

## INFLUENCE OF PARAMETERS OF MODIFYING OXYGEN-CONTAINING ATMOSPHERE ON OXYNITRIDING OF TITANIUM ALLOYS

I. M. Pohrelyuk,<sup>1,2</sup> V. M. Fedirko,<sup>1</sup> O. I. Yas'kiv,<sup>1</sup> Dong-Bok Lee,<sup>3</sup>  
and O. V. Tkachuk<sup>1</sup>

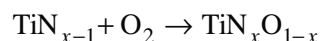
UDC 669.295:621.795

We study the influence of the parameters of modifying oxygen-containing atmosphere (the degree of rarefaction, temperature and time of modification) on the oxynitriding of titanium alloys. It is shown that, as the degree of rarefaction of the atmosphere increases and the temperature of modification decreases, the process of phase formation on the surface of titanium alloys evolves in the direction of formation of oxynitrides, whereas the period of modification does not affect the structural and phase state. As the oxygen content decreases, the composition of titanium oxynitride approaches the equiatomic composition. This guarantees the increase in surface microhardness and the improvement of the corrosion resistance of titanium alloys in oxygen-free acids.

**Keywords:** titanium alloys, surface engineering, oxynitriding, parameters of modification, oxynitrides, nitrides, oxides, oxygen, nitrogen.

Due to the complete mutual solubility of isomorphous TiO and TiN [1], it is possible to form  $\text{TiN}_x\text{O}_{1-x}$  titanium oxynitrides that not only inherit the characteristics of binary oxide and nitride but also, for some compositions, are better than the indicated compounds [2–4]. This is why these compounds are more promising as functional coatings, including the coatings formed on titanium alloys.

Among the methods of oxynitriding under the conditions of thermodiffusion saturation from the controlled gaseous atmosphere, the technological procedure according to which ternary compounds are formed by modifying nonstoichiometric titanium nitrides with oxygen according to the reaction



should be regarded as preferable [5, 6]. In this scheme, the procedure of thermodiffusion saturation of titanium with nitrogen (nitriding) is performed prior to its controlled modification with oxygen (oxynitriding). The effect of this treatment depends both on the parameters of saturation in nitrogen and on the characteristics of modifying atmosphere.

In what follows, we study the influence of the parameters of modifying oxygen-containing atmospheres on the oxynitriding of titanium alloys.

### Procedure of Investigations

We study  $10 \times 15 \times 1$  mm specimens of VT1-0 commercially pure titanium and  $\alpha$ -(PT-7M), pseudo- $\alpha$ -

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<sup>1</sup> Karpenko Physicomechanical Institute, Ukrainian National Academy of Sciences, Lviv, Ukraine.

<sup>2</sup> Corresponding author; e-mail: pohrelyuk@ipm.lviv.ua.

<sup>3</sup> Sungkyunkwan University, School of Advanced Materials Science & Engineering, Suwon, South Korea.

(VT20), and  $(\alpha + \beta)$ -(VT6s) titanium alloys preliminarily polished to  $R_a = 0.4$  mm, washed in alcohol, and dried.

The phase compositions of the surface layers are determined by the X-ray phase diffraction analysis (XPDA) carried out with the help of a DRON-3.0 diffractometer with Bragg–Brentano focusing scheme in the monochromatic  $\text{CuK}\alpha$ -radiation. The anodic voltage of the X-ray tube is equal to 30 kV and the current through the tube to 20 mA. To determine the locations of diffraction maxima in the image and the lattice constants identified according to the JCPDS-ASTM data file, we used the Sietronix, Powder Cell 2.4, and FullProf software packages.

The oxynitride phase is identified according to the reference X-ray diffraction pattern of titanium oxynitride with equiatomic composition. It was obtained by modeling the structure according to the Levi model [7] in which, unlike the model presented in Pearson's Handbook [8] for a completely disordered structure, the presence of disordering is allowed solely for the nonmetallic sublattice [the N and O atoms randomly occupy the  $(1/2 \ 1/2 \ 1/2)$  positions, whereas the titanium atoms necessarily occupy the  $(0 \ 0 \ 0)$  positions].

The microhardness over the section of subsurface layers was measured with a PMT-3M device under a load applied to the indenter of 0.49 and 0.98 N. The microstructure of the subsurface layers was studied by using an "Epiquant" metallographic microscope and an EVO-40XVP scanning electron microscope equipped with an INCA Energy system for microanalysis.

The procedure of oxynitriding is carried out by delivering a controlled oxygen-containing medium into the system in the final stage of nitriding (in the process of cooling). As a result, the controlled oxidation of the already formed nitrides (oxynitriding) runs from the maximum temperature of saturation down to the temperature at which the interaction of titanium with nitrogen and oxygen is still intense (from  $T_M$  to  $500^\circ\text{C}$ ) (Fig. 1).

