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The mechanism of the impurity redistribution between phases of variable and constant compositions

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The problem with describing the redistribution of impurities at the interface between phases of variable and constant composition is closely related to the impossibility of thermodynamically determining chemical potential for a phase of constant composition as a derivative by a variable of the impurity concentration. It is shown that the deviation of the chemical potential of a variable composition phase from its equilibrium value, determined by the common tangent to the Gibbs energies of the interacting phases, can be chosen as the thermodynamic force for the impurity transfer at interface between phases of constant and variable composition. The equations of the phase field dynamics and of the impurity redistribution is derived from non-equilibrium thermodynamics. The results of numerical modeling show qualitative compliance with the expected behavior and are presented in the form of graphs of the concentration distribution and the phase field.

Keywords: phase transformations, stoichiometric phases, phase field method.

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The process of impurity redistribution under phase changes in the solutions with the participation of phases, where no impurities dissolve, was studied within the phase field method. Such phases with fixed stoichiometric ratio are called „stoichiometric" in contrast to variable composition phases (VCP) [1]. Stoichiometric phases (SP) are present in most technical alloys [2]. The relevance of the study of processes to generate the materials containing SPs, depends on their impact at strength characteristics [3] and is still maintained [4].

The phase field method [5] is most sought after in the theoretical description of the microstructure formation process, since it relies on the thermodynamics of equilibrium states of solutions based on Gibbs potentials [1]. The latter as the functions of concentrations and temperature are produced from the experiment and are interpolated between the equilibrium states using the parameter of order φ (phase field). For the SP the Gibbs energy defines the dependence of energy on temperature at certain composition [6].

The objective of the study is theoretical description of isothermal redistribution of the impurity between the fluid phase of solution Al–Y with initial (molar) concentration $x(\mathbf{r},0)$ and one of SPs (Al_2Y) with (molar) concentration of impurity x_0. Fig. $1,a$ shows a typical example of molar densities for real Gibbs potentials $G^L(x,T_0)$ of fluid phase and $G^S(T_0)$ for SP Al_2Y at temperature $T_0 = 1173\,\mathrm{K}$ [6]. Previously the processes of SP formation in Al–Y were studied many times experimentally [7]. The isothermality condition suggests that the temperature is homogeneous in space, but may change with time. In virtue of difference between the coefficients of thermal conductivity and diffusion by orders of magnitude, the impact of the temperature distribution at the phase transition in this objective with two phases is not relevant.

The main obstacle to the theoretical description of phase changes with the participation of SP is the absence of chemical potential in them. The VCP chemical potential is [1] derivative $\mu = \partial G(x,T)/\partial x$, which determines the driving forces both for the transfer of the impurity via the phase boundaries and for the movement of the boundary itself [8]. Since the molar concentration of impurity x_0 in SP is fixed, the absence of the derivative by concentration for SP makes the direct transfer of the phase-field description of VCP dynamics [8] to the SP case impossible. Attempts are known [9] to replace the SP Gibbs energy with „narrow" parabolic function of the composition, considering the growth and degradation of the SP as VCP. Since the result directly depends on the artifacts of selection (for example, function curvature), such approach is ambiguous and incompetent, as shown further.

The alternative approach was used by Miura [4,10] and was continued in paper [11]. This approach takes into account the diffusion of the impurity only inside a fluid phase. Incorrect description in the redistribution of the impurity at the phase boundary in this approach manifests itself in the form of appearance of a „plateau" at $\varphi = 0.5$ in the phase field curves [11].

Let us consider the conditions of phase growth according to Hillert [1] (fig. $1,a$). At fluid phase concentration x in the interval of $x_1 < x < x_2$ the SP Al_2Y must grow, since the tangent to the curve $G^L(x,T_0)$ passes higher $G^S(T_0)$. The latter means there is a driving force for

