EXTERNAL FORCE FIELD DURING DIFFUSION - SEDIMENTATION IN CONDENSED MATTER

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Abstract

In this paper numerical description of the external force field during interdiffusion is discussed. Two methods of modeling the sedimentation process is presented. Mainly, the steady state and evolutionary approximation. The proposed approaches based on the generalized Darken method. The main equations is the mass conservation and equation of motion. Thus, the simultaneous action of backstress, external forces and Kirkendall shift during interdiffusion in metals is described by self-consistent scheme. The diffusion flux is than determined by both, chemical and mechanical potentials.

Key words: sedimentation, Darken method, equation of motion

1. INTRODUCTION

In 1947 Kirkendall (Smigelskas & Kirkendall, 1947) reported the results of his famous experiment on the interdiffusion between copper and zinc. During the diffusion annealing the movement of the interface was observed. This phenomena is known as Kirkendall effect. This effect plays an outstanding role in description of interdiffusion process. It is the evidence of vacancy mechanism of diffusion in metals. The key reason of the plane movement is the difference in intrinsic diffusion coefficients in diffusion couple. That was the most important assumption made by Darken (Darken, 1948). From different diffusion coefficients Darken determined the drift velocity, for binary alloys:

$$v^{drift} = \left(D_A - D_B \right) \frac{\partial N_A}{\partial x} \qquad (1)$$

where: v^{drift} [$m \ s^{-1}$] denote the drift velocity, D_i [$m^2 \ s^{-1}$] is the intrinsic diffusion coefficient of the i-th component and N_i its molar ratio.

In fact, the drift velocity can be compared with the vacancy migration. The vacancies migrate from the material with the lower diffusion coefficient into the material with the higher diffusion coefficient.

At present the new processes are tested in order to develop new materials. Such process is sedimentation in metals. One of the first sedimentation machine was developed in 1970 by Barr and Smith (1969) and Anthony (1970). They investigated the sedimentation of Au atoms in elemental metals (K, In and Pb) with low melting temperatures under maximum acceleration fields of $1\text{-}2\text{x}10^5$ g. In 1996, Mashimo et al. developed an ultracentrifuge apparatus that can generate an acceleration field up to 10^6 g for long times at high temperatures (Mashimo et al., 1996).

In this paper a model describing the sedimentation process - diffusion under external force field is proposed. The model is based on the mass conservation law and equation of motion. After Darken two velocities are introduced, mainly the diffusion and drift velocity. Additionally for the first time the va-

cancy concentration during the sedimentation process is calculated. From the vacancy concentration, the most likely place of voids formation can be determined.

2. MATHEMATICAL MODEL

In this paragraph the mathematical model of the sedimentation process is discussed. The two different approaches are presented, mainly the steady state and evolutionary algorithms. Both methods based on the generalized Darken method. The evolutionary algorithm can be determined by solving the mass conservation law:

$$\frac{\partial N_i}{\partial t} + \nabla \bullet (N_i v_i) = 0 \qquad (2)$$

where: v_i [$m\ s^{-1}$] is the overall velocity acting on the i-th component and N_i the molar ratio of the i-th component. The molar ratio is defined as the quotient of molar concentration, c_i [$mol\ m^{-3}$] and overall concentration, c [$mol\ m^{-3}$] of the mixture:

$$N_i = \frac{c_i}{c} \qquad (3)$$

The following relations hold in the mixture:

$$c = \frac{1}{\Omega} = \sum_{i=1}^{r} c_i, \qquad \Omega = \sum_{i=1}^{r} \Omega_i N_i \qquad (4)$$

where: Ω [$m^3\ mol^{-1}$] and Ω_i [$m^3\ mol^{-1}$] denotes the overall and i-th component molar volume, respectively.

The mass density of the i-th component, ρ_i [$kg\ m^{-3}$], defined as a measure of the mass, M_i [$kg\ mol^{-1}$], of substance contained in any volume and the overall mass density, ρ [$kg\ m^{-3}$], is defined as follow:

$$\rho_i = M_i c_i, \qquad \rho = \sum_{i=1}^{r} \rho_i \qquad (5)$$

The overall component velocity defined in Eq. (2), after Darken (Darken, 1948) is defined as a sum of the diffusion, v_i^d [$m\ s^{-1}$], and drift, v^{drift} [$m\ s^{-1}$] velocity:

$$v_i = v_i^d + v^{drift} \qquad (6)$$

The drift velocity is an average velocity for each component, the drift velocity can be defined from the volume continuity equation (Danielewski & Wierzba, 2010):

$$v^{drift} = -\sum_{i=1}^{r} N_i v_i^d \qquad (7)$$

The diffusion velocity can be defined by Nernst-Planck formulae (Nernst, 1889; Planck, 1890).

