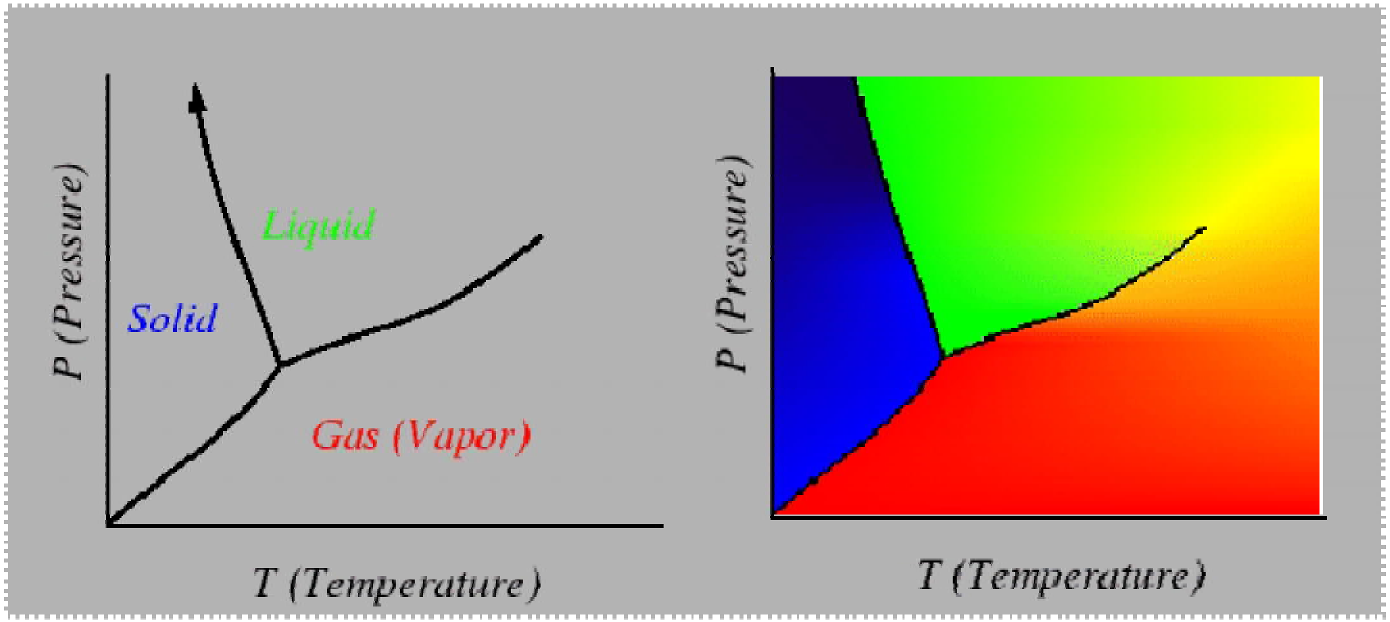
Chapter 7

Phase Diagrams



Outline

- Definitions and basic concepts
- Phases and microstructure
- Binary isomorphous systems (complete solid solubility)
- Binary eutectic systems (limited solid solubility)
- Binary systems with intermediate phases/compounds
- The iron-carbon system (steel and cast iron)

Definitions: Components and Phases

- **Component :** chemically recognizable species (Fe and C in carbon steel, H_2O and NaCl in salted water).
  A binary alloy contains two components, a ternary alloy – three, etc.
- **Phase :** a portion of a system that has uniform physical and chemical characteristics. Two distinct phases in a system have distinct physical or chemical characteristics (e.g. water and ice) and are separated from each other by definite phase boundaries.

Definitions: Components and Phases

- A phase may contain one or more components.
- A single-phase system is called homogeneous, systems with two or more phases are mixtures or heterogeneous systems.

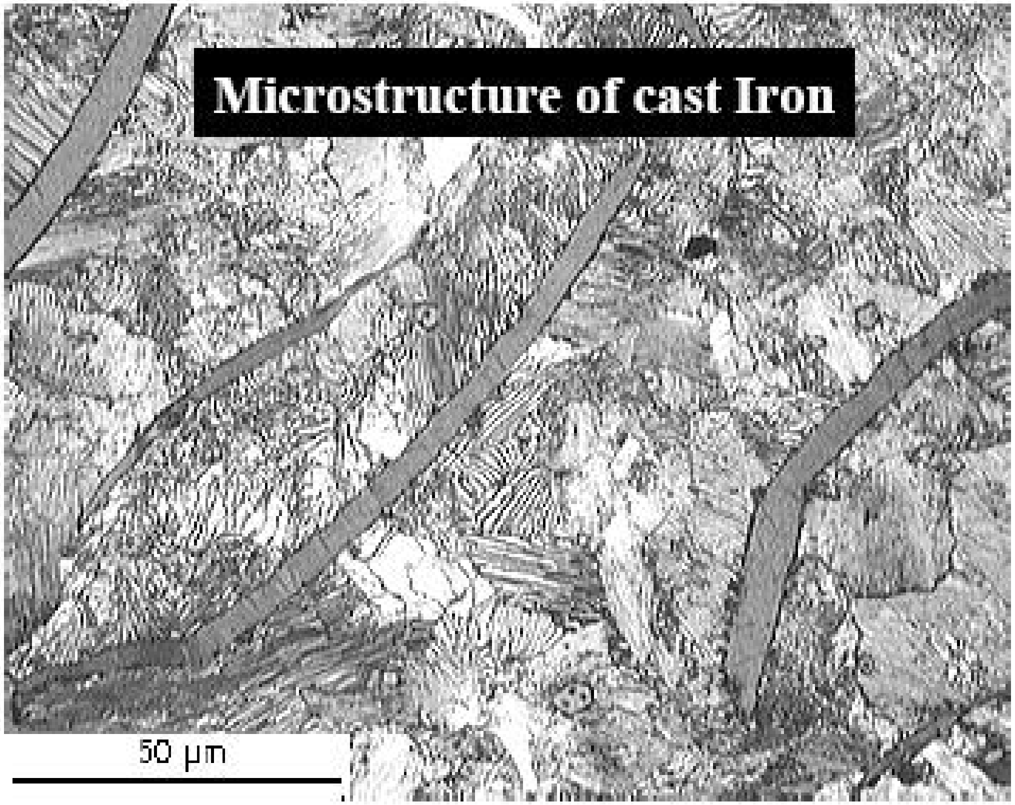
Definitions: Solubility Limit

- **Solvent :** host or major component in solution.
- **Solute :** minor component.
- **Solubility Limit** of a component in a phase is the maximum amount of the component that can be dissolved in it (e.g. alcohol has unlimited solubility in water, sugar has a limited solubility, oil is insoluble).
- The same concepts apply to solid phases: Cu and Ni are mutually soluble in any amount (unlimited solid solubility), while C has a limited solubility in Fe.

Microstructure

- The properties of an alloy depend not only on proportions of the phases but also on how they are arranged structurally at the microscopic level.
- Thus, the microstructure is specified by:
  - The number of phases,
  - Their proportions,
  - And their arrangement in space.

This is an alloy of Fe with 4 wt.% C. There are several phases. The long gray regions are flakes of graphite. The matrix is a fine mixture of BCC Fe and Fe_3C compound.



Phase diagrams will help us to understand and predict the microstructures like the one shown in this photo.

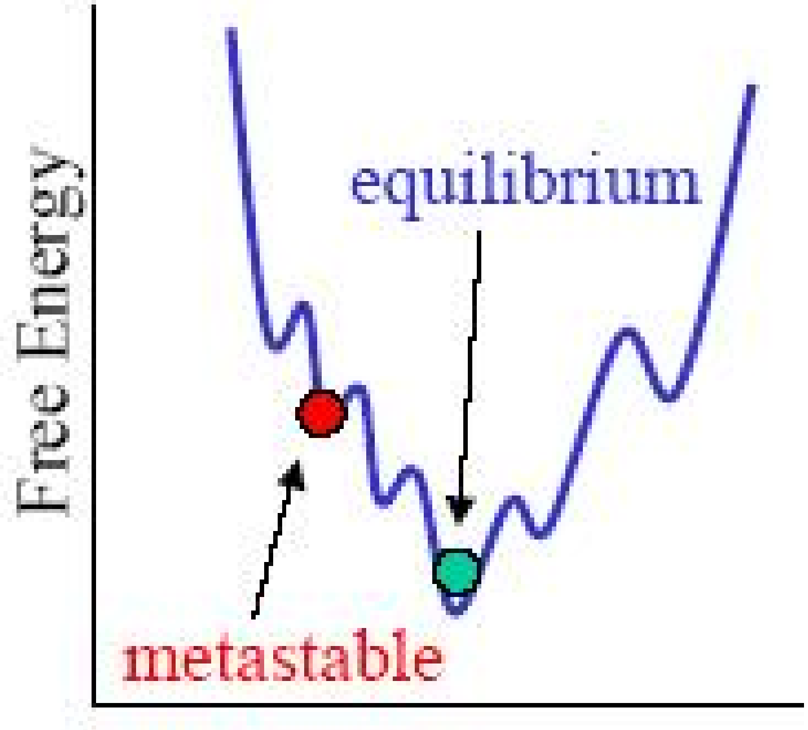
Equilibrium and Metastable States

- A system is at equilibrium if at constant temperature, pressure and composition the system is stable, not changing with time.
- Equilibrium is the state that is achieved given sufficient time.
- But the time to achieve equilibrium may be very long (the kinetics can be slow) that a state along the path to the equilibrium may appear to be stable.
- This is called a metastable state.

Equilibrium and Metastable States

In thermodynamics, equilibrium is described as the state of system that corresponds to the minimum of the thermodynamic function called the free energy of the system.

