Structure and properties of titanium after nitriding in a plasma of pulsed hollow cathode glow discharge

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Abstract. The paper reports on a study of the structure, phase composition and mechanical characteristics of a modified surface layer of VT1-0 titanium after nitriding in the plasma of pulsed and stationary non-self-sustained glow discharge. It was revealed that after nitriding in a pulsed glow discharge, the volume fraction of nitride phase (Ti$_2$N, TiN) in the surface layer of VT1-0 titanium is higher than that in the nitrided layer obtained by exposure to a plasma of steady glow discharge at the same nitriding temperatures, average ion current density at the surface and ion energy. As a result, the hardness of the surface layer of samples obtained by nitriding in pulsed discharge mode exceeds that of samples treated in steady glow discharge mode. Wear resistance of titanium after nitriding in the plasma of a pulsed glow discharge is approximately four times higher than that of titanium without treatment and 1.5 times higher than that achieved by nitriding in a steady glow discharge plasma.

1. Introduction
Titanium alloys with their unique combination of mechanical, physical and processing properties such as high specific strength, low density, high corrosion resistance and high-temperature strength are widely used in airspace systems, medicine, etc. [1]. Among the drawbacks of titanium alloys, especially of unalloyed ones, are low hardness, and dissatisfactory tribotechnical characteristics [2]. One of the ways to improve tribotechnical and mechanical characteristics of components and parts is to expose them to ion plasma nitriding; furthermore a treatment in low-pressure discharge plasma is 2-3 times faster than in an abnormal glow discharge plasma. The process of nitriding in a low-pressure discharge plasma at the same temperature of treated items can be intensified by increasing the saturation capacity of the medium in the pulsed glow discharge mode. The concept is based on the fact that a pulsed discharge creates a plasma of higher concentration as compared to a steady glow discharge, hence the number of active states of nitrogen-containing gas is significantly higher. The duration of the pause between pulses should be selected in such a way that the concentration of plasma does not have enough time to decrease significantly. If that is achieved, the nitriding process continues during the pause between pulses. In a pulsed mode of plasma generation, the dynamic change of the composition of the layer adsorbed on the surface of titanium significantly differs from nitriding in a stationary plasma. If certain conditions are met, the total number of nitrogen atoms diffused into the material, hence the hardness of the treated layer, may significantly increase once treated by a pulsed glowing charge plasma. After nitriding in the plasma of a non-self-sustained glow discharge at temperature of 600-700 °C, the resulting surface hardness titanium and durability of VT1-0 are several times higher than in the original state [3].

The purpose of this paper is to compare the results of research of structure, phase composition and mechanical characteristics of the surface layer of VT1-0 titanium samples after nitriding in the plasma of pulsed and stationary non-self-sustained glow discharge.
2. Material and research techniques

The nitriding experiments with technically pure VT1-0 titanium were carried out with the plasma of both stationary and pulse periodic low-pressure non-self-sustained glow discharge with a hollow cathode using a test bench described in [3]. To investigate the peculiarities of plasma generation in a non-self-sustained glow discharge with a hollow cathode, internal walls of the stainless steel vacuum chamber were used as the hollow cathode for a glow discharge. It is noted in [4] that during the nitriding of titanium alloys it is desirable to have no dispersed steel electrodes in the chamber volume, as the deposition of dispersed iron on the titanium surface may block propagation of nitrogen into titanium. Thus in order to eliminate disperse iron, the research used a screen of 1-mm-thick titanium, the internal walls of which served as the hollow cathode for the discharge (figure 1). Electrons were emitted into the glow discharge from the plasma of auxiliary arc discharge with a cold hollow cathode [5] that, in combination with the grid arc discharge anode, served as the source of electrons 3. The exit aperture of this source was covered with two anode grids – a stainless steel grid 5 with cells measuring 0.4×0.4 mm and a titanium grid 6 with cells measuring 1×1 mm. Thus, inside the hollow cathode, all the electrode parts exposed to ion bombardment were made of titanium alloys. A turbomolecular pump was used to create vacuum in the chamber with minimum pressure of 5·10⁻³ Pa.

