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Publisher: Taylor & Francis

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## Philosophical Magazine

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tphm20>

### Competition between Kirkendall shift and backstress in interdiffusion revisited - simple analytic model

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Published online: 03 Mar 2014.

To cite this article: A. Gusak, B. Wierzb<sup>a</sup> & M. Danielewski (2014): Competition between Kirkendall shift and backstress in interdiffusion revisited - simple analytic model, Philosophical Magazine, DOI: [10.1080/14786435.2013.878053](https://doi.org/10.1080/14786435.2013.878053)

To link to this article: <http://dx.doi.org/10.1080/14786435.2013.878053>

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## Competition between Kirkendall shift and backstress in interdiffusion revisited – simple analytic model

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(Received 1 October 2013; accepted 18 December 2013)

We present the first simple analytical description of the interdiffusion process where the competition between the Kirkendall shift and the backstress is considered. It is shown that two diffusion subzones are formed; these sections are linked to the fast and slow diffusing component. During the interdiffusion process, the stress effect does not vanish.

**Keywords:** Kirkendall shift; backstress; interdiffusion; stress effect; vacancy distribution

‘Every physical law must have mathematical beauty’

Paul Dirac

### 1. Introduction

Complexity of interdiffusion is, first of all, due to the difference of mobilities of different species. Difference of mobilities leads to the numerous phenomena: the lattice shift, the stress generation and relaxation, the non-equilibrium distribution of vacancies and voiding, the evolution of dislocation network, often to the diffusion-driven grain-boundaries motion, sometimes to the bifurcations and instabilities of markers distributions [1–12]. In this work, we consider one-dimensional interdiffusion in a two-component alloy, in which intrinsic diffusivities (mobilities) are composition invariant. The diffusion flux (in standard Darken approach, it means the flux in the moving lattice reference frame) depends on the gradient of the diffusion potential,

$$J_i^d = -M_i c_i \frac{\partial \mu_i}{\partial x}. \quad (1)$$

The diffusion potential gradient is a generalized thermodynamic driving force and reflects the change of energy due to the diffusion (motion) of atoms. The overall component flux is a sum of diffusion and drift counterparts:  $J_i = J_i^d + c_i v$ . Interdiffusion

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proceeds under constraint of almost constant total volume, that is, we neglect the deviations from Vegard's law. This constraint means zero divergence of overall volume flux density [9]:

$$\frac{\partial}{\partial x} (\Omega_A J_A + \Omega_B J_B) = 0. \quad (2)$$

In planar diffusion couple with concentration gradient along  $x$ -axis, it immediately leads to

$$\Omega_A J_A + \Omega_B J_B = k(t). \quad (3)$$

In the closed diffusion couple that does not exchange mass with the surrounding  $k(t) = 0$  and we get finally:

$$\Omega_A J_A + \Omega_B J_B = 0. \quad (4)$$

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

$$\Omega_i J_i = M_i c_i \Omega_i \frac{\partial \mu_i^{\text{ch}}}{\partial x} + \Omega_i c_i v = D_i^* \varphi \frac{\partial N_i}{\partial x} + N_i v. \quad (5)$$

The thermodynamic factor equals  $\varphi = \frac{N_A}{kT} \frac{\partial \mu_A^{\text{ch}}}{\partial N_A} = \frac{N_B}{kT} \frac{\partial \mu_B^{\text{ch}}}{\partial N_B}$ , where  $N_i$  is the atomic fraction ( $N_A + N_B = 1$ ).

Below we will concentrate on the kinetic effects that are related to difference of mobilities, namely on the stress generation and relaxation. So-called concentration stresses have been analysed in textbooks and will not be considered here [3,13]. Therefore, we will assume the constant and equal atomic volumes ( $\Omega_A \cong \Omega_B \cong \Omega$ ). In the closed diffusion couple, it implies that its overall volume is constant as well. Difference of mobilities  $M_i = D_i^*/kT$ , in other words, of the tracer diffusivities  $D_i^*$  leads to 'contradiction' with constraint of constant volume. Interdiffusion leads to the accumulation of matter at the side of slower component of the diffusion couple. Due to the volume constraint, Equation (2), nature just must find some ways to reduce this accumulation to zero. One can distinguish at least three basic ways of the accumulation reduction:

- (1) *Kirkendall effect* – movement of lattice from slower diffusant side towards the faster diffusant side with some drift velocity,  $v$ , that is common for both components and measured by inert markers frozen within moving lattice. The only driving force is chemical potential,  $\mu_i = \mu_i^{\text{ch}}$  and the local drift velocity is determined by constraint of the constant volume. Thus, from Equations (4) and (5), we get:

$$\Omega J_A + \Omega J_B = \left( -D_A^* \varphi \frac{\partial N_A}{\partial x} + N_A v \right) + \left( -D_B^* \varphi \frac{\partial N_B}{\partial x} + N_B v \right) = 0. \quad (6)$$

