# PHYSICO-CHEMICAL AND TRIBOLOGICAL PROPERTIES OF NITROGENED LAYERS OF STRUCTURAL STEEL

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## Introduction

The presented work is a continuation of the problem of solving practical and theoretical principles of vacuum-diffusion gas-discharge processes, in which the mechanisms of processes of formation of modified surface layers of metals under the interaction of regime (temperature, medium saturation, medium pressure in gas-discharge chamber and saturation time) and energy (current density) and voltage at the electrodes of the discharge chamber) parameters. On the basis of the obtained experimental data it is planned to formulate the position of practical use of a fundamentally new technological process with optimization of combining its mode and autonomous saturation parameters, which would fully correspond to the formation on the surface of structures corresponding to increasing reliability and durability of machine parts. The authors rely on the developed fundamentally new energy model of the nitriding process in the glow discharge, the main feature of which is the priority of those subprocesses in strengthening the surface layers of metals, which in specific operating conditions of parts are most appropriate [1].

Analysis of the literature [2, 3, 4] showed that all known theoretical models of ionic nitriding processes are largely hypothetical, because the hypotheses underlying them are not always and not fully confirmed experimentally. A number of such models do not have an analytical justification, there are no criteria for optimizing nitrided surfaces, and thus methods of managing the nitriding process in order to achieve the required performance characteristics. The accumulation of a large amount of technological data, which do not have a generalized theoretical basis, not only does not contribute to the development of practical application of ion-plasma hardening of parts, but often leads to opposite consequences, because the accumulated results do not take into account real operating conditions.

In the planned cycle of works, fundamentally new provisions of the theory of diffusion gas-discharge processes of ionic nitriding of metals are formed, which are based on the priority of energy approaches [1]. From such positions theoretical processes of diffusion gas-discharge methods of ionic nitriding were not considered by domestic and foreign researchers, but they open absolutely new opportunities of studying of the thin mechanism of the phenomena and their practical application in the field of strengthening of metal surfaces.

**Materials for research**

To study the effect of BATR, structural steels of the following grades were selected: 45 - high-quality carbon, 40X - chromium and 38HMUA - chromium-aluminum with molybdenum of high quality, as the most commonly used for nitriding in the glow discharge.

**Research methods**

Anhydrous nitriding in the glow discharge was carried out at the industrial plant UATR-1 of the Podolsk Scientific Physical and Technological Center (PNFC) of Khmelnytsky National University. The installation belongs to the model of diode type on a direct current and was in addition completed with heating elements placed in the gas-discharge chamber that gave the chance to change arbitrarily energy parameter - size of voltage U, and value of current density I (the relation of current to the total area of details a combination of arbitrarily set voltage and pressure of the gas mixture and nitriding time ($\tau$ = 4 hours).

**Nitriding modes**

Since the impact on the structure, phase composition, and hence on the performance characteristics of nitrided steels temperature, composition of the gaseous medium and nitriding time has been comprehensively studied in the works of many authors, for example, [2, 5, 6], and based on many years of experience materials and parts in PNPTC accepted: duration of nitriding - 4 h, the composition of the gas mixture - 80% N2 (nitrogen) + 20% Ar (argon) and temperature - 833K. Voltage and current are selected experimentally, based on the experience of previous studies. The current density was found as the ratio of the current to the cathode surface area, ie took into account the sum of the surface areas of the samples and the suspension. Technological modes of BATR are given in table.1

The specific power of the glow discharge in the gas discharge chamber was determined by the formula:

$$w=UxI/S=Uxj,$$

where S is the surface area of the cathode.

**Table 1. Parameters of BATR modes**

| Mode parameter value | Sequence number of the experiment | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1*/1** | 2 | 3 | 4*/4** | 5 | 6 | 7*/7** | 8 | 9 |
| Pressure p, Pa | P1=53,2 | | | P2=106,4 | | | P3=159,6 | | |
| Strain U, B | 1100/680 | 820 | 515 | 840/610 | 515 | 300 | 700/540 | 515 | 300 |
| Current density j, A / m2 | 11,0/15,3 | 7,2 | 3,2 | 13,2/16,4 | 7,2 | 2,8 | 15,8/17,2 | 12,8 | 7,2 |
| Specific power of the glow discharge w, kW / m2 | 12,1/10,4 | 5,9 | 1,65 | 11,1/10,0 | 3,71 | 0,84 | 11,1/9,3 | 6,6 | 2,2 |

* The results of experiments without additional heating of the samples

To verify the position of [6] that "each power and discharge corresponds to a certain pressure of the gas medium" was conducted a second series of experiments with the same mode parameters as experiments 1 *, 4 *, 7 * of the first series, but using suspension of other sizes (cathode surface area), which led to changes in voltage and current density (modes 1 **, 4 **, 7 **; see table 1).

