Influence of nitrogen pressure and electrical parameters of a glow discharge on the process of ion plasma nitriding of steel

V O Oskirko, I M Goncharenko, A P Pavlov, A N Zakharov and V A Semenov
Institute of High Current Electronics SB RAS, 2/3 Akademichesky Ave., Tomsk, 634055, Russia
E-mail: oskirkovo@gmail.com

Abstract. The influence of the working gas pressure on the electrical parameters of the glow discharge and the structure of diffusion hardened layers in the process of ion-plasma nitriding of steel AISI 5140 was investigated. The experiments were carried out in the pressure range of 70–500 Pa, while the power (18 kW), the temperature of the samples (550 °C) and the processing time (6 hours) remained unchanged. The change in gas pressure was accompanied by a change in discharge voltage in the range from 560 to 1800 V and current density from 3.2 to 1.1 mA cm⁻². It is shown that the change in the pressure of nitrogen leads to a change in the energy and density of the particles flows acting on the workpieces. Metallographic and X-ray analysis showed that the surface layers formed at different pressures differ in length, structure, and phase composition. In particular, the maximum width of the diffusion zone of 460 microns was achieved at an operating pressure of 250 Pa. The increase and decrease in pressure leads to a decrease in the length of the diffusion zone and an increase in the compound layer to 26 μm.

1. Introduction
Ion-plasma nitriding (IPN) is a surface hardening treatment process that allows to increase the hardness, wear resistance and corrosion resistance of the surfaces of steels.

An important advantage of IPN, compared with traditional methods of gas nitriding, is the wider possibilities of technological control and regulation of the process of diffusion saturation. In addition to the traditional technological parameters, such as the composition of the nitrogen-containing medium, temperature and processing time, in the IPN also applies the adjustment of gas pressure and electrical discharge parameters (voltage, current, power, duty cycle in pulse mode). The working pressure and electrical parameters of the discharge are highly dependent on each other, as well as on the way plasma is excited. Usually the process can be carried out in a wide range of pressures, for example, nitriding in a glow discharge is carried out in a mixture of nitrogen and hydrogen at a pressure of 200–1000 Pa. Increasing the pressure allows you to increase the plasma concentration and density of the ion current flowing to the workpiece. This leads to an increase in the density of the flow of reactive gas particles saturating its surface. On the other hand, lowering the pressure can reduce the number of particles collisions in the plasma. As a result, the particles reach the surface of the workpiece with greater energy, which contributes to the formation of vacancies in the surface layers and increases the efficiency of cleaning from natural oxide, which prevents the diffusion process. As a rule, the pressure value is selected experimentally, based on the installation capabilities, the required properties of the modified layer and the steel grade. A number of works are devoted to the choice of optimal pressure.
For example, in [1] it is shown that an increase in the gas pressure leads to an increase in the thickness of the compound and diffusion layers formed during the processing of high-speed steel. However, an increase in pressure during the processing of stainless steel causes the opposite effect – a decrease in the thickness of these layers [2, 3, 4, 5]. In [6] experiments on nitriding of low alloy steel AISI 5140 in a system with an active screen were carried out. The change in gas pressure from 100 to 500 Pa had no noticeable effect on the thickness of the layers. The use of the hollow cathode effect made it possible to reduce the working pressure of the gas in the system.

This paper presents the results of experiments on the nitriding of AISI 5140 steel in the classical nitriding system in a glow discharge without active screens. It was possible to stabilize the discharge power and the temperature of the workpiece in a wide range of pressures (70–500 Pa) due to the use of a high-voltage power supply with an adaptive output volt-ampere characteristic. The paper considers the influence of gas pressure on the electrical parameters of the glow discharge, the kinetics of formation, composition and properties of the hardened layer.

2. Methodology and materials
The experiments were carried out on a modernized vacuum unit with a vacuum chamber volume of \( V = 1 \) m\(^3\). Modernization of the installation was to replace the standard DC discharge power source based on the transformer and rectifier with a thyristor arc suppression circuit with a next-gen equipment with the ability to switch the type of work from DC to pulse modes. This type of power supply (APEL-N-24 DC-2000A) was developed and produced by the team of the company "Applied electronics". This PS was used to power the glow discharge in the interelectrode space between the parts being processed (cathode) and the water-cooled walls of the discharge chamber (anode) (figure 1).

