2009 fall

Phase Transformation of Materials

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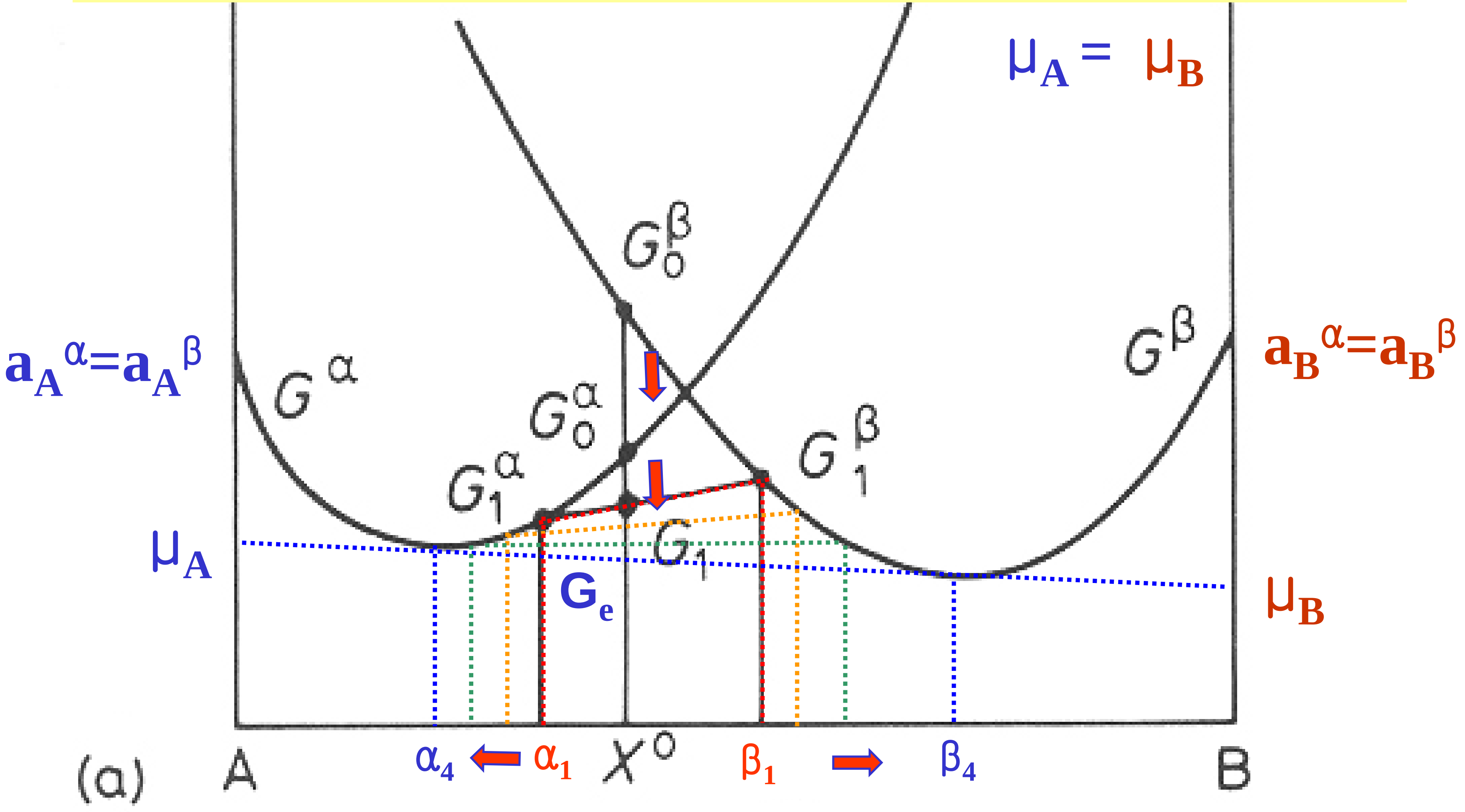
Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

Equilibrium in Heterogeneous Systems

In X^0, $G_0^\beta > G_0^\alpha > G_1$ ➡ $\alpha + \beta$ 로 분리 ➡ 두상의 화학 포텐셜 일치



$\mu_A = \mu_B$

$a_A^\alpha = a_A^\beta$

$a_B^\alpha = a_B^\beta$

Contents for today's class

- Binary phase diagrams

1) Simple Phase Diagrams

2) Systems with miscibility gap

4) Simple Eutectic Systems

3) Ordered Alloys

5) Phase diagrams containing intermediate phases

1) Simple Phase Diagrams

가정: (1) completely miscible in solid and liquid.

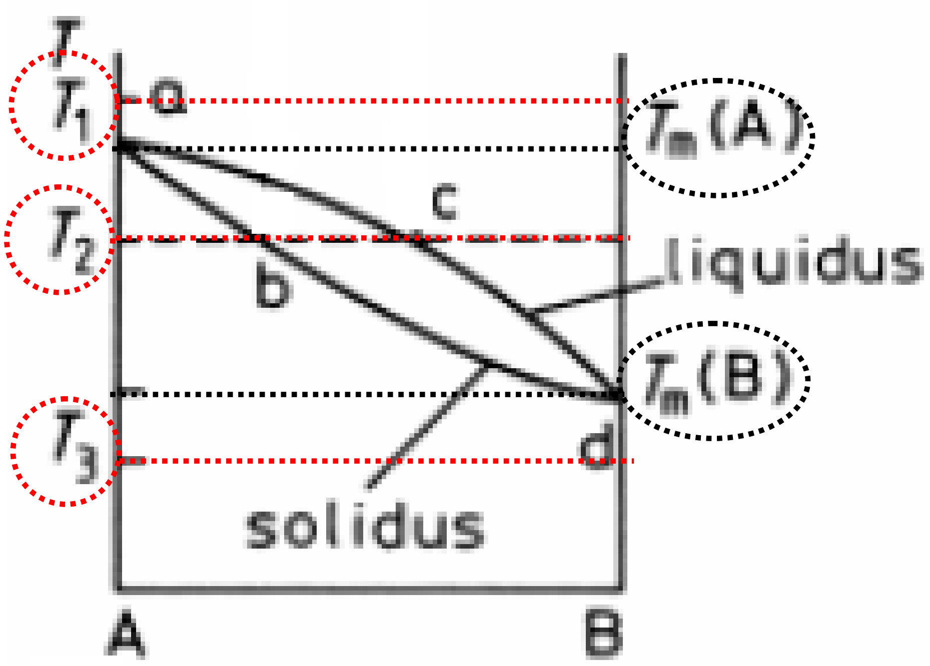
(2) Both are ideal soln.

$$\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0$$

(3) $T_m(A) > T_m(B)$

(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$

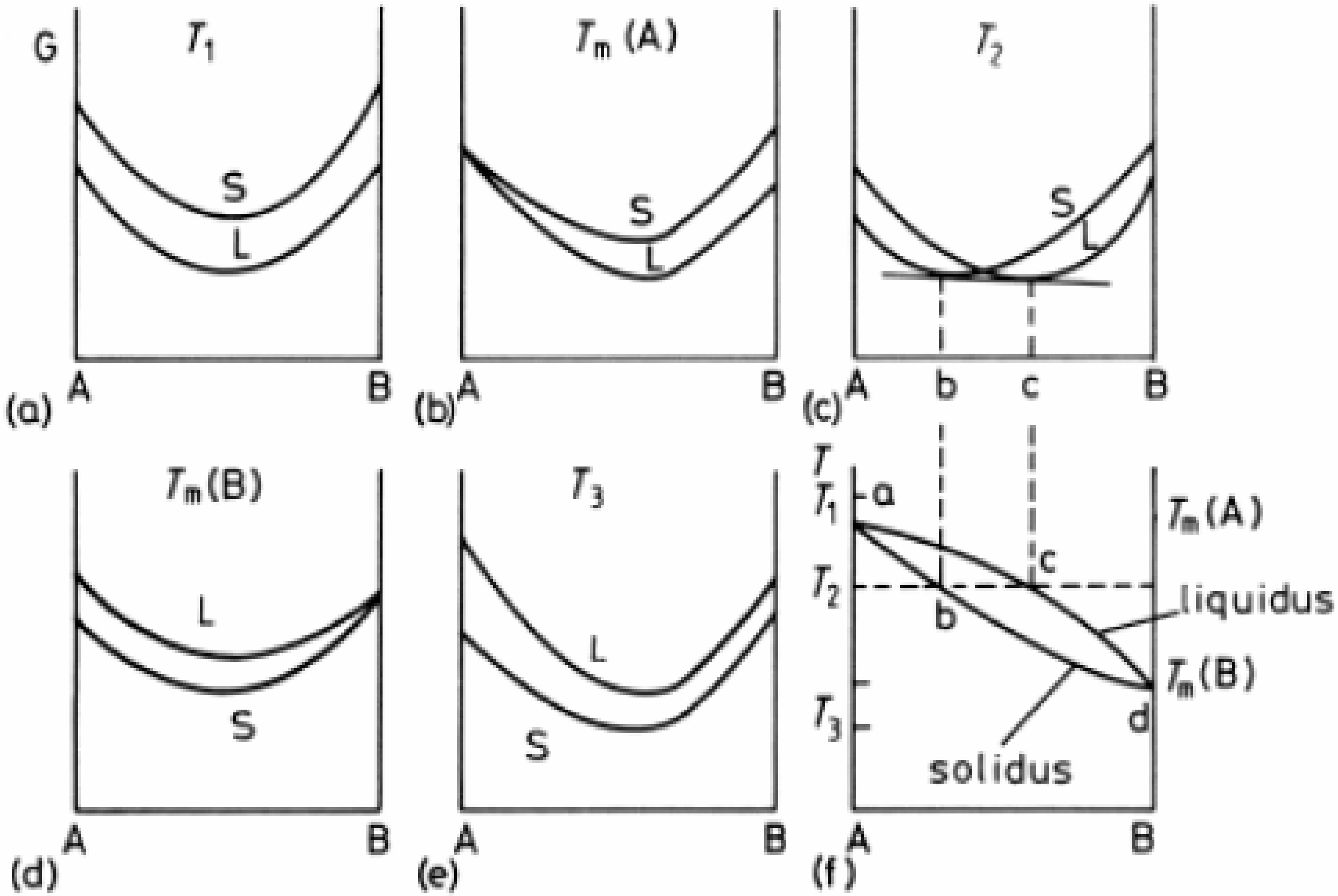
Draw G^L and G^S as a function of composition X_B at T_1, $T_m(A)$, T_2, $T_m(B)$, and T_3.



1.5 Binary phase diagrams

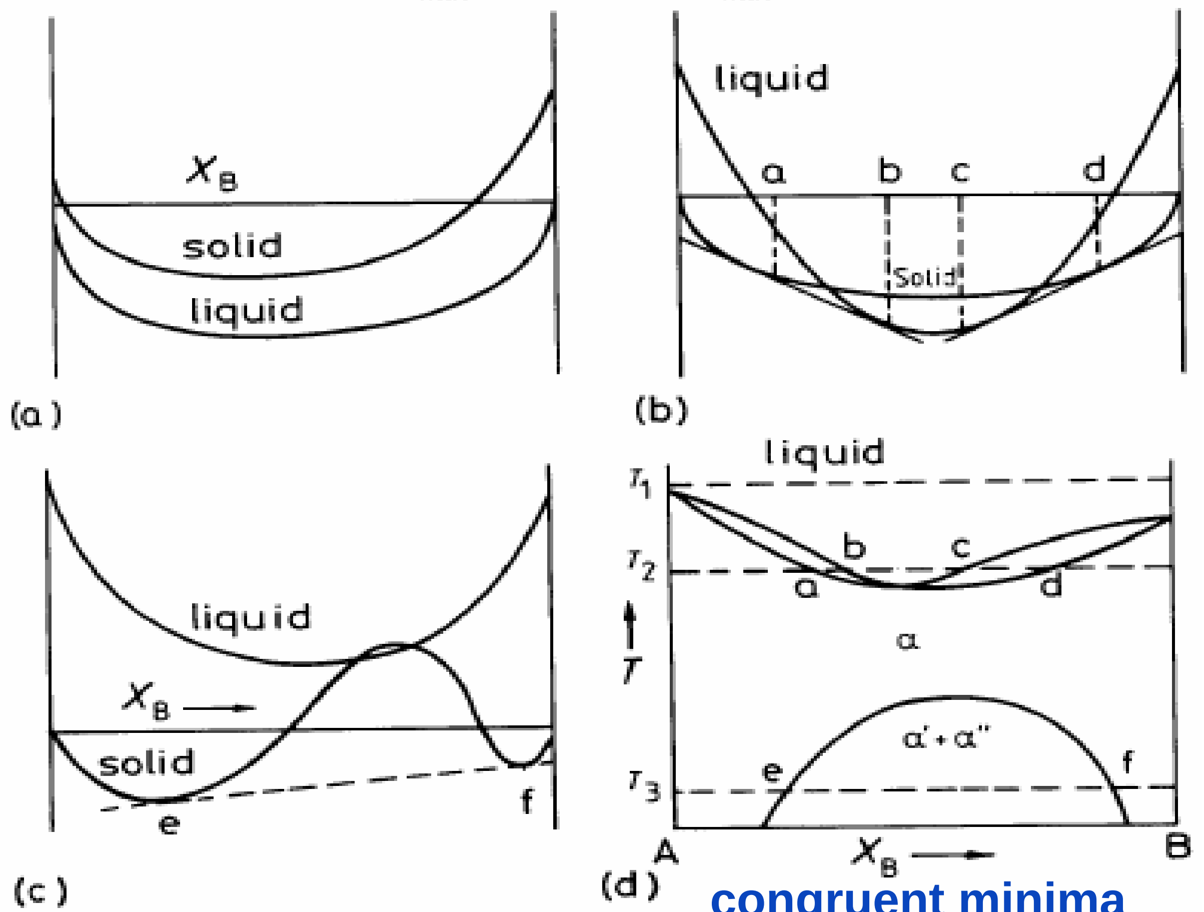
1) Simple Phase Diagrams

가정: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.
(3) $T_m(A) > T_m(B)$
(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$



2) Systems with miscibility gab

$$\Delta H^{L}_{mix} = 0 \qquad \Delta H^{S}_{mix} > 0$$

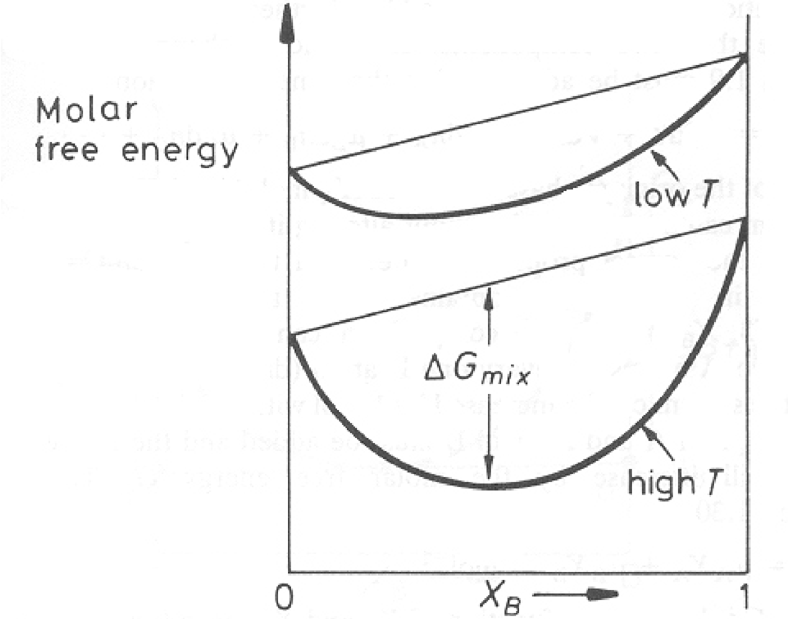


congruent minima

How to characterize G^s mathematically in the region of miscibility gap between e and f ?

