

MODELING THE PRECIPITATION KINETICS IN SYSTEMS WITH STRONG HETEROPHASE FLUCTUATIONS

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The hierarchy of the Becker-Döring rate equations is used to consider the influence of heterophase fluctuations on the kinetics of precipitation in supersaturated solid solutions, including the nucleation stage and the crossover to the final Ostwald ripening regime. Numerical simulation shows that a quasi-stationary distribution of solute clusters forms in the region of small sizes. This population of small clusters (heterophase fluctuations) is separated by a gap from the distribution of coarsening precipitates. The scaling behaviour of the precipitate size distribution during the later stage of decomposition is consistent with the Lifshits-Slyozov theory of coarsening.

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1. INTRODUCTION

The properties of many industrial alloys are controlled by the precipitation of second phase particles. Traditionally, the precipitation kinetics in supersaturated metastable solid solutions is considered in terms of three distinct stages: (i) nucleation of stable clusters of the precipitating phase, (ii) independent diffusion growth of these clusters, and (iii) coarsening (Ostwald ripening) that involves the growth of large precipitates at the expense of dissolving small ones, driven by an overall reduction in the interface energy. There exists an important class of alloys in which precipitate-matrix interface energy is low. Usually these precipitates are coherent with the matrix and resistant to coarsening. Examples of such alloys include nickel superalloys [1], copper bearing high strength low alloy steels (HSLA) [2,3], aluminum alloyed with scandium [4,5] etc. Due to precipitation of a high density of coherent, nanometer sized particles these alloys exhibit substantial strength. This effect can be beneficial or detrimental depending on alloy application. For example, model Fe-Cu alloys have received much attention because of the influence of irradiation on the precipitation of copper-rich particles in ferritic steels and the related steel hardening and embrittlement of reactor pressure vessels [6,7].

The processes of nucleation, growth and coarsening in the system of coherent precipitates with low interface energy can occur simultaneously, which makes interpretation of the alloy behavior difficult. The interface energy affects the nucleation rate, the precipitate growth as well as drives the coarsening process through the capillarity effect. Existing models of the later stage of decomposition consider only large coarsening precipitates and solute monomers, whereas the population of subcritical clusters is ignored. However, even in undersaturated solid solutions a steady-state distribution of small-sized clusters forms due to continuous nucleation and decay of unstable clusters. In 1939 Frenkel has named this distribution the heterophase fluctuations (HF) [8]. In this communi-

cation we consider the effect of HF on the kinetics of precipitation in binary alloys. At a low interface energy and/or high temperatures the HF may contribute considerably to the overall balance of solute atoms and influence both the nucleation and coarsening stages.

2. THE MODEL

Consider a binary alloy supersaturated with a component that will be called the solute in the following. The alloy may contain second phase precipitates which are assumed to consist of the pure solute component. All precipitates are approximated as spherical in shape. Our goal is to describe the evolution of the precipitate size distribution function (DF) which is defined as the time-dependent concentration $f(n,t)$ of solute clusters of a given size n varying over the range from solute dimers to large precipitates. We will use an approach known in the literature as the Becker-Döring model [9] or the Master equation approach. According to this model the kinetic equations for cluster concentrations are defined by the rates at which clusters absorb a solute atom and lose a solute atom due to thermal evaporation. Only solute monomers are assumed to be mobile, i.e. direct collisions of clusters are not considered within the Becker-Döring model

$$\frac{\partial f(n,t)}{\partial t} = J_{n-1,n} - J_{n,n+1}, \quad n = 2, 3, \dots \quad (1)$$

$$J_{n-1,n} = W^+(n-1)f(n-1,t) - W^-(n)f(n,t), \quad (2)$$

where $f(1,t) \equiv C_1$ is the concentration of mobile monomers (all concentrations are defined in terms of atomic fractions). In the diffusion-limited case the absorption and emission rates $W^+(n)$ and $W^-(n)$ are given by