We used commercially pure molecular nitrogen ( $\geq 0.4$  vol.%) cleaned from oxygen and moisture (down to  $\leq 0.05$  vol.%) as a result of passage through a capsule filled with silica gel and titanium chips heated over the temperature of saturation. To remove natural oxide films and prevent the formation of new films, the specimens were heated to the temperature of saturation  $T_N$  in a vacuum of  $10^{-3}$  Pa .

The oxynitriding performed in this way depends both on the parameters of nitriding (temperature  $T_N$ , the time of isothermal holding  $\tau_N$ , and the pressure of nitrogen  $p_{\text{N}_2}$ ) and on the parameters of modification with oxygen (the degree of rarefaction of the modifying medium  $p_{\text{O}_2}$ , the temperature of modification  $T_M$ , and its duration  $\tau_M$ ). The results of oxynitriding are known depending on the parameters of nitriding [9, 10]. In what follows, we study the influence of the parameters of modification with oxygen on oxynitriding for  $T_N = 950^\circ\text{C}$ ,  $\tau_N = 1$  and 5 h, and  $p_{\text{N}_2} = 10^5$  Pa .

## Results and Discussion

As a result of realization of the procedure of oxynitriding (Fig. 1) in the course of rarefaction of the oxygen-containing medium to 100 Pa, dull chalky oxide films are formed on the surfaces of titanium alloys. The incoherence of the structures formed on the surfaces of titanium oxide and titanium nitride, the difference between their physical properties (e.g., between the coefficients of thermal expansion [1]), and large thicknesses of oxide films are responsible for the formation of the critical residual stresses in the surface layers. This leads to the cracking and cleavage of oxide films. Hence, we can conclude that the modifying oxygen-containing media rarefied below 100 Pa are unsuitable for oxynitriding.

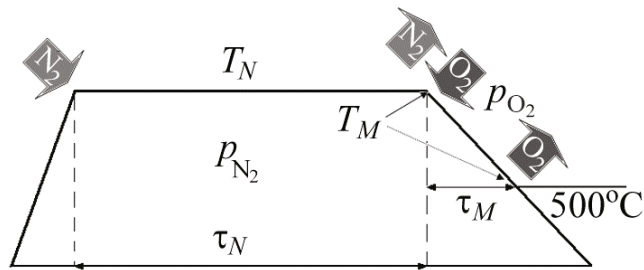


Fig. 1. Schematic diagram of the oxynitriding of titanium alloys.

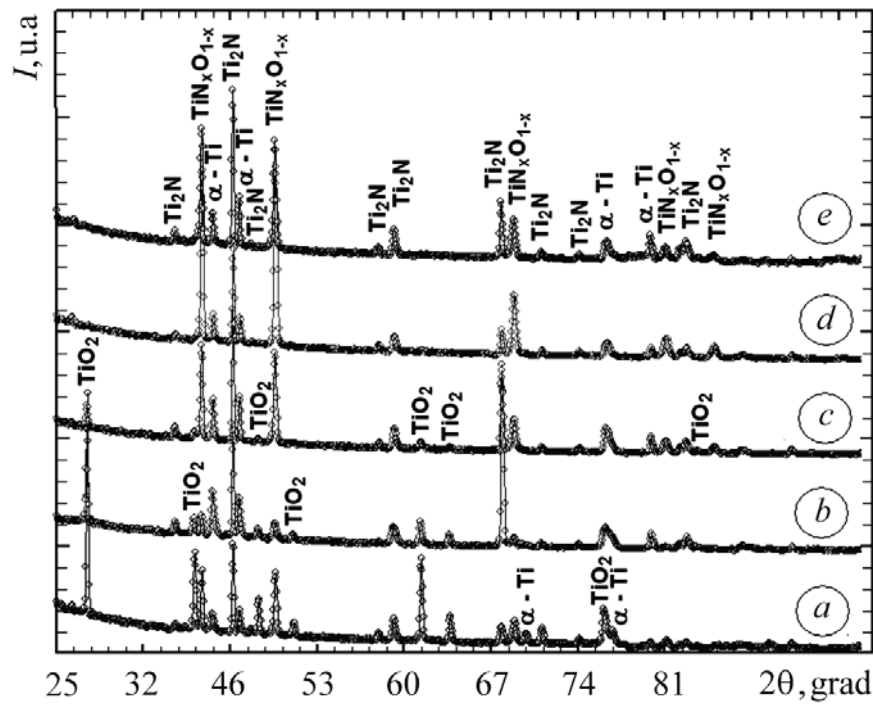
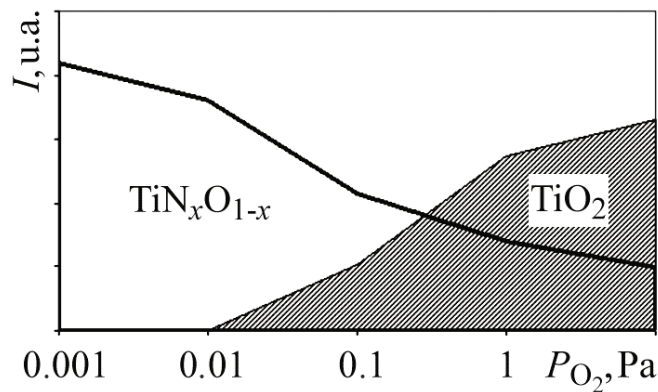


