MATHEMATICAL PHYSICS ANALYSIS OF SURFACE HEATING AND MODIFICATION DURING LASER TREATMENT OF MATERIALS (SURVEY)

É. N. Sobol', A. L. Glytenko, and B. Ya. Lyubov

UDC 621.78:535.211

INTRODUCTION

One of the promising directions of laser technology is the action on the composition and structure of surface layers of materials in order to alter their mechanical, chemical, electromagnetic, and other properties [1-9]. Surface modification under laser heating is realized by phase transformations and chemical reactions whose course in time is governed mainly by heat and mass transfer processes. The concentration of physical and mathematical models of such processes is based to a considerable extent on the theory of heat conduction and diffusion with the most essential features of the object under investigation taken into account [10, 11]. Concepts of phase, interphasal boundaries are used here (i.e., it is assumed that the transition zone thickness is negligibly small as compared with the characteristic dimensions of the domains under consideration), and the isotropy of space and the validity of the fundamental laws of heat and mass transfer are also assumed [10, 12].

The classical theory of heat conduction can turn out to be inapplicable in the case of the action of highly intense energy fluxes on real materials and it becomes necessary to extend the Fourier law (for instance, by expanding the magnitude of the heat flux in a power series in the temperature gradient [13]), to consider deviations from the Fick law in inhomogeneous solids [14], to take account of the boundedness of the rate of thermal perturbation propagation and, therefore, to apply heat conduction equations of hyperbolic type [10, 15, 16].

Among the general features of the action of laser radiation should be the change in time and space of the thermal sources, the nonisothermy of the progressing processes, the high rate of change of the temperature limiting the role of the mass transfer or the processes on the phase interface boundary. It is assumed in the classical formulation of the Stefan problem that is utilized extensively to analyze phase transitions in condensed media [10, 12, 17-20] that the phase transition occurs at the equilibrium temperature T_k = const. Under laser treatment conditions, an additional kinetic condition relating the velocity of phase interface boundary motion to its temperature should be taken into account. If the kinetics of the phase transition or the thermally activated chemical reaction is governed by the probability of atom passage through the interphasal boundary, then in conformity with [12]

$$v = v_0 \exp\left(-\frac{E}{RT}\right)\left\{1-\exp\left(-\frac{\Delta G}{RT}\right)\right\}. \tag{1}$$

If the phase boundary motion is constrained by mass transfer, then the kinetic equation should be obtained from the solution of the appropriate mass transfer equation and can have a more complicated form [12, 14, 21].

The purpose of this paper is to survey publications of recent years on the laser heating, melting, crystallization, and amorphization, as well as to consider the features of laser hardening of alloys and the kinetics of new phase layer formation during thermochemical reactions on solid body surfaces. The main attention will hence be spent on a sequential analysis of the role of the kinetic condition in problems of laser treatment of materials.

1. PROBLEMS OF THE THEORY OF HEATING

The features of a laser heat source and problems of heating by concentrated energy fluxes are described in detail (see [1-4, 9, 22], and the literature cited there). The circle of problems having sufficiently simple analytic solutions is limited to individual cases of plate and half-space heating by fixed [4, 9, 23] and rapidly moving (uniformly and rectilinearly) heat sources [4, 24]. To obtain approximate solutions describing the temperature fields for a Gaussian

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Scientific-Research Center on Technological Lasers, Academy of Sciences of the USSR, Troitsk. I. P. Bardin Central Scientific-Research Institute of Ferrous Metallurgy, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 3, pp. 357-374, March, 1990. Original article submitted September 20, 1989.

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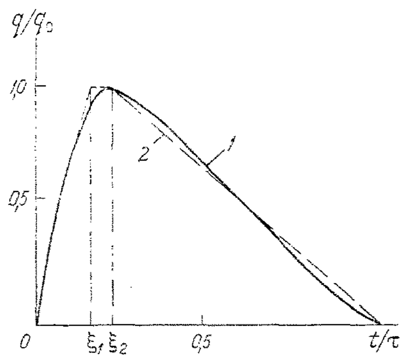

Fig. 1

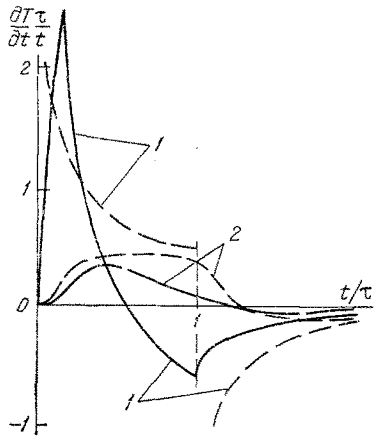

Fig. 2

Fig. 1. Laser pulse shape (1) and its approximation (2).

Fig. 2. Time dependence of the temperature rate of change $\partial T/\partial t\ \tau/T_0$ at a different distance from the surface: dashed curves for a rectangular pulse, and solid curves for trapezoidal; 1) $\hat{x} = 0$; 2) $\hat{x} = 0.5$ ($\hat{x} = x(2\sqrt{a\tau})^{-1}$).

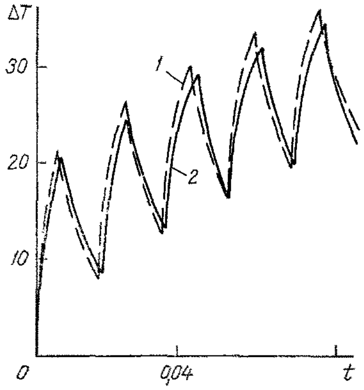

Fig. 3. Change in the surface temperature of a molybdenum specimen under pulse-periodic laser treatment: 1) computation; 2) experiment [29]; $q_0 = 317$ W/cm^2; $\tau = 9\cdot10^{-3}$ sec; $\tau f = 0.5$. ΔT, K; t, sec.

source, the saddle point method is used in [25, 26]. The computational formulas are complicated significantly in the case of real objects for treatment.

Since many articles utilized in machine construction and subjected to laser hardening are cylindrical in shape, we examine the mathematical model of heating a cylinder of radius R by a thermal source of power P that moves over the surface at the angular velocity ω and the linear velocity v_z (along the cylinder generator) [27]. If the temperature field T_i is associated with the i + 1-th rotation of the source, then $T=\sum_{i=0}^{m} T_i$ in the m + 1-th rotation. The heat conduction boundary value problem is written in a cylindrical coordinate system as

$$\begin{gathered}\frac{\partial^2 T_i}{\partial r^2}+\frac{1}{r}\frac{\partial T_i}{\partial r}+\frac{1}{r^2}\frac{\partial^2 T_i}{\partial \varphi^2}+\frac{\partial^2 T_i}{\partial z^2}=\frac{1}{a}\frac{\partial T_i}{\partial t},\\ \lambda\left.\frac{\partial T_i}{\partial r}\right|_{r=R}=\frac{P}{R}\,\delta(\varphi-\varphi_i)\,\delta(z-v_z t),\ i=0,\ 1,\ \ldots,\ m,\\ \varphi_i=\omega t-2\pi i,\quad \tau_0 m\leqslant t\leqslant \tau_0(m+1),\quad \tau_0=2\pi/\omega.\end{gathered} \tag{2}$$

