



ISSN: 2350-0328

**International Journal of Advanced Research in Science,
Engineering and Technology**

Vol. 7, Issue 11, November 2020

Properties of Surface Diffusion Nitride-Oxide Layers on Low-Carbon Steels

Kholikul Karshievich Eshkabilov, Sherzod Alimardonovich Berdiev, Aziz Teshavaevich Kurbanov, Jahongir Shodmonkulovich Rabbimov

Candidate of Technical sciences, Associate Professor, Department of “Technological Machines and Equipment”, Faculty of Oil and Gas, Karshi Engineering and Economic Institute

Senior Lecturer, Department of “Technological machines and equipment”, Faculty of Oil and Gas, Karshi Engineering and Economic Institute

Scientific Applicant, Department of “Technological machines and equipment”, Faculty of Oil and Gas, Karshi Engineering and Economic Institute

2nd year Master’s Student, Department of “Technological machines and equipment”, Faculty of Oil and Gas, Karshi Engineering and Economic Institute

ABSTRACT: The article describes the technology of hardening the surface by nitration of low-carbon steels and subsequent oxidation in water vapor. The kinetics of the formation of diffusion composite nitride-oxide coatings were studied, and technological methods of obtaining the nitride layer in the oxidation of the nitride layer in the first and second stages of nitrogen saturation in the atmosphere of water vapor were studied.

The modes of obtaining a carbonitride layer in ferrite and pearlite areas of low-carbon steel for further oxidation with the formation of an oxide layer due to denitrogenation of the nitride layer have been established. The corrosion properties and the intensity of running-in of the obtained nitride-oxide layer have been studied.

KEYWORDS: low carbon, nitriding, oxidizing, nitride, carbonitride, oxycarbonitride, porosity, denitrating, decarburization, corrosion resistance, running-in.

I. INTRODUCTION

Ensuring the required reliability and durability of machine parts and tools operating under conditions of friction and corrosion is carried out mainly through chemical-thermal treatment. The choice of the optimal method for chemical and thermal treatment of metal products depends on many factors related to both the specific properties of diffusion layers and the conditions of their operation, the expected technical and economic effects and environmental features. From this point of view, in this direction in the world mechanical engineering, preference is given to low-temperature nitriding processes (below the Ac1 transformation temperature) [1-3].

Due to the manufacturability of the process, the most widespread are the processes of gas nitriding and its varieties [3-5]. In all cases, during nitriding of steel below the temperature of the eutectoid transformation of the “Fe-N” system in various saturating media, predominant diffusion of nitrogen occurs.

II. MAIN PART

In works [6-9] devoted to the development of technological processes of low-temperature nitriding methods of steel products, which result in diffusion layers with the best tribological and anticorrosive properties, special attention is paid to establishing relationships between the structure, phase composition of the layers and their properties. Knowledge of these dependencies allows you to choose the right diffusion layers in terms of the expected performance properties.

Below the temperature of the eutectoid transformation of the “Fe-N” system, due to the low temperatures of the process and the absence of phase transformations in steel, no significant changes in the shape and size of the parts to be



hardened are observed, no mechanical processing is required, and therefore the process is a finishing surface treatment. It should be noted that low-temperature processes are more economical than high-temperature ones in terms of energy consumption and in many cases, this factor should determine their choice.

Nitriding is a multipurpose process by which hardening is achieved through the formation of a nitrided layer consisting of a surface nitride zone and a diffusion sublayer - an internal nitriding zone (IDA) [2-6]. The main advantage of the gas nitriding process is the ability to control the structure and phase composition of the resulting surface diffusion nitrided compositions.

To study the physicochemical and physicomachanical properties of the composite nitride - oxide layer obtained on low-carbon structural steels, the processes of combining gas nitriding in dissociated ammonia, followed by oxidation of the nitride layer in water vapor, were studied. In this case, on the samples at the first stage of saturation, a nitride layer of different phase composition was obtained, which at the second stage of the process were subjected to oxidation in water vapor.

The surface nitride zone of various phase composition and SBA on samples of low-carbon and low-alloy structural steels were obtained in the range of ammonia dissociation $\alpha = 30-85\%$ at the first stage of saturation. The duration of the first stage was 0.5-3 hours, and oxidation in water vapor was carried out in the time interval $\tau = 0.5-1.0$ hours. The saturation temperatures were chosen below the temperature of the eutectoid transformation of the "Fe-N" system.

