Controlled thermogasocyclic nitriding processes

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Abstract: *The existing basic nitriding methods do not exploit many of the potential opportunities. To intensify it and increase its efficiency, this paper considers and proposes a new method of low-temperature nitriding, which makes it possible to optimise the classical process and reduce the consumption of ammonia from 2 to 10 times, reduce 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 properties. During the experiment, gas-cyclic and thermogasocyclic nitriding of armco iron was carried out on an experimental setup, which included a system for monitoring and maintaining the temperature in the working volume, a gas supply system, monitoring the flow rate and degree of ammonia dissociation, cleaning and drying gas, as well as two electromagnetic gas valves controlled from the control panel, allowing the processes to be carried out automatically. As a result, a new method of low-temperature nitriding has been developed – under the conditions of a thermo-gas cycle. This method consists in periodic alternation of saturation cycles during flow nitriding and resorption of the nitrided layer with the maximum possible decrease in the saturating capacity of the atmosphere. The proposed new method of thermogasocyclic nitriding is a new, effective hardening technology that allows to reduce the consumption of saturating gas and emissions into the atmosphere by up to 10 times, the nitriding time by 4-6.5 times, and also to increase the thickness of the diffusion layer by 2-6 times without reducing the physical and mechanical properties. A new technological parameter has been established – the duration of half-cycles, which allows simply and effectively regulating the phase composition and structure of the layer in order to obtain the required physical and mechanical properties.*

Key Words: *nitriding, thermo-gas cycles, duration of the half-cycles, saturation, denitriding*

1. INTRODUCTION

One of the main directions of modern materials science and heat treatment is the creation of materials with a higher complex of properties and the development of new strengthening technologies for their effective application in modern mechanical engineering. At the present time, the way of obtaining new materials has basically been exhausted, and it is not necessary to expect obtaining compositions that could significantly exceed the physicochemical properties of the known ones. The increasing complexity of alloy building and the related increase in the content of hardening phases in them, for example, in high-speed steels, leads, on the one hand, to an increase in the service characteristics of alloys, and on the other, to a simultaneous decrease in their technological plasticity at various stages of production, starting from forging and rolling and ending with cutting and grinding. So, for example, the yield of long steel at metallurgical plants for standard high-speed steel of R6M5 grade is 4-6 times higher than for complex-alloyed, less ductile steel of R12M4K8F2 grade, which has a higher hardness and high cutting properties.

In this regard, in the last decade, there has been a tendency to improve the service characteristics of materials, to ensure their high reliability and environmental protection of products by improving existing technologies for obtaining materials and their heat treatment. Due to the fact that the existing basic nitriding methods do not use many potential opportunities for the efficiency increase, this paper discusses and proposes a new method of low-temperature nitriding, which makes it possible to optimise the classical process and 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 properties [1], [2], [3]. Here, the kinetics of the formation of nitrided layers of great thickness is investigated during the cyclic method of feeding ammonia into the working chamber and cyclic temperature change. It should be noted that the processes of resorption (denitrogenation) of the layer, which depend on the duration of the half-cycles of saturation and resorption, are also of great importance in the formation of the layer [4], [5].

2. MATERIALS AND METHODS

Armco iron, which is a model material for microstructural analysis, and the KhVG low-alloy tool steel, samples from which were tested for wear, were subjected to nitriding. The standard treatment for steels of this type is quenching and deep drawing, but they can also be hardened by nitriding, since this type of chemical-thermal treatment improves the wear resistance and heat resistance of the tool surface, which is responsible for its performance properties. Gas-cyclic and thermogasocyclic nitriding was carried out on an experimental setup [6], including a system for monitoring and maintaining the temperature in the working volume, a gas supply system, monitoring the flow rate and degree of dissociation of ammonia, purifying and drying gas, as well as two electromagnetic gas valves controlled from the control panel, which allows to carry out processes in automatic mode [7], [8], [9].

The determining factor for the acceleration of saturation is the diffusion coefficient, which, as is known, depends mainly on the temperature and concentration gradient [10]. Therefore, to accelerate the process and the possibility of its regulation, a thermal cycle is proposed instead of isothermal holding during conventional flow nitriding [11]. Similar studies related to temperature effects were carried out in [12], [13], [14], [15], [16].

