

## RADIATION-ACOUSTIC EFFECTS AT DIAMOND-LIKE COATING DEPOSITION FROM THE FLOW OF HYDROCARBON IONS AND THEIR INFLUENCE ON KINETIC PROCESSES

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Based on the model of the nonlocal thermoelastic peak (NTP) the ion generalized to the case of the ion of polyatomic molecule, the acoustic effect of low-energy ion of a hydrocarbon molecule during plasma-ion deposition of diamond-like carbon coating is investigated. The generation of a stress wave takes place as a result of the combined action of mechanisms associated with the rapid transfer of energy, momentum, and additional volume to the NTP volume. The magnitude, shape, and spatial dependence of the stress pulse generated by  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_6\text{H}_6$  ions have been studied with absorption taken into account. The possibility of accelerating the diffusion of interstitial defects, as well as the possibility of brittle fracture of the coating at the interface with the substrate under the action of acoustic pulses from deposited hydrocarbon ions, is discussed.

### INTRODUCTION

Experiments show that low-energy ions ( $E \sim 1$  to 10 keV) bombarding the solid body surface affect the structure and properties of the body at depths significantly exceeding the length of the ion's path. One of the examples of such a long-range effect is the so-called radiation-stimulated diffusion of implanted ions in the process of irradiation. The distribution of introduced impurities depending on the irradiation time, ion energy, and matrix temperature was studied in [1–3]. The depth of impurity penetration in all investigated cases significantly exceeded the projected length of the ion path of such energy. Another example of the long-range effect of ions on the target structure is the treatment of thick (tenths of micron) opaque carbon films with  $\text{Ar}^+$  ions, as a result of which their transparency increases. The thickness of the film exceeded the length of the ion path ten times [4, 5].

The purpose of the work is to prove that acoustic pulses excited by single hydrocarbon ions during plasma-ion deposition of carbon coating can cause structural rearrangement, in particular, accelerated migration of defects and brittle fracture at a significant distance (up to tens of nanometers) from the coating surface. In contrast to the time-consuming methods of molecular dynamics, the proposed macroscopic approach allows obtaining results in analytical form, which greatly facilitates their analysis.

In the course of theoretical studies, the concept of the nonlocal thermoelastic peak (NTP) of the ion that developed by us earlier for monoatomic ions [6] was widely used. Further consideration is carried out in relation to the ion of a hydrocarbon molecule  $\text{C}_n\text{H}_{n_1}$ , where  $n$  and  $n_1$  are the number of carbon and hydrogen atoms, respectively, included in the molecule. As will be shown below, ions of polyatomic molecules excite, as a rule, more powerful acoustic pulses, compared to carbon ions of the same energy, which increases their influence on transfer and destruction processes.

### MODEL OF THE NTP OF HYDROCARBON ION

When determining the characteristics of the thermoelastic peak generated by the ion of hydrocarbon molecule, we take into account the fact that the molecule, falling into the target substance, disintegrates into its atoms, which fly with speeds equal in magnitude and direction, and equal to the speed of the original molecule. The kinetic energy  $E_C$  of the C atom entering the molecule is equal to

$$E_C = 12E / (12n + n_1). \quad (1)$$

When the condition  $n_1 \ll 12n$  is met (that is the most common case), the acceptable approximation of the energy of carbon atom is  $E_C = E/n$ . For energy of the hydrogen atom, we have:

$$E_H = \frac{E}{12n + n_1} \approx \frac{E}{12n} \ll E_C. \quad (2)$$

Each ion of the fragmented molecule forms its NTP independently of other ions of the molecule. The analysis shows that the size of the peaks formed from carbon ions significantly exceeds the characteristic distance between them, which is determined by the lengths of the carbon-carbon bonds of the hydrocarbon molecule. Let's introduce the parameter  $l_{CC}$  – the maximum distance between carbon atoms in the molecule, which is estimated from the lengths of carbon-carbon bonds. For  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_6\text{H}_6$ , the  $l_{CC}$  parameter is 0, 0.12, and 0.46 nm, respectively. The condition  $l_{CC} \ll 2R(E_C)$  means that there is the almost complete spatial-temporal coincidence of carbon peaks. Here  $R(E_C)$  is the initial radius of the carbon ion peak with energy  $E_C$ . As a result, the thermoelastic peak is formed, the initial radius of which is  $\sim R(E_C)$ . Similarly, the thermoelastic peak is formed from each of the hydrogen atoms included in the original molecule. Calculation using the SRIM2000 package [7] shows that the peaks of hydrogen ions (ie, protons) lie inside the combined carbon peak. Thus, if we neglect some

inhomogeneity of the energy distribution associated with proton peaks, it can be assumed that as a result of implantation of the hydrocarbon molecule ion with energy  $E$ , the thermoelastic peak with a radius  $R(E/n)$  and energy content  $E\eta(E/n)$  is formed. For simplicity of the analysis, we assumed  $l_{CC} = 0$ , since it does not significantly affect the results. Here  $\eta(E)$  is the fraction of phonon losses of the  $C^+$  ion with energy  $E$ . Note that in this approximation the parameters of the NTP of the  $CH_4^+$  ion coincide with those of the NTP of  $C^+$  ion.

