

Study of the Properties of Oxide Coatings Formed on Titanium by Plasma Electrolytic Oxidation Method

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Abstract

The development of the modern industry requires to develop high-performance, environmentally friendly methods for the production of light structural material surface coatings. The use of products and structures made of titanium and its alloys with high wear resistance and corrosion resistance prevails in many industries, in particular in the aerospace industry, shipbuilding, and transport engineering. Nowadays, the application of the plasma electrolytic oxidation method, a promising metal surface treatment method, is of increasing interest. Besides this method is called microarc oxidation. The objective of this work is to study the properties of oxide coatings obtained on titanium alloys under the influence of rapid pulsed effects of the plasma electrolytic oxidation process. Oxide composite coatings were obtained in various electrolyte solutions in this work. Oxide coatings are characterized by high wear resistance. It has been established in tribological tests that the wear resistance of the coating is increased by 2–15 times compared with an uncoated sample. The friction coefficient curves obtained for coated samples show that there is no destruction of the coating to the base. The breaking-in area is marked in the curves. The friction surfaces are adjusted to each other and go to a stable friction mode. The latter results in the friction coefficient decrease and wear rate decrease.

1. Introduction

Nowadays titanium and its alloys are widely used in aerospace and other industries due to their high specific characteristics. However, there are areas of application where the use of these alloys is limited by their low hardness and wear resistance. Therefore, the problem of surface modification of titanium alloys is relevant.

Given this, the method of plasma electrolytic oxidation (PEO), a relatively new method used to treat the valve metals surface, is of interest [1–3]. A characteristic feature of PEO is the use of surface microdischarges to form a coating having a very significant and specific effect on the coating formed [4–7].

The oxide coatings obtained due to microplasma treatment in electrolyte solutions have high ad-

hesion to the substrate [8, 9], wear resistance [10–12], heat resistance [13], and corrosion resistance [14]. Oxide coatings are characterized by different porosities [15, 16]. This property of the coating enables us to use it as bioactive materials when modifying the surface of titanium, magnesium and their alloys [17, 18]. The coating composition depends on the substrate material and electrolyte composition. The method is environmentally friendly compared to the traditional anodizing method.

The microarc oxidation (MAO) process can be implemented using stationary and slowly varying energy impacts limiting the widespread use of the method due to the large power consumption. Currently, the microarc oxidation methods are started to be used with fast-flowing (pulsed) energy effects where the voltage change rate reaches 10^8 V/sec, and the current density – 600 A/dm² [19]. This mode enables to form coatings with much lower energy costs.

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Tribological studies are not always performed when studying the wear resistance of coatings. High microhardness oxide coatings containing rutile TiO_2 in their composition are assumed to be wear-resistant [20]. Alongside with that, the coating microhardness is not always proportional to their wear resistance.

The objective of this work is to study the physical and mechanical properties of oxide coatings obtained on titanium and its alloys under the influence of rapid pulsed effects of the plasma electrolytic oxidation process.

2. Experimental part

A unit consisting of a two-electrode electrochemical cell and a power source was used to study the modification of titanium and its alloy surfaces. The cell consisted of a bath, an auxiliary electrode made of stainless steel and a working electrode, i.e. a metal sample. The surface of the auxiliary electrode was 50 times more than the surface of the working electrode. The diagram of the experimental unit is shown in Fig. 1.

“Corundum M0” pulsed power source of thyristor type was used as a source of power. “Corundum M0” power supply enables to form alternating positive and negative voltage pulses of a trapezoidal shape. When using pulses of this form, the supplied energy is used the most complete, while the duration of the pause between pulses is sufficient so that there is no strong overheating of the near-electrode layer.

The PEO process conditions: anode current pulse duration is $250 \pm 25 \mu\text{s}$; cathode current pulse duration is $5 \pm 0.5 \text{ ms}$; pause between anode and cathode current pulses is $250 \pm 0.5 \mu\text{s}$; repetition frequency of the anodic and cathodic pulses is $50 \pm 0.5 \text{ Hz}$; voltage is within 360–365 V; current density is within 110–114 A/dm^2 , process time is 600 sec.

