

## CADiff – THE INTER AND REACTIVE DIFFUSION SIMULATION TOOL

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### Abstract

The CADiff software is presented in the paper. The method based on the extended Darken and Wagner models, allows to simulate the inter and reactive diffusion processes. The diffusion fluxes are defined in the volume fixed reference frame. The Darken method is extended to include the non ideal alloys showing different partial molar volumes and boundary conditions taking into account both the diffusion and the surface reactions.

The CADiff simulation tool allow to compute a wide range of interdiffusion processes starting from the Fick constitutive diffusion flux formula to the combined Darken-Onsager approach. They allow to model pure interdiffusion in multi-component systems as well as a wide class of the reaction-diffusion problems associated with solid state chemistry, corrosion, surface treatment etc.

**Key words:** diffusion, interdiffusion, reactive diffusion, oxidation, selective oxidation, Wagner method, chemical interdiffusion

## 1. INTRODUCTION

The quantitative simulation tools of the coupled diffusion processes and material behavior can be very useful in testing material stability and estimating required properties. The departures of the ideal solid structure are thermodynamically unavoidable and very often diffusion determines the overall reaction rate. The method to combine the fundamental formulae of the diffusive mass transport in solutions (interdiffusion) with kinetic processes (heterogeneous reaction) is presented in this paper. The Computer Aided Diffusion tool (CADiff) is a simulation software which allows to simulate the inter diffusion and reactive diffusion processes in multicomponent systems.

Both Onsager based (Murch and Belova, 2005; Manning, 1971) and Darken (1948) methods are commonly used to describe diffusion in solids and are self consistent with nonequilibrium thermodynamics. The Darken method published in 1948 launched entirely new understanding of the diffusion processes in solids, namely in binary systems. The method was based on the Nernst-Planck (Nernst, 1889; Planck, 1890) and Smigelskas and Kirkendall (1947) works. The key Darken postulate that the total mass flow is a sum of the diffusion and drift flows, was applied for the description of the diffusion in binary solid solution. The Darken method was extended by Holly and Danielewski (1994) to include the multicomponent alloys. The Danielewski-Holly method describes the process in the bounded mixture (i.e., in the diffusion couple of the finite

thickness) showing the constant total concentration and the variable diffusivities of the components. In this paper Darken method for multi-component alloys is further extended to include the Vegard law (1921) instead of the assumption of the constant molar volume of the system.

The reaction diffusion process in binary system was analyzed by Wagner (1952; 1956; 1956; 1959), who studied the conditions necessary for selective oxidation of the ideal Ni-Pt alloy. He derived an appropriate analytical expression and obtained the qualitative agreement between the experimental (Kubaschewski and von Goldbeck, 1949) and calculated values of the reaction rate. Wagner was the first to notice that the oxidized component enters the oxide phase as a result of the surface reaction and of the diffusion through alloy-oxide interface. The non-reacting elements diffuse into the interior of the alloy (Wagner, 1952).

Gesmundo et al. applied Wagner model and his analytical solution to model the oxidation of two-phase alloy (Gesmundo et al. 1993; 1997). Also Danielewski and Filipek et al. used the Wagner boundary condition for the binary alloy in the case of multicomponent alloy. Consequently, they have neglected the fluxes of non-reacting components (Danielewski, Filipek et al. 2000; 2001).

**2. INTERDIFFUSION IN MULTICOMPONENT SOLID SOLUTIONS**

The CADiff software is based on the mass conservation law:

$$\frac{\partial c_i}{\partial t} = - \operatorname{div}(J_i^d) - \operatorname{div}(J_i^D) \quad i=1, \dots, r$$

$$\left[ \begin{array}{c} \text{evolution} \\ \text{of} \\ \text{concentration} \end{array} \right] = - \left[ \begin{array}{c} \text{diffusional} \\ \text{flux} \end{array} \right] - \left[ \begin{array}{c} \text{Darken} \\ \text{flux} \end{array} \right]$$

