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Modelling of Microstructural Evolution of Titanium During Diffusive Saturation by Interstitial Elements

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1. Introduction

Titanium and titanium alloys are the most promising structural materials for the products of the contemporary aircraft and spacecraft engineering, medicine. The complex of characteristics of such products strongly depends on the properties of their surface layers. One of the efficient method of their hardening is the thermodiffusive saturation with interstitial elements, in particular nitrogen or oxygen (Fedirko & Pohrelyuk, 1995; Panasyuk, 2007). Such high-temperature interaction with these interstitial elements is accompanied by not only the formation and growth of a nitride or oxide film, but also the significant dissolution of nitrogen or oxygen in the base metal. The competition of these processes complicates significantly the study of the kinetics and mechanism of such an interaction. In this case, useful information can be obtained from results of an investigation of the high-temperature interaction of titanium in an atmosphere with a decreased nitrogen or oxygen pressure, which simultaneously generates practical interest, because deep diffusion layers without a continuous nitride or oxide film on a titanium surface can be formed (Fedirko & Pohrelyuk, 1995; Panasyuk, 2007). The incubation period of formation of such a film depends to a large degree on the partial gas pressure and saturation temperature. Attempts to choose purposefully an optimal nitrogen or oxygen pressure and temperature–time parameters of such a thermochemical treatment failed. This is due to the complexity and diversity of the interactions of titanium with rarefied gas-containing atmospheres, the absence of data on parameters that characterize surface phenomena, and a large spread (up to two orders of magnitude) of available data on the diffusion

coefficient of nitrogen or oxygen in titanium (Panasyuk, 2007; Metin, 1989; Kofstad, 1966). This is why investigations (experimental and theoretical) aimed at elucidating the kinetic regularities and peculiarities of the distribution of interstitial elements in a surface layer, which determines the changes of its physicomechanical characteristics, are urgent.

Diffusive processes determine changes of properties of surface layers of the structural materials in many cases, for example, in the process of their thermochemical treatment or in the conditions of operation at high temperature. However, the diffusion in solids is often accompanied by the structural phase transformations. These processes are interconnected and interdependent: diffusion of the elements can stimulate structural phase transformations, and the latter change the conditions of diffusion. It is difficult to describe these processes analytically. Titanium, which undergoes the polymorphic transformation at $T_{\alpha \leftarrow \beta} = 882\ ^0C$ (Fromm & Gebhardt, 1976), is interesting for such theoretical and experimental investigations, in particular its high-temperature interaction with nitrogen or oxygen. Due to high affinity of these elements with titanium nitride or oxide layer forms and grows on the surface. Unlike many alloying elements, in particular vanadium, molybdenum, which are β-stabilizers, above mentioned interstitial elements are α-stabilizers, which can stimulate structural phase transformations in titanium. The microstructural evolution during $\alpha \leftrightarrow \beta$ phase transformation as a result of migration of β-stabilizers is presented in (Malinov et al., 2003). However, the authors did not take into consideration the role of nitrogen as α-stabilizer in the structural transformations. It was demonstrated (Matychak, 2009) in the studies of interconnection of nitrogen diffusion and structural phase transformations during high-temperature nitriding that, in particular, under the rarefied atmosphere, the continuous nitride layer on the surface was absent for a long time.

The aim of work is:

- to establish the kinetic peculiarities of interaction of titanium with the interstitial element A (nitrogen or oxygen) at the temperature lower and higher than temperature of allotropic transformation $T_{\alpha \leftarrow \beta}$;

- to investigate experimentally and model analytically the process of diffusive saturation of α-titanium with the interstitial element from a rarefied atmosphere taking into account the surface phenomena;

- to model the interdependence of the processes of external supply of the interstitial element to the surface and its chemosorption with diffusive dissolution and segregation on defects, caused by the chemical interaction with the titanium atoms;

- to estimate the influence of temperature-time parameters of treatment on the depth of diffusion zone and change of its microhardness;

- to establish the kinetic peculiarities of diffusive saturation of titanium with the interstitial element caused by the structural phase transformations.

2. Thermodiffusion saturation of titanium with interstitial elements from a rarefied atmosphere at $T < T_{\alpha \leftrightarrow \beta}$

2.1. Physicomathematical model

2.1.1. Phenomenology of surface phenomena

Let us consider the interaction of α-titanium with a rarefied gas atmosphere in a temperature range which is below the temperature of the $\alpha \leftrightarrow \beta$ allotropic transformation. In such a system, peculiarities of the interaction predominantly manifest themselves on the titanium surface as a result of adsorption, chemisorption, chemical reactions, generation of point defects, and the formation of two-dimensional structures. Along with phase formation, which includes these processes on the surface, the transfer of the interstitial element in the depth of titanium, i.e., its diffusive saturation, plays an important role. Experimental data indicate that, for rather long exposures, at certain rarefaction of the interstitial element, only islands of a nitride or oxide film, rather than a continuous film, are formed on the titanium surface (Fedirko & Pohrelyuk, 1995). In this case, the kinetics of saturation is sensitive to the interstitial element transfer to the surface of titanium and the intensity of surface processes. Thus, the surface interstitial element concentration depends on time. The defectiveness of the metal and its influences on the diffusion activity and reactivity of the interstitial element also play an important role. Due to lattice defects, in particular vacancies, dislocations of the surface layer, the probability of inequilibrium segregations of the interstitial element increases as a result of the chemical interaction with titanium, which introduces changes in the diffusive saturation of titanium with the interstitial element. That is why it is incorrect to describe analytically the kinetics of saturation with the known Fick's equation by setting constant values of the surface concentration (the first boundary-value task). This indicates the actuality and importance of an adequate choice of boundary conditions for the formulation of the corresponding diffusion problem. To do this, it is necessary to have a clear notion of the interrelation of the physico-chemical processes on a surface and near it.

The interaction of titanium with a rarefied gas atmosphere can be schematically illustrated by following processes with relevant parameters characterizing them (Fig. 1):

a. transport of the interstitial element molecules to a metal surface followed by their physical adsorption, dissociation, and chemisorption (the mass transfer coefficient h, cm/sec);

b. segregation of the interstitial element on defects in a contact layer (with a mass capacity ϖ, cm) as a result of the chemical interaction with the metal (the rate of reaction k, cm/sec);

c. diffusion of the interstitial element in α-titanium (diffusion coefficient D, cm^2/sec).

Processes enumerated in clause a) can be interpreted as a two-stage reaction which consists of a diffusive stage, described by the constant rate h_D, and a stage of chemisorption at a constant rate h_R. Then, according to the law of summation of kinetic resistances, we have
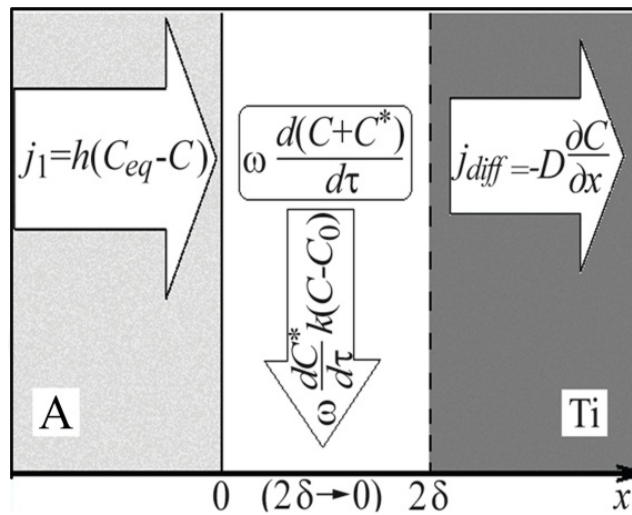
Figure 1. Scheme of mass fluxes in the Ti–A system

$h^{-1} = h_D^{-1} + h_R^{-1}$. The introduced kinetic parameters ($P_i = D$, h, k) of the model representation characterize the aforementioned thermoactivated physicochemical processes with the corresponding activation energies (E_i), according to the dependence $P_i = P_{0i} \exp(-E_i/RT)$. The effective parameters h and k depend not only on temperature, but also largely on the partial pressure of interstitial element and defectiveness of the material. That is why they are usually calculated from specific experimental data of the kinetics of saturation. In particular, the experimental data for the spatial distribution of the interstitial element in surface layer of titanium after various exposure time (τ_1 and τ_2) allow to use a graphical method to compute the mass transfer coefficient h and the surface content (C_{eq}) of nitrogen which is in equilibrium with the atmosphere (Fig. 2) (Matychak et al., 2009).
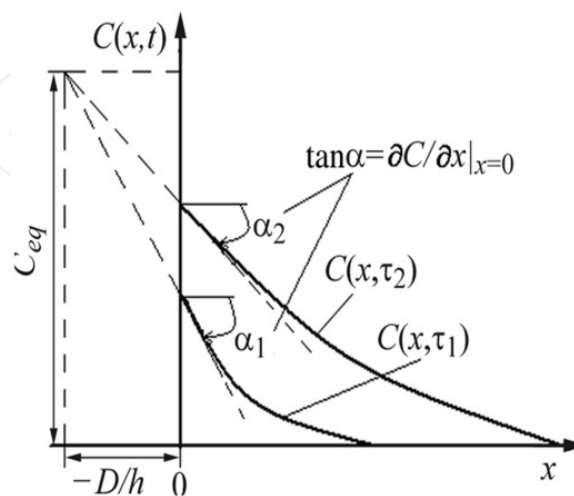
Figure 2. Graphical method for the determination of the h and C_{eq} parameters

Let us represent the inequilibrium processes mentioned in clauses (a) – (c) in the formulation of the diffusion problem through the adequate setting of the boundary conditions of mass exchange on the surface.

