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THE KIRKENDALL SHIFT AND FRENKEL EFFECT DURING MULTI-COMPONENT DIFFUSION PROCESS

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Abstract. *In this paper the phenomenological process related to the evolution of the ternary and higher system is discussed. The two coupled phenomena related to the difference in diffusion coefficients will be presented by numerical investigations - mainly the Kirkendall and Frenkel effects. Such a difference leads to the: lattice shift, stress generation and relaxation, non-equilibrium distribution of vacancies and voiding. The generalized Darken method (bi-velocity) of the multi-component system is formulated. The approximation method allows for determination the evolution of the voids. Thus the relaxation time for the vacancies in terms of mean migration length and vacancy diffusion coefficient in case of multicomponent system will be formulated. Moreover, the void evolution in Fe-Pd system will be calculated.*

1 INTRODUCTION

The Navier-Stokes set of equations is a theoretical model for continuum fluid dynamics where the local thermodynamic equilibrium holds. However, this equations encounters some challenging difficulties for non-continuum flows. This phenomena was widely studied in the gas community, where the gas density is usually very low. In recent years, non-continuum flows have also attracted much attention with the rapid development in microelectromechanical systems. However, due to the finite Knudsen number effect, the continuum-equilibrium assumption may break down and the model will fail to work for these flows [1, 2, 3].

In the recent years Brenner proposed new model based on the fluid velocity [4, 5, 6]. He introduced one single additional term into each of the momentum and energy equations. Generally Brenner assumed that the mass velocity in the hydrodynamics equations should be replaced by volume velocity which relates to the flux of volume rather than mass [4, 5, 6].

On the other hand, diffusion community knows very well an alternative way of providing volume conservation. Namely, it is a lattice drift (Kirkendall effect) caused by the vacancy flux divergence leading to dislocation climb and subsequently to the construction of extraplanes in accumulation region and dismantling atomic planes in depleting region [7, 8, 9]. The drift velocity is than 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, $\mu_i = \mu_i^{ch}$, the volume flux is given by:

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

In this paper the intrdiffusion in solid state description will be formulated. The mass, heat, volume continuity equation, flux definition and vacancy evolution equation will be presented. We will focus on the kinetic effects that are related to difference of mobilities, namely on the stress generation and relaxation [3,10]. Interdiffusion leads to the accumulation of matter at the side of slower component of the diffusion couple. Due to the volume constraint, nature just must find some ways to reduce this accumulation to zero. This reduction, will be realized here by introduction of: 1) Kirkendall effect; 2) Backstress effect and 3) non-equilibrium vacancy distribution. The last paragraph will present the results of the model mainly, the voids evolution during interdiffusion process in Fe-Pd system.

2. THE MASS AND HEAT EQUATIONS

Mass conservation law. Consider multicomponent mixture, where ρ_i denote the *i*-th component density. The evolution of the density is described by the equation:

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div}\left(\rho_i v_i\right) = 0 \qquad (1)$$

where $J_i = \rho_i v_i$ is the overall flux of the *i*-th component and v_i denote its volume velocity (the medium velocity). We do not take into account mass production or consumption in this equation.

Heat balance. Diffusive flux can influence the heat balance. The heat flux can be defined after Fourier (for isotropic material) as:

$$J^q = -k \text{ grad } T \qquad (2)$$

where k denote the thermal conductivity and T is the temperature. We can define the enthalpy of the system according to internal energy density as:

$$h = u + \frac{\operatorname{tr}\left(\sigma\right)}{\rho} \qquad (3)$$

The differential form of the above equation is:

$$\left.\frac{D\rho h}{Dt}\right|_v = \left.\frac{D\rho u}{Dt}\right|_v + \left.\frac{D\operatorname{tr}\left(\sigma\right)}{Dt}\right|_v \approx \sum_i \left.\frac{D\rho_i u_i}{Dt}\right|_{v_i} + \left.\frac{D\operatorname{tr}\left(\sum_i \Omega_i^m \rho_i \sigma\right)}{Dt}\right|_{v_i} \qquad (4)$$

where $\left.\frac{DT}{Dt}\right|_v$ denote the Lagrange derivative defined over the velocity v:

$$\left.\frac{DT}{Dt}\right|_v = \frac{\partial T}{\partial t} + v \text{ grad } T, \qquad (5)$$

Assuming, that the changing enthalpy in time is proportional to its specific heat and temperature, the following equation can be written:

$$\left.\frac{Dh}{Dt}\right|_v = c_p \left.\frac{DT}{Dt}\right|_v \qquad (6)$$

Finally, by introducing Eqs. (2) - (6) into the energy conservation law and the mechanical parts are neglected, than the final heat transport equation can be derived:

$$\rho c_p \left.\frac{DT}{Dt}\right|_v \approx \mathrm{div}\left(k \text{ grad } T\right) \tag{7}$$

