RESEARCH ARTICLE

NITRO-OXIDATION PRODUCTS FROM STRUCTURAL STEELS

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Abstract

The article examines the technology of nitro-oxidation, which consists of nitriding in separated ammonia at the first stage and oxidation in water vapor at the second stage of the process, studied the structure and phase composition of the diffusion nitride-oxide layer, providing high physico-mechanical and physicochemical surface characteristics, competitively capable of galvanic strategies of getting a coating, the conceivable outcomes of regulating the structure and phase composition of the nitride-oxide layer are being investigated to obtain a diffusion coating composition with predetermined properties.

Introduction:

Low-temperature gas nitriding of structural steels is frequently carried out at temperatures of 400-600 °C, as a result of which steels gain high hardness, high wear resistance, corrosion resistance, high endurance constrain, and cavitation resistance [1, p. 256].

Nitro-oxidation, as a process that provides unique surface characteristics of steel in combination with tall fatigue strength, is as of now successfully used in various branches of machine building to reinforce a wide range of parts instead of electroplated chromium coatings [2, p. 320; 5, pp. 238-243].

The Main Findings And Results:

Amid nitro-oxidation, a combined diffusion layer is formed, consisting of a surface oxide zone, a carbon-nitride zone, and a diffusion sublayer - an internal nitriding zone (INZ). Figure 1 shows the structure of the nitride-oxide layer, which provides surface characteristics that are competitive to galvanic coating methods.

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According to the technological sequence of operations, nitro-oxidation is carried out according to a one-stage scheme of a continuous process or according to a combined process scheme: nitriding followed by oxidation, preliminary oxidation followed by nitriding, or according to a three-stage scheme, which consists in preliminary oxidation, nitriding and subsequent oxidation [6, p. 278; 8, pp. 10-15].

In Russia, a combined nitro-oxidation process based on Nitroc, as an alternative to hard chrome plating, was tested to harden the pistons of brake cylinders. At the first stage of the process, a diffusion layer is formed by the Aichelin method in a mixture of ammonia and exogas at a temperature of 600-620 °C. After polishing, the pistons are oxidized at a temperature of 350 °C, which allows an increase in corrosion resistance by 7-13 times than that of chrome-plated parts [10, pp. 23-24; 11, pp. 1-5].

The nitrate process, created in Britain in accordance with the patent of Cyril Dawes (Cyril Dawes, British patent # 1011580) is carried out in the temperature range 550 - 620 °C in an atmosphere of ammonia and exogas followed by short-term oxidation. At the same time, two zones are microstructurally uncovered in the carbo-nitride layer: a zone with controlled porosity and, located behind it, a non-porous zone.

**Currently, three process schemes are being industrially implemented:**

- Nitrotec process in an ammonia-exogas atmosphere with the formation of a layer with a black oxide surface zone and corrosion resistance superior to zinc galvanic coatings.

- Nitrotec-S process with additional mechanical polishing before oxidation, with corrosion and wear resistance superior to chrome plated coatings.

- Nitrotec-C process for low carbon and low alloy steels, including carburizing or nitro-carburizing before nitro-oxidation. This process is recommended for wear parts with high contact loads.

Nitrotec processes are successfully used not only for hardening a wide range of parts, but also in metallurgical production for surface treatment of rolled products instead of electroplated chrome coatings. In particular, MacSteel (USA) has launched the production of nitro-oxidized rolled products in the form of rods and pipes from 45 and 45GM steels. Corrosion resistance in salt fog conditions is guaranteed after the Nitrotec process - 100 hours, after the Nitrotec-S - 250 hours. Nitroxidized rolled products are used for the manufacture of parts for hydraulic machines, cylinders, pistons, plungers.

Acceleration of the nitriding process can also be accomplished by pre-oxidation. A thin oxide layer with a thickness of no more than 0.5 μm, created at the primary stage of the process, is diminished with hydrogen amid the
subsequent gas nitriding, providing a relatively clean surface, whereas, due to a diminish in the concentration of alloying elements, the diffusion of nitrogen in the strong solution is accelerated and the nitriding process is intensified.

