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## Diffusion of Nitrogen and Phase–Structural Transformations in Titanium

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The process of high-temperature nitridation ( $T = 950^\circ\text{C}$ ) of titanium is investigated analytically and experimentally. The role of nitrogen as  $\alpha$ -stabilizer in forming of nitride layer and diffusion zone, which contains three layers (layer of  $\alpha$ -phase, layer of  $\alpha + \beta$ -phase, and layer of  $\beta$ -phase), is shown. The approximate solution of formulated task is obtained for diffusion of nitrogen in such a heterogeneous medium, taking into account the motion of interfaces. The constants of parabolic growth of layers are calculated. It allows foreseeing the kinetics of their growth and distribution of nitrogen in diffusion zone. The microstructure evolution of diffusion zone (after processing times of 1 h and 5 h), which is caused by the phase–structural transformations during diffusion of nitrogen, is fixed experimentally.

Аналітично й експериментально досліджено процес високотемпературного азотування ( $T = 950^\circ\text{C}$ ) титану. Відображено роль азоту як  $\alpha$ -стабілізатора у формуванні нітридного шару та тришарової дифузійної зони (шар  $\alpha$ -фази, шар  $\alpha + \beta$ -фази і шар  $\beta$ -фази). Одержано наближений розв'язок сформульованої задачі щодо дифузії азоту в такому неоднорідному середовищі з урахуванням переміщень міжфазних меж. Розраховано константи параболічного росту шарів, що уможливило передбачити кінетику їх росту і розподіл азоту в дифузійній зоні. Експериментально зафіксовано еволюцію мікроструктури газонасиченого шару (після витримок у 1 і 5 годин), зумовлену структурно-фазовими перетвореннями під час дифузії азоту.

Процесс высокотемпературного азотирования ( $T = 950^\circ\text{C}$ ) исследован аналитически и экспериментально. Отображена роль азота как  $\alpha$ -стабилизатора в формировании нитридного слоя и трёхслойной диффузионной зоны (слой  $\alpha$ -фазы, слой  $\alpha + \beta$ -фазы и слой  $\beta$ -фазы). Получено приближенное решение сформулированной задачи относительно диффузии азота в такой неоднородной среде с учётом перемещения межфазных границ. Рассчитаны константы параболического роста слоёв, что дало возможность предви-

деть кинетику их роста и распределение азота в диффузионной зоне. Экспериментально обнаружена микроструктурная эволюция диффузионной зоны (после времени обработки 1 и 5 часов), которая обусловлена фазово-структурными превращениями во время диффузии азота.

**Keywords:** nitridation of titanium, kinetics, diffusion, phase-structural transformations.

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## 1. INTRODUCTION

It is necessary to have comprehensive knowledge (experimental and theoretical) about the kinetics of the processes of interaction of elements taking into consideration the influence of process parameters and phase-structural state of the material for forecasting of surface strengthening of titanium alloys after nitriding. Titanium undergoes polymorphic transformation at  $T_{\alpha\leftrightarrow\beta} = 882^\circ\text{C}$  [1]. Previously, it was investigated the kinetics of nitriding of titanium and  $(\alpha + \beta)$ -titanium alloys at temperatures of  $T < T_{\alpha\leftrightarrow\beta}$  analytically and experimentally [2]. The microstructural evolution during  $\alpha \leftrightarrow \beta$ -phase transformation because of migration of  $\beta$ -stabilizers is presented in [3]. However, the authors did not take into consideration the role of nitrogen as  $\alpha$ -stabilizer in the structural transformations. The influence of nitrogen as  $\alpha$ -stabilizer during nitriding of titanium at temperatures of  $T > T_{\alpha\leftrightarrow\beta}$  under the rarefied atmosphere without forming of continuous nitride layer on the surface was investigated earlier in [4]. The aim of this work is to create the physical and mathematical model for diffusion saturation of titanium at temperatures  $T > T_{\alpha\leftrightarrow\beta}$  under medium with high nitrogen potential; establish the kinetic peculiarities of such nitriding analytically and experimentally caused by the phase-structural transformations in the diffusion zone.

