Series lectures of phase-field model

12. Coherent Phase Equilibria

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Free energy and composition of mixture

- The free energy of α-β phase mixture,

$$F = zF_\alpha + (1-z)F_\beta + F_{\text{el}} \qquad 0 \le z \le 1$$

where F_α and F_β are the molar free energies of the α and β phases and the phase fraction of α, z and the elastic strain energy arose by misfit strain between α and β phases, F_{el}.

- The composition of bulk alloy c of A-B binary system is

$$c = zc_\alpha + (1-z)c_\beta$$

where c_α and c_β are concentrations of B of α and β phases.

Misfit strain

- As a first assumption,

$$\varepsilon^\circ = \frac{a_\beta - a_\alpha}{a_\alpha}$$

where a_β and a_α are lattice parameters of β and α phases and the misfit strain is given by

$$\varepsilon = \varepsilon^\circ \left| c_\alpha - c_\beta \right|^k$$

- The elastic strain energy of isotropic material is assumed by

$$F_{\text{el}} = \frac{z(1-z)VE(\varepsilon^\circ)^2(\bar{c}_\alpha - \bar{c}_\beta)^{2k}}{1-\nu}$$

where E is Young's modulus and ν is Poisson's ratio and V is the molar volume in the reference state.

Free energy in polynomial form

- Molar free energy of each phase can be approximately given by

$$F_\alpha = \mu_{\mathsf{A}}^e (1 - c_\alpha) + \mu_{\mathsf{B}}^e c_\alpha + a_0 \left(c_\alpha - c_\alpha^e\right)^2$$

$$F_\beta = \mu_{\mathsf{A}}^e (1 - c_\beta) + \mu_{\mathsf{B}}^e c_\beta + b_0 \left(c_\beta - c_\beta^e\right)^2$$

where c_α^e and c_β^e are the compositions of the two phases under the equilibrium and μ_{A}^e and μ_{B}^e are chemical potentials of A and B at incoherent equilibrium.

- Introduce the normalized compositions for convenience,

$$\bar{c}_\alpha = 1 - 2\frac{c_\alpha - c_\alpha^e}{c_\beta^e - c_\alpha^e} \qquad \bar{c}_\beta = 1 - 2\frac{c_\beta - c_\alpha^e}{c_\beta^e - c_\alpha^e} \qquad \bar{c} = 1 - 2\frac{c - c_\alpha^e}{c_\beta^e - c_\alpha^e}$$

Reduced free energy

The reduced free energy

$$\phi = az\big(1-\bar{c}_\alpha\big)^2 + b(1-z)\big(1+\bar{c}_\beta\big)^2 + Az(1-z)(\bar{c}_\alpha - \bar{c}_\beta)^{2k} \tag{1}$$

where

$$\phi = F - \big[\mu^e_{\mathsf{A}}(1-c) + \mu^e_{\mathsf{B}}c\big]$$

$$a = a_0\frac{\big(c^e_\beta - c^e_\alpha\big)^2}{4} \qquad b = b_0\frac{\big(c^e_\beta - c^e_\alpha\big)^2}{4}$$

$$A = \frac{VE\big(\varepsilon^\circ\big)^2\big(c^e_\beta - c^e_\alpha\big)^{2k}}{2^{2k}(1-\nu)}$$

The mass conservation requires

$$\bar{c} - z\bar{c}_\alpha - (1-z)\bar{c}_\beta = 0 \tag{2}$$

To apply Lagrange multiplier, we multiply L and we have

$$L\big(\bar{c} - z\bar{c}_\alpha - (1-z)\bar{c}_\beta\big) = 0$$

$k = 0$ case

For simplicity we assume $a = b = 1$ and $k = 0$. We have

$$\phi = \phi + L\big(\bar{c} - z\bar{c}_\alpha - (1 - z)\bar{c}_\beta\big)$$

take the derivative with respect to $\bar{c}_\alpha$ it have to be 0 to minimize the free energy.

