PHASE BOUNDARY INSTABILITY DURING PHASE CONVERSION UNDER PRESSURE

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The problem of instability of the boundary of a spherical nucleus during solidification of gases under diffusion growth conditions was considered in [1, 2]. The question of stability of a planar boundary between two phases during phase conversion was first formulated in [3], which considered solidification of one of the components of a binary alloy. However, as was noted in [2], [3] suffers from the serious shortcoming that it does not consider the decrease in velocity of the front motion with time. The problem of development of distortions in a planar phase boundary with time was solved in [2] in the linear approximation with consideration of the fact that diffusion cannot supply the quantity of dissolved material necessary to insure motion of the planar front at constant velocity. The present study will consider development of instability over time in spherical and planar phase boundaries during phase conversion under pressure in the linear approximation. Mathematically this problem differs from that considered in [1-3] in that it considers the change in supersaturation with pressure δp as a function of time, which has a significant effect on instability development. The time change of δp can either be specified, or produced by a change in volume upon phase transition (synthesis in a constant-volume high-pressure chamber, in a regulated high pressure chamber, or in shock waves). We will also examine development of instability in a spherical phase boundary with consideration in the thermal conductivity equation of the finite rate of motion of the phase conversion front and the temperature dependence of the thermal conductivity coefficient. A possible mechanism for formation of polycrystals of varying dispersion is considered. The results obtained can be applied to diffusion synthesis of a new phase when the concentration of the dissolved material is a function of time. Such a situation occurs, for example, in the process of diffusion synthesis of diamond under pressure, in which case the pressure drop in the chamber produced by the phase transition leads to a decrease in the concentration of dissolved graphite in the catalyst.

1. Formulation of the Problem. It is known that motion of the new phase boundary in phase transitions of the first sort is accompanied by liberation or absorption of heat. In the case of diffusionless phase transitions, no matter what the phase transition mechanism, as a rule the process of thermal relaxation is the slowest process in the system, so that growth of the new phase is controlled by heat liberation from the boundary where the phases contact each other. The problem can be solved in the isotropic approximation by assuming that elastic stresses which develop in the conversion process do not affect the rate of phase motion boundary. This is possible in the case where the stresses developing during front motion are relaxed by plastic deformation, i.e., the rate of phase transition front motion is less than the plastic deformation rate.

To describe the development of phase boundary distortions over time in the linear approximation we write the thermal conductivity equation for the first phase:

$$\partial T/\partial t = \chi_1 \Delta T. \tag{1.1}$$

On the phase boundary the condition

$$T|_{s} = T_{0} \left(1 - 2\alpha / \left(\rho_{2} q R \right) \right)$$
(1.2)

must be satisfied. Removing the thermal flux from the phase transformation boundary leads to motion of the latter:

$$-\kappa_1 \partial T / \partial \mathbf{v}|_s = \rho_2 q v_{\mathbf{v}}. \tag{1.3}$$

The condition

$$T_{\infty} = T_0 \left(1 - 2\alpha / (\rho_2 q R_*) \right) \tag{1.4}$$

defines the critical nucleus size R_{\star} . Here T_0 is the temperature on the plane boundary between the two phases in equilibrium; χ_1 , thermal diffusivity of phase 1; ρ_2 , density of the

Troitsk. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 5, pp. 132-138, September-October, 1988. Original article submitted November 20, 1986.

nucleus; q, heat of phase transition; α , surface tension coefficient; R, radius of the nucleus; , thermal conductivity coefficient of phase 1; v_{ν} , normal velocity of phase conversion front; T_{∞} , temperature of phase 1 at large distances from the front.

The phase boundary is constantly in thermodynamic equilibrium, and change in temperature on the planar phase contact boundary is defined by the Clapeyron-Clausius equation

$$\Theta = T_0 - T_\infty = T_\infty \left(V_1 - V_2 \right) \, \delta p/q \tag{1.5}$$

(where V = $1/\rho_1$, V₂ = $1/\rho_2$ are the specific volumes of phases 1 and 2).