**Metallographic research**.

Cylindrical samples after BATR were cut on a diametrical plane (received two half-cylinders). The obtained planes were ground and polished by washing with distilled water and subjected to etching in a 3% alcoholic solution of nitric acid ($HNO_3$).

Measurement of the thickness of the nitride zone was performed on a microscope MIM-10, which allows quantitative analysis of the phase and structural composition of nitrided surfaces.

Microhardness was determined on a microhardness tester PMT-3 at a load of 0.98N with fixation of microhardness values both on the surface and at a distance from it 0; 25; 50; 100; 200; 300; 500 μm.

**X-ray phase analysis** was performed on a DRON-3 diffractometer in the filtered radiation of the iron anode in the range of angles θ from 20° to 100° with a scanning step of 0.1° and an exposure time of 10s. X-rays were taken from the surface to the depth of the nitrided layer.

**Tribological research**.

Experimental studies of samples for wear resistance were performed on a universal machine for testing materials for friction model 2168UMT.

Analysis of literature sources [2, 5] allows to determine as factors that have the most significant impact on the course of tests and their results, the following characteristics: friction scheme - "disk - finger"; friction without lubricant; counter body material - steel SHH15 with hardness of the base HRC61; pressure in the contact zone p = 16 MPa; the controlled parameter is the linear wear h, which was defined as the change as a result of the passage of a section of length l of the linear size of the sample, measured along the normal to the friction surface.

As the friction path passed, the step of fixing the test results changed (Table 2).

**Table 2. Periodicity of measurement of test results**

| Friction path section L, m | 0 – 50 | 50 – 200 | 200 – 400 | 400 – 1000 | more 1000 |
|---|---|---|---|---|---|
| Measuring step l, m | 5 | 10 | 25 | 50 | 100 |

The tests were stopped in the event of catastrophic wear.

Influence of BATR energy parameters. For greater clarity, the set of technological processes is represented by the scheme (Fig. 1), where the numbers near the points correspond to the number of the corresponding mode, and the lines connecting them correspond to the same pressures of the gas mixture: p1 = 53.2 PA, p2 = 106.4 Pa and p3 = 159.6 Pa. Points 1, 4, 7 correspond to the modes carried out without an additional heating source, ie with interdependent ATP parameters (each pressure of the gas mixture corresponds to a certain combination of voltage and current at the electrodes of the discharge chamber).

Analysis of the obtained dependence shows (Fig. 1) that with increasing pressure of the gas mixture p3> p2> p1 for BATR without additional heating increases the current with decreasing voltage in the discharge chamber, and the specific power w is approximately the same 11.1… 12.1 kW / m2 (modes 1 *, 4 *, 7 *). and 9.3… 10.4 kW / m2 (modes 1 **, 4 **, 7 **) when changing the shape of the suspension (cathode surface area). The latter is achieved by automatically changing the current density j and voltage U according to the change in gas pressure.

