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Void Formation during Diffusion – Two-Dimensional Approach

DOI 10.1515/htmp-2015-0049
Received March 2, 2015; accepted June 23, 2015

Abstract: The final set of equations defining the interdiffusion process in solid state is presented. The model is supplemented by vacancy evolution equation. The competition between the Kirkendall shift, backstress effect and vacancy migration is considered. The proper diffusion flux based on the Nernst–Planck formula is proposed. As a result, the comparison of the experimental and calculated evolution of the void formation in the Fe-Pd diffusion couple is shown.

Keywords: diffusion, Frenkel effect, backstress

Introduction

The difference in diffusion coefficient of components causes several effects during mass transport process. Most often Kirkendall and Frenkel effects occur [1, 2]. Kirkendall effect (lattice drift) caused by the vacancy flux divergence leads to dislocation climb and subsequently to the construction of extra planes in accumulation region [3–5]. The drift velocity is then generated. This constraint means zero divergence of overall volume flux density:

$$\frac{\partial}{\partial x}\sum_{i=1}^{r}\Omega_i^m J_i = 0.$$

When the only driving force is chemical potential gradient, $\mu_i = \mu_i^{\mathrm{ch}}$, the volume flux is given by

$$\Omega_i^m J_i = D_i^* \varphi \frac{\partial \rho_i}{\partial x} + \rho_i v.$$

In this paper the generalized description of the interdiffusion in solid state will be shown. The final set of equations: mass and volume continuity; flux relation and vacancy evolution equation will be formulated. Moreover, the kinetic effects related to the difference of mobilities, namely the stress generation and relaxation [3, 6], vacancy migration and void formation will be discussed. Due to volume constraint, interdiffusion leads to the accumulation of matter, and thus this accumulation must be reduced to zero. This reduction will be realized by the introduction of (1) Kirkendall effect; (2) backstress effect and (3) non-equilibrium vacancy distribution (Frenkel effect). Void evolution during interdiffusion process in Fe-Pd system will be presented.

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Mathematical formulation

Consider a multicomponent mixture, where ρ_i denotes the ith component density. The evolution of the density is described by the mass conservation law:

$$\frac{\partial \rho_i}{\partial t} + \mathrm{div}(\rho_i v_i) = 0, \tag{1}$$

where $J_i = \rho_i v_i$ denotes the overall flux of the ith component and v_i is its volume velocity (the medium velocity). The overall fluxes and velocities of the mass in the mixture (alloy) are defined by the volume frame of reference:

$$\begin{aligned} &\rho\Omega^m v = \sum\nolimits_i \left(\rho_i\Omega_i^m v^{\mathrm{drift}} + \rho_i\Omega_i^m v_i^d\right) \\ &\text{where } v := v^{\mathrm{drift}} + v^d = v^{\mathrm{drift}} + \sum\nolimits_i \rho_i\Omega_i^m v_i^d, \end{aligned} \tag{2}$$

where $i = 1,\ldots, r$ and r denotes the number of components. $N_i^m = \rho_i/\rho$ is the molar fraction.

During an arbitrary transport process, when volume is affected by the distribution of every component mixture, the volume continuity equation [7] follows:

$$\sum\nolimits_i \frac{\partial \rho_i \Omega_i^m}{\partial t} + \sum\nolimits_i \mathrm{div}\left(\rho_i\Omega_i^m v_i\right) = 0. \tag{3}$$

The final form of eq. (3) can be rewritten in the form that allows to determine the drift velocity:

$$\mathrm{div}\ v^{\mathrm{drift}} = -\mathrm{div}\left(\sum_{i=1}^{r}\rho_i\Omega_i^m v_i^d\right). \tag{4}$$

In one-dimensional space the drift velocity can be expressed by analytical function (after integration):

$$v^{\mathrm{drift}} = -\sum_{i=1}^{r}\rho_i\Omega_i^m v_i^d. \tag{5}$$

However, in two or free dimension space eq. (4) should be solved by numerical method, e.g. by replacing the drift velocity by its potential, i.e. $v^{\mathrm{drift}} = \mathrm{grad}\ u^{\mathrm{drift}}$ and then

rewriting the second-order partial derivatives with second-order finite difference approximations. Thus, the Poisson equation is derived. Finally, the iterative update of the Jacobi iteration can be used.

