HEAT TRANSFER PROCESSES IN PHASE CONVERSIONS UNDER THE ACTION OF INTENSE ENERGY FLUXES

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1. Introduction. In various processes of the treatment of materials by concentrated energy fluxes, as a rule, the thermal action of a plasma flux or laser or electron beam is used. Therefore, one of the most important problems of the physics of interaction of radiation with matter is the development of a thermal model of the laser breakdown of materials, the fundamentals of which have been developed in [1, 2]. The construction of an adequate theory of phase transitions under the action of intense energy fluxes is associated, in particular, with the solution of boundary problems of heat conduction for regions with mobile boundaries.

In the one-dimensional case, the simplest formulation of the problems considered in this review include the heat-conduction equation and the energy balance at the phase interface

$$\frac{1}{a}\frac{\partial T}{\partial t}=\frac{\partial^2 T}{\partial x^2},\quad x\geqslant y(t),\quad y(0)=0, \tag{1}$$

$$-\varkappa\frac{\partial T}{\partial x}\Big|_{x=y(t)}=q(t)-Qv(t),\quad v(t)\equiv\frac{dy}{dt}. \tag{2}$$

If such factors as the nonuniformity, nonstationarity, and spatial boundedness of the heat transfer processes, the temperature dependences of the vaporization rate and properties of the material, and diffusional phenomena, which are significant in a real situation, are taken into account, the formulation of the corresponding problems is considerably complicated; classical methods of heat-conduction theory become inappropriate for their solution, and it is necessary to use special mathematical means and approximate methods [3-10]. Some of these problems, relating to the problem of surface evaporation of metals, were considered in the review [11], in which works published up to the middle of 1977 were taken into account. The problem of heat conduction with a surface heat source of constant intensity and an additional kinetic relation between the velocity of phase-interface motion v and the evaporation temperature T_e

$$v=v_*\exp\left(-\frac{E_e}{T_e}\right) \tag{3}$$

was analyzed in [11].

No consideration was given in [11] to the problems of melting and transformation in the solid phase, nor to processes of the laser destruction of nonmetallic materials, for which the bulk nature of light-energy absorption becomes significant, while the destruction kinetics may not only be determined by the heat transfer, but also limited by diffusion, change in concentration of the free electrons, or other processes. In these cases the formulation of the heat-conduction problem is supplemented by the appropriate boundary conditions.

The present review is devoted to the consideration of these questions with generalization of the data of [11], taking account of recent work. Consideration is limited here to analytical methods of investigation of heat transfer processes, and nothing is said regarding questions of radiation screening [2, 12], problems of melt motion — see [13-15] and the literature cited there — and instability of the form of the phase-transition surface [17-19]; the information regarding diffusional photothermochemistry included in [20-22] is supplemented.

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2. Nonsteady Melting (Ablation) of Materials. The problem of kinetics of the change in size and temperature of a melting body is one of the most important in heat-conduction theory and has formed the subject of many works. Here consideration is restricted predominantly to nonsteady problems, for which the law of phase-interface motion is not specified and must be determined in the course of solution. It is assumed here that heat transfer in the liquid occurs according to the Fourier law or is totally absent, which is characteristic of the cases when the melt moves ideally or "instantaneous" removal of the melt (ablation of the material [23]) occurs.

In the one-dimensional case, processes of melting, crystallization, and diffusion are described by a single mathematical model, and for an arbitrary law of interface motion the temperature field may be found in the form of the series [8, 24]

$$T(x, t) = T_s(t) + \sum_{n=1}^{\infty} \frac{1}{a^n (2n)!} \frac{\partial^{n-1}}{\partial t^{n-1}} \left\{ \frac{dT_s}{dt} [y(t) - x]^{2n} \right\} - \sum_{n=0}^{\infty} \frac{1}{a^n (2n+1)!} \frac{\partial^n}{\partial t^n} \left\{ \frac{\partial T}{\partial x}\Big|_{x=y(t)} [y(t) - x]^{2n+1} \right\}. \quad (4)$$

In analyzing problems of melting, Eq. (3) is usually not taken into account; the temperature of the phase interface is taken to be equal to the melting point

$$T(y, t) = T_m. \quad (5)$$

Under definite simplifying assumptions, the equation for the desired law of phase-boundary motion may be obtained directly from the boundary problem, without calculating the temperature field [25-28]. The approach developed in [24-28] has been used to investigate a series of specific problems of melting under the action of a concentrated energy flux [29-33].

The nonsteady problem of the melting of a semiinfinite body under the action of a surface heat source of constant intensity was apparently first considered in [34]. The introduction of dimensionless variables reduces the problem in Eqs. (1), (2), and (5), with the boundary conditions $T(x, 0) = T_b$, $T(\infty, t) = T_b$, to a system depending on the parameter $\eta = c(T_m - T_b)Q_m^{-1}$. The cases when $\eta = 0$ and $\eta = \infty$ were considered in [34]. The initial stage of the melting process was investigated for any η by the method of successive approximation in [35]. An iterative process was constructed on the basis of the assumption that the term $v\eta dT/dg$ appearing on passing from Eq. (1) to the moving coordinate system $g = x - y$ is small.