Table 1 shows the main parameters of PS. It has an adaptive output current-voltage characteristic and two modes of operation: low-voltage (LV) and high-voltage (HV). When switching from one mode to another, the output current and output voltage control range changes. This solution allows to provide high discharge power in a wide range of operating gas pressure.

![Diagram](image)

**Table 1. Parameters PS APEL-N-24PDC-2000A.**

| Parameters         | LV mode   | HV mode   |
|--------------------|-----------|-----------|
| Voltage            | 100–1000 V| 200–2000 V|
| Current            | 0.4–44 A  | 0.2–22 A  |
| Avg. power         | up to 24 kW| 32 A      |
| Max. pulse current | 64 A      | 64 A      |
| Stabilization mode | voltage, current, power | voltage, current, power |
| Pulse frequency    | 1–100 kHz |           |
| Duty cycle         | 10–80 % (+ DC mode) |           |

As a test load, which allows to simulate a real technological chemical-thermal process, a workpiece whose mass together with the tooling was 130 kg was used. In addition, samples for further research were installed on the surface of this workpiece. Steel AISI 5140 (0.4% C, 1.0% Cr, 0.5% Mn, 0.17–0.37% Si) was used as the test samples material. In the initial state before nitriding, AISI 5140 steel was a ferritic-pearlitic in structure. The samples were cylinders with a diameter of 25 mm and a height of 10 mm. The surface of the samples before nitriding was machined by grinding and polishing with abrasive materials to the finish surface roughness \( Ra = 0.027 \) microns. The microhardness of the material of the initial substrates throughout the entire volume was \( HV_{0.05} = 280 \) kgf\( \cdot \)mm\(^2\).

Plasma nitriding treatment was carried out in an atmosphere of pure nitrogen at three pressures of the working gas: 70, 250 and 500 Pa. Before carrying out each experimental process, the reactor
loaded with workpieces and was evacuated to a base pressure $P = 10$ Pa, and then there was the two-time flushing of the discharge volume with nitrogen up to a pressure $P = 10^3$ Pa without the initiation of a glow discharge. Processing of workpieces took place in three stages. At the first stage, the workpieces were cleaned and heated in a pulse-frequency mode from RT to 550 °C. This mode provided for the suppression of arcing and reducing the time to reach the temperature of nitriding. At the second stage, an isothermal exposure of 6 hours duration was carried out at one of three pressure values. Power supply stabilized discharge power $W = 18$ kW in DC mode. At the final stage, after switching off the discharge, the workpieces were cooled in vacuum to room temperature for at least 10 hours.

The properties and composition of nitrided layers were studied by x-ray diffraction, optical and scanning electron microscopy, and by microhardness measurements. The phase composition and structure of the samples were investigated by XRD-6000 diffractometer on CuK$_\alpha$-radiation. Phase composition analysis was performed using PDF 4+ databases, as well as full-profile analysis program POWDER CELL 2.4.

The microstructure of the samples surface and samples cross-sections was investigated using optical metallographic microscope. The depth of hardening of nitrided layers was measured by the values of increased microhardness on the cross-section from the surface of the treated samples to the hardness of the initial substrate material. An optical microscope-hardness tester with a Vickers diamond indenter was used as a microhardness test instrument.

A quantitative chemical analysis of the ratio of elements located in the surface layer of the samples was carried out using an XRF-1800 X-ray fluorescence scanning spectrometer.

3. Results and discussion

To begin, consider how the gas pressure in the chamber affects the electrical parameters of the discharge. The graph in figure 2 shows how the discharge current and voltage change when the gas pressure changes. Markers on the graph indicate the working points at which the samples were obtained. The dotted line allows you to predict the behavior of current and voltage within the study range and beyond.

![Figure 2. Coordinates of operating points on the current-voltage characteristic at an average discharge power of 18 kW and nitrogen pressure of 70, 250 and 500 Pa.](image)

Increasing the pressure from 70 to 500 Pa leads to a triple increase in the discharge current. Since the discharge power remained constant, the increase in current was accompanied by a threefold decrease in voltage. The discharge resistance, in this case, changes approximately 9 times. The adoptive output voltage-current characteristic of the power supply allows to maintain high discharge power under conditions of multiple changes in the discharge resistance. Figure 2 shows the operating ranges of the power supply within which the operating point can move. The working area consists of two parts, which correspond to the high-voltage and low-voltage mode of operation.

