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ION-PLASMA NITRIDING OF INNER CYLINDRICAL SURFACES OF PRODUCTS

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ABSTRACT

Technological modes of pulsed ion-plasma nitriding of inner cylindrical surfaces with application of a hollow perforated anode were developed. It results in formation of diffusion coatings, consisting of areas of different chemical and phase composition. Maximum concentration of nitrogen is observed in the areas opposite holes in the anode, which are made at a certain distance at a certain angle. Accordingly, these same areas contain a hard phase from iron nitride, discretely arranged in a soft matrix of α-iron. Testing under the conditions of dry friction of metal against metal showed that the wear resistance of specimens, taken from different areas of the nitrided specimens, is 3–5 times higher than in the initial non-nitrided specimen that is indicative of a high wear resistance and good prospects for their further investigation.

KEYWORDS: ion-plasma nitriding, discrete-matrix coatings, technological modes, wear resistance, inner cylindrical surfaces

INTRODUCTION

Compared to other nitriding methods, ion-plasma nitriding has a number of technical and economic advantages such, as minimal energy- and labour-intensiveness of the process, high values of contact endurance and fatigue strength of the hardened surface. More over, it allows removing chemical contaminants, which are released into the environment at application of the traditional treatments: chemical, electrochemical, salt and other.

Alongside the environmental friendliness and cost-effectiveness of the process, ion-plasma nitriding allows producing diffusion layers of the specified composition and structure, both with the nitride zone on the surface, and without it. In the first case, high corrosion and wear resistance of friction surfaces is ensured, but crack resistance decreases, and in the second case the alternating loading resistance under the conditions of high pressure and temperature is increased.

Ion-plasma nitriding also allows solving the problem of strengthening especially deep holes, the length of which is greater than their diameter tens of times and that is a rather complex task practically for all the surface engineering methods and requires further studies.

Numerous studies, by both local and foreign researchers are devoted to nitriding technologies, including combined saturation of the steel surface by nitrogen and carbon (carbonitriding) [1–4].

Work [5] gives the results of nitriding by high-density plasma with hollow tubular cathode of small-sized specimens from martensitic stainless steel AISI 420-J2 at the temperature of 673 K. It led to formation of a nitrided surface layer up to 80 μm thick and 31 at.% nitrogen concentration on its surface. In work [6] studies were also performed on nitriding in the hollow cathode mode of products of microtube type from steels AISI 304 and AISI 316 of 5.5 to 30.0 mm length with inner diameter from 0.58 to 16.9 mm and outer diameter from 0.88 to 21.5 mm. A mixture of nitrogen and hydrogen gases was passed through a hole, the internal surface hardness rising to more than 800 *HV*.

Authors of work [7] conducted ion nitriding of tubular specimens from 32CrMoV12-10 steel with hole diameter of 6 and 8 mm and 500 mm length at the temperature of 500 °C for 6 h with a mixture of hydrogen and nitrogen gases. The length of the nitrided layer was 234 mm at hole diameter of 8 mm and 138 mm at hole diameter of 6 mm. Thus, the length of the nitrided layer decreased with decrease of the hole diameter. The nitrided surface consisted of a composite layer on the surface and diffusion transition zone. The specimen surface hardness increased by 100 %. The authors of [8] applied gas nitriding for treatment of bores of small arms of the diameter from 5.56 to 12.5 mm from 38HMJ steel in NH_3 ammonia environment. It resulted in formation of a hardened layer approximately 220 μm thick with subsurface microhardness of 900 *HV*. Here a white layer of iron nitrides with $\varepsilon + \gamma'$-phase structure of 12–15 μm thickness formed on the surface. It has a high hardness and corrosion resistance, but low crack resistance.

Crack and wear resistance of nitrided layers can be significantly improved by forming discrete structures, which are ever wider applied in different mechanical engineering sectors [9].

