Phase Transformations

Diffusion

Byeong-Joo Lee
POSTECH-CMSE

References

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Diffusion Coefficient – Inter Diffusion

Diffusion Coefficients

- Intrinsic, Inter (Chemical), Self, Tracer, Tracer Impurity Diffusion Coefficient
- Intrinsic diffusion coefficients are not measurable, but can be calculated using Darken's equation

□ Darken's equation

▷ with respect to some fixed reference plane

- $J_A = -D_A \dfrac{\partial n_A}{\partial x}$

$J_B = -D_B \dfrac{\partial n_B}{\partial x}$ (n_i : concentration of i)

- $J_A + J_B + J_V = 0$

Difference between $|J_A|$ and $|J_B|$, thus the flux of vacancies causes a movement of the reference plane (at a velocity, v)

$\rightarrow \quad J_V = -J_A - J_B = n_t v$ (n_t : # of total atoms per volume)

Assume that molar volume of A and B is equal to each other.
($n_t = n_A + n_B =$ constant)

$\therefore \quad v = (D_A - D_B) \dfrac{\partial N_A}{\partial x}$ (N_A : mole fraction of A)

Diffusion Coefficient – Inter Diffusion

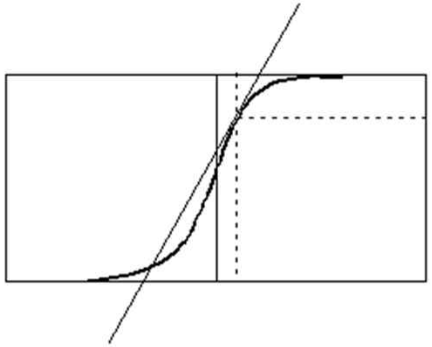
▷ with respect to volume fixed frame,

$$\tilde{J}_B = J_B + N_B n_t v = J_B - N_B (J_A + J_B)$$

$$= -(N_B D_A + N_A D_B)\frac{\partial n_B}{\partial x} \qquad = -\tilde{D}\frac{\partial n_B}{\partial x}$$

$$\therefore \quad \tilde{D} = N_B D_A + N_A D_B$$

ex)



Distance of marker plane from Matano plane : 0.01 cm

Annealing time : 18000 sec

on marker plane : $N_A = 0.65$, $N_B = 0.35$

$$\tilde{D} = 5.5 \times 10^{-8}\ \text{cm}^2/\text{sec}$$

$$\frac{\partial N_A}{\partial x} = 2.44\ \text{cm}^{-1}$$

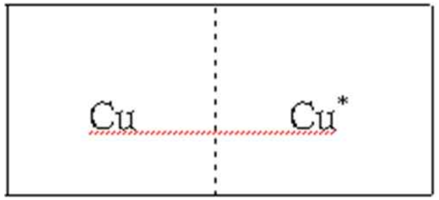
$$\cdot \quad v = \frac{x}{2t} = \frac{0.01}{2 \times 18000} = 2.78 \times 10^{-7}\ \text{cm/sec}$$

$$5.5 \times 10^{-8} = 0.35\ D_A + 0.65\ D_B$$

$$2.78 \times 10^{-7} = 2.44\ (D_A - D_B)$$

Diffusion Coefficient – Self/Tracer Diffusion

☐ Self Diffusion Coefficient



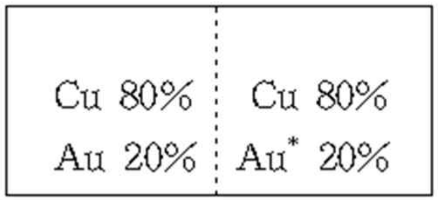
$$\tilde{D} = N_B D_A + N_A D_B$$

$$D_A = D_B = D$$

$\tilde{D}$: constant

※ determination of $\tilde{D}$: Grube method

☐ Tracer Diffusion Coefficient



$$N_{Au} + N_{Au^*} = 20\%$$

$$D_{Au} = D^*_{Au} = D(N_{Au} + N_{Au^*}) = \text{constant}$$

$D^*_{Au} \leftarrow$ Grube method

Diffusion Coefficient – Intrinsic Diffusion Coefficient

☐ Intrinsic Diffusion Coefficient

· $J_A = - D_A \dfrac{\partial n_A}{\partial x} = - D_A n_t \dfrac{\partial N_A}{\partial x}$

· ideal solution

$$\mu_A = {}^{o}G_A + RT \ln N_A , \qquad \frac{\partial \mu_A}{\partial x} = \frac{RT}{N_A} \frac{\partial N_A}{\partial x}$$

· $J_A = - \dfrac{D_A}{RT} n_A \dfrac{\partial \mu_A}{\partial x}$

$\quad = - B_A n_A \dfrac{\partial \mu_A}{\partial x} \qquad (B_A$: mobility)

· Non-ideal solution

$$\mu_A = {}^{o}G_A + RT \ln N_A \gamma_A$$

$$\frac{\partial \mu_A}{\partial x} = \frac{RT}{N_A} \left[\frac{\partial N_A}{\partial x} + N_A \frac{\partial \ln \gamma_A}{\partial x} \right]$$

$$J_A = - B_A RT n_t \frac{\partial N_A}{\partial x} \left[1 + N_A \frac{\partial \ln \gamma_A}{\partial N_A} \right]$$

$$\therefore D_A = B_A RT \left[1 + N_A \frac{\partial \ln \gamma_A}{\partial N_A} \right]$$

※ Tracer Diffusion

· $D_A^* = B_A^* RT \left[1 + N_{A^*} \dfrac{\partial \ln \gamma_{A+A^*}}{\partial N_{A^*}} \right]$

$\quad = B_A^* RT$

$$B_A^* = B_A$$

$$\therefore D_A = D_A^* \left[1 + N_A \frac{\partial \ln \gamma_A}{\partial N_A} \right]$$

Diffusion Coefficient – Inter Diffusion Coefficient

□ Inter-diffusion Coefficient

· $\tilde{D} = N_B D_A + N_A D_B$

$$= N_B\, D_A^* \left[1 + N_A \frac{\partial \ln \gamma_A}{\partial N_A}\right] + N_A\, D_B^* \left[1 + N_B \frac{\partial \ln \gamma_B}{\partial N_B}\right]$$

· Gibbs-Duhem Eq.

$$N_A\, d\mu_A + N_B\, d\mu_B = 0 \quad \rightarrow \quad N_A \frac{d\mu_A}{dN_A} = N_B \frac{d\mu_B}{dN_B}$$

$$\frac{d\mu_i}{dN_i} = \frac{RT}{N_i}\left[1 + \frac{d\ln \gamma_i}{d\ln N_i}\right]$$

$$\rightarrow \quad \left[1 + \frac{d\ln \gamma_A}{d\ln N_A}\right] = \left[1 + \frac{d\ln \gamma_B}{d\ln N_B}\right]$$; thermodynamic factor

$$\therefore\ \tilde{D} = (N_B\, D_A^* + N_A\, D_B^*)\left[1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A}\right]$$

Diffusion Coefficient – Modeling

- Inter-diffusion Coefficient in a binary alloy
  - linked to intrinsic diffusion by the Darken's relation

$$\tilde{D} = (N_B D_A^* + N_A D_B^*)\left[1 + \frac{d \ln \gamma_B}{d \ln N_B}\right]$$

- Intrinsic diffusion Coefficient
  - composed of mobility term (Tracer Diffusion) and thermodynamic factor

$$D_B = D_B^*\left[1 + \frac{d \ln \gamma_B}{d \ln N_B}\right]$$

- Tracer diffusion Coefficient – as a function of composition & temp.

$$D_B^*(N_B, T) = D_B^o(N_B) \cdot e^{-Q_B(N_B)/RT}$$

$D_B^*(N_B = 0)$: tracer impurity diffusion coefficient

$D_A^*(N_B = 0)$: self-diffusion of A in the given structure

$$D_B^*(N_B = 0) \cong D_A^{*self}$$

- Linear composition dependence of Q_B in a composition range $N_1 \sim N_2$

$$Q(N) = Q\left(\frac{n_1}{n_1+n_2}N_1 + \frac{n_2}{n_1+n_2}N_2\right) = \frac{n_1}{n_1+n_2}Q_1 + \frac{n_2}{n_1+n_2}Q_2$$

  - assuming composition independent D^o

$$D_B^*\left[\frac{n_1}{n_1+n_2}N_1 + \frac{n_2}{n_1+n_2}N_2\right] = D_B^o \cdot e^{-\left[\frac{n_1}{n_1+n_2}Q_1 + \frac{n_2}{n_1+n_2}Q_2\right]/RT} = D_{N_1}^{*\,\frac{n_1}{n_1+n_2}} \cdot D_{N_2}^{*\,\frac{n_2}{n_1+n_2}}$$

❖ Tracer diffusion Coefficient at an intermediate composition is a **geometrical mean** of those at both ends – from experiments