2. Instability in the Motion of Spherical Nucleus Phase Boundaries. The spherically symmetric solution of Eq. (1.1) in a coordinate system fixed to the phase conversion front with neglect of heat liberation inertia is

$$T(r) - T_{\infty} = -\frac{\Theta_R R \int\limits_{R}^{r} \exp\left\{-z \frac{r}{R}\right\} \frac{dr}{r^2}}{E_2(z)} + \Theta_{Rs}$$
(2.1)

where $z = R \frac{dR}{dt} / \chi_1$; $E_2(z) = \int_{1}^{\infty} \exp\{-zt\} \frac{dt}{t^2}$; $\Theta_R = T_R - T_{\infty} = \Theta(1 - R_*/R)$ (as follows from Eqs. (1.2), (1.4)). Substituting Eq. (2.1) in Eq. (1.3), we have

$$T_{q}z = \frac{\rho_{1}}{\rho_{2}} \Theta_{R} \frac{\mathrm{e}^{-z}}{E_{2}(z)}$$

$$(2.2)$$

 $(T_q = q/C, where C is the specific heat).$

When the form of the nucleus deviates from spherical, for its temperature and radius we take the following

$$T' = T(r) + \sum_{l,m} \left(\frac{R}{r}\right)^{l+1} f_{lm}(r) Y_{lm}(\Omega), \quad R' = R(t) + \sum_{l,m} \xi_{lm}(t) Y_{lm}(\Omega)$$
(2.3)

 $(Y_{lm}(\Omega)$ are spherical harmonics). Linearizing the boundary conditions (1.2), (1.3) with respect to ξ with the aid of Eq. (2.3), we obtain

$$\frac{\partial T}{\partial r}\Big|_{R} \xi_{lm} + f_{lm}(R) = -\frac{T_{0}\alpha (l-1) (l+2)}{\rho_{2}qR^{2}} \xi_{lm}, \qquad (2.4)$$

$$\rho_{2}q\frac{d\xi_{lm}}{dt} = -\varkappa_{1}\frac{\partial^{2}T}{\partial r^{2}}\Big|_{R} \xi_{lm} + \varkappa_{1}\frac{l+1}{R} f_{lm}(R) - \varkappa_{1}\frac{\partial f_{lm}}{\partial r}\Big|_{R}.$$

Substituting Eq. (2.3) in Eq. (1.1), we find an equation for definition of $f_{lm}(r)$:

$$\frac{d^2 f_{lm}}{dr^2} + \left(\frac{z}{R} - \frac{2l}{r}\right) \frac{df_{lm}}{dr} - \frac{z(l+1)}{Rr} f_{lm} = -\frac{1}{\chi_1} \left(\frac{r}{R}\right)^{l+1} \frac{d\xi_{lm}}{dt} \frac{\partial T}{\partial r}.$$
(2.5)

For sufficiently high phase boundary velocity the major change in temperature will occur in a thin boundary layer with little curvature. We take r = R(t) + y, y << R. In the first approximation, in place of Eq. (2.5), we write

$$\frac{d^2 f_{lm}}{dy^2} + \frac{1}{R} \left(z - 2l\right) \frac{d f_{lm}}{dy} - \frac{z \left(l+1\right)}{R^2} f_{lm} = \frac{T_q}{\chi_1} \frac{\rho_2}{\rho_1} z \frac{d\xi_{lm}}{dt} \exp\left\{-\frac{z}{R} y\right\}.$$
(2.6)

The required solution of Eq. (2.6), vanishing at infinity, is

$$f_{lm} = A_{lm} \exp k_1 y + \frac{T_q}{\chi_1} \frac{\rho_2}{\rho_1} \frac{R}{l-1} \frac{d\xi_{lm}}{dt} \exp\left\{-\frac{z}{R}y\right\}$$

$$\left(k_1 = -\frac{1}{2R} \left(z - 2l + \sqrt{z(z+4) + 4l^2}\right)\right).$$
(2.7)