The analysis of relaxation processes showed that taking into account the ionization (inelastic) losses of the implanted ion does not change the estimate of the thermal energy density in the NTP. Using the position of the mathematical model of the nonlocal thermoelastic peak of monatomic ion [6], we come to the conclusion that the initial radius of the NTP ion of hydrocarbon molecule is determined with acceptable accuracy by the expression  $R(E/n) = L(E/n)/2 + R_T$ , where  $R_T = 2\sqrt{\kappa\tau}$  is the radius of thermal smearing of the point heat source during the ion-ion relaxation time,  $\kappa \approx 10^{-2} \text{ cm}^2/\text{s}$  is the coefficient of the thermal conductivity of the target material (diamond-like carbon coating),  $\tau$  is the time of ion-ion relaxation, which is actually the formation time of the NTP. Functions  $\eta(E)$  and  $L(E)$  were determined using SRIM2000 [7]. The presence of  $n$  thermal peaks of  $C^+$  ions, which coincide in space and time, leads to the revision of the limit of applicability of the NTP model of the hydrocarbon ion in direction of significant increase in acceptable energies, compared to the  $C^+$  ion. So, for example, computer modeling showed that the NTP model for the  $C_6H_6$  ion is suitable up to energy  $E = 10 \text{ keV}$ .

The analysis of the momentum transfer process from the primary ion to the carbon coating material was also performed. It is shown that, despite a significant part of the energy  $E(1 - \eta(E/n))$  contained in ionization losses (in excited electrons), the share of momentum they carry is negligibly small. The last circumstance is a consequence of the insignificance of the mass of electrons constituting ionization losses compared to mass of hydrocarbon molecule. Thus, it is shown that the transfer of momentum from the primary ion to the substance in the NTP, with a sufficient degree of accuracy, is determined by the expression  $P = \sqrt{2MnE}$ , where  $M$  is the mass of the carbon atom.

### ACOUSTIC IMPULSE FROM THE NTP

The generation of acoustic stresses is caused by the pulsed change in the volume of the NTP due to thermal expansion and introduction of additional volume by the primary ion, as well as the transfer of momentum from the ion to the substance of the NTP [8]. In the problem of excitation of the acoustic pulse by the NTP of the low-energy ion, there are three characteristic times: the relaxation time of phonon losses  $\tau = (2 \dots 5) \cdot 10^{-14} \text{ s}$  (it is also the relaxation time of the transmitted pulse); the

time of acoustic relaxation of NTP  $t_s = 2R/s \sim (1 \dots 5) \cdot 10^{-13} \text{ s}$ ; and the cooling time of NTP  $t_T = R^2/4\kappa \sim 10^{-11} \text{ s}$ . Here  $R$  is the initial radius of the NTP,  $s$  is the longitudinal sound velocity of the target material. The evaluation of the characteristic times shows that the relation  $\tau \ll t_s \ll t_T$  is fulfilled. In view of this, the thermal, as well as the impulse, impact on the material of the peak can be considered as an instantaneous load.

To find out the dependence of the amplitude of the acoustic pulse on the NTP parameters and the target characteristics, the task of exciting elastic oscillations by the spherical region in the infinite homogeneous isotropic elastic body, which acquires the energy of phonon losses  $E\eta(E/n)$ , momentum  $P = \sqrt{2MnE}$ , and additional volume  $nV_I$  was considered. Accordingly, three mechanisms of elastic oscillation generation were considered.

**Thermoacoustic mechanism.** The rapid increase in the volume of the NTP due to thermal expansion during heating due to phonon losses of the ion  $E\eta(E/n)$  excites thermoacoustic stresses  $\sigma_T$ . The system of equations of thermoacoustics [9], neglecting thermal conductivity during the formation of the acoustic pulse, leads to the single equation regarding the amplitude of the acoustic displacement:

$$\frac{\partial^2 \vec{u}}{\partial t^2} - s^2 \Delta \vec{u} = -\frac{\Gamma}{\rho} \frac{\partial \varepsilon(\vec{r}, t)}{\partial \vec{r}}, \quad (3)$$

with zero initial conditions

$$\vec{u}(\vec{r}, 0) = 0; \quad \partial \vec{u}(\vec{r}, 0)/\partial t = 0, \quad (4)$$

where  $\vec{u}(\vec{r}, 0)$  is the amplitude of the longitudinal acoustic displacement wave excited by the NTP,  $t$  is the time since the occurrence of the NTP,  $\vec{r}$  – the radius vector from the center of the NTP to the point of observation,  $\varepsilon(\vec{r}, t)$  is the heat energy density in the NTP,  $s$ ,  $\rho$ , and  $\Gamma$  are the longitudinal speed of sound, density and parameter Grüneisen coating material, respectively. In the “wave zone”, that is, under the condition  $r_0 \gg R$  where  $R$  is the effective radius of the NTP, the expression was obtained for the amplitude of the acoustic stress pulse [9]:

$$\sigma(\vec{r}_0, t) = \frac{\Gamma}{4\pi s^2 r_0} \frac{\partial}{\partial t} \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} \frac{\partial \varepsilon(\vec{r}, t - (r_0 - x)/s)}{\partial t} dx. \quad (5)$$

