THE EFFECT OF NITRIDING TEMPERATURE ON THE FORMATION OF SURFACE LAYERS OF VANADIUM-TITANIUM ALLOY Ti–6Al–4V

© 2025 V. L. Vorobyev*, V. S. Gladysheva, S. G. Bystrov, P. V. Bykov, V. Ya. Bayankin, and A. L. Ulyanov

Udmurt Federal Research Center, Ural Branch of the Russian Academy of Sciences, Izhevsk, Russia

**e-mail: Vasily_L.84@udman.ru*

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Abstract. In this work, using the methods of atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction analysis (XRD), the features of the formation of surface morphology, chemical and phase composition of near-surface and surface layers during ion-plasma processing of the Ti–6Al–4V (VT6) alloy in a glow discharge plasma of N+ ions were studied. depending on the temperature of the samples. It has been shown that increasing the sample temperature from 300 to 700ºC during processing leads to an increase in the surface roughness parameters *Ra* and *Rz*, due to the formation of titanium nitrides Ti_2N and TiN on the surface of the alloy. Based on the conducted research, it is assumed that the formation of thin near-surface layers (~20 nm) during treatment in nitrogen plasma without heating and with heating to 300ºC is determined by the oxidation processes of alloy components, and when processing with heating to 500 and 700ºC by nitrogen diffusion processes.

Keywords: *titanium alloy VT6, titanium nitrides, nitriding, chemical and phase composition, surface morphology, X-ray photoelectron spectroscopy*

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INTRODUCTION

Titanium alloys are widely used in various fields of technology due to their high strength, plasticity and low biotoxicity. The problem of developing technologies for modifying the surface of titanium alloys to increase their hardness, wear resistance, corrosion resistance and biocompatibility is relevant [1, 2]. One of the widely used methods for modifying titanium alloys is ion-plasma treatment of their surface. In particular, methods of diffusion saturation with nitrogen in glow and arc discharge plasma are used [3–9], as well as irradiation with N ion flows.$^+$[10–12].

In most cases, nitriding is carried out at high (800–900 ° C) temperatures for many hours. However, at high temperatures (exceeding the temperature of the polymorphic α→β transformation), nitriding of low-alloy titanium alloys leads to microstructure changes associated with grain growth. Nitriding of high-alloy titanium alloys, especially those alloyed with elements that lower the temperature of the polymorphic α→β transformation, is accompanied by changes in phase composition. Grain growth, changes in structural and phase composition lead to changes in the properties of titanium alloys and, consequently, require additional heat treatment operations to restore the structure and properties in the bulk of the products. Therefore, it is necessary to search for solutions that allow nitriding of titanium alloys under mild conditions (glow discharge, short processing time, relatively low temperatures). The structural simplicity of the nitriding equipment is also important, so that the developed technology can be applied in production later. In addition, to understand the mechanisms of the nitriding process and its purposeful regulation, it is relevant to study the chemical state and elemental composition of the surface of titanium alloys before and after modification. In view of the above, the aim of the work was a comprehensive study of surface morphology, formation of chemical and phase composition of surface and near-surface layers of titanium alloy VT6 during nitriding in glow discharge plasma depending on the nitriding temperature.

EXPERIMENTAL PART

Samples of titanium alloy VT6 were plates 10 mm long, with a cross-section of 8×2 mm. The composition of the samples in the initial state: Ti – base, Al – 6 wt.%, V – 4 wt.%. Since the samples were cut from a rolled sheet, their surface layers were in a work-hardened state. Therefore, in order to remove internal stresses and restore the microstructure, the samples were subjected to recrystallization annealing at a temperature of 800ºC with a holding time of 30 minutes followed by cooling together with the furnace before ion-plasma nitriding. After that, the surface of the samples was mechanically ground with sandpaper of P120, P320, and P1200 grit sizes. Then the samples were polished on felt with sequential application of suspensions with abrasive particle sizes of 9, 3, and 1 μm. The final stage of sample surface preparation was cleaning in an ultrasonic bath in organic solvents.

Ion-plasma treatment of the samples was carried out in a vacuum unit based on VUP-4M. The sample was placed in a quartz reactor inside the vacuum chamber, and the plasma was ignited only in the quartz reactor. Ultra-high purity nitrogen with a volume concentration fraction of 99.9999% was supplied to the quartz reactor. The gas composition is presented in Table 1. After preliminary evacuation to a pressure of ~ 1 Pa, nitrogen was admitted into the reactor chamber up to a residual pressure of 10 Pa. The sample served as the cathode. A high DC voltage of 500 V was applied between the anode and cathode. A glow discharge plasma with a plasma current of 40 mA was ignited in the reactor chamber.

