
Phase Transformations

Diffusion

Byeong-Joo Lee
POSTECH-CMSE



포항공과대학교
Pohang University of Science and Technology

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

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

$$\cdot J_A = - D_A \frac{\partial n_A}{\partial x}$$

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

$$\cdot J_A + J_B + J_V = 0$$

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

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

Assume that molar volume of A and B is equal to each other.

$$(n_t = n_A + n_B = \text{constant})$$

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



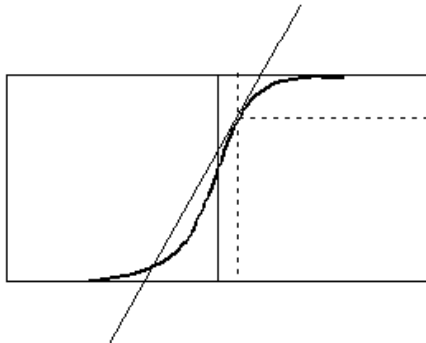
Diffusion Coefficient – Inter Diffusion

▷ with respect to volume fixed frame,

$$\begin{aligned}\mathcal{J}_B &= J_B + N_B n_t v = J_B - N_B (J_A + J_B) \\ &= - (N_B D_A + N_A D_B) \frac{\partial n_B}{\partial x} = - \bar{D} \frac{\partial n_B}{\partial x}\end{aligned}$$

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

ex)



Distance of marker plane from Matano plane : 0.01 cm

Annealing time : 18000 sec

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

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

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

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

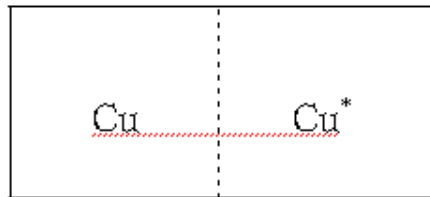
$$5.5 \times 10^{-8} = 0.35 D_A + 0.65 D_B$$

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



Diffusion Coefficient – Self/Tracer Diffusion

☐ Self Diffusion Coefficient



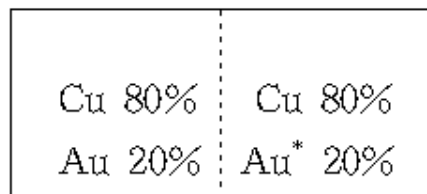
$$\bar{D} = N_B D_A + N_A D_B$$

$$D_A = D_B = D$$

$\bar{D}$: constant

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

☐ Tracer Diffusion Coefficient



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

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

$D_{Au^*}^*$ ← Grube method



Diffusion Coefficient – Intrinsic Diffusion Coefficient

□ Intrinsic Diffusion Coefficient

$$\cdot J_A = - D_A \frac{\partial n_A}{\partial x} = - D_A n_t \frac{\partial N_A}{\partial x}$$

· ideal solution

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

$$\begin{aligned} \cdot J_A &= - \frac{D_A}{RT} n_A \frac{\partial \mu_A}{\partial x} \\ &= - B_A n_A \frac{\partial \mu_A}{\partial x} \quad (B_A : \text{mobility}) \end{aligned}$$

※ Tracer Diffusion

· Non-ideal solution

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

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

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

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

$$\begin{aligned} \cdot D_A^* &= B_A^* RT \left[1 + N_A \frac{\partial \ln \gamma_{A+A^*}}{\partial N_A} \right] \\ &= B_A^* RT \end{aligned}$$

$$B_A^* = B_A$$

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



Diffusion Coefficient – Inter Diffusion Coefficient

□ Inter-diffusion Coefficient

$$\begin{aligned} \cdot \quad \bar{D} &= N_B D_A + N_A D_B \\ &= N_B D_A^* \left[1 + N_A \frac{\partial \ln \gamma_A}{\partial \ln N_A} \right] + N_A D_B^* \left[1 + N_B \frac{\partial \ln \gamma_B}{\partial \ln N_B} \right] \end{aligned}$$

· Gibbs-Duhem Eq.

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

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

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

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



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

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



Diffusion Coefficient – Modeling

- 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°

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

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

- the same for the D° term

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

- ❖ Both Q° & Q are modeled as a linear function of composition



Modeling of Multi-Component Diffusion - Basic Assumption

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

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

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

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

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

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



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

$$\bullet \quad J_i = - L_i \nabla \mu_i$$

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

$$n^* = n \quad \text{for substitutional solution}$$

$$n^* = n + 1 \quad \text{for interstitial solution (including vacancy)}$$

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

$$\begin{aligned} J_k &= \tilde{J}_k - u_k \sum_{i \in S} \tilde{J}_i = \sum_{i \in S} \delta_{ik} \tilde{J}_i - \sum_{i \in S} u_k \tilde{J}_i = \sum_{i \in S} (\delta_{ik} - u_k) \tilde{J}_i \\ &= - \sum_j^{n^*} [\sum_{i \in S} (\delta_{ik} - u_k) L_i \frac{\partial \mu_i}{\partial u_j} V_S] \nabla C_j \end{aligned}$$

$$\bullet \quad L_i = u_i y_{Va} M_{iVa}$$

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

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



Mathematical Formalism of Multi-Component Diffusion Coefficient

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

- $J_k = - \sum_{j=1}^{n^*} \left[u_k y_{Va} \Omega_k \frac{\partial \mu_k}{\partial u_j} \right] \nabla C_j$ 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