The microstructure of the diffusion layer was investigated from cross-sectional sections on a Neophot-21 microscope at a magnification of up to x1000.

The phase composition of oxide layers obtained at different oxidation temperatures on pre-nitrided samples using filtered cobalt and iron K_{α} radiation was studied using the X-ray method on the Dron-3 setup. Tests for the general corrosion resistance of the diffusion layers were carried out by holding in a 3% aqueous solution of sodium chloride.

The running-in properties of the coatings were investigated on a SMTs-2 friction machine according to the "roller-block" scheme under dry friction conditions.

The surface morphology and microstructure of the nitride-oxide layer were studied using a JEOL JSM-25 scanning electron microscope and a SEM-EVO MA 10 scanning microscope (Carl Zeiss, Germany), the structures' compositions were determined using an energy-dispersed elemental analyzer of the Energy- Dispersive X-ray spectrometer (EDS-Oxford Instrument).

III. RESULTS AND DISCUSSION

In low-temperature gas nitriding, the best corrosion and wear-resistant properties of the nitride layer are ensured by obtaining sufficiently dense nitride layers with the minimum possible number of pores. In this case, it is necessary to ensure the condition of external friction by achieving a guaranteed positive gradient of the properties of mutually contacting surfaces.

As a result of the combined nitriding technology processes followed by oxidation, the nitride layer at the first saturation stage in dissociated ammonia with a minimum number of pores can be obtained only in intervals below the eutectoid temperature for the "Fe-N" phase diagram (below 591 ° C) (Fig. 1, a). An increase in the saturation temperature above the eutectoid one, although it leads to an increase in the thickness of the resulting nitride layer, however, its porosity significantly increases and the hardness of the nitride layer itself decreases (Fig. 1, b).

Carrying out the nitriding process with a stepwise change in the nitrogen potential in the furnace atmosphere allows a slight increase in the thickness of a denser nitride layer. Therefore, the nitriding process of low-carbon steels at the first stage of saturation must be carried out first at high nitrogen potentials of the atmosphere (in the range of $\alpha = 30-45\%$) with a further decrease in the value of the nitrogen potential of the atmosphere (transition to the range of $\alpha = 70-85\%$),

i.e. a two-step change in the nitrogen potential in the process of saturation in the medium of dissociated ammonia (Fig. 1, c).

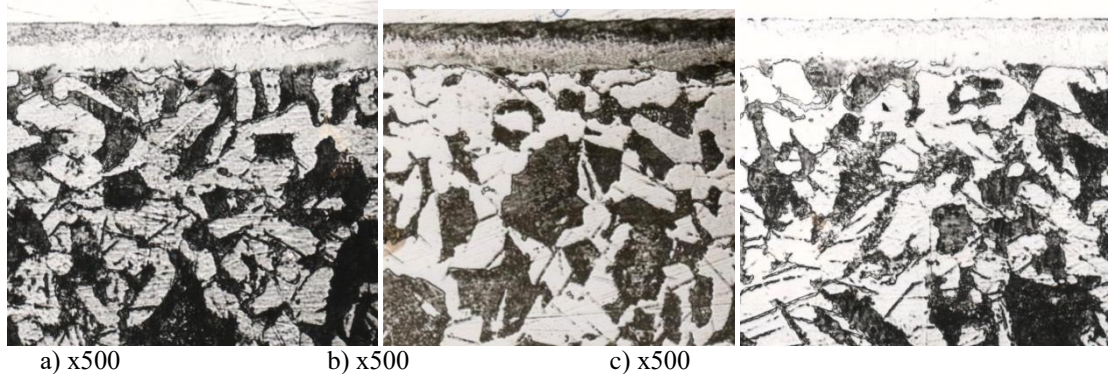


Figure: 1. Microstructure of nitrided layers after various modes of processing steel 20 a - nitriding at 580 0C; b - nitriding at 620 0C; c - nitriding at 580° C with a two-stage change in the nitrogen potential.

