2019 Spring

"Phase Equilibria *in* Materials"

04.10.2019

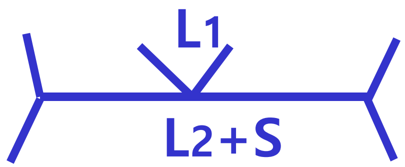
Eun Soo Park

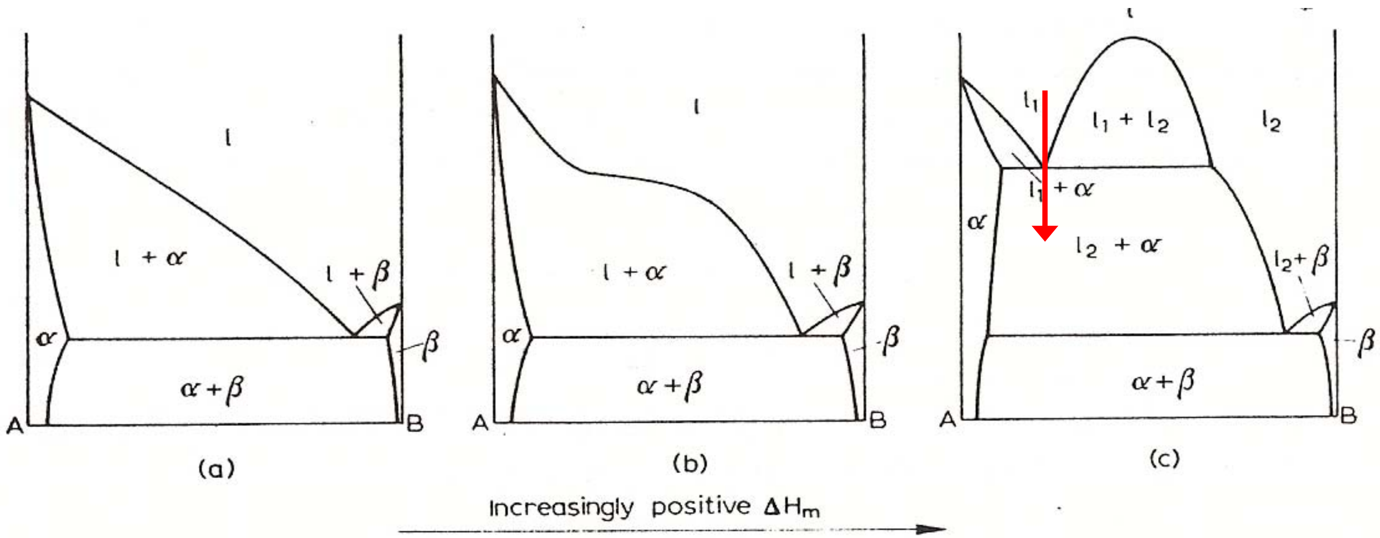
Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

* Monotectic reaction:

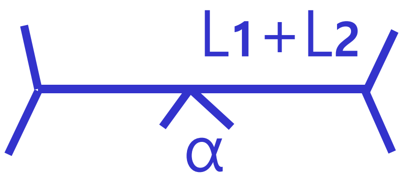
Liquid1 ↔Liquid2+ Solid



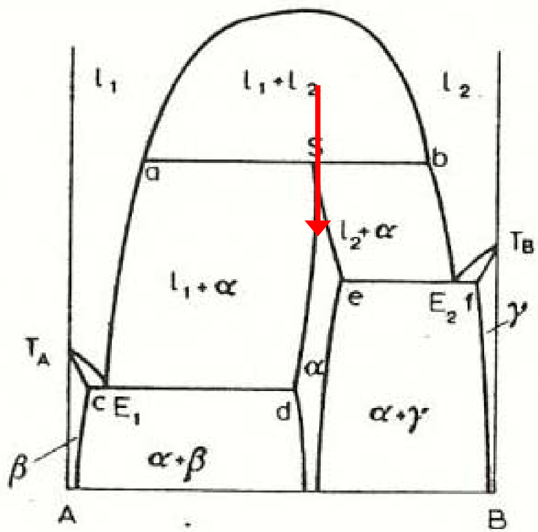


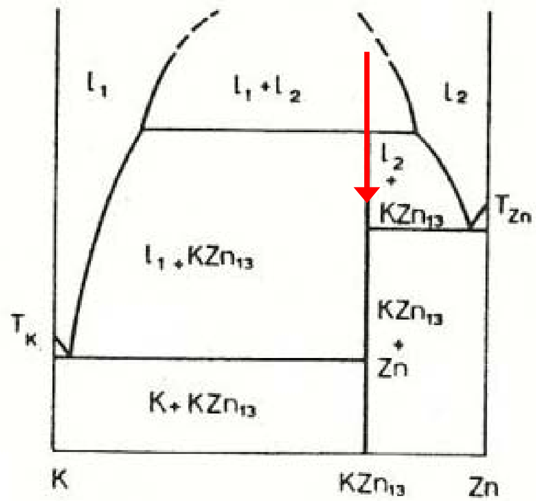
* Syntectic react

Liquid1+Liquid2



K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

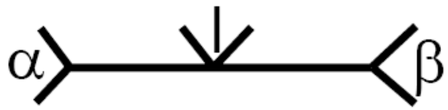
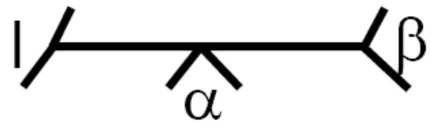
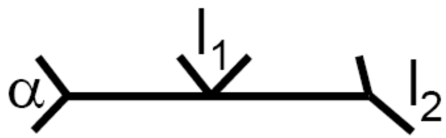
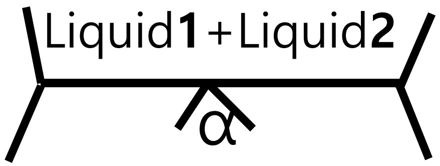




Contents for previous class

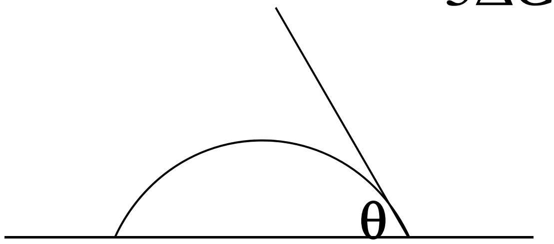
Review of Invariant Binary Reactions

Positive ΔH_m

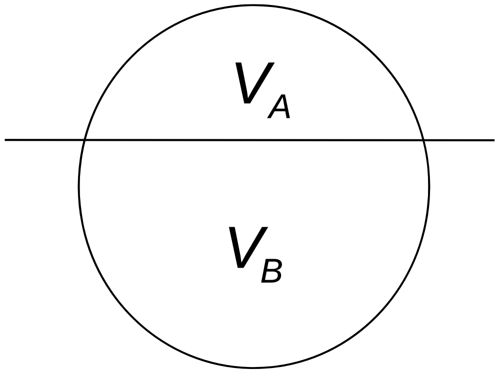
Eutectic $l \rightleftarrows \alpha + \beta$		Al-Si, Fe-C
Peritectic $l + \beta \rightleftarrows \alpha$		Fe-C
Monotectic $l_1 \rightleftarrows \alpha + l_2$		Cu-Pb
Syntectic reaction Liquid**1**+Liquid**2** $\leftrightarrow$ α		**K-Zn, Na-Zn, K-Pb, Pb-U, Ca-Cd**

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot \frac{(2 - 3\cos\theta + \cos^3\theta)}{4}$$



$$\Delta G_{het}^* = S(\theta)\Delta G_{\mathrm{hom}}^*$$

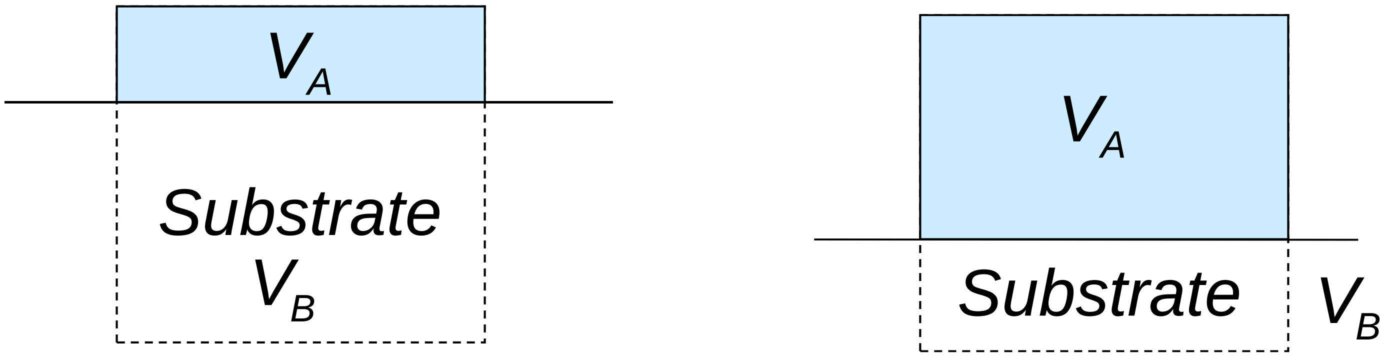


$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right)$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

How about the nucleation at the crevice or at the edge?

How do we treat the non-spherical shape?



Good Wetting **Bad Wetting**

$$\Delta G^*_{sub} = \Delta G^*_{homo}\left(\frac{V_A}{V_A + V_B}\right)$$

Effect of good and bad wetting on substrate

Contents for today's class

Chapter 6
Binary Phase Diagrams: Reactions in the Solid State

* Eutectoid reaction: $\alpha \leftrightarrow \beta + \gamma$

* Monotectoid reaction: $\alpha_1 \leftrightarrow \beta + \alpha_2$

* Peritectoid reaction: $\alpha + \beta \leftrightarrow \gamma$

Chapter 7
Binary Phase Diagram: Allotropy of the Components

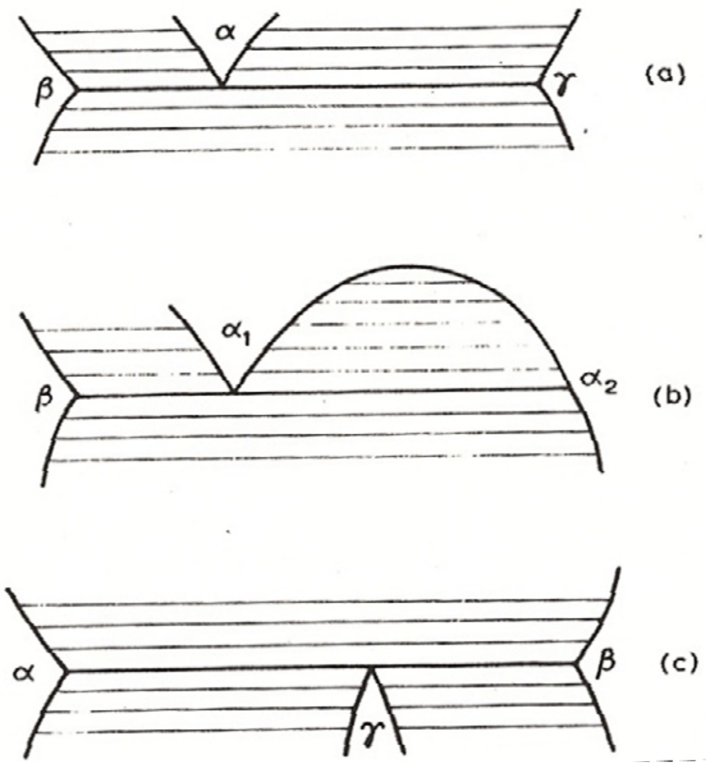
* SYSTEMS IN WHICH ONE PHASE IS IN EQUILIBRIUM WITH THE LIQUID PHASE

* SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE

* Metatectic reaction: $\beta \leftrightarrow L + \alpha$ Ex. Co-Os, Co-Re and Co-Ru

Chapter 6
Binary Phase Diagrams: Reactions in the Solid State

~ Only the kinetics of the reaction differ



Eutectoid reaction: $\alpha \leftrightarrow \beta + \gamma$

Monotectoid reaction: $\alpha_1 \leftrightarrow \beta + \alpha_2$

Peritectoid reaction: $\alpha + \beta \leftrightarrow \gamma$

* **Transformation can only proceed if $-\Delta G_{bulk} > +\Delta G_{interface} + \Delta G_{strain}$**

By nucleation and growth mechanism

~ Strain energy factor

~ nucleation sites of transformation

Disordered atomic arrangement at <u>grain boundaries</u> will reduce the strain energy factor and the interfacial energy needed to nucleate a new phase.

➡ **The finer the grain size, and hence the larger the grain boundary area, the more readily will the transformation proceed. "allotropic transformation"**

Iron-Carbon System

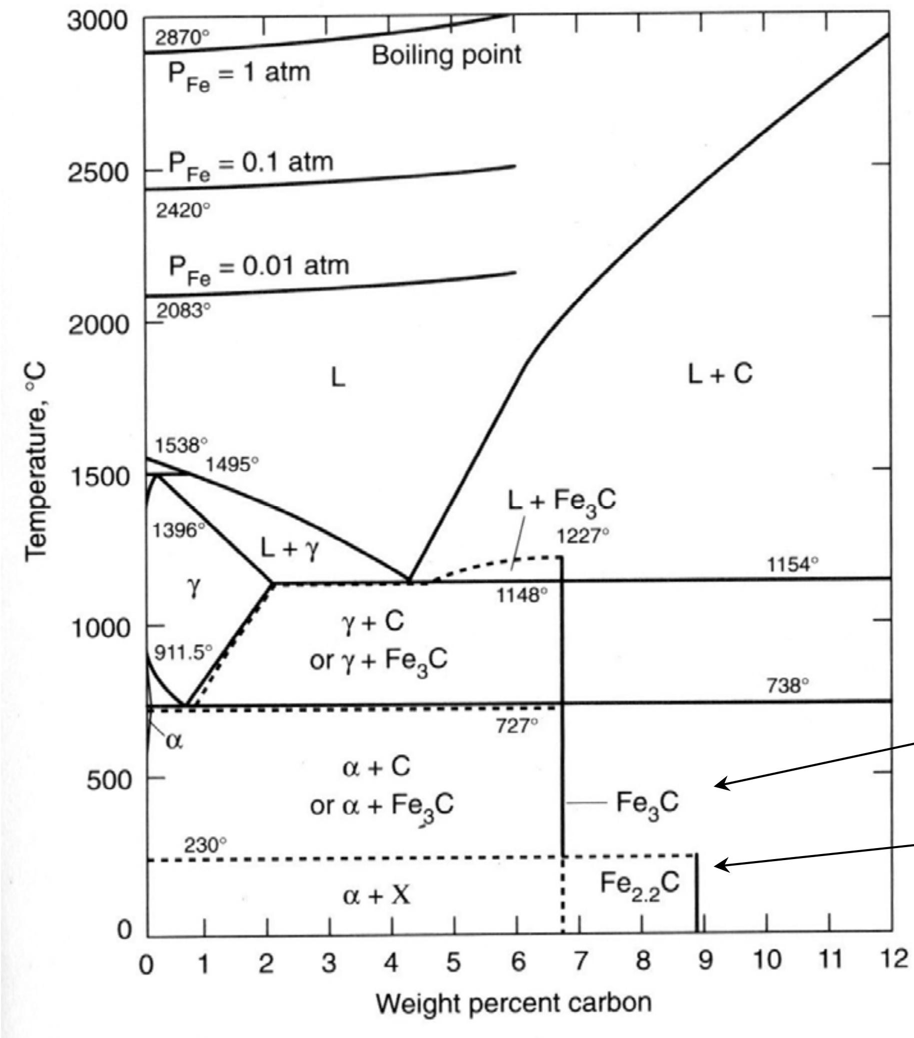


Diagram is not ever plotted past 12 wt%

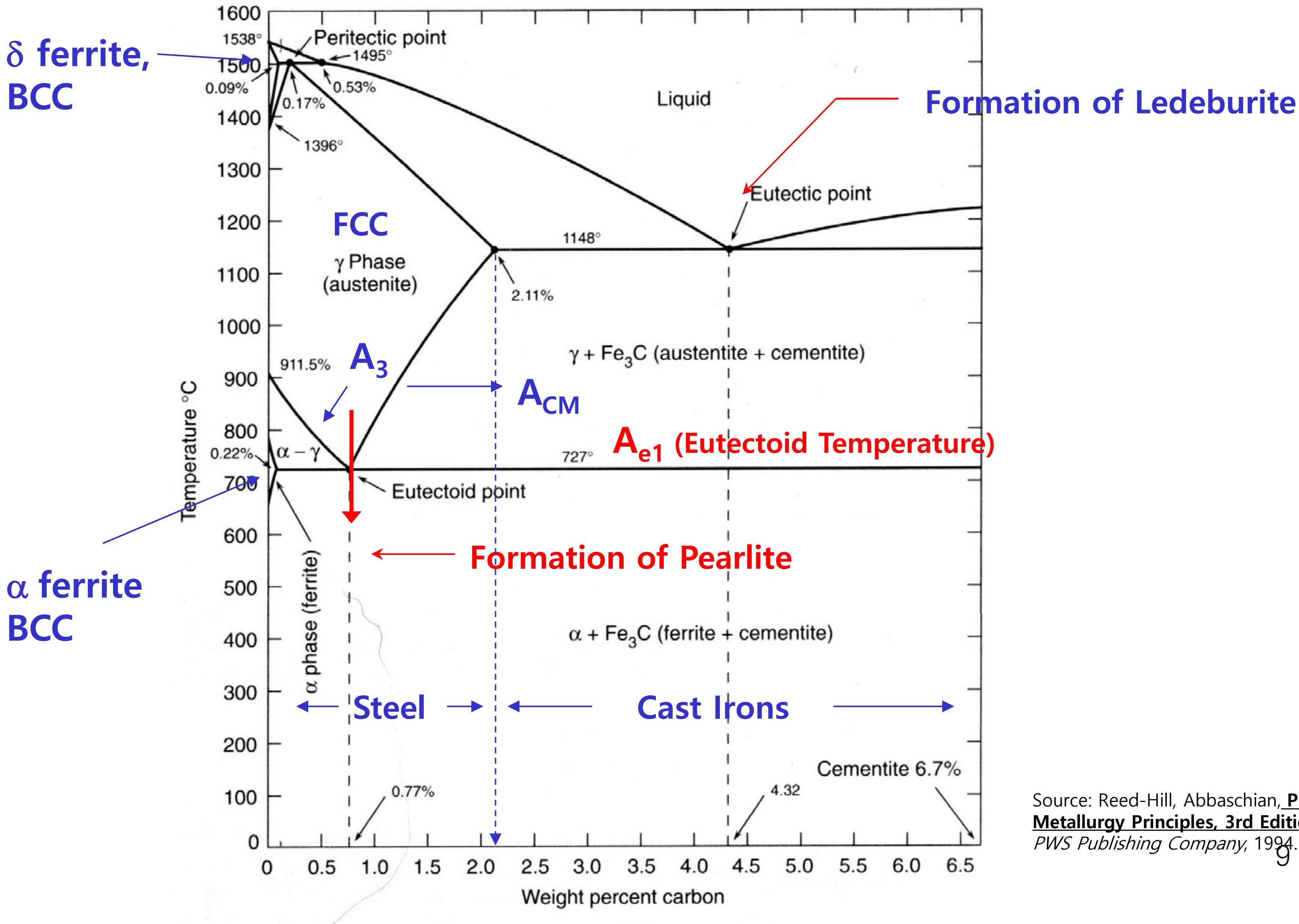
Cementite

Hägg carbide

Source: Reed-Hill, Abbaschian, **Physical Metallurgy Principles, 3rd Edition**, *PWS Publishing Company*, 1994.

