



ACADEMICIA
An International
Multidisciplinary
Research Journal
 (Double Blind Refereed & Peer Reviewed Journal)



DOI: 10.5958/2249-7137.2021.00910.1

MICRO STRUCTURAL AND X-RAY ANALYSIS OF NITRO-OXIDATED ANTENED STEELS

Eshkobilov Kh.K*; Berdiev Sh. A; Kamolov B.S*****

*Associate Professor,
 Candidate of Technical Sciences,
 Karshi Engineering and Economic Institute,
 UZBEKISTAN

**Senior Teacher,
 Karshi Engineering and Economic Institute,
 UZBEKISTAN

***Independent Researcher,
 Karshi Engineering and Economic Institute,
 UZBEKISTAN

ABSTRACT

The article examines the structural and phase changes of surface diffusion nitride-oxide coatings obtained in the process of nitriding in a gas medium followed by oxidation in water vapor of ferrite-pearlite steels, as well as the effect of phase changes on corrosion properties. The combination of the process of gas nitriding in an ammonia medium followed by oxidation in water vapor (nitro-oxidation) consists in the fact that at the first stage of saturation, nitriding is carried out in a gas atmosphere, and at the second stage, the nitride layer is oxidized in superheated steam.

KEYWORDS: *Ferrite, Pearlite, Nitriding, Oxidation, Diffusion Coating, Nitride Layer, Oxide Layer, Corrosion Resistance.*

INTRODUCTION

During nitriding of metals and alloys, multiphase surface diffusion coatings are formed on the surface of the work piece, consisting of a nitride zone and an internal nitriding zone, which provides a wide range of physic mechanical and physicochemical characteristics of nitrated materials. In order to expand the field of application of nitriding, combinations of the process

with other methods of surface hardening are used. At the same time, the intensification of the process, regulation of the structure and structure, as well as modification of the phase composition of the surface nitride layer with the achievement of the required property, taking into account the specific operating conditions of the processed product [1-4], is achieved.

Although the combination of the nitriding process with other methods of chemical-thermal treatment is carried out in a parallel or sequential scheme, in all cases the formation of the surface nitride layer during nitriding depends on the potential of the saturating medium; compositions of nitriding gas and nitriding alloy. During nitriding, according to the “iron-nitrogen” phase diagram, a nitride layer is formed on the surface of the work-piece, consisting of ϵ -phase, $(\epsilon+\gamma')$ - phase and γ' - phase. Under the high-nitrogen ϵ -phase, there is a mixture, followed by a thin γ' -phase. The boundary advancement of the γ' -phase significantly increases the average nitrogen content in the zone of internal nitriding [5-6].

THE MAIN FINDINGS AND RESULTS

When the nitriding process is combined, of all known saturating media, the most dynamic are gaseous atmospheres, which make it possible to obtain any structural sets and a different range of depths of diffusion layers. 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. At the initial stage of diffusion, the nitrogen concentration corresponds to the formation of a high-nitrogen nitride layer (ϵ -phase) with a change in the value of the nitrogen potential in the atmosphere; the phase composition of the nitride layer also changes. The final structures and phase components of the nitride layer are obtained after cooling the nitride layer [7-9].

The combination of the process of gas nitriding in an ammonia medium followed by oxidation in water vapor (nitro-oxidation) consists in the fact that at the first stage of saturation, nitriding is carried out in a gas atmosphere, and at the second stage, the nitride layer is oxidized in superheated steam. As a result of oxidation of the nitride layer, nitride, carbo-nitride, oxy-carbonitride layers and a zone of internal nitriding with an enriched γ' -phase are obtained, which are each responsible for certain corrosion or wear-resistant properties [10-12].

To improve the service characteristics of products made of low-carbon steels, the difference in the physicochemical properties of the structure - ferrite and pearlite in the steel matrix, especially in the surface zone, requires the need for chemical-thermal treatment to obtain diffusion coatings in terms of increasing their corrosion properties in atmospheric conditions and wear resistance under various conditions of friction. One of the ways to achieve this goal is to obtain an equilibrium structure of the diffusion nitride-oxide layer on low-carbon steel products.

