

The structure, phase composition and mechanical properties of titanium alloy exposed to the ion-plasma nitriding

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Abstract. This paper investigates the structure, phase composition and mechanical properties of titanium alloy exposed to ion-plasma nitriding at 550 °C for 2, 4 and 8 hours in pure nitrogen atmosphere. Nitriding leads to an increase in nitrogen concentration in the near-surface layer, formation of α -Ti(N) solid solution, TiN, changes in the microstructure and microhardness of the surface: a decrease in roughness, an increase in microhardness, and, consequently, a decrease in the coefficient of friction.

Keywords: ion-plasma nitriding, titanium alloy, phase composition, microhardness, roughness, friction coefficient.

1. Context and motivation

Titanium alloys are used in medicine, aviation, and shipbuilding due to their low density, high strength, and corrosion resistance. However, titanium alloys are characterized by low tribological properties. The reason for this disadvantage is the high reactivity of the product surface, as well as insufficient hardness. Therefore, in order to achieve the required set of properties, titanium alloys should be subjected to hardening treatment. One of the types of chemical heat treatment is nitriding. Lately, there has been a consistent rise in scientific and industrial interest in employing vacuum-plasma diffusion techniques for the chemical-thermal surface treatment of materials and products [1, 2]. Among a wide variety of methods, the most promising nitriding method is ion-plasma nitriding due to the more rapid procedure, as the presence of the diffusing substance in an atomic or ionized state increases the rate of dopant penetration, and higher hardness of nitrided parts [3–5].

2. Experimental procedure

In this study, the object of research is a titanium alloy after ion-plasma nitriding (IPN) at the temperature of 550 °C for 2, 4, and 8 hours in the atmosphere of pure nitrogen. The elemental and phase composition, as well as the mechanical properties of the alloy, are studied.

3. Structure and phase composition

In this study, the object of research is a titanium alloy after ion-plasma nitriding (IPN) at the temperature of 550 °C for 2, 4, and 8 hours in the atmosphere of pure nitrogen. The elemental and phase composition, as well as the mechanical properties of the alloy, are studied. Energy-dispersive X-ray spectroscopy of the elemental composition revealed the presence of different alloying elements, such as Al, V, Mo, and Zr (Al is α -stabilizer, V and Mo are β -stabilizers) and Zr (neutral element). Nitrogen concentration raised from the 0.4 wt.% to 3.2 wt.% with an increase in nitriding time from 2 to 8 hours. Glancing X-ray diffraction method determined that the main phase is α -Ti (hexagonal low-temperature phase) and β -Ti (cubic high-temperature phase) is also present. The preferential orientation for the α -Ti diffraction line corresponds to α -Ti (101). The results of the study of the samples corresponding to different nitriding times are presented in Fig. 1. The analysis of the results showed that with increasing nitriding time the intensity of the diffraction lines of α - and β -Ti decreases, which is especially noticeable in the example of the peaks of α -Ti (101) and β -Ti (110). This can be explained by the increase in the thickness of the diffusion layer, as well as the gradual formation of a nitride film on the surface of the sample, preventing the penetration of X-rays. The graphs show that the diffraction peaks from α -Ti have an asymmetric shape, which is explained by

the next factors: firstly, the presence of nitrogen dissolved in the matrix phase in the surface layer; secondly, the superposition of peaks from the matrix titanium α -Ti and solid solution introduction α -Ti(N); thirdly, dispersed phase Ti_2N , which in accordance with the nature of the formation of additional phases in the process of IPN should precede the formation of titanium nitride TiN. However, the presence of this phase is not observed in the X-ray diffraction images, which can be explained either by the overlapping of peaks too thin for its detection, or by the nitrogen concentration on the sample with a treatment time of 4 hours insufficient for the Ti_2N formation. The formation of an additional TiN phase on the side faces of the sample was found to occur at 8 hours of processing time (Fig. 1). The visible evidence of TiN formation is the appearance of a golden-like coloration on the surface of the sample. Analysis of X-ray diffraction patterns of samples at increasing nitriding time revealed a shift of α -Ti diffraction lines to lower angles with increasing treatment time (Fig. 2). Therefore, there is a need to investigate the changes in the crystal lattice parameters.