Industrial implementation of nitro-oxidation began in the middle of the last century, when the company Degussa in Germany introduced a process of soft nitriding in cyanide-cyanate baths called Tenifer. For the intensification of the Tenifer process, the Degussa Firm (Germany) proposed the “QPQ” process, which includes preliminary oxidation of the processed products when they are heated in air to 350 °C and after preliminary oxidation, the parts are transferred to a cyanate bath, where the nitriding process is carried out at 580 °C in within 30-180 minutes. The thickness of the carbonitride zone on the pre-oxidized parts is 25% higher than on the unoxidized ones [11, pp. 1-5].

The development of the Tenifer process, including the “QPQ” process, was carried out on the basis of the use of in the initial state non-toxic baths based on cyanates and carbonates. The disadvantage of these processes is the formation of toxic cyanides, the amount of which amid normal operation increases to 0.5-3%, and determines the fulfillment of extra requirements for environmental protection.

Currently, the industry uses various options for nitro-oxidation technologies, which are carried out in various saturating media, forming a nitrided diffusion layer with a surface nitride, carbo-nitride and oxycarbonitride zone covered with a dark dense oxide film with unique decorative and anti-corrosion properties.

Materials:-
The study of the kinetics of the formation of diffusion nitride-oxide coatings amid nitro-oxidation was carried out on standard steels of grades 20, 40X, 45. The combined technology of obtaining protective coatings was created in relation to structural steels used for the manufacture of parts operating in conditions of atmospheric corrosion and low wear - and medium stacked friction units. Commercial ammonia was used as a saturating gas in the first stage and superheated steam in the moment stage.

Nitriding followed by vapor oxidation of the samples was carried out as follows: after reaching the required temperature in the furnace volume, the time started to number and the degree of ammonia dissociation was observed every 15 + 20 minutes using a water dissociometer.

When implementing the technology at the first stage, saturation was carried out in dissociated ammonia at various degrees of dissociation, and at the second stage, it was oxidized in superheated steam.

Methods:-
To study the growth kinetics of the hardened layer of steel samples, metallographic studies of transverse sections of the processed samples were carried out. The microstructure of the hardened layers was studied using a “Neophot-21” optical microscope and a SEM-EVO MA 10 scanning microscope (Carl Zeiss, Germany).

The micro-hardness along the depth of the diffusion layer was measured according to State-Standard 9450-76 on a PMT-3 micro-hardness tester. The micro-hardness was measured on thin sections in the direction perpendicular to the hardened surface and was determined as the arithmetic mean of five measurements. At the same load, the change in micro-hardness along the layer thickness was estimated. The effective thickness of the diffusion layer was taken as the distance from the surface of the area with a hardness of 250-300 MPa higher than the matrix hardness.

The study of the phase composition of the hardened layers of steel samples was carried out by the method of X-ray structural analysis on a DRON-3 installation in iron and cobalt filtered radiation. The phase composition was determined by comparing the obtained inter-planar distances \((d / n)\) with tabulated values \((d / n)\) for nitride and oxide phases, taking into account the ratio of the intensities of the lines of the corresponding plane [12; 13, p. 863].

For a comparative characteristic of the corrosion properties of coatings, the method of exposure to neutral salt fog in accordance with State-Standard 9.308-85 was used. Corrosion tests were carried out in a KTK-500 chamber. A 3% NaCl solution in water was used as an aggressive medium [14, p. 58].
Results:
When nitriding in an ammonia atmosphere, due to its thermal dissociation in the working space of the furnace, on the surface of parts made of steel and alloys agreeing to the “Fe-N” system, multilayer diffusion coatings are shaped, consisting of a surface nitride zone and a diffusion sublayer – an internal nitriding zone (INZ). In this case, nitride crystals can develop only in a saturated solid solution, since the maximum nitrogen concentration is reached only on the surface; the nitride Me$_{2-3}$N or MeN forms a continuous surface layer.

