
EVOLUTION OF NEW PHASE CLUSTERS AT THE INITIAL STAGES OF BINARY ALLOY DECOMPOSITION DESCRIBED IN TERMS OF A MODIFIED THEORY OF NUCLEATION

M. PASICHNYI,¹ A. SHIRINYAN,² J. SCHMELZER³

¹**B. Khmelnytskyi Cherkasy National University**

(81, Shevchenko Blvd., Cherkasy 18031, Ukraine; e-mail: pasichnyy@ukr.net)

²**Taras Shevchenko National University of Kyiv**

(2, Prosp. Academician Glushkov, Kyiv 03680, Ukraine; e-mail: aramshirinyan@ukr.net)

³**Institute of Physics, Rostock University**

(43-45, Wismarsche Str., Rostock 18051, Germany; e-mail: juern-w.schmelzer@uni-rostock.de)

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The work considers the thermodynamics and the kinetics of initial decomposition stages in a supersaturated binary solid solution in the framework of the modified nucleation theory. The specific surface energy is considered as a function of intensive state parameters of both the cluster and the matrix, which allows one to uniformly describe clusters of critical, subcritical, and supercritical size. The analysis was performed in two stages. On the first one, the optimal size dependences of the compositions of new phase clusters were determined by analyzing the macroscopic equations of growth of nuclei. On the second stage, we solved a kinetic equation to describe the evolution of the size distribution function of new-phase clusters along this optimal composition line. The effect of various kinetic factors on the behavior of the distribution function and characteristics of new-phase clusters was studied. The obtained distributions demonstrate a possibility of the existence of bimodal size distributions of new-phase clusters.

1. Introduction

A huge experimental material accumulated in the field of the theory of phase transitions in solid bodies cannot be understood without theoretical researches and numerical modeling. With regard for the intensive development of the computational technique, the method of numerical simulation of processes with phase transitions acquired the highest importance for studying the nature of physical properties of solid bodies aimed at the creation of new substances with preassigned physical characteristics. In this respect, a special role is played by first-order phase transitions and, particularly, the alloy decomposition.

In theory and experiments, one distinguishes three successive stages of the alloy decomposition: nucleation, independent growth of new-phase particles, and coalescence (or Ostwald ripening stage) [1–4]. On the first stage, a metastable homogeneous alloy is transformed

into a two-phase (heterogeneous) one by means of the initiation of new-phase particles and the simultaneous growth of already formed supercritical clusters. On the second stage, the volume of the new phase increases due to the growth of supercritical clusters. Moreover, their number remains almost invariable. Nuclei grow independently until the diffusion regions of different new-phase particles start overlapping or the supersaturation becomes so small that it will impede the further growth of all clusters. The last evolution stage of new-phase particles at the decomposition is the coalescence that has been experimentally known for a long time and was first described qualitatively by Ostwald. On this stage, the volume fraction of the new phase is approximately constant, the supersaturation becomes very small, whereas the process is accompanied by the growth of large particles due to the dissolution and the vanishing of small nuclei. In the case of infinite small supersaturations, the coalescence is described by the Lifshitz–Slyozov–Wagner (LSW) solution, in which it is assumed that new-phase particles are located so far from each other that they interact only through the matrix. The LSW theory determines the law of nucleus growth and yields a unified size distribution function of new-phase particles. At the same time, due to the necessity of considering the properties of critical, subcritical, and supercritical clusters that can depend on their size and composition, the problem of description of initial stages of the decomposition in many-component media remains unsolved and urgent [5–9].

In this work, we consider a generalization of the Gibbs approach to the case of homophase fluctuations in order to describe the kinetics of first-order phase transitions in the case of the decomposition of a binary solution. This field was studied in a number of works [10–13] demon-

strating that the growing new-phase particles can have a composition differing both from the composition in the solution and that of the new macroscopic phase, whereas the critical size, nucleation barrier, and nucleation rate can differ from the respective parameters determined by the classical Gibbs theory for heterophase systems.

The purpose of this paper is to study the main thermodynamic and kinetic characteristics of a binary system on the initial stage of nucleation of a new phase based on theoretical assumptions and a numerical modeling of the corresponding kinetic equations. It will be shown that the situations, where the particle size distribution on the transient stages of nucleation and new phase growth becomes bimodal, can be realized.

The paper is organized as follows. First, we briefly consider the problem statement in the thermodynamic approximation (Section 2). After that, we will solve the problem of description of a new phase composition as a function of the size (Section 3). Then the basic kinetic equations and the quantities under study will be put down in the framework of the mean-field model and the calculation algorithm will be described (Section 4). In the last part, we present the main result of this problem in the case of the invariable initial supersaturation (Section 5) and the concluding remarks (Section 6).