$$0 = 2z\big(1 - \bar{c}_\alpha\big) - Lz \tag{3}$$

Take the derivative with respect to $\bar{c}_\beta$

$$0 = 2(1 - z)\big(1 + \bar{c}_\beta\big) - L(1 - z) \tag{4}$$

Take the derivative with respect to z

$$0 = \big(1 - \bar{c}_\alpha\big)^2 - \big(1 + \bar{c}_\beta\big)^2 + A(1 - 2z) + L\big(\bar{c}_\alpha - \bar{c}_\beta\big) \tag{5}$$

- By algebraic manipulation, we have the solutions for Eqs. 3 to 5,

$$\bar{c}_\alpha = 1 - \frac{A\bar{c}}{4-A} \qquad \bar{c}_\beta = -1 - \frac{A\bar{c}}{4-A} \qquad z = \frac{1}{2} + \frac{2\bar{c}}{4-A} \tag{6}$$

  when $\bar{c}$ is determined, rest of the values are determined.
- With values in Eq. 6, the reduced energy in $\alpha + \beta$ two phase region is

$$\phi_{\alpha+\beta} = \frac{A}{4} - \frac{A\bar{c}^2}{4-A}$$

  the compositional derivative of ϕ is

$$\frac{d\phi_{\alpha+\beta}}{d\bar{c}} = -\frac{2A\bar{c}}{4-A}$$

  Since

$$0 \leq z \leq 1$$

- For $A < 4$,

$$-1 + \frac{A}{4} < \bar{c} < 1 - \frac{A}{4}$$

- For $A > 4$,

$$1 - \frac{A}{4} < \bar{c} < \frac{A}{4} - 1$$

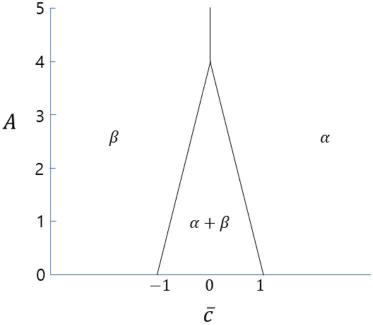
it is easily shown this solution no longer minimizes ϕ.

- When $z = 1$, $\bar{c} = \bar{c}_\alpha$,

$$\phi = (1 - \bar{c})^2$$

- When $z = 0$, $\bar{c} = \bar{c}_\beta$,

$$\phi = (1 + \bar{c})^2$$



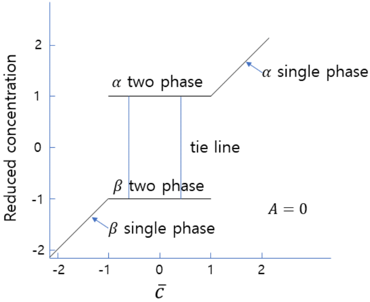
Incoherent equilibria

For incoherent case,

$$A = 0$$

it means that

$$\bar{c}_\alpha = 1 \qquad \bar{c}_\beta = -1$$

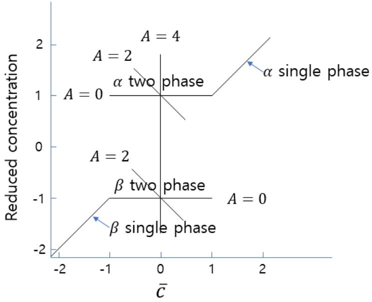


Coherent equilibria

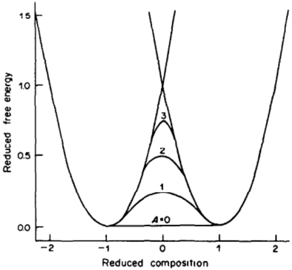
Even though $A \neq 0$,

$$\bar{c}_\alpha - \bar{c}_\beta = 2 \qquad 0 \leq z \leq 1$$

and when $A > 0$, $\bar{c}_\alpha$ and $\bar{c}_\beta$ increase as A increases.



Free energy function of alloy compositions



When $A \geq 4$, two phase region does not exist. When $A = 0$, incoherent case, the concentrations of α and β phases are fixed within the region. However, if elasticity exists, $A > 0$, concentrations of two phases are not constant within two phase region.

