Low energy implantation of nitrogen ions by extended beam with a ballistic focusing in a stainless steel

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Abstract. The results of experiments on low-energy nitrogen ions implantation in stainless steel AISI 321 are presented. The treatment was carried out with a pulsed beam of nitrogen ions obtained using a ballistic system of ion focusing. The source of ions was nitrogen plasma of a non-independent gas arc discharge with a heated cathode. It was shown that the specimen surface is subjected to ion etching, which leads to the formation of a well, whose profile depends on the ionic exposure parameters. In addition, when treating specimen in such a system, the surface hardness increases up to 4 times. The increase in hardness occurs due to the formation of a modified layer in the surface, with a thickness of up to 50 microns, containing iron and chromium nitrides.

1. Introduction
Improving the performance properties (hardness, wear resistance, etc.) of stainless steel products is an important scientific and technical problem, in the solution of which the aircraft and engine-building industries, the automotive industry, the space industry, etc. are interested in. Currently, one of the most popular methods for improving the properties of products is the surface modification, which involves changing the surface properties of the product material without changing its bulk properties. This approach is often sufficient and cheaper. To modify the surface, the methods are often used, which imply the changes in the elemental and phase composition of the surface layers of materials by adding additional substances to the surface. Among such methods, the ion-plasma methods, using substances in the ionized state, seem attractive. The method of ion implantation has gained widespread currency. It is realized when tens to hundreds of kiloelectronvolts (keV) of energy are added to ions of matter that is added to the surface [1]. However, this method is limited by the magnitude of the projection path of ions in the surface (tens of monolayers). Another common method of changing the elemental and phase composition of the surface is the diffusion saturation method [2], which involves heating the treated product to temperatures (400–800°C), at which the diffusion of the atoms of the added substance allows to get modified layers of tens-hundreds of micrometers per unit-tens of hours. The process of diffuse saturation of the surface with nitrogen atoms is called nitriding and it has gained widespread currency in industry. Nitriding of stainless steels is usually performed at temperatures under 600 °C, this is due to the temperature stability of iron nitrides. It is this maximum treatment
temperature that was chosen for our experiments to obtain the maximum diffusion rate. It was shown in [3] that an increase in the ion current density leads to an intensification of the nitriding process, at the same time, delivering several hundred eV of energy to ions allows both to carry out effective ionic cleaning of the surface from oxides formed on it and to perform their low-energy implantation [4]. To increase the pulse density of the ion current, a ballistic focusing system of the ion beam in a spherical configuration was proposed [5]. The use of this system for treatment of AISI 5140 steel showed a good result. The disadvantage of this system can be considered a small treatment area (about 2 cm²). In this connection, a similar system of a cylindrical configuration was developed, which allows to treat surfaces of a larger area [6].

This paper presents the results of experiments on low-energy implantation of stainless steel with nitrogen ions in a ballistic focusing system of an ion beam in an extended configuration. The source of nitrogen ions was the plasma of a non-independent arc gas discharge with a heated cathode.

2. Description of the experimental setup

The experiments were carried out on an installation with a vacuum chamber size of 900 mm×900 mm×1100 mm, which was pumped out with a turbomolecular pump with a capacity of 1000 l s⁻¹ to a pressure not worse than 5·10⁻² Pa. The generation of gas plasma was carried out by PINK source in the axial configuration [7]. The ion beam ballistic focusing system was a box-shaped case with a rectangular base with sizes of 120 mm×240 mm, one side of which was covered with a metal grid with a cell of 0.5 mm×0.5 mm and a geometric transparency of ≈ 53 % in the form of a part of the cylinder element of ∅ 150 mm (figure 1a).

