



Surface Structural–Phase Modification of Structural Steels during Gas Nitriding

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ABSTRACT: The formation of a composite nitride layer in an ammonia atmosphere with the addition of carbon– and oxygen–containing gases during gas nitriding is considered. The conditions for the formation of cementite during nitriding of steel and the influence of carbon in the matrix on the release of cementite are given. After oxidation of the nitride layer, modified nitride compositions with stable gradient structural–phase states were obtained.

KEYWORDS: carbonitride, cementite, corrosion, oxycarbonitride, diffusion nitride–oxide coating, nitride, reactive diffusion, lesions.

Recently, new chemical–thermal processes have been developed in the world mechanical engineering, in particular, combined methods of nitriding and its varieties, which make it possible to increase the operational reliability of machine parts and tools, their durability and instead of environmentally harmful galvanic methods of coating.

Nitriding as a method of surface hardening with obtaining a variety of modified diffusion compositions of nitride phases on various parts of machines and mechanisms made of steels and alloys is one effective and common method. Therefore, it has found the widest application in cases where the main reason for the destruction of parts is corrosion processes under the influence of the corrosive environment.

In order to regulate the structure and phase composition of the resulting surface diffusion nitrided layer and from the point of view of resource saving, various combinations of liquid, ionic and gas nitriding processes have been developed. Among them, more advanced, energy–saving, environmentally friendly processes that improve the quality of the resulting diffusion layer and control the phase composition of the nitride coating, depending on the required performance characteristics, taking into account the actual conditions of the parts, the combination of the gas nitriding process with other methods of surface saturation becomes more acceptable.

At present, a large number of various options for technological processes for obtaining diffusion nitride coatings have been developed. Despite the large number of options for technological processes of nitriding and methods for obtaining nitrogenous surface layers, the obtained nitride diffusion coatings have basically the same structure. The obtained ordinary diffusion layers can be characterized by the thickness of the diffusion zone, the concentration of saturating elements and the structure of the layer.

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When carrying out the process of gas nitriding followed by oxidation in water vapor (nitrooxidation), the intensification and quality of the formed nitrided layer at the first stage of nitriding depends on the degree of ammonia dissociation and temperature, as well as the composition of the saturating atmosphere. By changing these parameters, it is possible to achieve regulation of the phase composition and structure of the nitride layer, the formation of one or another composition of the composition of nitride phases in the surface diffusion zone. In this case, the quantitative content of carbon in the steel matrix is important, which participates simultaneously with nitrogen in diffusion processes during the decarburization period.

According to the “Fe–N” phase diagram, at a higher eutectoid temperature for the “Fe–N” system, a γ -eutectoid is formed, in general, depending on the degree of dissociation and temperature, a composite nitride layer consisting of ϵ - and γ' -phases is formed on the surface of the steel and an internal nitriding zone (Fig. 1). In this case, modification of the nitride layer with the formation of a different ratio of nitride phases and regulation of the structure of the diffusion layer is achieved by varying the nitrogen potential of the atmosphere.

During nitriding, diffusion processes proceed by the introduction and replacement of atoms of the storable element into the crystal lattice in the steel matrix, as well as by the boundary diffusion of atoms into the base metal.

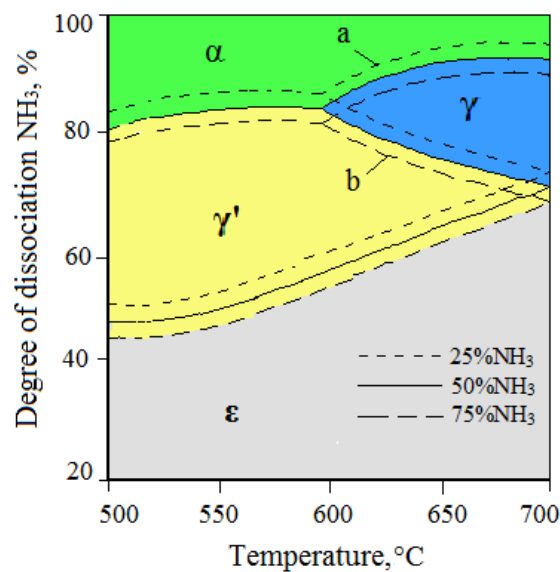


Fig. 1. Phase equilibrium of the “Fe–N” system in dissociated ammonia with additives of its preliminary dissociation

