can be obtained by eliminating surface defects (microcracks and micropores).

Keywords: plasma electrolytic oxidation, anatase, rutile, structure, phase.

Introduction

The manufacture of modern implants for traumatology and dentistry requires careful research and selection of the product material and surface treatment. Titanium alloys are the most widely used in surgery because of their bioinertness and corrosion resistance [1]. The disadvantage of using alloys, for example, Ti-6Al-4V is the content of harmful alloying components, and the use of pure titanium is hampered by insufficient strength. The solution to the problem of reducing the harmful alloying components of the metal can be found in introducing modern technology of nano-structuring into production [2]. Various methods of surface treatment have improved osseointegration and biocompatibility of titanium and titanium alloys [3], among which plasma electrolytic oxidation (PEO) has significant advantages. PEO — an ecologically pure and high-manufacturing process that makes it possible to obtain coatings with good adhesion, developed porosity for integrating osteoblast cells [4].

Recently, the PEO process has attracted considerable interest as an economically efficient, ecologically pure, and highly efficient technology for the deposition of porous and well-adhesive ceramic pellicles on Ti surfaces [5].

The features of PEO coatings lead to a process similar to anodizing of alternating current. In both processes, the metal substrate and counter electrode are conductively coupled to a power source and immersed in an aqueous electrolyte. However, in PEO, an alternating current is supplied under conditions of a higher voltage than during anodizing, which leads to the development of different surface morphologies [6].

The resulting porous oxide layer contains species obtained from the substrate and electrolytes [7]. Moreover, this porous oxide pellicle consists of an inner dense layer and an outer porous one [8]. The properties of formed PEO coatings depend on several factors, including processing time, electrical parameters, electrolyte composition, and substrate. One of these parameters, which have a great influence on the properties of PEO coatings, is the chemical composition of the electrolyte, which can be changed by changing the concentration of the components or adding various additives. By adding various additives to the electrolyte (calcium hydroxide Ca $(OH)_2$, sodium phosphate Na_3PO_4, sodium hydroxide (NaOH), sodium phosphate silicate (Na_2SiO_3), sodium tetraborate ($Na_2B_4O_7$), and sodium fluoride (NaF) can be obtained on coatings based on hydroxyapatite and calcium phosphates [7–9].

The addition of nano– and microparticles in electrolytes can have a significant effect on the phase composition, microstructure, thickness and, consequently, on the corrosion properties of PEO coatings on titanium and its alloys. In most cases, particles can participate in PEO coatings by applying electrophoretic force and mechanical stirring. These two reinforcements transfer the negatively charged particles suspended in the electrolyte onto the oppositely charged conductive substrate. The particles are then incorporated into the PEO coating. Particles, entering, filling and sealing micropores, reduce the porosity of PEO coatings and modify the microstructure. This improved microstructure reduces the penetration of destructive ions from the coating into the substrate. It leads to an increase in the corrosion resistance of PEO coatings.

Changing the chemical composition of the electrolyte, oxidation time and electrical parameters (density, mode and frequency of current) in PEO contributes to obtaining films of biocompatible oxide — anatase (TiO_2) and to develop the surface relief in order to have a beneficial effect on the osseointegration of the implant surface in the recipient's body.

Experimental

As a substrate material for processing, we chose square-shaped samples of Ti6Al4V titanium alloy with a size of 20 mm × 20 mm × 3 mm. Table 1 illustrates the composition of the Ti6Al4V titanium alloy. The samples were ground and polished (using SiC paper with grain sizes from 100 to 2000 and using GOI paste (abrasive ability 0.3–0.1 μm)), washed with distilled water, and then dried before the PEO. For the deposition of coatings, PEO baths with different compositions were used (Table 2). In addition, 4 g of KOH (potassium hydroxide) was added to all baths to increase the conductivity of the electrolyte. The Ti6Al4V sample acted as an anode and a stainless steel container was used as a cathode. The PEO processes were performed using a constant voltage (270 V) for 5 minutes. The power source was a powerful rectifier, giving the maximum output value of 360V/100A as direct current. Using the cooling system, the temperature of the electrolyte during the experiments was cooled below 40°C. The samples were washed with distilled water and dried in a flow of cold air after each treatment. A schematic representation of the PEO installation is shown in Figure 1.