Mathematical Formalism - Application to Binary and Ternary Solutions

□ Application to binary and ternary solutions

▷ Application to an Fe-M substitutional binary solution

$$\begin{aligned}
 J_M &= -[y_{Fe} y_M \Omega_M \left(\frac{\partial \mu_M}{\partial y_M} - \frac{\partial \mu_M}{\partial y_{Fe}} \right) - y_M y_{Fe} \Omega_{Fe} \left(\frac{\partial \mu_{Fe}}{\partial y_M} - \frac{\partial \mu_{Fe}}{\partial y_{Fe}} \right)] \nabla C_M \\
 &= - \left[y_{Fe} y_M \Omega_M \frac{d\mu_M}{dy_M} - y_M y_{Fe} \Omega_{Fe} \frac{d\mu_{Fe}}{dy_M} \right] \nabla C_M \\
 &= - \left[y_{Fe} \Omega_M RT + y_M \Omega_{Fe} RT \right] \left(1 + \frac{d \ln \gamma_M}{d \ln y_M} \right) \nabla C_M
 \end{aligned}$$

※ 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

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



Mathematical Formalism - Application to Binary and Ternary Solutions

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

▷ Application to the Fe-C interstitial binary solution

$$\begin{aligned} J_C &= - y_C y_{Va} \Omega_C \left(\frac{\partial \mu_C}{\partial y_C} - \frac{\partial \mu_C}{\partial y_{Va}} \right) \nabla C_C \\ &= - y_C y_{Va} \Omega_C \frac{d\mu_C}{dy_C} \nabla C_C \\ &= - \Omega_C RT \left(1 - \frac{2y_C y_{Va}}{RT} \cdot L_{Fe Va, C} \right) \nabla C_C \end{aligned}$$

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

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



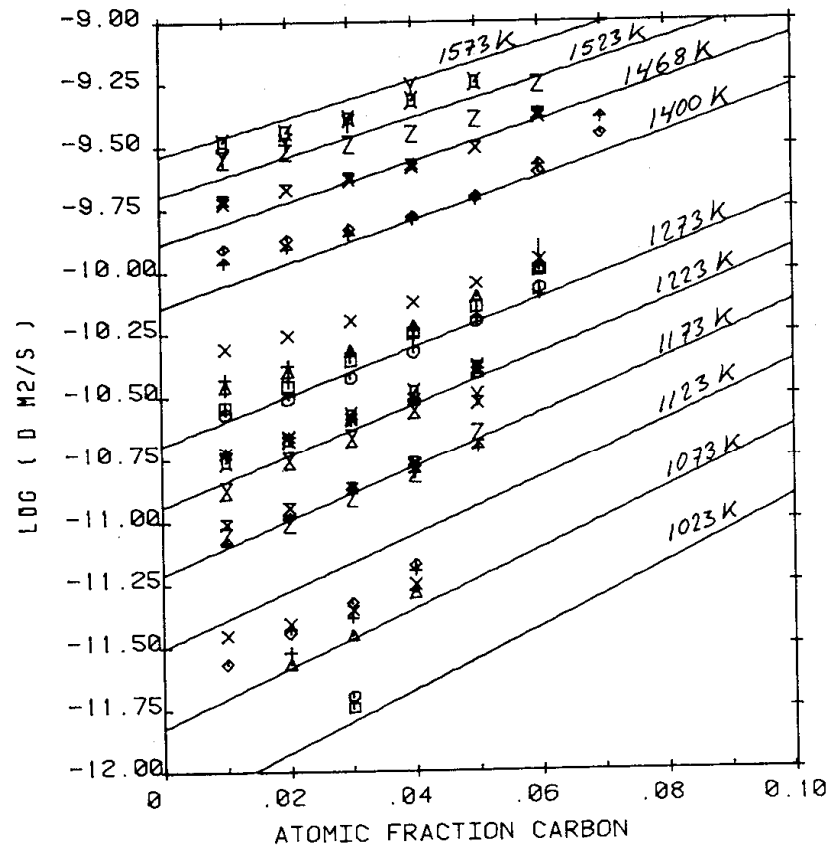
Mathematical Formalism - Application to Binary and Ternary Solutions

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		8.06	157.0	—	773-873	IIIa(i) 212
Bi	Pb		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	—	
0-0.7 (wt.%)	$\left\{ \begin{array}{l} 0 \\ 5.8 \\ 10.6 \\ 20.2 \end{array} \right\}$	(γ)	$\left\{ \begin{array}{l} 0.04 + 0.08 c \\ 0.04 + 0.08 c \\ 0.03 + 0.1 c \\ 0.03 + 0.06 c \end{array} \right\}$	$\left\{ \begin{array}{l} 131.3 \\ 127.7 \\ 125.2 \\ 120.8 \end{array} \right\}$		1 273-1 473	IIa(i) 146
			(c = wt.%C)				
C	Fe		3.94×10^{-3}	80.2	—	313-623	Various 215
0-0.1	(α)		$D = 4.53 \times 10^{-3} [1 + y_c(1 - y_c) 8339.9/T] \exp [-(T^{-1} - 2.221 \times 10^{-4} \times 17767 - 26436 y_c)]$				
γ -range			$y_c = x_c/(1 - x_c),$	$x_c = \text{mol fraction of C}$			42
α -range			$\text{Log } D = -0.9064 - 0.5199\chi + 1.61 \times 10^{-3}\chi^2$			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).

