

EFFECT OF THE RAREFACTION OF AN OXYGEN-CONTAINING MEDIUM ON THE FORMATION OF TITANIUM OXYNITRIDES

I. M. Pohrelyuk, V. M. Fedirko, and O. V. Tkachuk

UDC 669.295:621.795

We study the effect of the rarefaction of an oxygen-containing medium (0.001 to 10 Pa) on the formation of oxynitrides on the surface of VT1-0 titanium and its OT4, PT-7M, VT20, and VT6s alloys in the course of modification of nitrides formed in molecular nitrogen at a temperature of 850°C. The initiation of titanium oxynitrides becomes more intense as the rarefaction increases from 10 to 0.001 Pa. We also show that the surface microhardness increases after oxynitriding as compared with nitriding, and the depth of the hardened layer is determined by isothermal holding in nitrogen.

At present, coatings based on ternary interstitial compounds, in particular, titanium oxynitrides become more and more important. As compared with binary compounds (oxides, nitrides), these coatings possess better operating properties (hardness, wear and corrosion resistance, high-temperature strength, etc.) [1–3]. This can be explained by a nonlinear change in the parameters of the electron structure of oxynitrides and in the type of chemical bond between atoms in the crystal lattice depending on the composition of this compound [4, 5]. For the oxynitriding of titanium alloys by means of modification of the nitride layers with oxygen, the optimal temperature range (750 to 950°C) has been determined earlier, but the optimal degree of rarefaction of the oxygen-containing medium has not been substantiated [6].

In the present work, we study the effect of oxygen partial pressure on the oxynitriding of titanium alloys by means of modification of the nitride layers with oxygen.

Procedure of Investigations

We used specimens made of commercially pure VT1-0 titanium, PT-7M α -alloy, OT4 and VT20 pseudo- α -alloys, and VT6s ($\alpha + \beta$)-alloy, $10 \times 15 \times 1$ mm in size. The specimens were polished ($R_a = 0.4 \mu\text{m}$), washed in alcohol, and dried. Afterwards, they were heated to the nitriding temperature in vacuum 10 mPa and saturated in molecular nitrogen under atmospheric pressure at 850°C. We used commercially pure nitrogen, which was cleaned by passing it through a capsule with silica gel and heated titanium chip so that the oxygen and moisture content should be not more than 0.05%. Then the specimens were subjected to isothermal holding in nitrogen for 5 h and cooled to 500°C in a rarefied oxygen-containing medium (0.001 to 10 Pa), and afterwards the chamber was vacuumized.

We determined the phase composition of the surface layers by X-ray phase analysis on a DRON-3.0 diffractometer in monochromatic $\text{CuK}\alpha$ -radiation with focusing by the Bragg–Brentano scheme. The voltage on the anode of the X-ray tube was 30 kV, and the current through it was 20 mA. For data processing, we used DHN-PDS and CSD program packages.

Karpenko Physicomechanical Institute, Ukrainian Academy of Sciences, Lviv, Ukraine.

Translated from *Fiziko-Khimichna Mekhanika Materialiv*, Vol. 44, No. 1, pp. 56–60, January–February, 2008. Original article submitted December 7, 2007.

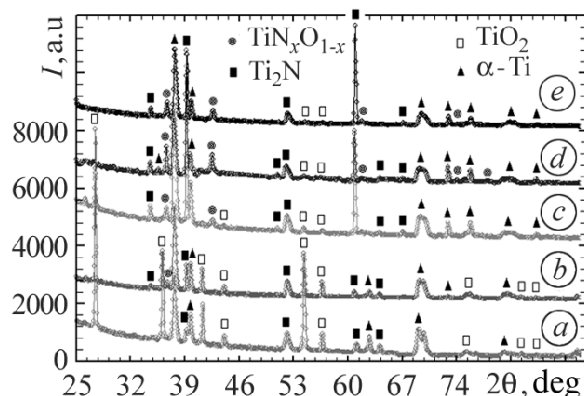


Fig. 1. Diffraction spectra taken from the surface of commercially pure VT1-0 titanium after oxynitriding under different rarefactions of the oxygen-containing medium (p_{O_2} , Pa): (a) 10, (b) 1, (c) 0.1, (d) 0.01, (e) 0.001.

