

Thermal Stability of the Structure and Phase Composition of Titanium Treated with Compression Plasma Flows

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Abstract—The results of studying the structure and phase composition of the surface layer of commercial pure VT1-0 titanium treated with compression plasma flows in nitrogen atmosphere and annealed in the temperature range of 400–900°C for 1 h are presented. Using the X-ray diffraction method, the α -Ti(O) solid solution is found to form in the titanium surface layer at 500°C, without pretreatment with plasma, and to transform into the titanium oxide TiO₂ (rutile) phase at 600°C. Pretreatment of titanium with compression plasma flows promotes the formation of α -Ti(N) solid solution decreasing the rate of surface oxidation and increasing the initial temperature of rutile formation to 700°C, which indicates enhancement of the thermal stability of this structure.

Keywords: titanium, titanium oxide, rutile, oxidation, thermal annealing, compression plasma flows, phase composition

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INTRODUCTION

Modification of the structure and phase composition of surface layers of metals and alloys aimed at improving their physical and mechanical parameters is one of the problems considered in materials science. Ion/electron beam [1–7] and plasma [8–10] approaches to surface treatment have become the most prevalent today. In many cases, surface modification is accompanied by the production of various nonequilibrium structures, such as oversaturated solid solutions, intermetallic phase inclusions, or nanocrystalline structures. However, there is the problem of the thermal stability of these structures, which is quite important in view of the frequent practical use of parts, including with modified surfaces, under outdoor conditions at high temperatures. In this paper, we consider the formation of oxygen-based compounds on the surface, which can diminish the positive effect achieved upon preliminary modification of the surface.

Earlier studies [11–13] showed the unique possibility of using compression plasma flows generated by quasi-stationary plasma accelerators to modify the surface layers of metals and alloys. These experiments show that the use of such flows, unlike conventional approaches involving intensive electromagnetic (laser) radiation and beams of charged particles (ions and electrons) to treat materials, promotes a considerable

increase in the depth of the modified layer reaching tens of micrometers. This is due to a combination of a high density of the absorbed energy measured at tens of J/cm², and rather long lifetime of the plasma flow (100 μ s), which results in melting of the surface layer and, due to hydrodynamic intermixing of the melt, promotes an increase in its thickness due to the convective mechanism of heat transfer. The direct treatment of materials with compression plasma flows produces small-crystalline, including nanocrystalline, structures, metastable solid solutions, and intermetallic phases, while a thin surface layer becomes enriched with atoms of the plasma gas (nitrogen). All this promotes, first of all, improvement of the mechanical characteristics of the modified layer (microhardness and wear resistance) [14, 15].

Because of the widespread application of titanium and its alloys, compression plasma treatment is aimed at both improvement in their tribological characteristics [16] and minimization of the toxic impurity concentration in the surface layer of titanium alloys used for medical purposes [17]. However, no studies of the thermal stability of the structures by their heating in air have been carried out. In this paper, the results of studying the thermal resistance of titanium modified by compression plasma flows in the temperature range of 400–900°C are presented.

EXPERIMENTAL

Samples of commercially pure titanium VT1-0 alloy of the dimensions 10×10 mm and thickness 3 mm were examined in the experiment. The samples were exposed to compression plasma flows generated in a compact magnetoplasma compressor in a residual nitrogen atmosphere (pressure 400 Pa) [18, 19]. In order to achieve the uniform melting of surfaces, the studied samples were treated with plasma flows in the mode of five consecutive pulses, 100 μ s each, with intervals of 20 s. The accumulating system of capacitors facilitating the treatment of titanium samples was preliminary charged to 4 kV; the distance between the electrode and the sample surface was 12 cm. Calorimetric studies performed to determine the maximum attainable temperature of the entire sample volume by means of a thermocouple probe, assuming complete transformation of the absorbed energy into thermal energy, showed that the density of the energy transferred to the surface layer was 13 J/cm² per pulse at the used exposure parameters [20].

