SURFACE HARDENING OF THE TOOLS BY NITROOXIDATION

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Abstract. *In order to increase the corrosion resistance and wear resistance as well as the resistance of cutting tools made of high-speed steels, the article presents the results of the study of the possibility of using a combined method of surface hardening, consisting in nitriding in ammonia at the first stage and oxidation of the nitride layer in water vapor at the second stage. The formation of a thin dense oxide film consisting of one magnetite and a dense nitride layer under it as well as the following zone of internal nitriding were studied on the surface to be strengthened. It is studied that the combined process at the first stage at pre-eutectoid temperature for the system "Fe-N" taking into account the temperature intervals of martensitic transformation of residual austenite and at the second stage at pre-eutectoid temperature for the system Fe-O at tempering temperature intervals allows to obtain a diffusion nitride-oxide layer with the necessary structures and properties on the surface of high-speed steels.*

Keywords: *diffusion nitride layer, nitrooxidation, surface oxide layer, zone of internal nitriding.*

Introduction

In the technological process of heat treatment of tools made of high speed steel, the high-tempering operation after quenching is of great importance. When vacationing by conventional methods, uneven oxides are formed on the surface of the tool, which greatly spoil the appearance of the tool, as a result of which it is necessary to chemically clean the surface of the processed products.

To improve wear resistance and protection against atmospheric corrosion during their storage, a high tempering of the tool is carried out in an atmosphere of water vapor to obtain diffusion oxide layer on their surface. At the same time, the obtained surface oxide layer improves machinability during metal cutting.

Surface hardening of cutting tools made of high-speed steels can serve as one of the ways to increase their durability. One of the methods to improve the wear resistance and corrosion resistance of the properties of cutting tools is the nitrooxidation process. In this case, with a combination of low-temperature nitriding processes in an ammonia atmosphere and subsequent oxidation, an inner nitriding zone is formed on the surface of the product at the first stage of the nitriding process, and a thin and dense oxide layer is formed at the second saturation stage due to surface de nitriding.

The technological regimes of the processes of low-temperature gas nitriding and oxidation in water vapor, as well as tempering after quenching, allow the combination of processes of low-temperature gas nitriding with subsequent oxidation in superheated steam.

Oxidation of high speed steels.

Tools such as drills, taps and mills made of high-speed steels are usually quenched by subsequent high tempering in an atmosphere of superheated steam, after which the oxide layer on the surface serves as an effective method of protection against atmospheric corrosion. Vacation in the atmosphere of superheated steam is one of the types of combination of thermal and chemical-thermal treatment. In this case, the surface of the instruments heated to 450-600^{0}S interacts with oxygen of superheated steam and oxidizes with the formation of a thin oxide film on the surface.

The thickness of the oxide film on the surface, depending on the temperature-time regimes and conditions of the oxidation process in an overheated pair, ranges from 3-30 mkm. At the same time, the regimes of conducting high tempering are not consistent with the modes of transformation of residual austenite into marten site, because of which some structural strengths of the product change.

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The use of high tempering in an atmosphere of superheated steam of products from high speed steels after quenching is usually carried out after grinding. This leads to secondary hardening of the surface, and here the need arises to restore residual austenite to martensite.

The oxidation of the surface of metals and alloys in water vapor is determined by many factors, the most important of which include the composition of the oxidizing oxygen-containing gas phase, the temperature of oxidation and the duration of exposure to the oxidizing atmosphere, the composition of the steel, as well as the structure and condition of the surface. According to the state diagram for the Fe-O system, it follows that in the technically interesting region of iron alloys with oxygen, three types of oxides are formed: ferrous oxide FeO (wustite), ferrous oxide Fe_3O_4 (magnetite), iron oxide Fe_2O_3 (hematite) .

FeO - has a significant number of defects in the crystal lattice, and is stable only at a higher eutectoid temperature for the state diagram "Fe-O". Fe_3O_4 has a cubic spinel-type lattice with the parameter a 0,838 nm. Although magnetite, as well as wustite, contains an excess of oxygen, the magnitude of this excess is small.

In works devoted to vapor oxidation, it is shown that the diffusion permeability of magnetite and hematite in comparison with wustite permeability is insignificant and this determines their best protective properties against corrosion. When oxidized with water vapor, the oxide film consists of Fe_3O_4 oxide, which in some cases is prone to cracking, which facilitates the growth of the oxide film. Moreover, its crystals grow on an open external surface and are prone to cracking, cracking and peeling.

