



Article Effect of Machine Pin-Manufacturing Process Parameters by Plasma Nitriding on Microstructure and Hardness of Working Surfaces

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Abstract: This work concerns two stages of research into plasma nitriding (change of nitriding steel and modification of nitriding parameters). In the first stage, pins obtained from currently used steel were compared with pins made of an alternative material available on the market, using the same nitriding process parameters. As a result of the metallographic tests carried out, in the first case, the presence of a thin, porous, and heterogeneous nitrided layer or its absence was found, with the core in its raw state and not thermally improved. In the second case, the presence of a nitrided layer of small thickness with noticeable porosity on the surface of the sample was found, but with a core after heat treatment (incorrect process parameters). Therefore, modification of the parameters of the nitriding process was proposed, in terms of a mixture of gases, currents, time, and temperature of the nitriding process. As a result, a satisfactory effective thickness of the nitrided layer was obtained, consisting of a white near-surface zone with ε and $\varepsilon + \gamma'$ -type nitrides with a thickness of 8.7 to 10.2 μ m, and a dark zone of internal nitriding with γ' nitrides. The nitrides layer was continuous, compact, and well adhered to the steel surface. In the core of the samples, the presence of a fine-needle tempering sorbite structure with a small amount of fine bainite, which is correct for the steel after heat treatment and nitriding, was found. The most favorable parameters of the ion nitriding process were gas flow rate (1.5 L/min N; 0.4 L/min H; 0.3 L/min Ar); currents (BIAS—410 V 4.0 A, SCREEN—320 V 4.0 A); time (26 h and 35 min); and temperature (550 °C).

Keywords: pins; wear; heat treatment; chemical treatment; plasma nitriding

1. Introduction

Both in everyday life and in industry, products that can make our lives easier, better and safer are very important. With this in mind, there is a constant need to improve the approach to production. One aspect of product improvement is the need for increasingly efficient and cost-effective manufacturing methods. To ensure cost-effective production, especially for large-scale industrial processing, this approach requires continuous process improvement. The key in this aspect is surface engineering, which includes the use of traditional and innovative technologies to obtain a product surface with better properties compared to the existing ones [1,2]. One of the methods of improving the surface properties of the product is the treatment of its surface after production, usually aimed at its hardening. The need to harden the surface of materials, especially metals, is now more in demand than ever. This is due to the systematically growing demand for metallic materials that, with high hardness, show high strength, resistance to abrasive wear, and, very importantly, are obtained at reduced production costs. Modern surface-treatment methods most often include chemical vapor deposition (CVD), physical vapor deposition (PVD), cladding, and plasma nitriding [1–6].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Nitriding is one such surface-treatment method that is critical to modern industry. It is used in many fields, including machine, automotive, and tool industries [3,7–15]. The nitriding process guarantees the improvement of the surface properties, primarily alloy steels intended for nitriding, while maintaining minimum dimensional tolerances and high abrasion resistance. In addition to increasing the surface hardness, wear resistance, and corrosion resistance, nitriding can lead to an improvement in the fatigue strength of the component. This is possible due to the formation of appropriate phases with increased volume, causing the occurrence of compressive stresses in the surface layer.

This is possible because iron in Fe–C alloys occurs in various allotropic forms, which, combined with appropriate alloy additions, favors the formation of phases strengthening their surface in the nitriding process [16–19]. Up to a temperature of 912 °C, the Fe α variety occurs, crystallizing in the BCC lattice. Between the temperatures of 912 and 1394 °C there is a Fe γ variety crystallizing in the FCC lattice, and in the temperature range of 1394 to 1538 °C, there is a high-temperature Fe δ variety crystallizing in the BCC lattice. The phases occurring in the iron–nitrogen system are shown in the phase equilibrium diagram in Figure 1.



Figure 1. The Fe—N equilibrium phase diagram [20].

The graph shows that the solubility of nitrogen in Fe α is low and reaches a maximum at 590 °C. At this temperature, the solubility is 0.10% and decreases rapidly with decreasing temperature, so that at 200 °C it is only 0.004%. This interstitial solution of nitrogen in the iron is called nitrogen ferrite.

There are two interstitial vacancies in the Fe α lattice where nitrogen can be located. The radius of octahedral and tetrahedral vacancies is 0.019 nm and 0.052 nm, respectively [11]. Even though the radius of the N atom is 0.07 nm, it was found that it is in smaller octahedral vacancies in the Fe α lattice, thus causing the expansion of the Fe α lattice, an increase in internal stresses, and solution strengthening [20–23].

The solubility of nitrogen In Fe γ is much higher, and this solution, called nitrogen austenite, is stable only at temperatures higher than 590 °C. The greatest solubility of nitrogen in Fe γ is 2.80% at 650 °C, and then decreases to 2.35% at the eutectoid temperature. Nitrogen austenite with such a composition decomposes eutectoidly into a mixture of Fe α (N) nitrogen ferrite and the γ' phase. This eutectoid, formed during slow cooling, is called braunite. By rapid cooling, however, nitrogen austenite can be supercooled to temperatures at which nitrogen martensite is formed as a result of diffusion-free transformation.

