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Hydrogen-free nitriding of carbon steels and gray cast irons pre-hydrogenated in a glow discharge

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A glow discharge nitriding method has been developed, which includes preliminary hydrogenation of metal surfaces and promotes the intensification of diffusion processes during nitriding in a plasma chamber. Both hydrogenation and nitriding processes are carried out sequentially in the same discharge chamber and do not require any additional equipment. The combination of hydrogenation and subsequent glow discharge nitriding is expected to increase the number of phase structural components of the nitrided layer, particularly the ε- and γ´-phases, which will significantly improve its physicochemical and operational properties such as strength, ductility, corrosion resistance, and fatigue strength. The increase in the thickness of the nitride layer reaches its maximum at an argon content of 20%. With a further increase in argon content, the thickness of the nitride layer decreases for all studied materials. This is presumably due to internal stresses exceeding the strength limits of the materials, resulting in relaxation through massive dislocation emission to the surface, micropore formation, and a decrease in hydrogen pressure in internal voids—referred to as collectors. Preliminary ion-plasma hydrogenation in an environment with 20% argon content followed by glow discharge nitriding made it possible to increase the thickness of the nitride layer in the studied materials by approximately 1.7 times. Additionally, corrosion-mechanical wear resistance in a buffer solution of citric acid with pH 6.5 increased by 1.45 to 1.62 times compared to conventional methods. Cavitation–erosion resistance in a 3% NaCl solution increased by 4.7, 5.3, and 8.9 times for steels 20, 45, and cast iron SCH 20, respectively.

Keywords: hydrogenation, nitriding, wear resistance, cavitation-erosion resistance.

Безводневе азотування вуглецевих сталей та сірих чавунів, попередньо наводненних у тлуючому розряді. *Д.В. Здоренко, М.С. Стечишин, А.В. Мартинюк, Н.М. Стечишина, Ю.В. Цимбалюк*

Розроблений спосіб азотування в тліючому розряді, який включає попереднє наводнювання поверхонь металів, що сприяє інтенсифікації дифузійних процесів азотування в газорозрядній камері Процеси наводнювання і азотування проводяться почергово в одній і тій же газорозрядній камері та не потребують якогось додаткового обладнання. В результаті суміщення наводнювання і наступного азотування в тліючому розряді очікується збільшення кількості фазових структурних складових азотованого шару, зокрема ε і γ´–фаз, що значно підвищує його фізико-хімічні та експлуатаційні характеристики: міцність і пластичність, корозійну стійкість, втомну витривалість. Зростання товщини нітридного шару максимальне за вмісту аргону 20%. Із зростанням вмісту аргону товщина нітридного шару зменшується для всіх досліджених матеріалів. В разі збільшення аргону понад 20% внутрішні напруження перевищують межу міцності матеріалів і відбувається їх релаксація

через масовий вихід дислокацій на поверхню, утворення мікропор та зниження тиску водню у внутрішніх пустотах – колекторах. Попереднє іонно-плазмове наводнювання в середовищі з 20% вмістом аргону та наступне азотування в тліючому розряді дозволило приблизно в 1,7 рази збільшити товщину нітридного шару досліджених матеріалів, а корозійно-механічна зносостійкість у буферному розчині лимонної кислоти із pH 6,5 підвищилася в 1,45 ... 1,62 рази в порівнянні з відомим способом. Кавітаційно–ерозійна стійкість матеріалів у 3%-му розчині NaCl збільшилася в 4,7, 5,3 і 8,9 рази, відповідно для сталей 20, 45 і СЧ20.

1. Introduction

As noted in [1], various methods can be used to perform hydrogenation prior to chemical-thermal treatment (CTT). The most commonly used approaches are: 1) the electrolytic method under cathodic polarization in electrolytes; 2) the chemical method using acidic environments or hydrogen sulfide-containing solutions; 3) hydrogenation in a glow discharge.

The first two methods do not require special equipment, are performed at room temperature, and involve minimal energy consumption. The third method requires specific equipment and entails some energy costs. However, the combination of hydrogenation and subsequent glow discharge nitriding is expected to increase the thickness of the nitrided layer, which significantly improves its physicochemical and operational properties: strength and ductility [2], corrosion resistance [3], and fatigue endurance [4].

