GENERALIZATION OF THE KOLMOGOROV–JOHNSON–MEHL–AVRAMI THEORY TO THE CASE OF NON-UNIFORM NUCLEATION

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UDC 548.5

An expression for the phase volume fraction in a system with a position-dependent nucleation rate is derived in the framework of a geometric-probabilistic approach. As examples of such systems, the following cases are considered: a) a planar layer with nucleation on the mid-plane, an infinitely long cylinder with nucleation on the axis, and a sphere with nucleation at the center; b) nucleation on random planes, on straight lines, and at points in the infinite space. In these cases, the volume fractions are derived for both the time-dependent nucleation rate and the time-dependent growth velocity. The equivalence of the processes of homogeneous nucleation and nucleation at points is established. The obtained results can be used for the analysis of phase transformations starting on grain boundaries (which are modeled by random planes), on grain edges or other linear objects, and at impurity particles.

1. Introduction

The probabilistic phenomenological approach to the description of a phase transformation is based on the notion of centers of a new phase, around which the accretion of a substance proceeds at some rate. Respectively, two functions are used: the nucleation rate $I(t)$ of new-phase centers and their growth velocity $\tilde{u}(t, \mathbf{n})$. The aim is to derive the temporal characteristics of the process, such as the volume fraction $X(t)$ of the new phase, the size distribution function of the grains formed, etc.

The accretion of a substance around a new-phase center proceeds with the linear rate

$$\tilde{u}(t, \mathbf{n}) = u(t)c_0(\mathbf{n}), \tag{1}$$

where $\mathbf{n}$ is a unit vector directed outward from this center; the function $c_0(\mathbf{n}) \equiv c_0(\theta, \phi)$ is such that the extreme points of the vectors of length $c_0(\mathbf{n})$ drawn from the origin in all directions $\mathbf{n}$ form a convex surface. From (1), the size of a nucleus in the direction $\mathbf{n}$ is

$$\tilde{R}_{\mathbf{n}}(t', t) = R(t', t)c_0(\mathbf{n}), \tag{2}$$

where $R(t', t) = \int\limits_{t'}^{t} u(\tau)d\tau$ is the radius of a spherical nucleus. The increment of the nucleus volume by dt in the direction n is equal to $d\tilde{V}_{\mathbf{n}}(t', t) = R^2(t', t)dR(t', t)c_0^3(\mathbf{n})d\Omega$, $d\Omega = \sin\theta d\theta d\phi$ is the solid-angle element. Hence, the volume of a nucleus at t is $\tilde{V}(t', t) = V(t', t)c_0^3$, where

$$c_0^3 = \frac{1}{4\pi}\int\limits_{\Omega} c_0^3(\mathbf{n})d\Omega, \tag{3}$$

and $V(t', t) = (4\pi/3)R^3(t', t)$ is the volume of a spherical nucleus. Setting $g \equiv (4\pi/3)c_0^3$, we obtain $\tilde{V}(t', t) = gR^3(t', t)$, where g is the shape constant.

Under the condition that the model restrictions established by Kolmogorov [1] are fulfilled (they are examined in [4] in detail), the following expression for the volume fraction $Q(t)$ of the material untransformed is obtained in the framework of the Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [1-4]:

$$Q(t) = \exp\left[-Y(t)\right], \quad Y(t) = \int\limits_{0}^{t} I(t')\tilde{V}(t', t)dt'. \tag{4}$$

The result of the Kolmogorov's approach can be formulated as follows: the probability for an arbitrary point O' of a system to remain untransformed at time t is given by (4). In other words, this is the probability that no center of a new phase appears inside the critical region for the point O' ($\tilde{V}(t',t)$ is the volume of the critical region at t').

Thus, the nucleation rate in the classical KJMA theory can depend on time, but it does not depend on coordinates. In the present paper, the extension of the KJMA theory to the case of a position-dependent nucleation rate is carried out. To do this, the critical region method is used. Earlier, it was applied by the author to the problem of calculating the volume fractions of competing phases [5]. It should be pointed out that the critical region concept itself was introduced by Kolmogorov in [1], though no specific term for this region was used therein.

