

Generalized Darken's Method; from Diffusional Structures to Nonparabolic Diffusion

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Abstract. The generalized Darken method for multicomponent interdiffusion is presented. Its solution enables one to obtain an exact expression for the evolution of component distributions in closed and open systems, for arbitrary initial distributions and time dependent boundary conditions. The model allows to study the evolution of the composition of the solid solution because of its thermal treatment, evaporation and/or oxidation. Introductory commentary on some of the more current experimental and mathematically oriented results (nonparabolic diffusion) as well as the modified Navier-Stokes equation with additional diffusional terms are included.

INTRODUCTION

The results presented here benefitted immensely from the Darken concepts [1]. The starting point was his fundamental concept in interdiffusion studies which states that as in other media, in solids the flux of a given element equals its diffusional flux (in an internal reference frame) when added to the drift (convection) flux. What is presented here is a sampler of contributions we have made to that field over the last ten years. These contributions were possible due to the tremendous progress made in the modern theory of partial differential equations. The experiments were possible due to collaboration with several Laboratories. In the section that follows, we will put forth the formulation of a generalized Darken method of interdiffusion, GDM, and the method for finding its solution.

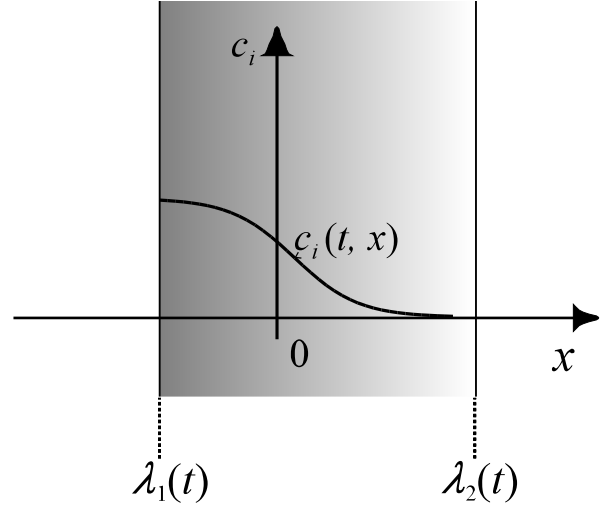
The metallic alloys and ceramic materials are usually a multicomponent and multiphase. Thus, the understanding of the interdiffusion in solutions containing an unrestricted number of components is stimulating and productive. Such systems often show variable mobilities and exchange mass with the surrounding. Moreover, initial distributions are arbitrary. Although general phenomenological relations for interdiffusion are available, these are hardly simple and their effective solutions are few and narrowed mainly to the closed systems. Investigations of multicomponent systems are usually limited to the determination of interdiffusion coefficients [2], because of experimental difficulties, are few for systems with more than three components. The mathematical model of interdiffusion [3, 4] and the concept of generalized (i.e., weak) solution allow to obtain an exact expression for the evolution of component distributions in a closed system as well as in an open one. Finally, we have included an introductory commentary on some of the more current experimental and mathematically oriented results (nonparabolic diffusion) as well as the modified Navier-Stokes equation with additional diffusional terms. Though this results have not yet been verified on an experimental level, they still offer exciting new frontiers.

THEORY

We start with the generalized Darken's phenomenological scheme. The particulars of this method for the closed system [5] and the more general description of interdiffusion that incorporates the equation of motion can be found elsewhere [3, 4]. In case of multicomponent solutions the force, being a result of concentration gradient, gives rise to diffusion of a particular element. The velocity of diffusion was defined by Darken in the internal reference frame: $v_{id} = -D_i \text{grad}(\ln c_i)$. All diffusional fluxes are coupled and their local changes influence the common mixture drift velocity (v) [1]. Depending of a

branch of knowledge, the drift velocity is called as translation, convection and flow velocity. Such description of diffusion in solid solutions is a base of Darken model. Its core is a postulate of existence of the unique drift velocity that is induced by diffusion of mixture components. When external forces are marginal (gravity, electrical fields), the interdiffusion process can be treated as pure diffusional mixing. The Darken model was restricted to a binary solid solution and to a simple initial and boundary conditions [1].

The change of the mass distribution in every free *bounded body*, e.g., in diffusional couple, implies its translation to maintain an initial position of the *body* mass center (i.e., when external force fields and initial velocity are negligible, then the position of the *body* mass center does not vary with time). This conclusion leads to generalization of the boundary conditions, which is essence of the GDM [3]. We state that the position of the system boundary depends usually on time, a *quasi-free boundary*, Figure 1. The main goal is to predict the distribution of all elements as a function of time.