The temperature range was determined in accordance with the iron-nitrogen diagram, where there are critical points separating regions with different phase compositions. [17], [18],

[19], [20]. The correct choice of the temperature range of thermal cycling is an important condition in the study of the influence of gas and thermogasocyclic effects on the nitriding process [21], [22] Therefore, the temperature range was chosen so that the process of saturation with nitrogen (the first stage of the cycle during nitriding) occurs below the temperature of the eutectoid transformation according to the "iron-nitrogen" phase diagram, i.e. at temperatures below 591°C. During nitriding of the studied samples, this temperature was 520°C. Then, the samples were denitrified (the second stage of the cycle), for which the ammonia supply was switched off, that is, the ammonia pressure in the working space of the furnace remained constant for some time [23], [24]. The upper limit of thermal cycling during nitriding of the samples was 620°C. The degree of dissociation of ammonia in each first half-cycle was monitored every 15-20 min using a water dissociometer. At a saturation temperature of 520°C, the degree of dissociation of ammonia was 25-30%, at a temperature of 620°C – 40-45%. On every second half-cycle, the degree of dissociation increased and amounted to 68-70% at 520°C and 94-98% at 620°C. The study of the microstructure after nitriding was carried out on a Neophot-21 microscope with a digital attachment, and the distribution of nitrogen over the thickness of the nitrided layer was obtained by scanning on an X-ray spectral microscope analyser. Wear tests were carried out on a machine simulating the cutting process. The friction path was 200 m.

3. RESULTS AND DISCUSSIONS

The technology of thermogasocyclic nitriding consists in the periodic alternation of saturation cycles during flow nitriding and resorption of the nitrided layer with the maximum possible decrease in the saturating capacity of the atmosphere. In this case, additional intensification occurs due to the two-stage process – during thermogasocyclic nitriding, saturation and resorption (denitriding) occur at different temperatures. This technology provides effective regulation of the phase composition of the diffusion layer using a new technological parameter – the half-cycle duration – and leads to a reduction in the saturation gas consumption due to the maximum use of each gas portion at the saturation stage. In addition, the environmental requirements for the processes of chemical and thermal treatment are met by reducing harmful gas emissions into the atmosphere.

With a cyclic change in temperature, a cyclic phase transformation also occurs in the layer, that is, a transition from the low-temperature region, i.e. below the temperature of the eutectoid transformation (591°C), where nitrogenous pearlite exists, to the region of stable austenite, and vice versa. This transformation is accompanied by grain refinement in the layer and, accordingly, large diffusion movements with the simultaneous existence of two or more phases with different crystal lattices and different volumes; an increase in the length of the boundaries, and, consequently, an increase in the proportion of boundary diffusion, which is quite active. To further accelerate the denitriding process, the volume change factor in iron-nitrogen alloys was used during the eutectoid transformation: both the formation of nitrogenous pearlite and the nitriding process are accompanied by an increase in volume, i.e. thermodynamically initiate each other. The combination of these factors contributes to the acceleration of the saturation process, leads to an increase in the intensity of nitrogen diffusion and an increase in the thickness of the nitrided layer.

The total time of the cyclic nitriding process was 6 hours. Each cycle consisted of two half-cycles equal in time, the duration of each half-cycle being respectively 0.5; 1; 1.5 and 3 hours. In the first half cycle, the surface is saturated with nitrogen. In this case, as is known, the nitride zone is intensively formed, and the process is most active, in accordance with Fick's

law and according to the results of experiments, for the first half hour or hour. Therefore, the half-cycle time corresponded only to the active saturation regions. In the second half-cycle (the stage of resorption), due to the cessation of the ammonia supply, the nitrided layer dissociates, since the nitrogen potential drops to almost zero, and molecular nitrogen is passive with respect to iron.

The nitride zone consists of metastable phases in which nitrogen is active and diffusible. As a result, a high concentration gradient is created at the border of the nitride zone and the zone of internal nitriding, and concentration levelling begins, i.e., the outflow of nitrogen goes mainly into the metal, accelerating the process of layer formation.

And this cycle is repeated several times. As a result, nitrogen is "pumped" deep into the metal. Repetition of such cycles leads to the formation of thicker diffusion layers during nitriding compared to conventional nitriding at the same temperatures in a continuous flow of ammonia.

The increase in the total thickness of the nitrided layer obeys a parabolic dependence and, in general, with a decrease in the duration of half-cycles, the total thickness of the layer increases, and, mainly, due to the internal nitriding zone (INZ) (Figure 1). With an increase in the duration of half-cycles, the layer thickness decreases, which is associated with the actively passing process of denitriding at the 2nd stage of the cycle.

