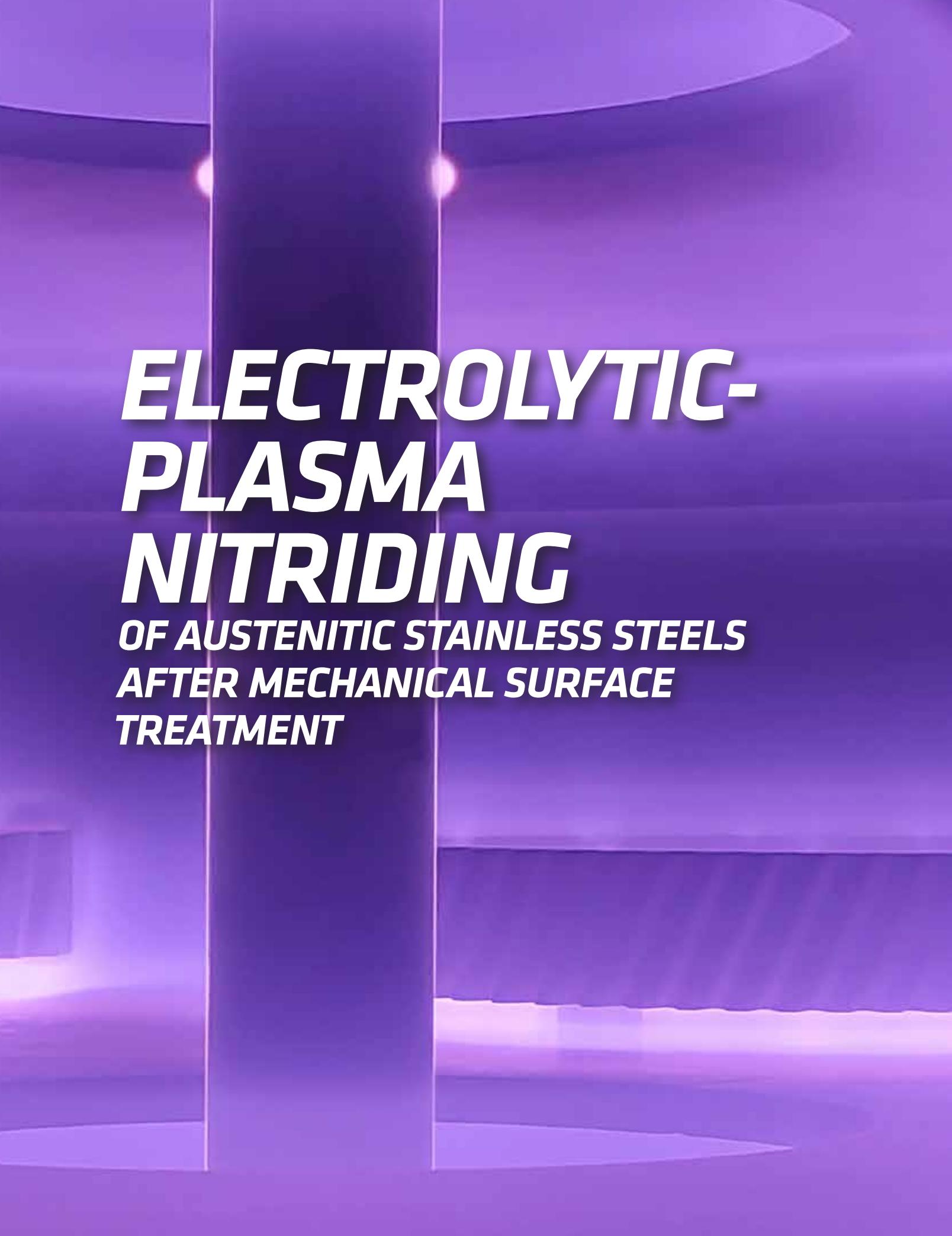


The background is a deep purple with a central vertical column and horizontal bands. There are glowing light effects, including two bright spots on the upper part of the central column and a horizontal band of light near the bottom. The overall aesthetic is futuristic and scientific.

ELECTROLYTIC- PLASMA NITRIDING

***OF AUSTENITIC STAINLESS STEELS
AFTER MECHANICAL SURFACE
TREATMENT***

A combined process – preliminary shot peening followed by electrolytic-plasma nitriding – was developed and investigated, providing a significant enhancement of nitrogen diffusion efficiency and the formation of expanded austenite in AISI 321 steel.

By **BAUYRZHAN RAKHADILOV, ZARINA SATBAYEVA, ALMASBEK MAULIT, NURLAT KADYRBOLAT, and ANUAR RUSTEMOV**

In this work, the effect of preliminary mechanical surface treatment on the kinetics of formation, phase composition, and functional properties of the nitrided layer during electrolytic-plasma nitriding (EPN) of austenitic stainless steel 12Kh18N10T (AISI 321) was investigated. In contrast to traditional approaches, for the first time, this work establishes a direct correlation between the degree of surface deformation induced by shot peening and the formation of the expanded austenite (γ N) phase under low-temperature plasma conditions. Quantitative X-ray phase analysis revealed a lattice parameter expansion of $\Delta a/a_0 \approx 1.4\text{--}1.8\%$ and a gradual transformation of γ -Fe $\rightarrow$ γ N without the formation of CrN nitrides at moderate intensity of preliminary treatment. According to SEM/EDS data and microhardness profiles, a multilayer structure was formed, consisting of a thin surface film of CrN/Fe₄N, a developed γ N zone with a thickness of 1215 μm , and a stable austenitic γ -Fe matrix. The surface microhardness increases to 880 ± 20 HV, while the friction coefficient decreases to 0.35-0.40, corresponding to a wear reduction of approximately 55% compared to the initial steel. The results provide a mechanistic understanding of nitrogen diffusion through defect-enriched subsurface layers and show that optimal preliminary deformation ($d = 6$ mm, $v = 40$ Hz, $t = 20$ min) promotes controlled formation of the γ N phase with minimal lattice instability. The proposed combined approach — shot peening + EPN — is an effective method for producing wear- and corrosion-resistant surfaces of austenitic steels under atmospheric plasma conditions.

1 INTRODUCTION

Austenitic stainless steels are widely used in power engineering, chemical machinery, and biomedical systems due to their high corrosion resistance, ductility, and structural stability during operation over a wide temperature range [1]. However, the low surface hardness and insufficient wear resistance limit their use in friction units, and in chloride-containing environments, localized corrosion (pitting and crevice) may occur [2,3]. Enhancing the durability of such materials requires the improvement of surface engineering methods aimed at strengthening while preserving corrosion resistance. One of the most effective methods of surface modification is nitriding — a process of diffusion saturation with nitrogen that leads to the formation of hard nitride phases and supersaturated solid solutions [4]. However, during conventional high-temperature nitriding (500-580°C), chromium nitrides precipitate, causing local depletion of Cr in the matrix and a reduction in passivating properties [5,6]. In addition, the dense FCC lattice of austenite slows down nitrogen diffusion, making the process less efficient without additional activation methods [2].