Free energy is a function of the internal energy of a system, and also the randomness or disorder of the atoms or molecules (or entropy)



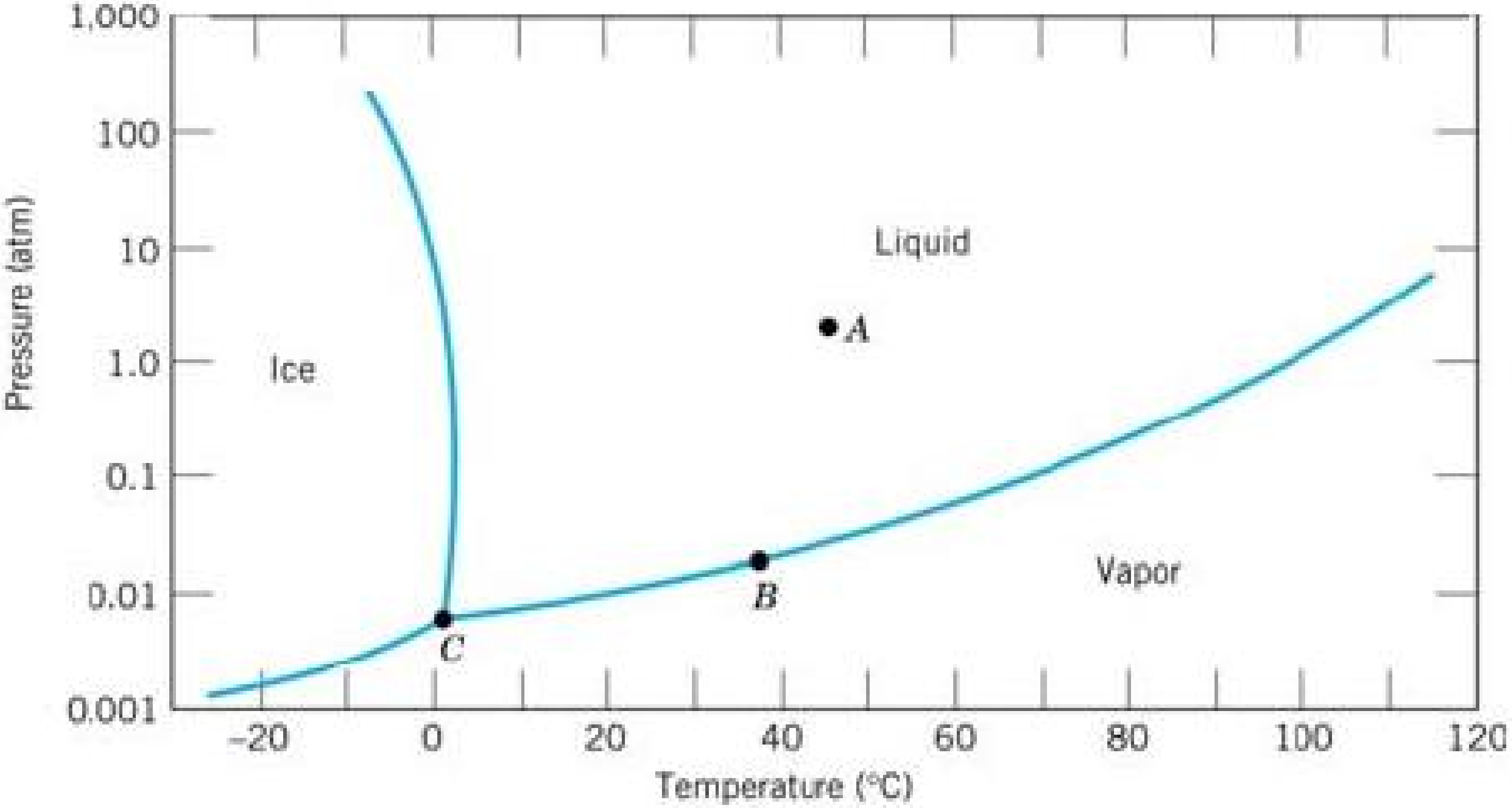
Equilibrium and Metastable States

Thermodynamics tells us that:

- Under conditions of a constant temperature and pressure and composition, the direction of any spontaneous change is toward a lower free energy.
- The state of stable thermodynamic equilibrium is the one with minimum free energy.
- A system at a metastable state is trapped in a local minimum of free energy that is not the global one.

Phase diagram

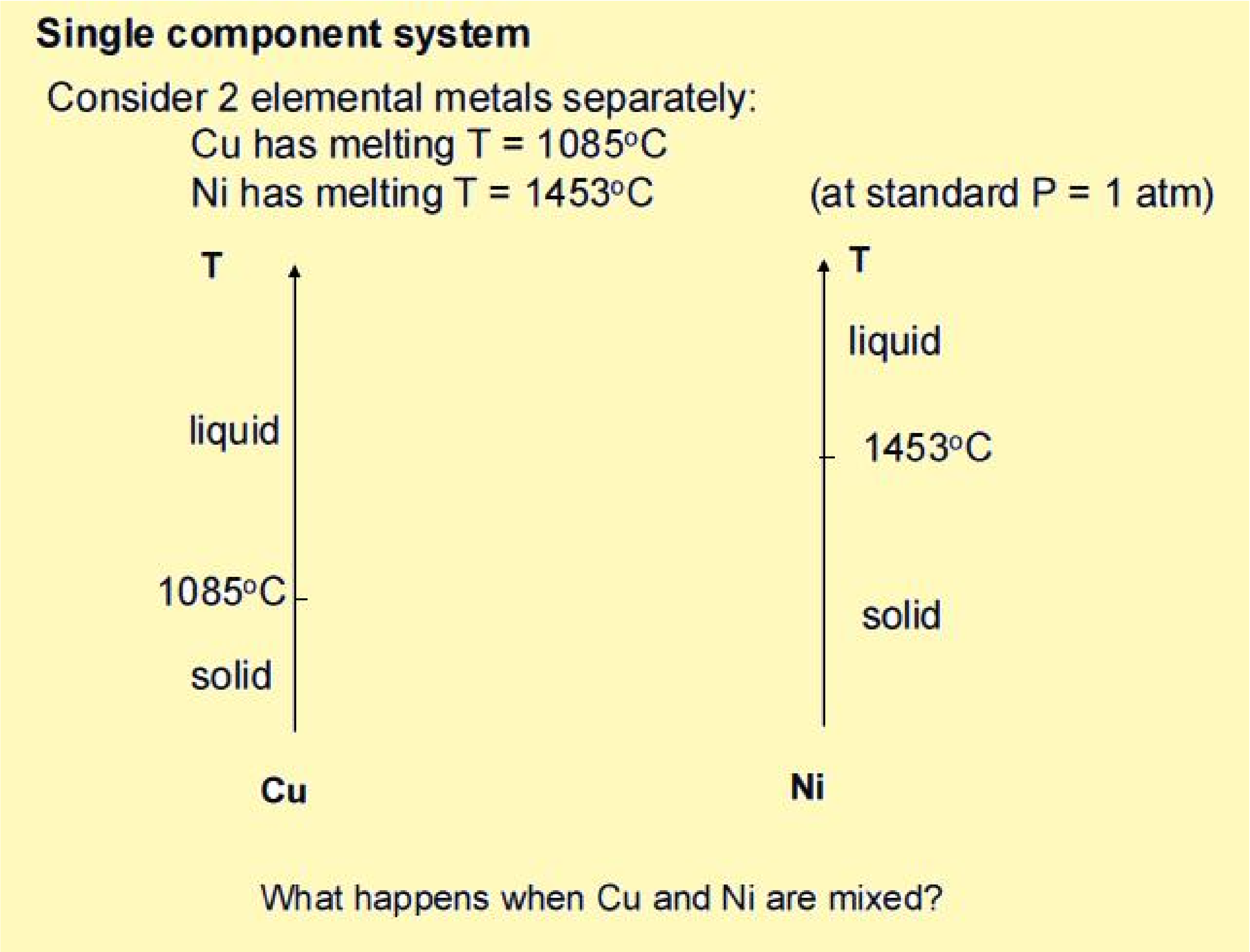
A phase diagram: graphical representation of the combinations of temperature, pressure, composition, or other variables for which specific phases exist at equilibrium.
For H_2O, a typical diagram shows the temperature and pressure at which ice (solid),water (liquid) and steam (gas) exist.


1,000
100
10
1.0
0.1
0.01
0.001
Pressure (atm)
-20
0
20
40
60
80
100
120
Temperature (°C)
Ice
Liquid
Vapor
A
B
C

Phase diagram

- A phase diagrams show what phases exist at equilibrium and what phase transformations we can expect when we change one of the parameters of the system (T, P, composition).
- We will discuss phase diagrams for binary alloys only and will assume pressure to be constant at one atmosphere.
- Phase diagrams for materials with more than two components are complex and difficult to represent.

Unary System



Single component system

Consider 2 elemental metals separately:

Cu has melting T = 1085°C

Ni has melting T = 1453°C (at standard P = 1 atm)

What happens when Cu and Ni are mixed?

Binary Isomorphous Systems (I)

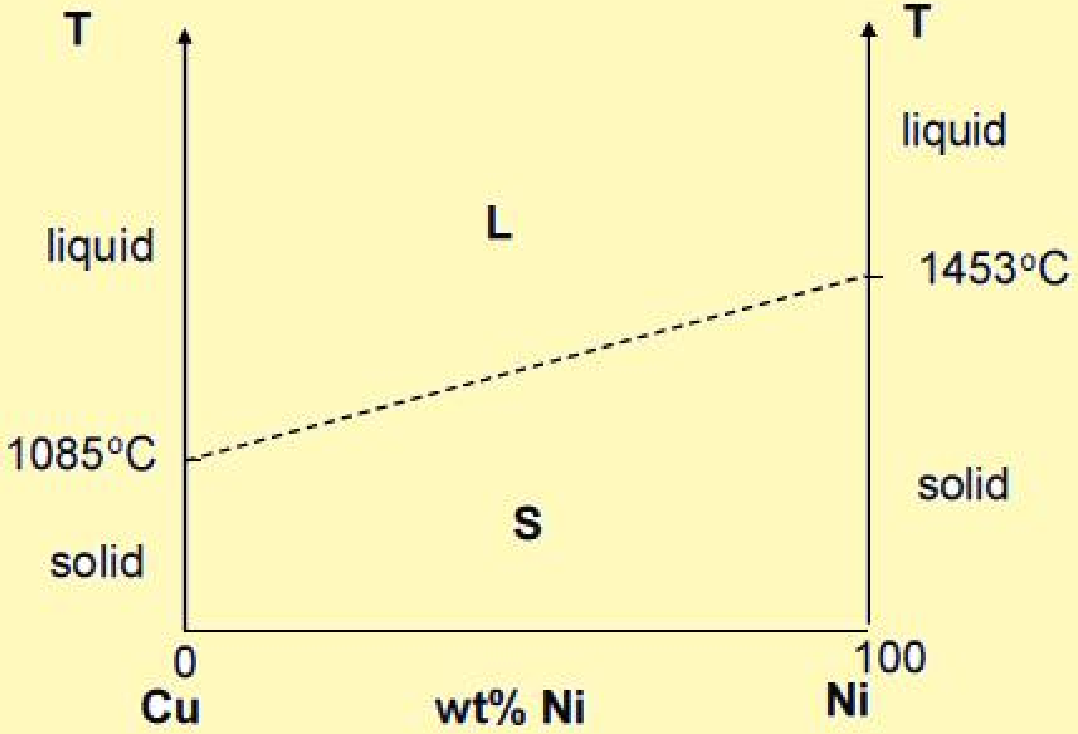
- **Isomorphous system:** complete solid solubility of the two components (both in the liquid and solid phases).
- Three phase region can be identified on the phase diagram:
- Liquid (L) , solid + liquid (α +L), solid (α)
- **Liquidus** line separates liquid from liquid + solid
- **Solidus** line separates solid from liquid + solid.

