PLASMA OXIDIZED Ti6Al4V AND Ti6Al7Nb ALLOYS FOR BIOMEDICAL APPLICATIONS

Bartosz Pązik[1], Jacek Grabarczyk[1]*, Damian Batory[1], Witold Kaczorowski[1], Barbara Burnat[2], Małgorzata Czerniak-Reczulska[1], Marcin Makówka[1], Piotr Niedzielski[1]

[1] Institute of Materials Science and Engineering, Lodz University of Technology, 1/15 Stefanowskiego St. 90-924 Lodz, Poland
[2] Department of Inorganic and Analytical Chemistry, University of Lodz, 12 Tamka St., Lodz, Poland
*e-mail: jacek.grabarczyk@p.lodz.pl

Abstract

Titanium and its alloys are one of the most popular metallic materials used in medicine for many years. Their favorable mechanical properties, high corrosion resistance and good biotolerance in an environment of tissues and body fluids, cause that they are widely used as construction material of orthopaedic dental and neurological implants. Their disadvantages are poor tribological properties manifested by high coeffi-cient of friction, scuffing and tendency to formation of adhesive couplings. In many research centers the works on improving the unfavorable tribological properties of titanium alloys are conducted. They rely on the use of modern methods of surface treatment including the thermo-chemical methods (nitriding, carburizing, oxidation) and the synthesis of thin films using PVD and CVD methods. In the presented work the glow discharge oxidation was applied to improve the surface properties of two-phase Ti6Al4V and Ti6Al7Nb titanium alloys. The results include a description of the obtained structure of the surface layer, surface topography, micro-hardness, wear ratio and corrosion resistance. The obtained results indicate changes in the surface layer of the material. The surface hardness was more than doubled and the depth of increased hardness region was up to 85 microns. This, in turn, several times decreased the wear rate of the modified materials while reducing the wear rate of the countersample. At the same time the carried out thermo-chemical treatment did not cause any structural changes in the core material. The oxidation process preferably influenced the corrosion properties of titanium alloys. Both, significant increase in the corrosion potential (approx. 0.36 V), as well as increased polarization resistance were observed. The modified surfaces also retained a high resistance to pitting corrosion.

Keywords: *titanium alloys, plasma oxidizing, tribology, wear, corrosion*

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Introduction

Titanium and its alloys due to the unique physical and chemical properties become more widely used in various industries, including aerospace, automotive, energy, ship-building, chemical and food industries as well as in medicine [1,2]. This is due to the small weight, high mechanical strength and Young's modulus twice lower in comparison to steel. Titanium alloys are characterized by the highest relative strength of all metallic materials up to a temperature of 600°C [2-4]. Covered by a thin oxide layer, mainly TiO_2, are resistant to atmospheric agents, sea water and many chemicals [5]. A number of characteristics of titanium in particular its alloys, makes them widely used in medicine for the production of medical instruments and implants. This is mainly due to the high relative strength, good corrosion resistance (in particular to physiological fluids and certain medications), high biocompatibility and ability to osseointegration. Titanium alloys have a relatively low Young's modulus of all metallic materials used for implants, which is the most similar to the one of the bone. Therefore they are most often used for pins of prostheses and acetabulum clamps. They are also used for dental and various spinal implants [4,6-8].

Based on the literature reports, among others Refs. [13-15], a beneficial effect of the oxidation of titanium and its alloys on the improvement of their corrosion resistance was confirmed. This treatment helps to increase the thickness and integrity of the oxide layer, which protects against corrosive agents. The most common methods for the oxidation of titanium alloys include an oxidation in fluidized bed, gas and plasma techniques [8,15]. In Refs. [14,16,17] the effect of oxidation in a fluidized bed on the properties of titanium is presented. In all cases, the thicknesses of the obtained layers were very small, not exceeding 10 μm. However, even such a thin layer enriched with oxygen helped to improve the tribological properties. In works [18-21] the effect of glow discharge oxidation on the tribological and mechanical properties of titanium alloys, primarily Ti6Al7Nb and Ti6Al4V, is presented. In each work the carried out oxidation process allowed a significant increase in hardness. The thickness of the obtained layers was greater than in the case of oxidation in a fluidized bed, ranging from 30 to about 105 μm for the plasma oxidation at a temperature of 850°C and time of 3 h [18]. Nowadays there are many works presenting the oxidation process as a hardening treatment, of which the main task is to improve the mechanical and tribological properties of the substrate. The difficulties encountered during the processes of oxidation of titanium and its alloys include very thin diffusion range and possible brittleness of the resulting layers, which excludes the modified material from its further application.

