

Gradient structural-phase states and properties of surface layer after nitro-oxidation

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Abstract. The phase equilibrium is considered, the formation of nitride phases during gas nitriding due to the presence of carbon in the iron steel matrix in all formed structural-phase states of the nitride layer, carbides are released, the dispersion and dispersion of which in the nitride layer depends on the nitrogen potential of the saturating atmosphere. During subsequent oxidation in water vapor, simultaneously with the formation of a surface oxide film during the exposure period, especially in water vapor with additives of complexion agents, during reaction-diffusion, gradient structural-phase states of low-nitrogen carbonitride, oxycarbonitride, and nitride phases are formed in the nitride layer. At the same time, the presence of oxygen in the furnace atmosphere positively affects the formation of the nitride layer and the internal nitriding zone. The corrosion resistance of gradient nitride-oxide diffusion coatings depends on the presence of a surface oxide layer consisting of magnetite and the ratio of modified nitrides and γ' -phase composition. At the same time, in the composition of the nitride layer, the composition of oxycarbonitrides with a larger proportion of the γ' -phase has the highest corrosion resistance with a lower rate of development of corrosion damage on the surface. The presence of a surface oxide layer in the structural-phase states of the nitride-oxide layer, providing a positive property gradient, can provide conditions for external friction during sliding friction.

1 Introduction

Surface hardening of steels by creating controlled technologies for obtaining a modified composite nitrided layer by combining the nitriding process with other surface hardening processes is widely used in modern mechanical engineering [1,2]. Combinations of liquid, ionic, and gas nitriding processes are carried out by various methods of mechanical, thermomechanical, thermal, and chemical-thermal hardening, as a result of which, to improve the service characteristics of steel and alloy products, a diffusion gradient layer is obtained modified with different compositions, structures, and compositions of nitride phases [3-5].

Due to the environmental problem in liquid technologies, the high cost and difficulty of processing products of complex configuration, recently special attention has been paid to the development of low-temperature short-term gas nitriding processes with the study of gradient structural-phase states, both in the surface nitride layer and in the diffusion nitriding zone [6,7].

In the process of gas nitriding for the formation of modified diffusion composite coatings on the surface of machine parts and tools, regulation of the structure and composition of both the nitride layer and the internal nitriding zone is achieved in a single-stage nitriding process by changing the nitrogen potential of the atmosphere, introducing various carbon and oxygen-containing gases, as well as preliminary oxidation [8, 9]. The structure and composition of nitrided layers with process intensification is regulated in two-stage or three-stage nitriding processes with a combination of oxidation processes [10, 11].

In the process of nitro-oxidation, when nitriding is performed at the first stage in an ammonia atmosphere, followed by oxidation at the second stage in water vapor, a diffusion nitride-oxide coating is formed on the surface of which an oxide film is located. In this case, the nitride layer under the oxide film during the

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oxidation process will undergo phase changes with the formation of oxygen-doped nitride and carbonitride phases [12, 13].

During nitriding, the structure and composition of the steel matrix, as well as the size of the grain in the structure, to some extent determines the diffusion processes, in volume and along grain boundaries, the latter which occurs at a much higher rate than in the bulk of the grain. During the nitriding of steel and alloys, the formation of compositions of nitride phases in diffusion processes is achieved mainly with a change in the temperature-time regimes of the processes and a change in the nitrogen potential of the saturating atmosphere [14, 15].

In the nitro-oxidation, it becomes possible to obtain compositions of modified nitride phases alloyed with oxygen, which determine the gradient of the structural-phase states of nitrated layers on the surface of processed products from medium-carbon and low-alloy steels and the criteria for choosing diffusion nitrated coatings with certain phase compositions with known corrosion and wear-resistant properties [16].

2 Methods

The process of nitro-oxidation was carried out in the first stage by nitriding in an atmosphere of dissociated ammonia and the second stage by oxidation in water vapor. To increase the oxygen potential during oxidation, aqueous solutions of complexions were used: a 5% solution of hydroxyethylidene diphosphonic acid (HEDP) and a 5% solution of Trilon B [18].

Metallographic analysis of treated steel samples was performed on transverse sections using a Neophot-21 light microscope and a JEOL JSM-25 scanning electron microscope [19].

The main study was carried out on steel grade 40X with the composition: C - 0.41 %, Si - 0.22 %, Mn - 0.55 %, Cr - 0.016 %, Ni - 0.022 %, P - 0.96 %, S - 0.06 %.

Qualitative phase X-ray diffraction analysis of the diffusion nitride and nitride-oxide layers was studied on the Dron-3 installation using filtered cobalt $K\alpha$ radiation. Diffraction angles were recorded in the range $2\theta=20-130$ deg, at 1 and 2 deg/min sample rotation rates. The phase composition was determined by comparing the obtained interplanar spacing (d/n) with tabulated values (d/n) for nitride and oxide phases, taking into account the intensity ratio of the corresponding plane [20].