The surface was modified in VT1-0 and VT5 titanium alloy samples of rectangular shape 3 mm

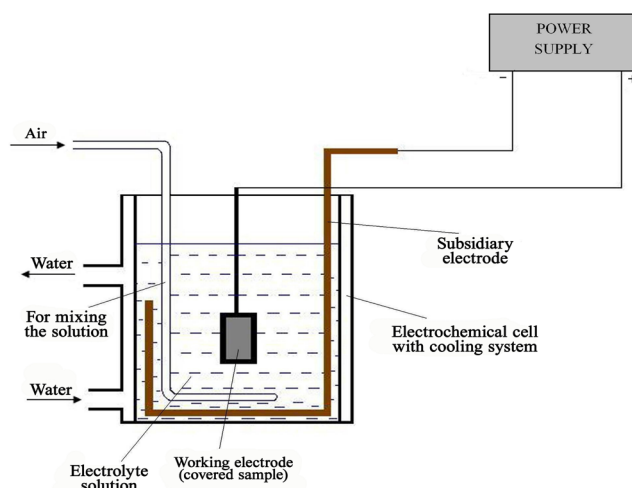


Fig. 1. Diagram of the experimental unit.

thick and sized of $20 \times 40 \text{ mm}$ and $15 \times 40 \text{ mm}$. The alloys compositions are shown in Table 1.

Preliminarily the samples were ground to remove any oxide film and scratches. Then the surface was cleaned from organic impurities, the samples were washed with distilled water, a solution of ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$ and again with distilled water. Then the samples were dried at room temperature.

Alkaline electrolyte solutions were used as electrolytes with the compositions specified in Table 2.

The surface microhardness of oxide coatings obtained on titanium and its alloy was studied with the help of a Vickersat KB 30S hardness gage made by Pruftechnik GmbH with a load of 200 g.

Tribological studies of the wear resistance of oxide coatings obtained on titanium samples were performed with the help of a TNT-S-AH0000 high-temperature tribometer. Besides, we used a 3 mm ball indenter made of WC alloy to study the tribological properties of coatings.

Tribological test conditions: the load was 1N, linear speed was 4 cm/s, measurements were carried out at $25 \text{ }^\circ\text{C}$, air humidity was 50%, track radius was 3 mm, number of revolutions was 1000.

Table 1
Composition of alloys

Brand	Mass fraction of chemical elements, %											
	Ti	Al	V	Mo	Zr	Si	Fe	Oxygen	Hydrogen	Nitrogen	Carbon	Other impurities
VT1-0	Base	-	-	-	-	0.10	0.25	0.20	0.010	0.04	0.07	0.30
VT5	Base	4.5-6.2	1.2	0.8	0.30	0.12	0.30	0.20	0.015	0.05	0.10	0.30

Table 2
Composition of electrolytes

Electrolyte No.	Electrolyte composition	Concentration, g/l
1	Disodium phosphate 12 hydrate	40
	Sodium tetraborate 10 hydrate	30
	Boric acid	22
	Ammonium fluoride (NH ₄ F)	10
2	Sodium phosphate 3-sub. 12 hydrate	70
	Aluminum oxide (1.1– 1.5 micron) powder	20
3	Disodium phosphate 12 hydrate	40
	Sodium tetraborate 10 hydrate	30
	Boric acid	22
	Ammonium fluoride (NH ₄ F)	10
	Sodium metavanadate	1.0

Wear resistance was estimated for the track depth area measured using MICROMEASURE 3Dstation, a non-contact 3D-profilometer. A three-dimensional image of the surface and automatic calculation of the track area were displayed on the profilometer. A thin layer of aluminum 50–60 nm thick was deposited on the samples to increase the reflective properties of the surface.