A layer consisting only of an internal nitriding zone (Fig.1, zone α) is formed while maintaining the nitrogen potential of the atmosphere at the level of the limiting solubility of nitrogen in α (γ') – solid solution and during saturation at a higher dissociation of base metal nitrides. In this case, it is necessary to take into account the factor that the nitrogen 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. However, the atmospheric potential does not give an estimate of the layer formation rate.

The nitrogen potential of the atmosphere of the medium depends on the saturation temperature, the degree of dissociation of ammonia and can vary over a wide range with the introduction of diluents gases and, depending on their chemical nature, a modification of the phase composition and structure of the diffusion nitride coating is achieved. In this case, when adjusting the nitrogen concentration in the nitride layer and doping with carbon, oxygen and simultaneously doping with oxygen and carbon of the nitride layer, it gives a range of possibilities for modifying the nitride coating, with the formation of gradient layers with different structural and phase states. In this case, the formed gradient of structural–phase states of the surface diffusion coating determines the physicochemical and physico–mechanical properties of the hardened product.

To carry out controlled low–temperature short–term nitriding processes with modification of the nitride layer on the steel surface, when used as a saturating atmosphere in a mixture of ammonia diluted with its preliminary dissociation products (Fig. 1), as well as with inert gases and with additives of carbon and oxygen–containing gases, the stability of high–nitrogen gases increases nitride phases and expands the area of their existence on the phase equilibrium diagrams of the “Fe–N” system (Fig. 1., a and b).

During gas nitriding in an ammonia atmosphere with the introduction of carbon–containing gases, cementite (Fe_3C) is formed along with nitride phases, and an increase in the concentration of hydrocarbon components expands the region of existence of Fe_3C and ϵ -phase. In the region of the zone, the presence of cementite and ϵ -phase due to their mutual solubility on the basis of cementite, nitrocarbide alloyed with nitrogen of the $\text{Fe}_3(\text{NC})$ type is formed and on the basis of the ϵ -phase alloyed with carbon – carbonitride $\text{Fe}_{2-3}(\text{CN})$ (ϵ' -phase). In the presence of oxygen in the composition of the saturating medium, the formation of a phase of nitrides doped with oxygen is possible: oxynitrocarbides $\text{Fe}_3(\text{ONC})$ and oxycarbonitrides $\text{Fe}_3(\text{OCN})$ (ϵ'' -phase).



The formation of a nitride layer in a mixture of ϵ -phase+Fe₃C, γ' -phase+Fe₃C and the zone of internal nitriding α +Fe₃C also occurs during nitriding in dissociated ammonia of structural steels, due to the presence of carbon in the steel matrix during decarburization. In this case, the carbon in the matrix simultaneously participates in the formation of the nitride layer and the ϵ' -phase and Fe₃C are formed, the formation of the latter occurs more noticeably with an increase in the carbon content in the steel matrix.

In steel with a ferrite-pearlite structure, the formation of Fe₃C in the pearlite part proceeds especially strongly, in some cases, with an increased, carbon content due to the limited solubility of carbon in cementite, the formation of a mixture of Fe₃C and graphite is also possible.

The rate of the process during nitriding can be estimated from the activity of the atmosphere used for chemical-thermal treatment.

Atmospheric activity (A_k) is determined by two factors: thermodynamic and kinetic. The thermodynamic factor is analyzed as the difference between the current atmospheric potential (π_N) and the equilibrium potential (π_{N^0}) for a given phase or nitrogen concentration. The greater the potential difference $\pi_N - \pi_{N^0}$, the greater the Gibbs energy of the reaction of the interaction of iron with ammonia.

