

NITRIDING IN A LOW-TEMPERATURE GAS ENVIRONMENT AND OXIDATION OF THE FORMED NITRIDE LAYER IN WATER VAPOR

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Abstract

The article examines the structural and phase changes in surface diffusion nitride-oxide coatings obtained during nitriding in a gas environment followed by oxidation of ferrite-pearlite steels in water vapor, as well as the influence of phase changes on the corrosion properties.

Keywords: Ferrite, pearlite, nitriding, oxidation, diffusion coating, nitride layer, corrosion resistance.

Introduction

During nitriding of iron and its alloys in an environment containing ammonia at the saturation temperature of the eutectoid according to the "iron-nitrogen" phase diagram, the surface nitride zone consists of successive layers:

The formation of the ϵ' -phase occurs only during nitriding of steel and alloys in the presence of carbon in their matrix and has a carbonitride character. Therefore, noticeable formation of this type of nitride is characteristic only during nitriding of carbon steel and alloys.

Methods

In the first stage of nitrooxidation for oxidation in water vapor, the processes of obtaining a nitride layer by nitration in ammonia were studied. As mentioned above, the pre-eutectoid and eutectoid temperature ranges were studied for the "iron-nitrogen" system. The microstructure of the nitride layers obtained after nitriding at a temperature of 620°C oxides FeO Fe₂O₃, Fe₃O₄, and at an oxidation temperature of 550°C the oxide layer consists of one Fe₃O₄.

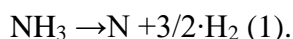
Fig. 5.

At the nitriding temperature above the eutectoid temperature (at 620 °C), a columnar structure of the surface zone is observed in the nitrogen layer, its large crystals have a value equal to the thickness of the ϵ -phase.[1] A small number of pores and cracks are noted between the crystals, the boundaries between the crystals are very open. ξ - and ϵ -phase layers have a lot of pores, the walls of which are oxidized (Fe₂O₃) upon cooling.

Results and its Discussion

The ability to predict the structure and properties of the nitrided layer on the surface of structural and carbon steels is of great importance for optimizing the process technology and subsequent processing of processed products.

Under certain thermodynamic conditions (temperature, pressure), ammonia dissociates in accordance with the reaction:



During the saturation process, a certain nitrogen potential is formed and during the process, the nitrogen potential equilibrium occurs. According to the relation (1), the resulting atomic nitrogen diffuses into the metal surface forming metal nitrides FeN.

To estimate the ratio of the partial pressure of ammonia to hydrogen, the equilibrium constants (K_a) can be used:

$$K_a = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}} \cdot \frac{1}{a_N} \quad (2),$$

where: P_{NH_3} - partial pressure of ammonia;

$P_{\text{H}_2}^{3/2}$ - partial pressure of hydrogen;

a_N - nitrogen activity or nitrogen potential.

During nitriding, a solid solution of nitrogen is formed in the $\alpha\text{-Fe}$, γ' and ε - phases. At constant temperature and pressure, the equilibrium constant will be constant, so equation (2) can be written as follows:

$$a_N = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}} \quad (3).$$

To ensure the diffusion of nitrogen into the material, it is necessary that the nitrogen potential of the saturating medium be greater than the nitrogen content in the metal:

$$a_N^{\text{FC}} \succ a_N^{\text{Me}} \quad (4).$$

Equation (4) characterizes the initial stage of diffusion, since with the formation of the nitride layer (γ' and ε - phases), the value of the nitrogen potential must satisfy the condition:

$$a_N^{\text{FC}} > a_N^{\gamma'} > a_N^{\varepsilon} \quad (5).$$

In short-term nitrooxidation processes, the nitriding process first occurs with the formation of a nitride layer.

In all cases, the formation of the nitride layer and the internal nitriding zone in pure iron occurs in accordance with the "Fe-N" diagram.

In iron-based alloys, the formation of the diffusion layer is accompanied by counter-diffusion of carbon in the opposite direction, depending on the amount of dissolved carbon in the α -iron. This can be characterized by the following relationship:

$$\mu_C^{\text{FC}} < \mu_C^{\text{Me}} \quad (6).$$

Only when carbon-containing components are added to the atmosphere does the ratio (6) become more complicated.