Mechanical properties						Heat treatment			
						Quenching		Tempering	
σ_y, MPa	σ_t, MPa	δ, %	ψ, %	a_h, J/cm^2	*HB*	Temperature, °C	Cooling medium	Temperature, °C	Cooling medium
961	1118	21	64	107	195	850–40	Oil	620–60	Water

The principle of a discrete structure consists in replacement of the continuous structure of the surface layer by a discrete-matrix one that greatly improves the limit state of the surface (contact loads, critical deformations of the base, crack resistance, fatigue life), compared to a continuous coating of the same thickness, composition and hardness.

Considering the insufficient research into the phenomena taking place on the discrete structure surface, and absence of its design methods, many studies were directed at optimal design of a discrete structure, allowing for residual stresses [10].

Dimensions and configuration of individual areas are calculated, proceeding from the conditions of minimizing the level of stress-strain state during mechanical and temperature impact, and they are determined by analytical and numerical methods.

The discrete-matrix structure is formed by ion-plasma method using diverse screens, patterns, masks, also in the form of metal grid [11, 12]. The grid geometrical parameters are selected, proceeding from calculation of a discrete area dimensions and continuity with provision of a minimal level of residual stresses in the surface layer. The distance between the screen and backing determines the shape of the edge of an individual discrete area.

Thus, development and investigation of the methods of forming the discrete-matrix structure is one of the relevant tasks in the problem of improvement of physico-mechanical properties of the surface.

The objective of this work is strengthening the inner surfaces of cylindrical holes by forming discrete-matrix coatings at ion-plasma nitriding.

INVESTIGATION PROCEDURE

Investigations were conducted with application of an experimental vacuum unit, fitted with a source of constant regulated voltage, high-frequency generator and pulse modulator, made with vacuum electronic instruments GU-81M. Owing to their characteristics, these instruments automatically limit the current and load by a preset value and interrupt the arcing process, which is accompanied by explosion-like local destruction of the cathode surface.

Experiments were conducted on tubular specimens of outer diameter of 30 mm, and inner diameter of 12 mm and length of 240 mm. The main material was 40KhN2MA steel, as its composition and properties are close to those of a material, from which it is possible to make arms barrels that is highly relevant now for improvement of the defense capability of Ukraine. Chemical composition of this steel is as follows, wt.%: 0.41 C; 0.31 Si; 0.57 Mn; 0.003 S; 0.017 P; 0.8 Cr; 1.37 Ni; 0.07 W; 0.01 V; 0.21 Mo; 0.18 Cu; 0.001 Ti; 0.016 Al; 0.009 N, and its mechanical properties and heat treatment in keeping with the certificate of quality are given in the Table.

Microhardness measurements on the inner surfaces were performed over the microsection using PMT-3 hardness meter with 50 g loading on the indenter; wear resistance was determined by shaft-block schematic, the counterbody was a rod of 10 mm diameter from carbon steel, quenched to 28–35 *HRC* hardness. The coating microstructure and chemical composition were determined in scanning electron microscope REM-1061, fitted with energy-dispersive microanalyzer OXFORD x-act. Diffractometric analysis was conducted using X-ray diffractometer Rigaku Ultima IV.

INVESTIGATION RESULTS

The nitriding process was conducted in the mode of an anomalous glowing discharge, when the entire surface of the cathode electrode (of the part in our case) participates in the discharge and is covered by plasma glow. Voltage in such a discharge is equal to hundreds of volts, and the part current density is up to 10 mA/cm^2.

Parameters of the mode of high-frequency pulsed nitriding that ensures stable burning of the anomalous glowing discharge are given below:

Pressure in the process chamber, Pa	25–350
Voltage U, kV	0.8–1.0
Current density, mA/cm^2	9
Pulse frequency f_0, kHz	10
Pulse ratio Q	1.5–2.0
Process duration, h	5–6

A mixture of 75 % N_2 + 25 % Ar was used as the working gas, and pure argon was applied for surface cleaning at the initial stage.

Specimen temperature during nitriding did not exceed 580 °C. It was regulated by varying such parameters of the pulsed power supply mode as voltage and pulse ratio.

