

Nitriding HS6-5-2 Steel in Inductively Coupled Plasma

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This article presents research on the possibility of obtaining a hardened surface layer via nitriding in coupled plasma (ICP) for HS6-5-2 steel. The subject of the investigation was the influence of the process parameters on the properties of the obtained layers. The surface layers were characterized using an optical microscope, SEM (Scanning Electron Microscope), EDS (Energy Dispersive Spectroscopy), XRD (X-Ray Diffraction), and a microhardness tester. The generator power was changed gradually from 500 W to 2 kW and the tests were carried out for various process durations, from 15 to 45 minutes at a set pressure. The obtained results show the possibility of obtaining nitrided surface layers with a thickness of up to 0.1 mm and a significant increase in hardness in a very short time.

Keywords: plasma, nitriding, surface layer, hardness

Highlights

- The maximum hardness of about 1100 HV was obtained: an increase in hardness by 350 % in relation to the starting material.
- Nitrided layers with a thickness of 100 μm were obtained following a very short process: 45 minutes.
- The influence of process parameters on the properties of the nitrided layers is shown.
- The nucleation and growth mechanism of the nitrided layers obtained by this method is described.

0 INTRODUCTION

The constant development of technology means that there is a need to optimize the functional properties of materials used in the production of tools and machine parts. On one hand, this process can be achieved by producing tool materials with better properties, which requires the use of expensive alloying additives in a multi-stage technological process [1] and [2]. On the other hand, research to modify the surface layer to obtain new, more favourable functional features of ready-made tools is being carried out. Despite significant progress in the development of surface engineering, methods for increasing the durability and reliability of tools and structural elements, especially those of small dimensions, still cause problems [3] and [4]. One of the most frequently used technologies, especially for small dimension elements, is nitriding [5] to [7]. Nitriding done by the classical thermochemical treatment method leads to ϵ (Fe_{2-3}N) and γ' (Fe_4N) [8] to [10] brittle layer formation. In the case of gaseous-controlled processes, it is possible to control the phase composition of the layers, but the processes take a relatively long time, even for thin layers [11]. Plasma-assisted nitriding is presented in the literature on the subject primarily concerning ionic discharge, which is the phenomenon of accelerating particles in an electric field. The high kinetic energy of ions is created as a result of the potential difference between the electrodes, both in the glow discharge of direct current and in the high-frequency electric field. In

the first case, the existence of strong field strength is obvious and directly dependent on the potential difference applied to the electrodes. In high-frequency plasma discharge, the discharge is obtained between opposite electrodes as a result of applying a high-energy and high-frequency signal from a generator to them. Such plasma is called “capacitively coupled plasma” (CCP). The generator can be connected by means of electrodes directly to the discharge area or by galvanic isolation of one of the electrodes using a capacitor or an insulator.

The disadvantage of the direct variant of connecting the linings with the discharge is the possibility of contamination of the treatment atmosphere with matter from the electrodes due to their contact with the plasma. In the case of isolating one of the electrodes, due to the different masses and the related mobility of ions and electrons, the high frequency of electrode polarization changes means that heavy ions cannot keep up with the changes in the electric field. As a result, a constant, non-discharged charge accumulates on one of the electrodes, causing the electrode to be polarized with a constant voltage. This phenomenon is called “autopolarization”, and its consequence is the creation of a strong, directed electric field, which accelerates the ions, by giving them high kinetic energy, causing the spraying of the processed samples. This is the main reason that this method of plasma production cannot be used to nitride objects while keeping their surface and edges intact.

Another disadvantageous effect of the directed electric field is the shadow phenomenon, which makes it necessary to change the position of the workpieces during the process [12]. It should be emphasized, however, that CCP plasma is used in numerous industrial applications in which high ion energy is useful, e.g., ion etching, surface cleaning, or expanding.

The use of inductively coupled plasma obtained in a strong magnetic field due to the flow of Foucault currents eliminates the occurrence of an accelerating electric field. The magnetic field of the solenoid causes the flow of eddy currents both in the gas region and in the workpiece, which simultaneously fulfil two tasks: they resistively heat both the gas (nitrogen) creating a plasma ring discharge and the workpieces to the penetration depth, where the value depends on the resistivity of both the ionized gas and the sample and frequency. Multiple ionization of particles in a low-temperature non-isothermal plasma [13] makes it an effective source of the nitriding agent and can be used for diffusive saturation of metals. However, the use of such an induced plasma for steel nitriding is practically unknown, as single works on a laboratory scale [14] have only been recognized. In contrast, inductively coupled plasma is widely used for the physical deposition of various types of coatings [15].

