

Intensified Saturation of Iron with Nitrogen by the Method of Thermogasocyclic Nitriding

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Abstract—Here, we describe the thermogasocyclic-nitriding method, which consists in multiple alternation of process stages with high and low nitrogen potential conducted at temperatures lower and higher, respectively, than the temperature of the eutectoid transformation in the Fe–N system. The phase composition of the nitrided layer after various operation modes and kinetics of the growth of its individual regions have been studied. The possibilities of intensifying the nitriding process and regulating the phase composition of the layer by an appropriate choice of process parameters, namely, the number of half cycles and their duration, have been demonstrated.

Keywords: nitriding, thermogasocycling, nitrided layer, microstructure, phase composition

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The technology of nitriding of metals and alloys is widely used in industry for surface hardening of machine parts and tools. At present, a large number of technological modifications for this process exist and are used to increase the service life of machines [1–3]. The common use of this method of thermochemical treatment (TCT) is due to its clear advantages in comparison with other TCT methods. First of all, they include the possibility to control the phase composition and structure of the diffusion layer in a wide range, which ensures the achievement of properties desired in each particular case, namely, hardness, wear resistance, corrosion resistance, fatigue strength, etc.

Each of the phases of the nitrided layer possesses characteristic properties, and their combination determines the properties of the nitrided product. Analysis of modern knowledge of the mechanisms of wear, corrosion failure, and other surface properties allows us to formulate requirements for the phase composition of the nitrided layer for various operating conditions of products.

Thus, the surface nitride zone provides running-in of surfaces in friction conditions and increases resistance to corrosion. During wear in a high specific pressure mode, a multilayer structure consisting of a surface nitride zone and a doped internal nitriding zone is considered to be optimal. For products exposed to dynamic wear and impact loads, a developed internal nitriding zone with a relatively small surface nitride layer needs to be created. In some cases, a diffusion layer without the nitride zone is required,

consisting only of the internal nitriding zone on the basis of a solid solution.

The phase composition of the nitrided layer is traditionally controlled by monitoring the nitrogen potential of the saturating atmosphere, which is maintained at the level of nitrogen solubility in a particular phase of the Fe–N system. In classical furnace gas nitriding, this is successfully done by using multicomponent media: ammonia diluted with nitrogen, air, oxygen, carbon-containing gases, and ammonia cracking products [3, 4].

The main disadvantage of the nitriding process is the length of time required for the process. This results in a search for methods to intensify saturation and solve problems of resource conservation and environmental safety, which is directly related to a decrease in ammonia consumption.

It is known that the limiting stage of the nitriding process in most cases is the diffusion of nitrogen in the metal to be saturated. Thus, the main factor in the intensification of the process is the increased temperature, which provides increased diffusion mobility of the active ions and, as a consequence, the accelerated growth of the layer. However, the limits of the increase in the temperature of the process are limited by the conditions that phase transformations need in order to proceed. This explains the fact that high-temperature nitriding processes are used only for a limited range of materials [5]. Other ways to intensify the nitriding process are also widely known, which are based on increased activity of the gaseous medium, for exam-

ple, nitriding in a glow discharge [6, 8], and use of other types of energy influence [9, 10].

Studies show that the acceleration of the formation of the diffusion layer is facilitated by gasocyclic processes with changing nitrogen potential at its individual stages [11, 12]. Thus, nitriding with an alternating supply of ammonia and air makes it possible to reduce the formation time of the diffusion layer in alloyed steels by 1.5–4 times [13, 14]. The mechanism of the intensification in this case is related to the control of the composition and structure of the surface nitride zone of the ϵ -phase, which reduces the diffusion mobility of nitrogen and prevents its penetration into the internal nitriding zone.

On the other hand, the resulting highly nitrogenous ϵ -phase can become an additional source of nitrogen when its resorption (denitrogenation) is provided. This can be realized by lowering the nitrogen potential at the stage following the saturation. Multiple repetition of nitriding and denitrogenation stages makes it possible to increase the diffusion layer. Thus, the classical gasocyclic process includes the alternation of processing stages with high and low nitrogen potential at the same temperature. At the same time, the gasocyclic process provides significant saving of the saturating gas, ammonia.

