SIMULATION OF NANOCRATER FORMATION DURING LASER-INDUCED PHASE TRANSITIONS

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Abstract *A theoretical study of the process destruction of a solid surface under the action of a powerful radiation impulse is carried out. The peculiarities of the dynamics the surface destruction of the material and the features of the space-time dynamics of the gaseous phase were studied. This phase occurs as a result of local phase changes on the surface of the irradiated material. The differential equation to describe the dynamics of the corrosion crater formation on a solid surface was researched. This equation is analyzed together with equation of near-surface pressure dynamics. The asymptotic analysis for crater equation gives the basis to assert that mathematical interpretation of process of destruction corresponds to actual temporal dynamics of formation of a crater on the substance. The numerical simulation of the formation of a nanocrater with a model form of an active laser impulse is given. The test calculations correspond to experimental observation and theoretical ideas about the process of development of a corrosion crater under laser pulsed irradiation.*

KEYWORDS: LOCAL PHASE CHANGES, POWERFUL RADIATION IMPULSE, CORROSION CRATER, PRESSURE

1. Introduction

Laser radiation (laser doping, annealing, heat treatment, coating, etc.) is used in many modern surface treatment (modification) technologies. Possibility of local influence on small surfaces, high speed heating, and manoeuvrability in laser beam controlling make laser methods of material modification more and more attractive. A lot of experimental and theoretical investigations are closely related to the problem of solid matter surface destruction by short high-power laser impulses. These technologies may, in particular, be useful in recording information, labeling and other technological applications.

Therefore development of theory of intense energy flow interaction with matter surface which takes into account local phase transformations during surface destruction is may be the most consecutive scientific approach.

2 Preconditions and means for resolving the problem

2.1 Experimental studies

Contemporary lasers and laser systems generate femtosecond impulses (1 fs=10^{-15} s). Femtosecond laser systems with light impulse duration 10–1000 fs allow obtaining under focusing enormous light intensity over 10^{13} W/cm^2. After falling on solid matter surface such high intensity impulses can, under some conditions, lead to considerable damages of this surface and are of special interest [1-10]. . Examples of such a damage are shown on fig. 1

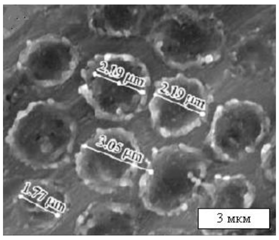

Fig.1 *Microcraters obtained by femtosecond laser titanium irradiation [10]*

The damages made by laser impulse are various on their form. The surface destruction may be accompanied by fusing as well as not fusing of crater edges. According to experimental estimations characteristic level of energy, from which active destruction of surface begins practically without formation of liquid phase exceeds 10 ÷ 100 MW/cm^2 depending on material. If the flow is substantially higher than this value, considerable part of energy of laser radiation is outlaid on a direct phase solid-gas transition. A liquid phase in the area of treatment is practically absent in this case. Such streams represent the main interest of this research.

The formation of a corrosive crater on the surface of such a media depends on both the power flow parameters and the properties of the specific substance. This research is aimed at studying theoretically the dynamics of the crater formation and all the accompanying processes. In the case of destruction under real conditions the removal of a substance from the solid phase and its transfer into the gas one can occur not only directly from the surface in the form of individual atoms, but also through micro-clusters and micro-droplets which cannot but be formed in the gaseous phase.

2.2 Criterion for surface destruction in laser irradiation without crater melting

Flows that cause surface destruction without melting are of basic interest in this research. To define limit, which separates treatment with formation of the liquid state and treatment which is not accompanied with surface melting, we will consider the superficial layer of matter on an area with the size equal to the cross-section of laser impulse. To prevent liquid phase appearing on the solid surface, its temperature during impulse action has to amount, at least, critical value T_c, without going out the borders of the matter state phase surface which belongs exceptionally to the hard phase. Thus pressure in this near surface area of hard phase must also exceed some critical value P_c. As a laser impulse is considered, a necessary condition at which the system gets in the noted area is: $P_c<q_s(1+R)$ where q_s – power of electromagnetic wave falling on the matter surface, R – light reflectivity, c – light speed.

