Interdiffusion Studies in Co-Fe-Ni Alloys

R. Filipek[1,a], M. Danielewski[1], R. Bachorczyk[1,2]

[1] AGH University of Science and Technology, al.Mickiewicza 30,
30-059 Krakow, Poland
[2] Joint Research Centre, Petten, the Netherlands
[a] rof@agh.edu.pl

Abstract. Interdiffusion in Co-Fe-Ni alloys was studied in 1373-1588 K temperature range. The Danielewski-Holly model was used for the description of the interdiffusion process in ternary Co-Fe-Ni diffusion couples both for the finite and infinite geometry. Using the inverse method the average intrinsic diffusivities of components in the Co-Fe-Ni system were calculated and compared with the results of the other authors. The activation energies of cobalt, iron and nickel intrinsic diffusion have been found in 1373-1588 K temperature range.

Introduction

The phenomenological description of interdiffusion proposed by Darken [1] is widely accepted for the binary systems. The Darken method was extended by Danielewski and Holly [2]. It describes the process in the bounded mixture (i.e., diffusion couple of finite thickness) showing constant concentration (e.g., in solid or liquid solutions) and for variable diffusivities of the elements. We derived an exact expression describing the evolution of components distributions [3] during interdiffusion in multi-component systems.

In this paper we will present: *i)* some aspects of the mathematical model of interdiffusion, *ii)* the inverse method which allows calculation the diffusion coefficients in the multi-component system, *iii)* results of interdiffusion studies in the Co-Fe-Ni system, iv) comparison of the results with the results of other authors.

Mathematical Model of Interdiffusion

The Danielewski-Holly model of interdiffusion is an initial boundary-value problem for partial differential equations, namely for the equations of mass conservation. The details of the model for multi-component systems have already been published [5,4]. For readers convenience a brief description of the model is presented below. The model describes diffusion in solid solutions.

Data: 1) intrinsic diffusivities of the components: $D_1,\ldots,D_r$, 2) time of the process duration: $\hat{t}$, 4) thickness of the system: 2Λ and average molar concentration of the system: c.

Physical laws: 1) the law of the mass conservation of an *i*-th component:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x} \qquad (i = 1,\ldots,r). \tag{1}$$

where the flux, J_i, is a sum of the diffusion flux $-D_i \dfrac{\partial c_i}{\partial x}$, and drift flux $c_i \upsilon$ [1], r denotes number of components in the system.

2) *Postulate of the constant mixture concentration*: $\sum_{i=1}^{r} c_i = c = const.$

Initial and boundary conditions: 1) the initial concentration profiles of the components in the system $c_i(0,x) = \overset{0}{c}_i(x)$, where $x \in [-\Lambda, \Lambda]$ 3) fluxes of the components through the boundary. Here $J_i(t,\pm\Lambda) = 0$. i.e,, the system is closed.

Unknowns: 1) the concentration profiles of all elements as a function of time $c_i(t,x)$ and 2) the drift velocity $\upsilon(t,x)$.

Mathematical Solution to the Model

In order to solve the formulated problem we define new variable $w_i(t,x)$ that has a physical interpretation and denotes a deviation of the *i*-th element mole fraction from its average in the alloy (from now on, the variable $w_i(t,x)$ is called "molar deviation"):

$$w_i(t,x) := N_i(t,x) - \bar{N}_i \tag{2}$$

where $\bar{N}_i$ is an average mol fraction of *i*-th element in the alloy. Using the new variable w_i, the interdiffusion problem can be transformed as follows [5]:

$$\frac{\partial w_i}{\partial t}(t,x) = \frac{\partial}{\partial x}\left[D_i \frac{\partial w_i}{\partial x}(t,x) - \left(w_i(t,x) + \bar{N}_i\right)\sum_{j=1}^{r} D_j \frac{\partial w_j}{\partial x}\right] \tag{3}$$

$$w_i(0,x) = \overset{o}{w}_i(x).$$

We will seek the weak solution [6] to the problem (3). It has two advantages: *i)* we can in the natural way set the initial conditions given by the steep functions (very common e.g. in multi-layers wafers and thin films); *ii)* the weak solution allows easy transition to the approximate solution and offers the numerical method for its solving. The detailed information on the solution of the interdiffusion problem Eq. (3) (Faedo-Galerkin's approximate solution) has been already published [3].

In the next section the method which allows determination of the average intrinsic diffusivities in multi-component systems is presented.

