# Three-Dimensional Interdiffusion Under Stress Field in Fe-Ni-Cu Alloys

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We present the method of solving the mechanochemical transport problem in multicomponent solid solutions, namely, the method of quantitative description of the interdiffusion (ID) under the stress field. We postulate that the velocities appearing in the momentum balance equation should be the drift and diffusion velocity. The energy, momentum, and mass transport are diffusion controlled, and the diffusion fluxes of the components are given by the Nernst-Planck formulas. The diffusion depends on the chemical potential gradient and on the stress that can be induced solely by the diffusion as well as by the boundary conditions. The key results lie in the interpretation of the Navier-Lamé equation for the deformed regular crystal, where the concentrations are not uniform and ID occurs. The presented coupling of the Darken and CALPHAD methods with the momentum balance equation allows for quantitative analysis of the transport processes occurring on entirely different time scales. It is shown that the proposed method is effective for modeling transport processes in Fe-Ni-Cu alloys. We demonstrate the case of ID in a planar plate, and predict slower penetration and accumulation. The experimental results confirm theoretical predictions.

## 1. Introduction

Experiments made in the 19th century showed that diffusion in solids is as real as it is in liquids. Already in 1896, Roberts-Austen[1] measured the diffusion of gold in lead and calculated its diffusivity down to 100 °C. Unfortunately, for the next 60 years the concept of conservation of the lattice sites (in solids) and Fick's laws dominated. In 1935, Gorsky[2] analyzed the interaction of diffusion and stress. The idea was to treat a diffusing atom as a center of dilatation that creates a local stress field. Alefeld et al.[3] considered other local contributions such as an externally applied stress. Larché and Cahn[4,5] studied various aspects of the Gorsky concept, such as the effect of stress on the

mobility, the stresses due to the compositional inhomogeneities, and the stress influence on the boundary conditions. The dependence of the local flux* on the geometry and nonhomogeneity of the entire specimen was considered by them as a failure of local Fick's law and explained as an effect of nonlocal factors. Finally, Larché and Voorhees[6] formulated the model of diffusion in the presence of stress based on the usual equilibrium thermodynamics of fluids. All of the above models are limited to the diffusion of various components in the conserved solid lattice (solute).

The entirely new understanding of diffusion in multicomponent systems started with Kirkendall experiments on the interdiffusion (ID) between copper (Cu) and zinc (Zn). They proved that diffusion by direct interchange of atoms, the prevailing idea of the day, was incorrect. In 1946, Kirkendall, along with his student, Alice Smigelskas[7] showed movement of the interface between the "initially different phases" due to ID. They showed that the different intrinsic diffusion fluxes of the components cause swelling (creation) of one part and shrinking (annihilation) of the other part of the diffusion couple. The key conclusion was that local movement of a solid (its lattice) due to the diffusion is a real process and that the lattice sites are not conserved in a solid. Once the solid solution is nonuniform and the mobilities differ from each other, then a vast number of phenomena can occur (i.e., Kirkendall marker movement occurs, Kirkendall-Frenkel voids might be formed, and stresses are generated).

The concepts initiated by Kirkendall played a decisive role in the development of the diffusion theory. In 1948,

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*Fick's first law, and the Nernst-Planck and the Onsager formulas relate the local diffusion flux to the local gradient of the, for example, concentration, chemical potential, and electric field. Thus, they are all local laws.

Darken[8] explained the Kirkendall shift observed during the ID in solids by postulating the existence of local drift velocity in solids. Thus, almost a century after Fick, Darken showed again that diffusion in the solid phase proceeds analogously to that in liquids. Nowadays, the drift velocity in solids is universally accepted and is by some authors called convection.[9]

The ID and stress (i.e., the mechanochemical transport problem at constant temperature) was studied by only a few authors. The key results are by Stephenson[9] and Beke.[10] Stephenson[9] limited the stress problem to noncompressible flow only, and was able to avoid mathematical and numerical difficulties. Beke[10] analyzed the stress problem in binary alloys and used relations analogous to those in the Stephenson approach. The different partial molar volume and mobility of the diffusing species generate an imbalance in the volume transport. This is equivalent to the creation of a nonuniform stress-free strain that couples the drift velocity field and the strain. Finally, Boettinger et al.[11] analyzed lateral deformation of the hypothetical binary diffusion couple due to the ID.

