Structure and properties of commercially pure titanium nitrided in the plasma of a low-pressure gas discharge produced by a PINK plasma generator

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Abstract. The paper analyzes the surface structure and properties of commercially pure VT1-0 titanium nitrided in the plasma of a low-pressure gas discharge produced by a PINK plasma generator. The analysis demonstrates that the friction coefficient of the nitrided material decreases more than four times and its wear resistance and microhardness increases more than eight and three times, respectively. The physical mechanisms responsible for the enhancement of strength and tribological properties of the material are discussed.

1. Introduction
Titanium and its alloys are widely used in industry and medicine due to their low specific weight, high corrosion resistance, and biological compatibility [1]. However, the materials display low hardness and low wear resistance, and this is a barrier to further extension of their applications. One of the promising ways to enhance the functional properties of materials, including titanium and its alloys, is their diffusion doping [2] which nitrogen is often used for. Nitriding considerably increases the surface strength and wear resistance of materials, make them less prone to tears, and provide their high cavitation and corrosion resistances in atmosphere, fresh water, and vapor. The deformation of materials during nitriding is minimal and their nitrided layers are easily grinded and polished.

The aim of the present study is to analyze the surface structure and properties of commercially pure titanium subjected to low-temperature nitriding.

2. Materials and methods of study
The material under study was commercially pure VT1-0 titanium [3], hereinafter also Ti, shaped as plates of thickness 4.5 mm and dimensions of 15 × 15 mm. The surface of the specimens was subjected to nitriding in the plasma of a low-pressure gas discharge produced by a PINK plasma generator which provides the possibility to increase the plasma density at comparatively low discharge operating voltages, vary the discharge current irrespective of the latter and of the pressure in the working chamber, and produce the plasma with no microdroplets [4]. The pressure at which a discharge operates in such systems can be varied from ~0.1 to ~5 Pa, making possible efficient ion cleaning of treated surfaces. The energy of bombarding ions is controlled using an additional bias

voltage of 20–1000 V, and this allows one to control the rate of surface etching and vary the temperature of treated objects in the range 200–700°C. In our study, nitriding was realized at a temperature of 500 °C, 600 °C, and 650 °C for 1–5 h. Before nitriding, the specimens were mechanically polished to a roughness of Ra = 0.02 μm. One of the flat surfaces of each specimen (let term it the specimen back) was tightly pressed to the specimen holder and the other surface (its face) was free. The nitriding temperature was measured at the specimen holder with the use of a chromel-alumel thermocouple the thermal junction of which was insulated from the holder by a quartz cup. The structure of the modified material was examined by optical and scanning electron microscopy. The phase composition was determined by X-ray diffraction analysis. The surface properties were studied by estimating the microhardness, wear resistance, and friction coefficient.

3. Experimental results and their discussion

Tests of the specimens at an indenter load of 0.5 and 0.2 N show that the surface hardness of the treated material is more than three times higher than that of the untreated one (Fig. 1). The data in Fig, 1 suggest that the hardness of VT1-0 titanium depends on both the temperature and duration of nitriding. Nitriding at 500 ºC fails to provide surface hardening and this is likely because of low nitrogen penetration into the surface layers. Conversely, nitriding at 600 °C and 650 °C does reveal surface hardening the degree of which is higher on the face of the specimens (Fig. 1, *a*) and lower on their back (Fig. 1, *b*). The surface hardening of both the face and back of the Ti specimens nitrided at 650 °C is damping (Fig. 1, curves *5* and *6*). The surface hardening of the specimen face nitrided at 600 °C is also damping (Fig. 1, *a*, curves *3* and *4*); on the back of the specimens, the surface hardness increases linearly with nitriding duration (Fig. 1, *b*, curves *3* and *4*).