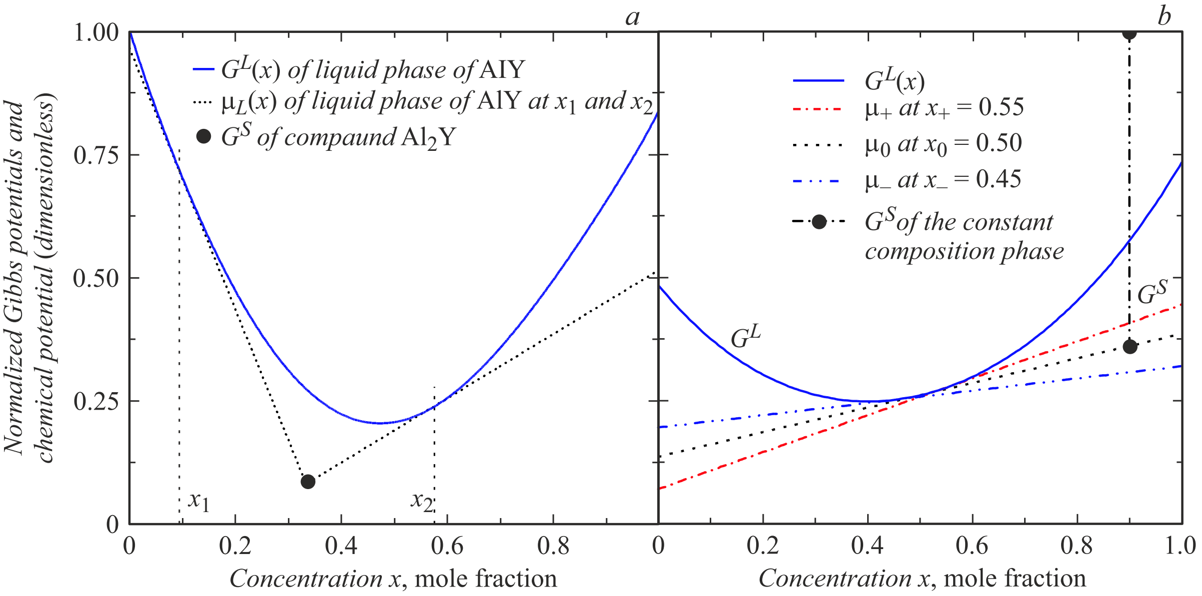

Figure 1. a — dimensionless potentials [7] of fluid phase Al–Y and SP Al_2Y. The solid line shows the dependence of the molar density of potential G^L on molar concentration Y. Molar density of SP Gibbs potential Al_2Y G^S is marked with a black circle. The dotted line shows the chemical potentials of the fluid phase in the equilibrium positions of the fluid and SP (points x_1, x_2) at $T = 1173$ K, the dashed lines show equilibrium concentrations x_1 and x_2. b — dimensionless model. Gibbs potentials of variable (G^L) and fixed (G^S) composition phases. The change in the chemical potentials of the fluid phase is shown against the change in the impurity concentration. The inclined dotted and dash-and-dot lines correspond to the SP chemical potentials for concentrations $x_0 = 0.5$, $x_+ = 0.55$ and $x_- = 0.45$, the vertical dash-and-dot line fixes the position of point G^S in the fixed composition phase, the other designations correspond to fragment a.

the SP growth. At the initial concentration x beyond the interval $x_1 < x < x_2$ the tangent to the fluid phase is below the SP Gibbs energy, which corresponds to SP dissolution. To consider the transfer of the impurity at the phase boundary, let us conditionally draw in fig. 1, b the model Gibbs potentials G^L VCP and G^S SP, and also chemical potentials $\mu_0(x_0)$, $\mu_+(x_+)$, $\mu_-(x_-)$ for the concentration values $x_0 = 0.55$, $x_+ = 0.5$, $x_- = 0.45$. The conditions of the phase equilibrium are reduced to the presence of the common tangent between the phases: $\mu_0(x_0)$. Accordingly, the equilibrium VCP in respect to the SP will be the VCP with concentration x_0. If the concentration in VCP differs from the equilibrium one ($x_+ > x_0$ or $x_- < x_0$, fig. 1, b), its chemical potential will differ from $\mu_0(x_0)$, therefore the system changes to the equilibrium, pushing out (or pulling inside) some of SP impurity. As a result the concentration in the VCP changes, trying to reach the equilibrium one x_0. In fig. 1, b this corresponds to the balancing of chemical potentials $\mu_\pm(x_\pm) \Rightarrow \mu_0(x_0)$ Therefore, the thermodynamic force defining the impurity transfer through the boundary between the SP and VCP is related to the deviation of the VCP potential $\mu(x)$ from its equilibrium value μ_0. This means that the flow of the impurity between the phases is proportionate to the deviation of the VCP chemical potential from the equilibrium value μ_0:

$$J_D \propto \mu^L(x) - \mu_0. \tag{1}$$

Going back to fig. 1, a, note that the tangents to the curve of the fluid phase Gibbs potential $G^L(x)$, passing through the value G^S SP at concentration x_0, define the concentrations x_1 and x_2, when the phases are equilibrium [1]. Let the share $p(\varphi) = \varphi^2(3 - 2\varphi)$ of the volume unit correspond to SP Al_2Y, and $p(1 - \varphi) = 1 - p(\varphi)$ — to the fluid phase share. In SP (S) the parameter of order $\varphi = 1$, inside the fluid phase volume (L) $\varphi = 0$. Values of field $0 < \varphi < 1$ correspond to the phase interface [6]. Neglecting the change in the substance density at the phase boundaries and recalculating the Gibbs potentials per unit of volume, for interpolation of the energy by phases with account of the surface energy $(\nabla\varphi)^2$ we note the following [6]:

$$G(t) = \int \Big((1 - p(\varphi))G^L(x, T_0) + p(\varphi)G^S(T_0) + Wg(\varphi) + \frac{1}{2}\sigma(\nabla\varphi)^2\Big)dV, \tag{2}$$

where function $g(\varphi) = \varphi^2(1 - \varphi)^2$ — potential barrier between the thermodynamically stable phases of height W. Parameters of the functionality (2) are expressed via the coefficient of surface energy χ and half-width of the diffuse boundary δ [9]:

$$\sigma = 3\chi\delta, \qquad W = \frac{6\chi}{\delta}. \tag{3}$$

The average concentration of the impurity in the volume unit of solution $\langle x \rangle = (1 - p(\varphi))x + p(\varphi)x_0$ (where $x_0 = 0.33$ — impurity concentration in SP Al_2Y, x — impurity concentration in VCP) is subordinate to the

