Hardening of cutting tools by combined gas nitriding method

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Abstract. In order to improve the strength properties of cutting tools made of high-speed steels, the article presents the results of a study of the possibility of using a combined method of surface hardening, which consists in nitriding in an ammonia medium at the first stage and oxidizing the nitrided layer in water vapor at the second stage. The formation of a thin dense oxide film consisting of a single magnetite and a dense nitride layer under it as well as a zone of internal nitriding following it are studied on the surface to be strengthened. It is established that the combination of the process in the first stage by zaevtektoidnoj temperature for the system "Fe-N" the temperature intervals of martensite transformation of residual austenite and the second step by zaevtektoidnoj temperature for the system "Fe-O" according to temperature intervals and tempering after hardening allows you to get the diffusion nitride-oxide layer with the desired structures and properties on the surface of high-speed steel.

1. Introduction

Currently, as building materials in construction stores, you can find a wide range of cutting tools, one of which is a drill designed for drilling a wide variety of materials that differ not only in shape and size, but also in their purpose.

One widespread type of drill is wood drills, which are made of high-speed steel. In the technological process of heat treatment of high-speed steel tools, it is important to perform a high tempering operation after quenching. When tempering using conventional methods in a furnace atmosphere, uneven oxides are formed on the surface of the tool, which greatly spoil the appearance of the tool, as a result of which the surface of the processed products is chemically cleaned [1-3].

For tools made of high-speed steels after quenching, high tempering is carried out in an atmosphere of superheated steam, after which a uniform and non-porous oxide layer is formed on the surface, which serves as the only effective method of protection against atmospheric corrosion. Vacation in an atmosphere of superheated steam is a type of chemical-thermal treatment. The surface of steel products heated to 450-600 °C, interacting with water vapor, undergoes intensive oxidation; a thin oxide film is formed on it [4 – 6].

To improve wear resistance and protect against atmospheric corrosion during storage, high tool tempering is carried out in an atmosphere of water vapor to obtain thin oxide layer on their surface. At the same time, the resulting surface oxide layer improves the machinability by cutting [7,8].

Tempering in the atmosphere of superheated steam of tools made of high-speed steels is usually carried out after grinding products, which can cause secondary hardening of the surface and here it is necessary to restore the residual austenite to martensite, based on the conditions of heat treatment of products made of high-speed steels.
Increased wear-resistant and anti-corrosion properties of cutting tools are achieved by nitriding in various nitrogen-containing saturating media, in particular by nitriding in an ammonia atmosphere, in which diffusion processes occur much faster than in nitrogen [9-12].

Nitriding is a multi-purpose process that strengthens a wide range of metals and alloys, structural, tool, corrosion-resistant and heat-resistant steels, etc. After nitriding in the hardened layer, the formation of diffusive surface nitride zones and an internal nitriding zone is achieved, which are each responsible for establishing certain properties of the hardened products [13-18].

Various tools – drills, milling cutters, taps, reamers and other tools of high-speed steels as a finishing chemical - thermal treatment are subjected to nitriding to obtain a thin surface layer consisting mainly of nitrides (ε+γ') - phase and a diffusion zone of internal nitriding (Feₐ[N]) located behind it.

Compatibility of technological modes of low-temperature gas nitriding and oxidation processes, as well as tempering after quenching of tools allows combining nitriding processes with subsequent oxidation in water vapor to further improve the service characteristics of tools made of high-speed steels [19-21].

The production of diffusion layers on the surface of metals and alloys is determined by many factors, the most important of which include the composition of the saturating gas phase, the temperature and duration of exposure to the furnace atmosphere, the composition of steel, as well as the structure and condition of the treated surface.

2. Methods

Combinations of nitriding technology with subsequent oxidation were carried out by saturation at the first stage in dissociated ammonia and further oxidation in water vapor on samples made of R6M5 steel with a diameter of 10 mm and a thickness of 5 mm. Samples made of R6M5 steel used in mass production are quenched at a temperature of 1210-1230 °C and tempered in the temperature range of 550-600 °C. 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 process of nitriding cutting tools made of high speed steel was carried out at temperature range of 500-550 °C with a duration of 0.5-2.0 hours, at different values of the degree of dissociation of ammonia in the second stage, often removing the samples from the furnace was processed by oxidation in water steam.

