Eutectic Systems

- The simplest kind of system with two solid phases is called a eutectic system.
- A eutectic system contains two solid phases at low temperature. These phases may have different crystal structures, or the same crystal structure with different lattice parameters.
- Examples:
  - Pb (FCC) and Sn (tetragonal) - solder systems
  - Fe (BCC) and C (graphite - hexagonal) - cast irons
  - Al (FCC) and Si (diamond cubic) - cast aluminum alloys
  - Cu(FCC) and Ag(FCC) – high temperature solder

Cu/Ag Eutectic System

- Copper and Silver are both FCC, but their lattice parameters and atomic radii are very different, so they have limited solubility in the solid state.
- There are two solid stable phases α and β, and at high temperatures there is a eutectic reaction where the solids α, β and the liquid coexist.

$$L(C_E) \underset{\textit{Cooling}}{\overset{\textit{Heating}}{\rightleftharpoons}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

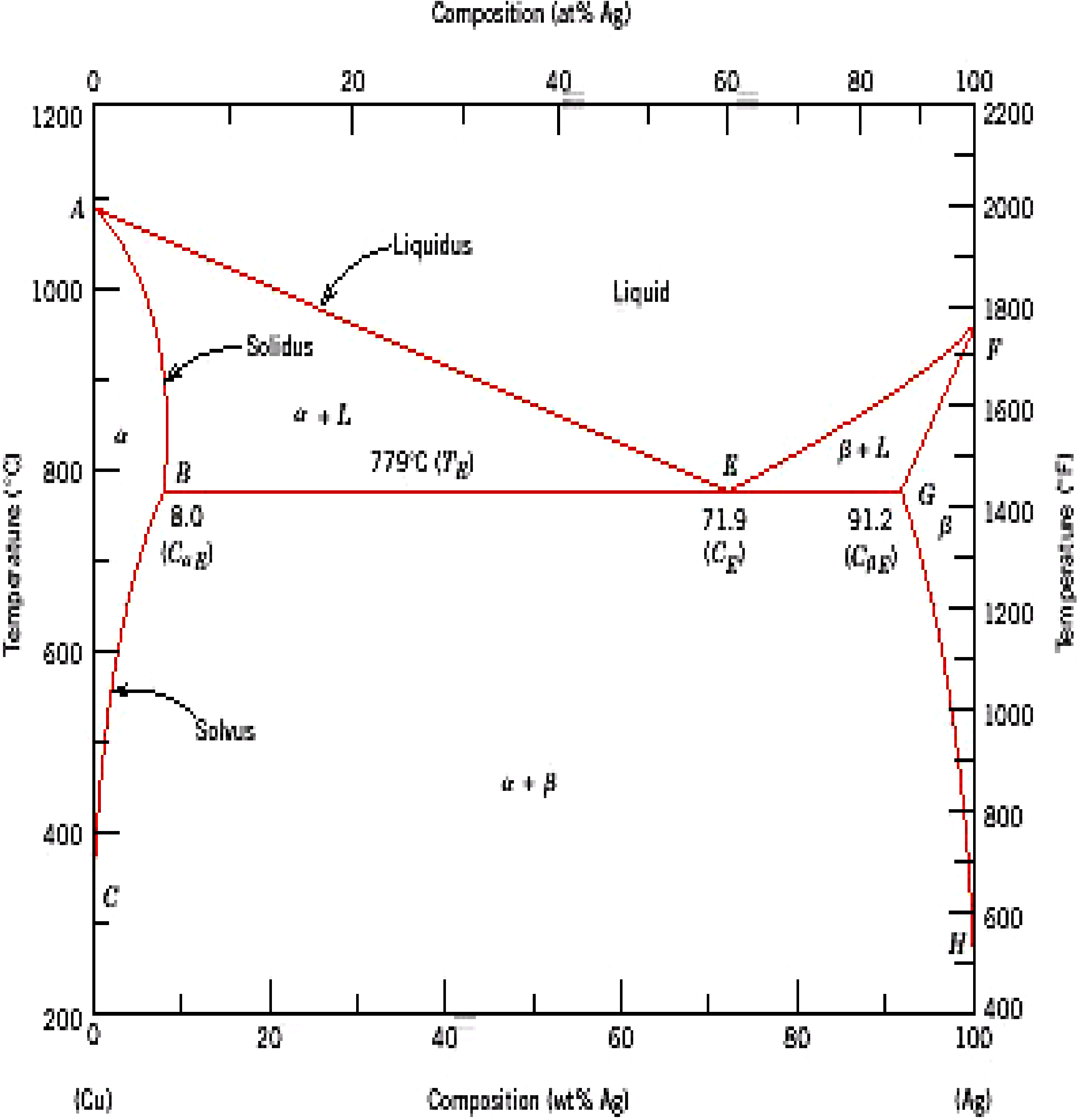


FIGURE 9.6 The copper–silver phase diagram. (Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski, Editor-in-Chief, 1990.

Cu – Ag System

Cu: α phase

Ag: β phase

Eutectic means "easily melted" in Greek

Point E: invariant point (eutectic point)

BG line: isotherm line

AB: Solidus line

FG:

BC: Solvus line

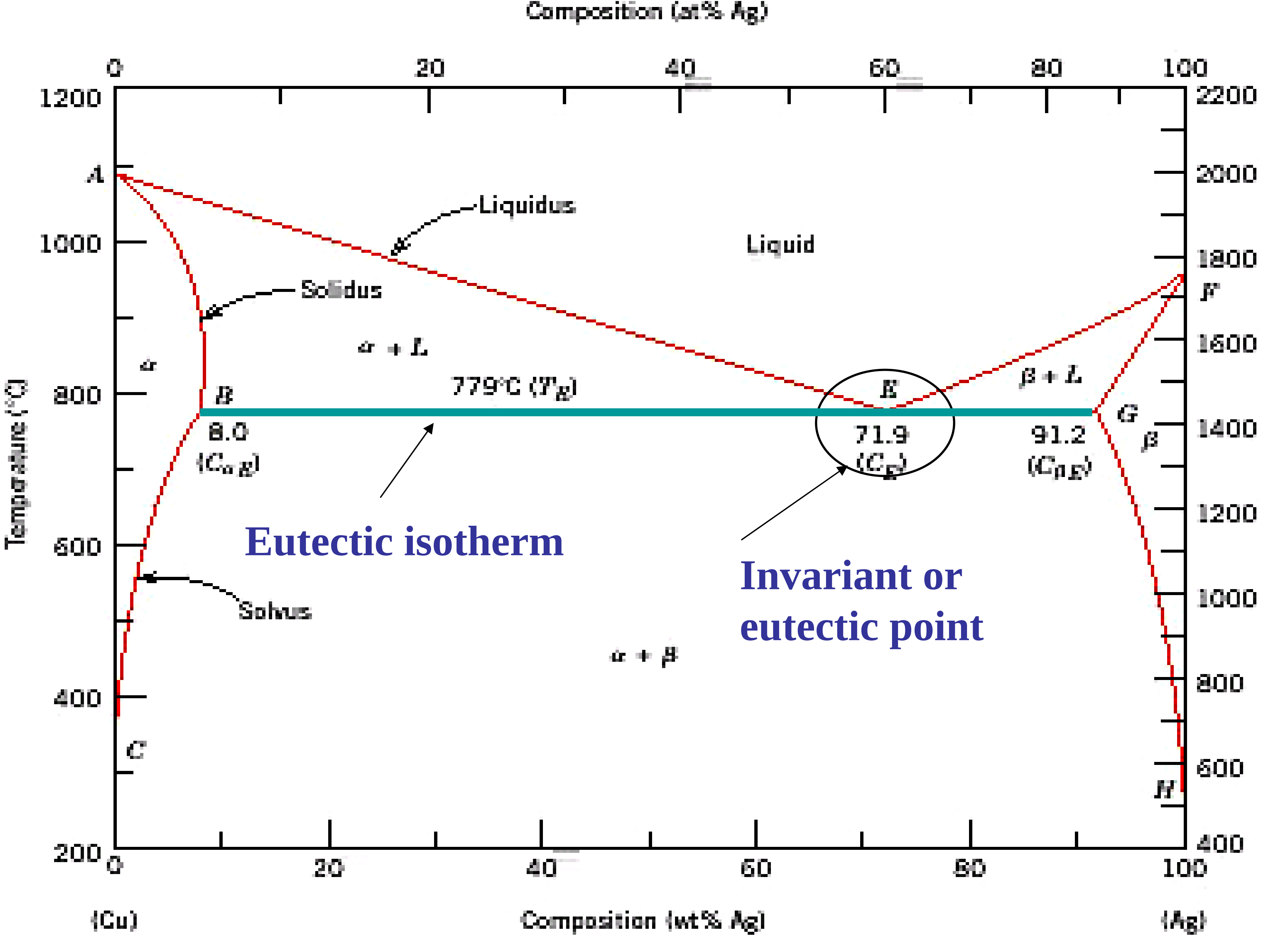
GH:

AE: Liquidus line

EF:

BEG: Solidus line, isotherm line

T_E: eutectic isotherm



Composition (at% Ag)
0
20
40
60
80
100
1200
1000
800
600
400
200
2200
2000
1800
1600
1400
1200
1000
800
600
400
A
Liquidus
Liquid
Solidus
F
α + L
α
800
B
779°C (T_E)
E
β + L
G
8.0
($C_{\alpha E}$)
71.9
(C_E)
91.2
($C_{\beta E}$)
β
Temperature (°C)
Eutectic isotherm
Invariant or
eutectic point
Solvus
α + β
C
H
0
20
40
60
80
100
(Cu)
Composition (wt% Ag)
(Ag)

Eutectic Reaction:

$$L(C_E) \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

For copper-silver system:

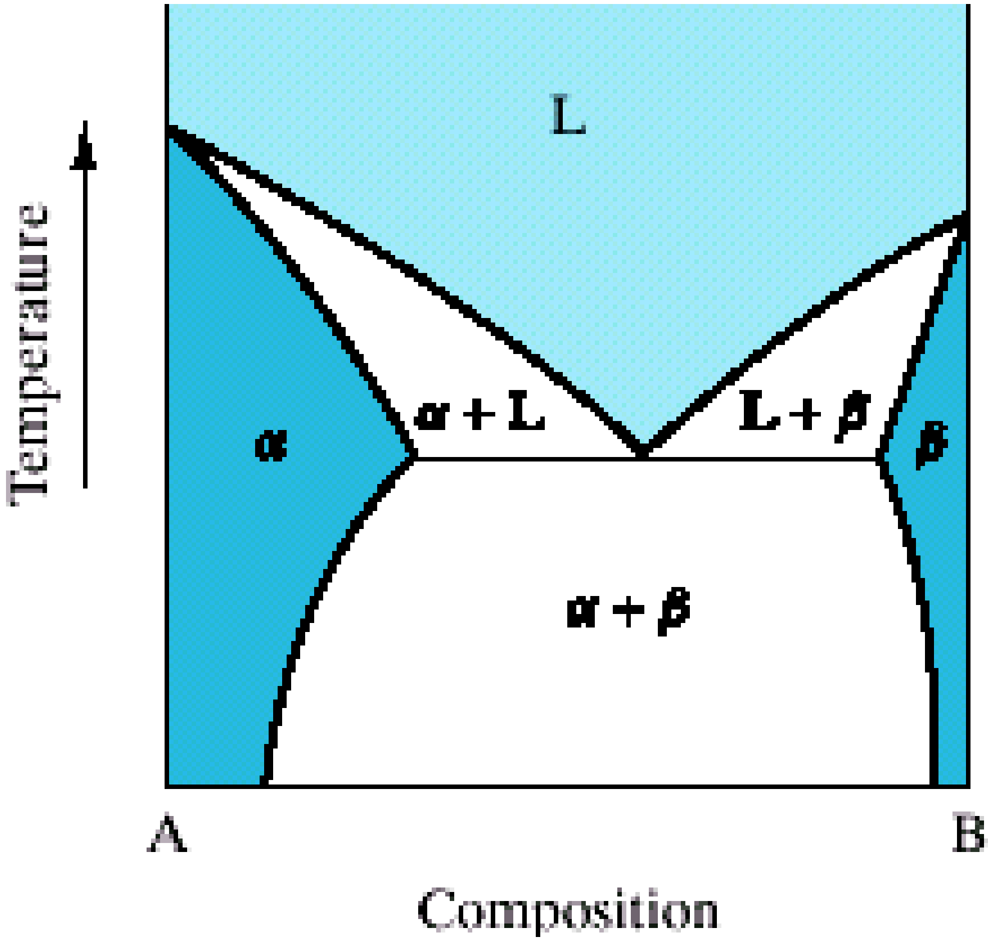
$$L(71.9\text{wt\%Ag}) \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \alpha(8.0\text{wt\%Ag}) + \beta(91.2wt\%Ag)$$

Eutectic or invariant point - Liquid and two solid phases co-exist in equilibrium at the eutectic composition C_E and the eutectic temperature T_E.

Eutectic isotherm - horizontal solidus line at T_E.