The component flux, $J_i \equiv \rho_i v_i$, should be expressed by the proper constitutive formula. Moreover three additional effects should be introduced, mainly (1) Kirkendall, (2) backstress and (3) vacancy generation into the flux expression.

The **Kirkendall effect** means the movement of lattice from slower diffusant side towards the faster diffusant side with some drift velocity, v^{drift}. Thus this effect results in diffusion flux as follows:

$$J_i = \rho_i v_i^d + \rho_i v^{\text{drift}}, \tag{6}$$

The diffusion flux is defined by the Nernst–Planck flux equation [8, 9], which in general form reads:

$$J_i = \rho_i B_i \operatorname{grad}\mu_i + \rho_i v^{\text{drift}}, \tag{7}$$

where μ_i is the generalized diffusion potential of the ith component.

Backstress effect – the diffusion potential is affected by the internal stress effect – stress gradient appearing due to attempt of matter accumulation. Each diffusing atom of both species is affected by common stress force:

$$\operatorname{grad}\mu_i^{\text{Int}} = -\operatorname{grad}\left(\Omega_i^m p^{\text{Int}}\right). \tag{8}$$

Non-equilibrium vacancy distribution – the diffusion potential is a difference of component chemical and common vacancy potentials, $\mu_i = \mu_i^{\text{ch}} - \mu^V$, and equalization of the diffusion fluxes instead of lattice shift is provided by the non-equilibrium vacancy gradient appearing due to attempt of matter accumulation. Role of effective force here is played by the gradient of vacancy chemical potential, proportional to the gradient of deviation of vacant sites fraction from its local equilibrium value:

$$\mu^V = -kT \ln \frac{\rho_V}{\rho_V^{\text{eq}}}. \tag{9}$$

Finally, the diffusion potential is a sum of component chemical, common vacancy and stress potentials, $\mu_i = \mu_i^{\text{ch}} + \mu^V + \mu_i^{\text{Int}}$, defined as follows:

$$\begin{aligned}\operatorname{grad}\mu_i = &- kT\frac{1}{\rho_i}\operatorname{grad}\rho_i - \frac{kT}{\rho_V^{\text{eq}}}\operatorname{grad}\left(\rho_V - \rho_V^{\text{eq}}\right)\\ &- \operatorname{grad}\left(\Omega_i^m p^{\text{Int}}\right).\end{aligned} \tag{10}$$

The internal pressure, p^{Int}, is a result of the difference in the diffusion coefficients of the components and difference in the lattice in diffusion couple (pressure generated by interdiffusion process):

$$\frac{\partial p^{\text{Int}}}{\partial t} = -\frac{E}{3(1-2\upsilon)}\operatorname{div}\left(\sum_{i=1}^{r}\rho_i\Omega_i^m v_i^d\right). \tag{11}$$

The last equation defining the model is the vacancy exchange equation defined as

$$\frac{\partial \rho_v}{\partial t} - \operatorname{div}\sum_{i=1}^{r}\rho_i B_i \operatorname{grad}\mu_i + \frac{\rho_v - \rho_v^{\text{eq}}}{\tau_v} = 0, \tag{12}$$

where N_v is the vacancy molar fraction, j_v is the vacancy flux. N_v^{eq} and τ_v denote the vacancy equilibrium molar fraction and relaxation time, respectively.

To calculate void formation, in one-dimensional system, during the interdiffusion process one additional equation should be introduced, mainly, the void radii evolution [10, 11]:

$$\frac{dR}{dt} = D_V\left(N_V - N_V^{\text{eq}}\right)\left(\frac{1}{L_V} + \frac{1}{R}\right), \tag{13}$$

where L_V denotes the mean free path of vacancies and the vacancy diffusion coefficient is defined as $D_V = \dfrac{\sum_{\substack{j,i=1\\ j>i}}^{r} D_i^I D_j^I}{N_V \sum_{\substack{i,j=1\\ i\neq j}}^{r} D_i^I N_j}$.

