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RADIATION-STIMULATED DIFFUSION IN PLASMA-ION DEPOSITION OF COATINGS

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The diffusion of defects in a carbon coating when its surface is bombarded with heavy low-energy ions is theoretically studied, taking into account a sharp increase in the rate of kinetic processes in nonlocal thermoelastic peaks (NTPs) of ions, i.e., in superheated nanometer regions that arise around ion trajectories in the target material. The thermal energy density in NTP is comparable to or exceeds the activation energies of many physical and chemical processes, as a result of which their contribution to the total diffusion of defects in the near-surface layer of the target can be significant. Based on the NTP model, expressions were obtained for the average diffusion coefficient in the near-surface layer of the target, controlled by a beam of incident ions, as well as for the diffusion acceleration index. The dependences of the diffusion acceleration index on the ion energy are presented for various species of ions at selected activation energies and ion flux densities. Numerical calculation of the obtained expressions using the SRIM2000 software package showed that, at the selected ion flux density *J*, diffusion acceleration occurs only for processes with the activation energy exceeding a certain threshold value determined by the value of *J*, the type and energy of the ions.

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INTRODUCTION

Kinetic transfer processes occurring due to thermal movement and interaction of microparticles play the important role in the solid under irradiation. Transfer processes include diffusion, viscosity, creep, thermal diffusion, thermal conductivity, electrical conductivity, thermoelectric phenomena, etc. Of particular interest is the diffusion of radiation defects in amorphous and nanocrystalline coatings during their deposition from a beam of low-energy ions. This interest is due to the fact that this process directly affects the structure of the coating: the degree of defects and intrinsic stresses in the coating.

In accordance with experimental data, the rate of diffusion of impurities in the irradiated substance increases. The distribution of introduced impurities depending on irradiation time, ion energy and matrix temperature was studied in [1–3]. The penetration depth of impurities for all studied cases significantly exceeded the projective path length of ions of a given energy.

Another example of the long-range effect of incident ions on the target structure is the increase in the transparency of carbon films when they are treated with Ar^+ ions with energy E ~ 1.2 eV. The thickness of the film exceeded the ion path length by tens of times [4]. All this requires explanation within the framework of existing views about processes in a solid body under irradiation.

In [5], the mechanism of "radiation shaking" was proposed, the essence of which was that during the generation and annihilation of the Frenkel pair, the wave of elastic stress is formed in the material, associated with the change in atomic volume. The interaction of such waves with defects lowers their migration barriers and promotes their movement.

In [6], radiation stimulation of diffusion processes was associated with the deviation of the temperature dependences for the frequencies of atomic transitions from equilibrium positions from the Arrhenius law.

Previously, we proposed a mechanism for remote influence on defects, according to which elastic stress pulses excited in nonlocal thermoelastic peaks (NTPs) of ions bombarding the target surface interact with defects [7–9]. The excitation of such pulses by ions of carbon, noble gases, and hydrocarbons bombarding the surface of the carbon coating, as well as by Ti^+ and Cr^+ ions during the deposition of nitride coatings, was studied. In particular, it was shown that such pulses are capable of "sweeping out" interstitial defects from nanocrystallites of size $d \le 30$ nm and accelerating their migration over distances $d \le 100$ nm.

At the same time, the question of the influence of high temperature in the NTPs of ions on the diffusion rate remains unclear. As is known, the rate of any kinetic process depends significantly on temperature, so it is obvious that in NTPs characterized by high overheating temperatures, the diffusion rate increases significantly compared to the substance located outside the ion peaks. However, it is not clear whether its acceleration in nanometer-sized objects such as NTP ions can significantly change the average rate of diffusion in the irradiated material.

In this work, using the NTP ion model, we theoretically study the diffusion of defects in coating when its surface is bombarded with heavy low-energy ions, in particular, ions from the flow of which the coating is deposited.

MATHEMATICAL MODEL

In [10], based on computer modelling using the SRIM2000 package [11] of energy transfer from the ion to atoms of a substance and taking into account relaxation processes, it was shown that phonon energy losses of the low-energy ion are contained in the nanometer region that arises around the trajectory of the ion in the material target, i.e., in nonlocal thermoelastic

peak (NTP). The thermal energy density in NTP is comparable to the activation energy of many physical and chemical processes. According to the analysis, the peak can be approximated by the spherical segment containing the phonon losses of the ion $\eta(E)E$, centered at the middle of the mean projective path of the ion *L(E)* with initial radius

$$R(E) = 2\sqrt{\kappa\tau} + L(E)/2 . \quad (1)$$

Here E is the ion energy; τ is the thermalization time (ion-ion relaxation time); κ is the thermal diffusivity coefficient ; ρ is the density of the target substance, and $\eta(E)$ the fraction of ion energy converted into phonon excitations.

