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MODIFICATION OF NITRIDE COATING UNDER ION BOMBARDMENT

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Abstract

A model of nitride coating treatment by a combined beam of aluminum and boron ions is presented. Results of numerical investigation of the model are mechanical stresses in the work area, phase and chemical composition of the coating at an arbitrary instant of time and toward the end of the treatment process for varying technological parameters. On the basis of a notion of generalized plane stress-strain state it is shown that explicit differentiation between diffusion and thermal stresses is possible in individual cases only. In the simplest case the problem is reduced to described in the literature stress problem of a plate characterizing by thickness graded properties. Results of numerical investigation are in qualitative and quantitative agreement with the experimental data.

Key words: *mathematical simulation, phase and chemical composition, diffusion zone, thermal and diffusion stresses*

1. INTRODUCTION

Coatings based on titanium nitride TiN have been widely used in practice for the purpose of increasing the wear resistance of cutting tools. However, more detailed investigations of the properties of these coatings have revealed a number of disadvantages that have limited the prospects of their use in industry. In particular, TiN-based coatings exhibit a low oxidation resistance.

The use of high-energy ion beam bombardment makes it possible to synthesize coatings with a structure and phase composition varying in depth, i.e. the so-called gradient coatings [1-3].

Experimental investigations of the structure of the coating subjected to ion beam treatment cannot provide detailed information that is necessary for revealing the processes responsible for the formation of a particular structure. In this case, additional information can be obtained from the mathematical simulation. Furthermore, the appropriate simulation of the technological process is necessary for the optimization of the technological procedures and for the proper choice of their parameters.

2. MATHEMATICAL STATEMENT OF THE PROBLEM

Let us assume that a titanium nitride (TiN) coating is deposited in some way or another on a sample of α iron (Fig. 1). Then, the sample is treated with a beam of Al+ and B+ ions. The ion beam treatment leads to the implantation of ions into the surface layer of the coating followed by its heating. The substrate is also heated as a result of heat conduction. A more intensive heat removal can be achieved when the substrate contacts a material with high thermal conductivity, which is not always the case. Additional heat losses occur through radiation from the surface. The ion beam treatment is

accompanied by the redistribution of elements and the formation of different compounds and phases in the surface layer of the coating.

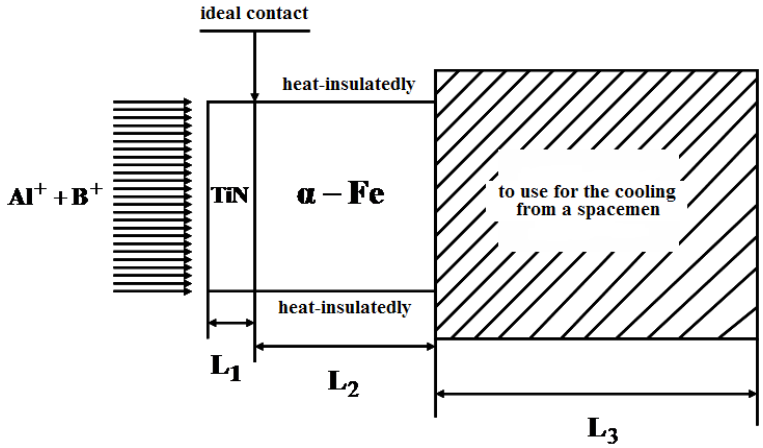


Fig.1 Conventional scheme of coating modification by a combined ion beam

If heating surface is homogeneous, lateral surfaces are heat-insulated and the sample has sufficiently large thickness then the heat conduction and diffusion problems can be considered as one-dimensional. Due to smallness of the coating and the substrate (L_1 and L_2) in comparison with heat penetration width which can be formed in the sample during the observation period the model is simplified and instead of the heat conduction equation we get the heat-balance equation [4]:

$$\left(c_1\rho_1 L_1 + c_2\rho_2 L_2 + c_3\rho_3 L_3\right)\frac{\partial T}{\partial t} = -\sigma\varepsilon\left(T^4 - T_e^4\right) + q_{eff}\, f(t) + \int_0^{L_1}\sum_{i=1}^{4} Q_i\varphi_i \mathrm{d}z \qquad (1)$$

where $q_{eff} \equiv \frac{\sqrt{\pi}}{2} q_0 erf\left(bL_1 + a\right) = m_3 h_{3,eff} + m_4 h_{4,eff}$, parameters m_3, m_4, $h_{3,eff}$, $h_{4,eff}$ are assessed from the experimental data matching [4]. The first term on the right-hand side of the equation (1) describes a heat loss obeying the Stefan-Boltzmann law. The second and the third terms are sums of sources such as from external heating and chemical reactions correspondingly.

