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【論 文】

The Generalized Solutions in Non-Equilibrium Thermodynamics

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Generalized solutions play an important role in the modern theory of partial differential equations. The mathematical model of interdiffusion in the bounded mixture (*i.e.* layer) showing constant concentration (*e.g.* in solid or liquid solutions) and variable diffusivity of the components is presented. Using the idea of generalized solution, we will show an exact expression for the evolution of components distribution. The experimental results for ternary Co-Ni-Fe alloy are presented. We present the practical solution of the interdiffusion in multi layer materials and uphill diffusion (diffusional structures) in ternary diffusional couples of finite thickness. Presented model allows for many conclusions to be derived. The key massage is a great potential of generalized Darken model of interdiffusion in describing the mass transport in solid solutions. We show that modern mathematics now-days allows for the modelling, practical calculation and the better understanding of the real transport problems.

1. Introduction

Today's dynamic simulations of transport processes are powerful and widely used, *e.g.* by the space industry and in the advanced control systems on modern plants. Yet, we still make little use of dynamic modelling of complex thermochemical processes. This article will show the desktop simulation of complex mass transport process namely, the interdiffusion in multicomponent solid solutions.

Many processes in solids require the redistribution of mass over macroscopic distances. This redistribution occurs through a random process called diffusion (interdiffusion in multicomponent media) and its macroscopic description rests on specific differential equation called the continuity equation. Its solutions are used for widely different problems, from heterogeneous reactions to heat treatment of alloys from interdiffusion in liquid electrolytes to the motion of molecules in biological membranes. Apparently, there is a growing demand for the more advanced modelling of the real, practical systems. The polycrystalline, multiphase materials and nonplanar geometries are the basic examples.

The phenomenological description of diffusion proposed by Onsager[1,2] dominates interdiffusion study. An Onsager phenomenological scheme is useful in describing the behaviour of a closed system but in an open system the translation velocity usually does not vanish.[3] Consequently, the general case of interdiffusion in multicomponent system and many other complex transport processes cannot be satisfactorily described by a simple extension of the methods currently used.

The developments of modern mathematics offer an alternative approach, which is based on the idea of the generalized solution, *i.e.* week solution. It allows the quantitative description of very complex transport processes. It allows for the generalization of Darken phenomenological model of interdiffusion. In the modern theory of partial differential equations generalized solutions play a fundamental role. There are two reasons why we need to apply the generalized solutions: i) such formulation of the practical problems in the natural way

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allows to deal with the initial conditions given by the step functions and with nonhomogeneous objects (*e.g.* containing interfaces, *math:* containing singularities), ii) the generalized solution allows easy transition to the approximate solution and offers the numerical methods of its solving.

2. A generalized solution of the interdiffusion in an open, multicomponent bounded system

Although a general phenomenological relations for interdiffusion are available, these are hardly simple and their effective solutions are few and narrowed to the closed systems. Investigations of multicomponent systems are usually limited to the determination of interdiffusion coefficients.4) Such studies are almost entirely restricted to metallic alloys and, because of experimental difficulties, are few for systems with more than three components.5)

The different phenomenological description of interdiffusion has been proposed by Darken.6) It rests on the postulate that mass flux in ponderable media is a sum of diffusional and drift (translation) flow. The renewed interest in Darken's idea is seen in the recent approaches to interdiffusion in binary solid solutions.7) This paper introduces the reader to the generalized Darken's phenomenological scheme and presents recent experimental results. The particulars of this model for the closed system8) and the more general description of interdiffusion that incorporates the equation of motion can be found elsewhere.9)

