

THERMOCHEMICAL TREATMENT

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EFFECT OF TEMPERATURE AND DEGREE OF RAREFACTION OF THE OXYGEN-BEARING MEDIUM ON THE PROCESS OF OXYNITRIDING OF TITANIUM ALLOYS

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Dependence of the physicochemical characteristics of surface layers of titanium alloys on the mode of oxynitriding, i.e., the temperature of saturation in the nitrogen-bearing medium and the degree of rarefaction of the oxygen-bearing medium in the process of oxygen modifying of the formed nitride layer, is studied. The conditions ensuring formation of a homogeneous oxynitride layer on the surface are determined.

Keywords: titanium alloys, oxynitriding, oxygen-bearing medium, microstructure, phase composition.

INTRODUCTION

Titanium oxynitrides have high operating properties, especially wear and corrosion resistance [1 – 3]. This makes the oxynitrides an appropriate material for functional coatings on titanium alloys.

The determining factor for forming oxynitrides on the surface of titanium alloys by modifying the nitride layers with oxygen is the quality of the initial nitride, its stoichiometry in particular. In its turn, this depends on the temperature and time parameters of nitride formation. The absence of data on the effect of the temperature and time parameters of the process of formation nitride film on the composition of the oxynitride and on the conditions of its modification with oxygen prevents purposeful formation of oxynitrides with specific composition and appropriate physicochemical characteristics.

The aim of the present work consisted in studying the physicochemical properties of surface layers obtained by modifying the nitride layers formed by isothermal hold in a medium of molecular nitrogen at 850 and 950°C in a rarefied (0.001 – 10 Pa) oxygen-bearing medium.

METHOD OF STUDY

We studied specimens 10 × 15 × 1 mm in size fabricated from VT1-0 (technically pure titanium) and PT-7M α -alloys,

OT4 and VT20 pseudo- α -alloys, and VT6s ($\alpha + \beta$)-alloy. The specimens were preliminarily polished ($Ra = 0.4 \mu\text{m}$), washed in alcohol, and dried. The saturation was performed at 850 and 950°C in molecular nitrogen of atmospheric pressure. We used technically pure nitrogen that was cleaned from oxygen and moisture by passing through a capsule with silica gel and titanium chips heated above the saturation temperature before feeding into the working space of the furnace. The isothermal hold in the saturation was 5 h. Heating to the nitriding temperature was performed in 10^{-3} Pa vacuum; cooling from the nitriding temperature to 500°C was performed in an oxygen-bearing medium (air) rarefied to 0.001 – 10 Pa. After this the chamber was evacuated.

The phase composition of the surface layers was determined with the help of x-ray phase analysis using a DRON-3.0 diffractometer in monochromatic copper K_{α} radiation with focusing in the mode of Bragg – Bretano. The anode voltage of the x-ray tube was 30 kV at a current of 20 mA. In order to obtain and process the data we used DNH-PDS, CSD, and PCW software.

The microstructure of the specimens was studied on angle laps using an Epiquant microscope equipped with a camera and a computer for obtaining images in digital form. The microhardness over the cross section of the surface layers was measured using a PMT-3M device at a load of 0.49 N on the indenter.