To prevent chromium nitride precipitation, low-temperature

nitriding ($\leq 450^\circ\text{C}$) has been developed, in which nitrogen dissolves in the austenite lattice, forming a metastable supersaturated phase — expanded austenite (S-phase) [7]. This structure combines high hardness ($\sim 1,000\text{--}1,200$ HV) with retained corrosion resistance, as it is not accompanied by CrN formation [8,9]. Borgioli [2] showed that the stability and formation of the S-phase are determined by the balance between the nitrogen diffusion rate and its chemical bonding; however, the mechanisms of these processes under different types of plasma treatment have not been fully studied [7]. Among nitriding technologies, the most widely used are gas nitriding, plasma (ion) nitriding, and electrolytic-plasma nitriding. Gas nitriding is carried out in an ammonia atmosphere but often leads to the formation of coarse nitride phases and a reduction in corrosion resistance [5]. Plasma nitriding, based on glow discharge in a vacuum, provides more uniform saturation at lower temperatures [9,10]; however, it requires complex equipment and is limited by the size of the treated parts.

An alternative is electrolytic-plasma nitriding (EPN), in which plasma is formed in the near-surface layer of the electrolyte under the action of pulsed discharges [11,12]. The method combines electrochemical action and local plasma heating, providing a high density of active species, accelerated saturation, and a reduced processing time compared to gas and vacuum-plasma nitriding [13]. In addition, EPN is carried out at atmospheric pressure, which makes the technology suitable for treating large-sized components [14].

Nevertheless, during EPN of austenitic steels, the hardened layer thickness is limited, which is attributed to the presence of a passive oxide film and the low diffusion mobility of nitrogen [14]. To increase the efficiency of the process, methods of preliminary mechanical treatment are actively used, creating a defective and nanostructured surface that promotes accelerated mass transfer [15,16,17,18]. In particular, shot peening and ultrasonic impact treatment form a zone with a high density of defects and residual stresses, which reduces the activation energy of diffusion and increases the saturation rate [17,19]. Shen et al. [15] showed that preliminary shot peening doubles the thickness of the nitrided layer during plasma nitriding of AISI 304, while Hashemi et al. [18] observed an increase in surface microhardness by 10-15%. Similar patterns have also been observed for nanostructured surfaces obtained by the SMAT method, where the growth of the nitrided layer reaches 40-50% [19]. Despite this, most studies have been carried out for vacuum-plasma technologies, whereas investigations on the effect of preliminary work hardening on electrolytic-plasma nitriding are extremely limited [11,14,20,21,22]. In particular, quantitative relationships between shot peening parameters, the degree of surface defectiveness, and the kinetics of S-phase

formation during EPN have not been established.

Despite extensive studies on gas and ion nitriding of austenitic steels [1-10, 15-19], the effect of preliminary mechanical surface treatment on the kinetics of electrolytic-plasma nitriding (EPN) remains poorly understood. Most published studies are devoted to vacuum-plasma or ion methods, whereas systematic investigations of EPN of pre-strained surfaces are practically absent. To date, a quantitative relationship between the defect structure of the surface, the characteristics of the plasma discharge, and the nitrogen diffusion rate during EPN has not been established. Thus, there is a clear scientific gap related to the influence of preliminary work hardening on the formation of the phase composition and properties of coatings obtained by the EPN method.

The present work is aimed at filling this scientific gap: The goal is to study the effect of preliminary shot peening on the saturation kinetics, structure, and properties of layers formed during electrolytic-plasma nitriding of 12Kh18N10T steel. This will make it possible to optimize combined processing modes and ensure an increase in surface hardness and wear resistance.

2 MATERIALS AND METHODS

Samples made of austenitic stainless steel 12Kh18N10T (foreign equivalent — AISI 321) with dimensions of $60 \times 60 \times 20$ mm were used for preliminary mechanical surface treatment. Hot-rolled sheet steel was used. The chemical composition of 12Kh18N10T steel is as follows: iron (Fe) 70.67%, chromium (Cr) 18.57%, nickel (Ni) 9.7%, manganese (Mn) 0.19%, titanium (Ti) 0.21%, silicon (Si) 0.23%, copper (Cu) 0.29%, carbon (C) 0.12%, phosphorus (P) 0.01%, sulfur (S) 0.01%. Before treatment, the surfaces of the samples were ground and then rinsed with distilled water to remove abrasive residues and contaminants. The preliminary mechanical treatment was carried out on a universal vibration stand SVU-2 (Figure 1), at the Engineering Center «Strengthening Technologies and Coatings». The stand is a single-mass sub-resonant-type unit. Structurally, the unit consists of stationary and vibrating parts. The oscillating part is designed as two parallel platforms to which an inertia-type vibration exciter is attached. The exciting force is generated by a system of unbalanced masses rotating by means of an electric motor. The SVU-2 unit is equipped with a control panel featuring a timer that allows setting the treatment duration over a wide range (from 0.1 seconds to 24 days) and a frequency controller that enables adjustment of vibration frequency from 1 to 50 Hz. The design includes eight vibration chambers made of ShKh15 steel, each with a volume of 100 cm^3 , allowing simultaneous processing of several samples under different conditions.

The essence of the preliminary mechanical surface treatment method lies in the impact of metallic balls with diameters ranging from 1 to 15 mm on the sample, placed in a chamber that is set into oscillatory motion within a specified frequency range by a vibration exciter. The vibration energy causes chaotic movement and repeated impacts of the balls on the sample surface, resulting in its strengthening and modification of the microrelief. To determine the optimal parameters of the preliminary mechanical treatment, the ball diameter (3, 4, 6, and 7.5 mm), treatment time, and vibration frequency were varied. The chamber was filled with metallic balls to approximately 80% of its volume. Based on the analysis of surface roughness and microhardness, the optimal treatment mode was selected. Next, for the electrolytic-plasma nitriding process, cubic samples with dimensions of $20 \times 20 \times 20$ mm were prepared (Figure 2). Before the process, the samples were thoroughly rinsed with distilled water to remove abrasive residues and contaminants. An aqueous solution consisting of 10% sodium carbonate (Na_2CO_3), 20% urea ($\text{CO}(\text{NH}_2)_2$), and 70% distilled water was used as the electrolyte, providing stable

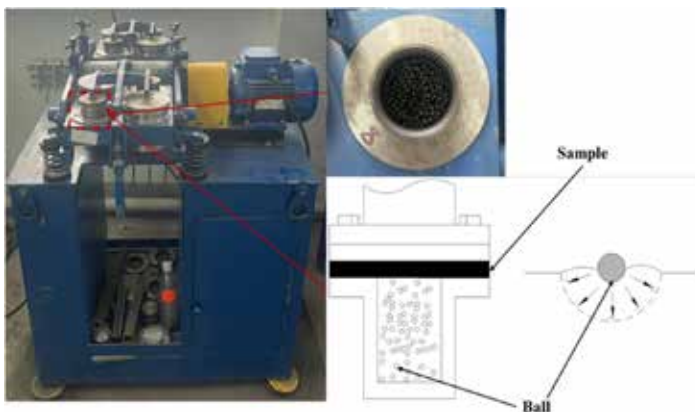


Figure 1: Diagram of the experimental setup for vibro-impact mechanical surface treatment (SVU-2 stand).

plasma burning and effective nitrogen diffusion into the surface layer of the material.