After being treated with compression plasma flows, the titanium samples were annealed in a muffle furnace for 1 h. The temperature of aging varied from 400 to 900°C with an accuracy of 10°C. Then the heated samples were cooled in ambient conditions. In order to discern the effect of compression-plasma-flow treatment raw titanium samples were also exposed to thermal annealing.

The morphology of the surface of the treated and annealed samples was studied using scanning electron microscopy (SEM) with a LEO 1455 VP microscope. The phase composition of the oxidized titanium layers were studied with the help of X-ray analysis using an UltimaIV Rigaku diffractometer in the parallel beam geometry using copper radiation ($\lambda = 0.154178$ nm). Diffractograms were recorded with the detector moving 2 degrees a minute with a step of 0.05°.

RESULTS AND DISCUSSION

In its initial state, titanium contained only the low-temperature crystalline α phase with a hexagonal lattice. According to the results of the phase analysis (Fig. 1), titanium kept its hexagonal low-temperature α phase after thermal annealing in air at 400°C without pretreatment with compression plasma flows. Determination of the lattice parameters of α -Ti shows that at this annealing temperature the unit-cell parameters do not change, which allows us to exclude oxygen penetration upon heating. It is known, that a thin (few tens of nanometers) oxide layer is usually formed on the surface of titanium preventing oxygen from penetration into it from the surrounding medium. An increase in the thermal-annealing temperature to 500°C results in the formation of additional diffraction lines with a weak intensity in the form of “shoulders” of α -Ti diffraction lines from the smaller diffraction

angles. These are most apparent in diffraction lines corresponding to reflections from crystallographic planes (002) and (102). With an increase in the annealing temperature to 600°C, the relative intensity of these additional lines increases. These lines can be associated with the formation of a solid solution on the basis of the low-temperature phase of titanium and oxygen α -Ti(O), which is often interpreted as one of the low titanium oxides Ti₃O or Ti₂O with the same crystalline structure as α -Ti [21]. The diffraction properties of the solid solution phase of α -Ti(O) are detected up to 800°C (Fig. 2).

According to the equilibrium diagram of the titanium–oxygen state [22], the maximum oxygen solubility in the low-temperature phase of titanium reaches 30 at %. The solid solution of α -Ti(O) is a low-temperature phase of titanium whose hexagonal lattice is deformed due to the dissolution of oxygen atoms penetrating from the surface on account of diffusion processes. Since the atomic radius of oxygen (0.074 nm) is smaller than that of titanium (0.146 nm), oxygen atoms dissolve in the α -Ti crystal lattice becoming embedded in its pores. The radius of the oxygen atom considerably exceeds the size of the octahedral (0.060 nm) and tetrahedral (0.033 nm) pores in the titanium hexagonal lattice; therefore, it deforms, and its parameters are increased. Using the Gaussian function for the mathematical separation of diffraction reflections into components we can determine the lattice parameters of the α -Ti(O) solid solution. Hence, when the annealing temperature increases from 500 to 800°C, parameter a increases from 0.2935 to 0.2959 nm, and parameter c increases from 0.4738 to 0.4766 nm (Fig. 3). The structure hexagonality parameter (c/a), about 1.61, remains almost unchanged during thermal annealing. The increase in the lattice parameters of the solid solution can indicate an increase in the oxygen content with rising temperature.

At an annealing temperature of 600°C, the phase of TiO₂ oxide (rutile) starts to form in the titanium surface layer, which is reflected by diffraction line 110 at diffraction angle $2\theta = 27.41^\circ$. At annealing temperatures of 700–800°C, we observe an intense increase in the volume content of TiO₂ oxide which becomes the dominant phase after heat treatment at 900°C. The tetragonal lattice parameters of this phase are $a = 0.4596$ nm and $c = 0.2964$ nm.

Comparison of the lattice parameters of α -Ti(O) solid solution and TiO₂ titanium oxide shows that with increasing annealing temperature due to increasing oxygen concentration in the surface layer, the lattice parameter a of the α -Ti(O) solid solution increases until it reaches (or exceeds) the lattice parameter of the oxide. This condition is met at 600°C, when the formation of TiO₂ oxide starts.

