THE EFFECT OF SELF-SATURATION IN AN ALLOY AS A CRITERION OF THE BEGINNING OF THE COALESCENCE STAGE

A.S. SHIRINYAN, M.P. KUDIN

UDC 539.2 ©2008 B. Khmel'nyts'ky Cherkasy National University (81, Shevchenko Blvd., Cherkasy 18031, Ukraine; e-mail: shirinyan@phys.cdu.edu.ua, aramshirinyan@ukr.net)

A numerical solution of the problem concerning the diffusioncontrolled process of growth and coalescence of new-phase particles in the mean field approximation is discussed. The model allows one to investigate the main stages of the decay (the stage of independent growth, intermediate stage, and coalescence), as well as transitions between them, in detail. It is shown that the size dispersion of new-phase particles at the stage of independent growth decreases. It is obtained that, in the framework of the mean field approximation, one can observe the self-saturation effect at the initial stage of coalescence. Self-saturation is characterized by the "inverse" behavior of saturation, namely by the increase of the concentration of dissolved atoms corresponding to a new phase, as well as by the "inverse" behavior of the mean and critical radii of new-phase particles - their decrease. The amplitude of this effect is small and depends on both the volume fraction of the new phase and the initial supersaturation. The result was verified for various initial size distributions of particles. The self-saturation effect can be considered as a criterion (indicator) of the beginning of the coalescence stage.

1. Introduction

A special role in the production of composite materials, protective coatings, integrated circuits in microelectronics, powder alloys, and high-temperature semiconductors is played by the reaction diffusion, i.e. the diffusion accompanied by the appearance and the competitive growth of particles of a new phase. In theory and experiments, one distinguishes four successive stages of alloy decay: nucleation, stage of independent growth of new-phase particles, intermediate (transient) stage, and coalescence (Ostwald ripening stage) [1–4].

At the first stage, a metastable homogeneous alloy becomes two-phase and heterogeneous after the nucleation. At the second one, the volume of the new phase increases, and nuclei grow independently until the diffusion regions of different new-phase particles start to overlap. Then the intermediate stage of weak diffusion long-range interaction comes. The last stage of the alloy decay, the coalescence, is described by the Lifshits–Slezov (LS) analytic solution in the space of relative sizes, where the growth of large particles of the new phase at the expense of small nuclei is taken into account. The LS theory is constructed within the model of mean field approximation for the concentration field [5, 6]. It determines the law of growth of nuclei and results in a unified size distribution function of new-phase particles. At the same time, the problem of description of the decay at initial stages remains unsolved and urgent [7]. The development of computer technique allows one to use methods of numerical simulation of the processes with phase transformations and to obtain results that improve the understanding of the processes of decay and give a detailed description of the indicated problem.

The given paper is aimed at the investigation of the influence of the initial size distributions of new-phase particles on the kinetics of initial decay stages by means of numerical simulation. In our paper, we won't consider the first stage, namely the stage of nucleation. Therefore, the alloy is considered to be two-phase (containing the nuclei of a new phase) from the very beginning. We'll see that the approximation of mean concentration field can give the result (unknown till now) that consists in the possibility of the self-saturation of a system at the intermediate stage of decay before coalescence.

2. A Model of Mean Field Approximation

Let's consider the supersaturated solid solution of a binary alloy with the initial composition C_{α} (the atomic concentration of *B* component in the initial alloy). We suppose that nuclei of the new phase are spherical and located at such a distance from one another that their concentration fields don't overlap at the beginning. This situation can be reached if the initial supersaturation C_{α} and the volume fraction of the new phase are specified as small. Under such conditions, the probability of the fluctuation appearance of new particles of the new phase is low. In this approximation, the entry of a substance to a new-phase particle is determined by both the equilibrium concentration \bar{C} far from the nucleus and thermodynamic parameters of the system, i.e. it is controlled by volume diffusion [6, 8].

The balance equation of a substance at the mobile boundary of a new-phase nucleus can be presented in the form

$$\left\{C_n - C_{\alpha,n}\left(R_i\right)\right\} \frac{\partial R_i\left(t\right)}{\partial t} = D \left.\frac{\partial C}{\partial r}\right|_{r=R_i(t)}.$$
(1)

Here, $C_{\alpha,n}(R_i)$ denotes the equilibrium concentration in the solution at the interface of the *i*-th nucleus and the alloy (Fig. 1), r and $C \equiv C(r)$ stand for the variable radius and concentration in the neighborhood of the *i*-th nucleus, respectively, C_n is the concentration of atoms of B sort in new-phase particles (the same for all nuclei), *i* is the number of particles (changes from unity to the general number of nuclei existing at a certain time moment), $R_i(t)$ represents the radius of the *i*-th newphase particle, and D is the diffusion coefficient for Batoms in the solution.