Table 1. Composition of ultra-high purity nitrogen gas used for plasma ignition in the reactor chamber

No. item	Parameter name	Concentration, vol.%
1	Volume fraction of nitrogen	not less than 99.9999%
2	Volume fraction of oxygen	not more than 0.00001%
3	Volume fraction of water vapor in gaseous nitrogen	not more than 0.00005%
4	Volume fraction of the sum of carbon-containing compounds in terms of CH_4	not more than 0.00001%
5	Volume fraction of hydrogen	not more than 0.00005%

The samples were treated both without heating and with heating using a built-in heater. A platinum-rhodium-platinum thermocouple was attached to the heater table. The treatment time for each sample was 60 minutes. For convenience of presenting the results, we introduce sample designations, which are given in Table 2.

Table 2. Sample designation

Sample No.	Treatment
1	Initial alloy VT6
2	VT6 in N plasma $^+$
3	VT6 in N plasma $^+$ with heating to 300ºC
4	VT6 in N plasma $^+$ with heating to 500ºC
5	VT6 in N plasma $^+$ with heating to 700ºC

The chemical composition of the surface layers was studied by X-ray photoelectron spectroscopy (XPS) using SPECS and ES2401 spectrometers with Mg K α–radiation (1253.6 eV). The energy scale of the spectrometers was calibrated using the binding energies of Au 4 f 7/2 (84.0 eV) and Cu 2 p 3/2 (932.8 eV). Sample charging control was not used as the samples had sufficient conductivity. The full width at half maximum (FWHM parameter) of the Au 4 f 7/2 peak was 1.0 eV. Processing of spectral data and concentration calculations were performed using the Casa XPS software (Version 2.72-r22116). Layer-by-layer elemental analysis was carried out during surface etching with argon ions with an energy of 4 keV and a current density of 30 μA/cm ^{2} . The surface etching rate was ~1 nm/min, and the relative error in determining the concentration of elements was ±3 at.%.

The morphology of the sample surfaces was studied using a SOLVER P47 PRO atomic force microscope in contact mode. Image processing was performed using Image Analysis 3.5.0 software. For each sample, the average arithmetic surface roughness (*Ra*) and the height of the profile irregularities at ten points (*Rz*) were calculated from images of 9 areas with a base size of 2×2 μm. The measurement error for *Ra* and *Rz* (standard deviation, SD) was calculated. The average sizes of blocks on the sample surfaces were calculated using the Grain Watershed subroutine (figures "boundaries of grains" and "average size") for 5×5 μm frames. Images with surface section profiles along a selected line were obtained (figures section analysis and height profile) for 5×5 μm frames.

The X-ray diffraction (XRD) analysis was performed on a MINIFLEX-600 diffractometer using Co K α-radiation. X-ray phase analysis was carried out using software package [13]. The analysis depth was ~ 9-10 μm.

Microhardness measurements of the samples were conducted by indentation method on a PMT-3M device with an indenter load of 10 g and a dwell time of 10 s at this load. A diamond pyramid with a vertex angle of 136º was used as the indenter. At the selected load, the indenter penetration depth was ~3 μm. At least 20 measurements were made on each sample.

RESULTS AND DISCUSSION

Studies conducted by atomic force microscopy (AFM) indicate that ion-plasma treatment of the alloy in N $^+$ ion plasma, especially at higher temperatures, leads to changes in surface morphology. The surface morphology of the initial sample represents a typical example of the surface condition after mechanical grinding and polishing (Fig. 1a). No significant changes in the surface morphology of samples treated in N $^+$ ion plasma without heating and with heating up to 300ºC were observed. After ion-plasma treatment in N $^+$ ion plasma with sample heating to temperatures of 500 and 700ºC, certain features appear in the surface morphology (Fig. 1c, d). These features manifest as round-shaped blocks appearing across the entire surface. Changes in surface morphology during ion-plasma treatment with increasing sample temperature are also reflected in the values of surface roughness parameters *Ra* and profile irregularity height *Rz* , calculated from ten points (Table 3). The values of these parameters for the initial surface and the surface after treatment in N^+ ion plasma without heating and with sample heating to 300ºC correspond to each other within the experimental error. After treatment in N^+ ion plasma with sample heating to temperatures of 500 and 700ºC, an increase in these parameters is observed. For example, the roughness parameter *Ra* after treatment at 700ºC increased approximately 3 times (Table 3).

