INTRINSIC STRESSES IN MULTI-COMPONENT NITRIDE COATINGS PRODUCED BY PLASMA IMMERSION ION IMPLANTATION

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In model of nonlocal thermoelastic peak of low energy ion the process of intrinsic stress formation in the multi-component coatings CrN, $Cr_{0.5}Al_{0.5}N$, TiN, $Ti_{0.5}Al_{0.5}N$, deposited by vacuum arc method from ion beams Cr^+, $Cr^+_{0.5}Al^+_{0.5}$, Ti^+, $Ti^+_{0.5}Al^+_{0.5}$ in direct current (DC) and pulsed potential modes is investigated. The calculations of the intrinsic stress σ in the coatings depending on bias potential U at different deposition regimes and temperatures are carried out. It has been shown that growth of Al ion content in the mixed beam of incident ions increases stress $\sigma(U)$ in the deposited coating whereas growth of deposition temperature decreases it. Transition from the DC mode of deposition to the pulsed potential one leads to reduction of intrinsic stress maximum and shifts it in area of higher potentials. Comparison of theoretical results with experimental data permits estimating value of activation energy of defect migration.

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INTRODUCTION

The coatings based on nitrides of Ti and Cr with improved operational characteristics (hardness, wear, corrosion, radiation and heat resistances) are formed mainly by vacuum arc and plasma − ion deposition [1]. The intrinsic compression stresses, which, on the one hand, increase the hardness of coatings, but, on the other hand, may cause their destruction, arise during deposition. Determination of intrinsic stresses and their dependence on the deposition process parameters and thermal characteristics of the coating are necessary to choose the optimum mode of deposition and to control quality of the deposited coatings.

According to model proposed in [2] the intrinsic stress is formed as result of stress generation due to defect formation during ion implantation and stress relaxation during migration defects in point thermal peaks (PTP) of ions. Obtained formula gave qualitative explanation of the observed stress dependence on the ion energy and satisfactory quantitative agreement with experimental results.

However, the use of PTP model for description of stress relaxation seems to be not quite correct, because it does not take into account the nature of interaction between the implanted ions and atoms of the target material, which determines the energy content and the size of the formed thermal peak. In this regard, the model can not in principle explain the experimentally observed dependence of intrinsic stresses arising from the deposition temperature T_0. Its agreement with experimental data is achieved by activation energy u at values of u = 3 ... 14 eV, far exceeding the known values for defect migration. Besides the charge state of the ions and the deposition mode of coating do not take into account in the model.

In [3, 4], the modified formula for intrinsic stress calculation which uses the model of nonlocal thermoelastic peak (NTP) of ion is proposed. According to this model, the NTP of the low-energy ion is overheated and overpressured nanometer-sized region, arising around the ion path in the coating material as a result of thermalization of ion phonon losses. This formula allows us to calculate the stress in one-component coatings deposited from ion flows with different charging in modes of direct current (DC) and pulsed bias potentials and at different deposition temperatures.

In this paper we present a generalized formula for the calculation of intrinsic stresses in the multi-component coatings at the deposition of mixed ion beam, and the results of calculations of intrinsic stress σ in coatings CrN, $Cr_{0.5}Al_{0.5}N$, TiN, $Ti_{0.5}Al_{0.5}N$, deposited by vacuum arc of beams of Cr^+, $Cr^+_{0.5}Al^+_{0.5}$, Ti^+, $Ti^+_{0.5}Al^+_{0.5}$ ions in modes of DC and pulsed potential on substrate and comparison with experimental data.

INTRINSIC STRESSES IN THE COATINGS DEPOSITED FROM MIXED ION BEAM

The formula for calculating the intrinsic stresses in the multi-component coatings at deposition of mixed beam of differently charged ions is derived in accordance with the scheme, originally proposed in [2] and modified in [3-5] for the NTP model of low-energy ion in the cases of DC and pulsed potential mode. The expression for the intrinsic stress, the detailed derivation of which in the most general case is given in [5], has the form:

$$\sigma(U,T_0) = \frac{AE_Y}{1-\Pi} \frac{\sum\limits_{j=1}^{m}\sum\limits_{i=1}^{n}\chi_{ij}\left[ft_p\zeta_j\left(i\left(U+U_0+E_{0ij}\right)\right)+\left(1-ft_p\right)\zeta_j\left(i\left(U_1+U_0+E_{0ij}\right)\right)\right]}{1+\sum\limits_{j=1}^{m}\sum\limits_{i=1}^{n}\chi_{ij}\left[ft_p w_j\left(i\left(U+U_0+E_{0ij}\right),T_0\right)+\left(1-ft_p\right)w_j\left(i\left(U_1+U_0+E_{0ij}\right),T_0\right)\right]}. \qquad (1)$$

