INTRINSIC STRESS FORMATION IN MULTI-COMPONENT COATINGS PRODUCED BY PLASMA ION DEPOSITION IN MODES OF DC AND PULSE BIAS POTENTIALS

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In the model of nonlocal thermoelastic peak of low-energy ion a formula for intrinsic stress in multi-component material deposited from mixed beam of differently charged ions in modes of DC and pulse bias potentials is derived. Calculation of intrinsic stress σ depending on bias potential U in coating Cr-Al-N deposited from mixed ion beam Cr(50%)Al(50%) is executed at different modes and substrate temperatures T_0. It is shown that maximum of $\sigma(U)$ in pulse bias potential mode shifts towards higher U as compared with DC mode whereas increase of T_0 leads to opposite effect.

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INTRODUCTION

Multi-component nanostructure coatings, based on nitrides of Al, Ti, Cr, Mo, Zr, Nb, Hf, are recently considered as the leading candidates for device component protection as they combine improved operational characteristics such as hardness, durability, corrosion and radiation resistance. Such coatings are widely used for hardening of cutting tools, compressor and turbine blades, as well as friction pairs, operated in extreme conditions [1]. There are proposals on the use of nitride coatings as protective coatings of fuel elements and other components of the primary circuit of nuclear reactor [2].

Such coatings are formed mainly by vacuum-arc and plasma-ion deposition. The essential feature of these methods is appearance of intrinsic stresses in the deposited coatings. These stresses, along with beneficial effects, manifested in the creation of dense and tough coatings, can cause negative consequences, such as cracking, peeling and flaking coatings [3]. The knowledge of intrinsic stresses depending on the deposition parameters is necessary for the quality control of deposited coatings.

A number of works are devoted to the theoretical study of the origin and role of intrinsic stress in the coating by ion deposition. It is worth to notice that wide use of molecular dynamics simulations allowed to establish many characteristics of films growing at the chosen values of ion energy, substrate temperature, etc. [4]. However, to control the intrinsic stress we have to possess equations relating intrinsic stress to deposition parameters, i. e. species and energy of the ions, temperature and deposition regime. These equations can be obtained only as a result of physically-based mathematical modeling of the intrinsic stress origination.

C.A. Davis proposed a simple model in which intrinsic stress is formed as a result of two simultaneous but differently directed processes: 1) stress generation due to ion implantation and 2) stress relaxation due to thermally activated processes of migration in the point thermal peaks (PTP) of ions. In case of DC bias potential the Davis's model gives the dependence of intrinsic stress σ on ion energy E [3]:

$$\sigma(E) \sim \frac{E_Y}{1-\Pi} \frac{E^{1/2}}{\xi + w_0(E)}, \tag{1}$$

where E_Y и Π are the Young modulus and the Poisson ratio of the target material, respectively, ξ is the ratio of the total flux of deposited atoms J_a to the ion flux J. The number of thermally activated transitions w_0 generated by ion are calculated within PTP model:

$$w_0(E,u) \approx 0{,}016(E/u)^{5/3}, \tag{2}$$

where u is the activation energy of defect migration.

The Davis'es model permitted explaining the appearance of intrinsic stresses in the coating at plasma ion deposition. Derived formula (1) provided a qualitative explanation of the observed dependence of the stresses on the ion energy and quantitative agreement with experimental results by a suitable choice of u parameter.

Nevertheless, this model has some shortcomings. First of all, the use of PTP formalism contradicts to the fact of nonlocality of energy transfer from ion to target material. Therefore formula (1) can't explain the experimentally observed dependence of the stress on deposition temperature. Moreover, its agreement with the experimental data is achieved at values u, far exceeding the known values for the defect migration. Among other shortcomings of the PTP model one should be noted its inherent inconsistency, as the model is built only for the case of zero temperature environment and at the same time assumes the constancy of the heat capacity and it independence on temperature.

We have proposed a modification of the formula Davis, based on the model of a nonlocal thermoelastic peak (NTP) of low-energy ion, i. e. overheated and overpressured nanometer-sized region arising around the ion path in the target material as a result of thermalization of elastic losses of ion [5]. According to the model, the NTP of low-energy ion is approximated by spherical segment adjacent to the target surface. The main parameters of the NTP are the radius

$$R(E,t) = l(E)/2 + R_T(t) \tag{3}$$

and the energy content

$$E_{ph} = \eta(E)E. \tag{4}$$

Here $l(E)$ is the average projective range, and $\eta(E)$ is the relative part of phonon losses of the ion, calculated using the software package SRIM2000; $R_T(t)$ is the radius of "smearing" of the point heat source for time *t*. The center of the NTP is situated in the middle of the average projected range of the ion *l*.

