MODELING THE PROCESS OF MELT SOLIDIFICATION ON THE SURFACE OF A MATERIAL

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Dynamic methods of thermal processing for metals and alloys are widely used at present. Of special interest is the technology of thermal processing in rapidly occurring processes involving modern equipment such as lasers, explosives, etc. [1]. Such processes are characterized by the action of high pressure and temperature values on materials. Under such action various structural and phase transitions occur within the material under extremal heating and cooling conditions [2]. It thus becomes possible to produce materials with certain desirable properties. In particular, metastable materials with an amorphous or finely dispersed structure have been produced [3].

Carrying out experimental studies on the principles of thermal processing at superhigh heating and cooling rates involves definite difficulties, and in some cases is simply not possible. A theoretical analysis of thermal processes usually leads to classical mathematical models of thermal conductivity and Stefan-type problems [4]. However for satisfactory estimates of the quantitative and qualitative characteristics of material structure formation it is necessary to consider the kinetics of new phase formation.

The present study will carry out a numerical analysis of formation of amorphous and finely dispersed crystalline structures in thin surface layers of a melt during rapid cooling.

A thin melted layer on the surface of a material can be obtained by the action of concentrated energy fluxes [2]. A high cooling rate is achieved by heat removal into the depths of the cold substrate. The structure of the solidified melt depends on the dynamics of the temperature regime, the value of the cooling rate, and the thermophysical characteristics of the material. In fact, the kinetics of new crystalline phase formation in the supercooled melt are determined by its viscosity and relaxation time, which increase with drop in temperature.

The formation of a new phase brings about fluctuations or spontaneity as a function of the degree of supercooling.

In the case of rapid supercooling of the melt the liquid phase is absolutely unstable and from the kinetic viewpoint spontaneous formation and growth of new phase nuclei is most probable. For spontaneous nucleus formation the size of the critical nucleus is of atomic order of magnitude, and change in the size of the new phase nucleus occurs due to combination or detachment of individual atoms which overcome the potential barrier. The nucleus distribution function over size obeys the fundamental kinetic equation obtained under the condition that growth is accomplished solely by attachment of individual atoms through the potential barrier in an activated manner [5].

We will consider the process of cooling of a thin layer of melt in ideal contact with the cold substrate. The problem of the "composite wall" can be described by thermal processes of amorphous film production by modern technology (explosion of melted drops or spreading on a rapidly rotating drum, etc.).

We take the mathematical formulation of the problem in the form

$$CR\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right) + RL\frac{\partial}{\partial x}\int_2^\infty f(x, n, t)\,dn; \tag{1}$$

$$T|_{t=0} = \begin{cases} T^*, & 0 \leqslant x \leqslant \Delta S, \\ T_0, & \Delta S \leqslant x \leqslant S; \end{cases} \tag{2}$$

$$\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0, \quad \left.\frac{\partial T}{\partial x}\right|_{x=S} = 0; \tag{3}$$

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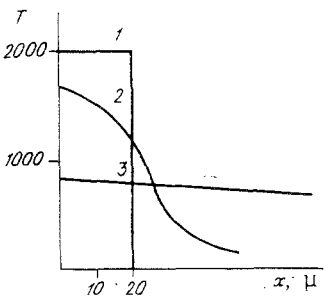

Fig. 1

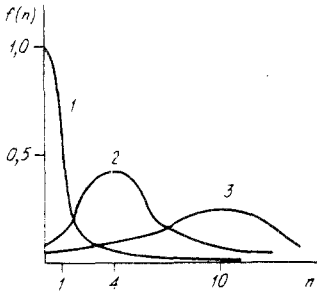

Fig. 2

$$\frac{\partial f}{\partial t} = 0{,}5\frac{\partial^2}{\partial n^2}(f(n,t)[P_+(n) + P_-(n)]) + \frac{\partial}{\partial n}(f(n,t)[P_-(n) - P_+(n)]), \tag{4}$$

$$P_\pm(n) = n^*\nu \exp\left[-\frac{U}{kT} \pm \frac{d\Delta F(n)}{dn}\right];$$

$$f(n)|_{t=0} = \frac{N}{r_a n^*}\exp\left[-\frac{\Delta F(n)}{kT}\right]; \tag{5}$$

$$f(n,t)|_{n=\infty} = 0; \tag{6}$$

$$\left(\alpha\frac{\partial f}{\partial n} + \beta f\right)\Big|_{n=1} = 0. \tag{7}$$

