Web of Scientists and Scholars: Journal of Multidisciplinary Research

Volume 3, Issue 5, May - 2025 **ISSN (E):** 2938-3811

COMBINED TECHNOLOGY OF THE PROCESS OF GAS NITRIDING WITH SUBSEQUENT OXIDATION IN WATER VAPOR OF LOW- AND MEDIUM-CARBON STEELS

Sh. A. Berdiev
Senior Lecturer, Karshi State Technical University, Karshi

Abstract
Increasing the corrosion resistance of a large number of metal products made from ordinary quality steel and ordinary low-carbon steel, from low-alloy structural steels, as well as rolling obtained by industrial smelting, made from structural steels and operating under low contact loads in conditions of atmospheric corrosion can be achieved by a combined low-temperature nitriding process.

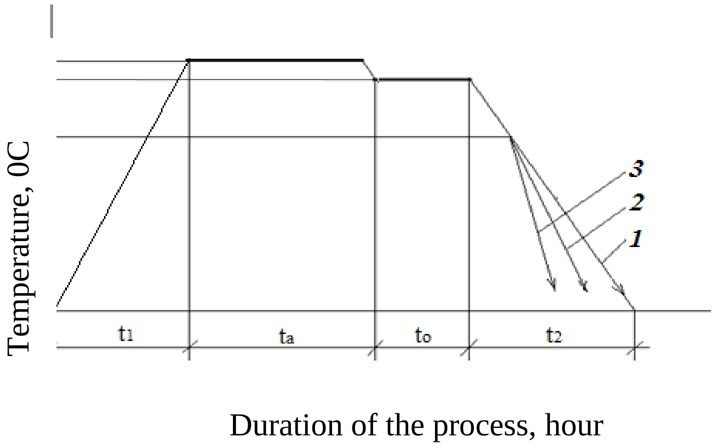
Keywords: Ferrite, pearlite, nitriding, oxidation, diffusion coating, nitride layer, corrosion resistance.

Introduction

The process flow diagram of the combined nitroxidation process is shown in Fig. 1.

When carrying out the nitroxidation process according to the given process flow diagram, the following options were adopted:

- nitriding at the hypereutectoid temperature (620 ± 10^0C);
- nitriding at the hypereutectoid temperature (620±100C) and oxidation at temperatures: $T_2 = 580\pm10^0$C and $T_3 = 550\pm10^0$C;
- nitriding at hypoeutectoid temperature $T_2 = 580^0$C; - nitriding at hypoeutectoid temperature (580 ± 10^0C) and oxidation at temperatures: $T_2 = 580\pm10^0$C and $T_3 = 550\pm10^0$C.



T1 = 580 ^{0}C, T2 = 550 ^{0}C, T3 = 550^{0}C, T4 = 400 ^{0}C, t1 – heating time; ta – nitriding time, to – oxidation time, t_2 – cooling time. 1 – cooling with furnace, 2 – cooling in oil, 3 – cooling in water.

Figure 1 - Flow chart of the continuous-sequential two-stage nitroxidation process.

During cooling after the nitroxidation process, various cooling methods were used: cooling with a furnace (line 1), cooling in oil (line 2) and cooling in water (line 3).

Therefore, when carrying out the process, the actual saturation temperatures were measured with deviations within ±10^{0}C.

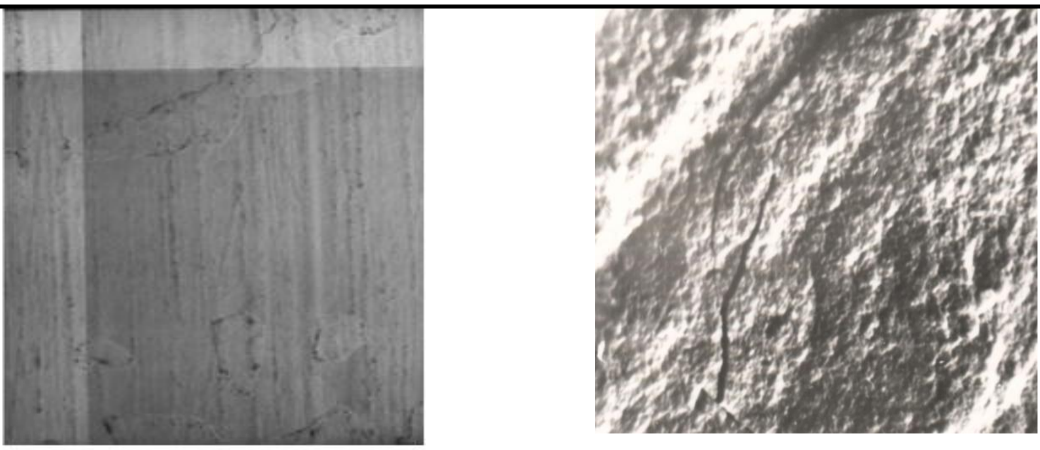
The technological scheme for carrying out nitroxidation includes the following technological operations:

- heating of parts in an atmosphere of dissociated ammonia to a temperature of 580°C ±10°C (T_a);
- isothermal holding (saturation) at this temperature with the degree of ammonia dissociation established for a given batch of parts taking into account their composition;
- oxidation in water vapor at a temperature (T_o) of 550±10°C;
- cooling.

The oxide layer obtained at an oxidation temperature of 580°C consists of a mixture of oxides. When cooled rapidly, such an oxide film cracks and peels off. In Fig. 2 it is evident that although after nitroxidation the surface is smoother than the surface of the nitrided sample, traces of local peeling and cracking of the oxide film are visible. The peeling of the oxide film along the interface with the nitride zone apparently occurs due to the formation of the FeO phase between the nitride layers and the oxide film. This is confirmed by the results of sclerometric analysis of the hardened surface nitride-oxide layer, in the presence of an oxide consisting of FeO between the nitride and oxide layers, due to which the oxide layer peels off from the nitride layer and peeling occurs (Fig. 3).

The morphology of the surface of nitroxidized samples when cooled in air to a temperature of 400 ^{0}C and subsequently in oil of the surface layer of oxides on samples with a nitride-oxide coating is more uniform, especially to some extent the rough surface is smoothed out after processing and the micropores are filled with oil during cooling (Fig. 4).

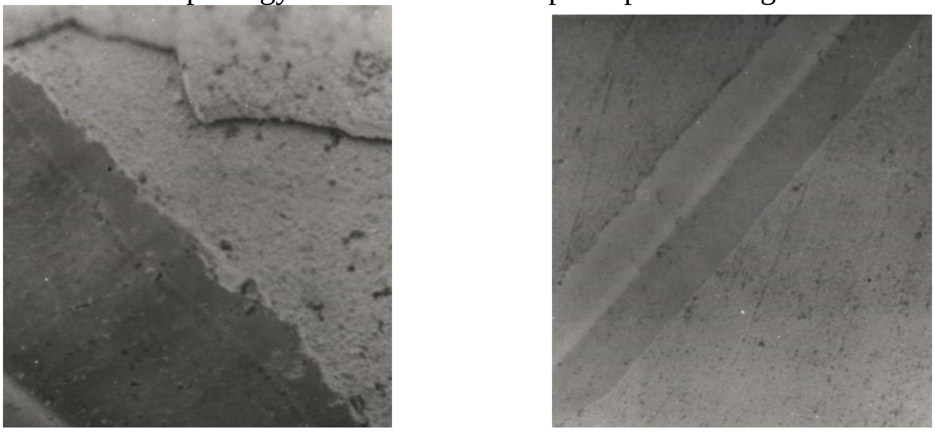
During nitroxidation, a combined diffusion layer is formed, consisting of a surface oxide zone, a carbonitride and oxycarbonitride zone, and then a diffusion sublayer follows – the internal nitriding zone (INZ). In all cases, at the first stage of saturation, predominant diffusion of nitrogen occurs,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



a) x1000 b) x1000

a – peeling, upon cooling in air, nitroxidation at a temperature of 580⁰C; b – cracking upon cooling in air, nitriding at 580⁰C and oxidation at 550⁰C.

Figure 2 – Surface morphology of nitroxidized samples upon cooling in air.