Pulse frequency on the level of 10 kHz was established, proceeding from the conditions of preventing the anomalous glow discharge transition into the arc discharge, which damages the surface of products and may lead to rejects. Thus, application of pulsed nitriding mode ensures stability of the process of diffusion saturation of the surface without electric breakdowns or arcing, and the mode of anomalous glow discharge is realized in keeping with the volt-ampere characteristic of electric discharge. Pulse ratio has an important role in this process, its reduction leading to localization of the plasma volume in the tubular specimen. It can be compensated by voltage increase. However, it causes overheating on the specimen surface, resulting in undesirable structural transformations. The uniformity of plasma combustion was indirectly evaluated by specimen heating using thermocouples located on specimen edges and in its middle. If the glow discharge is uniformly distributed along the entire specimen length, the temperature difference between the thermocouples does not exceed 10 °C.

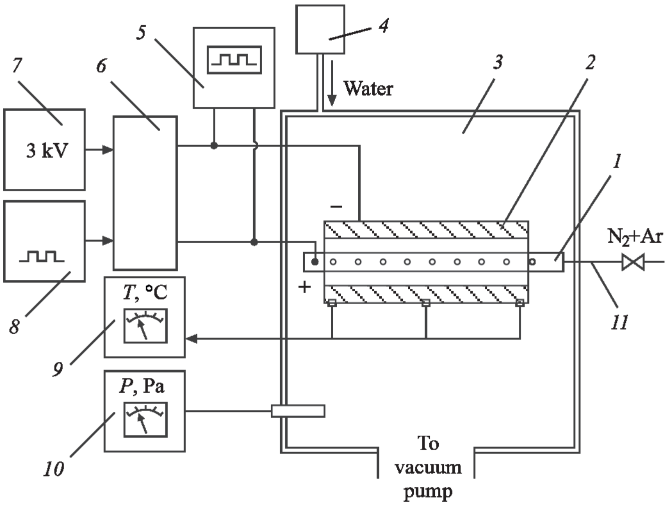

Figure 1. Schematic of an experimental unit for ion-plasma nitriding: *1* — tubular anode with holes for gas feeding; *2* — hollow nitrided cathode-specimen; *3* — vacuum chamber; *4* — vacuum chamber water-cooling block; *5* — oscillograph; *6* — modulator; *7* — DC source with voltage regulation; *8* — pulse generator with variable frequency and ratio; *9* — thermocouples and temperature measuring device; *10* — device for measuring the chamber pressure; *11* — vacuum lead valve for working gas

Nitriding of inner surfaces of holes in tubular specimens was realized as follows: a tubular anode of 5 mm diameter with side holes and one end plugged was coaxially installed inside the specimen, the anode open end was connected to a pipeline for feeding working gas of 75 % N_2 + 25 % Ar, so that the gas entered through the anode side holes into the specimen cavity and then escaped into the vacuum chamber, which was continuously pumped down (Figure 1). The cathode-specimen and the anode were fixed by special insulators mounted on a common continuous platform.

Holes in the tubular anode were arranged so as to prevent overlapping of nitrided zones with maximum nitrogen concentration (Figure 2, *a*). Taking into account the anode outer diameter, and inner diameter of the hollow cathode, as well as distribution of nitrogen concentration field over the cross-section, the holes were made every 20 mm at an angle of 120°.

The experimental specimen (Figure 2, *b*) was cut up so that a complex of studies could be performed. In the middle part, specimen No.1 was cut out in the form of a ring for microscopic investigations, then specimens Nos 2 and 3 were cut off in the form of semi-rings for wear resistance testing by shaft-sleeve scheme. On the specimen surface one can also see a hole for mounting a tubular thermocouple, which was placed into a ceramic case to ensure electric decoupling.

