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Vacuum-arc Nitriding of Carbon Steels Having Low Tempering Temperature

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Abstract: Studies have been made into a new possibility of modifying the surface of steels having a low tempering temperature by nitriding them in a vacuum-arc gas discharge followed by heat treatment (heating, quenching and tempering). Generally, nitriding of hardened steels takes place at a temperature of about 500°C, and thus this process appears impossible for steels with tempering temperatures of the order of 200... 300°C. It is demonstrated here that a single ion-plasma nitriding of high-carbon steel with the composition of 0.9% C, 1% Cr, 1% Si, followed by heat treatment, provides the nitrided layer of 2.5 mm in depth, with the hardness between 9 and 11 GPa. Within the range of X-rays penetration, the nitride-hardened layer of the surface is defined as the nitrogen austenite-alpha ferrite mixture, which shows high wear resistance and impact toughness. This layer contributes, in particular, to three-/four-foldin crease in the operational life of cutting punches (made of this steel and used in the manufacture of metal sieves) as opposed to the punches that have undergone conventional heat treatment. After repeated nitriding of the same steel and its subsequent heat treatment according to standard technologies the nitrided layer thickness becomes nearly twice as large, and that allows for multiple regrinding of steel tools. A computer analysis of related publications entered into three International Databases (INIS, MSCI, SCOPUS) has been carried out.

Keywords: Vacuum Arc Discharge, Vacuum Arc Gas Discharge, Ion-plasma Nitriding, Heat Treatment, Carbon Steel

1. Introduction

About a hundred years ago, Academician A. F. Ioffe established a significant effect of the surface condition on the mechanical properties of materials [1]. Among various ways of modifying the surface of steels, and thus, improving their physical and technical properties, we mention here nitriding.

Nowadays, ion-plasma nitriding of steels [2, 3, 8] is widely used throughout the world (Figures 1, 2).

For the computer analysis of publications on ion-plasma nitriding in a vacuum, use was made of the data from the International Databases, viz., International Nuclear Information System - INIS (1990-2020), Materials Science Citation Index - MSCI (1992-2011), SCOPUS (1990-2020).

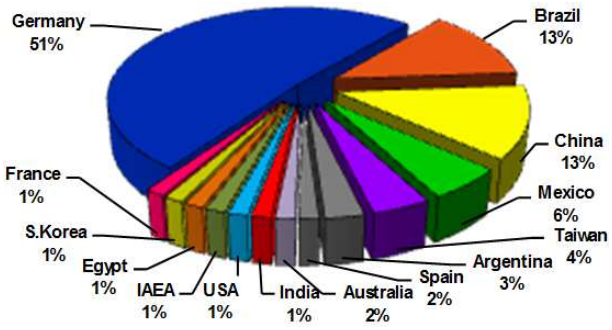

Figure 1. *Distribution of related publications by different countries.*

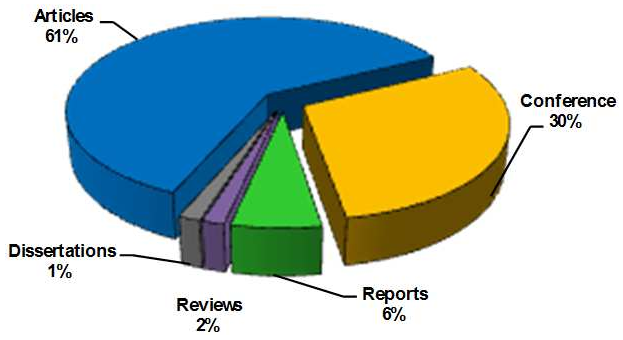

Figure 2. *Distribution of data by the mode of publications: articles, conference proceedings, reports, reviews.*

The analysis of the data from the mentioned three databases has revealed great interest in ion-plasma nitridings hown by many countries, as evidenced by a large number of conference proceedings. The number of publications has been continuously increasing from year to year until 2018 (Figure 3).

