Diffusion

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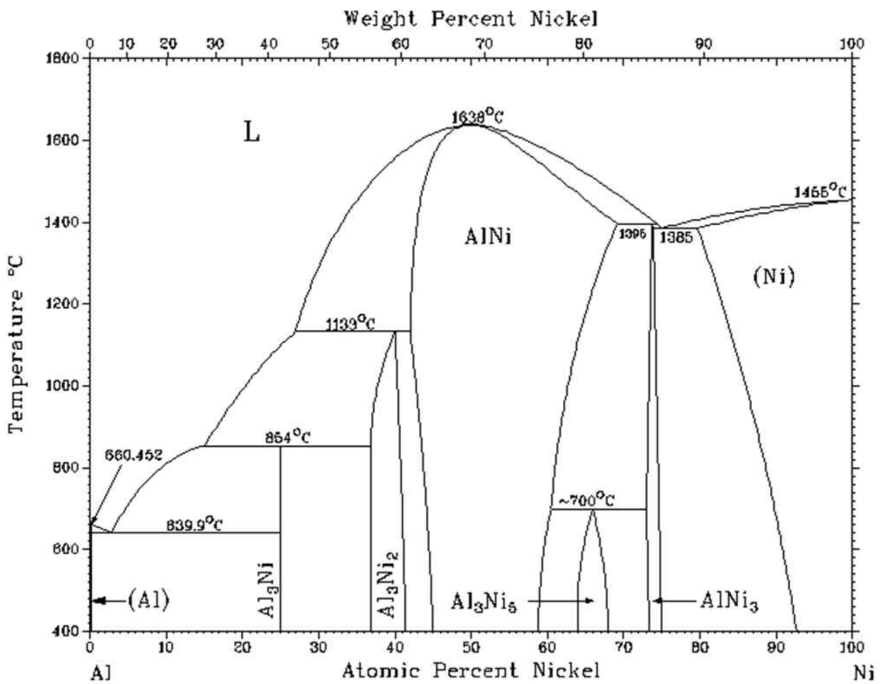
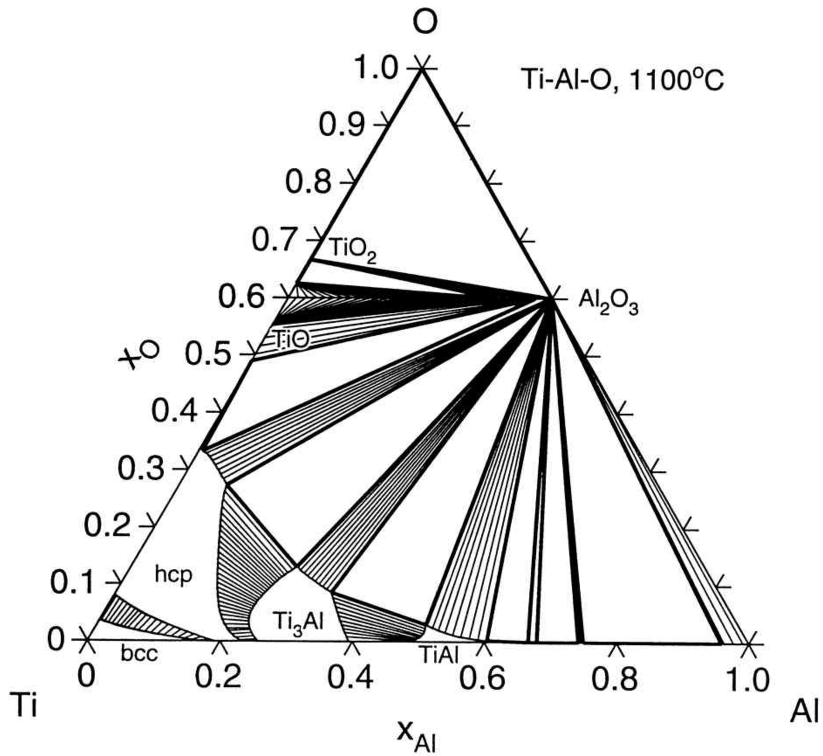
Diffusional Reactions – binary & multicomponent systems

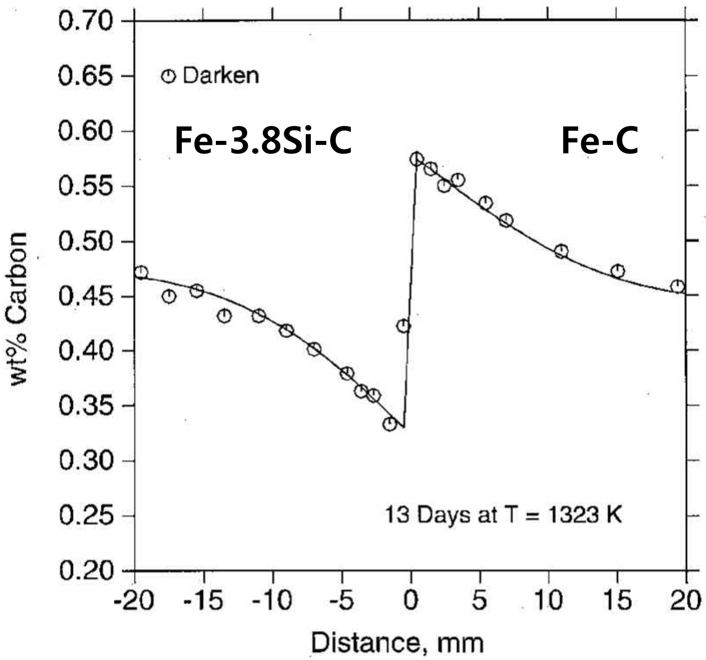




Multicomponent Diffusion

Darken's uphill diffusion

B.-J. Lee, J. Phase Equilibria 22, 241 (2001).



Diffusion between multiphase layers

A. Engström, Scand. J. Metall. 24, 12 (1995).

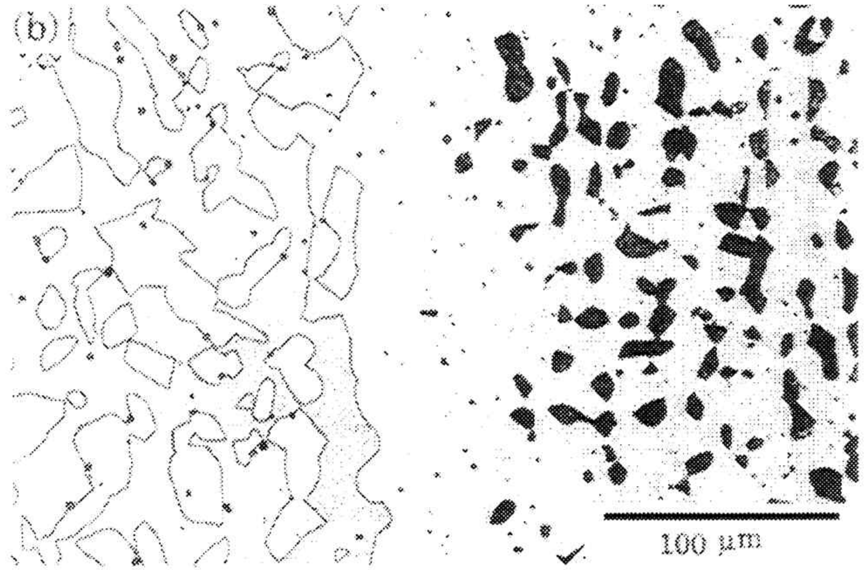


Fig. 14. (a) Microstructure of couple k5-k7 after a diffusion anneal at 1100°C for 100 h. (b) Same as (a) but different scale.

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Definition

Homogenization phenomena by non-convective mass transport due to chemical potential or electrochemical potential difference in a multicomponent single phase

▷ Linear rate law : Phenomenological eq.

result = A · cause

· Fourier's law of heat conduction

$$\dot{q} = -K \cdot \nabla T$$

· Fick's law of diffusion

$$J = -D \cdot \nabla C$$

· Ohm's law of electrical conduction

$$J = -\sigma \cdot \nabla \phi$$

· Newton's law of viscous flow

$$\tau_{xy} = -\eta \cdot \frac{\partial v_x}{\partial y}$$

⇒ for isotropic cases & for small deviation from equilibrium and with only direct effect

⇒ for Non-isotropic cases

$$\vec{J} = -[D_{ij}] \nabla C$$

General Phenomenological Equation

▷ $J_i = -D_i \nabla C_i + D_i^{'} (\nabla C_j)^2 + D_i^{''} (\nabla C_j)^3 + \cdots$

⇒ First term approximation near thermodynamic equilibrium

▷ General Phenomenological Equation

$J_i = -L_{ij} \nabla C_j + L_{iT} \nabla T + L_{i\phi} \nabla \phi + \cdots$

⇒ Direct effect : mass transport due to concentration gradient

⇒ Cross effect :

- thermomigration
- electromigration
- thermoelectricity
- pyroelectricity, piezoelectricity

Fick's 1st law

▷ Fick's 1st law

$$J_i = -D_i \frac{\partial C_i}{\partial x}$$

unit of D : $cm^2\ sec^{-1}$

▷ Order of D

· metal	:	$D \simeq 10^{-8}$ cm^2/sec near T_m
· semiconductor	:	$D \simeq 10^{-12}$
· liquid	:	$D \simeq 10^{-4} \sim 10^{-5}$
· gas	:	$D \simeq 10^{-1}$
· oxide	:	anion (−) $D_- \simeq 10^{-8} \sim 10^{-10}$
		cation (+) $D_+ \simeq 10^{3} \sim 10^{4} \times D_-$

Fick's 2nd law

▷ Fick's 2nd law

$$\frac{d}{dt}\int_v C\,dv = -\oint_A \vec{J}\cdot\vec{n}\,dA = -\int_v \nabla\cdot\vec{J}\,dv$$

· continuity equation

$$\frac{\partial C}{\partial t} = -\nabla\cdot J$$

$$: \vec{J} = -D\nabla C \quad\Rightarrow\quad \frac{\partial C}{\partial t} = \nabla\cdot(D\nabla C)$$

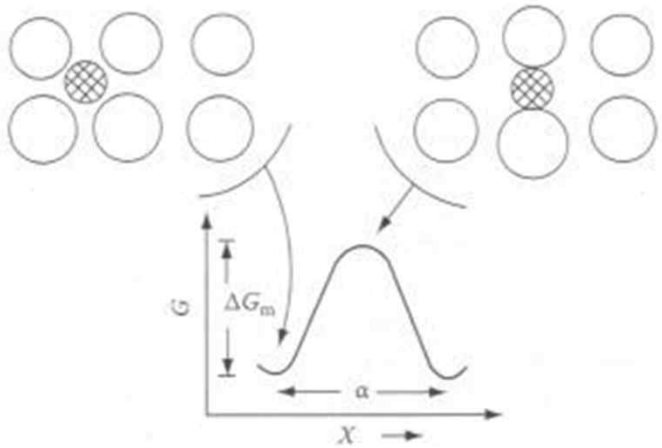
$$: \mathit{if}\ D \neq D(C) \quad\Rightarrow\quad \frac{\partial C}{\partial t} = D\nabla^2 C$$

· if ∃ source or sink

$$\frac{d}{dt}\int_v C\,dv = -\int_S \vec{J}\cdot d\vec{\sigma} + \int_v \dot{q}\,dv$$

$$\Rightarrow \frac{\partial C}{\partial t} = -\nabla\cdot J + \dot{q}$$

More about Diffusion Coefficient – Thermal Activation



As a thermally activated process

$$D_B = \frac{1}{6}\Gamma_B \alpha^2$$

$$\Gamma_B = z\upsilon \exp\frac{-\Delta G_m}{RT}$$

$$D_B = \left[\frac{1}{6}\alpha^2 z\upsilon \exp\frac{\Delta S_m}{R}\right]\exp\frac{-\Delta H_m}{RT}$$

$$D_B = D_{B0}\exp\frac{-Q_D}{RT}$$

for interstitial diffusion $Q_D = \Delta H_m$

How about for substitutional diffusion?

Steady State Solution of Diffusion

▷ Steady state

· $\frac{\partial C}{\partial t} = 0 \quad \Rightarrow \quad J = constant$

$\Rightarrow D = -\frac{J}{\partial C/\partial x}$

※ D can be determined by measuring C and C gradient

▷ Steady state solution

: $\nabla \cdot (D \nabla C) = 0$

: $if \ D \neq D(C) \quad \Rightarrow \quad D \nabla^2 C = 0$: Laplace Eq.

· for 1-dim. case

· Cartesian : $D \frac{d^2C}{dx^2} = 0;$ $\quad C = A + B x$

· Cylindrical : $D \left(\frac{d^2C}{dr^2} + \frac{1}{r} \frac{dC}{dr} \right) = 0;$ $\quad C = A + B \ln r$

· Spherical : $D \left(\frac{d^2C}{dr^2} + \frac{2}{r} \frac{dC}{dr} \right) = 0;$ $\quad C = A + \frac{B}{r}$

Non-Steady State Solution of Diffusion

Non-Steady State Solution

; steady state solution form as $t \rightarrow \infty$

- Error-fn. form : Superposition
  - -. Short time solution
  - -. Initial stage of diffusion $(\delta/L << 1)$

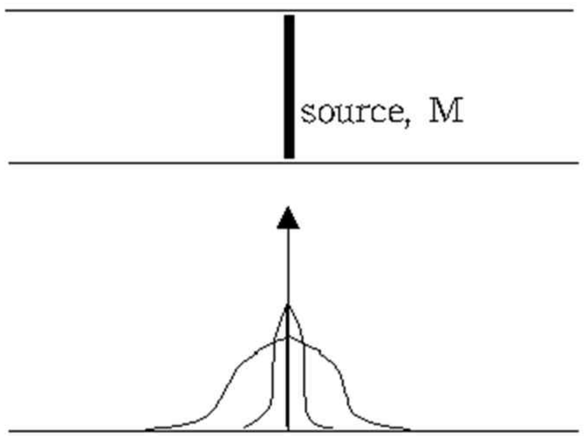
- Trigonometric-series sol. : Separation of variable
  - -. Long time solution
  - -. Late stage of diffusion

- Boltzman-Matano Analysis

Non-Steady State Solution of Diffusion - Superposition Principle

☐ Superposition Principle

▷ Thin film source (planar source)



$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2}$$

$$C(|x|>0,\ t=0) = 0$$
$$C(x=0,\ t=0) = \infty$$
$$C(|x|\rightarrow\infty,\ t) = 0$$

$$C(x,t) = \frac{A}{t^{1/2}}\exp\left(-\frac{x^2}{4Dt}\right)$$

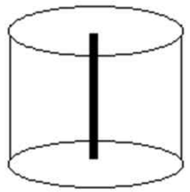
$$\int_{-\infty}^{\infty} C(x,t)\ dx = M \qquad \rightarrow \qquad A = \frac{M}{\sqrt{4\pi D}}$$