Determining the functions $l(E)$ and E_{ph} we can calculate the volume

$$V = \frac{4\pi}{3}\left(R^3 - \frac{3}{8}R_T{}^2 l - R_T{}^3/2\right) \qquad (5)$$

and the average temperature of the NTP

$$T(E,t,T_0) = \frac{E_{ph}(E)}{\rho C V(E,t)} + T_0 . \qquad (6)$$

Here ρ, C, and T_0 are the mass density, the specific heat and the initial temperature of the target material, respectively. For simplicity, arguments of functions V, R, l and R_T are omitted in Eq. (5).

Repeating reasoning of Davis [3] we have obtained the following modified formula for intrinsic stress in the DC mode [7]:

$$\sigma(E,u) \sim \frac{E_Y}{1-\Pi}\cdot\frac{\sqrt{E}}{\xi + w(E,u)} . \qquad (7)$$

Coinciding by the structure with Eq. (1), the Eq. (7) comprises the function $w(E,u,T_0)$ of the number of thermally activated transition, calculated in NTP model:

$$w(E,u,T_0) = n_0 \nu \int_0^{\tau_c} V(t,E)\, \mathrm{e}^{-\frac{u}{k_B T(t,E,T_0)}}\, dt , \qquad (8)$$

where k_B is the Boltzmann constant, n_0 is the concentration of atoms in target, ν is the atom oscillation frequency, and τ_c is the NTP lifetime.

The modified formula was used to explain a number of regularities observed in the deposition of DLC and BN coatings in DC mode. However, the use of mixed beams of differently charged ions and pulse bias potential mode requires another revision of the formula for intrinsic stress in coating.

The purpose of this work is the derivation of the formula for intrinsic stress in coating deposited from mixed beam of differently charged ions in modes of DC and pulse bias potentials, and the use resulting formula for calculation of intrinsic stress in nitride coating of Cr-Al-N deposited from ion flux of Cr(50%) Al (50%) in DC and pulse bias potentials modes at different deposition temperatures.

MATHEMATICAL MODEL

In the course of deriving formula for intrinsic stress we followed the reasoning used in [3]. Particularly, the expounded model as the Davis'es model, is based on the hypothesis of a linear dependence between volumetric deformation of the target material and density of defects produced from the ion scattering on the atoms of the target. In [8], based on the linear theory of Sigmund cascade collisions, it has been suggested that the rate of defects formation per unit area $\dot{n}_d$ associated with a flux density of the incident ions J, and ion energy E by the expression $\dot{n}_d \sim JE^{1/2}$. However, it should be noted that this dependence arising from the model assumptions is the only analytical approximation which satisfactorily describes the process of defect production only at sufficiently high energy of the incident ion $E >> E_d$, where E_d is the energy of the defect formation. In this paper, we use the dependence for $\dot{n}_d$, given by direct calculation of the part of the ion energy that is used for the production of vacancies $\upsilon(E)$ created by ions with energy E. Calculation of function $\upsilon(E)$ was performed using SRIM2000 in option "Detailed Calculation with full Damage Cascade" [9]. We assume that each vacancy corresponds to interstitial forming together Frenkel pairs. In accordance with the definition of the function $\upsilon(E)$, the number of point defects (Frenkel pairs), formed by the primary ion is equal to $E\upsilon(E)/E_d$. We assumed in calculation $E_d = 25$ eV. It should also take into account the contribution to the volumetric deformation of the primary ion, which is constant for all ions of the same species with energies $E > E_s$ permitting to penetrate the surface of the solid body ($E_s \sim 10$ eV). As a result, the expression for the rate of defects formation can be presented as:

$$\dot{n}_d \sim J\left[\frac{E\,\upsilon(E)}{E_d} + \Upsilon\right], \qquad (9)$$

where Υ is the own contribution of the primary ion in volumetric deformation due to its implantation in terms of the contribution of Frenkel pairs. Since the volume deformation is proportional to the stress, the expression (9) also characterizes the rate of growth of intrinsic stresses due to the defects formation.