  - the same for the D^o term

$$D_B^*(N_B, T) = e^{\ln D_B^o(N_B)} \cdot e^{-Q_B(N_B)/RT} = e^{Q_B^o(N_B)} \cdot e^{-Q_B(N_B)/RT}$$

❖ **Both Q^o & Q are modeled as a linear function of composition**

Modeling of Multi-Component Diffusion - Basic Assumption

$$V_m = \sum_{k=1}^{n} x_k V_k$$

$$V_k = V_S \qquad \text{for } k \in \text{S (substitutional)}$$

$$V_k = 0 \qquad \text{for } k \notin \text{S}$$

$$V_m = \sum_{k=1}^{n} x_k V_k = V_S \sum_{k \in S} x_k$$

$$C_k = \frac{x_k}{V_m} = \frac{x_k}{\sum_{j \in S} x_j} / V_S = u_k / V_S$$

$$u_k = x_k / \sum_{j \in S} x_j$$

Modeling of Multi-Component Diffusion - Reference Frame

$$\sum_{k=1}^{n} V_k J_k = 0$$

$$\sum_{k \in S} J_k = 0$$

$$\tilde{J}_k = J_k - u_k \sum_{i \in S} J_i$$

Mathematical Formalism of Multi-Component Diffusion Coefficient

☐ Mathematical formalism of the multicomponent diffusion coefficients

- $J_i = - L_i \nabla \mu_i$

- $J_i = - L_i \sum_j^{n^*} \frac{\partial \mu_i}{\partial C_j} \nabla C_j = - \sum_j^{n^*} [L_i \frac{\partial \mu_i}{\partial u_j} V_S] \nabla C_j$

  $n^* = n$ for substitutional solution

  $n^* = n + 1$ for interstitial solution (including vacancy)

- translation to guarantee the number fixed frame wrt. substitutional atoms

$$J_k = \tilde{J}_k - u_k \sum_{i \in S} \tilde{J}_i = \sum_{i \in S} \delta_{ik} \tilde{J}_i - \sum_{i \in S} u_k \tilde{J}_i = \sum_{i \in S} (\delta_{ik} - u_k) \tilde{J}_i$$

$$= - \sum_j^{n^*} [\sum_{i \in S} (\delta_{ik} - u_k) L_i \frac{\partial \mu_i}{\partial u_j} V_S] \nabla C_j$$

- $L_i = u_i \, y_{va} \, M_{iVa}$

  $\Omega_i = y_{Va} \, M_{iVa} \, V_S$ for substitutional i

  $\Omega_i = M_{iVa} \, V_S$ for interstitial i

Mathematical Formalism of Multi-Component Diffusion Coefficient

- $J_k = -\sum_{j=1}^{n^s} [\sum_{i \in S} (\delta_{ik} - u_k) u_i \Omega_i \frac{\partial \mu_i}{\partial u_j}] \nabla C_j$ for substitutional k

- $J_k = -\sum_{j=1}^{n^s} [u_k y_{Va} \Omega_k \frac{\partial \mu_k}{\partial u_j}] \nabla C_j$ for interstitial k

- for each sublattice (normal lattice & interstitial site)

  $\sum_j \nabla C_j = 0$

※ One can remove ∇C_j term where j means solvent atom in the substitutional sublattice and vacancy in the interstitial sublattice.

$$J_k = -\sum_{j=1}^{n-1} D_{kj}^n \nabla C_j$$

- $D_{kj}^n = \sum_{i \in S} (\delta_{ik} - u_k) u_i \Omega_i \left(\frac{\partial \mu_i}{\partial u_j} - \frac{\partial \mu_i}{\partial u_n} \right)$ for substitutional k

- $D_{kj}^n = u_k y_{Va} \Omega_k \left(\frac{\partial \mu_k}{\partial u_j} - \frac{\partial \mu_k}{\partial u_n} \right)$ for interstitial k

☐ Application to binary and ternary solutions

▷ Application to an Fe-M substitutional binary solution

$$J_M = -[y_{Fe}\, y_M\, \Omega_M \left(\frac{\partial \mu_M}{\partial y_M} - \frac{\partial \mu_M}{\partial y_{Fe}}\right) - y_M\, y_{Fe}\, \Omega_{Fe} \left(\frac{\partial \mu_{Fe}}{\partial y_M} - \frac{\partial \mu_{Fe}}{\partial y_{Fe}}\right)] \nabla C_M$$

$$= -[\ y_{Fe}\, y_M\, \Omega_M \frac{d\mu_M}{dy_M} - y_M\, y_{Fe}\, \Omega_{Fe} \frac{d\mu_{Fe}}{dy_M}\ ] \nabla C_M$$

$$= -[\ y_{Fe}\, \Omega_M\, RT + y_M\, \Omega_{Fe}\, RT\ ] \left(1 + \frac{d\ln \gamma_M}{d\ln y_M}\right) \nabla C_M$$

※ for an Fe-M-M* ternary system

using the relations : $\nabla C_{Fe} = 0$

$\nabla C_M + \nabla C_{M^*} = 0$

$\Omega_M = \Omega_{M^*}$

one can derive

$$J_{M^*} = -\ \Omega_M\, RT\, \nabla C_{M^*}$$

- $$D_{kj}^{n} = u_k \, y_{Va} \, \Omega_k \left(\frac{\partial \mu_k}{\partial u_j} - \frac{\partial \mu_k}{\partial u_n} \right)$$ for interstitial k

▷ Application to the Fe-C interstitial binary solution

$$J_C = - \, y_C \, y_{Va} \, \Omega_C \, \left(\frac{\partial \mu_C}{\partial y_C} - \frac{\partial \mu_C}{\partial y_{Va}} \right) \, \nabla C_C$$

$$= - \, y_C \, y_{Va} \, \Omega_C \, \frac{d\mu_C}{dy_C} \, \nabla C_C$$

$$= - \, \Omega_C \, RT \left(1 - \frac{2 y_C y_{Va}}{RT} \cdot L_{Fe\,Va,C} \right) \nabla C_C$$

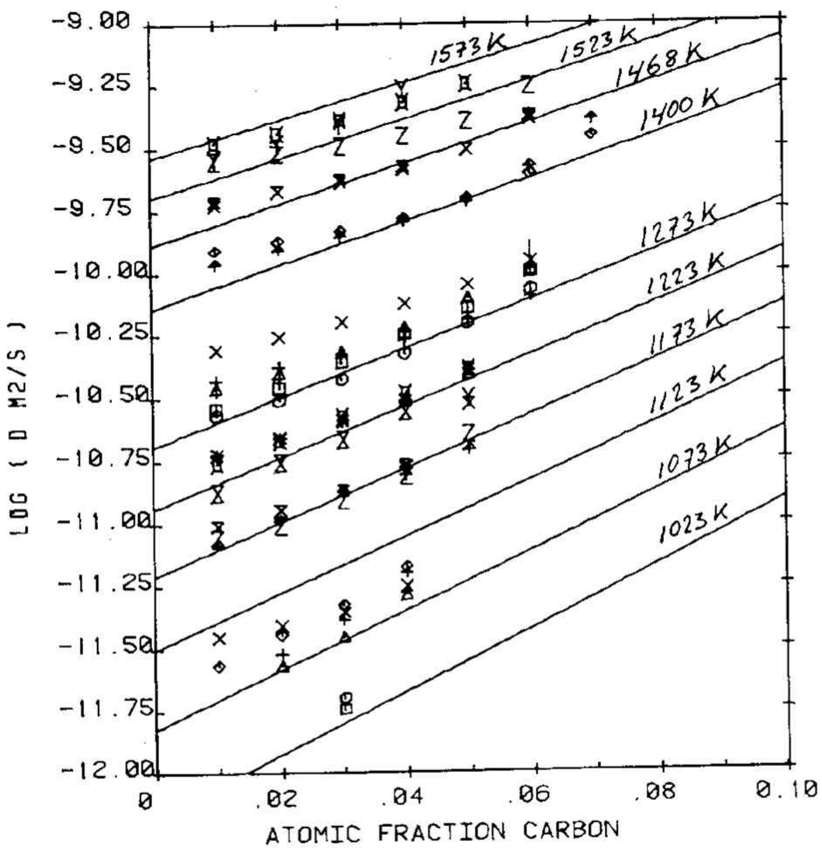
$$\Omega_C \, RT = 4.529 \cdot 10^{-7} \exp\left[- \frac{(1 - 2.221 \cdot 10^{-4} \cdot T)}{RT} (-72007 y_C + 147723 y_{Va}) \right]$$

[J. Ågren, *Scripta Metall.* 20, 1507 (1986)]