A proprietary stand for nitriding in high-frequency plasma was designed and built to perform the tests (Fig. 1). The device consists of a high-frequency generator set with an inductor, which contains a reactor inside. The set of vacuum pumps allows the appropriate vacuum to be obtained. Nitrogen with a purity of 99.999 % is taken from a cylinder via the mass flow controller.

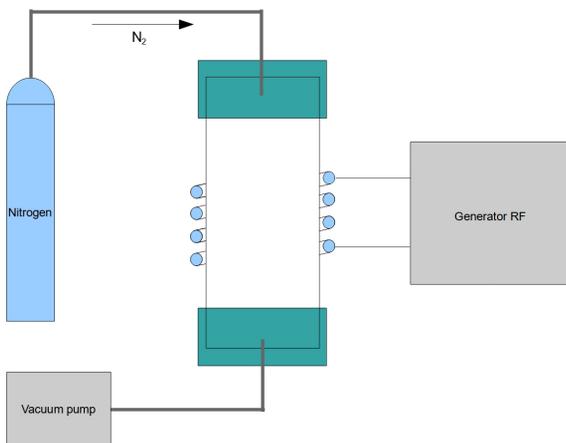


Fig. 1. Block diagram of the device for Inductively Coupled Plasma

As part of this work, the HS6-5-2 steel was subjected to tests. Cutting tools made of this steel, including the drills, taps, and reamers most commonly used in industry and households, constitute a specific group: they are exposed to work in very difficult conditions. Practice shows that small-size tools are not sharpened but replaced with new ones [16]. Therefore, the modification of the surface by nitriding in inductively coupled plasma, leading to a numerous increase in their durability while maintaining high core impact strength, is economically justified.

1 EXPERIMENTAL PROCEDURE

The samples used for the tests were HS6-5-2 steel bars with a diameter of 4 mm, a length of 50 mm with the composition in accordance with the standard shown in Table 1. The samples were in the raw steel state (without heat treatment).

Table 1. Standardized chemical composition [wt. %] of HS6-5-2 steel

C	Cr	Mo
0.80 to 0.88	3.80 to 4.50	4.70 to 5.20
V	W	Si
1.70 to 2.10	5.90 to 6.70	Max 0.45

The samples were nitrided in a stand built for nitriding in inductively coupled plasma discharge with a frequency from a band intended for industrial, scientific, and medical (ISM) applications, in a continuous operation mode. The device was made of a reactor in the form of a quartz tube, 750 mm long and 100 mm in diameter, and was connected to a set of vacuum pumps, which included a turbomolecular pump and a scroll pump. The operating pressure of the process under a nitrogen atmosphere of 99.9999 % purity was 100 Pa, and its flow was controlled by a mass flow controller (MFC). The plasma discharge took place within a coil made of a copper pipe with a diameter of 8 mm and was powered by a generator with a frequency of 27.12 MHz. The power was changed in steps ranging between 500 W, 1 kW, 1.5 kW, and 2 kW. The samples placed in quartz glass process tables were nitrided at constant pressure and changed the duration of the process (15 min, 30 min, 45 min) for the set generator power.

The cross-section microstructures of specimens were observed using a Nikon MA200 optical microscope (Nikon Instech Co., Ltd., Tokyo Japan). The microstructure and chemical composition of the surface layers were also investigated by using a

scanning electron microscope (SEM) JEOL JSM-6610 LV (JEOL Ltd., Tokyo Japan) equipped with an energy dispersion spectroscope (EDS) X-MAX 80 Oxford Instruments (Oxford Instruments Group, Abingdon, United Kingdom). The X-ray diffraction (XRD) was done on a device from PANalytical Empyrean (Malvern Panalytical Ltd, Malvern, United Kingdom). The source was an x-ray tube with cobalt anode-emitting characteristic radiation ($\text{CoK}\alpha = 1.74 \text{ \AA}$). Primary beam optic consisted of Goebel mirror for Co radiation, fixed divergence slit 0.5 deg, Soller slit 0.04 rad, and mask 10 mm. Diffracted beam optic consisted of parallel plate collimator 0.18 deg, Soller slits 0.04 rad and proportional Xe detector.

