

Article

Electrolytic Plasma Nitriding of Medium-Carbon Steel 45 for Performance Enhancement

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Abstract: This article analyzes the effect of electrolytic plasma nitriding on the performance of medium-carbon steel 45 under increased mechanical loads and in aggressive environments. Nitrided samples in carbamide electrolytes, both with and without the addition of ammonium nitrate, were compared to the initial material. SEM with EDX and XRD analysis was used to examine the microstructure and phase composition of nitrided samples. Wear resistance was studied using the ‘ball-on-disk’ method and Vickers microhardness testing, while corrosion resistance was studied using potentiodynamic polarization curves. The study results show that the sample without ammonium nitrate demonstrated better mechanical and corrosion properties due to a more homogeneous and denser nitride layer, approximately 10 μm thick, containing phases FeN and Fe₄N. Its wear resistance doubled compared to that of the initial sample. The sample treated in an electrolyte with the addition of ammonium nitrate demonstrated a higher current density (2.8672×10^{-5} A/cm²) and a lower corrosion potential (−0.565 V) compared to the initial sample ($i_{\text{corr}} = 1.8971 \times 10^{-5}$ A/cm², $E_{\text{corr}} = -0.480$ V) and the sample without ammonium nitrate ($i_{\text{corr}} = 1.7315 \times 10^{-5}$ A/cm², $E_{\text{corr}} = -0.376$ V). This is due to the formation of an uneven nitride layer and the presence of microcracks on the surface.

Keywords: electrolytic plasma nitriding; nitride layer; aqueous electrolyte; wear resistance; diffusion saturation; surface modification



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1. Introduction

Medium-carbon steel, containing approximately 0.3% to 0.6% carbon, is widely used for the production of various machine-building parts, such as shafts, gears, fasteners, and studs. Its popularity is due to its low cost and balanced properties of strength, ductility, and suitability for heat treatment [1,2]. Due to the exposure of these parts to high mechanical and thermal stresses, as well as shock load, additional surface modification is required to improve their operational characteristics. Surface modification processes are essential for enhancing the mechanical properties of materials, such as wear resistance, hardness, and durability. The most common methods include quenching, cementation, nitrocementation, and nitriding. Quenching increases hardness and strength through martensite transformation, but it can also cause internal stresses and deformations. Cementation diffuses carbon into steel, creating a hardened surface layer while maintaining a strong core, but it requires a long processing time. Nitrocementation combines the benefits of nitriding and cementation, enhancing hardness and corrosion resistance. Nitriding, especially electrolytic

plasma nitriding, forms solid nitride compounds on the surface at relatively low temperatures, reducing the risk of deformation and cracking while providing high wear resistance and corrosion protection. Among these methods, nitriding is considered gentler, as it is typically performed at relatively low temperatures and does not involve the decomposition of austenite during cooling. As a result, thermal and transformational deformations contribute less to distortion compared to cementation or induction hardening [3,4]. The gas nitriding of medium-manganese forging steel has shown that this method significantly increases surface hardness (up to 950 HV) due to the formation of nitride phases. However, the process requires a long treatment time of more than 10 h and high temperatures, which may limit its use for parts sensitive to thermal effects [5]. Ionic nitriding [5,6] allows for greater nitrogen diffusion depth and the precise control of the process temperature. It is also characterized by lower energy consumption and the ability to process complex shapes, but it requires more sophisticated equipment. Electrolytic plasma nitriding (EPN) [7–10] is characterized by a high processing speed and low energy consumption, making it preferable for mass production. Additionally, it is more environmentally friendly, as it does not use toxic gases.

One of the main advantages of EPN is a significant increase in microhardness. A number of studies have shown that after EPN, the microhardness of the surface layer can reach 1050–1130 HV, which is due to the formation of nitride phases such as γ' -Fe₄N and ϵ -Fe_{2–3}N [11,12]. Phase transformations significantly increase the mechanical strength of steel and improve its resistance to thermal influences [13–15]. Additionally, in nitrided layers, phase structures remain stable even after subsequent heat treatment, ensuring the durability of the improved characteristics [12,16]. These solid phases form as a result of the steel surface being saturated with nitrogen at high temperatures, which leads to an increase in the material's resistance to mechanical loads [17,18]. The wear resistance of steel increases significantly after the application of EPN. Studies show that the coefficient of friction decreases from 0.61 to 0.52 after processing, and the wear resistance increases by more than 70 times [19–21]. This is due to the formation of a solid nitride layer on the steel surface, which provides high resistance to abrasive wear and reduces the wear rate even under intense mechanical loads [19,22,23]. The corrosion resistance of steel 45 after EPN is significantly increased due to the formation of a protective layer consisting of iron oxides and nitrides. Studies show that the density of the corrosion current decreases from 23 $\mu\text{A}/\text{cm}^2$ for untreated steel to 8 $\mu\text{A}/\text{cm}^2$ after EPN [12,17,24,25]. This confirms the effectiveness of EPN in improving the corrosion resistance of steel, which makes it more suitable for use in aggressive environments [19,20].

The composition of the electrolyte has a significant effect on the thickness of the nitride layer during the electrolytic plasma nitriding of steel. For example, a study by the authors of [26–28] showed that the addition of ammonium nitrate to the electrolyte increases the thickness of the nitrided layer on steel by increasing the concentration of active nitrogen ions in plasma, which accelerates the process of nitrogen diffusion into steel. In another study [29], it was found that using an electrolyte with sodium carbonate promotes the formation of deeper nitrided layers due to increased nitrogen release on the surface and a rise in plasma temperature. The research by the authors of [27] also confirms that choosing an electrolyte with a highly alkaline composition increases the thickness of the nitrided layer due to more intensive electrolyte reactions and the increased activity of nitrogen compounds. In addition, the use of electrolytes with various additives, such as sulfates, fluorides, and chlorides, makes it possible to change the nature of the formation of the oxide and nitride phases, which makes it possible to expand the range of operational properties of medium-carbon steels after EPN [30–33].

This article focuses on studying the effect of increasing nitrogen concentration by adding ammonium nitrate on the quality of the nitrided layer, its microstructure, and the wear and corrosion resistance of steel 45. The novelty of this work lies in an integrated approach to optimizing the electrolyte composition for electrolyte plasma nitriding, which not only improves surface characteristics but also establishes a foundation for future

studies on electrolyte composition. The aim of this study is to identify the wear mechanism of steel products after nitriding under various processing conditions and to develop recommendations for improving wear resistance when using this treatment method.

