Journal of Applied Mechanics and Technical Physics, Vol. 48, No. 2, pp. 208–212, 2007

GROWTH OF A NEW PHASE IN A SUBSTANCE IN A METASTABLE STATE

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UDC 536.42

A model of kinetics of phase transitions in a substance in a metastable state is proposed, where the probability of extensive nucleation owing to homogeneous mechanisms is rather large; the model is an alternative to Kolmogorov's model. The use of this model is demonstrated to offer analytical solutions that describe both the crystallization processes with similar densities of the liquid and solid phases and, for instance, the kinetics of nucleation and growth of bubbles in surface boiling. Solutions obtained by Kolmogorov's model and by the present model coincide at the initial stage of the process where the volume fraction of the new phase is small.

Key words: *phase transitions, metastable state, nucleation.*

Fluctuation nucleation of centers of a new phase is possible in a substance in a metastable state. The nuclei can be formed both inside the volume of the pure substance (homogeneous nucleation) and on impurity particles or foreign surfaces (heterogeneous nucleation). The nucleation frequency J and the growth rate of the nuclei v depend on the degree of metastability of the medium ε (overcooling, oversaturation, etc.). An important problem is to find the time-dependent behavior of the fraction X of the volume occupied by the new phase and the number of nucleation centers N for prescribed values of J and v.

One of the first works, where an attempt was made to solve this problem as applied to kinetics of volume crystallization of an overcooled metallic melt, was the paper by A. N. Kolmogorov [1]. He demonstrated that the dependence of the fraction of the crystalline mass X (ratio of the volume of the crystallized substance to the initial volume) on time is described by the relation

$$X(t) = 1 - \exp\Big(\int\limits_0^t J(\tau)V(t-\tau)\,d\tau\Big), \tag{1}$$

where V is the crystallite volume. The densities of the liquid and solid phases in this model are assumed to be identical.

It follows from Eq. (1) that the fraction of the crystalline mass asymptotically approaches unity (i.e., the time of the phase transition actually tends to infinity), which disagrees with the physics of the process: it is obvious that the phase-transition time is finite if at least one nucleus appears in the volume because the growth rate of the centers of the new phase and the nucleation frequency are finite. It should be noted that there is always a probability that no nuclei appear at all, but this probability for an isolated system with a finite volume V_0 "catastrophically" tends to zero for $t \gg t^* = 1/(JV_0)$ (t^* is the characteristic time of expectation of the emergence of the center of the new phase).

In general, there is always some arbitrariness in the technique of obtaining deterministic solutions in stochastic processes [2, 3]. In many papers, these processes are modeled by Monte Carlo methods (see, e.g., [4]). We will try to solve the problem posed, based on model considerations different from Kolmogorov's theory, like, e.g., in [5] in analyzing surface boiling. Let there be a volume occupied by a metastable phase of a certain substance. In the course of the phase transition, this volume is gradually filled by a new phase (which is stable in this state).

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Nucleation is possible only in the region that has not yet passed to the new phase state. Hence, the time-dependent behavior of the fraction X of the volume occupied by the new phase is described by the integral equation

$$X(t) = \int_0^t J(\tau)(1 - X(\tau))V(t - \tau)\, d\tau, \tag{2}$$

where V is the volume of the center of the new phase. For volume nucleation of the new phase, Eq. (2) is valid if the densities of the new and parent phases are identical (a more generic dependence with different densities of the phases for spontaneous volume vaporization was derived in [6]). In addition to volume nucleation, the centers can also be formed on heterogeneous surfaces. In this case, Eq. (2) describes the contact area of the new phase with the heterogeneous surface on a unit surface area as a function of time. The quantity V is understood here as the contact area of the nucleus of the new phase with the surface. Note that the surface and volume formation of the new phase (for similar densities of both phases) are united by spatial "freezing-in" of the nuclei. Let us consider this class of problems in more detail. The mechanism of "collision" of the growing centers is not considered in the present paper.