Non-Steady State Solution of Diffusion - Superposition Principle

· Layer Deposition

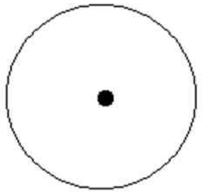
$$C(x,t) = \frac{M}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

· Line source



$$C(r,t) = \frac{M}{4\pi D t} \exp\left(-\frac{r^2}{4Dt}\right)$$

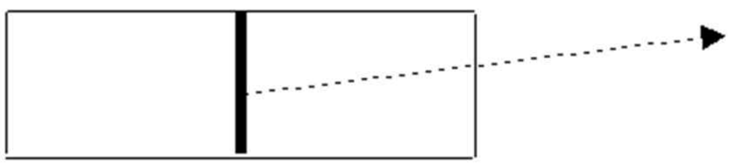
· Point source



$$C(r,t) = \frac{M}{(4\pi D t)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

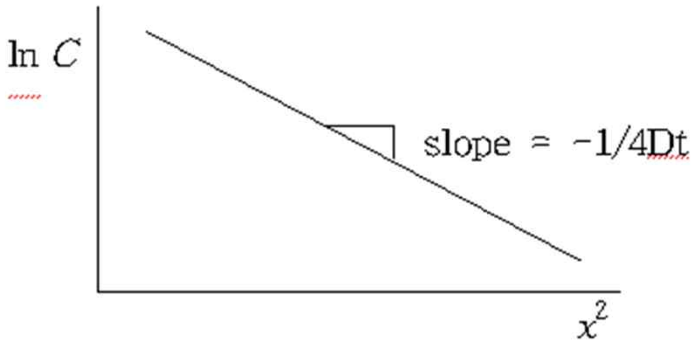
Non-Steady State Solution of Diffusion – Application of Superposition Principle

※ Application – Measurement of D^*



$$C(x,t) = \frac{M}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

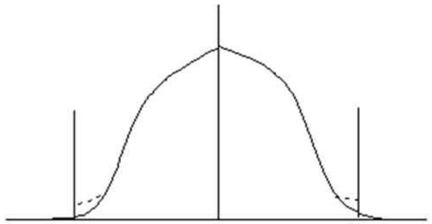
$$\ln C = -\frac{x^2}{4Dt} + \ln\frac{M}{\sqrt{4\pi Dt}}$$



Non-Steady State Solution of Diffusion – Leak Test & Error Function

※ Leak Test

: reflection at the boundary in the case of finite dimension and long time



$$R = \frac{2\int_{x_o}^{\infty} C(x,t)\,dx}{\int_{-\infty}^{\infty} C(x,t)\,dx} \quad \text{should be} << 1$$

$$R = \frac{\int_{x_o}^{\infty} e^{-x^2/4Dt}\,dx}{\int_{0}^{\infty} e^{-x^2/4Dt}\,dx} = \frac{2\sqrt{Dt}\int_{\frac{x_o}{2\sqrt{Dt}}}^{\infty} e^{-\eta^2}\,d\eta}{2\sqrt{Dt}\,\sqrt{\pi}/2} = erfc\left(\frac{x_o}{2\sqrt{Dt}}\right)$$

· for error range of 0.1%

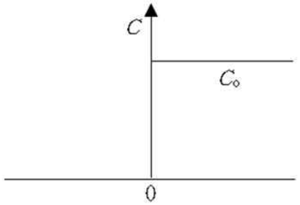
$$erfc\left(\frac{x_o}{2\sqrt{Dt}}\right) << 0.001 \quad \Rightarrow \quad \frac{x_o}{2\sqrt{Dt}} \simeq 2.5$$

※ Error function

- $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2}\,d\eta$
- $erf(0) = 0$
- $erf(\infty) = 1$
- $erf(-z) = -erf(z)$
- $erf(z) \simeq z \quad (z < 0.6)$

Non-Steady State Solution of Diffusion – Semi-Infinite Source

▷ Semi-infinite source (diffusion couple)

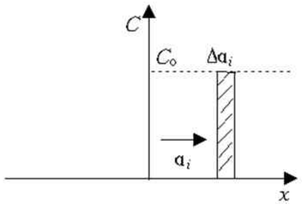


$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$C(x>0,\ t=0) = C_o$

$C(x<0,\ t=0) = 0$

- consider superposition of infinite number of thin film at $0 < x < \infty$
- for i-th thin film



$$C_i = \frac{C_o\,\Delta\alpha_i}{\sqrt{4\pi Dt}}\exp\left(-\frac{(x-\alpha_i)^2}{4Dt}\right)$$

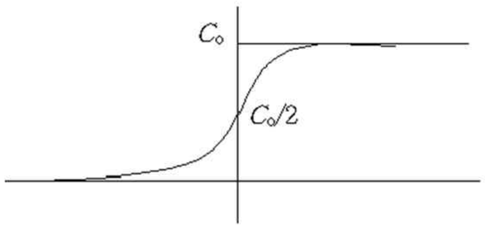
$$\Rightarrow\ C(x,t) = \sum_i^{\infty} C_i = \int_0^{\infty}\frac{C_o}{\sqrt{4\pi Dt}}\exp\left(-\frac{(x-\alpha_i)^2}{4Dt}\right)d\alpha$$

set $\dfrac{x-\alpha}{\sqrt{4Dt}} = \eta,\qquad d\alpha = -2\sqrt{Dt}\,d\eta$

$$C(x,t) = -\frac{C_o}{\sqrt{\pi}}\int_{x/2\sqrt{Dt}}^{-\infty} e^{-\eta^2}\,d\eta$$

$$= \frac{C_o}{\sqrt{\pi}}\left\{\int_{-\infty}^{0} e^{-\eta^2}\,d\eta + \int_0^{x/2\sqrt{Dt}} e^{-\eta^2}\,d\eta\right\}$$

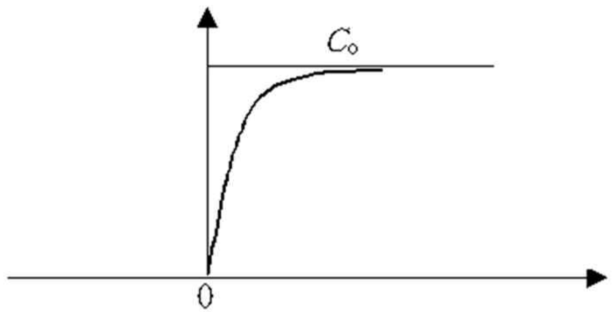
$$= \frac{C_o}{2}\left\{1 + \frac{2}{\sqrt{\pi}}\int_0^{x/2\sqrt{Dt}} e^{-\eta^2}\,d\eta\right\}$$



$$\therefore\ C(x,t) = \frac{C_o}{2}\left\{1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right\}$$

Non-Steady State Solution of Diffusion – Semi-Infinite Source

※ Diffusion out process



$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

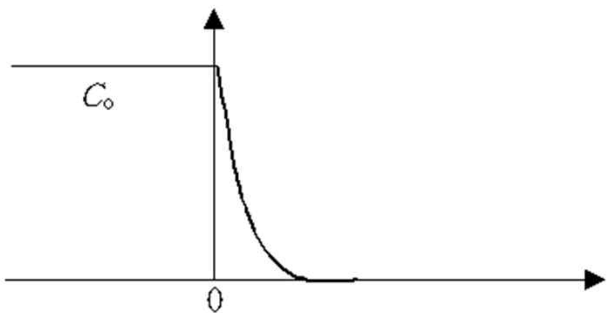
$C(x>0,\ t=0) = C_o$

$C(x<0,\ t=0) = 0$

$C(x<0,\ t>0) = 0$

$$\therefore\quad C(x,t) = C_o\, erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

※ Carburization



$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$C(x>0,\ t=0) = 0$

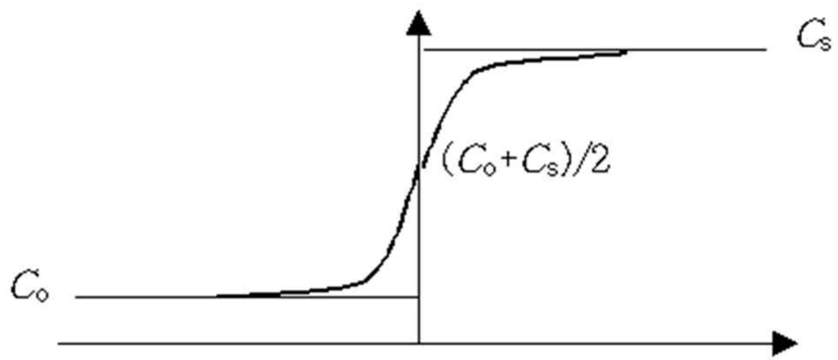
$C(x<0,\ t=0) = C_o$

$C(x<0,\ t>0) = C_o$

Non-Steady State Solution of Diffusion – Semi-Infinite Source

※ Generally

- $C(x,t) = A + B \, erf\left(\frac{x}{2\sqrt{Dt}}\right)$
- A, B : determined from initial condition

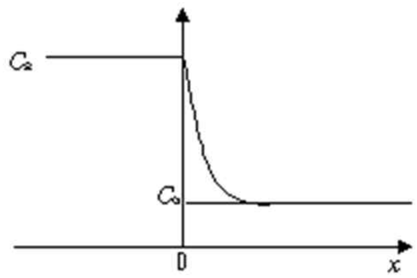


$C(x>0,\ t=0) = C_s$

$C(x<0,\ t=0) = C_o$

$$\therefore \frac{C - C_o}{C_s - C_o} = \frac{1}{2}\left\{1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right\}$$

※ Other methods for carburization



$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$$C(x>0,\ t=0) = C_0$$
$$C(x=\infty,\ t) = C_0$$
$$C(x\le 0,\ t) = C_s$$

1. set $y \equiv \dfrac{x}{\sqrt{t}}$

$$\frac{\partial C}{\partial t} = \left(\frac{\partial C}{\partial y}\right)\left(\frac{\partial y}{\partial t}\right) = -\frac{y}{2t}\left(\frac{\partial C}{\partial y}\right)$$

$$\frac{\partial C}{\partial x} = \left(\frac{\partial C}{\partial y}\right)\left(\frac{\partial y}{\partial x}\right) = \frac{1}{\sqrt{t}}\left(\frac{\partial C}{\partial y}\right), \qquad \frac{\partial^2 C}{\partial x^2} = \frac{1}{t}\left(\frac{\partial^2 C}{\partial y^2}\right)$$

set $P = \left(\dfrac{\partial C}{\partial y}\right)$

$$-\frac{y}{2t}P = \frac{D}{t}\left(\frac{\partial P}{\partial y}\right) \Rightarrow -\frac{y}{2}P = D\left(\frac{\partial P}{\partial y}\right) \Rightarrow -\frac{y}{2D}dy = \frac{dP}{P}$$

$$P = \frac{\partial C}{\partial y} = A\exp\left(-\frac{y^2}{4D}\right)$$

$$dC = A\exp\left(-\frac{y^2}{4D}\right)dy$$

$$C - C_s = A\int_0^y \exp\left(-\frac{y^2}{4D}\right)dy$$

set $\lambda^2 = \dfrac{y^2}{4D}$, $\quad dy = 2\sqrt{D}\,d\lambda$

$$C - C_s = 2\sqrt{D}A\int_0^{\lambda}\exp(-\lambda^2)\,d\lambda = 2\sqrt{D}A\int_0^{\frac{x}{2\sqrt{Dt}}}\exp(-\lambda^2)\,d\lambda$$

for $\lambda = \infty$

$$C_0 - C_s = 2\sqrt{D}A\int_0^{\infty}\exp(-\lambda^2)\,d\lambda = \sqrt{\pi D}A$$

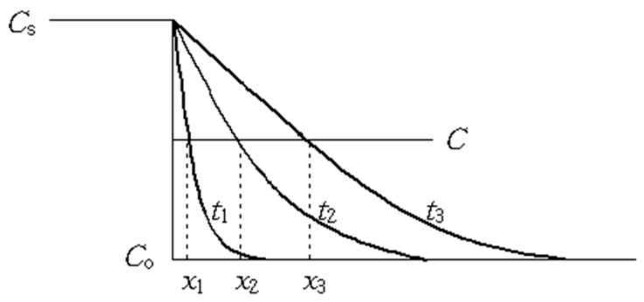
$$A = (C_0 - C_s)/\sqrt{\pi D}$$

$$\frac{C - C_s}{C_0 - C_s} = \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}}\exp(-\lambda^2)\,d\lambda = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\therefore \frac{C - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Non-Steady State Solution of Diffusion – Semi-Infinite Source

※ Application



for a constant C

$$y = \frac{x_1}{2\sqrt{Dt_1}} = \frac{x_2}{2\sqrt{Dt_2}} = \frac{x_3}{2\sqrt{Dt_3}}$$

· $y = 0.477, \quad erf(y) = 0.50$

$$\text{for } \frac{C-C_o}{C_s-C_o} = 0.5,$$

$$y = 0.477 = \frac{x}{2\sqrt{Dt}} \; ; \qquad \frac{x}{\sqrt{Dt}} \simeq 1$$

$\Rightarrow$ diffusion distance, $x = \sqrt{Dt}$

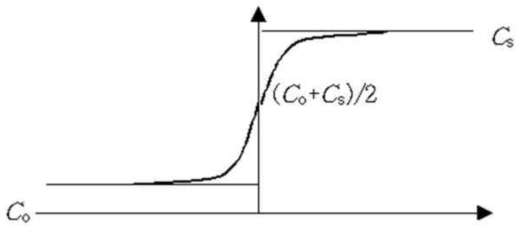
ex) carburization, at 1000 °C for 1 hr.

$$D_C = 3\times10^{-7} \text{ cm}^2/\text{sec}$$

$$x = \sqrt{Dt} = 0.033 \text{ cm} = 0.33 \text{ mm}$$

Non-Steady State Solution of Diffusion – Semi-Infinite Source

※ Other methods for diffusion couple



· $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$$C(x>0,\ t=0) = C_s$$
$$C(x<0,\ t=0) = C_o$$
$$C(x=\infty,\ t) = C_s$$
$$C(x=-\infty,\ t) = C_o$$

· Fourier transformation

$$F(k,t) = \int_{-\infty}^{\infty} C(x,t)\, e^{ikx}\, dx$$

$$C(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(k,t)\, e^{-ikx}\, dk$$

· $$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial t}\left[\frac{1}{2\pi}\int_{-\infty}^{\infty} F(k,t)\, e^{-ikx}\, dk\right] = \frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{\partial F(k,t)}{\partial t}\, e^{-ikx}\, dk$$

· $$D\frac{\partial^2 C(x,t)}{\partial x^2} = \frac{1}{2\pi}\int_{-\infty}^{\infty} -Dk^2 F(k,t)\, e^{-ikx}\, dk$$

