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Finite size effect in spinodal decomposition of nanograined materials

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Decomposition of solid solution taking into account the grain boundaries segregations is considered in the framework of generalized Cahn-Hilliard model for finite systems. Two types—"stripe" and "drop-wise"—of the surface-directed decomposition found below spinodal depend on concentration of a wetting component. We demonstrate that grain boundaries segregations are able to drastically change the phase equilibrium inside the grain when its size becomes less than the critical value. As a result, decomposition of the solid solutions easily appears for nanograined materials.

1. Introduction

Unconventional phase and structural transformations occurring in materials under severe mechanical treatment attract great interest due to the perspectives of technological application of this phenomenon [1]. In spite of remarkable efforts of researchers the nature and mechanisms of phase transformations of alloys in nanocrystalline state remains a subject for discussions [2–5]. If amorphization and formation of solid solutions from immiscible component can be comprehensible in terms of direct mechanical mixing of atoms in shear bands [2, 3], then for explanation of decomposition phenomena one should assume an important role of the thermodynamic factors and diffusion mass transfer [4, 5]. One of the key conditions for appearance of the phase instability is obtaining maximum fragmentation of alloys and formation of the nanograined state [1]. This clearly indicates a significant role of grain boundaries (GB) in initiation of phase transformations under intensive plastic deformation.

As commonly accepted the grain boundaries are preferable places for segregation of one of alloy components. In the case when parameters of an alloy lie over solubility limit (i.e. when solid solution is stable) the thickness of the GB precipitates remains small during an isothermal exposure. When alloy parameters are between spinodal and binodal the interfaces are preferred places for heterogeneous nucleation of a new phase. In subcritical region when homogeneous state of an alloy is unstable with respect to spinodal decomposition, interface stimulates appearance of concentrating waves propagating from the boundary into a sample. The latter phenomenon first discovered in polymer mixtures has been profoundly studied in the recent time (see review [6]) and has been defined as surface directed spinodal decomposition (SDSD).

The concept of SDSD [6] based on the consideration of the isolated boundary and therefore, can not explain the influence of grain size L on phase stability of an alloy under severe mechanical treatment. Generally speaking, the features of behavior of nanograin materials must originate from relatively high fraction of the boundary atoms comparable with a core of grain [1, 7]. The development of phase instability when value L decreases may be related, for example, with stress fields of geometrically necessary defects appearing under plastic deformation [1] or with intensive generation of point defects accompanying grain-boundary sliding [4, 5]. In this paper we pay attention to factors of the geometric nature which can qualitatively change the whole picture of the phase stability of an alloy. We show that in nanograined materials a fraction of component segregated on GB can be comparable with a core of grain and grain-boundary segregations become critical for alloy phase stability.

Here we analyze the role of a size factor in phase stability of solid solutions in a wide range of parameters both in a subcritical region and beyond it. We consider decomposition kinetics in the framework of generalized nonlinear Cahn-Hilliard model, whose microscopic derivation is given in [8]. An unexpected result is the loss of alloy stability when grain size L becomes smaller less than some value L_c even if its parameters are beyond the critical region. Such change of alloy state stability has a threshold character that enables us to speak about size effect in phase instability of nanograined alloys.

2. Generalized Cahn-Hilliard model allowing for surface segregations

For study of the decomposition kinetics in AB binary alloy we use a lattice model with a direct exchange of

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A and B type neighboring atoms [9]. Such description of diffusion processes is not quite realistic because in solids mass transfer goes according to vacancy mechanism. Nevertheless, we believe that using of the direct exchange approximation allows us to describe correctly the main qualitative peculiarities of decomposition. Moreover, as shown in [8], taking into account vacancy exchange mechanism leads to similar results for the case of the locally-equilibrium distribution of vacancies.