For each of the elements initially contained in the coating with implanted ions, the transfer equation can be written in the form

$$\frac{\partial y_k}{\partial t} = -\frac{\partial}{\partial z} J_k + w_k + b^{-1}\rho_1 V_k M_k^{-1} F(t,z),\ k = 1,2,3,4 \qquad (2)$$

Here, w_k is the sum of sources and sinks of the given element in the volume due to the chemical reactions, V_k is the maximum "velocity" of the external flow of particles of the k^{th} type (for aluminum ions, k=3; for boron ions, k=4) (obviously, the maximum particle velocity is determined by the accelerating voltage), M_k is the molar mass of particles of the k^{th} type (kg/mol), J_k is the mass flow of the component due to the concentration diffusion, and ρ_1 is the density of the coating.

The function F approximates the experimentally observed distribution of implanted ions in the case where the thermally activated processes can be ignored. The function F formally reflects physical processes that are not explicitly included in the model (e.g. the internal friction and the ion transfer

due to the internal stresses generated in the surface layer). It is assumed that the function F can be represented in the form

$$F(t,z)=f(t)\cdot f_2(z),$$

where $f_2(z)=\exp\left(-\left(\frac{z-a}{b}\right)^2\right)$.

The parameters a and b have to be determined from the comparison with the experiment..

The pulsed character of the external ion source is reflected by the function

$$f(t)=\begin{cases}1,(t_i+t_p)\cdot(n-1)\le t<(t_i+t_p)\cdot(n-1)+t_i\\0,(t_i+t_p)\cdot(n-1)+t_i\le t<(t_i+t_p)\cdot n,\end{cases}$$

where n is the number of the pulse.

In the simplest variant of the model, which disregards the possible acceleration of the diffusion due to the activation [5, 6] or the influence of internal stresses, we can write for J_k, mol/m^2s

$$J_k=-D_k\frac{\partial y_k}{\partial z}, \tag{3}$$

Here, D_k is the diffusion coefficient of the element in the coating (m^2/s) depending on the temperature according to the Arrhenius law:

$$D_k=D_{k0}\exp(-\frac{E_{k0}}{RT}),$$

where E_{k0} is the activation energy of diffusion and D_{k0} is the preexponential factor.

The total sources and sinks obey the equation

$$w_k=\sum_{j=1}^{r}\nu_{kj}\varphi_j, \tag{4}$$

where r is the number of reactions; φ_j is the rate of the j^{th} reaction (mol/m^3 s); ν_{kj} is the stoichiometric coefficient of the k^{th} component in the j^{th} reaction.

With due regard for the available results of the experimental investigations of the structure and composition of the coatings after completion of the ion beam treatment process [7, 8] and elsewhere, among the potentially possible reactions, we choose the following reactions

$$Ti+Al+B+N\rightarrow TiAlBN \text{ (the formation of the solid solution) (I)}$$

$$Ti+2B\rightarrow TiB_2 \text{ (the exothermic reaction) (II)}$$

$$Ti+B\rightarrow TiB \text{ (the exothermic reaction) (III)}$$

$$Al+12B\rightarrow AlB_{12} \text{ (the exothermic reaction) (IV).}$$

Reaction (I) corresponds to the formation of the $Ti_{1-x}Al_xB_2$ and Ti_3AlN phases.

Since other compounds were not revealed in the experiments, other reactions were not included in the model. Nonetheless, there can appear other compounds under nonequilibrium conditions, whereas the coating compositions experimentally obtained in [7, 8] correspond to those formed after the treatment and "relaxation" in the course of cooling.

Consequently, the kinetic functions of reactions (I) – (IV) can be written in the form

$$\varphi_1 = k_1 y_1 y_2 y_3 y_4 \exp\left(-\frac{E_1}{RT}\right); \varphi_2 = k_2 y_1 y_4^2 \exp\left(-\frac{E_2}{RT}\right);$$
$$\varphi_3 = k_3 y_1 y_4 \exp\left(-\frac{E_3}{RT}\right); \varphi_4 = k_4 y_3 y_4^{12} \exp\left(-\frac{E_4}{RT}\right). \quad (5)$$

For nondiffusing compounds, we can write the following kinetic equations

$$\frac{\partial y_k}{\partial t} = w_k, \; k = 5,6,7,8 \quad (6)$$

According to the scheme of reactions (I)–(IV), we have

$$w_1 = -(\varphi_1 + \varphi_2 + \varphi_3); \; w_2 = -\varphi_1; \; w_3 = -(\varphi_1 + \varphi_4);$$
$$w_4 = -(\varphi_1 + 2\varphi_2 + \varphi_3 + 12\varphi_4); \quad (7)$$
$$w_5 = \varphi_1; \; w_6 = \varphi_2; \; w_7 = \varphi_3; w_8 = \varphi_4$$

If under the experimental conditions the coating for the diffusion process has an "infinite thickness" (i.e., the thickness of the coating considerably exceeds the typical diffusion scale) then the diffusion problem is closed by the simple boundary conditions:

$$x = 0 : J_k = 0; \; x \to \infty : J_k = 0. \quad (8)$$

At the initial instant of time, the concentrations of the elements are specified as follows:

$$t = 0 : C_1 = C_{10}; C_2 = C_{20}; C_k = 0, \; k = 3-8 \quad (9)$$

The problem is solved numerically with the use of the special algorithm described in [9]. According to this algorithm, the heat conduction and the diffusion problems are solved using different but matched difference schemes. Since the temperature distribution over the coordinate is ignored in the model under consideration, the algorithm is reduced to the matching of the time steps in the diffusion and heat sub-problems according to the characteristic rates of the heat conduction and diffusion processes. The system of kinetic equations is solved independently by the Runge-Kutta method with the automatic choice of the step at each step of solving the heat problem.