The excitation of the acoustic pulse by the instantaneously and uniformly heated spherical region was analyzed. The expression for the amplitude of the stress pulse in the wave zone has the form:

$$\sigma_T(y, r) \cong \sigma_{Tm}(y-1) [\Theta(y-2) - \Theta(y)], \quad (6)$$

where  $y = (st - r + R(E/n_C))/R(E/n_C)$ ;  $\Theta(x)$  – is the Heaviside's “unit”;  $\sigma_{Tm} = \Gamma E \eta(E/n) R(E/n_C) (2rV(E/n))^{-1}$ ,  $V(E)$  – is the volume of the near-surface NTP of carbon ion with energy  $E$ , for which the following expression was obtained [6]:

$$V(E) = \pi \left[ \frac{2}{3} R(E)^3 + \frac{L(E)}{2} R(E)^2 - \frac{1}{3} \frac{L(E)^3}{8} \right]. \quad (7)$$

We emphasize that it is legitimate to use the initial parameters of the NTP to determine the acoustic stresses, since the condition  $\tau \ll 2R/s$  is fulfilled. The time is counted from the moment of arrival of the leading edge of the pulse at the observation point  $r$ .

In Fig. 1 shows the universal function  $\sigma(y)/\sigma_m$ , which specifies the shape of the stress pulse generated by the instantaneously arising thermal field with the uniform distribution of absorbed energy over the sphere. In this case, the acoustic response is the spherically symmetric bipolar stress wave that propagates from the NTP volume with the longitudinal speed of sound  $s$  and decreases with distance according to the law  $\sigma \sim r^{-1}$ .

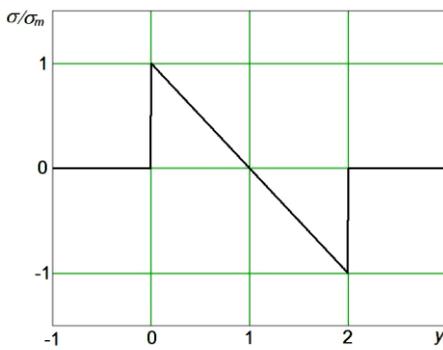


Fig. 1. Thermoacoustic stress generated by spherical NTP

**Deformation mechanism.** The rapid increase in the volume of the NTP by the amount of the introduced volume  $nV_I$  excites the deformation stresses  $\sigma_D$ . Here,  $V_I$  is the introduced volume of  $C^+$  ion. In the approximation of the uniform distribution of the introduced volume  $nV_I$  in the volume of the NTP, it is possible to obtain the amplitude of deformation stresses  $\sigma_D(r,t)$  from (6) after the substitution  $\Gamma E \eta(E/n) \rightarrow KnV_I$ , where  $K$  is the bulk compression modulus of the target material. As a result, we get:

$$\sigma_D(y,r) \equiv \sigma_{Dm}(y-1) [\Theta(y-2) - \Theta(y)], \quad (8)$$

where  $\sigma_{Dm} = KnV_I R(E/n_C) (2rV(E/n))^{-1}$ . It is clear that the acoustic pulse excited by the deformation mechanism coincides in shape with the thermoacoustic pulse shown in Fig. 1, however, in this case it is necessary to put  $\sigma_m = \sigma_{Dm}$ .

Thus, the deformation pulse, like the thermoacoustic one, is the bipolar wave that has the maximum (compressive stress) on the leading front ( $y = 0$ ) and the equal minimum (stretching stress) on the rear front ( $y = 2$ ).

**Impact (dynamic) mechanism.** The generation of the stress wave also occurs as a result of the transfer of the ion momentum to the substance in the NTP volume during the ion-ion relaxation time  $\tau$ . Considering the condition  $\tau \ll 2R/s$ , it can be assumed that the ion NTP, being at rest at  $t < 0$ , instantly acquires speed

$v = \sqrt{2MnE}/(\rho V(E/n))$  at the moment  $t = 0$ . This acceleration of the spherical NTP causes wave excitation of the elastic medium. In the hydrodynamic approximation, the acoustic stress field in the wave zone is given by the expression [10]:

$$\sigma_I(\vec{r}, y, \theta) = -\sigma_{Im}(r, \theta) e^{-y} \sin\left(y - \frac{\pi}{4}\right), \quad (9)$$

where  $\sigma_{Im}(\vec{r}, \theta) = sR(E/n) \sqrt{2MnE} \cos\theta (V(E/n)r)^{-1}$ ,  $\theta$  is the angle between the radius-vector  $\vec{r}$  and the momentum of the primary ion;  $M$  is the mass of the carbon atom. The impact stress is the spherical wave with the effective spatial length  $\lambda \sim 2R(E)$ , which diverges from the NTP at the longitudinal sound velocity  $s$  and decreases with distance as  $r^{-1}$ . Its amplitude  $\sigma_I$  is proportional to the momentum of the primary ion and depends on the angle  $\theta$  according to the law  $\sigma_I \sim \cos\theta$ . For the direction  $\theta = 0$ , the amplitude of the impact pulse is maximum. In the direction perpendicular to the velocity vector of the incident ion, the amplitude of the impact component is zero.

In Fig. 2 shows the universal form (time dependence) of the impact acoustic pulse in the wave zone in the dimensionless variables  $y$  and  $\sigma_I/\sigma_{Im}$ . The calculation is made for the case when the detection point lies on the direction  $\theta = 0$ .

