Structural-phase transformations during nitro-oxidation of steels and surface properties

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Abstract. Structural and phase changes in the surface diffusion layer during gas nitriding of steel were studied, with the formation of a crystallographic structure of the nitride layer for subsequent oxidation in water vapor. The conditions for forming carbides and nitrocarbides with simultaneous diffusion of nitrogen and decarburization of the steel matrix are determined depending on the nitrogen potential of the saturating medium.

The structural-phase states of the surface diffusion layer with a stepwise change in the nitrogen potential during nitriding at the first stage and followed by oxidation at the second stage, the formation of a surface oxide layer, as well as the conditions for participation in mutual diffusion processes of carbon in the nitride layer, decarburized from the steel matrix with the formation compositions of modified nitride phases.

The nitride-oxide layer's corrosion properties and gradient properties in various structural-phase states of nitride phase compositions have been studied.

1 Introduction

In the world of mechanical engineering, to improve the performance properties of a wide range of parts made from metals and alloys by surface hardening, chemical-thermal treatment methods are used, in particular, various nitriding methods. During nitriding, surface hardening is achieved due to the formation of a nitrided layer consisting of a surface nitride zone and a diffusion sublayer - an internal nitriding zone. The main advantage of the gas nitriding process with others is the compatibility of the process with other methods of thermal and chemical-thermal treatments; as a result, by controlling the structure and modifying the phase composition of the surface nitride layer, it is possible to control the characteristics of the resulting diffusion composite coatings [1-4].

One promising method of creating a high-quality modified nitride layer with the required properties is a combination of a low-temperature gas nitriding process with other methods of chemical heat treatment, in particular carrying out the process followed by steam oxidation (nitro-oxidation) [4-9].

The formation of modified nitrided layers on the surface, possessing a complex of physical, mechanical, and physical and chemical properties simultaneously, can be achieved by preliminary, simultaneous, or sequential oxygen doping of the surface nitride

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layer. To intensify the nitriding process, the technology is carried out simultaneously by adding a certain amount of oxygen (up to 5 % by weight) or air in the saturating medium and preliminary or sequential oxidation in water vapor [4,5]. To regulate the phase composition, the nitriding process is carried out in two or three stages with a combination of the oxidation process [6-12].

Improving the operational properties of parts made of low- and medium-carbon steels is possible by using surface hardening as a result of nitro-oxidation with the creation of gradient structural-phase states consisting of nitride, carbonitride, and oxycarbonitride phases with a thin oxide film on the steel surface [5,7,10,13]. In this case, the resulting composition of nitride phases, depending on the composition and structure, may have certain properties necessary for the specific operation conditions of steel products.

To achieve the best structural-phase state gradient on the surface, various composite coatings with predetermined properties are applied [13-16]. To further improve the quality of diffusion coating and develop effective nitro-oxidation methods for surface hardening of products made of medium-carbon steels, it is important to find out the kinetics of formation and structural-phase transformations both in the nitride layer during nitriding and in the oxide layer during oxidation.

2 Methods

The nitro-oxidation process is carried out by a combination of gas nitriding in ammonia dissociation step change in the first saturation stage at temperatures below eutectoid (591 °C) for the "Fe-N" system and oxidation in the second stage in water vapor at above and below eutectoid temperatures (570 °C) for the "Fe-O" system. The materials used for the study were steel 45 after enhancement.

To study the growth kinetics of the hardened layer of steel samples, metallographic studies of cross-slips of machined samples were carried out. The microstructure of the hardened layers was studied with an optical microscope "Neophot - 21" and with the help of images made on a scanning electron microscope JSM-25 of "JEOL" company [17].

Qualitative phase X-ray diffusion analysis of the nitride and nitride-oxide layers was carried out by X-ray diffusion analysis on the installation of DRON-3 in iron and cobalt filtered K_α - radiation. The phase composition was determined by comparing the obtained interplanar distances (d/n) with the tabulated values (d/n) for the nitride and oxide phases, taking into account the ratio of the line intensities of the corresponding plane [18,19].

The surface morphology and microstructure of the nitride-oxide layer were studied using a scanning microscope SEM-EVO MA 10 (Carl Zeiss, Germany); the compositions of the structures were determined using an energy-dispersive elemental analyzer brand Energy-Dispersive X-ray spectrometer (EDS-Oxford Instrument).

For comparative characterization of the corrosion properties of the coatings, the method of exposure to neutral salt fog was used, and the tests were carried out in the KTK-500 chamber, as an aggressive medium was used 3% NaCl solution in water [20].