The experiment was carried out on an electrolytic-plasma thermochemical treatment unit equipped with a 40 kW DC power supply and a specialized processing chamber containing a plasma torch, as shown in Figure 3.

The nitriding process of the samples was carried out as follows: First, the working bath (5) was filled with the electrolyte; using a pump (4) installed at the bottom of the bath; the electrolyte was directed through pipelines (8) into the plasma torch (3) in the processing chamber (2); after passing through the plasma torch, the liquid returned to the bath through drain openings, ensuring a closed circulation loop; the electrolyte flow rate was maintained within 4-7 L/min, while the cooling water in the heat exchanger circulated at a rate of 3-6 L/min, allowing the electrolyte temperature to be kept within 40-50°C as the samples were heated to 500-550°C; the sample (6) was fixed in the holder so its working area was at a distance of 2-3 mm from the opening of the conical partition, through which the electrolyte jet entered, serving as a cooling and temperature-stabilizing medium; the anode (7) was connected to the positive pole of the power supply (1), and the samples, serving as the cathode, were connected to the negative pole. At the initial stage, a voltage of 320 V was applied for 10 seconds to rapidly heat the samples to the saturation temperature. Then, the voltage was reduced to 180 V, and the treatment was carried out for 10 minutes, maintaining the sample temperature within 500-550°C by adjusting the electrolyte circulation rate [23].

The surface roughness parameter R_a was measured using an HY2300 profilometer (Anytester, Hefei Co., Ltd., Hefei, China). X-ray phase analysis was performed on an Xpert PRO PANalytical diffractometer (PANalytical BV, Almelo, The Netherlands) at an anode voltage of 40 kV and a current of 30 mA, using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) in the 2θ range of 30-90°, with a step size of 0.02° and an acquisition time of 0.5 seconds per step. Phase processing and identification were carried out using the HighScore Plus v3.0.5 software package.



Figure 2: Samples after mechanical treatment prepared for electrolytic-plasma nitriding.

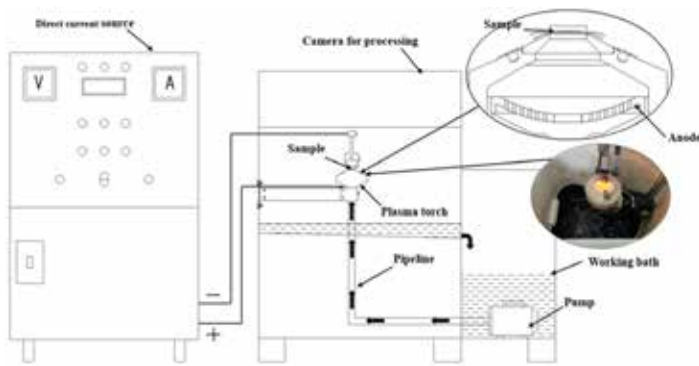


Figure 3: Setup for electrolytic-plasma nitriding of steels [23].

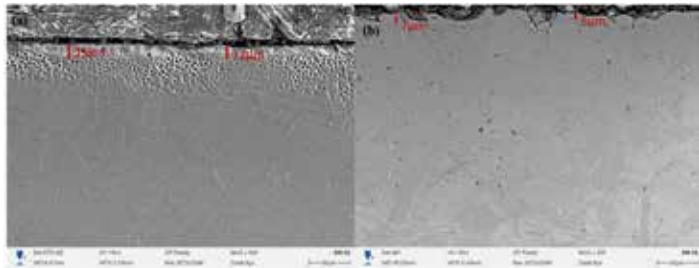


Figure 4: SEM microstructure of the cross-section of 12Kh18N10T (AISI 321) steel after electrolytic-plasma nitriding: (a) after mechanical surface treatment, (b) before mechanical surface treatment.

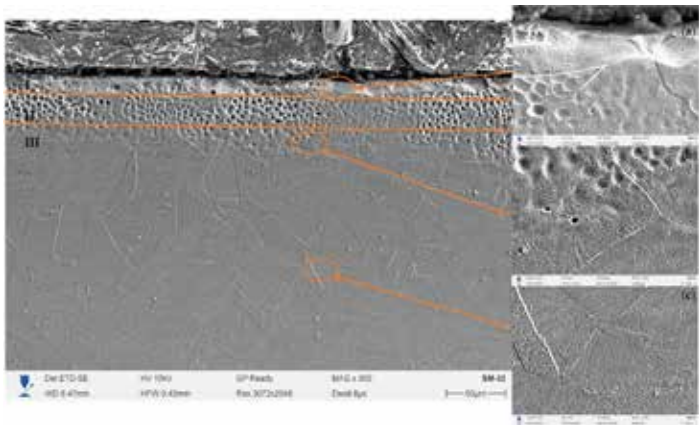


Figure 5: SEM microstructure of the cross-section of 12Kh18N10T (AISI 321) steel after preliminary mechanical surface treatment and subsequent electrolytic-plasma nitriding (sample 3), ×300 magnification: I – nitride zone; II – transition zone; III – initial structure. (a-c) – SEM images of the corresponding layers at ×2000 magnification.

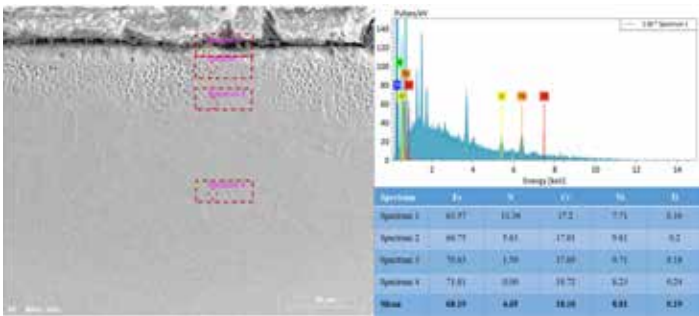


Figure 6: Local EDS analysis along the depth of the nitrided layer (sample 3) of austenitic stainless steel 12Kh18N10T (AISI 321).