The inverse problem of interdiffusion. Let's define the symbol $w_i^{\hat{t}}$ – calculated molar deviation of *i*-th element for time $\hat{t}$ and diffusion coefficients $D_1, \ldots D_r$. Calculations can be performed using Danielewski-Holly model (solution to the problem (3)) for the following data: *1)* initial molar deviation distributions of elements $\left(\overset{o}{w}_1(x), \ldots, \overset{o}{w}_r(x)\right)$ in the alloy; *2)* time of process duration $\hat{t}$; 3) $\hat{w}_1, \ldots \hat{w}_r$ – known (experimental) molar deviation distributions of elements in the alloy after the time $\hat{t}$. Let's define error function, *err*, given by the formula:

$$err\left(D_1, \ldots, D_r\right) := \int_{-\Lambda}^{\Lambda} \sum_{i=1}^{r} \left(\hat{w}_i(x) - w_i^{\hat{t}}(x)\right)^2 \tag{4}$$

We are looking for such parameters $D_1, \ldots D_r$ which minimize error function (4). Determined numbers $D_1, \ldots D_r$ are approximate diffusion coefficients.

The calculation of the diffusion coefficients is a problem of minimization of the function *err* in *r*-dimensional space – Eq. (4), where *r*, as before, means the number of elements in the alloy. The evaluation of error function involves iterations in which we solve the interdiffusion problem (3) for any numbers $D_1, \ldots D_r$ inserted in the place of the diffusion coefficients. To obtain effective minimization procedure we have used: *i)* sequential quadratic programming [7], ii) multi-dimension downhill simplex method [8], iii) evolutionary operation algorithm [9]. The resulting software was used to compute the diffusivities in the Co-Fe-Ni system.

Interdiffusion in Co-Fe-Ni Alloys

The interdiffusion in the Co-Fe-Ni alloys was examined by Vignes and Sabatier [10, 11]. They had performed detailed study of diffusion in Co-Fe-Ni alloys at 1408 and 1588 K. Using Kirkaldy analysis [12] they obtained the matrix of interdiffusion coefficients in a wide range of compositions. The binary Co-Fe, Co-Ni and Fe-Ni systems were of great interest as well [10,11,13-18]. The Co-Fe-Ni alloys can be treated as ideal and consequently the thermodynamic interactions can be neglected [11, 19].

We have studied interdiffusion in the Co-Fe-Ni system in the 1273 - 1588 K temperature range. Using the Danielewski-Holly model and the inverse method we have calculated average intrinsic diffusion coefficients of Co, Fe and Ni as a function of temperature. The calculated intrinsic diffusivities give full description of interdiffusion process in the Co-Fe-Ni system, i.e. allow computing the distribution profiles of the elements.

Experimental Procedure

Cobalt, iron and nickel (99.98 pct purity) were used as initial materials. The binary alloys Co-Ni, and Fe-Ni were induction melted to form 1 cm diameter rods. After homogenization in 1573 K for 48 hours in argon atmosphere the rods were sectioned into discs of 1 mm thick with a diamond impregnated cut-off wheel to have parallel faces. The disks were carefully ground and polished using standard metallographic preparation. The compositions of materials were determined by a chemical analysis and the level of homogeneity of materials used in subsequent diffusion experiments were determined by EDS analysis. The actual compositions of samples used for diffusion experiments were Co–51.3±0.1 wt. % Ni and Fe–51.9±0.1 wt. % Ni. The two disks each of the different alloy were assembled together in molybdenum jig forming a diffusion couple. The couples were heat treated in argon atmosphere at temperatures and for the periods of time shown in the Table 1. The partial oxygen pressure in argon was monitored during experiment and was lower then 10^{-6} atm. After annealing each specimen was cut perpendicular to the direction of diffusion and polished using standard metallographic preparation. The concentration profiles were analysed by point-to-point counting techniques using scanning microscope XL300 Philips equipped with EDS Oxford Link Isis Detector and standard ZAF corrections.

Table 1. The examined diffusion couples.

Diff. couple	T [K]	Time [h]
P1	1273	68
P2	1323	50
P3	1373	140
P4	1423	85
P5	1473	59
P6	1523	24
P7	1588	17
P8	1588	131

Table 2. Calculated average intrinsic diffusion coefficients.