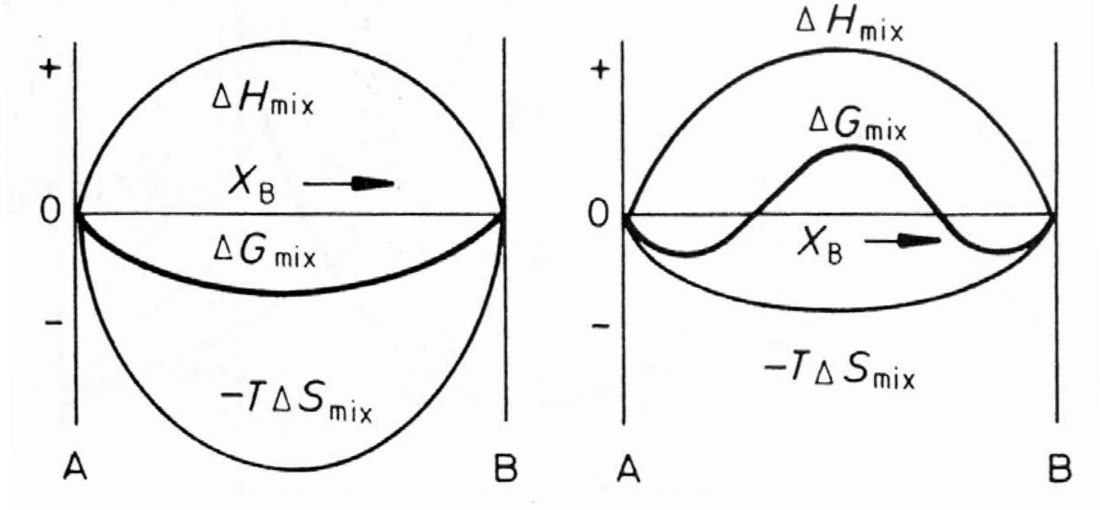
Ideal Solutions

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



Regular Solutions

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



(c) $\Omega > 0$, high T

(d) , $\Omega > 0$ low T

Reference state

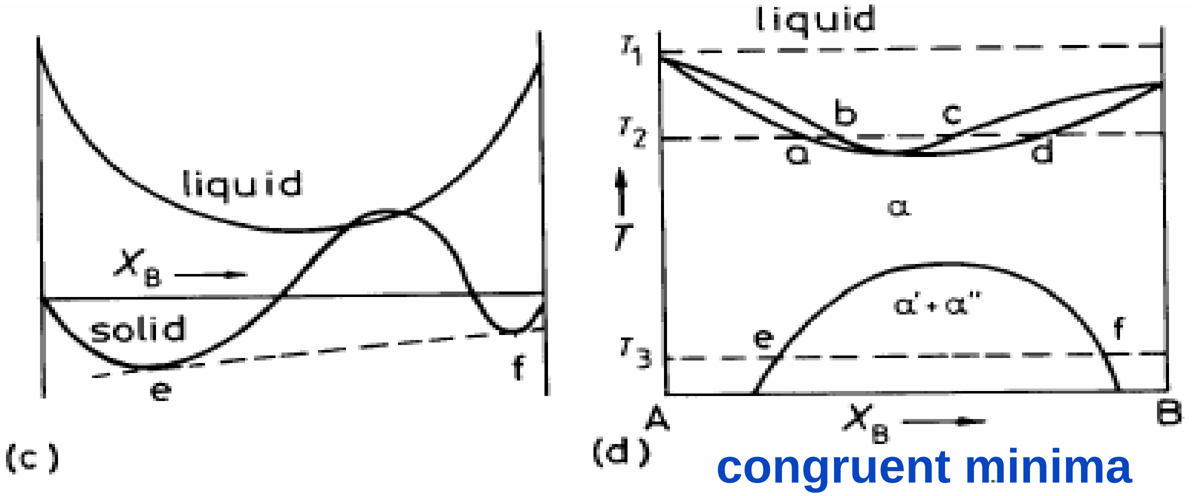
Pure metal $G_A^0 = G_B^0 = 0$

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

2) Systems with miscibility gab

$$\Delta H^{L}_{mix} = 0 \qquad \Delta H^{S}_{mix} > 0$$

- When A and B atoms dislike each other, $\Delta H_{mix} > 0$
- In this case, the free energy curve at low temperature has a region of negative curvature, $\frac{d^2G}{dX_B^2} < 0$
- This results in a ‘miscibility gap’ of α´ and α˝ in the phase diagram



congruent minima

1.5 Binary phase diagrams

4) Simple Eutectic Systems $\Delta H_{mix}^{L} = 0 \quad \Delta H_{mix}^{S} >> 0$

- **ΔH_m>>0 and the miscibility gap extends to the melting temperature.**

(when both solids have the same structure.)

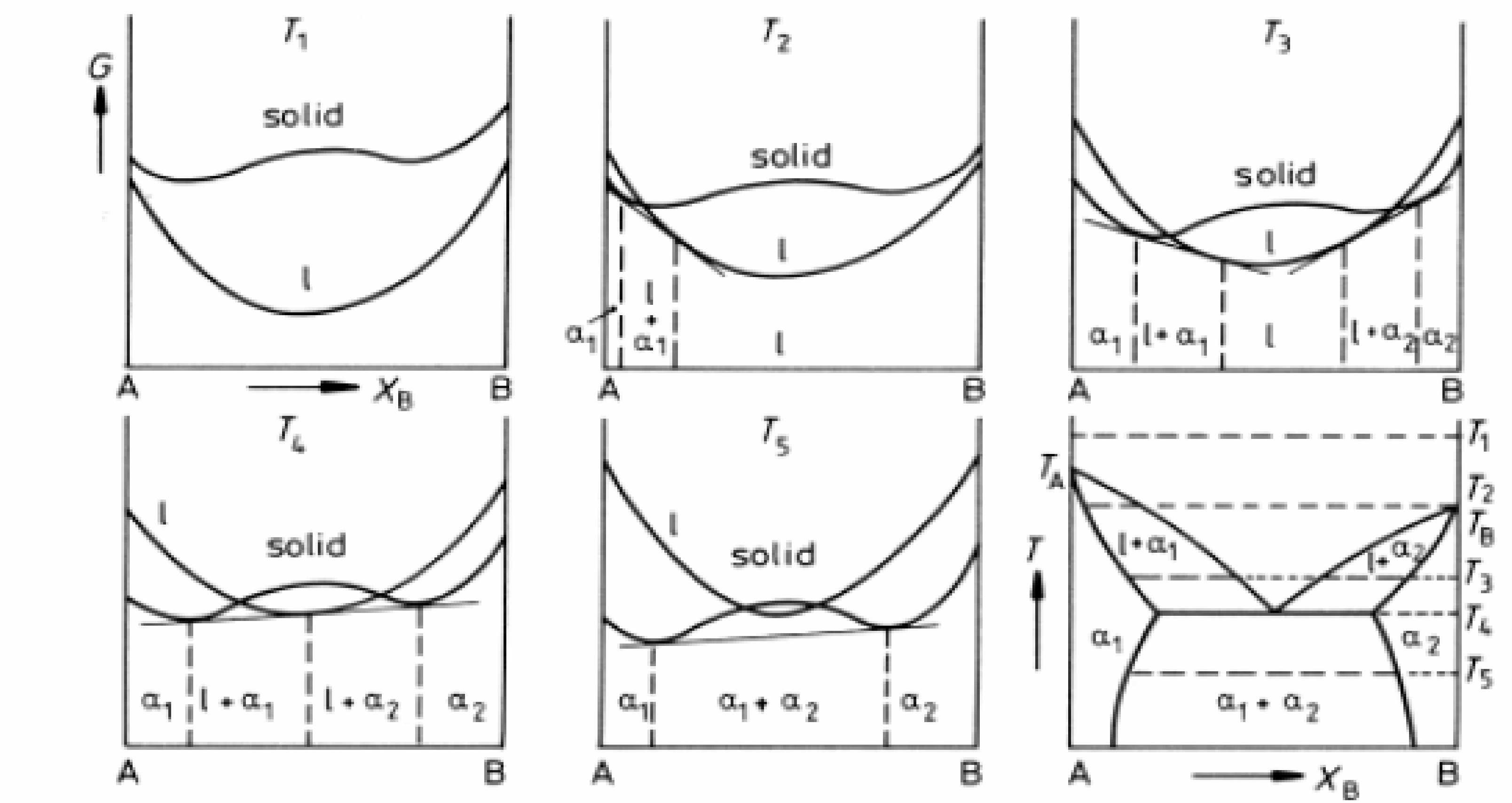


Fig 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure. (After A.H. Cottrell, *Theoretical Structural Metallurgy*, Edward Arnold, London, 1955,©Sir Alan Cottrell.)

(when each solid has the different crystal structure.)