The kinetic factor is determined by the rate constant of the ammonia decomposition reaction (K), the time (τ) and the presence of a diluents gas, in particular an oxygen-containing gas (α).

The kinetic factor is estimated based on the Temkin equation for the decomposition of ammonia:

$$dP_{NH_3}/dt = -K P_{NH_3}/P_{H_2}^{3/2} \quad (1)$$

The solution of equation (2) in general form is described by the equation:

$$F \frac{(\beta - a)}{(1 - a)} - F(b) = k\tau(cp)^{3/2} \quad (2)$$

where: P – the total pressure in the furnace

β – determined from the expression: $P_{NH_3} = (1 - \beta)P$

a, b, c – coefficients depending on the type of diluents gas.

For oxygen, air, water vapor: $a = X$ – the volume fraction of the diluents gas, $b = 0$, $c = \frac{1 - x}{3 - x}$

The kinetic factor $F \frac{(\beta - a)}{(1 - a)}$ determines the presence of free nitrogen on the surface, while the greater the dissociation of ammonia, the more active nitrogen appears per unit time.

Based on the dependence of atmospheric activity on thermodynamic and kinetic factors, atmospheric activity is considered as the product of the probabilities of thermodynamic and kinetic factors:

$$A_k = F \frac{(\beta - a)}{(1 - a)} (\pi_N - \pi_{N^0}) \quad (3)$$

Since oxygen is present in the furnace atmosphere during gas nitriding, for example, the presence of water vapor in the composition of technical ammonia and oxidation of the furnace wall, etc., can be their causes. In some cases, to intensify the processes of gas nitriding, oxygen or water vapor, are added in certain concentrations. For gas processes, the phase composition of the formed diffusion layer is predicted depending on the composition of the atmosphere and the temperature of the process when calculating the nitrogen and oxygen potentials of the atmosphere.

In particular, during oxynitriding in ammonia with oxygen additives, the conditional nitrogen potential of the atmosphere can be described by the following equation:

$$\pi_N = \frac{\lambda \cdot (1 - a)[0.5(1 + \lambda) + \alpha\lambda]^{1/2}}{[3/2\alpha\lambda - 0.5(1 - \lambda)]} \quad (4)$$

where: α – the degree of dissociation of ammonia;
 λ – proportion of ammonia mixed with oxygen.

In accordance with equation (4), phase equilibria in the “Fe–N–O” system during oxynitriding in ammonia with oxygen additives, with an increase in the degree of ammonia dissociation and the temperature of the process, the oxidizing ability of the atmosphere decreases.

Presence of oxygen should not cause oxidation of the hardened parts at the nitriding stage. According to equation (4), with the degree of dissociation of ammonia $\alpha=30\%$ and the oxygen content of 5%, no oxide is formed on the surface of the parts, but π_N and, consequently, the rate of the process increases. With an increase in the oxygen concentration to 10%, the formation of Fe_3O_4 oxide is possible at 500 – 520 °C and $\alpha = 45-50 \%$.

When oxygen, air, carbon dioxide, water vapor and their mixtures are introduced into the ammonia–hydrogen atmosphere, increasing the nitrogen potential contributes to the intensification of the process. At the same time, the composition of the atmosphere is calculated so that the nitrogen potential of the atmosphere corresponds to the ratio: $P_{NH_3}/P_{H_2}^{3/2} \geq 3$, and the oxygen content (water vapor and other oxidants) is below the iron oxidation limit. The amount of introduced oxygen (oxygen–containing agent) is determined by the oxygen potential of the atmosphere $\pi_o = \frac{P_{H_2O}^2}{P_{H_2}}$, at which iron oxidation does not yet occur. By changing the parameters of the atmosphere, it is possible, in accordance with the diagram, to control the structure and phase composition of the layer, changing the ratio of nitride (carbonitride) phases in the nitride zone and forming an oxide film of Fe_3O_4 at the final stage of the process. In this case, it is possible to form a nitride–oxide coating of various gradient structural phase states by carrying out the process of gas nitriding with preliminary and subsequent oxidation to obtain modified nitride coatings with certain phase compositions or from compositions of various ratios of modified nitrides.

