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Model of the Subsurface Overheating of Carbon Samples upon Laser Impact in Liquid Nitrogen

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Abstract—A qualitative model describing the subsurface overheating of carbon samples exposed to femtosecond laser irradiation in liquid nitrogen is proposed for purposes of simulation. To a large degree, the model has universal applicability. A distinctive feature of this model is the principle of interactive control, which allows investigated characteristics to be adapted to observed experimental data.

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INTRODUCTION

Processes that occur under the action and propagation of femtosecond laser radiation determine the wide use of means and ways of creating, shaping, and controlling the properties of micro- and nanostructures. The use of ultrashort laser pulses continually allows us to improve the accuracy of processing and predict its results. Combining high energy and ultrashort duration, pulsed laser radiation lets us achieve local conditions in a field of action sufficient for removing, structuring, or changing the phase composition of a material. Femtosecond laser ablation is one of the most popular and widely used laser means of removing material. Over the fairly long time of studying this complex multiscale phenomenon, the main principles of femtosecond laser ablation have been elaborated, a phenomenological description of them was compiled, and the hierarchy of interrelated processes was established [1–3]. However, an integrated picture from the absorption of the energy of an ultrashort laser pulse to the thermal relaxation of a system has yet to be fully obtained, due to uncertainty regarding the effects of a pulse and the time scales of the processes that occur.

The development of such models, particularly when using femtosecond laser radiation, is complicated by the attempt to consider as many parameters of the phenomenon and experimental conditions as possible. Instead of one model, a hierarchical structure is formed whose components are themselves models of some interrelated processes and phenomena. A certain degree of accuracy and fair universality is of course achieved by using complex models, but extraordinary difficulties arise in their implementation. These are associated not only with the difficulties of solving the equations themselves (some numerical calculations are too cumbersome and unsuitable for analyzing experimental data), but also with problems of determining the coefficients and values of the specific parameters that these equations contain. This is especially noticeable when the model is intended to describe a single parameter or value for a problem of a particular case, e.g., determining the propagation of a temperature front inside a sample near the surface on which laser radiation is acting. A complex model is in this case a superposition of other models describing individual physical processes. With an actual experiment, the result is often distorted by the effects of unconsidered factors, unknown coefficients, or errors in determining the parameters of the experiment.

STATEMENT OF THE PROBLEM

Processes initiated by the action of femtosecond laser radiation on samples cooled to liquid nitrogen temperature differ substantially from those that occur under normal conditions in air . This could be due to a change in the duration of electron–phonon interaction as a result of strong cooling of the material. The question then arises as to the applicability of the generally accepted sequence of events or phenomena that occur during laser ablation with ultrashort laser pulses under normal conditions, their dominance, and the length of each process. Based on the results from the experiments in [4], we may conclude that temperature and pressure rise sharply, accompanied by a change in the phase composition at a certain depth in the sample, followed by movement of the crystalline structures formed in the bulk to the surface. We may assume that the times of crystal structure formation are much longer than that of the action of a single femtosecond laser pulse. The energy contribution from a single pulse is also insufficient for the growth of such a

