



Formation of oxynitrides on titanium alloys by gas diffusion treatment

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ABSTRACT

The regularities formation of oxynitride layers on titanium with diffusion treatment has been investigated. Commercially pure titanium, α -, pseudo- α -(Ti–Al–V–Mo–Zr) and $(\alpha + \beta)$ -(Ti–Al–V) alloys were used. Oxynitrides were formed by the modifying of titanium nitride with oxygen according to the following scheme: $TiN_x + O_2 \rightarrow TiN_xO_{1-x}$. The oxynitriding process was carried out by introducing the controlled oxygen-containing medium into the system at finish stage of nitriding (during cooling). The influence of nitriding parameters (temperature, nitriding time, nitrogen partial pressure) and oxynitriding parameters (temperature, oxynitriding time, oxygen partial pressure) on phase composition as well as mechanical and corrosion properties of the oxynitride coatings were studied. It was determined that the intensity of oxynitriding is more efficient when TiN_x is near its lower limit of homogeneity and increases with lowering of oxygen partial pressure in range 0.0001...0.01 Pa and temperature of oxynitriding in range 1223...923 K. The corrosion properties of oxynitride coatings were improved at higher nitrogen contents in the oxynitride compounds.

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1. Introduction

Titanium alloys have a wide range of applications including machinery, aircraft components, the chemical industry and biomedicine because of their high strength-to-weight ratio, elasticity, corrosion resistance and biocompatibility [1,2]. The leading role of titanium in many sectors of industries is also conditioned by the number of possibilities for surface engineering. One promising way of surface engineering titanium alloys is through the formation of coatings based on oxynitrides TiN_xO_{1-x} . These materials are isomorphic to the well studied binary compounds (TiN and TiO) [3]. However, oxynitrides have achieved a great importance because of their high microhardness, wear and corrosion resistance, which exceed the properties of both nitrides and oxides [4–6]. In particular, titanium oxynitrides are widely used in medicine and chemical industries because of excellent combination of chemical and mechanical properties [7,8].

Many techniques, including diffusion, plasma-based, ion-plasma, detonation, laser and high-energy methods, are currently available in order to improve the hardness, corrosion and wear resistance of

titanium alloys [9–13]. Thermodiffusion treatment is well studied and, therefore, remains a promising technique for surface engineering titanium alloys. This technique can be used to regulate the structural and phase states of the near-surface layers, treat the workpieces of the arbitrary configuration (including poles) and precisely control the process. While titanium has a strong affinity for oxygen and nitrogen, oxynitriding with the thermodiffusion treatment offers a flexible approach for controlling the composition, the structure and the dimensions of the processed zone.

The most optimal way to form the oxynitride is to modify titanium nitride with oxygen according to the following process: $TiN_x + O_2 \rightarrow TiN_xO_{1-x}$ [4,14]. However, filling oxygen atoms into the vacancies in a non-metal nitride sublattice, having significant stoichiometric deviations, is a more energy efficient process than the modification of stoichiometric nitride [15]. Therefore, the oxygen-reducing reactions on the surface of nonstoichiometrical nitride are more active and determine the phase-structural state of the near-surface layers, as well as the composition of oxynitride.

This technological process for the oxynitriding process consists of two stages in a single technological mode. These stages are the thermodiffusion saturation of titanium with nitrogen (nitriding) and the modification of the nitride surface with oxygen (oxynitriding). The effects of this treatment depend on both the nitriding parameters and the parameters of oxygen-containing medium. The purpose of this work was to investigate the influence of the nitriding and oxynitriding parameters on the formation of oxynitride layers on titanium alloys.

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2. Experimental details

2.1. Sample preparation

Commercially pure (c.p.) titanium and α -, pseudo- α -(Ti-(5.5–7.0)Al-(0.8–2.5)V-(0.5–2.0)Mo-(1.5–2.5)Zr) and $(\alpha + \beta)$ -(Ti-(5.3–6.5)Al-(3.5–4.5)V) alloys were used in this study. The titanium sheets were received with a defective surface layer as a result of rolling and etching. Therefore, this layer was removed through polishing with a 0.1 μm grade diamond paste in order to reduce the roughness, R_a , to at least 0.4 μm . Then the samples were degreased in benzene and washed with deionized water prior to the treatment.

2.2. Thermodiffusion treatment

For the nitriding process, the samples were heated at 1123 K and 1223 K in the reaction chamber with a controlled gas media. The gas environment was controlled with the assigned gas-dynamic parameters. The oxygen and moisture in the nitrogen atmosphere were removed by filtering the gas through a silica gel filter and heating the titanium chips at 50 K above the saturation process temperature. The oxygen content in the nitrogen was ≤ 0.0005 –0.01%, whereas the content in unpurified nitrogen was about 0.5%.

Prior to nitriding the samples were heated in a vacuum of 10^{-3} Pa in order to remove the natural oxide films and to avoid the formation of new ones during heating to the process temperature. The heating rate was 0.04 K/s. The processing time ranged from 1 to 15 h. After isothermal exposure, the samples were cooled at an average cooling rate of 100 K/h. The nitrogen partial pressures were 10^5 and 10 Pa.

The oxynitriding process was carried out by the puffing of controlled oxygen-containing medium into the system at the final stage of the nitriding (during cooling) (Fig. 1). Consequently, the controlled oxidation of the pre-formed nitride occurred between the nitriding temperature and the temperature limited by the active interaction between titanium and oxygen (773 K). The oxygen partial pressure was within 10^{-4} – 10^1 Pa.

