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THE ROLE OF CARBIDES IN FORMATION OF SURFACE LAYER ON STEEL X153CrMoV12 DUE TO LOW-PRESSURE NITRIDING (VACUUM NITRIDING)

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The mechanism of formation of surface layer on steel X153CrMoV12 in the process of vacuum nitriding (low-pressure nitriding) in a universal vacuum furnace in an atmosphere of dissociated ammonia at a pressure of 30×10^2 Pa (30 mbar) is studied by the methods of light microscopy and measurement of microhardness. The chemical composition of the nitrided layers is determined.

Key words: tool steel, vacuum nitriding, microstructure, carbides, hardness.

INTRODUCTION

The articles subjected to heat and thermochemical treatment include cutting tools, molds and dies. They experience intense loads both mechanical and thermal. High durability of such tools can be provided by using appropriate materials, but the optimum properties can only be formed by heat and thermochemical treatment [1 – 3].

Nitriding, carburizing and nitrocarburizing are the most widely used methods of thermochemical treatment among the various methods elevating the surface properties of structural elements. Controlled nitriding is employed in many industries due to its numerous advantages. The range of the steel grades subjected to nitriding widens. Today, nitriding is applied not only to the steels specially intended for this kind of treatment but also to the traditional heat-hardenable, carburizing, stainless, acid-resistant and tool steels [4].

To meet the growing expectations of improvement of the mechanical properties and corrosion resistance of nitrided steels, the nitriding processes should include control of the growth of the internal nitrided layer and of the nitride layer on the surface. Nitriding should not only provide a high hardness of the surface and but also a great depth of the zone of internal nitriding. Special attention should be devoted to the layer of nitrides lying directly under the surface. This layer is decisive for formation of such properties as corrosion resistance and wear resistance [5].

The characteristics of nitrided layer in recent aircraft and vehicle articles impose limitation on the thickness of iron nitrides on the surface. Such layers should have a high hardness and a good ductility. When the thickness of the iron nitrides is limited, it is possible to observe all the dimensional tolerances of the articles [1, 5].

Gas nitriding is a permanently advanced method of thermochemical treatment. Recent nitriding regimes provide different alternation of nitrided layers depending on the required operating properties. The process of gas nitriding is controllable through regulation of the nitrogen potential [6]. In the present work we used the principles of the Nitrovac nitriding technology.

The Nitrovac technology is very efficient. Specifically, a method based on its principles has been used for strengthening machine parts operating under the conditions of rolling and sliding friction such as cogwheels, splines, and pump and valve components [1]. The nitriding gas in the method is ammonia, which dissociates on the surface of the charge under reduced pressure and at a temperature ranging from 400 to 600°C. The saturation with nitrogen may be expressed quantitatively by the following relation:

$$A = \Delta G \frac{\Gamma}{N},$$

where A is the thermodynamic stimulus of nitriding, ΔG is the change in the thermodynamic potential of the system during the process, Γ is the number of ammonia molecules absorbed on 1 cm² of the surface of the alloy, and N is the Avogadro number.

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Decrease in the pressure of the atmosphere in the nitriding process lowers the adsorption of the molecules of NH_3 on the surface of the steel (Γ) at simultaneous growth in the nitrogen potential in the atmosphere (ΔG) [7].

Since the parameters of the process are fully controllable, the formed nitrided layers may have any phase composition. The Nitrovac process helps to avoid formation of brittle ϵ and ζ iron nitrides, but the formed layers consist of a diffusion zone or contain an additional thin layer of an iron γ' -nitride (which is desirable if the part has to be protected from adhesive wear). Being very hard and plastic the γ' -layer reduces the friction factor of rubbing surfaces [8].

The aim of the present work was to study the mechanism of formation of surface layer on steel X153CrMoV12 (Polish NC11LV) during nitriding in low-pressure atmospheres.

METHODS OF STUDY

We studied specimens of tool steel X153CrMoV12 (1.60% C, 0.28% Si, 0.30% Mn, 12% Cr, 0.85% Mo, 0.70% V).

The specimens were nitrided in a universal vacuum furnace in an atmosphere of dissociated ammonia at a pressure of 30×10^2 Pa (30 mbar). The process parameters were as follows: the temperature 560°C, the flow rate of ammonia 7.5 dm³/h, the nitriding time 0.5, 1.0, 2.0 and 3.0 h.

The structure was observed with the help of a Nikon Eclipse 200 confocal microscope. The objects of the metallographic study were etched in nital (MilFe), i.e., a 4% solution of HNO_3 in ethanol.

The Vickers hardness was measured according to the PN EN ISO 6507-1 1999 Standard using a KB universal hardness meter. Three series of measurements were made for each specimen to calculate the average value. The hardness of the specimens nitrided for 0.5 h was measured at a distance of 60 μm from the surface, because this depth corresponded to the hardness of the core.