· $$\frac{\partial F(k,t)}{\partial t} = -Dk^2 F(k,t) \ ; \qquad \frac{dF(k,t)}{F(k,t)} = -Dk^2\, dt$$

· $$F(k,t) = Ae^{-Dk^2 t}$$

$$F(k,0) = A = \int_{-\infty}^{\infty} C(x,0)\, e^{ikx}\, dx = \int_0^{\infty} C_s\, e^{ikx}\, dx + \int_{-\infty}^{0} C_o\, e^{ikx}\, dx$$

· $$\begin{aligned} C(x,t) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} F(k,t)\, e^{-ikx}\, dk \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} A\, e^{-Dk^2 t}\, e^{-ikx}\, dk \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-Dk^2 t}\, e^{-ikx}\, dk\left[\int_0^{\infty} C_s\, e^{ikx'}\, dx' + \int_{-\infty}^{0} C_o\, e^{ikx'}\, dx'\right] \end{aligned}$$

· $$\begin{aligned} &\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-Dk^2 t}\, e^{-ikx}\, dk \int_0^{\infty} C_s\, e^{ikx'}\, dx' \\ &= \frac{C_s}{2\pi}\int_0^{\infty} dx' \int_{-\infty}^{\infty} e^{-Dk^2 t}\, e^{-ik(x-x')}\, dk \\ &= \frac{C_s}{2\pi}\int_0^{\infty} dx' \int_{-\infty}^{\infty} e^{-Dt\left(k^2 + \frac{ik(x-x')}{Dt}\right)}\, dk \\ &= \frac{C_s}{2\pi}\int_0^{\infty} dx' \int_{-\infty}^{\infty} e^{-Dt\left(k + \frac{i(x-x')}{2Dt}\right)^2}\, e^{-\frac{(x-x')^2}{4Dt}}\, dk \\ &= \frac{C_s}{2\pi}\sqrt{\frac{\pi}{Dt}}\int_0^{\infty} e^{-\frac{(x-x')^2}{4Dt}}\, dx' \\ &= \frac{C_s}{2\pi}\sqrt{\frac{\pi}{Dt}}\cdot 2\sqrt{Dt}\int_{-\frac{x}{2\sqrt{Dt}}}^{\infty} e^{-\lambda^2}\, d\lambda \\ &= \frac{C_s}{\sqrt{\pi}}\left(\frac{\sqrt{\pi}}{2} + \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\lambda^2}\, d\lambda\right] \\ &= \frac{C_s}{2}\left(1 + \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\lambda^2}\, d\lambda\right] \end{aligned}$$

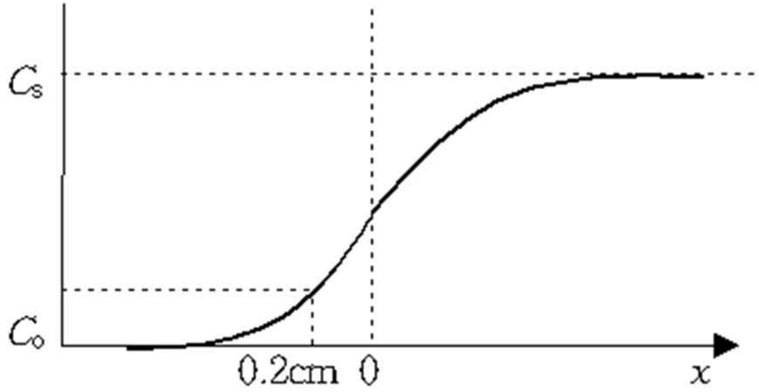
· $$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-Dk^2 t}\, e^{-ikx}\, dk \int_{-\infty}^{0} C_o\, e^{ikx'}\, dx' = \frac{C_o}{2}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\lambda^2}\, d\lambda\right]$$

$$\begin{aligned} \therefore\ C(x,t) &= \frac{C_s + C_o}{2} + \frac{C_s - C_o}{2}\, erf\left(\frac{x}{2\sqrt{Dt}}\right) \\ &= C_o + \frac{C_s - C_o}{2}\left(1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right) \end{aligned}$$

Determination of Diffusivity – Grube method

1. Grube method

· when $D \fallingdotseq$ constant



· $C(x,t) = C_o + \frac{C_s - C_o}{2}\left(1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right)$

· given values

Cs = 50 %

Co = 40 %

t = 40 hrs = 144000 sec

· at x = - 0.2 cm, C = 42.5 %

$$0.425 = 0.4 + \frac{(0.5 - 0.4)}{2} \cdot \left(1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

$$erf\left(\frac{x}{2\sqrt{Dt}}\right) = -0.5$$

$$\frac{x}{2\sqrt{Dt}} = -0.477$$

$$D = 3.04 \times 10^{-7}\ \mathrm{cm^2/sec}$$

: average value of the diffusivity for the interval.

Determination of Diffusivity – Boltzmann-Matano

2. Boltzmann-Matano Method

· when D $\neq$ constant

$$\cdot\ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) = \frac{\partial D}{\partial x}\cdot\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2}$$

· set $y \equiv \frac{x}{\sqrt{t}}$

$$\cdot\ \frac{\partial C}{\partial t} = \left(\frac{\partial C}{\partial y}\right)\left(\frac{\partial y}{\partial t}\right) = -\frac{y}{2t}\left(\frac{\partial C}{\partial y}\right)$$

$$\cdot\ \frac{\partial C}{\partial x} = \left(\frac{\partial C}{\partial y}\right)\left(\frac{\partial y}{\partial x}\right) = \frac{1}{\sqrt{t}}\left(\frac{\partial C}{\partial y}\right),$$

$$\cdot\ \frac{\partial D}{\partial x} = \left(\frac{\partial D}{\partial y}\right)\left(\frac{\partial y}{\partial x}\right) = \frac{1}{\sqrt{t}}\left(\frac{\partial D}{\partial y}\right),$$

$$\cdot\ \frac{\partial^2 C}{\partial x^2} = \frac{1}{t}\left(\frac{\partial^2 C}{\partial y^2}\right)$$

$$\cdot\ -\frac{y}{2}\frac{\partial C}{\partial y} = \frac{\partial D}{\partial y}\cdot\frac{\partial C}{\partial y} + D\frac{\partial^2 C}{\partial y^2}$$

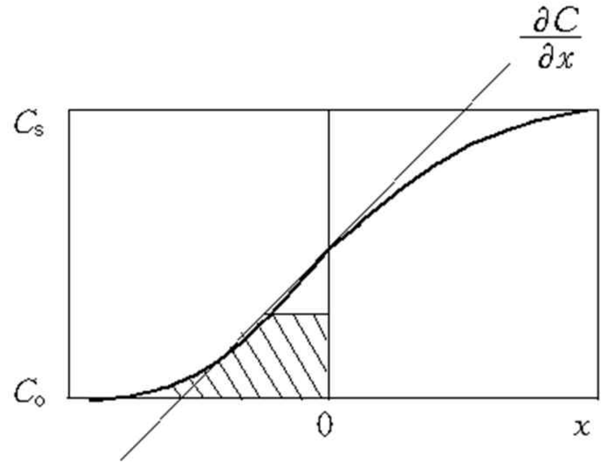
$$= \frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right)$$

$$\cdot\ -\frac{y}{2}\,dC = d\left(D\frac{\partial C}{\partial y}\right)$$

$$D\frac{\partial C}{\partial y} = -\frac{1}{2}\int_{C_o}^{C} y\,dC$$

$$D = -\frac{1}{2}\cdot\frac{\partial y}{\partial C}\cdot\int_{C_o}^{C} y\,dC$$

$$\therefore\ D = -\frac{1}{2t}\cdot\frac{\partial x}{\partial C}\cdot\int_{C_o}^{C} x\,dC$$



Non-Steady State Solution of Diffusion – Separation of Variable

☐ Separation of Variable

▷ $$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

· $C(x,t) = X(x)\cdot T(t)$

$$\frac{1}{DT}\frac{dT}{dt} = \frac{1}{X}\frac{d^2X}{dx^2} = -\lambda^2$$

· $\frac{dT}{dt} + \lambda^2 DT = 0$; $T(t) = e^{-\lambda^2 Dt}$

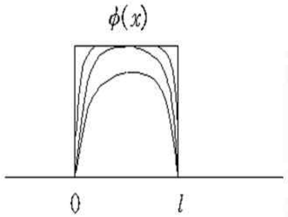
$\frac{d^2X}{dt^2} + \lambda^2 X = 0$; $X(x) = A\cdot\cos\lambda x + B\cdot\sin\lambda x$

▷ $$C(x,t) = \sum_n (A\cdot\cos\lambda_n x + B\cdot\sin\lambda_n x)\, e^{-\lambda_n^2 Dt}$$

· λ_n : from B.C.

· initial condition

$C(0<x<l, t=0) = \phi(x)$



· boundary condition

$C(x=0,t) = 0 \rightarrow A = 0$

$C(x=l,t) = 0 \rightarrow \lambda l = n\pi,\quad \lambda_n = \frac{n\pi}{l}\quad (n = 1,2,3,\cdots)$

▷ $$C(x,t) = \sum_n^{\infty} B_n\cdot\sin\lambda_n x\cdot e^{-\lambda_n^2 Dt} = \sum_n^{\infty} B_n\cdot\sin\frac{n\pi}{l}x\cdot e^{-\frac{n^2\pi^2}{l^2}Dt}$$

· by Orthogonality Theorem

$$C(x,0) = \sum_n^{\infty} B_n\cdot\sin\frac{n\pi}{l}x = \phi(x)$$

$$B_m\int_0^l \left(\sin\frac{m\pi}{l}x\right)^2 dx = \int_0^l \phi(x)\,\sin\frac{m\pi}{l}x\,dx = B_m\frac{l}{2}$$

$$B_m = \frac{2}{l}\int_0^l \phi(x)\,\sin\frac{m\pi}{l}x\,dx$$

· if $\phi(x) = C_o$

$$B_m = \frac{2}{l}C_o\int_0^l \sin\frac{m\pi}{l}x\,dx = \frac{2C_o}{m\pi}[1-\cos m\pi] = \frac{4C_o}{m\pi}\quad \text{if } m = 2j+1$$

1. $\sin(n+m)x = \sin nx\cos mx + \cos nx\sin mx$

$\sin(n-m)x = \sin nx\cos mx - \cos nx\sin mx$

$\sin(n+m)x + \sin(n-m)x = 2\sin nx\cos mx$

$\sin(n+m)x - \sin(n-m)x = 2\cos nx\sin mx$

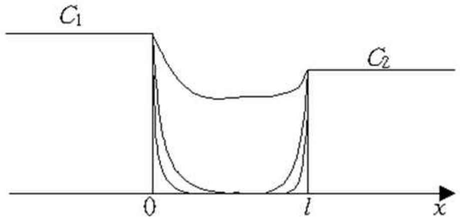
2. $\cos(n+m)x = \cos nx\cos mx - \sin nx\sin mx$

$\cos(n-m)x = \cos nx\cos mx + \sin nx\sin mx$

$\cos(n+m)x + \cos(n-m)x = 2\cos nx\cos mx$

$\cos(n+m)x - \cos(n-m)x = -2\sin nx\sin mx$

Non-Steady State Solution of Diffusion – Separation of Variable

※ 

$$C(0<x<l, t=0) = 0$$
$$C(x\leq 0, t) = C_1$$
$$C(x\geq l, t) = C_2$$

$$\Rightarrow \quad u(x,t) = \sum_n^{\infty} B_n \cdot \sin\lambda_n x \cdot e^{-\lambda_n^2 Dt}$$

$$\lambda_n = \frac{n\pi}{l} \quad (n = 1,2,3,\cdots)$$

$$B_n = \frac{2}{l}\int_0^l [-V(x)] \sin\frac{n\pi}{l}x\, dx$$

· It is impossible to determine B_n from initial condition (by orthogonality theorem)
→ find steady state solution, V(x), and change the form of solution C(x,t) as

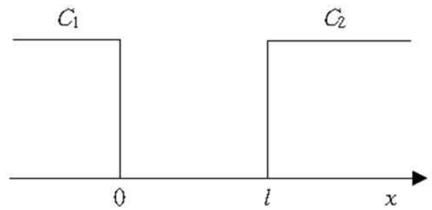
$$C(x,t) = u(x,t) + V(x)$$
$$u = C - V$$

V : steady state
u : nonsteady state

· from $\frac{\partial^2 V}{\partial x^2} = 0 \quad \rightarrow \quad V(x) = C_1 + \frac{C_2 - C_1}{l}x$

$$u(x,t) = C(x,t) - V(x)$$
$$= C(x,t) - C_1 - \frac{C_2 - C_1}{l}x$$

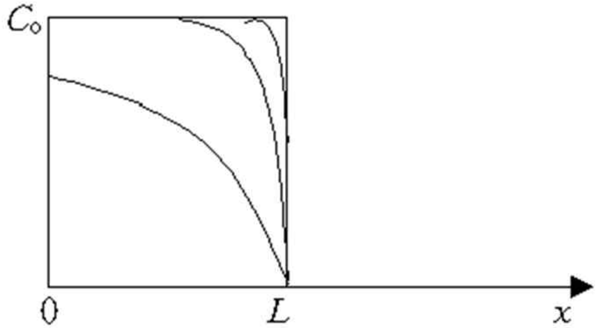
· $u(0<x<l, t=0) = -V(x)$
$u(x\leq 0, t) = 0$
$u(x\geq l, t) = 0$



$$C_1 = C_2 = C_o$$
$$C = u + V$$
$$V = C_o$$

· $u(x,t) = -\frac{4C_o}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)} \cdot \sin\frac{(2j+1)\pi}{l}x \cdot e^{-\frac{(2j+1)^2\pi^2}{l^2}Dt}$

※ Impermeable Coating of one side

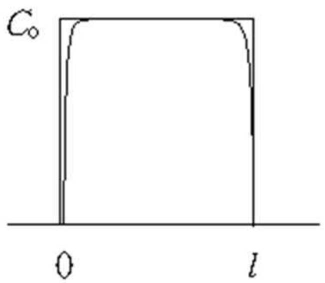


$$C(0 < x < l, t = 0) = C_o$$

$$C(x = L, t) = 0$$

$$\frac{\partial C(x = 0, t)}{\partial x} = 0$$

· considering the case

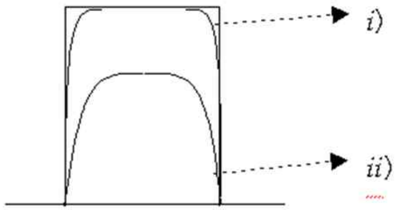


$$x' = x - \frac{l}{2} \quad ; \quad x = x' + \frac{l}{2}$$

$$L = \frac{l}{2} \quad ; \quad l = 2L$$

Non-Steady State Solution of Diffusion – Separation of Variable

※ Accuracy of trigonometric infinite series



i) $l > 10\sqrt{Dt}$

$$C/C_o = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C/C_o = erf\left(\frac{l-x}{2\sqrt{Dt}}\right)$$

ii) $l < 10\sqrt{Dt}$

$$C/C_o = \frac{4}{\pi}\sum_{j=0}^{\infty}\frac{1}{(2j+1)}\cdot\sin\frac{(2j+1)\pi}{l}x\cdot e^{-\frac{(2j+1)^2\pi^2}{l^2}Dt}$$