## 2. THERMODYNAMIC ANALYSIS

According to the phase diagram (Fig. 1), titanium undergoes polymorphic transformation (change of crystal lattice from h.c.p. to b.c.c.) at  $T_{\alpha\leftrightarrow\beta} = 882^\circ\text{C}$  [5]. We will be interested in high-temperature ( $T > T_{\alpha\leftrightarrow\beta}$ ) interaction of titanium with the gaseous medium with the high nitrogen potential. Under these conditions, according to the phase diagram (Fig. 1), titanium nitrides ( $\text{TiN}$ ,  $\text{Ti}_2\text{N}$ ) as products of chemical reactions and solid solutions of nitrogen in  $\alpha$ - and  $\beta$ -phases because of diffusion dissolution of nitrogen in titanium matrix and structural transformations are stable in the system. In particular, in the nitrogen concentration range  $0 < C_N < C_{23}$ , solid solution of nitrogen in  $\beta$ -phase is

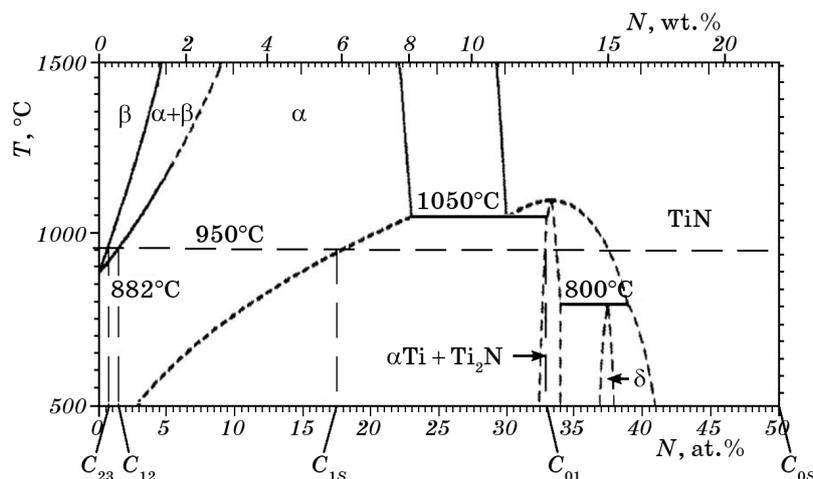


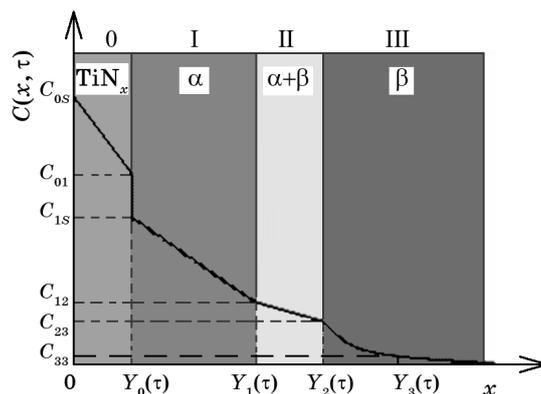
Fig. 1. Titanium–nitrogen phase diagram [5].

stable, while in the concentration range  $C_{12} < C_N < C_{1S}$ , solid solution of nitrogen in  $\alpha$ -phase, and in the concentration range  $C_{23} < C_N < C_{12}$ , solid solutions of nitrogen in both  $\alpha$ - and  $\beta$ -phases can coexist.

It should be noted that in  $\alpha$ -phase the solubility of nitrogen is high enough at temperature of nitriding and can reach, for example, for  $T = 950^\circ\text{C}$  17.5 at.% against 0.75 at.% in  $\beta$ -phase. At the same time, coefficient of diffusion of nitrogen in  $\alpha$ -phase is on two-three orders less than in  $\beta$ -phase (Fig. 1).

