ON THE KINETICS OF POLYCRYSTAL SHOCK MELTING

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A superheated crystal is thermodynamically stable with respect to small internal perturbations. Experimentally, however, superheating is difficult to achieve because of the serious disturbance of the thermodynamic state of the crystal originating at the surface (which, as a rule, is wetted by the liquid phase of the same substance [1, 2]). This disturbance, of course, cannot be eliminated, however slow the rate of heating. Superheating is possible only under dynamic conditions – when the heating time is less than the time required to establish phase equilibrium. In principle, this condition can be fulfilled by rapid volume heat release, for example, in shock compression.

Let us consider the melting time for a rapidly heated polycrystalline solid. It is assumed that the melting point T_* and the heat of fusion q do not change in the process of establishing phase equilibrium, which, generally speaking, holds true only at constant pressure.

In the relaxation zone of the phase transition in a shock wave the pressure P changes by a certain quantity ΔP, which, however, usually satisfies the condition $P^{-1}\Delta P \ll 1$ (an exception is the case when the shock adiabat and the melting point curve intersect at a small angle). The change in T_* is then of the order [3]:

$$\frac{\Delta T_*}{T_*} \sim \frac{n-1}{n}\,\frac{\Delta P}{P+\pi} \quad \text{or} \quad \frac{\Delta T_*}{T_*} \ll 1, \qquad \frac{\Delta q}{q} \ll 1 .$$

Here it has been assumed that $n > 1$ and $\pi \sim 10^4$-10^5 atm. Hence, in solving the heat conduction equation we may assume that $T_* = \langle T_* \rangle$ and $q = \langle q \rangle$, where $\langle T_* \rangle$ and $\langle q \rangle$ are the mean values of T_* and q in the relaxation zone.

The second assumption is that only the surfaces of the monocrystals are centers of fusion. This assumption does not limit the generality of the treatment, if the monocrystals are small enough for the process of melting to conclude before liquid phase nuclei can form in the interior of the monocrystal.

However, since the kinetics of volume nucleation and the quantitative criterion of crystal smallness in the abovementioned sense are not considered here, the estimate obtained below should be regarded as an estimate of the upper limit of the melting time τ for monocrystals of arbitrary size. The processes taking place at the melting surface can be assumed inertialess* within certain limits of superheating, as long as the rate of fusion is limited by the thermal conductivity. The limits of applicability of this treatment will be considered later.

If the intensity of the shock wave is sufficient to melt only a small portion of the monocrystal, then the location of the surface of the solid phase during the process of melting can be assumed fixed, and τ is determined by the time for equalization of the temperature T of the monocrystal, whose surface is maintained at $T = T_*$, while the initial temperature $T_0 > T_*$. The temperature equilization time, which depends on the shape of the monocrystal, is of the order

$$\tau \approx 0.1\, a^2 / \varkappa \tag{1}$$

(for example, for a spherical or cubic shape [5]). Here a is the linear dimension of the monocrystal, $\varkappa$ is the thermal diffusicity. According to (1) the width of the relaxation zone of a shock wave with a mass velocity U relative to the front is $\sim 0.1\, U a^2/\varkappa$.

At larger shock wave intensities, the melting process may be significantly accelerated owing to displacement of the monocrystal boundary. In order to estimate the melting time in this case, let us consider the auxiliary one-dimensional problem of the melting of a semi-infinite medium having an initial temperature T_0 independent of the coordinate x and a moving plane boundary x_1, at which the temperature T_* is given. The position of the boundary x is determined by the quantity of heat necessary for melting reaching x_1 from the region of the solid phase.

The mathematical formulation of the problem consists in the following: it is required to solve the equation of heat conduction:

$$\frac{\partial T}{\partial t} = \varkappa \frac{\partial^2 T}{\partial x^2} \tag{2}$$

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*Cases involving the anomalously slow kinetics of surface melting, characteristic of substances whose liquid phase is vitreous and distinguished by its extremely high viscosity, are an exception. Such substances may be considerably superheated by a heat flux from the surface [4].

with the initial conditions $T(x, 0) = T_0 = \text{const} > T_*$, $x > 0$, $T(0, 0) = T_*$ and a boundary condition (conservation of quantity of heat during melting) that may be conveniently represented in integral form:

$$qx_1 = x_1 c(T_0 - T_*) + c\int_{x_1}^{\infty}(T_0 - T)\,dx \tag{3}$$

where c is the specific heat of the crystal.*

From the parameters of the problem and the variables x and t it is possible to construct only one independent dimensionless variable $y = x(2\varkappa t)^{-1/2}$, on which depends the dimensionless "temperature"

$$z = \frac{T - T_*}{T_0 - T_*}.$$

In dimensionless quantities Eq. (2) becomes

$$z'' + yz' = 0. \tag{4}$$

The solution of Eq. (4) is the integral

$$z = A\int_{y_1}^{y} e^{-1/2\, r^2}\,dr \quad (y \geqslant y_1); \qquad z = 0 \quad (0 \leqslant y < y_1) \qquad \left(\frac{1}{A} = \int_{y_1}^{\infty} e^{-1/2\, y^2}\,dy\right). \tag{5}$$

In determining A it was assumed, that $z = 1$ when $y = \infty$.