Substituting Eq. (2.7) in Eq. (2.4) with the aid of Eqs. (2.1) and (2.2), we find

$$\frac{d\xi_{lm}}{\xi_{lmdt}} = \frac{\chi_1 z \left(\sqrt{z (z+4) + 4l^2 - z - 2}\right)}{2R^2 h} - \frac{\chi_1 T_0 \gamma \left(z+2 + \sqrt{z (z+4) + 4l^2}\right) (l-1) (l+2)}{2\rho_2 q R^3 h} \left(h = 1 - \frac{1}{l-1} (z+k_1 R), \gamma = \frac{\alpha}{\rho_2 q}\right).$$
(2.8)

For z >> 1, $R >> R_{*}$, it follows from Eq. (2.2) that

$$z = \frac{2\Theta}{T_q - \Theta} - \frac{\Theta}{T_q}.$$
(2.9)

For the instability increment [2], which compares growth in the deviation ξ to growth of the nucleus itself R, we obtain

$$\lambda_{l} = \frac{d}{dt} \ln \frac{\xi_{lm}(t)}{R(t)} = \frac{\chi_{1} z \left(\sqrt{z(z+4)+4t^{2}}-z-2(1+h)\right)}{2R^{2}h} - \frac{\chi_{1} T_{0} \gamma (t-1) \left(t+2\right) \left(z+2+\sqrt{z(z+4)+4t^{2}}\right)}{2\rho_{2} q R^{3} h}.$$
(2.10)

Equation (2.10) gives a correct result for z << 1, since the solution of Eqs. (2.5), (2.6) in this case is $f_{\ell m} = A_{\ell m}$ and Eq. (2.3) is a solution of Eq. (1.1). It is evident from Eq. (2.10) that with growth of the nucleus, perturbations with an ever increasing ℓ lose stability. Instability first develops for a given ℓ at

$$R_{cl} = \frac{\varkappa_{1} T_{0} \gamma \left(l-1\right) \left(l+2\right) \left(z+2+\sqrt{z \left(z+4\right)}+4l^{2}\right)}{\rho_{2} q \chi_{1} z \left(\sqrt{z \left(z+4\right)}+4l^{2}-z-2\left(1+k\right)\right)}.$$
(2.11)

For z << 1, R >> R_x from Eq. (2.2) we obtain $z = \rho_1 \Theta / (\rho_2 T_q)$ and instability first develops for $R_{c3} \simeq 40 \varkappa_1 \gamma T_0 / (\rho_2 q \chi_1 z)$ at $\ell = 3$, as in [2]. It should be noted that $R_{c\ell}$ for z >> 1 is significantly smaller than for z << 1. Moreover, at z >> 1 perturbations with various ℓ become unstable at practically the same time as compared with perturbation stability loss at z << 1.

In a constant-volume chamber nuclei grow under conditions of falling pressure, produced by the phase transition. In this case the expression for the instability increment (for $z \ll 1$)

$$\lambda_{l} = \frac{\varkappa_{1}T_{\infty}\left(V_{1}-V_{2}\right)\left(l-2\right)}{\rho_{2}q^{2}R^{2}} \delta p_{0} - \frac{\varkappa_{1}T_{\infty}\alpha}{\rho_{2}^{2}q^{2}R^{3}} \left[2\left(l-2\right) + \left(l^{2}-1\right)\left(l+2\right)\right] - \frac{4}{3}\pi NT_{\infty}\varkappa_{1}K_{1}\left(V_{1}-V_{2}\right)^{2}\left(l-2\right)R \quad (2.12)$$

can be obtained from Eqs. (2.10) and (1.5) with $\delta p = \delta p_0 - \frac{4}{3} \pi N K_1 \frac{V_1 - V_2}{V_2} R^3$. Here δp_0 is the initial supersaturation; N is the number of nuclei per unit volume; K_1 is the modulus of volume compression of phase 1.

