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Incorporation of vacancy generation/annihilation into reactive diffusion concept – Prediction of possible Kirkendall porosity

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ABSTRACT

The reactive diffusion concept represents an approved handy tool for simulation of diffusive phase transformations in binary systems. The local value of the site fraction of a particular component, obtained by solution of diffusion equation, determines its affiliation to a phase or to an interface, to which the respective chemical potentials and kinetic coefficients, used in diffusion equation, can be assigned. The reactive diffusion concept is now generalized to account for intensity of non-ideal sources and sinks for vacancies, which allows the treatment of the Kirkendall effect and an according prediction of formation of pores. The new concept is demonstrated on an instructive example showing the kinetics of phase transformation, shift of the Kirkendall plane and evolution of site fraction profiles. Local supersaturation by vacancies indicates the possible formation of pores.

1. Introduction

Reactive diffusion is now an established concept to study the kinetics of one or more product phases (intermetallic compounds) between two parent phases of a binary system. Standard models work with sharp interfaces between all phases with infinite mobility and mostly do not take care about the role of sources and sinks for vacancies. Since jumps of the chemical composition exist at interfaces, corresponding mass balances at the interfaces must be employed. For details concerning both theoretical and experimental aspects of standard models we refer to the book edited by Dayananda and Murch [1], the work by van Loo [2], and the recent papers by Wang et al. [3] and Paul [4]. It should be mentioned that in the last decade also the phase field method was applied to reactive diffusion within a rather extensive mathematical framework, see Park and Arróyave [5–7].

Recently Erdélyi and Schmitz [8] applied the classical reactive diffusion concept to diffusive phase transformations in binary system by introducing respective thermodynamic factors. Inspired by Erdelyi and Schmitz the authors [9] provided a modification of their concept by working directly with chemical potentials denoted as the *direct chemical potential concept*. This new concept has proven to meet automatically the physical (and mathematical) contact conditions at the infinitely mobile interfaces and is, from the point of view of computational efforts, extremely efficient. The papers [8,9] deal with the simulation of phase transformations in one dimension. Recently the authors extended the direct chemical potential concept also to a two-dimensional configuration [10] with option to three dimensions. However, all the concepts discussed above do not treat sufficiently the role of sources and sinks for vacancies responsible for the very prominent Kirkendall effect. Moreover, in many binary systems also Kirkendall pores (voids) appear, see Seitz [11] in the first volume of Acta Metallurgica and the instructive overview by Bhadesia [12].

As typical system exhibiting Kirkendall pores the Cu-Sn-system shall be mentioned. The reader is referred to recent experimental works [13–15] and, particularly with respect to Kirkendall pores formation, see Figs. 1 and 2 in [16], Figs. 3, 4, 7 and 8 in [17], Figs. 3, 4 and 8 in [18], Figs. 1, 3 and 4 in [19], Fig. 1 in [20], Figs. 3 and 8 in [21] and Fig. 7 in [22]. In many cases, the Kirkendall pores detach from the migrating Cu/ε interface and are dispersed in the $\varepsilon-$ phase, see [23] for a respective model. We provide also a detailed example of the Kirkendall porosity at the interface between the Cu- and $\varepsilon-$ phase, see Fig. 1.

It shall be mentioned that the detailed understanding of kinetics of a Cu-Sn-system forming two intermetallic phases, namely the $\varepsilon-$ and $\eta-$ phase, requires treatment of coupling of bulk and grain boundary diffusion, see [24], as well as the formation of Kirkendall pores. Understanding the formation of Kirkendall pores makes it necessary to treat properly the vacancy generation and annihilation in the whole system which means the nonequilibrium

