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INFLUENCE OF THE INERT GAS PRESSURE ON INTRINSIC STRESS IN DIAMOND-LIKE COATING DEPOSITED FROM VACUUM ARC CARBON PLASMA[†]

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Within the framework of the model of the nonlocal thermoelastic peak of low-energy ion, the formation of intrinsic stress in a carbon coating deposited from the vacuum arc plasma in the argon atmosphere is theoretically studied. It is shown that the flow of particles bombarding the deposited coating contains, along with C^+ ions, also Ar^+ ions involved in the formation of intrinsic stress in the coating. The flux density of Ar^+ ions resulting from ionization losses of C^+ ions passing through the argon atmosphere is proportional to both the flux density of C^+ ions and the density (pressure) of argon. Expressions are obtained for the intrinsic stress in the deposited carbon coating depending on the bias potential on the substrate and the argon pressure for the cases of both constant and pulsed potentials. The analysis of the obtained expressions shows that the intrinsic stress in the carbon coating decrease with increasing argon pressure.
Keywords: Diamond-like carbon coatings; Plasma-ion deposition; Vacuum arc; Argon atmosphere; Thermal peaks; Intrinsic stress; Growth rate
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Diamond-like carbon (DLC) coatings are of significant interest for applications associated with extreme tribological conditions, providing high efficiency, performance and reliability. The strong covalent sp^3 bonding in ta-C coatings provides high mechanical hardness, toughness, chemical and thermal stability, making them highly suitable for harsh tribological conditions, including high speeds, loads and temperatures.

Due to the unique combination of properties, thick microcrystalline diamond-like films are most preferred for use in tools, while thinner nanocrystalline DLC coatings are widely used for surface modification of parts used in mechanical engineering, aerospace, medicine, micromechanics, and other industries. Such coatings are characterized by low coefficient of friction, chemical inertness, biocompatibility and high radiation resistance. [1-5].

The development of equipment and processes for high-quality DLC deposition over the large area is the urgent and important task, the solution of which will increase the productivity of the process, as well as expand the list of processed articles. In addition, there is a great need for the deposition of diamond-like carbon on the surface of articles with complex shapes (cylindrical, spherical and others, for example, the friction joints of endoprostheses). Improving the characteristics and functional properties of DLC is impossible without knowledge of the physical mechanisms which determine the deposition rate and the processes of formation of the structure and phase composition of the coating material. Therefore, it is important to theoretically study the mechanisms of DLC synthesis, to reveal the role of the bombardment of the growth surface with low-energy ions (from 0.1 to ~ 1 keV) in the sputtering and activation of radiation-stimulated processes and the effect of deposition conditions on intrinsic stress in the coating.

The important type of the process of DLC production is the deposition of carbon coatings from the carbon plasma of the vacuum arc in sufficiently rarefied atmosphere of the inert gas. For obtaining coatings with parameters providing the best performance characteristics, such as hardness and high adhesion to the substrate, it is necessary to investigate the dependence of the properties of coatings on the type of inert gas and its pressure. The key parameter providing the above properties of the DLC is the intrinsic stress arising during the coating deposition.

In this paper, we study the dependence of intrinsic stress in the deposited coating on the pressure of the inert gas in the atmosphere of working installation.

MATHEMATICAL MODEL

We will assume that the flux of C^+ ions is deposited on the substrate surface in atmosphere of easily ionized inert gas, argon. As a result, the mixture of ion fluxes falls on the deposited surface: the flux j_1 of C^+ ions knocked out from the cathode and the flux j_2 of Ar^+ ions generated when gas atoms collide with the flux of C^+ ions. Assuming that the number of ionized Ar atoms is small compared to the initial amount, the following expression can be written for the flux j_2:

$$j_2 = \alpha P j_1 , \quad (1)$$

Here P is the argon pressure, α is the coefficient that, generally, depends on the design of the installation.

