Modification of 40X13 steel at high-intensity nitrogen ion implantation

A I Ryabchikov, D O Sivin, O S Korneva, P S Ananin, S V Dectyarev

National Research Tomsk Polytechnic University, 30 Lenin Avenue, 30, Tomsk, 634050, Tomsk, Russia

E-mail: oskar@tpu.ru

Abstract. This paper presents the results of the formation of deep modified layers in 40X13 steel using a high-intensity repetitively pulsed nitrogen ion beam with a current density up to 0.25 A/cm^2. An arc generator with a hot cathode provided the DC nitrogen plasma flow. A plasma immersion approach was used for high-frequency, short-pulse very intense nitrogen ion beam formation. A grid hemisphere with radii of 7.5 cm was immersed in the plasma. Negative bias pulses with an amplitude of 1.2 kV, a pulse duration of 4 μs, and a pulse repetition rate of 10^5 pulses per second were applied to the grid. The substrates were implanted at the temperature of 500 ˚C and various processing times ranging from 20 to 120 minutes with 1.2 keV nitrogen ions using a very-high current density up to 0.25 A/cm^2 ion beams. The work explores the surface morphology, elemental composition, and mechanical properties of deep-layer modified 40X13 steel after low ion energy, very-high-intensity nitrogen ion beam implantation.

1. Introduction

Surface modification is a widespread method for changing the structure or chemical composition of various materials to improve their performance characteristics.

A low-energy nitriding is a promising and intensively developing technology for hardening of metallic materials. Because of the hardness of nitrided layer and the stresses occurring therein, wear resistance, corrosion resistance and resistance to long loads increase regardless of the strength characteristics of a part.

The development of ion-plasma nitriding technology is primarily related to the search for the optimal source of nitrogen plasma. As a rule, sources based on a melting, arc, high-frequency discharge are used for a nitriding process [1, 2]. The following important parameters affecting the nitriding process are the intensity of the ion flux on the workpiece surface and the energy of the nitrogen ions.

A number of theoretical and experimental studies [3–5] have shown the possibilities of using low-energy nitrogen ion beams at ion current densities up to 5 mA/cm^2 for the formation of deep implanted layers. A theoretical model for the formation of deep nitrogen-containing layers after high-current ion implantation was proposed in [3]. The main factor affecting the depth of dopant diffusion is a high density of ion current but not an ion energy. The authors of [6, 7] first demonstrated the possibility of plasma-immersion formation of high-intensity repetitively pulsed beams of low-energy ions with a current density of up to 1 A/cm^2 because of the ballistic focusing in the equipotential space. The present work is devoted to the study of some regularities in the variation of elemental composition, morphology, microstructure and micro-hardness of 40X13 steel after high-dose high-intensity irradiation with a low-energy nitrogen ion beam.

2. Experimental installation and research technique

Nitrogen ion implantation was carried out on an experimental installation equipped with a turbo-molecular pump. The vacuum chamber was previously evacuated to a pressure of 10^{-3} Pa. An arc source of a gas-discharge plasma with a hot cathode was used to generate a nitrogen plasma [8]. The source formed the plasma when nitrogen was injected into the working chamber to a pressure of 0.6 Pa at an arc discharge of 25 A. The formation of high-intensity repetitively pulsed fluxes of low-energy nitrogen ions was carried out by a plasma-immersion ion extraction method with subsequent ballistic focusing [6]. The focusing system made of a steel grid with a cell size of 1.8x1.8 mm, as a part of a sphere with a radius of 7.5 cm was placed opposite the plasma generator at a distance of 10 cm. The grid electrode was mounted on the end surface of a cylinder 15 cm in diameter. The grid electrode and the cylinder with a closed end surface formed an equipotential space for transportation and ballistic focusing of an ion beam. To form an ion beam, a repetitively pulsed negative bias potential with an amplitude of 1.2 kV was applied to the system, at a pulse duration of 4 μs and a frequency of 10^5 Hz.

The shape of the grid electrode in the form of a part of the sphere provided the ballistic focusing of nitrogen ions under the condition of the volume beam charge neutralization. Because of the ballistic focusing, an ion beam with a current of 0.35 A was formed on the sample placed in the region of the system focus. The current density distribution along the beam cross-section was measured using diaphragms with diameters from 5 mm to 20 mm. It is shown in figure 1.

