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DEVELOPMENT OF NITRIDING IN RUSSIA.[1] FOURTH PERIOD (1980 – PRESENT TIME): NEW DIRECTIONS IN THE DEVELOPMENT OF LTCTT

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By the beginning of the 1980s nitriding in Russia gave rise to numerous processes united under the general title of "low-temperature chemicothermal treatment" (LTCTT).

The traditional processes of LTCTT widely used in industry were developed continuously with full or partial removal of the weak points of classical gas nitriding. As a rule, problems were solved by creating new saturating media. However, virtually any of the developed LTCTT technologies had disadvantages. To a considerable degree this was caused by the absence of means for optimization of the processes.

By the late 1970s rather accurate qualitative and quantitative models of the carbon potential of furnace atmosphere were created in gas carburizing. The industry produced equipment for indirect determination of the value of the carbon potential in time. The development of this equipment went through stages of glass gas analyzers, dew point devices, and infrared detachable gas analyzers for immersed oxygen probes.

In LTCTT progress was much slower. Industry produced only simple portable dissociometers and some infrared ammonia analyzers. In most practical cases the phase composition of the surface layer was controlled using four variable parameters, namely, the temperature, the time, the degree of dissociation of ammonia, and the degree of dilution of ammonia by other gases.

One of the causes of this lagging was the small number of works devoted to the creation of quality models of nitrogen potential, though it was well known that the potential (concentration) of the saturating element on the surface of a treated part is responsible for the rate of the process and the properties of the part.

In the early 1980s the concept of nitrogen potential was formulated as a quantity determined by the ratio of the partial pressures of the gas components according to the reactions of formation of nitrides in the nitrided material [1 – 4].

The nitrogen potential π_N was represented as a function of the partial pressures of ammonia and hydrogen. However, due to the imperfection of the technique of gas analysis and great difficulties with its practical realization, the nitrogen potential was determined in terms of the partial pressures calculated by an equation involving the composition of the atmosphere at the inlet to the furnace, the degree of dissociation of ammonia α, and the pressure p in the furnace, i.e.,

$$\pi_N = \frac{\lambda_{NH_3}(1-\alpha)(1+\alpha\lambda_{NH_3})^{1/2}}{(1.5\lambda_{NH_3}\alpha + \lambda_{H_2})^{3/2}} p^{-1/2}, \tag{1}$$

where λ_{NH_3} and λ_{H_2} are the volume fractions of ammonia and hydrogen in the atmosphere.

The use of this formula was assumed to provide the possibility of determining the nitrogen potential with the use of simple devices, i.e., flowmeters for determining the flow rates of ammonia and dissociated ammonia and a dissociometer for determining the degree of dissociation of ammonia in the furnace.

Another important aspect was the understanding of the physicochemical processes formulated at that time. The idea was that individual ammonia molecules are ionized by electrons of the metal, which have received an energy exceeding the escape barrier due to the temperature and the existence of weak electrostatic fields in furnaces with radiation heating. A negative ion of ammonia "sticks" to the surface of the metal and dissociates on it. The nitrogen atom formed as a result is adsorbed by the surface and passes into the solid solution. As the nitrogen concentration in the surface layer increases, new phase transformations occur. The concentration of nitrogen

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[1] For the beginning of this series see MSHT No. 7, 1999 and Nos. 1 and 5, 2000.

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in the surface layer is determined by the value of the nitrogen potential.

When the degree of the dissociation of ammonia α, i.e., the amount of hydrogen in the gas phase, increases, π_N decreases. Experimental data [3, 5] make it possible to obtain dependences of the equilibrium potential C_N^i on the content of nitrogen in the α- and ε-phases in nitriding in dissociated ammonia, namely,

$$\pi_N^\alpha = 5.17 \times 10^{-5} \exp\left(\frac{8933}{T}\right) C_N^\alpha; \tag{2}$$

$$\pi_N^\varepsilon = 2.33 \times 10^{-5} \exp\left(\frac{1045}{T}\right) \times \left(\frac{11.12 - C_{\min}^\varepsilon}{C_{\min}^\varepsilon - 5.94}\right)\left(\frac{C_N^\varepsilon - 5.94}{11.12 - C_N^\varepsilon}\right), \tag{3}$$

where $C_{\min}^\varepsilon = 3.01 + 0.0179T - 0.154 \times 10^{-4} T^2$ is the temperature dependence of the minimum solubility of nitrogen in the ε-phase of the nitrided layer (obtained by processing experimental data in accordance with the Fe – N diagram).