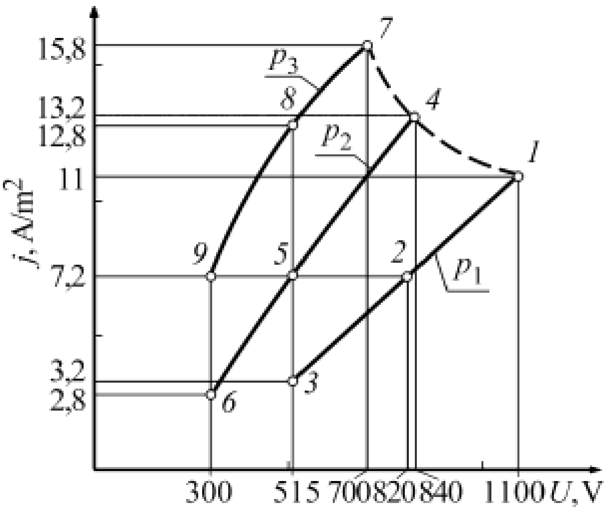



**Fig.1. The nature of changes in energy parameters U and j**

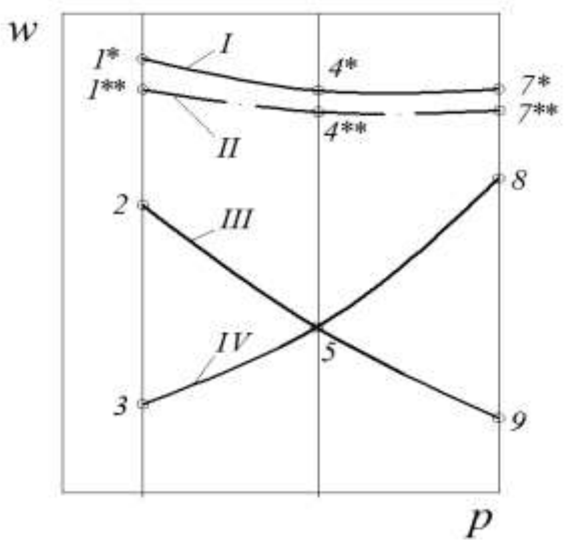



**Fig.2. Dependence of the specific power of the discharge W on the pressure of the gas mixture: I, II - without additional heating; III, IV - with autonomous modes (with additional heating of the camera)**

In the case of BATR with independent energy regimes, much smaller values of j and U are required to maintain the glow discharge in the chamber, for example, modes 9 and 7 at pressures p3 and modes 6 and 4 and 3 and 1 at pressures p2 and p3, respectively. In this case, when U = const (modes 3, 5, 8) to maintain the glow discharge requires an increase in j, and when j = const (modes 2, 5, 9), on the contrary, decreases U with increasing pressure of the gas mixture. It follows that the energy parameters are closely related to the pressure of the gas mixture. Therefore, Fig. 2 shows the dependences of the change in the specific power of the glow discharge w from the pressure of the gas mixture of the river. Curves I, II in Fig. 2 II - additional series of experiments, less energy losses). We have completely different dependences for BATR with autonomous energy parameters (Fig. 2, curves III, IV). In this case, at U = const with increasing pressure (modes 3, 5, 8 in Fig.1 and 2) w increases, and at j = const (modes 2, 5 and 9 in Fig.2), on the contrary, decreases. Figure 2 also shows that the use of energy parameters of BATR can significantly reduce the energy consumption of the nitriding process.

The results of research presented in [6] indicate the existence of an extreme relationship between the specific power of the discharge and the pressure of the gas mixture. The authors note that the pressure of the gaseous medium, which corresponds to the maximum specific power of the discharge, provides a nitrided layer of the greatest thickness. However, it should be noted that such conclusions are based on the results of nitriding copper tubes 30 mm long with an inner diameter of 1.6; 3.6; and 5.7 mm, but the features of nitriding of small diameter holes are associated with the effect of a hollow cathode [8] and it is unlikely that this allows the results to be extended to parts or samples of other configurations. Moreover, the extreme nature of the dependence w = f (p) decreases with increasing inner diameter of the tubes [6].

In our experiments conducted on cylindrical samples, completely different results were obtained (Fig. 2, curves I and II). By the way, similar results were obtained in [9] on samples of ellipsoidal shape, which ensured the absence of field concentrators. In any case, the question of the influence of the energy characteristics of the calf discharge on the physicochemical characteristics of the nitrided layer remains unclear and requires further research. Therefore, the thicknesses of the diffusion zone h and the nitride zone hN were found for the samples nitrided according to the above regimes. The results of the measurements are shown in table 3.

Assuming hardness as a basic parameter to assess the thickness of the nitrided layer (DSTU 20495-2005), we can conclude that it maintains the same trend - with decreasing energy parameters of the BATR process, the thickness of the nitrided layer decreases. This pattern is characteristic of the thickness of the nitride zone (Table 3.)

Analysis of the results (table 3) shows that with decreasing specific power of the electric discharge in the gas discharge chamber, the thickness of the layers h and hN also decreases and at w = 0.84 and 1.65 kW / m2 nitride zone on the studied steels is absent, but there is only the diffusion zone, which is absent only on 40X steel, which is explained by significantly higher energy costs for the formation of chromium nitrides. At the same time at w = 2.2 kW / m2 (mode 9 in Fig.1) there are no nitride and diffusion zones (table 3), which indicates the importance of comparing theoretical models of the formation of the incident particle flux with the real characteristics of the electric discharge in gases which should include the field voltage in the field of cathodic voltage drop, current density, cathode temperature, pressure and composition of the gaseous medium.