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



Mathematical Formalism - Application to Binary and Ternary Solutions

▷ 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

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

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

$$y_C + y_{Va} = 1$$

$$y_{Fe} + y_M = 1$$

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

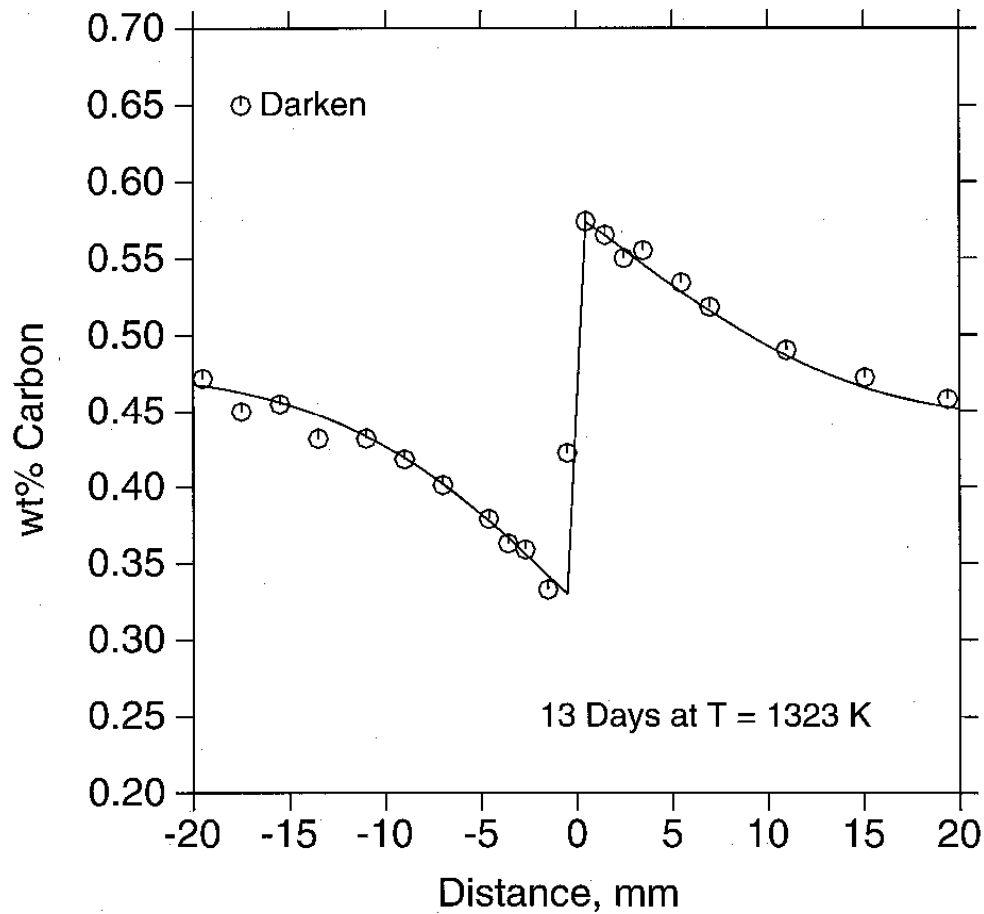
$$D_{CC} = y_C y_{Va} M_{CVa} \left(\frac{d\mu_C}{dy_C} \right)_{y_M} V_S$$

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

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



Multi-Component Diffusion Simulation – Darken's uphill diffusion



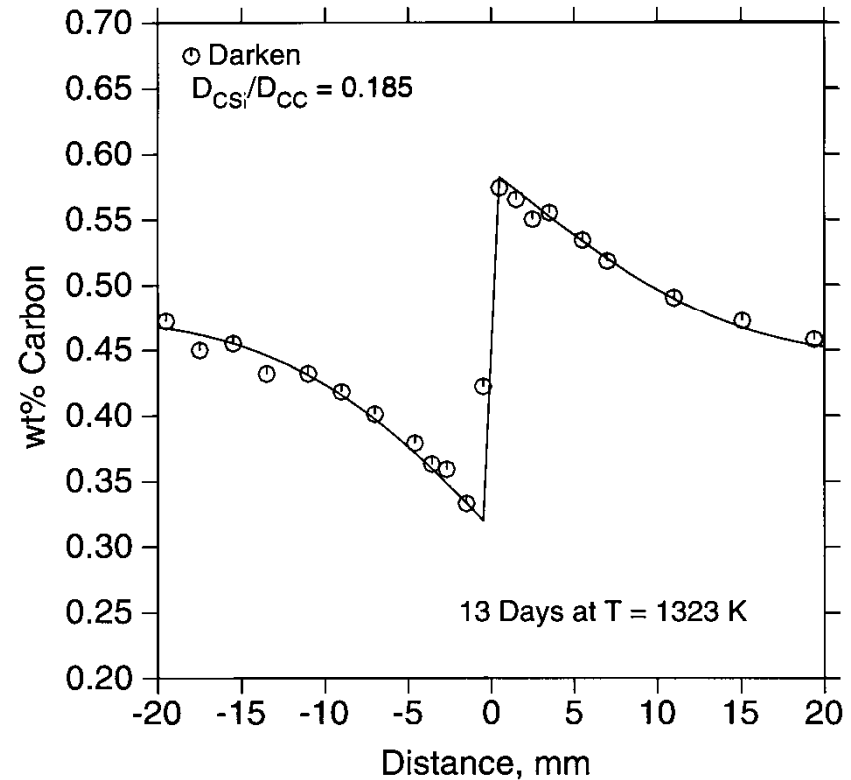
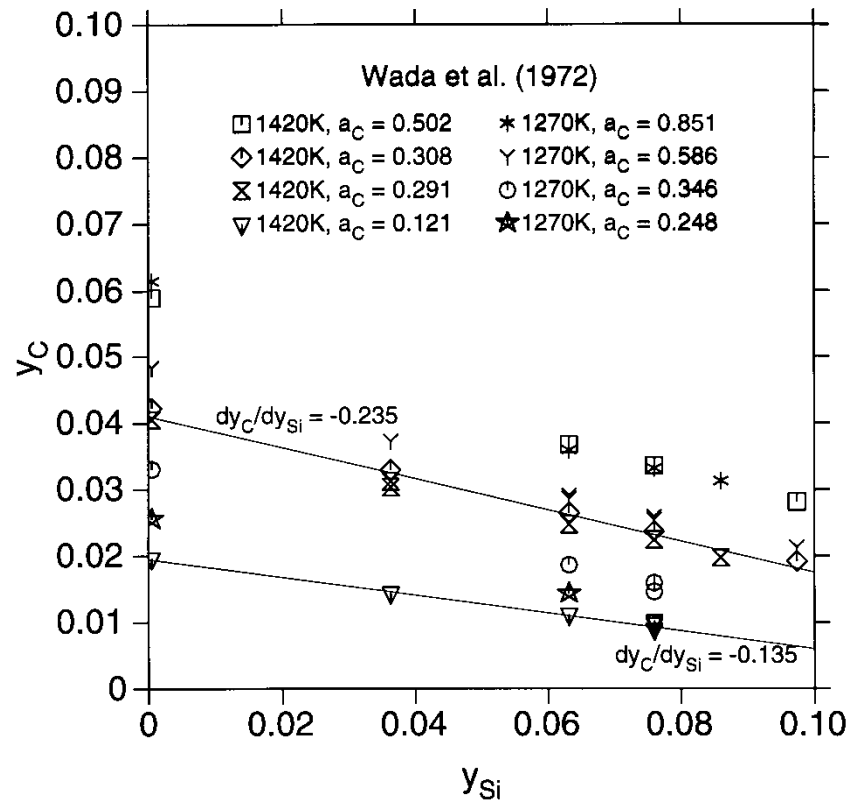
Fe-3.8Si-C