Sustaining the nitrogen potential at the level of nitrogen solubility in this or that phase we can obtain a layer consisting of only α-solid solution, form a "lower" nitride (γ′-phase) on the surface, or obtain an ε-phase with a low content of nitrogen. It is recommended to control the nitrogen potential by diluting the ammonia with fully dissociated ammonia, oxygen, air, carbon-bearing gases, etc. [1, 4]. However, the authors of [3, 5] assumed that the simplest way to change the nitrogen potential consisted in changing the degree of dissociation of ammonia in the furnace. The higher the degree of the dissociation of ammonia in the furnace, the lower is π_N. At a nitriding temperature of 520°C and a degree of dissociation of 25% the potential $\pi_N \geq 1.5$; at 60 – 80% dissociation the potential $\pi_N \leq 0.3$ [1]. By changing the degree of the dissociation of ammonia (the nitrogen potential) in the furnace at any nitriding temperature we can regulate the phase composition and the nitrogen content in the ε-phase and the other phases. In addition, it is shown in [6] that saturation in an atmosphere of ammonia and products of its partial dissociation can accelerate the nitriding process by a factor of 1.5 – 1.8 when the value of the nitrogen potential is controlled.

Thus, the method for determination of the nitrogen potential developed by the school of Yu. M. Lakhtin made it possible to control the nitriding process.

However, some constraints inherent in the given method hampered its wide application. For example, the technique for determining the nitrogen potential was based on the measurement of gas flow rates, comparing their values, and measuring the partial pressure and the degree of dissociation of ammonia in the furnace, i.e., at least four gauges and quite intricate computational devices were required for determining a single parameter. In addition, the determination of the saturating capacity in terms of the partial pressures of the components of the gas phase did not provide the desired reproducibility of the results.

The next step in the development of indirect control of nitrogen potential was the creation of an ion gauge for direct measurement of the degree of dissociation by Lakhtin's school. It is based on the phenomenon of ionization of gas molecules in their thermal dissociation [7]. An automated ion dissociometer makes it possible to measure the ion potential within 0.1 – 7% in a temperature range of 450 – 700°C. At the same time, a method and a device have been created for controlling the nitriding process by evaluating the change in the physical properties of the steel directly in that process [7, 8].

Having studied the phenomena that occur in nitriding the disciples of Yu. M. Lakhtin worked on the mathematical description of the process and developed software for computer monitoring of the production processes and simulation of diffusion processes in nitriding [9 – 12]. This created prerequisites for complex automation of the processes of LTCTT.

In the end of the 1980s the Moscow Highway Engineering Institute (MHEI) in cooperation with the Freiburg Mining Academy (FMA) (Germany) performed a series of works devoted to testing a solid-electrolyte probe as a means for indirect determination of the saturating capacity of the ammonia furnace atmosphere in gas nitriding [3].

It should be noted that the solid-electrolyte gas analyzer is a sensitive element fabricated from stabilized zirconia, and its operation is based on the oxygen-anion conduction caused by the difference in the partial pressures of oxygen in the external and internal volumes of the solid-electrolyte cell (SEC), which commonly has the form of a test tube. It is obvious that in this case it is necessary to have a gas containing a constant and quite high amount of oxygen for comparison. As a rule, the gas is air. If the outer surface of the test tube is washed by the furnace atmosphere with an extremely low oxygen content ($10^{-14} - 10^{-18}$%), and its interval cavity is filled with air (20% O_2), an electromotive force arises between the two surfaces, which is quite measurable (from 1000 to 1200 mV (the e.m.f. of the SEC)).

By the beginning of the 1980s correlations were discovered and used between the partial pressure of oxygen and the content of carbon in the surface layer of carburized steel.

Researchers of the MHEI and FMA made an attempt to use such a gauge for indirect determination of the degree of dissociation of ammonia in gas nitriding. The external surface of the solid electrolyte cell was washed by the furnace atmosphere; for comparison, the same furnace atmosphere but preliminarily heated to the temperature of full dissociation of retained ammonia was fed into the internal cavity. The heating was performed in a special device inside the probe. The diagram of the sensitive element of the probe is presented in Fig. 1.