In the case of a position-dependent nucleation rate, expression (4) must be replaced by

$$Q(\mathbf{r}_0,t) = \exp\left[-Y(\mathbf{r}_0,t)\right], \tag{5}$$

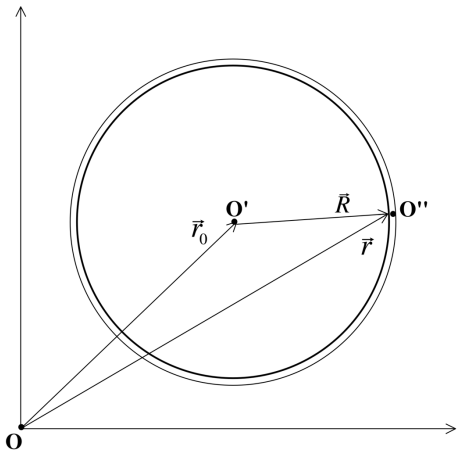
where $\mathbf{r}_0$ is the radius vector of the point O'.

The functions $Y(t)$ and $Y(\mathbf{r}_0,t)$ calculated according to the algorithm of (1) are expressed in terms of an integral over the critical region. So, for the problem considered here, $Y(\mathbf{r}_0,t)$ must have the form

$$Y(\mathbf{r}_0,t) = \int\limits_{t_0}^{t} dt' \int\limits_{\tilde{V}(t',t)} I_{\mathbf{r}_0}(\mathbf{r}',t')d^3\mathbf{r}'. \tag{6}$$

Thus, the Kolmogorov's method is a "differential" one with respect to time, but an "integral" method with respect to the spatial variable. That is, the finite quantity $\tilde{V}(t',t)$ is used, by deriving expressions (4) and (5).

The proposed method differs from the Kolmogorov's one in that it is a "differential" method with respect to both the time and spatial variables: the differential of $V(t',t)$ is used to derive the volume-fraction expression. As a result, the solution is expressed in terms of integrals over the time variables only, which is convenient for the analysis of the dependences obtained [5]. Therefore, this method as a "finer" instrument for calculating the volume fractions is more effective in some cases. In particular, this advantage manifests itself in solving the present problem: it is naturally to operate with dV rather than V in the case of a position-dependent nucleation rate.



The framework used to derive the expression for the volume fraction in the case of a position-dependent nucleation rate

As a special case of systems with inhomogeneous nucleation rates, the nucleation on different i-dimensional objects, $i < 3$ (surfaces, lines, and points), is considered here; the nucleation rate can be represented as a δ-function of coordinates in these cases.

The paper is organized as follows. In Section 2, the general expression for the volume fraction for a position-dependent nucleation rate is derived. In Section 3, the expressions for the volume fractions of an infinite plate with nucleation on the mid-plane, an infinite cylinder with nucleation on the axis, and a sphere with nucleation at the center are obtained. The problem of calculating the volume fractions when the nucleation occurs on planes, straight lines, and at points randomly distributed in the infinite space is solved in Section 4. A discussion of the results is given in Section 5.

2. Calculating the Volume Fraction in the Case of a Position-Dependent Nucleation Rate

Let us introduce a reference frame with the point O as the origin (Figure). We seek the probability $dX(t)$ that the point $O'(\mathbf{r}_0)$ randomly chosen in the system will be transformed in the time interval $[t, t+dt]$. In order that this event take place, it is necessary and sufficient that the following two conditions be satisfied: 1) the point O is not transformed before time t; 2) a new-phase nucleus that can transform the point O' in the time interval $[t, t+dt]$ appears at any time t', $0 \le t' \le t$; we call this nucleus a critical one. Let $Q(\mathbf{r}_0,t)$ and $dY(\mathbf{r}_0,t)$ denote the probabilities of the first and second events, respectively. We deal with nuclei of spherical shape

below. The case of an arbitrary shape allowed by the Kolmogorov's model can be considered similarly without basic difficulties. Consider the space-time scheme of the process, in which both conditions are fulfiled.

Let us specify the spherical region of radius $R(t',t)$ with the center at the point O', the critical region. At time t', the region boundary is moving toward the center with velocity $u(t')$, so that the radius decreases from its greatest value $R(0,t) \equiv R_m(t)$ to $R(t,t) = 0$. As this happens, the fulfilment of condition 1) implies that the appearance of new-phase nuclei is forbidden within this region in the time interval $0 \le t' \le t$. In [1], the function Q(t) is calculated from this condition directly. In the present approach, we use condition 2) for its calculation.