### 3. PHYSICO-MATHEMATICAL MODEL

Let us consider the process of isothermal saturation of titanium at temperatures higher than temperature of polymorphic transformation ( $T > T_{\alpha \leftrightarrow \beta}$ ). In this case, the initial microstructure of titanium has  $\beta$ -modification. According to the thermodynamic analysis, the following scheme of the nitrated surface layer of titanium is suggested (Fig. 2). During the interaction of titanium with nitrogen, nitride 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  $\alpha$ -phase of titanium significantly nitrogen-enriched because of high solubility of the nitrogen in  $\alpha$ -phase of titanium. This layer is formed and it grows during nitriding because of diffusion dissolution of nitrogen and structural transformations in titanium, because nitrogen is  $\alpha$ -stabilizer. The layer III ( $Y_2(\tau) < x < \infty$ ), which borders on the titanium matrix, at the temperature of saturation, is  $\beta$ -phase of titanium enriched by nitrogen. Between the first and third layers, the layer II ( $Y_1(\tau) < x < Y_2(\tau)$ ), which is the disperse mixture of



**Fig. 2.** Scheme of distribution of nitrogen concentration at nitriding of titanium at temperature of  $T > T_{\alpha \leftrightarrow \beta}$ .

$\alpha$ - and  $\beta$ -phases enriched by nitrogen, is formed, and it grows.

It will be done some model assumptions for analytical description of the process of nitriding. The aim of nitriding of titanium samples is strengthening of their surface layers and the object of analytical investigation of the kinetics of diffusion saturation of titanium by nitrogen the half-space ( $0 \leq x < \infty$ ) has been chosen. Nitride film is formed immediately on titanium surface, and the surface nitrogen concentration does not change with time and corresponds to stoichiometric titanium nitride (TiN). On the interfaces, the nitrogen concentrations corresponding to equilibrium phase diagram are constant (Fig. 1).

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

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

Here,  $C_i(x, \tau)$  is nitrogen concentration,  $x$  is spatial coordinate,  $\tau$  is time,  $D_i$  is nitrogen diffusion coefficient; index  $i = 0$  corresponds to  $\text{TiN}_x$  layer ( $0 < x < Y_0(\tau)$ ),  $i = 1$ — $\alpha$ -Ti layer ( $Y_0(\tau) < x < Y_1(\tau)$ ),  $i = 2$ — $(\alpha + \beta)$ -Ti-layer ( $Y_1(\tau) < x < Y_2(\tau)$ ),  $i = 3$ — $\beta$ -Ti layer ( $Y_2(\tau) < x < \infty$ ). It should be noted that diffusion coefficient  $D_2$  is the averaged effective diffusion coefficient of nitrogen in  $(\alpha + \beta)$ -Ti layer [2].

Initial conditions ( $\tau = 0$ ):

$$C_i(x, 0) = 0, \quad Y_i(0) = 0 \quad \text{for } x > 0. \quad (2)$$

Boundary conditions ( $\tau > 0$ ):

$$C_0(0, \tau) = C_{0S}, \quad C_3(\infty, \tau) = 0, \quad C_0(Y_0(\tau), \tau) = C_{01}, \quad C_1(Y_0(\tau), \tau) = C_{1S}, \quad (3)$$

$$C_1(Y_1(\tau), \tau) = C_2(Y_1(\tau), \tau) = C_{12}, \quad C_2(Y_2(\tau), \tau) = C_3(Y_2(\tau), \tau) = C_{23}.$$

The motion of interfaces will be set by the parabolic dependences:

$$Y_0(\tau) = 2\beta_0\sqrt{D_0\tau}, \quad Y_1(\tau) = 2\beta_1\sqrt{D_1\tau}, \quad Y_2(\tau) = 2\beta_2\sqrt{D_2\tau}. \quad (4)$$