The crystal cell parameter a for 4 hours of nitriding compared to 2 hours of nitriding increases by 0.03%, and for 8 hours compared to 2 hours – by 0.1% (Fig. 3). As the treatment time increases, nitrogen atoms, penetrating into the octahedral pores of the titanium crystal lattice, increase its cell and form the α -Ti(N) solid solution. As a result, compressive residual stresses (compressive microstresses) appear in the modified layer.

The parameter c shows a non-linear character of change: when passing from 2 hours of nitriding to 4 hours, a decrease by 0.08% (relative to the parameter taken for 2 hours of treatment) is observed, and when passing from 4 hours of nitriding to 8 hours of nitriding, an increase by 0.06% (relative to the parameter taken for 4 hours of treatment) and a decrease by 0.02% (relative to the parameter taken for 2 hours of treatment) are observed (Fig. 4.). The different character of change of parameters a and c of hexagonal lattice α -Ti is explained by anisotropy of properties.

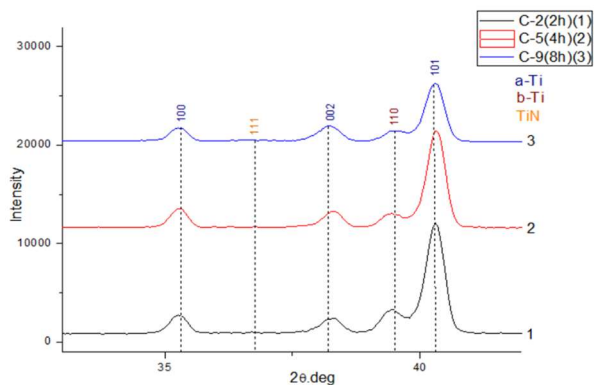


Fig. 1. X-ray diffraction of the sample Ti-6.2Al-2.3V-2.2Zr-1.8Mo-0.4N at 2, 4, 8 hours of nitriding

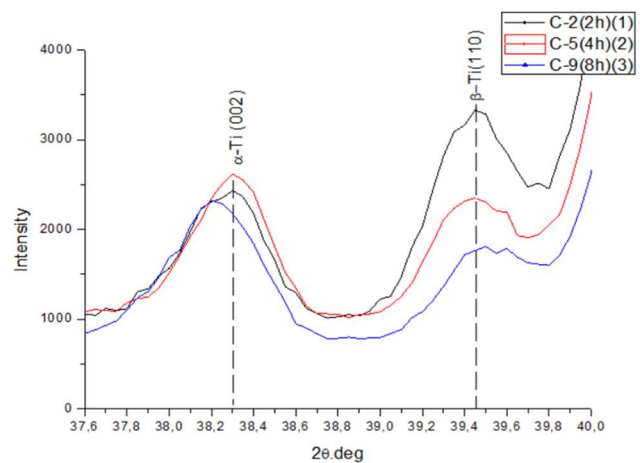


Fig. 2. Shift of α -Ti diffraction peaks towards smaller diffraction angles of the sample Ti-6.2Al-2.3V-2.2Zr-1.8Mo-0.4N at 2, 4, 8 hours of nitriding

The size parameter of the coherent scattering region shows the following pattern of change: at processing times 2 and 4 hours, it is almost unchanged, but when the processing time is increased to 8 hours, it increases by 33% (Fig. 5). This behavior is explained by the reasons described earlier.

The character of microstrain variation correlates with the character of variation of crystal lattice parameters (Fig. 6).

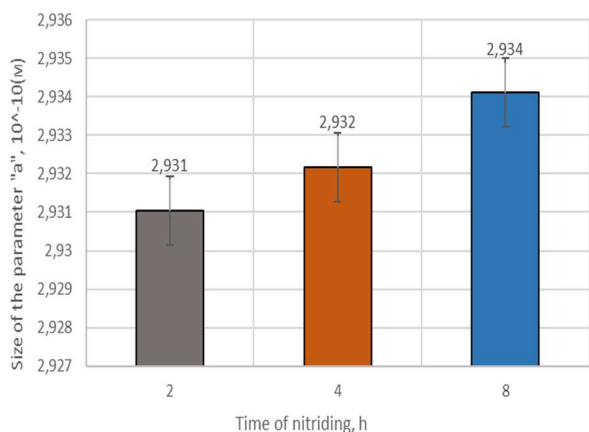


Fig. 3. Variation of the lattice parameter a as a function of processing time.