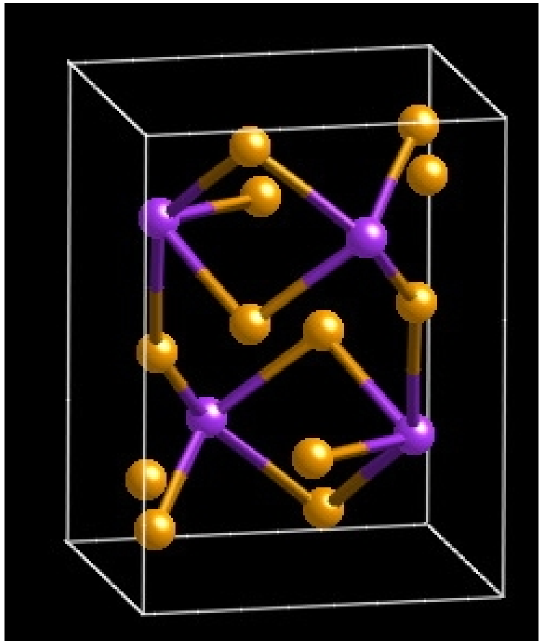
Iron Carbon Phase Diagram

Eutectoid reaction: $\gamma \leftrightarrow \alpha + Fe_3C$



Source: Reed-Hill, Abbaschian, **Physical Metallurgy Principles, 3rd Edition**, *PWS Publishing Company*, 1994.

Cementite – What is it?



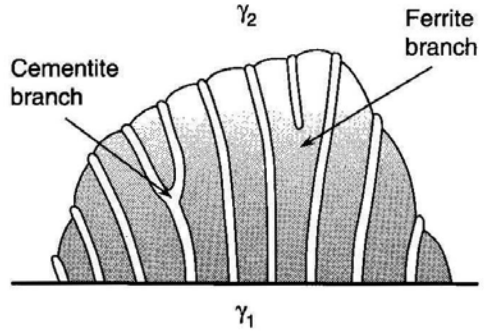
Iron Carbide – Ceramic Compound

Purple: Carbon atoms
Orange: Iron atoms

- <u>Cementite has an orthorhombic lattice</u> with approximate parameters 0.45165, 0.50837 and 0.67297 nm.
- There are twelve iron atoms and four carbon atoms per unit cell, corresponding to the formula Fe_3C.

Source: http://www.msm.cam.ac.uk/phase-trans/2003/Lattices/cementite.html
H. K. D. H. Bhadeshia

Pearlite: What is it?



- The eutectoid transformation:

γ (0.77% C) $\longrightarrow$ α (0.02%C) + Fe_3C (6.67%C)

- Alternate lamellae of ferrite and cementite as the continuous phase

- Diffusional Transformation

- "Pearlite" name is related to the regular array of the lamellae in colonies. Etching attacks the ferrite phase more than the cementite. The raised and regularly spaced cementite lamellae act as diffraction gratings and a pearl-like luster is produced by the diffraction of light of various wavelengths from different colonies

Pearlite

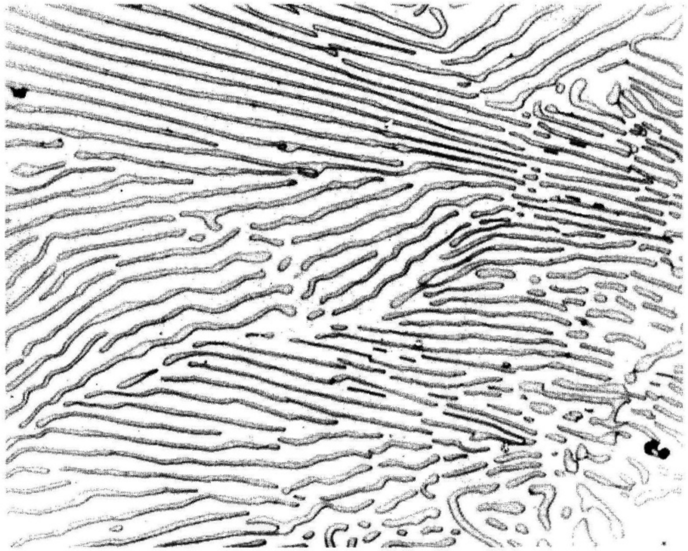


Fig. 18.6 Pearlite consists of plates of Fe_3C in a matrix of ferrite. (Vilella, J. R., *Metallographic Technique for Steel*, ASM Cleveland, 1938.) 2500X.

Reed-Hill, Abbaschian, 1994, [5]

- **Two phases appear in definite ratio by the lever rule:**

$$\alpha = \frac{6.67 - 0.77}{6.67} \approx 88\%$$

$$cementite = \frac{0.77 - 0}{6.67} \approx 12\%$$

- **Since the densities are same (7.86 and 7.4) lamellae widths are 7:1**

- **Heterogeneous nucleation and growth of pearlite colonies – but typically grows into only 1 grain**

Lamellae Nucleation

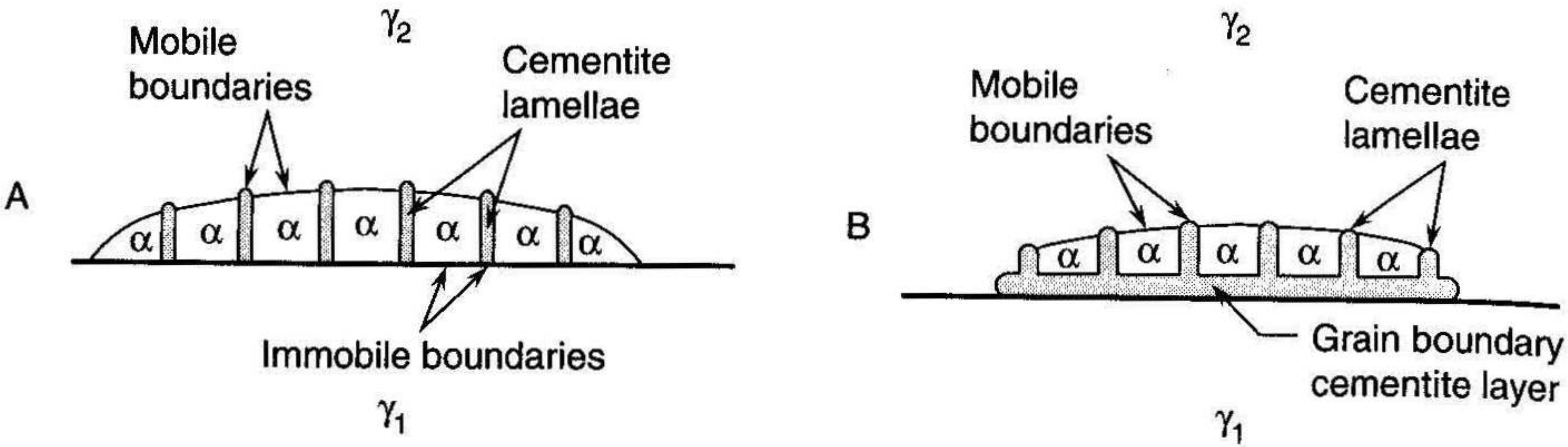


Fig. 18.7 The two primary methods of nucleating pearlite. (A) Nucleation of pearlite at an austenite grain boundary (Pitsch-Petch relation). (B) Nucleation of pearlite at a grain-boundary layer of cementite (Baryatski relation).

Reed-Hill, Abbaschian, 1994

Lamellae Nucleation

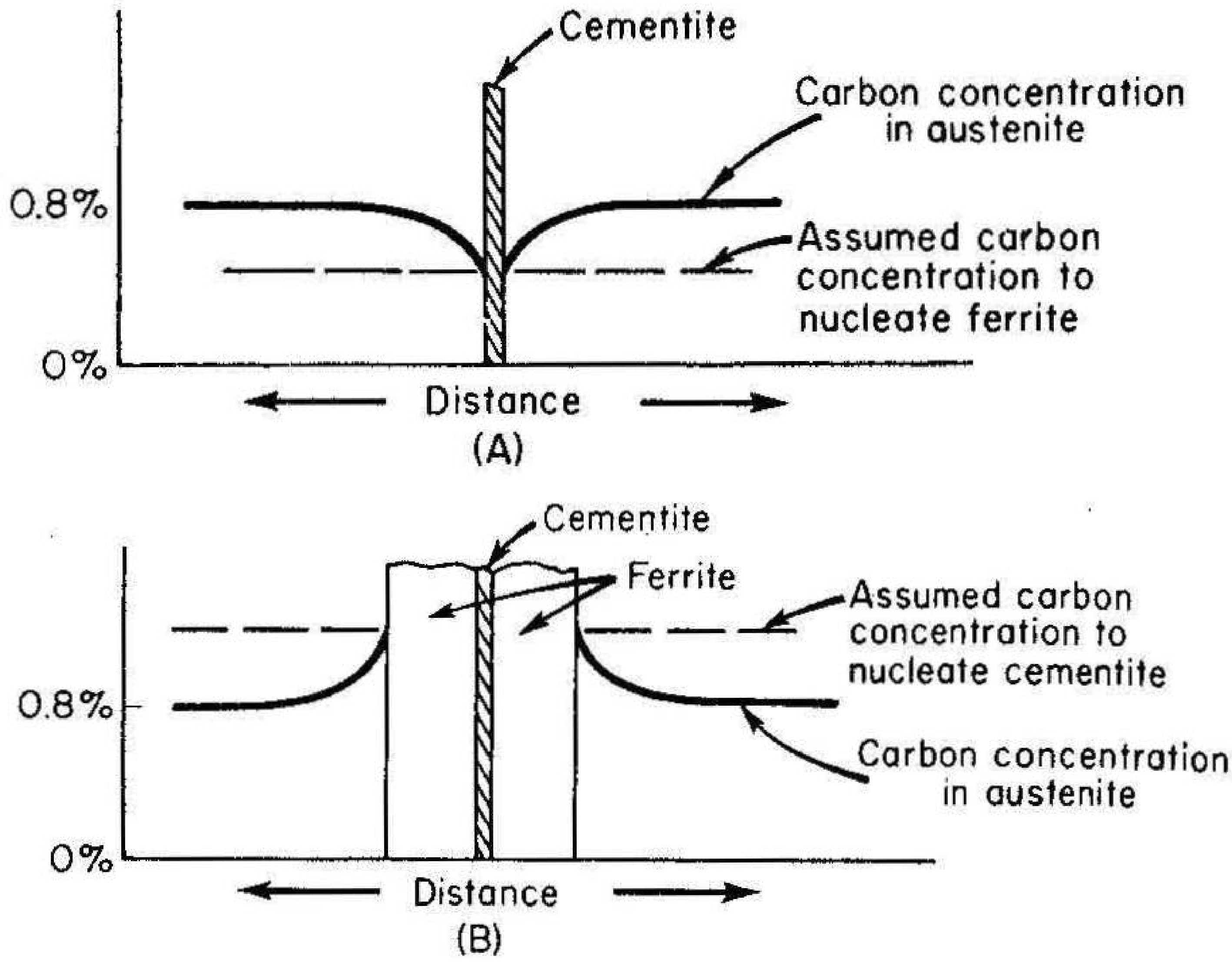


Fig. Growing cementite and ferrite lamellae may nucleate each other.

Reed-Hill, Abbaschian, 1994

Eutectic Solidification (Kinetics)

If α is nucleated from liquid and starts to grow, what would be the composition at the <u>interface</u> of α/L determined?

→ rough interface (diffusion interface) & local equilibrium

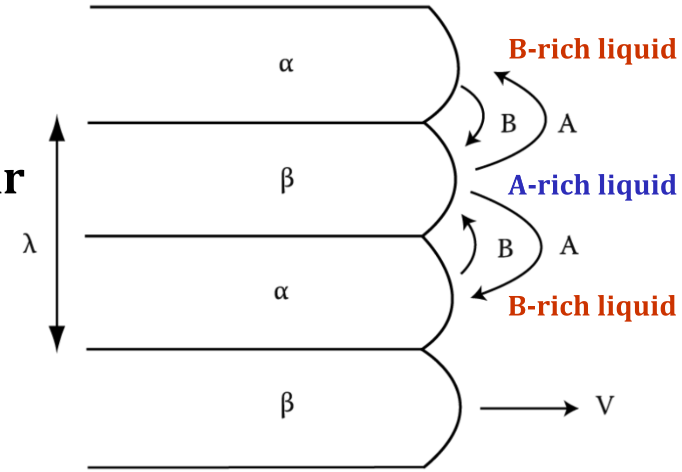
How about at β/L? **Nature's choice? Lamellar structure**

$$\rightarrow G = G_{bulk} + G_{interface} = G_0 + \gamma A$$

$$\sum A_i \gamma_i + \Delta G_S = minimum$$

Interface energy + Misfit strain energy

interlamellar spacing →



Eutectic solidification

: diffusion controlled process

1) λ↓ → eutectic growth rate↑

but 2) λ↓ → α/β interfacial E, $\gamma_{\alpha\beta}$↑

→ lower limit of λ

➡ <u>fastest growth rate at a certain λ</u>

What would be a role of the <u>curvature</u> at the tip?

→ Gibbs-Thomson Effect

Interlamellar Spacing

- **Interlamellar spacing λ is almost constant in pearlite formed from γ at a fixed T.**
- **Temperature has a strong effect on spacing – lower T (large ΔT) promotes smaller λ.**
  - **Pearlite formed at 700°C has λ ~ 1 mm and Rockwell C – 15.**
  - **Pearlite formed at 600°C has λ ~ 0.1 mm and Rockwell C – 40.**
- **Zener and Hillert Eq. for spacing (eq. 4.39):**

$$\lambda = \frac{4\sigma_{\alpha / Fe_3C} T_E}{\Delta H_V \Delta T}$$

IH5: derive λ with maximum growth rate at a fixed ΔT (eutectic case)

σ_{a/Fe_3C} = Interfacial energy per unit area of a/Fe_3C boundary
T_E = The equilibrium temperature (Ae_1)
ΔH_V = The change in enthalpy per unit volume
ΔT = The undercooling below Ae_1

Effect of Undercooling on λ

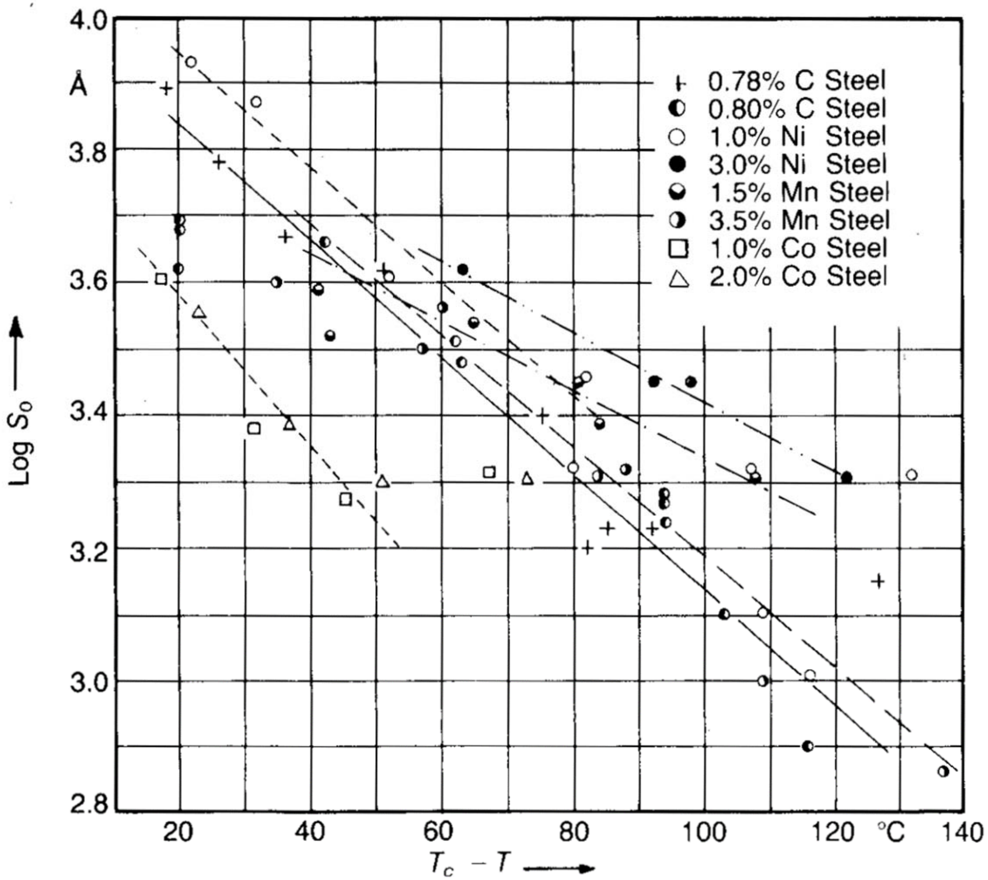
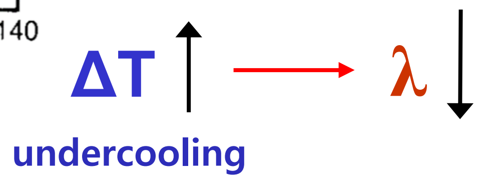


Fig. 2.4. Average true interlamellar spacings of pearlite, S_o, as a function of undercooling below Ae_1 for various steels as indicated. (Ref 2.1)

*Krauss, **Steels**, **1995***



Effect of Interlamellar Spacing

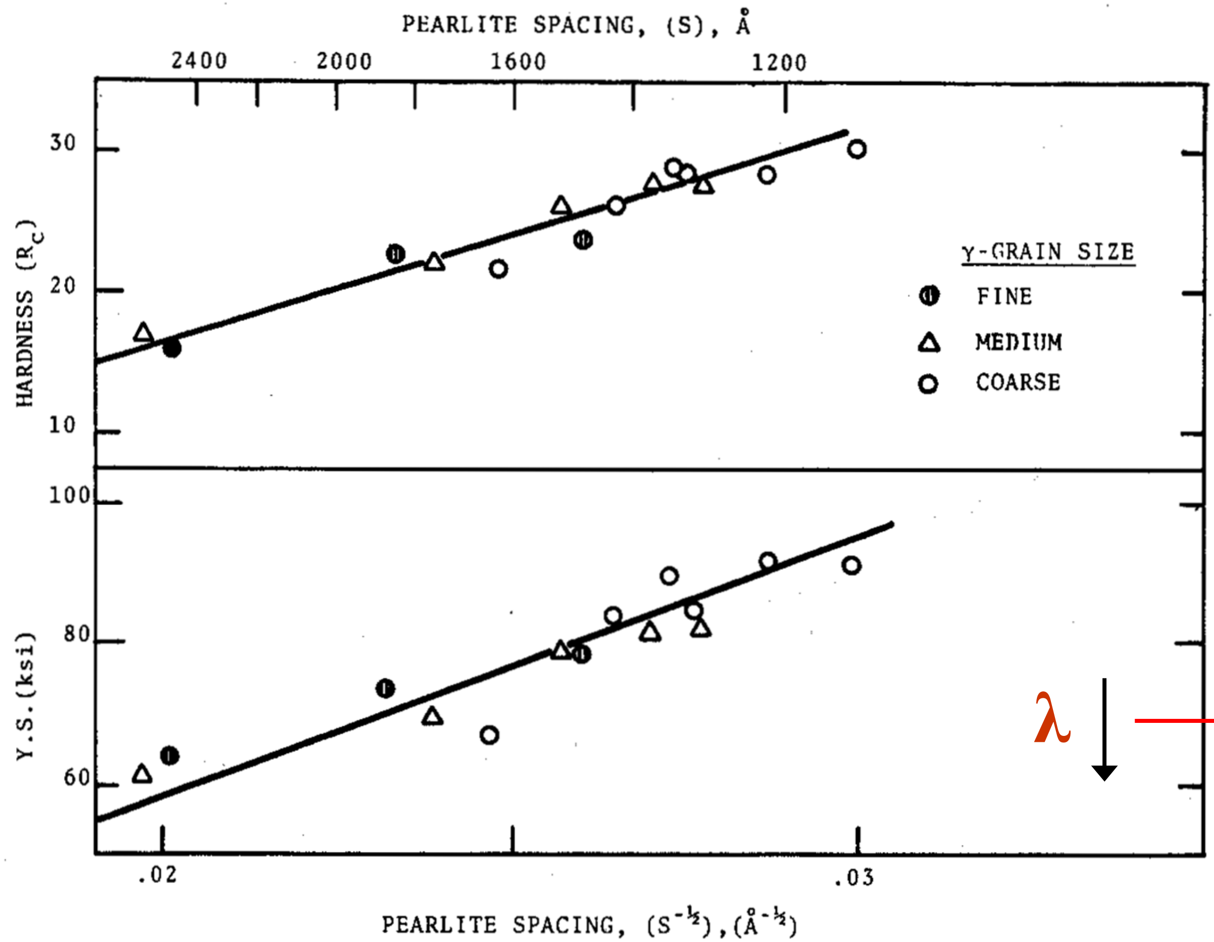
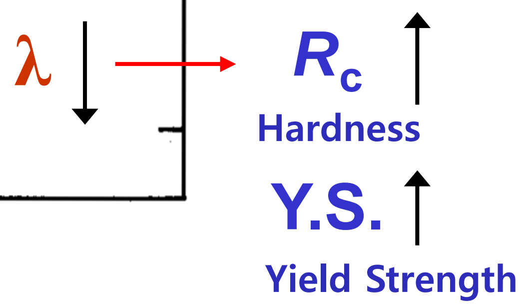


FIG. 16—*Yield strength and hardness versus pearlite interlamellar spacing* [49].