3. ANALYSIS OF NUMERICAL RESULTS

The parameters a and b have been assessed numerically, from the comparison of relative atomic concentrations Al and B in the surface layer of the coating toward the end of the treatment process with experimental data [4] for irradiation dose under which the diffusion processes and chemical reactions are not activated. It is shown on the fig.2.

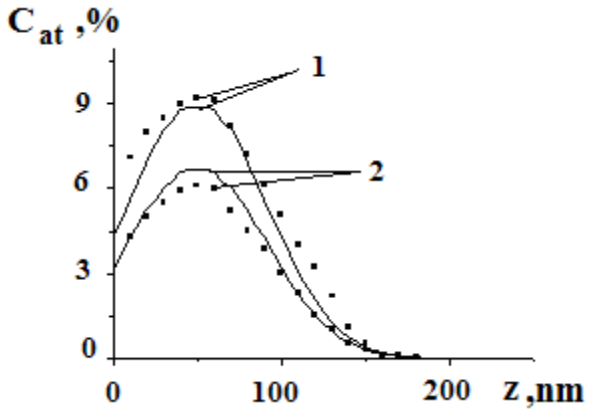


Fig. 2. Distribution of implanted ions in the coating for $D = 10^{17}$ ions/cm^2.
$q_{m,3} = 2.0 \cdot 10^{-10}$ *mol/(cm^{2}s)*, $q_{m,4} = 1.5 \cdot 10^{-10}$ *mol/(cm^{2}s)*
Solid curves represent the results of theoretical calculations and symbols ▪ indicate the experimental data ([4]).
1 is for Al^+, 2 is for B^+

An increase in the irradiation dose, the treatment time, and the initial heating (the initial temperature of the sample) can bring about the diffusion redistribution of all elements and chemical transformations. In order to evaluate the formal kinetic parameters of the chemical reactions, we use the standard apparatus of the chemical thermodynamics [10]. The rate constants of the chemical reactions were evaluated from the standard thermodynamic formulas according to the procedure described in [11].

The time dependencies of the average temperature of the sample for varying irradiation modes are plotted in Fig.3. It is evident that the higher the irradiation dose, the higher the temperature. At the irradiation dose $D = 10^{17}$ *ions/cm^2*, the temperature doesn't exceed 30-40°C, which is in agreement with the experimental data.

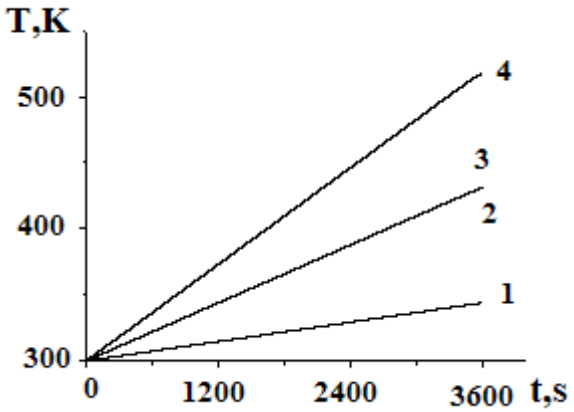


Fig. 3. Time dependencies of the sample temperature at different irradiation doses:
1– $D = 10^{17}$ *ions/cm^2*, 2– $D = 3.25 \cdot 10^{17}$ *ions/cm^2*, 3– $D = 4 \cdot 10^{17}$ *ions/cm^2*, 4– $D = 6 \cdot 10^{17}$ *ions/cm^2*

Each calculation provides complete information on the dynamics of the distribution of the molar concentration of the "unbound" elements and chemical compounds, as well as the distribution of atomic concentrations of the Ti, Al, B, and N elements at an arbitrary instant of time and toward the end of the treatment process.

It is evident that an increase in the irradiation dose leads to an increase in the height of the maxima in the distributions of implanted ions and an increase in the depth of the minima in the Ti and N distributions. This is connected with expenditures of the elements on the formation of the chemical compounds and the solid solution. At the maximum irradiation dose, there arises an interesting effect: the solid solution at the first instants of time is formed in the region corresponding to the maximum of implanted ions (fig. 4). Then, the maximum in the distribution of the solid solution (y_5) ceases to change, but the reaction of the formation of the *TiAlBN* solid solution propagates in both directions, i.e., deep into the coating and toward the surface. The total content of the solid solution in the surface layer of the coating increases with an increase in the irradiation dose. This also agrees with the experimental results.

