

# diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

## **Theoretical model for an interaction between titanium and binary rarified gas medium with taking into account the segregation of the impurity on the interface and in the bulk of the metal.**

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### **Introduction**

Surface layers of construction materials (Me) can be strengthened by the thermal diffusion saturation of interstitial impurities: nitrogen, boron, carbon and oxygen. In order to form deep strengthened (diffusion) layers without the formation of the nitride film on the surface, the method of nitriding of titanium under reduced nitrogen pressure is quit effective [1]. For the better result the two-component mixture of interstitial elements, for example, boron-nitrogen containing medium G(N,B) should be used [2]. However, there are no detailed descriptions of such a thermal and chemical treatment [1] because of the complexity and variety of high temperature processes, which appear simultaneously in the metal-gas (Me-O) system, particularly at initial stages. They determine the kinetics of the interaction Me-O by the formation of the either diffusion zone or new phases. The defects of crystal lattice in diffusion layer, such as vacancies, dislocations or other nonuniformities (in other words there are locally distributed energy disturbance) and chemical reaction which influence on process of mass transfer cause to increasing the possibility of

nonequilibrium segregation. Therefore, experimental and theoretical studies are necessary in order to bring the light on the physical nature of interaction mechanisms on the different stages in the Me-G system.

Today, analytical researches of interaction between different media (including titanium interaction with gases) are far from complete ones due to poor description of its different stages, especially initial stages [3, 4]. It is important to understand the physical nature of phenomena determined by the interaction mechanisms, which include the internal (defects, grain boundary) as well as external (time, temperature, pressure) factors.

Therefore, we propose to distinguish the role of separate processes in general phenomenon of interaction Me-G, to estimate relative contribution of each process taken separately and to reveal conditions of dominating some processes in comparison with others.

The aim of the work is to describe the mathematical model for the diffusion of interstitial elements in the titanium which interacts with the rarefied boron-nitrogen containing medium in consideration of their non equilibrium segregation, and to estimate influence of time-temperature parameters as well as surface phenomena.

### **1. Phenomenological physical-mathematical model of interaction Me(Ti) - G(N,B).**

Let us consider the interaction of the titanium with the boron-nitrogen containing medium under the rarefied atmosphere  $10 \dots 10^{-1}$  Pa in the temperature range 750-850°C (below the temperature of the titanium polymorphic transformation). The numerous experimental data [1] indicate that: during 6-25 hours there is no nitride film on the titanium

surface; kinetics of nitriding is sensitive to diffusion supply of nitrogen to titanium surface; surface concentration of nitrogen depends on the time. In such conditions The analytical description of the kinetics of nitriding (boriding) by known Fick's equation with setting constant value of the surface concentration (1<sup>st</sup> diffusion boundary conditions) would be not correct. On the whole, in different stages of reactive diffusion, the time dependence of the concentration of the diffusant on the interface is essentially different [5]. Therefore, for definition of mass transfer of interstitial impurity, it is necessary to analyze the processes in the bulk of subsystems (Me and G), in the nonequilibrium medium, kinetics depends on an external and internal mass transfer.

The high-temperature interaction between the metal Me and a gaseous medium G begins from the moment of their contact ( $\tau=0$ ) at the interface. The mass transfer of gaseous component in the bulk plays an important role. With time, the consequences of interaction are perceptible in the bulk of the metal and in the medium. They are caused by mutual processes which realize: a) on the interface - absorption, chemisorptions, chemical reactions, formation of the two-dimensional structures, defect appearance; b) in the volumes of subsystems (diffusion, defects segregation, internal chemical and structure transformations).

It is well known, that the thermodynamic conditions as the driving force determine the phase formation. The sudden change of chemical potential of the impurity on the interface and the sufficient penetrability of the interface boundary are necessary conditions to begin the flow of the impurity. Then impurity migrates to the subsystem, where its chemical

potential is lower. The system once disturbed from balance in the moment of interaction tends to attain a new equilibrium state. At such system, the metastable intermediate phases can exist during the some time (even a long time [6]). In this case, the chemical potential of impurity takes on intermediate quasi-stationary values. Also, the unsoundness of metals plays an important role. However, the intensity of surface reaction and the mobility of diffusant (diffusion factor) are more essential factors affecting on the interaction between Me – G .