Constraint of constant volume in the form of Equation (4) immediately gives famous Darken expressions for the drift velocity:

$$v = (D_B^* - D_A^*) \varphi \frac{\partial N_B}{\partial x} \quad (7)$$

and for the volume interdiffusion flux:

$$\Omega J_B = -(N_A D_B^* + N_B D_A^*) \phi \frac{\partial N_B}{\partial x} \equiv -\tilde{D} \frac{\partial N_B}{\partial x}, \quad (8)$$

where effective Darken interdiffusivity equals:

$$\tilde{D} = (N_A D_B^* + N_B D_A^*) \phi. \quad (9)$$

- In a case of large difference of mobilities and atomic fractions not too close to zero or unity, Darken interdiffusivity is determined mainly by the faster diffusant.
- (2) *Backstress effect* (osmotic pressure – this notion being introduced by Bokstein and Shvindlerman [14]). In this case, the diffusion potential is a sum of chemical and common stress forces,  $\mu_i = \mu_i^{\text{ch}} + \mu^{\text{stress}}$  and equalization of the diffusion fluxes (the local volume conservation = conservation of the lattice sites) instead of lattice shift is provided by the stress gradient appearing due to attempt of matter accumulation. Each diffusing atom of both species is affected by common stress force:  $F = -\partial \mu^{\text{stress}} / \partial x = \Omega \partial \sigma / \partial x$ , where  $\sigma = -p = 1/3 S p \sigma_{ik}$  is hydrostatic part of the stress tensor. In a planar diffusion couple with concentration gradient along  $x$ -axis, one has [3]:

$$\sigma_{xx} = \sigma_{xy} = \sigma_{xz} = 0, \quad \sigma_{yy} = \sigma_{zz} = \frac{1}{2} S p \sigma_{ik} = \frac{3}{2} \sigma. \quad (10)$$

Force is the same for both species and in general the drift velocity under common stress force and chemical potential will be now different, due to different mobilities, and this is a main difference with Darken analysis. In the ‘ideal case’, action of force should lead to the zero drift term. Thus, the volume fluxes are purely diffusional ( $v = 0$ ) and are given by Nernst–Einstein relation [15], Equation (1):

$$\Omega J_i = -D_i^* \phi \frac{\partial N_i}{\partial x} + N_i \frac{D_i^*}{kT} F = -D_i^* \phi \frac{\partial N_i}{\partial x} + N_i \Omega \frac{D_i^*}{kT} \frac{\partial \sigma}{\partial x}. \quad (11)$$

Then, the constraint of constant volume, Equation (4), will give:

$$\Omega J_A + \Omega J_B = \left( -D_A^* \phi \frac{\partial N_A}{\partial x} + N_A \frac{D_A^*}{kT} F \right) + \left( -D_B^* \phi \frac{\partial N_B}{\partial x} + N_B \frac{D_B^*}{kT} F \right) = 0 \quad (12)$$

and one obtains the magnitude of backstress force:

$$F = \Omega \frac{\partial \sigma}{\partial x} = \frac{D_B^* - D_A^*}{N_A D_A^* + N_B D_B^*} kT \phi \frac{\partial N_B}{\partial x} \quad (13)$$

and an expression for interdiffusion flux:

$$J_B = -J_A = -\frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*} \phi \frac{\partial N_B}{\partial x} \equiv -D_{NP} \frac{\partial N_B}{\partial x}. \quad (14)$$

Effective interdiffusivity here is sometimes called Nernst–Planck diffusivity [6,13],

$$D_{NP} = \frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*} \phi \quad (15)$$

It is controlled by the slower component, contrary to Darken case. Backstress effect is well known in electromigration community, after Herring explanation of Blech experiments with Al strips [16,17]. Electromigration issues will not be discussed here.

- (3) *Non-equilibrium vacancy distribution.* This way of providing local volume conservation was first analysed in details by Nazarov and Gurov [18]. In this case, 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.

Formally, this way is very similar to previous one (and was presented one year earlier than osmotic pressure concept). 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:

$$F_V = -\frac{\partial \mu_V}{\partial x} = -\frac{\partial}{\partial x} \left( kT \ln \frac{N_V}{N_V^{\text{eq}}} \right) \cong -\frac{kT}{N_V^{\text{eq}}} \frac{\partial (N_V - N_V^{\text{eq}})}{\partial x} \quad (16)$$

Role of non-equilibrium vacancy distribution is important at the initial stages of interdiffusion when the width of diffusion zone is less or by the order of magnitude comparable with the mean migration length of vacancies [5,19]. This length depends on dislocation density and is typically of micron or sub-micron size. The effective interdiffusivity of Nazarov-Gurov coincides with Nernst-Planck expression, Equation (15).

In this work, we do not assume the equalization of the diffusion fluxes by some unique way at any time moment and consider the following question: what way or combination of ways of satisfying constant volume constraint is actually used by nature at various stages of interdiffusion? In other words, what is the interrelation between Kirkendall shift, stress gradient and non-equilibrium vacancy distribution at different stages of the interdiffusion process and at various positions within the diffusion zone?