2.3. Characterization methods

The X-ray analysis was carried out using a diffractometer with $\text{CuK}\alpha$ -radiation at a voltage of 35 kV and a current of 20 mA. The tube focusing system was made using Bregg–Brettano method. The scan step was 0.05° . The step counting time was 5 s. The diffraction pattern profiles were refined by the Rietveld method with two different pseudo-Voigt function using Powder Cell 2.4 program [16]. R_p (R-pattern) and R_{wp} (R-weighted pattern) were used as numerical criteria of fit. Titanium oxynitride was identified using the standard diffraction pattern obtained in accordance with the model by Levi et al. [17]. This model assumed that the non-metal sublattice was disordered (the N and O atoms randomly occupied the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$

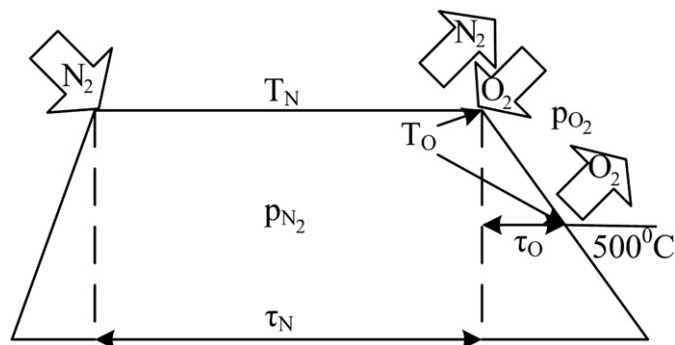


Fig. 1. Scheme of oxynitriding of titanium alloys.

positions, whereas the Ti atoms occupied the (0 0 0) positions). The accuracy of lattice parameter measurement was $\pm 0.0002 \text{ \AA}$. No preferred orientations were observed on the non-treated titanium specimens. Therefore, the texture effect was not considered in present study.

The surface microhardness (H , GPa) was characterized at loadings of 0.49 and 0.98 N. Microhardness measurement was used to estimate the integral hardness of surface layer after treatment.

3. Results and discussion

The formation of oxynitrides is conditioned by the thermodynamic probability of reaction between titanium nitride and oxygen. Titanium oxynitride $\text{TiN}_x\text{O}_{1-x}$ is formed as result of modification of nonstoichiometrical nitride with oxygen. In this case nitrogen atoms are replaced with oxygen atoms. In the course of time the certain level of nitride oxidation is reached. It is accompanied by the decreasing of nitrogen content in oxynitride. Oxynitride of extremal composition is transformed to titanium dioxide TiO_{2-x} (Fig. 2).

The oxynitriding process depends on both the nitriding parameters (e.g. nitriding temperature T_N , nitriding duration τ_N , nitrogen partial pressure P_N) and oxynitriding parameters (T_O , τ_O , and P_{O_2}). Since the nitriding parameters determine the stoichiometry of titanium nitride [18], the influence of the nitriding parameters T_N , τ_N , and P_N on the composition and the properties of the oxynitride coatings were investigated.

3.1. Influence of the nitriding parameters on the phase composition and properties of the oxynitride coatings

3.1.1. Influence of the nitriding temperature T_N

The mononitride coating, with a nearly stoichiometric composition of $\text{TiN}_{0.98}$ with a lattice parameter of 0.42401 nm, was formed by nitriding of c.p. titanium at 1223 K for 5 h in nitrogen at atmospheric pressure ($P_N = 10^5$ Pa). The lattice parameter reduced to 0.4239 nm when the temperature was lowered to 1123 K, corresponding to a composition of $\text{TiN}_{0.88}$. The color of the nitride surface was yellow at 1123 K and golden at 1223 K.

The surface color changed after the oxynitriding process. At 1123 K, the color was uneven and consisted of tints ranging from orange to blue depending on the type of alloy. The lilac or lilac-gray tints on the surface of all samples confirmed the presence of the oxynitride phase [19]. At 1223 K, the color of the oxynitrided surface became more homogeneous and was either lilac-gray or dark golden (for the α - and pseudo- α -alloys, respectively). The color difference for alloys can be explained by the formation of the oxynitrides with different compositions.

The lattice parameters of the oxynitrides were 0.42464 nm and 0.42544 nm at $T_N = 1123$ K (c.p.Ti) and $T_N = 1223$ K, respectively. It indicated that the oxynitride lattice parameter depends on the oxygen

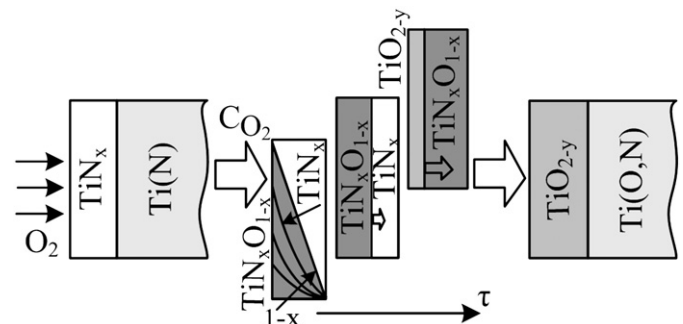


Fig. 2. An evolution of phase composition of surface layers of Ti alloys at oxynitriding.

(or nitrogen) content [20], and the amount of oxygen in $\text{TiN}_x\text{O}_{1-x}$ decreased with increasing of the nitriding temperature.