A peculiar layer, which occupies a  $(0, \delta)$  zone of the metal and the  $(-\delta, 0)$  of the medium (fig 1a), is forming in the subsystems after the contact Me(Ti) - G(N,B) in the neighborhood of the interface. This duplex layer is unstable, with defected structure. This layer is observed as a quasi-

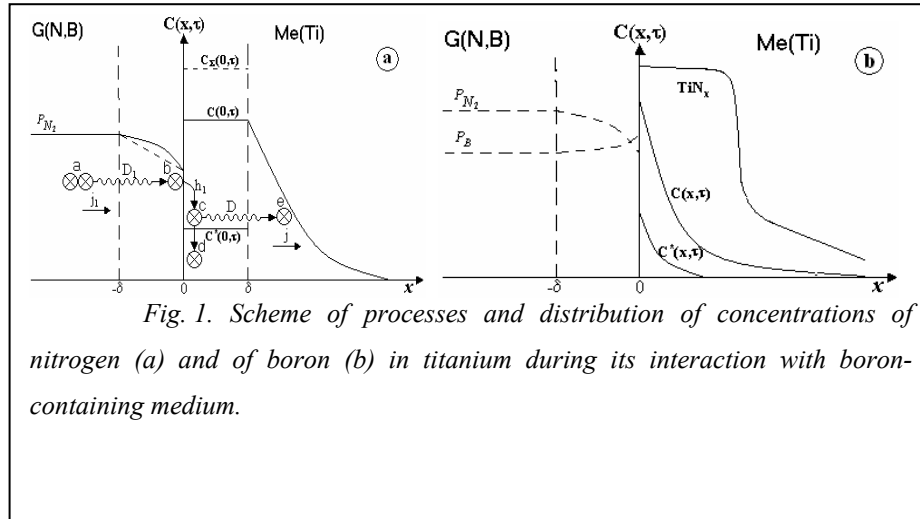


Fig. 1. Scheme of processes and distribution of concentrations of nitrogen (a) and of boron (b) in titanium during its interaction with boron-containing medium.

phase, or a solution on the metal surface [7]. Using such definition of the contact layer and carrying out thermodynamic analysis (energy of

compounds formation —  $|\Delta G_{\text{TiN}}| > |\Delta G_{\text{TiB}}|$  [8], solubility of impurities in titanium -  $C_{\text{N}}^{\text{max}} > C_{\text{B}}^{\text{max}}$ , diffusion coefficients  $D_{\text{N}}^{\text{Ti}} > D_{\text{B}}^{\text{Ti}}$ ) with taking into account kinetic and structural features, the mathematical model of interaction in system Me(Ti) - G(N,B) (subject to  $P_{\text{N}_2} > P_{\text{B}}$ ) is offered. Gas-saturated zone is formed due to diffusion of nitrogen in the titanium according to scheme on the fig.1:  $a \rightarrow b$ - diffusion in gaseous medium (parameter - diffusion coefficient  $D_1$ ) ;  $b \rightarrow c$ - physical absorption, dissociation and chemisorption  $h_1$ ;  $c \rightarrow d$ - chemical reaction ( $k$ );  $c \rightarrow e$ - dissolution and diffusion in the metal ( $D$ ).

The diffusion of boron is realized by the similar scheme (fig.1b.) but with some peculiarities. At the first, due to decreasing of the partial pressure of nitrogen in the neighborhood of the interface, partial pressure of the boron can increase. On the other hand, the diffusion of the boron in the titanium surface layer follows the diffusion front of the nitrogen. Therefore, this layer is defective and can be presented like the solid solution of the nitrogen in the titanium Ti(N) or like the nonstoichiometric nitride  $\text{TiN}_x$  (under high partial pressure of nitrogen media  $P_{\text{N}_2}$ ). The presence of defects of the crystal lattice in the surface layer causes to increase the boron mass transfer and the possibility of its segregation on the defects in the forms of chemical compounds (borides).

Thus, the interaction between the titanium and the rarefied boron-nitrogen containing media (in the first approximation with omitting the mutual influence of elements) will be considered as nitriding of the titanium with the following boron saturation.

### 1.1. Mathematical description of nitriding of titanium.

For object of investigation, we take semispace, because in whole, the changes are applied only to the surface layer, which has less thickness than titanium sample. Then, in order to find the distribution of impurity concentration  $C(x,\tau)$  in solid solution, we formulate the following boundary – initial value problem:

$$D\partial^2 C / \partial x^2 = \partial C / \partial \tau \text{ at } \tau > 0, \quad 0 < x < \infty, \quad C(x,0) = C(\infty,\tau) = C_0. \quad (1)$$

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

Here,  $C_{eq}$  is the quasi-equilibrium magnitude of the surface impurity concentration ( $C_{eq} = d \cdot C_{eq}^-$ , where  $d$  is coefficient of equilibrium impurity distribution between the metal and the medium,  $C_{eq}^-$  is determined by the partial pressure of impurity in the medium). In the case of quasistationary state ( $(dC / d\tau = 0)$ ) or by omitting the contact layer ( $\omega = 0$ ) correspondingly to eq.2, we obtain typical 3<sup>rd</sup> boundary condition:  $-D\partial C / \partial x|_{x=0} = h[C_{eq} - C(0,\tau)]$  [9]. It shows, that all atoms, which precipitate on the surface, diffuse in metal with distributing according to the diffusion laws. In this equation, if  $D \rightarrow 0$  then  $C(0,\tau) = C_{eq}$ , in other words, the concentration on the surface is equal to the equilibrium concentration. It is independent of time and becomes on the instant. However, correspondingly to boundary condition (2), if the diffusion in the bulk is lacking ( $D \rightarrow 0$ ), we have:

$$C(0,\tau) = C_{eq} - (C_{eq} - C_0) \exp[-(h+k)\tau / \omega]. \quad (3)$$

Thus, the contact layer with capacity  $\omega$  plays the role of mini reservoir.