We follow approach [10] describing the evolution of the distribution of alloy components starting from a master equation in a mean field approximation. In continuum limit which is valid for sufficiently slow change of concentrations $C_{\rm i}(\mathbf{r})$ (it is valid for a long-range interatomic interaction, in particular) the master equation transforms into nonlinear kinetic equation in a form [8]:

$$\frac{\partial C_{\rm A}}{\partial t} = -\vec{\nabla}\vec{J}_{\rm A} \tag{1}$$

$$\vec{J}_{\rm A} = -\omega_{\rm A}(1-\Psi C_{\rm A}C_{\rm B})\vec{\nabla}C_{\rm A} + \Psi C_{\rm A}C_{\rm B}\frac{R_{\rm int}^2}{6}\omega_{\rm A}\vec{\nabla}\Delta C_{\rm A} \tag{2}$$

The Equations 1 and 2 are similar to Cahn-Hilliard-Cook equation, but unlike the latter the effective surface energy of an inhomogeneities (the last term in the right part (2)) turn out to be dependent on concentrations. The fluxes of components $\vec{J}_{\rm i}$ satisfy the condition $\vec{J}_{\rm A}+\vec{J}_{\rm B}=0$ and diffusion mobility of atoms is equal to: $\omega_{\rm A}=\omega_{\rm B}=\omega$. The parameter $R_{\rm int}$ has an order of the typical length of interatomic interaction [8]. The value Ψ is dimensionless energy of mixing

$$\Psi = \frac{1}{kT}(2\Phi_{\rm AB}-\Phi_{\rm AA}-\Phi_{\rm BB}),$$

$$\Phi_{\rm ij} = \frac{1}{V}\int \varphi_{\rm ij}(\mathbf{r})\,d\mathbf{r} \tag{3}$$

$\varphi_{\rm ij}(\mathbf{r})$ is the interaction energy between i and j-type atoms, located at a distance $\mathbf{r}$ from each other. Below a spinodal curve (region C in Fig. 1) described by an equation

$$1-\Psi C_{\rm A}C_{\rm B}=0 \tag{4}$$

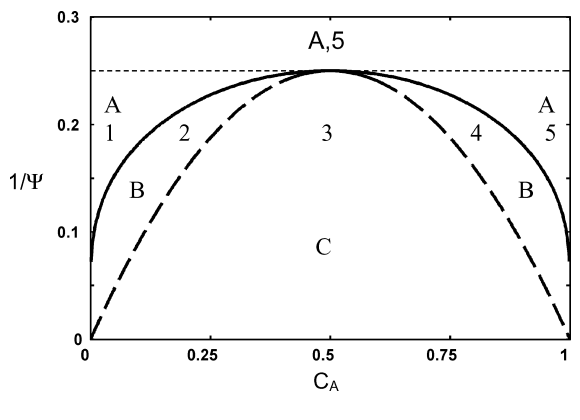

Figure 1 Equilibrium phase diagram of regular solid solution. Solid line corresponds to a solubility curve, dashed — to a spinodal.

a loss of stability of homogeneous solid solution takes place. A new phase appears due to the formation of nuclei and their subsequent growth between curves 1 and 2 (region B).

As it doing in models SDSD (see [6]), we do not consider a mechanism of the interaction of alloy components with boundary and take into account GB modified by introducing the deviation of chemical potential $\mu^{\rm i}$ of the alloy component $\mu_{\rm b}^{\rm i}(\mathbf{r})=\mu^{\rm i}(\mathbf{r})-\mu_0^{\rm i}$ near the boundary from its bulk value $\mu_0^{\rm i}$.

The spatial heterogeneity of the chemical potential near GB results in an extra contribution to the flux

$$\vec{J}_{\rm i}^{\rm b} = -M\vec{\nabla}\mu_{\rm b}^{\rm i}(\mathbf{r}) \tag{5}$$

where M is mobility of components. Applying Einstein relation the value M can be presented in the form $M=\omega C_{\rm A}C_{\rm B}/kT$.

In models describing SDSD [6] the interaction of only the nearest neighbor's atoms is taken into account and one assumes that a thickness of the adjacent to GB layer (where $\mu_{\rm b}^{\rm i}\neq 0$) is very small. As a result, the dependence $\mu_{\rm b}^{\rm i}(\mathbf{r})$ has the δ-wise form and is introduced in kinetic equations via boundary conditions. The distinguished feature of the nanocrystalline materials is the wide adjacent region with properties differing from the bulk ones. According to experimental data [1] the thickness of such region ξ is approximately 1 nm, i.e. comparable with the grain size in nanocrystalline materials. The reasons for it may be connected with a special non-equilibrium state of the GB and, with noticeable lattice distortions near GB in nanocrystalline materials, in particular. We take a model form of the $\mu_{\rm b}^{\rm i}(\mathbf{r})$ dependence

$$\mu_{\rm b}^{\rm i}(x) = \frac{q_{\rm i}}{2(1+(x/\xi)^2)} \tag{6}$$

where x is a coordinate in direction perpendicular to GB; q characterizes chemical potential change at the boundary. The results of numerical calculations show that decomposition kinetics is low-sensitive to the choice of $\mu_{\rm b}^{\rm i}(x)$ dependence and is mostly determined by $q_{\rm i}$ and ξ parameters. Note, that Equation 6 introduces a long-range influence of GB on phase stability. As we show below, this feature plays an important role in the problem under consideration.

