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Model of Nanostructure Formation on Solid Surface Melted by Laser Pulse

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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 titan pieces irradiated by ArF-laser are shown.

Keywords: Surface Nanostructure, laser pulses, Stefan Problem, Nucleation Theory, Material Melting.

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1. INTRODUCTION

It's necessary to control process of nanostructuring and develop basic physics of new effective methods producing structures with characteristic size less than 100 nm on surface of industrial materials. In [1-4] a method of "direct" laser nanostructuring by nanosecond lasers have been considered. These lasers are of great interest because of their low cost and usability in comparison with femto- and pico- counterparts [5]. For that matter it is required to create method of theoretical estimation for sizes of nanostructures produced.

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 we consider the process of material melting occurring as a result of laser impact and the Stefan problem with the corresponding boundary conditions is solved. In the second part we consider the process of a melted layer cooling at the expense of heat transmission into the solid phase in combination with a nucleation theory explaining the formation of crystalline seeds [6]. 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 titanium.

2. KINETICS OF NANOSTRUCTURE FORMATION ON SOLID SURFACE MELTED BY LASER PULSE

2.1 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 [7].

Consider a semi-infinite one-dimensional block of metal at initial temperature $T = T_{in}$ for $x \in [0,\infty]$ (see Fig. 1a). 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). Using heat equations for each phase with corresponding boundary conditions we have

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

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

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

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

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

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

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

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

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

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

Setting of the problem in the form of (1-5) with replacing (4) by (7) is reasonable if the temperature of

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

material surface achieves phase transition point during the time $t_0 << \tau$ and the temperature of liquid phase varies slightly during further process $t_0 < t < \tau$.

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

$$\frac{T(\tau) - T(t_0)}{T(t_0)} << 1\,. \quad (10)$$

Combining (1), (2), (3), (5) and (7), we obtain (13) where $u = x/\sqrt{2t}$, $y(t) = \beta\sqrt{2t}$, β is a constant value.

The solution of (6) yields the value ß determining a phase boundary velocity. Considering $\alpha_1 = \alpha_2$ and substituting (11), (12), and (13) to (6), we obtain transcendental equation to define β (14)

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

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

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

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

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

2.2 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 [7]. 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 $(T_0 - T_к)/T_к << 1$, then we can consider the liquid temperature to be permanent and equal T_k. Nonstationary distribution of solid phase temperature is approximated by:

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

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 (see Fig. 1b).

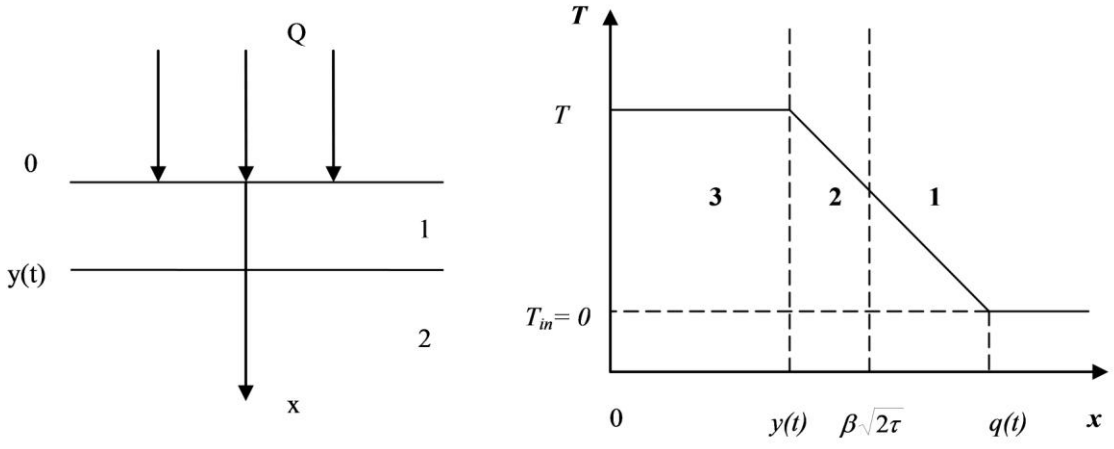
To define $y(t)$ and $q(t)$ we use variation principle based on adding the vector field $\mathbf{H}(x,y,z,t)$ in basic heat conduction law [8]. Going over to generalized coordinates $\mathbf{H} = \mathbf{H}(q_1,q_2,...q_n,x,y,z,t)$ we have a system of differential equations for unknown q_i [9].