Binary Isomorphous Systems

2 components

Complete liquid and solid solubility

Expect T_m of solution to lie in between T_m of two pure components



For a pure component, complete melting occurs before T increases (sharp phase transition). But for multicomponent systems, there is usually a coexistence of L and S.

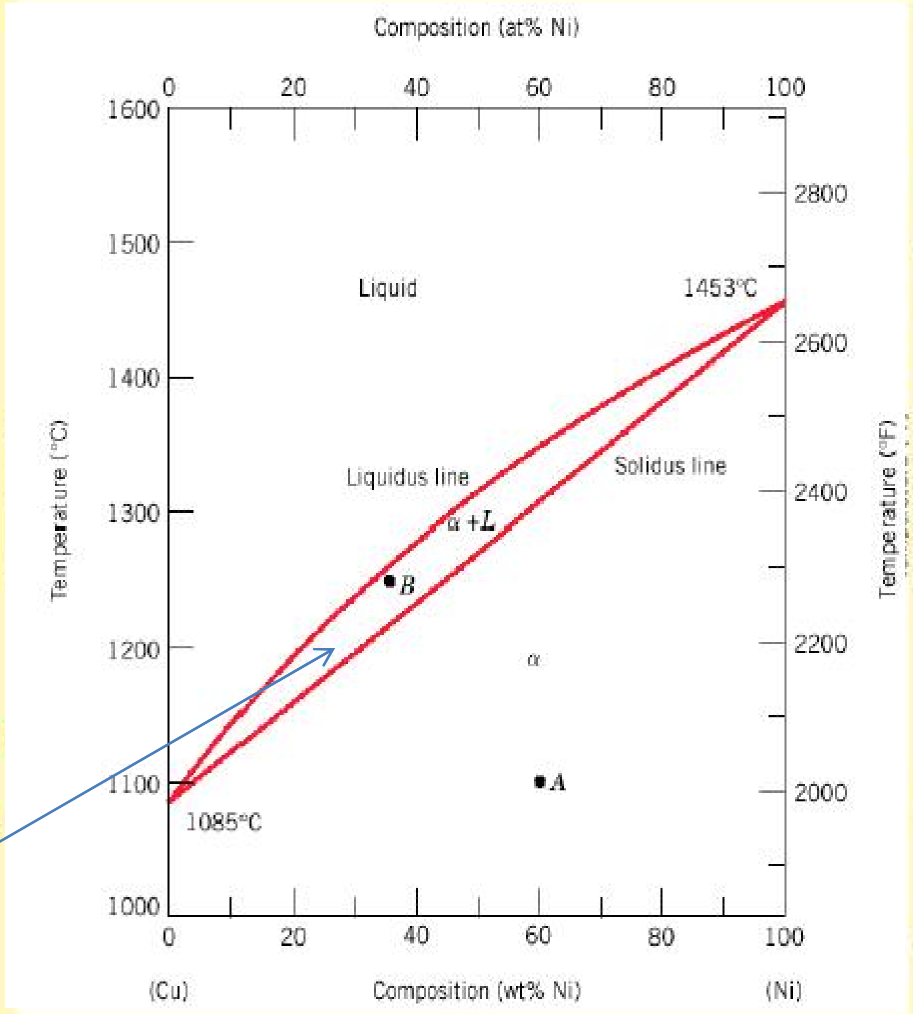
Binary Isomorphous Systems (II)

Example of isomorphous system Cu-Ni

The complete solubility occurs because:-

1. both Cu and Ni have the same crystal structure, FCC
2. similar radii
3. electronegativity
4. valence

Binary Isomorphous Systems



Solid-liquid coexistence region

What can we learn from this phase diagram?

1. **Phase(s) present.**

A: solid (α) only

B: solid and liquid

2. **Composition of those phases**

A: 60 wt% Ni

B: 35 wt% Ni overall (how about in L and S separately?)

3. **Amount of the phases.**

A: 100% α phase

B: % solid and % liquid?

Binary Isomorphous Systems (II)

- In one-component system melting occurs at a well-defined melting temperature.
- In multi-component systems melting occurs over the range of temperatures, between the solidus and liquidus lines.
- Solid and liquid phases are in equilibrium in this temperature range.

Interpretation of Phase Diagrams

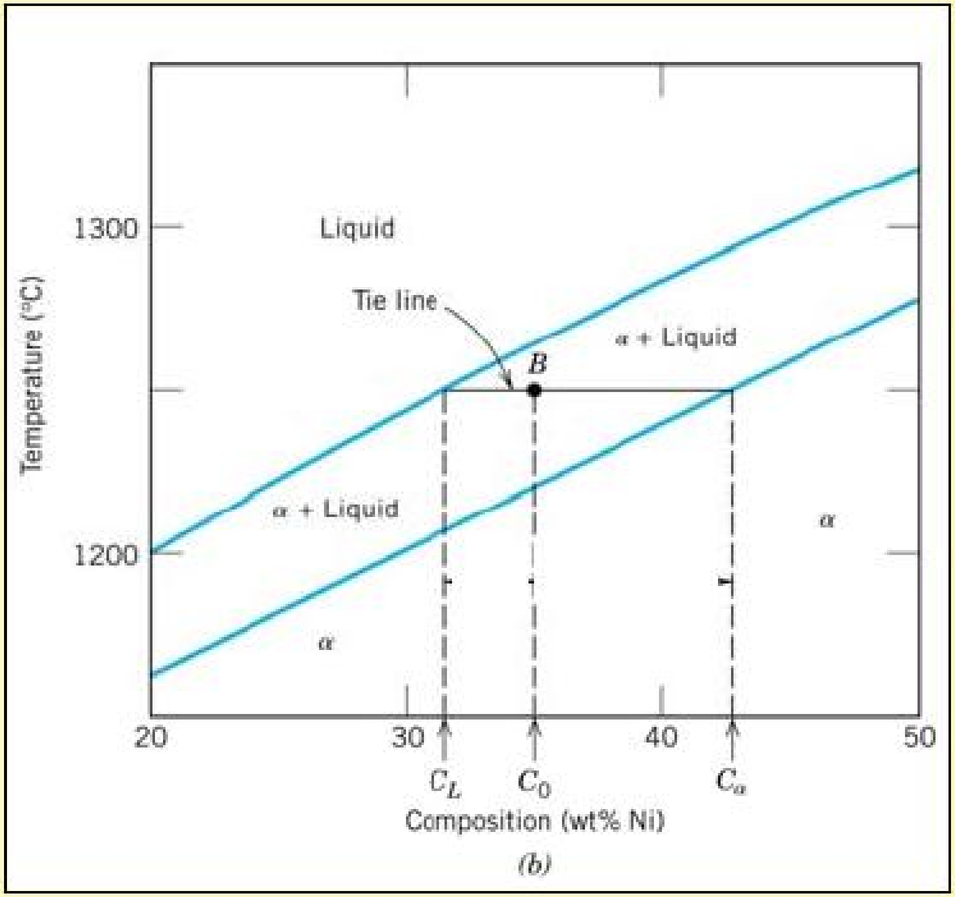
For a given temperature and composition we can use phase diagram to determine:

1) The phases that are present
2) Compositions of the phases
3) The relative fractions of the phases

Finding the composition in a two phase region:

1) Locate composition and temperature in diagram.
2) In two phase region draw the **tie line** or isotherm.
3) Note intersection with phase boundaries. Read compositions at the intersections.

The liquid and solid phases have these compositions.



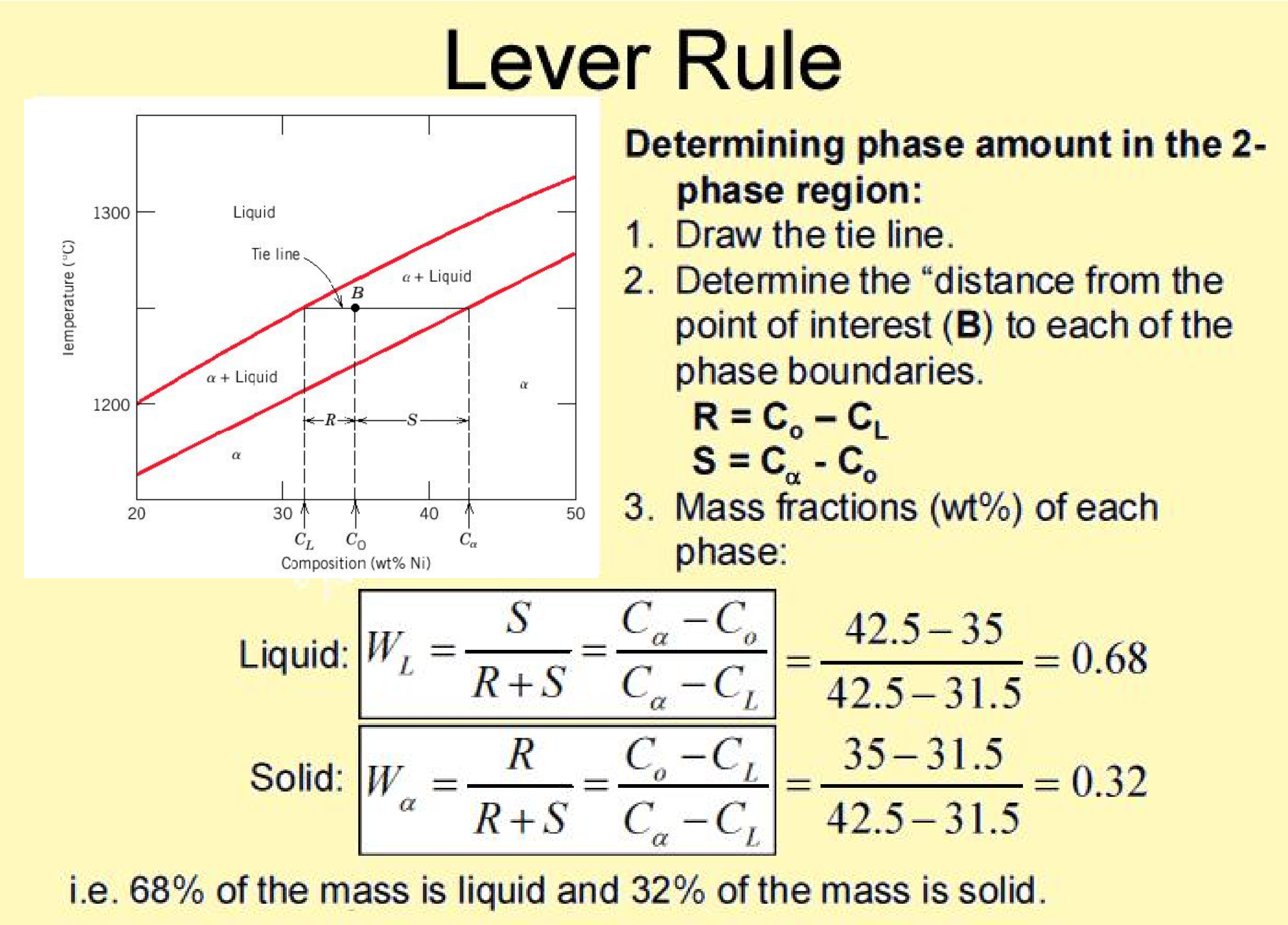
Determining phase composition in 2-phase region:

1. Draw the tie line.
2. Note where the tie line intersects the liquidus and solidus lines (i.e. where the tie line crosses the phase boundaries).
3. Read off the composition at the boundaries:

   Liquid is composed of $\mathbf{C_L}$ amount of Ni (31.5 wt% Ni).

   Solid is composed of $\mathbf{C_\alpha}$ amount of Ni (42.5 wt% Ni).

The Lever Rule



Lever Rule

Determining phase amount in the 2-phase region:

1. Draw the tie line.
2. Determine the "distance from the point of interest (**B**) to each of the phase boundaries.

   $R = C_o - C_L$

   $S = C_\alpha - C_o$
3. Mass fractions (wt%) of each phase:

Liquid: $$\boxed{W_L = \frac{S}{R+S} = \frac{C_\alpha - C_o}{C_\alpha - C_L}} = \frac{42.5-35}{42.5-31.5} = 0.68$$

Solid: $$\boxed{W_\alpha = \frac{R}{R+S} = \frac{C_o - C_L}{C_\alpha - C_L}} = \frac{35-31.5}{42.5-31.5} = 0.32$$

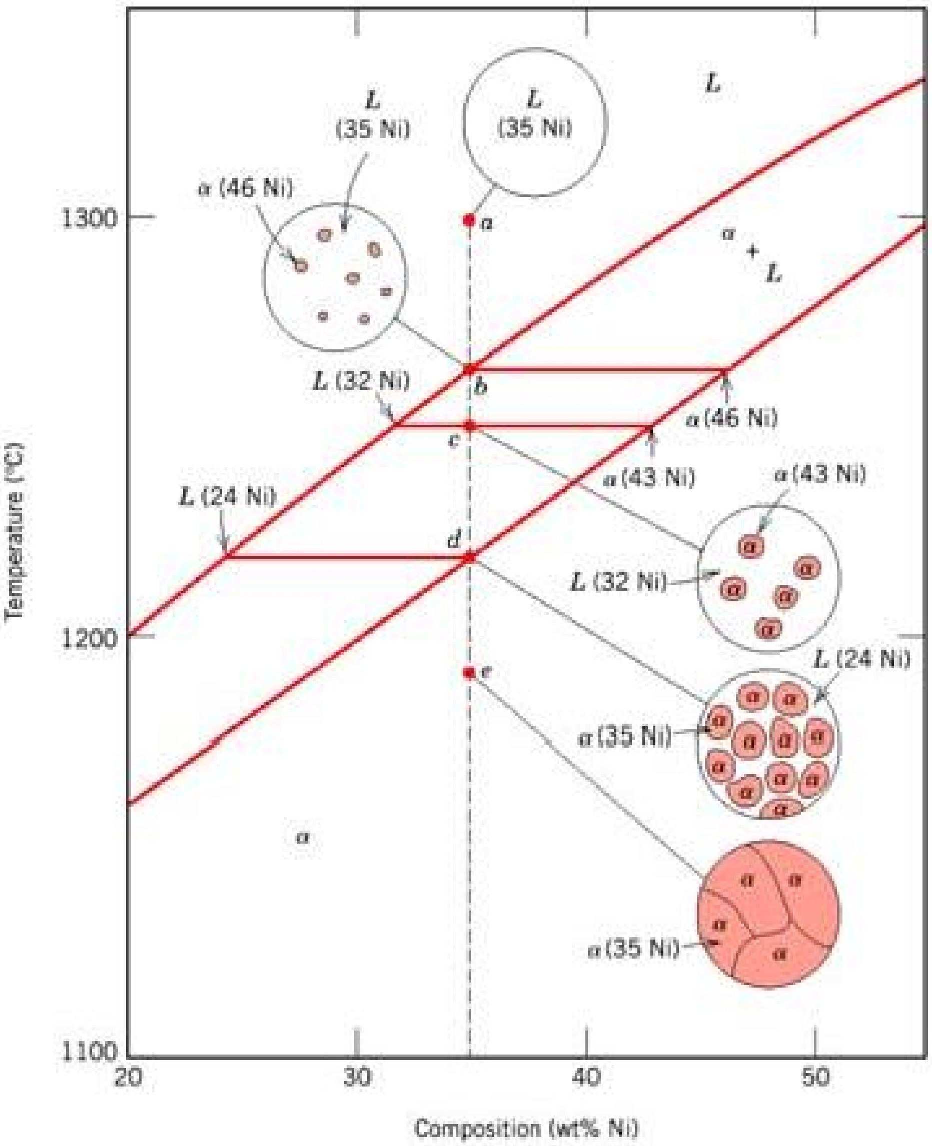
i.e. 68% of the mass is liquid and 32% of the mass is solid.

Development of microstructure in isomorphous alloys

Equilibrium (very slow) cooling

- Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line.
- The composition of the solid and the liquid change gradually during cooling (as can be determined by the tie-line method.)
- Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.

a (T>1260° C): start as homogeneous liquid solution.
b (T ~ 1260° C): liquidus line reached. α phase begins to nucleate. C_α= 46 wt% Ni; C_L = 35 wt% Ni
c (T= 1250° C): calculate composition and mass fraction of each phase.
d (T~ 1220° C): solidus line reached.
Nearly complete solidification.
C_α= 35 wt% Ni; C_L = 24 wt% Ni
e (T<1220° C): homogeneous solid solution with 35 wt% Ni.



Example problem

- 65 wt% Ni – 35 wt% Cu alloy is heated to T within the α+L region.

α-phase contains 70 wt% Ni, determine:

a. Temperature of the alloy.

b. Composition of the liquid phase.

c. Mass fraction of both phases.

Development of microstructure in isomorphous alloys

Non-equilibrium cooling

Fast cooling, but how fast?

→ Fast w.r.t. diffusion.

Since diffusion rate is especially low in solids, consider case where:

Cooling rate >> diffusion rate in solid

Cooling rate << diffusion rate in liquid

(equilibrium maintained in liquids phase) a’ ($T>1260^o$ C): start as homogeneous liquid solution.

b’ ($T \sim 1260^o$ C): liquidus line reached. α phase begins to nucleate.

$C\alpha = 46$ wt% Ni; CL = 35 wt% Ni

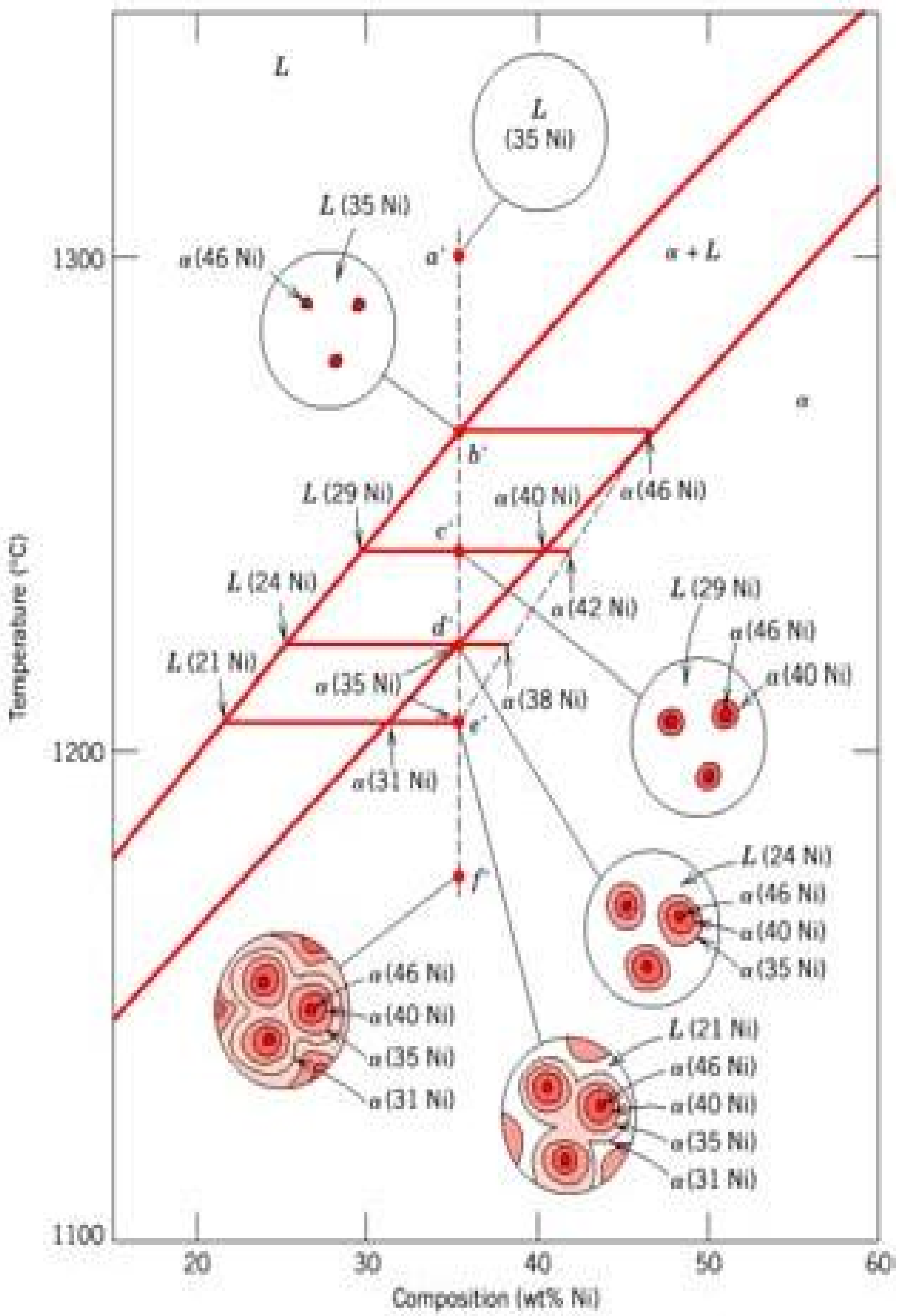
c’ ($T= 1250^o$ C): solids that formed at pt b’ remain with same composition (46wt%) and new solids with 42 wt% Ni form around the existing solids (Why around them?).