Taking into account, that on the critical isotherm of gas phase for arbitrary pressure P and volume V_Γ the state equation $PV_\Gamma = \nu R_\Gamma T_c$ is holding, where ν is a molar gas amount, it is possible to estimate the value of pressure P_c, which provides implementation of the above condition. This value can be estimated from the next considering. In order that a liquid phase did not appear, a hard phase after a phase transition must get on an isotherm which with a temperature not below than critical isotherm with a temperature T_c. Examining a critical isotherm, we will get the sought threshold value P_c for which gas state equation will acquire a kind $PV_\Gamma^{(c)} = \nu R_\Gamma T_c$ In this equation remains indefinite volume $V_\Gamma^{(c)}$so far. For its estimation it is possible to take advantage of fact, that in the moment of phase state transition from solid to gas, the change of volume $V_T \to V_\Gamma$ is not so substantial comparing to the similar change for other points of isotherm T_c. (where this change is large). That is why a volume $V_\Gamma^{(c)}$ can be estimated counting it practically equal to the proper volume of hard phase $V_T^{(c)}$. As one mol volume of hard matter V_μ is determined by ratio: $V_\mu = \mu/\rho_0$, where μ is molecular mass, and ρ_0 is density, the volume of ν molls is obviously equal to $V_\Gamma^{(c)} = \nu\mu/\rho_0$. Using this value of volume in state equation $P_c V_\Gamma^{(c)} = \nu R_\Gamma T_c$ in place of $V_\Gamma^{(c)}$ we will get an estimation: $P_c = \rho_0 R_\Gamma T_c/\mu$, and a sufficient condition for a flow q_s will look in this case like:

$$q_s > \frac{\rho_0 R_\Gamma T_c c}{\mu} \cdot \frac{1}{1+R}$$

In practice such estimation is interesting for an initial flow q, which is related to the flow q_s which passed in a solid by correlation $q_s = (1-R)q$. Then for the initial value of flow we get:

$$q > \frac{\rho_0 R_\Gamma T_c c}{\mu} \cdot \frac{1}{1-R^2}$$

After this formula estimations were made for concrete materials. They show that, for example, for aluminum the superficial value of stream must meet condition $q \geq \frac{6\cdot 10^{13}}{1-R^2}$ W/cm^2, for copper and chrome $q \geq \frac{9\cdot 10^{13}}{1-R^2}$ W/cm^2 for tungsten $q \geq \frac{1{,}5\cdot 10^{14}}{1-R^2}$ W/cm^2, for titan $q \geq \frac{7{,}6\cdot 10^{13}}{1-R^2}$ W/cm^2, for potassium $q \geq \frac{4\cdot 10^{12}}{1-R^2}$ W/cm^2. As evidently, such estimations do not contradict experimental information [11]. Consequently, here we will name flows intensive, if they meet condition got before.

3 Solution of the problem

The model of the destructive process proposed in the paper was built on the basis of a system of inhomogeneous equations of mechanics of a continuous medium.

At action of irradiation on a surface there is a coexistence of the two, solid and gas, media due to local phase transitions. Using the three boundary conditions, namely [9]:

— the condition of a mass flux balance

(1) $$\rho_s (\boldsymbol{v_s} \cdot \boldsymbol{n}) - \rho_s (\boldsymbol{v_{0s}} \cdot \boldsymbol{n}) = 0,$$

— the condition impulse flow balance

(2) $$P_s n_i + \frac{1}{c}(n \cdot q_s) + \rho_s (n \cdot v_s)(v_s^i - v_{0s}^i) + P_{ij}^{0s} n_j = 0,$$

— condition of energy flow balance near the phase boundary:

(3) $$(\boldsymbol{n}\cdot\boldsymbol{v_s})\left(\rho_s H_s + \rho_s \frac{\boldsymbol{v_s^2}}{2}\right) + L_0(\boldsymbol{n}\cdot\boldsymbol{q_s}) - L\lambda_s(\boldsymbol{n}\cdot gradT)_s - -(\boldsymbol{n}\cdot\boldsymbol{v_s})\rho_s U_{0s} = 0.$$

has allowed us to formulate three equations which are characterized, in the main, by gas parameters and describe the dynamics of a crater formation – eq. (1), dynamics of a plasma plume formation – eq. (2) and dynamics of behavior of the basic macroscopic quantities of the process – eq. (3)

