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Abstract

The paper describes the model of nanostructure formation on solid surface by nanosecond laser pulses melting the material. Stefan problem with corresponding boundary conditions is solved in combination with nucleation theory. It is found that typical size of surface nanostructure formed depends on energy and duration of laser pulse. For comparison of theoretic and experimental results various industry material (germanium, titanium, zirconia dioxide) pieces irradiated by ArF-laser are shown.

Introduction

In recent years nanostructures in solids have been attracting ever greater attention from researchers because they are promising objects for applications in various fields of science and engineering. Both ordered and disordered ensembles of nanoparticles are new artificially created materials whose widespread use is associated with their unique properties.

In this work we study the mechanism responsible for the formation of nanostructures at the surface of solids under the action of nanosecond laser pulses. Two parts can be mentioned by the solution of this task. In the first part, the process of material melting occurring as a result of laser impact is being considered and the Stefan problem with the corresponding boundary conditions is being solved. In the second part, the process of a melted layer cooling at the expense of heatsink into the solid phase bulk together with a theory explaining the formation of crystalline seeds is being considered [1]. As a result, we obtain the expression for the characteristic size of nanostructures depending on the pulse duration and energy. To compare calculated and experimental data, we study the action of pulses of an ArF laser with a wavelength of 193 nm on the surface of a number of widely used materials (titanium, germanium, zirconia dioxide).

Model of nanostructure formation

Melting stage

Surface layer begin to melt if energy density and width of laser pulse are high enough. When laser pulse ends, surface layer cool down and freeze by means of heat transmission into solid phase [2].

Consider a semi-infinite one-dimensional block of metal at initial temperature $T = T_{in}$ for $x \in [0, \infty]$ (see fig. 1). The metal is heated with heat flux of pulsed laser radiation. The flux causes the metal to melt down leaving an interval $[0, y(t)]$ occupied by metal melt, where $y(t)$ is moving boundary of two phases (liquid and solid).
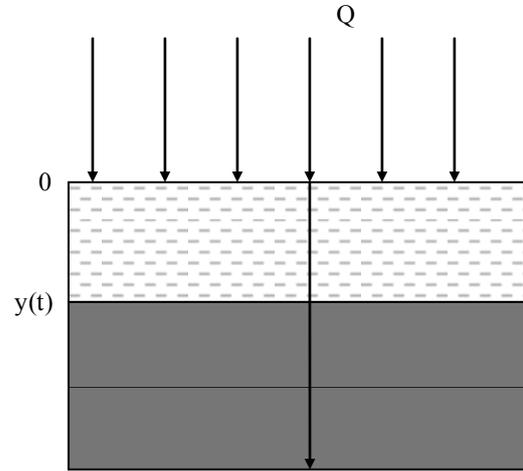

Fig.1. Schematic representation of heat flux Q incoming on metal surface.

Using heat equations for each phase with corresponding boundary conditions we have

$$\frac{\partial^2 T_1}{\partial x^2} = \frac{1}{a_1}\frac{\partial T_1}{\partial t}, 0 < x < y(t), \qquad (1)$$

$$\frac{\partial^2 T_2}{\partial x^2} = \frac{1}{a_2}\frac{\partial T_2}{\partial t}, y(t) < x < \infty, \qquad (2)$$

$$T_2(x,0) = T_2(\infty, t) = T_{in}, \qquad (3)$$

$$\frac{\partial Q(t)}{\partial t} = -\lambda \frac{\partial T_1}{\partial x}\Big|_{x=0}, \qquad (4)$$

$$T_1\big|_{x=y(t)} = T_2\big|_{x=y(t)} = T_k, \qquad (5)$$

where a, λ, c are temperature conductivity, thermal conductivity, and specific heat capacity correspondingly; ρ is a material density; $Q(t)$ is an energy absorbed per unit area during $t < \tau$, where τ is a pulse duration; T_k is a melting temperature. Liquid phase is denoted by number 1, solid phase is denoted by number 2.

$$Q(\tau) = H\rho y(\tau) + \int_0^{y(\tau)} C_2\rho(T_k - T_{in})dx + \int_0^{y(\tau)} C_1\rho(T_1 - T_k)dx + \int_{y(\tau)}^{\infty} C_2\rho(T_2 - T_{in})dx \qquad (8)$$