In the grain boundary, the expression (2) contains the operator  $d/d\tau$ , which allows one to describe the kinetics of the reagent accumulation on the interface. The difference between the diffusion flux of the impurity  $j_1$  with reducing the variable  $x$  to 0 from the left side of the interface ( $x=-0$ ), and  $j$  at  $x \rightarrow +0$ , determines the kinetics of the impurity accumulation in the neighborhood of the interface via a chemical reaction. Such accumulation takes place in the contact layer with the averaged capacity  $\omega$  on defects, which play role of the "traps" for the diffusant.

If the chemical reactions with formation of compounds  $TiN_x$  can occur in the system, then the impurity concentration at the surface layer for the binding state (in compounds) has the following form

$$C^*(0, \tau) = \left( \frac{k}{\omega} \right) \int_0^\tau [C(0, t) - C_0] dt. \quad (4)$$

Parameter  $k$  describes the intensity of reaction. The total impurity concentration in the neighborhood of interface is represented by the expression

$$C_\Sigma(0, \tau) = C(0, \tau) + C^*(0, \tau). \quad (5)$$

Thus, among all adsorbed atoms of impurity, only part from them is dissolved in the metal and diffuses in the bulk. The rest segregate near surface as compounds (Fig. 1a). In analytical form, the solution of equation for  $C(x, \tau)$  (here  $\bar{C}(x, \tau) \equiv (C(x, \tau) - C_0)/(C_{eq} - C_0)$  is normalized

concentration that describes distribution of impurity of the solid solution ) is [10] following:

$$\bar{C}(x, \tau) = h(h+k)^{-1} \operatorname{erfc}\left[x/(2\sqrt{D\tau})\right] - h[q_2^{-1}F_2(x, \tau) - q_1^{-1}F_1(x, \tau)]/(D\Delta). \quad (6)$$

here

$$\begin{aligned} F_1(x, \tau) &= \exp(q_1 x + q_1^2 D \tau) \operatorname{erfc}\left[q_1 \sqrt{D\tau} + x/(2\sqrt{D\tau})\right], \\ F_2(x, \tau) &= \exp(q_2 x + q_2^2 D \tau) \operatorname{erfc}\left[q_2 \sqrt{D\tau} + x/(2\sqrt{D\tau})\right], \\ q_1 &= (1 + \Delta)/(2\omega), \quad q_2 = (1 - \Delta)/(2\omega), \quad \Delta = \sqrt{1 - 4\omega(h+k)/D}. \end{aligned}$$

The formula which describes the surface concentration of the unbound impurity takes on the form

$$\bar{C}(0, \tau) = h/(h+k) - [f_2(\tau)/q_2 - f_1(\tau)/q_1]h/(D\Delta), \quad (7)$$

here

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

The surface concentration of impurity  $C^*(0, \tau)$ , which exists in compounds and the total concentration on the surface  $C_\Sigma(0, \tau)$  are determined by equation (Eq. 4) and (Eq. 5), respectively. Using the dependence (Eq. 6) for  $C(x, \tau)$  and (Eq. 7) for  $C(0, \tau)$ , one can determine the total mass transfer of impurity  $\Delta M_\Sigma(\tau)/S$  during the time  $\tau$  per square of surface contact and the mass change  $\Delta M(\tau)/S$  caused only by diffusion dissolution. Then, we have

$$\Delta M_\Sigma(\tau)/S = h \int_0^\tau [C_{eq} - C(0, t)] dt, \quad \Delta M(\tau)/S = \int_0^\tau j(x=+0, t) dt. \quad (8)$$

The density of diffusion flux in metal is determined as

$$j(x=+0, \tau) = -D \partial C / \partial x \Big|_{x=+0} = h(C_{eq} - C_0)[f_2(\tau) - f_1(\tau)]/\Delta. \quad (9)$$