Carrying out the process of gas nitriding in partially dissociated ammonia at temperatures closer to the eutectoid temperature for the “Fe-N” system accelerates the nitriding process and reduces the nitrogen content in the ϵ -phase due to its intense migration into the depth of the layer. In this case, the surface hardness slightly decreases, but the physical and mechanical properties of the surface layer itself do not decrease. The nitrogen concentration in the ϵ - and γ' -phases at a given temperature and the phase composition of the diffusion layer are determined by the nitrogen potential of the atmosphere [2].

By changing the parameters of the atmosphere, it is possible to regulate the structure and phase composition of the layer, by changing the ratio of nitride phases in the nitride zone and by

forming an oxide film of Fe_3O_4 at the final stage of the process. The atmospheric potential is a thermodynamic quantity and indicates the possibility of forming a layer of a given phase composition and a certain concentration of saturating elements. When carrying out the nitro-oxidation process in a production environment, it is very difficult to measure the partial pressure in the furnace. In this regard, the nitrogen potential is usually controlled by the change in the dissociation of ammonia in the furnace atmosphere [13-14].

By maintaining the nitrogen potential at the level of nitrogen solubility in one or another phase, a layer consisting of iron nitrides and alloying elements can be formed on the surface of metals and alloys, and it is also possible to form an γ' -phase (low nitride) or ϵ -phase with low nitrogen content.

METHODS

To develop a production controlled technology of the process and the theoretical foundations of the technology of the combined nitriding process followed by oxidation in water vapor for surface hardening of low-alloy steel, the dependences of the composition and structure of the nitrided and oxide layers on the chemical composition of steels and technological parameters of the process were studied. Investigated industrial steels 20, 45 and 40X after annealing with a ferrite - pearlite structure.

During nitrooxidation to obtain the required effective thickness of the diffusion surface nitride layer, nitriding is carried out at a temperature of 500-580⁰C with an exposure of 3-5 hours. Metallographic analysis of the treated steel samples was carried out on transverse sections using a Neophot-21 light microscope.

The qualitative phase X-ray diffraction analysis of the diffusion nitride and nitride-oxide layers was studied using a Dron-3 diffract meter using filtered cobalt $K\alpha$ - radiation. The general corrosion resistance of the treated samples was investigated in a 3% NaCl solution.

RESULTS AND DISCUSSIONS

During nitriding followed by oxidation, a combined diffusion layer is formed, consisting of a surface oxide zone, a carbo-nitride and oxy-carbonitride zone, followed by a diffusion sublayer - an internal nitriding zone (INZ). In all cases, at the first stage of saturation, predominant nitrogen diffusion occurs, and the structure and phase composition of the diffusion nitride layer is determined by the phase diagram for the "Fe-N" system.

Since during the interaction of ferrite and pearlite with the environment in separate phases, due to the difference in electrode potentials, anodic and cathodic reactions occur; which cause electrochemical corrosion, as well as the difference in plastic properties and hardness of the phases, sharply reduce the surface physical and mechanical properties during their operation.

From a theoretical point of view, on steels the main structures of which are grains of ferrite and pearlite, due to the difference in the rate of diffusion processes during nitriding, the formation of a nitride layer over the depth of the metal occurs unevenly. Therefore, in order to obtain a uniform controlled nitride layer during gas nitriding in an atmosphere of dissociated ammonia, subsequent oxidations of the nitride layer in water vapor were carried out to obtain a thin oxide layer.

During gas nitriding in dissociated ammonia at saturation above the eutectoid temperature (5910C) for the “iron-nitrogen” system, the resulting diffusion nitride layer, depending on the cooling method, consists of a porous $\xi + \varepsilon$ -phase, $\varepsilon + \gamma'$ -phase, γ -phase and it is followed by a zone of internal nitriding (Figure 1, a). The high-nitrogen $\xi + \varepsilon$ -phase has a columnar structure and upon cooling it is easily oxidized by atmospheric oxygen and always forms a thin porous oxide film consisting of Fe_2O_3 on its surface.