Oxide coating thicknesses were determined with the help of a QuaNix-1500 thickness gauge with digital indexing.

3. Results and discussions

The plasma electrolytic oxidation method enables to modify the surface of titanium and its alloys and to obtain coatings with various properties. The properties of the coatings are affected by both the electrolyte composition and the microplasma process modes [21].

In this work, alkaline electrolyte solutions were used to obtain oxide coatings. When choosing electrolytes, we proceeded from the fact that phosphate ions contribute to an increase in electrochemical polarization since they form barrier films on the base metal surface. When borates are in a solution during microplasma discharges, solid and heat-resistant boroxide compounds are formed on the sample surface. Fluoride compounds increase the hardness of the synthesized coating. When alumina powder is introduced into the solution, powder particles can be incorporated into the coating composition [22].

The coating was formed in a pulsed mode, where the duration of the anode current pulse was $250 \pm 25 \mu\text{s}$; the cathode current pulse duration was $5 \pm 0.5 \text{ ms}$; the pause between the anodic and cathodic current pulses was $250 \pm 25 \mu\text{s}$; repetition rate of anode and cathode pulses $50 \pm 0.5 \text{ Hz}$. In all electrolyte solutions, dense uniform oxide coatings are formed on the samples. The thickness of the oxide coatings was 10–21 microns.

Table 3
Microhardness of uncoated samples and oxide coatings obtained in various electrolytes based on VT1-0 and VT5 alloys

Measurements No.	Microhardness of VT1-0 alloy without coating and with oxide coatings obtained in electrolytes 1–3 (Table 2), HV				Microhardness of VT5 alloy without coating and with oxide coatings obtained in electrolytes 1–3 (Table 2), HV			
	Without coating	1	2	3	Without coating	1	2	3
1	200	648	629	415	348	665	640	585
2	234	683	274	522	402	636	518	563
3	253	559	593	497	418	591	537	713
4	240	556	520	728	369	1016	864	549
5	241	716	422	509	368	1155	659	580
6	257	575	411	461	342	678	626	520
Average	237.5	622.8	474.8	512.5	374.5	790.2	640.7	585.0

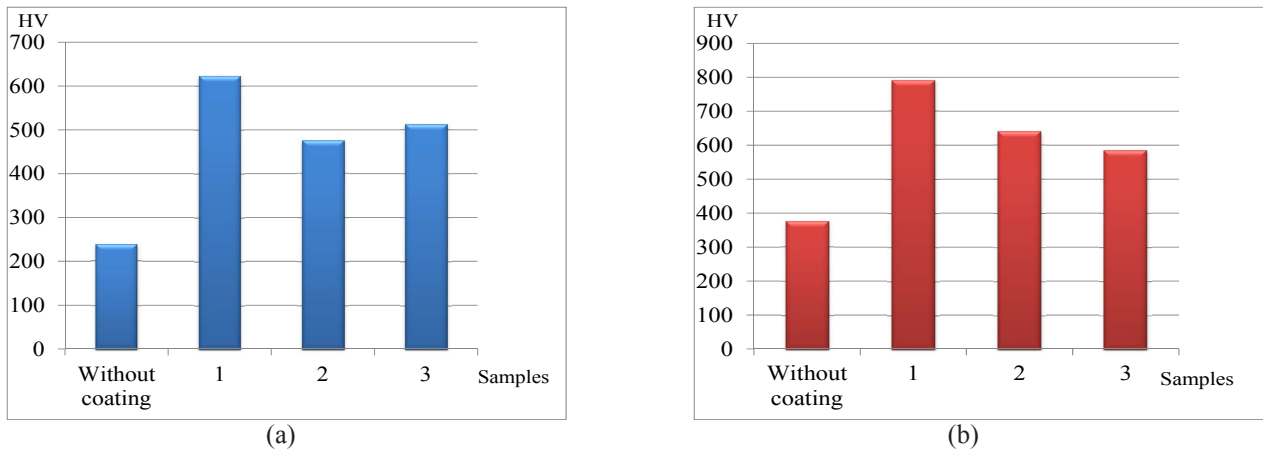


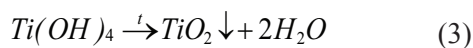
Fig. 2. Data for microhardness of the coatings obtained on VT1-0 (a) and VT5 (b) alloys in Electrolytes 1, 2, 3 (Table 2) as compared with samples without coating.