Together with the discharge current and voltage, under these conditions, the flux density and the energy of the particles acting on the surface to be treated change. As you know, when processing a
workpiece its surface is bombarded with energy ions and energy neutrals, as well as neutrals with low thermal energy. Ions are accelerated in the dark cathode space adjacent to the surface of the workpiece. Fast ions collide with gas molecules in the cathode layer, losing energy and increasing the concentration of energy neutrals. The number of collisions depends on the free path of the ion \( \lambda \) and the width of the cathode layer \( L \). The width of the cathode layer can be determined by the Child-Langmuir equation [7]:

\[
L = \left( \frac{4e_0}{9J} \right)^{\frac{1}{2}} \left( \frac{4q}{M} \right)^{\frac{1}{2}} V_c^{\frac{1}{2}},
\]

where, \( J \) – cathode current density, \( q \) – electron charge \( (1.6 \times 10^{-19} \text{ C}) \), \( M \) – ion mass \( (4.66 \times 10^{-26} \text{ kg for } N_2^+) \), \( V_c \) – cathode voltage and \( e_0 \) – vacuum permittivity \( (8.85 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}) \). It is assumed that the ground ionic state is \( N_2^+ \). The free path of the ion depends on the gas pressure and is equal to:

\[
\lambda = \frac{kT}{P \sigma}
\]

where, \( k \) – Boltzmann constant \( (1.3 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}) \), \( P \) – gas pressure, \( \sigma \) – ionization cross section \( (2.5 \times 10^{-15} \text{ cm}^2) \) [8]. Using the model developed by Davis and Vanderslice, it is possible to determine the average energy of ions entering the cathode [9, 10]:

\[
\frac{dN}{dE} = \frac{N_i L}{2 \lambda} \left( 1 - \frac{E}{V_c} \right)^{\frac{1}{2}} \exp \left[ -\frac{L}{\lambda} + \frac{L}{\lambda} \left( 1 - \frac{E}{V_c} \right)^{\frac{1}{2}} \right],
\]

where, \( N_i \) – number of ions entering the cathode dark space, \( E \) – ion energy. The average energy of the ions bombarding the cathode is:

\[
E_i = V_c \left[ 2 \frac{\lambda}{L} - 2 \left( \frac{\lambda}{L} \right)^2 + 2 \left( \frac{\lambda}{L} \right)^2 \exp \left[ -\frac{L}{\lambda} \right] \right]
\]

Ions are an essential component of the nitriding process, but not the only one. Energetic neutrals, which were formed as a result of collisions, also affect the workpiece surface. Their number and average energy can be calculated using the following formulas:

\[
N_n = N_i \frac{L}{\lambda},
\]

\[
E_n = V_c \frac{\lambda}{L} \left[ 1 - 2 \frac{\lambda}{L} + 2 \left( \frac{\lambda}{L} \right)^2 \right] \exp \left[ -\frac{L}{\lambda} \right]
\]

Table 2 presents the process parameters at different gas pressures in the chamber, calculated using the formulas (1–6).

| № | \( P \) (Pa) | \( U \) (V) | \( I \) (A) | \( J \) (mA·sm\(^{-2}\)) | \( W \) (kW) | \( L \) (mm) | \( \lambda \) (mm) | \( L/\lambda \) | \( E_i \) (eV) | \( E_n \) (eV) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 70 | 1700 | 10.6 | 1.1 | 7.5 | 0.53 | 14 | 242 | 104 |
| 2 | 250 | 800 | 22.5 | 2.3 | 18 | 3.2 | 0.17 | 19 | 85 | 38 |
| 3 | 500 | 560 | 32.0 | 3.2 | 21 | 2.1 | 0.09 | 24 | 46 | 21 |

The results of the calculations presented in table 2 show that in the range of pressure changes from 70 to 500 Pa, there is a significant change in the energy of ions and neutrals in the cathode layer. To compare the number of collisions of ions in the cathode layer, you can use the \( L/\lambda \) ratio. With a
decrease in pressure from 500 to 70 Pa, the $L/\lambda$ ratio decreases by more than one and a half times. The increase in the number of collisions and the voltage in the cathode layer leads to a fivefold increase in the average energy of ions $E_i$ and energetic neutrals $E_n$. At the same time, due to the decrease in the discharge current, the density of the ion flow $J$ decreases three times. According to (5), the number of energy neutrals resulting from collisions of ions with gas molecules in the cathode layer decreases five times with a decrease in pressure from 500 to 100 Pa.