Oxidation of a nitride layer obtained at a higher eutectoid temperature always leads to its oxidation along the wall of columnar nitrides and, due to the porosity of the formed oxide layer, the rate of the denitro-genation process will always be higher than the rate of oxidation. When the nitride layer is oxidized in these temperature ranges, the total thickness of the nitride layer decreases due to the dissociation of the high-nitrogen nitride.

A mixture of the $\varepsilon + \gamma'$ -phase in the nitride layer is formed during the cooling period, due to the difference in nitrogen concentration along the depth of the layer (Figure 1, a). The formation of the γ -phase is characteristic of the nitride layer obtained at a higher eutectoid temperature. Especially, the formation of the γ -phase occurs with a decrease in the carbon content in the steel matrix, since the presence of carbon in the matrix participates in the formation of a nitride layer of a carbo-nitride nature and upon cooling, some part of the γ -phase closer to the internal nitriding zone transforms into carbo-nitride or γ' -phase in a mixture with the zone internal nitriding.

In low-carbon steels, the zone of internal nitriding formed in a mixture with the γ -phase, during saturation, practically does not have a significant effect on any properties of the processed material (Figure 1, a). By choosing certain methods of cooling in the zone of internal nitriding in the boundary of the pearlite part, it is possible to obtain martensite, bainite, or depleted retained austenite in the ferritic part.

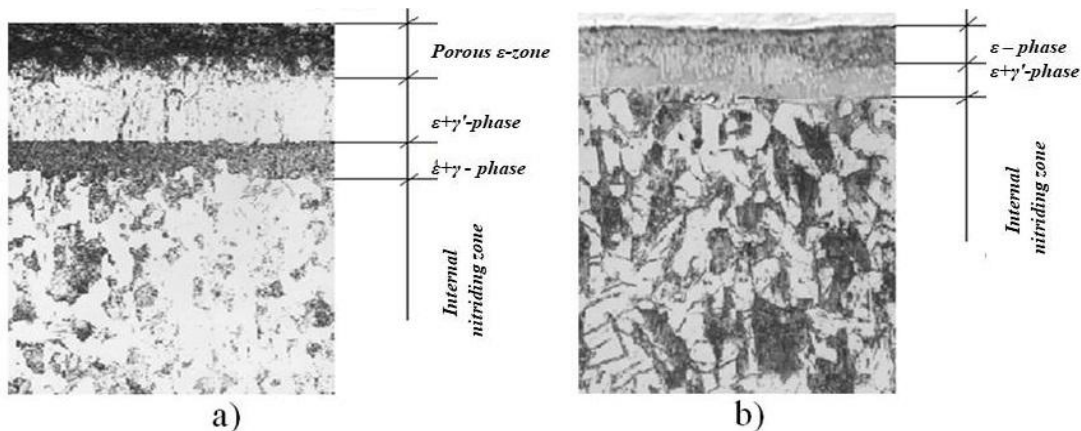


Figure 1. Microstructure of steel 20 after nitriding at a temperature of 6200C (a) and 580⁰C (b) in a dissociated atmosphere for 3 hours.

When nitriding below the eutectoid temperature (580⁰C), a denser structure is formed on the surface of steel 20 than the nitride layer obtained at a higher eutectoid temperature (Figure 1, b). The surface ε -phase has fewer pores, consists of a mixture of high-nitrogen nitride and carbo-nitride phases, and carbo-nitrides are formed by the diffusion of atomic nitrogen from the

saturation medium and the simultaneous decarburization of the steel matrix in the zone of the nitride layer.

The mixture of $\varepsilon + \gamma'$ -phases forming behind the high-nitrogen ε -phase in the nitride layer, the forming during the cooling period has dispersed structures due to the uneven distribution of carbon in the steel matrix. Since the carbon content in ferrite is 0.02% C, and in pearlite 0.8% C. At saturation below the eutectoid temperature for the "iron-nitrogen" system, the γ -phase is not formed (Figure 1, b).

The composition of the zone of joints formed on low-carbon steels during processes of their saturation with nitrogen from the saturating atmosphere and carbon from the pearlite part due to its decarburization has a significant effect on the structure and phase composition of the nitride layer and on the performance characteristics of the hardened products. Determination of the composition of the nitride and carbonitride zones depending on the parameters of the saturating atmosphere in the range of certain temperatures is very difficult due to the different shapes and dimensions of ferrite and pearlite in the structure of the work-piece.