Data: 1) intrinsic diffusivities: D_1, \dots, D_r ($D_i = D_i(c_1, c_2, \dots, c_{r-1})$), 2) initial position of the right end of the system: Λ (the right border of the one-dimensional diffusional couple of thickness $d = 2\Lambda$), 3) time of the process duration: t^* , 4) arbitrary initial distribution of the elements: $\overset{\circ}{c}_1(x), \dots, \overset{\circ}{c}_r(x)$ for $-\Lambda \leq x \leq \Lambda$ such that

the condition of constant concentration of the mixture is fulfilled: $\sum_{i=1}^r \overset{\circ}{c}_i = c$.

Physical laws follow the original Darken concept:

1) *the law of the conservation* of an i -th element (equation of continuity). The law that tells that the local change of concentration of the i -th element is a result of its net in or an outflow only:

$$\frac{\partial c_i}{\partial t} = - \frac{\partial j_i}{\partial x} \quad (i = 1, \dots, r). \quad (1)$$

Following Darken drift flow idea we postulate that the flux of an i -th element is a sum of the diffusional flux and translation flux:

$$j_i = -D_i(c_1, \dots, c_{r-1}) \frac{\partial c_i}{\partial x} + c_i v. \quad (2)$$

In the original Darkens' treatment the diffusional flux was postulated to be a Fickian flow. Often, the more general formulae of diffusional flow can be transformed to Fick's form. Thus, the flux of the i -th element can be more generally expressed by:

$$j_i = c_i \mathbf{B}_i F_i + c_i v, \quad (2a)$$

where B_i is mobility of the i -th component and F_i denotes a local force acting on the i -th component -

usually gradient of the (electro)chemical potential ($F_i = -\partial\mu_i/\partial\mathbf{x}$). The equation (2) is the constitutive flow formula postulated for as the generalized Darken method. In the case of interdiffusion problems in non-ideal and ionic solid solutions eq. (2a) must be used. Such reformulation will be shown in the next section.

2) *Postulate of the constant mixture concentration*, i.e., the equation of state, which tells that the sum of concentrations of all elements at any position and for every time is constant:

$$c_1 + \dots + c_r = \text{constant} = c. \quad (3)$$

Initial conditions: 1) *positions of the left and right ends of the system:* $\lambda_1(0) = -\Lambda$, $\lambda_2(0) = \Lambda$, where indexes "1" and "2" denote the left and right end¹ of the system. 2) *initial density distributions of the elements in the system:*

$$c_1^0(x), \dots, c_r^0(x) \text{ for } -\Lambda \leq x \leq \Lambda \quad (4)$$

Boundary conditions. Two different conditions were postulated for an open and closed system:

1) In the closed system *the relation between the velocity of boundaries* ($d\lambda_j/dt$) and flux at these boundaries has form:

$$\frac{d\lambda_j}{dt} = u(t, \lambda_j(t)) \quad \text{for } j = 1, 2; \quad (5)$$

i.e., we postulated that the velocity of the boundary equals the velocity of the local mass center, u , at this boundary. Otherwise, e.g., if the velocity u differs from the velocity of the boundary, the atoms would "jump out" of the system. These boundary conditions do not imply constant densities at the boundaries. In the closed system the gradients of all components at both boundaries vanish [5].

2) We postulate that when the *mass flow through the boundary occurs*, i.e., system is open, then, the flux of i -th component at the boundary equals its flow through the boundary [3]:

$$j_i(t, -\Lambda) = j_{iL}(t) \quad \text{for } i = 1, 2, \dots, r; \quad (6)$$

$$j_i(t, \Lambda) = j_{iR}(t) \quad \text{for } i = 1, 2, \dots, r. \quad (7)$$

The functions at the right side of equations (6) and (7) have to be known. They can be calculated from the predicted or known rates of reaction at the boundaries or from the other experimental data.

Unknowns: The data, laws, initial and boundary conditions allow to compute: 1) positions of the boundaries, $\lambda_1(t)$, $\lambda_2(t)$, as a function of time, 2) concentrations of all elements as a function of time and position, $c_i(t, \mathbf{x})$ and, 3) the drift velocity in the system as a function of time and position, $v(t, \mathbf{x})$.

Reformulation of the problem. Mathematics that is behind steps that are listed below is arduous for non-mathematician. It results in: the variational form of initial-boundary value problem of GDM, the proof of existence and uniqueness of its solution and finally the effective numerical methods of finding the solution.

