The local–nonequilibrium kinetics of growth of stoichiometric compounds under isothermal condition: phase–field approach

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Abstract. The presence of line (stoichiometric) compounds in alloys of light metals greatly improves their mechanical and strength properties. The formation of Al₃Y and Al₂Y line compounds in a highly supercooled Al–Y melt is investigated using the phase field method and numerical modeling of the directional solidification of the melt. The main problem in the phase-field description of phase transitions in line compounds is finding the driving forces of these transitions. One of the possible ways to handle this problem is development of a thermodynamically consistent phase-field approach based on the minimization of the full Gibbs energy of the system, nonequilibrium thermodynamics and separation of diffusion processes in different phases. The resulting equations are analyzed in the equilibrium case. The model dynamics is examined numerically for the case of the one-dimensional problem of directional solidification of the Al–Y melt under isothermal condition. The analysis of the numerical solutions shows that initially the transformation of the melt from liquid to solid happens due to the driving forces of the phase transition, while further formation of the spatially–nonhomogeneous laminated structure is caused by the interfacial barriers.

1. Introduction
Many insoluble intermetallic precipitates, or precipitates with extremely small solubility, are known as “line compounds”. The free energy of these compounds, by definition, is represented by a single value at a given temperature. The phase-field description of stoichiometric compound growth, similarly to the description of growth of phases with variable composition, poses serious challenges, since the derivative of the free energy with respect to concentration does not exist. One of the possible solutions is the approximation of the line compound free energy by the parabolic function of its composition [1, 2]. Hu with co-authors [3] pointed out the inconsistency of this approach and noted the difficulties encountered in processing the logarithmic contributions to the Gibbs potentials [4]. Hu presented [3] a thermodynamically more consistent view on the solidification kinetics of stoichiometric phases. His assumption about equality of chemical potentials of the compound and variable composition phase leads to the tangent construction for the driving forces of the phase transition. However, in paper [3] the diffusion equation is written for average concentrations of different phases, without consideration of dynamic peculiarities in each phase. It is easy to show that if diffusion in different phases
is separated, then we get the correct equation of interaction between the compounds and the phases with variable composition.

As an example let us consider the phase-field description and modeling of peritectic reaction which is frequently encountered in technologically important materials (e.g., steels, brass, bronze, intermetallic compounds, magnetic materials and YBa$_2$Cu$_3$O$_x$ superconductors). Many interesting microstructures have been found during directional solidification of peritectic alloys, which have attracted much attention since the last decade. In the present work, in order to investigate the growth behavior of the Al$_3$Y phase as a peritectic phase modeling of the directional solidification haves been performed for the Al–Y peritectic alloy previously examined experimentally [5].

2. Formulation of the problem

We consider an isothermal problem of phase transformations in the melt of Al–Y with the average molar concentration $x_1$ of yttrium and suggest that this concentration is limited to some small interval the $x_1 \approx 0.25$ atomic fraction. Then we assume that there is a small temperature gradient of $G=20$ K/mm and the initial temperature is equal to $T_0 = 980^\circ$C, Fig. 1. Under these conditions except the liquid phase only two solid stoichiometric phases are relevant. Dependences of the densities of Gibbs potentials [6] of liquid and stoichiometric compounds on the concentration of solutes are shown in Fig. 2 in relative values.

![Figure 1. A part of the Al–Y phase diagramm.](image1)

![Figure 2. Gibbs potentials of Al$_2$Y, Al$_3$Y stoichiometric compounds and liquid at $T = 1253$ K (980$^\circ$C).](image2)