Results

In this section the experimental and calculated results of interdiffusion and void formation will be shown. The calculations will be analysed in two-dimensional space. The simulation results will be verified with diffusion couple experiments in Fe-Pd binary system (Figure 1). The void radii will be estimated and the results for

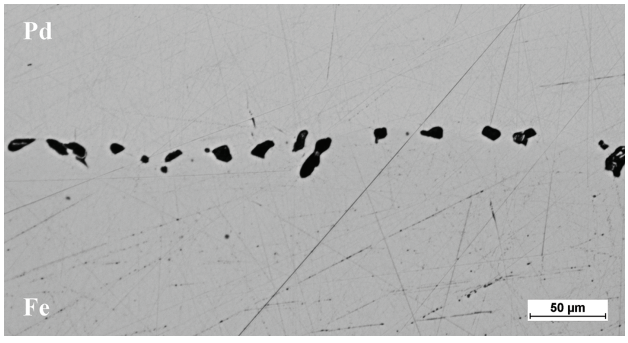

Figure 1: The experimental results of Frenkel effect (voids formation) during diffusion between pure Fe and Pd after 150 h at 1,273 K.

different calculation times will be presented. The following set of equations will be solved:

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div}\left(\rho_i v_i^d + \rho_i v^D\right) = 0 \quad \text{on}$$
$$\Omega \backslash \Omega_V \ - \text{mass conservation}$$

$$\frac{\partial \rho_v}{\partial t} - \operatorname{div} \sum_{i=1}^{r} \rho_i B_i \operatorname{grad} \mu_i + \frac{\rho_v - \rho_v^{\text{eq}}}{\tau_v} = 0 \quad \text{on}$$
$$\Omega \backslash \Omega_V \ - \text{vacancy exchange}$$

$$\frac{\partial \rho_i}{\partial t} = \frac{\partial \rho_V}{\partial t} = 0 \quad \text{on} \quad \Omega_V \ - \text{void growth}$$

where $\operatorname{grad}\mu_i = -kT\frac{1}{\rho_i}\operatorname{grad}\rho_i - \frac{kT}{\rho_V^{\text{eq}}}\operatorname{grad}\left(\rho_V - \rho_V^{\text{eq}}\right)$. This set of equations will be supplemented with boundary conditions:

$$\rho_i v_i^d = 0 \quad \text{on} \quad \partial\Omega \quad - \text{diffusion flux on the boundary}$$

The subset Ω_V denotes the position of the voids. The voids are initially introduced into the calculation mesh. Thus only the growth will be simulated. In two-dimensional space no additional equation for radii is needed.

In Fe-Pb system the voids growth on the iron reach side of the diffusion couple. We assume that in Fe-Pd system the mean migration length for vacancy is $L_V = 10^{-8}$m. The diffusion coefficient was calculated from Boltzmann-Matano analysis (from known experimental results of diffusion in Fe-Pd system at 1,273 K for 150 h – Figure 1). The results for different calculation times are shown in Figures 2– 5.

The estimated voids radii for different times are shown in Figure 6. It is clearly shown that the dependence is a parabolic one.

Conclusions

The presented method allowed the calculation of the interdiffusion process when Kirkendall, Frenkel and backstress effects are introduced. It was shown that the vacancy evolution in all diffusion calculations to approximate the real process should be introduced. The vacancies agglomerate in places where initially void was introduced as in real diffusion experiments. The results

