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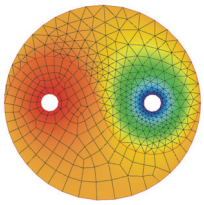
AKAPIT

COMPUTER METHODS IN MATERIALS SCIENCE
Informatyka w Technologii Materiałów

Vol. 13, 2013, No. 2



THE MIGRATION OF KIRKENDALL PLANE DURING DIFFUSION

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Abstract

In this study some aspects of Kirkendall and lattice plane migration in binary diffusion couples are studied by means of numerical simulations by bi-velocity method. The bi-velocity method (Darken method) base on the postulate of the unique transport of the mass due to diffusion. The method deal with the 1) composition dependent diffusivities, 2) different partial molar volumes of components, 3) the stress field during the diffusion process and 4) entropy production. It is shown that the method allows for calculation the trajectory of the Kirkendall plane in binary diffusion couples.

Key words: kirkendall plane, bi-velocity method, interdiffusion, trajectory

1. INTRODUCTION

In recent years, both experimental characterization and computer simulations have revealed many new phenomena that are not yet fully explained by existing theories and models. A list of examples include: (i) multiple Kirkendall planes (bifurcations), (ii) stability of individual Kirkendall plane, and (iii) discontinuity of the Kirkendall velocity at moving interphase boundaries (van Dal at al., 2001; van Loo at al., 1990).

The Kirkendall effect (Smigelskas & Kirkendall, 1947) always accompanies interdiffusion, manifests itself in many phenomena, the migration of inclusions inside the diffusion zone, the development of porosity, generation of stress and in plastic deformation of the material. These diffusion-induced processes are of concern in a wide variety of structures including composite materials, coatings, weld junctions, thin-film electronic devices (Boettinger at al., 2007; Gusak, 2010).

While the Darken's treatment of diffusion has withstood the test of time, the efforts directed towards its implementation into physics and thermodynamics are far from being accepted. The reason may be attributed to the inherent experimental difficulties involved in the measurement of material velocities. The rationalization and formal description of the Kirkendall effect are by no means trivial. Regardless of intensive work in this field, a number of fundamental questions still remains to be answered. Is the Kirkendall plane unique? In other words, could the inert particles placed at the initial contact interface migrate differently in the diffusion zone, so that two (or more) "Kirkendall planes" can be expected? (van Dal at al., 2001).

Experiments confirm that the “fiducial markers” may have different trajectories. However the existing methods dealing with Kirkendall trajectories do not quantify the bifurcations, trifurcations, nonstability and discontinuity (van Loo at al., 1990).

The bi-velocity method is a generalization of Darken method of interdiffusion. The method based on the rigorous mathematical derivation of mass, momentum and energy conservations (Danielewski

ISSN 1641-8581

& Wierzba, 2010). It allows to calculate the densities, drift velocity, energy and entropy densities in multicomponent systems. The method can be used when the gradient of the mechano-chemical potential (from fairly well known thermodynamic properties) and diffusivities as a function of concentrations (from measured tracer diffusivities) are known. The method is limited to the axiatoric part of the stress tensor only, i.e. the rotations of the system are neglected (rot $\upsilon = 0$). The purpose of this paper is to use the bi-velocity method to calculate the Kirkendall trajectory (position of the Kirkendall plane).

2. THE BI-VELOCITY METHOD (DANIELEWSKI AT AL., 2010)

The core of the bi-velocity method is the mass balance equation:

$$\frac{\partial \rho_i}{\partial t} = -\frac{\partial}{\partial x}\left(J_i^d + J_i^{drift}\right), \qquad i = 1,2\,, \quad (1)$$

where ρ_i is the mass density; J_i^d and J_i^{drift} denote the diffusion and drift flux, respectively.