The Navier-Stokes equation was "revisited" recently by Brenner.[12] He postulated a revision of Newton's law of viscosity appearing in the deviatoric stress tensor in the Navier-Stokes equation for the case of compressible fluids, both gaseous and liquid. The postulated modification is equivalent to the Darken concept of the drift velocity that had already been postulated in the case of a solid phase.[13] In the present work, the Navier-Lamé equation describes the momentum conservation in a multicomponent regular crystal. An effect of the different time scales for mechanical (stress) and chemical (ID) processes explains the effect of the geometry and boundary conditions of the entire system on the ID. Thus, the hierarchical structure of a solid explains the different time scales observed during the mechanochemical transport process. There are no new fundamental laws, only new phenomena, as one considers a different length scale.[14]

In a previous study,[15] the authors presented the method of description of ID in solids and liquids. Due to the introduction of the partial Cauchy stress tensor and pressure approximations, the method was unsuccessful in practical applications. In what follows, only widely accepted formulas are used, and the authors avoid the concept of partial stress tensor. The coupling of the Darken method with the momentum balance equation allows for an effective, quantitative analysis of the isothermal transport process (ID) in the iron (Fe)-nickel (Ni)-Cu alloys.

## 2. Theory

The authors analyzed the mass, momentum, and energy transport in a multicomponent regular crystal. This analysis was based on: the Darken method for a multicomponent solution (the continuity equations and the Vegard law as an equation of state at equilibrium); the Navier-Lamé momentum balance equation; the energy conservation formulae; and the CALPHAD method to compute chemical potentials.

The Darken method for multicomponent solutions (DMMS) is based on the Darken postulate that the total mass flow is a sum of diffusion and drift flow.[16] The force arising from local gradients causes the atoms of a particular component to move with a velocity, which in general may differ from velocity of the other components. The medium is common for all of the species and diffusion fluxes that affect the common drift velocity $\upsilon^{\text{drift}}$. The physical laws that govern the pure ID process (i.e., when stresses are negligible) are continuity equations, and the postulate that the total molar concentration of the solution is constant. The extended Darken method in one dimension[16] allows modeling the positions of the solution boundaries, densities, and the drift velocity. Physical laws in DMMSs are the same as in original Darken model. All the important differences are in the formulation of the initial and boundary conditions. The DMMSs allow the modeling of ID for arbitrary initial distribution of the components, in a case of moving boundaries, of the reactions at interfaces and in many other situations. The uniqueness and existence of the solution, the effective methods of numerical solution, and the successful modeling of the "diffusional structures" (up-hill diffusion) proved the universality of Darken's drift concept. The DMMSs are used here to describe mechanochemical transport problem in a multicomponent solution, namely, the ID in a nonideal solution (alloy), in a system in which stresses are nonnegligible, and in three dimensions. Moreover, it is assumed that the mobilities are isotropic (regular crystal) and that no source of internal stresses, such as dislocations, exists.

The use of the CALPHAD method, the Vegard law, and the mechanochemical time scales will be described in the next sections.

### 2.1 The Darken Method for Multicomponent Solutions and Stress

The core of the DMMS method is the mass balance equation:

$$\frac{\partial \rho_i}{\partial t} = -\text{div} J_i, \qquad i = 1, \ldots, r \tag{Eq 1}$$

where $\rho_i$ is the mass density and $J_i$ denotes the flux of $i$-th element that contains the diffusive and the drift terms:

$$J_i = \rho_i \upsilon_i = J_i^d + \rho_i \upsilon^{\text{drift}} = \rho_i \upsilon_i^d + \rho_i \upsilon^{\text{drift}}, \qquad i = 1, \ldots, r \tag{Eq 2}$$

where $\upsilon^{\text{drift}}$ denotes the drift velocity, $r$ the number of components in the solution, $J_i^d$ and $\upsilon_i^d$ are the diffusion flux and diffusion velocity of $i$-th component, respectively.

The drift velocity is a result of deformation, $\upsilon^\sigma$, and of the Darken drift velocity, $\upsilon^D$. Thus:

$$\upsilon^{\text{drift}} = \upsilon^D + \upsilon^\sigma \tag{Eq 3}$$

The mass balance equation can be written in the internal reference frame (relative to the drift velocity). Thus, from Eq 1 and 2 it follows:

$$\left.\frac{D\rho_i}{Dt}\right|_{v^{\text{drift}}} = -\text{div}J_i^d - \rho_i \text{div}v^{\text{drift}} \qquad i = 1, \ldots, r \qquad \text{(Eq 4)}$$

The derivative in Eq 4 is called Lagrangian, substantial, or material derivative:

$$\left.\frac{D\rho_i}{Dt}\right|_{v^{\text{drift}}} = \frac{\partial \rho_i}{\partial t} + v^{\text{drift}} \, \text{grad} \, \rho_i \qquad \text{(Eq 5)}$$

and it gives the rate of density changes at the point moving with an arbitrary velocity; here it is the drift velocity.