$$W^+(1) = 2 \frac{4\pi}{\omega} R(1)DC_1, \quad (3)$$

$$W^+(n) = \frac{4\pi}{\omega} R(n) D C_1, \quad n > 1, \quad (4)$$

$$W^-(n) = \frac{4\pi}{\omega} R(n) D C_1^R, \quad n > 1, \quad (5)$$

where ω is the atomic volume, $R(n)$ is the radius of the n -atomic cluster, D is the diffusion coefficient of solute atoms. C_1^R is the thermal equilibrium concentration of solute monomers at the precipitate boundary given by the Gibbs-Thomson relation

$$C_1^R = C_1^e \exp\left(\frac{2\gamma\omega}{Rk_B T}\right), \quad (6)$$

where C_1^e is the solute monomer concentration at equilibrium with the bulk solute phase and γ is the precipitate-matrix interface energy.

The total number of solute atoms is kept constant

$$C_1 + \sum_{n=2}^{\infty} n f(n, t) = Q, \quad (7)$$

where Q is the atomic fraction of solute atoms.

The solid solution is supersaturated if $C_1 > C_1^e$. The excess amount of solute atoms forms clusters of the new phase. The well-known expression for the steady-state nucleation rate of stable clusters can be obtained from Eqs. (1) and (2)

$$J_{n-1, n} = J = \left[\sum_{n=1}^{\infty} (W^+(n) f_e(n))^{-1} \right]^{-1}, \quad (8)$$

where

$$f_e(n) = \frac{W^+(1) f(1)}{W^+(n)} \prod_{i=2}^n \frac{W^+(i)}{W^-(i)} \quad (9)$$

is the DF corresponding to the constrained equilibrium $J_{n-1, n} = 0$. The function $f_e(n)$ has the minimum at the critical size $n = n_{cr}$ defined by the relation

$$W^+(n_{cr}) = W^-(n_{cr}). \quad (10)$$

All clusters, smaller than the critical cluster, play an important role providing a "path" for nucleation of stable growing precipitates (Eq. (8) contains all cluster sizes). Even saturated stable solution ($n_{cr} = \infty$) contains HF in the form of the equilibrium distribution of clusters [8]. This means that the solute solubility is not identical to the solubility of monomers. The solubility should be defined as the total content of solute atoms in the saturated solution including solute atoms in subcritical clusters that form and decay due to fluctuations, i.e. in the capillary approximation used here the solute solubility is given by

$$\begin{aligned} C^e &= C_1^e + \sum_{n=2}^{\infty} n f_e(n) \\ &= C_1^e \left[1 + 2 \sum_{n=2}^{\infty} n^{2/3} \exp\left(-\beta \sum_{i=2}^n i^{-1/3}\right) \right], \end{aligned} \quad (11)$$

where $\beta = \frac{2\omega}{R_1 k_B T} \gamma$ is the dimensionless interface energy.

Fig. 1 shows the relative contributions of monomers and HF (the second term in Eq. (11)) to the solute solubility. It is seen that at small values of the parameter β the monomer concentration is low¹. In alloy systems with small values of the parameter β the majority of solute atoms belongs to immobile clusters and does not participate directly in diffusion decomposition. This means that the conventional models of nucleation and coarsening are valid for systems with $\beta \gg 1$; their application to systems with small values of β may result in erroneous interpretation of experimental data.

