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Repetitively-pulsed nitrogen implantation in titanium by a high-power density ion beam

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Abstract. The article presents the results of studies of the features and regularities of high-intensity nitrogen ion implantation into titanium using repetitively-pulsed beams with high average and pulsed power densities. It is shown that the method of low-energy high-intensity nitrogen ion implantation at current densities of 180, 140, 60, and 10 mA/cm^2 makes it possible to obtain wide ion-doped layers in titanium. The regularities of changes in both thickness and elemental composition of ion-doped layers depending on the ion current density have been established. It has been established that a wide diffusion layer is observed at ion current densities from 60 to 180 mA/cm^2. Nitrogen concentration in the diffusion layer increases with an increase in the ion current density. As a result of a long high-intensity implantation process at temperatures of 700 and 850 °C, the titanium microstructure deteriorates in the entire volume of the sample material. The article presents the transmission electron microscopy data showing that the modified layers at a depth of 10 μm consist of α-Ti, in the volume of which nanosized particles of δ-TiN with average size of 15.4 nm crystallize. Numerical simulation is used to study the change in temperature fields in titanium under the action of a pulsed and repetitively-pulsed ion beam with submillisecond duration on the surface with a power density from 20 to 30 kW/cm^2. The results of experimental studies of the pulsed impact of high-pulse ion beams on the titanium microstructure are discussed.

Keywords: ion beam, high intensity, high power, implantation, surface modification.

1. Introduction

A wide range of titanium alloy advantages, such as high strength, toughness and density, high corrosion resistance and low specific gravity make this material indispensable in mechanical engineering, instrumentation, aviation industry, etc. However, poor wear resistance, high friction coefficient, and low hardness lead to the need to strengthen the surface layers of titanium materials. There are many surface modification methods, for example, ion nitriding, ion-beam and electron-beam processing, ion-plasma deposition of coatings, modification by laser radiation, high-current electron beams, powerful plasma flows [1–8]. One of the efficient methods of surface modification is ion implantation, which makes it possible to significantly change the structure and phase composition of materials. In recent years, the method of high-intensity low-energy ion implantation has been actively developed [9]. The method is based on plasma-immersion extraction of ions from the free plasma boundary, their acceleration in a high-voltage sheath, followed by ballistic focusing, and allows forming high-density ion beams, which makes it possible to multiply the ion implantation fluence. Work [10] shows the possibility to implant nitrogen ions into AISI 5140 steel to a depth of up to 180 μm, with a 3-fold improvement in microhardness and 27-fold improvement in wear resistance as compared to the initial target material. One of the characteristic features of the metal and alloy modification by high-intensity low-energy ion implantation is due to the heating of the sample by an ion beam to high temperatures, which deteriorates the microstructure of the irradiated materials throughout the volume. Work [11] proposes a method to solve this problem due to the synergy of high-intensity ion implantation and pulsed or repetitively-pulsed energy impact of the ion beam on the irradiated surface.

This work focuses on the features and regularities of high-intensity nitrogen ion implantation in titanium using pulsed and repetitively-pulsed ion beams with a pulsed power density from 0.2 to 30 kW/cm^2.

2. Research methodology

High-intensity nitrogen ion implantation was carried out on a vacuum experimental setup equipped with a turbomolecular pump Turbo-V 1001 Navigator. The residual gas pressure in the working chamber was 10^{-3} Pa. Plasma generation was carried out using a gas-discharge plasma formed by non-self-sustained arc discharge with a thermionic and hollow cathodes "PINK" [12]. High-intensity nitrogen ion beam formation was carried out by a method of plasma-immersion ion extraction from free plasma boundary, their acceleration in a high-voltage sheath, followed by ballistic focusing, similar to the approach described in previous works [9, 13]. To generate low-energy ion beams, a focusing system was used in the form of a part of a sphere with a curvature radius of 75 mm, made of a metal mesh with a cell size of 1.8×1.8 mm^2. When the bias potential amplitude increased to 20 kV, a grid electrode with a cell size of 0.5×0.5 mm^2 and a curvature radius of 120 mm were used. The grid electrodes were connected to bias voltage pulse generator with a negative polarity. In the first case, the generator provided forming the negative bias potential pulses with an amplitude of 1.2 kV, at a repetition rate of 10^5 pulses/s and a pulse duration of 4 μs. In the second case, a pulsed voltage generator was used with a bias amplitude of 20 kV and a pulse duration of 500 μs. The ion current density was determined from the data of current measurements by a Rogowski coil on a collector with a size of 2×2 mm^2. In the case of high-intensity low-energy ion implantation, the maximum current density was 180 mA/cm^2. In studies of the synergy of high-intensity ion implantation and energy impact on the surface, the nitrogen ion current density was about 1500 mA/cm^2. The thickness of the ion-modified layer was determined using a scanning electron microscope Hitachi S-3400 N by metallography after chemical etching of thin sections. The elemental composition of the modified near-surface layer was analyzed and the nitrogen distribution depth in the transverse sections of the samples was determined by the X-ray spectral method on Bruker XFlash 4010 energy-dispersive attachment to a Hitachi S-3400 N electron microscope. Electron microscopic studies of titanium samples after nitrogen ion implantation were carried out on a transmission electron microscope. Foils for TEM studies were prepared according to the "cross-section" scheme by ion etching using an argon ion beam on an ION-SLICER EM-09100IS unit (Jeol, Japan).