To include an effect of the stress field, the DMMS[16] has to be further generalized. The more general form of the diffusion flux is the Nernst-Planck equation:[17,18]

$$J_i^d = \rho_i B_i F_i := \rho_i v_i^d \qquad \text{(Eq 6)}$$

where $v_i^d$, $B_i$, and $F_i$ are the diffusion velocity, the mobility of $i$-th component, and the force acting on it, respectively:

$$F_i = -\text{grad}\left(\mu_i + \frac{\Omega_i^V}{\sum\limits_{i=1}^{r} N_i \Omega_i^V} \Omega p\right) = -\text{grad}\left(\mu_i + \frac{\Omega_i^V}{\Omega^V} \Omega p\right)$$
$$= -\text{grad}(\mu_i + \mu_i^m) \qquad \text{(Eq 7)}$$

$$\mu_i^m = \frac{\Omega_i^V \Omega}{\sum\limits_{i=1}^{r} N_i \Omega_i^V} p \qquad \text{(Eq 8)}$$

where $\mu_i$ and $\mu_i^m$ denote the chemical and mechanical potential of the $i$-th component in the solution (alloy), respectively, $\Omega_i^V$ and $p$ are the standard partial molar volume (at $10^5$ Pa), and $p$ is the pressure.

Upon combining Eq 4, 6, and 7, the continuity equation becomes:

$$\left.\frac{D\rho_i}{D_t}\right|_{v^{\text{drift}}} = \text{div}(\rho_i B_i \text{grad}(\mu_i + \mu_i^m)) - \rho_i \text{div}v^{\text{drift}} \qquad i = 1, \ldots, r$$
$$\text{(Eq 9)}$$

The concentration of the solution is defined by:

$$c = \sum_{i=1}^{r} c_i = \sum_{i=1}^{r} \frac{\rho_i}{M_i} \qquad \text{(Eq 10)}$$

From Eq 2, the following relations for the flux and velocity of the $i$-th element hold:

$$J_i = c_i v_i^d + c_i v^D + c_i v^\sigma \qquad \text{(Eq 11)}$$

$$v_i = v_i^d + v^D + v^\sigma \qquad \text{(Eq 12)}$$

By summing Eq 11 for all components and using Eq 10 one gets:

$$\sum_{i=1}^{r} J_i = \sum_{i=1}^{r} c_i v_i = cv = \sum_{i=1}^{r} c_i v_i^d + cv^D + cv^\sigma = cv^d + cv^D + cv^\sigma$$
$$\text{(Eq 13)}$$

and from Eq 13 it follows:

$$v^d = v - v^D - v^\sigma = v - v^{\text{drift}} \qquad \text{(Eq 14)}$$

It is postulated here that the drift velocity is the sum of Darken drift velocity (generated by the ID) and the deformation velocity $v^\sigma$ (generated by the stress):

$$v^{\text{drift}} = v^D + v^\sigma \qquad \text{(Eq 15)}$$

Darken[8] postulated that diffusion fluxes are local and are defined exclusively by the local forcing (e.g., the chemical potential gradient, stress field, and electric field). He postulated the existence of the unique average velocity that he called the drift velocity. In the original article on the DMMS,[8] the Darken drift velocity, $v^D$, is given:[16]

$$\frac{\partial}{\partial x}\left(cv^D + \sum_{i=1}^{r} c_i v_i^d\right) = 0$$

Upon integrating, the above relation takes the form:

$$v^D = v*(t) - \frac{1}{c}\sum_{i=1}^{r} c_i v_i^d$$

The average, time-dependent velocity $v*(t)$ depends on the boundary conditions only[16] and in the closed system equals zero.[19] Consequently, the Darken drift velocity in the multicomponent one-dimensional mixture is given by:

$$v^D = -\frac{1}{c}\sum_{i=1}^{r} c_i v_i^d \qquad \text{(Eq 16)}$$

Equation 16 states that drift velocity compensates the non-balanced diffusional fluxes.

In this work, the authors generalize the original Darken concept to include the different molar volumes (Vegard law) and the deformation of an alloy. To include an effect of different molar volumes of the components, $\Omega_i^V$, it was already postulated that the Vegard law ($\Omega^V = \sum_{i=1}^{r} N_i \Omega_i^V$) is the equation of state for the nondeformed crystal (at $10^5$ Pa), as seen in Eq 7. The Vegard law implies the more general form of the Darken drift velocity:

$$v^D = -\left(\sum_{i=1}^{r} N_i \Omega_i^V v_i^d\right) \Bigg/ \left(\sum_{i=1}^{r} N_i \Omega_i^V\right) \qquad \text{(Eq 17)}$$

The diffusion velocity in Eq 17 is given by Eq 6. Thus, it depends on the stress, or more generally on the mechano-chemical potential gradient. The drift velocity, seen in Eq

15, can be computed from the momentum conservation formula.