Table 1

Chemical composition of Ti6Al4V alloy (weight percent)

Ti	Al	V	Fe	C	O	N	H
88.5–92.5	5.5–6.5	3.5–4.5	<0.25	<0.08	<0.13	<0.05	<0.012

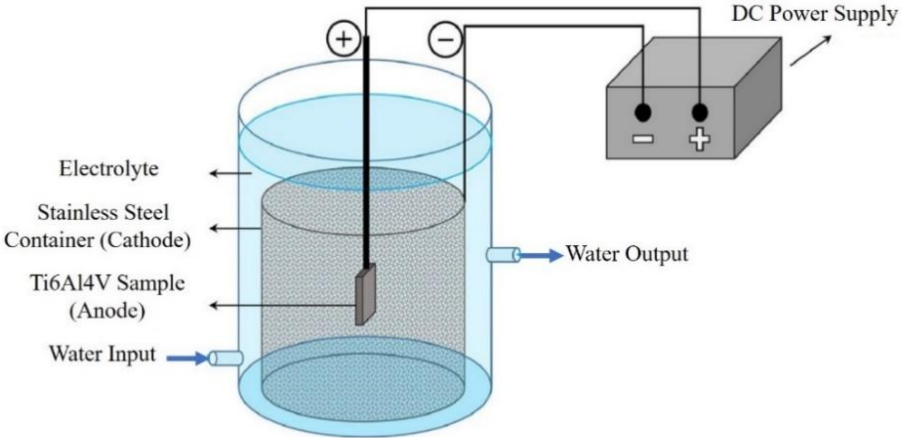

Figure 1. Schematic representation of the installation for PEO processing.

Table 2

Electrolyte composition for the PEO processes.

Electrolyte code	Electrolyte composition	Current density A/cm^2
H	20 g L^{-1} NaOH	26 A/cm^2
P	20 g L^{-1} Na_3PO_4	34 A/cm^2
S	20 g L^{-1} Na_2SiO_3	28 A/cm^2

The phase composition of the samples was studied by X-ray diffractometer X'PertPro (Philips Corporation, Netherlands) using CuKα radiation. Data processing and quantitative analysis were performed using PowderCell 2.4. The surface morphology was studied by scanning electron microscopy on a TESCAN MIRA scanning electron microscope with an electron-probe attachment for local microanalysis.

Results and Discussion

The chemical composition of the electrolyte significantly affects the acceleration of metal passivation and dielectric breakdown and, consequently, the formation of a thin insulating film [10]. Therefore, different electrolytes of different compounds (phosphate, silicate and hydroxide) were chosen here. In fact, a spark, known as a combustion phenomenon and an exothermic reaction containing an oxidizing agent, occurs as a result of absorption of a sufficient amount of oxygen. A micro-arc discharge leads to the eruption of molten substances from the discharge channels and the subsequent formation of micropores in the form of craters on the coating surface [11] (Figure 2).