2.1.2. Mathematical description

Since the aim of the diffusive saturation of a titanium sample is primarily to harden its surface layer, as an object of the analytic investigation of the kinetics of this process, we chose a half-space ($0 \leq x < \infty$) with the initial ($\tau=0$) interstitial element concentration $C(x,\tau=0)=C_0$. For the calculation of the concentration of dissolved interstitial element in the titanium sample it is need to solve Fick's diffusion equation considering initial and boundary conditions (Matychak et al., 2007):

$$D\partial^2 C(x,\tau)/\partial x^2 = \partial C(x,\tau)/\partial \tau \quad for \quad \tau > 0, \; 0 < x < \infty, \; C(x,0) = C(\tau,\infty) = C_0, \tag{1}$$

$$\omega \cdot dC/d\tau = h(C_{eq} - C) - k(C - C_0) + D\partial C/\partial x \quad for \quad x = +0. \tag{2}$$

Here C_{eq} is a quasiequilibrium surface concentration of the interstitial element, which depends on its partial pressure in the atmosphere.

The boundary condition (2) was proposed on the basis of notions of a contact layer with a thickness 2δ between the metal and the environment, in which processes of migration of an impurity and the chemical reaction of the first order (Fig. 1) occur (Prytula et al., 2005). Using a mathematical procedure (Fedirko et al., 2005; Matychak, 1999), this layer was replaced by an imaginary layer of zero thickness ($2\delta \rightarrow 0$) with a mass capacity ω. For such a transition, we introduced averaged characteristics of the contact layer, specifically the surface concentration of the impurity $C(+0,\tau)$. Note that neglecting the contact layer $\omega=0$, and, correspondingly, $k = 0$, from Eq.(2) we obtain the typical boundary condition of mass exchange of the third kind (Raichenko, 1981):

$$-D\partial C/\partial x\big|_{x=0} = h[C_{eq} - C(0,\tau)] \tag{3}$$

or even the simpler condition ($D/h \rightarrow 0$) of the first kind:

$$C(0,\tau) = \lim_{x\to+0} C(x,\tau) = C_{eq} = const \tag{4}$$

Let us point at the characteristic peculiarities of the proposed generalized boundary condition (2), which distinguishes it from the quasistationary boundary condition (3). The latter one reflects to a certain extent the real situation of the asymptotic approximation of the surface concentration to its equilibrium value. At the same time, according to condition (3), all atoms

adsorbed on the surface diffuse into the metal and are distributed in compliance with the law of diffusion. That is why, according to condition (3), when D→ 0, we have C(0,τ)=C$_{eq}$. That is, the surface concentration becomes equilibrium instantaneously and is independent of time. Thus, from the proposed generalized nonstationary boundary condition (2), in the absence of diffusion D→ 0 of the impurity in the volume of the metal, we have the following time dependence of its surface concentration:

$$C(0,\tau) = \frac{hC_{eq} + kC_0}{h+k} - \frac{h(C_{eq} - C_0)}{h+k} \exp\left[-\frac{(h+k)\tau}{\omega}\right],$$

(5)

which is determined by the intensity of surface processes. One more peculiarity of proposed non-stationary condition (2) concerns the action of the operator d/dτ, which describes the kinetics of accumulation of the interstitial element in the vicinity of the interface. In particular, the difference between the flux j$_1$ of the interstitial element from the environment to the surface (x=-0) and its diffusion flux j = j$_{diff}$ in the metal (x=+0) determine the kinetics of accumulation (segregation) of the interstitial element in the vicinity of the interface as a result of the chemical interaction (Fig. 1). The interstitial element is accumulated in the contact layer on defects modeled as "traps" for the diffusant. Then its concentration in the surface layer in the bound state (in nitride or oxide compounds) and its total concentration (in the solid solution and compounds) in the vicinity of the surface are computed from the relations

$$C^*(0,\tau) = \left(\frac{k}{\omega}\right)\int_0^\tau [C(0,t) - C_0]dt, \qquad C_\Sigma(0,\tau) = C(0,\tau) + C^*(0,\tau).$$

(6)

Thus, only a part of all adsorbed interstitial element atoms dissolves in the metal and diffuses in the volume. The remaining nitrogen atoms segregate in the form of compounds near the surface (Fig. 3).
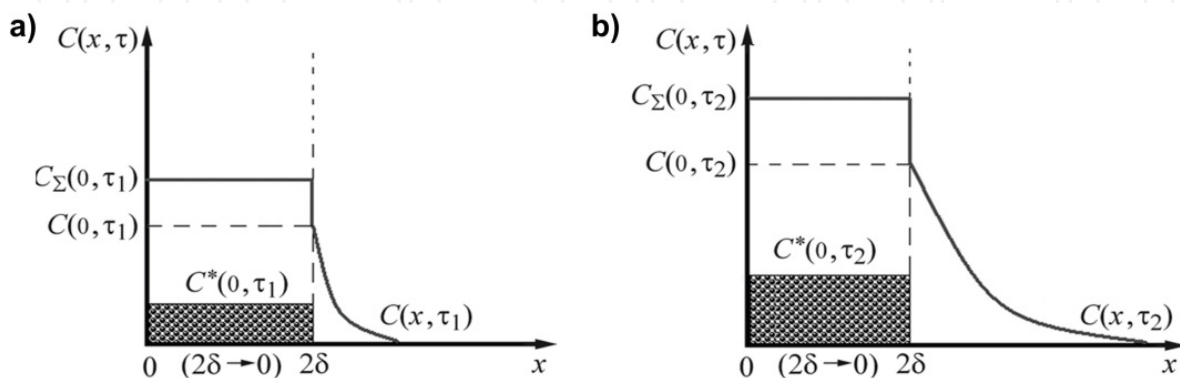
Figure 3. Evolution of the interstitial element distribution during diffusive saturation: (a: τ= τ$_1$, b: τ= τ$_2$; τ$_1$<τ$_2$

The evolution of spatial distribution of dissolved nitrogen in titanium (Fig. 3) during its thermodiffusive saturation gives a solution of the equations (1), (2), which in the analytic form is as follows (Matychak et al., 2007):

$$\overline{C}(x,\tau) = h(h+k)^{-1} erfc\left[x / (2\sqrt{D\tau}) \right] - h\left[q_2^{-1}F_2(x,\tau) - q_1^{-1}F_1(x,\tau) \right] / (D\Delta), \tag{7}$$

where

$$F_1(x,\ \tau) = \exp(q_1 x + q_1^2 D\tau) \cdot erfc[q_1\sqrt{D\tau} + x / (2\sqrt{D\tau})]] \ ,$$

$$F_2(x,\ \tau) = \exp(q_2 x + q_2^2 D\tau) \cdot erfc[q_2\sqrt{D\tau} + x / (2\sqrt{D\tau})]] \ ,$$

$$q_1 = (1+\Delta) / 2\omega , \quad q_2 = (1-\Delta) / 2\omega , \quad \Delta = \sqrt{1 - 4\omega(h+k) / D} \ .$$

Specifically, the surface concentration of dissolved interstitial element is

$$\overline{C}(0,\tau) = h / (h+k) - [f_2(\tau) / q_2 - f_1(\tau) / q_1] \cdot h / (D\Delta) , \tag{8}$$

where

$$f_1(\tau) = \exp(q_1^2 D\tau) \cdot erfc(q_1\sqrt{D\tau}) \ , \quad f_2(\tau) = \exp(q_2^2 D\tau) \cdot erfc(q_2\sqrt{D\tau}). \tag{9}$$

Here $\overline{C}(x,\ \tau) = (C(x,\ \tau) - C_0) / (C_{eq} - C_0)$ is the relative change of the interstitial element concentration in the solid solution in α-titanium. Its surface concentration $C^*(0,\tau)$ in the bound state and the total concentration $C_{\Sigma}(0,\tau)$ are determined by formulas (6).

The obtained results for the diffusive saturation of titanium with nitrogen under low partial pressure (1 Pa) in the temperature range of 750-850 ^{0}C (below the temperature of allotropic transformation) were confirmed by the experimental results (Matychak et al., 2009).

2.2. Technique and results of experimental tests

2.2.1. Methods

The samples (10×15×1 mm) of VT1-0 commercially pure titanium were investigated after an isothermal exposure at temperatures of 750, 800, and 850 ^{0}C for 1, 5, and 10 h in a rarefied (to 1 Pa) dynamic nitrogen atmosphere (the specific inleakage rate was 7×10^{-3} Pa/sec). Before treatment, samples were ground to R_a = 0,4 μm, washed in acetone and alcohol, and dried.

Upon loading the samples in an ampoule, the system was pumped down to a pressure of 10^{-3} Pa, then the nitrogen was blown through, and required parameters of the gas medium were set. Heating was performed at a rate 0.04 ^{0}C/sec. After an isothermal exposure, the samples were furnace-cooled in nitrogen (the mean cooling rate was 100 ^{0}C/h).