The initial energy E_0 of C^+ ions in the setup chamber is 20 to 25 eV (up to the thin near-surface layer near the substrate, where the ions are additionally accelerated by the bias potential). Modeling the passage of the low-energy C^+

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ion with such an energy through the argon atmosphere using the SRIM2000 software package shows that the following approximate expression for the average projective ion path is valid: L_C, cm = 0.076/P, where P is given in Torr units. The ionization loss of the C + ion can be estimated from the expression $\Delta E_{ion} \sim 0.3 E_0 D / L_C =$, where D is the characteristic distance traveled by the ion in the gaseous atmosphere of the vacuum chamber, specified in cm. The coefficient 0.3 corresponds to the fraction of ionization energy losses of the C^+ ion ~ 30%. The above estimate is valid under the condition $D < L_C$ that is satisfied at pressures P <10^{-3} Torr. Assuming that all ionization losses of the ion C^+ are spent on the formation of Ar^+ ions, we obtain the following estimate for the number of Ar^+ ions formed by one C^+ ion: $N_{Ar} \sim 10DP$, that is, $\alpha \sim$ 10D. Here we use the following average ionization potential of Ar I_{Ar} = 11.6 eV. For the coating deposition systems used, the conditions $P < 10^{-3}$ Torr and $D < 10^2$ cm are satisfied, whence $\alpha P < 1$ follows.

When deriving the formula for intrinsic stress, basically, the line of reasoning used in works [6-9] is repeated. At this, the model of a nonlocal thermal peak (NTP) of a low-energy ion is widely used - an overheated and overstressed nanometer region near the ion trajectory in the target material, in which thermalized phonon losses of the ion contain [10]. Computer simulation using the SRIM2000 software package [11] has shown that the NTP can be approximated by a spherical segment adjacent to the target surface, the center of which lies in the middle of the average projective range of the ion. The effective lifetime t_T, volume $V(t,E)$, and temperature $T(t,E,T_0)$ of the NTP of the ion are calculated within the framework of the previously developed model [10, 11]. So, the volume of the near-surface NTP is found by the formula

$$V(E,t) = \pi\left[\frac{2}{3}R(E,t)^3 + \frac{L(E)}{2}R(E,t)^2 - \frac{1}{3}\frac{L(E)^3}{8}\right], \tag{2}$$

where $R(E,t) = \dfrac{L(E)}{2} + 2\sqrt{\kappa(\tau+t)}$ is the radius of the NTP created by the ion with energy E at time t, $L(E)$ is the average projective range of the ion, $\tau \sim 10^{-13}$ s. is the ion-ion relaxation time; κ is the phonon thermal diffusivity of the coating material. Temperature $T(t,E)$ in the NTP is calculated from the equation that takes into account the dependence of the heat capacity on temperature [10, 12]:

$$\frac{\eta(E)E}{\rho\, C\, V(E,t)} = TD\left(\frac{\theta}{T}\right) - T_0 D\left(\frac{\theta}{T_0}\right), \tag{3}$$

where ρ is the density, $C = 3\nu_a k_B / M$ is the high-temperature limit of the heat capacity of the target material, $\eta(E)$ is the fraction of phonon losses of the ion with energy E in the target material, T_0 is the substrate temperature, θ is the Debye temperature of the target material, k_B is the Boltzmann constant, ν_a is the number of atoms in the molecule of the target material (for carbon coating ν_a = 1), $D(x)$ is the Debye function having the form [12]:

$$D(x) = \frac{3}{x^3}\int_0^x \frac{z^3\, dz}{e^z - 1}. \tag{4}$$

The lifetime $t_T(E)$ of the NTP is determined by the rate of its cooling. Assuming that the peak is cooled only by thermal conductivity, we obtain for the effective cooling time of the peak $t_T(E) = R(E,0)^2 / 4\kappa$. Functions $L(E)$ and $\eta(E)$ were calculated using the SRIM2000 software package [11]. The results of calculating the functions $\eta(E)$ for C^+ and Ar^+ ions in the carbon coating are shown in Fig. 1.

The dependences of the NTP volumes of C^+ and Ar^+ ions in the carbon coating on the ion energy are shown in Fig. 2.