Stone et al, 1975

Iron-Carbon (Fe-C) Phase Diagram

3 invariant points:

- Peritectic (*C*) [0.17%C]:

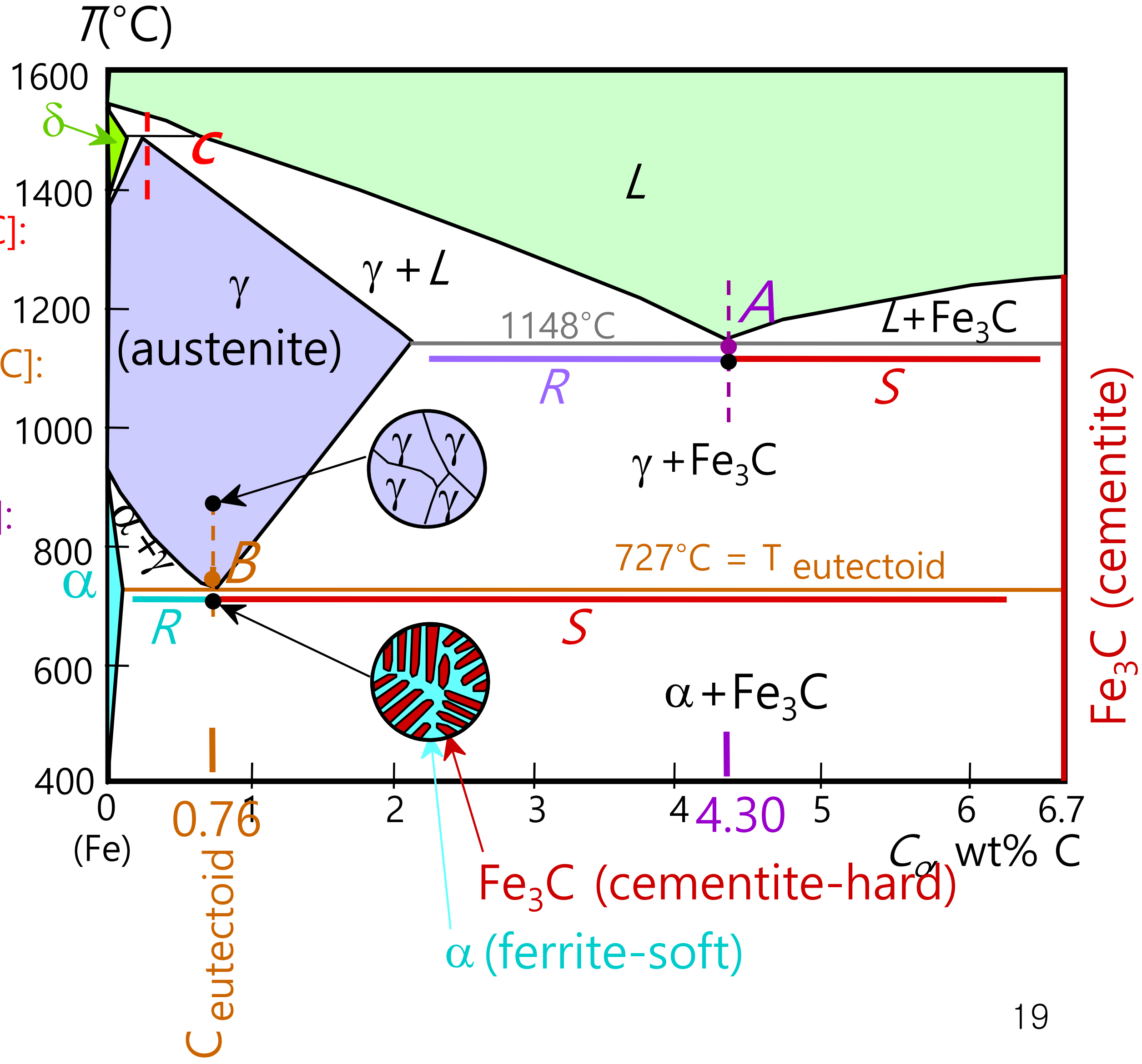
  L + δ ⇒ γ

- Eutectoid (*B*) [0.77 %C]:

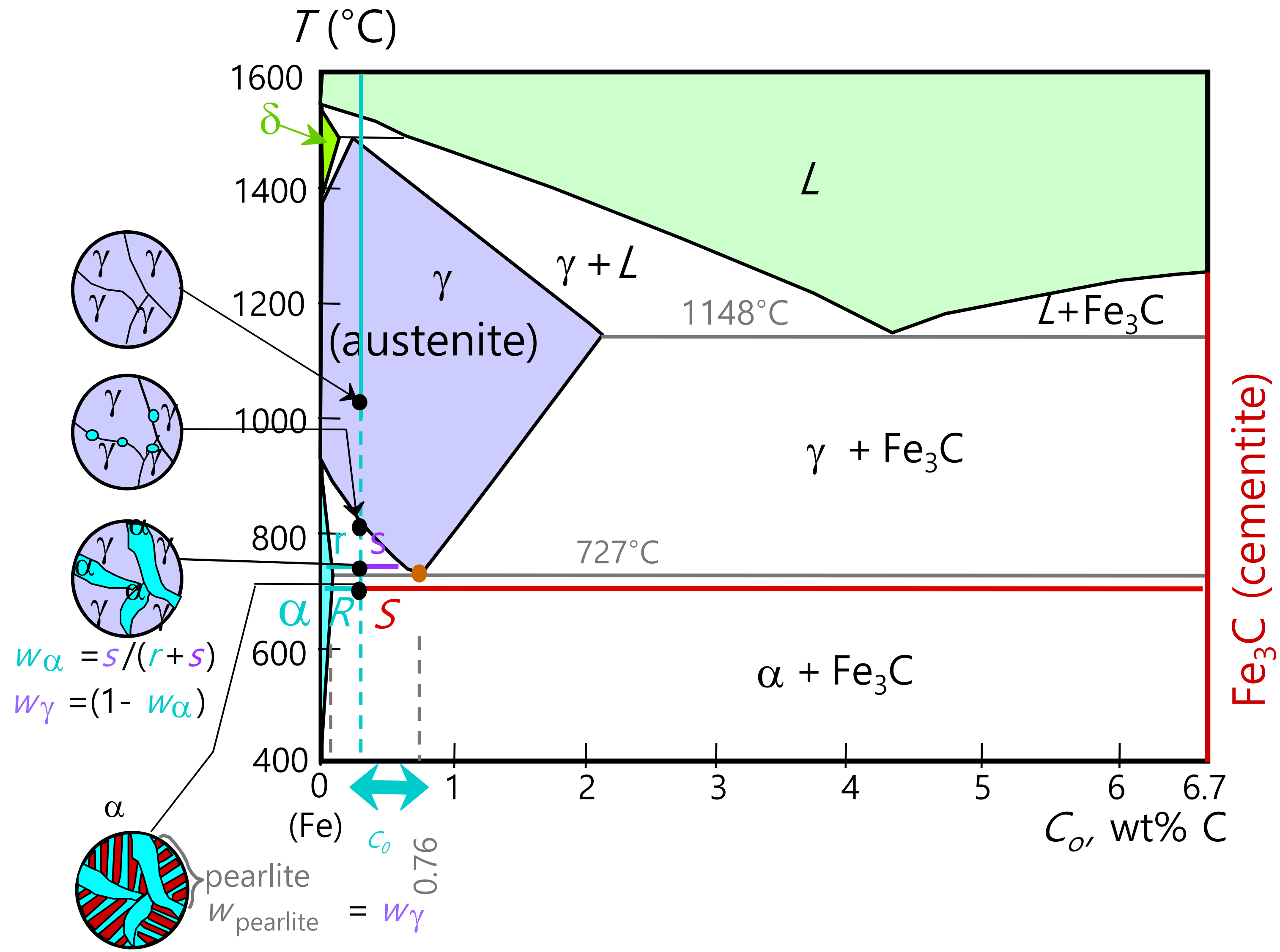
  $\gamma \Rightarrow \alpha + Fe_3C$

- Eutectic (*A*) [4.32 %C]:

  $L \Rightarrow \gamma + Fe_3C$



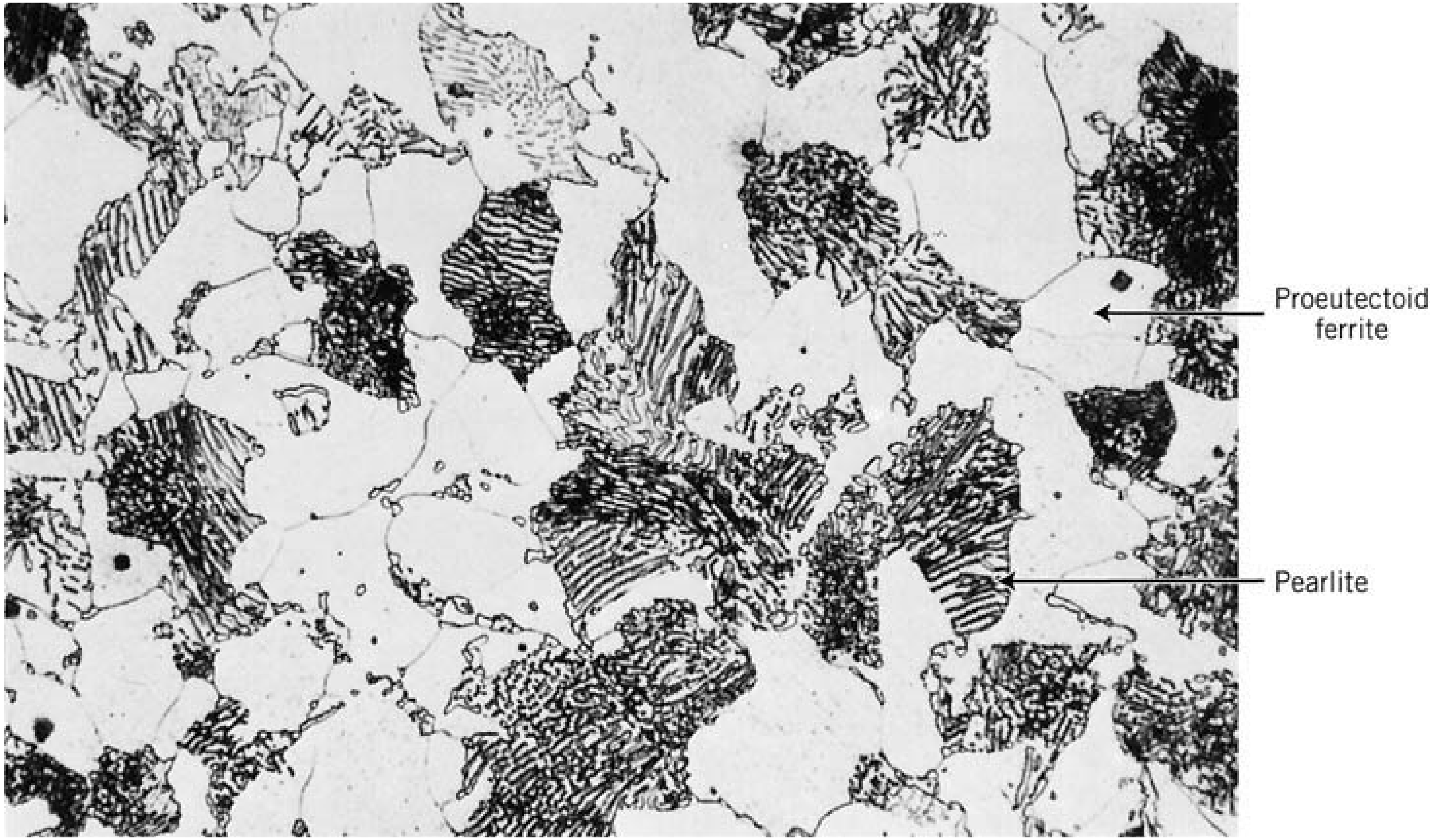
Hypoeutectoid Steel



$w_\alpha = S/(R+S)$

$w_{Fe_3C} = (1 - w_\alpha)$

Proeuctectoid Ferrite – Pearlite

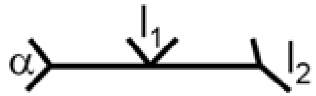


0.38 wt% C: Plain Carbon – Medium Carbon Steel

6.3 Monotectoid reaction: $\alpha_1 \leftrightarrow \beta + \alpha_2$

Monotectic

$l_1 \rightleftarrows \alpha + l_2$



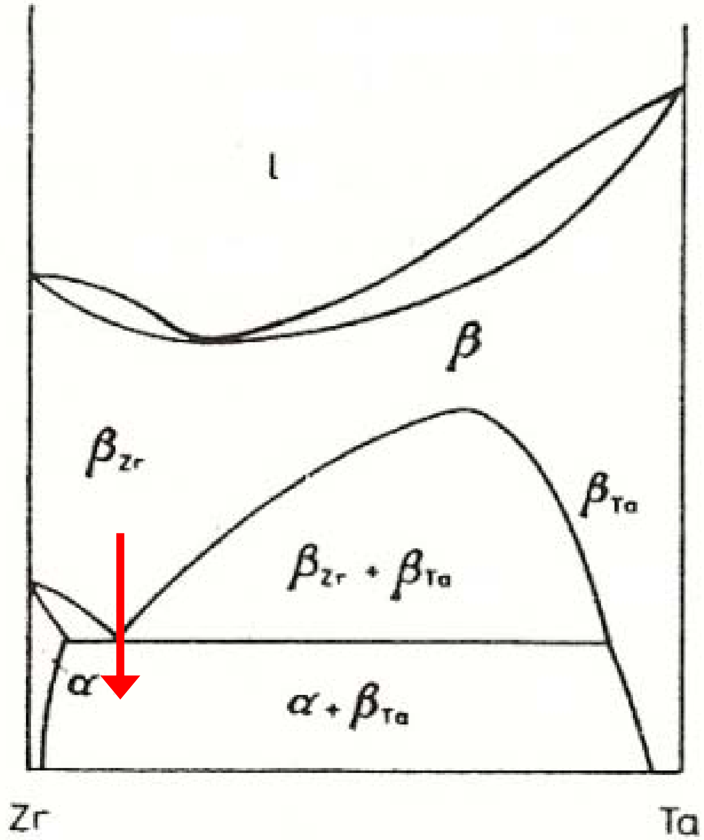


Fig. 93. The monotectoid reaction in the Ta–Zr system (schematic).

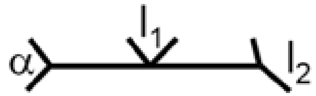
$\beta_{Zr} \leftrightarrow \alpha + \beta_{Ta}$

Both βZr and βTa have the same crystal structure (b.c.c.) but different lattice spacing.

Monotectoid reaction: $\alpha_1 \leftrightarrow \beta + \alpha_2$

Monotectic

$l_1 \rightleftarrows \alpha + l_2$



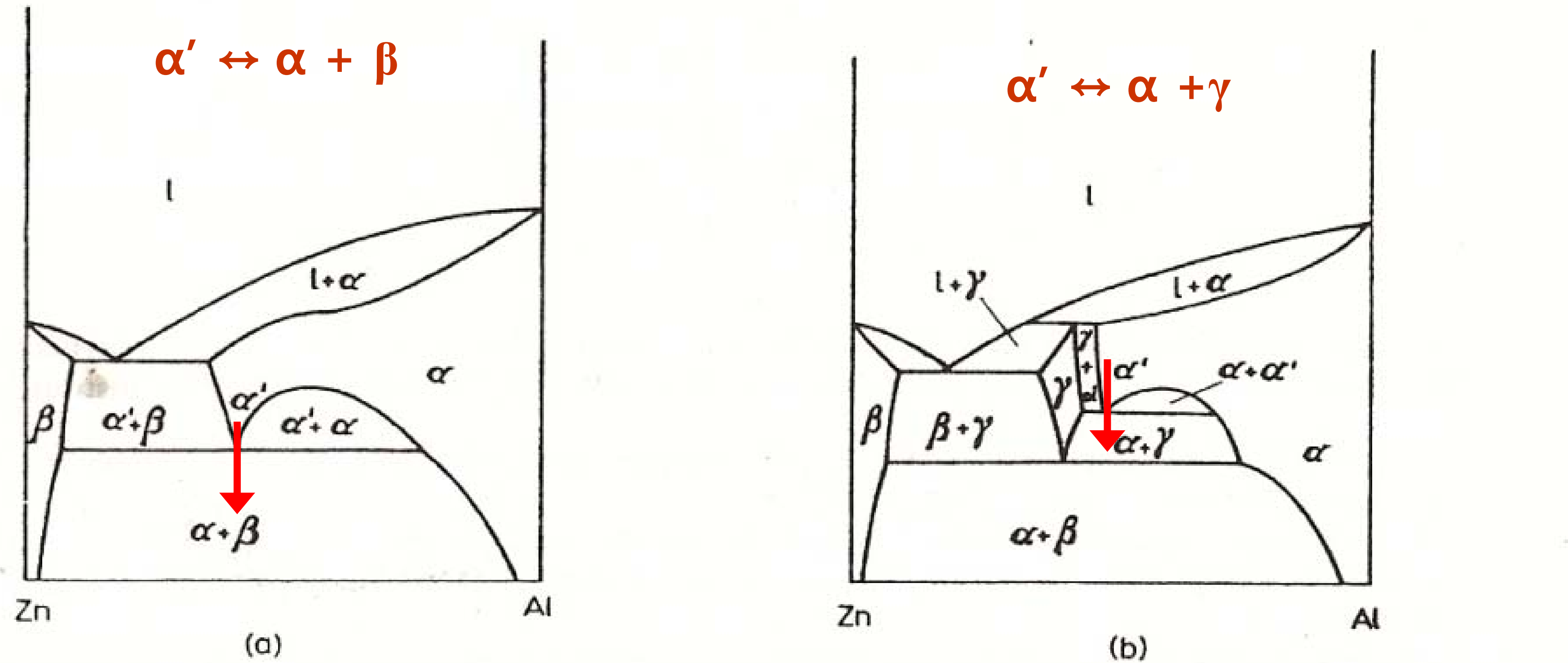


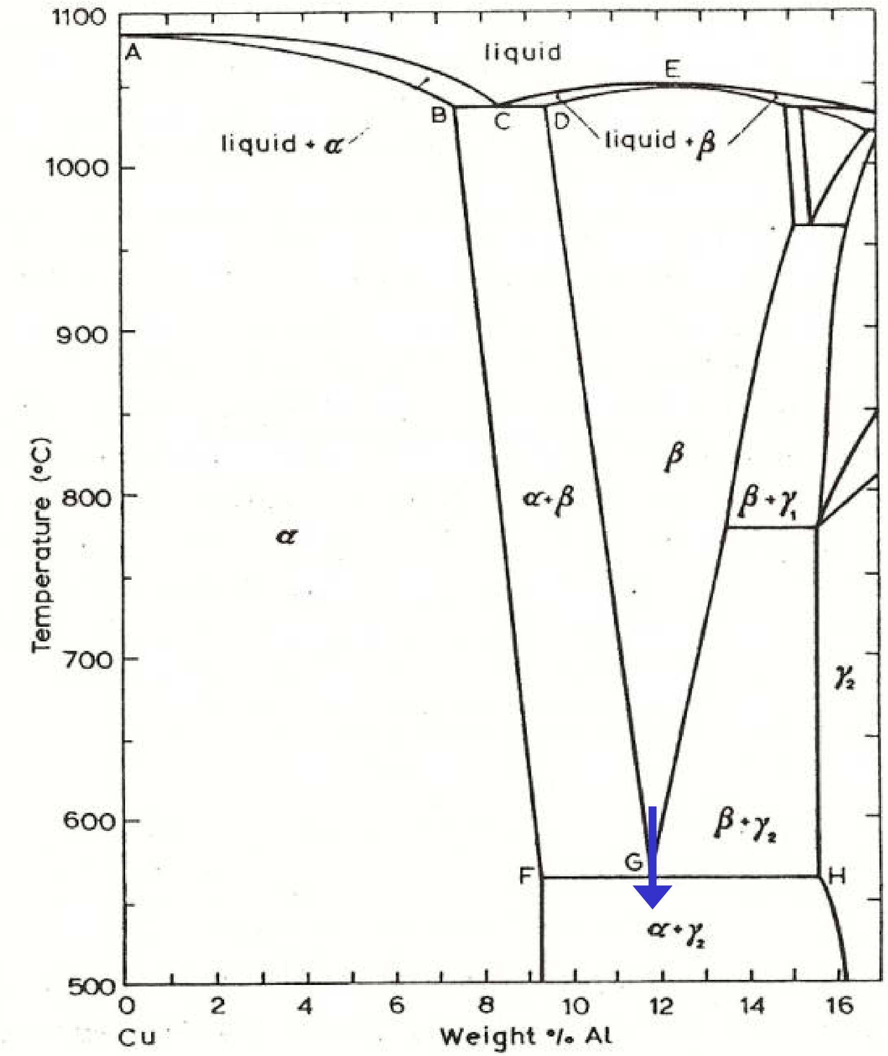
Fig. 94. The monotectoid reaction in the Al–Zn system (schematic). (a) Previously accepted phase diagram; (b) recently proposed modification.