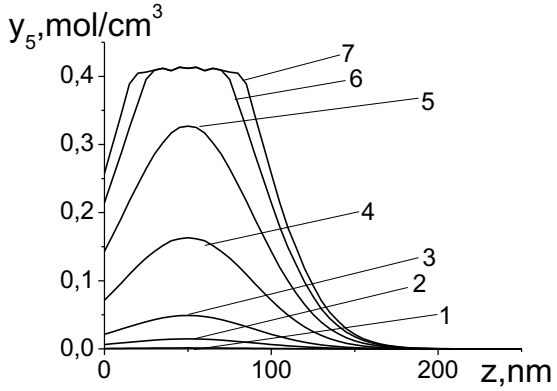


Fig. 4. Spatial distributions of the mole fractions of the *TiAlBN* solid solution (y_5) at different instants of time 1–9, 2–90, 3–300, 4–1000, 5–2000, 6–3000, 7–3600 s. for maximum irradiation dose $D = 6 \cdot 10^{17}$ *ions/cm*^{2}

It should also be noted that, at the chosen parameters, the TiB and TiB_2 compounds are formed in small amounts, whereas the AlB_{12} compound is not formed over the entire range of irradiation doses under investigation.

Numerical results and the experimental data at irradiation dose $D = 10^{17}$ *ions/cm*^{2} are presented in Table 1. It is seen, that agreement of the results is rather satisfactory. Numerical concentration values do not agree with the experimental data as far as parameters of the model have been assessed with a certain error. For instance, the diffusion coefficients used in our calculations are most likely underestimated and do not correspond to the diffusion coefficients D_k in the solid solution. In the real experiment, the treatment depth increases with an increase in the irradiation dose. This can be explained by acceleration of diffusion, for example, due to the activation of the elements in the surface layer [5, 6], which is ignored in the model.

Table 1

Comparison of the calculation data of relative atomic concentrations of pure elements *Ti, N, Al, B* with the experimental data [4]
at irradiation dose $D = 10^{17}$ *ions/cm²*

C_{at}, %	**Ti**	**N**	**Al**	**B**
	experiment			
D=10^{17} *ions/cm²*	50	38	9	5
	theory			
	56	28	9.2	6.8

It should be noted that in the result of irradiation by an ion beam at $D = 4 \cdot 10^{17}$ *ions/cm²* the content of the TiAlBN new phase amounts to 37 % what also agrees with the experimental data [4].

4. EVALUATION OF STRESSES AND DEFORMATIONS IN THE DIFFUSION ZONE

Assuming that deformations are small, we have used known models of thermo- and masselasticity to evaluate stresses and deformations [12, 13]. In this case

$$\sigma_{ij}^{e} = 2\mu\varepsilon_{ij} + \delta_{ij}\left[\lambda\varepsilon_{kk} - K\omega\right] \tag{10}$$

In the general case a stress problem includes equilibrium equations, Duamel-Neumann relations and compatibility equations incurring from Cauchy equations [14, 15].

We will examine the particular case of a slab with thickness graded properties. The slab is completely free from volume surface forces. The temperature and the concentrations are varying with the thickness only, i.e. $T = T(z)$. For these conditions we have:

$$\sigma_{xx} = \sigma_{yy} = f(z),\ \sigma_{zz} = \sigma_{xz} = \sigma_{yx} = \sigma_{zy} = 0. \tag{11}$$

Hence it follows that from the compatibility equations we have two equivalent equations:

$$\frac{\partial^2 \varepsilon_{yy}}{\partial z^2} = 0 \ \text{и}\ \frac{\partial^2 \varepsilon_{xx}}{\partial z^2} = 0. \tag{12}$$

It follows from (10) under condition (11):

$$\begin{gathered}\sigma_{xx} = 2\mu\varepsilon_{xx} + \left[\lambda\varepsilon_{kk} - K\omega\right];\\ \sigma_{yy} = 2\mu\varepsilon_{yy} + \left[\lambda\varepsilon_{kk} - K\omega\right];\ 0 = 2\mu\varepsilon_{zz} + \left[\lambda\varepsilon_{kk} - K\omega\right];\\ 0 = 2\mu\varepsilon_{xy};\ 0 = 2\mu\varepsilon_{yz};\ 0 = 2\mu\varepsilon_{xz}.\end{gathered} \tag{13}$$

Taking into account the symmetry of the problem we have: $\sigma_{kk} = \sigma_{xx} + \sigma_{yy} = 2\sigma_{yy} = 2\sigma$.