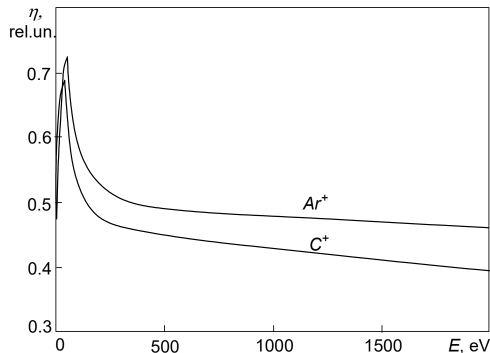

Figure 1. Phonon loss functions for C^+ and Ar^+ ions in the DLC coating.

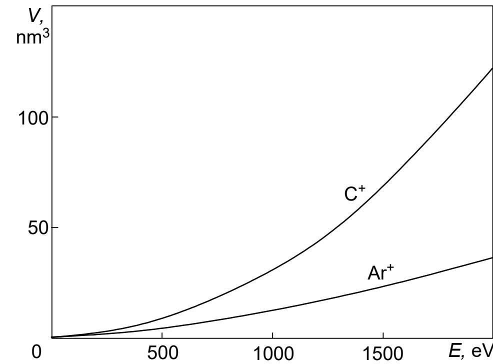

Figure 2. Volumes of NTP of C + and Ar + ions in the DLC coating depending on the ion energy

The results of calculating the NTP temperatures as functions of the ion energy are shown in Fig. 3. In the calculations, the substrate temperature was assumed to be T_0 = 300 K.

The data obtained on the characteristics of the NTP allow us descripting the intrinsic stress formation in the coating deposited from mixed flow of C^+ and Ar^+ ions. It is assumed that intrinsic stresses are formed as a result of two simultaneous but oppositely directed processes: 1) stress generation due to implantation of the incident ion beam and 2) stress relaxation due to thermally activated processes of defect migration in the NTP of ions [6]. In addition, the stated model [7–9], like the Davis's one [6], is based on the hypothesis of proportionality between the density of defects formed as a result of ion scattering by target atoms and the volumetric deformation of the target.

The rate of defects formation by ions of the *i*-th species, per unit surface of the coating, is proportional to the ion flux density j_i and the number of defects $\zeta_i(E)$ formed by one ion of the *i*-th species. In papers [6,7], the approximation $\zeta_i(E) \sim \sqrt{E}$ was used [13]. In this work, the defect formation functions are calculated numerically using the SRIM2000 program code [9, 11] (see Fig. 4).

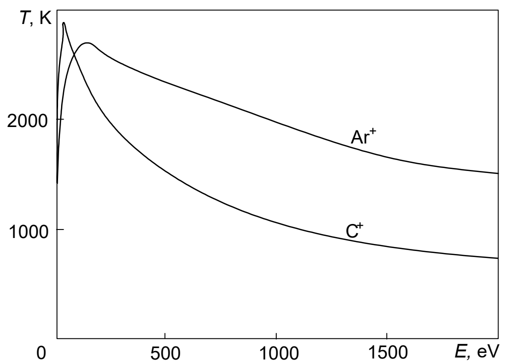

Figure 3. Temperatures in the peaks of C^+ and Ar^+ ions in the carbon coating depending on the ion energy.

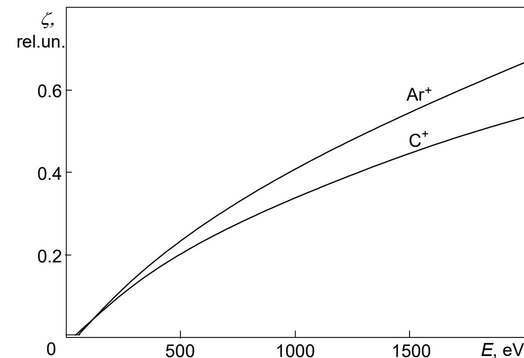

Figure 4. Functions of defect formation of C^+ and Ar^+ ions in the carbon coating.