Nitriding of high speed steels.

Nitriding is a multi-purpose process, which strengthens a wide range of metals and alloys, structural, tool, corrosion-resistant and heat-resistant steels, etc. After nitriding in the hardened layer, obtaining diffusion surface nitride zones and an internal nitriding zone are achieved, each of which is responsible for establishing certain properties of the processed products.

Various tools - drills, milling cutters, taps, reamers, etc. made of high-speed steels as a final chemical-thermal treatment are subjected to nitriding to obtain a thin surface layer consisting of nitrides $(\varepsilon+\gamma')$-phase and the diffusion zone of the internal nitriding (Fe_α).

The surface nitride zone on the processed products obtained after nitriding is responsible for properties such as corrosion resistance and wear resistance. Increase the hardness of the working surfaces of the tools, reduce the adhesion of the processed material to the tool material. The zone of internal nitriding obtained after low-temperature nitriding allows the operation of tools at elevated cutting conditions and increases tool life.

Regulation of the phase composition and structure of the nitride layer is achieved by changing the nitrogen potential of the saturating atmosphere and the establishment of the temperature-time regimes of the process. Maintaining the nitrogen potential at the level of nitrogen solubility in one or another phase, it is possible to obtain a layer consisting of an α-solid solution - $Fe_{\alpha\,[N]}$, iron nitrides and alloying elements, to form a nitride ε-phase, carbonitride ε'-phase, oxycarbonitride ε"-phase on the surface. It is recommended to regulate the nitrogen potential by diluting ammonia with fully or partially dissociated ammonia, oxygen, air, carbon-containing gases, etc. However, the simplest change in the atmospheric potential can be achieved by changing the degree of dissociation of ammonia in the furnace.

Since the degree of dissociation of ammonia is a function of many variables, for a given furnace load, shape of parts and saturation temperature, the degree of dissociation is mainly determined by the flow rate of ammonia, and therefore, its amount supplied to the furnace. The greater the flow of ammonia passing through the furnace, i.e., the greater its flow rate, the lower the dissociation. Under these conditions, most of the ammonia is not involved in the process of steel saturation with nitrogen and is a carrier gas.

Nitriding of a cutting tool made of high-speed steels is carried out under temperature-time conditions that do not affect the transformations of residual austenite into martensite or the transformations of martensite into austenite in a steel matrix.

The nitriding process of a cutting tool made of high speed steel is carried out at temperature intervals of 500-550°S for a duration of 0,5-2,0 hours, depending on the design and size of the tool, as well as the type of workpiece and operating conditions.

Nitrooxidation of high speed steels.

In order to further, improve the mechanical and physicochemical properties of the workpiece made of high-speed steels, the combined nitriding technologies were studied, which consisted of conducting gas nitriding at the first stage in an atmosphere of ammonia and further oxidation of the nitride layer in water vapor.

Drills made of P6M5 steel used in serial production were selected as the cutting tool. Material Composition: C=0,8-0,88%; Cr=3,8-4,4%; W=5,5-6,5%; Mo=5,0-5,5%; V=1,7-2,1%. The drill is hardened at a temperature of 1210-1230°S and tempering in the temperature range 550-600°S.

To study the kinetics of the formation of a nitride and oxide layer on the surface depending on the temperature and time parameters and to determine the nitride and oxide layer on P6M5 steel, samples with a diameter of 10 mm and a thickness of 5 mm from this steel were subjected to nitration in ammonia for 2 hours at the first stage at a temperature of 550°S in various values of the degree of dissociation of ammonia, in the second stage, frequently samples without being removed from the furnace were processed by oxidation in water vapor.

In the short-term process of low-temperature nitriding at the first stage of nitrogen saturation in an atmosphere of ammonia, a thin nitride layer is formed on the steel surface in the form of an non-etching part of the surface and a mixture of $(Fe_{\alpha\,[N])}+\gamma')$-phases is located behind it, followed by the internal nitriding zone (Figure 1, a).