The critical center appearing at t' must lie inside a spherical layer of thickness $dR(t',t) = (\partial R(t',t)/\partial t)dt$ at a distance $R(t',t)$ from the point O'. Let it appear in the volume element $dV(\mathbf{r})$ in the neighborhood of the point $O''(\mathbf{r})$ (Fig. 1), and let the probability of its appearance be $dP_{\mathbf{r}} = I(\vec{r},t)dt'dV(\mathbf{r})$.

In order to get the probability $dP_{\mathbf{r}_0}(t',t)$ of the appearance of a critical center at t', we must integrate $dP_{\mathbf{r}}$ over the critical region boundary. To this end, we introduce the spherical frame of reference with the point O' as the origin. The coordinates of the point O'' are $(R(t',t),\theta,\phi)$, where $R(t',t) = |\mathbf{r}-\mathbf{r}_0|$. The volume element $dV(\mathbf{r})$ is equal to $dV(t',t)d\Omega/4\pi$, where $dV(t',t) = 4\pi R^2(t',t)dR(t',t)$. The nucleation rate in this frame of reference is $I(\mathbf{r},t') \equiv I_{\mathbf{r}_0}(\mathbf{R},t') = I_{\mathbf{r}_0}(R(t',t),\theta,\phi;t')$ (the dependence of quantities on $\mathbf{r}_0$ is indicated below by an index). We introduce the notation

$$J_{\mathbf{r}_0}(t',t) = \frac{1}{4\pi}\int\limits_{\Omega} d\Omega I_{\mathbf{r}_0}(R(t',t),\theta,\phi;t'), \tag{7}$$

where the integration is over the whole solid angle.

In the case of an arbitrary nucleus shape allowed by the Kolmogorov's model, the critical region obviously has the same shape as the nucleus and the opposite orientation . In this case, the radius vector $\mathbf{r}(t',t)$ has length (2) with the replacement $c_0(\mathbf{n}) \to c(\mathbf{n}) \equiv c_0(-\mathbf{n})$ in this formula, so $I(\mathbf{r},t) = I_{\mathbf{r}_0}(R(t',t)c(\mathbf{n}),\theta,\phi;t')$, $d\tilde{V}_{\mathbf{n}}(t',t) = (1/4\pi)dV(t',t)c^3(\mathbf{n})d\Omega$, and the expression for $J_{\mathbf{r}_0}(t',t)$ becomes

$$J_{\mathbf{r}_0}(t',t) = \frac{1}{4\pi}\int\limits_{\Omega} I_{\mathbf{r}_0}(R(t',t)c(\mathbf{n}),\theta,\phi;t')c^3(\mathbf{n})d\Omega. \tag{8}$$

Thus, the desired probability

$$dP_{\mathbf{r}_0}(t',t) = J_{\mathbf{r}_0}(t',t)dt'dV(t',t). \tag{9}$$

The probability $dY_{\mathbf{r}_0}(t)$ for the critical center to appear in the time interval $0 \le t' \le t$ is obtained by integrating (9) over t':

$$dY_{\mathbf{r}_0}(t) = \left\{\int\limits_0^t dt' J_{\mathbf{r}_0}(t',t)\frac{\partial V(t',t)}{\partial t}\right\} dt. \tag{10}$$

Thus, the simultaneous fulfilment of conditions 1) and 2) leads to the equality

$$dX_{\mathbf{r}_0}(t) = Q_{\mathbf{r}_0}(t)dY_{\mathbf{r}_0}(t). \tag{11}$$

Since $X_{\mathbf{r}_0}(t) = 1 - Q_{\mathbf{r}_0}(t)$, expression (11) is a differential equation for $X_{\mathbf{r}_0}(t)$. Its solution with respect to the initial condition $X_{\mathbf{r}_0}(t_0) = 0$ is

$$X_{\mathbf{r}_0}(t) = 1 - \exp\left[-Y_{\mathbf{r}_0}(t)\right],$$

$$Y_{\overline{\tau}_0}(t) = \int\limits_{t_0}^{t} d\tau \int\limits_0^{\tau} dt' J_{\mathbf{r}_0}(t',\tau)\frac{\partial V(t',\tau)}{\partial \tau}. \tag{12}$$

The probability for the point O' to fall in the transformed part of the system is

$$X(t) = \frac{1}{V_0}\int\limits_{V_0} X_{\mathbf{r}_0}(t)d^3\mathbf{r}_0, \tag{13}$$

where the integration is over the system volume.