Setting Eq. (2.12) equal to zero, we obtain

$$R^4 + dR + e = 0, (2.13)$$

where $d = -\frac{3}{4} \frac{\delta p_0}{\pi N K_1 \rho_2 (V_1 - V_2)}; \ e = \frac{3}{4} \frac{\alpha}{\pi} \frac{[2 (l-2) + (l^2 - 1) (l+2)]}{\rho_2^2 (V_1 - V_2)^2 N K_1 (l-2)}$. Equation (2.13) has two positive

$$R_{1,2} = \sqrt{8y_1/4} \mp (-d/\sqrt{8y_1} - y_1/2)^{1/2}$$

$$(2.14)$$

$$y_1 = \sqrt[3]{-q + \sqrt{D}} + \sqrt[3]{-q - \sqrt{D}}, D = d^4/256 - e^3/27 > 0, q = -d^2/16$$

Near the values e/d and $\sqrt[3]{-d}$,

$$R_{1} \simeq \frac{\alpha \left[2 \left(l-2\right)+\left(l^{2}-1\right) \left(l+2\right)\right]}{\left(l-2\right) \rho_{2} \left(V_{1}-V_{2}\right) \delta \rho_{0}} \left[1 + \frac{4}{3} \pi \alpha^{3} \times \frac{\left(2 \left(l-2\right)+\left(l^{2}-1\right) \left(l+2\right)\right)^{3} N K_{1}}{\rho_{2}^{2} \left(V_{1}-V_{2}\right)^{2} \left(l-2\right)^{3} \left(\delta \rho_{0}\right)^{4}}\right]_{*}$$

$$R_{2} \simeq \left(\frac{3}{4} \frac{\delta \rho_{0}}{\pi N K_{1} \rho_{2} \left(V_{1}-V_{2}\right)}\right)^{1/3} - \frac{1}{3} \alpha \frac{\left[2 \left(l-2\right)+\left(l^{2}-1\right) \left(l+2\right)\right]}{\rho_{2} \left(V_{1}-V_{2}\right) \delta \rho_{0}}.$$
(2.15)

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Perturbations lose stability $(\lambda_{\ell} > 0)$ at $R_1 < R < R_2$. It follows from Eqs. (2.14), (2.15) that for a sufficiently large pressure drop in the chamber produced by the change in volume upon phase transition, perturbations with large ℓ become stable one after the other.

If there is a sufficient quantity of new phase nuclei in the constant-volume chamber, arbitrarily distributed over size, then at $\Theta_R \ll T_q$ and insignificant supersaturation δp a stage of coalescence sets in, caused by thermal diffusion, which is completely analogous to the coalescence stage in the diffusion process of new phase nucleus formation in decomposition of a supersaturated solid solution considered in [4]. The law of increase in mean and maximum

size of new phase nuclei is then
$$\langle R \rangle = R_* = \left(\frac{4}{9}\chi_1\beta t\right)^{1/3}$$
, $R_m = \frac{3}{2}\langle R \rangle (\beta = 2\alpha CT_0/(\rho_2q^2))$, and from Eq. (2.10) we obtain $\lambda_{\ell} < 0$ for all ℓ . Hence, in the coalescence stage, perturbations with any ℓ are stable. They diappear following the law $\xi_l = \xi_{l0} \left(\frac{t_0}{t}\right)^n$, where $n = (l-1) \left[\frac{9}{8}\frac{\rho_1}{\rho_2}(l+1)\right]$

 $(l+2) - \frac{1}{3}$; ξ_{l0} is the value of the initial perturbation with orbital moment l; t_0 is the in-

itial time.

