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Formation of microstructure and mechanical properties on internal cylindrical surfaces nitrided by ion-plasma method

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The paper studies the processes of active ion-plasma nitriding of the inner surface in the mode of abnormal glow discharge; a hollow cathode and a perforated tubular anode made of widely used high-quality steel 40CrNi2Mo are used. The structure and composition of the nitrided surfaces and the microhardness of the internal surfaces were investigated. The relationship between plasma treatment parameters, geometric features and microhardness has been established. Diffusion coatings with uneven nitrogen concentration and discrete layered structure were obtained. The nitrided surface consists of three zones: nitride, transition and diffusion. The nitrided layers have increased hardness; scratching revealed zones with higher hardness values located along the inner cylindrical surface.

Keywords: ion-plasma nitriding, hollow cathode, perforated anode, microhardness, sclerometry, internal cylindrical surfaces.

Формування мікроструктури та механічних властивостей на внутрішніх циліндричних поверхнях азотованих іонно-плазмовим методом. *І.А. Селіверстов, І.В. Смирнов, А.В.Чорний, В.В. Лисак, О.В. Ляшко, М.О. Сисоєв*

Робота була зосереджена на розробці процесів активного іонно-плазмового азотування внутрішньої поверхні в режимі аномального тліючого розряду з використанням полого катода і перфорованого трубчастого анода для широко використовуваної сталі 40ХН2МА. Досліджено структуру та склад азотованих поверхонь та мікротвердість внутрішніх поверхонь. Встановлено зв'язок між параметрами плазмової обробки, геометричними особливостями та мікротвердістю. Застосуванням перфорованого трубчастого анода були отримані дифузійні покриття з нерівномірною концентрацією азоту і утворюванням дискретних структур. Структура азотованої поверхні шарувата і складається з трьох зон: нітридної, перехідної та дифузійної. Азотовані шари мають з підвищену твердість, за результатами вимірювання мікротвердості методом HRV . Методом склерометрії виявлені зони з більш високим значенням твердості, які розташовані вздовж внутрішньої циліндричної поверхні.

1. Introduction

Nitriding is often used to improve the tribological properties and wear resistance of structural steels [1-3]. Among the methods, plasma nitriding is a widespread, environmentally friendly and energy-efficient technology [4].

This technology makes it easy to remove passive layers from the surface before nitriding. However, plasma nitriding of the inner surface is still a challenge [5-7]. With a small amount of work, we can state certain benefits from hardening the inner surface, in some cases increasing corrosion resistance with high tribomechanical properties. There are many applications that could benefit from such properties, such as numerous bushings in the engineering industry, machining long tubular parts such as small arms channels or biomedical products, etc.

Plasma nitriding of internal surfaces is associated with geometric features t of the tubular perforated anode and hollow cathode, which can lead to an extreme absence of plasma or the appearance of high-density plasma in certain areas [8]. As a result, zones with uneven nitrogen concentrations and the formation of discrete structures can form.

Replacing the continuous structure of the surface layer with a discrete matrix structure significantly improves the boundary state of the surface (contact loads, critical deformations of the base, crack resistance, durability) compared to a continuous coating of the same thickness, composition and hardness.

Due to the insufficient study of the phenomena occurring on the surface of a discrete structure and the lack of methods for its design, many studies have been aimed at the optimal design of a discrete structure with regard to residual stresses [9]. To form a discrete matrix structure using the ion-plasma method, various screens, stencils, masks, including microtexture printing, are used [10]. Thus, the development and study of methods for the formation of nitrided layers on internal surfaces is one of the most urgent tasks in surface engineering.

The aim of this work is:

1. To develop a plasma nitriding method using a hollow cathode and a tubular perforated anode to strengthen the internal cylindrical surfaces of holes by forming a surface layer with improved mechanical properties.
2. To determine the influence of plasma nitriding modes and design solutions of the hollow cathode and tubular perforated anode on the formation of microstructure and mechanical properties on internal cylindrical surfaces.

2. Experimental

The study was carried out using an experimental vacuum installation equipped with a constant regulated voltage source, a high-frequency generator, and a pulse modulator. These devices automatically limit the current and load to a predetermined value and interrupt the arc formation process.

In the experiments, tubular samples with an outer diameter of 30 mm, an inner diameter of 12 mm and a length of 240 mm were used. The main material was high-quality 40CrNi2Mo steel with the following chemical composition, 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. Heat treatment consisted of hardening and tempering (hardening temperature 850°C, cooling in oil, tempering at 620°C).