The surface microhardness data for uncoated and oxide coated samples obtained in various electrolyte solutions are shown in Table 3.

Comparative data for the microhardness of oxide coatings obtained on VT1-0 and VT5 alloys, compared with samples without coating are shown in Fig. 2.

An increase in surface microhardness by 1.5 or more times is observed for samples of coated VT1-0 and VT5 alloys formed in Solutions 1–3 (Table 2).

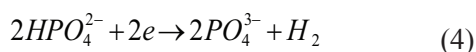
The highest VT1-0 titanium alloy microhardness is observed for the oxide coating obtained in electrolyte No. 1. At the same time, the microhardness increases by 2.6 times compared with the uncoated sample. In this electrolyte, coatings are formed on metals containing oxides of the base metal and electrolyte components. In the initial period of electrolysis, a thin layer of oxides is formed on the surface:



Oxygen in the form of ions penetrates through the film and causes further oxidation of the metal.

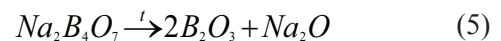
Layers containing both matrix elements (oxidizable material) and electrolyte solution elements are formed on the surfaces of products as a result of local high-energy exposure.

The alkali metal phosphate forms phosphate ions as a result of the reaction which



form a part of the coating as P_2O_5 oxide under the influence of high temperatures. This process can result in the coating hardness increase.

High voltage and developing high temperatures in the area of microplasma discharges lead to the formation of solid and heat-resistant organoboron compounds



In electrolyte solution No. 2, coatings are formed on the surface of titanium alloys similarly to reactions 1–4. Since the solution contains alumina, powder particles can form a part of the coating [23].

Electrolyte solution No. 3 is characterized by reactions 1–5. The introduction of sodium metavanadate in this electrolyte results in the formation of a black oxide coating. Obtaining a black color of the coating is most likely associated with the introduction of vanadium oxide into the coating formed under the influence of high temperatures during microarc discharge.

When studying the wear resistance of coatings, we obtained the following three-dimensional images of the samples surfaces with a track (Fig. 3), curves for changes in the friction coefficient (Fig. 4), data for the depth areas of wear tracks (Table 4).

Figure 3 shows three-dimensional images of sample surfaces with a track for VT1-0 alloy without and with coating obtained in electrolyte solutions No. 1, 2.

The obtained three-dimensional images of the samples surfaces with a track show that the width and depth of the track in a sample without coating significantly exceeds the width and depth of the tracks in samples with coating. It follows that the wear resistance of oxide coatings is higher than that of the original uncoated sample.