The temperature Ms (martensite start) in this case is lower than in steels and, in the alloy with eutectoid composition, it is only $35 \degree$ C.

The γ' phase is a solid solution based on iron nitride Fe₄N with a narrow homogeneity range. This phase is stable up to 680 °C and then changes to the hexagonal ε phase, which is a solid solution with a wide range of homogeneity. Like nitrogen austenite, the ε phase containing 4.55% nitrogen decomposes at 650 °C into a eutectoid mixture of γ and γ' phases.

The iron nitrides show low durability and decompose at higher temperatures, which can be seen in the example of the γ' phase. Due to this low stability, iron nitrides coagulate rapidly, even at low temperatures. The consequence of this is the low hardness of the surface of nitrided objects made of unalloyed steel because the dispersion of the formed nitrides quickly disappears.

More durable, and therefore less prone to coagulation, nitrides form nitrogen with transition metals that are components of alloy steels. These can be, for example, chromium nitrides CrN and Cr_2N and molybdenum nitrides MoN, titanium nitrides TiN, or others. The most durable AlN nitrides are formed by aluminum and therefore are used in special grades of steel intended for nitriding. Apart from other alloying additives, this element is also used.

The structure of the diffusion layers formed depends primarily on the nitriding temperature, the chemical composition of the nitriding atmosphere, and the chemical composition of the material of the nitrided objects.

As already mentioned, the nitrided sample is characterized by increased surface hardness, increased wear resistance, high fatigue strength, increased corrosion resistance, and high dimensional stability [1,24–37]. This is possible because a sufficiently high concentration of nitrogen on the steel surface determines the formation of Fe–N phases. If the concentration of nitrogen increases sufficiently, a layer of these compounds with very high hardness forms on the surface. Below this layer, a diffusion zone is formed, consisting of nitrogen in the interstitial solid solution with fine precipitations of alloy nitrides [1,24]. This mechanism of precipitation hardening of the diffusion zone depends largely on the number of elements that favor the formation of nitrides and on the concentration of nitrogen itself [38]. A simplified cross-sectional diagram of a typical nitrided sample is shown in Figure 2. The diffusion zone consists of interstitial nitrogen dissolved in the Fe α lattice and Fe alloy carbonitrides [39–41]. It has been shown that the high surface hardness obtained as a result of nitriding results from the precipitation of fine-grained alloy carbonitrides [42–44]. The latter is a consequence of the presence of strongly nitride-forming elements in the steel substrate, such as Al, Cr, Mo, Ti, Mn, Si, and V [43–45]. The hardness in the diffusion zone depends on the type and number of alloying elements in the steel [38,46]. In addition, in high-alloy steels, there is a reduction in the hardening depth after nitriding treatment due to the precipitation of alloy nitrides, which additionally limits the diffusion of nitrogen to the substrate [47].



Figure 2. A diagram of a typical cross-sectional view of a nitrided component. Shown is the compound layer with the diffusion region beneath. Please note that this diagram is not to scale.

Plasma nitriding is one of the modern techniques of thermo–chemical treatment, which is usually carried out with the use of nitrogen and hydrogen [48–52]. The process is carried out under reduced pressure where a voltage is applied between the samples and the walls of the furnace. A glow discharge with a high level of ionization (plasma) is generated around the part [48,49]. In the area of the workpiece surface that is directly bombarded with ions, nitrogen-rich nitrides form and break down, releasing active nitrogen to the surface. The ability to adjust the degree of cathodic sputtering, the selection of the appropriate current–voltage characteristics, and the ability to increase or decrease the pressure in the working chamber enables the formation of the structure of nitrided layers [53]. Plasma nitriding makes it possible to modify the surface according to the desired properties [53–56]. By adjusting the gas mixture (proportions), it is possible to obtain tailored layers and hardness profiles, from a surface free of a layer of low nitrogen compounds and up to 20 microns thick, to a layer containing nitride compounds and a solid solution diffusion zone. The wide temperature range allows many applications beyond the possibilities of gas or salt bath processes.

Traditional nitriding techniques most often lead to the formation of defects, such as the formation of brittle surface layers, and the effect of non-uniform edges. To eliminate these problems, especially in the case of plasma nitriding, appropriate nitriding furnaces have been developed [57–59]. One of the recent innovations in this field was the introduction of the innovative technology of Active Screen Plasma Nitriding (ASPN) [56–59]. ASPN nitriding ensures the uniform formation of nitrides that reflect the shape of the workpiece. This effect is achieved by glowing nitrogen-activating plasma on the mesh as well as on the nitrided detail, which guarantees no damage or burns caused by oversized plasma discharges on the detail. This minimizes the risk of damage to the elements subjected to electric arc treatment and uneven heating of elements of different dimensions, and removes or minimizes the polarization voltage, which is applied to the treated elements in traditional plasma nitriding [59–62].