From (13) we have

$$\varepsilon_{kk} = \frac{2\sigma}{3K} + \omega . \tag{14}$$

Substituting (14) in (13) we get

$$\varepsilon_{xx} = \sigma\left(\frac{\lambda+2\mu}{2\mu\cdot 3K}\right) + \frac{1}{3}\omega;\ \varepsilon_{yy} = \sigma\left(\frac{\lambda+2\mu}{2\mu\cdot 3K}\right) + \frac{1}{3}\omega;\ \varepsilon_{zz} = \frac{K\omega}{2\mu} - \frac{\lambda\varepsilon_{kk}}{2\mu}, \tag{15}$$

Then, from (12) we have

$$\frac{\partial^2 \varepsilon_{yy}}{\partial z^2} = \frac{\partial^2}{\partial z^2}\left[\frac{1-\nu}{E}\sigma_{yy} + \frac{1}{3}\omega\right] = 0, \tag{16}$$

$$\varepsilon_{xx} = \varepsilon_{yy} = C_1 + C_2 z,$$

$$\varepsilon_{zz} = \frac{K\omega - 2\lambda\varepsilon_{xx}}{2\mu+\lambda}.$$

By integrating the equation (16) we get a relation for stress tensor components $\sigma_{xx} = \sigma_{yy}$ written as:

$$\sigma_{yy} = \frac{E}{1-\nu}\left(-\frac{1}{3}\omega + C_1 + C_2 z\right). \tag{17}$$

The constants C_1 and C_2 in principle have to be assessed from zero boundary conditions for stresses on the edges of the slab. But it would mean that the stresses are equal to zero throughout the whole thickness excepting the particular case of linear z variation of temperature and concentration which is not satisfied in the general case. We can select the values of the constants C_1 and C_2 in such way [15] that for any temperatures $T(z)$ and concentrations $y_k(z)$ the resultant force and moment (per unit of lenght) caused by σ_{xx} and σ_{yy} have been equal to zero on the edges of the slab (which is compound in this case), i.e. so that:

$$\int_0^{L_1+L_2+L_3} \sigma_{yy} dz = 0 \text{ and } \int_0^{L_1+L_2+L_3} \sigma_{yy}\cdot z \cdot dz = 0. \tag{18}$$

Substituting (17) into (18):

$$\int_0^{L_1+L_2+L_3} \left[\frac{E}{1-\nu}\left(-\frac{1}{3}\omega + C_1 + C_2 z\right)\right] dz = 0 \tag{19}$$

$$\int_0^{L_1+L_2+L_3} \left[\frac{E}{1-\nu}\left(-\frac{1}{3}\omega + C_1 + C_2 z\right)\right]\cdot z \cdot dz = 0. \tag{20}$$

Let us introduce the following designations

$$f_1(t) = -\frac{1}{3}\int_0^{L1+L2+L3} \frac{E}{1-\nu}\cdot\omega\cdot dz, \tag{21}$$

$$f_2(t) = -\frac{1}{3}\int_0^{L1+L2+L3} \frac{E}{1-\nu}\cdot\omega\cdot z\cdot dz, \tag{22}$$

$$A = \int_0^{L1+L2+L3} \frac{E}{1-\nu}dz = \frac{E_1}{1-\nu_1}L_1 + \frac{E_2}{1-\nu_2}L_2 + \frac{E_3}{1-\nu_3}L_3,$$

$$B = \int_0^{L1+L2+L3} z\frac{E}{1-\nu}dz =$$

$$= \frac{E_1}{1-\nu_1}\frac{L_1^2}{2} + \frac{E_2}{1-\nu_2}\left(\frac{(L_1+L_2)^2}{2} - \frac{L_1^2}{2}\right) + \frac{E_3}{1-\nu_3}\left(\frac{(L_1+L_2+L_3)^2}{2} - \frac{(L_1+L_2)^2}{2}\right),$$

$$D = \int_0^{L1+L2+L3} z^2\frac{E}{1-\nu}dz =$$

$$= \frac{E_1}{1-\nu_1}\frac{L_1^3}{3} + \frac{E_2}{1-\nu_2}\left(\frac{(L_1+L_2)^3}{3} - \frac{L_1^3}{3}\right) + \frac{E_3}{1-\nu_3}\left(\frac{(L_1+L_2+L_3)^3}{3} - \frac{(L_1+L_2)^3}{3}\right).$$

Hence, we have the system of linear equations for finding of the integration constants C_1 and C_2:

$$\begin{cases} f_1(t) + C_1A + C_2B = 0: \\ f_2(t) + C_1B + C_2D = 0, \end{cases}$$

whence it follows

$$\begin{aligned} C_1 &= \frac{Df_1(t) - Bf_2(t)}{B^2 - AD} \\ C_2 &= \frac{Af_2(t) - Bf_1(t)}{B^2 - AD} \end{aligned} \tag{23}$$

Let us calculate integrals in $f_1(t)$ taking into account physical features of the problem under consideration. We have:

$$f_1(t) = -\frac{1}{3}\int_0^{L1+L2+L3} \frac{E}{1-\nu}\cdot\omega\cdot dz = -\frac{1}{3}\int_0^{L1} \frac{E}{1-\nu}\cdot\omega\cdot dz - \frac{1}{3}\int_{L1}^{L1+L2} \frac{E}{1-\nu}\cdot\omega\cdot dz - \frac{1}{3}\int_{L1+L2}^{L1+L2+L3} \frac{E}{1-\nu}\cdot\omega\cdot dz$$

or

$$f_1(t) = -\frac{1}{3}\left[I_1 + I_2 + I_3\right].$$

Indexes $1,2,3$ correspond to different parts of the sample in fig.1.