We set $a = b = 1$ and $k = 1$ in Eq. 1. We have the consistent formulation with the case of $k = 0$

$$\phi = \phi + L\big(\bar{c} - z\bar{c}_\alpha - (1-z)\bar{c}_\beta\big)$$

take the derivative with respect to $\bar{c}_\alpha$ it have to be 0 to minimize the free energy.

$$0 = 2z\big(1 - \bar{c}_\alpha\big) - 2Az(1-z)\big(\bar{c}_\alpha - \bar{c}_\beta\big) - Lz \tag{7}$$

Take the derivative with respect to $\bar{c}_\beta$

$$0 = 2(1-z)\big(1 + \bar{c}_\beta\big) - 2Az(1-z)\big(\bar{c}_\alpha - \bar{c}_\beta\big) - L(1-z) \tag{8}$$

Take the derivative with respect to z

$$0 = \big(1 - \bar{c}_\alpha\big)^2 - \big(1 + \bar{c}_\beta\big)^2 + A(1-2z)\big(\bar{c}_\alpha - \bar{c}_\beta\big)^2 + L\big(\bar{c}_\alpha - \bar{c}_\beta\big) \tag{9}$$

After algebraic manipulation of Eqs. 7 to 9,

$$A\left(\bar{c}_\alpha - \bar{c}_\beta\right)^2 + \left(1 - \bar{c}_\alpha\right)^2 - \left(1 + \bar{c}_\beta\right)^2 - 2\left(1 + \bar{c}_\beta\right)\left(\bar{c}_\alpha - \bar{c}_\beta\right) = 0 \quad (10)$$

$$A\left(\bar{c}_\alpha - \bar{c}_\beta\right) - \left(1 - \bar{c}_\alpha\right) - \left(1 + \bar{c}_\beta\right) = 0 \quad (11)$$

which means that $\bar{c}_\alpha$ and $\bar{c}_\beta$ are not dependent on $\bar{c}$. The solution of Eqs. 10 and 11 are

$$\bar{c}_\alpha = \frac{1}{A+1} \qquad \bar{c}_\beta = -\frac{1}{A+1}$$

Applying mass conservation in Eq. 2,

$$z = \frac{1}{2} + \frac{A+1}{2}\bar{c}$$

The minimized ϕ within $\alpha + \beta$ two phase region is

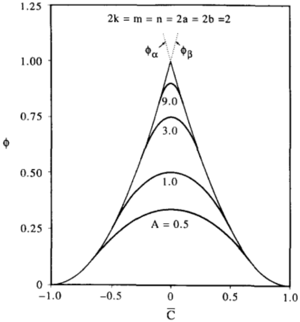
$$\phi_{\alpha+\beta} = -A\bar{c}^2 + \frac{A}{A+1}$$

When $z = 1$,

$$\bar{c} = \bar{c}_\alpha \qquad \phi = \phi_\alpha = (1 - \bar{c})^2$$

When $z = 0$,

$$\bar{c} = \bar{c}_\beta \qquad \phi = \phi_\beta = (1 + \bar{c})^2$$



Two phase region exists even if $A > 4$.

Phase diagram when $k = 1$

The boundary between $\phi_{\alpha+\beta}$ and ϕ_α is given by

$$(1-\bar{c})^2 = -A\bar{c}^2 + \frac{A}{A+1}$$

The double root is given by

$$\bar{c}_{\alpha/\alpha+\beta} = \frac{1}{A+1}$$

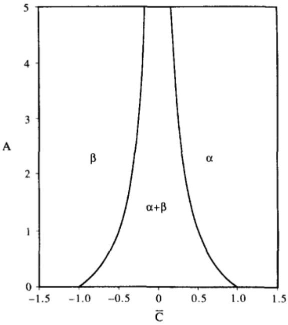
The boundary between $\phi_{\alpha+\beta}$ and ϕ_β is given by

$$(1+\bar{c})^2 = -A\bar{c}^2 + \frac{A}{A+1}$$

The double root is given by

$$\bar{c}_{\beta/\alpha+\beta} = -\frac{1}{A+1}$$

it means that two phase region always exists when $A \geq 0$.


5
4
3
2
1
0
A
β
α
α+β
−1.5
−1.0
−0.5
0
0.5
1.0
1.5
C̄