This work is the result of research and development activities carried out as part of the project entitled Regional Operational Program for the Lower Silesian Voivodeship for the years 2014–2020. As part of the project, actions were taken to modify the parameters of the technological process for the production of machine pins to improve the surface properties of the product. The research was carried out in two stages. In the first stage, they consisted of comparing the process from the point of view of the currently used steel with an alternative material, while maintaining the previously used parameters of the nitriding process. In the second stage, the parameters of the plasma nitriding process were modified.

2. Materials and Methods

The samples taken from the pins, which were plasma nitrided with Nitro-Tool technology in a vacuum furnace, using the ASPM method, were tested. Figure 3 shows a diagram of a vacuum furnace for nitriding using the ASPN method. During the tests, the ASPN nitriding method with active BIAS was used to obtain an even coverage with the nitrided layer.

In the first stage of the research, samples taken from pins currently manufactured by the Sacher Company, made of 38HMJ steel (designation according to the withdrawn PN—89/H84030.03 standard), in the state before and after the application of the plasma nitriding process, were tested. The parameters of the nitriding process typical for the company were used: gas flow rate (1.3 L/min N; 0.7 L/min H; 0.2 L/min Ar); currents (BIAS—420 V 5.0 A, SCREEN—320 V 3.0 A); time (26 h and 35 min); and temperature (510 $^{\circ}$ C).

As a result of the microscopic examination of samples subjected to heat-chemical treatment with the ion nitriding method, according to the parameters mentioned above, the presence of a thin, porous, and non-homogenous nitrided layer (or its absence) and a diffusion layer of small thickness was found on the surface of the sample with a raw, not thermally improved core.



Figure 3. Schematic illustration of ASPN: (a) bias-on and (b) bias-off.

After analyzing the obtained results, the possibility of using modern grades of steel, e.g., 33CrMoV12—9 or 32CrAlMo7—10 (designation according to PN EN ISO 683—5:2021—10) was proposed as an alternative to the currently used steel used for the production of pins. Due to the unavailability of these materials, 42CrMo4 steel (designation according to EN ISO 683—1:2018—09) was used in the tests. After machining, the pins were subjected to the nitriding process, each time using the same process parameters as in the case of the first thermo–chemical treatment.

However, these actions did not bring the desired effect. Therefore, steps were taken to modify the parameters of the nitriding process. Thus, four test trials were carried out. Each time a different process parameter was changed (gas mixture, currents, time, and temperature), with the others returning to their initial values. Individual parameters were changed in the following ranges: gas flow rate (1.3–1.5 L/min N; 0.4–0.7 L/min H; 0.2–0.3 L/min Ar); currents (BIAS: 410–440 V 4.0–5.0 A, SCREEN: 320–330 V 3.0–4.0 A); time (from 26 h and 35 min to 30 h and 38 min); temperature (510–550 $^{\circ}$ C).

In each case, the pins (dimensions \emptyset 35 × 75) were produced using CNC machines: HASS SL—20 (Hass Automation Inc., Oxnard, CA, USA) and HASS VF5 (Hass Automation Inc., Oxnard, CA, USA). The pins were then subjected to ion plasma nitriding using a Nitro-Tool furnace (AMP Heat Treatment Technologies Company, Świebodzin, Poland).

Test samples were cut using a Secotom precision cutting machine (Struers, Copenhagen, Denmark) and then embedded. A grinding and polishing machine by LaboSystem (Struers, Copenhagen, Denmark) was used for grinding and polishing the specimens.

The metallographic tests consisted of the determination of the chemical composition using the spectral method using a GDS 750 QDP glow discharge analyzer. During the analysis, the following parameters were used to ionize the inert gas: U = 1250 V, I = 45 mA, 99(.9)% Ar (Leco, St. Joseph, MI, USA). The obtained results were the arithmetic mean of at least five measurements and the X-ray energy dispersion spectroscopy method (SEM Quanta 250 FEI with EDS detector by Oxford Instruments). The WDS by Oxford Instruments was also used for comparative purposes (for carbon and nitrogen content); measurement of the hardness distribution on the cross-section was carried out using a Vickers hardness tester MMT—X7B (Matsuzawa Co., Tokyo, Japan) under conditions compliant with PN EN ISO 6507—1:2018—05, as well as analysis of the microstructure of the core, nitrided layer and determining the thickness of the layer nitrided, using an Eclipse MA-200 metallographic microscope (Nikon, Tokyo, Japan), under conditions compliant with PN—82/H—04550. Microscopic observations were carried out on samples non-etched and etched with nital-Mi1Fe (5 % alcohol solution HNO₄). Nital etching made it possible to visualize the microstructure of individual zones, i.e., the surface containing characteristic types of nitrides and the core without nitrides.