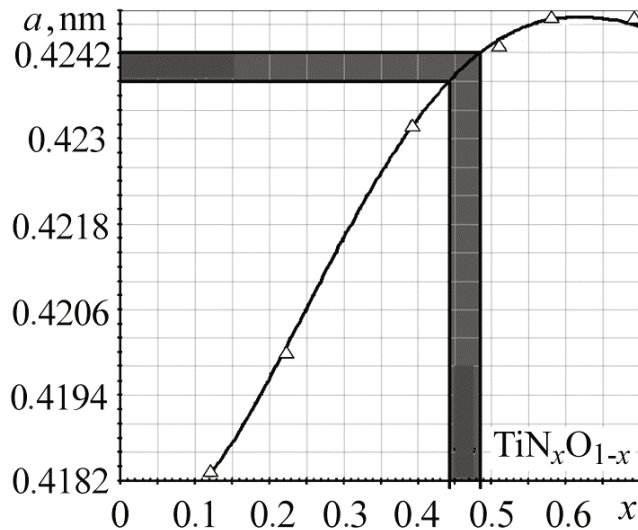
Fig. 2. X-ray diffraction patterns of the surface of commercially pure VT1-0 titanium after oxynitriding in modifying oxygen-containing media rarefied to  $p_{O_2}$ : (a) 10, (b) 1, (c) 0.1, (d) 0.01, (e) 0.001 Pa.

We illustrate the dependence of oxynitriding performed according to the outlined technological procedure on the degree of rarefaction of the modifying oxygen-containing medium  $p_{O_2}$  within the range 0.001–10 Pa. The upper bound of this range is determined by the technical characteristics of the applied equipment.

As a result of the modification of nitrided layers in oxygen-containing media rarefied to 10 Pa, we observe the formation of gray-blue oxide films on the surfaces of titanium alloys. In this case, titanium nitride oxidizes to the  $TiO_2$  oxide in the rutile modification. In the X-ray diffraction patterns taken from the surfaces of the alloys, parallel with a large number of intense reflexes of the oxide phase, we record the lines of the oxynitride phase and less intense lines of the lower titanium nitride ( $Ti_2N$ ) (Fig. 2a). They also contain the lines of  $\alpha$ -titanium with elevated interplane distances, which reveals the formation of transition layers of a solid solution of interstitial elements in  $\alpha$ -Ti separating the coating from the matrix.



