KINETICS OF PHASE TRANSFORMATIONS IN THE ORDERED NANOGRAINED ALLOYS

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Abstract. The effect of grain boundaries (GB) on phase stability and transformation kinetics has been investigated in framework of simple model which takes into account a competition between ordering and chemical decomposition processes. It was shown that a deviation of alloy parameters near GB from bulk values can essentially change the equilibrium of an alloy and precipitation kinetic. In particular, GB segregation can stimulate the surface directed decomposition of the ordered phase; the decrease of the ordering energy near GB results in formation of the concentration inhomogeneity which coexists together with ordering in the bulk. The effect of GB appears significant for small grain size, when the GB segregation is able to change the alloy composition inside the grains. These results allow understanding the mechanism of the phase instability of alloys subjected to severe plastic deformation.

1. INTRODUCTION

The phenomenon of the phase instability which is observed in nanograined mechanically driven alloys is attracting a considerable attention because of fundamental interest and possible technological applications [1,2]. Two possible mechanisms of this phenomenon are under discussion: (i) kinetic, related with moving of the system faraway from equilibrium during severe deformation [1] and (ii) thermodynamic, connected with changes in equilibrium conditions of the alloy due to a stored energy and structure evolution [2]. There are few doubts that changes in thermodynamic conditions under severe exertion play important role in the development of the phase instability, however a mechanism of this phenomena is still unclear and debatable [3,4].

The severe deformation results in fragmentation of the alloy and produce number of the non-equilibrium grain boundaries (GB) [5]. Traditionally GB's considered as preferable area for the segregation one of the components or promotion of the

heterogeneous new phase nucleation [6]. Recently attention was drawn to another aspect of this problem, i.e. the role of the inner boundaries in transformation kinetics and pattern formation [7-9]. In particular, the interfaces can stimulate the appearance of concentration waves propagating inside a sample (so called surface directed spinodal decomposition phenomena, SDSD [10]). Moreover, as it shown in Refs. [8,9], the non-equilibrium GB can essentially change the phase equilibrium of an alloy if size of grain become smaller a critical value. In this case decomposition can start beyond of the region spinodal instability of the coarse grained alloy when segregated fraction becomes comparable with rest part of alloying elements in grain [8].

The model [8] predict the appearance of the concentration inhomogeneity with special morphology (front of the concentration waves is parallel to GB) due to variation of the chemical potential in virtue of GB. In Ref. [9] the kinetics of the precipitation was considered with taking into account both changes in chemical potential and the diffusion

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mobility of the alloy components near GB. As it was shown, the increase of diffusion mobility results in formation of lamellar structure propagating from GB inside grain and variation in morphology from lamellar to drop-like type structure take place when composition change. These results point out that change in the equilibrium condition nearby GB will provoke of instability in nanograined alloys. However, the chemical decomposition of solid solutions is rather special case of the phase instability under deformation which was realized, for example, in Ni-Cu [11]. More common scenario of the phase instability should be including the formation of new phase particles. At the same time a question about GB effect on the phase formation and interplay between chemical decomposition and new phase formation is still unclear.

In this paper we generalize the model [8,9] to more realistic case of the phase instability in nanograined materials by considering of ordering alloys and taking unto account both the chemical decomposition and the precipitation of ordered phase. We analyze the decomposition in the polycrystalline alloys and show that GB essentially exert on kinetic and morphology of the precipitation. In particular, both chemical decomposition and phase separation can be realized in one sample due to deviation equilibrium condition in GB area from core one.

