
THEORY
OF METALS

Decomposition of Equilibrium Interphase Boundary in Substitutional Alloys upon Mechanical Alloying

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Abstract—The vacancy-flux-induced decomposition of an interphase boundary in substitutional alloys has been considered. The interphase boundary decomposition has been described using the nonequilibrium thermodynamics approach, which considers a heterogeneous system to be continuous medium, including the interphase boundary. A hypothesis of local equilibrium in the thermodynamics of a continuous medium has been substituted for a more general hypothesis that takes into account the nonlocal dependence of thermodynamic forces and fluxes on order parameters. The interpretation of the formation of spatial composition modulations during the mechanical alloying of pure metallic Cu–Co, Cu–Fe, and Fe–Cr–Sn powder mixtures has been given.

Keywords: nonlocal thermodynamics, heterogeneous systems, substitutional alloys, mechanical alloying, spatial composition modulations

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INTRODUCTION

Mechanical alloying of pure metallic Cu–Co, Cu–Fe, and Fe–Cr–Sn powder mixtures results in composition heterogeneity with the period of spatial concentration modulations of about 2 nm and an amplitude of more than 10% [1–3]. The initial stage of spinodal decomposition is characterized by the same parameters of composition modulation.

The Mössbauer study of mechanically alloyed Fe, Cr, and Sn powders indicated spatial composition modulations of up to 10 at % with a period of several nanometers [3]. This composition distribution was observed after the 20-min medium-temperature annealing of the compacted samples. Spinodal decomposition was observed in Fe–Cr–Sn alloys after the annealing of preliminary quenched samples. Annealing for 30 h results in the formation of a modulated structure with parameters typical of mechanically alloyed samples. The study of the composition distribution in a Fe–Cr–Sn sample immediately after mechanical alloying and compaction (before annealing) suggests that this distribution is characteristic of an equilibrium two-phase alloy. Medium-temperature annealing, which activates the processes of composition redistribution, results in a transition to a state

identical to the initial (linear) stage of spinodal decomposition.

The high positive mixing energy of Cu–Fe and Cu–Co alloys does not allow the creation of chemically homogeneous samples using quenching for the study of spinodal decomposition. A direct comparison with the mechanical alloying processes is not possible. The composition distribution of mechanically alloyed Cu–Fe and Cu–Co samples seems to be similar to the composition distributions of other systems during their spinodal decomposition.

In work [1], after mechanical alloying, the mixture of Cu–Co powders was compacted at a pressure of 0.5 GPa at room temperature. Then, medium-temperature annealing was carried out for 2 h at a temperature of 400°C. The composition distribution in some local regions of the sample was found to have a form that corresponds to the sharp concentration modulations, which may indicate the linear stage of spinodal decomposition. Fourier analysis showed that the period of these modulations was 2 nm.

The mechanical alloying of the mixture of Cu–Fe powders also results in the composition modulations with parameters that correspond to the linear stage of spinodal decomposition [2]. In contrast to Cu–Co, the samples were not annealed and the powder mix-

[†] Deceased.

ture after mechanical alloying was compacted at room temperature and at a pressure of 5 GPa.

Composition modulations are observed only in some regions of the mechanically alloyed Cu–Co and Cu–Fe samples. The composition in other regions is constant. These regions with the homogeneous composition contain up to ~19 at % Cu (copper-depleted regions) and up to ~14 at % Fe (iron-depleted regions). These values differ significantly from the equilibrium solubility limits 1–3 at % Cu and 1–3 at % Fe, respectively. Thus, copper (iron)-enriched and depleted regions in the sample can be considered to be regions with homogeneous compositions, but are in a nonequilibrium state. The width of the nonequilibrium interphase boundary is ~2 nm [2], which is similar to that of the equilibrium interphase boundary.

One sample contains regions with different quality and quantity characteristics of the composition distribution, which, in our opinion, is associated with the difference in factors that determine the conditions for generating vacancies during severe plastic deformation. The process of severe plastic deformation is related to polycrystal structure evolution. This process depends in a complicated way on the distribution and the activity of vacancy sources and sinks; therefore, the same sample contains both regions whose composition is close to equilibrium phases and regions with modulated structures [2].

There are several stages of spinodal decomposition. At the initial (linear) stage, a modulated structure is spontaneously formed from a homogeneous metastable alloy. Next stages are diffusion-induced growth and structure coarsening. The process is completed by the formation of equilibrium phases separated by interphase boundaries. The linear stage of decomposition proceeds rapidly because it is controlled by powerful thermodynamic stimuli. Subsequent stages are controlled by diffusion, so they occur slowly. The necessary condition for the onset of composition redistribution during mechanical alloying is the compaction of the powder mixture of pure metals preliminarily subjected to mechanical treatment. As a result, a nonequilibrium alloy is formed in which the composition distribution is the same as that in an equilibrium alloy based on mutually insoluble components. Its nonequilibrium state manifests during subsequent annealing at medium temperatures close to room temperature. This leads to the redistribution of the composition and the formation of spatial modulations with parameters that are characteristic of the linear stage of spinodal decomposition. Annealing at higher temperatures leads to diffusion-induced growth and structure coarsening, as occurs in the case of classical spinodal decomposition. The result of the redistribution of the composition during mechanical alloying is a transition from a state with parameters characteristic of an equilibrium two-phase alloy to a nonequilibrium state in the form of composition modulations. Anneal-

ing temperatures of 273–400°C correspond to the conditions under which vacancy migration becomes possible [4]. The composition redistribution is associated with the inverse Kirkendall effect.

Redistribution effects do not always occur directly during mechanical treatment; however, in some cases, they are delayed. This is because the formation of the sources of nonequilibrium vacancies during mechanical treatment is a necessary but not sufficient condition for the appearance of the inverse Kirkendall effect. The second condition is the creation of the possibility of vacancy migration. This effect is well illustrated by the processes that occur during the mechanical treatment of NiPd alloy. This alloy consists of components with unlimited solubility and is homogeneous in the initial state. Separation into components was detected during milling [5]. The maximum separation of components in NiPd alloy was observed in the temperature range of 293–403 K. However, no alloy separation was observed at a milling temperature of 80 K, but medium annealing at 553 K again led to maximum alloy separation. Here, the delayed effect of composition redistribution is caused by the fact that sources of nonequilibrium vacancies are formed at the temperature of liquid nitrogen, when vacancy migration is impossible. An increased temperature is required to activate the migration of nonequilibrium vacancies.

In the case of the mechanical alloying of Cu–Fe, Cu–Co, and Fe–Cr–Sn, the effects of composition redistribution also arise not directly during mechanical treatment, but rather after compaction and medium-temperature annealing.

APPROACH TO THE THERMODYNAMIC DESCRIPTION OF HETEROGENEOUS ALLOYS

The above analysis of the experimental data [1–3] suggests that the initial state during mechanical alloying is characterized as two-phase, unlike the final state (spatial composition modulations), which cannot be described as a two-phase system. The analysis also showed that a key role in the evolution of composition distribution is played by the fluxes of nonequilibrium vacancies. It makes sense to describe this process in theoretical terms of the nonequilibrium thermodynamics of a heterogeneous system, which is considered to be a continuous medium, including interphase boundaries. The implementation of this approach faces three problems.

