

2019 Fall

Introduction to Materials Science and Engineering

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Contents for previous class

Chapter 11

Phase Diagrams

- **Equilibrium** $dG = 0$ **Lowest possible value of G**
No desire to change ad infinitum
- **Phase Transformation** $\Delta G = G_2 - G_1 < 0$
- * **Single component system** One element (Al, Fe), One type of molecule (H₂O)
: Equilibrium depends on **pressure** and **temperature**.
- * **Binary system (two components)** → A, B
: Equilibrium depends on not only **pressure and temperature**
but also **composition**.
- **Binary System** mixture/ solution / compound

- Solubility

- Unlimited Solubility

- Hume Rothery' Conditions

- Similar Size
 - Same Crystal Structure
 - Same Valance
 - Similar Electronegativity

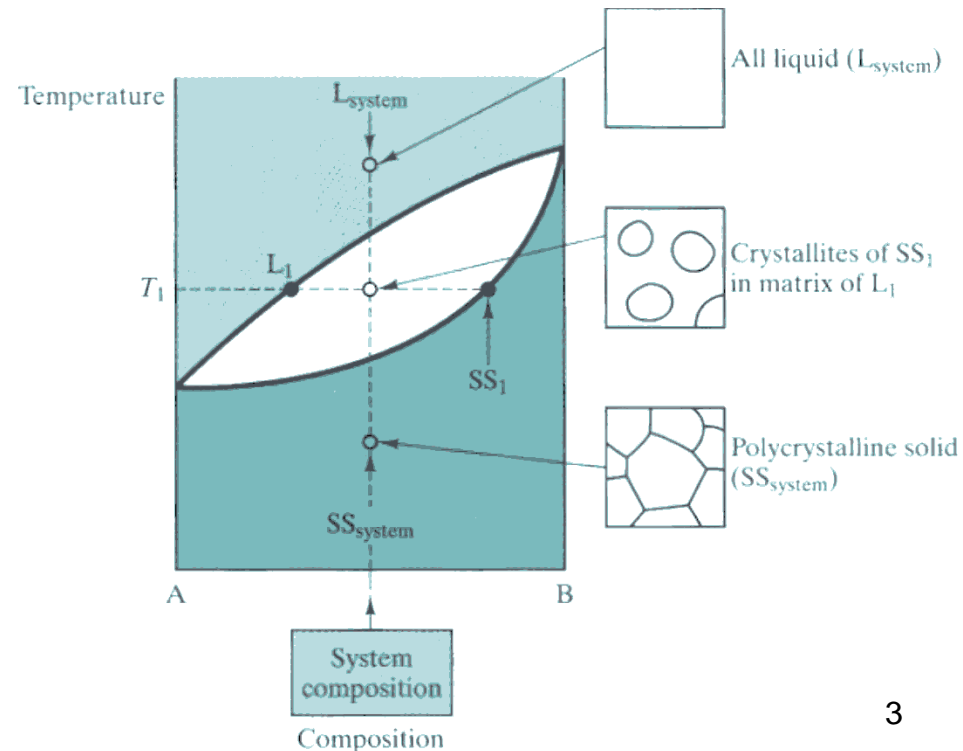
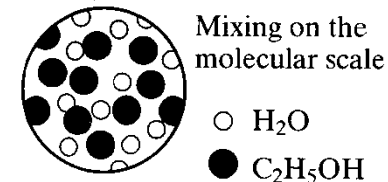
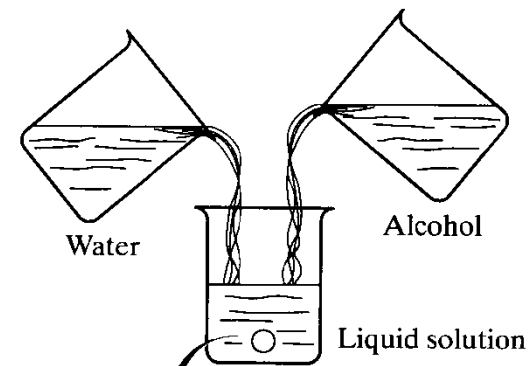
- Implies single phase

- Limited Solubility

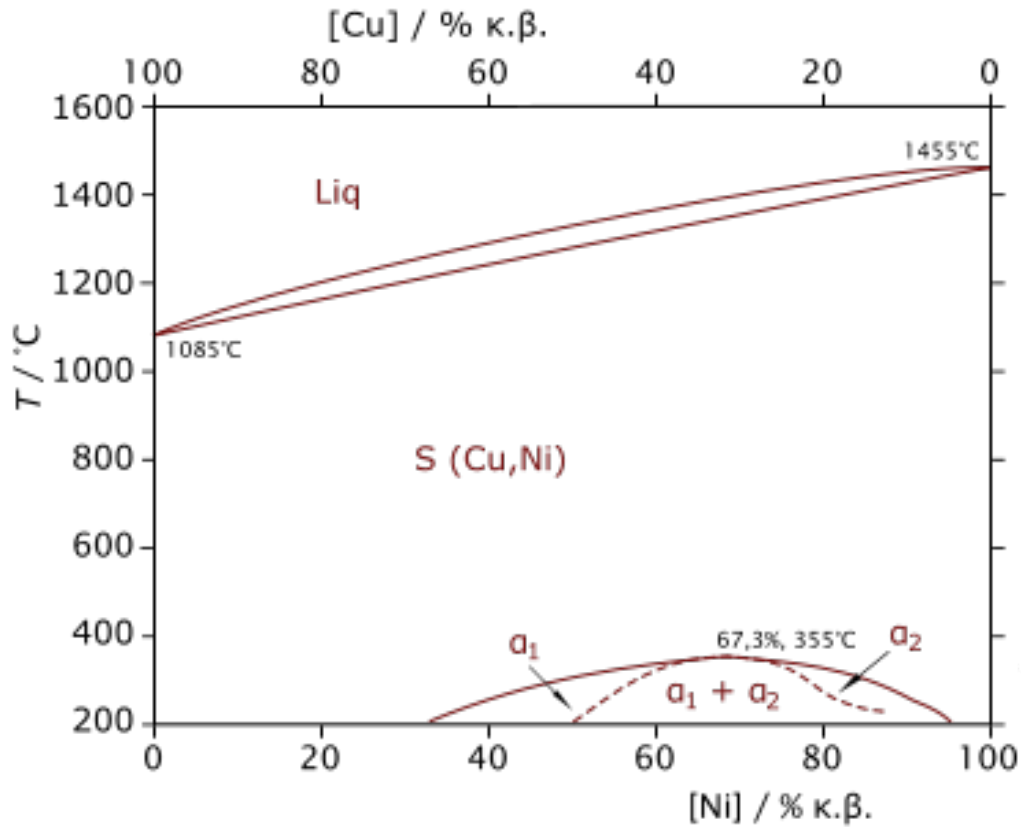
- Implies multiple phases

- No Solubility

- oil and water region

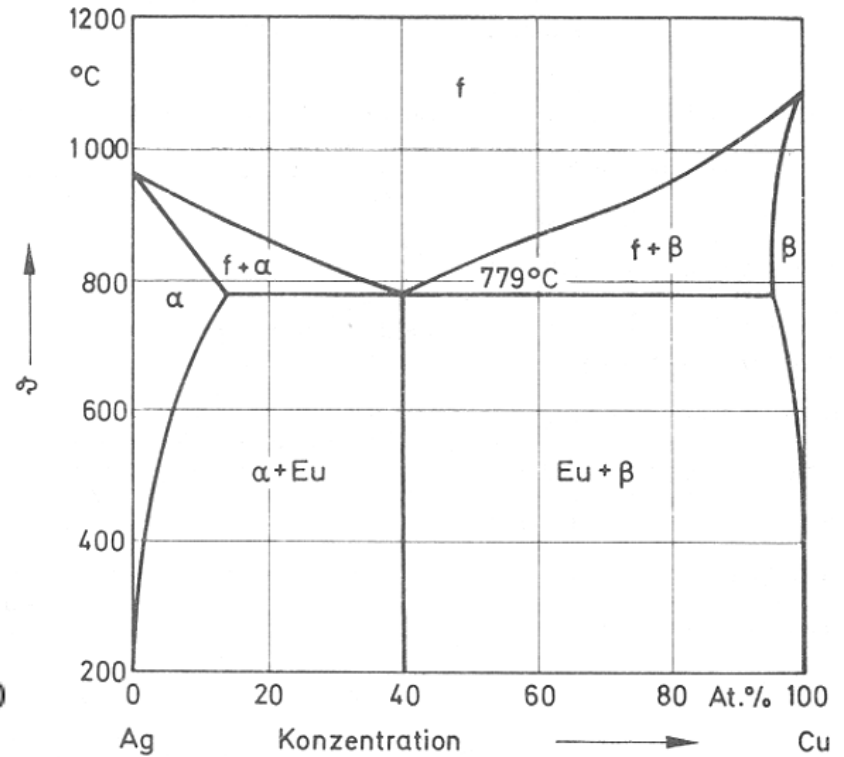


Cu-Ni Alloys



complete solid solution

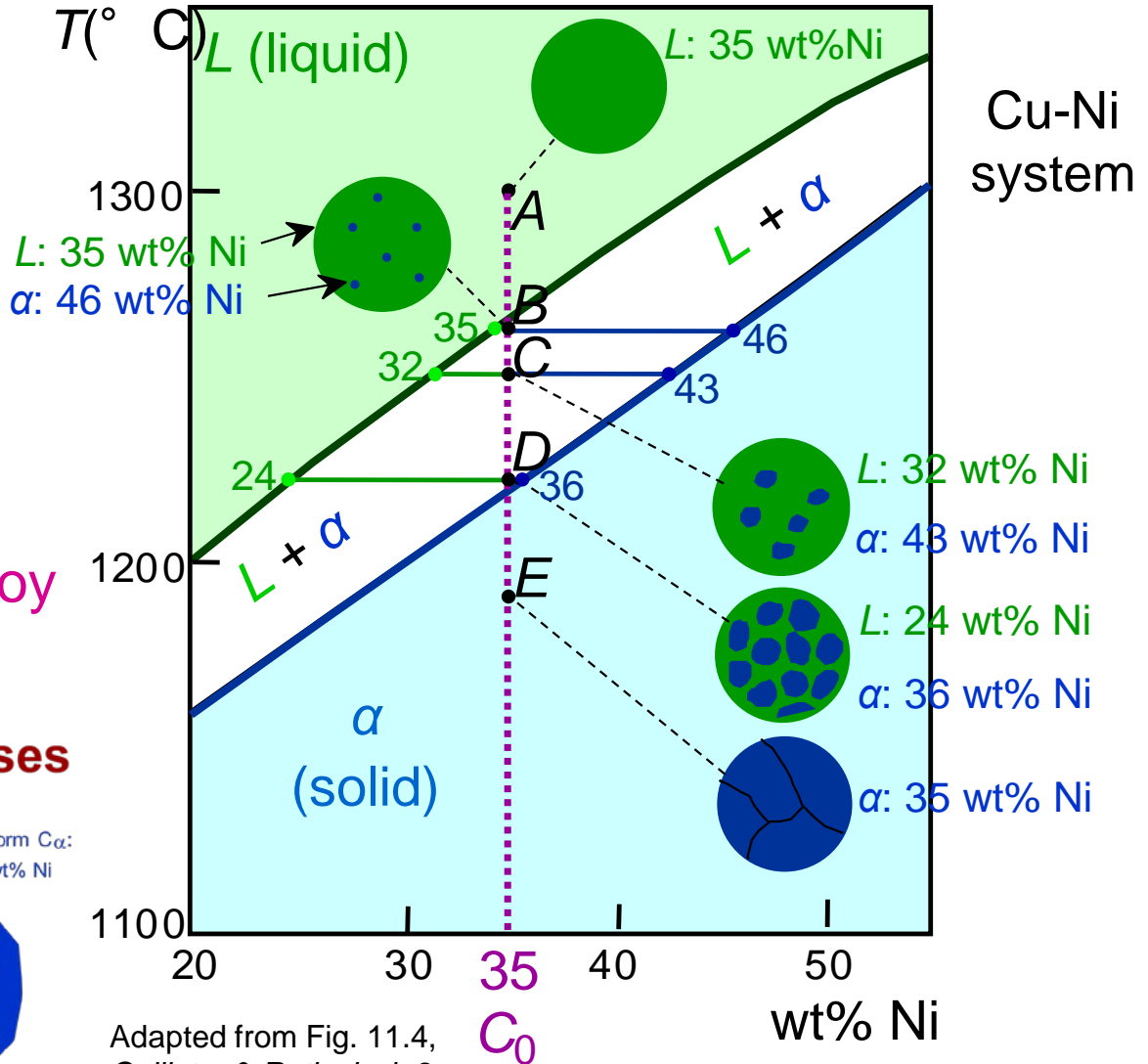
Cu-Ag Alloys



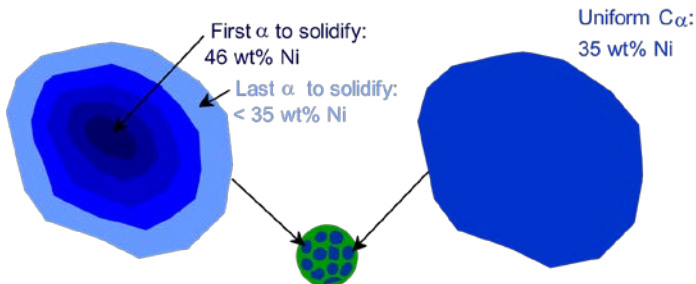
limited solid solution

- Cooling of a Cu-Ni Alloy

- Phase diagram: Cu-Ni system.
- Consider microstructural changes that accompany the cooling of a $C_0 = 35 \text{ wt\% Ni}$ alloy



- Cored vs Equilibrium Phases



Chapter 11: Phase Diagrams

What we will learn about

I. Component, Phase, Equilibrium

→ Phase diagram (Gibb's phase rule)

II. one component phase diagram

two component phase diagram

: solubility limit (Hume-Rothery Rule)

III. Isomorphous Binary Phase Diagram

: tie line, lever rule

IV. Binary-Eutectic Systems

V. Binary invariant reaction

: Eutectic, Eutectoid, & Peritectic

- Ternary, Quarternary phase diagram

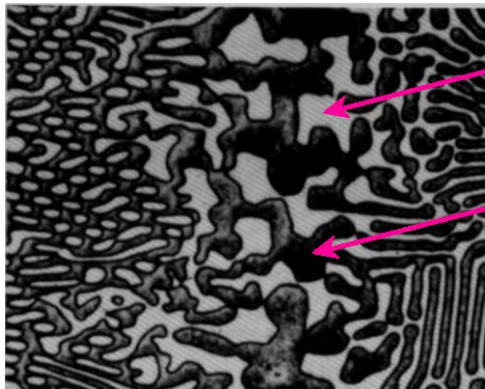
- Phase transformation

IV. Binary-Eutectic Systems

2 components

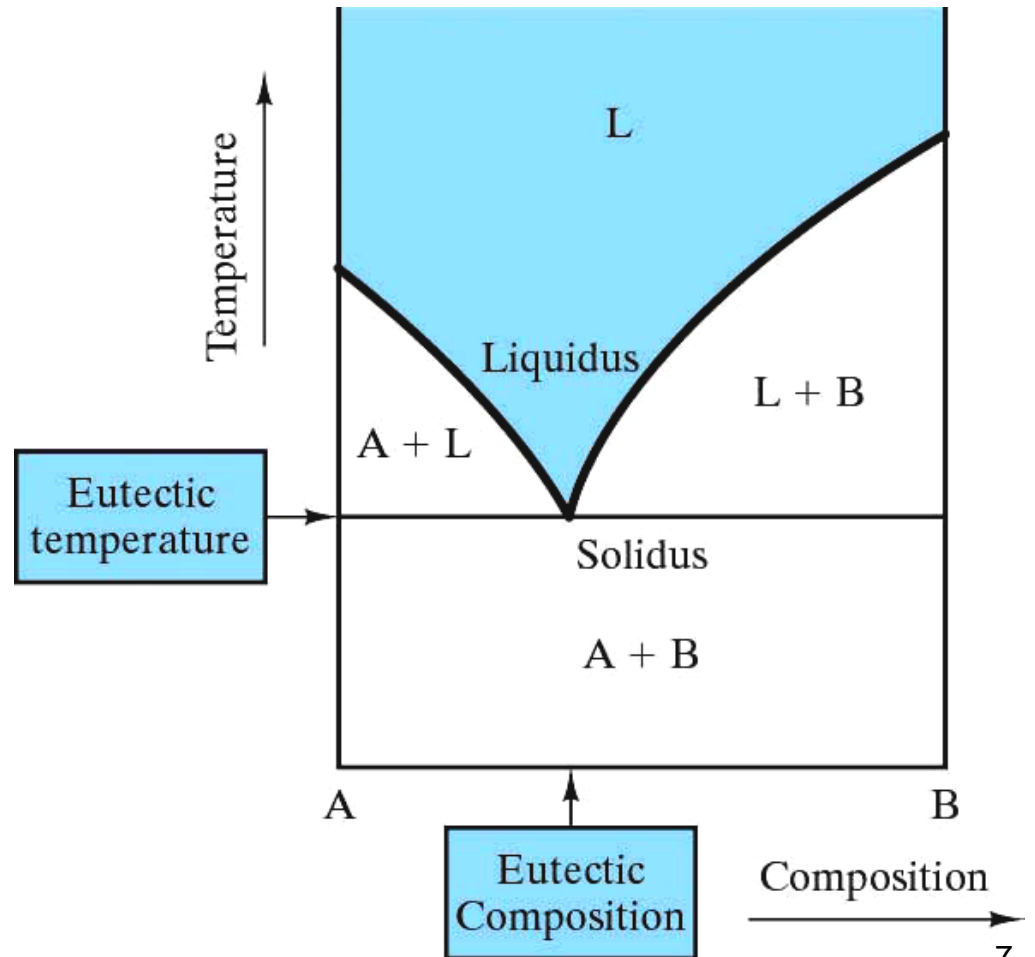
has a special composition with a min. melting T .

Eutectic reaction
 $L \rightarrow \alpha + \beta$



β (light phase)

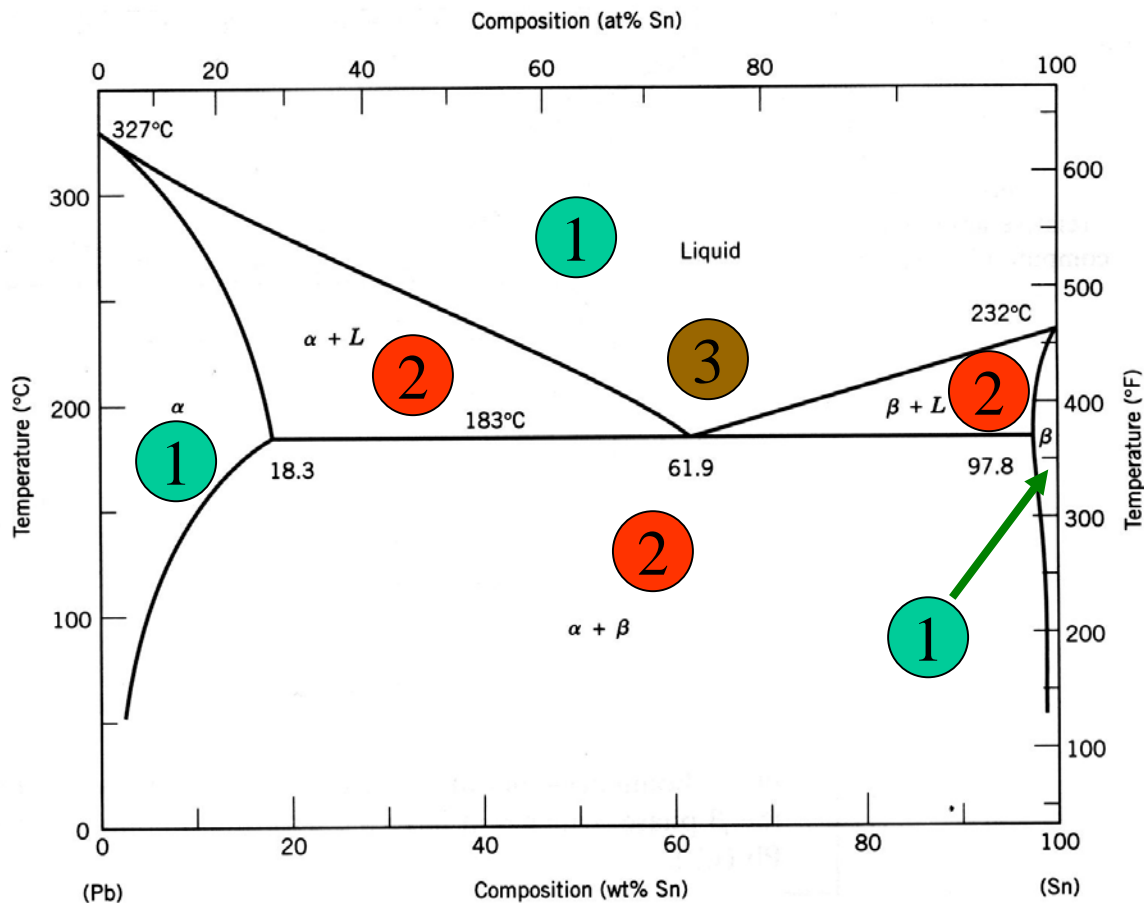
α (dark phase)



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

$$F = C - P + 1$$

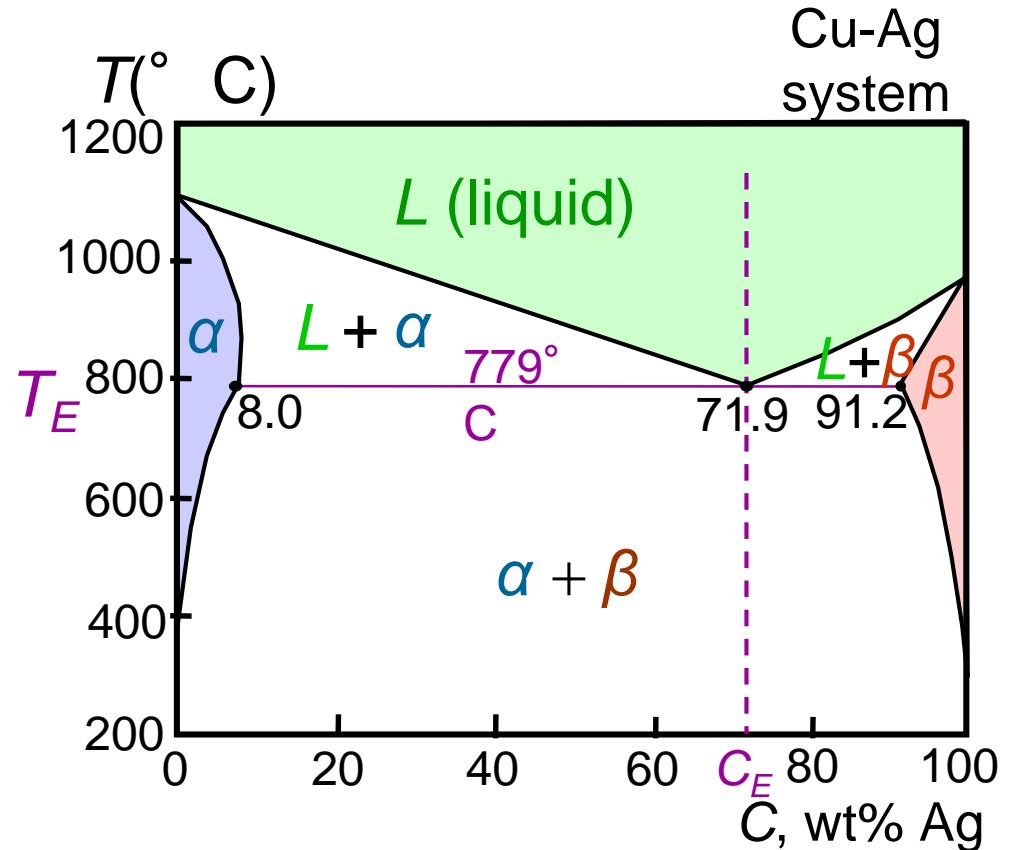
$$= 2 - 3 + 1$$

$$= 0$$

can't vary T or composition

EX 1: Cu-Ag Eutectic System

- 3 single phase regions (L , α , β)
- Limited solubility:
 α : mostly Cu
 β : mostly Ag
- T_E : No liquid below T_E
- C_E : Composition at temperature T_E



• Eutectic reaction

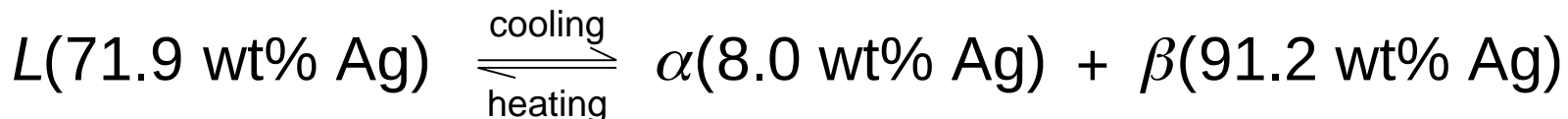
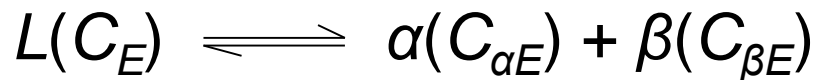


Fig. 11.6, Callister & Rethwisch 9e

[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

EX 2: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 150° C, determine:
 - the phases present

Answer: $\alpha + \beta$

- the phase compositions

Answer: $C_\alpha = 11$ wt% Sn
 $C_\beta = 99$ wt% Sn

- the relative amount of each phase

Answer:

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_0}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 0.67$$

$$W_\beta = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 0.33$$

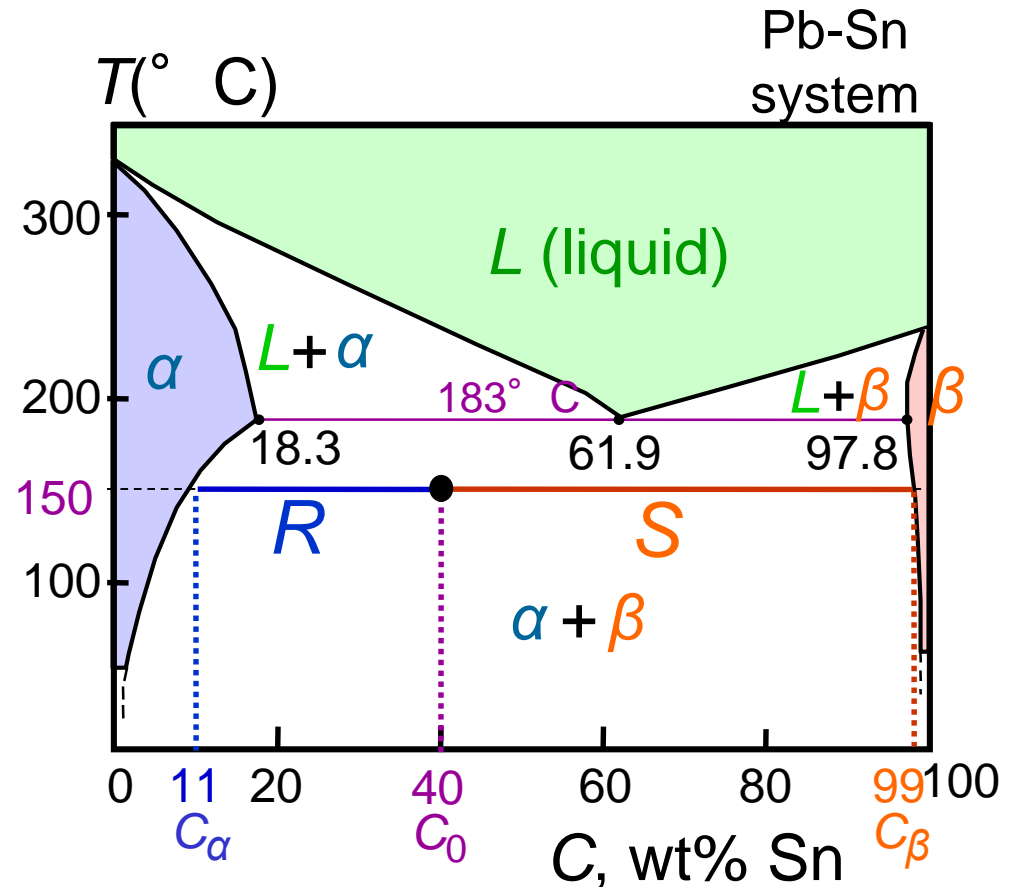


Fig. 11.7, Callister & Rethwisch 9e.
 [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

EX 2: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220° C, determine:
 - the phases present:

Answer: $\alpha + L$

- the phase compositions

Answer: $C_\alpha = 17$ wt% Sn
 $C_L = 46$ wt% Sn

- the relative amount of each phase

Answer:

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$

$$= \frac{6}{29} = 0.21$$

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$

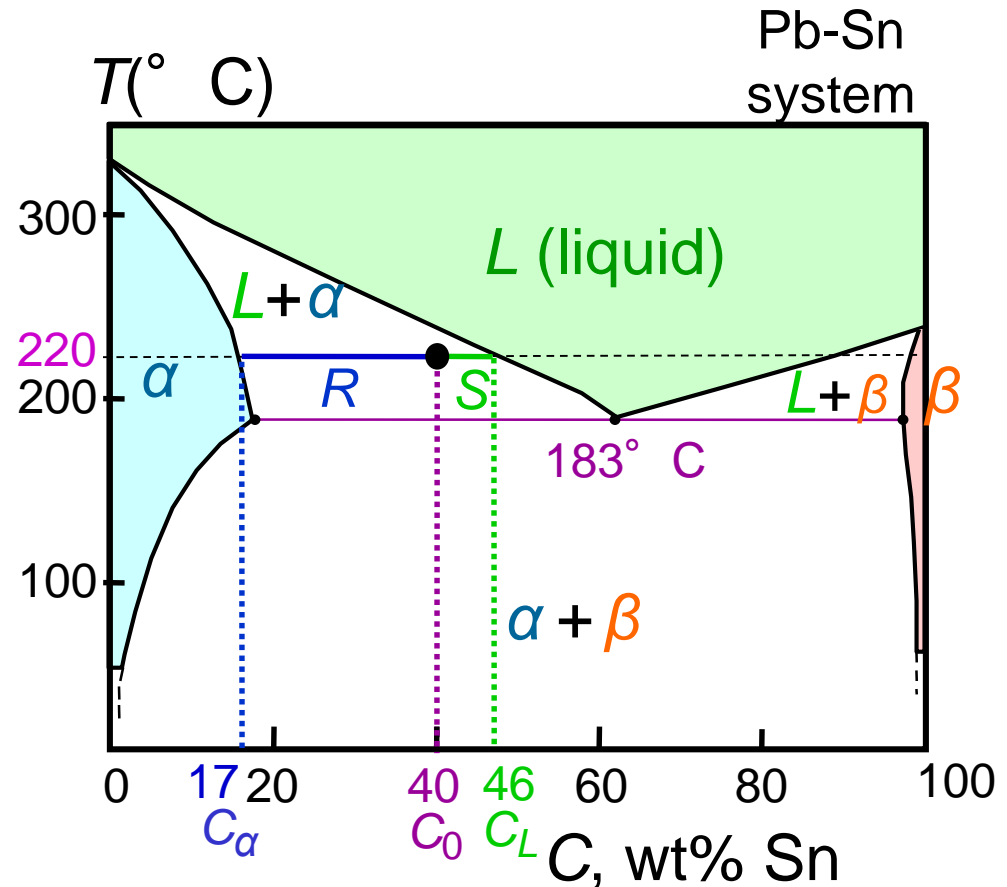


Fig. 11.7, Callister & Rethwisch 9e.
 [Adapted from *Binary Alloy Phase Diagrams*,
 2nd edition, Vol. 3, T. B. Massalski (Editor-in-
 Chief), 1990. Reprinted by permission of ASM
 International, Materials Park, OH.]

Microstructural Developments in Eutectic Systems I

- For alloys for which $C_0 < 2 \text{ wt\% Sn}$
- Result: at room temperature -- polycrystalline with grains of α phase having composition C_0

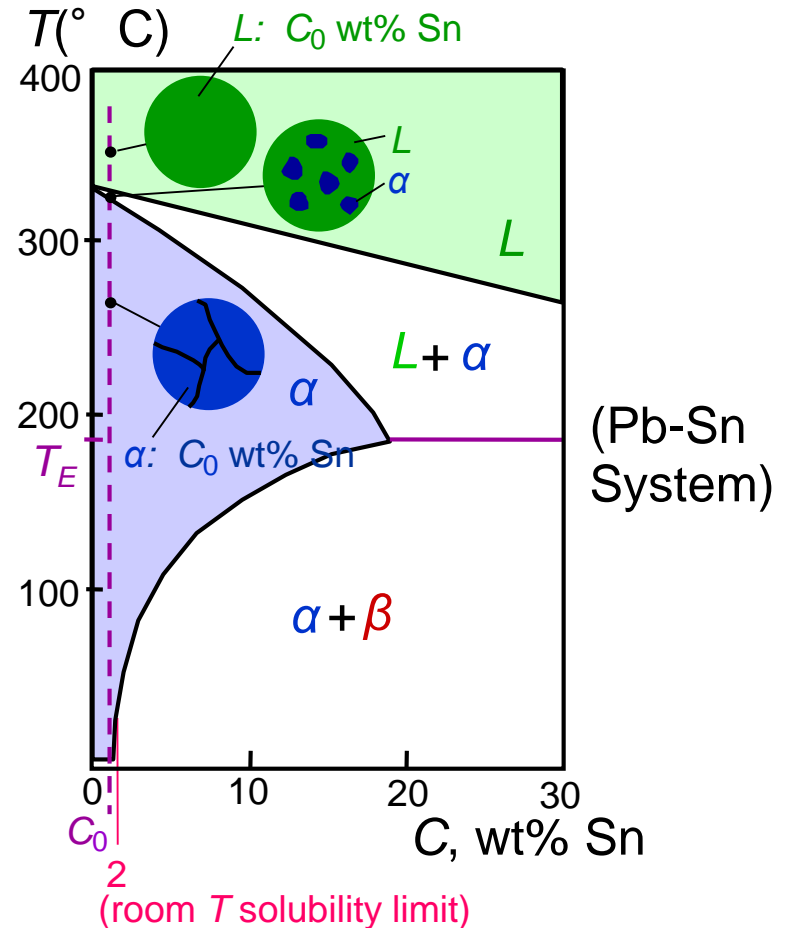


Fig. 11.10, Callister & Rethwisch 9e.

Microstructural Developments in Eutectic Systems II

- For alloys for which $2 \text{ wt\% Sn} < C_0 < 18.3 \text{ wt\% Sn}$
- Result: at temperatures in $\alpha + \beta$ range -- polycrystalline with α grains and small β -phase particles

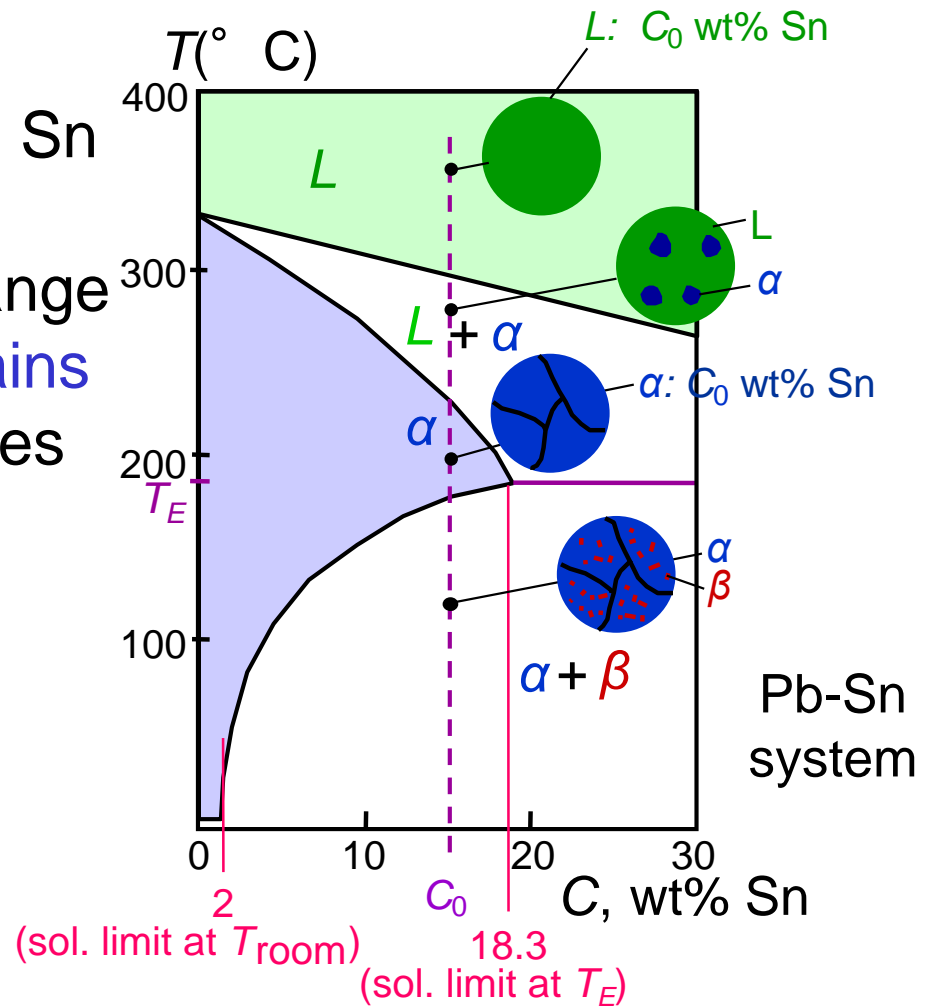


Fig. 11.11, Callister & Rethwisch 9e.

Microstructural Developments in Eutectic Systems III

- For alloy of composition $C_0 = C_E$
- Result: Eutectic microstructure (lamellar structure)
-- alternating layers (lamellae) of α and β phases.

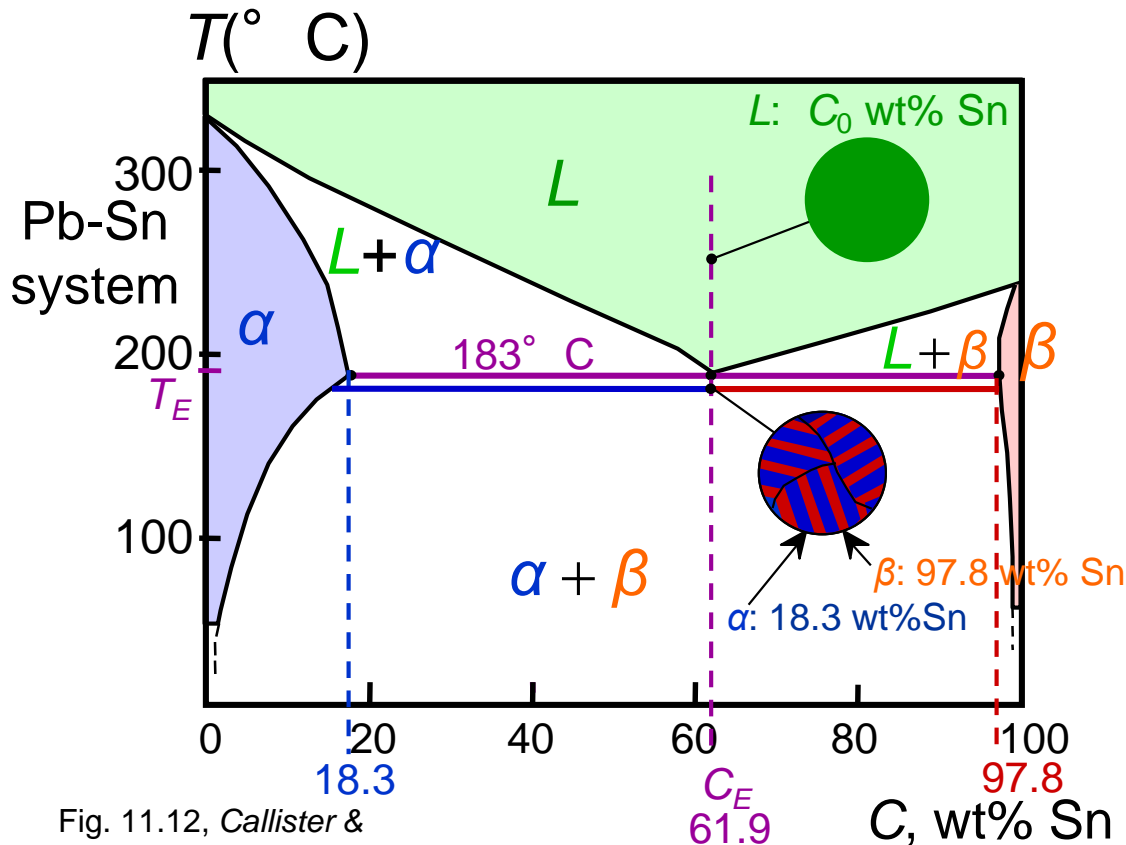


Fig. 11.12, Callister & Rethwisch 9e.

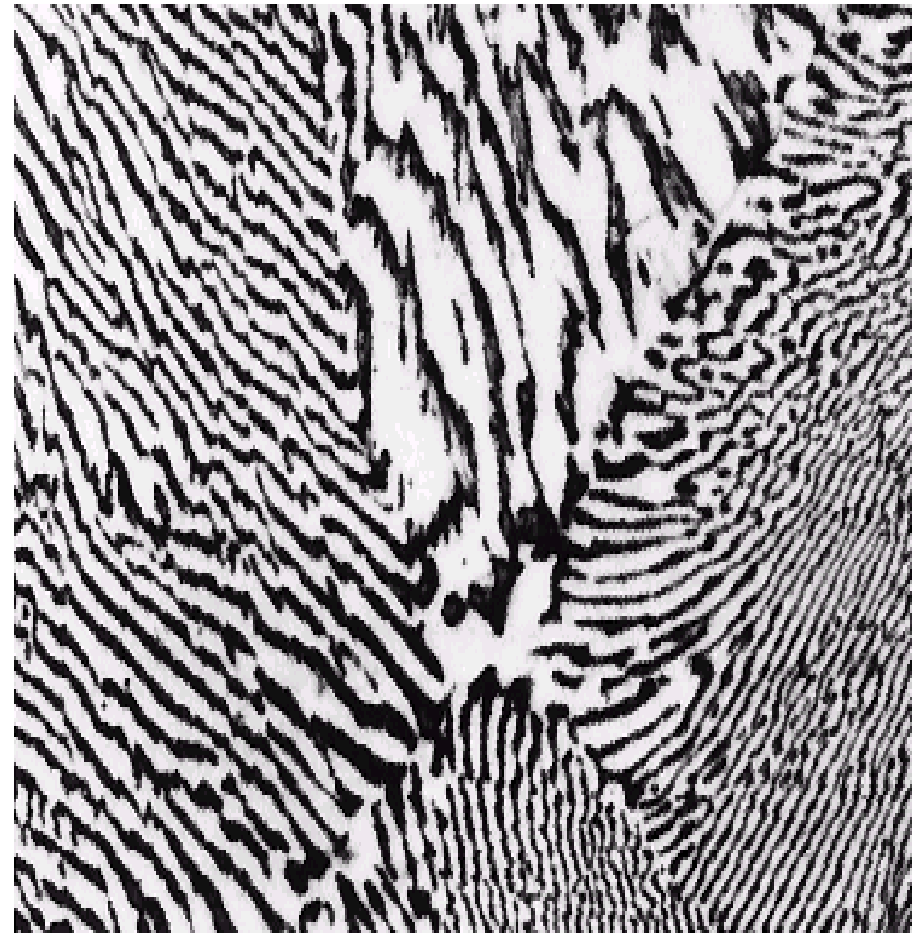
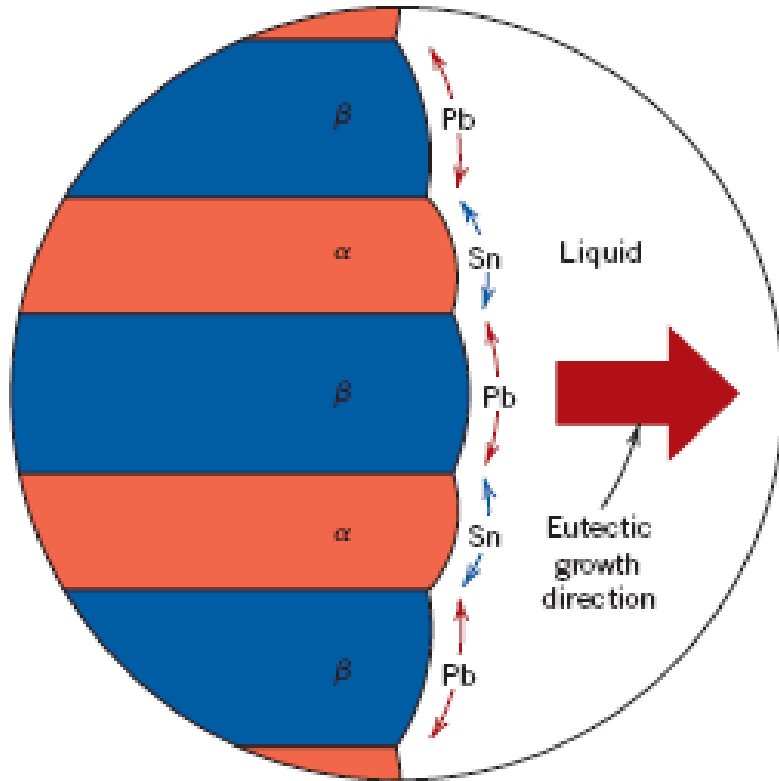
Micrograph of Pb-Sn eutectic microstructure



160 μm

Fig. 11.13, Callister & Rethwisch 9e. (From *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

Lamellar Eutectic Structure



Figs. 11.13 & 11.14, *Callister & Rethwisch 9e*.
(Fig. 11.13 from *Metals Handbook*, 9th edition, Vol. 9,
Metallography and Microstructures, 1985. Reproduced by
permission of ASM International, Materials Park, OH.)

Microstructural Developments in Eutectic Systems IV

- For alloys for which $18.3 \text{ wt\% Sn} < C_0 < 61.9 \text{ wt\% Sn}$
- Result: α phase particles and a eutectic microconstituent

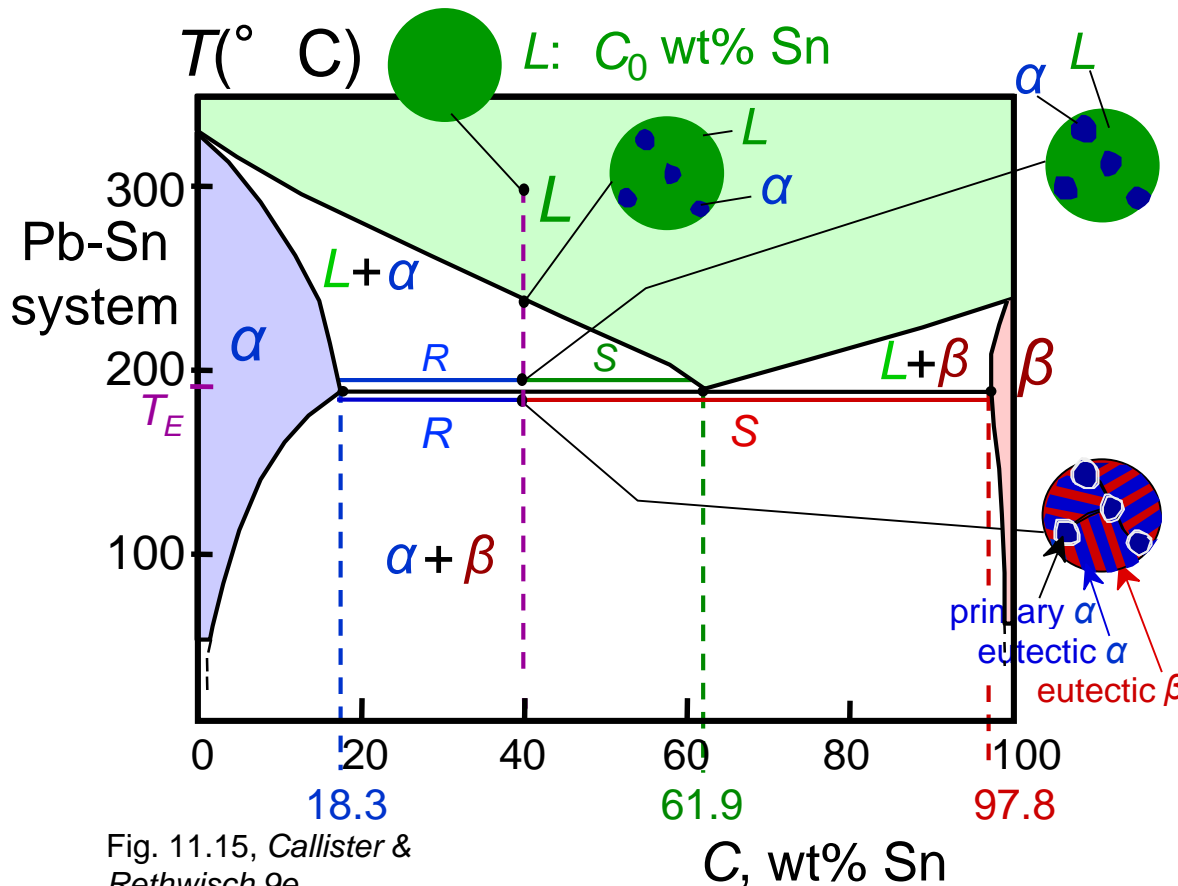


Fig. 11.15, Callister & Rethwisch 9e.