Expression (13) is the desired volume fraction of the material transformed according to the geometric definition of probability [6]. If the system is infinite, then expression (13) is regarded as the limit at $V_0 \to \infty$. However, it is important that finite-size domains naturally obey this expression. Thus, the expressions obtained can also be regarded as a generalization of expression (4) to the case of a finite-size domain. Even though the nucleation rate inside the domain does not depend on $\mathbf{r}$, the function $X_{\mathbf{r}_0}(t)$ depends on $\mathbf{r}_0$. The reason for this is that, generally, only a part of the critical region for the point O' lies inside the domain. The size of this part depends on $\mathbf{r}_0$. Equation (13) in this case yields the volume fraction averaged over a great number of identical domains, since the transformed fraction of an individual domain is a random quantity.

3. Nucleation on Plane, on a Straight Line, and at a Point

We use the indices s, l, and c for a plane, a straight line, and a point, respectively. Let $I_i(t)$ $(i = s,\ l,\ c)$ be

the specific nucleation rates: I_s (I_l) is the number of centers appearing on unit area (length) per unit time, and I_c is the probability for the center to appear at the point per unit time. Using the δ-shaped representation of the volume nucleation rates $I_v^{(i)}(\mathbf{r},t)$ [e.g., $I_v^{(c)}(\mathbf{r},t) = I_c(t)\delta(\mathbf{r})$] and following the computational procedure of Section 2, we can derive the desirable volume fractions. However, it is simpler to get the result by the critical region method immediately.

The critical region for the point O' at time t' is the sphere of radius $R(t',t)$. Either a part of the plane of area $S_{r_0}(t',t) = \pi\left[R^2(t',t) - r_0^2\right]$ (a part of the straight line of length $l_{r_0}(t',t) = 2\left[R^2(t',t) - r_0^2\right]^{1/2}$) or the point can be located inside it. Let us define the time $t_m(t,r_0)$ by the equation

$$R(t_m,t) = r_0. \tag{14}$$

At $t' > t_m$, the object under consideration is outside the critical region.

In order that the point O' be untransformed at time t, the new-phase center is forbidden to appear in the time interval $0 \le t' \le t_m(t,r_0)$ on the circle of area $S_{r_0}(t',t)$, on the segment of length $l_{r_0}(t',t)$, and at the point O. The probabilities $Q_{r_0}^{(i)}(t)$ of these events can be calculated by the method of [1]; the result is obvious:

$$Q_{r_0}^{(i)}(t) = \exp\left[-\int\limits_0^{t_m(t,r_0)} I_i(t')\zeta_{r_0}^{(i)}(t',t)dt'\right], \quad r_0 < R_m(t), \tag{15}$$

$$\zeta_{r_0}^{(i)}(t',t) = \begin{cases} S_{r_0}(t',t), & i = s, \\ l_{r_0}(t',t), & i = l, \\ 1, & i = c, \end{cases}$$

$$Q_{r_0}^{(i)}(t) = 1, \quad r_0 > R_m(t), \tag{16}$$

since the object is outside the critical region in this case at all t' [Eq. (14) has no solution].

Let the plane be in the middle of a plate of thickness $\varepsilon_s = 2L$, let the straight line be the axis of a cylinder with cross-sectional area $\varepsilon_l = \pi L^2 \equiv s$, and let the point be the center of a sphere of volume $\varepsilon_v = (4\pi/3)L^3 \equiv v$. By $\sigma = (2L)^{-1}$, $\lambda = s^{-1}$, and $n = v^{-1}$, we denote the mean area, the mean length, and the mean number of points in unit volume, respectively.

To get the fraction of a material of the plate transformed (nucleation occurs on the middle plane), we integrate the function $X_{r_0}^{(s)}(t) = 1 - Q_{r_0}^{(s)}(t)$ over r_0 according to (13):

$$X^{(s)}(t) = 2\int\limits_0^L X_{r_0}^{(s)}(t)\frac{dr_0}{2L}. \tag{17}$$

By t^*, we denote the time at which the nucleus appearing at $t' = 0$ reaches the plate boundary: $R_m(t^*) = L$. At $t < t^*$ ($R_m(t) < L$), this integral reduces, in view of (16), to

$$X_1^{(s)}(t) = 2\sigma\int\limits_0^{R_m(t)} X_{r_0}^{(s)}(t)dr_0 =$$

$$= 2\sigma R_m(t)\int\limits_0^1 X_\xi^{(s)}(t)d\xi, \quad \xi = r_0/R_m. \tag{18}$$

At $t > t^*$, we use expression (17) for the volume fraction which can also be represented as

$$X_2^{(s)}(t) = \int\limits_0^1 X_\kappa^{(s)}(t)d\kappa, \quad \kappa = r_0/L. \tag{19}$$

Finally, we obtain

$$X^{(s)}(t) = \eta(t^* - t)X_1^{(s)}(t) + \eta(t - t^*)X_2^{(s)}(t), \tag{20}$$

where $\eta(x)$ is the symmetric unit function [7].

