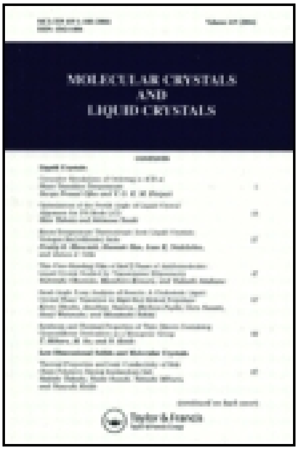

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Interdiffusion in Oxide Solid Solutions, Simulation of the Process and Calculation of Intrinsic Diffusivities

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Interdiffusion in Oxide Solid Solutions, Simulation of the Process and Calculation of Intrinsic Diffusivities

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A modified form of the generalized Darken's model of interdiffusion is presented in the case of solid solution oxides of the (A, B,..)O type, i.e., binary, ternary and higher oxides. 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 interfaces are allowed are shown. The model allows to study the evolution of the composition in the multicomponent system occurring as a result of its thermal treatment and/or intercalation, e.g., allows to predict the concentration profiles of all elements in the vicinity of interfaces (at the reaction zone). We show the simulation of the evolution of composition of the NiO-CoO solid solutions at high temperatures. We will show that the generalized Darken model allows to obtain the quantitative data on the interdiffusion in open systems as well as describe the complex mass transport processes in solid solutions.

Keywords: interdiffusion; computer simulation; intrinsic diffusivities; chemical diffusion; ternary oxides

INTRODUCTION

The commercial metallic and growing number of ceramic materials are usually a multicomponent and multiphase. In this work we will show the recent progress in understanding the interdiffusion in a single phase solid solution containing an unrestricted number of components ($r \geq 2$) that show variable mobilities and the interdiffusion in an open system. We restrict our model to single phase solid solutions only and will demonstrate its capability in future applications for multiphase systems. The mathematical model of interdiffusion in one-dimensional system showing constant total concentration and variable diffusivity of the components is a base of our approach[1,2]. Using the idea of generalized solution, we have obtained an exact expression for the evolution of component distributions in an closed and open systems, e.g., intercalated material.

THEORY

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[3]. Such studies are almost entirely restricted to metallic alloys and, because of experimental difficulties, are few for systems with more than three components. This paper introduces the reader to the generalized Darken's phenomenological scheme. The particulars of the generalized Darken's model (GDM) for the closed system[4] and the more general description of interdiffusion that incorporates the equation of motion can be found elsewhere[1,2].

The model of interdiffusion in the multicomponent solid solution

In case of multicomponent solutions the force, being a result of concentration gradient, gives rise to diffusion of particular element. The gradient of chemical potential causes the atoms of the particular element to diffuse with a certain velocity. This velocity of diffusion was defined by Darken in the internal reference frame (i.e., lattice frame of reference) as the diffusional velocity, $v_{id} = -\mathrm{D}_i\,\mathrm{grad}\left(\ln c_i\right)$. All diffusional fluxes are coupled and their local changes influence the common mixture drift velocity (v). The drift velocity (Darkens term) is synonym of translation (plastic deformation and interdiffusion), convection (interdiffusion and stress) and flow velocity (open systems and liquid solutions with convection). The above description of diffusion in alloys (generally solid solutions) is called Darken model of interdiffusion[5].

Following Darken drift flow postulate we state that the flux of *i*-th element is a sum of the diffusional flux $\left(\varrho_i v_{\mathrm{d}\,i}\right)$ and drift flux $\left(\varrho_i v\right)$:

$$\varrho_i v_i = \varrho_i v_{\mathrm{d}\,i} + \varrho_i v . \qquad (1)$$

Following the original Darkens' formulation, we postulate that the diffusional flux is an Fickian flow. Thus, the flux of the *i*-th element becomes:

$$\varrho_i v_i = -D_i \frac{\partial \varrho_i}{\partial x} + \varrho_i v , \qquad (2)$$

where D_i is intrinsic diffusivity of the *i*-th component that can depend on the composition of the solid solution, i.e., $D_i := D_i\left(\varrho_1, \varrho_2, \ldots, \varrho_r\right)$. The Eq. (2) is the constitutive flow formulae postulated for the generalized Darken model of interdiffusion. Thus, the interdiffusion problems in ionic solid solutions and non-ideal solutions will have to be reformulated to such a form. Examples of such reformulation will be shown in the next section.