and

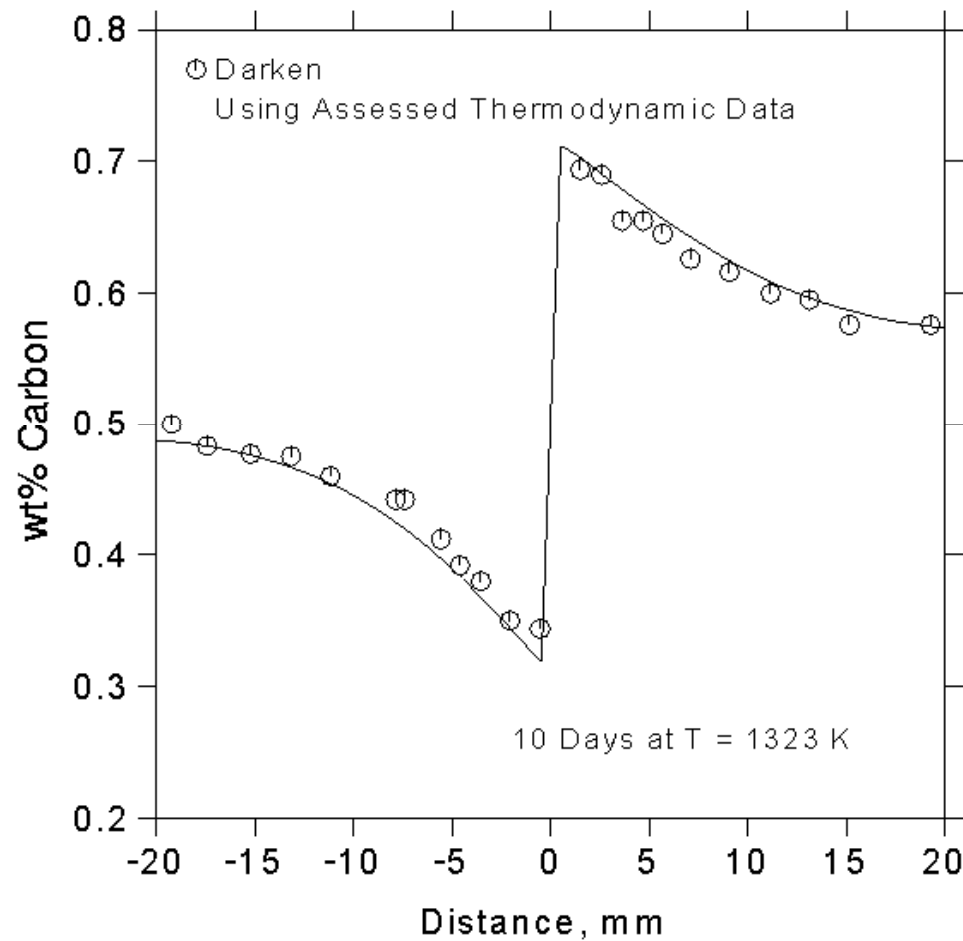
Fe-C



Multi-Component Diffusion Simulation – Darken's uphill diffusion



Multi-Component Diffusion Simulation – Darken's uphill diffusion



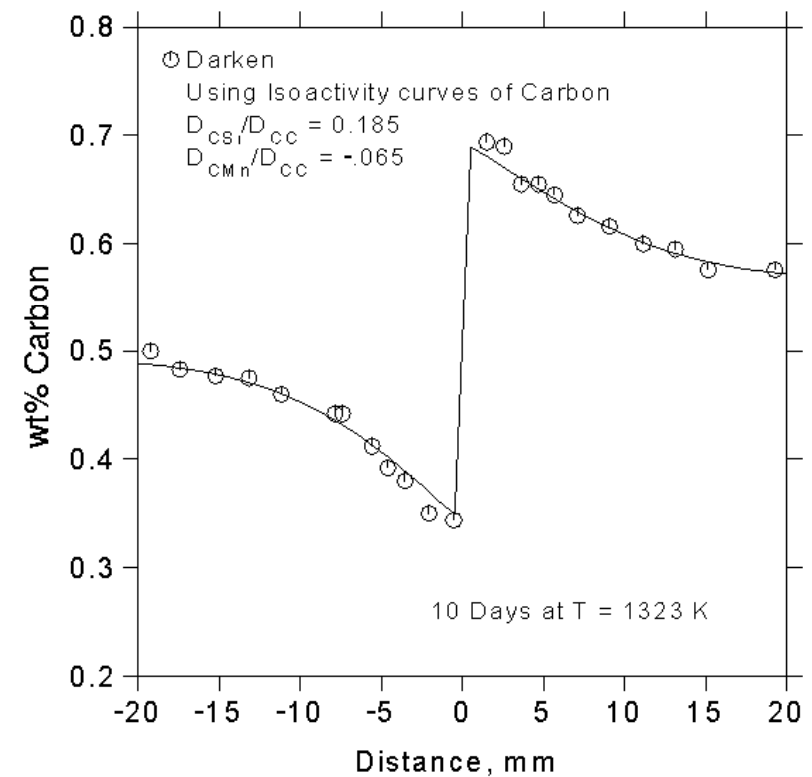
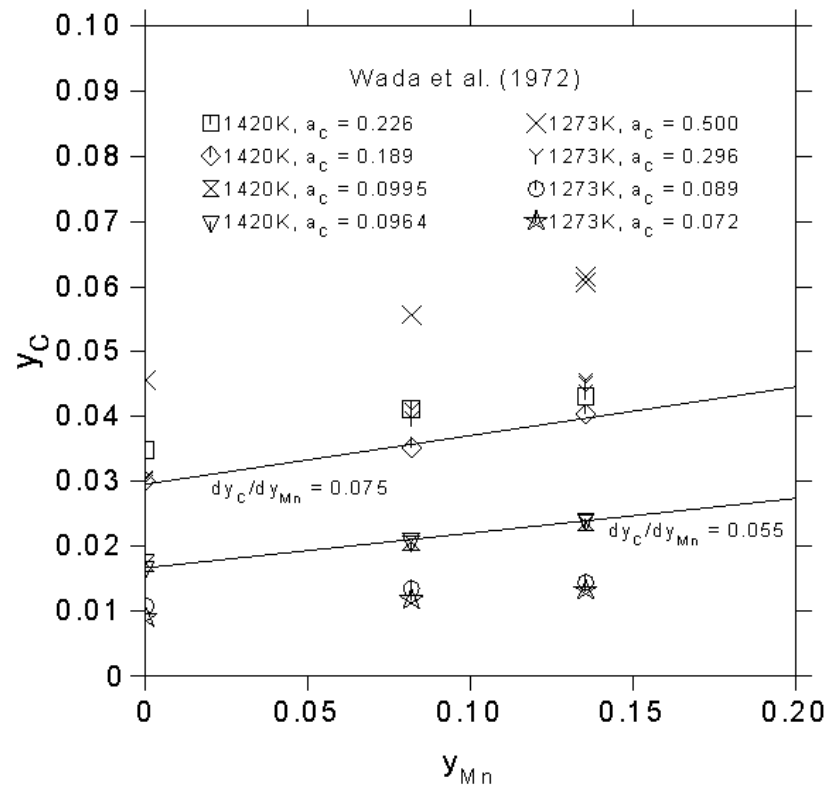
Fe-3.8Si-C

and

Fe-6.45Mn-C



Multi-Component Diffusion Simulation – Darken's uphill diffusion



