Influence of hydrogen content on ion nitriding of coarse-grained and ultrafine-grained VT6 titanium alloys

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Abstract. This work investigates low-temperature ion nitriding of coarse-grained VT6 titanium alloy performed at the temperature of 600°C with different hydrogen contents (0–30% H₂). The optimum hydrogen content identified during the experiments with coarse-grained samples was used to further nitride ultrafine-grained VT6 titanium alloy at the temperature of 500°C. Microhardness distribution diagrams of and optical microstructure images were obtained; brittleness of the nitrated layer was estimated.

1. Introduction
Titanium alloys demonstrate high specific mechanical properties, which assures their widespread use in aircraft manufacturing, mechanical engineering and the production of medical implants. However, low performance characteristics of the surface due to low hardness, tendency to sticking and scoring when used in friction units adversely affect the durability of parts made from titanium alloys [1].

Formation of ultrafine-grained (UFG) structures in titanium alloys by severe plastic deformation (SPD) is increasingly used to improve their mechanical properties in recent decades [2, 3]. However, although SPD increases physical and mechanical properties of VT6 titanium alloy, its surface undergoes considerable wear during operation.

There are several methods to efficiently increase wear resistance of titanium alloy surfaces. Among them, ion nitriding [4] has several advantages over other hardening methods (such as, gas nitriding in furnaces, laser hardening, etc.), i.e. high rate of surface saturation with nitrogen, ecological purity of the process, control over phase composition at all stages, possibility of local nitriding of individual parts of the sample. However, despite the existing advantages and the high rate of saturation with nitrogen, nitriding titanium alloys still remains a long process (lasts more than 10 hours); moreover, it is carried out at high temperatures (800–1000°C) [5]. Treatment of UFG titanium alloys is impossible under such thermal conditions due to recrystallization and subsequent growth of grains, which leads to a decrease in mechanical characteristics of the base material. Therefore, ion nitriding of UFG titanium alloys at reduced temperatures (450–500°C) is of high interest.

It is known [6, 7] that the composition of a gas medium during ion nitriding significantly affects the structure, properties, phase composition and growth kinetics of a modified layer. Adding argon to the gas mixture allows accelerating the growth of the diffusion zone while reducing the nitried layer (which mainly consists of titanium nitrides and alloying elements) due to the sputtering of the nitried layer during bombardment by heavy argon ions. The presence of hydrogen in the working gas mixture during nitriding increases nitrogen diffusion due to removing the nanocrystalline layer on the titanium alloy surface, which inhibits nitriding [8, 9]. In another mechanism proposed by [10], the presence of
hydrogen in the nitriding medium leads to the formation of $\text{H}^+$, $\text{NH}^+$ and $\text{NH}_2^+$ radicals, which have a catalytic effect on the nitriding kinetics and, therefore, increase the efficiency of nitriding. Thus, the efficiency of ion nitriding can be increased by varying ratios of components in a gas mixture. However, there are no data on the effect of hydrogen content in a three-component gas mixture (nitrogen – argon – hydrogen) at low-temperature ion nitriding of titanium alloys ($T \leq 600^\circ\text{C}$) on their technological parameters (surface temperature and the difference of potentials required to maintain the operating temperature) and the properties of the modified layer (hardness, hardening depth, phase composition).

This work investigates the effect of hydrogen content in a gas mixture on the structure and mechanical properties of a two-phase coarse-grained (CG) and UFG VT6 titanium alloys at low-temperature ion nitriding.

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

| Table 1. Chemical composition (%) of VT6 titanium alloy. |
|----------------|---|---|---|---|---|
| Ti                | 88.24 | Al | 6.5 | V | 5.1 |
| Fe                | 0.1 | Si | 0.03 | C | 0.02 |
| N                 | 0.01 |

The samples were nitrided under $T = 600\pm10^\circ\text{C}$ 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 $300^\circ\text{C}$. Diffusion saturation occurred in a three-component gas mixture of $\text{N}_2$, Ar and $\text{H}_2$ having the ratios given in table 2.

