

INFLUENCE OF LATTICE RELAXATION ON THE KINETICS OF SPINODAL DECOMPOSITION OF SOLID SOLUTIONS

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UDC 669.112:544.015.4

Within the framework of the medium-field approximation, it has been shown that lattice relaxation can stabilize a solid solution relative to small fluctuations of the composition, causing the kinetics of spinodal decomposition of the alloy to substantially change. The metastable state diagram has been constructed and the kinetics of transformations with allowance for the lattice relaxation has been investigated. It has been found that the decomposition develops by the mechanism of growth of eutectoid-type colonies or twin lamellas from the region with a disturbed homogeneity.

Keywords: diffusion, spinodal decomposition, metastable phases, eutectoid colonies.

Introduction. The structural properties of steels and alloys are dependent on their structural-phase composition, e.g., Guinier–Preston lamellar zones in Al–Cu alloys determine the strength of duralumins used in the aircraft industry [1]. Pearlite colonies appearing in decomposition of metastable austenite are the basic structural components of annealed steels used for manufacture of rails and reinforcement [2]. Copper precipitates of the interfacial composition in the α -Fe matrix ensure the high plasticity and fracture toughness of steel products [3].

Equilibrium thermodynamics [4] is limited in its capabilities because it predicts volume fractions of precipitates on long standing, whereas an analysis of the precipitation morphology requires approaches making it possible to study the kinetics of transformations. The simplest diffusion equations describing the stability loss by a solid solution at lower-than-average temperatures (spinodal decomposition (SD)) have been proposed by Cahn and Hillard [5]. These equations make it possible to consider the SD kinetics, which includes a few stages: wave instability, coalescence of concentration waves, and evaporation of droplets [6]. However, the SD kinetics in complex interactions (effects of long-range interaction, ordering, unmatching, etc.) calls for further study. In particular, the mechanisms of autocatalysis of lamellas in eutectoid decomposition of alloys, the features of formation of Guinier–Preston zones, and role of lattice deformations in the formation of regular microstructures are not quite clear.

Alloys with a tendency toward ordering, in which decomposition from the metastable region of the phase diagram developed by the mechanism of growth of eutectoid-type colonies, and metastable precipitates of the interfacial composition were formed in decomposition from the instability region, have been considered in [7]. In the present work, it is shown, within the framework of the medium-field method, that lattice deformations accompanying the formation of concentration inhomogeneities can stabilize a solid solution relative to small fluctuations of the composition. In this case the ideas of decomposition of metastable phases turn out to be applicable to the solid solution. In particular, growth of the colonies and the formation of metastable precipitates of the interfacial composition are possible in decomposition from different regions of the phase diagram.

1. Formulation of the Model. In the medium-field approximation, the density of the free energy of mixing of an alloy is determined by the formula

$$f(C_A) = \sum_{\sigma=A,B} (\Phi_{\sigma\sigma} - \Phi_{\sigma\sigma}^0) C_{\sigma} + (\Phi_{AB} - \Phi_{\sigma\sigma}) C_A C_B + kT (C_{\sigma} \ln C_{\sigma}), \quad (1)$$

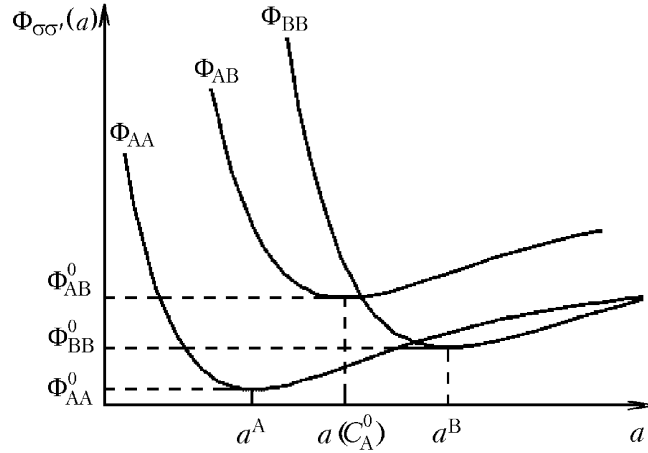


Fig. 1. Energies $\Phi_{\sigma\sigma'}$ vs. lattice parameters; Φ_{AA} and Φ_{BB} are minimized in pure substances, Φ_{AB} has its minimum at $a = a(C_A^0)$.

