

Model of cratering by single ions in heavy metals

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Abstract. In the model of the nonlocal thermoelastic peak (NTP) of ion the theoretical investigation of nanocratering in targets of heavy metals at bombardment by ions Xe^+ with energy from 25 eV up to 30 keV is carried out. Simulation using program package SRIM2008 has shown possibility of formation of subsurface singly connected cascade with energy capacity sufficient for arising of the droplet sputtering for Ag targets. Calculations have shown opportunity of cratering on surface of Ag flat targets with yield strength <0.1 GPa at bombardment by Xe^+ ions with energy $E > 10$ keV. Craters are not formed on Pt flat targets. Possible influence of nanoscale roughness on cratering by single ions is discussed.

1. Introduction

Interest in formation of defects on the surface of structural materials at ion bombardment is related to the development of nanotechnology, demanding for its implementation tools that are able to create and/or modify nanoscale objects. To use fast heavy ions bombarding solid surface as such a tool, it is necessary to investigate related phenomena and, above all, the processes of droplet/cluster sputtering and nanocratering by single ions [1].

The sputtering of metal targets by heavy ions may exhibit as a macroscopic effect, to obey the laws of thermodynamics and continuum mechanics. High temperatures and pressures arising in cascades of excited atoms after thermalization can lead to melting, evaporation and subsequent ejection of target material in the form of vapor, polyatomic clusters or droplets, which provides sputtering factors $S \gg 10$ [2]. The surface is subjected to increased erosion with the formation of nanometer-sized craters. [1-3].

The evaporation model [4,5], the shock wave model [6,7], the brittle fracture model [8,9] were offered for description of nonlinear sputtering processes. In last years, except for analytical research methods, methods of molecular dynamics are widely used allowing to trace the spatial - temporal evolution of the atom ensemble near the ion path during the transition from nonequilibrium state to state, obeying thermodynamic laws.

The model of cratering associated with arising of subsurface overheated nanoscale regions containing the molten material flowing away under action of thermoelastic stress was proposed in [10]. However, the above model can not explain the experimentally observed cases of nanoparticle ejection at the ion bombardment of heavy metals (gold) [3]. In addition, the analytical methods used in [1-10], do not have sufficient universality and do not give complete understanding of cratering and cluster sputtering. Also, the use of the molecular dynamics for cratering analysis is associated with

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very time-consuming calculation. It is therefore of interest to develop a simple physical model for analysis the process of cratering and for determination main parameters that influence on cratering.

In [11, 12] the model of the droplet sputtering based on the concept of the nonlocal thermoelastic peak (NTP) of the ion has been proposed. In this model, the minimal permissible energy $E_{\min} \sim 10$ eV of the ion is determined by opportunity of thermodynamic description of physical processes in NTP. The maximal permissible energy E_{NTP} of the ion is determined by a qualitative structural change of the cascade, resulting in formation of several weakly connected overheated regions determined by parameters of subcascades forming them. The value E_{NTP} depends on ion species and target material. To determine E_{NTP} the detailed statistical analysis of overheated region was required which has permitted estimating probability of acceptable parameters of the region [13].

In this paper, the cratering on surface of Ag and Pt targets with nanoparticle ejection at bombardment by single Xe^+ ions with energy from 25 eV to 30 keV is investigated in the NTP model. The range of ion energies causing droplet sputtering and cratering is determined. The influence of target surface roughness on cratering is discussed.

2. Mathematical model

Cratering is related to the transition of the target material in a liquid state in the NTP volume and ejection of molten mass. At $E \leq E_{\text{NTP}}$ the simulation results obtained by the well-known program package SRIM2008 have shown that cratering of a heavy metal can be related to arising of the ion NTP [11,12]. The resulting peak can be approximated by a spherical segment adjacent to the target surface and containing the phonon loss of ion energy E_{ph} . Initial temperature and phase state of the material in the NTP are determined by the average density of thermal energy:

$$\varepsilon(E, d) = \frac{E_{ph}}{V(E, d)}. \quad (1)$$

Here $V(E, d)$ is the NTP volume, depending on ion energy E and effective size d of target crystallite.