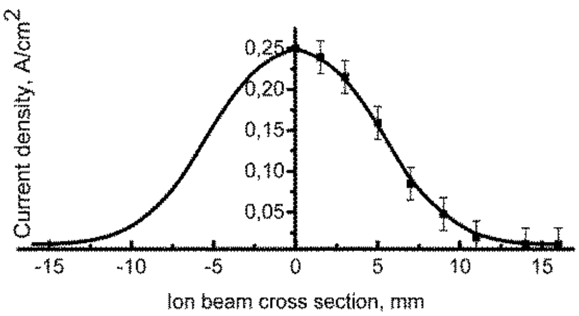


Figure 1. The distribution of the ion current density j along the nitrogen ion beam cross section.

Figure 1 shows that the ion beam has a significant inhomogeneity in the current density distribution along the cross section. The maximum ion current density was 0.25 A/cm^2. 40X13 high-temperature steel was chosen for nitriding. The samples were in the form of cylinders with a diameter of 20 mm and a height of 5 mm. Implantation was carried out by nitrogen ions with an energy of 1.2 keV for 20, 60, 90 and 120 minutes. Implantation was done at a temperature of 500 °C. Heating of the samples to a temperature of 500°C was performed by an ion beam for 20 minutes. The ion-beam heating time of the samples was additional for all irradiation regimes and was not included in the total implantation time. The temperature of the samples during the irradiation was monitored by an isolated thermocouple mounted on the reverse side of the target.

Studies of the surface relief of the samples were carried out on a three-dimensional non-contact profilometer "STIL 3D Micromesure". The change in the Vickers micro-hardness distribution along the thickness of the modified layer was carried out on a "Nano Hardness Tester" at a load of 50 mN. The elemental composition of the ion-alloyed surface layer was analyzed using energy dispersive spectrometer "Bruker XFlash 4010" attached to scanning electron microscope "Hitachi S-3400N". To more clearly identify the metallographic structure on the transverse sections, ion-modified samples were etched in a mixture of nitric acid (1 part), hydrochloric acid (3 parts) and glycerol (2 parts).

3. Experimental results and discussion

3.1. Ion surface sputtering at high-intensity implantation

High-intensity ion implantation at current densities of tens and hundreds of mA/cm^2 causes large irradiation fluences. A change in the ion current density from 0.25 A/cm^2 at the centre of the beam to 0.01 A/cm^2 at a distance of 8 mm from the centre of the beam causes a decrease in the fluence from 4.5×10^{21} ion/cm^2 to 0.2×10^{21} ion/cm^2 during 120 minute irradiation. The multiple increase in the ion current density contributes to an increase in the coefficient and, correspondingly, the diffusion rate of implanted atoms deep into the material of the samples. The competing factor is the proportionally increasing ion sputtering of the surface. Figure 2 shows the cross section profiles of the nitrided sample surfaces in the central region of the craters of sputtered surfaces by a focused ion beam at irradiation times with nitrogen ions of 20 min, 60 min, 90 min and 120 min.