It was assumed that the concentration of oxygen in both mixtures should be the same, while the concentration of hydrogen should differ. In the medium of fully dissociated am-

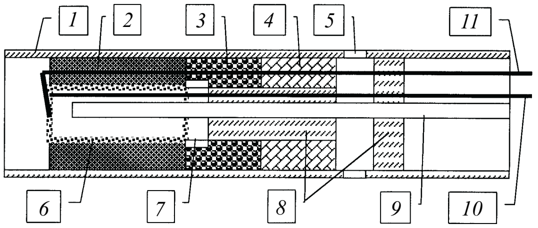

Fig. 1. Diagram of the sensitive element of oxygen probe designed by the FMA: *1*) external ceramic tube; *2*) sealing; *3*) heating; *4*) catalyst; *5*) feeding of the furnace atmosphere into the dissociator; *6*) solid-electrolyte cell; *7*) feeding of dissociated ammonia into the solid-electrolyte cell; *8*) ceramic bushes; *9*) removal of dissociated ammonia from the solid-electrolyte cell; *10*) internal electrode; *11*) gas electrode.

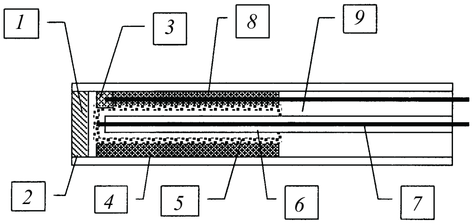

Fig. 2. Diagram of the sensitive element of oxygen probe TDK-1M6A: *1*) filter; *2*) external ceramic tube; *3*) titania powder; *4*) sealing; *5*) solid-electrolyte cell; *6*) external ceramic tube; *7*) air electrode; *8*) gas electrode; *9*) cavity for feeding air into the solid-electrolyte cell.

monia the content of hydrogen should be much higher and, consequently, the proportions of H_2O/H_2 should differ. A hypothesis was put forward, according to which the content of water in the atmosphere should be constant. In this case, it is sufficient to determine the content of hydrogen in the furnace atmosphere in order to find the degree of dissociation of ammonia. Then the amount of retained ammonia in the furnace atmosphere is a constant quantity determined by the temperature. Thus, having determined the e.m.f. of the SEC we can calculate the nitrogen potential by the formula

$$\pi_{\mathrm{N}} = \frac{p_{\mathrm{NH}_3}}{p_{\mathrm{H}_2}^{3/2}}. \tag{4}$$

However, the tests performed in the pilot installation at the MHEI showed that "in gas nitriding the state of the equipment, the composition of the mixture, and the random proportion of the partial pressures H_2O/H_2 were interdependent" [3].

It should be noted that after the union of Germany researchers of the FMA and the Process Electronic Company declared the beginning of commercial production of oxygen probes for determining the nitrogen potential in gas nitriding. Wide-scale production was started in 1995. However, already in 1997 practical application of these devices showed that the used method of indirect determination of the nitrogen potential had limited possibilities. In 1998 Process Electronic stopped the production of the oxygen probe for ammonia furnace atmospheres.

The method of using a classical oxygen probe as a means for indirect determination of the saturating capacity of the furnace atmosphere in gas nitriding was suggested in the works of V. M. Zinchenko and V. Ya. Syropyatov [13 – 15].

The nitrogen potential was determined as the content of nitrogen in an iron (steel) specimen after its through saturation in an atmosphere with a specific composition at a specific temperature, i.e., in a specimen placed under equilibrium conditions with the gas phase. It was suggested that a foil sample should be used for direct determination of the nitrogen potential.

A new design of oxygen probe TDK-1M6A (Fig. 2) was suggested, in which the comparison gas was air. The choice of a cardinally new material for the gas electrode (titania powder) provided stable operation of the SEC at a temperature exceeding 400°C. This made the use of a special heating device in the structure of the probe unnecessary. The basic dependences of the nitrogen concentration in specimens of the foil sample on the SEC e.m.f. for conventional nitriding temperatures are

$$\log \mathrm{Np} = \frac{1}{1.2167}\left(\frac{10.082(E-797.2)}{T} - 3.363\right), \tag{5}$$

where Np is the nitrogen potential of the atmosphere (the content of nitrogen in the specimen of the foil sample in wt.%), E is the electromotive force of the solid-electrolyte cell in mV, and T is the temperature in K.

Such an approach simplified considerably the prediction of the phase composition of the surface layer of the nitrided steel. When determining the nitrogen potential expressed in terms of the nitrogen concentration in iron with the help of an oxygen probe placed directly in the chamber of the furnace, it is sufficient to compare the obtained result with the binary Fe – N diagram for finding the phase composition. A foil sample is used as a means for periodic checking of the oxygen probe.

The new model of the nitrogen potential made it possible to create quite simple software for computer simulation of the diffusion processes that occur in gas nitriding and for monitoring of the actual technological processes [15].