Fig. 1. AFM images of the surface morphology of the studied samples: (a) - initial sample; (b) - N^+ plasma with sample heating to 300ºC; (c) - N^+ plasma with sample heating to 500ºC; (d) - N^+ plasma with sample heating to 700ºC.

Table 2. Sample designation

Sample #	Processing
1	Initial Ti6Al4V alloy
2	Ti6Al4V in N^+
3	Ti6Al4V in N^+ plasma with heating to 300ºC
4	Ti6Al4V in N^+ plasma with heating to 500ºC
5	Ti6Al4V in N^+ plasma with heating to 700ºC

It can be assumed that the observed changes in surface morphology are a consequence of structural-phase transformations occurring in the near-surface and surface layers of the samples under conditions of ion-plasma treatment. Another mechanism leading to changes in surface morphology can be attributed to surface sputtering [14, 15]. However, due to the low energy of N^+ ions (about 500 eV), their small mass, and based on the peculiarities of the formation of chemical and phase composition, which will be discussed below, it can be assumed that the sputtering process is a secondary mechanism of surface morphology formation under these processing conditions. For example, the growth of surface roughness and the appearance of blocks begins to manifest clearly only at elevated processing temperatures.

Fig. 2. Element distribution profiles in titanium alloy Ti6Al4V samples in the initial state (a) and after treatment in nitrogen plasma without heating (b).

XPS studies of the elemental and chemical composition of thin surface layers of the samples showed that the initial surface is characterized by a rather deep layer of natural titanium oxides up to ~ 20 nm (Fig. 2a). The presence of a thick titanium oxide film on the surface of the investigated alloy is a consequence of the high mutual chemical activity of titanium and oxygen atoms [16]. After treatment in N^+ ion plasma without heating the samples, an increase in oxygen concentration in the near-surface layers is observed compared to the oxygen concentration in the original sample (Fig. 2b). The distribution of elements in the near-surface layers of samples treated at different temperatures is presented in Fig. 3. Attention should be paid to changes in the nitrogen and oxygen distribution profiles. These profiles, combined into one graph, are separately presented in Figure 4. From the data provided, it follows that when treated in N^+ ion plasma without heating and with heating of samples to 300°C, no accumulation of nitrogen in the near-surface layers is observed.

The maximum concentration to which it accumulates does not exceed 15 at.% (Fig. 4a). After treatment of samples in N^+ ion plasma with higher heating temperatures, especially at 700°C, intensive saturation of the surface with nitrogen occurs (Fig. 4a). The nitrogen concentration at 700°C reaches ~37-40 at.%. At the same time, starting from a depth of ~5 nm, the concentration profile of nitrogen distribution, as in the sample treated at 500°C, reaches values that change insignificantly with further depth.

Fig. 3. Distribution profiles of elements in titanium alloy VT6 after treatment in N^+ ion plasma with heating of samples to 300°C (a); 500°C (b); 700°C (c).

Fig. 4. Distribution profiles of nitrogen (a) and oxygen (b) in VT6 samples treated in N^+ ion plasma under various conditions: initial sample (1), N^+ ion plasma without sample heating (2) and with heating to temperatures of 300°C (3); 500°C (4); 700°C (5).

Therefore, starting from this depth and under given treatment conditions, the concentration profiles of nitrogen distribution reach saturation. From the oxygen distributions (Fig. 4b), on the contrary, it follows that during plasma treatment without heating and with heating of samples to 300°C, there is an increase in oxygen concentration in the near-surface layers, associated with oxidation processes of the alloy components. With increasing nitriding temperature, the oxygen concentration decreases, and in the sample treated at a temperature of 700°C , it becomes even lower than the oxygen concentration in the original sample (Fig. 4b).

Also, from the distributions of elements presented in Fig. 3, it can be noted that in the near-surface layers of samples after ion-plasma treatment, an increase in carbon concentration is observed. On the original surface, the carbon concentration at depths from ~ 1 nm and more is ~ 3-5 at.%. After ion-plasma treatment, especially at higher temperatures (500°C and 700°C), an increase in carbon concentration is observed (Fig. 2b and Fig. 3a-c). On the surface, the carbon concentration reaches values of 50-70 at.%. However, this is a typical case for a metallic surface after being exposed to air. The increase in carbon content in the near-surface layers is a consequence of adsorption and diffusion of carbon from the residual atmosphere of the vacuum chamber during the ion-plasma nitriding process. Carbon enters the residual atmosphere of the vacuum chamber from the oil pumping system of the device. For example, at depths from ~5 nm and more, the carbon concentration, depending on the treatment mode, varies in the range of 4-10 at.% (Fig. 3a-c). This is approximately twice as much as on the original surface. However, this is significantly lower than the concentrations of nitrogen, titanium, and oxygen, which determine the formation of surface layers.