In nitriding, the structure of the steel matrix and grain sizes are of small importance, which to a few extents determine the volumetric diffusion and diffusion along the grain boundaries, the latter which happens at a much higher rate than within the bulk of the grain. In this manner, when nitriding steel and alloys, the intensification of diffusion forms is achieved mainly with alter in the temperature-time regimes of the processes and alter in the nitrogen potential of the saturating atmosphere.

When nitriding iron and its alloys in an environment with a high nitrogen potential, the surface nitride diffusion coating consists of sequentially located layers Fe$_2$N (ξ-фаза)→Fe$_2$$_3$N (ε-фаза)→Fe$_4$N (γ′-фаза). The ξ-phase is formed as a result of phase recrystallization upon cooling in those regions of the ε-phase in which the nitrogen concentration is 11.0-11.35% (by weight). The saturation temperature and the cooling method play an important role here.

The ε-phase formed at a higher eutectoid temperature for the “Fe-N” system (590 °C) often contains a large amount of micro-pores formed due to the meta-stability of nitride phases, from which nitrogen tends to be released in free form. The ε-phase formed above the eutectoid temperature has a columnar structure, at the boundaries of grains and micro-pores, as well as developed voids of volumes, an accumulation of atomic nitrogen appears, which, upon cooling, passes into a molecular state. Oxidation of the pore walls occurs during the cooling of the treated surfaces with atmospheric oxygen with the formation of oxide Fe$_2$O$_3$ (Fig. 1).

The required structure and phase composition of the nitride-oxide layer is achieved under optimal processing conditions, with obtaining a low-nitrogen ε'-phase (Fe$_2$$_3$ (NC)), ε'"-phase (Fe$_2$$_3$ (NCO)) and γ'-phase (Fe$_4$N) of a certain ratio a thickness of 25-30 microns and a surface layer of Fe$_3$O$_4$ oxide with a thickness of 1-3 microns [8].

As our further studies showed, in order to obtain an oxycarbonitride layer having a certain ratio of ε'-, ε'"- and γ'-phases in the nitride zone and a dense oxide layer consisting of one magnetite, the oxidation process can be carried out in water vapor with the addition of complexones, in particular HEDP (hydroxyethylidenediphosphonic acid).
The microstructure of the nitride-oxide layer obtained after nitro-oxidation at the second stage of oxidation with the addition of HEDP to the composition of water vapor has a dense composite layer. In this case, a composite diffusion layer is formed, consisting of a dense surface oxide zone.

**Fig 3:** Microstructure of the nitride-oxide layer on steel 45.

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**Treatment mode:**
Nitriding - 580°C, 3 hours; oxidation - 550°C, a - 1 hour and b - 2.5 hours in water vapor with additions of 5% HEDP.

In order to clarify the nature of the dissociation of the nitride phase, the nitride layer was oxidized in water vapor with HEDP additives for 2.5 hours. In this case, the thickness of the oxide layer increases, and the precipitation of dispersed nitride particles in the diffusion zone is detected (Fig. 3, b).

X-ray diffraction analysis showed that the surface oxide layer consists of almost one oxide - magnetite, and an increase in the intensity of the Fe$_3$O$_4$ oxide line is found than the intensity of the Fe$_3$O$_4$ line obtained under the same conditions of nitrooxidation, carried out by oxidation in water vapor without additive.

It is important that the nitride sublayer grows deep into the nitrided layer with the formation of lower nitride ε'-, ε''- and γ'-phases due to the high-nitrogen 13-phase obtained by nitriding at the first stage.

According to the above technology, samples of steel 20 were processed. The results of studying the surface layer showed that after nitriding in the usual way (t$_{as}$=580°C, t$_{as}$=3 hour. α=45-60%), the micro-hardness of the nitride layer in the ferrite part was HV = 4, 73 GPa, and in the pearlite part HV = 6.35 GPa. After nitro-oxidation over the entire surface, almost identical values of micro-hardness were obtained equal to HV = 8.58 GPa. In this case, the increase in the intensity of the lines of the 14- and 15-phase of the nitride layer differs sharply from the intensities of the lines of the corresponding phases of the nitride layer obtained after nitriding.