2. FORMULATION OF MODEL

As in Ref. [8], we use two-component AB lattice gas model to describe of the transformation kinetics of alloy. The energy of alloy in cluster variation approximation [12] can be presented by expansion:

$$E = E_0 + \sum_i V_1^i n_i + \sum_{i \neq j} V_2^{ij} n_i n_j +$$

$$\sum_{i \neq j \neq k} V_3^{ijk} n_i n_j n_k + \dots, \qquad (1)$$

where V_1^i, V_2^{ij}, V_3^{ijk} are so called effective parameters of the cluster interactions, n_i are occupation numbers equal 1 if solute atom (atom type A for certainty) occupy site i and zero in opposite case, E_0 is configuration independent part of energy. In homogeneous case the onsite energy V_1^i is constant which determined by the solution enthalpy for dilute alloy, but in polycrystalline materials where value V_1^i in GB area deviate from bulk one the second term in Eq. (1) is depending on distribution of alloy component.

Here we are interesting in a qualitative features of the transformation kinetics and will neglect three-

fold and higher order of the interactions between solute atoms and employ simple mean field approximation (see [13,14]) which don't take into account correlation effects. Then free energy can be written as

$$F = \sum_i V_1^i c_i + \frac{1}{2} \sum_{i,j} V_2^{ij} c_i c_j +$$

$$kT \sum_i \left(c_i \ln c_i + (1 - c_i) \ln(1 - c_i) \right), \qquad (2)$$

where $c_i = <n_i>$ is local concentration of the component A (brackets mean averaging over canonic ensemble). The parameter of the pair interaction V_2^{ij} is determined as the energy change when two remote atoms A move toward each other to positions separated by vector $r_i - r_j$. Because this procedure include appearance A-A and B-B bonds instead two A-B bonds, the value V_2^{ij} coincide with mixing energy of alloy for corresponding coordination sphere

$$V_2^{ij} = V_{AA}(r_i, r_j) + V_{BB}(r_i, r_j) - 2V_{AB}(\qquad (3)$$

For statistically uniform alloy $V_1(r_i) = const$, $V_2^{ij} = V(r_i - r_j)$ and the depending on distribution of the alloy component part of energy, ΔE, can be presented as expansion over concentration waves [15]

$$\Delta E = \frac{N}{2} V(0) c^2 + \frac{N}{2} \sum_s V(k_s) \eta_s^2, \qquad (4)$$

where N is number of atoms, $V(k_s) = \sum_r V(r) \exp(-i k_s r)$ is Fourier transform of the mixing energy, k_s is wave vector for superstructure s type, η_s is order parameters proportional to the amplitude of concentration wave. However, the method of the concentration waves is not quite appropriate for describing of the heterogeneous alloy. In this case more correct is using a local order parameters that distinguish of the concentrations in the two sublattices. Using the simultaneously evolving sublattices (SES) ansatz [13], we can now define the local average concentration C_i and the local order parameter η_i by

$$C_i = \left(c_i^{(1)} + c_i^{(2)} \right) / 2, \ \eta_i = \left(c_i^{(1)} - c_i^{(2)} \right) \qquad (5)$$

where $c_i^{(n)}$ be the concentration of atoms type A on site i in sublattice n. We will assume for simplicity that alloy contains two equivalent sublattices. In particular, for BCC based alloy it takes place for k_s vector which correspond B2 structure. In this case
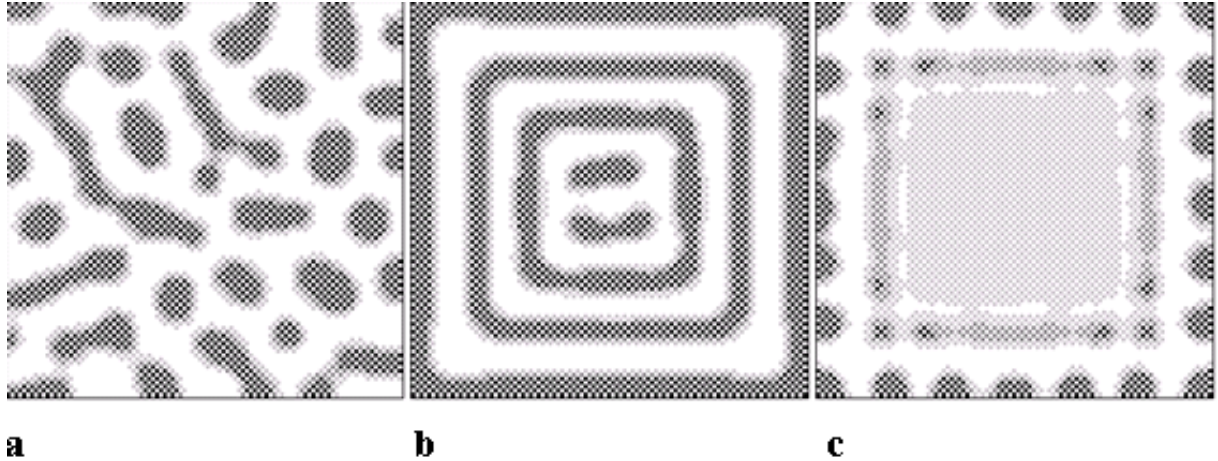
a **b** **c**