To study the microstructure of the nitrided samples, after etching in a 10% oxalic acid solution, a scanning electron microscope SEM3200 (CIQTEK Co., Ltd., Hefei, China) was used. Microhardness was measured using a FISCHERSCOPE HM2000 instrument (Helmut Fischer

Sample	d, mm	t, min	v, Hz	Filling	Ra, μm	HV
1	3.0	20	40	80%	4.43	445.2
2	4.0	20	40	80%	2.19	388.9
3	6.0	20	40	80%	2.05	497.8
4	6.0	10	40	80%	3.36	439.9
5	6.0	30	40	80%	4.96	574.9
6	6.0	20	50	80%	2.54	514.6
7	6.0	20	30	80%	3.81	396.2
8	7.5	20	40	80%	3.03	515.6

Note: In all experiments, the containers were filled with metallic balls up to 80% of their volume. The selected modes (samples 3, 6, and 8) for subsequent electrolytic-plasma nitriding are highlighted in bold.

Table 1: Effect of metallic ball mechanical treatment parameters on surface roughness and microhardness (80% filling).

GmbH, Sindelfingen, Germany) under a load of 100 mN. Friction tests were carried out on a universal tribological tester TRB3 (Anton Paar, North Ryde, Austria) using the “ball-on-disk” method in accordance with ASTM G99 standard [24]. The test was conducted under dry friction conditions at a temperature of $25 \pm 1^\circ\text{C}$ and a sliding speed of 0.05 m/s. A 100Cr6 steel ball was used as the counterbody under a load of 10 N, and the friction coefficient was determined after the sample had traveled a distance of 60 m.

3 RESULTS AND DISCUSSION

3.1 Microstructure and Elemental Gradient

Comparison of the parameters of the preliminary mechanical treatment showed that the optimal mode should provide a compromise between the reduction in surface roughness and the increase in microhardness, both necessary for stable microarc ignition and accelerated nitrogen diffusion during EPN (Table 1). Compared to the initial surface ($R_a = 3.93 \mu\text{m}$; $HV = 236$), the best balance is achieved in three optimal modes: sample 3 ($d = 6 \text{ mm}$, $t = 20 \text{ min}$, $v = 40 \text{ Hz}$, filling 80%), which provides the minimum roughness $R_a = 2.05 \mu\text{m}$ with high microhardness $HV = 497.8$; sample 6 ($d = 6 \text{ mm}$, $t = 20 \text{ min}$, $v = 50 \text{ Hz}$), where a moderate $R_a = 2.54 \mu\text{m}$ is accompanied by increased work hardening $HV = 514.6$; and sample 8 ($d = 7.5 \text{ mm}$, $t = 20 \text{ min}$, $v = 40 \text{ Hz}$), demonstrating a combination of $R_a = 3.03 \mu\text{m}$ and the maximum $HV = 515.6$ among the selected modes, reflecting the higher impact energy of larger balls. The remaining variants are inferior in terms of combined criteria: For example, increasing the treatment time to 30 minutes (sample 5) yields a peak hardness of $HV = 574.9$ but is accompanied by an unacceptable increase in roughness ($R_a = 4.96 \mu\text{m}$), while reducing the frequency to 30 Hz (sample 7) worsens both parameters. Therefore, for subsequent electrolytic-plasma nitriding, samples 3, 6, and 8 were selected as the most appropriate, providing a smooth yet work-hardened surface ($R_a \approx 2.0\text{--}3.0 \mu\text{m}$; $HV \approx 500\text{--}516$), favorable for uniform microarc discharge and the formation of a high-quality nitride layer.

In Figure 4a, a uniform and dense surface layer with a thickness of about 12–15 μm is observed, corresponding to the expanded austenite (γN) zone. The structure is characterized by uniform contrast, absence of pores and nitride phase precipitates, indicating a metastable solid solution of nitrogen in the $\gamma\text{-Fe}$ lattice. The surface of the layer exhibits a more developed morphology with rounded craters caused by microplasma discharges, but without signs of overheating or local melting. The formation of a thicker γN layer after mechanical treatment is associated with an increased defect density of the crystal lattice and a higher dislocation density, which facilitates nitrogen diffusion into the metal. Similar results were reported in studies [25,26], where mechanical surface strengthening prior to nitriding promoted accelerated growth of expanded austenite.

In contrast, in Figure 4b, for the sample without preliminary mechanical treatment, the thickness of the hardened layer is only

5-7 μm , while the structure is less contrasted and contains individual microdefects along the layer boundary. The absence of active diffusion centers and the lower surface energy limit nitrogen penetration, leading to the formation of a thinner γN zone. A slight inhomogeneity is also observed in the near-surface region, indicating local variations in the plasma exposure intensity. Mechanical surface treatment prior to electrolytic-plasma nitriding has a significant effect on the nitrogen diffusion kinetics and the thickness of the formed hardened layer. The increase in the γN zone thickness to 12-15 μm after preliminary work hardening is explained by the higher number of crystal lattice defects and the formation of a substructure that facilitates accelerated interstitial nitrogen penetration.

Figure 5 shows the SEM microstructure of the cross-section of 12Kh18N10T (AISI 321) steel after preliminary mechanical surface treatment and subsequent electrolytic-plasma nitriding at a temperature of 500°C, voltage of 180 V, and duration of 10 minutes. The microstructure of the hardened layer exhibits a clearly defined zonal morphology and consists of three regions: I — nitride zone, II — transition zone, and III — initial austenitic structure. Detailed images of these zones at $\times 2,000$ magnification are shown in fragments (a-c).

The upper part of the layer (zone I) is represented by a dense and continuous near-surface structure about 1-2 μm thick, exhibiting increased contrast. This zone is characterized by the formation of a thin nitride film containing fine-dispersed chromium and iron particles (CrN , Fe_4N), which are formed as a result of surface supersaturation with active nitrogen ions. The uniformity and absence of pores indicate the stability of the plasma discharge and the uniformity of nitriding in the near-surface region. Such microstructural features are typical of low-temperature electrolytic-plasma saturation modes, where intense surface interaction occurs without significant melting or metal erosion.

Beneath the surface nitride zone lies the transition zone (II), about 10-15 μm thick, which constitutes the main hardened region. Here, the expanded austenite (γN) phase is formed — a metastable solid solution of nitrogen in the $\gamma\text{-Fe}$ lattice, free from chromium nitride precipitates. The microstructure of this zone is characterized by fine grains and uniform contrast, reflecting the high defect density of the crystal lattice and the presence of significant internal compressive stresses. Such features are caused by the interstitial incorporation of nitrogen atoms, which leads to an increase in the lattice parameter and the formation of expanded austenite. The observed subgrain boundaries and characteristic diffusion flow lines in micrographs (b) indicate active atomic migration processes in the near-surface region. The thickness of this zone is consistent with the results obtained at similar temperatures in studies [27,28], where the formation of a γN structure without CrN precipitates was also observed at temperatures up to 550°C. During EPN, microdischarges are localized at the protrusions of the surface microrelief and produce short-term local melting/boiling; when polished across this zone, such craters are cut and appear as rounded dark cavities with a diameter of about 0.5-2 μm , arranged in a band parallel to the surface. Below in depth (region III), the matrix without pores is observed, showing characteristic slip traces.