In this case, the diffusion potential is a sum of component chemical and common vacancy and stress potentials,  $\mu_i = \mu_i^{\text{ch}} - \mu_V + \mu^{\text{stress}}$ . Consequently, we need interrelation between lattice drift, backstress and non-equilibrium vacancy concentration. Recently, a linear interrelation between drift velocity and stress gradient was suggested [20], but the factor of proportionality remained a fitting parameter. On the other hand, there is simple link between divergence of drift velocity and the rate of stress evolution [21], see also similar relation for electro-migration [22], both can be used at least in the case when the plasticity limit is not reached. Namely, when the divergence of drift velocity is determined by the vacancy generation/annihilation rate, which means generation or annihilation of lattice sites. This means dilatation of alloy leading to stress:

$$\frac{\partial v}{\partial x} = -\frac{N_V - N_V^{\text{eq}}}{\tau_V} = -\frac{1}{B} \frac{\partial S p \sigma_{ik}}{\partial t}, \quad (17)$$

where  $B$  is the bulk modulus.

In this paper, we at first write down the full set of equations with account of all above-mentioned factors. The possible voiding will be not considered.

## 2. Theory

### 2.1. Formulation of the problem; the self-consistent set of equations

Simultaneous evolution of concentration profiles, lattice drift, stresses and non-equilibrium vacancies implies that diffusion potential that is sum of chemical potential, stress and vacancy terms. The problem is described by the set of 4 differential equations, where  $N_A$ ,  $\sigma$ ,  $N_V$  and  $v$  are unknowns:

$$\frac{\partial N_A}{\partial t} = -\frac{\partial}{\partial x} \left( -D_A^* \varphi \frac{\partial N_A}{\partial x} + N_A \Omega \frac{D_A^*}{kT} \frac{\partial \sigma}{\partial x} + N_A \frac{D_A^*}{N_V^{eq}} \frac{\partial (N_V - N_V^{eq})}{\partial x} + N_A v \right) \quad (18)$$

$$\frac{\partial N_B}{\partial t} = -\frac{\partial}{\partial x} \left( -D_B^* \varphi \frac{\partial N_B}{\partial x} + N_B \Omega \frac{D_B^*}{kT} \frac{\partial \sigma}{\partial x} + N_B \frac{D_B^*}{N_V^{eq}} \frac{\partial (N_V - N_V^{eq})}{\partial x} + N_B v \right) \quad (19)$$

$$\begin{aligned} \frac{\partial N_V}{\partial t} = & -\frac{\partial}{\partial x} \left( (D_B^* - D_A^*) \varphi \frac{\partial N_B}{\partial x} - \Omega \frac{N_A D_A^* + N_B D_B^*}{kT} \frac{\partial \sigma}{\partial x} - \frac{N_A D_A^* + N_B D_B^*}{N_V^{eq}} \frac{\partial (N_V - N_V^{eq})}{\partial x} + N_B v \right) \\ & - \frac{N_V - N_V^{eq}}{\tau_V}, \end{aligned} \quad (20)$$

$$\frac{\partial \sigma}{\partial t} = \frac{1}{3} \frac{\partial S p_{ik}}{\partial t} = -\frac{B}{3} \frac{\partial v}{\partial x}, \quad (21)$$

The components conservation law, Equations (18) and (19), describes the redistribution of components with account of chemical driving forces, stress gradient, non-equilibrium vacancy gradient and lattice drift. Equation (20) does the same for vacancies, taking the sinks and sources of vacancies into account in relaxation approximation, that is, using an approximation of effective medium [23]. Last Equation, (21), relates stress and drift velocity in hydrostatic approximation. It does not take into account the relaxation by dislocation sliding and therefore is applicable only for an undercritical stresses. The relaxation time for vacancies,  $\tau_V$ , can be expressed in terms of mean migration length:

$$\tau_V = \frac{L_V^2}{D_V} \approx \frac{N_V L_V^2}{N_A D_A^* + N_B D_B^*}. \quad (22)$$

Summation of Equations (18)–(20) immediately gives relation between the drift velocity distribution and local vacancy concentration:  $\partial v / \partial x = -(N_V - N_V^{eq}) / \tau_V$ . As we already mentioned, non-equilibrium vacancy distribution influences the interdiffusion process only at the initial stages of interdiffusion in massive diffusion couples when the diffusion zone width is about or less than the vacancy mean migration length. So, in micro-metric or nanometric systems, we should take non-equilibrium vacancies into account. The full numeric analysis of the set (18)–(21) will be made elsewhere. In this paper, we shall limit ourselves to comparably long annealing times when the non-equilibrium vacancies are already not important, but the stresses are still crucial. In this case, we can treat  $(N_V - N_V^{eq})$  term as negligible in Equations (18), (19) and exclude (20) from our analysis. Consequently, problem reduces to