Melt ejection from the NTP is due to elastic unloading of stressed state arising into its volume. Stress in NTP is mainly determined by the sum of the thermal stress caused by thermal expansion of target material in the NTP volume, and some intrinsic stresses having other nature. Provided occurrence of phase transition the thermoelastic stresses arising in the NTP can be written as:

$$\sigma_T(E, d) = \int_0^{\varepsilon(E, d)} \Gamma(\varepsilon) d\varepsilon, \quad (2)$$

where $\Gamma(E)$ is the effective Gruneisen parameter connecting $\sigma_T(E, d)$ and $\varepsilon(E, d)$.

The Gruneisen parameter of the target material varies significantly with density of thermal energy in the NTP. At σ_T calculation the following components of heat expansion were taken into account:

1) material expansion at its heating to melting point; 2) expansion at melting; 3) melt expansion at heating up to temperature corresponding to energy density in the NTP. Further calculations were performed assuming that Gruneisen parameters for these processes are constants. This approximation is acceptable for materials under consideration. In σ_T calculation the values of effective Gruneisen parameter of the target material is equal to Γ_s and Γ_l in the solid and liquid state, respectively, and Γ_m in transient state “solid $\rightarrow$ liquid”. Here $\Gamma_m = \zeta K / (q_m \rho)$, where ζ is the specific volume change at target material melting, q_m is the specific heat of melting, K and ρ are the effective bulk modulus and density of target material, respectively. Values ε_{m1} , ε_{m2} and ε_{b1} are the energy densities of the melting beginning, the melting end and the boil beginning, respectively. In this case,

the general expression (2) transforms to:

$$\begin{aligned}\sigma_T(E, d) = & \Gamma_s \varepsilon \Pi(\varepsilon; 0, \varepsilon_{m1}) + [\Gamma_s \varepsilon_{m1} + \Gamma_m (\varepsilon - \varepsilon_{m1})] \Pi(\varepsilon; \varepsilon_{m1}, \varepsilon_{m2}) \\ & + [\Gamma_s \varepsilon_{m1} + \Gamma_m (\varepsilon_{m2} - \varepsilon_{m1}) + \Gamma_l (\varepsilon - \varepsilon_{m2})] \Pi(\varepsilon; \varepsilon_{m2}, \varepsilon_{b1}) \\ & + [\Gamma_s \varepsilon_{m1} + \Gamma_m (\varepsilon_{m2} - \varepsilon_{m1}) + \Gamma_l (\varepsilon_{b1} - \varepsilon_{m2})] \Pi(\varepsilon; \varepsilon_{b1}, \infty),\end{aligned}\quad (3)$$

where

$$\Pi(x; a, b) = \begin{cases} 0, & x \in (-\infty, a) \cup [b, \infty); \\ 1, & x \in [a, b), \quad (b > a). \end{cases}$$

Cratering with ejection of molten material is possible if the elastic energy W_{el} of the melt spent on drop ejection exceeds energy W_s spent on formation of drop and crater surfaces. Therefore, the criterion of droplet sputtering and cratering has the form:

$$W_{el} \geq W_s. \quad (4)$$

Critical parameters of the NTP corresponding to droplet sputtering initiation (the critical volume V_c of the NTP and the critical number $Y_c = V_c \rho / M$ of atoms in the NTP, where M is the atom mass of target material) are determined from equation $W_{el} = W_s$.

The elastic energy W_{el} of the melt spent on droplet ejection was estimated by formula:

$$W_{el}(E, d) = \lambda \frac{[\sigma_T(E, d) + \sigma_i]^2}{2K} V(E, d). \quad (5)$$

The parameter λ determines the relative fraction of the elastic energy spent on drop formation and its detachment from target surface. Precise λ calculation is possible by solving equations of continuum mechanics, but it lies beyond the scope of this paper. Therefore, λ parameter is the free model parameter, which depends on surface geometry and the NTP position. Let's estimate λ value basing on the following considerations.