Binary Eutectic System

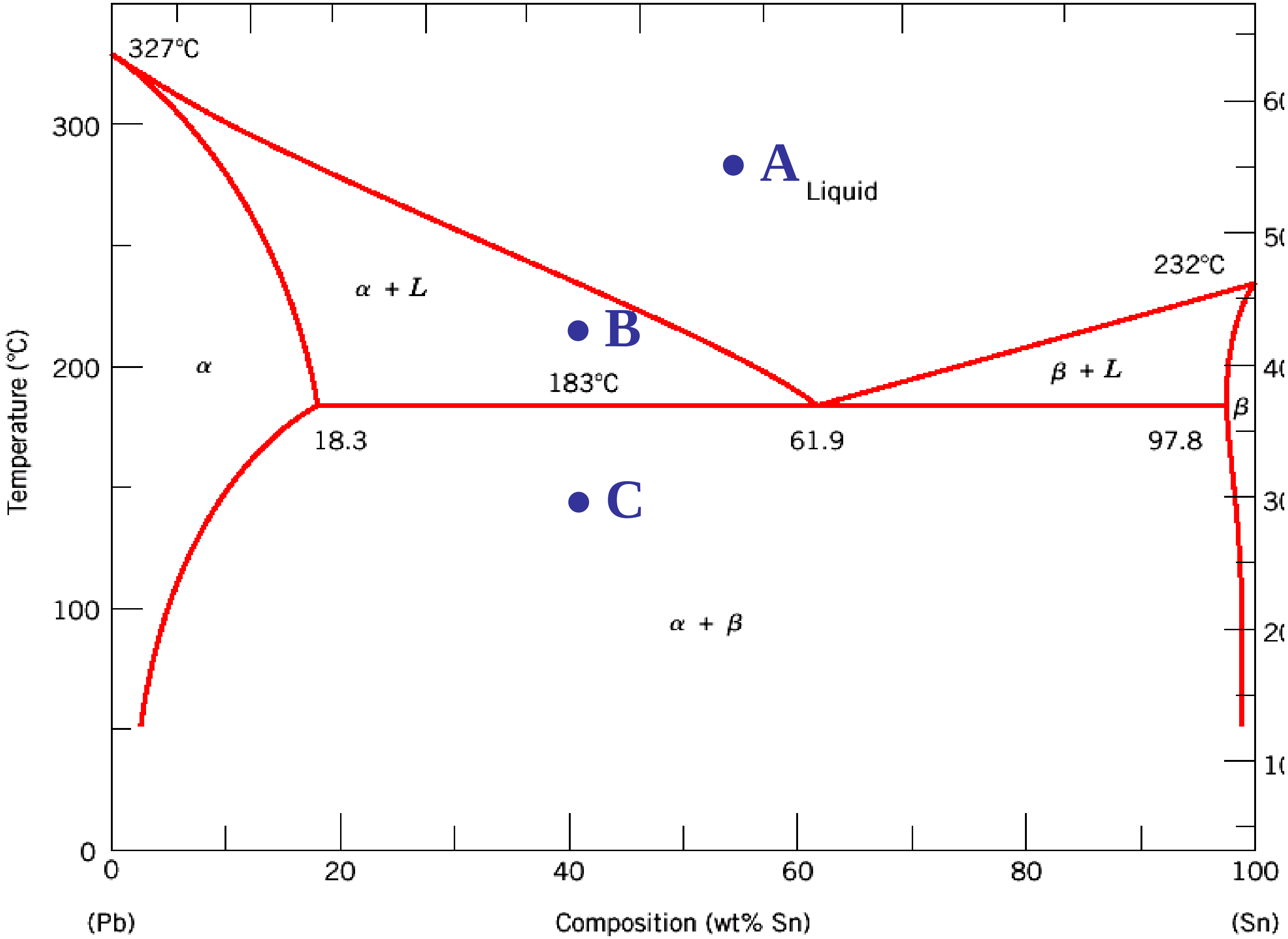
Eutectic reaction – transition from liquid to mixture of two solid phases, $\alpha + \beta$ at eutectic concentration C_E.



At most two phases can be in equilibrium. Three phases (L, α, β) may be in equilibrium only at a few points along the eutectic isotherm. Single-phase regions are separated by 2-phase regions.

Binary Eutectic System

Compositions and relative amounts of phases are determined from the same tie lines and lever rule, as for isomorphous alloys--demonstrate



Example

For Point ***C***: 40wt%Sn-60wt%Pb alloy at 150^{o}C

a) What are the phases present?
b) What are the compositions of the phases present?
c) Mass fraction?
d) Volume fraction at 150^{o}C?

Knowing that the densities of Pb and Sn are 11.23 and 7.24g/cm^3, respectively

a) At C, α and β phases coexist

b) Draw Tie Line at ***150ºC***:

For α-phase:

C_α = 10%

→10wt%Sn–90wt%Pb

For β-phase:

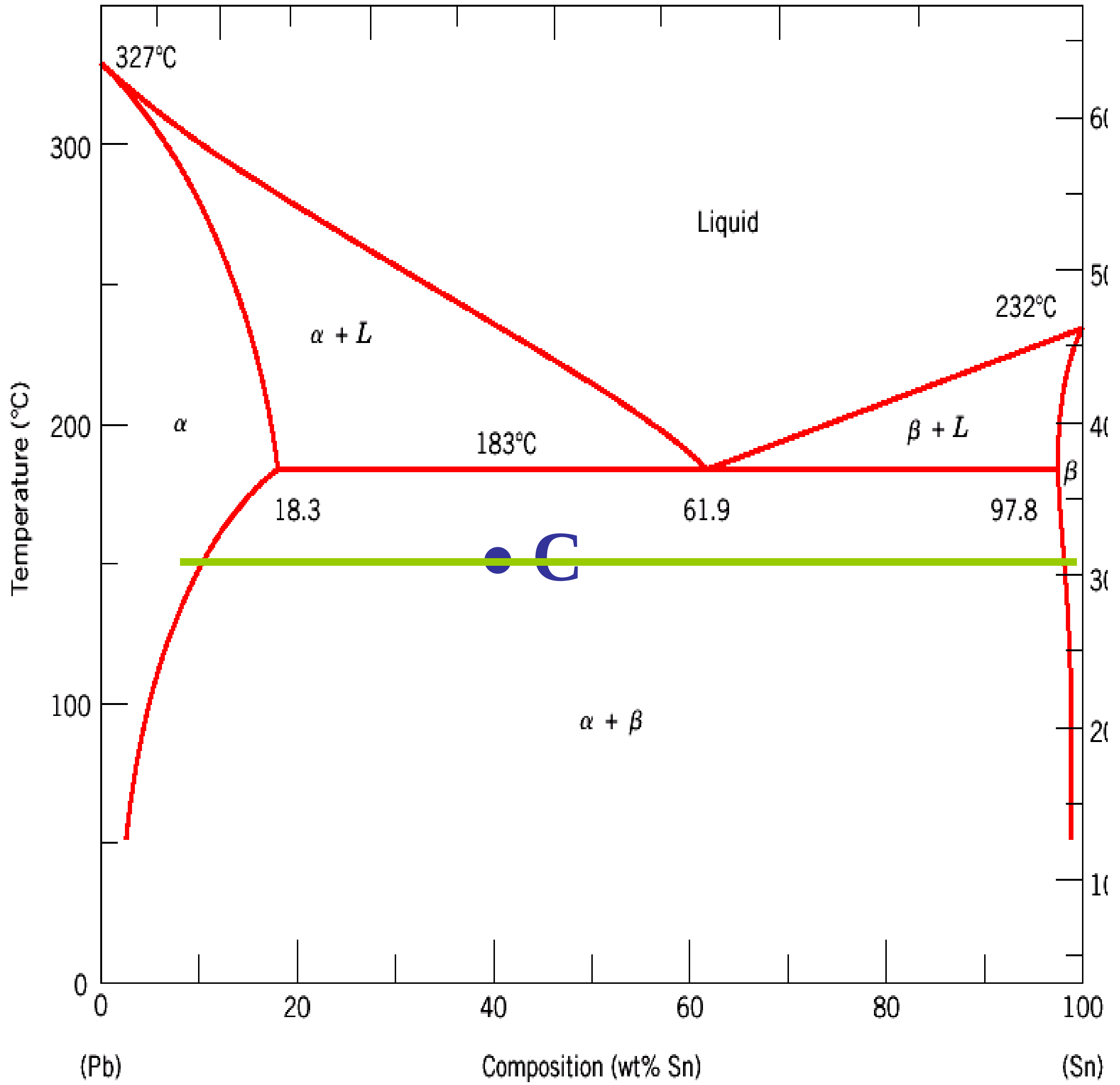
C_β = 98%

→98wt%Sn–2wt%Pb

c) Mass fraction:

$$W_\alpha = \frac{C_\beta - C_1}{C_\beta - C_\alpha} = \frac{98-40}{98-10} = 0.66$$

$$W_\beta = \frac{C_1 - C_\alpha}{C_\beta - C_\alpha} = \frac{40-10}{98-10} = 0.34$$



d) volume fraction:

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta} = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

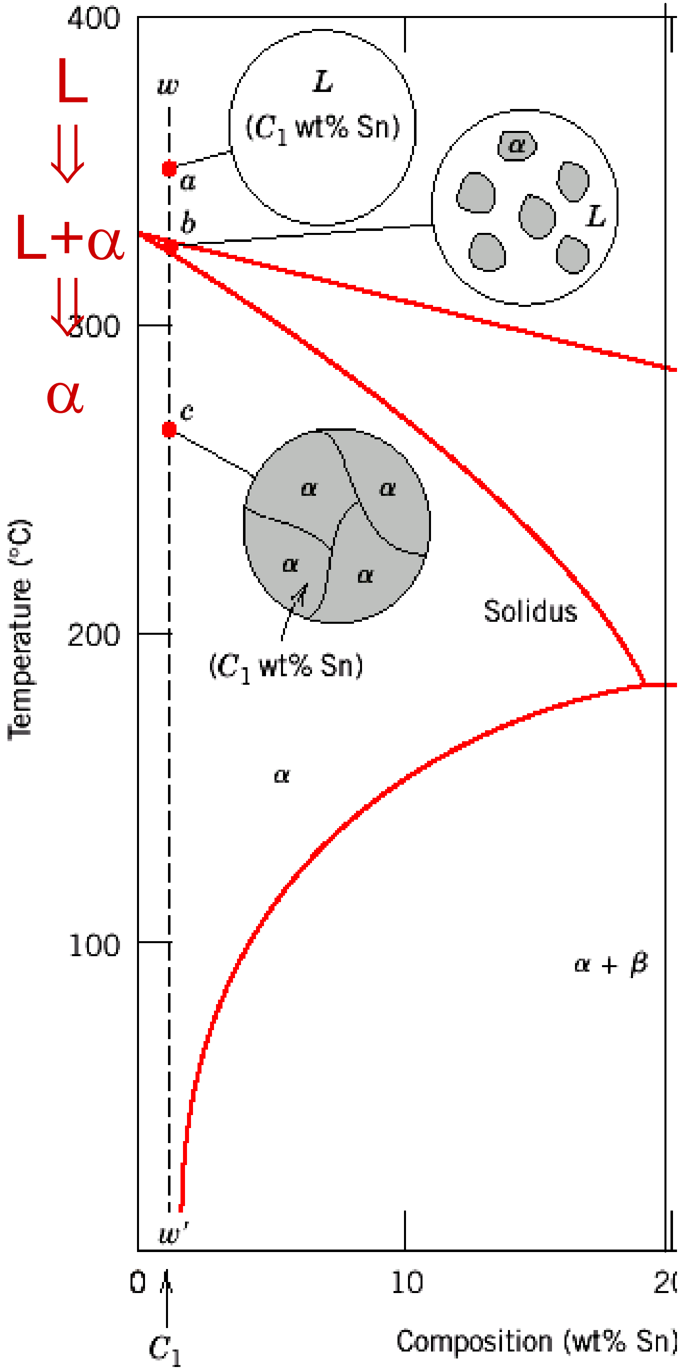
Where:

$$\rho_\alpha = \frac{100}{\dfrac{C_{Sn(\alpha)}}{\rho_{Sn}} + \dfrac{C_{Pb(\alpha)}}{\rho_{Pb}}} = \frac{100}{\dfrac{10}{7.24 g.cm^{-3}} + \dfrac{90}{11.23 g.cm^{-3}}} = 10.64 g.cm^{-3}$$

$$\rho_\beta = \frac{100}{\dfrac{C_{Sn(\beta)}}{\rho_{Sn}} + \dfrac{C_{Pb(\beta)}}{\rho_{Pb}}} = \frac{100}{\dfrac{98}{7.24 g.cm^{-3}} + \dfrac{2}{11.23 g.cm^{-3}}} = 7.29 g.cm^{-3}$$

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta} = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}} = \frac{\dfrac{0.66}{10.64}}{\dfrac{0.66}{10.64} + \dfrac{0.34}{7.29}} = 0.57$$

$$V_\beta = 1 - V_\alpha = 1 - 0.57 = 0.43$$

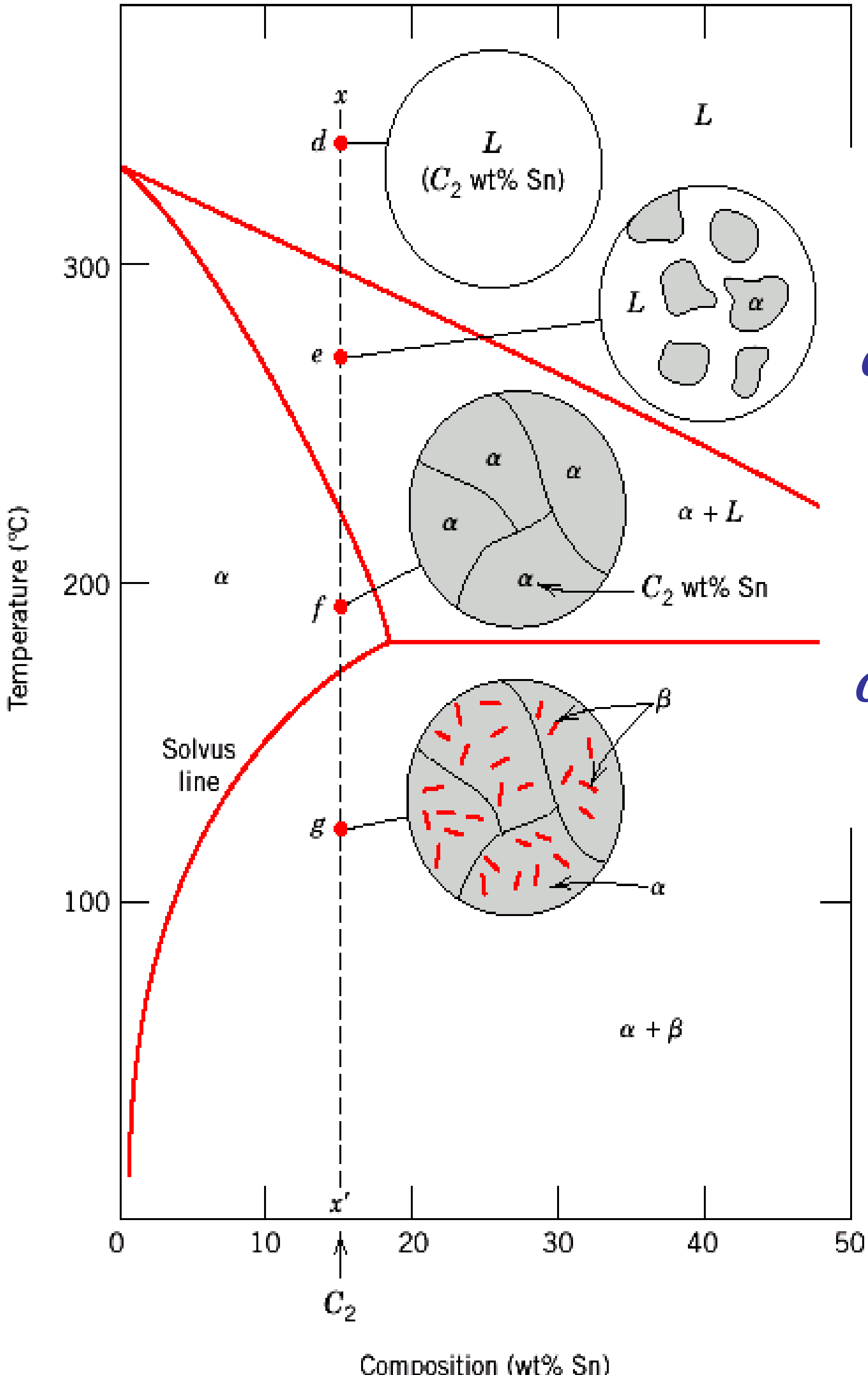


Development of microstructure in eutectic alloys (I)

Several types of microstructure formed in slow cooling an different compositions. Cooling of liquid lead/tin system at different compositions.