In the process of subsequent oxidation in water vapor of the nitride layer obtained at a lower eutectoid temperature (Figure 2, a), a thin oxide layer is formed on the surface of the nitride layer due to denitrogenation of the nitride layer (Figure 2, a and b).

A denser nitride layer for its further oxidation is obtained at a nitriding temperature below the eutectoid temperature with a stepwise change in the degree of dissociation of ammonia. Since at the beginning of the process it is desirable to withstand a low nitrogen potential due to the activity of the treated surface until the concentration of nitrogen in the diffusion layer is obtained within the formation of the ε -phase.

In the diffusion layer, after reaching the nitrogen concentration corresponding to the formation of a high-nitrogen nitride phase in an atmosphere of constant nitrogen potential, the process of decarburization of the matrix is accelerated in the opposite direction to the diffused atomic nitrogen, as a result of which the rate of nitrogen diffusion decreases. In this case, on the surface, the probability of the formation of molecular nitrogen and the accumulation of carbon from the matrix causes micro-porosity of the formed layer.

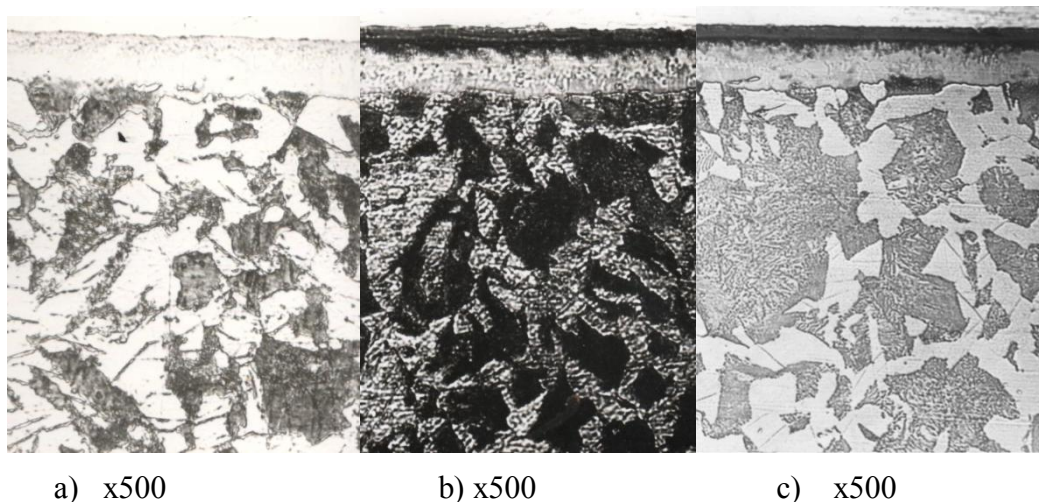
The subsequent increase in the nitrogen potential ensures a constant rate of nitrogen diffusion through the nitride layer. In this case, boundary diffusion of carbon from pearlite towards ferrite occurs due to the displacement of the atmosphere by nitrogen. The redistribution of nitrogen and carbon in the ferrite and pearlite zones favorably affects the formation of a carbonitride layer, both in the ferrite and pearlite parts of the formed surface nitride layer, giving them the same carbonitride character. As a result of such a change in the nitrogen potential of the saturating atmosphere during nitriding, it is possible to obtain a denser structure of a mixture of ε -phase nitride and ε' -phase carbonitride in the surface layer for its further oxidation (Figure 2, a).

After oxidation of the nitride layer in water vapor, an oxide layer forms on the surface of the nitride layer due to denitrogenation of the nitride layer, and at the same time diffusion of an oxygen atom into the interior of the nitride layer occurs.

When nitriding is combined with subsequent oxidation in water vapor during saturation of the nitride layer with carbon of the steel matrix, a carbonitride ε' -phase is formed, and then, due to

the diffusion of oxygen in the carbonitride phase during oxidation, an oxycarbonitride ϵ'' -phase is formed [9, 12].