Microhardness on the internal surfaces was measured by the cross-section of the microgroove on a PMT-3 hardness tester with an indenter load of 50 g; the scratch test method was used with a Vickers indenter at a movement speed of 8 mm/min and a load of 40 g according to the 'face forward' scheme.

The microstructure and chemical composition of the coatings were determined using a scanning electron microscope REM-106I with an OXFORD x-act energy dispersive microanalyzer. XRD analysis was performed using a Rigaku Ultima IV X-ray diffractometer.

3. Results and discussion

The nitriding process was carried out in the mode of an anomalous glow discharge, in which the entire surface of the cathode electrode – the sample - is covered with a plasma glow. The voltage during this discharge was 850 V, and the current density on the part was up to 10 mA/cm^2. The process duration was 5...6 hours. The nitriding process mode was selected in accordance with previous studies in [11].

A gas mixture of 75 % N_2 + 25 % Ar was used, and pure argon was used for surface cleaning. The sample temperature during nitriding did not exceed 580 °C.

For nitriding the internal surfaces of the holes in tubular samples, a hollow perforated anode with a diameter of 5 mm with side holes and one end plugged was coaxially installed in the middle of the sample; the open end of the anode was connected to a pipeline for supplying 75% N_2 + 25% Ar working gas. Along the anode at an angle of 120º, holes with a diameter of 1 mm for gas outlet were made every 20 mm (Fig. 1).

After the nitriding process, the samples were prepared for testing. The results of scan-

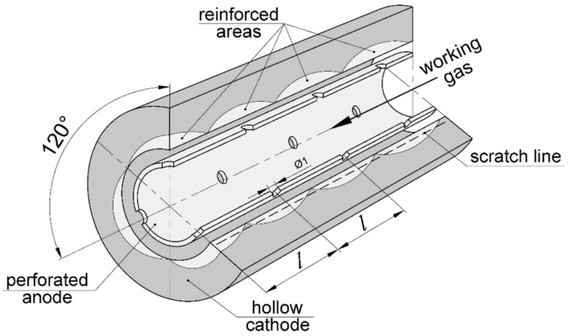


Fig. 1 Hollow cathode element with perforated anode

ning microscopy and chemical analysis showed that ion-plasma nitriding of internal surfaces using a hollow perforated anode resulted in the formation of diffusion coatings with different chemical and phase compositions (Fig. 2).

The results of chemical analysis in three zones according to Fig. 2 are given in Table 2, and the distribution of elemental concentrations deep in the surface of the nitrided layer is shown in Fig. 3. The concentration of elements from the surface to the centre was determined with a step of 1.88 μm deep into the sample at a distance of 90-100 μm, and the nitrogen concentration was reduced to standard values for high-quality 40CrNi2Mo steel.

The surface layer (Zone I), where the ε-phase was formed, is a very thin, 8 μm thick, and has a brittle structure. After nitriding, the nitrogen content on the surface of zone 1 reaches 8.97 wt.% (26.38 at.%). According to the iron-nitrogen diagram, at a nitrogen concentration of about 20 at.%, iron nitrides will be formed, mainly Fe_2N, which leads to a maximum microhardness near the surface at 3.65 GPa.

The near-surface layer is 15 μm thick (Zone II), where the γ' phase of nitrided ferrite was formed. Consisting mainly of Fe_4N nitrides, the chemical composition of the nitrided surface in zone 2 differs from both the initial and the nitrided layer: the nitrogen content reaches 6.25 wt. % (20.8 at. %).

Zone III is a diffusion sublayer with a granular pearlite structure, consisting of α- and γ'-phases with the formation of predominantly Cr, Ni and Mo carbides of alloying elements of steel on nitrides, which additionally contribute to an increase in the solubility of nitrogen in the α-phase. Zone III, where the nitrided layer was formed, also underwent changes in its chemical composition: the amount of nitrogen decreased to 3.5 wt. % (12.6 at. %) at a distance of 25 μm, and the last zone at the boundary with the base has a nitrogen content of 1.57 wt. (5.96 at. %) at a distance of 46.25 μm. At a distance of about 100 μm, the amount of nitrogen is 0.57 wt. (2.22 at. %).