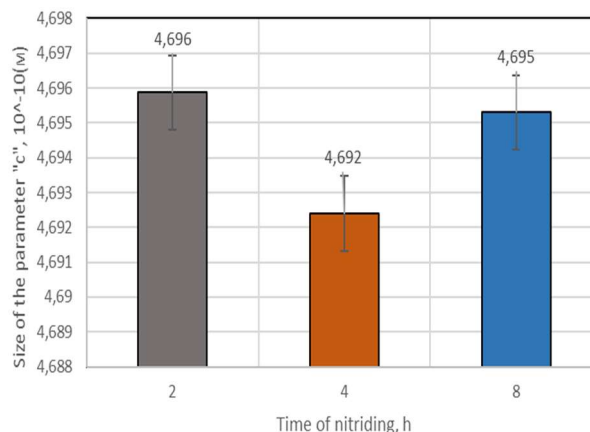


Fig. 4. Variation of the lattice parameter c as a function of processing time.

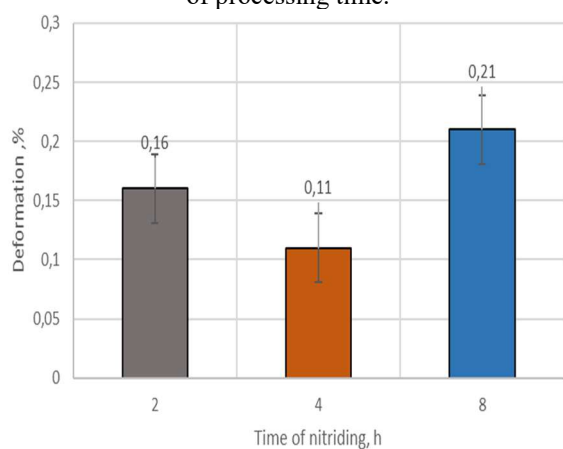


Fig. 5. Variation of crystal lattice microstrain as a function of processing time.

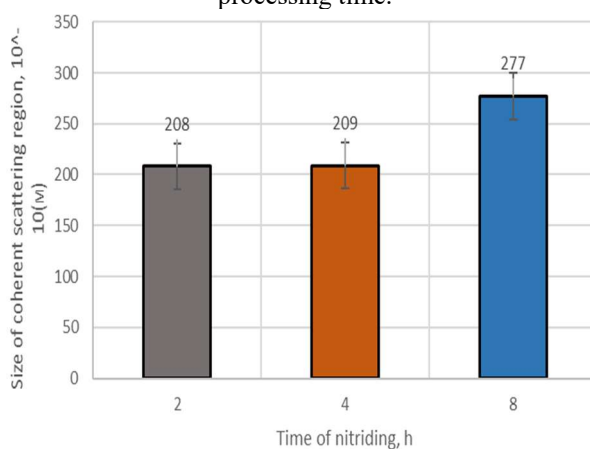


Fig. 6. Variation of coherent scattering region size as a function of nitriding time.

4. Mechanical properties

Based on the changes in the elemental and phase composition of the surface, modifications in the mechanical properties of the surface layers of titanium alloys should be observed after nitriding. It should be noted that the value of the nitrogen sputtering coefficient in the non-nitrided sample under these processing conditions is 0.63, while for TiN the coefficient is 0.84, which significantly affects the formation of the nitride film, sputtering the surface with nitrogen ions. As the nitriding time increases, the rate of nitrogen saturation slows down, which is associated with the formation of a TiN film on the surface, preventing the penetration of nitrogen into the diffusion layer. The change in microhardness may be associated with an increase in the yield limit due to the formation of a solid solution of incorporation. The microhardness studies of the samples showed an increase of 10% when the nitriding time increased from 2 to 8 hours for all loads, which is due to the formation of a solid solution of incorporation α -Ti(N), nitride film at a nitriding time of 8 hours. It should be noted that as the load on the pyramid increases, there is a decrease in the microhardness of all the samples under consideration, which is likely due to the increase in the contribution of the hardness of the titanium located below the diffusion layer and the layer of titanium nitride, to the obtained values with an increase in the load on the pyramid (Fig. 7).