Here C, R, and λ are the specific heat, density, and thermal conductivity of the wall material — discontinuous functions (which are assumed piecewise-constant); L is the latent heat of fusion; T* is the melt temperature; T_0 is the substrate temperature; U is the activation energy for a single atom; ν is the Debye frequency; k is the Stefan–Boltzmann constant; n* is the number of atoms on the nucleus surface; $P_\pm$ is the probability of attachment or detachment of an atom; r_a is the atomic radius; N is the number of atoms in the system; f is the nucleus distribution function over size, normalized to unity $\int_1^\infty f\,dn = 1$; α, β are kinetic coefficients; $d\Delta F(n)/dn = -H(T_f - T(t))/T_f$ is the driving force of the process under spontaneous growth conditions; T_f is the fusion temperature; H is the phase transition enthalpy per atom; and ΔF is the change in free energy.

Thermal conductivity equation (1) contains a kinematic term on its right side, which plays the role of a volume heat source during solidification of the melt. The initial temperature conditions of Eq. (2) have a discontinuity on the contact line $x = \Delta S$, while for the distribution function in the equilibrium state we have Eq. (5). The boundary conditions of Eq. (3) for the thermal portion of the problem are taken with the assumption of thermal insulation of exterior surfaces of the wall. For the distribution function f of Eq. (6) a natural condition is the absence of very large new formations as $n \to \infty$. Equation (7) defines a zero particle flux in size space at n = 1 [6].

For the numerical realization of the problem an implicit Krank–Nicholson difference scheme with discrete representation of the basic kinetic equation (4) was used:

$$f(n,\ t+\Delta t) - f(n,\ t) = -f(n,\ t)\Delta t[P_+(n,\ t) + P_-(n,\ t)] +$$
$$+f(n+1,\ t)P_-(n+1,\ t)\Delta t + f(n-1,\ t)P_+(n-1,\ t)\Delta t.$$

We will consider the case of solidification of melted Fe with a temperature T_f = 2000°C and thickness ΔS = 20 μm in contact with a cold (Fe) substrate.

Figures 1 and 2 show characteristic temperature distributions and functions f in the composite wall at various times (lines 1-3 for 10^{-6}, $2\cdot10^{-6}$, $5\cdot10^{-6}$ sec). The calculated values of the temperature fields show practically no differences from similar calculations performed for solutions by classical Stefan models. Since the temperature gradients over time dT/dt (cooling rates) reach values of 10^9-10^6 deg/sec, spontaneous generation of the new phase occurs and the chosen mathematical formulation is valid.

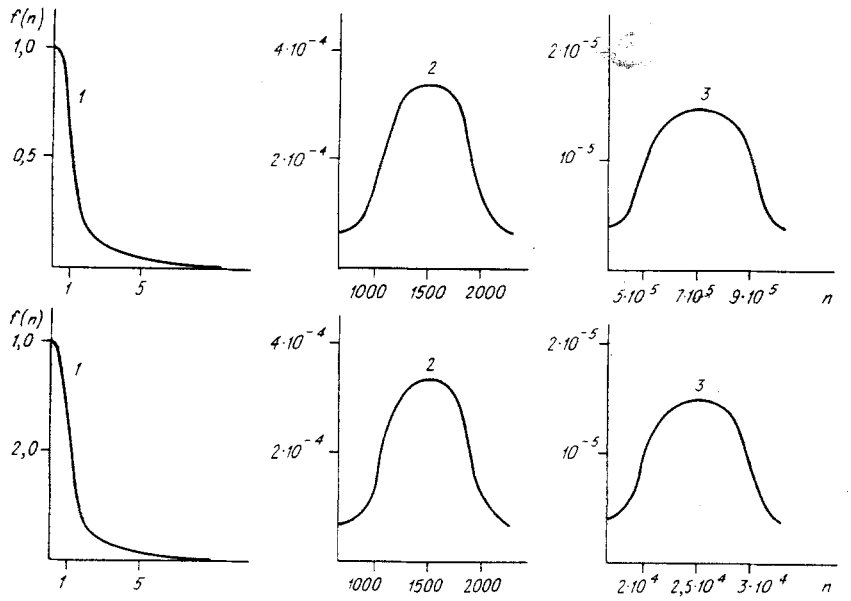

Fig. 3

The change in structure of the solidifying melt can be traced from the behavior of the distribution function f(x, n, t). Figure 3a illustrates the form of f(x, n, t) at a fixed point in the melt x = 10 μm at various times: t = 0, $2\cdot10^{-5}$, $4\cdot10^{-5}$ sec (lines 1-3). Figure 3b shows the distribution function at the specific time t = $2\cdot10^{-5}$ sec for the points x = 1, 10, 20 μm (lines 1-3).

