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THERMOMECHANICAL EFFECTS WHEN ATOMIC CLUSTER FALLS ONTO COATING SURFACE

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The model of nonlocal thermoelastic peak (NTP) of the ion is generalized for the case of multi-atomic cluster bombarding the surface of solid body. The condition for the occurrence of the subsurface NTP is formulated, and its geometric dimensions, volume, and thermal energy density are determined depending on energy and the number of atoms in the cluster. The analysis of processes of droplet sputtering of solids during irradiation with atomic clusters is carried out based on the thermodynamic approach. The condition for droplet sputtering in the case of bombardment of solid with clusters is formulated.

INTRODUCTION

Atomic clusters and their beams play an essential role in modern material synthesis technologies. Their use as a tool for processing solid objects and for depositing coatings is of paramount importance for the synthesis of nanostructured materials and the development of industrial processes based on nanotechnology.

Clusters can play both positive role, such as accelerating the growth of nanostructured films, and the negative one, such as deteriorating the quality of coatings. Clusters, like macroparticles, are often present as impurities at plasma-ion deposition of coatings, so it is necessary to study their effect on the quality of the deposited coating.

Scientific literature discusses the use of cluster beams for the production of nanostructured materials with the unique set of optical, magnetic, mechanical, and catalytic properties. Cluster beams can be used both for thin film deposition and substrate erosion, depending on the kinetic energy of the cluster [1].

Molecular dynamics methods have been frequently used to study the interaction of clusters of different energies with solid targets. For example, in [2] studied the formation of the crater caused by the energetic impact of the Cu_n cluster (n = 3, 43) with energy from 5 to 20 keV on the Cu surface. The influence of the target cohesion energy on the crater size was also studied, and the inverse-square dependence was obtained.

In [3], experiments on target surface smoothing using the high-energy cluster impact are reported. Thin films were obtained by cluster beam deposition. Experiments demonstrate that kinetic energy E of clusters is important parameter determining the mode of interaction of the cluster with the surface. These modes can vary from soft landing to implantation. Thus, reflective thin films were deposited without ionization and acceleration of cluster beams, while for the purposes of cluster impact lithography, ionized clusters must be accelerated to energy above 10 eV/atom to achieve surface erosion through the formation of nanometer craters.

Theoretical studies of the interaction of clusters bombarding solid surfaces have mainly been qualitative and descriptive in nature. Thus, the analysis of thermal and mechanical effects when the cluster falls on the surface of the coating depending on the energy E and the number of atoms n in the cluster is an important task.

Previously, we proposed and developed the model of the nonlocal thermoelastic peak (NTP) of the low-energy ion bombarding the surface of solid [4]. In this work, the NTP model is generalized for the case of the multi-atomic cluster. This allows to consider all the diversity of thermal, mechanical, and kinetic effects at the interaction of the incident cluster with the target material within the single approach. In particular, we determine NTP geometric dimensions, volume, and thermal energy density in the cluster depending on energy and number of atoms in the cluster. A qualitative and quantitative analysis of the processes of droplet sputtering of surface of solid during bombardment with atomic clusters was performed based on the thermodynamic approach. The study is based on the example of carbon cluster C_n with restricted number of atoms $n < 10$. The latter condition was chosen in order to limit the consideration of not too high overheats $T < 10^4$ K in the cluster's NTP, so as not to take into account the occurrence of shock waves near the NTP.

MODEL OF NTP OF ATOMIC CLUSTER

Let us determine the geometric dimensions of the cluster. Assuming that the cluster is spherical in shape, we obtain the following expression for the radius of the cluster:

$$R_c(n) = \left(\frac{3Mn}{4\pi\rho_c}\right)^{1/3}, \qquad (1)$$

where M is the mass of the atom; ρ_c is the cluster material density, and n is the number of atoms in the cluster.

Let us discuss possible scenarios of interaction between the cluster and the target depending on its energy E. If the condition is satisfied $E < nE_f$, where $E_f \sim 10$ eV is the surface energy of the target material, then the cluster atoms cannot penetrate the target material. In this case, the atoms of the cluster are located on the surface of the target, concentrating on it

in the form of undeformed or deformed clusters, or evaporating in gaseous form, depending on the ratio between the energy density in the cluster and the thermal characteristics of the cluster material. This deposition mode is commonly referred to as "soft landing" of the cluster.