The opposite process of stress relaxation is determined by the number of thermally activated transitions of atoms in the NTP of ion defined by the expression (8). Rate of defects decrease $\dot{n}_R$ per unit area is proportional to the number $w(E,u,T_0)$ of thermally activated transition of atoms, caused by one ion, to the part of atoms which are in metastable states n/n_0, and to the flow of implanted ions J:

$$\dot{n}_R = (n/n_0)\, J w(E,u,T_0), \qquad (10)$$

where n is the concentration of defects.

The resulting velocity per unit area of defects implantation into the film, is equal to $J_a n/n_0$. On the other hand, the resulting velocity of the defects introducing is given by the difference between the rate of defect production due to the ion implantation and the rate of their loss due to thermally activated migration. Consequently, the steady-state condition, i. e., constancy of defects density, leads to the relation:

$$J_a \frac{n}{n_0} = \dot{n}_d - \dot{n}_R . \qquad (11)$$

We assume that the deposited flow consists of m different species, and each species is presented by ions with charges from 1 to n (in units of the proton charge), and the part of species j with charge i is equal to χ_{ij}.

Generally, we can take $n \le 5$. Note that some of components χ_{ij} may be equal to zero, for example, if there are no ions with charge of *i* in flow of *j*-th species. In case of a mixed beam of differently charged ions in the formation and drift of defects simultaneously involves all *m* species, each species is presented by ions of *n* different energies, determined by the charge *i* of the ion and the bias potential *U*. As a result, the expression for the rate of defects formation can be represented as:

$$\dot{n}_d \sim J\sum_{j}^{m}\sum_{i=1}^{n}\chi_{ij}\zeta_j\left(i\left(U+U_f+E_{0ij}\right)\right), \qquad (12)$$

where we include notation $\zeta_j(E) = E\upsilon_j(E)/E_d + \Upsilon_j$; U_f is the floating potential; E_{0ij} is the reduced initial energy of *j*-th species with charge *i*. Similarly, the rate of decrease of defects is given by

$$\dot{n}_R = \frac{n}{n_0}J\sum_{j=1}^{m}\sum_{i=1}^{n}\chi_{ij}w_j\left(i\left(U+U_f+E_{0ij}\right),T_0\right). \qquad (13)$$

Substituting $\dot{n}_d$ and $\dot{n}_R$ in (11), extracting the term n/n_0 from obtained equation, and accepting $J_a = J$ (only ions deposits) we get:

$$\frac{n}{n_0} \sim \frac{\sum_{j=1}^{m}\sum_{i=1}^{n}\chi_{ij}\zeta_j\left(i\left(U+U_f+E_{0ij}\right)\right)}{1+\sum_{j=1}^{m}\sum_{i=1}^{n}\chi_{ij}w_j\left(i\left(U+U_f+E_{0ij}\right),T_0\right)}. \qquad (14)$$

By assumption, the bulk deformation ε is proportional to the fraction of the implanted defects n/n_0. Compressive stress σ acting in the plane of the thin coating is associated with deformation by equation $\sigma = E_Y\varepsilon/(1-\Pi)$. The result is:

$$\sigma(U) = \frac{AE_Y}{1-\Pi}\frac{\sum_{j=1}^{m}\sum_{i=1}^{n}\chi_{ij}\zeta_j\left(i\left(U+U_f+E_{0ij}\right)\right)}{1+\sum_{j=1}^{m}\sum_{i=1}^{n}\chi_{ij}w_j\left(i\left(U+U_f+E_{0ij}\right),T_0\right)}. \qquad (15)$$

Here A is the normalization constant depending, in general, on species and coating material.

Let us consider the effect of the pulse potential mode on the intrinsic stress in deposited coating. The shape of the pulse bias potential on the substrate is shown in Fig. 1.