There are three main competing and complementary processes occurring during nitriding: (I) nitride formation on the surface, (II) diffusion of nitrogen into the modified layer and (III) surface sputtering. Each process includes many components (sub-processes) [11]. Priority is given to the most energy-efficient sub-processes [12]. Since the change in gas pressure leads to a significant change in the energy of the particles, it can lead to a change in the parameters of the modified layers.

Figure 3 shows photos of cross sections taken with an optical microscope. In all three modes a compound layer is observed on the sample surface. It has a white color and is characterized by a high nitrogen content. The thickness of compound layers is different. With a pressure (250 Pa) the compound layer has the smallest thickness – 14–16 microns. Increasing the pressure to 500 Pa leads to an increase in the width of the compound layer to 25–27 microns. The same thing happens when the pressure drops to 70 Pa.

![Figure 3. Micrographs of the modified layer. Nitrogen pressure are 70, 250 и 500 Pa.](image)

Table 3 presents the results of the microhardness measurement. All samples have a surface hardness of more than 800 kgf-mm$^2$, which corresponds to the hardness of the compound layer. The maximum hardness (960 kgf-mm$^2$) is obtained at a pressure of 250 Pa. The width of the diffusion zones was estimated by measuring the microhardness of the cross sections. The microhardness distribution over the depth of nitrated samples is shown in figure 4.

| Pressure (Pa) | 70  | 250 | 500 |
|--------------|-----|-----|-----|
| Surface microhardness (HV$_{0.05}$) | 840 | 960 | 840 |
| Compound layer (µm) | 26.1 | 15.6 | 27 |
| Diffusion zone (µm) | 300 | 460 | 390 |

All samples demonstrate high hardness. The diffusion zone corresponds to an area where the hardness is higher than that of the source material. In 6 hours of nitriding at the same temperature of the experimental samples in all modes, an extended diffusion zone was formed, several hundred
micrometers thick. The width of the diffusion zone also depends on the pressure, but unlike the compound layer, at a pressure of 250 Pa it has a maximum value of ~ 500 µm (figure 4b). The minimum width (~ 300 µm) of the diffusion zone was observed when the working gas pressure was reduced to 70 Pa with a simultaneous increase in the discharge voltage to 1800 V (figure 4a).

Since the power of the discharge and the temperature of the workpieces did not change during the experiments, it can be assumed that this is a result of changes in the energy and concentration of particles acting on the surface.

The high ion current density and the concentration of energetic neutrals at elevated pressure lead to the fact that more particles are able to participate in sorption processes. At elevated pressure, high-energy particles create a large number of vacancies in the surface layers. In both cases, conditions are provided for the rapid penetration of nitrogen into the surface layers. The result is a thick compound layer, which in turn acts as a barrier to the diffusion of nitrogen into the depth of the metal. Therefore, the rate of formation of the diffusion zone is reduced. At pressures near 250 Pa, a superposition of these effects is likely to be provided. At intermediate values of the particle flux density and their energy, the rate of penetration of nitrogen into the surface compound layer decreases. The concentration of nitrogen becomes insufficient for the formation of a thick compound layer therefore nitrogen diffuses faster into the depth, forming the thickest diffusion zone.

The processing of AISI 5140 steel in a glow discharge of pure nitrogen without the addition of hydrogen is accompanied by phase transformations with the formation of nitrides in the structure (figure 5). With increasing pressure of the working gas, the intensity of the matrix reflections from α-Fe on diffractograms sharply decreases. This confirms the presence of a zone of nitrides and a zone of solid solution of large thickness (see figure 3 and 4). Nitrogen doping increases the volume fraction of the following main dominant phases: ε(Fe2–3N) and γ'(Fe4N) (table 4). According to X-ray analysis data the α-Fe lattice parameter in the surface layer after nitriding with a gas pressure of 70 Pa greatly exceeds the value of the initial sample (2.886 and 2.877 nm respectively). This indicates a high
concentration of nitrogen in this area of the treated material. It should be noted that for steel nitrated at elevated pressure, the lattice parameter for the $\alpha$-phase matters close to the source material. Probably, in the absence of a high density of grain boundaries, the diffusion of nitrogen in the condition of high ion energy at a pressure of 70 Pa in the samples occurs predominantly through the grain body. Under these conditions, the zone of internal nitriding is depleted in nitrogen, which mainly concentrates in the nitride part of the hardened surface.