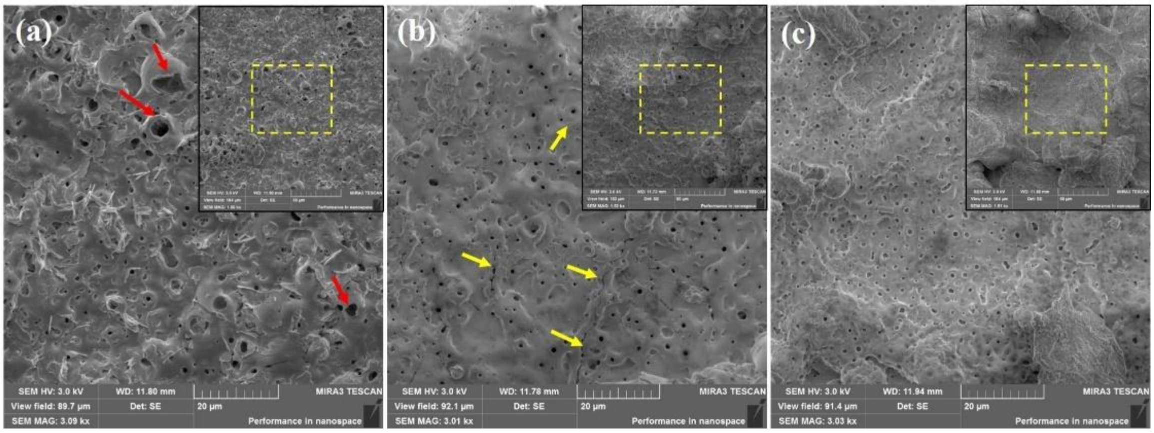

Figure 2. Surface morphology of PEO coatings of various electrolytes
(a) H, (b) P, (c) S

The spark voltages due to the nature of the electrolytes (electrolyte composition) were different for each electrolyte (Table 2). The composition of the electrolyte affects the intensity and size of microcharges and the volume of gas evolution of various electrolytes. On the surface of the sample prepared in electrolyte (H), there are several dark black spots, which can be caused by the large size and high intensity of the generated sparks at the points of low dielectric strength on the coating surface during the process.

The surface morphology of various coatings formed on Ti6Al4V titanium alloys is shown in Figures 2, 3. The coatings made with different electrolytes exhibited completely different microstructures. All coatings, due to the formation of micropores as a result of discharges accompanied by an avalanche of electrons at the interface between the electrolyte and the oxide layer, showed a typical structure of PEO, which contained micropores in the form of craters. When molten oxides leave the discharge channels and meet the surrounding electrolyte, they quickly solidify, and pores are formed on the coating surface [11]. On the other hand, a large amount of gas is formed on the discharge channels, which is then released into the electrolyte. At the early stage of the PEO process, the intensity of sparks and the amount of gas generated in the exhaust channels are much higher. Due to the gas ejection, molten oxides are thrown out of the outlet channels, they cannot fill the outlet channels, and, accordingly, a large number of micropores are formed. Due to a decrease in the intensity of sparks, the volume of gases formed in the discharge channels decreases to some extent [12].