2.1 The phenomenological description and the mathematical model of interdiffusion in the multicomponent solid solution

In case of multicomponent solutions the force, being a result of concentration gradient, causes the atoms of the particular element to move with a velocity (v_1), which may differ from the velocity of atoms of the other elements. Because the medium is common for all elements the fluxes are coupled and their local changes can influence the common mixture translation velocity (v). The above phenomenon is called interdiffusion.5) When external forces are negligible, the interdiffusion process can be treated as pure diffusional mixing. Nevertheless, the change of the mass distribution in the diffusional couple (*bounded body*) implies its translation to maintain an initial position of the *body* mass centre (*i.e.* when external force fields and initial velocity are negligible, then the position of the *body* mass centre does not vary with time). This conclusion leads to generalization of the boundary conditions, which is essence of our model.9-11) We state that the position of the *free* mixture boundary depends usually on time. The main targets of the model are to predict a concentration distribution of the elements for an arbitrary time (*i.e.* to calculate the evolution of distributions as a function of time) and/or to calculate the diffusivities, when the elements' distributions are known.12) The trem *formulation of the problem* is used here to mean an initial boundary-value problem for partial differential equations, namely for the equations of mass conservation. The formulation of the interdiffusion problem is a mathematical idealization, which consists of: i) data, ii) unknowns, iii) physical laws and relevant assumptions, iv) initial and boundary conditions. In this paper the retarded form of the generalized model of interdiffusion is presented.

Data:

1) molecular masses of the elements: $M_1, \ldots, M_r$,
2) diffusivities of the elements: $D_1, \ldots, D_r$, (may depend on composition),
3) initial position of the right end of the system (*i.e.* the border of the diffusional couple): Λ,
4) time of the process duration: t^*,
5) initial density distribution of the elements in the diffusional couple:

$$\overset{\circ}{\rho}_1(x), \ \ldots, \ \overset{\circ}{\rho}_r(x) \qquad -\Lambda \le x \le \Lambda$$

such that the condition no.6 in data is satisfied.

6) initial concentration of the mixture (see also next section):

$$c = \sum_{i=1}^{r} \frac{1}{M_i} \overset{\circ}{\rho}_i$$

Physical laws:

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

$$\frac{\partial \rho_i}{\partial t} = -\frac{\partial}{\partial x}(\rho_i v_i) \qquad (i = 1, \ldots, r) \tag{1}$$

where the reactions within the interdiffusion zone are not allowed. Following Darken drifts flow idea we postulate that the flux of i-th elements ($j_i = \rho_i v_i$) is a sum of the diffusional flux ($j_{d,i} = \rho_i v_{d,i}$) and translation flux ($\rho_i v$):

$$\rho_i v_i = -D_i \frac{\partial \rho_i}{\partial x} + \rho_i v$$

where diffusional flux ($j_{d,i} = \rho_i v_{d,i} = -D_i \cdot \partial \rho_i / \partial x$) is defined by the Fick'ian formula.

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

$$\frac{1}{M_1}\rho_1 + \ldots\ldots + \frac{1}{M_r}\rho_r = \text{constant} = c \tag{2}$$

This assumption can be used for solid or liquid solutions and when free volume of mixing and the gradient of pressure or stress are negligible.

It can be noted that the number of equations ($r+1$) equals the number of unkowns ($\rho_1, \ldots, \rho_r, v$).

Initial conditons:

1) *positions of the left and right ends of the mixture*: $\lambda_1(0) = -\Lambda$, $\lambda_2(0) = \Lambda$, where indexes "1" and "2" denote the left and right end of the mixture, respectively. Let us remember that in the presented dynamical model of interdiffusion the positions of the mixture ends can be affected by the interdiffusion process and/or external forces[9] and are functions of time,

2) *initial density distributions of the elements in the mixture*:

$$\rho_i(0, x) = \overset{\circ}{\rho}_i(x) \qquad \text{for } i = 1, \ldots, r$$

Boundary conditions:

1) *relation between the velocity of boundaries* ($d\lambda_j/dt \equiv \dot{\lambda}_j(t)$) *and mass flux at the boundaries*:

$$\dot{\lambda}_j(t) = u(t, \lambda_j(t)) \qquad (j = 1, 2) \tag{3}$$

In still simpler words, we postulate that the velocity of the boundary equals the velocity of the local mass centre of the mixture, u, at the boundary. It is apparent because otherwise, *e.g.* if the velocity u differs from the velocity of the boundary, the particles would jump out (leave) the surface of the diffusional couple. The above boundary conditions do not imply a constant density of the elements at the boundaries, which can vary during interdiffusion process.