In this case of lead-rich alloy (0-2 wt% of tin) solidification proceeds in the same manner as for isomorphous alloys (e.g. Cu-Ni) that we discussed earlier.

Development of microstructure in eutectic alloys (II)



L

⇓

$\alpha + L$

⇓

α

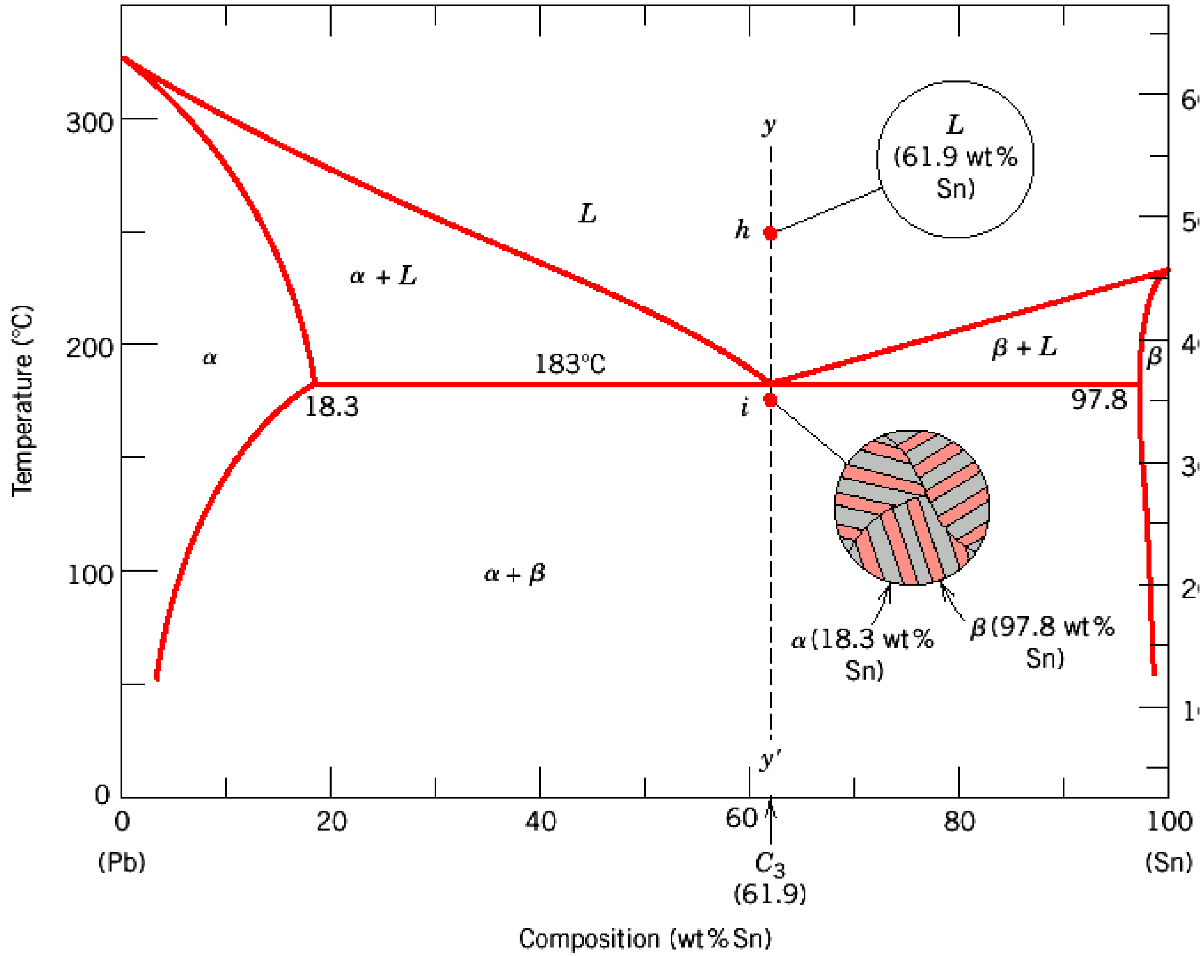
⇓

$\alpha + \beta$

At compositions between room temperature solubility limit and the maximum solid solubility at the eutectic temperature, β phase nucleates as the α solid solubility is exceeded at solvus line.

Development of microstructure in eutectic alloys (III) Solidification at the eutectic composition (I)

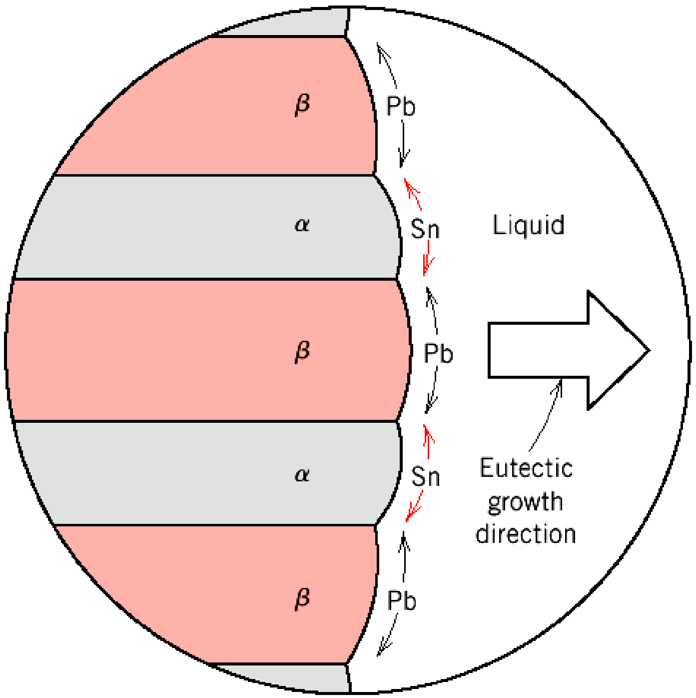
No changes above eutectic temperature, T_E. At T_E liquid transforms to α and β phases (eutectic reaction).



$$L \rightarrow \alpha + \beta$$

Development of microstructure in eutectic alloys (IV)
Solidification at the eutectic composition (II)

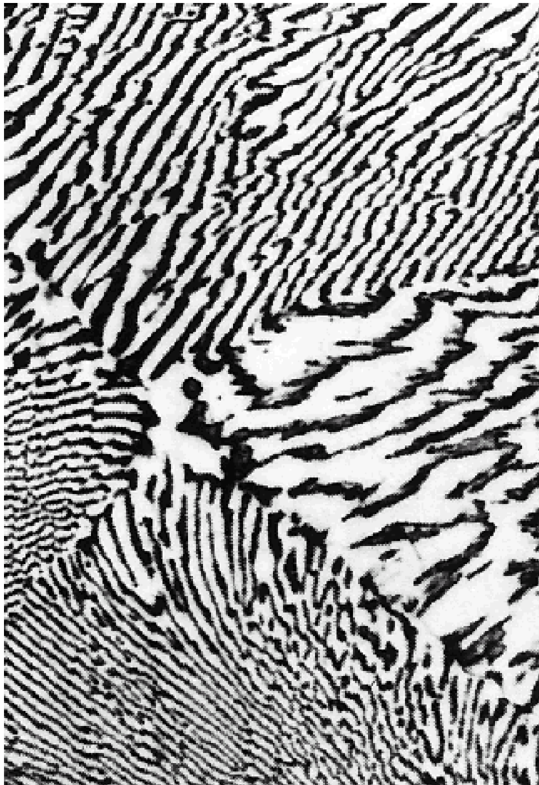
Compositions of α and β phases are very different → eutectic reaction involves redistribution of Pb and Sn atoms by atomic diffusion. Simultaneous formation of α and β phases results in a layered (lamellar) microstructure:called eutectic structure.



Formation of eutectic structure in lead-tin system.

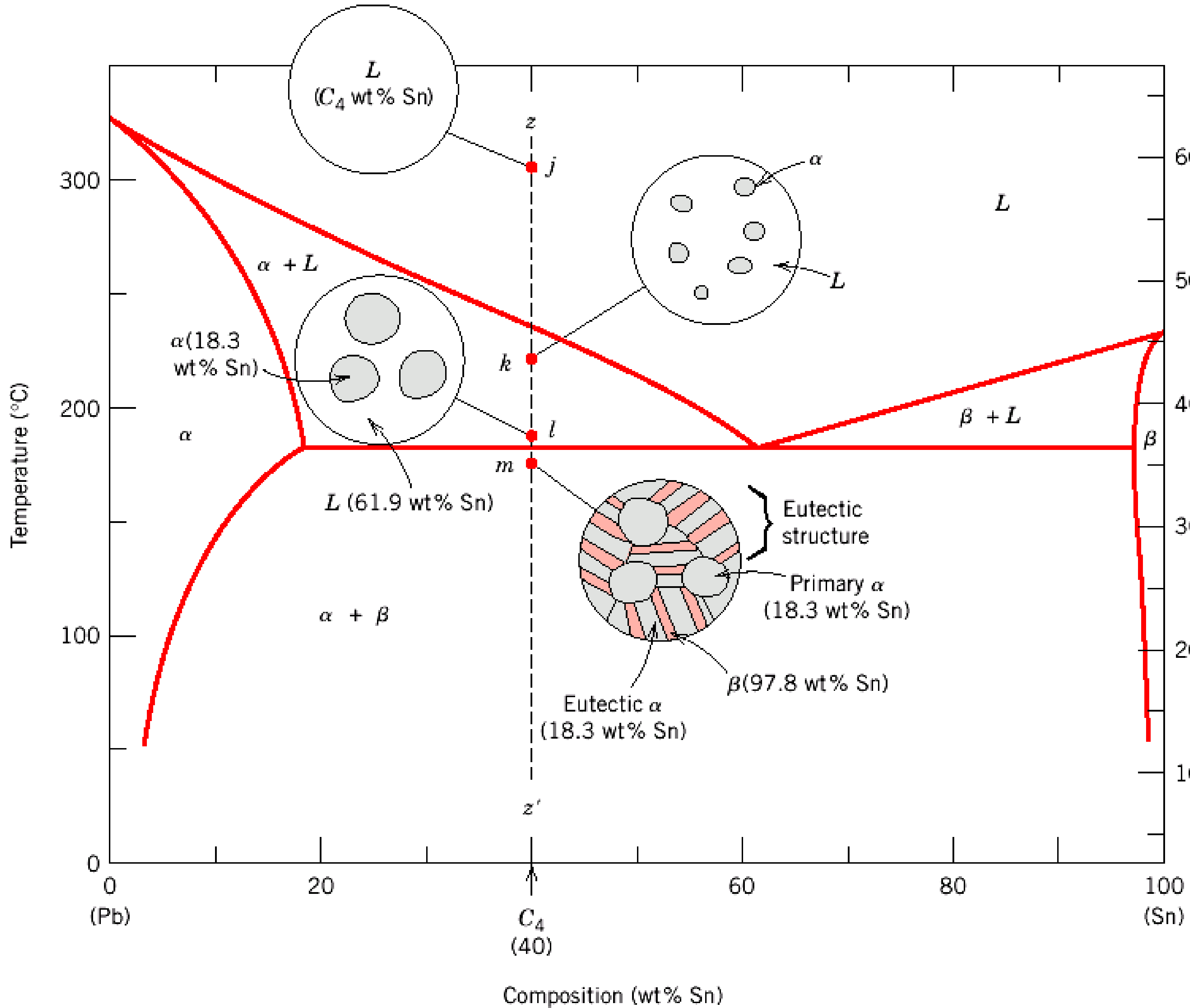
Dark layers are lead-reach α phase.

Light layers are the tin-reach β phase.



Development of microstructure in eutectic alloys (V) Compositions other than eutectic but within the range of the eutectic isotherm

Primary α phase is formed in the $\alpha + L$ region, and the eutectic structure that includes layers of α and β phases (called eutectic α and eutectic β phases) is formed upon crossing the eutectic isotherm.