Corrosion tests were carried out in the KTK-500 chamber. A 3% solution of NaCl in water was used as an aggressive medium at a rain gauge constant of $2 \text{ cm}^3/\text{h}$, temperature $-26 \text{ }^\circ\text{C}$. During the daily inspection of samples treated according to different modes, the time of the appearance of the first foci of corrosion and the area of corrosion damage as a percentage of the entire estimated area were recorded.

Microhardness over the depth of the diffusion layer, taking into account the relaxation properties of the hardened layer on the MTI-3M installation by pressing the indenter onto the surface of the samples at room temperature. With automatically performed loading and unloading with smooth control of the indenter movement speed in the range from 0.05 to $7 \text{ }\mu\text{m/s}$, as well as recording loading, holding, and unloading diagrams in the coordinates "load-indenter penetration depth". During testing, the values were calculated using the corresponding formulas [21].

3 Results and Discussions

At the first stage of nitro-oxidation in systems with an internal nitriding zone and two nitrides $\text{Fe}_4\text{N} \rightarrow \text{Fe}_{2-3}\text{N}$ are formed on the steel surface depending on time, and at high nitrogen concentrations, the formation of gradient layer structures consisting of $\text{Fe}_2\text{N} \rightarrow \text{Fe}_3\text{N} \rightarrow \text{Fe}_4\text{N}$ nitrides and internal nitriding zone is observed. Improving the performance properties of products is achieved by obtaining compositions of these nitride phases.

For a composite nitride coating, optimization of the phase composition and structure of the surface nitride zone is achieved by controlling the nitrogen concentration in the nitride layer to obtain nitride phases of one or another composition, which is possible by varying the nitrogen potential (π_n) of the atmosphere during saturation, as well as by doping the nitride coating with oxygen and carbon. During structural and phase changes in the nitride coating, it is important to change the nitrogen potential of the atmosphere, which determines the structure and phase composition of the diffusion zone, the surface of which is subjected to further oxidation. The nitrogen potential of the medium depends on the saturation temperature and the degree of ammonia dissociation (α) (Fig. 1).

In the ranges of high nitrogen potential, corresponding to low ranges of ammonia dissociation, a nitride phase with a high nitrogen concentration (ε -phase) is formed on the surface; The formation of the zone of internal nitriding occurs at low nitrogen potentials, corresponding to high values of the degree of ammonia dissociation (Fig. 1).

According to (Fig. 1) the phase equilibrium, depending on the temperature and the degree of dissociation on the steel surface up to the eutectoid temperature for the "Fe-N" system (590°C), it is possible to form composite nitrided coatings consisting of the $\varepsilon \rightarrow \gamma'$ phases at temperatures above the eutectoid $\varepsilon \rightarrow \gamma' \rightarrow \gamma$ phases.

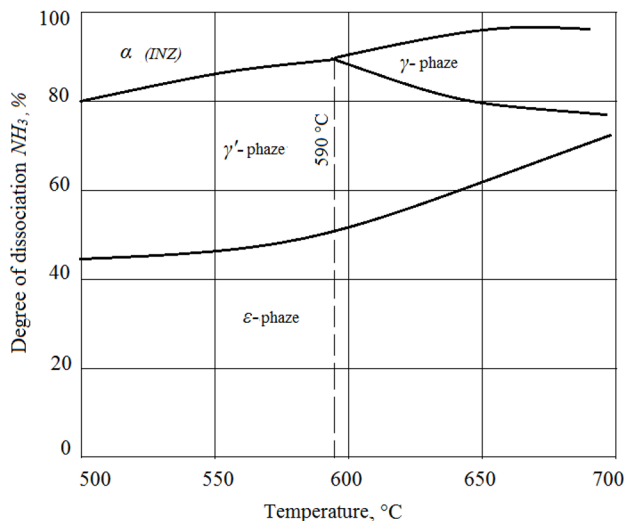


Fig. 1. Phase equilibrium of "Fe-N" system in atmosphere of dissociated ammonia.

When using an ammonia medium with the addition of gases-diluents, which has different chemical natures, the nitrogen potential of the saturating medium changes depending on the saturation temperature and the degree of ammonia dissociation. For example, when carbon-containing gases are introduced into the ammonia atmosphere, along with nitride phases, the formation of Fe_3C in the nitride layer is thermodynamically probable, and the region of existence of high-nitrogen $\text{Fe}_{2,3}\text{N}$ nitride phases, and Fe_3C expands with an increase in the concentration of hydrocarbon components (Fig. 2).