Tribological tests of the samples showed a decrease in the friction coefficient by 2.8 times for 8 hours of nitriding compared to 4 hours of processing, which may be due to the formation of a nitride film, causing the increase in surface microhardness and a decrease in its roughness (Fig. 8). For 2 hours of nitriding, large fluctuations in the value of the friction coefficient are observed, which may

be due to the sputtering of nitrogen on the surface of the sample, abrasive wear, typical for titanium alloys. With an increase in nitriding time, the running-in zone significantly decreases, which may be due to the formation of a nitride film and a decrease in surface roughness.

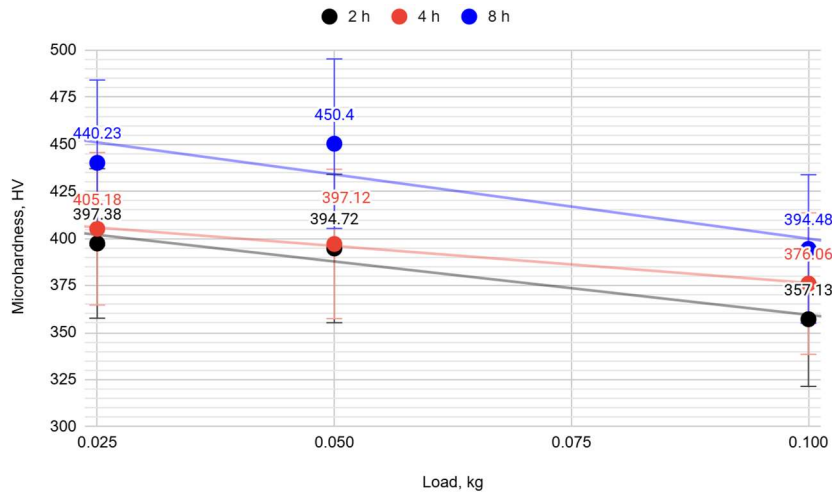


Fig. 7. Change in microhardness of surface layers of the titanium alloy Ti-6.5Al-2.3V-2.2Zr-1.8Mo during nitriding over various time intervals.

Also, the method of profilometry was used to study wear tracks. Analytically obtained data indicate a decrease in the width and area of wear tracks for 2 and 4 hours. It should be noted that when considering the profilogram for 8 hours of nitriding by this method, no wear track is observed, measurement of the width, area of the track by the profilometry method is not possible. The track depth for 2 hours of nitriding is 522 nm (Fig. 9) and 436 nm (Fig. 10) for 4 hours. For 8 hours of nitriding, the wear track depth measured by AFM is 180 nm (Fig. 11).

The study of the surface of the samples by the method of atomic force microscopy revealed that with an increase in nitriding time, a decrease in surface roughness is observed. This can also be explained by the sputtering of the surface with nitrogen ions, the formation of a thin layer of TiN. The following values of the root mean square deviation of the sample profile were obtained: for 2 hours of nitriding, $Rq = 237$ nm, for 4 hours $Rq = 127$ nm, for 8 hours $Rq = 120$ nm. This indicates that with an increase in time, the surface is smoothed, which is associated with the sputtering of surface layers with nitrogen ions, the formation of a nitride film.

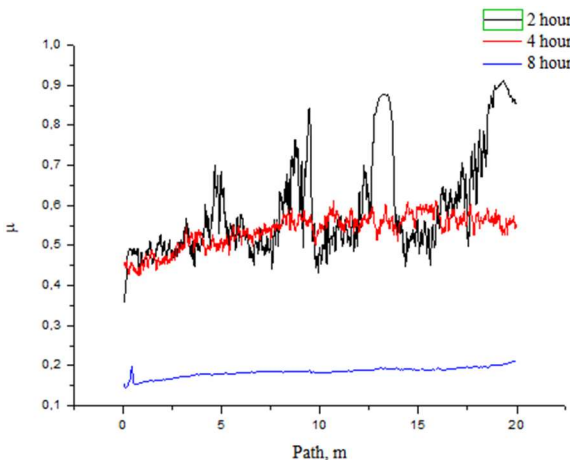


Fig. 8. Change in friction coefficient as a function of path at different nitriding time intervals.