### 2.2 The Mechanochemical Transport Problem in the Multicomponent Solution

For all of the processes that obey the mass conservation law and when the chemical and/or nuclear reactions are not allowed (the reaction term can be omitted), the equation of mass conservation holds for every component as well as their mixture (Eq 1).

**2.2.1 Stress and Strain Relations.** The general form of the equation of motion for an elastic solid is very complex. We will use the results that come out for an isotropic material. In such a case, the equation of motion is the vector equation $\mathbf{f} = (\lambda + \mu)$graddiv$\mathbf{u} + \mu$divgrad$\mathbf{u}$, where $\mathbf{f}$ is the density of the force induced by the displacement vector $\mathbf{u}$. It shows that isotropic material (regular crystal) is completely described by the two elastic constants. To get the equation of motion, one can set $\mathbf{f} = \rho(\partial^2\mathbf{u})/\partial t^2$, and by ignoring any body forces, like gravity, one gets:[20]

$$\rho\frac{\partial^2\mathbf{u}}{\partial t^2} = (\lambda + \mu)\text{graddiv}\mathbf{u} + \mu\text{divgrad}\mathbf{u}. \qquad \text{(Eq 18)}$$

An elastic body is defined as a material for which the stress tensor is an exclusive function of a deformation tensor $\mathbf{F}$,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}(\mathbf{F}) \qquad \text{(Eq 19)}$$

In this work, it is assumed that the displacements are small. In such a case, the displacement gradient $\mathbf{H}$ is defined as the gradient of the displacement vector ($\mathbf{u} = \mathbf{x} - \mathbf{X}$):

$$\mathbf{H} = \text{grad}\mathbf{u} = \mathbf{F} - \mathbf{1} \qquad \text{(Eq 20)}$$

and the strain tensor is the symmetric part of $\mathbf{H}$:

$$\varepsilon = \frac{1}{2}(\mathbf{H} + \mathbf{H}^\mathrm{T}) \qquad \text{(Eq 21)}$$

where

$$\varepsilon_{kl} = \varepsilon_{lk} = \frac{1}{2}(u_{k,l} + u_{l,k}) \qquad \text{(Eq 21A)}$$

The constitutive equation of an isotropic, linear, and elastic body is known as Hooke's law:[21]

$$\boldsymbol{\sigma} = (\lambda\mathbf{tr}\varepsilon)\mathbf{1} + 2\mu\varepsilon \qquad \text{(Eq 22)}$$

where $\lambda$ and $\mu$ denote the Lame coefficients:

$$\lambda = \frac{vE}{(1+v)(1-2v)} \quad \text{and} \quad \mu = \frac{E}{2(1+v)} \qquad \text{(Eq 23)}$$

where $E$, as shown previously, denotes the Young modulus and $v$ is the Poisson ratio.

The divergence of the stress tensor defined by the Eq 22 can be expressed:[21]

$$\text{div}\boldsymbol{\sigma} = (\lambda + \mu)\,\text{graddiv}\mathbf{u} + \mu\text{divgrad}\mathbf{u}. \qquad \text{(Eq 24)}$$

The local pressure is defined by:

$$p = -\frac{1}{3}\text{tr}\boldsymbol{\sigma} \qquad \text{(Eq 25)}$$

where $\sigma$ is the Cauchy stress tensor.

The Navier-Lamé equation describes the momentum balance in an isotropic solid:[22]

$$\rho\frac{D\upsilon}{Dt}\bigg|_\upsilon = \text{div}\sigma + \rho f_b \qquad \text{(Eq 26)}$$

where $\sigma$ and $f_b$ denote the overall Cauchy stress tensor (as in Eq 24) and body force, respectively.

**2.2.2 The Energy Conservation Law.** Finally, from the mass and momentum conservation equations one can derive the energy conservation law for an isotropic crystal:

$$\sum_{i=1}^{r}\rho_i\frac{D}{Dt}(Ts + \mu_i + \mu_i^m + V^{\text{ext}})\bigg|_\upsilon = \sigma{:}\text{Grad}\upsilon + \eta\text{Grad}\upsilon^{\text{drift}}{:}\text{Grad}\upsilon$$
$$+ \rho\upsilon\text{grad}V^{\text{ext}} - \text{div}\,J_q \quad \text{(Eq 27)}$$

When the external force fields do not depend on time $V^{\text{ext}} = V^{\text{ext}}(x)$, then it further reduces to:

$$\sum_{i=1}^{r}\rho_i\frac{D}{Dt}(Ts + \mu_i + \mu_i^m)\bigg|_\upsilon = \sigma{:}\text{Grad}\upsilon + \eta\text{Grad}\upsilon^{\text{drift}}{:}\text{Grad}\upsilon$$
$$- \text{div}\,J_q \qquad \text{(Eq 28)}$$

where the heat flux is given by appropriate formula. Equations 27 and 28 express the first law of thermodynamics.

