
PHYSICAL METALLURGY. THERMAL AND THERMOCHEMICAL TREATMENT TECHNOLOGIES

Influence of Preliminary Oxidation on the Subsequent Nitriding

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Abstract—The interaction of oxidation atmospheres with metals and alloys and the influence of an oxide film on the formation of a hardened layer upon the subsequent nitriding are considered.

Keywords: controlled atmosphere, oxide film, energy barrier, dissociation, chemisorption

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INTRODUCTION

Methods of metal and alloy hardening upon interaction with gases found wide use in various areas of mechanical engineering and instrument-making industries. Gas media represent controlled atmospheres interacting with metals and alloys during thermal treatment. The properties of metals and metallic alloys are determined, to a great extent, by the content (even in small amounts) of atoms of such gases as oxygen, nitrogen, and carbon.

INTERACTION IN METAL–GAS SYSTEMS

Metal–gas systems are interesting, because solid interstitial solutions are formed in them and also because of the formation of specific intermediate phases, such as hydrides, oxides, and nitrides. In some cases, these compounds have unique mechanical and physicochemical properties and can be used as dispersed reinforcing elements in composite materials and as protection coatings on metallic structures. Chemical thermal treatment such as oxidation and nitriding is based on the interaction of metals with oxygen and nitrogen.

The reactions of metals with gases can be classified as follows: the reactions that do not lead to the formation of chemical compounds on the surface and the reactions that form such compounds. There are also reactions in which molecules of a chemical compound (for example, oxides) are formed on the surface and the subsequent diffusion (for example, of nitrogen) occurs through a thin film of this chemical compound.

The reactions with the formation of a chemical compound on the metal surface are most abundant. When a chemical compound layer is formed on the metal surface, the participants of the “metal and gas” reaction turn out to be separated from each other, and their further interaction occurs only in the case if at

least one of the substances diffuses through a separating film. This results in the situation where the reaction rate is governed, in many cases, by the mass transfer through the chemical compound film rather than the reaction itself. If the lattice of the chemical compound contains cationic defects, the metal ions diffuse to the film–gas phase interface and interact with the gas at the interface. For anionic defects, gas ions diffuse to the chemical compound–metal interface and interact with the metal at this interface.

Thus, both boundary reactions and transfer processes occur. The boundary reactions are the dissociation of gas molecules with the simultaneous chemisorption of gas atoms and their transition to the film lattice, and the transfer of metal ions and electrons to the film followed by the interaction of gas ions with the metal at the metal–film interface and by the interaction of metal ions with the gas at the film–gas interface. The transfer processes include the diffusion of metal cations and gas anions that is caused by the gradient of chemical potentials through the film at the sites of defects, diffusion along the grain boundaries of a chemical compound, penetration through pores and discontinuities, and transfer processes in thin films due to spatial charges and electric field.

MECHANISM OF FORMATION OF OXIDE FILMS ON METALS

Presently, one of the most abundant concepts on the interaction of gases with metals is the Minkevich–Wagner theory, according to which cations and anions rather than atoms of interacting substances diffuse through the crystalline lattice of the formed surface layer. The transfer mechanism depends on defects of the surface layer and differences in the chemical potentials between the surface layer and gas and between the metal and surface layer. These features of the interaction of gases with metals can clearly be