The x-ray analysis of the distribution of the chemical elements was performed with the help of a HITACHI S3000-N scanning electron microscope with an EDS (energy dispersive spectrometer) attachment. We plotted the maps of the distribution of each element in the surface layer of the specimens.

RESULTS AND DISCUSSION

The microstructure of ledeburitic tool steel X153CrMoV12 for cold working consists of tempered martensite with coarse-grained (ledeburitic) primary carbides with unidirectional distribution and secondary carbides. The distribution of the hardness in the layers after nitriding of different duration is presented in Fig. 1. After 0.5-h nitriding the hardness increases little (to 642 $HV_{0.1}$). The thickness of the layer is about 30 μm . After nitriding for 2 h the hardness attains

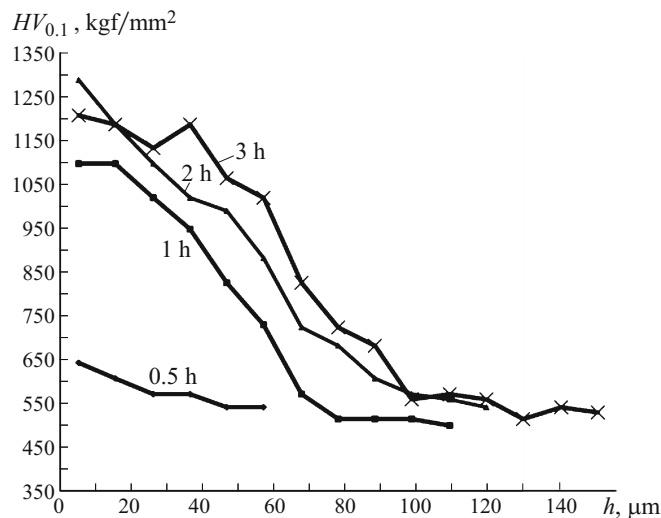


Fig. 1. Distribution of the hardness of the surface layer in steel X153CrMoV12 after 0.5 – 3-h nitriding at 560°C (h is the distance from the surface). The duration of the nitriding process is given at the curves.

1300 $HV_{0.1}$ near the surface; the thickness of the layer is 90 μm . The primary carbides transform into carbonitrides. After 3-h nitriding the hardness in the surface zone is about 1200 $HV_{0.1}$ and the thickness of the layer is 130 μm (Fig. 1).

Figure 2 presents the microstructure of steel X153CrMoV12 after nitriding of different duration. It can be seen from Fig. 2a that after nitriding for 0.5 h the microstructure is represented by tempered martensite, coarse primary carbides and secondary carbides. In some regions of the surface we can detect very thin (below 0.1 μm) layers of nitrides of a γ' -phase (Fe_4N), which have formed mostly in the presence primary carbides. A darker zone of internal nitriding is not detectable. After 1-h nitriding the saturation of the steel with nitrogen increases (Fig. 2b). The zone of internal nitriding is well manifested. Phase γ' forms only in the presence of primary carbides, and surface layer exhibits a nitride net. The net has formed at a specific distance from the surface and grown from the grain boundaries of primary carbides. This means that nitrogen diffuses into the metal over grains of primary carbides, reaches the boundary of a carbide particle, and then diffuses over the boundaries of the grains of the matrix of the former austenite forming a net of precipitates of a γ' -phase. In addition, the color of some carbide regions changes for gray, which indicates saturation of the carbides with nitrogen. The transformation of the carbides into carbonitrides causes carbon saturation of the austenite surrounding the carbides; the carbon hinders the diffusion of nitrogen through the grains and precipitates on the grain boundaries in the form of a net of a γ' -phase.

Figure 2c presents the microstructure of nitrided layer on steel X153CrMoV12 after 2-h nitriding. In this case the structure also contains an ϵ -phase ($\text{Fe}_{2.3}\text{N}$). The layer includes a zone of internal nitriding, where the γ' -phase has the