$$\frac{\partial N_A}{\partial t} = -\frac{\partial}{\partial x} \left( -D_A^* \varphi \frac{\partial N_A}{\partial x} + N_A \Omega \frac{D_A^*}{kT} \frac{\partial \sigma}{\partial x} + N_A v \right), \quad (23)$$

$$\frac{\partial N_B}{\partial t} = -\frac{\partial}{\partial x} \left( -D_B^* \varphi \frac{\partial N_B}{\partial x} + N_B \Omega \frac{D_B^*}{kT} \frac{\partial \sigma}{\partial x} + N_B v \right), \quad (24)$$

$$\frac{\partial \sigma}{\partial t} = -\frac{B}{3} \frac{\partial v}{\partial x}. \quad (25)$$

Summation of (23) and (24) gives:

$$v = (D_B^* - D_A^*) \varphi \frac{\partial N_B}{\partial x} - \frac{\Omega}{kT} [(1 - N_B) D_A^* + N_B D_B^*] \frac{\partial \sigma}{\partial x} + k(t) \quad (26)$$

In the closed system, due to the boundary conditions,  $k(t)$  equals zero. It is so in the infinite diffusion couple whereat infinities (the left and right margins) the drift velocity vanishes. Substitution of Equation (26) with zero constant into Equation (24) gives

$$\frac{\partial N_B}{\partial t} = \frac{\partial}{\partial x} \left( (N_A D_A^* + N_B D_B^*) \varphi \frac{\partial N_B}{\partial x} \right) - (D_B^* - D_A^*) \frac{\partial}{\partial x} \left( N_B (1 - N_B) \frac{\partial(\sigma \Omega / kT)}{\partial x} \right) \quad (27)$$

Taking spatial derivative of both parts of Equation (26) and substituting it into right-hand side part of (25) one gets:

$$\frac{\partial(\sigma \Omega / kT)}{\partial t} = -\left( \frac{B \Omega}{3kT} \right) \frac{\partial}{\partial x} \left( (D_B^* - D_A^*) \varphi \frac{\partial N_B}{\partial x} \right) + \left( \frac{B \Omega}{3kT} \right) \frac{\partial}{\partial x} \left( (N_A D_A^* + N_B D_B^*) \frac{\partial(\sigma \Omega / kT)}{\partial x} \right) \quad (28)$$

Equations (27) and (28) form a full set for description of intermixing and stress evolution during interdiffusion when the non-equilibrium vacancy concentration is negligible and the intrinsic components diffusivities are constant. Substitution of solution,  $\sigma(t, x)$  and  $N_B(t, x)$ , into (26) gives a spatial distribution of drift velocities.

## 2.2. Analytical expressions

To have possibility of some analytical expressions, let us consider below the incremental diffusion couples with small initial steps of composition,

$$N_B^R - N_B^L \ll (N_B^R + N_B^L)/2 \quad (29)$$

In this case, the set (27)–(28) can be reduced to the system of two coupled linearized equations for two non-dimensional functions:  $N_B = N_B(t, x)$  and  $\Psi = \Omega \sigma(t, x) / kT$ , with almost constant coefficients:

$$\frac{\partial N_B}{\partial t} = D_{11} \frac{\partial^2 N_B}{\partial x^2} + D_{12} \frac{\partial^2 \Psi}{\partial x^2} \quad (30)$$

$$\frac{\partial \Psi}{\partial t} = D_{21} \frac{\partial^2 N_B}{\partial x^2} + D_{22} \frac{\partial^2 \Psi}{\partial x^2} \quad (31)$$



Here, interdiffusion matrix is:

$$\begin{aligned} D_{11} &= (N_A D_B^* + N_B D_A^*) \varphi, & D_{12} &= -N_A N_B (D_B^* - D_A^*), \\ D_{21} &= -\frac{B\Omega}{3kT} (D_B^* - D_A^*) \varphi, & D_{22} &= \frac{B\Omega}{3kT} (N_A D_A^* + N_B D_B^*) \end{aligned} \quad (32)$$

Interdiffusivity matrix has two eigenvalues that follow from the conditions  $D^{(1)} + D^{(2)} = SpD_{ik} \equiv D_{11} + D_{22}$  and  $D^{(1)}D^{(2)} = \det D_{ik} \equiv D_{11}D_{22} - D_{12}D_{21}$ :

$$\begin{aligned} D^{(1)} &= \frac{1}{2} \left( SpD_{ik} + \sqrt{(SpD_{ik})^2 - 4 \det D_{ik}} \right), & D^{(2)} &= \frac{1}{2} \left( SpD_{ik} - \sqrt{(SpD_{ik})^2 - 4 \det D_{ik}} \right), \\ D^{(1)} &> D^{(2)} \end{aligned} \quad (33)$$