In the last decade a method for diagnosing processes that occur both in the technological atmosphere and on the saturated surface in LTCTT in a glow discharge appeared in Russia [16]. The method and the device for its realization developed by N. M. Ryzhov have made it possible to create a system for control over the processes of ion chemicothermal treatment, i.e., nitriding, nitrocarburizing, and carburizing [17]. The method provides control and regulation of the carburizing and nitriding capacities of the ionized atmosphere

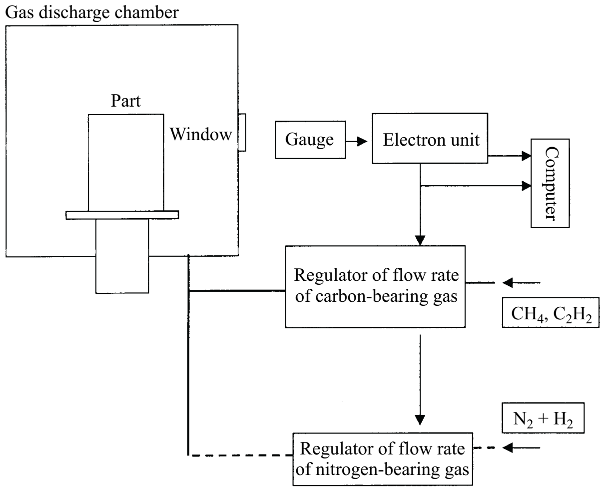

Fig. 3. Block diagram of automated system for controlling ion chemicothermal treatment.

from the density of the current of carbon- and nitrogen-bearing particles created and transferred by the glow discharge from the gas medium to the saturated surface of the part and makes it possible to determine the concentration of carbon and nitrogen in the process of diffusion saturation, sustain it at the requisite level on the saturated surface, and determine the beginning of the phase transformation on the saturated surface, i.e., the formation of particles of excess carbides, carbonitrides, or carbon black. The created system for controlled diffusion saturation (Fig. 3) includes a block of equipment, control gauges, and a mathematic model of the process with appropriate software. The software allows the researcher to simulate the diffusion process in a real time mode and determine the distribution of the concentration of the saturating elements over the thickness of the diffusion layer. The method makes it possible to optimize the parameters of ion chemicothermal treatment from the standpoint of stable creation of a quality diffusion layer and from the standpoint of the technical and economic parameters.

In the same period S. A. Gerasimov obtained new data on the mechanism of phase transformations in the diffusion layer [18, 19]. Specifically, he established experimentally that in nitriding of aluminum-bearing steels a metastable aluminum nitride with a f.c.c. lattice segregates in the diffusion layer. It turned out that all segregations in the bulk of a grain (coherent, semi-coherent, and incoherent) are nitrides with a f.c.c. lattice, similar to the γ'-phase. The use of modern methods allowed the researchers to determine the nature of the grain boundary segregations in the diffusion layer that had earlier been classified as iron nitrides (carbonitrides) enriched with alloying elements. The increase in the size and volume fraction of these segregations during the entire evolution of the nitriding processes was a factor worsening the properties of the treated parts. It was shown that grain boundary segregations in the diffusion zone of the nitrided layer were represented by ferrite. This made it possible to explain many problems arising in the formation of the nitrided layer. Specifically, the presence of ferrite with highly dense nitrides of light elements causes the embrittlement of grain boundaries and diminishes the impact toughness of nitrided steels. Ferrite, with its high diffusivity, is the conductor of nitrogen over grain boundaries. These results create new possibilities for solving many problems of LTCTT.

However, the possibilities of the development of LTCTT were limited to a considerable degree by the absence of clear concepts of the physicochemical processes that occur at the gas/metal interface. This made researchers return to the problem of the initial interaction between the saturating medium and the surface of the metal and to the nature of diffusion of nitrogen in gas nitriding (pure or a reaction one).

Though the theory of pure diffusion dominated in gas nitriding in those years, there still exists an opinion that reaction diffusion is the primary one. This was unambiguously stated in the works of S. F. Yur'ev [20], A. N. Minkevich [21], G. N. Dubinin [22 – 24], and others. This opinion is based on experimental results that allowed the researchers to conclude that the nitride layer forms virtually always and immediately.

V. M. Zinchenko, V. V. Barelko, and V. Ya. Syropyatov assumed that processes at the gas/metal interface could be principally changed towards activation of the predominantly solid-solution mechanism by treating ammonia on catalysts.