(1)

where:  $c_i = c_i(t, x)$  denotes the concentration of the  $i$ -th component,  $J_i^d = J_i^d(t, x)$  and  $J_i^D = J_i^D(t, x)$  denote the diffusion and darken flux of  $i$ -th component, respectively. The overall flux is defined as a sum of the diffusion and Darken fluxes,  $J_i = J_i^d + J_i^D$ . Depending on the availability of the data and required accuracy, CADiff allows selecting the constitutive equations for the overall flux. The main engine of the CADiff uses the Darken-Onsager flux formula:

$$J_i = \sum_{j=1}^r L_{ij} X_j + J_i^D, \quad i=1, \dots, r \quad (2)$$

where:  $L_{ij}$  – phenomenological transport coefficients,  $X_j$  – the force acting on the diffusing component. The Onsager constitutive equations are based on the definition of the phenomenological transport coefficients (Murch and Belova, 2005):

$$L_{ii} = c_i B_i \frac{\left( \sum_{k=1, k \neq i}^r N_k B_k \right)}{\sum_{k=1}^r N_k B_k}, \quad i=j, \quad i=1, \dots, r,$$

(3)

$$L_{ij} = -c_i B_i \frac{N_j B_j}{\sum_{k=1}^r N_k B_k}, \quad i \neq j, \quad i, j=1, \dots, r,$$

(4)

where:  $N_i, B_i$  – molar ratio and mobility of  $i$ -th component, respectively.

One can show that the transport coefficients in equation (4) are symmetrical (Onsager, 1931), i.e.,  $L_{ij} = L_{ji}, \quad i \neq j$ .

The forces in equation (2),  $X_j$ , are defined as chemical potential gradients only:

$$X_j = -\operatorname{grad} \mu_j^{ch} \quad (5)$$

In CADiff, the thermodynamic and kinetic data can be introduced by the user as analytical functions or assuming ideality sweeping statement ( $a_i=c_i$ ).

**3. DIFFUSION FLUX IN MULTICOMPONENT SYSTEMS**

The Darken flux,  $J_i^D$ , is generated during interdiffusion due to locally unbalanced diffusion fluxes. It is computed relatively to the volume fixed reference frame (Danielewski and Wierzba; Wierzba and Danielewski, 2007):

$$J_i^D = c_i v^D = -c_i \sum_{j=1}^r \frac{c_j \Omega_j}{c \Omega} v_j^d \quad (6)$$

where:  $v^D = v^D(t, x)$  – Darken velocity that is common for every component,  $v_i^d = v_i^d(t, x)$  – the diffusion velocity of the  $i$ -th component,



$c = c(t, x) = \sum_{i=1}^r c_i(t, x)$  - the overall molar concentration in the alloy,  $\Omega_i$  - the partial constant molar volume of the  $i$ -th component. The overall volume of the alloy,  $\Omega = \Omega(t, x)$ , is defined using the Vegard law (Vegard, 1921):

$$\sum_{i=1}^r \frac{\Omega_i}{\Omega} N_i = \sum_{i=1}^r \frac{\Omega_i c_i}{\Omega c} = \sum_{i=1}^r \Omega_i c_i = 1 \quad (7)$$

CADiff software enables to simulate the diffusion process using different constitutive equations for the flux. When different partial molar volumes are considered,  $\Omega_i \neq \Omega_j$ ,  $i \neq j$ , the diffusion fluxes are than defined in the volume fixed reference frame. Consequently the diffusion fluxes are multiplied by the correction factor,  $f_i = \Omega_i/\Omega$  (Danielewski and Wierzba 2007). The following constitutive equations are allowed in CADiff:

1) The Darken-Onsager flux:

$$J_i = f_i \sum_{j=1}^n L_{ij} X_j + J_i^D, \quad i = 1, \dots, r \quad (8)$$

2) The Onsager flux:

$$J_i = f_i \sum_{j=1}^r L_{ij} X_j, \quad i = 1, \dots, r \quad (9)$$

3) The Darken-Nernst-Planck flux:

$$J_i = f_i c_i B_i X_i + J_i^D, \quad i = 1, \dots, r. \quad (10)$$

4) The Nernst-Planck diffusion flux (Nernst, 1889; Planck, 1890):

$$J_i = c_i B_i X_i, \quad i = 1, \dots, r \quad (11)$$

5) The Fick-Darken flux:

$$J_i = -D_i \text{grad } c_i + J_i^D, \quad i = 1, \dots, r \quad (12)$$

6) The Fick flux, equation (12), without Darken velocity and with assumption that molar volumes are equal to each other, becomes 1<sup>st</sup> Fick law:

$$J_i = -D_i \text{grad } c_i, \quad i = 1, \dots, r \quad (13)$$

Equation (10) follows from Eq. (8) when:  $L_{ij} = 0$ , when  $i \neq j$  and  $L_{ii} \approx c_i B_i$ ,  $i = 1, \dots, r$ .