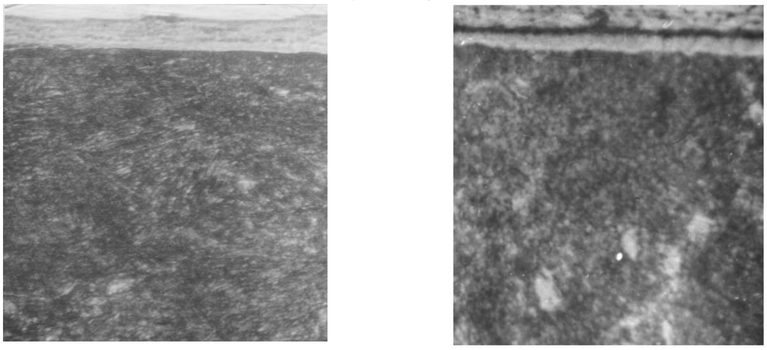
In all cases, when saturated with nitrogen, a sequentially arranged composite layer is formed on the surface consisting of the ε-phase → γ'-phase → mixture $(Fe_{\alpha\,[N]}+\gamma')$-phases → the internal nitriding zone, according to the state diagram of the “Fe-N” system. The regulation of the structure of the nitride layer is achieved by changing the nitrogen potential of the atmosphere, maintaining which at the level of the limiting solubility of nitrogen in one or another phase, it is possible to form a diffusion zone based on the internal nitriding zone or a composite layer with a given nitride phase.

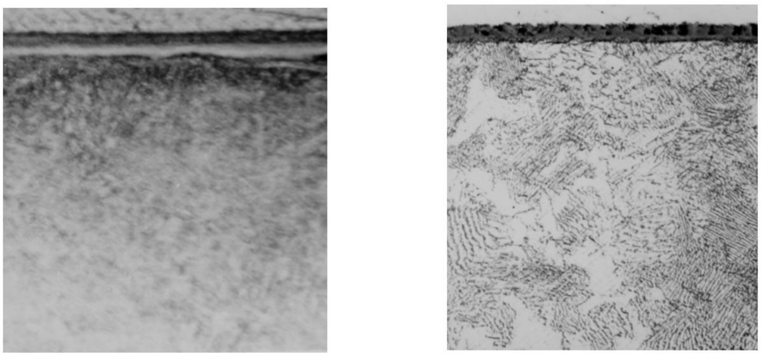
As a result of studying the effect of the degree of ammonia dissociation on the thickness and composition of the diffusion layer at lower eutectoid temperatures, it is shown that the formation of a developed zone of high nitrogen nitride (ε-phase) at a significant total layer thickness is characteristic of processes with a degree of ammonia dissociation $\alpha<50$ %, however, the porosity of the nitride layer increases for its further oxidation. When the degree of ammonia dissociation $\alpha>50$ %, the thickness of the nitride zone decreases and the amount of high-nitrogen nitride of the ε-phase decreases, and the low-nitrogen nitride of the γ'-phase increases, the porosity of the nitride layer disappears.

In the nitride layer, the formation of the ε'-phase of a carbonitride character obtained upon saturation in an atmosphere of ammonia occurs only when nitriding the steel due to the presence of carbon in the steel matrix, since only in the presence of carbon in the nitride layer a carbonitride phase is formed. In the process of nitrogen diffusion from the atmosphere and due to the back diffusion of carbon from the steel matrix during decarburization, especially at the boundaries of the nitride layer and the internal nitriding zone, the formation of the ε'-phase is more likely.

In order to obtain a hardened layer by nitriding followed by oxidation in water vapor, high-speed steel samples were processed in a pure ammonia atmosphere with a dissociation degree $\alpha>50$ % at a temperature of 550°S for 2 hours and at the same temperature, the samples were oxidized in water vapor. Microstructures of samples previously nitride and oxide in water vapor of various durations are shown in Figure 1.

When superheated steam is introduced into the atmosphere in the nitride layer due to a change in the partial pressure ratios $NH_3:H_2$ towards $H_2O:H_2$, the nitride layer begins to be nitride with the formation of a thin surface oxide layer, which, after the formation of a certain thickness, prevents the formation of a barrier layer and inhibits nitrogen diffusion deep in the metal. As a result, during oxidation, a thin oxide film is formed on the surface of the nitride layer (Figure 1, a), with further oxidation, the thickness of the oxide film increases due to the de-nitrated nitride layer (Figure 1, b), after a long duration of oxidation, the nitride layer completely dissociates and a surface oxide forms layer (Figure 1,c).





a) x500 b) x500

c) x500 d) x500

Figure 1. Microstructure of samples nitriding at a temperature of 550°S (a) and oxidation in water vapor at the same temperature for a duration of: b - 0,5 hours; c - 1,0 hour and d - 1,5 hours.