Here,  $\beta_j$  ( $j = 0, 1, 2$ ) 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  $Y_j(\tau)$ , there are as follow:

$$\begin{aligned} -D_0 \frac{\partial C_0}{\partial x} \Big|_{x=Y_0(\tau)-0} + D_1 \frac{\partial C_1}{\partial x} \Big|_{x=Y_0(\tau)+0} &= (C_{01} - C_{1S}) \frac{dY_0(\tau)}{d\tau}, \\ D_1 \frac{\partial C_1}{\partial x} \Big|_{x=Y_1(\tau)-0} = D_2 \frac{\partial C_2}{\partial x} \Big|_{x=Y_1(\tau)+0}, \quad D_2 \frac{\partial C_2}{\partial x} \Big|_{x=Y_2(\tau)-0} &= D_3 \frac{\partial C_3}{\partial x} \Big|_{x=Y_2(\tau)+0}. \end{aligned} \quad (5)$$

It is difficult to solve the diffusion task (1)–(5) in analytical form. The method of approximate solution of above-mentioned task [6] should be used. The linear distribution laws of the nitrogen concentrations in nitride layer and in the first two layers of diffusion zone corresponded to the quasi-stationary state is accepted, and Gauss law for the distribution of nitrogen in the third layer is:

$$\begin{aligned} C_0(x, \tau) &= C_{0S} - (C_{0S} - C_{01}) \frac{x}{Y_0(\tau)}, \\ C_1(x, \tau) &= C_{1S} - (C_{1S} - C_{12}) \frac{x - Y_0(\tau)}{Y_1(\tau) - Y_0(\tau)}, \\ C_2(x, \tau) &= C_{12} - (C_{12} - C_{23}) \frac{x - Y_1(\tau)}{Y_2(\tau) - Y_1(\tau)}, \\ C_3(x, \tau) &= C_{23} \operatorname{erfc} \frac{x - Y_2(\tau)}{2\sqrt{D_3\tau}}. \end{aligned} \quad (6)$$

The chosen functions  $C_i(x, \tau)$  satisfy the initial (2), boundary conditions (3) and the differential equations (1). The following set of transcendental equations for calculating the parameters  $\beta_j$  ( $j = 0, 1, 2$ ) was obtained by the conditions of mass balance on interfaces (5) and relation (4):

$$\frac{A_0}{2\beta_0} \left[ \frac{1}{\beta_0} - \frac{1}{A_1\gamma_0(\beta_1 - \beta_0\gamma_0)} \right] = 1, \quad \frac{\beta_1 - \beta_0\gamma_0}{A_2\gamma_1(\beta_2 - \beta_1\gamma_1)} = 1, \quad \frac{2(\beta_2 - \beta_1\gamma_1)}{A_3\gamma_2\sqrt{\pi}} = 1. \quad (7)$$

Having solved the set of equations (7), we obtain:

$$\begin{aligned}\beta_0 &= A_0(\sqrt{B^2 + 2/A_0} - B)/2, \quad \beta_1 = \beta_0\gamma_0 + A_2A_3\gamma_1\gamma_2\sqrt{\pi}/2, \\ \beta_2 &= \beta_1\gamma_1 + A_3\gamma_2\sqrt{\pi}/2,\end{aligned}\quad (8)$$

where

$$\begin{aligned}B &= 1/(A_1A_2A_3\gamma_0\gamma_1\gamma_2\sqrt{\pi}), \quad \gamma_0 = \sqrt{D_0/D_1}, \quad \gamma_1 = \sqrt{D_1/D_2}, \quad \gamma_2 = \sqrt{D_2/D_3}, \\ A_0 &= \frac{C_{0s} - C_{01}}{C_{01} - C_{1s}}, \quad A_1 = \frac{C_{0s} - C_{01}}{C_{1s} - C_{12}}, \quad A_2 = \frac{C_{1s} - C_{12}}{C_{12} - C_{23}}, \quad A_3 = \frac{C_{12} - C_{23}}{C_{23}}.\end{aligned}$$