Both α and α′ are face-centered cubic phases, differing only in lattice spacing.

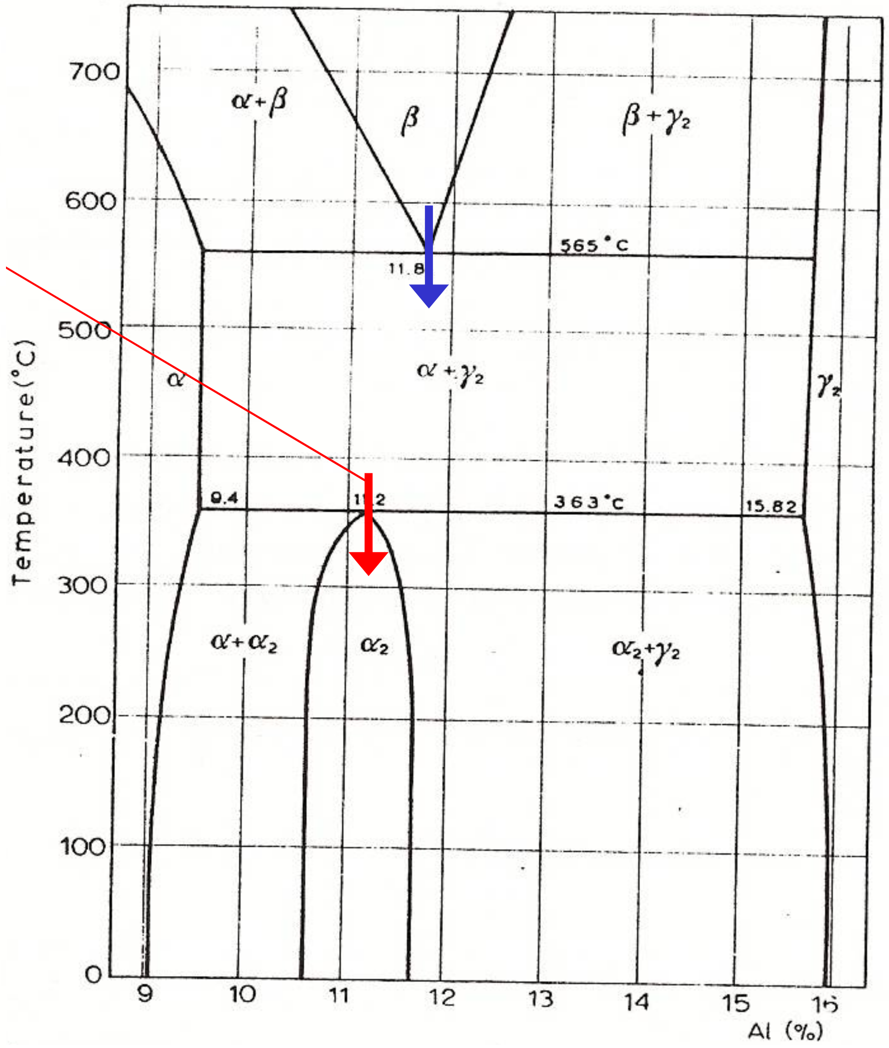
Peritectoid reaction: α + β ↔ γ

Peritectic

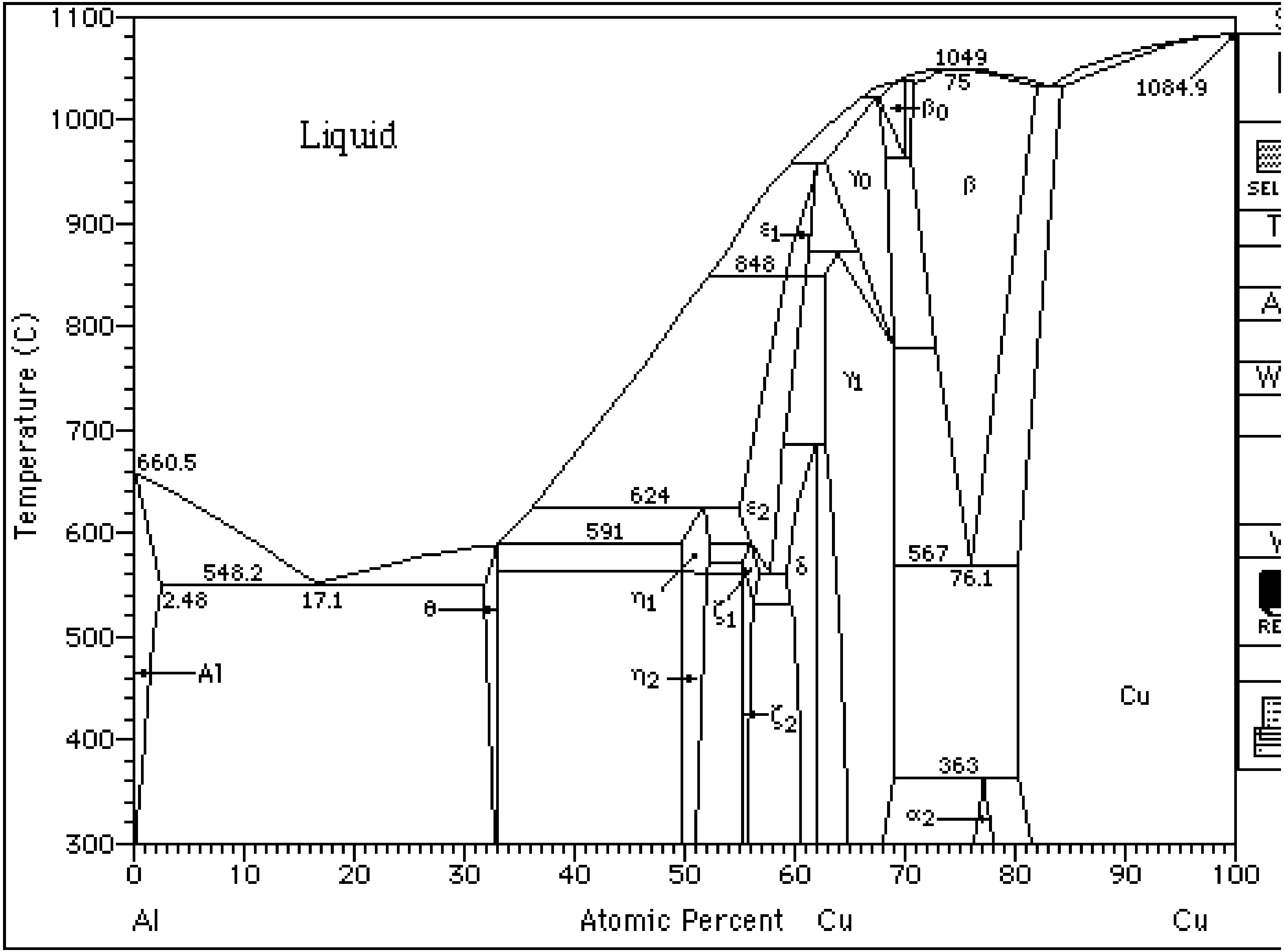
l + β ⇄ α



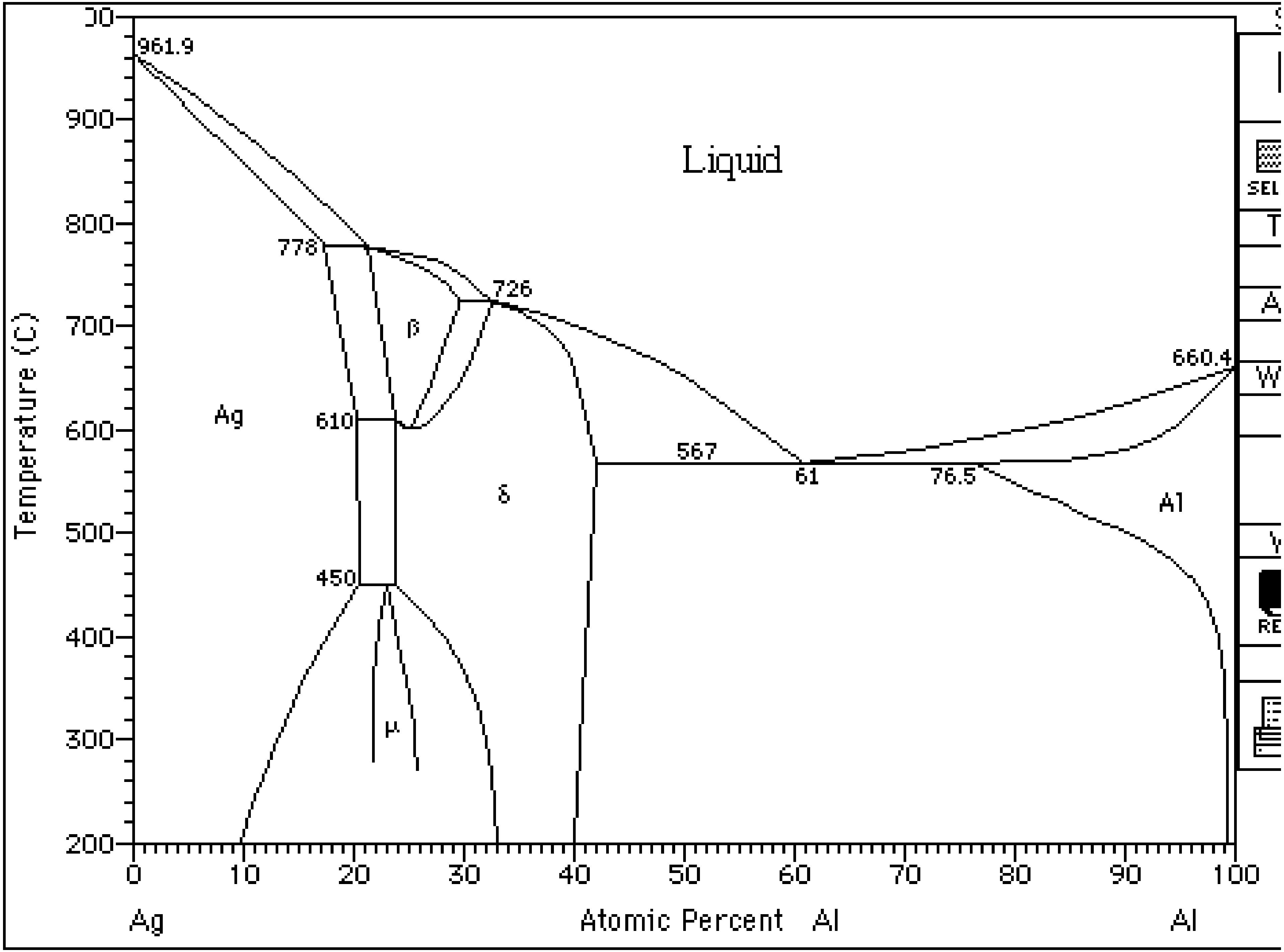
Cu-Al phase diagram



Revision of Cu-Al phase diagram



Liquid
1100
1000
900
800
700
600
500
400
300
Temperature (C)
1049
75
1084.9
β0
γ0
β
ε1
848
γ1
660.5
624
ε2
591
548.2
2.48
17.1
θ
η1
ζ1
δ
567
76.1
Al
η2
ζ2
Cu
363
α2
0
10
20
30
40
50
60
70
80
90
100
Al
Atomic Percent Cu
Cu

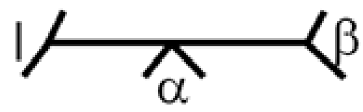


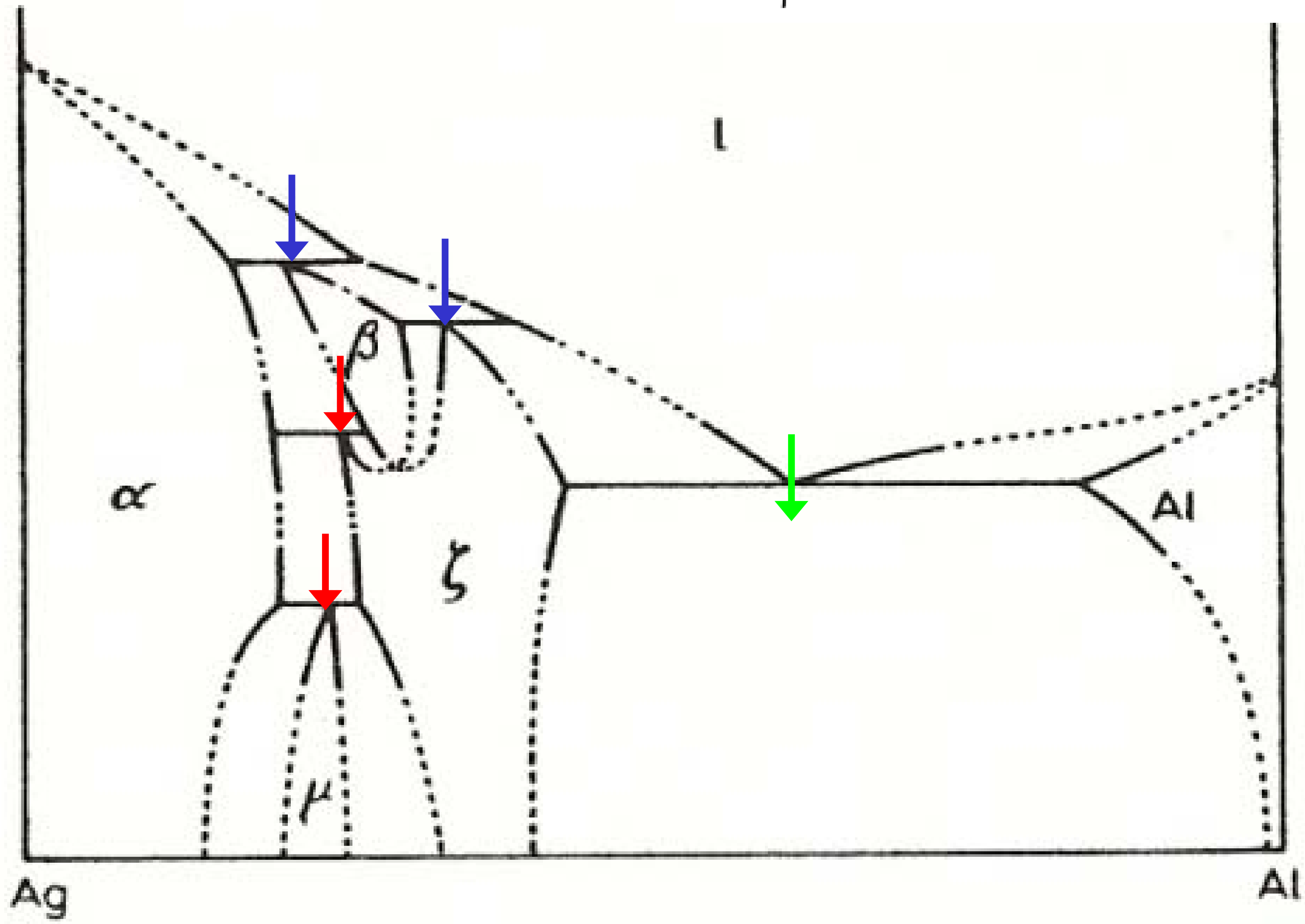
Liquid
961.9
778
726
660.4
610
567
61
76.5
450
β
δ
μ
Ag
Al
Temperature (C)
Atomic Percent Al
Ag
Al

Peritectoid reaction: $\alpha + \beta \leftrightarrow \gamma$

Peritectic

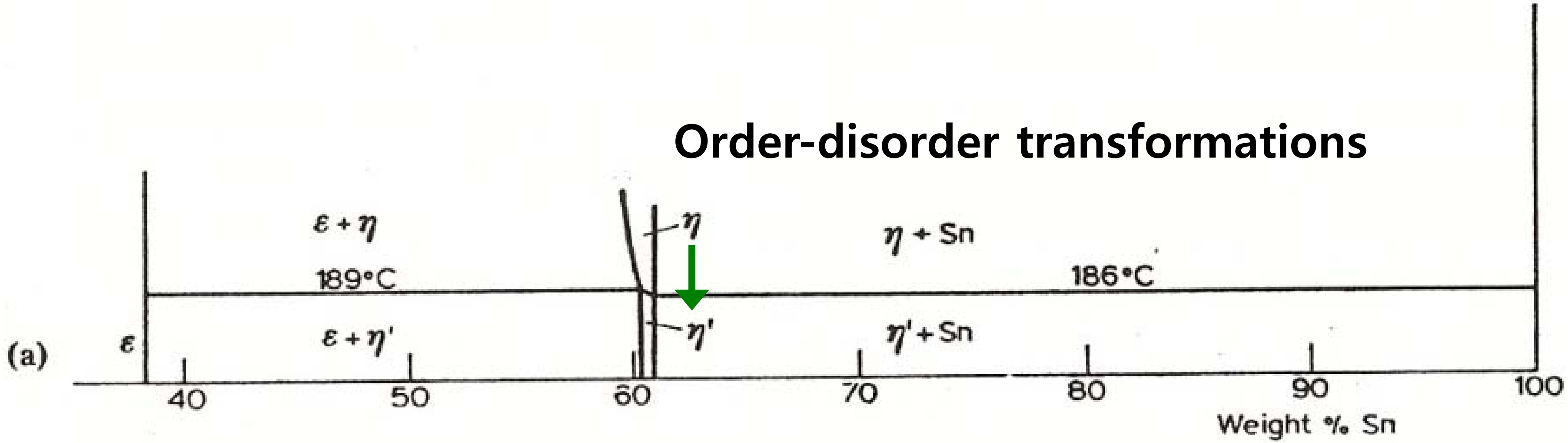
$l + \beta \rightleftarrows \alpha$





Ag-Al phase diagram (schematic)