During nitrooxidation of structural steels, a diffusion nitride–oxide coating is formed on the surface, consisting of a surface thin oxide zone, followed by a nitride zone, and the nitride zone is followed by an internal nitriding zone (Fig. 2).

The nitride layer was oxidized in water vapor with a change in the composition of the oxidizing atmosphere. At the same time, to increase the oxygen potential, aqueous solutions of complexions were used as an oxidizing atmosphere: a 5% solution of hydroxyethylidene diphonic acid (HEDP) and a 5% solution of Trilon B.

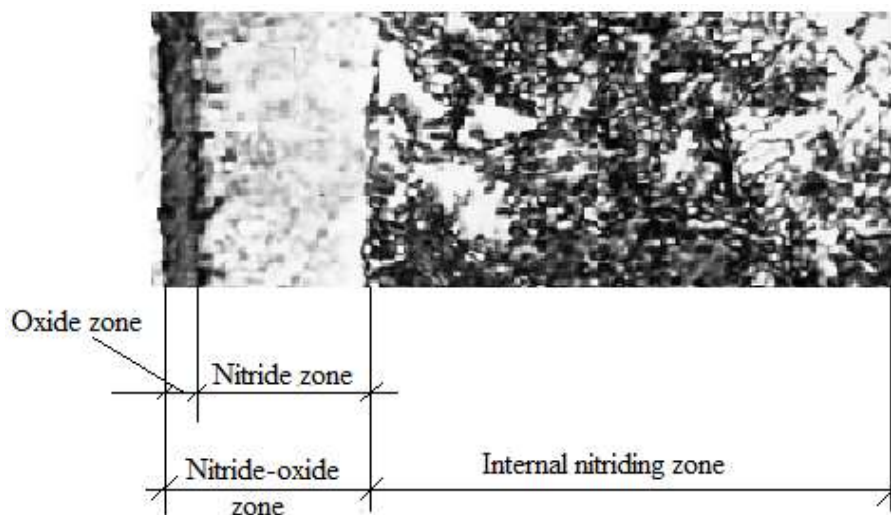


Fig. 2. Microstructure of the nitride–oxide diffusion layer after nitrooxidation

The phase distribution over the depth of the nitride–oxide layer on steel 45 was studied using the Dron–3 installation by layer–by–layer X–ray diffraction analysis. In this case, the samples were processed in the same technological modes of nitrooxidation. The nature of the change in the high–nitrogen ϵ –phase depending on the chemical nature of the oxidizing atmosphere was studied (Fig. 3).

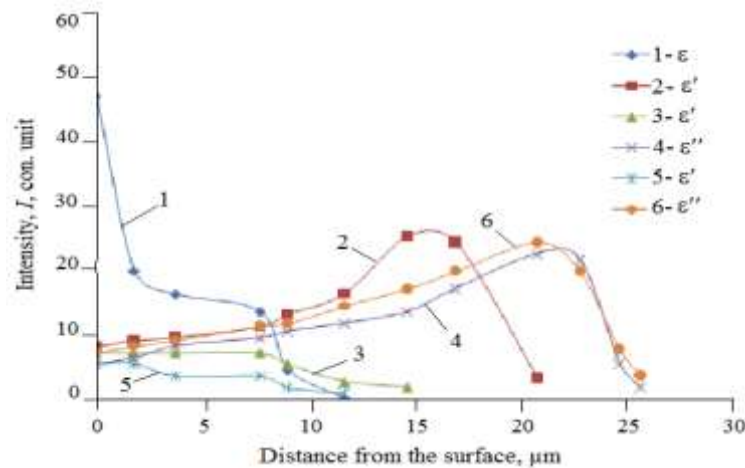


Fig. 3. Distribution of the ϵ -phase content according to the results of layer-by-layer X-ray analysis of treated steel samples

Nitriding – 2 hours $\alpha=30-45\%$ + 1 hour $\alpha=45-60\%$; 1,2 – nitriding; 3,4 – nitriding followed by oxidation in vapors of a 5% aqueous solution of HEDP; 5,6 – nitriding followed by oxidation in vapors of a 5% aqueous solution of Trilon B.