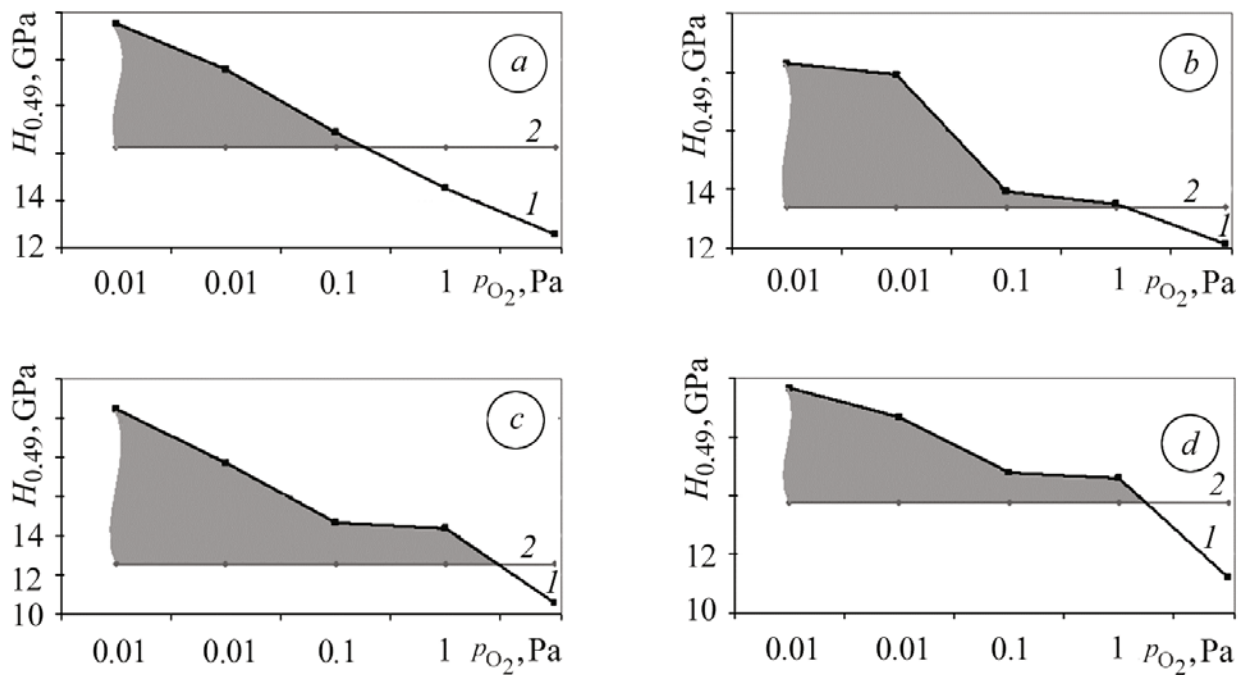
**Fig. 3.** Dependences of the relative intensities of diffraction maxima (110) of the  $\text{TiO}_2$  phase and diffraction maxima (111) of the  $\text{TiN}_x\text{O}_{1-x}$  phase in the X-ray diffraction patterns taken from the surfaces of commercially pure VT1-0 titanium oxynitrided at  $950^\circ\text{C}$  on the degree of rarefaction of the modifying oxygen-containing medium.



**Fig. 4.** Dependence of the lattice parameter of  $\text{TiN}_x\text{O}_{1-x}$  on the content of nitrogen (the solid line corresponds to the data taken from [12]).

As the degree of rarefaction of the atmosphere increases to 1–0.1 Pa, the rate of the process of oxidation becomes much lower, which manifests itself in the decrease in the intensity of the diffraction maxima of  $\text{TiO}_2$  oxide and their number. At the same time, the number and intensities of reflexes of the oxynitride phase increase (Figs. 2b, c). The surfaces of the specimens become lilac-gray or dark golden (PT-7M, VT20), which also confirms the presence of the oxynitride phase (together with the data of XPDA) [11]. The difference between the colors of the surfaces of different alloys is, most likely, explained by the formation of oxynitrides of different chemical compositions.

In the case where the oxygen-containing atmosphere is rarefied to 0.01–0.001 Pa, the process of formation of titanium oxynitrides is predominant (Fig. 3). In this case, reflexes of the oxide phase are absent in the X-ray diffraction patterns but the oxynitride phase is represented by the complete spectrum of diffraction maxima (Figs. 2d, e).



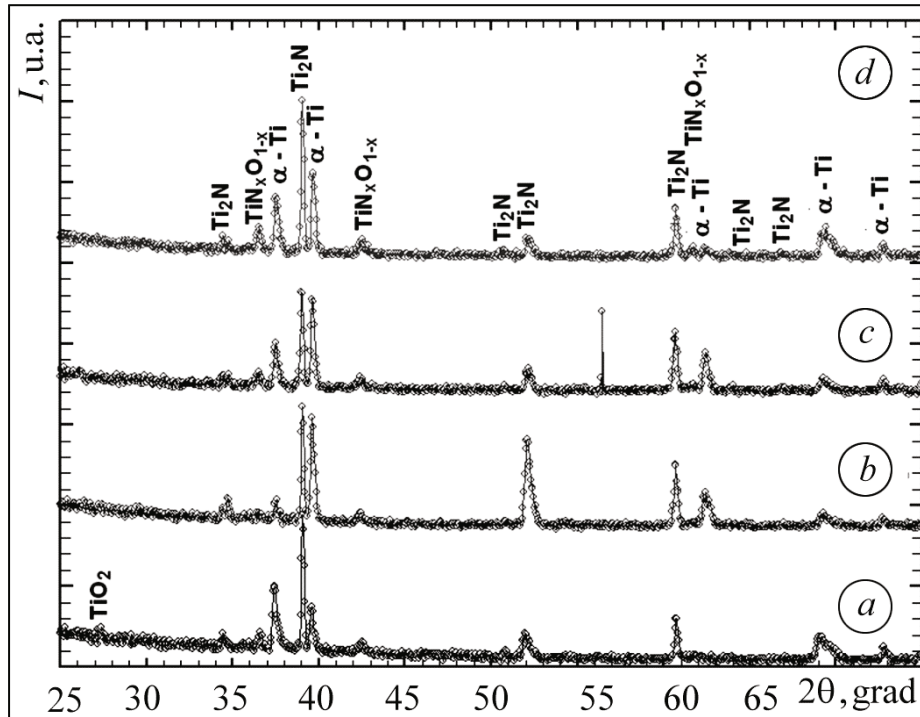
**Fig. 5.** Dependences of the surface microhardness of oxynitrided titanium alloys (curve 1) on the degree of rarefaction of the oxygen-containing atmosphere: (a) VT1-0, (b) PT-7M, (c) VT20; (d) VT6s (curve 2 corresponds to the surface microhardness after nitriding).