Fig. 2. The typical patterns of wave stage decomposition in alloy starting from uniform initial state (a), in appearance of GB that is changing the ordering energy (b) or diffusion mobility of one component (c) at $C_{A0}=0.25$, $\Psi = 4.8$, $\Xi = 6$, $L = 100R$, $\phi = 0$. $\zeta = 5R$, $\delta\Psi = 0.1\Psi_0$ (b), $\zeta = 2R$, the atoms mobility nearby GB in twice bigger of the bulk value (c).

the free energy of alloy (per atom) can be presented as

$$f(\mathbf{r}_i) = V_1^i C_i + \frac{1}{2}\sum_j V_{ij} C_i C_j +$$

$$\frac{1}{2}\sum_j \left(V_{ij}^{(11)} - V_{ij}^{(12)}\right)\eta_i \eta_j +$$

$$kT\sum_{n=1,2}\left(c_i^{(n)}\ln c_i^{(n)} - \left(1 - c_i^{(n)}\right)\ln\left(1 - \quad (6)\right.$$

where $V_{ij}^{(11)}$, $V_{ij}^{(12)}$ are mixing energies inside one and between unlike sublattices, determined by Eq. (3) when atoms belong the same or different sublattices, correspondingly. In continual limit, assuming that concentrations $C(\mathbf{r})$ and order parameter η_r change slowly, *i.e.* $C(\mathbf{r+a}) \approx C(\mathbf{r})+\mathbf{a}\nabla C(\mathbf{r})$, $\eta(\mathbf{r+a}) \approx C(\mathbf{r})+\mathbf{a}\nabla\eta(\mathbf{r})$ (it is correct, in particular, for

a long-range interatomic interaction), the density of free energy (6) can be presented as

$$f = f_{loc}(\mathbf{r}) + f_{nloc}(\nabla C, \nabla\eta),$$

where f_{nloc} is non-local contribution which describe the interphase boundaries energy and depend on the gradient of order parameters,

$$f_{loc} = kT\left(\phi C + \Psi C(1 - C) - \Xi\eta^2\right) +$$

$$kT\sum_{n=1,2}\left(c^{(n)}\ln c^{(n)} + \left(1 - c^{(n)}\right)\ln\left(1 - \quad (7)\right.$$