We note that lines on the diffractograms, which correspond to reflections from the crystallographic planes of α -Ti, are recorded in the samples exposed to

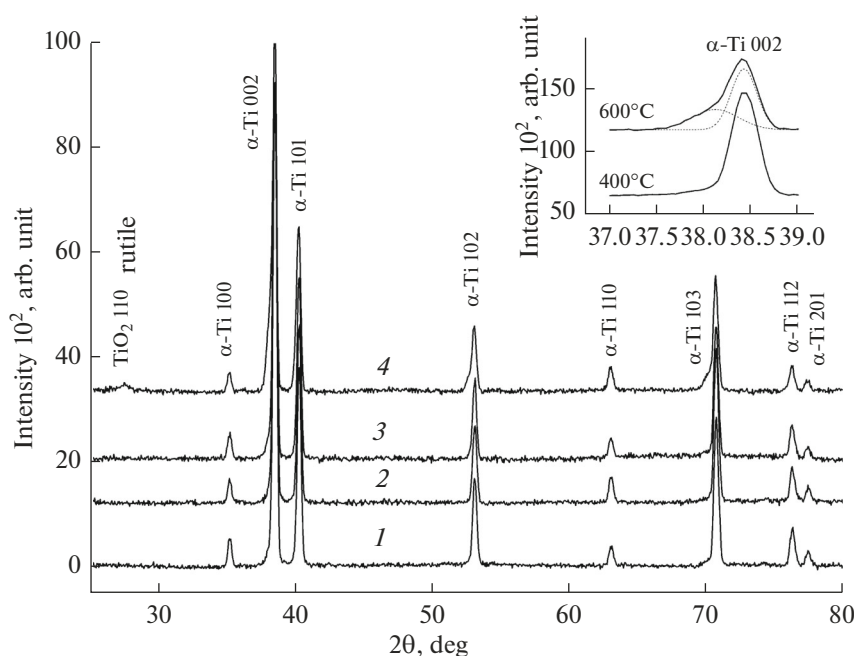


Fig. 1. Diffractograms of titanium before (1) and after thermal annealing in air at temperatures: 400°C (2), 500°C (3), and 600°C (4) (insert shows the results of deconvolution of the diffraction line 002 of α -Ti).

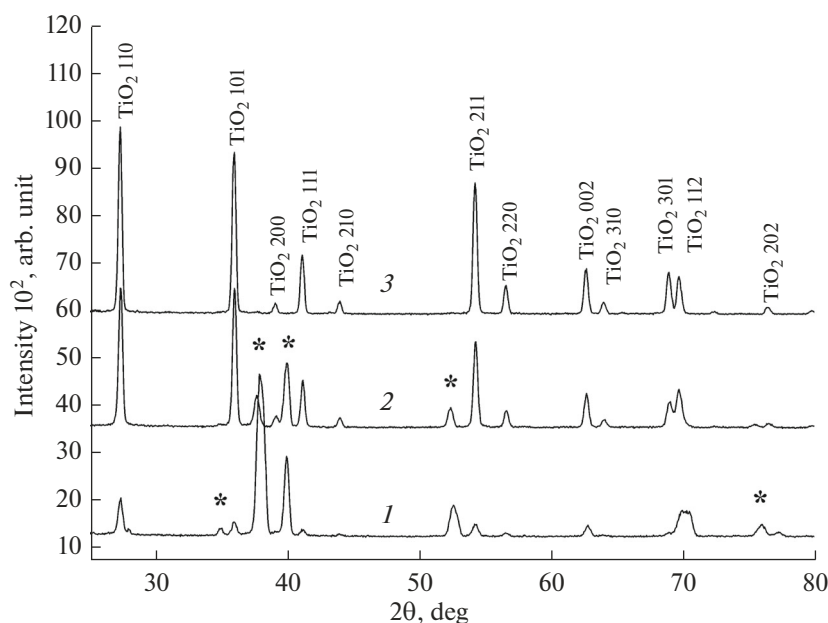


Fig. 2. Diffractograms of titanium after thermal annealing in air at temperatures: 700°C (1), 800°C (2), and 900°C (3). Asterisks mark reflections of α -Ti(O) phase.