The same expression is applied for volume fractions of the cylinder with nucleation on the axis and the sphere with nucleation at the center. We have

$$X_1^{(l)}(t) = \int\limits_0^{R_m(t)} X_{r_0}{}^{(l)}(t)\frac{2\pi r_0 dr_0}{s} =$$

$$= 2\pi\lambda R_m^2(t)\int\limits_0^1 X_\xi^{(l)}(t)\xi d\xi, \tag{21}$$

$$X_2^{(l)}(t) = 2\int\limits_0^1 X_\kappa^{(l)}(t)\kappa d\kappa \tag{22}$$

for the cylinder and

$$X_1^{(c)}(t) = \int\limits_0^{R_m(t)} X_{r_0}^{(c)}(t)\frac{4\pi r_0^2 dr_0}{v} =$$

$$= 2\pi n R_m^3(t) \int\limits_0^1 X_\xi^{(c)}(t)\xi^2 d\xi, \quad (23)$$

$$X_2^{(c)}(t) = 3\int\limits_0^1 X_\kappa^{(c)}(t)\kappa^2 d\kappa \quad (24)$$

for the sphere. At the constant nucleation and growth rates, the integrals in the latter case are evaluated yielding the following explicit time dependence:

$$X_1^{(c)}(t) = \frac{6}{(I_c t^*)^3}\left\{\frac{(I_c t)^3}{6} - \frac{(I_c t)^2}{2} + I_c t - 1 + e^{-I_c t}\right\}, \quad (25)$$

$$X_2^{(c)}(t) = 1 - \frac{6e^{-I_c(t-t^*)}}{(I_c t^*)^3}\left\{\frac{(I_c t^*)^2}{2} - I_c t^* + 1 - e^{-I_c t^*}\right\}, \quad (26)$$

where $t^* = L/u$.

4. Nucleation on Random Planes, on Straight Lines, and at Points

4.1. Derivation of the expressions for volume fractions

In view of the generality of the approach used, we consider these three cases simultaneously.

Let either planes (straight lines) or points be distributed randomly in the infinite system. In deriving the volume fractions of a material transformed on the nucleation on these objects, we use the critical region method. We choose accidentally a point O' in the system and seek the probability $Q^{(i)}(t)$ that it will be untransformed at time t. The critical region for the point O' at the time $t' = 0$ is a sphere of radius $R_m(t)$. Let it either be intersected by N planes (straight lines) or include N points. By r_k, we denote the distance from point O' to the kth object, k=1,...N. The probability $q_N^{(i)}(\{r_k\},\ t)$ for the point O' to be untransformed at time t at the given N and the realization of the set $\{r_k\} = \{r_1, r_2, ..., r_n\}$ is a product of probabilities (15):

$$q_N^{(i)}(\{r_k\}, t) = \prod_{k=1}^{N} Q_{r_k}^{(i)}(t) =$$

$$= \prod_{k=1}^{N} \exp\left[-\int\limits_0^{t_m(t,r_k)} I_i(t')\zeta_{r_k}^{(i)}(t', t)dt'\right], \quad i = s, l, c. \quad (27)$$

The desired function $Q^{(i)}(t)$ is obtained by averaging $q_N^{(i)}(\{r_k\},\ t)$ over all r_k and N:

$$Q^{(i)}(t) = \sum_{N=0}^{\infty} P^{(i)}(N) \int\limits_0^{R_m(t)} \cdots \int\limits_0^{R_m(t)} q_N^{(i)}(\{r_k\}, t)\times$$

$$\times f^{(i)}(r_1, ..., r_N)dr_1...dr_N, \quad (28)$$

where $f^{(i)}(\{r_k\})$ is the distribution function of the set $\{r_k\}$, and $P^{(i)}(N)$ is the probability of the given N.

