New nitriding process of high-alloyed maraging steel for cryogenic operation

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Abstract. The paper considers the gas nitriding process with cyclic alternation of atmospheres: ammonia and an ammonia mixture with air for strengthening the corrosion-resistant high-alloyed steel 03Cr11Ni10Mo2Ti, designed to operate at cryogenic temperatures. The formation in steel of a nitrided layer of 130—150µm thickness with increased microhardness (more than 12GPa) is shown experimentally. During the final stage in the ammonia and air environment, iron oxides remain in the compound zone, and a sharp drop in hardness is observed at the border of the core. At the completion of the cyclic process with the stage of saturation in ammonia, a nitrides zone is formed based on the $\gamma'$-phase, the layer thickness increases (up to 180...200µm) and the microhardness profile is smoothed, which reduces the risk of embrittlement.

1. Introduction
Corrosion-resistant maraging steels alloyed with chromium and nickel are used for loaded parts operating in aggressive atmospheric conditions (turbomachine disks, gear wheels, spindles, worms, aircraft parts). Steels with a reduced carbon content operate at cryogenic temperatures due to the stabilization of retained austenite: steel 03Cr11Ni10Mo2Ti – at -70°C/-196°C, steel 03Cr12Ni10MoTi – at -253°C. These steels are designed for use as treated by nitriding [1]: nitriding is carried out at temperatures of 540...550°C for 36 hours in ammonia with a dissociation degree 25...40%. In this case, nitrided layers with increased hardness of a thickness of 0.20...0.25 mm are formed. Nitriding maintains the required level of toughness at low temperatures, obtained during preliminary heat treatment, which consists of quenching and tempering. The corrosion-resistant zone is 50...60% of the thickness of the nitrided layer.

In recent years, ion and plasma nitriding methods have been widely used as an alternative to furnace and liquid nitriding. Ion-plasma nitriding is reasonably considered a progressive method of surface hardening, the advantage of which is the formation of layers with a given thickness, phase composition and hardness on the outer surfaces of parts [2-4]. Ionic and plasma nitriding is successfully used for hardening of austenitic and martensitic steels [4-6]. Thus, for maraging high-strength steels, methods of ion-plasma nitriding have been developed, which make it possible to reduce the process temperature (up to 400...450°C) and obtain a nitrided layer with high hardness without a surface zone of chemical compounds in a short time [7]. However, the thickness of the hardened layer does not exceed 20 µm. The disadvantage of the process is also an increase in the...
roughness of the steel surface.

Gas nitriding technologies are being improved towards processes intensifying, that may be achieved by using multicomponent atmospheres, including techniques of thermal and gas cycling. Thus, cyclic processes with alternating supply of ammonia and air are not inferior to the processes of ion-plasma nitriding in terms of the rate of formation of the nitrided layer; such processes create additional possibilities for regulating the phase composition of the layer and obtaining the desired properties [8, 9].

The aim of this work is to study a new process of gas nitriding with cyclic alternation of atmospheres, consisting of ammonia and air, as applied to high-alloy maraging steel.

2. Materials and methods

The studies were carried out on samples of steel 03Cr11Ni10Mo2Ti; the chemical composition is presented in table 1.

| Table 1. Chemical composition of steel 03Cr11Ni10Mo2Ti |
|--------------------------------------------------------|
| Fe  | C     | Cr    | Ni    | Mo    | Ti    | Si   | Mn    | S    | P    |
| Bal | ≤0.03 | 10-11.3 | 9.0-10.0 | 1.8-2.3 | 1.0-1.4 | ≤0.15 | ≤0.1 | ≤0.01 | ≤0.01 |

The gas nitriding processes were carried out in a two-zone shaft furnace with a gas intake system, which allows one to carry out processes in ammonia-air atmospheres with air concentrations from 10 to 90 vol.%. The temperature control of the heaters is carried out by thermocouples in the upper and lower zones. The presence of two heating zones with separate control ensures uniform temperature distribution over the working space of the furnace (±3°C).

The process temperature was 580°C. At the stages of the process, the cycles of ammonia supply were alternated with cycles of the supply of a mixture of ammonia and air into the working space. The nitrogen potential of the atmosphere is regulated by changing the ratio of the volumetric concentrations of air (50...70%) and ammonia. The addition of air to the saturating atmosphere causes a sharp temperature rise in the container due to the reaction of hydrogen with oxygen. The temperature increase depends on the concentration of air in the mixture: the overheating was 60°C for 70% air, and it amounts 40°C for 50% of air. Thus, the cyclic air supply causes micro-cycling of the temperature in the oven (Fig. 1).