heat treatment in the temperature range of 400–600°C and disappear at higher temperatures. The lattice parameters of α -Ti remain almost unchanged in the case of temperature growth: $a = 0.2948$ – 0.2950 nm, $c = 0.4682$ – 0.4687 nm ($c/a = 1.58$). The obtained values correspond to reference data for the low-temperature phase of titanium. Hence, they emerge due to the

presence of unoxidized titanium near the surface layer, apparently, localized under a layer of α -Ti(O) solid solution. At 700–900°C, no diffraction reflections from the unoxidized titanium phase are detected, which can be the result of a considerable increase in the layer depth corresponding to the formation of the α -Ti solid solution; the layer depth is ≈ 7 μ m and

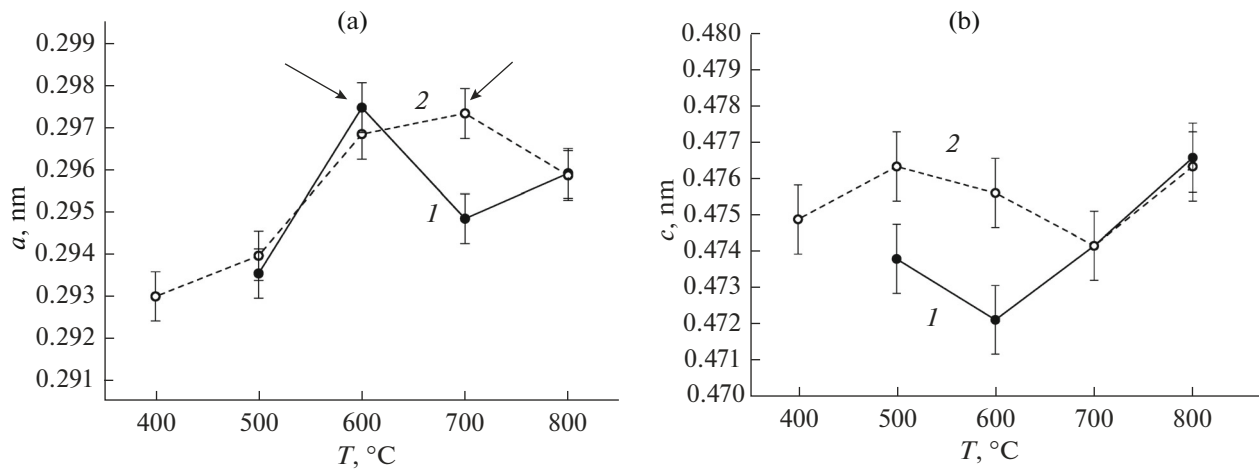


Fig. 3. Lattice parameters a (a) and c (b) of the solid solutions α -Ti(O) (1) and α -Ti(N,O) (2) as functions of the annealing temperature (arrows mark the modes starting TiO_2 titanium-oxide formation).

becomes comparable to the depth measured by means of X-ray diffraction. Indeed, at a mean diffusivity of $4.6 \times 10^{-11} \text{ cm}^2/\text{s}$ of oxygen atoms in the titanium lattice at 700°C [23], the mean depth of oxygen penetration during annealing is $\approx 6 \mu\text{m}$ and grows with an increase in the annealing temperature.