Taking into account (6) an extra contribution to the flux in normal to GB direction can be written as

$$J_{\rm i}^{\rm b} = \frac{\omega C_{\rm A}C_{\rm B}q_{\rm i}}{kT\xi^2(1+(x/\xi)^2)^2} \tag{7}$$

After substituting the total flux $J_{\rm i}+J_{\rm i}^{\rm b}$ defined by expressions (2), (7) into Equation 1 we come to a kinetic equation describing a phase evolution in non-ideal solid solution taking into account GB segregations.

3. Decomposition kinetics allowing for GB segregations: Results of numerical calculations

Numerical solution of kinetic equation was carried out for a two-dimensional case assuming a rectangular form and an equal size of all grains. We applied boundary conditions which follow from the mirror-symmetrical distribution of concentrations with respect to each GB. Note, that such boundary conditions ensured zero fluxes via GB automatically. A homogeneous distribution of concentrations $C_i = C_{i0}$ with small occasional fluctuation were imposed as an initial state; further the time evolution of distribution $C_i(\mathbf{r})$ has been studied at different alloy parameters Ψ, C_{A0} for regions 1–5 (Fig. 1). For certainty we assume that $\mu_b^B < 0, \mu_b^A = -\mu_b^B$, i.e. B species is wetting GB component. In the figures below the dimensionless time τ and distance is given in L^2/ω and L units correspondingly.

3.1. Surface-Directed Spinodal Decomposition (SDSD)

In Fig. 2a–f intermediate stages of the decomposition developing when alloy parameters lie in region 3 (Fig. 1) are shown. In this case even small perturbations on boundaries give rise to SDSD. Small fluctuations introduced at initial concentration distribution develop faster in adjacent to GB regions. As a result a structure repeating the shape of grain (Fig. 2a–c) is formed. A similar picture of the surface provoking spinodal decomposition was observed earlier in SDSD model [6].

As seen in Fig. 2a–c, two distinguished types of SDSD are possible: "stripe-wise" (Fig. 2a) and "drop-wise" (Fig. 2b and c). Separation of two types of spinodal decomposition seems to be justified and for the case of the absence of fluctuations on the boundaries (see Fig. 2d–f). The results of calculations enables us to conclude that there exists a certain critical concentration C_{A0}^{crit} dividing regions of the "stripe" and "drop" SDSD. First regime appears for comparable concentrations C_{A0} and C_{B0} (near 0.5); second regime—when concentration one of species is small (close to a spinodal boundary). The physical reason for existence of two types of SDSD is clear enough. The migration of atoms at considerable distances (in the wave propagation direction) would be necessary for ensuring "stripe-wise" decomposition if one of components is present in small concentration. Therefore, for certain composition $C_{A0} < C_{A0}^{crit}$ a wave front appears to be unstable and is split into "drops" in results of the redistribution of atoms in the transverse direction.

3.2. Decomposition of metastable solid solutions

Beyond region 3 small fluctuations in the initial distribution do not affect transformation kinetics. Therefore, below we show the results of calculations when homogeneous state was chosen at the initial moment of time. The kinetics of decomposition in region 2 differs for small and large grain sizes. If the grain size L is larger