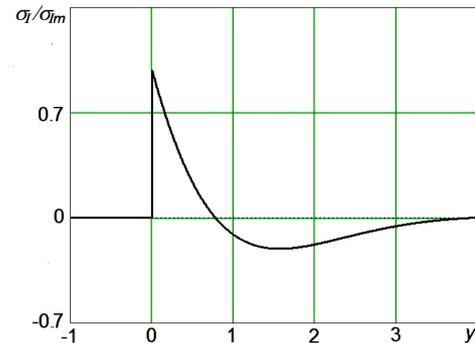


Fig. 2. Universal function of the time dependence of the impact pulse excited by the spherical NTP

As one can see from Fig. 2, the impact acoustic pulse is the bipolar wave, which has the maximum (compressive stress) at the leading front ( $y = 0$ ) and the minimum (tensile stress) at the time of  $y = 1.57$ . At the same time, the half-waves of compression and rarefaction are sharply asymmetric: compressive stresses are about 5 times larger than tensile stresses, but the half-wave of rarefaction is stretched out in time by about the same number of times.

The total amplitude of the acoustic pulse is given by the expression:

$$\sigma(y, r, \theta) = \sigma_T(y, r) + \sigma_D(y, r) + \sigma_I(y, r, \theta). \quad (10)$$

In Fig. 3 shows the acoustic pulses that are excited in the diamond-like coating (DLC) by the ions of hydrocarbon molecules with energy  $E = 100$  eV, formally calculated for the distance  $r = R(E/n)$  from the center of the NTP (case  $\theta = 0$ ). To obtain the value of the acoustic stress at the point  $r \gg R(E/n)$  it is

necessary to take into account the geometric factor and multiply the data shown in Fig. 3, on  $R(E/n)/r$ .

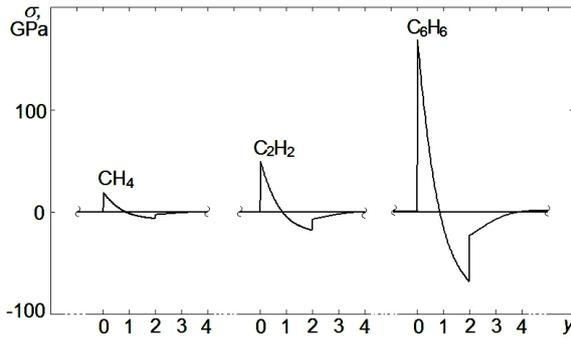


Fig. 3. Acoustic pulses excited in the DLC by ions of hydrocarbon molecules with energy  $E = 100 \text{ eV}$  ( $\theta = 0$ )

The effective duration of the total acoustic pulse, as well as its components, is  $\Delta t \sim 2R(E/n)/s \sim 10^{-13} \text{ s}$ , it decreases with the number of carbon atoms in the hydrocarbon molecule and increases with the energy of the ion (Fig. 4).

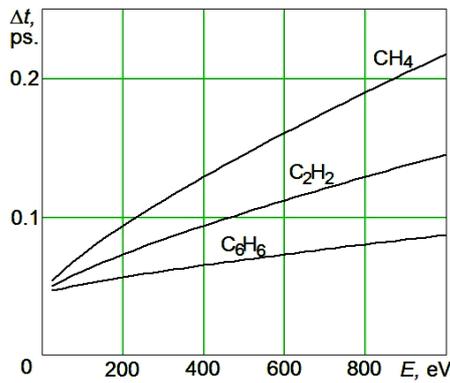


Fig. 4. Dependence of the effective duration of the acoustic pulse excited by the NTP ion on the ion energy for various ions of hydrocarbon molecules

Based on the fact that the maxima of all three components of the acoustic pulse are reached at the leading front ( $y = 0$ ), the maximum amplitude of the total acoustic pulse is given by the expression

$$\sigma_m(E, \theta) = \sigma_{Tm}(E) + \sigma_{Dm}(E) + \sigma_{Im}(E, \theta) \cos \theta. \quad (11)$$

In Fig. 5 shows the dependence of the maximum of the total amplitude of the acoustic pulse on the ion energy for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_6\text{H}_6$  ions in DLC at  $\theta = 0$ .

As can be seen from the presented material, the acoustic response of the material to the bombardment of the hydrocarbon molecule ion is the powerful pulse with the amplitude of tens of gigapascals and subpicosecond duration which decreases with distance according to the law  $\sigma \sim 1/r$ . Such pulses expire quickly when passing through the target material. However, if harmonic oscillations  $u_\omega \sin \omega t$  are characterized by the decay with distance according to the law  $\sim u_\omega e^{-\beta(\omega)r}$ , then for a time-limited pulse, which is a superposition of harmonics with frequencies from the interval

$0 \leq \omega \leq s/2R(E/n_C)$ , the decay law is determined by the total contribution of all components and is no longer exponential. As a result, the shape of the pulse, its duration and the law of spatial decay also change.