- decay rate : $R = \dfrac{|(j+1)th\ term|}{|j\ th\ term|} \sim e^{-\frac{8(j+1)\pi^2}{l^2}Dt}$
- 1st term approximation

$$C/C_o = \frac{4}{\pi}\sin\frac{\pi x}{l}\cdot e^{-\frac{\pi^2}{l^2}Dt}$$

$$R = \frac{|2nd\ term|}{|1st\ term|} = \frac{\frac{4}{\pi}\frac{1}{3}\sin\frac{\pi x}{l}\ e^{-\frac{9\pi^2 Dt}{l^2}}}{\frac{4}{\pi}\sin\frac{\pi x}{l}\ e^{-\frac{\pi^2 Dt}{l^2}}} = \frac{1}{3}\ e^{-\frac{8\pi^2}{l^2}Dt}$$

- for 0.1% accuracy

$$\frac{e^{-8\pi^2 Dt}}{l^2} \le 0.003 \quad \Rightarrow \quad if\ l \le 4\sqrt{Dt},\ \text{1st term approx. with 0.1\% accuracy}$$

Non-Steady State Solution of Diffusion – Separation of Variable

※ Average concentration

· $$\overline{C}(t) = \frac{1}{l}\int_0^l C(x,t)\,dx$$

$$= \frac{8C_o}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^2}\cdot e^{-\frac{(2j+1)^2\pi^2}{l^2}Dt}$$

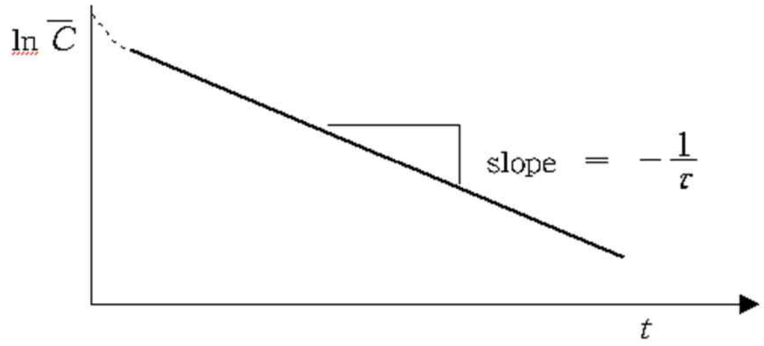
· 1st term approximation for $l < 4\sqrt{Dt}$

$$\overline{C}(t) = \frac{8C_o}{\pi^2}\cdot e^{-\frac{\pi^2 D}{l^2}t}$$

$$= \frac{8C_o}{\pi^2}\cdot e^{-t/\tau}$$

where $\tau = \frac{l^2}{\pi^2 D}$: relaxation time

· $\ln\overline{C} = A - \frac{t}{\tau}$

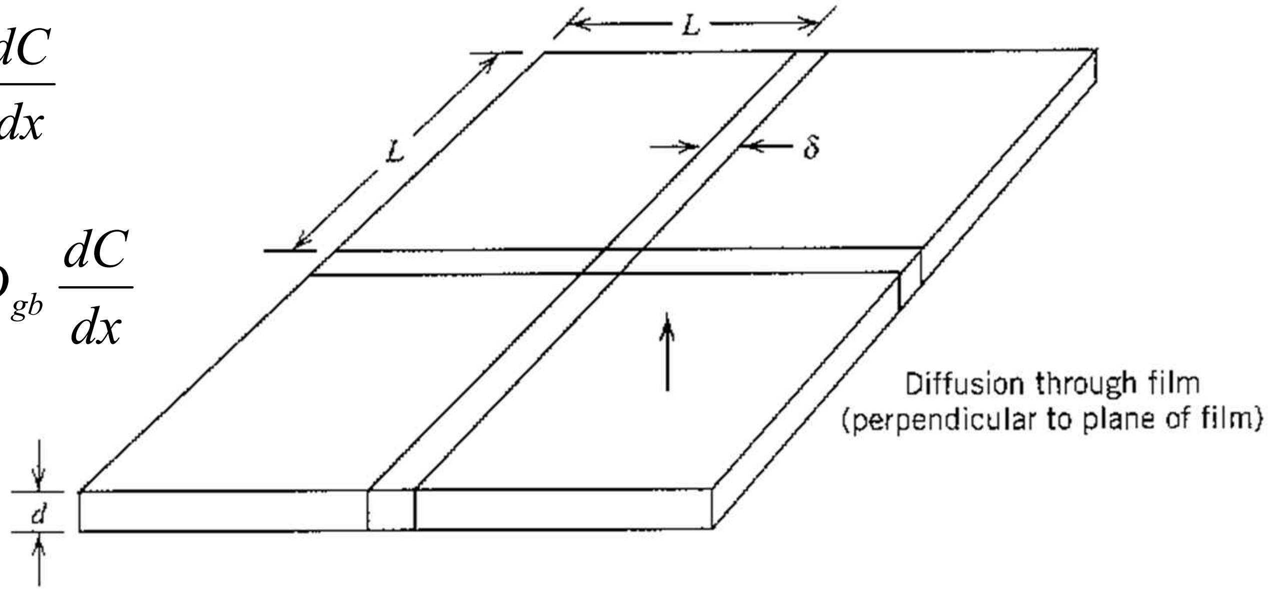


∴ applicable to vacancy annihilation in metal,
with l : grain size or inter dislocation distance

Diffusion along High Diffusion Path – Grain Boundary Diffusion Model

$$J_L = \frac{m_L}{L^2 t} = -D_L \frac{dC}{dx}$$

$$J_{gb} = \frac{m_{gb}}{2\delta L t} = -D_{gb} \frac{dC}{dx}$$



$$\dot{m}_L = -D_L L^2 \frac{dC}{dx}$$

$$\dot{m}_{gb} = -2 D_{gb} \delta L \frac{dC}{dx}$$

$$\frac{\dot{m}_{gb}}{\dot{m}_L} = \frac{2\delta D_{gb} L \frac{dC}{dx}}{D_L L^2 \frac{dC}{dx}} = \frac{\delta D_{gb}}{D_L}\frac{2}{L}$$

Diffusion Simulation – Finite Difference Method

$$\frac{\partial C}{\partial x} = \frac{C_{i+1}^{j} - C_{i-1}^{j}}{2\Delta x}$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{C_{i+1}^{j} - 2C_{i}^{j} + C_{i-1}^{j}}{(\Delta x)^2}$$

$$\frac{\partial C}{\partial t} = \frac{C_{i}^{j+1} - C_{i}^{j}}{\Delta t}$$

Diffusion Simulation – Finite Difference Method

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

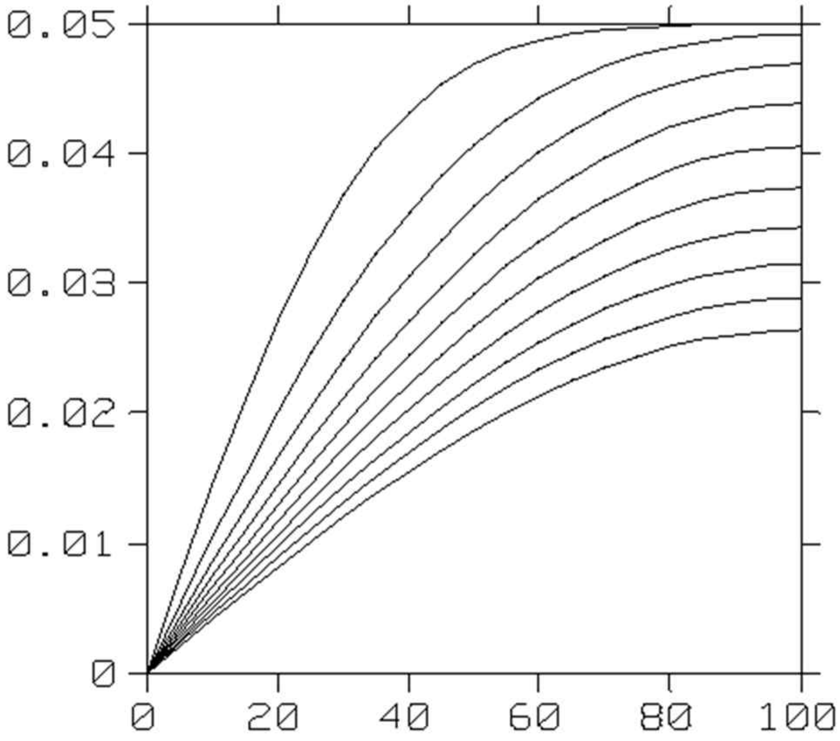
$$\Delta t \le \frac{(\Delta x)^2}{2D}$$

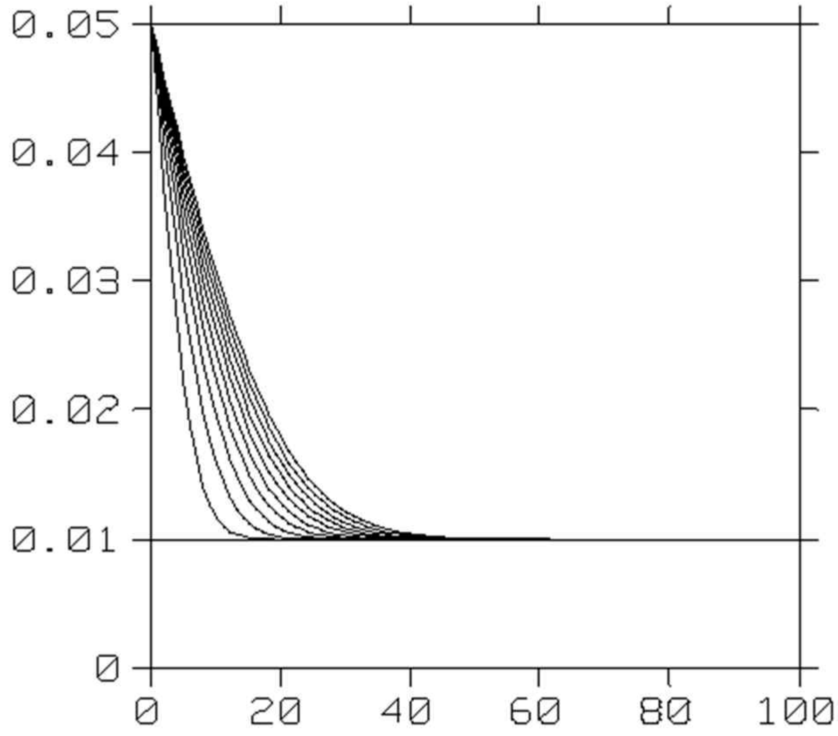
$$C_i^{j+1} = C_i^j + D\frac{(\Delta t)}{(\Delta x)^2}(C_{i+1}^j - 2C_i^j + C_{i-1}^j)$$

Diffusion Simulation – Finite Difference Method

```fortran
      implicit integer (i-n)
      implicit double precision (a-h,o-z)
      dimension U(1000), UF(1000)
c
      write(*,'(a)',advance='NO') ' Length of Simulation (micro-m) ? '
      read(*,*) XL
      write(*,'(a)',advance='NO') ' Initial Composition (U-fraction) ? '
      read(*,*) Uini
      write(*,'(a)',advance='NO') ' Boundary (Left-end) Composition ? '
      read(*,*) U0
      write(*,'(a)',advance='NO') ' Diffusion Coefficient (cm^2/sec) ? '
      read(*,*) D
      write(*,'(a)',advance='NO') ' Reaction Time (sec) ? '
      read(*,*) Tend
      write(*,'(a)',advance='NO') ' number of grid ? '
      read(*,*) n
c
      D = 1.d+08 * D
      dx = XL / dble(n-1)
      dt = 0.25d0 * dx * dx / D
      dtdx = D * dt / dx / dx
c
      xiter = Tend / dt
      nprnt = idint(xiter/10.d0)
c
c     initial condition
c
      U  = Uini
      UF = Uini
      time = 0.d0
      iter = 0
      open(unit=1,file='result.exp',status='unknown')
      write(1,'(a,f12.6)') '$ time = ', time
      write(1,'(f6.2,f12.6,a)') 0.d0, uf(1), '  M'
      do i = 2, n
        write(1,'(f6.2,f12.6)')  dble(i-1)*dx, uf(i)
      enddo
c
c     Boundary condition
      U(1)  = U0
      UF(1) = U0
      U(n+1) = U(n-1)
c
    1 iter = iter + 1
      time = time + dt
      do i = 2, n
        uf(i) = u(i) + dtdx * ( u(i+1) - 2.d0*u(i) + u(i-1) )
      enddo
      uf(n+1) = uf(n-1)
c
      u = uf
c
      if(mod(iter,nprnt) .eq. 0) then
        write(1,'(a,f12.6)') '$ time = ', time
        write(1,'(f6.2,f12.6,a)') 0.d0, uf(1), '  M'
       do i = 2, n
          write(1,'(f6.2,f12.6)')  dble(i-1)*dx, uf(i)
       enddo
      endif
c
      if(time.lt.tend) goto 1
      stop
      end
```

Diffusion Simulation – Finite Difference Method





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

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

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

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

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

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

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

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

Diffusion Coefficient – Self/Tracer Diffusion

□ Self Diffusion Coefficient

Cu	Cu^*

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

$$D_A = D_B = D$$

$\tilde{D}$: constant

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

□ Tracer Diffusion Coefficient

Cu 80%	Cu 80%
Au 20%	Au^* 20%

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

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

D^*_{Au} ← Grube method

☐ Intrinsic Diffusion Coefficient

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

· ideal solution

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

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

$= - B_A n_A \frac{\partial \mu_A}{\partial x}$ (B_A : mobility)

· Non-ideal solution

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

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

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

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

※ Tracer Diffusion

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

$= B_A^* RT$

$$B_A^* = B_A$$

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

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.