In the study of diffusion processes, significant attention is paid to the role of dislocations [5-9]. It has been established that diffusion along edge dislocations has the lowest activation energy. A.N. Minkevich [5] and S.Z. Bokshtein [6] explain the acceleration of diffusion by the fact that an increase in the concentration of dislocations or their intensive movement increases the density of vacancies, and the immediate proximity of dislocations can also contribute to the continuous formation of new dislocations [7–9].

At the same time, it is known that during hydrogenation, the density of vacancies, dislocations, and other crystal lattice defects increases in the surface layers of metals and alloys, which leads to an increase in microhardness and the appearance of residual compressive stresses in the surface layers, reaching 80–100 MPa [10]. Hydrogen (due to the high pressure of molecular hydrogen in internal “collectors”) also promotes the formation of porosity, local lattice distortions, the initiation and growth of microcracks, and even the restoration of cementite crystals in pearlite grains (decarburization) [11–13], all of which enhance the nitrogen diffusion coefficient. Moreover, during hydrogenation, grain boundaries of metals thicken due to the diffusion of S, Ar, and Sb along the grain boundaries, which weakens cohesion and consequently lowers the activation energy for diffusion of saturating elements [14].

From the above, it is evident that performing hydrogenation prior to glow discharge nitriding promotes the intensification of diffusion processes in the plasma discharge chamber. It should be emphasized that hydrogenation and nitriding processes are carried out sequentially in the same chamber and do not require any additional equipment [15].

2. Experimental

Nitriding of the samples was carried out using a UATR-1 unit designed for surface modification of parts, tools, and equipment by means of hydrogen-free glow discharge nitriding (HF-GDN) or similar diffusion vacuum processes. A key feature of this unit is the use of hydrogen-free gas mixtures (nitrogen-argon) as the saturating medium during the nitriding process, which eliminates hydrogen embrittlement of the metal surface. The absence of hydrogen in the saturating medium — a strong reducing agent that neutralizes oxygen — necessitates the use of highly pure gases (99.99%) and a high degree of sealing in the gas supply system and vacuum chamber. Even a small amount of oxygen (0.1%) can lead to oxide formation on the metal surface, drastically reducing nitrogen diffusion into the metal. Therefore, unlike systems that operate with hydrogen-containing atmospheres (such as ammonia or nitrogen-hydrogen mixtures), this unit includes an oxygen trap in the gas supply system to neutralize residual oxygen before the gas enters the vacuum chamber [16].

Cavitation–erosion wear resistance of the nitrided samples was investigated using a setup equipped with a magnetostrictive vibrator (MSV). The device includes an ultrasonic generator UZDN-A with a power of 150 W, vibration frequency of 22 kHz, and concentrator amplitude range of 5–85 μm. The setup is described in detail in [17]. It includes a dual-circuit cooling system with oppositely wound coils and devices for monitoring the near-surface

temperature of the samples during cavitation. As shown in prior testing [18], this dual-circuit system eliminates the influence of temperature factors on the intensity of cavitation–erosion wear of the sample surfaces.

For comprehensive investigation of corrosion–mechanical wear (CMW) of materials in a wide range of loads and working environments, a laboratory rig for end-face friction testing has been developed [19]. It makes it possible to obtain data on the kinetics of changes in electrode potential, friction and wear characteristics, surface temperature in the contact zone and the nature of friction depending on the potential of the system electrode.

The wear resistance of nitrided samples was evaluated under a load of 4 MPa and a sliding speed of 1 m/s in a buffer solution of citric acid with pH 6.5. Wear was assessed based on changes in the linear dimensions of the samples during testing.

The average surface temperature of the sample was measured using an electronic self-recording potentiometer KSP-2-23 at a distance of 1 mm from the friction surface. A chromel-alumel thermocouple with a diameter of 0.5 mm was used for this purpose.

Wear resistance of the friction pair was also evaluated by measuring the linear wear of the samples and recording the friction force. The friction force was measured by a strain-gauge method. The steady-state coefficient of friction was determined from friction torque diagrams recorded by a chart recorder. Linear wear was measured using an MKM dial gauge with a resolution of 1 μm.

The top sample, made of U8A steel hardened to HRC 61...63, featured two 3 mm-wide grooves on the working surface to ensure free access of the medium to the contact area. The bottom sample was made from the test material. The initial surface roughness of the samples was R_a = 0.63. Heating of the samples in the contact zone did not exceed 393 K, thus avoiding structural transformations.