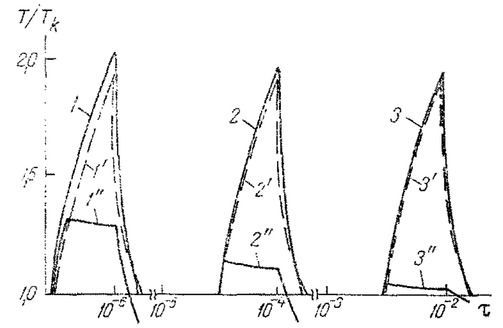

Fig. 4

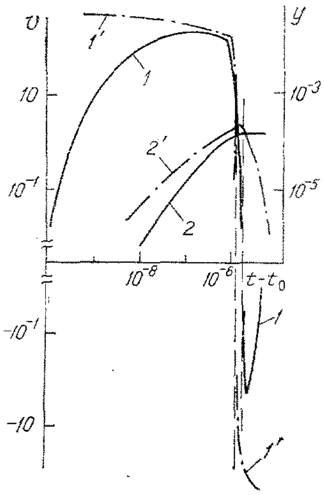

Fig. 5

Fig. 4. Temperature change during melting on a specimen surface (1, 1′, 2,2′, 3,3′) and on the interphasal boundary (1″, 2″, 3″), $t_0/\tau = 0.3$; 1, 1′, 1″) $q = 2.45 \cdot 10^6$ W/cm^2, $\tau = 10^{-6}$ sec; 2, 2′, 2″) $q = 2.45 \cdot 10^5$, $\tau = 10^{-4}$; 3, 3′, 3″) $q = 2.45 \cdot 10^4$, $\tau = 10^{-2}$, 1′, 2′, 3′) solutions in a Stefan formulation.

Fig. 5. Velocity of motion (1, 1′) and position of the interphasal boundary (2, 2′) during melting and subsequent crystallization: $q = 2.45 \cdot 10^6$ W/cm^2, $t_0 = 3 \cdot 10^{-7}$ sec, 1′, 2′) solution in a Stefan formulation. v in cm/sec, y in cm, t — t_0 in sec.

The solution of (2) by an operational method yields for $(R - r)R^{-1} \ll 1$ and $2\sqrt{at}R^{-1} \ll 1$ [27]

$$T = \frac{P}{2\pi\lambda v_\varphi} \sum_{i=0}^{m} \frac{1}{\Delta t_i} \exp\left[-\frac{(R-r)^2 + (z - v_z\xi_i)^2}{4a\Delta t_i}\right], \tag{3}$$

where $v_\varphi = \omega R$; $\Delta t_i = 1 - \xi_i > 0$; $\xi_i = (\varphi + 2\pi i)\omega^{-1}$.

In the case of a distributed thermal load the temperature field in the near-surface layer of a cylindrical body has the form

$$T(r, \varphi, z) = \sum_{i=0}^{m} \int_{\psi_i}^{t-\xi_i} d\eta \int_{v\xi_i - d/2}^{v\xi_i + d/2} \frac{qdz'}{2\pi\lambda\eta} \exp\left[-\frac{(R-r)^2 + (z - z')^2}{4a\eta}\right]. \tag{4}$$

Here $q = Pd^{-2}$, $\psi_i = 1 - \xi_i - t_d$ for $t - \xi_i > t_d = dv_\varphi^{-1}$ and $\psi_i = 0$ for $t - \xi_i < t_d$. In certain particular cases (4) is simplified and can be utilized for engineering computations. For instance, for linear heat sources stretched along and across the z axis, (4) yields respectively

$$T = \frac{qd}{2\pi\lambda v_\varphi} \sum_{i=0}^{m} \sqrt{\frac{a}{\pi\Delta t_i}} \exp\left[-\frac{(R-r)^2}{4a\Delta t_i}\right] \left\{\operatorname{erf}\left(\frac{b_{i,1}}{\sqrt{\Delta t_i}}\right) - \operatorname{erf}\left(\frac{b_{i,2}}{\sqrt{\Delta t_i}}\right)\right\},$$

$$T = \frac{qd}{2\pi\lambda} \sum_{i=0}^{m} \left\{E_1\left[\frac{(R-r)^2 + (z - v_z\xi_i)^2}{4a(t - \xi_i)}\right] - E_1\left[\frac{(R-r)^2 + (z - v_z\xi_i)^2}{4a(t - \xi_i - t_d)}\right]\right\}.$$

Здесь $b_{i,1} = (z - v_z\xi_i + d/2)(2\sqrt{a})^{-1}$, $b_{i,2} = (z - v_z\xi_i - d/2)(2\sqrt{a})^{-1}$.

Here $b_{i,1} = (z - v_z\xi_i + d/2)(2\sqrt{a})^{-1}$, $b_{i,2} = (z - v_z\xi_i - d/2)(2\sqrt{a})^{-1}$.

The development of pulse-periodic lasers and the technology of multipulse treatment requires analysis of the temperature fields with the influence of the previous laser pulses taken into account [5, 28]. Approximating the time

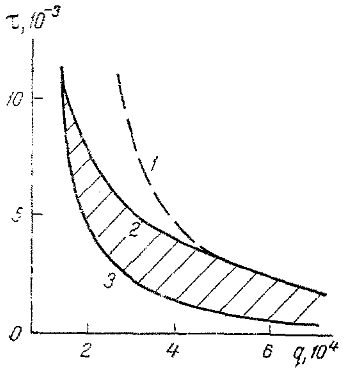

Fig. 6. Domain of allowable laser amorphization regimes (shaded): 1) $\tau = \tau^v$; 2) $\tau = \tau_0$; 3) $\tau = \tau_m$ (τ_m and τ_v are the surface heating times to the melting and boiling temperatures, respectively; τ_0 is the ultimately allowable pulse duration). τ, sec; q, W/cm^2.

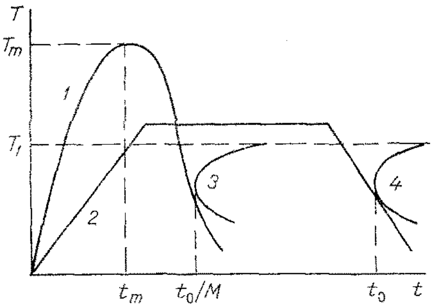

Fig. 7. Nature of the temperature change with time during tempering of steel: 1, 2) temperature mode of laser and traditional thermal treatment; 3, 4) austenite dissociation diagrams during laser and traditional tempering.

shape of a separate pulse by a trapezoid (Fig. 1) for $\tau f \ll 1$, we write the surface temperature in the form

$$\hat{T}(0, \xi) = \hat{T}_n(0, \theta) + \sum_{k=1}^{n-1} \frac{\alpha^*}{(\theta + k\hat{\tau})^{1/2}}, \tag{5}$$

where $T = T/T_0$; $T_0 = 2q_0\sqrt{a\tau}/\pi/\lambda$; $\xi = t/\tau = (n-1)\hat{\tau} + \theta$; $\hat{\tau} = (\tau f)^{-1}$; $\alpha^* = (1 + \xi_2 - \xi_1)/4$; $\xi_1 = t_1\tau^{-1}$; $\xi_2 = t_2\tau^{-1}$; $0 \leq \theta \leq \hat{\tau}$; θ is the time from the beginning of the last pulse, $\hat{T}_n(0, \theta) = \frac{2}{3}\sum_{i=0}^{3} \frac{(-1)^i(\theta - \xi_i)^{3/2}}{\xi_1(\delta_{0,i} + \delta_{1,i}) - (1 - \xi_2)(\delta_{2,i} + \delta_{3,i})}$; $\delta_{i,j}$ are Kronecker deltas (i, j = 0, 1, 2, 3). For rectangular pulses $\hat{T}_n(0, \theta) = \sqrt{\theta} - \sqrt{\theta - 1}$.