Commercially-pure gaseous nitrogen was used, which, according to a technical specification, contained not more than 0.4 vol. % of oxygen and 0.07 g/m³ of water vapor. Before feeding in the reaction space of a furnace, nitrogen was purified from oxygen and moisture by passing through a capsule with silica gel and titanium chips heated to a temperature higher by 50 °C than the saturation temperature. After every 3–4 tests, to restore the efficiency of the system for purification of nitrogen, silica gel was annealed at 180 °C for 3–4 h, and titanium chips were replaced by new ones. Due to this, the oxygen concentration in nitrogen ranged from 0.01 to 0.03 vol. %.

The microstructure of "oblique" microsections of samples was studied with a "Epiquant" microscope equipped with a camera and a computer with digital image analysis software.

The surface hardening was assessed based on the microhardness measured with a PMT-3M unit under a load of 0.49 N. As the depth of a nitrided layer, the depth of a zone was accepted in which the microhardness was higher than that of the core by δH=0.2 GPa (Fedirko & Pohrelyuk, 1995).

2.2.2. Results of experimental investigations

An analysis of experimental data of the influence of the partial nitrogen pressure on the saturation of titanium alloys during nitriding indicates that, in the range of rarefaction of the active gas 0.1–10 Pa (the specific inleakage rate ranged from 7×10^{-2} to 7×10^{-4} Pa/sec), the kinetics of nitriding is sensitive to processes related to the nitrogen feed to the gas–metal interaction zone (Fedirko & Pohrelyuk, 1995). Under such conditions, in a certain time range, which depends on the nitriding temperature, one can maintain the dynamic equilibrium between the adsorbed nitrogen and nitrogen transported by diffusion in the depth of the titanium matrix and shift significantly in time the beginning of the formation of a continuous nitride film. Metallographic analysis of the surface of VT1-0 titanium samples nitrided in this range of gas-dynamic (1 Pa; 7×10^{-3} Pa/sec) and temperature–time (750-850 °C; 5 h) parameters confirmed the absence of a continuous nitride film on their surfaces (Fig. 4). Instead of it, we observe the initiation and growth of nitride islands, predominantly between grains (Fig. 4 a-c).
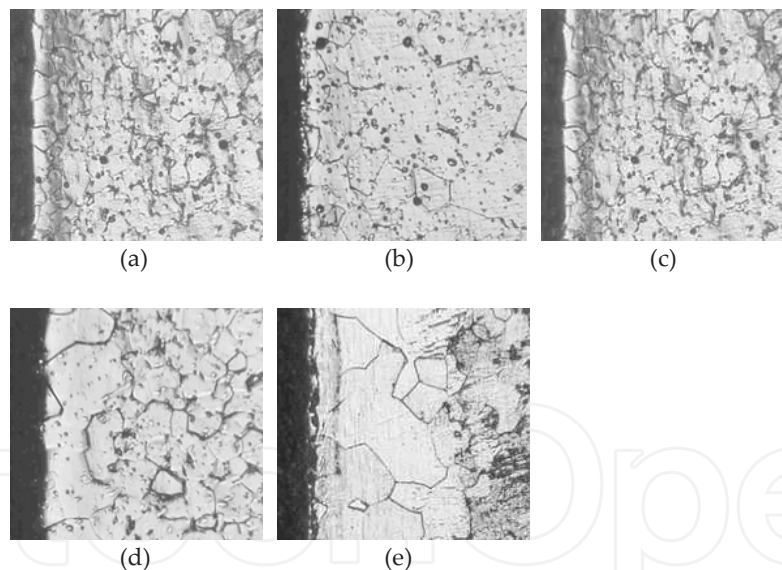

| (a) | (b) | (c) | (d) |
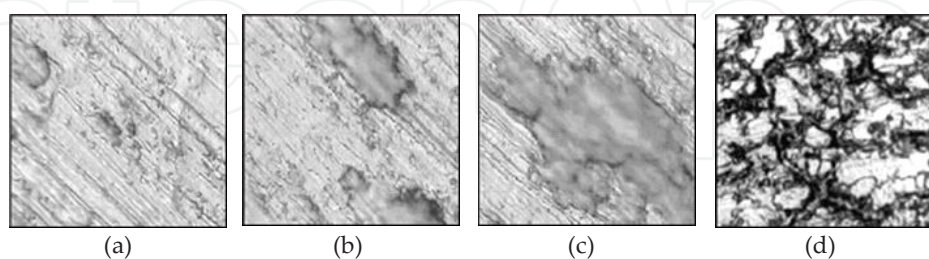
Figure 4. Surface of VT1-0 titanium after nitriding in a rarefied dynamic nitrogen atmosphere (1 Pa): (a) 750 °C, 5 h; (b) 800 °C, 5 h;(c) 850 °C, 5 h; (d) 850 °C, 10 h

After an exposure for 10 h at 850 °C (Fig. 4 d), almost all grain boundaries contain nitrides, which favor the formation of a surface network from nitride inclusions and the formation of the corresponding surface topography. The dissolution of nitrogen in titanium stabilizes an

α-solid solution, the layer of which increases in thickness as the temperature–time parameters increase; its grains are etched less than the matrix (Fig. 5).

The surface microhardness of titanium changes as a result of nitride formation. After nitriding at 750 and 800 ^{0}C for 5 h and at 850 ^{0}C for 1 h when nitride formation is not very intensive, which is evidenced by reflexes of relative intensity of the nitride of lower valence (Ti$_2$N), the surface microhardness of titanium ranges from 4.4 to 7.3 GPa (Fig. 6). As the exposure time increases to 5 – 10 h at 850^{0}C when nitride islands cover a major part of the surface of the alloy, it rises to 10–13 GPa. The temperature–time nitriding parameters affect the surface micro-hardness of titanium and the depth of the nitrided layer, which increases monotonically in thickness with the temperature and time of exposure in a nitrogen-containing atmosphere (Fig. 6 c, d). Temperature influences analogously the surface microhardness for a given exposure time (Fig. 6 a). The effect of the time of saturation at 850 ^{0}C is somewhat different. As the exposure time increases from 1 to 5 h, the microhardness increases 2.5 times, and as the exposure time increases from 5 to 10 h, it rises only by 1.67 GPa (Fig. 6 b).


(a)   (b)   (c)

(d)   (e)

Figure 5. Microstructure of surface layers of VT1-0 titanium nitrided in a rarefied dynamic nitrogen atmosphere (1 Pa): (a) 750 ^{0}C, 5 h;(b) 800 ^{0}C, 5 h; (c) 850 ^{0}C, 1 h; (d) 850 ^{0}C, 5 h; (e) 850 ^{0}C, 10 h

Curves of the distribution of the microhardness over a cross-section of the hardened surface layers shift in the direction of higher values of the hardness with increases in the saturation temperature (Fig. 7 a) and saturation time (Fig. 7 b). During nitriding at a temperature of 850 ^{0}C for 5 h, the surface hardening of titanium is more significant than those at 750 and 800 ^{0}C and the same exposure time (Fig. 7 a).
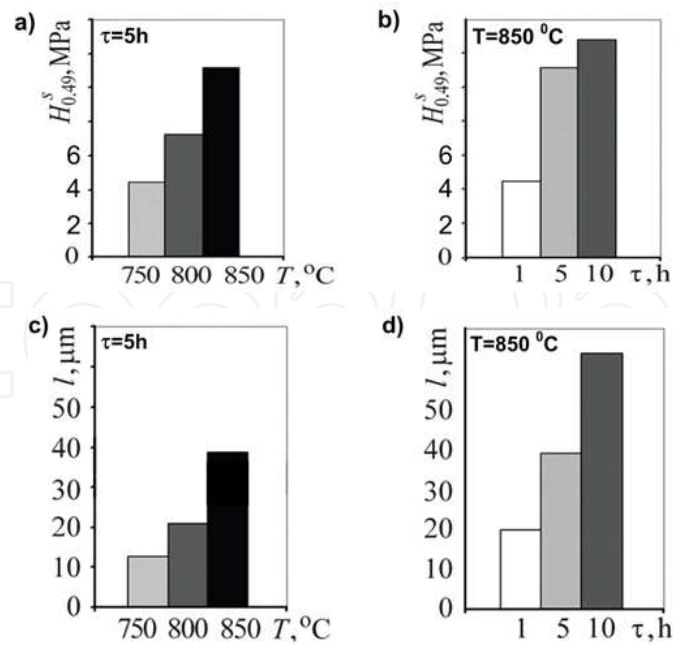
Figure 6. Dependences of the surface microhardness (a, b) and the depth of the hardened zone (c, d) on the temperature–time nitriding parameters of VT1-0 titanium in a rarefied dynamic atmosphere (1 Pa)
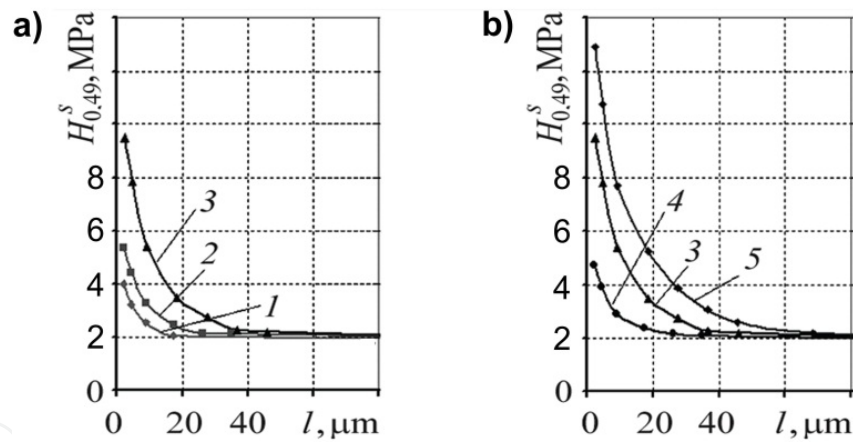
Figure 7. Distribution of the microhardness over the cross-section of surface layers of VT1-0 titanium nitrided in a rarefied dynamic atmosphere (1 Pa) depending on the temperature (a) and time of an isothermal exposure (b): (1) 750 ⁰C, 5 h; (2) 800 ⁰C, 5 h; (3) 850 ⁰C, 5 h; (4) 850 ⁰C, 1 h; (5) 850 ⁰C, 10 h

