Physica A 484 (2017) 482–487

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

The vacancies formation and agglomeration under centrifugal force

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HIGHLIGHTS

- Vacancy migration due to external force.
- Vacancy agglomeration in the lower gravity region.
- The evolutionary algorithm for sedimentation.

ARTICLE INFO

Article history:
Received 26 January 2017
Received in revised form 31 March 2017
Available online 20 May 2017

Keywords:
Vacancies
Sedimentation
Diffusion

ABSTRACT

In this paper the vacancies formation and agglomeration under centrifugal force — sedimentation will be analyzed. The evolutionary algorithm for diffusion and vacancy evolution will be shown. The model predicts the location of vacancies agglomeration during the sedimentation process — the most probably place of voids formation. The computed results will be compared with experiments in Cu–brass diffusion couple. The influence of the centrifugal force on the vacancies migration will be presented.

1. Introduction

The completely new understanding of diffusion process has started with Kirkendall experiments [1]. The Kirkendall effect is a motion of the boundary between the two metals – Matano interface – during the interdiffusion process. The movement of the fast component in the diffusion couple is balanced by the plane shift, generation and migration of the vacancies. Thus, the fluxes of the binary diffusion couple, j_A, j_B and vacancies, j_V are conserved:

$$j_A + j_B + j_V = 0. \tag{1}$$

The first macroscopic model describing the Kirkendall effect was proposed by Darken [2] in 1948. The Darken model assumes, that during the diffusion process additional drift velocity exists, which is common for each component. The drift velocity, v^{drift} was defined by assumption of constant overall molar concentration:

$$v^{drift} = (D_A - D_B)\,\frac{\partial N_A}{\partial x} \tag{2}$$

where D_i and N_i denote the intrinsic diffusion coefficient and molar ratio of the ith component, respectively.

The Darken model was further the basis of its generalization for multicomponent systems [3,4], introduction of self stress [5–7], thermodynamics consistency [8], voids formation [9,10] and multiphase systems [11].

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http://dx.doi.org/10.1016/j.physa.2017.05.018
0378-4371/

A strong gravitational field has direct effects on the atomic scale, which can induce sedimentation of atoms or structural change [12,13]. The centrifugal forces can influence the chemical component concentration, isotopes segregation [14], formation of an atomic-scale graded structure in condensed matter [15].

One of the first sedimentation model in condensed matter was presented by Mashimo [16]. The model based on the Fick's first law for diffusion flux:

$$J_i = -\sum \left(D_{il1}\nabla C_l\right) + \sum \left(\frac{D_{il2}}{RT} g\left(M_j - M_j^*\right)\right) \tag{3}$$

where two different kinetic coefficients were introduced, namely: diffusion coefficient – D_{il1} and unknown sedimentation coefficient – D_{il2}. C_l denote the concentration, g the gravity force and M_j molecular mass of the component. The model was successfully solved in binary—BiSb system. However, the sedimentation coefficient has no physical meaning.

The diffusion under external gravitational field can be derived also from Maxwell relations:

$$\frac{1}{2}\frac{M_1}{N_A}\bar{\upsilon}_1^2 = \frac{1}{2}\frac{M_2}{N_A}\bar{\upsilon}_2^2 = \frac{3}{2}kT \quad \text{or} \quad M_1\bar{\upsilon}_1^2 = M_2\bar{\upsilon}_2^2 = 3RT \tag{4}$$

where: M_i denotes the molar mass of the ith component—a mass of one mole of this substance. N_A is an Avogadro number and $\bar{\upsilon}_i^2$ is an average velocity. The stress field acting on the components can be derived from Dalton law:

$$p = \frac{1}{3}M_1c_1\bar{\upsilon}_1^2 + \frac{1}{3}M_2c_2\bar{\upsilon}_2^2 = (c_1 + c_2)\,RT. \tag{5}$$

Assuming the local mechanical equilibrium, the momentum equation can be rewritten in the following form:

$$-\,\text{grad}\; p + \rho r\omega^2 = -\text{grad}\; p + \rho\omega^2\left(M_1c_1 + M_2c_2\right) = 0 \tag{6}$$

where: c_i the molar concentrations of the ith component in the mixture, p denote the internal pressure, r the radii and ω the centrifugal velocity. The concentration is a measure of the number of particles contained in any volume. $\rho_i = M_ic_i$ denotes the mass density of the ith component, it is a measure of the mass of substance contained in any volume. $\rho = \sum_{i=1}^{r}\rho_i$ the overall mass density. Combining Eqs. (5) and (6) the following relation hold:

$$-\,RT\text{grad}\;\left(c_1 + c_2\right) + r\omega^2\left(M_1c_1 + M_2c_2\right) = 0 \tag{7}$$

by using simple algebraic transformation, Eq. (7) can be rewritten in the following form:

$$-\,RTc_1\text{grad}\ln c_1 - RTc_2\text{grad}\;\ln c_2 + r\omega^2M_1c_1 + r\omega^2M_2c_2 = 0. \tag{8}$$

After rearranging and assuming, that the potential is a part of chemical and gravitational force acting on the component ($\mu_i = \mu_i^{ch} + V_i^g$ and $F_i^g = -\text{grad}V_i^g$):

$$c_1\left(-RT\text{grad}\;\ln c_1 + r\omega^2M_1\right) + c_2\left(-RT\text{grad}\;\ln c_2 + r\omega^2M_2\right) = c_1\left(-\text{grad}\;\mu_1^{ch} + F_1^g\right) + c_2\left(-\text{grad}\;\mu_2^{ch} + F_2^g\right) = 0 \tag{9}$$

where: $\text{grad}\;\mu_i^{ch} = RT\text{grad}\;\ln c_i$ and $F_i^g = r\omega^2M_i$.

Form, Eq. (9) the diffusion potential in gases equals:

$$c_1\left(-\text{grad}\;\mu_1^{ch} + F_1^g\right) + c_2\left(-\text{grad}\;\mu_2^{ch} + F_2^g\right) = c_1\left(-\text{grad}\;\mu_1^{ch} - \text{grad}V_1^g\right) + c_2\left(-\text{grad}\;\mu_2^{ch} - \text{grad}V_2^g\right) = 0. \tag{10}$$

Consequently:

$$c_1\text{grad}\;\mu_1 + c_2\text{grad}\;\mu_2 = 0. \tag{11}$$

Form Eq. (11) in gravity field at steady state ($F_i^g = M_ig$, $h = x$ and $-\text{grad}\;(M_igh) = -M_ig$). The two possible solution exists:

$$c_i\text{grad}\;\mu_i = 0 \tag{12}$$

and

$$c_1\text{grad}\;\mu_1 = -c_2\text{grad}\;\mu_2. \tag{13}$$

The second solution, Eq. (13) is not stationary, thus it is non-physical one. Concluding, the only one stationary solution is Eq. (12). The concentration can be approximated as:

$$\text{grad}\;\left(RT\ln c_i + M_igh\right) = 0 \quad \Rightarrow \quad \ln c_i = -\frac{M_ig}{RT}h \tag{14}$$

and finally:

$$c_i\left(h\right) = c_i\left(0\right)\exp\left(-\frac{M_ig}{RT}h\right). \tag{15}$$