T [K]	Intrinsic diffusion coefficients [$cm^2 s^{-1}$]		
	Fe	Co	Ni
1273	$4.97 \cdot 10^{-12}$	$1.53 \cdot 10^{-12}$	$7.86 \cdot 10^{-13}$
1323	$1.78 \cdot 10^{-11}$	$3.83 \cdot 10^{-12}$	$3.42 \cdot 10^{-12}$
1373	$5.78 \cdot 10^{-11}$	$1.53 \cdot 10^{-11}$	$1.14 \cdot 10^{-11}$
1423	$1.21 \cdot 10^{-10}$	$3.44 \cdot 10^{-11}$	$2.67 \cdot 10^{-11}$
1473	$3.22 \cdot 10^{-10}$	$1.06 \cdot 10^{-10}$	$5.14 \cdot 10^{-11}$
1523	$4.86 \cdot 10^{-10}$	$1.43 \cdot 10^{-10}$	$1.23 \cdot 10^{-10}$
1588	$1.20 \cdot 10^{-9}$	$4.28 \cdot 10^{-10}$	$2.35 \cdot 10^{-10}$

Experimental Results

The diffusion couples investigated in the present work (Table 1) and the experimental concentration profiles in the Co-Fe-Ni system for several diffusion couples are presented in the Figure 2. Having experimental concentration profiles and using the inverse method the average intrinsic diffusion coefficients of Co, Fe and Ni were calculated, Table 2. The diffusion coefficients of cobalt, iron and nickel in the range between 1373–1588 K follow Arrhenius equation (see Fig. 1):

$$D = D_0 \exp\left(-\frac{E_A}{RT}\right) \tag{5}$$

Using standard linear regression analysis for each component the preexponential factor D_0, activation energy E_A and its error (Table 3) were calculated. The calculated in this work intrinsic diffusivities of Co, Fe and Ni show good agreement with the results of other authors for the ternary Co-Fe-Ni system [11] and for the binary Fe-Ni [15,18,20], Co-Fe [18] and Co-Ni [13,17,18] alloys (see Fig. 3).
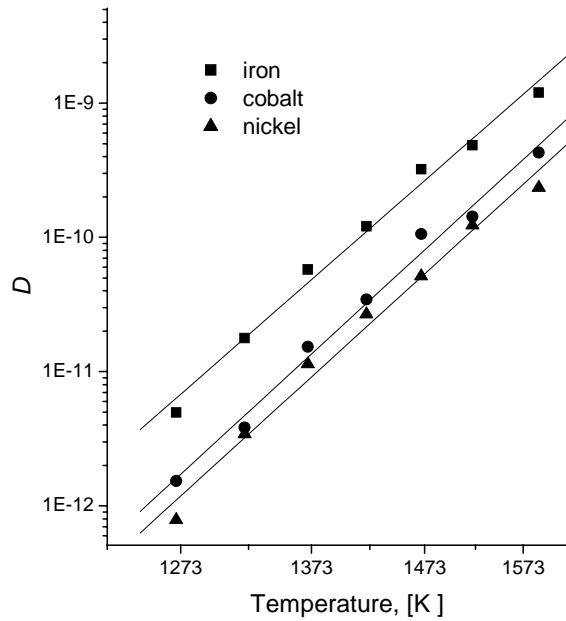

Figure 1. Temperature dependence of Co, Fe and Ni intrinsic diffusivities in the Arrhenius plot.

Table 3. Activation energy and preexponential factor for Co-Fe-Ni alloy in 1273 – 1588 K temperature range.

Element	E_A $[kJ\ mol^{-1}]$	D_0 $[cm^2\ s^{-1}]$
Fe	289±13	4.62
Co	304±13	4.45
Ni	301±15	2.38