2. Thermodynamic Approximation — Modified Gibbs Nucleation Theory

Let us imagine that a two-component system is transferred to a metastable state between the binodal and spinodal curves. Under such conditions, the system must decompose sooner or later, and this process will start from the nucleation of a new phase with the following growth of such particles. The composition of the growing new-phase clusters will differ from that of the initial matrix and will acquire the composition and structure of the new phase in the process of evolution.

The Gibbs classical nucleation theory (CNT) determines the characteristics of a critical new-phase nucleus in the approximation of heterophase fluctuations and compositions differing from the parent one [14]. When using the CNT for the description of the phase formation, the free energy of the system is approximately considered in the one-dimensional space of sizes of new-phase nuclei. Moreover, such an inclusion of the new phase has all macroscopic properties of the newly formed phase (with the constant surface tension and specific bulk free energy). The classical approximation can be valid only in the case where the linear dimensions of such nucleus are much larger than the thickness of the

surface layer. But the linear size of a nucleus is not a parameter of the theory; it is determined from the maximum condition of the energy of the whole system. In addition, the classical approximation often appears inaccurate for the quantitative description. For example, in the case of the condensation from the vapor phase (where all data are known with good accuracy), the empirical nucleation rates differ from those calculated according to the CNT by several orders of magnitude (for nonane (C_9H_{20}), this difference is equal to five orders of magnitude [15]). The CNT based on the Gibbs approximation for an abrupt interface between a nucleus and a metastable parent phase predicts a nonzero energy barrier of transformation for any supercoolings and appears invalid for the description of the spinodal decomposition. J.W. Gibbs understood that the capillary approximation is inappropriate for small new-phase particles. Therefore, he introduced a surface tension dependent on the surface curvature. This idea was subsequently developed by R.C. Tolman who introduced an additional parameter [15, 16]. However, its determination also encounters a number of problems, as it changes depending on the supersaturation (size), and even the sign of this parameter is doubtful [17].

In the authors' opinion, a whole number of the mentioned problem questions can be solved using the recently proposed modified nucleation theory. For new-phase clusters, this theory specifies a dependence of the nucleus surface energy on the concentrations inside a nucleus and in the matrix [10–13]. Another essential difference of this consideration from the Gibbs classical approach is that it takes clusters of arbitrary compositions and sizes into account. In the framework of this modification, one can determine the compositions of nuclei of all sizes, while the resulting composition curve is called an optimal trajectory. The obtained trajectories allow one to proceed from solving a two-dimensional problem to the quasideimensional analysis. In the general case, one should solve a two-dimensional problem in the space of the number of atoms of a certain sort [18].

First, we consider the thermodynamics of the decomposition of a supersaturated binary solid solution that occurs by means of the nucleation and the growth of clusters of a new α -phase in the matrix of the parent β -phase. In this case, the appearance of a new-phase particle results in the classical change of the Gibbs potential of the system [10–13]