Judging by the microstructure of steel with composite oxynitride layers, we can say that the oxide layer develops uniformly over the nitride layer due to the dissociation of nitrogen on the nitride surface, further prolonged oxidation of which leads to the disappearance of the high nitrogen nitride layer.

In the zone of internal nitriding, under the nitride layer, mixtures of the ($Fe_{\alpha[N]}+\gamma'$)-phases develop. The depth of the ($Fe_{\alpha [N]}+\gamma'$)-phases first increases due to nitriding in the first stage of nitrogen saturation, and in the second stage of the oxidation process due to the dissociation of a high nitrogen nitride layer (Figure 1, d).

Based on the presence of a nitride oxide layer on the surface, which is responsible for properties such as corrosion resistance and wear resistance with the creation of a positive surface gradient during friction, it is necessary to obtain a developed nitride oxide layer, and to increase the structural strength it is necessary to obtain a developed mixture ($Fe_{\alpha[N]}+\gamma'$)-phases and SVA. In the zone of internal nitriding with prolonged oxidation, the low-nitrogen nitride of the γ'-phase develops well in the form of a lamellar structure mixed with Feα [N].

An X-ray method was used to study the phase composition of the oxide layers obtained at various temperatures on the surface of previously nitriding samples obtained at the DRON-3 setup. The following phases in the oxide layers are revealed on the diffraction patterns: at an oxidation temperature of 550°S - Fe_3O_4, Fe_2O_3, at 580°S - FeO, Fe_3O_4, Fe_2O_3. The main phase of oxide layers at an oxidation temperature of 550°S. Fe_2O_3 oxide grows on the surface of the Fe_3O_4 phase, probably during cooling, it adheres poorly to the oxide layer, and is easily removed from the surface by friction. The FeO oxide found in the oxide layers obtained at a temperature of 580°S is located by a thin film at the boundary of the oxide and nitride zones.

The growth rate of Fe_3O_4 oxide at an oxidation temperature of 580°S is much higher, however, with an increase in the duration of exposure, the growth rate slows down and, when oxidized for more than 1 hour, the intensity of Fe_3O_4 oxide lines at two temperatures is almost the same.

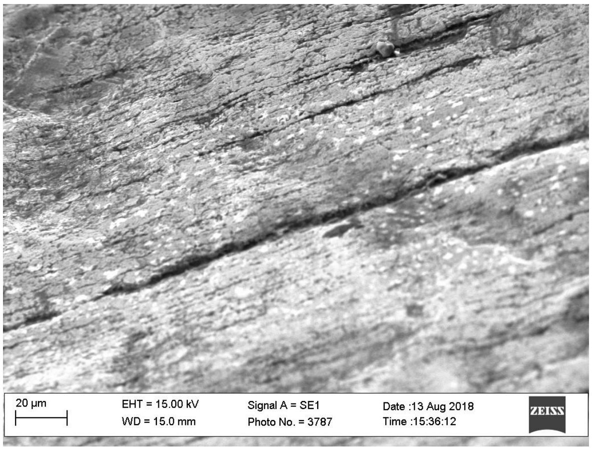
It should be noted that only oxides covering the surface with a continuous layer can have practical application. An oxide film obtained at an oxidation temperature of 550°S is denser, with a small number of defects and has better adhesion strength, which makes it possible to consider a temperature of 550°S to be preferred for vapor oxidation.

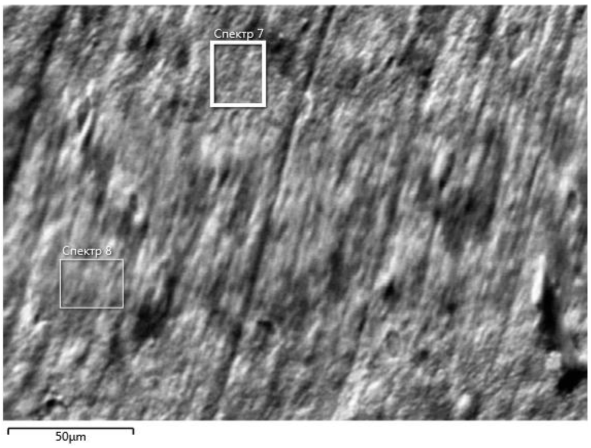
The oxide layer obtained on the nitride surface at a temperature of 580°S is composed only upon their rapid cooling, and upon slow cooling of FeO in the oxide layer below the eutectoid transformation it decomposes according to the formula: $FeO \rightarrow Fe_3O_4+Fe_\alpha$ and the resulting Fe_α is the source of the appearance of the first corrosion centers under the influence of the external environment, as well as during the decomposition of FeO, the formation of Feα between oxide and nitride layers leads to a decrease in the adhesion strength of the oxide layer to nitride and, with an increase in the FeO reflection, its decomposition causes Although a small thickness of Feα is formed, as a result of which peeling of the oxide layer occurs. Therefore, in order to avoid the formation of FeO and Feα during the oxidation of the nitride layer, it is necessary to carry out oxidation at a lower eutectoid temperature for the state diagram for the “Fe-O” system.