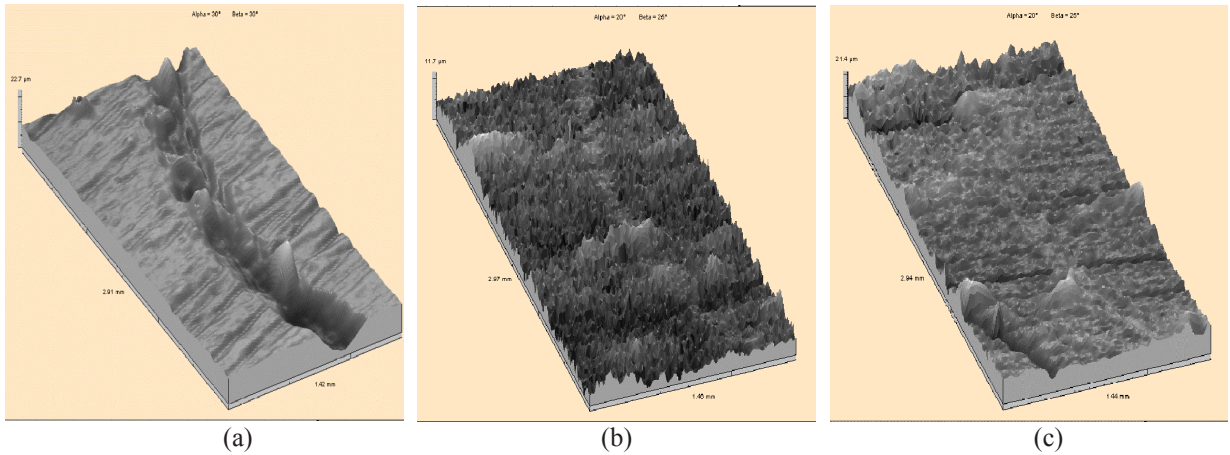


Fig. 3. Three-dimensional image of the samples surfaces with a track for VT1-0 alloy: (a) without coating, (b) with a coating obtained in electrolyte No. 2 (Table 2), (c) with a coating obtained in electrolyte No. 1 (Table 2).

The analysis of the friction coefficients of the coatings (Fig. 4) shows that there are breaking-in areas in the tribosystem where the friction surfaces adjust to each other. Besides, stages with stable friction conditions and a practically constant and

relatively low wear rate can be seen there. There is no sharp change in the friction coefficient characteristic for coating destruction. Oxide coatings are not destroyed and do not wear up to the base under the given test conditions.