Materials and Methods

The tested materials were two-phase titanium alloys: Ti6Al4V and Ti6Al7Nb, in the form of samples cut from the rod. The chemical composition of the alloys was in line with ISO 5832-2 (Ti6Al4V) and ISO 5832-11 (Ti6Al7Nb) standards. The differences in the microstructure of the two materials in the initial state (FIG. 1) result from different thermal treatments which were applied at the stage of production. Both alloys were annealed at 750°C. Ti6Al7Nb alloy was annealed for a period of 75 min and cooled in air, whereas Ti6Al4V alloy was annealed for a period of 120 min and cooled with the furnace.

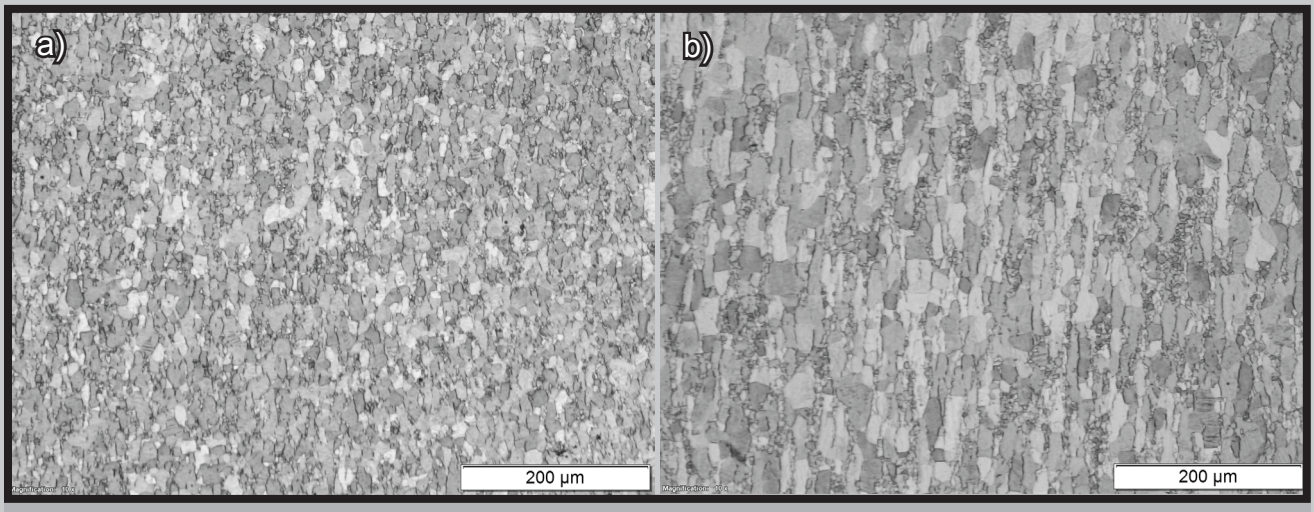

FIG. 1. Optical microscope images of initial microstructure of the titanium alloys: a) Ti6Al4V and b) Ti6Al7Nb.

The samples were grinded and mirror polished using colloidal silica suspension. Before the oxidation process the substrates were ultrasonically cleaned in acetone bath for 10 min and dried using a compressed air.

The process of diffusion strengthening by interstitial oxygen atoms was conducted in Ar/O_2 plasma. The samples were mounted on W electrode and placed in a quartz tube of the vacuum furnace. The annealing was conducted in a DC pulsed glow discharge in Ar atmosphere and pressure of 9 Pa. The plasma parameters during the whole process were kept at the same level: U = 850-1000 V and I = 50-60 mA. As soon as the temperature reached 900°C oxygen was introduced into the chamber at constant flow ratio O_2/Ar equal to 1/6. Oxygen was supplied for 60 s and then it was cut and the discharge took place only in an atmosphere of argon for 10 min. A total of 20 cycles were conducted to obtain the oxidized surface layers. After the process the batch was slowly cooled down with the furnace in continuous glow discharge in argon.

Microstructural examination was carried out using scanning electron microscope JEOL JSM-6610LV. Before the observation the prepared cross sections were etched by Kroll's reagent (1.5 ml of HF, 4 ml of HNO_3, 94 ml of H_2O). The roughness measurements were made with use of HOMMEL TESTER profilometer. The roughness parameters were examined before and after the plasma oxidation procedure.

