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ION NITRIDING OF TITANIUM COATINGS OBTAINED WITH THE HELP OF A LIQUID-METAL CARRIER

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INTRODUCTION

Nitriding is one of the most effective kinds of chemicothermal treatment that provides special physicochemical and mechanical properties in surface layers of steel parts. It was established in [1, 2] that volume alloying of steels with titanium accelerates their nitriding considerably. The deepest nitriding without deterioration of the surface hardness is observed in steels containing 1.5 – 2.0% Ti and 0.15 – 0.20% C at a Ti/C ratio ≥ 10. We have developed and studied in [3, 4] a method for diffusion saturation of steel surfaces with metals with the use of a liquid-metal eutectic carrier for transporting the alloying element to the surface of a part.

It seems expedient to combine titanizing from a liquid-metal carrier with nitriding in order to obtain layers with specified properties on the surface of austenitic corrosion-resistant steels. The choice of these steels is determined in the first place by the impossibility of their heat hardening. In the present work, we studied the laws of nitrogen saturation of metallic coatings, which are preliminarily deposited from a liquid-metal carrier on a steel surface from a glow discharge.

METHODS OF STUDY

We deposited a titanium coating on steel 08Kh18N10T by the method of [3]. The liquid-metal carrier was a eutectic alloy Bi – 47.3% Pb with an additive of 2% Ti in the form of a powder. The saturation was performed for 10 h at 1100°C. The thickness of the diffusion layer of titanium was 0.23 – 0.28 mm; the microhardness was 290 – 320 *HV*. Specimens with preliminarily deposited coatings were nitrided in a glow discharge in gaseous nitrogen of special purity (GOST 9293–74), in a nitrogen–hydrogen mixture (50% N_2 + 50% H_2), and in dissociated ammonia. Nitrogen was cleaned of water vapors by silicagel and of oxygen by titanium sponge heated to 550°C. The gas medium was fed into the chamber for ion nitriding through needle leaks. The amount of the fed gas was controlled with the help of rotameters. The flow rate of the gas medium was 15 – 30 liters/h.

In order to sustain a stable temperature in the workspace of the furnace, we designed and fabricated a system for temperature control maintained manually and automatically with controlled stages of "heating," "norm," and "overheating." The ion-nitriding chamber was evacuated to a pressure of $p = 0.532$ Pa. At this pressure we performed cathode sputtering. The voltage of the discharge in the chamber was 1600 V, the current was 0.1 A, and the temperature of the parts did not exceed 250°C. The duration of cathode sputtering was 0.3 h. As a result, the surface of the specimens was depassivated and thus prepared for nitrogen saturation.

The saturation was performed with indirect heating of the parts and ion bombardment at a voltage of about 300 V and a current of 2 A. The pressure of the gas medium in nitriding $p = 6.65 – 7.98$ hPa, the temperature was varied from 650 to 920°C, and the duration of the process was varied from 10 min to 10 h. After a technological hold, the parts were cooled in a gas flow. The obtained layers were studied by metallographic analysis and measurement of the microhardness (the load on the indenter $P_{\text{ind}} = 0.2$ N).

RESULTS AND THEIR DISCUSSION

Let us consider the effect of the temperature–time regimes of nitriding on the microstructure and distribution of the microhardness over the thickness of titanium–nitrogen layers on steel 08Kh18N10T.

Effect of the temperature. After nitriding at 650°C, an unetched nitride layer (a "white" layer) is formed on the surface of the parts (Fig. 1*a*). It has a hardness of 1427 *HV*. Under this layer lies a thin layer with a microhardness of 1207 *HV*, and then follows a fine-grained layer (about 0.11 mm) of a solid solution of nitrogen in a titanium coating on the steel (a zone of internal nitriding). The microhardness of the matrix is 264 *HV*. After nitriding at 750°C, the succession of layers is preserved (Fig. 1*b*). The microhardness of the layers obtained at 650 and 750°C differs (Fig. 2); after nitriding at 750°C, it is higher (for example, the microhardness of the nitride layer is 1600 *HV*).