During oxidation with the achievement of the required density of the oxide layer counteracting denitrogenation and decarburization of the matrix under the oxide layer, depending on the concentration of nitrogen, carbon and oxygen, upon cooling of the nitride layer, mixtures of ϵ -, ϵ' - and ϵ'' -phases are formed, followed by $\epsilon'' + \gamma'$ -phases (Figure 2, b and c).



a - nitriding at a temperature of 580°C for 3 hours; b - nitriding at a temperature of 580°C for 3 hours; subsequent oxidation at a temperature of 580°C for 0.5 hour; c - nitriding at a temperature of 580°C for 3 hours; subsequent oxidation at a temperature of 550°C for 1.0 hour.

Figure 2. Microstructure of steel 20 after nitriding (a) and nitrooxidation (b and c).

The oxide film obtained on the nitride surface at a higher eutectoid temperature for the “iron-oxygen” system (570°C) has a micro-porous structure, and wustite (FeO) is also detected on X-ray diffraction patterns upon rapid cooling (Figure 3, a). With slow cooling, wustite is not detected on X-ray diffraction patterns, because when the processed sample is slowly cooled, most likely wustite decomposes according to the formula: $\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}\alpha$.

The nitride layer located under the oxide layer has a heterogeneous structure due to a mixture of carbonitride and oxycarbonitride phases, due to the microporosity of the oxide layer. Since the denitrogenation process in a microporous oxide film remains long and with an increase in the thickness of the oxide film, the activity of carbon during decarburization will be greater than the diffusion of oxygen through the barrous oxide layer.

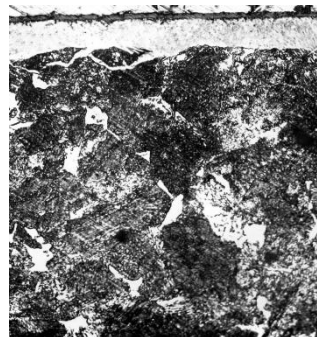
In order to avoid the formation of wustite and the formation of equiphase structures of nitride and magnetite monoxide (Fe_3O_4), the oxidation process must be carried out at a lower eutectoid temperature for the “iron-oxygen” system, in particular in the temperature range 500-550°C (Figure 2, c). In this case, the resulting oxide layer has a dense structure and consists of one oxide Fe_3O_4 , and the resulting oxide layer acts as a barre layer preventing denitrogenation, since due to the dissociation of the high-nitrogen ϵ -phase, a more uniform distribution of nitrogen, carbon and oxygen in the nitrided layer with uniform and constant the formation of the oxycarbonitride layer of the ϵ'' -phase at different durations of the oxidation process (Figure 2, b).

The study of the microstructure and X-ray diffraction analyzes of the nitrooxidation process on steels 45 and 40X also confirms the formation of a uniform oxide layer consisting of Fe_3O_4 monoxide and a mixture of a surface oxide film of a nitride layer in a mixture of an oxycarbonitride ϵ'' -phase and γ' -nitride, it is possible to obtain a uniform nitride layer on the surface of ferrite and pearlite on annealed steels (Figure 3, a and b).

For surface hardening of parts operating in a corrosive environment, for wear at low contact loads, a nitrooxide layer is used; consisting of a developed nitride zone and a thin surface oxide zone, which provides better wearing-in of rubbing surfaces and corrosion resistance. Low-nitride layer consisting of ϵ' - , ϵ'' - - and γ' -phases, therefore, for the formation of a carbonitride layer on the ferrite surface, it is necessary to set the oxidation time of the nitride layer based on the diffusion of carbon from the pearlite part to the ferrite part; to obtain a uniform carbonitride or oxycarbonitride layer under the oxide layer.



a) x500



b) x500

a - nitriding at a temperature of 580°C in an ammonia atmosphere with a degree of dissociation of ammonia $\alpha = 45\text{-}60\%$ and followed by oxidation at a temperature of 550°C for 0.5 hours. b - nitriding at a temperature of 580°C in a mixture of $0.75\% \text{NH}_3 + 0.25\% \text{H}_2$ for 3 hours and followed by oxidation at a temperature of 550°C for 0.5 hours.

Figure 1. Microstructure of steel 45 (a) and 40X (i) after nitrooxidation.