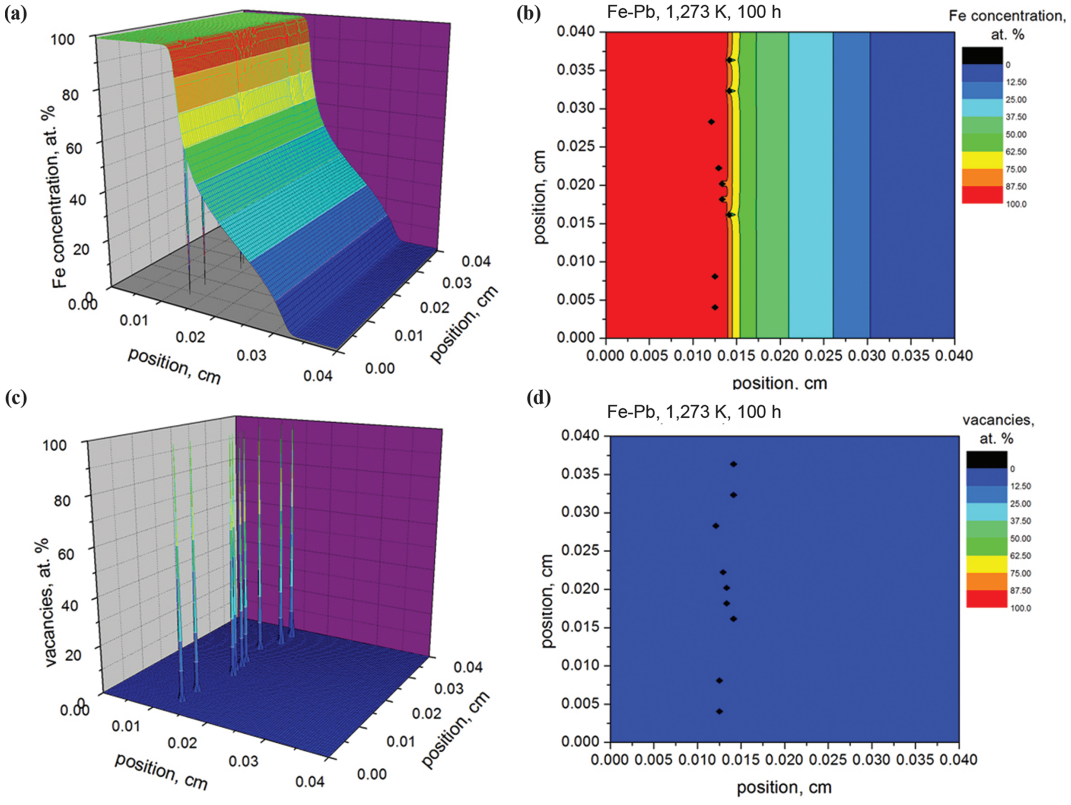

Figure 2: The simulation results of the Fe concentration (a)–(b) and voids formation (vacancies evolution) (c)–(d) in Fe-Pd system after annealing at 1,273 K for 100 h.