The hardness distribution on the cross section profile was obtained for load of 100 g. with use of the Knoop indenter. The distance between the particular indentations was 10 µm.

Tribological parameters (coefficient of friction (CoF) and resistance against wear) were determined using ball on disc method. The investigations were performed under load of 10 N with the sliding speed 0.1 m/s on a distance of 1000 m. As the counterpart ¼ inch ZrO_2 ball was used. The tests were performed under temperature of 20 ±1°C and relative humidity of 50 ±2%. After the tests both, the wear tracks on the samples and wear scars on the countersamples were measured and used to determine their wear rates. For each sample and countersample four measurements were registered and the results were averaged.

Corrosion measurements were carried out using PGSTAT 302N potentiostat with NOVA 1.11 software. The measurements were performed in a thermostated electrochemical vessel in PBS (Phosphate Buffered Saline) solution at 37°C. Before the measurement electrolyte solution was deoxygenated with argon for 30 min. An active surface of samples was approx. 0.785 cm^2. The reference electrode was a saturated calomel electrode (E = 0.236 V_{SHE}), and the auxiliary electrode was a platinum gauze. Corrosion tests were carried out using electrochemical methods. The corrosion potential E_{cor} was measured in an open circuit (OCP) while recording the potential of the sample relative to the reference electrode for 1800 s. The value of polarization resistance, R_p, was determined according to Stern–Geary method in a scanning range of ± 20 mV vs. E_{cor} potential at the rate of 0.3 mV/s. Potentiodynamic characteristics were measured in a wide range of anodic polarization starting at potential E_{cor} – 0.2 V to 4 V with the scan rate of 1 mV/s.

Results and Discussion

After the oxidation processes significant changes in the surface layer of titanium alloys can be observed (FIG. 2). The subsurface layer of α-Ti, stabilized by the diffusion of oxygen, is visible. Next appears the oxygen diffusion zone which is a mixture α-Ti and β-Ti grains with the predominance of the former. The microstructure of vanadium containing alloy appears to be more fine-grained, especially in the case of the α-Ti regions.

For both modified materials a noticeable strengthening of the subsurface regions can be observed. The obtained hardness values compared to the unmodified materials are more than twice. With increasing distance from the surface the hardness decreases rapidly (FIG. 3). Based on both, the hardness distribution on the cross-section and SEM examinations the thickness of oxygen diffusion zone was estimated. In the case of all modified substrates its range was c.a. 85 µm which is in agreement with results presented in works [18-21].

After the oxidation procedure the coefficient of friction negatively increased for both modified alloys. Note, that prior to the ball on disc tests the plasma oxidized samples were polished to remove the top surface porous oxide layer. The initial value of CoF for Ti6Al4V alloy was 0.45, whereas for Ti6Al7Nb it was 0.46. The plasma oxidation process increased the values of CoF up to 0.72 and 0.74, respectively. As stated earlier in order to obtain the low roughness of the analyzed alloys, close to the one prior to oxidation process, both alloys were mirror polished. The polishing procedure made it possible to remove the outer layer of oxides, negatively influencing the surface topography, and, at the same time, not to affect the strengthening effect of the plasma treatment. Roughness parameters of Ti6Al4V and Ti6Al7Nb alloys before and after the plasma oxidation are presented in TABLE 1.