Equation (12) can be derived from Eq. (10). By assuming i) the ideality sweeping statement ( $a_i = c_i$ ) and ii) the equal partial molar volumes of components:

$X_i = -\text{grad}(\mu_i^0 + RT \ln c_i) = -RT \text{grad} c_i$ , where:

$\mu_i^0$  is standard chemical potential,  $R$  and  $T$  denote the gas constant and temperature.

#### 4. BOUNDARY CONDITIONS

The CADiff software enables to simulate the diffusion process in both open and closed systems. The user can use different boundary conditions:

1) In closed system all fluxes at all boundaries are equal zero,

$$J_i(t, 0) = J_i(t, \lambda_R) = 0, \quad i = 1, \dots, r \quad (14)$$

2) The boundary condition in the case of reactive diffusion processes (system exchanging mass with surrounding) states that the flux of the arbitrary element through interface is equal to its diffusion flux in alloy at interface, e.g., for the right boundary it is:

$$J_i^d(t, \lambda_R(t)) = J_i(t, \lambda_R(t)), \quad (15)$$

where: flux through interface,  $J_i(t, \lambda_R(t))$ , is a known or computed function of time,  $\lambda_R(t)$  denote the position of the right boundary.

In this work we assumed that the boundary flux is a result of chemical reaction  $J_i[t, \lambda_R(t)] = J_i^{ch}(t)$  (Wagner, 1952). The reaction flux can be introduced by:

1) The analytical, known function to simulate the arbitrary process. The user has a possibility to introduce different fluxes for every component.

2) In the case of oxidation the fluxes can be introduced based on the Wagner method (1952).

Wagner was first to notice that the oxidized component enters the oxide phase as a result of the surface reaction and of the diffusion through alloy-oxide interface. The non-reacting element diffuse into the interior of the multi-component alloy (Wagner, 1952).

The flux of A (oxidized component) through the alloy-oxide interface (due to the diffusion from the alloy) is given by (Danielewski and Wierzba, 2008):

$$J_A(t, \lambda_R(t)) = (c_A(t, \lambda_R(t)) - c(t, \lambda_R(t))) \frac{d\lambda_R}{dt} \quad (16)$$

In a case of multi-component alloy it is necessary to compute inward fluxes of the all non-reacting components. These fluxes result from the consumption of oxidized component of the alloy,  $d\lambda_R/dt$



(Danielewski and Wierzba, 2008):

$$J_i(t, \lambda_R(t)) = c_i(t, \lambda_R(t)) \frac{d\lambda_R}{dt} \quad \text{for } i = 1, 2, \dots, r-1 \quad (17)$$

The Wagner method allows to compute the flux of A-component (oxidized) in the oxide as a function of the instantaneous rate constant (chemical potential of A at the interface) (Danielewski and Wierzba, 2007):

$$J_A^{ch}(t) = c_A^{ox} \frac{k(t)}{X(t)} = \frac{c_A^{ox} k(t)}{\sqrt{2 \int_0^t k(\tau) d\tau}}, \quad (18)$$

where:  $c_A^{ox}$  – the oxidized component concentration in the oxide,  $k(t)$  – instantaneous rate constant,  $X(t)$  – thickness of the product layer.

The thickness of the oxide can be defined as:

$$X(t)^2 = 2 \int_0^t k(\tau) d\tau. \quad (19)$$

The interdiffusion in the alloy and the reactive diffusion in the oxide are coupled by the flux of reacting component through the interface. The total flux of reacting component A, through the alloy-oxide interface is a result of reaction (alloy consumption). One can derive the equation describing the flux of oxidized component through the interface (Danielewski and Wierzba, 2008):

$$J_A[t, \lambda_R(t)] = \{1 - N_A[t, \lambda_R(t)]\} \frac{c_A^{ox} k(t)}{\sqrt{2 \int_0^t k(\tau) d\tau}}$$

$$k(t) = \frac{1}{RT} \int_{\mu_A''}^{\mu_A'(t, \lambda_R)} D_A^{ox} d\mu_A^{ox} \quad (20)$$

where:  $\mu_A'$ ,  $\mu_A''$  – the chemical potentials of A in the oxide at the alloy-oxide interface and at the oxide-gas interface, respectively,  $D_A^{ox}$  – self-diffusion coefficient of oxidized component,  $\mu_A^{ox}$  – the chemical potential of oxidized component.