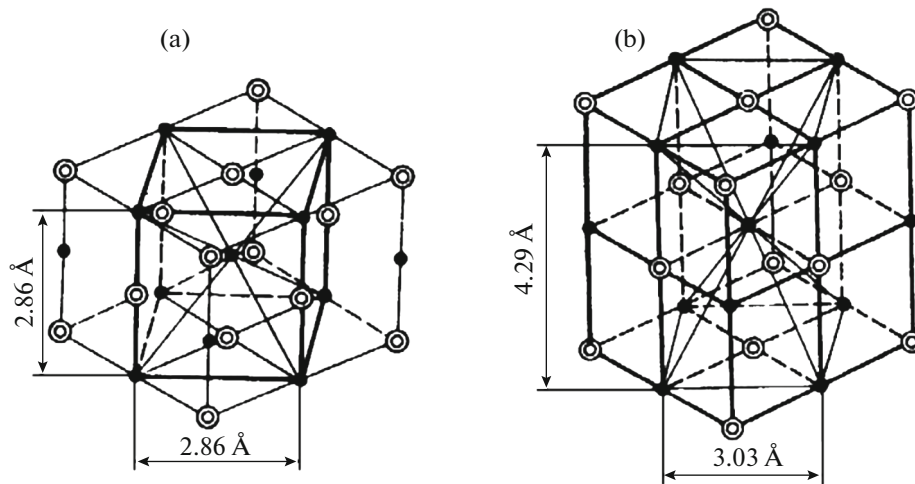


Fig. 1. Scheme of the transition of the iron lattice to the wustite lattice upon oxidation (black signs are iron ions, and white signs are oxygen ions): (a) before a change in the lattice parameters and (b) after a change in the parameters of the iron lattice to those of the wustite lattice.

monitored for oxidation [1, 2]. For example, alkaline and alkaline-earth metals react with oxygen rather rapidly even at room temperature. The molecular volume of the oxide formed is smaller than the atomic volume of the metal, resulting in the formation of a porous layer of oxide, through discontinuities in which oxygen from the gas phase penetrates directly to the metal surface, and the process rate is determined by the reaction rate at the gas–metal interface.

For another group of metals, especially heavy metals, the molecular volume of the formed metal oxide is larger than the atomic volume of the metal lying under the oxide. Therefore, closely spaced to the metal compact coatings are formed, as a rule, upon oxidation. The lower the difference in interatomic distances of the metal and oxide lattices, the easier the formation of these perfect coatings. Thus, under certain conditions, the oxide is a compact pseudo-coherent layer to which the type of lattice and metal–substrate interatomic distances are “imposed” [3]. The stability of this pseudo-coherent layer depends on the interatomic interaction forces between the oxide and metal and on the elastic properties of the oxide. The higher the compressibility of the oxide, the more stable its pseudo-coherent state. The crystalline oxide formed is pseudo-coherent to the metallic substrate if the lattice parameters of the metal and oxide differ less than by 15%. If the difference in these parameters exceeds 15%, an oxide layer with the intrinsic type of the crystalline lattice is formed. In the first case, a growing oxide crystal is thermodynamically unstable and a compact oxide layer is formed only under the conditions of equal lattice parameters of the oxide and oxidized metal. In the second case, the formation of a crystalline lattice inherent in this oxide starts after the complete coating of a metallic surface with an oxide layer. This can take place due to the cracking of the

coating, plastic deformation of the external layer of the oxidized metal, or recrystallization [1, 4, 5].

Metal oxidation is related to some change in the crystalline lattice, but the orientational relationships between the oxide and metal are retained. The surface film during formation tends to take the structure of the low-lying metal. For example, the body centered lattice of iron transforms into the simple cubic lattice of ferrous oxide without preliminary decomposition, so that the [100] direction in the iron lattice coincides with the [110] direction in the oxide lattice (Fig. 1) [4, 5].

The main theories of the initial oxidation at relatively low temperatures were generalized in [6] (see table).

The main regularities of the oxidation of pure metals are also valid for alloys, but a complicated character of diffusion processes and the formation of oxides of a more complicated composition should be taken into account in this case.

Thus, the compositions, the structures, and the properties of oxide films being independent phases should be taken into account.

According to the thermodynamic regularities, in the general case, Fe_2O_3 , Fe_3O_4 , and FeO form from the surface to the volume.

EXPERIMENTAL

The following nitriding steels with 1.5–13% Cr of various classes were studied: pearlitic steels (40Kh, 40KhFA, 30KhMVS, 20Kh3MVF, 30Kh3MF1, 20Kh3VA, 38KhNMFA), martensitic steels (40Kh9S2, 20Kh13, 30Kh13, 40Kh13) ferritic steels (08Kh12), martensitic–ferritic steels (12Kh13), and ledeburitic steels (Kh12M and R6M5). These steels