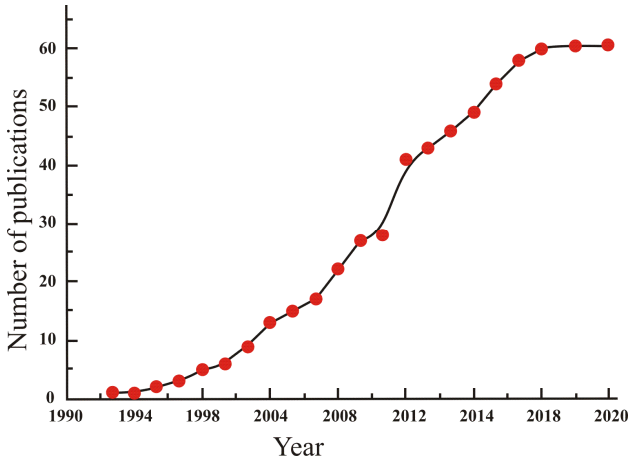

Figure 3. *Cumulative increase of the number of publications introduced in Databases.*

However, in recent years, publications have practically ceased, despite the fact that a number of issues still remain unclear, among them the ones considered in the proposed article.

Nitriding is one of the priority areas of research in this respect, considering good combination of high physical and mechanical properties at a moderate cost. Of prime importance is the development of nitriding processes for steels, the tempering temperature of which is at the level of 200-300°C, while generally, nitriding occurs at temperatures of about 500°C.

It is known that the wear resistance of steel products is determined by the compromise between hardness, impact toughness and plasticity of their surface. The introduction of nitrogen into steel improves these characteristics [2].

There are various methods of nitriding, including ionic and ion-plasma nitration (in the plasma of a vacuum-arc gas discharge) [3, 4, 8], which will be considered at some length below.

By one theory [2, 3], the ion nitriding process is carried out in a sealed closed volume in a rarefied NH_3 or $N_2 + H_2$ gas medium. A glow discharge is initiated between the cathode (sample) and the anode. Gas ions with high energy bombard the surface of the sample, heat it, depassivate and change the fine structure of the surface; intensify chemical processes, adsorption and diffusion, as a result of which the surface gets saturated with nitrogen and its compounds with metals, thus increasing the hardness and other physical properties of the sample. The ionic composition of ammonia plasma near the cathode is a mixture of NH_2^+ and NH_3^+ ions, and in the nitrogen plasma - $N_2^+$and N^+ ions. Thes puttered iron atoms in the glow discharge plasma combine with nitrogen to form iron nitride, which is adsorbed on the cathode surface. Under the action of bombardment, the deposited Fe_2N nitride decomposes ($Fe_2N \rightarrow Fe_3N \rightarrow Fe_4N$) with the formation of lower nitride and atomic nitrogen, which diffuses deep into the metal and forms a zone of internal nitriding, while the nitrogen-depleted iron is sputtered into the plasma [2, 3]. This process is continuously repeated.

Thus, according to this theory, the nitride phases formed in the plasma and deposited on the cathode (nitrided sample) surface, serve as an independent source of atomic nitrogen.

By another theory [4], the presence of atomic nitrogen in the near-cathode plasma gives rise to nitrides on the iron surface, which are then partially decay due to the ion bombardment, yielding the atomic nitrogen, one part of which diffuses to the bulk-volume of iron, and the other part comes back to the plasma. So, the nitrided layer consists of iron-nitrogen compounds and the solid solution of nitrogen in the iron lattice.

However, studies into nitriding processes have cast some doubt upon the reality of the above-described model. In 1974, an article was published [5], the author of which convincingly demonstrated that for the nitriding of steel the only essential factors are the sufficient temperature of the process and presence of nitrogen atoms. In 1983, information appeared on the nitriding of steel in a glow discharge in the ammonia atmosphere at application of positive potential to the samples, i.e., without sample surface sputtering [6]. Later on, by nitriding of steels with the use of substrates made of Armco iron, and titanium in an Ar-N mixture, and also, high speed steel (6% W, 5% Mo) substrates in nitrogen, it was demonstrated that the nitriding of steels in a low-pressure vacuum-arc discharge (i.e., discharge with a hot-cathode arc as an electron emitter) takes place provided that necessary conditions are met. These are the required operating temperature and the «floating» potential, i.e., in the absence of surface sputtering [7].

The later experiments showed that the same results (including physico-technical characteristics) of nitriding in the arc gas (two-stage) discharge at the same temperature of the samples were obtained at both the negative (sample–cathode) and positive (sample–anode) polarities of the substrate [8, 9].

