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Technology of Nitro-Oxidation of Structural Steels

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ABSTRACT: In article presents technologies for producing surface nitroxide diffusion coatings having various phase compositions and structures. The physicochemical and physicomechanical properties of diffusion nitride and nitroxide layers on the surface of structural steels are considered. In order to obtain a nitroxide layer on the surface of structural steels with specified structures and phase compositions, we study the change in the nitride layer during oxidation in water vapor.It is established that during oxidation in water vapor by creating a dense oxide layer on the surface of the nitride one can control the phase composition of the nitride layer and obtain the necessary structure

KEYWORDS: Gas nitriding, nitrooxidation, phase composition, structure, nitroxide layer, composite layer, internal nitriding zone, morphology, microstructure, corrosion resistance, microhardness, wear resistance, running-in, complexones, high nitrogen phase, low nitrogen nitride

I. INTRODUCTION

Currently, the processes of low-temperature chemical-thermal treatment of steel products are carried out in a wide temperature range in various saturating environments. The most widespread of the low-temperature methods of chemical-thermal treatment is the process of nitriding and combining the nitriding process with other low-temperature processes. Improving the service characteristics of products is achieved by optimizing the structure of the diffusion layer for various operating conditions of machine parts and tools.

The disadvantages of the standard gas nitriding process are the long duration of the technological cycle, the uncontrollability of the process, the low quality of the diffusion layer and the lack of technological support for optimizing the properties of nitrided coatings for various grades of structural and tool steels and alloys.

The world industry uses various options for combined nitriding technologies - nitrooxidation, which are carried out in various saturating media, forming a nitrided diffusion layer with a surface nitride or carbonitride zone coated with a dark oxide film with unique decorative and anticorrosion properties.

According to the technological sequence, the nitrooxidation process is carried out according to a single-stage scheme or according to a combined process scheme: nitriding followed by oxidation, pre-oxidation followed by nitriding, or according to a three-stage scheme consisting in preliminary oxidation, nitriding and subsequent oxidation.

The nitriding process is not regulated by the nitrogen potential of the atmosphere, which does not allow varying the properties of diffusion coatings in accordance with the operational requirements for the products and intensifying the saturation rate. It should be noted that the vast majority of chemical-thermal treatment processes are controlled by almost only two technological parameters: temperature and processing time.

In this work, the nitrooxidation process is considered as a method of regulating the phase composition of the diffusion nitride layer obtained after nitriding in an atmosphere of ammonia and subsequent oxidation in water vapor

II. SIGNIFICANCE OF THE SYSTEM

In article presents technologies for producing surface nitroxide diffusion coatings having various phase compositions and structures.The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. METHODOLOGY

Steel 20 and steel 45 in the delivery state were used as materials for studying the nitrooxidation process.A metallographic analysis of the treated steel samples was carried out on transverse sections using a Neophot-21 light microscope in the magnification range 500-1000.

Qualitative phase X-ray diffraction analysis of the diffusion nitride and nitride oxide layer was studied using a Dron-3 diffractometer using filtered cobalt and iron Kα radiation.

The total corrosion resistance of the treated samples was investigated in a 3% NaCl solution.The surface morphology and the study of the microstructure of the nitroxide 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).

When studying the morphology and spectral analyzes of the surface of the nitride oxide layer, the working distance was 8.5 mm

IV. EXPERIMENTAL RESULTS

During nitrooxidation, a combined diffusion layer is formed, consisting of a surface oxide zone, a carbonitride and hydroxycarbonitride zone, and then a diffusion sublayer — the internal nitriding zone (CVA). In all cases of the first saturation stage, predominant nitrogen diffusion occurs, and the structure and phase composition of the diffusion nitride layer is determined by the state diagram for the Fe-N system.

In the process of gas nitriding, the regulation of the structure of the nitrided layer is achieved by increasing the temperature and using mixed atmospheres due to the dilution of ammonia with nitrogen, hydrogen, nitrogen-hydrogen mixtures, oxygen, air, etc.

The regulation of the structure of the nitrided 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 layer based on SVA or a composite layer with a given nitride phase (Figure 1).