Thus, the total rate of defect formation by the mixed beam of ions of two species is determined by the expression:

$$\dot{n}_d(U) \sim j_1\zeta_1(E_1(U)) + j_2\zeta_2(E_2(U)). \tag{5}$$

Using (1), we obtain from (5):

$$\dot{n}_d((U)) \sim j_1(\zeta_1(E_1(U)) + \alpha P\zeta_2(E_2(U))). \tag{6}$$

Here we used the notation $E_i = q_i(U + U_0) + E_{0i}$, q_i is the charge of the *i*-th species ion, U_0 is the floating potential, E_{0i} is the initial energy of the *i*-th species ion.

The opposite process of stress relaxation is determined by the number of thermally activated transitions $w_i(E)$ of atoms in the NTP of the *i*-th species ion with energy *E*.
Function

$$w_i(U) = n_0\nu\int_0^{t_T} V_i(t, E_i)\, e^{-\frac{u}{k_B T_i(t, E_i, T_0)}}\, dt\,, \tag{7}$$

specifies the number of thermally activated transitions in the NTP of the ion, which determine the migration rate of defects with the activation energy *u* and, therefore, the stress relaxation rate at the target temperature T_0.

The rate of defect loss, per unit area, is proportional to $w_i(E)$, to the fraction of defects n/n_0 and to density of the implanted ion flux j_i. After summing up the contributions of two species ions to the migration process, we obtain the following expression for the rate of defect loss:

$$\dot{n}_R(U) = \frac{n}{n_0}\left[j_1 w_1(E_1) + j_2 w_2(E_2)\right] = j_1\frac{n}{n_0}(w_1(E_1) + \alpha P w_2(E_2)). \tag{8}$$

The resulting rate, per unit area, with which defects are implanted in the film, is equal to $j_1 n/n_0$. Here we have taken into account that only ions of the 1st species (carbon ions) build up the coating. On the other hand, the resulting rate of introduction of defects is set by the difference between the rate of appearance of defects due to implantation and

the rate of their loss due to thermally activated migration. Consequently, the condition of constancy of density of defects leads to the relation:

$$j_1 \frac{n}{n_0} = \dot{n}_d - \dot{n}_R . \tag{9}$$

Substituting $\dot{n}_d$ and $\dot{n}_R$ from Eqs. (6), (8) in Eq. (9) and expressing in the resulting equation the fraction n/n_0 of implanted ions in the film, we obtain for intrinsic stress in the case of the constant bias potential (so called the direct current (DC) mode):

$$\sigma(U,P) = \frac{AE_Y}{1-\Pi} \frac{\zeta_1(E_1(U)) + \alpha P \zeta_2(E_2(U))}{1 + w_1(E_1(U)) + \alpha P w_2(E_2(U))}, \tag{10}$$

where E_Y and Π are the Young's modulus and the Poisson's ratio of the coating material, correspondingly. Here, we used the relationship $\sigma = E_Y \varepsilon/(1-\Pi)$ between stress σ and volumetric deformation ε, which is determined by the density of defects n/n_0. Coefficient *A* is found by comparing the theoretical curve with the experimental data.

Expression (10) was generalized to the case of the pulse potential mode [8]. Intrinsic stress in the pulse potential mode is given by the expression:

$$\sigma(U,P) = \frac{AE_Y}{1-\Pi} \frac{\left(\zeta_1(E_1(U)) + \alpha P \zeta_2(E_2(U))\right) ft_p + \left(\zeta_1(E_1(0)) + \alpha P \zeta_2(E_2(0))\right)(1-ft_p)}{1 + \left(w_1(E_1(U)) + \alpha P w_2(E_2(U))\right) ft_p + \left(w_1(E_1(0)) + \alpha P w_2(E_2(0))\right)(1-ft_p)}, \tag{11}$$

where, t_p is the duration of the high voltage pulse, *f* is the pulse repetition rate.

When calculating the intrinsic stress in the deposited coating, it is necessary to take into account the deposition temperature T_0, which can vary significantly with the energy of the deposited ions, since the ion flux heats the coating surface. In the approximation of the linear theory of thermal conductivity with constant coefficient of thermal conductivity and in the stationary mode, the deposition temperature T_0 is related to the bias potential *U* by linear dependence:

$$T_0(U) = T_{00} + \lambda q\left[(U_0 + E_0)(1-ft_p) + (U + U_0 + E_0) ft_p\right](1+\alpha P), \tag{12}$$

where T_{00} is the temperature of the non-irradiated substrate. The average charge *q* of C^+ and Ar^+ ions, according to experimental data, is, with sufficient accuracy, equal to the elementary (proton) charge. The value λ depends on the technical parameters of the coating deposition installation. The value of λ was chosen from the condition that the deposition temperature was equal to its experimental value at known energy of the deposited ions.