$$\Delta G = -n\Delta\mu + \sigma A, \quad (1)$$

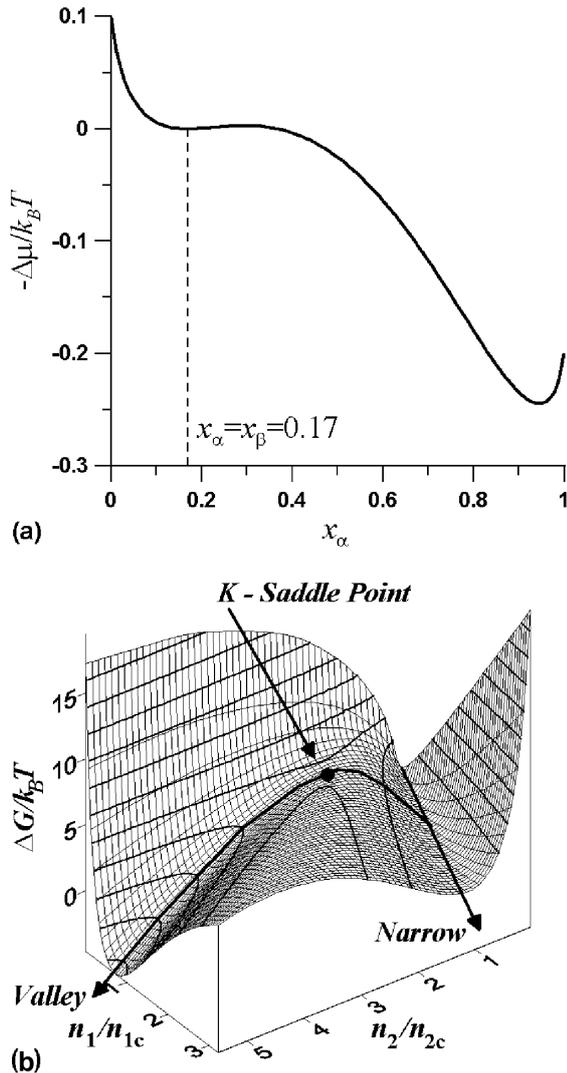


Fig. 1. (a) Thermodynamic driving force of transformation as a function of the composition of a new-phase nucleus; (b) Surface of variation of the Gibbs potential of the system at the formation of a new-phase nucleus as a function of the numbers of atoms of the first and second sorts, respectively. Point K is a “saddle point” corresponding to the critical nucleus and the nucleation barrier

where n denotes the number of atoms in a new-phase nucleus consisting of n_1 atoms of the first component and n_2 atoms of the second one, $\Delta\mu$ is the thermodynamic driving force of transformation per one atom of a nucleus, σ is the surface energy density of the interface, and A is the surface area.

The thermodynamic driving force of the phase transformation is presented by the expression for a regular solid solution [10–13, 19]:

$$\Delta\mu = -k_B T f(x_\alpha, x_\beta), \quad (2)$$

$$f(x_\beta, x_\alpha) = (1 - x_\alpha) \left[\ln \left(\frac{1 - x_\alpha}{1 - x_\beta} \right) + 2 \frac{T_c}{T} (x_\alpha^2 - x_\beta^2) \right] + x_\alpha \left\{ \ln \left(\frac{x_\alpha}{x_\beta} \right) + 2 \frac{T_c}{T} [(1 - x_\alpha)^2 - (1 - x_\beta)^2] \right\}. \quad (3)$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, T_c is the critical temperature of the decomposition dome, x_α stands for the composition of a new-phase nucleus, and x_β denotes the composition of the parent phase.

For the sake of simplicity, we consider that nuclei of the new α -phase have a spherical form and neglect the effects related to elastic deformations and their energy contribution. In this work, we consider the initial decomposition stages, on which the depletion of the medium still can be neglected, and the average composition of the parent β -phase can be considered constant. The specific surface energy depends on the difference in the compositions of the new and parent phases [11, 12] and has the form of the square dependence

$$\sigma = \tilde{\sigma} (x_\alpha - x_\beta)^2. \quad (4)$$

The following thermodynamic analysis is performed for such parameters: $\frac{T}{T_c} = 0.7$; $\frac{\tilde{\sigma} c_\alpha^{-2/3}}{k_B T} = 0.53$, where c_α is the volume density of the new phase (number of atoms in unit volume); and $x_\beta = 0.17$. For these parameters, the number of atoms in the critical nucleus amounts to $n_{1c} = 36.25$ atoms of the first sort and $n_{2c} = 62$ atoms of the second sort. The barrier value is equal to $\Delta G_c = 3.86 k_B T$, whereas the critical nucleus composition is $x_{\alpha c} = 0.61$.

The thermodynamic driving force for the chosen parameters and the surface of variation of the Gibbs potential of the system in the case of the formation of a new-phase nucleus are presented in Fig. 1. The region of the parent phase represents a “narrow” (right side of Fig. 1, b) and goes along the ray x_β . A characteristic feature of the “narrow” is a zero variation of the Gibbs potential (1) along it and the composition corresponding to the parent phase. The new phase is presented by a “valley” (left side of Fig. 1, b), in which the variation of the Gibbs potential is negative for large sizes. The nucleation of new-phase particles represents a fluctuation transition of nuclei from a “narrow” of the parent phase to a “valley” of the new phase by means of overcoming the energy barrier (saddle point K in Fig. 1, b). The growth of new-phase particles can be presented by some curve on the surface of variation of the Gibbs potential. This curve must correspond to the composition of the parent

phase for small-size nuclei and to the macrophase composition for large-size ones. Moreover, it is supposed that this trajectory passes through the critical point corresponding to the “saddle point” of the surface of variation of the Gibbs potential of the system. The question of interest is which way of overcoming the barrier will be optimal for all nuclei?