This shows that a homogeneous layer of titanium oxynitrides is formed on the surface. The fact of predominance of lilac-pink tints in the surface colors also confirms the predominance of the oxynitride formation.

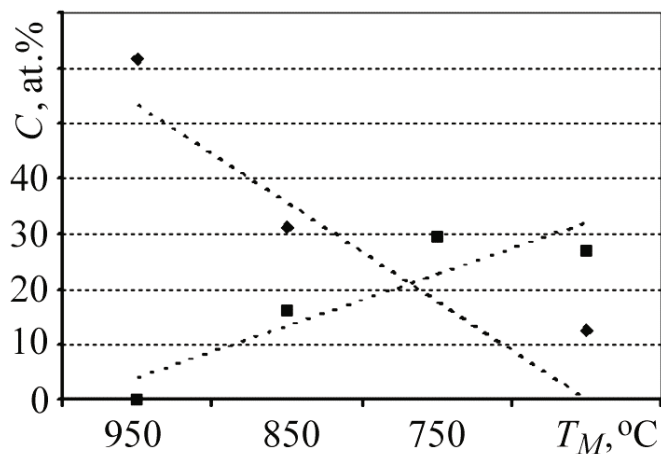
The lattice constant of the oxynitrides formed on commercially pure VT1-0 titanium increases as the pressure of the modifying atmosphere decreases from 10 to 0.001 Pa (Fig. 4). This is why, in view of the dependence of the lattice constant of titanium oxynitrides on the oxygen (nitrogen) content [12], we can conclude that, under these conditions, the amount of nitrogen in the ternary compound increases and, hence, the amount of oxygen decreases. The composition of titanium oxynitrides formed on the titanium surface is close to the equiatomic composition:  $TiN_{0.44-0.48}O_{0.56-0.52}$  (for VT1-0).

The results of the durometric and X-ray phase-diffraction analyses of the surface layers of titanium alloys after oxynitriding show that, for  $p_{O_2} = 0.001-0.01$  Pa, when the formation of oxynitrides is more intense than the formation of oxides, the composition of oxynitrides formed on the surface determines the microhardness of titanium alloys. The maximum hardening effect of oxynitriding, namely,  $\Delta H = H_M^S - H_N^S$  (the increment of the surface microhardness of titanium alloys after modification with oxygen as compared with the level of microhardness after nitriding) is also attained within the indicated pressure range (Fig. 5).

Within the range  $p_{O_2} = 0.1-10$  Pa, the attained degrees of oxidation of nitrides become so high that oxynitrides begin to transform into titanium oxides (Fig. 2) and, as a result, the effect of oxynitriding becomes much weaker or absolutely absent (Fig. 5). In this case, the surface microhardness of titanium alloys depends on the qualitative and quantitative characteristics of the oxide film, which substantially affects the integral value of microhardness of the modified surface. The oxynitriding of VT20 titanium alloy proves to be the most efficient procedure (from the viewpoint of attainment of the maximum surface hardening).