$$v_i^d = B_i F_i \qquad (8)$$

where: v_i^d [$m\ s^{-1}$] denote the diffusion velocity of the i-th component, B_i [$mol\ kg^{-1}\ s$] its mobility and F_i [$mol\ kg^{-1}\ m\ s^{-2}$] denote the forces acting on the i-th component during the diffusion process. In the case of gravity induced diffusion, the forces can be defined as:

$$F_i = -\nabla \mu_i = -\nabla \mu_i^{ch} - \nabla \mu_i^m - \nabla (M_i gx) \qquad (9)$$

where μ_i^{ch} [kg mol^{-1} m^2 s^{-2}] and μ_i^m [kg mol^{-1} m^2 s^{-2}] denote the chemical and mechanical potential gradient, respectively. The g [$m\ s^{-2}$] denote the gravitation and x [m] is the position.

Finally, during the sedimentation process the diffusion velocity can be rewritten in the following form:

$$v_i^d = -B_i \nabla \mu_i^{ch} - B_i \nabla \mu_i^m - B_i \nabla (M_i gx) \qquad (10)$$

The mechanical potential in case of the sedimentation process can be defined from the equation of motion assuming the mechanical equilibrium, thus:

$$-\nabla p + \rho r \omega^2 = 0 \quad \Rightarrow \quad \nabla p = \rho r \omega^2 \quad (11)$$

where: p [$kg\ m^{-1}\ s^{-2}$] denote the pressure and ω [s^{-1}] is angular speed.

Finally, the mass conservation, after simple algebra, can be rewritten in the form:

$$\frac{\partial N_i}{\partial t} + \nabla \bullet (-B_i RT \mathrm{grad} N_i - B_i N_i \Omega_i \rho r \omega^2 -$$
$$B_i N_i M_i r \omega^2 + N_i v^{drift}) = 0 \qquad (12)$$

In case of the steady state approximation, the time derivative of concentration is equal zero, thus the mass conservation in one dimension takes the form:

$$-B_i RT \nabla N_i - B_i N_i \Omega_i \rho r \omega^2 - B_i N_i M_i r \omega^2 + N_i v^{drift} = 0 \qquad (13)$$

Moreover, in the steady state we assume, that the drift velocity is equal zero, thus:

$$-B_i RT \nabla N_i - B_i N_i \Omega_i \rho r \omega^2 - B_i N_i M_i r \omega^2 = 0 \qquad (14)$$

Consequently, in steady state, the equation describing the molar ration is:

$$\nabla \ln N_i = -\frac{(\Omega_i \rho + M_i) r \omega^2}{RT} \qquad (15)$$

3. NUMERICAL PROCEDURE

Both presented approximations based on the method of lines to solve numerically the ordinary differential equations (ODEs) system resulting from the space discretization (Schiesser, 1991). The uniform grid, which contained 100 mesh points along the x direction, respectively, was used and the concentrations and drift velocity were defined at points x_k. The applied discretization led to the system of ODEs in time variable. The evolutionary method based additionally on the adaptive step-size Runge–Kutta-Fehlberg modification. The six evaluations of the functions from the fifth-order Runge–Kutta algorithm were used to make other combinations implemented in the fourth-order Runge–Kutta method. The difference between these two estimates served as an estimate of the truncation error. Hence, the step size was adjusted (Press et al., 1992). The results of the proposed methods are compared and discussed.

4. RESULTS

In this section both steady state and evolutionary approximations are compared. The hypothetical data is used to simulate the binary sedimentation process in one dimension. The data used for calculation of the hypothetical binary sedimentation process are presented in table 1.

Table 1. *The data used for calculation of the sedimentation process in hypothetical binary alloy*

Component	Atomic mass, M_i	Molar volume, Ω_i	Initial composition, at. %	Diffusion coefficient, $D_i = B_i/RT$
1	150	18	50	$1 \cdot 10^{-5}$
2	100	16	50	$2 \cdot 10^{-6}$

The angular speed was 215 000 rev/min and the distance from the edge 3,65 cm.

The result of the calculations of the hypothetical sedimentation process by steady state and evolutionary algorithms is shown in figure 1. The result from steady state is straight line opposite to the evolutionary algorithm - parabola. Thus the accuracy of steady state is lower. In the formal calculations the evolutionary algorithms should be used.
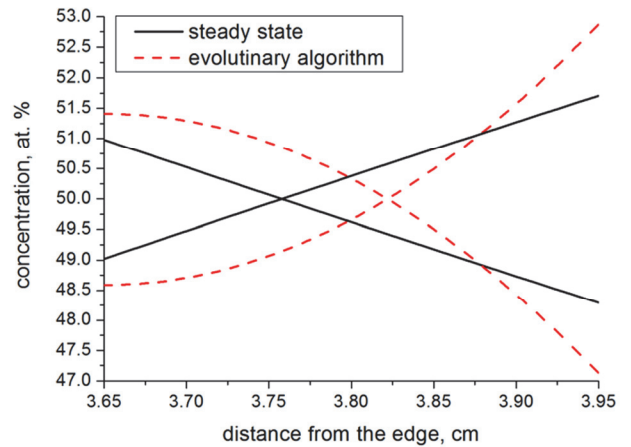