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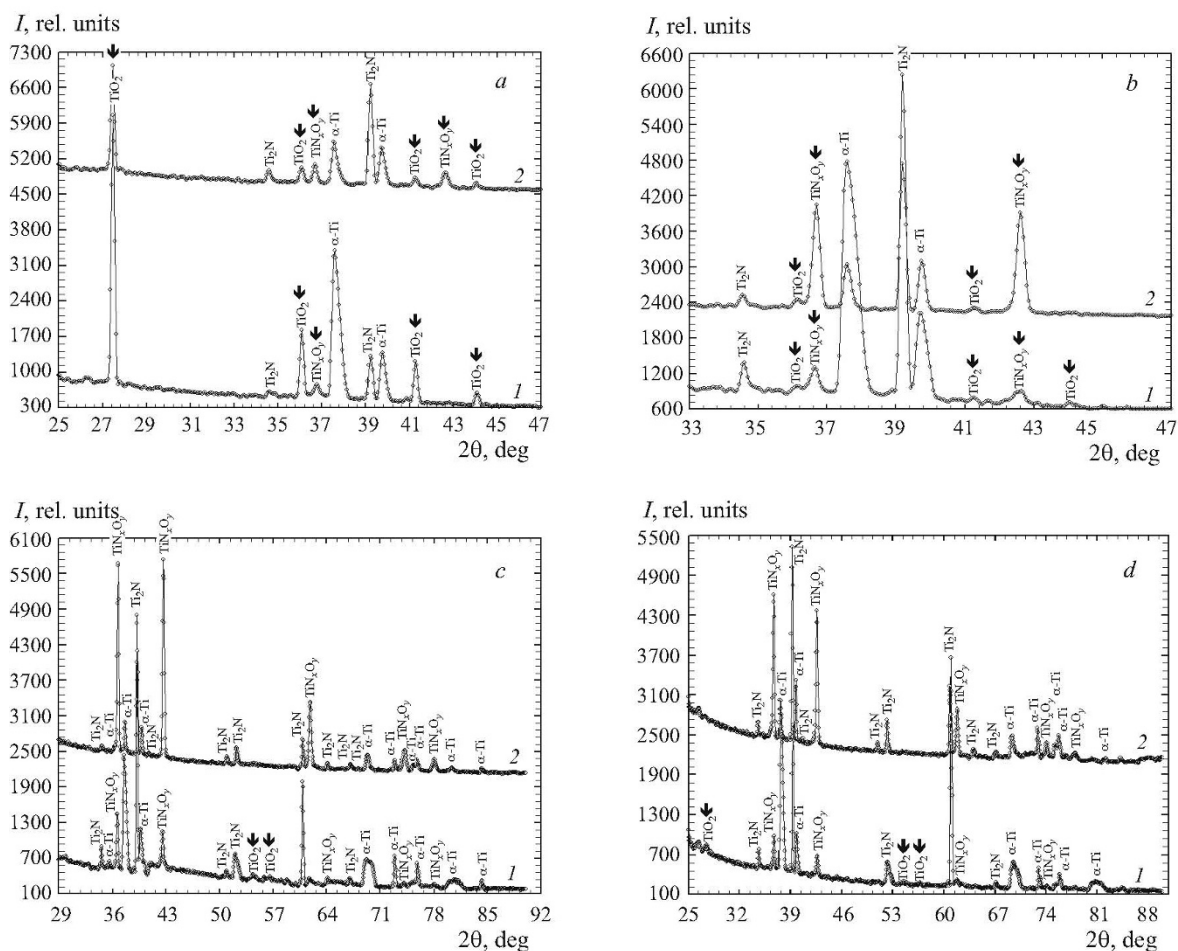


Fig. 1. Diffractograms taken from the surface of technically pure titanium VT1-0 after oxynitriding at 850°C (1) and 950°C (2) at different rarefaction of the oxygen-bearing medium: a) 1 Pa; b) 0.1 Pa; c) 0.01 Pa; d) 0.001 Pa.

RESULTS AND DISCUSSION

In the process of isothermal hold at 950°C in atmospheric-pressure nitrogen the surface of titanium alloys is covered by a film of titanium mononitride with composition close to the stoichiometric one. This is confirmed by the lattice parameter $a = 4.2354$ nm of the nitride formed on the surface of titanium due to nitriding in the temperature-time mode without feeding a rarefied oxygen-bearing medium in the cooling stage. At a lower saturation temperature ($t_s = 850^\circ\text{C}$) the titanium nitride formed on the surface contains a higher number of vacancies in the nonmetallic sublattice (the lattice parameter $a = 4.2146$ nm). In the case of cooling in a rarefied oxygen-bearing medium the nitride layers formed in the isothermal hold in a medium of molecular nitrogen are modified with oxygen, i.e., the titanium alloy undergoes oxynitriding. Filling of the vacancies in the nonmetallic sublattice of the nitride formed at a lower nitriding temperature with oxygen atoms is more favorable from the standpoint of energy than modification of stoichiometric nitride. For this reason, under the same conditions of modification the oxidation-reduction reactions on the surface of the

nonstoichiometric nitride occur more rapidly, which will later determine the structure and phase composition of the surface layers and the composition of the oxynitrides.