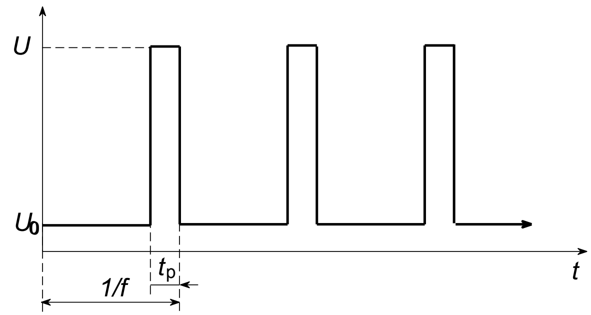

Fig. 1. The shape of the pulse bias potential

For the *j*-th species with charge *i* in pulse potential mode the ions of two different energies $i\left(U_0+U_f+E_{0ij}\right)$ and $i\left(U+U_f+E_{0ij}\right)$ are alternately deposited. Let duration and frequency of high-energy pulses are t_p and *f*, respectively. Thus duration of period when the target is irradiated with low energy ions is $f^{-1}-t_p$. At sufficiently high pulse duration material deposited during the pulse can be seen as a solid layer of macroscopic thickness. Intrinsic stress arising in each layer should be calculated using Eq. (15), wherein *U* is the bias potential on the substrate which forms the layer. In this case, the coating can be regarded as multi-layer sandwich, and the equilibrium stress can be calculated taking into account the stress and the thickness of each layer [10]. However, if the effective thickness of each layer does not exceed the interatomic distance *a*, then we can assume that the coating is formed by a mixture of ions of two different energies (the approach of the mixed beam), and the fractions of ions with energies $i\left(U_0+U_f+E_{0ij}\right)$ and $i\left(U+U_f+E_{0ij}\right)$ are $1-ft_p$ and ft_p, respectively. Criterion of applicability of the latter case has the form:

$$f >> J_a a^2. \qquad (16)$$

Assuming for estimates $J_a = 3\cdot10^{16}$ cm$^{-2}\cdot$s^{-1}, $a = 2{,}5\cdot10^{-8}$ cm, we obtain from (16) condition: $f >> 20$ Hz. During deposition of coatings in a pulse potential mode they are usually used frequency $f = 1\ldots20$ kHz, so the criterion (16) is carried out by a wide margin, and to describe the stress arising in the coating we should use approximation of the mixed beam. In this case, the Eq. (15) for intrinsic voltage is converted to the form:

$$\sigma(U,T_0) = \frac{A\sum_{j}^{m}\sum_{i=1}^{n}\chi_{ij}\left[ft_p\zeta_j\left(i\left(U+U_f+E_{0ij}\right)\right)+\left(1-ft_p\right)\zeta_j\left(i\left(U_0+U_f+E_{0ij}\right)\right)\right]}{1+\sum_{j}^{m}\sum_{i=1}^{n}\chi_{ij}\left[ft_pw_j\left(i\left(U+U_f+E_{0ij}\right),T_0\right)+\left(1-ft_p\right)w_j\left(i\left(U_0+U_f+E_{0ij}\right),T_0\right)\right]}. \qquad (17)$$

Eq. (17) describes the intrinsic stress arising during multi-component coating deposition from a beam containing mixture of different species in modes of DC ($ft_p = 1$) and the pulse bias potential $ft_p < 1$ on the substrate.

RESULTS AND DISCUSSION

For correct calculation of intrinsic stresses in deposited coatings one should take into account deposition temperature T_0, which can vary significantly with changing of ion energy. Let suppose that thermal regime of substrate obeys linear law of thermal conductivity with constant coefficient of heat conductivity Then, as it can be shown, T_0 is associated with bias potential *U* by the following linear dependence in the steady state conditions:

$$T_0(U) = T_{00} + \lambda \sum_{j}^{m} \sum_{i=1}^{n} \chi_{ij} i \Big[ft_p \left(U + U_f + E_{0ij} \right) + \\ + \left(1 - ft_p\right)\left(U_0 + U_f + E_{0ij}\right)\Big], \quad (18)$$

where T_{00} is the temperature of non-irradiated substrate. Parameter λ is proportional to the flux density of deposited ions and depends on structural features of installation for coating deposition. The value of λ is chosen from the condition of equality the deposition temperature to its experimental value at a certain energy of deposited ions.

Formula (18) was used to calculate intrinsic stresses in multicomponent nitride coatings deposited from a mixed beam of ions. We assumed $ft_p = 0.12$ and $ft_p = 1$ at calculations in DC and pulse potentials modes, respectively. Also, we put, $\lambda = 0.1$, $U_f = 20$ V, $U_0 = 0$.

Data for the charges and the initial energies of ions presented in [11] was used for calculation of the intrinsic stresses in the CrAlN coating.

Fig. 2 shows the results of calculation of the stress $\sigma(U)$ in nitride coating Cr-Al-N, deposited from mixed flux of ions Cr(50%)Al(50%) and at different modes and temperatures of deposition. As it is seen from Fig. 2, the value and shape of intrinsic stresses depends essentially on the mode and the deposition temperature. Pulse potential mode allows to reduce significantly the maximum value of the stress. Maximum of curve $\sigma(U)$ in pulse potential mode shifts to the side of higher U values as compared with DC mode. At the same time the increase of T_0 leads to the opposite effect. To determine the amplitude, it is necessary to determine the constant A, that is possible only by comparing the calculation results with experimental data.