### 2.3 Initial Boundary Value Problem of Stress and Interdiffusion

The derived laws of mass conservation (Eq 9), momentum (Eq 26), and energy (Eq 28) form the set of second-order partial-differential equations. In this work, the external forcing is not analyzed, and consequently they become:

$$\frac{D\rho_i}{Dt}\bigg|_\upsilon^{\text{drift}} = \text{div}(\rho_i B_i\text{grad}(\mu_i + \mu_i^m)) - \rho_i\text{div}\upsilon^{\text{drift}} \quad i = 1,\ldots,r$$

$$\rho\frac{D\upsilon}{Dt}\bigg|_\upsilon = \text{div}\sigma$$

$$\sum_{i=1}^{r}\rho_i\frac{D}{Dt}(Ts + \mu_i + \mu_i^m)\bigg|_\upsilon = \sigma{:}\text{Grad}\upsilon + \eta\text{Grad}\upsilon^{\text{drift}}{:}\text{Grad}\upsilon$$
$$- \text{div}\,J_q$$

where:

$$\text{Div}\sigma = (\lambda + \lambda')\text{grad div}\upsilon^{\text{drift}} + \lambda'\text{Div grad}\upsilon^{\text{drift}}$$

$$\mu_i^m = \frac{\Omega_i^V \Omega}{\displaystyle\sum_{i=1}^{r} N_i \Omega_i^V} p$$

$$\upsilon^d = \upsilon - \upsilon^D - \upsilon^\sigma = \upsilon - \upsilon^{\text{drift}}$$

$$p = -\frac{1}{3}\text{tr}\sigma \quad \text{and} \quad \upsilon^D = -\left(\sum_{i=1}^{r} N_i \Omega_i \upsilon_i^d\right)\bigg/\left(\sum_{i=1}^{r} N_i \Omega_i\right).$$

The chemical potential is a known function of the composition and the temperature, and is computed using the Calphad method. The initial conditions are given by the known initial distribution of components and the zero initial momentum of the system:

$$\rho_i(0, x) = \rho_i^0(x) \quad \text{for} \quad i = 1, 2, \ldots, r \tag{Eq 29}$$

$$\sum_{i=1}^{r} \rho_i(0, x)\upsilon^{\text{drift}}(0) + \sum_{i=1}^{r} \rho_i(0, x)\upsilon_i^d(0, x) = 0 \tag{Eq 30}$$

**2.3.1 The Boundary Conditions.** Through the left boundary, $-\Lambda(t)$, and the right boundary, $\Lambda(t)$, there is no mass flow during the experiment $t^*$, and external pressure is constant:

$$J_{i,\text{L}}(t), J_{i,\text{R}}(t) = 0 \quad \text{for} \quad t \in [0, t^k], \quad i = 1, 2, \ldots, r \tag{Eq 31}$$

$$p_{\text{L}}(t), p_R(t) = \text{const.} \quad \text{for} \quad t \in (0, t^k) \tag{Eq 32}$$

### 2.4 Nondimensionalization

For the purpose of numerical treatment, further analysis is carried out in terms of nondimensional variables and equations. The proper dimensionless formulation allows the separation of terms (e.g., the mass diffusion from the longitudinal waves in the crystal in nonequilibrium). One can introduce the following nondimensional symbols:

1) Dimensionless length:

$$x' = \frac{x}{L} \tag{Eq 33}$$

where $L$ denotes the characteristic diffusion distance (e.g., the jump length of the diffusing atoms).

2) Dimensionless velocity:

$$\upsilon' = \frac{\upsilon}{\upsilon^*} \tag{Eq 34}$$

where $\upsilon^*$ is a characteristic velocity. When the diffusion of mass is considered, it is equal to self-velocity $\upsilon^* = \text{D}^*/L$.

3) Dimensionless time:

$$t' = \frac{\text{D}^*}{L^2}t = \frac{\upsilon^*}{L}t = f t \tag{Eq 35}$$

where $\text{D}^*$ and $\upsilon^*$ denote the self-diffusion coefficient, and self-velocity, $f$, is the frequency of the effective jumps of the diffusing atoms. In a multicomponent system, the average diffusivity might be considered.