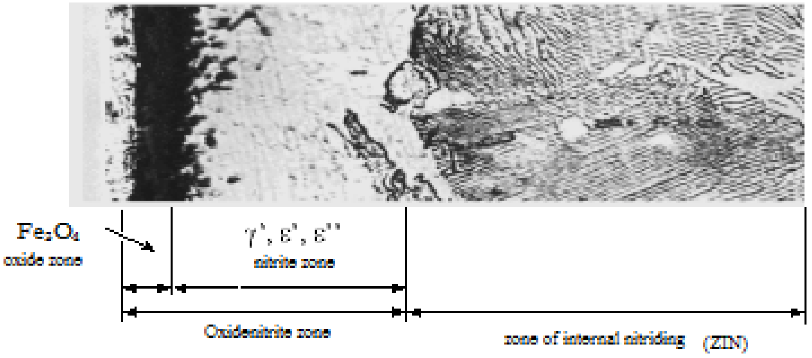


Figure 1. The structure of the nitrooxidized layer

By adjusting the phase composition and structure of the nitrided layer, depending on the nitrogen potential and the composition of the saturating medium, the following are formed on the surface of the processed materials: internal nitriding zones (SVA); composite layers γ′-phase + SVA or ε + γ′-phase + SVA. The phase composition and structure of the surface oxide layer are regulated to obtain the necessary nitrooxidized layer with desired operational properties, subsequent oxidation is carried out in an atmosphere of air, oxygen, water vapor and with the addition of other oxygen-containing components. In the operational plan, each zone of the nitrooxidized layer has certain service characteristics.

Recently, for surface hardening of parts operating in a corrosive environment, for wear at low contact loads, a nitroxide layer is used, consisting of a developed nitride zone and a thin surface oxide zone, which provides better rubbing surfaces and corrosion resistance.

Here, preference is given to the subsurface nitride zone, consisting of the ε phase and γ′phase, it is desirable to obtain the ε phase with a lower nitrogen content, having a carbonitride or oxycarbonitride character.

For parts working under conditions of fatigue, at elevated temperatures, a nitroxide layer with a developed diffusion sublayer - ZVA is used, and for tools operating in the mode of dynamic wear and impact loads, an SVA is formed on the surface without a brittle surface nitride layer.

The formation of a nitroxide coating on structural steels by nitrocarburizing and subsequent short-term oxidation in pure oxygen yields a layer with good antifriction characteristics that are not prone to setting and at the same time providing better running-in of the sliding friction unit in the initial period of wear.

It is known that nitrides have a high affinity for oxygen and a thermodynamic assessment of the interaction of iron and its nitrides with oxygen has been shown that iron nitrides interact more actively with oxygen than iron (Figure 2).

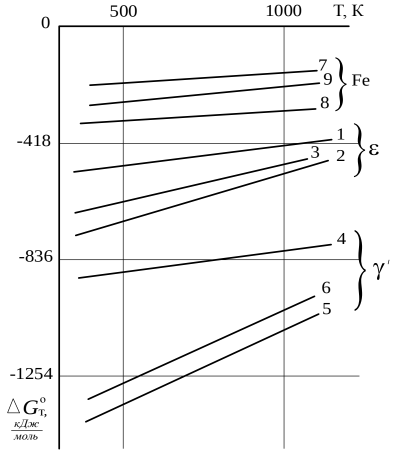


Figure 2.Temperature dependence of isobaric-isothermal potentials by the reaction of oxidation of iron nitrides.

The calculated isobaric-isothermal potential by the reaction of the formation of oxides at 500 °C is $G_o t$ = 209-293 kJ/mol, for $Fe_{2\text{-}3}N$ $\Delta G_o t$ = 481-711 kJ / mol and for Fe_4N it is $\Delta G_o t$ = 878-1463 kJ/mol. The resulting nitroxide zones are more plastic than oxide Fe_2O_3 films on a metal matrix.

The fatigue resistance of nitrooxidized parts is determined by the thickness and properties of the internal nitriding zone, and the phase composition, thickness and structure of the oxide and carbonitride zones determine the corrosion resistance and wear resistance of the parts. Optimum tribological and corrosion-protective properties are achieved with an oxycarbonitride layer with a dense oxide surface zone consisting of magnetite (Fe_3O_4) with a thickness of 1 to 3 microns. A change in the phase composition of the oxide zone with the formation of FeO and Fe_2O_3 oxides is accompanied by loosening of the layer and leads to a deterioration in corrosion resistance. The presence of FeO oxide leads to cracking of the oxide film and its peeling from the surface.