In the case of the short-time range, we get

$$\bar{C}(0, \tau) \approx \frac{h\tau}{\omega} \left[ 1 - \frac{4}{3} \cdot \sqrt{\frac{D\tau}{\pi\omega^2}} + \frac{\tau}{2} \cdot \left( \frac{D}{\omega^2} - \frac{h+k}{\omega} \right) \right]. \quad (10)$$

$$j(x=+0, \tau) = 2h(C_{eq} - C_0) \sqrt{D\tau/(\pi\omega^2)}. \quad (11)$$

as well as for the long-time range these quantities is represented as

$$\bar{C}(0, \tau) \approx \frac{h}{h+k} \left[ 1 - \exp\left[-(h+k)^2 \tau / D\right] \cdot \operatorname{erfc}\left[(h+k) \sqrt{\frac{\tau}{D}}\right] \right] \approx \frac{h}{h+k} \left[ 1 - \frac{1}{h+k} \sqrt{\frac{D}{\tau}} \right], \quad (12)$$

$$j(x=+0, \tau) = \frac{h}{h+k} (C_{eq} - C_0) \sqrt{\frac{D}{\pi\tau}}. \quad (13)$$

Thus, using nonstationary boundary condition of the mass transfer on the interface (2), we obtain equations (9) and (11) which describe the density of the diffusion flux of the impurity in the metal. The density depends on time. This dependence differs from one  $j \sim 1/\tau^{1/2}$  [9]. It contains fallibility at  $\tau \rightarrow 0$ . In this case the density of flux goes to the infinity. In the equations (9) and (11), the appearance of the finite parameters of surface reactions eliminates this paradox.

## 1.2. Mathematical description of boriding of titanium.

Let us formulate the task for the description of kinetics of the boron diffusion in the defective nitride layer of the titanium  $\text{TiN}_x$  (fig. 1b). In view of the kinetic aspect, the defects play role of traps for diffusant. Therefore, Fick's equation with addition member which takes into account a presence of the "traps" zone in the diffusion and boundary conditions of mass changing with fixation of time dependences of boron concentration on both side of interface is used [11]. We obtain

$$\begin{aligned} Dd^2C/\partial x^2 &= \partial C/\partial \tau + K(C-C_0), \\ \partial C^*/\partial \tau &= K(C-C_0), \quad \tau > 0, \quad 0 < x < \infty. \end{aligned} \quad (14)$$

$$\begin{aligned} C(x,0) &= C(\infty, \tau) = C_0, \quad C^*(x,0) = 0, \\ -D\partial C/\partial x|_{x=+0} &= h_\beta [d_\beta C^\beta(-0, \tau) - C(+0, \tau)] \end{aligned} \quad (15)$$

Here  $C(x, \tau)$  is the concentration of boron dissolved in  $\text{TiN}_x$ ,  $D$  is the diffusion coefficient of boron;  $C^*(x, \tau)$  is the concentration of boron segregated on the defects due to chemical interaction with titanium. In other words, this is the concentration of the boron in binding state – complexes which is considered as separate low-motioned components. The parameter  $K$  characterises the intensity of the boron capturing by “traps”;  $d_\beta = C_m/C_m^\beta$  is the coefficient of the equilibrium boron distribution between the titanium and medium, parameter  $h_\beta$  is the coefficient of the boron mass transfer.

It should be noted, that in general, the parameters  $D, h_\beta, K$  are functions of the time and distance. However, in the proposed model, they have effective constant values.

We suppose that concentration of boron  $C^\beta(-0, \tau)$  at the left side of interface is changing with time from  $C_0^\beta$  for  $\tau = 0$  to stationary (quasi-equilibrium) value  $C_m^\beta$  according to dependence

$$C^\beta(-0, \tau) = C_m^\beta - (C_m^\beta - C_0^\beta) \exp(-K_\beta \tau). \quad (16)$$

The following expression represents the assumption that chemical reaction has first order:

$$dC^\beta(-0, \tau) / d\tau = -K_\beta [C^\beta(-0, \tau) - C_m^\beta],$$

here  $K_\beta$  is parameter of rate of reaction.

Using an operating method of Laplace transformation the solution of the problem is obtained in the form

$$\begin{aligned} \bar{C}(x, \tau) &\equiv \frac{C(x, \tau) - C_o}{C_m - C_o} = \int_0^\tau F(\tau - \theta) \Phi(x, \theta) d\theta, \\ \bar{C}^*(x, \tau) &\equiv \frac{C^*(x, \tau)}{C_m - C_o} = K \int_0^\tau \int_0^\theta F(\theta - \vartheta) \Phi(x, \vartheta) d\vartheta d\theta, \quad \bar{C}_\Sigma(x, \tau) = \bar{C}(x, \tau) + \bar{C}^*(x, \tau), \end{aligned} \quad (17)$$