Taking account of the trapezoidal pulse shape results in the fact that the maximal surface temperature is achieved during the pulse and not at the time of its termination as in the case of a rectangular pulse, and permits determination of the maximal heating and cooling rates while the heating and cooling rates for rectangular pulses tend to infinity (Fig. 2) [29].

Comparison of computational (by using (5)) and experimental dependences of the surface temperature on the time is presented in Fig. 3 [29]. Formula (5) can be used also to compute the metal surface cold-working parameters by pulse-periodic laser radiation. As is shown in [30], the thermomechanical stresses occurring for definite values of q, f

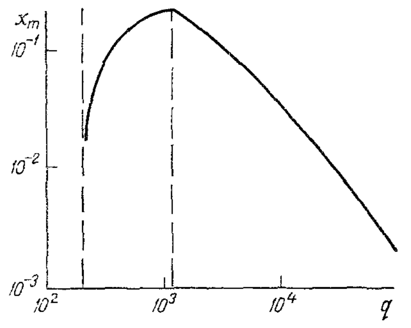

Fig. 8

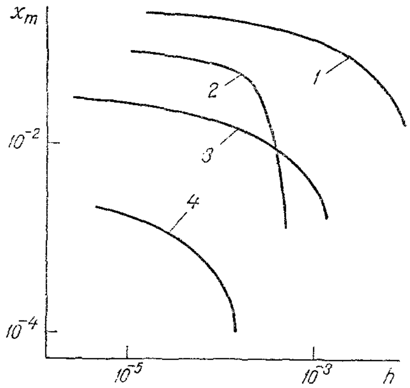

Fig. 9

Fig. 8. Maximal degree of steel tempering x_m for different energy flux densities, x_m in cm.

Fig. 9. Dependence of the maximal degree of hardening x_m on the interlamellar spacing h of pearlite structure: 1) $q = 1.16 \cdot 10^3$ W/cm^2; 2) $3 \cdot 10^2$; 3) 10^4, 4) 10^5. h, cm.

and τ result in a local plastic flow and an increase in dislocation density in the metal surface layer, which increases the mechanical strength on the one hand, and lowers the surface ray strength threshold on the other.

Therefore, the solution of the simplest heating problems in a linear formulation permits analytic expressions to be obtained for qualitative estimates, and even for a quantitative computation of laser surface modification regimes in a number of cases and can also be utilized to construct the solutions of more complex, including nonlinear, problems [20, 31]. Numerical methods [32] are successfully used to obtain detailed quantitative information about laser heating parameters for real materials.

2. SURFACE MELTING, CRYSTALLIZATION AND AMORPHIZATION

Melting and crystallization are mutually symmetric processes of boundary motion between a liquid and solid body and (in the case of a planar interphasal boundary) can be considered by using a single mathematical model describing the kinetics of a phase transition of the first kind [12, 14, 18]. The simplest one-dimensional formulation of the heat conduction problem without taking account of melt motion and temperature dependences of the material characteristics for the liquid (i = 1) and solid (i = 2) phases in the case of laser heating has the form [10, 17]

$$\frac{1}{a_i}\frac{\partial T_i}{\partial t} = \frac{\partial^2 T_i}{\partial x^2}, \quad i = 1,\ 2, \tag{6}$$

$$-\lambda_1 \frac{\partial T_1}{\partial x}\bigg|_{x=0} = \begin{cases} q, & t \leqslant \tau, \\ 0, & t > \tau, \end{cases} \tag{7}$$

$$-\lambda_1 \frac{\partial T_1}{\partial x}\bigg|_{x=y} = Q\frac{dy}{dt} - \lambda_2 \frac{\partial T_2}{\partial x}\bigg|_{x=y}, \tag{8}$$

$$\frac{\partial T_2}{\partial x}\bigg|_{x=\infty} = 0, \quad T_2|_{x=\infty} = 0. \tag{9}$$

For a sufficiently slow temperature change (for relatively small q) the phase boundary temperature differs insignificantly from the equilibrium value and the Stefan formulation of the problem (6)-(9) is valid with the condition

$$T_1(y,\ t) = T_2(y,\ t) = T_k. \tag{10}$$

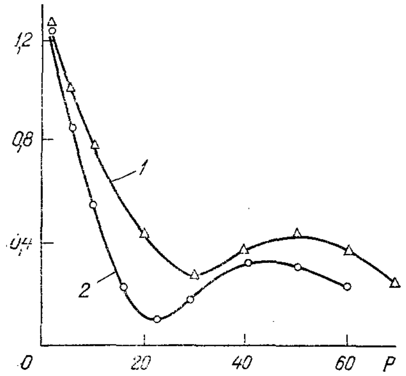

Fig. 10. Dependence of the degree of calcite decomposition S on the external pressure P_e; ($\tau \simeq 1$ msec, pulse energy 22 J): 1) treatment in a nitrogen atmosphere; 2) in a carbon dioxide gas atmosphere. S, mm; P, atm.

The temperature field

$$T(x, t_0) = T_k \left\{ \exp\left(-\frac{x^2}{4at_0}\right) - \frac{x}{2}\sqrt{\frac{\pi}{at_0}}\,\mathrm{erfc}\left(\frac{x}{2\sqrt{at_0}}\right)\right\}$$

that occurs at the time of the beginning of melting $t_0 = \pi(T_k\lambda/2q)^2a^{-1}$ is taken as initial condition.

A large number of papers (see [3, 10, 12, 14, 15, 17, 33], and the literature cited there) is devoted to investigation of the melting and crystallization processes in a Stefan formulation. Typical additional assumptions taken in solution of the problem (6)-(10) are neglecting the heat of phase transition [34] and heat removal in the solid phase [32], the assumption of rapid mixing or instantaneous removal of the melt being formed [4, 10, 31]. A numerical solution of the problem (6)-(10) without these assumptions is obtained in [35].

The disadvantage of the Stefan formulation of the problem is the neglect of the kinetic relationship that sets up a dependence of the process rate on the degree of overheating or overcooling of the phase boundary with respect to T_k. The motive force of the process is the difference in the chemical potentials $\Delta\mu$ in the solid and liquid phases. For melting $\Delta\mu < 0$ and the excess T_k increases the motive force and mobility of the atoms, resulting in rapid growth of the potentially possible velocity of phase boundary motion. Consequently, the Stefan formulation turns out to be acceptable in many situations for the analysis of melting [10]. In the crystallization case, overcooling increases the motive force but the atom mobility diminishes whereupon the dependence of the crystallization rate on ΔT has a maximum. The influence of overcooling on the crystallization kinetics is examined in detail in the monographs [12, 17, 33].