Additional prerequisites for intensified nitriding and regulating the phase composition of the layer are created by the thermogasocyclic process, which involves changed temperature at various stages of the process. The increased temperature at stages with low nitrogen potential is a factor in the acceleration of the process of resorption of high-nitrogen nitride phases with the corresponding increased concentration of active nitrogen in the solid solution. The task is to determine the parameters of the thermogasocyclic process that affect the phase composition of the diffusion layer and the rate of its formation.

The purpose of this work is to study the kinetics of the growth and phase composition of a nitrided layer in iron under the conditions of the thermogasocyclic process.

Gasocyclic and thermogasocyclic nitriding of ARMCO iron were studied experimentally according to the scheme shown in Fig. 1. For several cycles (N), the active saturation stage in pure ammonia alternates with the passive stage, which is carried out when ammonia is not supplied, i.e., at a nitrogen potential close to zero.

The duration of the stages is the same in each process and is characterized as the half cycle duration. The initial stage is always active; depending on the type of the final stage, two options were provided: the “asymmetric” process ended with the passive stage (with an even number of half cycles), while the “symmetric” process ended with the active stage (with an

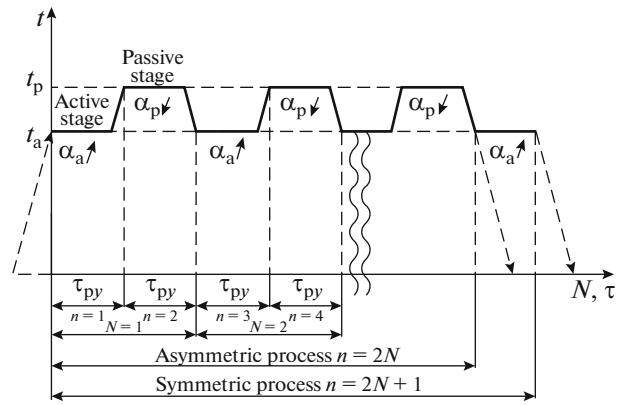


Fig. 1. Scheme of the process of thermogasocyclic nitriding.

odd number of half cycles). The main parameters of the process are the following:

t_a	temperature of the active stage
t_p	temperature of the passive stage
τ_{hc}	half-cycle duration
$n = 2N$	number of half cycles.

The temperature of the thermocycling stages was chosen in accordance with the Fe–N state diagram for the possibility of phase transitions during the change of stages. The temperature of the active saturation stage in ammonia is $t_a = 520^\circ\text{C}$, which makes it possible to compare the results obtained with classical nitriding. Temperature of the passive stage $t_p = 620^\circ\text{C}$ is chosen to be slightly higher than the eutectoid temperature of the Fe–N system (591°C), on the one hand, to ensure the most complete dissociation of ammonia, and, on the other hand, to prevent the growth of the grain upon heating. To compare the thermocycling effect with the isothermal gasocyclic process, experiments were also carried out at equal temperatures of the active and passive stages: $t_a = t_p = 520^\circ\text{C}$ and $t_a = t_p = 620^\circ\text{C}$.

The degree of dissociation of ammonia in the active stage α_a was regulated to be 25–30 and 40–45% at saturation temperatures of 520 and 620°C , respectively. In the passive stage, the degree of dissociation α_p was 68–70 and 94–98% at 520 and 620°C , respectively.

The total duration of all “asymmetric” processes is the same and equal to 6 h; the number of cycles N varied from 1 to 6. At the same time, the number of half cycles n ranged from 2 to 12 depending on the chosen parameter of the half-cycle duration τ_{hc} (ranged from 3 to 0.5 h). For the “symmetric” process, the final stage of nitriding in ammonia lasting from 0.5 to 1 h was added to the scheme mentioned.

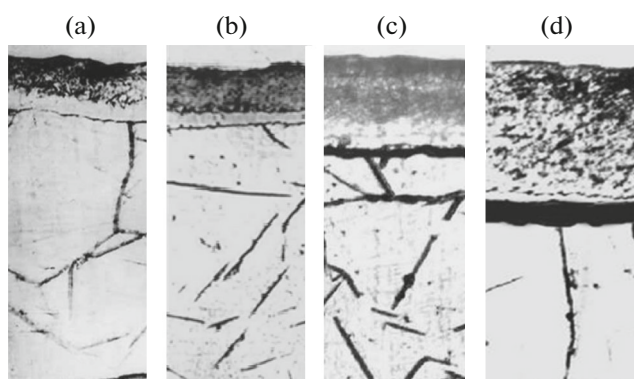


Fig. 2. Microstructure of ARMCO iron after nitriding for 6 h: (a) traditional nitriding in ammonia at 520°C; (b) gasocyclic nitriding at 520°C, the number of half cycles is 6; (c) thermogasocyclic nitriding at 520/620°C, the number of half cycles is 6, "asymmetric process"; (d) thermogasocyclic nitriding at 520/620°C, the number of half cycles is 6 + 1 with additional active stage of 0.5 h, "symmetrical process." Magnification 1000 \times .