RESULTS AND DISCUSSION

In Fig. 5 shows the dependence of intrinsic stress on the bias potential for different values of the parameter αP in both cases of the direct current (DC) and pulse potential regimes. The calculations were performed for the case of the absence of the argon atmosphere $\alpha P = 0$, and for the case of $\alpha P = 1$. As can be seen from the Fig. 5, the addition of Ar^+ ions to the flow of incident particles does not change behavior of dependence *σ(U)* but leads to a certain decrease of intrinsic stress in the deposited carbon coating.

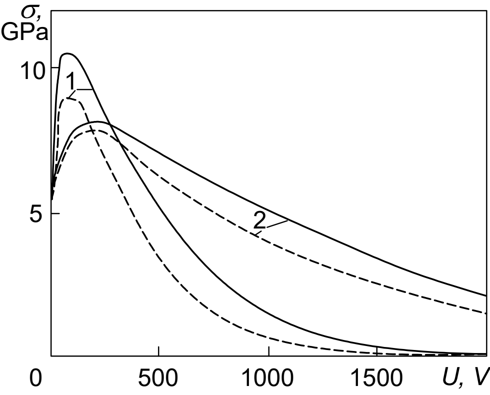

Figure 5. Dependence of intrinsic stress in deposited carbon coating on bias potential at different pressures of inert gas. Curves 1 – the case of the DC regime (ft_p = 1), curves 2 – the case of the pulse potential regime (ft_p = 0.12). Solid curves correspond to $aP = 0$, and dashed curves correspond to $\alpha P = 1$.

To study the dependence of intrinsic stress on the inert gas pressure *P*, we represent expression (10) in the form:

$$\sigma(P) = B\frac{1+aP}{1+bP}, \tag{13}$$

where

$$B(U) = \frac{AE_Y}{1-\Pi}\frac{\zeta_1(E_1(U))}{1+w_1(E_1(U))}, \tag{14}$$

$$a(U) = \frac{\alpha\zeta_2(E_2(U))}{\zeta_1(E_1(U))}, \tag{16}$$

$$b(U) = \frac{\alpha w_2(E_2(U))}{1+w_1(E_1(U))}. \tag{17}$$

are the positive definite functions of the bias potential *U*.

For given values of *U*, the parameters B, a, b are constants. Constant *B* is equal to the intrinsic stress in the coating obtained at zero inert gas concentration. It can be seen from (13) that the intrinsic stress is the fractional-rational function of pressure *P*. The behavior of the fractional-rational function (13) with the change in the argument *P* depends on the ratio between its coefficients *a* and *b*. So, at zero concentration of the inert gas (at *P* = 0) we have $\sigma(0) = B, \quad \sigma'(0) = B(a-b)$. Thus, the slope of the stress curve is proportional to the difference *(a-b)* near the point *P* = 0. As the pressure *P* increases, the function $\sigma(P)$ tends to the asymptotics Ba/b.

Analysis of Eq. (11) shows that it can also be represented as the fractional-rational function of pressure *P*:

$$\sigma_1(P) = B_1\frac{1+a_1P}{1+b_1P}, \tag{18}$$

where

$$B_1(U) = \frac{AE_Y}{1-\Pi}\frac{\zeta_1(E_1(U))ft_p + \zeta_1(E_1(0))(1-ft_p)}{1+w_1(E_1(U))ft_p + w_1(E_1(0))(1-ft_p)}, \tag{19}$$

$$a_1(U) = \frac{\alpha\left[\zeta_2(E_2(U))ft_p + \zeta_2(E_2(0))(1-ft_p)\right]}{\zeta_1(E_1(U))ft_p + \zeta_1(E_1(0))(1-ft_p)}, \tag{20}$$

$$b_1(U) = \frac{\alpha\left[w_2(E_2(U))ft_p + w_2(E_2(0))(1-ft_p)\right]}{1+w_1(E_1(U))ft_p + w_1(E_1(0))(1-ft_p)}. \tag{21}$$

Dependence of intrinsic stress on the parameter αP for three different bias potentials is shown in Fig. 6. The solid curves correspond to the DC regime deposition whereas the dashed curves – to the pulse potential regime.