Setting of the problem in the form of (1-5) with replacing (4) by (7) is reasonable if the temperature of material surface achieves phase transition point during the time $t_0 \ll \tau$ and the temperature of liquid phase varies slightly during further process $t_0 < t < \tau$.

$$T(t_0) = T_k, \qquad (9)$$

$$\frac{T(\tau) - T(t_0)}{T(t_0)} \ll 1. \qquad (10)$$

Combining (1), (2), (3), (5) and (7), we obtain

Taking into account that on the moving boundary latent heat of melting H is absorbed, we obtain

$$\lambda_1\left(\frac{\partial T_1}{\partial x}\right)\Big|_{x=y(t)} = H\rho\frac{dy}{dt} + \lambda_2\left(\frac{\partial T_2}{\partial x}\right)\Big|_{x=y(t)} \qquad (6)$$

To simplify the solution we replace (4) by boundary condition

$$T_1(0,t) = T_0 = T_1(0,\tau) > T_k, \qquad (7)$$

where T_0 is a temperature of molten metal on the surface. It is defined by heat balance equation

$$T_1 = T_0 + (T_k - T_0) \cdot \frac{erf\frac{u}{\sqrt{2a_1}}}{erf\frac{\beta}{\sqrt{2a_1}}}, \qquad (11)$$

$$T_2 = T_{in} - (T_{in} - T_k) \cdot \frac{erf\frac{u}{\sqrt{2a_2}}}{erf\frac{\beta}{\sqrt{2a_2}}}, \qquad (12)$$

where $u = x / \sqrt{2t}$, $y(t) = \beta\sqrt{2t}$, β is a constant value. Using (11), (12) and (8), we get

$$T_0 = T_k + \frac{Q(\tau)/\sqrt{\tau} - \sqrt{2}H\rho\beta - 2C_2\rho(T_k - T_{in})\sqrt{a_2}\exp\left(-\frac{\beta^2}{2a_2}\right)/\sqrt{\pi}\,erfc\frac{\beta}{\sqrt{2a_2}}}{2C_1\rho\sqrt{a_1}(1 - \exp\left(-\frac{\beta^2}{2a_1}\right))/\sqrt{\pi}\,erf\frac{\beta}{\sqrt{2a_1}}} \qquad (13)$$

The solution of (6) yields the value β determining a phase boundary velocity. Considering $a_1 = a_2$ and

substituting (11), (12), and (13) to (6), we obtain transcendental equation to define β

$$2c\rho(T_k - T_{in})\sqrt{\frac{a}{\pi}} = \left\{\sqrt{2}H\rho\beta\left[\exp\left(\frac{\beta^2}{2a}\right) - 2\right] + \frac{Q(\tau)}{\tau}\right\}erfc\frac{\beta}{\sqrt{2a}}. \qquad (14)$$

The solution to equation (14) allows us to calculate melting depth of different materials irradiating with laser pulses of various duration and energy.

Crystallization Stage

After laser pulse ends a phase transition process starts. Liquid phase transforms into solid one. The crystallization with nanostructure formation occurs if cooling rate of molten metal is high enough [2]. To determine the cooling rate we need to solve the problem of molten layer cooling into solid phase.

In this case initial distribution of temperatures is given by expression of T_2 from (12) at the moment

of laser pulse ending. If the melt depth is low and the overheat of liquid phase is defined by $(T_o - T_\kappa)/T_\kappa \ll 1$, then we can consider the liquid temperature to be permanent and equal T_k. Nonstationary distribution of solid phase temperature is approximated by:

$$T(x,t) = T_k\frac{x - q(t)}{y(t) - q(t)}, x \ge y(t). \qquad (15)$$

To simplify the calculation we assume that $T_{in} = 0$. In (15) $y(t)$ and $q(t)$ are the laws of motion of temperature boundaries $T = T_k$ and $T = T_{in} = 0$, correspondingly. Taking this into account, we have that sort of temperature distribution at some instant.

To define $y(t)$ and $q(t)$ we use variation principle based on adding the vector field $H(x, y, z, t)$ in basic heat conduction law [3]. Going over to generalized coordinates $H = H(q_1, q_2, ...q_n, x, y, z, t)$ we have a system of differential equations for unknown q_i [4].

