Some aspects of the nitriding process of parts in machine construction

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Abstract. Nitriding is the most common and effective surface hardening method. Such chemical-thermal treatment is capable of increasing surface hardness, contact endurance, wear and seizure resistance, as well as heat resistance and corrosion resistance of a wide range of machine parts. This process of surface hardening has found its application in many branches of modern mechanical engineering. The operational requirements for the parts led to the need to replace high-temperature methods of chemical-thermal treatment (carburizing, high-temperature nitrocarburizing, etc.) for hardening processes at lower temperatures (500-650 °C), namely nitriding. This replacement was facilitated by the latest technological developments in the field of various nitriding methods. The scientific developments obtained to date make it possible to gradually eliminate such disadvantages of nitriding as a significant duration of the process, increased fragility of the surface layer, insufficient values of contact endurance, and labor intensity of the process [1, 2].

1. Introduction
Nitriding is the most common and effective method of surface hardening. Such chemical-thermal treatment is capable of increasing surface hardness, contact endurance, wear and seizure resistance, as well as heat resistance and corrosion resistance of a wide range of machine parts. This process of surface hardening has found its application in many branches of modern mechanical engineering. The operational requirements for the parts, came to the conclusion to replace high-temperature methods of chemical-thermal treatment (carburizing, high-temperature nitrocarburizing, etc.) for hardening processes at lower temperatures (500 - 650 °C), namely nitriding. This replacement was facilitated by the latest technological developments in the field of various nitriding methods. The scientific developments obtained to date make it possible to gradually eliminate such disadvantages of nitriding as a significant duration of the process, increased fragility of the surface layer, insufficient values of contact endurance, labor intensity of the process [1 - 3]. Despite the fairly widespread use of the nitriding process in the practice of various areas of mechanical engineering, there are still a lot of unresolved issues associated mainly with the mechanism of structure formation in the formation of a diffusion layer [2 - 6]. It is the structural features of the nitride layer and the matrix itself that determine the performance of machine parts and, consequently, the choice of steels, pretreatment technologies and the
nitriding technology itself. Therefore, today the prediction and modeling of the formation of structure and properties in the diffusion layer during nitriding is a rather urgent problem [7 - 9].

2. Modeling the processes occurring during nitriding

Modeling the processes occurring during nitriding is the most effective method for developing a technological process. The use of computational methods makes it possible to obtain rather promptly information about the main properties of the hardened layer, about the rate of diffusion and structures of forming processes, about the formation of nitride and carbon nitride layers with varying temperature and time regimes. Simulation of various nitriding processes makes it possible for a simple and prompt solution of many technological problems to control and manage saturation modes of diffusion layers, predict the final results and the possibility of developing innovative processing modes. At the same time, taking into account the complexity and high cost of carrying out a large number of experiments makes mathematical modeling of nitriding processes a particularly promising research method.

Mathematical models describing the dependences of the depth of the nitride layer and surface hardness on the values of temperature and duration of chemical-thermal treatment of steel during ionic nitriding can be represented as a polynomial of the second degree [1, 3]:

\[ y_i = b_0 + a_1 x_1 + a_2 x_2 + a_3 (x_1^2 - \beta) + a_4 (x_2^2 - \beta) + a_5 x_1 x_2 \]  

(1)

where - \( a_i \) are the estimated coefficients, \( \beta \) – is the parameter calculated depending on the number of points of the core of the compositional plan \( 2n-p \), the shoulder of "star" points \( a \) and the number of points in the plan by the formula:

\[ \beta = \frac{\sum_{j=1}^{N} x_j^n}{\sum_{j=1}^{N} x_j} \]  

(2)

The procedure for estimating the coefficients of the model, checking its adequacy and statistical analysis of accuracy are given in [1, 2]. The resulting model of the depth of the hardened layer, depending on the normalized values of temperature and duration of chemical heat treatment, has the form:

\[ y = 295,55556 + 42,5085 \cdot x_1 + 280,056 \cdot x_2 - 9,211 \cdot x_1^2 + 33,289 \cdot x_2^2 + 13,75 \cdot x_1 \cdot x_2 \]

(3)

The mathematical model describing the effect of the temperature and duration of nitriding on the values of the surface hardness of the nitride layer, in general form, is represented as follows:

\[ y = 9,8 - 0,8335 \cdot x_1 + 1,30026 \cdot x_2 + 0,09853 \cdot x_1^2 - 0,80147 \cdot x_2^2 - 0,75 \cdot x_1 \cdot x_2 \]

Checking the significance of the coefficients showed that the coefficient \( a_3 \) can be considered insignificant, therefore, the model is converted to the form:

\[ y = 9,8 - 0,8335 \cdot x_1 + 1,30026 \cdot x_2 - 0,80147 \cdot x_2^2 - 0,75 \cdot x_1 \cdot x_2 \]  

(4)

Response surfaces in factor space in a given planning area are presented in [2, 3].