Studying the kinetics of the formation of a nitrided layer on the surface and the microstructure of the samples after nitriding and subsequent oxidation in water vapor, it can be stated that the nitride layer obtained at a lower eutectoid temperature for the Fe-N system, although it has less thickness than the nitride layer obtained at a higher eutectoid temperature , it has a denser structure than the nitride layer obtained at hypereutectoid temperature and having surface micropores after the steam oxidation process is healed with the formation of iron oxides Fe_3O_4.

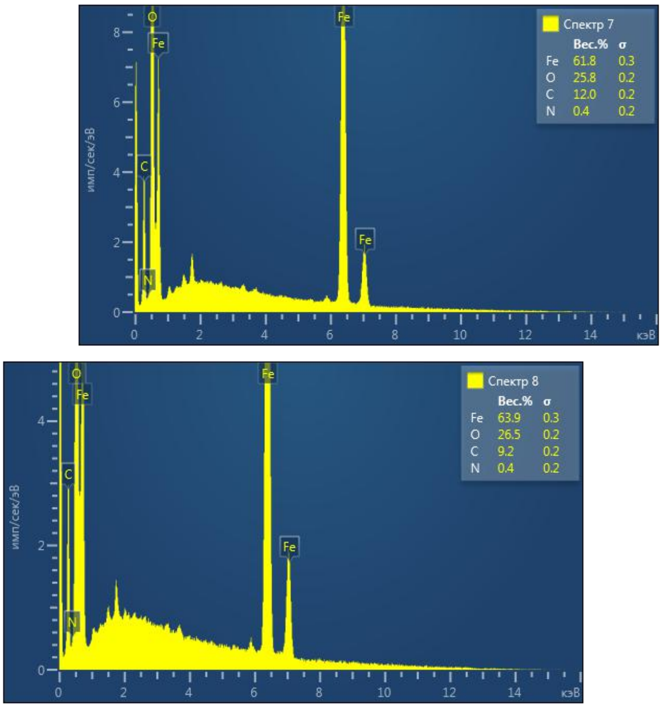
The surface morphology and the study of the microstructure of the nitride oxide layer were studied using a SEM-EVO MA 10 scanning microscope (Carl Zeiss, Germany), the composition of the structures was determined using an Energy-Dispersive X-ray spectrometer (EDS-Oxford Instrument))

In studying morphology and spectral analyzes of the surface of the nitride oxide layer, the working distance was 8.5 mm. Images were obtained at various scales (Figure 2 and Figure 3). The drill was tested with a diameter of 10 mm, made of high-speed steel P6M5 after hardening by nitriding and subsequent oxidation in water vapor at a temperature of 550°S. In order to find out the wear of the nitride oxide layer on the drills, the drills were studied after surface hardening (Figure 2). Only were studied after the drill was run with a total working time of more than 5 hours during the drilling of plates from Steel 20 (Figure 3).





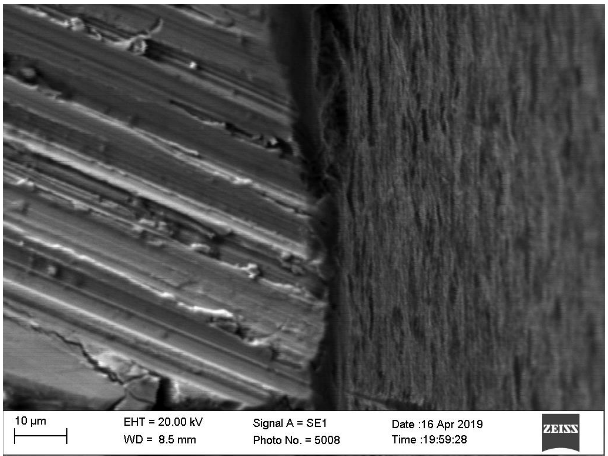
a) b)