The nitride zone with high surface characteristics consists of γ ’(Fe_4N) and ε (Fe_3N) phases. Moreover, the ε -phase is depleted in nitrogen and X-ray diffraction is detected in the form of two isomorphic phases: an isomorphic carbonitride phase, designated as ε ’with lattice parameters: a = 0,269; c = 0,436 nm and carbonitride phase with lattice parameters: a = 0,267; c = 0,436 nm.

As our studies have shown, the corrosion resistance of the nitrooxidized layer depends on the ratio of γ ’and ε phases in the nitride zone.

Figure 3 shows the dependence of the time of occurrence of the first corrosion centers in a 3% aqueous solution of steel 45 salt after nitrooxidation with the addition of water vapor. With an increase in the amount of the γ’ phase in the nitride zone to 75%, the time until the appearance of the first centers of corrosion increases, reaching 910–960 hours at 75% of the γ ’phase. A further increase in the amount of γ ’phase is accompanied by a decrease in corrosion resistance. The presence of an oxide layer positively affects the corrosion properties of the nitroxide layer (Figure 3, line 1).

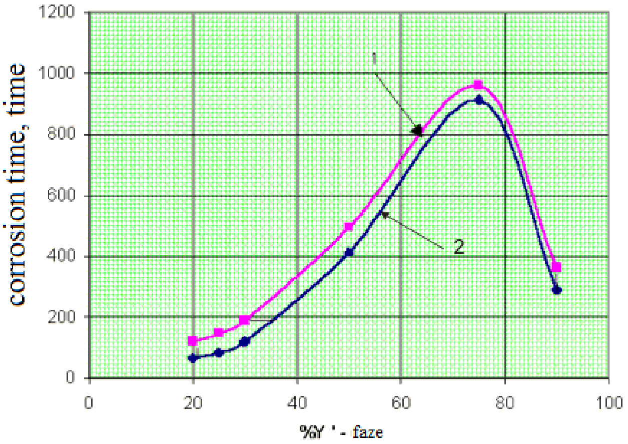


Figure 3. The effect of the concentration of the γ’-phase in the nitrooxidized zone of steel 45 on the appearance of the first foci of corrosion in a 3% NaCl solution. Nitriding at 580 °C, 3 hours + oxidation in water vapor 550 °C; 0,5 hours; 1 - with an oxide layer; 2 - without oxide layer.

Figure 4 for the same test conditions shows the change in the corrosion area from the test time for the nitride layer with 50 and 75% γ ’phases. It should be noted that in the experiments performed, the thickness of the oxide zone was 1–5 µm.

During nitrooxidation, a composite layer practically consisting of the γ′ phase can be obtained by a two-stage change in the nitrogen potential of the atmosphere at 560-580 °C, and preliminary dissociation of ammonia αo = 25%, while maintaining the dissociation of the ammonia mixture at saturation α = 55-75% and a duration of 1.5 -3 hours.

The resulting nitride layer has an even and non-etched appearance predominantly consisting of the γ′ phase (Figure 5).

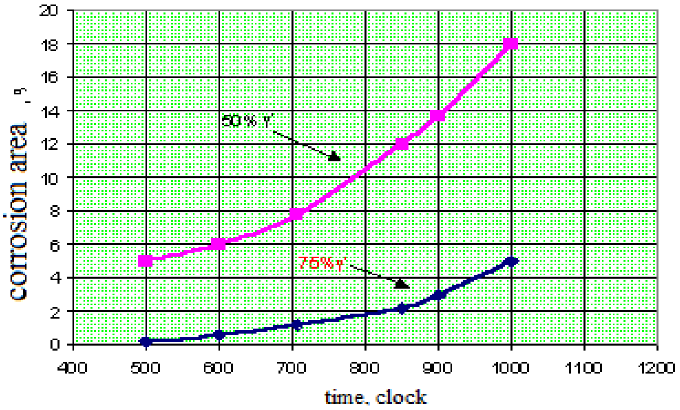
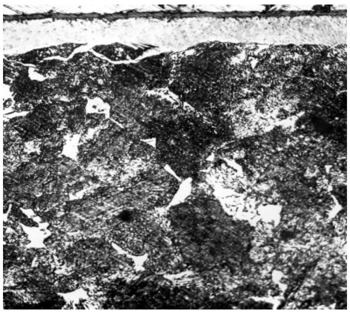