In this case, the concentration distribution in the matrix (not far from the i-th particle) at any time moment is determined from the diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial r} \left(D \frac{1}{r^2} \frac{\partial C}{\partial r} \right)$$

where C is the concentration of atoms of B sort in the solution in the neighborhood of new-phase particles. The solution of the last equation for the decay process limited by diffusion can be found with regard for the condition for the process to be quasistationary: $\frac{\partial C}{\partial t} = 0$. In the spherical coordinate system, by taking the boundary and limiting conditions for the concentration profile $C(r = R_i) = C_{\alpha,n}(R_i)$ and $C(r \to \infty) = \overline{C}(t)$ into account, the solution has the following form:

$$C(r) = \bar{C}(t) + \frac{C_{\alpha,n}(R_i) - \bar{C}(t)}{r}R_i.$$
(2)

Here, $\overline{C}(t)$ representing the average concentration of a substance in the solution after the nucleation in the process of decay is the function of time and will be determined from the mass conservation law. Hence, the distribution of the concentration C(r) in the neighborhood of a nucleus will also vary with time.

The substitution of expression (2) into Eq. (1) will give the equation of growth of new-phase particles in an supersaturated alloy with the composition $\bar{C}(t)$:

$$\frac{dR_i(t)}{dt} = \frac{D}{R_i} \frac{\bar{C}(t) - C_{\alpha,n}(R_i)}{C_n - C_{\alpha,n}(R_i)}.$$
(3)

 C_{C_n} $C_{\alpha,n}(R_1)$ \overline{C} $C_{\alpha,n}(R_2)$ R_1 R_2

Fig. 1. Concentration field close to new-phase particles of various sizes. C_n – concentration in new-phase particles, $C_{\alpha,n}(R_i)$ – equilibrium concentration in the solution at the *i*-th "new-phase particle – alloy" interface, \bar{C} – concentration of the substance in the solution far from the nucleus

For the further investigation, it's necessary to determine the quantities C_n and $C_{\alpha,n}(R_i)$. They characterize the growth rate (3) and can be determined knowing the thermodynamic parameters for the alloy and new-phase particles. Let's consider the model of the appearance of a new intermediate phase from an supersaturated ideal solid solution having the initial composition C_{α} . The Gibbs potentials (energy per atom) for the initial and new phases are defined by the formulas

$$G = kT \left(c \ln \left(c \right) + (1 - c) \ln \left(1 - c \right) \right) + G_0,$$

$$G_n = \Delta G,$$
 (4)

respectively, where the solid solution has the concentration dependence for the Gibbs potential of the alloy, while the new phase has a strict stoichiometry of the C_n composition, G_0 represents the enthalpy of the mixing of atoms, k is the Boltzmann constant, T is the absolute temperature, and G_n denotes the thermodynamic stimulus of creation of the new phase (Fig. 2).

With regard for the equilibrium of the phases existing in the solution, one can find the equilibrium concentration $C_{\alpha,n}(R_i)$ at the "solution-new phase" interface (taking the curvature of the surface of a newphase particle with radius R_i into account, we pass to the simplified notation $C_{\alpha,n}$), by using the equality of the chemical potentials:

$$G_n - G_0 + \frac{2\sigma}{\rho R_i} - kT \bigg[C_{\alpha,n} \ln \left(C_{\alpha,n} \right) + (1 - C_{\alpha,n}) \times \bigg]$$



Fig. 2. Concentration dependences of the thermodynamic characteristics of phases: σ – surface tension; $2\sigma/R$ – effective decrease of thermodynamic stimulus (energy per atom) under condition of the presence of a spherical surface with radius R; C_n – concentration in new-phase particles, C_{α} – initial composition in the solution; and $C_{\alpha,\infty}$ – equilibrium composition on the plane "new-phase particle – solution" interface (when $2\sigma/R \rightarrow 0$)

$$\times \ln (1 - C_{\alpha,n}) + (C_n - C_{\alpha,n}) \ln \frac{C_{\alpha,n}}{1 - C_{\alpha,n}} \bigg] = 0.$$
 (5)

