2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

09.17.2009

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Contents for previous class

- Gibbs Free Energy in Binary System

$$G_1 = X_A G_A + X_B G_B \quad J/mol$$

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

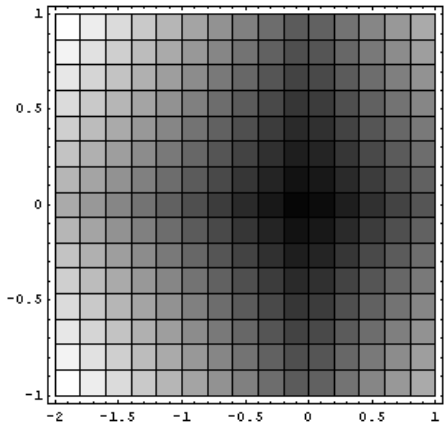
Ideal solution ($\Delta H_{mix}=0$) $\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$

$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

- Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A, will be proportional to dn_A.

$$dG' = \mu_A \, dn_A \qquad (T, P, n_B: \text{constant})$$



μ_A : **Chemical potential of A or partial morlar free energy of A**

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P,n_B} \qquad \mu_B = \left(\frac{\partial G'}{\partial n_B}\right)_{T,P,n_A}$$

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B \qquad \text{(for variable T, P)}$$

Contents for today's class

CHAPTER 1 & 2

- Binary System

  - Gibbs Free Energy in Binary System

    Ideal solution and Regular solution

  - Chemical potential and Activity

  - Equilibrium in Heterogeneous Systems

Regular Solutions

Ideal solution : $\Delta H_{mix} = 0$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Quasi-chemical model assumes that heat of mixing, ΔH_{mix}, is only due to the bond energies between adjacent atoms.

Structure model of a binary solution

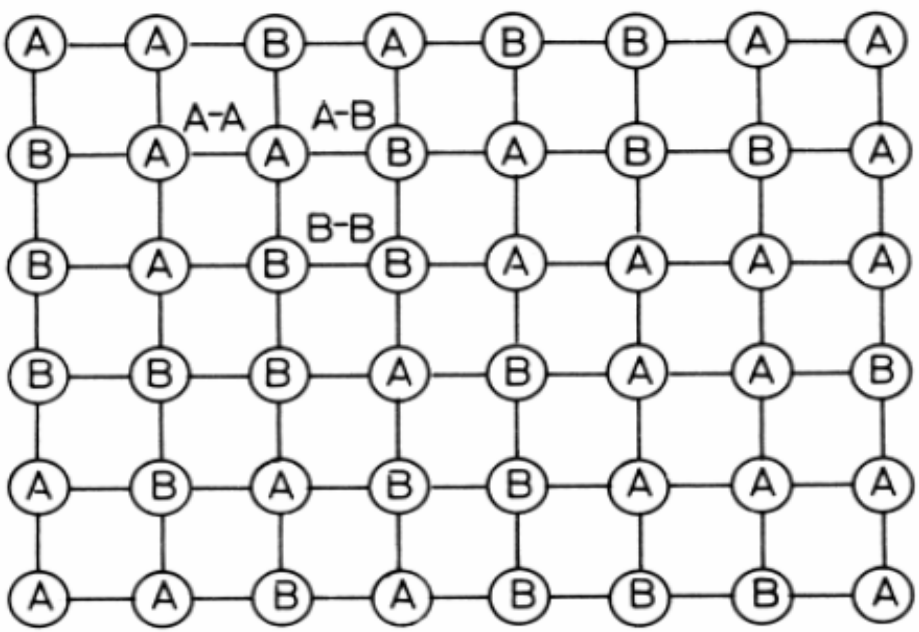


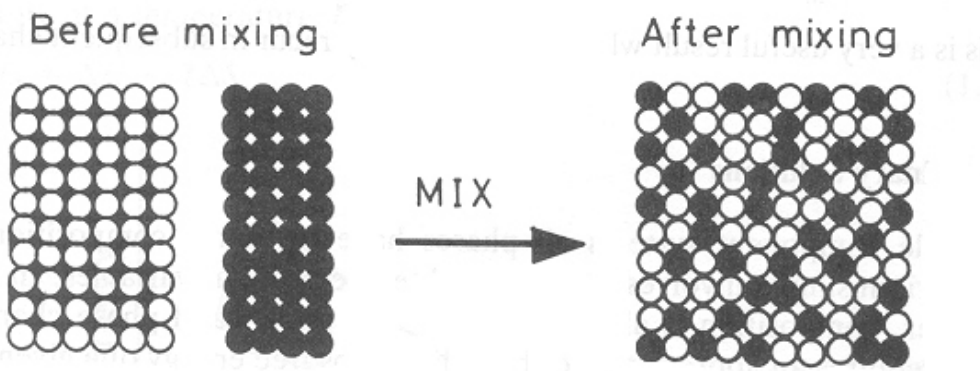
Fig. 1.13 The different types of interatomic bond in a solid solution.

Regular Solutions

	Bond energy	Number of bond
A-A	ε_{AA}	P_{AA}
B-B	ε_{BB}	P_{BB}
A-B	ε_{AB}	P_{AB}

Internal energy of the solution

$$E = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\varepsilon_{AB}$$



$$\Delta H_{mix} = P_{AB}\varepsilon \quad \text{where } \varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})_5$$

Regular Solutions

Completely random arrangement

$$\varepsilon = 0 \quad \Rightarrow \quad \varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

$\Delta H_{mix} = 0$ ideal solution

$P_{AB} = N_a z X_A X_B$ bonds per mole

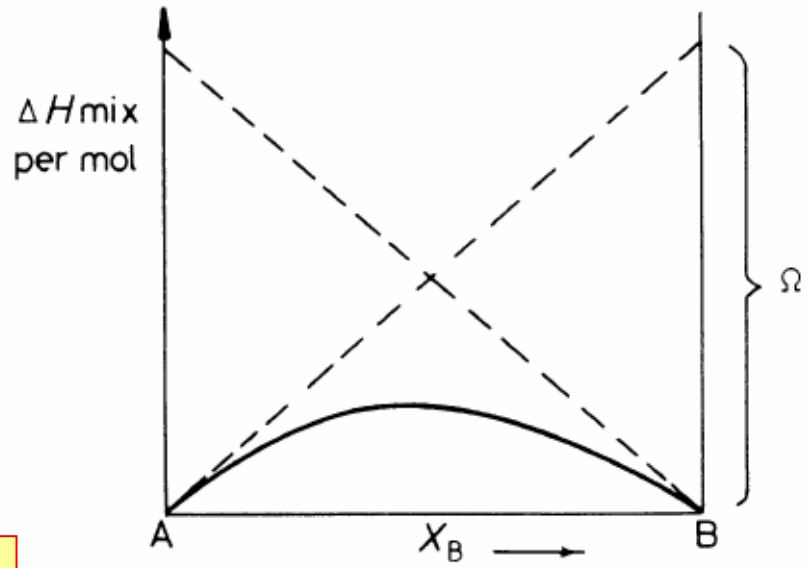
N_a : Avogadro's number

z : number of bonds per atom

$\varepsilon < 0 \rightarrow P_{AB} \uparrow$ $\varepsilon > 0 \rightarrow P_{AB} \downarrow$

$\varepsilon \approx 0 \quad \Rightarrow \quad \Delta H_{mix} = P_{AB}\varepsilon$

$\Delta H_{mix} = \Omega X_A X_B$ where $\Omega = N_a z \varepsilon$



Ω >0 인 경우

Regular Solutions

Fig. 1.14 The variation of ΔH_{mix} with composition for a regular solution.