2.3. Assessment of the temperature–time parameters of nitriding and analysis of results

It is known that the profile of nitrogen concentration in the surface layer of titanium substantially affects its physicomechanical properties. For experimental investigations of hardened nitrided layers, the method of layer-by layer testing of microhardness, which substantially depends on the content of dissolved nitrogen in titanium, is widely used. Let us use a known linear dependence of change of the microhardness on the concentration of an interstitial impurities in titanium (Korotaev et al., 1989):

$$H(x,\tau) = H_0 + a \cdot [C(x,\tau) - C_0] \qquad (10)$$

Then the relative change in the microhardness in the diffusion zone due to dissolved nitrogen (neglecting the contribution of nitride inclusions) is as follows:

$$\bar{H}(x,\tau) = [H(x,\tau) - H_0]/[H_{max} - H_0] \equiv \bar{C}(x,\tau) \qquad (11)$$

Here H_0 is the microhardness of the initial titanium sample, H_{max} is the microhardness of titanium at a maximum concentration of dissolved nitrogen $C_{max}=C_{eq}$, and a is the proportionality coefficient. Relation (11) indicates the possibility to plot the calculated relative concentrations $\bar{C}(x, \tau)$ of nitrogen and experimental data of the relative change in the microhardness $\bar{H}(x, \tau)$, on the same ordinate axis.

The roles of the time parameter and temperature are illustrated by analytic curves of the nitrogen content (Fig. 8, Fig. 9, Fig. 10), constructed from relations (6) – (8), and experimental data (see Fig. 4) using relation (11). For analytic calculations the following parameters were used: for T=750 ^{0}C – D =1•10^{-11} cm^2/sec, h=1•10^{-8} cm^2/ sec; for T=800 ^{0}C – D = 3.4•10^{-11} cm^2/sec, h = 3•10^{-8} cm/sec; for T = 850 ^{0}C – D=1•10^{-10} cm^2/sec, h=1•10^{-7} cm/sec; ω = 10^{-5} cm, k/h = 0.002. Diffusion coefficients of nitrogen were calculated according to the dependence $D = D_0 \exp(-E/RT)$, where D$_0$=0.96 cm^2/sec, E=214.7 kJ/mole (Metin & Inal, 1989). An analysis of these curves gives grounds for the following conclusions.

For an isothermal exposure T=850 ^{0}C in nitrogen, with increase in the saturation time, both the surface concentration of dissolved nitrogen C(0, τ) (curve 1) and its concentration in nitride inclusions C*(0, τ) (curve 2), as well as its total content C$_\Sigma$(0, τ) (curve 3, Fig. 8 a), increase.
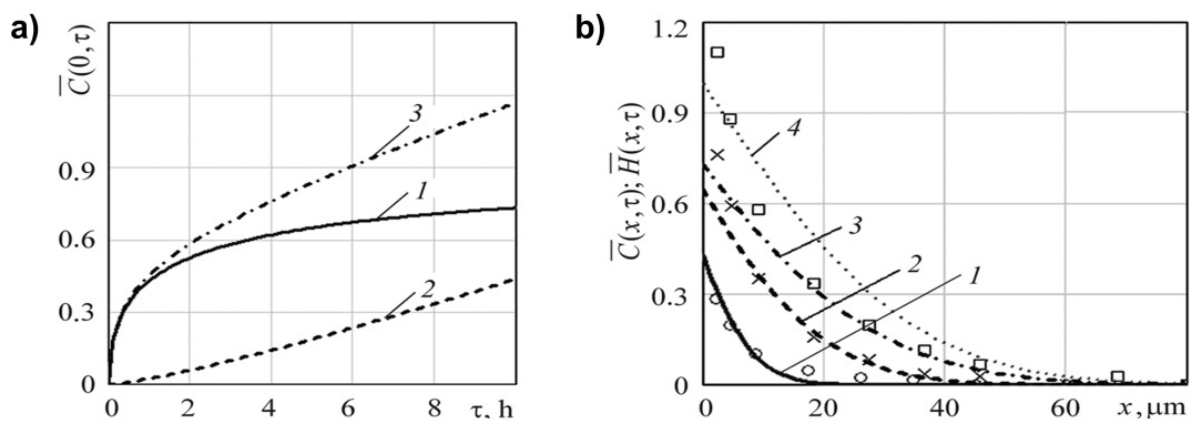
Figure 8. Time dependence of the surface nitrogen content ((a): curve (1) in the solid solution$C(0, \tau)$; (2) in nitride inclusions $C^*(0, \tau)$; (3) total content $C_\Sigma(0, \tau)$and its distribution in the surface layer of titanium (b) for different exposure times: (1), τ = 1 h; (2) τ = 5 h, (3) and (4) τ = 10 h (curve (4) was constructed for the condition $C(0, \tau)$=const,$h \to \infty$) at a nitriding temperature T = 850 ^{0}C. Marks correspond to experimental data (H(x, τ))

The nitrogen content in the surface layer and the depth of the diffusion zone change additively as the exposure time (curves 1 – 3, Fig. 8 b) and the temperature of the isothermal exposure (curves 1 – 3, Fig. 9) change.

On the whole, the analytic calculations of content profiles correlate well with the experimental results of relative changes in the microhardness of the surface layer (Fig. 8 b, Fig. 9). The corresponding curves have a monotonic character; the microhardness over the cross-section of the sample decreases gradually in the depth of the metal until it attains values characteristic for titanium. At the same time, there are insignificant disagreements between the theoretical and experimental results. In particular, for short exposures, the zone of change of the micro-hardness extends to a larger depth than the value which follows from the nitrogen distribution (Fig. 8 b). This can be explained by an insignificant content of oxygen, which is characterized by a larger diffusion mobility than nitrogen. For larger exposure times when the percentage of nitrogen is larger than that of oxygen, this effect is leveled.
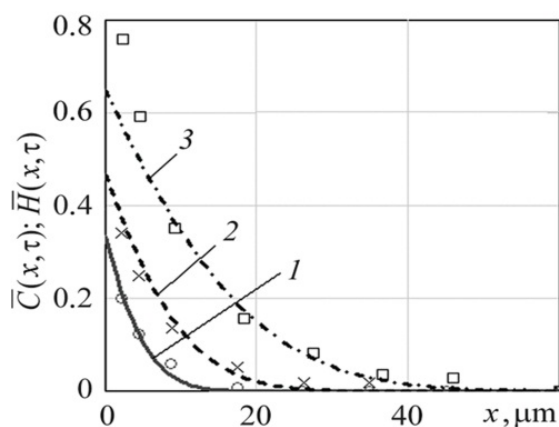

Figure 9. Distribution of nitrogen in the surface layer of titanium after an exposure $\tau = 5$ h for different saturation temperature: (1), 750 ^{0}C; (2), 800 ^{0}C; (3), 850 ^{0}C. Marks correspond to experimental data $\bar{H}(x, \tau)$

Some disagreement between the calculated nitrogen distribution and experimental data of change in the microhardness is also observed near the surface, particularly as the time (Fig. 8 b) and temperature (Fig. 9) of the treatment increase. In our opinion, this is due to the influence of nitride inclusions, the content of which increases under such conditions, on the microhard-ness. That is why it is more expedient to use the modified dependence (11) with allowance for such an influence.

Not only data of the surface concentration of nitrogen (correspondingly, the hardness as well), but also data of its concentration at a certain distance from the surface and the depth of the nitrided layer depending on the temperature–time parameters are of practical interest. The corresponding curves (Fig. 10) were constructed for the same parameters as in the preceding figures. It should be noted that the depth of the diffusion zone was determined behind the front of propagation of the relative nitrogen concentration $\bar{C} = 0.02$, which corresponds to a change in the microhardness by an amount $H_\delta = 0.2$ GPa, equal to the error in its measurements.