3. Wear on the nitride surface

One of the reasons for the failure of many parts is the wear of the working surfaces during operation in friction units. To solve this problem, expensive materials are used, which are necessary for the manufacture of parts, with high hardness, wear resistance, etc. Experimental data on the determination of the hardness and thickness of nitride surface layers of steels of different grades by the nanoindentation
method are presented. The dependence of the change in the layer hardness on the current power during nitriding has been determined. For the study were taken samples of steel of different grades, the composition of which is presented in [10, 11]. Determination of the thickness and hardness of the modified layer was carried out using a Nano hardness tester "Nano Hardness Tester" company CSEM by the Vickers method. The Vickers method uses a diamond pyramid with an apex angle between opposite faces equal to $136^\circ$. Hardness is defined as the ratio of the load to the surface area of the print or its projection. Since nanoindentation examines the layer in the nanometer range, and the indenter size is 5 $\mu$m, the surface roughness, cracks, and inhomogeneity of the chemical composition have a significant effect on the measurement result; therefore, the samples are pre-polished and the area with the least number of defects is selected during indentation. The maximum load on the indenter was 50 mN. An example of indentation is shown in Figure 1.

![Image](matrixindentationonthesamplenr.3.png)

**Figure 1.** Matrix indentation on the sample nr. 3.

![Image](dependenceofthechangeincharnessonthedepthofthenitride.png)

**Figure 2.** Dependence of the change in hardness on the depth of the nitride layer.

The primary obtained dependence of hardness on penetration depth has peaks and valleys that arise from the errors described above. But the hardness in the nitride layer changes smoothly, therefore, during data processing, an interpolation operation was used in order to reduce the error. Since the samples were polished, the roughness error is small. The instrumental error is determined by the standard. For this, the indenter pierces a quartz sample, then the device independently adjusts this error. The dependences of hardness on depth are shown in Figure 2, and a comparison of the initial and maximum hardness in the table [10, 11]. From the obtained dependences it follows that on the surface of the nitride layer the maximum value of hardness, when moving along the cross section of the sample in the direction from the nitride surface, the value of hardness decreases. At a certain depth of the layer, the hardness does not change, and from this it can be concluded that this value corresponds to the initial hardness of the sample, and this depth is the depth of the nitride layer.

**4. Gas-cyclic and thermo-gas-cyclic nitriding**

Nitriding was subjected to ARMCO iron, 105MnCrW11 alloy steel, the samples of which were subjected to wear tests. Standard processing for steels of this type - hardening and low tempering, but
they can also be hardened by nitriding, because this type of chemical-thermal processing allows to increase the resistance to wear, thermal, corrosion of products [12 - 14]. Gas-cyclic and thermo-gas-cyclic nitriding was performed on an experimental installation, which includes the control and temperature maintenance system in the work space (oven). Gas supply system, control of ammonia consumption and dissociation value, gas cleaning and drying. At the same time, two solenoid valves for gases, controlled and controlled to order, and the possibility in automatic mode to act on the technological parameters of the nitration process.

The factor that has accelerated the enrichment process is the diffusion coefficient, as it is better known is influenced by temperature and concentration gradient. Therefore, in order to speed up the process and the possibility to regulate it, a thermocycle was proposed instead of isothermal treatment at a normal nitriding by gas flow. The temperature range was determined in accordance with the iron-carbon diagram, where there are critical points, which divide the domain into phases by content. The correct choice of the temperature range for the thermocycle process is a condition for researching the influence of cyclic gas and thermo-gas on the nitriding process. Therefore, the temperature range was chosen so that the process when nitrogen diffuses into iron (the first stage of the nitriding cycle) takes place below the temperature of eutectoid transformations according to the “iron-nitrogen” state diagram, iron-nitrogen at a temperature below 591°C. When researching the nitride samples, the temperature was in the limits of 490 - 540°C. Then the dissociation of the nitride layer was performed (the second stage of the cycle), the supply of ammonia is interrupted, the pressure in the furnace for a period of time remaining constant.

The upper limit of the nitriding cycle was 620°C. The value of ammonia dissociation in each first half-cycle was checked every 15-20 minutes. using the water disosciometer. At the enrichment temperature 520°C the dissociation value with ammonia was 25-30%, at temperatures of 620°C - 40-45%. At each second half-cycle, the dissociation value with ammonia increased and constituted 68-70%, at a temperature of 520°C and 94-98%, at a temperature of 620°C.

The microstructure research after nitriding was performed on the “VEGA TS 5130” microscope, and the distribution of nitrogen on the nitriding depth was obtained by scanning with X-ray spectral analyzer. The wear resistance research was performed on the installation, which models the cutting process. The road traveled is equal to 200 m [14, 15]. Thermo-gas-cyclic nitriding technology is based on the periodic alternation of cycles when nitrogen diffuses into the iron during nitriding by gas flow and dissociation of the nitride layer to a maximum possibility of reducing the atmospheric saturation property.
At the same time, the additional intensification takes place at the expense of carrying out the process in two phases - at the thermo-gas-cyclic nitriding the nitrogen enrichment process takes place, at the second dissociation which is carried out at different temperatures. This technology ensures an effective regulation of the phase structures of the diffusion layer, with the help of a new technological parameter - the duration of the half-cycle - and allows reducing gas consumption at the expense of maximum use at each gas consumption volume at the stage when nitrogen diffuses into iron. At the same time, the requirements for ecology are improved, which are advanced compared to the chemical-thermal processing processes, by reducing the harmful gases released into the environment.