- Just above T_E :
 - $C_{\alpha} = 18.3 \text{ wt\% Sn}$
 - $C_L = 61.9 \text{ wt\% Sn}$
 - $W_{\alpha} = \frac{S}{R+S} = 0.50$
 - $W_L = (1 - W_{\alpha}) = 0.50$
- Just below T_E :
 - $C_{\alpha} = 18.3 \text{ wt\% Sn}$
 - $C_{\beta} = 97.8 \text{ wt\% Sn}$
 - $W_{\alpha} = \frac{S}{R+S} = 0.73$
 - $W_{\beta} = 0.27$

Hypoeutectic & Hypereutectic

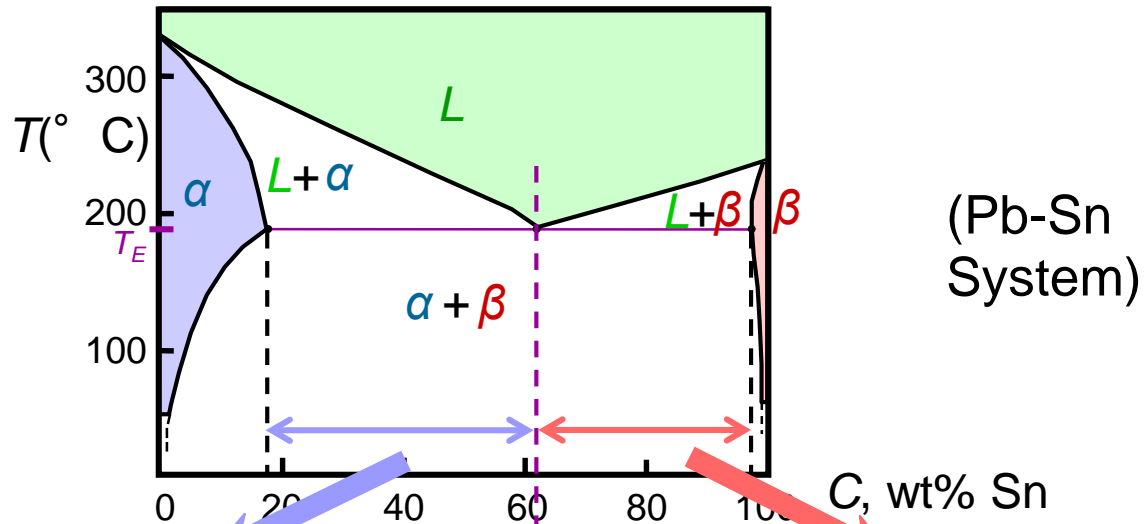


Fig. 11.7, Callister & Rethwisch 9e. [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

hypoeutectic: $C_0 = 50 \text{ wt\% Sn}$

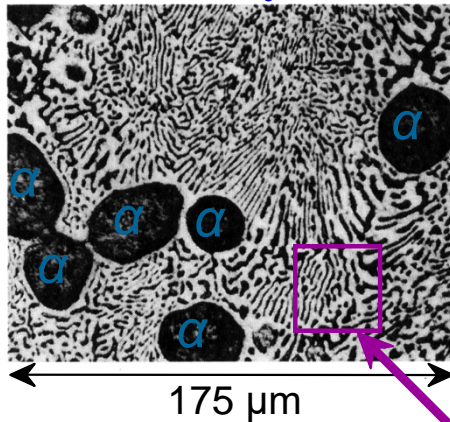


Fig. 11.16, Callister & Rethwisch 9e.

eutectic
61.9

eutectic: $C_0 = 61.9 \text{ wt\% Sn}$

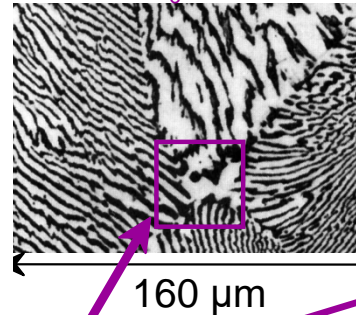
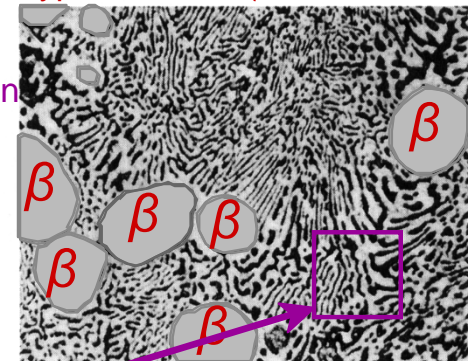


Fig. 11.13, Callister & Rethwisch 9e.

hypereutectic: (illustration only)



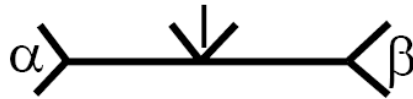
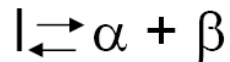
Adapted from Fig. 11.16, Callister & Rethwisch 9e. (Illustration only)

(Figs. 11.13 and 11.16 from *Metals Handbook*, 9th ed., Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

Review of Invariant Binary Reactions

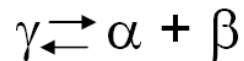
Eutectic Type

Eutectic



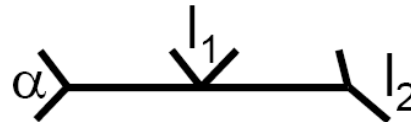
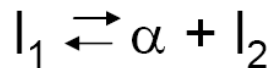
Al-Si, Fe-C

Eutectoid



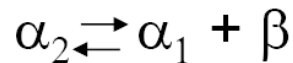
Fe-C

Monotectic



Cu-Pb

Monotectoid



Al-Zn, Ti-V

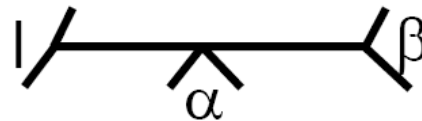
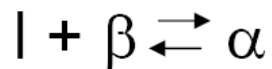
On cooling one phase going to two phases

Metatectic reaction: $\beta \leftrightarrow L + \alpha$ **Ex. Co-Os, Co-Re, Co-Ru** ¹⁸

Review of Invariant Binary Reactions

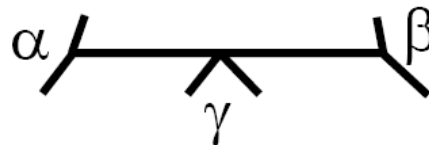
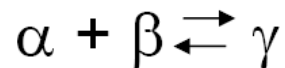
Peritectic Type

Peritectic



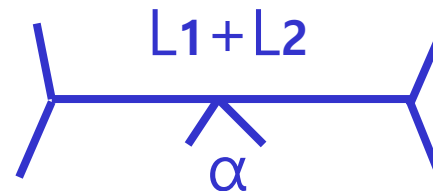
Fe-C

Peritectoid



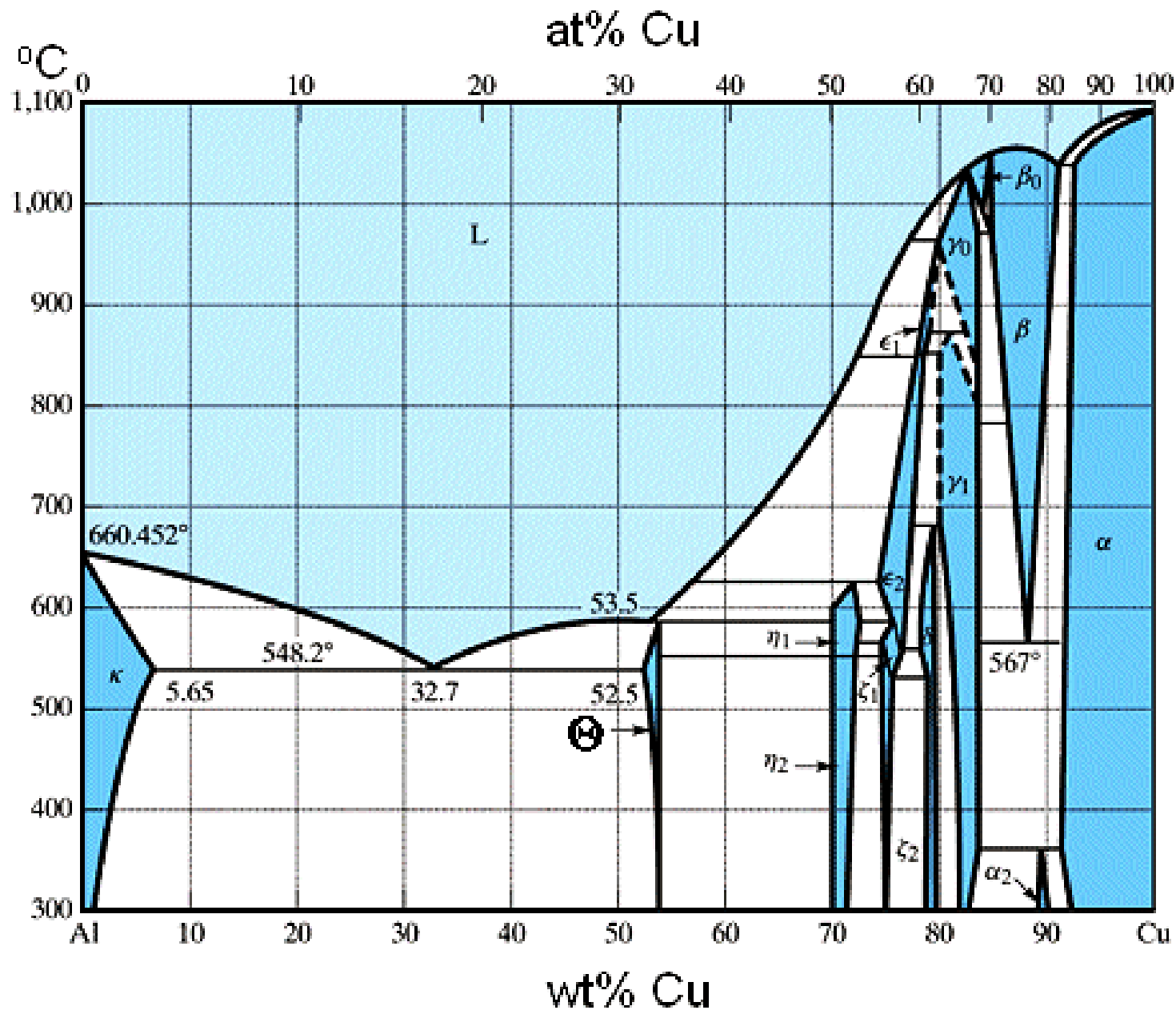
Cu-Al

Syntectic reaction



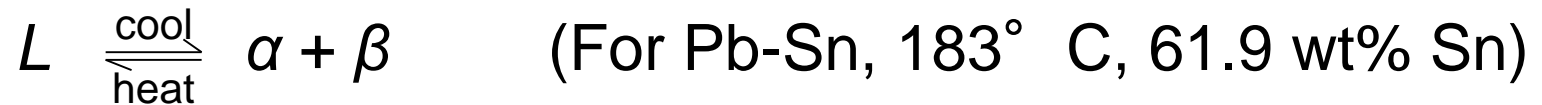
K-Zn, Na-Zn,
K-Pb, Pb-U, Ca-Cd

On cooling two phases going to one phase

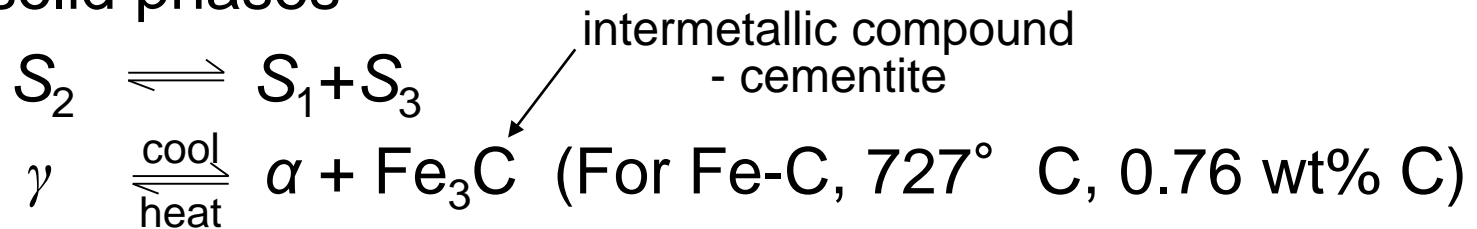


V. Eutectic, Eutectoid, & Peritectic

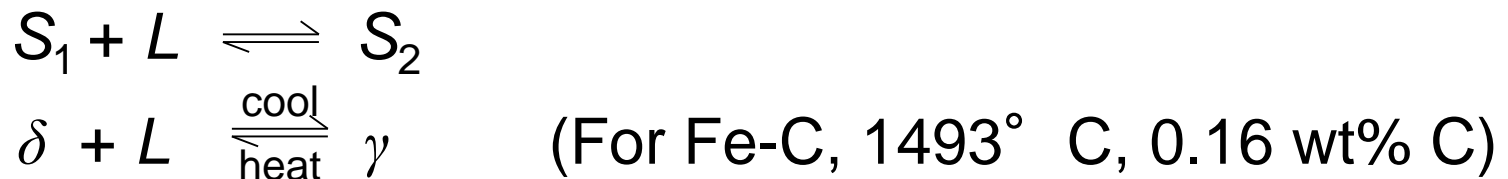
- **Eutectic** - liquid transforms to two solid phases



- **Eutectoid** – one solid phase transforms to two other solid phases



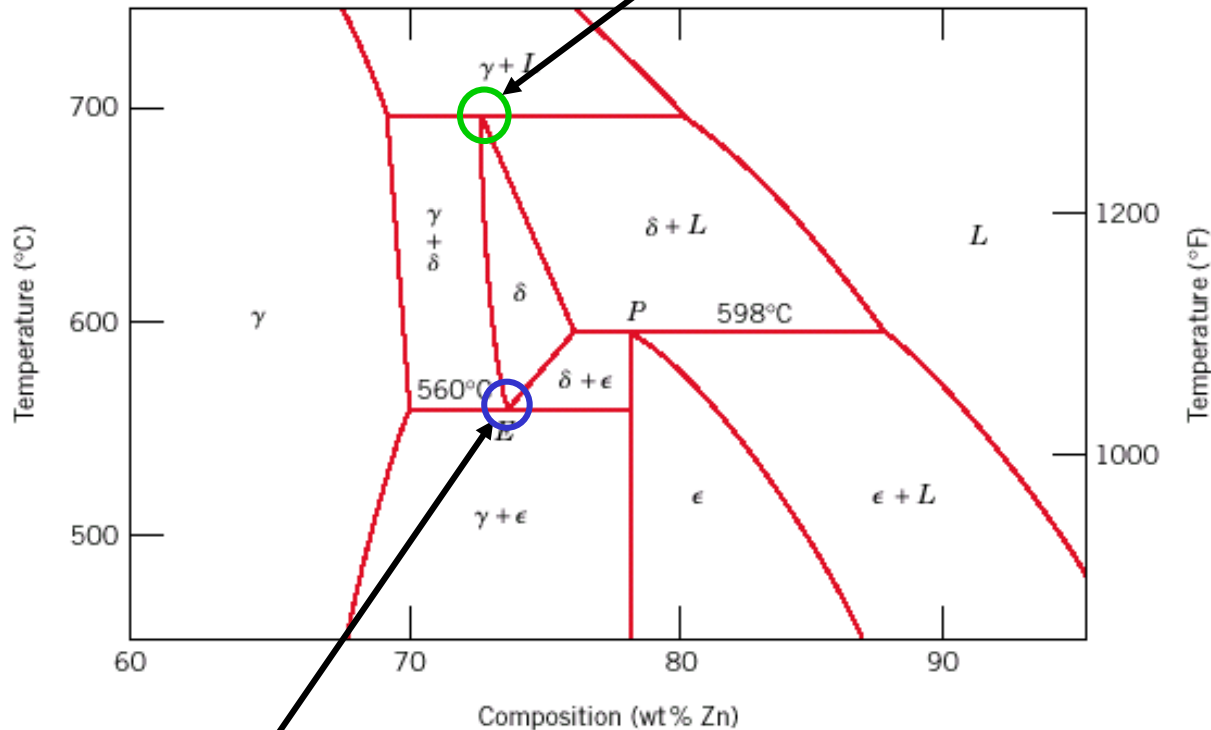
- **Peritectic** - liquid and one solid phase transform to a second solid phase



a. Eutectoid & Peritectic

Cu-Zn Phase diagram

Peritectic transformation $\gamma + L \rightleftharpoons \delta$



Eutectoid transformation $\delta \rightleftharpoons \gamma + \epsilon$

Fig. 11.20, Callister & Rethwisch 9e.
[Adapted from *Binary Alloy Phase Diagrams*,
2nd edition, Vol. 2, T. B. Massalski (Editor-in-
Chief), 1990. Reprinted by permission of
ASM International, Materials Park, OH.]

b. Congruent vs Incongruent

Congruent phase transformations: no compositional change associated with transformation

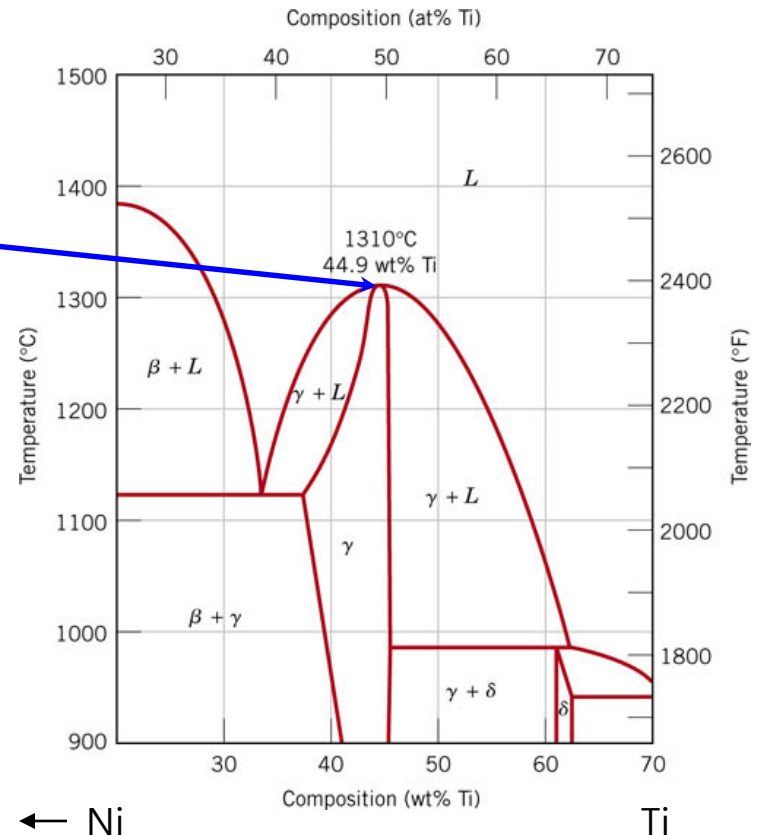
Examples:

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

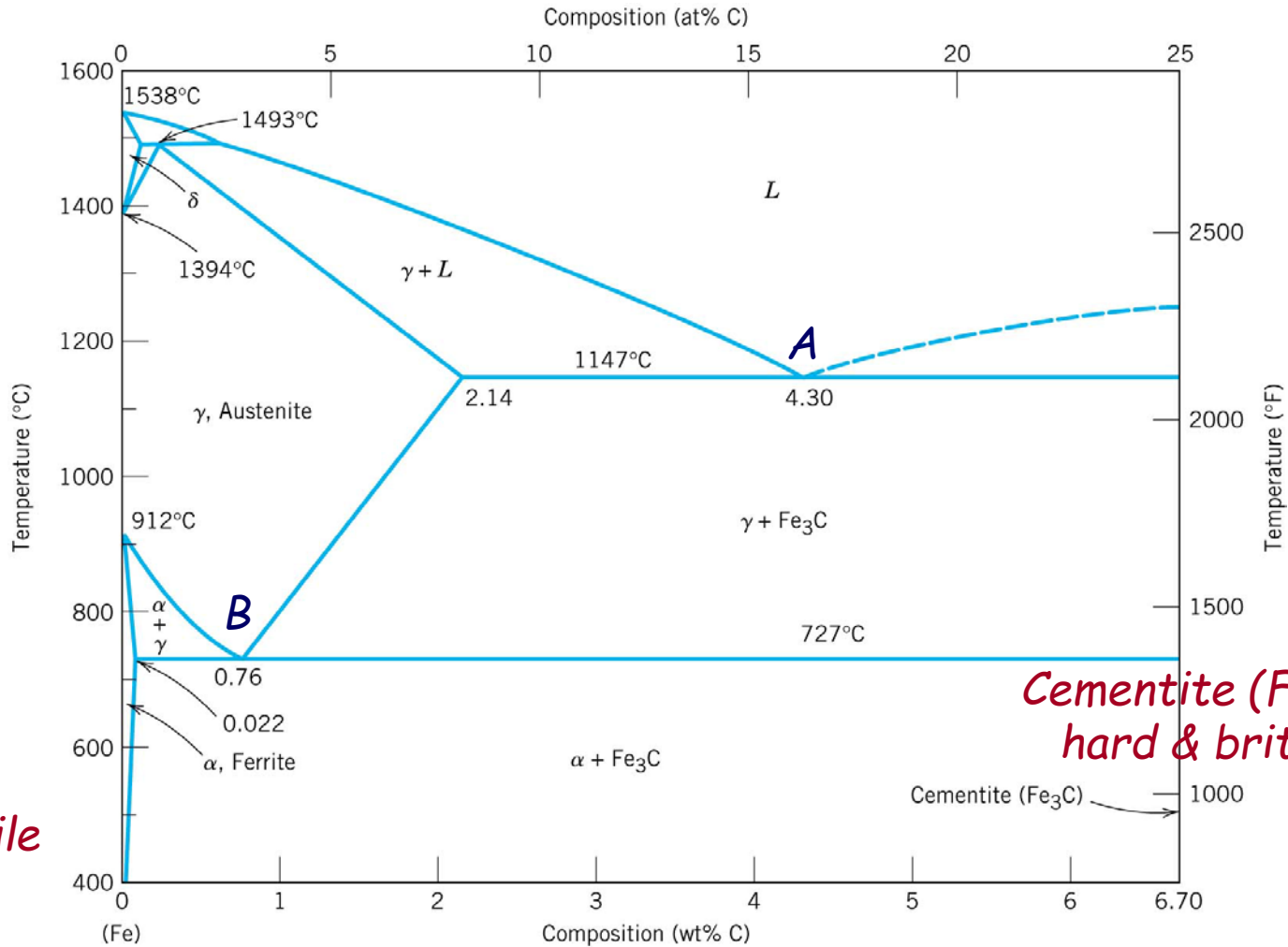
Incongruent phase transformation: at least one phase will experience change in composition

Examples:

- Melting in isomorphous alloys
- Eutectic reactions
- Peritectic Reactions
- Eutectoid reactions



c. Fe-C phase diagram



γ iron
austenite
(FCC)

α iron
Ferrite
(BCC)
soft & ductile

Cementite (Fe_3C)
hard & brittle

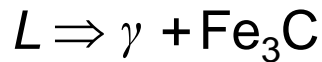
A; eutectic
B; eutectoid

C concentration	0.008w%	2.14w%	6.7w%
	iron	steel	cast iron

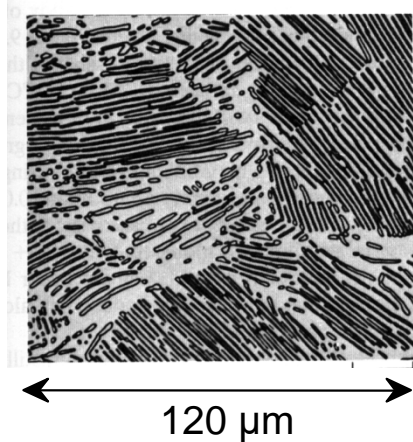
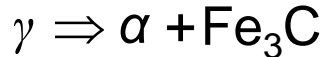
Iron-Carbon (Fe-C) Phase Diagram

- 2 important points

- Eutectic (A):



- Eutectoid (B):



Result: Pearlite = alternating layers of α and Fe_3C phases

Fig. 11.26, Callister & Rethwisch 9e.
(From *Metals Handbook*, Vol. 9, 9th ed.,
Metallography and Microstructures, 1985.
Reproduced by permission of ASM
International, Materials Park, OH.)