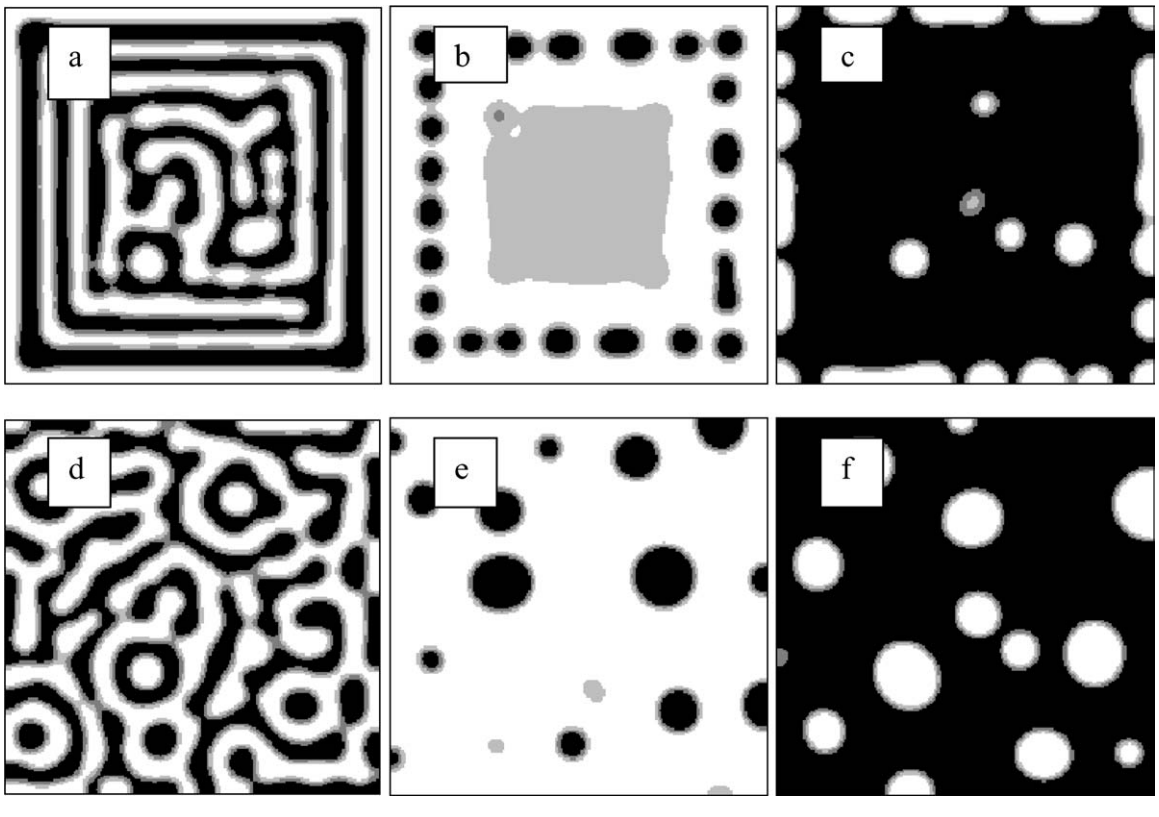

Figure 2 Wave stage of SDSD (a–c) and spinodal decomposition in the absence of perturbation on boundaries (d–f) with different alloy composition. In the initial distribution 200 small random Gauss fluctuations have been introduced. $\Psi = 5.3$, $L = 80R_{int}$, $\xi = 2R_{int}$. In this system $C_{A\beta}^{eqv} = 0.10$, $C_{A\beta}^{spin} = 0.25$. (a) $C_{A0} = 0.5, q' = 1.0, \tau = 0.02$; (b) $C_{A0} = 0.27, q' = 1.0, \tau = 0.04$; (c) $C_{A0} = 0.73, q' = 0.1, \tau = 0.08$; (d) $C_{A0} = 0.5, \tau = 0.02$; e) $C_{A0} = 0.27, \tau = 0.16$; (f) $C_{A0} = 0.73, \tau = 0.16$.