L

$\Downarrow$

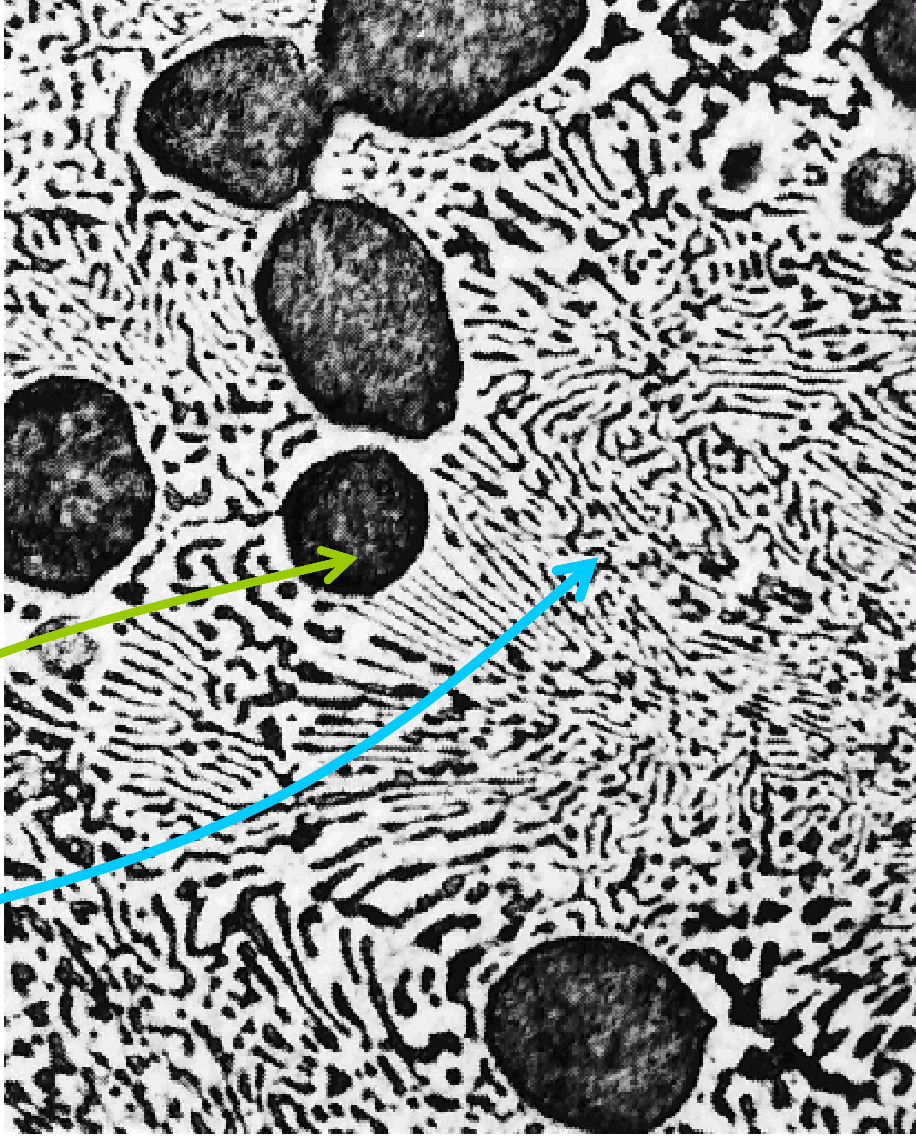
α+L

$\Downarrow$

α+β

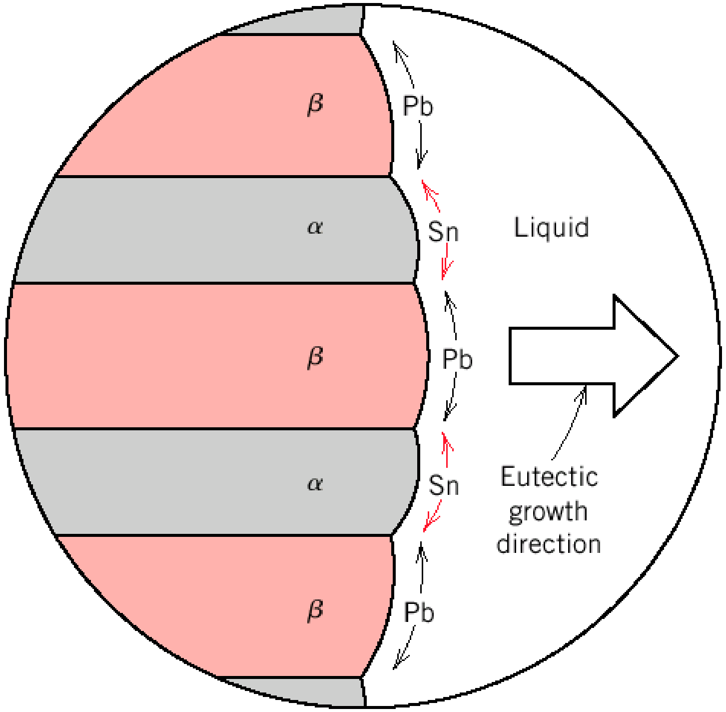
Development of microstructure in eutectic alloys (VI)

Microconstituent – element of microstructure having a distinctive structure. For case described on previous page, microstructure consists of two microconstituents, primary α phase and the eutectic structure.



Although the eutectic structure consists of two phases, it is a microconstituent with distinct lamellar structure and fixed ratio of the two phases.

Compositions of α and β phases are very different → eutectic reaction involves redistribution of Pb and Sn atoms by atomic diffusion. Simultaneous formation of α and β phases results in a layered (lamellar) microstructure:called eutectic structure.



Formation of eutectic structure in lead-tin system.

Dark layers are lead-reach α phase.

Light layers are the tin-reach β phase.

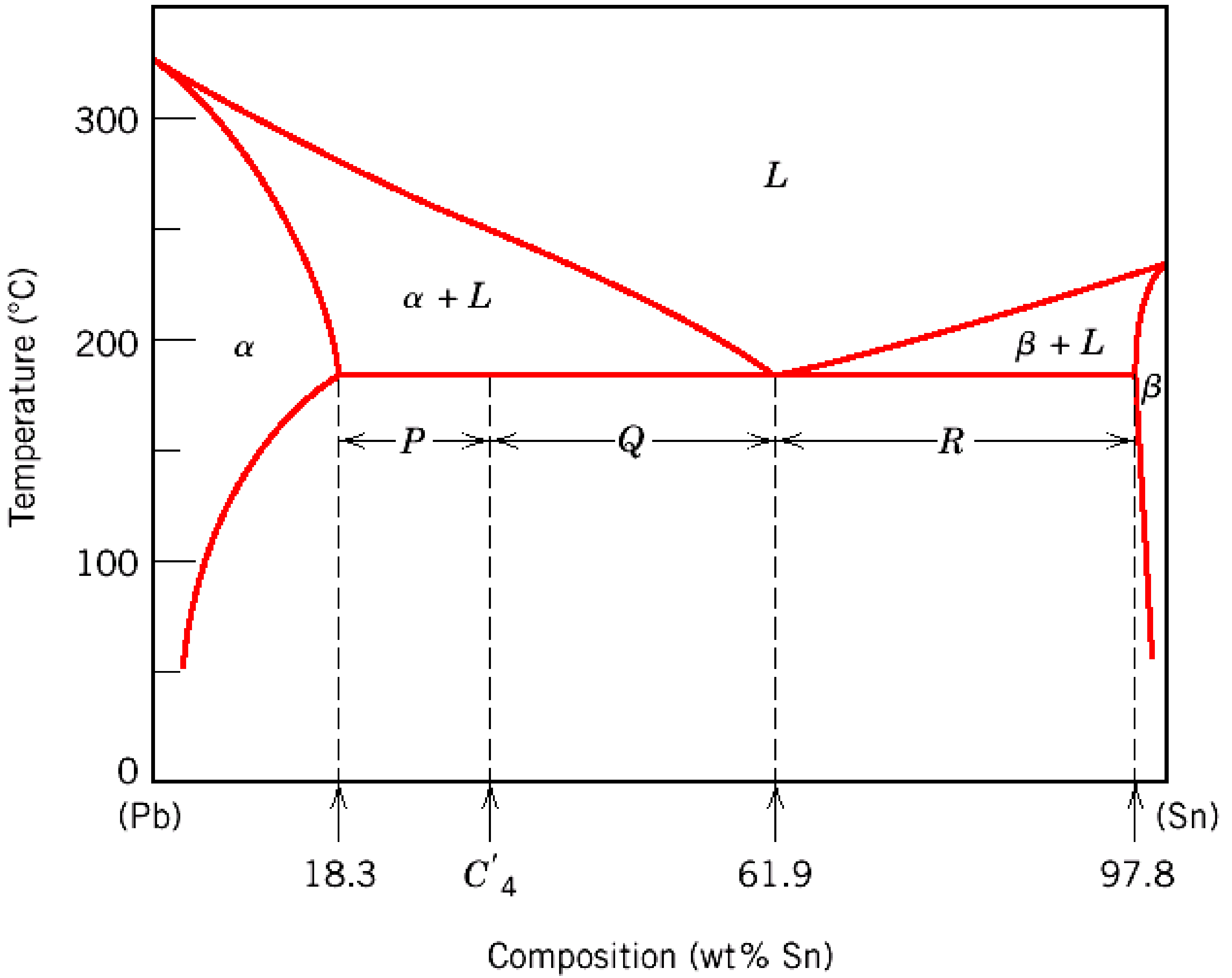
Relative amounts of microconstituents?

Eutectic microconstituent forms from liquid having eutectic composition (61.9 wt% Sn)

Treat the eutectic as if it were a separate phase and apply lever rule to find relative fractions of primary α phase (18.3 wt% Sn) and eutectic structure (61.9 wt% Sn):