In order to deduce the expression for$f^{(i)}(\{r_k\})$, we first choose the parametric space for every kind of the object. In the case of points, the parametric space is the coordinate space itself: the point is determined by the coordinates (r, θ, ϕ); the volume element is $dv = r^2 \sin\theta dr d\theta d\phi$. We assume that the points are distributed according to the Poisson law: the probability for the point to be in the volume element dv is equal to $\gamma_c dv$ and does not depend on either volume element shape or position. We divide the volume $V_m(t) = (4\pi/3)R_m^3(t)$ of the critical region into layers of thickness dr, $dv(r) = 4\pi r^2 dr$. Further, we use the following property of the Poisson process [6]: the probability for the kth point to be in the volume element dv_k under the condition that there are N points in the whole volume $V_m(t)$ is equal to dv_k/V_m (the distribution over volume is uniform). Going from v_k to r_k, we find that the probability for kth point to be at the distances $[r_k, r_k + dr_k]$ is equal to $4\pi r_k^2 dr_k/V_m$. Also, all the distances r_k are independent quantities. Consequently,

$$f^{(c)}(\{r_k\}) = \prod_{k=1}^{N} f^{(c)}(r_k), \quad (29)$$

where $f^{(c)}(r_k) = 3r_k^2/R_m^3$.

A plane is uniquely determined by two angles θ, ϕ and the length r_k of the perpendicular to it from the point O'. The measure element for planes in the parametric space (r, θ, ϕ) is $dE^{(s)} = \sin\theta dr d\theta d\phi$ [8]. We also assume the Poisson distribution for planes: the probability for a plane to be in the "volume" element $dE^{(s)}$ is $\gamma_s dE^{(s)}$. Further, we similarly derive expression (29) with $f^{(s)}(r_k) = 1/R_m$ for the set $\{r_k\}$ distribution.

Let us determine a straight line by its direction θ, ϕ and the polar coordinates r, β of the intersection point of this line with the plane perpendicular to it and passing

through the point O'. Thus, the measure element is $dE^{(l)} = rdrd\beta d\Omega$, and, for the Poisson distribution of straight lines (with the parameter γ_l), the probability for the kth line to be at the distances $[r_k,\, r_k + dr_k]$ from the point O' is $f^{(l)}(r_k)dr_k = 2r_k dr_k/R_m^2$.

Returning now to expression (28), we see that the N-dimensional integral is equal to $w_i^N(t)$, where

$$w_i(t) = \int\limits_0^{R_m(t)} Q_r^{(i)}(t) f^{(i)}(r) dr. \tag{30}$$

Averaging with the use of $P^{(i)}(N) = \alpha_i^N \exp(-\alpha_i)/N!$ yields

$$Q^{(i)}(t) = \sum_{N=0}^{\infty} \frac{\alpha_i^N}{N!} e^{-\alpha_i} w_i^N = e^{-\alpha_i(t)(1-w_i(t))}. \tag{31}$$

We determine the parameter α_i for every kind of the object. For points: $\alpha_c = \bar{N} = V_m(t)n$. For planes, we express α_s in terms of σ. The area S_r of the plane part located inside the critical region is equal to $\pi(R_m^2 - r^2)$. Its mean value is

$$\bar{S}_r = \pi \int\limits_0^{R_m(t)} \left(R_m^2 - r^2\right) \frac{dr}{R_m} = \frac{2}{3}\pi R_m^2.$$

The mean area in unit volume is $\sigma = \bar{S}_r \bar{N}/V_m = \bar{S}_r \alpha_s / V_m = \alpha_s / 2R_m$, which yields

$$\alpha_s = 2\sigma R_m. \tag{32}$$

For straight lines, it is easy to similarly get

$$\alpha_l = \pi \lambda R_m^2. \tag{33}$$

Substituting α_i into (31), we find the fraction of a material transformed in every case:

$$X^{(i)}(t) = 1 - \exp\left(-X_1^{(i)}(t)\right), \tag{34}$$

where $X_1^{(i)}(t)$ are given by expressions (18), (21), and (23).