The phase composition of oxide layers obtained at different oxidation temperatures on pre-nitrided samples was studied by x-ray method at the DRON-3 facility [22,23].

The surface morphology and microstructures of the nitride-oxide layer were studied using a SEM-EVO MA 10 scanning microscope (Carl Zeiss, Germany), the structure compositions were determined using an Energy-Dispersive X-ray spectrometer (EDS-Oxford Instrument). When studying the morphology and spectral analysis of the surface of the nitride-oxide layer, the working distance was 8.5 mm.

3. Results and Discussions

According to the nitriding theory, the regulation of the phase composition of the nitrided layer is achieved by changing the nitrogen potential of the saturating atmosphere. By maintaining the nitrogen potential at the level of nitrogen solubility in one or another phase, a layer consisting of an a-solid solution - Feₐ[N], iron nitrides and alloying elements can be formed on the surface of the nitride ε-phase, carbonitride ε'-phase, oxycarbonitride ε''-phase, low nitride γ'-phase with a low nitrogen content. 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, part shape, and saturation temperature, the degree of dissociation is mainly determined by the
rate of flow of ammonia, and therefore the amount of ammonia 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 does not participate in the process of steel saturation with nitrogen and is a carrier gas.

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

During the short –term process of low-temperature nitriding, at the first stage of nitrogen saturation in an ammonia atmosphere, a thin nitride layer is formed on the steel surface in the form of a non-etching part of the surface, followed by a mixture of (Fe$_{a[N]}$+γ') phases, followed by an internal nitriding zone (INZ) (Fig. 1,a).

In all cases, when nitrogen is saturated, a sequentially arranged composite layer is formed on the surface consisting of the ε-phase → γ’-phase → mixture (Fe$_{a[N]}$+γ') → phase → INZ, according to the state diagram of the Fe-N system. Regulation of the structure of the nitrided layer is achieved by changing the nitrogen potential of the atmosphere, which is maintained at the level of the maximum solubility of nitrogen in a particular phase, it is possible to form a diffusion zone based on INZ or a composite layer with a given nitride phase.

As a result of studying the influence of the degree of ammonia dissociation on the thickness and composition of the diffusion layer at a lower eutectoid temperature, it is shown that the formation of a developed zone of high-nitrogen nitride (ε-phase) with a significant total layer thickness is characteristic of processes with the degree of ammonia dissociation α<50%, but the porosity of the nitride layer increases for its further oxidation. If the degree of dissociation of ammonia, α>50% decrease the thickness of the nitride zone and the quantity of high-carbon nitride ε-phase decreases, and low nitride γ’-phase increases, the porosity of the nitride layer is removed.

In the nitride layer, the formation of the ε’-phase of a carbonitride character obtained by saturation in the atmosphere of ammonia occurs only during nitriding of steel due to the presence of carbon in the steel matrix, since only in the presence of carbon in the nitride layer is the carbonitride phase formed. During the diffusion of nitrogen from the atmosphere and due to the reverse diffusion of carbon from the steel matrix during decarburization, especially at the boundaries of the nitride layer and the INZ, the formation of the ε’-phase is more likely.

In order to obtain a hardened layer by nitriding followed by oxidation in water vapor, samples of high-speed steels were processed in an atmosphere of pure ammonia, with a degree of dissociation α>50% at a temperature of 550 °C for 2 hours and at the same temperature, the samples were oxidized in water vapor. The microstructures of samples pre-nitrided and oxidized in water vapor of various durations are shown in Fig. 1.