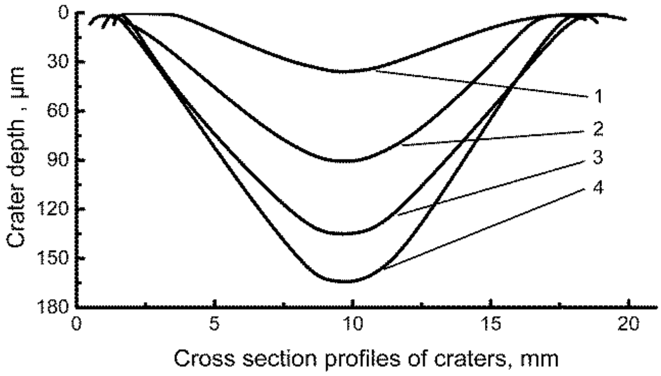


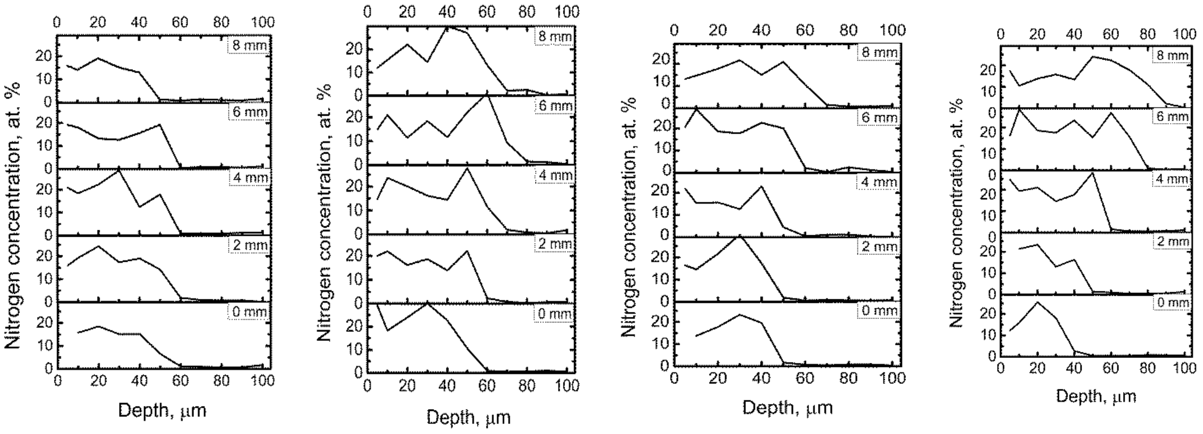
Figure 2. The cross section profiles of sample surfaces in the central region of 40X13 steel craters after sputtering with nitrogen ions at different irradiation times: 1 – 20 min; 2 – 60 min; 3 – 90 min; 4 – 120 min.

The obtained cross section profiles of the sample surfaces show that the depth of the crater increases with increasing of the time and, accordingly, the fluence of the sample irradiation. The depth at the centre of the crater at a minimum time of sample ion treatment of 20 minutes (ion irradiation fluence 7.5×10^{20} ion /cm^2) was 36 µm. After a two-hour ion implantation (irradiation fluence with nitrogen ions 4.5×10^{21} ion/cm^2), the crater depth in its central region increases to 166 µm. There is also a slight change in the diameter of the crater depending on the conditions of irradiation. A sixfold increase in the fluence of ion irradiation causes an increase in the crater diameter from 15 mm to 18 mm.

3.2. Distribution of nitrogen concentration along the depth of implanted samples

The spatial distribution of implanted nitrogen along the depth of the target was measured at different distances from the target edge at the centre of the sputtered crater and at distances of 2, 4, 6 and 8 mm from it. Figure 3 shows concentration profiles of nitrogen distribution along the depth in the samples modified for 20, 60, 90 and 120 min.

On a sample nitrated at the ion irradiation fluence of 7.5×10^{20} ion/cm^2 (20 min), the distribution at various points of the crater is relatively uniform along the thickness of the nitrogen layer. From the centre of the crater to 6 mm from it, the thickness of the layer is 55-60 µm, and at the extreme point of the sample at a distance of 8 mm the thickness of the layer decreases by 10 µm. Tendencies of changes in nitrogen distribution profile along the depth at various points in the crater with increasing time and fluence of ion irradiation are significantly different. At the centre of the crater at the maximum ion current density, an increase in the irradiation time from 20 to 120 minutes is accompanied by a gradual decrease in the depth of the nitrided layer from 60 µm at 20 minutes to 40 µm at 120 minutes of ion implantation. At a 4 mm distance from the centre of the crater, the width of the ion-nitrided layer is approximately 60 µm and there is no clear dependence on time and fluence of ion irradiation. An obvious nitrided layer thickness tendency depending on the irradiation time is observed at the points of the crater corresponding to a 8 mm distance from the centre. After twenty-minute irradiation, the thickness of the layer does not exceed 50 µm with increasing time to 60 minutes, the thickness of the layer increases to 70 µm, and at 120 minute ion implantation the layer width exceeds 90 µm. The maximum nitrogen concentration, as follows from figure 4, approaches 30 at.%.

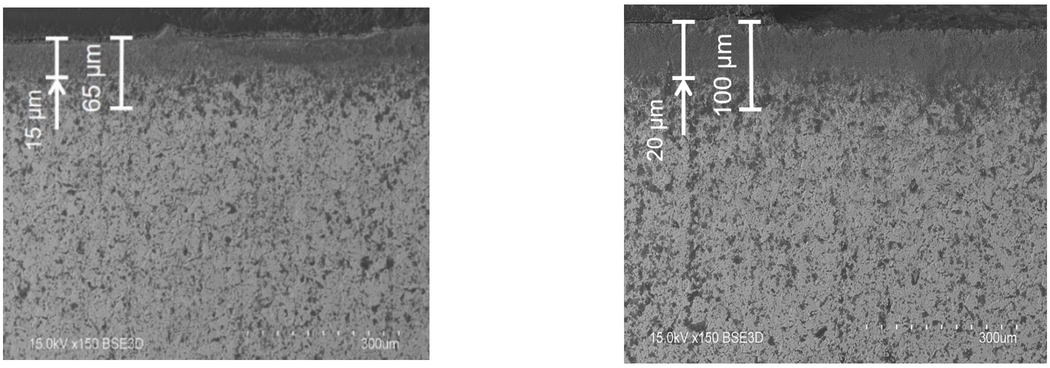


a) b) c) d)

Figure 3. Concentration profiles of nitrogen dopant distribution along the depth obtained at various distances from the centre of the sputtering crater, for samples modified at different times of nitrogen ion implantation : a – 20 min; b – 60 min; c – 90 min; d – 120 min.