4) Dimensionless concentration:

$$c_i' = \frac{c_i - \langle c_i \rangle}{\langle c_i \rangle} \tag{Eq 36}$$

where $\langle c_i \rangle$ denotes the average concentration in the mixture.

5) Dimensionless flux:

$$J_i' = \frac{1}{\upsilon^*\langle c_i \rangle}J_i \quad \text{or} \quad J_i' = \frac{1}{\langle \upsilon_i^* \rangle\langle c_i \rangle}J_i \tag{Eq 37}$$

## 3. Results and Discussion

There exists a solution of the above model. At present the authors solve this problem numerically using the finite differential method in one dimension. In this work, studies of diffusion couples are based on the Cu-Fe-Ni system at 1273 K. The Cu-Fe-Ni system was chosen because it is a single phase over a wide range of compositions and because its thermodynamic properties are fairly well known. Moreover, it is the only ternary alloy in which the tracer diffusivities are measured.[23] Thus, it offers a unique opportunity to test

**Table 1  Tracer diffusivities and Young modulus at 1273 K for Fe-Ni and Ni-Cu alloys**

| Alloy composition, wt.% | | | Tracer diffusion coefficients, m² · s⁻¹ | | | |
|---|---|---|---|---|---|---|
| Cu | Fe | Ni | $D_{\text{Cu}}$ | $D_{\text{Fe}}$ | $D_{\text{Ni}}$ | Young modulus, GPa |
| … | 80.3 | 19.7 | $7.52 \times 10^{-15}$ | $4.95 \times 10^{-16}$ | $2.33 \times 10^{-16}$ | 115 |
| … | 50.4 | 49.6 | $2.52 \times 10^{-15}$ | $3.08 \times 10^{-16}$ | $3.25 \times 10^{-16}$ | 120 |
| … | 99 | 1 | $1.92 \times 10^{-15}$ | $6.71 \times 10^{-16}$ | $3.24 \times 10^{-16}$ | 120 |
| 67 | … | 33 | $1.08 \times 10^{-15}$ | $4.23 \times 10^{-16}$ | $4.15 \times 10^{-16}$ | 70 |
| 41.9 | … | 58.1 | $1.92 \times 10^{-15}$ | $6.71 \times 10^{-16}$ | $3.24 \times 10^{-16}$ | 100 |
| 52 | … | 48 | $4.19 \times 10^{-14}$ | $1.26 \times 10^{-14}$ | $3.74 \times 10^{-15}$ | 90 |
| 86 | … | 14 | $1.92 \times 10^{-15}$ | $6.71 \times 10^{-16}$ | $3.24 \times 10^{-16}$ | 60 |
| … | 24.1 | 75.9 | $1.92 \times 10^{-15}$ | $6.71 \times 10^{-16}$ | $3.24 \times 10^{-16}$ | 117 |
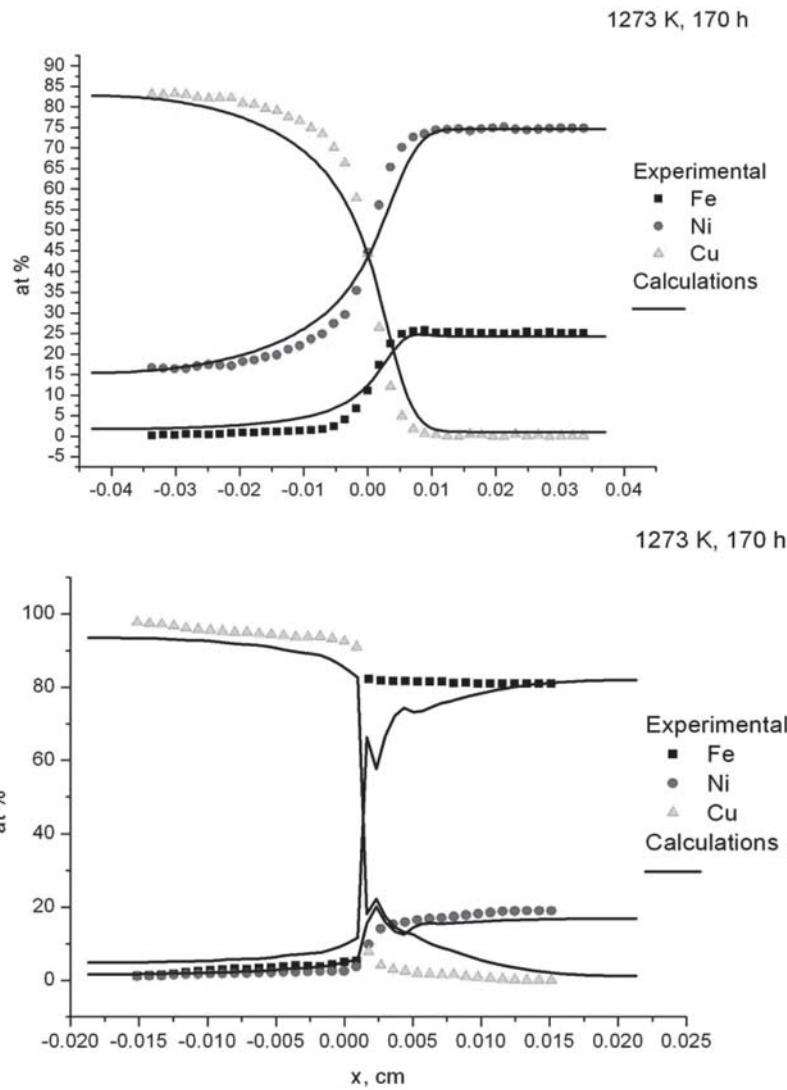
**Fig. 1** The experimental versus computed concentrations of components in the Fe-Ni-Cu couple, using the Darken method for multi-component solid solutions[16]