At the first stage of saturation with nitrogen, the lower temperature limit can be based on the conditions for obtaining a nitride layer of the required thickness. In order to achieve the required corrosion properties in practice, the thickness of the nitride layer is generally obtained more than 10 μm , having a non-porous structure. The production of developed, non-porous nitride layers is ensured in the temperature range 550-590° C and 3-5 hours. The thickness of the nitride layer in the dissociated ammonia obtained under such saturation conditions is in the range of 10-25 microns, the maximum value of the thickness is reached with a stepwise change in the nitrogen potential during saturation.

From a technological point of view, in the process of nitriding, obtaining nitride layers in which pores would be completely absent is practically impracticable. Therefore, the subsequent oxidation of the nitride layer contributes to a decrease in porosity and other defects in the nitride layer arising in the process of saturation with nitrogen and in the process of cooling the processed products.

During oxidation of the nitride layer, first, denitrogenation occurs on the surface with the formation of Fe_α which, depending on the oxidation temperature at above the eutectoid temperature for the “Fe-O” system (570 0C), FeO oxide is formed and below the eutectoid temperature, Fe_3O_4 oxide is formed. During the oxidation process, a thin oxide layer is formed on the porous surface of the nitride layer, microporosity and defects in the nitride layer are filled with oxides, which give an additional increase in the surface properties of the nitride layer (Fig. 2, a).

With the formation of an oxide film on the surface of the nitride layer, the growth of the thickness of the oxide film naturally slows down, and the oxidation reaction can even stop or slow down, the kinetics of which is determined by diffusion processes through the oxidized layer of metal and oxygen ions. Therefore, the technological modes of the nitride layer oxidation process depend on the composition and structure of steels, the kinetics of surface denitrogenation, the structural and phase composition of the nitride layer, the growth of the oxide film thickness, etc.

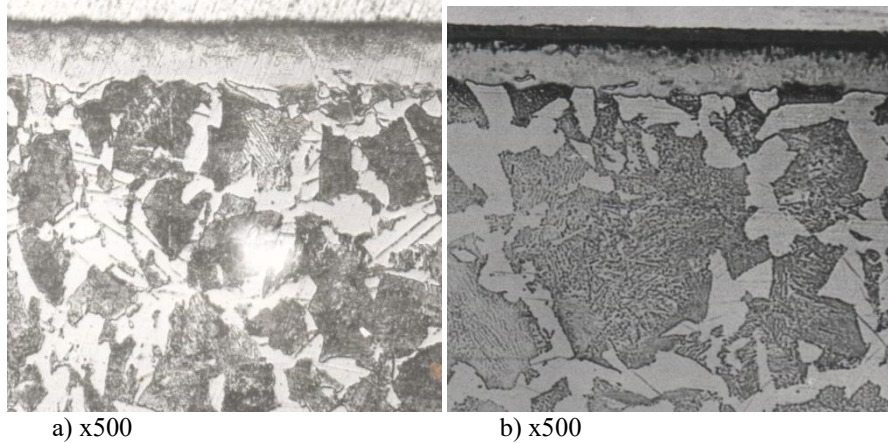


Figure: 2. Microstructure of nitride - oxide layers on steel 20. Nitriding at 580 ° C; a - oxidation at 550 ° C for 0.5 hour; c - oxidation at 550 ° C for 1.0 hour.

According to the regularities of nitrogen diffusion in steel during nitriding, a nitride layer is formed on the surface, in which the ϵ -phase with a high nitrogen content is located first, then the γ' -phase with a low nitrogen content, followed by a solid solution of nitrogen in α -Fe (internal nitriding zone Fe_α). Therefore, during the oxidation of the nitride layer in superheated steam, only the surface part of the nitride layer undergoes denitrogenation [11, 12]. In this case, due to the high-nitrogen nitrides, the formation of a lower nitride zone occurs, the thickness of which begins to grow at the beginning of oxidation. Subsequently, the thickness of the nitride zone decreases due to the dissociation of iron nitrides and the diffusion of nitrogen simultaneously into the furnace atmosphere and into the inner zones of the nitrified layer (Fig. 2, b)