When the nitriding temperature is increased to 920°C, the succession of the layers is the same, but their microhard-

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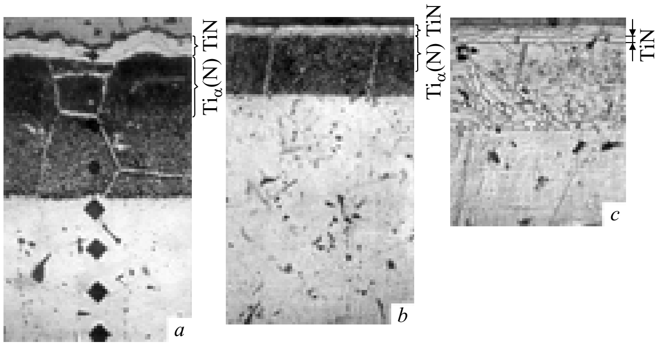

Fig. 1. Microstructure of a titanium–nitrogen coating on steel 08Kh18N10T deposited by nitriding by the following regimes: *a*) 650°C 3 h, × 270; *b*) 750°C 2.5 h, × 200; *c*) 920°C 3 h, × 200.

ness and appearance change (Figs. 1*c* and 2*d*). The microhardness of the unetched nitride layer is 1635 *HV*. The layer of the solid solution of nitrogen in the diffusion titanium coating resembles nitrided layers of ($\alpha + \beta$)-titanium alloys with $Ti_\alpha \rightleftarrows Ti_\beta$ phase transformation at 882°C [5, 6]. The lighter inclusions have a microhardness of 1109 *HV*. They are represented by hard nitride compounds. The matrix of this layer is a solid solution of nitrogen with a microhardness of 403 *HV*. Below the boundary separating the titanium–nitrogen layer and the steel, the microhardness decreases to that of the core.

Effect of the nitriding time. The titanium–nitrogen layer grows the most intensely in a 3-h isothermal hold (Figs. 1 and 2). A longer hold causes a certain increase in the thickness of the unetched nitride layer and the microhardness of the zone of the solid solution of nitrogen in the diffusion titanium layer. The hardness of the "white layer" remains virtually at the same level. After a 1-h hold, the diffusion layer is represented by a solid solution of nitrogen in titanium nitride inclusions distributed in a mosaic manner. There is no continuous zone of nitrides. The duration of the hold influences substantially the distribution of the microhardness over the thickness of the layer. The increase in the hold time increases the thickness of the unetched nitride layer from 0.016 to 0.019 mm and somewhat raises the microhardness of the zone of the solid solution of nitrogen in the diffusion titanium layer. At holds up to 1 h long, the curve of the distribution of the microhardness decreases smoothly from the surface into the depth of the titanium coating. The microhardness of the near-surface layers at $t_n = 950°C$ and $\tau_n = 10$ min and $\tau_n = 30$ min is 670 and 1150 *HV* respectively ($P_{ind} = 0.5$ N).

Effect of the pressure and the composition of the gas medium. The pressure of the gas medium influences the parameters of the glow discharge, which imposes constraints on this characteristic. A change in the pressure within 1.33 – 3.99 hPa does not change the thickness and the microhardness of the titanium–nitrogen layer. As the pressure is increased to 7.98 hPa, the process intensifies and a nitride layer appears.