Assuming one-dimensional approximation we conclude that only half-wave propagating to surface involves in drop formation and detachment. Therefore, the value $\lambda = 0.5$ may be taken for fraction of the elastic energy of the NTP spent on drop formation in the case of flat target surface. However, the estimate λ should change in case of a non-planar surface if its radius of curvature is comparable to the NTP radius R_{NTP} . In case of a convex surface, fraction of elastic energy in the wave interacting with the surface increases ($\lambda > 0.5$). Analogously, in case of a concave surface, fraction of elastic energy going on drop formation and detachment decreases ($\lambda < 0.5$). In case of rough surface the droplet sputtering process becomes the probabilistic one since the fraction of the elastic energy spent on drop formation varies depending on surface geometry near ion incidence point.

Analysis showed that molten material ejection in the form of single spherical drop is the least energy-consuming. It allows estimating the minimum energy needed for surface formation of drop and crater, using the formula:

$$W_s(E, d) = \sqrt[3]{36\pi} \beta \delta (V(E, d))^{2/3}, \quad (6)$$

where δ is the surface tension of the target material in liquid state, β is the growth factor which is equal to the ratio of additionally formed square to the square of the spherical drop. In the case of the flat surface the value of β lays in range from 1 (drop ejection from liquid or plastic material without

cratering, ($\mu \ll K$ where μ is the average shear modulus of target material) up to ~ 2 (drop ejection from a rigid material with formation of the cavity replicating the NTP shape). For arbitrary combination of "ion-target" the value of β is determined by model stated in [14]. According to this model the crater is represents as an axially-symmetric hollow which surface is formed by rotation along vertical axis of two conjugate arcs with radii $R_1 = \delta / \sigma_Y$ and $R_2 = 2R_1 + (R_{NTP} - 2R_1) \cdot \Theta(R_{NTP} - 2R_1)$. Here σ_Y is the yield strength of the target material, $\Theta(x)$ is the unit Heaviside function. Factor β , the shape, diameter and the depth of the crater are determined on the assumption that the crater forms in the complex process of drop ejection by the action of two opposing forces - surface tension and elasticity/stiffness of the target material. Details of determining the value of β for flat target surface are given in [14]. In case of a rough surface the value β varies depending on the surface curvature at the point of ion incidence.

3. Results and discussion

The simulation performed using the program package SRIM2008, has allowed to determine the shape and geometric parameters of NTPs generated in the heavy metal targets (Ag, Pt) by ions Xe^+ with energy $E \leq E_{NTP}$ bombarding target surface, as well as the energy phonon loss E_{ph} of ions [12].

Value E_{NTP} increases with increase of the crystallite size d . The maximum admissible energies E_{NTP} for polycrystalline, nanocrystalline ($d = 2$ nm) and amorphous target of Ag (Pt) have the following values: 20 (25) keV, 16 (21) keV and 13 (17) keV, respectively. The obtained values of NTP parameters have allowed to estimate thermal energy density in the resulting NTP, to check fulfillment of the criterion of droplet sputtering and cratering (4), to determine minimal E_1 and maximal E_2 values of ion energy ensuring droplet sputtering, to calculate the yield of droplet sputtering and crater dimensions.

Figure 1 shows the functions of number of atoms in the NTP $Y(E, d)$ and the critical number of atoms $Y_c(E)$ satisfying starting condition $W_{el} = W_s$ of droplet ejection from NTP of Xe^+ ion for targets of crystalline Ag (figure 1(a)) and amorphous Pt (figure 1(b)). Calculation of functions $Y_c(E)$ for bulk Pt and Ag targets was performed at $\lambda = 0.5$ and β values calculated by expressions from [14].

