2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

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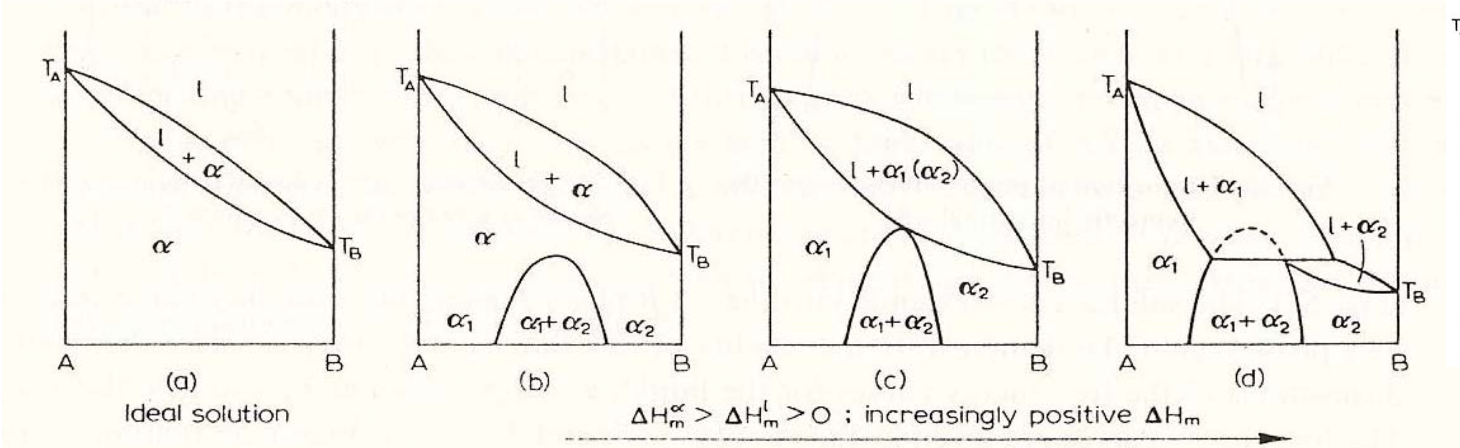
Contents for previous class

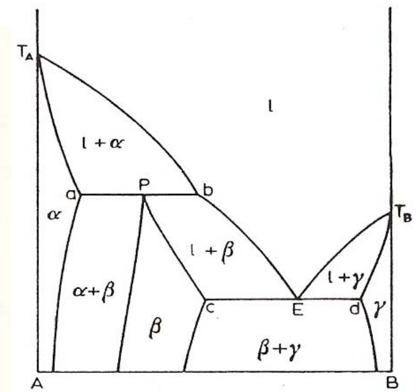
- Gibbs Phase Rule $F = C - P + 2$ (from T, P)

- Invariant reaction

$l \rightleftharpoons \alpha + \beta$	eutectic reaction	(*e.g.* Ag–Cu system)
$\gamma \rightleftharpoons \alpha + \beta$	eutectoid reaction	(*e.g.* C–Fe system)
$l_1 \rightleftharpoons \alpha + l_2$	monotectic reaction	(*e.g.* Cu–Pb system)
$\alpha \rightleftharpoons \beta + l$	metatectic reaction	(*e.g.* Ag–Li system)
$l + \alpha \rightleftharpoons \beta$	peritectic reaction	(*e.g.* Cu–Zn system)
$\alpha + \beta \rightleftharpoons \gamma$	peritectoid reaction	(*e.g.* Al–Cu system)
$l_1 + l_2 \rightleftharpoons \alpha$	syntectic reaction	(*e.g.* K–Zn system)

- Peritectic reaction



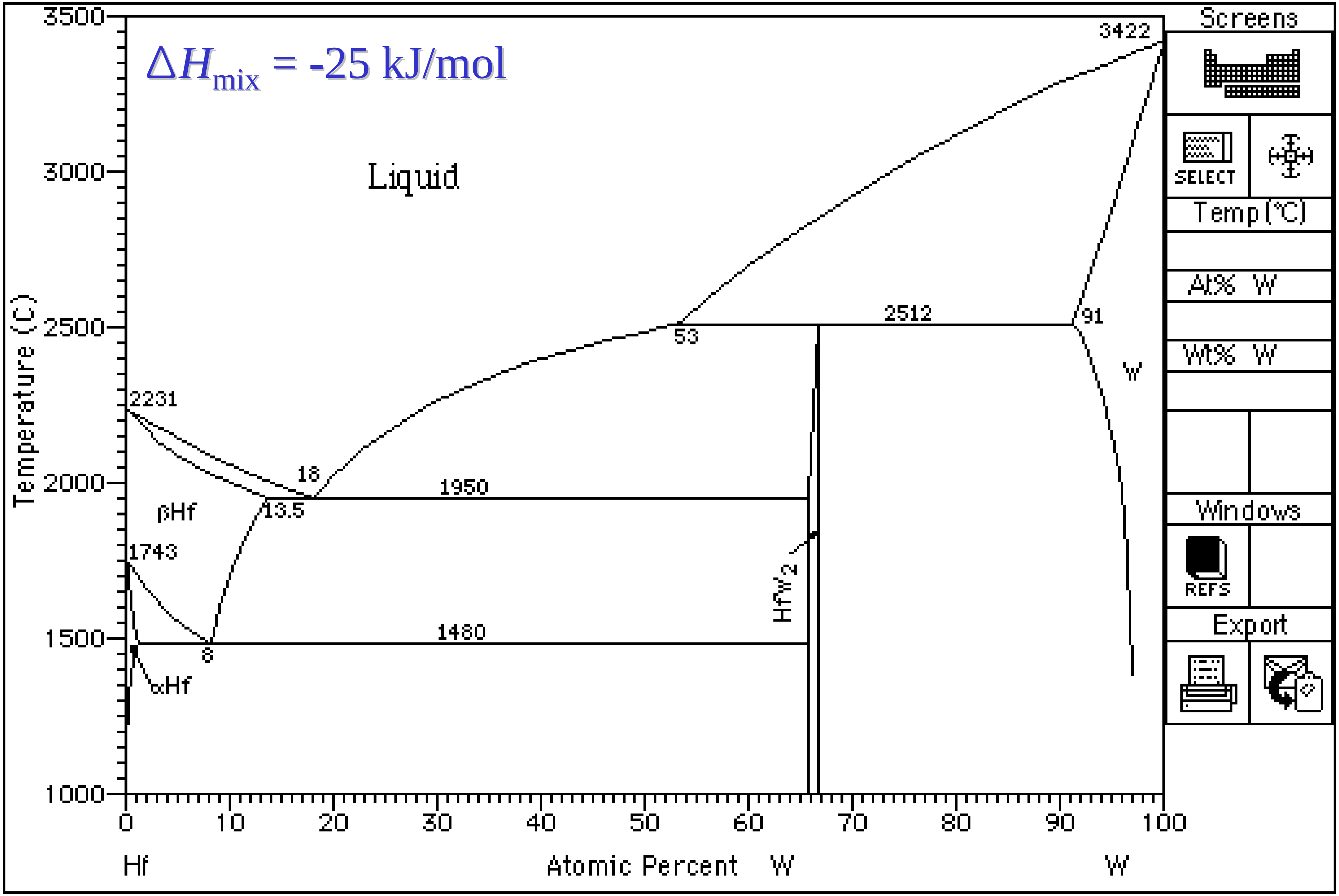


- Congruent transformation

a melting point minimum, a melting point maximum, and a critical temperature associated with a order-disorder transformation

Congruent melting : $S_{x1} \xrightarrow{\text{melting}} L_{x1}$

Incongruent melting : $S_{x1} \xrightarrow{\text{melting}} L_{x2}$



ΔH_mix = -25 kJ/mol
Liquid
3422
2512
91
53
W
2231
18
1950
βHf
13.5
1743
1480
8
αHf
HfW2
3500
3000
2500
2000
1500
1000
Temperature (C)
0
10
20
30
40
50
60
70
80
90
100
Hf
Atomic Percent W
W
Screens
SELECT
Temp (°C)
At% W
Wt% W
Windows
REFS
Export

Peritectic solidification

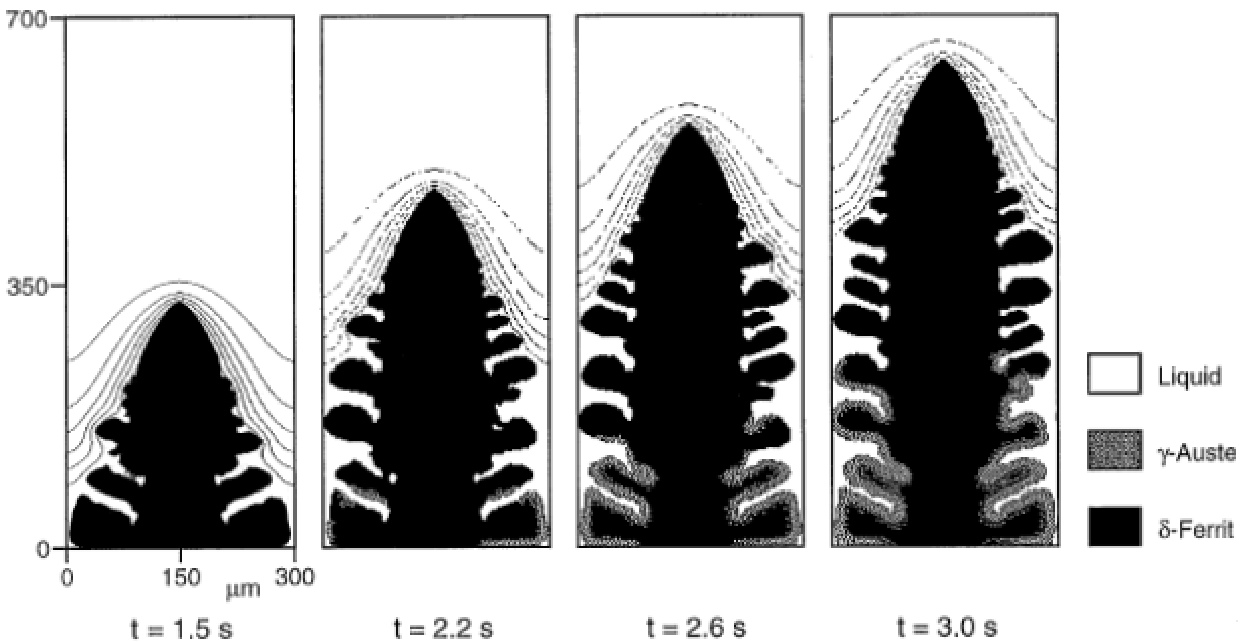
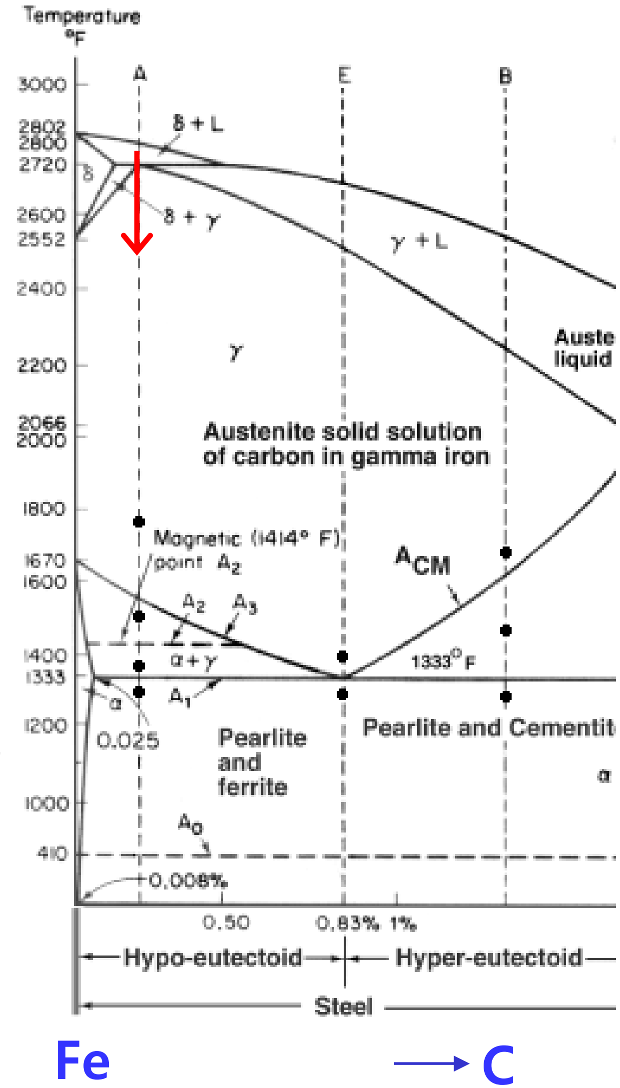


Figure 7. Phase-field simulation of peritectic reaction [3].