In all these cases, at the same temperature of the samples under positive or negative potentials, the formation rates of the nitrided layers, the their structure and physical characteristics were approximately the same. The fact of positive-polarity nitriding of samples denies the model of nitride formation in a gaseous medium, since the surface bombarded by electrons is not sputtered. And thus, the nitriding model associated with the nitrided surfaces puttering is denied.

All these nitriding processes provide the thickness of the nitrided layer at the level of several tens of microns. For cutting tools, in most cases, the optimal thickness is about 35-40 microns [8]. However, these thickness values are clearly insufficient for machine parts.

There are known the processes of vacuum-arc nitriding of high-speed steels with their subsequent heat treatment [10, 11], which make it possible to obtain nitrided layers in hardened steels with thickness of 2 mm and more. These studies dealt only with high-speed steels. However, studies of relatively cheap steels having low tempering temperatures, which cannot be nitrided by common methods, are of no less interest, since the temperature of the products during their nitriding (about 500°C) is higher than their tempering temperature. In particular, this applies to the 9 KhS steel of composition 0.9% C, 1% Cr, 1% Si (with tempering temperatures of 200... 300°C).

As an example of steels having low tempering steels, the present paper deals the processes of ion-plasma nitriding of steel 9 KhS (its composition see above) with its subsequent heat treatment [13].

2. Experimental Technique

2.1. Schematic Diagram of the Installation

Figure 4 shows a schematic diagram of the installation, which explains the essence of the vacuum-arc ion-plasma nitriding of steel products.

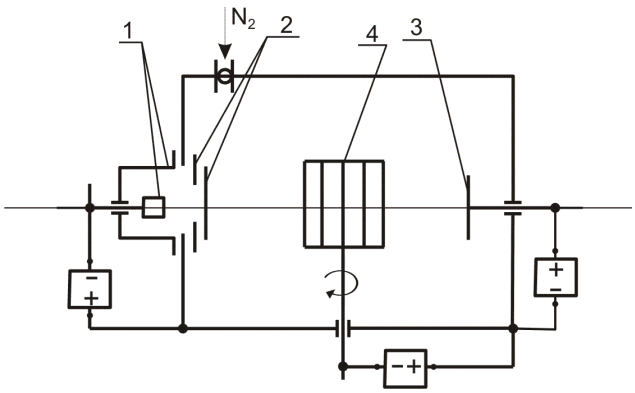

Figure 4. *Schematic diagram of a vacuum-arc installation for ion-plasma nitriding: 1 - vacuum-arc evaporator, 2 – power supply for the first stage of the arc discharge, 3–screen, 4-additional anode.*

The installation has a vacuum-arc evaporator 1, the outlet of which is closed by a screen 2 which passes neither the metal component of the plasma, nor the droplets, but passes the gaseous (in this case, nitrogen) plasma. The vacuum chamber also contains an additional anode 3. In the center of the vacuum chamber there is a rotary device 4, on which the products to be nitrided are located. The chamber is evacuated to a high vacuum, nitrogen is admitted to a pressure of about 0.5 Pa, and the evaporator 1 is turned on. The gas-metal plasma is generated in the evaporator, the gas component of which penetrates into the volume of the vacuum chamber and is drawn to the anode 3. Thus, an arc gas discharge is formed in the chamber, the ions of which are used for nitriding the products (figure 4).

For nitriding the samples made of steel 9 KhS, a negative potential ranging from 1 to 1.2 kV was applied to the rotary device 4, there by controlling the sample temperature in the range from 500 to 550°C. Thus, a two-stage arc discharge is created, the first stage of which presents the plasma of a conventional vacuum-arc evaporator, the second is the gas discharge between screen 2 and additional anode 3 (Figure 4). The second-stage plasma of the discharge is used to heat the samples during nitriding.

Heating of metal samples up to temperatures of 420-590°C is carried out in the second-stage gas plasma by bombarding the samples with ions (or electrons) on applying negative (or positive) potential to them By changing the potential value at the nitrided products one can control their temperature, and hence, their properties, such as the phase composition, the depth of nitrided layers, etc. The properties of the nitrided layers can also be controlled by changing the pressure and composition of the nitrogen - argon mixture. The main components of the gas vacuum arc discharge are the molecular nitrogen ions N_2^+ and the excited nitrogen molecules in various metastable states, while the plasma contains a fairly large number of neutral nitrogen atoms, reaching 10^{10} n/cm^3 [8].