Smithells Metals Reference Book, 1992

	0–0.2		1.0	226.1	—	1 073–1 373	IIa(i)	38
			Very little variation of $\tilde{D}$ with c					
Be	H							
			2.3×10^{-7}	18.42	—	473–1 273	IIIb	86
Be	Mg							
0–sol. limit			8.06	157.0	—	773–873	IIIa(i)	212
Bi	Pb							
0–2.0			0.018	77.0	—	493–558	IIa(i)	39
C	Co							
			8.72×10^{-3}	149.3	—	723–1 073	IIa(i), p.c.	158
~0.1–0			0.31	153.7	—	1 073–1 673	IIIa(i)	216
C	Co	Fe						
	78.5		0.472	157.0	—	1 123–1 373	IIIb(ii)	41
0.48	89.4		0.442	157.0	—	1 123–1 385		
0–0.7 (wt.%)	0	(γ)	$0.04 + 0.08\,c$	131.3		1 273–1 473	IIa(i)	146
	5.8		$0.04 + 0.08\,c$	127.7				
	10.6		$0.03 + 0.1\,c$	125.2				
	20.2		$0.03 + 0.06\,c$	120.8				
				(c = wt.%C)				
C	Fe							
0–0.1	(α)		3.94×10^{-3}	80.2	—	313–623	Various	215
γ-range	$D = 4.53 \times 10^{-3}[1 + y_c(1 - y_c)8339.9/T]\exp[-(T^{-1} - 2.221 \times 10^{-4} \times 17\,767 - 26\,436 y_c)]$							
			$y_c = x_c/(1 - x_c)$,	x_c = mol fraction of C				42
α-range	$\mathrm{Log}\,D = -0.9064 - 0.5199\chi + 1.61 \times 10^{-3}\chi^2$					233–1 140	Combined data, several sources	40
			$\chi = 10^4/T$					

Mathematical Formalism - Application to Binary and Ternary Solutions



John Ågren, Scripta Metallurgica 20, 1507-10 (1986).

$$D_C = 4.53 \cdot 10^{-7}\left(1+y_C(1-y_C)\frac{8339.9}{T}\right)\exp\left\{-\left(\frac{1}{T} - 2.221 \cdot 10^{-4}\right)(17767 - y_C 26436)\right\} \quad m^2 s^{-1}$$

▷ Application to the Fe-M-C interstitial ternary solution

$$J_C = -y_C\, y_{Va}\, \Omega_C\left(\frac{\partial \mu_C}{\partial y_C} - \frac{\partial \mu_C}{\partial y_{Va}}\right)\nabla C_C - y_C\, y_{Va}\, \Omega_C\left(\frac{\partial \mu_C}{\partial y_M} - \frac{\partial \mu_C}{\partial y_{Fe}}\right)\nabla C_M$$

$$J_M = -\left[y_{Fe}\, y_M\, \Omega_M\left(\frac{\partial \mu_M}{\partial y_C} - \frac{\partial \mu_M}{\partial y_{Va}}\right) - y_M\, y_{Fe}\, \Omega_{Fe}\left(\frac{\partial \mu_{Fe}}{\partial y_C} - \frac{\partial \mu_{Fe}}{\partial y_{Va}}\right)\right] \nabla C_C$$

$$- \left[y_{Fe}\, y_M\, \Omega_M\left(\frac{\partial \mu_M}{\partial y_M} - \frac{\partial \mu_M}{\partial y_{Fe}}\right) - y_M\, y_{Fe}\, \Omega_{Fe}\left(\frac{\partial \mu_{Fe}}{\partial y_M} - \frac{\partial \mu_{Fe}}{\partial y_{Fe}}\right)\right] \nabla C_M$$

Multi-Component Diffusion Simulation – for C in Fe-C-M ternary system

$$J_C = -D_{CC}\nabla C_C - D_{CM}\nabla C_M$$

$$J_C = -u_C y_{Va} M_{CVa}\left(\frac{\partial\mu_C}{\partial u_C} - \frac{\partial\mu_C}{\partial u_{Va}}\right)V_S\nabla C_C - u_C y_{Va} M_{CVa}\left(\frac{\partial\mu_C}{\partial u_M} - \frac{\partial\mu_C}{\partial u_{Fe}}\right)V_S\nabla C_M$$

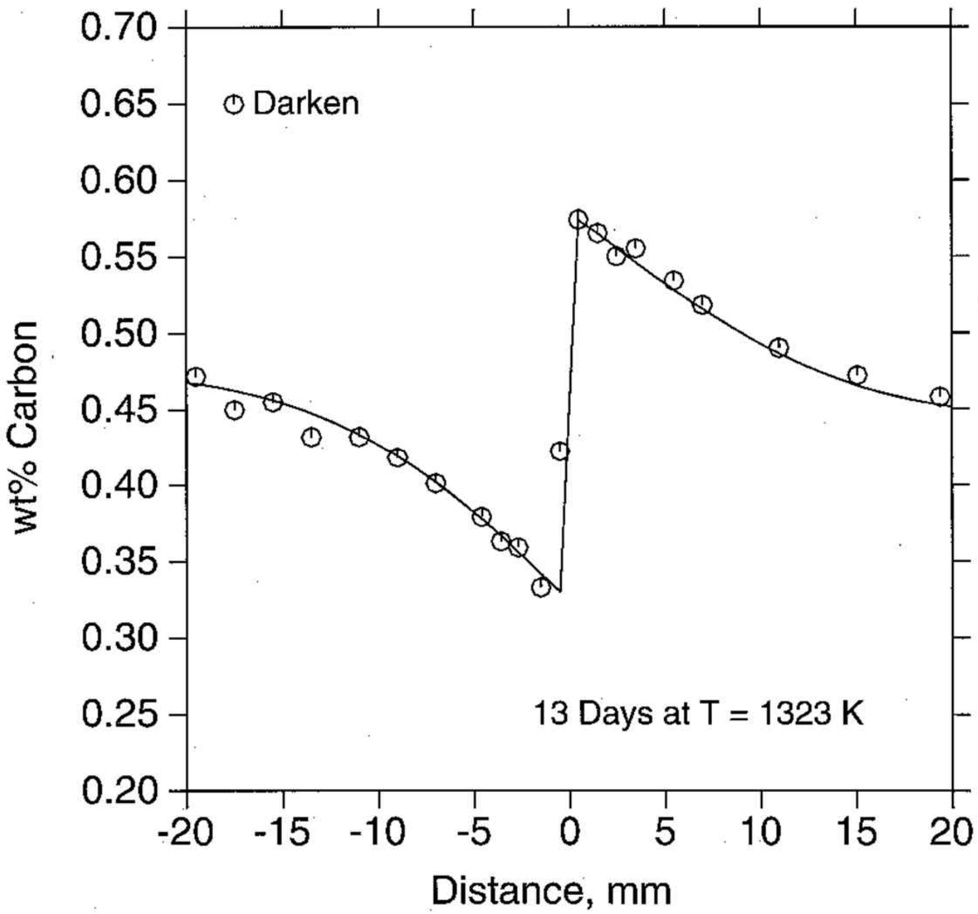
$$y_C + y_{Va} = 1 \qquad\qquad y_{Fe} + y_M = 1$$

$$J_C = -y_C y_{Va} M_{CVa}\left(\frac{d\mu_C}{dy_C}\right)V_S\nabla C_C - y_C y_{Va} M_{CVa}\left(\frac{d\mu_C}{dy_M}\right)V_S\nabla C_M$$

$$D_{CC} = y_C y_{Va} M_{CVa}\left(\frac{d\mu_C}{dy_C}\right)_{y_M} V_S \qquad\qquad D_{CM} = y_C y_{Va} M_{CVa}\left(\frac{d\mu_C}{dy_M}\right)_{y_C} V_S$$

$$D_{CM} / D_{CC} = \left(\frac{d\mu_C}{dy_M}\right)_{y_C} / \left(\frac{d\mu_C}{dy_C}\right)_{y_M} = -\left(\frac{dy_C}{dy_M}\right)_{\mu_C}$$