3. Investigating the regularities of high-intensity low-energy ion implantation

Nitrogen ion implantation into titanium samples was carried out at temperatures of 500, 700, and 850 °C for one hour. In contrast to nitrogen implantation in steel AISI 5140, AISI 321 [10,13], when significant diffusion took place at temperatures of about 500 °C, the regime of nitrogen ion implantation into titanium at the same temperature did not give positive results, since this temperature is not sufficient for intensification of diffusion processes [14]. Fig.1 shows graphs of the nitrogen dopant distribution over the samples' depth at target temperatures of 700 and 850 °C. As can be seen from Fig.1, at a target temperature of 700 °C, the maximum value of the nitrogen concentration is about 4 at.% near the surface, then it sharply decreases. As the target temperature rises to 850 °C, a significant ion-doped layer broadening is observed. The maximum nitrogen dopant concentration rises to 17 at.%. The width of a layer with a high concentration reaches 40 μm, and a layer with a low concentration of ~5 at.% persists for several tens of micrometers. The influence of the ion implantation fluence on the doped layer depth, its microstructure and phase composition was studied on samples irradiated at a temperature of 850 °C. Fig.2 shows a photograph of a metallographic section corresponding to a maximum fluence of $1.6 \cdot 10^{21}$ ion/cm^2. Under irradiation, a continuous ion-modified layer is formed near the surface, the thickness of which varies significantly depending on the ion implantation fluence. The maximum thickness of the ion-doped layer is 50 μm when nitrogen ions are implanted with a current density of 180 mA/cm^2 and a fluence of $1.6 \cdot 10^{21}$ ion/cm^2. As the fluence decreases to $0.1 \cdot 10^{21}$ ion/cm^2, the layer depth decreases to ~15 μm. A continuous ion-modified layer corresponds to a high nitrogen concentration of ~10–17% a.u. (Fig.3). Along with it, in accordance with the nitrogen concentration distribution over depth, there is a diffusion layer with a thickness of 400 μm. At the maximum value of the ion current density, the nitrogen concentration in the diffusion layer is about 5 at.%. When the current density decreases to 60 mA/cm^2, the concentration is almost halved. At a current density of 10 mA/cm^2 the diffusion layer actually disappears.

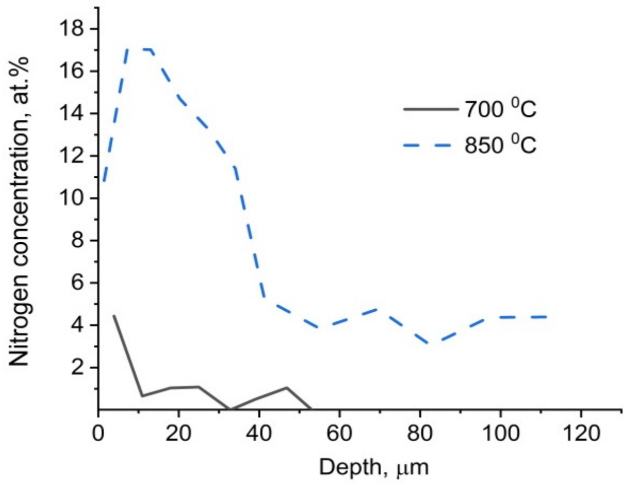

Fig.1. Profiles of nitrogen dopant distribution over the titanium samples' depth.