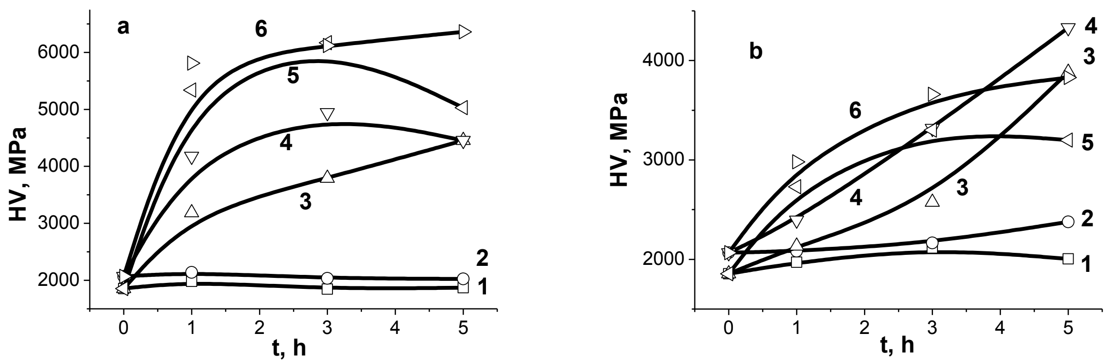

Figure 1. Surface microhardness HV of the specimen face (a) and back (b) vs the duration of nitriding **t** at 500 °C (1, 2), 600 °C (3, 4), and 650 °C (5, 6); P = 0.5 N (1, 3, 5); P = 0.2 N (2, 4, 6).

Nitriding in the low-pressure gas discharge plasma with ion bombardment of the Ti surface causes its etching. The roughness of both the specimen back and face (Fig. 2, curves *1*, *2* and *3*, *4*, respectively) increases whatever the nitriding temperature. At the same nitriding temperature and time, the roughness of the specimen face is 1.5-2.0 times higher than that of the specimen back.

Titanium and its alloys, despite their good strength and corrosion properties, are of limited use as structural materials because of their low wear resistance. The wear resistance of Ti-based alloys, where its high values are required, is increased by special surface treatment (nitriding, deposition of wear-resistant coatings, implantation). Figure 3 shows dependences of the friction coefficient on the number of loading cycles (friction track length, number of revolutions with respect to a counterbody made of hard VK8 (WC-Co) alloy) for the back and face of the nitrided Ti specimens. It is seen that the minimum friction coefficient of the specimen back is 0.13 (Fig. 3, *a*, stage *1*), and after ~50 cycles, the friction coefficient reaches ~0.46 and then, with regard to its fluctuation, varies in the range 0.38–0.54 (Fig. 3, *a*, stage *2*). Note that the friction coefficient of untreated VT1-0 titanium reaches ~0.46 even in the first cycles and then, with regard to its fluctuations, varies in the range 0.38–0.56. The face of the nitrided Ti specimen features a rather extended initial stage of wear with a low (0.09–0.23) and stable friction coefficient (Fig. 3, *b*, stage *1*), suggesting that the wear at this stage is mostly abrasive. Following the initial stage, the friction coefficient and its fluctuation amplitude increases, reaching values close to those of commercially pure VT1-0 titanium (Fig. 3, *b*, stage *2*).

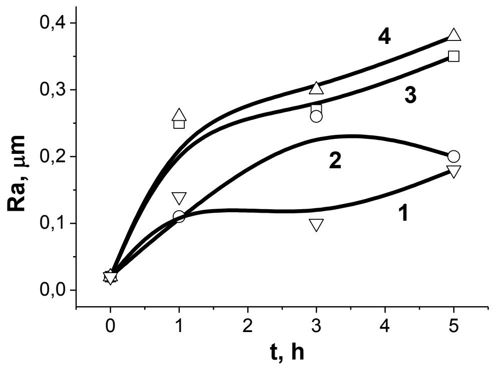

Figure 2. Surface roughness Ra of the specimen back (1, 2) and face (3, 4) vs the duration of nitriding **t** at 600 °C (2, 3) and 650 °C (1, 4).

Figure 4 shows 3D images of wear tracks for the initial and nitrided Ti specimens. It can be concluded from the images that the initial Ti specimens undergo mostly adhesive wear (Fig. 4, *a*) in which volumes of the material are torn from its depth, transferred from one friction surface to another, and the thus formed jogs affect the conjugate surface [5]. The wear track of the nitrided specimen is smooth (Fig. 4, *b*, *c*), suggesting that the wear is abrasive and is due to cutting or scratching. A comparative profilometric analysis shows that the surface hardness of the specimen nitrided at 650 °C for 3 h increases more than three times, its friction coefficient decreases more than four times, and this increases the wear resistance of the specimen more than eight times.