Peritectic solidification

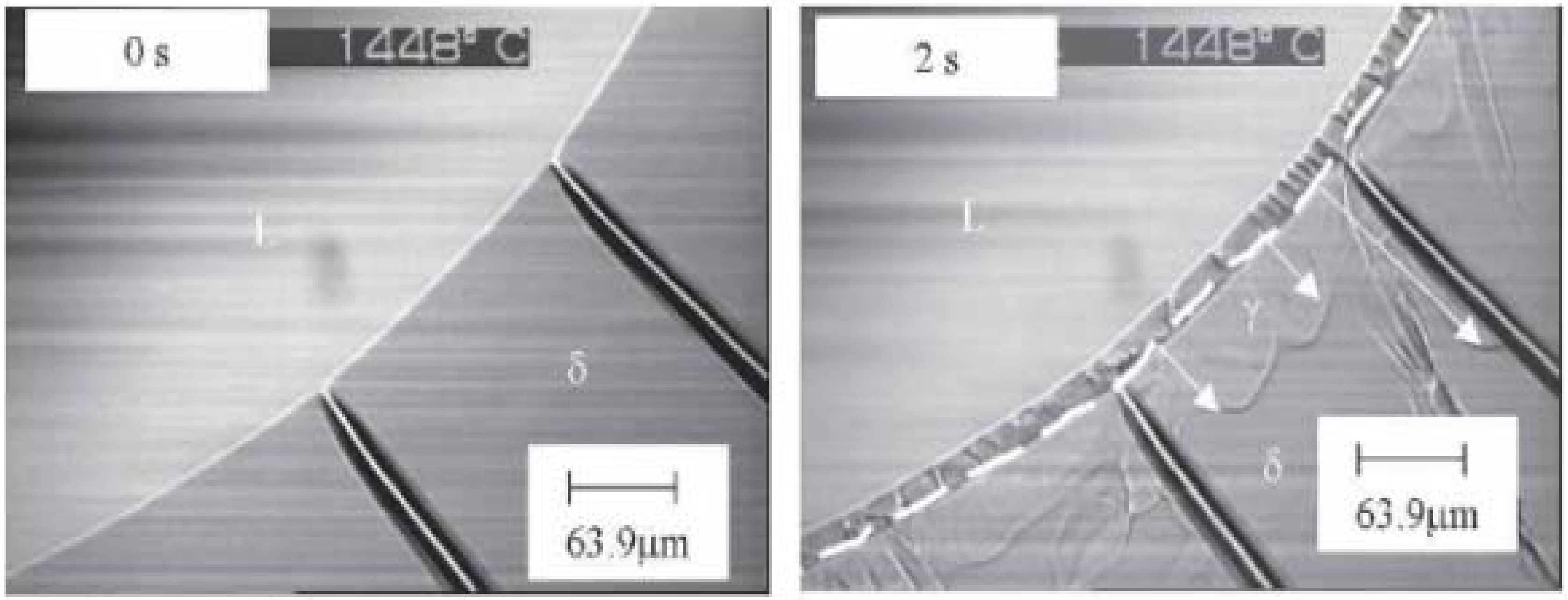


Figure 5. Peritectic reaction in Fe-0.18 pct C alloy: cooling rate =10 K/min [2].

Peritectic solidification

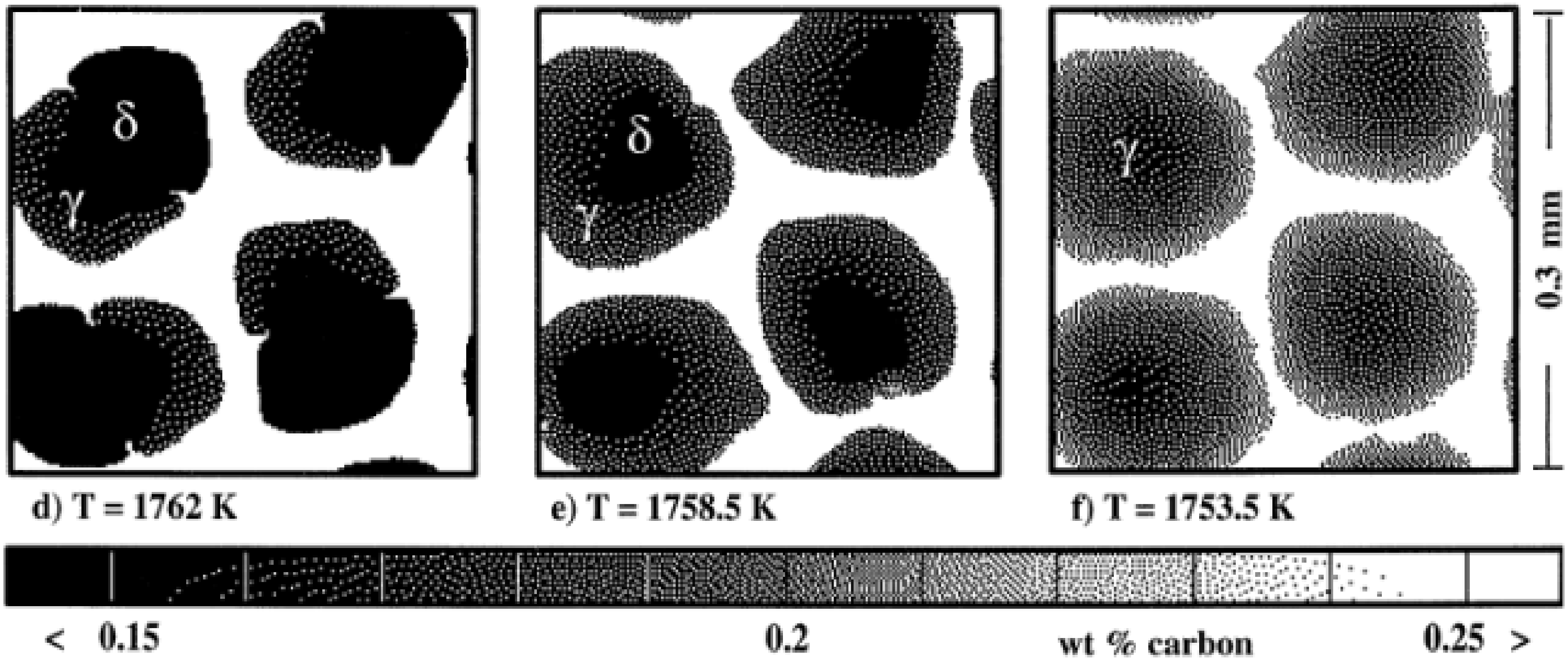


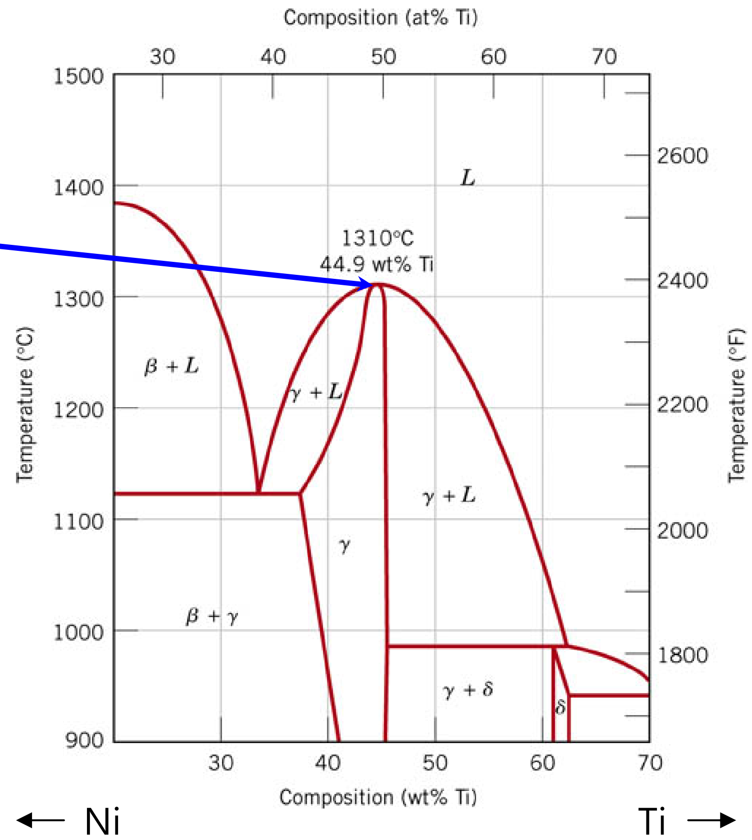
Figure 6. Phase-field simulation of peritectic reaction [3].