The fluxes. The overall flux and velocity of the mass are defined by the volume drift and diffusion velocities:

$$\rho\Omega^m v = \sum_i \left(\rho_i\Omega_i^m v^{drift} + \rho_i\Omega_i^m v_i^d\right) \qquad \text{where } v := v^{drift} + v^d = v^{drift} + \sum_i \rho_i\Omega_i^m v_i^d , \tag{8}$$

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

The volume drift velocity. During an arbitrary transport process when volume is affected by the distribution of every mixture component and the stress field, from the Liouville theorem it follows:

$$\sum_i \frac{\partial\rho_i\Omega_i^m}{\partial t} + \sum_i \mathrm{div}\left(\rho_i\Omega_i^m v_i\right) = \mathrm{div} v^\sigma . \tag{9}$$

We consider here a multicomponent solution in a closed system, where partial molar volumes and elastic properties do not depend on composition, $\Omega_i \neq f\left(N_1,\ldots,N_r\right)$. Thus, the volume can be only affected by the external forces:

$$\mathrm{d}|\Omega|/\mathrm{d}t = \int_{\partial|\Omega|} v^\sigma \, \mathrm{d}x . \tag{10}$$

where: υ^σ is a velocity generated by external forces (elastic deformation). Introducing Euler relation ($\sum_i \rho_i\Omega_i^m = \rho\ \Omega^m \equiv 1$) and Eq. (8), (9) allow to calculate the drift velocity of the mixture:

$$\sum_i \mathrm{div}\left(v^{drift} + \rho_i\Omega_i^m v_i^d\right) = \mathrm{div} v^\sigma \tag{11}$$

Denoting the Darken velocity, v^D as:

$$v^D = -\rho_i\Omega_i^m v_i^d \tag{12}$$

The final form of the drift velocity can be rewritten in the form:

$$\mathrm{div}\ v^{drift} = \mathrm{div}\left(v^\sigma + v^D\right) \tag{13}$$

Equation (13) defines the drift velocity of the system. In one dimension the drift velocity can be expressed by analytical function as:

$$v^{drift} \approx v^\sigma + v^D \tag{14}$$

In this paper we will consider, additionally four more effects: 1) Kirkendall effect, 2) Backstress 3) vacancy generation effect and 4) thermal gradient

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 follow:

$$J_i = \rho_i v_i^d + \rho_i v^{drift}, \qquad (15)$$

The diffusion flux is defined by the Nernst-Planck flux equation [11,12] which in general form reads:

$$J_i = \rho_i B_i \operatorname{grad}\mu_i + \rho_i v^{drift}, \qquad (16)$$

where μ_i is the generalized diffusion potential of the *i*-th 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:

$$\operatorname{grad}\mu_i^{Int} = -\operatorname{grad}\left(\Omega_i^m p^{Int}\right) \qquad (17)$$

Non-equilibrium vacancy distribution - the diffusion potential is a difference of component chemical and common vacancy potentials, $\mu_i = \mu_i^{ch} - \mu^V$, 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:

$$\mu^V = -kT \ln \frac{\rho_V}{\rho_V^{eq}} \qquad (18)$$

Temperature distribution - the isothermal heat transmitted by moving the atom in the process of jumping a lattice site less the intrinsic enthalpy [13, 14]:

$$\operatorname{grad}\mu^T = -\frac{1}{T} Q^* \operatorname{grad}T \qquad (19)$$

where: Q^* is defined as heat of transport. Finally, the diffusion potential is a sum of component chemical and common vacancy and stress potentials, $\mu_i = \mu_i^{ch} - \mu^V + \mu_i^{Int} + \mu^T$. Consequently, the gradient of the diffusion potential is defined as follow:

$$\mathrm{grad}\mu_i = -kT\frac{1}{\rho_i}\mathrm{grad}\rho_i - \frac{kT}{\rho_V^{eq}}\mathrm{grad}\left(\rho_V - \rho_V^{eq}\right) - \mathrm{grad}\left(\Omega_i^m p^{Int}\right) - \frac{1}{T}Q^*\mathrm{grad}T \qquad (20)$$

Internal pressure - the internal pressure is a result of the difference in the diffusion coefficients of the components and difference in the lattice in diffusion couple [15]:

$$\frac{\partial p^{Int}}{\partial t} = -\frac{E}{3\left(1-2\upsilon\right)}\mathrm{div}\left(v^{\sigma} + v^{d}\right), \ (21)$$

where: the overall diffusion velocity is defined as:

$$v^d = \sum\nolimits_i \rho_i \Omega_i^m v_i^d \qquad (22)$$

Vacancy exchange. The last equation defining the model is the vacancy exchange. The equation is defined as:

$$\frac{\partial \rho_v}{\partial t} - \mathrm{div}\sum_{i=1}^{r} \rho_i B_i \,\mathrm{grad}\mu_i + \frac{\rho_v - \rho_v^{eq}}{\tau_v} = 0 \qquad (23)$$