When calculating the pulse passing through the absorbing medium, the dispersion of the sound velocity can be neglected and limited only to absorption, since absorption leads to the disappearance of harmonics with the large dispersion from the pulse spectrum. In this case, taking into account the effect of the absorbing medium on the acoustic pulse is reduced to the integral transformation of the amplitude in the medium without absorption and dispersion:

$$u_{at}(r, t) = \frac{1}{\pi} \int_{-\infty}^t u(r, \tau) \int_0^\infty e^{-\beta(\omega)r} \cos[\omega(t - \tau)] d\omega d\tau. \quad (12)$$

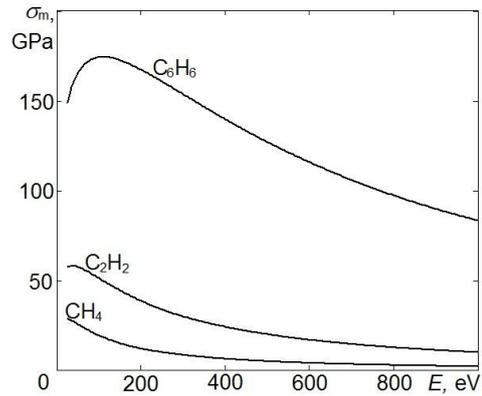


Fig. 5. Dependence of the maximum total pulse amplitude on the ion energy for various hydrocarbon ions

In the most important case  $\beta(\omega) = \beta\omega^2$ , characteristic of absorption in amorphous bodies and dielectric single crystals, we obtain the following dependence on  $r$  for the point thermal peak [8,12]:

$$\sigma_{at}(r) \cong \frac{\Gamma E \eta (E/n)}{\sqrt{2\pi e} \beta_2 s^2} \frac{1}{r^2}. \quad (13)$$

The resulting expression describes the distance dependence of the amplitude of the acoustic pulse also for the non-local peak, but only for the interval  $r > r_{at}(E, n) = 4R(E/n)^2 / (\beta s^2) \sim 3...10 \text{ nm}$ . At smaller distances, the expression for the amplitude of the acoustic pulse obtained without taking into account absorption should be used for estimations.

Analogous considerations make it possible to obtain approximate expressions for the deformation and impact components of the acoustic pulse. As a result, for the full amplitude of the acoustic pulse from the NTP of the hydrocarbon molecule ion, we obtain the following expression:

$$\sigma_{at}(\vec{r}) \approx \begin{cases} \frac{R}{2r} \frac{\Gamma E \eta + KnV_1 + 2s\sqrt{2MnE} \cos \theta}{V}, & R < r < r_{at}, \\ \frac{\Gamma E \eta + KnV_1 + 2s\sqrt{2MnE} \cos \theta}{\sqrt{2\pi e} \beta s^2 r^2}, & r_{at} < r. \end{cases} \quad (14)$$

Here, for brevity, we use the notations  $R = R(E/n)$  and  $V = V(E/n)$ .

At  $r \sim r_{at}(E/n)$ , the acoustic stress amplitude of the passes from one asymptotic dependence to another. Note that the limiting distance  $r_{at}(E/n)$  increases with the energy  $E$  of the ion and decreases with the number of carbon atoms  $n$  in the hydrocarbon molecule.

The acoustic pulse in the interval  $r > r_{at}(E/n)$  turns into a bipolar antisymmetric wave, the spatial length of which depends weakly on the radius of the NTP and increases with the distance  $r$  according to the law  $\lambda(r) \approx s\sqrt{\beta r}$ . In this range of distances, absorption leads to a power-law (not exponential) dependence on the distance, and the pulse amplitude depends only on the integral characteristics of the NTP:  $E$ ,  $\eta(E)$ ,  $V_I$ ,  $n$  and does not depend on the radius of the NTP. The independence of the pulse amplitude and duration on the NTP size allows the use of the “point” approximation for ions with energy  $E \gg 1$  keV, although the spherical NTP model may no longer be applicable to them. The relative contributions of different mechanisms to the total acoustic pulse remain valid in this interval as well.

### FRAGILE DESTRUCTION

Acoustic stresses arising near the NTP of heavy, low-energy ions are large enough to lead to brittle destruction of the material. Dynamic strength of metals is  $\sigma_d \sim 1$  HPa. Such stress occurs, for example, when the material is instantly heated to temperatures  $T \geq 10^3$  K, which are characteristic of the NTP of low-energy ions. An additional contribution to acoustic stress is made by deformation and impact (dynamic) generation mechanisms. It should be noted that the leading front of the stress pulse, which has the largest value, is the compressive stress and cannot cause brittle destruction of the material. The possibility of destruction occurs when the pulse reaches the boundary with a material that has a lower acoustic rigidity and is reflected from it with repolarization.

Let's discuss the possibility of brittle destruction in the immediate vicinity of the near-surface NTP. In the region of peak localization, the stress is a superposition of the spherical bipolar wave diverging from the volume of the peak and reflected from the free boundary of the target, and static thermoelastic stress present in the material near the peak. The analysis shows that the contribution of static compressive stress leads to the fact that compressive stresses constantly prevail near the near-surface NTP, and, therefore, brittle fracture is impossible here [11].