Next, we'll look at the case of clusters with energy

$$E > nE_f, \qquad (2)$$

sufficient for its atoms to penetrate beneath the surface of the target.

When a cluster hits the target substance, it breaks down into atoms that fly off at the same speed and direction as the original cluster. The kinetic energy E_1 of an atom in cluster C_n is equal to

$$E_1 = E/n. \qquad (3)$$

Upon entering the target material, the atom is transformed into the ion, whose motion and interaction with the target particles can be studied using the SRIM software package [5]. As shown in previous works, the bombarding ion creates the overheated and overpressured nanometer-sized region, i.e., NTP.

Each atom of the disintegrated cluster forms its own non-local thermoelastic peak independently of other ions in the cluster. The NTP of the cluster is the superposition of the NTPs of its constituent ions (Fig. 1). As a result, the NTP of the cluster coincides with the NTP of the atom in the longitudinal length $L(E_1)$, but differs in the transverse dimension by the diameter of the cluster $2R_c$. Thus, the shape of the cluster's NTP at the initial moment of time is close to the segment of flattened spheroid adjacent to the target surface with the longitudinal semi-axis

$$R_l(0,E,n) = \frac{L(E/n)}{2} + R_T(0), \qquad (4)$$

and transverse half-axis

$$R_\perp(0,E,n) = \frac{L(E/n)}{2} + R_T(0) + R_c(n). \qquad (5)$$

Here $L(E)$ is the average projective range of the atomic ion with energy E, $R_T(t)$ is the radius of diffusion of thermal phonons over time t [4]. The center of the NTP of the cluster lies at distance $L(E/2)/2$ from the target surface. The thermal energy of the cluster is equal to $E\eta(E/n)$, where $\eta(E)$ is the relative fraction of phonon losses of the single-atom ion.

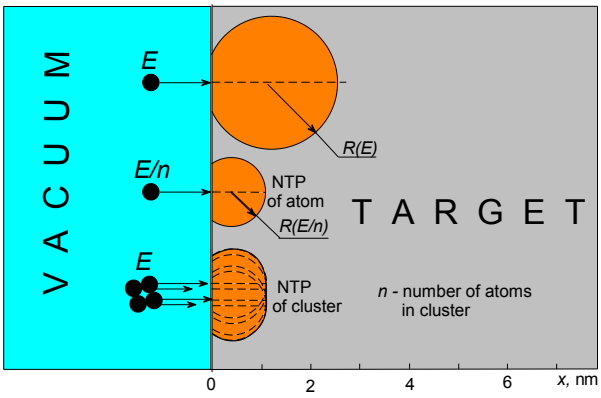

Fig. 1. Scheme of formation of the NTP of multi-atom cluster in the target

Given the axial symmetry, the volume of NTP of the cluster $V_c(E,n)$, with sufficient accuracy, is given by the expression

$$V_c(E,n) \simeq V(E/n)\left[\frac{R_1(E/n)+R_c(n)}{R_1(E/n)+R_c(1)}\right]^2, \qquad (6)$$

where

$$V(E) = \pi\left[\frac{2}{3}R(0,E)^3 + \frac{L(E)}{2}R_1(0,E)^2 - \frac{1}{3}\frac{L(E)^3}{8}\right] \qquad (7)$$

is the volume of the NTP of the atomic ion with energy E.

Fig. 1 shows that the NTP of a cluster is a nanometer region of matter that is smaller than the NTP of the atom that make up this cluster, with the same energy E. As a result, the energy density $\varepsilon(E,n)$ in the NTP cluster

$$\varepsilon(E,n) = \frac{E\eta(E/n)}{V_c(E/n)} \qquad (8)$$

is significantly higher than that of the NTP of the single-atom ion with the same energy, and it increases with the increase in the number of atoms n in the cluster (Fig. 2).

The results of the calculations suggest that the energy density in the NTP of the cluster can exceed both the melting point and the boiling point of the target material even at relatively small numbers of atoms n in the cluster. This requires taking into account nonlinear thermomechanical effects (sputtering, cratering, generation of powerful pulses).