Regular Solutions

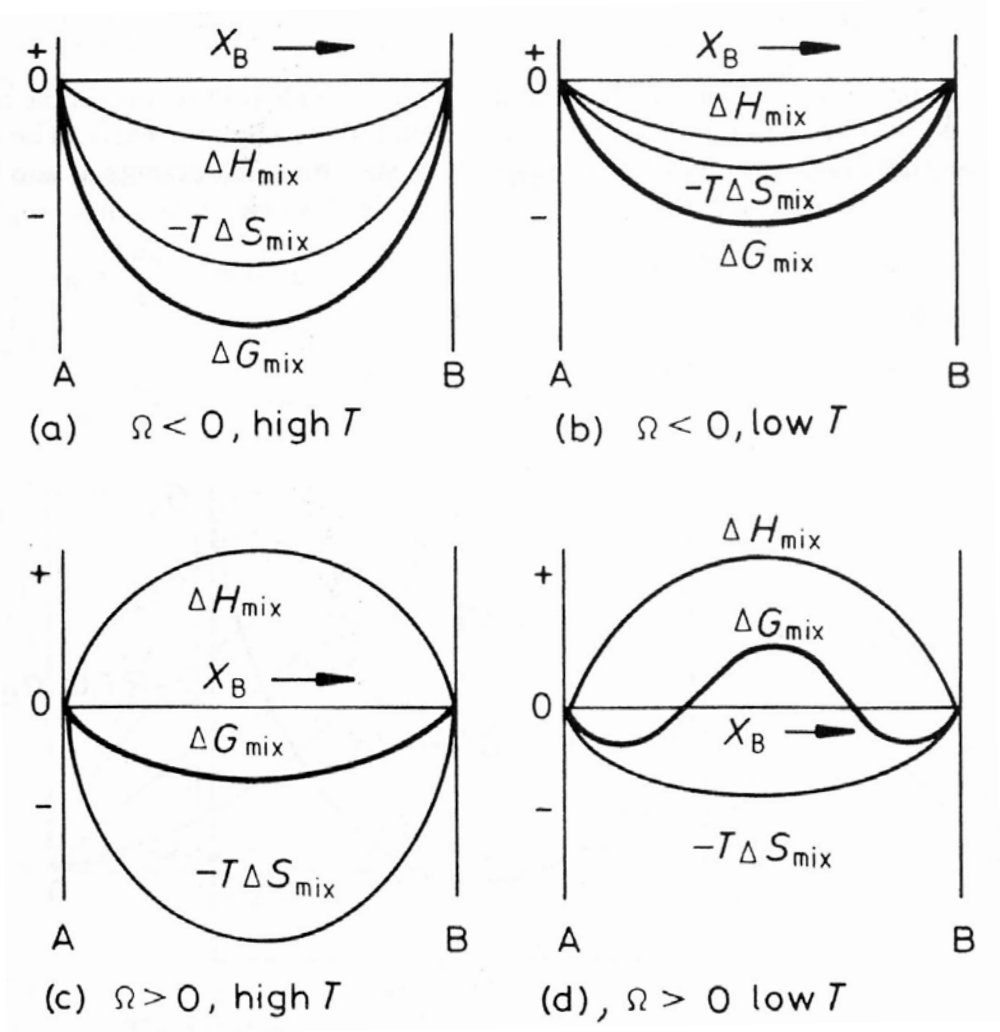
$$G_2 = G_1 + \Delta G_{mix}$$

$$G = X_A G_A + X_B G_B + \underbrace{\Omega X_A X_B}_{\Delta H_{mix}} + \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{-T\Delta S_{mix}}$$

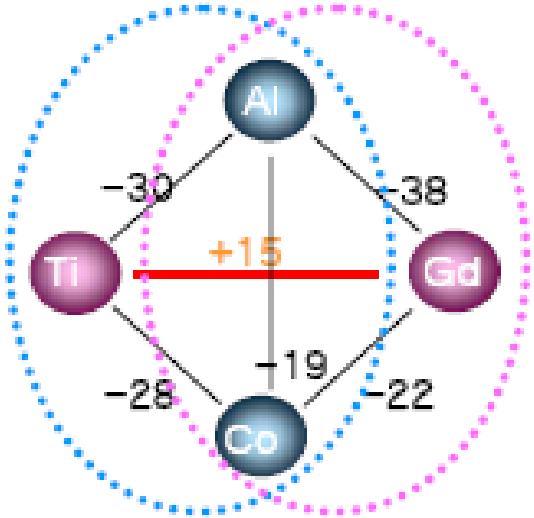
Reference state

Pure metal $G_A^0 = G_B^0 = 0$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



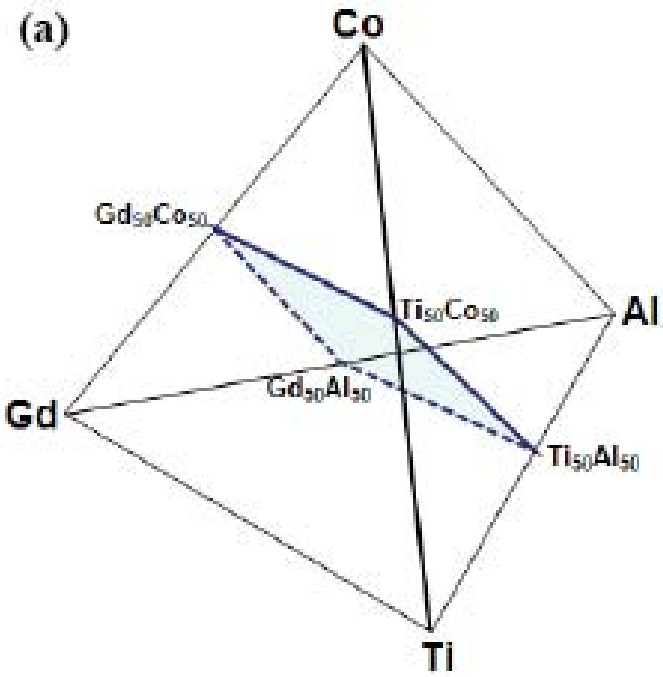
Synthesis of metallic glass composites using phase separation phenomenon

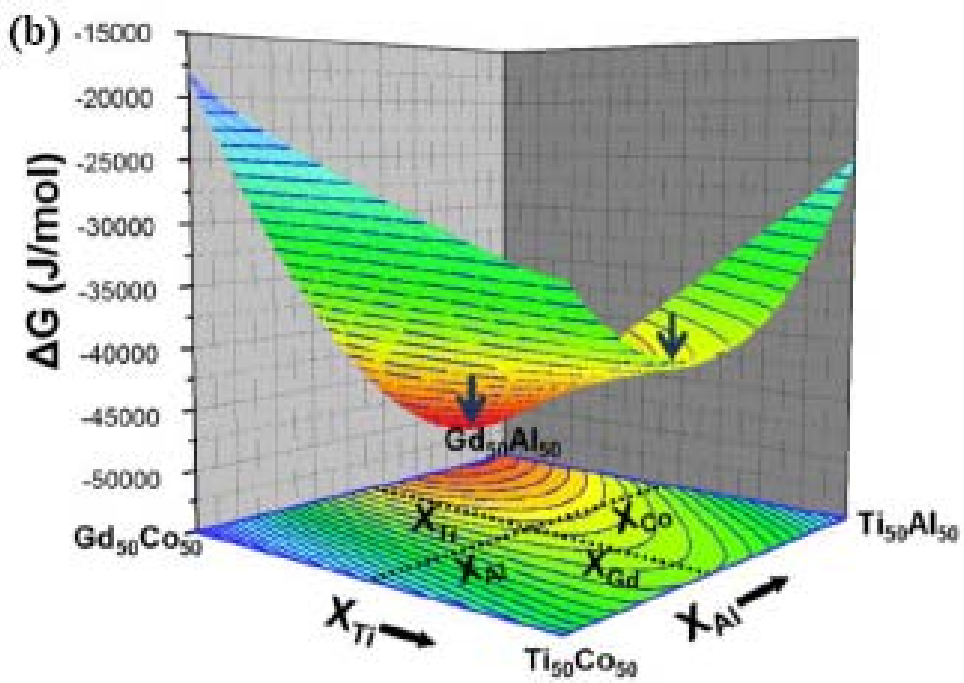


Possibility of two phase !!!