One can define a new variable $w_i(t, \mathbf{z})$, the shifted deviation of the i -th element mole fraction from its average in the system (briefly: the shifted deviation):

$$w_i(t, \mathbf{z}) := \frac{1}{c} c_i(t, \mathbf{x}) - \bar{m}_i(t), \quad (8)$$

¹Positions of the system ends can be affected by diffusion and external forces [3], are functions of time.

where $\bar{m}_i(t)$ denotes the mean mole fraction of the i -th element: $\bar{m}_i(t) := m_i(t)/(2\Lambda M_i \mathbf{c})$ and, $m_i(t)$ is the mass of the i -th element per unit of a system surface. The definition (8) leads to the expressions [3] for: $\frac{\partial w_i}{\partial z}(t, z)$, $w_i(0, z)$ and $v_i(t, z)$. In an open system (when the mass of the i -th element per unit of a system surface can depend on time) the problem of interdiffusion becomes:

$$\frac{\partial w_i}{\partial t}(t, z) = - \frac{d}{dz} \left(-D_i \frac{\partial w_i}{\partial z}(t, z) + \left\langle \mathbf{D}, \frac{\partial \mathbf{w}}{\partial z}(t, z) \right\rangle + K(t) \right) (w_i(t, z) + \bar{m}_i(t)) - \frac{d\bar{m}_i(t)}{dt} \quad (9)$$

$$w_i(0, z) = w_i^0(z) \quad (10)$$

$$\mathbf{c}(w_i(t, -\Lambda) + \bar{m}_i(t)) v_i(t, -\Lambda) = j_{iL}(t) \quad (11)$$

$$\mathbf{c}(w_i(t, \Lambda) + \bar{m}_i(t)) v_i(t, \Lambda) = j_{iR}(t) \quad (12)$$

for $i = 1, \dots, r$, where $w = (w_1, \dots, w_r)$ and $\mathbf{D} = (D_1, \dots, D_r)$ are vector functions of the shifted deviations of all elements and diffusivities [3],

$$\left\langle \mathbf{D}, \frac{\partial \mathbf{w}}{\partial z}(t, z) \right\rangle = \sum_{i=1}^r D_i \frac{\partial w_i}{\partial z}(t, z)$$

denotes the scalar multiplication (in \mathbb{R}^r) and $K(t)$ is defined in the next section, in definition of the generalized solution of GDM, see eq. (13).

Equations (10) - (12) are the reformulated initial and boundary conditions, coupled with Eq. (9) form a system of r -differential equations where unknowns are shifted deviations, w_i . They form the initial-boundary value problem for GDM.

Generalized solution is a concept widely used in modern theory of partial differential equations, e.g., in hydrodynamics. It allows for computation of solutions for complex transport problems. Contrary to classical methods in which the primary goal is to find the analytical function that allows to compute solution for a given arbitrary set of initial and boundary values, the generalized solution allows usually to compute the much more complex and broader class of problems. Even a brief presentation of this method exceeds the size and scope of this paper. Thus, only some basics will be presented below.

In the method shown below we multiply both sides of partial differential equation by a term (a certain known function). At first look the problem becomes more complex. Nevertheless, immediate profit is the simplification of boundary conditions and transformation of formulae to the forms that allow for application of well-developed methods. Usually equation(s) will finally become simpler and "solvable." The basic steps in the case of the GDM are presented below.

Let us take some continuous function $\boldsymbol{\phi}(z) = (\phi_1(z), \dots, \phi_r(z))$, which has a square integrable derivative $\frac{d\boldsymbol{\phi}}{dz}(z)$ that is defined almost everywhere in the system, everywhere where the solution is to be found, i.e., $z \in [-\Lambda, \Lambda]$. We multiply Eq. (9) by $\phi_i(z)$ and sum all the formulae. If we integrate the obtained equality(ies) with respect to z within the range $\int_{-\Lambda}^{\Lambda}$, we can shift the derivatives from the right-hand side of Eq. (9) into functions ϕ_i , which by our assumption are differentiable. Consequently, we can consider a solution $w(t, z)$, which does not have second spatial derivative,

$\partial^2/\partial z^2$. By the analogous treatment the initial conditions (10) can be written:

$$\int_{-\Lambda}^{\Lambda} w(0, z) \cdot \phi(z) dz = \int_{-\Lambda}^{\Lambda} \overset{\circ}{w}(z) \cdot \phi(z) dz,$$

where $\overset{\circ}{w}(z)$ is a given known function of the initial shifted deviations of all elements.