The first problem is that the Onsager approach aimed at studying processes in homogeneous systems is used to describe diffusion [6]. A special feature of this approach is the constructing the entropy balance equation for describing a continuous medium using the Lagrange method. The heart of the Lagrange method is the study of processes in a fixed material

element, which does not exchange matter with surroundings. In thermodynamics, it is equivalent to a closed system. The description of relaxation to phase equilibrium in a heterogeneous system should be based on the concept of an open system, since equilibrium is achieved through the exchange of matter between phases [7]. Therefore, the Euler method is preferable for deriving the entropy balance equation in the case of the nonequilibrium thermodynamics formulated for heterogeneous systems. It deals with the exchange of matter between a fixed-volume element and its surroundings, which is equivalent to the idea of an open system in thermodynamics.

The second problem is related to the fact that diffusion in substitutional alloys is not the same as the independent migration of atoms of alloy components. It must be taken into account that the movement of an atom from one position to another implies the movement of a vacancy in the opposite direction to the atom. This means that, in the thermodynamic description, the gradient of the chemical potential of the components cannot be considered the sole driving force of diffusion. To adequately describe diffusion, a gradient of some quantity, which includes the chemical potentials of components and vacancies, should be used as a driving force.

The third problem is that the classical version of the local equilibrium hypothesis cannot be used for the thermodynamic description of heterogeneous systems. According to this hypothesis, in all regions of a heterogeneous system, including the interphase boundary, the chemical potential should be considered as a function of the local values of the following intensive variables: state (T, p) and order parameters (ρ, c_k).

State and order parameters in the context of thermodynamics can be determined as follows. In equilibrium, the state parameters (T, p, μ_k) have the same values in all parts of the system. The order parameters (s, ρ, c_k) describe the difference between the system phases, when the system is in an equilibrium state. In the case of a binary alloy that consists of mutually insoluble components, the concentration of one of the components can be considered as an order parameter. The phases of the system far from the interphase boundary can be considered as homogeneous. The values of the order parameter remain the same within the same phase, but they are different in neighboring phases. This makes it possible to refine the condition for the phase equilibrium in the binary two-phase alloy [7]

$$\mu_{A1}(T, p; c_{A1}^e) = \mu_{A2}(T, p; c_{A2}^e) = \text{const}, \quad (1)$$

where $\mu_{A1,2}$ is the chemical potential of component A and $c_{A1,2}^e$ is the equilibrium concentration of a component in the first and second phases. Here, the chemical potentials of the component in the phases are two

different concentration functions. The equilibrium condition for describing a heterogeneous system in terms of a continuous medium can be written as

$$\mu_A(T, p) = \text{const}. \quad (2)$$

Here, this means that, at equilibrium, the chemical potential remains constant in any region of the heterogeneous system, including the interphase boundary. Far from the boundary, the order parameter (concentration) is constant, so Eq. (2) gives the same result as Eq. (1). The order parameter sharply changes at the vicinity of the boundary. Therefore, the chemical potential should be selected as a function of the order parameter, which ensures the simultaneous fulfillment of Eq. (1) in phase regions and the constancy of its value near the interphase boundary. This problem can be solved using functional Φ_Γ of the order parameter. Here, Γ is an arbitrary intensive variable that is an order parameter, e.g., density or component concentration.

Functionals have been previously used in thermodynamic descriptions, e.g., by Khachatryan in the form of a free energy functional to analyze modulations in the spatial composition in alloys with anisotropy of elastic properties [8], but their use was limited. Using the relationship between the free energy and the chemical potential, we can show the structural similarity between the expressions given in [8] and those obtained in this work. The main difference is in the form of coefficients at derivatives in expressions we obtained (see, e.g., Eq. (9)).

The functional can be expressed in general form as

$$\begin{aligned} & \Phi_\Gamma(x, y, z, t) \\ &= \int_{-\infty}^{+\infty} dt' \iiint_V dx' dy' dz' \Gamma(x', y', z', t') \\ & \quad \times \delta_\Phi(\Delta x, \Delta y, \Delta z, \Delta t). \end{aligned} \quad (3)$$

The kernel of the functional is taken to be normalized as follows:

$$\int_{-\infty}^{+\infty} dt' \iiint_V dx' dy' dz' \delta_\Phi(x', y', z', t') = 1. \quad (4)$$

All of the physical properties that are essential for a real system are taken into account by choosing the form of the kernel of the functional. For example, in order to satisfy the causality principle, the Heaviside function as a function of time may be included as a factor in the expression for the kernel of the functional; whereas the case with no preferential direction requires the dependence of the kernel of the functional on only the length of the spatial interval.

In the case of diffusion in alloys, the temporal part of the functional may be neglected, with the assumption the time of transferring the information about the

state is extremely short, since the transfer occurs through the field of elastic stresses, whereas the speed of sound is many orders of magnitude faster than the rate of diffusion. In addition, to study diffusion in an isotropic medium (bcc or fcc lattice), let us consider only one-dimensional cases. Finally, in the case with no preferential direction, the dependence of the kernel of the functional on the coordinate difference will be considered even. As a result, we get

$$\Phi_{C_A}(x) = \int_{-\infty}^{+\infty} dx' C_A(x') \delta_{\Phi}(|x - x'|). \quad (5)$$

Now, the equilibrium condition of the two-phase system can be written in the form

$$\mu_A(T, p; \Phi_{C_A}) = \text{const}. \quad (6)$$

The kernel will be considered to be described by a delta-like distance function. The kernel radius is taken to be three lattice parameters, since the intensity of the elastic stress field of a point source is decreased by an order of magnitude at a distance of three lattice parameters. Let an atom of a component embedded in the matrix of another component be considered as a perturbing source. In this case, a nonlocality range is about 2 nm, which qualitatively coincides with the width of the diffuse interphase boundary in alloys and with the linear size of composition modulations formed at the initial stage of spinodal decomposition.

Assuming that the integrand only slightly changes at a distance of the functional kernel radius, the expression can be expanded as

$$\Phi_{C_A}(x) \cong C_A(x) + \Lambda^2 \frac{\partial^2 C_A}{\partial x^2} + \dots, \quad (7)$$

where Λ is the dimensional quantity of the order of the kernel radius.

The equilibrium condition (6) can approximately be written as

$$\mu_A \left(C_A(x) + \Lambda^2 \frac{\partial^2 C_A}{\partial x^2} \right) = \text{const}. \quad (8)$$

The expansion of the left-hand side of Eq. (8) enables the transformation of the integral equation to a differential one, which describes a certain dependence of a component concentration near the equilibrium interphase boundary, at which the chemical potential remains constant both within phase regions and near the interphase boundary. This equation has the form

$$\Lambda^2 \frac{d\mu_A}{dC_A} \frac{\partial^2 C_A}{\partial x^2} + \mu_A(C_A) = \text{const}. \quad (9)$$

The order parameters in heterogeneous systems are internal thermodynamic degrees of freedom. Their appearance is associated with the collective interaction of the particles of matter, which forms the struc-

ture of various phases. The collective interaction within the macroscopic description leads to the non-local dependence of the chemical potential on an order parameter, which manifests not only in equilibrium state, as was shown above, but also in nonequilibrium heterogeneous systems.

As a result, to describe heterogeneous systems in terms of a continuous medium, the hypothesis of local equilibrium should be extended to create a suitable version of the Onsager approach.

Let us formulate a new hypothesis as follows:

(i) Assume that a heterogeneous system can be divided into small regions and, within each region, all expressions for equilibrium systems are valid.

(ii) The arguments of chemical potentials are taken to be corresponding functionals, rather than local values of intensive variables. For example, instead of density ρ and component concentration, which play the role of order parameters in vapor–liquid systems and alloys, the arguments will be Φ_{ρ} and Φ_{C_i} .