where $\Phi_{\sigma\sigma'} = \sum_i \varphi_{\sigma\sigma'}(\mathbf{r} - \mathbf{q}_i)$ are the energies of interaction of the atom of the $\sigma = A, B$ sort at the node \mathbf{r} with the lattice filled with atoms of the σ' sort, which are computed by summation of the values of the pair potentials $\varphi_{\sigma\sigma'}$ with the atoms at a distance \mathbf{q}_i (i are the lattice nodes), $\Phi_{\sigma\sigma'}^0$ are the values of these energies in pure substances, and C_σ is the local concentration of atoms of the σ sort; $C_A + C_B = 1$.

Lattice deformations involve the change in the interatomic distances q_i and hence in the energies $\Phi_{\sigma\sigma'}$. Therefore, in the case of inhomogeneous deformations the energies $\Phi_{\sigma\sigma'}$ are dependent on coordinates: $\Phi_{\sigma\sigma'} = \Phi_{\sigma\sigma'}(\mathbf{r})$. If deformations are due to the local change in the chemical composition, these energies turn out to be dependent on concentrations: $\Phi_{\sigma\sigma'} = \Phi_{\sigma\sigma'}(C_\sigma(\mathbf{r}))$, although interatomic interactions are described, as previously, by the pair potentials $\varphi_{\sigma\sigma'}$. In the general case the dependences $\Phi_{\sigma\sigma'}(C_\sigma)$ are nonmonotonic.

Let us restrict our consideration to the simplest situation where the lattice deformations accompanying the decomposition of the alloy are caused by the difference in the atomic radii of components A and B, and the long-range elastic concentration stresses are disregarded. The dependence of the lattice parameter on the concentration of the component may be thought of as being linear: $a(C_A) = a^A C_A + a^B C_B$, which is known as the Vegard law [4]. In the process of decomposition of the alloy, the energies Φ_{AA} and Φ_{BB} approach their minima Φ_{AA}^0 and Φ_{BB}^0 attained in decomposition into pure elements (Fig. 1). Conversely, the minimum of $\Phi_{AB}(C_A)$ can be realized in the region of interfacial concentrations for a certain $C_A = C_A^0$, $0 < C_A^0 < 1$. From what has been said above, we approximate $\Phi_{\sigma\sigma'}$ as follows:

$$\Phi_{\sigma\sigma} = \Phi_{\sigma\sigma}^0 + \zeta(1 - C_\sigma), \quad \Phi_{AB} = \Phi_{AB}^0 + \varepsilon(C_A - C_A^0)^2, \quad \zeta > 0, \quad \varepsilon > 0. \quad (2)$$

In this case $f(C_A)$ has a nearly classical form [4]; however, the dimensionless energy of mixing is dependent on the concentration $\tilde{\Psi} = \tilde{\Psi}(C_A)$:

$$\frac{f(C_A)}{kT} = \tilde{\Psi}(C_A) C_A C_B + \sum_{\sigma=A,B} C_\sigma \ln C_\sigma, \quad (3)$$

$$\tilde{\Psi}(C_A) = \Psi + 2Y(C_A - C_A^0)^2, \quad \Psi = \frac{2\Phi_{AB}^0 - \Phi_{AA}^0 - \Phi_{BB}^0 - \zeta}{kT}, \quad Y = \frac{\varepsilon}{kT}.$$

The values of Ψ and Y are comparable, since the pair-interaction energies can substantially change for lattice deformations of 3–5% [8]. We note that the specific form of approximation (2) has no effect on the qualitative regularities of the decomposition, which are discussed below and are related to the nonmonotonic dependence $\tilde{\Psi}(C_A)$.