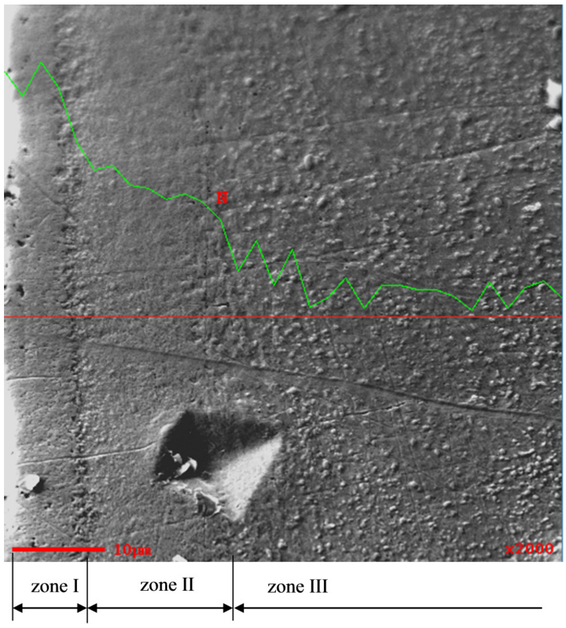


Fig. 2 Structure of the nitrided surface with the distribution of nitrogen concentration from the surface to the middle of the sample

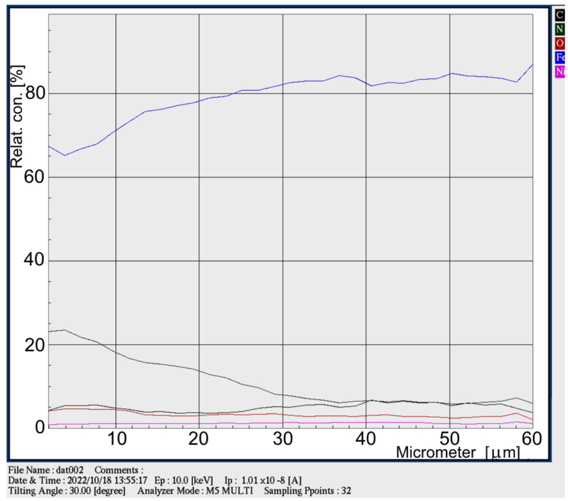
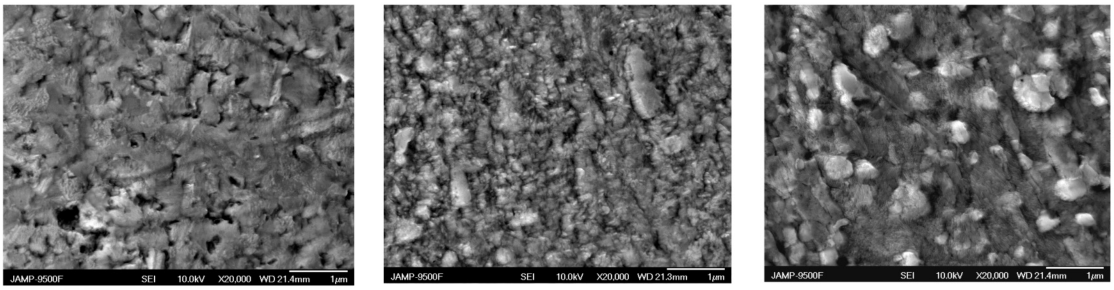


Fig. 3. Distribution of element concentrations from the surface to the middle of the nitrided layer

Table 1 - Chemical analysis in three zones.

Elements	I	II	III
C	4.9	2.1	2.9
N	19.7	14.0	4.7
O	3.4	1.3	1.9
Fe	70.4	81.3	88.7
Ni	0.9	1.1	1.4
Cr	0.1	0.1	0.4
Mo	0.5	0.2	0.0



I) II) III)

Fig. 4. Structures of the nitrided layer a) in zone I, b) in zone II, c) in zone II c (magnification x20000)

The structures of the nitrided surface in different zones are shown in Fig. 4

The results of local chemical analysis of individual structural components are shown in Fig. 5 and Table 2.

The results of chemical analysis show that the highest concentration of nitrogen (11.2 at.%) and carbon (15.9 at.%) is found in light-colored spherical globules (point 1). These globules also contain the maximum amounts of chromium (3.3 at.%) and molybdenum (1.1 at.%). Iron is also distributed unevenly: a maximum of 83.6 at.% is in the matrix phase (point 2) and a minimum of 67.1 at.% is in the globules (point 1).

Based on this distribution of chemical elements, it can be assumed that the spherical globules are complex carbonitrides of iron, chromium and molybdenum.

The scratch tracks and indenter imprints allowed us to determine the microhardness along the sample; the distribution of average microhardness values had similar results from the surface to the middle (Fig. 6.a, b) and was in the range from 3.65 GPa to 2.44 GPa, respectively. The microhardness of 2.44 GPa corresponds to the average value of the base material.