Multi-Component Diffusion Simulation – Darken's uphill diffusion

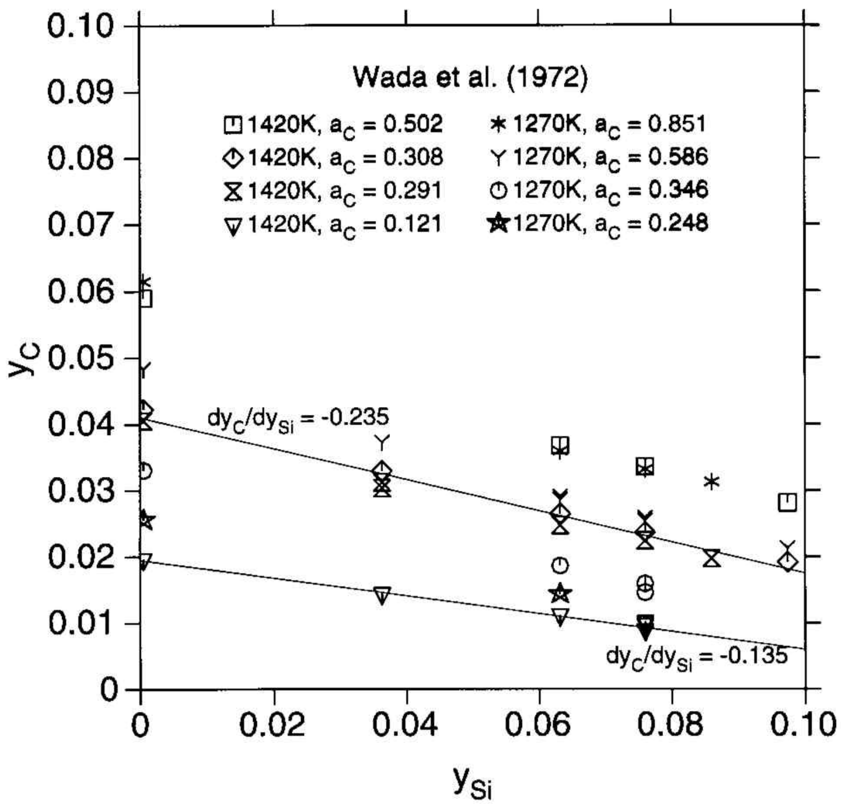


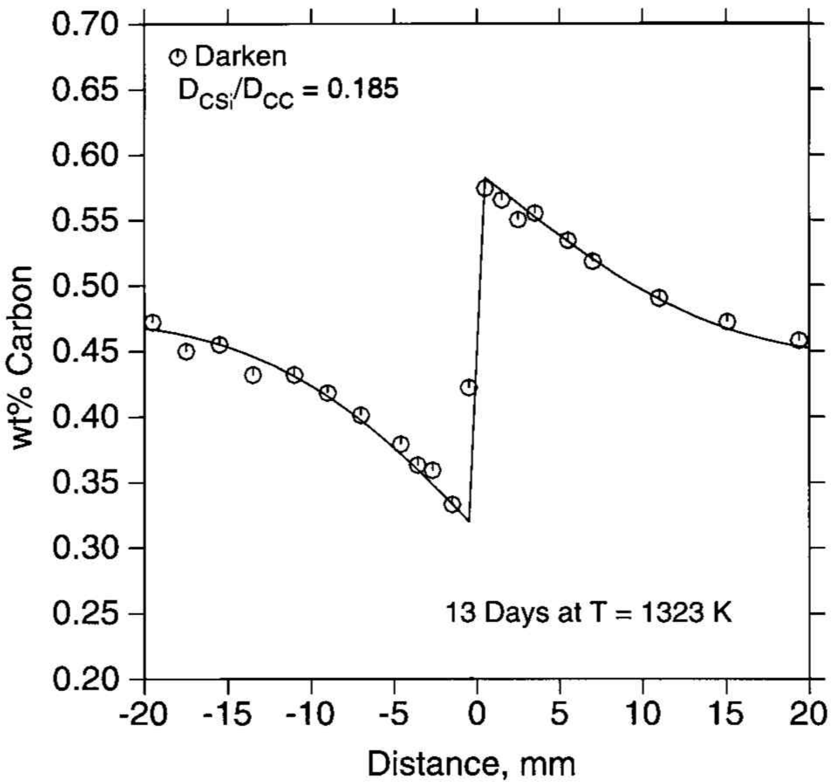
Fe-3.8Si-C

and

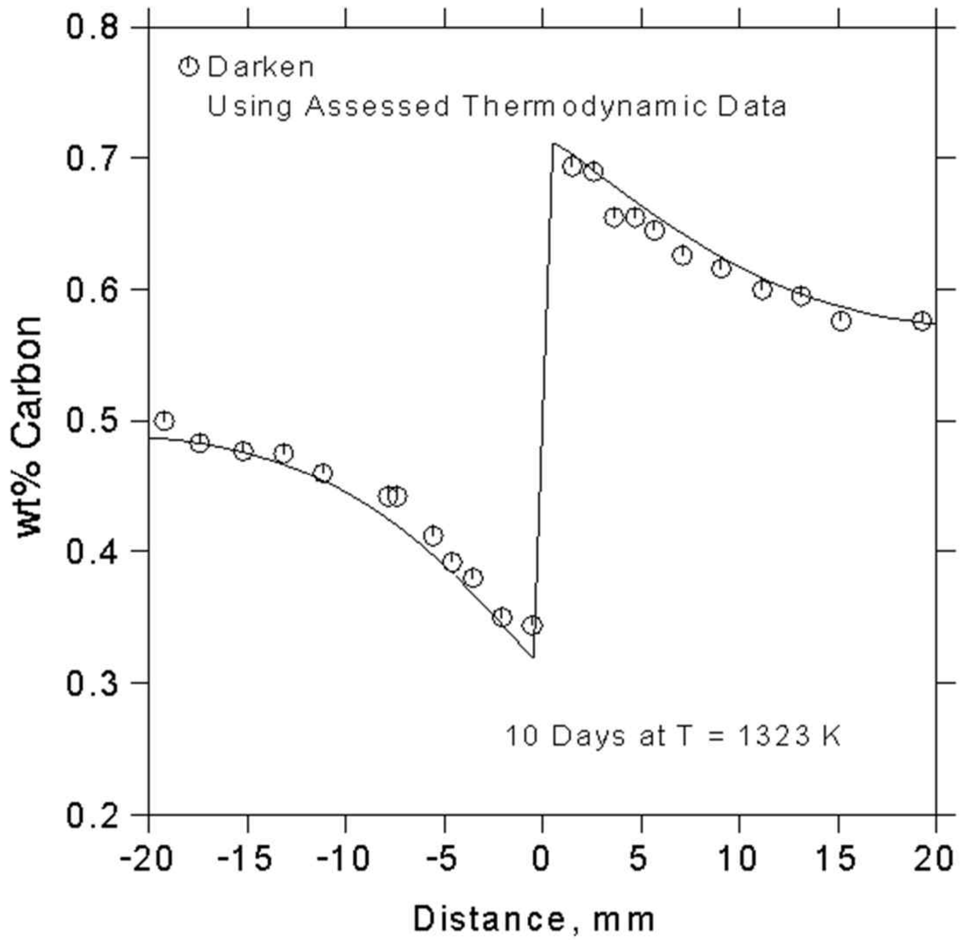
Fe-C

Multi-Component Diffusion Simulation – Darken's uphill diffusion





Multi-Component Diffusion Simulation – Darken's uphill diffusion

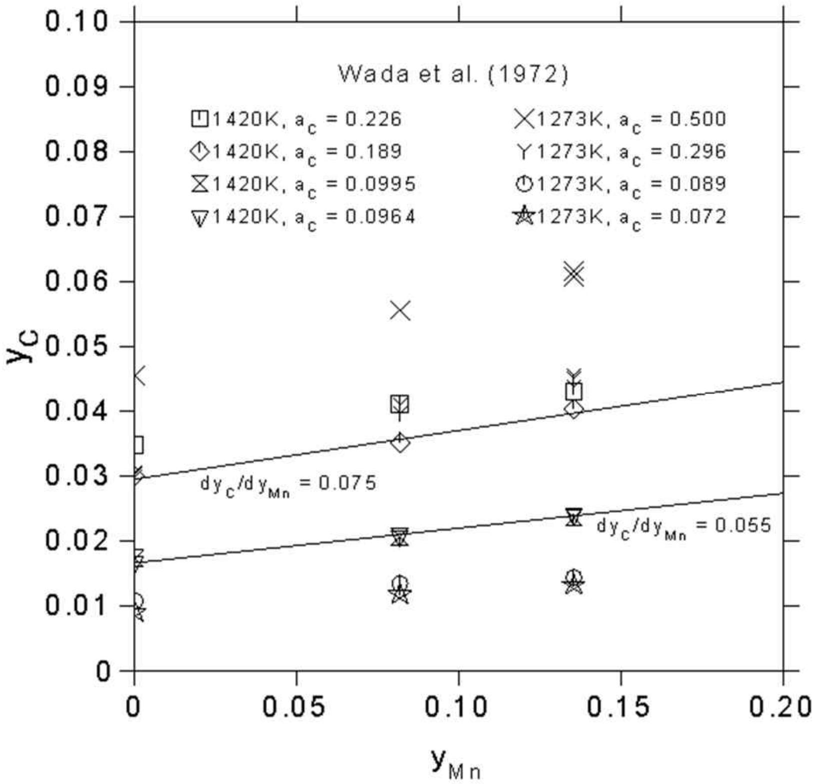


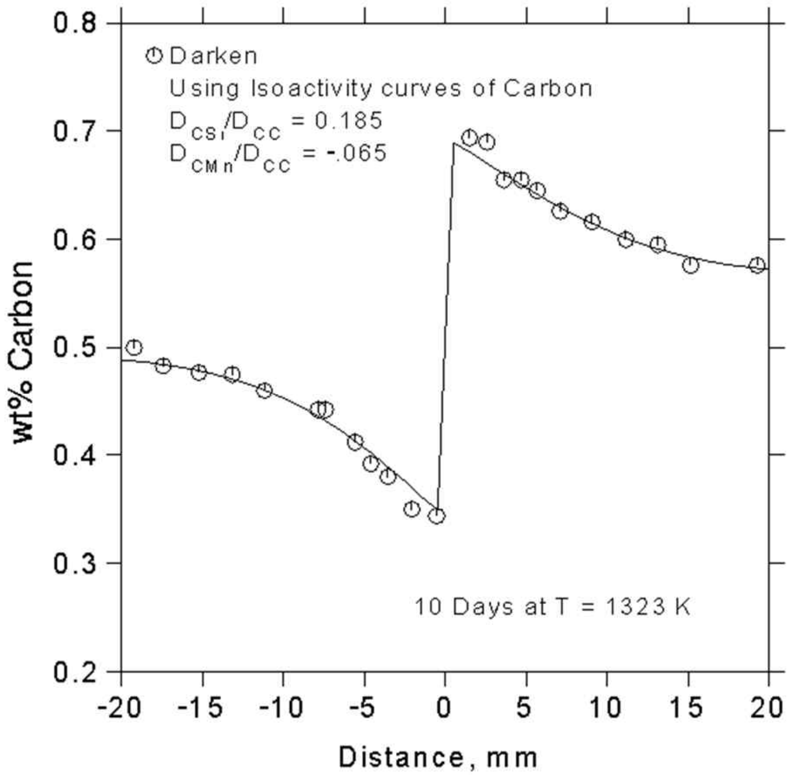
Fe-3.8Si-C

and

Fe-6.45Mn-C

Multi-Component Diffusion Simulation – Darken's uphill diffusion





Multi-Component Diffusion Simulation – FDM approach for Fe-Si-C

$$\frac{\partial C_k}{\partial t} = -\nabla \cdot J_k = \sum_{j=1}^{n-1} \nabla \cdot (D_{kj}^n \nabla C_j)$$

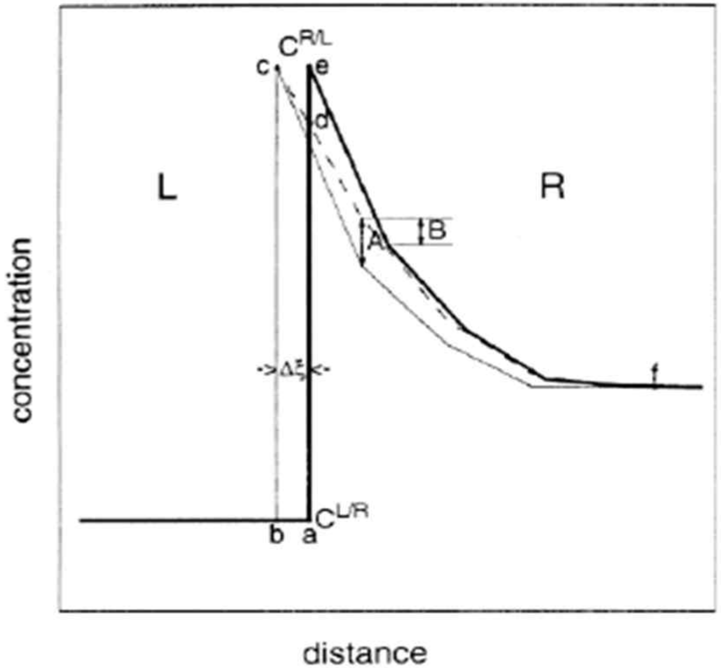