Let's write the law of conservation of matter under the conditions of the existence of new-phase particles:

$$C_{\alpha}V_{\text{tot}} = C_n \frac{4}{3}\pi \sum_{i=1}^{N(t)} R_i^3 + \bar{C}(t) \left\{ V_{\text{tot}} - \frac{4}{3}\pi \sum_{i=1}^{N(t)} R_i^3 \right\}.$$
(6)

Here, V_{tot} stands for the alloy volume, N(t) is the number of new-phase particles that changes in time. The atomic density ρ in new-phase particles and that in the parent phase are considered to be the same. It's worth noting the fact that Eq.(6) doesn't consider a change of the concentration $\bar{C}(t)$ caused by the presence of the concentration profile (Fig. 1) close to a newphase particle. According to the performed analysis, such a specification doesn't change the generality of the obtained results and will be presented in a separate work.

Thus, we obtain that conditions (5), (6) and the law of growth (3) are sufficient to describe the evolution of the decaying system. Unfortunately, it's impossible to find an analytic solution of such a system except for the case of the zero initial supersaturation and infinitely large time intervals where the LS theory is applicable. That's why we'll perform a numerical analysis for various initial supersaturations and try to clarify the behavior of the basic quantities that describe the decay in the system.

3. Basic Quantities That Describe the System

As one can see from Eq.(3), the growth rate of a newphase particle essentially depends on its radius. As a minimal value of the radius R_{\min} at which this equation makes sense, one can accept the value for which the condition $C_{\alpha,n} (R = R_{\min}) = C_n$ is satisfied (Fig. 1). The substitution into Eq.(5) gives

 $R_{\min} =$

=

$$= \frac{2\sigma}{\rho kT[C_n \ln C_n + (1 - C_n) \ln (1 - C_n)] - \rho (G_n - G_0)}$$

That's why we'll remove any particle having the radius $R \leq R_{\min}$ from the system, while the vanishing volume will be redistributed in the system due to the self-consistent conservation law (6).

Let's define the critical radius $R_{\rm cr}$ as such a value of the radius of a new-phase nucleus, at which the rate of growth in expression (3) changes the sign and equals zero: $C_{\alpha,n}(R_{\rm cr}) = \overline{C}$. Particles whose radius is lower than the critical one will decrease in the indicated deterministic model up to the minimum acceptable value, whereas particles whose radius is higher than the critical one will increase in size. We can write

$$R_{\rm cr} = 2\sigma / \left\{ \rho kT \left[\bar{C} \ln \bar{C} + \left(1 - \bar{C} \right) \ln \left(1 - \bar{C} \right) + \left(C_n - \bar{C} \right) \ln \frac{\bar{C}}{1 - \bar{C}} \right] - \rho \left(G_n - G_0 \right) \right\}.$$

The following characteristic parameter is the mean radius $\bar{R}(t)$ of new-phase particles that can be determined by means of arithmetic averaging: $\bar{R}(t) = \sum_{i=1}^{N(t)} R_i(t)/N(t)$. It's worth noting that, in the process of evolution of the system, all values of $R_i(t)$ and N(t) change. In addition, if the dimensions of nuclei $R_i(t)$ are known, the total volume of new-phase particles will be presented as $V_n(t) = \sum_{i=1}^{N(t)} \frac{4}{3}\pi R_i^3(t)$, whereas the volume fraction of the new phase will have the form $\tilde{V} = V_n(t)/V_{\text{tot}}$.

The numerical solution of problem (3)–(6) also allows one to observe the energy parameters that characterize the stability of the system. For example, one can calculate the surface energy of all nuclei: $E_s = \sigma \sum_{i=1}^{N(t)} 4\pi R_i^2$. The volume energy of the alloy with regard

for the part of nuclei will be determined as $E_V = \{V_{\text{tot}} - V_n(t)\}\rho G(\bar{C}) + V_n(t)\rho G_n$. The total energy of the system will be derived by means of summation: $E = E_V + E_s$.