Of particular importance is the diffusion of oxygen into the nitride layer and the formation of oxygen compounds with iron. At an oxidation temperature of the nitride layer equal to above the eutectoid temperature for the Fe-O system, upon rapid cooling of the samples, FeO oxide is detected by X-ray diffraction, and upon slow cooling it decomposes according to the formula: $FeO \rightarrow Fe_3O_4 + Fe_\alpha$. Fe_α formed during the decomposition between the oxide and nitride layers sharply affects the adhesion strength of the oxide layer to the nitride layer, due to the presence of Fe_α , cracking of the oxide layer occurs, and with the accumulation of matrix carbon in this zone, peeling of the oxide layer can occur (Fig. 3, a). At oxidation below the eutectoid temperature for the "Fe-O" system, no defects are found on the surface of the oxide layer (Fig. 3, b).

When implementing the technology for oxidizing the nitride layer under industrial conditions in order to obtain stable results of hardening, the oxidation process in superheated steam must be carried out in the temperature range up to 550 ° C, the phase composition of the oxide layer consists mainly of the oxides Fe_3O_4 and Fe_2O_3 . Fe_2O_3 oxide forms upon cooling on the surface of Fe_3O_4 , which leaves when the surface is slightly abraded.

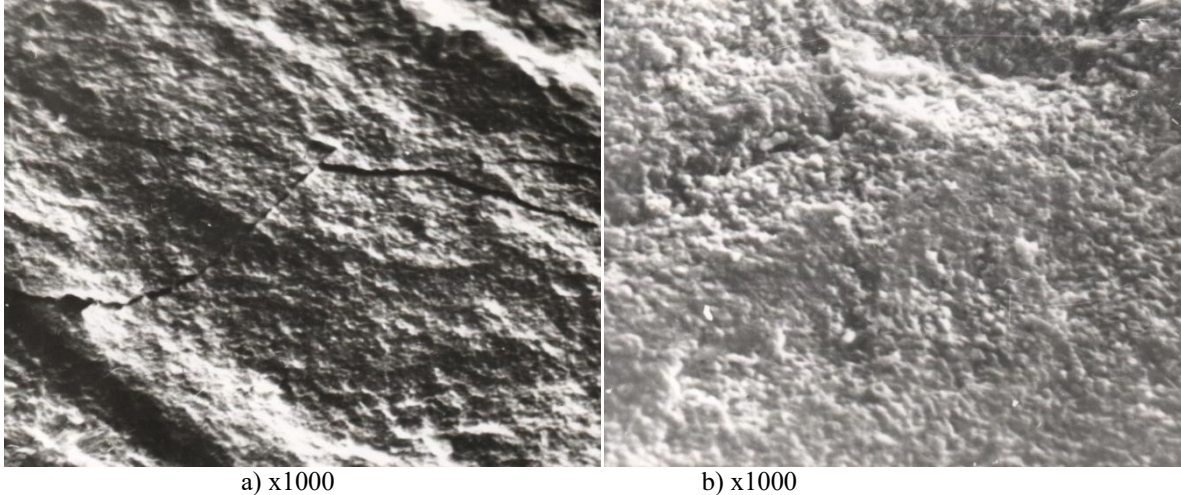


Figure: 3. Surface morphology of treated steel specimens 20, Nitriding at 580 ° C; a - oxidation at 580 ° C for 1.0 hour; c - oxidation at 550 ° C for 1.0 hour

When the nitride layer is oxidized, the structure and phase composition in the nitride layer change. The formation of the phase composition of the nitride layer depends on the initial surface structure and the carbon content in the steel matrix. Diffusion of nitrogen during nitriding in ferrite and pearlite occurs at different speeds, iron nitrides are formed in the ferrite part according to the “Fe-N” system, and in the pearlite part according to the “Fe-C-N” system.

During nitriding, as pearlite is saturated with nitrogen, the pearlite decarburizes, part of the carbon leaves in two directions: diffusion of carbon into ferrite occurs together with nitrogen from the atmosphere and decarburization. Part of the carbon in pearlite participates in the formation of a carbonitride layer, and at the same time, due to the diffusion of carbon from the pearlite part and nitrogen from the atmosphere in the ferrite part, a phase composition of a carbonitride character is also formed. In general, the surface diffusion nitride layer has a carbonitride character - Fe (N, C) due to the presence of carbon in the steel matrix (Fig. 4, a).