The processes were carried out on a modified unit for traditional nitriding in flowing ammonia, which incorporated a system for monitoring and maintaining temperature in the working volume and a system for gas supply, controlling the flow and degree of dissociation of ammonia, and purification and drying of gas. Two electromagnetic gas valves controlled by a monitoring panel were used to cut off the flow of ammonia at the passive stage, which makes it possible to conduct the processes in the automatic mode.

Nitrided samples were placed in a working container at the level of the working area. The container was then sealed and connected to the gas main. Within 5–10 min, the container was purged with ammonia to remove air. Then, the operating flow rate of ammonia was set and the container was placed in an oven heated to the operation temperature.

Microstructure of nitrided samples was studied using a Neophot metallographic microscope with a digital adapter and an EVO MA10 scanning electron microscope. Phase X-ray-diffraction analysis was carried out on a DRON-2 device. The nitrogen distribution over the thickness of the nitrided layer was determined by the scanning method using a Link-System micro-X-ray spectral analyzer.

Experimental studies of the microstructure and phase composition of ARMCO iron after gasocyclic and thermogasocyclic processes have shown that the structure of the nitrided layer in iron corresponds to the laws governing the separation of phases in accordance with phase transformations in the Fe–N system. In all operation modes of the process, a nitride zone and a diffusion sublayer of the internal nitriding zone are observed in the diffusion layer (Fig. 2).

The nitride zone contains a layer of the ϵ -phase of Fe_3N with high nitrogen content and a sublayer of the

γ -phase of Fe_4N . The internal nitriding zone consists of a nitrogen-doped α -solid solution $\text{Fe}_\alpha(\text{N})$ with inclusions of the γ -nitride of a characteristic needle shape. A dark eutectoid layer ($\alpha + \gamma$) is observed under the nitride zone during the gasocyclic or thermogasocyclic processes with a passive stage at a temperature of 620°C (see Figs. 2c, 2d).

It was found that nitriding under thermogasocyclic conditions increases the thickness of the diffusion layer as compared with traditional nitriding and saturation under isothermal gasocyclic conditions. The greatest effect of intensification is achieved in the "symmetric" process, in which the final stage is saturation in conditions of increased nitrogen potential. When conducting the process with the following parameters: $t_a = 520^\circ\text{C}$, $t_p = 620^\circ\text{C}$, and number of half cycles $n = 12 + 1$ (half-cycle duration is 0.5 h), the total thickness of the nitrided layer was found to almost triple in comparison with the usual nitriding in flow ammonia.

The mechanism for accelerating the growth of the nitrided layer by thermocycling at temperatures above and below the eutectoid temperature layer is that phase transitions occur in it with a periodicity equal to the number of half cycles. When passing from the passive to the active half cycle, due to a decrease in temperature from 620 to 520°C, the eutectoid transformation of nitrous austenite into nitrous perlite consisting of $\text{Fe}_\alpha(\text{N})$ and the γ -phase takes place in a narrow zone of the layer. This transformation is accompanied by an increase in volume, which contributes to an intense outflow of incoming nitrogen from the surface of the sample.

In addition, these transformations are accompanied by grain refinement, i.e., an increase in the extent of grain boundaries, and, consequently, activation of the boundary diffusion of nitrogen.

Intense penetration of nitrogen into the deep parts of the layer during thermogasocyclic nitriding was confirmed experimentally by analyzing the distribution of nitrogen concentration in the depth of the sample (Fig. 3). It can be seen that the thickness of the region with an increased nitrogen concentration is much larger than the thickness of this zone when nitriding in flowing ammonia. The values of the maximum nitrogen concentrations calculated from the intensity of the characteristic radiation peaks are 12 wt % of N after thermogasocyclic nitriding and 8.5% wt % of N after the usual nitriding.