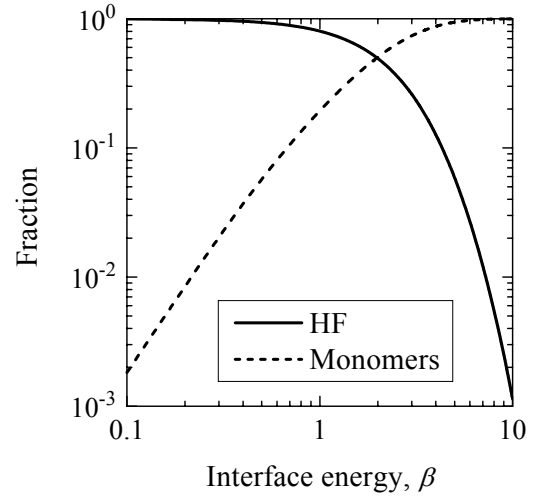


Fig. 1. Relative contributions of monomers and HF to the solute solubility versus the interface energy

To investigate the influence of HF on homogeneous nucleation and coarsening of precipitates we track the full particle size DF through the cause of transformation. We use the numerical method described in [11]. To reduce the number of equations solved simultaneously we keep the original discrete Eqs. (1) and (2) up to 200 atoms in clusters; for larger sizes Eqs. (1) and (2) are transformed to a partial differential equation of the Fokker-Planck type for a continuous size variable, which allows coarse-graining of the numerical mesh. The combined set - the discrete equations and the continuous Fokker-Planck equation - is solved numerically by the method of lines [12].

3. RESULTS AND DISCUSSION

In simulations we used dimensionless time

$$\tau = 4\pi R_1 \omega^{-1} D t. \quad (12)$$

The solubility was fixed at the value $C^e = 0.2\text{at}\%$, then the equilibrium concentration of solute monomers C_1^e was calculated as a function of the parameter β

¹ As an example, the interfacial energy of coherent Ni_3Al particles precipitating in Ni-Al alloys is 14 mJ/m^2 [10] and the value of β is estimated as $\beta \approx 700/T$.

using Eq. (11). Fig. 2 shows formation of the precipitate size DF in the supersaturated solid solution during aging. The DF is defined in terms of cluster radius

$$F(R, \tau) = \frac{3}{\omega} \left(\frac{4\pi}{3\omega} \right)^{1/3} n^{2/3} f(n, \tau), \quad (13)$$

where $\omega = 1.2 \times 10^{-29} \text{ m}^3$. In the initial state the matrix contains only solute monomers with the concentration $Q = 2 \text{ at}\%$. To analyze the simulation results the population of precipitates is divided into two groups: (i) small clusters (HF with $R < R^* = 1 \text{ nm}$); and (ii) large precipitates. The density of HF N_{hf} , the precipitate density N_p and the mean precipitate radius R_p are given by relations

$$N_{hf} = \int_{R_2}^{R^*} F(R, \tau) dR, \quad N_p = \int_{R^*}^{\infty} F(R, \tau) dR, \quad R_p = \int_{R^*}^{\infty} R F(R, \tau) dR, \quad (14)$$

where R_2 is the dimer radius.

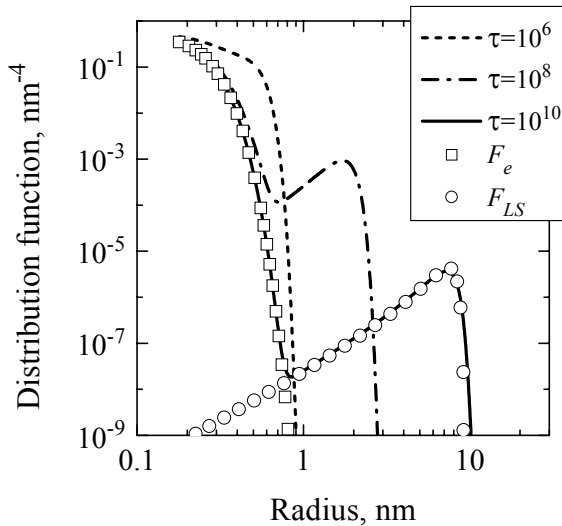


Fig. 2. Evolution of DF at $\beta = 0.5$ Boxes show the quasi-stationary distribution of HF (see Eqs. (9),(13)); circles correspond to the Lifshitz-Slyozov distribution