Microhardness on the depth of the diffusion layer was measured on a microhardness tester PMT-3. Microhardness was measured on the slits in the direction perpendicular to the hardened surface by indentation of a diamond indenter on the surface of the treated samples. The change in microhardness along the layer thickness was evaluated under the same load. The distance from the surface of the area with hardness at 2,5÷3,0 GPa above the hardness of the matrix was taken as the effective thickness of the diffusion layer.

3 Results and Discussions

During gas nitriding in an ammonia atmosphere due to its thermal dissociation in the working space of the furnace, multilayer diffusion composite coatings are formed on the surface of parts made of steel, according to the system "Fe-N". In this case, nitride crystals can grow only in a saturated solid solution, as the maximum nitrogen concentration is achieved only on the surface of the nitride Fe_3N or Fe_4N continuous surface layer. In this case, the presence of carbon in the steel matrix and grain size is of no small importance, which determines the rate of diffusion processes along the volume and along the grain boundaries, the latter of which occurs at a much higher rate than in the volume of the grain.

At higher eutectoid temperature in the system "Fe-N" (590 °C) on the surface of the nitride zone with a higher concentration of nitrogen in the ε-phase with the content of carbon in the steel matrix due to the metastability of nitride phases the surface has a morphological texture with lots of micropores. In the high-nitride nitride phase at the boundaries of columnar grains in the developed voids of the volumes during cooling, there is an accumulation of atomic nitrogen, carbon, and iron carbides in the ε-phase area, while in the γ'-phase area, which has a crystallographic texture, the formation of iron carbides Fe_3C occurs because of the lower solubility of carbon in it (Fig. 1, a). Moreover, molecular nitrogen, carbon, and carbide accumulation in the ε-phase is arranged in a spherical form at equidistant distances from the surface.

During oxidation in water vapor, the walls of columnar grains are oxidized to a greater depth, the micropores are filled with oxides, and the formation of porous oxide structures layers consisting of a mixture of Fe_2O_3, Fe_3O_4, and Fe_3O_4, as well as γ-eutectoid under γ'-phase is noted (Fig. 1, b).

a) *b)*
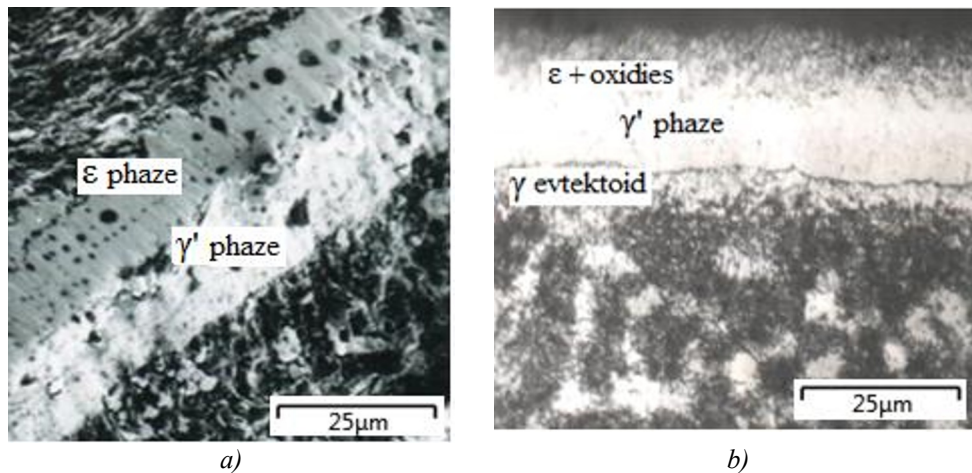
a is nitriding-620 °C, 3 h; *b* is nitriding-620 °C, 3 h; oxidation-620 °C, 0,5 h in water vapor

Fig. 1. Microstructure of nitrided (a) and nitroxidized (b) layers on steel 45.

During nitriding composite diffusion coating consisting, at temperatures below eutectoid, of three single-phase zones regardless of the nitrogen saturation potential in dissociated ammonia, the nitride zone has a crystallographic texture. The presence of matrix carbon at its decarburization against the nitrogen movement occurs by alloying the nitride phase of carbon accompanied by the formation of the carbonitride phase $Fe_3(NC)$. When cooling in places of higher concentration of carbon formed carbides Fe_3C and nitrocarbides $Fe_3(CN)$,

which is detected as dark components in the microstructure in the area of the nitride zone (Fig. 2).