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

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

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

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

Diffusion Coefficient – Inter Diffusion

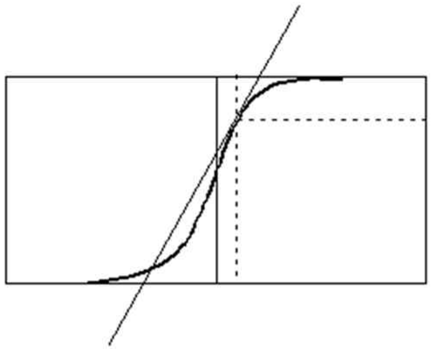
▷ with respect to volume fixed frame,

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

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

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

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 – 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 ~ N_2

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

➢ 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**

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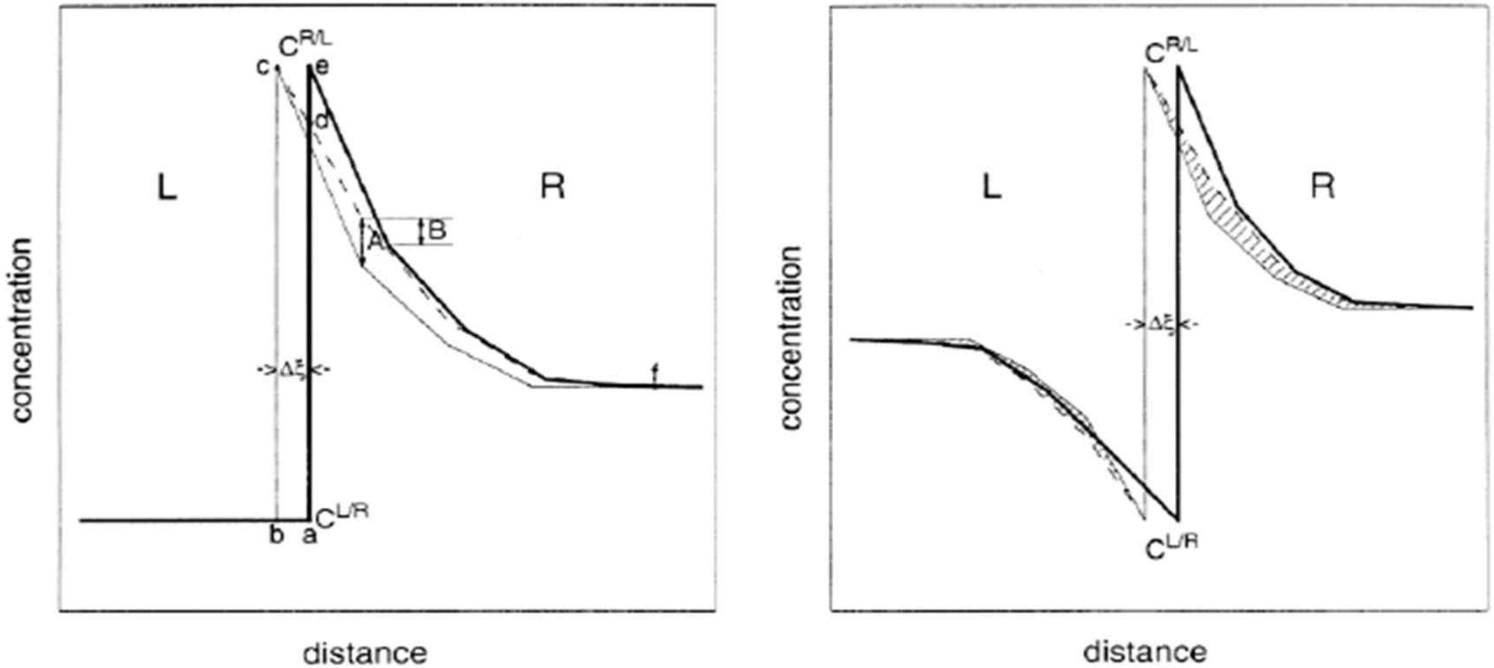
www.postech.ac.kr/~calphad

Moving Boundary Problem – Basic Equation

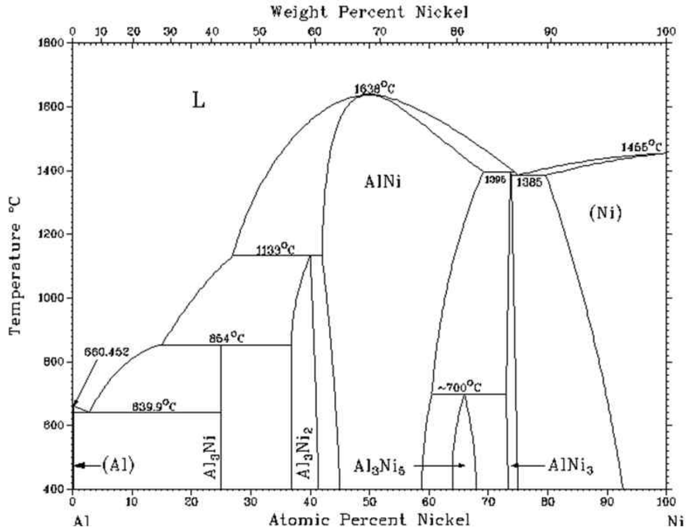


$$v^R C_k^{R/L} - v^L C_k^{L/R} = J_k^{R/L} - J_k^{L/R}$$

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

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

Binary Diffusion



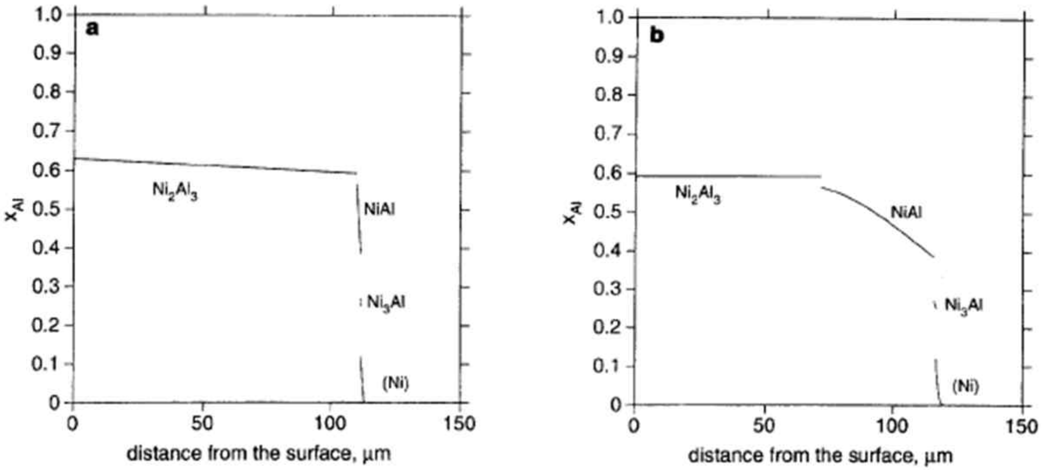
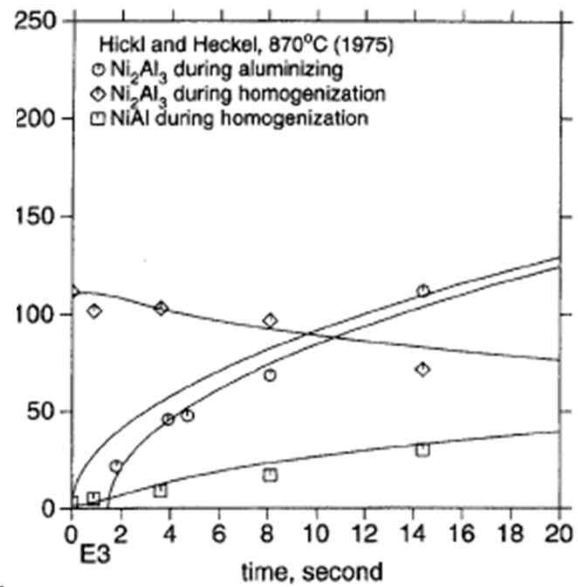


Fig. 7. Simulated composition profile of Al (a) after aluminizing of Ni for 14400s at 870°C and (b) after continued homogenization for 22500s at the same temperature.



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

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

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

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

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

※ 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

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

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

▷ Application to the Fe-C interstitial binary solution

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

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

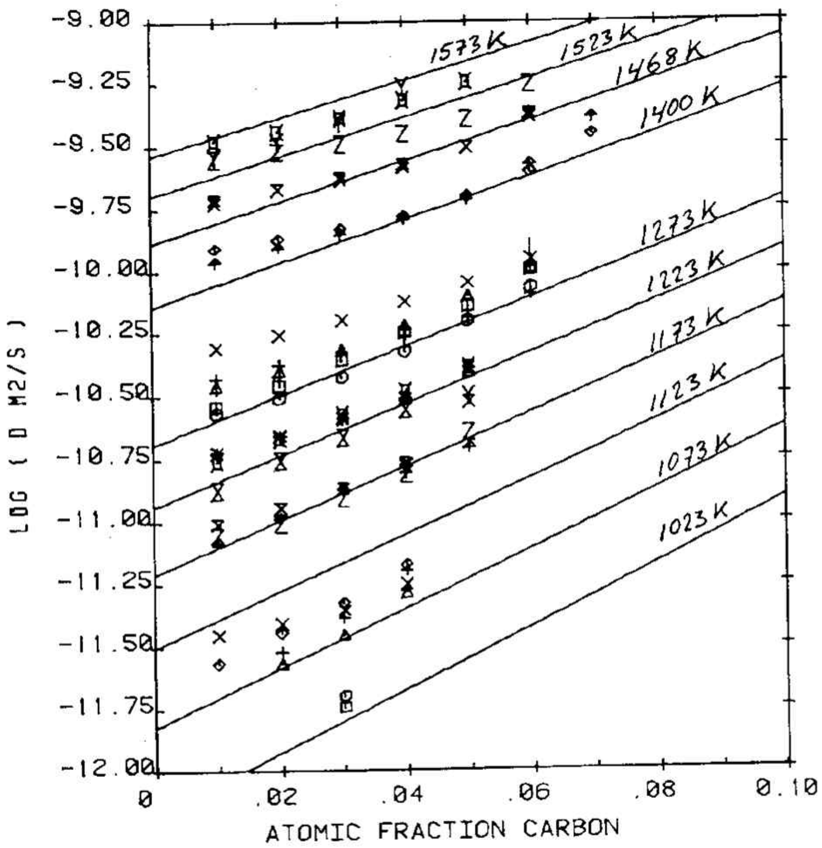
$$= -\ \Omega_C\, RT \left(1 - \frac{2 y_C y_{Va}}{RT} \cdot L_{Fe:Va,C} \right) \nabla C_C$$

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

[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
$\sim$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	$D=4.53\times10^{-3}[1+y_c(1-y_c)8339.9/T]\exp[-(T^{-1}-2.221\times10^{-4}\times17\,767-26\,436y_c)]$							
			$y_c=x_c/(1-x_c)$,		x_c = mol fraction of C			42
α-range	$\operatorname{Log} D=-0.9064-0.5199\chi+1.61\times10^{-3}\chi^2$					233–1 140	Combined data, several sources	40
			$\chi=10^4/T$					



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

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

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

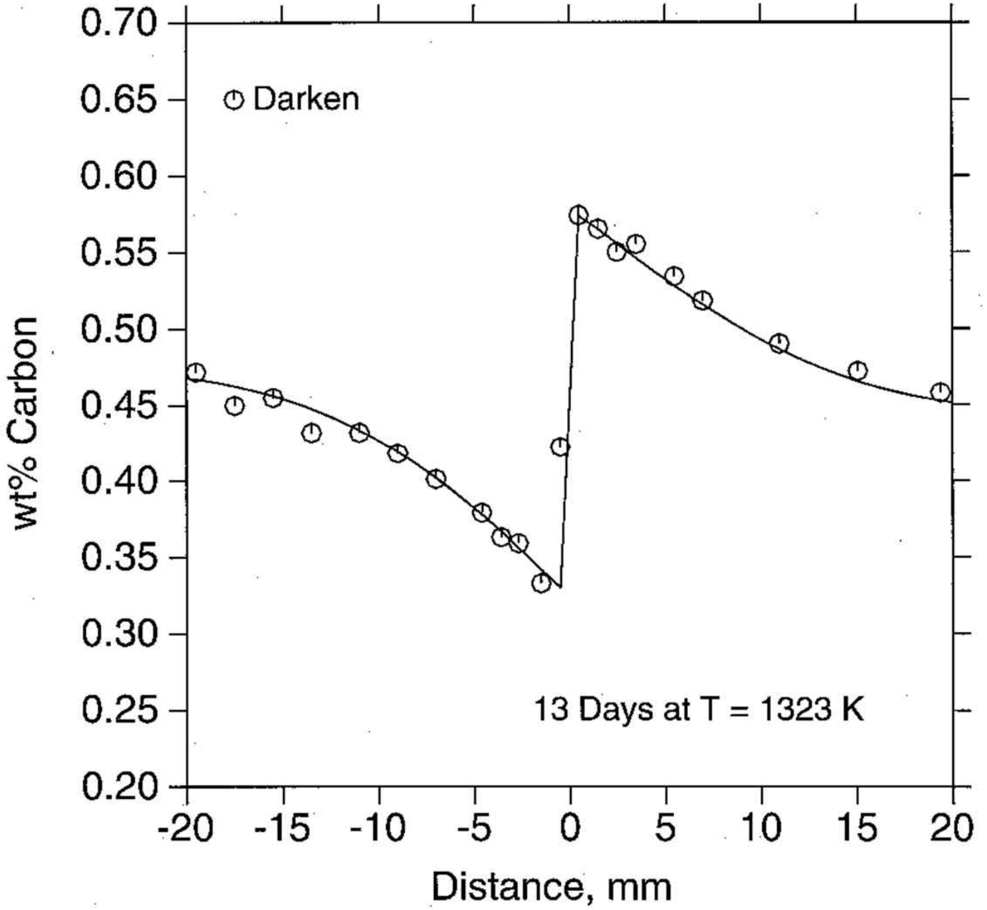
$$y_C + y_{Va} = 1 \qquad\qquad y_{Fe} + y_M = 1$$