In our one-dimensional case we consider that only $q(t)$ is generalized coordinate, and $y(t)$ is prescribed time function. Therefore $y(t)$ is defined by subsidiary equation which is not concerned with variation principle. Using heat balance equation on phase boundary:

$$\lambda\left(\frac{\partial T}{\partial x}\right)_{x=y} = \rho H\left(\frac{dy}{dt}\right)$$

and (15), we get

$$\dot{y}(q - y) = -\frac{\lambda T_k}{\rho H}\,. \quad (16)$$



a b

Fig. 1 – Heat flux incoming on metal surface (a) and temperature distribution in instant t (b)

Further, applying variation principle for generalized coordinate $q(t)$, we have:

$$(\frac{16}{15}\dot{q}+\frac{3}{5}\dot{y})(q-y)=\frac{8}{3}a\,. \qquad (17)$$

Then we solve the system of equations (16), (17) at corresponding initial conditions [9] and using the equation $y(t) = 0$, we get the total crystallization time

$$t_{cryst}=\frac{\gamma\alpha^2}{2\Delta(\delta+\gamma)}\left(\left[1+\frac{(\delta+\gamma)\beta\sqrt{2\tau}}{\gamma\alpha}\right]^2-1\right). \qquad (18)$$

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 [7] is defined by:

$$\frac{dr}{dt}=\nu_0 d\exp(-U/kT)[1-\exp(-\Delta\mu/kT)]\,, \qquad (19)$$

where υ_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 ($\Delta\mu = h(T_к - T)/T_k$, 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:

$$\int_0^{\beta\sqrt{2\tau}}\frac{T(x,\tau_0)dx}{\beta\sqrt{2\tau}}=T_k-\Delta_0\,, \qquad (20)$$

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 (19) and taking into consideration $[T_k - T(t)]/T_k = \varepsilon t/T << 1$ and $h \sim 0.1U$, we obtain the size of nucleating center of solid phase in supercooled liquid:

$$r(t)=\nu_0 d\exp\left(-\frac{U}{kT_k}\right)\frac{kT_k^2}{U\varepsilon}\left\{\frac{h}{U+h}-\exp\left(-\frac{U\varepsilon t}{kT_k^2}\right)+\frac{U}{U+h}\exp\left[-\frac{\varepsilon t(U+h)}{kT_k^2}\right]\right\}\approx R\left[1-\exp\left(-\frac{U\varepsilon t}{kT_k^2}\right)\right], \qquad (21)$$

where

$$R=\frac{\nu_0 d\exp(-U/kT_k)kT_k^2 h}{\varepsilon U(U+h)}\,.$$

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 (20), hence $\Delta_0 = kT_k^2/U$. Now we can find τ_0 from (20) and then we can define the cooling rate and the characteristic size of nucleating center.

3. EXPERIMENT

The formation of surface nanostructures were observed on specimens of titanium at a multipulse irradiation by nanosecond (20 ns) ArF-laser with wavelength of 193 nm.

In our experiments we use a simple method of "direct" laser nanostructuring, which does not require the use of projection masks, the surface shielding with small (micro-, nano-) particles, or the interference of two or more laser beams on the surface of material. The analysis of irradiated surface profiles is carried out by an atomic-force microscope (AFM).

The intensity of the laser radiation takes the maximum value in the center of the spot and fall to its pe-

riphery. As a consequence, at multipulse irradiation of the same surface plot the deep crater appears in the center of the spot. There is the removal of the material from this crater. Only a surface melting is observed on the laser spot periphery, where the intensity of laser radiation reduces. 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).

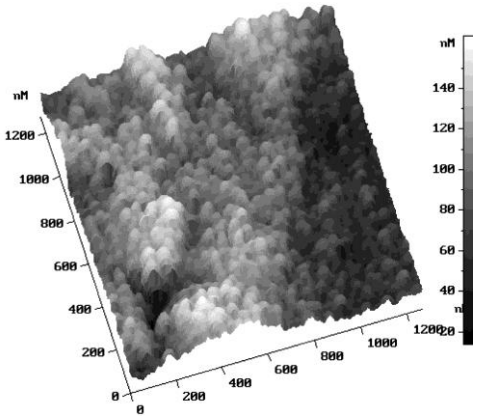


Fig. 2 – 3D photograph of relief in the peripheral low-intensity region at the titanium surface after irradiation by nanosecond ArF-laser with wavelength of 193 nm

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.

4. CONCLUSIONS

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

The solution of the Stefan problem for the melting of the surface layer in combination with the nucleation theory denotes a dependence of the cooling rate and characteristic sizes of nanorelief on the duration and energy of the 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 as a result of the action of nanosecond pulses of an ArF- laser with a wavelength of 193 nm. The calculation of the formed nanostructure parameters for titanium gives a value on the order of 60 nm that agrees well with the experimental results.

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