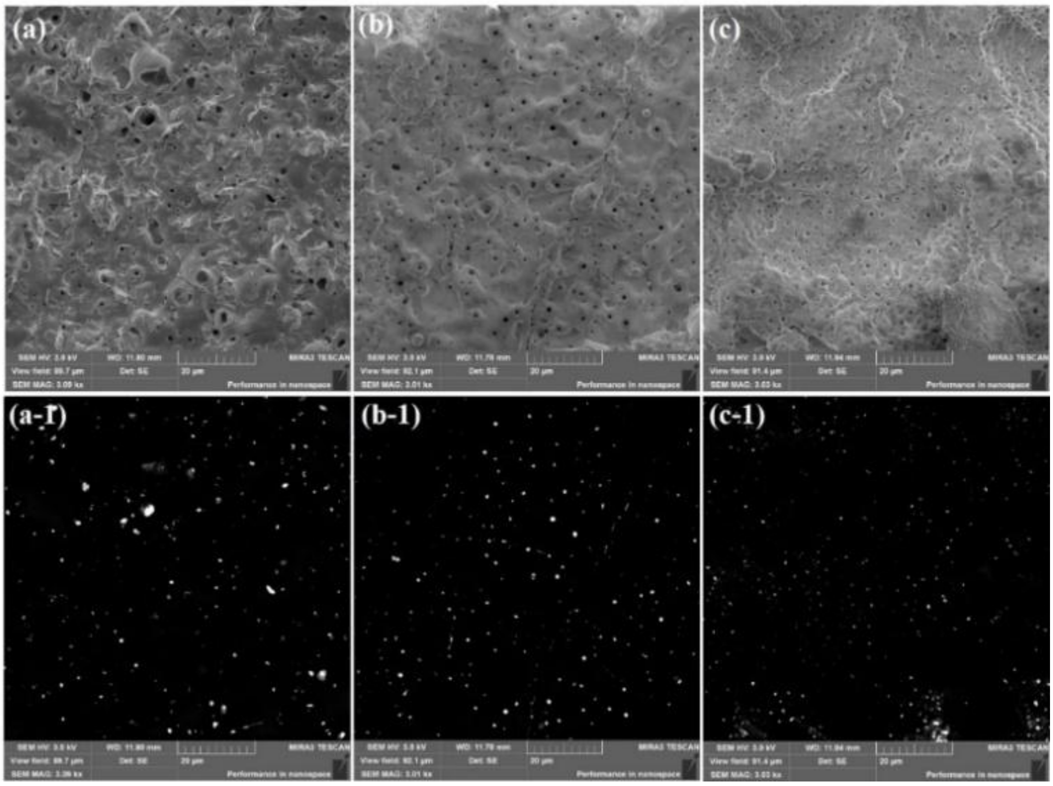

Figure 3. Pore distribution of PEO coatings in various electrolytes
(a, a-1) H, (b, b-1) P, (c, c-1) S.

In PEO processes, the characteristics of sparks and the amount of gas release affect the morphology of the coating surface. Larger sparks result in more and fewer micropores, while smaller sparks create more and smaller micropores and, consequently, form a more uniform structure. The average size of micropores and the percentage of porosity of the coatings are shown in Figure 4. According to Figures 3 and 4, it is obvious that due to the large number of small sparks and a small amount of gas evolution, the electrolyte coating (S) (Figure 3 (c, c-1)) possessed the smallest (with a porosity of 1.22 %), the smallest (with an average size of 0.48 microns) micropores. In this sample, the micropores are well distributed over the coating surface and are identical in size. The sample prepared in electrolyte (H) (Figure 3 (a, a-1)) had some large micropores with inhomogeneous dispersion, as well as large spherical condensation products formed by the rapid growth of the coating as a result of strong discharges [13]. In addition, the largest average micropore size (1.49 μm) was associated with electrolyte preparation (H). On the surface of the sample (P), several micropores and many microcracks were observed (Figure 3 (b, b-1)). Microcracks appear during the coating growth process due to the release of thermal stress and discharge activity [14]. Thus, the high temperature of the plasma discharges leads to the melting of oxides around the discharge channels, followed by rapid cooling with the electrolyte. Then, a rapid change in temperature causes the appearance of microcracks [15]. Although the average size of micropores in the sample (P) was smaller, and the percentage of porosity was higher compared to the sample (H).