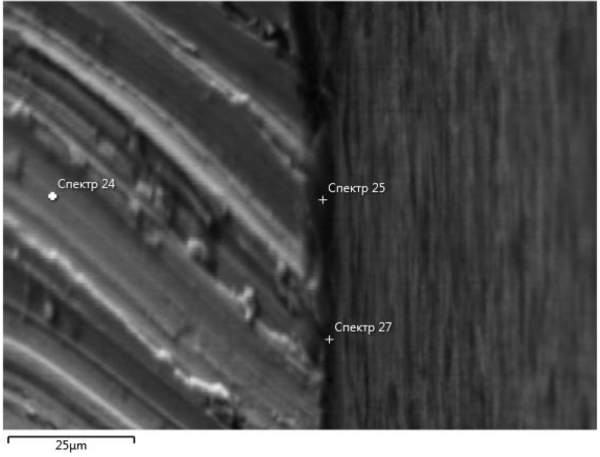


c) d)

Figure 2. Morphology and spectrograms from a surface with an oxynitride layer of P6M5 steel. a - surface morphology; b - place of taking spectra on the surface; c - spectrogram from the point "Spectrum 7"; d - spectrogram from the point "Spectrum 8".

In the process of drilling, the diffusion nitride-oxide coating in the cutting part of the tool is still worn out (in the non-working part is preserved) under the influence of the cutting force during friction in contact with the processed material. In the future, the depths of solid solutions of nitrogen $Fe_{\alpha[N]}$, dispersed γ'-phase and zones of internal nitriding are responsible for using the tool in the drilling process. Therefore, it is necessary to have more developed solid solutions of nitrogen along the depth of the surface along the depth of the matrix of the workpiece. It is appropriate to note here that the strength properties of the cutting tool are not only ensured by the formation of $Fe_{\alpha[N]}$ solid solutions, but nitrides of alloying elements that are part of the material of the cutting tool also enter into the main decisive factors in increasing the tool life.





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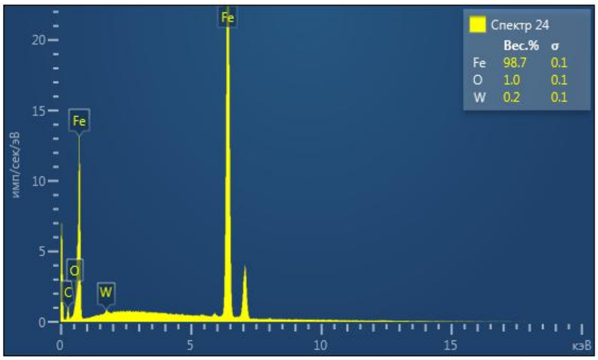
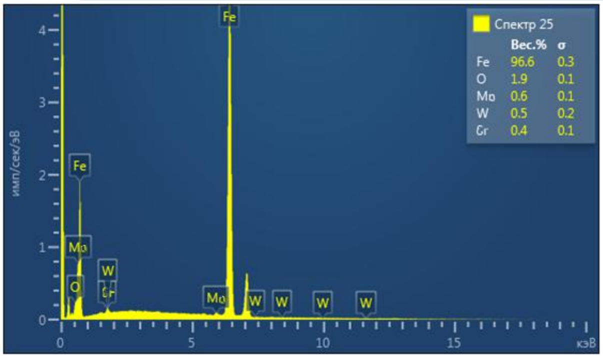


	Вес.%	σ
Fe	98.7	0.1
O	1.0	0.1
W	0.2	0.1



	Вес.%	σ
Fe	96.6	0.3
O	1.9	0.1
Mo	0.6	0.1
W	0.5	0.2
Cr	0.4	0.1

в) г)