| Table 2. Working gas composition. |
|----------------|----------------|
| No. | Working gas composition |
|-----|--------------------------|
| 1   | 40% -$\text{N}_2$, 60%-$\text{Ar}$ |
| 2   | 40% -$\text{N}_2$, 50%-$\text{Ar}$, 10%-$\text{H}_2$ |
| 3   | 40% -$\text{N}_2$, 40%-$\text{Ar}$, 20%-$\text{H}_2$ |
| 4   | 40% -$\text{N}_2$, 30%-$\text{Ar}$, 30%-$\text{H}_2$ |

UFG structure of VT6 titanium alloy was obtained by equal-channel angular pressing [11] (figure 2a) in two modes. In the first mode, the billet was heated to $700^\circ\text{C}$, and then twice forced through channels intersecting at the angle of $120^\circ$. 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 [11]: 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°) with a Struers DuraScan hardness testing machine. The static load applied to the diamond indenter for 10 s was 490.5 mN (50 g).

The microstructure of the samples was studies with an Olympus GX-51 optical microscope. Thin sections of the titanium alloy were etched using an etchant of 10% HF–15% HNO₃–75% H₂O to reveal the structure of the sample.

### 3. Experimental Results and Discussion

Heat treatment of titanium alloys is commonly used to stabilize their structure and mechanical properties through the whole volume of the material. Figure 3 shows an optical image of the VT6 titanium alloy structure after annealing at the temperature of 800°C. It has been established that the structure consists of small equiaxial elongated crystallites of the α-phase with the mean size of 8 μm, while the β-phase is distributed along the boundaries of the α-phase and has an elongated drop-like and needle-like shape.

After two ECAP cycles, a fragmented structure with elongated primary α grains of about 7 μm and the volume fraction of about 40% has formed in the titanium alloy (figure 3b). After six ECAP cycles, the material microstructure has changed significantly into a bimodal material, which consists of a finely dispersed α+β matrix with inclusions of large α-crystallites of about 6 μm mean size and a volume fraction of about 35% (figure 3c).

![Figure 3. Initial microstructure of VT6 titanium alloy: a – coarse-grained microstructure after annealing; b – ultrafine-grained microstructure after two ECAP cycles; c – ultrafine-grained microstructure after six ECAP cycles.](image)

Figure 4 shows the microstructure of VT6 titanium alloy after nitriding at different hydrogen and argon contents of a working gas mixture.

Image analysis has showed the absence of visible structural changes in the volume of the material, the absence of boundary between the solid solution of α and β-titanium (diffusion zone) and the base after low-temperature nitriding. This is due to the fact that nitriding was carried out at temperatures
below the polymorphic transformation. It is known [12] that the structure does not change under such conditions; an $\alpha$-solid solution is released from a $\beta$-phase and a phase separation is observed at nitriding temperatures above the polymorphic transformation.

The surface layer is saturated with nitrogen, the driving force being a concentration gradient in ion nitriding. Because of the penetration of nitrogen into the surface, elastic lattice distortions occur, which causes an increase in the hardness of the modified layer. Distortion grows and, consequently, the hardness increases with an increase in nitrogen concentration. To assess the effect of hydrogen content on the depth of the hardened layer, and, therefore, on its growth kinetics, curves of hardness distribution over the depth of the modified layer were obtained (figure 5).

![Figure 4](image1.png)

**Figure 4.** Optical images of VT6 titanium alloy microstructure after nitriding at different hydrogen contents of a working gas mixture: a – 0% H$_2$, b – 10% H$_2$, c – 20% H$_2$, d – 30% H$_2$.

![Figure 5](image2.png)

**Figure 5.** Dependence of microhardness distribution along the depth of the hardened layer on hydrogen content of a working gas mixture.

![Figure 6](image3.png)

**Figure 6.** Dependence of hardened layer thickness on hydrogen content in a working gas mixture.
The analysis of the curves (figure 5) has showed that the addition of 20% hydrogen into a gas mixture increases surface microhardness from 460 HV\(_{0.05}\) (at hydrogen-free nitriding) to 530 HV\(_{0.05}\). Further increase in the hydrogen content to 30% leads to a decrease in microhardness to 460 HV\(_{0.05}\). This is probably due to the fact that hydrogen has a smaller atomic radius compared to nitrogen, diffuses more actively into the lattice and occupies the pore space, thereby reducing the amount of nitrogen that the titanium lattice (\(\alpha\) and \(\beta\)) can accommodate. The intensity of nitrogen diffusing into the VT6 titanium alloy surface was estimated from the growth rate of the hardened layer. The dependence of the thickness of the hardened layer on hydrogen content was obtained based on microhardness measurements over the depth of the modified layer (figure 6).