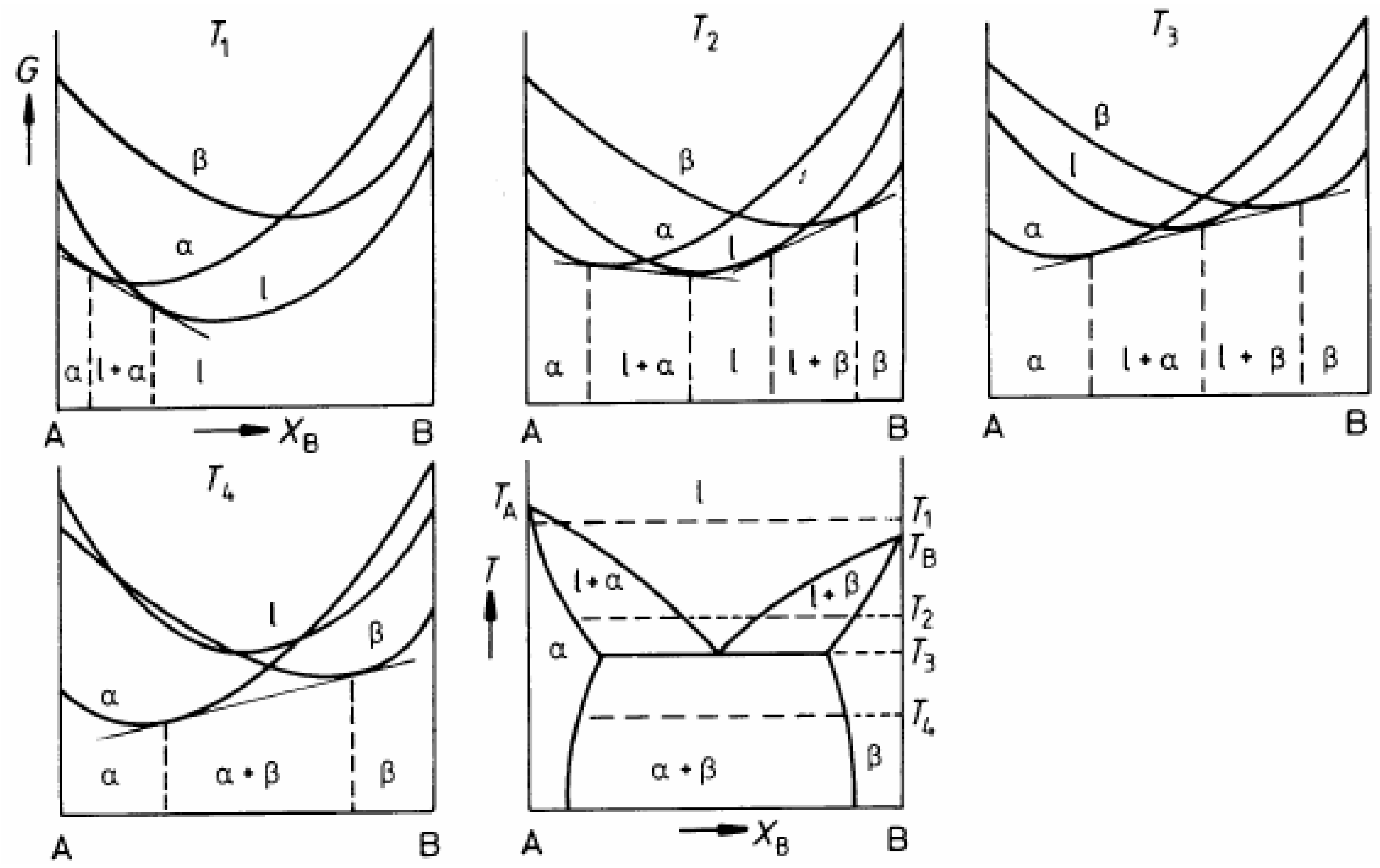


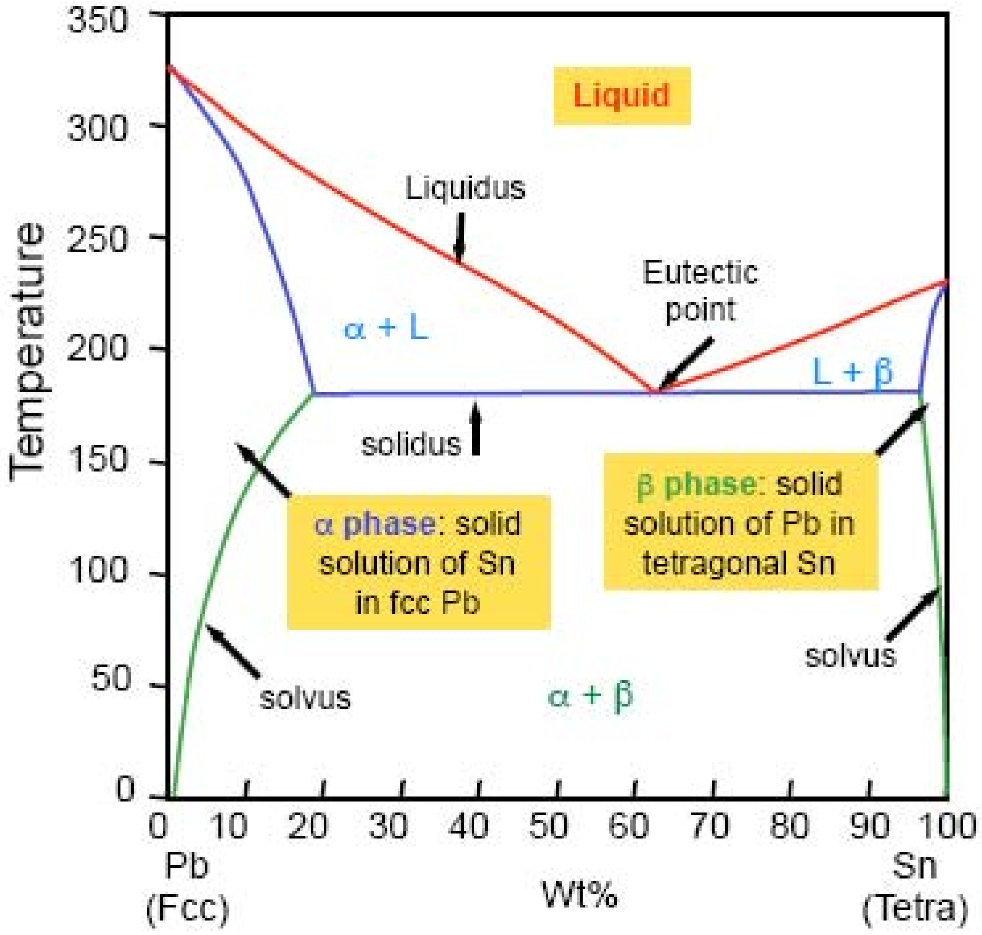
Fig. 1.33 The derivation of a eutectic phase diagram where each solid phase has a different crystal structure. (After A. Prince, *Alloy Phase Equilibria*, Elsevier, Amsterdam, 1966.)

Eutectic Systems

The Pb-Sn system is characteristic of a valley in the middle. Such system is known as the **Eutectic** system. The central point is the Eutectic point and the transformation though this point is called Eutectic reaction: **L**✦α+β

Pb has a fcc structure and Sn has a tetragonal structure. The system has three phases: L, α and β.

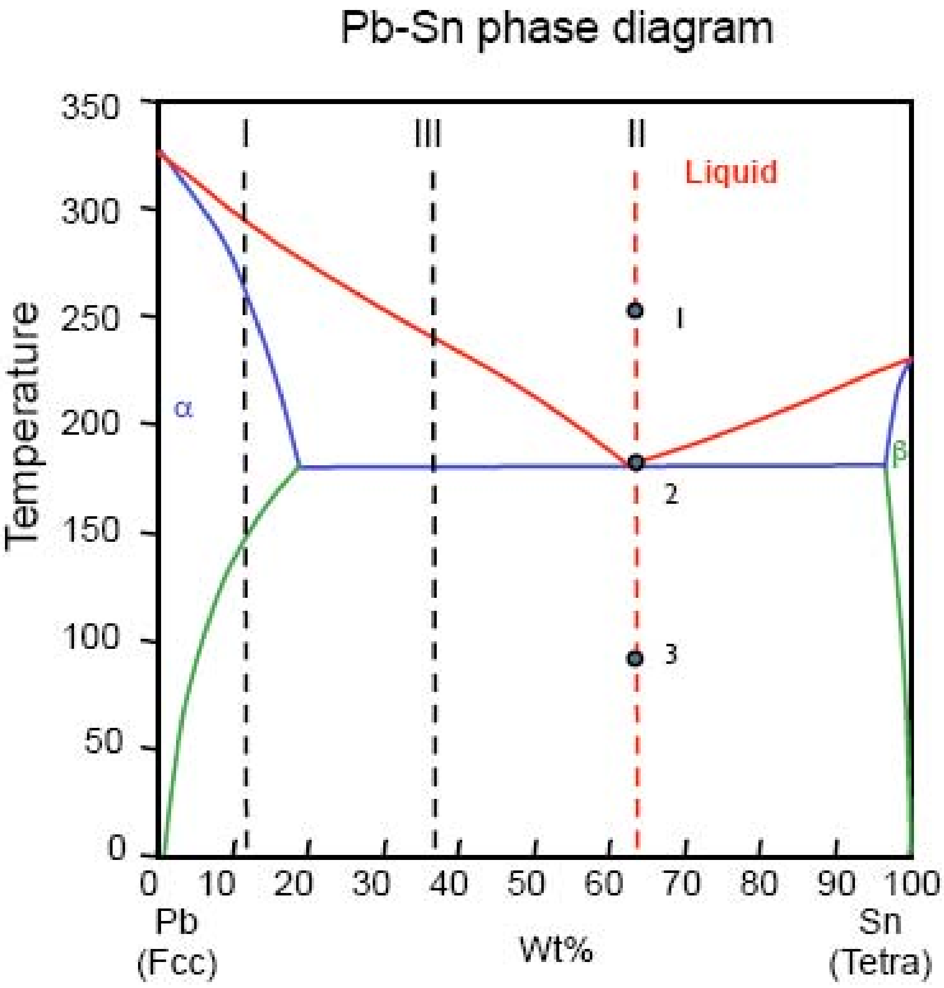
Pb-Sn phase diagram



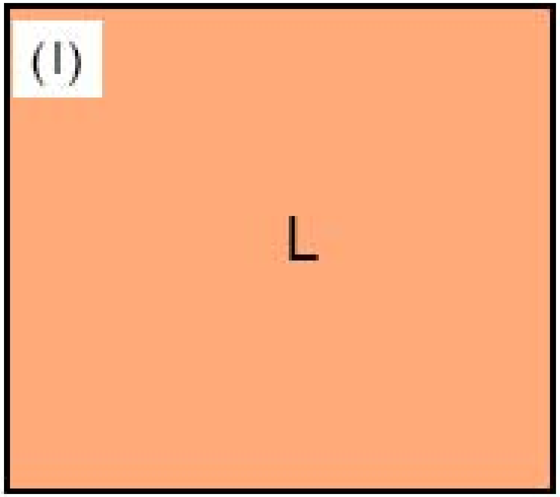
1.5 Binary phase diagrams

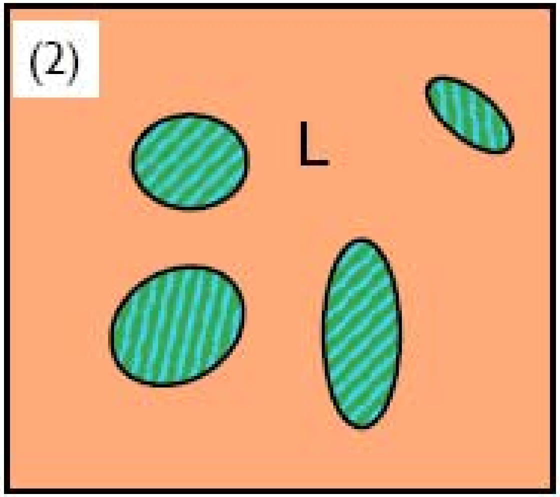
Solidification of Eutectic Systems

Alloy II:
At point 1: Liquid
Solidification starts at eutectic point (where liquidus and solidus join)
At point 2: L✦$(\alpha+\beta)$ (eutectic reaction)
The amounts of α and β increase in proportion with time.
Solidification finishes at the same temperature.
At point 3: $\alpha+\beta$
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.

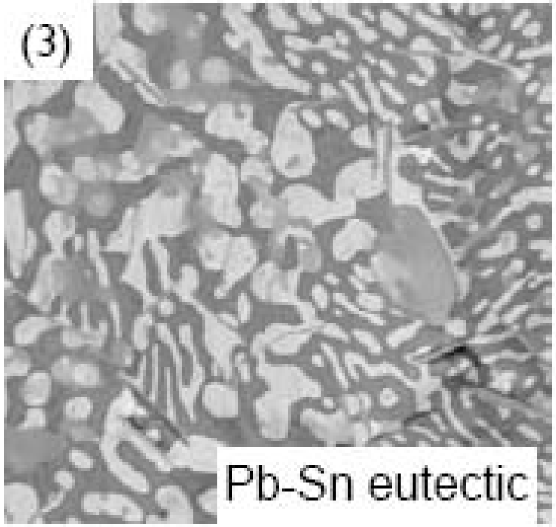


1.5 Binary phase diagrams





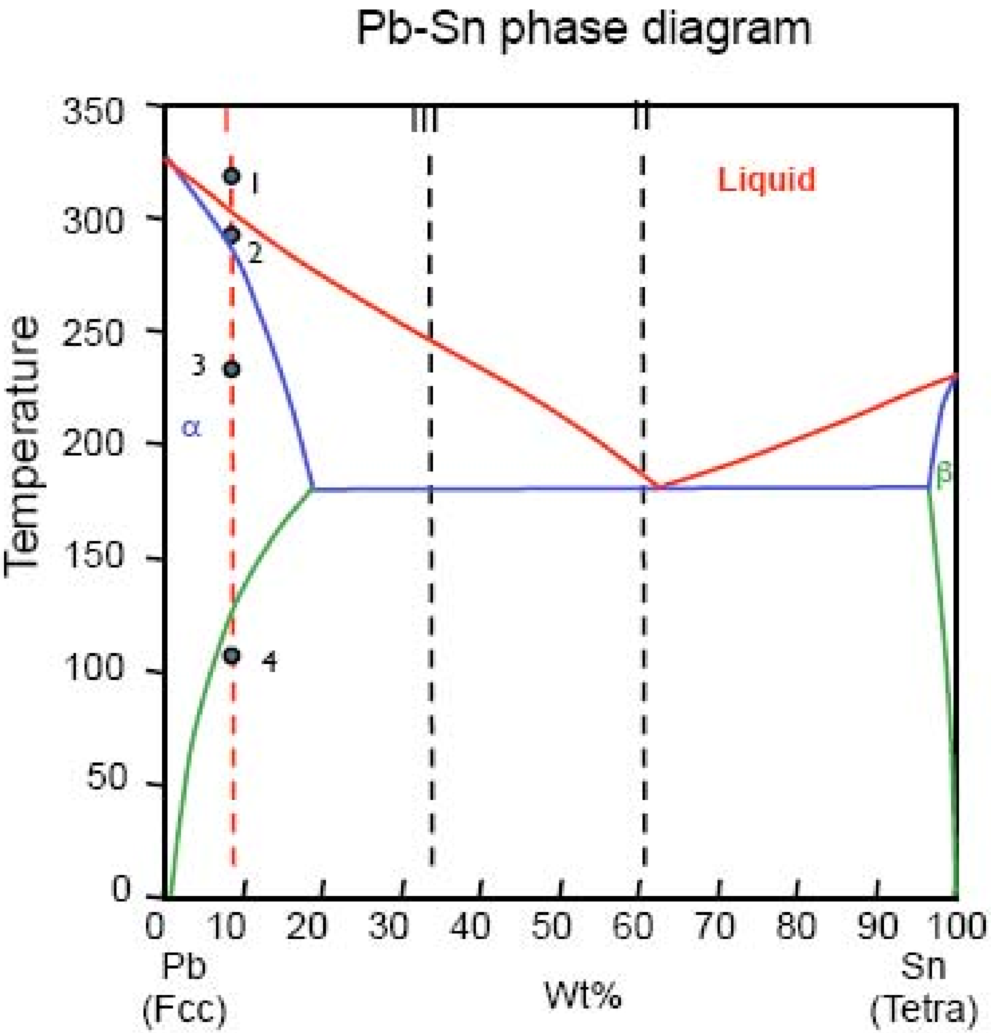
Nucleation of colonies of α and β laminates



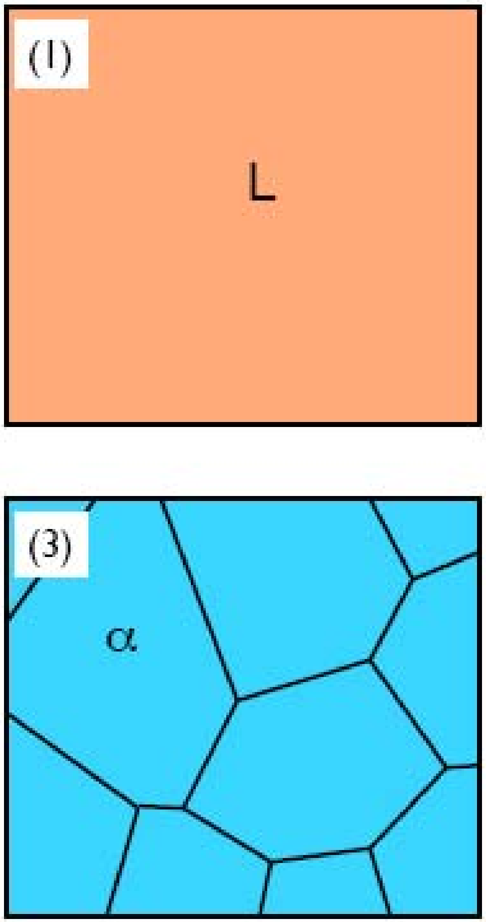
Eutectic structure of intimate mix of α and β to minimise diffusion path

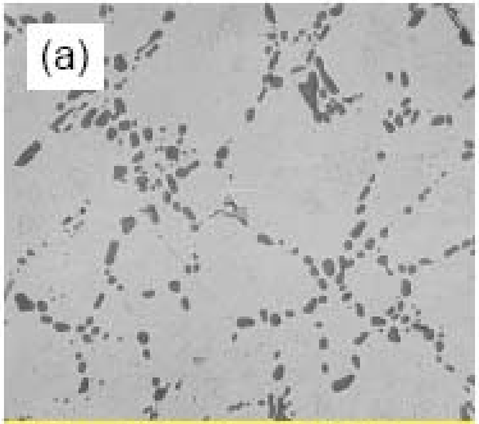
Solidification of Eutectic Systems

Alloy I:
At point 1: Liquid
Solidification starts at liquidus
At point 2: L+α
The amount α ↑ with ↓ T
Solidification finishes at solidus
At point 3: α
Precipitation starts at solvus
At point 4: α+β
Further cooling leads to formation and growth of more β precipitates whereas Sn% in α decreases following the solvus.