3.1.2. Influence of the nitriding time t_N

The composition of TiN_x increases not only with increasing of the temperature, but also with increasing of the process time t_N . In particular, the lattice parameter shifted from 0.42302 to 0.4236 nm for the pseudo- α -alloy when t_N was increased from 5 to 10 h (at $T_N = 1223$ K). The lattice parameter shifted from 0.42337 \rightarrow 0.42401 \rightarrow 0.42436 nm for the c.p. Ti with increasing t_N from 1 to 5 to 10 h ($T_N = 1223$ K). It indicated that the composition of TiN_x becomes more stoichiometric with increasing of the nitriding time.

The lattice parameter of the oxynitride $\text{TiN}_x\text{O}_{1-x}$, formed after oxynitriding at $T_N = 1223$ K increased with respect to the process time (Fig. 3). For the pseudo- α -alloy, the lattice parameter increased from 0.4242 to 0.4249 nm with increasing t_N from 1 to 5 h. For the ($\alpha + \beta$)-alloy, the lattice parameter increased from 0.42340 to 0.42382 nm for 5 and 10 h, and for the c.p. Ti, the lattice parameter increased from 0.42398 to 0.42544 to 0.4261 nm with increasing t_N from 1 to 5 to 10 h. In Fig. 3, the oxygen amount in the oxynitride compound decreased with increasing t_N .

The X-ray analysis confirmed that the oxynitrided layer consisted of oxynitride ($\text{TiN}_x\text{O}_{1-x}$), nitride (Ti_2N) and rutile dioxide (TiO_2). The formation of the oxide was caused by the nitride oxidation after the maximum composition of oxynitrides was formed [19]. The temperature-time parameters influenced the correlation between the above phases. For example, the amount of oxide decreased with increasing nitriding time, regardless of the temperature (Fig. 4).

3.1.3. Influence of the nitrogen partial pressure P_N

After nitriding the coating consists of external TiN_x and internal Ti_2N nitrides. Changes in the nitrogen partial pressure P_N influenced the composition of TiN_x . In particular, when reducing the P_N from atmospheric pressure to 10 Pa, the lattice parameter of TiN_x decreased from 0.42442 to 0.42354 nm (for pseudo- α alloy, at $T_N = 1123$ K and $t_N = 5$ h). It indicates that the nitride deviated from the stoichiometric values with decreasing of the nitrogen partial pressure.

After oxynitriding at $P_N = 10$ Pa, the X-ray analysis revealed that rutile TiO_2 (up to 1.14 vol.%) appeared in surface layer. On the other hand, after oxynitriding at $P_N = 10^5$ Pa, the oxide did not form, and the oxynitride consisted of more nitrogen (the lattice parameter was 0.42475 versus 0.42423 nm).

3.1.4. Influence of the nitriding parameters on the microhardness of the oxynitride coatings

Table 1 shows the surface microhardness of the Ti-alloys after nitriding and oxynitriding at various conditions. These results indicate that, regardless of the nitriding temperature T_N and the process time

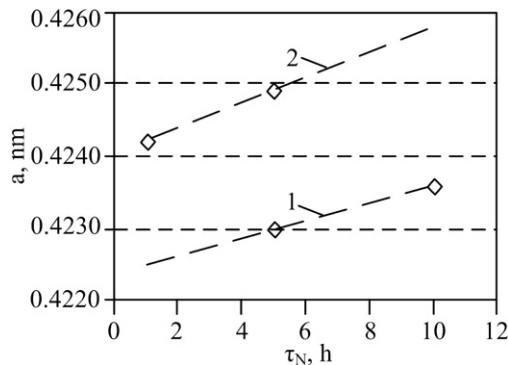


Fig. 3. Dependence of lattice parameter (a , nm) of TiN_x (curve 1) and $\text{TiN}_x\text{O}_{1-x}$ (curve 2), formed on pseudo- α alloy at nitriding and oxynitriding on process time (τ_N , h) ($T_N = 1223$ K).

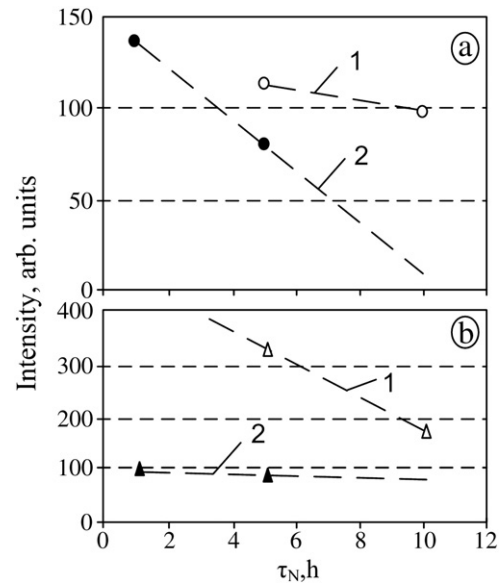


Fig. 4. Dependence of relative intensity of titanium dioxide reflex (111) on the diffraction patterns of c.p. titanium (a) and pseudo- α alloy (b) after oxynitriding at $T_N = 1123$ K (1) and 1223 K (2) with nitriding time (τ_N , h).