$W_e = P / (P+Q)$ **(eutectic)**

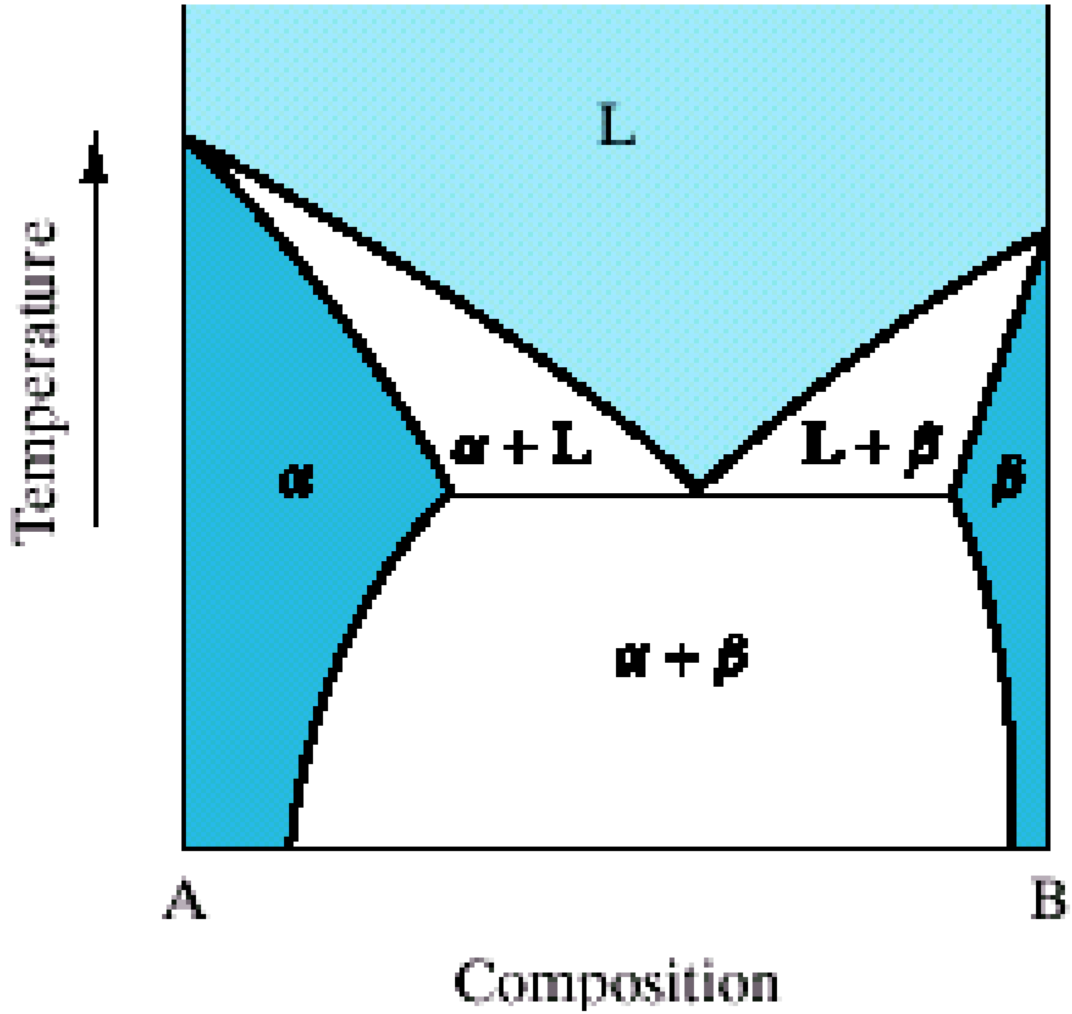
$W_{\alpha'} = Q / (P+Q)$ **(primary)**



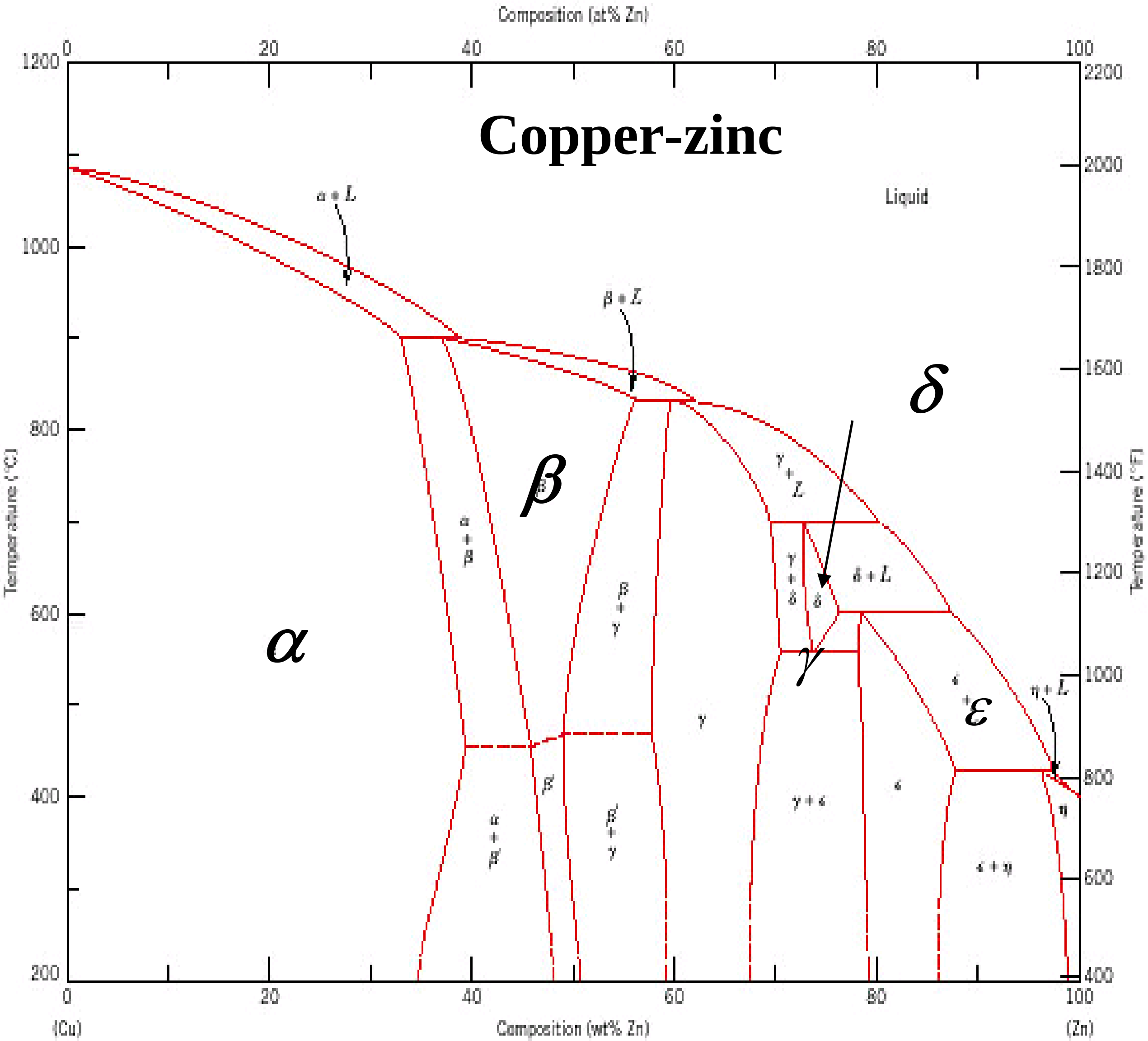
300
200
100
0
Temperature (°C)
L
α + L
α
β + L
β
P
Q
R
(Pb)
(Sn)
18.3
C′4
61.9
97.8
Composition (wt% Sn)

Equilibrium Diagrams Having Intermediate Phases or Compounds

Terminal solid solution:
a solid solution that exists over a composition range extending to either composition extremity of a binary phase diagram



Equilibrium Diagrams Having Intermediate Phases or Compounds



Intermediate solid solution:

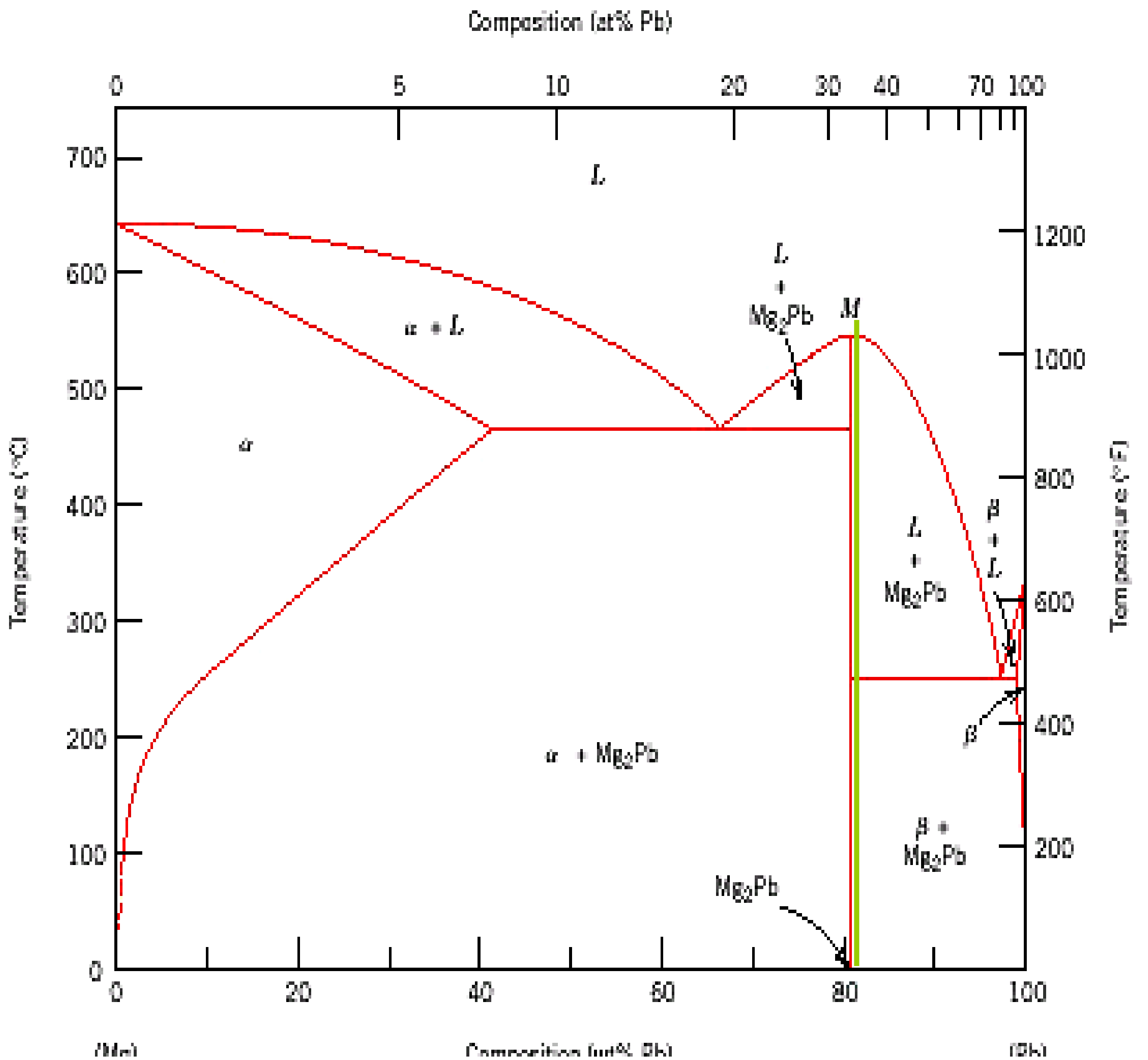
α and η: two **terminal** solid solution

β, γ, δ, & ε are **intermediate** phases

Intermetallic Compounds

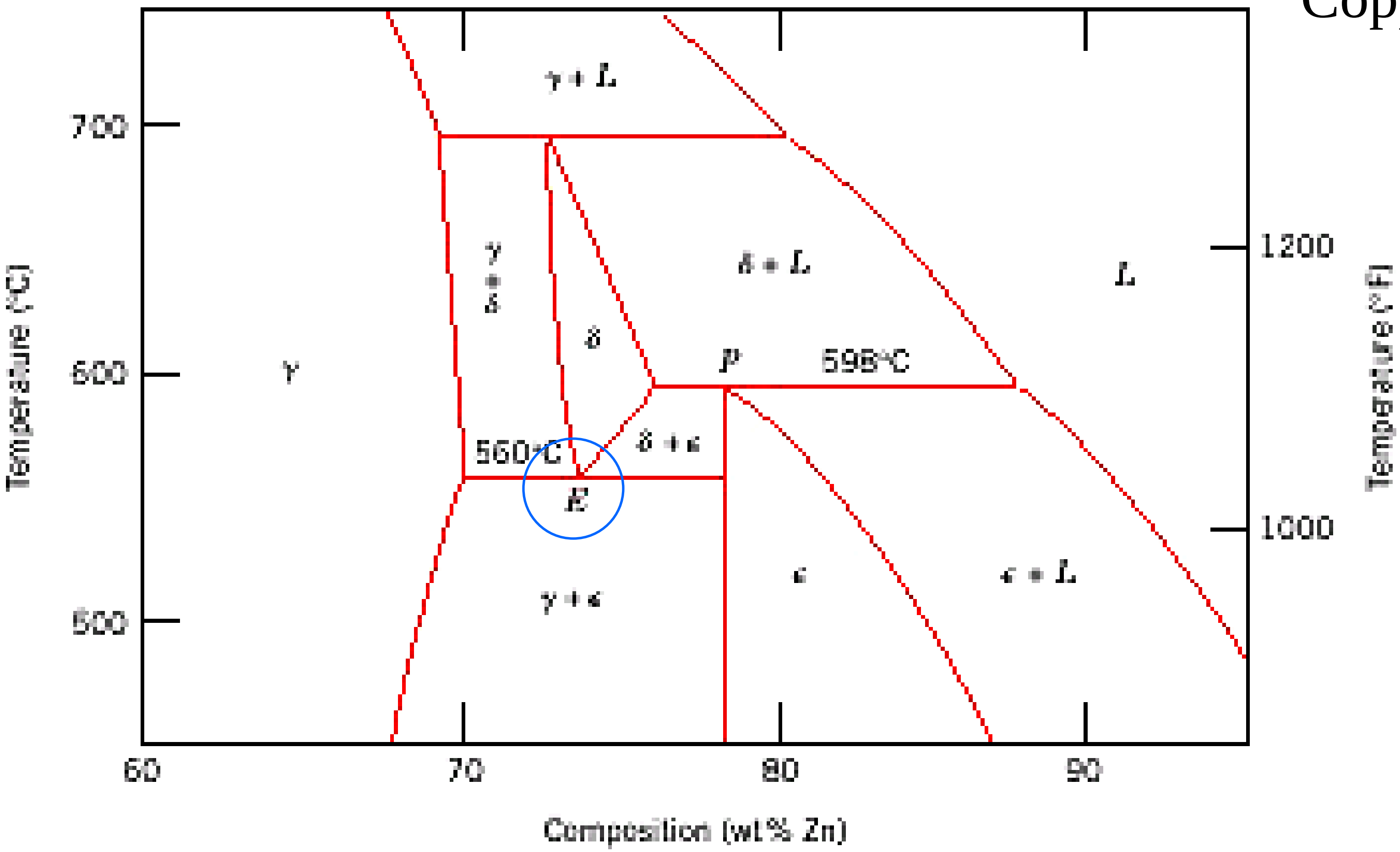
Ex: magnesium-lead phase diagram:

Intermetallic compound: Mg_2Pb can exist by itself only at the precise composition of 19wt%Mg – 81wt%Pb



Eutectoid Reaction (Invariant Point E at 560°C)

Copper-zinc

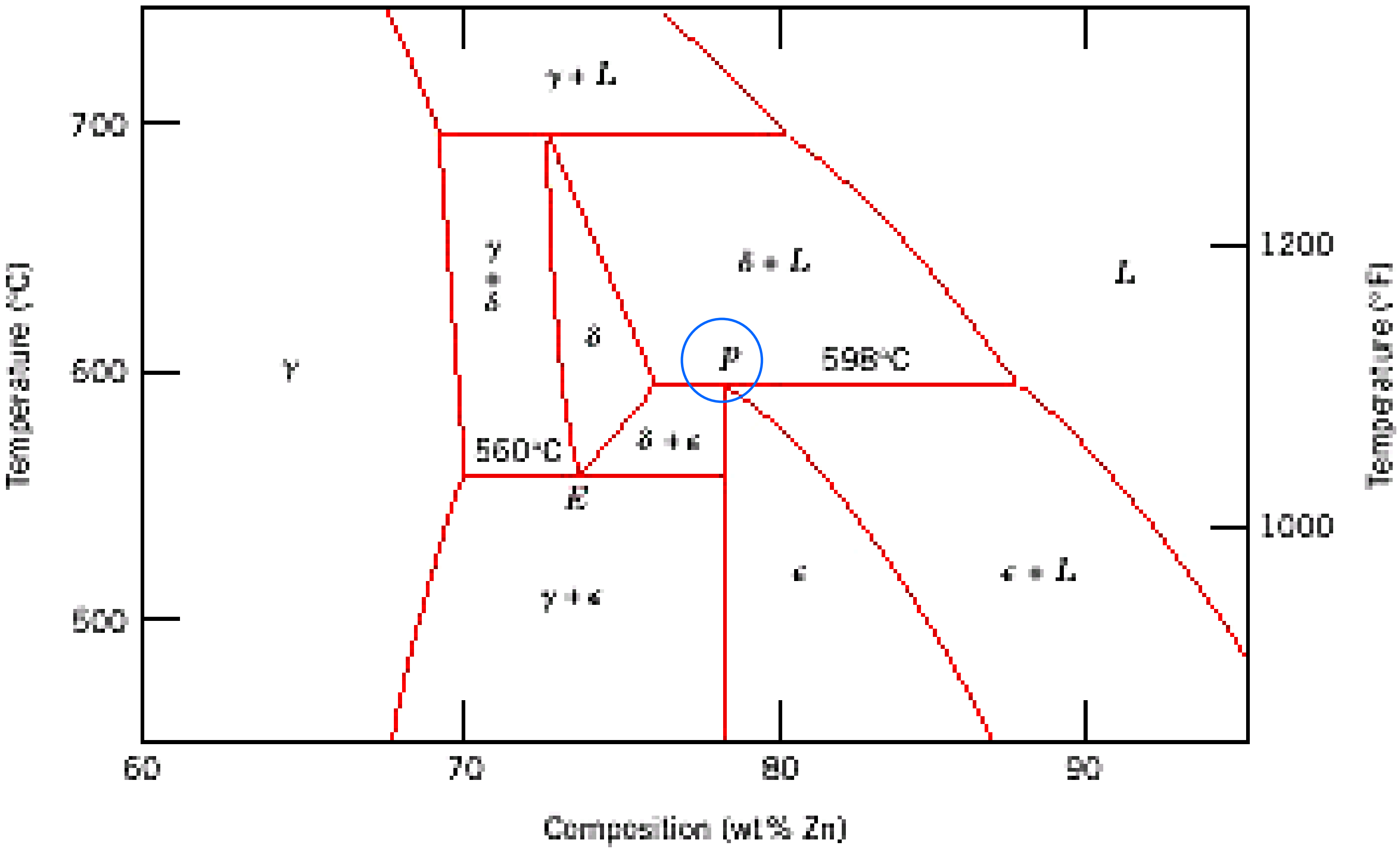


$$\delta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \gamma + \varepsilon$$

Eutectoid reaction

Peritectic Reaction (Invariant Point P at 598°C)