A similar problem of the growth of a crystal in the case of a constant flux through the surface $x = 0$ was considered in [36], where the introduction of the dimensionless variables

$$X = \frac{xq}{aQ}, \quad Y = \frac{yq}{aQ}, \quad \tau = \frac{tq^2}{aQ^2}, \quad \theta = \frac{c(T_m - T)}{Q} \quad (6)$$

reduces the problem to a form not including any parameters:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial X^2}, \quad \frac{\partial \theta}{\partial X}\Big|_{X=Y} = -\frac{dY}{d\tau}, \quad Y(0) = 0,$$
$$\theta(Y, \tau) = \theta(X, 0) = 0, \quad \frac{\partial \theta}{\partial X}\Big|_{X=0} = -1. \quad (7)$$

Then, using Eqs. (4) and (5), an equation is obtained for the function $Y(\tau)$:

$$\sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \frac{d^{n+1}}{d\tau^{n+1}} [Y^{2n+1}(\tau)] = 1. \quad (8)$$

The solution of Eq. (8) may be found, e.g., in the form $Y(\tau) = \sum_{k=0}^{\infty} A_k \tau^k$, and the temperature field calculated using a computer exhaustively describes the process [8, 36].

In [37-42] and elsewhere, the integral Goedman method was used for the analysis of problems of melting and ablation; in this method the heat-conduction equation is replaced by the heat-balance equation obtained as a result of integrating Eq. (1) with respect to x over the limits from 0 to L(t), where L(t) is the thickness of the thermal boundary layer. Specifying the temperature profile in the form of a function of L and x, and substituting it into the

heat-balance equation and the boundary condition (2), a system of two equations with unknowns v and L is obtained. A definite modification of the Goedman method [43] allows the accuracy of calculation to be significantly increased, and allows the power-law and exponential dependence of the energy flux density on the time to be taken into account [44].

In [45], the problem of nonsteady melting is linearized by approximating the temperature field using an exponential function. The solution is found by series expansion of the relations obtained after performing a Laplace transformation.

In [46-50], the Biot variational method [51] was used; this method is based on the introduction of the thermodynamic equivalent of the Lagrangian function in mechanics and is also associated with the concept of a thermal layer, the temperature profile in which is approximated by a power law. In [52], the ablation problem for a semiinfinite body was solved by the variational method outlined in [53]. In contrast to the Biot method, this approach allows the function v(t) to be obtained in explicit form.

The methods of similarity and dimensionality theory have been used to find self-similar solutions of problems of melting under the action of a point heat source in the cases of plane, axial, and spherical symmetry [54-56].

The self-similar solution of the two-dimensional problem of the melting of a semiinfinite body heated by a moving heat source in the form of a strip was obtained in [57]. Nonsteady melting under the action of a bulk heat source was considered in [58].

Taking account of the spatial boundedness of the melting body significantly complicates the analysis of the process. For a body of spherical form, the problem of melting is not equivalent to the problem of crystallization, on account of the presence of the initial crystal dimension R_0. Melting of a spherical crystal in an infinite melt heated to a temperature $T_b > T_m$ was investigated in [31]. The heat transfer satisfying the Fourier law was considered separately for two regions: $R(t) \leqslant r \leqslant R_0$, $r \geqslant R_0$, with the corresponding matching conditions; an integral equation was obtained for the function R(t). The kinetics of the process depends strongly on the parameter η. If $|\eta| \ll 1$, melting extends over a considerable time, and the law of interface motion is found in the form $R(t) = \left[R_0 + \sum_{n=1}^{\infty} \eta^n B_n(\tau)\right]^{1/2}$, where $\tau = at R_0^{-2}$. When $|\eta| > 1$, the crystal melts rapidly, and the solution of the problem is expediently obtained in the form of a power series in $\sqrt{\tau}$.

In [32], the problem of the melting of a heated spherical crystal was considered in the case when the stored energy is insufficient for complete melting. In the case when $\tau \gg 1$, the solution is obtained in the form

$$R(\tau) = R_\infty + \sum_{n=1}^{\infty} A_n \exp\left\{-\left(\frac{\pi n R_0}{R_\infty}\right)^2 \tau\right\}, \quad R_\infty = R_0(1+\eta)^{1/3}.$$

Melting of a plate of finite thickness was investigated in [30, 48-50, 59]. It is assumed that the melt is removed rapidly from the surface of the body. The formulation of the problem includes Eqs. (1), (2), (5) for the region $0 \leqslant x \leqslant y(t)$ (the coordinate origin is at the midpoint of the plate, which is heated symmetrically from the surfaces $x = \pm l$ by constant energy fluxes), the initial conditions $T(x, 0) = f(x)$, $y(0) = l$, and the adiabatic symmetry condition

$$\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0. \tag{9}$$

The solution of the problem is sought in the form [29]

$$T(x, t) = \sum_{n=0}^{\infty} \frac{x^{2n}}{a^n (2n)!} \frac{d^n}{dt^n} \sigma(t). \tag{10}$$