3. Results and Discussion

3.1. Testing of Currently Produced Pins-38HMJ Steel

In the first stage, metallographic tests were carried out on samples taken from pins made of 38HMJ steel (outdated designation according to the withdrawn PN—89/H84030.03 standard), delivered by the company before and after the nitriding process. The results of the analysis of chemical composition obtained by the GDS method of the base steel samples for nitriding are presented in Table 1.

Table 1. Results of chemical composition analysis of base steel samples intended for nitriding.

Ordinal Number	Element	Chemical Composition of Steel (%mass)
1	С	0.392
2	Cr	1.270
3	Al	0.763
4	Mn	0.401
5	Si	0.308
6	Мо	0.166
7	Ni	0.086
8	Ti	0.004
9	Р	0.006
10	S	0.001

Based on the analysis of the chemical composition, it was confirmed that the closest equivalent of the material from which the samples were made is 38HMJ steel (according to withdrawn PN—89/H84030.03).

3.1.1. Microscopic Observations of Pins in Raw State

Microscopic observations of non-etched samples taken from pins in their raw state showed the presence of an increased number of non-metallic inclusions, mainly in the form of oxides and brittle silicates (Figure 4a). This indicates the low quality (metallurgical purity) of the tested material. After etching the reagent, a very finely dispersed, partially banded pearlitic structure with grains of free ferrite was found (Figure 4b).



Figure 4. A sample taken from the pin before nitriding—38HMJ steel: (**a**) Increased number of non-metallic inclusions in the form of oxides and brittle silicates. Non-etched state; (**b**) Partially banded pearlitic-ferritic structure. Etched state.

This structure is typical for materials cooled from hot working temperatures (raw state) and is an incorrect structure, as it is the initial structure for steel before the nitriding process. It can cause a significant reduction in strength properties, and in particular cause cracks and chipping, and reduce the fatigue resistance of nitrided details.

In this case, it can be stated that no thermal improvement procedure was applied before the ion nitriding process.

3.1.2. Microscopic Observations of Pins after Nitriding

Based on the conducted microscopic examinations of nitral-etched samples after nitriding, the presence of a ferritic-pearlitic banded structure, typical of the raw state after hot plastic working, was found in the core (Figure 5). This indicates that the heat treatment required before the nitriding process was not applied. The nitrogen content on the surface of the samples after nitriding was an average of 8.50 $\%_{mass}$ (EDS and WDS for comparison).



Figure 5. Sample after nitriding—core. Longitudinal section. Highly banded, heterogeneous ferritic structure with very finely dispersed pearlite. Etched state.

In the surface zone, a nitrided layer was found with a total metallographic thickness of about 0.2 mm (Figure 6), consisting of a very thin white near-surface layer with ε and $\varepsilon + \gamma'$ -type nitrides, 5 to 10 µm thick, and a dark nitriding zone with the γ' nitride lattice forming a lattice on the former austenite grain boundaries.



Figure 6. Nitrided layer in the corner of the sample after nitriding, etched state: (a) Visible bright, uneven, and very thin layer of ε , $\varepsilon + \gamma'$ -type nitrides and a dark zone of internal nitriding with γ' nitride precipitates forming a lattice on the former austenite grain boundaries; (b) Enlarged part of the area shown in Figure 7.



Figure 7. Nitrided layer on the sample surface after nitriding. Visible bright, uneven, and very thin layer of ε , $\varepsilon + \gamma'$ -type nitrides and a dark zone of internal nitriding with γ' nitride precipitates forming a lattice on the former austenite grain boundaries. Etched state.

Changes in the thickness of the nitride layer ε and $\varepsilon + \gamma'$ in the range from 2 to 5 µm and porosity features were observed locally (Figure 6a). In addition, a continuous network of nitrides distributed γ' along the grain boundaries of the former austenite was found. The transition zone from the nitrided layer to the core has the correct structure. Summing up, the obtained structure is incorrect, showing a high tendency toward cracks and chipping of the surface layer during operation.

On the other hand, a dendritic bainitic structure was found in the core of the samples with precipitates of sorbite and troostite in the interdendritic spaces. This is an unacceptable defect, indicating a complete lack of application of thermal improvement after the plastic working process before the nitriding process or the use of incorrect technology in the thermal improvement process. It should be mentioned that the thickness of the nitrided layer should be from approx. 0.5 mm to approx. 0.7 mm. The small thickness of the nitrided layer requires a uniform, hard and resilient substrate, protecting the above-mentioned layer against its collapse and chipping under the action of local pressures.

In addition, it was found that in many places around the circumference of the sample, the nitrided layer was irregular, thicker in some places—place No. 1, thinner in some places—place No. 2 in others (Figure 7) or there is no such layer (Figure 8).



Figure 8. Nitrided layer on the surface of the sample after nitriding. Visible dark zone of internal nitriding with precipitates of γ' nitrides forming a lattice on the boundaries of former austenite grains and no layer of ε , $\varepsilon + \gamma'$ nitrides on the surface. Etched state.