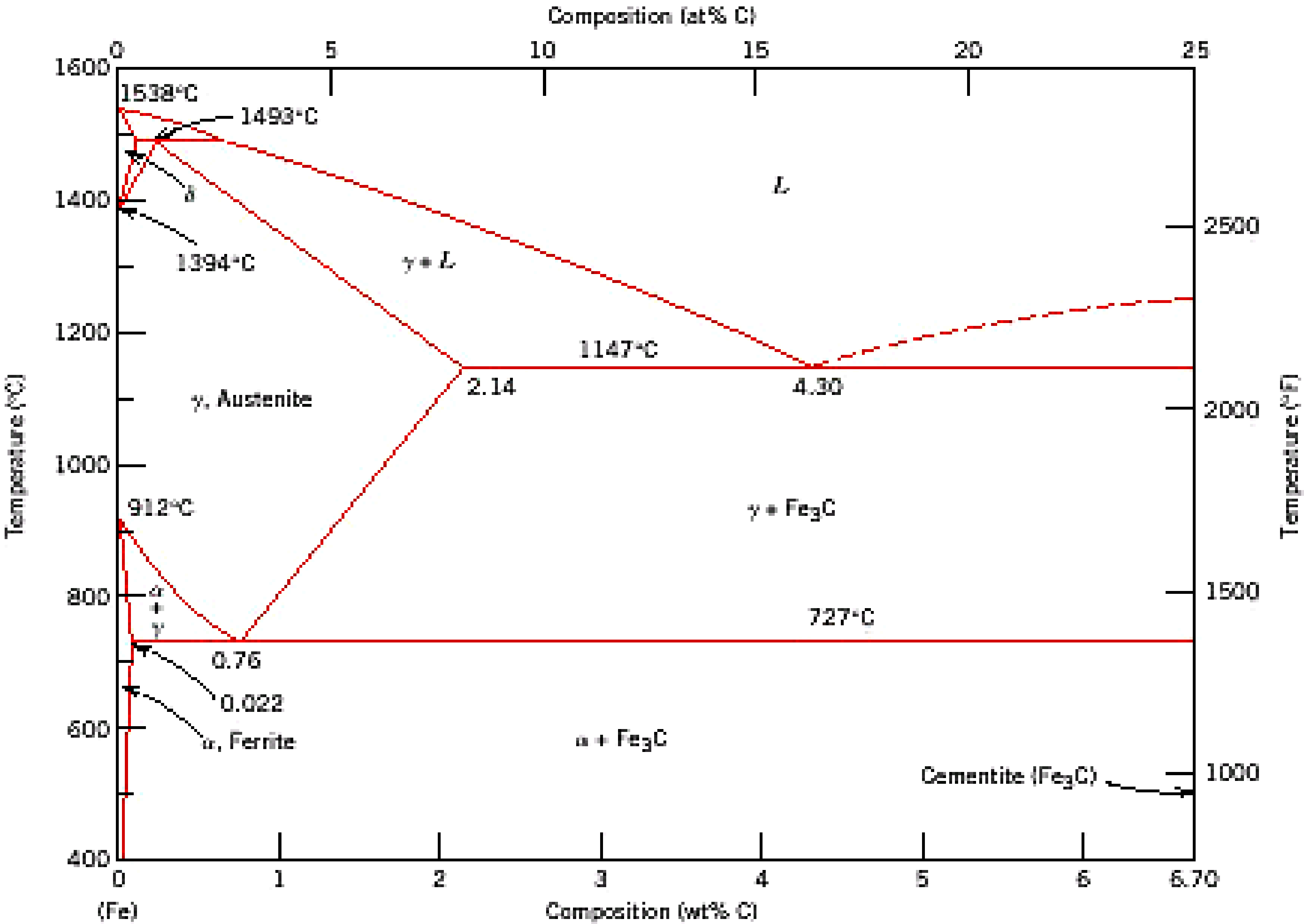
Copper-zinc



$$\delta + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \varepsilon$$

Peritectic reaction

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



Reactions

Peritectic L + δ = γ
at T=1493^{o}C and 0.18wt%C

Eutectic L = γ + **Fe_3C**
at T=1147^{o}C and 4.3wt%C

Eutectoid γ = α + **Fe_3C**
at T=727^{o}C and 0.77wt%C

Max. solubility of C
in ferrite=0.022%
in austenite=2.11%

Phases Present

L

δ ferrite delta
Bcc structure
Paramagnetic

γ austenite
Fcc structure
Non-magnetic
ductile

α ferrite
Bcc structure
Ferromagnetic
Fairly ductile

Fe_3C cementite
Orthorhombic
Hard, brittle

Phases in Fe–Fe_3C Phase Diagram

- **α-ferrite - solid solution of C in BCC Fe**
  - Stable form of iron at room temperature.
  - Transforms to FCC g-austenite at 912 °C
- **γ-austenite - solid solution of C in FCC Fe**
  - Transforms to BCC δ-ferrite at 1395 °C
  - Is not stable below the eutectic temperature (727 ° C) unless cooled rapidly.
- **δ-ferrite solid solution of C in BCC Fe**
  - It is stable only at T, >1394 °C. It melts at 1538 °C
- **Fe_3C (iron carbide or cementite)**
  - This intermetallic compound is metastable at room T. It decomposes (very slowly, within several years) into α-Fe and C (graphite) at 650 - 700 °C
- **Fe-C liquid solution**

Comments on Fe–Fe_3C system

C is an interstitial impurity in Fe. It forms a solid solution with α, γ, δ phases of iron

Maximum solubility in BCC α-ferrite is 0.022 wt% at 727 °C. BCC: relatively small interstitial positions

Maximum solubility in FCC austenite is 2.14 wt% at 1147 °C - FCC has larger interstitial positions

Mechanical properties: Cementite (Fe_3C is hard and brittle: strengthens steels). Mechanical properties also depend on microstructure: how ferrite and cementite are mixed.

Magnetic properties: α -ferrite is magnetic below 768 °C, austenite is non-magnetic

Classification.

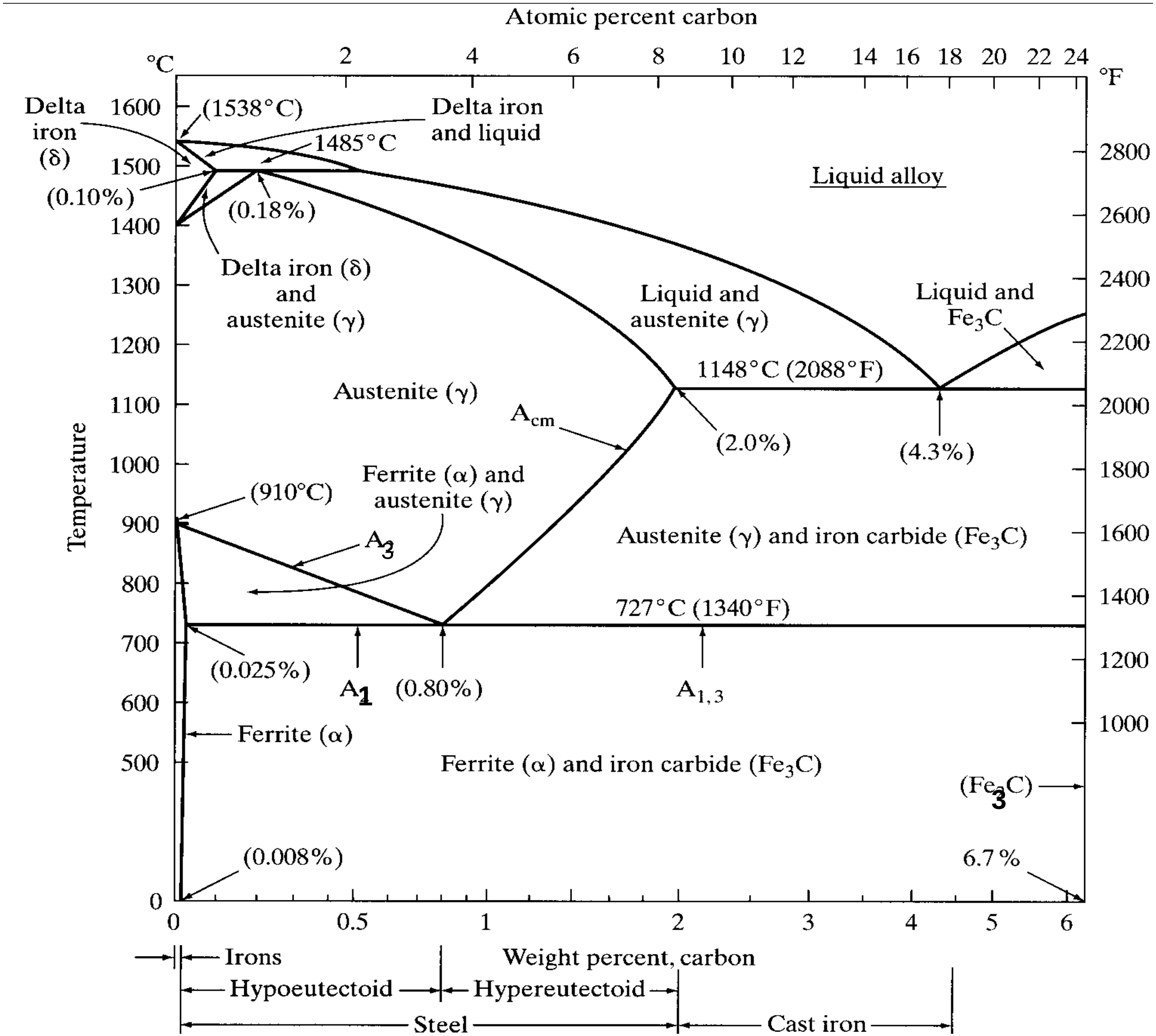
Three types of ferrous alloys:

Iron: $<$ 0.008 wt % C in α-ferrite at room T

Steels: 0.008 - 2.14 wt % C (usually $<$ 1 wt %)

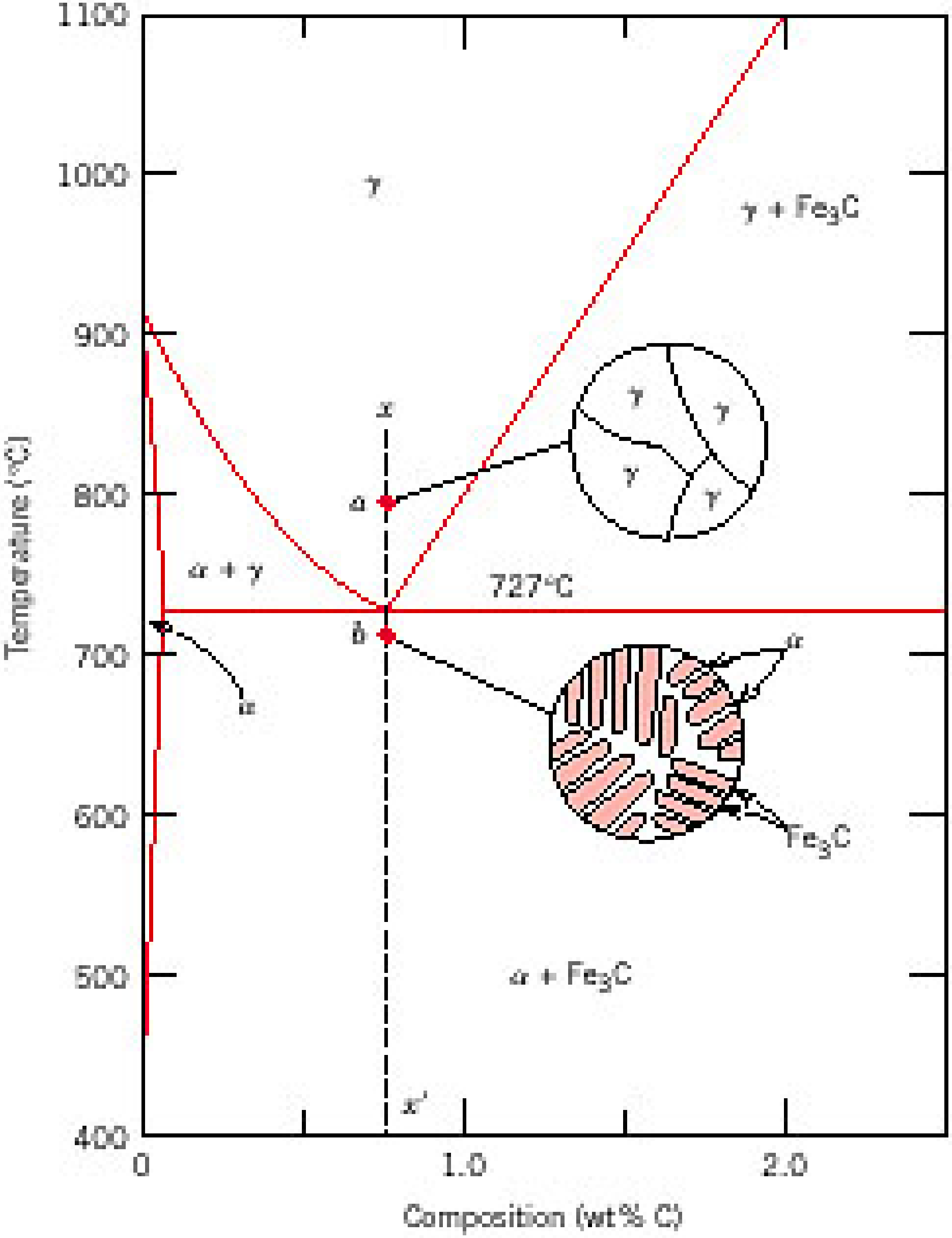
α-ferrite + Fe_3C at room T

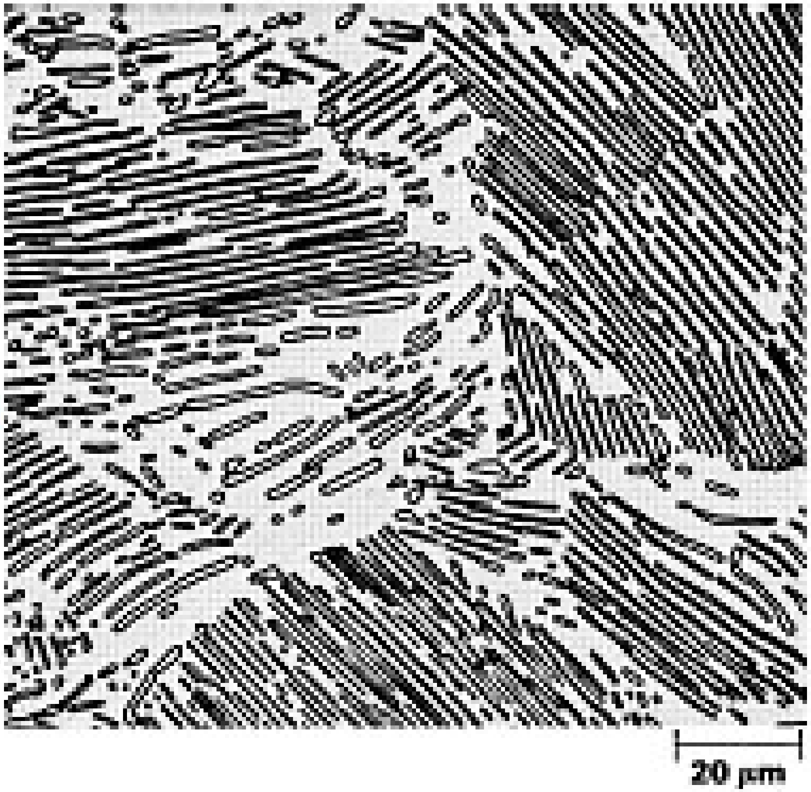
Cast iron: 2.14 - 6.7 wt % (usually $<$ 4.5 wt %)