Scratch tests revealed local areas of increased hardness from 6.89 GPa to 4.56 GPa with a size of approximately 200 μm along and 100 μm deep in the sample with a high nitrogen content of 9.7 wt. % (29.8 at. %) (Figs. 7, 8).

Table 2 - Chemical analysis of structural components (at.%)

Elements	point1	point 2
C	15.9	6.91
N	11.2	5.8
O	0.4	1.2
Fe	67.1	83.6
Ni	1.1	1.3
Cr	3.3	0.9
Mo	1.1	0.3

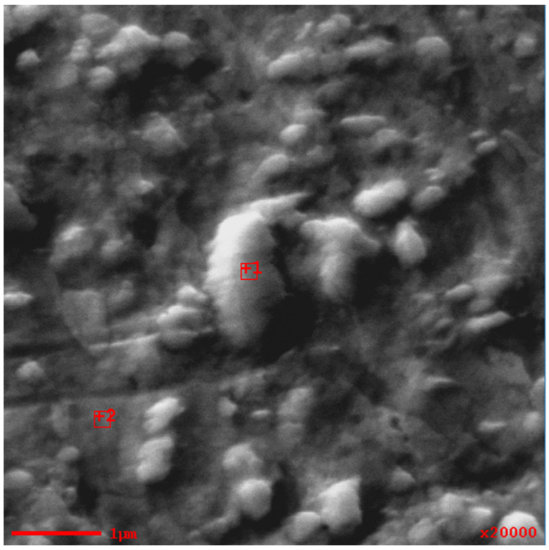


Fig. 5. Location of points for analyzing the chemical composition of structural components

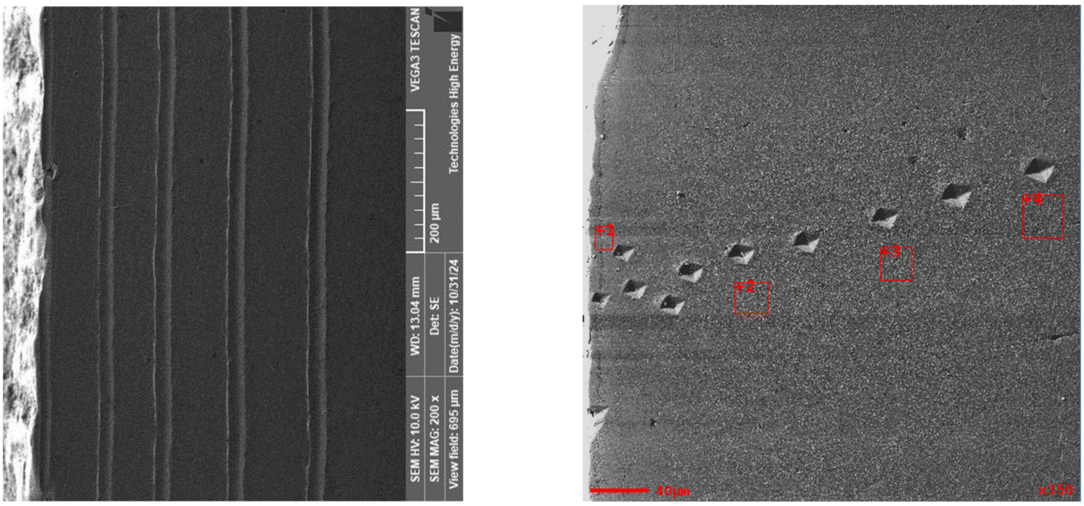
The formation of such areas was detected near the structural location of the hole in the anode through which nitrogen was supplied. The distribution of nitrogen along the scan line is also uneven with characteristic peaks (Fig. 8).

The presence of these localized areas is probably due to a higher concentration of gaseous nitrogen (high plasma density) in the flow zone through the anode hole and, possibly, additional stress concentrators on the surface formed after mechanical processing of the inner cylindrical surface.

4. Conclusions

On the basis of comprehensive experimental studies of microstructure, mechanical properties and chemical composition using modern research methods, the effectiveness of the ion-plasma nitriding method for strengthening internal cylindrical surfaces has been established. The main conclusions are as follows:

1. Technological modes of pulsed ion-plasma nitriding of internal surfaces have been



a) b)

Fig. 6. General view of scratch tracks (a) and indentation marks (b) for determining microhardness