τ_N , oxynitriding considerably strengthened the surface compared to nitriding. The strengthening effect of oxynitriding ΔH is the increase in the surface microhardness after oxynitriding compared to nitriding ($\Delta H = H^s_O - H^s_N$; where H^s_O is surface microhardness after oxynitriding and H^s_N is surface microhardness after nitriding). ΔH was larger at higher T_N and longer τ_N (Fig. 5) because the temperature and process time determined the phase composition of the coating and the chemical composition of the nitride TiN_x . During the oxynitriding process, the nitrogen content in the oxynitride was larger and the strengthening effect ΔH was higher when the stoichiometry of TiN_x did not deviate as much.

For the Ti-alloys, the maximum strengthening effect was observed for the c.p. titanium (Fig. 5). The difference between the other alloys was not significant. The ΔH decreased with the transition from α - to ($\alpha + \beta$)-alloys.

To confirm the effects of the TiN_x composition on the surface strengthening, the c.p. titanium underwent nitriding under different conditions using the process modes in Fig. 1 (Mode 1: $T_{N1} = 1123$ K, $\tau_{N1} = 3$ h, $P_{N1} = 10^5$ Pa; Mode 2: $T_{N2} = 1223$ K, $\tau_{N2} = 1$ h; $P_{N2} = 10^5$ Pa). The nitride coatings were of similar thicknesses (about 1–3 μm) but different compositions (lattice parameters of 0.4215 and

Table 1
Surface microhardness $H_{0.98}$, GPa of titanium alloys after oxynitriding.

Alloy	Nitriding time τ_N , h		
	1	5	10
$T_N = 1123$ K			
c.p. titanium	10.70/12.70	11.80/14.30	13.30/16.50
α -titanium	8.00/8.50	10.80/12.80	11.70/14.10
pseudo- α (Ti–Al–V–Mo–Zr)	6.40/7.10	10.60/12.20	11.00/12.90
($\alpha + \beta$) (Ti–Al–V)	9.10/9.60	10.90/12.00	11.60/13.40
$T_N = 1223$ K			
c.p. titanium	14.30/17.90	15.90/20.00	15.40/19.80
α -titanium	10.60/11.10	12.00/14.40	13.00/15.70
pseudo- α (Ti–Al–V–Mo–Zr)	9.60/10.30	11.60/13.40	12.50/14.60
($\alpha + \beta$) (Ti–Al–V)	10.80/11.40	11.70/13.00	12.70/14.30

Note: numerator – after nitriding, denominator – after oxynitriding at identical time and temperature parameters.

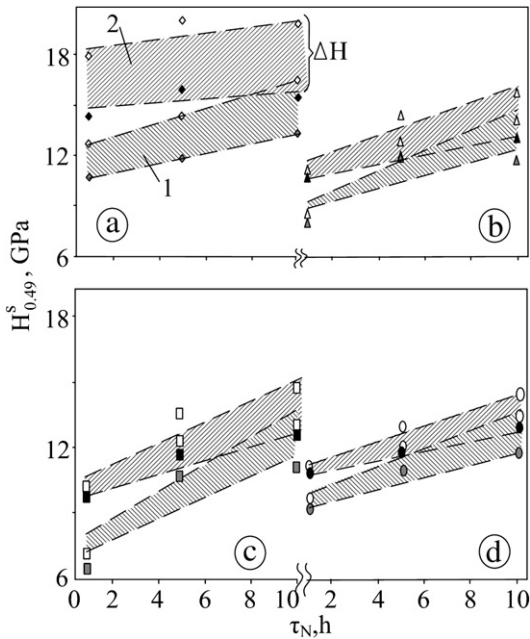


Fig. 5. Dependence of surface microhardness of c.p. titanium (a), α -titanium (b), pseudo- α -alloy (Ti-Al-V-Mo-Zr) (c) and $(\alpha + \beta)$ -alloy (Ti-Al-V) (d) on time and temperature parameters of nitriding (dots with dark background) and oxynitriding (dots with light background) (1–1123 K, 2–1223 K).

0.4225 nm, respectively). The strengthening effect of oxynitriding was lower for the less stoichiometric nitride (2.0 GPa versus 2.6 GPa) whereas these coatings were oxynitrided at identical conditions ($P_{O_2} = 0.001$ Pa, $T_O = 1123$ K, $\tau_O = \tau_{cooling}$, from T_O to 773 K).

The strengthening effect of the oxynitriding process was influenced by changes in the nitrogen partial pressure. For instance, at $P_N = 10$ Pa, the microhardness was 0.2 GPa, whereas at $P_N = 10^5$ Pa the microhardness was 1.7 GPa (Fig. 6).

It could be summarized that the intensity of oxynitriding is more efficient when the nonstoichiometric nitride TiN_x is near its lower limit of homogeneity (Fig. 7). At the same time, the strengthening effect of oxynitriding is larger when the composition of nitride is close to the upper limit of homogeneity.

3.2. Influence of the oxynitriding parameters on the phase composition and properties of the oxynitride coatings

For these investigations, the nitriding process was performed at $T_N = 1223$ K, $\tau_N = 1$ and 5 h, and $P_N = 10^5$ Pa.

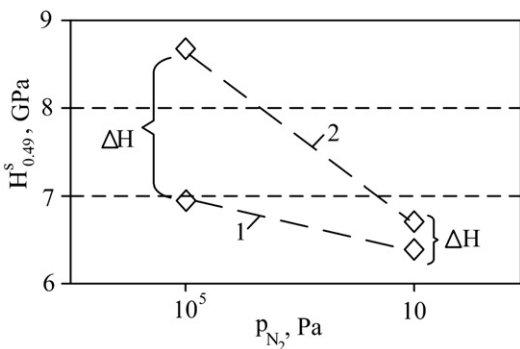


Fig. 6. Dependence of surface microhardness of pseudo- α -alloy (Ti-Al-V-Mo-Zr) on nitrogen partial pressure P_N after nitriding (1) and oxynitriding (2).