There E_Y and Π are the Young's modulus and Poisson's ratio of the coating material, t_p is the rectangular pulse duration of potential with an amplitude U, f is the frequency of pulse repetition, U_0 is the floating potential, U_1 is the potential applied to the substrate between pulses, χ_{ij} and E_{0ij} are the ion part of j sort with charge i (in units of the proton charge) and the initial energy per unit of charge of these ions, respectively. The summation is executed over m ion sorts and n ion charge states, and

$$\sum_i \sum_j \chi_{ij} = 1 . \qquad (2)$$

It is assumed that the deposited flux contains only ions and no neutral atoms. The function ζ_j defines the deformation dependence on ion energy E, caused by defect formation of j-th sort ion. Function

$$w_j\left(E,u,T_0\right) = n_0 \nu \int_0^{\tau_c} V_j\left(t,E\right) e^{-\frac{u}{k_B T_j\left(t,E,T_0\right)}} dt \qquad (3)$$

defines the number of thermally activated transitions in the NTP of j-th sort ion at deposition temperature T_0. There k_B is the Boltzmann constant, n_0 is the concentration of the coating atoms, f is the frequency of the atom vibration, τ_c is the NTP lifetime, and $V_j\left(t,E\right)$ and $T_j\left(t,E,T_0\right)$ are the NTP volume of j-th sort ion and the temperature in it, u is the migration activation energy of point defects. Functions ζ_j, $V_j\left(t,E\right)$ and $T_j\left(t,E,T_0\right)$ are calculated by the program code SRIM2000 [6] and at the values of n_0, coating density, thermal characteristics, which are typical for CrN, CrAlN, TiN, TiAlN coatings of micron thickness. Parameter A and the value of u were determined by comparing of the theoretical curve with the experimental data.

The deposition temperature T_0 can vary significantly with changes in the deposited energy ions E. So it is necessary to take into consideration. The value of T_0 affects the total peak temperature determining migration rate of defects and, consequently, the stress relaxation rate. Deposition temperature is associated with the ion energy by linear dependence in the approximation of linear heat equation with constant thermal conductivity coefficient of substrate K and in the stationary thermal mode. Temperature of absorbing surface of substrate with thickness h, reverse side of which is at constant temperature T_{00}, can be represented as:

$$T_0\left(E\right) = \frac{Jh}{K} E + T_{00} = \lambda E + T_{00} , \qquad (4)$$

where J is ion flux. The deposition temperature is linear function of the potential on the substrate U, because the energy E_{ij} of the j-th sort ion with charge i is related to U by ratio $E_{ij} = i\left(U + U_0 + E_{0ij}\right)$. In view of the multi-component flow of differently charged deposited ions, the expression for the substrate temperature can be represented as:

$$T_0\left(U\right) = T_{00} + \lambda \sum_{j=1}^{m} \sum_{i=1}^{n} \chi_{ij} i \left[f t_p E_{ij} + \left(1 - f t_p\right) E_{1ij} \right], \qquad (5)$$

where $E_{1ij} = i\left(U_1 + U_0 + E_{0ij}\right)$. This parameter λ is proportional to the flux density of the deposited ions but is inversely proportional to the thermal conductivity coefficient of the target material, and also depends on the structural features of facility for coating deposition. The value λ is chosen from the condition that the deposition temperature is equal to its experimental value at known potential U.

RESULTS AND DISCUSSION

Expression (1) allows determining the value of the intrinsic compressive stress σ in the coatings deposited from a mixed beam of ions in modes of direct current (DC) and pulsed potentials. Calculation of stresses for nitride coatings TiN and $Ti_{0.5}Al_{0.5}N$ (CrN and $Cr_{0.5}Al_{0.5}N$) was carried out under the following deposition parameters and deposited coatings: f = 24 (12) kHz, T_0 = 473 (400) K, t_p = 5 (12) μs and E_Y = 450 (400) GPa, Π = 0.23 (0.3), λ = 0.1 (0.3). Values of χ_{ij} and E_{0ij} parameters for coatings were taken from the book [7].

Fig. 1 shows the dependence of the intrinsic compressive stresses in the deposited coatings CrN, $Cr_{0.5}Al_{0.5}N$, TiN, $Ti_{0.5}Al_{0.5}N$ on the bias potential U (curves 1-4) in DC (dotted lines) and pulse (solid line) potentials.