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

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

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

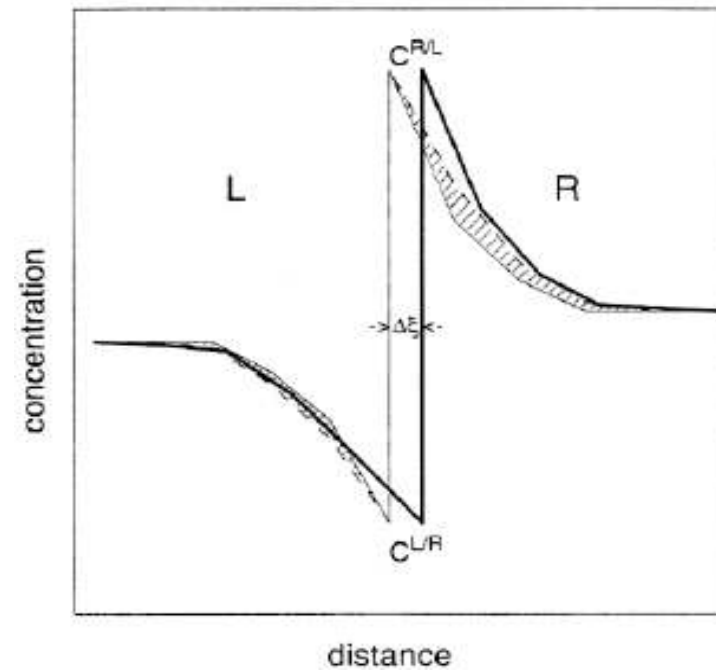
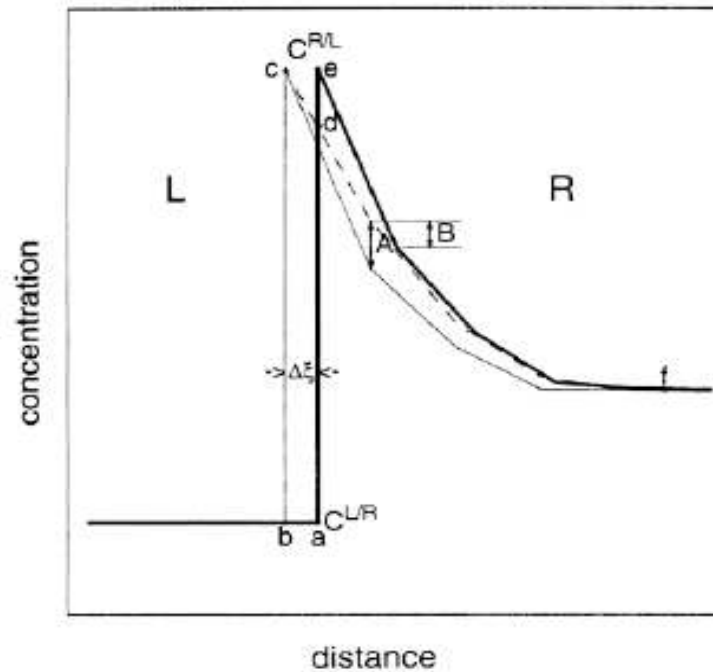
$$\frac{\partial C_{Si}}{\partial t} = \frac{\partial}{\partial x} \left[D_{SiC} \frac{\partial C_C}{\partial x} + D_{SiSi} \frac{\partial C_{Si}}{\partial x} \right]$$