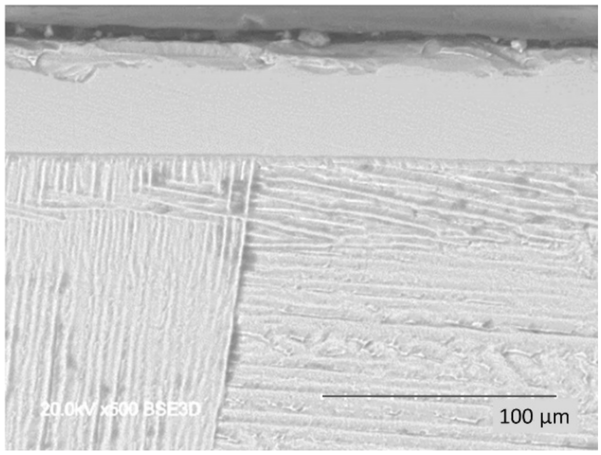

Fig.2. Micrograph of a thin section of titanium modified at ion implantation fluence of $1.6 \cdot 10^{21}$ ion/cm^2 and temperature of 850 °C.

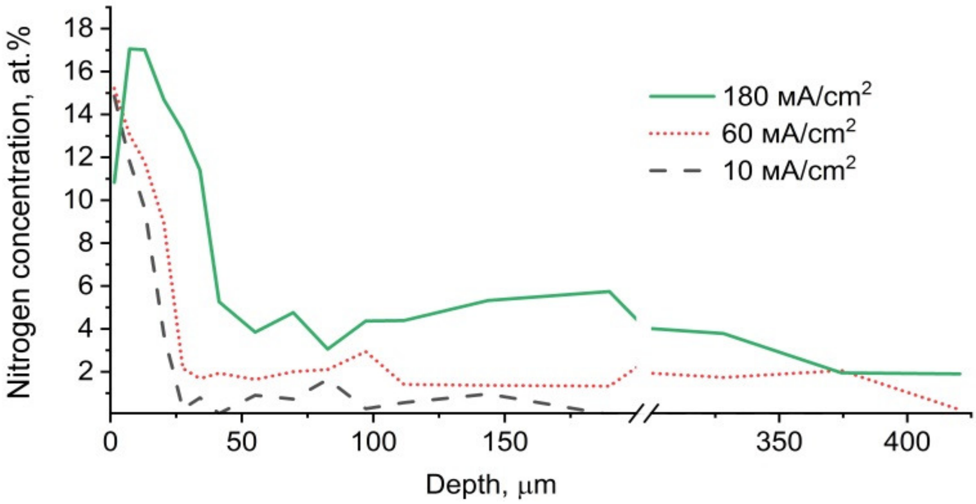

Fig.3. Profile of nitrogen concentration distribution in a sample implanted at a temperature of 850 °C.

Fig.4 shows the results of electron microscopic studies of the microstructure and phase composition of a titanium sample implanted with nitrogen ions in cross-section. It can be seen from the presented images that the microdiffraction patterns obtained from the modified sample surface (Fig.4b) and at a distance of 10 μm from its surface (Fig.4c) have the same appearance. In particular, the microdiffraction patterns contain intense point reflections characteristic of a titanium matrix with a hexagonal close-packed structure, as well as ring reflections, which have a lower intensity. Identification of microdiffraction patterns (Fig.4b,c) made it possible to establish that the α-Ti matrix grains presented on the implanted sample surface have the zone axes [003] and $[\bar{1}1\bar{1}]$. Ring reflections, which are also present in the microdiffraction patterns of the sample under study, correspond to reflections (111), (200), and (220) of the TiN δ-phase. At that, according to the TEM data, the formation of $TiN_{0.3}$ (hcp) in the titanium surface layers with depth of up to 10 μm was not detected, which may be due to its localization in the modified titanium layers that are more distant from the implanted surface. Electron microscopy showed that the implanted samples contain a large number of particles belonging to δ-TiN phase. The size of the formed phase particles lies in a narrow range from 8 to 33 nm, and their average size is 15.4 nm (standard deviation σ_d = 4.35 nm). Therefore, the modified titanium sample is α-Ti containing nanosized particles of titanium nitride δ-TiN.