Then we solve this system of equations at corresponding initial conditions [4] and using the equation $y(t) = 0$, we get the total crystallization time

$$t_{cryst} = \frac{\gamma \alpha^2}{2\Delta(\delta + \gamma)} \left(\left[1 + \frac{(\delta + \gamma)\beta\sqrt{2\tau}}{\gamma\alpha} \right]^2 - 1 \right) \quad (16)$$

where $\alpha = \sqrt{\pi a \tau} \cdot erfc(\beta / \sqrt{2a}) \cdot \exp(\beta^2 / 2a)$, $\gamma = 16\lambda T_k / 15\rho H$, $\delta = 8/3a + 3\lambda T_k / 5\rho H$, $\Delta = 15/16\gamma$.

The crystallization is determined by formation and growth of nucleating centers in molten metal. The nuclei growth rate [2] is defined by:

$$\frac{dr}{dt} = v_0 d \exp(-U/kT)[1 - \exp(-\Delta\mu/kT)] \quad (17)$$

$$r(t) = v_0 d \exp\left(-\frac{U}{kT_k} \right) \frac{kT_k^2}{U\varepsilon} \left\{ \frac{h}{U+h} - \exp\left(-\frac{U\varepsilon t}{kT_k^2} \right) + \frac{U}{U+h} \exp\left[-\frac{\varepsilon t(U+h)}{kT_k^2} \right] \right\} \quad (19)$$

The size of crystallized nucleating center $r(t)$ approach to limit value in a time of relaxation $\tau_0 = kT_k^2/\varepsilon U$, which is characteristic time of this process. On the other hand the characteristic time is concerned with the cooling rate by $\tau_0 = \Delta_0/\varepsilon$, where Δ_0 is the supercooling in (18), hence $\Delta_0 = kT_k^2/U$. Now we can find τ_0 from (18) and then we can define the cooling rate and the characteristic size of nucleating center.

Experiment

We use a simple method of "direct" laser nanostructuring [5, 6]. It requires only one laser beam irradiating material without any projection masks, micro- and nanoparticles shielding the surface, or interference of two or more laser beams on the material surface. The formation of micro- and nanostructures were observed on specimens of titanium, germanium and ceramics based on zirconia dioxide at a multipulse irradiation by nanosecond (20 ns) ArF-laser with wavelength of 193 nm. The analysis of irradiated surface profiles was carried out by an atomic-force microscope (AFM).

where v_0 is a Debye frequency of atom oscillation in supercooled liquid, U is an activation energy for atom transition, kT is a thermal energy, d is a characteristic size per atom, $\Delta\mu$ is a difference of atom chemical potentials in supercooled liquid at temperature of T and phase change temperature of T_k ($\Delta\mu = h(T_k - T)/T_k$, where h is a heat of phase change per atom).

As a characteristic time of nuclei growth passes the size of nucleating centers almost stop to change. In this interval of time the molten layer temperature becomes equal to $T_k - \Delta_0$, where Δ_0 is supercooling at which the nuclei growth practically stops. Therefore, the characteristic time of the process τ_0 is defined by:

$$\int_0^{\beta\sqrt{2\tau}} \frac{T(x, \tau_0)dx}{\beta\sqrt{2\tau}} = T_k - \Delta_0, \quad (18)$$

where $\beta\sqrt{2\tau}$ is a molten layer depth.

We can write the average cooling rate of molten metal as $\varepsilon = \Delta_0/\tau_0$, and the change of molten layer temperature as $T(t) = T_k - \varepsilon t$. Integrating (17) and taking into consideration $[T_k - T(t)]/T_k = \varepsilon t/T \ll 1$ and $h \sim 0.1U$, we obtain the size of nucleating center of solid phase in supercooled liquid:

AFM-analysis shows that the formation of surface nanostructure occurs in peripheral low-intense part of irradiation zone. For example, there are nanostructures with characteristic sizes of 300-600 nm and 50-60 nm on titanium surface (see Fig. 2). The calculation with the help of the model described above for titanium gives a value of 60 nm at the energy density of 6 J/cm². The estimation of size parameters for a nanostructure formed under given conditions agrees well with the experiment.

AFM-analysis of germanium samples shows that in the peripheral low-intensity region there are nanostructures with period from 40 to 120 nm and amplitude from 40 to 70 nm (see Fig. 3). They appeared after 20 pulses of radiation with frequency of 2 Hz and energy density of 4 J/cm². The calculation for germanium gives a value of 12 nm at the energy density of 2 J/cm².