d’ ($T\sim 1220^o$ C): solidus line reached. Nearly complete solidification.

p g

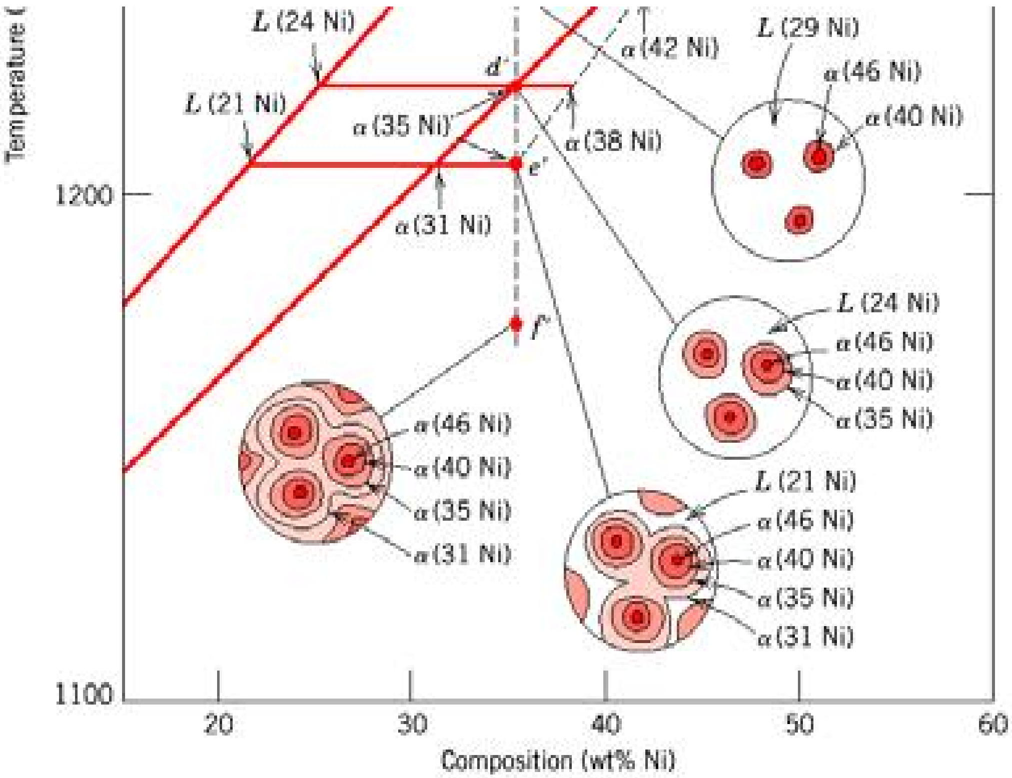
- Previously solidified regions maintain original composition and further solidification occurs at 35 wt% Ni.

e ($T<1220^o$ C): Non-equilibrium solidification complete (with phase segregation).



Note that the center of each grain is rich in Ni (freezes first), with compositional gradient to edge of grain: **segregation**

- The resulting microstructure is termed a **cored structure**



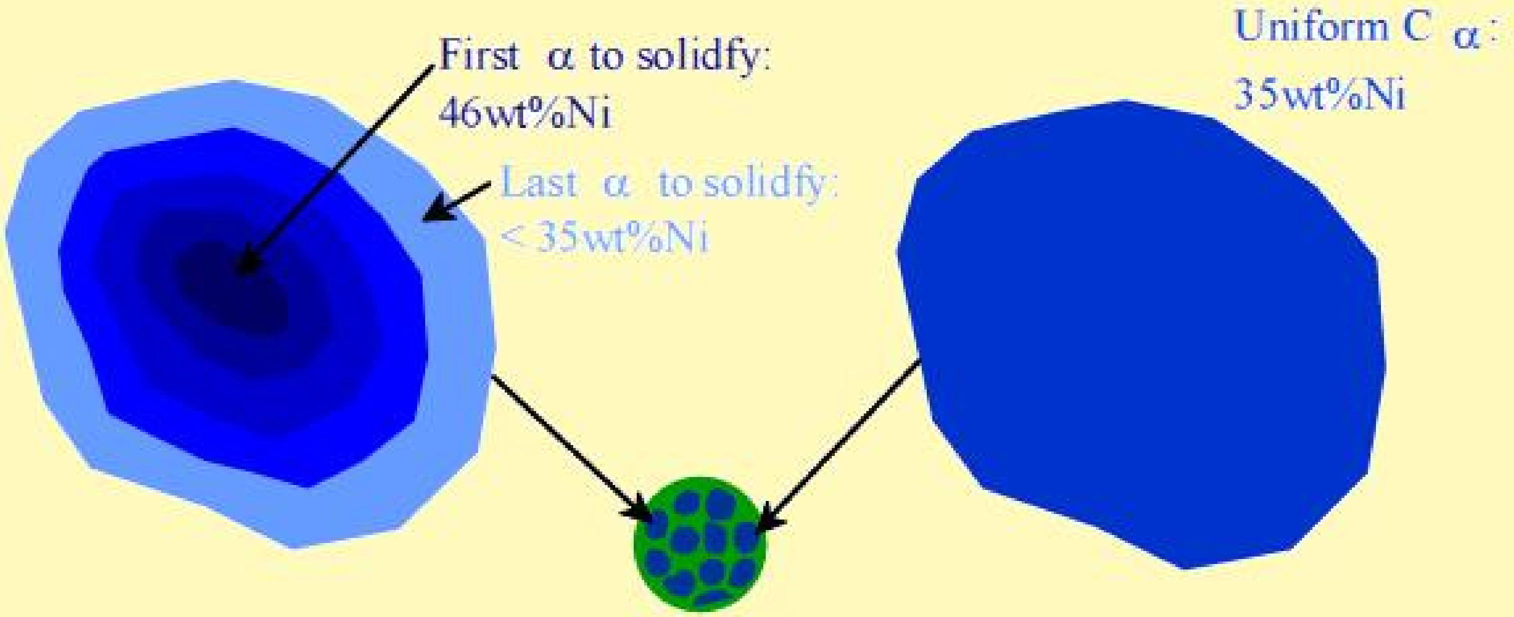
On re-heating, GBs will melt first, this can lead to premature mechanical failure!

Cored vs. Equilibrium phases

- C_α changes as we solidify.
- Cu-Ni case: First α to solidify has C_α = 46wt%Ni.
  Last α to solidify has C_α = 35wt%Ni.

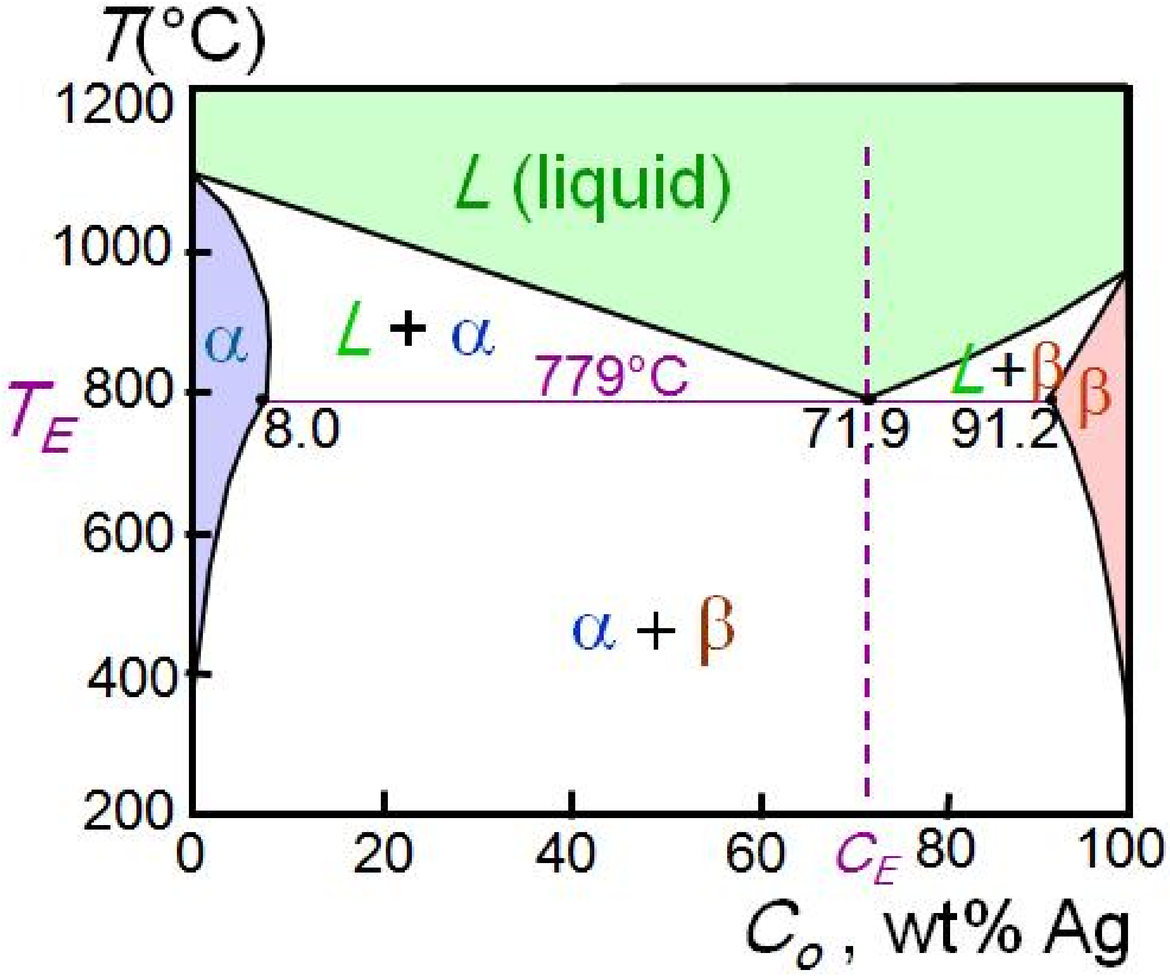
- Fast rate of cooling:
  Cored structure