Microstructures of the nitride layer obtained at different values of the nitrogen potential (π_N) during nitriding in dissociated ammonia below the eutectoid temperature with the study of the distribution of carbides in the nitride layer (Fig. 2). During nitriding at low atmospheric nitrogen potentials the formation of carbides and nitrocarbides in the nitride layer occurs by accumulation in the surface area (Fig. 2, a), and at medium values of the nitrogen, potential is distributed disorderly with reinforced dimensions in the nitride layer (Fig. 2, b). A more uniform distribution of carbides and nitrocarbides over the nitride layer occurs during nitriding with high atmospheric nitrogen potential (Fig. 2, c), but further oxidation results in the accumulation of carbides and nitrocarbides under the oxide layer (Fig. 3, a).

Carbides and nitrocarbides (dark components) are distributed over the surface even after oxidation, breaking the continuity of the surface oxide layer, which during oxidation at 580 °C on the surface occurs in enlarged sizes (Fig. 4, a), and at oxidation temperature below the eutectoid for the "Fe-O" system in smaller amounts with large sizes in places of accumulation (Fig. 4, b). This is proved by elemental compositions in the obtained spectrograms from the surface of nitride-oxide coatings oxidized at 580 ° C (Fig. 4, c) and at 550 ° C (Fig. 4, d), where with decreasing oxidation temperature, the carbon content on the surface decreases, and the oxygen content increases.

The high nitrogen concentration on the surface at saturation is a driving force for diffusion. Therefore it is important to consider the participation of carbon in the diffusion processes in the nitride layer during the decarburization of the steel matrix. Conducting the nitriding process with a change in the nitrogen potential of the atmosphere with a decrease in the nitrogen potential during the saturation period allows the participation of carbon in the diffusion processes during the nitrogen saturation period.

The high nitrogen concentration on the surface of the nitride layer at saturation is a driving force for further nitrogen diffusion. Therefore it is important to consider the simultaneous participation of carbon in the diffusion processes in the nitride layer itself during decarburization of the steel matrix.

When nitriding in dissociated ammonia, a denser nitride layer for further oxidation is obtained by saturation in an ammonia atmosphere in the first stage with a high nitrogen potential of the atmosphere and further with a decrease in the nitrogen potential of the atmosphere, which contains carbides and nitrocarbides in smaller amounts in the microstructure (Fig. 2, d). The oxidation in the second stage of the nitride layer at a temperature of 550 °C, obtained by the nitro-oxidation process with a step change in the nitrogen potential in the first stage, allows obtaining a uniform surface oxide layer of dense structure as a result of which the resulting coating has a gradient structure consisting of a surface oxide layer and nitride layer under it (Fig. 3, b).

Reducing the temperature at the second stage of the nitro-oxidation process naturally causes a slowdown of decarburization of the steel matrix, and the carbon in the nitride zone is involved in the process of interdiffusion in the nitride zone to form a carbonitride Fe(NC) and oxycarbonitride Fe(NCO) phase. At the boundary of the nitride layer with the zone of internal nitriding in the part of the nitride due to the predominance of boundary diffusion forms a toothed-wave structure γ'-phase, between the teeth of which the cementite is released, due to the limited solubility of carbon in the nitride phase, as evidenced by a decrease in the decarburization rate of the matrix with decreasing temperature nitro-oxidation process (Fig. 3, b).

The main phase of oxide layers at oxidation temperatures of 550 °C and 580 °C is Fe_3O_4. Oxide Fe_2O_3 grows on the surface of the Fe_3O_4 phase, probably in the cooling process. Oxide FeO, found in oxide layers obtained at 580 °C and 620 °C, has a thin film at