Let us illustrate the dependence of the effect of oxynitriding in the process described on the nitriding temperature and on the degree of rarefaction of the oxygen-bearing medium.

After modification of the nitrated layer formed at $t_s = 850$ and 950°C in an oxygen-bearing medium rarefied to 10 Pa the surface of the tested titanium alloys is coated with an oxide film with dominant gray-blue color. In this mode of oxynitriding oxygen participates actively in the oxidation of titanium nitride forming a TiO_2 oxide in rutile modification. The diffractograms taken from the surfaces of the alloys exhibit a considerable number of intense reflections of an oxide phase and low-intensity lines of a lower Ti_2N nitride against the background of the titanium matrix. After saturation at 950°C the diffractograms of the specimens contain traces of an oxynitride phase the relative intensity of which is inconsiderable. After saturation at 850°C reflections of the oxynitride phase are undetectable.

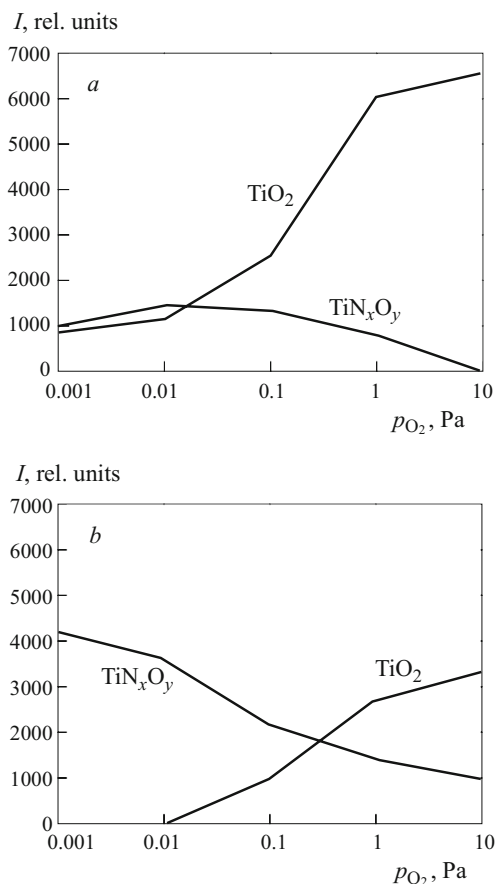


Fig. 2. Relative intensity I of diffraction reflections of TiO_2 (110) and TiN_xO_y (111) in the surface layers of specimens as a function of the rarefaction of the oxygen-bearing medium in the process of oxynitriding at 850°C (a) and 950°C (b).

When the rarefaction of the oxygen-bearing medium is increased to 1–0.1 Pa, the oxide formation is substantially decelerated; this is reflected in an decrease in the intensity of the diffraction maxima of the TiO_2 oxide and in their number. At the same time, the number and the intensity of reflections of the oxynitride phase increase. It should be noted that after saturation at 950°C the process of formation of oxynitrides upon increase in the rarefaction from 10 to 0.1 Pa occurs more intensely than after saturation at 850°C. This is reflected in growth in the number and intensity of reflections of the oxynitride phase on the diffractograms and in decrease in the intensity of reflections of the oxide phase (Fig. 1a and b).

The surface of specimens of all the alloys subjected to such saturation acquires a violet color. This very color accompanies formation of oxynitride phases in the process of high-temperature oxidation of compact poreless specimens of titanium nitride [4]. As a result of saturation of the alloys at 850°C in an oxygen-bearing medium rarefied to 1 Pa the surface layer of the specimens chips off; for all the other modes of oxynitriding, detachment of the surface layers has not been observed.