During oxidation in superheated steam of low-carbon steels, the nitride layer is mainly denitrogenated with the formation of iron oxides, further growth of the oxide layer due to the density of the oxide slows down and oxygen diffusion into the carbonitride layer predominantly occurs with the formation of a diffusion layer of an oxycarbonitride nature - Fe (N,C,O). This circumstance can be confirmed especially by the formation of a nitride - oxide layer under the same processing conditions for annealed steel 45 with large structures of ferrite and pearlite (Fig. 4, b).

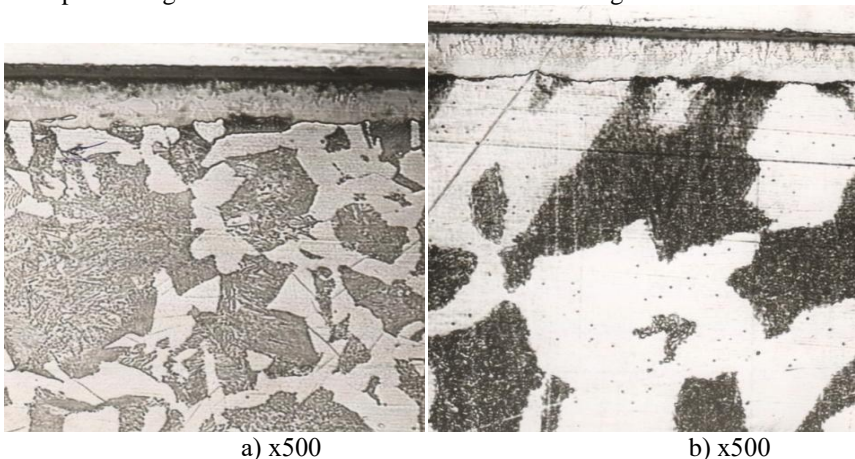


Figure: 4. Microstructure of treated nitride - oxide layers: nitriding at 580 ° C for 3 hours and oxidation at 550 ° C for 1.0 hour. a - steel 20; b - steel 45 after annealing

Comparative corrosion tests of diffusion layers of different phase composition were carried out, the results of which are shown in Table 1.

According to the results of the comparative corrosion tests, the best corrosion properties during the time of the first corrosion foci (300 hours) and the growth of the corrosion area depending on the test duration (15% of the corrosion area during 400 test hours) showed an oxide layer with an oxycarbonitride sublayer. The oxycarbonitride layer was tested with the removal of the surface oxide layer, which showed additional protective properties of the oxide layer on the nitride surface.

Table 1
Corrosion resistance of diffusion layers on steel 20 after various modes of nitriding treatment with subsequent oxidation in a medium of 3% NaCl

Processing mode	Phase composition of the layer	Time of appearance of the first foci of corrosion, hour	Corrosion area / test duration, (Sk / So) / hour
Oxidation: $T_{ok}=550^{\circ}C$; $\tau_{ok}=0,5$ hour	α, Fe_3O_4, Fe_2O_3	6	90/144
Nitriding: $T_{az} = 580^{\circ}C$; $\tau_{az}= 3$ hour	$Fe(NC), Fe_2O_3$	18	60/400
Nitriding: $T_{az} = 580^{\circ}C$; $\tau_{az} = 3$ hour; Oxidation: $T_{ok}=550^{\circ}C$; $\tau_{ok}=0,5$ hour.	$Fe(NC), Fe_3O_4$	64	39/400
Nitriding: $T_{az} = 580^{\circ}C$; $\tau_{az} = 3$ hour; Oxidation: $T_{ok}=550^{\circ}C$; $\tau_{ok}=1,0$ hour	$Fe(NCO), Fe_3O_4$	300	15/400
Nitriding : $T_{az} = 580^{\circ}C$; $\tau_{az} = 3$ hour; Oxidation: $T_{ok}=550^{\circ}C$; $\tau_{ok}=1,0$ hour	$Fe(NCO)$ With removal Fe_3O_4	274	18/400

It is known that to ensure the conditions of external friction, it is necessary to ensure a positive gradient of the properties of rubbing surfaces. Therefore, from the point of view of achieving an increase in wear resistance, it is very important to study the running-in of rubbing surfaces, since during this period there is an increase in the actual contact area, which leads to a decrease in specific pressures in the contact zone [13].