Hardness measurements were carried out using the Vickers method in conditions compliant with PN EN ISO 6507—1:2018 on the cross-section of the samples in the plane perpendicular to the nitrided surface in the cores of the samples taken from the pins before and after nitriding. A Matsuzawa hardness tester was used with a load of 1 kg (9807 N) operating for 15 s.

The average hardness of the base material in the core of the sample taken from the pin as supplied was found to be 255.8 HV1. The hardness in the core of the sample after the nitriding process does not show significant differences and amounts to 349.8 HV1, respectively.

In addition, measurements of the hardness distribution under the surface of the nitrided layer were made in two places on the sample after nitriding, using a Matsuzawa hardness tester with a load of 0.5 kg (4.904 N).

Determination of the thickness of the nitrided layer by measuring the hardness distribution was made in accordance with the PN—82/H—04550 standard. Hardness measurements were made along a line perpendicular to the surface of the sample at intervals of 50 µm. The measurement results are summarized in Tables 2 and 3.

Table 2. Measurement results of HV0.5 hardness distribution on the cross-section of the nitrided layer in the sample after nitriding—place No. 1.

Distance from the Surface (µm)	50	100	150	200	250	300	350	400	450	500	550	600	650	700
Hardness HV0.5	732.0	663.9	442.7	373.1	369.9	364.7	372.8	369.4	365	384.7	376.4	378.1	377.9	366.4

Table 3. Measurement results of HV0.5 hardness distribution on the cross-section of the nitrided layer in the sample after nitriding—place No. 2.

Distance from the Surface [µm]	50	100	150	200	250
Hardness HV0.5	761.2	729.9	567.9	396.9	390.1

As a result of hardness measurements, it was found that in the sample after nitriding in place No. 1, the effective thickness of the nitrided layer calculated up to the hardness of 500 HV0.5 is 0.13 mm (130 μ m), and the maximum hardness of 732 HV0.5 in place No. 1 occurs at a distance of up to 0.05 mm (50 μ m) below the sample surface. The hardness at a distance of approx. 0.2 mm from the surface is 373 HV0.5.

In the sample after nitriding in place No. 2, the effective thickness of the nitrided layer calculated up to the hardness of 500 HV0.5 is 0.18 mm (180 μ m), and the maximum hardness of 761.2 HV0.5 also occurs at a distance of up to 0.05 mm (50 μ m) below the surface of the sample. The hardness at a distance of about 0.2 mm from the surface is 396 HV0.5.

The obtained results indicate that 38HMJ steel should not be used for nitriding. It was proposed to use modern steel grades intended for nitriding, e.g., 33CrMoV12—9 or 32CrAlMo7—10 (designation according to PN EN ISO 683-5:2021—10), and in the absence of their availability, the use of 42CrMo4 steel (designation according to EN ISO 683-1: 2018—09).

3.2. Study of Pins Manufactured from Alternative Steel—42CrMo4

Due to the unavailability of 33CrMoV12—9 and 32CrAlMo7—10 steel, 42CrMo4 steel was used.

3.2.1. Pins before Nitriding

As a result of microscopic examinations carried out in the longitudinal and transverse direction to the direction of machining of the pins in the non-etched state, a small number of non-metallic inclusions was found, mainly in the form of point oxides, unevenly distributed (Figure 9a). After etching, a partially banded bainite structure of a dendritic character was found, with precipitates of sorbitol and troostite in the interdendritic spaces (Figure 9b).



Figure 9. Sample before nitriding, steel 42CrMo4: (a) Visible small number of non-metallic inclusions, mainly in the form of point oxides, unevenly distributed. Non-etched state; (b) Visible partially banded bainite structure of dendritic character with precipitates of sorbitol and troostite in interdendritic spaces. Etched state.

3.2.2. Pin Surface after Nitriding

The analysis of the results of EDS (WDS analysis was used for comparison purposes for carbon and nitrogen) measurements made on the cross-section of the correctly nitrided samples showed the highest nitrogen saturation on their surface and a systematic decrease in the concentration of nitrogen towards the core, unlike the other elements (Figure 10).



Element distribution											
(%mass)											
Measurement											
	No.										
	1	2	3	4	5	6					
Ν	8.51	7.33	6.71	4.55	3.10	2.05					
С	0.17	0.21	0.25	0.31	0.35	0.37					
Cr	1.04	1.14	1.17	1.20	1.22	1.26					
Al	0.73	0.75	0.74	0.75	0.74	0.76					
Mn	0.24	0.25	0.28	0.31	0.33	0.39					
Si	0.27	0.28	0.29	0.28	0.30	0.30					
Мо	0.11	0.10	0.12	0.13	0.12	0.15					
Fe	Rest										

Figure 10. EDS analysis of the elemental distribution of the sample after nitriding (cross-section). Etching state.