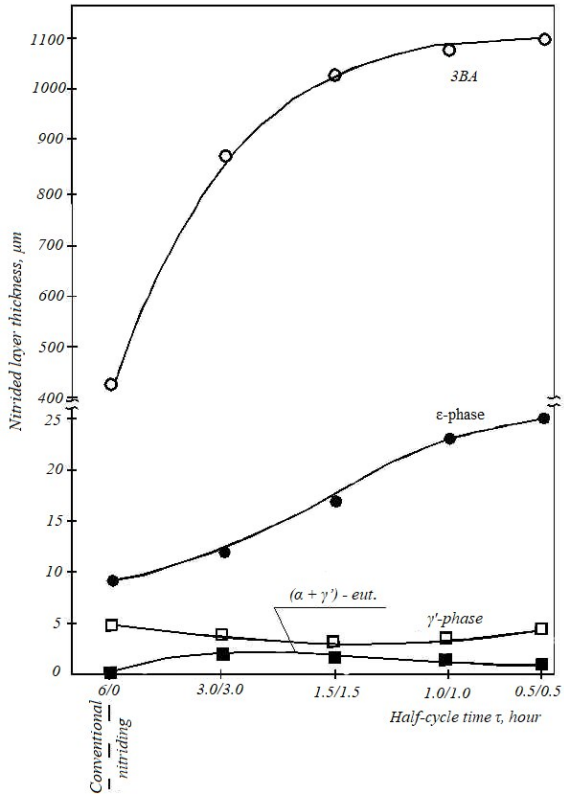
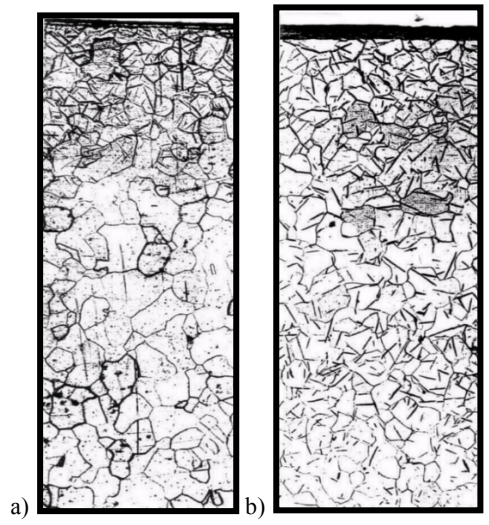


Fig. 1 – Dependence of the total thickness of the nitrided layer (nitride zone – ε- and γ′-phases, internal nitriding zone (INZ) and nitrogenous pearlite-eutectoid (α+γ′)) on the duration of half-cycles at the stage of nitriding and denitriding of armco iron. The total duration of the process is 6.5 hours. Temperature of nitriding – 520°C, denitriding – 620°C.

When comparing thermogasocyclic and conventional nitriding, a sharp increase in the total layer thickness is observed, which can be clearly seen on the microstructures (Figure 2)

by the characteristic needles of the γ′-phase. At the same time, the total depth increases, mainly due to INZ, which increases by about 6 times, and the nitride depth – 2 times compared to conventional nitriding.



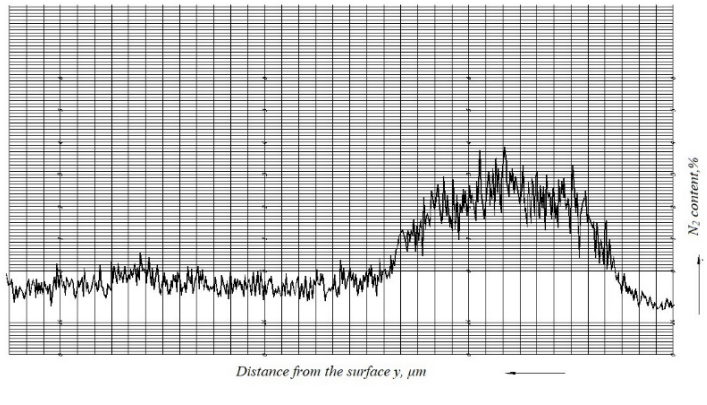
a) b)

Fig. 2 – Microstructures of diffusion layers on armco iron: a – conventional nitriding at 520°C in ammonia, 6 hours; b – thermogasocyclic nitriding (saturation temperature – 520°C, denitriding – 620°C). The duration of half-cycles is 0.5 hours. The total duration of the process is 6 hours, x100.

