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# Plasma electrolytic nitriding of alpha- and beta-titanium alloy in ammonia-based electrolyte

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ABSTRACT

The structure of alpha- and beta-titanium alloy, its microhardness, surface roughness, wear and corrosion resistance after anodic plasma electrolytic nitriding (PEN) in electrolyte containing ammonia were investigated. An X-ray diffractometer and a scanning electron microscopy (SEM) were used to characterize the phase composition of the modified layer and its surface morphology. Tribological properties of nitrided titanium alloy and their corrosion resistance are investigated. It was shown that the electrolyte containing ammonia and ammonium chloride provided the saturation of alloy with nitrogen and oxygen and formation $TiO_2$ with rutile structure and nitrogen solid solution in titanium. The anodic PEN at 800 °C during 5 min results in an increase in microhardness to 520 HV and a decrease in surface roughness by 4 times owing to anode dissolution of titanium. Friction coefficient of nitrided samples can be 4.4 times reduced through sliding with speed of 0.49 m/s and load of 208.6 N. These regimes enable to diminish wear rate of titanium alloy samples after their wear testing by 4 orders. The decrease in the sliding speed and load leads to the rise of friction coefficient and wear rate.



## 1. Introduction

Thermochemical treatment of titanium alloys is widely used to improve its surface properties, in particular for increasing the wear resistance [1]. Plasma electrolytic treatment has been also known for its advantages in diffusion saturation of titanium alloys. It is established that hardness of commercial pure titanium (CP-Ti) can be increased to 800 HV by means of cathode plasma electrolytic saturation with nitrogen and carbon using aqueous solution of carbamide and sodium carbonate [2] or to 1500 HV in solution of carbamide, triethanolamine, and formamide [3]. Microhardness of Ti6Al4V after its nitrocarburising in a solution of ammonium nitrate, ethanol, and glycerol reaches 2000 HV [4] or 2369 HV using a solution of triethanolamine and formamide [5]. This treatment enables to reduce weight loss of CP-Ti during wear testing 17 times [2] and Ti6Al4V by a factor 3248 [5]. Pulse saturation of CP-Ti with nitrogen and carbon is shown to result in the formation of nanocrystalline carbonitrides [6] and enhance of corrosion resistance of CP-Ti after its nitrocarburising in triethanolamine [7] or mixture of carbamide, formamide, and triethanolamine [3].

Plasma electrolytic nitriding (PEN) of titanium alloys is not thoroughly considered. Possible saturation of CP-Ti with nitrogen in electrolyte containing ammonia and ammonium chloride is shown [8]. It is found that the oxide layer on the titanium surface has micropores to 100 nm, through which the diffusing oxygen and nitrogen atoms are transported from vapour-gas envelope to metal. Similarly, migration of titanium atoms is carried forward from metal to envelope through these pores due to anodic dissolution. The thickness of the gas-enriched layer after nitriding is 20 μm. $TiO_2$ (rutile) is detected by X-ray analysis. In this case, elemental composition of surface layer is determined by spectra analysis of proton nuclear backscattering. It is revealed that oxygen diffusion prevails over nitrogen one when the PEN temperature is below 750 °C. The temperature rises to 780 °C results in the nitrogen concentration of 15 at.%. In this case, the oxygen concentration in the diffusion layer varies little [9]. This treatment is shown to promote increase in the corrosion resistance of CP-Ti in an aqueous solution of hydrochloric acid with an additive of protein-vitamin concentrate [10].

Anodic PEN of some low-alloy titanium alloys leads to an increase in their surface hardness up to 320–480 HV. Therefore, a positive effect of the anodic PEN on the wear resistance of CP-Ti was detected. The rise of the nitriding temperature up to 850 °C promotes the reduction of the friction coefficient from 0.7 for the untreated sample to 0.15. Wear testing shows that the weight loss decreases from 37 mg for the untreated sample to 0.52 mg for sample nitride at 800 °C [11]. Moreover, the increase in CP-Ti corrosion resistance in Ringer's solution is also noted.

According to the data obtained the cathode PEN of titanium alloys leads to a significant increase in their surface hardness and wear and

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corrosion resistance. It is also established that ammonia electrolyte enables to carry out anodic PEN of titanium with an increase in its surface hardness and wear resistance. Therefore, the aim of this work is to study the possibility of anodic PEN of titanium alloy VT22 in electrolytes containing ammonia and ammonium chloride with evaluation of wear and corrosion resistance of treated titanium samples. This alpha- and beta-titanium alloy was created on the base of system Ti-A1-Mo-V with additive of Fe and Cr [12] and is an analog of high-strength alpha-beta titanium alloy [13]. Alloy of VT22 can be effectively hardened after quenching, which can be easily performed at the anodic PEN by the electrolyte after the power supply is switched off. Proposed investigation includes the effect of the processing temperature on the surface roughness of samples, their microhardness, friction coefficient, weight wear, corrosion potential, and corrosion current density.

## 2. Materials and methods

### 2.1. PEN treatment

Cylindrical samples (∅ 10 × 15 mm) of titanium alloys VT22 (4–5.5% Mo, 4–5.5% V, 4.4–5.9% Al, 0.5–1.5% Fe, 0.5–2% Cr) were nitrided in a cylindrical electrolyzer with an axially symmetric electrolyte flow supplied through a nozzle located at the bottom of the electrolyzer [14]. Prior to the surface treatment, each specimen was ground with SiC abrasive paper grit size P320 to $R_a$ ~1.0 μm and ultrasonically cleaned with acetone. In the upper part of the electrolyzer, the electrolyte was overflowing into the sump and was further pumped through a heat exchanger at a rate of 3 l/min. The volume flow rate was measured with a RMF-0.16 GUZ flowmeter (accuracy of ±2.5%). The solution temperature was measured using thermocouple placed at the bottom of the chamber. The electrolyte temperature was maintained at 20 ± 1 °C. The samples were connected as the positive output and the electrolyzer was connected as the negative output of the DC power supply.

