Anodic plasma electrolytic saturation of the Ti6Al4V alloy with nitrogen and oxygen

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Abstract. The structure of the Ti6Al4V alloy, its microhardness, surface roughness, and wear and corrosion resistance after anodic plasma electrolytic saturation with nitrogen and oxidation of the surface were investigated. It was shown that an electrolyte containing ammonia and ammonium chloride provided the saturation of the alloy with nitrogen and oxygen and the formation of TiO₂ with rutile structure and a nitrogen solid solution in the alloy. The treatment at 750 °C during 5 min results in an increase in microhardness up to 790 HV and a decrease in surface roughness by 1.4-fold owing to the anode dissolution of titanium. The dry friction coefficient of the samples after treatment at 700 °C can be 3.5-fold reduced through sliding with a speed of 0.144 and a load of 105 N. These regimes allow diminishing the wear rate of samples of titanium alloy after their wear testing by 2 orders of magnitude. Corrosion resistance in Ringer's solution does not deteriorate after treatment at a low temperature, when an oxide layer forms on the surface.

1. Introduction
Alpha- and beta-titanium alloy Ti6Al4V and its Russian analogue VT6 are most widely used in modern industry due to a number of advantages [1]. These include high ductility and machinability, corrosion resistance, low thermal conductivity, etc. The poor wear resistance of Ti6Al4V, like that in other titanium alloys, can be improved by conventional thermal chemical treatment, particularly, nitriding. Long gas nitriding (up to 100 hours) can be significantly reduced to 3 hours by carrying out the process in pure nitrogen at a temperature of 1400 °C [2] or by plasma nitriding in an anomalous glow [3] as well as non-self-maintained discharge with the emission of N⁺, O⁺, and CᵅH₄⁺ ions [4]. Some coatings obtained by plasma electrolytic oxidation are characteristic by good biocompatibility and bactericidal properties [5]. Plasma electrolytic saturation (PES) of titanium alloys with atoms of light elements is a promising area, which permits to reduce the processing time to several minutes.

Cathodic nitrocarburising of commercial pure titanium in an electrolyte containing formamide and triethanolamine allows obtaining a thin carbonitride layer with a microhardness up to 2080 HV [6]. Saturation of commercial pure titanium with boron in a borax solution leads to the formation of nanocrystalline borides in the surface layer with an increase in the corrosion resistance in Ringer's solution [7]. Borocarburising of the Ti48Al2Cr2Nb alloy in a solution containing glycerol, borax and boric acid also results in the formation of nanocrystals in the surface layer [8]. Research has established an increase in the wear resistance of Ti6Al4V alloy after its cathodic carbonitriding in a
carbamide-based solution [9]. The wear rate decreases by 3 orders of magnitude under lubricant friction conditions against steel hardened to 50 HRC.

The anodic processes of PES are characterized by a decrease in surface roughness due to anodic dissolution and the absence of electric discharges, as well as additional saturation of the surface with oxygen. Anodic carburising of commercial pure titanium using an acetone-based solution allows increasing its surface hardness to 340 HV [10], and alpha- and beta-titanium alloy VT22 to 520 HV [11]. Anodic nitrocarburising of VT22 in a carbamide-based electrolyte shows positive results where microhardness of the layer reaches up to 780 HV [12]. Enhancement of the wear resistance of Ti6Al4V alloy is detected after its anodic carburising in an electrolyte containing ethylene glycol [13]. The weight wear rate after lubricant friction against the bearing steel as a counter body decreases by two orders of magnitude.

We could not find the results of PES of the Ti6Al4V alloy with nitrogen. It is known that anodic nitriding of commercial pure titanium in an ammonia-based electrolyte provides a significant decrease in the weight wear rate (by two orders of magnitude) with a slight increase in surface hardness to 220 HV [14]. Similar results are obtained after anodic nitriding of the alloy VT22 [15]. It is of interest to study the possibility of anodic nitriding of the Ti6Al4V alloy to enhance its wear resistance. Therefore, the aim of this work is to study the effect of the temperature of the anodic nitriding of the Ti6Al4V alloy in an ammonia electrolyte on the composition of the surface layer, its microhardness and roughness, as well as on wear resistance and corrosion resistance.

2. Experimental
Cylindrical samples (a diameter of 10 mm, a length of 15 mm) of titanium alloy Ti6Al4V were ground with SiC abrasive paper to a roughness of Ra (1.00 ± 0.10 μm) and ultrasonically cleaned with acetone. Vertically oriented samples were completely immersed in a cylindrical electrolyzer under the condition of a longitudinal flow of a cooled aqueous solution containing ammonium chloride (10 wt.%) and ammonia (5 wt.%) with a temperature of (20±2) °C. The electrolyte volume was 4 L, the duration of saturation with nitrogen and oxygen was 5 min. The electrolyte flow rate was measured with a RMF-0.16 GUZ flowmeter and maintained at 2.6 L/min. The samples were quenched in the same electrolyte by disconnecting the voltage after saturation with nitrogen and oxygen.