Below lies zone III, corresponding to the original austenitic structure. It is characterized by a coarse-grained morphology, low contrast, and the absence of phase transformations. The transition between layers II and III is gradual, confirming the diffusion nature of the hardened layer formation and the good metallurgical bonding of the modified zone with the substrate. Residual traces of plastic deformation caused by mechanical treatment are observed in this region; however, they do not compromise the integrity of the layer.

A comparison of the zone structures allows the conclusion that

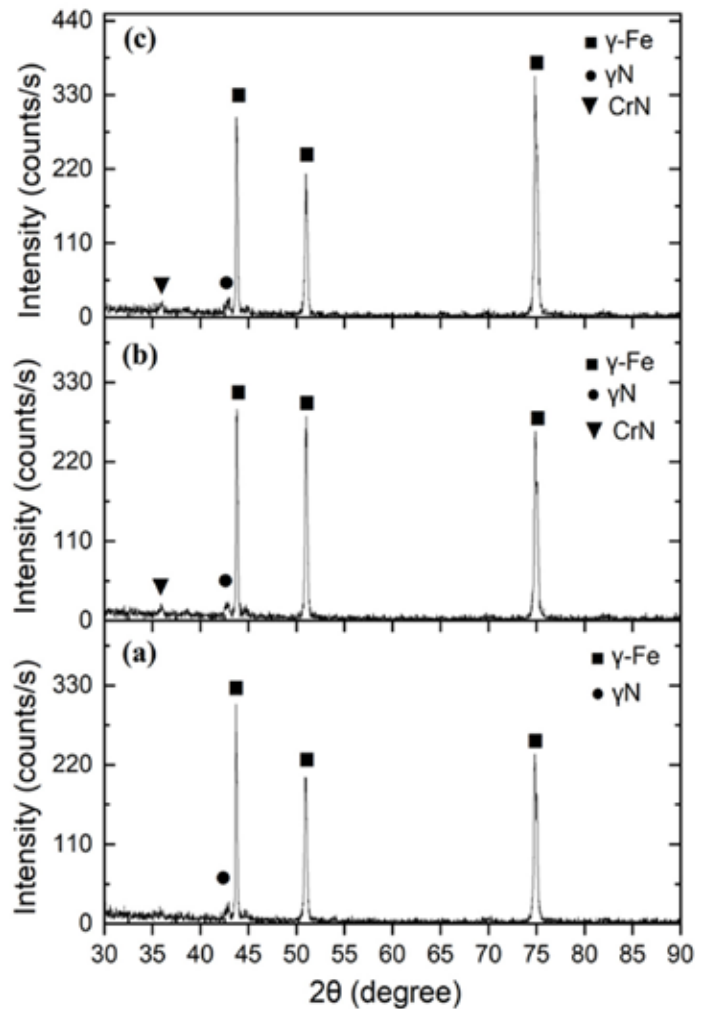


Figure 7: X-ray diffraction patterns of 12Kh18N10T (AISI 321) steel after electrolytic-plasma nitriding under different modes of preliminary mechanical treatment: (a) sample 6; (b) sample 8; (c) sample 3.

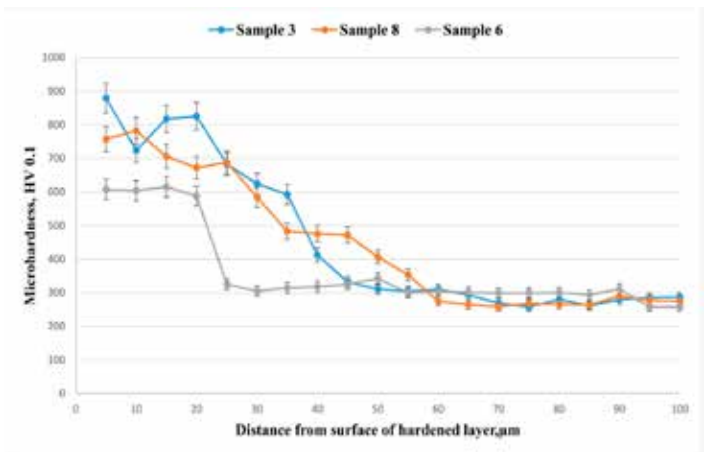


Figure 8: Distribution of microhardness HV0.1 as a function of distance from the surface of the hardened layer for samples 3, 8, and 6 after electrolytic-plasma nitriding. The vertical “whiskers” indicate the standard deviation (SD) based on a series of measurements ($n = 5$) at each point.

preliminary mechanical surface treatment significantly enhances the nitriding processes. The increased dislocation density, along with the presence of microrelief and microcracks after treatment, creates additional pathways for interstitial nitrogen diffusion, promoting the growth of the γN zone and a more uniform nitrogen distribution with depth. As a result, a multilayer system is formed: a thin nitride film,

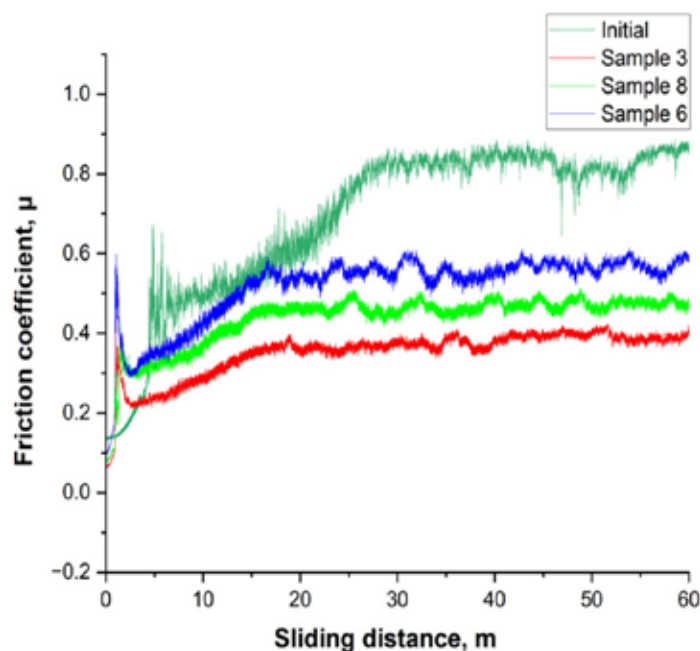


Figure 9: Friction coefficient (μ) as a function of sliding distance for the initial 12Kh18N10T (AISI 321) steel and samples 3, 8, and 6 after electrolytic-plasma nitriding.

between the hardened zone and the substrate, which ensures high adhesion strength of the coating.

The results of the EDS analysis (Figure 6) show a gradual decrease in nitrogen concentration from 11.36 at.% at the surface to 1.6 at.% at a depth of ~ 10 – 12 μm , and its almost complete absence in the core. At the same time, the proportion of iron and chromium increases, while the content of nickel and titanium remains stable. The obtained data indicate the formation of a stable chemical and structural gradient characteristic of low-temperature nitriding. The high nitrogen content in the near-surface zone leads to an expansion of the γ -phase lattice parameter and an increase in microhardness, while the gradual decrease in concentration toward the substrate prevents the formation of brittle CrN nitrides. Thus, the developed nitrogen distribution gradient confirms the effectiveness of the selected EPN mode and its compliance with the optimal conditions for the formation of functional γN layers with enhanced wear and corrosion resistance.