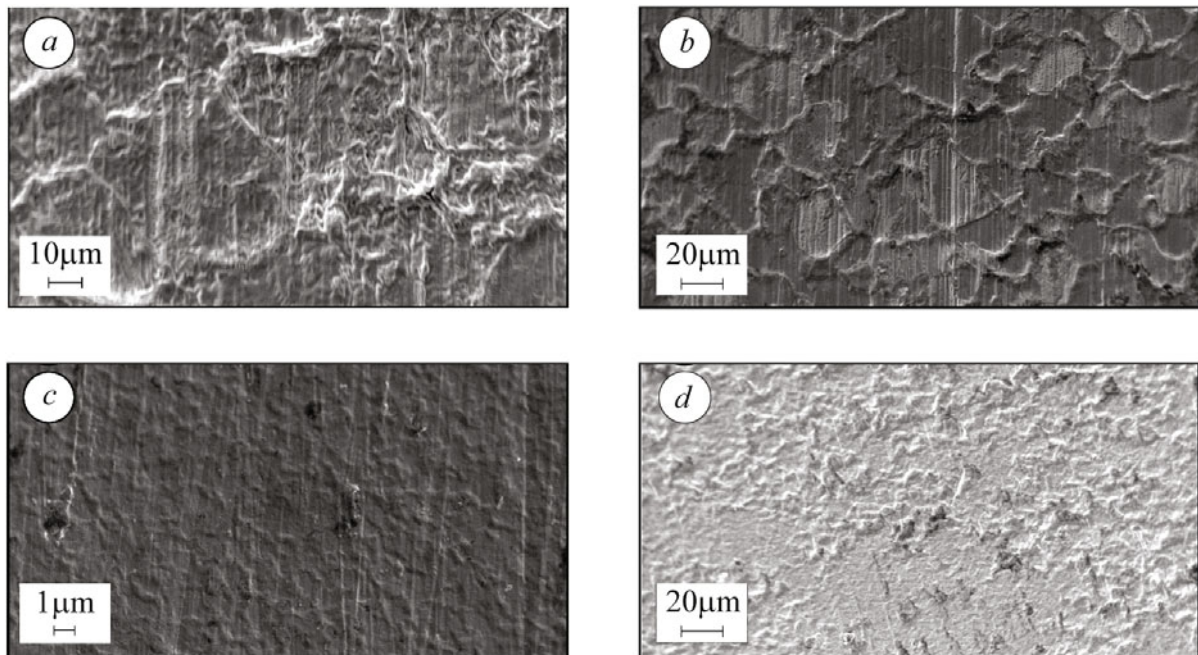


**Fig. 6.** X-ray diffraction patterns taken from the surface of commercially pure VT1-0 titanium after oxynitriding at different temperatures of the modifying oxygen-containing atmosphere ( $T_M$ ): (a) 950, (b) 850, (c) 750, (d) 650°C.



**Fig. 7.** Dependences of the concentrations of oxygen and nitrogen on the surfaces of oxynitrided specimens of commercially pure VT1-0 titanium on the temperature of modification  $T_M$  (according to data of micro-X-ray spectral analysis): (■) N, (◆) O.

To study the influence of the temperature of modification  $T_M$  on the oxynitriding of titanium alloys, nitride layers intended for oxygen modification were formed under the following conditions of chemical and thermal treatment:  $T_N = 950^\circ\text{C}$ ,  $\tau_N = 1$  h, and  $p_{N_2} = 105$  Pa. The temperature  $T_M$  varied in the range 950–650°C with steps of 100°C. The pressure of the oxygen-containing atmosphere  $p_{O_2} = 0.01$  Pa.



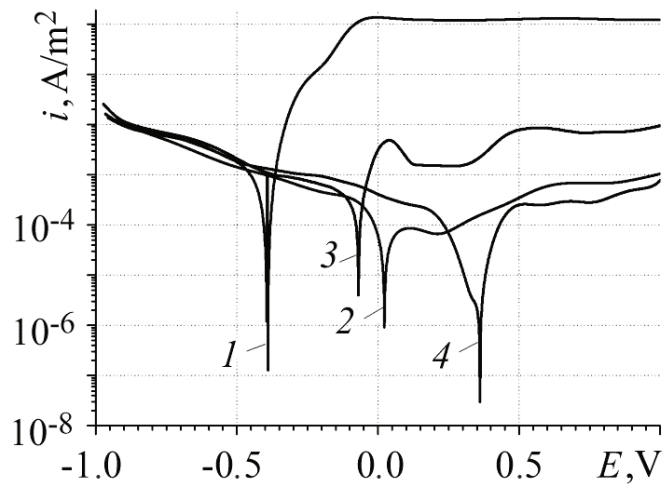
**Fig. 8.** Surfaces of VT1-0 (a), PT-7M (b), VT20 (c), and VT6s (d) titanium alloys after oxynitriding at a temperature of modification  $T_M = 650^\circ\text{C}$ .

**Table 1. Surface Microhardness  $H_{0.98}$  (GPa) of the Titanium Alloys after Oxynitriding Depending on the Temperature of Modification**

Alloy	Temperature of modification $T_M$ , °C			
	950	850	750	650
VT1-0	13.09	11.80	12.72	14.17
PT-7M	11.51	13.47	13.36	15.07
VT20	10.05	–	11.09	13.68
VT6s	11.02	–	11.48	12.53

As follows from the data of XPDA, the process of phase formation on the surfaces of alloys shifts in the direction of oxide formation as the temperature of modification increases. Thus, the reflexes of oxide phases are not recorded in the X-ray diffraction patterns taken from the surfaces of oxynitrided specimens of VT1-0 alloy modified at  $T_M = 660, 750,$  and  $850^\circ\text{C}$ . At the same time, a weak line (110) of  $\text{TiO}_2$  titanium oxide (rutile) is present in the spectra taken from the surfaces of the specimens modified at  $T_M = 950^\circ\text{C}$  (Fig. 6a).