Atomic percent carbon
°C
°F
Delta iron (δ)
(1538°C)
Delta iron and liquid
1485°C
(0.10%)
(0.18%)
Liquid alloy
Delta iron (δ) and austenite (γ)
Liquid and austenite (γ)
Liquid and Fe3C
1148°C (2088°F)
Austenite (γ)
Acm
(2.0%)
(4.3%)
Temperature
(910°C)
Ferrite (α) and austenite (γ)
A3
Austenite (γ) and iron carbide (Fe3C)
727°C (1340°F)
(0.025%)
A1
(0.80%)
A1,3
Ferrite (α)
Ferrite (α) and iron carbide (Fe3C)
(Fe3C)
(0.008%)
6.7%
Weight percent, carbon
Irons
Hypoeutectoid
Hypereutectoid
Steel
Cast iron

Eutectoid steel

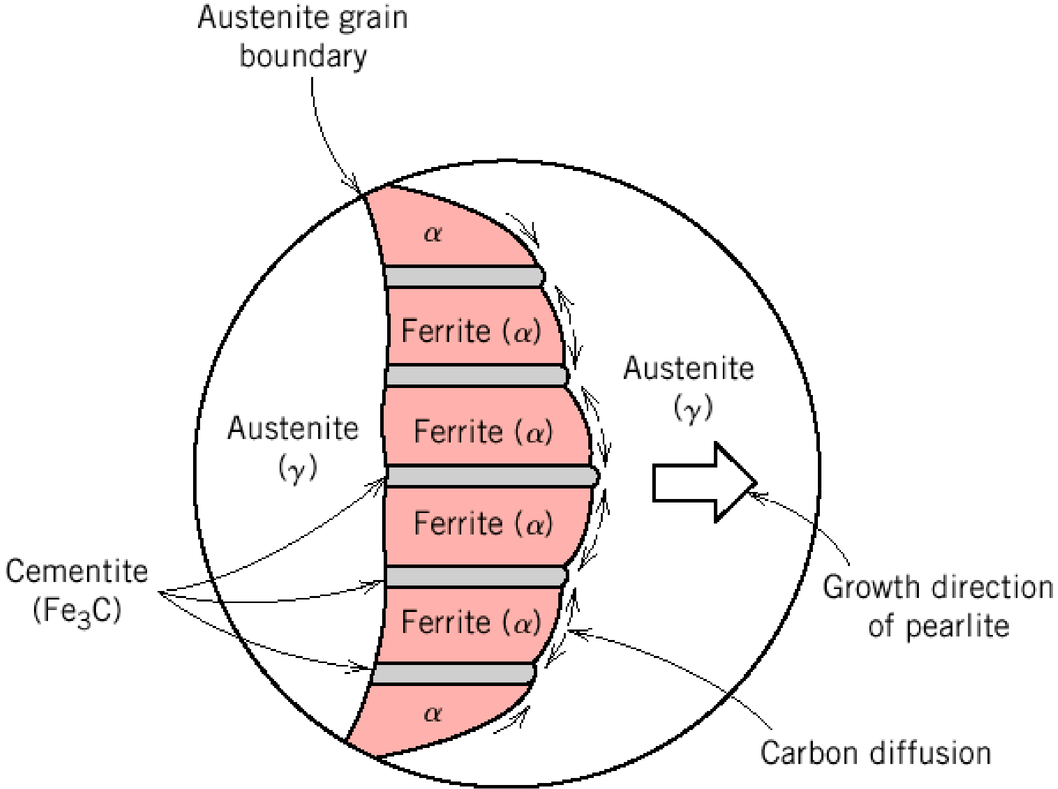




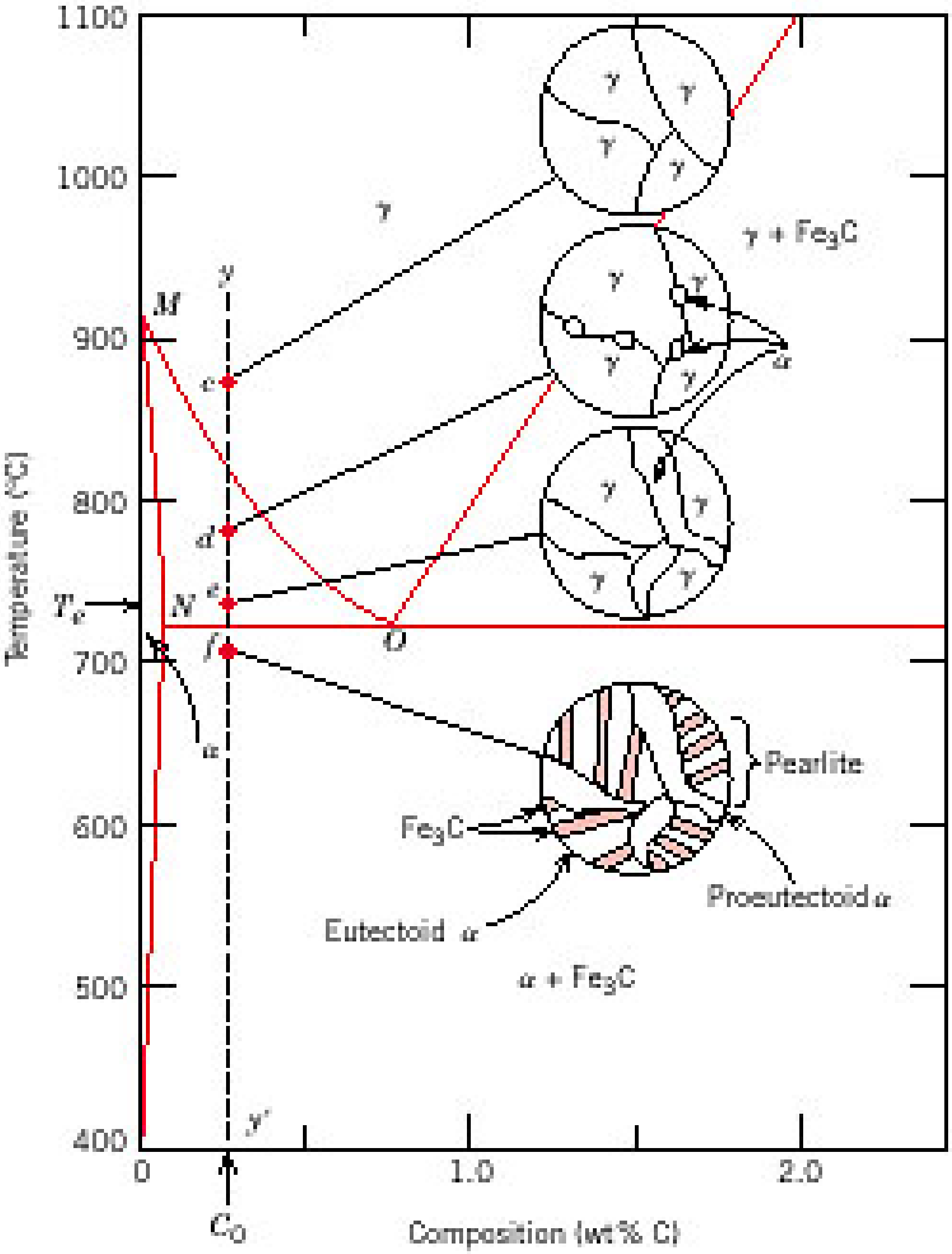
Microstructure of eutectoid steel

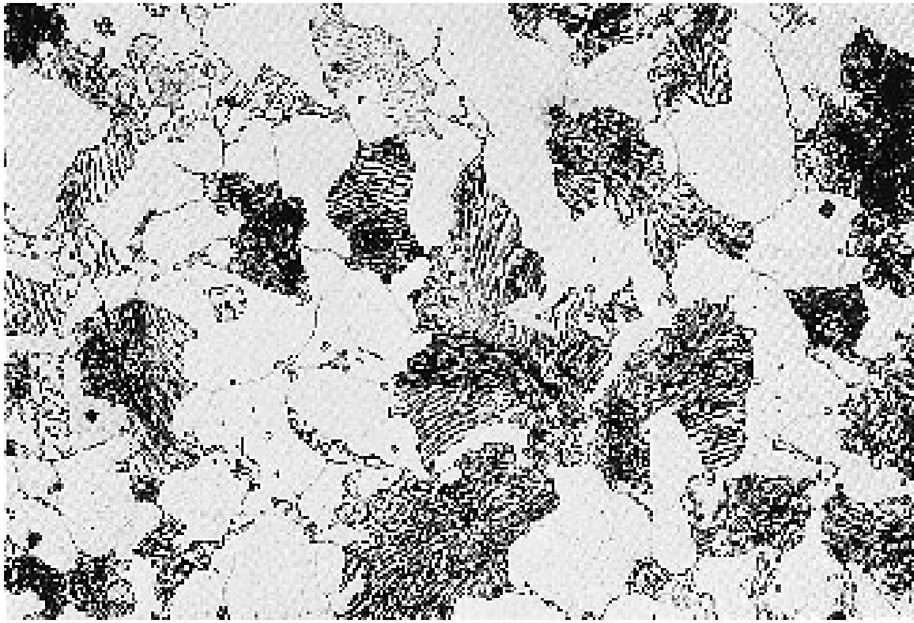
Alloy of eutectoid composition (0.76 wt % C) is cooled slowly: forms pearlite, layered structure of two phases: α-ferrite and cementite (Fe_3C)