Definition of the generalized solution of GDM in the open system: A function $w(t, z)$ is called a generalized solution of the problem (9) - (12) if and only if the identity:

$$\begin{aligned} \int_{-\Lambda}^{\Lambda} w(t, z) \cdot \phi(z) dz &= \int_{-\Lambda}^{\Lambda} \overset{\circ}{w}(z) \cdot \phi(z) dz - \int_0^t \int_{-\Lambda}^{\Lambda} F\left(w(\tau, z), \frac{\partial w}{\partial z}(\tau, z)\right) \cdot \frac{d\phi}{dz}(z) dz d\tau + \\ &+ \int_0^t K(\tau) \int_{-\Lambda}^{\Lambda} \left(w(\tau, z) \cdot \frac{\partial \phi}{\partial z}(z)\right) dz d\tau + \int_0^t (\phi(\Lambda) \cdot \Gamma_R(\tau) - \phi(-\Lambda) \cdot \Gamma_L(\tau)) d\tau + \int_{-\Lambda}^{\Lambda} (\phi(z) \cdot \bar{m}_i(0) - \bar{m}_i(t)) dz \end{aligned} \quad (13)$$

where

$$K(t) := \frac{1}{c} \sum_{i=1}^r j_{iL}(t) = \frac{1}{c} \sum_{i=1}^r j_{iR}(t)$$

$$\Gamma_{iL}(t) := K(t) \bar{m}_i(t) - \frac{1}{c} j_{iL}(t);$$

$$\Gamma_{iR}(t) := K(t) \bar{m}_i(t) - \frac{1}{c} j_{iR}(t)$$

$$\Gamma_L = (\Gamma_{1L}, \dots, \Gamma_{rL});$$

$$\Gamma_R = (\Gamma_{1R}, \dots, \Gamma_{rR})$$

holds for every ϕ .

In still simpler words generalized solution is a true solution if and only if it can be proved that equality does not depend on the form of function $\phi(z) = (\phi_1(z), \dots, \phi_r(z))$. Thus, the classical boundary-value problem (1) and (3) - (7) was reformulated to single-variational identity (13).

The final step is computation of the solution. An example of numerical method of solving the problem [6] and the procedures that allow to obtain the solution for an open system [7] were already published.

CHEMICAL INTERDIFFUSION

In order to effectively use the Generalized Darken Method (GDM) in the case of non ideal solid solutions the problem has to be reformulated to a form of Darken flow formula. The diffusional fluxes have to be expressed as a Fickian flows, that show variable diffusivities. The example of such reformulation is shown in this section in the case of postulated equation of state in the form:

$$\sum_{i=1}^r c_i = c \quad (14)$$

When the presence of the external forcings is negligible we postulate the following flow formula :

$$j_i = -B_i c_i \frac{\partial \mu_i}{\partial x} + c_i v, \quad (15)$$

where μ_i is the chemical potential of i -th element (e.g., expressed in the energy unit per atom) and $\mu_i = f_i(c_1, c_2, \dots, c_{r-1})$.

Upon assuming the Nernst-Einstein relation between the self diffusion and mobility ($D^* = B k T$), the diffusional flux in Eq. (2) can be expressed as the Fickian flow with intrinsic diffusivity that depends on

composition and diffusion path²:

$$j_i = -\mathbf{B}_i c_i \sum_{j=1}^r \left(\frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial x} \right) + c_i v = -k T \mathbf{B}_i c_i \sum_{j=1}^r \left(\frac{\partial \ln a_i}{\partial c_j} \frac{\partial c_j}{\partial x} \right) + c_i v, \quad (16)$$

or

$$j_i = -\mathbf{D}_i^* c_i \left(\left(\sum_{j=1}^r \frac{\partial \ln a_i}{\partial c_j} \frac{\partial c_j}{\partial x} \right) / \frac{\partial c_i}{\partial x} \right) \frac{\partial c_i}{\partial x} + c_i v = -D_i \frac{\partial c_i}{\partial x} + c_i v, \quad (17)$$

where k and T denote the Boltzman constant and the temperature. The intrinsic diffusivity is given by:

$$D_i = \mathbf{D}_i^* c_i \left(\left(\sum_{j=1}^r \frac{\partial \ln a_i}{\partial c_j} \frac{\partial c_j}{\partial x} \right) / \frac{\partial c_i}{\partial x} \right), \quad (18)$$

Thus, the intrinsic diffusivity is a function of concentrations and the diffusion path (function of the gradients of components):

$$D_i = \mathbf{D}_i \left(c_1, \dots, c_{r-1}, \frac{\partial c_1}{\partial x}, \dots, \frac{\partial c_{r-1}}{\partial x} \right). \quad (19)$$

The above formula differs from the one postulated in Generalized Darken Method:

$$D_i = \mathbf{D}_i(c_1, \dots, c_{r-1}), \quad (20)$$

Nevertheless we postulate that the solution of GDM in the case when intrinsic diffusivities are given by eq. (6) converge to the original problem (when intrinsic diffusivities are given by eq. (7)).