The constant of integration y_1 is determined by condition (3), which in dimensionless quantities has the form

$$y_1(b - 1) = \int_{y_1}^{\infty}(1 - z)\,dy \qquad \left(b = \frac{q}{c(T_0 - T_*)}\right). \tag{6}$$

In the general case y_1 is calculated from (5) and (6), which contain tabulated integrals. However, for $y_1 \gg 1$, the calculations can be carried to completion directly. It will be seen subsequently [formula (8)] that $y_1 \gg 1$ corresponds to almost complete melting $0 < b - 1 \ll 1$, assuming that $y_1 \gg 1$, we find

$$\int_{y_1}^{\infty} e^{-1/2 y^2}dy \approx \frac{e^{-1/2 y_1^2}}{y_1}, \quad \int_{y_1}^{y} e^{-1/2 r^2}\,dr \approx \frac{e^{-1/2 y_1^2}}{y_1} - \frac{e^{-1/2 y^2}}{y}$$
$$z \approx 1 - \frac{y_1}{y}\, e^{1/2\,(y_1^2 - y^2)} \qquad (y \geqslant y_1). \tag{7}$$

Substituting (7) in (6), we obtain

$$y_1(b - 1) \approx y_1 e^{1/2\, y_1^2}\int_{y_1}^{\infty} e^{-1/2\, y^2}\frac{dy}{y} \approx \frac{1}{y_1}, \qquad y_1 = (b - 1)^{-1/2} = \left[\frac{c(T_0 - T_*)}{q - c(T_0 - T_*)}\right]. \tag{8}$$

Reverting to the original variables, for the time for the liquid phase boundary to move from 0 to x_1 we get:

$$\tau_1 = \frac{x_1^2}{2\varkappa y_1^2} = \frac{x_1^2}{2\varkappa}\,\frac{q - c(T_0 - T_*)}{c(T_0 - T_*)} \approx \frac{x_1^2}{2\varkappa}\left[1 - \frac{c(T_0 - T_*)}{q}\right] \tag{9}$$

in accordance with (8) and $y_1 \gg 1$.

It follows from (7) that for $y > y_1$, T differs significantly from T_0 over the interval $\Delta y \sim 1/y_1$, i.e., over the interval $\Delta x \sim x_1/y_1^2$. Thus, for $y_1 \gg 1$ the volume of unmelted substance disturbed by thermal motion is small compared with the volume of liquid. For this reason the solution of the one-dimensional problem of the melting of a semi-infinite medium is applicable, to a good approximation, to the three-dimensional case of melting of a body of finite size. The melting time is then given by the formula

$$\tau \approx \left(\frac{a}{2}\right)^2\frac{1}{2\varkappa}\left[1 - \frac{c(T_0 - T_*)}{q}\right] \approx 0.1\,\frac{a^2}{\varkappa}\left[1 - \frac{c(T_0 - T_*)}{q}\right] \tag{10}$$

obtained from Eq. (9) by replacing x_1 by $a/2$ (since when $y_1 \gg 1$ the intensity of the shock wave is sufficient for melting to be almost complete).

Formula (10), obtained for $y_1 \gg 1$, formally coincides with (1) when $b^{-1} \ll 1$, i.e., for a wave intensity leading to only slight melting of the crystal. Thus, (10) correctly describes the limiting cases of slight and almost total fusion.

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*This problem is analogous to the problem of freezing [6], if the supercooled state of the liquid is considered.

In the intermediate region of shock wave intensities, equation (10) must be regarded as an interpolation. Further refinement of (10) would make sense only if the variety of size and shape of the monocrystals were taken into account.

Formula (10) reduces to $\tau = 0$ for $c(T_0 - T_*) = q$. Under these conditions, melting at the surface will proceed without heat being supplied. The rate of melting, however, will be limited by the activation time, not considered in this model, which, at the temperatures in question $(T - T_*) \approx q/c$, is of the order of 10 periods of vibration of a lattice point (the settled lifetime of a liquid molecule). This implies that the velocity of the phase boundary for $c(T_0 - T_*) \approx \approx q$ is of the order of 0.1 times the speed of sound. In a polycrystalline solid the relaxation zone of a shock wave, whose intensity is sufficient for total melting of the substance, thus has a width of about $10a$ or less. (If, as a result of melting, a two-wave configuration is formed, then this relates to the structure of the second wave. The two-wave configuration as a whole will not be stationary, and there is no limit on its width.)

In conclusion, it should be emphasized again that the above discussion relates to the upper limit of the melting time. Actually, for $c(T_0 - T_*) \approx q$ the melting time may be considerably less, since with such strong heating the state of the crystal may be close to the border of lability. (Molten metals have been supercooled [7] by $\Delta T \approx 0.2 T_*$. In view of the well-known symmetry of the processes of superheating and supercooling, we may expect superheating of the same order under conditions that exclude the surface effect. Then, however, the nuclei of the new phase still contain hundreds of molecules [7]. The time for these nuclei to develop [1] under shock melting conditions cannot be considered infinitely small. For this reason, shock melting may be nonhomogeneous even for a large degree of superheating.) A second factor, which may accelerate the process of melting, is the possible instability of the plane boundary of a superheated crystal, similar to dendritic solidification of a supercooled liquid [7].

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