Order-disorder transformations



Peritectoid reaction: η+ε ↔ η′ **Eutectoid reaction: η ↔ η′+ α**

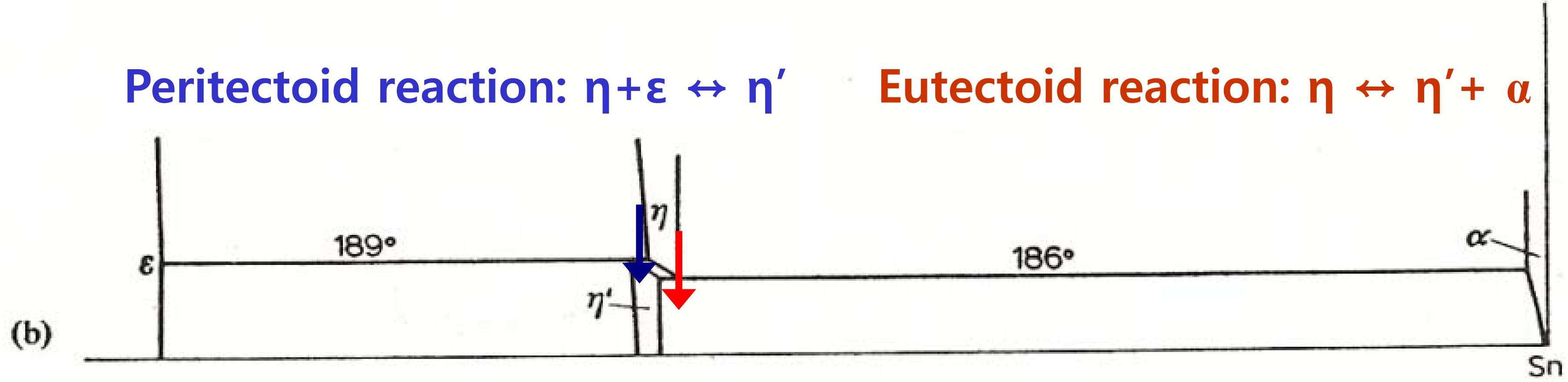


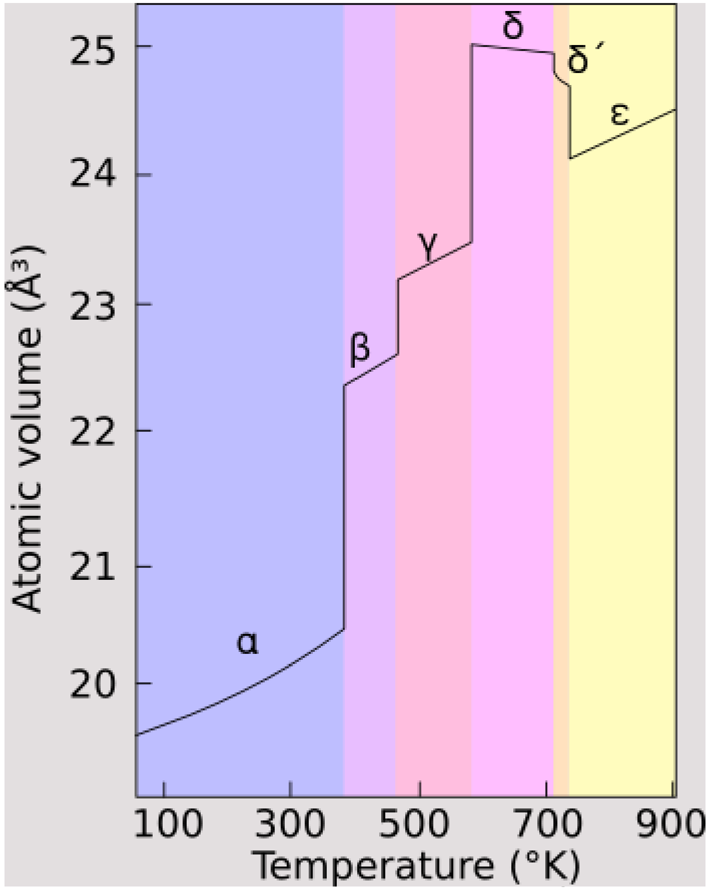
Fig. 97. (a) A part of the Cu–Sn phase diagram (after G. V. Raynor; courtesy Institute of Metals); (b) equilibrium relationships if the data in (a) are considered limiting cases of the peritectoid and eutectoid reactions.

CHAPTER 7

Binary Phase Diagrams. Allotropy of the Components

Several commercially important metals exist in more than one crystalline form.

Ex. Iron- three allotropes α, γ, δ



Titanium – two allotropes close-packed hexagonal α Ti stable at low temp. and body-centered cubic β Ti stable at high temp.

Plutonium – six allotropes _ the highest number of modifications

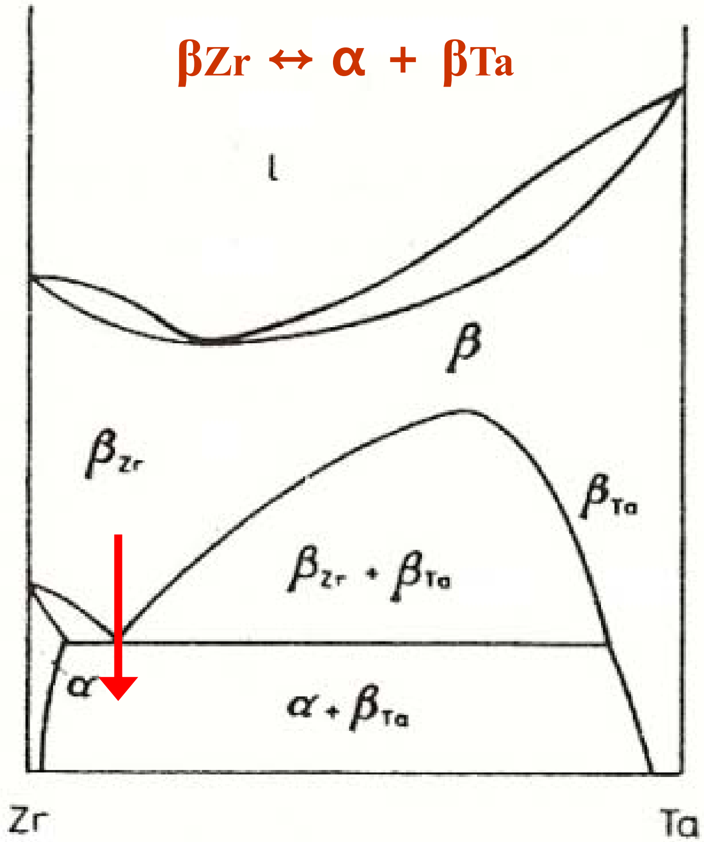
a. SYSTEMS IN WHICH ONE PHASE IS IN EQUILIBRIUM WITH THE LIQUID PHASE

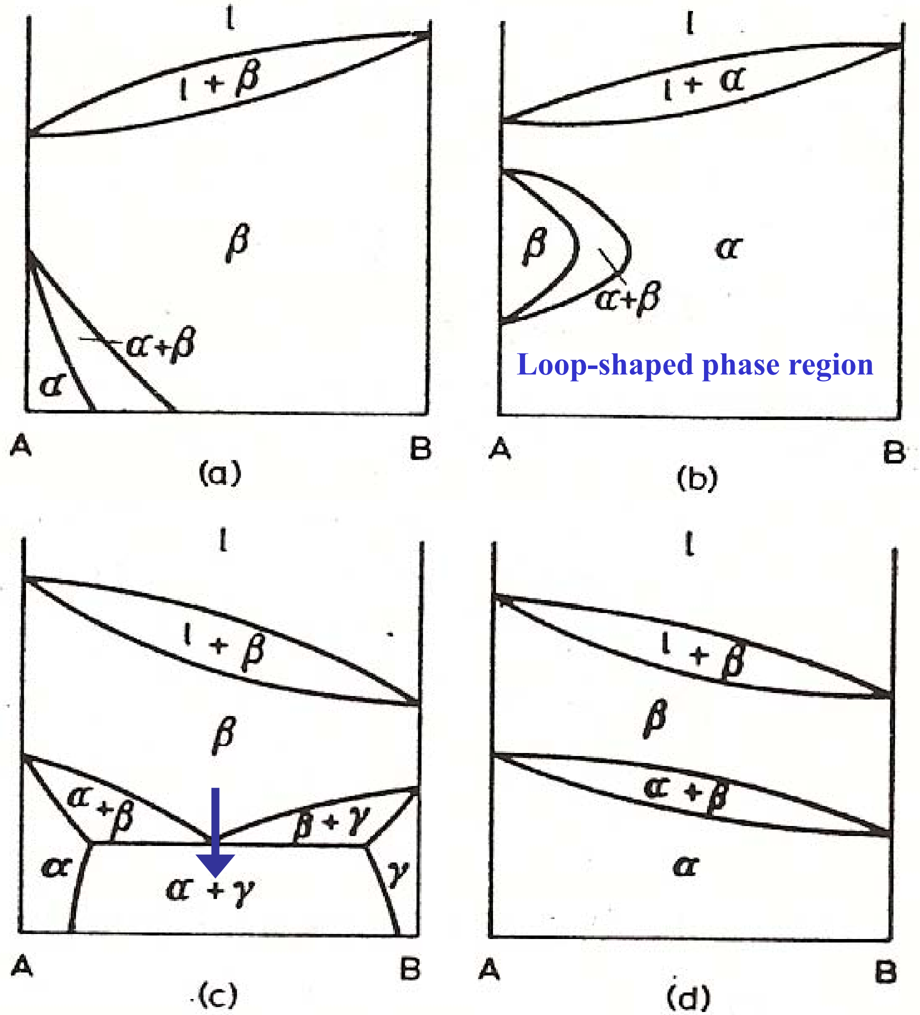
Such systems can be further divided according to whether the high temperature allotrope forms a continuous series of solid solutions with the other component or not.

7.1.1. The high temperature phase forms a series of solid solutions with the other component

Monotectoid reaction:

$$\beta Zr \leftrightarrow \alpha + \beta Ta$$



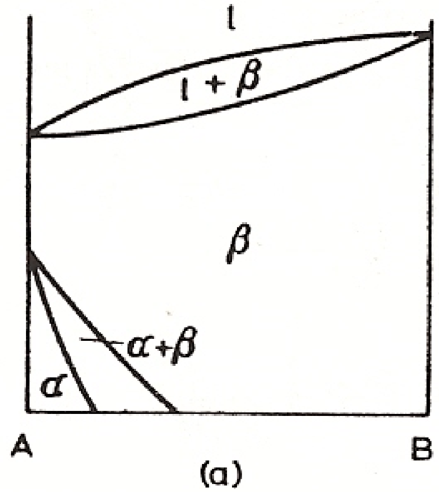


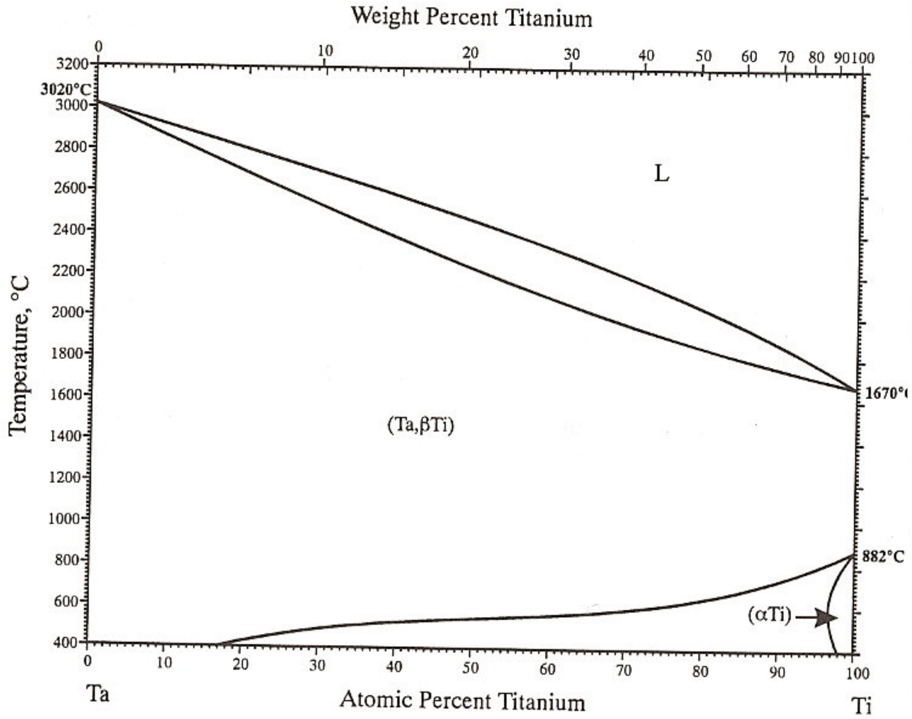
Eutectoidal decomposition

7.1.1. The high temperature phase forms a series of solid solutions with the other component

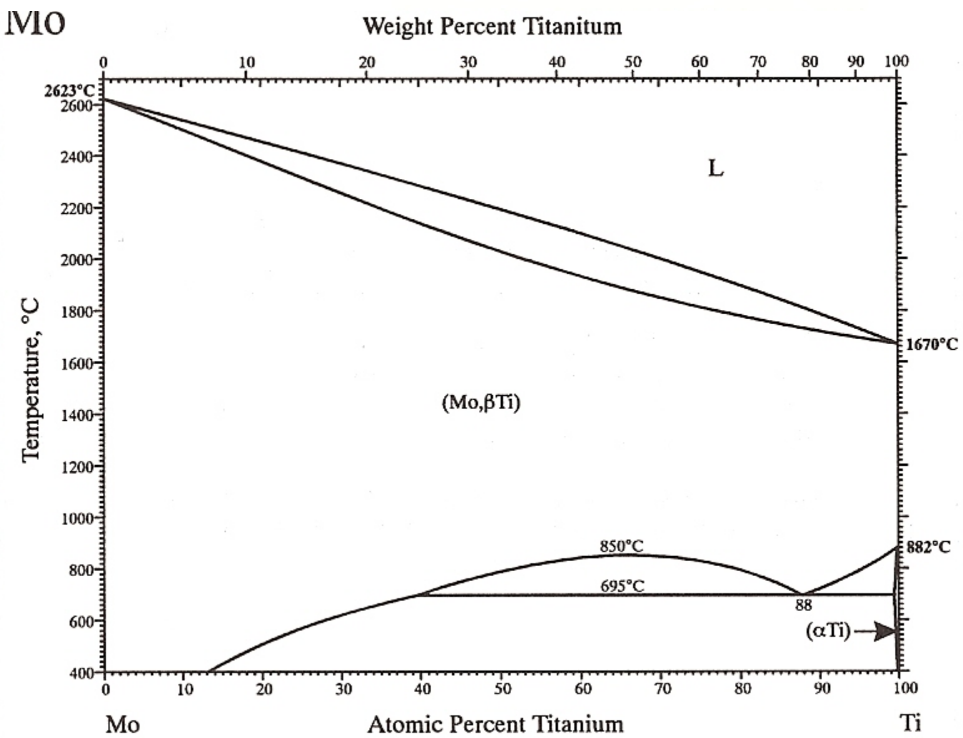
Types of phase diagrams formed when the high temperature allotrope forms a continuous series of solid solutions with the second component.

(a) single component have two allotropic modifications.





allotropic modification

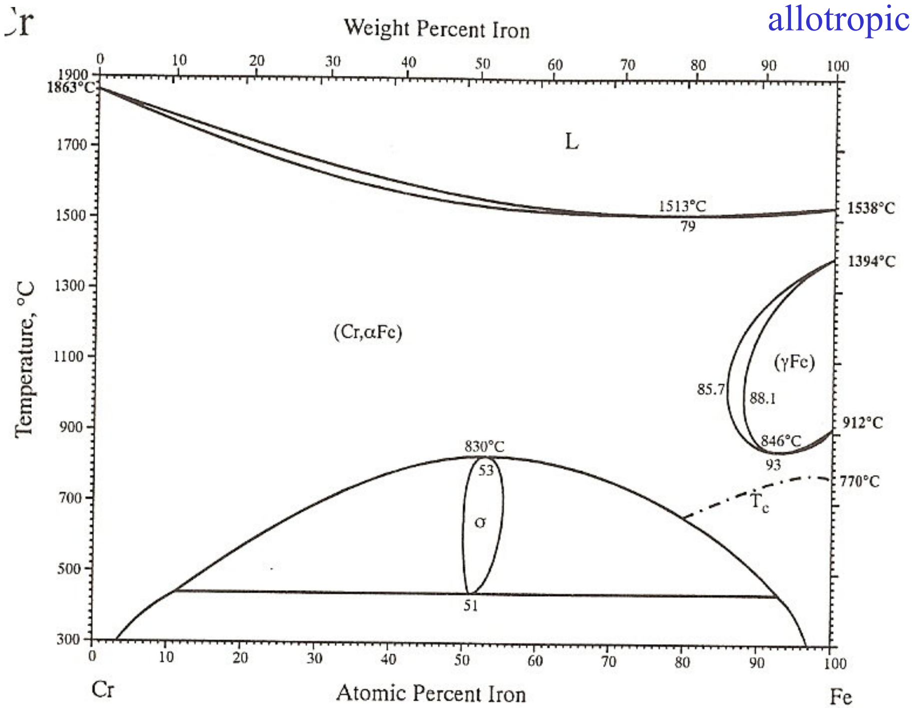


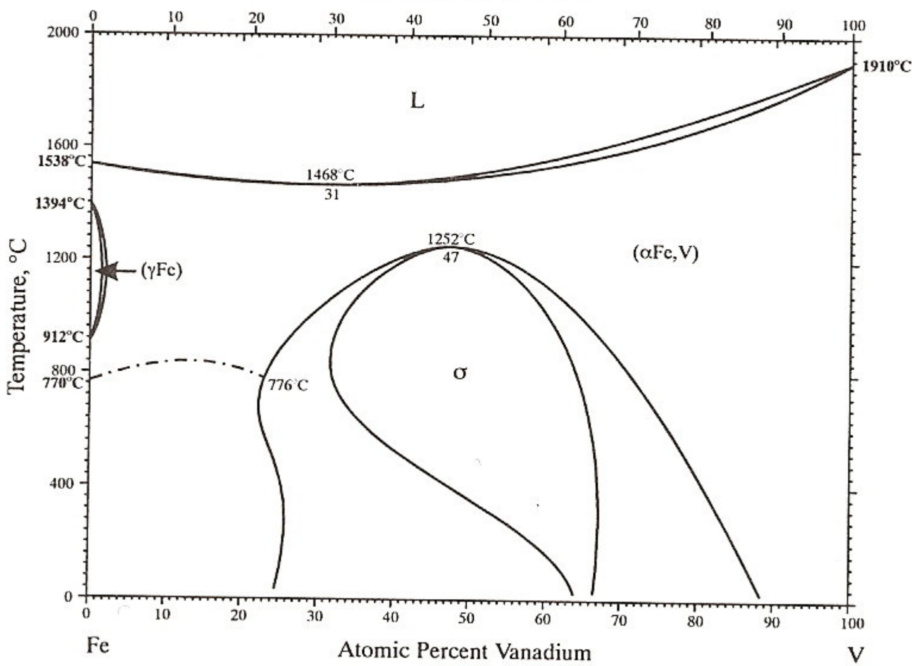
allotropic modification

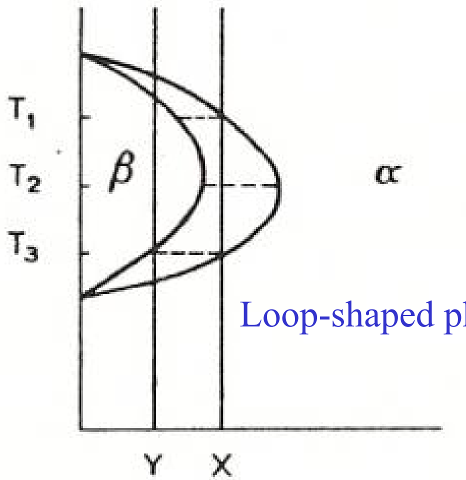
7.1.1. The high temperature phase forms a series of solid solutions with the other component

(a) single component have two allotropic modifications.

allotropic modification







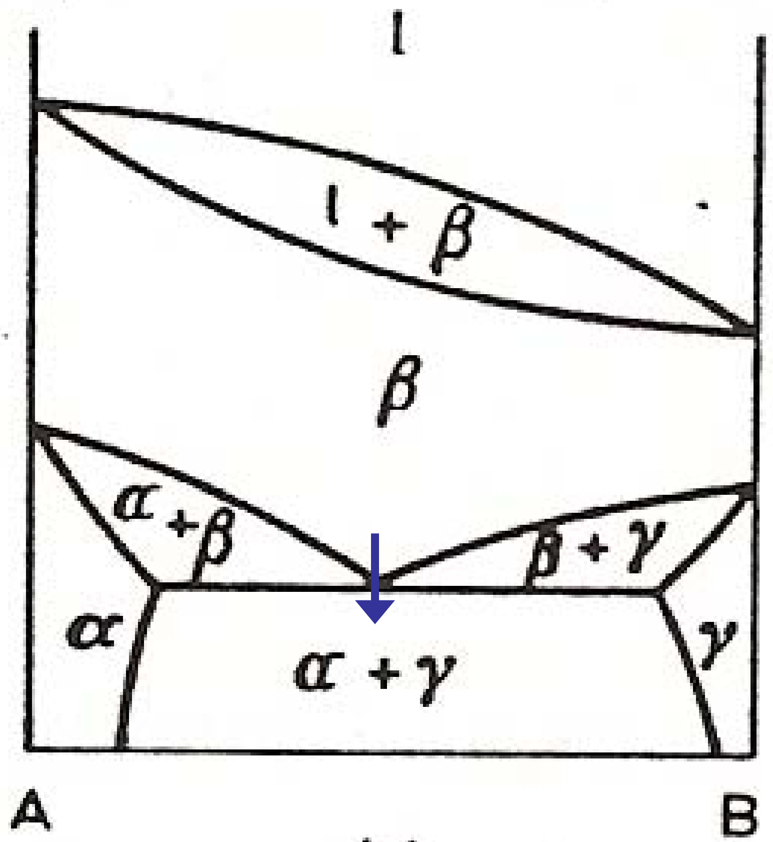
Loop-shaped phase region

Fig. 99. Cooling of alloys through the β loop.