As q increases, melting occurs under condition of a heat excess and the appearance of noticeable overheating of the phase boundary can be expected. Thus, experimental investigations of the melting process by short laser pulses [36] demonstrated the substantial role of the processes on the interphasal boundary and permitted estimation of the overheating that achieved 0.66 T_k.

An attempt is made in [37] at a theoretical explanation of the possibility of solid body overheating under laser action on the basis of the Frenkel' vacancy model [38] according to which melting sets in when the vacancy concentration exceeds a certain ultimately allowable value. It is assumed here that all the thermal energy is expended in vacancy formation while the melting rate is limited by their diffusion displacement. The weak spot of the vacancy model is that in real crystals the vacancy concentration to T_k is not very large (of the order of the atom concentration in a saturated vapor [38]) so that it is difficult to expect a substantial lowering of the melting activation energy because of interaction between vacancies. The joint solution of the thermal and diffusion problems is needed to construct a quantitative dependence $\Delta T(q)$ on the basis of a vacancy model. At the same time the existence of overheating during melting follows from the phenomenological equation (1). The limiting role of the processes on the phase separation boundary during melting and crystallization was analyzed on the basis of (1) in [35, 36, 39-44]. However, utilization of a number of approximations to describe the temperature field and the melting rate [41-43], neglect of the heat of phase transition, and overheating of the melt during analysis of the last crystallization [40] make estimation of the accuracy of the computations presented and the qualitative estimates difficult.

A more complete examination of melting and crystallization of a thin metal layer subjected to laser radiation is performed in [35, 44] by using the Biot variational method and numerical means. The solution of the problem (6)-(9) was here determined both with the kinetic equation (1) taken into account and in a Stefan formulation. The kinetics of

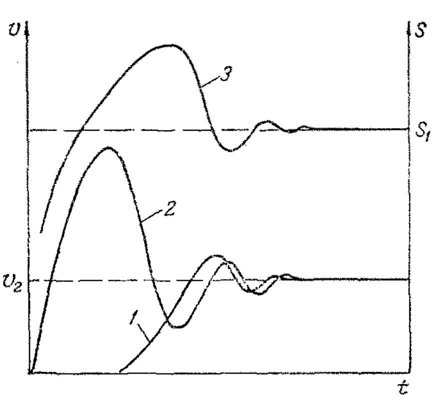

Fig. 11

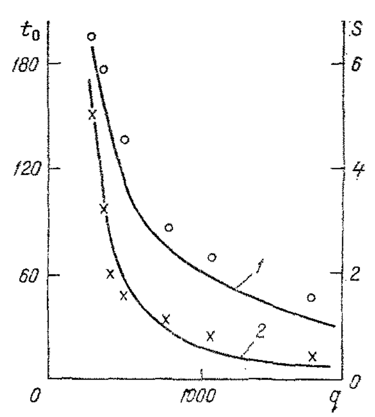

Fig. 12

Fig. 11. Nature of the time dependences of the motion velocities of the evaporation (1), decomposition (2) fronts and the new phase layer thickness (3).

Fig. 12. Theoretical (curves) and experimental (points) dependences of the new phase layer thickness (1) and the time of quasistationary calcite destruction regime build up (2) on the laser flux density. t_0, sec; S_1, mm.

the temperature change, the motion velocity and location of the phase separation boundary is shown in Figs. 4 and 5. Overheating and the melting rate grow in the initial melting stage. The maximal value of ΔT in Fig. 4 corresponds to the maximal value of v in Fig. 5. Further growth of the depth of melting results in a reduction in ΔT and v. An increase in the heat flux density specifies growth of ΔT and v. After termination of the laser pulse, the temperature and velocity of motion of the melting front decrease rapidly (Fig. 5) and the crystallization process starts that is developed in the reverse direction. Because of the rapid cooling of the melt, the crystallization rate passing through the maximum also diminishes and an uncrystallized layer of overcooled fluid, an amorphous layer, remains on the surface for definite laser pulse parameters. The condition necessary for amorphization of the surface has the form

$$\frac{\nu_0 d_0 L N_A R T_k^2}{\varepsilon E^2 l} \exp\left(-\frac{E}{RT_k}\right) < 1. \tag{11}$$

The laser pulse duration τ for amorphous layer formation should not exceed the ultimate allowable value $\tau_0(q)$. Since $\tau > \tau_m(q)$, the range of allowable values of τ increases as q grows (Fig. 6) and a minimal value q_{min} exists below which laser amorphization becomes impossible. Let us emphasize that the solution of the crystallization problem in the Stefan formulation does not, in principle, permit clarification of the amorphous layer formation condition since the rate of growth of the cooling does not result in formation of an overcooled layer but to acceleration of emergence of the crystallization front on the surface. Analysis shows [35, 44] that for small q thermodynamic equilibrium is set up more rapidly on the interphasal boundary than the change in the temperature field occurs, and the temperature of the phase separation boundary does not differ, in practice, from T_k (the Stefan formulation is applicable). As q grows, the heating and cooling rates increase and the role of the kinetic processes on the phase boundary rises.

Condition (11) is necessary but not sufficient for surface amorphization since the generation and growth of crystalline seeds in the bulk of the melt are possible in addition to the epitaxial crystallization examined above, where the bulk crystallization can become predominant for sufficiently high cooling rates [45-47].

For significant overcoolings ($\Delta T' \gtrsim 0.2T_k$) it is thermodynamically favorable to form crystalline seeds with dimensions on the order of the interatomic spacings [38, 48] and the crystallization rate of a layer melted by a laser beam is determined by the activation energy of the atom displacement in the melt [49-51]. Amorphization occurs if the cooling rate is sufficiently high, i.e., during achievement of the vitrification temperature domain ($T_g \sim 0.5T_k$) the crystalline coating is not formed successfully.

In conformity with [17], the kinetic equation for the crystalline seed size distribution function has the form

$$\frac{\partial f}{\partial t} = \nu_0 d_0 \exp\left(\frac{E}{RT}\right) \frac{\partial}{\partial \rho} \left\{\frac{d_0^3}{4\pi\rho^2} \frac{\partial f}{\partial \rho} - \frac{L N_A (1 - T/T_k)}{RT}\right\}. \tag{12}$$

Solution of (12) with the boundary conditions

$$f(\rho,\ x,\ t)|_{\rho=0} = \frac{N}{\rho_1},\quad f(\rho,\ x,\ 0)|_{\rho>0} = 0,\quad \lim_{\rho\to\infty} f(\rho,\ x,\ t) = 0$$

permits calculation of the fraction of melt being crystallized and the cooling rate ε_0 [51] needed for amorphization. The maximal pulse duration τ_0 at which surface amorphization is possible is determined by the expression

$$\tau_0 = \frac{40RT_k^2(5E(3RT_k)^{-1} - 1)}{\pi\varepsilon_0 E}. \tag{13}$$

Estimates for alloys on an iron base yield $\varepsilon_0 \sim 10^{10}$ K/sec, $\tau_0 \sim 3.6\cdot10^{-6}$ sec, $l \sim 3\cdot10^{-4}$ cm.