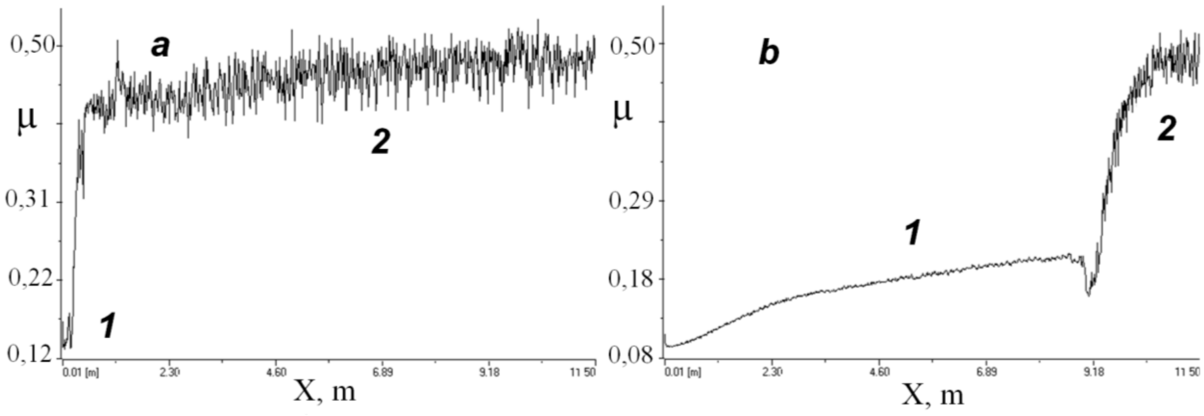

Figure 3. Friction coefficient **μ** vs the friction track length for the back (a) and face (b) of the Ti specimen nitrided at 650 °C for 3 h and tested with an indenter (VK8 ball) of diameter 3 mm at a track radius of 2 mm, applied load of 3 N, and indenter path of 11.5 m

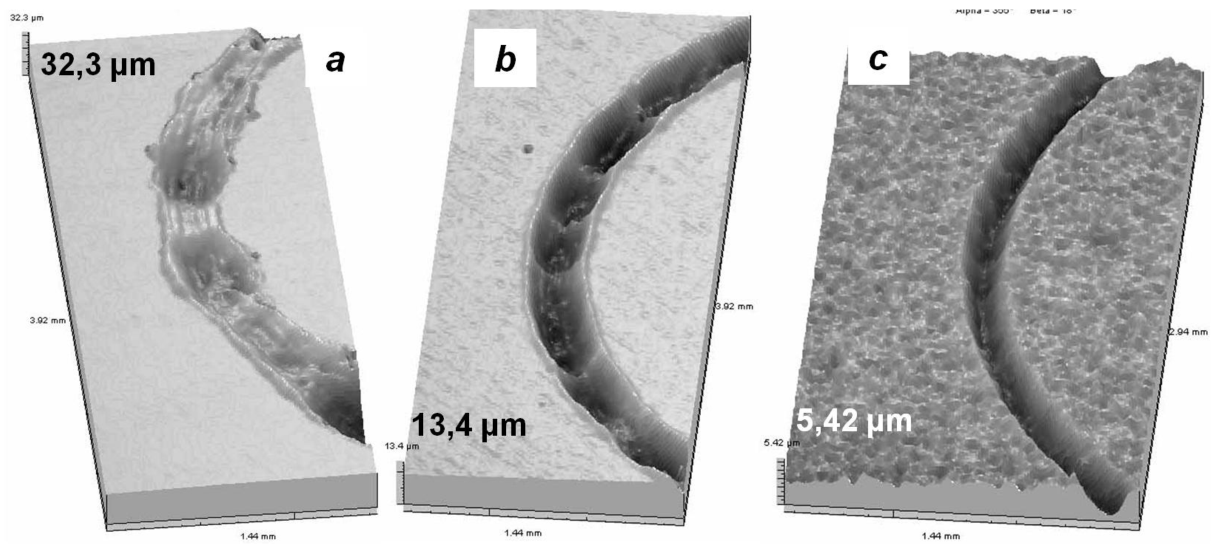

Figure 4. Images of wear tracks in the initial titanium (a) and titanium nitrided at 650 °C for 3 h (b) and tested with an indenter (VK8 ball) of diameter 3 mm at a track radius of 2 mm, applied load of 3 N, and indenter path of 11.5 m.