The number of nuclei N on a unit area, which are formed in a unit volume during the time t, is

$$N(t) = \int_0^t J(\tau)(1 - X(\tau))\, d\tau. \tag{3}$$

Let us pass to dimensionless variables $\bar{t} = t/t_0$, $\bar{V} = V/V_0$, and $\bar{J} = J/J_0$, where t_0, V_0, and J_0 are the characteristic time, volume of the nucleus (contact surface area), and nucleation frequency, respectively; t_0 is defined in a manner to satisfy the equality $J_0V_0t_0 = 1$. Then, Eqs. (2) and (3) can be written as

$$X(\bar{t}) = \int_0^{\bar{t}} \bar{J}(\bar{\tau})(1 - X(\bar{\tau}))\bar{V}(\bar{t} - \bar{\tau})\, d\bar{\tau}; \tag{4}$$

$$N(\bar{t}) = J_0t_0 \int_0^{\bar{t}} \bar{J}(\bar{\tau})(1 - X(\bar{\tau}))\, d\bar{\tau}. \tag{5}$$

If the degree of metastability of the medium ε remains constant in the process, the nucleation frequency J is also unchanged. Hence, we have $\bar{J} = 1$.

Let us consider some factors corresponding to different real physical processes, where Eqs. (4) and (5) have analytical solutions.

For $\bar{V}(\bar{t}) = \bar{t}^n$ $(n \in \mathbb{N})$, the integral equation (4) reduces to the differential equation (by means of differentiation $n + 1$ times)

$$\frac{d^{n+1}X(\bar{t})}{d\bar{t}^{n+1}} = n!\bar{J}(\bar{t})(1 - X(\bar{t})) \tag{6}$$

with the initial conditions

$$\frac{d^iX(0)}{d\bar{t}^i} = 0, \qquad i = 0, \ldots, n. \tag{7}$$

We consider volume crystallization of an overcooled melt. The centers of the new phase are crystallites, and the fraction of the volume occupied by the new phase is the fraction of the crystallized volume. The mechanism of crystal growth in the problem considered is assumed to be normal, and overcooling of the melt in the course of crystallization is constant ($\bar{J} = 1$). In this case, the radial growth rate of the crystal is $v_{\rm cr} = v_0 = {\rm const}$ [7]. Then, the volume of the nucleus is $V(t) = (4\pi/3)v_0^3t^3$. Passing to dimensionless variables, we obtain $\bar{V}(\bar{t}) = \bar{t}^3$ and $t_0 = ((4/3)\pi J_0v_0^3)^{-1/4}$. In this case, the solution of Eq. (6) with allowance for Eq. (7) has the form