It can be mentioned that the calculation of the thermodynamic factor in eq. (5) in general consists of finding the second derivative of the thermodynamic potential of the system:

$$\left(\sum_{j=1}^r \frac{\partial \ln a_i}{\partial c_j} \frac{\partial c_j}{\partial x} \right) / \frac{\partial c_i}{\partial x} = \frac{1}{c^2} \sum_{j=1}^r \left(\frac{\partial^2 G}{\partial y_i \partial y_j} \frac{\partial c_j}{\partial x} \right) / \frac{\partial c_i}{\partial x}. \quad (21)$$

and in the case of ternary and higher systems, the diffusion path has to be known. These all derivatives can be calculated from thermodynamic data and from the generalized Darken method.

Parabolic Interdiffusion. The problem (1) and (3) - (7) has a unique solution if it is parabolic [3]. The parabolicity can be explained upon introducing the measure of the mass dissipation in the system. It can be expressed in terms of w_i 's as follows:

$$\mathbf{W}(t) = \int_{-\Lambda}^{\Lambda} \left[\sum_{i=1}^r w_i(t, z)^2 \right] dz. \quad (22)$$

Since w_i is the local deviation of the molar ratio of the mixture i -th component from its average, the function $\mathbf{W}(t)$ represents the random deviation (variance) of molar ratio of the mixture components. If the system is parabolic, then [3, 4]:

²Diffusion path, gradients of all components, as function of time can be calculated using variational solution of the GDM.

$$\frac{dW}{dt} \leq 0 \quad (23)$$

and $W(t) \rightarrow 0$ when $t \rightarrow \infty$ [3]. Which means that the mixture mass dissipation decreases to zero with time increasing to infinity. Consequently, all system components become homogenous. Examples of such processes are shown in the next section.

Interdiffusion in Binary Alloy Showing Variable Intrinsic Diffusivities, Ag-Au Diffusional Couple

The main target is to show the usability of the GDM in modeling the diffusional processes in alloy in which intrinsic diffusivity depends on alloy composition of the alloy [8, 9]. The measured values of intrinsic diffusivities were approximated by polynomial fit and both functions consequently were used in eq. (9).

For calculating the solution of the problem of interdiffusion, Eqs. (9) - (12), the following data were used: thickness of the diffusional couple: $2\Lambda = 0.16$ cm; intrinsic diffusivities at 1177 K as shown in Figure 2; $c = 0.1$ molcm⁻³; time of the reaction $t^* = 8 \cdot 10^4$ s); the initial distribution was contact of pure Au and Ag plates.

It can be seen that computed results are in good agreement with the measured ones. Asymetry of distributions is seen on Figure 3.

Interdiffusion in Co-Ni-Fe alloys.

We will show that the change of concentration at the boundaries can be correctly predicted by GDM. For calculations the following data were used:

- 1) thickness of the diffusional couple: $2\Lambda = 0.1$ cm;
- 2) intrinsic diffusivities at 1588 K [10]: $D_{Co} = 6.31 \cdot 10^{-10}$, $D_{Fe} = 1.63 \cdot 10^{-9}$ and $D_{Ni} = 2.89 \cdot 10^{-10}$ cm²s⁻¹;
- 3) $c = 0.15$ molcm⁻³;
- 4) time of the annealing $t^* = 17$ and 131 hours;
- 5) the diffusional couple shown in Fig. 2 was formed by two alloy pellets of thickness $\Lambda = 0.05$ cm

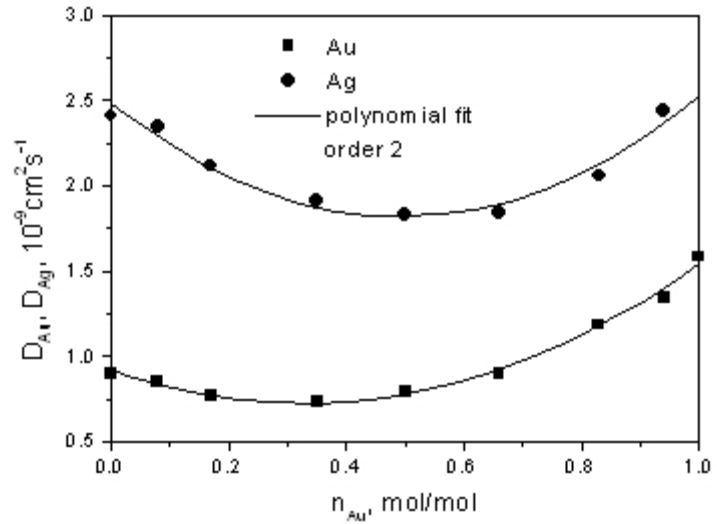


Figure 2. Intrinsic diffusivities in Ag-Au alloys at 1177 K [10].