Congruent vs Incongruent

Congruent phase transformation: no compositional change associated with transformation

Examples:

- **Allotropic phase transformations**
- **Melting points of pure metals**
- **Congruent Melting Point**



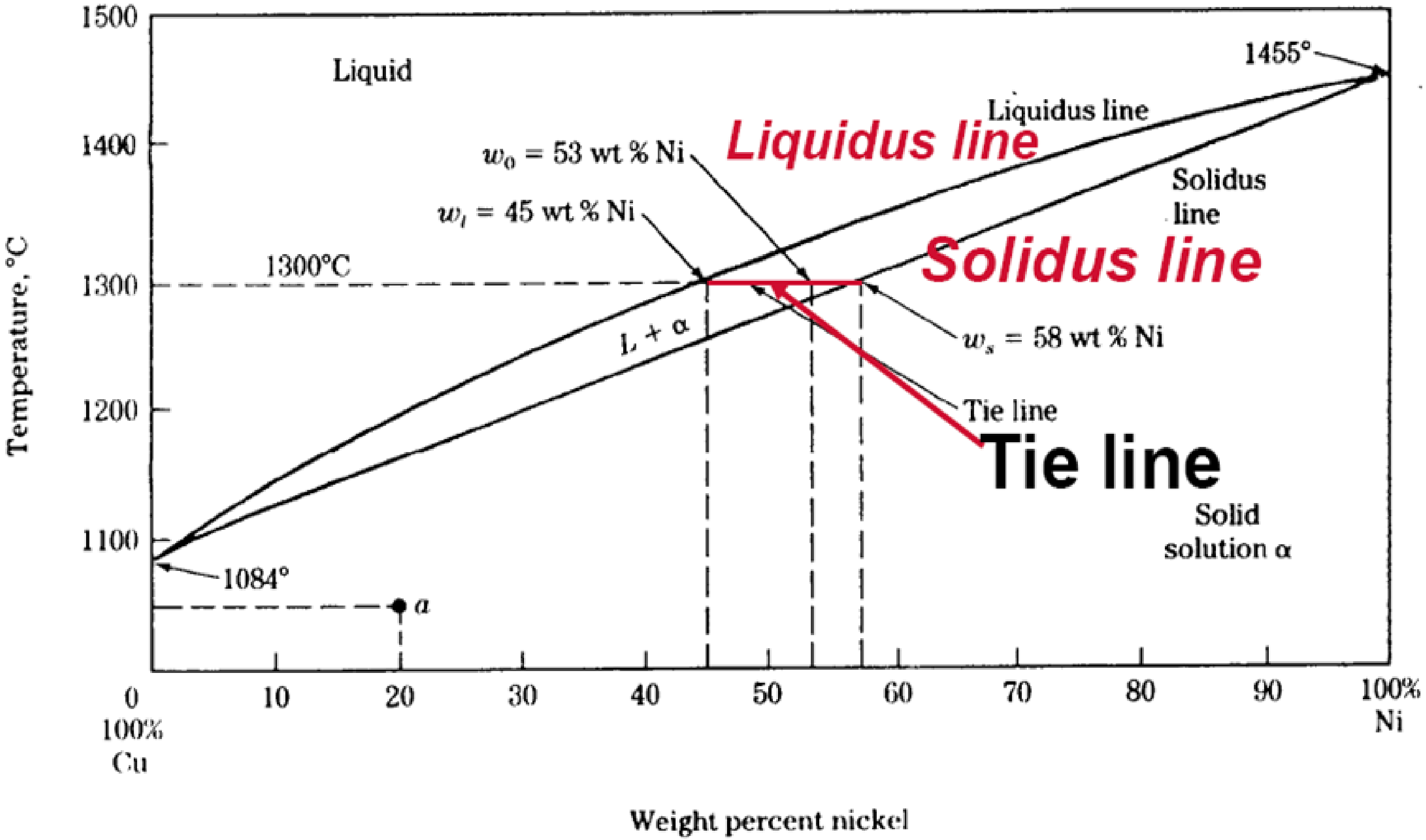
Incongruent phase transformation: at least one phase will experience change in composition

Examples:

- **Melting in isomorphous alloys**
- **Eutectic reactions**
- **Pertectic Reactions**
- **Eutectoid reactions**

Isomorphous systems contain metals which are **completely soluble** in each other and have **a single type of crystal structure.**

Cu-Ni: Binary Isomorphous Alloy Example



4.3.5. Non-stoichiometeric compounds

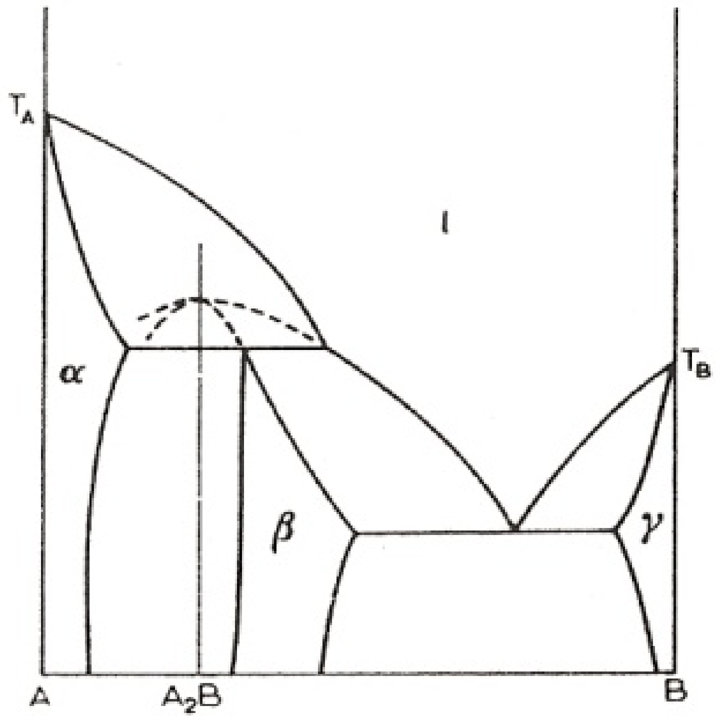


Fig. 74. A non-stoichiometric β phase based on the intermediate phase A_2B.

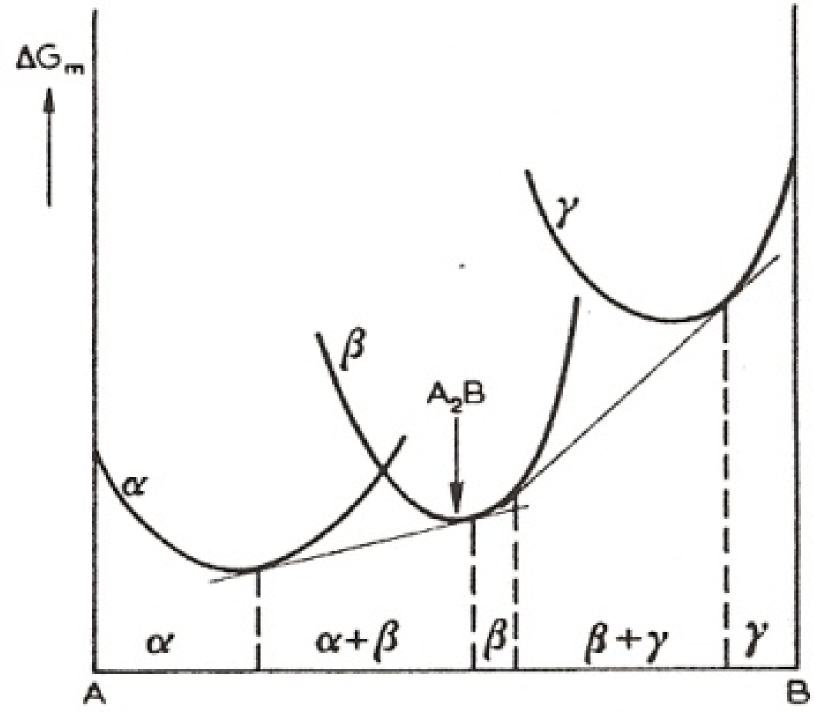
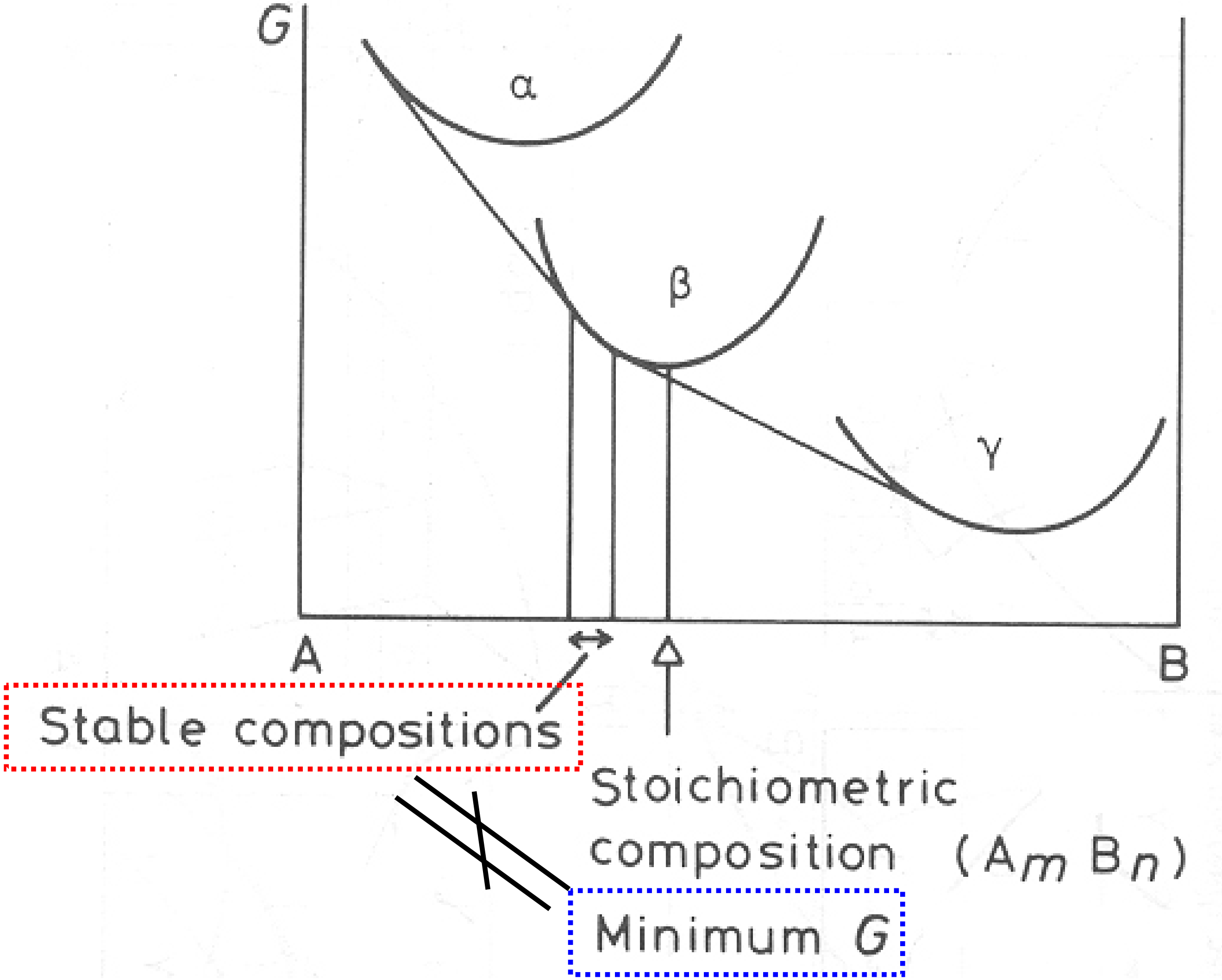


Fig. 75. Use of free energy curves to illustrate the occurrence of non-stoichiometric phases.