$$\frac{\partial C_C}{\partial t} = \frac{\partial}{\partial x}\left[D_{CC}\frac{\partial C_C}{\partial x} + D_{CSi}\frac{\partial C_{Si}}{\partial x}\right]$$

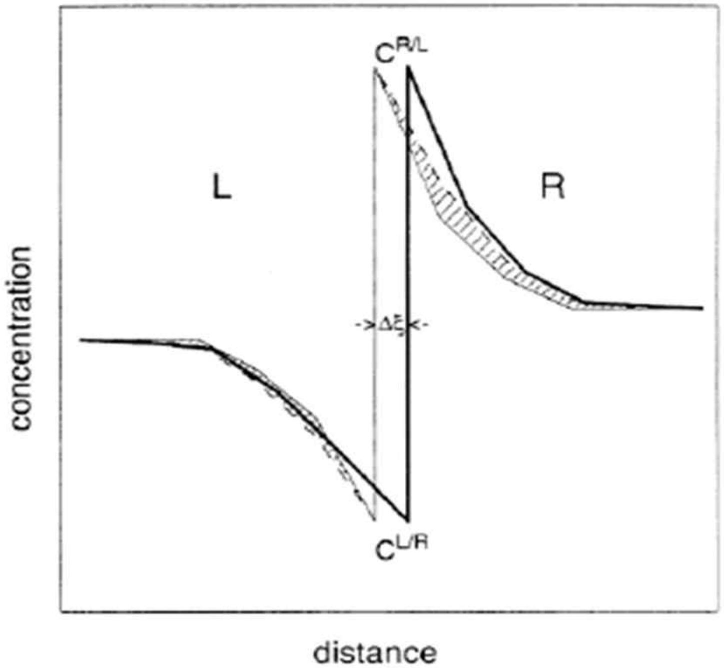
$$\frac{\partial C_{Si}}{\partial t} = \frac{\partial}{\partial x}\left[D_{SiC}\frac{\partial C_C}{\partial x} + D_{SiSi}\frac{\partial C_{Si}}{\partial x}\right]$$

$$\frac{\partial C_i}{\partial t} = \frac{C_i^{j+1} - C_i^j}{\Delta t}$$

$$\frac{\partial}{\partial x}\left[D_i\frac{\partial C_i}{\partial x}\right] = \frac{1}{\Delta x}\left[\frac{D_{i+1}+D_i}{2}\,\frac{C_{i+1}^j - C_i^j}{\Delta x} - \frac{D_i + D_{i-1}}{2}\,\frac{C_i^j - C_{i-1}^j}{\Delta x}\right]$$

Moving Boundary Problem – Basic Equation





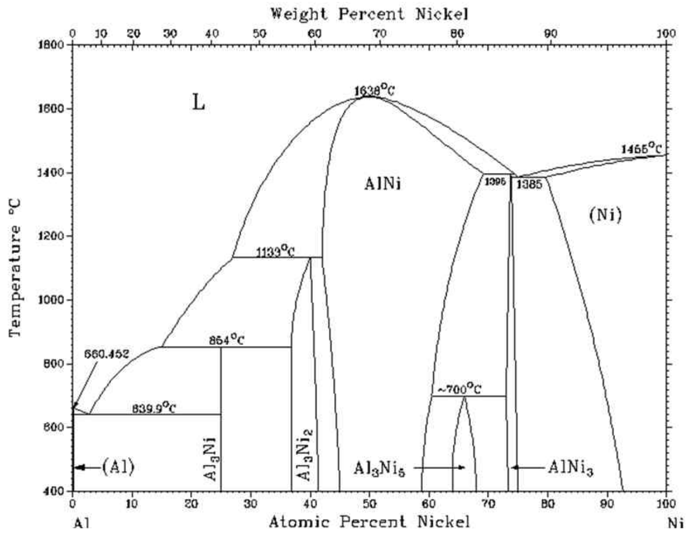
$$v^R C_k^{R/L} - v^L C_k^{L/R} = J_k^{R/L} - J_k^{L/R}$$