		T1	T2	T3	
X		α	α+β	α	
Y	α		β		α

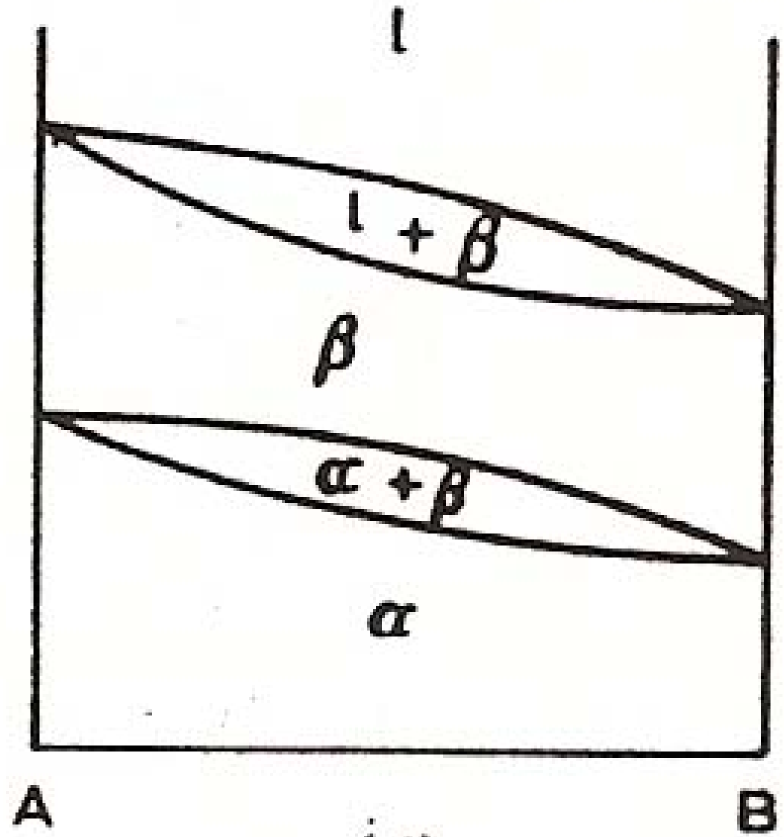
7.1.1. The high temperature phase forms a series of solid solutions with the other component

(b) Both components have two allotropic modifications.



(c)

Eutectoidal decomposition
of high temperature allotrope β into α and γ, the low temperature allotropes of components A and B respectively.

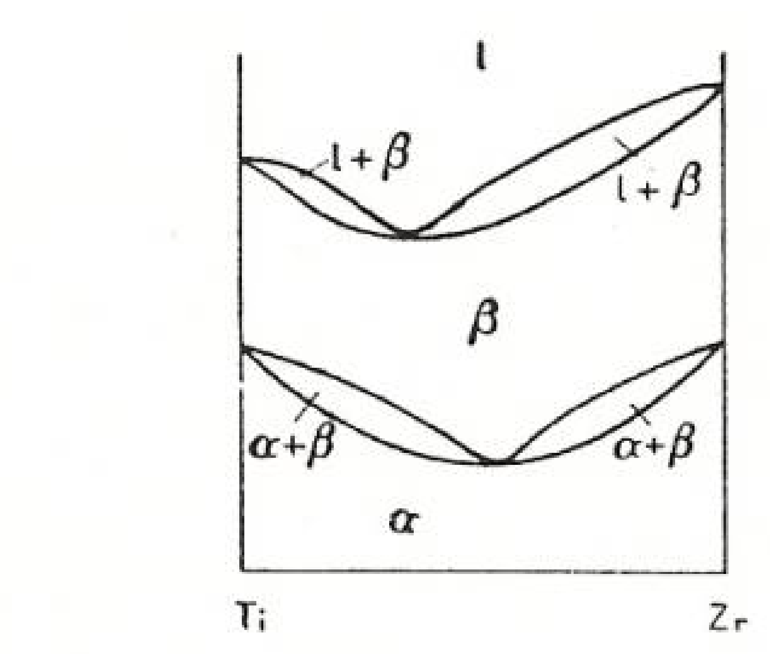


(d)

Complete series of solid solutions
are formed between each of the allotropes

7.1.1. The high temperature phase forms a series of solid solutions with the other component

(b) Both components have two allotropic modifications.



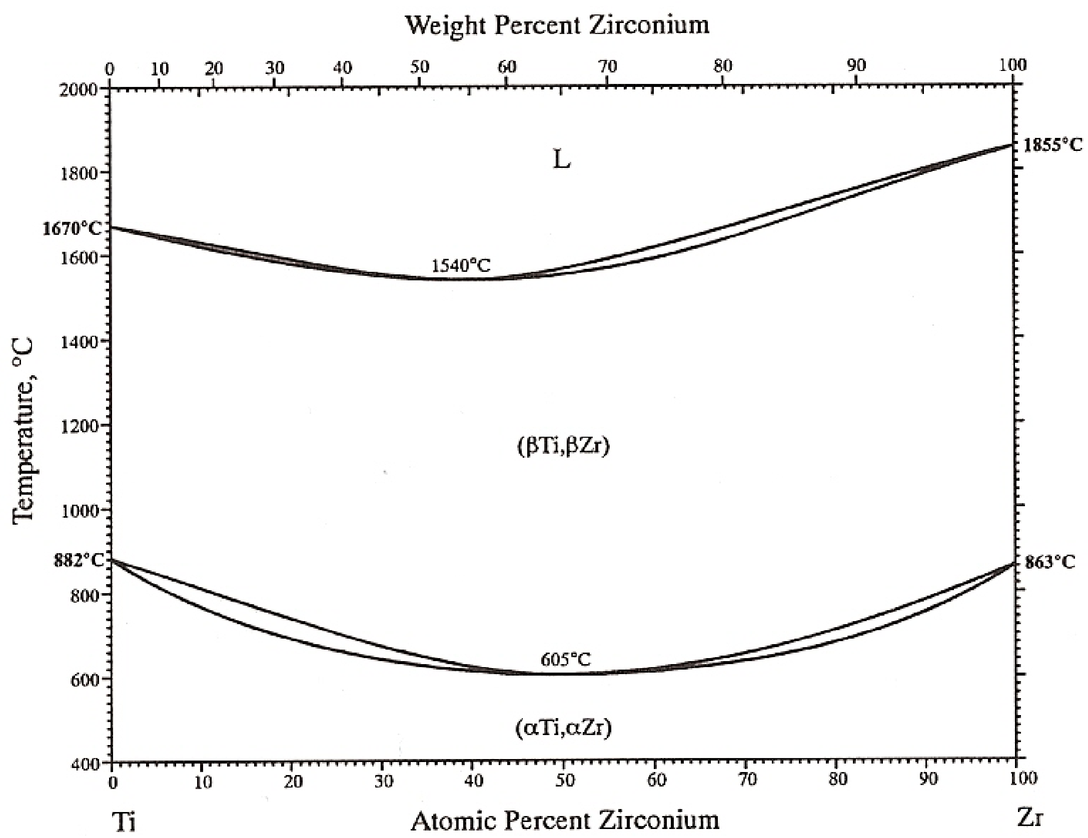
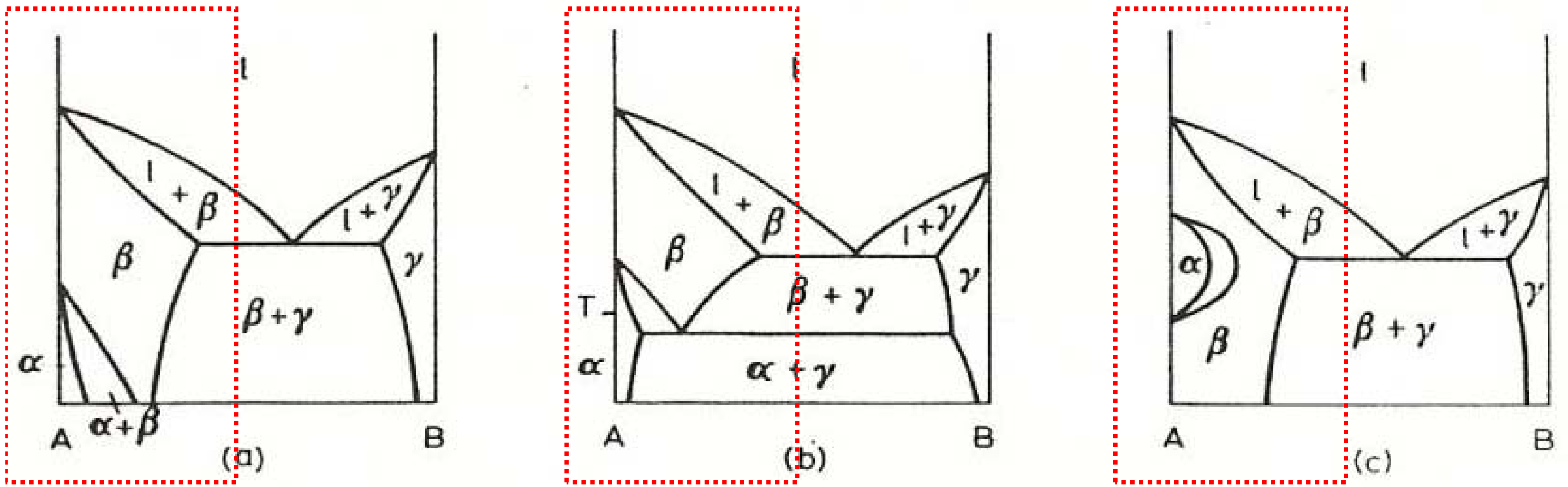


Fig. 100. The Ti–Zr phase diagram (schematic).

Complete series of solid solutions
are formed between each of the allotropes in the system Ti-Zr.

a. SYSTEMS IN WHICH ONE PHASE IS IN EQUILIBRIUM WITH THE LIQUID PHASE

7.1.2. Both phases form limited solid solutions with the other component

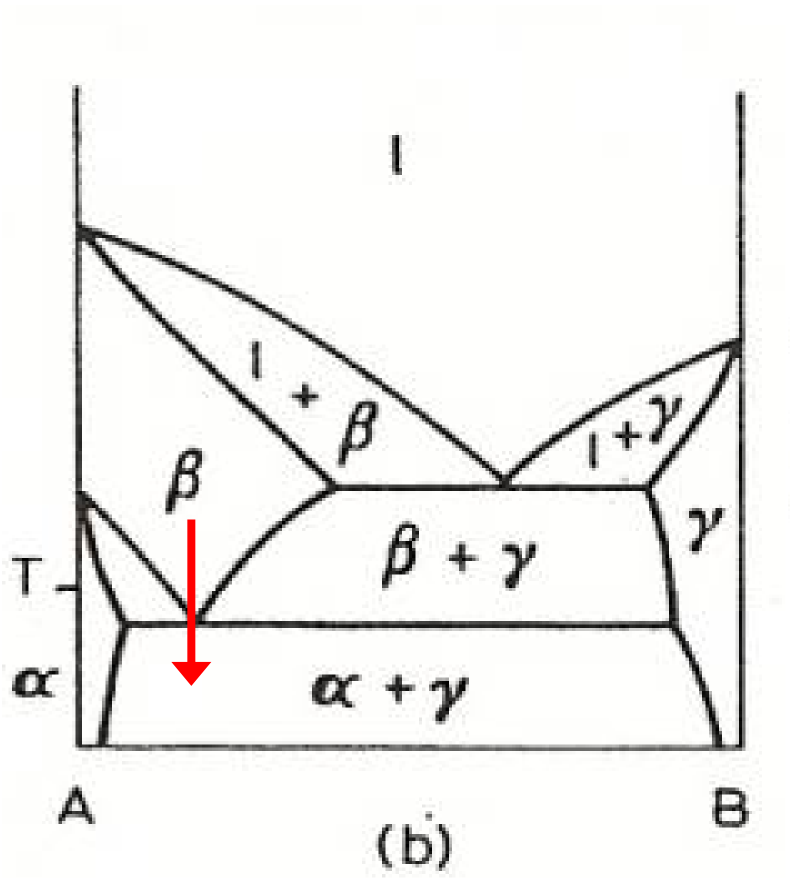


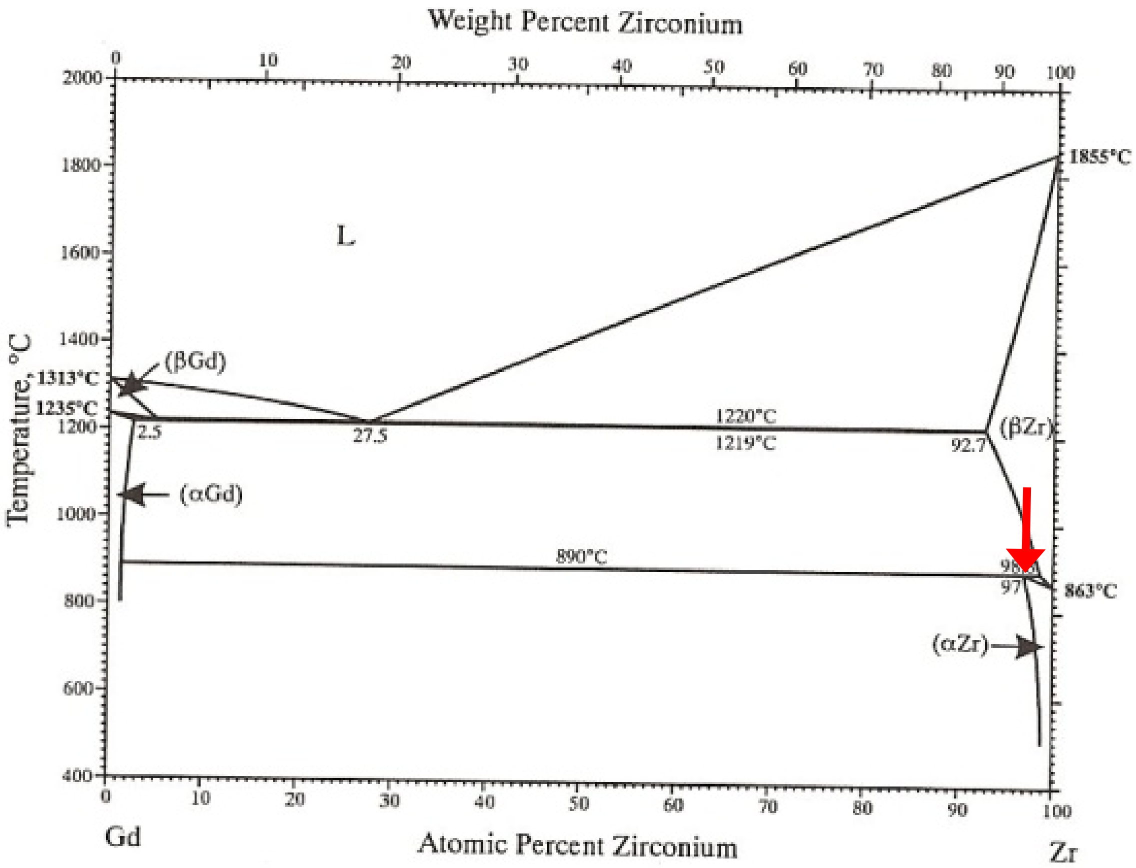
High-temperature β phase, as well as the low-temperature α phase form <u>limited solid solutions with component B</u>.