3. Search for Optimal Concentrations in Dependence on the Size of Nuclei

The optimal trajectory is found by solving a system of equations of growth and dissolution of nuclei in the subcritical and supercritical regions, respectively:

$$\frac{dn_i}{dt} = -\omega_{n_i, n_{i+1}}^{(+)} \frac{1}{k_B T} \frac{\partial \Delta G(n_1, n_2)}{\partial n_i}, \quad (5)$$

where t is the time. The index i corresponds to the sort of atoms and takes two values in the binary case. The frequency of attachment of atoms of the i -th component $\omega_{n_i, n_{i+1}}^{(+)}$ is determined by the expression [10–13, 19]

$$\omega_{n_i, n_{i+1}}^{(+)} = \frac{D_i^*}{a_\beta^2} 4\pi R^2 c_{i\beta}^{(s)}, \quad (6)$$

where D_i^* is the diffusion coefficient of the i -th component in an immediate vicinity of the nucleus surface, R is the particle radius, a_β is determined by the relation $\frac{4}{3}\pi (a_\beta)^3 = \frac{1}{c_\beta}$, and c_β is the volume density of the parent phase. The volume density of the i -th component close to the nucleus surface $c_{i\beta}^{(s)}$ is determined from the quasistationarity condition:

$$c_{i\beta}^{(s)} = \frac{c_{i\beta}}{1 + \frac{D_i^* R}{D_i a_\beta}}, \quad (7)$$

where D_i stands for the diffusion coefficient of the i -th component in the volume of the parent phase, and $c_{i\beta}$ is the volume density of the i -th component in the parent phase.

We consider, for simplicity, that the diffusion coefficients of the i -th component in an immediate vicinity of the nucleus surface and in the volume of the parent phases are equal to each other ($D_i^* = D_i$) and so are the volume densities of the parent and new phases: $c_\beta = c_\alpha$.

The calculation of the optimal trajectory according to the system of equations (5) starts from the critical point and its neighborhood and is performed independently for the subcritical and supercritical regions. Calculations in the supercritical region are limited only by the dimension of the computational scheme or the computer power

(of the order of 10^8 atoms). In the subcritical region, the trajectory ends at a point on the straight line corresponding to the parent phase concentration $x_\beta = 0.17$. At this point, the cluster contains the number of atoms $n_0 = n_{10} + n_{20}$, where n_{10} and n_{20} are the numbers of atoms of the first sort and the second one, respectively.

Let us consider the effect of diffusion mobilities of atoms on the shape of optimal-composition lines (Fig. 2). As one can see from the presented results, the difference between the trajectories is very significant in the subcritical region and almost inessential for supercritical nuclei. In addition, one can see that, for the considered cases $\frac{D_1}{D_2} = 1$ and $\frac{D_1}{D_2} = 10$, the composition x_α depends on the number of atoms n ambiguously, which testifies to a possibility of the existence of nuclei of equal sizes (with equal $n = n_1 + n_2$), but of different compositions (different n_1, n_2, x_α).

The obtained ambiguous correspondence of the compositions and the dimensions of new-phase clusters can become a “stumbling-block” for considering the kinetics of the decomposition process. That is why, in our further analysis, we proceed to the study of the quasione-dimensional problem in the space of the number of atoms of the second sort n_2 (the least numerous in the system) at the known relations between the compositions of various-size clusters according to the obtained optimal trajectories (Fig. 3). This will allow us to properly put down the kinetic equation of evolution for the cluster distribution function and to actually consider not only the size distribution of nuclei, but also the composition one.

It is also worth paying attention to the following interesting fact observed in the case of high mobilities of the first component. Comparing the obtained optimal trajectories with respect to the critical point (point K in Fig. 2), one can see that there exist subcritical new-phase nuclei, whose composition considerably differs from that of the critical cluster, whereas their dimensions exceed the critical one (the composition line lying to the left and above the point K in Fig. 2, a for $\frac{D_1}{D_2} = 10$). In such subcritical nuclei, $n > n_c$, $n_1 > n_{1c}$, and $n_2 < n_{2c}$.

4. Evolution of New-Phase Clusters

In order to describe the kinetics of the phase transition, we consider the distribution function $N(n_1, n_2, t)$ that represents the number of new-phase nuclei in unit volume of the alloy at the time moment t consisting of n_1 atoms of the first component and n_2 atoms of the second one. To use a kinetic equation of the “master-equation” type, it is necessary that the growth process occurs “step-