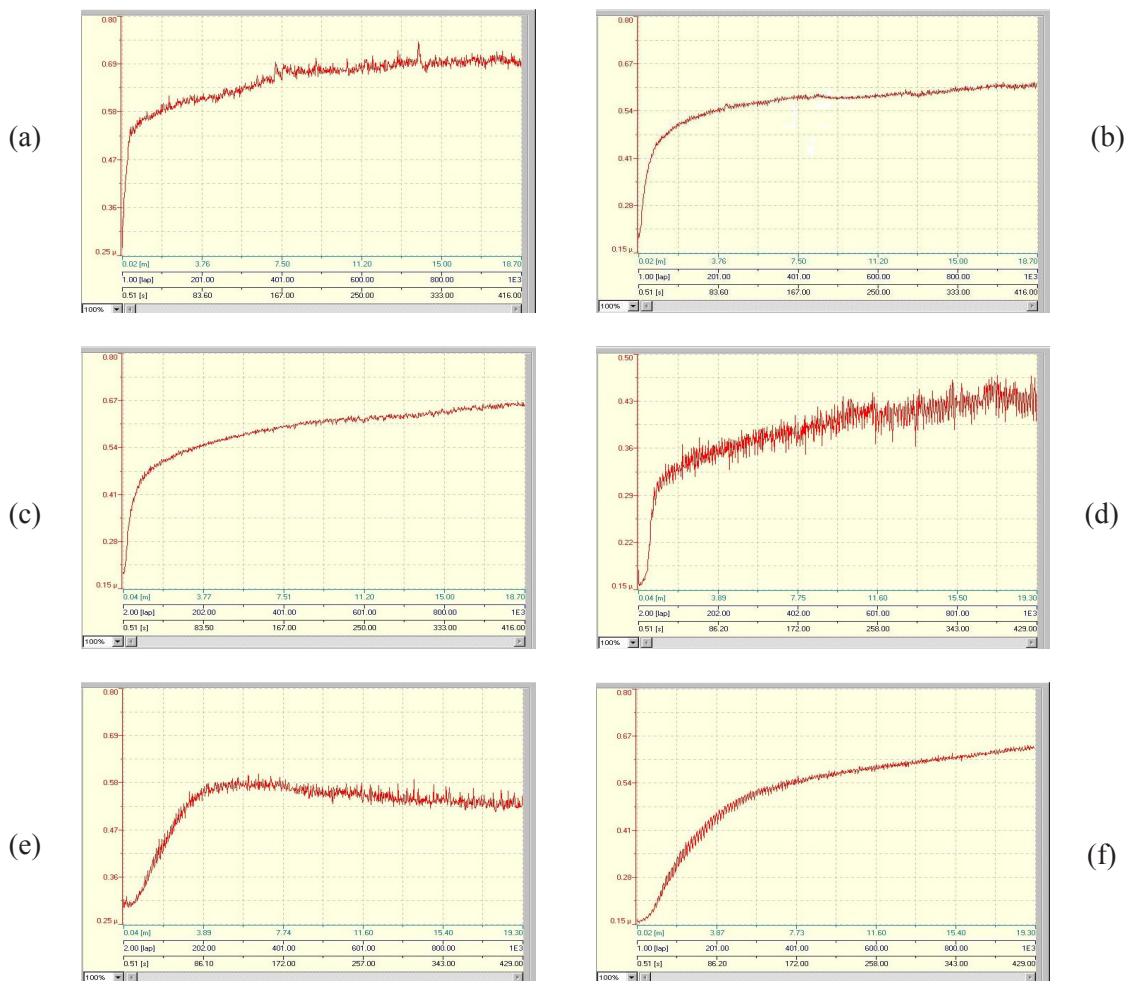


Fig. 4. Friction coefficient curves for coated VT 1-0 and VT5 alloys obtained in electrolytes 1–3 (Table 2): (a) – in electrolyte No. 1 on VT1-0 alloy; (b) – in electrolyte No. 2 on VT1-0 alloy; (c) – in electrolyte No. 3 on VT1-0 alloy; (d) – in electrolyte No. 1 on VT5 alloy; (e) – in electrolyte No. 2 on VT5 alloy; (f) – in electrolyte No. 3 on VT5 alloy.

Table 4
Track depth area data for VT1-0 and VT5 alloys with oxide coatings obtained in electrolyte solutions

No.	Track depth area, μm^2					
	1 electrolyte		2 electrolyte		3 electrolyte	
	VT1-0	VT5	VT1-0	VT5	VT1-0	VT5
1	240	198	48.9	213	145	148.6
2	286	185	25.7	372	81.5	144
3	569	105	149	331	242	190
4	358	105	28.5	339	193	150
5	76.3	148	124	492	190	123
6	347	166	83.2	627	94.9	163
7	177	198	160	939	179	80.7
8	225	185	65.6	468	155	195
9	157	105	35.0	581	218	143
Σ/n	270.6	155	79.9	484.7	166.5	148.6

The analysis of the profiles (tracks) obtained was performed using the Mountains Map Universal v.2.0.13 computer program. The program automatically determined the depth area of the track, at nine points equally spaced from each other along the entire length of the track (Table 4).

The arithmetic average of these track depth areas for VT1-0 titanium alloy is $1217.5 \mu\text{m}^2$, for VT5 alloy – $925.0 \mu\text{m}^2$. The data for the track depth areas are shown in Table 4 for oxide coatings obtained in various electrolyte solutions.

Comparative data on the wear resistance of coatings in the form of a diagram is shown in Fig. 5.

As can be seen from Fig. 5, oxide coatings obtained on VT1-0, VT 5 alloys are characterized with high wear resistance as compared with the uncoated sample. The data on tribological tests of oxide coatings obtained on VT1-0 alloy shows that the wear

resistance of the coating on sample 2 is increased by 15 times compared with the starting material. This coating is formed in an electrolyte containing an alkali metal phosphate with the addition of alumina powder. As a result of the electrophoresis effect, solid alumina particles can be incorporated into the coating composition. However, the oxide coating obtained in this electrolyte on VT5 alloy does not give such a high value of wear resistance. This is due to the fact that coatings can form on different alloys whose properties differ from each other under the same conditions in a solution of the same electrolyte [23]. Alloying additives which are part of the alloy affect the properties and composition of coatings.