The overall boundary fluxes of non reacting components, which are diffusing into the interior of the multi-component alloy, can be defined as (Danielewski and Wierzba, 2008):

$$J_i[t, \lambda_R(t)] = -N_i[t, \lambda_R(t)] \frac{c_A^{ox} k(t)}{\sqrt{2 \int_0^t k(\tau) d\tau}} \quad \text{for } i = 1, 2, \dots, r-1. \quad (21)$$

Equations (20) and (21) are the boundary conditions in the case of interdiffusion in multi-component alloy due to selective oxidation of A component.

## 5. THE REACTION OF AN IDEAL ALLOY

In such a case:  $\mu_i(\text{alloy}) = \mu_i^0 + RT \ln c_i$  and the local equilibrium at  $\lambda_R(t)$  implies  $\mu_A'(\text{oxide})(t) = \mu_A^0 + RT \ln c_A[t, \lambda(t)]$ . Thus, instantaneous rate constant becomes:

$$k(t) = \int_{c_A''}^{c_A'(t)} D_A^{ox} d \ln c_A = \int_{N_A''}^{N_A'(t)} D_A^{ox} d \ln N_A \quad (22)$$

where:  $N_A'(t) = N_A[t, \lambda_R(t)]$  – the molar ratio of A in the alloy at the alloy-oxide interface. Following the Wagner, the local equilibrium within the oxide implies (Wagner, 1952):

$$[N_A'(t)]^{4/z} p_{O_2}'(t) = p_{O_2}^{(e)} \quad (23)$$

where:  $p_{O_2}'(t)$  and  $p_{O_2}^{(e)}$  – the oxygen partial pressures at the alloy-oxide and (pure metal A)-oxide interface, respectively;  $z$  is the valence of A in oxide. Combining Eqs. (22) and (23):

$$k(t) = \frac{z}{4} \int_{p_{O_2}(t)}^{p_{O_2}''} D_A^{ox} d \ln p_{O_2} \quad (24)$$

where  $p_{O_2}'(t) = p_{O_2}(\text{alloy}|\text{oxide})$  and  $p_{O_2}'' = p_{O_2}(\text{oxide}|O_2)$  are oxygen pressures at interfaces.

## 6. INITIAL CONDITIONS

The initial distributions of the components can be introduced as a step function (Heaviside function) or any profiles given by the set of points. Thus, one can analyze processes in gradient materials, multi-layers, multiples materials and many others.



$$c_i(0, x) = c_i^0(x) \text{ for } i = 1, 2, \dots, r \quad (25)$$

Initial position of the right boundary of the mixture,  $\lambda_R(0) = \lambda_R^0$  (the thickness of the alloy) and the initial thickness of the product layer,  $X(0) = X^0$ .

## 7. RESULTS

In this section the comparison of oxidation in Ni-Pt alloy between the Wagner analytical solution, experimental data and our method is shown. The reaction rate is calculated from equation (24):

$$k(t) = 3D_A^{ox(0)} \cdot \left( (p_{O_2}''')^{1/6} - \left( p_{O_2}^{(e)} / [N_A(t, \lambda(t))]^2 \right)^{1/6} \right) \quad (26)$$

where:  $D_A^{ox(0)}$  – self-diffusion coefficient of A in oxide at standard conditions, at  $p_{O_2} = 1 [atm]$ . The Ni self diffusion coefficient in NiO is given by  $D_A^{ox} = D_A^{ox(0)} p_{O_2}^{1/6}$ .

Wagner assumed that Ni-Pt is an ideal solid-solution and that intrinsic diffusivities of Ni and Pt are equal and constant. Consequently:  $\tilde{D} = D_{Pt} = D_{Ni}$  (Wagner, 1952).

The following data were used for computation (Wagner, 1952):

- temperature:  $T = 1123 [K]$ ;
- self-diffusion coefficient of Ni in NiO at standard conditions:  $D_{Ni}^{ox(0)} = 1.8 \cdot 10^{-12} \left[ \frac{cm^2}{s} \right]$ ;
- the intrinsic diffusivities of Ni and Pt:  $\tilde{D} = D_{Pt} = D_{Ni} = 3.1 \cdot 10^{-12} \left[ \frac{cm^2}{s} \right]$ ;
- the oxidized component concentration in the oxide:  $c_A^{ox} = 8.97 \cdot 10^{-2} \left[ \frac{mol}{cm^3} \right]$ ;
- the oxygen partial pressure at the alloy-oxide interface:  $p_{O_2}^{(e)} = 9.1 \cdot 10^{-14} [atm]$ ;
- the oxygen partial pressure at the oxide-gas interface:  $p_{O_2}'' = 0.21 [atm]$ ;