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

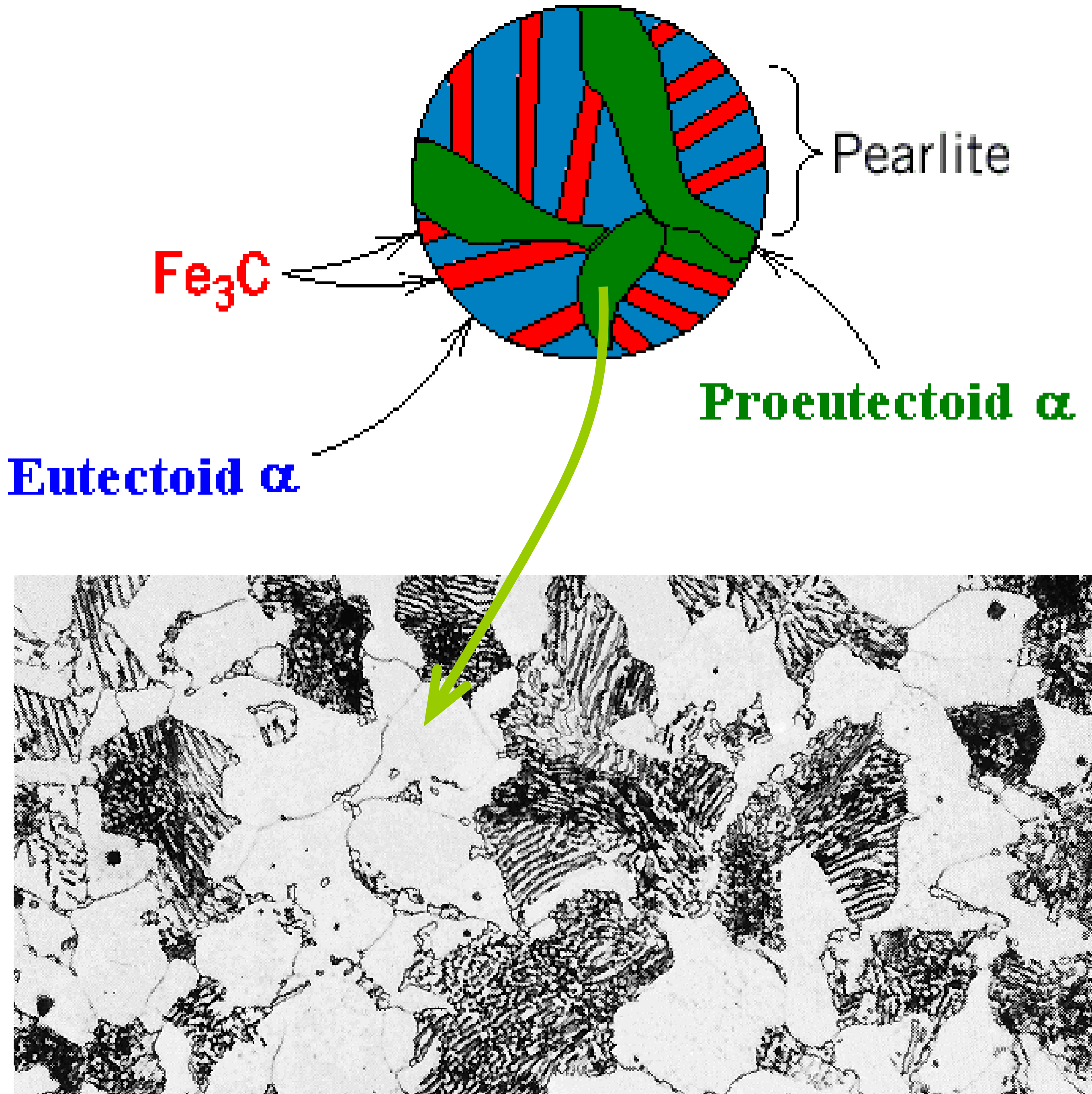


Hypoeutectoid steel

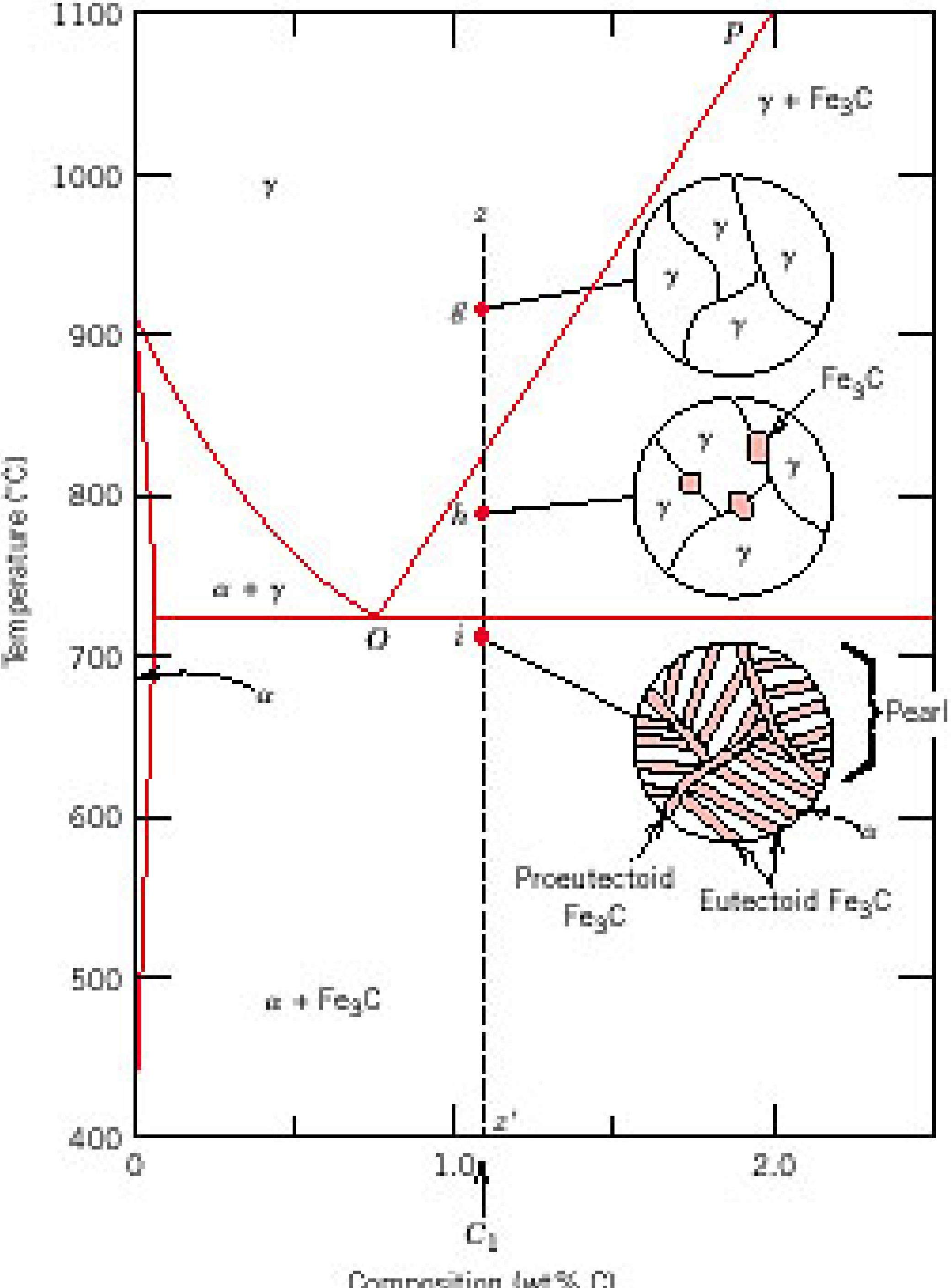




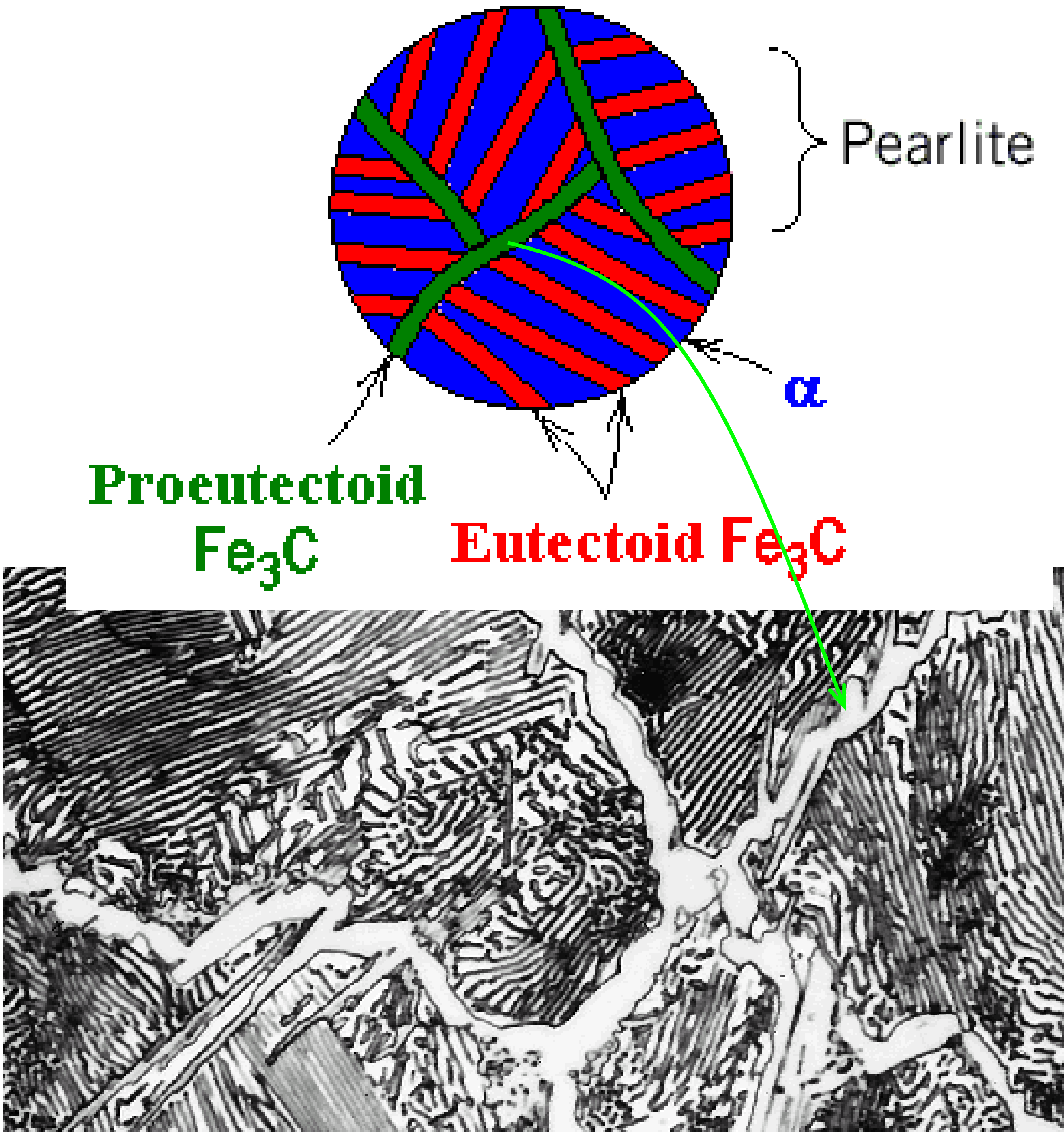
Hypoeutectoid alloys contain proeutectoid ferrite (formed above the eutectoid temperature) plus the eutectoid perlite that contain eutectoid ferrite and cementite.



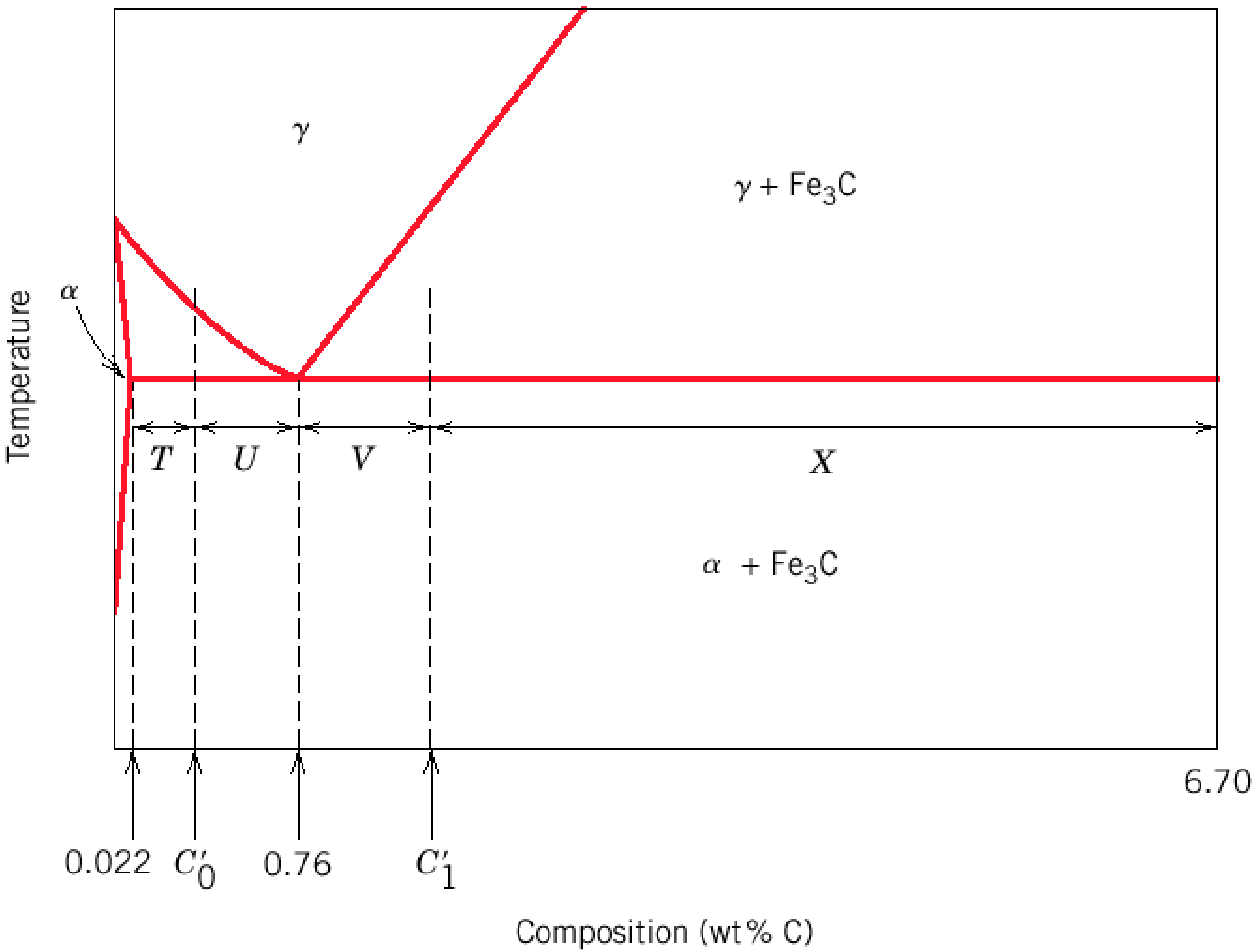
Hypereutectoid steel



Hypereutectoid alloys contain proeutectoid cementite (formed above the eutectoid temperature) plus perlite that contain eutectoid ferrite and cementite.



How to calculate the relative amounts of proeutectoid phase (α or Fe_3C) and pearlite?



Use the lever rule and a tie line that extends from the eutectoid composition (0.75 wt% C) to α (0.022 wt% C) for hypoeutectoid alloys and to Fe_3C (6.7 wt% C) for hypereutectoid alloys.

Example: hypereutectoid alloy, composition C_1

$$\text{Fraction of Pearlite} = W_P = \frac{X}{(V+X)} = \frac{(6.7 - C_1)}{(6.7 - 0.76)}$$

$$\text{Fraction of Proeutectoid Cementite} = W_{Fe3C} = \frac{V}{(V+X)} = \frac{(C_1 - 0.76)}{(6.7 - 0.76)}$$

Example

For alloys of two hypothetical metals ***A*** and ***B***, there exist an α, ***A***-rich phase and a β, ***B***-rich phase. From the mass fractions of both phases of two different alloys, which are at the same temperature, determine the composition of the phase boundary (or solubility limit) for both α and β at this temperature.

Alloy Composition	**Fraction of α phase**	**Fraction of β phase**
60wt%A – 40wt%B	0.57	0.43
30wt%A – 70wt%B	0.14	0.86

The problem is to solve for compositions at the phase boundaries for both **α** and **β** phases (i.e., **Cα** and **Cβ**). We may set up two independent lever rule expressions, one for each composition, in terms of **Cα** and **Cβ** as follows:

$$W_{\alpha 1} = 0.57 = \frac{C_\beta - C_{o1}}{C_\beta - C_\alpha} = \frac{C_\beta - 60}{C_\beta - C_\alpha}$$

$$W_{\alpha 2} = 0.14 = \frac{C_\beta - C_{o2}}{C_\beta - C_\alpha} = \frac{C_\beta - 30}{C_\beta - C_\alpha}$$

In these expressions, compositions are given in weight percent

A. Solving for **Cα** and **Cβ** from these equations, yield

Cα = 90 (or 90 wt% A-10 wt% B)

Cβ = 20.2 (or 20.2 wt% A-79.8 wt% B)