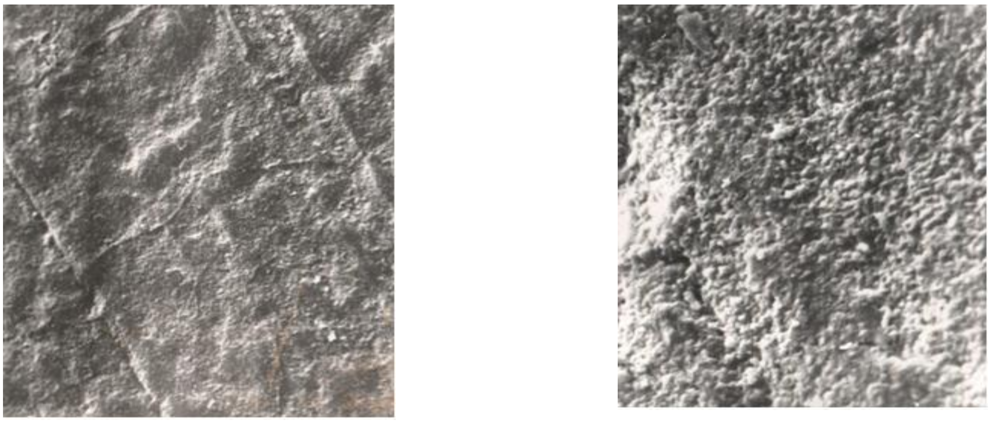


a) x1000 b) x500

a – peeling of the oxide layer obtained at a temperature of 580⁰C;

b – without defects when cooling in oil, oxidation at 550⁰C.

Figure 3 – Sclerometric analysis of the surface layer of oxides on samples with a nitride-oxide coating.



a) x1000 b) x1000

a – nitriding at a temperature of 580⁰C and oxidation at 550⁰C on samples with a more uniform surface;

b – nitriding at a temperature of 580^{0}C and oxidation at 550^{0}C on samples with a rough surface.
Figure 4 – Morphology of the surface of nitroxidized samples when cooling in oil in air of the surface layer of oxides on samples with a nitride-oxide coating.

In the process of gas nitriding, regulation of the structure of the nitrided layer is achieved by increasing the temperature and using mixed atmospheres by diluting ammonia with nitrogen, hydrogen, nitrogen-hydrogen-containing mixtures, oxygen, air, etc.

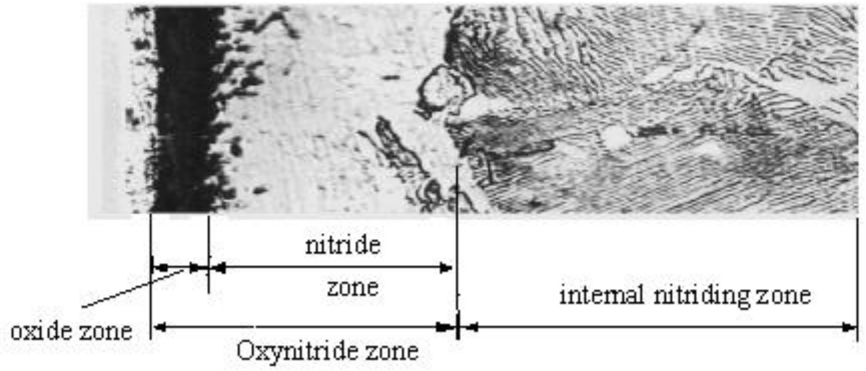


Figure 5 - Structure of the nitroxidized layer

Regulation of the phase composition and structure of the surface oxide layer to obtain the required nitroxidized layer with specified operational properties; subsequent oxidation is carried out in an atmosphere of air, oxygen, water vapor and with the addition of other oxygen-containing components.In operational terms, each zone of the nitroxidized layer has certain service characteristics.

Recently, for surface hardening of parts operating in a corrosive environment, for wear under low contact loads, a nitride-oxide layer has been used, consisting of a developed nitride zone and a thin surface oxide zone, which provides better running-in of rubbing surfaces and corrosion resistance.

Here, preference is given to the subsurface nitride zone, consisting of the ε-phase and the γ′-phase; it is desirable to obtain the ε-phase with a lower nitrogen content, having a carbonitride or oxycarbonitride character.

It is known that nitrides have a high affinity for oxygen and thermodynamic assessment of the interaction of iron and its nitrides with oxygen has proven that iron nitrides interact more actively with oxygen than iron (Fig. 6).

The calculated isobaric-isothermal potential of the reaction of oxide formation at 500 °C is $\Delta G^o_т$ =209-293 kJ/mol, for $Fe_{2\text{-}3}N$ $\Delta G^o_т$ = 481-711kJ/mol and for Fe_4N is $\Delta G^o_т$ = 878-1463 kJ/mol. The resulting nitroxide zones are more plastic than the oxide films of Fe_2O_3 on the metal matrix.