**Table 3. The thickness of the modified layer and the nitride zone of steels, nitrided in a glow discharge**

| Mode | The thickness of the modified layer, mm | | | The thickness of the nitride zone, μm | | |
|---|---|---|---|---|---|---|
| | Steel 45 | 40X | 38X2MЮA | Steel 45 | 40X | 38X2MЮA |
| 1 | 0,45 | 0,40 | 0,20 | 3,44 | 5,88 | 7,86 |
| 2 | 0,40 | 0,30 | 0,15 | 3,33 | 2,42 | 6,27 |
| 3 | 0,30 | 0,075 | 0,05 | 0 | 0 | 0 |
| 4 | 0,45 | 0,30 | 0,20 | 3,75 | 3,64 | 8,00 |
| 5 | 0,35 | 0,20 | 0,01 | 1,73 | 3,20 | 3,20 |
| 6 | 0,30 | 0 | 0,01 | 0 | 0 | 0 |
| 7 | 0,50 | 0,30 | 0,25 | 5,33 | 8,76 | 7,13 |
| 8 | 0,30 | 0,25 | 0,15 | 3,46 | 6,60 | 5,96 |
| 9 | 0 | 0 | 0 | 0 | 0 | 0 |

The latter determines the potential of the transition from dark to normal smoldering. The discharge transition potential for nitrogen-argon mixtures (20% N + 80% Ar) are according to the formula [1]:

$$U_{PTR}=(267,525+362,499P)+(24,3+433,2P)K_{PN}$$

where p is the pressure of the gas mixture; $K_{PN}$ = 0.25 is the ratio of the volume fraction of nitrogen.

For modes 3, 6 and 9 $U_{PTR}$, calculated by this formula is 462 V, 650 V and 838 V, but in fact it was 515 V, 300 V, and 300 V, respectively. That is why in mode 9 due to the absence of a glow discharge nitriding process is also absent and $h = h_N = 0$, and for modes 3 and 6 due to insufficient values of current density and, accordingly, insufficient value of specific power of electric discharge W no nitride layer is formed.

X-ray diffraction analysis data indicate that the structure and phase composition of nitrided steels also depend on the energy parameters of the discharge.

According to the results of X-ray diffraction analysis at the maximum values of energy parameters, a nitrided layer containing ε-, γ'- and α-phases is formed. Reducing the voltage and density of the discharge current leads to an increase in the proportion of γ'-phase (*$Fe_4N$*) in the nitride zone of the modified layer and, accordingly, to a decrease in the proportion of ε-phase (*$Fe_2N$*). At the minimum values of energy parameters, the formation of nitrides on the surface was not observed, the nitrided layer contained only the α-phase (Fig. 3 and Fig. 4).

It is known that the thickness and phase composition of the nitride zone determine its properties, and hence, ultimately, the properties of nitrided steel. Thus, the nitride zone containing only the γ′-phase is characterized by a sufficiently high ductility, while the zone containing the ε-phase has less ductility but higher corrosion resistance.