In analysed case:

$$\begin{aligned} SpD_{ik} &= D_B^* (N_A \varphi + N_B \frac{B\Omega}{3kT}) + D_A^* \left( N_B \varphi + N_A \frac{B\Omega}{3kT} \right), \\ \det D_{ik} &= \frac{B\Omega}{3kT} \varphi D_A^* D_B^*. \end{aligned} \quad (34)$$

Set of parabolic equations within diffusion couple with constant coefficients can be most simply solved by diagonalization of  $D$ -matrix, where  $D_{ik} = \sum_{n=1}^2 \sum_{m=1}^2 a_{in} (D^n \delta_{nm}) (a^{-1})_{mk}$ . It gives, in particular:

$$\begin{aligned} \frac{\partial}{\partial x} N_B(t, x) &= a_{11} \frac{\partial}{\partial x} w_1(t, x) + a_{12} \frac{\partial}{\partial x} w_2(t, x), \\ \frac{\partial}{\partial x} \left( \frac{B}{kT} \sigma(t, x) \right) &= a_{21} \frac{\partial}{\partial x} w_1(t, x) + a_{22} \frac{\partial}{\partial x} w_2(t, x), \end{aligned} \quad (35)$$

where

$$\begin{aligned} a_{11} &= 1, & a_{12} &= \frac{D^{(2)} - D_{22}}{D_{21}}, \\ a_{21} &= \frac{D^{(1)} - D_{11}}{D_{12}}, & a_{22} &= 1. \end{aligned} \quad (36)$$

The right-hand side terms in Equation (35) characterize two modes of interdiffusion:

$$\text{Faster mode: } \frac{\partial}{\partial x} w_1(t, x) = \frac{w_{1R} - w_{1L}}{\sqrt{\pi D^{(1)} t}} \exp\left(-\frac{x^2}{4D^{(1)} t}\right), \quad (37)$$

$$\text{Slower mode: } \frac{\partial}{\partial x} w_2(t, x) = \frac{w_{2R} - w_{2L}}{\sqrt{\pi D^{(2)} t}} \exp\left(-\frac{x^2}{4D^{(2)} t}\right). \quad (38)$$

We are interested here in the interaction (interplay) between the stress and concentration gradients. Initial step of stress is zero, initial step of composition is fixed,  $\Delta N_B = N_B^R - N_B^L$ . Thus, the steps of faster and slower modes are easily found as

$$\begin{aligned} \Delta w_1 &= a_{11}^{-1} \Delta N_B + a_{12}^{-1} \Delta(\Omega\sigma/kT) = a_{11}^{-1} \Delta N_B + 0 = \frac{a_{22}}{\det a_{ik}} \Delta N_B, \\ \Delta w_2 &= a_{21}^{-1} \Delta N_B + a_{22}^{-1} \Delta(\Omega\sigma/kT) = a_{21}^{-1} \Delta N_B + 0 = -\frac{a_{21}}{\det a_{ik}} \Delta N_B. \end{aligned} \quad (39)$$

Now, we can compare the two terms – concentration gradient and stress gradient terms – in the expression for drift velocity. Let us find the ratio of actual drift velocity (with account of arising stress gradients) with Darken expression for drift velocity (no stress):

$$\frac{v}{v^{\text{Darken}}} = \frac{(D_B^* - D_A^*)\varphi \frac{\partial N_B}{\partial x} - \Omega \frac{N_A D_A^* + N_B D_B^*}{kT} \frac{\partial \sigma}{\partial x}}{(D_B^* - D_A^*)\varphi \frac{\partial N_B}{\partial x}} = 1 - \frac{\Omega}{kT} \frac{(N_A D_A^* + N_B D_B^*) \frac{\partial \sigma}{\partial x}}{(D_B^* - D_A^*)\varphi \frac{\partial N_B}{\partial x}}. \quad (40)$$

Let us consider the case when the difference between backstress-mediated compensation and drift-mediated compensation is most pronounced, for example, when diffusivities of the components considerably differ. For example, let component A be much slower than B:  $D_A^* \ll D_B^*$ . In such a case

$$D^{(1)} \cong D_B^* \left( N_A \varphi + N_B \frac{B\Omega}{3kT} \right) \gg D^{(2)} \cong \frac{D_A^* \varphi}{N_A \frac{\varphi \cdot 3kT}{B\Omega} + N_B} \quad (41)$$

If, additionally,  $B\Omega N_B / (3kT \varphi N_A) \gg 1$  (which is typical for metallic solutions), then

$$\sqrt{\frac{D^{(1)}}{D^{(2)}}} \cong \sqrt{\frac{N_B^2 D_A^*}{\varphi D_B^*}} \ll 1 \quad (42)$$

$$a_{12} = (D^{(2)} - D_{22}) / D_{21} \cong N_B / \varphi, \quad (43)$$

$$a_{21} = (D^{(1)} - D_{11}) / D_{12} \cong -B\Omega / (3kT N_A),$$

$$\Delta w_2 / \Delta w_1 = -a_{21} / a_{11} = B\Omega / (3kT N_A) \quad (44)$$

Then, long but elementary algebra gives:

$$v(t, x) \approx \frac{1}{N_A} \sqrt{\frac{D^{(1)}}{\pi t}} \exp\left(-\frac{x^2}{4D^{(1)}t}\right) - \frac{3kT}{B\Omega} \sqrt{\frac{D^{(2)}}{\pi t}} \exp\left(-\frac{x^2}{4D^{(2)}t}\right), \quad (45)$$

$$\frac{v}{v^{\text{Darken}}} = \frac{1 + \frac{N_B B\Omega}{N_A kT \varphi}}{1 + \frac{N_B B\Omega}{N_A 3kT \varphi} \sqrt{\frac{D^{(1)}}{D^{(2)}}} \exp\left(-\frac{x^2}{4t} \left(\frac{1}{D^{(2)}} - \frac{1}{D^{(1)}}\right)\right)}. \quad (46)$$

Since second diffusion eigenvalue is much smaller, one obtains finally:

$$\frac{v}{v^{\text{Darken}}} = \frac{1 + \frac{N_B B\Omega}{N_A 3kT \varphi}}{1 + \frac{N_B B\Omega}{N_A 3kT \varphi} \sqrt{\frac{D^{(1)}}{D^{(2)}}} \exp\left(-\frac{x^2}{4D^{(2)}t}\right)}. \quad (47)$$

Equations (45) and (47) allow to examine the regions formed within the diffusion couple.

### 3. Results

Analysis of Equations (45) and (47) allows distinguishing three spatial regions:

*Internal zone:*  $|x| < \sqrt{D^{(2)}t} \cong \sqrt{D_A^* \phi t / N_B}$ . In this ‘internal zone’ in the vicinity of the Matano interface, the drift velocity is almost constant upon spatial coordinate and, of course, inversely proportional to the square root of time:  $v \cong \sqrt{D^{(1)}} / (N_A \sqrt{\pi t})$ . Actual drift velocity is much slower than the pure Darken case:  $v/v^{Darken} \cong \sqrt{D^{(2)}/D^{(1)}} \ll 1$ .

*Transient zone:*  $\sqrt{D_A^* \phi t / N_B} \cong \sqrt{D^{(2)}t} \ll |x| \ll \sqrt{D^{(1)}t} \cong \sqrt{B\Omega D_B^* N_B t / (3kT)}$  in which the drift velocity drops with increasing distance from the Matano interface:  $v(t, x) \cong \frac{1}{N_A} \sqrt{\frac{D^{(1)}}{\pi t}} \exp\left(-\frac{x^2}{4D^{(1)}t}\right)$ . Ratio of actual drift velocity to the pure Darken case is given by:  $v/v^{Darken} \cong 1 + \frac{B\Omega}{3kT\phi} \frac{N_B}{N_A}$ .

*External zone:*  $|x| > \sqrt{D^{(1)}t} \cong \sqrt{B\Omega D_B^* N_B t / (3kT)}$ . Diffusion zone is only approaching. In Figures 1–3, the concentration, drift velocity and stress distribution profiles found by analytical solution, Equations (35)–(45), are shown. Profiles were calculated with the assumption of the constant coefficients of diffusion matrix.

In Figures 4–6, the profiles calculated from numeric solution without assumption of constant coefficients of diffusion matrix are shown.

The internal and transient subzones are seen in the drift velocity and the normalized stress profiles of the finite diffusion couple. These sections are linked to the fast and slow diffusing component. The simplified assumption of the constant coefficients of the diffusion matrix results in the symmetry of the interdiffusion process, Figures 1–3. Contrary, more representative numerical computations based on Equation (32) shows strong asymmetry due to the composition dependence of the diffusion matrix coefficients, Figures 4–6. The qualitative agreement between analytical solution and numerical one can be seen. Nevertheless, the simplified assumptions in the analytical solution result in misrepresentative acceleration of the interdiffusion process.

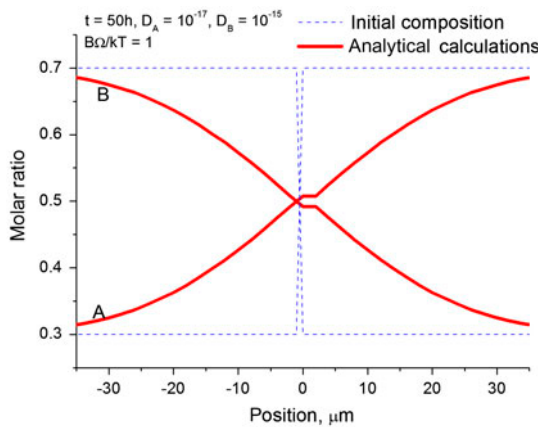


Figure 1. The concentration profiles in the finite diffusion couple. Constant coefficients of diffusion matrix are assumed.