The diffusion layers obtained on the surface of annealed steel 45, consisting of a surface oxide film of Fe_3O_4 with a thickness of 1-3 microns, with a lower hardness than an oxycarbonitride sublayer with a higher hardness, best provides a favorable positive gradient of the properties of contacting friction surfaces. Thus, the oxide layer has surface plastic properties, and a uniform thin oxide layer has a better adhesive strength to the nitride one. Therefore, they can be used to control the running-in process of rubbing surfaces, both in sliding friction pairs and in rolling friction pairs.

The burn-in intensity factor (K) of the nitride-oxide layer obtained under optimal processing conditions in the load range from 50 to 300 N shows that in all cases the oxycarbonitride layer provides a higher value of the burn-in intensity factor (K) with better burn-in than the nitride layer itself. layer obtained by the classical nitriding regime (Table 2).

Table 2
The value of the intensity factor of running-in layers obtained by various technological modes of processing on steel 45

Processing mode	Phase composition of the layer	Nitride layer thickness, microns	Oxide layer thickness μm	Running-in coefficient K
Nitriding: $T_{az} = 580^{\circ}C$; $\tau_{az} = 3$ hour	$Fe(NC), Fe_2O_3$	20-22	-	1,15-1,30
Nitriding: $T_{az} = 580^{\circ}C$; $\tau_{az} = 3$ hour; Oxidation: $T_{ok}=550^{\circ}C$; $\tau_{ok}=0,5$ hour.	$Fe(NC), Fe_3O_4$	23-25	1-3	3,70-3,85

Nitriding: $T_{az} = 580^{\circ}\text{C}$; $\tau_{az} = 3$ hour; Oxidation: $T_{ok} = 550^{\circ}\text{C}$; $\tau_{ok} = 1,0$ hour	$\text{Fe}(\text{NCO}), \text{Fe}_3\text{O}_4$	28-30	1-3	4,55-4,70
Nitriding: $T_{az} = 580^{\circ}\text{C}$; $\tau_{az} = 3$ hour; Oxidation: $T_{ok} = 550^{\circ}\text{C}$; $\tau_{ok} = 1,0$ hour	$\text{Fe}(\text{NCO})$ with removal Fe_3O_4	28-30	-	2,10-2,45

In general, the combination of the technology of gas nitriding in an ammonia atmosphere at a temperature of 550-580 ° C followed by oxidation in water vapor at a temperature of 550-560 ° C for 0.5-1.0 hours allows obtaining diffusion composite surface layers on products made of low-carbon structural steels. In this case, it is possible to control the structure and phase composition of the composite diffusion layer to obtain a nitride, carbonitride or oxycarbonitride character with a thin surface oxide film, the thickness of which varies within 1-3 microns. The resulting composite layer possesses the required corrosion resistance and wear, resistance at low and medium contact loads in conditions of dry and boundary sliding friction, operating in corrosive working environments.

IV. CONCLUSION

During gas nitriding in dissociated ammonia followed by oxidation in water vapor, a carbonitride layer is formed on the surface of products made of low-carbon steels at the first stage of nitriding in a ferrite and pearlite structure. The formation of a layer of carbonitride nature in the ferrite structure occurs due to the simultaneous diffusion: nitrogen from the atmosphere and carbon from the pearlite structure from the steel matrix.

During oxidation, the formed carbonitride layer undergoes denitrogenation on the surface and oxidation of the denitrogenized area with oxygen of the superheated vapor with the formation of a surface oxide film.

The nitride zone with high surface characteristics consists of the oxycarbonitride phase - Fe (N, C, O). The most corrosion-resistant is the oxycarbonitride phase mixed with lower nitride phases.

The formation of the oxycarbonitride and oxide layer of the optimal phase composition and structure is achieved by regulating the temperature and time regimes of each stage of the process. Corrosion resistance and wear resistance of products made of low-carbon steels is achieved by the formation of a diffusion layer with an optimal phase composition and structure, with the formation of an oxycarbonitride layer with a surface oxide film consisting of magnetite (Fe_3O_4) with a thickness of 1 to 3 μm .

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