Kinetics and theories of oxide film formation

Rate equation	Processes and conditions governing film growth rate
Linear	Adsorption on pure metallic surface with constant adhesion coefficient
Linear with temperature increase	Adsorption on pure metallic surfaces with increasing adhesion coefficient. Simultaneous adsorption and oxide growth
Logarithmic	Adsorption. Increase in activation energy with increasing gas flow. Transfer through thin films under electric field action. Electron transfer through film determining reaction rate. Electron flux governed by spatial charge in oxide film. Regions with low diffusion resistance. Decrease in effective surface area of volume diffusion. Oxide nucleation and growth. Increase in activation energy
Logarithmic, linear, etc.	Transfer through thin films under electric field action. Diffusion over pores
Inverse logarithmic	Ion transfer through thin oxide films under electric field action. Electron transfer caused by tunneling effect and transfer of metal cations from metal to oxide and then to oxide surface as nano-inclusions governing reaction rate, transfer of gas ions through oxide film as rate-determining factor

are applied for important parts. A necessary condition for hardening of these steels was the retention of the surface microgeometry. For this purpose, a hardened layer consisting only of the zone of internal nitriding of nitrides of alloying elements (CrN) and a solid solution of nitrogen in α -Fe was formed during nitriding.

Since the energy of chromium nitride formation is significantly lower than the energy of formation of iron nitrides [6, 7], the kinetic energy of nitrogen ions involved in nitriding should be decreased to exclude the formation of iron nitrides.

According to the aforesaid, oxide films were used as a barrier controlling the energy potential of active nitrogen ions for the subsequent nitriding of alloyed chromium steels. An oxide films were produced on the hardened surface during preliminary oxidation in an air atmosphere.

It is of interest to study the mechanism of formation of the barrier oxide film, as well as its structure and phase composition. For the oxide film to play the role of the barrier controlling the energy potential of active nitrogen ions and, thus, favoring the formation of the necessary structure under the oxide layer, the oxide film should have the corresponding thickness depending on the content of chromium in the steel.

An experiment on prolonged (2 h) oxidation of steels with different chromium contents was carried out in an air atmosphere in the temperature range from 450 to 591°C in order to determine the rate of oxide film growth. The published data [8] were taken into account: no substantial changes in the structure and thickness of the oxide layer are observed for low-temperature oxidation. The subsequent nitriding was conducted at 520–591°C in ammonia with a degree of dissociation of 30–45%.

The kinetics of the oxide film growth was monitored by the specific increase in the weight of the samples $\Delta P/S$, where ΔP is the increase in the sample weight due to oxidation (g) and S is the surface area of the sample (cm²).

Prior to oxidation, the surface area was measured with a fluid planimeter.

Assuming that the surface area of the sample is uniformly covered by an oxide film, its thickness was determined as a function of the oxide volume and the surface area of the sample. When determining the optimum thickness of the oxide film, we started from the fact that the process should occur in the range where all nitrides and iron nitride nucleation were completely absent. It was also taken into account that nitriding did not occur if the film thickness was greater than the optimum value and the standard nitriding process occurred to form iron nitrides if the film thickness was smaller than the optimum value.

RESULTS AND DISCUSSION

The following functional dependences were constructed by the results of $\Delta P/S$ determination:

$$\frac{\Delta P}{S} = f(\sqrt{\tau}), \quad (1)$$

where τ is the storage time (min).

A parabolic dependence of oxidation was established for all Fe–Cr alloys studied in the given temperature range.

The oxide film that is most uniform and optimum in composition and thickness is experimentally established to be formed on all samples in 15 min at 550°C. The calculations performed made it possible to estab-

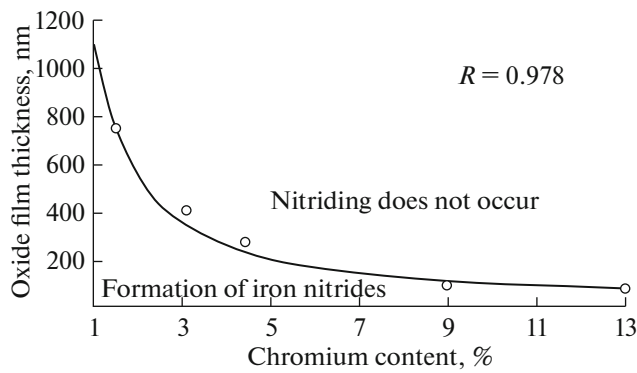


Fig. 2. Thickness (h_{ox}) of the oxide film formed on the surface before nitriding vs. the chromium content in steel.