In order to describe the state of the solution phase we confine ourselves to the ternary phase field $(\varphi_1, \varphi_2, \varphi_3)$, such that at each point of space the decomposition of unity should is satisfied:

$$\sum_{\alpha=1}^{3} \varphi_\alpha = 1. \quad (1)$$

The phase fields indices, 1, 2, 3, denote, respectively, the liquid, Al$_2$Y, and Al$_3$Y phases. Each of the phase field is equal to unity in the appropriate phase and zero in other phases. The unambiguity of the local phase state description is violated only near the interface with a small but finite thickness. Bulk properties of the phases (for example, the proportion of phases per unit volume) within the diffuse interfaces are interpolated by functions of the form:

$$\xi_\alpha = \varphi_\alpha^2 (3 - 2 \varphi_\alpha) + 2 \varphi_1 \varphi_2 \varphi_3, \quad \alpha \in \{1, 2, 3\}, \quad (2)$$
choice of which is determined by the requirement of the phases stability [7] and by the condition: $\sum_{\alpha=1}^{3} \xi_{\alpha} = 1$ following from $\left(\sum_{\alpha=1}^{3} \varphi_{\alpha}\right)^{3} = 1$.

### 3. Thermodynamics of multiphase systems

The thermodynamic potential determining the relaxation of a non-equilibrium isothermal system under the fixed pressure conditions is the Gibbs potential. The full Gibbs potential can be represented as: $G = \int \left( G_{eq} + G_{nc} + \lambda \left( \sum_{\alpha} \varphi_{\alpha} - 1 \right) \right) dV$, where $\lambda$ is the Lagrange multiplier, which ensures the condition (1). Neglecting the change of the molar volume, $v_{m}$, in the process of phase transition (and, consequently, internal stresses in the solidifying system), we present the full density of the Gibbs energy as the superposition of the molar Gibbs potentials of the equilibrium phases, $G^{\alpha}(T, x_{\alpha})$, in the form of:

$$G_{eq} = \frac{1}{v_{m}} \sum_{\alpha} \xi_{\alpha} G^{\alpha}(T, x_{\alpha}) + \sum_{\alpha<\beta} W_{\alpha\beta} \varphi_{\alpha}^{2} \varphi_{\beta}^{2}, \quad (3)$$

where the second term is similar to the well known $W$–potential with parameters $W_{\alpha\beta}$ which define the height of the potential barrier between the $\alpha$ and $\beta$ states. We should note that only the Gibbs potential density of the liquid depends on the concentration, namely $G^{(1)}_{ne} = G^{(1)}(T, x_{1})$, whereas for the other phases the Gibbs potential densities are functions only of temperature, $G^{(2,3)} = G^{(2,3)}(T)$, and the concentrations $x_{2}$ and $x_{3}$ are fixed.

The initial non-equilibrium of the liquid state leads to the necessity of the non-equilibrium contribution to the Gibbs potential density [8]: $G_{nc} = \frac{1}{2} \left( \beta J_{D}^{2} + \sum_{\alpha} \gamma_{\alpha} \dot{\varphi}_{\alpha}^{2} + \sum_{\alpha} \sigma_{\alpha} \nabla \cdot \varphi_{\alpha} \right)$, which describes the effects associated with the relaxation of the diffusion flux $J_{D}$, rate of the phase field change $\dot{\varphi}_{\alpha}$ and presence of interfaces $\frac{1}{2} \sigma_{\alpha} \nabla \cdot \varphi_{\alpha} \nabla \varphi_{\beta}$. The set of the parameters $\beta$, $\gamma_{\alpha}$, and $\sigma_{\alpha}$ is determined below.

### 4. The interface redistribution of the solute

The average concentration of the solute in all phases can be written as:

$$\bar{x} = \frac{1}{3} \sum_{\alpha=1}^{3} \xi_{\alpha} x_{\alpha}. \quad (4)$$

The total quantity of the solute satisfies to the conservation law. Since the liquid is the only phase with the variable composition then differentiating Eq. (4) on time we obtain the equation describing the change of the liquid concentration caused by changing the phase composition and bulk diffusion:

$$\dot{x}_{1} = -\nabla \cdot J_{D} - \sum_{\alpha,\beta} x_{\alpha} \frac{\partial \xi_{\alpha}}{\partial \varphi_{\beta}} \varphi_{\beta}. \quad (5)$$