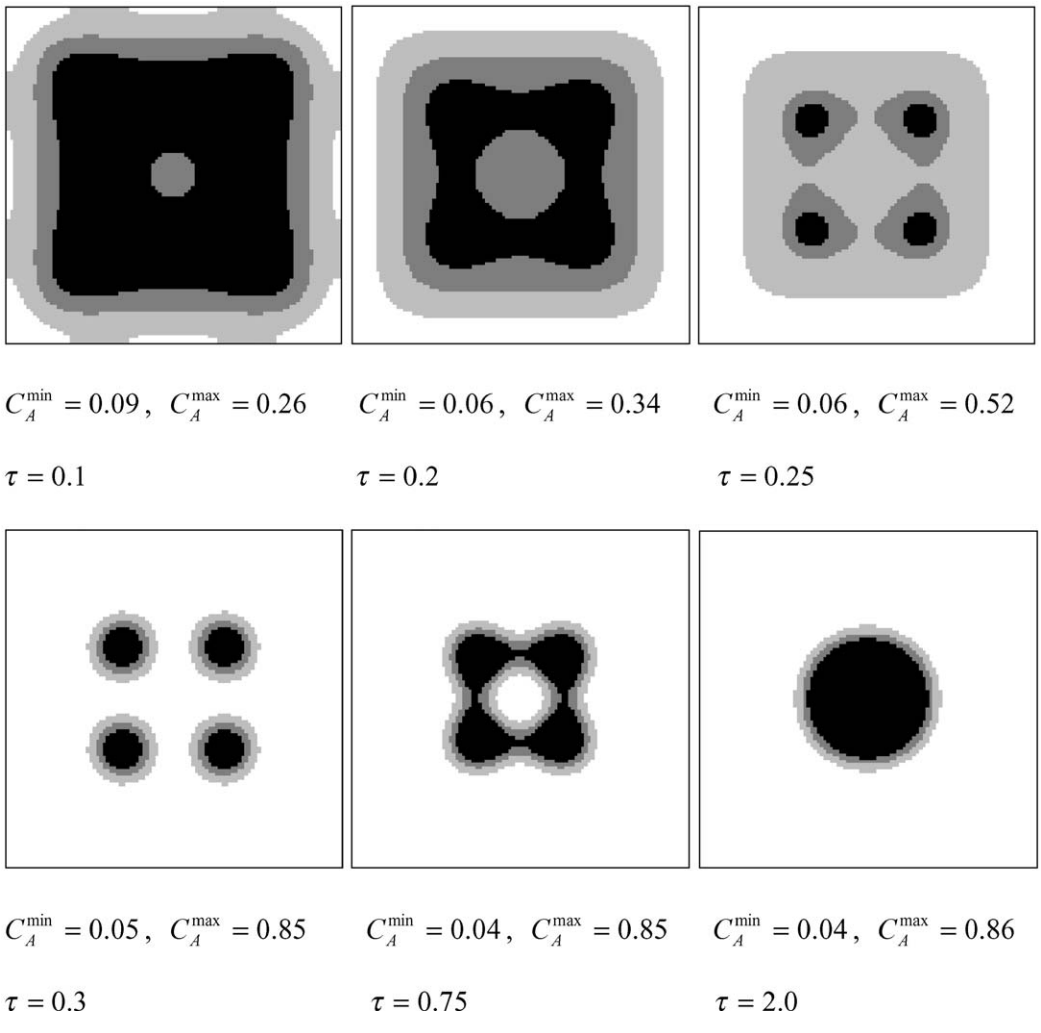

Figure 3 Decomposition kinetics of supersaturated solution under homogeneous perturbation on the boundary of a square region at $C_{A0} = 0.2$, $\Psi = 5.0$, $L = 40R_{\text{int}}$, $\xi = 4R_{\text{int}}$, $C_{A\beta}^{\text{eqv}} = 0.14$, $C_{A\beta}^{\text{spin}} = 0.28$, $q_0' = 1$, $\tau_0 = 0.1$.

than the critical value L_c, the decomposition completes by formation of wetting (B) component segregations on the GB. However, if $L < L_c$, the situation differs drastically (Fig. 3); instability of solid solution develops in the central part of grain. The reason for this phenomenon has a geometrical nature and is related with compositional changes in bulk due to segregations for small grain size. Due to the GB segregations the concentration of A component in central part of grain attains a value exceeding the thermodynamic stability threshold (Fig. 1, region 3). (In Fig. 3 the symbols a, b, c, d, e, f correspond to different times $\tau = 0.1, 0.2$ and so on respectively.) Decomposition usually begins with the formation of nuclei of a new phase (Fig. 3c) which move slowly to the centre and join together at long exposure times (Fig. 3d–f). Merging of the precipitates occurs according to "bridge mechanism" mentioned in [8].

The described above picture takes place when perturbation in chemical potential on GB appear instantaneously at the initial time. If the GB forms gradually (for example, by increase of disorientation due to accumulation of the lattice dislocation during plastic deformation) the redistribution of components will follow the variation in chemical potential. In this case for description of decomposition kinetics we introduced a temporary dependence of chemical potential on GB assuming that $q = q(1 - \exp[-\tau/\tau_0])$. At $\tau_0 = 1$ (slow variation of chemical potential with compare to characteristic diffusion time L^2/ω) decomposition develops more uniformly and segregation in the grain centre occurs without an intermediate stage of nuclei formation.