4.2. One more derivation of the Kolmogorov's formula

Consider the case of nucleation at points in greater details. In this case, expression (34) has the form

$$X^{(c)}(t) = 1 - \exp\left\{-4\pi n \int\limits_0^{R_m(t)} \left[1 - e^{-\int\limits_0^{t_m(t,r)} I_c(t')dt'}\right] r^2 dr\right\}. \tag{35}$$

Let us introduce the function $\bar{I}_v(t)$ via the equality

$$\bar{I}_v(t) = nI_c(t) \exp\left[-\int\limits_0^t I_c(t')dt'\right]. \tag{36}$$

Its integral is

$$n_0(t) = \int\limits_0^t \bar{I}_v(t')dt' = n\left\{1 - \exp\left[-\int\limits_0^t I_c(t')dt'\right]\right\}. \tag{37}$$

It is easily seen that the exponent in (35) is expressible in terms of $\bar{I}_v(t)$ as follows:

$$X^{(c)}(t) = 1 - \exp\left\{-4\pi \int\limits_0^{R_m(t)} r^2 dr \int\limits_0^{t_m(t,r)} \bar{I}_v(t')dt'\right\}. \tag{38}$$

Changing the order of integration, we obtain the Kolmogorov's formula:

$$X^{(c)}(t) = 1 - \exp\left\{-\int\limits_0^t \bar{I}_v(t') V(t', t) dt'\right\}. \tag{39}$$

It is seen that the function $\bar{I}_v(t)$ has the meaning of the mean volume nucleation rate.

In the limiting case of large values of $I_c(t)$, the function $\bar{I}_v(t)$ has a δ-shaped form: $\bar{I}_v(t) = n\delta_+(t)$, so expression (39) describes the case where all of the centers appear at $t' = 0$:

$$X(t) = 1 - \exp\left[-nV_m(t)\right]. \tag{40}$$

We now consider the limiting cases for planes. If the exponent in $Q_{r_0}^{(s)}(t)$ (15) is small (small nucleation and growth rates, small times), then expression (18) changes to

$$X_1^{(s)}(t) = \int\limits_0^t dt' \bar{I}_v(t') V(t', t), \quad \bar{I}_v(t') = \sigma I_s(t'). \tag{41}$$

In the case of a large value of the exponent, we have

$$X_1^{(s)}(t) = 2\sigma R_m(t). \tag{42}$$

The corresponding limiting cases for the system of random planes are obtained by substituting (41) and (42) into (34).

5. Discussion

As follows from the foregoing, the geometric-probabilistic approach in the form of the critical region method is efficient in the solution of various problems involved in calculating the volume fractions. The undoubted advantage of this approach is its rigor: the results are consequences of the initial premises. In the present work, the nucleation on i-dimensional objects is considered as an example of inhomogeneity. The expressions derived in the case of the nucleation on individual i-dimensional objects are used for calculating the volume fractions in infinite systems, in which these objects are distributed randomly. The nucleation at random points was considered for the first time by Avrami [3], who believed that phase transformation generally follows this scenario. The nucleation on random planes and straight lines was considered by Cahn [9] as applied to the problem of nucleation on grain boundaries and edges. The consideration was in the framework of the JMA approach, and the expressions for volume fractions at constant nucleation and growth rates were obtained. However, this approach, which is also called the mean-field approximation, is intuitive but not rigorous mathematically. It can yield both exact and approximate results. An example of the former is the Kolmogorov's formula which is also obtained in the JMA approach. As an example of the latter case, the volume fractions of competing phases can be considered: the JMA approach yields approximate expressions for them [5]. This was the reason for reconsidering the expressions in [9]. Their derivation performed in the present work supports the results in [9]: expressions (34) at constant nucleation and growth rates go into those obtained by Cahn. As is clear from the theory presented in Section 4, the exactness of the mean-field approach in this problem is a consequence of the Poisson distribution law for the objects and the premises of the Kolmogorov's model. Such a distribution is frequently found in physical systems. However, the cases of inhomogeneous distributions of objects are also possible. For example, the points (the particles, on which the nucleation occurs) can be nonuniformly distributed over a volume for various reasons (γ_c depending on r). These cases can also be considered in the framework of the theory given in Sections 4 and 2 with the corresponding modifications. In particular, the function $Q^{(i)}(t)$ calculated by the critical region method according to the scheme of Section 4 will depend on the radius vector $\mathbf{r}_0$ of the point O' in any frame of reference, so expression (13) must be used for calculating the volume fraction. The detailed consideration of these cases is beyond the scope of the present work.

Expression (41) shows that the phase transformation kinetics on the nucleation on random planes is described by the Kolmogorov's formula at the early stage of the process. After the exhaustion of places for the nucleation (the late stage of the process), only the one-dimensional growth of grains takes place [expression (42)]; the corresponding asymptotics for the volume fraction is $X^{(s)}(t) = 1 - \exp(-2\sigma R_m(t))$. So, the Avrami exponent $n_A(t) = \partial \ln(-\ln Q(t))/\partial t$ changes with time from 4 to 1 [9].