2. Materials and Methods

Samples of steel 45, the foreign equivalent of AISI 1045 steel, were prepared for EPN. The samples measured 15 mm × 15 mm × 10 mm. Before the start of the process, the surfaces of the samples were pretreated using a HYMP-2 grinding and polishing machine, achieving a surface roughness (R_a) of 1.0 ± 0.1 microns. After polishing, the samples were thoroughly rinsed with running water to remove any abrasive material residues and contaminants. The chemical composition of steel 45 is as follows (GOST 1050-2013): Fe: approximately 97%; C: 0.42–0.50%; Si: 0.17–0.37%; Cu: less than 0.25%; As: less than 0.08%; Mn: 0.50–0.80%; Ni: less than 0.25%; P: less than 0.035%; Cr: less than 0.25%; and S: less than 0.04%.

During the experiment, two types of electrolytes were used. Both electrolytes contained sodium carbonate as the plasma-forming component, and soda ash served as the nitrogen carrier. In the second electrolyte, 5% ammonium nitrate was added to increase the nitrogen concentration, as it contains a double nitrogen compound. Further increases in the concentration of ammonium nitrate led to unstable plasma combustion. The composition of the electrolyte used for EPN is shown in Table 1.

Table 1. Electrolyte composition.

Sample	Electrolyte Composition	Processing Parameters
Steel 45-1	10% sodium carbonate (Na_2CO_3) 20% carbamide ($\text{CH}_4\text{N}_2\text{O}$) 70% distilled water	320 V–20 s 180 V–7 min
Steel 45-2	10% sodium carbonate (Na_2CO_3) 15% carbamide ($\text{CH}_4\text{N}_2\text{O}$) 5% ammonium nitrate 70% distilled water	320 V–20 s 180 V–7 min

This experiment was conducted using an electrolytic plasma nitriding setup equipped with a 40 kW DC power rectifier and a specialized processing chamber containing the plasma torch, as shown in Figure 1.

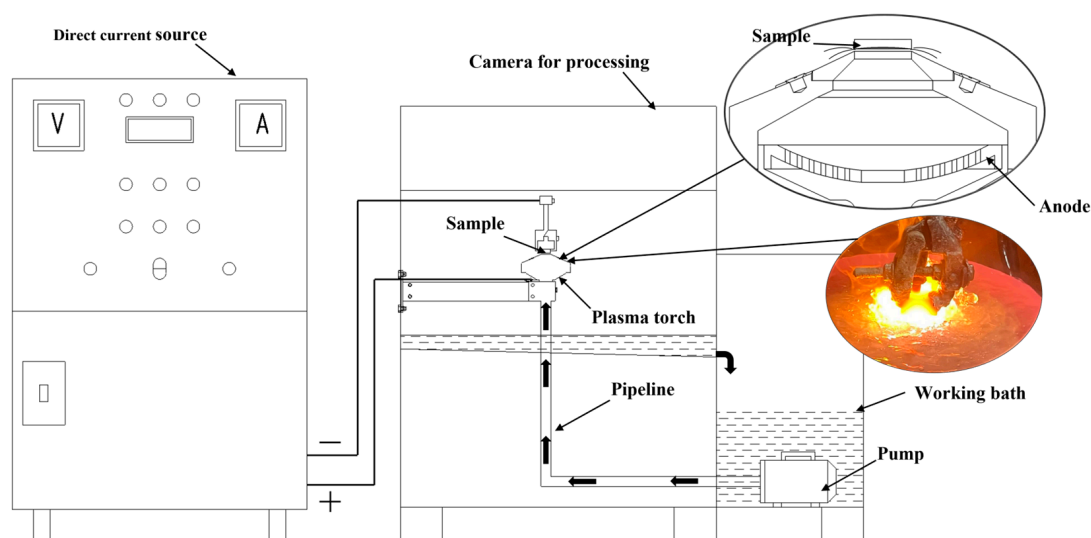


Figure 1. Installation for electrolyte plasma modification.

The nitriding process of the samples was carried out as follows: First, the working bath (5) was filled with the electrolyte. Then, using a pump (4) installed at the bottom of the bath, the electrolyte was supplied through pipelines (8) to the plasma torch (3), located in the processing chamber (2). After passing through the plasma torch, the electrolyte was returned to the working bath through specially provided drain holes, thus creating liquid circulation. The electrolyte supply rate was maintained in the range of 4–7 L/min, and the cooling water supplied to the heat exchanger circulated at a rate of 3–6 L/min. This allowed the electrolyte temperature to be maintained at 50–60 °C while the samples were heated to 700–800 °C. The samples (6) were fixed in the holder and immersed in the electrolyte, ensuring that the treated area was positioned 2–3 mm away from the opening of the cone-shaped partition. An electrolyte jet was supplied through this hole, providing cooling and temperature control for the samples. The anode (7) was connected to the positive pole of the power supply (1), while the samples, acting as the cathode, were connected to the negative pole. Afterward, a voltage of 320 V was applied to the samples for 20 s to quickly reach the saturation temperature. Then, the voltage was reduced to 180 V, and the treatment continued for 7 min, while the temperature of the samples was maintained in the range of 700–800 °C by regulating the electrolyte supply rate.

Figure 2 outlines the research roadmap. After completing the EPN process, cross-sectional samples were prepared by sectioning the treated specimens. These cross-sections were meticulously polished and etched to reveal the microstructure. Following this, light microscopy was employed to observe the microstructural changes. The microhardness of the treated layers was measured to evaluate surface hardness improvements post-nitriding. Additionally, XRD analyses were conducted directly on the nitrided surfaces to determine the phase composition and confirm the formation of nitrides. For tribological evaluation, wear tests were performed on the nitrided surfaces to assess resistance to friction. Lastly, the corrosion resistance of the specimens was tested using standard electrochemical techniques to evaluate the improvements imparted by the EPN treatment.