As seen from 3D-photographs the crystalline seeds have round form. This fact allows us to consider that process of material melting with further crystallization takes place. In the case of zirconia dioxide we observed another form of structures on

the irradiated surface. They are micro-cracks (at low intense laser radiation) and micro-ripples (at high intense laser radiation) with characteristic size of 1 up to 5 μm (Fig. 4).
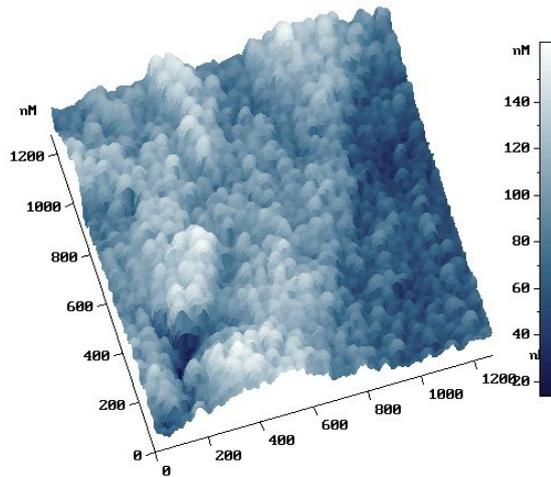

Fig.2. 3D photograph of titanium surface after irradiation by nanosecond ArF-laser with wavelength of 193 nm
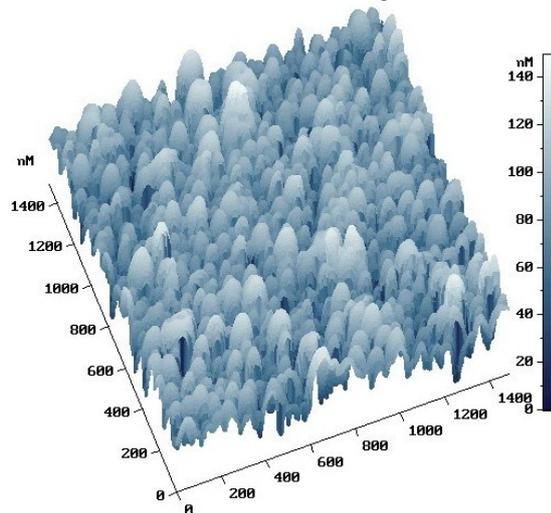

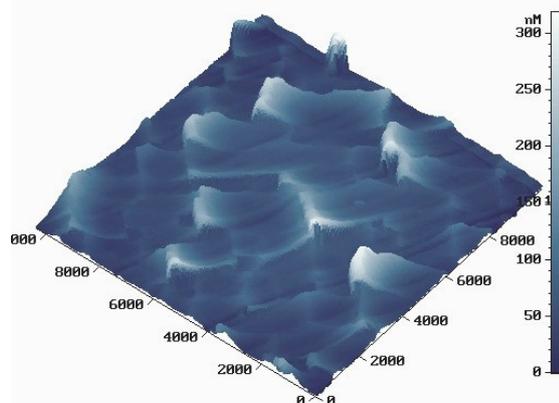Fig.3. 3D photograph of germanium surface after irradiation by nanosecond ArF-laser with wavelength of 193 nm

Fig.4. 3D photograph of zirconia dioxide surface after irradiation by nanosecond ArF-laser with wavelength of 193 nm

The calculation with the help of the model described above gives a big divergence with experimental data. Therefore we concluded that our model don't appropriate for this type of material because the melting process isn't dominant in this case. We are to consider different mechanism of nanostructure formation [7].

Results

The model for estimating the characteristic sizes of nanorelief formed on the solid surface as a result of melting by laser pulses is developed.

It is denoted the dependence of the cooling rate and characteristic sizes of nanorelief on the duration and energy of the laser pulse. This indicates the possibility of controling the processes responsible for the formation of nanostructures.

Investigations with the help of an atomic force microscope have proven the formation of the nanorelief at the surface of titanium, germanium, ceramics based on zirconia dioxide as a result of the action of nanosecond pulses of an ArF- laser with a wavelength of 193 nm. The calculation by means of the model gave good result agreement for titanium and germanium. For zirconia dioxide we gained a big divergence with experimental data and concluded that in this case mechanism of nanostructure formation differs from offered one.

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