In cyclic processes, the growth of the nitrided layer is mainly due to an increase in the thickness of the internal nitriding zone. Compared with traditional nitriding in ammonia at $t = 520^\circ\text{C}$ for 6 h, the thickness of the internal nitriding zone after the thermogasocyclic process increases from 400 to 870–1100 μm for the same 6 h depending on the number of half cycles.

The number of half cycles and their duration are the main parameters determining the degree of inten-

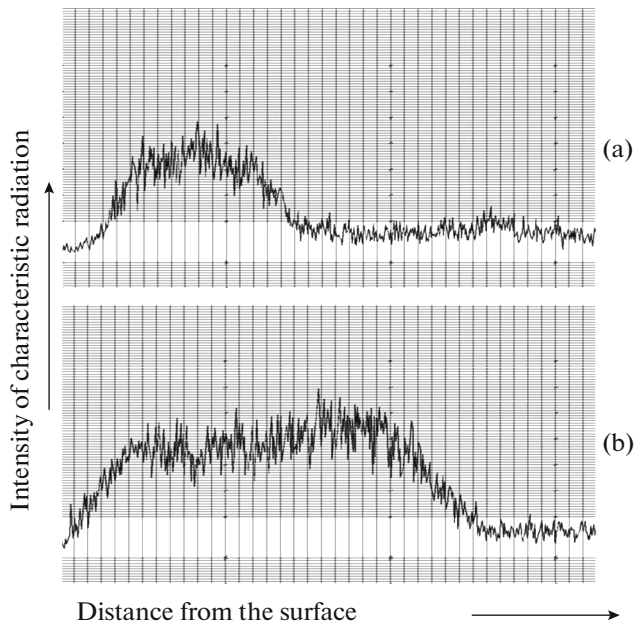


Fig. 3. Distribution of nitrogen in the bulk of nitride layer of ARMCO iron: (a) nitriding in flowing ammonia, 520°C, 6 h; (b) thermogasocyclic nitriding at 520/620°C, the number of half cycles is 12, the half-cycle duration is 0.5 h.

sification of the nitriding process: with increasing number of short half-cycles, the thickness of the inner nitriding zone increases (Fig. 4a). At the maximum number of short half cycles ($n = 12 + 1$) in our experiment, the thickness of the internal nitriding zone increases after gasocycling by 2.2–2.5 times, while after thermogasocycling it increases by 2.75 times in comparison with nitriding in flowing ammonia for the same time of the process. An increase in the temperature of the isothermal gasocyclic process from 520 to 620°C naturally accelerates the growth of the internal nitriding zone. The use of the thermogasocycle in the 520/620°C regime gives the highest acceleration of the layer growth, which, as noted above, is associated with repeated phase transformations promoting nitrogen diffusion.

The intensification of the growth of the inner nitriding zone with increasing number of short-term cycles (half cycles) during cyclic processes can be explained by the effect of “pumping” nitrogen into the metal due to repeated nitrogen saturation followed by resorption of the ϵ -phase. At the first active stage, the process of flowing nitriding takes place with the formation of a developed nitride zone on the surface consisting of sections of the ϵ - and γ' -phases. In this case, as is known, diffusion proceeds most intensely at the initial saturation phase and, then, in accordance with the parabolic law of the kinetics of nitriding, decays. The surface crust of the ϵ -phase increasing in thickness produces an additional decelerating effect on the

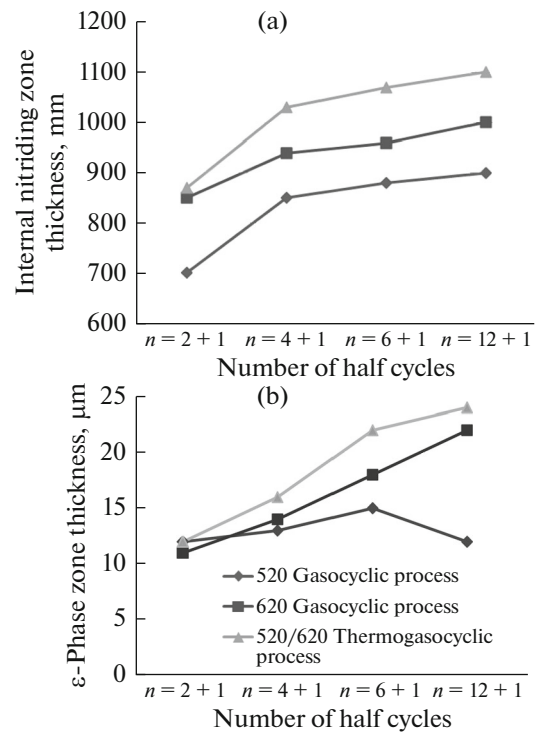


Fig. 4. Dependence of the thickness of the (a) inner nitriding zone and (b) nitride zone of the ϵ -phase on the number of half cycles of “symmetric” gasocyclic and thermogasocyclic processes completed in the nitriding stage after 0.5 h.

