MODELING OF METALS MELTING AND CRYSTALLIZATION UNDER THE ACTION OF ULTRASHORT LASER PULSE

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Summary. This paper is devoted to the numerical simulation of metals melting under the action of ultrashort laser pulse and crystallization of the melt. With the rapid laser heating, the kinetics of phase transitions differs significantly from that in the case of slow heating.

1 INTRODUCTION

The investigation of laser-induced phase transitions (for example melting and crystallization) in various materials has returned the scientific interest in recent years. It was found that the phase transitions by ultrashort laser pulse differ from that in the case of slow heating[1-4]. Processing of materials by ultrashort laser pulses opens up new possibilities for modifying properties. Under the action of ultrashort laser pulse high heating and cooling rates are achieved, which leads to overheating above the melting temperature[5] when heating and possible amorphization during cooling.

Many aspects of the interaction of laser radiation with matter requires analysis of the thermal effects with nonequilibrium thermodynamics.

2 MELTING

The modified vacancy model of melting, developed in the early 1990s[6], relies on that the structure of the melt can be considered as a crystal deformed by the vacancies. The model allows to use well developed methods of thermodynamic analysis of the crystals to analyze the properties of melt.

The fundamental postulates of the melting theory, based on an analysis of changes in the concentration of the vacancies, originally proposed by Frenkel[7,8], can be summarized as follows:

- the phenomenon of melting is associated with the sharp increase in the number of vacancies in the crystal during heating. To explain this, one must take into account the decrease in vacancy formation energy with increasing of its concentration;
- the latent heat of melting is associated with the increase in the vacancy concentration;
- the vacancies concentration increases due to their diffusion from the surface, so melting occurs from the surface.

According to this model the violation of long-range order during the melting occurs due to deformation of the crystal lattice by the vacancies (Fig. 1).
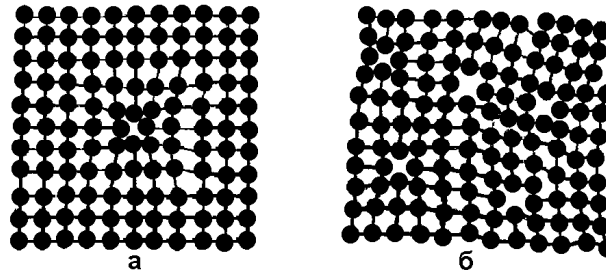
Figure 1. The scheme of the crystalline lattice distortion by the vacancies

At high concentrations of vacancies, when deformed regions overlap, the crystal lattice is deformed completely. In such crystal, deformed by the vacancies, the atoms surrounding a randomly chosen atom, located mainly around the same distance as in the crystal, but with some variation, i.e. short-range order is preserved. This scatter has the random character and increases rapidly with increasing of the distance from the selected atom.

The kinetics of the thermal motion in amorphous solids and liquids do not differ, that was predicted by Frenkel.

The state of the crystal, deformed by the vacancies, is described by its free energy F[4]:

$$F = En - \alpha n[1 - \exp(-nv)] - k_B T n \ln\left(\frac{Ne}{n}\right) \tag{1}$$

E – the energy of vacancy formation, n – the vacancy concentration, α – the vacancy interaction energy, v – the volume of vacancies interaction, N – the concentration of the lattice sites, T – the temperature, k_B – Boltzmann constant, e – the base of natural logarithm.

It is assumed that an increase vacancy concentration n increases the probability of their location at a distance from each other, that will reduce the total energy of vacancy formation. The formation energy of the pair of the interacting vacancies is less than that of two non interacting vacancies. So, the energy of the vacancies formation with consideration of its interaction is $F_v = En - \alpha n_n$ (n_n – is the amount of the vacancies in the interacting pairs), n_n can be defined as the product of the total number of vacancies n and the probability of that there is at least one vacancy in the volume v, which is defined by the radius of vacancies interaction, i.e. Poisson's law $n_n = n[1-\exp(-nv)]$.