Based on the conducted microscopic examinations, the presence of a nitrided layer with a metallographic thickness of approx. 0.3 mm was found (Figure 11). This layer consists of a white near-surface zone with nitrides of the ε and $\varepsilon + \gamma'$ -type with a thickness of 10 to 19 μ m, and a dark zone of internal nitriding with a network of γ' nitrides forming a mesh on the boundaries of former austenite grains.



Figure 11. Nitrided layer: (a) Visible bright layer of ε , $\varepsilon + \gamma'$ -type nitrides and a dark zone of internal nitriding with γ' nitride precipitates forming a lattice on former austenite grain boundaries; (b) Magnified fragment of the same area. Etched state.

In addition, it was found that in some places around the circumference of the sample, the nitrided layer was non-uniform and porous (Figures 11a and 12). Changes in the thickness of the nitride layer ε and $\varepsilon + \gamma'$ in the range of 4 to 7 µm and porosity were observed locally. A lattice of γ' nitrides distributed along the grain boundaries of the former austenite was also found. Moreover, the lack of an internal nitriding transition zone was observed. Locally, the hardness of the core was low and amounted to 320 HV1. It is an incorrect structure, showing a high tendency towards the cracking and chipping of the surface layer during operation.



Figure 12. Nitrided layer. Visible uneven and porous bright layer of nitrides of the ε and $\varepsilon + \gamma'$ -type, about 5 µm thick. A continuous grid of γ' nitrides located along the grain boundaries of the former austenite is visible. No internal nitriding zone. Etched state.

In the core of the sample, a dendritic bainitic structure was found with precipitates of sorbite and troostite in the interdendritic spaces, typical for materials cooled quickly from

hot working temperatures (typical for the raw state QT). This is an unacceptable defect, indicating a complete lack of application of the thermal improvement treatment after the plastic working process before the nitriding process or the use of an incorrect technology in the thermal improvement process.

As mentioned earlier, the thickness of the nitrided layer should be from about 0.5 mm to about 0.7 mm. The small thickness of the nitrided layer requires a uniform, hard and resilient substrate, protecting the above-mentioned layer against its collapse and chipping under the action of local pressures.

3.2.3. Measurements of Hardness of Samples Core after Nitriding

Core hardness measurements were made on the cross-section of the sample. The tests were carried out using the Vickers method in conditions compliant with PN EN ISO 6507—1:1999. As before, a Matsuzawa hardness tester with a load of 1 kg (9.807 N) operating for 15 s was used. As a result of the hardness measurements of the material in the core of the sample after the nitriding process, it was found that the average hardness of five measurements is 436.5 HV1.

3.2.4. Determination of Nitrided Layer Thickness

Determination of the thickness of the nitrided layer by measuring the hardness distribution was made in accordance with the PN—82/H—04550 standard. Hardness measurements were carried out using the Vickers method in conditions compliant with PN EN ISO 6507—1:2018 on the cross-section of the sample in the plane perpendicular to the nitrided surface. A Matsuzawa hardness tester was used with a load of 0.5 kg (4.904 N) operating for 15 s. Hardness measurements were made along a line perpendicular to the surface at intervals of 50 μ m.

As a result of the hardness measurements, it was found that the effective thickness of the nitrided layer calculated to a hardness of 500 HV0.5 is 0.35 mm. The results of hardness measurements are summarized in Table 4 and additionally in the form of a graph in Figure 13.

Table 4. Measurement results of HV0.5 hardness distribution on the cross-section of the nitrided layer in the sample after nitriding.

Distance from the Surface (µm)	50	100	150	200	250	300	350	400	450	500	550	600	650	700
Hardness HV 0.5	614.0	619.4	556.1	526.1	526.0	512.2	492.2	485.1	468.4	468.6	425.5	447.2	436.8	442.0



Hardness HV0.5

Figure 13. Hardness distribution in the nitrided layer with an HV load of 0.5 kg (4.904 N).

Referring to Section 3.2.2, it was found that reducing the nitrogen content from the surface towards to core of the samples caused changes in the microstructure from the formation of a white surface layer of ε -type nitrides, through a diffusion layer of ε + γ' -type nitrides, to the dark zone of γ' -type nitrides. This, in turn, resulted in a successive decrease in hardness, caused by a change in the types of nitrides in individual zones from the surface to the pin core.

As a result of the analyses carried out, it was found that the change in the material of 38HMJ steel to 42CrMo4 steel brought some improvement, but not as much as could be obtained using modern grades of steel, specially dedicated to the nitriding process.

To obtain a greater thickness of the nitrided layer, changing the parameters of the ion nitriding process was proposed, e.g., extending the nitriding time, changing the chemical composition of the nitriding atmosphere in the furnace, changing the BIAS potential, or possibly increasing the nitriding temperature. Before nitriding, it was necessary to carry out heat treatment, i.e., hardening from 880 °C in oil and tempering at 560 °C/1 h.