**Table 2   Initial compositions, the annealing time, and the average Young modulus of the diffusional couples used for simulations**

| Diffusion couple, wt.% | Average Young modulus, GPa | Time, h | Thickness of the diffusional couple, mm |
|---|---|---|---|
| 86Cu-14Ni\|24.1Fe-75.9Ni | 88.5 | 170 | 2 ± 0.1 |
| 24.1Fe-75.9Ni\|Cu | 77.5 | 170 | 2 ± 0.1 |

a complex method such as the combination of the Calphad and mechanical potential methods. The solid solutions in this system are not ideal, and consequently the diffusivities depend on composition.[23] The driving force for the diffusion in such a ternary system is the gradient of the mechanochemical potential, which can be calculated from the concentration profiles and using the known thermodynamic data of the system.

To calculate the concentration profiles in the Cu-Fe-Ni system, one has to specify the necessary input parameters: the activities of Fe, Ni, and Cu were calculated using the CALPHAD method and commercially available math software (Mathematica 5.1, Wolfram Research Inc., Champaign, IL); the atomic masses and partial molar volumes of components at $10^5$ Pa (Vegard), Young modulus and Poisson ratio.

The intrinsic diffusivities were computed as a function of the concentration of the components,[23] $D_i(c_1,c_2)$. Table 1 shows tracer diffusion coefficients for some selected compositions of the alloys. The initial compositions, the thicknesses of the diffusion couples, and their annealing time are shown in Tables 1 and 2. The density of Fe-Ni-Cu alloys was calculated, and consequently the partial molar volumes of components, $\Omega_i$, at 1273 K, $\Omega_i = M_i/\rho_i^T(alloy)$, where $M_i$ is the atomic mass. The densities of alloys at $T = 1273$ K were estimated using the following expression:[24]