An analysis of these curves confirms an adequate increase in the nitrogen content over the whole depth of the diffusion zone and the increase in the depth of this zone as the treatment time and temperature increase (curves 1–3, Fig. 10). It was found that, in the statement of the first boundary-value problem ($h \rightarrow 0$, $C(0, \tau) = Const$), overestimated values of the nitrogen concentration were obtained (curves 4 in Fig. 8 b Fig. 10). The calculated data show that the surface phenomena affect substantially not only the surface concentration of nitrogen (Fig. 10 a) (correspondingly, the surface hardness of titanium), but also the nitrogen content in layers more remote from the surface (Fig. 10 b), and the depth of the hardened diffusion zone (Fig. 10 c).
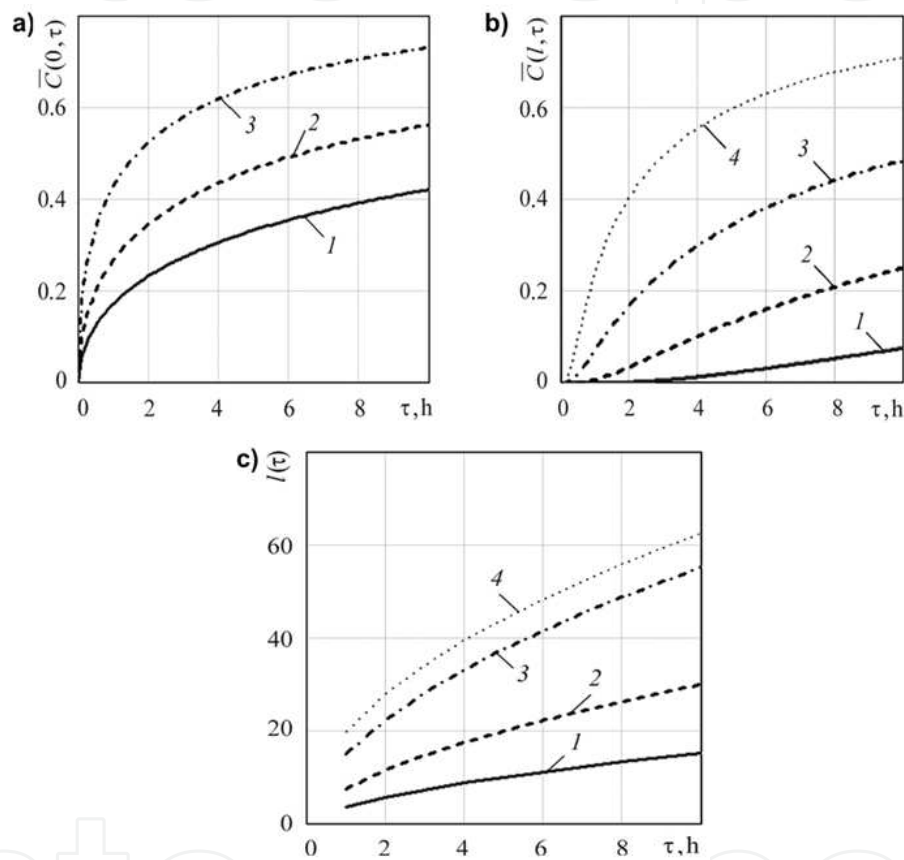
Figure 10. Time dependence of the content of dissolved nitrogen on the surface (a) and at a depth x = 10 μm (b), and the depth of the nitrided layer (c) for different saturation temperatures: (1) 750 ⁰C; (2) 800 ⁰C; (3, 4) 850 ⁰C (curves 4 were constructed for the condition $C(0, \tau)$ = const, h → ∞)

Thus, the presented results indicate the critical role of the surface phenomena (adsorption and chemisorption) in the kinetic regularities of nitriding of titanium in a rarefied atmosphere. The calculated data obtained on the basis of the solution of the diffusion task using the nonstationary boundary condition (2) indicate that its model representation reflects rather satisfactorily the main tendencies of the high-temperature interaction of titanium with rarefied nitrogen. For the provision of a specified hardened layer, the proposed model gives scientifically justified recommendations on external parameters (exposure temperature and time) of nitriding of titanium.

3. Kinetic peculiarities of thermodiffusion saturation of titanium with interstitial elements at T>T$_{\alpha \leftrightarrow \beta}$

3.1. Thermodynamic analysis

According to the phase diagram (Fig. 11 a, b), titanium undergoes allotropic transformation (change of crystal lattice from hcp to bcc) at T$_{\alpha \leftrightarrow \beta}$ = 882 ^{0}C (Fromm & Gebhardt, 1976).
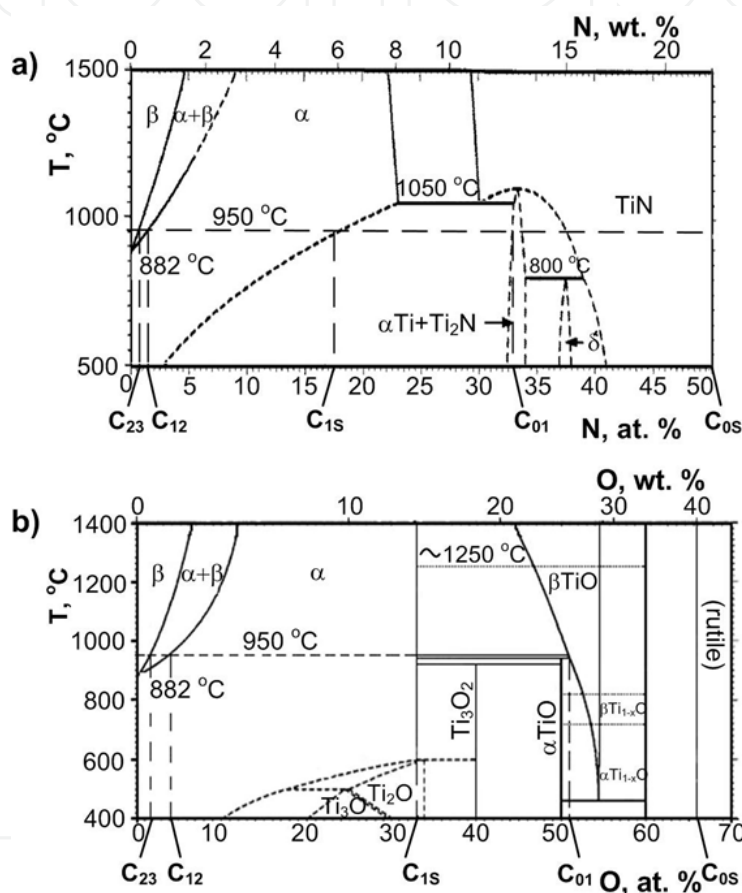
Figure 11. Ti-N (a) and Ti-O (b) phase diagrams (Fromm & Gebhardt, 1976)

We will be interested in high-temperature (T>T$_{\alpha \leftarrow \beta}$) interaction of titanium with the interstitial element A (A – N (nitrogen) or O (oxygen)). Under these conditions, according to the phase diagrams (Fig. 11 a, b), titanium nitrides or oxides (TiA$_x$) as products of chemical reactions and solid solutions of nitrogen or oxygen in α and β-phases of titanium are stable in the system.

In particular, in the concentration range $0 < C_A < C_{23}$ solid solution of interstitial element in β-phase is stable, while in the concentration range $C_{12} < C_A < C_{1S}$ – solid solution of interstitial element in α-phase. In the concentration range $C_{23} < C_A < C_{12}$ solid solutions of interstitial element in α- and β-phases can coexist.

It should be noted that the solubility of nitrogen and oxygen in α-phase is high in comparison with β-phase. At the same time, their diffusion coefficients in α-phase are by two orders lesser than in β-phase (Fedirko & Pohrelyuk, 1995; Fromm & Gebhardt, 1976; Panasyuk, 2007). The solubility and diffusion coefficient of oxygen in α- and β-phases are much higher in comparison with nitrogen.

3.2. Physico-mathematical model

Let us consider the process of isothermal saturation of titanium by nitrogen or oxygen at temperature higher than temperature of allotropic transformation ($T>T_{\alpha\leftarrow\beta}$). In this case the initial microstructure of titanium consists of β-phase. According to the thermodynamic analysis, the following scheme of the gas-saturated layer of titanium is suggested (Fig. 12) (Tkachuk, 2012).
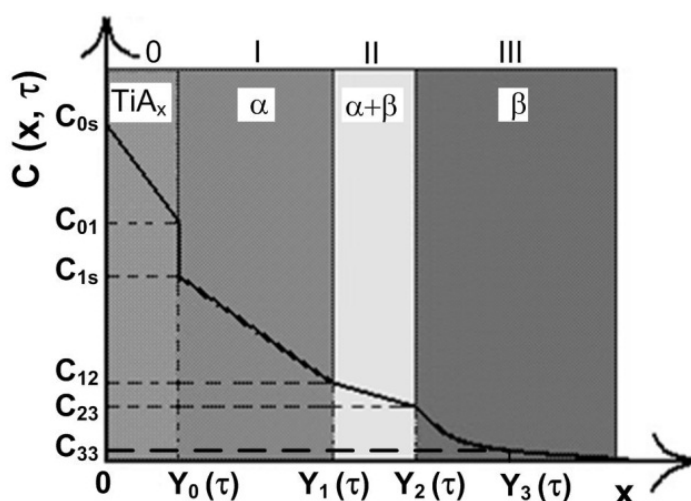
Figure 12. Scheme of the concentration distribution of interstitial element A (N or O) during saturation of titanium at $T>T_{\alpha\leftarrow\beta}$

During the interaction of titanium with nitrogen or oxygen nitride or oxide layer ($0 < x < Y_0(\tau)$) and diffusion zone are formed. The diffusion zone consists of three layers. The layer I ($Y_0(\tau) < x < Y_1(\tau)$), which borders on the nitride layer, is α-phase, significantly enriched in nitrogen or oxygen because of their high solubility in α-phase. This layer is formed and it grows during saturation because of diffusion dissolution of nitrogen or oxygen and structural transformations in titanium, because these interstitial elements are α-stabilizers. The layer III ($Y_2(\tau) < x < \infty$), which borders on the titanium matrix, at the temperature of saturation consists of β-phase enriched by nitrogen or oxygen. Between the first and third layers the layer II ($Y_1(\tau) < x < Y_2(\tau)$) is formed, which is the dispersed mixture of α- and β-phases, enriched in nitrogen or oxygen.