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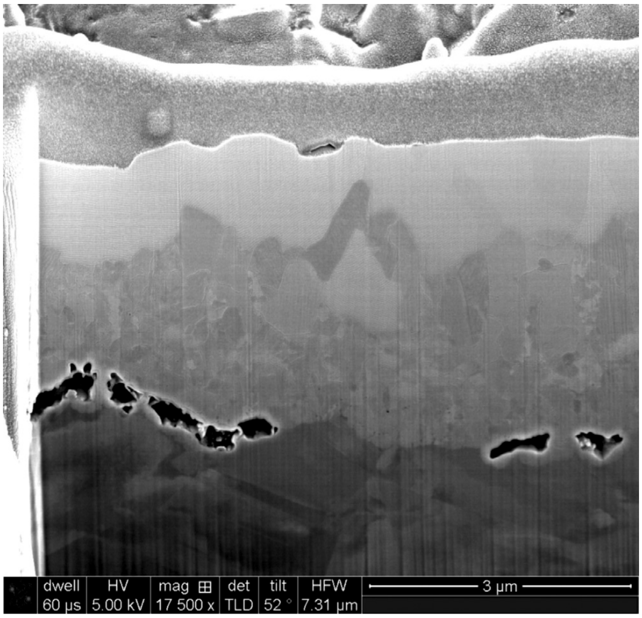

Fig. 1. Kirkendall pores at the $Cu/\varepsilon-$ interface built in the Cu-Sn diffusive couple (commercial Cu-Sn plate) during annealing 1000 h/150 °C.

vacancy redistribution problem. Pioneering theoretical papers were published by Nazarov and Gurov, started already in 1973 [25,26] and followed by Geguzin [27] in 1979, who classified the vacancy sinks/sources (s./s.) as K-s./s. (kinks/jogs in edge dislocations) and F-s./s. (so-called as Frenkel voiding). One has to assign the respective values of intensity of sources and sinks to both the bulk and the interface. Therefore, the goal of this paper is to modify the existing reactive diffusion concept to account for the role of non-ideal sources and sinks for vacancies in the system and calculate the spatial distribution of vacancies. The supersaturation of vacancies in different zones and at the interfaces can be interpreted as a measure for the formation of Kirkendall pores.

2. System definition

We assume a one-dimensional setting along the x-axis with y_0, $y_1 \equiv y$ and $y_2 \equiv 1 - y - y_0$ as site fractions of vacancies (component 0), component 1 and component 2, respectively. Interfaces and bulk are assumed as non-ideal sources and sinks for vacancies of different intensity expressed by the vacancy intensity coefficients $B \equiv B_{\text{int}}$ and $B \equiv B_{\text{bulk}}$ (see Eq. (9)), respectively. The reactive diffusion concept is treated by finite difference method on a non-equidistant grid, see e.g. [9]. Usually only one grid interval with the length Δx_{int} represents the interface, if the value of the site fraction y is outside the solubility limits of the adjacent phases (see Eq. (7)). The vacancy intensity coefficient attributed to the interface is then given by the product $U = \Delta x_{\text{int}} B_{\text{int}}$ which is, for convenience, supposed to be the same at all interfaces.

The vacancy mechanism ensures a constraint for diffusive fluxes as

$$j_1 + j_2 = -j_0. \tag{1}$$

According to Manning's theory, see details in [28–30], the fluxes are given by

$$j_k = -\sum_{i=1}^{2} L_{ik} \frac{d\mu_i}{dx}, \quad k = 1,2 \tag{2}$$

with the so-called Onsager coefficients L_{ik} as

$$L_{ik} = A_k \delta_{ik} + \frac{1-f}{f} \frac{A_i A_k}{A_1 + A_2}, \quad i,\ k = 1,2, \tag{3}$$

and the coefficients A_k as

$$A_k = \frac{y_0}{y_0^{eq}} y_k \frac{D_k}{\Omega RT}, \quad k = 1,2, \tag{4}$$

with f being the so-called vacancy correlation factor ($f = 0.7815$ for fcc and $f = 0.7272$ for bcc alloys). To demonstrate the concept, we assume that the molar volume Ω and the tracer diffusion coefficients D_k have the same values in all phases, R is the gas constant and T the absolute temperature.