the boundary of the oxide and nitride zones. At an oxidation temperature of 620 °C, due to more intensive growth of Fe_3O_4 and FeO, the oxide layer represents mixtures of all oxides, which are proved in numerous studies, dedicated to the formation of oxide phases on the surface during steam oxidation of steel [21-23] is characterized by significant friability, which leads to reduction of surface corrosion properties.
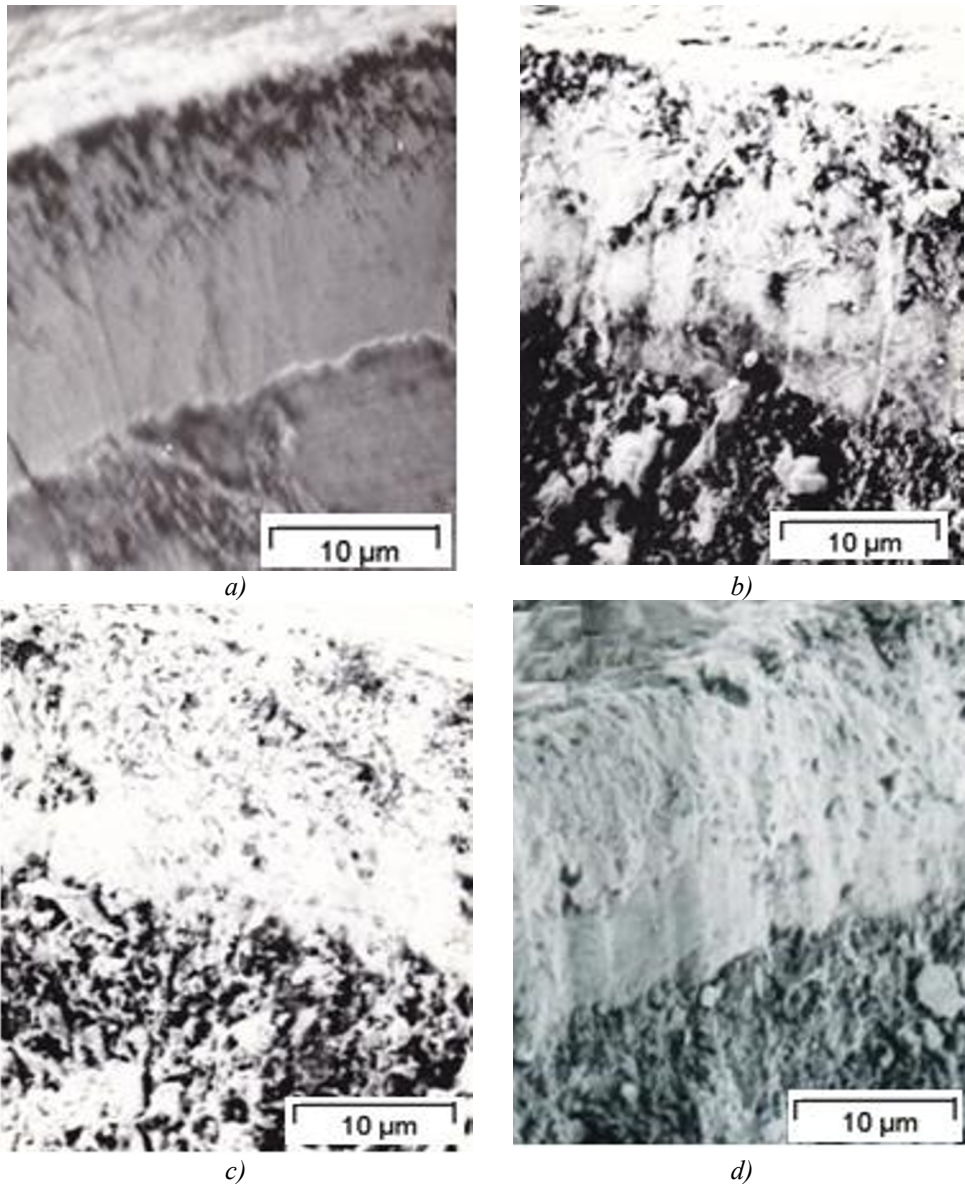

