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Abstract

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ON THE INFLUENCE OF ELASTIC-RELAXATION STRESSES ON THE CRYSTALLIZATION OF VERY VISCOUS LIQUIDS

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The influence of elastic stresses on the melting of solids was considered in ([1]). Analogous phenomena may occur in the crystallization of very viscous liquids, since the latter possess elastic properties (for glasses, for example, the shear modulus is $\sim 5 \cdot 10^{11}$ dyn/cm^2).

Since in an amorphous medium elastic stresses decay with time, their influence on crystallization is manifested in the case when the growth of the crystal outstrips the relaxation of the stresses. Apparently this is always the case, since for an atom to pass from the liquid phase into the solid a time τ_0 is required, equal to the time of a single change in the position of equilibrium, whereas for relaxation of stresses several such jumps must occur. The relaxation time τ is determined by the rearrangement of the structure of the liquid within preservation of short-range order and, owing to the chaotic character of the motion, is equal to the diffusion time over the corresponding characteristic distance $D = nd$, where d is the mean interatomic distance. It is easy to see that $\tau \sim n^2 \tau_0$. For ordinary liquids $n = 3 \div 4$, and for very viscous liquids it is still larger, so that $\tau > 10\tau_0$.

The probability of the fluctuational formation of nuclei of the solid phase in very viscous liquids is practically equal to zero, and we shall not touch upon this question, assuming that, as a result of the influence of impurities, there always exist nuclei that have overcome the surface barrier. We shall regard the growing crystals as spherical, which is quite permissible at the initial stage of the process.

If at the boundary of the crystal there is a stress $\sigma_{rr}(R) = -\delta p$ (this will occur in the case when the density of the crystal ρ_2 is greater than the density of the amorphous phase ρ_1), the melting temperature, according to the Clapeyron-Clausius equation, will be lowered. Namely, if crystallization is carried out at temperature T_1, a crystal of radius R will be in equilibrium with the medium when

$$\sigma_{rr}(R) = \left(\frac{T_0 - T_1}{T_c}\, q\rho_2 - \frac{2\alpha}{R}\right)\frac{1}{3\beta} \equiv \sigma_{rr}^{(0)}, \tag{1}$$

where T_0 is the melting point of a plane undeformed surface; q is the heat of transition per gram; α is the coefficient of surface tension; 3β is the relative change of density upon crystallization.

If $\sigma_{rr}(R) > \sigma_{rr}^{(0)}$, the crystal will melt; but if $\sigma_{rr}(R) < \sigma_{rr}^{(0)}$, the crystal grows, the characteristic time of the process in both cases being τ_0.

It is evident that under certain conditions relation (1) is fulfilled. Then for some time the growth of the crystal is determined by the relaxation of stresses. Taking (1) as the boundary condition, let us consider the problem of crystal growth caused by the indicated process.

Let the Young' s modulus and Poisson' s ratio in the amorphous phase and in the crystal be equal, respectively, to E_1, σ_1 and E_2, σ_2. The components of the vector

and the strain tensors u_i and u_{ik}, and the stress tensor σ_{ik}, belonging to the different media, we shall likewise denote by the indices (1) and (2). We shall assume that Hooke' s law holds in the crystal:

$$\sigma_{ik}^{(2)} = \frac{E_2}{1+\sigma_2}\left(u_{ik}^{(2)} + \frac{\sigma_2}{1-2\sigma_2} u_{ll}^{(2)}\right). \tag{2}$$

Both in the crystal and in the amorphous phase the equilibrium conditions are satisfied,

$$\frac{\partial \sigma_{ik}^{(1,2)}}{\partial x_k} = 0. \tag{3}$$

In the amorphous phase, the elastic-relaxation stresses are described by the interpolation equation for very viscous liquids (see, for example, ([2]))

$$\frac{d\sigma_{ik}^{(1)}}{dt} + \frac{1}{\tau}\sigma_{ik}^{(1)} = \frac{E_1}{1+\sigma_1}\frac{du_{ik}^{(1)}}{dt}. \tag{4}$$

At the boundary $r = R$, in addition to (1), the equilibrium condition is fulfilled,

$$\sigma_{rr}^{(1)}(R) = \sigma_{rr}^{(2)}(R) \tag{5}$$

and conservation of the amount of substance,

$$u_r^{(2)} - u_r^{(1)} = \beta R. \tag{6}$$

The spatial distribution of the corresponding quantities is given by the known formulas of the theory of elasticity. The quantities entering the boundary conditions have the form

$$\sigma_{rr}^{(1)} = \frac{2E_1}{1+\sigma_1} a(t) \frac{1}{r^3}; \qquad u_r^{(1)} = \frac{b(t)}{r^2};$$

$$\sigma_{rr}^{(2)} = \frac{c(t)E_2}{1-2\sigma_2}; \qquad u_r^{(2)} = c(t)r, \tag{7}$$

where a and b are related by the equation:

$$\dot{a} + \frac{1}{\tau} a = -\dot{b}. \tag{8}$$

Eliminating a, b, and c, we find the equation for the growth of the crystal

$$\left(\frac{1+\sigma_1}{2E_1} + \frac{1-2\sigma_2}{E_2}\right) \frac{d}{dt} R^2 \left(\frac{T_0 - T_1}{T_0} q\rho_2 R - 2\alpha\right) +$$

$$+\frac{1}{\tau} R^2 \frac{1+\sigma_1}{2E_1} \left(\frac{T_0 - T_1}{T_0} q\rho_2 R - 2\alpha\right) = 3\beta^2 R^2 \frac{dR}{dt}. \tag{9}$$