According to SEM data (Figure 4 and Figure 5), the structure of the modified layer exhibits a multilayer configuration typical of low-temperature EPN:

- » Surface nitride film 1–2 μm thick ($\text{CrN}/\text{Fe}_4\text{N}$),
- » Transition zone 10–15 μm thick consisting of expanded austenite (γN),
- » Stable γ -Fe substrate.

The transition zone is characterized by a fine-grained structure and high contrast, indicating intense lattice distortions. The Cr and Ni contents remain virtually unchanged, confirming the absence of local chromium depletion that could impair corrosion resistance. Such a distribution ensures a smooth transition of mechanical properties and high adhesion between the modified layer and the base metal. As seen from the elemental distribution profile, the nitrogen concentration decreases from 17 at.% at the surface to less than 1 at.% at a depth of 20 μm , which corresponds to a diffusion saturation mechanism. However, the EDS method has limited sensitivity to low atomic number elements and does not allow detailed visualization of local enrichment and depletion regions. In a recent study [29], it was shown that the use of EPMA provides high spatial resolution for elemental distribution mapping. In future work, EPMA is planned to be used to refine the structure of the γN layer.

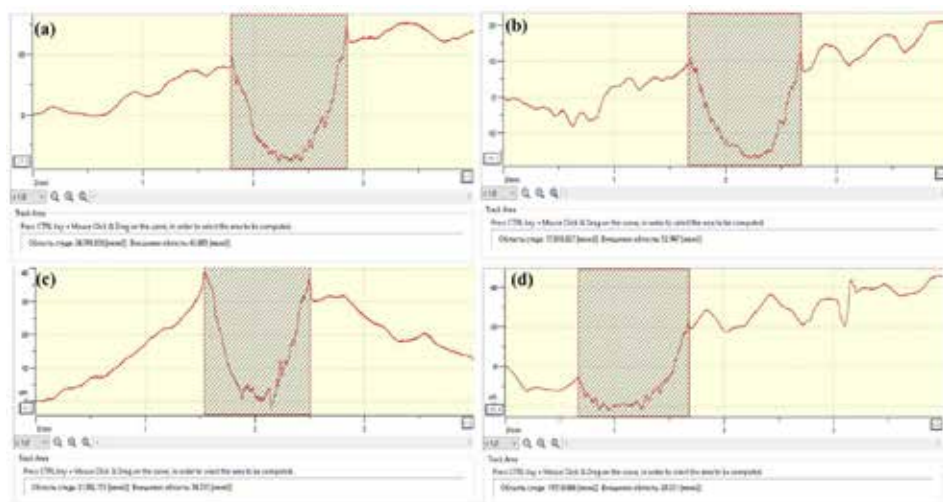


Figure 10: Cross-sectional profilograms of wear tracks of 12Kh18N10T (AISI 321) steel after tribological tests in the initial state and after electrolytic-plasma nitriding under different modes of preliminary mechanical treatment. (a) initial, (b) sample 6, (c) sample 8, (d) sample 3.

a developed expanded austenite region, and a stable austenitic substrate. Such a combination provides an optimal balance between high surface hardness, adhesion, and preservation of corrosion resistance.

In Figure 5, the SEM study of the cross-section of 12Kh18N10T (AISI 321) steel after electrolytic-plasma nitriding shows a clearly pronounced zonal structure, indicating the diffusion nature of saturation. In the near-surface region, a dense, porous-granular layer with pronounced contrast is observed, corresponding to the γN -phase of supersaturated austenite. Deeper in the layer, the structure gradually becomes more homogeneous, with a decrease in the number of micropores and dislocation accumulations, indicating a transition to the sublayer of deformed γ -austenite and further to the original γ -matrix. Such a gradient structure of the layer confirms the diffusion mechanism of nitrogen incorporation during electrolytic-plasma treatment and the preservation of a smooth structural transition

3.2 Phase Evolution During EPN

X-ray phase analysis shows that, in all cases, the matrix retains its austenitic FCC structure: Intense γ -Fe reflections are observed at $2\theta \approx 43^\circ$, 50° , and 74° , corresponding to the (111), (200), and (220) planes. At the low-angle side of the (111) peak, a broadened shoulder is observed in the region of $2\theta \approx 41$ – 42° , which is characteristic of expanded austenite γN (S-phase), formed as a result of supersaturation of the γ -Fe lattice with nitrogen atoms. For sample 3 (Figure 7a), the γ -Fe peaks remain sharp, and the γN shoulder is weakly expressed; nitride phases such as CrN are absent.

This indicates the predominance of nitrogen in solid solution and the formation of a stable single-phase γ -Fe(N) structure without chromium nitride precipitates. Such an X-ray pattern indicates a uniform nitrogen distribution under limited saturation, which is typical for moderate surface work hardening that creates optimal conditions

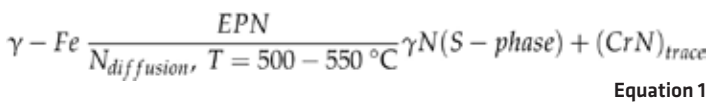
for diffusion without local supersaturation. In sample 8 (Figure 7b), the γ N shoulder becomes more pronounced, and a weak CrN (111) reflection appears in the region of $2\theta \approx 37^\circ$. The increase in the γ N peak intensity reflects a higher degree of nitrogen incorporation into the γ -Fe lattice, while the appearance of the nitride phase indicates the onset of local CrN precipitation under increased surface defect density. Such behavior is associated with the larger ball size used during mechanical treatment ($d = 7.5$ mm), which promotes deeper work hardening and increases dislocation density, thereby accelerating nitrogen diffusion into the metal.

The most pronounced changes were recorded for sample 6 (Figure 7c), which was treated at an increased vibration frequency ($\nu = 50$ Hz). The γ N peak becomes more intense and shifts toward lower angles, indicating a significant lattice parameter expansion due to the high concentration of interstitial nitrogen. At the same time, a weak appearance of CrN (111) is observed, with its intensity remaining significantly lower than that of the γ -Fe peaks. This indicates the partial nucleation of nitride inclusions while maintaining the dominant γ N phase, representing a state close to the solubility limit of nitrogen in austenite.

A comparison of the samples demonstrates a consistent evolution of the phase composition: from γ -Fe + weak γ N (without CrN) in sample 3 to γ -Fe + γ N + traces of CrN in samples 8 and 6. The enhancement of γ N reflections and the appearance of CrN correlate with the increased energy intensity of mechanical treatment, which leads to higher defect density, accelerated nitrogen diffusion, and a greater degree of lattice supersaturation. At the same time, in all cases, the main γ -Fe matrix is preserved, confirming the metastable nature of the γ N phase and the absence of global austenite decomposition.

