Low-temperature ion nitriding of VT6 titanium alloy with UFG structure

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Abstract. This work describes the effect of low-temperature ion nitriding on the mechanical and operational properties of the titanium alloy VT6 with the ultrafine-grained structure. Ion nitriding of the alloy was carried out at $T=450-600$ °C and $p=300$ Pa in a gas mixture of argon and nitrogen during 6 hours. Low-temperature nitriding at the temperature ≥550 °C leads to a decrease in the microhardness of the material base. The optimum processing temperatures are 450-500 °C. The formation of the UFG structure and subsequent nitriding increases wear resistance by 28%.

1. Introduction
Titanium alloys occupy an important place among modern structural materials due to the unique combination of their physical, mechanical and technological properties. Low density, high corrosion resistance, high specific strength and heat resistance make these alloys essential in aircraft industry. However, titanium alloys have low hardness and thus low surface wear resistance [1–3]. Therefore, new methods to improve mechanical and tribological properties of titanium alloys are of high interest.

One promising approach to increase the strength of structural materials is their intensive plastic deformation (IPD). IPD makes it possible to obtain materials of the ultrafine-grained (UFG) structure with the average grain size of less than 1 μm and predominantly high-angle grain boundaries, which ensures high strength [4–6].

Despite high physical and mechanical properties of UFG titanium alloys, their surface is subject to intensive wear under contact loads. At present, nitriding in a glow discharge (ion nitriding) is widely used to enhance the operational characteristics of the surface layers of engineering parts [7–9]. However, traditional ion nitriding of titanium alloys is carried out in a high temperature range (850–950 °C) with a long exposure time (24–48 hours) [10–11], which inevitably leads to a decrease in the mechanical properties of the material base due to polymorphic ($\alpha \rightarrow \beta$) transformations. Besides, it is inherently impossible to process titanium alloys with the UFG structure under such thermal conditions because their grains are growing at high temperatures due to recrystallization. In turn, the growth of the grains leads to a decrease in the mechanical characteristics of the material base. Therefore, ion nitriding of titanium alloys should be carried out in a low temperature range (450-600 °C) in order to prevent the growth of grains and maintain the operational characteristics of the material.

Herein, we demonstrate the effect of low-temperature ion nitriding on the microhardness and wear resistance of the ultrafine-grained titanium alloy VT6.
2. Materials and methods

A series of experiments was carried out to investigate the effect of hydrogen content in a gas mixture on ion nitriding of the coarse-grained and ultrafine-grained titanium alloy VT6. ELU-5M was used for thermal and thermochemical treatment of samples in vacuum; the scheme of the nitriding system is given in figure 1.

![Figure 1. Scheme of the glow discharge nitriding system: 1 – power source, 2 – electrode-anode, 3 – sample (cathode), 4 – vacuum chamber.](image)

Samples from the two-phase titanium alloy VT6 were used in the experiments: UFG and CG samples, the latter pretreated by heat (annealed at $T=800^\circ$C). The chemical composition of the material is given in table 1.

|     | Ti  | Al  | V   | Fe  | Si  | C   | N   |
|-----|-----|-----|-----|-----|-----|-----|-----|
| %   |     |     |     |     |     |     |     |
|     | 88.24 | 6.5 | 5.1 | 0.1 | 0.03 | 0.02 | 0.01 |

The samples were nitrided under $T=600\pm10^\circ$C and $p=300\pm5$ Pa during $t=6$ h. Diffusion saturation was preceded with ion beam cleaning in an Ar medium when the surface temperature of the samples did not exceed 300 °C.

UFG structure of the titanium alloy VT6 was obtained by equal-channel angular pressing [12] (figure 2a) in two modes. In the first mode, the billet was heated to 700 °C, and then twice forced through channels intersecting at the angle of $\Phi=120^\circ$. In this mode, the billet was rotated at $90^\circ$ clockwise along the longitudinal axis (figure 2b) after each passage. In the second mode, the billet was heated to 960 °C during 30 minutes in a furnace in the first cycle; the pressing temperature was 600 °C in the next five cycles; the angle and route were similar to the first mode.

![Figure 2. Schematic diagram of equal-channel angular pressing [12] (a) – scheme; (b) – route.](image)

The microhardness of the hardened layer was measured with a Vickers test on an angle lap section (at the angle of $6^\circ$) with a Struers DuraScan hardness testing machine. The static load applied to the diamond indenter for 10 s was 490.5 mN (50 g).
Standard pin-on-disk wear tests were performed using a Nanovea tribometer to assess the tribological characteristics. The force of 4 N was exerted on a metal ball of 3 mm in diameter made of bearing steel SHKH15; the ball rotated at the speed of 500 rpm.