diffusion penetration of nitrogen under the nitride zone.

At the passive stage, due to a reduced nitrogen potential close to zero, no high-nitrogen phases form and the growth of the nitride zone ceases. On the contrary, dissociation of nitrides takes place and active nitrogen is released. A significant gradient of nitrogen concentrations at the boundary of the nitride zone and the internal nitriding zone is created (see Fig. 3b), which is the driving force for its moving into the bulk of the metal.

In contrast to the diffusion process in the case of nitriding in an ammonia atmosphere directed only into the bulk of the metal, in the case of denitrogenation with zero nitrogen potential, the nitrogen diffusion occurs from the nitride zone in both directions, into the depth of the layer and outward, to the surface of the sample. Diffusion flows directed oppositely affect the character of the formation of phases in the diffusion layer at the subsequent active stage of the cycle.

Since the rate of denitrogenation, like the rate of nitriding, changes with time according to a damped curve, the process of nitride resorption is most active in the initial phase. Multiple repeated short-term stages of saturation and resorption give the greatest effect of increasing the thickness of the layer with an increased concentration of nitrogen.

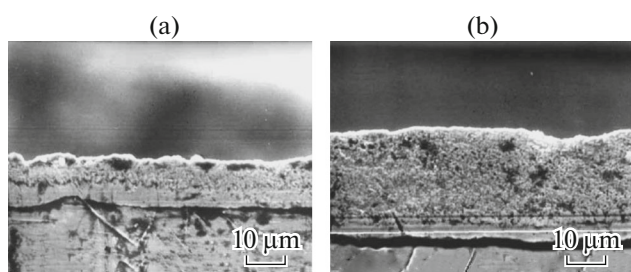


Fig. 5. The structure of the nitride zone in ARMCO iron (a) after traditional nitriding in ammonia at 520°C for 6 h and (b) after thermogasocyclic nitriding at 520/620°C for 6 h at a number of half cycles of 12 + 1. SEM images, magnification 1500×.

Thermogasocyclic nitriding in the “symmetric” regime promotes the accelerated growth of not only the internal nitriding zone, but also the nitride zone, mainly due to the growth of the ϵ -phase. However, a significant effect is achieved only with a large number of short half-cycles (Fig. 5). When the process was carried out during 6 h and consisted of one active and one passive stage lasting for 3 h with additional nitriding for 0.5 h, there is no significant effect on the formation of the ϵ -phase (see Fig. 4b).

An increase in the number of half cycles and a decrease in their duration intensifies the growth of the ϵ -phase zone. For the isothermal process at 620°C and the thermogasocyclic process, the maximum thickness of the ϵ -phase is achieved at $n = 12 + 1$ and has been found to be 2.2–2.4 times higher, respectively, than the usual nitriding. The isothermal gasocyclic process at 520°C, for which the maximum thickness of the ϵ -phase corresponds to number of half-cycles $n = 6 + 1$, is an exception.

After the “asymmetric” process, the thickness of the ϵ -phase is significantly lower (see Fig. 2c) due to its resorption. It has been found that, in the thermogasocyclic process, the complete resorption of the ϵ -phase occurs when the passive stage lasts 3 h (Fig. 6, $n = 2$). It can be concluded that, for longer cycle times, the denitrogenation process prevails over the nitriding process. At low cycle durations, on the contrary, the saturation process proceeds more intensely than the resorption process.

To a lesser extent, the parameters of the number and duration of half cycles affect the thickness of the nitride zone of the γ' -phase and thickness of the eutectoid zone: for all regimes of the thermogasocyclic process, they vary within 3–5 and 2–4 μm , respectively.