Polymorphism: **the ability of a solid material to exist in more than one form or crystal structure** (Both α and β are allotropes of A)

Eutectoid reaction: α ↔ β + γ

Peritectoid reaction: α + β ↔ γ





Simple eutectic system with solid-soild phase transitions

b. SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE

L+ α & L + β or L + β & L + γ or L + γ & L + δ

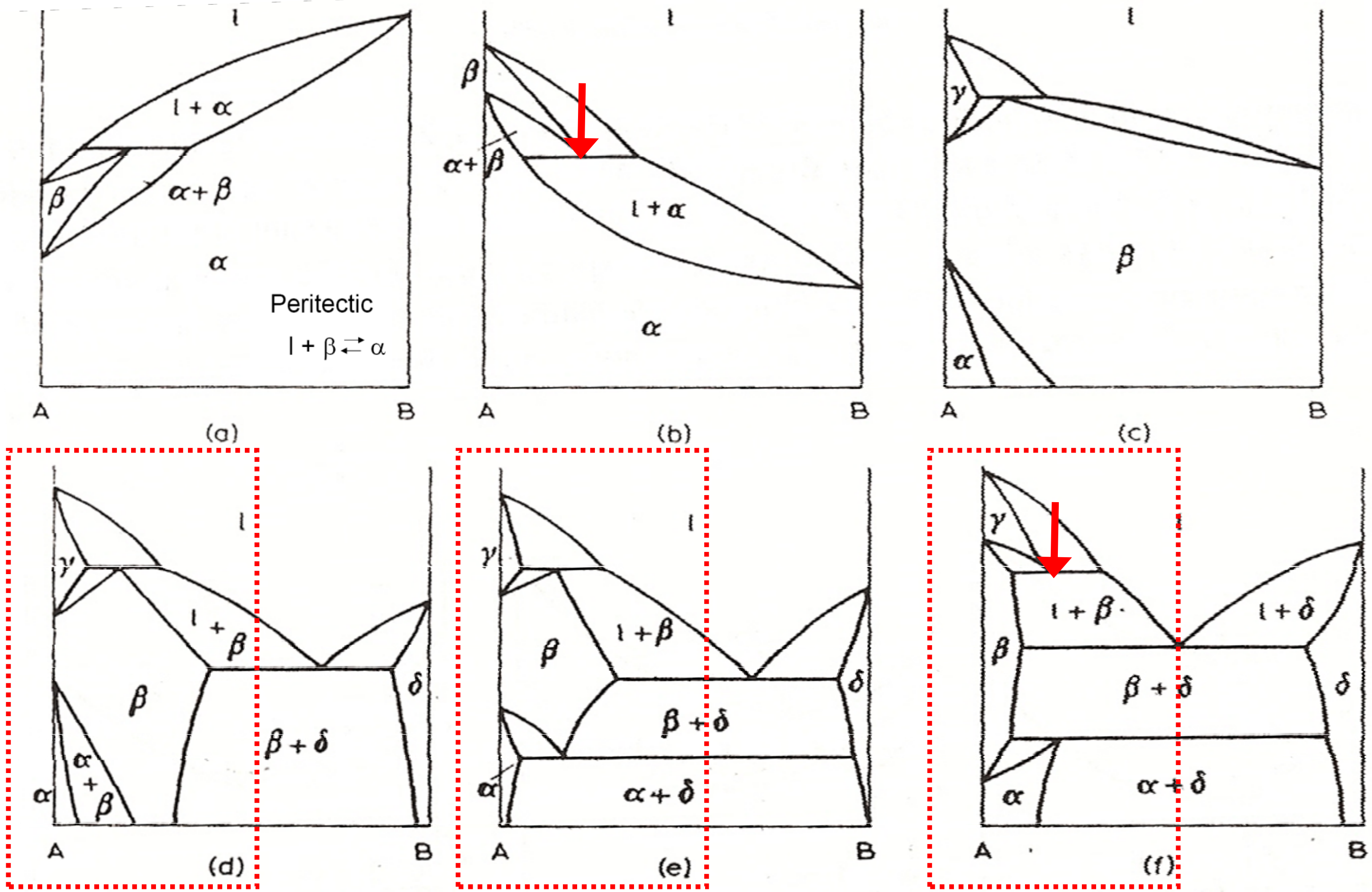


Fig. 102. Examples of phase diagrams in which both allotropes are in equilibrium with the melt.

Metatectic reaction: β ↔ L + α   **Ex. Co-Os, Co-Re and Co-Ru**

Metatectic reaction: β ↔ L + α   Ex. Co-Os, Co-Re and Co-Ru

(Both α and β are allotropes of A)

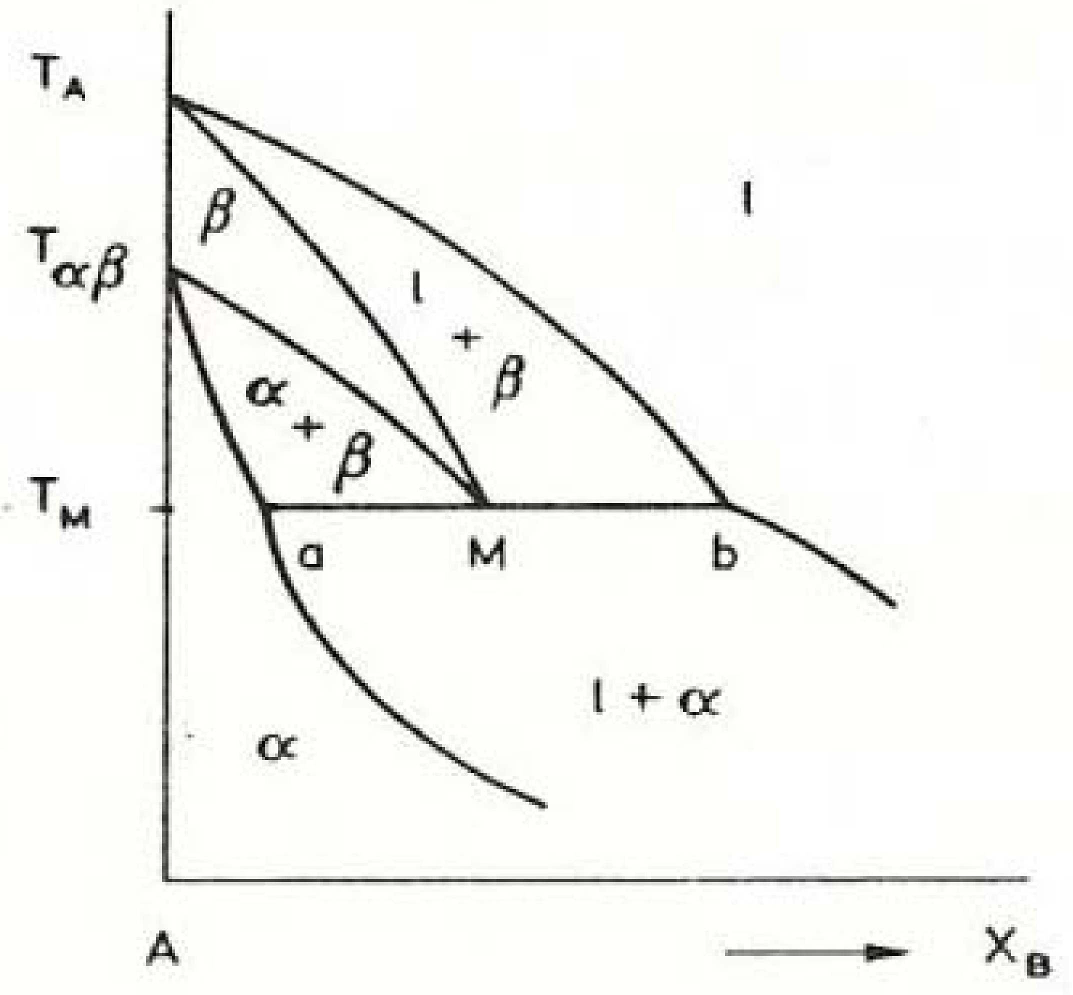


Fig. 103. The metatectic reaction.

Metatectic reaction: β ↔ L + α   Ex. Co-Os, Co-Re and Co-Ru

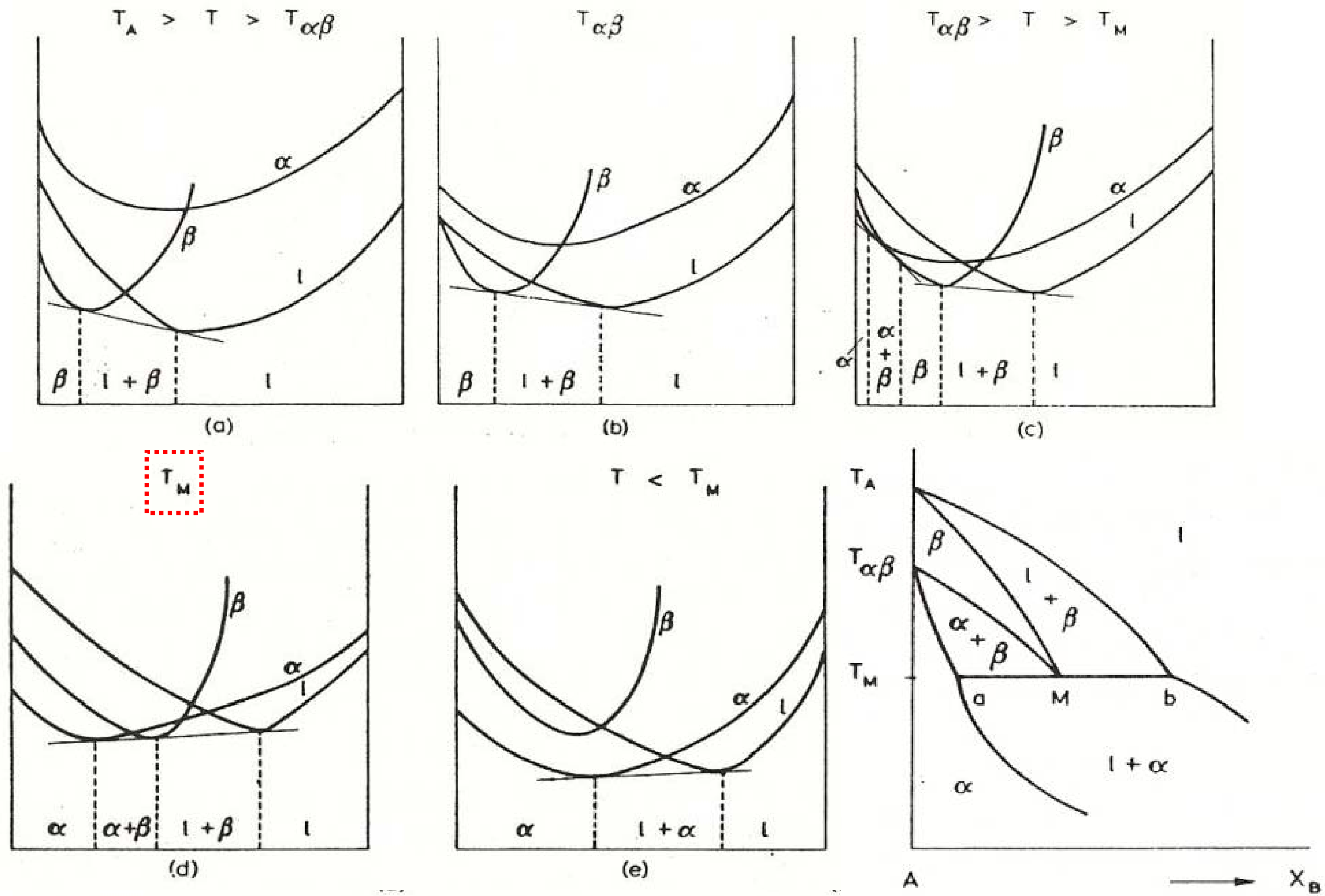
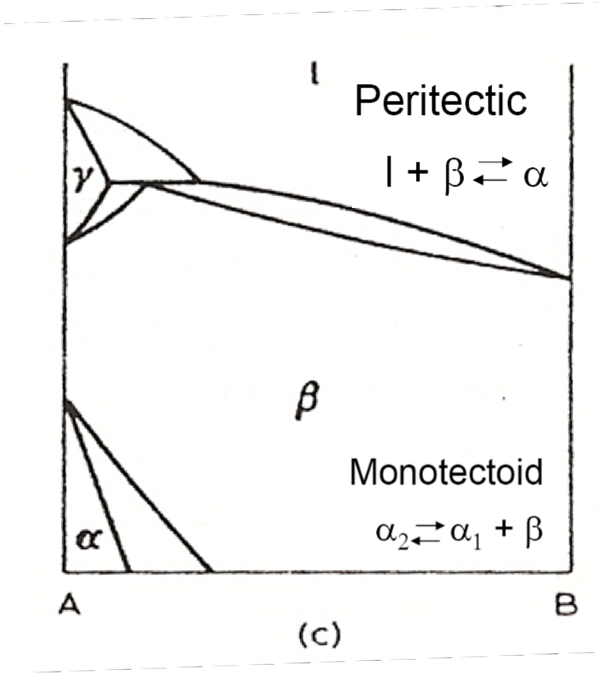
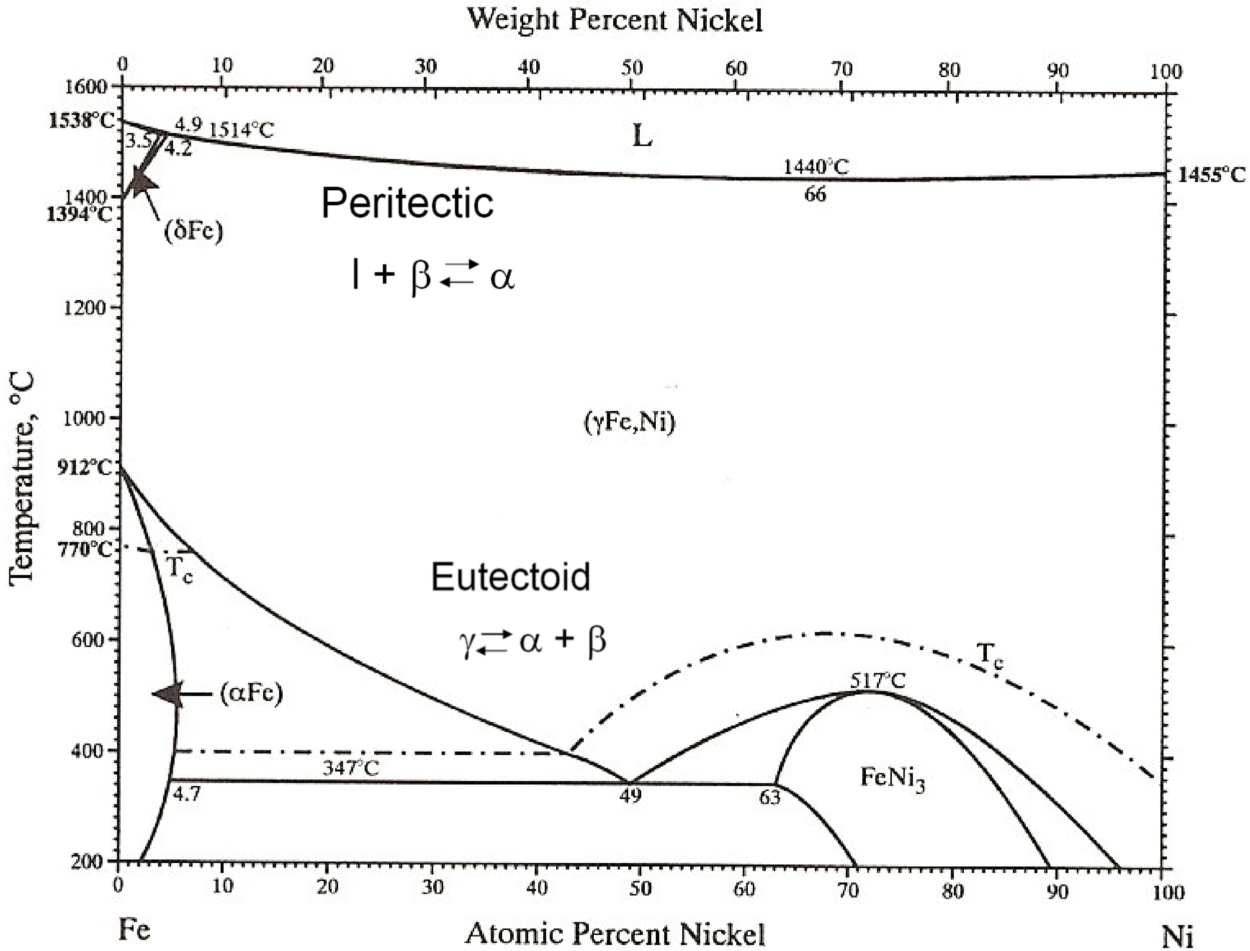


Fig. 104. Derivation of the metatectic phase diagram (Fig. 103) from the free energy curves for the liquid, α and β phases.

b. SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE

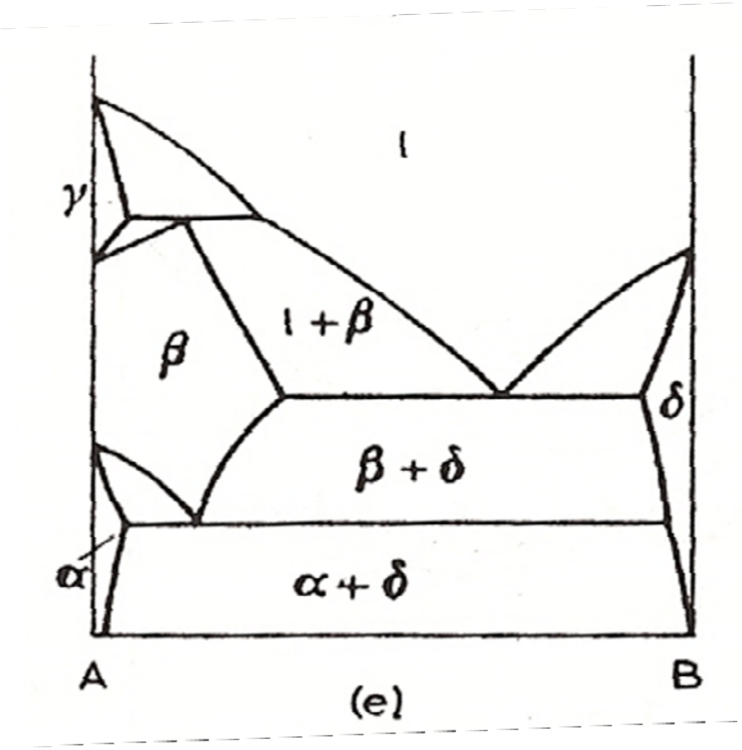
L+ α & L + β or L + β & L + γ or L + γ & L + δ

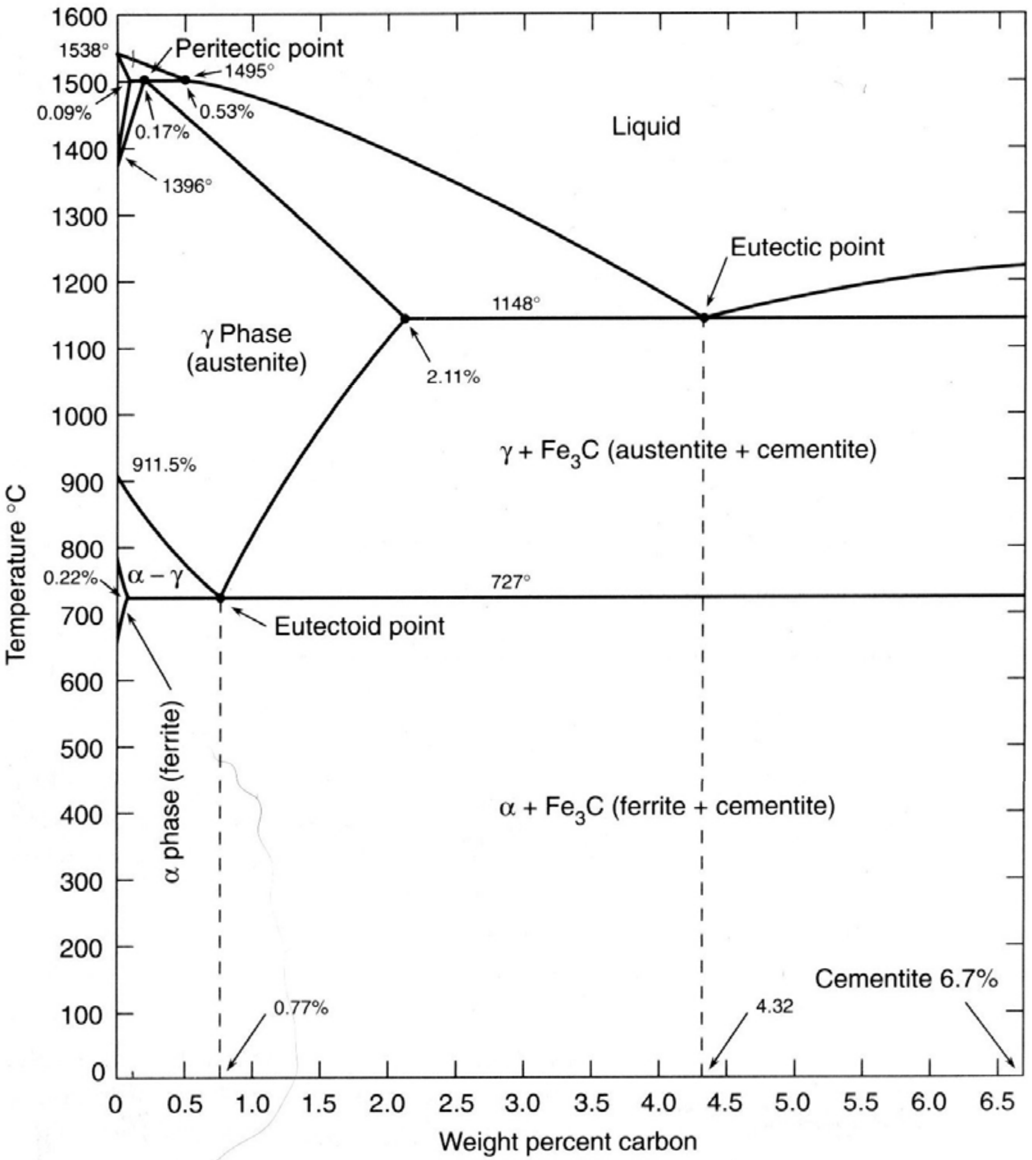




b. SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE

L+ α & L + β or L + β & L + γ



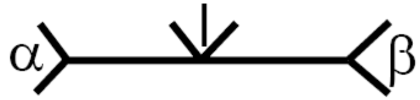


Review of Invariant Binary Reactions

Eutectic Type

Eutectic

$l \rightleftarrows \alpha + \beta$



Al-Si, Fe-C

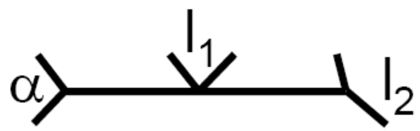
Eutectoid

$\gamma \rightleftarrows \alpha + \beta$

Fe-C

Monotectic

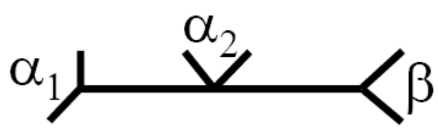
$l_1 \rightleftarrows \alpha + l_2$



Cu-Pb

Monotectoid

$\alpha_2 \rightleftarrows \alpha_1 + \beta$



Al-Zn, Ti-V

On cooling one phase going to two phases

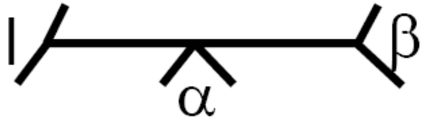
Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru**

Review of Invariant Binary Reactions

Peritectic Type

Peritectic

$l + \beta \rightleftarrows \alpha$



Fe-C

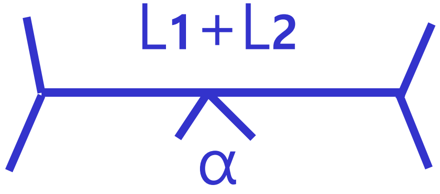
Peritectoid

$\alpha + \beta \rightleftarrows \gamma$

Cu-Al

Syntectic reaction

$Liquid_1 + Liquid_2 \leftrightarrow \alpha$



K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

On cooling two phases going to one phase

MIDTERM: **April 19 10-12 AM**

Scopes: Text ~ page 117/ Teaching note ~10

QUIZs and Homeworks

Eutectic Solidification (Kinetics)

If α is nucleated from liquid and starts to grow, what would be the composition at the interface of α/L determined?