The initial volume of near-surface NTP is found by the formula

$$V_{NTP}(E) = \pi\left[\frac{2}{3}R(E)^3 + \frac{L(E)}{2}R(E)^2 - \frac{1}{3}\frac{L(E)^3}{8}\right]. \quad (2)$$

The temperature in the peak is determined by numerically solving the equation [10]:

$$\frac{\eta(E)E}{\rho C V_{NTP}(E)} = TD\left(\frac{\theta}{T}\right) - T_0 D\left(\frac{\theta}{T_0}\right), \quad (3)$$

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; T_0 is the average temperature of the target (coating), θ is the Debye temperature of the target material; k_B is Boltzmann's constant; ν_a is the number of atoms in molecule of substance (for the carbon coating θ = 2250 K, ν_a = 1), and $D(x)$ is the Debye function, which has the form:

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

The lifetime of NTP is determined by thermal conduction processes:

$$\tau_L = \frac{R^2}{4\kappa}. \quad (5)$$

Let us dwell on determining the parameters of the NTP of ions of hydrocarbon molecules when they are implanted into the carbon coating. As shown in [9], as a result of implantation of the ion of a C_nH_{n1} molecule with energy E, the thermoelastic peak with radius $R_C(E/n)$ and energy content $E\eta_C(E/n)$ is formed, where $R_C(E)$ and $\eta_C(E)$ are the parameters of the NTP of the C^+ ion in the carbon coating.

When the coating is bombarded with the ion flux with the flux density J, in its near-surface layer there are simultaneously $J\tau_L$ peaks, per unit surface of the target. The total volume occupied by the NTPs is equal to

$$V(E) = V_{NTP}(E) J\tau_L . \quad (6)$$

All peaks are located in the near-surface layer, the thickness of which is equal to the height of the NTP $h(E) = L(E)/2 + R(E)$ and numerically coincides with the volume of the layer, per unit area.

In accordance with the Arrhenius law, the dependence of the diffusion coefficient on absolute temperature T has the form:

$$D(T) = D_0 \exp\left(-\frac{\varepsilon}{k_B T}\right), \quad (7)$$

where ε is the activation energy of the diffusion and k_B is the Boltzmann's constant.

The average diffusion coefficient over the surface layer is given by the expression

$$\bar{D}(E) = D_0\left[\frac{V(E)}{h(E)}e^{-\frac{\varepsilon}{k_B T(E)}} + \left(1 - \frac{V(E)}{h(E)}\right)e^{-\frac{\varepsilon}{k_B T_0}}\right]. \quad (8)$$

Let us introduce the index of the acceleration of diffusion in material under irradiation in comparison with the diffusion coefficient of non-irradiated material:

$$k_D(E) = \frac{\bar{D}}{D(T_0)} = \frac{V(E)}{h(E)}e^{-\frac{\varepsilon}{k_B T(E)} + \frac{\varepsilon}{k_B T_0}} + 1 - \frac{V(E)}{h(E)}. \quad (9)$$

As estimates show, in the entire range of ion energies E < 1 keV the inequality is satisfied with a large margin

$$V(E) << h(E). \quad (10)$$

Therefore, expression (9) takes on the form:

$$k_D(E) = \frac{JV_{NTP}(E)\tau_L(E)}{h(E)}e^{\frac{\varepsilon}{k_B}\left(\frac{1}{T_0} - \frac{1}{T(E)}\right)} + 1. \quad (11)$$

Expression (11) allows us to study the influence of the energy of incident ions E on the rate of defect diffusion with a particular activation energy ε.

RESULTS AND DISCUSSION

The main characteristics of the NTP of C^+, Ar^+ and hydrocarbons ions in the carbon coating, necessary for calculating diffusion coefficients (7), as well as expressions (8), (11), are given in [9, 10]. For carbon coating, ρ = 2.4 g/cm^3, $\tau = 2\cdot10^{-14}$ s, were taken $\kappa = 10^{-2}$ cm^2/s. When determining the average projective path of the ion *L(E)* and the fraction of phonon losses $\eta(E)$, the SRIM2000 software package was used [11].

Analysis of expression (11) showed that the diffusion acceleration index begins to significantly exceed 1 only at defect migration activation energies $\varepsilon >$ 0.6 eV. In Fig. 1 shows the acceleration coefficients for the diffusion of defects with activation energy ε = 0.6 eV when bombarding the carbon coating with flows of C^+, Ar^+, $C_2H_2^+$ and $C_6H_6^+$ ions (curves 1–4, respectively). The flux density for all species of ions was taken equal to $J = 3\cdot10^{17}$ cm$^{-2}\cdot$s^{-1}. As can be seen

from the Fig. 1, at such an activation energy, there is practically no acceleration of diffusion for the entire considered ion energy range $25 < E < 1000$ eV. However, as the activation energy increases, the rapid increase in the rate of such radiation-stimulated diffusion is observed. So, in Fig. 2 shows similar dependences of the diffusion rate acceleration indexes with activation energy $\varepsilon = 1$ eV. As can be seen from the Fig. 2, diffusion with such activation energy accelerates from 10^3 to 10^4 times or more, depending on the type of ions. In Fig. 3 shows the dependences of the diffusion acceleration indexes k_D on the activation energy ε in the range $0.5 < \varepsilon < 1$ eV, confirming the above.