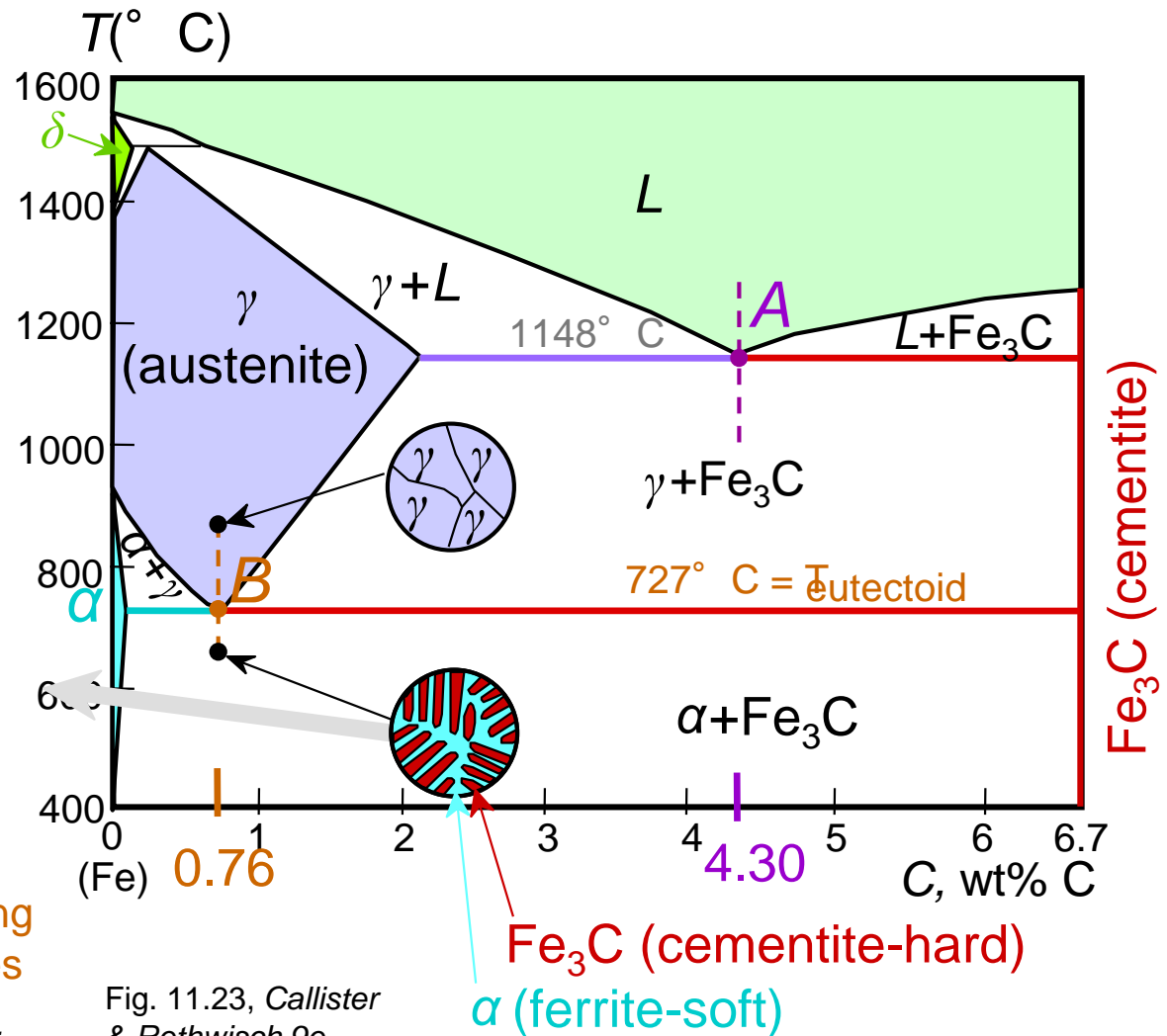
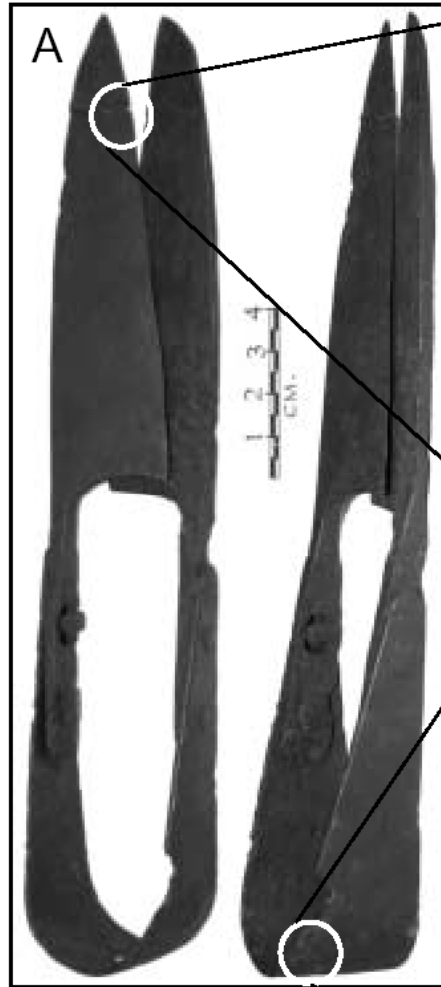
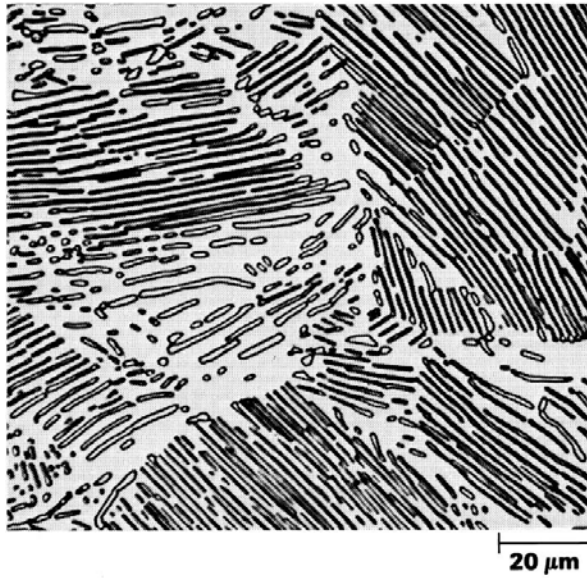


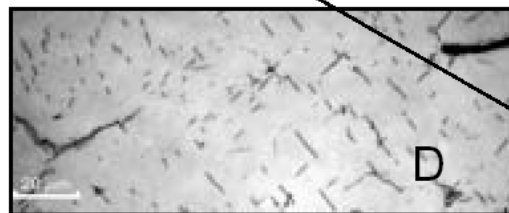
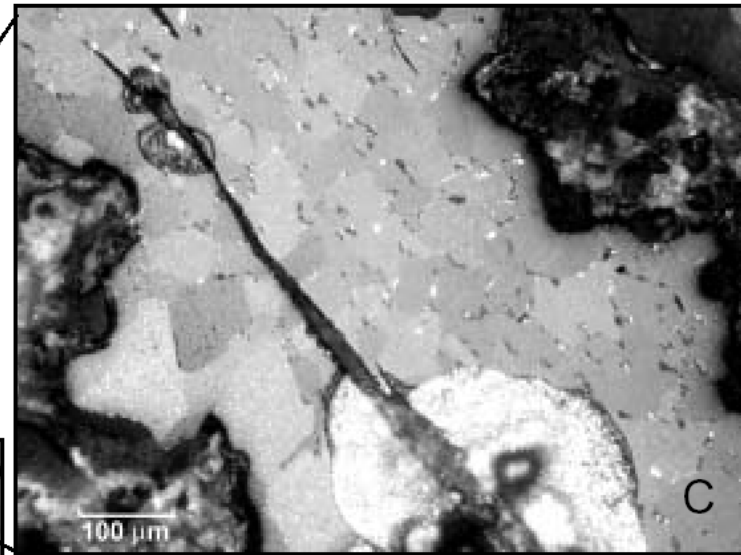
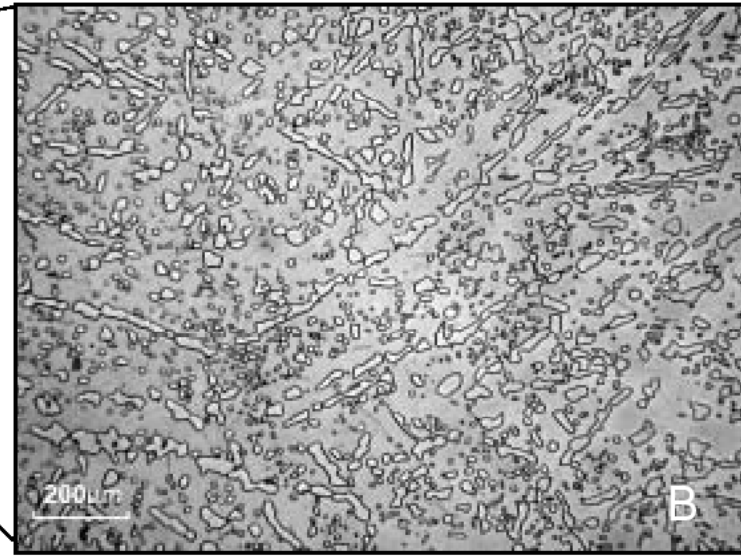
Fig. 11.23, Callister & Rethwisch 9e.

[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition,
Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted
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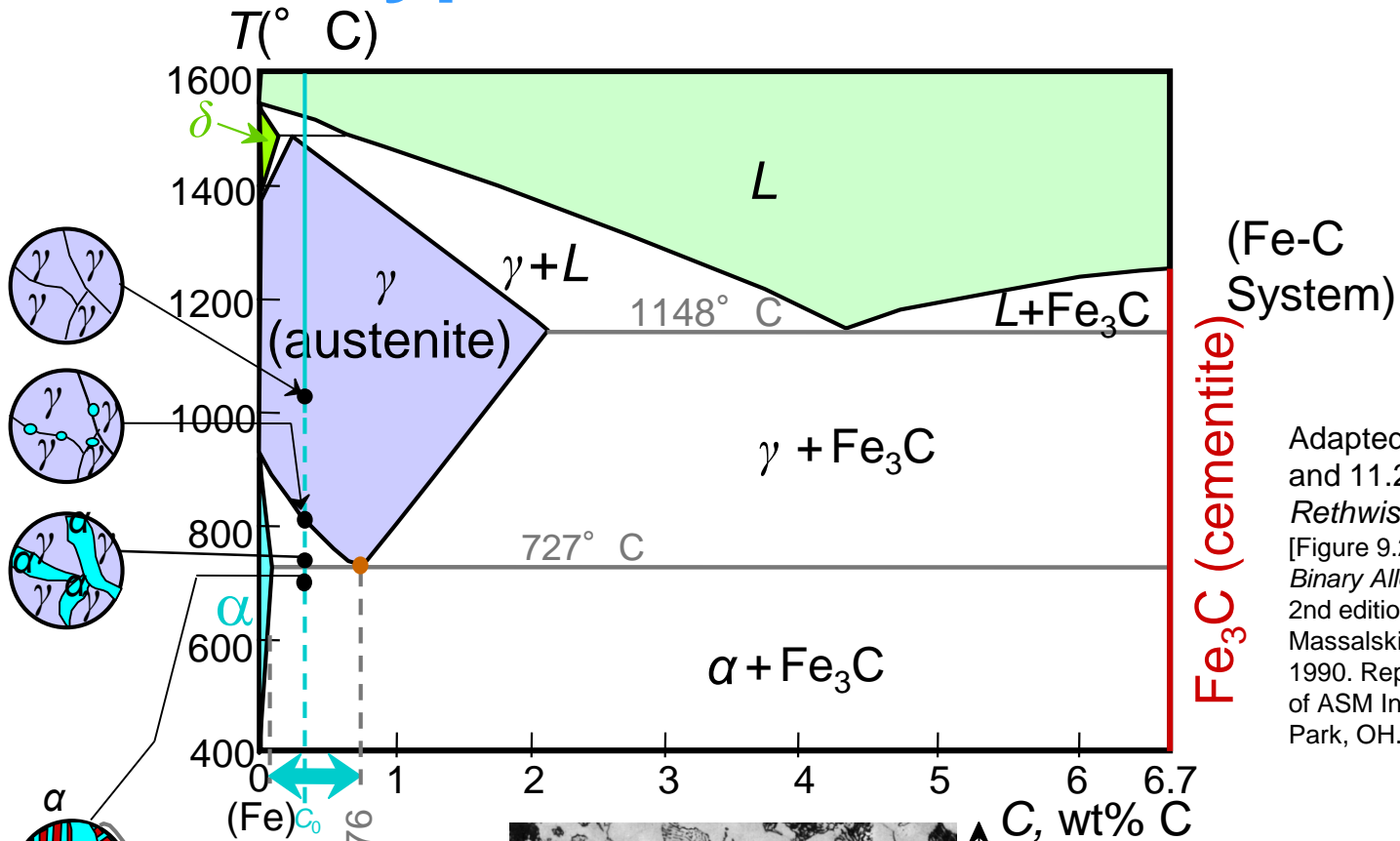
Pearlite microstructure



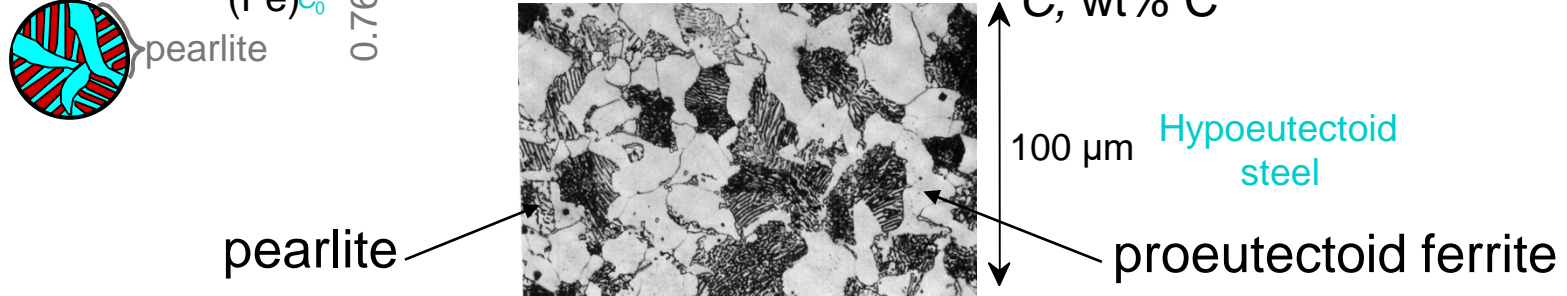
Cementite
(Fe₃C)



Hypoeutectoid Steel

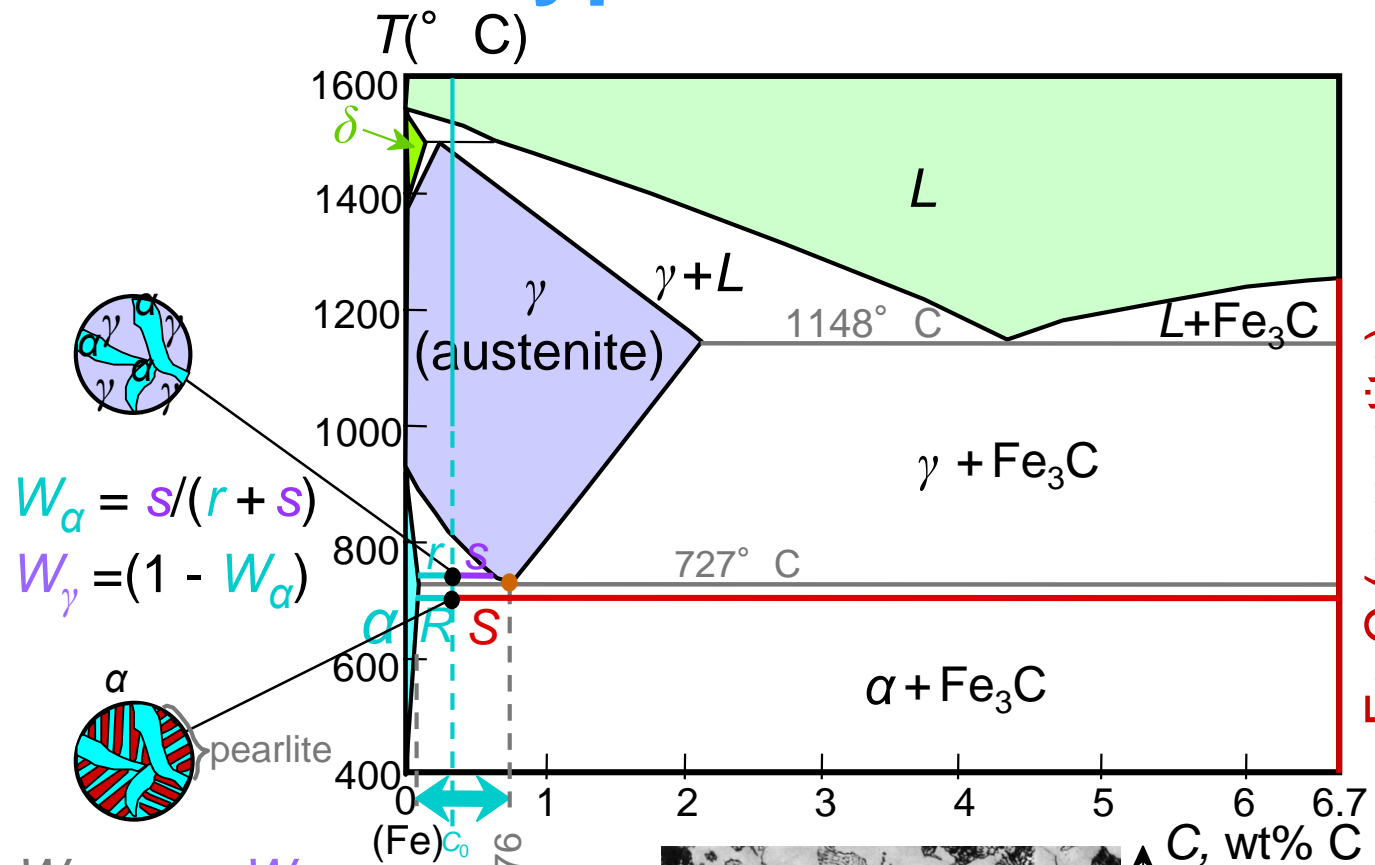


Adapted from Figs. 11.23 and 11.28, *Callister & Rethwisch 9e*.
 [Figure 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



Adapted from Fig. 11.29, *Callister & Rethwisch 9e*.
 (Photomicrograph courtesy of Republic Steel Corporation.)

Hypoeutectoid Steel



(Fe-C System)

Adapted from Figs. 11.23 and 11.28, Callister & Rethwisch 9e.
 [Figure 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

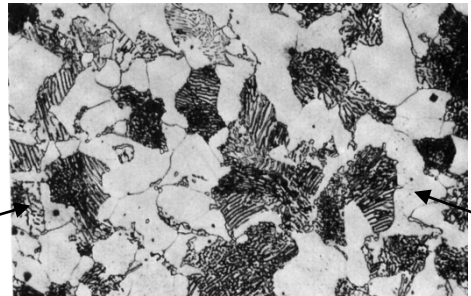
$$W_\alpha = s / (r + s)$$

$$W_\gamma = (1 - W_\alpha)$$

$$W_{pearlite} = W_\gamma$$

$$W_{\alpha'} = S / (R + S)$$

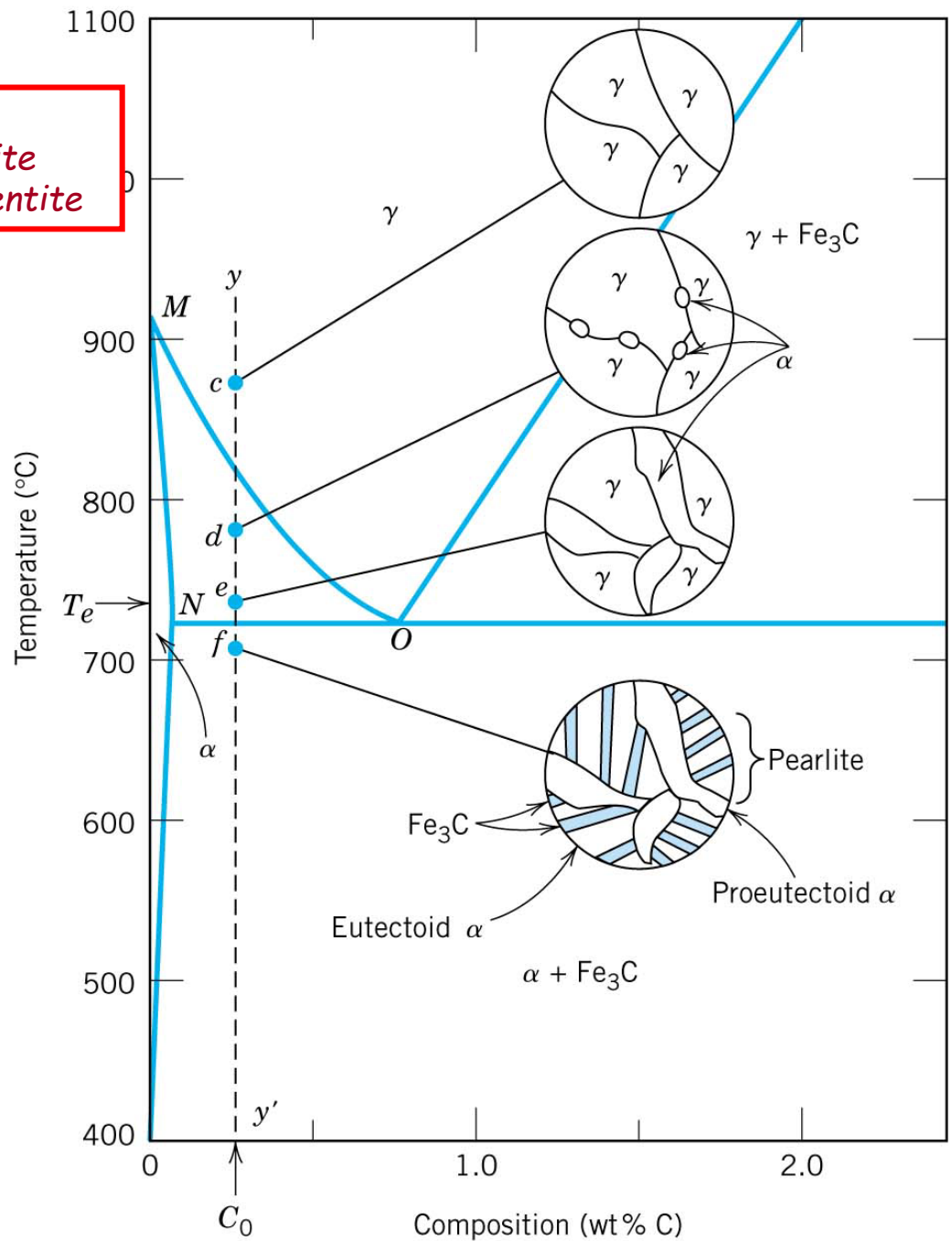
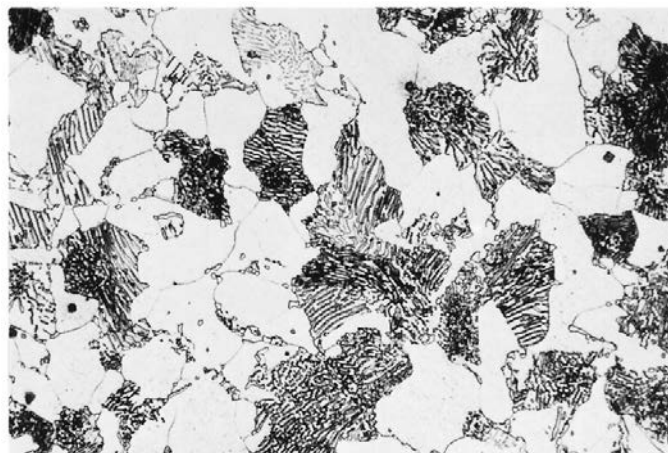
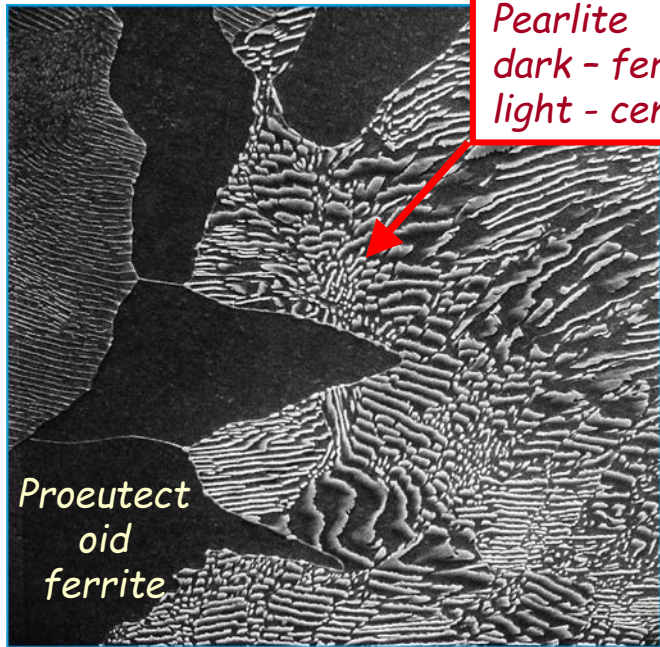
$$W_{Fe_3C} = (1 - W_{\alpha'})$$



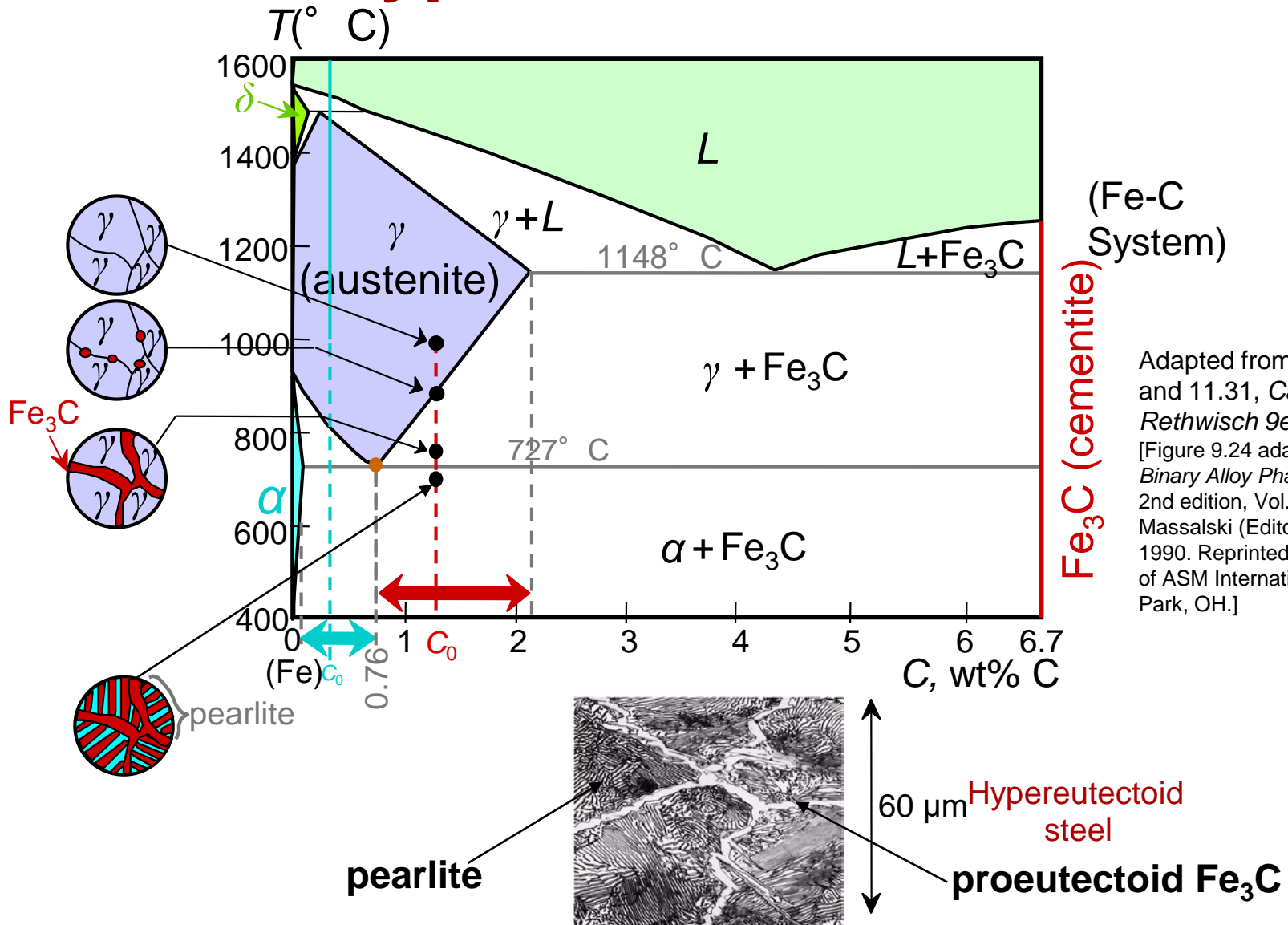
100 μm Hypoeutectoid steel
 proeutectoid ferrite

Adapted from Fig. 11.29, Callister & Rethwisch 9e. (Photomicrograph courtesy of Republic Steel Corporation.)