→ **Ti-Al-Co, Gd-Al-Co**

Fig. 1 (a) Composition section selected by rectangular plane intersection in quaternary Gd-Ti-Al-Co composition tetrahedron. (b) Gibbs free energy surface of liquid phase at 1000 K for the composition section given in (a). This Gibbs free energy surface shows two minima (arrows) implying that the phase separation can occur in that region.





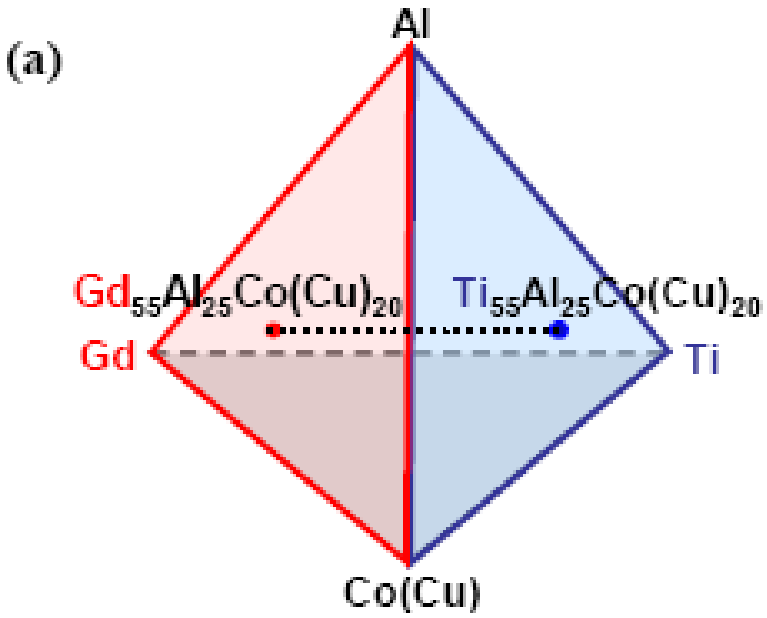
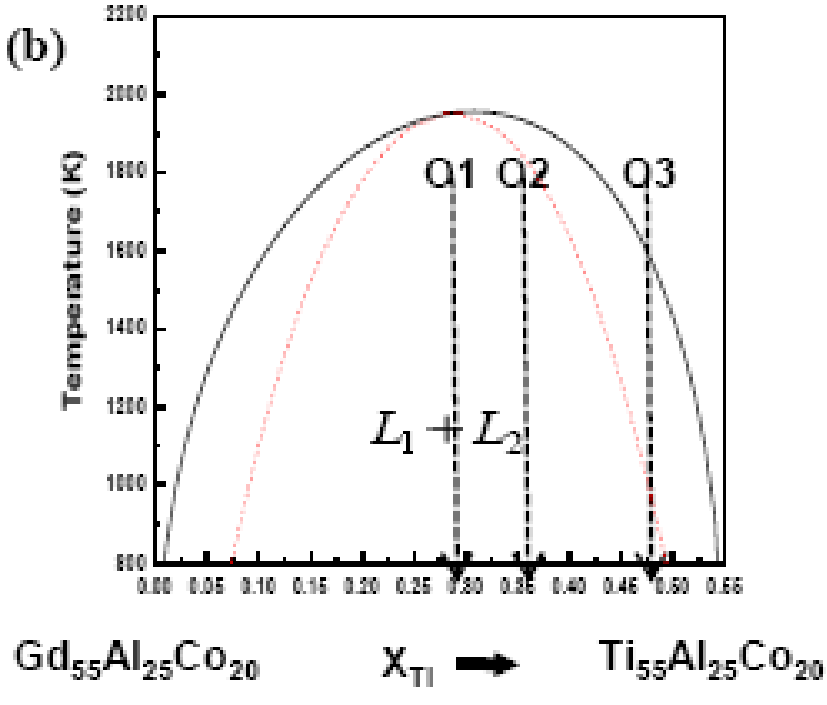


Fig. 2 (a) Representation of composition line in quaternary Gd-Ti-Al-Co(Cu) composition tetrahedron. Selected composition line is parallel to Gd-Ti binary edge line having positive heat of mixing. (b) and (c) Calculated miscibility gap (solid line) and spinodal locus (dashed line) in pseudo-binary section for the liquid phase in $Gd_{(55-X)}Ti_XAl_{25}Co_{20}$ and $Gd_{(55-X)}Ti_XAl_{25}Cu_{20}$, respectively.



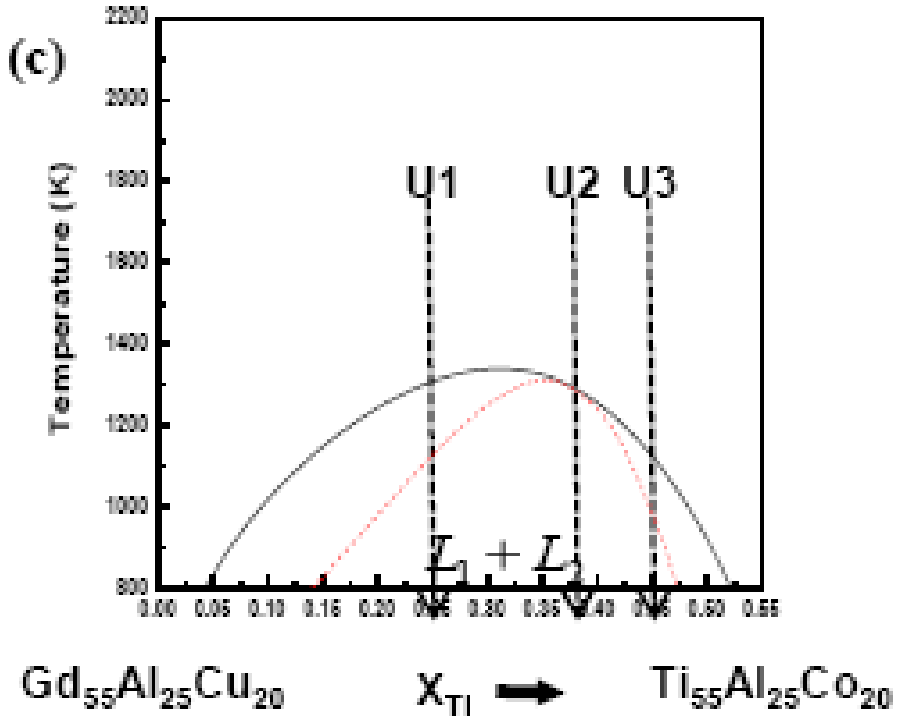


Fig. 3 (a) ~ (c) BF TEM image and corresponding SADP obtained from melt-spun $Gd_{25}Ti_{30}Al_{25}Co_{20}$ (O1), $Gd_{18}Ti_{37}Al_{25}Co_{20}$ (O2) and $Gd_{6}Ti_{49}Al_{25}Co_{20}$ (O3) ribbon, respectively.