The nitride zone with high surface characteristics consists of γ’ (Fe_4N) and ε (Fe_3N) phases. The ε phase is depleted in nitrogen and is revealed by X-ray diffraction as two isomorphic phases: the isomorphic carbonitride phase, designated as the ε′ phase with lattice parameters:

a=0.269; c=0.436 nm, and the carbonitride phase with lattice parameters: a=0.267; c=0.436 nm.

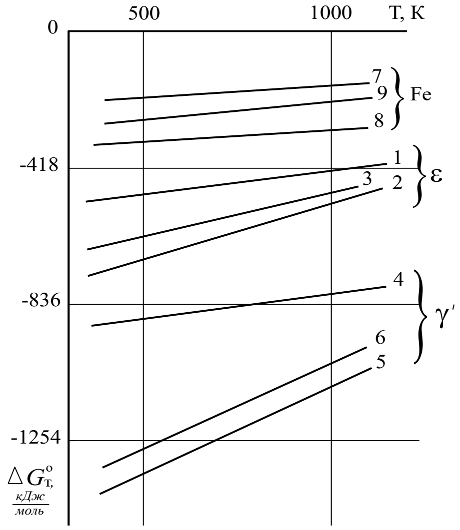


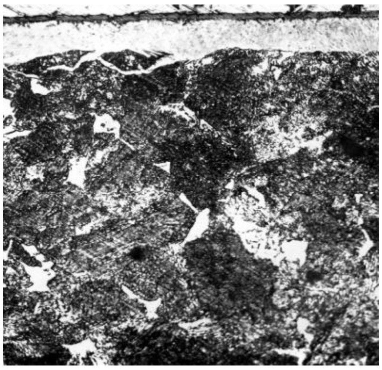
Figure 6. Dependence of isobaric-isothermal potentials of the oxidation reaction of iron nitrides on temperature.

As our studies have shown, the corrosion resistance of the nitroxidized layer depends on the ratio of γ'- and ε - phases in the nitride zone.

During nitroxidation, a composite layer consisting essentially of the γ'- phase can be obtained by a two-stage change in the nitrogen potential of the atmosphere at 560 - 580 °C, and preliminary dissociation of ammonia α_o = 25% with maintaining the dissociation of the ammonia mixture at saturation α = 55-75% and a duration of 1.5-3 hours.

The resulting nitride layer has a smooth and non-etching appearance, consisting mainly of the γ'-phase (Fig. 7). Subsequent oxidation of the γ'-phase in water vapor at a temperature of 540-550 °C for 0.5-1 hour on the surface can be obtained a uniform oxide layer with a thickness of 1-3 μm. The resulting nitride - oxide layer has better corrosion properties.

One of the rejection signs of nitrided parts is surface peeling associated with low plasticity, leading to the development of fatigue processes during elastic deformation and embrittlement during repeated plastic deformation.



x500

Figure 7. Microstructure of the nitroxide layer on 40X steel after nitriding at a temperature of 580^0C in a mixture of 0.75% NH_3+0.25% H_2 for 3 hours and followed by oxidation at a temperature of 550^0C for 0.5 hours.

The required structure and phase composition of the oxynitride layer is achieved under optimal processing conditions, with the production of a low-nitrogen ε′-phase (Fe_{2-3}(NC)), ε′′-phase (Fe_{2-3} (NCO)) and γ′-phase (Fe_4N) of a certain ratio with a thickness of 25-30 µm and a surface layer of Fe_3O_4 oxide with a thickness of 1-3 µm.

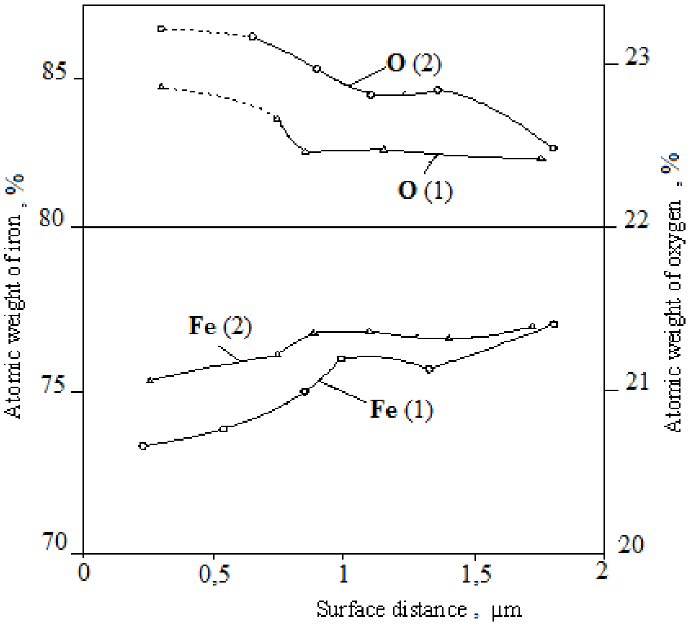
Figure 8 shows the microstructure of the oxynitride layer obtained by nitriding in an ammonia environment at 580°C for 3 hours and oxidized in water vapor with the addition of 5% HEDP at 550°C for 1.0 hour. In this case, a combined diffusion layer is formed, consisting of a dense surface oxide zone, a nitride zone, and a ZVA.