Hypoeutectoid Steel



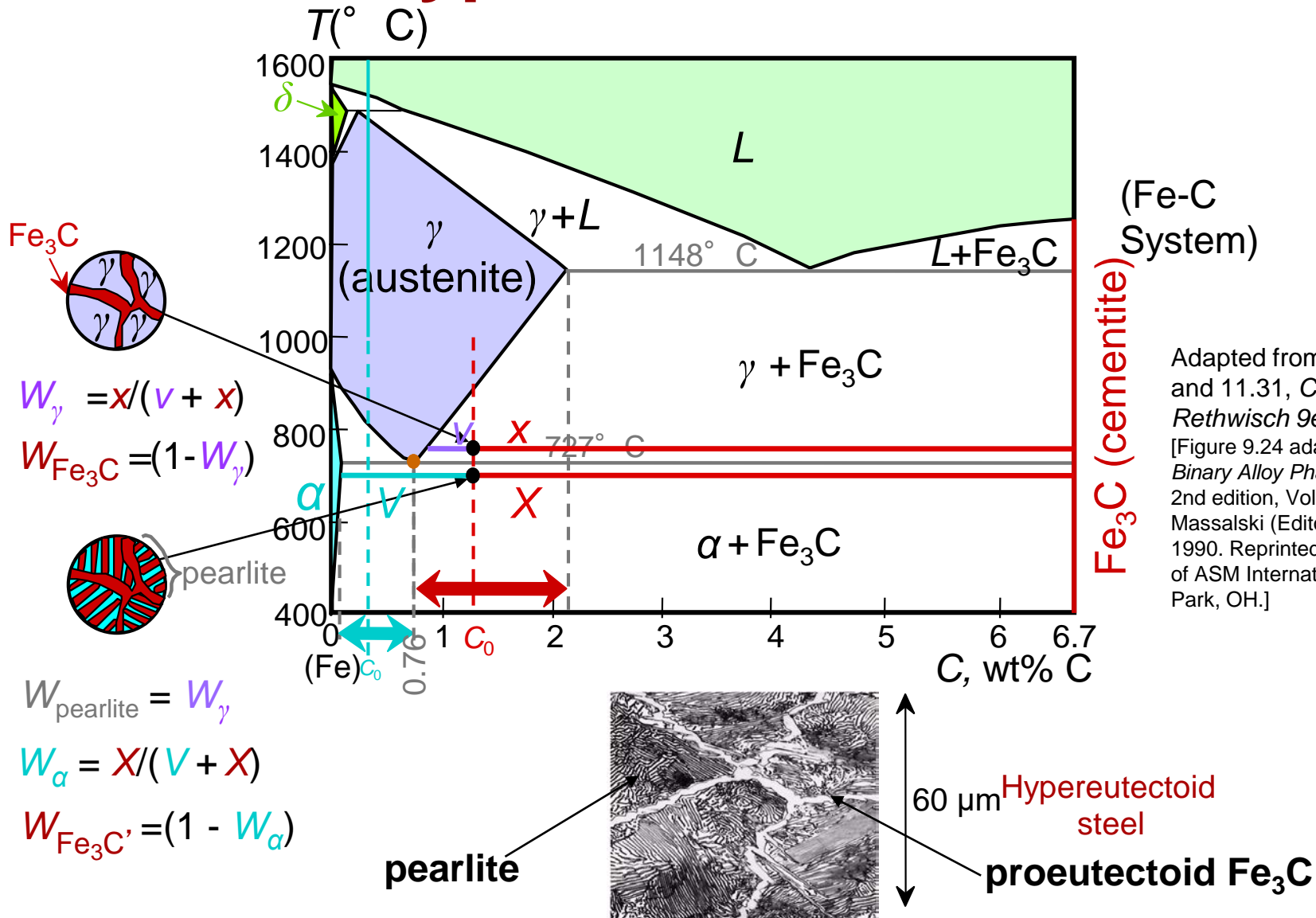
Hypereutectoid Steel



Adapted from Figs. 11.23 and 11.31, Callister & Rethwisch 9e.
 [Figure 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Adapted from Fig. 11.32, Callister & Rethwisch 9e.
 (Copyright 1971 by United States Steel Corporation.)

Hypereutectoid Steel



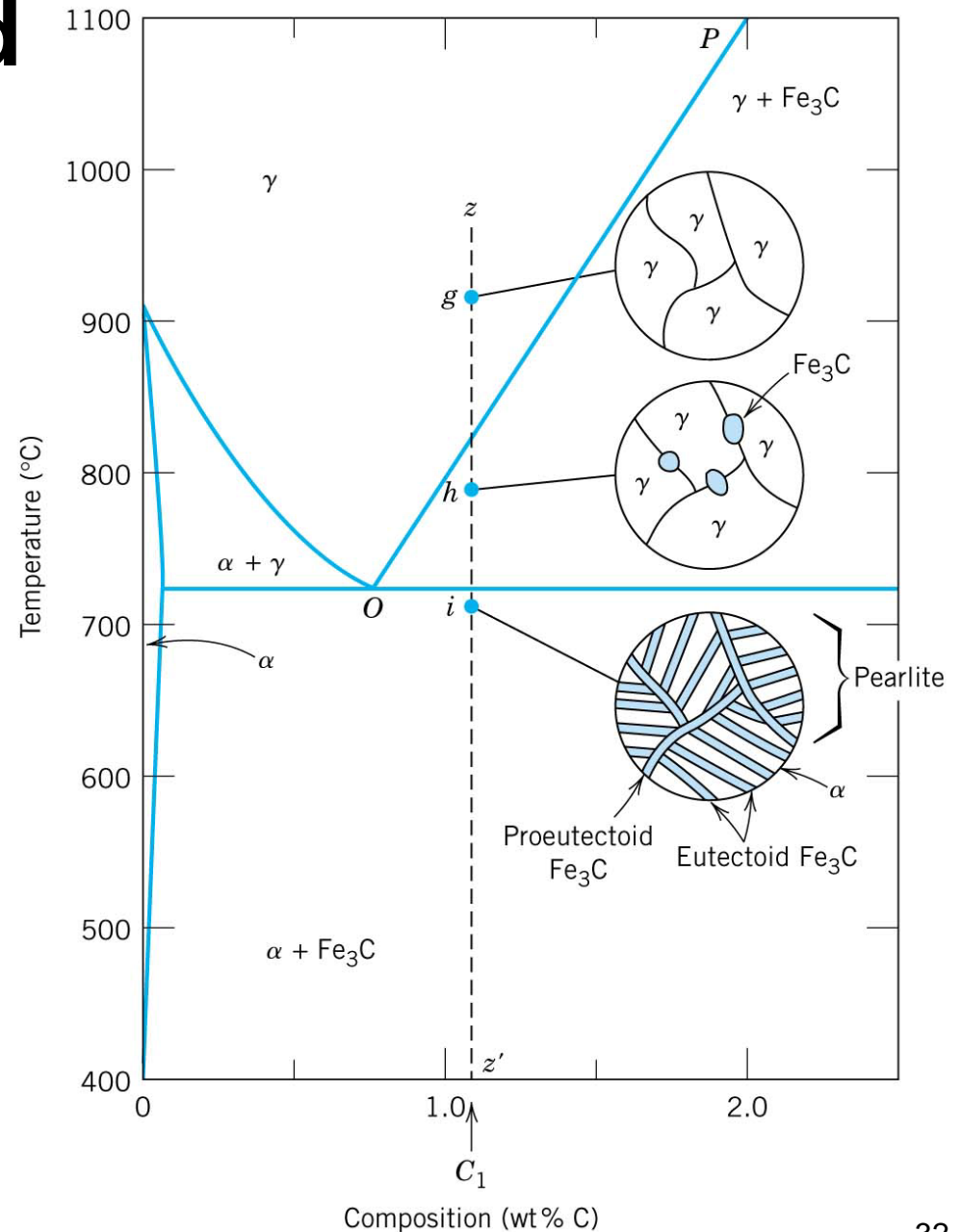
Adapted from Fig. 11.32, *Callister & Rethwisch 9e*.
 (Copyright 1971 by United States Steel Corporation.)

Hypereutectoid Steel

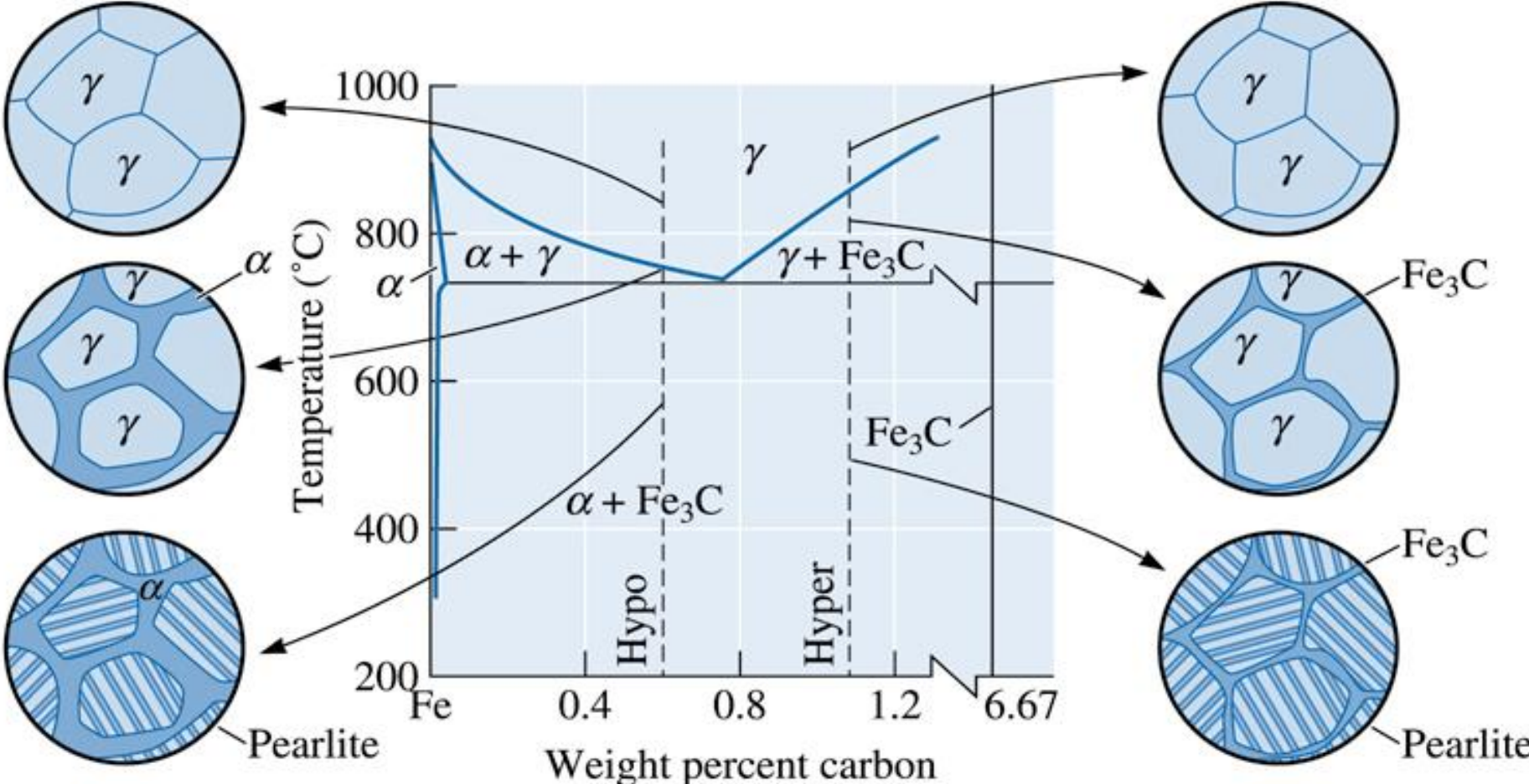


Pearlite

Proeutectoid
cementite



Evolution of microstructure of hypoeutectoid and hypereutectoid steels during cooling



Example Problem

For a 99.6 wt% Fe-0.40 wt% C steel at a temperature just below the eutectoid, determine the following:

- a) The compositions of Fe_3C and ferrite (α).
- b) The amount of cementite (in grams) that forms in 100 g of steel.
- c) The amounts of pearlite and proeutectoid ferrite (α) in the 100 g.

Solution to Example Problem

a) Using the RS tie line just below the eutectoid

$$C_{\alpha} = 0.022 \text{ wt\% C}$$

$$C_{\text{Fe}_3\text{C}} = 6.70 \text{ wt\% C}$$

b) Using the lever rule with the tie line shown

$$W_{\text{Fe}_3\text{C}} = \frac{R}{R+S} = \frac{C_0 - C_{\alpha}}{C_{\text{Fe}_3\text{C}} - C_{\alpha}}$$

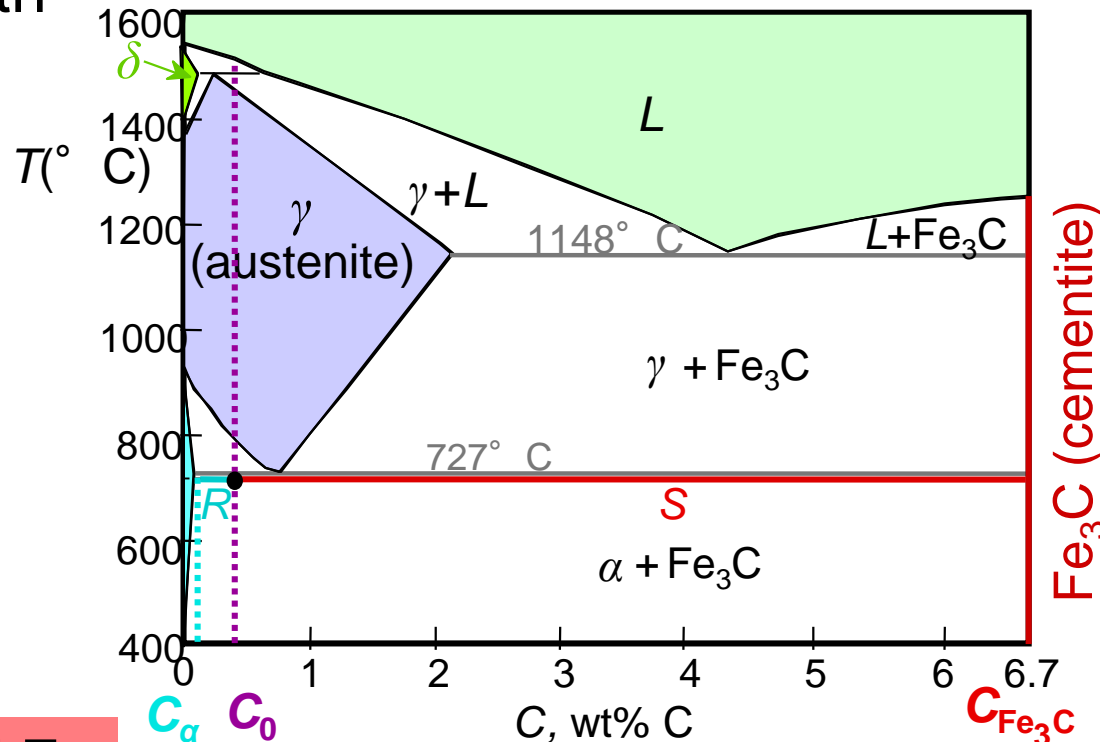
$$= \frac{0.40 - 0.022}{6.70 - 0.022} = 0.057$$

Amount of Fe_3C in 100 g

$$= (100 \text{ g}) W_{\text{Fe}_3\text{C}}$$

$$= (100 \text{ g})(0.057) = \mathbf{5.7 \text{ g}}$$

Fig. 11.23, Callister & Rethwisch 9e.
[From *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



Solution to Example Problem (cont.)

- c) Using the VX tie line just above the eutectoid and realizing that

$$C_0 = 0.40 \text{ wt\% C}$$

$$C_\alpha = 0.022 \text{ wt\% C}$$

$$C_{\text{pearlite}} = C_\gamma = 0.76 \text{ wt\% C}$$

$$W_{\text{pearlite}} = \frac{V}{V+X} = \frac{C_0 - C_\alpha}{C_\gamma - C_\alpha}$$

$$= \frac{0.40 - 0.022}{0.76 - 0.022} = 0.512$$

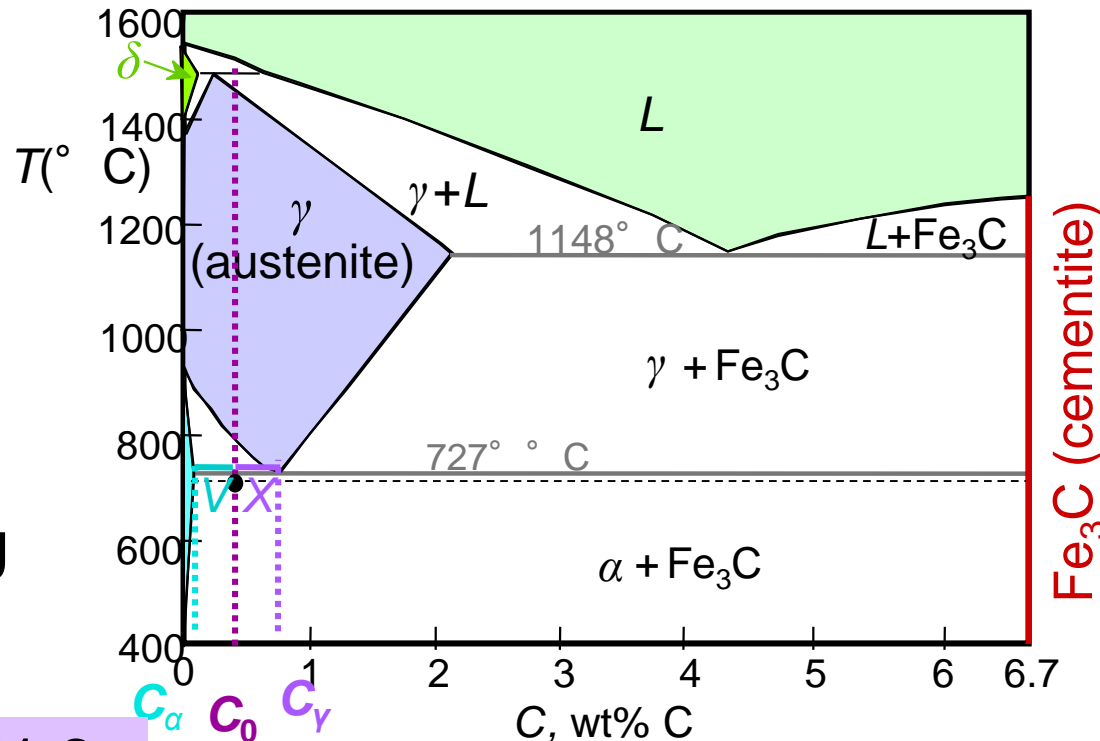
Amount of pearlite in 100 g

$$= (100 \text{ g}) W_{\text{pearlite}}$$

$$= (100 \text{ g})(0.512) = 51.2 \text{ g}$$

Fig. 11.23, Callister & Rethwisch 9e.

[From *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



Alloying with Other Elements

- $T_{\text{eutectoid}}$ changes:

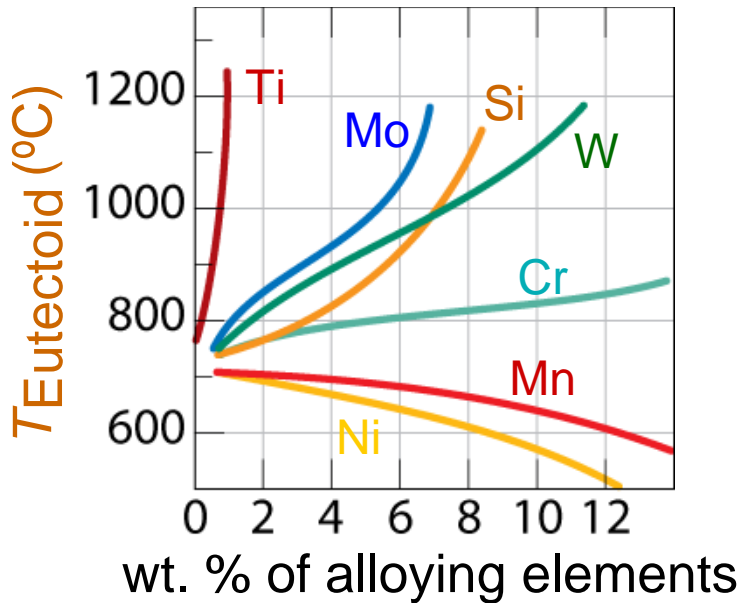


Fig. 11.33, Callister & Rethwisch 9e.
(From Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

- $C_{\text{eutectoid}}$ changes:

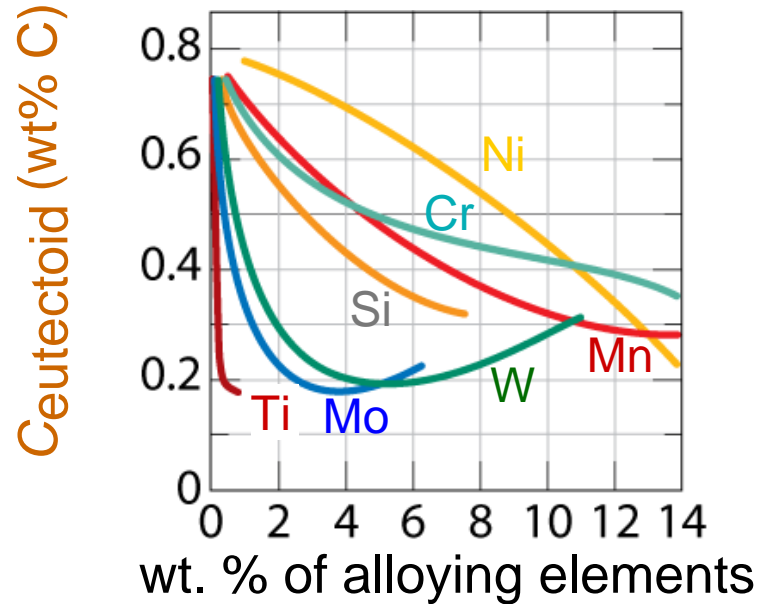
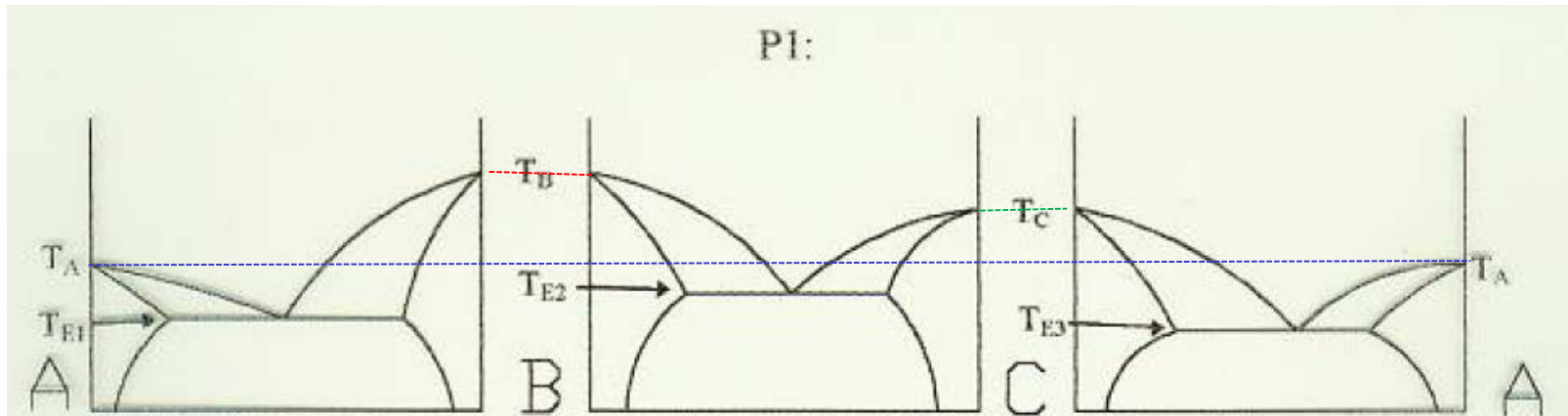


Fig. 11.34, Callister & Rethwisch 9e.
(From Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

Ternary Eutectic System (with Solid Solubility)