When saturated with a carbon-containing ammonia atmosphere (during nitrocarburizing) in the nitride layer due to the simultaneous diffusion of nitrogen and carbon, and also due to the mutual solubility of $\text{Fe}_{2,3}\text{N}$ (ε -phase) and Fe_3C (cementite), phases of the $\text{Fe}_{2,3}(\text{NC})$ carbonitride type are formed (ε' -phase) and nitrocarbide $\text{Fe}_3(\text{CN})$, respectively. Forming the $\text{Fe}_4(\text{NC})$ phase doped with carbon in the nitride layer and $\text{Fe}(\text{NC})$ in the internal nitriding zone is possible.

The presence of free nitrogen and hydrogen in a saturating atmosphere in a large amount increases the region of existence of a high-nitrogen ε -phase (Fig. 2, line 1) and leads to an increase in the content of cementite, as well as carbonitride $\text{Fe}_{2,3}(\text{NC})$ and nitrocarbide $\text{Fe}_3(\text{CN})$

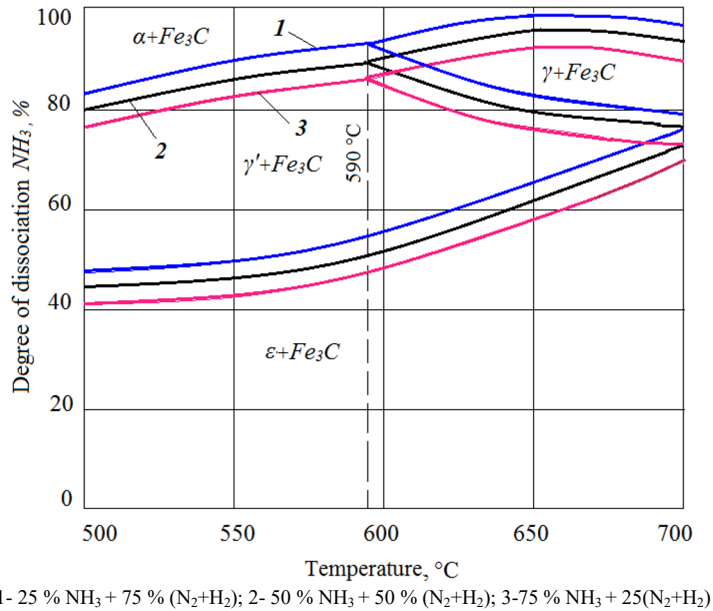


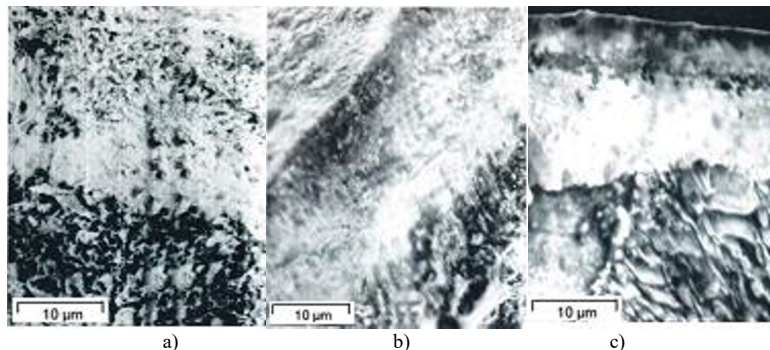
Fig. 2. Phase equilibrium of "Fe-N-C" system in atmosphere of dissociated ammonia.

With the content of free nitrogen and hydrogen in the saturating atmosphere in a smaller amount, the region of existence of the high-nitrogen ϵ -phase and the content of cementite, respectively, carbonitride $\text{Fe}_{2-3}(\text{NC})$ and nitrocarbide $\text{Fe}_3(\text{CN})$ decrease (Fig. 2, line 3).

With an increase in the nitriding temperature, the region of existence of the ϵ -phase and γ' -phase also increases; however, at a higher eutectoid temperature (590 °C) for the «Fe-N» system, due to the significant superiority of boundary diffusion, the formed ϵ -phase on the surface has a morphological texture (columnar structure), during oxidation, which is oxidized to a greater depth in the ϵ -phase [22]. At lower eutectoid temperatures, the ϵ -phase has a crystallographic texture, which is most likely to be created for further oxidation of the nitride layer with a developed surface ϵ -phase [6].

The microstructure of 40X steel after nitriding in various degrees of ammonia dissociation was studied (Fig. 3, a and b). In the microstructure of the nitride layer, carbides Fe_3C and nitrocarbides $\text{Fe}_3(\text{CN})$ in (dark components) are found, which, at a low degree of ammonia dissociation, are released in the form of a particle (Fig. 3, a), and the most scattered form of fine particles during the process of stepwise change in the degree of dissociation ammonia (Fig. 3, b). Such precipitation of carbides and nitrocarbides, although in small quantities, is found at the boundary of the oxycarbonitride surface layer, which is formed in the process of oxidation, and the nitride layer, which is subjected to denitriding (Fig. 3, c).