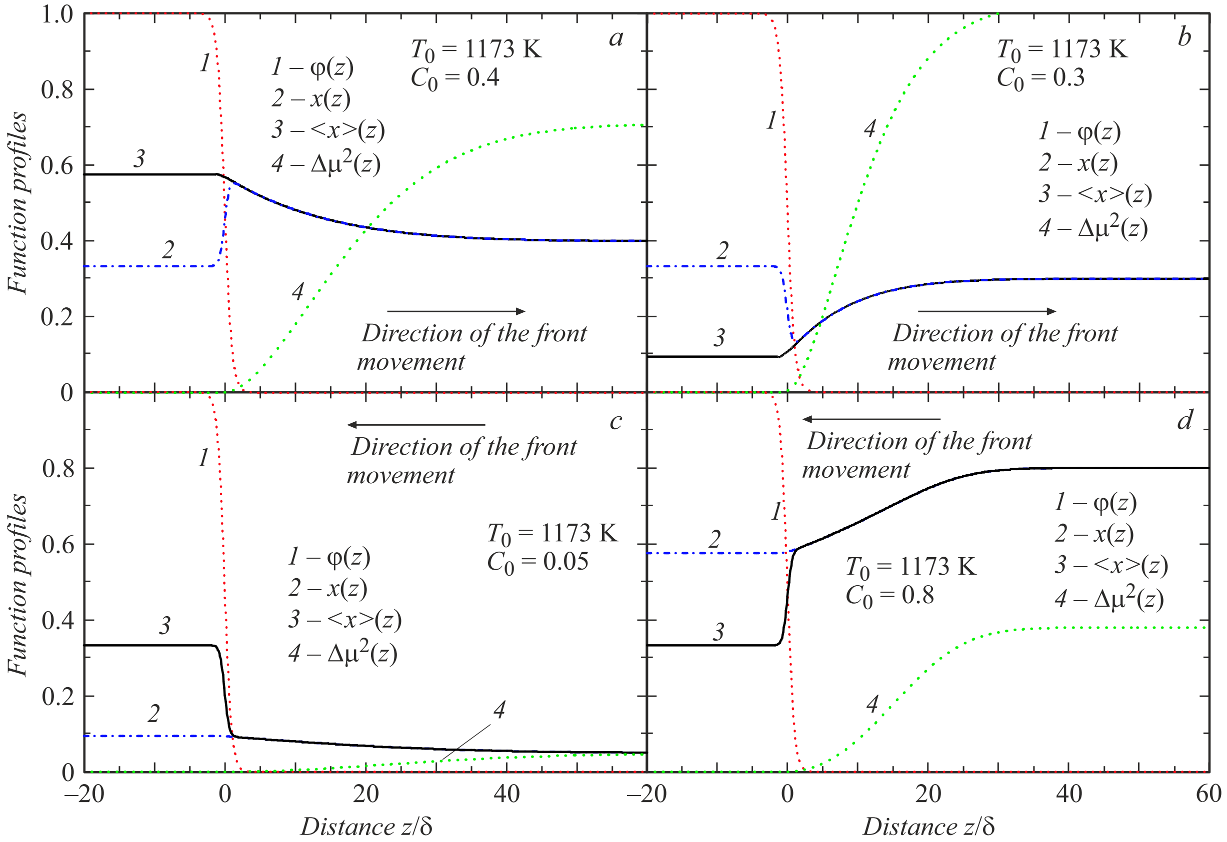

Figure 2. Profiles of $x(z)$, $\varphi(z)$ and $\langle x\rangle$ concentration along the space interval at temperature $T_0 = 1173\,\mathrm{K}$. Inside the diffuse boundary (at $\varphi \to 1$) the deviation of the chemical potential of the fluid phase from the equilibrium value $(\mu^L - \mu_0)^2 \to 0$. *a* — initial concentration of the impurity in the fluid phase $C_0 = 0.4$ $(x_0 < C_0 < x_2)$; *b* — $C_0 = 0.3$ $(x_1 < C_0 < x_0)$; *c* — $C_0 = 0.05$ $(C_0 < x_1)$; *d* — $C_0 = 0.8$ $(x_2 < C_0)$.

conservation principle and may only change due to the diffusion flow J_D, then

$$(1-p)\frac{\partial x}{\partial t} = -(x_0 - x)\frac{\partial p}{\partial t} - (1-p)\nabla \cdot J_D, \qquad (4)$$

since diffusion may only happen in the share $(1-p)$ of the volume unit occupied by VCP.

Requesting the subtraction of full Gibbs energy (2) [9] and assuming that the homogeneous boundary conditions of the second kind were met for φ, and the diffuse flow at the area boundary turns zero, we get the phase field relaxation equations and the expression for J_D. In the dimensionless variables for the numerical modeling of the problem with account of (3) we have

$$\frac{\partial \varphi}{\partial t} = \nabla^2 \varphi - 2g' - \Delta\tilde{\Omega} p', \qquad (5)$$

where $p' = dp/d\varphi$, $g' = dg/d\varphi$ — derivatives with respect to the argument of functions $p(\varphi)$, $g(\varphi)$. The difference of grand potentials is equal to $\Delta\tilde{\Omega} = \tilde{G}^S - \tilde{G}^L - \tilde{\mu}^L(x_0 - x)$. With account of replacement (1) the full flow is $J_D = -\alpha\nabla\big((1-p)(\tilde{\mu}^L - \tilde{\mu}_0)\big)$, which leads to the following diffusion equation

$$(1-p)\frac{\partial x}{\partial t} = -(x_0 - x)\frac{\partial p}{\partial t} + (1-p)\alpha\nabla^2\big((1-p)(\tilde{\mu}^L - \tilde{\mu}_0)\big). \qquad (6)$$

Values with the tilde ($\Delta\tilde{\Omega}$, $\tilde{G}^\alpha$, $\tilde{\mu}$) in (5), (6) are renormalized values. Usually the diffusion processes are slower than the kinetic processes in the front, which provides estimate $\alpha \approx 10^{-2}$. Note that expression (6) is divided into two contributions: Fick volume diffusion ($J_D \propto \nabla\mu^L$) and contribution ($J_D \propto \Delta\mu\nabla p$), providing for transfer of the impurity between the phases.

For the numerical solution to equation (6) the explicit finite-difference algorithm was used in the area $p(\varphi) < 0.98$. At $p(\varphi) \geq 0.98$ in virtue of the small share of the fluid phase it was assumed at it is balanced with SP, which corresponds to $x = x_{1,2}$ (depending on the initial concentration of the solution). The algorithm stability was determined empirically. The limitation by time increment is $\Delta t \leq 0.1141\Delta z^2$, where Δz — space increment.