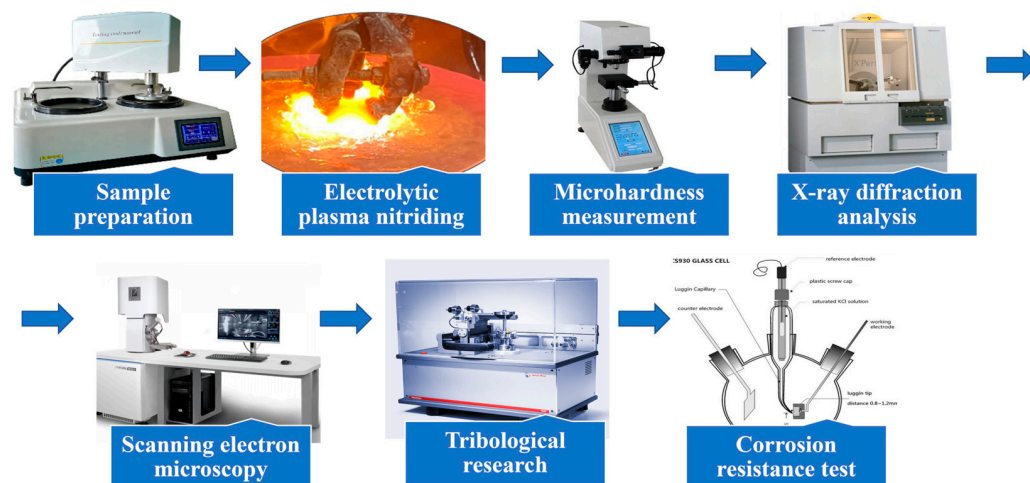


Figure 2. Roadmap of completed research.

X-ray phase analysis was performed on the X'Pert PRO (PANalytical BV, Lelyweg 1, Almelo, The Netherlands). During this study, a voltage of 40 kV and a current of 30 mA were applied to the anode copper tube. Cu-K α radiation ($\lambda = 1.541 \text{ \AA}$) was used in the range from 30° to 100°, with a shooting step of 0.02° and a counting time of 0.5 s/step. The phase analysis of the obtained diffractogram lines was carried out using the HighScore Plus software package. A TESCAN MIRA 3 LMH scanning electron microscope (TUSCAN, Brno, Czech Republic) was used to study the microstructure and elemental analysis of nitrided samples after etching with 3% nitric acid. The coefficient of friction was measured on a universal tribometer TRB3 (Anton Paar, Graz, Austria) using the 'ball-on-disk' method, following ASTM G133. The tests were carried out under dry friction conditions, with the

samples sliding along the steel surface of the counter body at a speed of 0.05 m/s, at a room temperature of 25 ± 1 °C. The vertical load on the samples was 10 N, and 100 Cr6 steel was used as the counter body material. The coefficient of friction was determined after the sample traveled a friction path of 60 m. The microhardness of the samples as measured using a Metolab 502 device according to the Vickers method (HV), following GOST R ISO 6507-1-2007 (Metolab LLC, Moscow, Russia). The following parameters were used for the measurements: a load of 10 g and a holding time of 10 s.

Corrosion resistance was assessed using a CS300 galvanostat–potentiostat (Corr test Instruments, Wuhan, China). The samples were tested in an open area of 1 cm² at room temperature (25 °C) in a 3.5% NaCl solution by weight. A three-electrode cell system was used, with a silver chloride electrode serving as the reference electrode and a platinum electrode as the auxiliary electrode. Before each polarization experiment, the sample was immersed in the electrolyte for 60 min to allow the open-circuit potential (OCP) to stabilize. The corrosion potential and current density were obtained from the polarization curve using the Tafel extrapolation method for four samples. The potential was scanned between −0.1 and 0.1 V relative to the OCP at a scanning rate of 0.5 mV/s. Each sample was tested three times, and the results were analyzed using CS Studio 6 software (version 6.3) [33].

3. Results and Discussions

In the provided comparison of phase transformations for samples nitrided in urea solutions with and without the addition of ammonium nitrate (Figure 3), the X-ray diffraction (XRD) analysis reveals some clear distinctions between the two samples. For sample (a), nitrided in a solution containing sodium carbonate and urea (Figure 3a), the diffraction pattern shows the formation of a nitride–martensite layer, which primarily consists of FeN and Fe₄N compounds. This indicates a significant diffusion of nitrogen into the surface, leading to the formation of these iron nitrides [26]. For sample (b), nitrided in a similar electrolyte but with the addition of ammonium nitrate (Figure 3b), the XRD analysis reveals a more complex nitrided structure. In addition to the FeN and Fe₄N phases seen in sample (a), this sample also shows the presence of Fe₃N, suggesting that the introduction of ammonium nitrate promotes the formation of higher-order nitrides. The presence of oxide layers (FeO, Fe₂O₃, and Fe₃O₄) in both samples is attributed to high-temperature oxidation caused by water vapor during the electrolytic plasma nitriding process in aqueous electrolytes, as supported by [34]. However, the second sample exhibits a more diverse phase composition in the nitride layer, likely due to the catalytic effect of ammonium nitrate, which alters the nitrogen diffusion and reaction kinetics during nitriding. A direct comparison of the two figures shows that the addition of ammonium nitrate in the electrolyte leads to a broader range of nitride phases, particularly the inclusion of Fe₃N, which is absent in the first sample. This suggests that the electrolyte composition significantly influences the phase composition and, consequently, the mechanical properties of the nitrided layer.

A study of the structure SEM analysis of the modified layer after nitriding in an electrolyte composed of sodium carbonate and carbamide showed the formation of a complex multilayer microstructure (Figure 4). The first zone consists of remnants of the oxide layer, formed during high-temperature exposure, followed by the second zone, a nitride FeN and Fe₄N layer with a thickness of about 10 µm (Figure 4a). As shown in Figure 4b, the non-etching white nitride layer penetrates evenly into the depth. The deep layers located below the nitride layer demonstrate the presence of martensite and pearlite grains, which indicates the preservation of elements of the original ferrite–pearlite structure. This indicates that the nitriding process affected only the upper layers of the material, leaving the main structural elements of the original steel unchanged. The incomplete hardening observed in these layers may be associated with insufficient heat treatment or inadequate nitrogen exposure time. However, even a partial transformation of the structure contributes to an improvement in the mechanical properties of steel.