is local part of free energy, $\Psi(\mathbf{r}_i) = -1/2kT\sum_j V_{ij}$, $\Xi(\mathbf{r}_i) = -1/2kT\sum_j \left(V_{ij}^{(11)} - V_{ij}^{(12)}\right)$, $\phi = V_1/kT - \Psi$ is the so-called dimensionless asymmetric potential [14] which can be written also as $\sum (V_{AA}(\mathbf{r}_j) - V_{BB}(\mathbf{r}_j))/kT$.
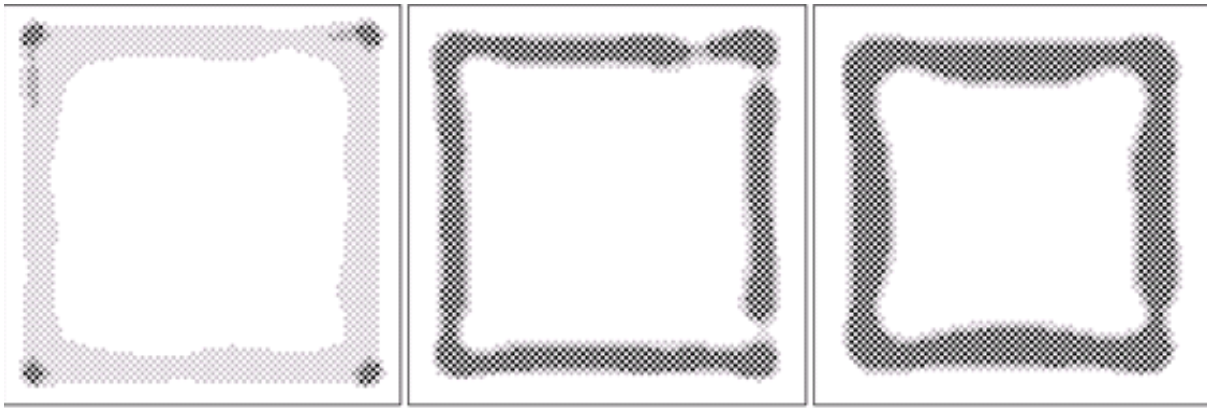
$$\tau = 0.25 \qquad\qquad \tau = 0.50 \qquad\qquad \tau = 2.0$$

Fig. 3. The typical patterns of wave stage decomposition in alloy starting from uniform initial state (a), in appearance of GB that is changing the ordering energy (b) or diffusion mobility of one component (c) at $C_{A0}=0.20$, $\Psi = 4.8$, $\Xi = 6$, $L = 100R$, $\phi = 0$. $\zeta = 5R$, $\delta\Psi = -0.5\Psi_0$. The dimensionless time τ is $t\left(\omega_A^{(0)} + \omega_B^{(0)}\right)C^V / 2L^2$.

In general, the function $f_{loc}(C,h)$ has few minima correspond the different possible states (stable or metastable) of system. Because the ordering is control by short range diffusion and develop for shorter time in comparison with redistribution of alloy components, we use the locally equilibrium ordering approximation, when ordering parameter $\eta(\boldsymbol{r})$ is fully determined by value of concentration $C(\boldsymbol{r})$ through Bragg-Williams equation [15]

$$\frac{(C-\eta)(1-C-\eta)}{(C+\eta)(1-C+\eta)} = \exp\left[-2\Xi\eta\right]. \qquad (8)$$

In this case, the dependence $f(C)$ has three minima; one of them at $C = 0.5$ corresponds to stoichiometric ordered state and two other minimums at values C nearby to 0 and 1. A scenario of phase transformation depend on relation between Ψ and Ξ. When $\Xi < 0$ and $\Psi > 0$ the central minimum on $f(C)$ is absent; and only spinodal decomposition on disordered phases is possible. If $\Psi > \Xi > 4$ then central minimum on $f(C)$ is local and ordered state becomes metastable; in this case decomposition on disordered phases take place but through a transient ordered stage [16,17].

Here we focus on the case $\Xi > \Psi > 0$ when the decomposition with formation of the equilibrium ordered phase is possible. The corresponding mean-field phase diagram (Fig. 1) contains the solid solution (α, β), ordered alloy (γ) and two phase ($\alpha + \gamma$,

$\beta + \gamma$) regions; the spinodal lines shown by the dashed curves. The decomposition kinetics depends on position of the parameters of an alloy on the phase diagram and its deviation near GB from bulk values.