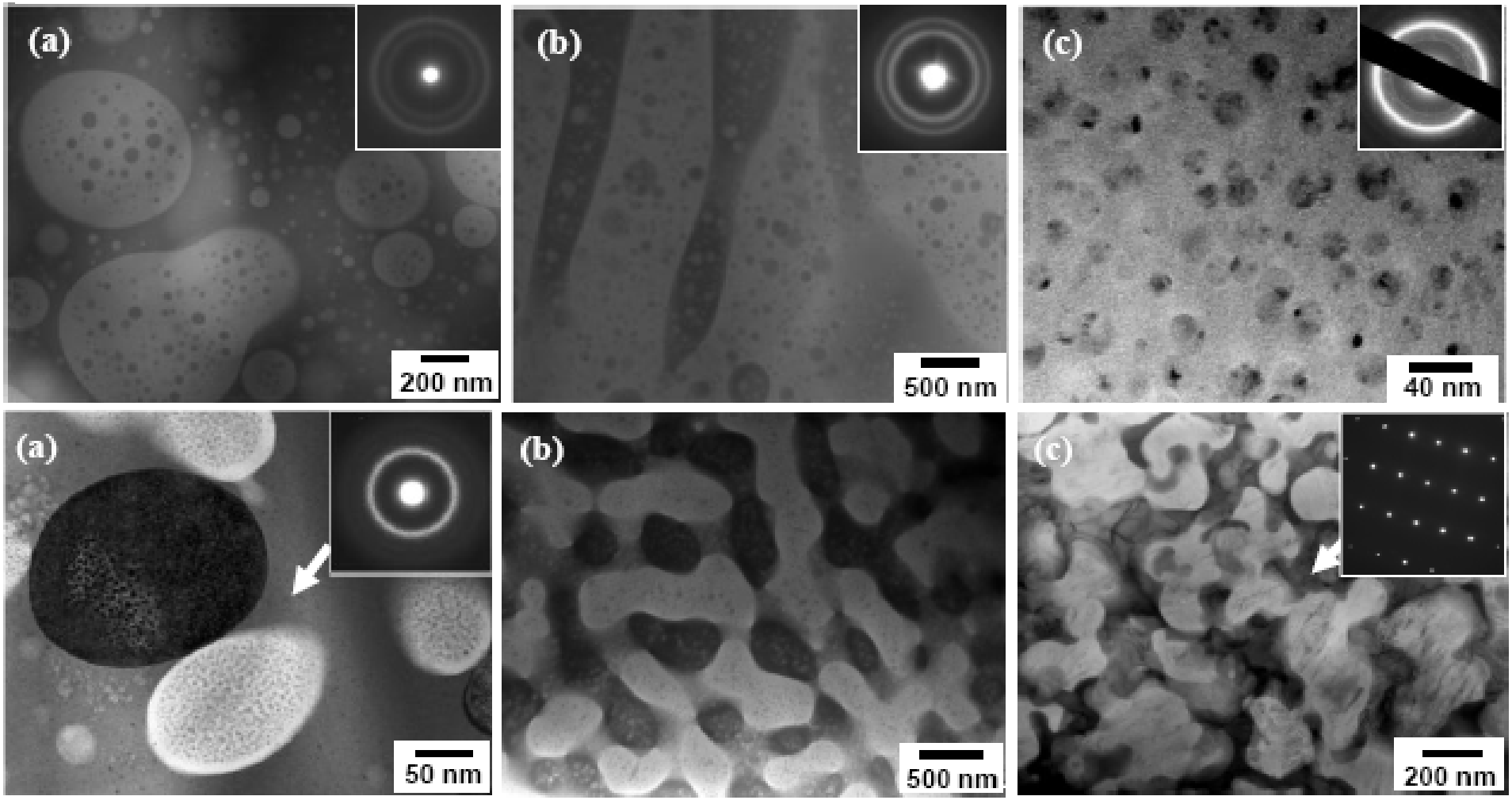
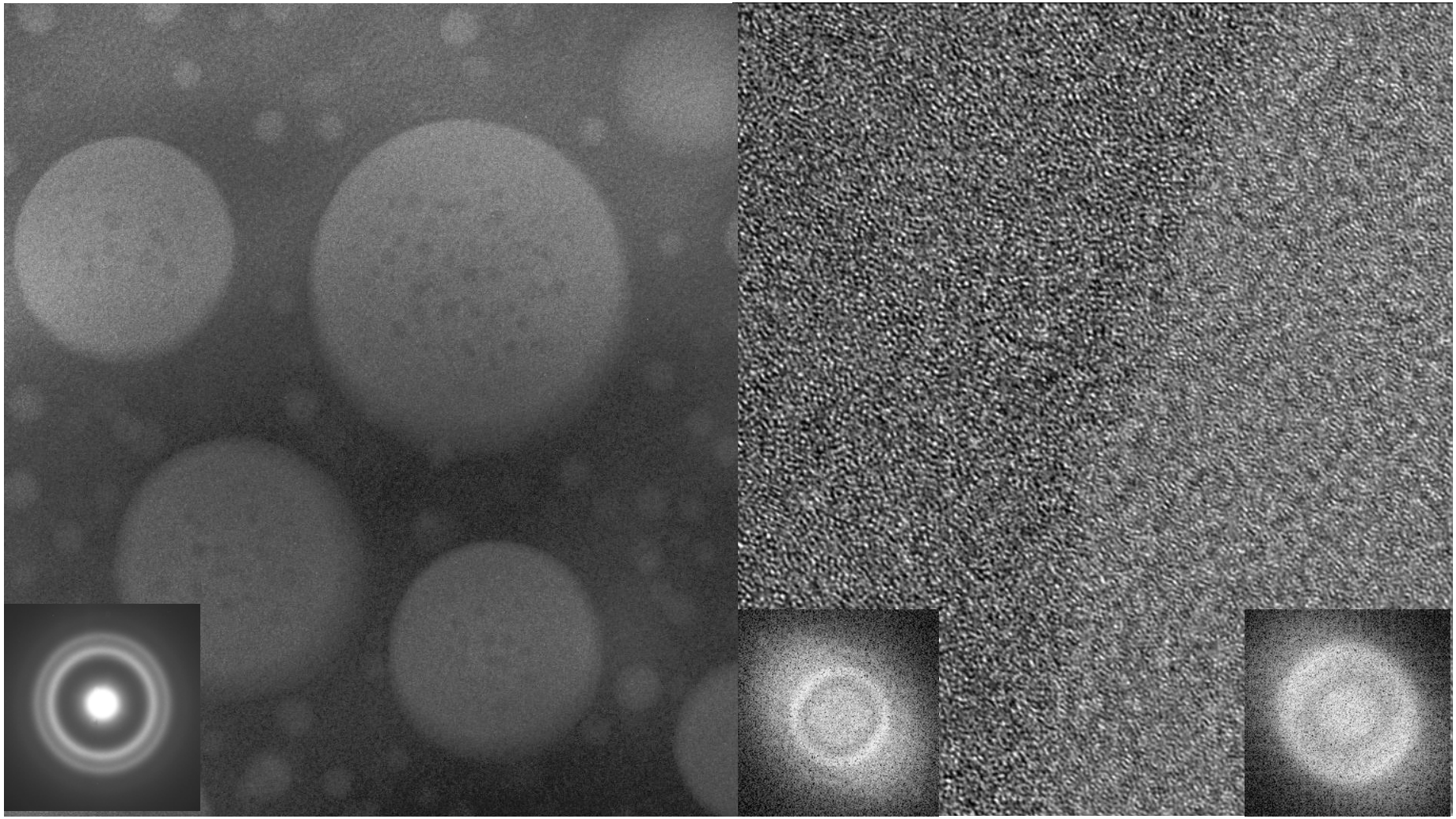
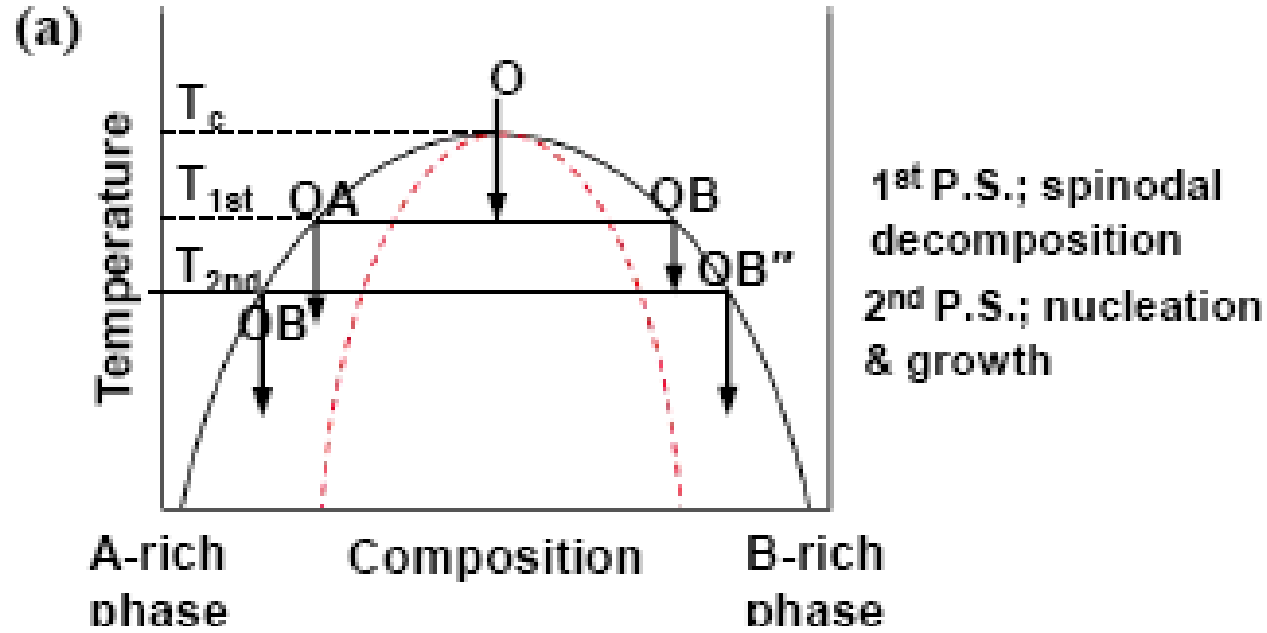