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

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

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

Multi-Component Diffusion Simulation – Darken's uphill diffusion

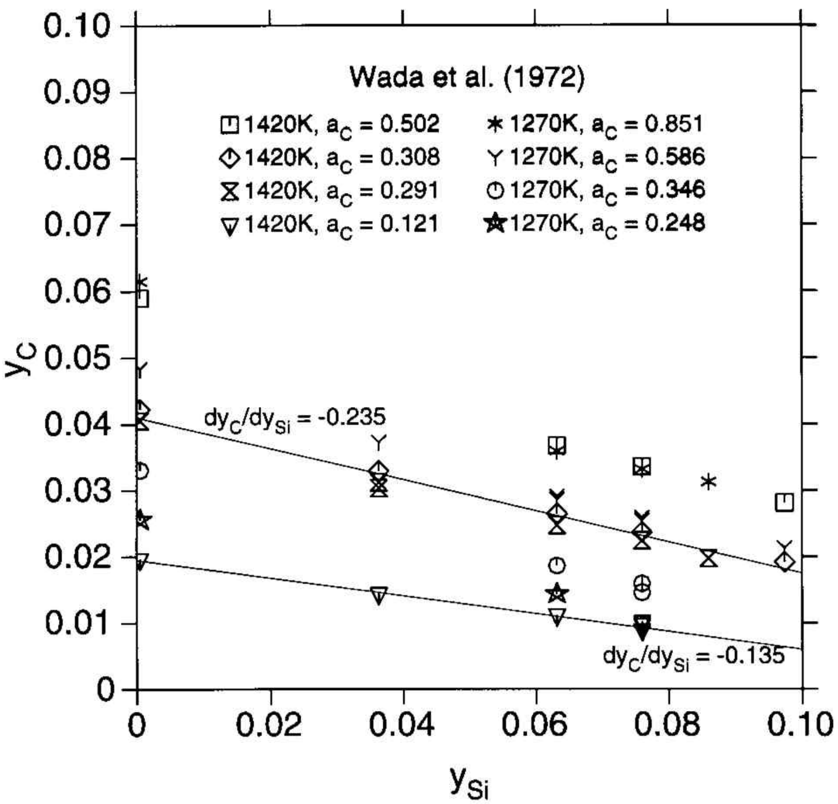


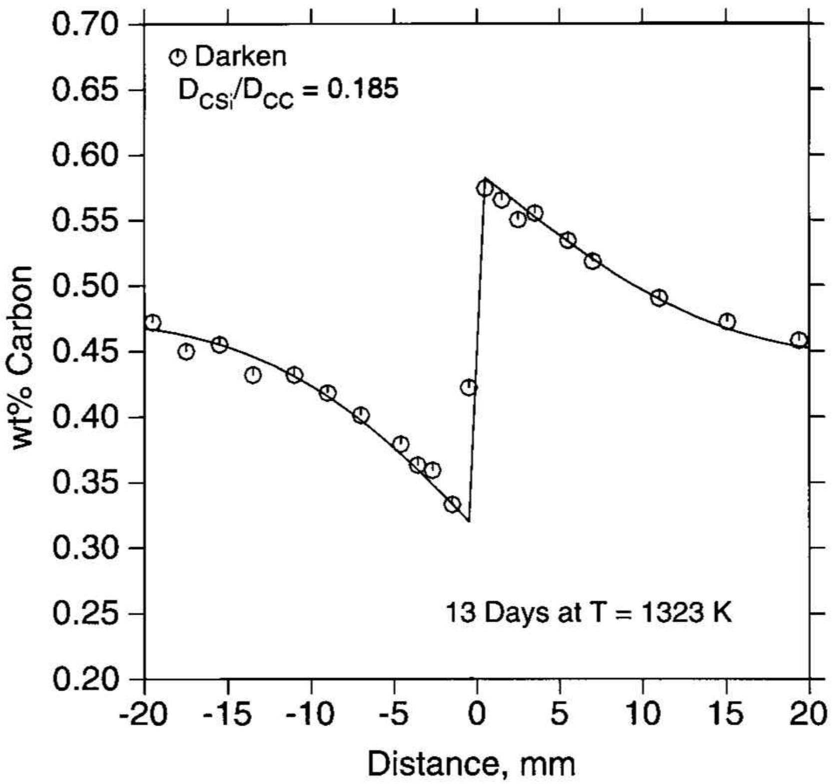
Fe-3.8Si-C

and

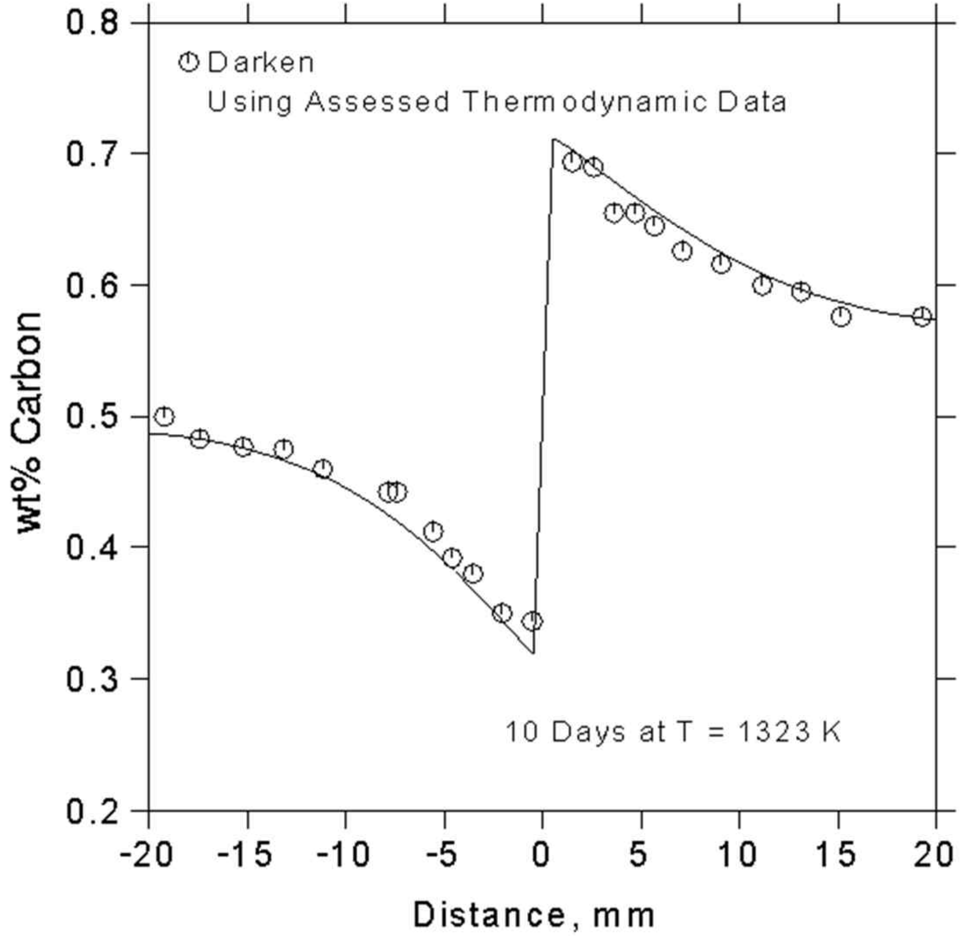
Fe-C

Multi-Component Diffusion Simulation – Darken's uphill diffusion





Multi-Component Diffusion Simulation – Darken's uphill diffusion

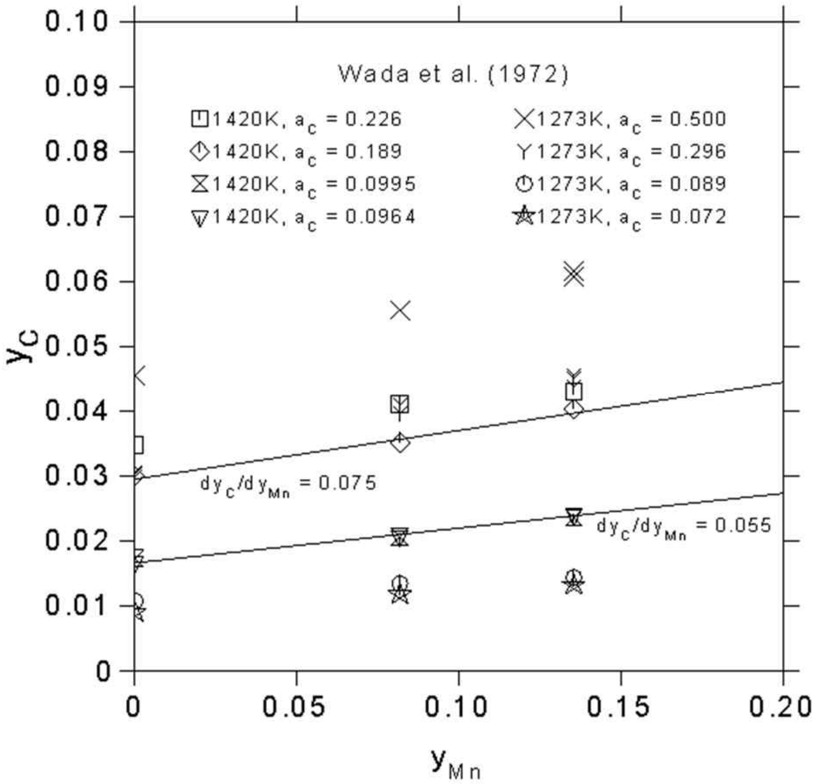


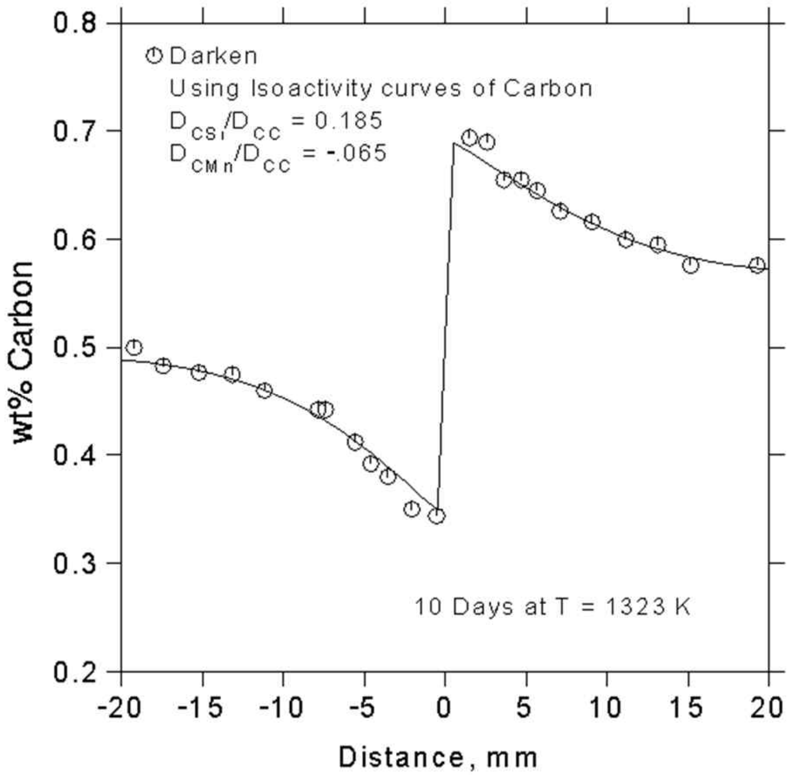
Fe-3.8Si-C

and

Fe-6.45Mn-C

Multi-Component Diffusion Simulation – Darken's uphill diffusion





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

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

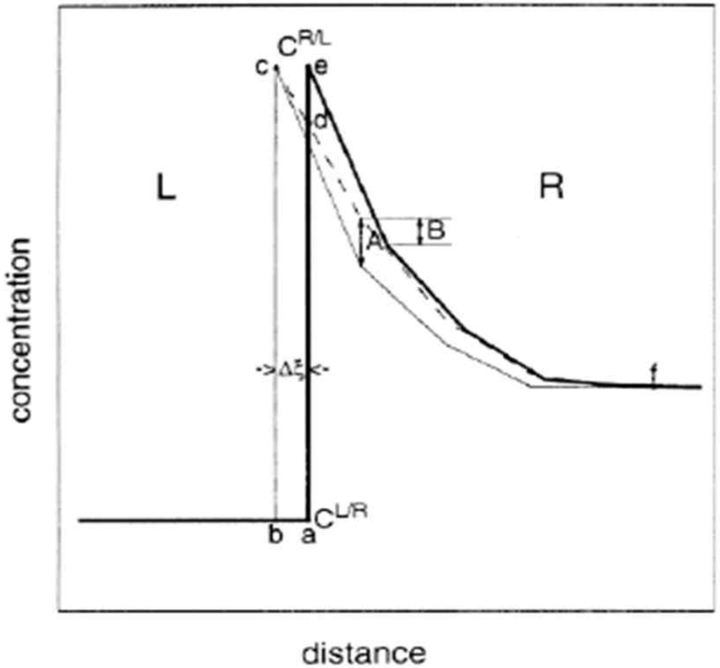
$$\frac{\partial C_C}{\partial t} = \frac{\partial}{\partial x}\left[D_{CC}\frac{\partial C_C}{\partial x} + D_{CSi}\frac{\partial C_{Si}}{\partial x}\right]$$

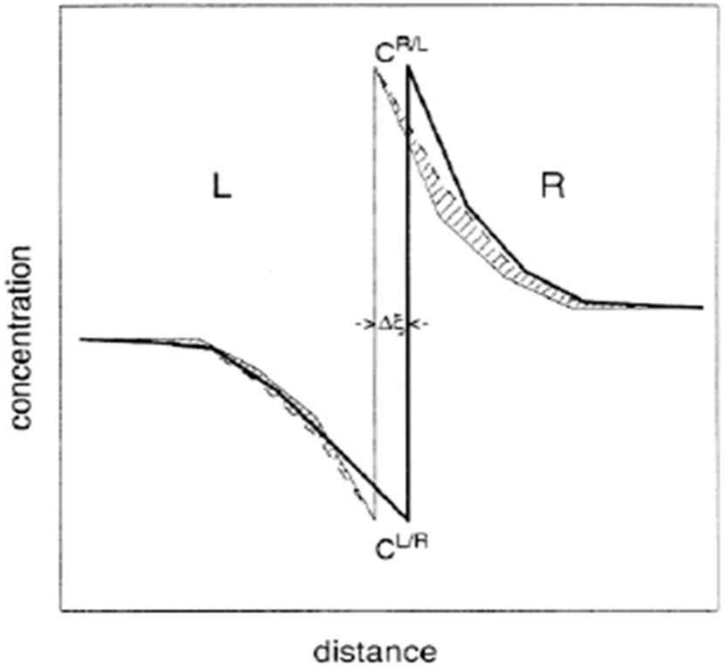
$$\frac{\partial C_{Si}}{\partial t} = \frac{\partial}{\partial x}\left[D_{SiC}\frac{\partial C_C}{\partial x} + D_{SiSi}\frac{\partial C_{Si}}{\partial x}\right]$$