4.3.5. Non-stoichiometeric compounds

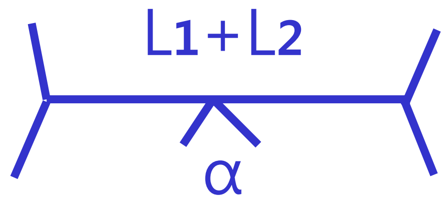


Contents for today's class

- Monotectic reaction: $Liquid_1 \leftrightarrow Liquid_2 + solid$

- Synthetic reaction:

  $Liquid_1 + Liquid_2 \leftrightarrow \alpha$



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

- Binary Phase Diagrams: Reactions in the Solid State

  * Eutectoid reaction: $\alpha \leftrightarrow \beta + \gamma$
  * Monotectoid reaction: $\alpha_1 \leftrightarrow \beta + \alpha_2$
  * Peritectoid reaction: $\alpha + \beta \leftrightarrow \gamma$

- 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

$\Delta G_m = NCX_A(1-X_A) + NkT[X_A \ln X_A + (1-X_A)\ln(1-X_A)]$ where, $C = Z[H_{AB} - (H_{AA} + H_{BB})/2.$

Here, C is an energy term, and k is bolzmann's constant (energy/temperature).

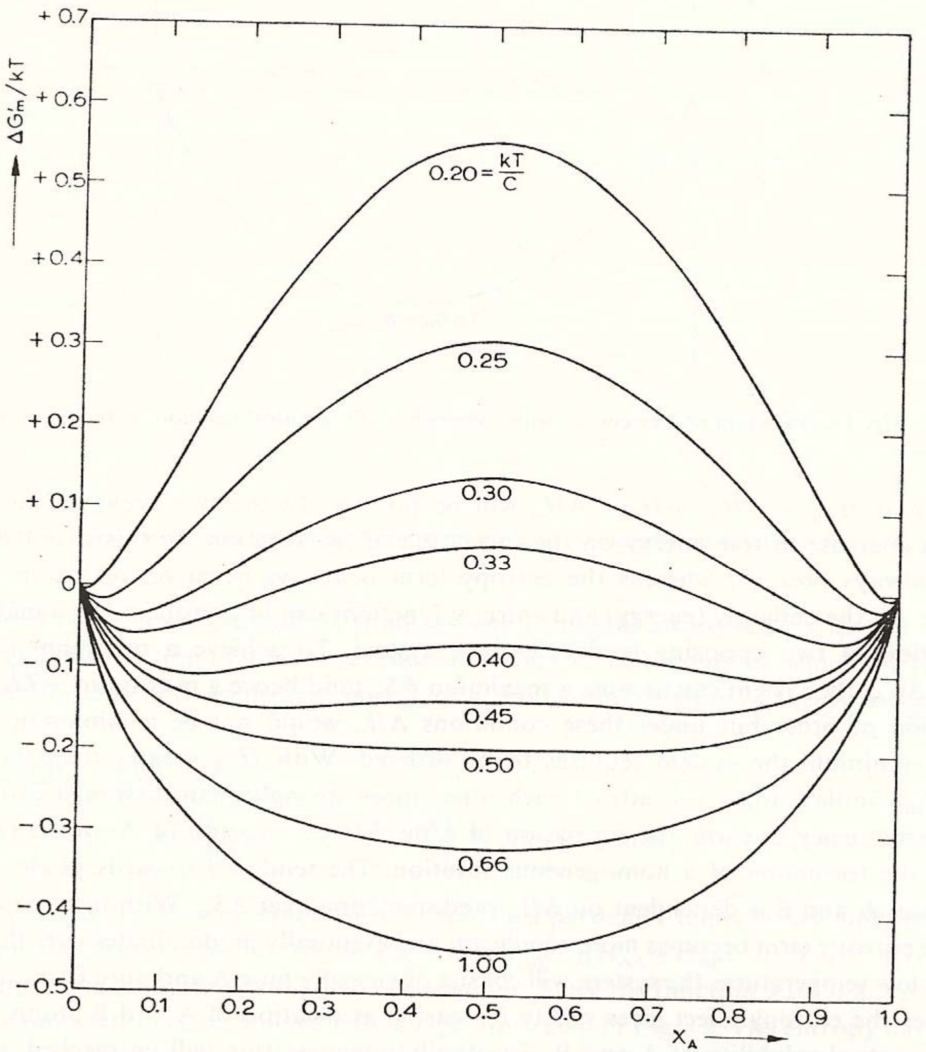
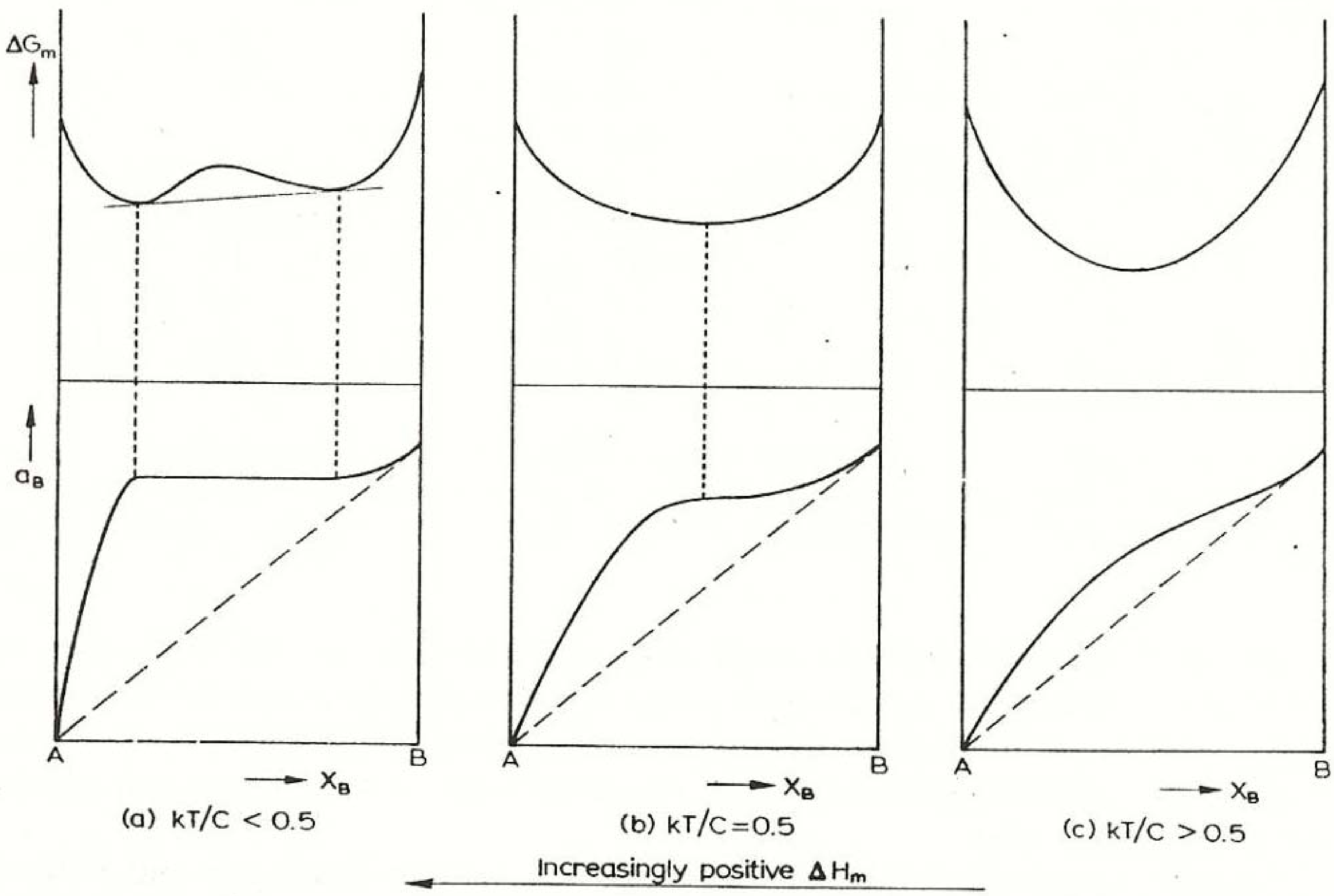
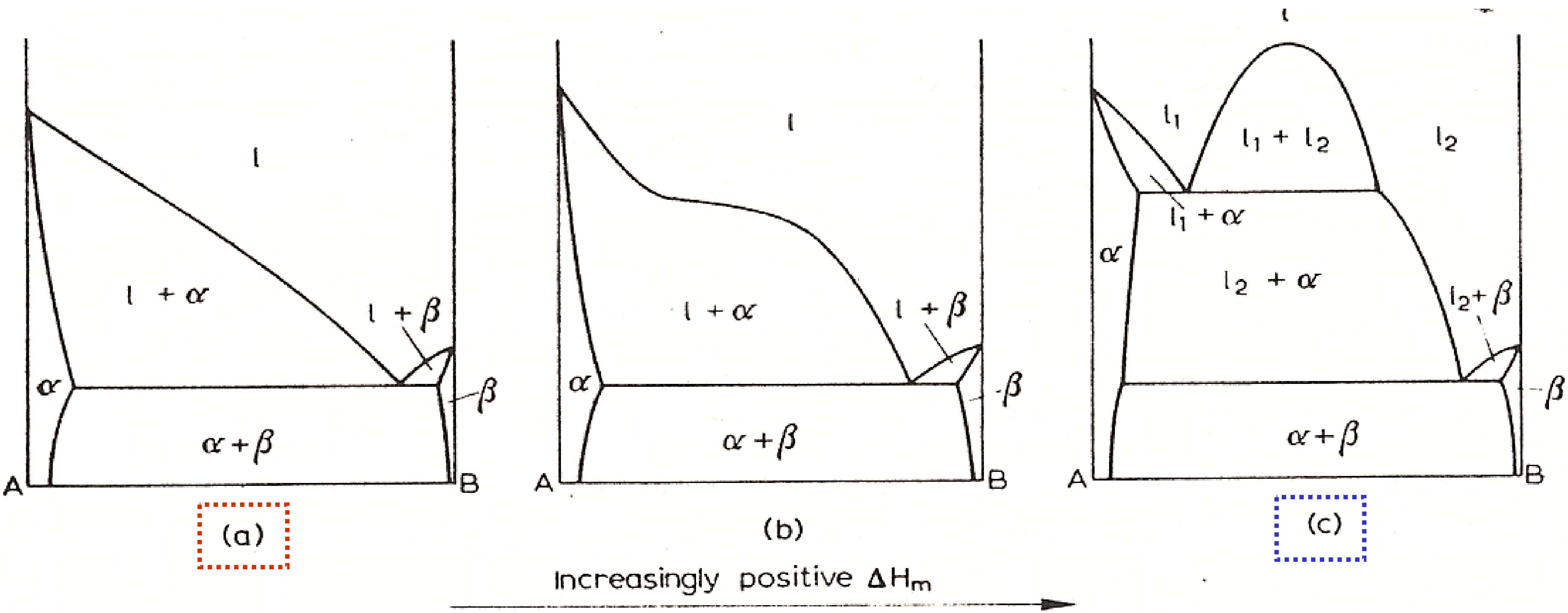


Fig. 14. Variation of free energy with composition for a homogeneous solution with $\Delta H_m > 0$. Free energy–composition curves are given for various values of the parameter kT/C.