In addition to the above-mentioned integral characteristics, the described model allows one to construct the size distribution of new-phase particles and to investigate the behavior of the particle size distribution function f(R), where f(R)dR is the number of particles whose sizes lie between R and R + dR at the time moment t. The results obtained for the distribution function f(R) at the last stage (coalescence) will be compared with the results of the LS theory. The latter uses the space of mean values, where the parameter is presented by the ratio of the radius of the particle $R_{i}(t)$ to the mean radius $\overline{R}(t)$ rather than the particle radius itself. That's why we'll consider the relative radius of the *i*-th particle: $u_i(t) = R_i(t)/\bar{R}(t)$. Respectively, the distribution function in such a space $f(u_i) \equiv f(u_i(t), t)$. We've constructed it in the form of bar charts and normalized in such a way that $f(u_i)$ represents a part of the general number of new-phase particles with sizes from u_i to $u_i + du_i$.

For the obtained distribution, the variance (DR or Du), slope (Sku), and peak sharpness (Kru) of the distribution function are determined by the formulas

$$DR = \sqrt{\frac{\sum_{i=1}^{N(t)} (R_i - \bar{R})^2}{N(t)}}, \quad Du = \sqrt{\frac{\sum_{i=1}^{N(t)} (u_i - 1)^2}{N(t)}},$$

$$Sku = \frac{\sum_{i=1}^{N(t)} (u_i - 1)^3}{N(t) (Du)^3}, \quad Kru = \frac{\sum_{i=1}^{N(t)} (u_i - 1)^4}{N(t) (Du)^4} - 3.$$
(7)

Hereinafter, $\overline{R} \equiv \overline{R}(t)$, $\overline{u} = 1$ represents the mean size in the space of relative sizes $u_i(t)$. The slopes Sku and the peak sharpnesses Kru of the distribution function in the spaces of common sizes and relative sizes coincide: (SkR=Sku, KrR=Kru).

Thus, the algorithm of simulation of the decay kinetics of a binary alloy will be as follows: a) the initial composition C_{α} and thermodynamic parameters of the phases are specified; b) at the first stage, we imitate the nucleation and introduce new-phase particles with the general number N(t = 0) and their initial sizes $R_i(t = 0)$, which determines the distribution function $f(u_i)$ and the initial volume fraction of the new phase; c) the composition in the alloy after the nucleation stage $\bar{C}(t=0)$ is determined by formula (6); d) the sizes of particles at further time moments $R_i(t>0)$ are found by formula 3); e) with the obtained values, we investigate all the indicated characteristics of the ensemble of new-phase particles and the quantities describing the decay. Then the procedure c)-e) is repeated.

The numerical solution presented in the given paper was realized by means of programming in the Borland C++ builder 6.0 programming environment with the help of Euler's method with automatic timestep variation.

4. Simulation Results

When simulating the nucleation, we set various initial size distributions of new-phase particles $f(\mathbf{R})$. Here, we'll restrict ourselves to the consideration of only two types of distributions (namely four Gaussian distributions and an exponential one) emphasizing the new result. The parameters of the distributions considered in the given paper are presented in Table 1.

As an example for the further discussion, let's consider alloy (b) from Table 1, where all nuclei of the new phase after the simulated nucleation stage were supercritical. Experimentally, such a situation can be created by means of the rapid overcooling of an alloy. The evolution of the distribution function of the chosen system is depicted in Fig. 3, while the evolution of its thermodynamic parameters is presented in Fig. 4.

The analysis testifies to the presence of all basic stages of the evolution of the system during the decay, namely the stage of independent growth, intermediate stage, and coalescence. In addition, one can trace the behavior of the basic quantities during the transitions from one stage to another in detail.

4.1. Stage of independent growth

In this case, at first $\overline{C}(t) \approx \text{const}$, and the growth equation (3) acquires the form

$$\frac{dR_i}{dt} = \frac{D}{R_i} \frac{\bar{C}(t) - C_{\alpha,\infty} - \frac{\gamma}{R_i}}{C_n - C_{\alpha,\infty} - \frac{\gamma}{R_i}} \approx \frac{D}{R_i} \frac{\bar{C}(t) - C_{n,\infty}}{C_n - C_{n,\infty}} \approx \frac{\text{const}}{R_i}.$$
(8)

This means that: a) at the stage of independent growth, nuclei grow following the parabolic law (8); b) the rates dR_i^2 / dt of change of the areas of particles of different sizes are the same; c) for two particles of different sizes



Fig. 3. Evolution of the size distribution function of new-phase particles following the variation of their sizes (bar charts are obtained numerically) and its comparison with the LS function (solid curve): a – initial distribution after nucleation, b – end of the stage of independent growth, the beginning of the intermediate stage, c – end of the intermediate stage, d – beginning of the coalescence stage