The measured values of intrinsic diffusivities were approximated by polynomial fit and both functions consequently were used in eq. (9).

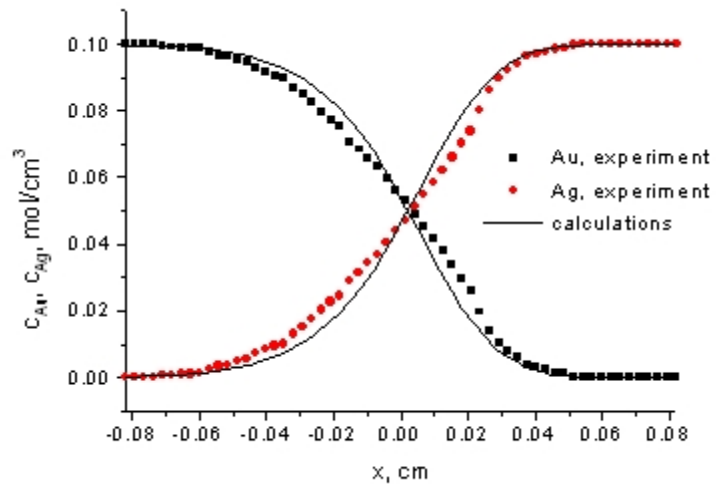


Figure 3. Interdiffusion in Au-Ag alloy at 1177 K.

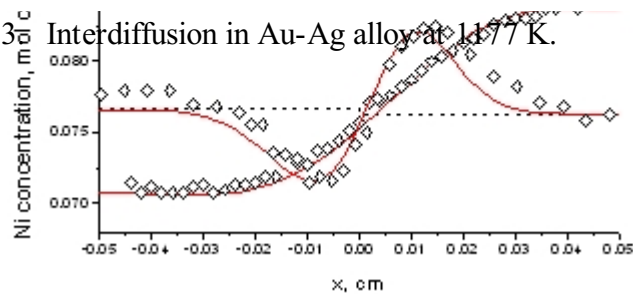


Figure 4. Experimentally measured and computed distributions of elements in diffusional couple Fe-52Ni|Co-51Ni annealed at 1588 K for 17 and 131 h.

each, having composition: Fe-52Ni and Co-51Ni in wt%.

Fig. 4 shows the initial distribution and the measured and calculated concentration profiles. The interdiffusion process generates the diffusional structure [3] of initially uniform nickel distribution, i.e., uphill diffusion of nickel. It may be noted that in the finite system (diffusional couple) its life time is limited and, after 131 hours annealing time diffusional structure diminishes. These results show that interdiffusion in finite system changes concentrations of components at the boundaries [5]. An example of a diffusional couple with more complex initial distribution is shown in Fig. 5. It shows experimentally measured and computed distributions of elements in ternary diffusional couple Co-51Ni|Fe-52Ni|Co-51Ni annealed at 1573 K for 48 hours.

In the next section we demonstrate an example of the non parabolic process governed by GDM. Such a process does not satisfy the parabolicity condition, eq. (23).

Non parabolic interdiffusion. In the case of multicomponent mixture ($r \geq 3$) it was demonstrated an example of diffusivities, $\Theta_1, \dots, \Theta_r$, which does not

satisfy the GDM parabolicity condition [3], i.e., an example of diffusivities providing that diffusional profiles are invariant to x/\sqrt{t} . In such a case one can speculate on the possibility of a gradient "blow-up" of the solution. One of us (W.K.) has found the initial conditions providing non parabolic behavior of the GDM solution.

The initial spatial distributions of molar ratios of arbitrary elements in ternary mixture, $\eta_i(z)$, are given by the following formulae

$$\eta_i(z) = \begin{cases} \delta_i + m_i & b \leq z \leq \Lambda \\ \frac{\delta_i}{b} z + m_i & -b \leq z \leq b \\ -\delta_i + m_i & -\Lambda \leq z \leq -b \end{cases}$$

where Λ , b , δ_i and m_i are constants.

For calculations the following data were used: 1) $\Lambda = 0.2$ cm; 2) intrinsic diffusivities: $D_1 = D_3 = 1 \cdot 10^{-5}$ and $D_2 = 10$ cm² h⁻¹; 3) $c = 0.15$ mol cm⁻³; 4) time of the process $t^* \in (1 \div 1 \text{ h})$; 5) the initial composition of the diffusional couple, eq. (24), shown in Fig. 6, where: $b = 0.02$ cm; $\delta_1 = 0.155367$; $\delta_2 = m_2$; $\delta_3 = -m_3$; $m_1 = 0.7768$; $m_2 = 0.03389$ and $m_3 = 0.18926$.