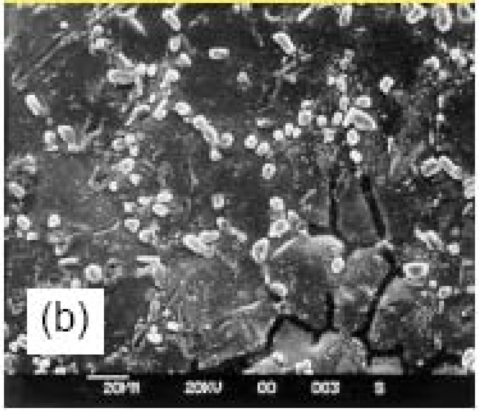


1.5 Binary phase diagrams





Precipitates in a Al-Si alloy;
(a) optical microscopy,
(b) scanning electron microscopy of fracture surface

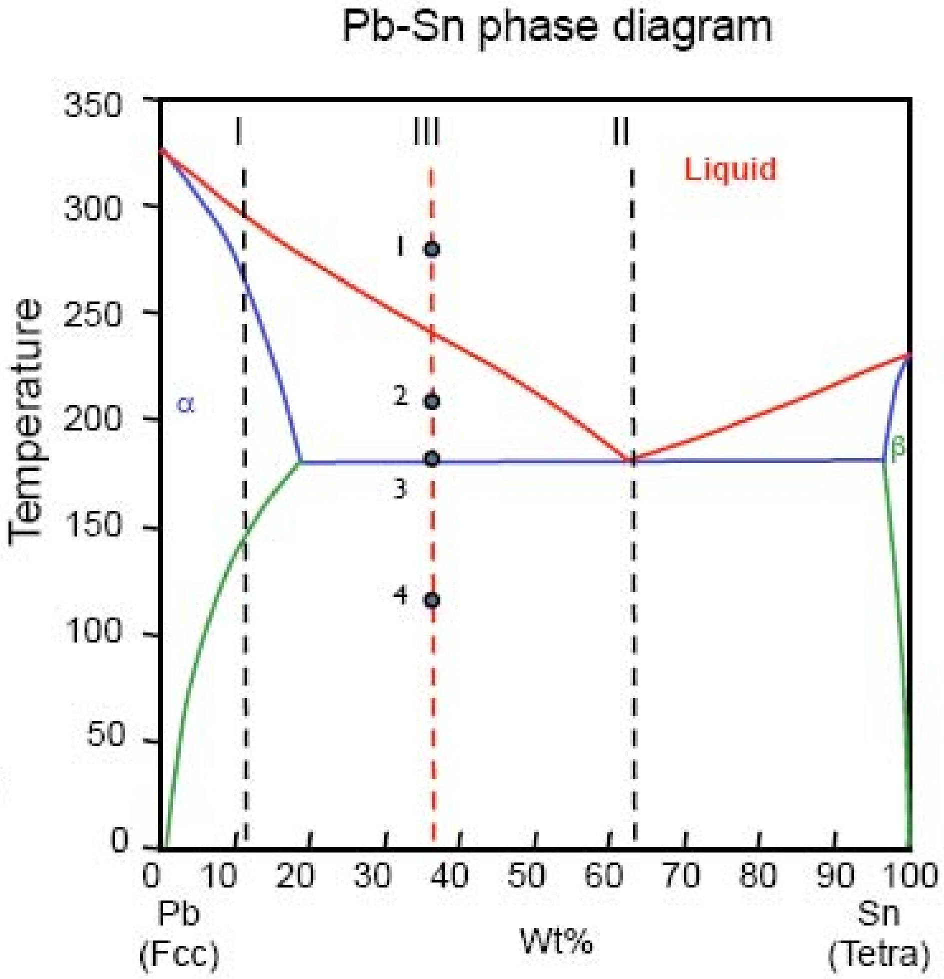


1.5 Binary phase diagrams

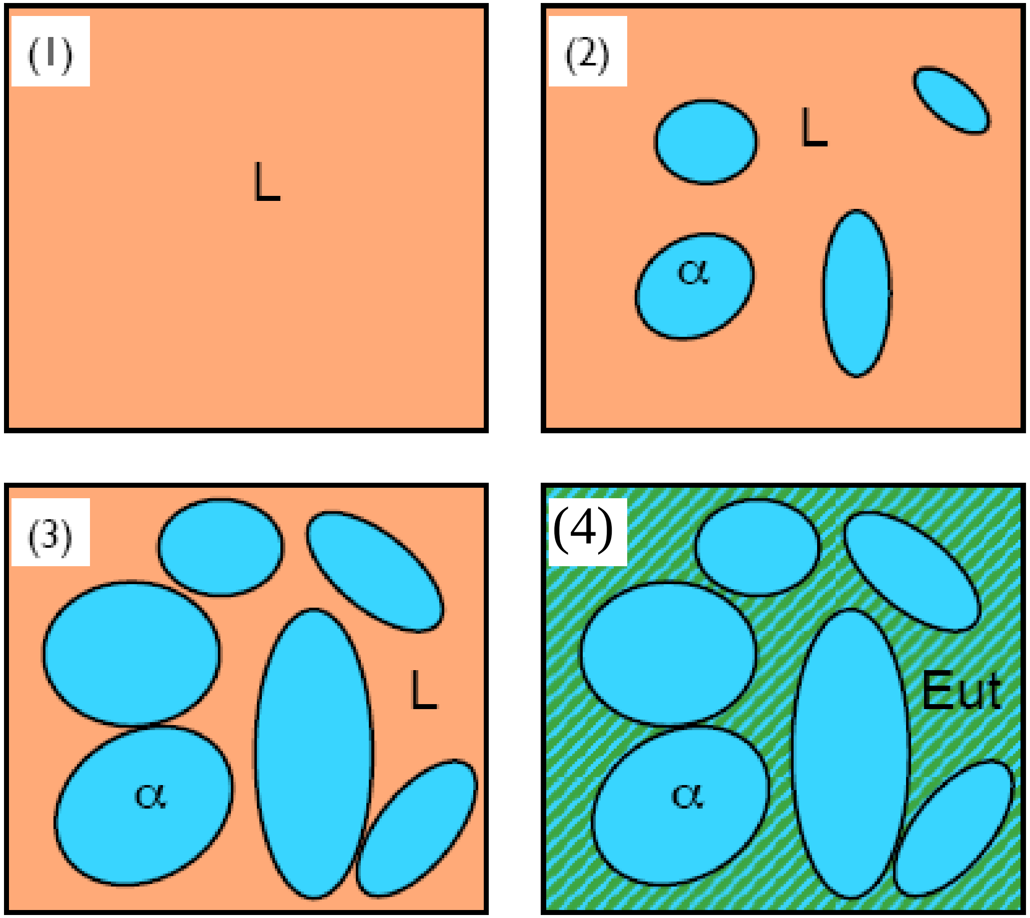
Solidification of Eutectic Systems

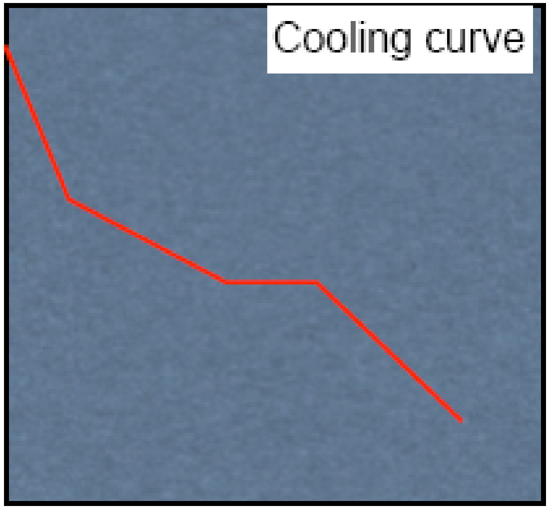
Alloy III:
At point 1: Liquid
Solidification starts at liquidus
At point 2: L✦L+α (pre-eutectic α)
The amount α ↑ with ↓T
At point 3: L✦ (α+β) (eutectic reaction)
Solidification finishes at the eutectic temperature
At point 4: α+β (pre-eutectic α + (α+β) eutectic mixture)
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.

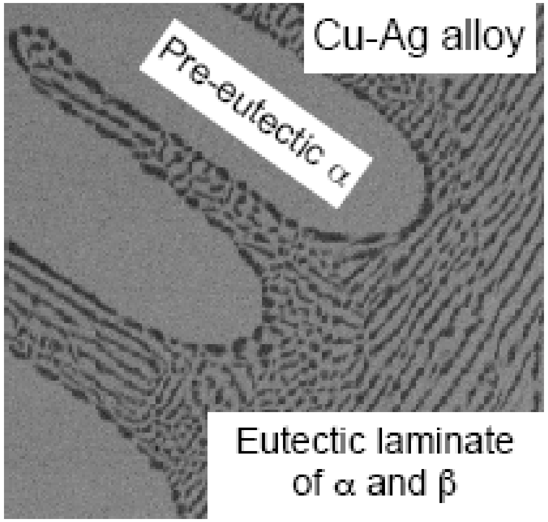
The cooling curve of this alloy is a combination of the two cooling curves shown in slide 9.