Metallographic analysis after hydrogen-free glow discharge nitriding (HFGDN) was conducted on cylindrical samples cut along the diametral plane (two semi-cylinders were obtained). The exposed surfaces were ground and polished under distilled water flow and etched in a 3% nitric acid (HNO_3) solution in ethanol. The thickness of the nitride zone was measured using a MIM-10 microscope, which allows quantitative analysis of the phase and structural composition of the nitrided surfaces.

Microhardness was measured with a PMT-3 microhardness tester under a 0.98 N load, with hardness readings taken at the surface and at depths of 0, 25, 50, 100, 200, 300, and 500 μm from the surface.

X-ray phase analysis of the nitrided samples was carried out using a DRON-3 diffractometer with filtered radiation from an iron anode. Measurements were taken over an angular range of 2θ = 20° to 100° with a scanning step of 0.1° and an exposure time of 10 seconds. X-ray diffraction data were obtained from the surface into the depth of the nitrided layer.

3. Results and discussion

Based on the above, the prior hydrogenation of metals and alloys before chemical-thermal treatment (CTT), particularly hydrogen-free glow discharge nitriding (HFGDN), is expected to intensify nitrogen diffusion saturation processes. To obtain comparative data, parallel nitriding in glow discharge was carried out on samples with preliminary hydrogenation in a hydrogen medium at a pressure of 265 Pa and a temperature of 570 °C for one hour without argon, as well as hydrogenation with argon addition.

The addition of argon during hydrogenation in an ionized hydrogen medium significantly enhances the "hydrogen-induced strain hardening" of the metal crystal lattice. This manifests as an increase in the density of dislocations, vacancies, and the stress state of surface layers at the submicrostructural level [13, 20]. Hydrogenation in glow discharge with ionized hydrogen and argon was conducted using the same equipment and, most importantly, under the same conditions as the subsequent nitriding in a nitrogen–argon gas mixture. This eliminates the need for additional energy costs or time typically required for reheating and cooling the chamber.

After the hydrogenation stage, the hydrogen–argon gas mixture is collected into a cylinder for reuse. The discharge chamber is then filled with a nitrogen–argon gas mixture in a 75:25 volume ratio, respectively. The process parameters for hydrogenation and nitriding in glow discharge were selected based on prior studies [21–23], with further adjustments made during the course of this study.

Table 1 presents the results of nitriding for 40Kh steel and SCh20 cast iron with and with-

Table 1. Wear properties of nitrided 40Kh steel and SCh20 cast iron using the developed method (upper data –thickness of the nitride zone, μm; lower data – time of wear 30μm/m, *h*)

Material	Nitriding without adding argon	Nitriding with the addition of argon, vol. %		
		15	20	25
Steel 40Kh	17...20 2600	29...32 3640	30...33 3780	29...32 3590
Cast iron SCH20	20...23 2250	31...33 3370	35...40 3650	25...30 3310

out argon addition during the preliminary hydrogenation stage.

Hydrogenation was performed in a hydrogen atmosphere both without and with the addition of 15–25 vol.% argon at a pressure of 265 Pa and a temperature of 570°C for 1 hour. Glow discharge nitriding (GDN) was carried out under the same pressure and temperature in an atmosphere containing 75 vol.% nitrogen and 25 vol.% argon for 4 hours. For comparison purposes, parallel nitriding was performed on similar specimens previously hydrogenated in pure hydrogen without argon, under identical conditions (pressure – 265 Pa, temperature – 570°C, hydrogenation duration – 1 hour).

Under these selected conditions of hydrogenation and nitriding, the microhardness of the nitrided coatings obtained by the proposed method did not differ significantly from that obtained using the conventional GDN method and amounted to 7.8–8.2 GPa for 40Kh steel, and 8.0–8.5 GPa for SCh20 cast iron.

Wear resistance tests were conducted using a face-friction test machine under a load of 4 MPa and a sliding speed of 1 m/s in a buffer solution of citric acid with pH = 6.5. Wear resistance was evaluated by measuring changes in the linear dimensions of the samples during wear testing. Based on the data of Table 1, the thickness of the nitride zone in the coating formed by the proposed method (Author's Certificate USSR No. 1324334) increased by a factor of 1.5 to 1.9, while wear resistance improved by 1.45 to 1.62 times, compared to the conventional method.