In the following context we assume as initial phase a solid solution (superscript SS) of components 1 and 2, which allows formulating the chemical potential in the frame of ideal solution as

$$\text{Phase SS}: \quad \mu_1^{\text{SS}} = RT\ \ln(y), \quad \mu_2^{\text{SS}} = RT\ \ln(1 - y - y_0). \tag{5}$$

We consider also two intermetallic phases denoted as IMP1 and IMP2 and described by the chemical potentials, according to the concept presented in [9,10], as

$$\begin{aligned} \text{Phase IMP1}: \quad & \mu_1^{\text{IMP1}} = g_{01} + W_1(2y - y^2 + y_{\text{m1}}^2 - 2y_{\text{m1}}), \\ & \mu_2^{\text{IMP1}} = g_{01} + W_1(-y^2 + y_{\text{m1}}^2), \end{aligned} \tag{6.1}$$

$$\begin{aligned} \text{Phase IMP2}: \quad & \mu_1^{\text{IMP2}} = g_{02} + W_2(2y - y^2 + y_{\text{m2}}^2 - 2y_{\text{m2}}), \\ & \mu_2^{\text{IMP2}} = g_{02} + W_2(-y^2 + y_{\text{m2}}^2). \end{aligned} \tag{6.2}$$

The quantities g_{01} and g_{02} represent the values of minima of the molar Gibbs energies of IMP1 and IMP2 at y_{m1} and y_{m2}, resp. The solubility limits y_{eq1}, y_{eq6} for the SS, y_{eq2}, y_{eq3} for the IMP1 and y_{eq4}, y_{eq5} for the IMP2 phases are given by the local equilibrium conditions at contact between the phases as

$$\mu_1^{\text{SS}}(y_{\text{eq1}}) = \mu_1^{\text{IMP1}}(y_{\text{eq2}}), \quad \mu_2^{\text{SS}}(y_{\text{eq1}}) = \mu_2^{\text{IMP1}}(y_{\text{eq2}}), \tag{7.1}$$

$$\mu_1^{\text{IMP1}}(y_{\text{eq3}}) = \mu_1^{\text{IMP2}}(y_{\text{eq4}}), \quad \mu_2^{\text{IMP1}}(y_{\text{eq3}}) = \mu_2^{\text{IMP2}}(y_{\text{eq4}}), \tag{7.2}$$

$$\mu_1^{\text{IMP2}}(y_{\text{eq5}}) = \mu_1^{\text{SS}}(y_{\text{eq6}}), \quad \mu_2^{\text{IMP2}}(y_{\text{eq5}}) = \mu_2^{\text{SS}}(y_{\text{eq6}}). \tag{7.3}$$

The contact conditions can be determined numerically as solutions of sets of two non-linear Eqs. (7.1)–(7.3) providing the values of pairs $(y_{\text{eq1}}, y_{\text{eq2}})$, $(y_{\text{eq3}}, y_{\text{eq4}})$ and $(y_{\text{eq5}}, y_{\text{eq6}})$, respectively. The difference between the solubility limits for each intermetallic phase is controlled by the values of W_1 and W_2. The chemical potentials outside the solubility limits (in the interface) are calculated as equal to those for the respective solubility limits, e.g. $\mu_1(y) = \mu_1^{\text{IMP1}}(y_{\text{eq3}}) = \mu_1^{\text{IMP2}}(y_{\text{eq4}})$, for $y \in (y_{\text{eq3}}, y_{\text{eq4}})$, which defines the "interface rule". The values of chemical potentials μ_1 and μ_2 are calculated according to the value of y by means of Eqs. (5) or (6.1–2) or according to the "interface rule".

The chemical potential of vacancies is calculated in the framework of the ideal solution model and assumed, for simplicity, as independent of the phase as

$$\mu_0 = RT \ln(y_0 / y_0^{eq}). \tag{8}$$

The rate of generation of vacancies at non-ideal sources and sinks in the bulk is described, according to [28], Sections 4–6 there, as

$$\alpha = -\frac{\mu_0 - \sigma_H \Omega}{K\Omega} \tag{9.1}$$

with σ_H being the hydrostatic stress and K as a material parameter. For a stress-free system Eq. (9.1) can be rewritten as

$$\alpha = -\frac{\mu_0}{K\Omega} = -B\mu_0 \tag{9.2}$$