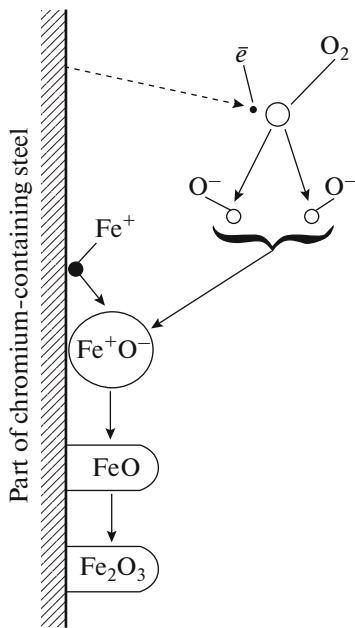


Fig. 3. Scheme of oxide film formation on the chromium-containing steel surface upon the isothermal storage in air.

lish the dependence of the oxide film thickness on the Cr content in the steel (Fig. 2). As can be seen from Fig. 2, the thickness of the oxide film in high-chromium steels is in a nanosized range.

The rate of saturation of the layer with nitrogen in chromium steels after preliminary oxidation also obeys a parabolic law. The solubility of nitrogen increases with the chromium content in Fe–Cr binary alloys, resulting in an increase in the amount of absorbed nitrogen determined from the weight increase.

Model of oxide film formation upon isothermal storage in air is based on the classical concepts on chemical thermal treatment mechanisms. The process starts from the dissociation of oxygen molecules to

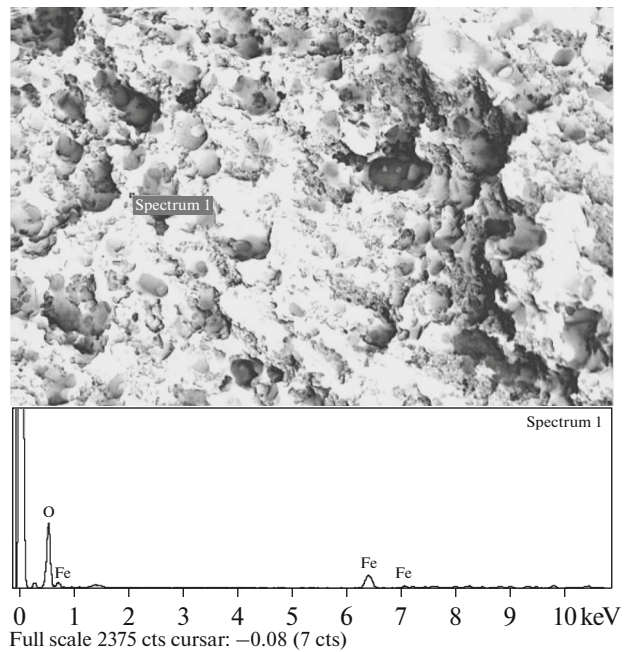


Fig. 4. SEM image of the oxide film ($\times 24000$) on the steel surface and the spectrum of elements recorded from the marked fragment of the structure (HITACHI S-800 scanning electron microscope with an INCA X-ACT X-ray spectral analyzer).

ions, and their adsorption on the surface and diffusion deep into the metal occur (Fig. 3). The penetration rate of oxygen atoms into the metal is determined by the classical equation of diffusion

$$\frac{dn}{dt} = D \frac{\partial^2 n}{\partial x^2}, \quad (2)$$

where n is the oxygen concentration. The phase transformation with the formation of iron oxide occurs in oxide as the oxygen concentration close to its stoichiometric content is achieved. Thus, a thin film of iron oxides is formed (Fig. 4).

The oxide film on the surface recorded using a HITACHI S-800 scanning electron microscope with an INCA X-ACT X-ray spectral analyzer is shown in Fig. 4. The peaks of O and Fe in the X-ray pattern confirm the formation of iron oxide.