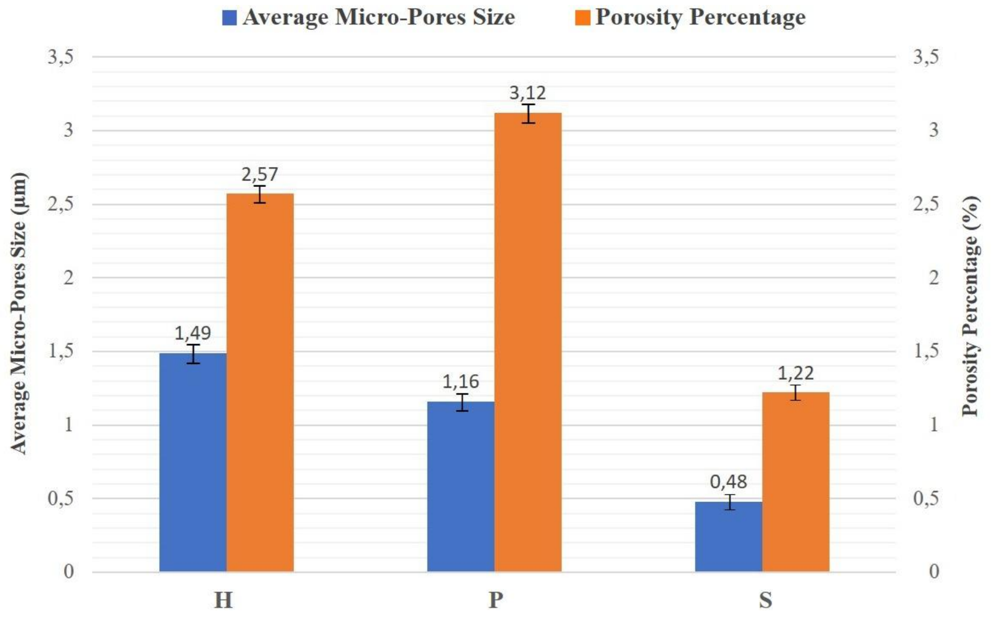

Figure 4. Average size of micropores and percentage of porosity of PEO coatings in various electrolytes.

Anatase, rutile, and brookite are the three main polymorphs of titanium oxide (TiO_2). In fact, TiO_2 and especially anatase are considered biocompatible. In addition, rutile has higher stability, high hardness, and, therefore, better mechanical properties and higher density than anatase. The temperature is low in the first stage of the PEO process. Thus, the anatase phase is formed earlier than rutile. With an increase in the applied voltage and current density, the temperature rises, and anatase is converted to rutile at 1461 °C, which is a more stable TiO_2 phase at high temperatures [16]. Diffraction patterns of coatings obtained in various electrolytes are shown in Figure 5. As can be seen in the figure, all coatings consisted of both rutile and anatase crystalline phases. The diffractogram of the (H), (P) and (S) electrolytes did not reveal the peaks of the crystalline phases associated with the $PO_4^{3—}$ and $SiO_3^{2—}$ anions. This means that these anions included only oxygen in the coatings.

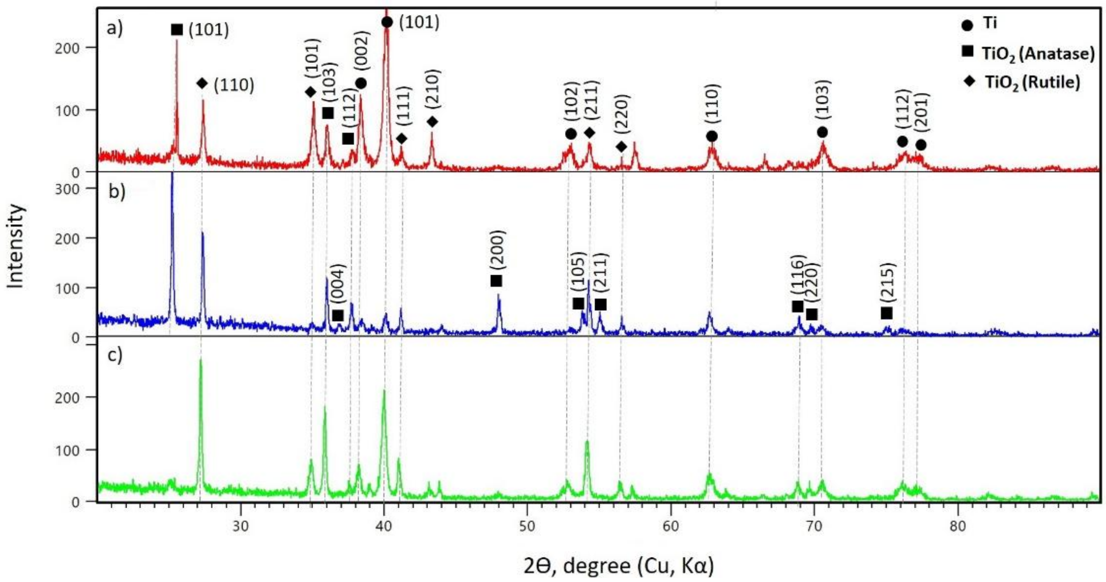

Figure 5. X-ray diffraction patterns of PEO coatings obtained in various electrolytes (a) H, (b) S, (c) P.

Quantitative analyses were performed using PowderCell 2.4. Table 3 shows the data of X-ray phase analysis.

Table 3

Results of X-ray phase analysis.