The diffusion flux, $J_i^d = \rho_i \upsilon_i^d$, in a case when no external forces are considered is given by the Nernst-Planck equation (Nernst, 1889; Planck, 1890):

$$J_i^d = c_i \upsilon_i^d = -c_i \frac{D_i}{RT}\frac{\partial}{\partial x}\left(\mu_i^{ch} + \Omega_i p\right), \qquad i = 1,2\,, \quad (2)$$

where υ_i^d denote the diffusion velocity, μ_i^{ch} is the chemical potential, D_i the intrinsic diffusion coefficient and Ω_i and M_i are partial molar volume and molecular mass of the i-th component, respectively; R and T are the gas constant and temperature, p denote the pressure field acting on the components. The density ρ_i is related with concentration, $\rho_i = M_i c_i$.

To calculate the drift flux the Volume Continuity Equation (VCE) is used. The differential form of VCE follow:

$$\sum_{i=1}^{2} \rho_i \Omega_i M_i \left(\upsilon_i^d + \upsilon^{drift}\right) = 0\,. \quad (3)$$

The drift velocity, υ^{drift}, of the mixture can be defined:

$$\upsilon^{drift} = -\sum_{i=1}^{2} \rho_i \Omega_i M_i \upsilon_i^d\,, \quad (4)$$

The pressure, p, generated during diffusion process is described by the Cauchy stress tensor. Thus, the pressure evolution can be approximated from dilatation of ideal crystal:

$$\frac{dp}{dt} = -\frac{E}{3(1-2v)}\frac{\partial}{\partial x}\left(\sum_{i=1}^{2} \rho_i \Omega_i M_i \upsilon_i^d\right), \quad (5)$$

where E and v are the Young modulus and Poisson ratio, respectively.

The bi-velocity allow also to calculate the energy and entropy conservations. Assuming the time independent external forcing $(\partial V^{ext}/\partial t = 0)$, the internal energy conservation law becomes:

$$\rho_i \frac{\partial u_i}{\partial t} + \rho_i \left(\upsilon_i^d + \upsilon^{drift}\right)\frac{\partial u_i}{\partial x} = -\Omega_i c_i\, p \frac{\partial\left(\upsilon_i^d + \upsilon^{drift}\right)}{\partial x} \quad (6)$$

where u_i denote the internal energy. The overall internal energy, u, of the mixture can be calculated from components counterparts $\rho u = \sum_{i=1}^{2} \rho_i u_i$.

Finally, the entropy, s, when diffusion is not negligible can be calculated from partial Gibbs-Duhem relation, $Ts_i = u_i - \mu_i^{ch} - \Omega_i M_i\, p$ and $\rho s = \sum_{i=1}^{2} \rho_i s_i$.

3. RESULTS

In this paper the three different methods of calculation of the position of Kirkendall plane in the binary A-B diffusion couples are shown and compared. Mainly, 1) the "curve method" (Aloke, 2004; Gusak, 2010), 2) the "trajectory method" and 3) "entropy approximation". The first two methods base on the drift velocity and its integral the last method assumes that the position of the Kirkendall plane is defined by the local maximas of the entropy distribution.

The "curve method". The Kirkendall velocity can be calculated from the drift velocity, equation (4). Assuming the diffusion process in the binary system and that the partial molar volumes are constant and equal, $\Omega_i = \Omega_j\ \forall i, j$, the drift velocity can be rewritten in the following form:

$$\upsilon^{drift} = -\Omega\left(c_1 \upsilon_1^d + c_2 \upsilon_2^d\right) \quad (7)$$

From Euler theorem the overall molar volume equal to the inverse of the overall concentration, $\Omega = 1/c$. Thus:

$$\upsilon^{drift} = -\left(N_1\upsilon_1^d + N_2\upsilon_2^d\right) \tag{8}$$

where the molar ratio, $N_i = \frac{c_i}{c}$. Substituting equation (2) the drift velocity in a binary system when pressure filed is neglected can be rewritten in the following form:

$$\upsilon^{drift} = N_1\frac{D_1}{RT}\frac{\partial\mu_1^{ch}}{\partial x} + N_2\frac{D_2}{RT}\frac{\partial\mu_2^{ch}}{\partial x} \tag{9}$$