3.3. Metallographic structure of ion-modified samples

Metallographic analysis of transverse sections of samples modified by high-intensity implantation of low-energy nitrogen ions revealed a two-layer structure. Figure 4 shows characteristic micrographs of the sample after ion treatment with a fluence of 2.25 x 10^{21} ion/cm^2 (60 min). The photographs were made at the centre of the sputtered crater (figure 4a) and at a radius of 8 mm (figure 4b).



a) b)

Figure 4. Microphotographs of metallographic sections of a sample irradiated with nitrogen ions with an energy of 1.2 keV for 60 minutes: a - at the centre of the crater, b - at a distance of 8 mm.

The microphotographs show that the thickness of the continuous near-surface layer at the centre of the crater is approximately 50 µm, and with increasing distance from the centre of the crater to 8 mm the thickness increases to a maximum value of 80 µm. Below the continuous near-surface layer, there is a thin diffusion layer no more than 15 µm at the centre of the crater and 20 µm at a distance of 8 mm from it.

Based on the metallographic studies of sections of modified samples, radial distributions of ion-modified layer thickness were obtained from the time of ion implantation, presented in figure 5.

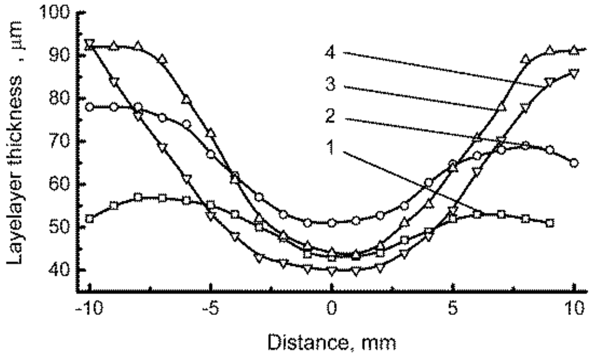
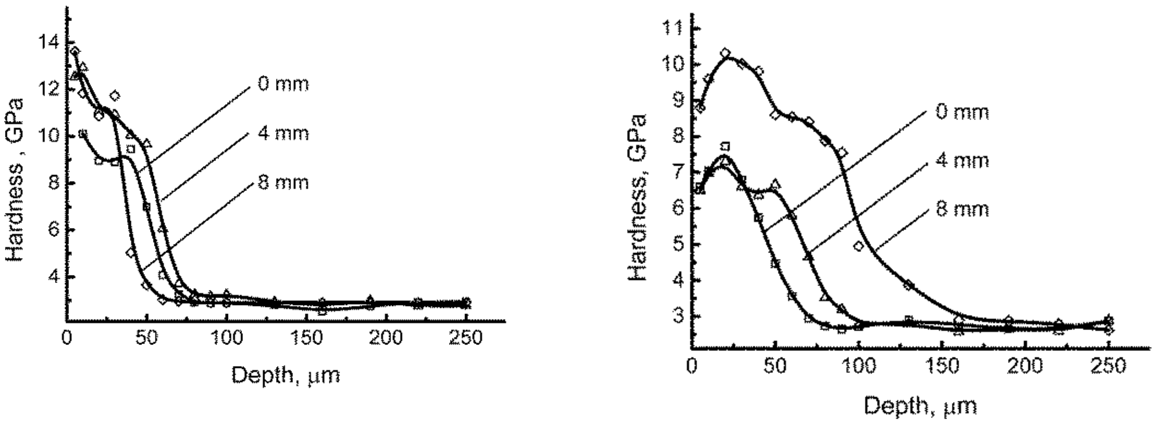


Figure 5. Dependences of the ion-modified layer thickness on the time of ion implantation (1 – 20 min, 2 – 60 min, 3 – 90 min, 4 – 120 min) at different distances from the axis of the ion beam symmetry.