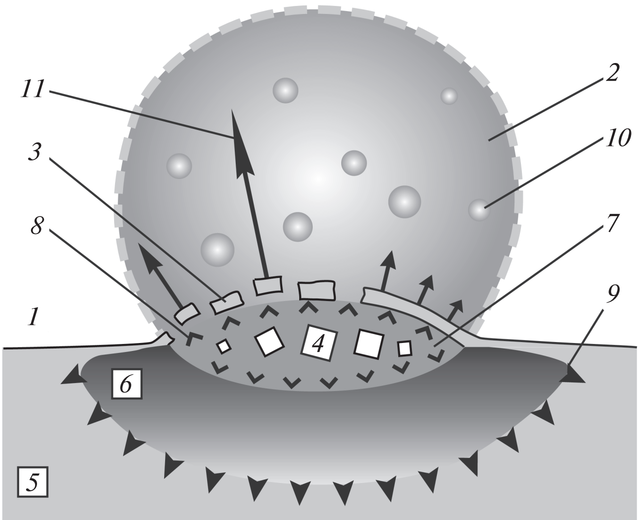

Fig. 1. Scheme of the physical processes of subsurface overheating during the interaction between femtosecond laser radiation and a carbon material in liquid nitrogen: (*1*) liquid nitrogen; (*2*) vapor–gas region (the region of effective heat exchange between the sample's surface, the products of ablation, and the volume of liquid nitrogen); (*3*) subsurface layer; (*4*) carbon microcrystals; (*5*) glass-carbon target; (*6*) region of heat transfer to the volume of the material, (*7*) region of subsurface overheating; (*8*) front of pressure propagation/growth; (*9*) front of temperature propagation due to thermal conductivity; (*10*) evaporated nitrogen; (*11*) direction of surface layer material ejection.

structure, so the energy accumulates in a subsurface layer, stimulating crystal growth up to a particular moment (until the structure is ejected when the surface opens by overcoming the threshold of the pressure difference, at a considerable excess of stresses, and so on). We may therefore assume that some calculations for nanosecond laser ablation [5] are also valid here.

Figure 1 schematically shows the dynamics of the development of physical processes. During the action of a femtosecond laser pulse, energy is transferred to the electronic subsystem of the material. The duration of this process is comparable to that of the laser pulse. A photoelectric avalanche is created with a subsequent transfer of energy through electron–phonon interaction. The rise in the stressed state of the crystal lattice is due to a nonstationary increase in temperature and pressure in the region of the redistribution of the electron–phonon energy. The expansion of this region should develop uniformly in all directions relative to the nominal center, but this does not happen because of the highly nonequilibrium conditions of the system. The expansion of this area deep into the material is limited by the lattice mobility as a result of the strong cooling of the sample volume. The removal of heat is in turn limited by the thermal conductivity. The expansion of the material's volume is more intense in liquid nitrogen due to the lower density of the medium. Conditions are thus formed in the direction of the medium (liquid nitrogen) that favoring cooling of the sample surface (a drop in pressure, expansion of the material into less dense regions of the medium, heat exchange with the medium, and so on). Due to low heat transfer and the impossibility of expanding into the interior, conditions for a substantial increase in temperature and pressure are created in the direction of the bulk of the material; this in turn leads to structural changes in the lattice of the material. The above mechanism behind the processes accompanying energy exchange in the system correlates with the results of experimental studies.

The experimental conditions in [4] were used as the basis for our model describing subsurface overheating. A femtosecond laser system with the following parameters were used in that work: wavelength, 800 nm; pulse duration, 50 fs; frequency of pulse repetition, 1 kHz; and average power, 0.5 W. An open cryostat was assembled to fix and cool the carbon samples. After thermal stabilization (cooling) of the sample, it was treated with laser radiation as the thickness of the liquid nitrogen layer was varied. Highly oriented pyrolytic graphite and glassy carbon were used as samples.

The totality of processes and mechanisms that arise from the action of femtosecond laser radiation on carbon samples in liquid nitrogen thus contain too many factors and conditions that affect the final result. Starting with the scattering of laser radiation by nitrogen vapors, the spatial modulation of the laser beam, the interaction between femtosecond laser radiation and low-temperature samples, and other processes that accompany an experiment, we cannot possibly consider all such processes, at least at this stage of our research. We also cannot construct a satisfactory and all-encompassing model of an experiment or correctly incorporate it into any known model [1–3]. The aim of this work was thus to construct a very simplified model that does not cover all aspects of the phenomenon but nevertheless ensures an adequate simulation. This is of fundamental importance in describing and analyzing an experiment, particularly with such processes as subsurface overheating and changes in the phase composition of a material. As a result, we developed a single property model. First, it is assumed that there are some areas of uncertainty regarding domains Δ_t and Δ_x (temporal and spatial, respectively). Second, we propose using average values of the parameters (in our equations, coefficients are assumed to be constant). Third, the use of fitting parameters is in this case inevitable.