Fig. 2. Microstructure of nitride layer on steel 45 at different nitrogen potentials: Nitriding-580 °C, 3 h: a - π_N <2; b-2< π_N <3.5; c - 4< π_N <5.5; d-2 h (4< π_N <5.5) + 1 h (2< π_N <3.5)
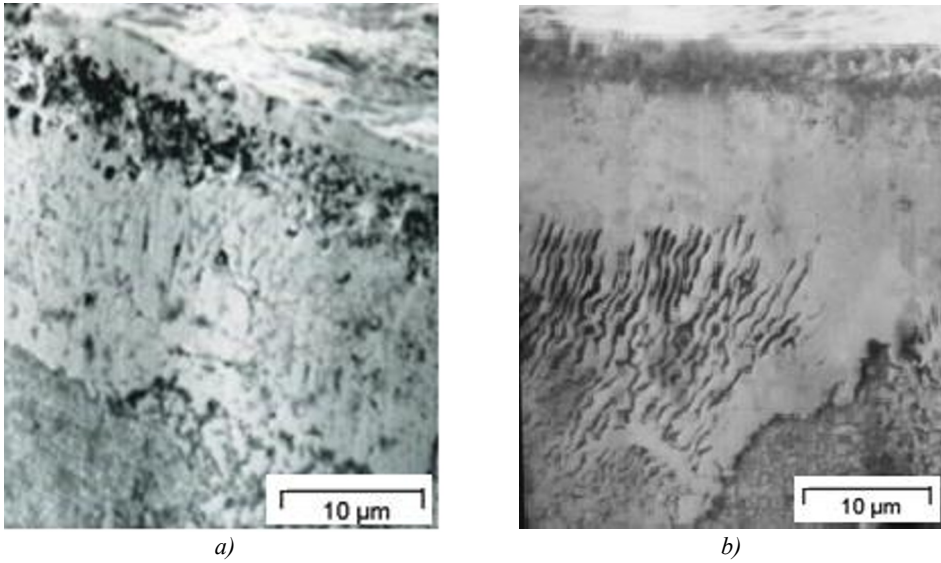
Fig. 3. Microstructure of nitride oxide layer on steel 45 in different modes of nitro-oxidation: Nitriding - 580 °C, 3 hours: *a*-oxidation – 580 °C, 1 hour; *b*-oxidation -550 °C, 1 hour
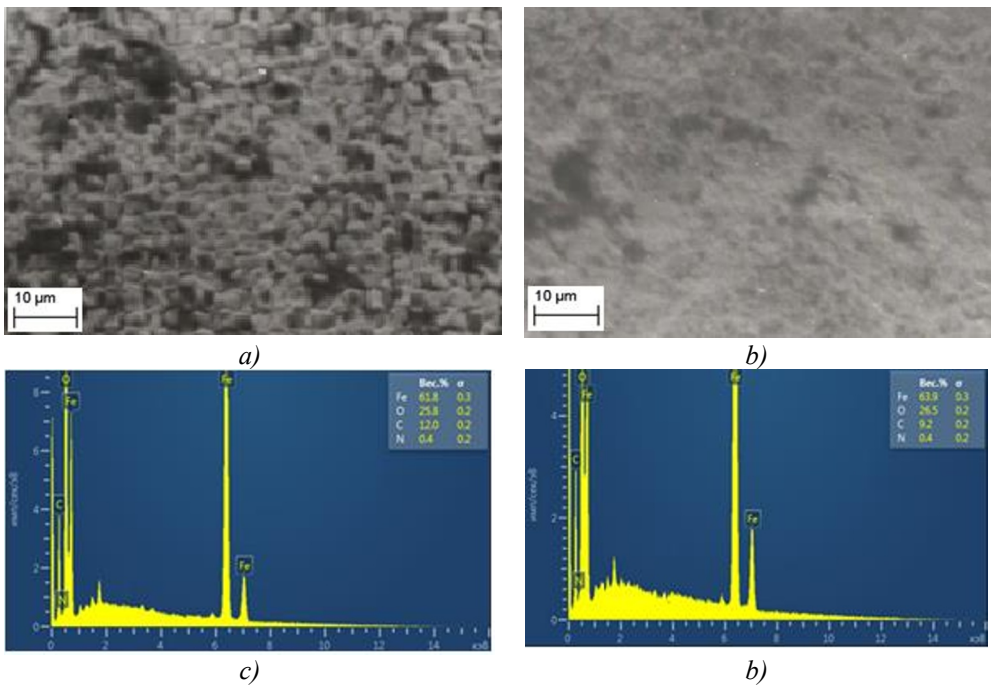

Fig. 4. Morphology and spectrogram of surface of nitride-oxide layer on steel 45: Nitriding – 580 °C, 3 hour: oxidation – 580°C, 1 hour; *a* - surface morphology; *b* - spectrogram; oxidation -550 °C, 1 hour; *c*-surface morphology; *d*-spectrogram from surface

To improve the corrosion properties, the most responsible is the presence of an oxide layer on the surface consisting practically of a single magnetite Fe_3O_4 [21], which can be obtained during the oxidation process by reducing the temperature in the second stage of nitro-oxidation at 550 °C, below the eutectoid temperature for the system "Fe-O". Changing

the intensity of the nitride-oxide layer phase lines during nitro-oxidation in different oxidation modes is shown in Fig. 5.

After the nitro-oxidation process, the structure of the composite diffusion coating consists of a surface oxide zone and a modified nitride zone, which has in its composition compositions of nitrides, carbonitrides, as well as carbon- and oxygen-doped nitride phases.

The phase composition of the nitride phases at the first stage of nitriding changes depending on the nitrogen potential of the saturating atmosphere, and at the second stage of oxidation in the presence of oxygen from the saturating atmosphere and simultaneously proceeds interdiffusion of nitrogen and carbon in the nitride layer. Depending on the time of oxidation of the nitride layer is formed oxygen-doped phases - oxynitrides Fe(NO) and oxycarbonitrides Fe(NCO) in various ratios. Phase changes in the nitride layer with the formation of oxynitrides and oxycarbonitrides in the presence of oxygen in the saturating atmosphere during nitriding are confirmed in [24,25]. The ratio of oxygen- and carbon-doped nitride phases during isothermal aging in water vapor with simultaneous formation of a surface oxide layer varies depending on the duration of the process, which allows the formation of the necessary compositions of modified nitrides with different phase compositions.

