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Linear-parabolic transition in reactive diffusion – A concept of kinetic modelling

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ABSTRACT

In Erdélyi and Schmitz (2012) a flexible concept for the computational description of the phase formation and growth in solid state reactions was described. Unlike in other established approaches, it is not required to predefine and trace phase boundaries by dividing surfaces or similar concepts. We show how to extend the concept to the transition between linear to parabolic growth kinetics. Although no interphase boundaries are predefined, it is nevertheless possible to correctly describe the impact of interfacial transport barriers. This allows a transparent modelling of the linear-parabolic transitions in reactive diffusion.

1. Introduction

In established computational approaches to the diffusional processes of phase separation or interreaction, it is common practice to describe the appearing phase boundaries by some kind of dividing interfaces. The fluxes to both sides of the interface are evaluated in a dedicated manner to predict the migration of the boundary and so to allow the book-keeping of its momentary position, see e.g. [1] or [2]. In a recent work [3], we used an alternative concept of simulating reactive diffusion that avoided the mentioned book-keeping of the interfaces. Based on the appropriate thermodynamic driving forces, expressed by correct thermodynamic factors of chemical potentials, the algorithm predicts the phase transformations automatically, a concept that has been already discussed earlier [4]. But in contrast to this earlier report, now phase boundaries are not assigned to dividing interfaces anymore, but are simply related to volume slabs revealing a composition inside the forbidden concentration range of the two-phase regions. At first sight, this concept appears to be just a formal computational trick. However, focusing on nanodevices, it may even become the more realistic picture. A phase boundary cannot be infinitely sharp but may have a thickness of about a nanometer at least. So, the interface-related volume becomes significant in comparison to the total volume of a nanodevice.

In this article we develop and demonstrate how to describe the transition from linear to parabolic kinetics within the proposed computational concept. In phenomenological understanding of phase growth by solid state reaction, it is usually supposed that transfer of atoms through phase boundaries is hindered by different reasons. Whatever the reason is, extra potential barriers are supposed to be present at the phase boundaries which slow down the atomic transport [5,6]. Introduced as a concept of describing the kinetics of gas reactions, such as oxidation [7], the concept of linear growth was transferred to solid state reactions whenever a kinetic control by the interfaces had to be presumed [8,9]. While to the best of our knowledge no clear and undisputed case of linear interdiffusion kinetics has been reported for the reaction of pure metals (perhaps [10]), apparently clear experimental confirmations do exist for silicide reactions, e.g. [11–14]. A. Gusak [15] has presented arguments that a linear kinetic regime can hardly be observed in metallic thin films, provided sufficiently efficient vacancy sinks and sources. However, he also showed that non-equilibrium vacancies, eventually also other point defects, could force a significant linear regime at the transition between the early slow *Nernst – Planck* interdiffusion stage and the later fast *Darken* interdiffusion. So, the concept of linear growth seems to be relevant, even more so as it finds renewed interest in recent work on reactive diffusion in nanowires [16].

Our article is structured as follows. First, the basic concept of the suggested transport simulation is summarized. Then, in order to check its quantitative correctness, we derive an independent analytical solution of the reactive diffusion problem that can be

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applied to any arbitrary binary phase diagrams. A comparison with this innovative analytical solution confirms the validity of the kinetic simulation. But it also demonstrates deviations in early stages which gives rise to the main aim of this article, the modification of the kinetic concept to even simulate the effect of barriers at interfaces. Quantitative accuracy of this modification is demonstrated by comparison with the approximate description by Deal and Grove [7]. Finally, we demonstrate the flexible use of the simulation in describing complex cases comprising different relevant interfaces.

2. Basic equations of the kinetic simulation model

The following basic equations for numerical simulation were derived in Ref. [3] in the context of studying elastic stress and plastic relaxation in core shell nanostructures. For clarity, we repeat them here in a reduced form that is sufficient to describe the atomic transport by a vacancy mechanism, but disregarding the influence of mechanical forces.

2.1. Continuum equations of atomic transport

In order to calculate the change of composition in time and space by vacancy mediated diffusion, the equation

$$\frac{\mathrm{D}c_i}{\mathrm{D}t} = -\frac{1}{\rho}\nabla' \vec{j}_i - c_i s_v \quad \text{for } i = 1, \ldots, n, \tag{1}$$

is used for all n atomic components. The differential $\mathrm{D}/\mathrm{D}t$ is known as the *substantial (or material) derivative*. It gives the rate of change of any scalar quantity seen at a point which follows the motion of the material coordinate system. Moreover $\vec{j}_i$ is the flux of component i, ρ is the total material density (number of lattice sites per volume), c_i is the atomic fraction of component i, ∇' indicates the *divergent* calculated in the material coordinate system (see e.g. [3]), and s_v gives the rate of change of the atomic fraction of vacancies due to creation/annihilation.