In the case when alloy composition corresponds to region 4, the precipitates of a segregating component have thermodynamic stimulus to grow so that GB serves as a preferred site of heterogeneous nucleation of a new phase (Fig. 4). At the same time in the inner part of grain solid solution remains stable at any values of L.

3.3. Size effect in alloy decomposition

As mentioned above, in region 2 the kinetics of decomposition depends on grain size L if concentration of A component is less than 0.5 and $L < L_c$. This type of the finite size effect turns out to be possible even alloy parameters are located higher than a solubility limit (region 1). The evolution of the distribution A component in latter case is shown in Fig. 5. The size of a new phase precipitate in the grain is determined by a fraction of segregating component as distinct from the size effect for region 2 where magnitude of segregations depends mostly on the degree of initial supersaturation of the solid solution.

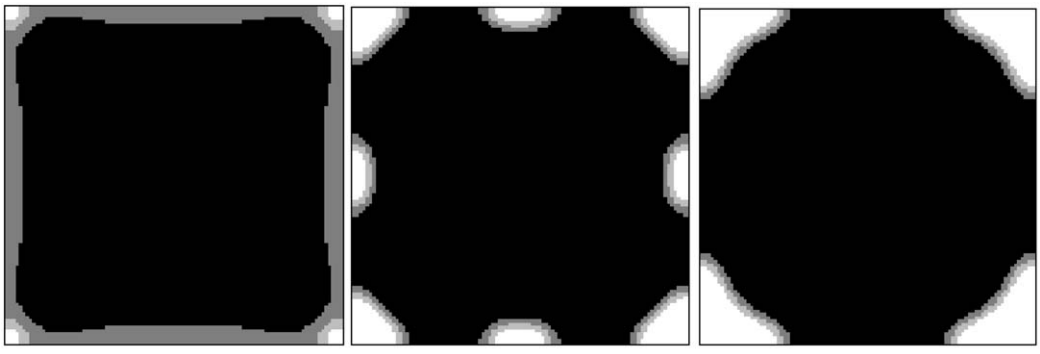

Figure 4 Decomposition kinetics of supersaturated solid solution under homogeneous perturbation on the boundary of a square region at $C_{A0} = 0.8$, $\Psi = 5.0$, $L = 40R_{int}$, $\xi = 4R_{int}$, $C_{A\beta}^{eqv} = 0.14$, $C_{A\beta}^{spin} = 0.28$, $q_0' = 1$, $\tau_0 = 0.1$.

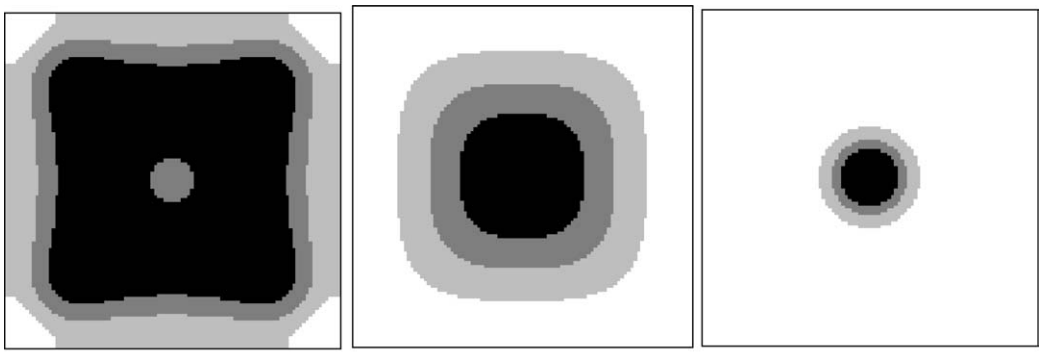

Figure 5 Decomposition kinetics of thermodynamically stable solid solution at homogeneous perturbation of chemical potential on boundary of a square region at $C_{A0} = 0.1$, $\Psi = 5.0$, $L = 30R_{int}$, $\xi = 4R_{int}$, $C_{A\beta}^{eqv} = 0.14$, $C_{A\beta}^{spin} = 0.28$, $q_0' = 3$, $\tau_0 = 0.1$.