Another situation occurs near the interface of the coating with the substrate, which is distant from the NTP by a rather large distance of  $r > 2R(E/n) \sim 3$  nm. When an acoustic pulse normally falls on the interface between two materials, the reflection coefficients  $D_{12}$  and transmission  $k_{12}$  are given by the expressions  $D_{12} = (\rho_2 s_2 - \rho_1 s_1) / (\rho_2 s_2 + \rho_1 s_1)$ ,  $k_{12} = 2\rho_2 s_2 / (\rho_2 s_2 + \rho_1 s_1)$ , where  $\rho_1, \rho_2$  are the densities of the materials, and  $s_1, s_2$  are the longitudinal velocities of sound. The acoustic pulse comes from material “1” to its border with material “2”. If the acoustic pulse from the DLC arrives at the boundary with the substrate that has a much lower rigidity (vacuum, polyethylene, silicon),

then  $D_{12} \cong -1$  and  $k_{12} \ll 1$ , i.e., the acoustic pulse is almost completely reflected with a change in sign. If the acoustic pulse arrives at the boundary with a material with the close acoustic rigidity, as in the case of the DLC on stainless steel substrate, then we have  $D_{12} \ll 1$  and  $k_{12} \simeq 1$ , that is, the acoustic pulse passes from the coating to the substrate, practically without being reflected and without changing in magnitude. Finally, if the acoustic rigidity of the substrate exceeds that of the coating, the pulse is reflected from the interface without repolarization, and the coating does not break down either.

The stress distribution in the coating near the boundary is obtained as the sum of direct and reflected stress pulses:

$$\sigma_{tot}(x, t) = \sigma(-x + st/R) + D_{12}\sigma(x + st/R), \quad (x \leq 0). \quad (15)$$

Here  $x=0$  is the coordinate of the boundary, on which the stress pulse comes from the negative half-space; moment  $t=0$  corresponds to the arrival of the leading front of the pulse at the interface.

In Fig. 6 shows the spatial distribution of stresses at different time points  $t = R(E/n_c)y/s$  near the boundary of the coating with the substrate that has a much lower rigidity, when the acoustic pulse excited by the nonlocal elastic peak of the  $\text{CH}_4$  ion with energy of 100 eV is incident.

As can be seen from Fig. 6, the repolarization of the pulse at the boundary and the combination of the reflected pulse with the direct that leads to the occurrence of significant tensile stress near the boundary, which can lead to brittle destruction (peeling) of the material. The maximum tensile stress is observed at distance  $R(E/n)$  from the boundary and is equal to  $\sim 1.2\sigma_m$  in magnitude, where  $\sigma_m$  is the maximum compressive stress in the direct impulse. Thus, the effect of brittle fracture must be taken into account when depositing nanometer DLC on materials with low stiffness, for example, on polymers.

The obtained pattern of stress distribution is correct if the distance from the NTP to the boundary does not exceed  $r_{crit}$ . Otherwise, it is necessary to take into account the effect of absorption on the amplitude of the acoustic pulse.

In Fig. 7 shows the dependence on the distance of the maximum of the acoustic stresses generated by the NTP of  $\text{CH}_4^+$  and  $\text{C}_6\text{H}_6^+$  ions of different energies in the DLC carbon coating. In connection with the above, Fig. 7 also displays the maximum tensile stresses that occur when the acoustic pulse is reflected from the boundary with a “soft” substrate, which is distant from the NTP by distance  $r$ .

The horizontal dash-dotted line shows the level of critical stress that causes brittle failure of the coating material, the vertical dashed-dotted lines mark the distances from the NTP corresponding to the critical stress for different ions. As can be seen from Fig. 7, the maximum coating thickness at which brittle fracture is possible does not exceed 10 nm for ions with energy of

less than 1 keV. That is, such a danger exists only for nanometer-thick films and coatings. For ions of higher energies, this thickness, of course, increases. So, as can be seen from Fig. 7, for  $C_6H_6^+$  ions with energy of 10 keV, the limit thickness is 20 nm.

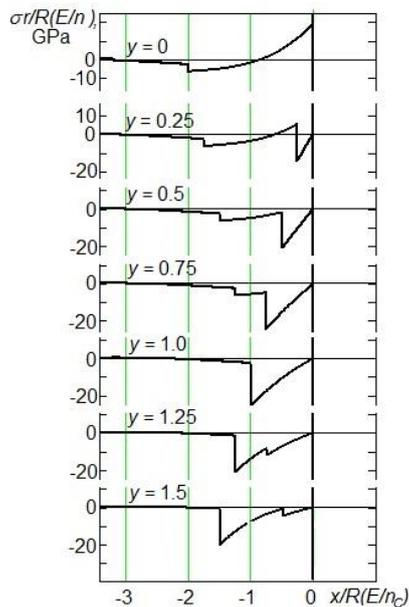


Fig. 6. Spatial distribution of stresses created by the acoustic pulse reaching the free boundary of the DLC film at different time points