T_A : Melting Point Of Material A

T_B : Melting Point Of Material B

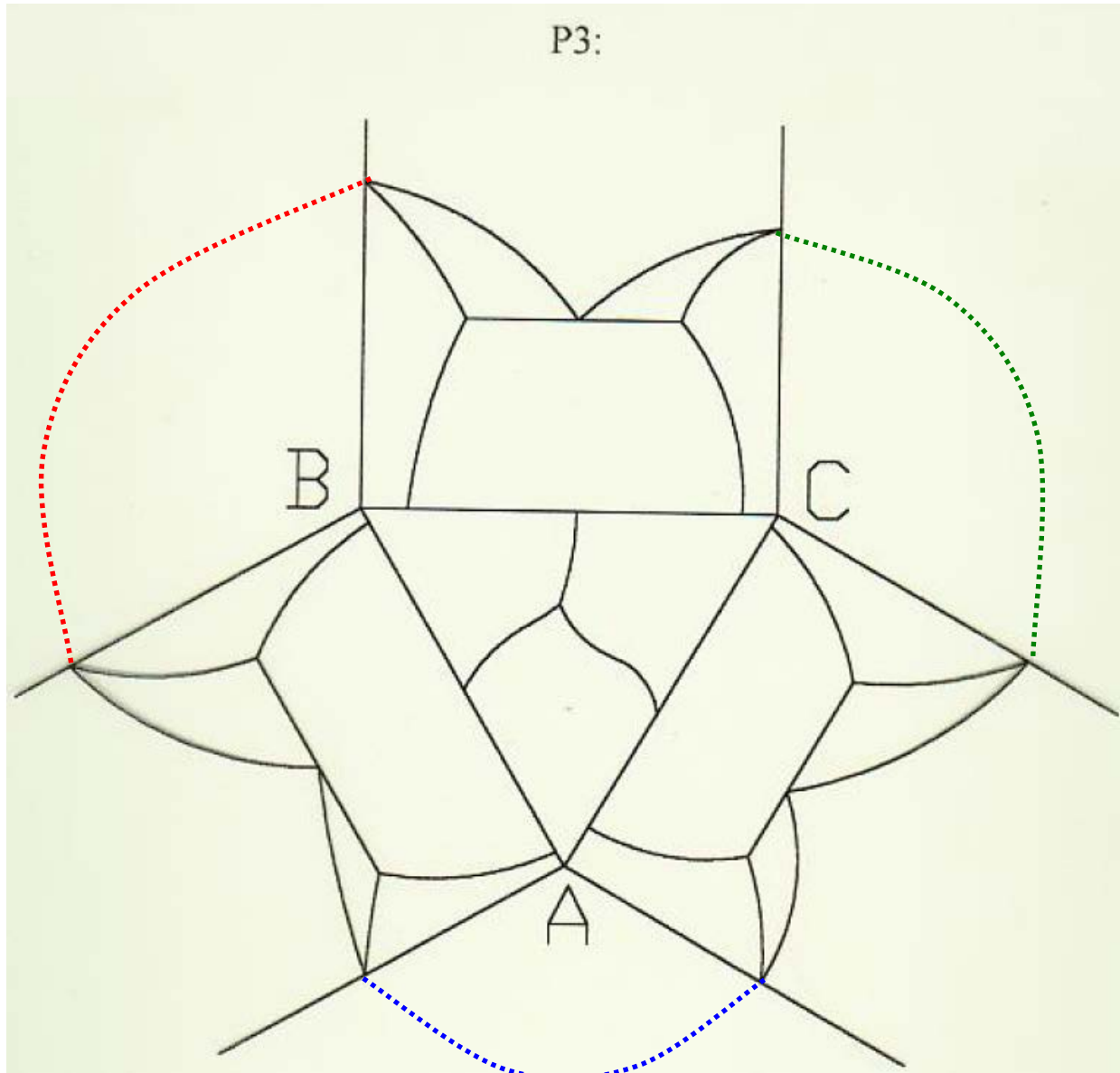
T_C : Melting Point Of Material C

T_{E1} : Eutectic Temperature Of A-B

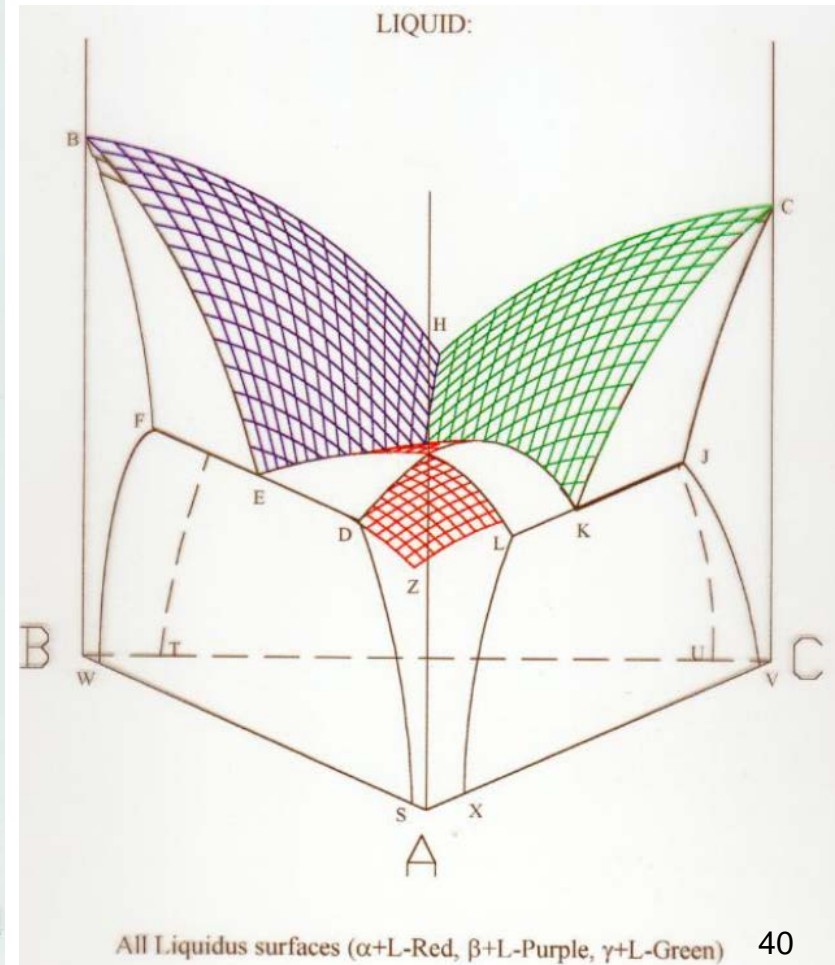
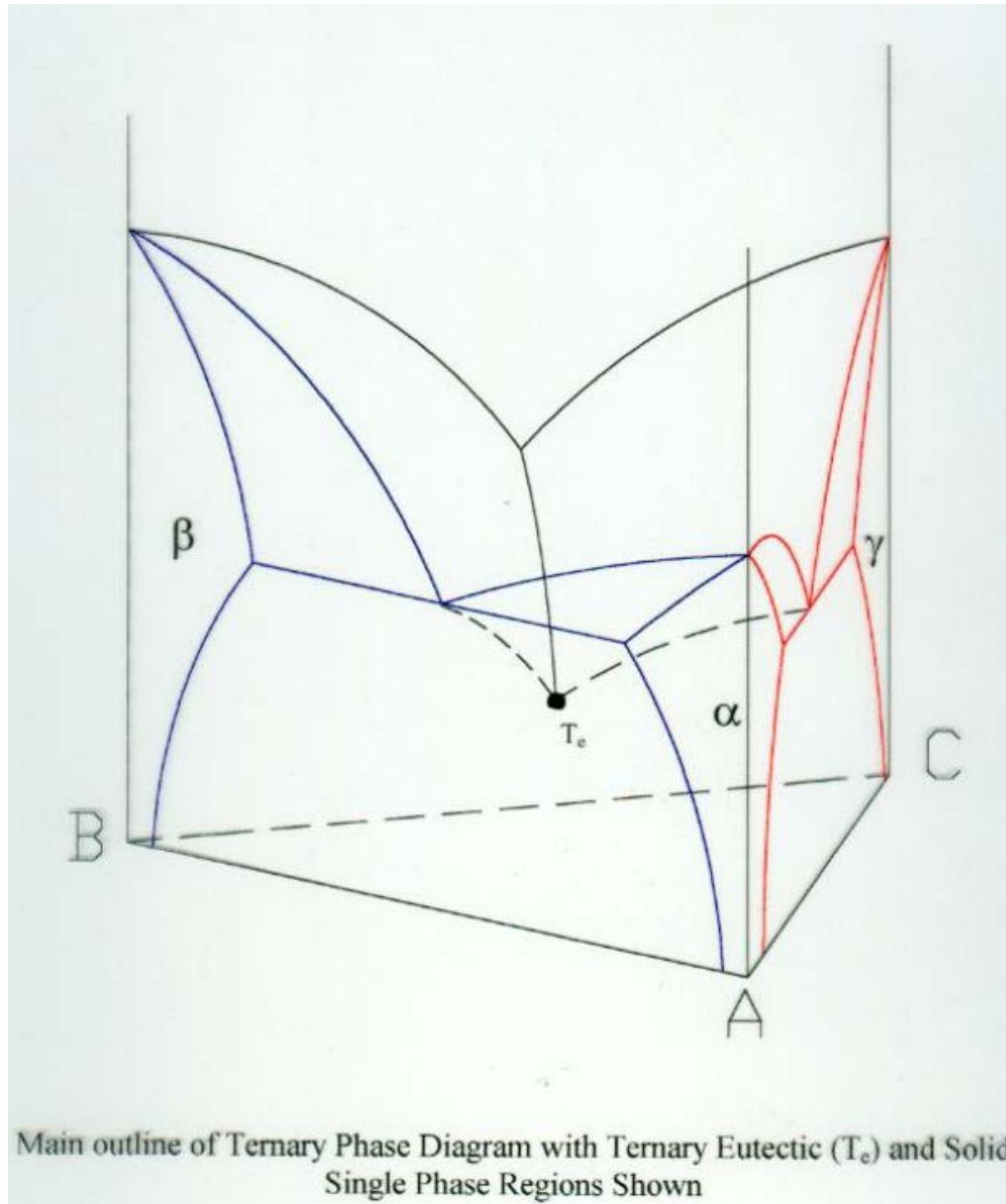
T_{E2} : Eutectic Temperature Of B-C

T_{E3} : Eutectic Temperature Of C-A

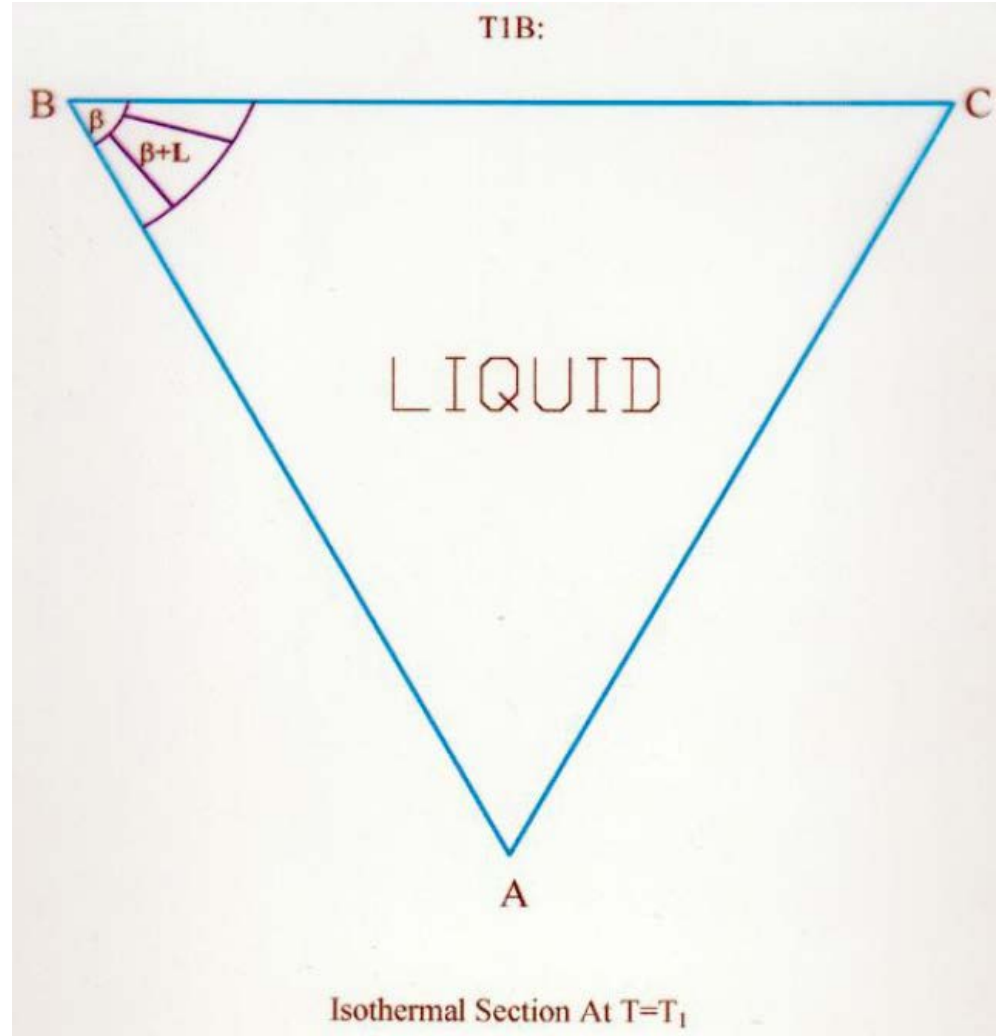
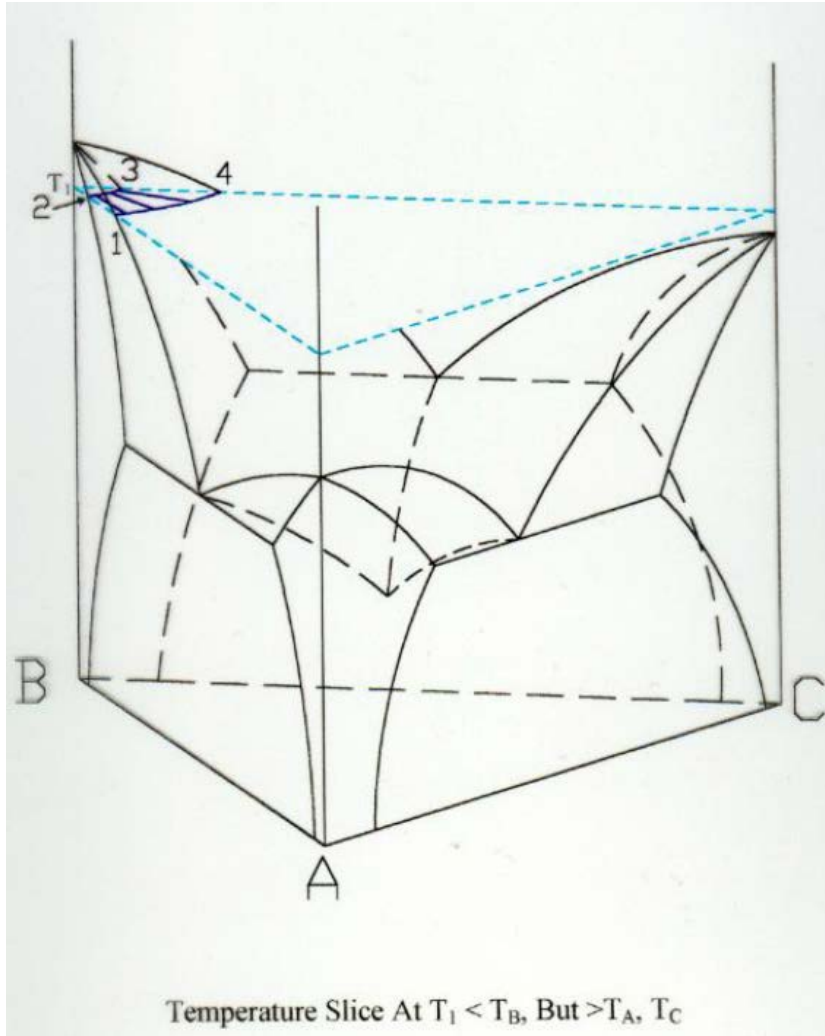
Ternary Eutectic System (with Solid Solubility)



Ternary Eutectic System (with Solid Solubility)

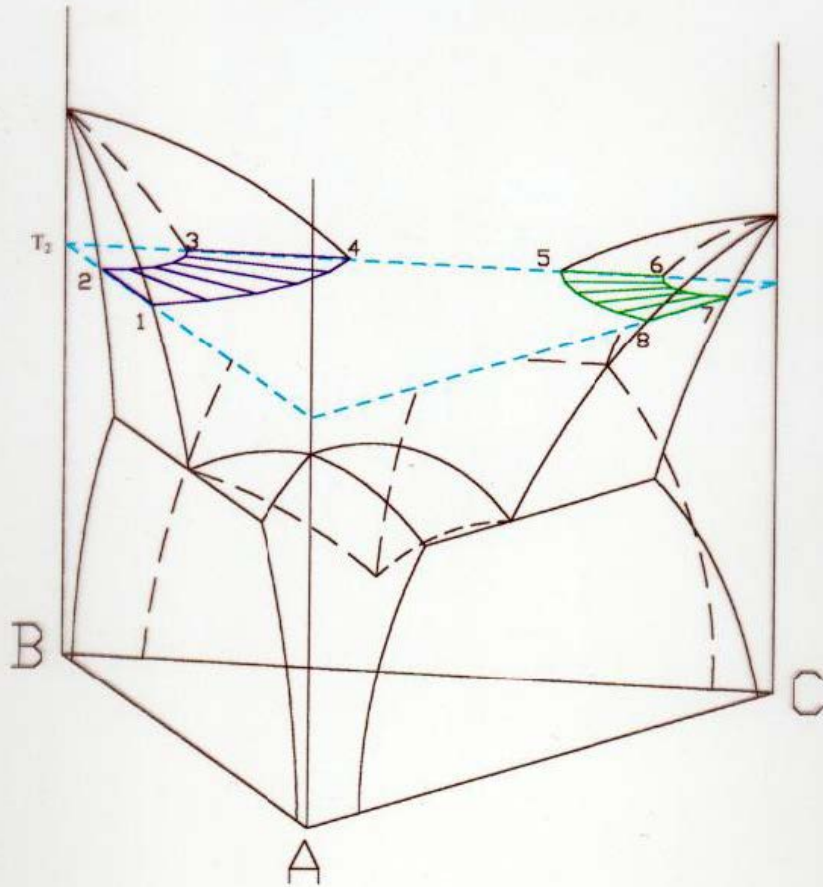


Ternary Eutectic System (with Solid Solubility)



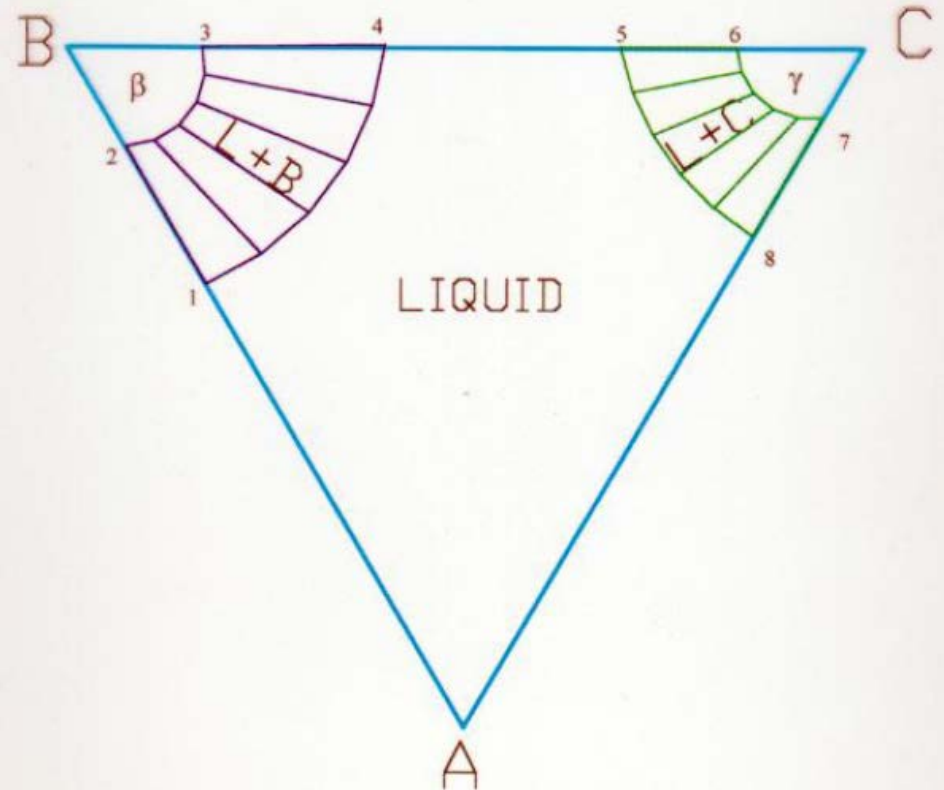
Ternary Eutectic System (with Solid Solubility)

T2A



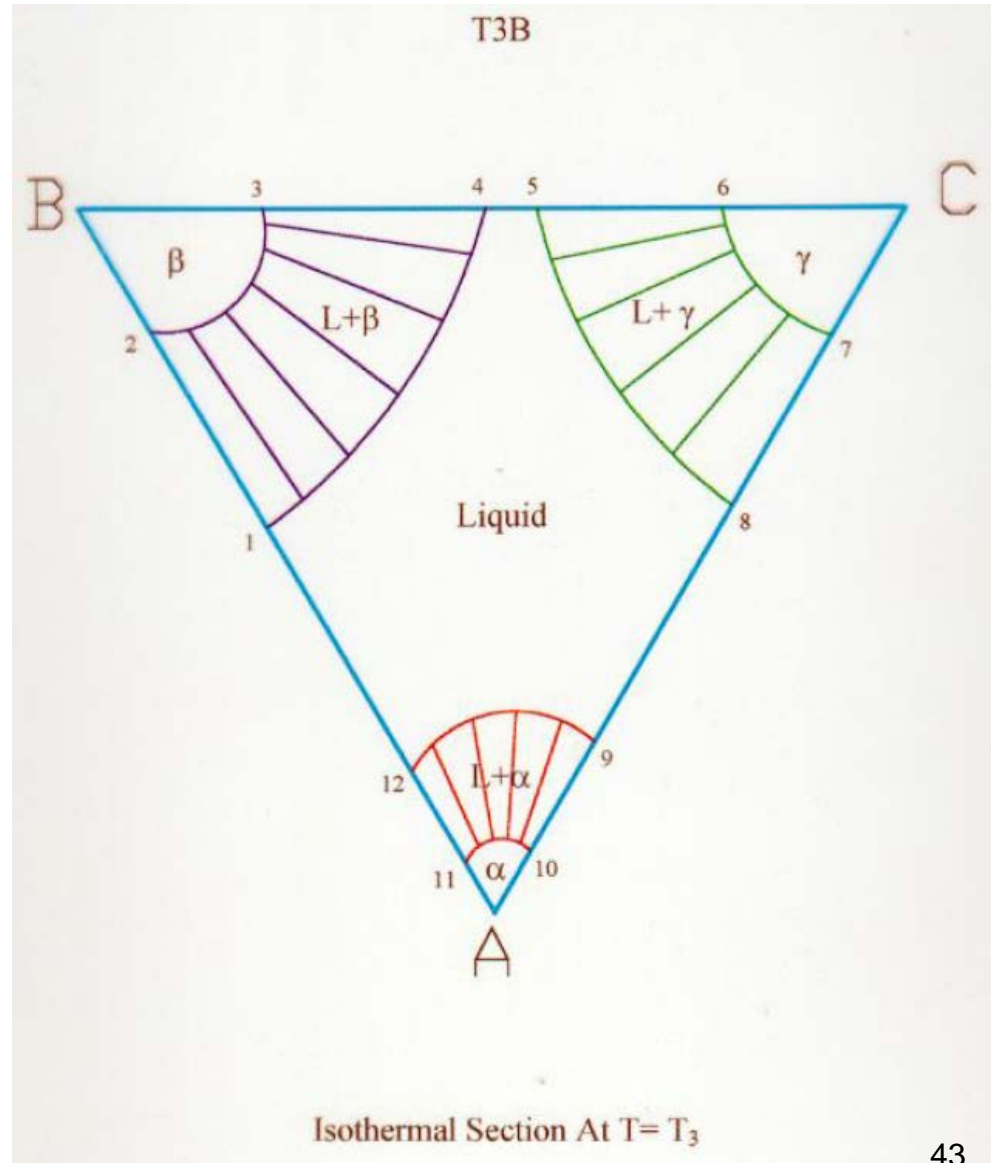
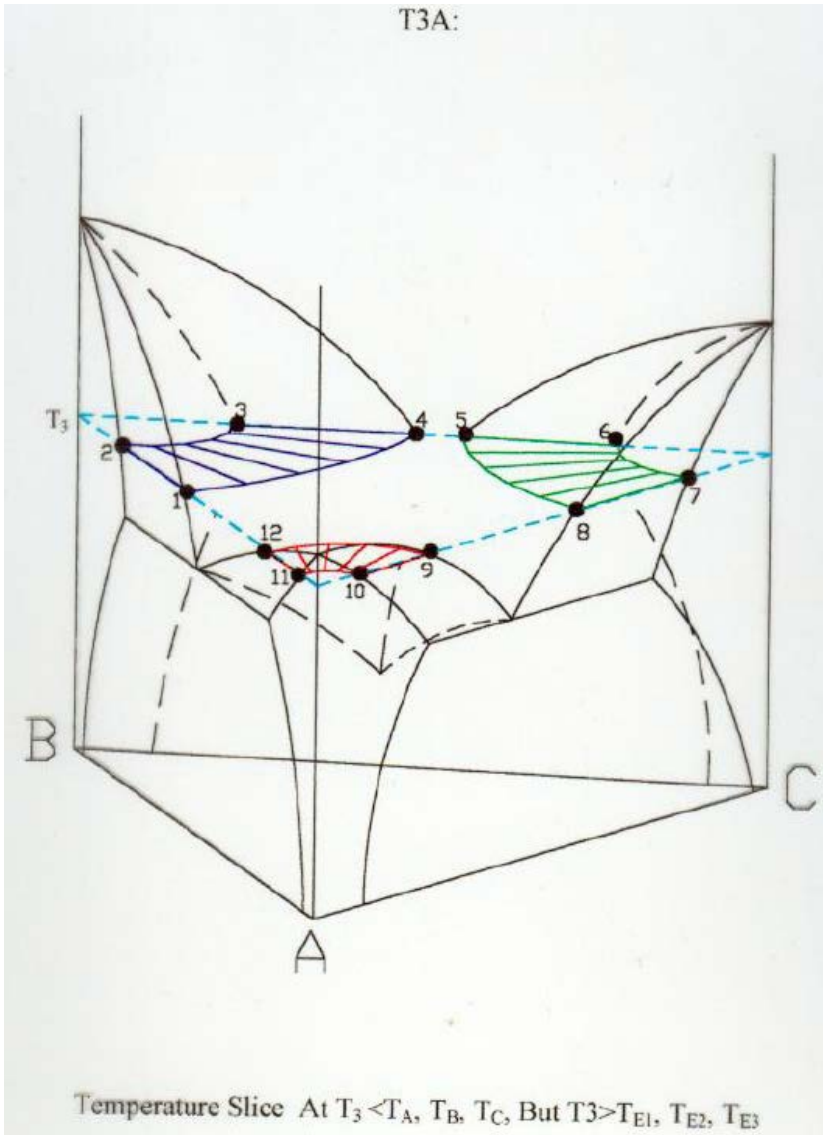
Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B, T_C$