Figure 4. Change in the corrosion area of nitrooxidized steel 45 depending on the exposure time in a 3% NaCl solution and the concentration of the γ’-phase in the nitroxide zone. Nitriding at 580 °C; 3 hours + oxidation in water vapor 550 °C; 0,5 hours;



x500

Figure 5. The microstructure of the nitroxide layer on steel 40X after nitriding at a temperature of 5800C in a mixture of 0,75% NH_3 + 0,25% H_2 for 3 hours and subsequent oxidation at a temperature of 5500C for a duration of 0,5 hours.

Subsequent oxidation of the γ′ phase in water vapor at a temperature of 540-550 °C for 0,5-1 hours on the surface, you can get a uniform oxide layer with a thickness of 1-3 microns. The obtained nitroxide layer possessing the best corrosion properties has wear resistance in the conditions of dry and boundary sliding friction 6-8 times greater than the nitrided layers obtained in an ammonia atmosphere at 580 °C for 3 hours. The increase in wear resistance is due to a decrease in the coefficient of friction of the nitroxide layer than the nitride layer obtained by nitriding (Figure 6).

It should be noted that the nitroxide layer obtained by nitriding for 5 hours and subsequent oxidation had almost the same wear-resistant characteristics.

To ensure the conditions of external friction, it is necessary to obtain a protective layer on the surface capable of repeated plastic deformation without hardening and fracture, providing minimum wear resistance of rubbing surfaces, reduced shear strength and a positive gradient of properties along the cross section of the hardened layer. This corresponds to a thin surface oxide layer consisting of almost one magnetite (Fe_3O_4).

One of the defective signs of nitrided parts is peeling of the surface associated with low ductility, leading to the development of fatigue processes during elastic deformation and embrittlement during repeated plastic deformation.

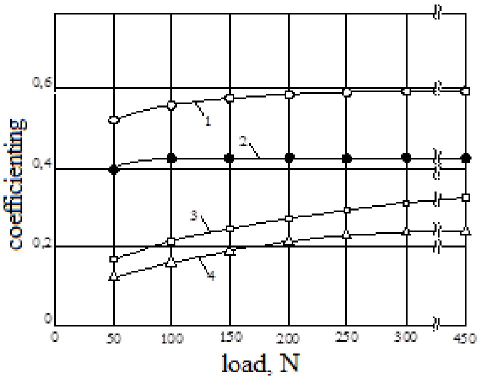


Figure 6. Change in the coefficient of friction depending on the applied load during dry friction. Friction pair "hardened steel 45-steel 45 with nitroxide layer". Vsk = 0,864 m / s.

The coefficient of run-in intensity (K) of the nitroxide layer shows that in all cases the nitroxide layer provides a higher value of the coefficient of run-in intensity (K) with a better run-in than the nitride layer obtained by the classical nitriding regime (Table 1).

Table 1
The value of the coefficient of the running-in time of the oxyzotized layers obtained according to various technological processing conditions on steel 45

Processing mode	**Layer phase composition**	**Thickness of the nitride layer, mkm**	**Oxide layer thickness, mkm**	**Running-in ratio, К**
Nitriding: T_a=580°C, τ_a=3 ч.	ε, ε′, γ′, Fe_2O_3	20-22	-	1,15-1,30
Nitriding: T_a=580°C, τ_a=3 ч., α=45-60% +oxide: $T_{ок}$=550°C, $\tau_{ок}$=1 ч	ε′, ε″, γ′, Fe_3O_4	28-30	1-3	3,70-3,85

The necessary structure and phase composition of the oxynitride layer is achieved under optimal processing conditions, with obtaining a low nitrogen ε′-phase ($Fe_{2-3}(NC)$), ε′′-phase (Fe_{2-3} (NCO)) and γ′-phase (Fe_4N) a certain ratio of 25-30 microns thick and a surface layer of Fe_3O_4 oxide 1-3 microns thick.