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[2]:

$$\left(\varrho_i v_i\right)\left(t, -\Lambda\right) = j_{i\mathrm{L}}(t) \quad \text{for} \quad i = 1, 2, \ldots, \mathrm{r} ; \qquad (3)$$

$$(\varrho_i v_i)(t, \Lambda) = j_{i\mathrm{R}}(t) \quad \text{for} \quad i = 1, 2, ..., \mathrm{r}. \tag{4}$$

The functions at right side of Eqs. (3) and (4) have to be known and can be calculated from the known rates of reaction at the boundaries or from the other experimental data (e.g. the rate of selective oxidation of multicomponent alloy). In the closed system the gradients of all components at both boundaries vanish[4]. Basing on modern theory of partial differential equations it has been proved the existence of the solution and its uniqueness. The variational form of initial-boundary value problem has been formulated for finding its solution.

CHEMICAL INTERDIFFUSION

In order to effectively use the GDM in the case of ionic solid solutions the flux formulae has to be reformulated to a form of Eq. (2), i.e., the diffusional flux has to be expressed as a Fickian flow showing variable diffusivity. Examples of such reformulation are shown in this section.

The diffusional flux of the ions in an (A, B, ...)X ionic solid solution under the case involving the presence of gradients of all components (and of nonmetal) can be expressed by the mobility of ions. Thus, the flux of the i-th element becomes:

$$\varrho_i v_i = B_i \varrho_i F_i + \varrho_i v, \tag{5}$$

where B_i denotes the mobility and F_i the force (or sum of all forces) acting on the i-th ion. Consequently when the presence of the external forcings is negligible Eq. (5) becomes:

$$\varrho_i v_i = -B_i \varrho_i \frac{\partial \mu_i}{\partial x} + \varrho_i v = -\mathrm{k}TB_i \varrho_i \frac{\partial \ln a_i}{\partial x} + \varrho_i v, \tag{6}$$

where k and T denote the Planck constant and the temperature and μ_i is the chemical potential of i-th element (expressed in the energy unit per single ion). Upon assuming: 1) the Nernst-Einstein relation between the self diffusion and mobility ($D^* = B\,\mathrm{k}\,T$) and 2) local equilibrium and existence of the equation of state for (A, B, ...)X ionic solid solution, the diffusional flux in Eq. (6) can be expressed as an Fickian flow with composition dependent intrinsic diffusivities:

$$\varrho_i v_i = -D_i^* \frac{\partial \ln a_i}{\partial \ln c_i} \frac{\partial \varrho_i}{\partial x} + \varrho_i v = -D_i \frac{\partial \varrho_i}{\partial x} + \varrho_i v, \tag{7}$$

where intrinsic diffusivity is given by:

$$D_i = D_i^* \frac{\partial \ln a_i}{\partial \ln c_i} = D_i^* \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right). \tag{8}$$

The analysis of the diffusion in ternary solid solution has been given by Wagner[6] in the case of the parabolic growth of an (A,B)O oxide on binary alloy. It became later a starting point for Gesmundo and Viani examination of interdiffusion in p-type oxide solid solutions[7].

We will demonstrate in a brief way that when electronic conductivity prevails the intrinsic diffusivities again can be expressed by Eq. (8). In such a case the non marginal diffusional flux of the electrons affects mobilities of ionic species (ambipolar mechanism of diffusion) and non negligible electric field is generated in the transport zone. Here again fluxes of ionic species and electrons in an (A, B, ...)X ionic solid solution under the case involving the presence of gradients of all components (including nonmetal) can be expressed by the mobility of ions. Thus, the flux of the *i*-th element can be expressed by Eq. (2). The presence of both the chemical and unknown electric field must be taken into account now. Thus, Eq. (5) becomes:

$$\varrho_i v_i = -B_i \varrho_i \left(\frac{\partial \mu_i}{\partial x} + z_i e \frac{\partial V}{\partial x} \right) + \varrho_i v , \tag{9}$$

where V denotes the electric potential generated as a result of movement of the charged species; e and z_i are the electric charge of electron and the valence of *i*-th specie respectively.

The diffusion of mass is the slowest mode of transport. Consequently, the Poisson equation can be avoided and the local electro neutrality postulate

$$\sum_{i=1}^{r} z_i j_{di} - j_e = 0 \tag{10}$$

correctly describes the charge transport. It must be emphasized that this equation is written in the internal reference frame thus, fluxes are the diffusional fluxes of all ionic species and of electrons. These fluxes must be expressed in mole units or as a number of particles. The electro neutrality equation allows to compute the unknown electric field. Upon substituting proper expressions for diffusional fluxes (left term of r.h.s. of Eq. (9)) in Eq. (10) the expression for the unknown electrical field can be calculated:

$$\frac{\partial V}{\partial x} = \frac{1}{e} \frac{-\sum_{i=1}^{r} c_i B_i z_i \frac{\partial \mu_i}{\partial x} + c_e B_e \frac{\partial \mu_e}{\partial x}}{\sum_{i=1}^{r} z_i^2 c_i B_i + c_e B_e} .$$