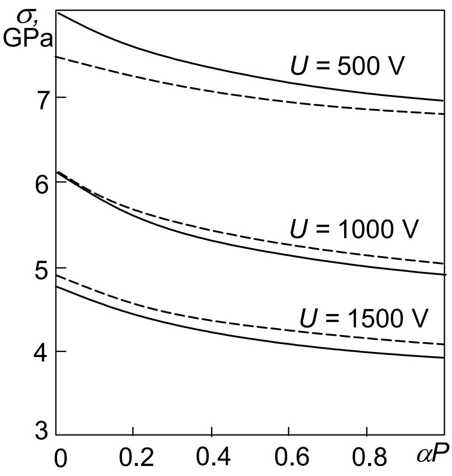

Figure 6. Dependence of intrinsic stress in the carbon coating on pressure of inert gas at different bias potentials on the substrate. The solid curves correspond to the DC regime (ft_p = 1), the dashed curves – to the pulse potential regime (ft_p = 0.12).

As can be seen from fig. 6, in the case under consideration, the condition is satisfied $a - b < 0$, since the intrinsic stress decreases with the increase in the pressure of the inert gas.

Note that the case of carbon coating deposition in the inert gas atmosphere differs from a similar case of deposition of the TiN coating, since in the latter case the increase in pressure led not to the decrease, but, on the contrary, to the increase in intrinsic stress in the TiN coating [14].

CONCLUSION

1. During the deposition of the carbon coating from the vacuum arc plasma in the argon atmosphere, the flow of particles, bombarding the deposited coating, consists of the mixture of C^+ and Ar^+ ions. The flux density of Ar^+ ions resulting from ionization loss of C^+ ions passing through the argon atmosphere is proportional to both the flux density of C^+ ions and the density (pressure) of argon.

2. Expressions are obtained for the intrinsic stresses in the deposited carbon coatings depending on the bias potential on the substrate for the modes of both the DC and the pulsed potential.

3. The analysis of the obtained expressions shows that the intrinsic stress in the case of deposition of the carbon coating in the argon atmosphere decreases with the increase of argon pressure *P*.

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ВПЛИВ ТИСКУ ІНЕРТНОГО ГАЗУ НА ВНУТРІШНІ НАПРУЖЕННЯ В АЛМАЗОПІДОБНОМУ ПОКРИТТІ, ЩО ОСАДЖУЄТЬСЯ З ВУГЛЕЦЕВОЇ ПЛАЗМИ ВАКУУМНОЇ ДУГИ

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В рамках моделі нелокального термопружного піка низькоенергетичного іона теоретично досліджується виникнення внутрішніх напружень у вуглецевому покритті, що осаджується з плазми вакуумної дуги в аргоновій атмосфері. Показано, що потік часток, які бомбардують покриття, що осаджується, містить поряд з іонами C^+ також іони Ar^+, що беруть участь у формуванні внутрішніх напружень в покритті. Щільність потоку іонів Ar^+, що виникли в результаті іонізаційних втрат іонів C^+, що проходять через атмосферу аргону, пропорційна як щільності потоку іонів C^+, так і щільності (тиску) аргону. Отримані вираження для внутрішніх напружень в вуглецевому покритті, що осаджується, залежно від потенціалу зміщення на підкладці і тиску аргону для випадків як постійного, так і імпульсного потенціалів. Аналіз отриманих виразів показує, що внутрішні напруження у вуглецевому покритті зменшуються зі збільшенням тиску аргону.

Ключові слова: алмазоподібні вуглецеві покриття, плазмо-іонне осадження, вакуумна дуга, атмосфера аргону, теплові піки, внутрішня напруга, швидкість росту