It is seen that the quasi-stationary distribution of solute clusters forms in the region of small sizes (Fig. 2). In the end of the nucleation stage a gap in the solute cluster distribution forms, which separates the population of small clusters (HF) from the distribution of large growing precipitates. The size width of the region of HF depends on interface energy and temperature (the parameter β); in particular, it increases with decreasing the interface energy. The simulated DF of small clusters is well described by Eq. (9) and (13). The leading edge of the distribution advances with time and large precipitates undergo a process of the Ostwald ripening. At the later stage of aging the shape of the precipitate DF is close to that predicted by the Lifshitz-Slyozov (LS) theory of coarsening [13]

$$F_{LS}(R, \tau) = \frac{N_p(\tau)}{R_p(\tau)} g\left(\frac{R}{R_p(\tau)}\right), \quad (16)$$

$$g(u) = \frac{4}{9} u^2 \left(\frac{3}{3+u} \right)^{7/3} \left(\frac{1.5}{1.5-u} \right)^{11/3} \exp\left(-\frac{u}{1.5-u}\right). \quad (17)$$

Fig. 3 shows the time dependence of the mean precipitate radius and the precipitate density calculated for several values of the parameter β that is proportional to the interface energy. It is seen that changing the parameter β has a pronounced effect on the onset of nucleation and crossover to the later coarsening stage. What is important here is that *the incubation period for nucleation increases with decreasing the interface energy*; in other words, despite low values of the critical size for nucleation the system evolves slowly.

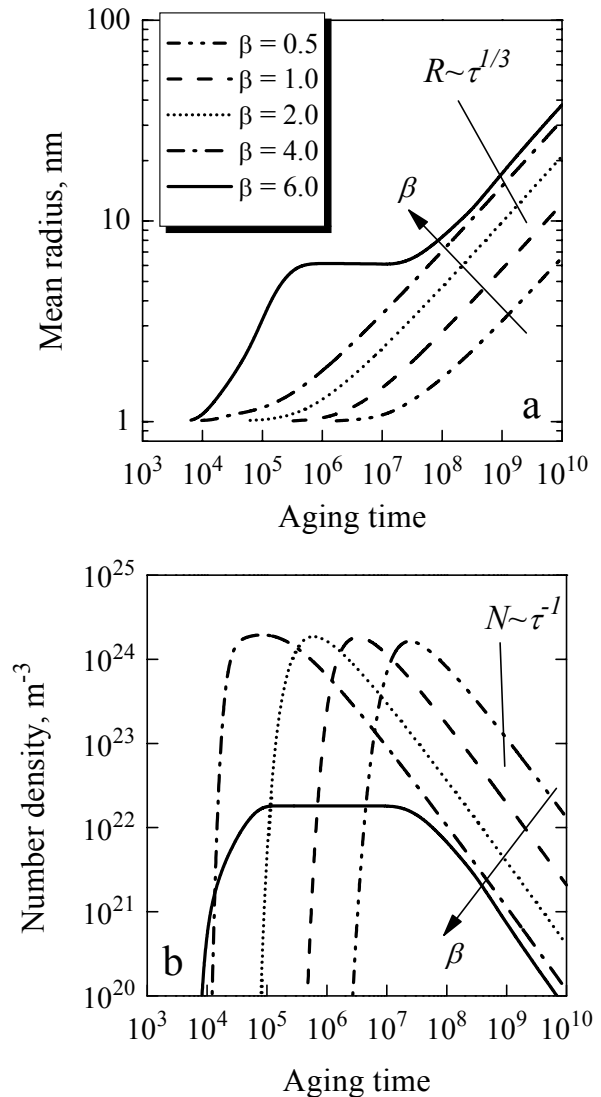


Fig. 3. Time dependence of the mean precipitate radius (a) and the precipitate density (b). The interface energy increases in the direction of arrows