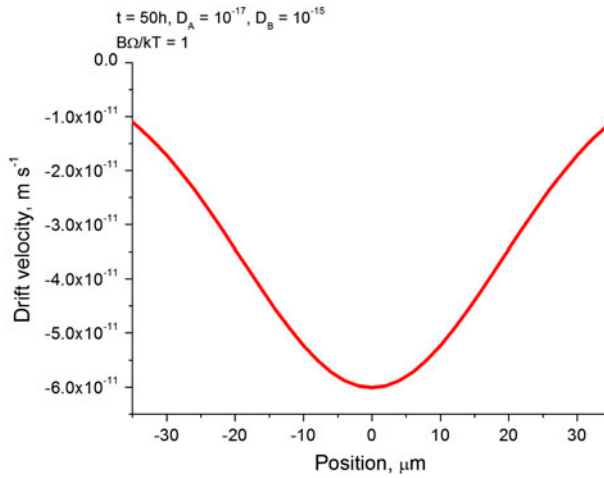


Figure 2. The drift velocity profile in the finite diffusion couple. Constant coefficients of diffusion matrix are assumed.

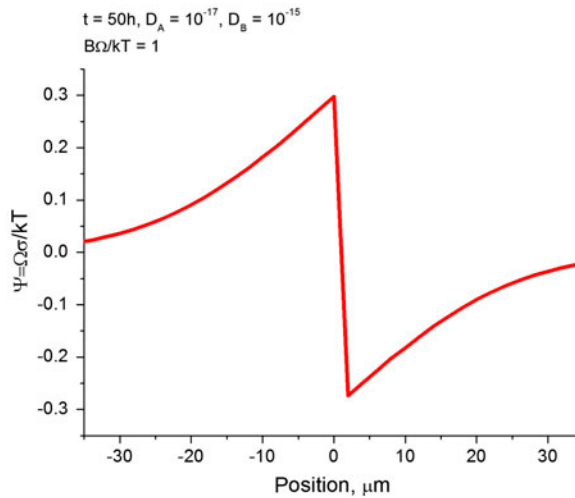


Figure 3. The normalized stress profile in the finite diffusion couple. Constant coefficients of diffusion matrix are assumed.

During the interdiffusion process, the stress effect does not vanish, Figures 3, 5 and 6. The comparison of the components distribution, Figures 4, shows that backstress effect retards the interdiffusion process.

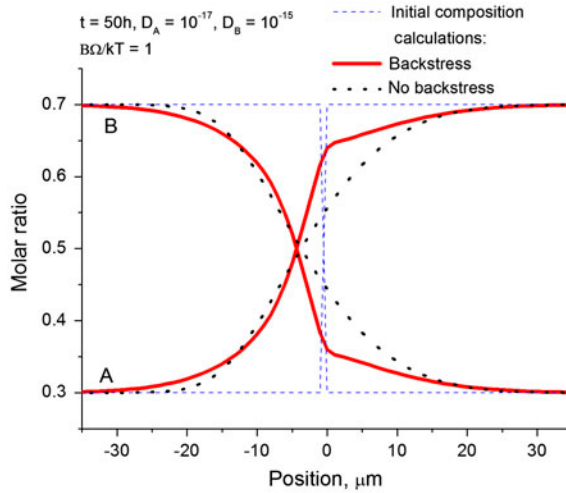


Figure 4. The concentration profiles in the finite diffusion couple. Coefficients of diffusion matrix depend on composition, Equation (32).

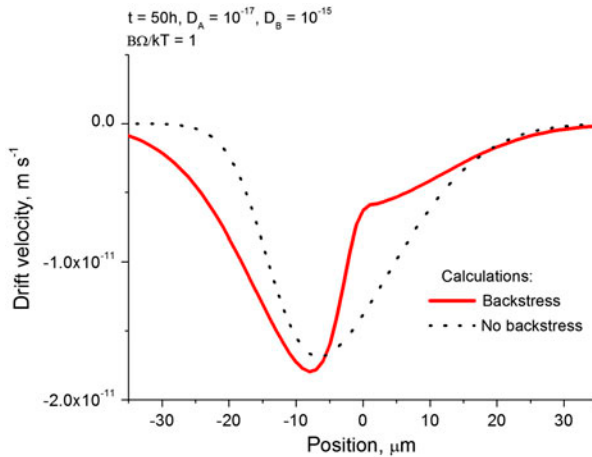


Figure 5. The drift velocity profiles in the finite diffusion couple. Coefficients of diffusion matrix depend on composition, Equation (32).

#### 4. Summary

The presented analysis of the interdiffusion process based on the Darken method and generalized diffusion potential to include the non-equilibrium vacancy concentration and the backstress effects.

- (1) The internal and transient subzones are formed during interdiffusion in planar diffusion couples; these sections are linked to the fast and slow diffusing component.