![Figure 1](image)

**Figure 1.** Ballistic ion focusing system (a) and experimental scheme (b).

The principle of the system operation was that the system was placed in the plasma generated by PINK generator at a distance of 180 mm from the end of its hollow cathode (figure 1b). A pulsed negative electrical bias was applied to the case with a grid and to the collector. Ions from plasma were accelerated in the direction of the case, partially passing through the grid inside the case. Due to the grid shape in the form of a part of the cylinder element, the ions, that have passed through the grid, fly in the radial direction and focus on the collector installed in the geometric center of the cylinder.
element. Specimen with sizes of 43 mm×20 mm×3 mm made of stainless steel 12Kh18N10T (analogue of AISI 321) were pre-wiped with gasoline and placed on the collector of the ballistic focusing system, the temperature of the specimen was measured with a chromel-alumel thermocouple on the back side. A collector with size of 45 mm×90 mm was structurally isolated from the system case, which made it possible to separately measure the ion current coming to it. The plasma generator was powered from a welding transformer with an output voltage of up to 70 V and a current of up to 200 A. The tungsten thermionic cathode of the plasma source was heated by a transformer with thyristor current adjustment and a frequency of 50 Hz. Accelerating voltage pulses were supplied by a specially designed source with output voltage of up to 2 kV and current of up to 3 A, as well as adjustable frequencies of up to 50 kHz and a pulse duty factor from 15 to 80 %.

The specimens were preliminarily cleaned and heated with argon ions with an energy of 1 kV for 20 minutes. Implantation was performed at a working nitrogen pressure of 0.5 Pa for 1 hour. After treatment, the specimens were cooled in the working chamber to a temperature below 70 °C, when pressure in the chamber was below 5×10^{-2} Pa.

In the process of performing experiments, the total current of the accelerating voltage source and the collector current, as well as the shape of the voltage pulses, were recorded by the LeCroy waveRunner 6050 oscilloscope on the Rogowski belts. The plasma generator was powered from a three-phase welding rectifier, and it was heated from a source with thyristor regulation, the discharge current and ion current pulses were modulated by the corresponding frequencies.

The relief investigations of the specimen were carried out on STIL 3D Micromesure optical profilometer, the surface hardness was measured with a PMT-3M microhardness meter, and X-ray diffraction investigations were performed on an XRD-6000 diffractometer. In the course of the study, transverse sections of the specimen were also made. Optical investigations of thin sections were performed on a µVizo-MET-221 optical microvisor.

### 3. Results and discussion

A series of experiments was carried out with three accelerating voltages (700, 1400 and 1800 V) and three duty factors of the accelerating voltage pulse (40, 60 and 80 %). The frequency of the voltage pulses remained unchanged and was 40 kHz. To keep the specimen at the same temperature (600 °C), the plasma density was changed by adjusting the discharge current of the plasma generator. The processing regimes are listed in table 1. The recorded average values of the ion current coming to the collector are also shown there.

| Regime number | Bias voltage (V) | Duty factor (in %) | Discharge current (A) | Collector average current (mA) | Total ion average current (mA) |
|---------------|------------------|-------------------|-----------------------|-------------------------------|-------------------------------|
| 1             | 700              | 40                | 120                   | 260                           | 1300                          |
| 2             | 700              | 60                | 67                    | 235                           | 1150                          |
| 3             | 700              | 80                | 38                    | 170                           | 950                           |
| 4             | 1400             | 40                | 50                    | 145                           | 830                           |
| 5             | 1400             | 60                | 28                    | 135                           | 740                           |
| 6             | 1400             | 80                | 20                    | 95                            | 610                           |
| 7             | 1800             | 80                | 12                    | 85                            | 560                           |

It is seen that with a decrease in the discharge current of the plasma generator, both total ion current and current to the collector decrease, even without changing the voltage pulse amplitude, but this does not lead to a decrease in the measured specimen temperature. This can be explained by the
improved ion beam focusing with an increase in the cathode layer width. Under conditions of constant accelerating voltage, the increase in the cathode layer width is due to a decrease in plasma density with a decrease in the discharge current of the plasma generator and reduces the influence of the form factor of a braided accelerating grid. The temperature of the specimen was measured with a thermocouple mounted on the back of the specimen in the middle and improving the ion beam focusing increases the power density directly opposite the thermocouple. Thus, the total power delivered by the ion beam to the entire surface of the specimen decreases. This should lead to an increase in the temperature gradient from the center of the specimen to its edges.