The many-fold improvement of the microhardness, wear resistance, and frictional properties of the Ti specimens nitrided in the low-pressure gas discharge plasma produced by the PINK generator is evidence for considerable changes in the material surface structure. The elemental composition and defect substructure of the Ti surface after nitriding were examined by optical and scanning electron microscopy for which the Ti specimens nitrided at 650 °C for 3 h were used.

The study shows that before nitriding the titanium represents a polycrystalline material with an average grain size of 25.8 μm. After nitriding at 650 °C for 3 h, the average grain size in its surface layers is 27.0 μm on the specimen back and 22.5 μm on the specimen face, which is close to the average grain size in the initial material (Fig. 5, *a*, *c*). In the grain volume of the nitrided specimen, a subgrain structure with an average subgrain size of 0.75 μm on the specimen back and 2.1 μm on the specimen face is formed (Fig. 5, *b*, *d*).

The grain and subgrain boundaries in the nitrided Ti specimen are decorated with second phase particles. The specimen back is characterized by an average particle size of 0.3 μm at the grain boundaries and 0.1 μm at the subgrain boundaries. For the specimen face, the average particle size at the grain and subgrain boundaries is 0.25 μm. The data of scanning electron microscopy shows that the nitrided specimen contains nitrogen atoms the concentration of which on the specimen back and face is 33 at. % and 36 at. %, respectively. Likely the second phase particles at the grain and subgrain boundaries are titanium nitride particles. And this is really so, as evidenced by X-ray studies which reveal the presence of an ε-phase (Ti_2N) with a content of 24.8 % on the specimen face. Assuming the formation of Ti_2N particles on the specimen back as well and taking into account the average particle size on both sides, the volume fraction of ε-phase particles is by estimate 1.8 %.

Nitriding, while involving the formation of nitride particles in the titanium, implies nitrogen saturation of the Ti lattice with its attendant distortion and change of its parameters. According to the X-ray data, the α-Ti lattice parameters in the nitrided titanium are a = 0.29454 nm, c = 0.47091 nm, c/a = 1.599, and $\Delta d/d = 2.7*10^{-3}$, whereas their table values for the α-Ti lattice are a = 0.29510 nm, c = 0.46970 nm, and c/a = 1.587. Thus, as evidenced by the change in the lattice parameters a and c, the Ti lattice is saturated with nitrogen.

The foregoing research data on the elemental composition, phase composition, and defect substructure in the nitrided surface layer of commercially pure VT1-0 titanium suggest that the strength and tribological properties of the material are increased through saturation of its lattice with nitrogen atoms, subgrain structure formation, and Ti_2N particle precipitation. When nitrided, the entire face of the Ti specimen is almost uniformly involved in Ti_2N precipitation, whereas this precipitation on the specimen back dominates at the grain and subgrain boundaries.