Considering Eq. (5) as the dynamic equation for the solute in liquid we should note that the original conservation law holds at every point of space and does not involve restrictions to any of the phases. In order to avoid explicit tracking of interfaces we assume that the concentration $x_{1}$ is some function defined at each point of space at each moment of time, while the physically observable quantity is the function of $c = x_{1} \xi_{1}$. Then from Eq. (5) we can see that in the space regions without the liquid the left part of Eq. (5) vanishes, although the right side of Eq. (5) is not equal to zero. In this case Eq. (5) defines the relationship between the diffusion flux and the growth rate of the Al$_{2}$Y and Al$_{3}$Y phases at the diffuse interface of the two stoichiometric phases. But these phases have a constant composition of the solute and thus there should not
be diffusion by definition. In order to remove this contradiction let us redefine Eq. (5) with the help of the Heaviside step function \( \theta(\xi_1) \), which is equal to one for a positive argument and to zero for a negative or zero values of the argument

\[
\dot{x}_1 \xi_1 = -\left( \nabla \cdot \mathbf{J}_D + \theta(\xi_1) \sum_{\alpha, \beta} x_\alpha \frac{\partial \xi_\alpha}{\partial \varphi_\beta} \dot{\varphi}_\beta \right).
\] (6)

However, in order to reproduce correctly Eq. (5) from Eq. (6) at each point of space we need to add to Eq. (6) the supplementary condition

\[
0 = (1 - \theta(\xi_1)) \sum_{\alpha, \beta} x_\alpha \frac{\partial \xi_\alpha}{\partial \varphi_\beta} \dot{\varphi}_\beta.
\] (7)

Due to the identity \( \theta(\xi_1) + (1 - \theta(\xi_1)) = 1 \), the sum of Eqs. (6) and (7) reproduces Eq. (5). The meaning of expression (7) is quite obvious: in the region without the liquid the growth rate of the stoichiometric phases should be constrained. In our case, when \( \varphi_1 = 0 \), condition (7) is equivalent to

\[
(1 - \theta(\xi_1)) \left( x_2 \dot{\varphi}_2 \frac{\partial \xi_2}{\partial \varphi_2} + x_3 \dot{\varphi}_3 \frac{\partial \xi_3}{\partial \varphi_3} \right) = 0
\]

or, in the absence of the liquid, we can choose \( \varphi_\alpha = \varphi \) and \( \varphi_\beta = 1 - \varphi \). After this we immediately find that \( \frac{\partial \xi_2}{\partial \varphi_2} = \frac{\partial \xi_3}{\partial \varphi_3} = p'(\varphi) = 6 \varphi (1 - \varphi) \). Then the previous condition is transformed in the following one \( (1 - \theta(\xi_1)) p'(\varphi)(x_2 - x_3) \dot{\varphi} = 0 \), which implies an obvious statement \( p'(\varphi)(x_2 - x_3) \neq 0 \) that holds within the diffuse interface between the stoichiometric phases \( \dot{\varphi} = 0 \).

5. The decrease of the Gibbs potential in the relaxation process

During relaxation to equilibrium monotonic decrease of the Gibbs potential takes place and taking into account relations (6) one can find that the time derivative of the Gibbs potential can be represented in the form

\[
\frac{dG}{dt} = \int \left( \mathbf{J}_D \mathbf{F}_D + \sum_{\alpha} \dot{\varphi}_\alpha \mathbf{F}_\alpha + \dot{\lambda} \mathbf{F}_\lambda \right) dV \leq 0.
\] (8)