2) We postulate that *when the mass flow through the boundary occurs*, *i.e.* the system is open, then, the gradients of components at the boundary are known functions.[10]

$$\frac{\partial \rho_i}{\partial x}(t, \lambda_1(t)) = \gamma_i(t) \qquad (i = 1, \ldots, r-1) \tag{4a}$$

These functions can be calculated, *e.g.* from the known rate of reaction at the boundary (interface). When the mass flow through the boundary does not occur (the system is closed) then, the gradients of all components at both boundaries vanish:[8]

$$\frac{\partial \rho_i}{\partial x}(t, \lambda_1(t)) = 0 \qquad (i = 1, \ldots, r) \tag{4b}$$

The unknowns: The above data, physical laws, initial and boundary conditions allow to compute:
1) positions of the mixture boundaries, $\lambda_1(t)$, $\lambda_2(t)$, 2) densities of all elements as a function of time and position, $\rho_1(t,x)$ and, 3) the mixture translation velocity as a function of time and position, $v(t,x)$.

Reformation of the problem. We define a new variable $w_i(t, z)$ the spatially shifted deviation of the i-th element mole fraction from its average in the mixture (called briefly the shifted deviation):

$$w_i(t, z) := \frac{1}{cM_i}\rho_i(t, x) - \overline{m_i}$$

where $\overline{m_i}$ denotes the mean mole fraction of the i-th element in the diffusional couple: $\overline{m_i} := m_i / 2\Lambda c M_i$ and, m_i is the total mass of the i-th element per unit surface of the mixture:

$$m_i = \int_{\lambda_1(t)}^{\lambda_2(t)} \rho_i(t, x)\,dx \tag{5}$$

The definition (5) allows to obtain the rescaled expressions for: $\partial w_i / \partial z\ (t, z)$, $w_i(0,z)$ and $v_i(t, z)$.[9] One can show that law of the mass conservation, Eq.(1), upon introducing above rescaled expressions becomes:

$$\frac{\partial w_i}{\partial t}(t, z) = -\frac{d}{dz}\left[D_i \frac{\partial w_i}{\partial z}(t, z) - (w_i(t, z) + \overline{m_i})\left(D \,\middle|\, \frac{\partial w}{\partial z}(t, z)\right)\right] \qquad i = 1, \ldots, r \tag{6}$$

where $w = (w_1, \ldots, w_r)$ and $D = (D_1, \ldots, D_r)$ are vector functions of the shifted deviations of all elements and intrinsic diffusivities[9] and $(\cdot \mid \cdot)$ denotes the scalar product in $\mathbb{R}^r$.

In a closed system, $\gamma_i(t) = 0$,[11] the problem of interdiffusion reduces further to:

$$\frac{\partial w}{\partial t}(t, z) = \frac{d}{dz}\boldsymbol{F}\left[w(t, z), \frac{\partial w}{\partial z}(t, z)\right] \tag{7}$$

$$w(0, z) = \overset{\circ}{w}(z) \tag{8}$$

$$\frac{\partial w}{\partial z}(t, -\Lambda) = \frac{\partial w}{\partial z}(t, \Lambda) = 0 \tag{9}$$

where $\boldsymbol{F}$ is the known function.[13]

The equalities (8) and (9) present the reformulated initial and boundary conditions, respectively. The equations (7)-(9) form a system of differential equations where unknowns are shifted deviations, w_i. They form the initial-boundary value problem for the interdiffusion in a closed system where initial distribution of elements is an arbitrary known function. One may remark that we have condensed the problem from "r+1" equations to one partial differential equation, Eq.(7).

2.2 Generalized solution

In this section an idea of the generalized solution is presented. Let us take some absolutely continuous function, $\varphi(z)$ which has a square integrable derivative $\mathrm{d}\varphi/\mathrm{d}z\ (z)$ defined almost everywhere in the diffusional couple - in the interval $[-\Lambda, \Lambda]$. If we multiply Eq.(7) by $\varphi(z)$ and integrate the obtained equality with respect to z within the range, $|^{\Lambda}_{-\Lambda}$, we obtain:

$$\int_{\Lambda}^{\Lambda} \frac{\partial w}{\partial t}(t, z) \cdot \varphi(z)\,\mathrm{d}z = \int_{\Lambda}^{\Lambda} \frac{\partial}{\partial z} \boldsymbol{F}\left(w(t, z), \frac{\partial w}{\partial z}(t, z)\right) \cdot \varphi(z)\,\mathrm{d}z \tag{10}$$

where $(\cdot)$ denotes the scalar product in $\mathbb{R}^r$. Integrating by parts the right-hand side of Eq.(10) and considering the condition (9) leads us to the following relation:

$$\int_{\Lambda}^{\Lambda} \frac{\partial w}{\partial t}(t, z) \cdot \varphi(z)\,\mathrm{d}z = \int_{\Lambda}^{\Lambda} \boldsymbol{F}\left(w(t, z), \frac{\partial w}{\partial z}(t, z)\right) \cdot \frac{\mathrm{d}\varphi}{\mathrm{d}z}(z)\,\mathrm{d}z \tag{11}$$