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

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



Moving Boundary Problem – Basic Equation

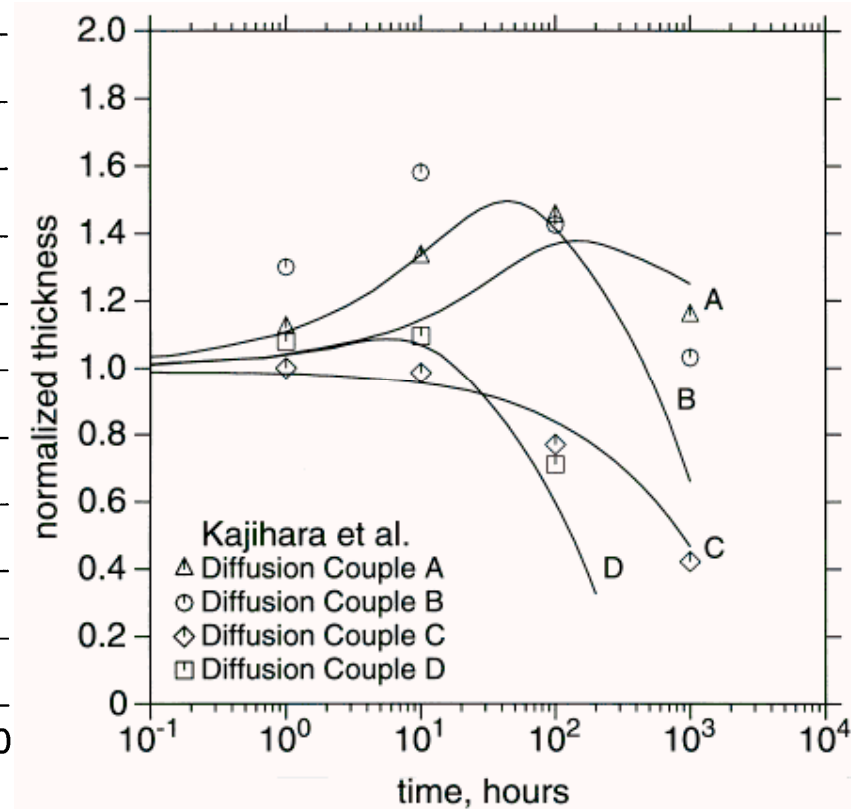
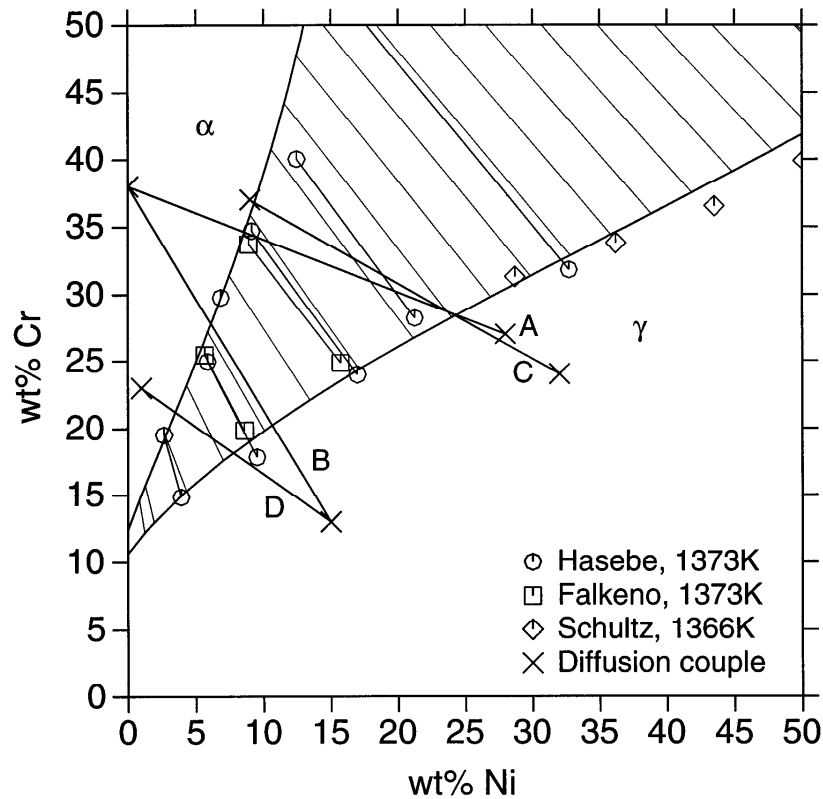


$$\begin{aligned} v^R C_k^{R/L} - v^L C_k^{L/R} &= J_k^{R/L} - J_k^{L/R} \\ &= v (C_k^{R/L} - C_k^{L/R}) \end{aligned}$$