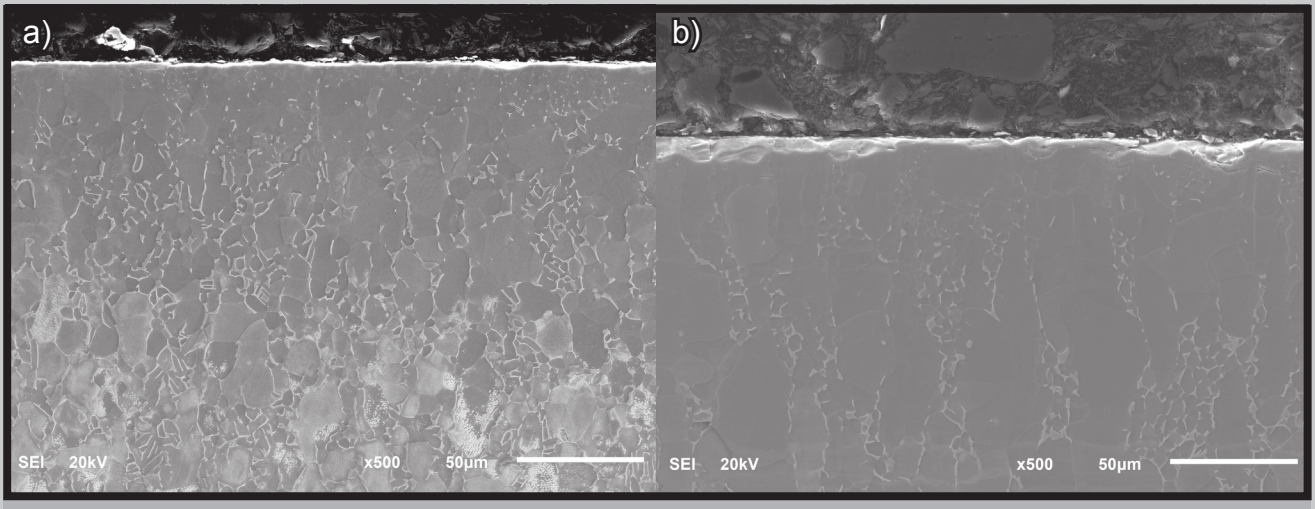

FIG. 2. SEM images of the microstructure after the plasma oxidation of: a) Ti6Al4V and b) Ti6Al7Nb.

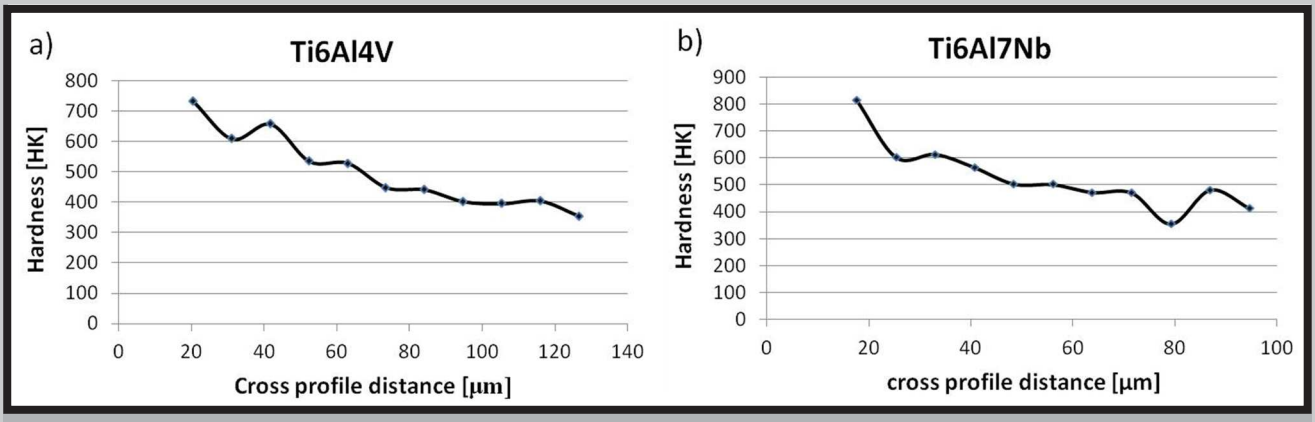

FIG. 3. Hardness distribution on the cross-section of the oxidized samples: a) Ti6Al4V and b) Ti6Al7Nb. The hardness is presented with respect to the distance from the surface of the sample.

TABLE 1. Roughness parameters of Ti6Al4V and Ti6Al7Nb alloys before and after the plasma oxidation.

Modification	Ti6Al4V				Ti6Al7Nb			
	Roughness parameters				Roughness parameters			
	Ra	Rp	Rz	Rmax	Ra	Rp	Rz	Rmax
Before	0.02	0.14	0.23	0.37	0.02	0.12	0.19	0.36
After oxidation	0.08	0.75	1.22	1.38	0.08	0.71	1.15	1.39
After oxidation and polishing	0.02	0.06	0.11	0.13	0.03	0.09	0.19	0.23

The wear rate (FIG. 4a) after the plasma oxidation was $0.171 \cdot 10^{-4}$ mm^3/Nm for Ti6Al4V alloy, which is one order of magnitude lower in comparison to the wear rate of unmodified sample. In the case of the Ti6Al7Nb alloy the wear rate after the plasma oxidation decreased seven times, giving the result $0.260 \cdot 10^{-4}$ mm^3/Nm. Also, the wear rate of the ceramic countersample (FIG. 4b) was significantly reduced. The obtained values of $0.066 \cdot 10^{-4}$ mm^3/Nm for the Ti6Al4V alloy, and $0.061 \cdot 10^{-4}$ mm^3/Nm for the Ti6Al7Nb alloy gave almost three times less wear rate of zirconium oxide countersample. The effect of reducing the wear rates during the tribological tests was obtained despite the fact that the coefficient of friction for both alloys noticeably deteriorated. This may be explained by the increased hardness of the surface and hence higher abrasion resistance. We did not observe the brittleness of the surface layer possibly caused by the oxidation process. The wear tracks were uniform and the values of CoF were stable and did not change during the entire test. The thickness of the modified surface layer (approx. 85 µm) has been found to be sufficient for bearing the applied load during the test.