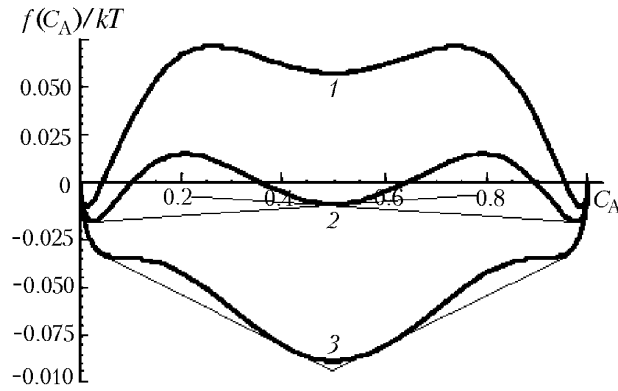


Fig. 2. Free energy of mixing vs. concentration of the component: 1) $\Psi = 3$, 2) 2.7, and 3) 2.4. $Y/\Psi = 1$; $C_A^0 = 0.5$.

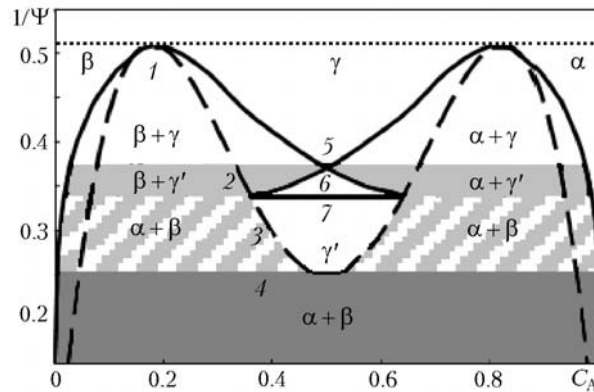


Fig. 3. State diagram of the alloy with a relaxing lattice ($C_A^0 = 0.5$): 1 and 2) regions of decomposition with precipitation of the $\alpha(\beta)$ phase and a stable γ or metastable solid solution γ' ; 3 and 4) regions of decomposition into α and β phases enriched with components A and B respectively; 5, 6, and 7) stable, metastable, and autocatalytically decomposing solid solution.

The transformation pattern is the most general for $Y/\Psi \approx 1$; then depending on temperature the plot of the function $f(C_A)$ has one to three minima: at low T , just the side minima are present on the plot; therefore, the traditional scenario of SD into equilibrium α and β phases enriched with A and B atoms respectively is realized [4–6]: the contribution of the entropy terms to the free energy (3) grows with T , resulting in the local and then absolute minimum of $f(C_A)$ when $C_A = C_A^0$ (Fig. 2). If the minimum is absolute, the solid solution γ remains stable in the region of interfacial concentrations; the local minimum, conversely, is responsible for the formation of metastable states of the interfacial composition γ' . From Fig. 2, it is clear that metastable states of two types are possible. At lower-than-average T , there is no common tangent to the neighboring concave portions of the $f(C_A)$ curve (Fig. 2, curve 1); therefore, no equilibrium of the metastable state with the α and β phases is reached. As is shown below, the decomposition of such a metastable alloy develops autocatalytically by the mechanism of colony growth from the regions with a disturbed homogeneity. Further increase in T leads to a metastable equilibrium between the $\alpha(\beta)$ phases and the γ phase (Fig. 2, curve 2); in this case the solid solution γ decomposes as a result of the growth of the precipitations of the α and β phases brought to the initial state.