Figures 6 and 7 show the initial

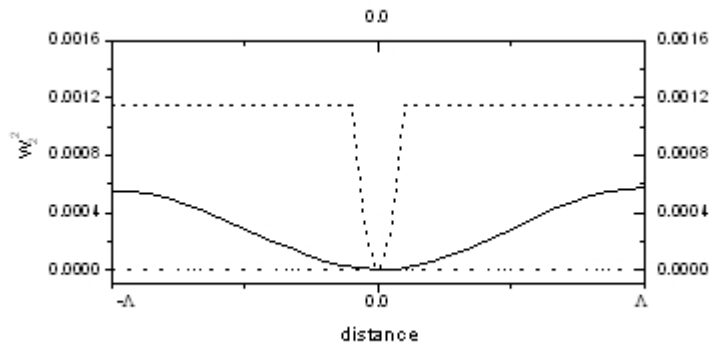
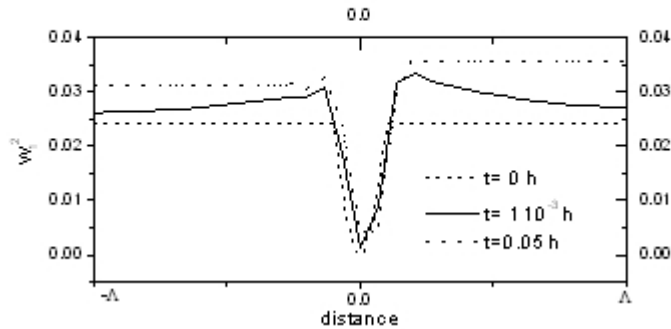
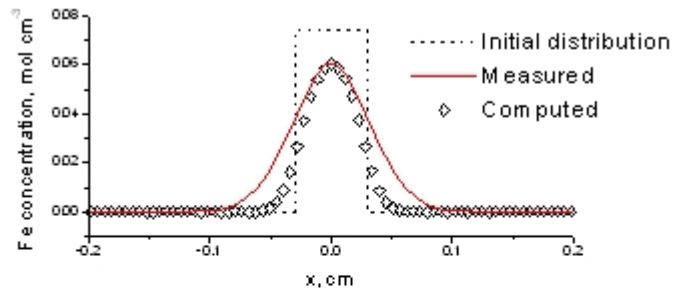


Figure 7. Non parabolic interdiffusion in ternary system. The evolution of the local deviation of molar ratio of the mixture components from the average value in the system, $w_i(z)$.

distribution and the calculated concentration profiles. The interdiffusion process generates the non parabolic diffusion, namely during the initial period of the process the system goes out of equilibrium at relatively fast rate. This can be seen clearly in Fig. 8 that shows the random deviation (variance) of molar ratio of the mixture components, $W(t)$, as a function of time.

It can be seen that during the initial period of the interdiffusion process (60 s), system goes out of equilibrium, i.e., random deviation of molar ratio of the mixture components increase. These results show that when diffusivities do not fulfil parabolicity condition [3] and specific initial distributions of elements are provided, the interdiffusion may become a non parabolic process. In the last section the momentum balance of mixture in which diffusion is considered will be presented.

Conservation of Momentum.

The alternative approach to phenomenological description of the interdiffusion was presented by Stephenson [11]. He analyzed the interaction between stress and diffusion [12]. The Stevenson approach base on the Darken's concept of the separation of diffusional and drift flows and takes into account the variable intrinsic diffusion coefficients [1]. His models are restricted to the semi-infinite one-dimensional system. To analyze real flow with diffusion, the momentum conservation law is necessary. However, the Navier-Stokes equations do not describe the diffusion of mass in a continuous medium.

Thus, no adequate formula that allows to analyze dynamics of interdiffusion is available.

All the above-mentioned models of transport base on the Darken's concept of the common medium drift velocity. Consequently (unavoidably when the three-dimensional problems are analyzed), this additional variable requires the formula which will balance number of unknowns and equations, requires a mathematical formula of momentum conservation.

The starting equation of the dynamics of solids is the general integral formula of momentum conservation

$$\frac{d}{dt} \int_{\Omega(t)} \rho \mathbf{u} \, dx = - \int_{\partial\Omega(t)} \rho \mathbf{u} \mathbf{u} \, dS + \int_{\Omega(t)} \rho \mathbf{f} \, dx + \int_{\partial\Omega(t)} \mathbf{t}(\mathbf{n}) \, dS, \quad (25)$$

where $\mathbf{t}(\mathbf{n})$ denotes the total strain tensor.