The samples for nitriding, made of technically pure VT1-0 titanium measuring 15×15×4 mm were placed in the centre on a titanium holder 4 at the level of the exit aperture of the electron source and rotated at 45° to the axis of the electron source as shown in figure 1. The samples were connected to constant negative bias voltage both in pulsed and stationary modes of glow discharge. Nitriding was performed at the temperature of samples of $T = 730 \, ^\circ C$, operating pressure of $p = 2 \, Pa$ in extra pure grade nitrogen and the time of $t = 2 \, hours$.

To ensure the required temperature of samples during the treatment at relatively low bias voltage $U_b \approx 85 \, V$, the average ion current density to the samples was around 6.8 mA/cm² in both discharge modes, the density of pulsed ion current during nitriding in a pulsed plasma amounted to around 13.2 mA/cm².

During the stationary glow discharge mode, the glow current was $I_d = 100 \, A$, glow discharge voltage was $U_d \approx 85 \, V$, and in the pulsed glow discharge mode at pulse frequency of $f = 1 \, KHz$ and pulse duty factor $\gamma = 50 \%$, in order to maintain the same temperature of samples, glow temperature was kept at $U_d \approx 150 \, V$ at average current of $I_d = 70 \, A$.

To assess the efficiency of titanium nitriding in a plasma of non-self-sustained glow discharge, operating in stationary and pulsed modes, we used the results of a microhardness (microhardness tester PMT-3, indentation load $P = 0.5 \, N$) and a nanohardness measurement (nanoindentation system TTX NHT² by CSM Instruments, indentation load $P = 0.03 \, N$) of the surface of nitrited samples. The thickness of the nitrited layer was determined by the distribution of nanohardness over the depth of treated samples.

![Figure 1. Experimental test bench (a) and current and voltage of non-self-sustained glow discharge at pulsed mode under $I_e = 150 \, A$, $p$ (N₂) = 1 Pa (b). In test bench: 1 – titanium hollow cathode of glow discharge, 2 – anode of glow discharge, 3 – source of electrons, 4 – holder with samples.](image-url)
The structure and the phase composition of samples prior to and after the treatment by the plasma of a stationary and pulse periodic low-pressure non-self-sustained glow discharge were measured using the optical (metallographic microvisor µVizio-MET-221), scanning electron microscopy (SEM-515 by Philips) and X-ray structural analysis (diffractometer Shimadzu XRD, copper Kα radiation). The analysis of phase composition was carried out using PDF 4+ databases and full-profile analysis software POWDER CELL 2.4.

The dry friction pin on disk technique with a Tribotechnik tribometer was used to measure surface durability. A VK8 hard alloy ball (6mm in diameter) was used as a counter body. The tests were carried out in the air at indenter load of 5 N and rotation speed of 25 mm/s. The sliding distance measured 60 m at the track radius of 2 mm. Comparative wear resistance tests were carried out with titanium samples in original condition and after nitriding in the plasma of a stationary and pulsed low-pressure non-self-sustained glow discharge. The wear intensity was assessed based on the dimension wear factor (mm³·N⁻¹·m⁻¹).

3. Results and discussion

The measurement results of surface microhardness of the samples after nitriding in a stationary and pulsed glow discharge are presented in table 1. In the original condition, microhardness of samples’ surface was HV₀.⁵=2 GPa, nanohardness HV₀.₀₀₃=3.1 GPa. Thus, the values of surface microhardness of titanium samples after nitriding were 55% and 85% higher for steady and pulsed glow discharge modes, respectively. The significant difference between the values of nanohardness and microhardness indicate a relatively thin modified layer formed on the surface of the samples.

The values of nanohardness of the surface of samples treated in pulsed glow discharge are approximately 30% higher than that of a stationary glow discharge, which is evidently related to a thicker nitride layer. A similar difference is observed in the measurement of microhardness, which may indirectly indicate both a larger volumetric fraction of hard phase in the surface layer of the metal, and a deeper nitrited layer.

| Discharge mode | Surface nanohardness HV₀.₀₀₃, GPa | Surface microhardness HV₀.⁵, GPa |
|----------------|-----------------------------------|----------------------------------|
| DC             | 9.9                               | 3.1                              |
| Pulsed         | 13                                | 3.7                              |

The measurements of nanohardness over depth (figure 2) have shown that nanohardness of the layer formed by nitriding of the sample in a pulsed mode was 25% higher than that of the sample treated in a stationary mode. The depth of the diffused layer for both nitriding modes is approximately the same, 50 µm.