Both the temperature and the concentration change explicitly in the coating. But the coating have been heated homogeneously, so that:

$$I_1 = \int_0^{L_1} \frac{E}{1-\nu} \cdot \omega \cdot dz = 3\frac{E_1}{1-\nu_1} \int_0^{L_1} \left[\alpha_T (T - T_0) + \sum_{k=1}^{n} \alpha_k \left(y_k - y_{k0} \right) \right] \cdot dz =$$

$$3\frac{E_1}{1-\nu_1} \alpha_{T,1} (\widetilde{T} - T_0) L_1 + 3\frac{E_1}{1-\nu_1} \int_0^{L_1} \left[\sum_{k=1}^{n} \alpha_k \left(y_k - y_{k0} \right) \right] dz.$$

In two other layers the concentrations do not change, so that:

$$I_2 = \int_{L_1}^{L_1+L_2} \frac{E}{1-\nu} \cdot \omega \cdot dz = 3\frac{E_2}{1-\nu_2} \alpha_{T,2} (\widetilde{T} - T_0) L_2$$

$$I_3 = \int_{L_1+L_2}^{L_1+L_2+L_3} \frac{E}{1-\nu} \cdot \omega \cdot dz = 3\frac{E_3}{1-\nu_3} \alpha_{T,3} \int_{L_1+L_2}^{L_1+L_2+L_3} (T - T_0) dz \approx 3\frac{E_3}{1-\nu_3} \alpha_{T,3} L_3 (T - T_0)$$

In a similar manner we proceed with the function $f_2(t)$. We have:

$$f_2(t) = -\frac{1}{3} \int_0^{L_1} \frac{E}{1-\nu} \cdot \omega \cdot z \cdot dz - \frac{1}{3} \int_{L_1}^{L_1+L_2} \frac{E}{1-\nu} \cdot \omega \cdot z \cdot dz - \frac{1}{3} \int_{L_1+L_2}^{L_1+L_2+L_3} \frac{E}{1-\nu} \cdot \omega \cdot z \cdot dz$$

or

$$f_2(t) = -\frac{1}{3} \left[J_1 + J_2 + J_3 \right],$$

where

$$J_1 = \int_0^{L_1} \frac{E}{1-\nu} \cdot \omega \cdot z \cdot dz = 3\frac{E_1}{1-\nu_1} \alpha_{T,1} (\widetilde{T} - T_0) \frac{L_1^2}{2} + 3\frac{E_1}{1-\nu_1} \int_0^{L_1} \left[\sum_{k=1}^{n} \alpha_k \left(y_k - y_{k0} \right) \right] \cdot z \cdot dz,$$

$$J_2 = 3\frac{E_2}{1-\nu_2} \alpha_{T,2} (\widetilde{T} - T_0) \left(\frac{(L_1 + L_2)^2}{2} - \frac{L_1^2}{2} \right),$$

$$J_3 = 3\frac{E_3}{1-\nu_3} \alpha_{T,3} \int_{L_1+L_2}^{L_1+L_2+L_3} (T - T_0) \cdot z \cdot dz \approx 3\frac{E_3}{1-\nu_3} \alpha_{T,3} (T - T_0) \left(\frac{(L_1 + L_2 + L_3)^2}{2} - \frac{(L_1 + L_2)^2}{2} \right).$$

Finally, we have different relations for different layers.

Thus, stresses in the coating can be evaluated by the following formula:

$$\sigma_{xx,1} = \sigma_{yy,1} = \frac{E_1}{1-\nu_1} \left[-\alpha_{T,1} \left(\widetilde{T} - T_0 \right) - \sum_{k=1}^{n} \alpha_k \left(y_k - y_{k0} \right) + C_1 + C_2 z \right], \; 0 \le z \le L_1. \qquad (24)$$

The first term in (24) is a function of t only, the rest of the terms are functions of t, z. This formula is for stresses in the diffusion zone.

In two other layers we have

$$\sigma_{xx,2} = \sigma_{yy,2} = \frac{E_2}{1-\nu_2}\left[-\alpha_{T,2}\left(\widetilde{T} - T_0\right) + C_1 + C_2 z\right],\ L_1 \le z \le L_1 + L_2, \tag{25}$$

$$\sigma_{xx,3} = \sigma_{yy,3} = \frac{E_3}{1-\nu_3}\left[-\alpha_{T,3}\left(T - T_0\right) + C_1 + C_2 z\right], L_1 + L_2 \le z \le L_1 + L_2 + L_3. \tag{26}$$