here

$$\begin{aligned} \Phi(x, \tau) &= \frac{1}{2} \left[ \exp(-x\sqrt{K/D}) \operatorname{erfc}\left(\frac{x}{2\sqrt{D\tau}} - \sqrt{K\tau}\right) + \exp(x\sqrt{K/D}) \operatorname{erfc}\left(\frac{x}{2\sqrt{D\tau}} + \sqrt{K\tau}\right) \right], \\ F(\tau) &= K_\beta (H^2 D) \exp(-K_\beta \tau) \int_0^\tau \exp(K_\beta \theta) \left[ \frac{1}{\sqrt{\pi}} \frac{1}{H\sqrt{D\theta}} - \exp(H^2 D \theta) \operatorname{erfc}(H\sqrt{D\theta}) \right] d\theta \\ H &= h_\beta / D, \quad C_m = d_\beta \cdot C_m^\beta. \end{aligned}$$

Such correlations describe the kinetics of the boron diffusion in the surface layer of the titanium. The boron diffusion is passed by the front of nitrogen diffusion. Equations (17) include phase-boundary and internally-volume chemical reactions. For the fixed period of the time, the calculations of  $C(x, \tau)$  allow us to get the boron distribution in solid solution. The boron distribution in the boron compounds can be obtained using the quantity  $C^*(x, \tau)$ . The sum  $C_\Sigma(x, \tau)$  is the experimentally found boron distribution.

Neglecting of kinetics of phenomena on the interface  $K_\beta \rightarrow \infty, h_\beta \rightarrow \infty$ , we obtain the diffusion process with taking into account “traps” only from one source. Then from eq. (17), we have

$$\bar{C}(x, \tau) = \frac{1}{2} \left[ \exp(-x\sqrt{K/D}) \operatorname{erfc}\left(\frac{x}{2\sqrt{D\tau}} - \sqrt{K\tau}\right) + \exp(x\sqrt{K/D}) \operatorname{erfc}\left(\frac{x}{2\sqrt{D\tau}} + \sqrt{K\tau}\right) \right],$$

$$\bar{C}^*(x, \tau) = \frac{K\tau}{2} \left[ \frac{e^{x\sqrt{K/D}} \left(1 + \frac{x}{2\sqrt{D\tau}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{D\tau}} + \sqrt{K\tau}\right) - e^{-x\sqrt{K/D}} \left(1 - \frac{x}{2\sqrt{D\tau}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{D\tau}} - \sqrt{K\tau}\right)}{2} \right] \quad (18)$$

At some moment  $\tau = \tau_1$ , the parameter  $K_\beta \tau$  becomes large. This fact corresponds to the approximation of boron concentration from the left side of interface up to the quasistationary value  $C_m^\beta$ . Then, from the right side of interface, the boron concentration is determined by relations:

$$\bar{C}(+0, \tau) = \frac{H^2 D}{H^2 D - K} \left[ 1 - e^{(H^2 D - K)\tau} \operatorname{erfc}(H\sqrt{D\tau}) - \frac{\sqrt{K}}{H\sqrt{D}} \operatorname{erf}(\sqrt{K\tau}) \right] - \frac{H\sqrt{D}}{K_\beta} e^{-K\tau} \left[ \frac{1}{\sqrt{\pi\tau}} - H\sqrt{D} \exp(H^2 D\tau) \cdot \operatorname{erfc}(H\sqrt{D\tau}) \right], \quad (19)$$

$$\bar{C}^*(+0, \tau) = K \int_0^\tau \bar{C}(+0, \theta) d\theta.$$

It should be noted, at  $C^\beta(-0, \tau) = C_m^\beta = \text{const}$  ( $K_\beta \rightarrow \infty$ ), the second term in the first correlation is equal to zero.

If we assume that  $D = \text{const}$ , then the following correlation between diffusion coefficient of boron and nitrogen is  $D_B^{TiB} < D_B^{Ti} < D_B^{TiN_x} < D_N^{Ti}$ . Thus, in difference with titanium boriding, when the thin boride film is forming, during saturation in the boron-nitrogen containing medium borides are forming on the deeper distance from surface. Therefore, using of such a media allows to form deep

strengthened layers due to dissolved nitrogen with additionally hardened by boron surface layer. Effectiveness of such a treatment is determined by temperature-time parameters and by the content of the medium (partial pressures of components).

Let us analyze of these factors for the nitriding process.

