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A new computational treatment of reactive diffusion in binary systems

J. Svoboda [a], F.D. Fischer [b,*]

[a] Institute of Physics of Materials, Academy of Sciences of the Czech Republic, CZ-61662 Brno, Czech Republic
[b] Institut für Mechanik, Montanuniversität Leoben, A-8700 Leoben, Austria

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ABSTRACT

Reactive diffusion is usually explained and simulated for a binary A–B diffusion couple used as a starting configuration. Various solution concepts for reactive diffusion are shortly discussed. If sharp interfaces between the developed new and/or parent phases with infinite mobility are assumed and act as ideal sources and sinks for vacancies, then the local equilibrium conditions at the interface are enforced. This is pronounced as jump in chemical composition given by a phase equilibrium diagram, and the corresponding local mass balance (conservation) at the interface must be taken into account. This represents a classical concept. However, there exist two further solution concepts, one working with the thermodynamic factors and the other one utilizing chemical potentials as unambiguous functions of the chemical composition. All three concepts are compared based on the solution of the same reference example by means of finite difference technique. Drastic differences appear between results obtained by the classical sharp interface concept as well as the chemical potential based concept (both providing identical results) compared to the use of the thermodynamic factor concept. The analysis of the results of simulations indicates that the solution concept based on thermodynamic factors produces artifacts in the treatment of reactive diffusion, if the most accurate discretization scheme is used.

1. Introduction and motivation

Reactive diffusion is understood in the literature, see e.g. theoretical treatments in [1–3] or experimental reports in [4,5], as the formation of one or more new (product) phases between two old (parent) phases under the assistance of diffusion. Let us assume as the simplest example a binary diffusion couple with the pure A-component on the left side and pure B-component on the right side of an interface as a one-dimensional starting configuration (coordinate x in the actual configuration). After a certain nucleation process along the interface, see e.g. the studies by Gusak and coworkers [6,7], one or more stable layers of new phases can develop between the parent phases. Moreover, also a certain molar fraction of B-component can be solved in the left phase and a certain molar fraction of A-component can be solved in the right phase, depending on the temperature, see the numerous phase diagrams for A–B-systems for solubilities.

Before discussing some solution concepts for the reactive diffusion process, it should be mentioned that also the wording "reaction diffusion" is used, see e.g. the book by Dybkov [8]. However, the wording "reaction–diffusion" (note the hyphen!) is usually applied to describe the evolution of local fractions of one or more substances, distributed in space, which change under the influence of *two* processes: "diffusion and local chemical reactions" (see WIKIPEDIA). In other words, in this case it is assumed that in each point of the system a mixture of different phases can coexist and their fractions change due to diffusion and due to local chemical reaction, the kinetics of which is usually described by a nonlinear function depending on the fractions.

However, in the micro-mechanical and thermodynamic models we allow only one phase (not a mixture of multiple phases) at any point of the system, and, thus, we prefer using the wording "reactive diffusion" as the most appropriate one for description of processes in the considered system, or in other words, "reactive diffusion" can be considered as a diffusive process accompanied by phase transformations.

Now some recently published concepts for the description of the reactive diffusion kinetics are discussed. Dybkov [8] uses a standard chemical approach in his book and introduces for each system a certain number of "reaction constants" describing the reactions at the interfaces and diffusion of components across the layers. In the case of interface reaction control linear growth occurs; for diffusion control the growth is parabolic. The search for the links amongst the reaction constants, interface mobilities, activity of sources and sinks for vacancies at the interface and bulk diffusion coefficients is not directly pronounced in the concept.

A further step in understanding has been done by van Loo and coworkers [9–11] or later by Paul and coworkers, see e.g. [12], who presented the physico-chemical approach. They introduce

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* Corresponding author. Tel.: +43 664 4424142; fax: +43 3842 46048.
E-mail address: mechanik@unileoben.ac.at (F.D. Fischer).

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an average inter-diffusion coefficient for each phase, and the ratios of the intrinsic diffusion coefficients of the species in each phase are considered as fitting parameters. This approach can treat not only the parabolic growth of the layers controlled by diffusion but also the splitting and motion of the Kirkendall planes, which can serve for the determination of the ratios of the intrinsic diffusion coefficients.

A crucial relation to be met in a solution concept is the mass balance at an interface. If a mathematical (sharp) interface is considered, the transport theorem of continuum mechanics teaches that the velocities of the interface relative to the lattice are generally different on both sides of the interface and they must be introduced into the mass balance for the actual configuration; for derivation, see e.g. [13] and its transferring to reference configuration in [14], Sect. 4 there. The difference in the interface velocity with respect to adjacent lattices is due to generation/annihilation of vacancies at the interface and/or due to different partial molar volumes of different components in different phases. Svoboda et al. published several papers on reactive diffusion, addressed to the Kirkendall effect by engaging the thermodynamic extremal principle, see e.g. [15], meeting the above mentioned mass balance as necessary constraint for the individual fluxes, see [16–18]. These papers deal with stoichiometric intermetallic phases taking into account the activity of sources and sinks for vacancies at the interfaces only or both in the bulk and at the interfaces. A recent contribution [19] deals also with the interaction of bulk diffusion and grain boundary/interface diffusion.