Substitution of (10) into (2), (5) gives a system of nonlinear equations, solution of which (by the method of successive approximation with the use of operational calculation) allows the unknown functions $\sigma(t)$ and y(t) to be found. The final expressions for y(t) are found in the form of a series [8, 30]. In particular, for the initial conditions approximated by the function $f(x) = T_b + A_1 x^2$, when $\tau = at l^{-2}$ is not too small, the following formula holds:

$$y(\tau) = l - \frac{l^2 q}{aQ_m}\left\{\tau - \frac{\theta_0}{3} + \frac{2\theta_0}{\pi 4}\sum_{k=0}^{\infty}\frac{\exp\left[-\pi^2\left(k+\frac{1}{2}\right)^2\tau\right]}{\left(k+\frac{1}{2}\right)^4}\right\}, \tag{11}$$

where $\theta_0 = 2\varkappa(T_m - T_b)(ql)^{-1}$. When $\tau \ll 1$, the solution is represented by a series of the form

$$\sum_{k=0}^{\infty}\left\{\left[\tau + \frac{1}{2}(2k+1)^2\right]\operatorname{erfc}\left(\frac{2k+1}{2\sqrt{\tau}}\right) - (2k+1)\sqrt{\frac{\tau}{\pi}}\exp\left[-\frac{(2k+1)^2}{4\tau}\right]\right\}. \tag{12}$$

It follows from the solution of the problem that at large τ the temperature of a nondissolving plate is equalized, and y becomes a linear function of τ.

Thus, the method considered in [8, 30] allows the process of melting to be described for any values of τ, taking account of an arbitrary initial temperature distribution, and is also found to be effective for the analysis of the melting of a cylinder and a sphere [30, 8].

An analogous problem of the melting of a plate of finite thickness with zero initial conditions was solved in [48-50] by the Biot method. Various possible conditions of melting, determined by the relation between t_0 and t_2, l and l_0, were considered in more detail; here l_0 is the characteristic distance at which the rate of boundary motion is influenced by the adiabatic condition (9), and depends on the thermophysical properties of the material and the energy flux density [50].

When $l_0 < l$, $t_0 < t_2$, two constant sections may exist on the curve of v(t): the first corresponds to the solution when the plate behaves as a semiinfinite body — $v_1 = q(Q_m + cT_m)^{-1}$; the second appears at the end of the process when the unmolten part is heated uniformly — $v_2 = qQ_m^{-1}$. This steady state is preceded by the corresponding transient conditions. In [48-50] approximate solutions were constructed (on the basis of a combination of the Biot method and perturbation theory) close to the steady states and then combined. Note that in [48-50] the dependence y(t) was obtained in parametric form, which hinders direct comparison with Eqs. (11), (12). The comparison in [49] with the results of [30] is not indicative, since only Eq. (11) was taken into account in the analysis, and the parameters of the problem were chosen so that the condition $\tau \ll 1$ was satisfied over most of the time interval, when series (11) converges poorly and series (12) must be used. When τ is not small, the two approaches give similar results. The use of the Biot method allows the temperature dependence of the thermophysical coefficients of the materials to be taken into account [47, 50].

3. Evaporation. In most cases of interest for technology, corresponding to moderate energy-flux energies, processes of laser evaporation are described within the framework of the Stefan problem [2, 11]. In contrast to problems of melting, kinetic relations of the type in Eq. (3) must be taken into account, as a rule, in evaporation problems. A review of problems of this type for a surface heat source was given in [11]. A method was outlined allowing the nonsteady problem (1)-(3) to be analyzed with an arbitrary initial condition f(x), for an arbitrary dependence of the energy flux density on the time q(t), taking account of the temperature dependences of the target properties [8, 11, 60, 61].

Representing the variable parameters by the power series

$$f(x) = \sum_{n=0}^{\infty}\omega_n x^n,\quad q(t) = \sum_{n=0}^{\infty}B_n(at)^{n/2},$$
$$v(t) = \sum_{n=0}^{\infty}\varepsilon_n(at)^{n/2},\quad A = \sum_{n=0}^{\infty}C_n(at)^{n/2}, \tag{13}$$

the temperature field is found in the form

$$T(x,\ t) = \omega_0 + \sum_{n=1}^{\infty}\left[\omega_n h_n\left(\frac{x}{2\sqrt{at}}\right) + v_n f_n\left(\frac{x}{2\sqrt{at}}\right)\right](at)^{n/2}. \tag{14}$$

Here h_n, f_n are Hermite functions [62]; B_n, C_n, ω_n, ν_n, ε_n are constant coefficients, between which there exist recurrence relations [60, 61]. Calculations of the velocity of motion and temperature of the phase boundary from (13), (14) agree satisfactorily with the results of numerical solution of the problem [63].

With laser irradiation of nonmetallic materials, and also with the action of an electron flux in a series of cases, the bulk character of light absorption by the material becomes significant, and the heat-conduction problem takes the form

$$\frac{1}{a}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + G(x,\ t),\ \varkappa \frac{dT}{dx}\bigg|_{x=y(t)} = Q_e v(t). \tag{15}$$

In the case where the Bouguer–Lambert absorption law is valid,

$$G(x,\ t) = q\varkappa^{-1}\mu \exp\{-\mu[x - y(t)]\}. \tag{16}$$

When $v = v_0 = \text{const}$, problem (15), (16) is solved by an operational method. Then [1]

$$T_0(g) = \frac{q\exp(-\mu g)}{\varkappa\left(\frac{v_0}{a} - \mu\right)} + \left[T_e - \frac{q}{\varkappa\left(\frac{v_0}{a} - \mu\right)}\right]\exp\left(-\frac{v_0}{a}g\right), \tag{17}$$

$$v_0 = v_* \exp\left(-\frac{E_e}{T_e}\right),\ v_0 = q(Q_e + cT_e)^{-1}. \tag{18}$$

Absorption laws differing from Eq. (16) (with irradiation of the material by an electron flux) and the corresponding temperature fields were considered in [64].