- Slow rate of cooling:
  Equilibrium structure



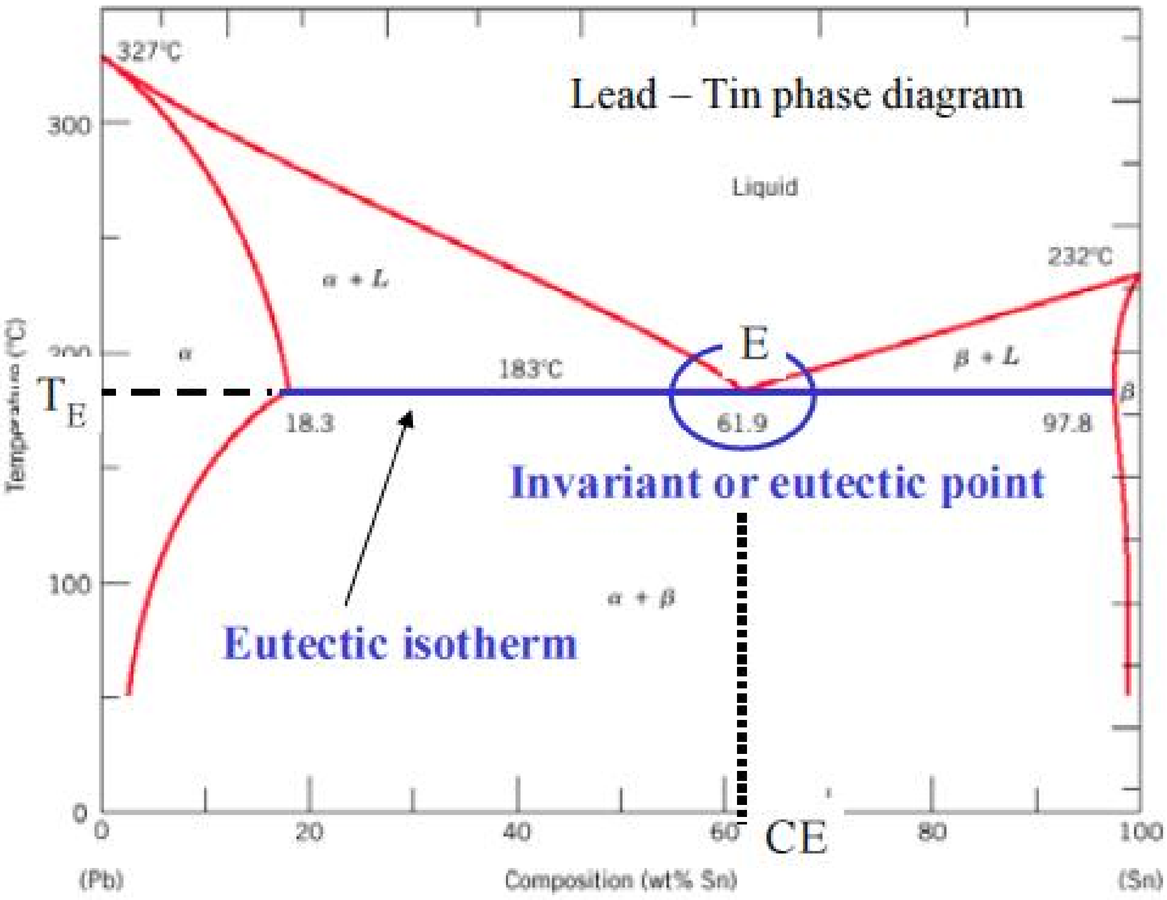
Binary Eutectic Systems

*E*utectic → "easily melted, has a special composition with a min. melting T"



Binary Eutectic Systems

- Single phase regions:
  - α-phase (solid solution rich in Cu).
  - β-phase (solid solution rich in Ag).
  - L-phase (liquid solution).
- Phase coexistence regions:
  - α+β phases (limited solubility of Ag in Cu and vice versa lead to 2 different solid solution phases).
  - α+L and β+L phase regions.
- Tie lines and Lever Rule can be applied in the 2-phase regions.
- Solvus line separates one solid solution from a mixture of solid solutions.



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 - the horizontal solidus line at T_E .

Example 1:

- For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find...

--the phases present: $\alpha + \beta$

--compositions of phases:

C_O = 40 wt% Sn

C_α = 11 wt% Sn

C_β = 99 wt% Sn

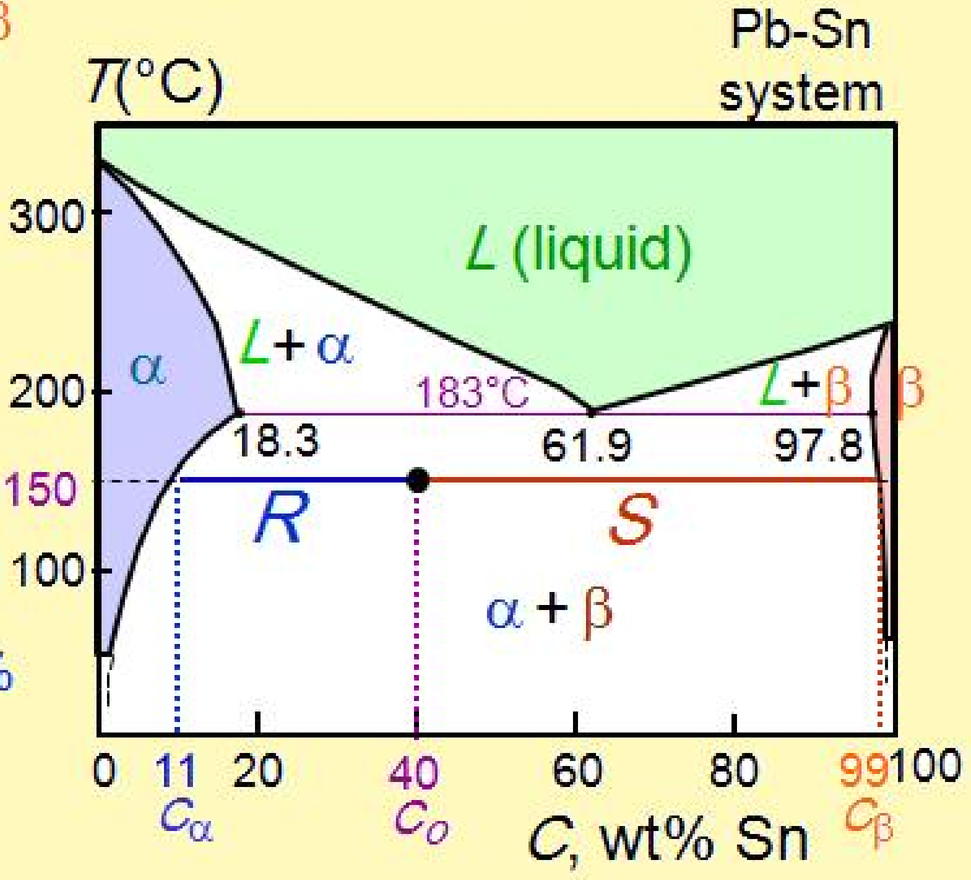
--the relative amount of each phase:

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

$$= \frac{99-40}{99-11} = \frac{59}{88} = 67 \text{ wt\%}$$

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

$$= \frac{40-11}{99-11} = \frac{29}{88} = 33 \text{ wt\%}$$



Example 2:

- For a 40 wt% Sn-60 wt% Pb alloy at 200°C, find...

  --the phases present: $\alpha + L$

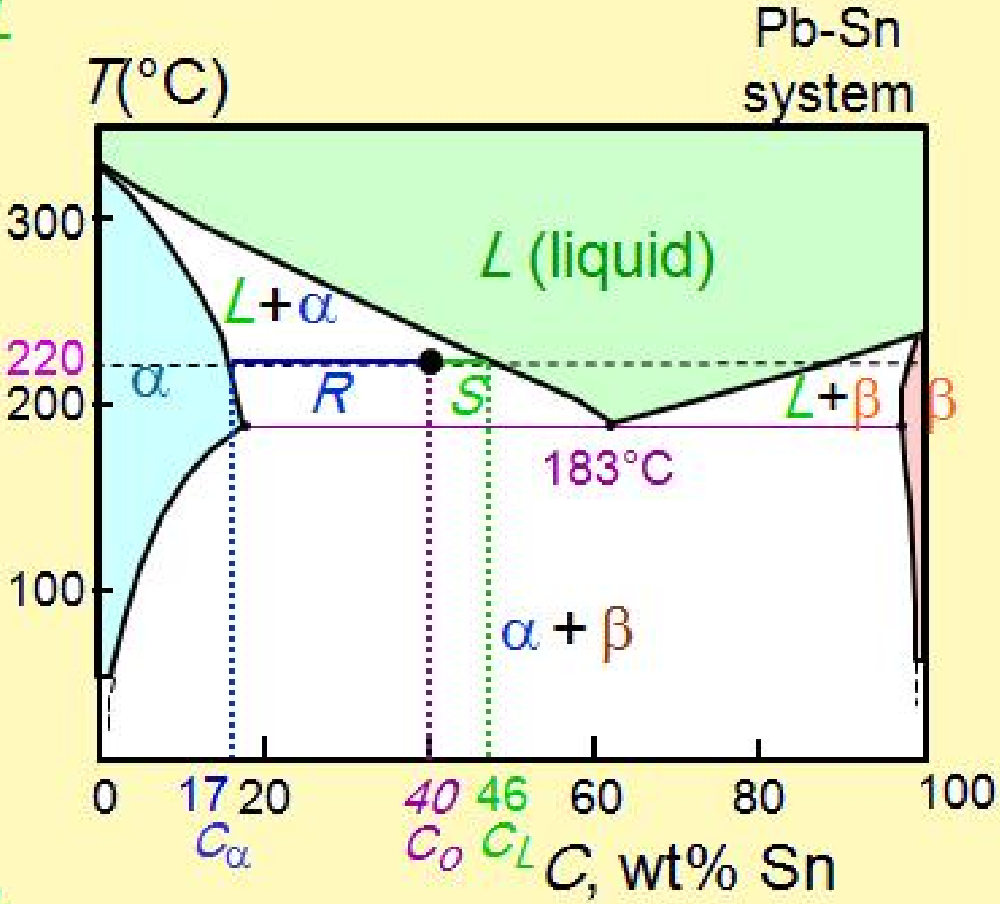
  --compositions of phases:

  $C_O = 40$ wt% Sn
  $C_\alpha = 17$ wt% Sn
  $C_L = 46$ wt% Sn

  --the relative amount of each phase:

$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$

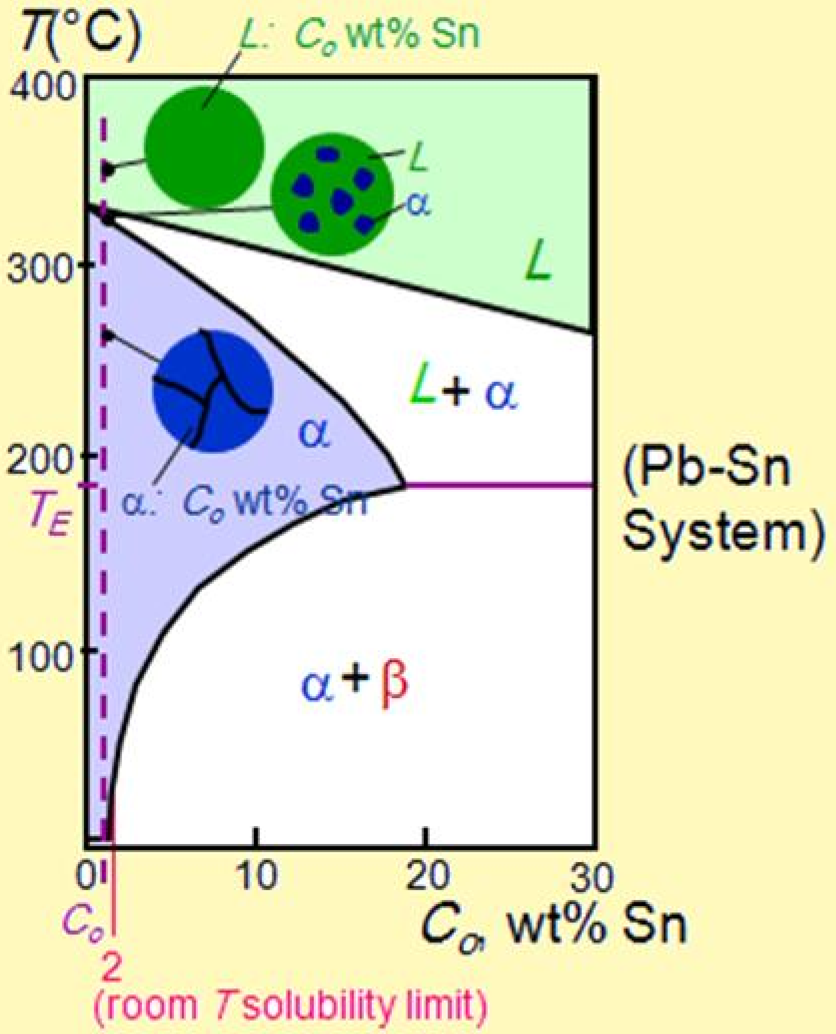


Microstructures in Eutectic Systems

- $C_o < 2$ wt% Sn
- Result:

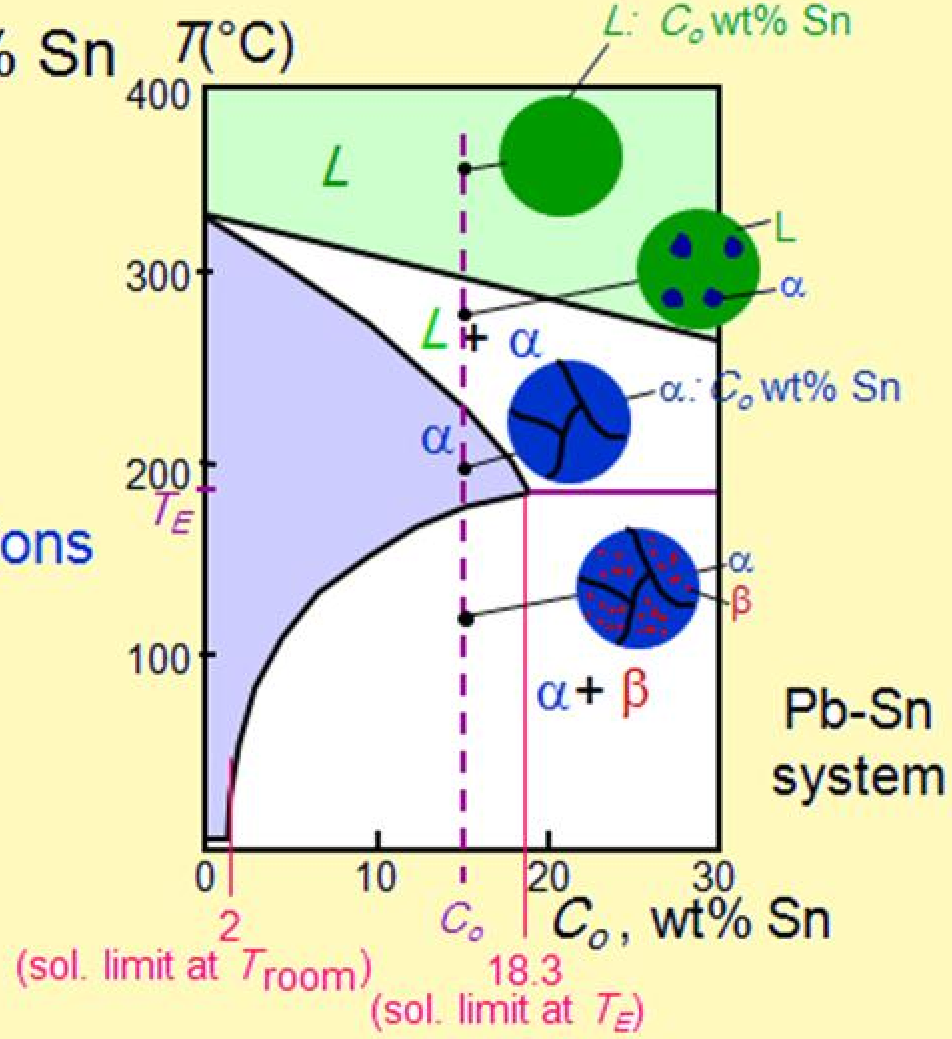
  --at extreme ends

  --polycrystal of α grains
  i.e., only one solid phase.



Microstructures in Eutectic Systems

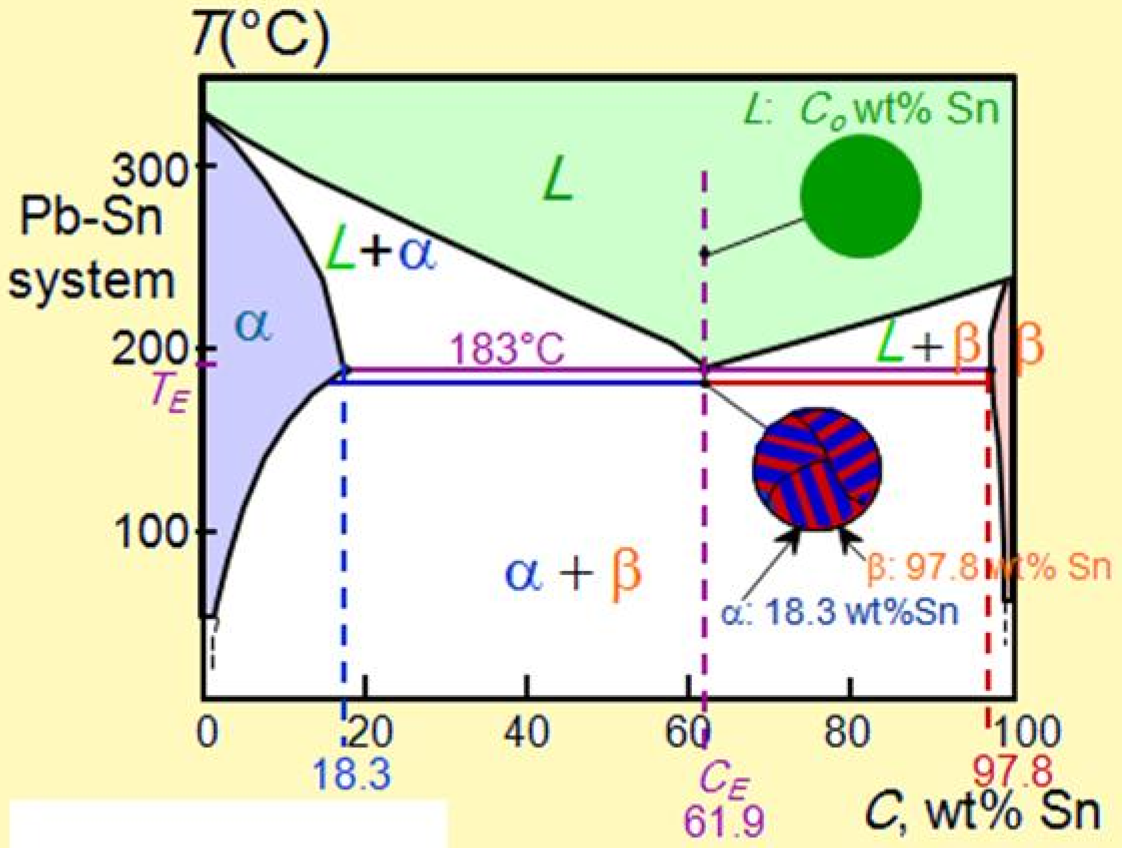
- 2 wt% Sn < C_o < 18.3 wt% Sn
- Result:
  - Initially liquid + α
  - then α alone
  - finally two phases
    - α polycrystal
    - fine β-phase inclusions