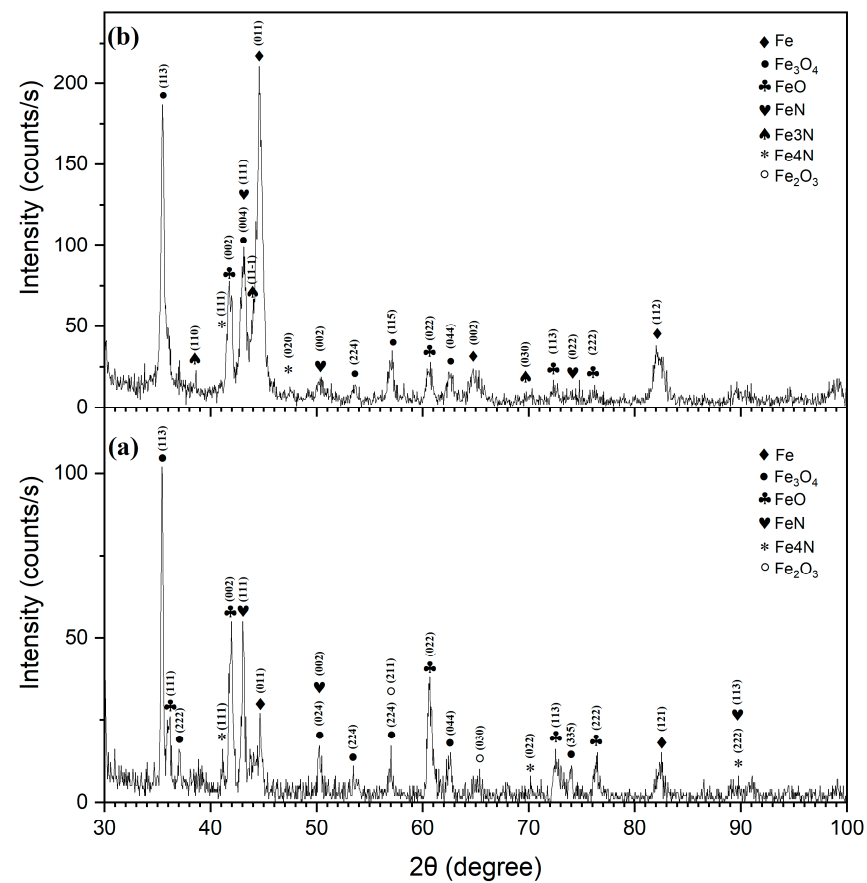


Figure 3. Diffractogram of surface layer of steel 45 after EPN: (a) Steel 45-1; (b) Steel 45-2.

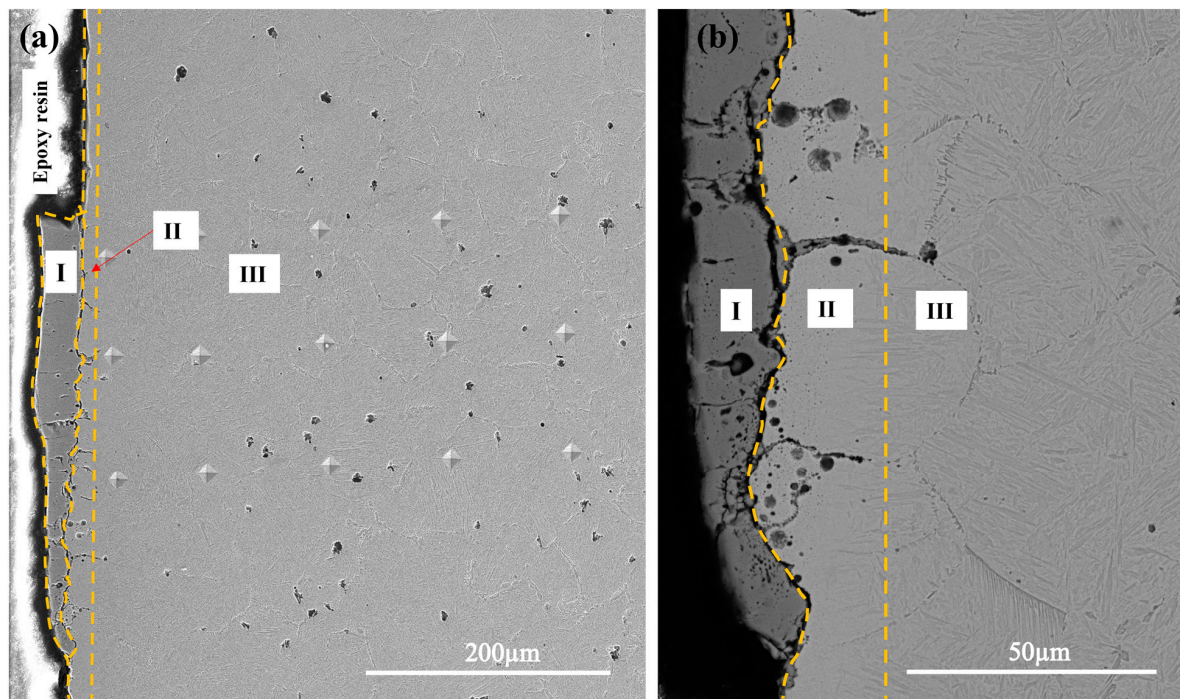


Figure 4. The results of the cross-sectional SEM analysis of nitrided Steel 45-1. (a) 500 $\times$ magnification: I—oxide layer; II—nitride layer; III—nitride-martensitic layer. (b) 2500 $\times$ magnification: I—oxide layer; II—nitride layer; III—nitride-martensitic layer.

In the Steel 45-2 sample, the oxide layer (first zone) is followed by a second zone consisting of a nitride–martensitic layer (Figure 5a) containing the phases FeN , Fe_3N , and Fe_4N , as confirmed by the results of X-ray phase analysis (Figure 3b). The absence of a non-etching white nitride layer is likely due to the added ammonium nitrate affecting the stable ignition of the plasma, requiring more processing time to fully saturate the lower layers with nitrogen. This layer, as shown in Figure 5b, mainly consists of needle-like martensite. The third zone consists of the initial ferrite–pearlite structure.