When the rarefaction of the oxygen-bearing medium was increased to 0.01 and 0.001 Pa at $t_s = 850^\circ\text{C}$ the coloring of the surface varied from orange to blue-green depending on the composition of the alloy. However, layers of violet or violet-gray color were observed in virtually all the alloys. In addition to the data of x-ray phase analysis this confirms the presence of an oxynitride phase. After saturation at 950°C the coloring of the surface of the specimens is more homogeneous, i.e., either violet-gray or dark-golden (alloys PT-7M and VT20). The difference in the coloring of the surface of the alloys seems to be explainable by formation of oxynitrides of different compositions with respect to nitrogen (oxygen).

The coloring of the surface of the specimens and the results of the x-ray phase analysis show that in the case of rarefaction of the oxygen-bearing medium to 0.01–0.001 Pa the process of formation of titanium oxynitrides prevails over the process of oxide formation (Fig. 2). This is especially well manifested for specimens treated at $t_s = 950^\circ\text{C}$. In this case reflections of an oxide phase are absent on the diffractograms and the oxynitride phase is represented by a full spectrum of diffraction maxima (Fig. 1b and d). This indicates formation of a homogeneous layer of titanium nitride on the surface. At $t_s = 850^\circ\text{C}$ the growth in the intensity of reflections of the oxynitride phase and the decrease in the number and intensity of reflections of the oxide phase on the diffractograms also reflect active oxynitriding.

It is known [4–6] that the change in the content of nitrogen (oxygen) in the oxynitride phase affects the parameter of its fcc lattice. As the rarefaction of the oxygen-bearing medium is increased from 1 to 0.001 Pa at $t_s = 850^\circ\text{C}$ the parameter of the lattice of the oxynitride formed on alloy VT1-0 increases as follows: 0.4227 nm \rightarrow 0.4239 nm \rightarrow 0.4240 nm \rightarrow 0.4240 nm. At $t_s = 950^\circ\text{C}$ in the rarefaction range of 10–0.001 Pa the lattice parameter changes as follows: 0.4238 nm \rightarrow 0.4240 nm \rightarrow 0.4242 nm \rightarrow 0.4238 nm \rightarrow 0.4241 nm. With allowance for the influence of the oxygen (nitrogen) content in titanium nitride on its lattice parameter [5] we may state that the content of the nitride component increases within the mentioned range of growth in the rarefaction of the oxygen-bearing medium and the content of the oxygen component in the ternary compound decreases (Fig. 3). However, the component composition of the oxynitride depends on the saturation temperature.

Oxynitriding (modifying of the formed nitrides with oxygen) at a lower saturation temperature yields oxynitrides with a higher content of the oxygen component. At a higher saturation temperature the range of the content of the oxygen (nitrogen) component in the formed oxynitrides is considerably narrower. For example, at $t_s = 850^\circ\text{C}$ the composition of the oxynitride is close to $TiN_{0.36-0.46}O_{0.64-0.54}$, whereas at 950°C it is close to $TiN_{0.44-0.48}O_{0.56-0.52}$ (Fig. 3). It should be noted that the composition of the oxynitrides obtained at $t_s = 950^\circ\text{C}$ is closer to the equiatomic variant than at $t_s = 850^\circ\text{C}$.

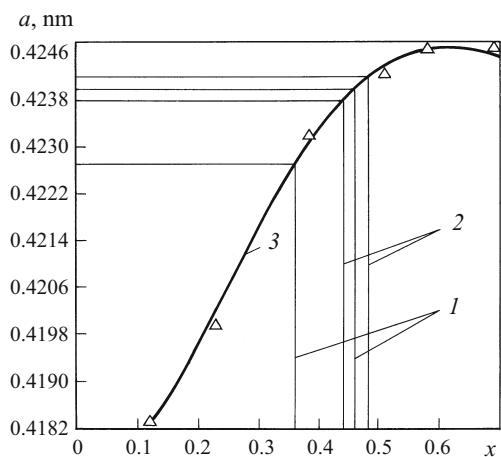


Fig. 3. Lattice parameter a as a function of the content of nitrogen component x in the $\text{TiN}_x\text{O}_{1-x}$ compound: 1) at 850°C ; 2) at 950°C ; 3) according to the data of [5].