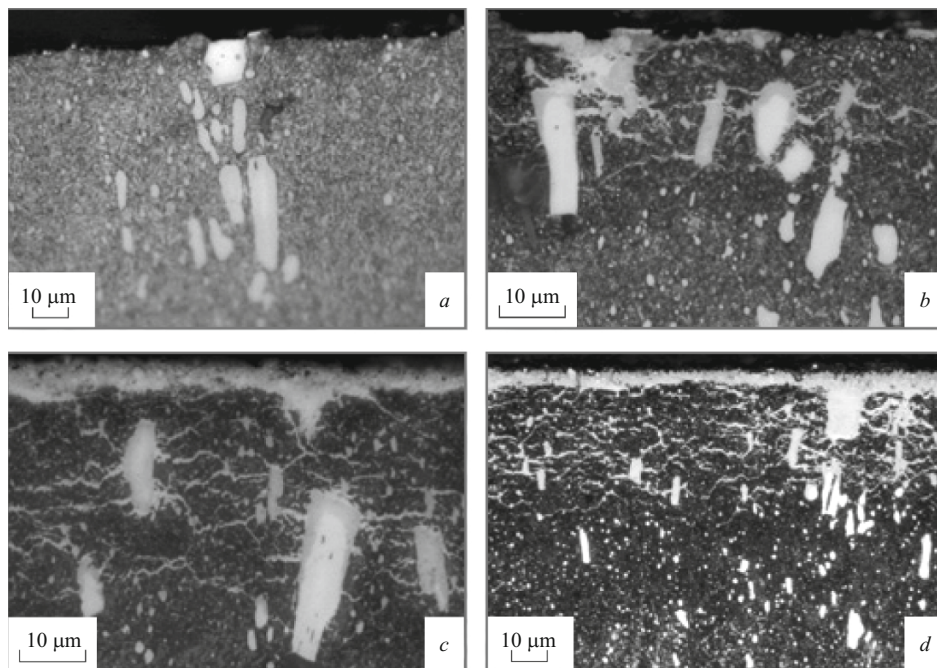


Fig. 2. Microstructure of the surface layer of steel X153CrMoV12 after nitriding at 560°C for 0.5 h (a), 1 h (b), 2 h (c), and 3 h (d): a) tempered martensite, coarse primary carbides, secondary carbides, and thin discontinuous layer of γ' -phase; b) γ' -phase near primary carbides and in the form of a net, diffusion zone; c, d) surface layer of $\epsilon + \gamma'$ iron nitrides, γ' -phase near primary carbides, net of γ' -phase over boundaries under the surface, diffusion zone.

form of a net, and a homogeneous mixture of $\epsilon + \gamma'$ phases formed on the surface. The primary carbides are saturated with nitrogen and have also transformed here into carbonitrides.

The microstructure of the diffusion layer on steel X153CrMoV12 after 3-h nitriding is presented in Fig. 2d. The formation of a nitride layer of ϵ -phase on the surface indicates a higher degree of surface saturation. The structure of the layer resembles that obtained in the preceding process. The layer of $\epsilon + \gamma'$ phases formed on the surface is followed by a layer of γ' -phase arranged over the boundaries of former

austenite grains, and then by a zone of internal nitriding. The primary carbides near the surface are fully saturated with nitrogen.

Formation of a γ' -phase under the surface of steel X153CrMoV12 may be undesirable due to the possibility of cracking and chipping of the surface caused by the presence of a hard nitrogen-saturated layer on grain boundaries. A qualitative x-ray analysis of the distribution of the chemical elements over points has proved that the dark spots on the carbides are nitrogen-saturated zones. Figure 3 presents SEM images of specimens with marked places of the analysis of the concentration of the chemical elements. Point 1 corresponds to carbide regions where the composition after the nitriding differs from that of the other carbides (see Fig. 2). As expected, these are nitrogen-saturated areas of primary carbides, where carbon has been partially substituted by nitrogen. The content of the chemical elements at point 1 (in wt.%) is as follows: 6.87 C(K_α), 6.40 V(K_α), 43.55 Cr(K_α), 32.62 Fe(K_α), 8.80 N(K_α), 0.14 Si(K_α), 1.48 Mo(L_α). At point 2 it is 12.47 C(K_α), 6.47 V(K_α), 41.08 Cr, 38.23 Fe(K_α), 0.13 N(K_α), 0.08 Si(K_α), 1.54 Mo(L_α).

Figure 4 presents a map of the distribution of the main chemical elements in the layer. The map shows that nitrogen is chiefly concentrated in the zone of primary carbides, which also contains a considerable amount of Cr and V. The analysis performed allows us to infer that when nitrogen diffuses over the grain boundaries of primary carbides, a part of it first forms carbonitrides or nitrides and may then diffuse from the carbonitrides promoting formation of a nitride net. The x-ray diffraction shows that the surface nitride layer is represented by a mixture of $\text{Fe}_{2.3}\text{N}$ and Fe_4N (Fig. 5).

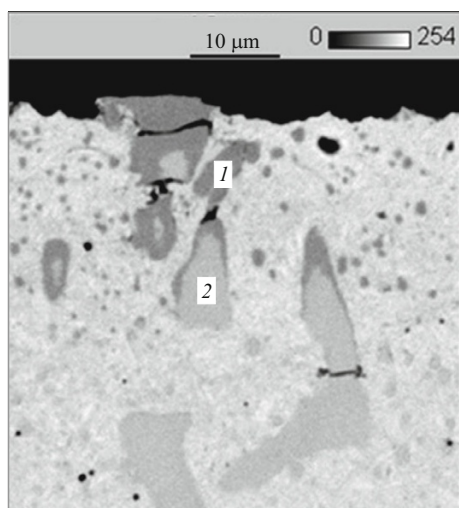


Fig. 3. EBSD image of steel X153CrMoV12 after nitriding: 1) dark part of primary carbide; 2) region of primary carbide without visible changes.