The first point of the new hypothesis completely repeats the local equilibrium hypothesis. As will be seen from the following, the second point means that the transition speed from one local state to another is determined by the spatial-temporal distributions of the parameters, rather than their local values.

THERMODYNAMIC DESCRIPTION OF DIFFUSION IN CONTINUOUS HETEROGENEOUS SYSTEMS

The expressions that describe thermodynamic forces in the case of a homogeneous (single-phase) system considered to be a continuous medium are derived from the Gibbs equation for a closed system [6]. A key moment in the study of heterogeneous systems is a consideration of the exchange of matter between phases; therefore, the Euler approach is required for their description as continuous media. In this approach, the Gibbs equation should be written taking into account the constant volume of a fixed region of space and the change in the total amount of matter in this region as follows:

$$dU = TdS + \sum_{k=1}^K \mu_{v_k} dN_k, \quad (10)$$

$$\sum_{k=1}^K N_k = N = \text{var},$$

μ_{v_k} is the molar chemical potential and N_k is the number of moles of substance k . We introduce the following specific values

$$u = \frac{U}{M}, \quad s = \frac{S}{M}, \quad v = \frac{1}{\rho} = \frac{V}{M}, \quad n_{mk} = \frac{N_k}{M}. \quad (11)$$

Here, V and M are the volume and the mass of the fixed element in medium. Now, the Gibbs equation can be rearranged as

$$d(\rho u) - Td(\rho s) - \sum_{k=1}^K \mu_{vk} d(\rho n_{mk}) + \left\{ \rho^2 d\left(\frac{1}{\rho}\right) + \rho \frac{1}{M} dM \right\} \times \left[u - Ts + \frac{p}{\rho} - \sum_{k=1}^K \mu_{vk} n_{mk} \right] = 0,$$

where n_{mk} is the number of moles per unit mass. This is then expressed in terms of component density ρ_k as

$$n_{mk} = \frac{\rho_k}{\rho M_{Ak}}, \quad (12)$$

where M_{Ak} is the mass of one mole of substance k .

The expression is then rearranged into the following form:

$$d(\rho u) - Td(\rho s) - \sum_{k=1}^K \mu_{mk} d\rho_k + \left\{ -\frac{1}{\rho} d\rho + \frac{1}{M} dM \right\} \times \left[\rho u - T\rho s + p - \sum_{k=1}^K \mu_{mk} \rho_k \right] = 0,$$

where μ_{mk} is the specific chemical potential

$$\mu_{mk} = \frac{\mu_{vk}}{M_{Ak}}.$$

Then, we turn to the limit of $V \rightarrow 0$, which is reasonable for the physically infinitely small volume of an element

$$M = \iiint_V \rho dV \rightarrow \rho V.$$

Since the volume is fixed according to the Euler approach, we have

$$dM \rightarrow d\rho \Delta V.$$

Then,

$$\frac{1}{M} dM \rightarrow \frac{1}{\rho} d\rho;$$

thus, we get

$$d(\rho u) - Td(\rho s) - \sum_{k=1}^K \mu_{mk} d\rho_k = 0$$

or, if we pass to the record in the form of a differential equation, we have

$$\frac{\partial(\rho s)}{\partial t} = \frac{1}{T} \frac{\partial(\rho u)}{\partial t} - \frac{1}{T} \sum_{k=1}^K \mu_{mk} \frac{\partial \rho_k}{\partial t}. \quad (13)$$

The entropy balance equation written in the local form (13) makes it possible to describe heterogeneous systems in terms of a continuous medium. To identify the flux and source of entropy, the general form of the local entropy balance equation is used as follows:

$$\frac{\partial(\rho s)}{\partial t} = -(\nabla, \mathbf{J}_S^0) + \sigma_S. \quad (14)$$

In this work, we will restrict our consideration to the study of diffusion; therefore, we write the relation between the flux and the source of entropy in the form

$$-(\nabla, \mathbf{J}_S^0) + \sigma_S = -\frac{1}{T} \sum_{k=1}^K \mu_{mk} \frac{\partial \rho_k}{\partial t}. \quad (15)$$

Using the local balance equations for component mass in the absence of chemical reactions [6], we find

$$-(\nabla, \mathbf{J}_S^0) + \sigma_S = \sum_{k=1}^K \frac{\mu_{mk}}{T} (\nabla, \mathbf{J}_k^0). \quad (16)$$

The relationship between the density of the local and the substantial fluxes of the component is

$$\mathbf{J}_k^0 = \mathbf{J}_k + \rho_k \mathbf{v}. \quad (17)$$

where \mathbf{J}_k is the density of the substantial component flux in the system of the mass center of a material parcel, i.e., the density of the diffusion flux, and \mathbf{v} is the velocity of the mass center of the material parcel in an arbitrary laboratory frame of reference.

Then,

$$-(\nabla, \mathbf{J}_S^0) + \sigma_S = \sum_{k=1}^K \frac{\mu_{mk}}{T} (\nabla, \mathbf{J}_k) + \sum_{k=1}^K \frac{\mu_{mk}}{T} (\nabla, \rho_k \mathbf{v}). \quad (18)$$

To simplify the calculations, let us consider the case of one component $K = 1$ without a loss of interesting features. Then, $\mathbf{J}_1 \equiv \mathbf{J} = 0$ and $J_j = 0$, since in this case there are no diffusion and chemical reactions. We also designate $\rho_1 \equiv \rho$, $\mu_{m1} \equiv \mu_m$. Therefore, instead of the previous record, we have

$$-(\nabla, \mathbf{J}_S^0) + \sigma_S = \frac{\mu}{T} (\nabla, \rho \mathbf{v}). \quad (19)$$

We use the relationships

$$\frac{1}{T} \mu (\nabla, \rho \mathbf{v}) = \left(\nabla, \frac{\mu \rho}{T} \mathbf{v} \right) - \left(\rho \mathbf{v}, \nabla \frac{\mu}{T} \right).$$

Then,

$$-(\nabla, \mathbf{J}_S^0) - \left(\nabla, \frac{\mu_m \rho}{T} \mathbf{v} \right) + \sigma_S = - \left(\rho \mathbf{v}, \nabla \frac{\mu_m}{T} \right). \quad (20)$$

Assuming for the density of the local entropy flux

$$\mathbf{J}_S^0 = - \frac{\mu_m \rho}{T} \mathbf{v},$$

we obtain for the density of the entropy source,

$$\sigma_S = - \left(\rho \mathbf{v}, \nabla \frac{\mu_m}{T} \right). \quad (21)$$

In the expression for σ_S , the only term that describes the appearance of matter flux when a temperature gradient and a chemical potential are retained. The Onsager approach developed by Dyarmati [6] does not consider this term, which makes it impossible to describe the interphase exchange in heterogeneous systems.

DIFFUSION IN BINARY SUBSTITUTIONAL ALLOYS

Interdiffusion is properly described by transitioning from an arbitrary laboratory frame of reference to that in which a crystal lattice is stationary and does not change during the process.