It was found by X-ray diffraction analysis (XRD) of the surface of the steels that the formed oxide film mainly contained oxide Fe_2O_3 (Fig. 5).

The layer-to-layer XRD gives the pattern of changes in the phase composition in depth (see Fig. 5). Iron oxides and α -Fe are observed in the near-surface zone. The oxides disappear with deepening, and only the solid solution of alloying elements and nitrogen with different concentrations are retained in α -Fe, which is observed from a change in the widths and heights of the diffraction patterns. Diffraction maximum (110) shifts toward larger reflection angles θ

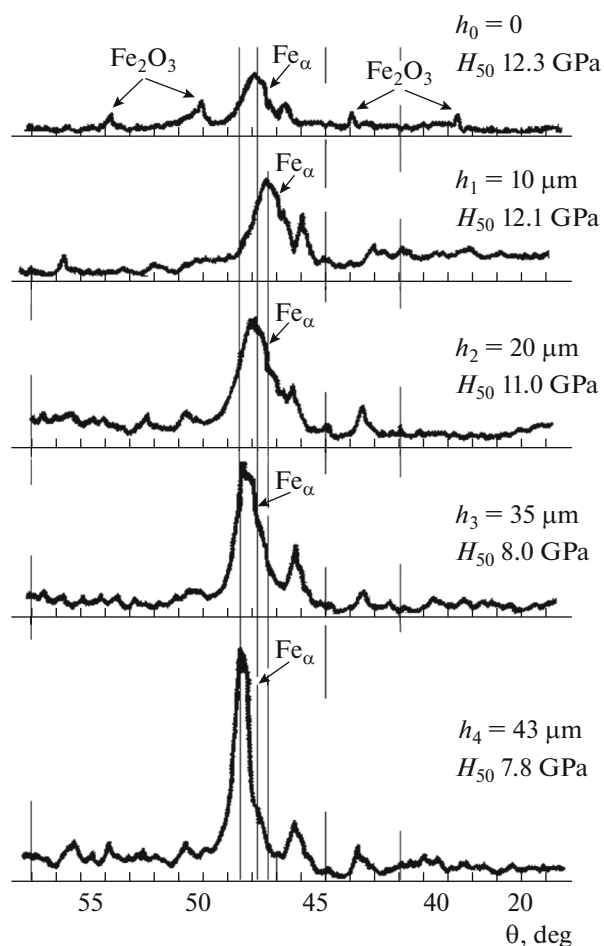


Fig. 5. Layer-by-layer X-ray diffraction patterns of R6M5 steel after nitriding through an oxide barrier: $t_n = 550^\circ\text{C}$, $\tau_n = 45$ min, and h_i is the distance from the surface.

and, at a depth of ~ 43 μm , corresponds to the initial state of the R6M5 steel.

The curves of element distribution over the thickness of the samples were obtained by electron spectroscopy. The thickness of the oxide layer was estimated from the length of the region of the curve with an increased oxygen concentration. For example, in the 20Kh3MVF steel, the oxide film thickness was about 200 nm (Fig. 6), which is close to the calculated value (see Fig. 2).

The mechanism of the subsequent formation of the nitrated layer depends on the oxide film and the nitriding time.

The model of formation of the internal nitriding zone under the oxide barrier in Fe–Cr binary alloys makes it possible to predict the phase composition of the layer. The mechanism of the nitrated layer formation under the oxide film is related to the following effects. Since free electrons are much more easily emitted from oxides than from metals [8, 9], the ionization of ammonia above the oxide film proceeds more

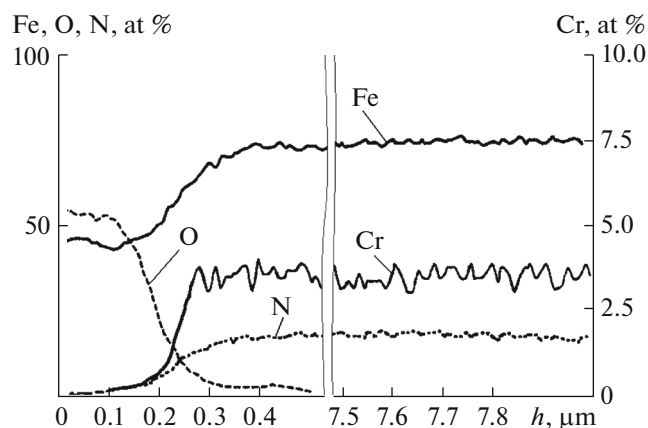


Fig. 6. Concentration profiles of elements across the layer thickness of 20Kh3MVF steel after oxidation and nitriding: $t_n = 540^\circ\text{C}$, $\tau_n = 45$ min (a Line Scan INCA-sight spectrometer), and h is the distance from the surface.