In the Figure 2 the experimental and calculated concentration profiles of Co, Fe and Ni (using the Danielewski-Holly model and intrinsic diffusivities from the Table 2) are compared.
The interdiffusion process generates the diffusion structure on initial nickel distribution, i.e., "uphill diffusion" of nickel. In the finite system (i.e., when the whole diffusion couple is affected by interdiffusion) its "life time" is limited (Fig. 4). The agreement between the calculated on the base of the Danielewski-Holly model and experimental profiles is observed both for the infinite (Fig. 3) and finite (Fig. 4) systems.
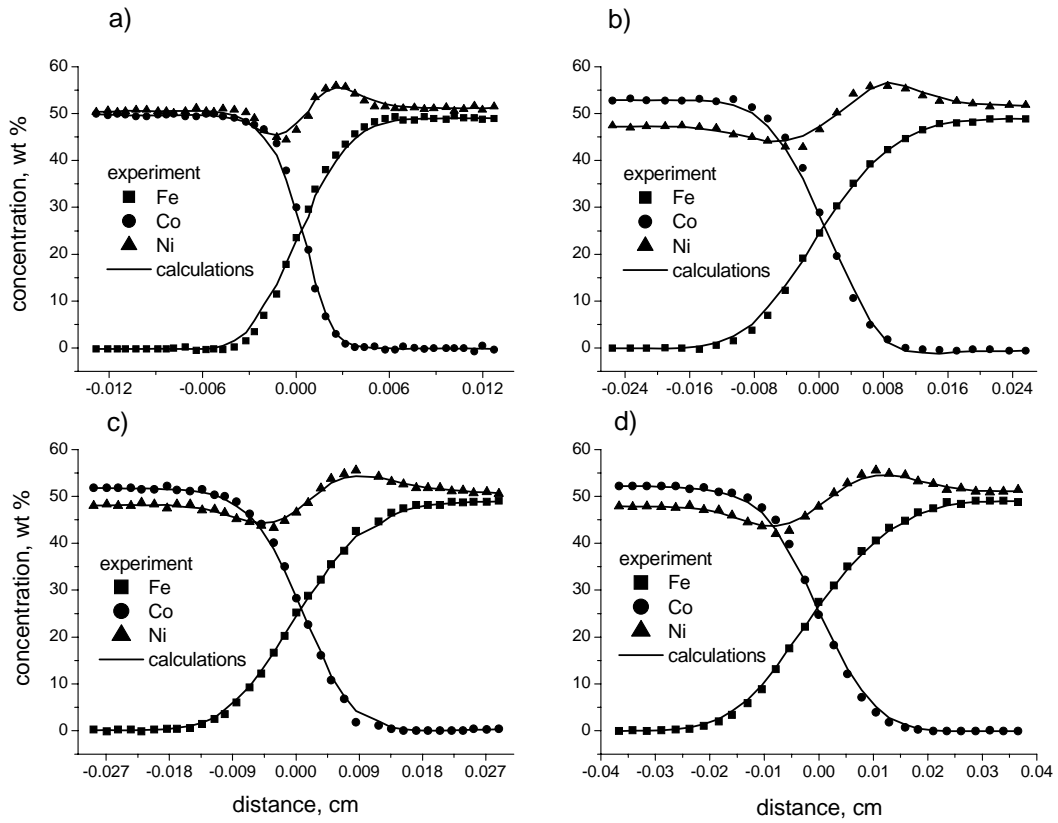
Figure 2. Interdiffusion in the Co-Fe-Ni diffusion couples: a) P2 1323 K and 50 h; b) P3 1373 K and 140 h; c) P4 1423 K and 85 h; d) P5 1473 K and 59 h.
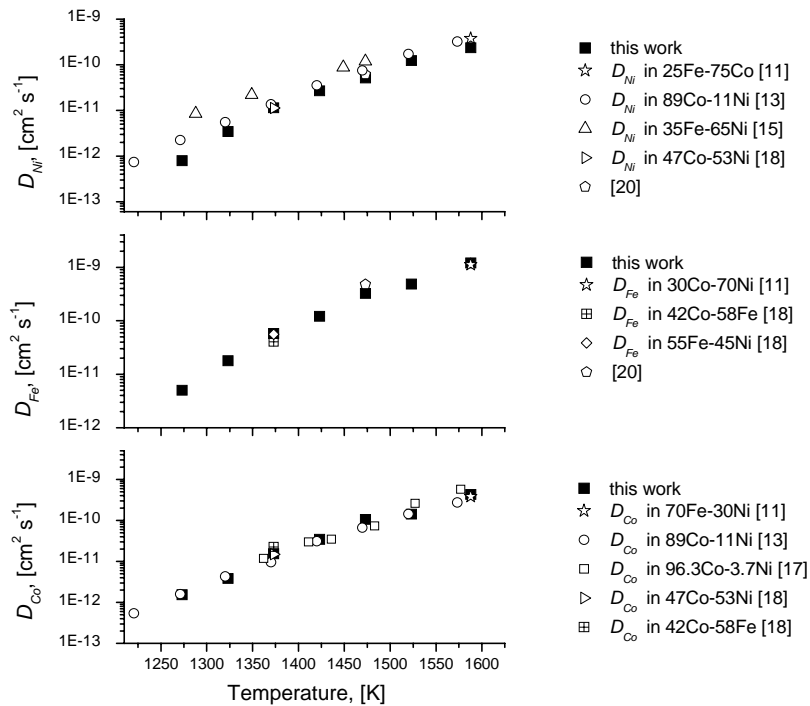