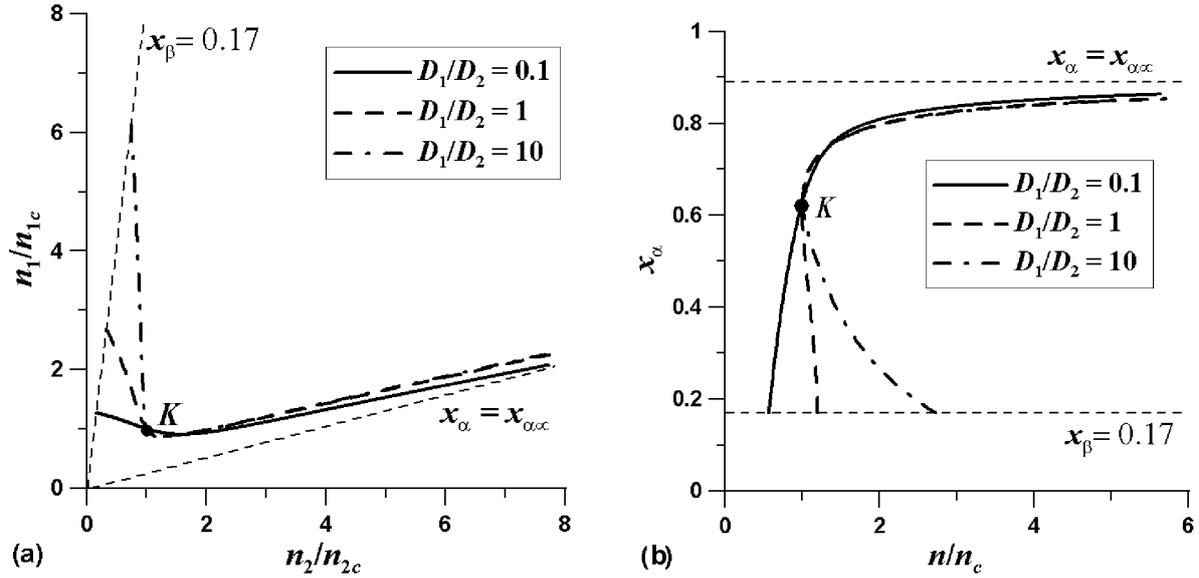


Fig. 2. (a) Optimal trajectories calculated for various relations between the diffusion coefficients of the components in the matrix; (b) Compositions of new-phase nuclei as functions of the total number of atoms in the nucleus determined along the optimal trajectories for various relations between the diffusion coefficients of the components in the matrix. Point K shows the parameters of the critical nucleus. The dotted line $x_\beta = 0.17$ corresponds to the parent phase composition. The dotted line $x_\alpha = x_{\alpha\infty}$ corresponds to the equilibrium composition of a new macrophase after the decomposition

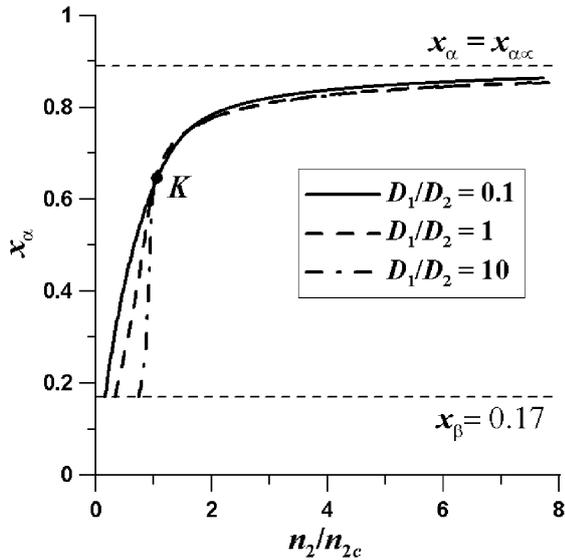


Fig. 3. Compositions of new-phase nuclei as functions of the number of atoms of the second component determined along the optimal trajectory for various relations between the diffusion coefficients of the components in the matrix

by-step” by means of the attachment or detachment of separate structural components. The optimal trajectory corresponds to a certain relation of the components in new-phase nuclei $n_1 = n_1(n_2)$. This gives a possibility

to proceed to the consideration of the distribution function of nuclei over the number of atoms of a certain sort, as the amount of the second component is determined by the above relation for the optimal trajectory. Performing the further analysis with the use of the distribution of nuclei over the number of atoms of the second component $N(n_2, t)$, we obtain the unambiguous dependences $n_1(n_2)$ and $x_\alpha(n_2)$ (Fig. 3).