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

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

Moving Boundary Problem – Basic Equation



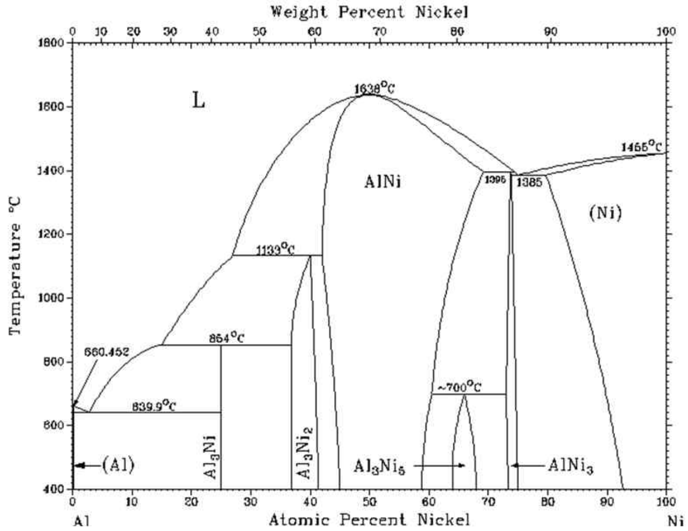


$$v^R C_k^{R/L} - v^L C_k^{L/R} = J_k^{R/L} - J_k^{L/R}$$

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

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

Binary Diffusion



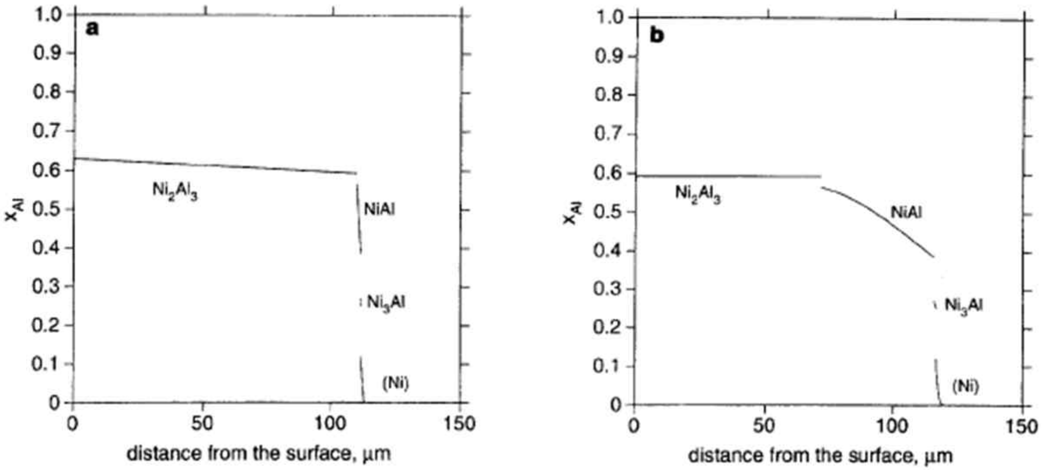
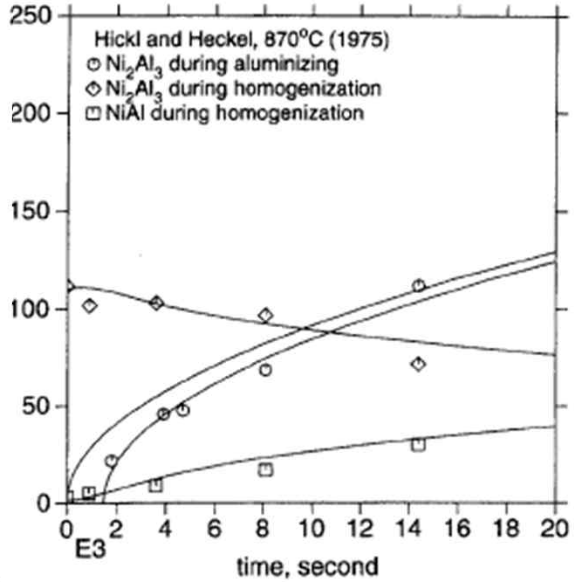
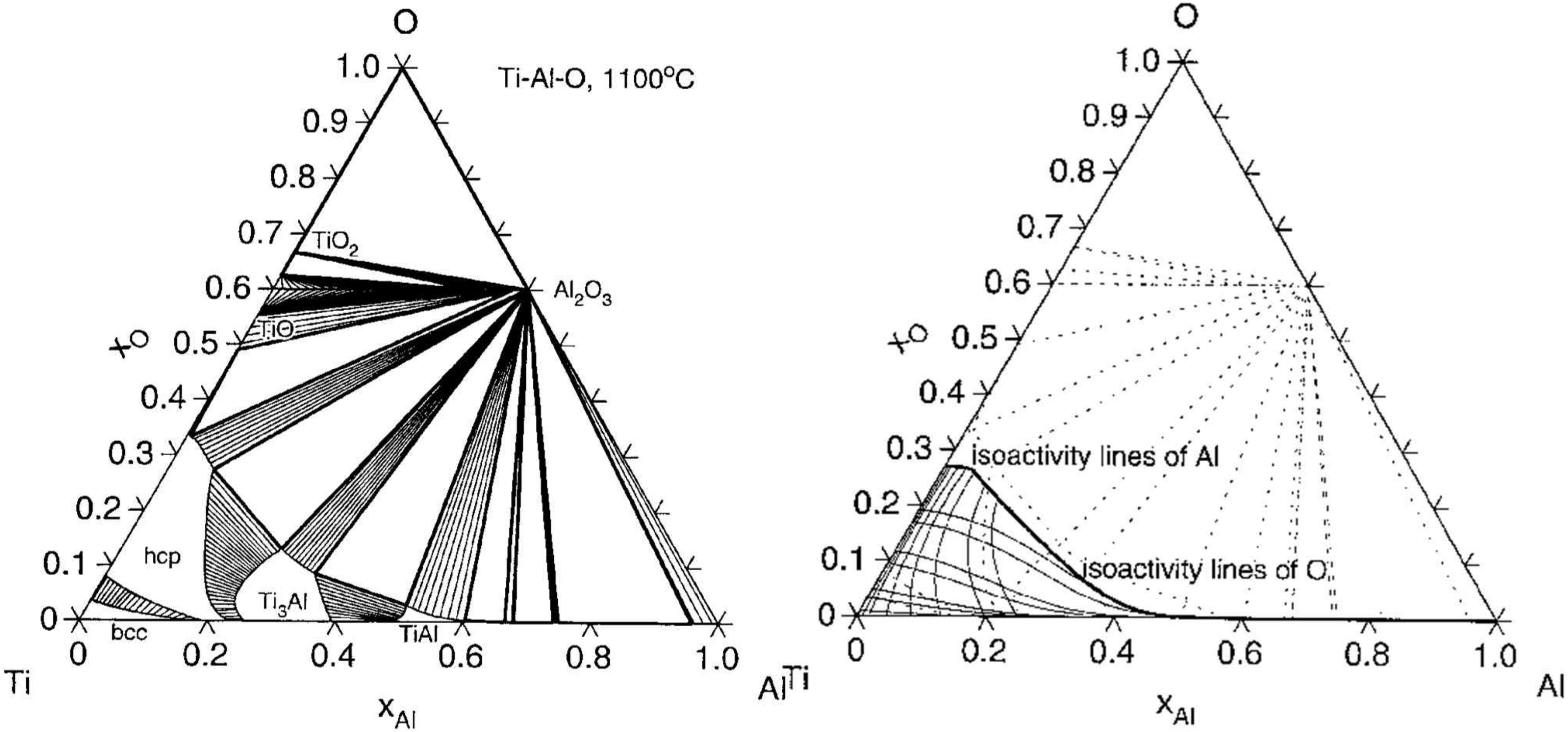


Fig. 7. Simulated composition profile of Al (a) after aluminizing of Ni for 14400s at 870°C and (b) after continued homogenization for 22500s at the same temperature.



Application to Interfacial Reactions – Ti/Al_2O_3 Reaction



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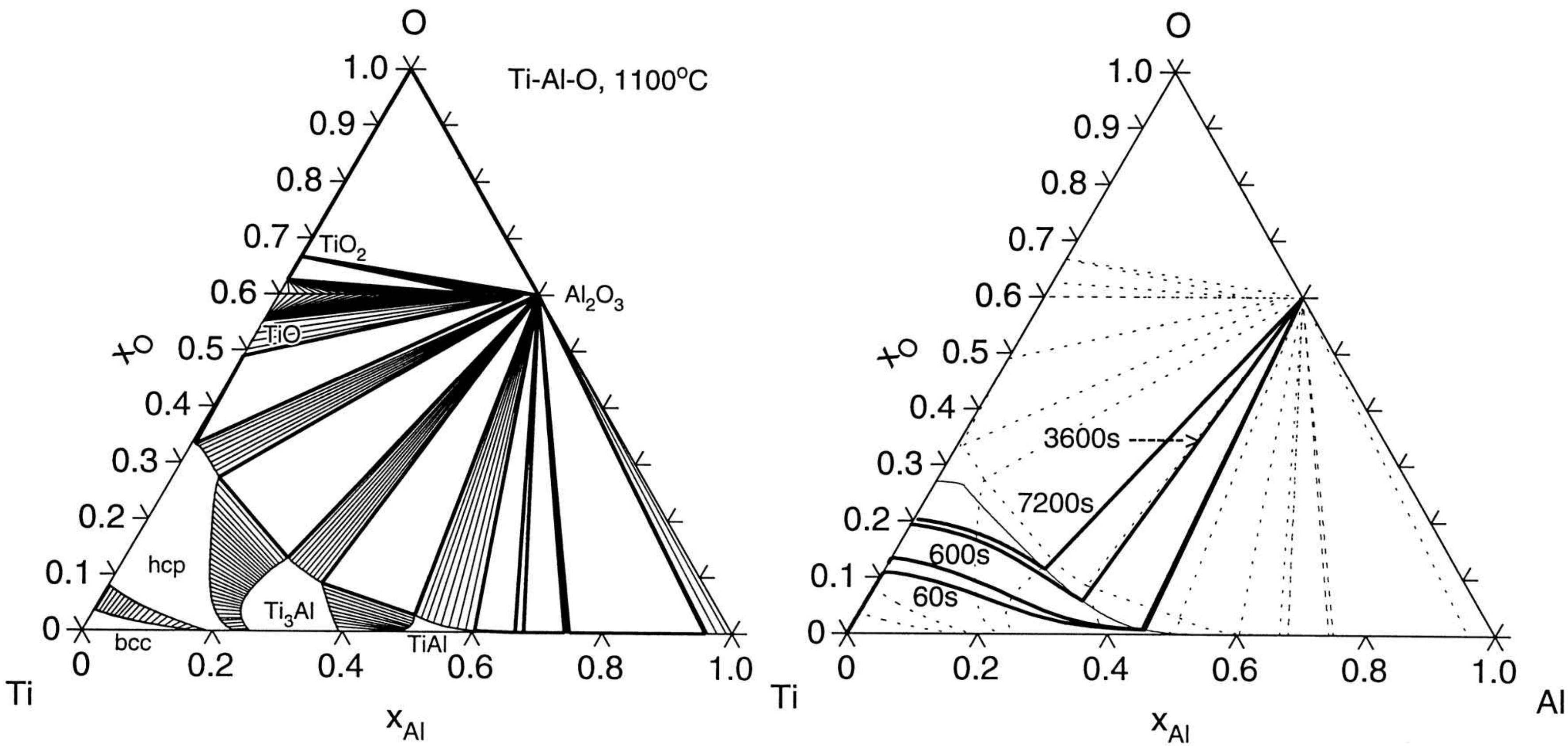

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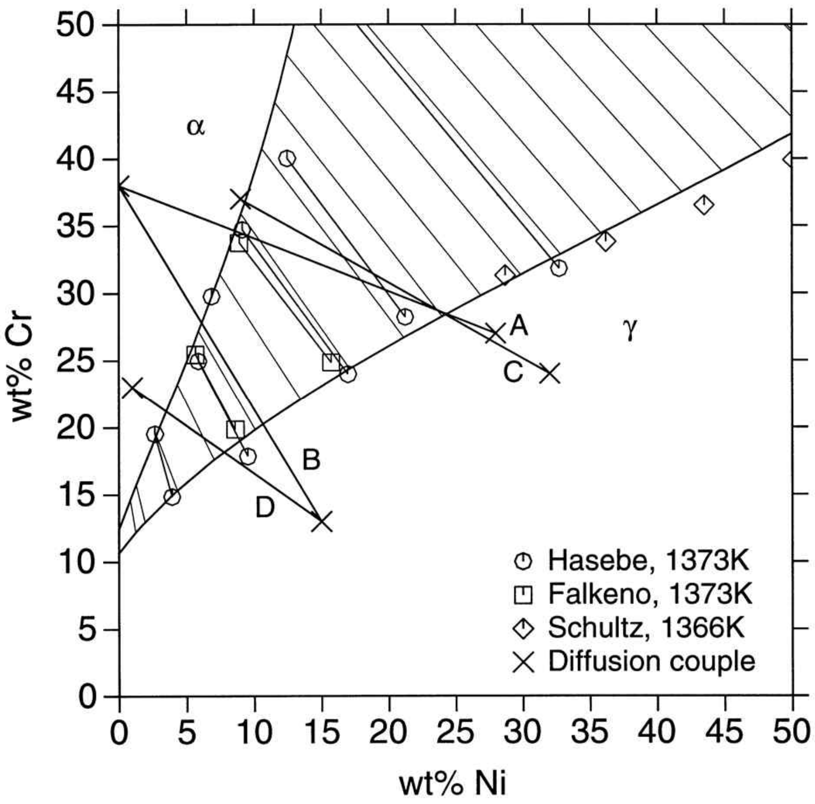
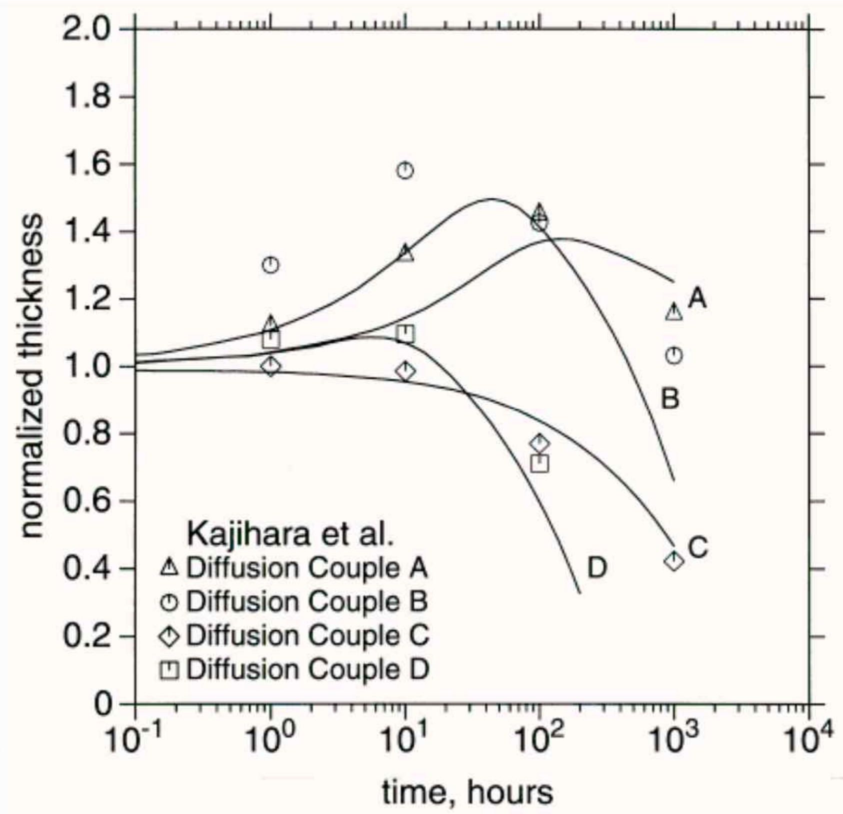
Multi-Component Diffusion Simulation – Case Study : Fe-Cr-Ni