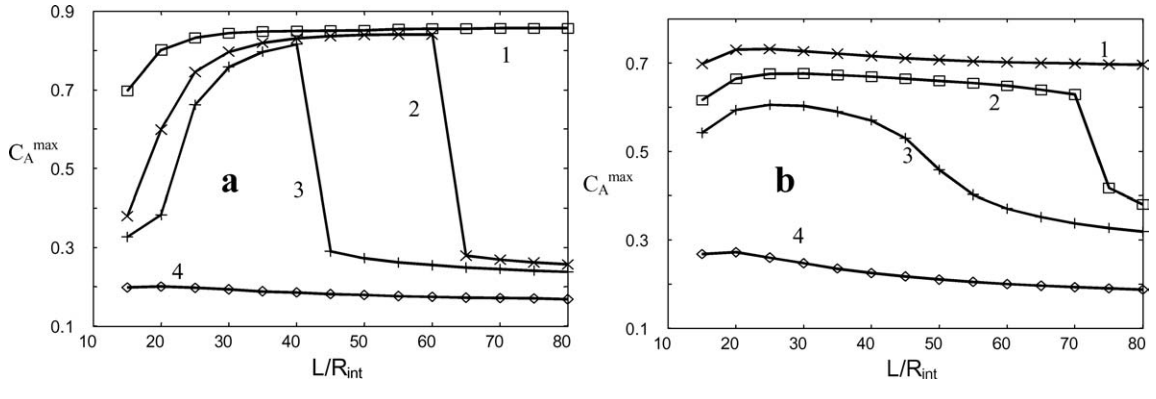

Figure 6 Dependence (in a stationary state) of maximum concentration of A component as a function of grain size at (a) $\Psi = 5.0$, $q_0 = 1$, $\xi = 4R_{int}$, $C_{A\beta}^{eqv} = 0.14$, $C_{A\beta}^{spin} = 0.28$ and $C_{A0} = 0.25$ (curve 1), 0.21 (2), 0.20 (3), 0.15 (4); (b) $\Psi = 4.24$, $q_0 = 3$, $\xi = 4R_{int}$, $C_{A\beta}^{eqv} = 0.30$, $C_{A\beta}^{spin} = 0.38$ and $C_{A0} = 0.28$ (curve 1), 0.25 (2), 0.23 (3), 0.15 (4).

For detailed analysis of the dependence of alloy stability on grain size we restricted ourselves to consideration of a simplest one-dimensional system. In Fig. 6a a dependence of the maximal value of the concentration C_A^{max}, which is attained inside the grain at $\tau \to \infty$ for the alloy with a homogeneous initial state and parameters from region 2 of a phase diagram are given. Near the subcritical region decomposition develops independently on grain size and $C_A^{max} \approx const$ (curve 1). Curves 2, 3 show size effect in alloy decomposition; when concentration C_{A0} decreases the solid solution becomes unstable for fairly small grains. Curve 4 corresponds to the situation when C_{A0} value is so small that an available GB segregation is not sufficient for

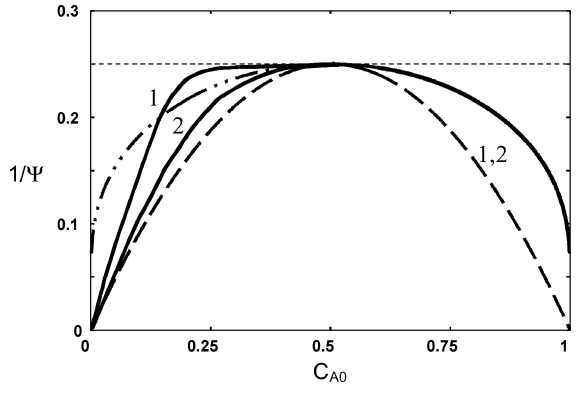

Figure 7 Diagrams of "conditional" spinodal at different grain sizes. Classical spinodal is shown by a dashed line, solubility curve-by a dash-dot line. $q_0 = 3$, $\xi = 4R_{\text{int}}$; $L = 40R_{\text{int}}$ (curve 1), $L = 250R_{\text{int}}$ (curve 2).

initiation of alloy decomposition. Curves 2, 3 have two typical features: a sharp jump at a certain size corresponding to precipitation of new phase and a smooth decrease of the maximum concentration value in the region of small sizes. The latter features in $C_{\text{A}}^{\max}(l)$ dependence related with attaining of the size segregations comparable with the critical nucleus of a new phase. In Fig. 6b analogous curves for the case of choice of the alloy parameters in region 1 of a phase diagram and $\Psi > 4$ are presented. In this case size effect is not so pronounced because of thermodynamically stable state of an alloy.