Of special interst is the effect of the temperature dependence of the thermal conductivity coefficient on development of phase boundary instability. In the approximation of slow phase boundary motion ($z \ll 1$) and neglect of inertia of heat removal from the boundary, the thermal conductivity equation for phase 1 can be written in the form

$$\operatorname{div}\left(\varkappa_{1} \operatorname{grad} T\right) = 0. \tag{2.16}$$

We will choose the simplest form of the thermal conductivity coefficient temperature dependence: $\varkappa_1 = \varkappa_{\infty}(1 + \lambda (T - T_{\infty}))$. Then the solution of Eq. (2.16) is

$$T - T_{\infty} + \frac{\lambda}{2} (T - T_{\infty})^2 = \frac{\left(\Theta_R + \frac{\lambda}{2} \Theta_R^2\right) R}{r} + \sum_{l,m} A_{lm} \left(\frac{R}{r}\right)^{l+1} Y_{lm}(\Omega).$$

Calculation of the instability increment for R >> $\rm R_{\star}$ yields

$$\lambda_{l} = \frac{\varkappa_{\infty} (l-2)}{\rho_{2} q R^{2}} \left(\Theta + \frac{\lambda}{2} \Theta^{2}\right) - \frac{\gamma \varkappa_{\infty} T_{0} \left(1 + 2\lambda \left(\Theta + \frac{\lambda}{2} \Theta^{2}\right)\right)^{1/2} (l^{2} - 1) (l+2)}{\rho_{2} q R^{3}}.$$
(2.17)

It follows from Eq. (2.17) that the value of R_{cl} characterizing the onset of instability for a perturbation with a given l is less for $\lambda < 0$ and greater for $\lambda > 0$ than at $\lambda = 0$.

3. Instability of a Planar Phase Boundary. We will consider the question of instability of a planar new phase front with the condition that δp is an arbitrary function of time. We will assume that the motion of the interphase boundary is slow in comparison to thermal conductivity. The solution of Eq. (1.1) is then

$$T(x, t) - T_{\infty} = \frac{T_{\infty} \left(V_1 - V_2 \right) \left(x - x_0 \right)}{2q \left(\pi \chi_1 \right)^{1/2}} \int_{0}^{t} \exp\left\{ -\frac{\left(x - x_0 \right)^2}{4\chi_1 \left(t - \tau \right)} \right\} \frac{\delta p(\tau) \, d\tau}{\left(t - \tau \right)^{3/2}}.$$
(3.1)

We describe the interphase boundary by the equation

$$x_{0} = \frac{\varkappa_{1} T_{\infty} (V_{1} - V_{2})}{(\pi \chi_{1})^{1/2} \rho_{2} q^{2}} \int_{0}^{\tau} \frac{\delta \rho (t - \tau)}{\sqrt{\tau}} d\tau.$$
(3.2)

We will study small perturbations of Eq. (3.1) in the manner of [2], first considering a single Fourier component. We take

$$T' = T(x, t) + f_k(x, t) e^{ik\varrho},$$
(3.3)

where $f_k(x, t)$ is a small temperature perturbation defining a small perturbation of the interphase boundary:

$$x_0' = x_0 + \xi_h(t) e^{ik\varrho}.$$
 (3.4)

The vectors ρ , k lie in the plane of the unperturbed phase boundary.

The boundary conditions (1.2), (1.3) linearized with respect to ξ have the form

$$f_k |_{x_0} + \frac{\partial T}{\partial x} \Big|_{x_0} \xi_k = -T_0 \gamma k^2 \xi_k; \qquad (3.5)$$

$$\rho_2 q \frac{d\xi_k}{dt} = -\kappa_1 \frac{\partial^2 T}{\partial x^2} \Big|_{x_0} \xi_k - \kappa_1 \frac{\partial f_k}{\partial x} \Big|_{x_0}.$$
(3.6)

It follows from Eqs. (3.3) and (1.1) that

$$\frac{\partial f_k}{\partial t} = \chi_1 \left(\frac{\partial^2 f_k}{\partial x^2} - k^2 f_k \right). \tag{3.7}$$