![Figure 2. Distribution of nanohardness over depth of VT1-0 titanium samples nitrited in a stationary and pulsed modes of non-self-sustained glow discharge. Dotted line – original nanohardness. Red – stationary mode, Black – pulsed mode.](image-url)
Figure 3 shows the surface structure of treated samples in a stationary and pulsed modes. The nitriding of titanium samples in the plasma of a low-pressure glow discharge is accompanied by the bombardment of material’s surface with accelerated ions, which leads to sputtering of the surface layer of the samples.

![Figure 3. SEM image of VT1-0 titanium samples after nitriding in a stationary glow discharge mode (a) and pulsed mode (b).](image)

In order to research the impact of the mode of plasma generation on the phase composition of the modified surface layer in more detail, X-ray tests diffraction patterns of VT1-0 titanium samples surfaces nitrited in a steady and pulsed glow discharge modes were obtained (figure 4).

![Figure 4. Portions of X-ray diffraction patterns of nitrited BT1-0 titanium samples: 1 – original sample; 2 – nitriding in a stationary mode; 3 – nitriding in a pulsed mode.](image)

The X-ray diffraction analysis shows that a multiphase structure is formed in the surface layer, which consists of α-Ti and nitride phases Ti₂N, TiN. The content of nitride phases in the surface layer of the samples nitrited in a stationary and pulsed glow discharge modes is shown in table 2. The main nitride phase is Ti₂N. The presented data clearly shows that the volumetric fraction of nitride phases is higher in the samples treated in the plasma of a pulsed glow discharge.
Table 2. The content of nitride phases in VT1-0 titanium samples nitried in a steady and pulsed glow discharge modes

| Discharge mode | Ti$_2$N, vol. % | TiN, vol. % |
|----------------|----------------|-------------|
| DC             | 11             | 3           |
| Pulsed         | 30             | 5           |

The comparative dry friction tribotechnical tests of the modified titanium have shown that after the nitriding in a steady and pulsed glow discharge modes, the intensity of wear of titanium is significantly reduced as compared to its original state. The wear factor of VT1-0 titanium in its original state is $7.99 \cdot 10^{-4}$ mm$^3$·N$^{-1}$·m$^{-1}$, after the nitriding in the plasma of a steady glow discharge – $2.98 \cdot 10^{-4}$ mm$^3$·N$^{-1}$·m$^{-1}$ and after the nitriding in the plasma of a pulsed glow discharge – $1.80 \cdot 10^{-4}$ mm$^3$·N$^{-1}$·m$^{-1}$. The increase in hardness and tribotechnical characteristics of the material is conditioned by the saturation of its crystalline lattice with nitrogen atoms and the formation of nitride phase particles (Ti$_2$N, TiN). The highest wear resistance is observed in titanium samples treated in the plasma of a pulsed glow discharge. The data is corroborated by the results of micro- and nanohardness, and phase composition measurements.

4. Conclusion
Nitriding of technically pure VT1-0 titanium samples was carried out in the plasma of non-self-sustained glow discharge in a stationary and pulsed glow discharge modes. The depth of nitrited layer at treatment time $t=2$ hours and operating pressure of 730 °C for both the modes measured 50 µm, however nanohardness over depth for the samples obtained by pulsed mode treatment was 25% higher than that for the stationary glow discharge mode. The pulsed glow discharge mode allows for a higher content of nitride phase (Ti$_2$N, TiN) in the nitrited VT1-0 titanium layer as compared to that in the modified layer using a stationary glow discharge mode. This leads to the fact that nanohardness of the modified layer obtained by nitriding in a pulsed mode is one quarter higher than that of the stationary glow discharge mode. Due to the fact that more nitride phase forms in the surface layer of titanium when nitried in the plasma of a pulsed glow discharge as compared to a stationary glow discharge mode, the wear resistance of titanium after such treatment is higher.

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