The hardness distribution of the nitrided layers was measured using a Vickers microhardness tester NEXUS 4305 (INNOVATEST Ltd., Maastricht, Netherlands). The surface hardness on the sample prepared for metallographic tests was measured at a distance of $10 \mu\text{m}$ from the edge of the sample and successively further inside the sample every $5 \mu\text{m}$. Measurements were made with 0.98 N load. The surface roughness profile parameters were tested with the T8000 RC profilometer by Hommel-Etamic. Parameter Ra arithmetic mean of the profile ordinates, was determined in accordance with the PN-EN ISO 4287:1999 standard.

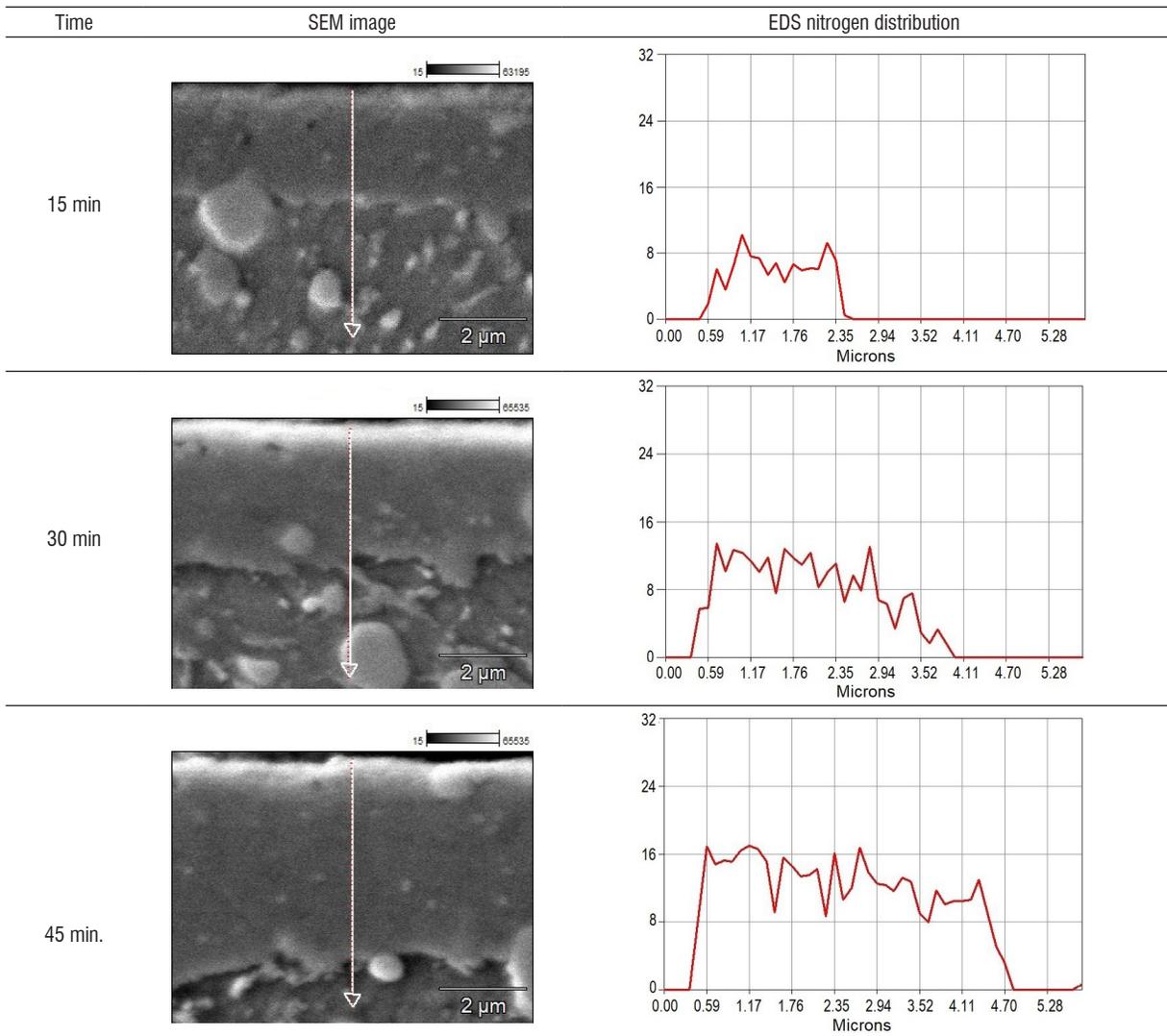


Fig. 2. Images of the SEM structures and the corresponding EDS nitrogen distributions obtained at a generator power of 500 W for different process times.

2 RESULTS AND DISCUSSION

As a result of the processes carried out at a generator power of 500 W, zones of nitride compounds on the surface were only obtained without an internal nitriding zone, regardless of time. Images of the SEM structures and the corresponding EDS nitrogen distribution distributions are shown in Fig. 2.

With a generator power of 500 W (Fig. 2), only the rudiments of the layer can be observed in the form of a white zone of nitride compounds: initially composed of γ' nitrides, and after longer dosing of nitrogen, transforming into ϵ nitrides. In this case, the internal nitriding zone was not obtained probably because of the low temperature of the samples, which was not sufficient to dissolve the nitrides and diffuse nitrogen into the samples. In the case of the shortest

time (15 min), the nitrogen content in the nitride zone was about 6 % by weight, which proves that it is mainly γ' nitride (Fe_4N). If the process is prolonged to 30 min, the nitrogen content increases, on average, to a level of about 10 % by weight. This value and the fact that the content exceeds 8 % prove that we are dealing with ϵ nitride ($\text{Fe}_{2.3}\text{N}$). Analogously, for a time of 45 min, the average nitrogen content is about 12 % by weight, so we are dealing with slightly more saturated nitrogen, specifically the nitride ϵ ($\text{Fe}_{2.3}\text{N}$).

These observations are consistent with the X-ray diffraction test (Fig. 3), where the spectra for the samples after 15 min and 45 min nitriding processes are presented. In the first case, the γ' (Fe_4N) nitrides are visible only. In the case of the longer process (45