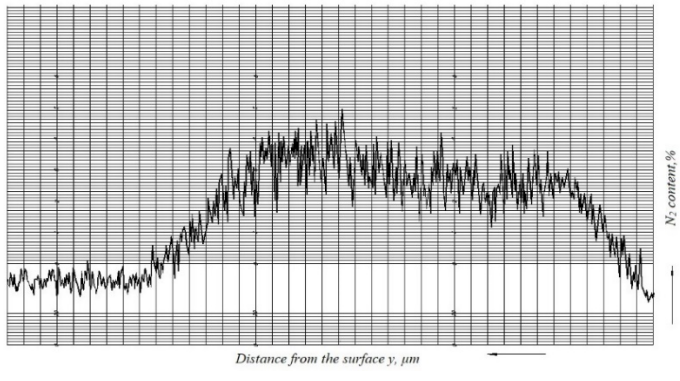
An increase in the intensity of the processes is also indicated by the curves of the distribution of radiation from nitrogen atoms (Figure 3) – with distance from the surface, the nitrogen content in the layer increases and reaches a maximum, moreover, in the depth of the layer.

It can be seen that the qualitative nature of the distribution of nitrogen over the thickness of the nitrided layer in the considered samples has the same form and is characterized by the fact that the maximum nitrogen content is very flat and is not on the surface in contact with the saturating medium, but inside the nitride zone, that is, at some distance from the surface of samples.

In addition, judging by the magnitude of the line reflection intensity, it can be noted that, firstly, the thickness of the layer with an increased nitrogen content increases upon passing from conventional nitriding to thermogasocyclic nitriding, and, secondly, the intensity of characteristic radiation in the nitride zone after thermogasocyclic nitriding significantly higher than after conventional nitriding.



a)



b)

Fig. 3 – Distribution of nitrogen over the thickness of the nitrided layer of armco iron: a – conventional nitriding, 6 h; b – thermogasocyclic nitriding, 6.5 h (saturation temperature – 520°C, denitriding – 620°C, half-cycle duration – 0.5 h each).

Microhardness measurements have shown that with thermogasocyclic nitriding, which takes 6.5 hours, it is possible to obtain the same surface hardness as with conventional nitriding, but only in 25-30 hours, i.e. nitriding time is reduced by 4-5 times. Thus, by changing only one technological parameter – the duration of half-cycles, on the surface of the hardened product, layers of different phase composition can be obtained with a certain combination of saturation and resorption processes. This makes it possible to apply this nitriding method for controlled processes, to obtain the required phases on the surface of the product, depending on the specific conditions of its operation. For example, during thermo-gas cycling of tool steels of the KhVG grade on the surface, it is advisable to simultaneously obtain a hard and plastic γ′-phase, and not a brittle ε-phase. In this case, nitriding should be carried out with a resorption stage and not a saturation stage. Nomograms of wear of specimens made of KhVG steels after conventional nitriding, gas-cyclic and thermogasocyclic nitriding are shown in Figure 4. It should be noted that in this case, as in other tests, the minimum wear is observed during thermogasocyclic nitriding, ending with the stage of resorption, in which the duration of half-cycles is 0.5 hours. The wear of the samples is almost 2.5 times less than during conventional nitriding. This can be explained by the formation on the surface during resorption of a harder than the ε-phase, γ′-phase.

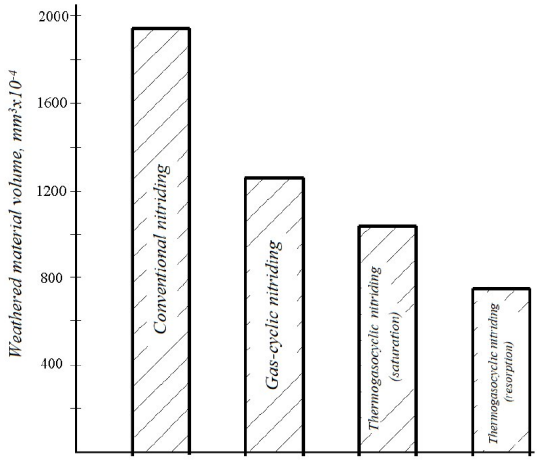


Fig. 4 – Nomographic chart of wear of samples made of KhVG steel after conventional nitriding, gas-cyclic and thermogasocyclic nitriding with a half-cycle duration of 0.5 h (nitriding temperature – 520°C, denitriding (resorption) – 620°C) and the final stage of saturation or resorption.

4. CONCLUSIONS

A new method of nitriding has been developed, which consists in periodic alternation of saturation cycles during flow nitriding and resorption of the nitrided layer with the maximum possible decrease in the saturating capacity of the atmosphere.

Thermogasocyclic nitriding is an effective new hardening method that allows reducing 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 properties, and improve the environmental aspects of the nitriding process in flowing ammonia.

A new technological parameter has been investigated – the duration of half-cycles, which allows simply and effectively regulating the phase composition and structure of the layer in order to obtain the required physical and mechanical properties. It has been established that the wear resistance of the KhVG steel, hardened by the thermogasocyclic nitriding, is 2.5 times higher than that of this steel in the conventional method.

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