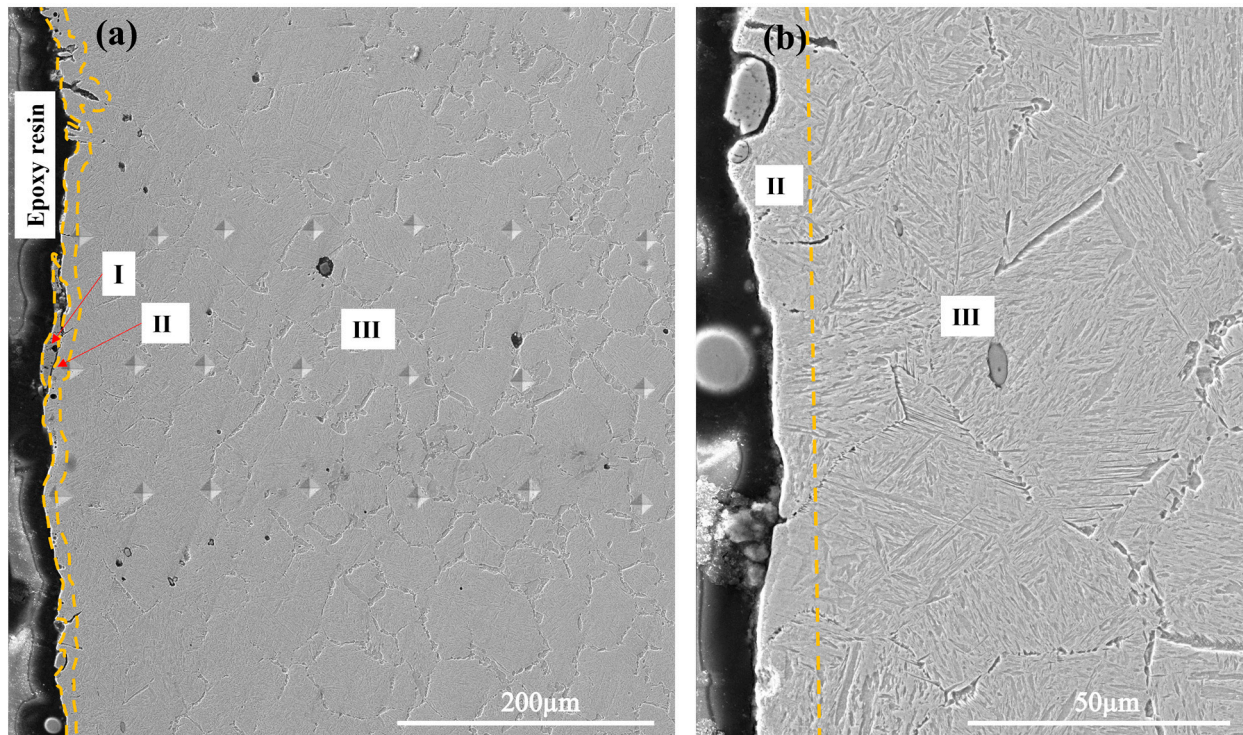


Figure 5. The results of the cross-sectional SEM analysis of nitrided Steel 45-2. (a) 500 $\times$ magnification: I—oxide layer; II—nitride–martensitic layer; III—initial layer. (b) 2500 $\times$ magnification: II—nitride–martensitic layer; III—transition zone.

The results of the EDX analysis of the Steel 45-1 sample in Figure 6 showed that a significant amount of iron oxides (51.18% oxygen) formed in the surface layer (Spectrum 26), with a low nitrogen content (2.44%), indicating surface oxidation after electrolytic plasma nitriding. In the transition zone (Spectrum 27), the nitrogen content is significantly higher (9.13%), which indicates the formation of iron nitrides, providing improved mechanical properties. In the deeper layer (Spectrum 28), the nitrogen concentration decreases to 2.56%, which indicates a decrease in nitrogen diffusion.

The results of the EDX analysis show that in the surface layers of the Steel 45-2 sample (Spectrum 29), a high oxygen content (52.03%) is observed, as shown in Figure 7, indicating a significant oxidation of the surface after electrolytic plasma nitriding, with a nitrogen content of 1.47%. Compared to the Steel 45-1 sample (Figure 6), the nitrogen content in the nitride zone (Spectrum 27) is significantly lower (2.44%), indicating less nitrogen penetration into the depth. In the deeper layers (Spectrum 31), the nitrogen content decreases to 1.76%.

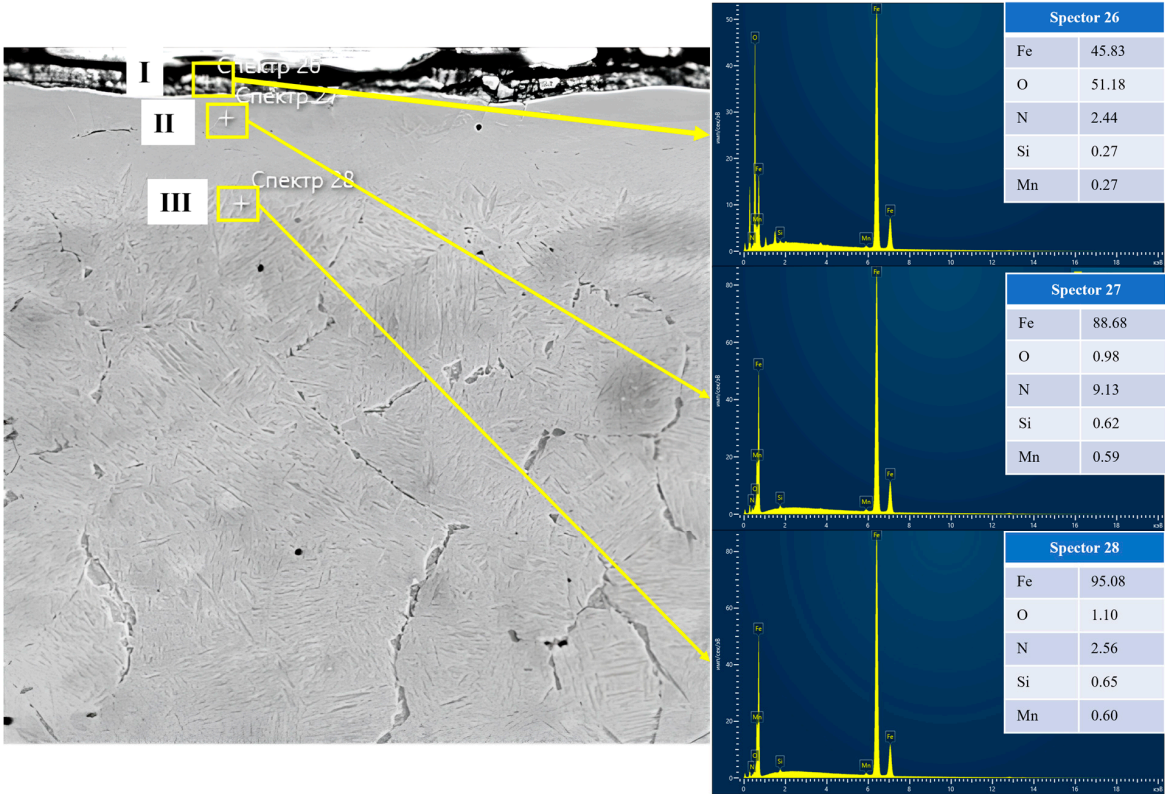


Figure 6. Results of EDX analysis of Steel 45-1 sample. I—oxide layer; II—nitride–martensitic layer; III—transition zone.