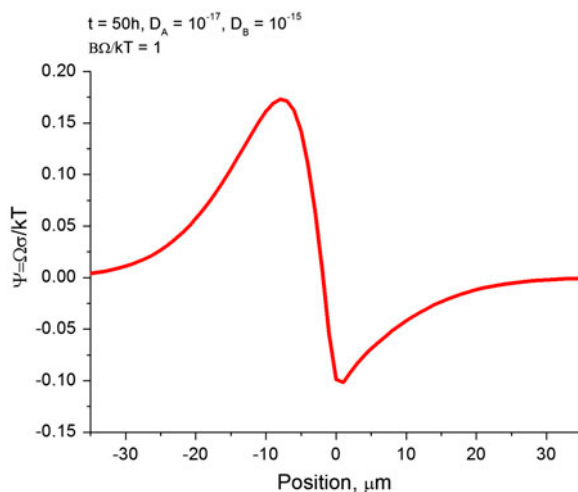


Figure 6. The normalized stress distribution in the finite diffusion couple. Coefficients of diffusion matrix depend on composition, Equation (32).

- (2) The numerical computations show strong asymmetry of the process due to the composition dependence of the diffusion matrix coefficients.
- (3) The qualitative agreement between analytical solution and numerical one was shown. The simplified assumptions in the analytical solution result in misrepresentative acceleration of the interdiffusion process.
- (4) During the whole interdiffusion process, the stress effect does not vanish. This backstress effect retards the interdiffusion process.
- (5) The non-equilibrium vacancy distribution influences the interdiffusion process only at the initial stages of interdiffusion in massive diffusion couples when the diffusion zone width is about or less than the vacancy mean migration length.
- (6) When the comparably long annealing times are calculated, the non-equilibrium vacancies are not important, but the stresses are still crucial.
- (7) The presented methodology can be extended to include three and more component alloys as well as different atomic volumes of the components and concentration-dependent intrinsic diffusivities.

### Acknowledgements

This work is supported by a National Science Center (Poland) decision no. DEC-2011/02/A/ST8/00280. One of the authors (AG) is grateful to AGH for hospitality and to the Ukrainian Ministry of Education and Science for support.

### References

- [1] A.D. Smigelskas and E.O. Kirkendall, *Trans. AIME* 171 (1947) p.130.
- [2] L.S. Darken, *Trans. AIME* 174 (1948) p.184.
- [3] Ya.E. Geguzin, *Diffusion Zone*, Nauka, Moscow, 1979 (in Russian).

- [4] F.J.J. Van Loo, Prog. Solid State Chem. 20 (1990) p.47.
- [5] K.P. Gurov and A.M. Gusak, Fiz. Met. Metalloved. 59 (1985) p.1062.
- [6] G.B. Stephenson, Acta Metall. 36 (1988) p.2663.
- [7] M.J.H. Van Dal, A.M. Gusak, C. Cserhádi, A.A. Kodentsov and F.J.J. Van Loo, Phys. Rev. Lett. 86 (2001) p.3352.
- [8] M.J.H. Van Dal, A.M. Gusak, C. Cserhádi, A.A. Kodentsov and F.J.J. Van Loo, Phil. Mag. A 82 (2002) p.943.
- [9] M. Danielewski and B. Wierzba, Acta Mater. 58 (2010) p.6717.
- [10] F.D. Fischer and J. Svoboda, Acta Mater. 58 (2010) p.2698.
- [11] B Wierzba, Philos. Mag. 91 (2011) p.3228.
- [12] M. Danielewski, B. Wierzba, A. Gusak, M. Pawelkiewicz, J. Janczak-Rusch, J. Appl. Phys. 110 (2011) 123705.
- [13] R.W. Balluffi, S.M. Allen, W.C. Carter and R.A. Kemper, *Kinetics of Materials*, Wiley, Hoboken, NJ, 2005.
- [14] S.Z. Bokstein, B.S. Bokstein and Zhukhvitskii, *Thermodynamics and Kinetics of Diffusion in Solids*, Oxonian Press, New Delhi, 1985.
- [15] M. Kizilyalli, J. Corish and R. Metselaar, Pure Appl. Chem. 71 (1999) p.1307.
- [16] I.A. Blech and C. Herring, Appl. Phys. Lett. 29 (1976) p.131.
- [17] K.N. Tu, J.W. Mayer and L.C. Feldman, *Electronic Thin Film Science for Electrical Engineers and Materials Scientists*, Macmillan, New York, 1992.
- [18] A.V. Nazarov and K.P. Gurov, Fiz. Met. Metalloved. 37 (1974) p.496.
- [19] A.M. Gusak, *Diffusion-controlled Solid State Reactions*, Wiley-VCH, Weinheim, 2010.
- [20] V.V. Turlo, A.M. Gusak and K.N. Tu, Philos. Mag. 93 (2013) p.2013.
- [21] B. Wierzba and M. Danielewski, Phil. Mag. 91 (2010) p.3228.
- [22] R. Kirchheim, Acta Metall. 40 (1992) p.309.
- [23] A.A. Turkin, (Phd thesis), Institute of Theoretical Physics, Ukrainian Academy of Science. Kharkov, 2010 (in Russian).