When superheated steam is introduced into the atmosphere in the nitride layer due to a change in the ratio of partial pressures NH$_3$:H$_2$ towards H$_2$O:H$_2$ begins denitriding of the nitride layer to form a thin surface oxide layer, which, after forming a certain thickness of the upper roller layer, prevents denitriding and forces the diffusion of nitrogen in the metal depth. As a result, during oxidation, a thin oxide film is formed on the surface of the nitride layer (Fig. 1,b). During further oxidation, the thickness of the oxide film increases due to the denitriding nitride layer (Fig. 1,c). after a long duration of oxidation, the nitride layer completely dissociates and a surface oxide layer is formed (Fig. 1,d).
If we judge by the microstructure of steel with composite oxynitride layers, we can say that the oxide layer develops evenly over the nitride layer due to the dissociation of nitrogen on the surface of the nitride layer, further prolonged oxidation of which leads to the disappearance of the high-nitrogen nitride layer.

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

Based on the presence of nitride-oxide layer on the surface which is responsible properties such as corrosion resistance and wear resistance with the creation of a positive gradient of the friction surface, you need advanced nitride-oxide layer, and for improving the structural strength necessary to obtain an advanced mixture (Fe$\alpha[N]$+$\gamma'$) phase and INZ. In the zone of internal nitriding, the low-nitrogen nitride of the $\gamma'$-phase develops well in the form of a lamellar structure in a mixture with Fe$\alpha[N]$ during prolonged oxidation.

The fractogram of the fracture surface shows that the nature of the fracture of the nitride-oxide layer (Fig. 2,a), the zone of the mixture (Fe$\alpha[N]$+$\gamma'$) -phase (Fig. 2,b) and INZ (Fig. 2,c) corresponds to a viscous fracture. The viscous properties over the entire depth of the nitrogen-saturated layer make it possible to increase the fatigue limit as a whole, which is a valuable mechanical property for cutting tools to increase their resistance during operation.

Diffractograms reveal the following phases in the oxide layers: at the oxidation temperature of 550 °C – Fe$_3$O$_4$, Fe$_2$O$_3$, at 580 °C - FeO, Fe$_3$O$_4$, Fe$_2$O$_3$. The main phase of the oxide layers at an oxidation temperature of 550 °C, Fe$_3$O$_4$ oxide grows on the surface of the Fe$_2$O$_3$ phase probably during cooling, it is poorly bonded to the oxide layer, and is easily removed from the surface by friction. The FeO oxide found in the oxide layers obtained at 580 °C is located as a thin film on the border of the oxide and nitride zones.
The growth rate of Fe$_3$O$_4$ oxide at an oxidation temperature of 580 °C is significantly higher, but with increasing exposure time, the growth rate slows down and when oxidized for more than 1 hour, the intensity of Fe$_3$O$_4$ oxide lines at two temperatures is almost the same.

It should be noted that only oxides that cover the surface with a solid layer can be used in practice. The oxide film obtained at an oxidation temperature of 550 °C is denser, has fewer defects, and has better adhesive strength, which makes it possible to calculate the temperature of 550 °C with the preferred one for steam oxidation.

The oxide layer obtained on the surface of the nitride at a temperature of 580 °C has in its composition only when they are rapidly cooled, and with slow cooling, FeO in the oxide layer below the eutectoid transformation decays according to the formula: FeO→Fe$_3$O$_4$ + Fe$_n$ and the resulting Fe$_n$ is the source of the first foci of corrosion under the influence of the external environment, as well as the decay FeO formation between the oxide and nitride layers Fe$_n$ leads to a decrease in the adhesion strength of the oxide layer to the nitride and an increase in reflex FeO its decay triggers the formation although a small thickness Fe$_n$ in which peeling of the oxide layer. Therefore, in order to avoid the formation of FeO and Fe$_n$ during the nitride layer oxidation, it is necessary to conduct oxidation at a lower eutectoid temperature for the state diagram for the "Fe-O" system.

By studying the kinetics of the formation of a nitrided layer on the surface and the microstructure of samples after nitriding and subsequent oxidation in water vapor, it can be argued 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 dense structure than the nitride layer obtained at a non-eutectoid temperature and having surface microdefects after the steam oxidation process is healed by the formation of iron oxides Fe$_3$O$_4$.