Taking into account the above we can write

$$\begin{aligned}\widetilde{\sigma}_{xx,2} = \widetilde{\sigma}_{yy,2} = \frac{E_2}{1-\nu_2}\left[-\alpha_{T,2}\left(\widetilde{T} - T_0\right) + \frac{1}{L_2}\int_{L1}^{L1+L2}\left(C_1 + C_2 z\right)dz\right] = \\ \frac{E_2}{1-\nu_2}\left[-\alpha_{T,2}\left(\widetilde{T} - T_0\right) + C_1 + \frac{C_2}{L_2}\left(\frac{\left(L_1 + L_2\right)^2}{2} - \frac{{L_1}^2}{2}\right)\right],\end{aligned} \tag{27}$$

$$\begin{aligned}\widetilde{\sigma}_{xx,3} = \widetilde{\sigma}_{yy,3} = \frac{E_3}{1-\nu_3}\left[-\alpha_{T,3}\left(T - T_0\right) + C_1 + C_2 z\right] = \\ \frac{E_3}{1-\nu_3}\left[-\alpha_{T,3}\left(\widetilde{T} - T_0\right) + C_1 + \frac{C_2}{L_3}\left(\frac{\left(L_1 + L_2 + L_3\right)^2}{2} - \frac{\left(L_1 + L_2\right)^2}{2}\right)\right].\end{aligned} \tag{28}$$

These expressions describe the macroscopic stresses which incorporate the contribution of the diffusion zone via C_1 and C_2.

In a similar manner we proceed with evaluation of deformations in layers 1 – 3:

$$\varepsilon_{xx,1} = \varepsilon_{yy,1} = C_1 + C_2 z, \tag{29}$$

$$\widetilde{\varepsilon}_{xx,2} = \widetilde{\varepsilon}_{yy,2} = C_1 + \frac{C_2}{L_2}\left(\frac{\left(L_1 + L_2\right)^2}{2} - \frac{{L_1}^2}{2}\right),$$

$$\widetilde{\varepsilon}_{xx,3} = \widetilde{\varepsilon}_{yy,3} = C_1 + \frac{C_2}{L_3}\left(\frac{\left(L_1 + L_2 + L_3\right)^2}{2} - \frac{\left(L_1 + L_2\right)^2}{2}\right).$$

and

$$\varepsilon_{zz,1} = \frac{K_1\left(3\alpha_{T,1}\left(\widetilde{T} - T_0\right) - \sum_{k=1}^{n}\alpha_k\left(y_k - y_{k0}\right)\right) - 2\lambda_1\varepsilon_{xx,1}}{2\mu_1 + \lambda_1},$$

$$\widetilde{\varepsilon}_{zz,2} = \frac{K_2\left(3\alpha_{T,2}\left(\widetilde{T} - T_0\right)\right) - 2\lambda_2\widetilde{\varepsilon}_{xx,2}}{2\mu_2 + \lambda_2},$$

$$\widetilde{\varepsilon}_{zz,3} = \frac{K_3\left(3\alpha_{T,3}\left(\widetilde{T} - T_0\right)\right) - 2\lambda_3\widetilde{\varepsilon}_{xx,3}}{2\mu_3 + \lambda_3}.$$

For numerical evaluation of stresses in the diffusion zone and the macroscopic stresses we need to know mechanical properties E_j, ν_j, $j = 1,2,3$ and coefficients $\alpha_{j,k}$ and α_T. Obviously, E_1, ν_1 change with change in composition, but dependencies $E_1(y_k)$, as a rule, are undetermined. Hence, we will limit ourselves to certain effective values (as it was taken into account in deriving of formulas). Let us assume

$$E_1 = 65\cdot10^3,\ E_2 = 195\cdot10^3,\ E_3 = 205\cdot10^3\ \text{N/cm}^2;\ \nu_1 = 0{,}3,\ \nu_2 = 0{,}28,\ \nu_3 = 0{,}3.$$

We will use the approximate approach described in [16, 17] for evaluation of $\alpha_{j,k}$. According to this approach the most widely used evaluation of a solute lattice contraction coefficient has the next form

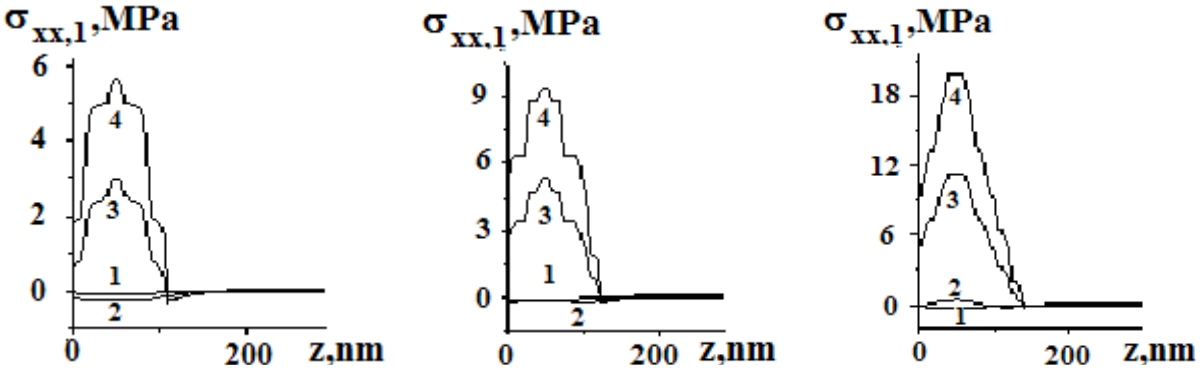
$$\alpha_k = \frac{1}{3}\frac{\omega}{\sum_{(i)}\omega_i}, \tag{30}$$

Here ω is the atomic (molecular, molar) volume of the component with the number k in its phase.