To calculate the dynamics of vacancy concentration we solve the equation of vacancies diffusion:

$$\mu \frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(D\mu \frac{\partial n}{\partial x}\right) \tag{2}$$

$\mu = \partial F/\partial n$ – the vacancy chemical potential, D – diffusion coefficient. The boundary conditions are the conditions for the thermal flow on the boundary: $q = D\varepsilon(n)\partial n(0)/\partial x$ ($\varepsilon(n)$ – the energy of formation and dilution of the vacancy).

The temperature's dynamics was calculated based on two-temperature model using the finite difference method[9,10]. The temperature during the picosecond laser pulse heating can be found by solving the system of equations:

$$c_e \frac{\partial T_e}{\partial t} - \frac{\partial}{\partial x}\left(\lambda_{Te} \frac{\partial T_e}{\partial x}\right) = \frac{q}{c_e} - k_{ei}\left(T_e - T_i\right) \tag{3}$$

$$c_i \frac{\partial T_i}{\partial t} - \frac{\partial}{\partial x}\left(\lambda_{Ti} \frac{\partial T_i}{\partial x}\right) = k_{ei}\left(T_e - T_i\right) + \frac{q_V}{c_i}$$

with initial and boundary conditions $\lambda_{Te}\dfrac{\partial T_e(0,t)}{\partial x} = \lambda_{Ti}\dfrac{\partial T_i(0,t)}{\partial x} = 0$, $\left.T_e\right|_{t=0} = \left.T_i\right|_{t=0} = T_n$, λ_e=2.37 W/(cm·K) – electron heat conductivity, λ_i=1 – lattice heat conductivity, c_e=0.04035 J/(cm^3·К) – electron heat capacity, c_i=2.43 J/(cm^3·К) – lattice heat capacity, k_{ei} – the electron-ion energy transfer coefficient, $q = \alpha_1(1-R)q_0 \exp(-\alpha_1 x)$ – the absorbed power density of laser beam, α_1 – absorption coefficient, q_0 – the peak power density of the absorbed laser beam, τ= 3·10^{-12}s – laser pulse duration, T_m=1235 К - the temperature of melting, T_n=473 К – the initial temperature, α=0.5756 eV – the energy of vacancies interaction, e=1.1 eV - the energy of vacancy formation, n_0=5.856·10^{22} cm^{-3}– the concentration of atoms, e_d=0.66 eV – the energy of the vacancy diffusion, v=1.421·10^{-20} sm^3 – volume of vacancy.

2.1 Results

The results of the numerical solution of the problem for the heating of silver by the laser pulse of microsecond duration are in good agreement[4] with experimental results[11].

Figures 2.a) and 2.b) shows the lattice temperature, and the melting depth for ultrashort pulses of different shapes. It is clear that the pulse shape significantly affects the temperature and rate of melting. Due to the short duration of the pulse time the melting depth is small during the pulse. A significant overheating above the melting point due to the fact that for the generation of vacancies at the surface and their diffusion takes time.
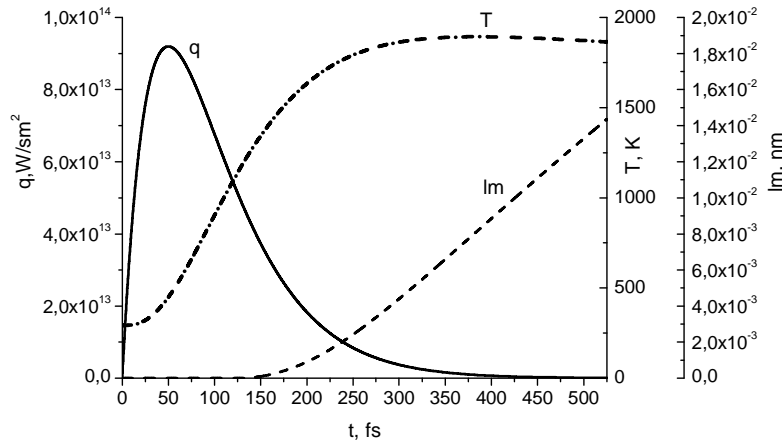
a)
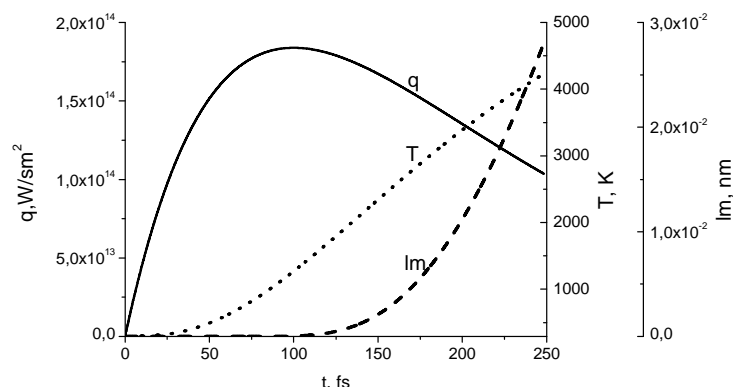
b)