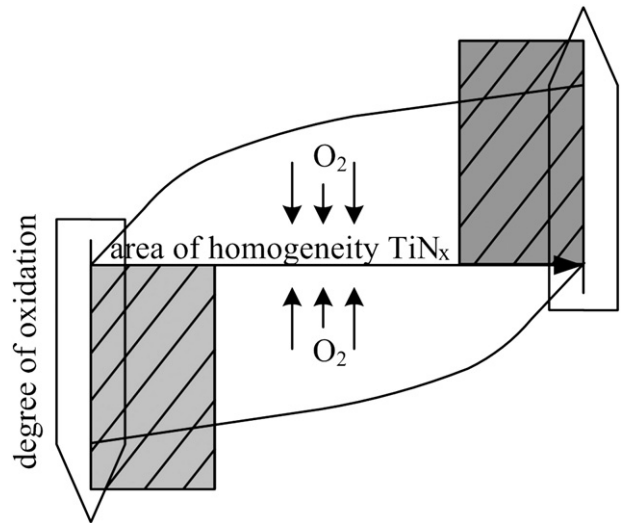


Fig. 7. Influence of nitride stoichiometry on degree of its modification by oxygen.

3.2.1. Influence the oxygen partial pressure P_O (0.0001–10 Pa) on the phase composition

A mat-lime colored oxide film formed on the surface after the oxynitriding at an oxygen partial pressure of 10 Pa. This film easily cracked and split off because of: 1) the incoherence of the oxide and nitride structures formed on the surface; 2) the difference between the thermal expansion coefficients [21]; and 3) the critical thickness of the oxide film, which caused considerable residual stresses in the surface layers. It can be concluded that the using of a medium with an oxygen partial pressure more 10 Pa is unacceptable for oxynitriding the Ti-alloys.

A gray-blue colored rutile TiO_2 film was observed after the oxynitriding at an oxygen partial pressure of 1 Pa. Oxynitride and nitride Ti_2N peaks with low relative intensities were observed in the diffraction spectrum (Fig. 8a).

Oxynitride started to form when the oxygen partial pressure was reduced to 0.1–0.01 Pa. The intensity of the TiO_2 peaks decreased, whereas the intensity of the TiN_xO_{1-x} peaks increased (Fig. 8b and c).

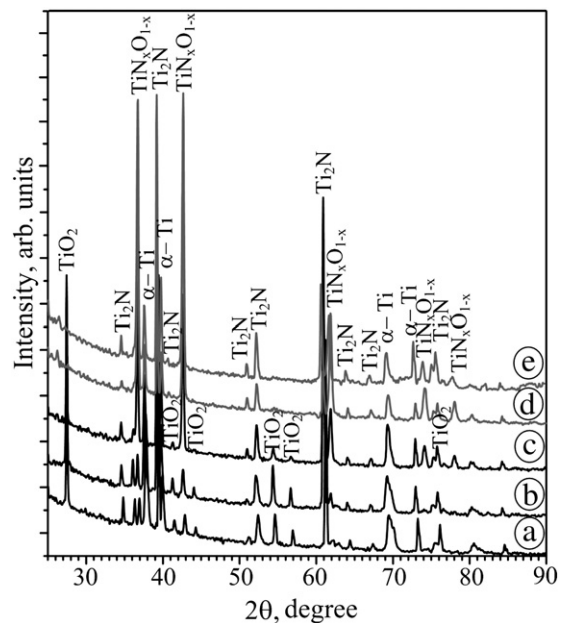


Fig. 8. Diffraction patterns of c.p. titanium after oxynitriding in dependence on oxygen partial pressure (P_O), Pa: a– 1; b– 0.1; c– 0.01; d– 0.001, e– 0.0001.

The surface color was homogeneous lilac gray or dark gold (for the α -alloy and the pseudo- α -alloy respectively). It corresponded to the presence of the oxynitride phase.

When the oxygen partial pressure was reduced to 0.001–0.0001 Pa, the oxide peaks were absent, whereas the oxynitride peaks were observed (Fig. 8d and e). It indicates that the oxynitride formation prevailed over the oxide formation under these conditions (Fig. 9). The lilac rose surface color also proved that the oxynitride formation dominates [19].

The lattice parameter of the oxynitrides increased with decreasing of the oxygen partial pressure from 1 to 0.0001 Pa (Fig. 10). It testifies that the amount of nitrogen in the oxynitride increased and the amount of oxygen decreased accordingly. Taking into consideration the dependence of the lattice parameter of the oxynitrides on the oxygen (nitrogen) content [4] the composition of the oxynitrides formed on the c.p. Ti was nearly equi-atomic ($\text{TiN}_{0.44-0.48}\text{O}_{0.56-0.52}$).

3.2.2. Influence of the oxygen partial pressure P_O (0.0001–10 Pa) on the surface microhardness

The microhardness measurements for the titanium alloys revealed that the maximum strengthening effect ΔH was observed after oxynitriding process at $P_O = 0.0001-0.001$ Pa, when the oxynitride formation prevailed over the oxide formation (Fig. 10).