3.3. Testing of Samples Taken from Pins Made of Nitrided 42CrMo4 Steel at Various Process Parameters

Before nitriding, the pins were subjected to heat treatment, i.e., hardening from 880 °C in oil and tempering at 560 °C/1 h. Then, samples taken from the pins after the nitriding process carried out in accordance with the parameters given in Table 5 were examined.

Samples		Gas Flow Rate (L/min)		Curr	rents	Time	Temperature (°C)	
No	Ν	Н	Ar	BIAS	SCREEN	(h/m1n)		
1	1.5	0.4	0.3	410V 4.0A	320V 3.0A	26/35	530	
2	1.3	0.7	0.2	440V 6.0A	330V 3.0A	26/35	510	
3	1.3	0.7	0.2	410V 4.0A	330V 3.0A	30/38	510	
4	1.3	0.7	0.2	410V 4.0A	330V 4.0A	26/35	550	

Table 5. Parameters of the nitriding process.

As a result of the conducted microscopic observations of the samples etched with nital, it was found that in the core of all samples, there is a structure of fine-needle tempered sorbite with a small amount of fine bainite with a hardness of 330 to 366 HV0.5. This structure is typical for 42CrMo4 steel in the heat-treated state after the ion nitriding process and is correct (Figures 14–17).

3.3.1. Sample No. 1-Microscopic Observations

In sample No. 1, a nitrided layer with a metallographic thickness of approx. 0.3 mm was found, consisting of a white near-surface zone with ε and $\varepsilon + \gamma'$ nitrides with a thickness of 8.7 to 10.2 µm and a dark internal nitriding zone with γ' nitrides. The layer of nitrides ε and $\varepsilon + \gamma'$ is continuous, compact and adheres well to the steel substrate.

In the core of the sample, there is a structure typical of fine-needle sorbite tempering, typical of 42CrMo4 grade steel in the tempered state (Figure 14). The structure of the heat–chemically treated layer is typical for glow-nitrided layers and is correct.



Figure 14. Nitrided layer in sample No. 1. Visible bright layer of ε , $\varepsilon + \gamma'$ -type nitrides and a dark internal nitriding zone with γ' nitride precipitates. Etched state.

3.3.2. Sample No. 2-Microscopic Observations

In sample No. 2, the presence of a nitrided layer with a metallographic thickness of approx. 0.1 mm was found, consisting of a white near-surface zone with ε and $\varepsilon + \gamma'$ nitrides with a thickness of 4.2 to 5.6 µm and a dark zone of internal nitriding with γ' nitrides. The layer of nitrides ε and $\varepsilon + \gamma'$ is continuous, compact and adheres well to the steel substrate.

In the core of the sample, there is a typical structure of fine-needle tempered sorbite, typical for steel grade 40HM in the QT state. The structure of the heat–chemically treated layer is typical for glow-nitrided layers and is correct. The microstructure of the nitrided layer in sample No. 2 is shown in Figure 15.



Figure 15. Nitrided layer in sample No. 2. Visible bright layer of ε , $\varepsilon + \gamma'$ -type nitrides and a dark internal nitriding zone with γ' nitride precipitates. Etched with Mi1Fe.

3.3.3. Sample No. 3-Microscopic Observations

In sample no. 3, a nitrided layer with a metallographic thickness of about 0.15 mm was found, consisting of a white near-surface zone with ε and $\varepsilon + \gamma'$ nitrides with a thickness of 5.6 to 6.2 µm and a dark zone of internal nitriding with γ' nitrides. The layer of nitrides ε and $\varepsilon + \gamma'$ is continuous, compact and adheres well to the steel substrate.

In the core of the sample, there is a typical structure of fine-needle tempered sorbite, typical for steel grade 40 HM in the QT state. The structure of the heat–chemically treated



layer is typical for glow-nitrided layers and is correct. The microstructure of the nitrided layer in sample no. 3 is shown in Figure 16.

Figure 16. Nitrided layer in sample No. 3. Visible bright layer of ε , $\varepsilon + \gamma'$ -type nitrides and a dark internal nitriding zone with γ' nitride precipitates. Etched state.

3.3.4. Sample No. 4—Microscopic Observations

In sample no. 4, a nitrided layer with a metallographic thickness of approx. 0.15 mm was found, consisting of a white near-surface zone with ε and $\varepsilon + \gamma'$ nitrides with a thickness of 4.3 to 5.0 µm and a dark zone of internal nitriding with γ' nitrides. The layer of nitrides ε and $\varepsilon + \gamma'$ is continuous, compact and adheres well to the steel substrate.

In the core of the sample, there is a typical structure of fine-needle tempered sorbite, typical for steel grade 40 HM in the QT state. The structure of the heat–chemically treated layer is typical for glow-nitrided layers and is correct. The microstructure of the nitrided layer in sample No. 4 is shown in Figure 17.



Figure 17. Nitrided layer in sample No. 4. Visible bright layer of ε , $\varepsilon + \gamma'$ -type nitrides and a dark internal nitriding zone with γ' nitride precipitates. Etched state.

