THE "SHORT-RANGE ORDERING" FACTOR UPON RIPENING

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The process of the diffusion-driven ripening in binary alloys has been considered for "large" volume fractions of the new phase. A simple "short-range order" model of ripening taking into account the correlations between neighbor particles has been proposed. The evolution of the particle size distribution has been investigated by using the parameters which characterize the width, kurtosis, and skew of a peak.

1. Introduction

In the growth of particles of a new phase when supersaturated alloys undergo a decomposition, we can distinguish such stages as the nucleation, growth of isolated particles, and their ripening. At the last stage of the decomposition, the particles of the new phase exhibit the tendency to reduce the interface between the phases and, accordingly, the surface energy of the system. The growth of large particles at the expense of small ones is considered as diffusion-driven.

The classical mean-field theory of ripening created by Lifshitz, Slezov [1, 2], and Wagner [3] for the decomposition of a supersaturated binary alloy predicts the law $\langle R \rangle \sim t^{1/3}$ for the variation of the particle size R in time t and the asymptotic distribution function of the particles over their dimensions, which does not depend on initial conditions. Experimental researches confirm the particle growth law derived in the Lifshitz—Slezov—Wagner (LSW) theory, but the measured particle distributions over their sizes are broader and less tilted to the right side.

Two basic assumptions have been used when constructing the LSW theory: (i) ripening is supposed considerably slower than diffusion, so that a quasi-stationary solution of the diffusion equation can be used and (ii) the environment around each particle is supersaturated to a certain mean degree which is considered identical for all precipitates (the mean-field approximation).

A further development of the LSW theory can be realized in two directions, namely, by considering both the correlation effects and the dependence of the diffusion coefficient on the concentration. The concept of diffusion screening was proposed in works [4—6]. The corresponding correction to the LSW theory is based on the idea that the concentration field around every isolated particle is determined, in general, by precipitates within a definite λ-sphere, the radius of which depends on the volume fraction of a new phase. As the concept of diffusion screening turns out basic in the analysis of experimental data, we will present its fundamentals in brief.

In a weak solution of component B in A, the variation of the concentration $c(t, \vec{\rho})$ of component B averaged over the volume L^3 that surrounds an arbitrary point $\vec{\rho}$, where L is the average half-distance between neighbor particles, (on the spatial scale of the ripening, $d^3\rho \approx L^3$) is described by the equation

$$\frac{\partial c(t, \vec{\rho})}{\partial t} = D\nabla^2 c - \int 4\pi r^2 \left.\frac{dr}{dt}\right|_\rho f(t, r|\vec{\rho})\, dr, \qquad (1)$$

where $f(t, r|\vec{\rho}) = f(t, r)$ is the distribution function normalized to the precipitate density

$$\int f(t, r)dr = n \approx 1/(4\pi L^3/3). \qquad (2)$$

The growth of a particle, with regard for the Gibbs—Thomson equation and the fact that the diffusion process is quasi-stationary, is described by the expression

$$\left.\frac{dr}{dt}\right|_\rho = \frac{D}{r^2}\left(r\Delta(t, \vec{\rho}) - \alpha\right), \qquad (3)$$

$\Delta(t, \vec{\rho}) = c(t, \vec{\rho}) - c^{eq}$, $\alpha = c^{eq}\frac{2\sigma\Omega}{kT}$, where c^{eq} is the equilibrium concentration in the case of the plane surface of a precipitate, σ is the surface tension, Ω is the molar volume, and T is the temperature.

Using the quasi-stationary approximation and combining (1)—(3), we obtain the equations of screening

$$\nabla_\rho^2\left(\Delta(\vec{\rho}) - \bar{\Delta}\right) = \frac{1}{\lambda^2}\left(\Delta(\vec{\rho}) - \bar{\Delta}\right),$$

$$\lambda = (4\pi n\langle r\rangle)^{-1/2}, \qquad (4)$$

It has the solution

$$\left(\Delta\left(\vec{\rho}\right) - \bar{\Delta}\right) \propto \frac{\exp\left(-\rho/\lambda\right)}{\rho}, \tag{5}$$

where λ is the screening length, which is expressed in terms of the average half-distance L between precipitates and the volume fraction f of the new phase as follows:

$$\lambda \approx \sqrt{L^3/\langle r\rangle} \approx \langle r\rangle f^{-1/2} = L \cdot f^{-1/6}. \tag{6}$$

The quantity $f = \langle r^3\rangle/L^3$ in Eq. (6) is the ratio of the total volume of particles to the volume of a sample.