Investigations of the surface profile of the specimen showed (figure 2) that during treatment the specimen were subjected to ion etching of different intensity with the formation of an extended etching well of different depth and width. In addition, it can be seen that the well can have a complex profile including several local relief minima, which indicates the nonideality of the ballistic focusing of the ion beam, which can be explained by a change in the shape of the grid during its heating. With a constant amplitude of the bias pulse (700 V), the etching well deepens with an increase in the duty factor of the bias pulse from 40 to 60% (figures 2ab), which is explained by the improved beam focusing.

Figure 2. Specimen surface profiles: a) regime 1; b) regime 2; c) regime 3; d) regime 4; e) regime 5; f) regime 6; g) regime 7.
A further increase in the pulse duty factor leads to a decrease in the well depth (figure 2c), probably due to a decrease in the ion current density at the collector. With an increase in the amplitude of the bias voltage from 700 to 1400 V (figures 2c–2f), the shape of the etching well becomes sharper. Such a change in the etching well shape is associated with improvements in focusing conditions with a decrease in the average current of ions arriving at the surface of the specimen. It is not possible to quantify the increase in the well depth due to the fact that different widths of the specimen areas are etched at different intensities. However, analyzing the well shape it can be stated that with an increase in the bias pulse amplitude, the ion etching efficiency in the region of the ion beam focus increased, despite the decrease in the total current of ions onto the specimen, and this led to the deepening of the well. Increasing the ion energy by increasing the accelerating voltage amplitude from 1400 to 1800 V, while simultaneously reducing the ion beam current from 95 to 85 mA, leads to a decrease in the well depth (figure 2g). This is probably due to the fact, that the ion beam focusing is not significantly improved, that is, the ion beam density at the focus decreases in proportion to the fall of the total current to the collector, and the increase in the ion energy does not lead to a significant increase in the ion sputtering coefficient, since in the range of energies from 1.8 to 2 keV, the dependence of this coefficient for almost all ion-target pairs is transferred to the saturation region [8]. Analysis of the surface profile of specimen shows that when treating using regime 1, there was no effective ion beam focusing, as evidenced by the absence of a clearly pronounced etching well on the surface of the corresponding specimen.

It is known that during nitriding of stainless steel, iron nitrides and alloying additives are intensively formed on its surface, which was confirmed by X-ray analysis (figure 3). The formation of these phases explains the increase in the surface microhardness, which was investigated for each specimen in the center of the etching well (center) and at a distance of 4–6 mm from it (periphery) (table 2).

Quantitative analysis of the X-ray diffraction pattern showed that the content of iron nitrides (Fe1–4N) in the surface layer exceeds 40 wt.%, and the content of chromium nitrides exceeds 20 wt.%. 

Figure 3. X-ray diffraction pattern of the specimen surface (regime 1).
Table 2. The specimen surface microhardness, indenter load 50 g.

| Regime number | Center   | Periphery |
|---------------|----------|-----------|
| 1             | 10.4     | 9.6       |
| 2             | 8.3      | 8.6       |
| 3             | 6.7      | 7.4       |
| 4             | 8.0      | 8.3       |
| 5             | 8.4      | 8.7       |
| 6             | 7.6      | 8.6       |
| 7             | 5.7      | 7.1       |

It can be seen (see table 2) that with the initial hardness of stainless steel of 3 GPa, after treatment, the surface hardness increased on all specimen both in the center of the etching well and at its periphery, at that, the highest hardness is observed on the specimen treated in regime 1.

Lower hardness in the center of the etching well compared to peripheral hardness (excluding the specimen treated in regime 1) may be associated with both more intense ion etching in the center of the well, and local overheating. Local intensive ion etching leads to a decrease in the modified layer thickness, and local overheating leads to grain growth and decay of iron nitrides.

Investigations of the transverse thin sections obtained with the AKASEL diamond suspension, without additional chemical etching, showed (figure 4) that two layers are clearly visible on all specimen: gray and white, located one under the other. The gray layer is an area saturated with iron nitrides and alloying additives, which is confirmed by X-ray diffraction patterns, and the white layer is probably the area of solid solution of nitrogen in iron. Layer thicknesses were measured for all treatment regimes (figure 5).