For $P_O = 0.01-1$ Pa, the strengthening effect of the oxynitriding process was substantially lower (Fig. 11), indicating that the oxynitrides transformed into oxides (Fig. 9). The surface microhardness depended on the qualitative and quantitative characteristics of the oxide film, which substantially contributed to the integral value of the surface microhardness.

The surface strengthening of the oxynitrided pseudo- α -alloy was the most effective as compared to other alloys.

3.2.3. Influence of the oxynitriding temperature T_O on the phase composition

The T_O was changed in the range from 923 K to 1223 K at 100 K intervals and the oxygen partial pressure was $P_O = 0.001$ Pa.

X-ray analysis indicates that after oxynitriding at $T_O = 923, 1023$ and 1123 K the oxide peaks were not observed, whereas at $T_O = 1223$ K a low intensity peak of TiO_2 (rutile) with indexes (110) appeared (Fig. 12). The phase transformation clearly shifted in the direction of the oxide formation with increasing of oxynitriding temperature.

The surface coloring and micro X-ray spectrometry analysis confirm this observation. The color of the titanium alloys changed from mainly violet to gold with decreasing T_O and decreasing of oxygen concentration C in the coating (Fig. 13). At $T_O = 1223$ K

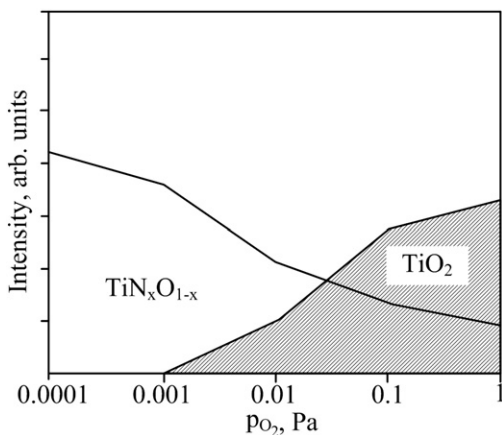


Fig. 9. Relative intensity of diffraction reflexes (110) of TiO_2 and (111) of $\text{TiN}_x\text{O}_{1-x}$ from c.p. titanium oxynitrided at 1223 K in dependence on oxygen partial pressure.

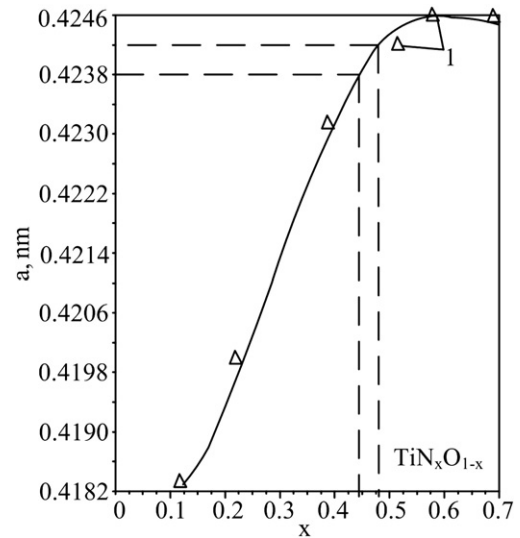


Fig. 10. Dependence of the lattice parameter on content of nitrogen in $\text{TiN}_x\text{O}_{1-x}$ (1 – according to [4]).

nitrogen was not observed and the oxygen concentration corresponded to titanium dioxide.

3.2.4. Influence of the oxynitriding temperature T_O on the surface microhardness

The surface microhardness after oxynitriding at $T_O = 1223$ K ranged from 10 to 13 GPa depending on the alloy. The proportion of oxynitride and nitride as well as the oxide film contributed to this

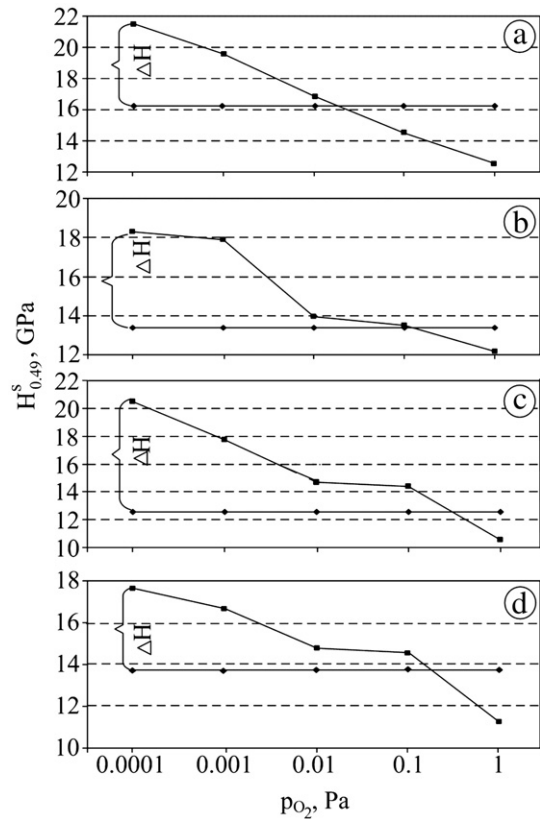


Fig. 11. Dependence of surface microhardness of titanium alloys on oxygen partial pressure at oxynitriding : a– c.p. titanium; b– α -alloy; c– pseudo- α -alloy (Ti–Al–V–Mo–Zr); d– $(\alpha + \beta)$ -alloy (Ti–Al–V) (horizontal line – surface microhardness after nitriding).