$$\rho_T = \rho_{T_m} - k(T - T_m) \qquad \text{(Eq 38)}$$

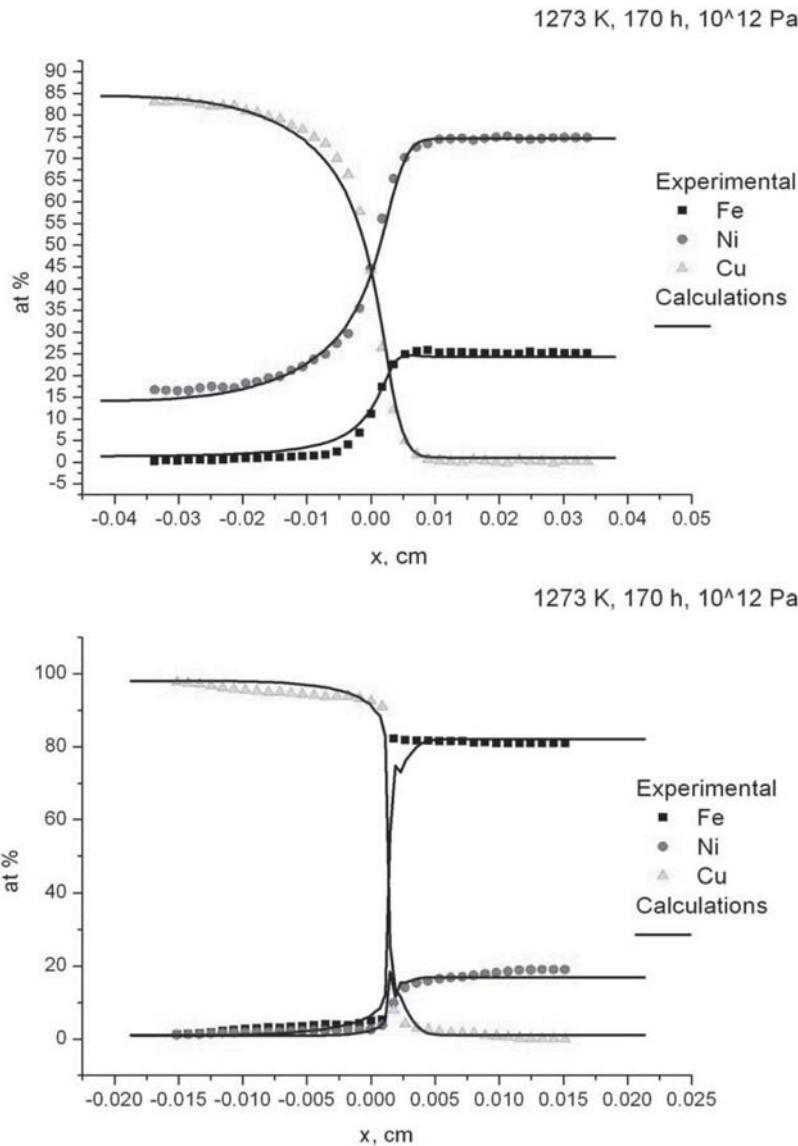1273 K, 170 h, 10^12 Pa



1273 K, 170 h, 10^12 Pa



**Fig. 2** The experimental versus computed concentrations of components in the Fe-Ni-Cu couple in this work (using the Darken method for multicomponent solid solutions with stress effect included)

where $T_m$ is the alloy melting point, $\rho_{T_m}$ is its density at melting point, $k$ (the coefficient of thermal expansion). Using data from the study by Lide[24] and Eq 38, the partial molar volumes of the components for Cu-Fe-Ni at $T = 1273$ K have been calculated: $\Omega_{Cu} = 7.92$ (cm$^3$ mol$^{-1}$); $\Omega_{Fe} = 7.66$ (cm$^3$ mol$^{-1}$]; and $\Omega_{Ni} = 7.21$ (cm$^3$ mol$^{-1}$). The alloy molar volume at $10^5$ Pa follows from Vegard's law.

There are no experimental or theoretical predictions of the Young modulus for Fe-Ni-Cu alloys at high temperatures. In this work, the Young modulus was estimated on the base of data for pure elements, and the Fe-Ni and Ni-Cu systems.[24-27] Thus, based on the temperature dependence of the Young modulus of Fe,[26] Fe-Ni,[25,27] Ni-Cu,[25] and Ni-based superalloys[28] the values of the Young modulus for Fe-Ni and Ni-Cu alloys at 1273 K were estimated (Table 1).

The Poisson ratio was estimated based on values for Fe-based alloys[29,30]: $v = 0.29$.

In Fig. 1, the Darken method was compared with the experimental data (without stress). The calculated concentration profiles of Cu, Fe, and Ni are compared with the experimental results, and show marked disagreement.

Figure 2 shows the comparison of the Darken method combined with the stress effect (this work) with the experimental data. The calculated concentration profiles of Cu, Fe, and Ni show good agreement with the experimental results.

Figures 1 and 2 show the measured and computed evolution of the concentrations. Comparison with experimental data shows that the formulated method of the quantitative description of the stresses in solids is self-consistent. They demonstrate that the presented mathematical description of

ID and stress is the effective tool for simulating such processes.

## 4. Summary

A mathematical description of ID in multicomponent systems was formulated. For the known thermodynamic data, the intrinsic diffusivities and the certain average mechanochemical properties of the alloy, the evolution of the concentration profiles, the pressure, and the drift velocity can be predicted.

The model was applied for the modeling of the ID in the Fe-Ni-Cu diffusion couples. The calculated concentration profiles were consistent with the experimental results.

The examples presented in this work show the potential of the model in describing ID in a wide range of diffusion-limited processes. An effective application of the model involves knowledge of the thermodynamics of the system and of the mechanical and kinetic data. The kinetic data—self diffusivities—can be obtained using, for instance, the radiotracer technique,[31] the inverse method, or computation when the mechanism of diffusion is known. Significant progress has been observed in the software. Programs like Thermo-Calc (Thermo-Calc Software, Stockholm, Sweden), FactSage (ESM Software, Inc, Hamilton, OH), or the CALPHAD database can be used as an effective tool in obtaining thermodynamic activities.

The Nernst-Planck flux formula was adapted to model the mechanochemical transport processes. The results show the prospect of the extension of DMMSs in future applications: electromigration; diffusion in electrolytes; biology; and nanoscale modeling.

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