T a b l e 1. Initial distributions and parameters of the systems under consideration

Parameters		Exponential			
	Alloy (a)	Alloy (b)	Alloy (c)	Alloy (d)	distribution
$(G_n - G_0)/\mathrm{kT}$	-7	-4	-9	-4	-5
$\sigma, J \cdot m^{-2}$	0.3	0.3	0.3	0.3	0.3
$D, \mathrm{m}^2 \cdot \mathrm{s}^{-1}$	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-10}
$ ho, \mathrm{m}^{-3}$	7×10^{28}				
T, K	700	700	700	700	700
$C_{\alpha}(t=0)$	0.002	0.05	0.002	0.02	0.02
C_n	0.9999	0.900	0.999	0.9999	0.98
$V_{\rm tot},{ m m}^3$	4.78×10^{-16}	3.29×10^{-16}	4.35×10^{-16}	3.2×10^{-14}	2.38×10^{-15}
R_{\min}, m	1.27×10^{-10}	2.41×10^{-10}	9.86×10^{-11}	2.22×10^{-10}	1.79×10^{-10}
$R_{\rm cr}(t=0), {\rm m}$	9.44×10^{-9}	7.85×10^{-10}	1.26×10^{-9}	1×10^{-8}	8.33×10^{-10}
$\bar{R}(t=0), m$	1.27×10^{-8}	2.41×10^{-8}	1.48×10^{-8}	1.11×10^{-8}	1.33×10^{-8}
$\bar{C}(t=0)$	0.001	0.041	2.4×10^{-4}	0.020	0.019
N(t=0)	50000	50000	50000	50000	800000
$\tilde{V}(t=0)$	0.001	0.01	1.75×10^{-3}	1×10^{-5}	1.25×10^{-3}
DR(t=0)	2.55×10^{-9}	4.84×10^{-9}	2.95×10^{-9}	2.23×10^{-9}	1.34×10^{-8}
$\mathrm{Du}(t=0)$	0.2	0.2	0.2	0.2	1.005
$\mathrm{Sku}(t=0)$	0.005	0.027	0.002	0.013	1.947
$\operatorname{Kru}(t=0)$	-0.004	-0.004	-0.016	-0.023	5.177



Fig. 4. Evolution of the basic parameters of the chosen system [alloy (b) in Table 1] at all stages: a – volume fraction of the new phase $\tilde{V}(t)$; b – mean $\bar{R}(t)$ (solid curve) and critical $R_{cr}(t)$) (dashed curve) radii of new-phase particles; c – mean concentration of the substance in the alloy $\bar{C}(t)$ (t^* – the time moment of maximal saturation), d – the fraction of vanished new-phase particles N(t)/N(t = 0). The time interval 0 < t < 1 s characterizes the stage of independent growth, the interval 1 s < t < 1.05 s corresponds to the intermediate stage, and the stage of Ostwald ripening comes for t > 1.05 s

 $R_1 > R_2$, the rates of growth $dR_1/dt < dR_2/dt$. Thus, particles with the least size will have the maximal rate of growth. As a result, in the process of independent growth of supercritical new-phase particles, their size distribution function will get narrow, while the radii of particles will tend to the highest possible size. It is just the behavior discovered by the numerical solution of the system of equations (3)–(6) at the beginning of the given stage (Fig. 3, a, b). The total number of particles N(t) doesn't change at this stage. All nuclei grow, as all of them are supercritical. One distinguishes conditionally three steps of the stage of independent growth: 1) the beginning of the stage with constant concentration and rapidly decreasing dispersion; 2) the step with minimal dispersion of new-phase particles and decreasing composition; 3) the last step of rapid growth of the critical radius $R_{\rm cr}$ getting equal to the average size $\bar{R}(t)$ (Fig. 4). In general, the stage is characterized by the following behavior of the basic characteristics: a) the volume fraction of the new phase rises; b) the mean and critical radii increase; c) the mean concentration of the substance in the solution gradually decreases; d) the

number of particles of the new phase remains constant. The details of the above-described behavior can be seen in Fig. 4. The completion of the stage is observed at the time moment $t_1 = 1$ s for the indicated parameters of the system presented in Table 1, alloy (b).