Sample	Detected Phases	Phase Structure Data in the Powder Cell Database		Structure Type	Phase Content wt.%
		Grid Type	Spatial Group		
P	Ti	hexagonal	P63/mmc (194)	D_{6h}^{4}	32
	TiO_2 (Anatase)	tetragonal	I41amd (141)	D_{4h}^{19}	15
	TiO_2 (Rutile)	tetragonal	P42/mnm (136)	D_{4h}^{19}	53
S	Ti	hexagonal	P63/mmc (194)	D_{6h}^{4}	46
	TiO_2 (Anatase)	tetragonal	I41amd (141)	D_{4h}^{19}	48
	TiO_2 (Rutile)	tetragonal	P42/mnm (136)	D_{4h}^{19}	6
H	Ti	hexagonal	P63/mmc (194)	D_{6h}^{4}	56
	TiO_2 (Anatase)	tetragonal	I41amd (141)	D_{4h}^{19}	18
	TiO_2 (Rutile)	tetragonal	P42/mnm (136)	D_{4h}^{19}	26

The wear resistance of various coatings formed on Ti6Al4V titanium alloys is demonstrated in Figure 6. The coatings made by different electrolytes showed completely different wear resistance. The lowest coefficient of friction (μ= 0.3) was indicated by the PEO coating (P). This may be due to many crystal phases of rutile. The sample prepared in electrolyte (H) represented a high wear coefficient (μ=0.52), this effect can be obtained by eliminating surface defects (micro-cracks and micropores).

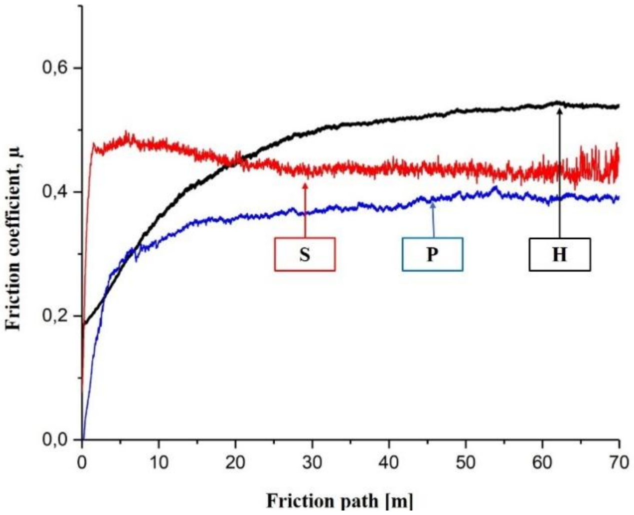

Figure 6. Results of tribological tests of PEO coatings of various electrolytes

Conclusions

The color and appearance, spark voltage and spark characteristics, surface morphology, phase composition and tribological behavior of coatings varied depending on the type of additive. The structures of the coatings formed using electrolytes containing Na_2SiO_3 additives were homogeneous and compact, with well-dispersed micropores. These technical characteristics were also associated with the formation of regular, uniform sparks during the coating process. The high electrical conductivity of the electrolyte containing Na_3PO_4 led to the formation of a coating containing relatively large micropores, with an irregular shape and distribution. Due to the release of thermal stresses during growth, this coating had micro-cracks. This coating has designated excellent wear resistance compared to other coatings. The good wear resistance of this coating is due to the high content of the rutile phase. The results of the PEO showed that the most homogeneous structure with lower porosity and numerous crystal phases of anatase were derived in a coating prepared in a silicate-based electrolyte. This mode is of practical interest from the point of view of obtaining a biocompatible coating.

