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Modelling of the influence of the vacancy source and sink activity and the stress state on diffusion in crystalline solids

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Abstract

Diffusion in solids is a well-known phenomenon that has many consequences in technology and material science. Modelling of diffusion-controlled processes requires both a reliable theory of diffusion and reliable kinetic coefficients, as well as other thermodynamic data. Often the classical Darken theory, valid for stress-free systems with ideal vacancy source and sink activity, is generalized to multicomponent systems with ideal vacancy source and sink activity. Nazarov and Gurov presented a theory for stress-free systems with no vacancy source and sink activity. Recently we published a general theory of diffusion that accounted for the role of non-ideal vacancy source and sink activity, as well as the stress state. Since diffusion theories are tested and diffusion coefficients measured usually on diffusion couples, this paper presents evolution equations based on that general theory for a diffusion couple. In the limit, the equations of the Darken theory and the Nazarov and Gurov theory are valid for ideal vacancy source and sink activity and no vacancy source and sink activity, respectively. Simulations for binary and ternary diffusion couples demonstrate the influence of the vacancy source and sink activity and the stress state on evolution of site fraction profiles of components and vacancies, and on the Kirkendall effect.

Keywords: Substitutional diffusion; Vacancies; Annihilation; Residual stresses; Non-equilibrium process

1. Introduction

Diffusion in stress-free solids was first described by Fick. His laws are used for the description of the interdiffusion in binary systems by the well-known Darken theory [1]. This theory, formulated for a one-dimensional setting, tacitly assumes ideal vacancy source and sink activity as well as shrinking or expanding only in the direction of diffusive fluxes. Onsager [2,3] showed that multicomponent interdiffusion can be described by a symmetrical matrix of kinetic coefficients. Manning [4] provided a model for a random alloy that allowed the matrix of kinetic coefficients to be calculated from diffusion coefficients. Manning's theory was then improved by the self-consistent theory of Moleko et al. [5]. Belova and Murch have presented an extensive overview of this topic [6]. The equations for interdiffusion in binary systems with no sources and sinks for vacancies were formulated in 1974 by Nazarov and Gurov [7]. Both the Darken theory and the Nazarov and Gurov theory were then unified in the theory by Gusak et al. [8–11], who first considered non-ideal vacancy source and sink activity. They showed that for non-ideal vacancy source and sink activity a "three-stage rule" for the shift of the Kirkendall plane exists: in the initial stage the "$\sqrt{t}$-rule" based on the Nazarov and Gurov kinetics can be observed, followed by a "t-rule" in the intermediate period, then returning to the "$\sqrt{t}$-rule" based on the Darken kinetics. Further recent studies on vacancy-mediated diffusion in binary alloys by Thornton et al. should also be mentioned [12–14].

Theories taking into account the influence of the stress state on diffusion in solids have been presented by several authors, one of the first being that of Stephenson [15]. A general concept for the kinetics of the diffusion was introduced by us in 2006 [16], which distinguishes between

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interstitial and substitutional components and vacancies, including the role of non-ideal vacancy source and sink activity. This concept considers the interaction of the diffusion process with the deformation process. The stress tensor and corresponding elastic strain energy (in other words, the so-called Eshelby tensor) represent the additional mechanical driving force for diffusion and generation/annihilation of vacancies. Very recently we applied the concept [16] to three-dimensional multicomponent diffusion in random alloys based on Manning's theory [17]. In contrast to previous treatments, this general theory systematically accounts for the influence of vacancy source and sink activity and of the stress state on both the kinetics of diffusion and the deformation of the system (known as Kirkendall effect). The concept is based exclusively on the knowledge of the tracer diffusion coefficients and thermodynamic state functions of the bulk phase. As a first step the theory has been successfully used for the treatment of diffusion and stress state development in thin layers [17,18]. However, a detailed analysis of diffusion in infinite multicomponent diffusion couples with non-ideal vacancy source and sink activity and accounting for the developing stress state is still missing.

The goal of this paper is the presentation of evolution equations based on the general theory [17] for infinite multicomponent diffusion couples accounting for vacancy-mediated diffusion, generation/annihilation of vacancies, stress development and deformation. In the limit, the Darken theory and the Nazarov and Gurov theory are valid for ideal and no vacancy source and sink activity, respectively. The influence of both the stress state and the vacancy source and sink activity on the evolution of site fraction profiles of vacancies and on the motion of the Kirkendall plane is simulated in stress-free binary and stress-subjected ternary infinite diffusive couples. The results of the simulations are discussed in detail.