Fig. 4 (a) ~ (c) BF TEM image and corresponding SADP obtained from melt-spun $Gd_{30}Ti_{25}Al_{25}Cu_{20}$ (U1), $Gd_{17}Ti_{38}Al_{25}Cu_{20}$ (U2) and $Gd_{10}Ti_{45}Al_{25}Cu_{20}$ (U3) ribbon, respectively.

Phase separation in metallic glasses




(a)
Temperature
T_c
T_{1st}
T_{2nd}
O
OA
OB
OB"
OB'
1st P.S.; spinodal decomposition
2nd P.S.; nucleation & growth
A-rich phase
Composition
B-rich phase

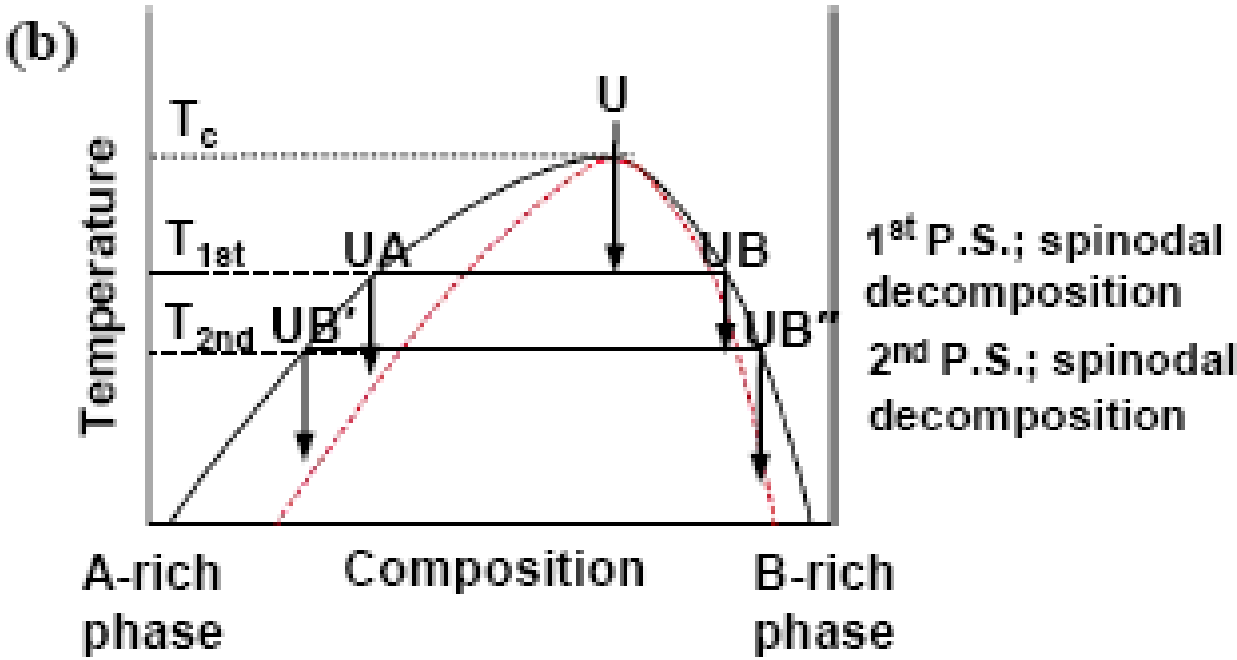
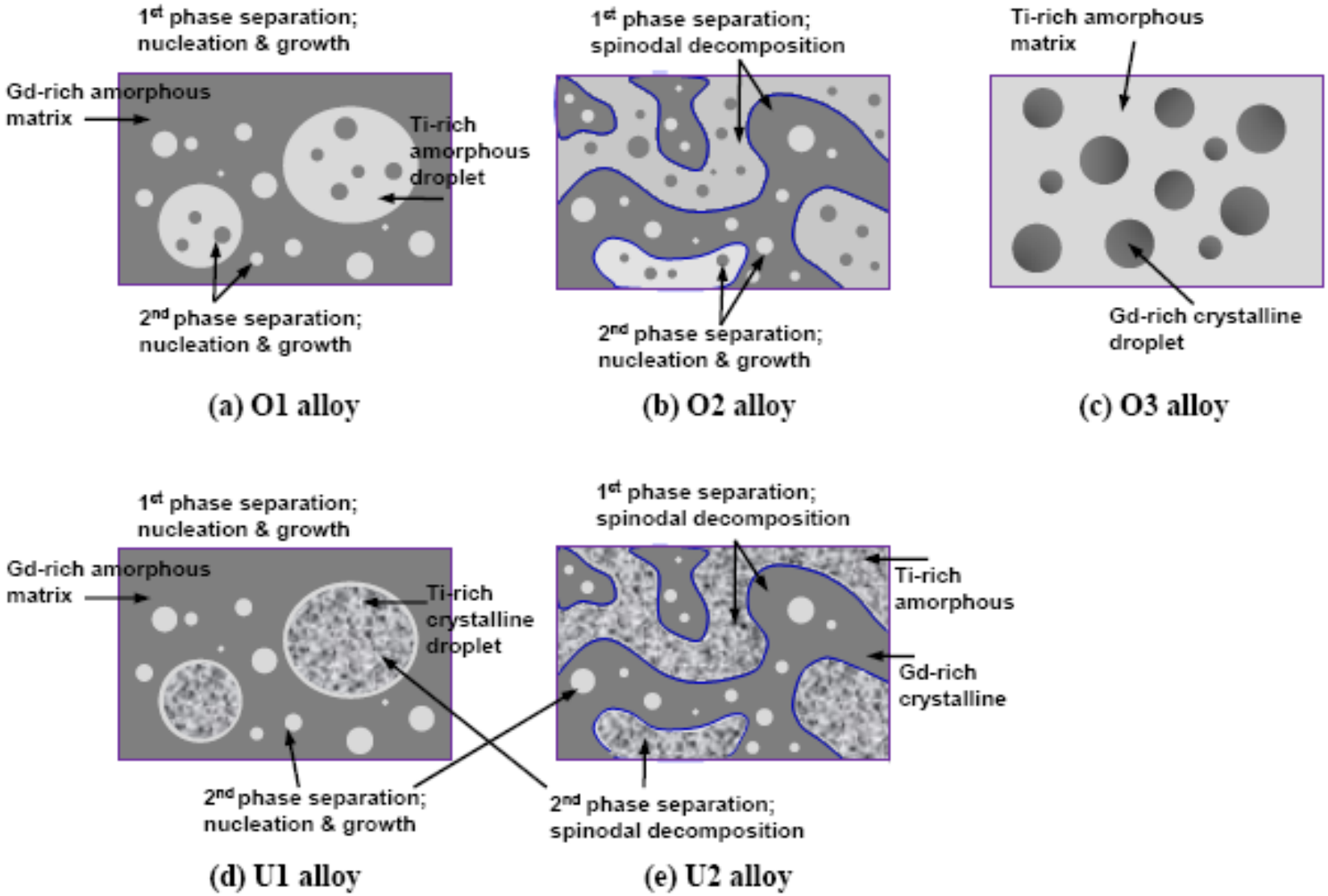