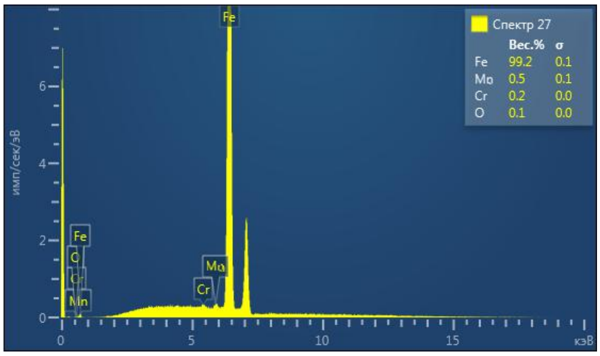


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Figure 3. Morphology and spectrograms from the surface of a drill made of P6M5 steel with an oxynitride layer after mining. a - morphology of the cutting part and the back side of the surface of the drill; b - place of taking spectra on the surface; c - spectrogram from the point "Spectrum 24"; g - spectrogram from the point "Spectrum 25"; d - spectrogram from the point "Spectrum 27".

The internal nitriding zone consists of a nitrogenous solid solution of the base metal, its nitrides and nitrides of alloying elements. In the zone of internal nitriding, nitrides of the base metal of iron (nitrides of the first kind) and nitrides of alloying elements (of the second kind) are released. Since the elements of P6M5 steel, such as Cr, W, Mo, V, have higher nitrogen thermodynamic activity than Fe, therefore, type II nitrides with a higher nitride forming ability than the Fe base metal give a large decrease in the specific volumetric energy in the internal nitriding zone.

When nitrogen diffuses into the doped matrix, a stable nitrogenous solid solution of alloying elements is formed, which are not prone to decay. With an increase in the nitrogen concentration in the internal nitriding zone during the oxidation process due to the dissociation of the highly nitrogenous nitride ε-phase, one can obtain the structures of a nitrogenous solid solution and nitrides of alloying elements (Figure 1, d).

The nitrides of alloying elements released during nitriding and also during oxidation due to the dissociation of the ε phase have a dispersed structure in a thread-like or lamellar form in the internal nitriding zone. This can be explained by the fact that, when nitrides of alloying elements are enlarged, a diffusion influx of not only nitrogen atoms, but also atoms of the alloying element is necessary. Since the flow of the alloying element is maximal at the grain boundary, the growth of nitrides of alloying elements mainly occurs along the grain boundaries.

The advantage of oxidizing the nitride layer on the surface of high-speed steels is the possibility of varying the temperature and duration of the oxidation process. By adjusting these modes, various stages of the process of separation of solid solutions and nitrides of alloying elements in the matrix can be fixed in an the internal nitriding zone. This makes it possible to achieve different levels of hardening along the depth of the matrix of the cutting tool to be nitrided.

CONCLUSION.

The results of the studies show that:

- Combinations of two types: nitriding in the first stage and subsequent oxidation in water vapor processes are a possible;
- in order to prevent martensitic transformation during nitriding, the process must be carried out below 550°S, and the developed zone of internal nitriding is achieved not only due to the solid solution and nitride of the base metal, solid solutions and nitrides of alloying elements are formed here, which favorably affect the properties of the alloy;
- alloying elements in the composition of high-speed steels from a thermodynamic point of view are more active towards nitrogen, which does not decompose upon isothermal exposure of the nitride layer in an atmosphere of superheated steam;
- when a combination of low-temperature nitriding is followed by oxidation on the surface of high-speed steels, diffusion composite layers are formed - a thin oxide layer due to surface dissociation of the nitride layer and below it a low-nitrogen nitride phase, then a mixture of nitrides and an inner nitriding zone;

- the process of oxidation of the nitride layer is necessary in the temperature range 550-570°S, which is in good agreement with the temperature range for the conversion of residual austenite to martensite and the state diagram for the Fe-O system, with the formation on the oxide surface consisting only of Fe_3O_4;
- during the oxidation of the nitride layer, the depth of the internal nitriding zone continues to grow with the formation of both solid solutions and nitrides of the base metal and alloying elements due to the high nitrogen nitride layer.

By combining the nitriding process with subsequent oxidation in water vapor by controlling one or another parameter at each stage of the process, it is possible to obtain a diffusion surface-hardened layer consisting of oxide, nitride, carbonitride, oxycarbonitride layers and a developed zone of internal nitriding of solid solutions and nitrides of the base metal and alloying elements. If necessary, you can get their compositions in various ratios.

Each obtained phase or phase mixture is responsible for certain conditions of the physic-mechanical and physic-chemical properties of the processed products, therefore, taking into account the operating conditions of tools made of high-speed steels and the establishment of technological parameters for a certain type of tool, there is the possibility of further improving their performance.

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