When the ideality sweeping statement is assumed, i.e. $\frac{\partial\mu_i^{ch}}{\partial x} = RT\frac{\partial \ln c_i}{\partial x}$ thus the drift velocity has its final form:

$$\upsilon^{drift} = \left(D_1 - D_2\right)\frac{\partial N_1}{\partial x} \tag{10}$$

In a diffusion controlled interaction, the Kirkendall plane is a plane of initial contact moving at parabolic dependence, thus the position of the Kirkendall plane:

$$\upsilon_K = \upsilon^{drift}(0,t) = \frac{dx}{dt} = \frac{x_K}{2t} \tag{11}$$

where υ_K is the positions of the Kirkendall plane at time $t = t^*$. The position(s) of the Kirkendall plane(s) can be found at the point of intersection(s) between the drift velocity curve and the straight line calculated from equation (11).

"The trajectory method". The position of the Kirkendall plane can also be calculated by following the marker during the diffusion process, equation (12).

$$x_K(t_2) = \int_{t_1}^{t_2}\upsilon^{drift}\left(x_K(t_1),t\right)dt \tag{12}$$

In each time the new position of the Kirkendall plane is calculated.

"The entropy approximation". In this studies it is postulated that the local maxima's calculated on the entropy distribution curve shows the positions of Kirkendall planes (the most favored places) in the diffusion couples.

Figure 1 shows the comparison of presented above methods of calculating the position of Kirkendall plane. The data used to calculate the diffusion process are presented in table 1.