(b)
Temperature
T_c
T_{1st}
T_{2nd}
U
UA
UB
UB"
UB'
1st P.S.; spinodal decomposition
2nd P.S.; spinodal decomposition
A-rich phase
Composition
B-rich phase

Fig. 9 Schematic drawings of the microstructures shown in Figs. 3(a)-(c) and 4(a)-(b) showing variation of microstructure depending on alloy composition and second phase separation mechanism.



Correlation between chemical potential and free energy

For 1 mole of the solution (T, P: constant)

G = E+PV-TS

$$G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$$

G = H-TS

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$\rightarrow \quad X_A X_B = X_A^2 X_B + X_B^2 X_A$$

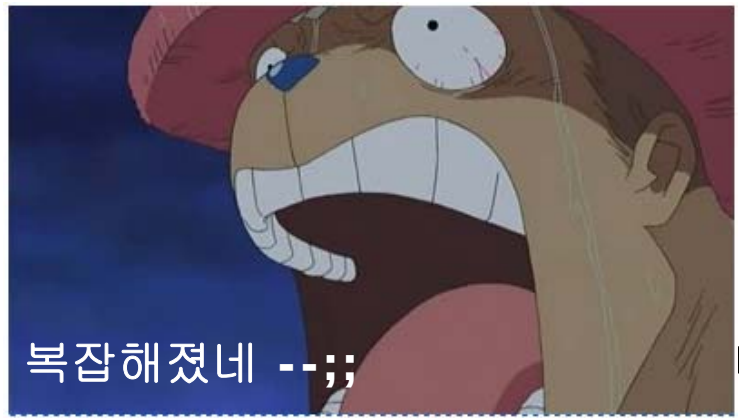
$$= X_A(G_A + \Omega(1-X_A)^2 + RT \ln X_A) + X_B(G_B + \Omega(1-X_B)^2 + RT \ln X_B)$$

Regular solution

$$\mu_A = G_A + \Omega (1-X_A)^2 + RT \ln X_A$$
$$\mu_B = G_B + \Omega (1-X_B)^2 + RT \ln X_B$$

$$\mu_A = G_A + RT \ln X_A$$
$$\mu_B = G_B + RT \ln X_B$$

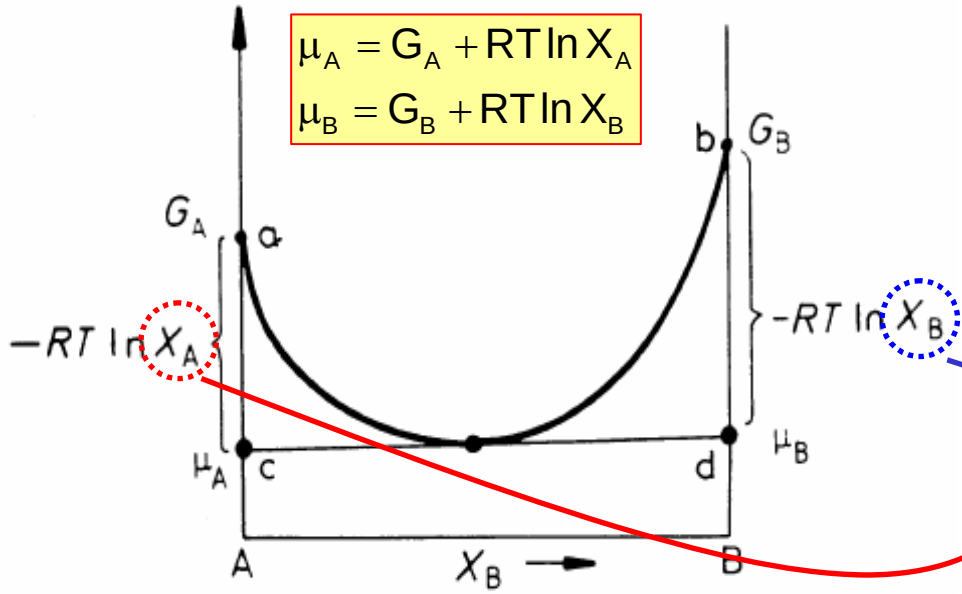
Ideal solution



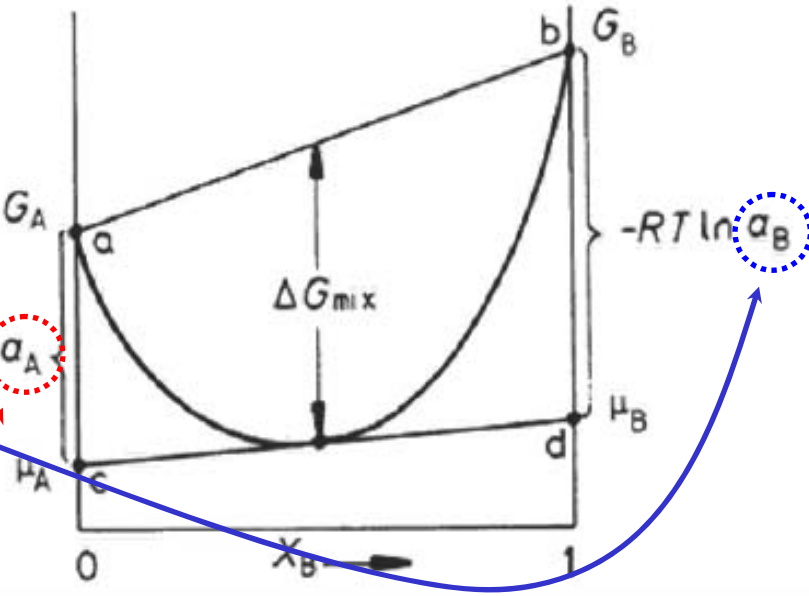
Activity, a : effective concentration for mass action