Images were obtained at various scales (Fig. 3 and Fig. 4). Drills with a diameter of 10 mm made of high-speed steel R6M5 were studied after their hardening by nitriding and subsequent oxidation in water vapor at a temperature of 550 °C. In order to determine the wear of the nitride-oxide layer on the drills, the drills were studied after surface hardening (Fig. 3) and after running the drill with a total duration of work for the drilling time of steel plates 20 more than 5 hours (Fig. 4).

During the drilling process, the diffusion nitride-oxide coating in the cutting part of the tool is still worn (in the non-working part it is preserved) under the influence of the cutting force during friction in contact with the material being processed. In the future, the depths of solid nitrogen solutions Fe$_{α[N]}$, dispersed γ'-phase, and internal nitriding zones are responsible for using the tool in the drilling process. Therefore, the depth of the surface must have a more developed solid solutions of nitrogen in the depth of the matrix of the processed product. Here it is appropriate to note that the strength
properties of the cutting tool are not only provided by the formation of solid solutions of $\text{Fe}_{\alpha}[\text{N}]$, but also nitrides of alloying elements that are part of the material of the cutting tool are the main decisive factors for increasing the tool's durability.

When nitrogen is diffused 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 high-nitrogen nitride phase $\text{Fe}_2\text{N}$ ($\varepsilon$-phase), the structures of the nitrogen solid solution and nitrides of alloying elements can be obtained (Fig. 1,d).

Released during nitriding and also during oxidation due to dissociation of the $\varepsilon$-phase of nitrides of alloying elements in the zone of internal nitriding has a dispersed structure in a filamentous or lamellar form. This can be explained by the fact that the enlargement of nitrides of alloying elements requires a diffusive influx of not only nitrogen atoms, but also atoms of the alloying element. Since the flow of the alloying element is maximal at the grain boundary, the growth of nitrides of alloying elements mainly occurs at the grain boundaries.

**Figure. 3.** Morphology and spectrograms from the surface with an oxynitride layer of P6M5 steel: a - morphology of the surface; b – place where spectra are taken on the surface; c – spectrogram from the point "Spectrum 7"; d – spectrogram from the point "Spectrum 8".
Figure. 4. Morphology and spectrograms from the surface of a P6M5 steel drill with an oxynitride layer after working out: a - morphology of the cutting part and the back side of the drill surface; b – the place where the spectra are taken on the surface; c – spectrogram from the point "Spectrum 24"; d – spectrogram from the point "Spectrum 25"; g – spectrogram from the point "spectrum 27".

The advantage of nitride layer oxidation on the surface of high-speed steels is the possibility of varying the temperature and duration of the oxidation process. By regulating these modes, various stages of the process of separation of solid solutions and nitrides of alloying elements in the matrix can be recorded in the INZ. This makes it possible to achieve different levels of hardening in the depth of the matrix of the processed cutting tool by nitriding.

4. Conclusions
The results of the research show that:
- combinations of two types of chemical and thermal treatment are possible: nitriding at the first stage and subsequent oxidation in water vapor;
- in order to prevent martensitic transformation during nitriding, the process must be carried out below 550 °C, and at the same time a developed zone of internal nitriding is achieved not only due to the solid solution and nitride of the base metal, but also 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 the thermodynamic point of view are more active to nitrogen, which does not disintegrate during isothermal exposure of the nitride layer in an atmosphere of superheated steam;
- when combining low – temperature nitriding with subsequent oxidation, diffusion composite layers are formed on the surface of high-speed steels-a thin oxide layer due to surface dissociation of the nitride layer and a low-nitrogen nitride phase below it, then a mixture of nitrides and an internal nitriding zone;
- the nitride layer oxidation process must be carried out in the temperature range of 550-570 °C, which is in good agreement with the temperature range of transformation of residual austenite into martensite and the state diagram for the Fe-O system, with the formation of an oxide on the surface consisting only of Fe₃O₄;
- when the nitride layer is oxidized, the INZ depth 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.

When combining the nitriding process with subsequent oxidation in water vapor by regulating a particular parameter at each stage of the process, it is possible to achieve 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 different ratios.

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

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