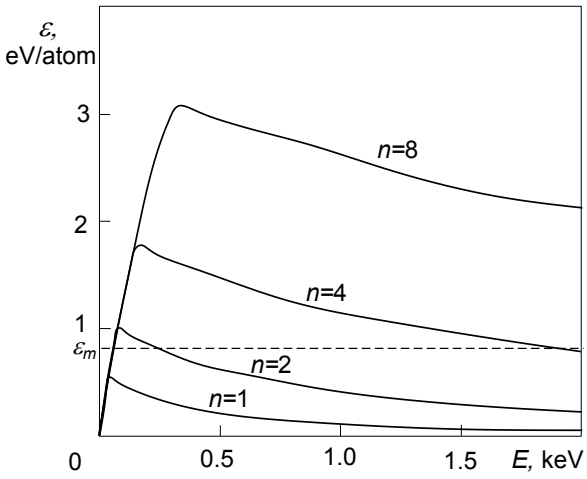

Fig. 2. Dependence of the density of thermal energy ε in the NTP of the carbon cluster C_n in carbon target on energy E at different numbers n of atoms in the cluster

DROPLET SPUTTERING AND CRATER FORMATION

It should be noted that linear cascade theory cannot explain the observed nonlinear effects, which indicate the manifestation of macroscopic forces in the volume of the NTP of the cluster [6]. Calculations using molecular dynamics methods are quite complex, especially with increasing numbers of atoms in the cluster. They do not give, which is very important, the analytical relationships between the initial parameters and the calculation results. Whereas the proposed model

makes it possible to perform the qualitative and quantitative analysis of the processes of sputtering of the solid body during irradiation with atomic clusters based on the simple thermodynamic approach.

Cluster implantation causes not only the spike in temperature but also instantaneous stress increase in the peak volume $\sigma_T(E)$, caused by thermal expansion. It is precisely this tension that can cause molten mass to be ejected from the NTP volume, resulting in droplet spraying and the formation of the crater on the target surface.

In general, in the presence of phase transitions with volume changes, the resulting thermoelastic stress σ_T can be written as [7, 8]:

$$\sigma_T(E,n) = \int_0^{\varepsilon(E,n)} \Gamma(\varepsilon) d\varepsilon , \qquad (9)$$

where $\Gamma(\varepsilon)$ is the generalized Grüneisen parameter, which relates the thermal energy density $\varepsilon(E,n)$ with the resulting thermoelastic stress $\sigma_T(E,n)$. When determining the peak thermoelastic pressure σ_T the change in material volume should be taken account of due to: 1) heating to the melting point; 2) melting; 3) heating the melt to a temperature corresponding to the energy density released in the NTP.

Further calculations were performed assuming that the Grüneisen parameter remains constant within the same aggregate state of matter. In this case, the general expression (9) becomes:

$$\begin{aligned}\sigma_{\mathrm{T}}(\mathrm{E},\mathrm{n}) = \\ = \Gamma_{\mathrm{s}}\varepsilon\,\Pi(\varepsilon;0,\varepsilon_{\mathrm{m1}}) + \left[\Gamma_{\mathrm{s}}\varepsilon_{\mathrm{m1}} + \Gamma_{\mathrm{m}}(\varepsilon-\varepsilon_{\mathrm{m1}})\right]\Pi(\varepsilon;\varepsilon_{\mathrm{m1}},\varepsilon_{\mathrm{m2}}) + \\ + \left[\Gamma_{\mathrm{s}}\varepsilon_{\mathrm{m1}} + \Gamma_{\mathrm{m}}(\varepsilon_{\mathrm{m2}}-\varepsilon_{\mathrm{m1}}) + \Gamma_{\mathrm{l}}(\varepsilon-\varepsilon_{\mathrm{m2}})\right]\Pi(\varepsilon;\varepsilon_{\mathrm{m2}},\varepsilon_{\mathrm{b1}}) + \\ + \left[\Gamma_{\mathrm{s}}\varepsilon_{\mathrm{m1}} + \Gamma_{\mathrm{m}}(\varepsilon_{\mathrm{m2}}-\varepsilon_{\mathrm{m1}}) + \Gamma_{\mathrm{l}}(\varepsilon_{\mathrm{b1}}-\varepsilon_{\mathrm{m2}})\right]\Pi(\varepsilon;\varepsilon_{\mathrm{b1}},\infty),\end{aligned} \qquad (10)$$

where the Π-shaped function is used

$$\Pi\ x;a,b\ = \begin{cases} 0, & x < a,\ x > b; \\ 1, & a \le x \le b, \quad b > a \end{cases}, \qquad (11)$$

Γ_s, Γ_l, and Γ_m are the values of the (effective) Grunaisen parameter of the target material in the solid and liquid states, as well as during its melting, respectively. Here $\Gamma_m = \zeta K/(q_m\rho)$, where ζ is the specific change in volume of the substance during melting., q_{m} is the specific heat of fusion, K and ρ are the effective bulk modulus and target material density, respectively. Energy density values ε_{m1}, ε_{m2}, and ε_{b1} correspond to the start of melting, the end of melting, and the start of boiling, respectively.