It should be noticed that parameters  $\beta_j$  depend on the values of nitrogen concentrations on interfaces and its diffusion coefficients, which in turn depend on the temperature. Taking the values of these parameters, which correspond to the saturation temperature  $T = 950^\circ\text{C}$ , according to relations (8), the constants  $\beta_j$  ( $j = 0, 1, 2$ ):  $\beta_0 = 0.183$ ,  $\beta_1 = 1.691$ ,  $\beta_2 = 0.782$  were calculated. The following values of diffusion coefficients were used here:  $D_0 = D_{\text{TIN}} = 3 \cdot 10^{-12} \text{ cm}^2/\text{s}$ ,  $D_1 = D_\alpha = 2.5 \cdot 10^{-9} \text{ cm}^2/\text{s}$ ,  $D_2 = 10D_1$  (from those reasonings that  $D_1 < D_2 < D_3$ ),  $D_3 = D_\beta = 3.2 \cdot 10^{-8} \text{ cm}^2/\text{s}$  [1, 5], and such values of nitrogen concentrations on interfaces:  $C_{0s} = 50$ ,  $C_{01} = 33$ ,  $C_{1s} = 17.5$ ,  $C_{12} = 1.5$ ,  $C_{23} = 0.75$  (at.%) (Fig. 1). Taking into consideration the correlation (4), the motion of interfaces will be presented as:

$$Y_0(\tau) = K_0\sqrt{\tau}, \quad Y_1(\tau) = K_1\sqrt{\tau}, \quad Y_2(\tau) = K_2\sqrt{\tau}, \quad (9)$$

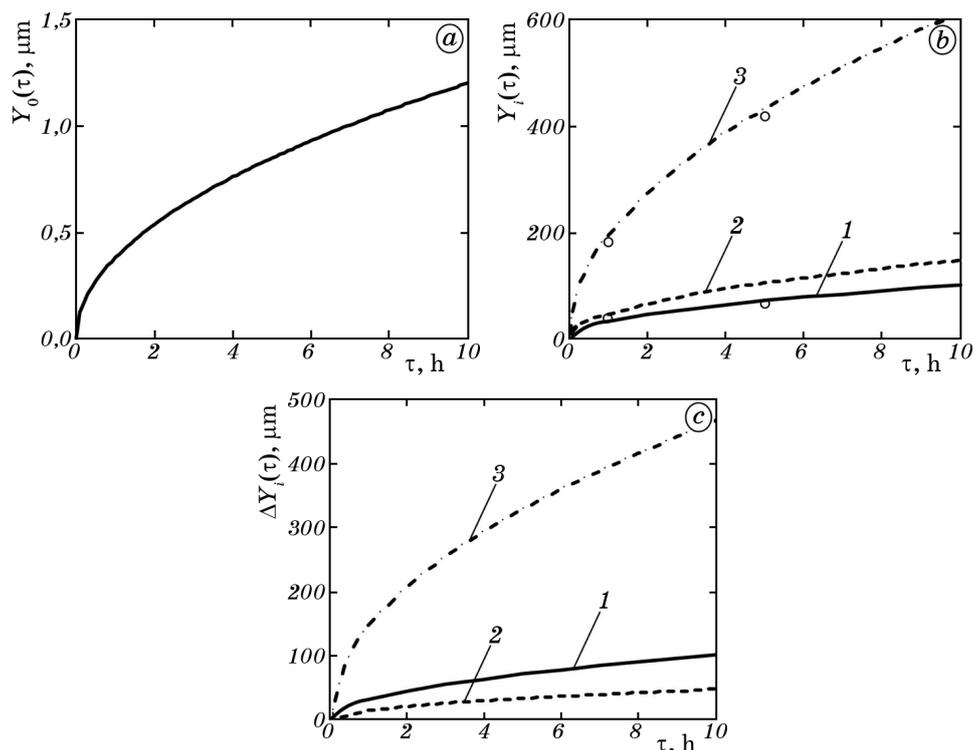
where  $K_0 = 2\beta_0D_0^{1/2}$ ,  $K_1 = 2\beta_1D_1^{1/2}$ ,  $K_2 = 2\beta_2D_2^{1/2}$  — constants of the parabolic growth of nitride layer and  $\alpha$ -,  $(\alpha + \beta)$ -layers of diffusion zone stabilized by nitrogen, respectively. In particular, these constants for saturation temperature  $T = 950^\circ\text{C}$  are such as