The fields of nitrogen concentration distribution over the cross-section of specimen No. 1 are given in Figure 3, *a*, which leads to the conclusion about the nouniformity of nitrogen distribution over the cross-section. The maximum concentration is observed from the side opposite the holes in the tubular anode. The curve of the change of nitrogen concentration in the cross-section (Figure 3, *b*) shows bends, the first small one at 15 μm distance from the surface with nitrogen concentration on the level of 21 at.% and the second one at 60 μm with nitrogen concentration on the level of 6 at.%. No further changes were observed which is related to the low sensitivity of the microanalyzer.

Figure 4, *a* shows the microstructure of a nitrided layer of specimen No. 1 in the area of maximum nitrogen concentration, where surface zones of different nitrogen concentration are observed, and Figure 4, *b* gives the microhardness variation, respectively.

Analysis of the results of determination of the nitrided layer chemical composition showed that the structure is layered, and it consists of several zones: nitride one on the surface where γ′-phase formed and nitrous ferrite. Alloying elements of chromium and

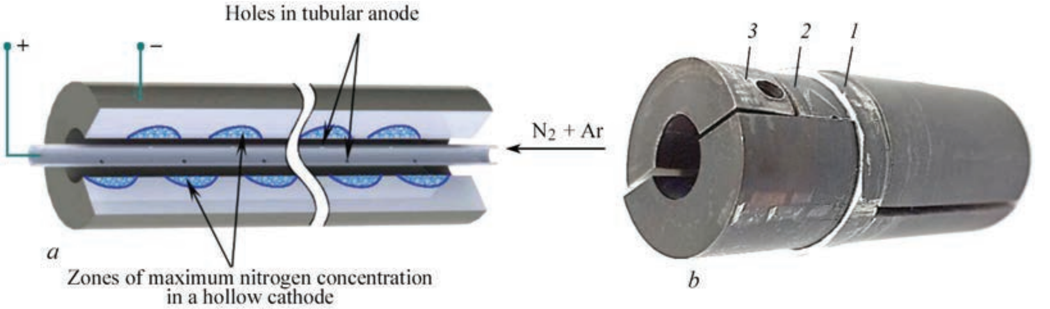

Figure 2. Schematic of location of diffusion zones of discrete-matrix nitriding along the tubular specimen (*a*) and experimental specimen (*b*), cut up into parts (*1–3*) to conduct microscopic investigations and microscopic tests

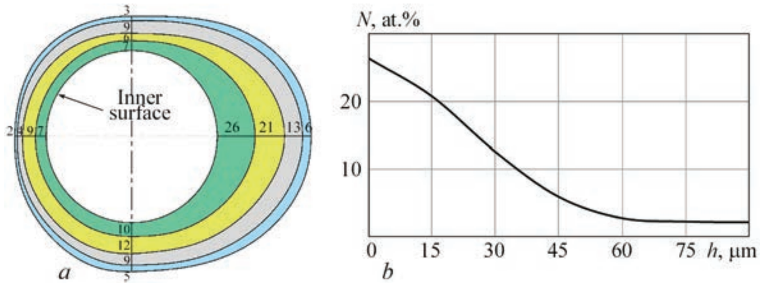

Figure 3. Distribution of nitrogen concentration (at.%) over the cross-section of specimen No. 1 (*a*) and radially from the center in the zone with maximum nitrogen concentration (*b*)

nickel dissolve in ferrite, and increase nitrogen solubility in α-phase, forming special nitrides. Precipitating in the fine-dispersed state these nitrides cause an increase in the nitrided layer hardness, predominantly in lower layer of the saturated zone. Chromium, as a transition element, actively interacts with nitrogen and improves nitrogen solubility in α-phase. Zone I with γ′-phase is very thin and brittle. After nitriding, nitrogen content on the surface of zone I reaches 8.97 wt.% (26.38 at.%). In keeping with iron-nitrogen constitutional diagram, iron nitrides will form at nitrogen concentration of about 20 at.%, which leads to maximum hardness on the level of 805 MPa near the surface. In zone II the chemical composition of the nitrided surface differs both from the initial and the nitrided layer: nitrogen content is up to 6.25 wt.% (20.8 at.%) at 6 μm distance. Zone III, where the nitrided layer formed, also demonstrated changes in the chemical composition: nitrogen amount decreased to 3.5 wt.% (12.6 at.%) at 25 μm distance, the last zone adjacent to the base has nitrogen content of 1.57 wt.% (5.96 at.%) at 46.26 μm distance. At the distance of approximately 100 μm the amount of oxygen is equal to 0.57 wt.% (2.22 at.%).