The main target of this approach was to move the derivative from function $\boldsymbol{F}$, Eq.(7), into function ψ, Eq.(11), which by our assumption is 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 (8) can be written:

$$\int_{\Lambda}^{\Lambda} w(0, z) \cdot \varphi(z)\,\mathrm{d}z = \int_{\Lambda}^{\Lambda} \overset{\circ}{w}(z) \cdot \varphi(z)\,\mathrm{d}z \tag{12}$$

where $w(z)$ is a given function (function of the initial shifted deviations of all elements).

Definition of the generalized solution: *A function* $w(t,z)$ *is called a generalized solution of the problem* (7)-(9) *if and only if the identity*:

$$\int_{-\Lambda}^{\Lambda} w(t, z) \cdot \varphi(z)\,\mathrm{d}z = \int_{\Lambda}^{\Lambda} \overset{\circ}{w}(z) \cdot \varphi(z)\,\mathrm{d}z - \int_0^t \int_{-\Lambda}^{\Lambda} \boldsymbol{F}\left(w(\tau, z), \frac{\partial w}{\partial z}(\tau)\right) \cdot \frac{\mathrm{d}\varphi}{\mathrm{d}z}(z)\,\mathrm{d}z\,\mathrm{d}\tau \tag{13}$$

(which is equivalent to the conjunction (7) and (8)) *holds for every* ψ.

Thus, the classical boundary-value problem (7)-(9) was reformulated to single variational identity (13). The final step is computation of solution, which bases on the idea of approximate solution. An example of the numerical method (the Galerkin method) of solving the problem (7)-(9) has already been presented.[13]

2.3 Interdiffusion in Co-Ni-Fe alloys

The experimental data and simulations of the interdiffusion processes in finite diffusional couples are shown in **Figs.1** and **2**. For calculations the following data were used:

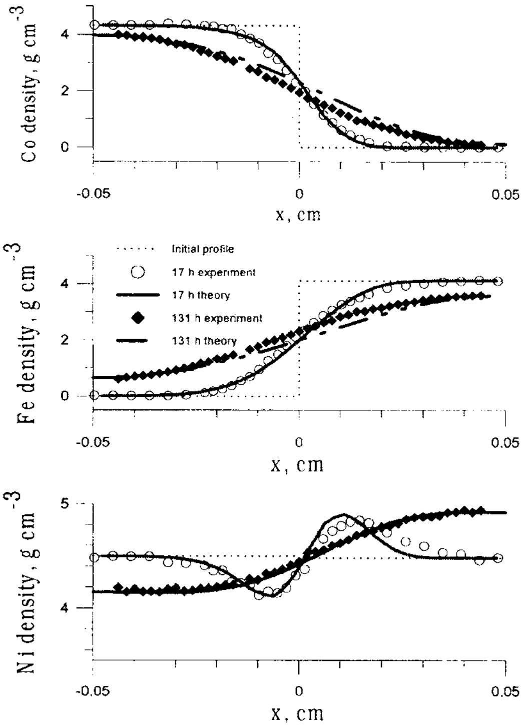

Fig.1 Interdiffusion in the Co-Fe-Ni finite diffusional couple at 1588 K. The experimental and calculated distributions of elements after 17 and 131 hours of the annealing time.