Fig. 1. *The comparisons of the steady-state and evolutionary algorithm for calculating the sedimentation process.*

The model can be easily supplemented with the vacancy evolution equation. Thus, the voids generation can be predicted. The detailed analysis of the voids generation and evolution can be found elsewhere (Wierzba & Skibiński, 2016). The following equation should be also calculated:

$$\frac{\partial N_v}{\partial t} - \text{div} \sum_{i=1}^{r} \rho_i B_i \, \text{grad} \mu_i + \frac{N_v - N_v^{eq}}{\tau_v} = 0 \qquad (16)$$

where: N_v is the vacancy molar fraction. The N_v^{eq} and τ_v [s] denote the vacancy equilibrium molar fraction and relaxation time, respectively. The data used in calculation is presented in table 2.

Table 2. *Data used in calculations of sedimentation process in BiSb system at 513 K (Regel & Glazov, 1982; Gorshkov, 2000)*

Component	Atomic mass, M_i [g mol^{-1}]	Molar volume, Ω_i [cm^3 mol^{-1}]	Initial composition [at. %]	Diffusion coefficient, D_i [cm^{2}s^{-1}]
Bi	208.98	21.31	70	$1.54 \ 10^{-5}$
Sb	121.76	18.19	30	$2.47 \ 10^{-6}$

In figure 2 the two-dimensional calculations of the vacancy profile is shown. The place of vacancy agglomeration is the potential place of voids formation.

5. CONCLUSIONS

In this paper two different methods of calculation the sedimentation process were discussed, namely the steady state and evolutionary algorithm. Both methods are based on the generalized Darken concept of interdiffusion with stress field. The stress was approximated from the equation of motion in
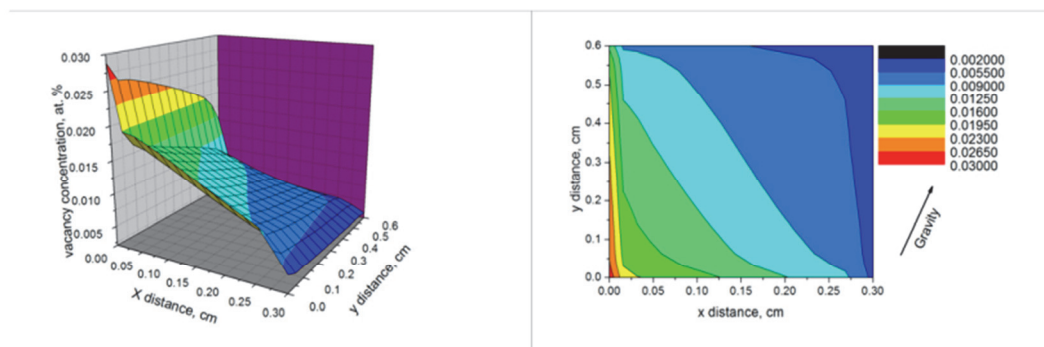
Fig. 2. *The calculated vacancy concentration profile during the sedimentation process in Bi-Sb system. The agglomeration of vacancies shows the place of voids formation.*

mechanical equilibrium. In our method, after Darken two velocities were introduced, namely the diffusion and drift velocity. The diffusion velocity based on the Nernst-Planck formulae. The diffusion potential was the sum of the chemical and mechanical potentials. The results of the calculations show, that the steady state could not be used in precise calculations. Moreover, the model can predict the vacancy concentration profile and place of voids formation. This is very important phenomena in e.g. microelectronics. The future investigations should focus on the influence of external forces onto the vacancy concentration and void generation.

ACKNOWLEDGEMENTS

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DYFUZJA POD WPŁYWEM POLA SIŁ ZEWNĘTRZNYCH - SEDYMENTACJA W CIELE STAŁYM

Streszczenie

W artykule zaprezentowana została numeryczna metoda charakteryzująca proces dyfuzji wzajemnej pod wpływem zewnętrznego pola sił. Zaprezentowano dwie metody modelowania procesu sedymentacji w ciele stałym - ewolucyjną oraz ustaloną w czasie. Zaproponowane metody bazują na uogólnionej metodzie Darkena. Podstawowymi prawami opisującymi proces są prawo zachowania masy oraz równanie ruchu. Matematyczny opis pozwala na równoczesną symulację pola naprężeń sprężystych oraz przesunięcia Kirkendalla podczas procesu transportu masy. Strumień dyfuzji jest zdefiniowany za pomocą potencjału chemicznego i mechanicznego.

COMPUTER METHODS IN MATERIALS SCIENCE