$$= v \ (C_k^{R/L} - C_k^{L/R})$$

$$\frac{d\xi}{dt} = \frac{J^{R/L} - J^{L/R}}{C^{R/L} - C^{L/R}}$$

Byeong-Joo Lee
www.postech.ac.kr/~calphad

Binary Diffusion



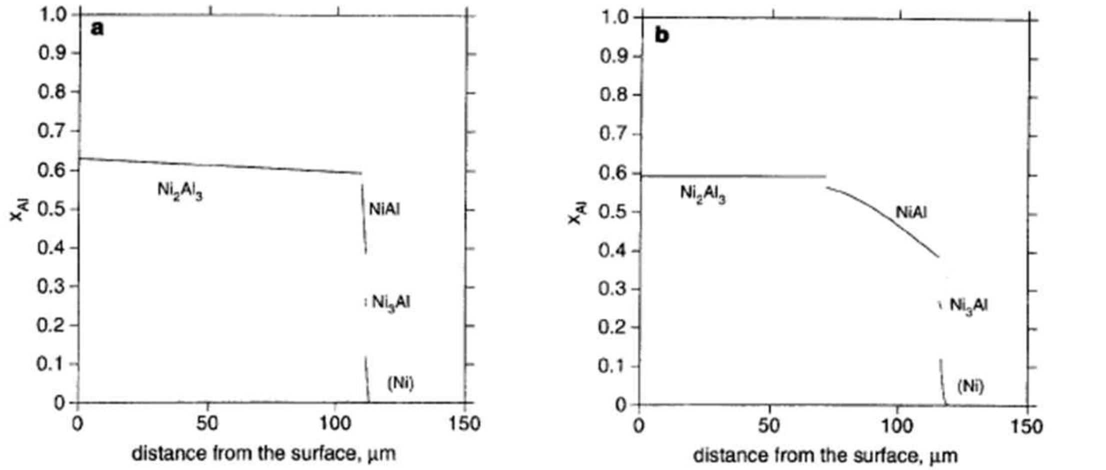
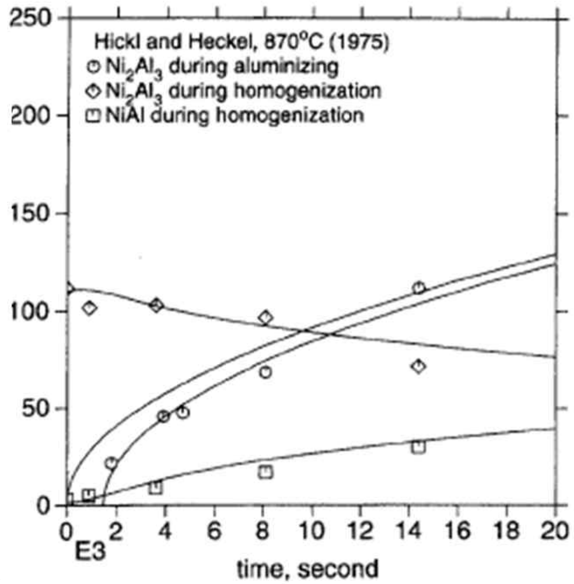
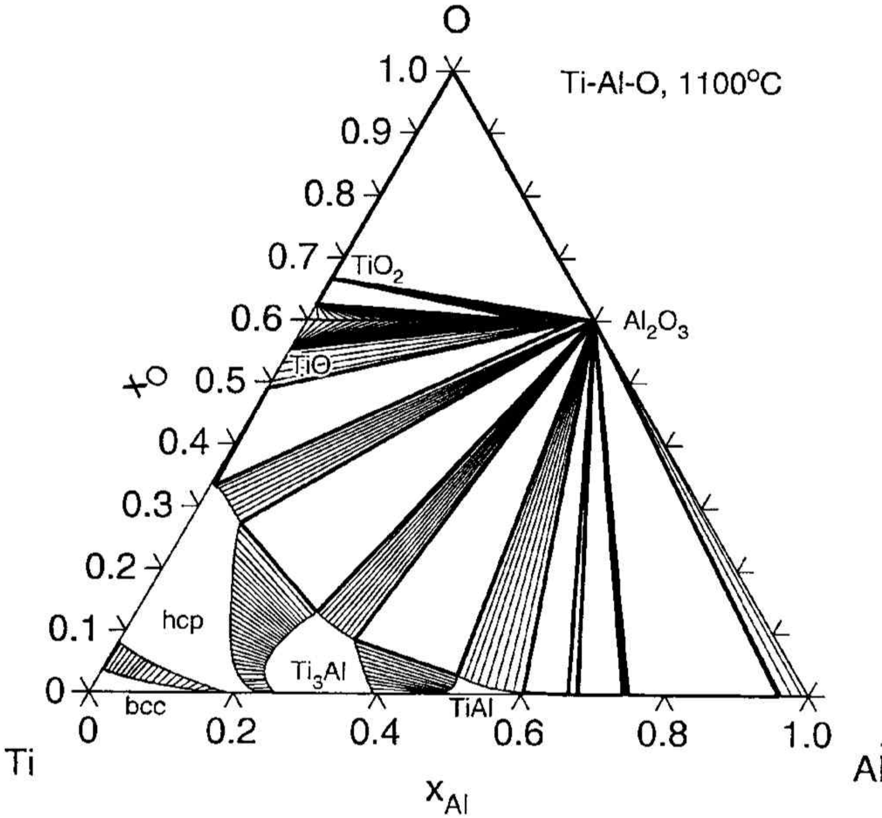
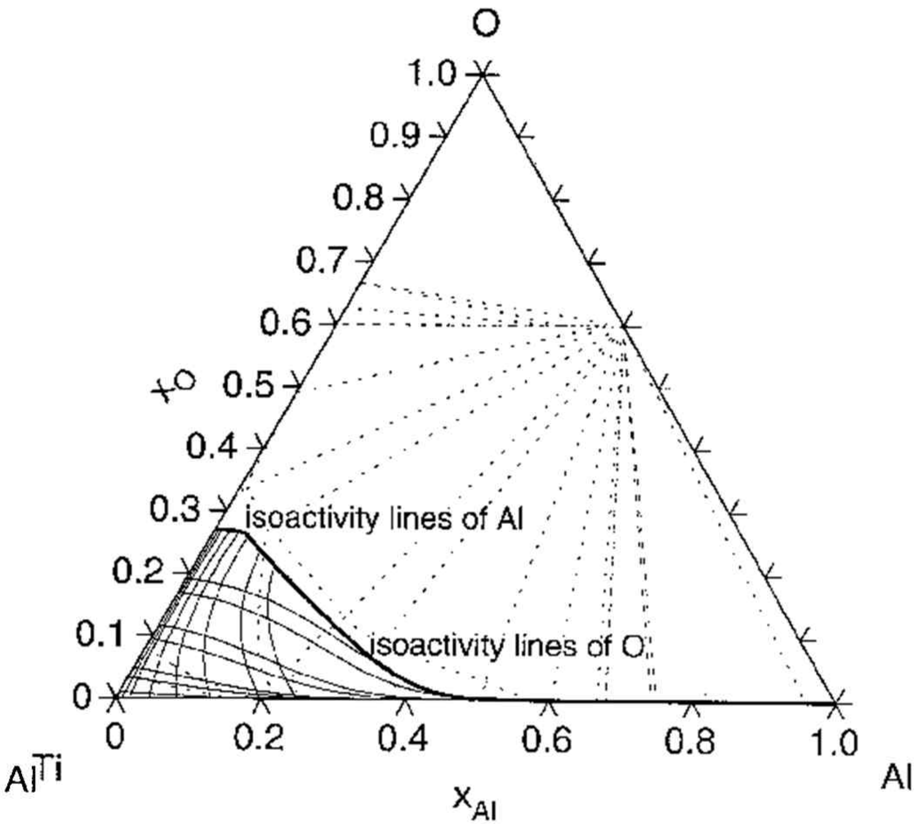


Fig. 7. Simulated composition profile of Al (a) after aluminizing of Ni for 14400s at 870°C and (b) after continued homogenization for 22500s at the same temperature.