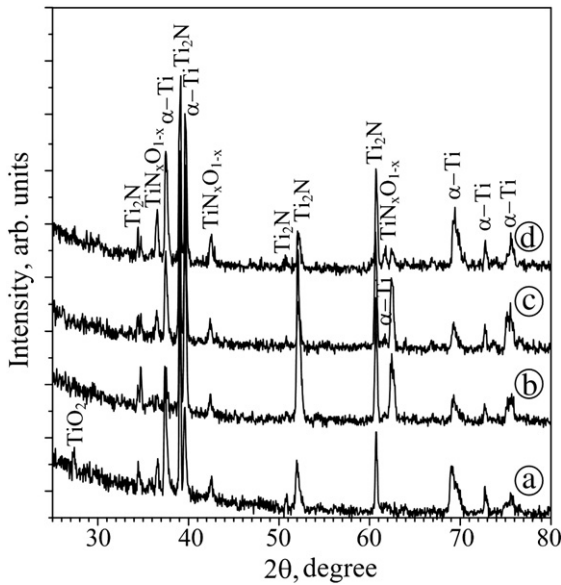


Fig. 12. Diffraction patterns from oxynitrided c.p. titanium in dependence on oxynitriding temperature (T_O): a– 1223; b– 1123; c– 1023; d– 923 K.

value. The surface microhardness increased with decreasing of T_O (Table 2) because of the extreme dependence of the microhardness of TiN_xO_{1-x} on the oxygen (nitrogen) content [19]. The microhardness was maximized for nearly equi-atomic compositions. The oxygen content in the TiN_xO_{1-x} decreased with decreasing T_O and the composition shifted towards the equi-atomic value.

3.2.5. Influence of the oxynitriding time τ_O on the surface microhardness

The dependence of the oxynitriding strengthening effect on the oxynitriding time τ_O was investigated. During these experiments, the process time was changed from 0 to 1.5 h and oxynitriding temperature was $T_O = 1223$ K.

From the X-ray analysis, the oxynitriding time did not influence on the phase-structural state of the surface layers. Low intensity of TiN_xO_{1-x} and nitride (Ti_2N) peaks and high intensity of α -titanium peaks with shifted positions were observed. The “sandwich” layer consisted of oxynitride, nitride and α -solid solution of nitrogen and oxygen in the titanium. The redistribution of the maximums of the oxynitride peaks confirmed the increase in the completeness of the oxynitride with increasing τ_O (replacement of N by O in the non-metal sublattice).

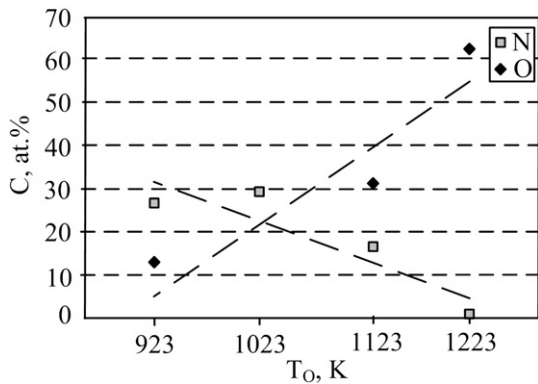


Fig. 13. Oxygen and nitrogen concentrations on the surface of oxynitrided c.p. titanium in dependence on oxynitriding temperature T_O (according to data of micro X-ray spectrum analysis).

Table 2 Surface microhardness $H_{0.98}$, GPa of titanium alloys after oxynitriding depending on oxynitriding temperature.

Alloy	Temperature of oxynitriding T_O , K			
	1223	1123	1023	923
c.p. titanium	13.09	11.80	12.72	14.17
α -titanium	11.51	13.47	13.36	15.07
pseudo- α (Ti–Al–V–Mo–Zr)	10.05	–	11.09	13.68
($\alpha + \beta$) (Ti–Al–V)	11.02	–	11.48	12.53

Both the surface microhardness and the surface roughness increased with increasing τ_O (Table 3). It can be explained by the structural changes in the surface layers of the oxynitrided titanium.

3.3. Electrochemical tests of the oxynitride coatings

The electrochemical analysis of the oxynitrided specimens of c.p. titanium was conducted in a 3% NaCl solution.

The anodic branch of the polarization curve of the surface oxynitrided at temperature $T_O = 1223$ K is characterized by the prolonged passive range (from 0.0 to 2.0 V) (Fig. 14a). However, the corrosion parameters (corrosion potential E_{cor} and current density i_{cor}) were worse as compared to the coatings after oxynitriding at lower T_O (Table 4). The anodic curves of these coatings exhibited an active–passive character. The passive current densities of the coatings formed at $T_O = 1123$ K were in 3–5 folds lower than the coatings formed at $T_O = 1223$ K. In the temperature range of 923–1123 K, the oxynitride formed at $T_O = 923$ K provided the best anticorrosive protection. The better anticorrosive characteristics of the coating with less oxygen in the oxygen-free acids can be explained by the decrease in the proportion of ionic bonding [22].

The corrosive characteristics of the coatings deteriorate with increasing of oxygen content in the oxynitrides as well as with increasing of surface roughness at longer oxynitriding times (Fig. 14b). The corrosion potentials of these coatings shifted to more negative values, and the corrosion current densities increased by two orders of magnitude (Table 5).