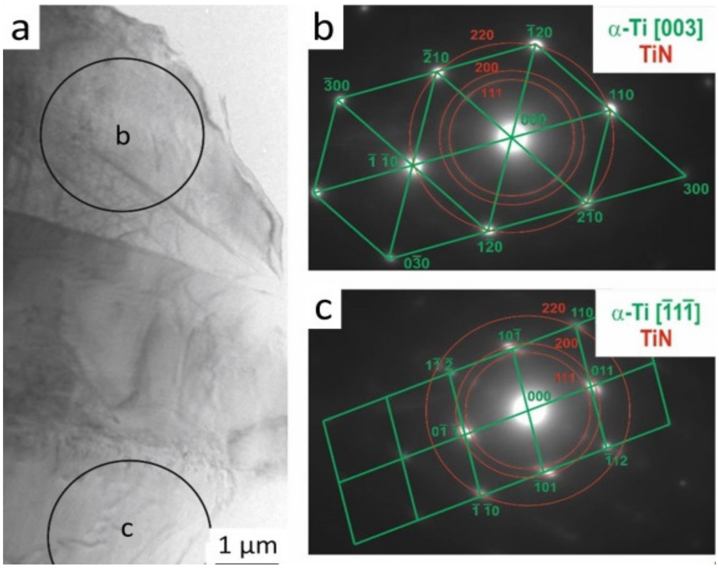

Fig.4. Electron microscopic images of titanium after high-intensity nitrogen ion implantation: a – bright-field image; b, c, – microdiffraction patterns and schemes for their indication. The circles show the sample areas from which the corresponding microdiffraction patterns were obtained.

It is important to note that the micrographs in Fig.2 demonstrate a significant change in the irradiated samples' microstructure even at great depths. This is due to the prolonged exposure to high temperature during high-intensity low-energy ion implantation. Grain growth takes place in the entire volume of the material. The possibility to solve the problem of microstructure deterioration in the entire volume of the irradiated material is proposed in [11]. The idea of the method is based on the synergy of repetitively-pulsed implantation by powerful submillisecond ion beams with the simultaneous energy impact of this beam on the near-surface layer of the material. To estimate the required ion beam parameters in such an irradiation regime, numerical simulation of the titanium sample's temperature fields was carried out under the influence of a nitrogen ion beam with a duration of 500 μs.

4. Simulation of the energy impact of a submillisecond ion beam on a titanium target

Numerical simulation was carried out using the program described in [15]. In this specific case, the model was modified in relation to the energy impact of a submillisecond pulsed nitrogen ion beam on a titanium target with thickness of 3 mm and a diameter of 40 mm.

Calculations have shown that a repetitively-pulsed nitrogen ion beam with a duration of 500 μs at a pulse frequency of 2 pulses/s and a pulsed power density of $2\cdot10^8$ W/m^2 provides heating of the irradiated target in the steady state up to a temperature of 647 °C (Fig.5). Pulsed impact of every next ion beam increases the near-surface layer temperature up to 1319 °C (Fig.6). With an increase in the power density of the pulsed beam to $2.5\cdot10^8$ W/m^2, the maximum temperature increases to

1487 °C, and at a power density of more than $3 \cdot 10^8$ W/m^2, pulsed melting of the surface should take place.

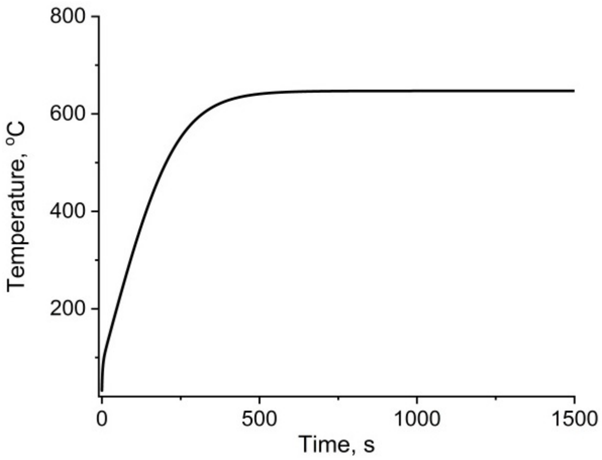

Fig.5. Dependence of the temperature in the center of a target made of titanium 3 mm thick on the time of its irradiation with a beam of nitrogen ions with a power density averaged over the period $Q_{average} = 2 \cdot 10^5$ W/m^2.