3. Experimental results and discussion

We obtained dependences of microhardness distribution over the depth of the hardened layer after ion-plasma nitriding in a glow discharge (figure 3) to assess the depth of the hardened layer. The dependency analysis showed that two ECAP cycles of UFG samples nitrided at 450 °C (figure 3a) increased the surface microhardness to 390 HV0.05; six ECAP cycles increased the surface microhardness to 405 HV0.05. The microhardness distribution is uniform with a smooth transition to the values of the material base. The depth of the hardened layer was ~18 μm in the samples with the coarse-grained (SC) structure and ~25 and 30 μm in the samples with the UFG structure after two and six cycles of pressing respectively. The increase in the depth of the modified layer in the samples with the UFG structure can be due to the fact that an increased volume fraction of grain boundaries and a higher density of dislocations occur in the material after SPD [13]. Literature data [14, 15] demonstrate that diffusion occurs mainly along grain boundaries. Moreover, the depth of the hardened layer increases in the sample with the increase in the number of ECAP cycles due to deformation. This fact indirectly confirms a higher diffusion in the sample with a smaller grain size and an increased density of defects in the lattice.

![Figure 3](image-url)

**Figure 3.** Microhardness distribution along the depth of the hardened layer in ultrafine-grained titanium alloy VT6 after ion nitriding in a glow discharge: (a) – 450 °C, (b) – 600 °C.

Significant softening of the material base occurs in both samples after ion-plasma nitriding at the temperature of 600 °C due to the grain growth and recrystallization. Two ECAP cycles of the sample increased the surface microhardness to 390 HV0.05; six ECAP cycles increased the surface microhardness to 440 HV0.05. Comparative results of the hardened layer thickness after ion-plasma nitriding in a glow discharge are given in table 2.

| Temperature, °C | Coarse-grained | ECAP, 2 cycles | ECAP, 6 cycles |
|-----------------|----------------|---------------|---------------|
| 450             | 18             | 25            | 30            |
| 500             | 27             | 32            | 46            |
| 550             | 30             | 40            | Softening     |
| 600             | Softering      | Softering     | Softering     |

SEM images of wear tracks (figure 4a, c, e) show that the initial samples with the SC and UFG structures had an adhesive wear. The tracks contained areas with the traces of setting, residues of the
material on the crests (selected area) and individual traces of breakaways, which are typical for adhesive wear [16].

**Figure 4.** SEM images of wear tracks of the samples in the initial state (a, c, e) and after nitriding at 450 °C (b, d, f): a, b – coarse-grained samples; c, d – ultrafine-grained samples after two cycles of ECAP; e, f – ultrafine-grained samples after six cycles of ECAP.

Ion nitriding in the CG samples (figure 4b) only slightly changed the nature of wear – the areas with the traces of setting remained; however, additional traces of microcuts appeared in the direction of friction. The sample after ion nitriding (ECAP, two cycles) demonstrated a mixed adhesive and abrasive wear pattern – significant risks appeared along the wear direction in addition to the adhesive wear characteristics named above (figure 4d). Such risks were probably formed due to sticking of particles of the thin surface nitride layer onto the ball, which resulted in an abrasive that contributed to surface micro-cutting. The wear mechanism differed significantly in the sample after nitriding (ECAP,
six cycles) and was predominantly abrasive as indicated by the nearly absent areas with sticking and breakaways of the material (figure 4f). This difference in the wear mechanism compared with the nitrided sample after two ECAP cycles is associated with different depths of the nitrided layer and the hardness of the base. Figure 5 presents the results of assessing wear resistance by the mass loss of the samples.

Figure 5. Mass loss of samples after tribological tests: (a) – initial state; (b) – after nitriding at 450 °C.

The diagram shows (Figure 5 a,b) that the formation of the UFG structure increased wear resistance by ~14% and ion nitriding at 450 °C lead to an increase in wear resistance by ~28%.

4. Conclusions

The study of low-temperature ion nitriding of the ultrafine-grained titanium alloy VT6 has shown that:
1) Low-temperature nitriding at the temperature of 550 °C and higher leads to a decrease in the microhardness of the material base. The optimum processing temperature range is 450-500 °C. The formation of the UFG structure in the titanium alloy makes it possible to increase the depth of the hardened layer to ~40% after ion-plasma nitriding in a glow discharge. Moreover, the depth of the hardened layer increases with an increase in the number of ECAP cycles due to an increase in the volume fraction of grain boundaries and the density of defects in the lattice. Diffusion occurs predominantly along grain boundaries during surface saturation with nitrogen; an increase in grain boundaries and defects leads to acceleration of diffusion.

2) The formation of the UFG structure and subsequent low-temperature nitriding at the temperature of 450 °C leads to an increase in wear resistance by 28%, compared with the initial coarse-grained sample. The increase in wear resistance of the ultrafine-grained sample after six cycles of ECAP occurs due to an extended hardened zone after nitriding.

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