The evolution of the size distribution function of new-phase clusters along the optimal trajectory is determined by a kinetic equation of the “master-equation” type [19]:

$$\begin{aligned} \frac{\partial N(n_2, t)}{\partial t} = & \tilde{\omega}_{n_2-1, n_2}^{(+)} N(n_2 - 1, t) - \tilde{\omega}_{n_2, n_2+1}^{(+)} N(n_2, t) + \\ & + \tilde{\omega}_{n_2, n_2+1}^{(+)} N(n_2 + 1, t) \exp \frac{\Delta G(n_2 + 1) - \Delta G(n_2)}{k_B T} - \\ & - \tilde{\omega}_{n_2-1, n_2}^{(+)} N(n_2, t) \exp \frac{\Delta G(n_2) - \Delta G(n_2 - 1)}{k_B T}. \end{aligned} \quad (8)$$

Equation (8) is put down in terms of the number of atoms of the second component n_2 . Nevertheless, the frequency of atom attachment $\tilde{\omega}_{n_2, n_2+1}^{(+)}$ should be considered with regard for the relation between the frequencies of attachment of atoms of the both components along the

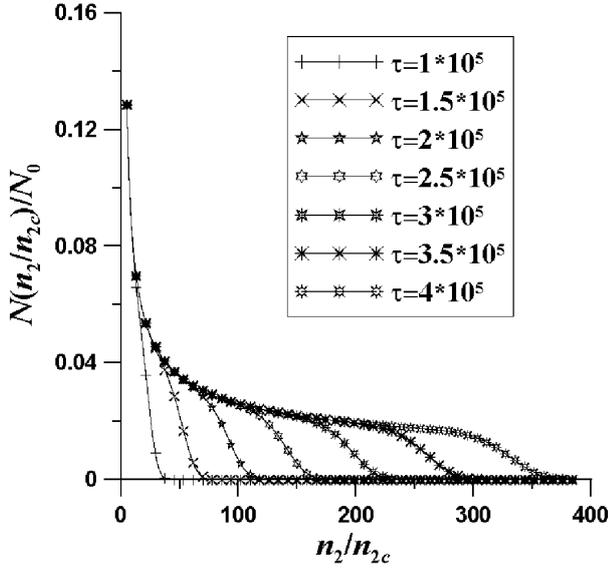


Fig. 4. Evolution of the distribution function of new-phase particles over the number of atoms of the second component for the case $\frac{D_1}{D_2} = 0.1$. The distribution function is determined by the relation $N\left(\frac{n_2}{n_{2c}}\right) = N(n_2) n_{2c}$

obtained trajectory [13]:

$$\tilde{\omega}_{n_2, n_2+1}^{(+)} = \frac{v_{2\alpha}^2}{\sum_{j=1}^2 \frac{v_{j\alpha}^2}{\omega_{n_j, n_j+1}^{(+)}}}, \quad (9)$$

where the quantities $v_{i\alpha} = \frac{dn_i}{dn}$ characterize the variation of the composition x_α of the new-phase cluster due to the change of the whole number of atoms in it and are calculated along the optimal composition trajectory.

Problem (8) is solved numerically with the use of the following initial and boundary conditions:

$$N(n_2, 0) = \begin{cases} N_0, & n_2 = n_{20}, \\ 0, & n_2 > n_{20}, \end{cases} \quad (10)$$

$$N(n_{20}, t) = N_0, \quad (11)$$

where n_{20} is the minimal number of atoms of the second sort in the new-phase nucleus obtained from calculating the optimal trajectory in the subcritical region, and N_0 is a constant.

The obtained system of equations (1)–(4), (8)–(11) allows us to obtain a self-consistent solution and to construct the size distribution functions $N(n_2, t)$ of new-phase clusters for various time moments. The problem was solved with the help of the Euler finite-difference scheme. To simplify the model, we introduced the dimensionless time $\tau = \frac{4\pi D_2^* c_\beta}{a_\beta^2} \left(\frac{3}{4\pi c_\alpha}\right)^{2/3} t$.

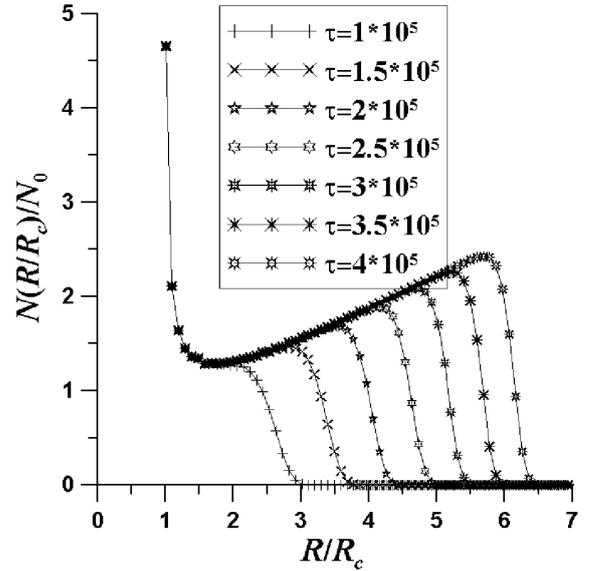


Fig. 5. Evolution of the distribution function of new-phase particles over radii for the case $\frac{D_1}{D_2} = 0.1$, where R_c is the radius of the critical nucleus