The increase in wear resistance of oxide coatings obtained in electrolytes 1 and 3 (Table 2) is 4.5 and 7.7 times more compared with the uncoated sample, respectively.

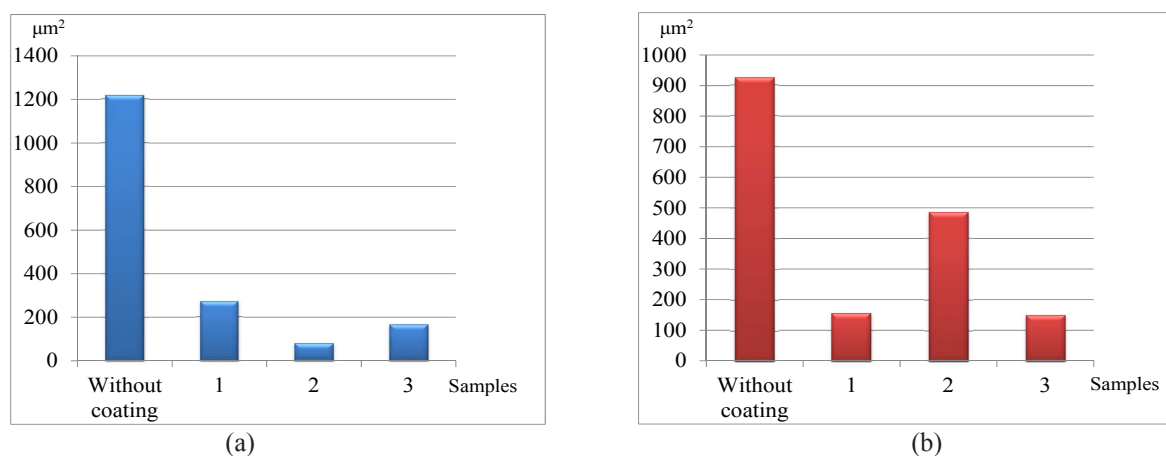


Fig. 5. Comparative wear resistance data for VT 1-0 and VT5 alloys without coating and with oxide coatings obtained in electrolytes 1–3 (Table 2): (a) – VT1-0 alloy; (b) – VT5 alloy.

The oxide coating on the VT5 alloy obtained in solutions 1 and 3 (Table 2) gives an increase in wear resistance compared with the uncoated sample by 5.9 and 6.3 times, respectively. A less wear-resistant oxide coating is formed in electrolyte No. 2, on VT5 alloy in comparison with the oxide coating on VT1-0 alloy. Apparently, this is due to the alloying additives of titanium VT5 alloy.

4. Conclusions

The modification process for the surface of titanium and its alloys in a pulsed anode-cathode mode with an anode current pulse duration of 250 μ s was studied. The process implementation at small values of the current pulse duration enables us to avoid the formation of a loose outer coating layer. The outer layer is formed as a dense one and may be functional. The surface microhardness of the oxide coatings obtained is 2 or more times higher compared with the samples without a coating. Studies of the wear resistance of oxide coatings showed a significant increase compared with an uncoated sample. The oxide coating obtained on the VT1-0 alloy in electrolyte 2 (Table 2) increases the wear resistance by 15 times in comparison with the initial sample without coating. In electrolytes 1 and 3 (Table 2), coatings are formed on the same alloy increasing the wear resistance by 4.5 and 7 times, respectively, compared with the uncoated sample. The highest wear resistance on the VT5 alloy is observed in the oxide coating obtained in solution 3 (Table 2). The introduction of sodium metavanadate into the solution makes it possible to obtain black coatings. A comparison of the data for the wear resistance of coatings obtained on VT1-0 and VT5 shows that the coatings formed on the unalloyed VT1-0 alloy have better performance (Fig. 5).

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