For analytical description of the process of saturation of titanium by nitrogen or oxygen some model assumptions should be done. The aim of thermochemical treatment of titanium samples is strengthening of their surface layer and as the object of analytical investigation of the kinetics of diffusion saturation of titanium the half-space ($0 \leq x < \infty$) has been chosen. Nitride or oxide

film is formed immediately. Surface concentration of nitrogen or oxygen does not change with time and corresponds to stoichiometric titanium nitride (TiN) or oxide (TiO₂). On the interfaces the nitrogen or oxygen concentration, corresponding to equilibrium concentration, according to the phase diagram is constant (Fig. 11 a, b).

The diffusion process in such heterogeneous system will be described by Fick's system of equations:

$$D_i \partial^2 C_i(x,\tau) / \partial x^2 = \partial C_i(x,\tau) / \partial \tau \ , \quad i = 0,1,2,3. \tag{12}$$

Here $C_i(x,\tau)$ and D_i are concentration and diffusion coefficients of the interstitial element; index i=0 corresponds to nitride TiN_x or oxide TiO_{2-x} layer ($0 < x < Y_0(\tau)$); i=1 – α-Ti layer ($Y_0(\tau) < x < Y_1(\tau)$); i=2 – ($\alpha+\beta$)-Ti layer ($Y_1(\tau) < x < Y_2(\tau)$); i=3 – β-Ti layer ($Y_2(\tau) < x < \infty$)).

Initial conditions (τ=0):

$$C_i(x,0) = 0, \quad Y_i(0) = 0 \quad for \ x > 0. \tag{13}$$

Boundary conditions (τ>0):

$$C_0(0,\tau) = C_{0S}, \quad C_3(\infty,\tau) = 0, \quad C_0[Y_0(\tau),\tau] = C_{01}, \quad C_1[Y_0(\tau),\tau] = C_{1S},$$
$$C_1[Y_1(\tau),\tau] = C_2[Y_1(\tau),\tau] = C_{12} \ , \quad C_2[Y_2(\tau),\tau] = C_3[Y_2(\tau),\tau] = C_{23} \ . \tag{14}$$

The motion of interfaces will be set by the parabolic dependencies (Lyubov, 1981):

$$Y_0(\tau) = 2 \cdot \beta_0 \cdot \sqrt{D_0 \cdot \tau} \ , \quad Y_1(\tau) = 2 \cdot \beta_1 \cdot \sqrt{D_1 \cdot \tau} \ , \quad Y_2(\tau) = 2 \cdot \beta_2 \cdot \sqrt{D_2 \cdot \tau} \ . \tag{15}$$

Here β_j (j=0,1,2) are dimensionless constants (for the specific temperature), which will be determined from the law of conservation of mass on the interfaces. Thus for diffusion fluxes on the interfaces $Y_j(\tau)$ are set:

$$-D_0 \frac{\partial C_0}{\partial x}\bigg|_{x=Y_0(\tau)-0} + D_1 \frac{\partial C_1}{\partial x}\bigg|_{x=Y_0(\tau)+0} = (C_{01} - C_{1S}) \frac{dY_0(\tau)}{d\tau} \ ,$$
$$D_1 \frac{\partial C_1}{\partial x}\bigg|_{x=Y_1(\tau)-0} = D_2 \frac{\partial C_2}{\partial x}\bigg|_{x=Y_1(\tau)+0} \ , \quad D_2 \frac{\partial C_2}{\partial x}\bigg|_{x=Y_2(\tau)-0} = D_3 \frac{\partial C_3}{\partial x}\bigg|_{x=Y_2(\tau)+0} \tag{16}$$

It is difficult to solve the equations system (12) – (16) in analytical form. The method of approximate solution of above mentioned task should be used (Lykov, 1966). It is accepted the linear distribution law of the concentration of the interstitial element in TiA_x layer (Fig. 12)

corresponded to the quasi-stationary state. It is accepted the same distribution law in the first two layers of diffusion zone. It was considered that in the third layer of diffusion zone the distribution of the interstitial element is realized by Gauss's law:

$$C_0(x,\tau) = C_{0S} - (C_{0S} - C_{01})\frac{x}{Y_0(\tau)}, \quad C_1(x,\tau) = C_{1S} - (C_{1S} - C_{12})\frac{x - Y_0(\tau)}{Y_1(\tau) - Y_0(\tau)},$$
$$C_2(x,\tau) = C_{12} - (C_{12} - C_{23})\frac{x - Y_1(\tau)}{Y_2(\tau) - Y_1(\tau)}, \quad C_3(x,\tau) = C_{23} erfc\frac{x - Y_2(\tau)}{2\sqrt{D_3\tau}}.$$

(17)

The chosen functions $C_i(x,\tau)$ satisfy the initial (13) and boundary (14) conditions as well as the differential equations (12). The following system of equations for calculating the parameters β_j (j=0,1,2) was obtained by the conditions of mass balance on interfaces (16) and relation (15) (Tkachuk et al., 2012):

$$\frac{A_0}{2\beta_0}[\frac{1}{\beta_0} - \frac{1}{A_1\lambda_0(\beta_1 - \beta_0\lambda_0)}] = 1, \quad \frac{(\beta_1 - \beta_0\lambda_0)}{A_2\lambda_1(\beta_2 - \beta_1\lambda_1)} = 1, \quad \frac{2(\beta_2 - \beta_1\lambda_1)}{A_3\lambda_2\sqrt{\pi}} = 1.$$

(18)

Having solved the system of equations (18), following equations were:

$$\beta_0 = A_0(\sqrt{B^2 + 2/A_0} - B)/2, \qquad \beta_1 = \beta_0\lambda_0 + A_2A_3\lambda_1\lambda_2\sqrt{\pi}/2,$$
$$\beta_2 = \beta_1\lambda_1 + A_3\lambda_2\sqrt{\pi}/2,$$

(19)

where

$$B = 1/[A_1A_2A_3\lambda_0\lambda_1\lambda_2\sqrt{\pi}], \quad \lambda_0 = \sqrt{D_0/D_1}, \quad \lambda_1 = \sqrt{D_1/D_2}, \quad \lambda_2 = \sqrt{D_2/D_3},$$
$$A_0 = \frac{C_{0S} - C_{01}}{C_{01} - C_{1S}}, \quad A_1 = \frac{C_{0S} - C_{01}}{C_{1S} - C_{12}}, \quad A_2 = \frac{C_{1S} - C_{12}}{C_{12} - C_{23}}, \quad A_3 = \frac{C_{12} - C_{23}}{C_{23}}.$$

The parameters β_j depend on concentration of nitrogen or oxygen on interfaces and their diffusion coefficients in α- and β-phases, which in turn depend on the temperature. In particular, for saturation temperature of T=950 °C the diffusion coefficients of nitrogen and oxygen in surface layers of titanium, and equilibrium concentrations of nitrogen and oxygen on interfaces, according to the corresponding phase diagrams (Fig. 11 a, b), are presented in Table 1.

Taking the values of these parameters, according to relations (19), the constants β_j for nitrogen and oxygen were calculated (Table 2).

A	D_0, cm²/ sec	D_1, cm²/ sec	D_2, cm²/ sec	D_3, cm²/ sec	C_{0s}, at. %	C_{01}, at. %	C_{1s}, at. %	C_{12}, at. %	C_{23}, at. %	C_{33}, at. %
N	3×10^{-12}	2.5×10^{-10}	2.5×10^{-9}	3.2×10^{-8}	50	33	17.5	1.5	0.75	0.25
O	2.5×10^{-11}	2.1×10^{-9}	2.1×10^{-8}	1.6×10^{-7}	66	51	33	4	2	0.25

Table 1. Diffusion coefficients of nitrogen and oxygen in the surface layer of titanium (Fedirko & Pohrelyuk, 1995; Fromm & Gebhardt, 1976; Panasyuk, 2007) and equilibrium concentration of nitrogen and oxygen on the interfaces at saturation temperature of T=950 °C

A	β_0	β_1	β_2	K_0, cm/ sec ¹/²	K_1, cm/ sec ¹/²	K_2, cm/ sec ¹/²
N	0.183	1.691	0.782	6.328×10^{-7}	5.348×10^{-5}	7.825×10^{-5}
O	0.082	1.481	0.789	8.175×10^{-7}	1.357×10^{-4}	2.288×10^{-4}

Table 2. Calculated constants β_j and K_j (j=0,1,2) at saturation temperature of T=950 °C

Taking into consideration the correlation (15), the motion of interfaces will be presented as:

$$Y_0(\tau) = K_0 \sqrt{\tau} \ , \quad Y_1(\tau) = K_1 \sqrt{\tau} \ , \quad Y_2(\tau) = K_2 \sqrt{\tau} \ , \tag{20}$$

where $K_0 = 2\beta_0 \sqrt{D_0}$, $K_1 = 2\beta_1 \sqrt{D_1}$, $K_2 = 2\beta_2 \sqrt{D_2}$ – constants of the parabolic growth of nitride or oxide layer and α, ($\alpha+\beta$) layers of diffusion zone stabilized by nitrogen or oxygen. In particular, for saturation temperature of T=950 °C these calculated constants are presented in Table 2.