Danielewski et al. [20] use in their concept the so-called "Stefan-condition" at moving interfaces, which differs obviously from the formulation of the mass balance in the actual configuration. Also interfaces of a given thickness between the individual phases are assumed in [20]. Dealing with thick interfaces makes it, however, necessary to consider the interface region as further distinct phase, for details see the studies [21,22]. Consequently, it is easier to work with a sharp interface and the proper mass balance there. Of course, the velocities of the interface relative to both adjacent lattices must be introduced.

Most recently Erdelyi and Schmitz presented a solution concept in [1] (denominated as "Erdelyi and Schmitz concept"), where they tried to avoid working with the interface and replaced the coupled problem of diffusion and interface migration by just the solution of a single modified diffusion equation expressed in the gradients of the site fractions and using thermodynamic factors. This concept was applied earlier only for intermixing of binary one-phase systems (and not reactive diffusion with moving interfaces) by Gusak et al., see [23] with references also to the remarkable research in the former Soviet Union, and Beke et al. [24] recently. If this idea worked also in multi-phase systems, this would be a significant simplification of the treatment in the field of reactive diffusion. A further concept can be dealing directly with the gradients of the chemical potentials and tracer diffusion coefficients instead of the gradients of the site fractions and the thermodynamic factors. In the following context we denote this concept as the "direct chemical potential concept".

We consider it now as a motivation to check if the Erdelyi and Schmitz concept of reactive diffusion [1] and the direct chemical potential concept lead to identical solutions as those based on rigorous treatment of the coupled problem of diffusion and interface migration. Since analytical solutions are not possible, numerical solutions are compared.

2. System definition

Let us choose a simple binary system of substitutional components A and B as used in [1], where y describes the site fraction of component A. For sake of simplicity we select a one-dimensional setting with the coordinate x in the actual configuration. One phase is supposed to be a solid solution (superscript SS) forming an ideal solution with the molar Gibbs energy given by

$$g^{\mathrm{SS}} = RT[y \ln y + (1-y)\ln(1-y)], \tag{1}$$

the second phase is supposed to be an intermetallic phase (superscript IMP), the molar Gibbs energy of which is approximated by

$$g^{\mathrm{IMP}} = g_0 + W(y - y_m)^2. \tag{2}$$

R is the gas constant, T the absolute temperature, g_0 the minimum value of the molar Gibbs energy of the IMP for y_m, and W characterizes the width of solubility in the IMP. Then the chemical potentials of individual components in individual phases are given by

$$\mu_A^{\mathrm{SS}} = RT \ln y, \tag{3.1}$$

$$\mu_B^{\mathrm{SS}} = RT \ln(1-y), \tag{3.2}$$

$$\mu_A^{\mathrm{IMP}} = g_0 + W(2y - y^2 + y_m^2 - 2y_m), \tag{3.3}$$

$$\mu_B^{IMP} = g_0 + W(-y^2 + y_m^2). \tag{3.4}$$

The solubility limits y_1^{eq} and y_4^{eq} in the SS and y_2^{eq} and y_3^{eq} in the IMP are given by the local equilibrium condition, solving the equations below for y_1^{eq}, y_2^{eq} and y_3^{eq}, y_4^{eq},

$$\mu_A^{\mathrm{SS}}(y_1^{eq}) = \mu_A^{\mathrm{IMP}}(y_2^{eq}), \tag{4.1}$$

$$\mu_B^{\mathrm{SS}}(y_1^{eq}) = \mu_B^{\mathrm{IMP}}(y_2^{eq}), \tag{4.2}$$

$$\mu_A^{\mathrm{SS}}(y_4^{eq}) = \mu_A^{\mathrm{IMP}}(y_3^{eq}), \tag{4.3}$$

$$\mu_B^{\mathrm{SS}}(y_4^{eq}) = \mu_B^{\mathrm{IMP}}(y_3^{eq}), \tag{4.4}$$

which can be determined numerically, see Fig. 1 with the data used in Sect. 5 of this paper.

We suppose that the molar volumes of both components and of vacancies in both phases are the same denoted by Ω. The bulk as well as the interfaces act as ideal sources and sinks for vacancies, which is in accordance with the so-called Darken concept, used also by Danielewski et al. [20]. Furthermore, we assume that the equilibrium vacancy site fraction is negligible with respect to one, the influence of the internal stress state plays a negligible role and the tracer diffusion coefficients D_A^{SS}, D_B^{SS}, D_A^{IMP} and D_B^{IMP} are independent of y.

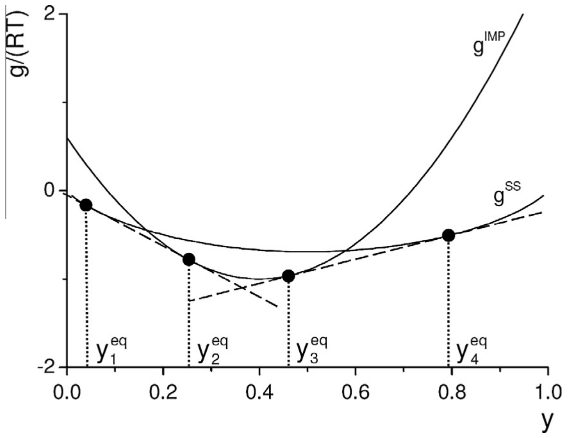

Fig. 1. Molar Gibbs energies of both phases showing the derivation of equilibrium site fractions at the interfaces.