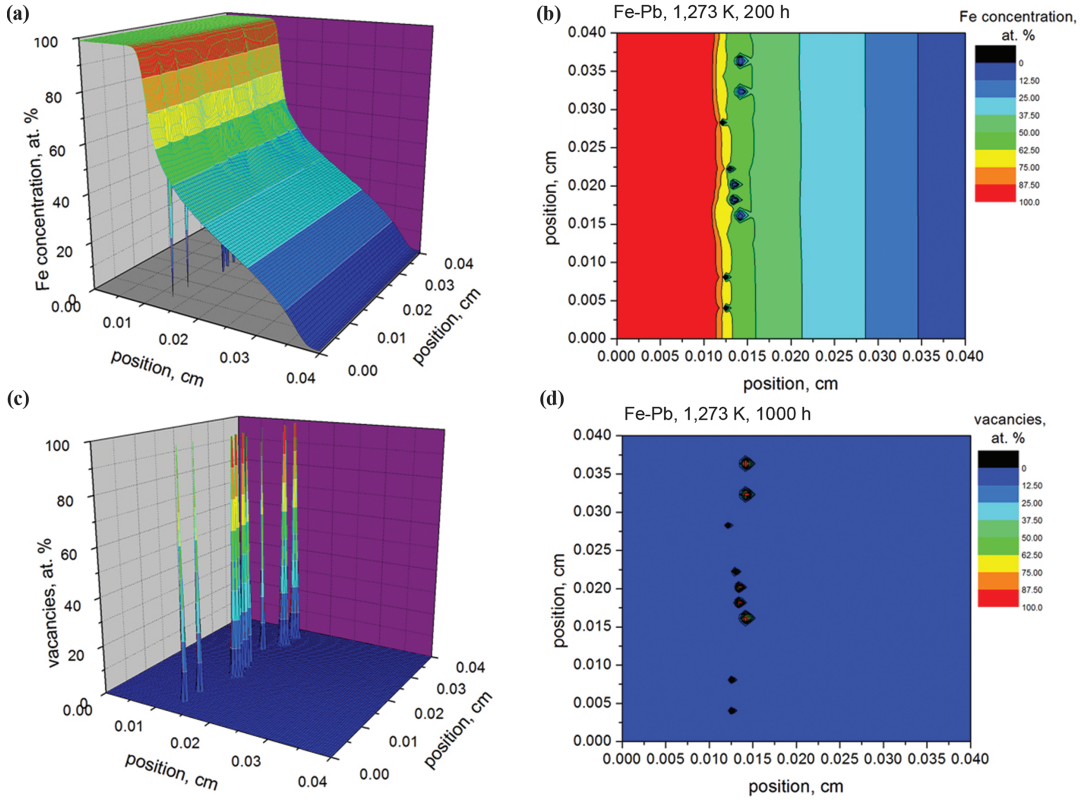

Figure 3: The simulation results of the Fe concentration (a)–(b) and voids formation (vacancies evolution) (c)–(d) in Fe-Pd system after annealing at 1,273 K for 200 h.

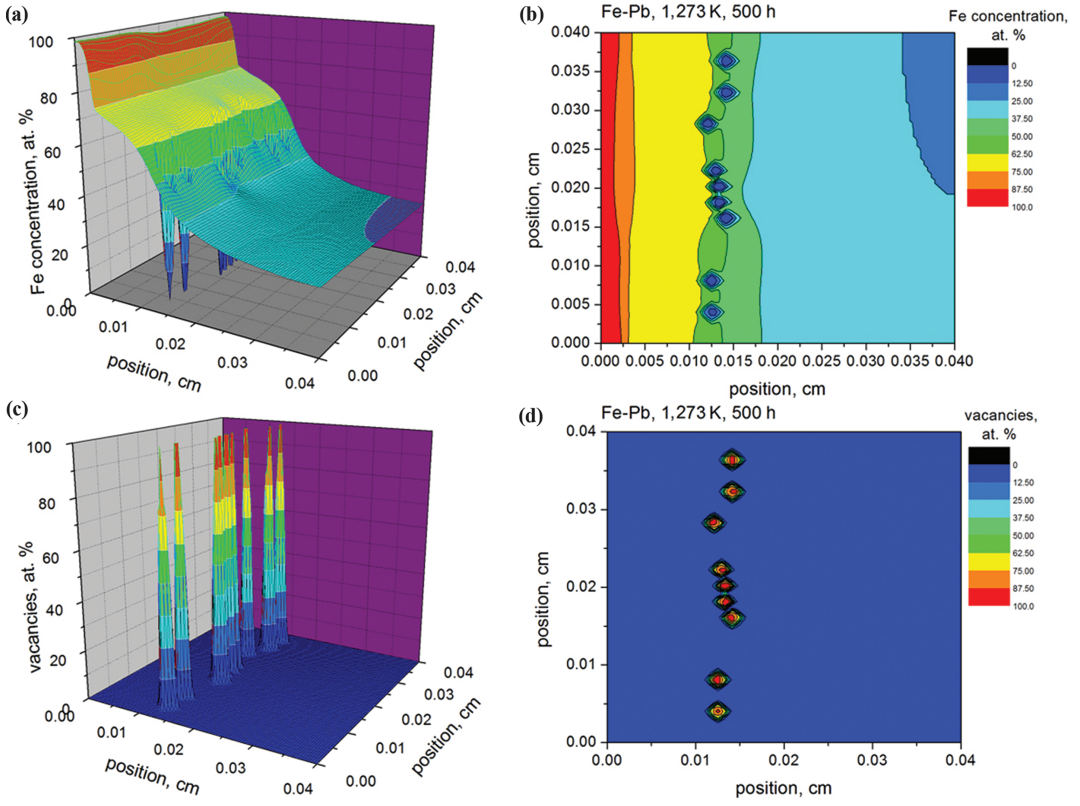

Figure 4: The simulation results of the Fe concentration (a)–(b) and voids formation (vacancies evolution) (c)–(d) in Fe-Pd system after annealing at 1,273 K for 500 h.