Dissociation of high-nitrogen nitrides takes place during isothermal aging of the nitrated layer. Released nitrogen diffuses in two directions from the concentration maximum in the layer, and changes in the nitrogen concentration in the layer also lead to changes in the ratio of ε- and γ' -phases. Deasotization of the surface in the oxidation process is determined by temperature, holding time, and atmosphere composition. After nitriding of medium carbon steels, two isomorphic hexagonal nitrides, referred to as ε- and ε'- phases, are formed in the nitride matrix because of the presence of carbon. At the same time, on the diffractogram, there is a stratification of reflexes ε-phase. The reflex phase, corresponding to large reflection angles θ, is denoted as carbonitride ε'-phase (Fig. 5).
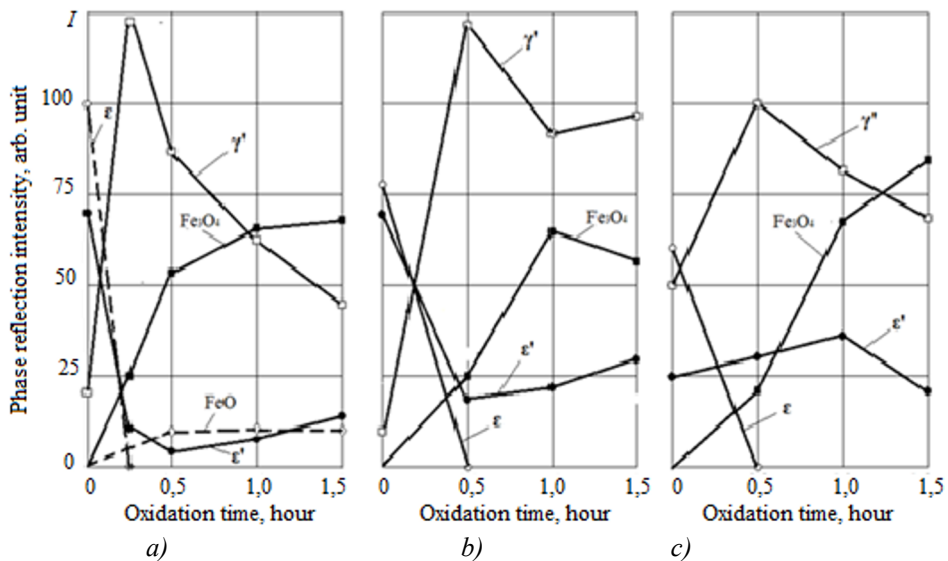

Fig. 5. Variation of intensity of lines $\varepsilon(101)$, $\varepsilon'(101)$, $\gamma'(200)$, Fe$_3$O$_4$(110), and FeO(200) of nitride layer depending on duration of oxidation of samples from steel 45. Radiation FeK$_\alpha$.: Nitriding at first stage -2 h ($4 < \pi_N < 5.5$)+1 h ($2 < \pi_N < 3.5$): a is nitriding – 620 °C, oxidation –620 °C; b is nitriding 580 °C, oxidation – 550 °C; c is nitriding -550 °C, oxidation – 550 °C

At the temperature of oxidation of the nitride layer, decomposition of ε-phase occurs within a short time of oxidation, and the oxide layer consists of a mixture of oxides Fe_3O_4 and FeO, and oxides FeO are metastable, and changes in the nitride phase occur, which at the beginning of oxidation their participation due to formation of γ'-phase increases, but over time becomes less because of the predominance of diazotization (Fig. 5, a).

The most stable changes in the nitride phases during nitriding with changes in the nitrogen potential of the atmosphere can be obtained by nitriding at temperatures below the eutectoid for the system "Fe-N" and oxidation in the second stage below the eutectoid temperature for the system "Fe-O" (Fig. 5, b and c). In these cases, the decomposition of high-nitrogen ε-phase occurs during 0.5 hours of oxidation with the formation of ε'-phase and γ'-phase, whose ratio changes with time (Fig. 5, b, and c). Further oxidation of nitride layers obtained at 580 °C is accompanied by an increase in the proportion of participation of nitride phases oxygen doping from the oxide layer due to a higher concentration of nitrogen in the nitride layer (Fig. 5, b), while in the nitride layer obtained at temperature 550 °C is the growth of oxide layer due to diazotization and dissociation of nitride layer (Fig. 5, c).