The exposure of titanium to compression plasma flows modifies its structure. One of the main effects of the treatment is the heat effect which provides heating and melting of the surface layer. According to solution of the classical thermal conductivity equation for titanium with corresponding energy parameters of the plasma flow, in this case, the maximum temperature on the sample surface reaches $2100\text{--}2200^\circ\text{C}$, and this is considerably higher than its melting point [24]. The depth of the melted layer is $5\text{--}7 \mu\text{m}$. The intense heat removal related to the volume of the unmelted part of the titanium sample triggers rapid crystallization at a typical cooling rate of about $10^6\text{--}10^7 \text{ K/s}$ and speed of the crystallization front of $1\text{--}2 \text{ m/s}$ [25]. Under such conditions of crystallization, a small-crystalline structure with a mean grain size less than $1 \mu\text{m}$ is formed. The corresponding diffraction-line broadening can implicitly indicate the formation of a small-crystalline structure in the surface layer of titanium after its exposure to compression plasma flows.

Since the magnetoplasma compressor chamber is filled with nitrogen, when compression plasma flows are generated, the titanium surface is saturated with nitrogen during its interaction with the plasma flow. This causes thickening of the thin nitrated surface layer, whose thickness does not exceed $1 \mu\text{m}$ [26] at the same parameters of treatment. The phase analysis carried out after the titanium sample was exposed to compression plasma flows reveals a phase containing nitrogen, i.e., the α -Ti(N) solid solution with a hexagonal lattice often designated as $\text{TiN}_{0.3}$ titanium nitride

[27]. The lattice parameters of the α -Ti(N) phase are: $a = 0.2945 \text{ nm}$ and $c = 0.4678 \text{ nm}$.

The thermal exposure of titanium at $400\text{--}600^\circ\text{C}$ after pretreatment with compression plasma flows causes an increase in the intensity and angular displacement of similar “shoulders” of diffraction lines of α -Ti (Fig. 4). In this case, they are the result of both the formation of α -Ti(N,O) solid solution, and the presence of dissolved atoms of oxygen in it. Since α -Ti(N,O) is formed in the immediate vicinity of the surface after surface exposure to compression plasma flows, we can expect α -Ti(N,O) solid-solution formation within the thermal-annealing procedure. The lattice parameter (mainly the c parameter), which is higher as compared with the corresponding parameter of the α -Ti(O) solid solution, indicates the formation of such a solid solution generated in titanium without exposure to compression plasma flows (Fig. 3).

When the annealing temperature increases to 700°C , an increase in the lattice parameter a of the α -Ti(N,O) solid solution is observed indicating growth of the oxygen concentration in the solution (Fig. 5). At 700°C , the a parameter exceeds the level of 0.2956 nm corresponding to the lattice parameter of the TiO_2 titanium oxide phase, the formation of which starts at this temperature. Moreover, as in the case of titanium-oxide formation without pretreatment with compression plasma flows, the beginning of growth of the TiO_2 oxide phase is characterized by the minimum lattice parameter c of α -Ti(O) and α -Ti(N,O) solid solutions (Fig. 3). At such lattice parameters, solid solutions feature the minimum hexagonality parameter 1.58 which is close to the tetragonality parameter of the TiO_2 titanium oxide phase (1.55). Thus, local regions of this solid solution with appropriate lattice parameters can become effective nuclei for the further growth of TiO_2 titanium oxide phase. Following from the obtained relationships, the lattice parameter of