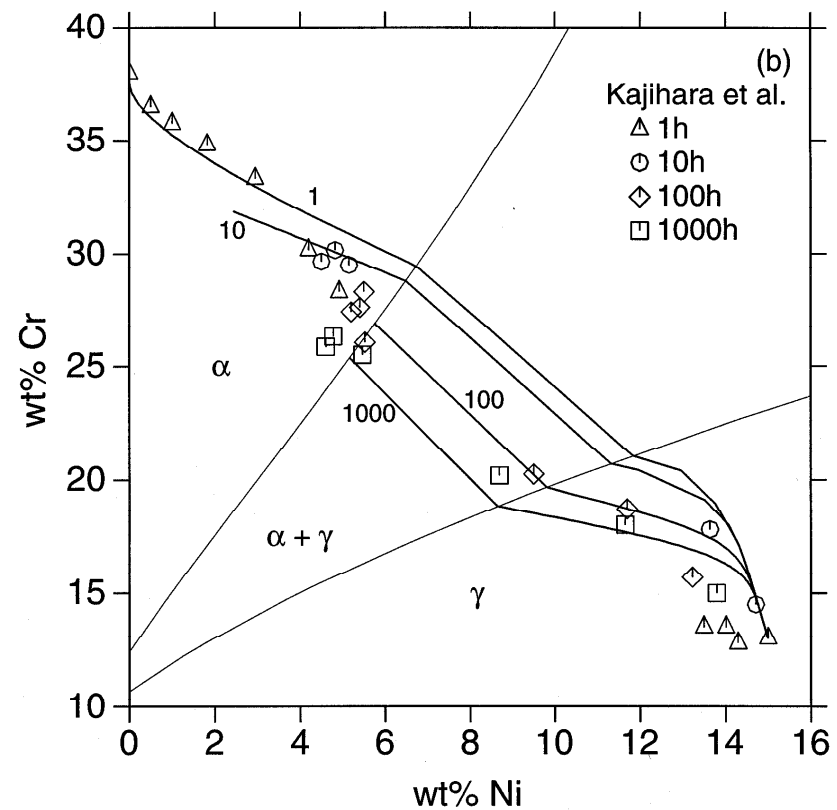
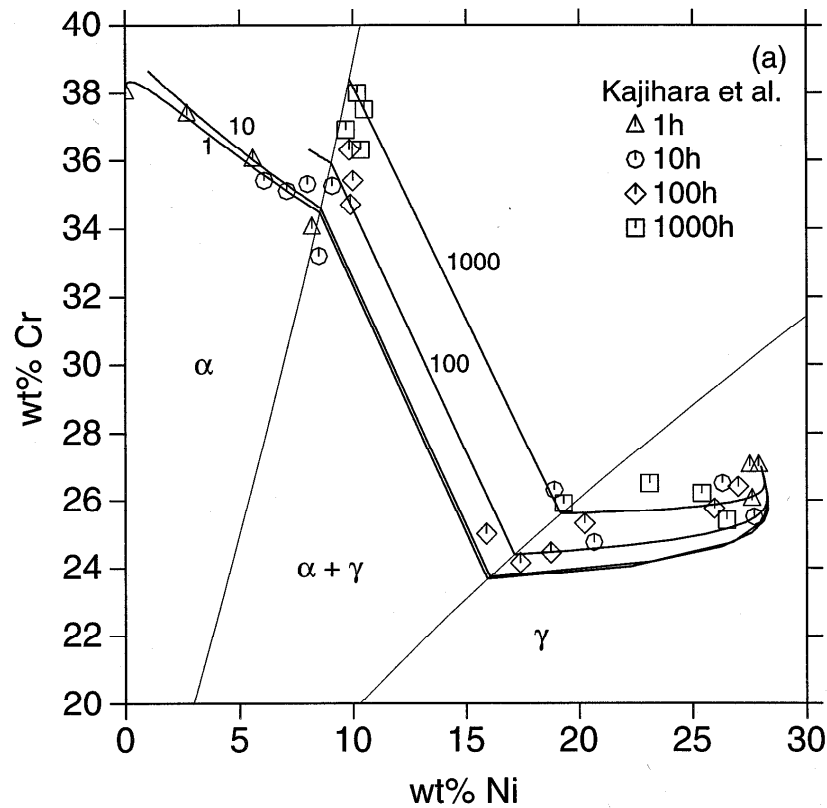
$$\frac{d\xi}{dt} = \frac{J^{R/L} - J^{L/R}}{C^{R/L} - C^{L/R}}$$