3.3.5. Samples from 1 to 4-Hardness Measurements

Determination of the thickness of the nitrided layer by measuring the hardness distribution was made in accordance with the PN—82/H—04550 standard. Hardness measurements were carried out using the Vickers method in conditions compliant with PN EN ISO 6507—1:2018 on the cross-section of the sample in the plane perpendicular to the nitrided

surface. During the measurements, a Matsuzawa hardness tester with a load of 0.5 kg (4.904 N) operating for 15 s was used. Hardness measurements were made along a line perpendicular to the surface at intervals of 50 μ m. The results of hardness measurements are summarized in Table 6.

Table 6. Results of hardness distribution measurements on the cross-section of sample No. 1.

Sample No. 1												
Distance from the surface [µm]	50	100	150	200	250	300	350	400	450	500		
Hardness HV 0.5	621.0	638.7	605.2	539.1	512.1	478.7	444.9	419.3	416.8	366.7		
	Sample No. 2											
Distance from the surface [µm]	50	100	150	200	250	300	350	400	450	500		
Hardness HV 0.5	529.7	499.3	461.9	438.9	420.0	386.1	375.6	359.5	359.0	330.3		
			S	ample No	. 3							
Distance from the surface [µm]	50	100	150	200	250	300	350	400	450	500		
Hardness HV 0.5	568.5	529.9	483.7	434.3	409.7	383.5	356.6	347.6	335.5	341.7		
Sample No. 4												
Distance from the surface [µm]	50	100	150	200	250	300	350	400	450	500		
Hardness HV 0.5	554.0	527.8	481.5	454.0	421.8	417.6	398.7	366.7	355.2	337.0		

As a result of hardness measurements, it was found that in sample No. 1, the effective thickness of the nitrided layer calculated to hardness 500 HV0.5 was 0.3 mm, in sample No. 2 the effective thickness of the nitrided layer was 0.1 mm, and in samples No. 3 and 4 the effective thickness of the nitrided layers were 0.15 mm. It can be concluded that the change in the parameters of the ion nitriding process of the 42CrMo4 steel material after thermal improvement resulted in an improvement in the quality of the nitrided layers, in particular in terms of their uniformity, thickness, and hardness. The most favorable set of parameters of the plasma nitriding process was obtained for sample No.1 (Table 5). Changing the parameters of the ion nitriding process improved the diffusion penetration of active nitrogen atoms toward the core of the nitrided samples. A higher concentration of active nitrogen atoms (not exceeding the limit value) favored the formation of a thicker layer of ε -type nitrides, a diffusion zone containing $\varepsilon + \gamma'$ -type nitrides, and a dark zone containing γ' -type nitrides. This, in turn, resulted in a higher surface hardness of the samples and a thicker hardened zone in the cross-section.

4. Conclusions

Tests have shown that 38HMJ steel in its raw state is not suitable for use on pins obtained by plasma nitriding. In its structure, the presence of many non-metallic inclusions with uneven distribution and inhomogeneous band structure of ferrite with finely dispersed pearlite was found. This shows the low quality of the material. Nitriding resulted in obtaining a thin, porous layer of ε -type nitrides and in some cases no layer at all.

At the same time, it was found that reducing the nitrogen content from the surface toward the core of the samples caused changes in the microstructure, most often from the formation of a white surface layer of ε -type nitrides, through a diffusion layer of ε + γ' -type

nitrides, to the dark zone of γ' -type nitrides. This, in turn, resulted in a successive decrease in hardness, caused by a change in the types of nitrides in individual zones from the surface to the pin core.

The use of 42CrMo4 steel in its raw state brought slightly better results. However, the obtained nitride layer showed uneven thickness and signs of porosity.

To obtain a greater thickness and uniformity of the layer of nitrided 42CrMo4 steel, initial heat treatment was carried out (quenching from 880 $^{\circ}$ C in oil and tempering at 560 $^{\circ}$ C/1 h) and modification of the parameters of the plasma nitriding process.

This brought the intended effect, and the most favorable set of parameters for the plasma nitriding process was gas flow rate (1.5 L/min N; 0.4 L/min H; 0.3 L/min Ar); currents (BIAS—410 V 4.0 A, SCREEN—320 V 4.0 A); time (26 h and 35 min); and temperature (550 °C). This facilitated the diffusion penetration of active nitrogen atoms from the surface towards the core of the nitrided samples. It was found that the concentration of nitrogen in the cross-section of the nitrided samples decreased towards the core, in contrast with the other elements. This allowed the obtaining of a continuous and compact layer of nitrides that was well adhered to the steel surface. A relatively thick and continuous white layer of ε -type nitrides appeared on the surface of the nitrided sample, guaranteeing the highest hardness, then a layer of ε + γ' -type nitrides of lower hardness and a dark zone of internal nitriding with γ' -type nitrides of the lowest hardness. On the other hand, in the core of the nitrided samples, the presence of the correct structure of fine-needle hardened sorbite with a small amount of fine bainite was found.

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