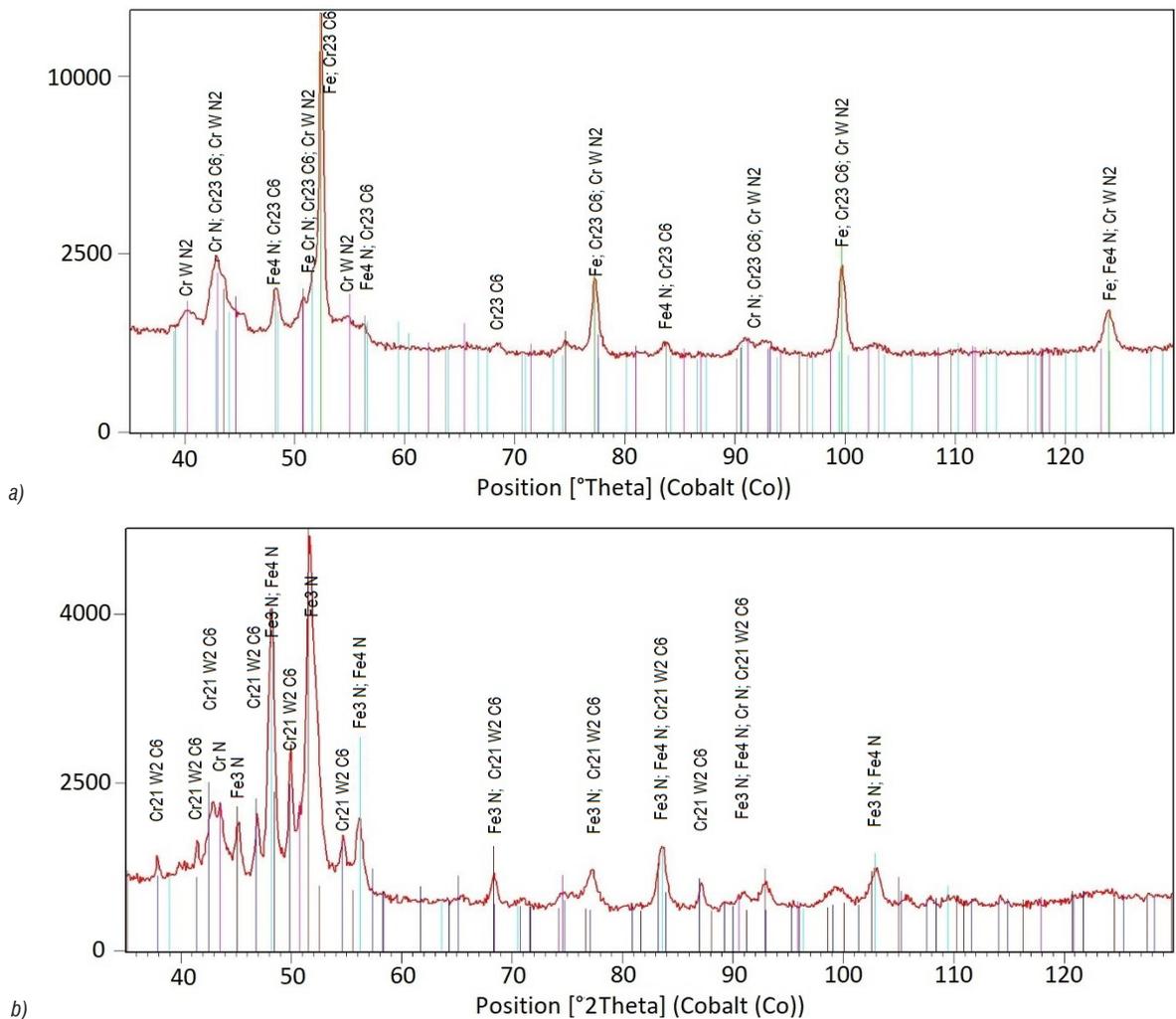


Fig 3. XRD spectra for nitrided samples at 500 W generator power, during a) 15 min and b) 45 min

min), the stress of nitrides ε (Fe_3N) and residuals of γ' (Fe_4N) are visible, respectively.

This may prove that the process of constituting nitrated layers takes place through the nucleation of γ' nitrides, which (together with a longer nitrogen supply) transform into ε nitride. However, with the indicated generator power, the obtained substrate temperature is too low and does not allow nitrogen diffusion deeper into the samples, as evidenced by the absence of an internal nitrating zone, and is confirmed by the lack of increase in the hardness of the sample directly under the nitride layer (the hardness at a depth of $10\ \mu\text{m}$ is about 300 HV). In contrast, surface hardness ranges from 960 HV, in the case of γ' nitride on the surface, to 700 HV for ε .

The processes carried out using higher generator powers allowed diffusion layers of various uniformity and thickness, as well as structural formation, to be obtained. The summary of the obtained structures is shown in Fig. 4.

The analysis of the photos shows that there is a clear correlation between the parameters of the process and the thickness and structure of the obtained layers. Increasing the generator power to 1 kW results in the appearance of the beginnings of the diffusion zone with a very irregular depth. A longer process time results in an increase in nitrogen saturation, but the layers are highly heterogeneous. At 1.5 kW, the diffusion layer is clearly visible but is not uniform and has an island structure, especially for shorter process times. It is clearly visible at shorter process times (e.g., for 15 min, the depth of the diffusion zone ranges from $26\ \mu\text{m}$ to $42\ \mu\text{m}$, but a white zone of nitride compounds appears on the surface above the areas of the thicker zone of internal nitrating). Increasing the time to 45 min makes the thickness uniform; however, the nitride compounds were not diffused. The use of a 2 kW generator results in even layers with a constant thickness after a 15 min process. However, an undiffused zone of nitride compounds is visible. Only