At the same time, as early as the 1930s some authors tested the effect of various catalysts on an ammonia atmosphere. Interesting large-scale tests of the effect of magnesia and other substances on the process of nitriding of steel 38KhMYuA were described in [25]. A layer 0.2 mm thick was obtained in 10 – 12 h instead of the 30 – 36 h in conventional nitriding. However, by the end of the 1940s this direction was undeservedly forgotten. Catalysts were placed in the class with accelerators [21] of the NH_4Cl type, i.e., with substances directly participating in reactions that occur at the gas/metal interface, and systematic studies devoted to the effect of catalysis on the nitriding process were not performed.

By the beginning of the 1980s workers of the laboratory of macrokinetics of the Institute for Problems of Chemical Physics of the Russian Academy of Sciences discovered intense sublimation of ions from the surface of platinum in an ammonia flow [26]. The sublimated ions are in a quasi-stable equilibrium, and after colliding with the inert gas molecules most return to the surface of the catalyst. The collision between platinum atoms and ammonia molecules causes ionization of the latter. It was established that platinum ions play the role of active centers of both ionization of ammonia and the chemical reaction of conversion of ammonia in the presence of oxygen. With increase in the ammonia content in the mixture the effect of catalytic ionization increases linearly, whereas the effect of conversion weakens. Oxygen, which is always present in the furnace atmosphere, fully passes into a bound form.

The discovered phenomenon [26] and subsequent studies lead to the development of a new series of catalysts with a cellular structure that differently affect the gas phase depending on the alloying of the matrix [27].

When such catalysts are used in gas nitriding the main problem consists in the changed nature of the interaction between the gas medium and the surface of the metal. It was assumed that this could be caused by powerful ionization of ammonia and formation of a large amount of intermediate, labile, highly adsorption-active, and short-lived formations such as nitrogen-, hydrogen-, and oxygen-bearing radicals, ions, and radical ions, or due to the incomplete oxidation of the ammonia and the initiation of processes similar to those occurring in an atmosphere of endothermic gas. It was expected that this would decelerate the formation of high-nitrogen phases and make the process of gas nitriding closer to the mechanism of pure solid-solution diffusion.

In order to check these ideas the researchers developed a catalytic unit "Oxycan" mounted in the furnace space at the place of feeding of the process gases. In the functional zone of the unit a catalyst was placed on a cloth base containing some metals (platinum, palladium, etc.) implanted in the fibers of the cloth. The process gases (ammonia, air, etc.) were fed by a conventional method, i.e., from commercial low-pressure gas pipes through a mixing device [28 – 30].

The saturation process in the new atmosphere differed radically from classical gas nitriding and other LTCTT processes in gas media. The differences included the formation of solid solutions of nitrogen in α-iron, which contained up to 1.4 wt.% N, the possibility of smooth regulation of the nitrogen potential within the range of 0.1 – 8.0 wt.% N by changing the partial pressure of oxygen in the atmosphere of the furnace, and the possibility of obtaining single-phase layers of a γ′- or ε-phase on the surface; when it was necessary to obtain an ε-phase on the surface, the content of nitrogen in it was provided at a level of at most 8 wt.%, which eliminated the high brittleness of this layer (Fig. 4). It is the formation of supersaturated solid solutions preceding the formation of secondary phases, which directly indicates that the process develops as pure diffusion. In this case there can be no doubt that pure diffusion is the primary process in nitriding performed in an atmosphere of catalytically treated ammonia, and the formation of the nitrided layer by this mechanism will provide the best quality of the treatment.

Thus, the use of a catalyst made it possible to change the mechanism of the interaction on the gas/metal interface in actual processes of gas nitriding, namely, to suppress the formation of nitrides in the initial stages of the saturation process and stimulate the process of pure diffusion. These results were used to develop a reliable method that involved the use of catalytically treated ammonia in the saturation process. The mentioned features of the new furnace atmosphere made it possible to develop a series of technological processes with much less defects, which considerably widened the application range of the LTCTT processes [29, 30].

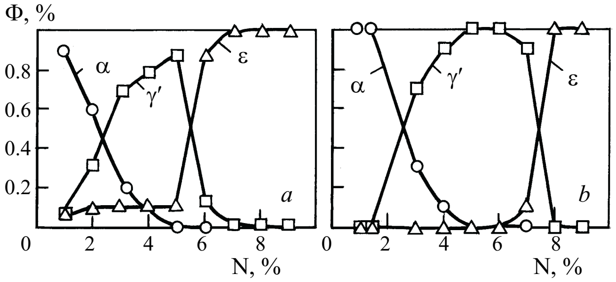

Fig. 4. Dependence of the phase composition (Φ-phase) of specimens of a foil sample on the content of nitrogen in classical (*a*) and catalytic (*b*) gas nitriding.