X-ray phase analysis (Figure 7) showed that, after nitriding, all samples retain the austenitic γ -Fe lattice of the FCC type. The formation of expanded austenite (γ N) is confirmed by the systematic shift in the (111) reflection toward lower diffraction angles ($\Delta 2\theta \approx 1.3$ – 1.6°). The corresponding lattice parameter expansion amounted to $\Delta a/a_0 \approx 1.4$ – 1.8% , indicating supersaturation of γ -Fe with nitrogen atoms incorporated into interstitial sites.

For sample No. 3, the diffraction pattern is characterized by a single-phase γ -Fe(N) structure with a pronounced γ N shoulder and no CrN peaks. For samples No. 6 and No. 8, weak CrN (111) reflections are observed at $2\theta \approx 37^\circ$, indicating partial nitride formation at higher deformation energy. This pattern demonstrates the presence of a threshold energy, the exceeding of which leads to local overheating and nitrogen segregation with the formation of CrN. The sequence of phase transformations can be expressed in Equation 1:



Thus, moderate preliminary deformation ($d = 6$ mm, 40 Hz) promotes predominant formation of the γ N phase, whereas excessive treatment leads to local decomposition of the supersaturated solid solution.

3.3 Mechanical Properties After EPN

Microhardness profiles (Figure 8) along the depth (HV_{0.1}) for the three modes show pronounced surface hardening followed by a monotonic decrease to the substrate level (~ 260 – 300 HV) at a depth of 70–90 μm . Sample 3 ($d = 6$ mm, 20 min, 40 Hz) exhibits a maximum surface hardness of ~ 880 HV at 5 μm and maintains ≥ 600 HV up to ~ 35 μm ; the effective depth of the hardened layer (down to ~ 300 HV) is ~ 58 – 60 μm . Sample 8 ($d = 7.5$ mm, 20 minutes, 40 Hz) shows a slightly lower surface hardness of ~ 750 – 780 HV but a comparable layer depth (~ 58 – 60

μm), while maintaining 450–500 HV in the 30–45 μm range. Sample 6 ($d = 6$ mm, 20 minutes, 50 Hz) is characterized by the lowest values: surface hardness of ~ 600 – 620 HV and a sharp “break” in the curve at 20–25 μm , dropping to ~ 320 HV, resulting in a layer thickness of ~ 25 – 30 μm . The obtained hierarchy ($3 > 8 > 6$ in terms of hardening level and depth) is consistent with the XRD phase analysis: samples 3 and 8 exhibit a more pronounced γ N phase (expanded austenite), providing higher hardness and greater hardening depth, whereas sample 6 contains a smaller fraction of γ N and forms a thinner layer.

Microhardness profiles (Figure 8) exhibit an exponential decrease with depth, which can be described by Equation 2:

$$HV(x) = HV_s + (HV_0 - HV_s) \exp\left(-\frac{x}{\delta}\right)$$

Equation 2

where HV_s is the surface hardness, HV_0 is the substrate hardness, and δ is the effective diffusion depth (~ 60 μm for sample No. 3). The surface hardness reaches 880 ± 20 HV, which is 3.7 times higher than that of the initial state. The increase in hardness directly correlates with the fraction of the γ N phase, confirming that strengthening is caused by lattice expansion and interstitial incorporation of nitrogen.

The behavior of the friction coefficient (μ) under dry sliding clearly distinguishes the initial steel from the nitrided samples, as shown in Figure 9. After a short running-in stage (first ~ 1 – 2 m), the initial state exhibits a high and noisy plateau with $\mu \approx 0.80$ – 0.90 , indicating intense formation and rupture of an oxide-abrasive third body. For sample 6, a lower and more stable level of $\mu \approx 0.55$ – 0.60 is established; however, the amplitude of fluctuations remains noticeable, and a tendency for an increase is observed at 40–60 m, which corresponds to the smaller thickness of the hardened layer (~ 25 – 30 μm) and the earlier involvement of the substrate in contact. Sample 8 exhibits intermediate behavior with a plateau of $\mu \approx 0.45$ – 0.50 , stable throughout the entire track length, reflecting a deeper hardened layer (~ 60 μm) and stable tribofilm formation.

The best result is shown by sample 3: after the running-in stage, the lowest plateau of $\mu \approx 0.35$ – 0.40 is formed with minimal signal noise, indicating stable performance of the γ N surface layer and a low proportion of adhesive/abrasive events. Compared to the initial state, the reduction in friction level is approximately 55% (sample 3), 45% (sample 8), and 35% (sample 6). Overall, this is consistent with the XRD and microhardness results: samples 3 and 8, which have a higher fraction of expanded austenite γ N and a thicker layer, provide lower and more stable friction, whereas sample 6, with a thinner modified layer, exhibits higher μ values and greater instability during prolonged sliding.

Figure 10 presents the cross-sectional profilograms of wear tracks obtained after tribological tests of austenitic stainless steel 12Kh18N10T samples in the initial state (a) and after electrolytic-plasma nitriding under different modes of preliminary mechanical treatment: sample 6 (b), sample 8 (c), and sample 3 (d). For the initial steel (Figure 10a), a wide and deep wear track profile is characteristic, with a wear area of $\approx 1.76 \times 10^4 \mu\text{m}^2$ and significant bottom roughness. Such morphology indicates the predominance of an adhesive-abrasive wear mechanism with plastic metal flow along the edges of the groove.

After electrolytic-plasma nitriding, a significant reduction in wear area and smoothing of the profile are observed. For sample 6 (Figure 10b), the depth of the wear track decreases by almost 1.5 times ($S = 2.67 \times 10^4 \times 1.95 \times 10^4 \mu\text{m}^2$), which is associated with the formation of a hardened layer 25–30 μm thick. However, the profile shape remains asymmetric, indicating partial destruction of the γ N layer in the central contact zone due to insufficient thickness and local involvement

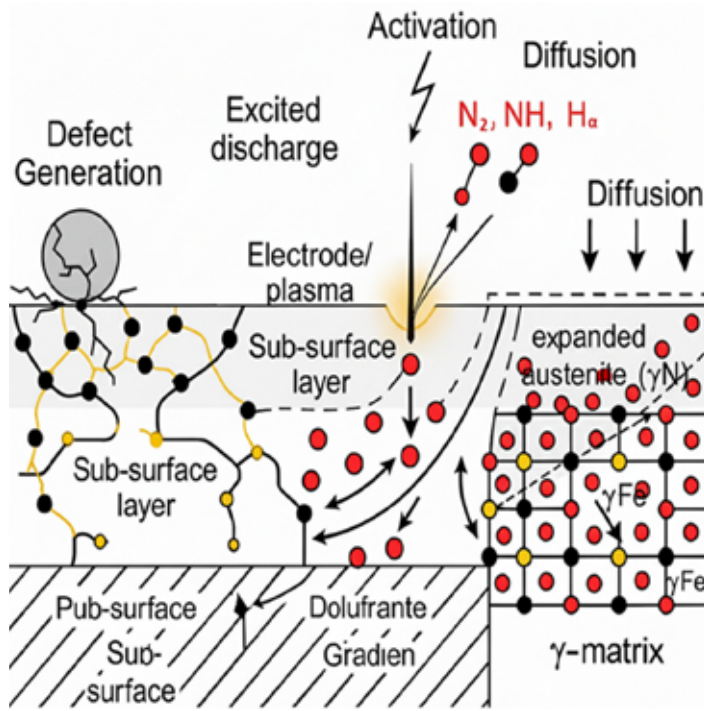


Figure 11: Mechanism of nitrogen diffusion through the defected subsurface layer during electrolytic-plasma nitriding of pre-strained austenitic steel 12Kh18N10T (AISI 321).