Diffusion processes in the nitride layer amid the production of the oxide layer occur mainly along the grain boundaries of the γ'-phase. In this case, the γ'-phase in the nitride layer will be covered by ε'-, ε''- phases in a reticular form. The separation of the high-nitrogen ε -phase occurs by the partial partition of the γ'-phase and the formation of the low-nitrogen ε'-phase due to carbon from the matrix and ε''-phase from the carbon of the matrix and oxygen from the saturating atmosphere.

When oxynitrogenation, a composite layer practically consisting of an γ'-phase can be obtained by a two-stage change in the nitrogen potential of the atmosphere at 560-580 °C, and by preliminary dissociation of ammonia α$_{a}$ = 25%, while maintaining the dissociation of the ammonia mixture at saturation α= 55-75% and a duration of 1.5-3 hours. The obtained nitride layer has an even and non-etched appearance, mainly consisting of a γ'-phase, the microstructure of which on steel 40X is shown in Fig. 4.
As our studies have shown, the corrosion resistance of the nitride-oxide layer depends on the ratio of $\gamma'$ and $\varepsilon$ phases in the nitride zone.

In fig. 4 shows the time dependence of the appearance of the first foci of corrosion in a 3% aqueous solution of sodium chloride steel 45 after oxynitriding with the addition of water vapor.

With an increase in the amount of lower nitride ($\gamma'$ phase) in the nitride zone up to 75%, the time before the appearance of the first foci of corrosion increases, reaching 910 - 960 hours at 75% of the $\gamma'$ phase. A further increase in the amount of phase 14 is accompanied by a decrease in corrosion resistance.

In figure 5 for the same test conditions shows the change in the corrosion area from the test time for a nitride layer with 50 and 75% $\gamma'$ phases.

It should be noted that in the experiments carried out, the thickness of the oxide zone was 1.5 μm.

Figure 4: Microstructure of the nitride-oxide layer on steel 40X after nitro-oxidation.
During oxidation, a dense oxide layer ensures uniform dispersion of the nitride layer and, thus, by setting the oxidation time, the necessary ratios of low-nitrogen phases in the nitride layer are achieved, which together have a surface oxide layer with the necessary physicochemical and physico-mechanical properties.

Optimal tribological and corrosion-protective properties are accomplished with a carbonitride layer with a surface dense oxide zone consisting of magnetite (Fe₃O₄) with a thickness of 1 to 3 microns. A change in the stage composition of the oxide zone with the formation of oxides FeO and Fe₂O₃ is going accompanied by the loosening of the layer and leads to a weakening in corrosion resistance. The presence of FeO oxide leads to the cracking of the oxide film and its delamination from the surface.

The nitride zone with high surface characteristics consists of αγ+ε phase. Moreover, the ε-phase is depleted in nitrogen and is revealed by X-ray diffraction in the form of two isomorphic phases: an isomorphic carbonitride phase, designated as ε'-phase with lattice parameters a = 0.269, c = 0.436 nm, and an oxycarbonitride phase, designated as ε''-phase with lattice parameters a = 0.267, c = 0.436 nm [8.15].

**Discussion:**
Depending on the technological modes of the process and on the composition of the nitrided alloy, it is possible to change the phase ratio in the nitride layer to obtain the required diffusion composite coating of a given phase composition and dispersion, which provides different physicochemical and physico-mechanical properties in the nitride layer. It is important to take into account that the structure of the nitride-oxide layer is formed not only at the saturation temperature, but also during subsequent cooling.

During the cooling period after nitro-oxidation, the α-solution decomposes, which, depending on the cooling rate, proceeds to a greater or lesser extent, the formation of a mixture of the α+γ'-phase. With slow cooling, in addition to granular nitrides of alloying elements, acicular nitrides of Fe₄N, which are released from the α-solution, may form.
Rapid cooling in water from the nitriding temperature suppresses the decomposition of the α-solution, and supersaturated nitrogenous ferrite is found at room temperature. Exposure at room temperature and especially at elevated temperatures causes the decomposition of the supersaturated α-solution.