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



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



Multi-Component Diffusion Simulation – between Multi-Phase Layers

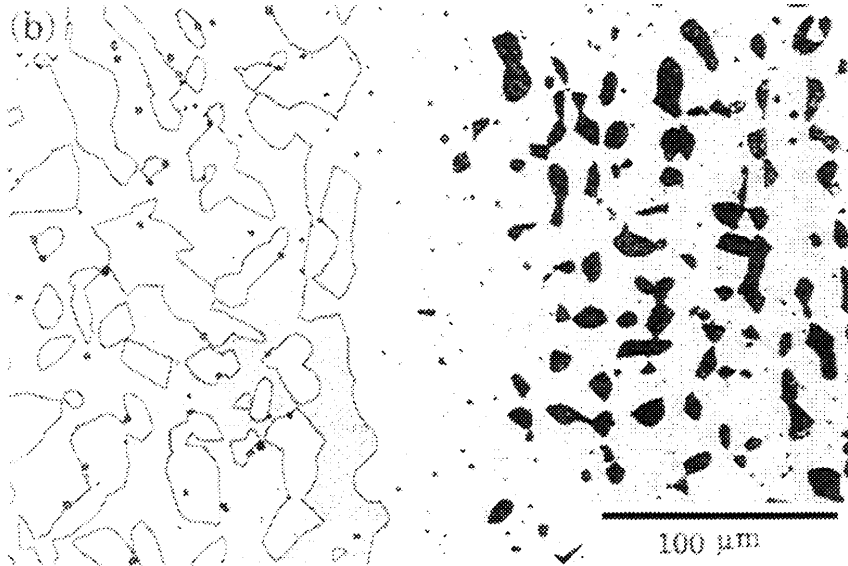


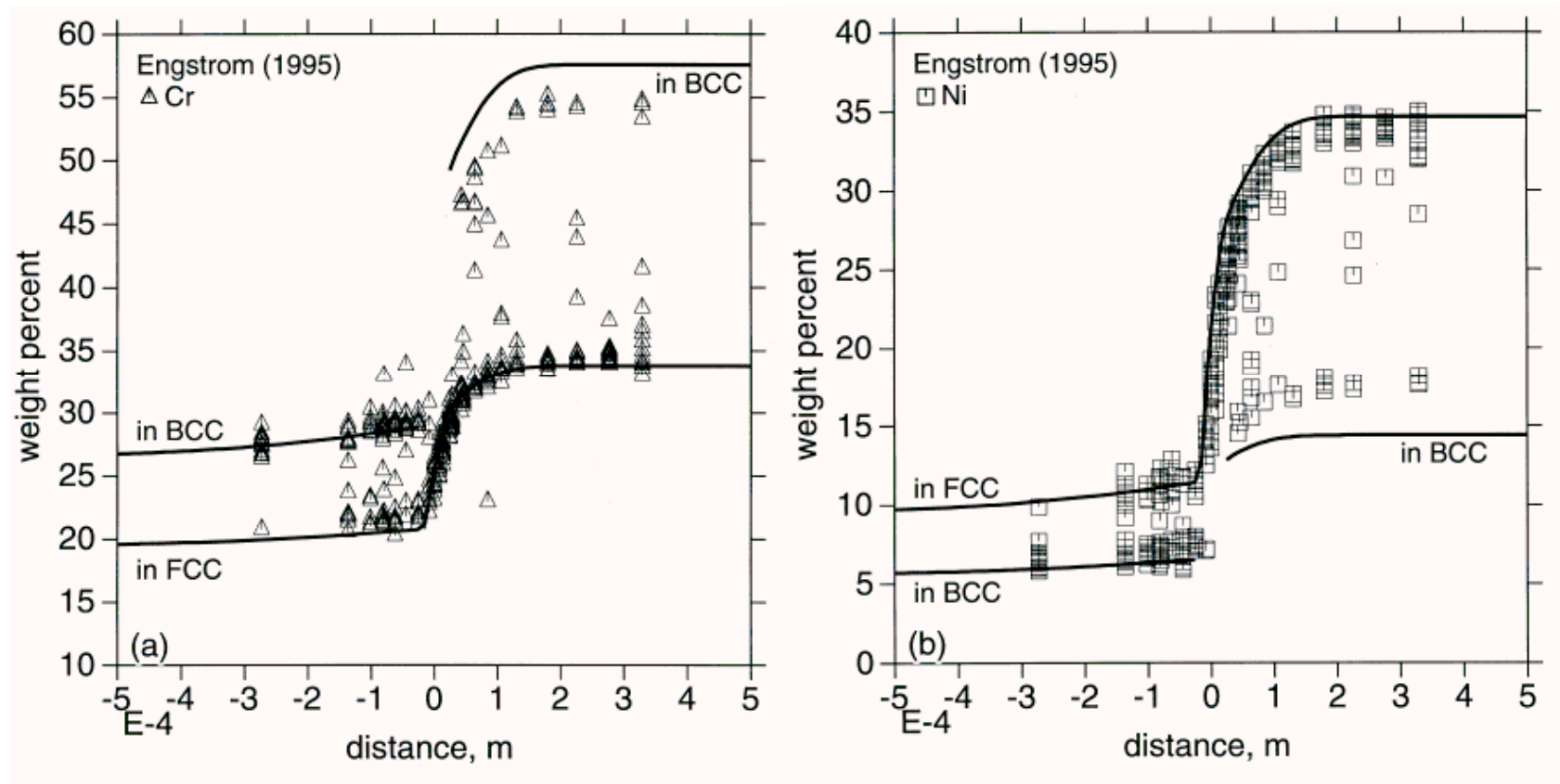
Fig. 14. (a) Microstructure of couple k5-k7 after a diffusion anneal at 1100°C for 100 h. (b) Same as (a) but different scale.

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

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



Multi-Component Diffusion Simulation – between Multi-Phase Layers



Multi-Component Diffusion Simulation – between Multi-Phase Layers