Here we designate by index "os" solid substance phase of and designate by index "s" gas. In the equations (1)–(3) *U, ρ, υ* respectively intrinsic energy of the continuous medium mass unit, density of this medium, and a convection velocity vector, P pressure exerting, P_{ij}^{0s} – the surface value of a stress tensor, H_s – a heat Gibbs function (enthalpy) describing macroscopic system state in thermodynamic equilibrium when entropy and pressure are the main independent variables; U_{0s} is intrinsic energy of the condensed matter mass unity; $\mathbf{Q} = q_s + \boldsymbol{q_s^T}$ – general energy flow in the medium, where q_s is an energy of a light flow and $\boldsymbol{q_s^T} = -\lambda_s(gradT)_s$ is an energy of a thermal flow L_0 is a light loss factor for the transition from gas to solid, L is a thermal loss factor for the transition gas-solid.

All boundary conditions are formulated in the local reference system, located on the boundary between the condensed media and the gas phase in the area of the impulse action. It is clear that when the solid surface does not destruct, the reference system will remain stationary relative to the observer. But when destruction occurs, then the chosen system in the area of this destruction is rigidly associated with a certain point of the surface of the solid medium, and moves along with it. That is, such a system describes the events directly at each individual point of the surface. Therefore, there is a need to establish a connection between the local and laboratory coordinate systems. The laboratory coordinate system is stationary relative to the surface prior to its destruction.

The shape of the crater at each fixed time point is determined as follows *z(t)=S(t, x(t), y(t))*. Here *S(t, x(t), y(t))* is the function of the shape of the surface of the formed crater (the crater shape function). For each moment of time, it determines a certain dependence *z* from *x* and *y*.

As a result of coordinate transformations from one system to another, ratios were obtained for velocities linking the two coordinate systems. The obtained ratios allow us to move from a local frame of reference, in which boundary conditions are formulated at the boundary of the separation of two phases to a laboratory frame of reference, in which the processes associated with destructive processing can be observed. At the expense of transformations, the equation of the dynamics of the crater formation relative to the laboratory frame of reference was obtained from the continuity condition. The feature of the equation is that the surface pressure that is included in the obtained equation is not constant. Therefore, the energy flow balance equation was used to determine the dynamics of the surface pressure.

A system of two differential equations was obtained. In dimensionless form:

– the crater dynamics equation

(4) $$\frac{\partial\Sigma}{\partial\theta} = \Pi^\beta \sqrt{1 + \left(\frac{\partial\Sigma}{\partial x}\right)^2 + \left(\frac{\partial\Sigma}{\partial y}\right)^2} \equiv \Pi^\beta N,$$

– the equation of the dynamics of near-surface pressure:

(5) $$\frac{\partial\Pi}{\partial\theta} = \left(-1 + \Lambda e_q \vartheta_\tau\right)\Pi^{\beta+\eta} - \Pi^{\beta+1} + \frac{e_q \vartheta_\tau \Pi^\eta}{\sqrt{1+\left(\frac{\partial\Sigma}{\partial x}\right)^2+\left(\frac{\partial\Sigma}{\partial y}\right)^2}} \equiv$$
$$\equiv \left(-1 + \Lambda e_q \vartheta_\tau\right)\Pi^{\beta+\eta} - \Pi^{\beta+1} + \frac{e_q \vartheta_\tau \Pi^\eta}{N}$$

In the equation (4) the parameter e_q determines the ratio of the flow that enters the surface of the matter q_s to the output flow q_0, i.e., in dimensionless units

$$e_q = \frac{q_s}{q_0} \equiv f(x,y)e^{-\Lambda M \Pi^{\beta+\eta}\Sigma},$$

where the function *f(x,y)* – determines the transverse shape of the stimulating impulse and adds to (4) an additional dependence on *x, y*, Λ – parameter determining the degree of interaction of the evaporable matter with the incident radiation, *M* – dimensionless parameter determined by equality:

$$M = \frac{q_0(\kappa-1)^2 L^2}{2\varphi_0^{3/2}\kappa^2 \rho_{0s}(\kappa+1)^{1/2}}.$$

Here κ is polytropic index, φ_0 is specific heat of the condensate - gas phase transition, *β≡(κ+1)/(2κ), η≡1/κ*. It is clear that in the presence of the destruction of the surface formed by the corrosion torch at the matter surface will significantly affect the factor e_q reducing it ($0 \leq e_q \leq 1$).