The radius of the λ-sphere, as well as the number of particles Z in it ($Z \approx \lambda^3/L^3 \approx f^{-1/2}$), grows if f tends to zero. It is this case that corresponds to the mean-field approximation in the LSW theory.

The analysis of the diffusion screening phenomenon is based on the use of the ripening scale with an "elementary volume" $1/n$ much smaller than the volume of the λ-sphere. However, such an approach does not work in the case where the screening length becomes of the order of or less than the average distance between neighbor particles. According to equality (6), we have

$$f \geq f^* = (1/2)^6 \approx 0.016.$$

In this case, the short-range order, i.e. the correlation between the dimensions of neighbor particles, can turn out important because, if the λ-sphere is reduced to the "first coordination sphere" of the particle, the mean-field approximation becomes incorrect.

2. Model of the Short-Range Order

For the analysis of the ripening kinetics in the case where the volume fraction of precipitates is greater than 2%, the following simplified model considering the correlations between the nearest neighbors is proposed.

At the initial moment, particles, the radii of which are randomly distributed about a certain value r_0, occupy the sites of the three-dimensional simple cubic lattice with the lattice constant H (Fig. 1). The variation of supersaturation around a particle is governed by the precipitates which fall into the sphere of the radius

$$L' = k\sqrt[3]{V^{\mathrm{tot}}/N^{\mathrm{tot}}}, \tag{7}$$

where V^{tot} is the sample volume and N^{tot} is the number of precipitates in the sample. The choice of a value for the parameter k allows one to assign the number of particles, the interaction with which at the initial moment is taken into account. The number of the "nearest neighbors" equals 6 for $k = 1.38$ and 32 for $k = 2.1$.
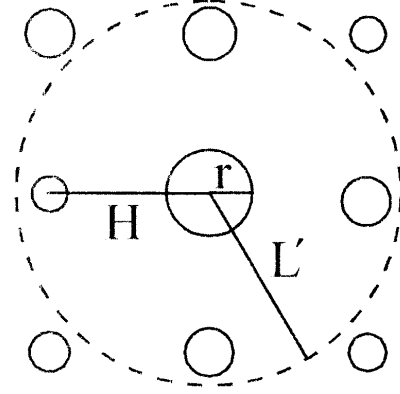

Fig. 1. Two-dimensional image of the precipitate lattice

Such precipitates generate the local supersaturation Δ_i around a particle, the ways to find which will be described below.

The quasi-stationary solution of the diffusion equation in the spherical coordinates, with regard for the fact that the average local concentration is reached at the "screening radius" rather than at the infinity, brings us to the modified equation of growth [7]

$$\frac{dr_i}{dt} = \frac{D}{r_i^2}\frac{(r_i\Delta_i - \alpha)}{1 - r_i/l_i}, \tag{8}$$

where $l_i < L'$ is the averaged distance to surrounding particles, the expressions for which and for Δ_i must be consistent. For $l_i \to \infty$, Eq. (8) takes the form (3).

In the simplest variant (case 1), the supersaturation created by the environment around a particle can be written as

$$\Delta_i = \frac{\alpha}{z_i}\sum_{j=1}^{z_i}\frac{1}{r_{i,j}} = \alpha\left\langle\frac{1}{r}\right\rangle_i, \tag{9}$$

where z_i is the number of neighbors of the i-th particle, which fall into the L'-region, and r_{ij} are their radii. Accordingly,

$$l_i^{-1} = \frac{1}{z_i}\sum_{j=1}^{z_i}\frac{1}{l_{i,j}}. \tag{10}$$

However, in this case, the smaller the radius of the particle, the larger its contribution to the concentration field. To avoid this circumstance, we consider the quantities Δ_i and l_i as given per unit area of the precipitate surface. This is case 2. Then,