a) b)

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.

Figure 8. Microstructure of the nitroxide layer on steel 45.

Figure 9 shows the distribution of elements by the depth of the oxide layer of nitroxidized samples of grade 45 steel treated by nitriding at 580°C for 3 hours and oxidized for 1.0 hour in water vapor and in water vapor with the addition of 5% OEDF.



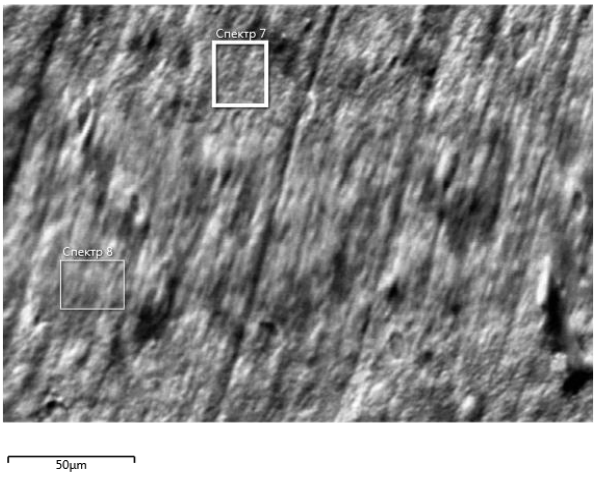
Nitriding at 580°C for 3 hours and oxidation: 1 - for 1.0 hour in water vapor; 2 - for 1 hour in water vapor with the addition of 5% OEDF. Steel 45.

Figure 9. Distribution of oxygen and iron by the depth of the oxide layer.

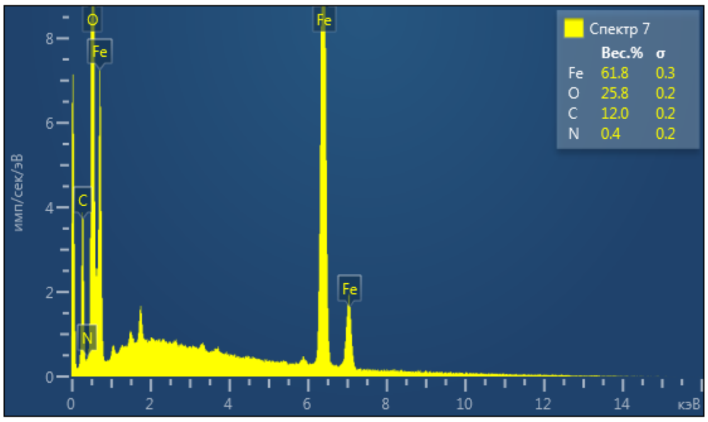
The formation of such a structure and composition of the oxide layer is probably due to the favorable condition of oxidation by oxygen located in the OEDP molecule, which provides the necessary oxygen potential of the saturating medium for the formation of an oxide layer consisting of almost one magnetite. The surface morphology and microstructure of the nitroxide layer were studied.

Two spectra were obtained in the image (Fig. 10, a). The study was carried out on nitroxidized samples with a diameter of 10 mm, made of steel 45 after their strengthening by nitriding and subsequent oxidation in water vapor.