For clarity, the results of preliminary tests are illustrated in Figures 1 and 2. In both cases of preliminary hydrogenation — with and without argon — an increase in the thickness of the nitride layer was observed (Figure 1). The maximum thickness was achieved at 20 vol.% argon. With further increases in argon content, the thickness of the nitride layer decreased for all tested materials. This trend is likely due to internal stresses exceeding the material strength limit, leading to relaxation through massive dislocation emission to the surface, formation of micropores, and a reduction of hydrogen pressure within internal voids (so-called "collectors").

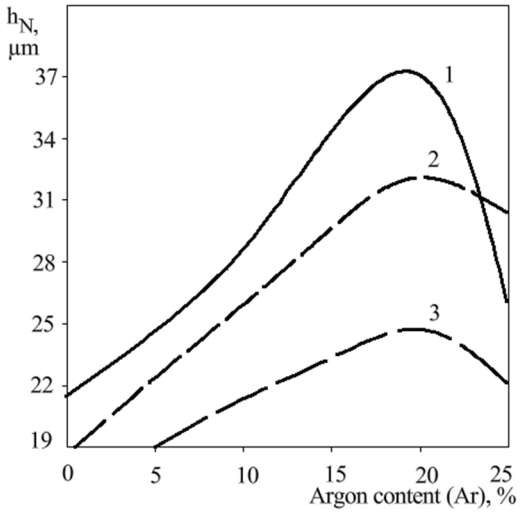

Fig. 1. Change in the thickness of the nitride layer h_N depending on the Ar amount (%) in the hydrogen mixture: 1 – cast iron SCh20; 2 – steel 40Cr; 3 – steel 45

Thus, preliminary ion-plasma hydrogenation in an atmosphere with 20% argon, followed by glow discharge nitriding, enabled an approximately 1.7-fold increase in nitride layer thickness.

Wear resistance tests also showed an increase by a factor of 1.5–1.6 compared to the conventional glow discharge nitriding (GDN) method. At the same time, the wear resistance of 40Kh steel (Figure 2, curve 1) was found to be higher than that of SCh20 cast iron (Figure 2, curve 2), despite the greater thickness of the nitride layer in the cast iron.

Taking into account the fatigue nature of corrosion-mechanical wear, the fatigue strength characteristics under both low-cycle and high-

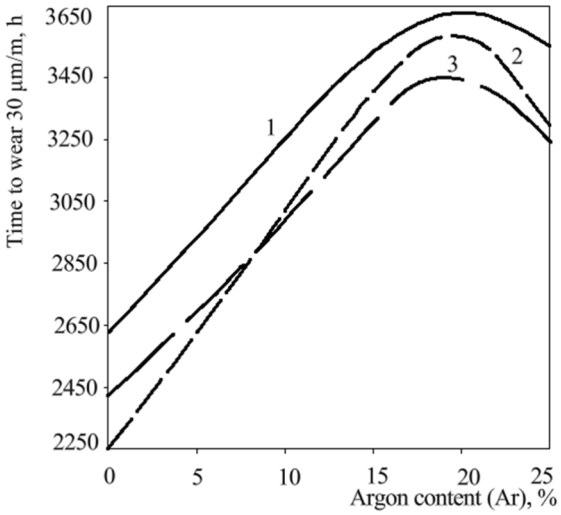

Fig. 2. Kinetics of wear of nitrided materials depending on the Ar amount in the hydrogen mixture: 1 – steel 40Cr; 2 – cast iron SCh20; 3 – steel 45

cycle loading are higher for steels than for cast irons, which explains the superior wear resistance of nitrided steels [25].

Furthermore, it has been established that fatigue failure sites develop within the diffusion layer located beneath the nitride zone, and the thickness of the nitride layer itself is not the determining factor for the intensity of wear processes in nitrided specimens [25, 26].

Similar results were obtained during the investigation of cavitation-erosion resistance of nitrided samples in a 3% aqueous sodium chloride solution (Fig. 3). After two hours of testing on the setup with a magnetostrictive vibrator (MSV) at an ultrasonic vibration frequency of 22 kHz and an amplitude of 36 μm, the wear resistance of nitrided samples without pre-hydrogenation increased by a factor of 5.3 for 45 steel (4.7 for 20 steel, and 8.9 for SCh20 cast iron). In the case of prior hydrogenation, the wear resistance of 45 steel increased by 7.5 times compared to the untreated 45 steel samples.

This effect can be explained by the improvement of both corrosion resistance and the physicomechanical properties of the surface layer, particularly an increase in the fatigue limit when exposed to aggressive environments.