The nonsteady problem (15), (16), (3) with the condition $T(\infty, t) = 0$ was investigated in [65] using an approach developed in [60]. The solution is sought close to the steady conditions (17), (18)

$$T(g,\ t) = T_0(g) + T_1(g,\ t),\ v(t) = v_0 + v_1(t). \tag{19}$$

Substituting (19) into (15), (3) and retaining only the terms linear in T_1 and v_1, a system of linear equations for T_1 and v_1 is obtained, and it is solved by the method of Laplace transformation. As a result the following expression is obtained for v_1:

$$\frac{v_1(t)}{v_0} = \exp\left(-\frac{v_0^2 t}{4a}\right)\sum_{i=1}^{3} A_i\{(\pi\mu^2 at)^{-\frac{1}{2}} - \nu_i \exp(\nu_i^2\mu^2 at)\operatorname{erfc}(\nu_i\mu\sqrt{at})\}, \tag{20}$$

where ν_i are the roots of the cubic polynomial [65], the form of which is independent of the initial temperature distribution $f(x)$;* A_i are constants (complex in the general case).

According to Eq. (20), the time t_0 to establish a constant value of the velocity of evaporation-front motion is (in order of magnitude) $a v_0^{-2}$ when $\mu \gg v_0 a^{-1}$; when $\mu \ll v_0 a^{-1}$, $t_0 \simeq (\mu v_0)^{-1}$.

In view of the sharp dependence of v on T_e defined by Eq. (3), the time t_1 to establish a steady value of the surface temperature is several times higher than t_0. A comparison of the theoretical [60, 61] and experimental [66] dependences of t_1 on q is shown in Fig. 1.

Analysis of the solution of Eq. (20) shows that with any real values of ν_i, the nonsteady addition v_1 tends monotonically to zero with increase in t. If there are two complex-conjugate roots among ν_i, the velocity v depends nonmonotonically on t and approaches v_0, performing damped oscillations (Figs. 2, 3). Until now, the problem has been considered in a one-dimensional formulation. The mathematical description of the phase-transition kinetics is evidently significantly complicated by taking into account that the heat transfer process is not one-dimensional and by the need to analyze the evolution of the form and dimensions of the phase interface. Nevertheless, under certain assumptions, this three-dimensional heat-conduction problem in a region with moving phase interfaces may be solved

*Therefore, $f(x) = 0$ was assumed in [65] to simplify the final results.

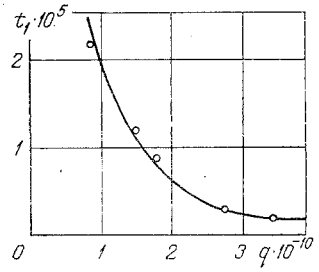

Fig. 1

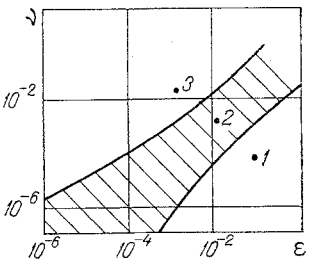

Fig. 2

Fig. 1. Theoretical [60] and experimental [66] dependences of t_1 on q; copper; t_1, sec; q, W/m^2.

Fig. 2. Region of existence of oscillatory conditions of evaporation (shaded).

when two phase transitions are taken into account: evaporation and melting [67]. The problem is formulated in the form

$$\frac{1}{a_i}\frac{\partial T_i(x, y, z, t)}{\partial t} = \nabla^2 T_i(x, y, z, t),\ T_2(\infty, t) = T_b,$$
$$-\varkappa_1 \frac{\partial T_1}{\partial n_1}\bigg|_e = q\cos\alpha_1 - Q_e\frac{dn_1}{dt},\ T_1|_e = T_e, \tag{21}$$
$$T_1|_m = T_2|_m = T_m,\ -\varkappa_1\frac{\partial T_1}{\partial n_2}\bigg|_m = -\varkappa_2\frac{\partial T_2}{\partial n_2}\bigg|_m + Q_m\frac{dn_2}{dt}.$$

The letters e and m here denote quantities corresponding to the evaporation and melting surfaces, respectively; i = 1, 2; i = 1 corresponds to the liquid and i = 2 to the solid material; the radiation is incident along the z axis. In this formulation of the problem, no account is taken of the heat propagation by the boundaries of the body and the spatial boundedness of the heat flux, and the possibility of motion of the melt is also ignored. Detailed analysis of the conditions under which the given assumptions are valid may be found in [61, 67, 68].

The solution of the problem in Eq. (21) is obtained in the form of a function of the single variable ξ:

$$T_i(\xi) = A_i\Phi_i(\xi) + B_i,\quad \Phi_i(\xi) = \int_\xi^\infty \frac{\exp(-\beta_i x)\,dx}{\sqrt{x(x+\varphi)}}. \tag{22}$$

Here $\beta_i = \rho v(2a_i)^{-1}$ and the following relation is valid for ξ:

$$\left(\frac{x}{\rho\xi}\right)^2 + \left(\frac{y}{\rho\xi}\right)^2\left(1 + \frac{\varphi}{\xi}\right)^{-1} = 1 - \frac{2}{\rho\xi}(z - vt). \tag{23}$$