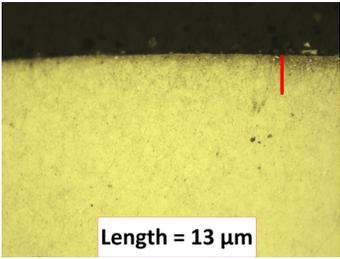
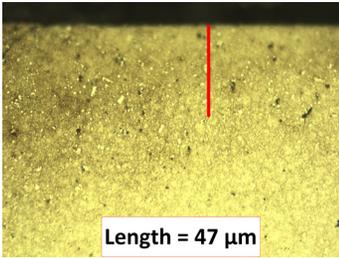
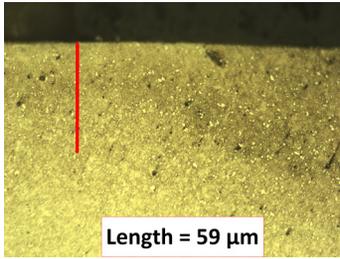
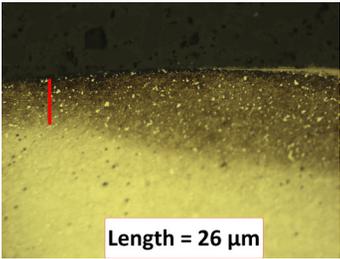
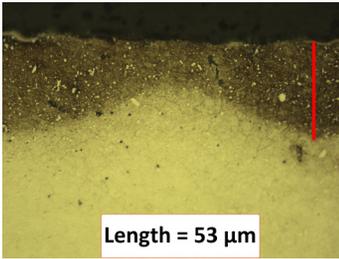
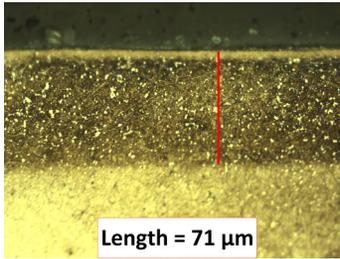
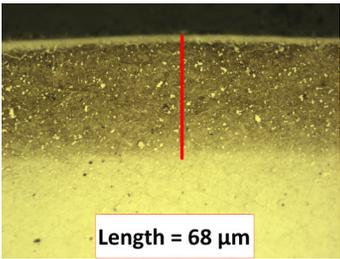
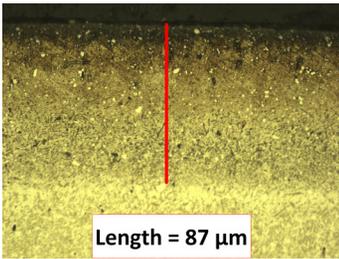
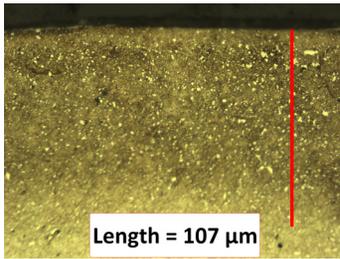
Generator power	Process time		
	15 min	30 min	45 min
1 kW	 Length = 13 μm	 Length = 47 μm	 Length = 59 μm
1.5 kW	 Length = 26 μm	 Length = 53 μm	 Length = 71 μm
2 kW	 Length = 68 μm	 Length = 87 μm	 Length = 107 μm

Fig. 4. Summary of metallographic structures obtained for different generator powers and process times

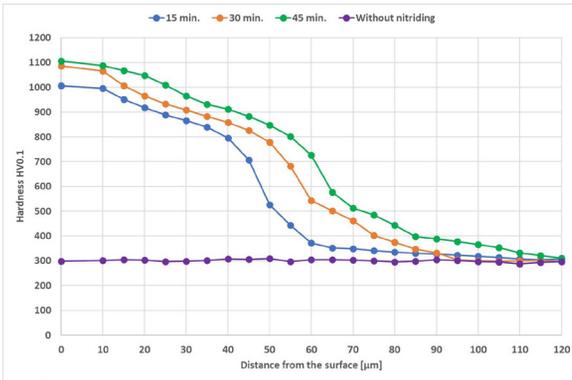


Fig. 7. Comparison of microhardness distribution of surface layers obtained with a 1 kW generator power for different process times