It's worth paying attention to the fact that, at this stage, an essential decrease of the size dispersion of new-phase particles can result in the distribution function similar to the Dirac delta-function. Only in the case where the critical radius reaches the mean one, the dispersion stops to decrease, and the intermediate stage of the decay comes (Fig. 3, b, c, the time interval 1 s < t < 1.05 s in Fig. 4).

4.2. Intermediate stage

According to the result obtained in this paper, in the previous publications of other authors, and in models based on other approximations, the mean radius at the intermediate stage remains constant and equal to the critical one [3].

In our numerical experiment, one can mark out at least two steps of this stage: 1) the step of a slow growth of the size dispersion of particles at almost constant mean sizes $\bar{R}(t) = R_{\rm cr}(t) \approx {\rm const}$; 2) the unknown before step of effective self-saturation of the alloy, essential reconstruction of the distribution function, and decrease of the critical and mean radii with simultaneous increase of the dispersion of particles [9]. The corresponding results are shown in Figs. 3 and 4.

The analysis implies that, with the beginning of the intermediate stage, the dispersion rises and the corresponding distribution function broadens (Fig. 3, b, c). At this stage, there takes place the essential reconstruction of the size distribution function of particles from the intermediate state to the form predicted by the LS theory (Fig. 3, b, c). Moreover, just at the step of effective "self-saturation", the distribution function broadens and acquires the form corresponding to the LS theory with the well-known values of the dispersion, slope, and peak sharpness of the particle size distribution function. A detailed investigation demonstrates that the nonmonotonicity discovered in the behavior of the parameters of the system represents a result of the application of the mean field model rather than testifies to the incorrectness of the scheme of numerical solution. This fact was verified by the use of various distributions, various volume fractions of the new phase, and various approximations to solve the key equations, as well as by the changes of steps of the numerical scheme and the refinement of the law of conservation of matter (6) with regard for the available concentration profile near new-phase particles.

It's worth paying attention to the fact that the amplitude of the indicated self-saturation effect isn't large and essentially depends on the initial conditions and parameters of the investigated system, namely on the ratio between the critical and mean radii and that between the maximally possible volume fraction of the new phase under the specified conditions and its initial volume fraction. The maximally possible volume fraction of the new phase can be determined from Eq.(6), by considering that new-phase particles have completely "obtained" matter from the solution to construct the phase. In this case, the substance concentration in the solution reaches its minimal value, whereas the volume fraction of the new phase - its maximum. The minimal concentration can be found from the equilibrium condition for the case of coexistence of one new-phase particle and the solution, i.e., from the rule of common tangent (5) to the concentration dependences of the Gibbs potentials (Fig. 2). Under such conditions, the second term on the right-hand side of Eq.(6) can be neglected, becvause it is of the second order of smallness. Thus, we can write

$$C_{\alpha}V_{\text{tot}} \approx C_n \sum_{i=1}^{N(t)} \frac{4}{3}\pi R_i^3 = C_n V_n, \quad \tilde{V}_{\text{max}} \approx \frac{C_{\alpha}}{C_n}$$

The self-saturation effect for all the initial distributions (Table 1) is shown in Figs. 5 and 6. It's worth noting that, in Figs. 5 and 6 and below, the letter near the number of the figure coincides with the notation of the chosen alloy in Table 1.

A small amplitude of the self-saturation effect [for example for case (b) of Table 1, the relative changes are as follows: $\Delta \bar{R}_2 / \Delta \bar{R}_1 \approx 4 \times 10^{-2}$, $\Delta \bar{C}_2 / \Delta \bar{C}_1 \approx 2 \times 10^{-4}$, $\Delta \tilde{V}_2 / \Delta \tilde{V}_1 \approx 10^{-4}$] complicates the possibility of experimental verification of the obtained result. At the same time, we obtain that an increase of the initial volume fraction of the new phase results in the growth of the amplitude of the indicated effect, i.e., in an increase of the relative changes of the concentration, the volume fraction of the new phase, and the mean radius during the self-saturation (Table 2).

The mean field approximation has restrictions and, in the general case, can't be applied to large volume fractions of the new phase, where one should take the diffusion interaction of new-phase particles into account [10]. Our preliminary analysis demonstrates that the allowance for the diffusion interaction doesn't change the main result concerning the presence of such an effect but



Fig. 5. Averaged composition of the substance in the solution near new-phase particles for various distributions. Amplitude and duration of the self-saturation effect for various initial systems: a-d – for alloys a-d in Table 1, e – for the exponential distribution. The self-saturation effect is absent for distribution (a)



Fig. 6. Evolution of the mean (solid curves) and critical (dashed curves) radii of new-phase particles. Amplitude, duration, and form of the self-saturation effect for various initial systems (notations the same as in Fig. 5)

can essentially influence the distribution function at the coalescence stage. This questionn will be considered in a separate work.