Thus, ion-plasma hydrogenation prior to hydrogen-free glow discharge nitriding increases the thickness of the nitride zone on the nitrided surfaces, enhances their corrosion resistance, and improves their capacity for structural transformation depending on the external loading conditions due to the formation of a barrier effect of the "debris layer" [27].

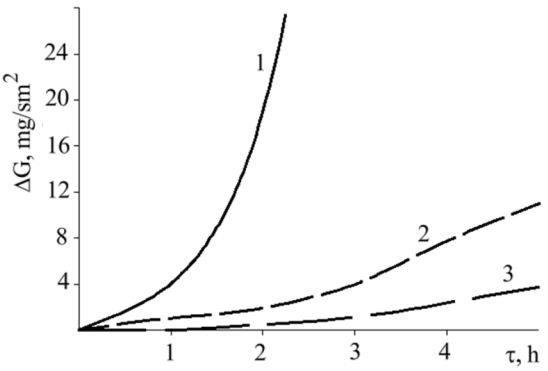

Fig. 3. Kinetics of mass loss during cavitation loading of steel 45 specimens in a 3% NaCl solution: 1 – untreated specimen (baseline condition); 2 – nitriding without prior hydrogenation; 3 – nitriding with preliminary ion-plasma hydrogenation with the addition of 20% argon.

4. Conclusions

1. Ion-plasma hydrogenation prior to glow discharge nitriding increases the thickness of the nitride zone on nitrided surfaces, enhances their corrosion resistance, and improves their corrosion-mechanical wear resistance due to an increased ability to undergo structural transformation depending on external loading conditions, caused by the barrier effect of the "debris layer".

2. Preliminary ion-plasma hydrogenation in an atmosphere containing 20% argon followed by glow discharge nitriding made it possible to increase the thickness of the nitride layer by approximately 1.7 times.

3. Due to the aforementioned factors, wear resistance under friction in an acidic environment increased by 1.5–1.6 times for structural steels 45, 40Kh, and gray cast iron SCh20 compared to traditional nitriding technology without preliminary hydrogenation. Cavitation-erosion resistance in a 3% NaCl solution increased by 4.7, 5.3, and 8.9 times for steels 20, 45, and gray cast iron SCh20, respectively.

References

1. M. S. Stechyshyn, M. Ye. Skyba, N. S. Mashovets', V. S. Kurskoy, and M. I. Tsepenyuk, The Effect of Pre-Hydrogenation on Thermodiffusion Chromizing and Cavitation Resistance of Carbon Steels and Gray Cast Iron, Metallofiz. Noveishie Tekhnol., 46, No. 12: 1173–1183 (2024) (in Ukrainian). DOI: 10.15407/mfint.46.12.1173
2. Stechyshyn M.S. Strength and Plasticity of the Surface Layers of Metals Nitrided in Glow Discharge / Stechyshyn, M.S., Stechyshyna, N.M.,