T2B



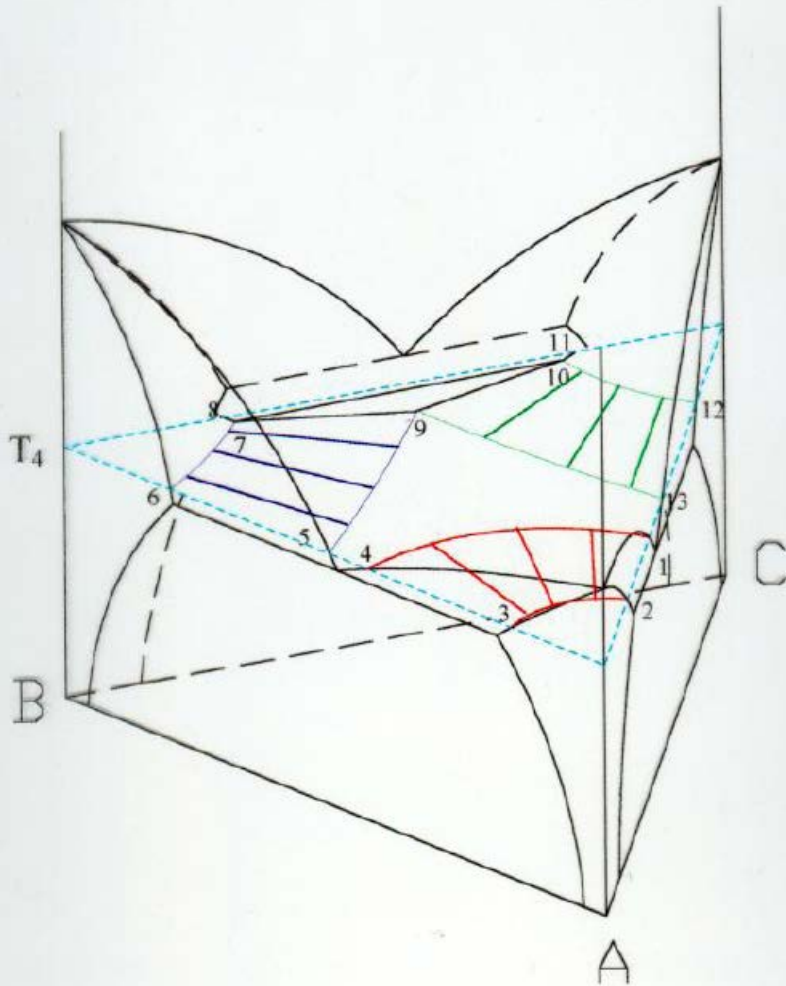
Isothermal Section At $T=T_2$

Ternary Eutectic System (with Solid Solubility)



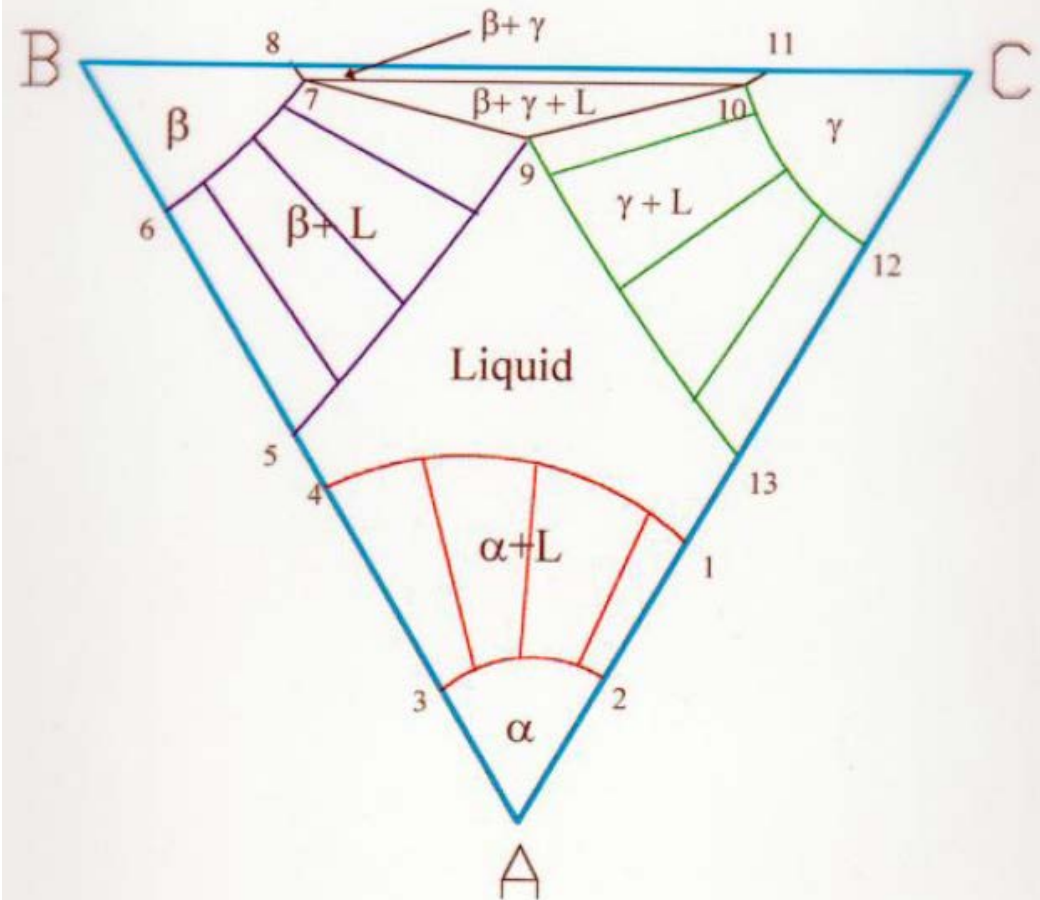
Ternary Eutectic System (with Solid Solubility)

T4A:



Temperature Slice At $T_4 < T_{E2}$ And $T_4 > T_{E1}, T_{E3}$

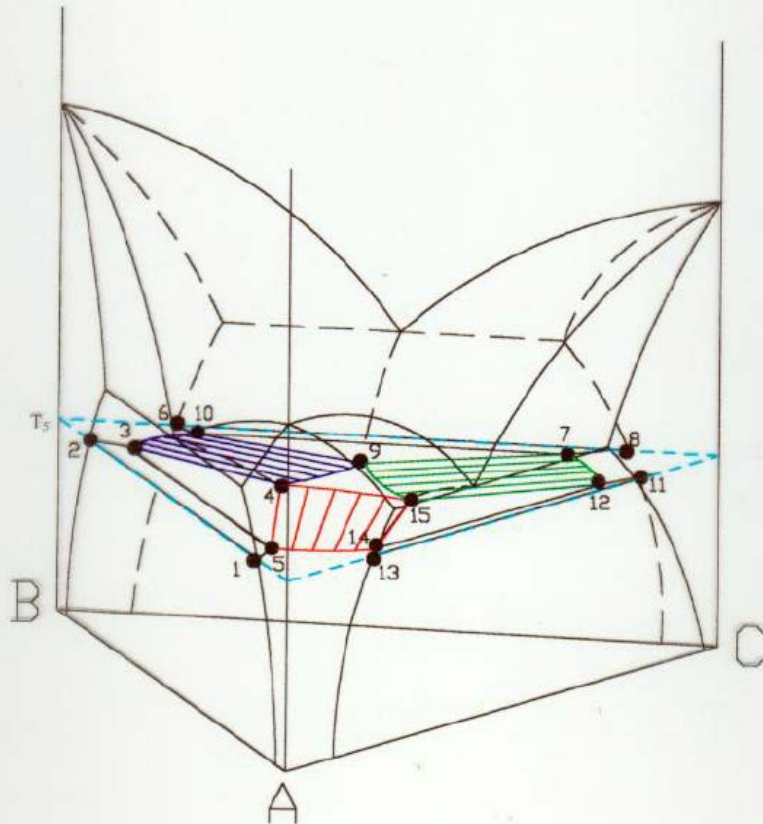
T4B:



Isothermal Section At $T = T_4$

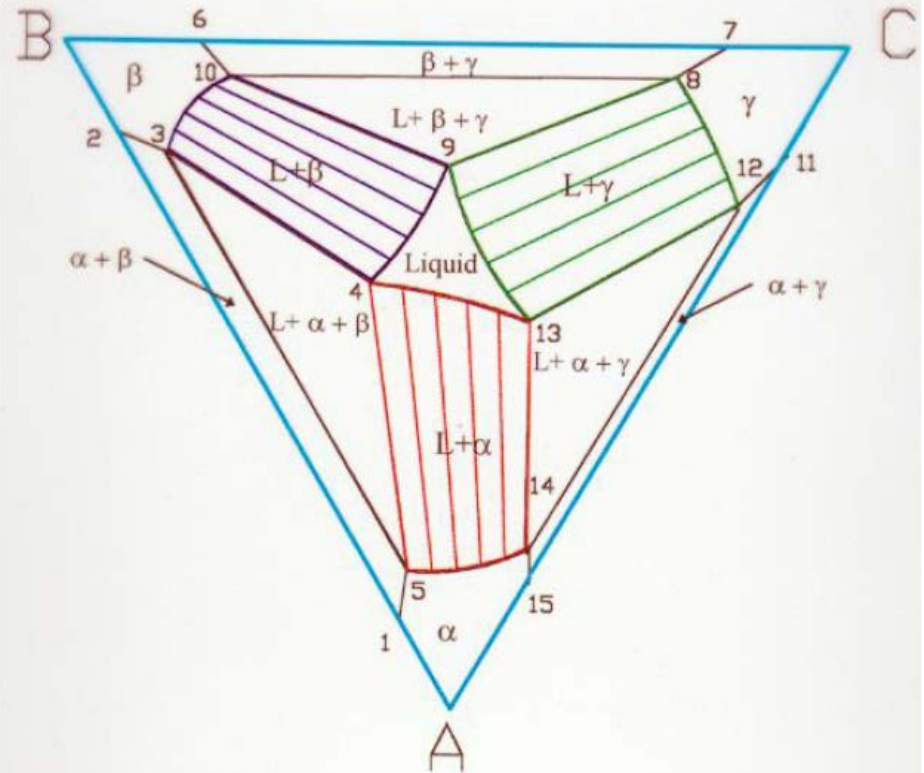
Ternary Eutectic System (with Solid Solubility)

T5A:



Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic

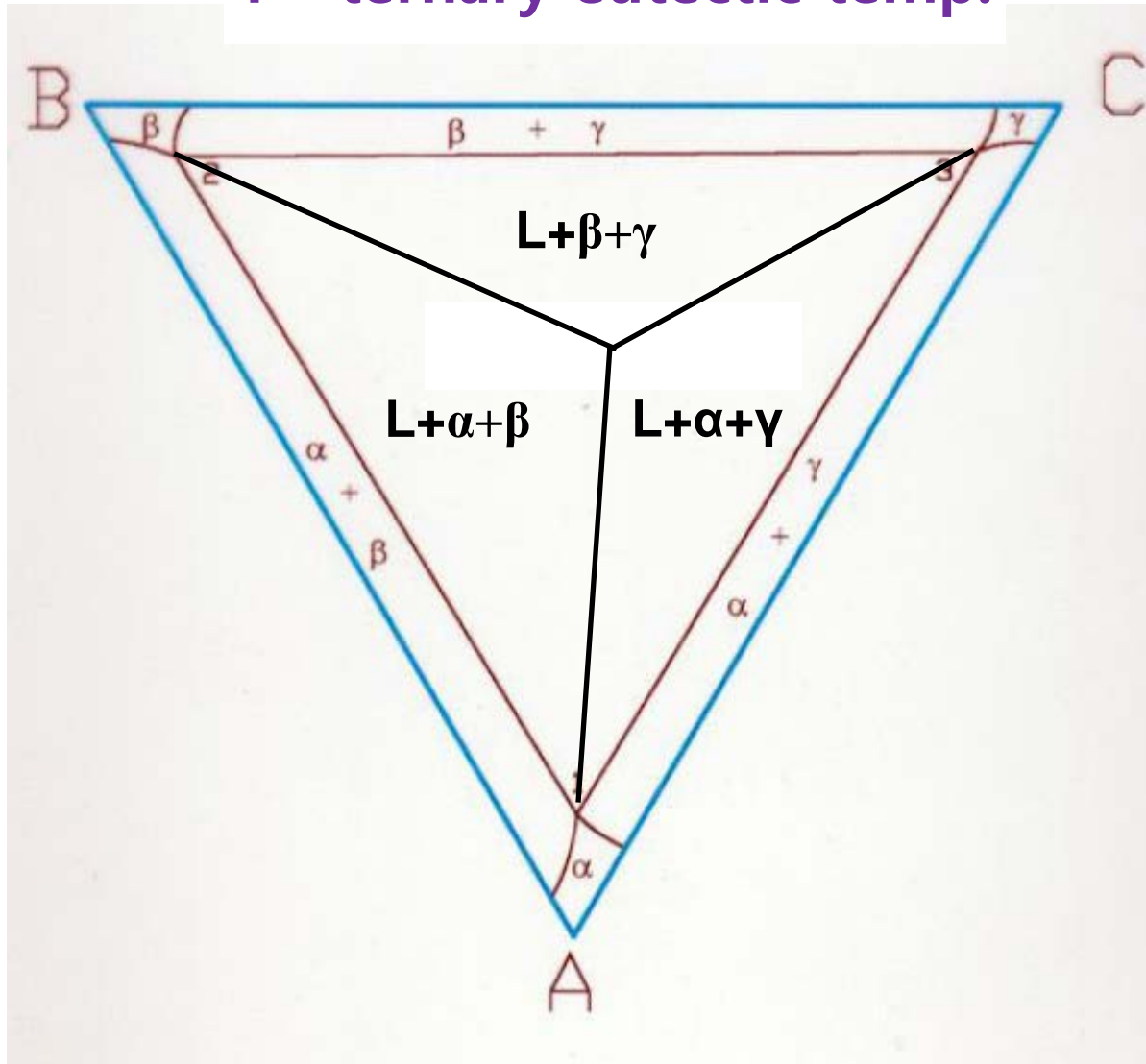
T5B:



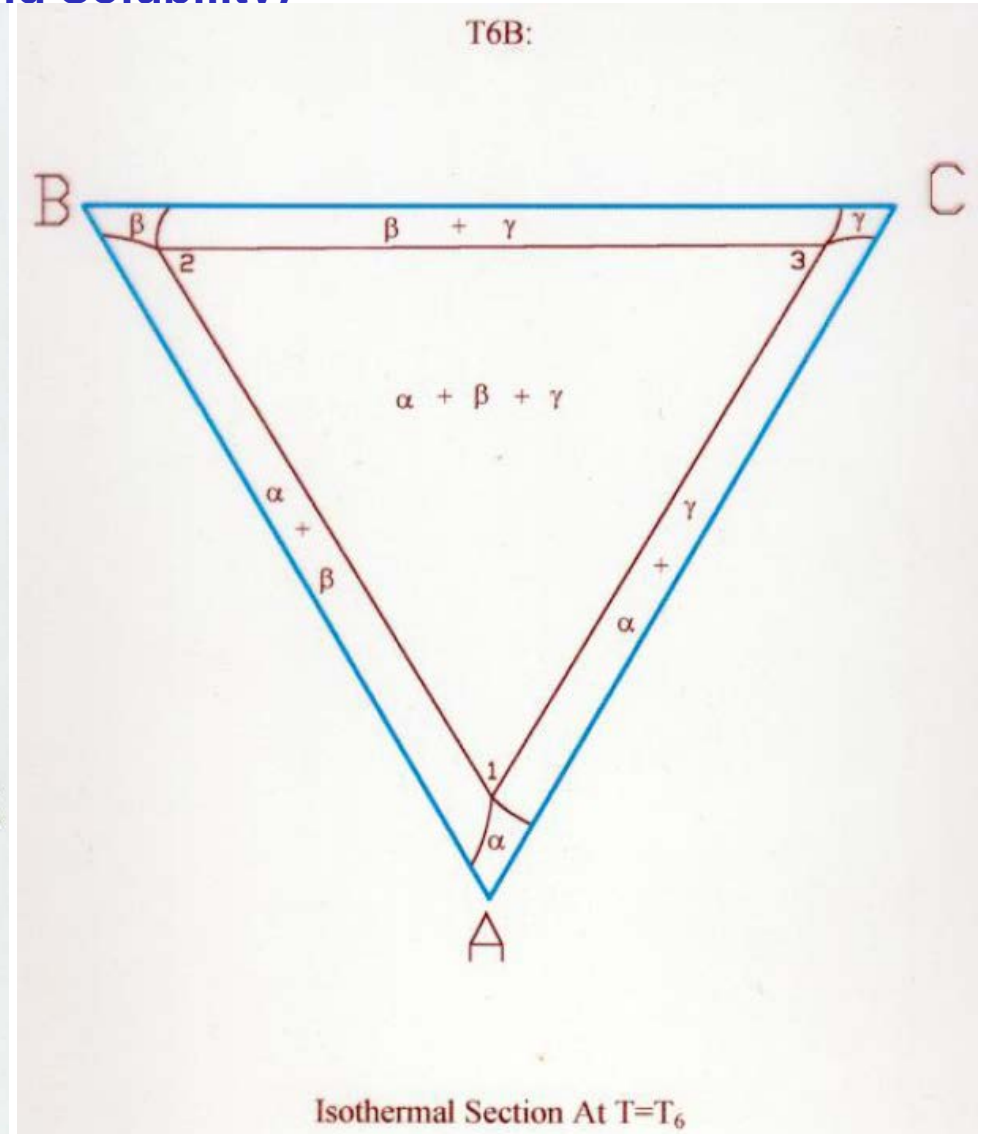
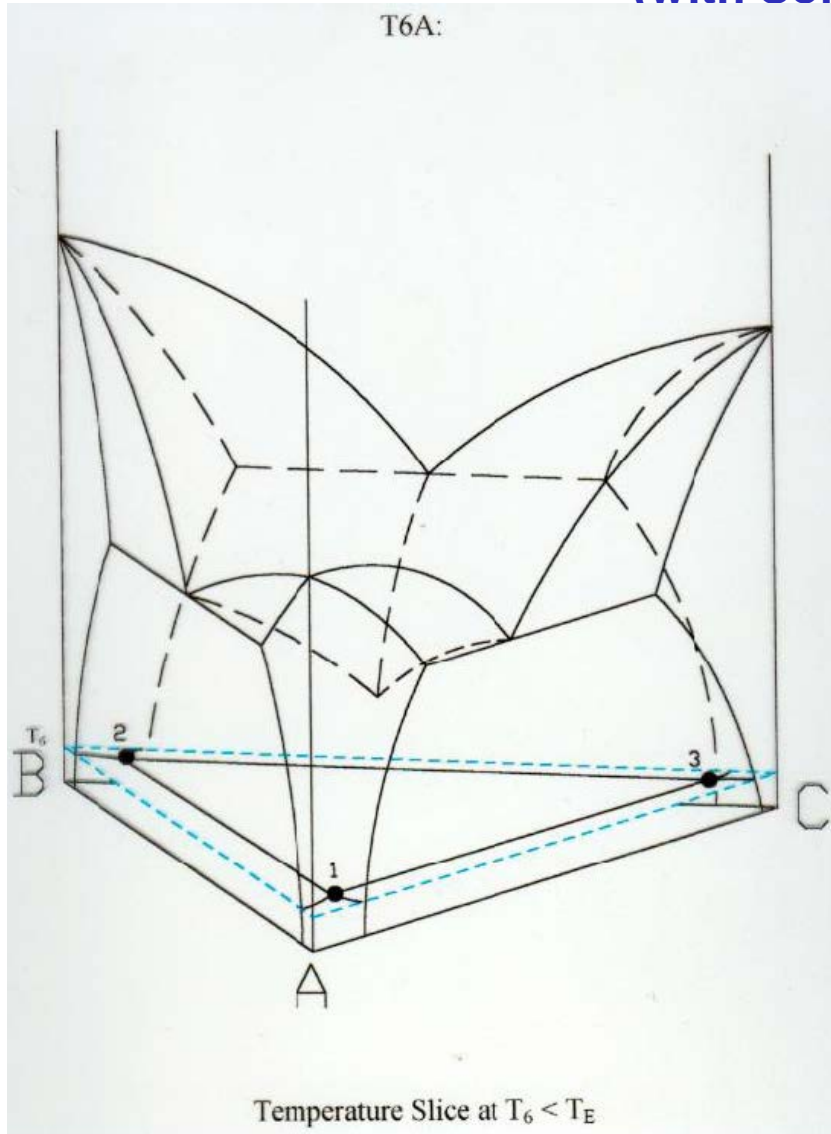
Isothermal Section At $T=T_5$

Ternary Eutectic System (with Solid Solubility)

$T =$ ternary eutectic temp.

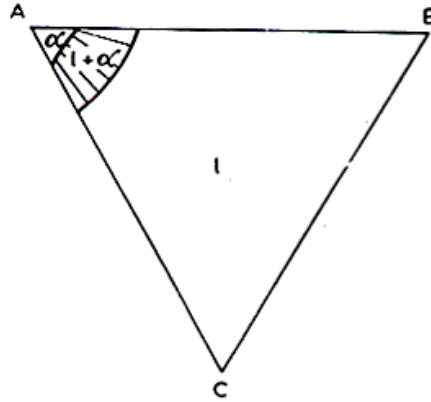


Ternary Eutectic System (with Solid Solubility)

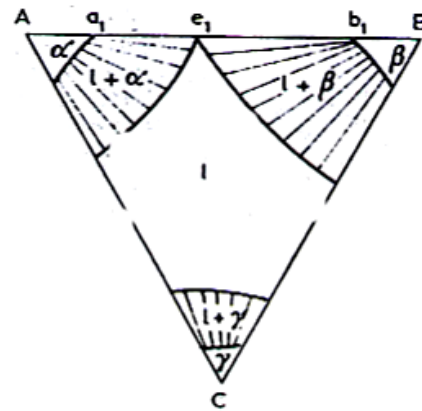


THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

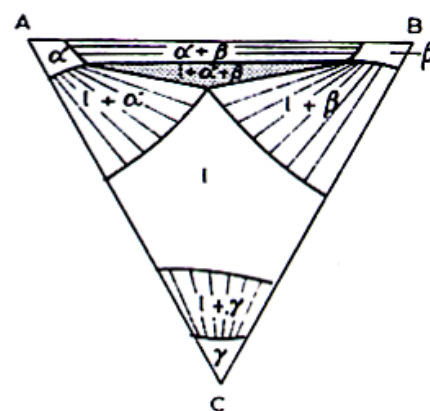
- Isothermal section ($T_A > T > T_B$)