One fact related to the one-dimensional asymptote (42) of the volume fraction is worth to note. It concerns the competitive formation of two or more different phases on a plane. Let two phases with nucleation and growth rates $I_{s,k}(t)$ and $u_k(t)$, k=1, 2, $u_2(t) > u_1(t)$, be formed simultaneously. As was shown in [5], the approximation of independent phases can be used in the given case for calculating the fractions of these phases. Thus, we have

$$Q^{(s)}_{r_0}(t) = \exp\left[-Y_{r_0,1}(t) - Y_{r_0,2}(t)\right], \tag{43}$$

$$Y_{r_0,k}(t) =$$

$$= \begin{cases} \int\limits_0^{t_{m,k}(t,r_0)} I_{s,k}(t') S_{r_0,k}(t',t)dt', & \mathrm{r}_0 < R_{m,k}(t), \\ 0, & \mathrm{r}_0 > R_{m,k}(t). \end{cases}$$

The total volume fraction $X^{(s)}(t)$ of a material transformed is obtained by integration of the expression $1 - Q^{(s)}_{r_0}(t)$ over r_0:

$$X^{(s)}(t) = 2\sigma R_{m,1}(t)\left\{\int\limits_0^1 \left[1 - e^{-Y_{\xi,1}(t) - Y_{\xi,2}(t)}\right]d\xi + \right.$$

$$\left. + \int\limits_1^{R_{m,2}/R_{m,1}} \left[1 - e^{-Y_{\xi,2}(t)}\right]d\xi \right\}, \tag{44}$$

where $\xi \equiv r_0/R_{m,1}$, $t < t^*$, and t^* is determined by the equality $R_{m,2}(t^*) = L$.

In the limiting case of large values of $Y_{\xi,2}(t)$, we have

$$X^{(s)}(t) = 2\sigma R_{m,2}(t). \tag{45}$$

Thus, the phase transformation is governed by the second (fast growing) phase. Grains of the first (slow-growing) phase are "immured" inside the layer of the

second one and cannot contribute to the increase of the transformed volume [10].

These results can be used to analyze the experimental data in the cases where the phase transformation starts on grain boundaries [10, 11].

In conclusion, let us dwell on expression (39) in more details. It shows that the process of nucleation at points can be regarded as the process of homogeneous nucleation with the appropriate nucleation rate (36). The inverse statement is also true: the process of homogeneous nucleation with the nucleation rate $I_v(t)$ can be represented as the process of nucleation at points. The corresponding specific nucleation rate $I_c(t)$ is easily derived from (36):

$$I_c(t) = \frac{I_v(t)}{n - \int\limits_0^t I_v(t')dt'} = \frac{I_v(t)}{n - n_0(t)}. \qquad (46)$$

The parameter n remains arbitrary under the single condition $n > n_0(t)$. The established equivalence of the processes of homogeneous nucleation and nucleation at points shows that the Avrami and Johnson–Mehl approaches are not alternative to each other [4], but reduce to each other by means of relations (36) and (46), respectively.

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Received 23.05.07

УЗАГАЛЬНЕННЯ ТЕОРІЇ КОЛМОГОРОВА–ДЖОНСОНА–МЕЙЛА–АВРАМІ НА ВИПАДОК НЕОДНОРІДНОГО ЗАРОДКОУТВОРЕННЯ

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Р е з ю м е

У рамках геометріко-ймовірностного підходу одержано вираз для об'ємної частки фази в системі з неоднорідною швидкістю зародження. Як приклади таких систем розглянуто такі випадки: *а*) плоский шар (зародження нової фази відбувається на серединній площині); нескінченний циліндр (зародження відбувається на осі); куля (зародження відбувається в центрі); *б*) зародження нової фази на випадкових площинах, прямих, в точках – у необмеженому просторі. У кожному випадку одержано вираз для об'ємної частки при залежних від часу швидкостях зародження і росту. Встановлено еквівалентність процесів гомогенного зародження і зародження в точках. Здобуті результати можуть бути використані для аналізу фазових перетворень, що починаються на межах зерен (які моделюються випадковими площинами), на ребрах зерен або інших лінійних об'єктах, а також на частинках домішок.