5. Results and Discussion of the Solutions of the Kinetic Problem

The evolution of the distribution function of new-phase nuclei for the particular case $\frac{D_1}{D_2} = 0.1$ is presented in Fig. 4. In the following description, the time variable τ in the designation of the distribution function will be omitted. The distribution functions over the number of atoms $N(n)$ or $N(n_2)$ monotonously decrease and develop toward larger sizes. The maximum at the left boundary corresponds to subcritical nuclei and is determined by the boundary condition (11).

The obtained distributions can be presented by the dependences in other units: in the size space, volume space, and so on. It is interesting to present the distribution function $N(R)$ in the space of sizes (radii) of new-phase particles, where $N(R) = 4\pi R^2 c_\beta N(n)$. In contrast to the distributions $N(n)$ over the number of atoms inside a nucleus, the size distribution functions $N(R)$ have a maximum in the supercritical region (Fig. 5). With increase in time, this maximum shifts to the right and grows in absolute value. The demonstrated results for the evolution of the distribution function do not qualitatively differ from those obtained earlier [19, 20].

Let us investigate the influence of various kinetic factors on the behavior of the distribution function and the characteristics of new-phase clusters. Of interest is the case of a high-mobility first component: $\frac{D_1}{D_2} = 10$. For this case, we used the composition profiles (Figs. 2 and

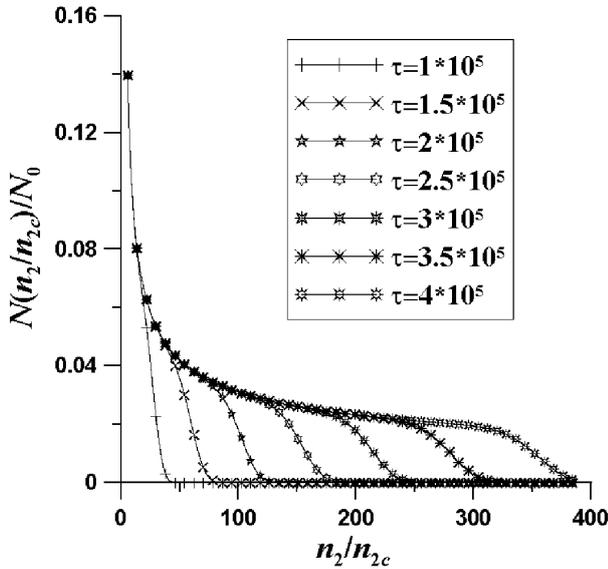


Fig. 6. Evolution of the distribution function of new-phase particles over the number of atoms of the second component for the case $\frac{D_1}{D_2} = 10$

3) and derived the respective solution. The form of the distribution function significantly depends on the choice of the space of variables. In particular, in the space of the number of atoms n_2 , the behavior of the distribution function of new-phase particles (Fig. 6) is similar to the previous one (Fig. 4).

At the same time, the shape of the radius distribution function $N(R)$ has a significant difference. In the region of sizes exceeding the critical one, there are two maxima (Fig. 7, a). Therefore, we call such a shape of the distribution function bimodal. The indicated bimodality is also characteristic of the size distribution function of the new phase volume $V(R) = \frac{n}{n_c} N(R)$ (Fig. 7, b). The peculiarity of such a bimodality consists in that the first maximum corresponds to nuclei supercritical in size and subcritical in composition $x_\alpha < x_{\alpha c}$, while the second one is related to those supercritical both in size and in composition $x_\alpha > x_{\alpha c}$. Let us consider this peculiarity from the viewpoint of the evolution of new-phase particles. A subcritical nucleus appears with the composition close to that of the parent phase $x_\alpha \approx x_\beta$ and the size $n > n_c$. In the process of evolution, the concentration of the second component in the nucleus grows with a simultaneous decrease of the size (Fig. 2) due to the fact that more mobile atoms of the first sort leave the nucleus. This process lasts until it reaches the critical region. In the supercritical region, the size grows simultaneously with the concentration. A detailed anal-