After switching the voltage, the samples were immersed in the electrolyte at a depth equal to their height. The voltage was measured using an LM-1 voltmeter (accuracy ±0.5%). The current was probed with an MS8221 multimeter. The sample temperature was measured with another MS8221 multimeter and M89-K1 thermocouple accuracy to 2% over a temperature range of 400–1000 °C. Temperature measurements were performed using thermocouple fixed in a hole made in the samples at a distance of 2 mm from the heated surface. The treatment time was 5 min. The treatment temperature varied from 650 to 900 °C with an increase in voltage of DC power supply from 140 to 225 V. After PEN samples were quenched in the electrolyte (hardening).

Aqueous solution of ammonia $NH_3$ (5 wt.%) and ammonium chloride $NH_4Cl$ (10 wt.%) was used as the working electrolyte. The solution concentration was regulated by measuring its density with a densimeter (accuracy ±0.001 g/cm$^3$).

### 2.2. Surface characterization

The phase composition of the surface layers after PEN was investigated with the use of an ARL X'tra X-ray diffractometer (Thermo Fisher Scientific) with Cu Kα radiation at a simple scanning in the theta-2theta-mode and scanning rate of 2°/min.

Quanta 3D 200i scanning electron microscopy (SEM) (FEI Company) was used to observe the surface morphology and cross-sectional with the subsequent elemental microanalysis after polishing and etching with the use of a 5% hydrofluoric acid solution in glycerol for 1 min.

The microhardness of the sample surface layer after PEN was measured on a PMT-3M apparatus at a loading of 50 g.

The surface roughness before and after PEN was investigated using a roughness tester TR200.

A pin-on-disk (208.6 N normal load, 0.49 m/s sliding speed, and 500 m sliding distance with hardened steel (50 HRC) disk) and a ball-on-disk (105 N normal load, 0.144 m/s sliding speed, and 100 m sliding distance with bearing steel ball (9 mm in diameter)) tribometers were applied to evaluate friction coefficient of the untreated and treated samples at lubricated conditions (engine oil "LITOL" containing petroleum oil with viscosity of 60–75 mm$^2$/s at 50 °C, lithium soap of 12-hydroxy acid and antioxidant additive). The weight loss was measured by an electronic balance with accuracy ±0.0001 g.

To assess corrosion properties of the treated surfaces, potentiodynamic polarisation tests (in Ringer's solution with sodium chloride (6.5 g/l), potassium chloride (0.42 g/l), calcium chloride (0.25 g/l), and sodium carbonate (1 mol/l) and with a sweep rate of 1 mV/s) were performed using a Biologic SP-150 potentiostat/galvanostat (Biologic Science Instruments). The potential was measured against a silver-silver chloride saturated electrode. Ringer's solution simulated human body fluid is used as a test media for comparison with the data of other authors.

## 3. Results and discussion

### 3.1. Phase composition

The anodic PEN in aqueous electrolytes results in oxidation of the samples' surface with formation of oxide layer. According to the data of X-ray analysis $TiO_2$ with rutile structure is formed on the titanium surface after PEN at all treatment temperatures (Fig. 1). It can be assumed that the main reaction of titanium oxidation is the following:

$$Ti + 2H_2O \rightarrow TiO_2 + 2H_2 \quad (1)$$

This reaction rate increases as the sample temperature rises. Hence, the amount of rutile grows.

The CP-Ti PEN in ammonia-based electrolyte reveals a similar result where titanium nitride has not been detected as well. Hence, anodic PEN differs sufficiently from cathode nitrocarburising where titanium carbonitrides of different composition are found [3,5,7] that is associated probably with a local increase in temperature of samples surface under the action of electric discharges.

### 3.2. Cross-sectional morphology and microhardness tests

Surface layer of the sample becomes enriched with titanium oxide and nitrogen forming a solid solution because of PEN of titanium alloy and its high-temperature oxidation at 650–700 °C (Fig. 2a and b). The PEN at 750–900 °C followed by quenching in electrolyte results in the structure change of the surface layer that corresponds to an incomplete

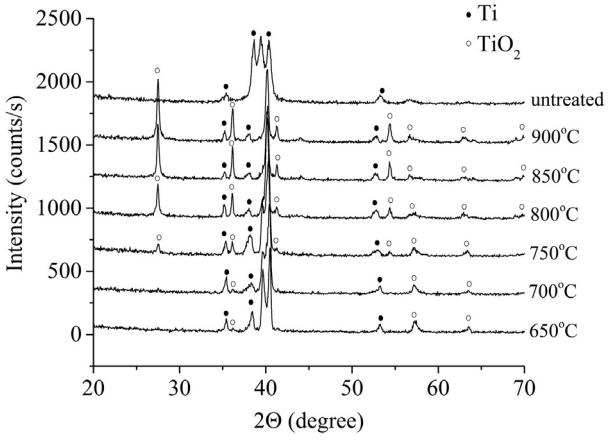


**Fig. 1.** X-ray diffraction patterns of surface layers before and after anode PEN at different treatment temperatures.