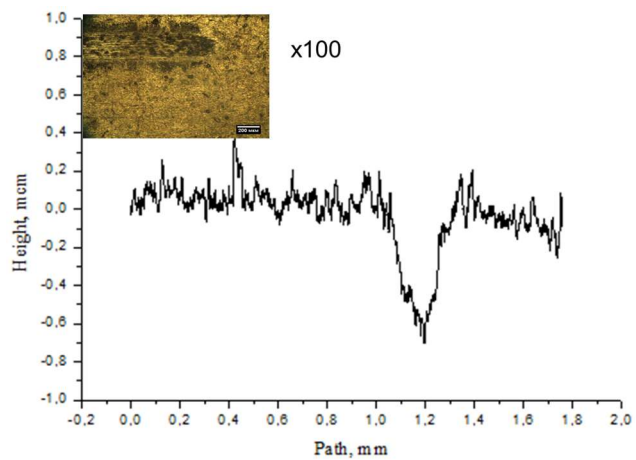


Fig. 9. Profilogram of the wear track for samples with 2 hours of nitriding.

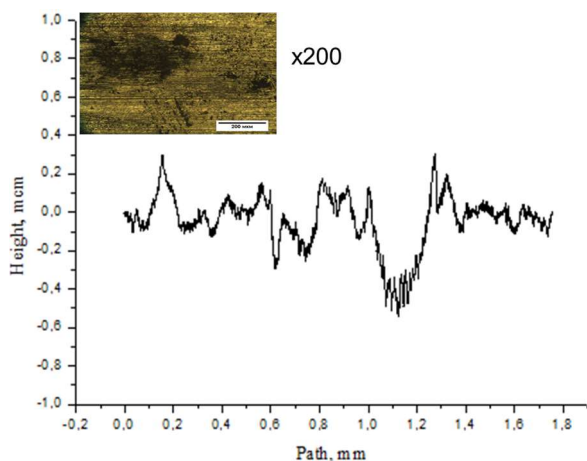


Fig. 10. Profilogram of the wear track for samples with 4 hours of nitriding.

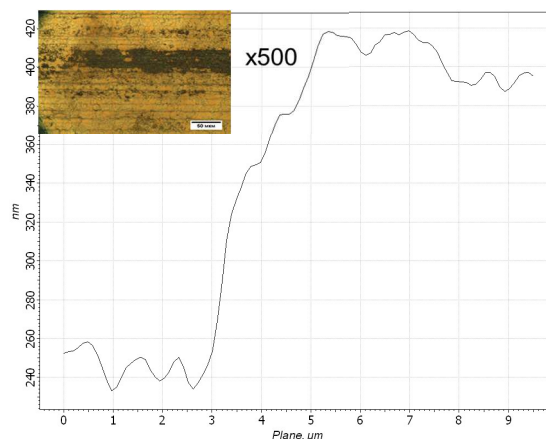


Fig. 11. Wear track depth for a specimen with 8 hours of nitriding.

Table 1. Mechanical properties of nitrided samples.

Processing time, h		2	4	8
Microhardness, HV	Load, 0.025 kg	397	405	440
	0.050 kg	395	397	450
	0.100 kg	357	376	394
Friction coefficient		0.45-0.90	0.56	0.20
Surface roughness Rq, nm		237	127	120
Depth of wear track, nm		522	436	180

5. Conclusions

An increase in the nitriding time of the samples from 2 to 8 hours leads to:

Increase in the concentration of nitrogen atoms N from 0.4 wt.% to 3.2 wt.%.

Appearance of TiN nitride. At 2 and 4 hours of nitriding the phase composition is the same: α -Ti is present (is the main phase) and β -Ti. The general scheme of the processes occurring during nitriding can be represented as: α -Ti \rightarrow α -Ti(N) \rightarrow Ti_2N \rightarrow TiN.

An increase in the parameter a of α -Ti from 0.2931 to 0.2934 nm. The lattice parameter increase is indicated by the shift of α -Ti diffraction peaks towards smaller diffraction angles due to the increase of N concentration in the α -Ti(N) solid solution and the occurrence of compressive stresses.

Increase in the size of the coherent scattering region from 21 to 28 nm.

Elevation in microhardness by 10% for loads of 0.025 kg, 0.050 kg, 0.100 kg.

Decrease of the friction coefficient by 2.8 times comparing 4 and 8 hours of processing time.

Diminishing the depth of the wear track shows a significant increase in the wear resistance of surface layers.

Reduction of roughness by a factor of 2 comparing 2 and 8 hours of processing time.

6. Acknowledgements

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7. References

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