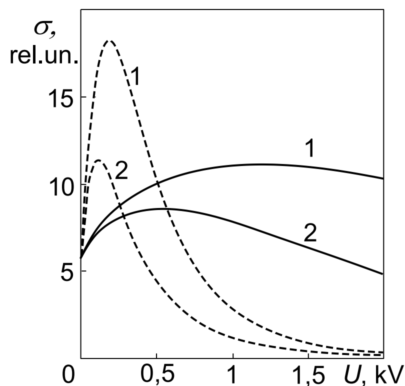

Fig. 2. Stresses σ(U) in the Cr-Al-N coating in DC (dashed curves) and pulse (solid curves) potential mode deposition with substrate temperature 473 K (curves 1) and 573 K (curves 2)

Pulse bias potential mode permits to obtain coatings with low stresses at relatively low deposition temperatures. That allows to deposite coating on materials with low temperature of tempering and significantly expands the assortment of materials which are used as substrates.

CONCLUSIONS

1. In model of nonlocal thermoelastic peak for low energy ion the formula for intrinsic stress in multi-component material deposited from mixed ion beam in DC and pulse potential modes was derived. The formula permits exploring the stress dependence on ion species, on the share content of ions in the deposited flux, on the bias potential and the substrate temperature.

2. Calculated the intrinsic stresses in Cr-Al-N coating precipitated from the mixed flux of the ions Cr(50%)Al(50%) at various temperatures and deposition modes. Coating deposition in pulse potential mode leads to a significantly smaller stresses at the maximum of curve of stresses $\sigma(U)$, rather than deposition in DC mode at the same temperature.

3. In pulse mode, the maximum of curve of stresses $\sigma(U)$ shifts to higher U values, compared with a DC mode. Increase of T_0 leads to the opposite effect.

4. Pulse potential mode permits to obtain coatings with low stresses at relatively low deposition temperatures, which allows to deposite coating on substrates with low temperature of tempering.

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ФОРМИРОВАНИЕ ВНУТРЕННИХ НАПРЯЖЕНИЙ В МНОГОКОМПОНЕНТНЫХ ПОКРЫТИЯХ, ОСАЖДАЕМЫХ В РЕЖИМАХ ПОСТОЯННОГО И ИМПУЛЬСНОГО ПОТЕНЦИАЛОВ СМЕЩЕНИЯ

А.И. Калиниченко, С.А. Козионов, В.Е. Стрельницкий

В рамках модели нелокального термоупругого пика низкоэнергетического иона получена формула для внутренних напряжений в многокомпонентном материале, осаждаемом из смешанного пучка разнозаряженных ионов в режимах постоянного и импульсного потенциалов. Проведен расчет зависимости внутренних напряжений σ от потенциала смещения U в покрытии Cr-Al-N, осаждаемом из смешанного потока Cr(50%)Al(50%) ионов при различных режимах и температурах осаждения T_0. Показано, что в режиме импульсного потенциала максимум кривой $\sigma(U)$ смещается в сторону больших значений U, по сравнению с режимом постоянного потенциала. Повышение T_0 ведет к обратному эффекту.

ФОРМУВАННЯ ВНУТРІШНІХ НАПРУЖЕНЬ У БАГАТОКОМПОНЕНТНИХ ПОКРИТТЯХ, ЩО ОСАДЖУЮТЬСЯ В РЕЖИМАХ, ПОСТІЙНОГО Й ІМПУЛЬСНОГО ПОТЕНЦІАЛІВ ЗМІЩЕННЯ

О.І. Калініченко, С.А. Козіонов, В.Є. Стрельницький

У рамках моделі нелокального термопружного піка низькоенергетичного іона отримана формула для внутрішніх напружень у багатокомпонентному матеріалі, що осаджується зі змішаного пучка різнозаряджених іонів у режимах постійного й імпульсного потенціалів. Проведено розрахунок залежності внутрішніх напружень σ від потенціалу зміщення U у покритті Cr-Al-N, що осаджується зі змішаного потоку Cr(50%)Al(50%) іонів при різних режимах і температурах осадження T_0. Показано. що в режимі імпульсного потенціалу максимум кривої $\sigma(U)$ зміщується у бік більших значень U, у порівнянні з режимом постійного потенціалу. Підвищення T_0 веде до зворотного ефекту.