2. Problem description

Let the system consists of two layers of one phase, which are of different chemical composition (diffusion couple) and are in contact along the x–y plane (see Fig. 1). Both the lower layer ($z > 0$) and the upper layer ($z < 0$) have the thickness $d/2$, $-d/2 \leqslant z \leqslant d/2$, with $0 < d < \infty$. The material is assumed to be elastic, described by the Young's modulus E and Poisson's ratio γ. The same elastic properties, independent of chemical composition, are addressed to both layers. Since the layers have infinite extent in the x- and y-directions, $-\infty < x < \infty$, $-\infty < y < \infty$, each plane $x = \text{const}$ and $y = \text{const}$ is a symmetry plane yielding spatially constant overall strain components $\varepsilon_x(x,y,z;t) = \bar{\varepsilon}_x(t)$, $\varepsilon_y(x,y,z;t) = \bar{\varepsilon}_y(t) = \bar{\varepsilon}_x(t)$ with t being the time. For $d \to \infty$ one can easily prove that the overall strains tend to 0, $\bar{\varepsilon}_x(t) = \bar{\varepsilon}_y(t) = 0$. As a consequence, only a principal stress state with the components $\sigma_x(z;t) = \sigma_y(z;t)$ and $\sigma_z(z;t)$ exists. The total body is assumed to be stress-free on its surface, so the following global equilibrium conditions exist:

$$\int_{-d/2}^{d/2} \sigma_x(z,t)dz = \int_{-d/2}^{d/2} \sigma_y(z,t)dz \equiv 0, \quad \sigma_z(z,t) \equiv 0. \tag{1}$$

Each layer consists of vacancies with a site fraction y_0 and n substitutional components, the site fractions of which are denoted by y_i, $i = 1,\ldots,n$. The site fractions enforce the constraint

$$y_0 + \sum_{i=1}^{n} y_i = 1. \tag{2}$$

Both layers contain non-ideal vacancy source and sink activity.

One can introduce the chemical potential for vacancies as

$$\mu_0 = R_g T \ln(y_0/y_0^{eq}) \tag{3}$$

with R_g being the gas constant, T the temperature and y_0^{eq} the equilibrium vacancy site fraction.

The vacancy source term α represents the number of vacancies generated during a time unit per number of site positions in the representative volume element and is assumed to have the form [17,18]

$$\alpha = -(\mu_0 - \Omega\sigma_H)/K_{bv}\Omega, \quad \boldsymbol{\alpha} = \alpha/3 \cdot \boldsymbol{\delta}, \ \boldsymbol{\delta} \text{ unity tensor.} \tag{4}$$

The quantity Ω is the molar volume assumed to be equal to partial molar volumes of all components. The hydrostatic stress is $\sigma_H = 2\sigma_x/3 = 2\sigma_y/3$ and K_{bv} is the bulk viscosity (for details, see [17]). The vacancy generation/annihilation is associated with a source/sink term α, with a corresponding eigenstrain rate tensor $\boldsymbol{\alpha}$.

Interdiffusion occurs between both layers and causes the Kirkendall effect. The evolution of the site fraction profiles y_i, expressed via $\dot{y}_i$ as their material time derivatives, is outlined in detail in Ref. [17] with respect to the actual configuration and follows for an ideal solution (which is assumed for sake of simplicity) for $i = 1,\ldots n$ as

$$\dot{y}_i = \frac{D_i}{y_0^{eq}}(y_0 y_i' - y_0' y_i)' - \alpha y_i + \frac{1-f}{f}\left[D_i y_i \frac{\sum_{k=1}^{n} D_k(y_k' y_0 - y_k y_0')}{y_0^{eq}\sum_{l=1}^{n} D_l y_l}\right]'. \tag{5}$$

Prime "′" denotes $\partial/\partial z$, defined in the actual configuration, and D_i are the tracer diffusion coefficients measured for equilibrium site fraction y_0^{eq} of vacancies (both D_i and y_0^{eq}

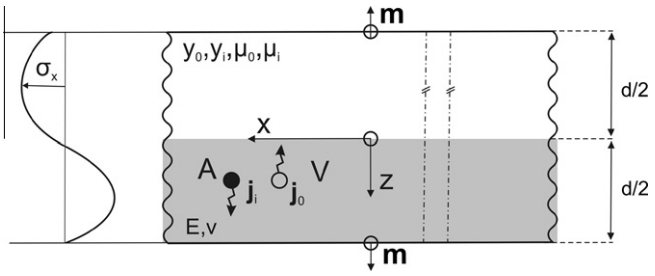

Fig. 1. Geometry of the system and introduction of internal variables.