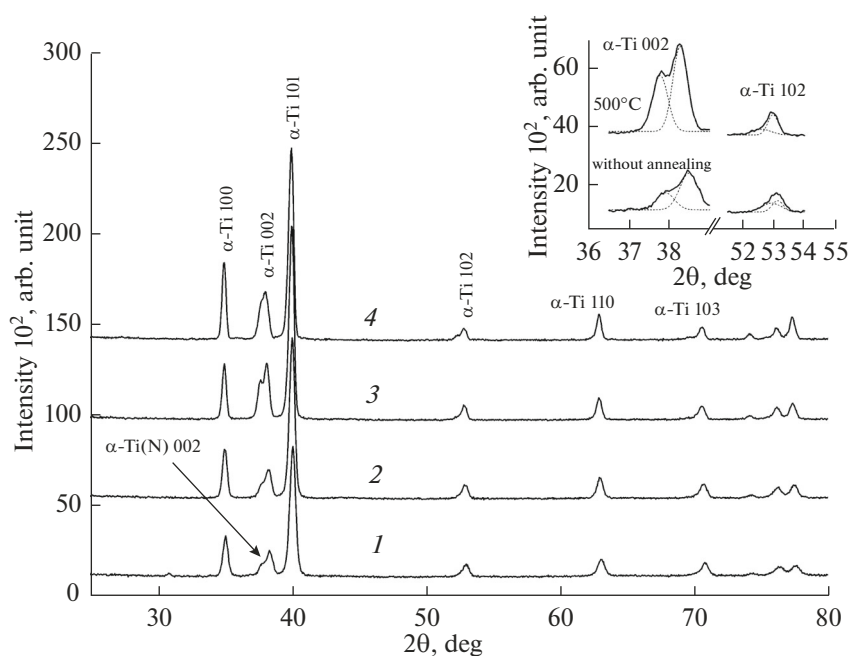


Fig. 4. Diffractograms of titanium treated with compression plasma flows before (1) and after thermal annealing in air at temperatures: 400°C (2), 500°C (3), and 600°C (4) (insert shows the results of deconvolution of the diffraction lines 002 and 102 of α -Ti).

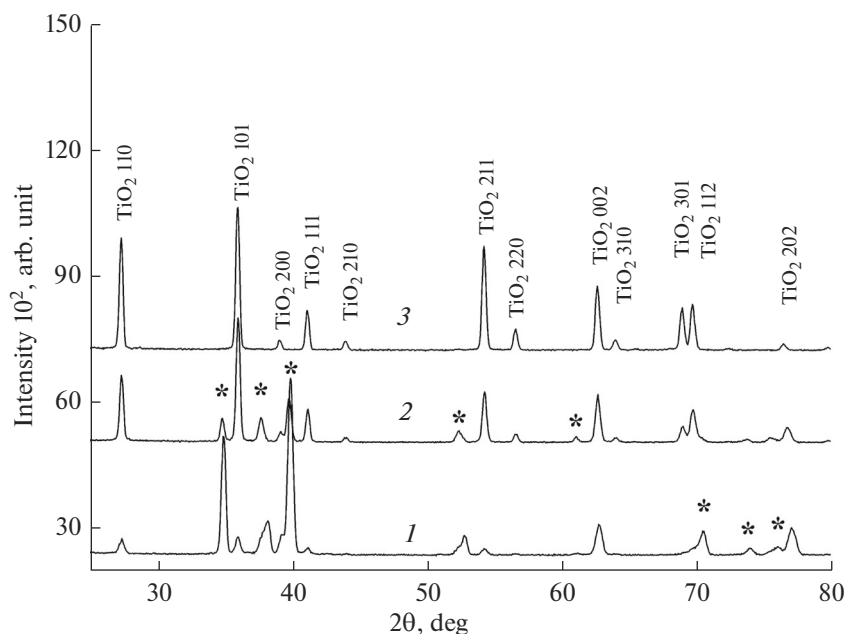


Fig. 5. Diffractograms of titanium treated with compression plasma flows after thermal annealing in air at temperatures: 700°C (1), 800°C (2), and 900°C (3). Asterisks mark reflections of the α -Ti(O) phase.

α -Ti(O) or α -Ti(N,O) solid solutions is an indicator of the start of the phase transition associated with the formation of titanium oxide. The overall pattern of phase transformations in titanium upon thermal exposure is presented in Fig. 6.

In Fig. 7, SEM images of the surface of titanium before carrying out thermal annealing are presented.