4. Conclusions

1. It was determined that oxynitride formation on the surface of titanium alloys is more intensive when T_A is higher, i.e. the deviation from stoichiometry of nitride is less. With the growth of T_A the content of oxygen in titanium oxynitride is decreased, and its composition is approached to equiatomic that provides the higher strengthening effect.
2. With the increase of isothermal exposure τ_A from 1 to 10 h the amount of oxide phase in the modified layers and content of oxygen in titanium oxynitride is decreased due to the change of composition of titanium nitride from less stoichiometric to more stoichiometric and composition of TiN_xO_{1-x} is approached to equiatomic.
3. It was determined that with decrease of nitrogen partial pressure p_{N_2} from 10^5 to 10 Pa nitride TiN_x with the greater deviation from stoichiometry is formed. When nitride formed at higher p_{N_2} after its modification by oxygen the content of oxide phase in surface

Table 3 Surface microhardness $H_{0.98}$, GPa and surface roughness R_a , μm of c.p. titanium after oxynitriding at different process time at $T_O = 923$ K.

Characteristics	Duration of oxynitriding τ_O , h			
	0	0.5	1	1.5
$H_{0.98}$, GPa	14.17	14.03	15.24	14.64
R_a , μm	0.73	0.81	0.84	0.86

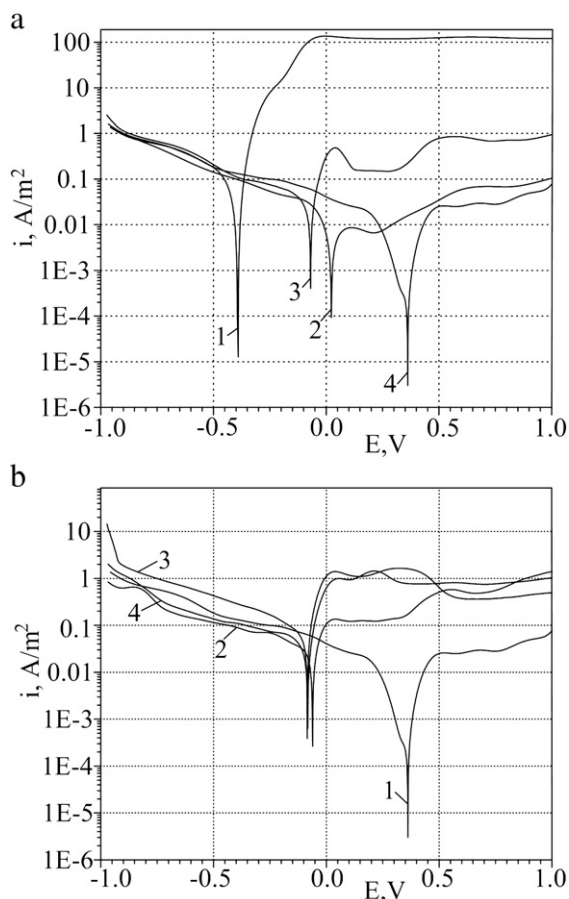


Fig. 14. Polarization curves measured in 3% NaCl from c.p. titanium after oxynitriding depending on temperature T_0 (a) (1–1223; 2–1123; 3–1023; 4–923 K) and time τ_0 (b) (1 – 0; 2 – 0.5; 3 – 1; 4 – 1.5 h).

layers and oxygen in titanium oxynitride are decreased. It provides the higher strengthening effect (1.7 GPa against 0.2 GPa).

4. With decrease of nitrogen partial pressure p_{O_2} from 1 to 0.0001 Pa at oxynitriding the phase formation is shifted from oxide to oxynitride formation, and oxygen content in titanium oxynitride is decreased. It provides the increase of surface microhardness of titanium alloys from 11 to 22 GPa.
5. It was determined that the level of surface microhardness of titanium alloys after oxynitriding at oxygen partial pressure 0.0001...0.01 Pa depends on oxynitride composition and grows with approaching of its composition to equiatomic. In this range of oxygen partial pressure the strengthening effect is presented. At oxygen partial pressure 0.1..1 Pa the level of surface microhardness is determined by an oxide film.
6. It was shown that with the decrease of oxynitriding temperature T_0 from 1223 to 923 K the phase transformation shifted toward oxynitride formation. Thus, oxygen content in titanium oxynitride is decreased, its composition is approached to equiatomic. It

Table 4

Corrosion potentials E_{cor} and current densities i_{cor} of c.p. titanium after oxynitriding at different temperatures T_0 .

T_0 , K	i_{cor} , A/m ²	E_{cor} , V
1223	1.5×10^{-2}	–0.9
1123	2.0×10^{-3}	0.02
1023	1.0×10^{-2}	–0.07
923	2.0×10^{-4}	0.36

Table 5

Corrosion potentials E_{cor} and current densities i_{cor} of c.p. titanium after oxynitriding at different process times τ_0 at $T_0 = 923$ K.

τ_0 , h	i_{cor} , A/m ²	E_{cor} , V
0.0	2.0×10^{-4}	0.36
0.5	1.5×10^{-2}	–0.06
1.0	1.5×10^{-2}	–0.08
1.5	2.0×10^{-2}	–0.08

provides the increase of surface microhardness from 10...12 to 12.5...15 GPa depending on alloy.

7. It is determined that with increase of process time at the oxynitriding temperature 1223 K from 0.5 to 1.5 h the content of oxygen component in titanium oxynitride is increased at maintenance of the phase-structural state of surface layers. The level of the surface strengthening is not changed sufficiently.
8. The corrosion properties of oxynitride coatings have been improved at higher nitrogen contents in the oxynitride compounds.

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