The XPDA data are in good agreement with the data of visual and micro-X-ray spectral analyses of the specimen surfaces. As  $T_M$  decreases, the color of the surfaces of titanium and its alloys changes, as a rule, from violet to golden, and the concentration of oxygen (nitrogen) on the modified surface decreases (increases) (Fig. 7).



**Fig. 9.** Polarization curves taken in a 3% NaCl solution on commercially pure VT1-0 titanium after oxynitriding at different temperatures of modification  $T_M$  (°C): (1) 950, (2) 850, (3) 750, (4) 650.

**Table 2.** Potentials  $E_{\text{cor}}$  and Corrosion Currents  $i_{\text{cor}}$  for VT1-0 Titanium after Oxynitriding at Different Temperatures  $T_M$

$T_M$ , °C	$i_{\text{cor}}$ , A/m <sup>2</sup>	$E_{\text{cor}}$ , V
950	$1.5 \cdot 10^{-4}$	-0.39
850	$2 \cdot 10^{-5}$	0.02
750	$1 \cdot 10^{-4}$	-0.07
650	$2 \cdot 10^{-6}$	0.36

Moreover, for  $T_M = 950^\circ\text{C}$ , nitrogen is absent on the surface and the amount of oxygen corresponds to the amount of titanium oxide.

The surface microhardness of titanium after modification of the nitride layer with oxygen at  $T_M = 950^\circ\text{C}$  varies, roughly speaking, within the range 10–13 GPa. It is clear that its values are affected not only by the oxynitride and nitride components of the modified layer but also by the thin surface oxide film. The surface microhardness of the oxynitrided alloys increases as the temperature of modification decreases as a result of deceleration of the process of oxide formation (Table 1). This is explained by the presence of extrema in the dependence of hardness of titanium oxynitrides on the oxygen (nitrogen) content [11, 14] with maximum for chemical compositions close to the equiatomic composition. As the temperature of modification decreases, the oxygen content of the oxynitride compound formed on the surfaces of alloys decreases and its composition approaches the equiatomic composition. The surfaces of the alloys oxynitrided at  $T_M = 650^\circ\text{C}$  are shown in Fig. 8.

As the temperature of modification becomes lower and the oxygen content of the oxynitride phase decreases, the fraction of ionic bonds in this phase also decreases which should lead to better anticorrosion charac-



teristics of the coating in oxygen-free acids [15]. This is confirmed by the results of potentiodynamic analysis of the specimens of oxynitrided VT1-0 titanium in a 3% NaCl solution (Fig. 9).

**Table 3. Surface Microhardness  $H_{0.98}$  and the Mean Arithmetic Deviation of the Surface Profile  $R_a$  of VT1-0 Titanium after Oxynitriding Depending on the Duration of Modification at  $T_M = 650^\circ\text{C}$**

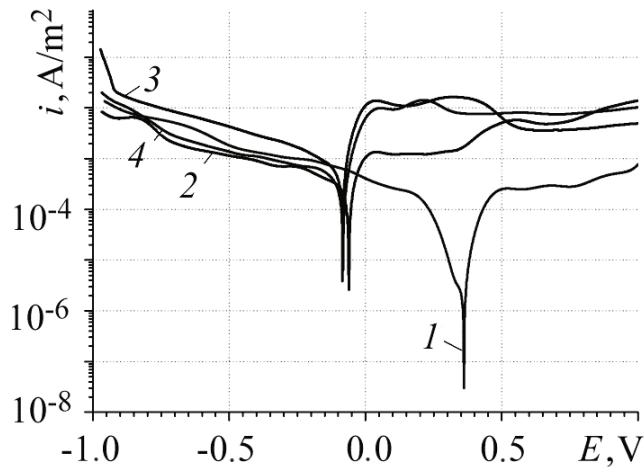
Characteristics	$\tau_M, \text{h}$			
	0	0.5	1	1.5
$H_{0.98}, \text{GPa}$	14.17	14.03	15.24	14.64
$R_a, \mu\text{m}$	0.73	0.81	0.84	0.86

**Table 4. Potentials  $E_{\text{cor}}$  and Corrosion Currents  $i_{\text{cor}}$  of VT1-0 Titanium after Oxynitriding at  $T_M = 650^\circ\text{C}$  for Different Periods of Modification  $\tau_M$**