From the analysis of the presented data, conclusions can be drawn about the following features of the formation of the elemental and chemical composition of thin near-surface layers of titanium alloy VT6 under treatment conditions in a glow discharge plasma of N^+ ions. When treated in N^+ ion plasma without heating and with low-temperature heating of samples up to 300ºC, the formation of surface layers with a depth of ~ 20 nm is determined, to a greater extent, by the oxidation processes of the alloy components, which can be attributed to processes of chemical nature. Oxygen atoms, due to their high chemical activity towards the alloy components, and especially to titanium atoms, enter into chemical interaction with them, forming their oxides. This process involves oxygen that was initially adsorbed on the alloy surface, as well as oxygen penetrating into the near-surface layers during ion-plasma treatment from the residual atmosphere of the vacuum chamber. At elevated treatment temperatures (500 and 700ºC), the formation of the chemical composition of the near-surface layers is determined by nitrogen diffusion processes.

Nitrogen diffusion processes can be attributed to processes of physical nature. With an increase in the treatment temperature, the mobility of alloy component atoms in the crystal lattice nodes and the diffusion mobility of nitrogen atoms increase. This leads to nitrogen penetrating through defects and grain boundaries into the near-surface, and then into the surface layers, accumulating in them. As will be shown below, this process is accompanied by the formation of titanium nitrides T_2N and TiN.

Analysis of XPS O1 *s* spectra using the technique of spectral decomposition into components indicates that oxygen is included in the composition of titanium oxides, titanium hydroxides with insignificant fractions of oxygen in C–O and O–H bonds (Fig. 5).

Fig. 5. XPS spectrum O1 *s* , obtained from a depth of ~ 20 nm, in a VT6 sample after plasma treatment without heating (a); with heating at 300ºC (b); 500ºC (c); 700ºC (d).

These oxygen states are detected in almost all samples. It should be noted that in samples treated at higher temperatures (500 and 700ºC), there are some overlaps from the lower electron binding energies (Fig. 5 c, d). These overlaps appear not only in the O1 *s* spectra, but also in the N1 *s* spectra (Fig. 6c, d). This is due to the fact that a state corresponding to titanium oxynitride TiN_xO_y is added to the chemical compounds mentioned above. In general, a detailed analysis of the XPS spectrum of N1 *s* shows that the predominant state of nitrogen atoms in all samples corresponds to the chemical bond of nitrogen with titanium atoms Ti–N (Fig. 6). The electron binding energy for the Ti–N bond in the N1 *s* spectrum is 397 eV. Titanium nitrides Ti_2N, TiN, as well as nitrogen atoms surrounded by titanium from the solid solution of the investigated alloy, contribute to this spectrum.

Thus, XPS data indicate that the formation of chemical compounds characteristic of titanium nitrides occurs already in the near-surface layers of the investigated samples under conditions of ion-plasma exposure at all treatment modes.

Fig. 6. XPS spectrum of N1 *s* obtained from a depth of ~20 nm in a VT6 sample after plasma treatment without heating (a); with heating at 300ºC (b); 500ºC (c); 700ºC (d).

The formation of titanium nitrides is confirmed by the analysis of Ti2 *p* -spectra (Fig. 7). In the initial state, the maximum of the Ti 2 *p* 3/2 line at the analysis depth of ~ 20 nm corresponds to 454 eV, and its Ti 2 *p* 1/2 doublet is separated from it by approximately 6.1 eV (Fig. 7, spectrum 1). This indicates the metallic state of titanium atoms in the initial sample at this depth. In this state, they are located at the nodes of the crystal lattice of the solid solution. After treatment under all nitriding modes, to a greater or lesser extent, we observe, firstly, a shift of the maximum lines of the Ti 2 *p* 3/2 and Ti 2 *p* 1/2 doublets toward higher energies and, secondly, a decrease in the distance between them (Fig. 7, spectra 2-5). This indicates a change in the oxidation state of titanium atoms and is a consequence of the formation of the above-mentioned compounds of oxides, nitrides, oxynitrides, and titanium hydroxides.

Fig. 7. XPS spectra of Ti2 *p* of VT6 samples obtained from a depth of ~ 20 nm, in the initial state (1); after plasma treatment without heating (2); with heating of samples to 300°C (3); 500°C (4); 700°C (5).