4.3. Coalescence stage

As was already noted above, the LS theory determines the temporal law of growth of particles as well as the explicit and unified form of the particle size distribution function. Using the mean field approximation, the LS theory in binary systems [5, 6] determines the law of temporal variation of the mean radius of new-phase particles: $\bar{R} \sim t^{\frac{1}{3}}$ for asymptotically remote times. The latter coincides with the law of growth of the critical radius $R_{\rm cr}(t)$.

In our numerical experiment, we observe both the beginning of coalescence and the coalescence stage itself that follows the LS theory. An early stage of coalescence can be also reached even at the beginning of the evolution of the chosen system in the case of the simultaneous choice of the initial supersaturation of the system, initial volume fraction of the new phase, and the distribution function close to that corresponding to the asymptotic LS function.

One can state that, at the given stage, the behavior of the obtained parameters of the system is similar to that described in the LS theory (Fig.3, d; Figs. 4–6). The parameters of the distribution function agree with those of the asymptotic distribution function following the LS theory (Table 3). The mean size and the number of new-phase particles also change depending on time similarly to the corresponding functions in the LS theory. The only exception is the sharpness of the peak of the distribution function which is very sensitive to the number of particles of the system.

5. Conclusions and Discussion

In the given paper, the decay of a binary supersaturated alloy is described using the mean field model and the diffusion-controlled process of growth of a new phase. We have described the stage of independent growth, intermediate and coalescence stages, and transitions between them. The proposed model and the numerical analysis allowed us to obtain new results for the initial and intermediate stages of the decay for a binary system. In particular, for large initial supersaturations, it was obtained that the size distribution function of particles at the stage of independent growth can tend to the function similar to the Dirac delta-function. At the intermediate stage, the distribution function is essentially reconstructed, whereas it acquires the form known from the LS theory at the coalescence stage.

One of the new obtained results is the "self-saturation effect" for the case of non-zero initial supersaturations, where, at the end of the intermediate stage, there takes place the "inverse behavior" of basic characteristics: the decrease of the mean size, critical size, and volume fraction of the new phase and the increase of the concentration. The amplitude of this effect is small, but the effect itself is clearly pronounced. This result was

T a b l e 2. Amplitude of the self-saturation effect for various initial parameters of the systems of Table 1

Initial system	$\frac{\Delta \bar{C}_2}{\Delta \bar{C}_1}$	$rac{\Delta \bar{R}_2}{\Delta \bar{R}_1}$	$\frac{\Delta \tilde{V}_2}{\Delta \tilde{V}_1}$	$\frac{\bar{R}(t=0)}{R_{\rm cr}(t=0)}$	$rac{ ilde{V}(t=0)}{ ilde{V}_{\max}}$	$rac{ ilde{V}ig(t^*ig)}{ ilde{V}_{ ext{max}}}$
Distribution (a)	-	-	-	1.344	0.49995	_
Distribution (b)	1.72×10^{-4}	0.04	1.65×10^{-4}	30.714	0.18	0.768
Distribution (c)	3.3×10^{-4}	0.21	3.3×10^{-4}	11.781	0.4995	0.936
Distribution (d)	4.52×10^{-4}	4.08×10^{-4}	4.58×10^{-4}	1.099	0.0005	0.074
Exponential	1.42×10^{-3}	0.179	1.4×10^{-3}	16.005	0.0618	0.678

Table 3	. Comparison	of the results	obtained in	the given	work	with t	those of	calculations	performed	according	\mathbf{to}
the LS theo	ory at the coal	lescence stage									