![Figure 5. XRD patterns of AISI 5140 low alloy steel for 6-h treatment time, at 550°C for 70, 250, 500 Pa.](image)

The distribution of the volume fraction of the $\varepsilon$($\text{Fe}_2\text{N}$) and $\gamma'$($\text{Fe}_4\text{N}$) phases strongly depends on the operating pressure. For example, ionic nitriding at a pressure of 70 Pa promotes the formation of a compound layer mainly containing the $\gamma'$-phase. The increase in pressure leads to the broadening of the lines on the diffractograms. This indicates an increase in internal stresses. For the $\varepsilon$-phase, with increasing pressure, an increase in the size of the coherent scattering region (CSR) is observed. In this case, the microstrain of the crystal lattice for this phase has a maximum at a pressure of 250 Pa, decreasing markedly with increasing or decreasing pressure values. For the $\gamma'$-phase the trend in the parameter $\Delta d/d^*$ changes to remains the same, the dimensions of CSR are inversely dependent on pressure, compared to the $\varepsilon$-phase.

**Table 4.** XRD patterns of AISI 5140 low alloy steel.

| $P$ (Pa) | Phase   | Content (%) | Lattice parameter (Å) | CSR (nm) | $\Delta d/d^*$\times 10^{-3} |
|---------|---------|-------------|------------------------|----------|-----------------------------|
| Before treatment | Fe       | 100         | $a = 2.8771$           | 62       | 3.6                         |
|         | Fe       | 4           | $a = 2.8866$           | 22       | 4.8                         |
| 70 Pa   | Fe$_3$N  | 6           | $a = 4.6683; c = 4.3787$ | 15       | 3.7                         |
|         | Fe$_4$N  | 90          | $a = 3.7969$           | 38       | 2.5                         |
|         | Fe       | 7           | $a = 2.8755$           | 18       | 0.9                         |
| 250 Pa  | Fe$_3$N  | 20          | $a = 4.6686; c = 4.3653$ | 22       | 5.6                         |
|         | Fe$_4$N  | 73          | $a = 3.7848$           | 32       | 8.9                         |
|         | Fe       | 9           | $a = 2.8757$           | 20       | 1.7                         |
| 500 Pa  | Fe$_3$N  | 24          | $a = 4.6951; c = 4.3606$ | 25       | 1.3                         |
|         | Fe$_4$N  | 67          | $a = 3.7938$           | 28       | 7.8                         |

Thus, by changing the nitrogen pressure while maintaining the temperature of the workpieces and the duration of the process, it is possible to change the phase composition and mechanical properties of the compound layer. For example, the predominance of the $\gamma'$-phase improves the strength and wear resistance of parts under high loads, while the $\varepsilon$-phase contributes to an increase in extreme pressure properties and is suitable for applications that are not subjected to shock loads or high local stresses [13, 14, 15].
4. Conclusion

As is known, the value of the working pressure in the process of ion-plasma treatment depends on the method of plasma excitation and the specific technical parameters of the equipment. The lower limit of gas pressure is determined by the value at which plasma can be excited and the required temperature is provided. This paper shows that the operating pressure range in a classical ion-plasma nitriding system based on a glow discharge can be significantly extended by using a power supply with a high output voltage and an adaptive output current-voltage characteristic.

Experiments carried out at a nitrogen pressure of 70, 250 and 500 Pa showed that in all three modes the formation of a nitrided layer consisting of a compound layer (15–27 microns) and a diffusion zone (300–460 microns) occurs. The dependence of the depth of the diffusion zone and the width of the compound layer on the gas pressure is complex. The greatest depth of the diffusion zone is provided at a pressure near 250 Pa, but in this mode the compound layer has a minimum width. We assume that this behavior is due to changes in the energy and concentration of particles acting on the workpiece surface.

The results of x-ray diffraction analysis showed that the phase composition of the compound layer changes when the pressure changes. The pressure reduction leads to a decrease in the volume content of ε-phase and an increase in γ-phase. The change in the phase composition is presumably due to an increase in the intensity of surface etching under conditions of an increase in the energy of the bombarding particles.

It has been experimentally shown that the use of a new type of power sources for the ionization of the working gas in a wide pressure range from 70 to 500 Pa, makes it possible to effectively conduct and control the processes of diffusion saturation of steels in a glow discharge by varying the nitrogen pressure. By changing the gas pressure at constant values of the workpiece temperature and the duration of the process, it is possible to control the structure, phase composition of the hardened layers, and, consequently, the performance properties of the finished products.

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