Expression (10) is obtained under the assumption that the thermal energy density is less than the threshold boiling energy density or slightly exceeds it. In this case, the contribution of vapor pressure to the energy of the elastic-stressed state can be neglected compared to the contribution of pressure arising from the integral thermal expansion of the solid and liquid phases, as well as from melting.

The detachment and ejection of molten material is only possible if the energy of the elastic-stressed state of the melt W_{el} exceeds energy W_s, that is necessary for the formation of the drop separation surface:

$$W_{el}(E,n) \ge W_s(E,n). \qquad (12)$$

The energy of the elastic-stressed state in NTP is estimated using the formula

$$W_{el}(E,n) = \frac{\left[\sigma_T(E,n)\right]^2}{2K} V_c(E,n). \qquad (13)$$

Considering that it is energetically preferable to eject the melt in the form of the single spherical drop, when the energy expense for the formation of the additional surface is minimal, we obtain the following expression for the energy required to form the drop surface and crater:

$$W_s(E,n) = \sqrt[3]{36\pi}\,\beta\delta\left(V_c(E,n)\right)^{2/3}. \qquad (14)$$

Here δ is the surface tension coefficient of the liquid target material, β is the coefficient equal to the ratio of the area of the additionally formed surface to the surface area of the spherical drop. The value of β lies in the range from 1 (drop ejection from a liquid or plastic ($\mu << K$) material without crater formation) to ~2 (drop ejection with the formation of the cavity which repeats the shape of the NTP).

When condition (12) is satisfied, the droplet sputtering coefficient S is determined by the number of atoms in the NTP:

$$S(E,n) = \rho V_c(E,n) \big/ \left(Am_p\right) \qquad (15)$$

and may exceed 10^3 already at E ~ 1 keV and n < 10 (the case of carbon clusters bombarding carbon coating).

The considered effect of droplet sputtering has no threshold in terms of the intensity of the irradiation flux and can occur even when bombarded by single clusters.

It should be noted that droplet sputtering of polycrystalline targets with single-atom ions is only possible for the heaviest metals (Au, U) bombarded with superheavy ions (Xe^+, Au^+, U^+). In the case of bombardment of material with clusters, the situation is more favorable for droplet sputtering. In this case, it is not difficult by varying the energy and number of atoms n in the cluster to select the size of the peak and the energy density in it so that the condition for droplet spraying (12) is fulfilled.

CONCLUSIONS

1. The model of the NTP of the monatomic ion is generalized for the case of the multi-atomic cluster. This allows us to calculate the size and thermodynamic characteristics of the NTP of the cluster and to consider the thermal, mechanical, and kinetic effects during the interaction of the incident cluster with the target material within the framework of the thermodynamic approach.

2. The conditions for droplet sputtering in the case of bombardment of solid material with clusters are formulated. It is shown that by changing the cluster energy and the number of atoms in the cluster, it is possible to ensure the energy density in the cluster's

NTP necessary to perform a particular task, for example, to deposit the coating or to erode the target surface.

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ТЕРМОМЕХАНІЧНІ ЕФЕКТИ ПРИ ПАДІННІ АТОМНОГО КЛАСТЕРА НА ПОВЕРХНЮ ПОКРИТТЯ

О.І. Калініченко, В.Є. Стрельницький

Модель нелокального термопружного піка (НТП) іона узагальнена для бомбардування поверхні твердого тіла багатоатомним кластером. Сформульовано умову виникнення підповерхневого НТП, а також визначено його геометричні розміри, об'єм та густину теплової енергії залежно від енергії та кількості атомів у кластері. Аналіз процесів крапельного розпилення твердих тіл під час опромінення атомними кластерами проведено на основі термодинамічного підходу. Сформульовано умову крапельного розпилення у випадку бомбардування твердого тіла кластерами.