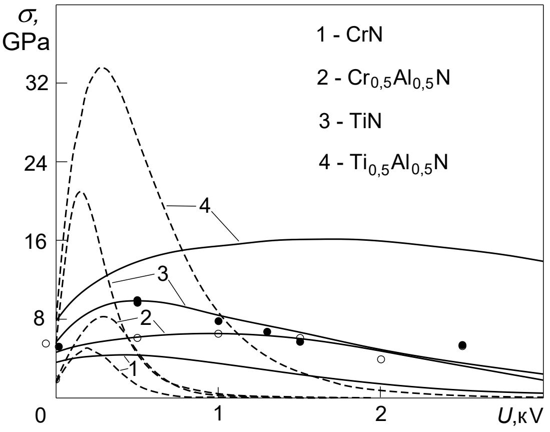

Fig. 1. The dependence of the intrinsic compressive stresses in the deposited coatings based on nitrides of Cr and Ti on substrate potential in modes of DC (dotted line) and pulsed (solid line) potential. Dark (light) circles are data from experiments for TiN($Cr_{0.5}Al_{0.5}N$) [8, 9] ([10])

Analysis has shown that the best agreement between the calculated curves with experimental data is achieved: for the stresses in TiN coating at the activation energy of defect migration u = 0.75 eV (solid curve 3) [8, 9]; for the stresses in the coating $Cr_{0.5}Al_{0.5}N$ at u = 0.85 eV (solid line 2) [10] (coating deposited in pulsed potential mode). The maximum of stress curve σ_{max} = 6.5 (10) GPa for coating $Cr_{0.5}Al_{0.5}N$ (TiN) is achieved at U = 1 (0.5) kV (solid curves 2 (3)), in accordance with the experimental data.

Activation energy values *u* <1 eV, obtained from comparison of theoretical curve with experimental data are consistent with the assumption that the origin of intrinsic stresses in the coating during plasma-ion deposition is associated with formation and subsequent migration of interstitial defects.

In the DC mode maximum of stress curve calculated at the same temperature is shifted towards lower values of *U* and reaches for $Cr_{0.5}Al_{0.5}N$ (TiN) coating the value σ_{max} = 8.3(21) GPa at U = 300(150) V (dotted curve 2 (3)). It is important to note that deposition in pulsed potential mode leads to lower maximum intrinsic stress than deposition in DC potential mode.

As can be seen from Fig. 1, increase of Al content leads to increase of stress in TiAlN (CrAlN) coatings and to shift of maximum stress in the direction of higher values *U*. The analysis also showed that the ratio between the stresses in the coatings deposited in DC and pulsed potential modes at a fixed temperature deposition depends essentially on content of Al.

Fig. 2 shows the results of calculations and experimental data for the intrinsic stress σ(*U*) in TiN and $Cr_{0.5}Al_{0.5}N$ coatings, deposited in pulsed potential mode at different deposition temperatures: T_0 = 400 K (curves 2 and 4, respectively) and 473 K (curves 1 and 3, respectively).

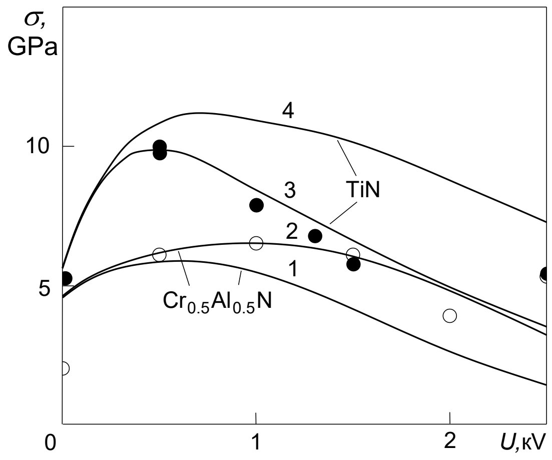

Fig. 2. Dependences of the intrinsic compressive stresses in the deposited coatings of TiN and $Cr_{0.5}Al_{0.5}N$ on substrate potential in pulsed potential mode, calculated at deposition temperatures T_0 = 473 K (curves 1, 3) and T_0 = 400 K (curves 2,4). Dark (light) circles are experimental data for TiN ($Cr_{0.5}Al_{0.5}$ N)[8,9]([10])

As can be seen from Fig. 2, the stresses σ and shape σ(U) curve strongly depends on the deposition temperature T_0. With increasing T_0 maximum stress is reduced and shifted to lower potentials. For coating $Cr_{0.5}Al_{0.5}N$ (TiN) stress maximum is σ_m ~ 6.5(11) GPa and it is achieved at deposition temperature T_0 = 400 K and U ~ 1(0.7) kV (curve 2 (4)). The stress maximum is reduced to the value of σ_m ~ 5.9(10) GPa at U ~ 0.6 (0.5) kV (curve 1 (3)) and at temperature of deposition T_0 = 473 K.