ideal solution

$$\mu_A = G_A + RT\ln X_A$$
$$\mu_B = G_B + RT\ln X_B$$



regular solution



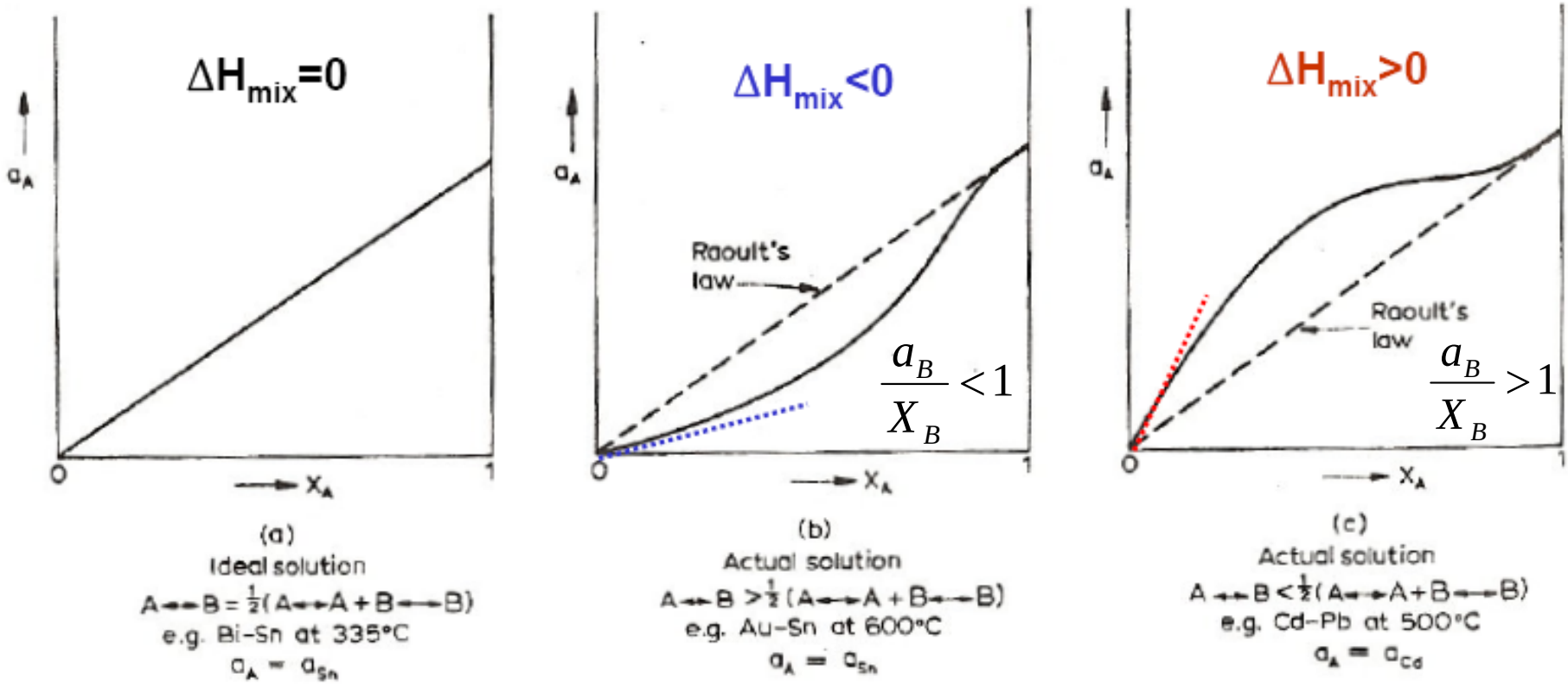
$$\mu_A = G_A + RT\ln a_A \qquad \mu_B = G_B + RT\ln a_B$$

$$\mu_A = G_A + \Omega(1-X_A)^2 + RT\ln X_A \qquad \mu_B = G_B + \Omega(1-X_B)^2 + RT\ln X_B$$

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1-X_A)^2 \qquad \ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1-X_B)^2$$

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient} \qquad \gamma_B = \frac{a_B}{X_B}$$