Our analysis shows that region of the alloy instability remarkably extends with the reduction of grain size. It enable us to speak about some kind of displacement of a spinodal curve. This displacement occurs asymmetrically affecting only that part of a phase diagram where alloy is enriched with a component disposed to formation of segregations on GB. In Fig. 7 classical spinodal is indicated by a dashed line, solubility curve- by a dash-dot line, "conditional" spinodals of two different grain sizes—by solid lines. As seen from Fig. 6, instability region of the finite size sample greatly expands compared with the infinite medium. In region $C_{\text{A0}} < 0.5$ instability degree of an alloy strongly depends on size, so that at small grain size alloy loses its stability even when the chosen initial parameters are located higher than the solubility curve ("conditional" spinodal goes higher than the solubility curve, respectively). When grain size is large, the "conditional" spinodal approaches the classical spinodal. In region $C_{\text{A0}} > 0.5$ GB segregations stimulate decomposition of metastable alloys by the conventional mechanism of the heterogeneous nucleation. (At the concentration above 0.5 (see Fig. 7) the curves 1 and 2 should be coincided to each other (solid line).) In this case overcooling into subcritical region do not lead to instability of solid solution (i.e. appearance of the GB segregations prevent spinodal decomposition).

4. Discussion

The additional term in chemical potential introduced by us in the GB region can be considered in fact, as an extra thermodynamic factor give rising to alloy decomposition. The results [11] of the experimental investigation of the decomposition under mechanical alloying of Ni-Pd—system with well-miscible components indicate the importance of such factor. As shown in Ref. [11], the decomposition near the room milling temperature is maximal and disappears at low and elevated temperatures. Moreover, the annealing at the medium temperatures of the preliminary milled sample leads to the further development of the decomposition. Due to the fact that kinetic factors (such as non-equilibrium vacancy fluxes) are not involved in the latter case, the process of transformation should be driven by the segregation formation. Decomposition at low temperatures is not realized, probably, due to retardation of diffusion processes. On the other side, the role of GB segregations at elevated temperatures appears to be small due to entropy factor. The significant magnitude of heterogeneities observable at intermediate temperatures indicate on important role of the GB segregations in alloy decomposition.

From the experimental investigations [12, 13] of influence of intensive plastic deformation on a magnetic state in Ni-Cu (alloy with low-temperature spinodal) it follows, that the plastic deformation of an alloy with initial parameters under spinodal curve results in the formation of concentration heterogeneities, namely, clusterization of Ni and Cu atoms. The clearest effects of clusterization or decomposition of alloy are observed at the grain sizes less than 10 nm. In this case, for deformed alloy (a degree of deformation $e \sim 95\%$) of initially uniform $Ni_{0.668}Cu_{0.332}$ the concentration heterogeneity can reach about 10% of Cu. These results are in accordance with the developed approaches, and also demonstrate the enhancement of thermodynamical stimulus of decomposition due to reduction of the grain size.

In summary, the analysis carried out in the framework of generalized Cahn-Hilliard model for finite size systems a considerable role of segregations on grain boundaries in the general picture of alloy decomposition induced by intensive plastic deformation was revealed. The existence of such segregations and their important role for decomposition was proved by the experiments in Ni-Pd and Ni-Cu systems [11–13] at transition to nanoscaled state.

The analysis of the surface directed spinodal decomposition with GB segregations displayed the two types of SDSD—"drop-wise" and "stripe-wise". From results of calculations one can conclude that there exists a certain critical concentration $C_{\text{A0}}^{\text{crit}}$ dividing regions of "stripe-" and "drop-wise" SDSD.

It was shown that thermodynamically unstable region for an alloy having finite size of grains greatly expands compared to an infinite medium. In case of $C_{\text{A0}} < 0.5$ the instability degree of alloy essentially depends on grain size including cases of decomposition of alloys with initial parameters lying in the solubility region of the phase diagram.

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