## **2. The influence of temperature-time parameters and surface phenomena on the kinetics of nitriding.**

Let us make some notes for introduced parameters of the model  $P_i$  ( $P_i=D, h, k$ ). The diffusive supply of nitrogen to the surface of titanium, its adsorption and chemisorption which are described by effective parameters  $h$  (coefficient of mass transfer), diffusion of nitrogen in titanium with coefficient  $D$  and chemical interaction (effective parameter  $k$ ) are physical-chemical processes. They are thermally active and are characterised by corresponding energies of activation with dependence  $P_i=P_{0i} \exp(-E_i /RT)$ . Namely, for the coefficient of diffusion of nitrogen [1], we have  $D_0=1.2 \cdot 10^{-2} \text{cm}^2/\text{s}$ ,  $E_D = 45250 \text{ cal/mol}$ . The coefficients of the diffusion of the nitrogen in the titanium at the research temperatures  $T_1=750^\circ \text{C}$ ,  $T_2=800^\circ \text{C}$  and  $T_3=850^\circ \text{C}$  are following:  $D_1=3 \cdot 10^{-12} \text{cm}^2/\text{s}$ ,  $D_2=8,4 \cdot 10^{-12} \text{cm}^2/\text{s}$  and  $D_3=2 \cdot 10^{-11} \text{cm}^2/\text{s}$ . The effective parameters  $h$  and  $k$  besides dependence on temperature, in the great bulk are depended on both a partial pressure and unsoundness of material. Therefore, in general, they should be defined from experimental data of the saturation kinetics.

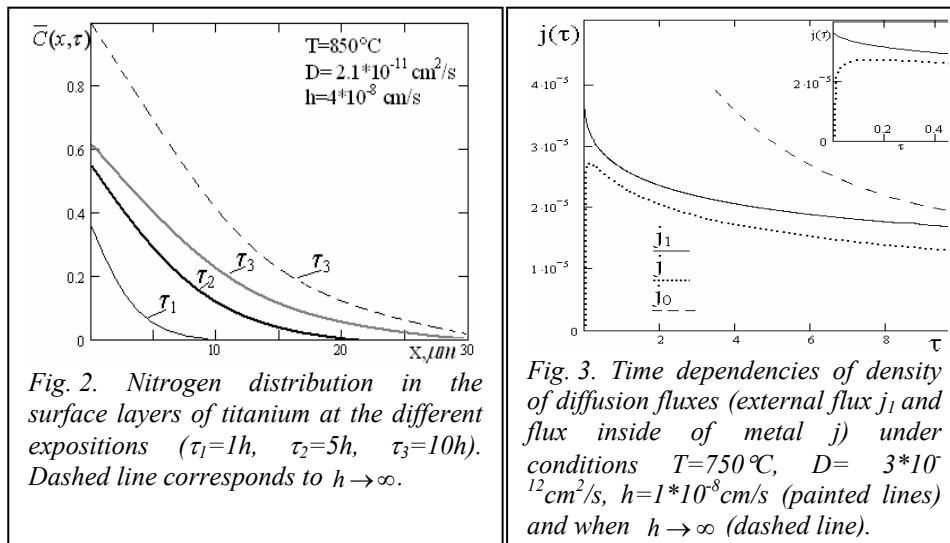
At some band of partial pressures  $P_{N_2}$ , the directly proportional dependence  $h \sim P_{N_2}$  can be assumed [12]. With taking into account the rate

of the parameter  $h$  according to literature data [12, 13] to analyse of kinetics of nitriding, we will use the following values  $h$  and  $k$ :

$$h_1=1 \cdot 10^{-8} \text{ cm/s}, h_2=4 \cdot 10^{-8} \text{ cm/s}, h_3=8 \cdot 10^{-8} \text{ cm/s} \text{ and } k=0,2 \cdot h.$$

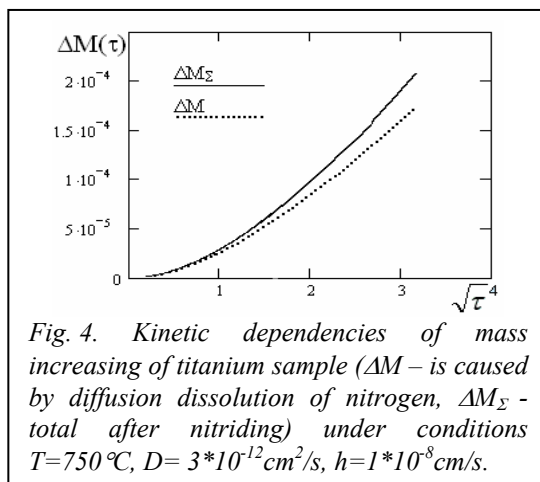
It must be noted that the equilibrium value of surface concentration  $C_{eq}$  depends on the partial pressure of the nitrogen too. For low partial pressures of nitrogen it is valid the relation  $C_{eq} \sim P_{N_2}$ . In the case of increasing the partial pressure, we have  $C_{eq} \sim \sqrt{P_{N_2}}$  [7]. We emphasise on this, because further, the figures of kinetic dependencies of concentrations ( $C$ ), of density of fluxes ( $j_1$  and  $j$ ) and of mass increasing ( $\Delta M$  and  $\Delta M_N$ ) with normalizing on  $C_{eq}$  will be shown.