When the mobility of electrons exceeds that of ionic species ($B_e \gg B_i$) it reduces to:

$$\frac{\partial V}{\partial x} = \frac{1}{e} \frac{\partial \mu_e}{\partial x} . \tag{11}$$

Upon substituting Eqs. (9) and (11), the flux in the external reference frame is given by:

$$\varrho_i v_i = -B_i \varrho_i \left(\frac{\partial \mu_i}{\partial x} + z_i \frac{\partial \mu_e}{\partial x} \right) + \varrho_i v ,$$

which upon taking into account that $\mu_i(uncharged) = \mu_i(charged) + z_i \mu_e$, reduces to formulae (6). Thus, again the intrinsic diffusivity is given by Eq. 8. The analysis of the ambipolar diffusion mechanism in oxides has been given by Wagner[8].

The thermodynamical factor can be calculated from thermodynamical data:

$$\frac{\partial \ln a_i}{\partial \ln c_i} = \frac{c_i}{RT} V_m \frac{\partial^2 G_m}{\partial y_i^2}$$

where V_m is molar volume of the system, G_m - its molar free enthalpy and y_i denotes mole fraction of *i*-th component.

INTERDIFFUSION IN NiO-CoO SOLID SOLUTION AT 1573 K

The main targets are to show the usability of the generalized Darken model in modeling the complex diffusional processes and the changes of density of elements in solid solution showing variable intrinsic diffusivities. For calculating concentra-tion profiles [9] the following data were used: 1) atomic masses of Ni, Co and O; 2) thickness of the sample ("diffusional couple"): $2\Lambda = 0.04$ cm; 3) variable intrinsic diffusivities of Co and Ni shown in Fig. 1 [7] and oxygen diffusivity $D_O \leq 1.0 \cdot 10^{-20} \mathrm{cm^2 s^{-1}}$; 4) $c = 0.18$ molcm^{-3}; 5) variable time of the reaction $t^* \in [0 \div 4 \cdot 10^4 \mathrm{s})$.

In present work we have included the thermodynamic factors that markedly affect the transport properties of the solid solution[5]. In Figure 2 the comparison of calculated concentration profiles for constant and variable intrinsic diffusion coefficients is shown.

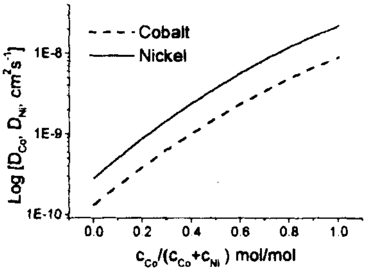

FIGURE 1 Intrinsic diffusivities of Co and Ni at 1573K as a function of Co molar fraction[7].

DISCUSSION

The simulation of interdiffusion in CoO|NiO diffusional couple shows great impact of variable diffusivities on distribution of Ni and Co, Fig. 2. It demonstrates that usual assumption of constant (e.g., average) intrinsic diffusivities can result in a large error and that such simplification is generally is not allowed in real systems. Our calculations of interdiffusion coefficients (not shown here) made evident the agreement of GDM with the already published results[7].

The results show the great potential of GDM in the modeling of interdiffusion in multicomponent oxide systems. The presented reformulation of the flux forulae

allows to study chemical interdiffusion in open systems. It allows to study the evolution of the composition in the multicomponent system occurring as a result of its thermal treatment and/or intercalation, e.g., allows to predict the concentration profiles of all elements in the vicinity of interfaces (at the reaction zone).
The existence and uniqueness of the solution of GDM[1] allows to formulate inverse problem of GDM. Thus, it allows for effective calculation of both constant [10] and variable intrinsic diffusivities. The details of the method and calculated diffusivities for non-ideal solid solutions will be published.

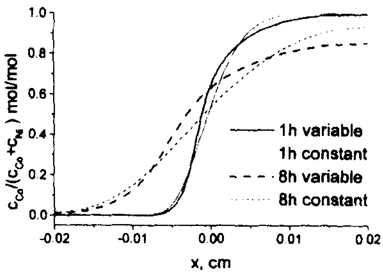

FIGURE 2 Computer simulation of interdiffusion in CoO|NiO diffusional couple at 1573K. Comparison of concentration profiles for constant and variable diffusion coefficients[7].

Acknowledgments
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