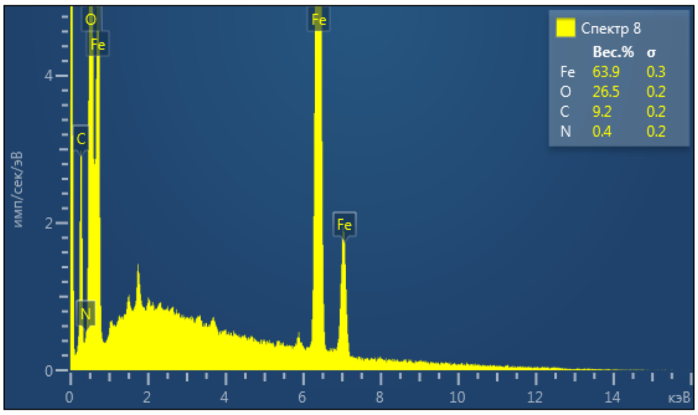
In order to determine the ratio of element concentrations on the surface of the nitroxide layer, spectrograms were taken at various points. The oxygen content on the surface is: in "spectrum 7" - 25.8%, and in "spectrum 8" - 26.5%. This confirms that on the surface the oxide consists only of Fe_3O_4, since at oxygen concentrations above 23.5% only Fe_3O_4 exists. (Fig. 10, a and b).



a)



b)



c)

a- surface morphology and spectral recording location; b- spectrogram from point "Spectrum 7"; c- spectrogram from point "Spectrum 8".

Figure 10. Morphology and spectrograms from the surface with a nitroxide layer of steel 45

What is important is the growth of the nitride sublayer into the depth of the nitrided layer with the formation of lower nitride ε′-, ε′′- and γ′-phases due to the high-nitrogen ε-phase obtained during nitriding at the first stage.

In order to clarify the nature of the nitride phase dissociation, the oxidation process of the nitride layer in water vapor with the addition of OEDF was carried out for 2.5 hours. The thickness of the oxide layer increases and the release of dispersed particles of nitride ε′-, γ′-phases is detected in the internal nitriding zone. Using the above-mentioned nitroxidation technology, samples of steel 20 were processed. The results of the surface layer study showed that after nitriding in the usual way (t_{az}=580°C, τaz=3 h, α=45-60%), the microhardness of the nitride layer in the ferrite part was HV=4.73 GPa, and in the pearlite part HV=6.35 GPa.

After nitroxidation over the entire surface, almost identical values of microhardness were obtained over the entire surface equal to HV=8.58 GPa. At the same time, the growth of the intensity of the lines of the ε′- and ε′′-phase of the nitride layer differs sharply from the intensity of the lines of the corresponding phases of the nitride layer obtained after nitriding.

Based on the data obtained, the following conclusions can be drawn:

- obtaining a nitride-oxide coating by nitriding at 580^0C in the first stage of the process and oxidation at 5500C, as well as by two-stage nitriding at the nitrogen potential in the first stage and oxidation in water vapor in the second stage, it is possible to achieve the desired results in regulating the phase compositions of both the nitride and oxide coatings;
- further development of research on regulating the phase composition of the nitride layer, with the achievement of the specified physicochemical and physicomechanical properties, it is necessary to study the processes of obtaining an optimal layer in terms of phase composition, structure, microporosity and formation rate, technologies combining a two-stage nitriding process using nitrogen potential followed by a steam oxidation process.

- by setting the time and selecting the saturating oxidation atmosphere, the necessary ratios of low-nitrogen phases in the nitride layer are achieved, which, together with the surface oxide layer, have the necessary properties;
- by regulating one or another nitroxidation parameter at each stage of the process, it is possible to obtain a diffusion surface layer consisting of oxide, nitride, carbonitride and oxycarbonitride nature;

Each obtained phase or phase mixture is responsible for certain conditions of the physical-mechanical and physical-chemical properties of the processed products made from low- and medium-carbon structural steels, taking into account their operating conditions.

References

1. Лахтин Ю.М. и др. Теория и технология азотирования. –М: Металлургия, 1981, 320 с.
2. Лахтин Ю.М., Коган Я.Д. Структура и прочность азотированных сплавов. – М., Металлургия, 1982, 176 с.
3. Гаврилова А.В. и др. // Металловедение и термическая обработка металлов., 1974. №3 С. 14-21.
4.Kh.K.Eshkabilov, Sh.A.Berdiyev, B.Kamolov.Hardening of cutting tools by combined gas nitridingmethod.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.
5. KholikulEshkabilov* ,SherzodBerdiyev .Structure and properties of the modified diffusion nitride-oxide surface layer //E3S Web of Conferences 264, 05054 (2021) https://doi.org/10.1051/e3sconf/202126405054 CONMECHYDRO - 2021