At lower eutectoid temperatures for the "Fe-N" system during the formation of the internal nitriding zone, the nitrogen source for its formation is the γ' -phase. At the same time, the formation of a phase at the boundary of the pearlite sections occurs more quickly due to the simultaneous diffusion of nitrogen atoms by the introduction and replacement of carbon atoms throughout the grain volume, mainly by the formation of the γ' -phase (Fe_4N), nitrocarbide $\text{Fe}_3(\text{CN})$ and iron carbide Fe_3C (Fig. 4, A). With carbon content an excess, graphite can be formed along with iron carbide, and the dark phase in the structure will have the composition of a mixture of Fe_3C +graphite (Fig. 4, B)



Nitriding -580 °C, 3 hours: a – $\alpha=30-45\%$; b – 2 hours $\alpha=30-45\%$ + 1 hour $\alpha=45-60\%$; c – oxidation –550 °C, 2,5 hours in vapors of 5% aqueous solution of HEDP

Fig.3. Microstructure of nitride (a and b) and nitride-oxide layer (c) annealed steel 40X

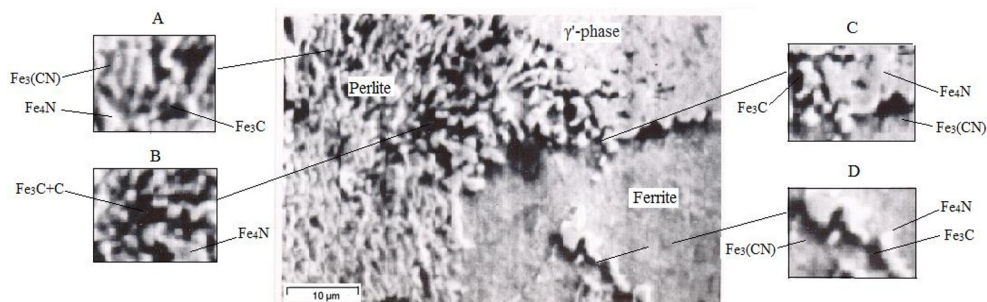


Fig. 4. Microstructure of nitrided layer at boundary of phase "nitride layer - zone of internal nitriding" on annealed steel.

Due to the low diffusion coefficient of nitrogen, $\text{Fe}(\text{NC})$ and $\text{Fe}_4(\text{NC})$ are formed in ferrite. As a result of simultaneous boundary diffusion of carbon and nitrogen in the γ' -phase, nitrocarbide $\text{Fe}_3(\text{CN})$ is formed at the grain boundaries of the ferrite, and with an excess carbon content between these phases form iron carbide, and the γ' -phase can also be engulfed by iron carbides (Fig. 4, C).

In the process of nitriding, due to the boundary diffusion of nitrogen and carbon, Fe_3C is formed within the grain boundaries, which is limited with the γ' -phase by nitrocarbide $\text{Fe}_3(\text{CN})$. Probably in the γ' -phase, $\text{Fe}_4(\text{NC})$ is formed in a scattered form, which gives a darkish tint to the region of the γ' -phase, the structure of which has mixtures of the Fe_4N phase (Fig. 4, D).

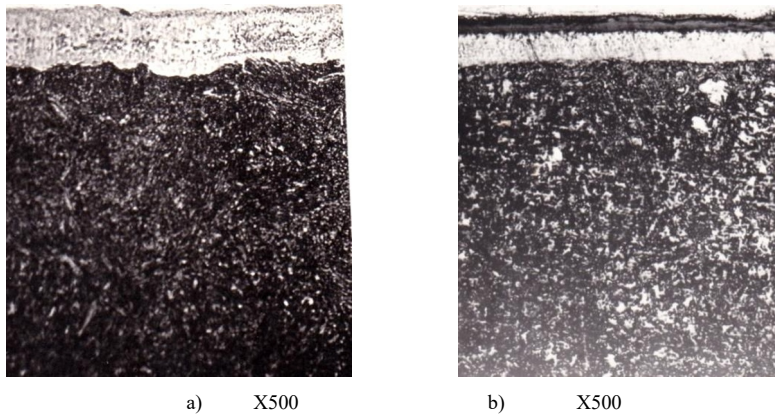
The carbon of the steel in the matrix affects the formation of gradient structural-phase states of the nitrided layer by forming various structural and phase components, both in the nitride layer and in the zone of internal oxidation. To achieve the required quality of the nitride layer with participation in diffusion processes in the nitride layer of the steel matrix carbon, according to the "Fe-N" phase state, it is necessary to ensure simultaneous diffusion of carbon and nitrogen, i.e., internal nitrocarburing, which makes it possible to obtain modified phase compositions in nitride layers with the required performance properties.