The amorphous state obtained because of laser melting is nonequilibrium, the possibility of its dissociation is governed exclusively by the atom mobility [52-56]. The main attention in investigation of amorphous layer stability is ordinarily paid to thermally activated dissociation [55] but thermomechanical stresses due to inhomogeneous heating of layers with different thermal expansion coefficients can also become a reason for destruction of the modified surface. Analysis of a model of mechanical exfoliation of an amorphous layer shows [57] that surface destruction does not occur if the magnitude of the residual stresses does not exceed a certain critical value $\sigma_0 < \sigma_m$ or if the amorphous layer thickness does not exceed

$$l_m = \frac{6E_2\gamma}{(1-\nu)\sigma_0^2}. \tag{14}$$

3. LASER HARDENING

The physical features of laser hardening are examined in an example of tempering iron carbide alloys [58-61]. The process of tempering steel that consists of freezing a supersaturated solid solution of carbon in iron can provisionally be separated into four stages: heating, $\alpha\to\gamma$ phase transformation, diffusion of the carbon redistribution in austenite and rapid cooling at rates exceeding the critical tempering rate (see Fig. 7). Two $\alpha\to\gamma$ transformation mechanisms are possible in solid bodies: shear (martensite) and fluctuation (diffusion) [12]. In contrast to slow heating at which the $\alpha\to\gamma$ transformation occurs at a constant temperature, the phase transition is realized under laser heating, in a temperature range whose magnitude increases as the heating rate grows [59, 60]. The kinetics of austenization in the fluctuation mechanism is limited by carbon diffusion from the cementite inclusions being dissolved to the growing austenite plates. Low carbon austenite is formed in a shear $\alpha\to\gamma$ transformation but a definite saturation of this austenite by carbon is necessary to obtain the hardening effect, otherwise, rapid cooling will result in low-carbon ferrite formation, i.e., a supersaturated solid solution of carbon in α iron (martensite) is not obtained [59]. Therefore, diffusion limits the laser hardening process for both the diffusion and the diffusion-free phase transition mechanisms, and the correct description of the laser hardening processes should be based on the combined analysis of the thermal and diffusion problems under conditions of an intense energy suppy for domains with moving boundaries [58-60, 62-64].

There is a sufficiently high number of publications ([65-68], say) in which the thickness δ of the hardened layer is determined by the position of the isotherm T_1. Such an approach results in satisfactory results for alloys with a sufficiently fine initial structure, but exaggerates the value of δ to some extent in the general case [60]. A concept introduced in [72, 73] of a shift in the critical points of the beginning and ending of the phase transitions is used to diminish the the discrepancy between the experimental and theoretical results in [69-71]. In conformity with (1), the shift of the critical points should actually occur but for relatively small q ($\sim10^4$ W/cm^2) that are ordinarily used in the laser tempering of alloys, the magnitude of the overheating is negligible (see section 2) so that the beginning and completion of austenitization of steel occurs near the equilibrium temperature T_1 [58, 59]. Consequently, the introduction of a shift in the critical points of the $\alpha\to\gamma$ transformation in the computational scheme is an artificial method that, although it does not correspond to the real physical situation, will permit matching the computed and experimental values of δ for an appropriate selection of the quantity ΔT. The common disadvantage of [65-73] is the lack of an analysis of the kinetics of the phase transformation and mass transfer process. The model proposed in [61] for the austenization of steel based on the joint examination of the thermal and diffusion problems explains overheating above the equilibrium temperature T_1 by the necessity to continue heating to assure displacement of the interphasal boundary a distance equal to half the interlamellar spacing. The diffusion problem in a growing austenite plate has the form

$$D(T)\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t},\quad y_1(t) \leqslant x \leqslant y_2(t), \tag{15}$$

$$C(y_1,\ t) = C_1(T),\quad C(y_2,\ t) = C_2(T), \tag{16}$$

$$(C_c - C_1)\frac{dy_1}{dt} = D\frac{\partial C}{\partial x}\Big|_{x=y_1}, \quad (C_2 - C_f)\frac{dy_2}{dt} = -D\frac{\partial C}{\partial x}\Big|_{x=y_2}, \tag{17}$$

$$D = D_0 \exp(-E/RT). \tag{18}$$

The functions $C_1(T)$ and $C_2(T)$ are determined by approximating the iron-carbon equilibrium diagram curves. The thermal problem can be examined in some formulation as a function of the laser treatment conditions [74].

The nonisothermal diffusion problem was investigated in [60-64]. The thickness of the tempered layer was computed on an electronic computer in [61] according to the size of the domain in which total austenitization, limited by carbon diffusion, proceeds successfully and whose cooling rate is greater than the critical value. The solution of the diffusion problem in an isothermal formulation for a constant D [14] was used here and the change in the diffusion coefficient and the equilibrium carbon concentrations with temperature on the austentie plate boundaries was taken into account by introduction of the effective temperature for each temperature range. The problem of austenization of a steel surface layer under the action of continuous laser radiation reduced to a system of integro-differential equations that were solved by using an electronic computer. The approximate analytic solution of the problem (15)-(18) was constructed in [60] by replacing the isothermal diffusion by the result of an equivalent isothermal process that occurs at the maximal temperature during the effective time $t_e < \tau$. An analogous approach was used earlier to investigate the kinetics of metal oxidation [75], it is sufficiently effective in those cases when the rate of the process grows abruptly as the temperature rises (see [62, 76, also].

In conformity with [60], the following formulas can be used

$$\delta = \delta_1 \simeq \frac{2}{\sqrt{\pi}}\sqrt{a\tau} - \frac{\lambda T_1}{q}, \quad h \leqslant BD_m\tau/2, \tag{19}$$

$$\delta = \delta_2 \simeq -\frac{\lambda T_1}{q} + \sqrt{\frac{1}{4}\left(\frac{\lambda T_1}{q} + \frac{4a\tau}{\pi}\,\frac{q}{\lambda T_1}\right)^2 - \frac{4ah^2}{\pi BD_m}}, \quad h > BD_m\tau,\ D_m = D(T_m) \tag{20}$$

to estimate δ as a function of the characteristic dimension h of the initial structure. The quantity B is determined from the solution of a system of transcendental equations [60]. It is essential that the quantity B be ten times greater during the shift transformation then for the diffusion $\alpha \to \gamma$ transition. As q and τ grow, the quantity δ grows until the surface temperature reaches the ultimately allowable value $T_2 \le T_k$. As q increases further, maintenance of $T = T_2$ on the surface requires an appropriate diminution in τ resulting in a lowering of δ. The maximal value of δ is achieved for

$$\tau_m = 4t_0\omega^{-2}, \quad q_m = \frac{1}{4}\sqrt{\frac{\pi}{at_0}}\,\lambda T_2\omega, \tag{21}$$

where $\omega = T_2T_0^{-1} + T_0T_2^{-1}$. Therefore, the optimal laser tempering conditions are determined by the thermophysical properties of steel, the values of the melting temperature, and the phase equilibrium as well as the position of the "nose" of the austenite dissociation diagram (Fig. 7). For given values of h and τ there exist a minimal value q_1, below which tempering is impossible even for the near-surface layer, and the maximum value

$$q_2 \simeq \frac{\pi\lambda T_k^2}{4T_1h}\sqrt{\frac{BD_m}{a}},$$

upon exceeding which the surface melts more rapidly than diffusion processes succeeded in occurring. The conditions for realizability of laser tempering reduce to the inequality

$$\left(\frac{T_1T_0}{T_2^2} + \frac{T_1}{T_0}\right)^2 < \pi BD_m t_0/h^2. \tag{22}$$