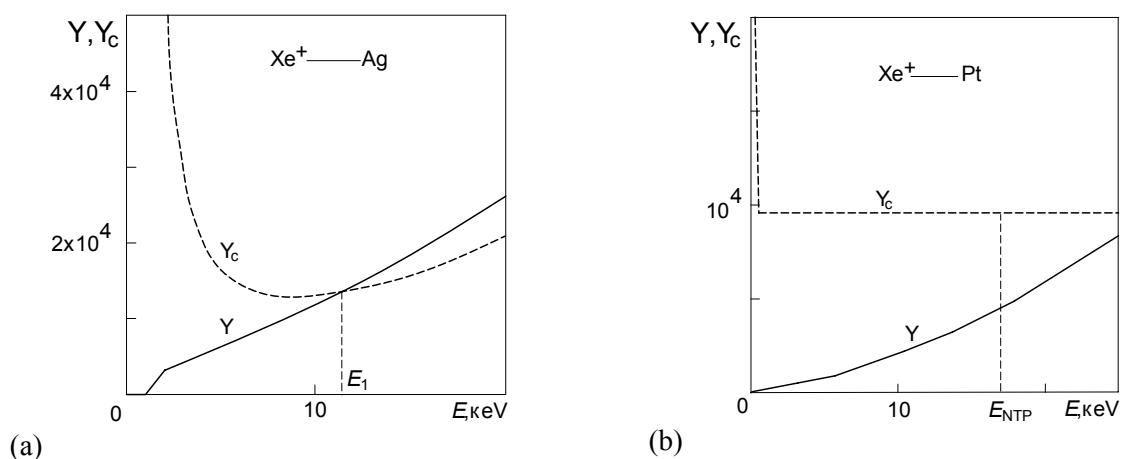


Figure 1. The number Y of atoms in the NTP of Xe^+ ions and critical number Y_c of atoms, corresponding to condition (4) in silver polycrystalline target (a), and platinum amorphous target (b) with flat surfaces ($\lambda = 0.5$). The threshold energies for Ag target are equal to: $E_1 \simeq 11.6$ keV; $E_2 = E_{NTP} = 20$ keV. For platinum amorphous target the criterion (4) is not satisfied at $E < E_{NTP}$.

As one can see from figure 1, for polycrystalline ($\beta = 1.016$) target of Ag the droplet sputtering is possible at $E \geq E_1 \approx 11.6$ keV. The largest value of sputtering yield is determined by the value $Y(E_2, d)$ where $E_2 \sim E_{NTP} \approx 20$ keV. For Pt targets with flat surface the droplet sputtering criterion (4) is not carried out even in the most favorable case of amorphous ($\beta = 1.012$) target. However, the last conclusion may change at ion bombardment of a rough surface. Thus, at ion incidence on convex section of a rough surface, the curvature radius of which is comparable to R_{NTP} , the fraction of elastic energy spent on drop detachment increases ($\lambda > 0.5$) in comparison with a case of a flat surface, and droplet sputtering may be possible [12]. At the same time, the fraction of elastic energy spent on drop detachment decreases at ion bombardment of a concave section of surface, and droplet sputtering is impossible. One should note, that such selective action of ion bombardment on convex sections of a rough surface should lead to surface smoothing, i.e. it appears as original «ionic polishing».

Figure 2 shows dependences of energy density ε in Xe^+ ion NTP on ion energy for amorphous (the curve 1), nanocrystalline (the curve 2, $d = 2$ nm) and polycrystalline (the curve 3) silver targets with flat surface, $\lambda = 0.5$ (see figure 2(a)), and platinum targets with a rough surface, $\lambda = 0.7$ (see figure 2(b)).

