

개인 과제물 I (Term Report)

Computer Simulation of Darken's Uphill Diffusion

Mathematical modeling of multicomponent diffusion coefficients

- 다원 합금계에서 Diffusion Coefficient 는 (n-1) 차원의 행렬 형태가 되며, Fe-M-C 3 원계에서 용질 C 와 M 의 확산 유속은 다음과 같이 표현된다.

Diffusion coefficient in an Fe-M-C ternary alloy forms a 2 x 2 matrix

$$\begin{aligned} J_C &= -y_C y_{Va} \Omega_C \left(\frac{d\mu_C}{dy_C} \right) \nabla C_C - y_C y_{Va} \Omega_C \left(\frac{d\mu_C}{dy_M} \right) \nabla C_M \\ &= -D_{CC} \nabla C_C - D_{CM} \nabla C_M \end{aligned}$$

$$\begin{aligned} J_M &= - \left(y_{Fe} y_M \Omega_M \frac{d\mu_M}{dy_C} - y_M y_{Fe} \Omega_{Fe} \frac{d\mu_{Fe}}{dy_C} \right) \nabla C_C \\ &\quad - \left(y_{Fe} y_M \Omega_M \frac{d\mu_M}{dy_M} - y_M y_{Fe} \Omega_{Fe} \frac{d\mu_{Fe}}{dy_M} \right) \nabla C_M \\ &= -D_{MC} \nabla C_C - D_{MM} \nabla C_M \end{aligned}$$

- 확산 유속은 농도 C 의 기울기를 이용하여 표현하지만 실제 simulation 에서는 V 와 C 를 곱한 U-fraction 이 사용된다.
In simulations, V (volume) is multiplied to C, yielding U-fraction.

Solution Thermodynamics

- Fcc Fe-M-C 침입형 고용상은 $(\text{Fe},\text{M})_1(\text{va},\text{C})_1$ 의 formula unit 을 이용하여 1 mol of formula unit 당 Gibbs free energy 를 다음과 같이 표현한다. Gibbs energy of $(\text{Fe},\text{M})_1(\text{va},\text{C})_1$ solution phase:

$$\begin{aligned}
 G_m = & y_{\text{Fe}} y_{\text{Va}} {}^o G_{\text{Fe:Va}} + y_{\text{M}} y_{\text{Va}} {}^o G_{\text{M:Va}} + y_{\text{Fe}} y_{\text{C}} {}^o G_{\text{Fe:C}} + y_{\text{M}} y_{\text{C}} {}^o G_{\text{M:C}} \\
 & + RT(y_{\text{Fe}} \ln y_{\text{Fe}} + y_{\text{M}} \ln y_{\text{M}}) + RT(y_{\text{Va}} \ln y_{\text{Va}} + y_{\text{C}} \ln y_{\text{C}}) \\
 & + y_{\text{Fe}} y_{\text{M}} y_{\text{Va}} L_{\text{Fe,M:Va}} + y_{\text{Fe}} y_{\text{M}} y_{\text{C}} L_{\text{Fe,M:C}} \\
 & + y_{\text{Fe}} y_{\text{C}} y_{\text{Va}} L_{\text{Fe:C,Va}} + y_{\text{M}} y_{\text{C}} y_{\text{Va}} L_{\text{M:C,Va}}
 \end{aligned}$$

- Darken 의 Uphill Diffusion 실험이 이루어진 fcc Fe-Si-C 고용상에 대한 열역학 parameter 는 다음과 같다. (J/mol)

Thermodynamic parameters

$${}^o G_{\text{Fe:Va}} = {}^o G_{\text{Fe}}^{\text{fcc}}$$

$${}^o G_{\text{Si:Va}} = {}^o G_{\text{Si}}^{\text{Diamond}} + 51000 - 21.8 \cdot T$$

$${}^o G_{\text{Fe:C}} = {}^o G_{\text{Fe}}^{\text{fcc}} + {}^o G_{\text{C}}^{\text{graphite}} + 77207 - 15.877 \cdot T$$

$${}^o G_{\text{Si:C}} = {}^o G_{\text{Si}}^{\text{Diamond}} + {}^o G_{\text{C}}^{\text{graphite}} - 20510 + 38.7 \cdot T$$

$$L_{\text{Fe,Si:Va}} = -125248 + 41.116 \cdot T - 142708(y_{\text{Fe}} - y_{\text{Si}}) + 89907(y_{\text{Fe}} - y_{\text{Si}})^2$$

$$L_{\text{Fe,Si:C}} = +143219.9 + 39.31 \cdot T - 216320.5(y_{\text{Fe}} - y_{\text{Si}})$$

$$L_{\text{Fe:C,Va}} = -34671$$

Derivation of Diffusion Coefficient

- Gibbs Energy 식으로부터 각 원소의 Chemical Potential 을 얻는 공식은 다음과 같다. To obtain chemical potential from Gibbs energy.