To describe the evolution of the average concentration distribution $C(\boldsymbol{r},t)$ we use a master equation in mean field approximation [13,14] for alloy that equilibrium properties are defined by free energy (7) and phase diagram in Fig. 1. In continuum limit which is valid for sufficiently slow change of concentrations $C(\boldsymbol{r})$ the mean field kinetic equation (MFKE) can be written in a form (for details of derivation MFKE for alloy without ordering see [9])

$$\frac{\partial C}{\partial t} = -\nabla \boldsymbol{J}, \ \boldsymbol{J} = M\left[-\frac{(1-\Psi Q(C,\mathrm{r})}{Q(C,\eta)}\right.$$
$$\frac{(1-\Xi Q(C,\eta))}{Q(C,\eta)}\nabla\eta + \frac{R^2}{2}\nabla(\Xi\Delta\eta + \mathrm{'}$$
$$\left.\frac{\nabla\phi}{2} + \left(C+\frac{1}{2}\right)\nabla\Psi + \eta\nabla\Xi\right], \qquad (9)$$

where $Q = (C + \eta)(1 - C - \eta)$, parameter R is characterize the width of interface boundary which we assume, for simplicity, the same for precipitation of ordered phase and chemical decomposition; the generalized mobility M is determined by
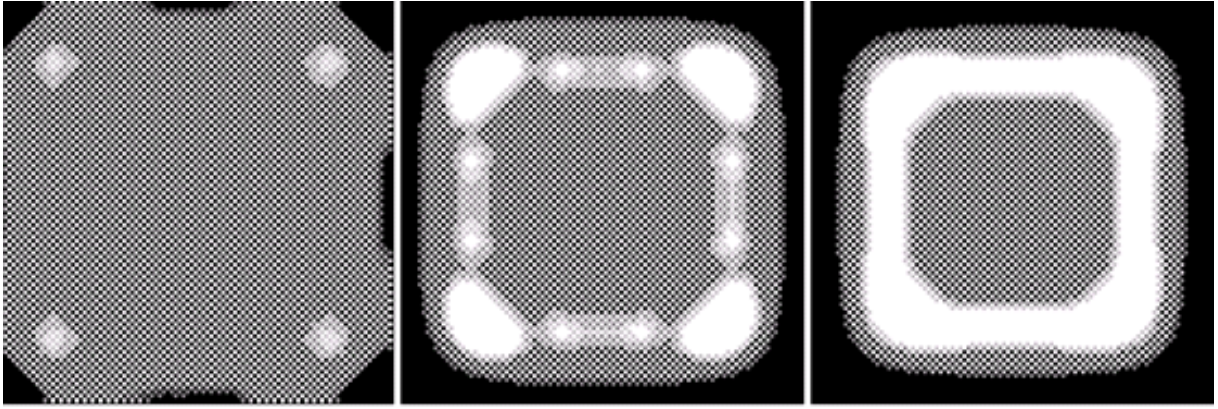
$\tau = 1.5$ $\qquad\qquad\qquad\qquad$ $\tau = 6.8$ $\qquad\qquad\qquad\qquad$ $\tau = 12$

Fig. 4. The typical patterns of wave stage decomposition in alloy starting from uniform initial state (a), in appearance of GB that is changing the ordering energy (b) or diffusion mobility of one component (c) at C_{A0}=0.50, Ψ = 4.8, Ξ = 6, L = 100R, ϕ_0 = 10, Φ_{AB} = -1. ζ = 7R, $\delta\phi$ = 0.5ϕ_0.

$$M = \frac{\omega_A^{(2)}\omega_B^{(2)}(C - \eta)(1 - C - \eta)C^v}{\omega_A^{(2)}(C - \eta) + \omega_B^{(2)}(1 - C - \eta)}$$

C^v is vacancy concentration which accepted independent of coordinate and equal an equilibrium value. The partial diffusion mobility $\omega_\alpha^{(n)}(\boldsymbol{r}) = \omega_\alpha^{(0)} \cdot \exp\left[E_\alpha^{(n)}(\boldsymbol{r}) / kT\right]$ is determined by the jump rate of atom α from site $\boldsymbol{r}$ of sublattice n to neighboring vacant site; where $E_\alpha^{(n)}$ is the energy of atom α in site $\boldsymbol{r}$ in initial position. Note, that value of barrier for atomic jump accepted invariable, as usually [13,14], and included in $\omega_\alpha^{(0)}$.