When the nitride layer is oxidized, the ratio of partial pressures of $\text{NH}_3:\text{H}_2$ changes. As a result, the thickness of the low-nitrogen nitride layer and the internal nitriding zone increase during oxidation. [1]

To develop a mathematical model and theoretical foundations for the technology of nitrooxidation of low-alloy carbon steel, the dependences of the composition and structure of the nitrided and oxide layer on the chemical composition of steels and technological parameters of the process were studied. Technical iron was used as a model alloy. Industrial steels 40X, P6M5 and steel 45 were also studied.

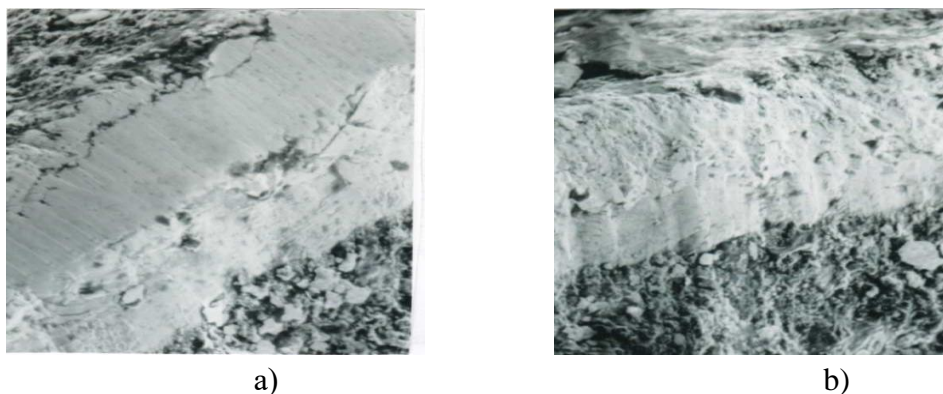


Fig. 1. Microstructure of the nitrided layer on steel 45 (a) and steel 40X (b)
Processing mode: Nitriding - 620 °C, 3 hours.

After saturation above the eutectoid temperature for the Fe-N system, a nitride zone with clearly defined columnarity is observed in the nitrided layer.

This zone consists of large crystals with wide boundaries between them and a large number of pores and cracks (Fig. 1, a and b). Such a layer structure excludes the further formation of a uniform oxide film. After nitriding at temperatures below the eutectoid (591°C), the layers have a smaller thickness, but a uniform structure.

There is no blockiness, the porosity of the layer is unnoticeable, and the pores themselves are small, rounded and isolated (Fig. 2). The addition of oxygen-containing components in small quantities to the composition of the saturating medium during oxidation, in particular complexones, has a beneficial effect on the formation of a dense surface oxide layer and the denitrification process during oxidation of the nitride layer is sharply reduced (Fig. 2, b).

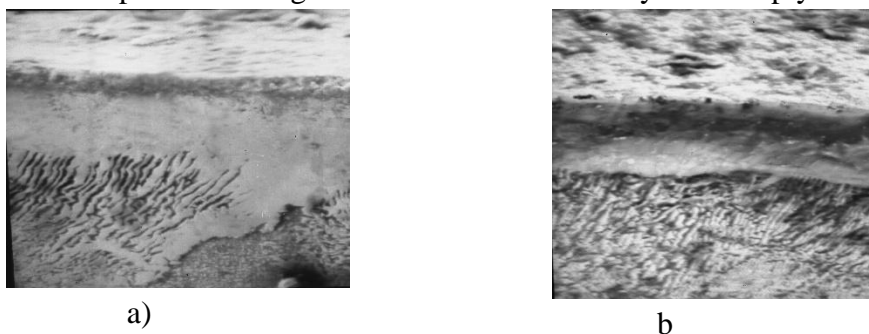


Fig. 2. Microstructure of the nitrooxidized layer on steel 45.

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% OEDF.

The results of the data obtained on the study of the influence of the degree of ammonia dissociation on the thickness and composition of the diffusion layer at a sub-eutectoid temperature (580°C) show that the formation of a developed zone of high-nitrogen nitride (ϵ -phase) with a significant total layer thickness is characteristic of processes with a degree of ammonia dissociation $\alpha < 30\%$ (Fig. 3, lines 2 and 3). [2]

However, this increases the porosity of the nitride layer.