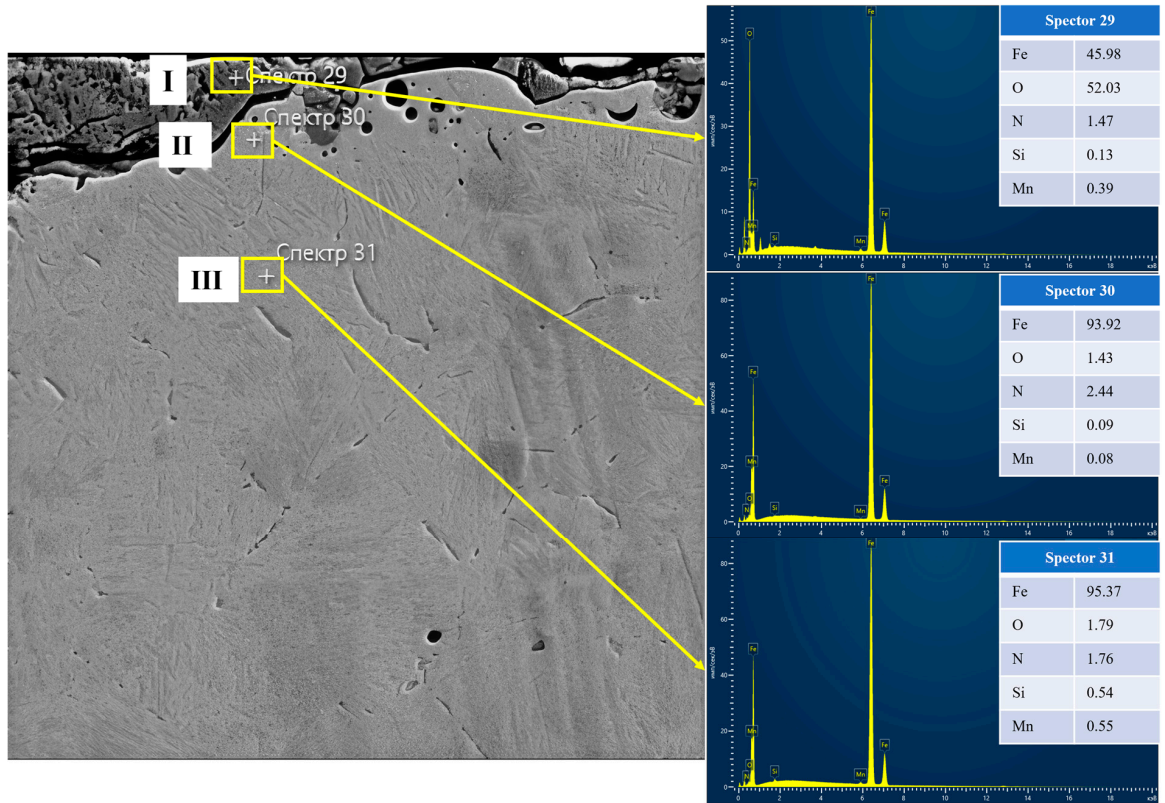


Figure 7. Results of EDX analysis of Steel 45-2 sample. I—oxide layer; II—nitride–martensitic layer; III—transition zone.

The microhardness data of the two samples, Steel 45-1 and Steel 45-2, show the characteristic patterns inherent in diffusion layers after nitriding (Figure 8). In both cases, hardness decreases as you move away from the surface. The Steel 45-1 sample demonstrates higher surface hardness values, indicating the effective formation of a nitride layer consisting of the FeN and Fe₄N phases, as confirmed by the results of EDX (Figures 6 and 7) and XRD analysis (Figure 3). It is important to note that the hardness of the nitride zone in Steel 45-1 is also more evenly distributed, which may indicate a higher-quality and more homogeneous diffusion process. At the same time, Steel 45-2 exhibits more pronounced hardness fluctuations, which may indicate an uneven distribution of nitride phases and a lower degree of alloying, both of which affect the characteristics of the diffusion zone.

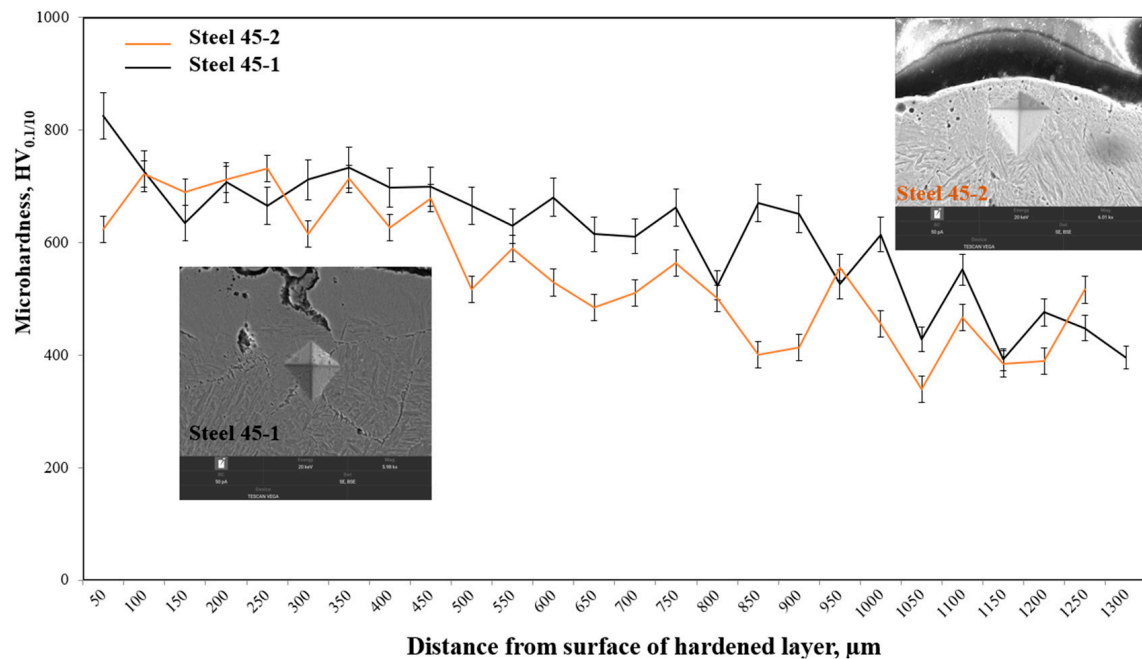


Figure 8. Results of microhardness distribution by depth.