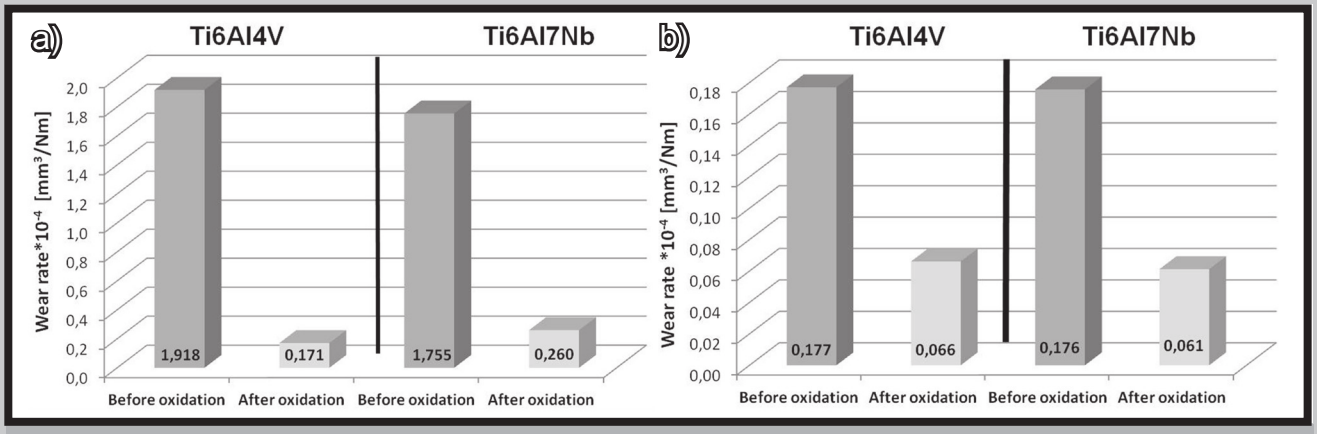

FIG. 4. Wear rates before and after the plasma oxidation of: a) Ti6Al4V and Ti6Al7Nb alloys, b) ZrO_2 countersamples.

TABLE 2. Corrosion parameters of the analyzed alloys.

Sample	E_{cor} (V)	R_p (MΩ cm²)	CR (μm/year)
Ti6Al4V before oxidation	-0.410 ±0.039	0.46 ±0.21	0.71 ±0.34
Ti6Al4V after oxidation	-0.049 ±0.021	1.25 ±0.20	0.22 ±0.03
Ti6Al7Nb before oxidation	-0.395 ±0.041	0.23 ±0.03	1.15 ±0.15
Ti6Al7Nb after oxidation	-0.021 ±0.054	2.35 ±0.15	0.11 ±0.01

Based on the corrosion studies the characteristic parameters characterizing the corrosion properties of the titanium alloys were calculated. The resulting mean values of E_{cor}, R_p and CR along with the standard deviations calculated from measurements of a series of three samples from each type are shown in TABLE 2.

Based on the values of corrosion parameters it can be seen that both titanium alloys have a similar resistance to corrosion - corrosion potential, polarization resistance and corrosion rate have a similar values, and any differences are within the measurement error. The plasma oxidation process resulted in a significant increase in the corrosion potential (approx. 0.36 V). The increase in the polarization resistance - approx. 3 times for the Ti6Al4V alloy, and approx. one order of magnitude for the Ti6Al7Nb alloy, was also observed. Higher polarization resistance provides a better corrosion resistance of the tested materials, which is also confirmed by the values of the corrosion rate presented in TABLE 2. In both cases, the corrosion rate of the modified alloys is lower and therefore it can be concluded, that the plasma oxidation procedure increased the corrosion resistance of studied alloys, wherein the observed effect was greater in the case of niobium containing Ti alloy.