$$K_0 = 6.33 \cdot 10^{-7} \text{ cm/s}^{1/2}, \quad K_1 = 5.35 \cdot 10^{-5} \text{ cm/s}^{1/2}, \quad K_2 = 7.8 \cdot 10^{-5} \text{ cm/s}^{1/2}. \quad (10)$$

Having found the constants of parabolic growth of the layers (10) and having used the relations (9), it is easy to foresee the kinetics of motion of interfaces (Fig. 3, *a, b*), and also time dependences of the change of thickness of nitride layer (Fig. 3, *a*) and  $\alpha$ -,  $(\alpha + \beta)$ - and  $\beta$ -layers of the diffusion zone (Fig. 3, *c*) in accordance with correlations:

$$\begin{aligned}\Delta Y_0(\tau) &= Y_0(\tau), \\ \Delta Y_1(\tau) &= Y_1(\tau) - Y_0(\tau) = \tilde{K}_1\sqrt{\tau}, \\ \Delta Y_2(\tau) &= Y_2(\tau) - Y_1(\tau) = \tilde{K}_2\sqrt{\tau},\end{aligned}\quad (11)$$

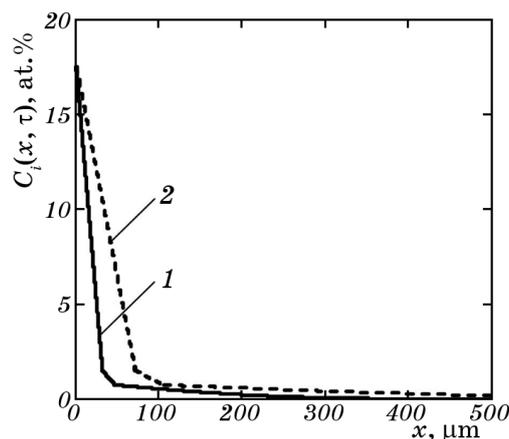
where  $\tilde{K}_1 = K_1 - K_0$ ,  $\tilde{K}_2 = K_2 - K_1$ .



**Fig. 3.** Kinetics of motion of interfaces: interface of nitride layer  $Y_0(\tau)$  (a); 1—interface  $Y_1(\tau)$ , 2— $Y_2(\tau)$ , 3— $Y_3(\tau)$ ,  $\circ$  — experiment (b); change of thickness of layers: 1—thickness of  $\alpha$ -layer, 2— $(\alpha + \beta)$ -layer, 3— $\beta$ -layer at nitriding of titanium at  $T = 950^\circ\text{C}$  (c).

It should be noted that  $\beta$  layer of diffusion zone is identified by the motion of conventional boundary with the specific nitrogen concentration, for example  $C_{33} = 0.25$  at.%. Based on relations (6), the concentration profiles of nitrogen in the diffusion zone of titanium after nitriding during 1 and 5 hours (Fig. 4) are calculated. It is clear that, according to the assumptions (4) with the increase of processing time, the motion of interfaces (Fig. 3, a, b) and, correspondingly, the growth of thickness of the different layers of the diffusion zone (Fig. 3, c) occur, according to the parabolic dependences proportionally to the corresponding constants of parabolic growth  $K_j$  i  $\tilde{K}_j$ .