In the process of nitrooxidation, the formation and uniformity of the surface diffusion nitride layer is significantly influenced by the presence of carbon in the steel matrix. In this case, carbon is in a free form in the matrix during the decarburization of pearlite and directly affects the development of the nitride layer by the formation of carbonitride phases during the nitriding process and oxycarbonitride phases during the oxidation of the nitride and carbonitride layers.

For parts operating under fatigue conditions at elevated temperatures, a nitride layer is used - an oxide layer with a developed diffusion sublayer of the internal nitriding zone, and for tools operating under dynamic wear and shock loads on the surface, an internal nitriding zone is formed without a brittle surface nitride layer.

It is known that nitrides have a high affinity for oxygen and the thermodynamic assessment of the interaction of iron and its nitrides with oxygen proved that iron nitrides interact more actively with oxygen than iron.

The dependences of the time of appearance of the first foci of corrosion in a 3% aqueous solution of NaCl for samples with a nitride – oxide coating were studied. With an increase in the amount

of γ' -phase in the nitride zone, the time until the first corrosion centers appear, reaching up to 450 hours. A further increase in the amount of γ' -phase is accompanied by a decrease in corrosion resistance. The presence of an oxide layer has a positive effect on the corrosion properties of the layer. It should be noted that in the experiments carried out, the thickness of the oxide zone was 1-5 microns.

Subsequent oxidation of the 13-phase in water vapor at a temperature of 540-550 ° C for 0.5-1 hour on the surface can obtain a uniform oxide layer with a thickness of 1-3 microns. The obtained nitroxide layer possesses the best corrosion properties, the time of appearance of the first centers of corrosion on which is 1056 hours.

The most corrosive properties are possessed by a nitride layer consisting of a mixture of ϵ' -, ϵ'' - and γ' -phases with a surface oxide layer consisting of Fe_3O_4 . This asserts that during the oxidation of the nitride layer, it is important to grow the nitride sublayer with the formation of lower nitride ϵ' -, ϵ'' - and γ' -phases due to the high-nitrogen 16-phase obtained during nitriding at the first nitriding stage.

CONCLUSION

The research results show that:

- The required structure and phase composition of the nitride-oxide layer is achieved under optimal processing conditions, with the production of low-nitrogen ϵ' -, ϵ'' - and γ' -phases and a surface layer of Fe_3O_4 oxide with a thickness of 1-5 microns.
- nitrooxidation of annealed steels with a ferrite - pearlite structure, it is possible to obtain a uniform surface diffusion layer with the required ratios of nitrogenous phases in the nitride layer;
- corrosion resistance depends on the ratio of nitride phases, the oxide layer consisting of Fe_3O_4 has the best adhesion strength.

Each obtained phase or phase mixtures are responsible for certain conditions of the physico-mechanical and physicochemical properties of the processed products, therefore, taking into account the operating conditions of the parts and setting the technological parameters of nitro-oxidation, it is possible to increase their reliability and durability.

REFERENCES

- [1] Lakhtin Yu. M., Kogan Ya. D. (1976) *Steel nitriding*. – Moscow: Mechanical engineering. – p. 256. (Лактин Ю. М., Коган Я. Д. Азотирование стали. – М.: Машиностроение, 1976. -256 с.)
- [2] Lakhtin Yu. M., Kogan Ya. D., Shpis GI, Bemer Z. (1991) *Theory and technology of nitriding*. – Moscow: Metallurgy. – p. 320. (Лактин Ю. М., Коган Я. Д., Шпис Г. И., Бемер З. Теория и технология азотирования. М.: Металлургия. 1991. 320 с.)
- [3] David Pye. (2003) *Practical Nitriding and Ferritic Nitrocarburizing*. ASM Publication. – p. 256.
- [4] Vanes S. E. (1984) The Nitrotec surface treatment process // *Met. and Mat.* V.1. № 4. – pp. 238-243.