The role of time parameter is shown by the curves that are plotted



according to equations of item 1.1 (Fig. 2-4). With increasing of the duration of expositions, the surface concentration of nitrogen and the depth of gas saturated zone increase; at the statement of the 1<sup>st</sup> boundary

task ( $h \rightarrow \infty, C(0, \tau) = const$ ), we have exceeding values of the concentration (fig.2). With taking into account of the nonstationary character of processes on the interface, the curves of density of internal diffusive flux ( $j$ ) has maximum; the maximal (finite) value of density of external flux ( $j_1$ ) corresponds to the start of the interaction. In the case

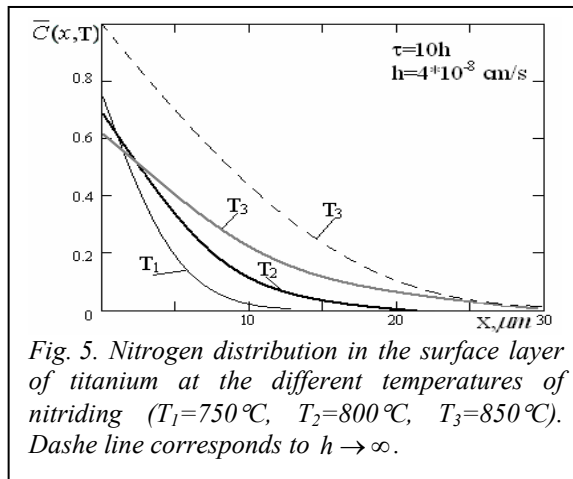


when  $C_{eq} = const$  the density of flux  $j \rightarrow 0$  at  $\tau \rightarrow 0$  (fig.3).

Fig.4 shows the deviation of mass increasing from parabolic law. For the small time it is caused by influence of surface phenomena. At the longer

exposition, it caused by chemical interaction between nitrogen and titanium.

The difference between  $\Delta M_{\Sigma}$  and  $\Delta M$  corresponds to the quantity of the nitrogen which is segregated near the surface.



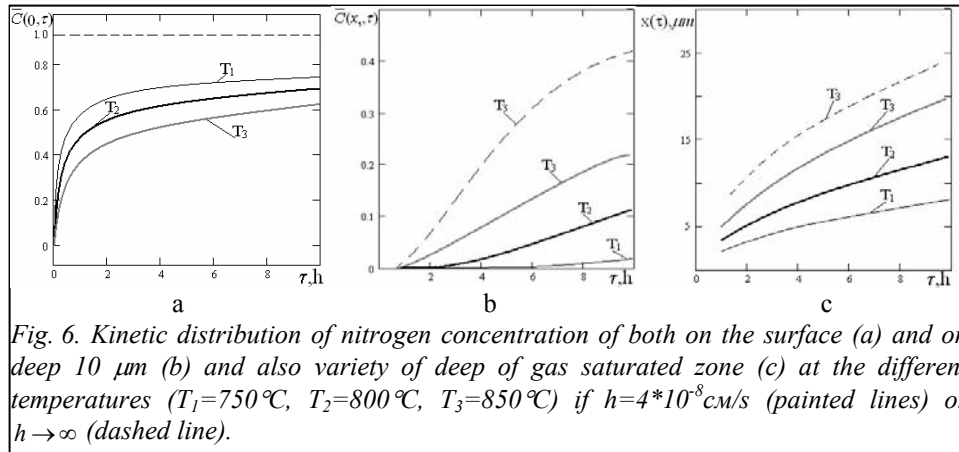


Fig. 6. Kinetic distribution of nitrogen concentration of both on the surface (a) and on deep 10  $\mu\text{m}$  (b) and also variety of deep of gas saturated zone (c) at the different temperatures ( $T_1=750^\circ\text{C}$ ,  $T_2=800^\circ\text{C}$ ,  $T_3=850^\circ\text{C}$ ) if  $h=4\cdot 10^{-8}\text{cm/s}$  (painted lines) or  $h\rightarrow\infty$  (dashed line).

The role of the temperature parameter is shown by the curves of the distribution of the nitrogen in the titanium at changing temperature (Fig. 5). At higher temperatures of isothermal nitriding, the depth of saturated zone is increasing (Fig. 5, 6c), however, the magnitude of surface concentration of nitrogen can decrease (Fig. 5, 6a) due to the intensive diffusion in the bulk of the metal (Fig. 6c). At the same time, concentration of nitrogen in the bulk of sample follows of additive dependence from temperature (Fig. 6b).