The titanium surface not exposed to compression plasma flows shows a developed relief that was apparently formed by plate deformation and rolling. After exposure to the plasma flows that caused melting, and subsequent solidification of the surface, its local smoothing is accompanied by the development of a specific relief stipulated by the crystallization of surface perturbations occurring in the melt during hydro-

$\alpha + \alpha(N)$	$\alpha + \alpha(N,O)$			$\alpha(N,O) + TiO_2$	TiO_2 2
α	$\alpha + \alpha(O)$	$\alpha + \alpha(O) + TiO_2$	$\alpha(O) + TiO_2$	TiO_2 1	
400	500	600	700	800	900 $T, ^\circ C$

Fig. 6. Diagram of the sequence of phase transformations in titanium upon thermal exposure without pretreatment (1) and after treatment with compression plasma flows (2).

dynamic processes. Crystals with cross-sectional dimensions not exceeding 1–3 μm stretched in the direction of growth were discovered during studies of the titanium-surface morphology after thermal annealing at 900 $^\circ C$ (Fig. 8). The crystals were found on the surfaces of both raw titanium and samples exposed to plasma pretreatment. Since titanium oxide TiO_2 is the single phase shown in X-ray patterns after annealing at 900 $^\circ C$, we can suppose that the crystals refer to this phase [28]. We note that the crystals formed have a columnar structure, which is displayed in places of their fracture, and their sizes and orientation are independent of plasma pretreatment.

It would be natural to suppose that diffusion migration, whose intensity increases with temperature, is the basic mechanism of oxygen penetration into the titanium surface layer. Apparently, two concurrent processes occur upon the oxidation of titanium exposed to pretreatment with compression plasma flows. Firstly, the formation of a small-crystalline structure induces an increase in the share of intra-grain boundaries which are paths for accelerated diffusion. Secondly, after exposure to plasma a nitrated layer is formed in immediate proximity to the titanium surface layer, and this is the $\alpha-Ti(N)$ solid solution, where oxygen diffusion is hampered. Thus, at the initial stages of oxidizing, when the bulk of oxygen is distributed across the nitrated layer, the process is slowed as compared with raw titanium. This provides an increase in the initial temperature of TiO_2 oxide formation to 700 $^\circ C$.

In [29], the model of growth of TiO_2 oxide on the surface of TiN titanium nitride is described under the assumption that within the oxidation procedure, in view of the high chemical affinity of titanium to oxygen, the diffusion of titanium atoms to the surface occurs. In this case, vacancies formed at lattice sites of

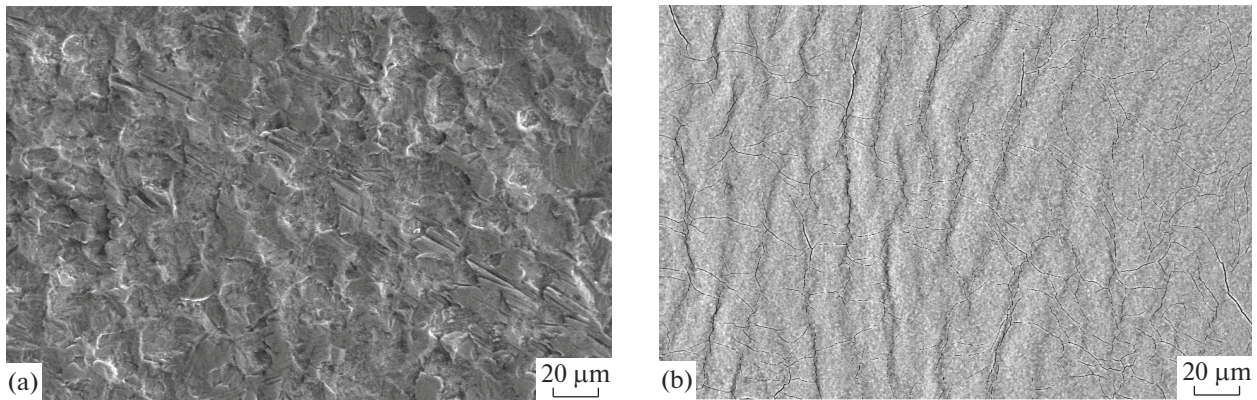


Fig. 7. SEM images of sections of the titanium surface: (a) in the initial state; (b) after treatment with compression plasma flows.