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

3. RESULTS.

In this section the results of interdiffusion and voids formation will be shown. The voids formation will be analyzed in two-dimmensional space. For experimental verification the Fe-Pd binary system was used. The voids radii will be estimated and the results for different calculation times will be shown. The following set of the equation will be solved:

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

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

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

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

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

The subset Ω_V denote the position of the voids. The voids are initially introduced onto the calculation mesh. Thus, only the growth will be simulated. In general, the voids growth on the faster diffusion couple side. 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 was $L_V = 10^{-8} m$. The diffusion coefficient was calculated from Boltzmann-Matano analysis (from known experimental results of diffusion in Fe-Pd system at 1273K for 150h [16]), i.e. at the concentration point $N_{Fe} = 0.75$ the diffusion coefficients was estimated as: $D_{Fe} = 1.17 \cdot 10^{-15}$ and $D_{Pd} = 9.27 \cdot 10^{-16}$ $m^2 s^{-1}$. The results for different calculation times are shown on figures 1-2.

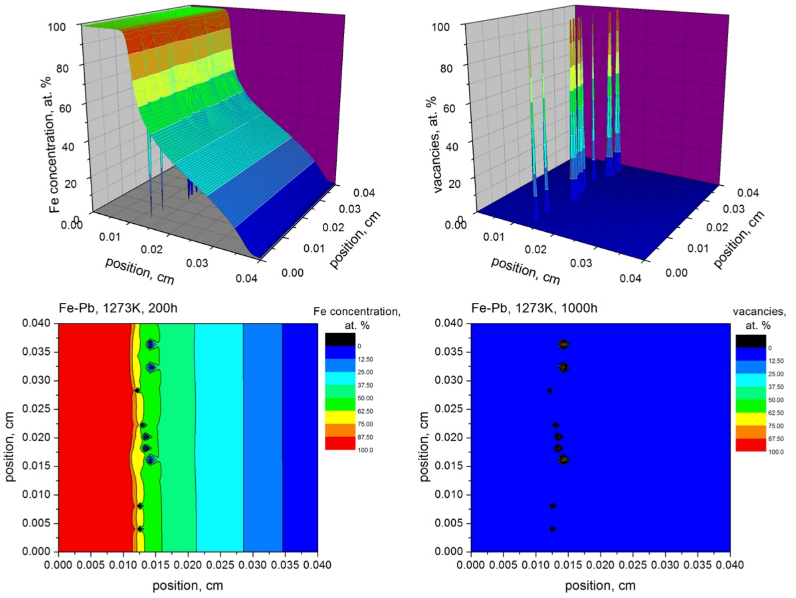

Figure 1. The simualtion results of the a) - c) Fe concentration and b) - d) voids formation (vacancies evolution) in Fe-Pd system after annealing at 1273K for 200h

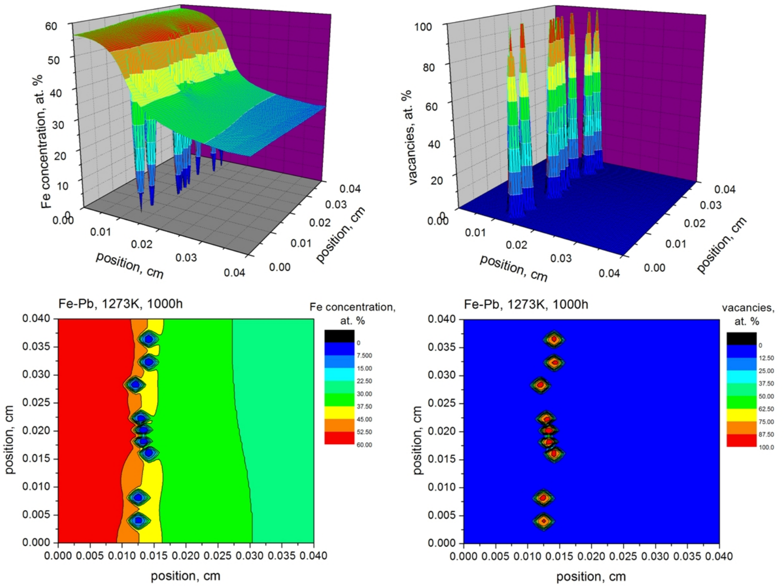

Figure 2. The simualtion results of the a) - c) Fe concentration and b) - d) voids formation (vacancies evolution) in Fe-Pd system after annealing at 1273K for 1000h

4. CONCLUSIONS.

Present paper shows the method which allow for calculation of the physical models of interdiffusion. The drift velocity was calculated in case of presence of the vacancy, backstress and chemical force fields. Moreover, it was shown, that the interdiffusion process can be influenced by the vacancy and heat fields. The model was checked by simulating voids growth during diffusion couple experiments. It was presented, that the voids are formed at the faster diffusion side of the diffusion couple. Moreover the radii of the void changes parabolically with time. In the future the simulation should take into account, that the voids are moving during the diffusion process.

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