intensely. An electric field accelerating the motion of formed nitrogen ions to the surface is formed about the unit because of ion emission from the oxide film. If the oxide film thickness is rather small (film is nanosized), a certain portion of the nitrogen ions penetrates through the film to the metal, losing the kinetic energy. This results in the formation of a nitrated layer under the oxide film to form nitrides with the lowest heat of formation. Thus, the oxide film, on the one hand, serves as a source of an electron flux that ionizes the gas of the saturating atmosphere, and on the other hand, it serves as a buffer zone absorbing a portion of the kinetic energy of the ions of this atmosphere and favoring the formation of a nitrated layer of a specified phase composition. The degree of energy loss by nitrogen ions is controlled by the thickness of the formed oxide barrier, which was shown to depend on the concentration of the alloying element (chromium) in the steel.

The model makes it possible to determine conditions for the formation of an internal nitriding zone in chromium steels. The zone consists of chromium nitrides only without the formation of iron nitrides. Since the heats of formation of iron nitrides Fe_4N and Fe_2N (-11 and -4 kJ/mol, respectively) are significantly higher than the heat of formation of chromium nitride CrN (-118 kJ/mol), their formation requires a higher energy of active nitrogen ions. The kinetic energy of nitrogen ions penetrating through the oxide barrier is sufficient for the formation of CrN but insufficient for the formation of iron nitrides. A modified layer consisting of a solid solution of nitrogen in α -Fe and dispersed chromium nitrides is formed under the oxide film (Fig. 7).

It was experimentally confirmed that the formation of nitrides Fe_4N and Fe_2N even on pure iron was excluded for nitriding through the oxide barrier. Subsequent aging of nitrated iron does not result in the

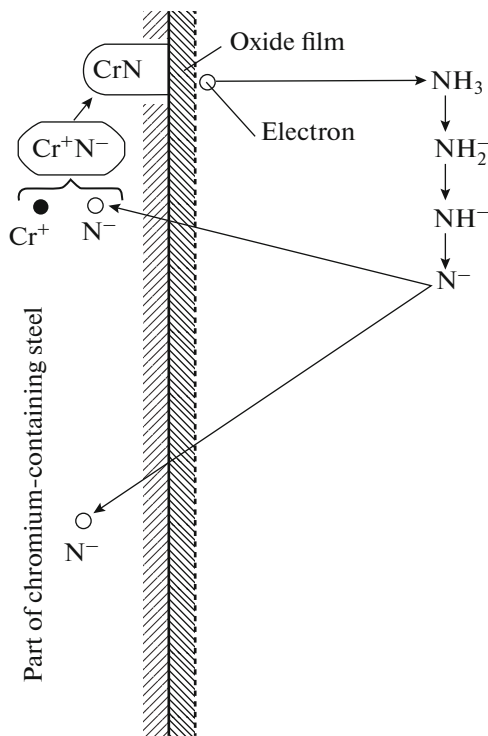


Fig. 7. Scheme of hardened layer formation under an oxide film during the nitriding of a chromium-containing steel.