Figure 2. Temporal behavior of the melting depth and the temperature on the surface of silver irradiated by femtosecond laser pulse: a) $q=q_m exp(-(t-t_m)^2/t_{m1}^2)/t_m$, $t_m=100$ fs, $t_{m1}=50$ fs $q_m=5\cdot10^{14}$W/sm², b) $q=q_m texp(-t/t_m)/t_m$, $t_m=100$ fs, $q_m=5\cdot10^{14}$W/sm²

Fig. 3 shows the changes in the concentration of the vacancies n_v and its equilibrium concentration n_v^e during the action of ultrashort laser pulse.
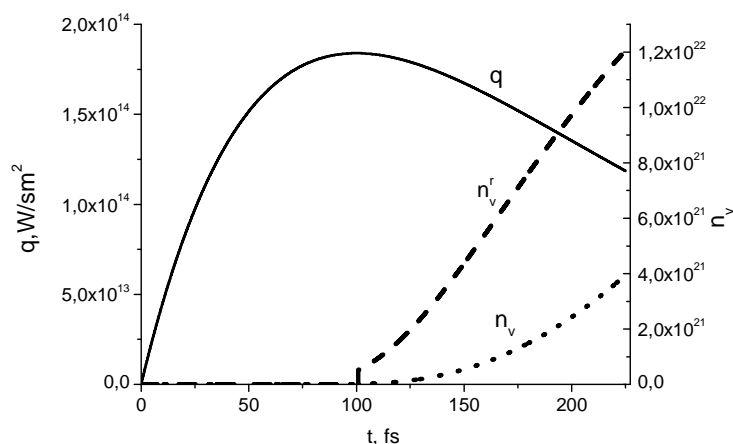

Figure 3. Temporal evolution of the vacancy concentration, $q=q_m texp(-t/t_m)/t_m$, $t_m=100$ fs, $q_m=5\cdot10^{14}$W/sm²

The heating rate during the laser excitation is defined by the extremely large rate of the energy supply. Under the picosecond laser pulses action the rate of the energy transfer from the electrons, heated to the temperatures of some tens of Kelvin, to the lattice can attain ~10^{14} W/cm³. The process of melting should differ from the well known melting in the quasi-stationary case.

The melting as a process associated with the restructuring of the structure has some typical times. The first is the restructuring time, the second is the time of the melting front movement which depends on the temperature.

It is possible to explain some interesting features of ultrafast melting using the vacancy model of melting. The constancy of the surface temperature during the laser melting and the presence of the energy flow to the melting front without the temperature gradient in the liquid layer are possible before the fluence attains the critical value. The critical value is determined by the vacancy generation rate and by the vacancy diffusion flow which, which determined by the vacancy concentration gradient on the melting front. The melting depth is determined by the laser fluence and the properties of the material.