Eq. (9) generalize Cahn-Hilliard model taking into account ordering in heterogeneous systems contained GB. Two first terms leads to decomposition when the alloy parameters crossing the disordered or ordered spinodal lines.

3. RESULTS OF CALCULATIONS

The decomposition kinetics in the presence of GB was studied by numerical solution of Eq's (9) and (8) for crystal contained the square *LxL* grains. For simplicity we consider a crystal with symmetric GB when distribution of concentrations $C(\boldsymbol{r})$ and order parameter $\eta(\boldsymbol{r})$ have mirror symmetry with respect to boundaries; it allows restricting oneself by calculations for one grain with appropriate boundary conditions. A homogeneous distribution of alloy components with small random fluctuations was

taken as an initial state for simulations. As early in Ref's [8,9], we assumed that disturbance of the thermodynamic parameters of alloy by GB has a long-range character with a typical length scale ξ:

$$\Psi = \Psi_0 - \delta_\Psi / \left(1 + x^2 / \xi^2\right),$$

$$\Xi = \Xi_0 - \delta_\Xi / \left(1 + x^2 / \xi^2\right),$$

$$\phi = \phi_0 - \delta_\phi / \left(1 + x^2 / \xi^2\right),$$

(10)

where $\delta\Psi$, $\delta\Xi$, $\delta\phi$ are parameters specifying the maximum disturbance amplitude, x is a distance from GB.

The kinetics of phase separation is depended on position of the parameters of alloys on the phase diagram and on relation between Ψ and Ξ. When $\Psi > 4 > \Xi$ the decomposition of disordered alloy take place; the role of GB in this case was studied previously in Ref's [8,9]. Here we consider the case $\Xi > \Psi > 0$ when the decomposition with formation of the ordered phase is possible. The results of calculations presented in Figs. 2-5, where the checkered pattern used to display ordered regions with dark and bright spots corresponding different sublattices and concentration of A component in each sublattice indicated by the gray scale. This way gives a vivid presentation of ordering and chemical decomposition simultaneously.
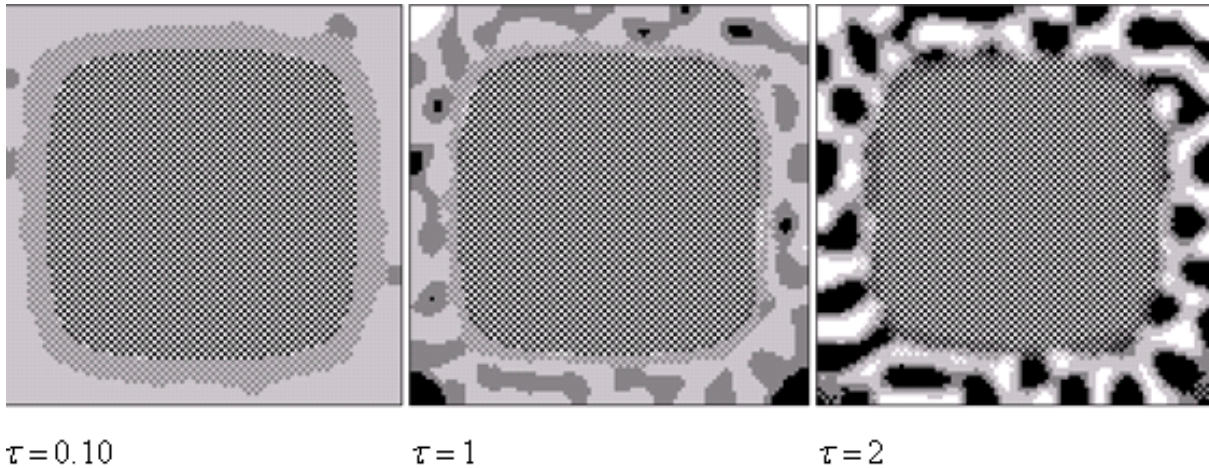
$\tau = 0.10$ $\tau = 1$ $\tau = 2$