If the alloy characteristics do not satisfy (22), then only partial tempering or tempering with surface melting is possible. Since the role of the shift mechanism of the $\alpha \to \gamma$ transformation grows during laser heating, the quantity B increases, the range of allowable regimes is broadened substantially and the possibility appears of hardening of those alloys for which the traditional tempering appeared to be impossible.

A more exact quantitative investigation of nonisothermal austenization of subsequent tempering is performed in [64]. The dependence $x_m(q)$ is presented in Fig. 8 while the influence of the initial structure on the thickness of the tempered layer is shown in Fig. 9. It follows from Fig. 9 and (20) that growth of the interlamellar spacing results in diminution of the hardened layer thickness.

Analysis of laser hardening of steels of noneutectic composition can be performed in an analogous manner on the basis of more complex diffusion problems [17, 59, 62]. A situation is possible in pre-eutectoid steels for which the pearlite is transformed into austenite by fluctuation means while the free ferrite is transformed by shift (with the formation of low-carbon austenite) [59]. Consequently, by changing the heating rate, the degree of inhomogeneity of the austenite and the dispersity of the carbide phase can be regulated. In steels of pre-eutectoid composition the incomplete dissolution of carbides and the regulatable austenite inhomogeneity permit realization of a more complete transformation of austenite into martensite, which assures a rise in hardness as compared with traditional tempering methods [62, 77].

One of the fundamental conditions for the formation of a tempered structure is sufficiently rapid cooling of the alloy for which the temperature curve does not intersect the C-shaped austenite dissociation diagram (see Fig. 7). The austenite features obtained during laser heat treatment (fine-graininess, inhomogeneity of the chemical composition, high lattice defect density) diminish its stability substantially and result in a shift of the dissociation diagram to the left, i.e., very much higher cooling rates are required than for the ordinary heat treatment of steel [59, 79]. When using handbook data [80] of t_0, T_0 in computations with (21) and (22), the errors in determining the optimal laser tempering regimes can be quite appreciable.

The magnitude of the shift of the C-shaped curve (Fig. 7) was investigated in [79]. Taking into account that austenite dissociation during a rapid change in temperature can be described by using the theory of isokinetic phase transition [12], we obtain for the dissociation diagram parameters [79]

$$T_0 = T_1\left[1 - \frac{2}{3}\sqrt{\frac{\beta\sigma^3}{3QE}}\right], \quad t_0 = \left[-\frac{\ln(1-\xi)}{F(T_0)}\right]^{1/n}, \qquad (23)$$

$$F(T) = \beta N\nu_0\left(\frac{2D_0}{h}\alpha\right)^3 \exp\left[-\frac{A_0 + nE}{RT}\right],$$

where n is a parameter whose value varies between 1 and 4 [12] depending on the mechanism and kinetics of the process.

In conformity with (23) T_0 is practically independent of the cooling rate, the degree of transformation and is diminished slightly as the diffusion activation energy grows. The quantity t_0 depends much more strongly on E. As E diminishes s times, t_0 diminishes M times

$$M = \eta \exp\left[\frac{E}{RT}(1 - s)\right]. \qquad (24)$$

Here η is the fraction of atoms taking part in the diffusion process with a lowered activation energy.

The reduction in E in the laser treatment of pre-tempered steel is due principally to an increase in the dislocation density. In this case $E/RT = 18$, $s = 0.5$, $\eta = 10^{-3}$ [12] and (24) yields $M = 10$. As steel hardens from the initial pearlite structure, crushing of the grain reduces to an increase in the role of the grain-boundary diffusion of carbon. Since $\eta \sim L^2$, where L is the characteristic grain size, then halving L results in a quadruple diminution of t_0.

4. NEW-PHASE LAYER FORMATION UNDER LASER THERMOCHEMICAL REACTIONS CONSTRAINED BY GAS TRANSFER

The limiting role of gas transfer is characteristic for different processes on a surface being exposed: in laser oxidation and reduction of metals, synthesis and decomposition of nitrides, carbides, and other compounds including high-temperature superconductors.

When analyzing laser thermochemical reactions that occur in a solid body with gas absorption or liberation, we will consider the absorbed energy flux q constant without examining thermooptical effects [81].

On the surface of an initial substance A subjected to laser radiation let a layer be formed of a new phase B of thickness S through which a gas C migrates. We write the chemical decomposition and synthesis reactions in the form $A \rightarrow B + C$ and $A + C \rightarrow B$, respectively. The direction of the reaction is governed by the sign of the Gibbs thermodynamic potential $\Delta G = \Delta H - T\Delta S$ where ΔH and ΔS are the changes in system enthalpy and entropy. In conformity with the theory of chemical equilibrium, the pressure on the chemical reaction front is related to the temperature by the Arrhesius law

$$P_S = P_0 \exp\left(-\frac{\Delta H}{RT_S}\right), \quad P_0 = \exp\left(\frac{\Delta S}{R}\right). \qquad (25)$$

The kinetics of the thermochemical reaction is governed by processes on the phase separation boundary and the mass transfer of the products (or components) of the reaction [12]. The reaction rate for thin layers is controlled by atom passage through the phase boundary and the velocity of transformation front motion is governed by (1). As the layer thickness S(t) increases, the heat and mass transfer through it are retarded and the process is limited by the kinetics of gas transfer when a certain value S_0 is exceeded [82]. Considering the new phase layers continous and considering gas diffusion, the experimental results can be explained qualitatively in many cases but quantitative agreement between theory and experiment is not always observed by far, where the difference can reach several orders of magnitude [83]. The real structure of the layers being formed, which are porous to some degree or other [82], must be taken into account for a more exact description of the kinetics of thermochemical reactions.