To relate the flux density and the entropy source in the case of diffusion without chemical reactions, we obtain

$$\begin{aligned} -(\nabla, \mathbf{J}_S^0) + \sum_{k=1}^K \left(\nabla, \left[\frac{\mu_{mk}}{T} (\mathbf{J}_k + \rho_k \mathbf{v}) \right] \right) \\ = \sigma_S + \sum_{k=1}^K \left([(\mathbf{J}_k + \rho_k \mathbf{v})], \nabla \frac{\mu_{mk}}{T} \right). \end{aligned} \quad (22)$$

Let us to introduce the local entropy flux as

$$\mathbf{J}_S^0 = - \sum_{k=1}^K \frac{\mu_{mk}}{T} (\mathbf{J}_k + \rho_k \mathbf{v}).$$

For the entropy source we obtain

$$\sigma_S = \sum_{k=1}^K \left((\mathbf{J}_k + \rho_k \mathbf{v}), -\nabla \left(\frac{\mu_{mk}}{T} \right) \right). \quad (23)$$

Since the exchange of momentum between components and between the lattice and components can be neglected in the consideration of diffusion in alloys, the effects associated with the mass do not play any role. This allows us to transfer from specific masses to densities expressed in the number of atoms of the component per unit volume. The following relationships are used:

$$\begin{aligned} \rho_k &= n_k m_{0k} = C_k n_0 m_{0k}, \\ \mathbf{J}_k &= \mathbf{J}_k n_0 m_{0k}, \\ \mu_{0k} &= \mu_{mk} n_0 m_{0k}, \end{aligned}$$

where n_k is the number of component atoms per unit volume, m_{0k} is the atomic mass, n_0 is the number of lattice sites per unit volume, C_k is the numerical density of a component, \mathbf{J}_k is the numerical flux of a component, and μ_{0k} is the chemical potential of a component per lattice site. Then, instead of Eq. (23), we have

$$\sigma_S = \sum_{k=1}^K \left((\mathbf{J}_k + C_k \mathbf{v}), -\nabla \left(\frac{\mu_{0k}}{T} \right) \right), \quad (24)$$

where \mathbf{v} is the velocity of the center of the quantity of the fixed material element (analog of the velocity of the center of a material mass) relative to an arbitrary laboratory frame of reference. The obtained equation contains an ambiguity related to the freedom of the frame of reference choice. As will be shown, physically correct results can be obtained by choosing a frame of reference in which the crystal lattice is stationary. Let the velocity of the mass center of a material element with respect to this frame of reference be denoted by u . Obviously, $u = v - v_r$, where v_r is the velocity of the crystal lattice with respect to an arbitrary frame of reference.

In terms of numerical flows, in the one-dimensional case, expression (22) can be written in the form

$$\begin{aligned} \frac{\partial}{\partial x} J_S^0 + \sum_{k=1}^K \frac{\partial}{\partial x} \left[\frac{\mu_{0k}}{T} (j_k + C_k u) \right] \\ + v_r \sum_{k=1}^K \frac{\mu_{0k}}{T} \frac{\partial C_k}{\partial x} = \sigma_S + \sum_{k=1}^K (j_k + C_k u) \frac{\partial}{\partial x} \left(\frac{\mu_{0k}}{T} \right). \end{aligned} \quad (25)$$

Let the local entropy flux be introduced in the form

$$J_S^0 = J_S^{01} + J_S^{02},$$

where the part that is invariant with respect to the Galileo transformation is defined in the usual way

$$J_S^{01} = - \sum_{k=1}^K \left[\frac{\mu_{0k}}{T} (j_k + C_k u) \right],$$

whereas the noninvariant part is defined by the expression

$$\frac{\partial}{\partial x} J_S^{02} = -v_r \sum_{k=1}^K \frac{\mu_{0k}}{T} \frac{\partial C_k}{\partial x}.$$

The velocity of the crystal lattice as a whole v_r is coordinate independent. Its change leads to proportional changes of J_S^{02} , which is a conventional convective term added to the local entropy flux.

Then, entropy production for a binary alloy with a cubic lattice (isotropy of diffusion properties) will be in the form

$$\begin{aligned} \sigma_S = -(j_A + C_A u) \frac{\partial}{\partial x} \left(\frac{\mu_{0A}}{T} \right) \\ - (j_B + C_B u) \frac{\partial}{\partial x} \left(\frac{\mu_{0B}}{T} \right). \end{aligned} \quad (26)$$

The relationship between the flux density of components and vacancies in the system of the material-quantity center, i.e., diffusion fluxes $j_{A,B,V}$, and the flux density in the lattice frame of reference gives the expression

$$j_{A,B,V} + C_{A,B,V}u = j'_{A,B,V}, \quad (27)$$

where $j'_{A,B,V}$ are the densities of the numerical fluxes of components and vacancies with respect to the crystal lattice. Since the jump of any atom results in the movement of a vacancy towards the atom in the case of the vacancy migration mechanism, the following relationship is fulfilled in the lattice frame of reference:

$$j'_A + j'_B + j'_V = 0. \quad (28)$$

For numerical concentrations, the following relation is true:

$$C_A + C_B + C_V = 1. \quad (29)$$

Under conventional conditions for metals,

$$C_V \ll C_{A,B}. \quad (30)$$

In the frame of reference associated with the center of a material quantity, the matter is stationary; therefore

$$j_A + j_B = 0. \quad (31)$$

Then, summing Eqs. (27) with allowance for the above relations, we obtain

$$j'_V \cong j_V = -u. \quad (32)$$

Consequently,

$$j_{A,B} = j'_{A,B} + C_{A,B}j'_V. \quad (33)$$

In view of Eq. (28), for diffusion fluxes, this can be written as

$$-j_B = j_A \cong C_B j'_A - C_A j'_B. \quad (34)$$

Equation (26) can be rewritten in terms of Eq. (27) as follows:

$$\sigma_S = -j'_A \frac{\partial}{\partial x} \left(\frac{\mu_{0A}}{T} \right) - j'_B \frac{\partial}{\partial x} \left(\frac{\mu_{0B}}{T} \right). \quad (35)$$

According to Onsager's ideology, the entropy production includes terms composed as products of fluxes and conjugate thermodynamic forces. In our case, Onsager's constitutive relationships between forces and fluxes have the form

$$j'_A = -L_{AA} \frac{\partial}{\partial x} \left(\frac{\mu_{0A}}{T} \right) - L_{AB} \frac{\partial}{\partial x} \left(\frac{\mu_{0B}}{T} \right), \quad (36)$$

$$j'_B = -L_{BA} \frac{\partial}{\partial x} \left(\frac{\mu_{0A}}{T} \right) - L_{BB} \frac{\partial}{\partial x} \left(\frac{\mu_{0B}}{T} \right). \quad (37)$$

In alloys, only isothermal diffusion is considered, whereas cross effects may be neglected as follows [9]:

$$j'_{A,B} = -\frac{L_{AA,BB}}{T} \frac{\partial \mu_{0A,B}}{\partial x}. \quad (38)$$

Equations (36)–(38) are derived to describe diffusion in substitutional alloys. However, they should be modified to account for the essence of the vacancy migration mechanism in an adequate way. First, let us rewrite Eq. (38) in the following equivalent form

$$j'_{A,B} = kL_{AA,BB} e^{\frac{\mu_{0A,B}}{kT}} \frac{\partial}{\partial x} \left(e^{-\frac{\mu_{0A,B}}{kT}} \right). \quad (39)$$

The quantity under the derivative sign has the form of probability

$$W_{A,B} = \left(e^{-\frac{\mu_{0A,B}}{kT}} \right). \quad (40)$$

Rewriting Eq. (39) in terms of the result (40), we obtain

$$j'_{A,B} = kL_{AA,BB} \frac{1}{W_{A,B}} \frac{W_{A,B}(x + \Delta x) - W_{A,B}(x)}{\Delta x}. \quad (41)$$