For substitutional M,

$$\mu_M = G_m + (1 - y_M) \left(\frac{\partial G_m}{\partial y_M} - \frac{\partial G_m}{\partial y_{Fe}} \right) = G_m + (1 - y_M) \frac{dG_m}{dy_M}$$

For interstitial C

$$\mu_C = \left(\frac{\partial G_m}{\partial y_C} - \frac{\partial G_m}{\partial y_{Va}} \right) = \frac{dG_m}{dy_C}$$

위 식에 따라 C chemical potential 이 다음과 같이 얻어짐을 확인하시오.

$$\begin{aligned} \mu_C = & -y_{Fe} {}^oG_{Fe:Va} - y_M {}^oG_{M:Va} + y_{Fe} {}^oG_{Fe:C} + y_M {}^oG_{M:C} \\ & - RT \ln(1 - y_C) + RT \ln y_C \\ & - y_{Fe} y_M L_{Fe,M:Va} + y_{Fe} y_M L_{Fe,M:C} \\ & + (1 - 2y_C) y_{Fe} L_{Fe:C,Va} + (1 - 2y_C) y_M L_{M:C,Va} \end{aligned}$$

D_{CC} 계산을 위해 다음을 또한 확인하시오.

$$\frac{d\mu_C}{dy_C} = \frac{RT}{1 - y_C} + \frac{RT}{y_C} - 2y_{Fe} L_{Fe:C,Va} - 2y_M L_{M:C,Va}$$

$$D_{CC} = y_C y_{Va} \Omega_C \left(\frac{d\mu_C}{dy_C} \right) = \Omega_C \cdot RT \left[1 - \frac{2y_C(1 - y_C)}{RT} (y_{Fe} L_{Fe:C,Va} + y_M L_{M:C,Va}) \right]$$

$$\Omega_C RT = M_o \exp \left[-\frac{1 - \beta T / T_l}{RT} [y_C \Delta H_C + (1 - y_C) \Delta H_{Va}] \right]$$

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

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

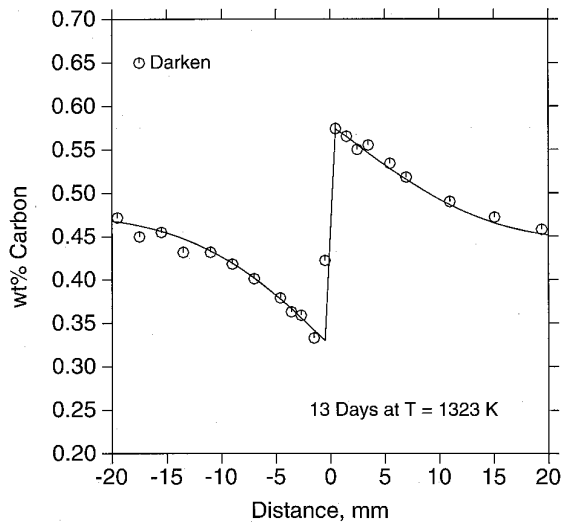
Simulation of Darken's Uphill Diffusion

- 다음의 Mobility 정보와 initial condition 을 이용하여 Darken 의 uphill diffusion 실험을 FDM 으로 simulation 하시오. (SI unit)

$$\Omega_{Fe}RT = 7.0 \times 10^{-5} \cdot \exp[-286000/RT]$$

$$\Omega_{Si}RT = 9.05 \times 10^{-3} \cdot \exp[-322465/RT]$$

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



- 각 시편 길이 (length) 50mm
- 왼쪽 시편 초기 조성 (left):
Fe - 3.8wt% Si - 0.478wt% C
- 오른쪽 시편 초기 조성 (right):
Fe - 0.441 wt% C
- 열처리 온도 (T) 1323 K
- 열처리 시간 (time) 13 days

실험 data (experimental data)

mm	wt% C	mm	wt% C
-19.5	0.472	0.5	0.574
-17.5	0.45	1.5	0.565
-15.5	0.455	2.5	0.55
-13.5	0.432	3.5	0.555
-11.0	0.432	5.5	0.534
-9.0	0.418	7.0	0.518
-7.0	0.401	11.0	0.49
-4.6	0.379	15.1	0.472
-3.6	0.363	19.4	0.458
-2.7	0.359	23.3	0.455
-1.5	0.333		
-0.5	0.422		