The diffusion coefficient of nitrogen in  $\beta$ -phase is on two-four orders higher than that in  $\alpha$ -phase and nitride layer that is why the thickness of  $\beta$  layer is much larger than the thickness of the other layers of diffusion zone (Fig. 3, a, c). If the thickness of nitride layer ( $Y_0(\tau)$ ) is less than 0.2% from the total thickness of diffusion zone ( $Y_3(\tau)$ ), the thickness of  $\alpha$ -,  $\alpha + \beta$ -, and  $\beta$ -layers will be 16, 8 and 76%.



**Fig. 4.** Concentration profiles of nitrogen in diffusion zone of titanium after its nitriding at  $T = 950^{\circ}\text{C}$  for two isothermal exposures: 1— $\tau = 1$  h, 2— $\tau = 5$  h.

At the same time, the different solubility of nitrogen in  $\alpha$ - and  $\beta$ -phases of titanium influences on the distribution of nitrogen in the diffusion zone. If the phase-structural transformations do not take place in the diffusion zone, the profile of nitrogen in this zone would have a small gradient because of the low solubility of nitrogen in  $\beta$ -phase. In fact, nitrogen, being  $\alpha$ -stabilizer, stimulates the  $\beta \rightarrow \alpha$ -phase transformations in the layers of the diffusion zone, adjacent to the nitride layer. As the solubility of nitrogen in  $\alpha$ -phase is much higher than that in  $\beta$ -phase, we can foresee that, in zone I, the profile of nitrogen will have a large gradient (Fig. 4) as well as the distribution of microhardness in this zone. It has been confirmed by the experimental investigations data.

#### 4. EXPERIMENTAL PROCEDURE

Commercially pure (c.p.) titanium with dimensions of  $10 \times 15 \times 4 \text{ mm}^3$  was investigated. The samples are polished ( $R_a = 0.4 \mu\text{m}$ ) and washed with deionized water before the treatment. The samples are heated to the nitriding temperature in vacuum of  $10^{-3} \text{ Pa}$ . Then, they are saturated with molecular nitrogen of the atmospheric pressure at the temperature of  $950^{\circ}\text{C}$ . The isothermal exposure in nitrogen was 1 and 5 h. After isothermal exposure, the samples were cooled in nitrogen to room temperature.

The microstructure of the nitride layers was studied using 'EPIQUANT' metallography microscope. Distribution of microhardness on cross section of surface layers of c.p. titanium after nitriding is estimated by measurement of microhardness at loading of 0.49 N.

## 5. 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 in nitrogen atmosphere. It indicates the increase of its thickness.

The diffusion zone is formed under titanium nitride layer (Fig. 5). It is difficult to find the layer II (Fig. 2) in this zone, which, according to the phase diagram (Fig. 1), probably has to form. However, two different parts, according to the structure of diffusion zone (zone A and zone B) are clearly fixed. Zone A is  $\alpha$ -phase of titanium formed during nitriding by nitrogen as  $\alpha$ -stabilizer. Its thickness, according to data of metallography analysis, increases from 20 to 45  $\mu\text{m}$  with the increase of duration of nitriding from 1 to 5 h. Zone B is  $\alpha$ -phase of titanium 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 microhardness distribution on cross section of surface layers of c.p. titanium after nitriding are presented in Fig. 6. On curves of microhardness, distribution zone A (layer I, Fig. 2) and zone B (probably, layer II + layer III, Fig. 2) are clearly seen.