Parameters	LS theory		Exponential			
		Alloy (a)	Alloy (b)	Alloy (c)	Alloy (d)	distribution
t	$\rightarrow \infty$	4.85	9.43	61.67	29.33	32.51
C_n	$\rightarrow 1$	0.9999	0.900	0.999	0.9999	0.98
C_{lpha}	$\rightarrow 0$	0.002	0.05	0.002	0.02	0.02
$\bar{R} = R_{\rm cr}$	$\sim t^{0.33333}$	$\sim t^{0.3}$	$\sim t^{0.32}$	$\sim t^{0.31}$	$\sim t^{0.34}$	$\sim t^{0.31}$
\tilde{V}	$\approx \text{const}$	$\sim t^{0.006}$	$\sim t^{0.0006}$	$\sim t^{0.0003}$	$\sim t^{0.015}$	$\sim t^{0.0008}$
N(t)	$\sim t^{-1}$	$\sim t^{-0.89}$	$\sim t^{-0.96}$	$\sim t^{-0.92}$	$\sim t^{-1.0}$	$\sim t^{-0.97}$
Du	0.215	0.23	0.228	0.231	0.218	0.242
Sku	-0.92	-0.76	-0.738	-0.738	-0.944	-0.558
Kru	0.675	0.5	0.52	0.548	0.728	0.228
$\max u$	1.5	1.456	1.453	1.496	1.372	1.5

verified by calculations performed for various initial distributions.

The physical reason of the self-saturation effect lies in the fact that there takes place the reconstruction of the size distribution function that acquires finally the form according to the LS theory, which is explained by the establishment of the distribution function that is in equilibrium relative to its form.

In our opinion, the self-saturation effect can be considered as an indicator of the beginning of the coalescence stage and as one of the criteria of applicability of the LS theory to the description of the decay at the coalescence stage.

The presented mean field model doesn't take the change of the concentration caused by the presence of a certain profile near new-phase particles into account. Such an analysis can be important at the coalescence stage for large volume fractions of the new phase, where one should allow for the diffusion interaction of newphase particles.

- 1. Ya.B. Zel'dovich, Zh. Eksp. Teror. Fiz. 12, 525 (1942).
- Ya.I. Frenkel, *Kinetic Theory of Liquids* (Nauka, Leningrad, 1975) (in Russian).
- V.V. Slezov and J.W.P. Schmelzer, in Annals of the Selected Papers Presented and/or Prepared in the Course of the Research Workshop Nucleation Theory and Application, edited by J.W.P. Schmelzer, G. Ropke, and V. Priezzchev (Dubna, JINR, 1999).
- A.S. Shirinyan and M.O. Pasichny, Bull. of Cherkasy State University. Physics: Proceedings of DIFTRANS'2001 36–37, 51 (2002).
- 5. I.M. Lifshitz and V.V. Slezov, Fiz. Tverd. Tela 1, 1401 (1959).

- E.M. Lifshits and L.P. Pitaevskii, *Physical Kinetics* (Pergamon Press, Oxford, 1981).
- M. Tokuyama and Y. Enomoto, Phys. Rev. Lett. 69, 312 (1992).
- B.Ya. Lyubov, Diffusion Processes in Inhomogeneous Solid Media (Nauka, Moscow, 1981) (in Russian).
- 9. A.S. Shirinyan and M.P. Kudin, Metalofiz. Nov. Tekhnol. (in press).
- 10. J.A. Marqusee and J. Ross, J. Chem. Phys. 80, 312 (1984).

Received 04.06.07. Translated from Ukrainian by H.G. Kalyuzhna

ЕФЕКТ САМОНАСИЧЕННЯ СПЛАВУ ЯК КРИТЕРІЙ ПОЧАТКУ СТАДІЇ КОАЛЕСЦЕНЦІЇ

А.С. Шірінян, М.П. Кудин

Резюме

Обговорюється чисельний розв'язок задачі контрольованого дифузією процесу росту та коалесценції частинок нової фази у наближенні середнього поля. Модель дозволяє детально дослідити основні стадії розпаду (стадію незалежного росту, перехідну стадію, коалесценцію) і переходи між ними. Показано, що дисперсія частинок нової фази за розмірами на стадії незалежного росту зменшується. Одержано, що в рамках наближення середнього поля може спостерігатися ефект самонасичення на початковій стадії коалесценції. Самонасичення характеризується "інверсною" поведінкою насичення, а саме зростанням концентрації розчинених атомів, що відповідають новій фазі. а також "інверсною" поведінкою середнього і критичного радіусів частинок нової фази – їх зменшення. Амплітуда цього ефекту є малою і залежить від об'ємної частки нової фази і початкового пересичення. Результат був перевірений для різних початкових розподілів частинок за розмірами. Ефект самонасичення може розглядатися як критерій (індикатор) початку стадії коалесценції.