One should note the clearly expressed maximum in the behavior of f(x, n, t), the amplitude of which falls off rapidly with passage of time. For the mean nucleus size we take the value of the maximum of the distribution function at the time of "freezing" of the process of new phase formation.

It is obvious that the distribution function at the moment of complete solidification of the melt determines the final size structure of the new phase nucleus. For a melt layer 20 μm thick the mean nucleus size (crystallite size in the solidified melt) comprises $5\cdot10^6$ atoms, or 0.017 μm assuming densely packed spherical grains.

At present there is interest in thermal processing of material surfaces by concentrated energy fluxes [2]. Studies have shown that the solidified melt on the surface has a fine-grain or even amorphous structure. In this connection it is important to know the principles of the process of surface cooling in order to control the structural transformations.

We will consider the action of a thermal flux q on the surface of a material over a short time interval Δt, which insures melting of a surface layer without significant destruction of material due to evaporation. In this case the process of melt cooling (see above) is preceded by a stage of surface heating which can be described mathematically by the classical Stefan problem:

$$CR\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right), \quad \begin{matrix}0<x<S,\\ 0<t<\Delta t;\end{matrix} \tag{8}$$

$$-\lambda\frac{\partial T}{\partial x}\Big|_{x=0} = q; \tag{9}$$

$$\frac{\partial T}{\partial x}\Big|_{x=S} = 0; \tag{10}$$

$$T|_{t=0} = T_0; \tag{11}$$

$$RL\frac{\partial\xi}{\partial t} = [q]|_{x=\xi},\ T|_{x=\xi} = T_* \tag{12}$$

(ξ is the coordinate of the moving melt–solid phase boundary, T_* is the equilibrium fusion temperature).

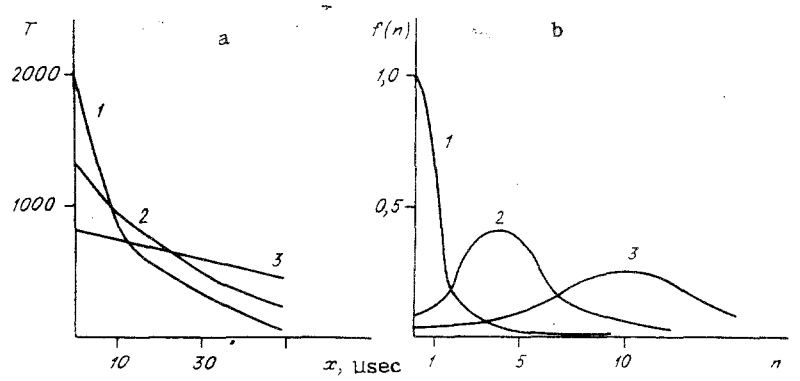

Fig. 4

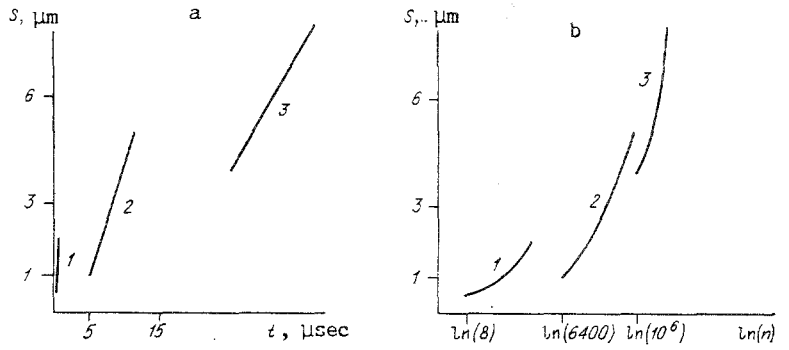

Fig. 5

The solution of the problem of Eqs. (8)-(12) at the moment that the action of the thermal flux is completed $t = \Delta t$ is then the initial temperature distribution for the subsequent problem of the "composite wall," Eqs. (1)-(7).