of the substrate in friction. For sample 8 (Figure 10c), the wear depth and area are even smaller ($S = 2.19 \times 10^4 \mu\text{m}^2$); the profile contour is symmetrical, and the track edges show no pronounced bulging. This confirms the stability and uniformity of the tribofilm, which is consistent with the optimal γN layer thickness ($\sim 60 \mu\text{m}$) and high microhardness ($\sim 750\text{--}780 \text{HV}$). The most favorable profile is exhibited by sample 3 (Figure 10d): minimal wear depth ($\sim 10 \mu\text{m}$), narrow contact zone ($S = 1.95 \times 10^4 \mu\text{m}^2$), and smooth contours, indicating high wear resistance and stable friction without seizure.

This confirms that under moderate preliminary mechanical treatment parameters ($d = 6 \text{ mm}$, $v = 40 \text{ Hz}$, $t = 20 \text{ min}$), an optimal expanded austenite γN layer is formed, providing a combination of high hardness, plasticity, and low friction coefficient ($\mu \approx 0.35\text{--}0.40$). Comparison of the profilograms confirms a direct correlation between wear morphology and the microstructural state of the layer: as the profile depth and track area decrease, the fraction of γN phase increases, CrN decreases, and the stability of the tribosystem improves. Wear profiles showed a decrease in wear track area from $1.76 \times 10^4 \mu\text{m}^2$ (initial state) to $1.95 \times 10^4 \mu\text{m}^2$ (sample No. 3) and a change in the dominant mechanism from adhesive–abrasive to mild oxidative wear, characterized by the formation of a stable tribofilm. The main mechanism of improved wear resistance and reduced friction is defect-assisted diffusion, which ensures stabilization of the γN phase and the formation of a self-lubricating surface layer during friction.

The specific volumetric wear (μ) was calculated using the classical tribological relationship in Equation 3:

$$\mu = \frac{V}{F \times S}$$

Equation 3

where

» μ : specific volumetric wear, $\text{mm}^3/(\text{N}\cdot\text{m})$.

» V : volume of the worn material, mm^3 , determined by integrating

the wear profile area.

» F : applied load, N .

» S : total sliding distance, m .

Analysis of the wear track profilograms (Figure 10) showed that electrolytic-plasma nitriding significantly reduces the depth and area of wear compared to the initial 12Kh18N10T (AISI 321) steel. The greatest reduction in wear parameters is observed for sample No. 3, which underwent preliminary mechanical treatment with optimal intensity ($d = 6 \text{ mm}$, $v = 40 \text{ Hz}$). This effect is attributed to the formation of a uniform and ductile γN phase possessing increased hardness and resistance to adhesive-abrasive damage.

Samples No. 6 and No. 8 show an intermediate reduction in wear, which is associated with partial formation of nitride phases and local reduction in the plasticity of the surface layer under more intense mechanical treatment. The calculation of specific volumetric wear showed a decrease in μ from $1.40 \times 10^{-3} \text{ mm}^3/(\text{N}\cdot\text{m})$ for the initial state to $0.92 \times 10^{-3} \text{ mm}^3/(\text{N}\cdot\text{m})$ for sample No. 3, corresponding to approximately a 35% reduction in material loss.

The obtained results confirm that moderate mechanical activation of the surface prior to EPN is a key factor in enhancing the wear resistance of austenitic steel.

3.4 Mechanism of Defect-Assisted Nitrogen Diffusion

Schematically, the mechanism of nitrogen transport during EPN (Figure 11) can be represented as follows:

1. Defect generation stage: Preliminary shot peening creates a high density of dislocations and grain boundaries that serve as channels for fast diffusion.

2. Activation stage: Cathodic discharges in the electrolyte generate active species N_2^+ , NH , and $\text{H}\alpha$ with energies of 3–5 eV, which are adsorbed on the defect sites of the surface.

3. Diffusion stage: Nitrogen atoms migrate along dislocation networks and sub-boundaries, reducing the effective activation energy of diffusion by approximately 0.5 eV compared to the untreated surface.

4. Phase stabilization stage: Residual compressive stresses suppress CrN precipitation and stabilize the supersaturated γN lattice up to 550°C .

This mechanism explains the accelerated layer growth and lattice expansion in pre-deformed samples and confirms that mechanical activation enhances both the thermodynamic and kinetic components of the plasma diffusion process

4 CONCLUSIONS

1. A combined process — preliminary shot peening followed by electrolytic-plasma nitriding (EPN) — was developed and investigated, providing a significant enhancement of nitrogen diffusion efficiency and the formation of expanded austenite (γN) in 12Kh18N10T (AISI 321) steel.

2. Mechanical treatment creates a defect-enriched subsurface layer with a high dislocation density and residual compressive stresses, which reduces the activation energy of nitrogen diffusion. As a result, the growth rate of the modified layer increases by more than two times compared to the untreated steel.

3. Under optimal preliminary treatment parameters ($d = 6 \text{ mm}$, $v = 40 \text{ Hz}$, $t = 20 \text{ minutes}$), a 12–15 μm thick layer is formed with a uniform nitrogen distribution and without chromium nitride precipitation. The surface microhardness reaches $\sim 880 \text{ HV}$, and the effective hardening depth is $\sim 60 \mu\text{m}$.

4. The fraction of the γN phase directly correlates with the improvement of tribological characteristics: The friction coefficient decreases to 0.35–0.40 (–55% compared to the initial state), and the wear track depth decreases from ~ 25 to $\sim 10 \mu\text{m}$.

5. Increasing the vibration frequency (≥ 50 Hz) or ball diameter (> 7.5 mm) causes excessive lattice deformation and partial formation of CrN, which reduces the plasticity and stability of the layer; therefore, a moderate level of mechanical activation is preferable.

6. The established relationship between deformation intensity, defect density, and nitrogen diffusion provides a basis for optimizing EPN parameters. The combined treatment enhances hardness, wear, and friction resistance without loss of corrosion resistance, opening prospects for its application in power engineering, mechanical engineering, and medical equipment. 🔥

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