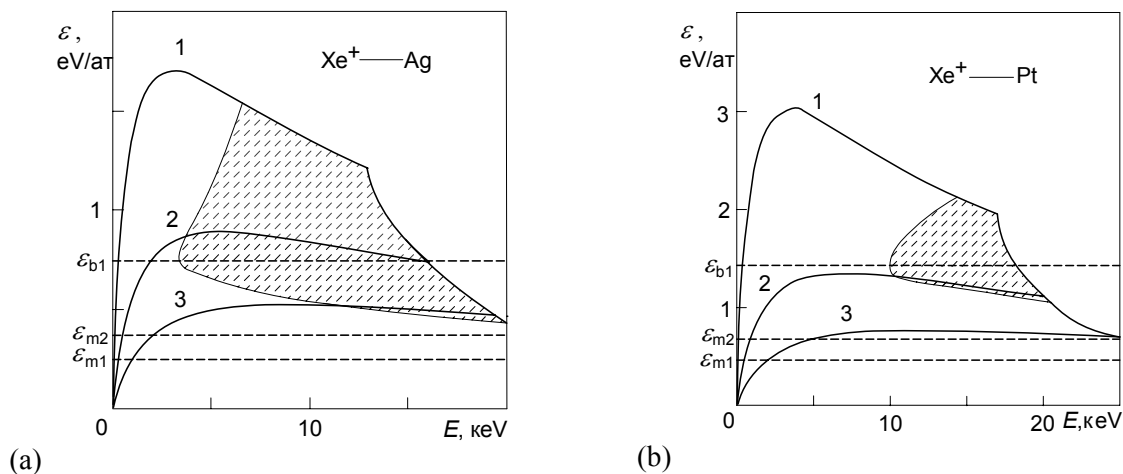


Figure 2. Thermal energy density ε in Xe^+ ion NTP depending on ion energy in amorphous (curve 1), nanocrystalline $d = 2$ nm (curve 2), polycrystalline (curve 3) targets: (a) silver target with flat surface ($\lambda = 0.5$); (b) platinum target with rough surface ($\lambda = 0.7$). Dashed lines correspond to the energy density of melting start point (ε_{m1}), melting end point (ε_{m2}), and boiling start point (ε_{b1}). Droplet sputtering and cratering are possible within hatched areas.

As one can see from figure 2, thermal energy density in the NTP $\varepsilon(E)$ decreases with d increasing, its maximum shifts to higher energies. For all Ag targets there is ion energy range, in which $\varepsilon(E)$ exceeds the value ε_{m2} to be necessary for the material full melting in NTP. Criterion of droplet sputtering (4) is met in hatched areas. The use of the equations derived in [14] enables to determine the size and the shape of forming craters which considerably depend on surface tension coefficient δ and yield strength σ_Y of target material. As a result of calculation, we obtain the following values of diameter D and depth H of crater. For Ag polycrystalline target ($\lambda = 0.5$, $\delta = 0.93$ J/m², $\sigma_Y = 0.02$ GPa) we have $D = 36$ nm, $H = 1.2$ nm. For Pt nanocrystalline ($d = 2$ nm) target ($\lambda = 0.7$, $\delta = 1.74$ J/m², $\sigma_Y = 0.07$ GPa) we obtain $D = 24$ nm, $H = 1$ nm.

Analogous calculations [11, 12] have shown opportunity of droplet sputtering and cratering at

bombardment of Au and U targets by single Xe^+ , Au^+ , U^+ ions of low energies.

The results can be used in nanotechnology for smoothing of heavy metal surfaces by heavy low-energy ions.

Conclusions

1. A simple model of cratering as a result of heavy metal droplet sputtering at low-energy ion bombardment is suggested. The criterion of droplet sputtering and cratering is obtained with a glance of surface irregularities.

2. It is shown that the criterion of droplet sputtering and cratering by Xe^+ ions is met for amorphous, nanocrystalline and polycrystalline Ag targets with yield strength $\sigma_Y < 0.1$ GPa, with flat surfaces or in the presence of nanoscale irregularities.

3. It is shown that the effect of the droplet sputtering is absent for platinum targets with flat surfaces. The cratering is possible in amorphous and nanocrystalline platinum targets with nanoscale irregularities.

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