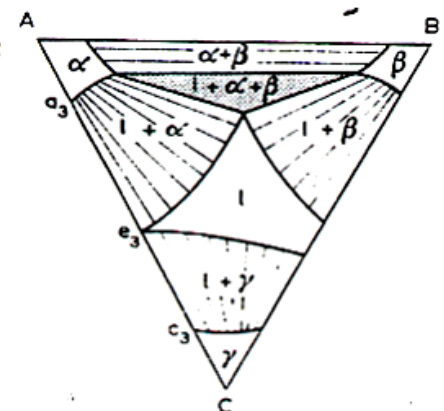
(a) $T_A > T > T_B$



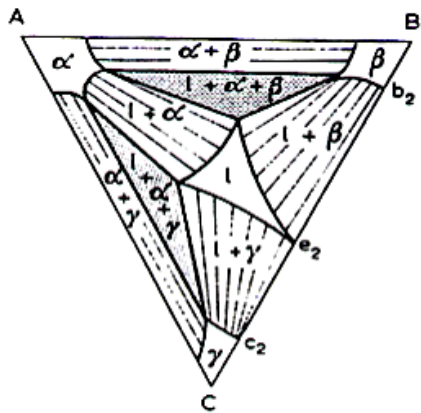
(b) $T = e_1$



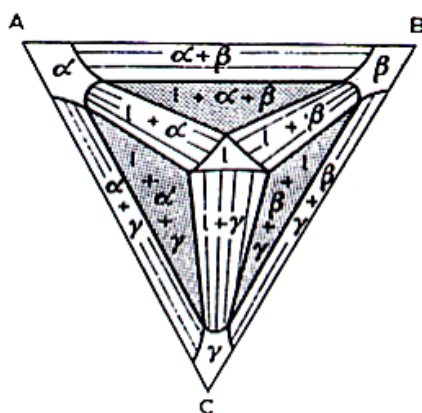
(c) $e_1 > T > e_3$



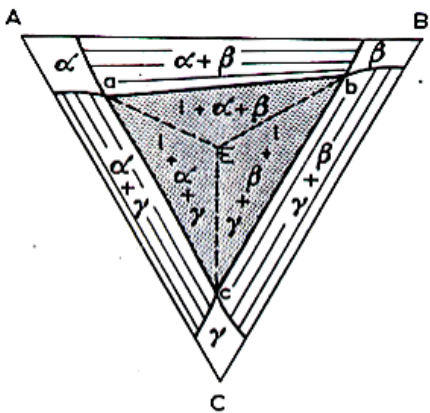
(d) $T = e_3$



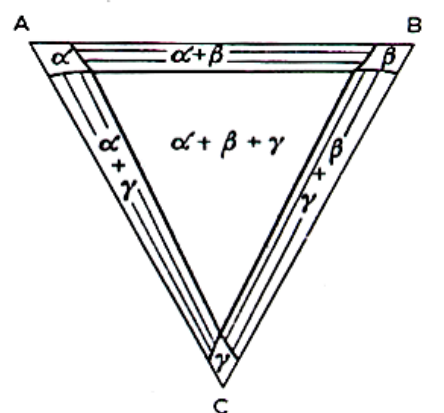
(e) $T = e_2$



(f) $e_2 > T > E$



(g) $T_A = E$



(h) $E = T$

THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section

Location of vertical section

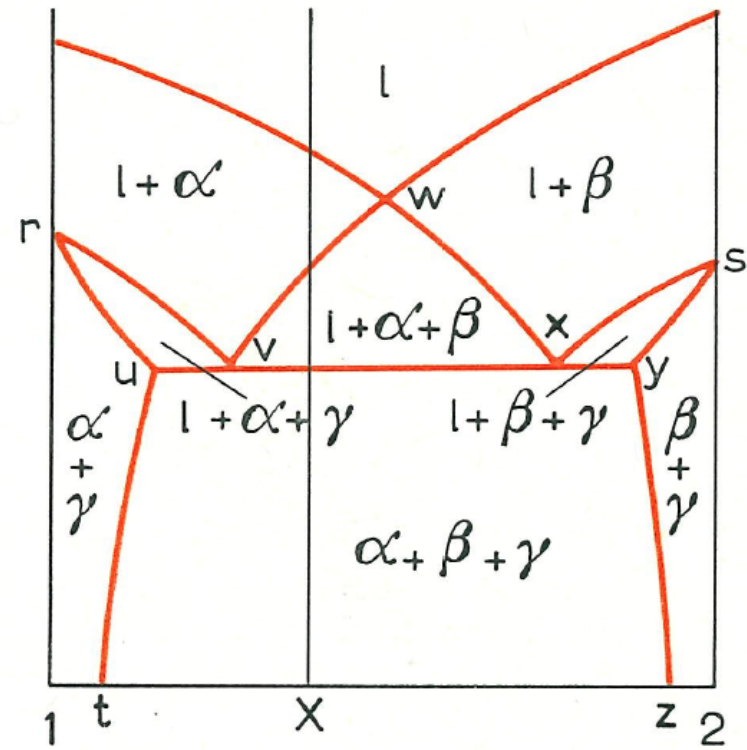
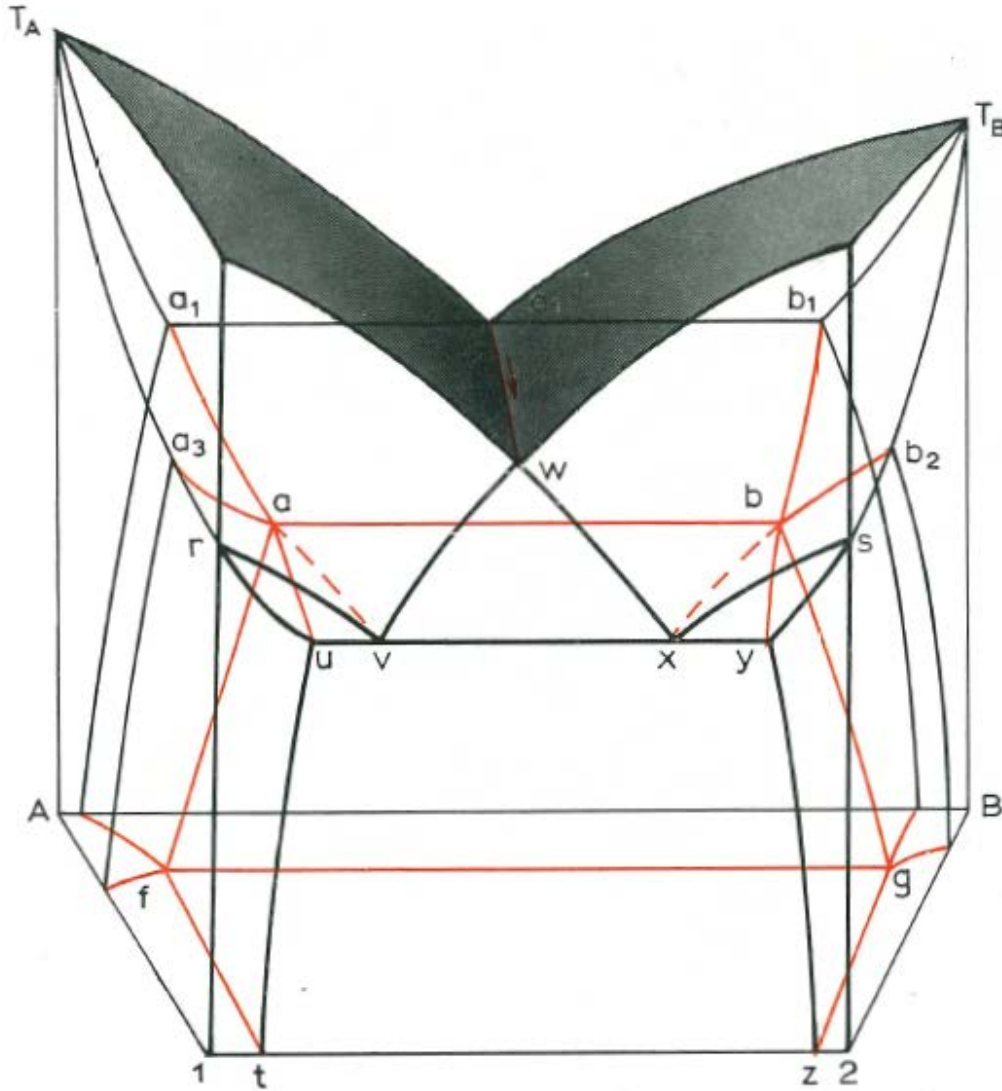


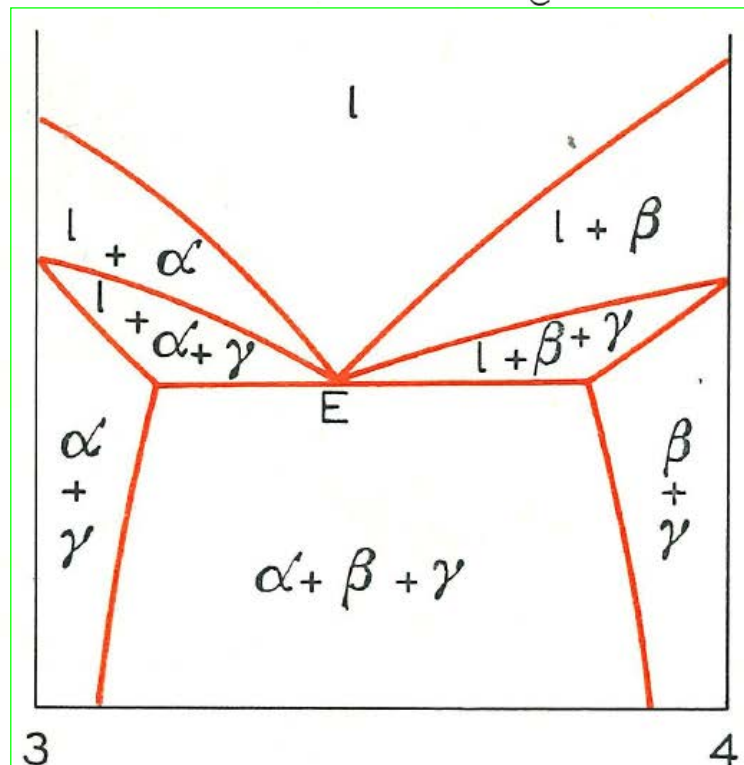
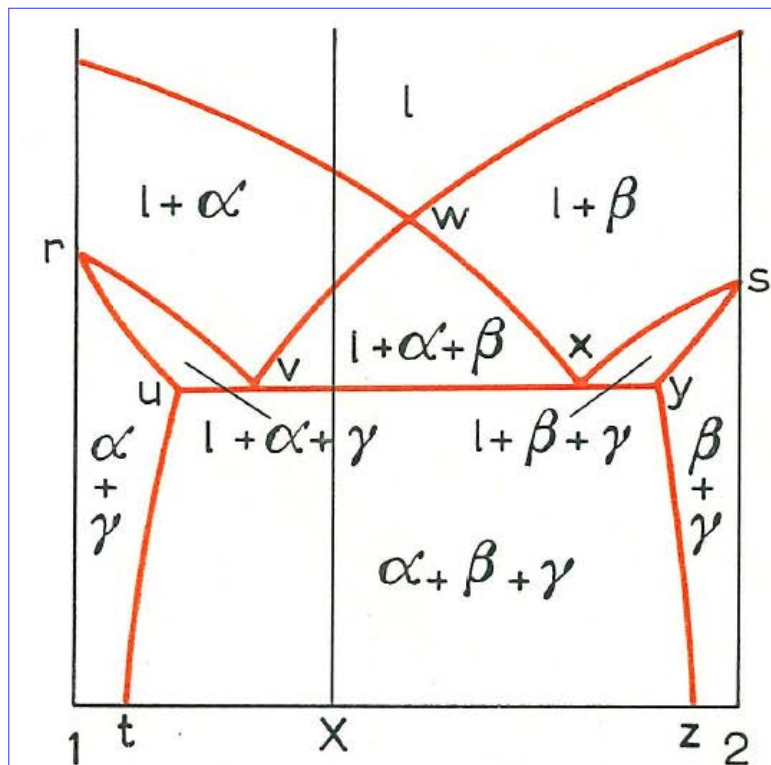
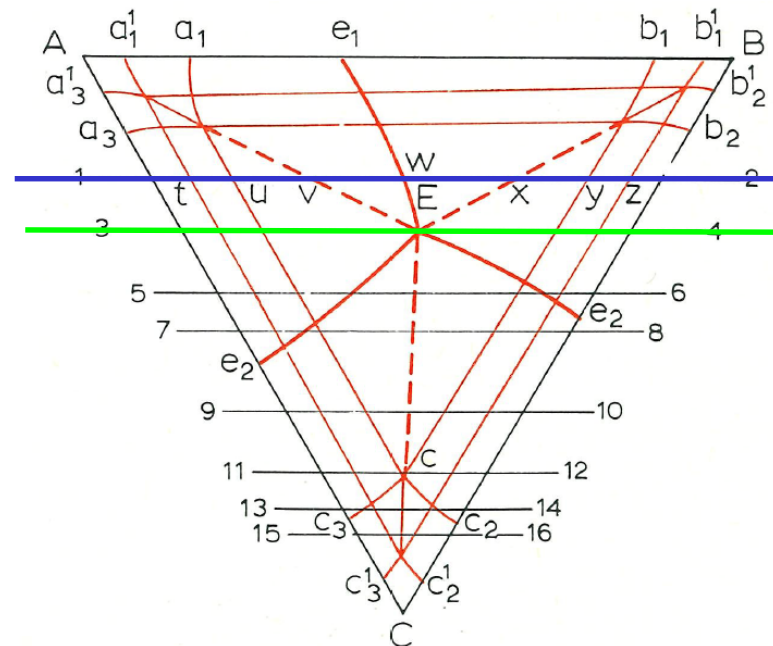
Fig. 179. Construction of vertical section 1-2.

THE EUTECTIC EQUILIBRIUM

$$(l = \alpha + \beta + \gamma)$$

Vertical section

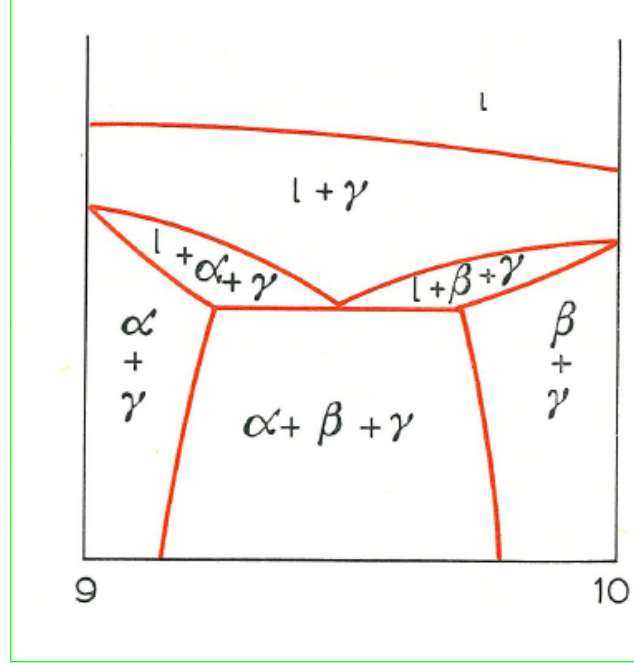
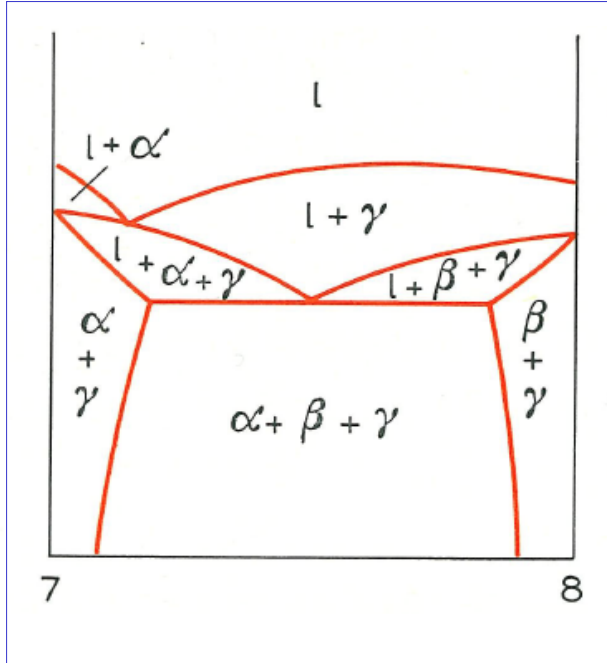
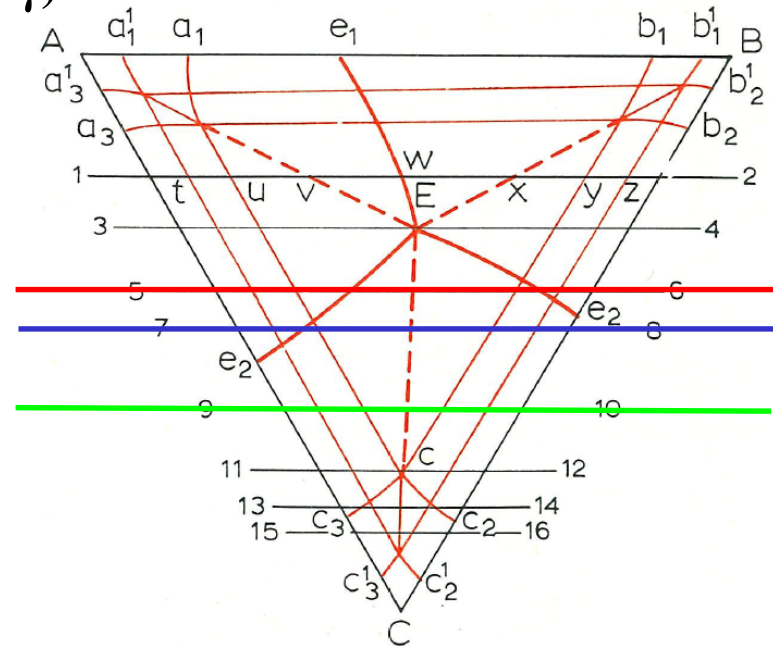
Location of vertical section



THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section

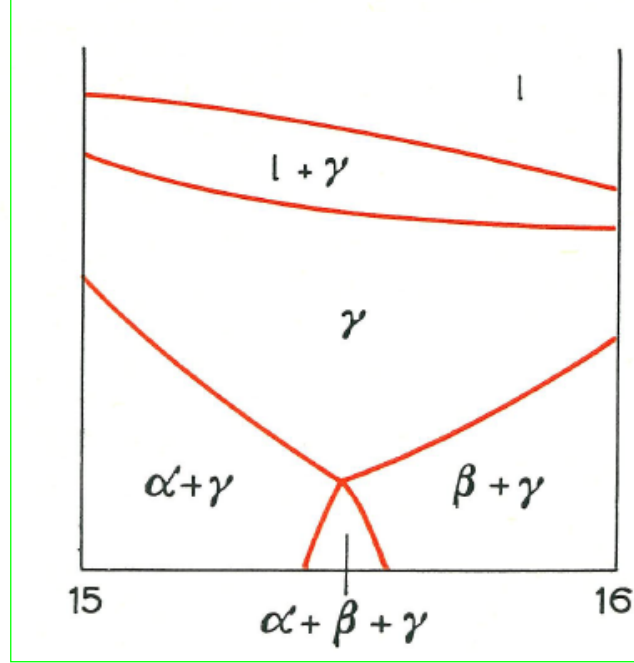
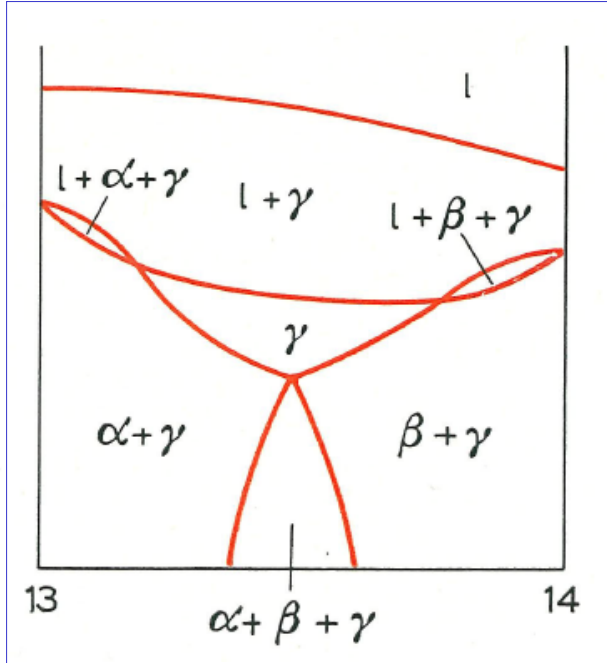
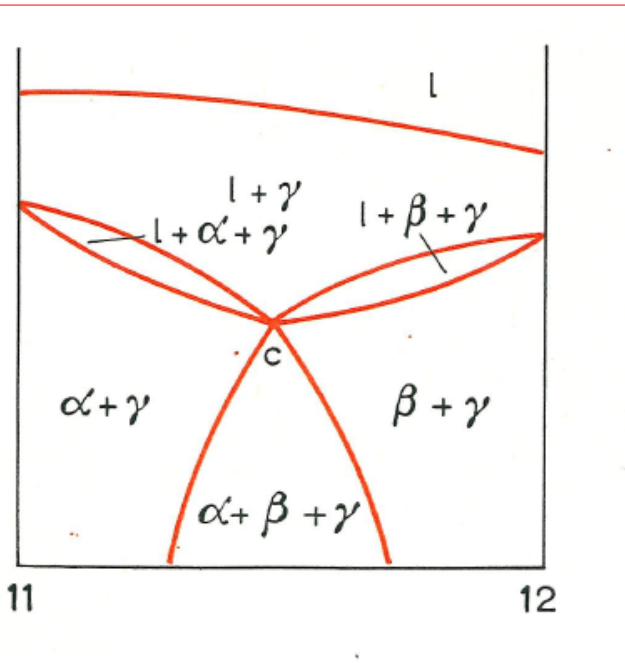
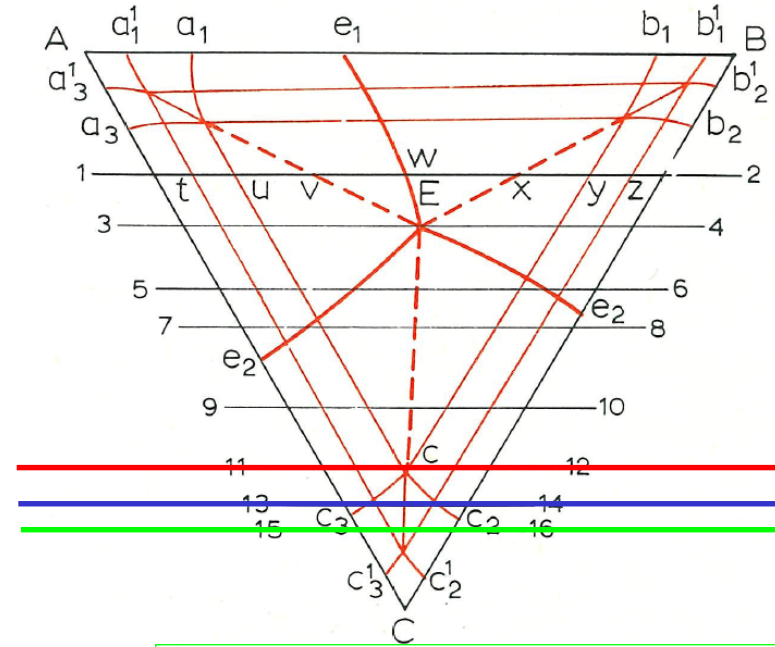
Location of vertical section



THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

Vertical section

Location of vertical section



< Quaternary phase Diagrams >

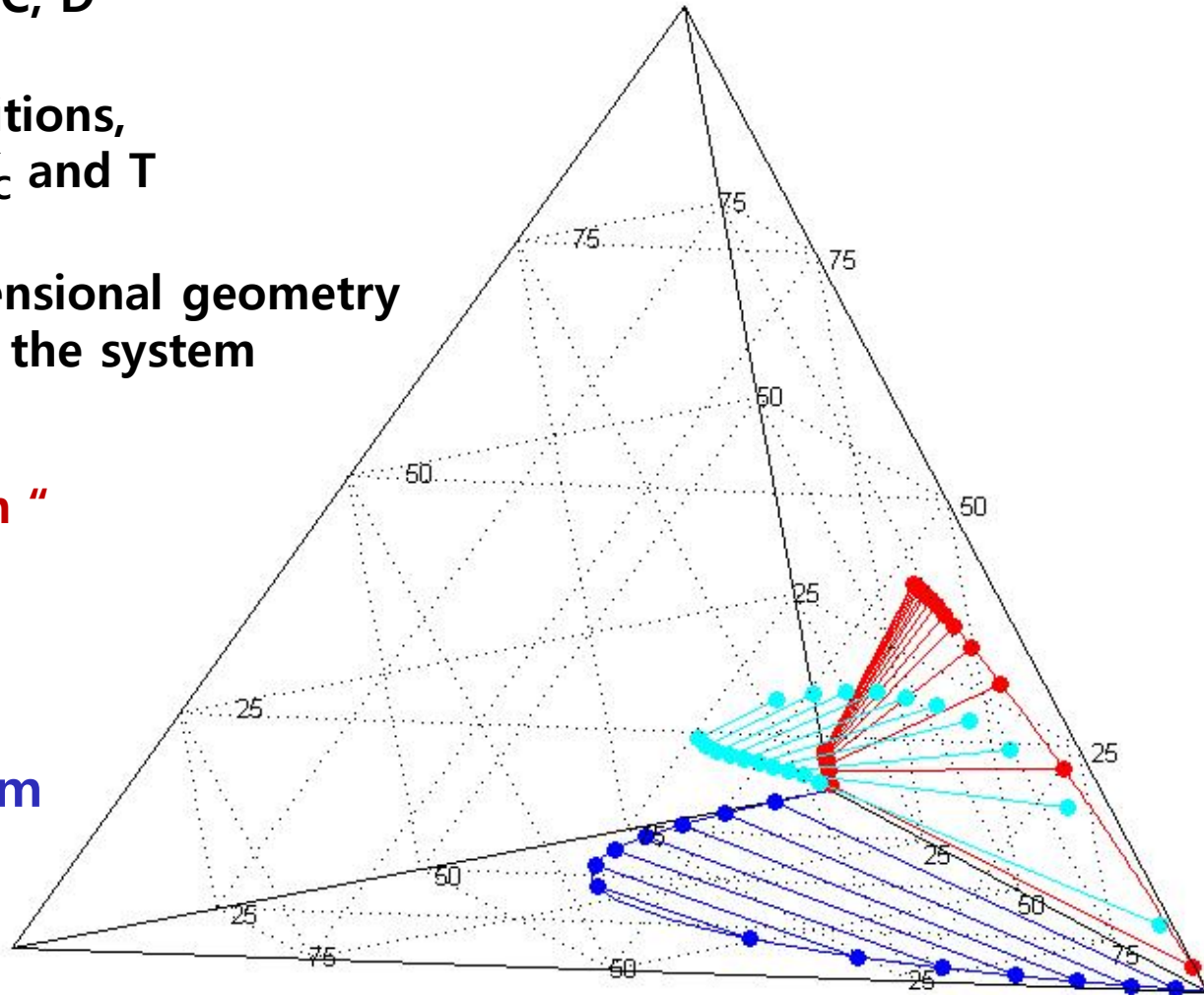
Four components: A, B, C, D

Assuming isobaric conditions,
Four variables: X_A , X_B , X_C and T

A difficulty of four-dimensional geometry
→ further restriction on the system

Most common figure:
" **equilateral tetrahedron** "

4 pure components
6 binary systems
4 ternary systems
A quaternary system



Microstructure-Properties Relationships

Alloy design &
Processing

Performance

“Phase Transformation”

Microstructure
down to atomic scale

Properties

“Tailor-made Materials Design”

Contents_Phase transformation course

**Background
to understand
phase
transformation**

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

**Representative
Phase
transformation**

(Ch4) Solidification: Liquid \rightarrow Solid

(Ch5) Diffusional Transformations in Solid: Solid \rightarrow Solid

(Ch6) Diffusionless Transformations: Solid \rightarrow Solid

Summary

- **Phase diagrams** are useful tools to determine:
 - the number and types of phases present,
 - the **composition** of each phase,
 - and the weight fraction of each phasegiven the temperature and composition of the system.
- The microstructure of an alloy depends on
 - its composition, and
 - whether or not cooling rate allows for maintenance of equilibrium.
- Important phase diagram phase transformations include **eutectic**, **eutectoid**, and **peritectic**.