Free energy and activity curves for (a) kT/C<0.5, (b) kT/C=0.5 (c) kT/C>0.5



Effect of very large positive deviations from ideality in changing the phase diagram from a eutectic to a monotectic reaction

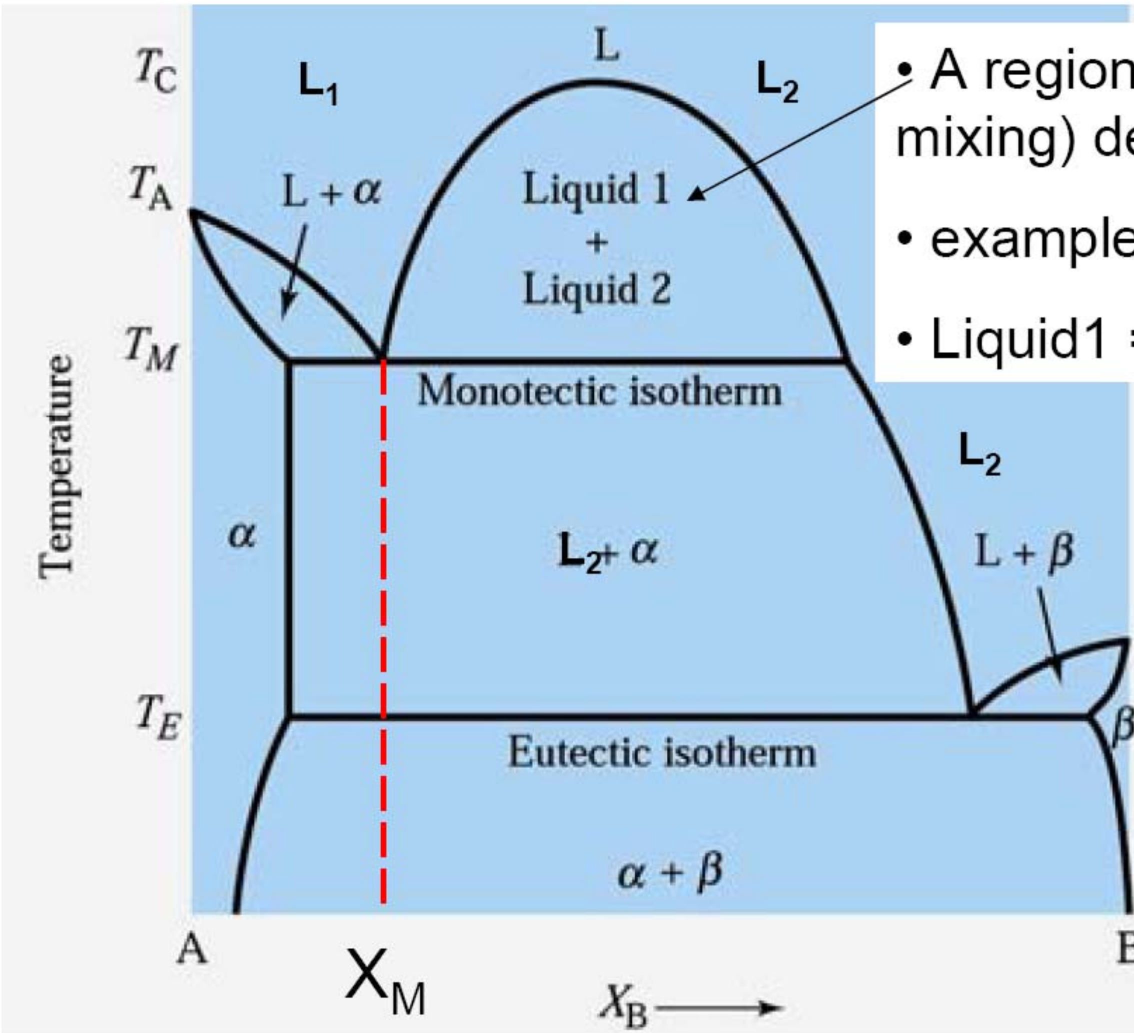


Eutectic reaction: Liquid ↔ α+β

Monotectic reaction: Liquid1 ↔ Liquid2+ solid

The reversible transition, on cooling, of a liquid to a mixture of a second liquid and a solid

Monotectic Phase Diagrams

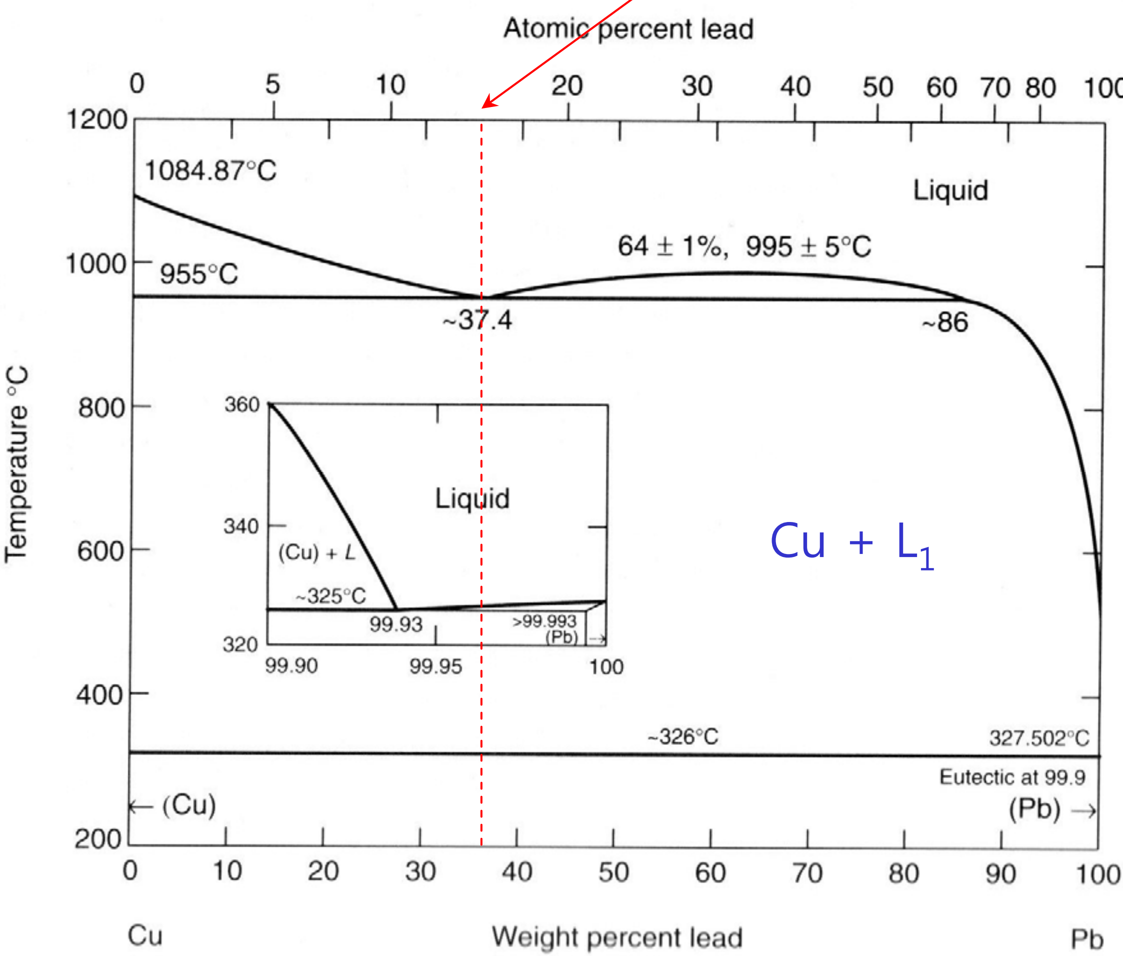


- A region of immiscibility (non-mixing) develops in the L phase
- example: oil and water
- Liquid1 = Liquid2 + α (solid)

G.A. Chadwick, Brit. J. App. Phys., 16 (1965) 1096

Monotectic

Monotectic Reaction: L $\underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}}$ L_1 + Solid



Pb and Zn do not mix in solid state:

- **RT: Cu in Pb < 0.007%**
- **RT: Pb in Cu ~ 0.002 – 0.005%**

	Crystal Structure	electroneg	*r* (nm)
Pb	FCC	1.8	0.175
Cu	FCC	1.9	0.128

26.8%

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

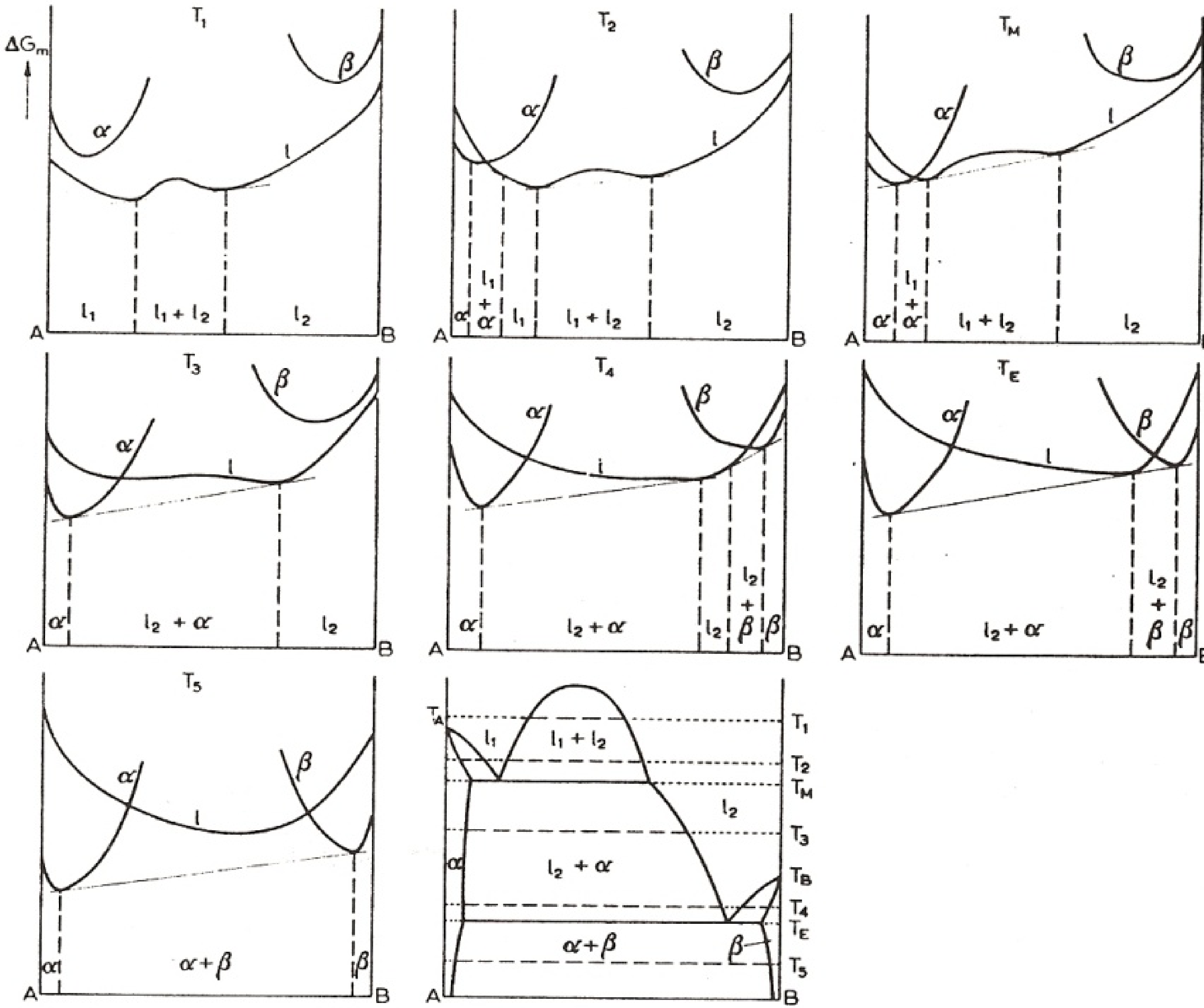


Fig. 85. Derivation of the monotectic phase diagram from the free energy curves for the liquid, α and β phases.