40X steels with a martensitic structure were investigated after nitriding (Fig. 5, a) and after nitro-oxidation (Fig. 5, b), with a study of the distribution of elements in the nitride layer (Fig. 6). From the point of view of ensuring the required quality of the resulting nitride layer with the participation of nitrogen and carbon of the steel matrix in the diffusion processes, the solution of the issue leads to the consideration of alloying the nitride phases with elements in the "Fe-N-C" phase states, with the production of modified phase compositions in nitride layers with predetermined operational properties.

Fig. 5 shows the microstructure of samples made of 40X steel with a martensitic structure after nitriding (Fig. 5, a) and after nitriding followed by oxidation in water vapor by holding at a temperature of 550 °C for 2.0 hours (Fig. 5, b). Subsequently, X-ray diffraction analysis of the surface of the treated samples and Auger spectral analysis were carried out to study the distribution of elements over the depth of the nitride and nitride

oxide layer (Fig. 6). Nitriding of the samples was carried out in a semi-industrial furnace with a volume of 0.67 m^3 after the previous nitro-oxidation process.

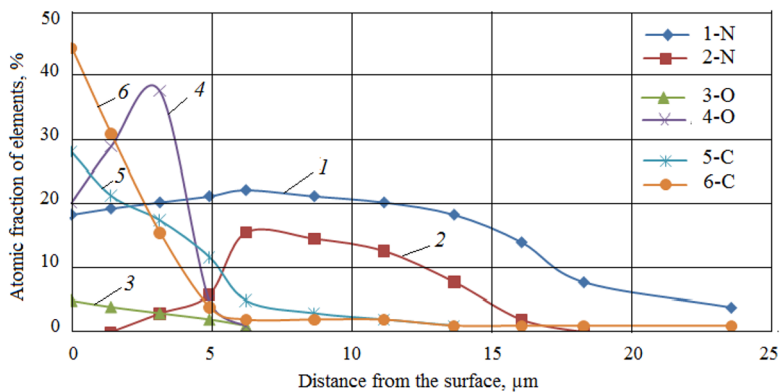
X-ray diffraction analysis in the nitride layer (Fig. 6, a) revealed Fe_3O_4 oxide and nitride phases of the ϵ -, ϵ' - and γ' -phases, and in the nitride-oxide layer (Fig. 6, b) Fe_3O_4 oxide and nitride phases ϵ' -, ϵ'' - and γ' -phases. After oxidation, the ϵ -phase (Fe_3N) is alloyed with carbon, and the carbonitride ϵ' -phase $\text{Fe}_3(\text{NC})$ is formed; in the dark parts of the nitride layer, the nitrocarbide ϵ' -phase $\text{Fe}_3(\text{CN})$ is formed, and when alloyed with carbon and oxygen, an oxycarbonitride ϵ'' -phase is formed $\text{Fe}_3(\text{NCO})$. Moreover, the formation of the oxycarbonitride ϵ'' -phase $\text{Fe}_3(\text{NCO})$ is possible based on nitrides $\text{Fe}_3(\text{NC})$ and $\text{Fe}_3(\text{CN})$, and $\text{Fe}_4(\text{NC})$ in grains of residual austenite.



Nitriding -580°C , 3 hours: a -without oxidation; b - oxidation -580°C , 2 hours in vapors of 5% aqueous solution of HEDP

Fig. 6. Microstructure of the nitride (a) and nitride-oxide layer on hardened steel 40X

After oxidation of the nitride layer in water vapor, a thin oxide layer is formed on the surface, depending on the rate of denitriding of the nitride layer, the thickness of which grows. In the initial period of oxidation, the surface high-nitrogen ϵ -phase in the nitride layer (Fig. 7, line 1) undergoes dissociation (Fig. 7, line 2) by simultaneous denitriding and; in the initial period, the growth of low-nitrogen nitride phases at the boundary with the internal nitriding zone, the formation of zones of internal nitriding due to the γ' -phase.



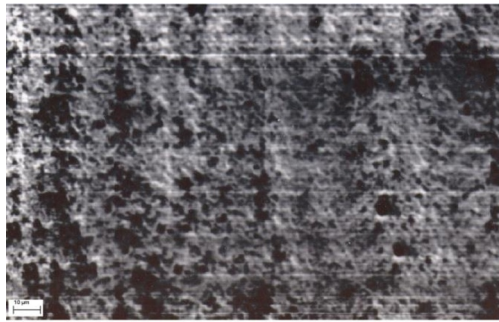
Lines 1,3,5 - nitriding: 580°C , 3 hours; lines 2,4,6 - nitriding at 580°C , 3 hours and subsequent oxidation in vapors of 5% aqueous solution of HEDP at 580°C , 2 hours.