The surface morphology and the elemental composition of the layer were studied using a VEGA 3 SBH electron microscope after polishing and etching samples for 1 min, using a 5 wt.% solution of hydrochloric acid in glycerol. The arbon concentration was subtracted to evaluate the layer composition under the assumption that this signal belongs to organic pollution. The structure was examined and microhardness was measured with a Falcon 503 (Innovatest) microhardness tester with a load of 50 g. The surface roughness was measured on a TR200 profilograph-profilometer.

A ball-on-disk (normal load 105 N, sliding speed 0.144 m/s, and sliding distance 100 m) against a bearing steel ball (9 mm in diameter) was applied to evaluate the wear rate and friction coefficient of the untreated and treated samples at dry and lubricated conditions (engine oil “LITOL” containing petroleum oil with a viscosity of 60–75 mm²/s at 50 °C, lithium soap of 12-hydroxy acid and an antioxidant additive). The weight loss was measured with electronic balance with an accuracy of ±0.1 mg. Corrosion tests were carried out in a three-electrode cell using an SP-150 Biologic potentiostat-galvanostat at a sweep rate of 1 mV/s. The potential was measured against a silver chloride saturated electrode. The surface of the sample was shielded, its side surface with an area of 0.32 cm² remained in contact with the solution. Ringer’s solution was chosen as a corrosive medium. The current density of corrosion was calculated by extrapolating the Tafel polarization curves.

3. Results and discussion
Anodic saturation of titanium alloys in aqueous electrolytes is always accompanied by the formation of an oxide layer, the morphology of which is shown in figure 1. The main part of the layer is represented by a smooth surface with small pores, which facilitate the diffusion of the saturating components and the liberation of dissolved metals. According to elemental analysis, the oxygen
content in the layer is \((34.5 \pm 0.5)\) wt.\%, which is close to the concentration of \(\text{TiO}_2\) (rutile), the formation of which was previously confirmed by X-ray analysis [13, 14]. The concentration of titanium is \((59.3 \pm 0.5)\) wt.\%, which also corresponds to rutile. The content of aluminum and vanadium is likewise reduced by 38–41%. A low chlorine content \((0.11 \pm 0.03)\) wt.\% indicates the participation of electrolyte anions in the anodic dissolution. Approximately the same composition, but with a higher oxygen concentration \((42.5 \pm 0.5)\) wt.\% is observed in dark areas with increased roughness.

Diffusion of oxygen and nitrogen reduces the stability of the \(\beta\)-phase and contributes to the martensitic transformation of the alloy with the formation of a supersaturated solid solution of the alloying components in titanium. The result of this transformation is an increase in the hardness of the alloy (figure 2). The lower surface hardness after saturation at \(700\) °C may be attributed to the absence of martensitic transformation owing to the insufficient diffusion of saturating components. The maximal thickness of the layer of increased hardness, exceeding \(0.25\) mm, is achieved at a saturation temperature of \(900\) °C, probably because of more intensive diffusion of nitrogen and oxygen. The surface roughness with respect to Ra parameter decreases at all saturation temperatures by 5–30%. The dependence of the roughness reduction on the saturation temperature is not detected due to uncontrolled partial exfoliation of the oxide layer.

![Figure 1. Top view of the oxide layer on the surface of the Ti6Al4V alloy after PES at 750 °C.](image1)

![Figure 2. Microhardness distribution in the surface layer of the Ti6Al4V alloy after PES at different temperatures (°C).](image2)

![Figure 3. The weight wear rate of the Ti6Al4V alloy processed at different temperatures after tribological tests.](image3)

![Figure 4. Polarization curves of corrosion tests for the Ti6Al4V alloy after PES at different temperatures. The test media is Ringer's solution.](image4)
Tribological tests show that the lubricant friction coefficient of samples treated at all temperatures is always lower than that of an untreated sample. No correlation between the friction coefficient and surface roughness Ra is found. The minimal friction coefficient, equal to 0.3, is observed after saturation at 850–900 °C, as well as the lowest wear rate (figure 3), which can result from the retention of lubricant in the pores of the oxide layer, which grows with increasing temperature. The dry friction coefficient decreases in comparison with the untreated sample only after saturation at low temperatures and reaches 0.15 at 700 °C, which is 3.5-fold less than that of the untreated sample. A minimum wear rate is also achieved under these conditions.

The results of corrosion tests show that the corrosion potential shifts in the positive direction only after treatment of the alloy at low temperatures up to 700 °C (figure 4). The minimum corrosion current density of 0.13 μA/cm² is observed after treatment at 700 °C, which is not too much higher than that of the untreated sample (0.08 μA/cm²).

4. Conclusions
The possibility of increasing the hardness and wear resistance of alpha- and beta-titanium alloy Ti6Al4V by means of the anodic plasma electrolytic saturation with oxygen and nitrogen in an electrolyte containing ammonium chloride (10 wt.%) and ammonia (5 wt.%) followed by quenching in the same electrolyte is shown. This treatment results in an increase in surface hardness up to 790 HV, a decrease in surface roughness from Ra 1.0 μm for the untreated sample to Ra 0.7 μm, and an increase in wear resistance by two orders of magnitude under the studied friction conditions.

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