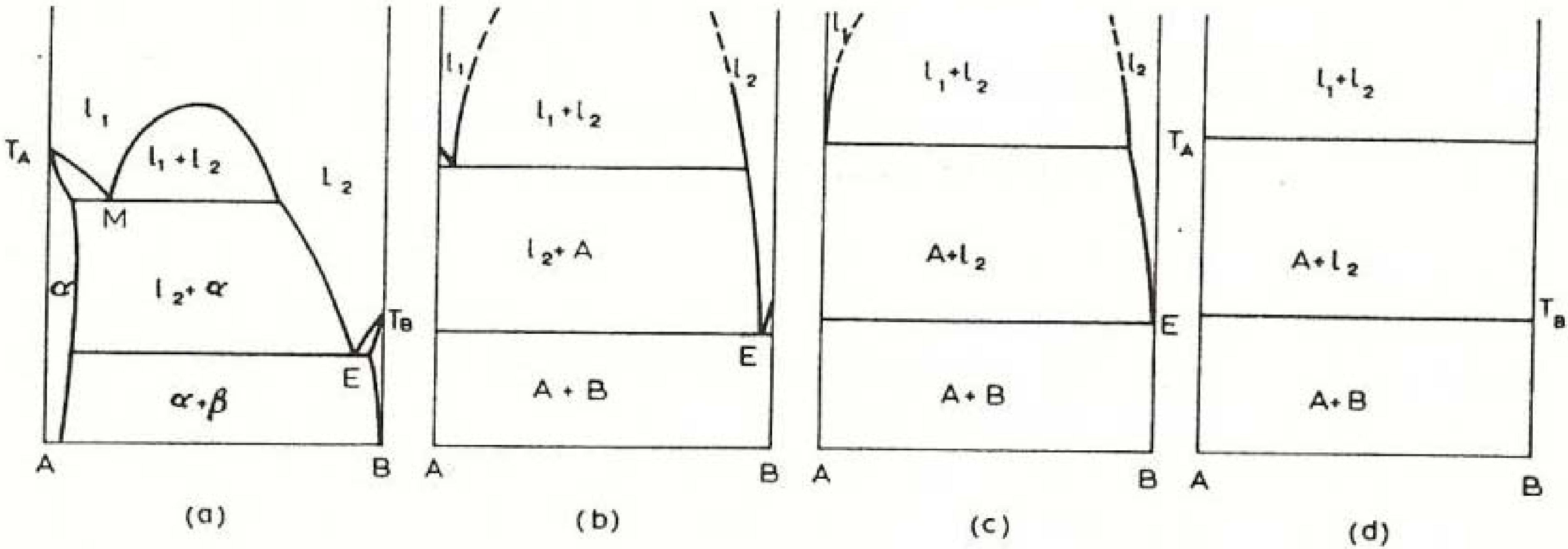
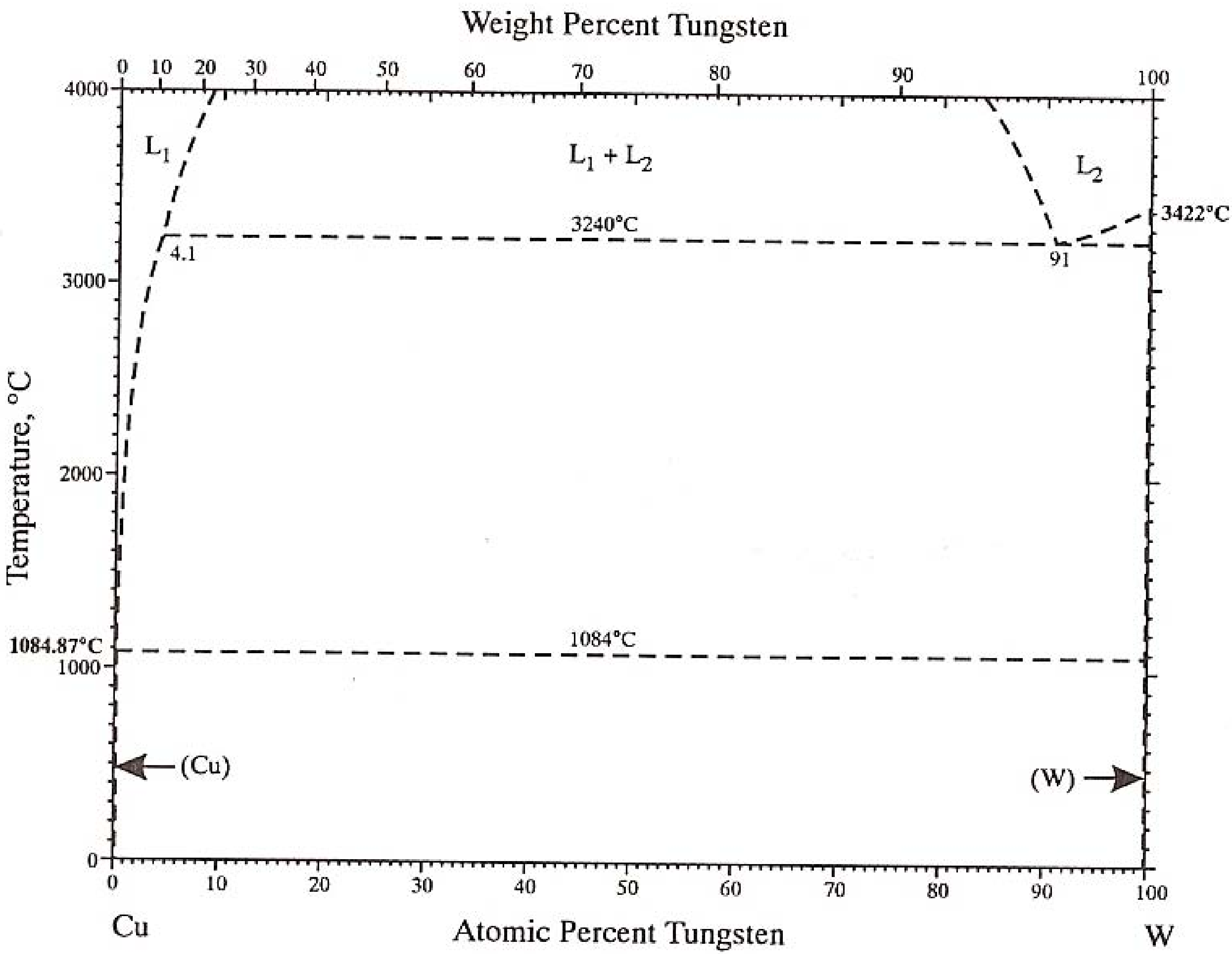


Fig. 86. Limiting form of the monotectic phase diagram.


Weight Percent Tungsten
0
10
20
30
40
50
60
70
80
90
100
4000
3000
2000
1000
0
1084.87°C
Temperature, °C
L1
L1 + L2
L2
3240°C
4.1
91
3422°C
1084°C
(Cu)
(W)
0
10
20
30
40
50
60
70
80
90
100
Cu
Atomic Percent Tungsten
W

Morphology in monotectic solidification

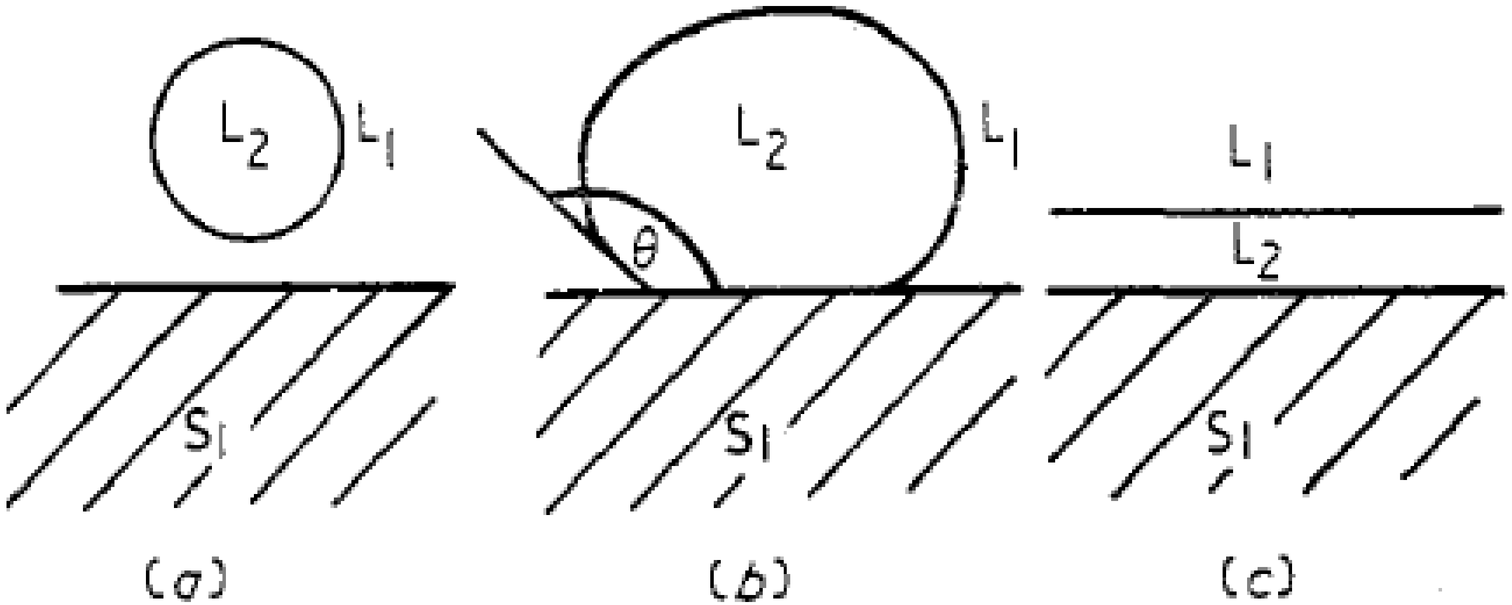
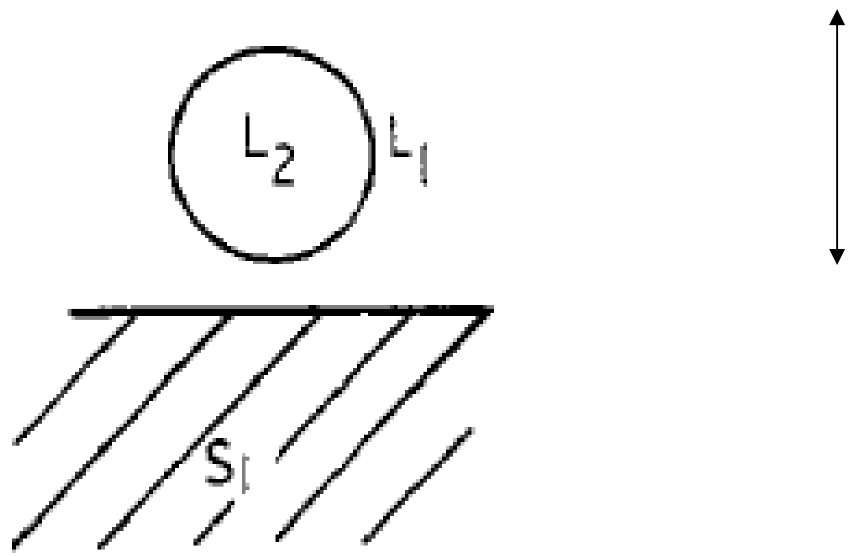


Figure 2. Solid–liquid interface morphology for different interfacial energy conditions: (*a*) $\gamma_{S_1L_2} > \gamma_{S_1L_1} + \gamma_{L_1L_2}$, (*b*) $\gamma_{S_1L_2} = \gamma_{S_1L_1} - \gamma_{L_1L_2} \cos\theta$, (*c*) $\gamma_{S_1L_1} > \gamma_{S_1L_2} + \gamma_{L_1L_2}$.