Analysis of the nitrided layer thicknesses with a modified structure confirmed that their total thickness varied depending on the distance from the centre of the crater, and hence also depending on the ion current density. Based on the data in figure 5, an increasing tendency in the thickness of the ion-modified layer is evident in all irradiation regimes with a decrease in the current density of nitrogen ions from 0.25 A/cm^2 to 0.08 A/cm^2. This behavior of the curves in figure 5 may indicate that when the current density of nitrogen ions increases above 0.08 A/cm^2, the ion sputtering rate of 40X13 steel surface increases in proportion to the increase in the number of particles falling on the target surface per unit time. Since the thickness of the ion-modified layer decreases, it should be assumed that the rate of nitrogen diffusion does not increase with increasing ion current density. As a result of the competition of target ion sputtering and implanted nitrogen dopant diffusion with an increase in the ion current density from 0.08 A/cm^2 to 0.25 A/cm^2, a gradual predominance of ion sputtering over diffusion is observed, which ultimately causes a gradual decrease in the thickness of the ion-doped layer. For the all of the treatment modes, the minimum thickness of the modified layer is observed at the center of the sputtering crater and equals to the values from 40 to 55 μm. The maximum thickness of the layer is 90 μm, which was observed at the distance of 8 mm from the ion beam center after 90 min of treatment.



a) b)

Figure 6. Distribution of micro-hardness along the depth of the hardened steel layer obtained at various distances from the centre of the sputtering crater, for samples modified at a time: a) – 20 min; b) – 120 min.

3.4. Regularities of micro-hardness variation of ion-modified 40X13 steel structures

Figure 6 shows the results of micro-hardness measurements along the depth of the hardened steel layer obtained at various distances from the centre of the crater sputtering. Analysis of micro-hardness value distribution along the depth of the nitrided layer showed that the micro-hardness in the near-surface layer of 40X13 steel correlated well with the nitrogen distribution at the depth of the target at different irradiation times shown in figure 3.

After 20 minute ion implantation, the maximum micro-hardness is observed in the surface layer, approaching 14 GPa (figure 6a). When depth increases to 50 μm, the micro-hardness gradually decreases to 9-10 GPa. At great depths from 50 to 70 μm, a sharp decrease in micro-hardness is observed to a level corresponding to the initial material (3 GPa). The largest layer width (100 μm) with microhardness in the range of 8-10 GPA is characterized for the sample modified during 120 min of ion processing, at the distance of 8 mm from the center of the sputtering crater.

4. Conclusion

The effect of high-dose nitrogen ion implantation into 40X13 steel was investigated using a high-intensity repetitively pulsed nitrogen ion beam with a current of 0.6 A at an ion energy of 1.2 keV at sample temperature of 500°C. The effect of an inhomogeneous radial distribution of the ion current density along the beam cross section in the range from 0.08 A/cm^2 to 0.25 A/cm^2 on the formation of the ion sputtering crater, the depth of nitriding and micro-hardness of the modified layers was considered. It was established that an increase in the irradiation fluence because of an increase in treatment time from 20 to 120 min caused an increase in the depth of the crater of ion sputtering from 36 μm to 166 μm. It was established that the width of the nitrided layer depended on the ion current density and treatment time. For all treatment regimes, increasing tendencies of the ion-modified layer thickness were noted with a decrease in the current density of nitrogen ions from 0.25 A/cm^2 to 0.08 A/cm^2. The maximum nitrogen penetration depth, 90 μm, was observed at a 120 minute treatment time in the region of ion current density of 0.08 A/cm^2 at a distance of 8 mm from the sputtering crater. Nitrogen implanted samples of 40X13 steel showed a significant increase in the hardness of the near-surface layer.

Acknowledgments

The work was carried out with the financial support of the Ministry of Education and Science of the Russian Federation in the framework of state assignments 3.2415.2017/4.6 and 3.7245.2017/6.7.

References

[1] Totten G E, Funatani K and Xie L 2004 *Handbook of Metallurgical Process Design* (CRC Press, NY, USA)
[2] Rakhit A K 2000 *Heat Treatment of Gears: A Practical Guide for Engineers* (ASM International, Materials Park, OH, USA)
[3] Wei R 1996 *Surf. Coat. Technol* **83** 218
[4] Goncharenko I I, Grigoriev S V, Lopatin I V, Koval N N, et al. 2003 *Surf. Coat. Technol.* **169–170** 419
[5] Gavrilov N V, Men'shakov A I 2012 *Tech. Phys.* **57** 399Ryabchikov A I, Ananin P S, Dektyarev S V, Sivin D O, Shevelev A E 2017 *Vacuum* **143** 447
[6] RyabchikovA I, Sivin D A, Ananin P A, Ivanova A A, Lopatin I B, Korneva O S and Shevelev A A 2018 *Surf.Coat.Technol* (in press)
[7] Lopatin I V, Akhmadeev Yu H and Koval NN 2015 *Rev. Sci. Instrum.* **86** 103301