Activity-composition curves for solutions



- **For a dilute solution of B in A ($X_B \rightarrow 0$)**

$$\gamma_B = \frac{a_B}{X_B} \cong \text{constant} \quad \text{(Henry's Law)}$$

$$\gamma_A = \frac{a_A}{X_A} \cong 1 \quad \text{(Rault's Law)}$$

ideal solution ~ random mixing

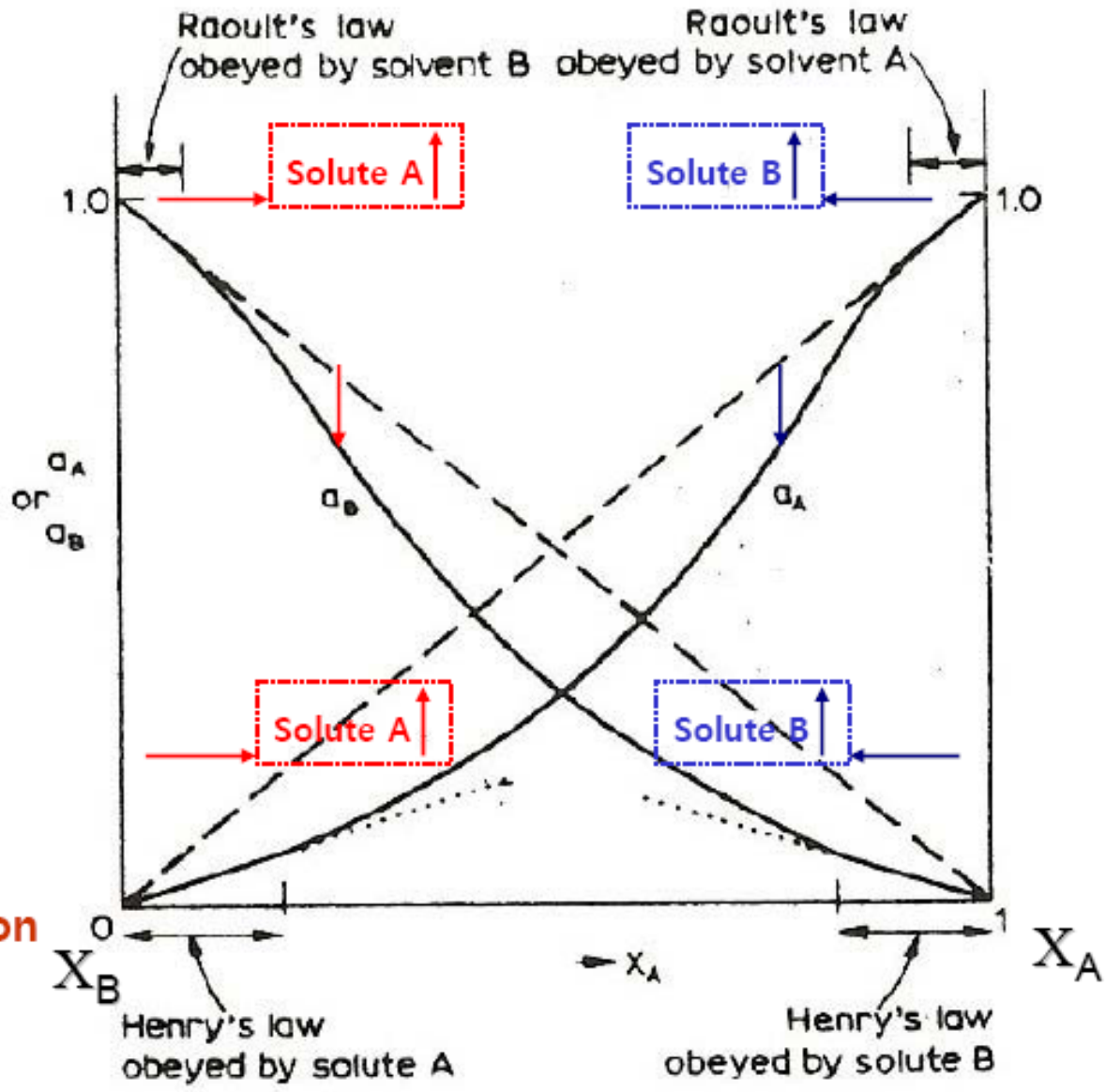
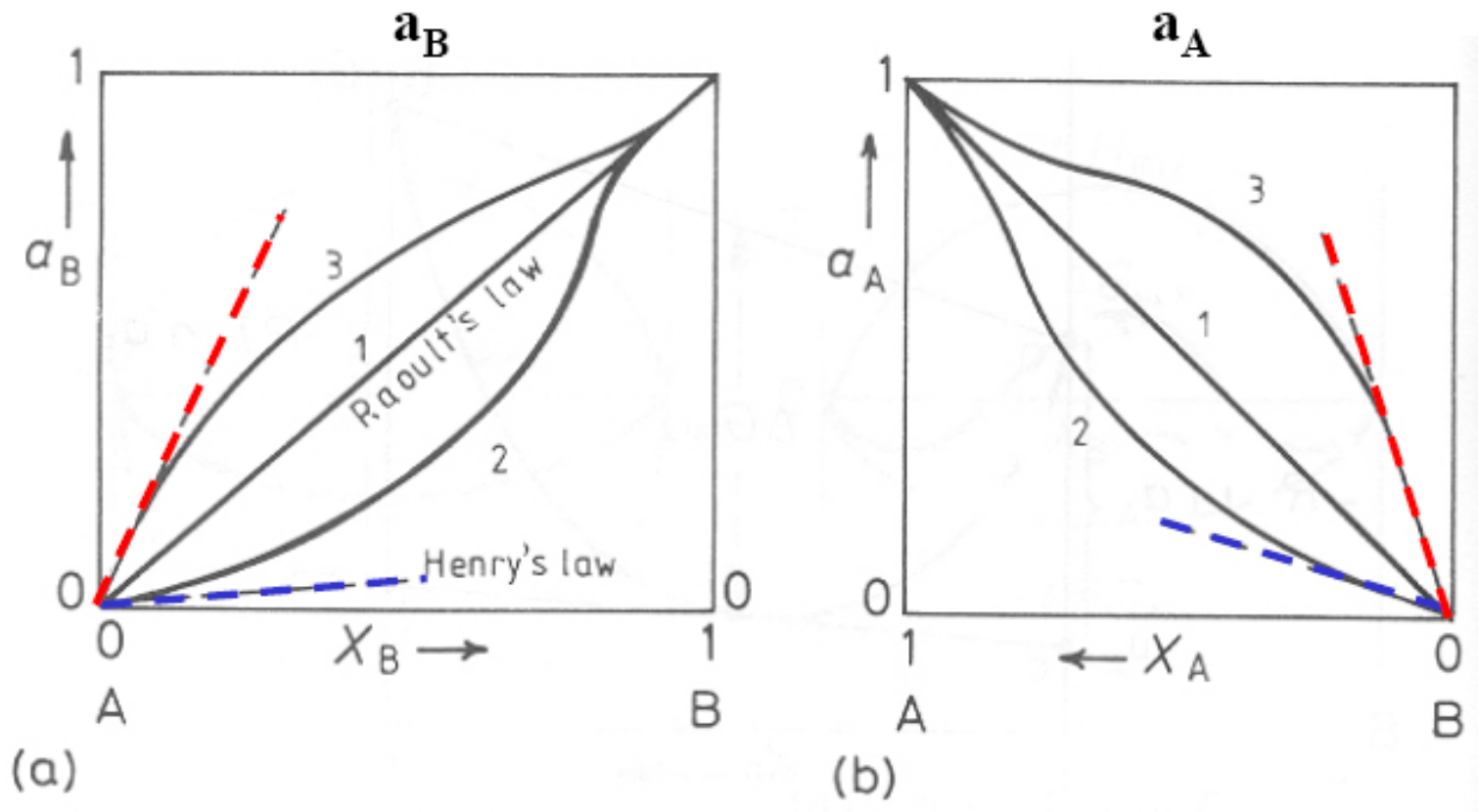


Fig. Raoult's law and Henry's law applied to actual solutions

Variation of activity with composition (a) a_B, (b) a_A



Line 1 : (a) $a_B=X_B$, (b) $a_A=X_A$ ideal solution…Rault's law

Line 2 : (a) $a_B<X_B$, (b) $a_A<X_A$ $\Delta H_{mix}<0$ ⇐ $\ln\left(\frac{a_A}{X_A}\right)=\frac{\Omega}{RT}(1-X_A)^2$

Line 3 : (a) $a_B>X_B$, (b) $a_A>X_A$ $\Delta H_{mix}>0$

Activity of a component is just another means of describing **the state** of the component in a solution.

degree of non-ideality ? $\rightarrow \dfrac{a_A}{X_A}$

$$\frac{a_A}{X_A} = \gamma_A, \quad a_A = \gamma_A X_A$$

γ_A : activity coefficient

$$\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1 - X_B)$$

$$\mu_A = G_A + RT\ln a_A$$

Activity or chemical potential of a component is important when several condensed phases are in equilibrium.

Chemical Equilibrium (μ, a) → multiphase and multicomponent

$$(\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \ldots), (a_i^{\alpha} = a_i^{\beta} = a_i^{\gamma} = \ldots)$$

$$(\mu_A^{\alpha} = \mu_A^{\beta} = \mu_A^{\gamma} = \ldots), (a_A^{\alpha} = a_A^{\beta} = a_A^{\gamma} = \ldots)$$

$$(\mu_B^{\alpha} = \mu_B^{\beta} = \mu_B^{\gamma} = \ldots), (a_B^{\alpha} = a_B^{\beta} = a_B^{\gamma} = \ldots)$$

$\vdots$

Contents for today's class

- **Binary System** mixture/ solution / compound
- **Gibbs Free Energy in Binary System**

$$G_1 = X_A G_A + X_B G_B \quad J/mol$$

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

Ideal solution ($\Delta H_{mix}=0$)

$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Regular solution

$$\Delta H_{mix} = P_{AB}\varepsilon$$

$$\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

where $\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

- **Chemical potential** and **Activity**

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,\,P,\,n_B}$$

- $\mu_A = G_A + RT\ln a_A$

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2$$

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$