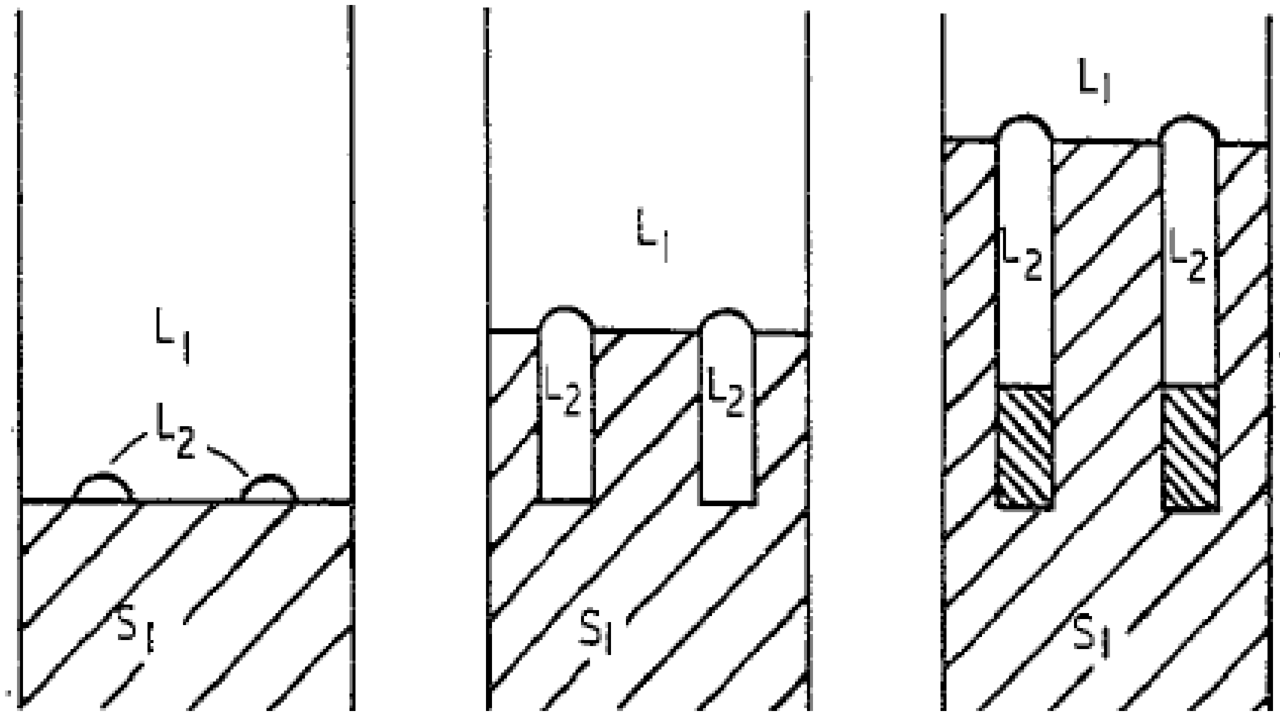
Case 1:

$$\gamma_{\alpha l_1} < \gamma_{\alpha l2} - \gamma_{l_1 l2}$$



Hg-Te single crystal

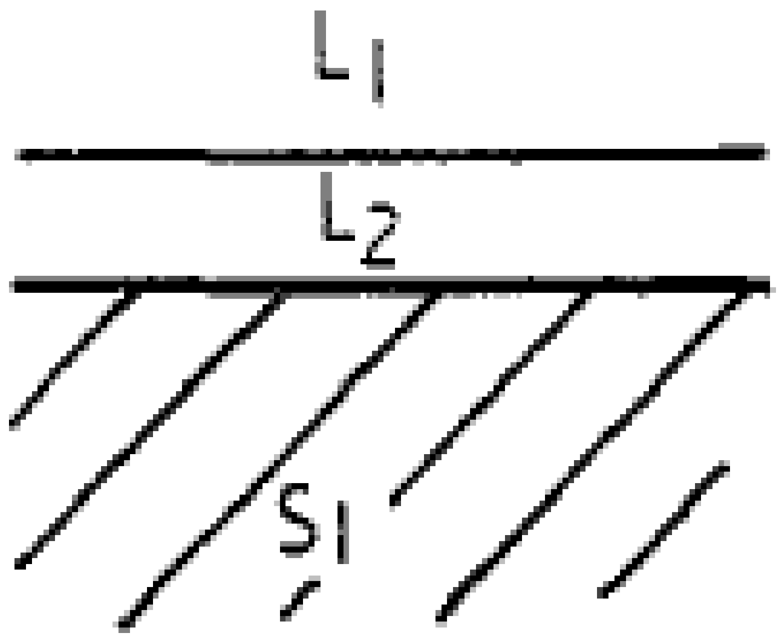
Case 2: $$\gamma_{\alpha l_1} = \gamma_{\alpha l 2} + \gamma_{l_1 l 2} \cos\theta$$



Growth mechanism of alloy of monotectic composition to produce a fibrous structure

$$\lambda \propto V^{-0.5}$$

Case 3: $\gamma_{\alpha l_1} > \gamma_{\alpha l2} + \gamma_{l_1 l2}$



Synthetic reaction

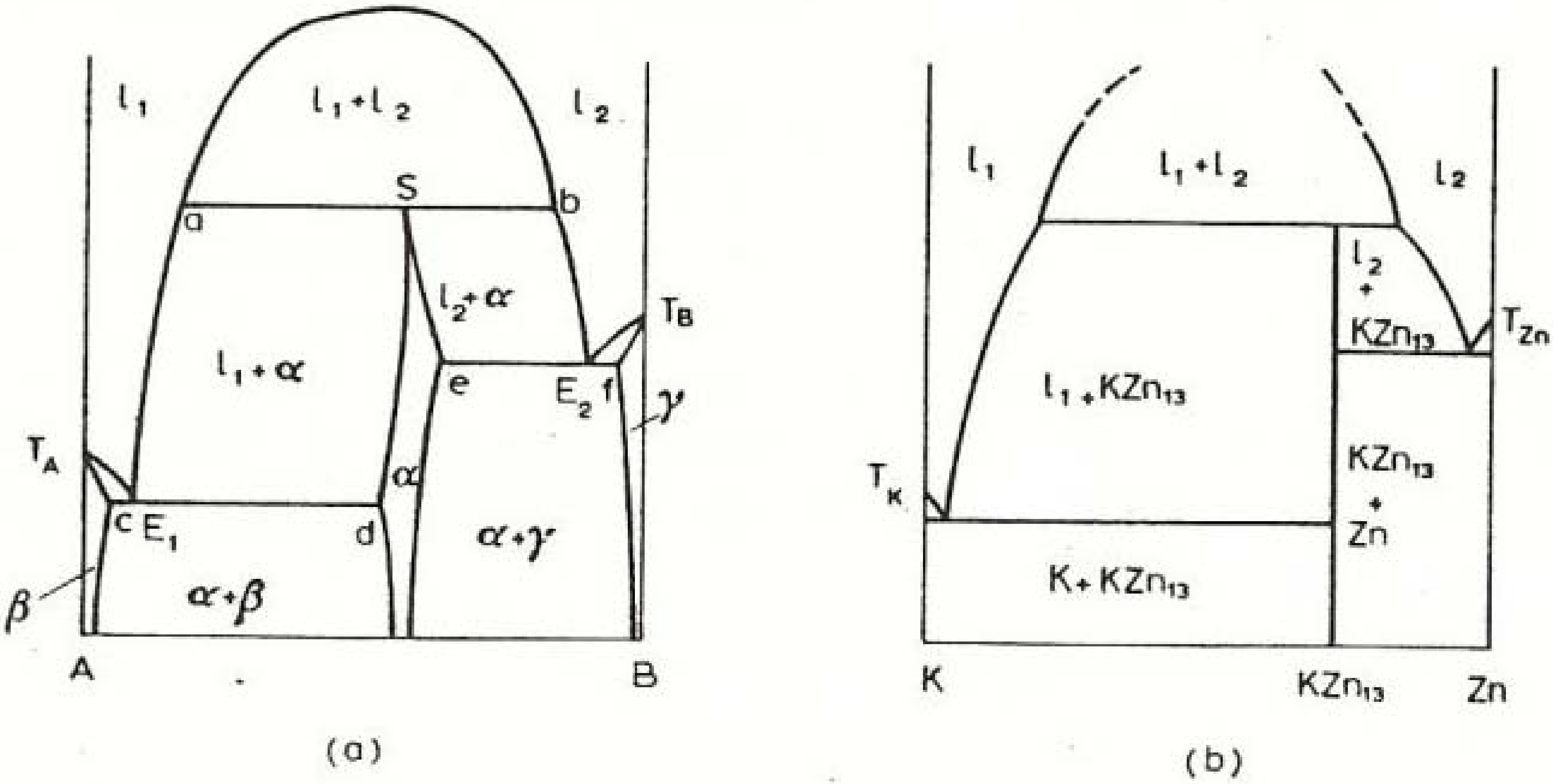


Fig. 87. Syntectic phase diagrams. (a) Schematic; (b) the K–Zn system.

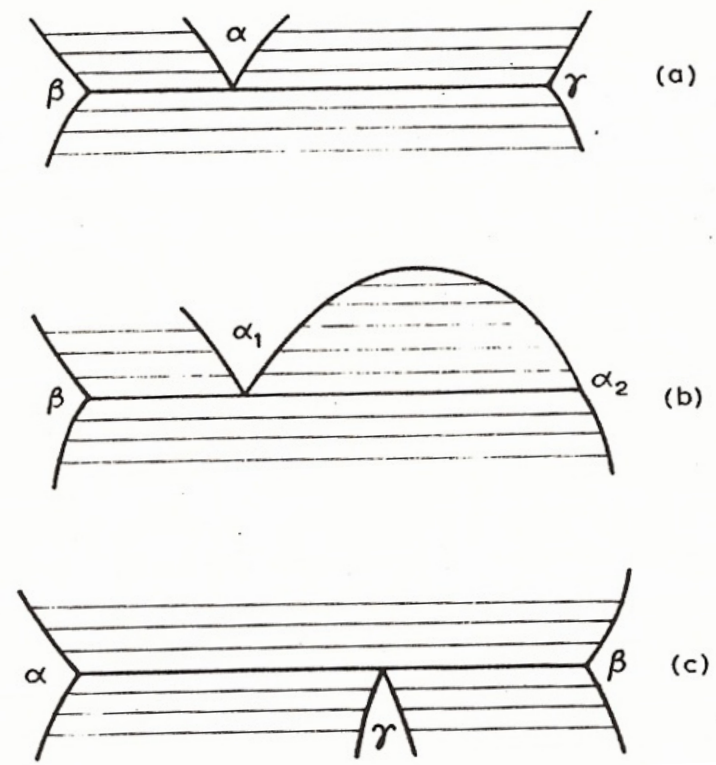
Ex. K-Zn, Na-Zn, K-Pb, Pb-U and Ca-Cd

Binary Phase Diagrams: Reactions in the Solid State

Eutectoid reaction: α ↔ β + γ

Monotectoid reaction: α1 ↔ β + α2

Peritectoid reaction: α + β ↔ γ



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

Disordered atomic arrangement at grain boundaries 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.