$$X(\bar{t}) = 1 - \cos((3/2)^{1/4}\bar{t})\cosh((3/2)^{1/4}\bar{t}). \tag{8}$$

We decompose Eq. (8) into a Taylor series

$$X(\bar{t}) = (6/4!)\bar{t}^4 - (6^2/8!)\bar{t}^8 + o(\bar{t}^8). \tag{9}$$

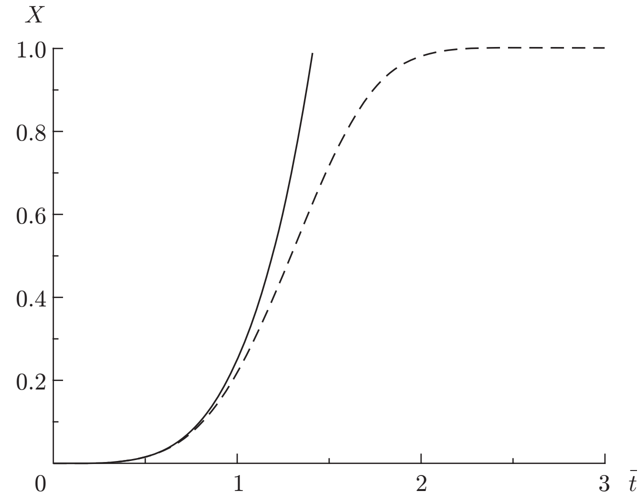

Fig. 1

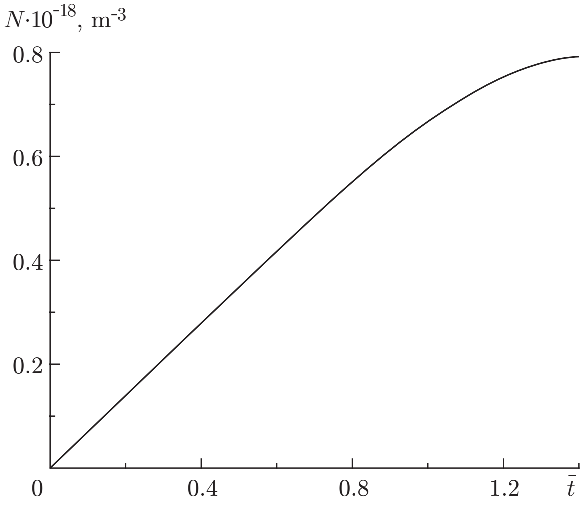

Fig. 2

Fig. 1. Fraction of the crystallized mass versus time for a constant growth rate of the crystal: the solid and dashed curves show the results calculated by Eqs. (8) and (10), respectively.

Fig. 2. Number of crystallites versus time for $J_0 = 10^{25}$ $(\mathrm{sec}\cdot\mathrm{m}^3)^{-1}$ and $v_0 = 10$ m/sec.

This equation contains only two first terms of the expansion, because it is obvious that each next term is much smaller than the previous one (at the characteristic times of the process). Moreover, the use of only the first term of the expansion in Eq. (9) also ensures high accuracy. Hence, the time of complete crystallization of the melt $t_{\rm cr}$ (when the fraction of the crystallized mass becomes equal to unity) can be readily found; $\bar{t}_{\rm cr} \simeq \sqrt{2}$ and $t_{\rm cr} = t_0\bar{t}_{\rm cr}$. For comparison, we also give the results for the crystallized mass fraction calculated by Kolmogorov's theory (1):

$$X(\bar{t}\,) = 1 - \exp(-\bar{t}^4/4). \tag{10}$$

It should be noted that the first term of the expansion of Eq. (10) with respect to $\bar{t}$ coincides with the first term of expansion (9). The subsequent terms of the expansion have an identical power, but the coefficients at these terms are different.

The results calculated by Eqs. (8) and (10) are plotted in Fig. 1. They are seen to be in good agreement for small values of $\bar{t}$.

Let us find the number N of crystallites formed in a unit volume of the melt as a function of time (5):

$$N(\bar{t}\,) \simeq (3\pi/4)^{1/4}\,(J_0/v_0)^{3/4}(\bar{t} - \bar{t}^5/20). \tag{11}$$

Dependence (11) is plotted in Fig. 2. It is seen that the nucleation rate of crystallites at the initial stage of the process is constant, because the fraction of the crystallized mass at this stage is yet low (see Fig. 1). In the course of crystallization of the melt volume, the volume of the parent phase and, hence, the nucleation rate of the centers of the new phase decrease.

The total number of crystallites formed is $N(\bar{t}_{\rm cr}) \simeq 0.8(J_0/v_0)^{3/4}$. Correspondingly, the mean grain size of the crystallized material is $R_{\rm cr} \simeq 0.7(v_0/J_0)^{1/4}$. In Kolmogorov's theory, the time of melt crystallization tends to infinity, but the number of nuclei formed is finite and equal to $N(\infty) \simeq 0.9(J_0/v_0)^{3/4}$.

Let us consider boiling on a flat surface. In this case, the centers of the new phase are vapor bubbles, and X is understood as the area of the "dry spot" on a unit area of the surface. Overheating of the liquid is assumed to be constant ($\bar{J} = 1$).

Under certain regime parameters, the radius R_b of the contact spot of the vapor bubble with the surface is determined by the relation [8] $R_b(t) = \sqrt{\varkappa t}$, where $\varkappa$ is a parameter of the process. Then the area of the contact spot is $V(t) = \pi\varkappa t$. Passing to dimensionless variables, we obtain $\bar{V}(\bar{t}\,) = \bar{t}$ and $t_0 = (\pi J_0\varkappa)^{-1/2}$. In this case, the solution of Eq. (6) with allowance for Eq. (7) has the form

$$X(\bar{t}\,) = 1 - \cos\bar{t}. \tag{12}$$

It follows from Eq. (12) that the boiling surface becomes completely dry at the time $\bar{t}_d = \pi/2$ and $t_d = t_0\bar{t}_d$.