$$\Delta_i = \alpha\sum_{j=1}^{z_i} r_{i,j}^2\frac{1}{r_{i,j}} \Big/ \sum_{j=1}^{z_i} r_{i,j}^2 = \alpha\langle r\rangle_i \Big/ \langle r^2\rangle_i, \tag{11}$$
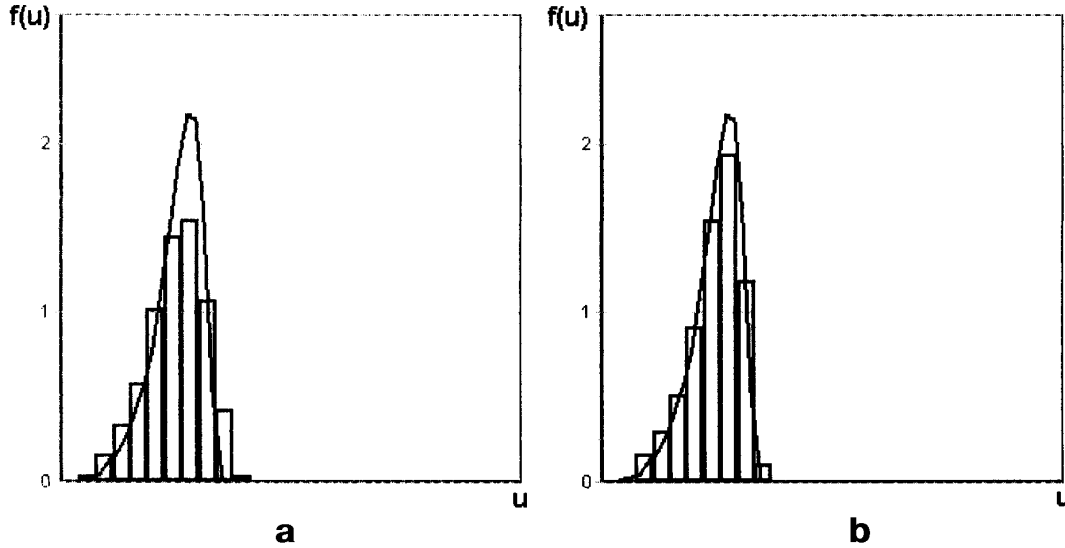
Fig. 2. Histograms of the size-distributions of particles obtained for various radii of the sphere of influence in case 2: (a) $f \approx 5\%$, $k = 1.38$ and (b) $f \approx 5\%$, $k = 2.1$. Solid curves correspond to the LSW-distribution

$$l_i^{-1} = \sum_{j=1}^{z_i} r_{i,j}^2 \frac{1}{l_{i,j}} \bigg/ \sum_{j=1}^{z_i} r_{i,j}^2. \tag{12}$$

The fulfillment of the conservation law (the almost constant volume of the new phase at the asymptotic stage) is ensured by the following normalizing condition:

$$p = \sum_{i=1}^{N} \frac{1}{1 - r_i/l_i} \bigg/ \sum_{i=1}^{N} \frac{r_i}{1 - r_i/l_i} \frac{\Delta_i}{\alpha}, \tag{13}$$

where the ratio $\frac{\Delta_i}{\alpha}$ is determined from expression (9) in case 1 and from expression (11) in case 2.

Thus, the equation governing the particle growth looks like

$$\frac{dr_i^3}{dt} = D\alpha \frac{\left(pr_i \left\langle \frac{1}{r} \right\rangle_i - 1 \right)}{1 - r_i/l_i}, \tag{14}$$

in case 1 and

$$\frac{dr_i^3}{dt} = D\alpha \frac{\left(pr_i \frac{\langle r \rangle_i}{\langle r^2 \rangle_i} - 1 \right)}{1 - r_i/l_i}. \tag{15}$$

in case 2.

3. Results

For each of the presented variants of the description of the local supersaturation around the particle, the relevant equation (11) or (14) was numerically solved. The solutions of the equations of growth, for various values of the input parameters f and k, made it possible

to obtain the distribution functions of the particle size (Fig. 2), which were compared with that predicted by the LSW theory.

The found distributions were analyzed by using the parameters which characterize the width s, skew w, and kurtosis K of the peak:

$$s = \left(\langle (u-1)^2 \rangle \right)^{1/2},$$

$$w = \left(\langle (u-1)^3 \rangle \right)/s^3,$$

$$K = \left(\langle (u-1)^4 \rangle \right)/s^4 - 3,$$

where $u = \frac{r}{\langle r \rangle}$. For the particle distribution in the LSW theory, we have $s = 0.215$, $w = -0.920$, and $K = 0.675$.