The analysis of the tribological test shows differences in the friction coefficients for the initial sample, as well as for nitrided Steel 45-1 and Steel 45-2, depending on the distance traveled (Figure 9). The starting material (green line) exhibits the highest coefficient of friction, which increases rapidly and stabilizes at around 0.6, indicating the absence of a protective nitride layer and a high level of wear. Steel 45-2 (red line), despite having a lower coefficient of friction compared to the initial sample, still shows values of around 0.4–0.5, indicating the presence of a nitride layer, though it is likely less dense or less stable. Steel 45-1 (blue line) shows the lowest coefficient of friction, which gradually increases to around 0.3. This indicates a more uniform and denser nitride layer, which provides improved tribological characteristics. It is important to note that, due to more saturated nitriding and the presence of nitride phases such as Fe₄N and FeN (Figure 3), Steel 45-1 shows the best results, reducing friction and wear.

Similar behavior was observed in studies of additive welding, where the improved wear resistance was attributed to the formation of multilayer carbon nanotubes and nickel particles, which provided a stable and durable structure [35]. In this research, the key role is played by the Fe₂N and Fe₄N phases, which form a strong barrier against contact with abrasive particles and reduce the likelihood of microcracks and fractures.

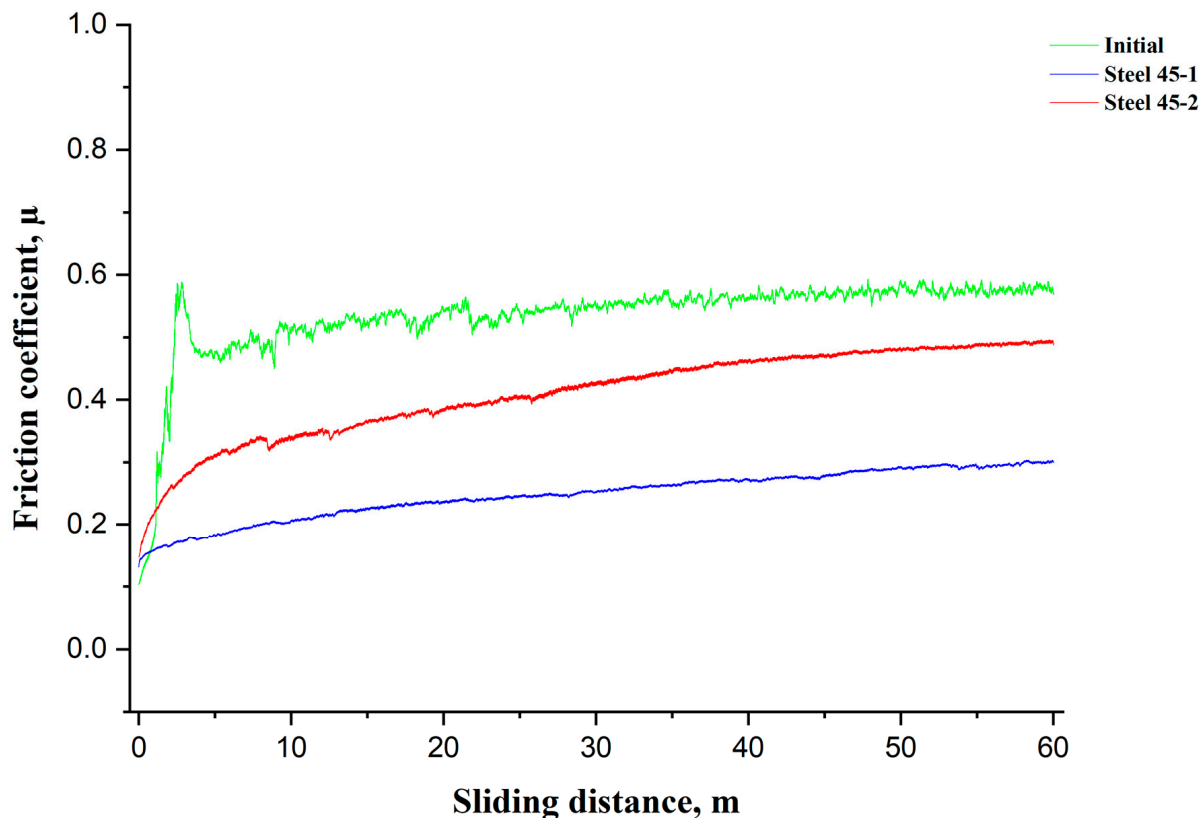


Figure 9. Results of coefficient of friction.

The corrosion test results in Figure 10 reveal significant differences in the corrosion resistance between Steel 45-1 and Steel 45-2. The Steel 45-1 sample demonstrates the highest corrosion resistance, as confirmed by its relatively high corrosion potential (-0.376 V) and the lowest corrosion current density (1.7315×10^{-5} A/cm²). This high corrosion resistance can be attributed to a more uniform nitrogen diffusion layer formed during the plasma nitriding process, which acts as an effective barrier against the penetration of aggressive media, such as chlorine ions commonly found in corrosion testing solutions. Despite the presence of microcracks in the Steel 45-1 sample, the diffusion of nitrogen into the material structures helps strengthen the protective layer, reducing the likelihood of localized corrosion attacks. Meanwhile, the Steel 45-2 sample exhibits significantly lower corrosion resistance. With a more negative corrosion potential of -0.565 V and the highest current density of 2.8672×10^{-5} A/cm², Steel 45-2 is more susceptible to the corrosion process. This can be explained by the uneven diffusion of nitrogen and the formation of numerous microcracks and oxide layers. These structural defects serve as pathways for the penetration of aggressive media, contributing to localized corrosion, especially at the ends of cracks. In addition, the thin nitride layer formed during nitriding proved insufficient for reliable protection against the corrosive environment, accelerating the material's degradation. The initial sample (designated as 'Initial') occupies an intermediate position between Steel 45-1 and Steel 45-2 in terms of corrosion resistance. Its corrosion potential is -0.480 V, and the current density is 1.8971×10^{-5} A/cm², indicating an average resistance compared to the nitrided samples. Although the nitriding process improved the mechanical properties of Steel 45-2, it also introduced defects such as oxides and cracks, which negatively impacted its corrosion resistance.