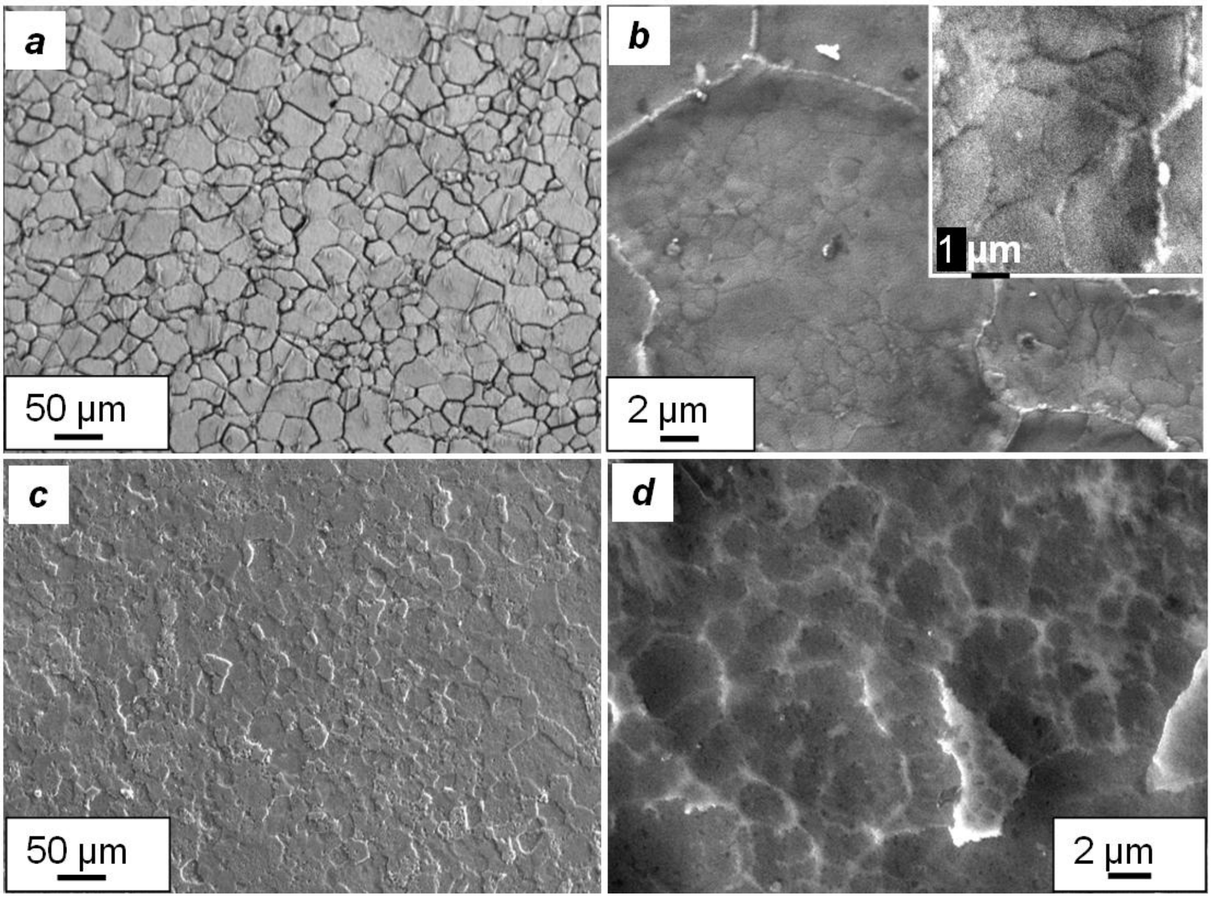

Figure 5. Surface structure on the back (*a*, *b*) and face (*c*, *d*) of commercially pure VT1-0 titanium nitrided at 650 °C for 3 h.

Formation of surface alloy is followed by change of strength characteristics of material. In Figure 1 the results of hardness change for the alloyed aluminum surface layer are presented. It is clear that the hardness and the Young's modulus of surface layer smoothly decreases from the values which is repeatedly exceeding strength characteristics of initial material to the values corresponding to A7 alloy. Therefore, the modified layer smoothly passes into the main volume of a sample. The boundary, which can contain concentrators of tension, is absent.

4. Conclusion

Thus, we analyzed the structure and properties of commercially pure VT1-0 titanium nitrided in the low-pressure gas discharge plasma produced by the PINK plasma generator. It is shown that the nitriding decreases the friction coefficient of the material more than four times and increases its hardness and wear resistance more than three and eight times, respectively. It is demonstrated that the strength and tribological properties of the material are enhanced due to nitrogen saturation of its lattice, subgrain structure formation, and Ti_2N particle precipitation. The research results allow us to suppose that the face of the Ti specimen is nitrided by intercrystalline mechanisms through diffusion at its internal interfaces and by intracrystalline mechanisms through diffusion at dislocation cores and interstitial sites of its crystal lattice. The back surface of the Ti specimen is nitrided mostly by intercrystalline mechanisms.

Acknowledgement

This work was supported by RSF grant (project No. 14-29-00091).

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