The dependence (figure 6) has showed that the depth of the hardened layer increases with an increase in the hydrogen content of a working gas mixture, i.e. the hardened layer thickness is 17 \(\mu\text{m}\) at hydrogen-free nitriding and increases to 45 \(\mu\text{m}\) at 10% H\(_2\) concentration. This is due to several mechanisms. Firstly, hydrogen reacts with residual and sputtered oxygen in the process of saturation in a vacuum chamber, thereby eliminating the barrier of an oxide film. Secondly, the presence of hydrogen in a nitrating medium leads to the formation of H\(^+\), NH\(^+\) and NH\(_2\)\(^+\) radicals, which have a catalytic effect on the kinetics of nitrogen diffusion into the titanium alloy surface as described in [10].

Since hydrogen is a harmful impurity for titanium and its alloys, indenter prints were analyzed (with the method designed at the All-Russian Scientific Research Institute of Aviation Materials (VIAM) [13]) to evaluate the effect of hydrogen content in a gas mixture on the fragility of the nitrided layer (figure 7).

![Figure 7](image_url)

**Figure 7.** Indenter prints in the nitrided layer of VT6 titanium alloy: a – after nitriding in a gas mixture with 10% H\(_2\); b – after nitriding in a gas mixture with 30%H\(_2\).

The study of indenter prints at the distance of 10 \(\mu\text{m}\) from the surface has showed that all prints fall under Group 1 according to VIAM scale when hydrogen content of a working gas mixture is below 20% and under Group 2 when the concentration increases up to 30%. It has been established that the above prints are valid in all cases.

It was established in [1, 14] that formation of a UFG structure increases the growth rate of a hardened layer. Treatment modes were selected based on the experiments performed for CG samples; then UFG VT6 titanium alloy samples were nitrided in a gas mixture with the 10% hydrogen content. Figure 8 demonstrates optical images of the UFG VT6 titanium alloy microstructure after ion nitriding. Analysis of the microstructure images (figure 8) has showed no visible structural changes in the material at the nitriding temperature of 500°C. No grain growth or release of secondary phases from the \(\alpha+\beta\) region have been detected, which indicates thermal stability of the UFG structure at the given nitriding temperature. The hardened layer does not stand out metallographically, there is no phase boundary between the diffusion zone and the base material.
Figure 8. Microhardness of UFG VT6 titanium alloy after ion nitriding in a glow discharge at 500°C: a – after two ECAP cycles; b – after six ECAP cycles.

Hardness distribution over the depth of the modified layer (figure 9) was analyzed to assess the dependence of the hardened layer depth on the initial structural state of VT6 titanium alloy.

Figure 9. Microhardness distribution over the depth of the hardened layer after nitriding VT6 titanium alloy at different hydrogen contents of a working gas mixture.

Analysis of the distribution (figure 9) has showed that the formation of the UFG structure led to an increase in the surface microhardness by 10% after nitriding; the depth of the hardened layer increased by 30% because nitrogen diffusion occurred mainly along the grain boundaries and there was a large number of grain boundaries and other structural defects that accelerated the diffusion process in UFG samples.

4. Conclusions
The study of the influence of hydrogen content in a gas mixture on the structure and properties of a two-phase VT6 titanium alloy during ion nitriding has demonstrated that:

- The diffusion rate increases by 2 times and the surface hardness of the hardened layer increases by 15% when adding 10% hydrogen to a gas mixture during ion nitriding of coarse-grained...
VT6 titanium alloy. A further increase in the hydrogen content of a gas mixture leads to a decrease in the depth of the modified layer;

- A change in the hydrogen content from 10 to 30% does not provoke embrittlement of the nitrided layer;
- Nitriding at the temperature of 500°C does not lead to the degradation of the UFG structure in VT6 titanium alloy obtained after ECAP;
- Pre-formed UFG structure in VT6 titanium alloy allows increasing the depth of the nitrided layer by ~ 30%.

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