Let us compare the results calculated by Eq. (12) with those predicted by Kolmogorov's theory. For the case considered, the theory predicts

$$X(\bar{t}\,) = 1 - \exp{(-\bar{t}^2/2)}. \tag{13}$$

As in the previous example, the first terms of the expansion of functions (12) and (13) with respect to $\bar{t}$ coincide $[X(\bar{t}\,) \simeq \bar{t}^2/2]$.

Let us find the dependence of the number of bubbles N formed on a unit area of the surface on time (5):

$$N(\bar{t}\,) = (J_0/(\pi\varkappa))^{1/2}\sin\bar{t}.$$

Then, the total number of bubbles formed is $N(\bar{t}_d) = (J_0/(\pi\varkappa))^{1/2}$.

Let us consider the case with an exponential dependence of the radius of the contact spot of the vapor bubble with the surface on time [8] $R_b(t) = R_0\exp{(t/T)}$, where R_0 and T are constants. In this case, the area of the contact spot is $V(t) = \pi R_0^2\exp{(2t/T)}$. Passing to dimensionless variables, we obtain $\bar{V}(\bar{t}\,) = \exp{(\alpha\bar{t}\,)}$, where $\alpha = 2t_0/T$ $[t_0 = (\pi J_0 R_0^2)^{-1}]$. The integral equation (4) is reduced to the differential equation (by differentiating the integral equation)

$$\frac{dX(\bar{t}\,)}{d\bar{t}} = \alpha X(\bar{t}\,) + \bar{J}(\bar{t}\,)(1 - X(\bar{t}\,)) \tag{14}$$

with the initial condition

$$X(0) = 0. \tag{15}$$

The solution of Eq. (14) with allowance for Eq. (15) has the form

$$X(\bar{t}\,) = \frac{\exp{((\alpha-1)\bar{t}\,)} - 1}{\alpha - 1}. \tag{16}$$

It follows from Eq. (16) that the time of drying of the boiling surface is $\bar{t}_d = (\ln\alpha)/(\alpha - 1)$; $t_d = t_0\bar{t}_d$. The total number of bubbles formed is

$$N(\bar{t}_d) = R_0^{-2}\Big(\frac{\alpha\ln\alpha}{(\alpha-1)^2} - \frac{1}{\alpha-1}\Big).$$

Let us compare the results obtained with those predicted by Kolmogorov's theory. According to this theory,

$$X(\bar{t}\,) = 1 - \exp{((1 - \exp{(\alpha\bar{t}\,)})/\alpha)}. \tag{17}$$

As in the previous examples, the first terms of the expansion of functions (16) and (17) with respect to $\bar{t}$ coincide $[X(\bar{t}\,) \simeq \bar{t}\,]$.

It follows from the above-given reasoning that the results predicted by Kolmogorov's theory coincide with the results obtained by the model proposed in the present paper only at the initial stage of the phase transition, when the volume occupied by the new phase is still small. Apparently, this is consistent with the assumption made in [1] that the emergence of new nuclei is an independent event, though this assumption is valid only if the number of nuclei in the volume is still small.

Note that the volume of the medium increases in such processes as volume degassing of an oversaturated solution, cavitation, etc., while the volume where the centers of the new phase can be formed remains almost constant. In this case, therefore, the time evolution of the volume concentration of the new phase is described as

$$X(t) = \int\limits_0^t J(\tau)V(t-\tau)\,d\tau \Big/ \Big(1 + \int\limits_0^t J(\tau)V(t-\tau)\,d\tau\Big).$$

The results obtained in the present work may be used to develop appropriate numerical methods and for their verification.

This work was supported by the Program of Support of Leading Scientific Schools of the Russian Federation (Grant No. NSh-6749.2006.8) and by the State Contract No. 02.442.11.7429.

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