With a positive potential at the samples, the electrons heat them up without sputtering the surface, i.e., the surface finishis not disturbed.

Therefore, as mentioned above, the coincidence of the data on nitriding at negative and positive potentials for high-speed steels indicates the absence of a noticeable contribution of molecular and atomic ions to the nitriding process. At that, only neutral nitrogen atoms have high activity upon saturation of the sample surface with nitrogen, and thus, the theory of the formation of iron nitrides in the plasma volume is not confirmed.

At the same time, nitriding with the use of an arc gas discharge at temperatures of 420... 590°C can significantly reduce the nitriding time and control the phase composition of the nitrided layer.

2.2. Diffractometric Research

Diffractometric studies of the samples were carried out

with a DRON-2.0 X-ray diffractometer in cobalt Co-Kα radiation, using a Fe selectively absorbing filter. Diffracted radiation was recorded by a scintillation detector. To determine the structure in depth, a layer-by-layer analysis of the surface was carried out. Qualitative (100) phase analysis of the samples was performed according to the International Database of Crystalline Compounds ICDDPDF-2. Quantitative phase analysis and determination of the phase lattice parameters were performed using the Rietveld method. Images of the surface after nitriding were obtained using a Nano SEM 425 scanning microscope.

2.3. Samples for Research

Cylindrical samples, 5 and 10 mm in diameters, made of unhardened steel 9 KhS, were used for the studies.

After preliminary preparation of their surface (cleaning, rinsing and drying), the samples were installed vertically on a rotating device in the upgraded BULAT-6 installation [8].

The vacuum chamber was preliminarily evacuated to a pressure of P = 0.01 Pa, then nitrogen was admitted to a pressure of 0.5 Pa; a negative potential of 1000 V was applied to the samples, and the nitriding process was carried out for 1 hour at a temperature of 500°C, followed by cooling in the vacuum chamber.

Then the samples were heated in a muffle furnace to a temperature of 860°C with subsequent quenching in oil and tempering at a temperature of 280°C.

The microhardness of the samples was measured with a PMT-3 microhardness tester at a load of 50 g.

3. Experimental Results

Under the above-given conditions, the ion-plasma nitriding of steel 9 KhS leads to the diffusion saturation of the surface with nitrogen and a small ionic sputtering of the surface layer (Figure 5).

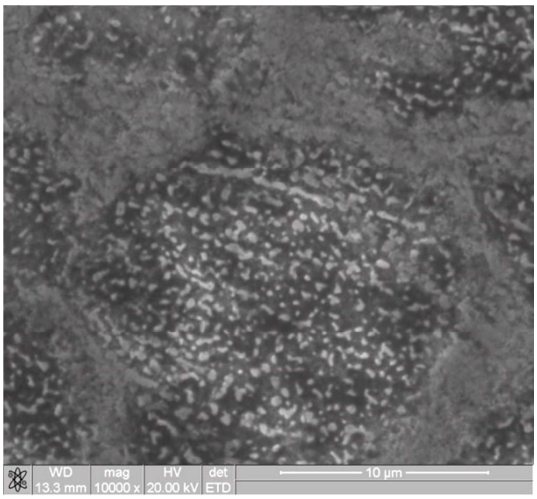

Figure 5. *Micrograph of the surface of steel 9 KhS after nitriding.*

The microhardness of the thus nitride surface of the steel reaches 9...11 GPa with a layer thickness of up to 50 microns.

After heat treatment (heating, quenching and tempering) the microhardness of the nitrided layer ranges between 8 and 11 GPa, and reaches a depth of 2.5 mm with the formation of a technological layer with a thickness of up to 150 microns and a hardness of 6...8 GPa (Figure 6).