A typical state diagram in this model is of the eutectoid form (Fig. 3). The phase-equilibrium curves shown as solid lines and the spinodals shown dashed have been obtained, according to [4], from the condition of equality of the chemical potentials of the phases and equality of the second derivative of the function $f(C_A)$ to zero respectively:

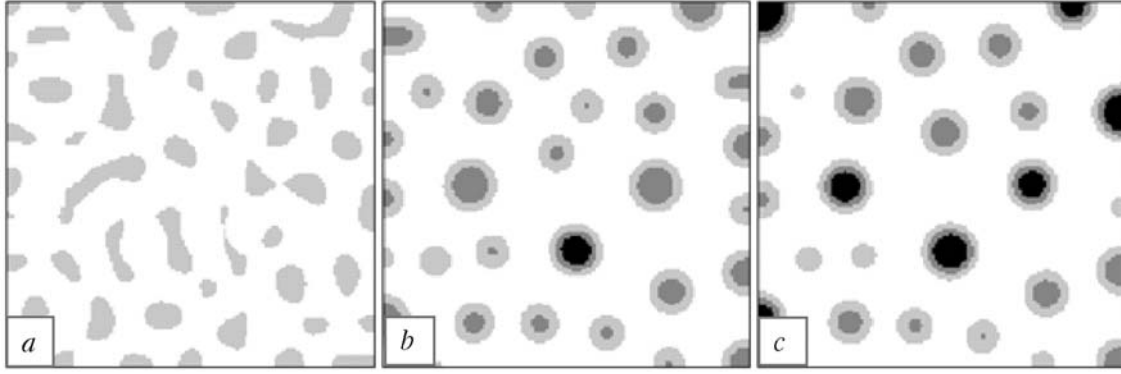


Fig. 4. Kinetics of formation of precipitates of the interfacial composition in decomposition of the alloy from the unstable homogeneous state with small Gaussian fluctuations: 1) $\tau = 10$, b) 80, and c) 160. $\langle C_A \rangle = 0.15$, $Y/\Psi = 1$, $\Psi = 3.4$, and $\Gamma/L = 0.03$.

$$\left. \frac{\partial f}{\partial C_A} \right|_{C_A=C_1} = \left. \frac{\partial f}{\partial C_A} \right|_{C_A=C_2} = \frac{f(C_2) - f(C_1)}{C_2 - C_1}, \quad \frac{\partial^2 f}{\partial C_A^2} = 0. \quad (4)$$

In regions 1 and 2, we have the decomposition with precipitation of the $\alpha(\beta)$ phase enriched with component A(B) and a stable solid solution γ (for region 1) or a metastable γ' phase of the interfacial composition (for region 2). In regions 3 and 4, the alloy decomposes into equilibrium α and β phases, but in region 3, the kinetics of decomposition is complicated by the presence of a spinodal bounding region 7. Regions 5, 6, and 7 correspond to the stable, metastable, and autocatalytically decomposing solid solution. There are critical ε values beginning with which the lower shaded region and then the dashed region of the phase diagram disappear. Conversely, as ε decreases, the lower shaded region expands with contraction of the remaining regions.

The decomposition kinetics is determined by Fick's laws [4]:

$$\frac{\partial C_A}{\partial t} = -\nabla \mathbf{J}_A, \quad \mathbf{J}_A = -M \nabla \mu. \quad (5)$$

To refine mobility we use the Einstein relation: $M = DC_A C_B / (kT)$, where D is the diffusion coefficient. The chemical potential μ is related to the density of the free energy of mixing by the equation [5]

$$\mu = \frac{\partial f}{\partial C_A} - \delta \Gamma^2 \Delta C_A, \quad (6)$$

where Γ is the small parameter having the meaning of the effective radius of interatomic interaction.

2. Simulation Results. Numerical solution of Eqs. (5) and (6) in which the energy $f(C_A)$ has been determined by formula (3) is carried out by the standard Runge–Kutta method in an $L \times L$ square domain. To determine the boundary conditions we assume that the concentration distribution beyond the square are mirror-symmetric relative to its boundaries. In the figures, different levels of concentration of component A (0 to 1) are marked by gray gradations. The time τ is given in dimensionless units D/Γ^2 . The diversity of qualitatively different variants of the diffusion kinetics occurs with variation of the parameters Ψ and Y and the average composition $\langle C_A \rangle$. Let us consider the most interesting cases where the kinetics of transformation is not evident from the state diagram.