It can be seen that the greatest thickness of the modified layers is observed on the specimen treated in regime 1 (figure 5a, shown on a different scale). This is probably due to the fact that under the conditions of this experiment there was no effective ion beam focusing due to the influence of the grid form factor. This led to the fact that, on the one hand, there was no excessive local ion etching of the surface, and on the other hand, since the total ion current in this regime was maximum, the average current density over the entire surface of the specimen was also maximum. This allows to suggest that to assess the efficiency of ionic saturation, it is not enough to consider the local density of the ionic current, but it is also necessary to operate with the ionic current density over sufficiently large (not less
than ones-tens of mm) areas. It looks logical when taking into account temperature and concentration gradients not only by depth, but also in transverse coordinates when evaluating diffusion. Analysis of the obtained transverse distributions does not allow to identify unambiguous correlations between the etching well depth and the thickness of the layers obtained. So for specimen treated at a bias voltage of 700 V in regimes 1 and 2 (figures 5ab and figures 2ab) the improvement in the ion beam focusing and, as a result, an increase in the etching well depth clearly leads to a local decrease in the thickness of layers in the beam focus area. A further improvement in focusing on the background of a decrease in the total ion current on the one hand leads to a decrease in the etching well depth, and on the other to a decrease in the thickness of the modified layers (figure 2c and figure 5c, respectively). This cannot be explained by an increase in the ion etching rate and, is probably, due to a decrease in the current density in the region of the ion beam focus and directly next to it. At a bias voltage of 1400 V, the situation is not unambiguous: in regimes 4 and 5, the thickness of the modified layers correlates with the etching well shape (figures 5de and figures 2de), that is, more intensive etching leads to thinning of the modified layers. However, in regime 6, a local increase in the thickness of the modified layers is observed in the region of the ion beam focus, that is, the maximum depth of the etching well (figure 5f and figure 2f), the same pattern is observed for the specimen treated in regime 7 (figure 5g and figure 2g).

**Figure 5.** Width of a gray layer (1) and a white layer (2) at the transverse sections of the specimen made of stainless steel, treated in different regimes: a) regime 1; b) regime 2; c) regime 3; d) regime 4; e)– regime 5; f) regime 6; g) regime 7.

Thus, a joint analysis of the surface profiles and thicknesses of modified layers of stainless steel specimen treated in regimes 6 and 7 allows to state that in the energy range of nitrogen ions above
700 V it is possible to create local ion chemical-thermal conditions, under which local increase in the ion current density will lead to an increase in the thickness of the modified layer, despite an increase in the efficiency of ion etching of the target material. For a more detailed study of this effect, additional experiments are needed.

4. Conclusion

Based on the work performed, the following conclusions can be drawn.

1) Treatment of stainless steel of grade AISI 321 was performed using ion-beam low-energy nitrogen implantation.

2) It is shown that during one hour the surface microhardness increases up to 4 times, at that, the surface is subjected to intensive ion etching with the formation of a wear well, the shape of which depends on the efficiency of the ion beam focusing and the ion energy of the beam.

3) It is shown that, depending on the treatment regime, the maximum surface hardness can be achieved both in the center of the etching well and at its periphery, which may be due to a complex of factors including the ion energy of the beam, the local density of the ion beam and the local temperature of the specimen surface.

4) It is shown that the local depth of the modified layer has a complex dependence on a complex of factors, such as: the ion energy of the beam, the local density of the ion beam and the local temperature of the specimen surface; and for the stainless steel of the grade under study, it can reach from 1.5 μm to 50 μm at the same fixed temperature of specimen of 600°C during one hour of treatment.

5) Obtaining the maximum thickness of the modified layers under conditions of poor focusing of the ion beam allows to suppose that to analyze and optimize the conditions of ion nitriding and low-energy implantation, it is necessary to provide both the local ion current density and a sufficiently large treatment area (at least 1–10 mm²).

6) Joint analysis of such local parameters of the treated surface of the specimen as the etching well depth and the modified layer thickness allows to state that during low-energy nitrogen implantation processes even in the energy range of nitrogen ions more than an order of magnitude above the target material sputtering threshold, it is possible to create conditions when local increase in the ion current density will lead to an increase in the modified layer thickness, despite an increase in the efficiency of material ion etching.

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