Table 1. Color of the Surface of Titanium Alloys Depending on the Rarefaction of the Oxygen-Containing Medium in the Course of Oxynitriding

Rarefaction, Pa	Alloy				
	VT1-0	PT-7M	OT4	VT20	VT6c
10	Gray-blue	Gray-blue	Gray-blue	Gray-blue	Brown
1	Light gray-blue	Light gray-blue	Light gray-blue	Light gray-blue	Light brown
0.1	Lilac-gray	Bright green	Green-brown	Pale green	Yellow-hot-brown
0.01	Lilac-gray	Lilac with bluish tint	Lilac	Lilac	Lilac
0.001	Aquamarine	Lilac	Pink	Lilac	Aquamarine

The microstructure of the alloys was studied on angle metallographic specimens with the use of an Epiquant microscope, equipped with a camera and a computer adapter for recording images in the digital form. The level of microhardness and its distribution over the cross section of the near-surface layers were evaluated on a PMT-3M instrument under a load on the indenter of 0.981 and 0.49 N, respectively.

Experimental Results and Discussion

After oxynitriding in an oxygen-containing medium rarefied to 10 Pa, a fairly dense oxide gray-blue film is formed on the surface of VT1-0 titanium and its OT4, PT-7M, and VT20 alloys (and a brown film on VT6s alloy) (Table 1). This is indicated by the presence of a significant quantity of intense reflections of TiO_2 titanium dioxide in the rutile modification in the diffractogram taken from the surface of VT1-0 (Fig. 1a). We found also lines of lower Ti_2N nitride against a background of the titanium matrix.

After oxynitriding under a rarefaction of the oxygen-containing medium of 1 Pa, the coloration of the surface of all alloys grows lighter. This fact demonstrates a change in the rate of oxidation of the surface and is corroborated by the data of X-ray phase analysis (a decrease in the intensity of oxide reflections). We recorded also a weak reflection of the reference line (111) of titanium oxynitride (Fig. 1b).

Here, the oxide coating exfoliates slightly on VT1-0 and OT4 alloy, more strongly on PT-7M and VT20, and practically completely on the specimens made of VT6s alloy. Obviously, this is caused by the incoherence of the structures of titanium oxide and nitride on the surface and by the difference in their physical properties, in particular, in the coefficients of thermal expansion [7], which induces significant residual stresses in the surface layers. As a result, the surface oxide film cracks and exfoliates.

If the rarefaction of the oxygen-containing medium is 0.1 Pa, the rate of oxide formation on the surface of titanium continues to recede: we observe a decrease not only in the intensity of the peaks of titanium dioxide in the diffractograms but in their quantity as well (Fig. 1c). At the same time, the surface of VT1-0 becomes lilac-gray, that of PT-7M, VT20, and OT4 alloys is bright green, pale green, and green-brown, respectively, and the surface of VT6s turns yellow-hot-brown. A violet (lilac) tint can be seen on the specimens of all alloys. Exactly such a tint accompanied the formation of the oxynitride phases in the course of high-temperature oxidation of compact nonporous specimens made of titanium nitride [8]. The results of X-ray phase analysis, in particular, an increase in the quantity and intensity of reflections of the oxynitride phase, confirm the more intense formation of titanium oxynitrides.

Under a rarefaction of the oxygen-containing medium of 0.01 Pa, on the surface of VT1-0 specimens, there arise titanium oxynitrides of lilac-gray color, which passes into yellow-hot at the edges. On the specimens of VT6s, VT20, and OT4 alloys, there are also oxynitrides of lilac color, and, on PT-7M, lilac with bluish tint (Table 1). As the rarefaction reaches 0.001 Pa, the oxynitride phase of pink and yellow-hot coloration is formed on OT4 alloy. The surface of VT20 alloy becomes lilac with violet setting, and that of VT1-0 aquamarine with variability colors. The layers of aquamarine, yellow-hot, and pink (along the edges) phases of titanium oxynitride are observed on VT6s alloy.

The colors of specimen surface and X-ray phase analysis show that, with increase in the rarefaction from 0.01 to 0.001 Pa, the formation of titanium oxynitrides predominates over oxide formation. This is indicated by an increase in the intensity of reflections of the oxynitride phase and a decrease in the quantity and intensity of reflections of the oxide phase in the diffractograms (Fig. 1d and e).

In general, as follows from the data of X-ray phase analysis, the relative content of the TiO_2 phase decreases from 50.03 to 3.26% as the rarefaction of the oxygen-containing medium changes from 10 to 0.001 Pa. Under a pressure of 0.001–0.01 Pa, the oxide phase is represented only by weak reflections (211) and (220). Thus, with increase in the rarefaction to 0.01–0.001 Pa, the formation of titanium oxynitrides predominates over the formation of the corresponding oxides.