4. Results and discussion

4.1 Analysis of phase trajectories of pressure at crater formation

To fulfill asymptotic estimates of the "behavior" of the crater formation as a function of time it is convenient to analyze the phase dependence curves $\frac{\partial\Pi}{\partial\theta}$ from *Π*. Consider a situation where the width of the incident beam is much greater than the depth of the crater and the intensity is distributed evenly across its cross section.

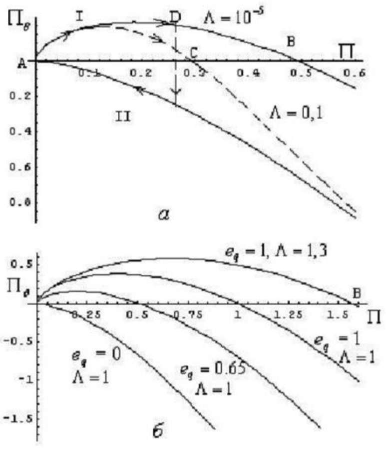

Fig.2 *Phase trajectories of two periods: a) curve I corresponds to the time when the impulse is acting, curve II corresponds to the time when the impulse is ended. b) corresponds to the time when the impulse is acting for different values of parameter Λ and e_q. Here we use the approximation Σ~1 and N~1.*

Arrows on fig. 2*a* designate the direction of the process movement of time pressure development indicate: the first stage (I) begins with point A, which is unstable for this stage (positive derivative $\frac{\partial \Pi}{\partial \theta}$), so the dependence change $\frac{\partial \Pi}{\partial \theta}$ from *Π* occurs along curve I to the moment of the impulse ending (indicated by D in the figure), or until the pressure reaches its maximum (Fig. 2*a* - points B or C). These points are stable - as soon as the curve crosses the axis Π the condition $\frac{\partial \Pi}{\partial \theta} < 0$ starts to be complied. This makes the process to return to point B (or C) again. At these points, the gas pressure remains constant until the impulse reached the end. As soon as the impulse is over, the transition to curve II occurs and the process begins to move along the curve until it reaches zero. In fig. 2*a* shows a dashed line that conventionally describes the dynamics of the process in the case of large ones Λ (an increase in this parameter physically means an increase in the interaction of radiation with the plasma-gas torch formed near the surface of matter). As can be seen from Fig. 2*b*, with $e_q \cong 1$ there are such values Λ, when in the point B, pressure value Π will be larger than unit. Also, for different values Λ at the similar e_q (on Fig. 2*b* are two curves that correspond $e_q \cong 1$) with increase Λ the value $\frac{\partial \Pi}{\partial \theta}$ increases in maximum.

4.2 Asymptotic study of the dynamics of the nanocrater formation

The dynamics of crater development on a solid surface under the action of a powerful laser impulse was investigated asymptotically (Fig. 3).

At the beginning of the formation of the crater the process has an explosive, power-law *θ*, character, and at reaching the maximum possible value of pressure (point B in Fig. 2*a*) - changes according to the linear law.