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The increase of the total thickness of the nitride layer is subject to parabolic dependence, with the decrease of the semi cycle duration the total thickness of the layer increases, due to the internal nitriding area (ZNI, figure 3). As the duration of the half-cycles increases, the thickness of the layer decreases, which is related to the process of dissociation of the nitride layer at the second stage of the cycle [15, 16].

When comparing thermo-gas-cyclic nitriding and ordinary nitriding, a sudden increase of the total layer is observed, it can be seen on microstructures (figure 4) according to those characteristics of the phases - $\gamma'$. At the same time, the total thickness increases especially on the account of ZNI, which increases approximately 6 times, that of nitrides - about 2 times compared to normal nitriding.

The increase in the intensity of the process is also shown by the radiation distribution curves from the nitrogen atoms (figure 5) - as it moves away from the surface, the nitrogen content in the layer increases and reaches its maximum value, especially in its depth. Obviously, the distribution of nitrogen on the thickness of the nitride layer in the investigated samples has the same character and are characterized by the fact that the maximum nitrogen content is very slow and is not on the surface of the samples.
which is in contact with the enrichment medium. In the internal nitride zone, at a distance from the sample surface. At the same time, taking into account the value of the intensity of the reflection of the lines, we can notice that, firstly, the thickness of the layer with high nitrogen content increases with the transition from ordinary to thermo-gas-cyclic nitriding, secondly, the intensity of radiation, and correspondingly the nitrogen content in the nitride area after thermo-gas-cyclic nitriding is obviously higher, compared to ordinary nitriding.

Figure 6 shows the results of the calculation of nitrogen consumption on the scanned curves. It can be seen that on the surface of the samples, which is in contact with the enrichment atmosphere, the nitrogen consumption is not high and constitutes about 3.5-4.8% (after meals). As the surface is removed, the nitrogen content in the layer increases and reaches a maximum value, for ordinary nitriding the nitrogen content increases maximum to 8.5%, and in the thermo-gas-cyclic - up to - 12%. This indicates that nitriding under the conditions of the thermo-gas-cyclic process is more intensive. At the same time, the maximum nitrogen content at its distribution curve on the layer thickness is very slow and moves in the depth of the layer when switching from ordinary to thermo-gas-cyclic nitriding, which can be clarified by intensifying the process of dissociation of the nitride layer in the material depth. The microhardness measurement showed: for the thermo-gas-cyclic nitriding which takes place 6.5 hours, we can obtain the same surface hardness as for the normal nitriding, only after 25-30 hours, the nitriding time was reduced by about 4-5 times.

Thus, by modifying only one parameter - the duration of the half-cycle, on the surface of the hardened product we can obtain layers with different phase structures at a corresponding correlation of the processes when nitrogen diffuses in iron and dissociation. Thus, we can use this method of nitriding to regulate the process, obtaining necessary phases on the surface of the product depending on the necessary operating conditions. As an example, in the thermo-gas-cyclic nitriding of 105MnCrW11 steel on the surface it is rational to obtain simultaneously the phase - γ hard and plastic yes not the phase - ε fragile. In this case the nitriding is necessary to complete it at the dissociation stage, nor how at the enrichment stage. The wear nomograms of 105MnCrW11 steel samples after conventional gas-cyclic nitriding and thermo-gas-cyclic nitriding are shown in Figure 7. We point out that, following the research, it was established that the minimum wear corresponds to the thermo-gas-cyclic nitriding, which ended with the dissociation stage, at which the duration of the half-cycle was 0.5 hours. The wear of the samples is about 2.5 times lower than the usual nitriding. This fact can be clarified that on the surface formed at dissociation the phase - γ 'yes not the phase - ε was formed [17 - 18].

5. Conclusions and results
A new nitriding method has been developed, which consists in periodic alternation of saturation cycles during flow nitriding and resorption of the nitride layer with the maximum possible decrease in the saturating capacity of the atmosphere. The method of thermo-gas-cyclic nitriding is an effective new method of strengthening parts that allows to reduce the consumption of ammonia from 2 to 10 times, the nitriding time by 4-6, 5 times with an increase in the thickness of the diffusion layer by 2-6 times without reducing the physical and mechanical characteristics, and also improve the environmental aspects of the nitriding process in flowing ammonia. A new technological parameter, the duration of
half-cycles, has been investigated, which allows simply from the point of view of implementation and effectively regulates the phase composition and structure of the layer in order to obtain the required physical and mechanical characteristics.

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