The solution satisfying the initial condition $R_{t=0} = R_1$ has the form

$$R \left(\frac{R - R_0}{R_1 - R_0}\right)^{\nu} = R_1 e^{-t/\tau_1}, \tag{10}$$

where

$$R_0 = \frac{2\alpha T_0}{(T_0 - T_1) q\rho_2} \quad \text{(critical size of the nucleus)};$$

$$\nu = \frac{1}{2} \left(1 - \frac{3\beta^2 E_1 E_2 T_0}{q\rho_2 (T_0 - T_1)[(1+\sigma_1)E_2 + (1-2\sigma_2)E_1]}\right),$$

$$\tau_1 = 2\tau \left(1 + \frac{2E_1}{E_2} \frac{1-2\sigma_2}{1+\sigma_1}\right). \tag{11}$$

The solution obtained describes the real process only under the condition $\dot{R} > 0$. In the opposite case, as is easy to see, for $\delta R > 0$, $\sigma_{rr} > \sigma_{rr}^{(0)}$, and condition (1) loses its force, and the crystal grows in a nonequilibrium manner if $R_1 > R_0$, and dissolves in the opposite case.

We shall assume that $R_1 > R_0$, i.e., that the surface barrier has been overcome. If $\nu > 0$, $\dot{R} < 0$. Elastic stresses do not determine the growth of the crystal. If $0 > \nu > -1$, then, under the condition

$$R < \frac{R_0}{1 - |\nu|}, \tag{12}$$

$\dot{R} > 0$. In this case condition (1) is fulfilled due to the influence of surface tension (the critical stresses are sufficiently small), and the growth of the crystal is determined by the relaxation of elastic stresses. Then the stresses fall below the critical value, and the growth of the crystal continues in a nonequilibrium manner (with characteristic time τ_0).

For $\nu < -1$, for any R, the increase of elastic stresses limits the growth of the crystal. As $t \to \infty$,

$$R \sim e^{-t/\tau_1(\nu+1)}. \tag{13}$$

For large ν and ν close to -1, the characteristic growth time is τ_0. Generalizing the results obtained, one may say that the growth time of the crystal is equal to $\tau_1(\nu+1)+\tau_0$ for $\nu < -1$, and to τ_0 for $\nu > -1$. Since τ_0 and τ_1 depend strongly on temperature (as $e^{U/kT}$), and $\nu \to \infty$ as $T_1 \to T_0$, the crystallization rate must also depend substantially on temperature.

Let $\tau_1 = \tau_1^{(0)} e^{U/kT_1}$, $\tau_0 = \chi_0 e^{U/kT_1}$, with $\chi_0 \ll \tau_1^{(0)}$ (see above). We shall find the degree of supercooling $\frac{T_0 - T_1}{T_0}$ at which the characteristic crystallization time is minimal. To do this we find the minimum of the expression $\tau_1(\nu+1)+\tau_0$. If the corresponding degree of supercooling lies in the interval $\nu < -1$, it will give the maximum crystallization rate. If it falls outside this interval, the maximum crystallization rate will be attained at $\nu = -1$.

In the calculations we shall assume that $T_0 - T_1 \ll T_0$ and $kT_0 \ll U_0$ (usually these conditions are always valid). We obtain

$$\left(\frac{T_0 - T_1}{T_0}\right)_{\max} = \frac{kT_0}{U}\left\{1 + \frac{kT_0}{U}\,\frac{qp_2\left[(1+\sigma_1)E_2 + (1-2\sigma_2)E_1\right]}{2E_1E_2\beta^2}\right\}. \tag{14}$$

This degree of supercooling may give ν both smaller and larger than -1. In the latter case, the maximum rate corresponds to the degree of supercooling

$$\left(\frac{T_0 - T_1}{T_0}\right)_{\max} = \frac{\beta^2 E_1 E_2}{qp_2\left[(1+\sigma_1)E_2 + (1-2\sigma_2)E_1\right]}. \tag{15}$$

Thus, we have shown that the maximum crystallization rate of very viscous liquids corresponds to a certain degree of supercooling, different from zero, just as occurs in ordinary liquids (3). However, the mechanism of this shift differs from that considered in (3) (the low probability of fluctuations under weak supercooling) and is associated with relaxation-elastic processes.

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Note: Figure translations are in progress. See original paper for figures.

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