Iron-Carbon System

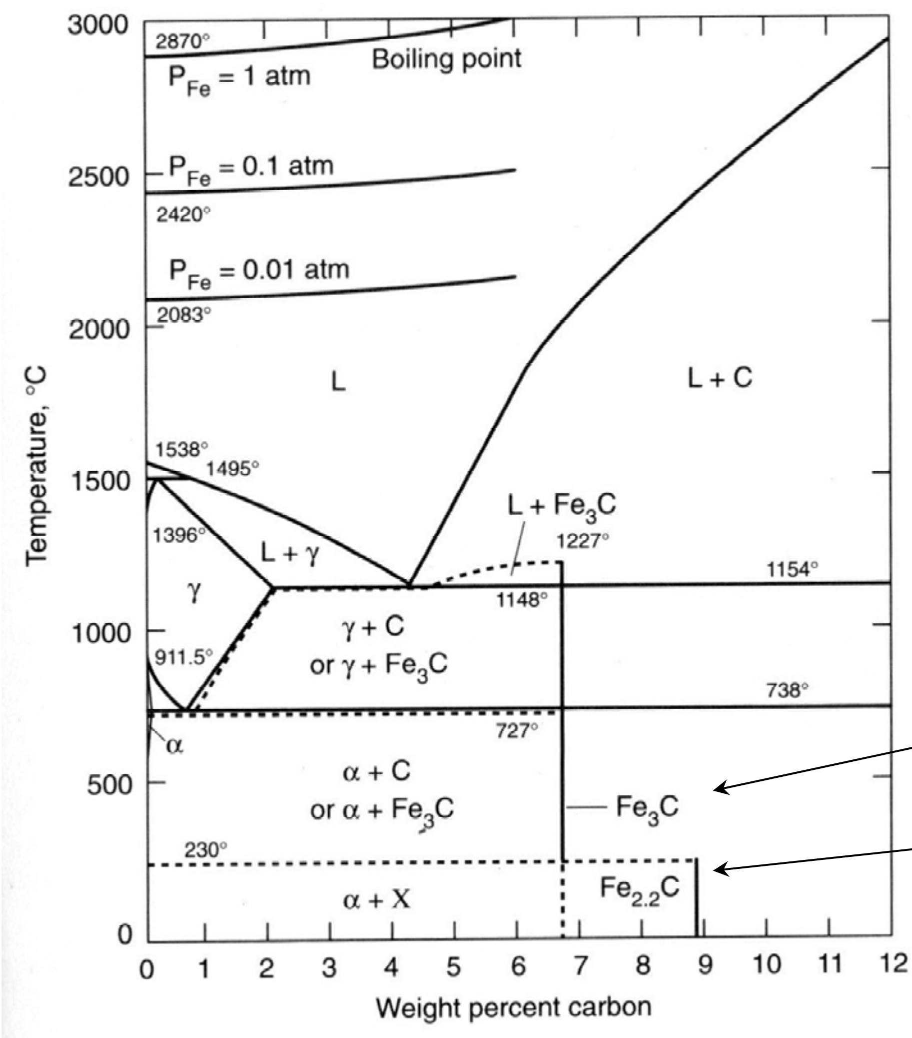


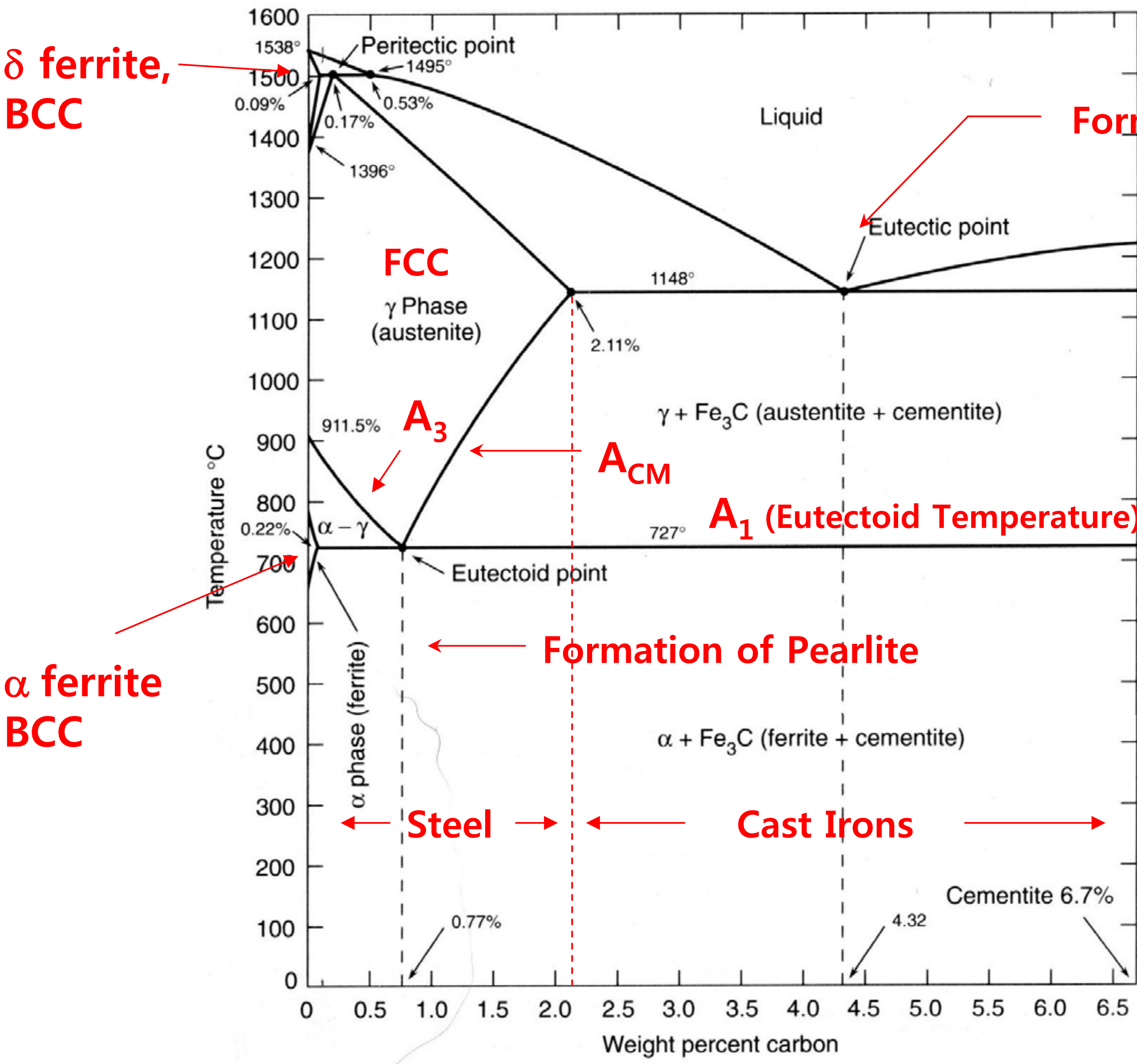
Diagram is not ever plotted past 12 wt%

Cementite

Hägg carbide

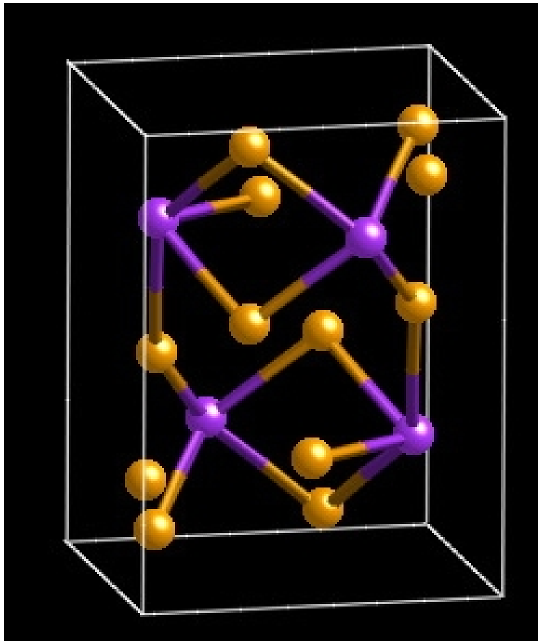
Source: Reed-Hill, Abbaschian, **Physical Metallurgy Principles, 3rd Edition**, *PWS Publishing Company*, 1994.

Iron Carbon Phase Diagram



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

Cementite – What is it?



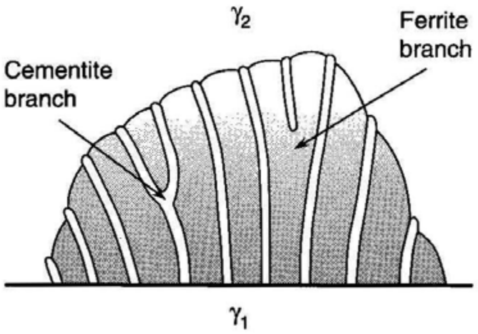
Iron Carbide – Ceramic Compound

Purple: Carbon atoms
Orange: Iron atoms

- Cementite has an orthorhombic lattice 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

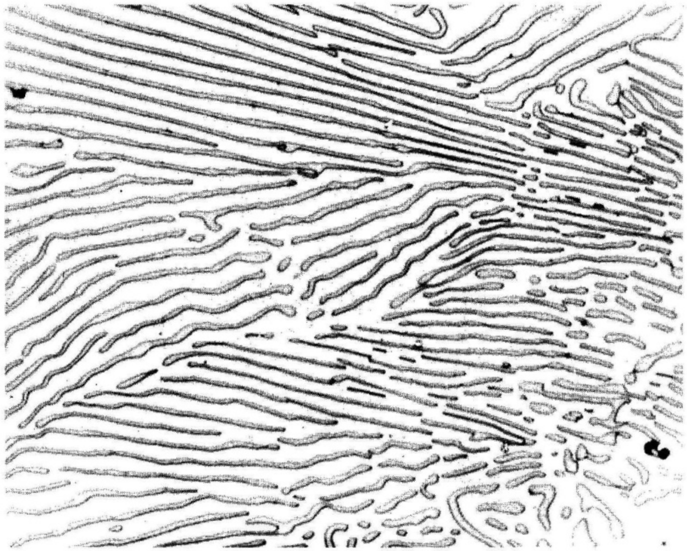


Fig. 18.6 Pearlite consists of plates of Fe_3C in a matrix of ferrite. (Vilella, J. R., *Metallographic Technique for Steel*, ASM Cleveland, 1938.) 2500X.

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**