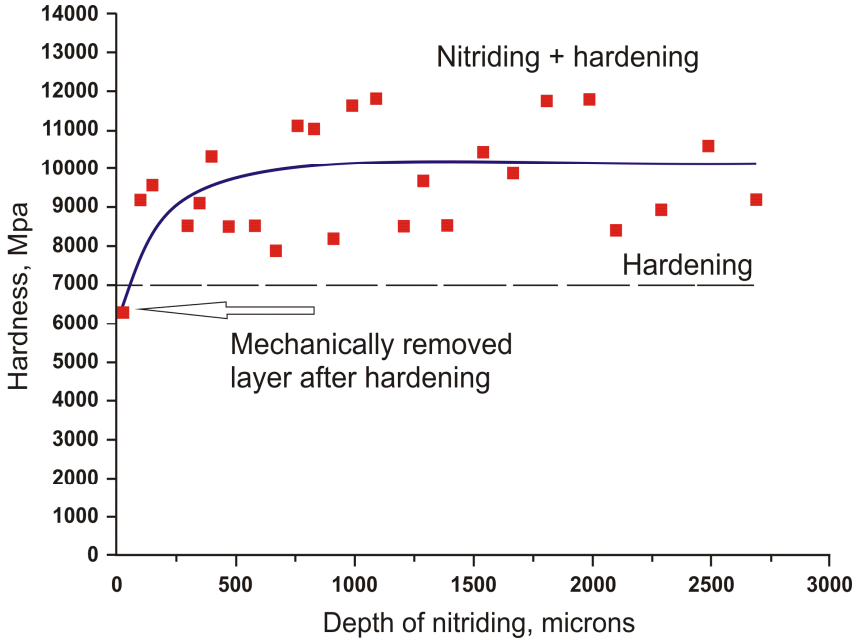

Figure 6. *Microhardness versus the depth of ion-plasma nitriding of the Ø5 mm sample made of heat-treated steel 9 KhS.*

Table 1 lists the X-ray diffraction data on the depth of nitration of the sample made of steel 9 KhS. The XRD patterns of the test samples are shown in Figure 7.

Table 1. *Phase composition and lattice parameters of the test sample.*

Sample No	Phase	Weight content, % wt	Lattice parameters, nm
No. 1. Initialsurface	Fe-α	100	a = 0.28646
No. 2. 50 microns removed from the original surface	Fe-α	100	a = 0.28652
No. 3. 100 microns removed from the original surface	Fe-α	100	a= 0.28655
No. 4. Surface after removal of 120 microns	Fe-γ	10.2	a = 0.3595
	Fe-α	89.8	a = 0.28760

On the surface of the test sample (Figure 7a), only Fe-α ferrite with the lattice parameter a=0.28646 nm was revealed. No traces of other phases were found within the sensitivity of the method.

After removal of 50 microns, the sample surface also exhibited only the Fe-α ferrite phase, and in comparison with the previous sample, the lattice parameter has slightly increased to be a=0.28652 nm. This increase is associated with the presence of dissolved nitrogen in the matrix (Figure 7b).

After removal of 100 microns (Figure 7c), again only the Fe-α ferrite phase was detected, and as compared to the previous sample, the lattice parameter was found increased within the measurement accuracy up to a=0.28655 nm. In this case, the hardness of the layer consisting of Fe-α ferrite is small and amounts to 5...6 GPa.