The equation for the phase field in the system (5) was solved implicitly with the help of a gradient-stable algorithm. The problem of unidimensional movement of the flat front along axis z was solved numerically. The integration area includes a space interval with size of 100δ broken down into 1000−4000 space increments. The boundary conditions for the phase field at the ends of the interval are the homogeneous conditions of the second kind. SP ($\varphi = 1$) is on the left, and on the right — the solution in VCP with concentration $x(0, z)$. The initial conditions are $x(0, z) = C_0 = \text{const}$ for the concentration in the fluid phase and $\varphi_0(z) = \frac{1}{2}(1 - \tanh(z - z_0))$ for the phase field.

Numerical calculations showed that at the initial concentration of the fluid phase impurity in the interval $x_1 < C_0 < x_2$ the phase boundary in the solution starts moving to the right to achieve the equilibrium state in the entire area (fig. 2, *a, b*). If $x_0 < C_0 < x_2$, the excess impurity is displaced to the fluid phase area, and a ledge is formed, which moves upstream the front (fig. 2, *a*). Otherwise, $x_1 < C_0 < x_0$, a dip is formed upstream the front. The impurity is pumped out of the fluid phase to form SP (fig. 2, *b*). At the initial concentration of solution $C_0 < x_1$ or at $C_0 > x_2$ the SP is dissolved (the front moves to the left, fig. 2, *c, d*), therefore the concentration of the solution upstream the front increases nearly to the equilibrium one, which complicates the SP dissolution process.

The obtained study results suggest the following. 1. The driving force to exchange the impurity at the phase boundary is the deviation of the VCP chemical potentials from the equilibrium values.

2. Numerical study of the isothermal unidimensional model shows its validity and agrees with the previously known facts.

3. Correct replacement (1) is confirmed by the absence of „non-physical“ numerical solutions for the phase field (in the form of a step at $\varphi = 0.5$ [11]).

4. If there is SP, the driving forces for the migration of the phase boundary are expressed via the VCP chemical potential. Therefore, all the attempts to interpolate the SP Gibbs potentials with the V P Gibbs potentials will be incorrect.

5. The model may serve as the basis for the computer modeling of real materials. The latter is relevant in connection with the development of the computer means to model the structure formation of the processes in the non-equilibrium states, including to study the glass formation processes [12].

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Hillert, *Phase equilibia, phase equilibria, phase diagrams and phase transformations. Their thermodynamic basis*, 2nd ed. (Cambridge University Press, Cambridge, 2008).

[2] D. Herlach, P. Galenko, D. Holland-Moritz, *Metastable solids from undercooled melts* (Elsevier, Amsterdam, 2007).

[3] J. Liu, X. Wang, A.P. Singh, H. Xu, F. Kong, F. Yang, Metals, **11**, 2054 (2021). DOI: 10.3390/met11122054

[4] H. Miura, Phys. Rev. E, **98**, 023311 (2018). DOI: 10.1103/PhysRevE.98.023311

[5] N. Provatas, K. Elder, *Phase-field methods in materials science and engineering* (Wiley-VCH, Weinheim, 2010).

[6] http://cpddb.nims.go.jp/cpddb/periodic.htm

[7] S.G. Menshikova, I.G. Shirinkina, I.G. Brodova, V.V. Brazhkin, Russ. Metall., **2019**, 135 (2019). DOI: 10.1134/S0036029519020150.

[8] V.G. Lebedev, JETP Lett., **115** (4), 226 (2022). DOI: 10.1134/S0021364022040075.

[9] M.S. Park, S.L. Gibbons, R. Arroyave, Acta Mater., **60**, 6278 (2012). DOI: 10.1016/j.actamat.2012.07.063

[10] H. Miura, Materialia, **31**, 101860 (2023). DOI: 10.1016/j.mtla.2023.101860

[11] S.A. Korobeynikov, V.G. Lebedev, V.I. Ladyanov, Tech. Phys., **69** (10), 1500 (2024)]. DOI: 10.61011/TP.2024.10.59352.110-24.

[12] C.P. Royall, F. Turci, T. Speck, J. Chem. Phys., **153**, 090901 (2020). DOI: 10.1063/5.0006998

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