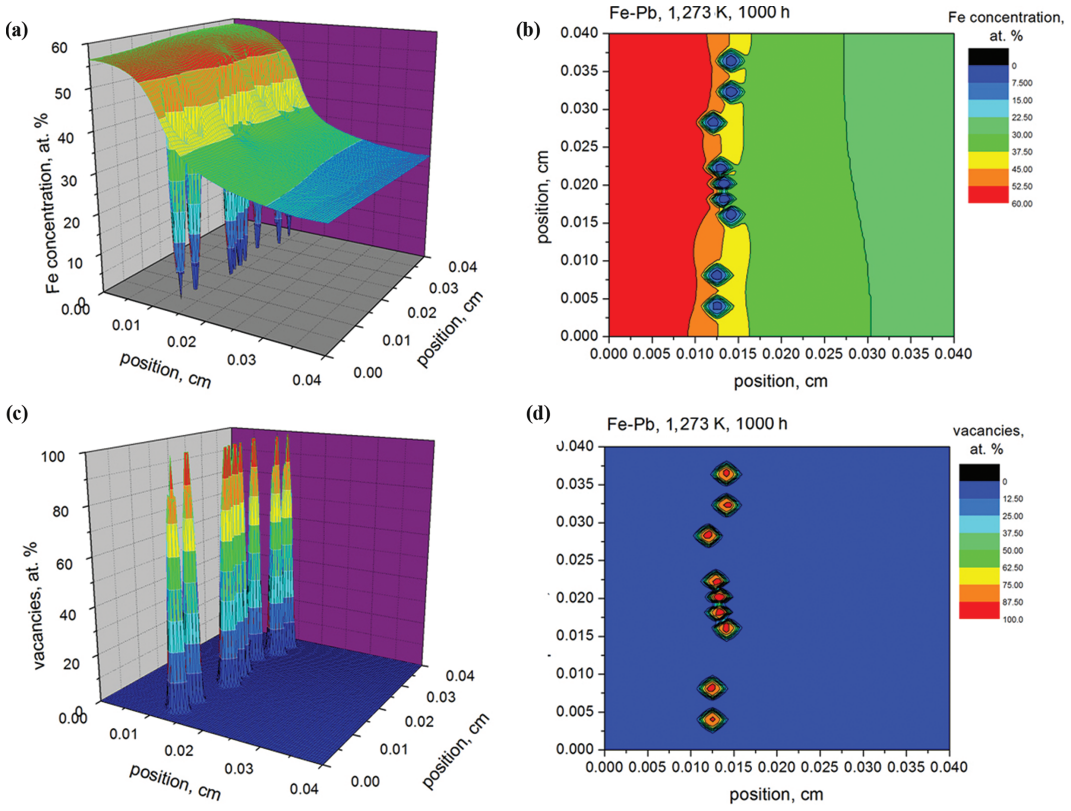

Figure 5: The simulation results of the Fe concentration (a)–(b) and voids formation (vacancies evolution) (c)–(d) in Fe-Pd system after annealing at 1,273 K for 1,000 h.

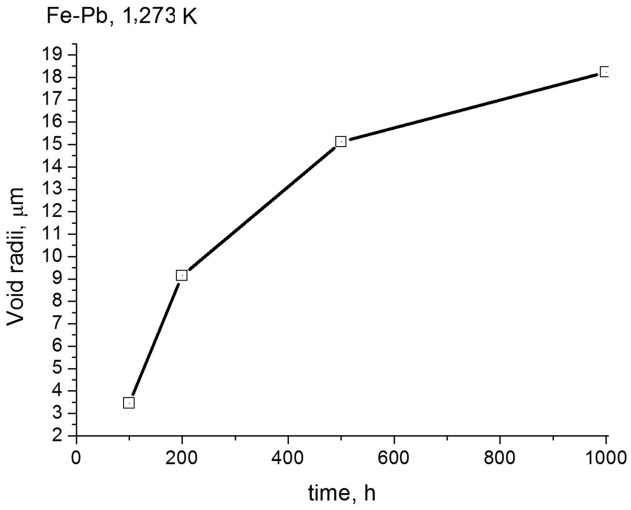

Figure 6: The estimated void radii for different simulation time.

of the model were verified with experimental results for Fe-Pb binary system. Moreover, it was presented that the average radii of the void change parabolically with time. In the future the dynamics of the voids should be introduced, mainly simulation should take into account that the voids are moving during the diffusion process.

Funding: This work has been supported by the National Science Centre (NCN) in Poland, decision number 2013/09/B/ST8/00150.

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