As is well known [4, 5, 8], a change in the nitrogen (oxygen) content in the oxynitride phase changes the parameter a of the face-centered cubic lattice of oxynitride (Fig. 2). As the rarefaction of the oxygen-containing medium increases from 1 to 0.001 Pa, the lattice parameter of formed titanium oxynitride grows (Table 2). Hence, with increase in the rarefaction (within the limits mentioned above), the content of oxygen component in the ternary compound decreases, and the composition of oxynitrides is close to $\text{TiN}_{0.36-0.46}\text{O}_{0.64-0.54}$.

One can trace (Fig. 3) the growth of the surface microhardness of specimens with increase in the rarefaction of the oxygen-containing medium, when phase formation on the surface of titanium alloys is shifted to the side of oxynitride formation. For all alloys under study, the greatest surface microhardness corresponds to rarefactions of 0.01–0.001 Pa. In addition, these values for VT1-0, OT4, and VT6s alloys are higher (1.2–1.4, 1.3–1.5, and 1.2 times, respectively) than the hardness of specimens after nitriding in nitrogen under atmospheric pressure with similar temperature-time parameters. For PT-7M and VT20 alloys, the range of higher, as compared with nitriding, values of the surface hardness is wider. The hardness of these alloys after oxynitriding is 1.8–1.9 and 2.0–2.1 times, respectively, higher than after nitriding. As follows from the dependence of oxy-

nitride hardness on its composition [5, 8], the surface microhardness of titanium alloys after oxynitriding under a rarefaction of 0.01–0.001 Pa is determined by the composition of surface oxynitride or, if the rarefaction is 0.1 to 10 Pa, by the surface oxide film.

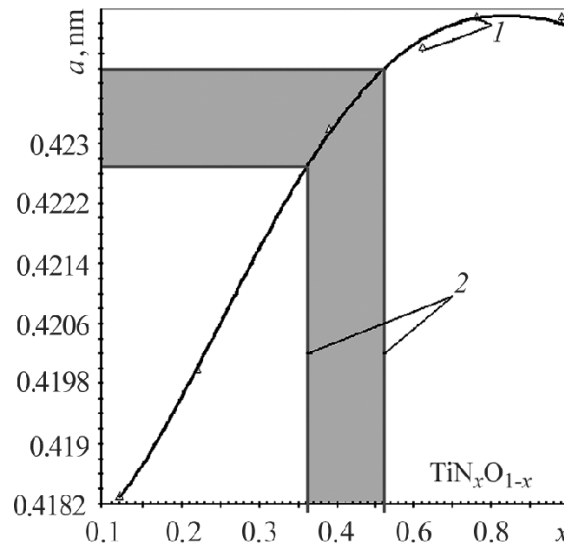


Fig. 2. Dependence of the lattice parameter a on the nitrogen content in $\text{TiN}_x\text{O}_{1-x}$ compound: (1) at 850°C, (2) according to [4].

Table 2. Lattice Parameter of the Oxynitride Phase (a , nm) Formed on VT1-0 after Oxynitriding at 850°C for Different Rarefactions of the Oxygen-Containing Medium

T , °C	P_{O_2} , Pa				
	10	1	0.1	0.01	0.001
850	—	0.4227	0.4239	0.4240	0.4240

The hardened surface layer, which is evaluated by the microhardness distribution over the cross section of specimens, includes a surface film and a diffusion sublayer, i.e., the solid solution of interstitial elements (nitrogen and oxygen, which are present in the reaction volume) in α -titanium, which is a consequence of mass transfer of components of the medium into the titanium matrix. The diffusion sublayer, in turn, consists of two parts. The first represents grains with a high microhardness due to their strengthening by nitrogen, and the second practically does not differ from the alloy matrix and is characterized by an insignificant microhardness gradient over its cross section (the level of saturation with nitrogen is substantially lower).

Depending on the rarefaction of the oxygen-containing medium, the depth of the hardened layer of titanium alloys does not change, which is connected with the conditions of oxynitriding and is determined only by isothermal holding in nitrogen at 850°C, as a result of which a layer of the solid solution of nitrogen in α -titanium of the corresponding thickness is formed.