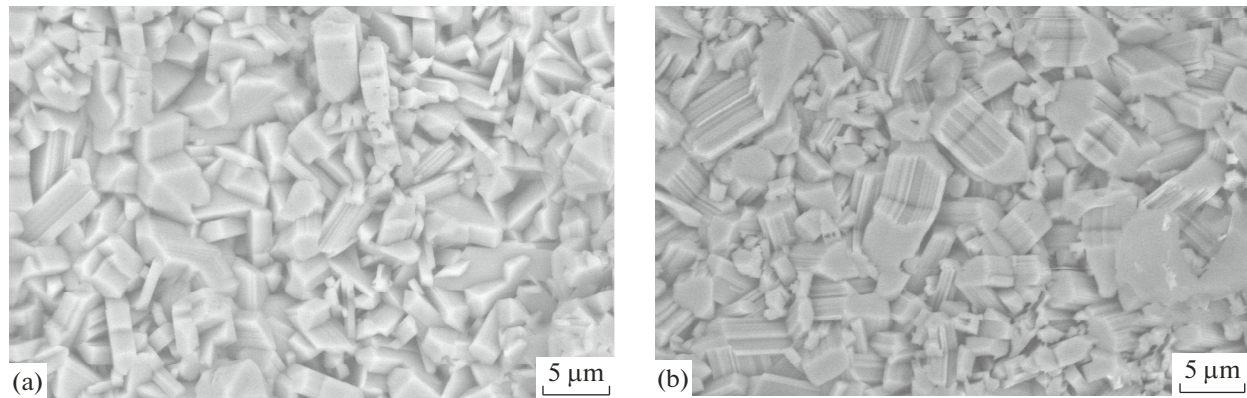


Fig. 8. SEM images of the titanium surface after thermal annealing at 900 $^\circ C$: (a) untreated sample; (b) after treatment with compression plasma flows.

the underlying metal are not occupied by atoms of titanium and eventually form clusters. Within these clusters, the boundaries between atoms of nitrogen drastically weaken forcing them to exist in the gas phase, which creates an interior mechanical pressure able to reach, by the our estimations, 300–400 MPa. This sequence of structural transformations is described by the general reaction: $\text{TiN} + \text{O}_2 \rightarrow \text{TiO}_2 + 1/2\text{N}_2$. The described mechanism can be expanded to the process of growth of the titanium-oxide phase in the α -Ti(N) solid solution produced after exposure to compression plasma flows. In this case, the interaction of atoms of oxygen with the surface induces titanium-atom migration to the surface forming vacant clusters filled by nitrogen. As shown above, growth of the phase of TiO_2 titanium oxide starts in local regions of either α -Ti(N,O) or α -Ti(O) solid solutions, when the lattice parameters reach certain values. Since the lattice parameter of the solid solution is less than that of TiO_2 titanium oxide, the lattice needs to be stretched to be transformed, which in the case of raw titanium can be arranged only by an increase in the oxygen concentration. When titanium is heated after exposure to plasma, the vacant clusters formed in it by the aforementioned mechanism are filled with nitrogen and create an additional inner pressure causing additional compression of the lattice. Consequently, the initial temperature of titanium-oxide formation rises.

CONCLUSIONS

Hence, the exposure of titanium to compression plasma flows generated in a nitrogen atmosphere modifies the structural phase state of the surface layer, namely, induces the formation of a small-crystalline structure and α -Ti(N) solid solution, which influence the process of oxidation during subsequent thermal exposure. It is discovered that when titanium, having been exposed to pretreatment with compression plasma flows, is treated at temperatures from 400 to 900°C, the surface nitrated layer is saturated with oxygen, the α -Ti(N,O) solid solution is formed, and the volume of TiO_2 titanium-oxide phase (rutile) increases. Exposure to compression plasma flows extends the temperature range of the thermal stability of titanium to 700°C—this is the temperature, at which the growth of the TiO_2 oxide phase starts.

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