With ammonia dissociation degree $\alpha > 50\%$, the thickness of the nitride zone and the amount of ϵ -phase on the surface of the layer decrease (Fig. 3).

The formation of the ϵ' -phase occurs only during nitriding of steel and alloys in the presence of carbon in their matrix and has a carbonitride character. Therefore, noticeable formation of this type of nitride is characteristic only during nitriding of carbon steel and alloys.

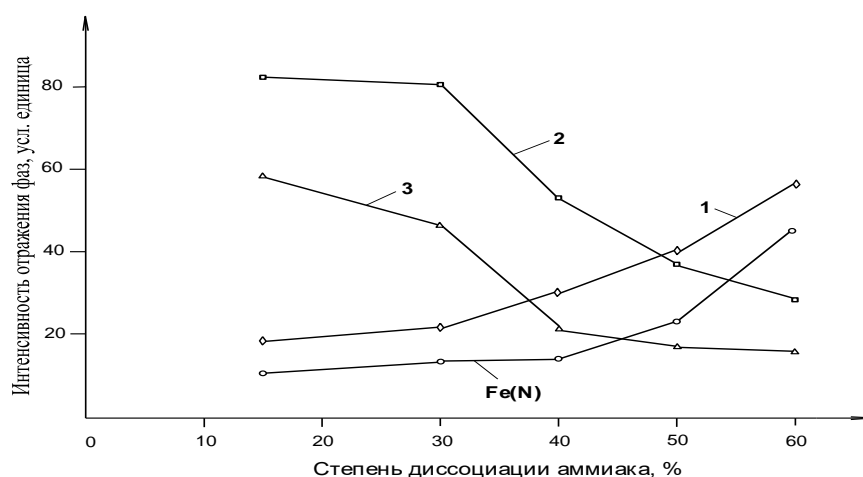


Fig. 3. Dependence of the intensity of phase lines on the degree of ammonia dissociation. Nitriding in an ammonia environment at a temperature of 580°C for 3 hours. 1 - γ' -phase (200); 2 - ϵ -phase (110) and 3 - ϵ' -phase (101).

Steel 40X, which has a martensitic structure, was studied as a structural steel. The samples were processed in an atmosphere of pure ammonia, with a degree of dissociation of $\alpha = 40 \dots 60\%$, at a temperature of 620°C – above the eutectoid temperature for the “Fe-N” system (option I), and some of the samples, without removing them from the furnace, were subjected to oxidation in water vapor for 1 hour at the same temperature (option II). The results of the study are shown in Fig. 4.

During oxidation, due to oxygen diffusion, denitrification and decarburization occur simultaneously in the lower nitride zone. A layer of oxycarbonitride character is formed on the surface (Fig. 2).

The nitride layer obtained at a higher eutectoid temperature (above 590°C) has a columnar structure and is also microporous. During the cooling period of the sample, the nitride layer is

oxidized from atmospheric oxygen, which is evidenced by the presence of oxygen after nitriding.

In order to obtain a complete picture of the change in the nitride layer during oxidation, samples of 40X steel were nitrided at a temperature of 580°C for 3 hours, oxidized at a temperature of 550°C below the eutectoid temperature for the “Fe-O” system for 1 and 2.5 hours. The results of the study are shown in Fig. 5.

It is worth noting the extremum (maximum) of the oxygen distributions, which corresponds to the beginning of the presence of nitrogen in the nitride layer.