3 CRYSTALLIZATION

The analysis of the crystallization process is based on modeling the formation of the crystalline phase nuclei and their growth. According to the model of "liquid - crystal deformed by vacancies," the crystallization of the melt corresponds to the transition of matter at temperature $T = T_m$ from the amorphous state, corresponding to the second minimum of the free energy with vacancy concentration n_2, into the crystalline state, corresponding to the first minimum with the concentration of vacancies n_1. The crystalline phase nucleus (assuming that the nucleus in amorphous solids and liquids have a spherical shape) originates when the concentration of vacancies fluctuationally decreases in a certain volume V of the amorphous phase, the free energy of this volume decreases[3]:

$$\Delta F = \Delta F_{ca}V + \gamma S = (F_c - F_a)V + 4\pi\gamma\left(\frac{3bv_a}{4\pi}\right)^{2/3},$$

(4)

V – volume of the nucleus of the crystalline phase, S – surface area of the crystalline phase nucleus, γ – the surface tension between the crystalline and amorphous phases (γ_{Ag}^{melt}=0,000002 J/sm^2), F_c – the potential barrier of the first minimum (see Fig. 4), F_a – the potential barrier of the second minimum, b – the number of atoms in the nucleus, v_a=V/b, v_a – the volume of the atom, radius of the nucleus r=$(3bv_a/(4\pi))^{1/3}$.
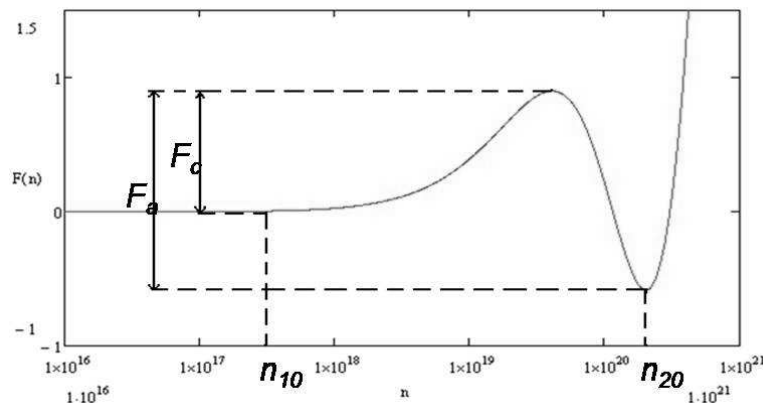

Figure 4. Scheme of the free energy potential barriers of the crystal at temperatures below the melting temperature.

If ΔF reaches $F_m V$, restructuring can occur, and the nuclei of a new phase can appear. So the probability of the formation of the crystalline phase nucleus in the amorphous phase can be defined as[3]:

$$p_{обр} = N_a \exp\left(\frac{-F_a V}{k_B T}\right),$$ (5)

(N_a - the concentration of atoms, k - Boltzmann constant).

The probability of the fluctuation extinction of the crystalline phase nucleus in this case can be defined as[3]:

$$p_{исч} = N_a \exp\left(-\frac{F_c V - \gamma S}{k_B T}\right).$$ (6)

Critical size of the nuclei is determined based on (4) assuming $\Delta F = 0$:

$$r_{кр} = -\frac{3\gamma}{F_c - F_a}.$$ (7)

The size distribution of nuclei, based on the probability of their formation and disappearance[3] can be written as:

$$m(r) = N_a \exp\left(-\frac{(F_c - F_a)V - \gamma S}{k_B T}\right).$$ (8)

The atoms adhere to the nucleus at a rate $\sim N_a^l S \exp\left(-\frac{F_a V + \gamma S}{N_a^l k_B T V}\right)$ (N_a^l- concentration of atoms in the amorphous phase). Rate of molecules escape from the nucleus can be defined as $\sim N_a^c S \exp\left(-\frac{F_c V - \gamma S}{N_a^c k_B T V}\right)$ (N_a^c-- the concentration of molecules in the crystalline phase). The growth rate of nucleus[3]:

$$V_s = \left(N_a^l S \exp\left(-\frac{F_a V + \gamma S}{N_a^l k_B T V}\right) - N_a^c S \exp\left(-\frac{F_c V - \gamma S}{N_a^c k_B T V}\right)\right)/\tau.$$ (9)

τ - the time order of the inverse Debye frequency

The nucleus can grow only when $F_c > F_a$, i.e. the formation of stable crystalline phase in the melt is possible only starting from temperature T_s, where $F_c = F_a$. Up to this temperature, the liquid can be supercooled at low cooling rates.