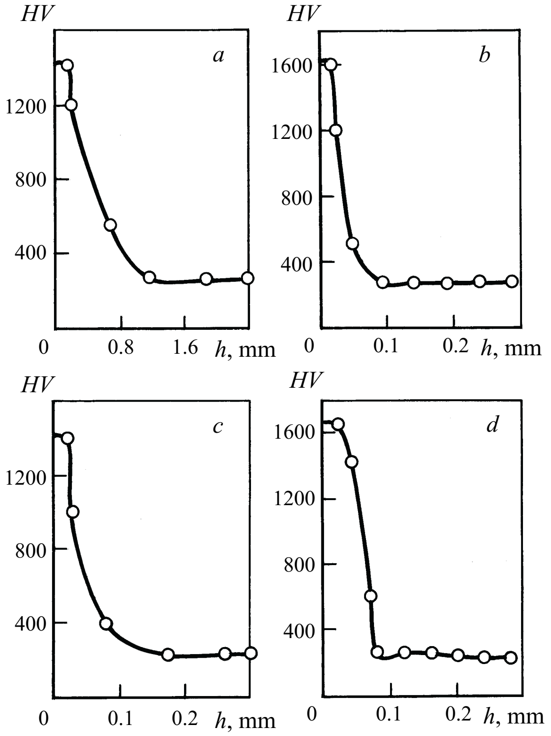

Fig. 2. Distribution of the microhardness over the thickness (*h* is the distance from the surface) of titanized coatings obtained by nitriding by the following regimes: *a*) 650°C 2 h; *b*) 750°C 2.5 h; *c*) 750°C 7 h; *d*) 920°C 3 h.

Studying the influence of the composition of the gas medium on the characteristics of the titanium–nitrogen layer (see Table 1), we established that the microhardness was minimum when the nitriding was performed in gaseous nitrogen. The microstructure of the titanium–nitrogen layer is independent of the composition of the gas medium. Layers with a higher microhardness are formed in nitriding in dissociated ammonia and in the nitrogen–hydrogen mixture. This seems to be connected with the ability of hydrogen to reduce the surface oxides, which promotes exchange reactions on the surface.

Ion nitriding of steel 08Kh18N10T without a titanium coating at 580°C for 7.5 h causes the formation of a diffusion layer 0.08 – 0.1 mm thick with a microhardness of 378 *HV* at the surface ($P_{ind} = 0.2$ N). Comparing the values of the

TABLE 1. Effect of the Composition of the Gas Medium on the Microhardness of the Titanium–Nitrogen Coating

Composition of the gas medium	t_n, °C	τ_n, h	*p*, hPa	*HV**
Nitrogen	920	3	7.98	1300
Ammonia (dissociated)	920	3	7.98	1450
Nitrogen–hydrogen mixture 50% N_2 + 50% H_2	920	3	7.98	1400 – 1600

* Microhardness of the surface layer.

microhardness of nitrided and titanonitrided specimens of steel 08Kh18N10T, we came to the conclusion that the higher microhardness of the latter was explainable by the formation of titanium nitrides. This is confirmed by the golden color of the titanium-nitrogen coating.

When nitrogen diffuses into the titanium coating finely dispersed titanium nitride forms. Penetrating the solid solution of titanium in iron and forming stable dispersed nitrides, nitrogen creates passages for easier diffusion of its new portions. The slow cooling after the nitriding is accompanied by segregation of titanium nitride over the grain boundaries.

The results of our study of ion nitriding of diffusion titanium coatings allow us to suggest the following mechanism of the nitriding process: when the surface of the steel with a titanium coating is bombarded by nitrogen ions, a layer of titanium nitrides forms. As a result of the local heating, this layer is partially decomposed, and the nitrogen formed in the decomposition of the nitrides diffuses into the matrix, creating a zone of solid solution of nitrogen in titanium. The nitrogen-depleted titanium again interacts with nitrogen ions. Thus, ion nitriding can provide a diffusion layer with an optimum structure and phase composition if we appropriately choose the parameters of the glow discharge, i.e., the pressure, the specific power, and the composition of the saturating atmosphere [7].

CONCLUSIONS

1. We established regular features of nitrogen saturation of titanium coatings preliminarily deposited from a liquid-metal carrier on steel 08Kh18N10T in a glow discharge.

2. In order to obtain a titanium–nitrogen layer with a maximum hardness of the surface, the process of ion nitriding should be performed in a medium of a nitrogen–hydrogen mixture at 750 – 800°C. The layer grows the most intensely at a hold of 3 – 7 h.

3. In ion nitriding, the pressure produces the greatest effect on the formation of the nitride layer that mainly consists of TiN nitrides. The optimum pressure providing a stable glow discharge for ion nitriding of coatings is 6.65 – 7.98 hPa.

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