Here, the numerator includes the difference between probabilities to find the system in a definite state at two points. This record adequately shows the situation in the case of the diffusion of a component according to the mechanism of direct jumps, e.g., the diffusion of interstitial atoms or the diffusion of an impurity in liquid and gas. But it does not describe the diffusion of a component in the case of the vacancy migration mechanism in a substitutional alloy. In the latter case, the migration of atoms and the counter migration of vacancies completely correlate with each other. In this case, it is necessary to take the difference between probabilities corresponding to the final and initial states. These states differ in the positions of atoms and vacancies located in two adjacent regions, which corresponds to the difference between $W_{A,B}(2)W_V(2)$ and $W_{A,B}(1)W_V(1)$. Taking into account that, before the transition, atoms A and B are localized in the region with coordinate x , vacancies in the region with the coordinate $x + \Delta x$, and they exchange places after the transition; thus, the equation changes as follows:

$$j'_{A,B} = \frac{kL_{AA,BB}}{W_{A,B}W_V} \times \frac{W_{A,B}(x + \Delta x)W_V(x) - W_{A,B}(x)W_V(x + \Delta x)}{\Delta x}. \quad (42)$$

Within the limit of $\Delta x \rightarrow 0$, we obtain

$$j'_{A,B} = kL_{AA,BB} \left(\frac{\partial \ln W_{A,B}}{\partial x} - \frac{\partial \ln W_V}{\partial x} \right). \quad (43)$$

Probability W_V is defined similarly to probabilities $W_{A,B}$, that is, by Eq. (40).

Let us consider the solid solution of components as nonideal, whereas the solution of vacancies as ideal in view of the condition $C_V \ll 1$. Then, their chemical potentials can be written in the form

$$\mu_{0A,B} = kT \ln(C_{A,B}\gamma_{A,B}) + \mu_{0A,B}^0, \quad (44)$$

$$\mu_{0V} = kT \ln C_V + \mu_{0V}^0, \quad (45)$$

$\gamma_{A,B}(C_{A,B})$ are the thermodynamic activities of components, and the values of $\mu_{0A,B,V}^0$ are independent of the concentrations. Let us assume that the spatial dependence only arises because of the inhomogeneity of the composition; then, $\mu_{0A,B,V}^0 = \text{const}$ and we obtain

$$j'_{A,B} = \frac{kL_{AA,BB}}{C_V C_{A,B} \gamma_{A,B}} \times \left(-C_V \frac{\partial}{\partial x} (C_{A,B} \gamma_{A,B}) + C_{A,B} \gamma_{A,B} - \frac{\partial C_V}{\partial x} \right). \quad (46)$$

Equation (46) coincides in form with the corresponding equation for the vacancy gas theory [9, 10], which has the form

$$j'_{A,B} = -C_V \frac{\partial}{\partial x} (C_{A,B} \omega'_{A,B}) + C_{A,B} \omega'_{A,B} \frac{\partial C_V}{\partial x}, \quad (47)$$

where $\omega'_{A,B}$ is the frequency of atom–vacancy transitions in the crystal lattice reference frame. The coincidence of the general form of the equation for the flux, which we derived from the thermodynamic description, with the appropriate equation for the vacancy gas theory can be achieved under the following conditions:

$$L_{AA,BB} = \frac{1}{k} C_V C_{A,B} \gamma_{A,B}, \quad \gamma_{A,B} = \omega'_{A,B}. \quad (48)$$

Let us write down the equation for the component flux in the lattice reference system using the self-diffusion coefficient of the component. When cross effects are neglected, this coefficient can be expressed in terms of the diagonal elements of the Onsager matrix of coefficients [9]. Therefore, it can be determined by the following expression:

$$D_{A,B}^* = k \frac{L_{AA,BB}}{C_{A,B}}. \quad (49)$$

The partial diffusion coefficients of components have the form

$$D_{A,B} = D_{A,B}^* g_{A,B}. \quad (50)$$

$g_{A,B}$ is the thermodynamic factor of the partial diffusion coefficient, which takes into account the nonideality of the solid solution

$$g_{A,B} = 1 + \frac{d \ln \gamma_{A,B}}{d \ln C_{A,B}}. \quad (51)$$

The equation for the component flux in the lattice frame of reference takes the form

$$j'_{A,B} = -D_{A,B} \frac{\partial C_{A,B}}{\partial x} + C_{A,B} \frac{D_{A,B}^*}{C_V} \frac{\partial C_V}{\partial x}. \quad (52)$$

Using Eq. (34), for the diffusion flux (the flux of component B is opposite in sign), we obtain

$$j_A = -D_D \frac{\partial C_A}{\partial x} + C_A C_B \frac{D_A^* - D_B^*}{C_V} \frac{\partial C_V}{\partial x}. \quad (53)$$

D_D is the interdiffusion coefficient in Darken's form

$$D_D = (C_A D_B + C_B D_A). \quad (54)$$

Using Eqs. (52), (28), and (32), we obtain the following expression for the vacancy flux

$$j_V = -V_V \frac{\partial C_V}{\partial x} + \frac{1}{C_V} (D_A - D_B) \frac{\partial C_A}{\partial x}, \quad (55)$$

where the vacancy diffusion coefficient is determined as

$$D_V = \frac{1}{C_V} (C_A D_A^* + C_B D_B^*). \quad (56)$$

If we express the vacancy concentration gradient from Eq. (55) and exclude it from Eq. (53), we obtain

$$j_A = -D_G \frac{\partial C_A}{\partial x} - \frac{C_A C_B}{C_V} \frac{D_A^* - D_B^*}{D_V} j_V. \quad (57)$$

Here, interdiffusion coefficient D_G is in the form proposed by Nazarov and Gurov in [11]

$$D_G = \frac{1}{C_V} \frac{D_A^* D_B^*}{D_V} g_G. \quad (58)$$

The thermodynamic factor of interdiffusion coefficient D_G is given by

$$g_G = 1 + C_A C_B \left(\frac{d \ln \gamma_A}{d C_A} + \frac{d \ln \gamma_B}{d C_B} \right). \quad (59)$$

For the activities of the components of regular solution, the following was obtained [9]

$$\ln \gamma_{A,B} = -\frac{C_B^2 Z E_{\text{mix}}}{kT}. \quad (60)$$

Here, Z is the coordination number, and the mixing energy is expressed through the pair interaction potentials of atoms in the form

$$E_{\text{mix}} = \Phi_{AB} - \frac{\Phi_{AA} - \Phi_{BB}}{2}. \quad (61)$$

When investigating the Kirkendall effect, the hypothesis of the local equilibrium gas of vacancies is used. According to this hypothesis, the vacancy concentration at a point is unambiguously determined by the local concentration of a component as follows: $C_V = C_V(C_{A,B})$, ($C_A + C_B = 1$). In this case, the substitution of $C_V(C_{A,B})$ in Eq. (53) allows one to reduce the problem to the interdiffusion of the alloy components [9]. The hypothesis of a locally equilibrium vacancy gas rests on the assumption that there are many vacancy sources/sinks at characteristic lengths of the alloy composition change and, as a result, this vacancy concentration is adjusted to the composition. This hypothesis was well justified in the study of diffusion, the driving force of which is the concentration gradients of components typical of metallurgical processes. In our case, the driving force is associated with thermodynamic factors, and the same occurs during

spinodal decomposition. The characteristic length of the change in the concentration curve is the same that the width of the equilibrium interphase boundary, which is about 2 nm. There are no vacancy sources/sinks at this distance; therefore, the equation for the flux in the form (57) at $j_V = 0$ should be used to describe the spinodal decomposition.