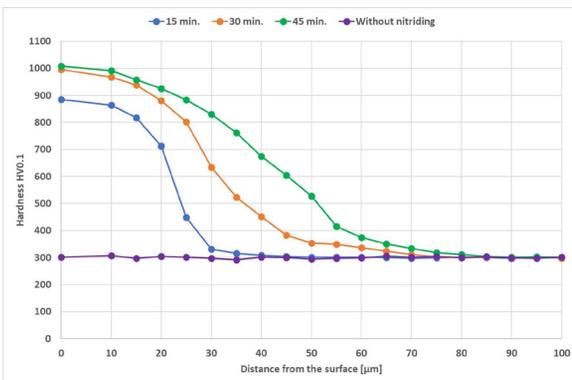


Fig. 8. Comparison of microhardness distribution of surface layers obtained with a 1.5 kW generator power for different process times

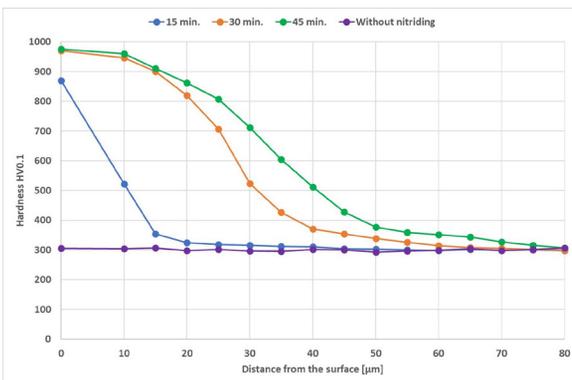


Fig. 9. Comparison of microhardness distribution of surface layers obtained with a 2 kW generator power, for different process times

Based on the hardness distributions made for a power of 1 kW, 1.5 kW, and 2 kW, the effective thicknesses of individual layers were determined in accordance with DIN 50190-3 (criterion 50 HV above the core hardness), while for the generator power of 500 W, the layer thickness was determined metallographically. Table 2 shows the thickness of the

obtained layers as a function of generator power and process duration.

When analysing the obtained layer thicknesses, it can be observed that, in line with theoretical predictions, the layer thicknesses increase along with generator power and with the extension of the process time. However, due to the thickness of the layers, their uniformity and phase structure, only the layers obtained with a generator power of 2 kW and process times of 30 min and 45 min are of practical importance for the application. In these cases, uniform layers were obtained without the white zone and the precipitation of nitrides at the grain boundaries of the former austenite, thus the most desirable for potential applications for small cutting tools.

It should be emphasized that the layers of usable thickness are obtained after a very short process (45 min). If counting a complete pump-down cycle, this time is approximately 1.5 hours. Compared to gas nitriding methods, for which the full cycle of such thickness is about 9 hours, this is a very good result. Comparison of the ionic or plasma methods with other methods of induction provides the following conclusions: the time is similar, but the inductively coupled plasma allows to eliminate the edge dissolution phenomenon and avoid the shadow effect.

Table 2. Summary of the thicknesses of the obtained layers as a function of generator power and process duration

Generator power	Process time		
	15 min	30 min	45 min
500 W	2.4 μm	4.0 μm	4.7 μm
1 kW	13 μm	47 μm	59 μm
1.5 kW	26 μm	53 μm	65 μm
2 kW	68 μm	87 μm	107 μm

3 CONCLUSIONS

1. It is possible to obtain nitrided layers with the correct structure in inductively coupled plasma. It is very important from a technological and economic point of view, i.e., a significant reduction of the process time with the possibility of full regulation of the structure of the layers, also without the zone of nitride compounds.
2. The possibility of nitriding in inductively coupled plasma on an industrial scale is also very important from an ecological point of view. The process uses inert nitrogen instead of toxic ammonia. In the new technology, there are also no emissions that require the utilization of post-process gases.

3. For samples made of HS6-5-2 steel with a diameter of 4 mm, it is best to conduct the process with a generator power of 2 kW.
4. The maximum hardness obtained on the raw material is about 1100 HV; hardness increases by 350 % in relation to the starting material.
5. Layers with functional properties of 100 μm thickness are obtained in a very short process lasting 45 min.

4 ACKNOWLEDGMENTS

The work has been done under Measure 1.2—Sectoral Research & Development programs of “Program Operacyjny Inteligentny Rozwój” 2014–2020 (Smart Growth Operational Program 2014–2020) co-funded by the European Regional Development Fund. The project: “Development of nitriding technology for machine parts and tools in inductively coupled plasma together with a device for its implementation.” Contract Number: POIR.01.01.01-00-0088/17.

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