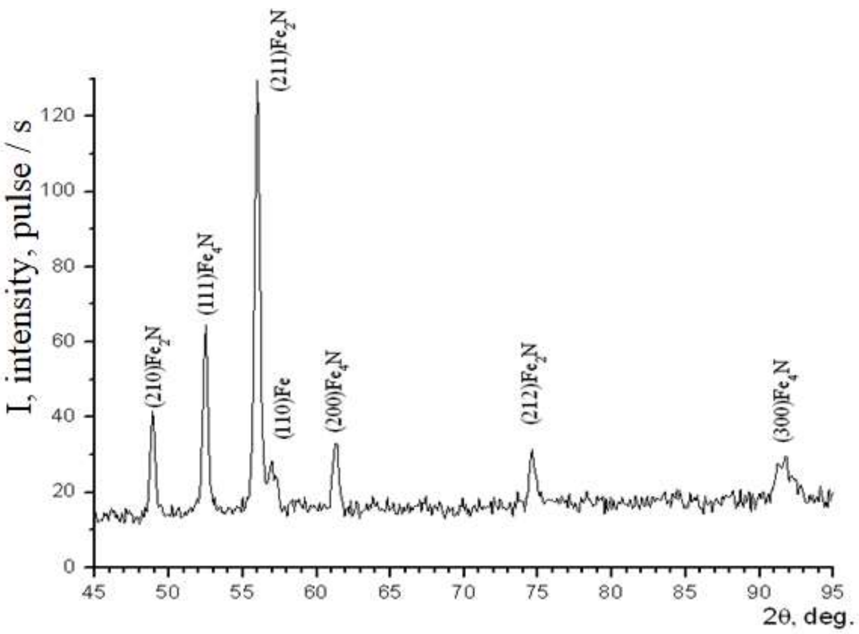
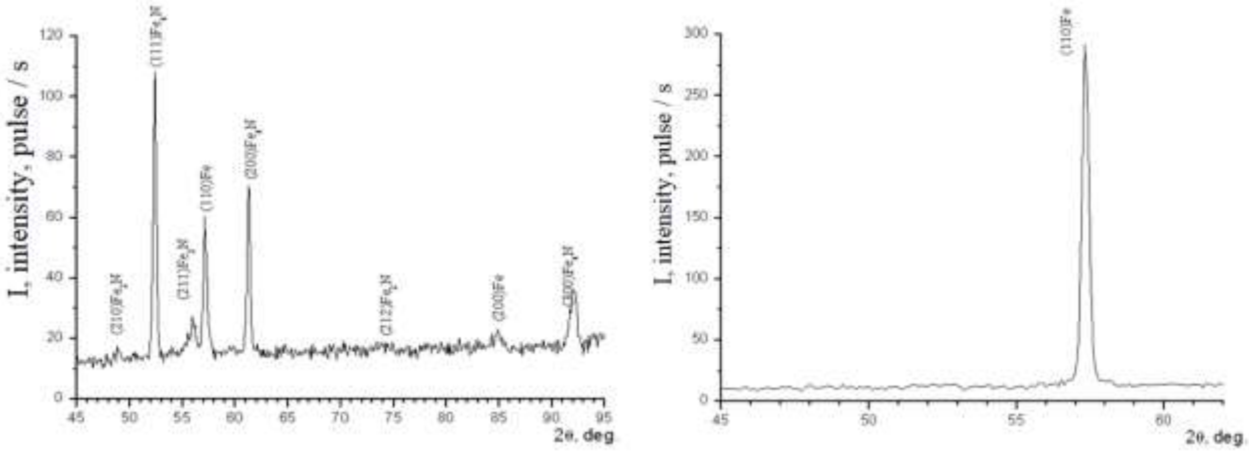



**Fig.3. Section of the diffraction pattern of the steel sample 40X (mode 7)**

The highest plasticity corresponds to the layer without the nitride zone. In general, the thinner the nitride zone, the more plastic is the nitrided layer, but the lower the resistance to abrasive wear, especially in dry friction [5].




a b

**Fig. 4. Section of the diffraction pattern of the steel sample 40X (mode 8 (a) and mode 9 (b))**

Thus, for parts operating in a corrosive environment and for wear at low contact loads, the BATR process should be carried out at the maximum possible values of voltage and current density, which will ensure the formation of ε-phase and, accordingly, high corrosion resistance and running friction surfaces. Reducing the values of energy parameters during BATR will increase the proportion of γ'-phase, and therefore can be recommended for parts operating at high dynamic loads under conditions of wear at high pressure; corrosion resistance will be reduced.

The dependence of the wear resistance of the modified surfaces on the energy parameters of the discharge was confirmed during tribological studies. As a result of experiments it was found that under conditions of dry friction for surfaces modified at higher energy values, the wear intensity (Fig. 5) and the run-in period (Fig. 6) decrease, and the period of constant wear increases, and with increasing content of alloyed elements in steel, this pattern becomes more pronounced. Of course, under other experimental conditions (for example, in the study of the obtained samples for corrosion resistance) the dependence of the tribological properties of nitrided surfaces on the current density and voltage at the electrodes of the chamber may be different, but in itself the existence of such dependence is not in doubt. which refutes the provisions of [10], according to which the energy characteristics of the discharge do not have a significant impact on the results of BATR.