The equations ξ = 1 and ξ = K define the evaporation and melting surfaces, respectively, in three-dimensional space; they take the form of elliptical paraboloids, one inside the other moving along the z axis at constant velocity v:

$$v = q\,[Q_e + Q_m + c\,(T_e - T_b)\,F(\beta_1)]^{-1},$$
$$F(\beta) = \frac{T_e - T_m}{T_e - T_b}\left[\frac{1}{\beta\exp(\beta)\sqrt{1+\varphi}\,[\Phi_1(1) - \Phi(K)]} - \frac{Q_m}{c\,(T_e - T_m)}\right]. \tag{24}$$

The constant coefficients A_i, B_i, K are determined from the boundary conditions of the problem. The quantity φ characterizes the degree of elongation of the phase interfaces along the y axis. When φ = 0, the phase interfaces take the form of paraboloids of revolution, while the functions Φ_i transform to integral indicative functions. As $\varphi \to \infty$, the functions Φ_i transform to supplementary integral probability functions, while the phase interfaces

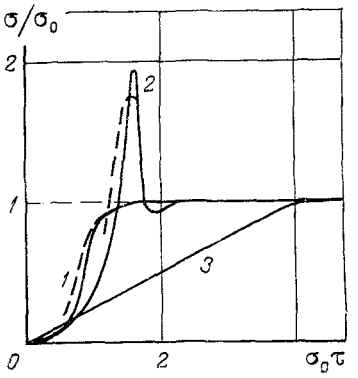

Fig. 3

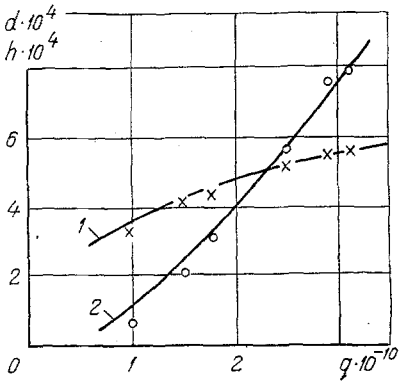

Fig. 4

Fig. 3. Dependence of velocity of evaporation-front motion on time [65]. Analytic (dashed) and numerical solutions; $\tau = \mu^2 at$, $\sigma = v(a\mu)^{-1}$, $\sigma_0 = v_0(a\mu)^{-1}$. Parameters corresponding to curves 1-3 are indicated on the (ν, ε) plane by points (see Fig. 2).

Fig. 4. Experimental and theoretical dependences of the crater depth h and diameter d in graphite on q [61]: $t = 4 \cdot 10^{-3}$ sec; 1) d; 2) h; h, d, m; q, W/m^2.

are elongated into a parabolic cylinder. The solution (22)-(24) includes the results obtained in [68-71] as particular cases. The function $F(\beta)$ characterizes the degree to which the destruction process is not one-dimensional. When $\beta \gg 1$, $F(\beta) \to 1$, and the process may be considered within the framework of the one-dimensional model. When $\beta < 1$, the heat transfer in the solid material increases significantly, and the energy capacity of destruction is inereased in comparison with the one-dimensional case.

The solution of Eq. (21) may be used in certain conditions [61, 67, 71] to calculate the parameters of the destruction process for various materials by laser radiation. A comparison of the results of calculation with experimental data on crater formation in graphite [61] is shown in Fig. 4. A comparison of the experimental [72] and theoretical [71] dependences of the productivity of the laser cutting of granite (the surface area of the cut per unit time) on the velocity of laser-beam motion is shown in Fig. 5.

The energy flux q absorbed by the material figures in the problems considered above; as a rule, q = const is assumed. At the same time, even with a constant magnitude of the incident flux density q_0, the absorbed power density $q = Aq_0$ may significantly change on account of the temperature dependence of the absorptive power of the material A or, e.g., for thin semitransparent films, on account of the dependence of A on the thickness of the evaporating layer.

For many metals, the temperature dependence of the absorbing power is satisfactorily approximated [13, 73] by the linear function $A = A_1 + A_2 T_s$. This dependence does not lead to significant complication of the problem if the evaporation process is considered in the quasisteady approximation [73]; for the initial stages of nonsteady evaporation, the dependence $A(T_s)$ may be taken into account [61] by means of the procedure of series expansion (13), (14). Oxidation of the metal significantly influences the change in absorbing power and hence the destruction kinetics [20, 74].

In the evaporation of transparent dielectrics, absorption of radiation with a nonlinear temperature dependence develops with thermal breakdown of the material around the absorbing inhomogeneities, which is accompanied by a sharp rise in free-electron concentration on account of thermal release of charge carriers in the valence band or on account of the thermal dissociation of multicomponent materials with subsequent partial ionization [75]. The absorbing power of the dielectric is determined by the relations

$$A = 1 - \int_0^\infty \mu[T(x)]\,dx, \quad \mu(T) = \mu_0 \exp\left(-\frac{E_r}{T_e}\right). \tag{25}$$

The system of equations describing the propagation of heat and emission of a transparent dielectric takes the form [75, 76]