Figure 3. The intrinsic diffusion coefficients by different authors in Co-Fe-Ni alloys for different temperatures.
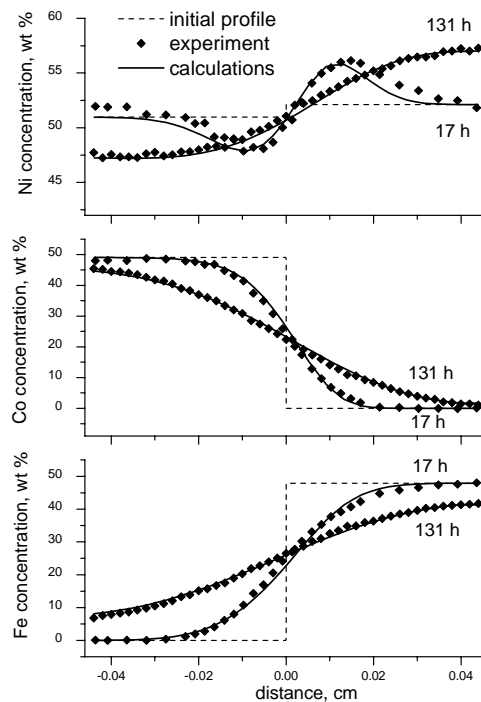
Figure 4. Interdiffusion in the Co-Fe-Ni diffusion couples P7 and P8 at 1588 K.

Summary

The generalized Darken method of interdiffusion allows a quantitative description of complex diffusion transport process for an unlimited number of elements. It allows to calculate diffusivities and concentration profiles both for the infinite and finite system. Using the Danielewski-Holly model, the interdiffusion in the Co-Fe-Ni system was analysed and satisfying agreement of the calculated concentration profiles and the experimental ones was observed. The calculated iron intrinsic diffusivity is higher than Ni and Co: $D_{Fe} > D_{Ni} \sim D_{Co}$ and is in good agreement with data for the binary systems [13-18]. The temperature dependence of Co, Fe and Ni intrinsic diffusion coefficients in whole examined temperature range (1373–1588 K) suggest one mechanism of diffusion. The values of activation enthalpy of Co, Fe and Ni are similar $300 \ kJ \ mol^{-1}$ and the

errors were estimated to be less than 5% and may suggest the vacancy mechanism of diffusion in this alloy. Confirmation of this hypothesis involves more complex and detailed examinations.

References

[1] L.S. Darken: Trans. AIME Vol. 174 (1948), p. 184

[2] K. Holly, M. Danielewski: Phys. Rev. B Vol. 50 (1994), p.13336.

[3] M. Danielewski, R. Filipek: J. Comp. Chem. Vol. 17 No. 13 (1996), p. 1497

[4] M. Danielewski, K. Holly, W. Krzyżański: Polish J. Chem. Vol. 68 (1994), p. 2031

[5] R. Filipek: Archives of Metallurgy and Materials Vol. 49 No. 2 (2004), p. 201

[6] L. L. Lions, Quelques Methodes de Résolution des Problémes aux Limites Non Linéaires, Dunod, Paris, 1969

[7] P.E. Gill, W. Murray, N.H. Wyight: *Practical optimalization, Academic Press*, 1981, p. 247

[8] J.A. Nelder, L. Mad: Computer Journal Vol. 7 (1965) , p. 308

[9] S.N. Ghani: Performance of global optimization algorithm for non-linear non-differentiable constraint objective functions, *IEEE International Conference on Evolutionary Comp*utations, Perth Western Australia, 1995, p. 320

[10] J.P. Sabatier, A. Vignes: Mém. Sci. Rev. Métall. Vol. 64 (1967) , p. 225

[11] A. Vignes, J.P. Sabatier: Trans. AIME Vol. 245 (1969) , p. 1795

[12] J.S. Kirkaldy, J.E. Lane: Can. J. Phys. Vol. 44 (1966) , p. 2059

[13] Ken-ichi Hirano, R.P. Agarwala, B.L. Averbach, Morris Cohen: J. Appl. Phys. Vol. 33 (10) (1962) , p. 3049

[14] J.I. Goldstein, R.E. Hanneman, R.E. Ogilvie: Trans. Metall. Soc. AIME Vol. 233 (1965) , p. 812

[15] E. Walsöe de Reca, C. Pampillo: Acta Metall. Vol. 15 (1967) , p. 1263

[16] T. Ustad, H. Sorum: phys. stat. sol. (a) Vol. 20 (1973) , p. 285

[17] B. Million, J. Kucera: Acta Metall. Vol. 17 (1969) , p. 339

[18] Yu.E. Ugaste, A.A. Kodentsov, F. van Loo: Phys. Met. Metallogr. Vol. 88 (6) (1999) , p. 598

[19] J.S. Kirkaldy and D.J. Young, *Diffusion in the Condensed State*, The Institute of Metals, London, 1987

[20] A. Kohn, J.Levasseur, J. Philibert, M. Wanin: Acta Metall. Vol. 18 (1970) , p. 163