An analysis of the obtained data shows that after nitriding steel 45, a high-nitrogen ϵ -phase and a carbonitride ϵ' -phase are formed in the nitride layer. During the oxidation period, the surface high-nitrogen ϵ -phase undergoes denitrogenation with the formation of Fe_3O_4 oxide and dissociation with the formation of the γ' -phase, the content of which increases during the oxidation period.

After oxidation with the formation of a surface oxide layer, the ϵ -phase simultaneously passes into the ϵ' -phase due to doping with matrix carbon, and the carbonitride ϵ' -phase is doped with oxygen and the oxycarbonitride ϵ'' -phase is formed. Moreover, the ϵ -phase is depleted in nitrogen and X-ray diffraction is detected in the form of two isomorphous phases: an isomorphous carbonitride phase, ϵ' with lattice parameters $a = 0.269$, $c = 0.436$ nm and ϵ'' -oxycarbonitride phase with lattice parameters $a = 0.267$, $c = 0.436$ nm.

After oxidation in the vapors of an aqueous solution with HEDP additives, the carbonitride ϵ' -phase still remains in the region of the ϵ -phase of the nitride layer, and during oxidation in the vapors of an aqueous solution with Trilon B additives, the carbonitride ϵ' -phase passes to the ϵ'' -phase, X-ray diffraction only traces of the ϵ' -phase are found in the surface zone of the nitride oxide layer.

The nitride zone with high surface characteristics consists of γ' -phase (Fe_4N) and ϵ'' -phase. As our studies have shown, the corrosion resistance of the oxycarbonitride layer depends on the ratio of γ' - and ϵ'' -phases in the nitride zone.

The time of appearance of the first centers of corrosion in a 3% aqueous solution of common salt of steel 45 after nitrooxidation with the addition of vapors of an aqueous solution of HEDP with an increase in the amount of lower nitride (γ' -phase) in the nitride zone up to 75% (the rest ϵ' - and ϵ'' -phase), the time before the appearance of the first centers of corrosion increases, reaching 910–960 hours at 75% γ' -phase.

After nitrooxidation with the addition of vapors of an aqueous solution of Trilon B with an increase in the amount of lower nitride (γ' -phase) in the nitride zone up to 80% (the rest of the ϵ'' -phase), the time before the appearance of the first centers of corrosion is also in the time interval of 910–960 hours, and the growth of the area affected by corrosion during the period of long-term testing decreases by 2–3 times than the nitride-oxide coating obtained after oxidation in the vapors of an aqueous solution of HEDP.

To improve wear-resistant characteristics during sliding friction of rubbing pairs operating in corrosive environments, the formation of diffusion coatings with a positive gradient of structural-phase states in a nitride-oxide coating is important from the point of view of providing external friction conditions.

Analyzing the formation of a nitride layer on the surface of structural steels during gas nitriding under various saturation conditions, we can conclude the following conclusions:



– the nitride layer after nitriding has compositions of nitride phases consisting of ϵ - and γ' -phases, the ratio of which depends on the degree of dissociation of the ammonia atmosphere and the temperature of the process, and in the presence of carbon-containing gases, an isomorphous carbonitride ϵ' -phase is formed;

– the formation of the carbonitride ϵ' -phase also occurs due to carbon in the steel matrix, which participates in diffusion processes and the presence of carbon in the layer due to its limited solubility in nitride phases leads to the release of cementite;

– during subsequent oxidation, reactive diffusion occurs in the nitride layer and the structure of the diffusion layer consists of two: the surface oxide zone and under it the nitride zone, which undergoes modification by the transition isomorphous to ϵ -nitride: when alloyed with carbon, a carbonitride ϵ' -phase is formed and when alloyed with carbon and oxygen forms an oxycarbonitride ϵ'' -phase;

– in nitrooxidation, there is a range of possibilities for the formation of a gradient of structural-phase states by obtaining one or another type of nitrides or their modified compositions;

– in the presence of a carbonitride ϵ' -phase, although it has a high corrosion resistance by the appearance of the first centers of corrosion, however, it has more corrosion damage over the area depending on time;

– nitride-oxide coating has high corrosion resistance, in which the composition of nitrides mainly consists of low-nitride γ' -phase (80%) and oxycarbonitride ϵ'' -phase.