According to the literature [25], the ε-phase Fe_xK has a wide area of homogeneity and varies from 2 to 3.5 at the boundary with the γ′-phase (about 6 % by mass) depending on the nitrogen concentration X.

Subsequent oxidation causes structural changes in the diffusion layer with the formation of the surface oxide layer with the subsequent location of the nitride layer under it, which in the process of oxidation as a result of interdiffusion, passes to quantitative phase changes, forming compositions of nitride phases in different ratios. This circumstance makes it possible to adjust the ratio of phases in the nitride layer to obtain a particular composition of compositions of nitride phases, creating the best gradient structural-phase states on the surface responsible for certain physical and mechanical and physical and chemical properties of hardened products made of medium-carbon steels.

Fig. 6 shows changes in the corrosion area of samples as a function of test time in a 3 % aqueous solution of table salt of steel 45 for the nitride layer with 50 and 75 % γ'-phase in the composition of nitride phases. It should be noted that in the experiments performed, the thickness of the oxide zone was - 1.5 μm.
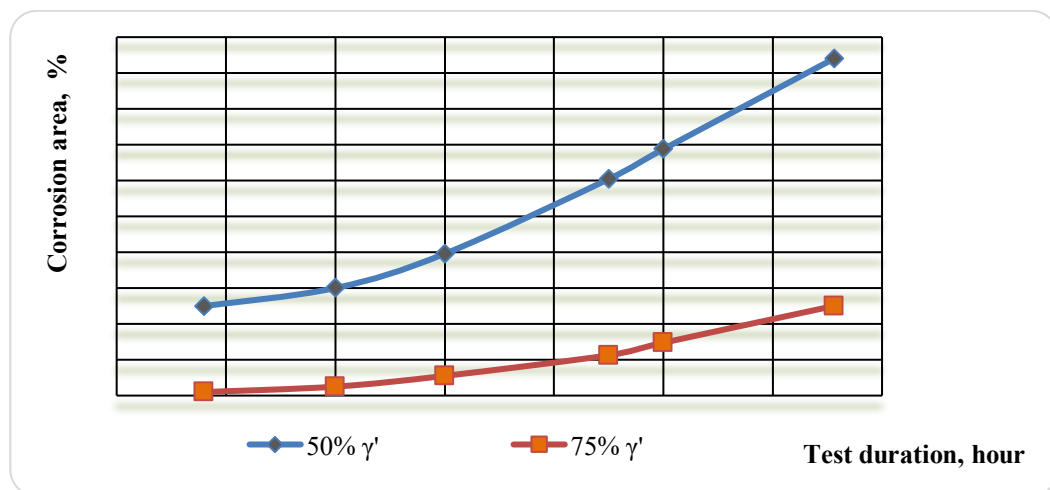

Fig. 6. Change in corrosion area of nitroxidized steel 45 depending on exposure time. Nitriding - 580 °C; 3 hours;   oxidation - 550 °C: 0.5 hours (50 % γ'-phase); 1 hour (75 % γ'-phase). Corrosive medium - 3 % aqueous NaCl solution.

The corrosion resistance of diffusion nitride oxide coating, which is one of the main operational properties of hardened products, when forming an oxide film on the surface of the nitrided layer on steel products increases. Here there are also opportunities to further improve corrosion resistance by adjusting the phase composition of the compositions of the phases in the nitride layer in the process of oxidation with the receipt of phase compositions consisting of γ'-phase content of about 75 %.

The surface of the nitride layer obtained by changing the nitrogen potential of the atmosphere (Fig. 2, d) is porous, and the surface microhardness is 3.5-4.0 GPa; after oxidation at 580 °C surface microhardness increases to 4.5-4.7 GPa, and at oxidation in temperature 550 °C for 1 hour reaches 5.5 GPa. The subsequent removal of the porous part of the nitride layer and the surface oxide film nitride-oxide layer reveals an increase in the surface microhardness of the nitride layer to 8.5 GPa.

The curves of microhardness distribution over the thickness of nitride and nitride-oxide coatings show that in all cases after nitro-oxidation, the microhardness in the nitrided layer increases (Fig. 6). The microhardness of the corresponding coating sections is practically independent of the nitriding duration, with increasing nitriding time an increase in the layer extent is observed. As shown by X-ray diffraction studies, the oxidation of the nitride layer results in the formation of a well-developed zone of ε'- and γ' - phases with high hardness, which leads to an increase in the hardness of the nitride layer after oxidation.