Fig. 7. Distribution of elements in nitride (lines 1, 3, 5) and nitride-oxide (lines 2, 4, 6) layers on hardened steel 40X.

On the surface of the nitride layer during a long oxidation process, the concentration of carbon from the steel matrix (Fig. 7, line 5) on the surface increases (Fig. 7, line 6) by reducing the carbon content in the nitride layer, as a result of which the probability of formation of iron carbide on the surface increases. The surface zone will generally consist of a mixture of iron oxides, carbides, and nitrocarbides (dark components) (Fig. 8).

After nitriding, oxygen is detected in the nitride layer (Fig. 7, line 3). The reasons for the presence of oxygen in the saturating atmosphere during the nitriding period can be different; during nitro-oxidation, the main sources of oxygen are the presence of water vapor in the composition of ammonia and oxides on the walls of the furnace formed in the previous nitro-oxidation process at the second stage of oxidation.

At the initial stage of the nitriding process, preliminary oxidation in chamber and shaft furnaces can occur at the stage of heating parts. In this case, oxidation is possible without a specially dosed supply of oxygen-containing gases since residual oxygen content in the furnace atmosphere is usually sufficient to form a thin oxide layer on the surface.



Nitrooxidation: nitriding -580 °C, 3 hours; oxidation – 580 °C, 1 hour in vapors of 5 % aqueous solution of HEDP at 580 °C, 2 hours.

Fig. 8. Morphology of surface of nitride–oxide layer on steel 40X.

It is known that the presence of oxygen in a saturating medium in a certain small amount intensifies the process of gas nitriding and the formation of a nitride layer in the presence of oxygen in a saturating medium with obtaining a layer of optimal phase composition and structure can be predicted based on thermodynamic analysis. By performing thermodynamic analysis for the liquid and gas oxynitriding processes, the corresponding calculation diagrams were constructed for choosing the modes of processing steels and alloys [6].

For gas processes, the phase composition of the formed diffusion layer is predicted depending on the composition of the atmosphere and the temperature of the process when calculating the nitrogen and oxygen potentials of the atmosphere. In particular, during nitriding in ammonia with oxygen additives, the conditional nitrogen potential of the atmosphere is determined by the following expression [6]:

$$\pi_N = \frac{\lambda \cdot (1 - \alpha)[0.5(1 + \lambda) + \alpha\lambda]^{1/2}}{[3 / 2\alpha\lambda - 0.5(1 - \lambda)]} \quad (1)$$

where α is the degree of dissociation of ammonia; λ - is proportion of ammonia mixed with oxygen.

The phase equilibria calculated following equation (1) in the "Fe-N-O" system during oxynitriding in ammonia with oxygen additives are shown in Fig. 9. With an increase in the degree of dissociation of ammonia and the temperature of the process, the oxidative capacity of the atmosphere decreases.

As follows from the generalized diagram (Fig. 9), with the degree of ammonia dissociation $\alpha=30\%$ and the oxygen content – 5 %, no oxide is formed on the surface of the parts, but π_N and the process speed increase. With an increase in the oxygen concentration to 10 %, forming Fe_3O_4 oxide is possible at 500–520 °C and $\alpha = 45\text{--}50\%$.

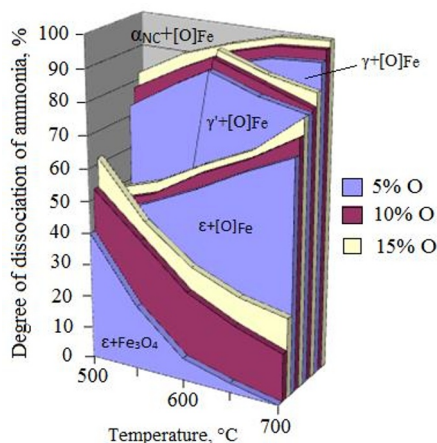


Fig. 9. Phase equilibria in "Fe-N-O" system during oxynitriding in mixture of ammonia and oxygen.

The amount of introduced oxygen (oxygen-containing agent) is determined by the oxygen potential of the atmosphere $\pi_o = P_{H_2O}^2/P_{H_2}^2$, at which the oxidation of iron does not yet occur. By changing the parameters of the atmosphere, it is possible, following the diagram (Fig. 6), to control the structure and phase composition of the layer by changing the ratio of nitride (carbonitride) phases in the nitride zone and forming an oxide film of Fe_3O_4 at the final stage of the process [22, 23].