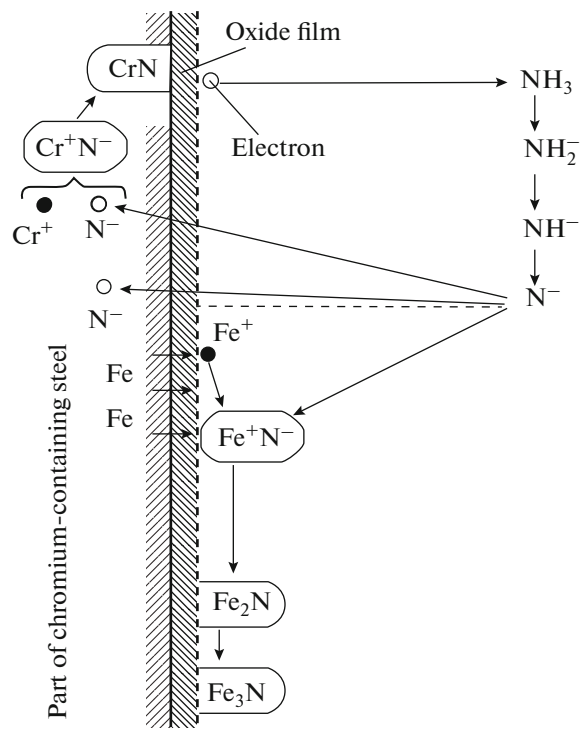


Fig. 9. Scheme of powdered ϵ -phase formation above an oxide film.

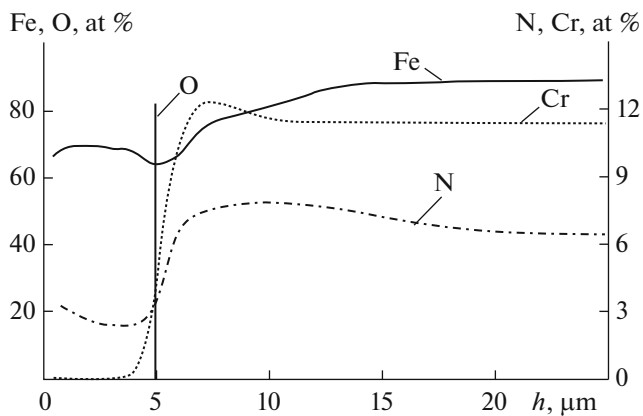


Fig. 8. Concentration profiles of elements across the layer thickness of 40Kh13 steel after oxidation and nitriding: $t_n = 580^\circ\text{C}$, $\tau_n = 4$ h (a Line Scan INCA-sighnit spectrometer), and h is the distance from the surface.

precipitation of secondary nitrides, and the structure represents nitrous ferrite.

As a result, a bilayer composite coating is formed on the surface: the surface layer of oxide Fe_2O_3 and the internal nitriding zone consisting of ferrite alloyed by nitrogen and dispersed particles of nitrides of alloying elements (first of all, CrN). This coating is formed upon short-term nitriding (shorter than 1 h).

The thickness of the diffusion layer increases with the nitriding time (more than 1.5 h), and a hardened layer separated by the oxide film into two zones is formed. A three-layer composite coating is formed: the surface layer of the nanopowder of the ϵ phase, the oxide phase under it, and the internal nitriding zone with coherent insertions of chromium nitrides (Fig. 8).

It was experimentally found that a powdered layer of the highly nitrous ϵ phase was formed above the oxide layer during prolonged nitriding. The formation of a powdered substance can be explained by the fact that nitrides are formed discretely, the melting temperature of nitrides is significantly higher than the nitriding temperature, and no particle sintering occurs. As a result, a low bond strength with oxide and, correspondingly, with the surface is observed. The powder size is $\sim 40\text{--}60$ nm, being a natural lubricant for the wear operation of units.

The scheme of formation of the layer of a finely dispersed powder of iron nitride on the surface is shown in Fig. 9. The nitride layer can be formed only in the case where iron interacting with nitrogen is observed on the oxide surface. It can be assumed that some iron atoms diffuse outside through the film due to concentration gradient. The reduction of iron with hydrogen from the oxide film is also possible.