REFERENCES

1. Lakhtin Yu.M., Kogan Ya.D., Shpis G.I., Byomer Z. Theory and technology of nitriding. – M: Metallurgy, 1991. – p. 320.
2. David Pye. Practical Nitriding and Ferritic Nitrocarburizing, ASM Publication, 2003. – p. 256.
3. Zinchenko V.M., Syropyatov V.Ya. New possibilities of gas nitriding as a method of anticorrosion treatment of machine parts. // Metal science and heat treatment of metals. No. 7. 1998. – p. 2–6.
4. Gerasimov S.A., Zhikharev A.V., Golikov V.A., Gress V.A., Zubarev G.I. Influence of preliminary heat treatment on the structure and properties of nitrided steels // Metal Science and Thermal Treatment of Metals. 2000. – No. 6. – p. 24–25.
5. Petrova L.G., Aleksandrov V.A., Zharov G.M. Surface hardening of steels by methods of chemical-thermal treatment in multicomponent media. // Strengthening technologies and coatings, 2012, No. 6 (90). – p. 18–22.
6. Kogan Y.D., Eshkabilov Kh.K. Oxynitriding of metallic articles. // Uproch. Tekhnol. Pokr. №6, 2006. – p. 10–16.
7. Palček P., Mintách R., Nový F., Chalupová M., Marônek M. Change of fatigue characteristics of deep drawing sheets by nitrooxidation. // Chemické listy, Vol. 105, Issue 16 (2011). – p. 539–541.
8. Petrova L.G., Aleksadrov V.A., Shestopalova L.P. Influence of pre-oxidation on the process of nitriding of steels containing chromium. // Bulletin of KhNADU. – Kharkov, 2008. – Issue. 46. – p. 82–85.
9. Kh.Eshkabilov, Sh.Berdiyev. Structure and properties of the modified diffusion nitride-oxide surface layer. E3S Web of Conferences 264, 05054 (2021). Conmechydro, 2021. 10.1051/e3sconf/202126405054.
10. Lazar R., Marônek M., Dománková M., Low Carbon steel treated by nitrooxidation process. // Strojjstvo extra, 2007, No. 4. – p. 86–89.
11. Kogan Ya.D., Solodkin G.A. Thermodynamic bases of controlled nitriding processes. // Metal science and heat treatment of metals, 1981, No. 4. – p. 16–20.
12. Zinchenko V.M., Syropyatov V.Ya., Prusakov B.A., Perekatov Yu.A. Nitrogen potential: the current state of the problem and the concept of development. – M.: Federal State Unitary Enterprise Publishing House “Mashinostroenie”, 2003. – p. 90.
13. Margulova T. X. The use of complexons in thermal power engineering. – M.: Energoatomizdat, 1986. – p. 280.
14. Freiman M.I., Makarov V.A., Bryskin I.E. Potentiodynamic methods in corrosion research and electrochemical protection. – L.: Chemia, 1978. – p. 58.
15. Eshkabilov Kh.K., Berdiev Sh.A. Controlled low alloy steel nitrooxidation technology. // International scientific and practical conference “World science”, “The goals of the World Science 2016”, January 27–28, 2016, Dubai, UAE. №2 (6), Vol.1. – p. 69–74.

Cite this Article: Kholikul Karshievich Eshkabilov (2023). Surface Structural-Phase Modification of Structural Steels during Gas Nitriding. International Journal of Current Science Research and Review, 6(4), 2697-2702