1.5 Binary phase diagrams

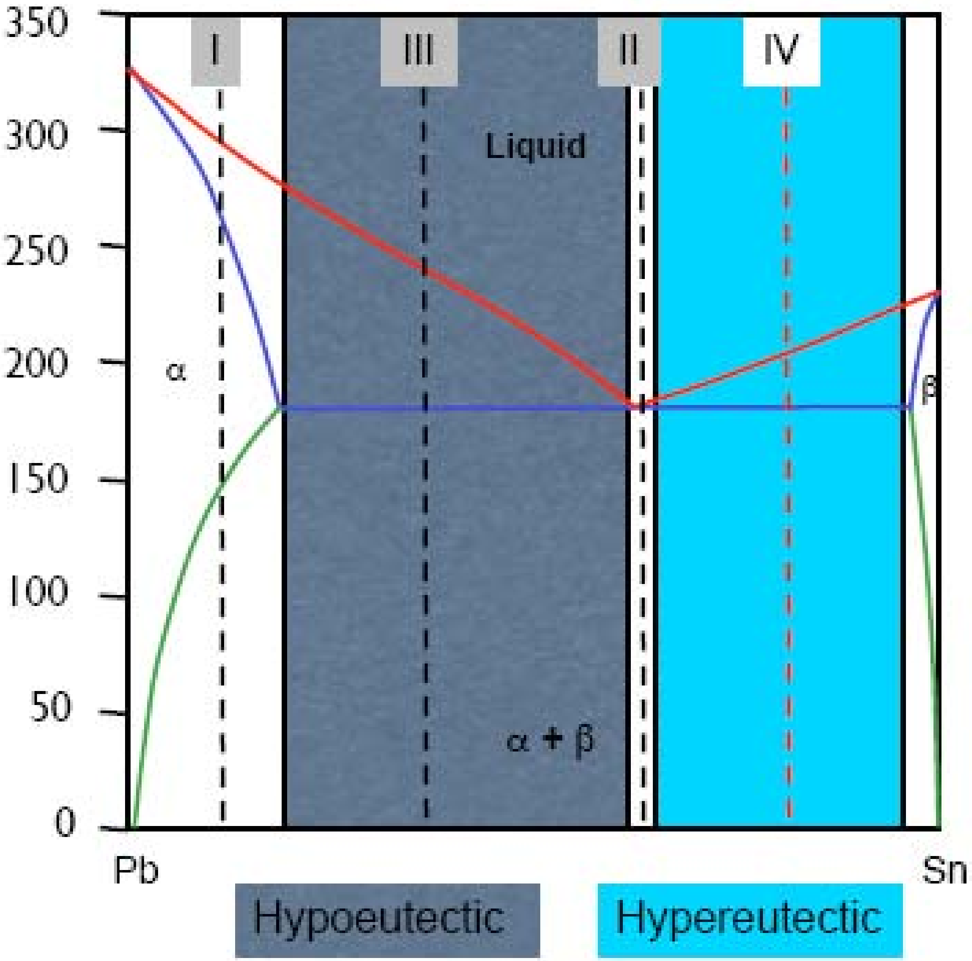




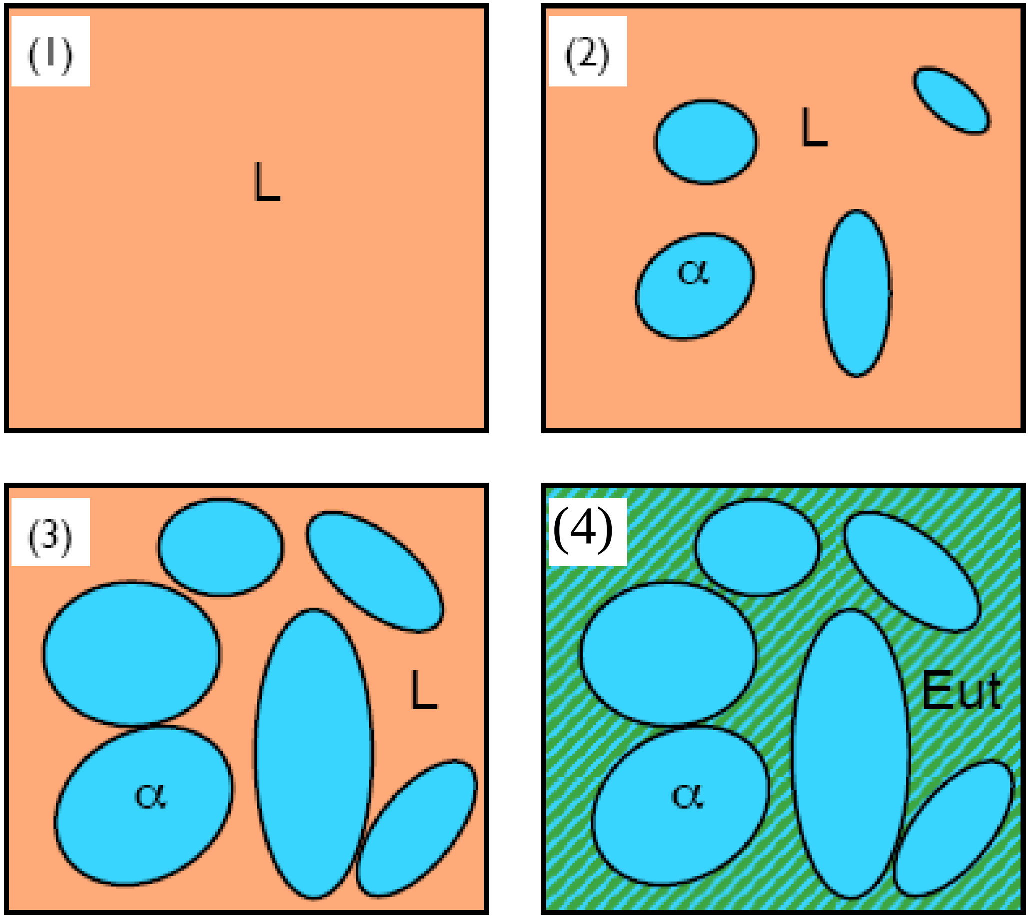


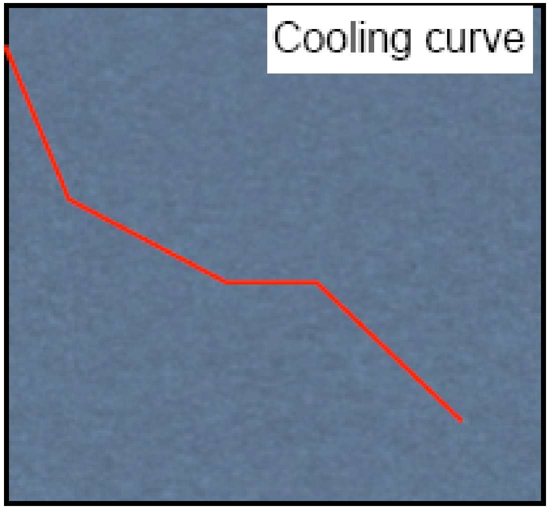
Solidification of Eutectic Systems

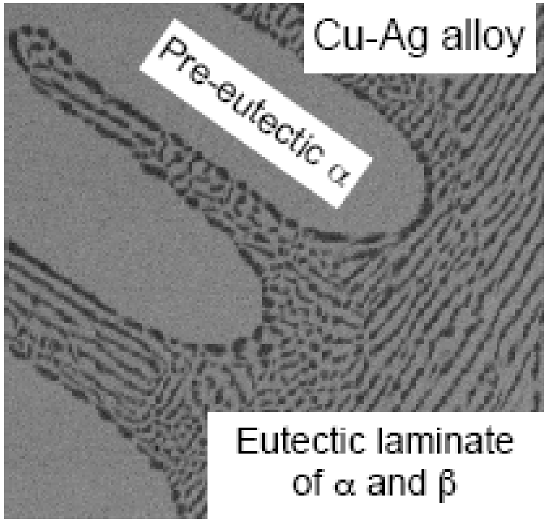
Can you describe the solidification process of alloy IV, including microstructure evolution, morphology of phases and cooling curve?



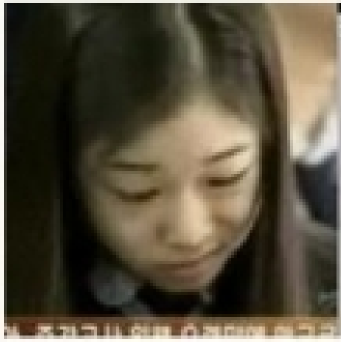
1.5 Binary phase diagrams




Cooling curve


Cu-Ag alloy

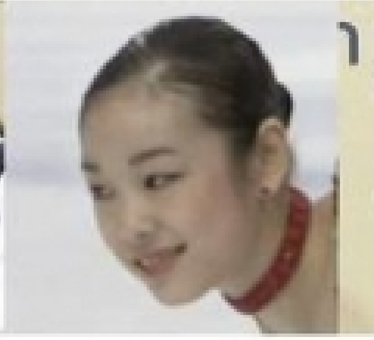
Eutectic laminate
of α and β



허탈

환희

집중

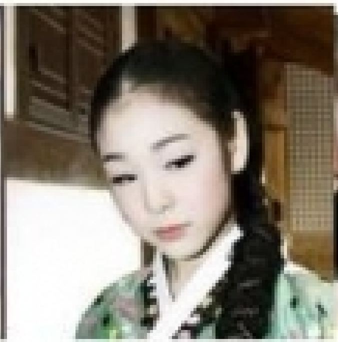


기쁨

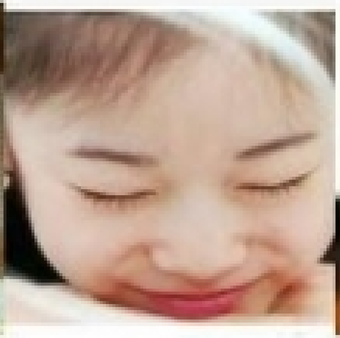
놀람

부끄러움

무아지경

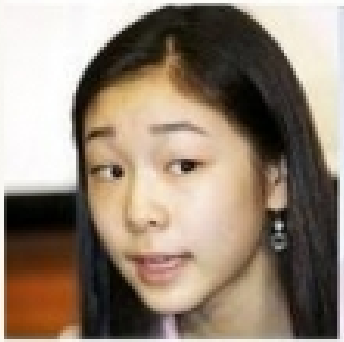


시침



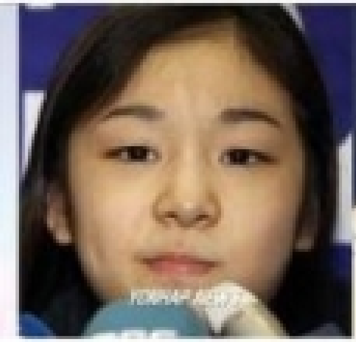
고통

분노

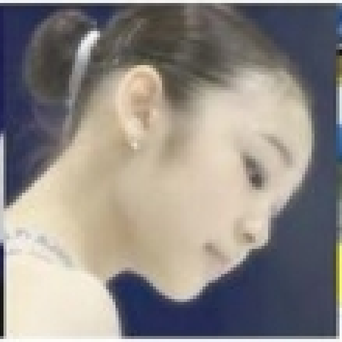


황당

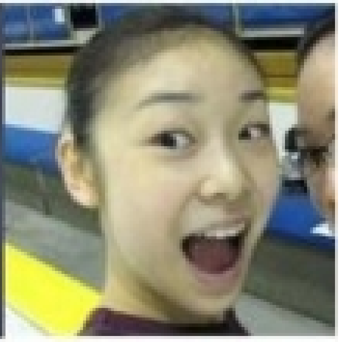
억울



난감



아름다움



반가움

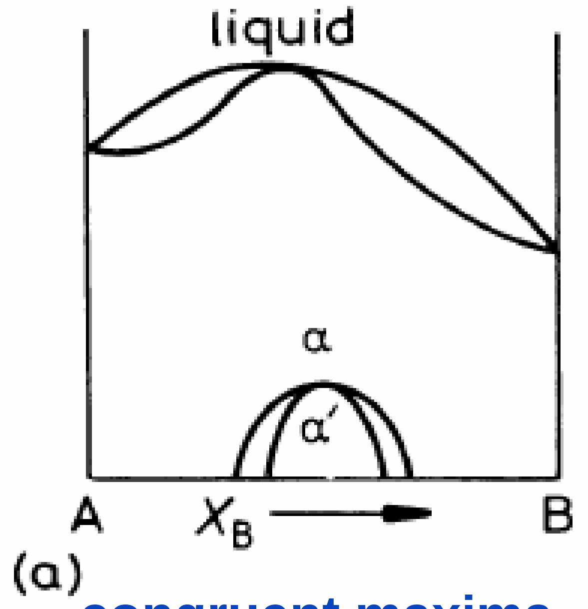
3) Ordered Alloys $\Delta H_{mix}^{L} = 0 \quad \Delta H_{mix}^{S} < 0$

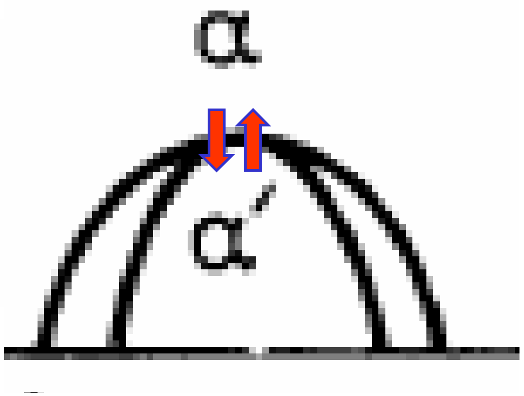
가. $\Delta H_{mix} < 0$ → A atoms and B atoms like each other.

How does the phase diagram differ from the previous case?

나. What would happen when $\Delta H_{mix} << 0$?

→ The ordered state can extend to the melting temperature.

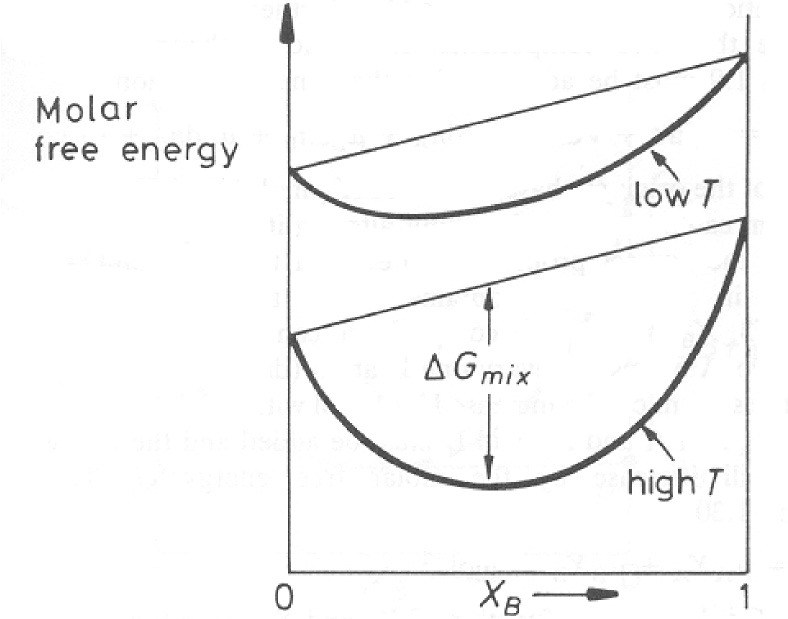




congruent maxima

Ideal Solutions

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

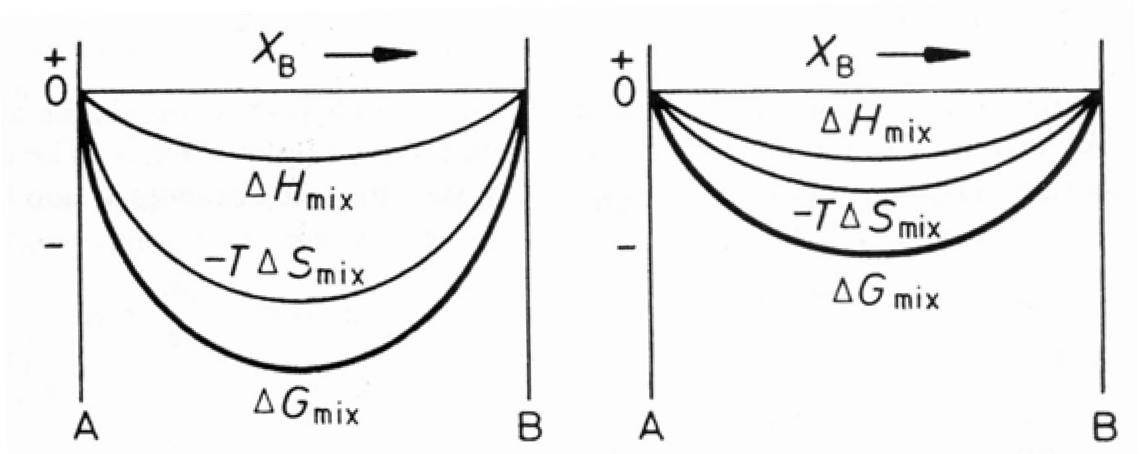


Regular Solutions

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

Reference state

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



(a) $\Omega < 0$, high T

(b) $\Omega < 0$, low T

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

1.5 Binary phase diagrams

Intermediate Phase

*** Solid solution**

→ random mixing

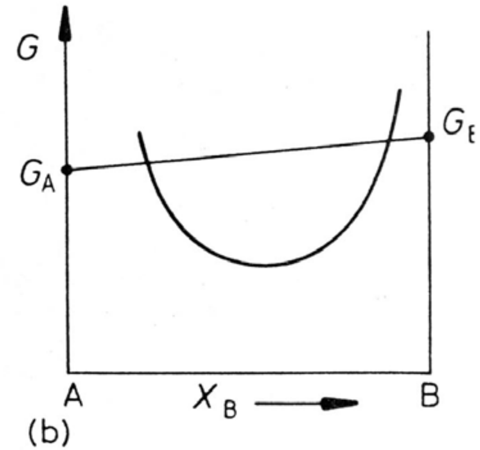
→ entropy ↑

negative enthalpy ↓

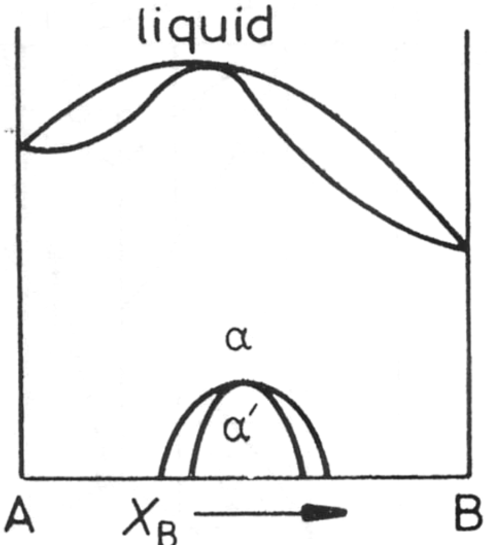
$$\boxed{\Delta H_{mix}^{S} < 0}$$

넓은 조성 범위

➔ G ↓



diate phases: (a) for an intermetallic com-
(b) for an intermediate phase with a wide



*** Compound : AB, A_2B…**

→ entropy ↓

→ covalent, ionic contribution.