When the rarefaction of the oxygen-bearing medium is increased and phase formation on the surface of titanium alloys shifts toward oxynitrides, the microhardness of the surface of the specimens grows (see Table 1). The highest values of microhardness on the surfaces of all tested alloys after oxynitriding at 850°C were obtained at rarefaction of the oxygen-bearing medium equal to 0.001 – 0.01 Pa, when the surfaces were coated with oxynitrides with composition closest to the equiatomic one. Such compounds exhibit a hardness of 2240 – 2650 HV [7]. At $t_s = 950^\circ\text{C}$ the range of rarefaction of the oxygen-bearing medium at which the formed compounds have maximum surface hardness widens to 0.001 – 0.1 Pa. The microhardness of the surface of the coating formed on alloys OT4 and VT6s due to oxynitriding at 850°C with cooling in a rarefied oxygen-bearing atmosphere is respectively 1.3 – 1.5 and 1.2 times higher than after nitriding in atmospheric-pressure nitrogen. At $t_s = 950^\circ\text{C}$ the growth in HV is more substantial, i.e., 1.1 – 2.2 and 1.6 – 1.9 times, respectively. The microhardness of the surface of alloys VT1-0, PT-7M, and VT20 after oxynitriding at 850°C is respectively 1.3 – 2.0, 1.8 – 1.9, and 2.0 – 2.1 times higher than after conventional nitriding at the same temperature.

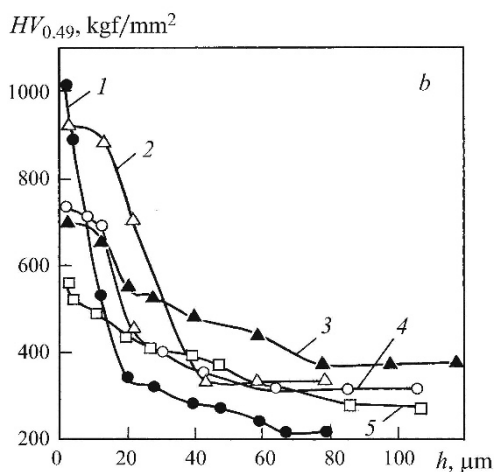
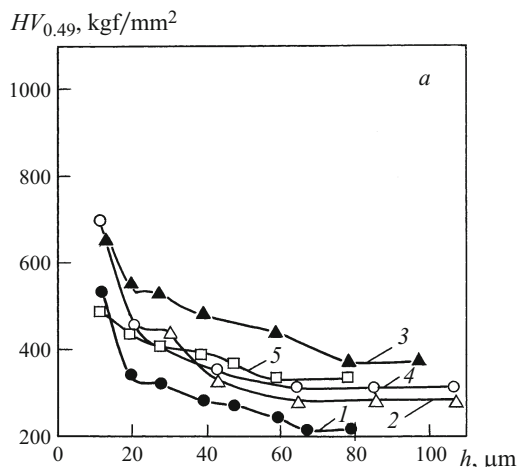


Fig. 4. Variation of microhardness over the thickness of surface layers of titanium alloys (h is the distance from the surface) after oxynitriding at 850°C (a) and 950°C (b) at rarefaction of the oxygen-bearing medium equal to 0.1 Pa: 1) VT1-0; 2) PT-7M; 3) VT20; 4) OT4; 5) VT6s.