Nitriding processes in products of catalytically treated ammonia and ion nitriding obey some general rules. In particular, it is known that the catalysis used by the author of [26] are a powerful source of charged particles in an ammonia flow at a temperature exceeding 300°C, which causes a considerable ionization of the gas. This factor also eliminates the formation of an excess nitrogen concentration in the layer (due to the more intense diffusion), and then the processes of structure formation, like in ion nitriding, are closer to equilibrium than in classical nitriding.

The use of LTCTT in processes of combined hardening of the surface was a principally new approach at that time. The main aim of such hardening consisted in combining the methods of surface treatment which provide formation of a hard substrate with deposition of very hard coatings of a micron thickness onto it by chemical (CVD) and physical (PVD) methods. In the presence of a hard substrate the working capacity of thin (5 – 7 μm) surface coatings increases markedly, causing a substantial increase in the wear resistance of cutting tools, for example. As applied to the nitriding process, the idea of such combination and creation of a kind of composite coating was first realized in the early 1980s by Lakhtin's disciples. The originality of the approach consisted in the fact that it was suggested to use nitriding after preliminary laser alloying of the surface of the steel. Nitriding was used with an aim to raise additionally the hardness of the surface created by laser alloying, thus removing the disadvantages of the laser treatment, first of all, the high difference in the internal stresses on the interface of the zone of the laser effect and the matrix.

It was shown in the works of O. V. Chudina [31 – 35] that the use of such a treatment is the most efficient when such elements as V, Cr, Mo, and Al are introduced into the composition during laser alloying. This provides an unusually high microhardness of the surface of medium-carbon steels (up to 2000 *H*), increases the wear resistance by a factor of 1.5 – 3 relative to nitrided nitralloys, redistributes the internal stresses, decreases substantially their gradient at the boundary of the zone of the laser effect, and thus removes one of the main disadvantages of laser treatment, i.e., the appearance of cracks in the near-matrix zone.

In the same years T. A. Panaioti and G. V. Solov'ev suggested processes of ion nitriding of titanium alloys in hydrogen-free media, which made it possible to reduce the time of nitrogen saturation by a factor of 10 – 15 as compared with conventional nitriding and perform ion nitriding of $(\alpha + \beta)$ titanium alloys at low temperatures (500 – 600°C) that corresponded to their aging temperature [36 – 39]. Such a treatment increases the resistance to abrasive wear (by a factor of 4) and erosive wear (by a factor of 10 – 40) without diminishing the structural strength of the material. For titanium alloys not hardened by quenching and aging ion nitriding is recommended at a high temperature (800 – 900°C). Methods were suggested for controlling the saturation capacity of the medium in ion nitriding of titanium and its alloys, which provide regulation of the phase composition and the thickness of the nitrided layer [40].

The research in the field of surface hardening of refractory metals and alloys, i.e., Nb, Ta, Mo, and W, was intensified considerably. A substantial contribution in this direction was made by T. A. Panaioti [41 – 47]. The main problem consisted in raising the strength and heat resistance of refractory metals with the use of an available material (nitrogen) and a relatively simple technology. These requirements were satisfied by nitriding, which provided an increase in the strength, hardness, wear resistance, high-temperature strength, and heat resistance of thin-sheet and thin-walled parts.

The use of glow discharge considerably widened the potential possibilities of nitriding of refractory alloys. The main advantages of ion nitriding relative to the conventional process are the possibility of controlling the characteristics of the obtained layer (the structure, the phase composition, and the thickness) aimed at providing the requisite combination of service properties of the parts and the possibility of nitrogen hardening (surface and volume) of any surface of a part with complex configuration.

Thus, the nitriding process was studied in Russia with due attention. As a method of hardening, nitriding in Russia went through all classical stages of development from pioneering scientific experiments, through numerous laboratory studies and pilot tests, to wide commercial use. The results allowed our specialists to convert the process in machine building plants of Russia and provide a high wear resistance, hardness, and corrosion and fatigue resistances of machine parts.

At the present time, this kind of CTT develops dynamically and is continuously improved by researches. The situation moves towards the implementation of the dream of the first enthusiasts of gas nitriding, who thought that this technology is a universal hardening method with unlimited possibilities.

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