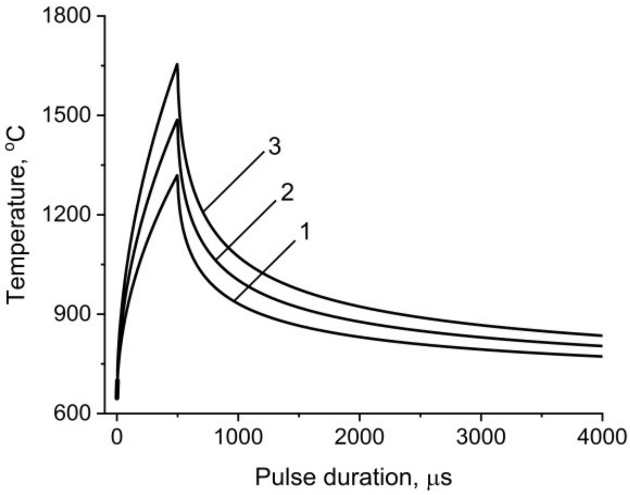

Fig.6. Time dependence of temperature in the steady state regime of titanium surface irradiation by a high-intensity beam of nitrogen ions with a pulsed power density: 1 – $Q_{pulse} = 2 \cdot 10^8$ W/m^2; 2 – $Q_{imp}= 2.5 \cdot 10^8$ W/m^2; 3 – $Q_{imp}= 3 \cdot 10^8$ W/m^2.

5. Experimental study of the submillisecond nitrogen ion beam's energy impact on titanium

The formation of an intense high-pulsed power nitrogen ion beams was carried out in the regime of plasma-immersion ion extraction from gas-discharge plasma. The plasma was generated using a gas-discharge source "PINK" [12]. A grid electrode with a cell size of 0.5×0.5 mm^2 was used to focus the ion beam. The high-voltage bias potential of negative polarity with a duration of 500 μs was formed by the power supply system of the ion and plasma source "Rainbow 5" in the inverse version. The ion current density in the focal region of the focused beam was determined from the result of measuring the ion current to a collector with size of 2×2 mm^2. The measurements showed that at bias potential amplitudes from 20 to 30 kV, the ion current density exceeded 1 A/cm^2, which provided the pulse power in the submillisecond ion beam in the range from 20 to 30 kW/cm^2.

Taking into account the numerical simulation results, the experiment on the repetitively-pulsed impact of a powerful submillisecond ion beam was carried out at an initial power density of 20 kW/cm^2. Initially, the sample was heated by a repetitively-pulsed nitrogen ion beam with the specified power density at a pulse frequency in the range of 2–5 pulses/s to a temperature of 647 °C. The average sample temperature was recorded by an isolated thermocouple. Subsequently, the samples were subjected to energy exposure by increasing the pulsed power density, up to a value providing pulsed melting of the surface.

The thin section microstructure analysis showed the following. At great depths, as well as in the entire volume of the sample material, no visible changes in the microstructure were observed. This means that the use of a high-power pulsed or repetitively-pulsed ion beam for high-intensity implantation can be carried out without damaging the matrix material microstructure in the main target volume. In the near-surface layer of an irradiated titanium target, with an increase in the pulsed power density to 30 kW/cm^2, a microstructure corresponding to pulsed melting was identified.

6. Conclusion

It is shown that the method of low-energy high-intensity nitrogen ion implantation at current densities of 180, 140, 60, and 10 mA/cm^2 makes it possible to obtain wide ion-doped layers in titanium. At a fluence of $0.1 \cdot 10^{21}$ ion/cm^2, the layer thickness is 15 µm, with a maximum nitrogen concentration of 16 at.% at the sample surface. With the increase in the irradiation fluence, the thickness of the ion-doped layer increases. At a fluence of $1.6 \cdot 10^{21}$ ion/cm^2, the thickness of the layer with a high nitrogen concentration of ~10–17 at.% reaches 50 µm. It was noted that at ion current densities from 60 to 180 mA/cm^2, a wide diffusion layer with a depth of up to 400 µm is observed. It is typical that with an increase in the ion current density, an increase in the nitrogen concentration in the diffusion layer is observed.

The results of transmission electron microscopy showed that the modified layers at a depth of 10 µm consist of α-Ti, in the volume of which nanosized particles of δ-TiN with average size of 15.4 nm crystallize. It is shown that the high temperature of the samples (700 and 850 °C) and the hour-long process of ion implantation contribute to a significant increase in the grain size in the entire volume of the sample. It has been shown by numerical simulation and experimentally that the use of repetitively-pulsed and pulsed beams of nitrogen ions with a high-pulse power with submillisecond duration provides the possibility of pulse heat of the near-surface ion-doped layer to temperatures conducive to radiation-enhanced diffusion of the introduced dopant. It is shown that a powerful ion beam can provide an increase in the temperature of the near-surface layer up to its melting. At great depths, as well as in the entire volume of the sample material, no visible changes in the microstructure were observed. This means that the use of a high-power pulsed or repetitively-pulsed ion beam for high-intensity implantation can be carried out without damaging the matrix material microstructure in the main target volume.

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