Using the quasisteady-state condition $\partial f_k/\partial t \ll \chi_1 k^2 f_k$, we obtain from Eqs. (3.5)-(3.7)

$$\xi_{k} = \xi_{0k} A(t) \exp\left[\int_{0}^{t} k(v_{0}(\tau) - v_{k}) d\tau\right],$$

$$v_{0}(t) = \frac{\kappa_{1} B \delta p_{0}}{(\pi \chi_{1} t)^{1/2}} + \frac{\kappa_{1} B}{(\pi \chi_{1})^{1/2}} \int_{0}^{t} \frac{\partial \delta p}{\partial \tau} (t - \tau)^{-1/2} d\tau,$$

$$v_{0}(t) = \frac{\kappa_{1} B \delta p_{0}}{(\pi \chi_{1} t)^{1/2}} + \frac{\kappa_{1} B}{(\pi \chi_{1})^{1/2}} \int_{0}^{t} \frac{\partial \delta p}{\partial \tau} (t - \tau)^{-1/2} d\tau,$$
(3.8)

$$v_{k} = \frac{T_{0} \gamma \varkappa_{1} k^{2}}{\rho_{2} q}, \quad B = \frac{T_{\infty} (V_{1} - V_{2})}{\rho_{2} q^{2}}, \quad A(t) = \exp\left\{-\frac{B \varkappa_{1}}{\varkappa_{1}} (\delta p(t) - \delta p_{0})\right\}.$$

The final result is

$$\xi(\rho, t) = A \int \xi_{0k} e^{ik\varrho} \exp\left[\int_{0}^{t} (v_0(\tau) - v_k) d\tau\right] \frac{d^2k}{(2\pi)^2}.$$
(3.9)

For example, let $\delta_{\mathbf{p}} = \omega t$. Then for a given t, the exponential in Eq. (3.8) is positive for $\frac{2\omega Bt^{1/2}}{(\pi\chi_1)^{1/2}} > \frac{T_0 \gamma k^2}{\rho_2 q}$, i.e., perturbations with $e k^2 < \frac{2(V_1 - V_2)\omega \rho_2 t^{1/2}}{\alpha (\pi\chi_1)^{1/2}} = k_c^2(t)$ are unstable. With increase

in t, perturbations with ever increasing k become unstable.

It follows from the integral of Eq. (3.9) at sufficiently large t that

$$\xi(\rho, t) \approx \int_{0}^{\infty} \xi_{\rho k} e^{ik\rho} \exp \varphi(k, t) \, k dk \sim \exp \varphi(k_m, t) \int_{0}^{\infty} \xi_{\rho k} e^{ik\rho} \exp \left\{ -\frac{1}{2} \left| \frac{\partial^2 \varphi}{\partial k^2} \right|_{km} (k-k_m)^2 \right\} k \, dk,$$

$$\varphi(k_m, t) \gg 1, \quad A \approx 1.$$
(3.10)

In Eq. (3.10) the function $\varphi(k, t) = \frac{4}{3} \varkappa_1 \frac{B \omega t^{3/2}}{(\pi \chi_1)^{1/2}} k - \varkappa_1 \frac{T_0 \gamma k^3 t}{\rho_2 q}$ is expanded in a series in k near

its maximum. (Since it is necessary that the condition $v_0(t)(t/\chi_1)^{1/2} \ll 1$ be satisfied, the maximum time t is limited and defined by the value of ω .)

The initial perturbations ξ_{0k} are unknown. We will assume that $\xi_{0k}k$ is a slowly varying function of k. Then from Eq. (3.10) we finally obtain

$$\xi\left(\rho,\,t\right) \sim \sqrt{\pi} \,\frac{\xi_{0k_m}k_m}{\sigma} e^{\phi(k_m,t)} \exp\left\{-\frac{\rho^2}{4\sigma^2}\right\} e^{ik_m\rho},$$
where $k_m = \frac{2}{3} \frac{\left[\omega\left(V_1 - V_2\right)\rho_2\right]^{1/2} t^{1/4}}{\alpha^{1/2} \left(\pi\chi_1\right)^{1/4}}; \ \sigma^2 = \frac{2\varkappa_1 T_0 \left[\alpha\omega\left(V_1 - V_2\right)\right]^{1/2}}{\rho_2^{3/2} q^2 \left(\pi\chi_1\right)^{1/4}} t^{5/4}; \ \varphi\left(k_m,t\right) = \frac{16}{27} \frac{\varkappa_1 T_0 \left[\left(V_1 - V_2\right)\omega\right]^{3/2} t^{7/4}}{\alpha^{1/2} q^2 \rho_2^{1/2} \left(\pi\chi_1\right)^{3/4}}.$ It

is evident that instability of the planar interphase boundary at sufficiently large times increases in this case as the exponential of $t^{7/4}$.