Figure 4a, b shows characteristic temperature distributions and functions f for action of a thermal flux of $q = 10^6$ W/cm^2 over a period $t = 9$ μsec (notation as in Figs. 1 and 2). The resultant property dependence differs slightly from that considered above (see Figs. 1 and 2).

The distribution function f(x, n, t) depends significantly on the melt cooling rate which is not constant over the process and varies significantly at different points within the melt thickness. However for points of a melted layer up to 20 μm in thickness the "frozen" distribution function has a practically identical form, which implies homogeneity over thickness of the structure.

Figure 5a, b shows calculations defining the melt depth achieved over time on the wall surface (material Fe) for various values of q and absence of evaporation ($q = 5\cdot10^6$, 10^6, $0.5\cdot10^6$ W/cm^2, lines 1-3). Figure 5b illustrates the dependence of mean grain size in the solidified melt upon melt thickness. For example, for a thermal flux $q = 10^6$ W/cm^2 acting over $t = 5$ μsec on the wall surface a melt thickness $\Delta S = 1$ μm can be obtained (Fig. 4a). For subsequent solidification of the melt one can expect a structure with mean crystallite size $n = 6400$ atoms or $d = 18.5\cdot10^{-4}$ μm.

Thus, we have presented a mathematical model for the thermal process occurring in a material upon action of a concentrated energy flux with consideration of the kinetics of crystalline phase formation. The expressions obtained permit evaluation of the size of the crystalline phase nuclei in the solidified melt, as well as the degree of its amorphization.

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VELOCITIES OF ELASTIC WAVES IN CONSOLIDATED GRANULAR MEDIA

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Zaikin [1] proposed a method of calculating the effective moduli of dry consolidated granular media on the basis of the solution of the problem of the elastic deformation of an individual grain. The model of intersecting spheres (MIS) was used to describe the structure of the pore space. A numerical procedure for calculating the velocities of elastic waves was also presented. As a result, a functional relationship was established between the velocities of longitudinal and transverse waves and the parameters of the pore space: porosity f and the product of the specific surface (per unit volume) and mean grain size $\eta = S_V\langle D\rangle$. Equations were presented for the velocities of the elastic waves in the case when the Poisson ratio of the material of the grains $\sigma = 0.25$.

In the present study, we use the approach referred to above to study the effect of the elastic properties of the solid phase on the effective elastic moduli of a granular medium. Results are presented from experimental studies of the structure of the pore space and the velocities of ultrasonic waves. These studies were conducted using specially prepared three-dimensional models of granular media.

As was established previously, the dependence of the effective moduli on the elastic parameters of the solid phase is determined solely by the Poisson's ratio of the latter. In our calculations, it varied within the range $0.05 \leq \sigma \leq 0.45$, with increments of 0.05. For each value of σ, we obtained the dependence of the velocities of the elastic waves on porosity and the type of packing of the grains (the number of contacts). Similar relations for $\sigma = 0.344$ are shown below. We used multiple regression analysis to approximate these relations with equations of the form

$$V_P^*/V_P = 1 - A_1 f - A_2\eta, \; V_S^*/V_S = 1 - A_3 f - A_4\eta. \tag{1}$$

The asterisks denote effective elastic parameters of the granular medium. We used nine values of σ to construct the regression equations for the coefficients of Eq. (1). Approximation of the coefficients A_1, A_2, A_3, A_4 by a cubic parabola gives results which are quite satisfactory (mean error no greater than 0.7%):

$$\begin{aligned} A_1 &= 0{,}722 + 0{,}029\sigma + 0{,}303\sigma^2 - 0{,}268\sigma^3, \\ A_2 &= 0{,}058 + 0{,}123\sigma - 0{,}494\sigma^2 + 1{,}16\sigma^3, \\ A_3 &= 0{,}685 + 0{,}0201\sigma + 0{,}05\sigma^2 + 0{,}147\sigma^3, \\ A_4 &= 0{,}0664 - 0{,}0225\sigma + 0{,}0277\sigma^2 - 0{,}133\sigma^3. \end{aligned} \tag{2}$$

With the use of Eqs. (1) and (2) to represent numerical results on the velocities of the elastic waves, the mean error of the prediction is no greater than 8%.

Before analyzing the expressions that have been obtained, let us discuss the MIS. The geometry of this model is determined by two dimensionless parameters. Since we are using f

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