The specified parameters are determined from the experimentally measured size-distributions of particles. For example, the quantity s varies within the limits of 0.26–0.29 for the ripening of the Ni_3Si precipitates in the binary alloys Ni–Si [8]. In the case of the ripening of Ni_3Ti particles in the Ni–Ti alloy, the values $s = 0.294$, $w = +0.308$, and $K = -0.216$ were obtained [9]. Similar experiments for the ripening of Ni_3Ge particles in Ni–Ge alloys gave $s = 0.292$, $w = -0.173$, and $K = -0.235$ [10].

In addition, the parameter

$$k_{gr} \equiv \frac{d\langle r \rangle^3}{dt}$$

which describes the particle growth rate was calculated at every time step. After some transient time interval, this parameter became constant.
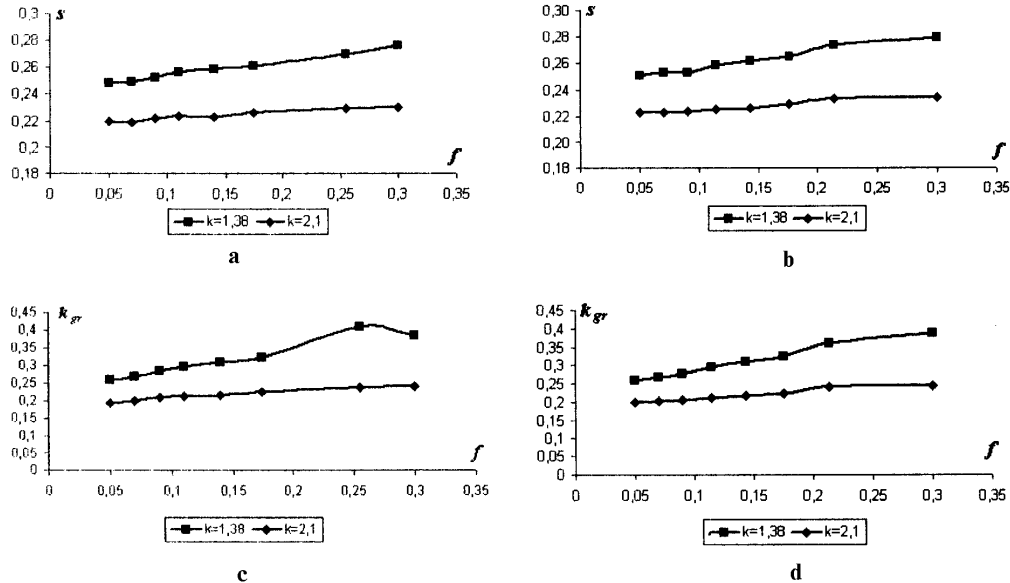
Fig. 3. Dependences of the parameters s and k_{gr} on the volume fraction f of the new phase for various values of the parameter k in case 1 (a,c) and 2 (b,d)

The behaviors of the parameters s and k_{gr} in time were also studied for different values of the volume fraction f of the new phase at given k. The averaged asymptotic values of those parameters for both the ways of the local supersaturation description are presented in Fig. 3. Here, the limiting cases are the values predicted by the LSW theory. The parameters w and K turned out less stable. Owing to the spatial confinement of the sample under investigation (the number of particles in the system only decreases), the task of calculating the asymptotic values is difficult. For the volume fraction f within the studied interval, the parameter w varies from -0.98 to -0.83 and the parameter K from 0.71 to 0.4 at $k = 2.1$, and the parameter w from -0.6 to -0.4 and the parameter K from 0.18 to -0.11 at $k = 1.38$.

4. Conclusions

Thus, the account of correlations between the nearest neighbors in the case of the "large" volume fractions of the new phase allows one to obtain the size-distributions of particles which are different from those predicted in the LSW theory and closer to experimental data.

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ФАКТОР "БЛИЗЬКОГО ПОРЯДКУ"
ПРИ КОАЛЕСЦЕНЦІЇ

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Р е з ю м е

Розглянуто процес дифузійно-контрольованої коалесценції у бінарному сплаві для випадку "великих" об'ємних часток нової фази. Запропоновано просту модель "близького порядку" коалесценції з урахуванням кореляцій між найближчими частинками. Досліджено отримані розподіли частинок за розмірами з використанням параметрів, що характеризують висоту, гостроту та нахил піка.