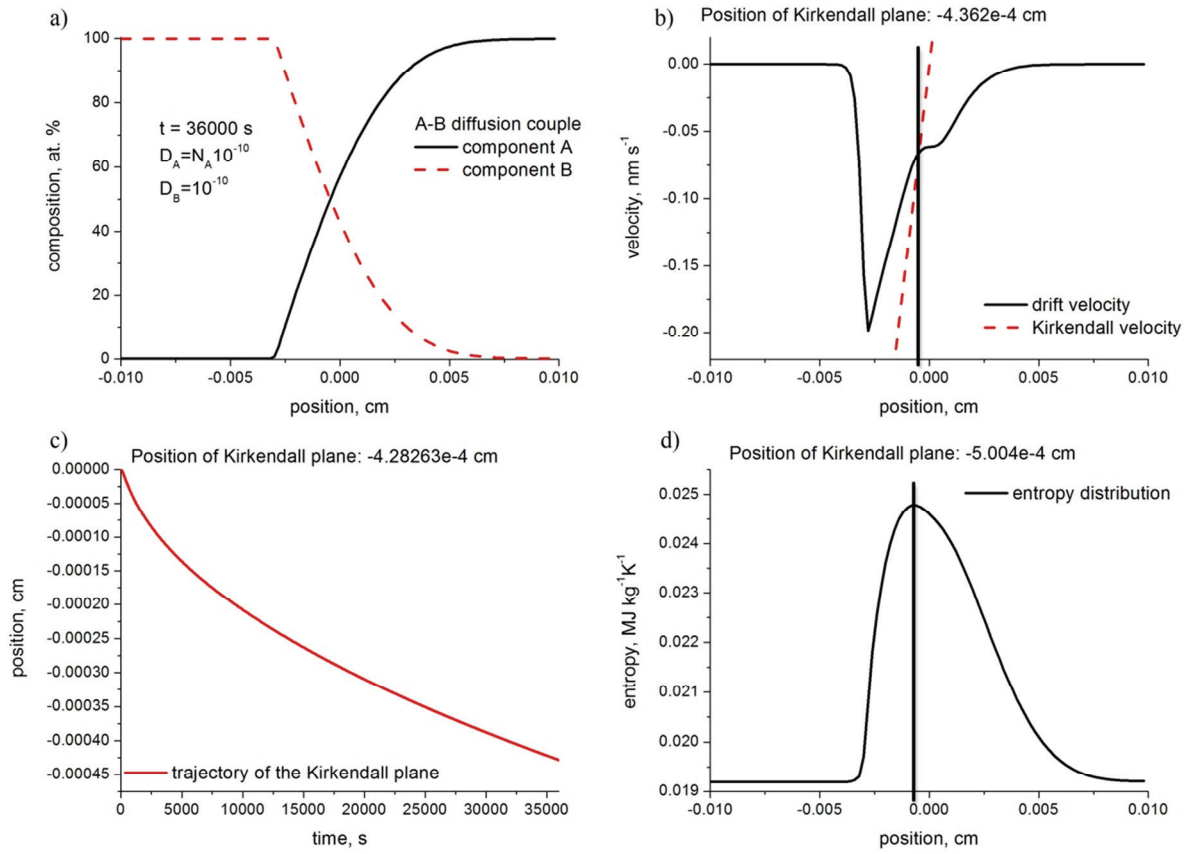

Fig. 1. *a) The concentration profile in binary A-B diffusion couple; The comparisons of the position of Kirkendall plane (vertical line) by different calculation methods: b) velocity curve; c) trajectory and d) entropy bi-velocity method.*

Table 1. *The data used in simulations of diffusion in binary A-B diffusion couple.*

T = 1273K; t = 36000 s; thickness, d = 0.02 cm	
A diffusion coefficient [$cm^2\ s^{-1}$]	B diffusion coefficient [$cm^2\ s^{-1}$]
$N_A \cdot 10^{-10}$	10^{-10}

The presented simulation results were calculated using the bi-velocity method. Figure 1 shows a) the concentration profile and comparison of the calculation of Kirkendall plane where different methods were used: b) the velocity curve; c) trajectory method and d) entropy bi-velocity method in a binary A-B diffusion couple.

Figure 1 shows that the three presented methods give similar results when only one position of the Kirkendall plane is expected.

4. CONCLUSIONS

The bi-velocity method for interdiffusion allows quantitative and qualitative description of the mass transport process in binary systems. The method based on the postulate that each component's velocity υ_i must be divided into two parts: υ_i^d the unique diffusion velocity, which depends on diffusion potential gradient and is independent of the choice of the reference frame; and the drift velocity υ^{drift}. The drift velocity, common for all components, allows to calculate the position and trajectory of the Kirkendall planes during diffusion process. The method effectively deals with (1) composition dependent diffusivities, (2) different partial molar volumes of components, (3) the stress field during the diffusion process and (4) entropy production. The model was applied for the modeling of the trajectory of the Kirkendall planes in a binary diffusional couples. The examples presented in this work show that the entropy curve can be used to approximate the position of the Kirkendall markers when the diffusion coefficients are composition dependant.

Acknowledgments. This work has been supported by the National Science Centre (NCN) in Poland, decision number DEC-2011/03/B/ST8/05970. The software CADiff available from author.

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KRYTERIA EWOLUCJI PŁASZCZYZNY KIRKENDALLA PODCZAS PROCESU DYFUZJI

Streszczenie

W artykule zaprezentowana została metoda dwu-prędkości pozwalająca na wyznaczenie ewolucji płaszczyzny Kirkendalla podczas procesu dyfuzji. Metoda dwu-prędkości jest uogólnieniem metody Darkena. Opiera się ona na całkowych prawach zachowania masy, pędu oraz energii. Algorytm obliczania trajektorii płaszczyzny Kirkendalla pozwala również na wyznaczenie: 1) stężeń składników, 2) prędkości dryftu, 3) energii oraz 4) produkcji entropii w wieloskładnikowych fazach skondensowanych. Pokazano, że metoda pozwala na poprawne wyznaczenie położenia płaszczyzny Kirkendalla podczas procesu dyfuzji w układach dwu-składnikowych.

Received: October 25, 2012
Received in a revised form: November 21, 2012
Accepted: : December 12, 2012