Analysis of the mass transfer mechanisms in porous layers shows [21] that the total gas flow is represented in the form $j = D_e \nabla\rho$, where $\nabla\rho$ is the gas density gradient and

$$D_e = \frac{A_1 T^r}{P + A_2 T^{r-1/2}} + KP + D_0 \exp\left(-\frac{E}{RT}\right). \tag{26}$$

The first term here corresponds to Knudsen flow and gas diffusion in pores, the second to hydrodynamic filtration, the third to solid-state diffusion, A_1, A_2, K, r, D_0 are constants [21], $P = (P_S + P_e)/2$, and P_e is the external gas pressure. In conformity with (26), D_e depends non-monotonically on P_e and T. An experimental dependence of the location of the calcite decomposition front S on P_e is presented in Fig. 10 [84]. An increase in the external pressure retards the chemical reaction that occurs with CO_2 liberation. However, for a definite value of P filtration, whose intensity increases abruptly with the growth of P, resulting in an increase in S, becomes the predominant mass transfer mechanism. As P_e approaches P_S the pressure gradient is small, the mass transfer is slowed down, and the quantity S diminishes.

Using the equation of state of an ideal gas $\rho = PM_c(RT)^{-1}$ and the mass conservation law, we obtain an expression for the velocity of the phase separation boundary motion

$$v = \pm\frac{M_A D_e (P_e - P_S)}{\gamma_A SRT}. \tag{27}$$

Here M_A, γ_A are the molecular weight and density of the initial substance, and the plus corresponds to the synthesis process and the minus to dissociation. Taking account of the density change, we find [21, 85]

$$\frac{dS^2}{dt} = \frac{2M_B D_e |P_e - P_S|}{RT\gamma_B}. \tag{28}$$

For a constant temperature the solution of (28) has the form

$$S = \sqrt{\frac{2M_B D_e |P_e - P_S|}{R\gamma_B T} t}, \quad v = \sqrt{\frac{M_B D_e |P_e - P_S|}{2R\gamma_B T t}}.$$

The growth rate of the new phase layer depends on the time, temperature, the pressure drop (that is determined by the external gas pressure and the temperature of the chemical reaction front), and also the effective gas transfer coefficient that depends, in turn, on the temperature and pressure. A change in the gas mass transfer mechanism can result in a non-monotonic dependence of the chemical reaction rate on the temperature [86, 87] and permits explanation, in particular, of the experimental results of laser oxidation of copper [83]. The effect of diminution of the copper oxidation rate during laser heating of a target in a definite temperature range is described in [83] and the cited explanation yields a quantity two orders of magnitude less than observed in test.

The surface temperature under laser heating conditions is maintained constant if the energy flux density diminishes [85]. For q = const a phase transformation occurs under nonisothermal conditions and overheating of the reaction products layer specifies the possibility of the origination of two process features. Firstly, the equilibrium gas pressure P_E grows sharply as the temperature rises and as the strength limit of the material is exceeded can result in its destruction. Such a low-energy mechanism explains the experimental results on laser destruction of marble [85, 88] and high-temperature superconductors (HTSC) [86, 87]. Thus the threshold ablation of $YBa_2CU_3O_x$ films by excimer laser pulses of 20-30 nsec duration is 0.1 J/cm^2, which agrees with 10% accuracy with the energy density needed for origination of a vibrational regime of HTSC decomposition with an oxygen pressure exceeding 10^3 atm [86]. Consideration of other destruction mechanisms results in the necessity of much higher energy expenditures [86].

The second feature of laser thermochemical reactions associated with overheating of the phase transition front is that for a sufficient duration of the laser action on the surface being exposed, another phase transition (melting, evaporation, or a different chemical reaction) can start and the problem with two moving phase separation boundaries must be considered to analyze the process. Let us examine such a problem in an example of calcite decomposition with simultaneous evaporation of the reaction product layer [85]. Formulation of the problem includes the heat conduction equations for the phases A and B, the condition for their ideal thermal contact, the energy balance on the evaporation surface and on the chemical reaction front, and also the kinetic conditions on the phase boundaries

$$\frac{1}{a_i}\frac{\partial T_i}{\partial t}=\frac{\partial^2 T_i}{\partial x^2},\quad i=A,\ B;\quad T_A(y_d,\ t)=T_B(y_d,\ t)=T_d(t),$$

$$-\lambda_B\frac{\partial T_B}{\partial x}\bigg|_{x=y_e}=q-Q_e v_e(t);\quad -\lambda_B\frac{\partial T_B}{\partial x}\bigg|_{x=y_d}=-\lambda_A\frac{\partial T_A}{\partial x}\bigg|_{x=y_d}+Q_d v_d(t),$$

$$v_e=v_0\exp\left(-\frac{Q_e M_B}{\gamma_B RT_e}\right),\quad v_p=\frac{M_A D_e(T,\ P)(P_E-P_e)}{\gamma_A S(t)RT_p(t)},\tag{29}$$

$$\frac{dS}{dt}=v_p(t)-v_e(t),\quad T_A(\infty,\ t)=0,\quad v_p=\frac{dy_p}{dt},\quad v_e=\frac{dy_e}{dt}.$$

Here the rate of layer growth equals the difference in the decomposition and evaporation boundary motion velocities.

For constant values of the temperature on the evaporation T_e and decomposition T_d boundaries, the problem (29) has a quasistationary solution in conformity with which both phase boundaries move at the identical constant velocity v_1 while the thickness of the new phase layer S_1 does not change with time. The quantities v_1, S_1, T_d and T_e are determined from the solution of a system of four equations

$$v_1=q\,[Q_e+Q_d+c_A T_d+c_B(T_e-T_d)]^{-1},\quad v_1=\frac{M_A D_e(P_E-P_e)}{\gamma_A S_1 RT_p},$$

$$v_1=v_0\exp\left(-\frac{Q_e M_B}{\gamma_B RT_e}\right),\quad S_1=\frac{a}{v_1}\ln\left[1+\frac{c_B(T_e-T_d)}{Q_d+c_A T_d}\right].\tag{30}$$

Analysis of the nonstationary problem shows that changes in the fundamental parameters with time are vibrational in nature (Fig. 11) [21, 86]. The number of vibrations and the buildup time of the quasistationary destruction regime depend on not only thermophysical processes but also on mass transfer kinetics. For a strong dependence of D_e on T (for instance, when filtration is the predominant transfer mechanism), the system can perform one-two vibrations, as was indeed observed in an investigation of the laser destruction of calcite [85]. A comparison between the experimental and theoretical dependences of the new phase layer thickness and the build-up time of the quasistationary regime on the energy flux density is presented in Fig. 12.

The quasistationary motion regime considered for the two phase boundaries does not hold in all cases. For certain combinations of the problem parameters the system (30) has no solution. The vibrations do not damp out, i.e., the limiting role of the mass transfer specifies the possibility of vibrational (with damping), self-vibrational or unstable thermochemical reaction regimes even for a constant absorbed radiation energy density. Let us note that gas temperature and pressure fluctuations in a definite range of parameters can also occur for one phase transition and exactly as the vibrational laser sublimation regimes [89] be of thermal nature. If volume light absorption by a substance is substantial, then the temperature maximum at a surface energy sink is at a certain distance from the surface being exposed. The phase boundary displacement in a hotter domain specifies the possibility of a short-time excess of the stationary value of the front velocity. Such a vibrational decomposition regime occurs, in particular, under the effect of ultraviolet radiation on $YBa_2Cu_3O_{7-x}$ [86].