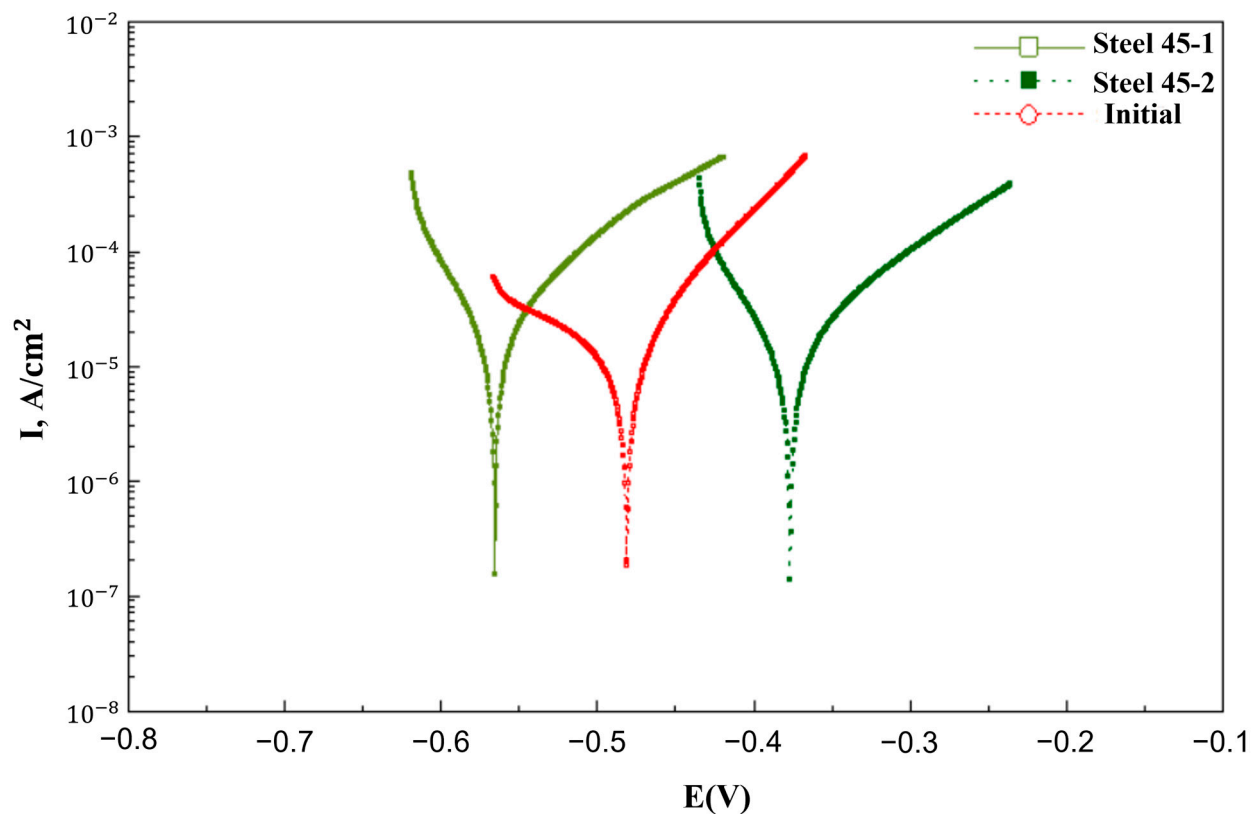


Figure 10. The results of the corrosion resistance test.

It can be assumed that unstable plasma combustion during plasma nitriding in an electrolyte containing 5% ammonium nitrate contributed to the formation of these defects. In the Steel 45-2 sample, nitrogen diffusion required more time under unstable plasma conditions, and exposure to high temperatures led to the formation of microcracks. As a result, these microcracks, along with the thin nitride layer, proved ineffective in protecting the steel from corrosion, leading to a more pronounced fracture. On the other hand, the Steel 45-1 sample, despite the presence of microcracks, benefited from a more uniform diffusion of nitrogen, which enhanced its corrosion resistance. Thus, it is evident that the uniformity of nitrogen diffusion and plasma stability during nitriding play a key role in determining the corrosion resistance of treated steel [34]. Plasma instability and rapid cooling in the Steel 45-2 sample likely contributed to its greater susceptibility to corrosion, while a more uniform and protective layer formed in the Steel 45-1 sample.

4. Conclusions

As a result of this study, the following conclusions can be drawn:

- XRD and SEM-EDX analyses showed that, as a result of electrolytic plasma nitriding, multilayered complex diffusion layers were formed. These layers consist of a surface oxide layer containing FeO, Fe₂O₃, and Fe₃O₄, followed by a white nitride layer with a thickness of about 10 µm, which contains the phases FeN, Fe₃N, and Fe₄N, and then a nitride–martensitic layer.
- The analysis of the tribological test shows that nitriding in carbamide solutions without the addition of ammonium nitrate yields the best result, with the coefficient of friction around 0.3. In comparison, the coefficient of friction for the original sample is about 0.6, proving that wear resistance doubled. The addition of ammonium nitrate did not yield the best result, as the coefficient of friction is around 0.5, likely due to the presence of a thin nitride layer.

- The results of the corrosion resistance test showed that the nitrided sample with the addition of ammonium nitrate has a poorer corrosion resistance compared to the sample without the addition of ammonium nitrate and the starting material. This is due to the formation of microcracks caused by high-temperature effects on the surface, as well as unstable plasma ignition, which did not allow for sufficient time for proper nitrogen saturation.
- In the future, it is planned to study the effect of processing time on nitrogen diffusion in various nitrogen-containing electrolytes and to determine the optimal electrolyte composition for stable plasma ignition and effective nitrogen saturation.

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