4. Mechanism for Formation of Polycrystals of Various Dispersions. It is obvious that the absence of increasing random perturbations during motion of the interphase boundary encourages production of a high-quality defect-free homogeneous crystal. It is also natural to assume that to produce a single-crystal, the initial form perturbations of nuclei with various & must attenuate with time. Consequently, large single-crystals can be grown only with a very small supersaturation, or during the coalescence stage. However in the case where the nucleus size R > R_{C3} and perturbations increase with time, one can propose a hypothesis concerning a possible mechanism for formation of polycrystals of various dispersions.

We will assume that the size of a crystallite in the polycrystal is the maximum size at which random perturbations of its form still decay with time. Beginning at some size, random perturbations of crystallite form can no longer be stabilized. They become nuclei of a new crystallite which grows together with the initial one (it is possible that the process of polycrystal formation passes through a stage of fractionation with subsequent merging together, but with lower system elastic and surface energy). Perturbations of various types which disturb nucleus form always exist under real conditions. From Eqs. (2.2), (2.8) it follows that $\xi_l \sim 1$

 $\xi_{al} \left(R/R_{c3} \right)^{(\sqrt{z(z+4)+4l^2}-z-2)/2\hbar}$, i.e., perturbations increase rapidly with increase in ℓ and R. There-

fore the characteristic scale of a crystallite in the polycrystal $R_{\mbox{cr}}$ ~ $R_{\mbox{c3}}.$ We will use Eq. (2.11) to estimate the size of a crystallite in the polycrystal for the case of the graphitediamond transformation. We have $\alpha \approx 10^{-4} - 10^{-3} \text{ J/cm}^2$, $V_1 - V_2 = 0.17 \text{ g/cm}^3$, $\rho_2 = 3.5 \text{ g/cm}^3$, and for $\delta p \approx 0.1$ GPa we obtain $R_{c3} \approx 10^{-4} - 10^{-3}$ cm, which corresponds to experimental data.

If the polycrystals grow under conditions of a pressure drop in the chamber, produced by the phase transition, then, as follows from Eqs. (2.14), (2.15), the polycrystalline nucleus is inhomogeneous: crystallites on the periphery are coarser than in the center.

The proposed mechanism for polycrystallite formation is kinetically and thermodynamically preferable to the known mechanism of spontaneous formation of a large quantity of new phase nuclei immediately over the entire volume, followed by subsequent growth and merger. In fact, as is well known [5], the number of nuclei (per sec, per cm³ of medium) which traverse

the critical region under steady-state conditions is $S = 2\left(\frac{\alpha}{T}\right)^{1/2} B(R_*) f_0(R_*)$, where $f_0(R_*) = 0$ $\frac{R_{*}^{2}}{v_{1}v_{2}}\exp\left\{-\frac{4\pi\alpha R_{*}^{2}}{3T}\right\}$; B(R_{*}) is the diffusion coefficient in dimensional space; v₁, v₂ are the vol-

ume of the phases per molecule.

With the aid of Eq. (2.2), we obtain

$$S = \frac{\varkappa_1 (\alpha T)^{-1/2} N_A^2 \rho_1}{4\pi M^2 (V_1 - V_2)} \left(\frac{dT}{dp}\right)^2 \delta p \exp\left\{-\frac{16}{3} \frac{\pi v_2^2 \alpha^3}{(v_1 - v_2)^2 T (\delta p)^2}\right\}$$
(4.1)

(where N_A is Avogadro's number and M is the molecular weight).

A diamond polycrystal ~1 cm in size contains ~10¹²-10⁹ crystallites. Yet, as follows from Eq. (4.1), the number of nuclei traversing the critical region is very small.

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