$\tau_M, \text{h}$	$i_{\text{cor}}, \text{A/m}^2$	$E_{\text{cor}}, \text{V}$
0	$2 \cdot 10^{-6}$	0.36
0.5	$1.5 \cdot 10^{-4}$	-0.06
1.0	$1.5 \cdot 10^{-4}$	-0.08
1.5	$2 \cdot 10^{-4}$	-0.08

In particular, the anodic branch of the polarization curve taken from the surface of nitrided titanium modified with oxygen at  $T_M = 950^\circ\text{C}$  is characterized by the longest passive region ( $\sim$  from 0 to 2 V). However, both the corrosion potential  $E_{\text{cor}}$  and corrosion current  $i_{\text{cor}}$  take the lowest values as compared with the corresponding characteristics of the coatings formed as a result of modification with oxygen at lower temperatures  $T_M$  (Table 2). It should be emphasized that the passivation currents are weaker than the currents formed in the coating modified at  $T_M = 950^\circ\text{C}$  by 3–5 orders of magnitude. The oxynitride coating modified at  $650^\circ\text{C}$  guarantees the best corrosion protection of the surface among the coatings modified with oxygen within the range  $850\text{--}650^\circ\text{C}$ .

We now analyze the dependence of the effect of oxynitriding performed according to the outlined technological procedure on the duration of modification  $\tau_M$  with oxygen. The period of isothermal holding at  $T_M = 650^\circ\text{C}$  varied from 0 to 1.5 h. According to the data of XPDA, the duration of modification at  $T_M = 650^\circ\text{C}$  does not affect the structural and phase state of the surface layers of titanium alloys. In the X-ray diffraction patterns taken from the surfaces of oxynitrided specimens, we detect weak lines of titanium oxynitride and  $\text{Ti}_2\text{N}$  nitride and intense peaks of  $\alpha$ -titanium with shifted interplane distances.



**Fig. 10.** Polarization curves taken in a 3% NaCl solution on commercially pure titanium after oxynitriding with holding in a modifying oxygen-containing atmosphere for  $\tau_M$  (h): (1) 0, (2) 0.5, (3) 1, (4) 1.5.

This may serve as an indication of the formation of a laminated modified layer formed by titanium oxynitride and titanium nitride separated from the titanium matrix by a layer of  $\alpha$ -solid solution of the interstitial elements (nitrogen and oxygen) in titanium. As the duration of modification increases, we observe the redistribution of intensity maxima of the oxynitride phase in the X-ray diffraction patterns, which confirms the increase in the degree of stoichiometry of oxynitride (substitution of O for N in the nonmetallic sublattice). The redistribution of intensity maxima of the  $Ti_2N$  nitride confirms the existence of leveling of the texture in direction (002) as  $\tau_M$  increases.

The indicated structural changes in the surface layers of oxynitrided titanium lead to changes in the level of surface hardening and in the surface topography (Table 3): the surface microhardness and the arithmetic mean deviation of the surface profile increase.

As the fraction of oxygen (fraction of ionic bonds) in the formed oxynitrides and the surface roughness increase with the duration of modification, the anticorrosion characteristics of the surfaces of oxynitrided titanium degrade (Fig. 10). Specifically, the corrosion potentials shift in the negative region and the corrosion currents increase by two orders of magnitude (Table 4).

## CONCLUSIONS

In the process of modification of titanium alloys in oxygen-containing atmospheres with degrees of rarefaction not lower than 100 Pa, we observe the formation of a surface oxide film susceptible to cleavage and exfoliation. As the degree of rarefaction increases from 10 to 0.001 Pa, the fraction of oxynitride in the coating increases and the fraction of oxide decreases. The nitrogen content of the ternary compound increases and, hence, the oxygen content decreases. In the oxygen-containing atmospheres rarefied to 0.001–0.1 Pa, the level of surface microhardness increases as compared with the case of nitriding and the rate of its growth becomes higher as the composition of oxynitride approaches the equiatomic composition.

As the temperature of modification decreases from 950 to 650°C, the process of phase formation shifts in the direction of formation of oxynitrides. In this case, the oxygen content of the oxynitride compound becomes lower and its composition approaches the equiatomic composition. The fraction of oxygen in the formed oxyni-

trides and the surface roughness of the coatings increase with the duration of modification. After oxynitriding, the corrosion resistance of the metal in a 3% NaCl solution increases with the nitrogen content of oxynitrides.

The present work was supported by the KICOS of Korea and the Ministry of Education and Science of the Ukraine within the framework of the Joint Ukrainian–Korean Research Program.

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