Let us denote the bulk density of the equilibrium Gibbs potential as \( \tilde{G}_\alpha = G_\alpha/v_m \) and the bulk chemical potential (more exactly the difference of the chemical potentials of the dissolved components) of the liquid phase as \( \tilde{\mu} = \mu/v_m = 1/v_m \partial G^{(1)}/\partial x_1 \). Then the coefficients in expression (8) can be easily found by algebraic manipulations. We devide the products of the Gibbs potentials with the phase fields rates at the diffuse interface into two parts \( \tilde{G}_\alpha \dot{\varphi}_\beta = \tilde{G}_\alpha \dot{\varphi}_\beta (\theta(\xi_1) + \theta(1 - \xi_1)) \) and assume that the phase field rates do not contribute to the rates of the system Gibbs potential in the regions where \( \theta(\xi_1) = 0 \) according to Eq. (7).

The coefficient of the change rate of the Lagrange multiplier is obviously equal to Eq. (1). Using the uncertainty of non-equilibrium thermodynamics [11] in the choice of fluxes (for the conservative order parameters) and rates (for the non-conservative order parameter), we can define the fluxes as \( \mathbf{J}_D = -M_D \mathbf{F}_D, \dot{\lambda} = -M_\lambda \mathbf{F}_\lambda, \dot{\varphi}_\alpha = -M_\alpha \mathbf{F}_\alpha \). The choice of mobility \( M_D > 0, M_\lambda > 0, M_\alpha > 0 \) guarantees fulfillment of the monotone decrease of the Gibbs potential (8).

We assume that \( M_\lambda \to \infty \), which assures satisfaction of Eq. (1). Expressing the mobility \( M_D \) via the diffusion coefficient in the liquid as \( D_L = M_D \partial \tilde{\mu}/\partial x_1 \), one can write the relaxation equations for the fluxes and phase fields in the form of

\[
\tau_D \mathbf{J}_D + \mathbf{J}_D = -D_L \nabla x_1,
\] (9)

\[
\tau_\alpha \dot{\varphi}_\alpha + \dot{\varphi}_\alpha = M_\alpha \left[ \nabla \left( \sigma_\alpha \nabla \varphi_\alpha \right) - \lambda - 2 \sum_{\beta \neq \alpha} W_{\alpha \beta} \varphi_\alpha \varphi_\beta^2 - \theta(\xi_1) \sum_{\beta} \frac{\partial \xi_\beta}{\partial \varphi_\alpha} (\tilde{G}_\beta - x_\beta \tilde{\mu}) \right],
\] (10)

where \( \tau_D = \beta M_D, \tau_\alpha = \gamma_\alpha M_\alpha \) are the relaxation times of the diffusion flux and phase fields.
6. Equilibrium conditions

Since all time derivatives and all fluxes tend to zero at equilibrium then from expression (9) it follows that the solute concentration in the liquid has a constant value \( x_1 = x_0 = \text{const} \), and, respectively, \( \dot{\mu} = \mu_0 = \text{const} \). Then Eq. (10) can be reduced to the following relationships

\[
\vec{\nabla} \left( \sigma_{\alpha} \vec{\nabla} \varphi_\alpha \right) - 2 \sum_{\beta \neq \alpha} W_{\alpha\beta} \varphi_\alpha \varphi_\beta^2 - \theta(\xi_1) \sum_{\beta} \frac{\partial \xi_\beta}{\partial \varphi_\alpha} \left( \tilde{G}_\beta^0 - x_\beta \tilde{\mu}_0 \right) - \lambda = 0. \tag{11}
\]

Next, let us consider the pairwise equilibrium of the \( \alpha \) and \( \beta \) phases. Due to the lack of third phase \( \varphi_\alpha = \varphi \) and \( \varphi_\beta = 1 - \varphi \). Denoting \( \sigma_{\alpha\beta} = \sigma_\alpha + \sigma_\beta \), and subtracting Eq. (10) for the \( \beta \) phase from Eq. (10) for the \( \alpha \) phase, we obtain:

\[
\vec{\nabla} \left( \sigma_{\alpha\beta} \vec{\nabla} \varphi \right) - W_{\alpha\beta} g'(\varphi) - p'(\varphi) \theta(\xi_1) \left( \tilde{G}_\beta^0 - \tilde{G}_\alpha^0 - (x_\beta - x_\alpha) \tilde{\mu}_0 \right) = 0. \tag{12}
\]