In the dashed region (see Fig. 3), the SD of the homogeneous alloy (with small Gaussian fluctuations) experiences the stage of precipitates of the interfacial composition $C_A \sim 0.5$ (Fig. 4), whose further decomposition requires no activation. However these precipitates turn out to be relatively stable at the interfacial stages of transformation. As $\langle C_A \rangle$ approaches the boundary of region 7, precipitates of the interfacial composition become larger and their stability

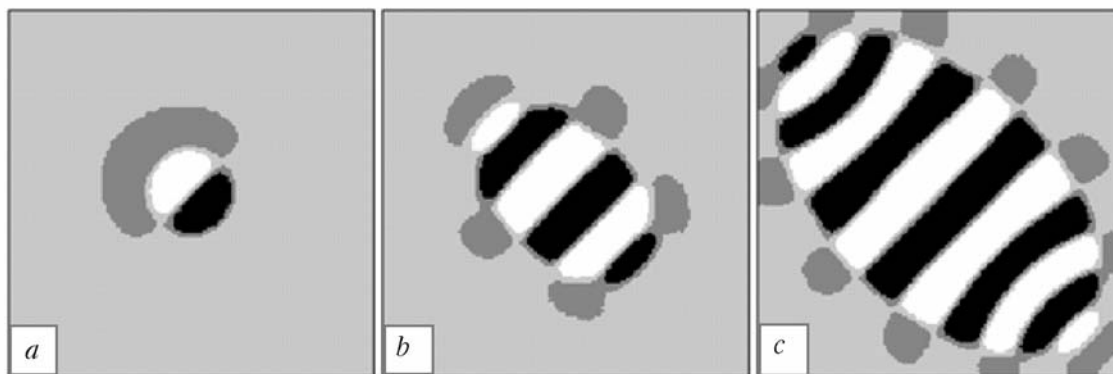


Fig. 5. Kinetics of growth of a colony in decomposition of the metastable solid solution, provoked by a pair of contacting nuclei of equilibrium phases: a) $\tau = 80$, b) 200 and c) 400. $\langle C_A \rangle = 0.50$, $Y/\Psi = 1$, $\Psi = 3.4$, and $\Gamma/L = 0.016$.

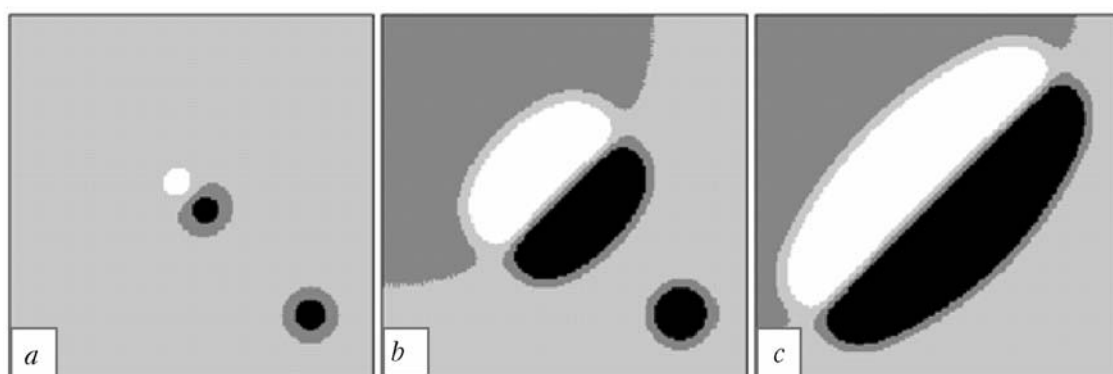


Fig. 6. Kinetics of growth of twin lamellas and evaporation of a single precipitate in the process of decomposition of the metastable phase: a) $\tau = 10^2$, b) $3 \cdot 10^3$, and c) 10^4 . $\langle C_A \rangle = 0.50$, $Y/\Psi = 1$, $\Psi = 2.9$, and $\Gamma/L = 0.016$.