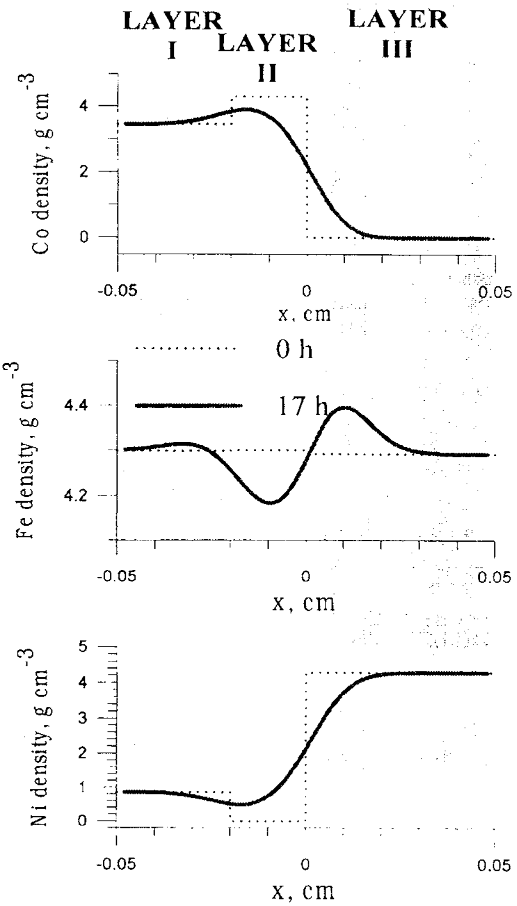

Fig.2 Interdiffusion in the Co-Fe-Ni finite multilayer diffusional couple at 1588 K. The calculated distributions of elements after 17 hours of the annealing time.

1) atomic masses of Co, Fe and Ni: 58.9333, 55.847 and 58.69 ;
2) thickness of the diffusional couple: $2\Lambda=0.1$ cm ;
3) diffusion coefficients at 1588 K[12] : $D_{Co}=6.31\cdot10^{-10}$, $D_{Fe}=16.25\cdot10^{-9}$ and $D_{Ni}=2.89\cdot10^{-10}$ cm^2 s^{-1} ;
4) $c=0.15$ mol cm^{-3} ;
5) time of the process (*e.g.* annealing) $t^*=17$ and 131 hours ;
6) the parameter of the Galerkin approximation[13] : $N=40$;
7) the diffusional couple shown in **Fig.1** was formed by two alloy pellets ($d=\Lambda=0.05$ cm) having composition: Fe-52Ni and Co-51Ni in wt%.

Figs.1 and **2** show the initial distribution and the measured and calculated concentration profiles. The interdiffusion process generates the diffusional structure of initially uniform nickel distribution, *i.e.* uphill diffusion of nickel, **Fig.1**. It may be noted that in the finite system (a finite diffusional couple) its life time is limited and after 131 hours annealing time diffusional structure diminishes. The experimental data and simulations show that homogenization time of the ternary diffusional couple is controlled by the transport of the component showing the lowest diffusivity.

The used here mathematical method allows for and arbitrary initial distribution of elements. Thus one can select very complex initial conditions, *e.g.* highly non regular initial data. In **Fig.2**. the interdiffusion in multilayered metallic plate is shown (total thickness 1 mm). The change of composition at the ends of the diffusional couple is observed. These results show that interdiffusion in some closed system changes concentrations of components at the boundaries.[8] The DYFSYM software used to compute evolution of densities was written in Borland C++ v.3.1. The demo version is available from the authors.[14] All computations were carried out using IBM-compatible PC Pentium 100 MHz. As with any numerical approach, the speed of our method depends on how much accuracy we need. The computations of evolution of the ternary system, **Fig.1** and **2** (the parameter of the approximation ($N=40$) required 10 and 20 minutes, respectively.

Discussion

The transport processes usually involve out- or inflow of a single or all elements from the system (*e.g.* the coating). The presented generalized Darken model of interdiffusion for the multicomponent, bounded system allows for simulation of such processes. The appropriate boundary conditions can be given for an open and also bounded systems and, can be applied for interdiffusion in wide selection of chemical processes.[9,10] The idea of generalized solution and its practical use for numerical calculations was introduced and showed. The experimental results and results of numerical calculations of interdiffusion in Co-Fe-Ni alloys were shown.

The model presented allows for many conclusions to be derived. The key massage is a great potential of generalized Darken model of interdiffusion in describing the mass transport in solid solutions. We show that modern mathematics now-days allows for the modelling, practical calculation and the better understanding of the real transport problems.

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