→ rough interface (diffusion interface) & local equilibrium

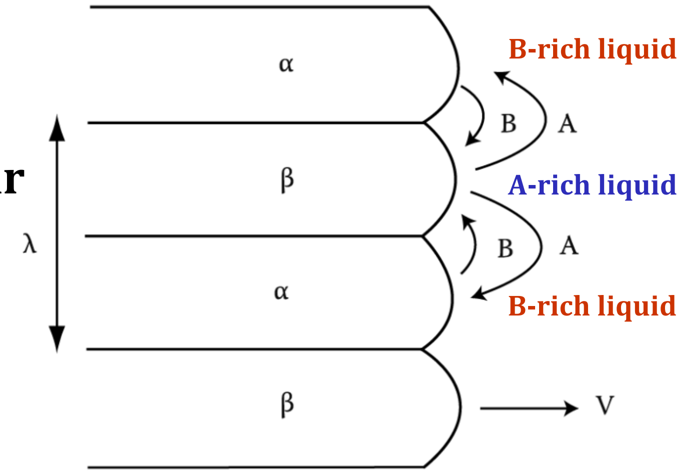
How about at β/L? Nature's choice? Lamellar structure

$\rightarrow\ G = G_{bulk} + G_{interface} = G_0 + \gamma A$

$$\sum A_i \gamma_i + \Delta G_S = minimum$$

Interface energy + Misfit strain energy

interlamellar spacing →



Eutectic solidification

: diffusion controlled process

1) $\lambda\downarrow$ → eutectic growth rate↑

but 2) $\lambda\downarrow$ → α/β interfacial E, $\gamma_{\alpha\beta}\uparrow$

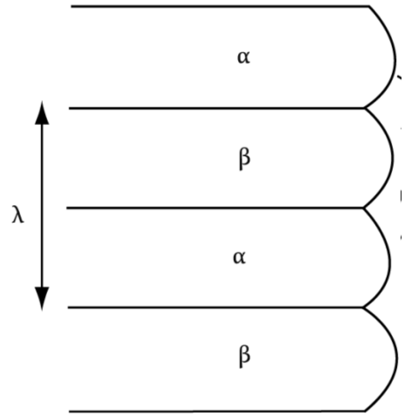
→ lower limit of λ

➡ fastest growth rate at a certain λ

What would be a role of the curvature at the tip?

→ Gibbs-Thomson Effect

Eutectic Solidification



How many α/β interfaces per unit length? $\rightarrow 1/\lambda \times 2$

For an interlamellar spacing, λ, there is a total of (2/ λ) m² of α/β interface per m³ of eutectic (단위 부피당 계면 E).

$$\Delta G = \Delta\mu \cong \frac{L\Delta T}{T_m}$$

$$\rightarrow \Delta G = \Delta\mu = \frac{2\gamma}{\lambda} \times V_m$$ Molar volume

Driving force for nucleation = interfacial E at eutectic phase

For very large values of λ, interfacial E~ 0

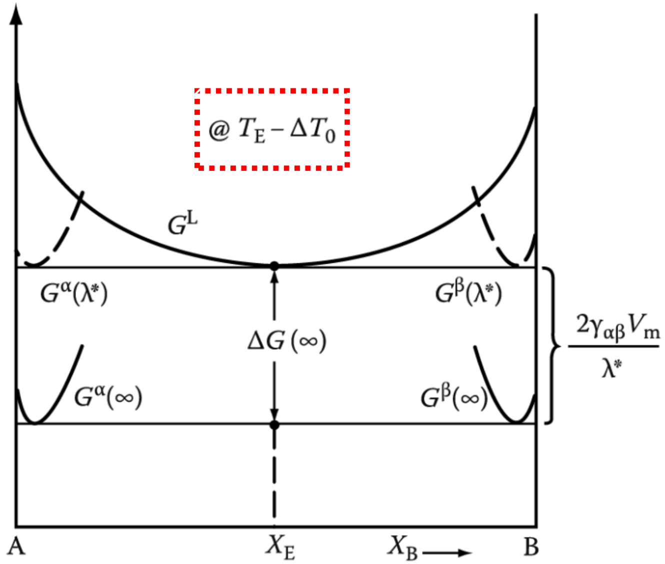
Total undercooling

$$\lambda \rightarrow \infty, \quad \Delta G(\infty) = \Delta\mu = \frac{\Delta H \Delta T_0}{T_E}$$

Interfacial E term

$$\Delta G(\lambda) = ? = -\Delta G(\infty) + \frac{2\gamma V_m}{\lambda}$$

Solidification will take place if ΔG is negative (-).



What would be the minimum λ?

Critical spacing, $\lambda^* : \Delta G(\lambda^*) = 0$

최소 층상 간격

$$\Delta G(\infty) = \frac{2\gamma V_m}{\lambda^*} \qquad \lambda^* = +\frac{2T_E\gamma V_m}{\Delta H \Delta T_0}$$

$$\lambda^* = +\frac{2T_E \gamma V_m}{\Delta H \Delta T_0} \rightarrow \textit{identical to critical radius}$$

in pure metal

Gibbs-Thomson effect

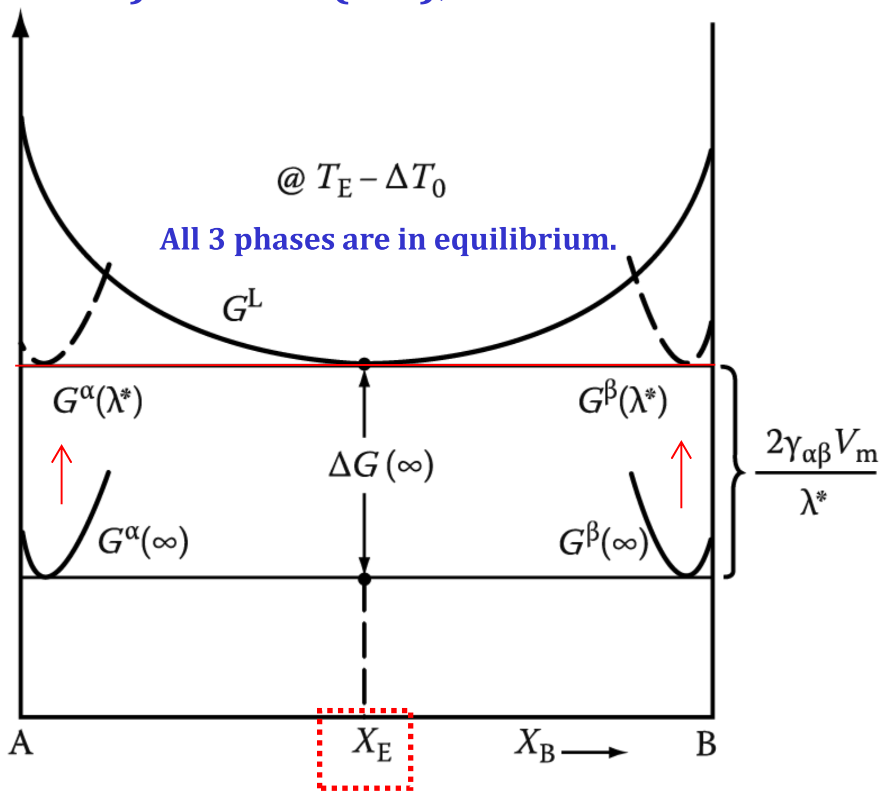
$$cf)\ r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T}$$

L_v : *latent heat per unit volume*

$L = \Delta H = H^L - H^S$

* Growth Mechanism: Gibbs-Thomson effect in a ΔG-composition diagram?

1) At λ=λ* (<∞),



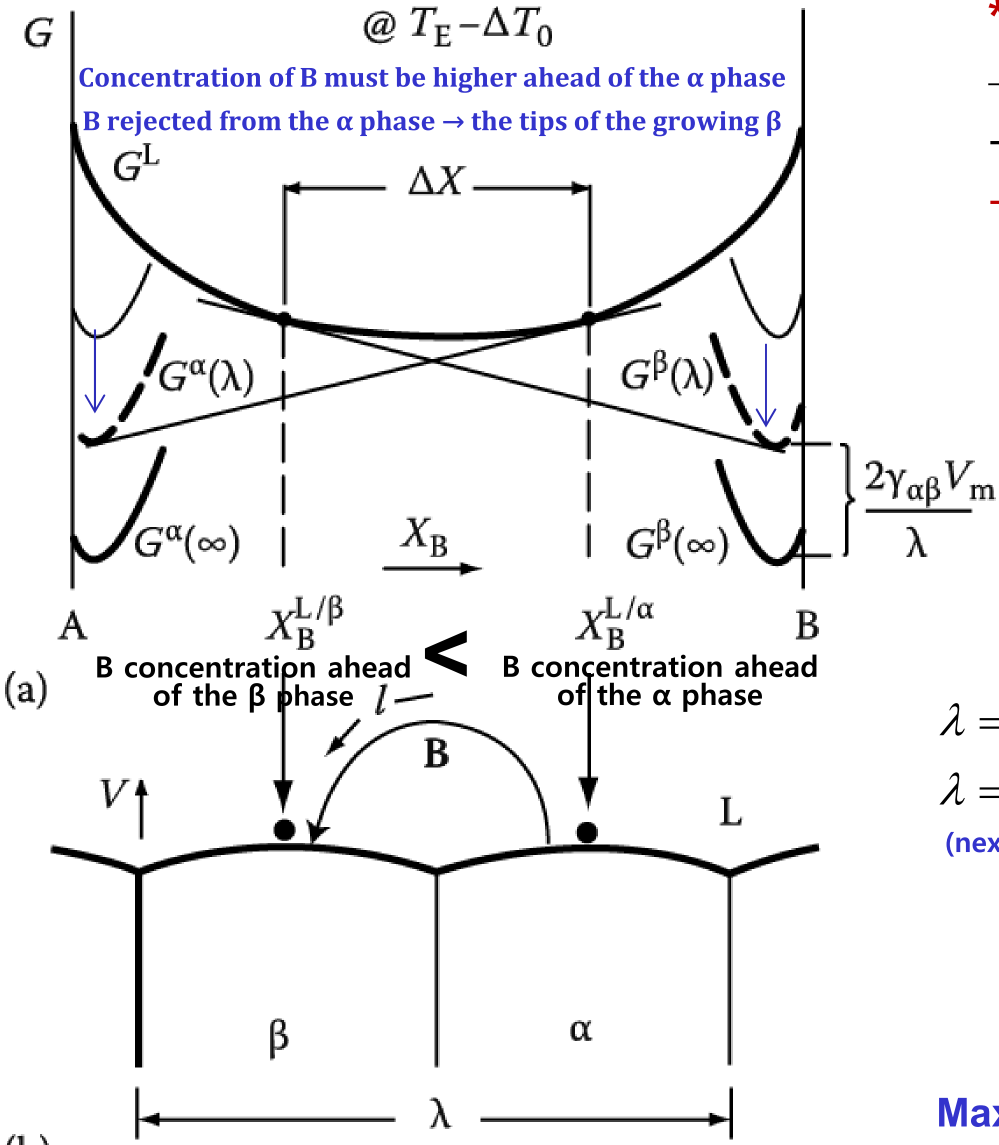
The cause of G increase is the curvature of the α/L and β/L interfaces arising from the need to balance the interfacial tensions at the α/β/L triple point, therefore the increase will be different for the two phases, but for simple cases it can be shown to be $\frac{2\gamma_{\alpha\beta}V_m}{\lambda}$ for both.

1) If λ=λ*, growth rate will be *infinitely slow* because the liquid in contact with both phases has the same composition, X_E in Figure 4.32.

2) At $\lambda = (\infty >)\ \lambda\ (> \lambda^*)$,

$\infty > \lambda > \lambda^*$, 총 계면에너지 감소로 G_α and G_β are correspondingly reduced.

$\rightarrow X_B^{L/\alpha} > X_B^{L/\beta}$



* Eutectic growth rate, v

→ if α/L and β/L interfaces are highly mobile

→ proportional to flux of solute through liquid

→ diffusion controlled process

$$v \propto D \frac{dC}{dl} \propto (X_B^{L/\alpha} - X_B^{L/\beta})$$

$\propto$ 1/effective diffusion distance.. 1/λ

$$v = k_1 D \frac{\Delta X}{\lambda}$$

$\lambda = \lambda^*, \Delta X = 0$

$\lambda = \infty, \Delta X = \Delta X_0$

(next page)

$$\Delta X = \Delta X_0 (1 - \frac{\lambda^*}{\lambda})$$

$$\Delta X_0 \propto \Delta T_0$$

$$v = k_2 D \frac{\Delta T_0}{\lambda} (1 - \frac{\lambda^*}{\lambda})$$

Maximum growth rate at a fixed $\Delta T_0 \rightarrow \lambda = 2\lambda^*$

Fig. 4.33 (a) Molar free energy diagram at $(T_E - \Delta T_0)$ for the case $\lambda^* < \lambda < \infty$, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

ΔX will it self depend on λ. ~ maximum value, ΔX_0

$$\lambda = \lambda^*, \Delta X = 0$$

$$\lambda = \infty, \Delta X = \Delta X_0$$

$$\Delta X = \Delta X_0 (1 - \frac{\lambda^*}{\lambda})$$

과냉도가 적을 경우,

$$\Delta X_0 \propto \Delta T_0$$

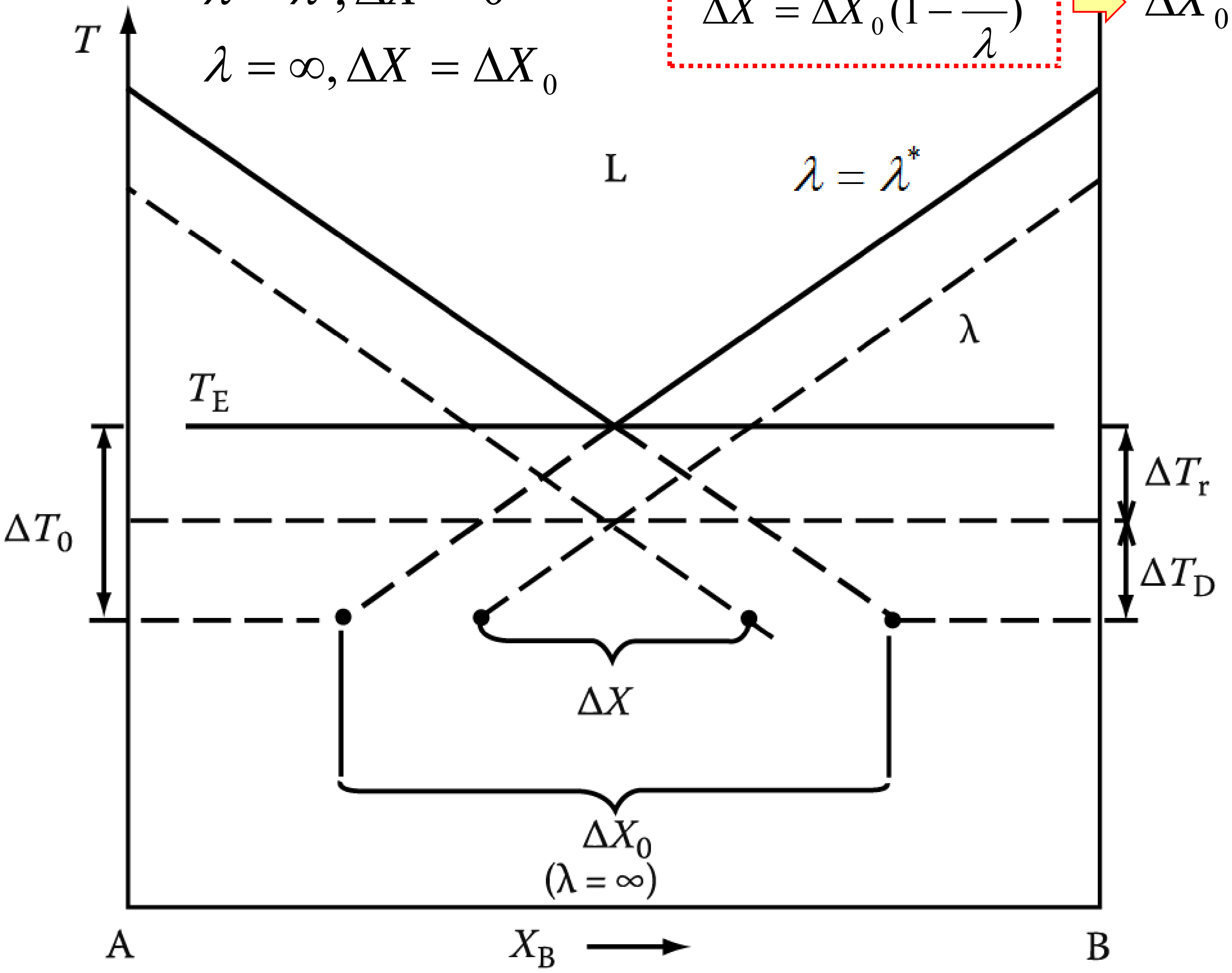


Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX_0 (exaggerated for clarity)