In FIG. 5 the potentiodynamic characteristics of the tested alloys, which can be used to evaluate their resistance to pitting corrosion are presented. The characteristics obtained for titanium alloys prior to the surface modification are typical of passive materials, but differ in the course depending on the alloy.

In both cases, at the potential of approx. 0 V begins a passive low-current range of the potentiodynamic characteristics (passive current density of 5-6 μA/cm²), and depending on the alloy it has a different width. The passive range of the Ti6Al4V alloy is very wide, and it ends at a potential of approx. 3 V. In the case of the Ti6Al7Nb alloy its range is narrower and ends just at a potential approx. 1.2 V. The observed increase in the corrosion current at higher potentials is associated with the processes of electrochemical oxidation of the titanium alloys surface. It was also confirmed by microscopic observations of the surface, performed after the polarization processes (data not shown here), which revealed the presence of corrosion damage. In contrast, the potentiodynamic characteristics of titanium alloys registered after the oxidation processes have a shape almost identical within the entire range of polarization. In both cases the Tafel's range of the characteristic is shifted towards higher potential values, and lower corrosion currents, whereas the further course of the characteristic is also typical for samples in the passive state. In any case, a sharp increase in current associated with pitting corrosion did not occur. The lack of the corrosion damage was also confirmed by the microscopic analysis of the surface.

To summarize, the performed examinations have shown, that the plasma oxidation allows the positive influence on the corrosion resistance of the analyzed alloys.

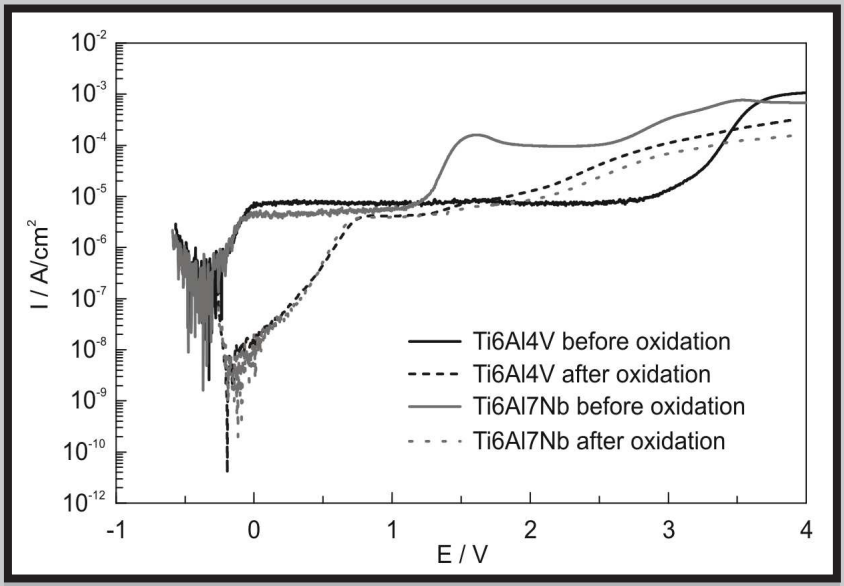

FIG. 5. Potentiodynamic characteristics of the investigated titanium alloys.

Conclusions

The conducted processes of diffusion strengthening of titanium alloys by interstitial oxygen atoms positively influenced the investigated properties. We managed to increase twice the hardness of the surface of the tested alloys and the thickness of the diffusion zone was estimated to be approx. 85 μm. These parameters resulted in a reduction of the wear rate determined in ball on disc tests. The registered value of the wear rate of the Ti6Al4V alloy decreased by one order of magnitude, whereas for the Ti6Al7Nb alloy it was 7 times lower. The lower values of wear rate were achieved despite the fact, that the friction coefficients, compared to the unmodified alloys, have increased from 0.45 to 0.7. The plasma oxidation of Ti alloys favourably affected their corrosion resistance. The value of the corrosion potential significantly increased (approx. 0.36 V). At the same time the polarization resistance increased three times for the Ti6Al4V alloy and 10 times for the Ti6Al7Nb alloy, which demonstrates the better corrosion resistance of the modified samples. The results of the potentiodynamic studies also confirmed a high resistance of the modified alloys against the pitting corrosion. As a drawback of the process of oxidation an increase in surface roughness can be pointed out. It results in the need of additional polishing treatment restoring the original surface smoothness and removing a thin surface layer of a porous oxide.

In summary, it can be stated that the plasma oxidation of titanium alloys favourably influenced the tribological and corrosion properties of both Ti6Al4V and Ti6Al7Nb alloys.

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