Martynyuk, A.V., Luk'yanyuk, M.M. // Materials Science: Springer (USA). – 2018. – 54 (5). – PP. 55 – 60. DOI: 10.1007/s11003-018-0156-5.
3. M. S. Stechyshyn, N. M. Stechyshyna, V. S. Kurskoi. Corrosion and Electrochemical Characteristics of the Metal Surfaces (Nitrided in Glow Discharge) in Model Acid MediaMarch 2018, Volume 53, Issue 5, pp 724–731.
4. Hirano M. Hydrogen-Free Plasma Nitriding Process for Fabrication of Expanded Austenite Layer on AISI 316 Stainless Steel Surface / Hirano M., Miura K., Ohtsu N. // Materials 2025. - 18(1). – p.140. https://doi.org/10.3390/ma18010140.
5. A. N. Minkevich, Chemical-thermal treatment of metals and alloys M: Mashinostroenie,1965 (in Russian).
6. S. Z. Bokshtein, Diffusion Processes, Structure, and Properties of Metals: (Springer US, 2013).
7. M.A. Krishtal, Diffusion mechanism in iron alloys. M: Mashinostroenie, 1972 (in Russian).
8. P. Anderson, J. Hirth, J. Lothe, Theory of Dislocations (Cambridge University Press, 2017)
9. I.K. Pokhodnya, V.I. Shvachko, S.V. Utkin, Materials Science 38, (2002). https://doi.org/10.1023/A:1020108328815.
10. M.Tamaki, Y. Tomii, N. Yamamoto, The role of hydrogen in plasma nitriding: Hydrogen behavior in the titanium nitride layer. January (2000) Plasmas & Ions 3(1):33-39. DOI:10.1016/S1288-3255(00)00108-8.
11. G. V. Karpenko, R. I. Kripyakevich, The influence of hydrogen on the properties of steel. Moscow: Metallurgizdat,1962 (in Russian).
12. V. I. Pokhmurs'kyi and K. B. Vasyliv, Mater. Sci., 48: 125 (2012).
13. V.I. Pokhmursky, V.V. Fedorov, Injection of water into diffusion processes in metals. Lviv: Phys.-Mech. Institute named after G.V. Karpenko NAS of Ukraine, 1998 (in Russian).
14. S. Rudenki, M. Kartsev, A. Korneev, A. Kunchenko, Y. Kunchenko, V. Marinin, V. Kovalenko, M. Bortnytska, T. Ryzhova, I. Lyashenko, and L. Martynenko, Science and Innovation, 18, No. 2: 66 (2022).
15. A.S. USSR No. 1324334. Method of combined processing of steel and cast iron products / A.I.Nekoz, N.A.Sologub, M.S.Stechishin., A.E.Rudyk, V.G.Kaplun. – Regulation decision of VNIIGPE from 1986 for application No. 3911489/02(83796).
16. Stechishina N.M. Corrosion-mechanical wear resistance of parts for grub production: monograph / N.M. Stechishina, M.S. Stechishin, N.S. Mashovets. – Khmnelnitsky: KhNU, 2022. – 181 p.(in Ukrainian).
17. Stechishin M.S. Cavitation-erosion wear resistance of dairy plant components: monograph / M.S. Stechishin, N.M. Stechishina, A.V. Martinyuk. – Khmelnitsky: KhNU, 2018. – 148 p. (in Ukrainian).
18. Nadya Stechyshyna. Method of assessment of cavitation-erosion wear resistance of metals in environments-electrolytes / Nadya Stechyshyna.1, Myroslav Stechyshyn1, Mykola Lukyanyuk1, Andriy Martynyuk, Mychailo Tsepenyuk, // Scientific Journal of TNTU - Tern.: 2023. vol 110, № 2, P. 68 –74
19. M.S. Stechyshyn, V.V. Lyukhovets, N.M. Stechyshyna, M.I. Tsepenyuk. Wear resistance of structural steels nitroded in cyclic-commuted discharge at limit modes of friction. // Problems of Tribology. – Khmelnytskyi: KHNU, 2022. V. 27. №3/105. P.27-33.
20. Pokhmursky V.I., Dalisov V.V., Golubets V.M. Increasing the durability of machine parts using diffusion coatings. K.: Nauk.dumka, 1998. 188 p. (in Russian).
21. M. Stechyshyn, M. Macko, O. Dykha, S. Matiukh, J. Musial. Tribotechnologies of strengthening and wear modeling of structural materials. Bydgoszcz: Foundation of Mechatronics Development, 2023. 196p.
22. Kaplun V. G., Kaplun V. G. Ion nitriding in hydrogen-free environments: monograph. Khmelnitsky: KhNU, 2015. 315 p. (in Russian).
23. Stechyshyn, M., Dykha, O., Stechyshyna, N., & Zdorenko, D. (2024). Methodology and results of the study of physical, mechanical and tribological characteristics of nitrided inner surfaces of long holes. Problems of Tribology, 29(2/112), 23–30. https://doi.org/10.31891/2079-1372-2024-112-2-23-30.
24. Pastukh I. M. Theory and practice of hydrogen-free nitriding in a glow discharge. Kharkov: National Scientific Center "Kharkiv Institute of Physics and Technology", 2006. 364 p.
25. M. S. Stechyshyn, M. E. Skyba, Yu. G. Sukhenko, M. I. Tsepenyuk Fatigue Strength of Nitrided Steels in Corrosion-Active Media of the Food Enterprises // Materials Science. - July 2019, Volume 55, Issue 1, pp 136–141.
26. Lakhtin Yu. M., Kogan Ya. D. Nitriding of steel. M: Mechanical Engineering. 1976. 256 p. (in Russian).
27. Stechyshyn M. S., Martynyuk A. V., Bilyk Y. M., Oleksandrenko V. P., Stechyshyna N. M. Influence of the ionic nitriding of steels in glow discharge on the structure and properties of the coatings // Materials Science. 2017. Vol. 53, No. 3. P. 343–349.