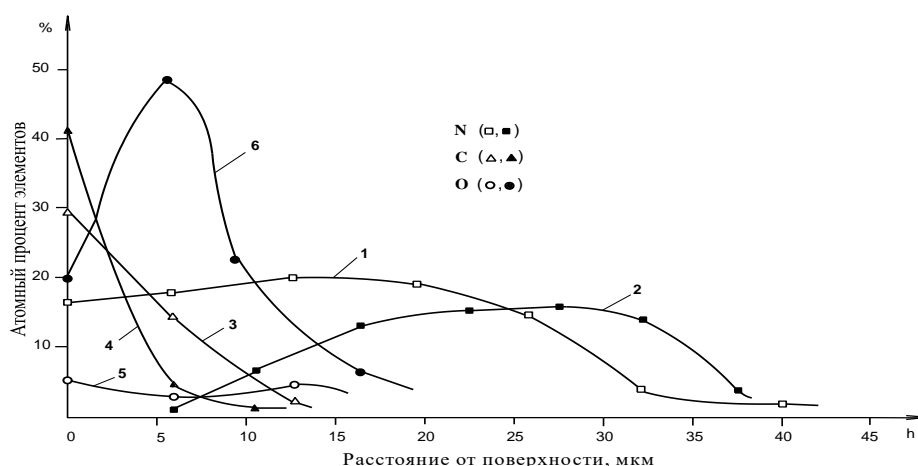


Fig. 4. Distribution of elements in the nitride layer after nitriding $t=620^{\circ}\text{C}$, $\tau=3\text{h}$. (lines 1,3,5) and nitriding followed by oxidation: $t=620^{\circ}\text{C}$, $\tau=3\text{h}$. (lines 2,4,6).

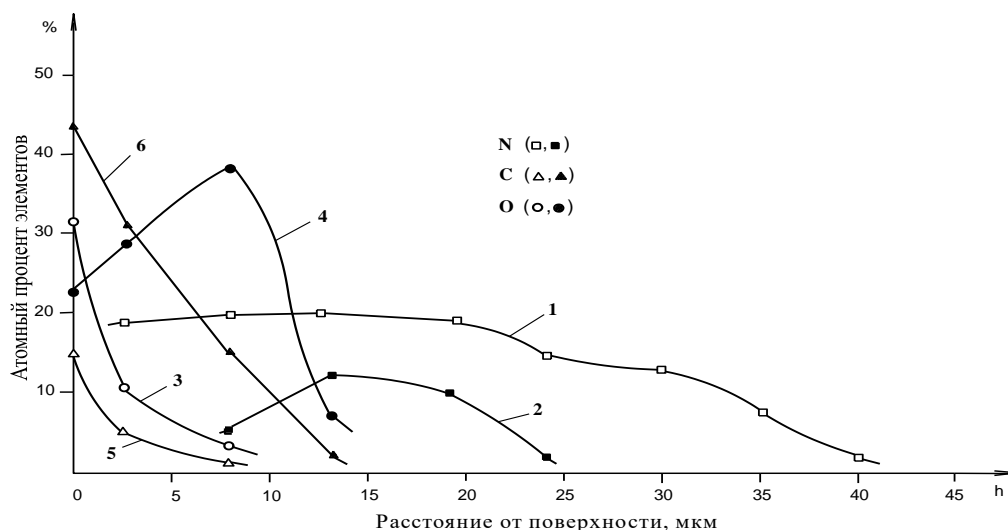


Fig. 5. Distribution of elements in the nitride layer after nitriding: $t=580^{\circ}\text{C}$, $\tau=3\text{h}$. and oxidation $t=550^{\circ}\text{C}$, $\tau=1\text{h}$. (lines 1,3,5) and $\tau=1\text{h}$. (lines 2,4,6).

As a result of the obtained data, it can be stated that under favorable conditions of oxidation of the nitride layer on carbon steels, it is possible to obtain controlled dense carbonitride,

oxycarbonitride layers, which have better physical, mechanical and physical-chemical properties than the nitride layer itself.

X-ray structural analysis of the processed samples was carried out, which confirmed the presence of a developed γ' -phase, ε' - a phase of carbonitride character, ε'' - a phase of oxycarbonitride character and at an oxidation temperature of 620°C oxides FeO Fe₂O₃, Fe₃O₄, and at an oxidation temperature of 550°C the oxide layer consists of one Fe₃O₄.

Thus, Auger spectral analysis, together with other research methods, allows us to obtain a picture of the layer-by-layer distribution of elements in nitroxidized steels. When studying the temperature and time dependencies of the formation of a hardening layer, based on its results it is possible to regulate the combined technology of nitroxidation during surface hardening of low-alloy carbon steels. [3]

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