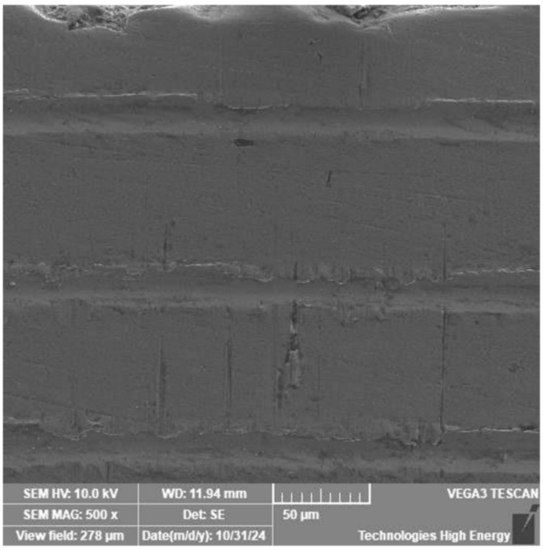


Fig. 7. General view of scratch tracks in the local area

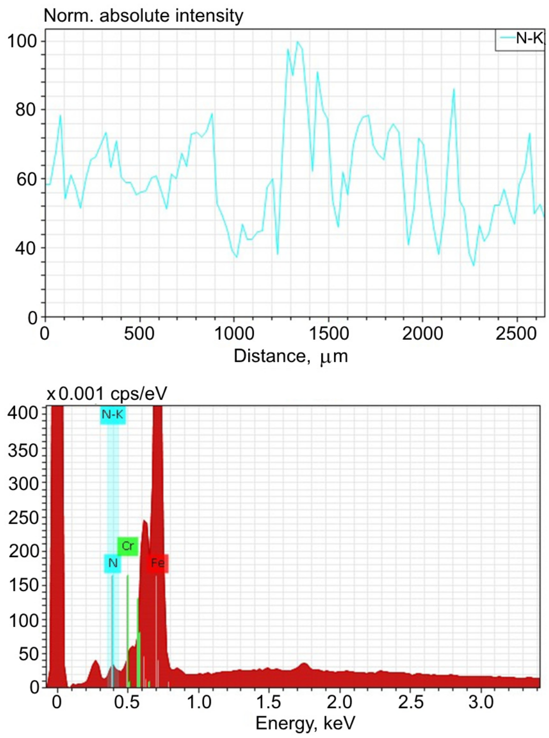


Fig. 8. Distribution of nitrogen concentration over the area near the anode hole

developed on the basis of an experimental vacuum installation equipped with a constant regulated voltage source, a high-frequency generator and a pulse modulator.

2. As a result of the research, it was established that ion-plasma nitriding of internal surfaces using a hollow perforated anode leads to the formation of structures with increased microhardness on the surface layer up to 3.65 GPa in the locations of holes, and local areas with increased microhardness up to 6.89 GPa.

References

1. T. Christiansen, M.A.J. Somers, *Surf. Eng.*, **21**, 445 (2005). https://doi.org/10.1179/174329405X68597.
2. T.Tsuchiyama, Y.Fujii, Y. Terazawa, K. Nakashima et al., *ISIJ Int.*, **48**, 861 (2008). https://doi.org/10.2355/isijinternational.48.861.
3. X. Zhang, J. Wang, H. Fan, D. Pan, *Appl. Surf. Sci.*, **440**, 755 (2018). https://doi.org/10.1016/j.apsusc.2018.01.225.
4. H. Aghajani, S. Behrangi Plasma Nitriding of Steels. Springer International Pub, (2016). https://doi.org/10.1007/978-3-319-43068-3.

5. I. Braceras, I. Ibanez, S. Dominguez-Meister, J. A.Sanchez-Garcia et al., *Surface and Coatings Technology*, **355**, 116 (2018). https://doi.org/10.1016/j.surfcoat.2018.04.057
6. K.Sumiya, S.Tokuyama, A.Nishimoto et.al., *Metals,* **11**(2), 366 (2021). https://doi.org/10.3390/met11020366.
7. T.Aizawa, K.Wasa, *Micromachines,* **8**, 157. (2017). https://doi. org/10.3390/mi8050157
8. S. Muhl, A. Perez, *Thin Solid Films,* **579**, 174 (2015). https://doi. org/10.1016/j.tsf.2015.02.066
9. B. A. Lyashenko, E Soroka, A. V. Rutkovskii, N. V. Lipinskaya, *Strength of Materials*, **34**(4), 402 (2002). https://doi.org/10.1023/A:1020344724002
10. T.Katoh, T.Aizawa, T.Yamaguchi, *Manufacturing Rev.*, **2**, 7 (2015). https://doi.org/ 10.1051/mfreview/2015004
11. I.V. Smirnov, A.V. Chornyi, V.V. Lysak, et al., *The Paton Welding Journal*, **11**, 21, (2022). https://doi.org/10.37434/tpwj2022.11.04