The internal nitriding zone lying under the oxide film is characterized by an enhanced nitrogen concentration (see Figs. 6, 8). A certain portion of this nitro-

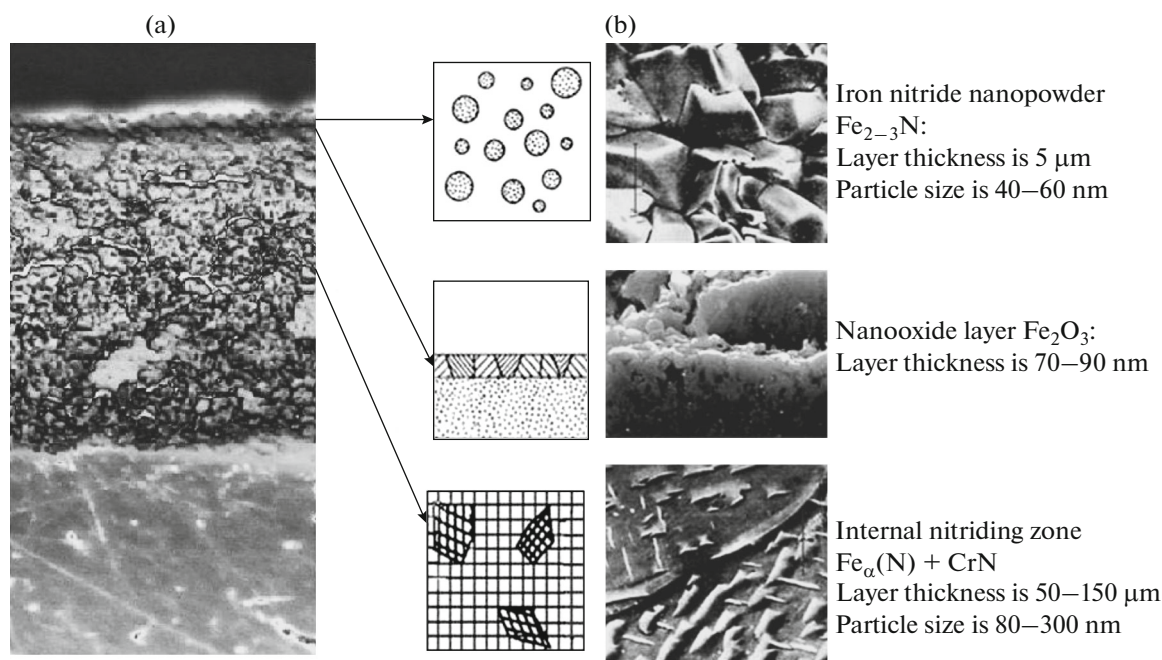


Fig. 10. Electronography of (a) oxynitrated layer of 40Kh13 steel ($\times 500$) and (b) nanostructure of the modified layer region.

gen is dissolved in ferrite, which is indicated by a change in the crystalline lattice parameter of the solid solution measured using layer-to-layer XRD by the broadening and shift of the α -Fe peaks in the diffraction patterns (see Fig. 5).

Thus, the oxide film makes it possible to form hardened composite nanostructured layers on the steel surface during subsequent nitriding (Fig. 10).

The study of the service characteristics of units with an oxide film on the surface hardened via the energetic oxide barrier showed the following. The presence of an oxide film favors a better running-in of the units and decreases the affinity to frictional seizure (cold welding) during contact of rubbing surfaces. The presence of a powdered substance of iron nitrides on the surface enhances the wear properties of the products.

The formation of surface films of secondary oxide structures (solid solutions of oxygen or oxides) is necessary to protect the rubbing surface from frictional seizure [10, 11]; i.e., a high affinity to oxygen of the surface activated during friction is required.

It should be mentioned that the formation of an oxide layer, which is based on the solid zone of internal nitriding, has high antifriction characteristics, does not tend to frictional seizure, and is very important for the workability of the friction system at the initial wear period (when local pressures are very high (considerably higher than that for steady wear) [11]). The oxide film formed on the surface can also improve the corrosion properties of the products [3].

CONCLUSIONS

(1) On the one hand, the oxide film formed on a surface serves as a source of an electron flux ionizing the gas of the saturating medium. On the other hand, the oxide film serves as an energy barrier absorbing portion of the kinetic energy of the ions of this atmosphere and, thus, makes it possible to form a hardened layer of nitrides of alloying elements.

(2) The presence of an oxide film favors better running-in and decreases the affinity to frictional seizure in contact of the rubbing surfaces of the products, and the nanopowder of iron nitrides formed on the surface acts as a natural lubricant for abrasion working parts.

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