In the case of severe plastic deformation, the vacancy fluxes are determined by the action of sources and sinks located in grain triple junctions [5]. Since the distance between them is greater than the grain size, the condition $j_V = \text{const}$ can be laid down to describe the diffusion at these scales. This also requires to investigate the vacancy-flux-induced decomposition of equilibrium diffuse boundaries using an expression for the diffusion flux similar to Eq. (57).

NONLOCALITY IN THERMODYNAMIC DESCRIPTION OF DIFFUSION IN BINARY HETEROGENEOUS ALLOYS

The new hypothesis was formulated above, which can replace the hypothesis of local equilibrium in the case of heterogeneous systems. According to this hypothesis, the argument of a chemical potential within the study of one-dimensional diffusion in substitutional alloys is the functional of an order parameter described by Eq. (5). One should take into account that nonlocality is associated with the nonideality of solid solution. Indeed, there are no phases in an ideal solid solution. The activity coefficients of the components characterize the difference between real solid solution and ideal one. They are associated with correlation effects and expressed through the interatomic interaction energy [9]. Relying on the above, suppose that the functional of an order parameter (functional of component concentration in our case) is only an argument of the component activities included in Eq. (44) for chemical potentials. For the chemical potentials of nonideal solid solutions, the following refined expression can be introduced:

$$\mu_{0A,B} = kT \ln(C_{A,B} \gamma_{A,B}(\Phi_{C_{A,B}})) + \mu_{0A,B}^0 \quad (62)$$

The expansion of functional (7) and the subsequent expansion of the activity coefficient in coordinates, Eq. (57) can be rearranged into a new equation for diffusion fluxes

$$j_A = \Lambda^2 \frac{D_A^* D_B^*}{C_V D_V} (1 - g_G) \frac{\partial^3 C_A}{\partial x^3} - D_G \frac{\partial C_A}{\partial x} - C_A C_B \frac{D_A^* D_B^*}{C_V D_V} j_V. \quad (63)$$

For regular solid solution, this equation takes the form

$$j_A = \Lambda^2 \psi C_A C_B \frac{D_A^* D_B^*}{C_V D_V} \frac{\partial^3 C_A}{\partial x^3} - \frac{D_A^* D_B^*}{C_V D_V} \times (1 - \psi C_A C_B) \frac{\partial C_A}{\partial x} - C_A C_B \frac{D_A^* D_B^*}{C_V D_V} j_V, \quad (64)$$

where ψ is the relative mixing energy

$$\psi = \frac{2ZE_{\text{mix}}}{kT}. \quad (65)$$

Let us put $j_V = 0$ when there are no vacancy fluxes specified by the external action. Then, Eq. (63) for the flux of a component becomes a balance equation that agrees with the equations of the theory of spinodal decomposition [12]. The difference is that the coefficient of the leading derivative is formally introduced as a small fitting parameter in the theory of spinodal decomposition. In our case, the coefficient is expressed through the diffusion parameters and the value of Λ , which is proportional to the radius of the functional kernel. This makes it possible to estimate the width of a nonequilibrium interphase boundary that is ~ 2 nm, which is in good agreement with the experimental data [2] for the nonequilibrium interphase boundary.

DECOMPOSITION OF INTERPHASE BOUNDARIES INDUCED BY VACANCY FLUX

Let us develop composition distribution in an alloy with allowance for the action of a constant vacancy flux in it. The equation specifying the stationary concentration curve can be written for a regular solid solution based on Eq. (64), provided that $j_A = 0, j_V = \text{const}$. This equation has the form

$$\Lambda^2 \psi \frac{\partial^3 C_A}{\partial x^3} - \left(\frac{1}{C_A C_B} - \psi \right) \frac{\partial C_A}{\partial x} = \frac{D_A^* D_B^*}{D_A^* D_B^*} j_V. \quad (66)$$

Twice integrating Eq. (66) yields an expression similar to the equation of nonlinear oscillations of the material point

$$\frac{1}{2} \Lambda^2 \psi \left(\frac{dC_A}{dx} \right)^2 - U(C_A) = a. \quad (67)$$

The function of concentration plays the role of the potential

$$U(C_A) = f(C_A) + j_V \Phi(C_A) + b C_A, \quad (68)$$

$f(C_A)$ is the free energy of a regular solid solution per lattice site, which is defined by the expression

$$f(C_A) = -\frac{1}{2} \psi (1 - C_A) C_A - C_A \ln C_A - (1 - C_A) \ln (1 - C_A). \quad (69)$$

Here, a , b are integration constants and Φ is determined by the expression

$$\Phi(C_A) = \int^{c_A} dC_A' \int^{c_A'} dC_A'' \times \frac{1}{\left(\frac{dC_A''}{dx}\right)} \left(\frac{1}{D_B^*(C_A'')} - \frac{1}{D_A^*(C_A'')} \right). \quad (70)$$

In equilibrium state, there is no vacancy flux ($j_V = 0$) and the curve of the interphase boundary is described by the following equation at $b = 0$ and $a = a_e$:

$$\frac{1}{2} \Lambda^2 \Psi \left(\frac{dC_A}{dx} \right)^2 - f(C_A) = a_e. \quad (71)$$

These values correspond to the condition when the straight line $y = a + bC_A$ touches the curve $f(C_A)$ at two points of minima, where $f(C_{A1,2}^e) = a_e$. In the theory of heterogeneous systems, this line is called the *conode*. This position of the conode with respect to the free energy curve provides the minimum free energy of the equilibrium system [13]. Concentration values at the points where the conode is in contact with the free energy curve correspond to equilibrium solubility limits $C_{A1,2}^e$, which for regular solid solution are determined by the following equation:

$$\frac{1}{2} \Psi(1 - 2C_A^e) = \ln \frac{1 - C_A^e}{C_A^e}.$$

This result coincides with the classical equilibrium theory for heterogeneous systems. An analysis based on Eq. (71) yields one more result in the form of the profile of the equilibrium diffuse interphase boundary of a binary substitutional alloy. The curve $C_A^e(x)$ of this profile is shown in Fig. 1.

The imposition of the vacancy flux shifts the potential curve downward and causes the composition modulations (curve $C_A(x; j_V)$ at the bottom of Fig. 1). To prove this it is convenient to introduce a new dependent variable that is analogous to the Lagrangian as follows:

$$L = T - U = \frac{1}{2} \Lambda^2 \Psi \left(\frac{dC_A}{dx} \right)^2 - f(C_A) + j_V \Phi(C_A). \quad (72)$$

Here $b = 0$, which ensures the transition to an equilibrium state when there is no vacancy flux, and T is the analog of the kinetic energy.