Upon completion of the impulse action, the crater formation is rapidly stopped, and when the situation is implemented under Λ>1 the explosive (Fig. 3*a*) process is gradually transformed into logarithmic and only then becomes linear. As the degrees of freedom increase, the magnitude Σ responds more slowly to the external laser effect

The approximate qualitative dynamics crater formation in this sequence is presented in Fig. 4

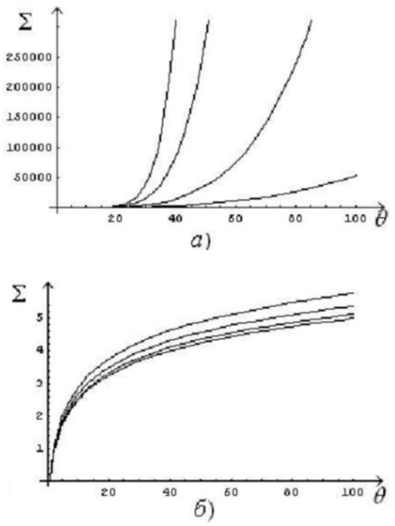

Fig. 3 *Asymptotic behavior of the formation of a crater under the influence of a laser power impulse*

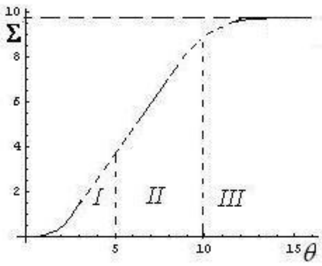

Fig. 4 *Formation of a crater under the influence of laser radiation according to asymptotic analysis*

Fig. 4 illustrates the formation of a crater in time. The first period (I) reproduces the formation of the crater at the beginning of the destruction of the surface. The second (II) is the dynamics of crater formation as the pressure approaches its maximum value. The last period (III) determines the change in the shape of the crater after the termination of the impulse, which is determined by asymptotic $\Sigma = \Pi_c^{\beta}\theta_\tau + \frac{25}{4\theta_\tau}$. Here Π_c is maximum value of pressure and θ_τ is dimensionless impulse length.

4.3 Numerical simulation of the dynamics of crater formation

A numerical simulation of the dynamics of crater formation was performed using the simplified formula

$$\frac{\partial S}{\partial t} = P\sqrt{1+\left(\frac{\partial S}{\partial r}\right)^2}$$

The initial conditions for this equation are obvious:

S (0, r) = 0, S (t, ∞) = 0.

Specified typical model of pressure caused by laser impulse:

$$P = \frac{1-\exp(-t^{10})}{1+\exp\big(10(t-\tau)\big)}\exp\left(\frac{r^2}{r_0^2}\right)$$

where τ is the laser impulse length, r_0 is beam width. The impulse lengths had femtosecond values at the values of the radiation flux q ~ 10 TW/cm^2. The function of the crater shape *S (t, r)* was calculated in nanometers.

In Fig. 5 shows the crater profiles for different time points. The origin coincides with the center of the laser impulse section.

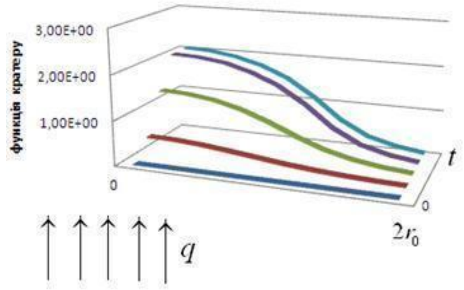

***Fig. 5** Dynamics of crater development over time*

5. Conclusion

The dynamics of the formation of corrosion crater on the surface of material subjected to destructive treatment is considered. The magnitudes of flows that lead to structural surface changes without surface melting were determined. They take values greater than 100 TW/cm^2 and depend on the properties of the irradiated material. Estimates were performed using phase diagrams, taking into account the local phase transformations of the solid surface under laser irradiation.

The phase diagrams of the equation of near surface pressure dynamics are analyzed. It is shown that the dynamics of the pressure, are significantly influenced by the parameters that determine the interaction of incident radiation with a plasma gas torch. Conformably these parameters define the process of forming a corrosion crater on the solid surface.

Asymptotic estimates of the dynamics of crater development have been performed. It is shown that the function of the shape of the crater surface is initially explosive and stabilizes in time after the ending of the affect impulse at arbitrary polytropic values. This indicates the internal consistency of the model.

The results of the numerical test calculations correspond to theoretical ideas about the process of a corrosion crater formation. Based on this, it can be argued that the constructed model theoretically describes the processes occurring on a solid surface under the influence of powerful femtosecond laser impulses.

The use of this model in the future may be useful for predicting changes on the surfaces of specific solid materials under the influence of high-power impulse radiation.

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