Oxynitriding of these alloys at 950°C promotes growth in the surface microhardness by a factor of 1.1 – 1.6, 1.3 – 1.4, and 1.3 – 1.5, respectively. Having analyzed the values of surface microhardness of the alloys after oxynitriding we came to a

TABLE 1. Microhardness of the Surface of Titanium Alloys after Oxynitriding at 850 and 950°C at Different Rarefaction of the Oxygen-Bearing Medium

Alloy	Surface microhardness $HV_{0.981}$, kgf/mm ² , at p_{O_2} , Pa					
	0	0.001	0.01	0.1	1	10
VT1-0	1530/1410	2100/2310	1900/2110	1320/1560	1260/1330	1140/1600
PT-7M	1200/1400	2310/1920	2160/1950	1760/1860	1290/1750	1310/1970
VT20	1100/1170	2250/1790	2340/1600	1330/1580	1250/1140	1000/1270
OT4	1750/1440	2220/1600	2550/2090	1610/2100	1270/1430	1000/1700
VT6s	1910/1540	2270/2650	2440/2400	1550/1930	1500/1390	1580/1410

Note. The numerators present the microhardness after nitriding at 850°C ; the denominators — after nitriding at 950°C .

conclusion that the process performed at both temperatures ensures higher hardening of the surface than nitriding.

Thus, in accordance with the dependence of the hardness of an oxynitride on its composition [4 – 6] the level of microhardness of the surface of titanium alloys is determined by the composition of the surface oxynitride at 850°C at rarefaction of 0.001 – 0.01 Pa and by the presence of oxide film on the surface at rarefaction of 0.1 – 10 Pa. At a higher saturation temperature (950°C) the microhardness of the surface is determined by the composition of the oxynitride at rarefaction of 0.001 – 0.1 Pa.

In the process of thermodiffusion saturation of titanium, formation of phases on the surface is accompanied by diffusion of the interstitial elements into the depth of the metal. This yields a transition diffusion zone with microhardness exceeding that of the matrix. The introduction of elements into the titanium matrix of each of the alloys is determined by their solubility and diffusion mobility and depends on the saturation temperature, the growth of which is accompanied by increase in the microhardness and thickening of the diffusion layer (Fig. 4). Specifically, after oxynitriding of titanium alloy OT4 at 850°C the thickness of the hardened layer by the data of a durometer study is about 53 – 55 μm. After increase in the saturation temperature to 950°C the more intense diffusion of nitrogen into the depth of the titanium matrix increases the thickness of the layer to 57 – 60 μm. According to the data of a metallographic analysis the thickness of the hardened layer increases from 19 – 23 μm to 33 – 38 μm upon growth in the saturation temperature from 850 to 950°C.

CONCLUSIONS

1. The phase composition of surface layers after oxynitriding depends on the saturation temperature and on the degree of rarefaction of the oxygen-bearing medium. At saturation temperature $t_s = 950^\circ\text{C}$ and rarefaction of the oxygen-bearing medium to 0.001 and 0.01 Pa the surface of titanium alloys is coated by a homogeneous layer of titanium

oxynitride; at $t_s = 850^\circ\text{C}$ the oxynitride is accompanied by titanium oxides.

2. In the process of saturation at 850°C the formed titanium oxynitrides have composition $\text{TiN}_{0.36-0.46}\text{O}_{0.64-0.54}$; saturation at 950°C yields $\text{TiN}_{0.44-0.48}\text{O}_{0.56-0.52}$. For the oxynitrides formed at $t_s = 950^\circ\text{C}$ the range of variation of the components is narrower and the composition is closer to the equiatomic one than at $t_s = 850^\circ\text{C}$.

3. Oxynitriding of titanium alloys ensures more considerable hardening of the surface than nitriding. The microhardness of the surface of titanium alloys is determined by the composition of the oxynitride formed on the surface at oxygen-bearing medium rarefied to 0.001 – 0.01 Pa ($t_s = 850^\circ\text{C}$) and to 0.001 – 0.1 Pa ($t_s = 950^\circ\text{C}$).

4. The thickness of the hardened layer of titanium alloys after oxynitriding is determined by the isothermal hold in nitrogen at the saturation temperature and is independent of the degree of rarefaction of the oxygen-bearing modifying medium.

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