At temperatures $T < T_s$ nucleus with volume $V > V^*$ begin to grow - crystallization starts. Vacancies, released during the crystallization, transfer to a liquid, so the total free energy of the body increases. The decrease of free energy occurs either by reducing the amount of the crystalline phase, either by reducing the vacancies concentration in the melt. So for the crystallization it is necessary the rate of vacancy transition from the crystalline phase into the liquid phase during the crystallization not to exceed the rate of vacancies "death". The increase of crystalline phase volume is proportional to the rate of vacancies "death". The rate of vacancies "death" can be estimated by[3]:

$$V_d \sim N_a^{2/3} \exp\left(-\frac{E_v + E_d}{k_B T}\right)\frac{S_{st}}{\tau} \tag{10}$$

E_d - activation energy of vacancies diffusion, S_{st}- the area of the surface vacancies runoff, E_v - energy of vacancy formation.

3.1 Results

   Here we present the results for computer simulation of crystallization due to generation of the crystalline nuclei and their growth during cooling with different constant rates. The results (Fig. 5) show that amount of crystalline phase depends on the cooling rate.
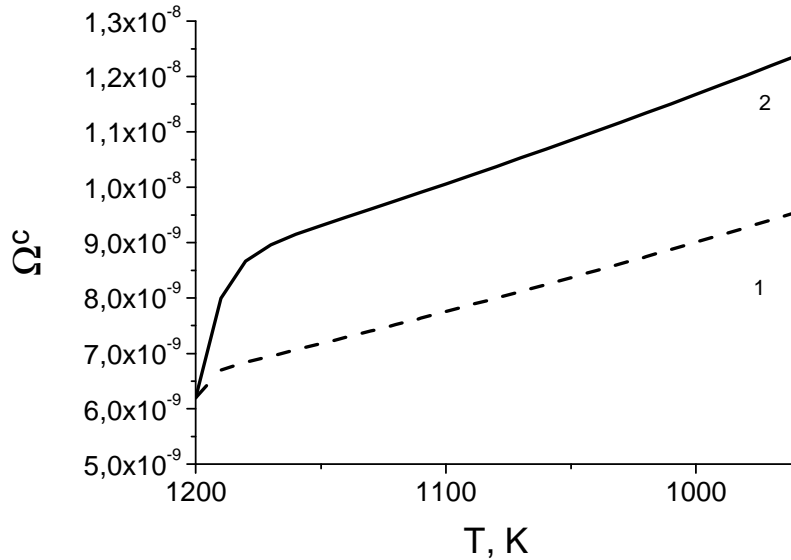

Figure 5. Temporal evolution of volumetric share of crystalline phase Ω_c for different rates of cooling: $1 - dT/dt = 10^{11}$K/s, $2 - dT/dt = 5 \cdot 10^{10}$K/s,

   If the melt during the heating does not have time to come to thermodynamic equilibrium due to high heating rates (such as laser heating), nucleation of the crystalline phase begins with the higher temperature and the probability of nucleus formation increases, the rate of nucleus growth increases, and therefore the critical cooling rate increases compared with the critical rate of hardening of the thermodynamic equilibrium of the melt.

   From the conditions of the phase transition it follows that the phase transition temperature may vary during heating and cooling. If the rate of temperature change is such that the phase does not have time to come into a stable thermodynamic equilibrium state, then, depending on the rate of temperature change, the temperature of the structural phase transition will change.

4   CONCLUSION

   The paper is devoted to the numerical study of the melting process of the metals exposed to ultrashort laser pulses and its subsequent crystallization. The vacancy model of melting

allows to explain some features of laser melting including overheating[4,6]. The estimates of the parameters of the process of crystallization of the melt showed the possibility of amorphization after the melting by ultrashort laser pulse.

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