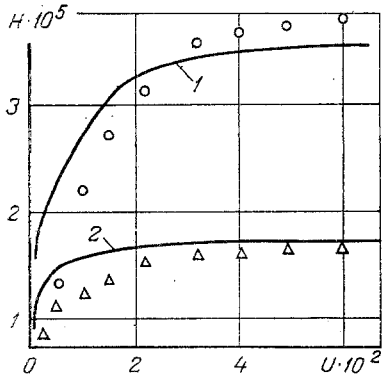

Fig. 5

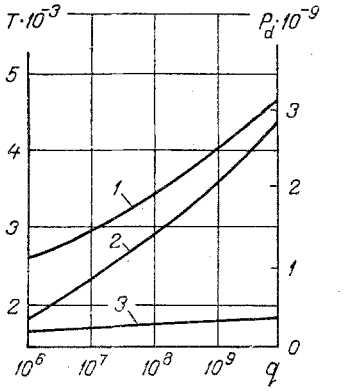

Fig. 6

Fig. 5. Theoretical and experimental dependences of the productivity of a laser knife H on the velocity of laser-beam motion U [72]. Radiation power 750 W: 1) $d_0 = 5 \cdot 10^{-4}$; 2) 10^{-3} m; H, m^2/sec; U, m/sec.

Fig. 6. Dependences of the basic characteristics of the quasi-steady process of evaporation and dissociation of $CaCO_3$ on q: 1) T_e; 2) P_d; 3) T_d; T, °K; P_d, N/m^2; q, W/m^2.

$$\frac{d^2T}{dz^2} \pm \frac{v}{a}\frac{dT}{dz} + G(T) = 0,\ G(T) = q\varkappa^{-1}\mu(T),$$
$$\varkappa \frac{dT}{dz}\Big|_{z=y} = \pm vQ_e,\ \frac{dq}{dz} = -q\mu(T), \qquad (26)$$
$$q(-\infty) = q_0,\ T(\infty) = 0,\ v = v_* \exp\left(-\frac{E_e}{T_e}\right).$$

Here the coordinate z is measured from the surface of maximum heat liberation, where the condition $(dG/dz)_{z=0} = 0$ is satisfied. The upper plus sign refers to the case when the radiation is incident on the evaporating surface from outside, and the lower minus sign refers to the case of incidence of the radiation from within the transparent material. In [76], an approximate solution of the problem in Eq. (26) was obtained under the condition $E_r \gg T$. Since the maximum temperature T_{max} is reached under the evaporation surface and the main contribution to light absorption comes from a small region of the dielectric at a temperature close to T_{max}, substituting a point source of intensity $q\varkappa^{-1}\delta(z)$ at the point z = 0 for the source function in the zero approximation leads to a solution of the heat-conduction equation (26) in the form

$$T^{(0)}(z) = \frac{q_1}{cv_0} u(\pm z) \exp\left(\mp \frac{v_0}{a} z\right) + \frac{q_1}{cv_0} u(\mp z) - \frac{Q}{c} \exp\left[\frac{v_0}{a}(\mp z - y)\right]. \qquad (27)$$

The absorbed density of the radiation flux $q_1 = Aq_0$ is determined by substituting (27) into (25). The temperature of the evaporating surface in the first approximation $T_e^{(1)}$ is calculated using (27), where $T = T_z^{(0)}$ is substituted into the T-dependent quantities. This procedure allows the dependences of the evaporation rate and the absorbing power on the intensity of the incident radiation to be obtained in the second approximation [76], with satisfactory agreement with the results of numerical solution [75].

It follows from the solution of the problem that since the temperature distribution is asymmetric with respect to T_{max}, the absorbing power of the input surface of the dielectric is found to be lower than in the case when the radiation is incident from the interior of the transparent material. With increase in laser-flux intensity, A decreases on account of the narrowing of the absorbing layer and the intensification of cooling action of evaporation. At sufficiently large q_0, the input and output surfaces correspond to identical values of A, and the kinetics of dielectric evaporation does not depend on the direction of incidence of the radiation.

In the presence of a metallic film at the surface of the transparent dielectric, the threshold at which destruction of the film–substrate system begins is found to be considerably lower than for a pure dielectric and for a massive metal, since a much smaller intensity is required for the destruction of a film that absorbs well than for the thermal breakdown of a transparent dielectric, while a much larger part of the radiation energy is released into the thickness of the material in the evaporation of massive metal than in the case of a dielectric substrate. The problem of heat conduction with evaporation of a metallic film on a transparent substrate was considered in [77], taking account of the dependence of the absorbing power of the film on its thickness, which varies in the course of destruction.

4. Dissociation in the Solid Phase. In the thermal dissociation of a series of chemical compounds (e.g., carbonates and hydrates of various metals, etc. [78]), no liquid phase is formed, but the liberated gases diffuse through a layer of solid decomposition products. With a relatively slow supply of heat, dissociation occurs at constant temperature T_c. With the action of intense energy fluxes, gas transfer through the layer of solid deposit limits the decomposition process, which is accompanied by increase in dissociation temperature $T_d > T_c$ and heating of the irradiated surface. This situation was considered in [79], where it was shown that taking diffusional processes into account leads to the appearance of the following relation between the velocity of dissociation-boundary motion and its temperature:

$$v_d = KMDP_d(\gamma sRT_d)^{-1}, \quad v_d = \frac{ds}{dt}. \tag{28}$$

In accordance with the Arrhenius law,

$$P_d = P^* \exp(-E_d T_d^{-1}). \tag{29}$$

Boundary condition (28) leads to a new group of heat-conduction problems of the type of the Stefan problem.