The Lagrangian satisfies the homogeneous nonlinear equation

$$\frac{d^2 L}{dC_A^2} - j_V \Lambda \sqrt{\frac{\Psi}{2} \frac{D_A^* - D_B^*}{D_A^* D_B^*}} \frac{1}{\sqrt{L + f}} = 0, \quad (73)$$

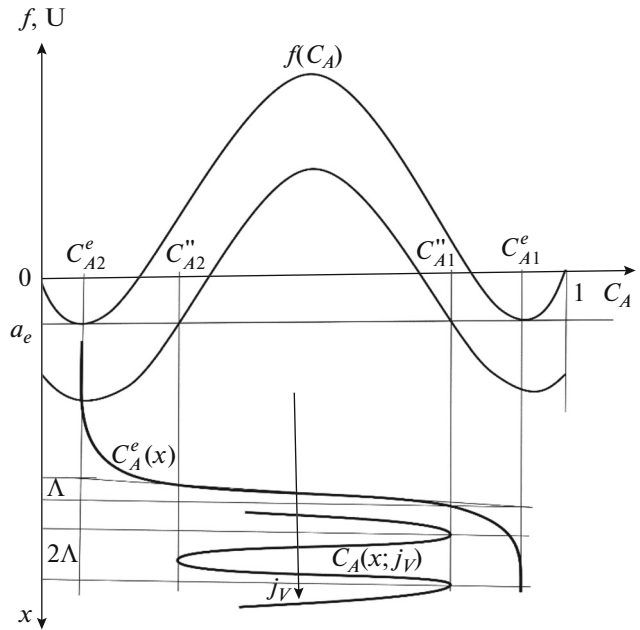


Fig. 1. Free energy $f(C_A)$ and potential function curves that result from perturbations in alloys induced by the vacancy flux in the upper part of the image. Equilibrium and non-equilibrium concentration curves at the bottom.

which makes it possible to create an iterative procedure for deriving a solution of the nonlinear oscillation equation.

In equilibrium, at $j_V = 0$, we obtain

$$\frac{d^2 L_0}{dC_A^2} = 0,$$

$$L_0 = T_0 - f = a_e,$$

from which it follows that

$$\frac{1}{2} \Lambda^2 \Psi \left(\frac{dC_A}{dx} \right)_0^2 - f(C_A) = a_e.$$

Then, by the first iteration, we get

$$\frac{d^2 L}{dC_A^2} = j_V \Lambda \sqrt{\frac{\Psi}{2} \frac{D_A^* - D_B^*}{D_A^* D_B^*}} \frac{1}{\sqrt{L_0 + f}}$$

or

$$\frac{1}{2} \Lambda^2 \Psi \left(\frac{dC_A}{dx} \right)^2 - f(C_A) \pm j_V \int^{c_A} dC_A' \int^{c_A'} dC_A'' \frac{1}{\left(\frac{dC_A''}{dx}\right)} \frac{D_A^* - D_B^*}{D_A^* D_B^*} = a_e. \quad (74)$$

The sign of the last term changes after passing through the inversion points of curve $C_A(x)$. The sign

should be selected in a way that ensures the intersection between the curve

$$U(C_A) = f(C_A) \pm j_V \int^{C_A} dC'_A \int^{C'_A} dC''_A \left| \left(\frac{dC_A}{dx} \right)_0 \right| \left(\frac{1}{D_B^*} - \frac{1}{D_A^*} \right)$$

and the conode, which is necessary for the existence of the inversion point of the curve.

The concentration gradient of a component can be estimated from the parameters of the equilibrium curve

$$\left| \left(\frac{dC_A}{dx} \right)_0 \right| = \frac{|C_{A1}^e - C_{A2}^e|}{\Lambda}$$

For the difference between the inverse self-diffusion coefficients, the simplest linear approximation will be applied, which allows one to vary the position of the point at which these quantities are equal, depending on the position of C_A^0 with respect to interval $(C_{A,1}^e, C_{A,2}^e)$

$$\frac{1}{D_B^*} - \frac{1}{D_A^*} = \frac{C_A^0 - C_A}{C_V d},$$

where d is the scale parameter with the dimension of the diffusion coefficient. This choice of the integrand for Eq. (74) and its integrating results in

$$\frac{(C_A - C_A^0)^2}{C_V d}.$$

This approximation gives the equation of nonlinear oscillations in the form

$$\frac{1}{2} \Lambda^2 \Psi \left(\frac{dC_A}{dx} \right)^2 - U(C_A) = a_e, \quad (75)$$

where

$$U(C_A) = f(C_A) - \frac{\Lambda |j_V| (C_A - C_A^0)^2}{d C_V |C_{A1}^e - C_{A2}^e|}.$$

The obtained form of the potential shifts the initial curve downward, and the shift is proportional to the vacancy flux. This causes the inversion points of the curve (see $C_A(x; j_V)$ curve shown at the bottom of Fig. 1). The distance between them along the Ox axis is of the order of the width of the equilibrium interphase boundary.

Equations (63) and (64) for the diffusion flux are analogous to those obtained within the framework of the nonequilibrium vacancy gas model [10, 14]. This model is a version of the semiphenomenological theory of K.P. Gurov [9]. The approach developed here and the nonequilibrium vacancy gas model are

completely consistent when the following conditions are met:

$$D_{A,B}^* = C_V \omega'_{A,B}, \quad \omega'_{A,B} = \gamma_{A,B}. \quad (76)$$

Since it follows from Eq. (76) that $D_{A,B}^* = C_V \gamma_{A,B}$, the vacancy gas theory imposes a restriction on the quantities that are regarded as independent in the thermodynamic theory of diffusion in alloys.

Taking into account that the nonequilibrium vacancy gas model is in agreement with the proposed version of nonequilibrium thermodynamics, provided that conditions (76) are met, it can be shown that allowance for nonlocality in both approaches also leads to identical equations. Thus, expression (64) for the component flux coincides with the corresponding expression in [14]. The latter was used to perform numerical calculations of the evolution of the component concentration, provided that the vacancy flux affected the equilibrium interphase boundary in a one-dimensional case [15]. As a result (see Fig. 2), it was shown that the vacancy flux decomposes the interphase boundary and leads to the formation of a modulated structure. For the simplicity of calculations, the relative mixing energy was chosen to be 4.24, which is slightly higher than a critical value of 4, below which no composition modulations occur. As a result, the numerical calculation yielded composition modulations with a relatively large spatial period.

In summary, the effect of a vacancy flux may cause the decomposition of an interphase boundary and the appearance of composition modulations instead, which may explain the data of [1–3].

DISCUSSION

The results of the composition redistribution during the mechanical alloying of the Fe–Cr, Cu–Co, and Cu–Fe powders were previously discussed in [10]. The discussion was based on the model of nonequilibrium gas of vacancies, which took into account the nonlocal composition dependence of the frequencies of atom–vacancy transition [14].

In the present work, a similar result was obtained based on the nonequilibrium thermodynamics method developed here to describe heterogeneous systems as continuous medium. This work demonstrates the potentials of a new approach using the experimental data that have already been interpreted in another theoretical description.