Intuitively, on the basis of the classical nucleation theory [14], completely opposite tendency can be expected. But this logic may lead to erroneous

conclusions. As an example, we would like to discuss here some results of ref. [15], in which a numerical precipitation model by Kampmann and Wagner [16] (KWN model) has been used to investigate the effect of interface energy, solute supersaturation, and diffusivity on the kinetics of precipitation in binary alloys. In the methodology of the KWN model the kinetics of small-sized clusters (HF) is not considered. Instead, the classical nucleation theory is used to derive the nucleation rate as a function of time and solute concentration. To simulate the precipitation kinetics the continuous time evolution is divided up into a number of small time steps. At each step new stable clusters are allowed to nucleate; for the existing precipitates a deterministic description is used. The radius of the newly formed precipitates is set to be slightly larger than the critical radius to enable these precipitates to grow. The precipitate size DF is used to calculate the precipitate volume fraction and the instantaneous mean concentration of solute monomers. In the next time step the updated concentration of monomers is used in calculating the nucleation rate and the deterministic growth rates of precipitates. It should be emphasized that both the model of this communication and the KWN model are based on the same physical assumptions. However, in contrast to results depicted in Fig. 3, in [15] in the framework of KWN model it has been found that the incubation period for decomposition decreases drastically when the parameter β decreases from 5 to 0.8. The reason of this discrepancy is that the KWN model is not physically justified for systems in which β is less or of order unity. As it has been written in [16] one of the main assumptions of the KWN model is the following: *those fluctuations formed in the nucleation regime which do not grow beyond the critical size do not influence the precipitation kinetics significantly; i.e. the number of fluctuations with subcritical size and, hence the fraction of solute atoms contained in them is negligibly small.*

According to Fig. 3; in the long-time limit the asymptotic behavior is consistent with the LS coarsening theory [13], i.e. $R_p \propto \tau^{1/3}$ and $N_p \propto \tau^{-1}$.

In the case of strong HF ($\beta = 0.5$) the atomic fraction of HF remains constant up to $\tau = 10^7$ (Fig. 4b) while in the system with small contribution of HF the nucleation stage is already completed (Fig. 4,a). The reason is that at low interface energy the driving force for evolution is low. Note that in the final state at $\tau = 10^{10}$ in the system with strong HF the concentration of mobile monomers is small (Fig. 4,b). This should be taken into account when using formulas of the LS theory for the experimental evaluation of material parameters. The point is that the mean precipitate radius obeys the asymptotic relation

$$R_p^3 = \frac{8}{9} \frac{\gamma\omega}{k_B T} D C_1^e t, \quad (18)$$

which well agree with our simulation results. This relation contains the equilibrium concentration of

monomers, but not the solute solubility. We have not found in the literature discussion of this issue.

We have also performed simulations of precipitation kinetics in the system with a size-dependent interface energy. It is known that the interface energy usually increases as the second phase particle grows from a small cluster into a distinct precipitate. The interface energy increases when precipitates lose coherency during growth. This means that small-sized precipitates may have low interface energy that controls the fraction of HF and the nucleation rate, while large observable precipitates have a higher value of the interface energy that controls the coarsening behavior. We have found that in this case (i) nucleation and coarsening processes are slow and (ii) at the intermediate stage of coarsening the precipitate DF is broader than the LS distribution function. The detailed description of these results will be presented elsewhere.