The role of partial pressure of nitrogen is represented by the curves on the Fig. 7. They are plotted for different

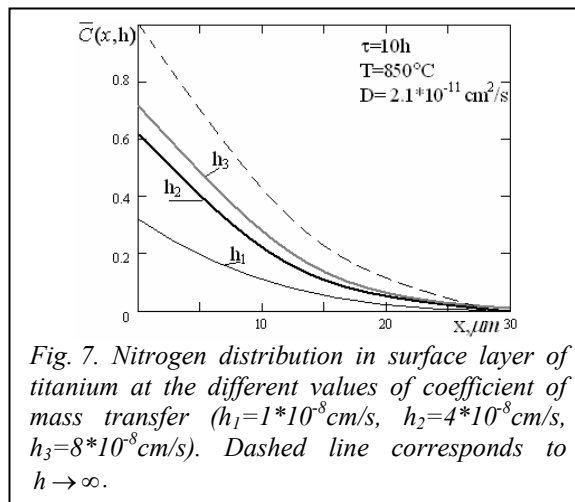


Fig. 7. Nitrogen distribution in surface layer of titanium at the different values of coefficient of mass transfer ( $h_1=1\cdot 10^{-8}\text{cm/s}$ ,  $h_2=4\cdot 10^{-8}\text{cm/s}$ ,  $h_3=8\cdot 10^{-8}\text{cm/s}$ ). Dashed line corresponds to  $h\rightarrow\infty$ .

values of the coefficient of nitrogen mass transfer ( $h$ ). With increasing of



partial pressure of nitrogen (on some region), the both a surface concentration and depth of nitriding layer increase.

### **Conclusions.**

1. Theoretical assumptions of physical-chemical processes of high-temperature interaction between titanium and boron-nitrogen containing medium in the temperature region 750-850° C are developed: a) it is proposed the mechanism of interaction according to which the gas saturated zone in titanium is formed due to the nitrogen saturation, whereas diffusion of the boron is realized in defect nitriding layer, where boron compounds segregate on the defects; b) physical-mathematical model of kinetic processes of the interaction, which includes the mutual dependence between diffusive supply of the impurity to the surface and its chemisorption with diffusion into bulk and non equilibrium segregation on the defects is offered.

1. Using nonstationery conditions of mass transfer on the interface, the kinetic regularities and features of diffusive saturation of titanium by interstitial elements (nitrogen and boron) are established. An additive dependence of both the concentration of impurity on the distant zone from the interface and the depth of saturated zone on duration and temperature of exposition and partial pressure is presented. Due to intensive diffusion in the bulk of the titanium at the longer exposition the concentration of the impurity near interface decrease; c) it is shown that there is extreme value of the internal flux near interface. The external flux is characterized by maximum of magnitude (finite value), which corresponds to the start of the interaction. Thus, due to offered equations the paradox according to which, if the surface concentration is constant and time of interaction decrease, the diffusive flux of impurity directs to infinity, is eliminated; in the calculations of mass parameter the separate value which is caused by segregation on the interface and in the bulk of metal due to which one mass increasing is deviated from the parabolic dependence was estimated.

### **References**

- [1] V. M. Fedirko, Y. M. Pohreliuk: *Nitriding of titanium and its alloys* (K.: Naukova dumka, 1995).
- [2] K. Wang, V.D. Krstic *Acta materiala* 51 (2003) 1809 – 1819.

- [3] A. M. Gusak, A. O. Bogatyryov: Metallofiz. Noveishie Teknol.-Vol. 16, № 9 (1994) p. 28-38.
- [4] L. N. Larikov: Metallofiz. Noveishie Teknol. Vol. 16, № 9 (1994), p. 3-27.
- [5] H. Sahlaoui, H. Sidhom, J. Philibert: Acta Materialia. 50, (2002) p.1383-1392
- [6] A.M. Gusak *Models of solid phases reactions* (Cherkassy: CNU, 2004)
- [7] L. L. Kunin, A. M. Golovin, U. I. Surovoi, V. M. Hohrin: (M.: Nauka, 1972)-p. 327.
- [8] A.Ronie, HSC Chemistry, ver 4.1 (Outkumpu Research Oy, Pori, Finland, 2000)
- [9] A. Raichenko *Mathematical theory of diffusion in applications* (K.: Naukova dumka, 1981)
- [10] A.Prytula, I.Pohreljuk, V. Vedirko, Ya. Matychak *Defects and diffusion forum*, Vols. 237-340 (2005) pp.1312-1318.
- [11] Ya. Matychak, O.Yeliseeva, V. Fedirko, V. Tcisar *Defects and diffusion forum*, Vols. 237-340 (2005) pp.733-738
- [12] V. Pavlyna, O. Yeliseeva, O. Lukianenko, A. Pichugin *Phisico-chemical mechanics of materials*, Vol 6,2003, p. 54-60.
- [13] T. Sobusiak *Nitriding technology Theory and practice*, 2003, pp.67-76.