The starting integral formula of the equation of momentum conservation in dynamics of fluids has a form [13] analogous to eq. (25). The key difference is substitution of the total strain tensor by the pressure tensor.

The development of the differential formula of law of momentum conservation in solids base on the careful subdivision of the total strain into elastic, plastic and stress-free strains while in case of fluids the properties of pressure tensor are of interest.

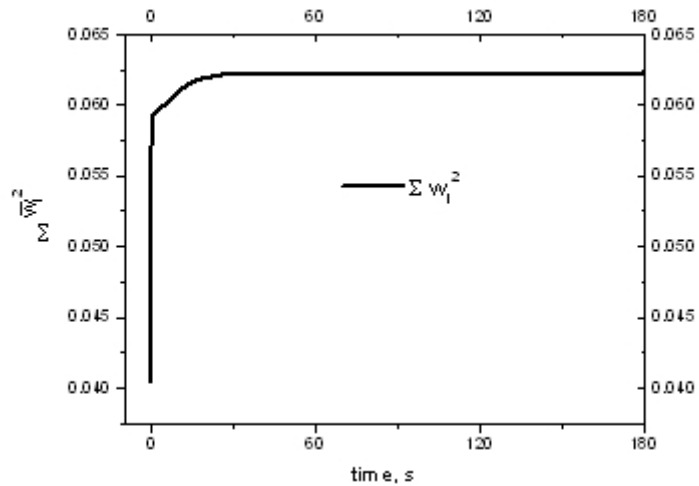


Figure 8. Nonparabolic interdiffusion in ternary system. The random deviation (variance) of molar ratio of the mixture components, $W(t)$, as a function of time.

In our treatment we based on the phenomenology of Navier-Stokes equations. In order to simplify the all derived formulae we restricted our analysis to the amorphous solids. We analyzed the motion of mixture in which mass flows from the region of higher mass density into the lower one [14]. In such a case the mass is transported as a result of pressure, viscosity, external forces and diffusion. The momentum balance of mixture in which diffusion is considered causes the new term to appear in the Navier-Stokes equation. Apart from terms responsible for pressure, viscosity and external forces there is the diffusional one. On the base of Newton's law we have obtained the equation of motion (local momentum conservation equation):

$$\rho \frac{D \mathbf{u}}{D t} \Big|_{\mathbf{u}} = - \nabla p + \text{Div} \boldsymbol{\sigma} + \mathbf{f} + \rho \frac{D \mathbf{v}_d}{D t} \Big|_{\mathbf{u}},$$

where $\rho \mathbf{v}_d$ denotes the average diffusional mass flux which can be expressed by any suitable formula, e.g. in the form of the Fickian flows.

The equation of motion has a form of Navier-Stokes equation, except the additional diffusional term

$$\mathbf{f}_d = \rho \frac{D \mathbf{v}_d}{D t} \Big|_{\mathbf{u}}.$$

It has been shown that the above diffusional term (diffusional force, \mathbf{f}_d) does not affects the internal energy of medium. Consequently the equation of internal energy conservation has the usual form:

$$\rho \frac{D \varepsilon}{D t} \Big|_{\mathbf{u}} = - p \text{div} \mathbf{u} + \sum_{i,j=1}^3 \frac{\partial u_i}{\partial x_j} \sigma_{ij} - \text{div} \mathbf{j}_q.$$

Finally we have examined the motion of the single component medium as a result of diffusion only, when the pressure ($p = \text{const.}$), viscosity ($\zeta = \eta = 0$) and external forces (\mathbf{f}_d) are negligible. We have concluded that in such a case the medium satisfies the well-known equation of diffusion:

$$\frac{\partial \rho}{\partial t} = \Theta \Delta \rho.$$

Though this results have not yet been verified on an experimental level, they still offer exciting new frontiers.

SUMMARY

- 1) The equations describing the interdiffusion process in the general case where the components' diffusivities vary with composition and the reactions of diffusing components at the boundaries are allowed are shown.
- 2) The reformulated variational form of interdiffusion in r-component solid solution that can exchange mass with a surrounding environment was derived (generalized Darken Method of interdiffusion).
- 3) A qualitative agreement between the computed and experimental results suggests that the postulated boundary conditions of GDM correctly describe the transport process in open systems.
- 4) The mathematical results of simulation of non parabolic diffusion show an exciting new possibilities in studying new group of processes.
- 5) Te modified Navier-Stokes equation with additional diffusional terms was shown. Though this results have not yet been verified on an experimental level, it still offers exciting new frontiers. Namely it may allow for quantitative modeling of interdiffusion in three-dimensional geometry.

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