→ enthalpy more negative ↓

$$\boxed{\Delta H_{mix}^{S} << 0}$$

좁은 조성 범위

➔ G ↓

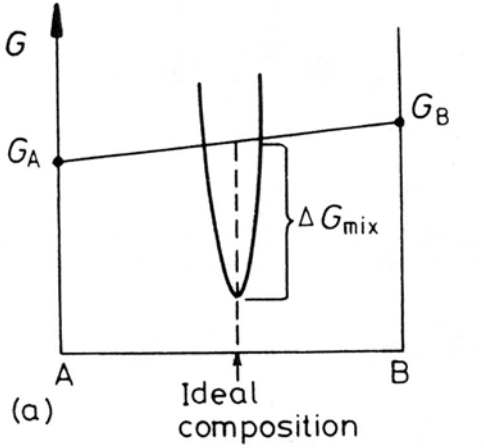
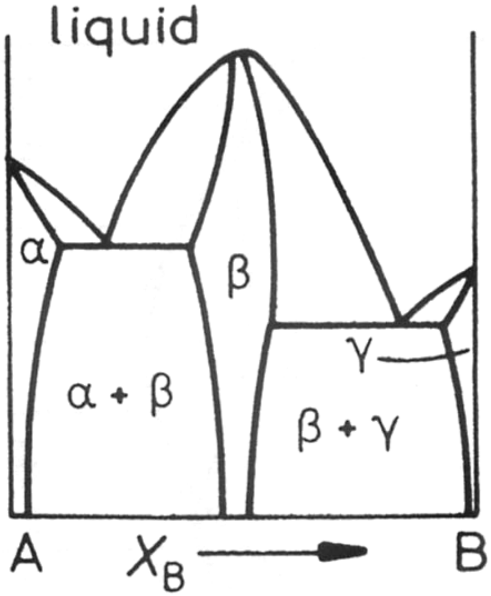
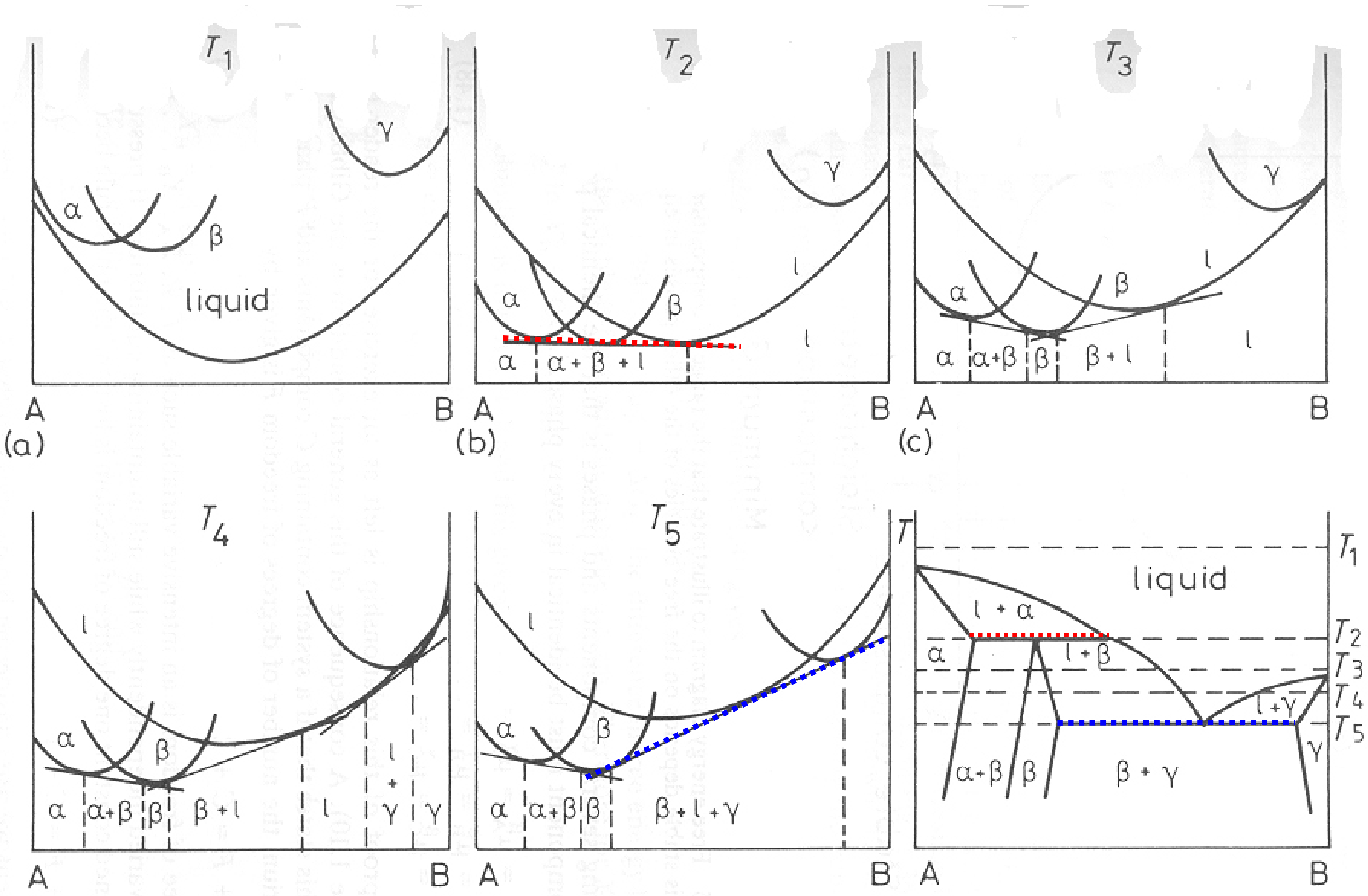


Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.



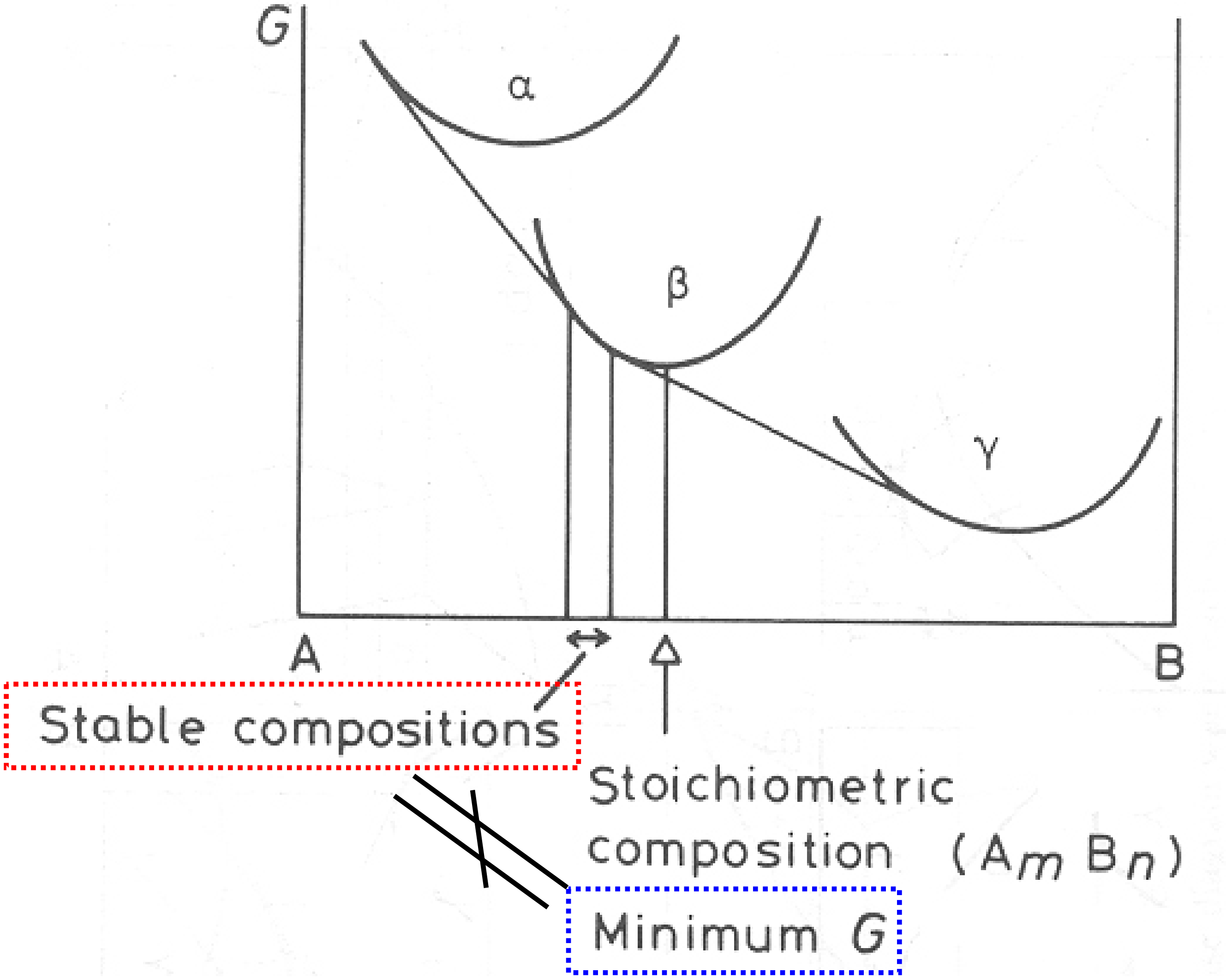
1.5 Binary phase diagrams

5) Phase diagrams containing intermediate phases



1.5 Binary phase diagrams

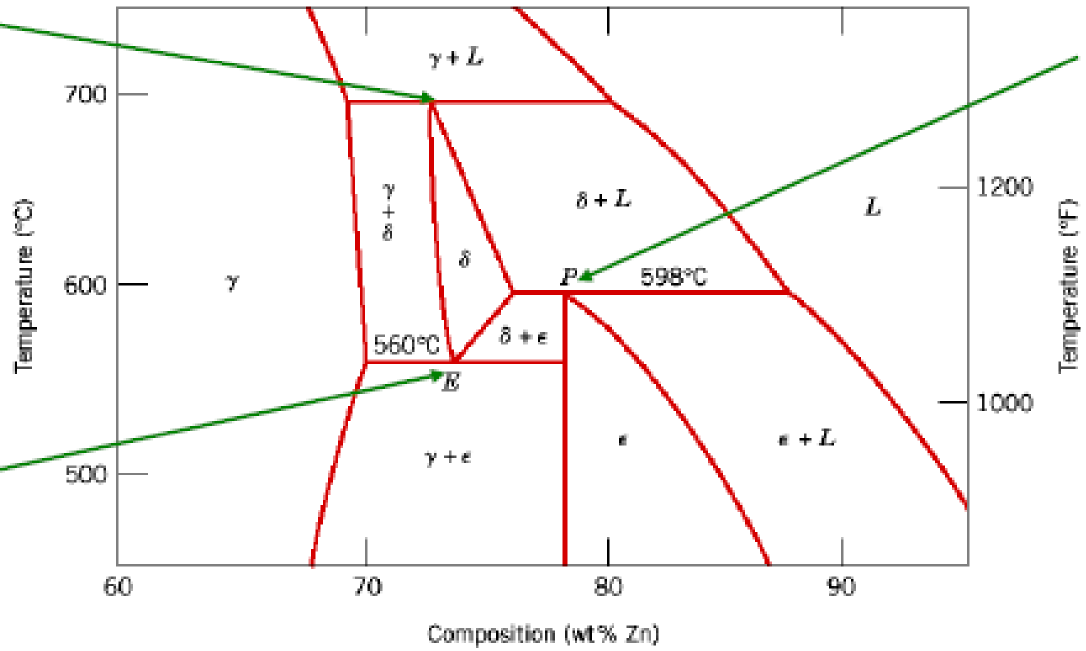
5) Phase diagrams containing intermediate phases



Cu-Zn Phase Diagram

Eutectoid and Peritectic Reactions

peritectic:
$\gamma + L \rightleftarrows \delta$



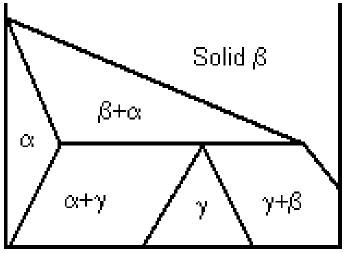
peritectic:
$\delta + L \rightleftarrows \varepsilon$

eutectoid:
$\delta \rightleftarrows \gamma + \varepsilon$

Eutectoid: one solid phase transforms into two other solid phases upon cooling

Peritectic: one solid and one liquid phase transform into another solid phase upon cooling

Peritectoid: two other solid phases transform into another solid phase upon cooling

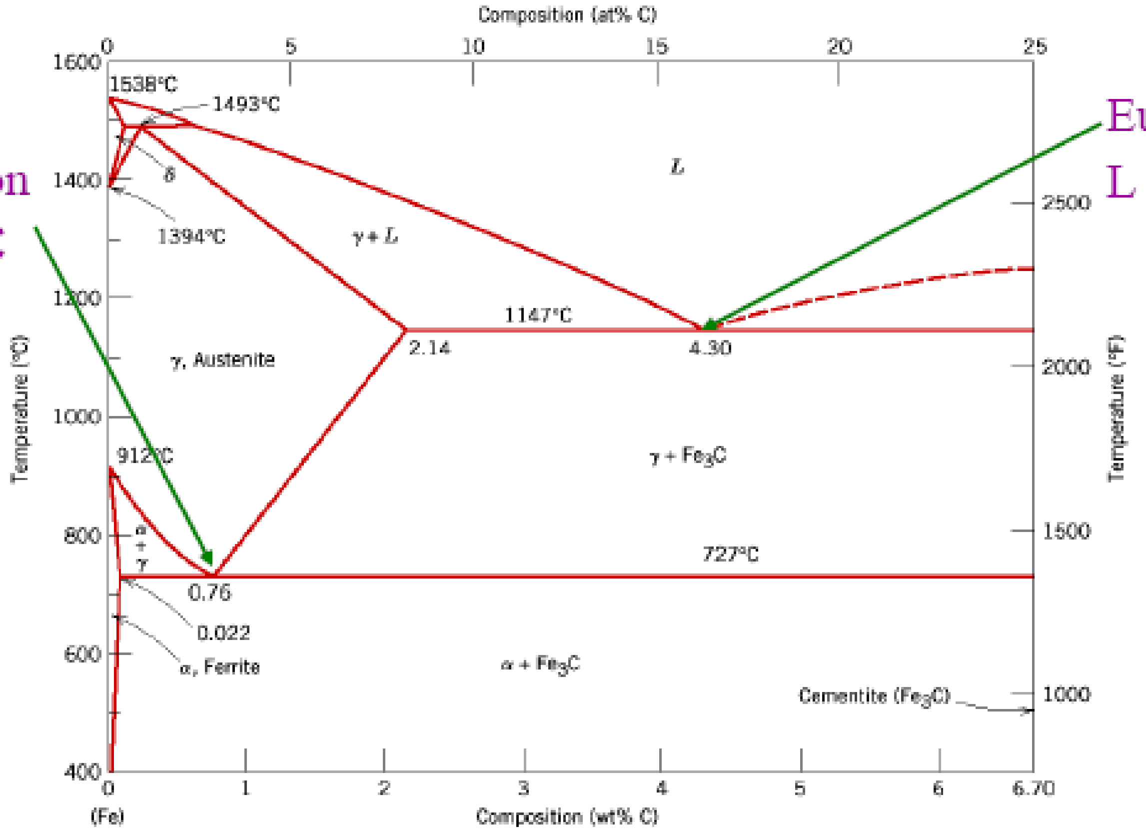


The Iron–Iron Carbide (Fe–Fe_3C) Phase Diagram

In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The Fe-C phase diagram is a fairly complex one, but we will only consider the part up to around ***7%*** *carbon of the diagram.*