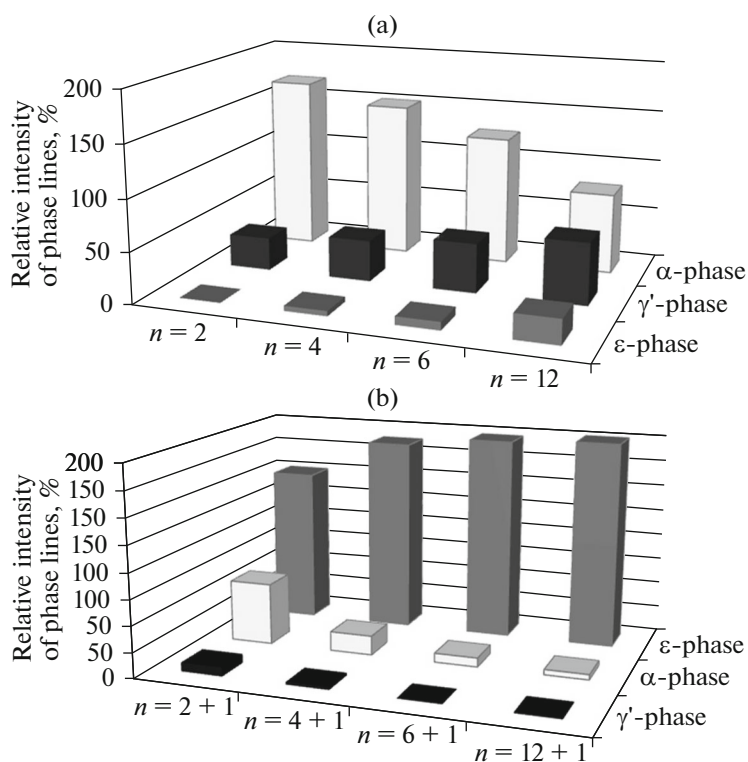


Fig. 6. Phase composition of the surface of ARMCO iron after thermogasocyclic processes at 520/620°C depending on the number of half cycles: (a) “asymmetric” process for 6 h; (b) “symmetric” process for 6 h with an additional stage of nitriding during 0.5 h.

The phase composition of the nitrified layer during thermogasocycling is strongly affected by the type of cyclic process, namely, the nature of its final stage. It has been found that “asymmetric” processes with the final stage of denitrogenation for any parameters of half cycles lead to the formation of a significant amount of the α -phase on the surface (see Fig. 6a). The intensity of the ε -phase lines is minimal and depends on the number of half cycles and their duration. “Asymmetric” processes, which end with a long-term stage of denitrogenation, make it possible to prepare a nitride layer based on the internal nitriding zone in the absence of the surface zone of the ε -phase.

The additional nitriding step (“symmetrical” process) contributes to the formation of the ε -phase (see Fig. 6b). The higher the degree of resorption of the nitride zone in the denitrogenation stage, the more intense the growth of the nitride zone at the final active stage. The most effective from the point of view of rapid formation of layers with a developed zone of the ε -phase are “symmetric” processes with a large number of half-cycles of short duration (0.5–1 h).

The completion of the process by the nitriding step leads to a sharp decrease of the intensities of the γ -phase and α -solid solution on the surface (see Fig. 6b).

Thus, the formation of a specific combination of the required phases in the nitrified layer can be realized by appropriately choosing the type of cyclic process, number of half cycles, and their duration. The parameters of the number of half cycles and their duration can be effectively used as regulators of the phase composition of the diffusion layer for gasocyclic and thermogasocyclic nitriding processes in order to achieve desired physicochemical properties.

CONCLUSIONS

The major conclusions are as follows. (1) The effect of intensification of iron saturation with nitrogen during the thermogasocyclic nitriding has been found, which manifests itself in an increase in the thickness, first of all, of the internal nitriding zone in comparison with its thickness obtained by nitriding in flowing ammonia of the same duration. The degree of intensification of the growth of the BA zone increases with an increase in the number of half cycles and a decrease in their duration. (2) Regimes of the thermogasocyclic nitriding in the conditions of “symmetric” and “asymmetric” processes differing in the type of the final stage of the process are proposed. When the process is completed by the active saturation stage, an intense growth of the nitride zone of the ε -phase is observed. (3) The following parameters of the thermogasocyclic process are determined: the number of half cycles and their duration, by means of which it is possible to regulate the phase composition of the nitrified layer.

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