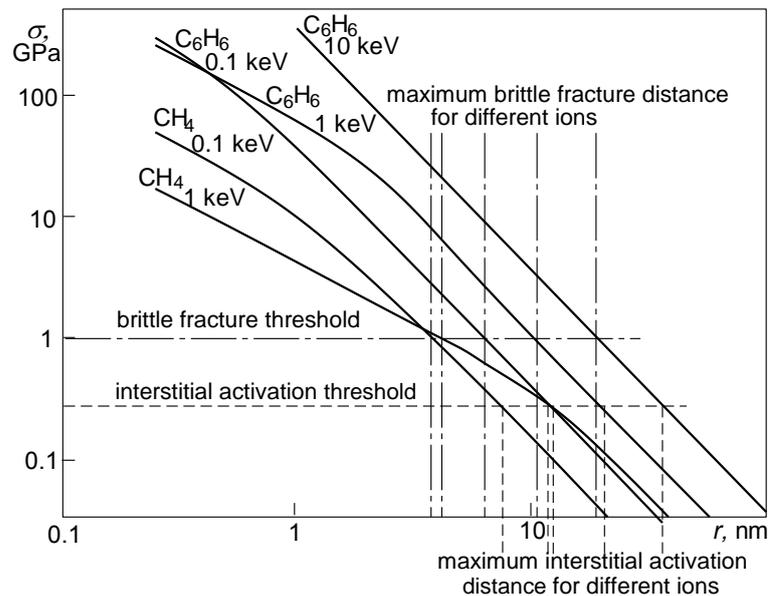


Fig. 7. Spatial dependence of acoustic stresses excited in DLC coating at implantation of  $CH_4^+$  and  $C_6H_6^+$  ions with energies of  $10^2$  and  $10^3$  eV

The limit of the area of activation of interstitial defects in the longitudinal direction is determined using the graph of the spatial dependence of acoustic stresses excited in diamond-like carbon by hydrocarbon ions (see Fig. 7). The horizontal dashed line shows the level of the critical stress that activates the movement of interstitial defects, the vertical dashed lines mark the distances from the NTP corresponding to the critical stress for different ions. As can be seen from Fig. 7, the dimensions of the activation region, where the over-

## ACCELERATION OF DEFECT MIGRATION

When the acoustic stress arising around the NTP exceeds the corresponding activation thresholds, various kinetic processes can be stimulated in the deposited material: diffusion of defects and impurities, structural rearrangement, and creep [12]. Thus, the equation for the boundary of the region  $\vec{r}_{is}(E, \theta, n)$ , inside which the acoustic pulse from the NTP activates the movement of interstitial atoms, has the form:

$$\sigma_{at}(\vec{r}_{is}(E, \theta, n)) = U_{is}/\Omega_{is}, \quad (16)$$

where  $U_{is}$  is the activation migration energy of the interstitial atom;  $\Omega_{is}$  is its volume. Taking  $U_{is} = 0.1$  eV,  $\Omega_{is} = 5 \cdot 10^{-23}$  cm<sup>3</sup> (the volume of the interstitial atom in carbon), we obtain  $\sigma_{is} = U_{is}/\Omega_{is} \sim 0.3$  GPa for the stress that activates the migrants. Activation will occur everywhere around the NTP, where the amplitude of the acoustic wave exceeds  $\sigma_{is}$ . The set of solutions  $\vec{r} = \vec{r}_{is}(E, \theta, n)$  of equation (16) lies on the surface of the ellipsoid of rotation extended in the direction  $\theta = 0$  due to dipole component in the amplitude  $\sigma_{at}(\vec{r})$ . This surface is the boundary of zone of interstitial activation.

barrier movement of migrants occurs, significantly depend on the type and energy of the ion. Thus, for the NTP of the  $CH_4^+$  ion with energy of  $10^2$  eV, the limit of the activation region is distant from the peak by distance of  $r_C(10^2) = 8$  nm, while in the case of the  $C_6H_6^+$  ion with energy of  $10^3$  eV, the limit is moved to 20 nm. Note that at a relatively small activation energy  $U_{is} \leq 0.1$  eV, which is characteristic of interstitial defects, the radius  $r_{is}$ , which determines the limit of the activation region, lies in the region  $r > r_{at}$ . In this

region, it is the absorption that determines the size and shape of the stress pulse. This also leads not to exponential, but to a slower power-law dependence of the stress on the distance  $\sigma_{at}(r) \sim 1/r^2$ . In this range,  $r_{is}$  increases both with energy and with the number of carbon atoms in the hydrocarbon molecule (see Fig. 7). In addition, in this range, the pulse amplitude depends only on the integral characteristics of the NTP, namely on  $E$ ,  $\eta(E)$ ,  $V_I$ , and  $n$ , and does not depend on the NTP size. This makes it possible to estimate the amplitude of the acoustic pulse for ions of high energies, for which the NTP model is no longer applicable. So, in Fig. 7 shows the distance dependence of acoustic stress excited by the  $C_6H_6^+$  ion with energy of 10 keV, for which the activation zone of the interstitial  $r_{is}$  is shifted to 40 nm.

It is likely that the influence of acoustic pulses generated by NTP ions is not limited to direct activation of defects. The well-known thermal activation of a kinetic process can accelerate the migration of defects by reducing the activation energy  $U$  in the stress field of the acoustic pulse from the NTP:

$$U_{ef}(E, n, \theta) \sim U - \Omega_{is} \sigma_{at}(\vec{r}(E, n, \theta)). \quad (17)$$

Here  $\Omega_{is}$  is the volume of the interstitial defect. The acceleration coefficient  $K$  of the kinetic process at the point  $\vec{r}$  where the acoustic stress is currently present is approximately equal to

$$K \simeq \exp\left\{\Omega_{is} \sigma_{at}(\vec{r}(E, n, \theta)) / (k_B T_0)\right\}, \quad (18)$$

where  $T_0$  is the temperature of the target,  $k_B$  is the Boltzmann constant. It can be seen from (18) that the lower the temperature of the target  $T_0$ , the greater the relative acceleration of the kinetic process due to acoustic activation. Estimates show that heavy ions, including hydrocarbon ions, can significantly accelerate the diffusion of interstitial defects at distances up to 300 nm at room temperature of the target material. Such an effect can ensure the defect-freeness of nanometer coatings deposited from ion flows of hydrocarbon molecules. This conclusion agrees with the available experimental data on the enlightenment of  $\sim 0.1 \mu\text{m}$  thick carbon films by  $Ar^+$  ions with energy of  $\sim 1 \text{ keV}$  [4, 5].