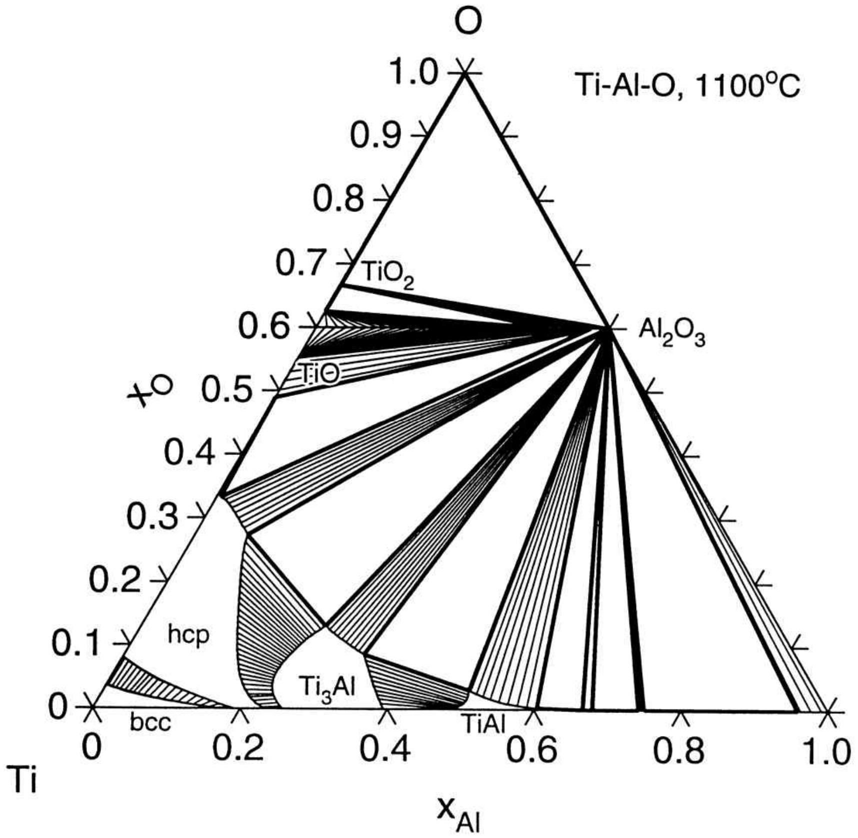


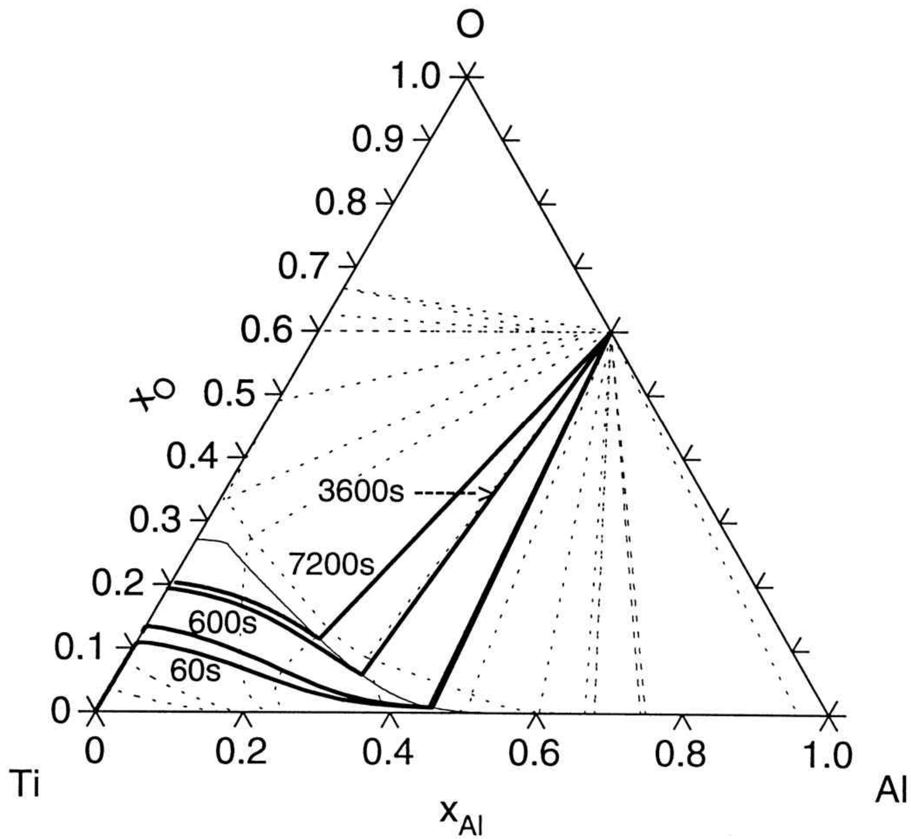
Application to Interfacial Reactions – Ti/Al_2O_3 Reaction



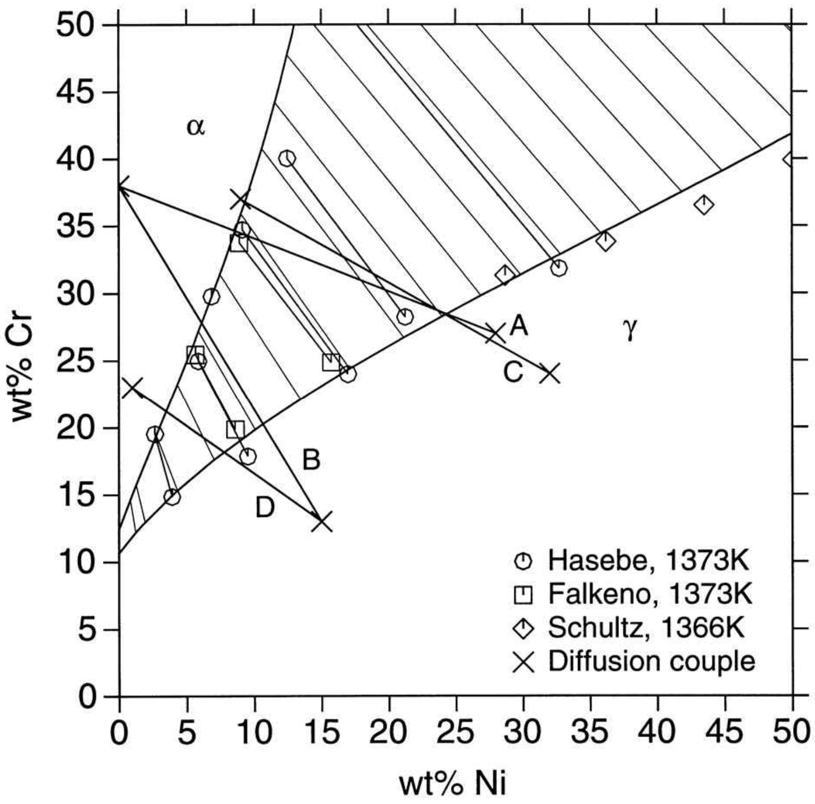


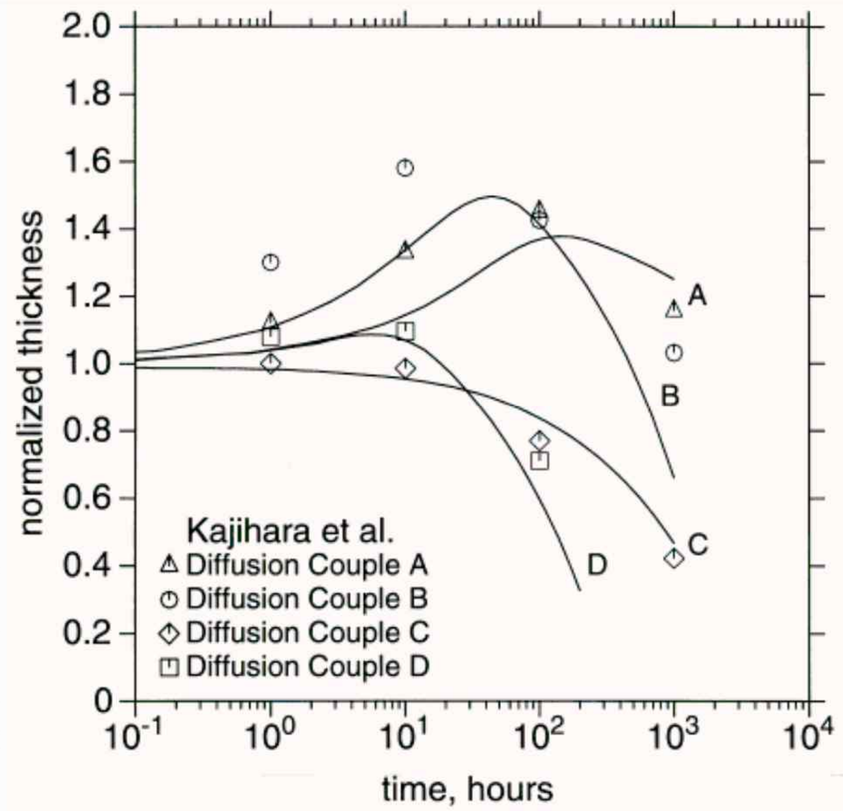
Application to Interfacial Reactions – Ti/Al_2O_3 Reaction