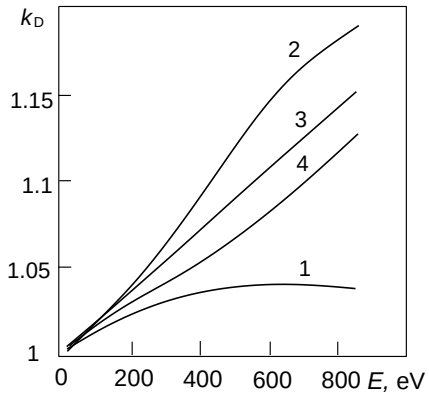

Fig. 1. Indexes acceleration of diffusion with activation energy ε = 0.6 eV when bombarding carbon coating with flows of C^+, Ar^+, $C_2H_2^+$, and $C_6H_6^+$ ions (curves 1–4, respectively)

It follows from the form of expression (11) that for relatively small J, at which the first term in (11) is less than unity, the diffusion rate is equal to the diffusion rate in the non-irradiated material and practically does not depend on J. With increasing flux density, the first term in (11) becomes the main one, while the diffusion rate changes proportionally to J. It should also be noted that as J decreases, the minimum activation energy at which diffusion begins to accelerate increases. Thus, at a flux density $J = 3 \cdot 10^{15} \text{cm}^{-2} \cdot \text{s}^{-1}$, a noticeable acceleration of diffusion occurs at $\varepsilon > 0.75$ eV.

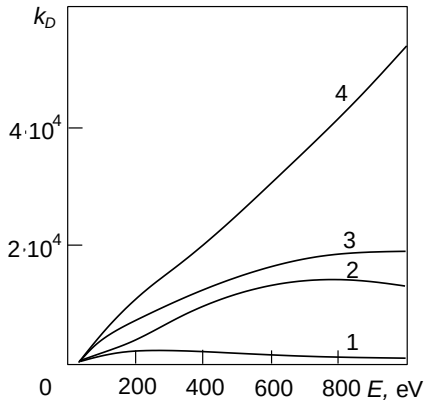

Fig. 2. Indexes acceleration of diffusion with activation energy ε = 1 eV when bombarding carbon coating with flows of C^+, Ar^+, $C_2H_2^+$, and $C_6H_6^+$ ions (curves 1–4, respectively)

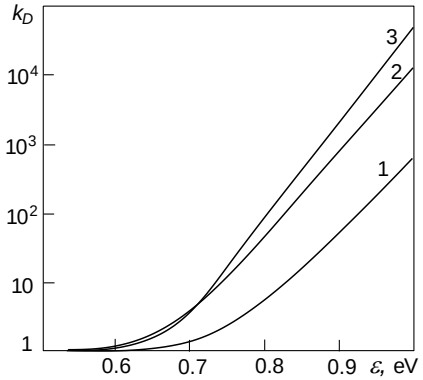

Fig. 3. Dependence of indexes acceleration of diffusion on activation energy ε when bombarding the carbon coating with flows of C^+, Ar^+, and $C_6H_6^+$ ions (curves 1–3, respectively) Ion energy E = 1000 eV

CONCLUSIONS

It is shown that the presence of superheated nanometer-sized regions near the trajectories of low-energy ions bombarding the target leads to an acceleration of diffusion in the surface layer of the target, controlled by the ion beam. Based on the model of the nonlocal thermoelastic peak of the low-energy ion, expressions are obtained for the average diffusion coefficient in the near-surface layer of the target controlled by the beam of incident ions, as well as for the diffusion acceleration index. The dependences of the diffusion acceleration index on the ion energy are presented for various types of ions at selected activation energies and ion flux densities. Numerical calculations showed that diffusion acceleration occurs only for processes with the activation energy exceeding a certain threshold value determined by the value of J, the type and energy of the ions. The minimum activation energy at which diffusion acceleration begins increases with decreasing flux density of incident ions.

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РАДІАЦІЙНО-СТИМУЛЬОВАНА ДИФУЗІЯ ПРИ ПЛАЗМОВО-ІОННОМУ ОСАДЖЕННІ ПОКРИТТІВ

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Теоретично досліджується дифузія дефектів у вуглецевому покритті при бомбардуванні його поверхні важкими низькоенергетичними іонами з урахуванням різкого збільшення швидкості кінетичних процесів у нелокальних термопружних піках (НТП) іонів – перегрітих нанометрових областях, що виникають навколо траєкторій іонів у матеріалі мішені. Щільність теплової енергії в НТП порівнянна з енергією активації багатьох фізичних та хімічних процесів, внаслідок чого їхній внесок у сумарну дифузію дефектів у приповерхневому шарі мішені може бути значним. На основі моделі НТП отримані вираження для середнього коефіцієнта дифузії в приповерхневому шарі мішені, контрольованому пучком іонів, що падають, а також для показника прискорення дифузії. Наведено залежність показника прискорення дифузії від енергії іона для різних видів іонів при вибраних енергіях активації та щільності потоку іонів. Чисельний розрахунок отриманих виражень з використанням програмного пакета SRIM2000 показав, що при обраній щільності потоку іонів J прискорення дифузії має місце тільки для процесів з енергією активації, що перевищує певне граничне значення, яке визначається величиною J, сортом і енергією іонів.