In this case, it is necessary to precisely coordinate the parameters of the oxidation process in the second stage of processing with the nitriding parameters in the first stage. Because the growth rate of the oxide layer on the surface of the nitride layer should be less than or equal to the rate of deazotization in the second stage. If they are not matched, an intermediate Feα phase can form, which leads to surface cracking or peeling of the oxide layer.

As our further studies have shown, in order to obtain a carbonitride and oxycarbonitride layer having certain ratios isomorphic to the ε phase: the ε′ and ε′′ phases, as well as the фазы phase in the nitride zone and a dense surface oxide layer consisting of of magnetite alone, the oxidation process can be carried out in water vapor with the addition of complexones, in particular, Trilon-B and HEDP.

Figure 7 shows the microstructure of the oxynitride layer obtained by nitriding in ammonia at 580 °C for 3 hours and oxidized in water vapor with 5% HEDP at 550 °C for 1.0 hour. In this case, a combined diffusion layer is formed, consisting of a dense surface oxide zone, a nitride zone, and an SVA

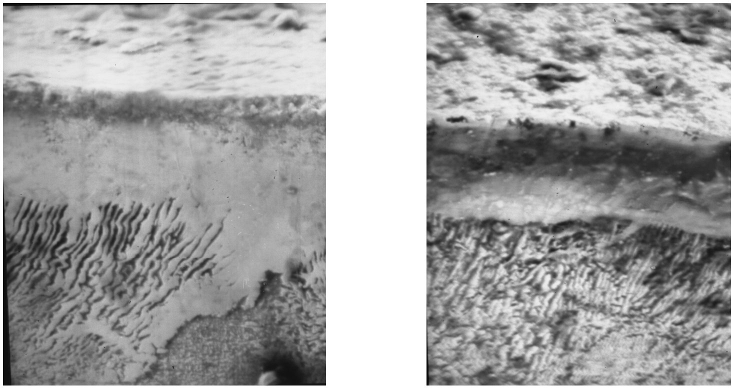

а)   б)

Figure 7.The microstructure of the nitroxide layer on steel 45. Processing mode: Nitriding 580 ° C, 3 hours; oxidation - 550 ° C, a - 1 hour and b – 2,5 hours in water vapor with the addition of 5% HEDP.

X-ray diffraction analysis showed that the surface oxide layer consists of almost one oxide, magnetite, with an increase in the intensity of the Fe_3O_4 line than the intensity of the Fe_3O_4 line obtained under the same conditions of nitrooxidation carried out by oxidation in water vapor without additives.

Figure 8 shows the distribution of elements over the depth of the oxide layer of nitrooxidized steel samples 45 treated with nitriding at 580 °C for 3 hours and oxidized for 1,0 hour in water vapor and in water vapor with 5% HEDP