Eutectoid reaction

$\gamma \leftrightarrow \alpha + Fe_3C$



Eutectic reaction

$L \leftrightarrow \gamma + Fe_3C$

$$\alpha\ (\mathbf{BCC}) \xleftrightarrow{912°C} \gamma\ (\mathbf{FCC}) \xleftrightarrow{1394°C} \delta\ (\mathbf{BCC}) \xleftrightarrow{1538°C} \textbf{liquid}$$

Pure iron

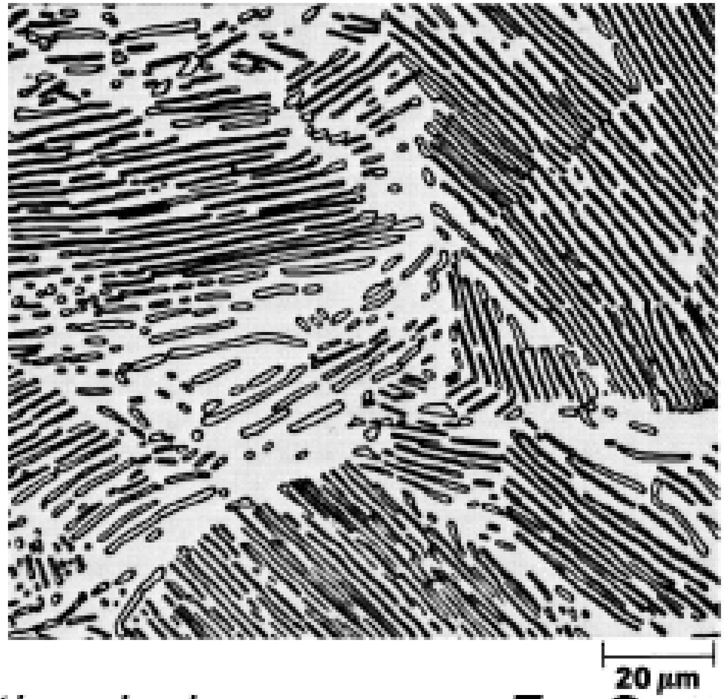
Development of Microstructure in Iron - Carbon alloys

- Microstructure depends on composition (carbon content) and heat treatment.
- In the discussion below we consider slow cooling in which equilibrium is maintained.

Eutectoid steel

When alloy of eutectoid composition (0.76 wt % C) is cooled slowly it forms a lamellar or layered structure of α and cementite (Fe_3C). This structure is called **pearlite.**

Mechanically, pearlite has properties intermediate to soft, ductile ferrite and hard, brittle cementite.



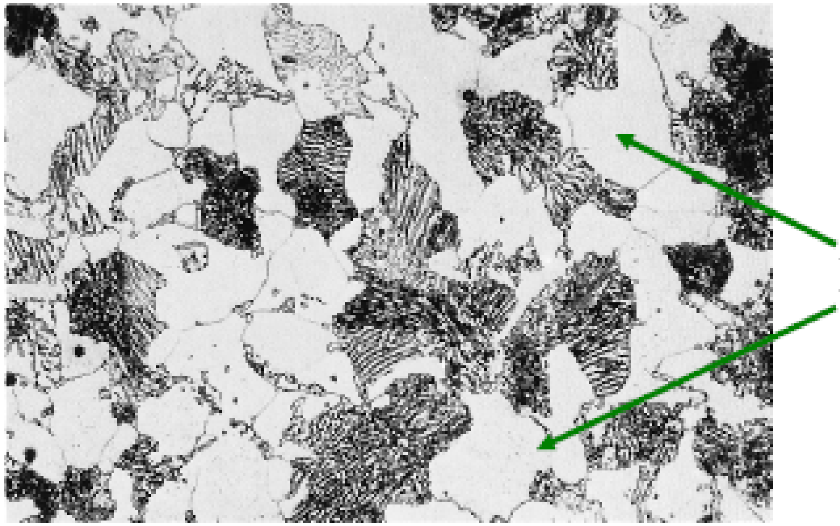
the dark areas are Fe_3C layers, the light phase is α -ferrite

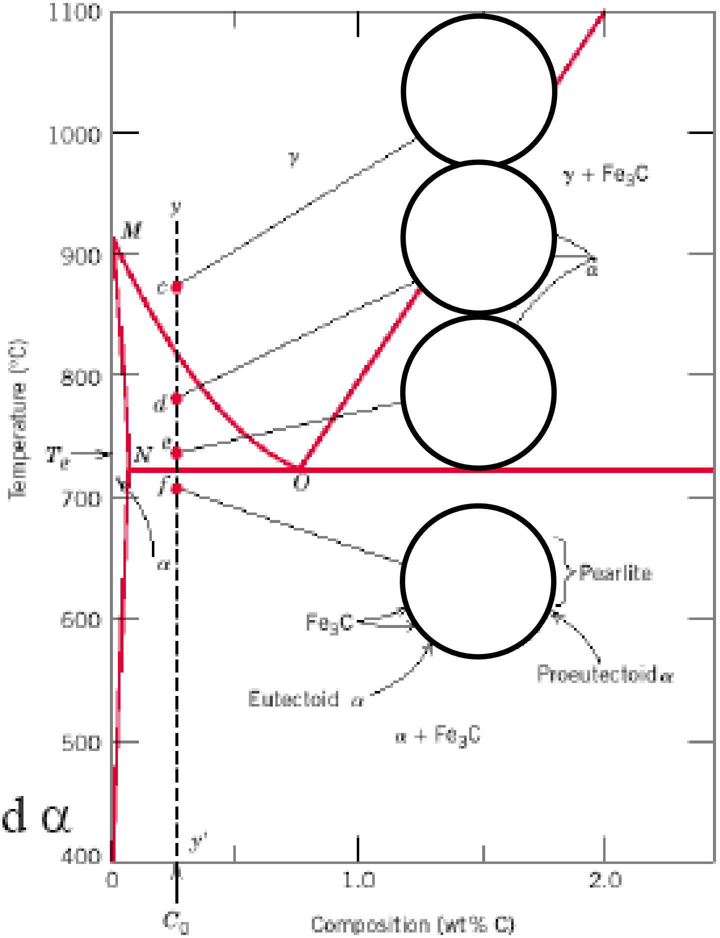
Microstructure of hypoeutectoid steel

Compositions to the left of eutectoid (0.022-0.76 wt % C) **hypoeutectoid** alloys

- *less than eutectoid* (Greek)

Hypoeutectoid alloys contain proeutectoid ferrite (*formed above the eutectoid temperature*) plus the eutectoid pearlite that contain eutectoid ferrite and cementite.



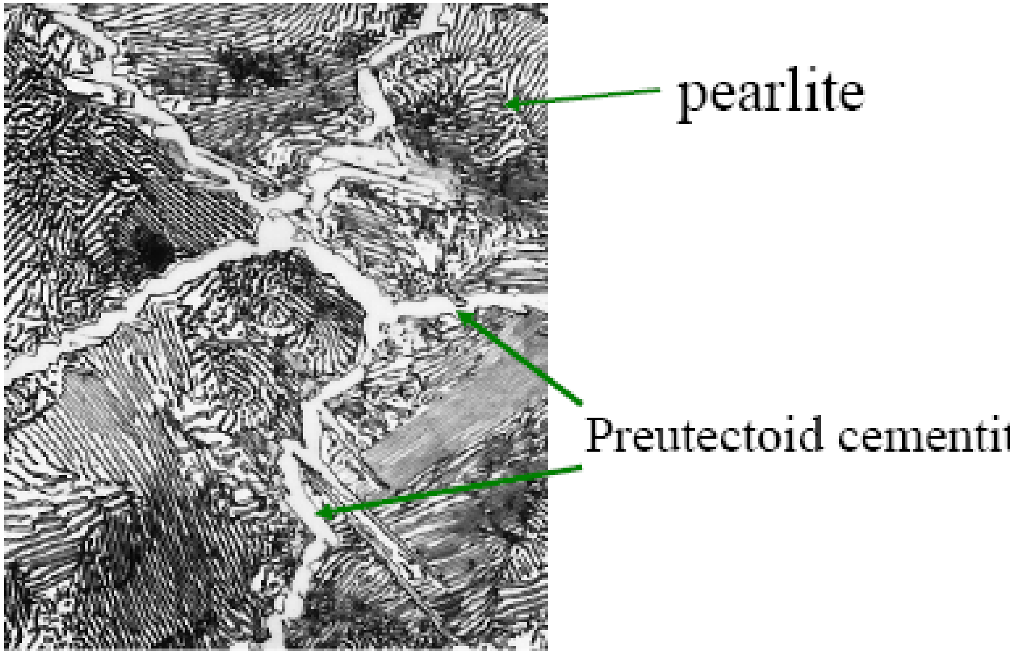


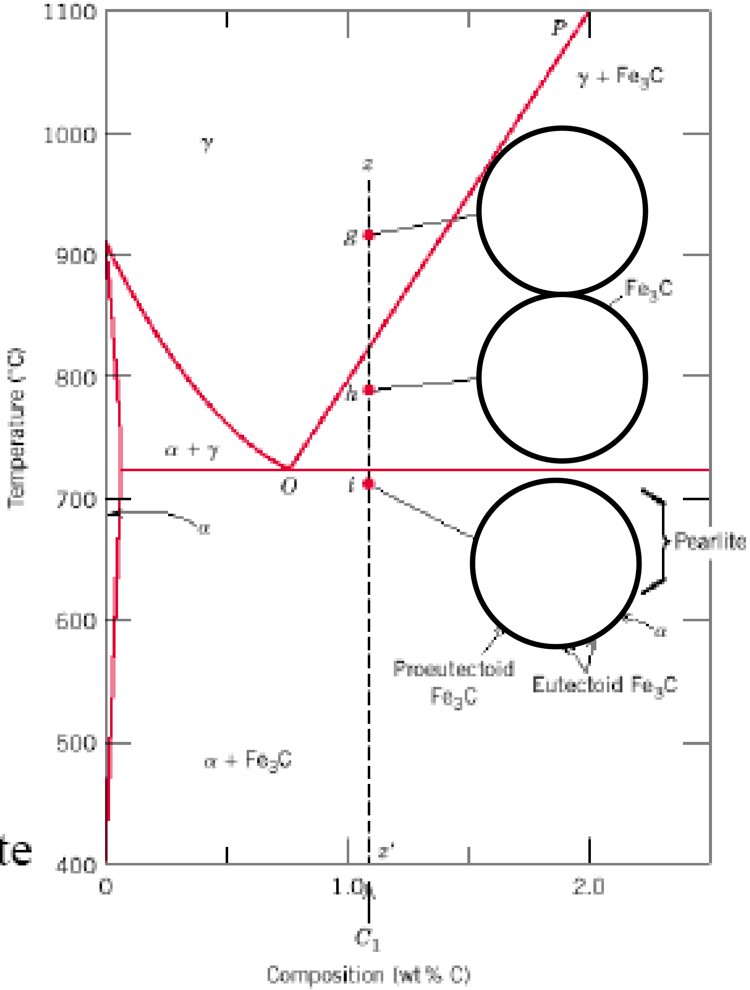
Microstructure of hypereutectoid steel

Compositions to the right of eutectoid (0.76 - 2.14 wt % C) **hypereutectoid** alloys.

- *more than eutectoid* (Greek)

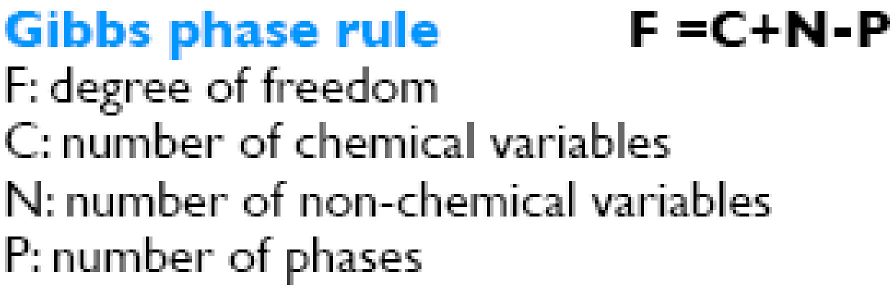
$$\gamma \rightarrow \gamma + \mathbf{Fe_3C} \rightarrow \alpha + \mathbf{Fe_3C}$$





The Gibbs Phase Rule

In chemistry, Gibbs' phase rule describes the possible number of degrees of freedom (F) in a closed system at equilibrium, in terms of the number of separate phases (P) and the number of chemical components (C) in the system. It was deduced from thermodynamic principles by Josiah Willard Gibbs in the 1870s.