It should be noted that relatively high heat conduction TiN, compared with CrN, leads to a decrease of temperature in the NTP ions into titanium nitride coatings that suppresses the migration of defects and stress relaxation. As a result, coatings based on TiN are characterized by higher level of intrinsic stresses at a fixed bias potential.

CONCLUSIONS

1. In framework of model of nonlocal thermoelastic peak the calculation of intrinsic stresses is carried out in the nitride coatings TiN and $Ti_{0.5}Al_{0.5}N$ (CrN and $Cr_{0.5}Al_{0.5}N$), deposited from a mixed beam of ions in the modes of DC and pulsed bias potential. The results of intrinsic stress calculations in coatings based on TiN(CrN), which are obtained for the pulsed potential mode at the activation energy of defect migration *u* = 0.75 (0.85) eV, respectively, agree with the experimental data.
2. The theoretical curves agree with the experimental data at the activation energy *u* <1 eV. This confirms the assumption that the origin of internal stresses in the coating during plasma ion deposition is associated with the formation and subsequent migration of interstitial defects.
3. It was shown that the intrinsic stresses decrease sharply with increasing deposition temperature in the modes of DC and pulsed bias potential.
4. It was shown that the intrinsic stresses increase with increasing of Al content in modes of DC and pulsed bias potential.

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ВНУТРЕННИЕ НАПРЯЖЕНИЯ В МНОГОКОМПОНЕНТНЫХ НИТРИДНЫХ ПОКРЫТИЯХ, ПОЛУЧАЕМЫХ МЕТОДОМ ПЛАЗМЕННО-ИММЕРСИОННОЙ ИОННОЙ ИМПЛАНТАЦИИ

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В рамках модели нелокального термоупругого пика иона низкой энергии анализируется процесс формирования внутренних напряжений в многокомпонентных покрытиях CrN, $Cr_{0.5}Al_{0.5}N$, TiN, $Ti_{0.5}Al_{0.5}N$, осаждаемых вакуумно-дуговым методом из пучков ионов Cr^+, $Cr^+_{0.5}Al^+_{0.5}$, Ti^+, $Ti^+_{0.5}Al^+_{0.5}$ в режимах постоянного и импульсного потенциалов на подложке. Проведен расчёт зависимости внутренних напряжений σ от потенциала смещения U в покрытиях при различных режимах и температурах осаждения. Показано, что увеличение содержания ионов Al в смешанном потоке падающих ионов повышает напряжения $\sigma(U)$ в осаждаемом покрытии, тогда как увеличение температуры осаждения снижает их. Переход от режима постоянного к режиму импульсного потенциала приводит к снижению максимума внутренних напряжений и смещению его в область более высоких потенциалов. Сравнение теоретических результатов с экспериментальными данными позволило оценить величину энергии активации миграции дефектов.

ВНУТРІШНІ НАПРУЖЕННЯ В БАГАТОКОМПОНЕНТНИХ НІТРІДНИХ ПОКРИТТЯХ, ЩО ОТРИМУЮТЬСЯ МЕТОДОМ ПЛАЗМОВО-ІМЕРСІЙНОЇ ІОННОЇ ІМПЛАНТАЦІЇ

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У рамках моделі нелокального термопружного піку іона низької енергії досліджується процес формування внутрішніх напружень в багатокомпонентних покриттях CrN, $Cr_{0,5}Al_{0,5}N$, TiN, $Ti_{0,5}Al_{0,5}N$, осаджуваних вакуумно-дуговим методом з пучків іонів Cr^+, $Cr^+_{0.5}Al^+_{0.5}$, Ti^+ , $Ti^+_{0.5}Al^+_{0.5}$ у режимах постійного та імпульсного потенціалів на підкладці. Проведено розрахунок залежності внутрішньої напруги σ від потенціалу зміщення U в покриттях при різних режимах і температурах осадження. Показано, що збільшення вмісту іонів Al в змішаному потоці падаючих іонів підвищує напругу $\sigma(U)$ в осаджуваному покритті, тоді як збільшення температури осадження знижує їх. Перехід від режиму постійного до режиму імпульсного потенціалу веде до зниження максимуму внутрішніх напружень та зміщенню його в область більш високих потенціалів. Порівняння теоретичних результатів з експериментальними даними дало можливість оцінити величину енергії активації міграції дефектів.