Figure 1 shows the oxidation rate constant,  $k_c$ , of Ni-Pt alloy as a function of initial Ni composition (i.e. Ni molar ratio,  $N_{Ni}^0 = c_{Ni}^0/c$ ). The rate constant in a case of Wagner model is given by his analytical

solution, Eq. (11) in (Wagner, 1952). To compare the experimental results (NiO thickness after 100 hours of oxidation (Kubaschewski and von Goldbeck; 1949)) and the CADiff simulations, the reaction rate is computed from the scale thickness,  $X(t^*)$ , after the actual reaction time ( $t^*$ ), i.e.,  $k_c = X(t^*)^2/2t^*$ .

The experimental results are by Kubaschewski and von Goldbeck (1949). They produced alloys from carbonyl nickel powder and pure platinum. The compressed powder mixtures were melted in Tamman furnace in vacuum, and the alloys were cooled slowly, rolled, and cut into small plates (12x6x0.5 mm), which were finally polished. In each experiment samples were oxidized in the alumina boats. Formation of nickel nitride was not observed. The samples were removed from the furnace after various periods of time and a micro-balance was used for non-continuous weighing, to the accuracy of  $\pm 0,002mg$ . After weighing, the alumina boats with the samples were returned to furnace and the weight increase was determined in several stages up a total 100h of the oxidation time.

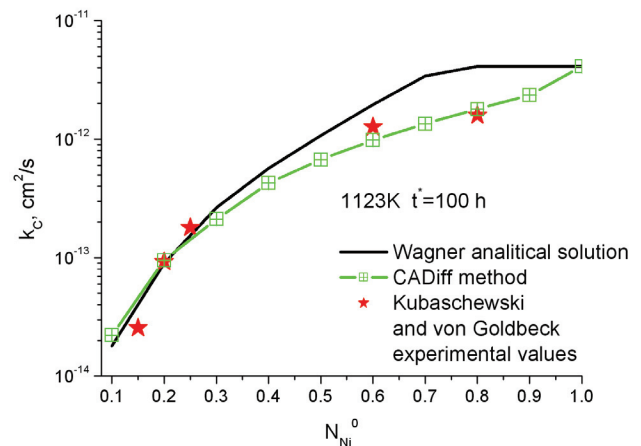


Fig. 1. Initial composition dependence (i.e. Ni molar ratio,  $N_{Ni}^0 = c_{Ni}^0/c$ ) of the oxidation rate,  $k_c$ , of Ni-Pt alloys at 1123 K. The dots show experimental data by Kubaschewski and von Goldbeck (1949); whereas the solid lines show the values calculated using the CADiff and the Wagner analytical solution, Eq. (11) in (Wagner, 1952).

Figure 1 shows that the CADiff software gives better approximation of the experimental data than the Wagner quasi-stationary solution.

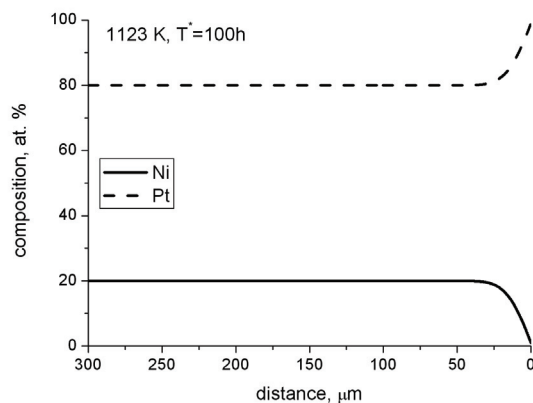
Wagner in his work calculated the oxidation rate for the quasi-stationary reaction period. He assumed the instantaneous, constant alloy composition (i.e. Ni molar ratio,  $N_{Ni} = c_{Ni}/c$ ) at the alloy-oxide interface. Consequently, the concentration of reacting metal in alloy at the alloy-oxide interface does not