Multi-Component Diffusion Simulation – Case Study : Fe-Cr-Ni





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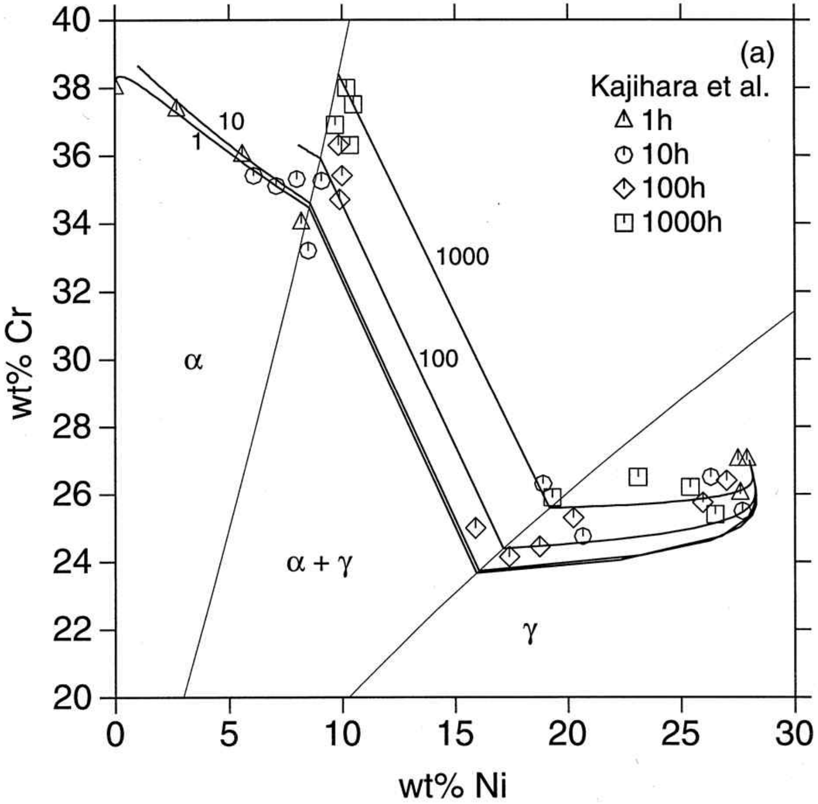
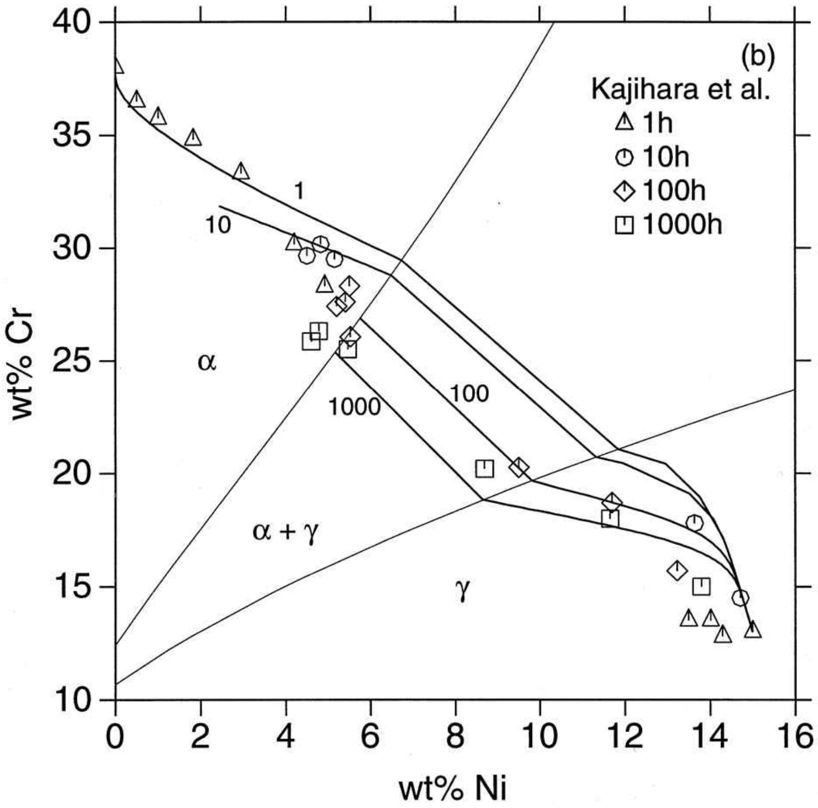




Multi-Component Diffusion Simulation – between Multi-Phase Layers

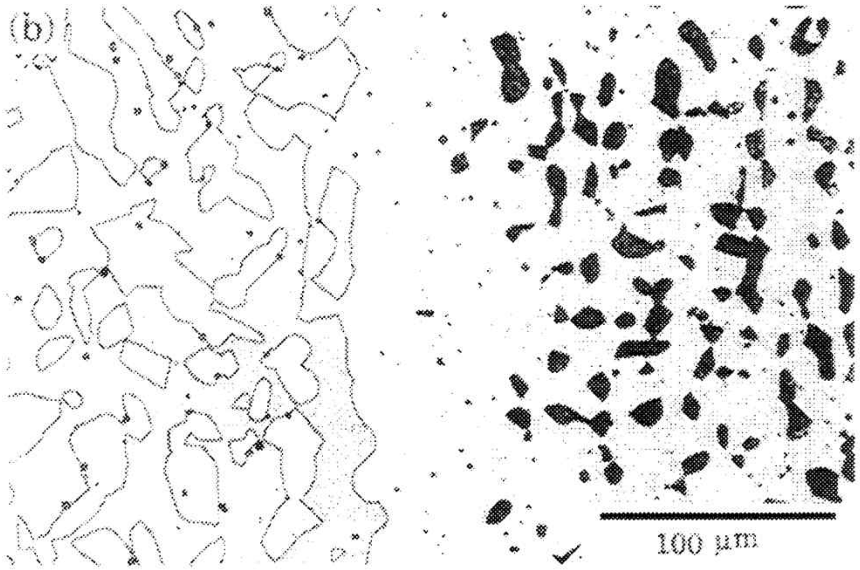
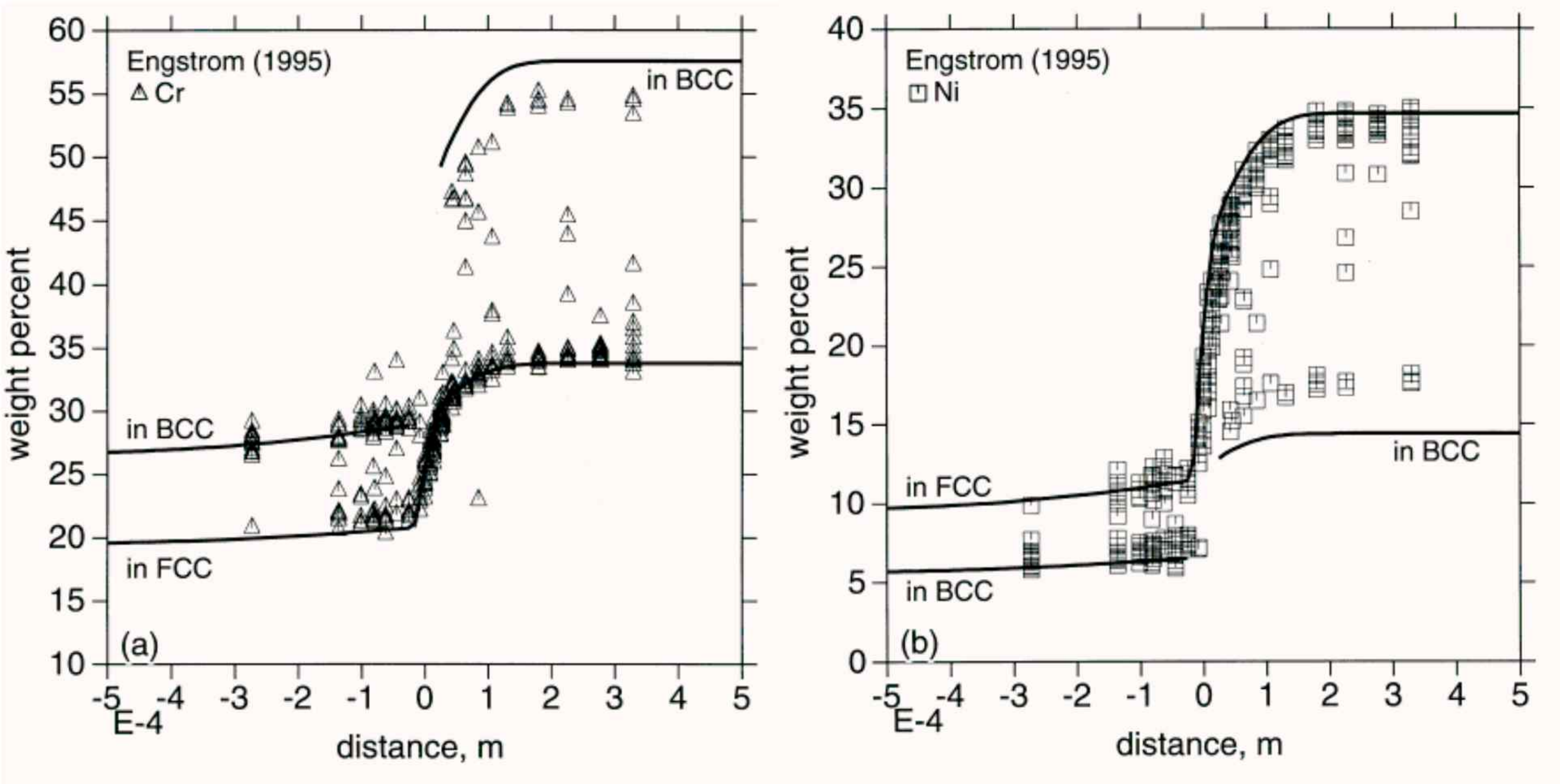


Fig. 14. (a) Microstructure of couple k5-k7 after a diffusion anneal at 1100°C for 100 h. (b) Same as (a) but different scale.

$$u_k = \sum_j p^j u_k^j$$

$$\Delta\xi = \frac{2(J_k^{R/L} - J_k^{L/R}) \cdot \Delta t + 2\Delta m_k^{corr}}{(u'^{R/L}_k + u'_{k,m+1} - u'^{L/R}_k - u'_{k,m})}$$

Multi-Component Diffusion Simulation – between Multi-Phase Layers



포항공과대학교
Pohang University of Science and Technology

Byeong-Joo Lee
www.postech.ac.kr/~calphad

Multi-Component Diffusion Simulation – between Multi-Phase Layers