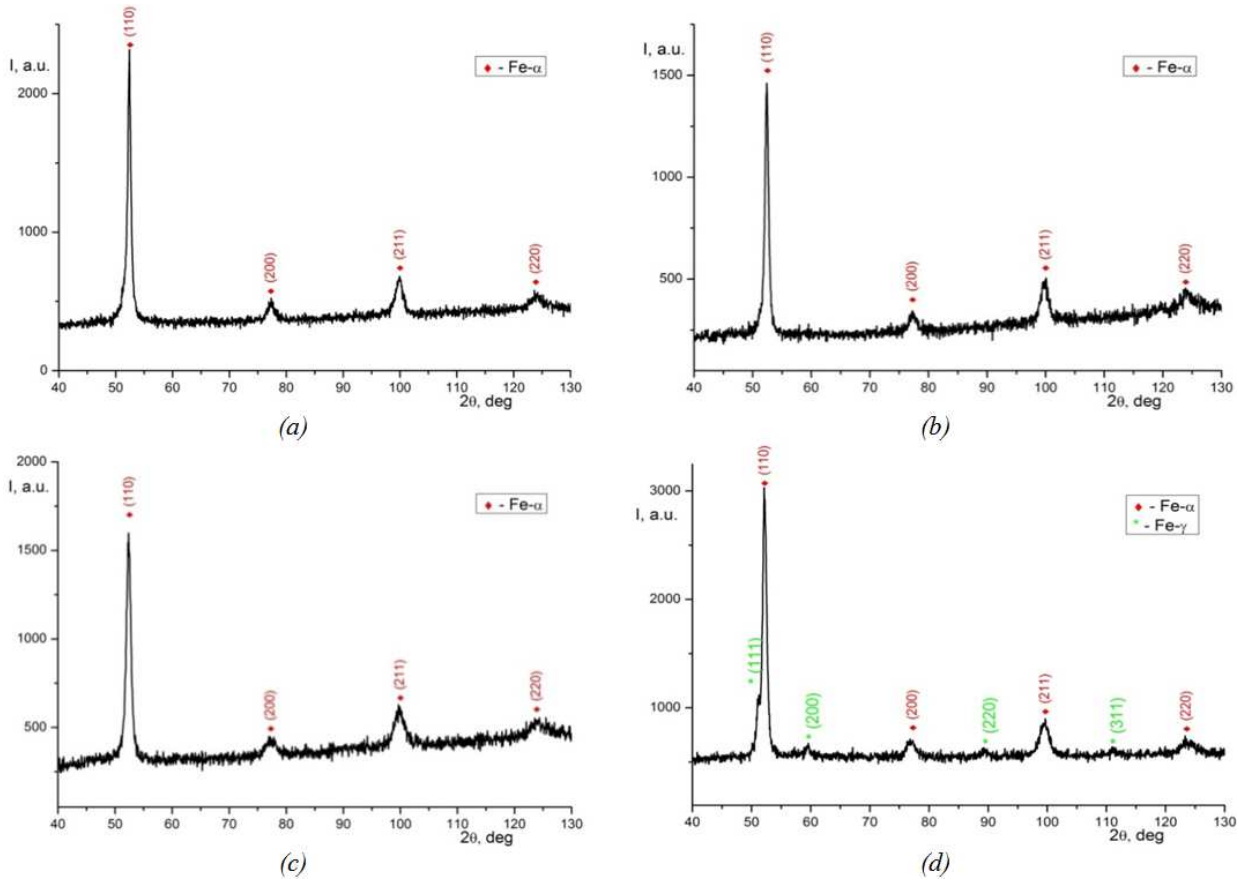

Figure 7. *Diffraction patterns of 9 KhS steel samples were measured after nitriding and heat treatment: (a) - original surface; (b) - surface after removal of 50 microns; (c) - after removal of 100 microns from the original; (d) - surface after removal of 120 microns from the original).*

Removal of the surface layer of the sample is carried out until the appearance of a layerhaving an increased hardness (8...11 GPa) at a depth of 120 microns from the surface. The X-ray diffraction studies of the sample surface after removing the low-hardness layer (Figure 7d) showed the presence of a mixture of two phases: ferrite Fe-α and nitrogenous austenite Fe-γ. No other phases, including nitrides, were found. The weight content of Fe-α ferrite in the sample is 89.8% wt, its lattice parameter is a=0.28760 nm. The sample also contains nitrogenous austenite, 10.2% by weight, its lattice parameter being a=0.3595 nm. To increase the depth of nitrationafter a single nitriding, the technology of double ion-plasma nitriding with heat treatment was applied. A sample of this steel with a diameter of 10 mm underwent nitriding followed by heat treatment two times in succession. In this case, the depth of the soft surface layer increased to 350 microns. This made it possible to increase the depth of the hard nitrided layer up to 5000 microns (Figure 8).

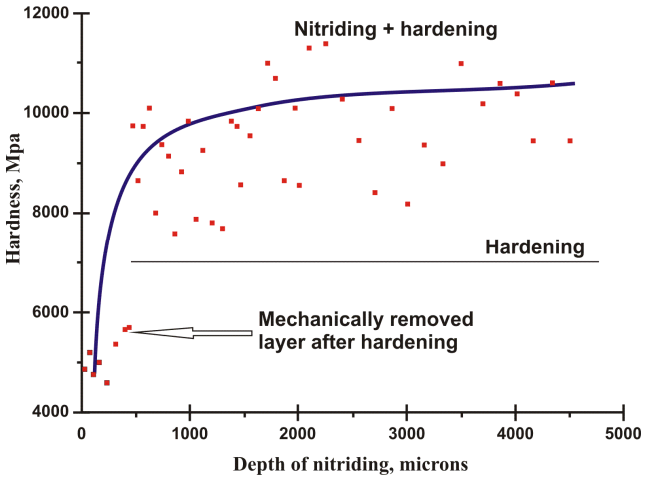

Figure 8. *Microhardness of the Ø10 mm 9 KhS steel sample as a function of the layer depth after double treatment.*

The microhardness of specimens from 9 KhS steel after double nitriding and heat treatment reaches 8...11 GPa to a depth of 5 mm [14, 15].