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Ti-6Al-4V плазмалық электролиттік тотығу әдісімен жабындарды жағу режимдерін зерттеу

Мақалада плазмалық электролиттік тотығу әдісімен *Ti-6Al-4V* титан қорытпасындағы керамикалық жабындар алынғандығы сипатталған. Плазмалық электролиттік тотығу әртүрлі химиялық құрамы бар электролиттерде жүргізілді және электролиттің макро— және микроқұрылымға әсерін, кеуектілік мөлшерін, фазалық құрамын және жабындардың тозуға төзімділігін бағалады. Натрий қосылыстарына негізделген электролиттің үш түрі қолданылды, соның ішінде фосфат, гидроксид және силикат. Электролиттің құрамы микрозарядтардың қарқындылығы мен мөлшеріне және әртүрлі электролиттердің газшығару көлеміне әсер етеді. Плазмалық электролиттік тотығу процестері тіркелген кернеу кезінде (270 В) 5 минут ішінде жүргізілді. Нәтижелер жабынның негізінен рутилден және TiO_2, анатазасынан тұратындығын көрсетті, бірақ аз кеуектілігі және көп кристалды фазалары бар біртекті құрылым силикат негізіндегі электролитте дайындалған жабындыда алынды. Электролиттердің дифрактограммасында $PO_4^{3—}$ және SiO_3^{2-} аниондарымен байланысты кристалды фазалардың шыңдары анықталған жоқ. Бұл аниондар жабындардың құрамына тек оттегі кіргенін білдіреді. Үлгілердің морфологиясы мен фазалық құрамы сәйкесінше сканерлейтін электронды микроскоп пен рентгендік дифрактометр көмегімен зерттелді. Тозуға төзімділік TRB^3 трибометрінде «шар-диск» әдісімен бағаланды, сонымен қатар, *Ti6Al4V* титан қорытпаларында түзілген әртүрлі жабындардың тозуға төзімділігі мүлдем басқа дәрежелерді көрсетті. Үйкелістің ең кіші коэффициенті (μ=0,3) фосфат негізінде алынған жабынмен көрсетілген. Бұл рутилдің кристалдық фазаларының көп болуына байланысты болуы мүмкін. Гидроксид негізіндегі электролитте дайындалған үлгі жоғары тозу коэффициентіне (μ=0,52) ие болды, бұл эффектіні бетіндегі ақауларды (микрожарықтар мен микрокеуектер) жою арқылы алуға болады.

Кілт сөздер: плазмалық электролиттік тотығу, анатаза, рутил, құрылым, фаза.

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Исследование режимов нанесения покрытий методом плазменного электролитического окисления на Ti-6Al-4V

В статье получены керамические покрытия на титановом сплаве *Ti6Al4V* методом плазменного электролитического окисления. Плазменное электролитическое окисление проводили в электролитах с различным химическим составом и оценивали влияние электролита на макро- и микроструктуру, размер пор, фазовый состав и износостойкость покрытий. Использовались три типа электролита на основе соединений натрия, включая фосфат, гидроксид и силикат. Состав электролита влияет на интенсивность, размер микрозарядов и объем газовыделения различных электролитов. Процессы плазменного электролитического окисления проводились при фиксированном напряжении (270 В) в течение 5 мин. Результаты показали, что покрытие, в основном, состояло из рутила и анатаза TiO_2, но однородная структура с меньшей пористостью и большим количеством кристаллических фаз анатаза была получена в покрытии, приготовленном в электролите на основе силиката. Дифрактограмма электролитов не выявила пиков кристаллических фаз, связанных с анионами PO_4^{3-} и SiO_3^{2-}. Это означает, что эти анионы включали в состав покрытий только кислород. Морфологию и фазовый состав образцов изучали с помощью сканирующего электронного микроскопа и рентгеновского дифрактометра соответственно. Износостойкость оценивалась методом «шар–диск» на трибометре *TRB*^{3}, притом износостойкость различных покрытий, сформированных на титановых сплавах *Ti6Al4V*, показала совершенно разную степень. Наименьший коэффициент трения ($\mu=0,3$) продемонстрировало покрытие, полученное на основе фосфата. Это, может быть, связано с большим количеством кристаллических фаз рутила. Образец, приготовленный в электролите на основе гидроксида, оказался с высоким коэффициентом износа ($\mu=0,52$), этот эффект может быть получен за счет устранения дефектов поверхности (микротрещин и микропор).

Ключевые слова: плазменное электролитическое окисление, анатаз, рутил, структура, фаза, дефекты поверхности.