Thermochemical reactions on the surface of solid bodies with oxygen absorption or liberation play a decisive role in HTSC dissociation and synthesis processes [87] and can be utilized for laser modification of HTSC films in order to superpose superconducting and insulating tracks [90-92], to crystallize amorphous layers [91], and change optical properties locally [92, 93].

As is shown in [92], the thresholds of an abrupt change in the light reflection and absorption coefficients are related to the beginning of intensive HTSC decomposition and are described well by a thermal model. The solution of the heat conduction problem for a film-substrate system with the real pulse shape taken into account yields [94]

$$\Phi=cThG(\tau)A^{-1}.$$

Here the function $G(\tau_0)$ describes the energy losses associated with the substrate. By approximating the time shape of the pulse by a step $q(t) = \varepsilon q_0$ ($\varepsilon = 1$ for $0 \leq t \leq \tau_1$ and $\varepsilon < 1$ for $\tau_1 < t < \tau$), we obtain [92]

$$G(\tau)=B^2\tau_1[(1-\varepsilon)F(\tau_1)+\varepsilon F(\tau_0)]^{-1},$$

$$F(\tau)=\exp(B^2\tau)\operatorname{erfc}(B\sqrt{\tau})+\frac{2}{\sqrt{\pi}}B\sqrt{\tau}-1.$$

The characteristic values of Φ for which stabilization of the optical properties is observed are related to termination of the decomposition process and can be computed by using a thermal model for sufficiently long laser pulses at which the mass transfer does not limit the chemical reaction. As experiments show, taking account of mass transfer becomes essential for $\tau \lesssim 10^{-7}$ sec [92] under exposure of YBaCuO films to CO_2 laser radiation.

Analysis of the conditions for completion of the phase transitions on a HTSC surface is associated with investigating the decomposition and subsequent melting of a multicomponent system as well as the kinetics of mass transfer under nonisothermal conditions.

CONCLUSION

The development of investigations of solid body surface modification processes proceeds in the direction of detailing the physical pattern of the phenomenon, the introduction of additional factors into the computational scheme, and the development of adequate mathematical methods. Coefficients here often appear in the theory whose determination can be an independent problem. More complicated models describe the process more exactly but their application is fraught with known difficulties. A sufficiently complete investigation can be performed for a combination of relatively simple approximate analytic solutions and detailed numerical computations for the most important particular cases.

A laser thermal source inserts definite features in different surface modification processes which appear in known proximity to mathematical models and generality of approaches to the solution of nonisothermal problems. We examined certain such general features, associated with the limiting role of processes on the phase separation and mass transfer boundary in this paper. Their analysis permitted clarification and description of a number of regularities and effects such as treatment of an amorphous layer and the conditions for its thermomechanical stability, the dependence of steel hardening process parameters on the state of its initial structure and heating rate, the non-monotonic nature of the dependences of the chemical reaction rate on the temperature and pressure, the optimal conditions of HTSC dissociation and synthesis, the change in the optical properties and low energetic mechanism of laser ablation of HTSC films, etc.

Let us note that a number of substantial questions remained outside the framework of the present survey both because of inadequate developments of some of them (for example, the regularities of laser hardening of doped alloys [58, 59] as well as phase transitions for which the concept of a phase separation boundary is unacceptable) and also in connection with their independent value (for instance, the hydrodynamic flow of a melt [3, 28, 95, 96], surface electromagnetic waves [97-99], development and interaction of different instabilities [100, 101], chemical reactions in gases and the liquid phase [8, 102, 103], etc.). Each of the listed questions deserves individual detailed analysis.

NOTATION

T_k, phase transition equilibrium temperature $\Delta T = T - T_k$, E, diffusion activation energy; v_0, constant on the order of the sound speed in a solid body; q, energy flux density; d, characteristic laser beam dimension; τ, laser pulse duration; f, pulse repetition rate; λ, heat conduction; a, thermal diffusivity; Q, heat of phase transition of unit volume; y and v, location and motion velocity of the phase separation boundary; ε, mean cooling rate; R, gas constant; l, maximal degree of melting; ν_0, mean frequency of atom passage through the phase boundary; d_0, characteristic length of the atom jump during passage from one phase to another; L = Q/N; N, number of atoms per unit volume; ρ_1, characteristic atom dimension; E_2, Young's modulus; ν, Poisson ratio; γ, specific energy of separation surface formation; δ, tempered layer thickness; C, carbon concentration; C_c, C_f, $C_1(T)$, $C_2(T)$, values of the carbon concentration in cementite, ferrite, and on the edges of an austenite plate, respectively; D, diffusion coefficient; D_e, effective mass transfer coefficient of gases; α, diffusion problem parameter [12]; σ, surface energy; β, grain shape parameter; ξ, degree of transformation; A_0, work of new phase seed formation; $\Phi = q\tau$, energy density; and c, specific heat per unit volume.

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MASS TRANSFER IN THE PROCESS OF PULSED LASER ALLOYING OF TITANIUM IN NITROGEN VAPORS

S. A. Astapchik, A. A. Uglov, I. Yu. Smurov, K. I. Tagirov, and T. N. Khat'ko

UDC 536.25:535.21

Thermocapillary mass transfer accompanying pulsed laser alloying of titanium in vapors of liquid nitrogen is studied. The impurity concentration fields are determined by the methods of numerical modeling. The numerical and experimental results are compared.

Mass transfer accompanying laser alloying of materials is the subject of intense scientific studies [1]. It has been shown in a number of experiments, for example, in [2-4], that the redistribution of impurities occurs practically over the entire depth of the melt pool. This in its turn results in the formation of different structures of the zones of alloying. Since in technological applications the characteristic pulsed laser exposure times do not exceed $\tau = 1\text{-}6$ msec the impurity can spread by the diffusion mechanism to a characteristic depth of several microns, while the melt pool is several hundreds of microns deep. Then forced convection in the melt pool is one of the main physical mechanisms for mass transfer over the entire depth of the pool and its determines the concentration field of the alloying component in the zone of laser action. In many cases, for relatively low energy flux densities, when evaporation is insignificant, thermocapillary convection is the dominant hydrodynamic process occurring in the melt. It is determined by the significant nonuniformity of the density of the incident energy flux over the radius of the heating spot and by the temperature dependence of the surface tension of the liquid metal. As a rule, the thermocapillary force is directed toward decreasing temperature, which gives rise to motion of the melt at the free surface from the center of the heating spot to the edges of the pool formed. In this paper we present the results of modeling of nonstationary thermocapillary mass transfer in a melt pool under pulsed action of laser radiation on titanium in a gaseous medium and we present experimental data on the alloying of titanium iodide in an atmosphere formed by the vapors of liquid nitrogen.

Model of Thermocapillary Mass Transfer. We shall study the nonstationary melting of a bulk sample of titanium by laser radiation. We assumed that the free surface of the melt pool is flat; the thermal conductivity and the thermal diffusivity of the liquid and solid phases as well as the density and dynamic viscosity of the melt are constant; the energy

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A. A. Baikov Institute of Metallurgy, Academy of Sciences of the USSR, Moscow. Physicotechnical Institute, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 3, pp. 375-380, March, 1990. Original article submitted May 15, 1989.

0022-0841/90/5803-0266$12.50