Having found the constants of parabolic growth of the layers, and having used the relations (20), it is easy to foresee the kinetics of motion of interfaces: $Y_0(\tau)$ – interface of nitride or oxide layer (Fig. 13 a), $Y_1(\tau)$ – interface of solid solution of interstitial element in α-phase (Fig. 13 b), $Y_2(\tau)$ – interface of mixture of solid solutions of interstitial element in α- and β-phases (Fig. 13 c), $Y_3(\tau)$ – interface of solid solution of interstitial element in β-phase (Fig. 13 d) at nitriding and oxidation of titanium at T=950 °C. One could notice that the last interface is identified by the motion of conventional boundary with the specific nitrogen or oxygen concentration, for example C_{33} = 0.25 at. %, that is from transcendental equation $C_3(Y_3(\tau), \tau) = C_{33}$.

Calculated constants $Y_i(\tau)$ (i=0,1,2,3) after isothermal exposures of 1 and 5 h during nitriding and oxidation of titanium at T=950 °C are presented in Table 3. It is clear that according to the assumptions (15) with the increase of processing time the motion of interfaces (Fig. 13 a, b, c, d) occur according to the parabolic dependences proportionally to the corresponding constants of parabolic growth K_j (j=0,1,2).

On the basis of relations (17) the concentration profiles of nitrogen (curves 1) and oxygen (curves 2) in the diffusion zone of titanium after nitriding and oxidation during 1 h (Fig. 14 a) and 5 h (Fig. 14 b) are calculated.
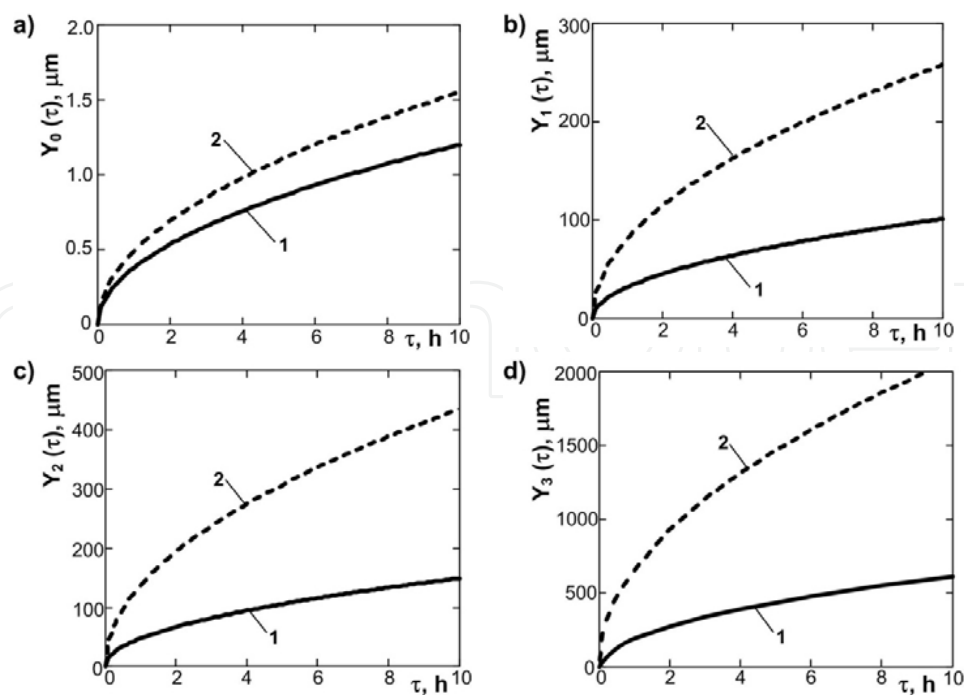
Figure 13. Kinetics of motion of interfaces $Y_0(\tau)$ (a), $Y_1(\tau)$ (b), $Y_2(\tau)$ (c) and $Y_3(\tau)$ (d) at nitriding (curves 1) and oxidation (curves 2) of titanium at saturation temperature of T=950 ^{0}C

The diffusion coefficient of nitrogen or oxygen in β-phase is by two-four orders higher than in α-phase and in nitride or oxide layers, that's why the thickness of β layer is much larger than the thickness of the other layers of diffusion zone (Fig. 13). If the thickness of nitride layer is less than 0.2% and oxide layer is less than 0.1 % of the total thickness of diffusion zone ($Y_3(\tau)$), the thickness of α, α + β and β layers will be 16, 8 and 76 % for nitriding and 12, 8 and 80 % for oxidation respectively.

A	τ = 1 h				τ = 5 h			
	Y_0, μm	Y_1, μm	Y_2, μm	Y_3, μm	Y_0, μm	Y_1, μm	Y_2, μm	Y_3, μm
N	0.4	32	47	194	0.85	72	105	433
O	0.5	81	137	658	1.1	182	307	1470

Table 3. Calculated $Y_i(\tau)$ (i=0,1,2,3) after isothermal exposures of 1 and 5 h at saturation temperature of T=950 ^{0}C

At the same time, the different solubility of nitrogen or oxygen in α and β-phases influences on the distribution of nitrogen or oxygen in the diffusion zone. When the structural phase transformations did not occur in the diffusion zone, the profiles of nitrogen and oxygen in this zone would be with a small gradients because of the low solubility of nitrogen or oxygen in β-phase. In fact, nitrogen and oxygen, being α-stabilizers, stimulate the β→ α phase transformation in the layers of the diffusion zone adjacent to nitride or oxide layer. And as the solubility

of nitrogen and oxygen in α-phase is much higher than in β-phase, it can be foreseen that in zone I the profiles of nitrogen and oxygen will have a large gradients (Fig. 14), and respectively the distributions of microhardness in this zone will have a large gradients. It has been confirmed by the literature data (Lazarev et al., 1985) and the experimental investigations' data on nitriding.
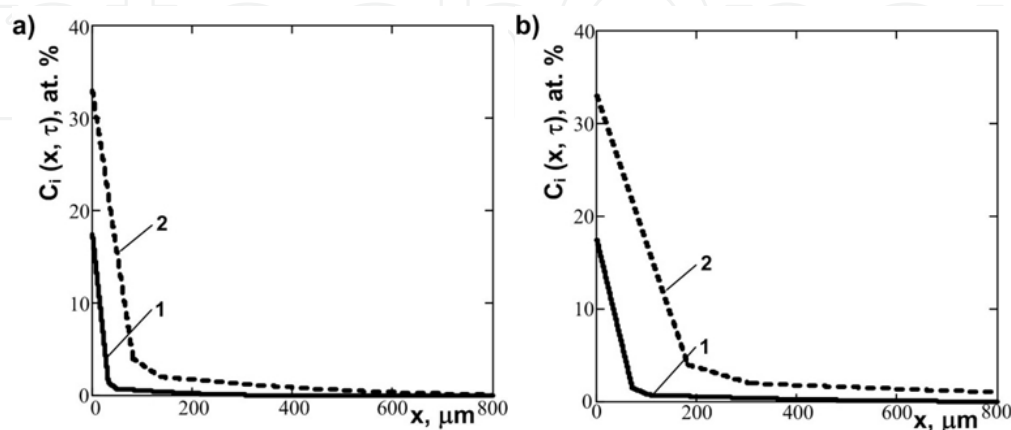
Figure 14. Concentration profiles of nitrogen and oxygen in diffusion zone of titanium after its saturation at T=950 ^{0}C for two isothermal exposures: a - τ = 1 h; b - τ = 5 h; curves 1 – for nitrogen, curves 2 – for oxygen

It was observed 2.5-3.0 times larger thickness of all layers of diffusion zone after oxidation comparing to nitriding (Fig. 13 b, c, d) as a result of the higher on order diffusion coefficients of oxygen in α- and β-phases compared to the diffusion coefficients of nitrogen (Table 1). Also the larger concentration gradient of oxygen in the layer I adjacent to oxide layer than concentration gradient of nitrogen in the layer I adjacent to nitride layer was received (Fig. 14). It is caused by higher solubility of oxygen in comparison with nitrogen in α-phase (Table 1).

3.3. Experimental procedure

Experimental investigation on the example of nitriding of titanium at the temperature of T=950 ^{0}C was conducted to check the validity of the above elaborated model representations.

Commercially pure (c.p.) titanium samples with dimensions of 10×15×4 mm were investigated. The samples were polished (R$_a$=0,4 µm), washed with deionized water prior to the treatment. The samples were heated to nitriding temperature in a vacuum of 10^{-3} Pa. Then they were saturated with molecular nitrogen of the atmospheric pressure at temperature of 950 ^{0}C. The isothermal exposure time in nitrogen was 1 and 5 h. After isothermal exposure the samples were cooled in nitrogen to room temperature.

The microstructure of nitride layers was studied by the use of metallographic microscope "EPIQUANT". Distribution of microhardness on cross section of surface layers of c.p. titanium after nitriding was estimated measuring microhardness at loading of 0.49 N.

3.4. Results and discussion

The nitride layer of goldish colour is formed on the surface of c.p. titanium after nitriding. Its colour is darkening with the increase of isothermal exposure time in nitrogen atmosphere. It indicates the increase of its thickness.

The diffusion zone is formed under titanium nitride layer (Fig. 15 a, b).