Figure 1. Time-temperature curves of cyclic nitriding (“Need for data” software): temperature splashes at “ammonia+air” stages: 1 — in the upper furnace zone; 2 — in the bottom furnace zone; 3 — in the reactor.
The analyses of the structure of nitrided samples were carried out: the microstructure of the nitrided layer were examined in the optical microscope METAM-LV 34; thickness and hardness of nitrided layers was determined on the PMT-3 device, and phase composition was determined by X-ray diffraction method on DRON-3 diffractometer.

3. Results and discussion

Alternation of saturation cycles with high and low nitrogen potential of the atmosphere contributes to the intensification of the nitriding process. At the saturation stage, a mixture of ammonia and air provides a high concentration of nitrogen in the near-surface layer; at the processing stage, nitrogen is moved from the surface to the depth of the layer in ammonia. When such cycles are repeated, nitrogen penetrates deeper, which leads to the formation of diffusion layers of greater thickness. There is an increase in the nitrided layer with a gradual decrease of the nitrogen concentration.

Experiments provided that during 12 hours nitriding with a high level of activity of the saturating atmosphere, a hardened layer is formed with a thickness of up to 130...150 microns, and with a hardness more than 12 GPA (Fig. 2, curve 1).

The accelerated growth of the diffusion layer is caused by microcyclic temperature fluctuations at the surface. Since the dissociation of ammonia occurs catalytically on the steel surface of the samples, it is in this region that hydrogen is bound by oxygen atoms. As a result, the effect of overheating is mostly appears in the near-surface area, that leads to an increase of the nitrogen concentration, and to the significant acceleration of diffusion processes.

![Figure 2. Microhardness profiles of steel after cyclic nitriding: 1 - “NH₃+air” final stage; 2 – “NH₃” final stage.](image)

However, the high concentration of oxygen in the saturating atmosphere results in the formation of iron oxides (Fe₃O₄) in the surface layer (Fig. 3). A compounds zone consists of iron oxides and nitrides (Fig. 4); it has increased brittleness as a consequence of its high microhardness and of the sharp drop in hardness at the layer/core interface (Fig. 2, curve 1). The compound zone is mainly consists of the ε-Fe₂N₃ phase (table 2).

A process with a final stage in pure ammonia (3 h) provides optimal hardness and reducing the brittleness of the layer due to the "dissolution" of the compound zone. Increase in the degree of ammonia dissociation in the saturating atmosphere leads to the deceleration in nitrogen penetration from the atmosphere into the surface layer. The increase in the nitrided layer (up to 180...200 microns) takes place due to the redistribution of nitrogen in depth. The maximum microhardness of the layer is slightly reduced (about 9.5 GPa), and the microhardness profile becomes smoother (Fig. 2, curve 2), that decreases stresses and risks of microcracks at the layer/core interface.
Another consequence of the dissolution final stage consists in the reduction of oxides that changes the phase composition of the compound zone. A low-nitrogen nitrides zone is formed, consisting mainly of $\gamma'$-Fe$_4$N phase (table 2); besides the X-ray diffraction pattern shows reflexes of a $\gamma$-Fe$_{0.7}$Ni$_{0.3}$ solid solution (Fig. 5). Such structure of the nitrided layer creates preconditions for wear resistance increase and for securing of the required toughness.

**Figure 3.** X-ray pattern of steel 03Cr11Ni10Mo2Ti after gas-cyclic nitriding with “NH$_3$+air” final stage.

| Table 2. Phase composition of nitrided steel 03Cr11Ni10Mo2Ti |
|-------------------------------------------------------------|
| Gas-cycling mode | Mole fraction of phases | $\varepsilon$-Fe$_3$N | $\gamma'$-Fe$_4$N | Fe$_3$O$_4$ | Fe$_2$(Ni) |
|------------------|------------------------|-----------------|-----------------|----------|-----------|
| “NH$_3$+air” final stage | 0.7969 | 0.0417 | 0.1614 | - |
| “NH$_3$” final stage | 0.0290 | 0.8744 | - | 0.0966 |

**Figure 4.** Micrograph of nitrided layer in steel 03Cr11Ni10Mo2Ti (x300).
4. Conclusion

The new nitriding process for maraging steel 03Cr11Ni10Mo2Ti, designed for operation at cryogenic temperatures, consists of a cyclic alternation of saturation stages in a mixture of ammonia and air, and the stages of resorption of the formed diffusion layer in ammonia. Gas-cyclic nitriding provides an intensification of the process of saturation of alloy steel with nitrogen due to the effect of microthermocycling. The optimal phase composition of the nitrided layer (nitride zone based on the γ'-phase without oxides) is formed during the final stage of the process with a lower nitrogen potential. During the final stage in pure ammonia, an increase in the thickness of the nitrided layer and a smooth microhardness profile are observed, which contributes to the preservation of plasticity and viscosity at a sufficiently high level of hardening.

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