Evaluation of the coefficients $\alpha_{j,k}$ by the formula (30) gives

$$\alpha_{Ti} \approx 0.083,\ \alpha_N \approx 0.136,\ \alpha_{Al} \approx 0.078,\ \alpha_B \approx 0.036.$$

For given experimental conditions the numerical stress analysis showed that an increase in the irradiation dose leads to an increase in the stresses in the coating. The maxima in the stress distributions are observed in the region corresponding to the maxima of implanted ions (fig. 5, a-c).



a) b) c)

Fig. 5. Spatial distributions of the stresses in the coating for a varying the irradiation dose for the

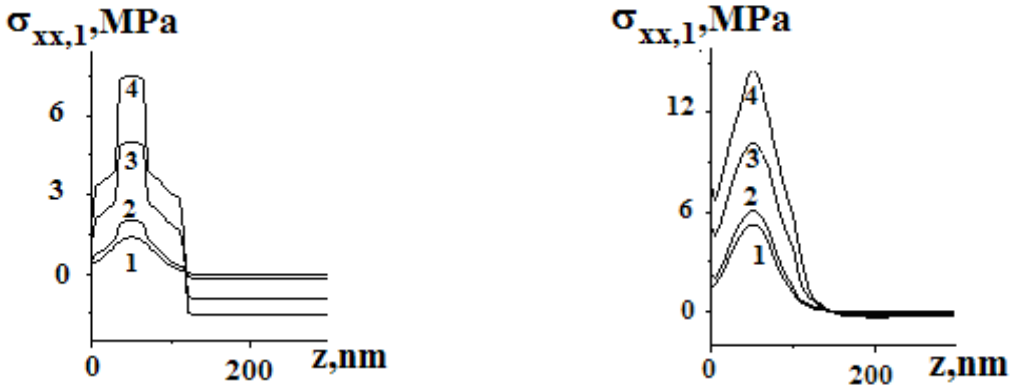
initial temperature of the surface $T_0 = 300K$ at instants of time t: 1–0,25; 2–1,25; 3–6; 4–10s.

a) $q_{m3} = 2 \cdot 10^{-10}$, $q_{m4} = 1.5 \cdot 10^{-10}$ mol/(cm^{2}s);

b) $q_{m3} = 4 \cdot 10^{-10}$, $q_{m4} = 3 \cdot 10^{-10}$ mol/(cm^{2}s);

c) $q_{m3} = 8 \cdot 10^{-10}$, $q_{m4} = 6 \cdot 10^{-10}$ mol/(cm^{2}s)

For high irradiation doses the maximum in the stress distribution diffuses (fig. 5, c). This is connected with redistribution of the elements as a result of the diffusion.



a) b)

Fig. 6. Spatial distribution of the stresses in the coating for a varying the irradiation dose for the initial temperature of the surface $T_0 = 773K$ at instants of time t: 1–0,25; 2–1,25; 3–6; 4–10s.

a) $q_{m3} = 2 \cdot 10^{-10}$, $q_{m4} = 1.5 \cdot 10^{-10}$ mol/(cm^{2}s);

b) $q_{m3} = 4 \cdot 10^{-10}$, $q_{m4} = 3 \cdot 10^{-10}$ mol/(cm^{2}s)

For an increasing in the initial temperature up to $T_0 = 773K$ and fixed flow q_{m3}, q_{m4} a qualitative change in behavior of stresses connected with the preceding activation of the diffusion and chemical transformations is observed (fig. 6.).

Complete calculation corresponding to the real time of treatment (1 hour) shows that the values of stresses in the diffusion zone are very high (about 6000 MPa) and it correlates with the experimental data. Numerical calculations of stresses can disagree with stresses observed in reality as far as there is a number of effects (such as change of thermophysical and mechanical properties) which have not been taken into account in the model under consideration.

5. CONCLUSIONS

We have examined the problem of modification of nitride coating by a combined ion beam accounting for formation of chemical compositions and phases with ions.

It was revealed that values of the diffusion coefficients corresponding to the reference data which was taken in our calculations are understated and do not correspond to values of these coefficients under conditions of high-energy treatment.

We have proposed a method of evaluation of stresses which appear in the diffusion zone during the process of material treatment by ion beams. Our evaluations take into account a contribution of not only diffusion but also chemical processes to irreversible deformations.

Theoretical results agree sufficiently with the experimental data.

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