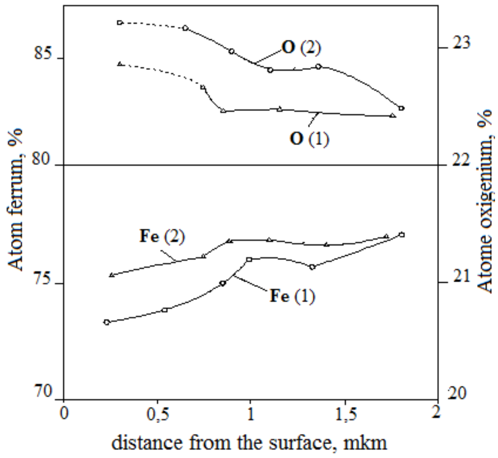
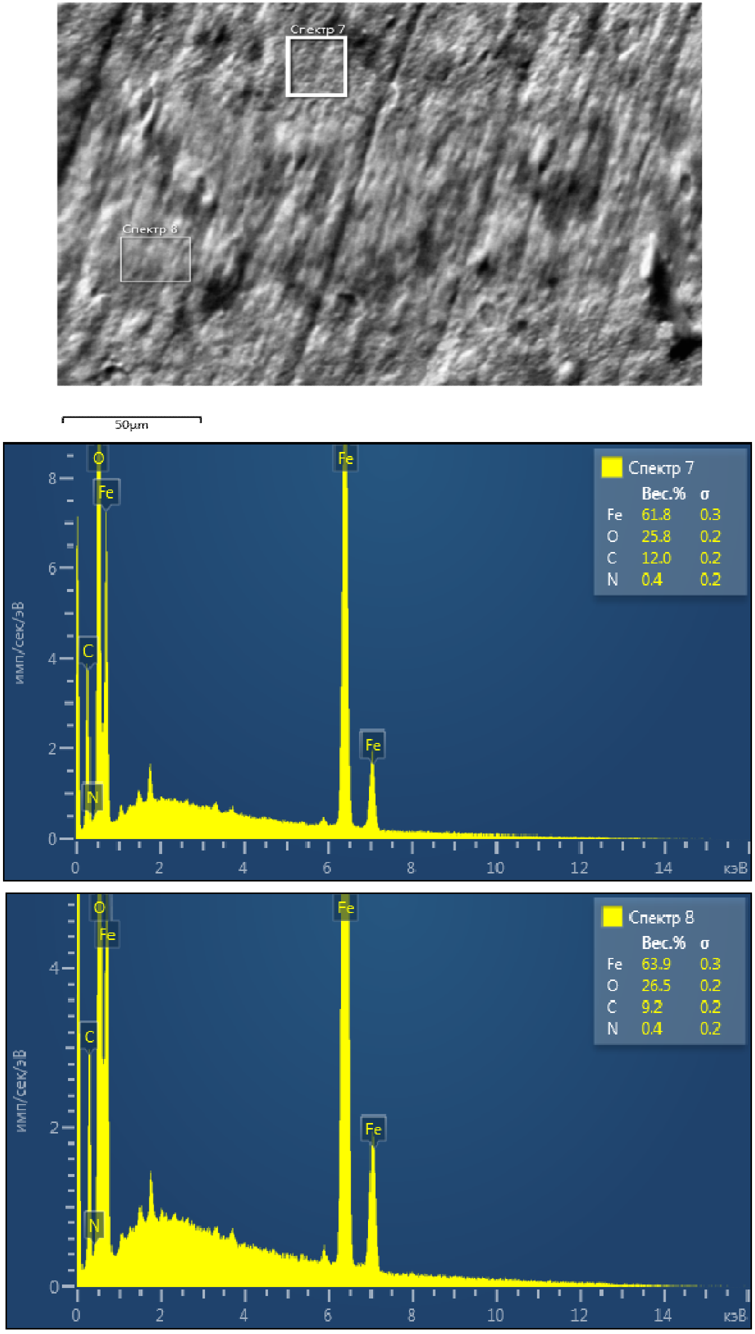


Figure 8.Distribution of oxygen and iron over the depth of the oxide layer.Nitridingat 580 °C for 3 hours and oxidation: 1 - for 1,0 hour in water vapor; 2 - for 1 hour in water vapor with the addition of 5% HEDP. Steel 45.

The use of an OEDP additive in water vapor during oxidation causes an increase in the oxygen concentration in the composition of the oxide layer. The resulting oxide layer has a dense structure consisting of one monoxide - magnetite. The formation of such an structure and composition of the oxide layer is likely due to the favorable condition for oxidation by oxygen located in the OEDP molecule, which provides the necessary oxygen potential of the saturating medium for the formation of the oxide layer, consisting of almost one magnetite. The surface morphology and the study of the microstructure of the nitrooxide layer were studied. Images were obtained at various scales (Figures 3 and 4). Nitrooxidized samples with a diameter of 10 mm, made of steel 45 after their hardening with nitriding and subsequent oxidation in water vapor, were studied. In order to clarify the ratio of the concentrations of elements on the surface of the nitroxide layer, spectrograms were taken at various points. The oxygen content on the surface is: in "spectrum 7" – 25,8%, and "spectrum 8" – 26,5%. This states that the oxide on the surface consists only of Fe_3O_4, according to the Fe-O diagram, only Fe3O4 exists in the zone of existence of the Feα + Fe_3O_4 mixture with oxygen concentrations above 23,5%. (Figure 9).