- [5] KoganYa.D., EshkabilovKh.K. (1992) Combination technology for obtaining nitride-oxide coatings on structural steels /*Scientific and Technical Conference on Complex Methods for Enhancing Reliability and Durability of Production Equipment Parts*/ Russian, Penza. – p. 14.
- [6] EshkabilovKh.K. (1992) Development of technology for nitrooxidation of machine parts operating under wear and corrosion conditions. Candidate of Technical Sciences. - Moscow. (ЭшкабиловХ.К. Разработка технологии нитрооксидирования деталей машин работающих в условиях износа и коррозии /Дисс. на соиск. уч. степ. к. т. н./ Москва, 1992.)
- [7] LakhtinYu.M. (1994) Oxygenation (Nitrooxidation) // *Metal Science and Heat Treatment of Metals*. No. 9. – pp. 2-5 (ЛахтинЮ. М. Оксизотирование (Нитрооксидирование) // *Металлургия*. 1994, №9. -С. 2-5)
- [8] EshkabilovKh.K., BerdievSh.A. (2016) Changes in the structure and composition of the nitride layer upon oxidation with water vapor // *Young Scientist*, No. 14. – Moscow. – pp. 204-207. (Эшкабилов Х.К., Бердиев Ш.А. Изменение структуры и состава нитридного слоя при оксидировании парами воды // *Молодой ученый*, №14// Москва, 2016. –С. 204-207.)
- [9] David Pye. (2003) *Practical Nitriding and Ferritic Nitrocarburizing*. ASM Publication. –p. 256.
- [10] KoganYa.D., EshkabilovKh.K. (1992) Obtaining diffusion nitride-oxide coatings by combined CTO technology. // *Materials and hardening technologies. Abstracts of reports. Republic scientific-technical conference*. - Kursk. – p. 66. (КоганЯ.Д., ЭшкабиловХ.К. Получение диффузионных нитрид-оксидных покрытий комбинированной технологией ХТО. // *Материалы и упрочняющие технологии. Тезисы докл. респ. науч.-техн. конф.*-Курск, 1992. – с.66.)
- [11] EshkabilovKh.K., EshkabilovO.Kh., BerdievSh.A. Corrosion resistance of steel 45 after nitrooxidation / Collection of scientific articles of the international scientific and technical conference dedicated to the 150th anniversary of the birth of Academician A.A. Baikova / *Modern problems and directions of development of metallurgy and heat treatment of metals and alloys*. –Kursk. September 18, 2020. – pp. 266-270. (ЭшкабиловХ.К., ЭшкабиловО.Х., БердиевШ.А. Коррозионная стойкость стали 45 после нитрооксидирования /Сборник научных статей международной научно-технической конференции, посвященной 150-летию со дня рождения академика А.А. Байкова/ *Современные проблемы и направления развития металловедения и термической обработки металлов и сплавов*. Курск, 18 сентября 2020 года. –С. 266-270.)
- [12] Kh.K.Eshkabilov, Sh.A.Berdiyev, B.Kamolov. Hardening of cutting tools by combined gas nitriding method. IOP Conference Series: Materials Science and Engineering, Volume 1030, VII *International Scientific Conference "Integration, Partnership and Innovation in Construction Science and Education"* (IPICSE 2020) 11th-14th November 2020, Tashkent, Uzbekistan. doi:10.1088/1757-899X/1030/1/012019.
- [13] LakhtinYu.M., KoganYa.D., Koltsov V.E., EshkabilovKh.K. (1992) *Method for chemical-thermal treatment of steel products. International patent certificate: SU 1765251 A1*. Moscow Automobile and Highway State Technical University, - Moscow. (Лахтин Ю.М., Коган Я.Д.,

Кольцов В.Е., Эшкабилов Х.К. Способ химико-термической обработки стальных изделий. Международная патентная свидетельства: SU 1765251 А1. МАДИ, Москва, 1992.)

[14] Eshkabilov Kh.K., Yurshev V.I. Nitrooxidation of steel products. / Materials of the All-Russian scientific and methodological conference. / *The university complex as a regional center of education, science and culture*. Orenburg, January 23-25, 2020. – pp. 787-793. (Эшкабилов Х.К., Юршев В.И. Нитроокисления стальных изделий. / Материалы Всероссийской научно-методической конференции. / Университетский комплекс как региональный центр образования, науки и культуры. Оренбург, 23–25 января 2020 года. –С. 787-793.)