MODEL OF SUBSURFACE OVERHEATING OF A TARGET BY A SERIES OF ULTRASHORT PULSES

Temporal Domain Δ_t

Let us consider an infinite line. Interval [0,1] simulates the target (in depth). The laser radiation falls normally onto the sample's surface and the left end of the segment corresponds to the target area. We assume that the initial distribution of temperature over the straight line is zero. Absorption of the energy of an ultrashort pulse heats the electron subsystem inside the target, after which the energy is transferred to the lattice by phonons (due to relaxation) and heat is diffused. This is all described by the familiar two-temperature model [5]. In other words, temporal range Δ_t, the stage of the pulse energy absorption and relaxation, is delineated. It is extremely short on the scale of treating the target with a series of impulses (up to several seconds with a repetition rate of 1 kHz).

Simulation Scenario 1 (Basic Scenario)

Let us consider the situation of exposure onto the target with a single pulse. We assume that the distribution function of temperature is $u(x,t-\tau_1)=0$ when $t<\tau_1$. At moment τ_1, an ultrashort impulse acts on the target. The electron cloud is then heated and relaxation occurs, forming the temperature profile of the target (the initial condition). Cooling then occurs in accordance with the heat transfer equation (homogeneous) for $t\geq\tau_1$. After a very short period of time (on the scale of treating the target with a series of pulses), a certain temperature profile is obtained. At the same time, the dynamics of its formation is not fully understood. We therefore propose that we simply consider initial condition $u(x,0)=\varphi(x)$ to be achieved at moment τ_1 when $\varphi(x)$ is the initial function. Domain Δ_t is in this case ignored. When $t>\tau_1$, the solution to homogeneous heat conduction equation $u_\tau=a^2u_{xx}$ (a zero function when $t<\tau_1$) can be expressed via Poisson's integral

$$u(x,t-\tau_1)=\frac{1}{2a\sqrt{\pi(t-\tau_1)}}\times\int_0^{+\infty}e^{-\frac{(x-y)^2}{4a^2(t-\tau_1)}}\varphi(y)dy. \quad (1)$$

A new pulse then arrives at subsequent moment in time $\tau_2>\tau_1$. It is considered independently of the previous pulse, but under similar conditions. As a result, when $t\geq\tau_2$, the temperature upon the action of two pulses is obtained by superimposing both solutions (according to the principle of superimposition), and so on.

The problem is finding the temperature profile at moment t. We know moments in time $\{\tau_k\}$ when ultrashort pulses arrive that satisfy condition $\tau_k<t$. The temperature profile is then expressed by the formula

$$\tilde{u}(x,t)=\sum_{\{\tau_k\}}u(x,t-\tau_k)$$
$$=\sum_{\{\tau_k\}}\left(\frac{1}{2a\sqrt{\pi(t-\tau_k)}}\int_0^{+\infty}e^{-\frac{(x-y)^2}{4a^2(t-\tau_k)}}\varphi(y)dy\right). \quad (2)$$

Spatial Domain Δ_x

An essential feature of this approach is the refusal to use boundary conditions, which are indispensable when studying processes of heat transfer during heating by, e.g., nanosecond pulses. This is a rough but very simple model that requires further improvement.

As noted above, when a material is heated by femtosecond laser pulses, the energy is transferred to the target via the photon-electron-phonon interaction sequence. After equilibrium is established, the processes are of a predefined nature and present a classical heat exchange scenario. However, complex processes that occur at the target boundary do not allow us to use these approaches when modeling heat exchange with a medium using boundary conditions, at least not without additional serious analysis. The very concept of a target surface, considered from the point of view of heat transfer, would seem to be an oversimplification. Here, we do not mean some conditions imposed directly on the temperature profile inside the target. The requirements are imposed on virtual continuations of the temperature distribution beyond the target. Instead of the target, we can conventionally consider some nominal body whose boundary is obtained by continuing the target boundary out to some fixed distance. It is assumed here that the thermal properties beyond the boundary of the target are the same as in the interior of the target itself. The zone of uncertainty that arises between the boundary of the nominal body and the target surface is treated as the Δ_x zone. This can certainly be called a superficial layer, but in our opinion, this is not entirely correct.