(a)   (b)
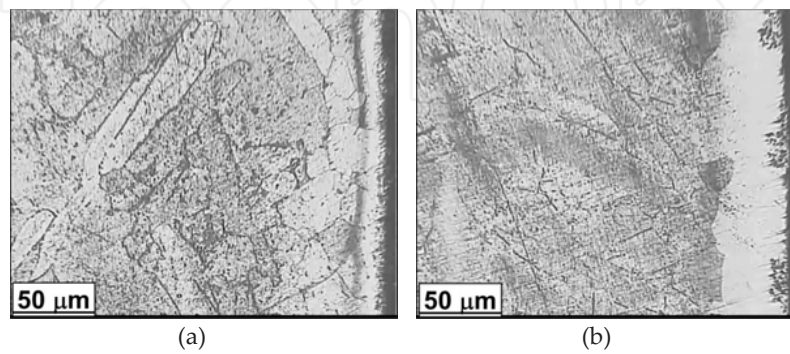
Figure 15. Microstructure of surface layer of c.p. titanium for nitriding at τ=1 (a) and 5 h (b) (T=950 ^{0}C, p=10^5 Pa)

It is difficult to find the layer II (Fig. 12) in this zone which, according to the phase diagram (Fig. 11 a) has to form. However, two parts of diffusion zone (zone A and zone B) of different structure are clearly identified. Zone A is α-phase formed during nitriding by nitrogen as α-stabilizer. Its thickness, according to data of metallographic analysis, increases from 20 to 45 μm with the increase of duration of nitriding from 1 to 5 h. Zone B is α-phase on the basis of solid solution of nitrogen, however formed as a result of $\beta \rightarrow \alpha$ transformation at cooling.

The results of investigation of character of distribution of microhardness on cross section of surface layers of c.p. titanium after nitriding are presented in Fig. 16 a. It is distinguished zone A (layer I, Fig. 12) and zone B (probably, layer II + layer III, Fig. 12) on curves of distribution of microhardness.
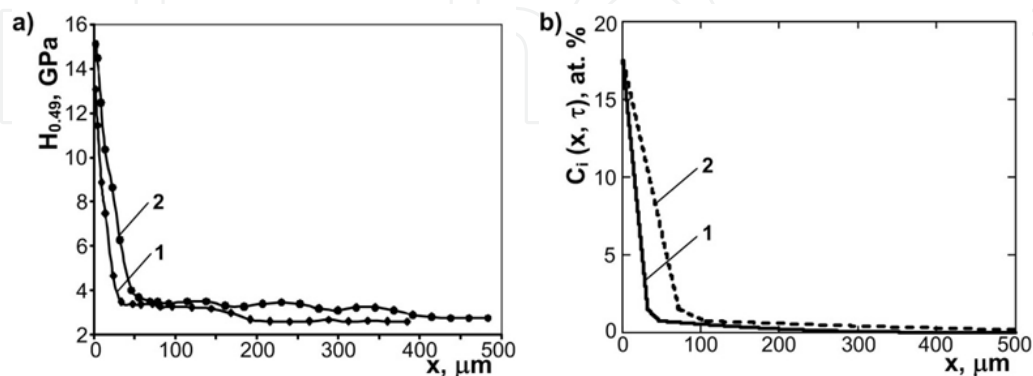
Figure 16. Distribution of nitrogen in diffusion zone of titanium (theory) (a) and distribution of microhardness on cross section of surface layer of c.p. titanium (experiment) (b) after its nitriding at T=950 ^{0}C and p=10^5 Pa for two iso-thermal exposure times: curve 1 – τ = 1 h; curve 2 – τ = 5 h

The large gradient of microhardness is characteristic for zone A. It is caused by $\beta \to \alpha$ transformation as a result of saturation by nitrogen as α-stabilizer and comparatively its high solubility in α-phase. With increasing distance from surface the microhardness is decreased sharply (Fig. 16 a) that is explained by decrease of nitrogen concentration (Fig. 16 b). The hardness of zone B is considerably less than zone A because of large difference of nitrogen solubility in α- and β-phases. The thickness of these zones is increased with the increase of duration of nitriding (Fig. 16 a). In particular, the thickness of zone A is 34 μm for τ= 1 h and 69 μm for τ=5 h. It can be noticed that this thickness is larger than corresponding thickness, determined by the data of metallographic analysis. The total depth of diffusion zone (zone A + zone B) is 185 μm for τ= 1 h and 425 μm for τ=5 h (Fig. 16 a).

The received analytical distribution of nitrogen (Fig. 16 b) and results of microhardness measurements (Fig. 16 a) confirm the correlation between model calculations and experimental data.

4. Conclusions

The process of high-temperature interaction of titanium with gaseous medium (nitrogen or oxygen) was modelled at temperatures $T<T_{\alpha \leftrightarrow \beta}$ and $T>T_{\alpha \leftrightarrow \beta}$ considering the surface processes and structural phase transformations.

The kinetics of surface processes is reflected by the mass balance equation, which takes into account the interaction of an external flux of impurities to the surface and its chemisorption with diffusion dissolution and segregation on defects as a result of a chemical interaction with titanium atoms.

The kinetics of diffusion saturation of α-titanium by nitrogen under rarefied atmosphere (1 Pa) in the temperature range of 750-850 ^{0}C was investigated experimentally and analytically. The influence of time and temperature parameters on the depth of the nitrided layer and a change of its microhardness was estimated.

It was shown the role of these interstitial elements as α-stabilizers in forming the diffusion zone which contains three layers based on α-phase, $\alpha+\beta$-phases and β-phase.

It was received the solution of the formulated task as for diffusion of nitrogen or oxygen in such a heterogeneous medium taking into account the motion of interfaces.

The constants of parabolic growth of layers were calculated. It allowed to foresee the kinetics of their growth and distribution of interstitial elements (nitrogen or oxygen) in diffusion zone.

The adequacy of the proposed model representations was confirmed by the results of experimental investigations on nitriding of titanium at T=950 ^{0}C. The microstructural evolution (after processing times of 1 and 5 h) of the diffusion zone which is caused by the structural phase transformations during diffusion of nitrogen was examined experimentally.

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References

[1] Fedirko, V. M. & Pohrelyuk, I. M. (1995). *Nitriding of Titanium and its Alloys*, Naukova Dumka, Kiev

[2] Fedirko, V. M., Matychak, Ya. S., Pohrelyuk, I. M. & Prytula, A. O. (2005). Description of the diffusion saturation of titanium with nonmetallic admixtures with regard for their segregation on the surface. *Materials Science*, Vol. 41, No. 1, pp. 39–46

[3] Fromm, E. & Gebhardt, E. (1976). *Gase und Kohlenstoff in Metallen*, Springer-Verlag, Berlin-Heidelberg-New York

[4] Kofstad, P. (1966). *High-Temperature Oxidation of Metals*, John Wiley & Sons, New York

[5] Korotaev, A. D., Tyumentsev, A. N. & Sukhovarov, V. F. (1989). *Disperse Hardening of Refractory Metals*, Nauka, Novosibirsk

[6] Lazarev, E.M., Kornilova, Z.I. & Fedorchuk, N.M. (1985). *Oxidation of Titanium Alloys*, Nauka, Moskow

[7] Lykov, A.V. (1966). *Theory of Heat Conduction*, Vysshaya shkola, Moskow

[8] Lyubov, B.Ya. (1981). *Diffusive processes in heterogeneous solids*, Nauka, Moskow

[9] Malinov, S., Zhecheva, A. & Sha, W. (2003). Modelling the nitriding in titanium alloys. *ASM International*, pp. 344–352

[10] Matychak, Ya. S., Fedirko, V. M., Pavlyna, V.S. & Yeliseyeva, O.I. (1999). The research of initial stage of oxide diffusion growth in Fe-Pb-O system. *Metallofizika i Noveishie Tekhnologii*, Vol. 21 № 2, pp. 78-83

[11] Matychak, Ya., Fedirko, V., Prytula, A. & Pohrelyuk, I. (2007). Modeling of diffusion saturation of titanium by interstitial elements under rarefied atmospheres. *Defect Diffusion Forum*, Vol. 261–262, pp. 47–54

[12] Matychak, Ya. S., Pohrelyuk, I. M. & Fedirko, V. M. (2009). Thermodiffusion saturation of α-titanium with nitrogen from a rarefied atmosphere. *Materials Science*, Vol. 45, No. 1, pp. 72-83

[13] Metin, E. & Inal, O. T. (1989). Kinetics of layer growth and multiphase diffusion in ion-nitrided titanium. *Metallurgical and Materials Transactions A*, Vol. 20A, pp. 1819–1832

[14] Panasyuk, V.V. (2007). *Strength and Durability of Airplane Materials and Structural Elements*, Spolom, Lviv

[15] Prytula, A. O., Fedirko, V. M., Pohrelyuk, I. M. & Matychak, Ya. S. (2005). Surface chemical reactions in processes of diffusion mass transfer. *Defect Diffusion Forum*, Vol. 237–240, pp. 1312–1318

[16] Raichenko, A. I. (1981). *Mathematical Theory of Diffusion in Supplements*, Naukova Dumka, Kiev

[17] Tkachuk, O., Matychak, Ya., Pohrelyuk, I. & Fedirko, V. (2012). Diffusion of nitrogen and phase-structural transformations in titanium, *Proceedings of International Workshop "Diffusion, Stress, Segregation and Reactions (DSSR-2012)"*, Svitanok, Cherkasy region, June, 2012