Спектр 7

	Вес.%	σ
Fe	61.8	0.3
O	25.8	0.2
C	12.0	0.2
N	0.4	0.2

Спектр 8

	Вес.%	σ
Fe	63.9	0.3
O	26.5	0.2
C	9.2	0.2
N	0.4	0.2

Figure 9. Morphology and spectrograms from a surface with a nitroxide layer of steel 45. a - surface morphology and place of taking the spectra; b - spectrogram from the point "Spectrum 7"; c - spectrogram from the point "Spectrum 8".

Important is the growth of the nitride sublayer in the depth of the nitrided layer with the formation of lower nitride ε′, ε′′ and γ′ phases due to the highly nitrogen phase obtained by nitriding in the first stage. In order to clarify the nature of the dissociation of the nitride phase, the nitride layer was oxidized in water vapor with HEDP additives for 2.5 hours. The thickness of the oxide layer increases and the release of dispersed particles of nitride ,-, γ′-phases in the zone of internal nitriding is detected.

Samples of steel 20 were processed using the above nitrooxidation technology. The results of studying the surface layer showed that after nitriding in the usual way (t_{az}=580 °C, τ_{az} = 3 hours, α = 45-60%), the microhardness of the nitride layer in the ferrite part was HV = 4 , 73 GPa, and in the pearlite part HV = 6,35 GPa. After nitrooxidation over the entire surface, almost the same values of microhardness over the entire surface equal to HV = 8,58GPa were obtained. In this case, the increase in the intensity of the lines of the ε′ andε′′ phases of the nitride layer differs sharply than the intensities of the lines of the corresponding phases of the nitride layer obtained after nitriding.

The mechanism of balancing the surface microhardness in the nitride layer claims that the dissociation of the high nitrogen ε phase and decarburization of the pearlite structure, although at the initial moment occurs with the formation of the surface α phase, the deazotization rate decreases further with the growth of the dense oxide layer on the surface. Diffusion of nitrogen from the high nitrogen ε phase occurs in the depth of the layer with the formation of a low nitrogen phase, and carbon in the transverse direction.

It is assumed that the diffusion processes in the nitride layer upon receipt of the oxide layer occur mainly along the grain boundaries of the γ′ phase. In this case, the γ′-phase in the nitride layer will be covered by ε′-, ε′′ -phases in a network form in the cross section of the oxycarbonitride layer. The dissociation of the highly nitrogen ε phase occurs by partial isolation of the γ′ phase and the formation of the faze phase due to carbon from the matrix and the ε′′ phase from matrix carbon and oxygen from the saturating atmosphere

V. CONCLUSION AND FUTURE WORK

The results of the studies show that:

- by setting the time and choosing a saturating oxidation atmosphere, it is possible to achieve the necessary ratios of the low nitrogen phases in the nitride layer, which together with the surface oxide layer possess the necessary properties;
- by controlling a nitrooxidation parameter at each stage of the process, it is possible to obtain a diffusion surface layer consisting of oxide, nitride, carbonitride, oxycarbonitride nature;
- optimaltribological and anticorrosion properties are achieved with a nitride layer with a dense oxide surface zone consisting of magnetite (Fe_3O_4) with a thickness of 1 to 3 microns;
- a nitride zone with high surface characteristics consists of γ ’(Fe_4N) and ε (Fe_3N) phases. Corrosion resistance depends on the ratio of γ’ and ε phases in the nitride zone. An increase in the amount of lower nitride (γ’ phase) in the nitride zone up to 75% is accompanied by an increase in corrosion resistance;
- the nitroxide layer, consisting of the γ′ phase and surface oxide Fe_3O_4, provides a positive gradient of properties, has a good run-in and a uniform surface oxide layer has better adhesion to nitride;

During nitrooxidation at the second stage of oxygen saturation with water in an atmosphere of water vapor by the addition of complexones (film former), it is possible to form a dense surface layer consisting of Fe3O4 oxide and a nitride layer composition that possess the necessary properties.

Each obtained phase or phase mixture is responsible for certain conditions of the physicomechanical and physicochemical properties of the processed products, therefore, taking into account the operating conditions of parts made of structural steels and the establishment of technological parameters of nitrooxidation, it is possible to achieve a further increase in their reliability and durability.

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