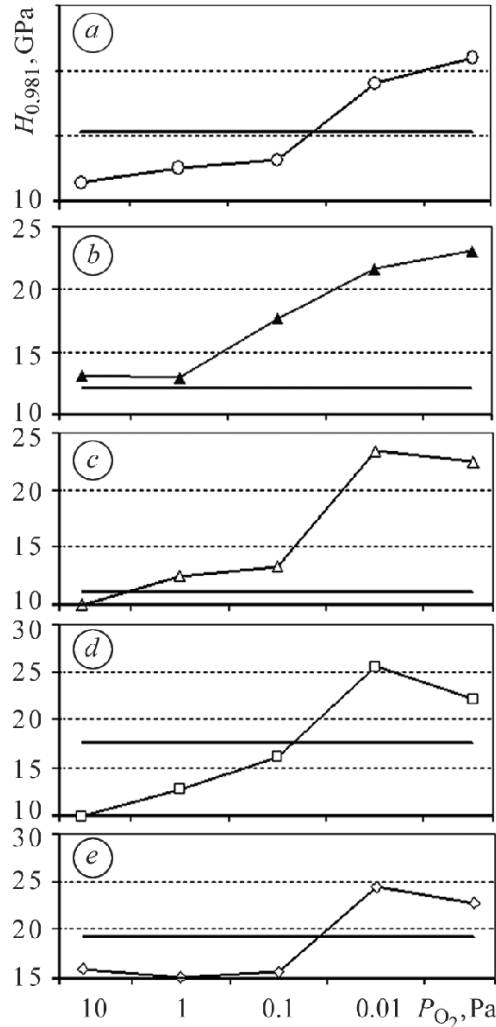


Fig. 3. Dependence of the surface microhardness H_{μ}^s of titanium alloys on the rarefaction of the oxygen-containing medium in oxynitriding: (a) VT1-0, (b) PT-7M, (c) VT20, (d) OT4, (e) VT6s. The solid line shows the surface microhardness after nitriding.

After nitriding of OT4 alloy, the depth of the hardened layer is about 62–64 μm , and, after modification of the nitrided layers with oxygen, it is equal to 53–55 μm . This difference can be explained by the fact that, in the course of nitriding, cooling from 850°C occurred in a nitrogen-containing medium, unlike oxynitriding, which favored further nitrogen diffusion and increased the thickness of the diffusion layer.

The depth of the hardened layer of PT-7M and VT6s alloys after oxynitriding is 50 to 55 μm . For commercially pure VT1-0 titanium, it grows to 65 μm and, for VT20 alloy, is maximum and constitutes about 75 μm .

CONCLUSIONS

With increase in the rarefaction of the oxygen-containing medium from 10 to 0.001 Pa, the formation of oxynitrides predominates on the surface of titanium alloys.

As compared with nitriding, oxynitrides formed under a rarefaction of the oxygen-containing medium of 0.01–0.001 Pa increase the surface microhardness of titanium alloys by a factor of 1.2–2.1.

A change in the rarefaction of the oxygen-containing medium in the course of oxynitriding does not affect the depth of the hardened layer of titanium alloys.

REFERENCES

1. N. Martin, O. Banakh, A. M. E. Santo, et al., “Correlation between processing and properties of TiO_xN_y thin films sputterdeposited by the reactive gas pulsing technique,” *Appl. Surf. Sci.*, **185**, 123–133 (2001).
2. J. Probst, U. Gbureck, and R. Thull, “Binary nitride and oxynitride PVD coatings on titanium for biomedical applications,” *Surf. Coatings Technol.*, **148**, 226–233 (2001).
3. N. Martin, R. Sanjines, J. Takadom, and F. Levy, “Enhanced sputtering of titanium oxide, nitride and oxynitride thin films by the reactive gas pulsing technique,” *Surf. Coatings Technol.*, **142–144**, 615–620 (2001).
4. S. I. Alyamovskii, Yu. G. Zainulin, and G. P. Shveikin, *Oxycarbides and Oxynitrides of Metals of the IVA and VA Subgroups* [in Russian], Nauka, Moscow (1981).
5. G. P. Shveikin, S. I. Alyamovskii, Yu. G. Zainulin, et al., *Compounds of Variable Composition and Their Solid Solutions* [in Russian], Ural Sci. Center, USSR Acad. Sci., Sverdlovsk (1984).
6. O. I. Yas’kiv and I. M. Pohrelyuk, “Formation of oxynitride layers on the surface of titanium,” in: *Proc. Conf. “Tooling-2000”* [in Ukrainian], Lviv (2000), pp. 94–99.
7. H. J. Goldschmidt, *Interstitial Alloys*, Butterworths, London (1967).
8. R. F. Voitovich, *Oxidation of Carbides and Nitrides* [in Russian], Naukova Dumka, Kiev (1981).