From the results of microhardness, studies of diffusion nitride-oxide coating can be concluded that the two-step nitro-oxidation mode in the surface layers is formed a continuous oxide film with a hardness of 4.5÷5.5 GPa, and behind it, the nitride zone, consisting mainly of ε'- and γ' - phase with hardness up to 8.5 GPa.
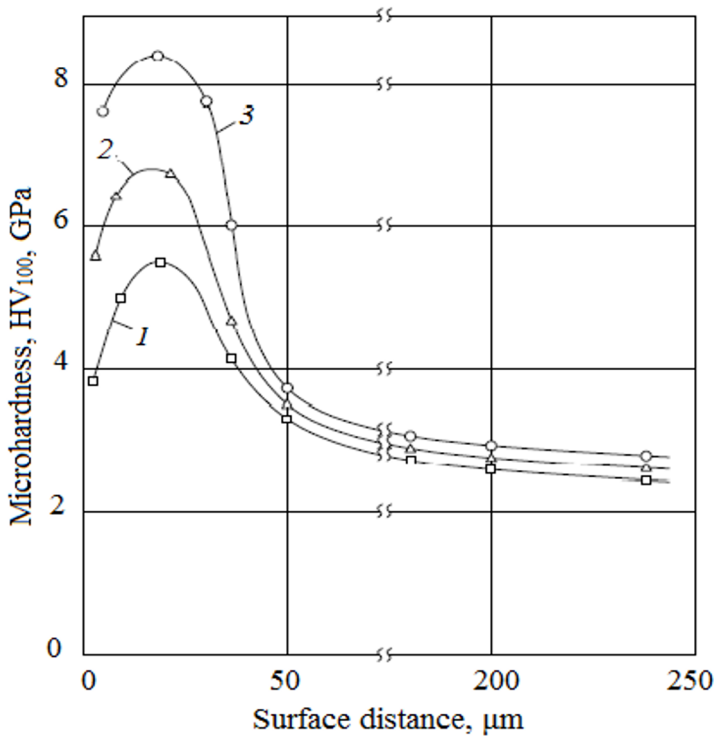

Fig. 7. Distribution of microhardness by layer depth. Nitriding - 580°C, 3 hours: 1 is no oxidation; 2 is oxidation -580 °C, 0.5 hours, 3 is oxidation 550 °C; 1 hr.

Structural-phase changes in the nitrided layer during oxidation are accompanied by diffusion of oxygen water vapor with replacement with nitrogen atoms on the surface with the formation of an oxide layer, nitrogen in two directions: diazotization into the atmosphere and interdiffusion deep into the metal, as well as the interdiffusion of carbon into nitrides from the steel matrix.

Depending on the technological regimes of the process of short-term low-temperature process of gas nitriding, a change in the nitrogen potential during the saturation period and the composition of the nitrided alloy can change the ratio of phases in the nitride layer, with obtaining diffusion composite coating with a given structure and compositions of nitride phases, with predetermined properties. It is important to consider that the gradient of structural-phase states is formed at the saturation temperature and during the subsequent cooling of the hardened products.

4 Conclusions

As a result of this research, it can be argued that the combination of gas nitriding technology with subsequent oxidation nitride layer with morphological structure does not provide a stable gradient of structural-phase states in the composite coating. Therefore it is necessary to have a crystallographic texture on the surface of products of medium-carbon steels, allowing the growth of a continuous oxide layer on the surface of nitride phases.

The structural-phase states of the nitroxidized layer are determined by the presence of the surface oxide layer and the regulation of the compositions of the nitride phases by interdiffusion of both nitrogens from the high-nitrogen nitride and carbon from the steel matrix. As a result, the surface nitride-oxide layers have a gradient structure and a regular arrangement relative to each other of the oxide and nitride layers with different structural-phase states.

Adjusting the nitrogen potential at saturation in an atmosphere of dissociated ammonia and carrying out the oxidation process at temperatures of the existence of one magnetite can be achieved to obtain a diffusion surface-strengthened layer consisting of oxide, nitride, carbonitride, oxycarbonitride nature, and developed zone of internal nitriding.

The presence of carbon in the steel matrix during decarburization is involved in diffusion processes in the nitride layer with the formation of carbonitride ε'-phase, so during oxidation, dissociation of high-nitrogen ε-phase transition into γ'-phase completely does not occur, the maximum content of which may be about 75%, and at these ratios, the nitride-oxide coating has improved corrosion resistance values.

During nitro-oxidation of medium-carbon steels in the second stage of the oxidation process in water vapor increases the microhardness of the nitride layer transition to low-nitride phases, and the surface oxide layer in hardness creates a positive property gradient, which is important for providing external friction conditions.

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