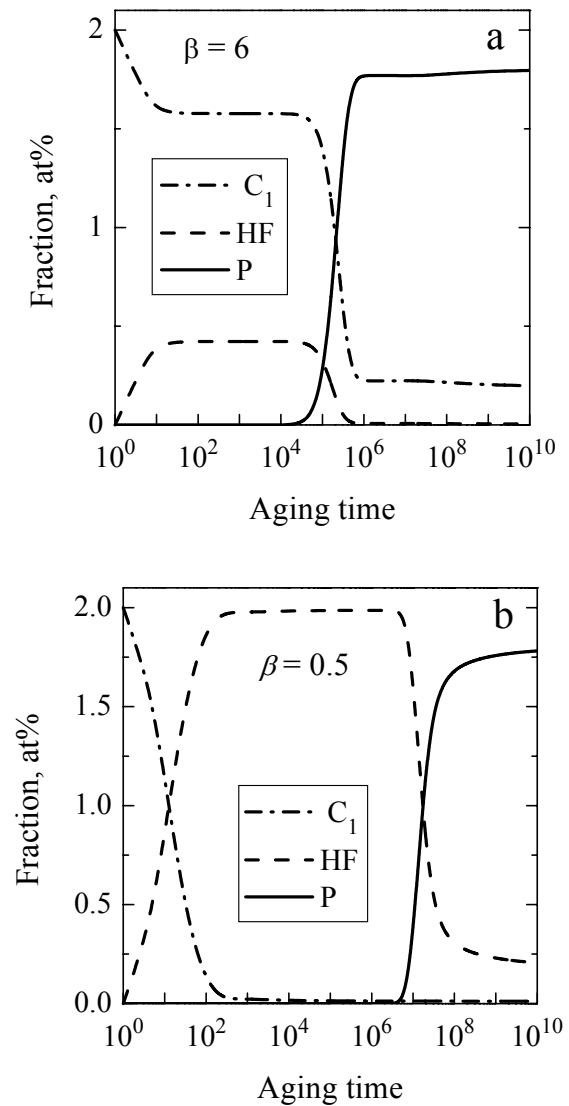


Fig. 4. Time dependence of atomic fractions of monomers (C_1), heterophase fluctuations (HF) and precipitates (P) in the system without HF at $\beta = 6$ (a) and in the system with strong HF at $\beta = 0.5$ (b)

4. CONCLUSIONS

Simulation of the precipitation kinetics in systems with strong HF ($\beta \lesssim 1$) shows that:

1. HF inhibit the homogeneous nucleation even in highly supersaturated solid solutions.
2. HF influence the shape of the precipitate size distribution function.
3. In the long-time limit the precipitate size distribution tends to a stable self-similar distribution close to the LS distribution.

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МОДЕЛИРОВАНИЕ КИНЕТИКИ РАСПАДА В СИСТЕМАХ С СИЛЬНЫМИ ГЕТЕРОФАЗНЫМИ ФЛУКТУАЦИЯМИ

А.А. Туркин, А.С. Бакай

Иерархия уравнений Бекера-Деринга используется для рассмотрения влияния гетерофазных флуктуаций на кинетику распада пересыщенных твердых растворов, включая стадию зарождения и переход к конечному режиму коалесценции. Численное моделирование показывает, что в области малых размеров формируется квазистационарное распределение мелких кластеров (гетерофазные флуктуации), которое отделено от распределения растущих выделений. Скейлинговое поведение распределения выделений по размерам на поздней стадии распада соответствует теории коалесценции Лифшица-Слезова.

МОДЕЛЮВАННЯ КІНЕТИКИ РОЗПАДУ В СИСТЕМАХ З СИЛЬНИМИ ГЕТЕРОФАЗНИМИ ФЛУКТУАЦІЯМИ

А.А. Туркін, О.С. Бакай

Ієрархія рівнянь Бекера-Деринга використовується для розгляду впливу гетерофазних флуктуацій на кінетику розпаду пересичених твердих розчинів, включаючи стадію зародження і перехід до кінцевого режиму коалесценції. Числове моделювання показує, що в області малих розмірів формується квазістаціонарний розподіл дрібних кластерів (гетерофазні флуктуації), що відокремлений від розподілу зростаючих виділень. Скейлінгова поведінка розподілу виділень за розмірами на пізній стадії розпаду відповідає теорії коалесценції Ліфшица-Сльозова.