Let us seek solutions to the equation that acquire certain equilibrium forms at the boundary of the body. We first consider two types of equilibrium. The first type is when the temperature of the medium is reached and maintained on the boundary of the body; i.e, it equals zero. The second type of equilibrium corresponds to when the temperature gradient is always zero at the boundary (it is assumed that the body is thermally insulated). In other words, we still introduce boundary conditions, but not on the surface of the target, which is of a virtual nature; a certain zone of uncertainty exists between the boundaries of the target and the nominal body. Let us consider the simplest variant, assuming that the thermal characteristics of the zone are identical to the properties of the target's material. This allows us to apply the heat conduction equation to the entire nominal body. This approach is attractive primarily because it generates temperature profiles that are realized by simple explicit formulas.

Simulation Scenario 2 (Choosing a Solution with Certain Specific Properties)

Points $x=0$ (the surface of the target) and $x=-\Delta_x$ (the boundary of the nominal body) correspond to the right and left boundaries of the layer. From the point of view of the analytical representation, the formulas are virtually identical to the expressions used above. Let us write the resulting formulas for a single pulse occurring at time τ (see above). The subscript corresponds to the first type of equilibrium; the superscript, to the second one.

$$U9x,t-\tau) = \frac{1}{2a\sqrt{\pi(t-\tau)}} \times \int_0^{+\infty} \left(e^{-\frac{(x-y)^2}{4a^2(t-\tau)}} \pm e^{-\frac{(x+y+2\Delta_x)^2}{4a^2(t-\tau)}} \right) \varphi(y)dy. \quad (3)$$

Solutions $U_{1,\Delta_x}(x,t-\tau)$, $U_{2,\Delta_x}(x,t-\tau)$ correspond to the first and second types of equilibrium. Their linear combination $\psi U_{1,\Delta_x}(x,t-\tau) + (1-\gamma)\, U_{2,\Delta_x}(x,t-\tau)$ is also the solution to the equation where γ is a parameter of the distribution profile. The initial conditions are naturally retained, but not the conditions at the boundary of the body. For example, if we assume $\Delta_x = 0$, $\gamma = 0.5$, the solution coincides with the basic scenario, i.e., the solution to the problem with no boundary conditions (see above).

First, the type of heat transfer between the target and the medium has a substantial effect on the formation of temperature profiles inside the target. Second, the actual process of interaction remains unclear, and is of an objective nature. There is an alternative: Either make considerable efforts to describe the exchange of heat between the target and the medium (not necessarily through the use of boundary conditions on the target surface), or assume that parameters Δ_x, γ are free and fit them. For example, we may initially assume that $\Delta_x = 0$. It would seem profiles $U_{1.0}(x,t-\tau)$, $U_{2.0}(x,t-\tau)$ $(x \geq 0)$ should then be considered virtual. But $\gamma U_{1.0}(x,t-\tau) + (1\ \gamma) U_{2.0}(x,t-\tau)$ probably models real profiles in a certain interval of γ. The consolidated formula used for a series of pulses is similar to (2).

As a first approximation to the choice of function $\varphi(x)$, we use the standard expression $\varphi(x) = (1-R)I_0\alpha e^{\alpha x}$, where R is the coefficient of reflection and I_0 is the intensity (power density) of radiation. The adjustment of the system will be based on the selection of a suitable absorption coefficient α, since this parameter regulates the form of the profile of a model. The use of a more complicated absorption function is of course also possible, so some modification of the system is thus allowed. At this stage, however, it is only a choice of α, since the remaining coefficients are constants and do not play a significant role.

MODELING RESULTS

We can write (3) as the sum of the solutions to the base scenario and the component that is used by assuming the existence of zone Δ_x and its effect on the temperature profile inside the target:

$$U(x,t-\tau) = u(x,t-\tau) + (2\gamma-1) \times \frac{1}{2a\sqrt{\pi(t-\tau)}} \int_0^{+\infty} e^{-\frac{(x+y+2\Delta_x)^2}{4a^2(t-\tau)}} \varphi(y)dy. \quad (4)$$

Each pulse leads to the same typical initial condition $\varphi(x) = (1-R)I_0\alpha e^{-\alpha x}$. We are interested in the process of temperature accumulation.