Results of diffractometric analysis (Figure 5) conducted near the surface of specimen No. 1 showed the presence of Fe_2N phase on the level of 7 %, the balance being α-Fe and Fe_3C at 92 and 1%, respectively.

Based on the obtained data on nitrogen concentration distribution over the specimen cross-section (Figure 3, *b*) showing the presence of a white nitride zone on the surface (Figure 4, *a*) that is confirmed by the results of diffractometric analysis (see Figure 5) we can conclude that application of ion-plasma nitriding of the inner surfaces using a hollow perforated anode results in formation of diffusion coatings, consisting of areas of different chemical and phase composition. Maximum nitrogen concentration is observed in the areas located opposite the holes in the anode, made at a certain distance (see Figure 2, *a*). Accordingly, the same areas contain a hard phase from iron nitride, which corresponds to increased wear resistance of the nitrided surface, i.e. there is every sign of the presence of a certain discrete arrangement of the hard nitride phase in a soft matrix of α-iron that corresponds to discrete-matrix coatings.

In order to confirm this conclusion and study the impact of discrete-matrix coatings produced by

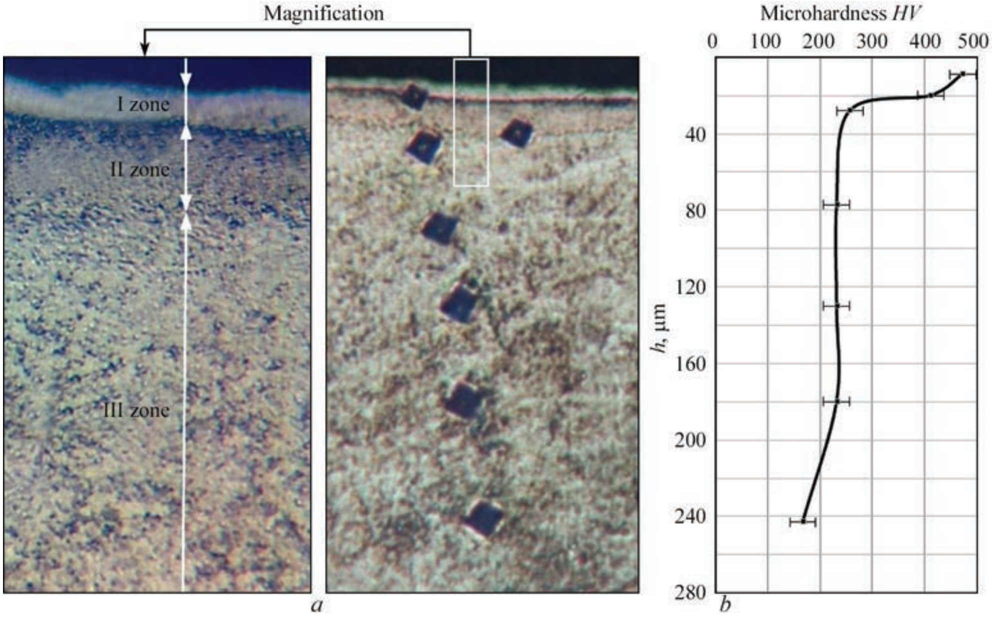

Figure 4. Microstructure of nitrided surface with maximum amount of nitrogen (*a*) and change of microhardness in the cross-section from the tubular specimen surface (*b*)