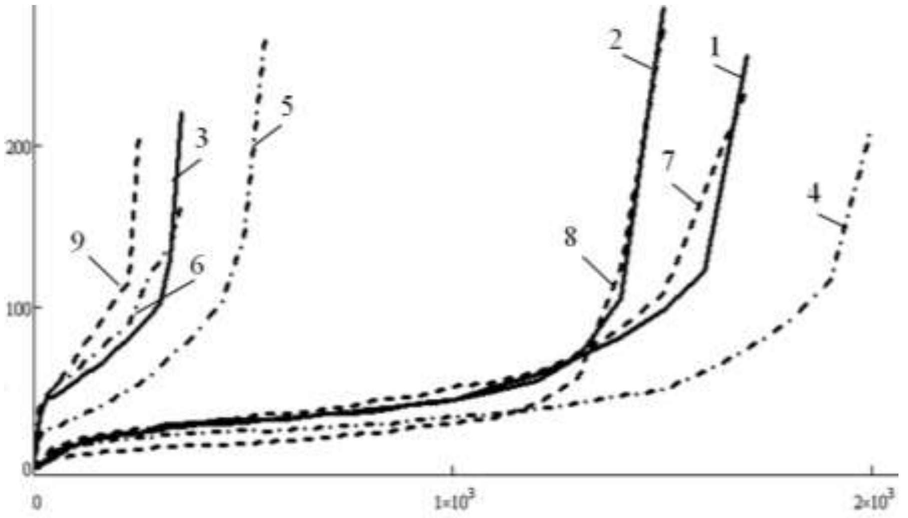



**Fig.5. Wear curves of steel 38KHMUA, nitrided in the glow discharge**

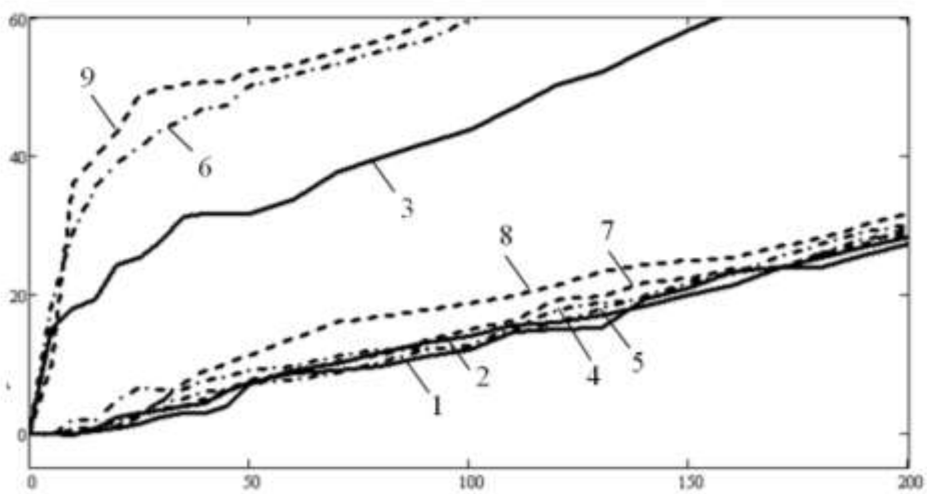



**Fig. 6. The running-in zone of the wear curve of steel 45 is nitrided in the glow discharge**

These data allow us to draw a very clear conclusion about the influence of voltage and current density on the characteristics of the modified layer, which determine the wear resistance of nitrided steels in the glow discharge, they are not just significant but crucial. Moreover, in the field of energy parameters of the regime there is a certain limit below which the ATP process generally loses its meaning, as it leads to unacceptable results, and this despite the fact that the values of the regime remain constant.

This means, in particular, that the set of traditionally fixed regime parameters (temperature, pressure, gas mixture composition and process duration) does not give an unambiguous idea of the conditions of the BATR process, and therefore cannot serve as a basis for predicting its results.

The list of factors that determine the BATR, given by the American researcher David Pye in [11], includes thirteen names.

Of course, taking all these indicators into account directly would make it incredibly difficult to manage the BATR process. However, they can be taken into account indirectly, because the influence of all these factors reflects the energy parameters of the process.

**Conclusions**

The paper presents a theoretical generalization and gives a new solution to the design and practical implementation of technological processes of nitriding in a glow discharge with independent parameters. As a result of the performed researches the following conclusions are formulated.

1 The current state of the controllability of the BATR process involves the use as a basic model of experimental developments, in which there are no provisions for establishing links between the input energy characteristics of the processing process and the final results. Provisions for the controlled provision of the necessary tribological characteristics of modified products have not been developed in practice, and those that are used as a result relate to a very narrow range of parameters.

4 The dependence of the main quantitative indicators of the modified layer, its structure and phase composition, as well as tribological characteristics on the energy parameters of the process is investigated. It is established that the increase of energy characteristics leads to: increase of surface hardness of the modified layer, its depth and thickness of the nitride zone; improvement of tribological properties - reduction of wear intensity and running-in zone; changes in the phase composition of steels, characterized by an increase in the proportion of γ'-phase in the nitride zone of the modified layer, which increases its ductility (compared to the nitride zone containing the ε-phase).

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