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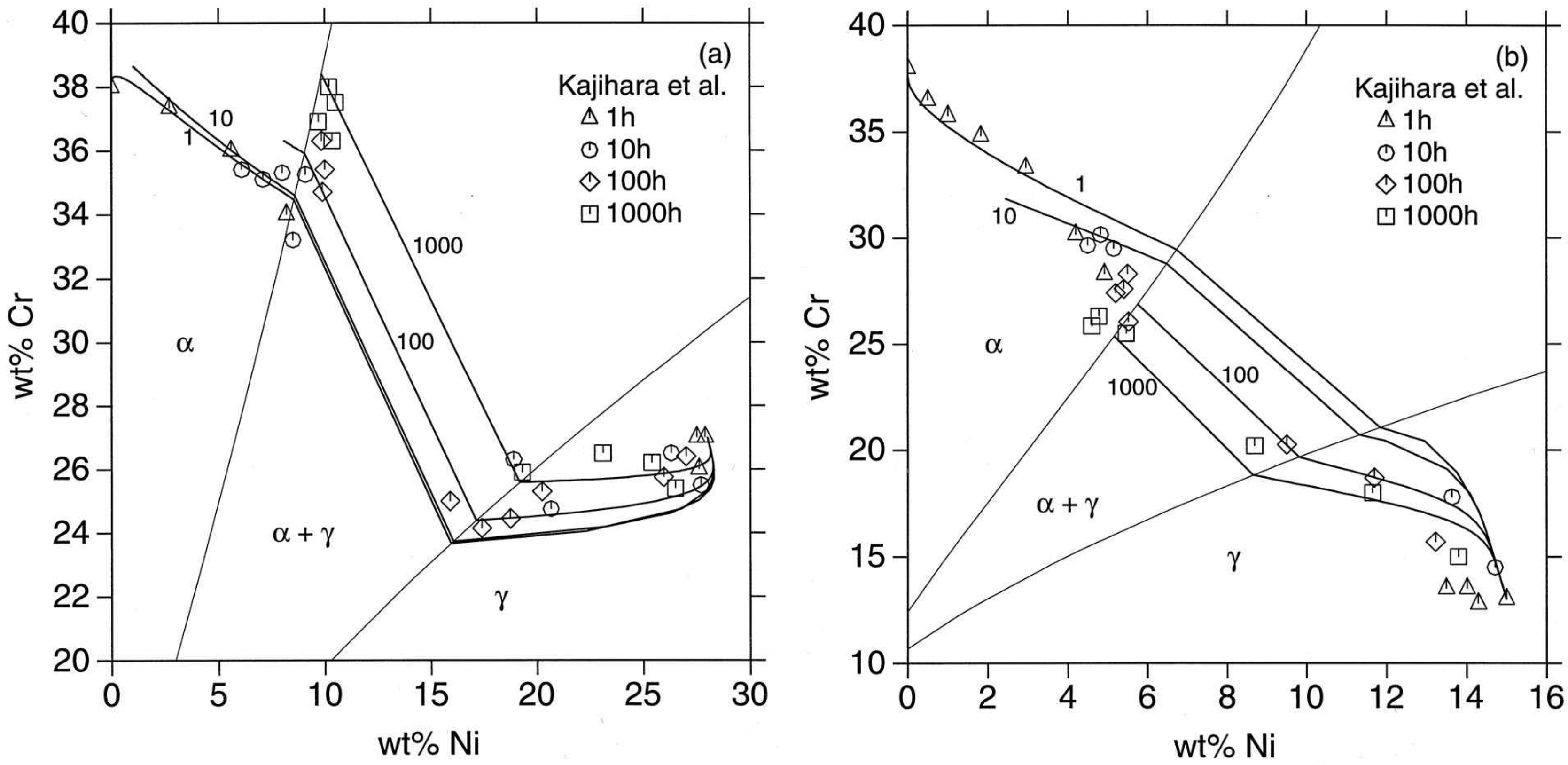


Multi-Component Diffusion Simulation – between Multi-Phase Layers

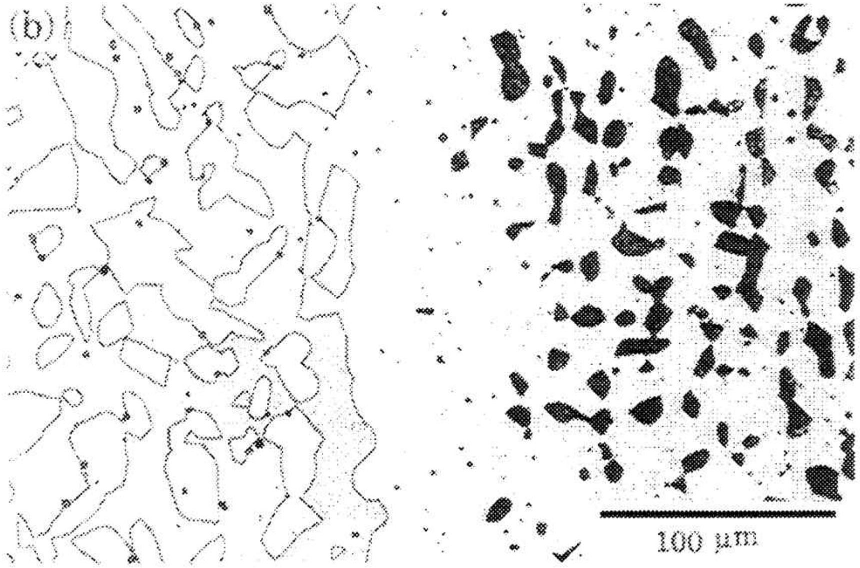
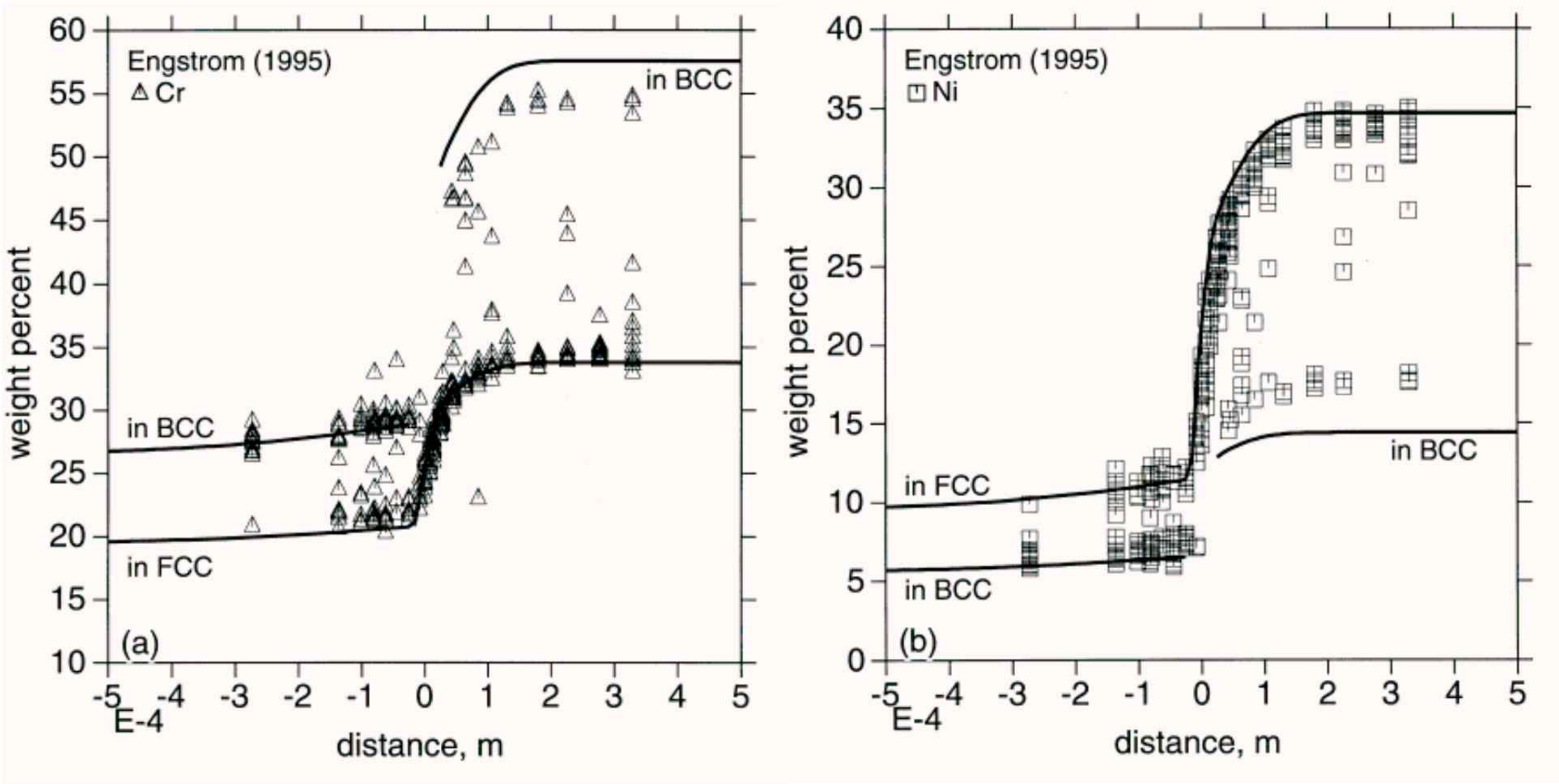


Fig. 14. (a) Microstructure of couple k5-k7 after a diffusion anneal at 1100°C for 100 h. (b) Same as (a) but different scale.

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

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

Multi-Component Diffusion Simulation – between Multi-Phase Layers



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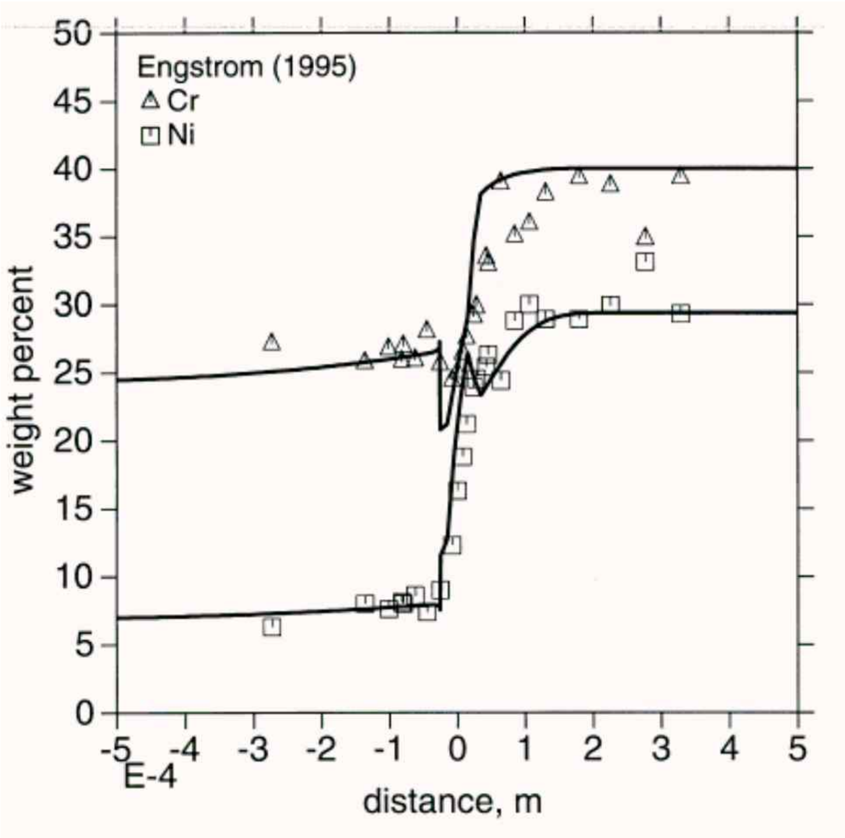

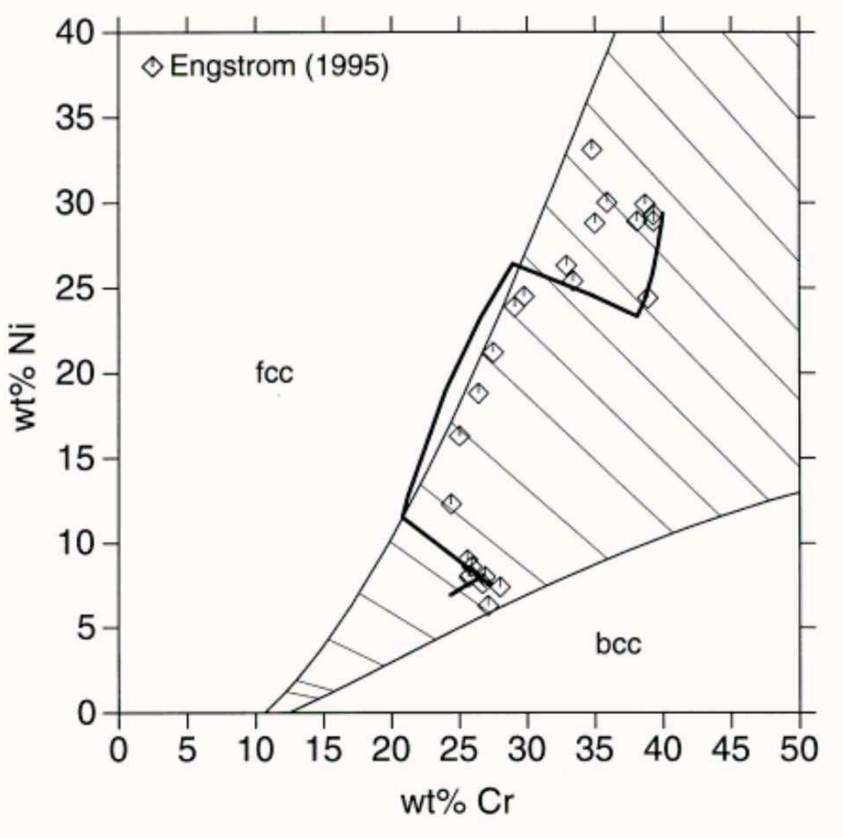

Further Readings