grows, and as the temperature increases and reaches region 2, they become metastable. In continuous diffusion models, the decomposition of metastable precipitates is only possible as a result of their evaporation due to the growth of the nuclei of equilibrium phases brought to the initial state [7]. In the region 7 confined between the spinodals (see Fig. 3), the homogeneous alloy is stable to small fluctuations of the composition but decomposes on bringing the critical nuclei of equilibrium phases to the initial state. In actual systems, such nuclei can appear spontaneously in the case of thermal fluctuations. Figure 5 gives the kinetics of decomposition induced by a pair of contacting nuclei. It can be seen that the decomposition develops autocatalytically: the precipitates of each phase contribute to the genesis of another phase in its vicinity. A colony consisting of parallel lamellas of nearly the same width results. A lengthwise growth of the colony is ensured by the atomic diffusion between neighboring lamellas over its front, whereas a growth in width results from the autocatalytic genesis of new lamellas. The rate of these processes generally differs; therefore, the colony is ellipsoidal in shape. Calculations show that the autocatalysis is enhanced with decrease in T ; therefore, the lamellas become narrower, and the colony is stretched perpendicularly to them.

Above region 7 is the existence domain of the metastable phase of the interfacial composition (see Fig. 3), which is quite narrow in the case $Y/\Psi \approx 1$ but expands with increase in Y/Ψ . In this domain, equilibrium with the solid solution γ is attained for single precipitates of the $\alpha(\beta)$ phases, but the pair of contacting nuclei develops into a double lamella (Fig. 6). The rate of elongation of this lamella is constant, whereas the rate of its broadening decreases with time, since the broadening requires atomic diffusion through the lamella. It is clear from Fig. 6 that a single nucleus of the equilibrium phase, brought to the initial state, is evaporated in the process of growth of the double lamella. Thus, among the possible mechanisms of decomposition of the metastable phase, the mechanism of growth of twin lamellas is preferable.

3. Discussion. It has been shown that allowance for the lattice relaxation leads to a significant change in the SD kinetics compared to the traditional ideas [4, 5]. Thus, precipitates of the interfacial composition can be formed in decomposition from the region of instability of the state diagram, whereas a growth of eutectoid colonies or twin lamellas is observed in decomposition from the metastable regions. The obtained results are true if the energy of mixing has its minimum in the permissible concentration range. Therefore, they are quite universal and can also be referred to the cases where the dependence $\tilde{\Psi}(C_A)$ is determined by other factors.

Nanosize precipitates of the interfacial composition, which are coherent with the matrix and were found initially in natural aging of Al–Ag, Al–Zn, and Al–Cu alloys, have been called Guinier–Preston zones [1]. A. G. Khachaturyan proposed that the ideas of metastable–equilibrium phases be used for their explanation [9]. The kinetics of formation and decomposition of metastable ordered states was considered in [7]. In the present work, it has been shown that with lattice relaxation, metastable states can be formed even in solid solutions. Precipitates of the interfacial composition $C_A \sim 0.5\text{--}0.7$ have recently been found at the initial steps of precipitation in the Fe–Cu alloy [3]. The reasons for the phenomenon remains to be elucidated, since the solubility of copper in the α -Fe matrix is low. Although the ionic radii of Fe and Cu atoms are very close, the assumption of the presence of the local $f(C_A)$ minimum in this system seems probable. The only alternative to this can be the influence of the impurities of other atoms that were present in the samples on the kinetics of decomposition.