When T_d = const, the solution of Eq. (28) takes the form

$$s(t) = \left(\frac{2MKDP_d t}{R\gamma T_d}\right)^{1/2}, \quad v_d(t) = \left(\frac{MKDP_d}{2R\gamma T_d t}\right)^{1/2}. \tag{30}$$

The parabolic law of boundary motion satisfies the classical Stefan boundary problem with the boundary condition: $T(0, t) = T_s$ = const. On heating the body by a surface energy flux, the law in Eq. (30) satisfies the solution of the thermal problem if $q = -\varkappa (\partial T/\partial x)_{x=0} \infty t^{-1/2}$ [79]. When q = const, the dissociation process is nonsteady (accompanied by increase in T_d, T_e, P_d) and may be investigated analogously to the problem of evaporation and melting without removal of the melt. In the initial stages of dissociation, the thin layer of solid product does not have a marked influence on the processes of heat and mass transfer, and the destruction kinetics is described by Eqs. (1)-(3), with the sole difference that E_e is replaced by E_d in Eq. (3).

Increase in thickness of the solid-deposit layer slows the processes of heat and mass transfer, which leads to increase in temperature of the irradiated surface; this, in turn, leads, after sufficient time of action of the heat source, to the development of the evaporation process. There then appears a second phase interface $y_e(t)$, which moves behind the dissociation surface $y_d(t)$. It follows from the solution of the corresponding heat-conduction problem [67, 79] that with constant q, T_d, T_s, quasisteady conditions of destruction are possible, with the two phase surfaces moving at the same velocity v and the thickness of the deposit layer $s = y_d - y_e$ remaining constant over time. In this case

$$v = \frac{q}{Q_e + Q_d + cT_e}, \quad s = \frac{a}{v} \ln\left[1 + \frac{c(T_e - T_d)}{Q_d + cT_d}\right]. \tag{31}$$

Equations (3), (28), (29), and (31) form a system of equations for determining the unknowns v, s, T_d, T_e, P_d. The results of solving this system [79] are shown in Fig. 6.

Analysis of the nonsteady stage shows that the transition from conditions of dissociation to conditions of dissociation with evaporation may occur in both a monotonic and nonmonotonic manner (Fig. 7). Nonmonotonic conditions arise because in definite conditions the

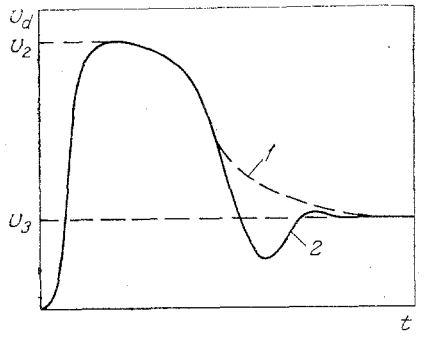

Fig. 7

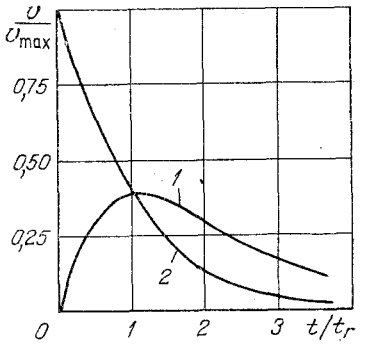

Fig. 8

Fig. 7. Character of the dependence of the dissociation rate v_d of marble on t: 1) monotonic; 2) nonmonotonic transition to quasisteady conditions of dissociation and evaporation.

Fig. 8. Change in rate of phase-interface motion as a function of time [81], taking account of (curve 1) and disregarding (curve 2) the finiteness of the rate of propagation of the heat perturbations.

evaporation surface begins to move more rapidly than the dissociation surface. The thickness of the deposit layer then decreases, gas diffusion and dissociation are promoted, and the velocities v_e and v_d equalize. The region of existence of oscillatory conditions of dissociation is determined analogously as for evaporation (see Sec. 3). The form of the time dependence of the dissociation rate shown in Fig. 7 is confirmed by experimental data on the laser destruction of marble [79].

5. Influence of the Finite Rate of Heat Propagation. In classical heat-conduction theory, the rate of propagation of the thermal perturbations ω is assumed to be infinite. However, under the action of high-intensity heat fluxes, it may be important to take account of the finiteness of ω for fast processes. The equation describing the heat transfer process in this case is of hyperbolic type, and its investigation for problems of heating and phase transitions under the action of intense energy fluxes [80-82] is based primarily on the work of Lykov [4, 83, 84]

$$\frac{\partial T}{\partial t} + t_r \frac{\partial^2 T}{\partial t^2} = a \frac{\partial^2 T}{\partial x^2}, \quad t_r = \sqrt{\frac{a}{\omega}}. \tag{32}$$

By modification of Stefan condition (2) and in view of [81], we obtain

$$-\varkappa \frac{dT}{dx}\bigg|_{x=y(t)} = q - Q\left(t_r \frac{d^2y}{dt^2} + \frac{dy}{dt}\right). \tag{33}$$

In [81], a series of steady and nonsteady problems of the type (32), (33) was considered. Steady conditions of evaporation of axisymmetric bodies of conical and needle-shaped form have been investigated by linearizing the model using the telegraph equation. Nonsteady evaporation has been considered approximately for a semiinfinite body, a cylinder, and a sphere.