The large gradient of microhardness is typical for zone A. It is caused by  $\beta \rightarrow \alpha$ -transformation because of saturation by nitrogen as  $\alpha$ -stabilizer and its comparatively high solubility in  $\alpha$ -phase. With the increase of distance from the surface, the microhardness is drastically decreases (Fig. 6) that is explained by the decrease of nitrogen concentration (Fig. 4). The hardness of zone B is considerably less than that of zone A because of large difference of nitrogen solubility in  $\alpha$ - and  $\beta$ -phases. The thickness of these zones is increased with the increase of duration of nitriding (Fig. 6). In particular, the thickness of zone A is

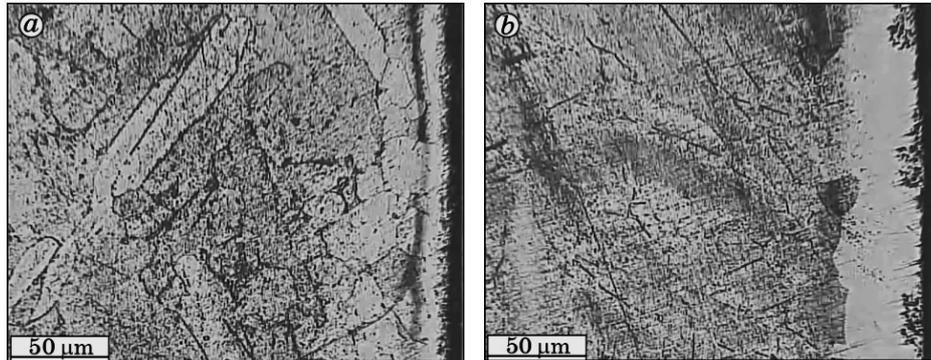


Fig. 5. Structure of surface layers of c.p. titanium after nitriding at  $\tau = 1$  h (a) and 5 h (b) ( $T = 950^\circ\text{C}$ ,  $p = 10^5$  Pa).

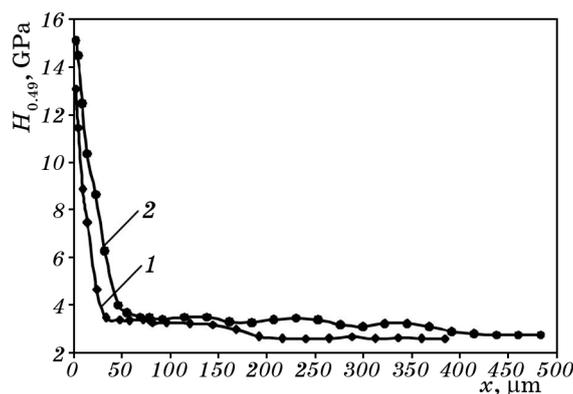


Fig. 6. Distribution of microhardness on cross section of surface layers of c.p. titanium after nitriding at  $\tau = 1$  h (1) and 5 h (2) ( $T = 950^\circ\text{C}$ ,  $p = 10^5$  Pa).

34  $\mu\text{m}$  for  $\tau = 1$  h and 69  $\mu\text{m}$  for  $\tau = 5$  h. It will be noticed that this thickness is larger than corresponding thickness, determined by the data of metallography analysis. The general depth of diffusion zone (zone A + zone B) is 185  $\mu\text{m}$  for  $\tau = 1$  h and 425  $\mu\text{m}$  for  $\tau = 5$  h (Fig. 3, b).

The obtained analytical distribution of nitrogen (Fig. 4) and results of measuring of microhardness (Fig. 6) confirm the correlation between model calculations and experimental data.

## 6. CONCLUSIONS

The kinetic peculiarities of diffusion saturation of titanium at temperature of  $T = 950^\circ\text{C}$ , which is higher than the temperature of  $\alpha \Leftrightarrow \beta$ -polymorphic transformation, are determined analytically and experimentally.

The role of nitrogen as  $\alpha$ -stabilizer in forming of multilayer diffusion zone is shown.

The analytical calculations of the kinetics of the layers of diffusion zone growth and the distribution of nitrogen in them correlate with the results of experimental investigations. The microstructure evolution (after processing times of 1 and 5 h) of the diffusion zone is fixed according to them.

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