The studies conducted by X-ray diffraction analysis provided information about changes in the structural and phase composition of the samples. They showed that in the initial state, the structural and phase composition of the samples is mainly represented by the α-Ti phase with a HCP crystal lattice (Fig. 8, X-ray pattern 1). After treatment in nitrogen plasma without heating and with heating of samples to 300°C, no visible changes in the X-ray patterns are observed (Fig. 8, X-ray patterns 2 and 3). This indicates that the phase composition of the samples treated under these modes does not undergo significant changes. After treatment in nitrogen plasma at higher temperatures (500 and 700°C), the titanium nitride phase Ti_2N with a volume fraction of 8 and 17 vol.%, respectively, is added to the α-Ti phase (Fig. 8, X-ray patterns 4 and 5). In addition, in the sample treated at the highest selected nitriding temperature (700°C), the titanium nitride phase TiN with a fraction of ~ 2 vol.% is added to the phase composition (Fig. 8, X-ray patterns 5).

Fig. 8. X-ray diffraction patterns of VT6 titanium alloy samples in the initial state (1); after treatment in N^+ ion plasma without heating (2); and with sample heating to temperatures of 300ºC (3), 500ºC (4); 700ºC (5).

Previously, in our work [17], we investigated the influence of N^+ ion implantation with an irradiation dose of 1018 ion/cm^2 on the formation of the structural-phase state of surface layers of VT6 alloy. Under these treatment conditions, the heating temperature of the samples under the ion beam did not exceed 300ºC. Nitrogen accumulation reaches concentrations of ~ 32 at.%, which corresponds to its accumulation in the sample after ion-plasma treatment at a temperature of 700ºC.

However, in the case of ion implantation, the preferential formation of the TiN phase is observed up to ~ 19 vol.%, while the proportion of the Ti_2N phase, on the contrary, is ~ 2 vol.%. These differences are related to the fact that the modification of the structural-phase composition is determined by the processes of ion implantation, chemical interaction of nitrogen with titanium atoms, formation of radiation defects and stress fields, under the influence of which radiation-stimulated diffusion of nitrogen ions occurs, rather than thermal diffusion.

Fig. 9. Relative change in microhardness of VT6 titanium alloy samples as a result of treatment in N^+ ion plasma without heating (2); with sample heating to temperatures of 300ºC (3); 500ºC (4); 700ºC (5).

Thus, from X-ray diffraction (XRD) studies, it follows that diffusion saturation with nitrogen during treatment in N^+ ion plasma with heating of samples to 500ºC and 700ºC occurs not only in the subsurface, but also in the surface layers and is accompanied by the formation of titanium nitrides Ti_2N and TiN as phase inclusions. Treatment in N^+ ion plasma without heating and with heating of samples to a temperature of 300ºC does not lead to the accumulation of nitrogen in the surface layers and the formation of titanium nitrides of sizes sufficient for particle identification by XRD method, which is a consequence of low diffusion mobility of nitrogen and alloy components, as well as oxidation processes of alloy components. The formation of titanium nitrides Ti_2N and TiN in the sample processed at 700ºC is accompanied by an increase in the microhardness of the samples by approximately 1.7 times (Fig. 9). With plasma treatment under other nitriding regimes, the microhardness values, within the experimental error, do not differ from the microhardness of the sample in the initial state.

CONCLUSIONS

It has been established that the surface of the VT6 titanium alloy, treated in N^+ ion plasma with heating of samples to 500ºC and 700ºC, consists of rounded blocks. It is assumed that this surface morphology is formed as a result of the formation of titanium nitrides Ti_2N and TiN in the surface layers of the samples.

It is shown that during nitriding of the VT6 alloy in the glow discharge plasma without heating and with heating of samples to 300ºC, a slight (up to ~15 at.%) saturation of the surface layers with nitrogen is observed, which is due to the low diffusion mobility of nitrogen at these temperatures and the oxidation processes of the alloy components.

At higher nitriding temperatures of 500 and 700ºC, the surface is saturated with nitrogen up to concentrations of ~35 at.%, accompanied by the formation of titanium nitrides Ti_2N and TiN, which is due to the predominant role of diffusion processes in the formation of surface layers under these processing conditions.

Ion-plasma nitriding at the highest of the selected processing temperatures (700ºC) leads to an increase in the microhardness of the samples by 1.7 times.

The conducted studies show the possibility of targeted modification of morphology, mechanical properties, chemical and phase composition of the surface and surface layers of VT6 alloy through treatment in N^+ ion plasma under mild conditions (at temperatures up to 700ºC).

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CONFLICT OF INTERESTS

The authors of this work declare that they have no conflict of interest.

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