## CONCLUSIONS

1. The acoustic effect of the single low-energy ion of hydrocarbon molecule falling on the diamond-like carbon coating was studied. The analysis showed that the generation of the stress wave occurs in the NTP i. e., in the nanometer region, where the energy and momentum transferred from the ion to the target particles are contained. The NTP model for the monatomic ion, which was developed earlier, was generalized to the case of hydrocarbon molecule ions when determining the space-time and energy parameters of the NTP.

2. The generation takes place as a result of the joint action of the following mechanisms: (a) thermoacoustic, associated with rapid heating of matter in the NTP; (b) deformation caused by the rapid introduction of the introduced volume of the ion into the volume of the

NTP; (c) impact, associated with the transfer of the ion momentum into the volume of the NTP.

In the linear acoustic approximation, the total amplitude of the stress pulse excited by the spherical NTP was found. The size and shape of the stress pulse generated by  $CH_4$ ,  $C_2H_2$ ,  $C_6H_6$  ions were investigated.

It was established that sound absorption affects the size and shape of the stress pulse at distances  $r > r_{at}$ . The extinction length  $r_{at}$  lies in the interval from 3 to 10 nm for the considered ions  $CH_4$ ,  $C_2H_2$ ,  $C_6H_6$  with energy from 100 eV to 1 keV. For a realistic quadratic dependence of the absorption coefficient on the frequency, the spatial attenuation of the stress amplitude is given by a power-law dependence  $\sigma_{at} \sim r^{-2}$  instead of the exponential that which is typical for harmonic oscillations. This relatively slower spatial decrease of the amplitude of the stress pulse expands the role of acoustic effects in the kinetic processes occurring in the material under ion radiation.

3. The spatial dependence of acoustic stresses generated by  $CH_4$ ,  $C_2H_2$ ,  $C_6H_6$  ions in DLC coating was studied in order to determine the influence on the processes of transport and destruction. Acceleration of the migration of interstitial defects takes place in the zone where the acoustic stress exceeds the limiting stress of defect activation  $\sigma_{is} = 0.3 \text{ GPa}$ . The maximum depth of acoustic activation is from 8 to 40 nm, increasing with energy and the number of carbon atoms in the incident ion. The activation zone has the shape of the ellipsoid of rotation, elongated in the direction  $\theta = 0$  due to the impact component in the amplitude of the stress pulse.

The possibility of the defects migration accelerating outside the activation zone by reducing the effective activation energy in the field of the acoustic wave excited by the NTP ion is discussed. Estimates show that hydrocarbon ions can significantly accelerate the diffusion of interstitial defects at distances up to 300 nm at room temperature in a diamond-like target. Such an effect can ensure defect-free nanometer coatings deposited from flows of hydrocarbon ions.

The possibility of destruction of the coating occurs when the acoustic pulse from the NTP reaches the boundary with a substrate with lower acoustic rigidity. The combination of direct and reflected pulses leads to the occurrence of significant tensile stresses near the boundary, which can lead to brittle fracture (to peeling) of the material. The maximum thickness of the coating, at which brittle failure at the boundary with the substrate is possible, lies in the range of 3 to 10 nm for ions  $CH_4$ ,  $C_2H_2$ ,  $C_6H_6$  with energy less than 1 keV, and the maximum thickness increases with increasing ion energy. This effect can be manifested when DLC are deposited on materials with relatively low rigidity, for example, on polymers.

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## РАДІАЦІЙНО-АКУСТИЧНІ ЕФЕКТИ ПРИ ОСАДЖЕННІ АЛМАЗОПОДІБНИХ ПОКРИТТІВ З ПОТОКУ ІОНІВ ВУГЛЕВОДНІВ ТА ЇХ ВПЛИВ НА КІНЕТИЧНІ ПРОЦЕСИ

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На основі моделі нелокального термопружного піка (НТП) іона, що була узагальнена на випадок іонів вуглеводневих молекул, досліджено акустичний ефект низькоенергетичного іона вуглеводневої молекули при плазмово-іонному осадженні алмазоподібного вуглецевого покриття. Генерація хвилі напруження має місце в результаті спільної дії механізмів, що пов'язані зі швидкою передачею енергії, імпульсу та додаткового об'єму в об'єм НТП. Досліджено величину, форму та просторову залежність імпульсу напруження, що генерується іонами  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$  з врахуванням поглинання. Обговорюється можливість прискорення дифузії міжвузольних дефектів, а також можливість крихкого руйнування покриття на межі з підкладкою під дією акустичних імпульсів від НТП іонів вуглеводнів, що осаджуються.