Modulated structures are frequent in decomposition of alloys (Ni–Au, Al–Ni, Au–Pt, Al–Zn, Cu–Ti, and others [9]) and are widely known in manufacturing practice (decomposition of metastable austenite into cementite and ferrite [2]). In the literature, two mechanisms of their genesis have been proposed: 1) when spontaneous decomposition from a homogeneous initial state with small fluctuations is developed [5]; 2) as a result of the compensation of far-range fields of elastic concentration stresses [9]. Modulated structures of the first type appear only in one-dimensional continuous models at the wave stage of decomposition; the period of modulation grows with temperature but is proportional to the effective radius of interatomic interaction and does not exceed several lattice parameters. In the second case the structural regularity grows with time, up to reaching the steady state, and the period is determined by far-range elastic fields. It follows from Section 2 that within the medium-field approximation, modulated structures also result from the decomposition in systems with a local $f(C_A)$ minimum. Such structures are nonequilibrium but are much more regular than those in the normal SD, since the metastable alloy is stable to fluctuations of the composition. The colonies are destroyed on long standing, since this requires atomic diffusion for distances of the order of the lamella width, which is much larger than the interatomic-interaction length, and an unstable equilibrium is attained for perfectly periodic concentration distributions [9]. The nonequilibrium of microstructures, the elliptic shape of colonies, and decrease in the modulation period with T are close to certain features of perlite transformation in steels [2].

Lamellar precipitates similar to those presented in Fig. 6 have been discussed in [9] where their appearance was determined by the optimum conjugation of crystal plates as a result of twinning. It follows from Section 2 that the formation of twin lamellas is also the preferred mechanism of decomposition of metastable phases. Bainite transformation in steel (precipitation of ferrite plates with pointed ends from metastable austenite), which is observed at temperatures lower than perlite-transformation temperatures, is an example of the appearance of such structures; the lattice transformation $\gamma \rightarrow \alpha$ acts an analog of lattice relaxation. However, discrete models should be used for analysis of transformations in steel, since continuous approaches lose their physical meaning for low concentrations of one component.

Conclusions. Thus, lattice relaxation can stabilize a solid solution relative to small fluctuations of the composition, which will cause the SD kinetics to change. It has been shown that precipitates of the interfacial composition are formed in decomposition from the region of instability of the phase diagram, and growth of eutectoid colonies or twin lamellas is observed in decomposition from metastable regions.

The author expresses his thanks to Director of the Private Corporation "Institute of Quantum Materials Science," Doctor of Sciences in Physics and Mathematics, Professor Yu. N. Gornostyrev for substantive discussions.

NOTATION

a and $a^{A(B)}$, lattice parameters in the alloy and pure substances, Å; C_σ , local concentration of atoms of the σ sort, $0 \leq C_\sigma \leq 1$; C_σ^0 , concentration corresponding to the local $f(C_\sigma)$ minimum; $\langle C_\sigma \rangle$, average concentration of

atoms of the σ sort, $0 \leq C_A \leq 1$; $C_{1(2)}$, equilibrium solubility limits, $0 \leq C_{1(2)} \leq 1$; D , diffusion coefficient, m^2/sec ; f , density of the free energy of mixing, eV ; \mathbf{J}_σ , flux of atoms of the σ sort, m/sec ; k , Boltzmann constant, $8.6 \cdot 10^{-5} \text{ eV}/\text{K}$; L , dimension of the sample, \AA ; M , mobility, $\text{m}^2/(\text{sec} \cdot \text{eV})$; \mathbf{q}_i , radius vector of the relative position of the lattice node, \AA ; \mathbf{r} , radius vector of a certain point of space, \AA ; T , temperature, K ; t , time, sec ; α and β , phases enriched with A and B atoms respectively; γ and γ' , stable and metastable solid solution; δ , surface energy, eV ; Γ , effective atomic-interaction radius, \AA ; ζ and ε , coefficients of the concentration dependence of the energies $\Phi_{\sigma\sigma}$, eV ; $\varphi_{\sigma\sigma'}$, energy of pair interaction of atoms of the σ and σ' sorts, eV ; $\Phi_{\sigma\sigma}$ and $\Phi_{\sigma\sigma'}^0$, energy of interaction of a σ atom with the lattice filled with σ' atoms in the alloy and pure substances, eV ; Y , dimensionless coefficient of the concentration dependence $\tilde{\Psi}(C_\sigma)$; $\tilde{\Psi}$ and Ψ , dimensionless total energy of mixing and its constant part; μ , chemical potential, eV ; τ , dimensionless time. Subscripts: i , sublattice node, 1, ..., N ; σ and σ' , sorts of A and B atoms.

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