The application of cutting punches of diameter 3 mm, used in the manufacture of sieves from 2 mm thicksheet steel, which underwent a single ion-plasma nitriding and heat treatment, showed an increase in their service life by 3-4 times as compared to hardened punches without nitriding.

4. Discussion of Results

As the X-ray diffraction studies have shown, the surface layer of the sample, subjected to a single ion-plasma nitriding and heat treatment, consists of Fe-α ferrite having a low hardness, which gradually increases with the increasing nitriding depth (Figure 6). After removal of 120 microns, the microhardness of the surface layer, consisting of a mixture of Fe-α ferrite and nitrogenous austenite Fe-γ (see Table 1), reaches a value ranging from 8 to 11 GPa.

This can be explained as follows. The layer on steel nitrided by the described method consists of a sequence of layers of the ε-phase $Fe_{2-3}N$, γ′-phase Fe_4N, nitrogenous austenite Fe-γ and ferrite Fe-α. When the nitrided layer is heated to the quenching temperature, all nitride phases decompose, and during the decomposition of the ε-phase, a layer of very soft porous iron is formed. From the nitride layers, nitrogen diffuses into the depth and outwards. In the process of quenching, the nitrogen resulting from the decomposition of the phases penetrates deep into the steel, there by displacing most of the carbon atoms owing to its higher mobility [12]. This is why the carbon atoms were not detected by X-ray diffraction.

In nitrogenous austenite the transfer of electrons from the nitrogen atom to iron is more intense than the exchange of electrons between carbon and iron atoms in carbonaceous austenite, this being indicative of an enhancement of the inter atomic bond. The spatial distribution of the charge in the lattice of nitrogenous austenite is more symmetric, i.e., with a smaller size of nitrogen ions, this contributes to a greater solubility of nitrogen in austenite in comparison with carbon.

The introduction of nitrogen makes it possible to reduce the carbon activity, i.e., to improve simultaneously the mechanical and corrosive properties of the finished product.

Nitrogen, unlike carbon, reduces the stacking fault energy, i.e., it splits dislocations. The splitting of dislocations leads to their strong interaction with nitrogen atoms, and also, to a decrease in the mobility of dislocations, which results in high values of the strain hardening coefficient, wear resistance and relaxation resistance [2].

Thus, nitrogen doping leads to the creation of austenite with a high concentration of stacking fault sand a heavily deformed lattice, thus ensuring the development of a structure with a high dislocation density after deformation. This makes it possible to create a layer with high mechanical characteristics. So, nitrogen enables one to obtain for steel a unique combination of strength, impact strength, corrosion resistance and ductility.

These physical and technical characteristics, in particular, cause an increase in the wear resistance of cutting punches by 3-4 times compared to punches with standard heat treatment.

5. Conclusions

1) The wear resistance of carbon steel products, having a low tempering temperature, can be increased through their heat treatment up to 500…590°C in the nitrogen medium of the gas vacuum-arc discharge (ion-plasma nitriding), followed by standard heat treatment (heating, quenching and tempering).
2) This technology provides the optimum combination of hardness, impact strength and ductility of nitrided layers at their thickness reaching 2 mm and more.
3) Single vacuum-arc nitriding of 9 KhS steel samples with subsequent standard heat treatment allows increasing their microhardnessup to 8...11 GPa to a depth of 2500 microns.
4) Double ion-plasma nitriding with heat treatment allows increasing the depth of the hardened layer with a hardness of 8...11 GPa up to 5000 microns.
5) The use of stamping punches after ion-plasma nitriding and heat treatment has shown an increase in their operational life by 3-4 times compared to similar punches but without nitriding.

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