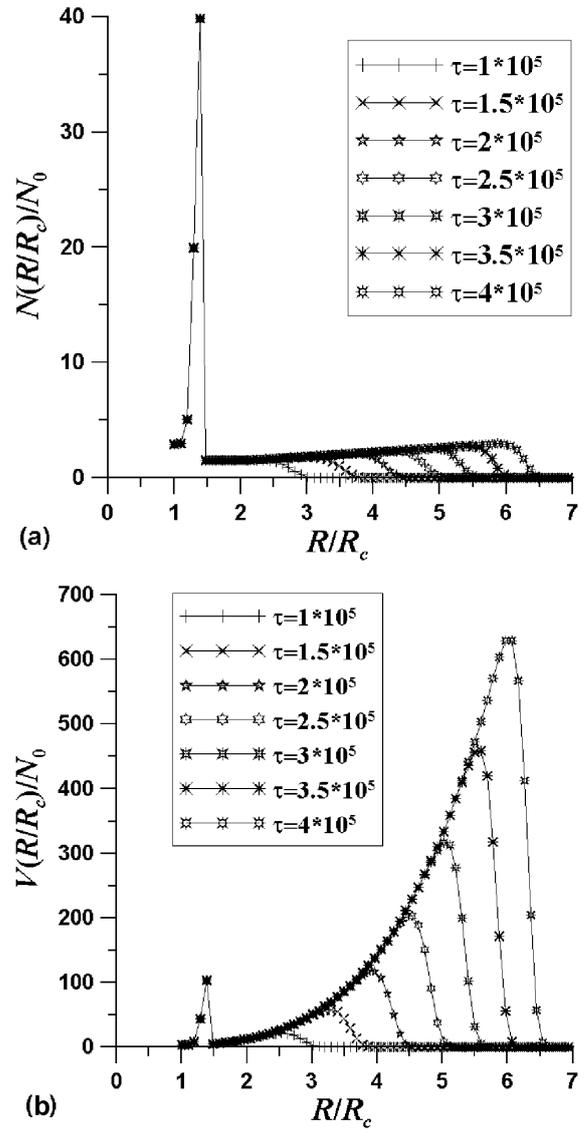


Fig. 7. Evolution of the relative size distribution function for the case $\frac{D_1}{D_2} = 10$: (a) — distribution of new-phase particles; (b) — distribution of the new phase volume

ysis of the distribution function in the space of radii demonstrates that the maximum for $n_2 < n_{2c}$ does not change in time due to the establishment of the stationary distribution of subcritical nuclei. The second maximum corresponding to supercritical particles $n_2 > n_{2c}$ shifts toward larger sizes and grows in absolute value.

Thus, the mechanism considered here can lead to bimodal size distributions of new-phase clusters already on the initial stage of the phase transition.

6. Conclusions

We simulated the behavior of the distribution function of new-phase particles in the case of a first-order phase transition (decomposition) in a binary supersaturated solid solution. The model uses the generalized Gibbs nucleation theory to obtain the optimal compositions of new-phase clusters. Such an approximation in the kinetics of the process can yield bimodal distribution functions (with no regard for the zero point) and demonstrates a possibility of the existence of the bimodality of the distribution functions related to a variation of the composition of new-phase nuclei on the nucleation stage. The problem of experimental verification of the presented theoretical results remains as yet open.

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ЕВОЛЮЦІЯ КЛАСТЕРІВ НОВОЇ ФАЗИ НА ПОЧАТКОВИХ ЕТАПАХ РОЗПАДУ БІНАРНОГО СПЛАВУ У МОДИФІКОВАНІЙ ТЕОРІЇ ЗАРОДКОУТВОРЕННЯ

М. Пасічний, А. Шірінян, J. Schmelzer

Резюме

У роботі розглянуто термодинаміку і кінетику початкових стадій розпаду в пересиченому бінарному твердому розчині у рамках модифікованої теорії зародкоутворення нової фази. Питому поверхневу енергію розглянуто як функцію інтенсивних параметрів стану як кластера, так і матриці, що дозволяє описувати кластери критичних, докритичних і закритичних розмірів єдиним чином. Аналіз проведено у два етапи. На першому етапі визначено оптимальні залежності складу кластерів нової фази від розмірів шляхом аналізу макроскопічних рівнянь росту зародків. На другому етапі розв'язано кінетичне рівняння для опису еволюції функції розподілу кластерів нової фази за розмірами вздовж оптимальної лінії складу. Досліджено вплив різних кінетичних факторів на поведінку функції розподілу і характеристики кластерів нової фази. Отримані розподіли демонструють можливість наявності бімодальних розподілів за розмірами кластерів нової фази.