Fig. 4. The typical patterns of wave stage decomposition in alloy starting from uniform initial state (a), in appearance of GB that is changing the ordering energy (b) or diffusion mobility of one component (c) at C_{A0}=0.50, $\Psi_0 = 4.8$, $\Xi_0 = 6$, $L = 100R$, $\phi_0 = 10$, $\Phi_{AB} = -1$. $\zeta = 7R$, $\delta\Xi = 0.5\Xi_0$.

In Fig 2 shown the wave stage of decomposition in the ordering alloy when the parameters are belonging to the field 3 in phase diagram (Fig. 1) as in absence of GB (a) as well in nanograined material (b,c). A local change of the asymmetric potential ϕ or mixing energy near GB leads to the segregation one of species at the boundary with further development of the SDSD. However, in contrast with chemical decomposition [10], we observed in this case the alternation of the order and disorder domains with repeated the shape of grain morphology (Fig. 2b). The increase of atoms mobility leads to local acceleration of transformations. The structure formed in the given case seems additionally modulated along GB. The further exposure will give rise to the growth of precipitates in perpendicular to GB direction. The similar result earlier was found in Ref. [18].

The formation of the GB segregations will change the composition in the core of grain and can give raise the finite size effects [8], if GB fraction is big enough. If the alloy parameters are belonging to the field 1 of phase diagram (Fig. 1), the precipitation of ordered phase in the bulk is possible only when the grain size is smaller than a critical value. If the alloy parameters are in field 2 of phase diagram and GB's are preferable for segregations of main component, the "two-layered" structure is realized nearby GB (Fig. 3) where chemical inhomogeneity regions alternate with the layers of ordered phase. If the initial state is located in the field 5, then the segregations at GB will force out the second component in the core of grain. Therefore, nearby GB the three-layered structure is formed (Fig. 4) included (i) segregations of A component, (ii) the layer of ordered phase and (iii) precipitates of B component migrating in bulk when time increase.

The decreasing of ordering energy Ξ nearby GB will lead locally to broadening of the disordered region 2 on phase diagram and makes preferable the decomposition into A+B (Fig. 5). When $\Psi > 4$ the decomposition will develop by conventional spinodal mechanism starting in adjacent to GB's areas and the fine structure of the alternated precipitates of α- and β-phase are forming. This finding shed a light on problem of the competition between chemical decomposition and ordering processes and shows that presence of GB in nanograin materials may evoke the decomposition of alloy which do not realize in infinite media due to preference of ordering.

4. SUMMARY

The model of spinodal decomposition in nanograined materials taking into account the variation of chemical potential and diffusion mobility of alloy components nearby GB's has been proposed in Ref's [8,9]. This model predicts the appearance of concentration waves propagating from boundaries inside of grains (chemical decomposition).

Here we are developing this approach and consider an effect of GB's on the kinetic of transformation in ordered alloys by using of the generalized lattice gas model with taking into account both chemical decomposition and new phase formation.

It was shown that in alloys subjected by intensive plastic deformation the non-equilibrium grain boundaries which cause lattice distortions in the adjacent regions can have significant influence on phase stability. The kinetic decomposition depends on deviation of the equilibrium conditions near grain boundary from bulk values. In particular, the segregation one of alloy component will shift locally the concentration in subcritical region of the phase diagram and stimulate of the phase separation in alloy which is stable in coarse grained material. Even if segregation is neglected (i.e. the deviation of the average composition nearby GB from bulk is small), the increase of the mixing energy in grain boundary area will change character of the transformation from ordering to the spinodal decomposition and give raise the appearance of the concentration oscillations along grain boundary with conservation of the atomic order inside grain. Thus, a competition between decomposition and ordering processes can result in unusual transformation behavior in nanograined materials which impossible to observe in coarse grain alloys.

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