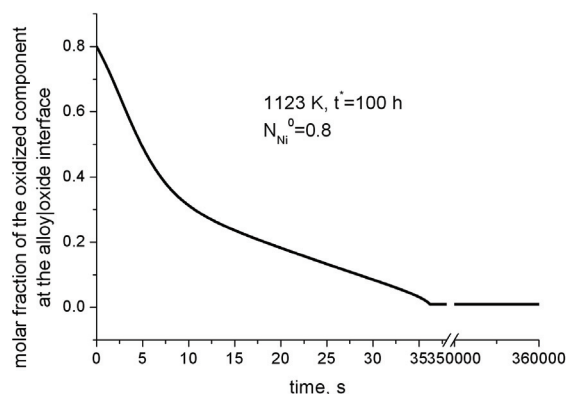


depend on time and is reached instantaneously (during the infinitesimally short period of time). Contrary, the CADiff allows to compute time dependent surface composition of the reacting alloy, see Fig. 2.

a)



and software (CADiff) can be further extended to model the more complex processes, e.g. the influence of the pressure on the diffusion (Danielewski and Wierzba; Wierzba and Danielewski, 2007).



b)

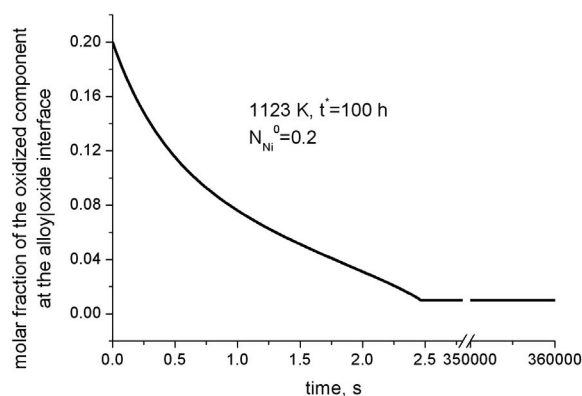
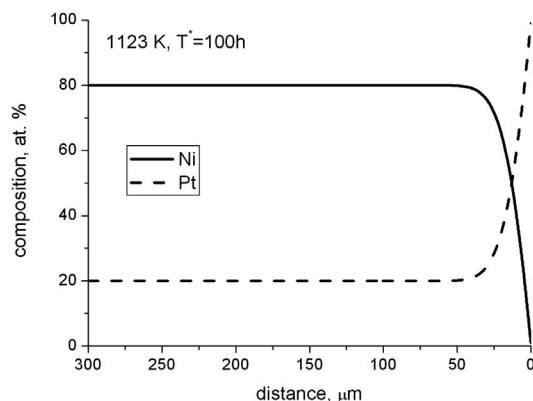


Fig. 2. The time dependence of the surface composition of the reacting Ni-Pt alloy and concentration profile; for a) 20Ni-Pt and b) 80Ni-Pt initial composition at 1123 K after 100 h.

## 8. CONCLUSIONS

The CADiff can be used for modelling both the inter and reaction diffusion processes in non-ideal systems. The method can be applied to predict 1) the time dependence of the reacting metal concentration at the alloy-oxide interface, 2) the instantaneous and the effective rate constants and 3) the life time of the material, i.e., the critical consumption of the reacting element. We defined the volume fixed frame of reference. In this unique frame all diffusion fluxes are expressed by the combined Onsager-Darken approach. The resulting system of physical laws, initial and boundary conditions (i.e., the initial boundary-value problem) allows using the Darken method in a case of non-ideal systems. One-dimensional geometry was considered as the first approach. The model

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## CADIFF – NARZĘDZIE DO SYMULACJI DYFUZJI WZAJEMNEJ I REAKCYJNEJ

### Streszczenie

W artykule zaprezentowana została metoda (model) oraz oprogramowanie CADiff. Metoda ta opiera się na uogólnionej metodzie Darkena dla układów wieloskładnikowych oraz modelu Wagnera. Pozwala ona na symulowanie zjawisk dyfuzji wzajemnej i reakcyjnej. Strumienie dyfuzyjne zdefiniowane zostały w objętościowym układzie odniesienia. Metoda Darkena rozwinięta została do symulowania zjawiska dyfuzji w układach otwartych uwzględniając różne objętości molowe składników.

Metoda oraz oprogramowanie CADiff umożliwia symulowanie zjawiska dyfuzji wzajemnej z wykorzystaniem wielu matematycznych opisów, między innymi: prawa Ficka, metoda Onsagera, połączone metody Onsagera i Darkena oraz uogólnionej metody Darkena. Umożliwia ona na symulowanie zarówno samego zjawiska dyfuzji wzajemnej (w układach zamkniętych) jak również zjawisk dyfuzji wzajemnej połączonych z reakcjami na granic.

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