In order for the equations for the material fluxes in our version of the Onsager method to be in agreement with analogous equations for the nonequilibrium vacancy gas theory, equation $D_{A,B}^* = C_V \gamma_{A,B}$ should be valid. However, the self-diffusion coefficients $D_{A,B}^*$ in nonequilibrium thermodynamics are determined through the diagonal elements of the

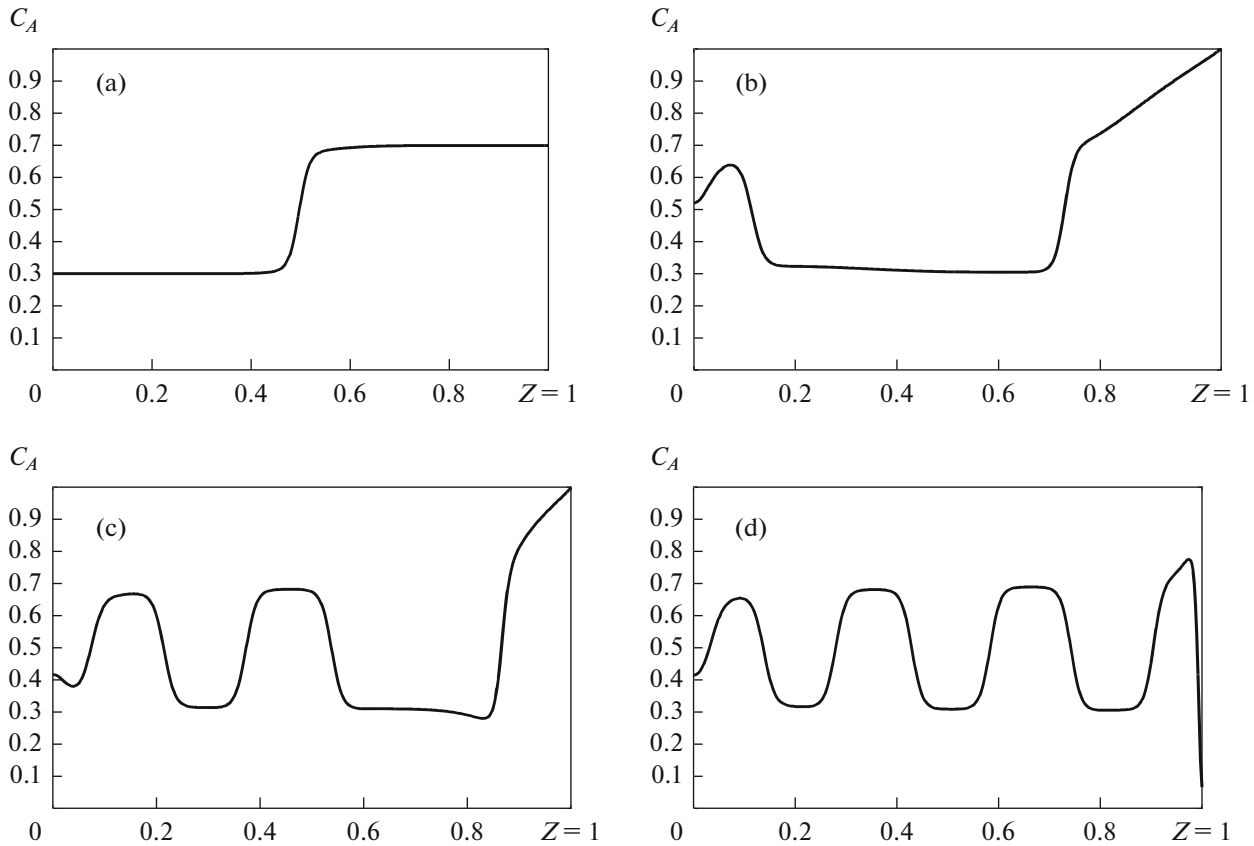


Fig. 2. Evolution of composition distribution during interphase boundary decomposition induced by vacancy flux crossing the boundary [15]: (a) initial stage and (d) final stage.

Onsager matrix (49), whereas the coefficients of thermodynamic activity $\gamma_{A,B}$ characterize the structure of the chemical potential (44). On the other hand, kinetic coefficients and the gradients of chemical potentials appear as factors in expressions for thermodynamic flows. That is, the chemical potentials and the coefficients of the Onsager matrix in linear nonequilibrium thermodynamics are considered to be independent quantities; therefore, the restriction $D_{A,B}^* = C_V \gamma_{A,B}$, which is imposed by the nonequilibrium vacancy gas theory, is unjustified and cannot be applied without further investigation. It is necessary to highlight several main aspects of the proposed version of the nonequilibrium thermodynamics of heterogeneous systems.

The first aspect is associated with a nonlocal dependence of fluxes and thermodynamic forces on order parameters. This nonlocality makes an allowance for the collective character of the interactions of material particles, which results in the formation of interphase boundaries. The formal aspect of accounting for the nonlocality is associated with the introduction of the dependence of thermodynamic quantities on the functionals of the order parameters, rather than the local values of these parameters in the analysis.

The small radius of the functional kernel makes it possible to expand the integrand in terms of coordinates, which automatically leads to singularly perturbed problems when writing the differential balance equations. An example of this problem is the theory of spinodal decomposition developed based on the Cahn–Hilliard approach [12]. When there are no vacancy fluxes in an equilibrium regular solid solution, we obtain results that are consistent with the classical equilibrium theory of heterogeneous systems.

The second aspect is associated with the change in the conjugate thermodynamic force of the flux of matter. It is chosen to be proportional to the difference in state probabilities that arise when these regions exchange atoms and the corresponding number of vacancies with each other, rather than the difference in chemical potentials in the neighboring regions of the alloy. The probabilities of local states with a certain concentration of components and vacancies are expressed in the form $W_{A,B,V} = \exp(-\mu_{0A,B,V}/kT)$, whereas the flux is proportional to

$$j'_{A,B} \sim \frac{W_{A,B}(x + \Delta x)W_V(x) - W_{A,B}(x)W_V(x + \Delta x)}{W_{A,B}(x)W_V(x)}.$$

As a special case, this approach includes the conventional version of the diffusion description. Indeed, if we suppose $W_V(x) = \text{const}$ and take into account the relationship between the probabilities and the chemical potential, for isothermal diffusion, we obtain the classical version

$$j'_{A,B} \sim (\mu_{0A,B}(x + \Delta x) - \mu_{0A,B}(x)).$$

Taking into account the above general equation for the thermodynamic force, it can be shown that the thermodynamic description of diffusion in substitutional alloys and vacancy gas theory are in agreement. The vacancy gas theory was tested on a wide experimental material.

The third aspect is associated with the application of the Euler method rather than the Lagrange method for deriving the entropy balance equation. A peculiar feature of the Lagrange method requires Gibbs equations to be used in a version that is unsuitable for analyzing open systems. This makes it impossible to derive the entropy balance equation for a heterogeneous system, which is considered to be a continuous medium. The Euler method rests on the idea of a selected fixed volume that can be considered as an open system. This makes it possible to derive an entropy balance equation for a heterogeneous system and to develop a version of the Onsager approach for it.

However, the problem emerges of choosing the frame of reference in which the relationship between thermodynamic forces and fluxes can be established. Otherwise, the freedom of flux values due to the possibility of change in the reference systems leads to physically meaningless results. In our case, we chose a frame of reference that is bound to the crystal lattice and, thus, equations for numerical diffusion fluxes were derived that were consistent with the expressions for the vacancy gas theory.

This choice of the frame of reference allows one to develop a thermodynamic approach that is simultaneously suitable for describing the Kirkendall effect, the spinodal decomposition of a homogeneous metastable solid solution, and the vacancy-flux-induced decomposition of an equilibrium interphase boundary. The latter made it possible to perform a semiquantitative interpretation of the experimental data on the composition distribution in the powders of pure metals during mechanical alloying.

The combination of these circumstances makes it possible to consider the choice of the frame of reference bound to the crystal lattice to be justified when determining the dependence of the fluxes on thermodynamic forces.

The choice of the coordinate system bound to the crystal lattice is the choice of the frame of reference that is associated with space, the metric of which is defined by the crystal lattice.

The advantage of choosing a frame of reference bound to space was recently discussed in detail in view

of the interpretation of new data on the distribution of matter in the universe in the context of quantum field theory [16, 17]. This coincidence may acquire significance in light of the model of the World Planck–Kleinert crystal, the analysis of which in terms of transport phenomena was carried out in [18].

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