In a mixture of ammonia and oxygen (4 liters of O_2 per 100 liters of NH_3), the nitriding rate is 2 times faster than conventional nitriding in ammonia. Introducing ~1 % oxygen into the ammonia-methane atmosphere also accelerates the formation of a layer under conditions of low-temperature nitrocarburizing (oxycarbonitriding) [24].

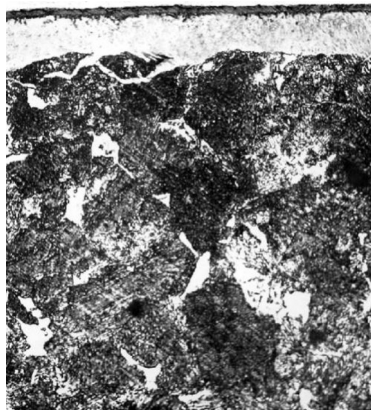
Released on the surface, oxygen, binding hydrogen, shifts the equilibrium of the ammonia dissociation reaction, increasing the nitrogen potential of the saturating medium. At the same time, it is necessary to take into account the Atmospheric potential does not give an estimate of the layer formation rate, is a thermodynamic quantity, and indicates the possibility of forming a layer of a given phase composition and a certain concentration of saturating elements.

A series of experiments were conducted to assess the corrosion resistance by obtaining a diffusion composite nitride-oxide coating (Fig. 10), forming a nitride layer with a stepwise change in ammonia dissociation at the first stage of nitriding. To obtain a nitride layer of various ratios of the nitride phase, the subsequent oxidation was carried out in water vapor and in the vapor of aqueous solutions of HEDP [25] and Trilon B complexes.

The structure of the surface layer consisted of Fe_3O_4 and a nitride layer, consisting of a composition of the nitride phase in various ratios; the composite coatings with the highest corrosion resistance to the corresponding processing modes are presented in Table 1.

The nitriding process was carried out at the first stage with a total duration of 3 hours: 2 hours with ammonia dissociation $\alpha=30-45\%$ in the stage and at the second stage 1 hour with dissociation $\alpha=45-60\%$. Subsequent oxidation was carried out at a temperature of 550 °C for 1 hour. During corrosion tests, at first (up to 400 hours of exposure), samples were examined daily, then once every three days. At the same time, the time of appearance of the first centers of corrosion of the base metal and the area of corrosion areas as a percentage of the entire estimated area were recorded (Table 1).

The results of corrosion tests showed that the corrosion resistance of the resulting nitride-oxide coating after oxidation significantly exceeds the corrosion resistance of the nitride layer not treated by oxidation. At the same time, along with the presence of an oxide layer consisting of Fe_3O_4 , the nitride layer, which undergoes a phase change during oxidation with the formation of an oxycarbonitride ϵ' -phase and an increase in the content of the γ' -phase, the corrosion resistance of the nitride-oxide layer is greatly increased under conditions of oxidation in water vapor with complexation additives.



X500

Nitrooxidation: nitriding $-580\text{ }^{\circ}\text{C}$, 3 hours; oxidation $-550\text{ }^{\circ}\text{C}$, 1 hour in vapors of 5 % aqueous solution of HEDP

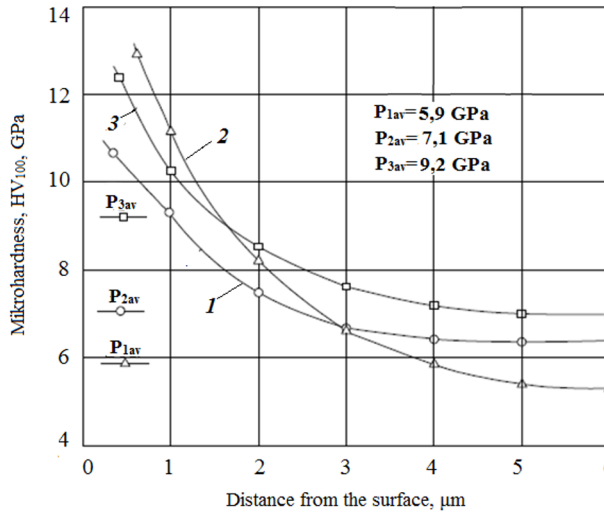
Fig. 10. Microstructure of diffusion nitride-oxide coating on annealed steel 40X after nitro-oxidation

Especially by increasing the content of the γ' -phase in the composition and the complete alloying of the ε' -phase carbonitride with oxygen to form the oxycarbonitride ε'' -phase in the process of oxidation in vapors of 5% aqueous solutions of Trilon B, the development of corrosion damage on the surface of the coatings for a long time is significantly reduced period.