Assuming that one of the phases is liquid (\( \theta(\xi_1) = 1 \)), we consider the case of the flat front. After integrating Eq. (12) along the normal direction for infinite limits taking into account the asymptotic boundary conditions for the phase field and the explicit form of the functions \( g(\varphi) = \varphi^2(1-\varphi)^2 \) and \( p(\varphi) = \varphi^2(3-2\varphi) \), we obtain the thermodynamic condition of equilibrium, which corresponds to the equality to zero of the driving force of the phase transition at the interface with the liquid [12]:

\[
\tilde{G}_\beta^0 - \tilde{G}_\alpha^0 - (x_\beta - x_\alpha) \tilde{\mu}_0 = 0. \tag{13}
\]

Taking into account the equilibrium conditions from (12) one can write by analogy with paper [14], the phenomenological parameters \( \sigma_{\alpha\beta} \) and \( W_{\alpha\beta} \) in the form \( \sigma_{\alpha\beta} = 6\chi_{\alpha\beta}\delta_{\alpha\beta} \) and \( W_{\alpha\beta} = 12\chi_{\alpha\beta}/\delta_{\alpha\beta} \), where \( \chi_{\alpha\beta} \) is the surface tension of the \( \alpha\beta \) interface and \( \delta_{\alpha\beta} = \sqrt{\sigma_{\alpha\beta}/2W_{\alpha\beta}} \) is the characteristic halfwidth of the diffusion front.

![Figure 3](image-url)  
**Figure 3.** The dynamics of the interfaces in the initial moment of time leads to uniform values of the phase fields, which afterwards delaminate into distinct phases.

7. Numerical simulation

For simplification of numerical simulation of the equations obtained one can assume that for all phases the relaxation times, the coefficients of surface tension and the halfwidth of the diffuse interface are approximately equal. Then we can write \( \tau_\alpha = \tau_0 = 10^{-11} \) s,
\[ \chi_{\alpha\beta} = \chi_0 = 0.87 \text{ J/m}^2, \]

where \( \chi_0 \) is equal to the surface energy of pure aluminium [13] and \( \delta_{\alpha\beta} = \delta_0 = 1.2 \times 10^{-9} \text{ m} \). Then, taking into account the equilibrium conditions we find:

\[ \sigma_\alpha = 3\chi_0\delta_0, \] \( \) and \( W_{\alpha\beta} = 12\chi_0/\delta_0 \). Assuming equality of the phase fields mobilities we can present them in the form of \( M_\alpha = \nu/3\chi_0\delta_0 \), where \( \nu = 8\times10^{-9} \text{ m}^2/\text{s} \). After the transition to dimensionless

variables the set of equations obtained is solved numerically using the explicit gradient–stable

algorithm [15]. Parameter \( \lambda \) is determined from the unit decomposition condition (1). The

simulation results are presented in Fig. 3 and Fig. 4.

8. Conclusions

The simulation results show that the proposed model provides the formation mechanism of the

spatially nonhomogeneous structure typical for peritectically transformations. The nucleation

of the solid phase in liquid happens due to the action of the driving force (13), while the formation

of interfaces is driven by the \( W \)–potential and takes place at greater time scales. Since the

isothermal model in which the temperature was nearly constant was used for the study of

peritectic transformations, the calculated composition of the final phase includes liquid, which

is not observed in the experiments. The reason is that our calculations do not take into account

the change of the temperature field in the sample up to complete solidification. This means that

one should also consider other phases, such as FCC phase of aluminum, which fall out from the

solution with the decreasing content of yttrium.

9. References

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