Comparison of the solutions of one-dimensional problems of phase transition at $t_r = 0$ and $t_r > 0$ show that when the classical heat-conduction equation — Eq. (1) — is used, the process of phase transition begins at a maximum rate, which may be as large as desired; taking account of the finiteness of the rate of heat propagation eliminates this singularity (Fig. 8). In addition, the use of the hyperbolic model allows the instability of the solution for sinusoidal temperature change at the body's boundary, a feature which is characteristic of the parabolic model, to be eliminated.

In [82], the one-dimensional problem of the melting and evaporation of a semiinfinite body was considered. Transforming Eq. (32) to a moving coordinate system, and noting that in comparison with the case $t_r = 0$, the quantities a and $\varkappa = ca$ in the heat-conduction equation and the boundary conditions are replaced by $a - t_r v^2$ and $c(a - t_r v^2)$, respectively, the solution is obtained, for the case of identical and constant velocity of the melting and evaporation interfaces, by the method of Laplace transformation, analogously to [69]. Comparison with the results of [69] shows that when $t_r > 0$ is taken into account, the tem-

perature front becomes steeper and the thickness of the melt layer less than in the case when $t_r = 0$. Since t_r is very small (for aluminum $t_r \approx 10^{-11}$ sec [4]), the influence of finiteness of the rate of heat propagation becomes pronounced only when q is sufficiently large (for Al when $q > 3 \cdot 10^{12}$ W/m^2).

6. Conclusions. Problems relating to the description of heat transfer processes have a series of features which distinguish them from the classical Stefan problem. First, what is regarded as specified is not the surface temperature, but the intensity of the surface or volume heat source. Second, the boundary condition in Eq. (5) is found to be applicable only in problems of melting. In evaporation or dissociation limited by diffusion, the kinetic relations (3), (28) between the velocity of phase-interface motion and its temperature must be taken into account. In crystallization problems this relation takes the forms [8]: $v \infty \Delta T$ (with a normal mechanism of crystal growth) and $v \infty \exp(-E/\Delta t)$ (with a laminar mechanism). Here ΔT is the supercooling at the crystallization front; E is the corresponding activation energy.

In addition, the absorbing power of the material and hence the intensity of the heat source may depend on the temperature and position of the phase-transition front. Self-similar quasisteady solutions of such problems may only be obtained in individual cases. It is typical for the given processes to be nonsteady.

In a series of cases, the velocity of phase-interface motion changes nonmonotonically in the course of steady-state establishment, even with constant energy-flux density. This feature of the process may be due to the bulk character of the energy absorption [65], the dependence of the optical properties of a thin film on its thickness [77], or the change in thermophysical properties of the target [85], or to the change in the mechanism of destruction of the material and the presence of two phase interfaces [79]. In [8, 86], the effect of crystal growth prior to solution was described; this effect is associated with the influence of surface-tension forces and the diffusional interaction of the melting inclusions.

Other features of Stefan problems include the instability of their solutions (in a certain range of parameters) and the infinite value of the velocity of phase-interface motion at initial instants of time. The mathematical model of the processes occurring may be significantly changed on taking account of the finite velocity of heat propagation, the hydrodynamics of the melt, the surface-tension forces, and the limiting role of diffusion. The investigation of these phenomena is one of the most urgent problems of the theory.

NOTATION

T, temperature; T_b, T_s, T_e, T_m, T_d, initial, surface, evaporation, melting, and dissociation temperatures; T_2, temperature of midpoint of plate; T_0, steady temperature field; $T_1 = T - T_0$, nonsteady corrections; t, time; t_0, time to establish a steady velocity of phase-interface motion; t_1, time to establish a steady surface temperature; t_r, heat-stress relaxation time; $t_2 = l^2 a^{-1}$, characteristic time of plate heating; l, half-thickness of plate; a, thermal diffusivity; x, z, coordinates; y(t), v(t), coordinate and velocity of motion of phase interface; v_0, steady value of v; $v_1 = v - v_0$, nonsteady correction; v_*, order of magnitude of the sound velocity in the target; $\varkappa$, thermal conductivity; q_0, density of incident energy flux; A, absorbing power; $q = Aq_0$, absorbed-power density; $q_1(z)$, effective energy flux density in transparent dielectric; Q, heat of phase transition per unit volume of material; E, heat of phase transition, expressed in degrees (the subscripts m, e, d refer to melting, evaporation, and dissociation, respectively); E_r, half the activation energy of the process of free-electron formation; $\eta = c(T_m - T_b)Q_m^{-1}$; c, specific heat per unit volume; $g = x - y(t)$, distance from the phase interface; X, Y, τ, θ, dimensionless coordinates, time, and temperature; A_n, B_n, K, ω_n, ν_n, ε_n, C_n, P^*, constant coefficients; R_0, R(t), R_∞, initial, current, and final radius of a melting crystal of spherical form; r, distance from the center of the sphere; f(x), initial temperature distribution; G, intensity of bulk heat source; μ, bulk absorption coefficient of light by the material; n_i, normal to the phase surface; α_i, angle between the corresponding normal and the direction of incidence of the radiation (i = 1, liquid; i = 2, solid material); $\delta(z)$, Dirac delta function; γ, M, density and molecular weight of material; P_d, equilibrium gas pressure at dissociation front; D, effective gas-transfer coefficient through layer of solid dissociation products; s, thickness of solid-deposit layer; ρ, minimum radius of curvature of evaporation surface; φ, degree of asymmetry of evaporation surface; h, crater depth; d, crater diameter; d_0, laser-beam diameter; R, gas constant; u(z), Heaviside function.

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