The total material density can be calculated from the partial material densities of the components i (ρ_i) and that of the vacancies (ρ_v): $\rho = \sum_{i=1}^{n}\rho_i + \rho_v$. Consequently, atomic fractions are related to the material densities by

$$c_i = \frac{\rho_i}{\rho} \quad \text{for } i = 1, \ldots, n \text{ and } i = v. \tag{2}$$

In turn, the total density ρ can also be expressed in terms of partial atomic volumes

$$\rho = \frac{1}{\sum_{i=1}^{n} c_i\Omega_i + c_v\Omega_v}. \tag{3}$$

The rate of vacancy creation/annihilation at a source/sink is considered to be proportional to the deviation of the current fraction of vacancies from the equilibrium one

$$s_v = K_{rate}\left(c_v^0 - c_v\right), \tag{4}$$

where the rate coefficient K_{rate} determines the effectiveness of sinks and sources. We emphasise that K_{rate} is not necessarily a constant but may vary, for instance, with spatial coordinates depending on the spatial distribution of the sinks and sources [17]. Note that other expression for s_v can be also used. See for instance in [18,19]. However, the present work is not intended to investigate the role of the different expressions for s_v.

In the case of a vacancy diffusion mechanism, the flux of component i can be written as [3,20]

$$\vec{j}_i = -\rho\frac{\mathscr{D}_i}{\mathrm{k}T} c_v c_i\left(\nabla'\mu_i - \nabla'\mu_v\right) \quad \text{for } i = 1, \ldots, n, \tag{5}$$

in which we have conveniently defined $\mathscr{D}_i = D_i^*/c_v^0$, with D_i^* being the tracer diffusion coefficient of the chemical component i [3,21]; k and T are Botzmann's constant and the absolute temperature. Furthermore, μ_i and μ_v are chemical potentials of component i and of the vacancy.

For the remaining of this article, we restrict to binary A-B alloys. If local equilibrium is fulfilled, the chemical potentials behave continuous. In this case Eq. (5) may also be expressed as

$$\vec{j}_i = -\rho\mathscr{D}_i\left(\Theta_i c_v \nabla' c_i - \Theta_v c_i \nabla' c_v\right) \quad \text{for } i = A, B \tag{6}$$

with the usual thermodynamic factors $\Theta_A = (\partial\mu_A/\partial\ln c_A)/\mathrm{k}T = \Theta_B$. It should be emphasized that Eqs. (5) and (6) are mathematically equivalent for a binary system. Therefore, in contrast to a recent critizism [22,23], it is always possible to derive suitable discretisation schemes for both variants so that identical results are achieved in numerical calculation.

If vacancy sinks and sources are so efficient that vacancy equilibrium holds (usually assumed for macroscopic systems), both variants of the transport equation may be further simplified:

$$\vec{j}_i = -\rho\frac{D_i^*}{\mathrm{k}T} c_i \nabla'\mu_i = -\rho D_i^*\Theta_i\nabla' c_i; \text{ for } i = A, B \tag{7}$$

and the sink term in Eq. (1) is neglected. Furthermore, mixing of the two components in the laboratory reference frame can then be described by a single exchange flux $\tilde{j} := j_A - c(j_A + j_B)$ Here and in the following c shall denote the atomic fraction of component A. The relevant driving force becomes the exchange potential $\tilde{\mu} := \mu_A - \mu_B$ so that the appropriate transport equation reads

$$\tilde{j} = \rho\frac{\widetilde{D}}{\mathrm{k}T} c(1-c)\nabla\tilde{\mu}, \tag{8}$$

with the interdiffusion coefficient

$$\widetilde{D}(c) = D_A^*(1-c) + D_B^* c. \tag{9}$$

2.2. Chemical driving forces

As a demonstration example, we consider a binary A-B systems that forms a single intermetallic phase, which stands in equilibrium to ideal solid solutions at both terminating sides of the phase diagram.

The Gibbs energy of mixing of an ideal binary solid solution (SS) is natural, while the Gibbs energy of the intermetallic phase (IM) shall be approximated by a second order polynomial, so

$$\begin{aligned} g^{SS} &= \mathrm{k}T[c\ln c + (1-c)\ln(1-c)], \\ g^{IM} &= -g_0 + V(c - c_m)^2. \end{aligned} \tag{10}$$

Here c_m denotes the stoichiometric concentration of component A in the intermetallic phase, and g_0 and V are parameters by which the existence range of the intermetallic phase can be adjusted.

With this, the chemical potentials of component A for the solid solution and the intermetallic phases are

$$\begin{aligned} \mu_A^{SS} &= \mathrm{k}T\ln c, \\ \mu_A^{IM} &= -g_0 + V\left(-c^2 + c_m^2 + 2c - 2c_m\right). \end{aligned} \tag{11}$$

As in the composition range $0\ldots c_1$ the solid solution is stable, the chemical potential is calculated from μ_A^{SS}; in the range $c_2\ldots c_3$, the intermetallic compound is the stable phase, so μ is calculated from μ_A^{IM}; and in the range $c_4\ldots 1$, it is calculated again from μ_A^{SS}. In the two-phase ranges $c_1\ldots c_2$ and $c_3\ldots c_4$, the chemical potential remains constant and equals to $\mu_A(c_1)$ and $\mu_A(c_3)$ calculated form either μ_A^{SS} or μ_A^{IM} (for the definition of the boundary con-