Gibbs phase rule $F = C + N - P$

F: degree of freedom
C: number of chemical variables
N: number of non-chemical variables
P: number of phases

In general, Gibbs' rule then follows, as:

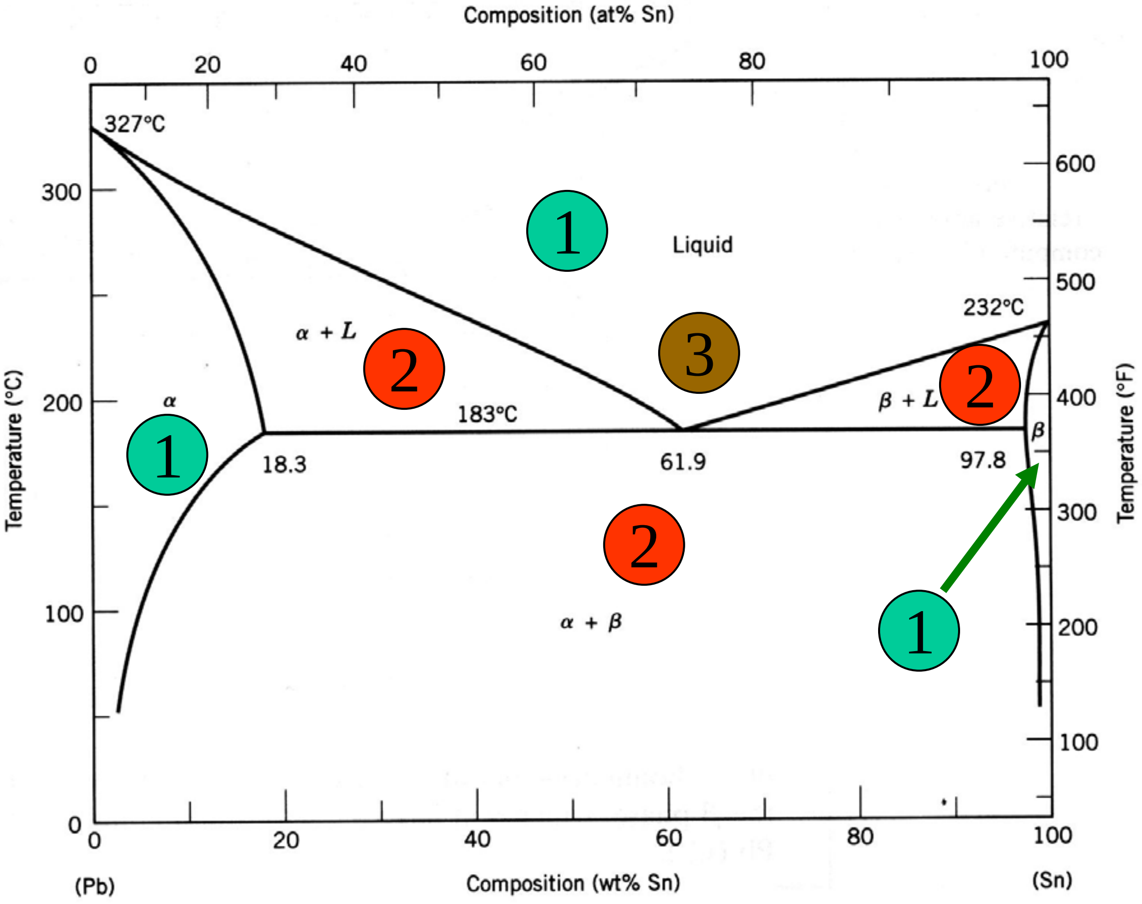
$$F = C - P + 2 \quad \text{(from T, P).}$$

From Wikipedia, the free encyclopedia

The Gibbs Phase Rule

For Constant Pressure,

P + F = C + 1



① **single phase**

F = C - P + 1

= 2 - 1 + 1

= 2

can vary T and composition independently

② **two phase**

***F* = *C* - *P* + 1**

= 2 - 2 + 1

= 1

can vary T *or* composition

③ **eutectic point**

F = C - P + 1

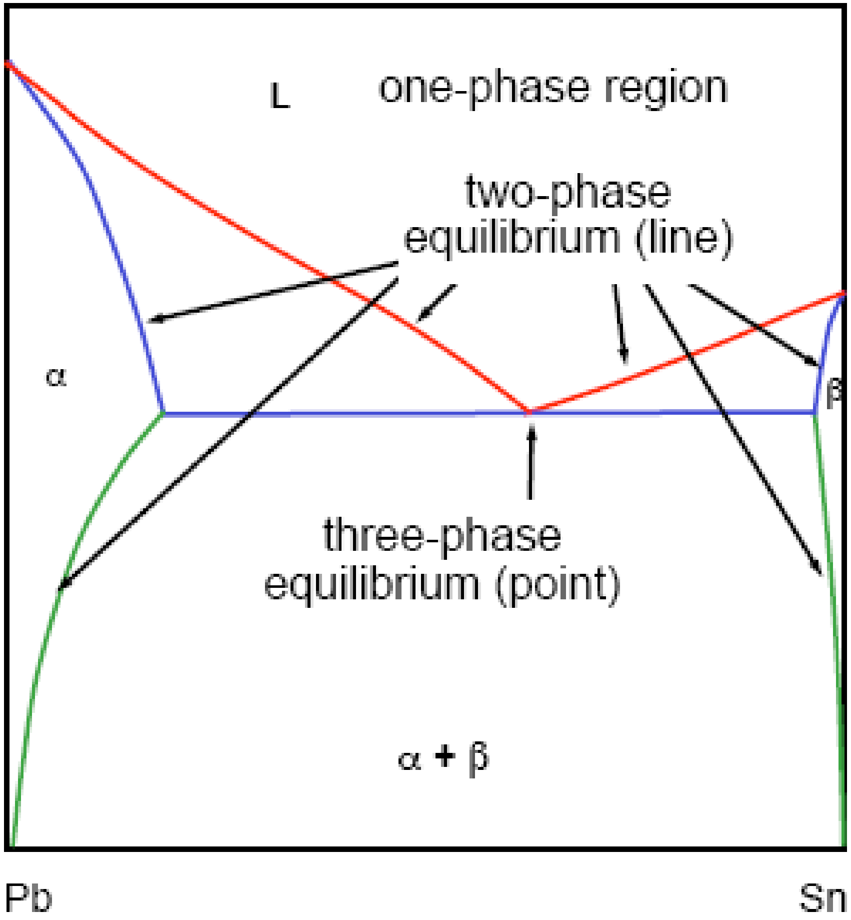
= 2 - 3 + 1

= 0

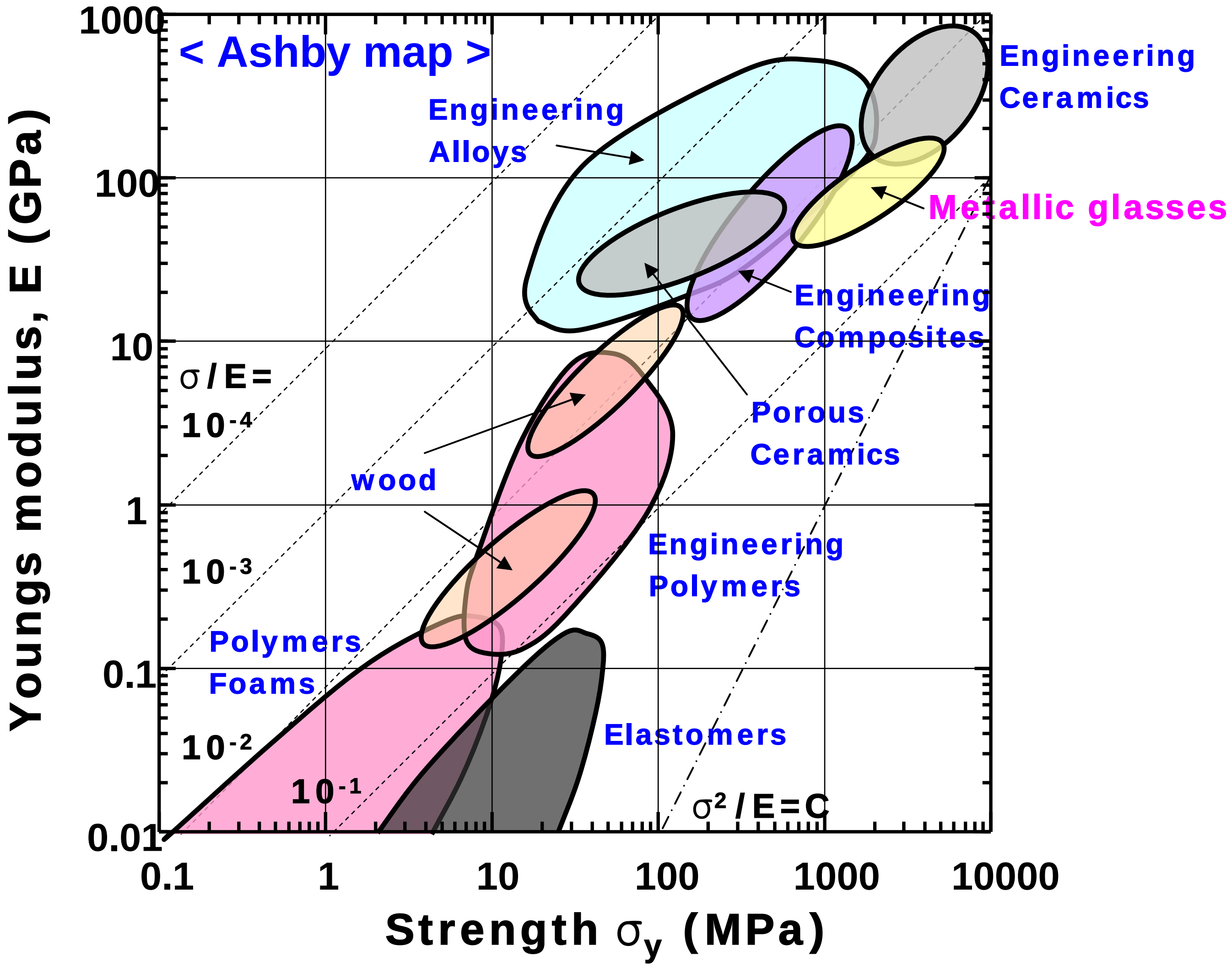
can’t vary T or composition

The Gibbs Phase Rule

Application of Gibbs phase rule:
For a binary system at ambient pressure:
C=2 (2 elements)
N=1 (temperature, no pressure)
For single phase: F=2: % and T (a region)
For a 2-phase equilibrium: F=1: % or T (a line)
For a 3-phase equilibrium: F=0, (invariant point)

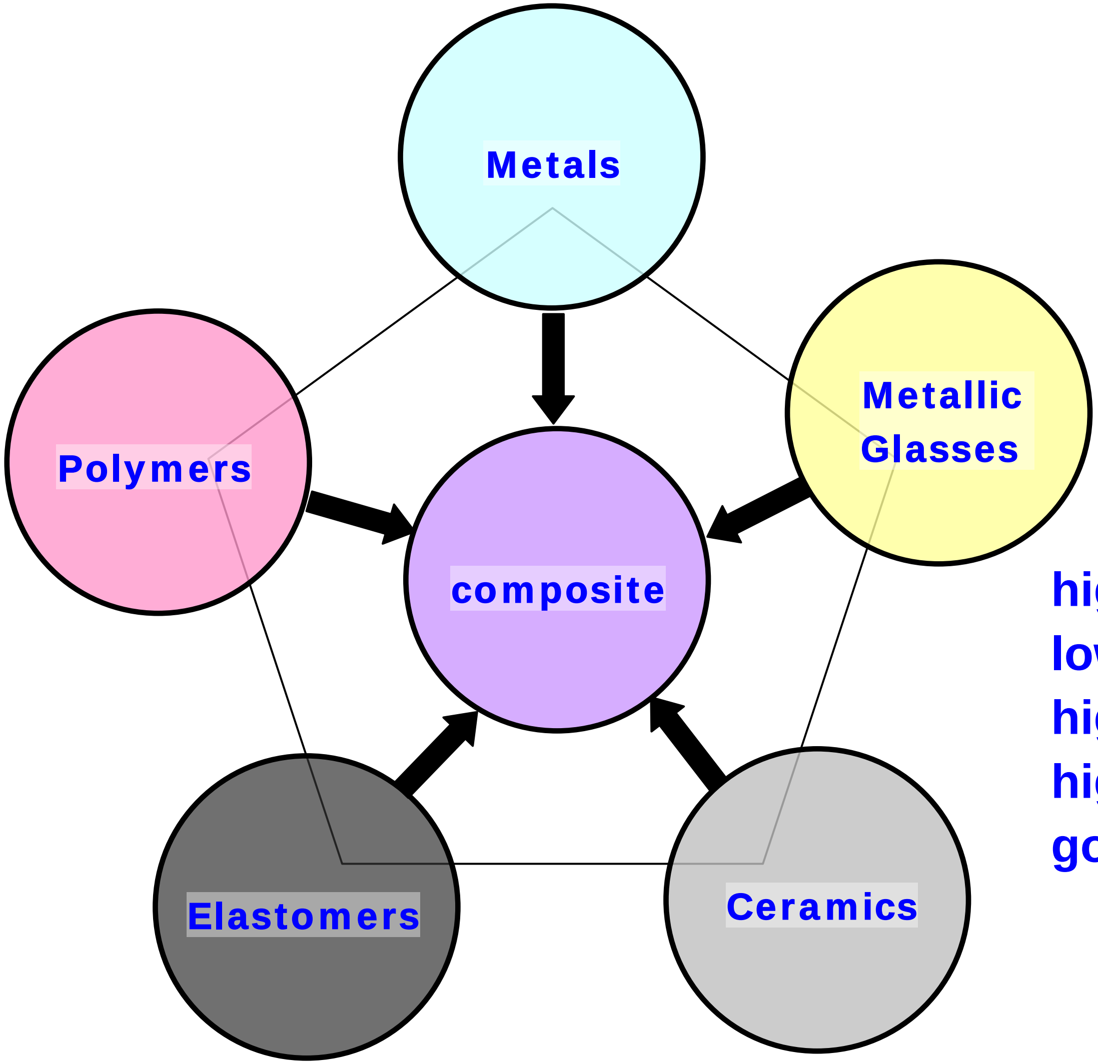


재 료 설 계


< Ashby map >
Engineering Ceramics
Engineering Alloys
Metallic glasses
Engineering Composites
Porous Ceramics
wood
Engineering Polymers
Polymers Foams
Elastomers
σ / E=
10-4
10-3
10-2
10-1
σ2 / E=C
Youngs modulus, E (GPa)
1000
100
10
1
0.1
0.01
0.1
1
10
100
1000
10000
Strength σy (MPa)

재 료 설 계

Menu of engineering materials



High GFA

High plasticity

higher strength
lower Young's modulus
high hardness
high corrosion resistance
good deformability
⋮

재료설계주제 제안

이번 학기에 깊이있게 조사해보고 싶은 재료 3 가지와 그 이유를 각 1 page 씩 정리하여 24일까지 제출하시오.

Ex) stainless steel/ Carbon nanotube/ Bio-material/ Dendrimer etc.

The Gibbs Phase Rule

Degree of freedom (number of variables that can be varied independently)

= the number of variables – the number of constraints

- Number of phases : p, number of components : c,
- # of controllable variable : composition (c-1)p, temperature : p, pressure : p
- # of restrictions :

(p-1)c from chemical equilibrium $\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \cdots = \mu_i^{p}$

p-1 from thermal equilibrium $T^{\alpha} = T^{\beta} = T^{\gamma} = \cdots = T^{p}$

p-1 from mechanical equilibrium $P^{\alpha} = P^{\beta} = P^{\gamma} = \cdots = P^{p}$

- Number of variable can be controlled with maintaining equilibrium

$$f = (c-1)p + p + p - (p-1)c - (p-1) - (p-1) = c - p + 2$$

$$f = c - p + 2$$

- If pressure is constant : $f = (c-1)p + p - (p-1)c - (p-1) = c - p + 1$