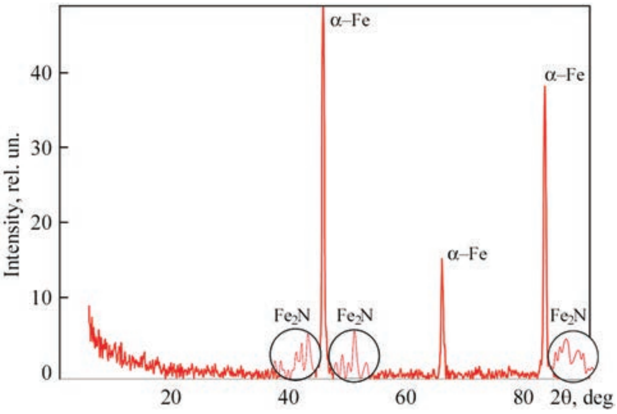

Figure 5. Diffractogram of the surface layer of specimen No. 1 in the area with maximum amount of nitrogen

ion-plasma nitriding on wear resistance, friction tests were conducted on specimens, cut out of various areas, which have different dimensions, have or do not have nitride zone I with a high nitrogen concentration on the surface and maximum hardness, respectively, that is demonstrated by wear results (Figure 6).

As we can see, the highest wear resistance was observed in specimen No. 3, cut out opposite the hole in the anode. After wearing of the nitride zone with maximum hardness, this specimen demonstrates a loss of mass with its uniform increase. Specimen No. 2 cut out with 15 mm shifting from the hole in the anode, demonstrates a uniform loss of mass, as in the case with specimen No. 3 that is attributable to a more homogeneous structure of the nitrided layer, however, the wear resistance is 1.8 times lower. In general, wear resistance of all the nitrided specimens after testing for 240 min is 2–3 times higher than that of the initial non-nitrided specimen. This is indicative of the good prospects for application of discrete-matrix coatings, and relevance of their further investigations. Obtained results are universal and can be applied for hardening other steels to be nitrided.

CONCLUSIONS

1. Technological modes were developed for pulsed ion-plasma nitriding of inner surfaces on the base of an experimental vacuum unit, fitted with a source of constant regulated voltage, high-frequency generator and pulse modulator. Owing to their characteristics, these instruments automatically limit the load current by a preset value and interrupt the arcing process, which is accompanied by explosion-like local destruction of the cathode surface of the specimen, which is inadmissible.

2. Conducted investigations showed that ion-plasma nitriding of inner surfaces with application of a hollow perforated anode, leads to formation of diffusion coatings, which consist of areas of different chemical and phase composition. Maximum concentration of nitrogen on the level of 8.97 wt.% (26.38 at.%) is found in areas, which were located opposite the holes in the anode, made at a certain distance at a certain angle. Accordingly, the same areas contain a hard phase from iron nitride, discretely located in the soft matrix of α-iron.

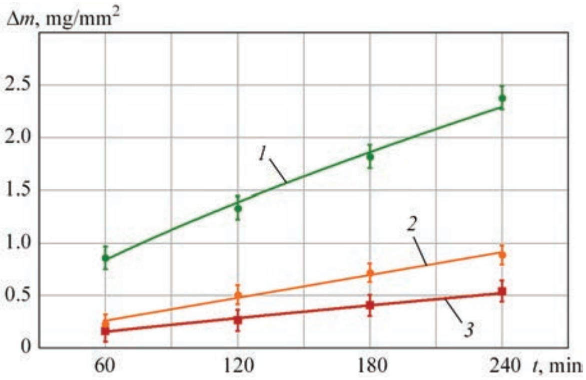

Figure 6. Kinetics of wear of 40KhN2MA steel specimens in the initial condition and after ion-plasma nitriding: *1* — initial specimen; *2*, *3* — nitrided specimens Nos 2 and 3, respectively

3. Testing under the conditions of dry friction of metal against metal showed that the wear resistance of specimens, taken from different areas of the nitrided specimens, is 3–5 times higher than that of the initial non-nitrided specimens that is indicative of their high wear resistance and attractiveness of their further studies.

4. Further on, proceeding from investigation results, it is planned to develop the technological schedule for specific tubular products, the inner holes of which are to be hardened by nitriding.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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