Table 1. Corrosion resistance of nitride-oxide layer on 40X steel specimens after various treatment modes in 3% NaCl medium

Oxidizing atmosphere	Phase composition of the nitride-oxide layer	Time of appearance of the first centers of corrosion, hour	Corrosion area/duration of the test, (S_k/S_0)/hour
No oxidation	$\varepsilon, \varepsilon', \gamma'(30\%)$	52–74	30/336
Water vapor	$\varepsilon', \varepsilon'', \gamma'(50\%), \text{Fe}_3\text{O}_4$	412–480	5/552; 15/912; 18/960
Water vapor with the addition of 5% HEDF	$\varepsilon', \varepsilon'', \gamma'(75\%), \text{Fe}_3\text{O}_4$	912–960	0/552; 3/960; 5/1056
Water vapor with the addition of 5% Trilon B	$\varepsilon'', \gamma'(80\%), \text{Fe}_3\text{O}_4$	912–960	0/552; 1/960; 3/1056

Fig.11 shows the change and average values of the microhardness of the nitride and nitride-oxide layer along the depth of the surface of annealed steel 40X, determined in the coating zone by extruding a diamond indenter onto the surface of the treated samples, which reflects the most accurate assessment of the surface microhardness in gradient structural-phase states of the surface layer.



Nitriding - 580 °C, 3 hours: 1-without oxidation; 2 - oxidation – 580 °C, 1 hour; 3-oxidation -550 °C, 1 hour

Fig. 11. Distribution of microhardness over surface layer depth on steel 40X

The microhardness of the surface after nitro-oxidation increases relative to the microhardness of the nitride layer obtained after nitriding, and the composition of the nitride-oxide layer formed after oxidation in water vapor with Trilon B additives has the highest microhardness values and reaches a value of 9.2 GPa. Such an increase in microhardness on the surface can be explained by phase transformations occurring in the nitride layer with the formation of low-nitrogen nitrides alloyed with oxygen and carbon ϵ -oxycarbonitride ($\text{Fe}_3(\text{NCO})$) and γ' -nitride, while the formation of oxygen-doped γ' -nitride $\text{Fe}_4(\text{NO})$ is possible and simultaneous doping with oxygen and carbon $\text{Fe}_4(\text{NCO})$.

In diffusion nitride-oxide coatings, especially the presence of a thin oxide layer consisting of almost one magnetite Fe_3O_4 with a hardness of 4.2–4.7 GPa creates on the surface of the modified nitride layer with a hardness of up to 9.2 GPa, the largest positive gradient of the property with the provision of external friction conditions at sliding.

4 Conclusions

During gas nitriding of carbon steels, depending on the degree of dissociation of the ammonia atmosphere in the nitride layer, decarburization of steel occurs to varying degrees, which, due to limited solubility in nitrides, is released in the form of carbides and nitrocarbides in the nitride layer.

In the process of nitriding at high degrees of ammonia dissociation, carbides and nitrocarbides occupy mainly surface micropores, and with a stepwise increase in ammonia dissociation during the saturation period, they disperse throughout the nitride layer in the form of fine particles, which makes it possible to attract carbide-forming carbon to the mutual diffusion of isothermal expos

Further oxidation of the nitride layer in water vapor, which is formed with a stepwise increase in the degree of ammonia dissociation, forms a gradient of the structure of the oxide-nitride layer, each structure of which can form different gradient phases, depending on the technological parameters of saturation, both during and during oxidation in water vapor.

A stable gradient of structural-phase states during nitro-oxidation is achieved in nitriding at the first stage with an increase in the degree of ammonia dissociation during the saturation period below the eutectoid temperature for the "Fe–N" system and oxidation in water vapor with the addition of complexation agents at below eutectoid temperatures for the "Fe–O" system. In this case, during the oxidation process, the nitride layer undergoes phase changes by forming a thin oxide film on the surface consisting of Fe_3O_4 .

Residual oxygen in the furnace atmosphere favorably affects the internal phase transformations in the nitride layer during the oxidation period. Interdiffusion of carbon forms carbonitrides, while carbon and

oxygen form oxycarbonitrides. In the boundary zone of the nitride layer in the zone of internal formation, the growth of the nitride layer occurs in the pearlite areas with the formation of a mixture of ε' -carbonitride, γ' -phase, iron carbide, and the ferrite in the zone of internal nitriding occurs the precipitation of the γ' -phase, and also in the grains of residual austenite can be formed $\text{Fe}_4(\text{NC})$.

The corrosion resistance of the nitride-oxide coating depends on the gradient of the structural-phase states of the diffusion nitride oxide layer; the nitride-oxide coating has the highest corrosion resistance, consisting of a surface oxide layer of Fe_3O_4 and a nitride sublayer with modified nitride compositions - a mixture of low-nitrogen ε'' -oxycarbonitride and with the largest amount of γ' -nitride.

A thin oxide layer is not only responsible for increasing the corrosion resistance but also creates a positive surface property gradient, which is important for providing external friction conditions.

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