Metastable nitride at low temperatures (up to 150 °C) has a maximum nucleation rate; therefore, the incubation period of isolation is minimal. With an increase in the temperature and duration of the process, Fe₄N nitride is released, which has a large work of the critical nucleus. At t>300 °C, only Fe₄N nitride is released, which corresponds to the well-known regularity: the lower the degree of saturation of the solid solution with respect to the stable nitride, the less intermediate transformations.

During nitriding, the matrixes blocks are refined, elastic stresses arise, and the lattice of the α-phase is distorted. Due to the development of a polygonized structure, a large number of additional diffusion channels appear, which allows nitrogen atoms to rapidly move deeper into the α-phase. During aging of iron-nitrogen compositions, the formation of metastable nitride Fe₁₆N₃ is observed, which, under certain temperature-time conditions of aging, is “replaced” by the more stable nitride Fe₄N.

In general, a nitrided surface composite layer consisting of a Fe₂,₃N and Fe₄N nitride zone is required to strengthen parts operating in a corrosive environment and under wear conditions at low contact loads. For a composite coating, the optimization of the phase composition and structure of the surface nitride zone is achieved by regulating the nitrogen concentration, by varying the nitrogen potential in nitride coatings and doping it with oxygen and carbon.

Since the regulation of the phase composition of the nitrided layer is achieved by changing the nitrogen potential of the saturating atmosphere, maintaining the nitrogen potential at the level of nitrogen solubility in one or another phase, it is possible to obtain a layer consisting of an α-solid solution - Fe₄[N], iron nitrides and alloying elements, to form on the surface nitride ε-phase, carbonitride ε'-phase, oxycarbonitride ε"-phase, low nitride γ'-phase with low nitrogen content. It is recommended to regulate the nitrogen potential by diluting ammonia with fully or partially dissociated ammonia, oxygen, air, carbon-containing gases, etc. However, the simplest change in the atmospheric potential can be achieved by changing the degree of dissociation of ammonia in the furnace.

Studying the kinetics of the formation of the nitrided layer on the surface and the microstructure of the samples after nitriding and subsequent oxidation in water vapor, it can be asserted that the nitride layer obtained at a lower eutectoid temperature for the “Fe-N” system, although it has less thickness than the nitride layer obtained at a higher eutectoid temperature, it has a denser structure than the nitride layer obtained at hypereutectoid temperature and having surface micro-pores after the process of vapor oxidation is healed by the formation of iron oxides Fe₃O₄.

**Conclusion:**
Judging by the microstructure of steel with composite oxynitride layers, it can be said that the oxide layer develops uniformly over the nitride layer due to the dissociation of nitrogen on the nitride surface, further prolonged oxidation of which leads to the disappearance of the high-nitrogen nitride layer.

Based on the presence of a nitride-oxide layer on the surface, which is responsible for properties such as corrosion resistance and wear resistance with the creation of a positive surface gradient during friction, it is necessary to obtain a developed nitride-oxide layer, and to increase the structural strength, it is necessary to obtain a developed mixture (Fe₄[N] + γ') - phases and INZ. In the zone of internal nitriding during prolonged oxidation, low-nitrogen nitride of the γ'-phase develops well in the form of a lamellar structure mixed with Fe₄[N].

The oxidation process of the nitride layer is necessary in the temperature range 550-570 °C, which is in good agreement with the temperature range of transformation of retained austenite into martensite and the phase diagram for the “Fe-O” system, with the formation of an oxide consisting only of Fe₃O₄ on the surface.

During the oxidation of the nitride layer, the INZ depth continues to increase with the formation of both solid solutions and nitrides of the base metal and alloying elements due to the high-nitrogen nitride layer.

By combining the nitriding process with subsequent oxidation in water vapor by regulating one or another parameter at each stage of the process, it is possible to achieve a diffusion surface-hardened layer consisting of oxide, nitride, carbonitride, oxycarbonitride layers and a developed zone of internal nitriding of solid solutions and base metal
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