When absorption coefficient $\alpha = 0$, the initial condition is a certain constant level of temperature. Cooling lowers the surface temperature of the target. As time goes by, the temperature front shifts into the interior of the target. After a while, the next impulse comes, which contributes its energy, raising the target temperature. The effect of each subsequent pulse thus results in overlapping with the previous temperature, and the overheating region shifts to the surface of the sample. After receiving the next portion of energy, the temperature front moves to the interior of the target, due to the thermal conductivity of the material.

Energy accumulation (when $\alpha > 0$) is more complicated. After transferring the energy of the first pulse to the lattice of the material, a characteristic initial condition is created in the form of a falling exponential, due to the thermal conductivity of the sample. Cooling at the boundary as a result of the processes described above lowers the temperature in the region of the target surface. The action of the second laser pulse leads to the formation of exactly the same temperature profile as the effect of the previous one, as a result of which a new pulse profile is superimposed on the one already propagating. The process of subsurface overheating in the interior of the target is initiated under the condition that the energy of one pulse is insufficient for overheating at the boundary. This process is cumulative and depends on the energy, the number of pulses, the frequency of their repetition, and the conditions of cooling at the target boundary.

The use of an additional term describing spatial zone Δ_x in modeling thus allows us to strike such a balance between the energies at which subsurface overheating takes place.

Figure 2 shows the plot of temperature as a function of the depth of the sample under the action of a series of femtosecond laser pulses, plotted according to the proposed model. This graph describes the distribution of the temperature front as a result of the action of a hundred pulses that have reached the surface of the target. By specifying the corresponding calculation parameters, we can obtain the temperature distribution at which phase transformations are possible. The areas corresponding to the actual physical state of the mathematical model are marked in the figure. The number *1* indicates the area of the development of a phase explosion when high temperature and

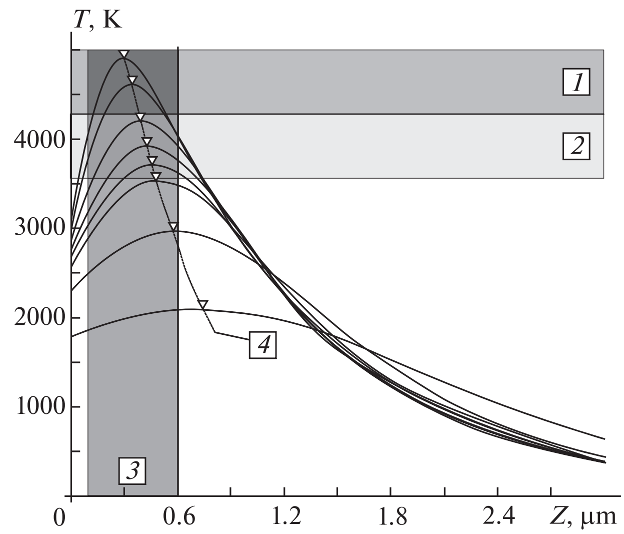

Fig. 2. Plot of temperature variation in the subsurface layer of the sample.

pressure are reached (the pressure parameter was not considered in this model, but it is considerable in an actual experiment). In the bulk of region *2* of subsurface overheating, phase transformations of carbon can occur under the effects of temperature and pressure, the formation of carbon crystals in particular. Region *3* shows the zones of possible phase transformations at a certain distance from the surface when the necessary temperature conditions are reached. Curve 4 reflects the dynamics of the shift of the temperature maximum to the surface of the sample, relative to the gained energy.

CONCLUSIONS

Our model of subsurface overheating allowed us to qualitatively estimate the distribution of temperature in the volume of a material. The temperature distribution was modeled as a result of energy transfer to the lattice of the material and the thermal effect observed in the target volume due to a series of femtosecond laser pulses. The phenomenon of subsurface overheating was confirmed. Using the principle of interactive control, we can adapt the model to different experimental conditions, and to the investigated phenomena in accordance with the observed experimental data. For more accurate physical estimates, we must also consider pressure, which has an exceptional effect on the growth of temperature in the investigated region. In order to improve the accuracy of assessing the impact of femtosecond laser radiation at low temperatures, we must therefore switch to multifactor evaluations of the processes that occur.

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