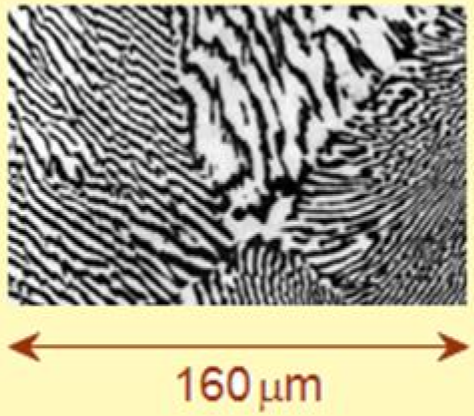
Pb-Sn system

Microstructures in Eutectic Systems

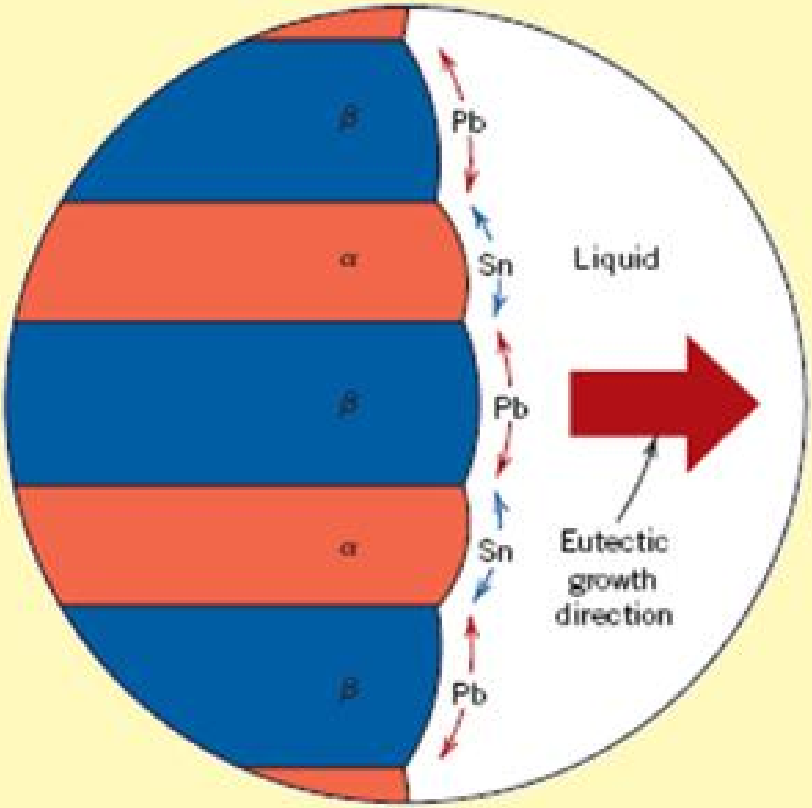
- $C_o = C_E$
- Result: Eutectic microstructure (lamellar structure)
  --alternating layers (lamellae) of α and β crystals.

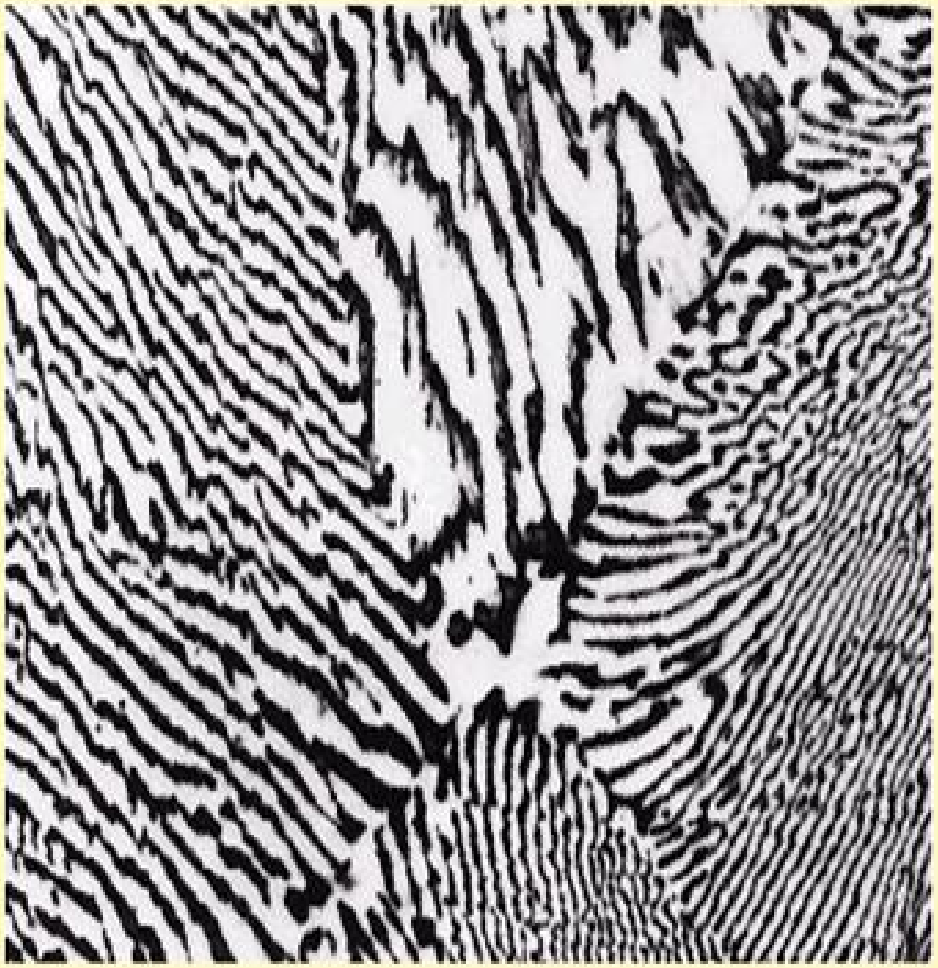


Micrograph of Pb-Sn eutectic microstructure



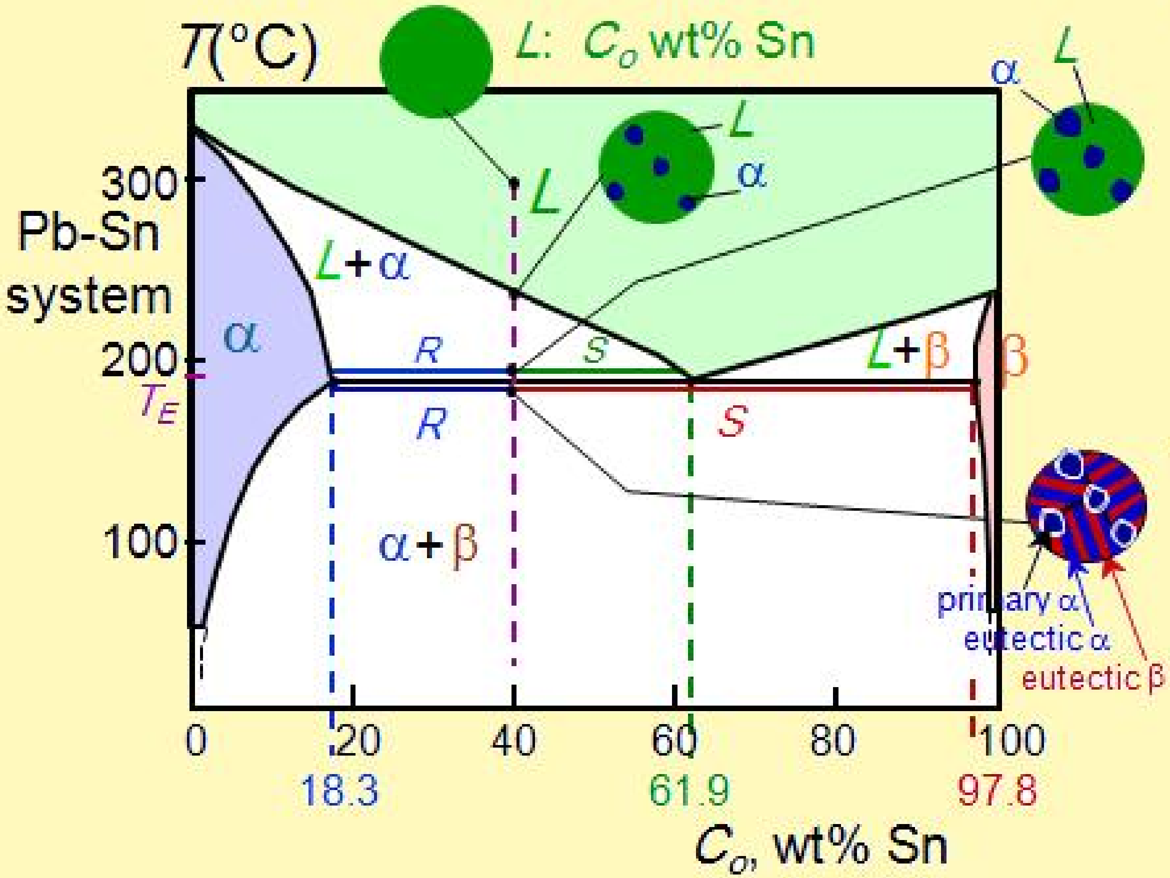
Lamellar Eutectic Structure





Microstructures in Eutectic Systems

- 18.3 wt% Sn < C_o < 61.9 wt% Sn
- Result: α crystals and a eutectic microstructure



- Just above T_E:

C_α = 18.3 wt% Sn

C_L = 61.9 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 50 \text{ wt\%}$$

$$W_L = (1 - W_\alpha) = 50 \text{ wt\%}$$

- Just below T_E:

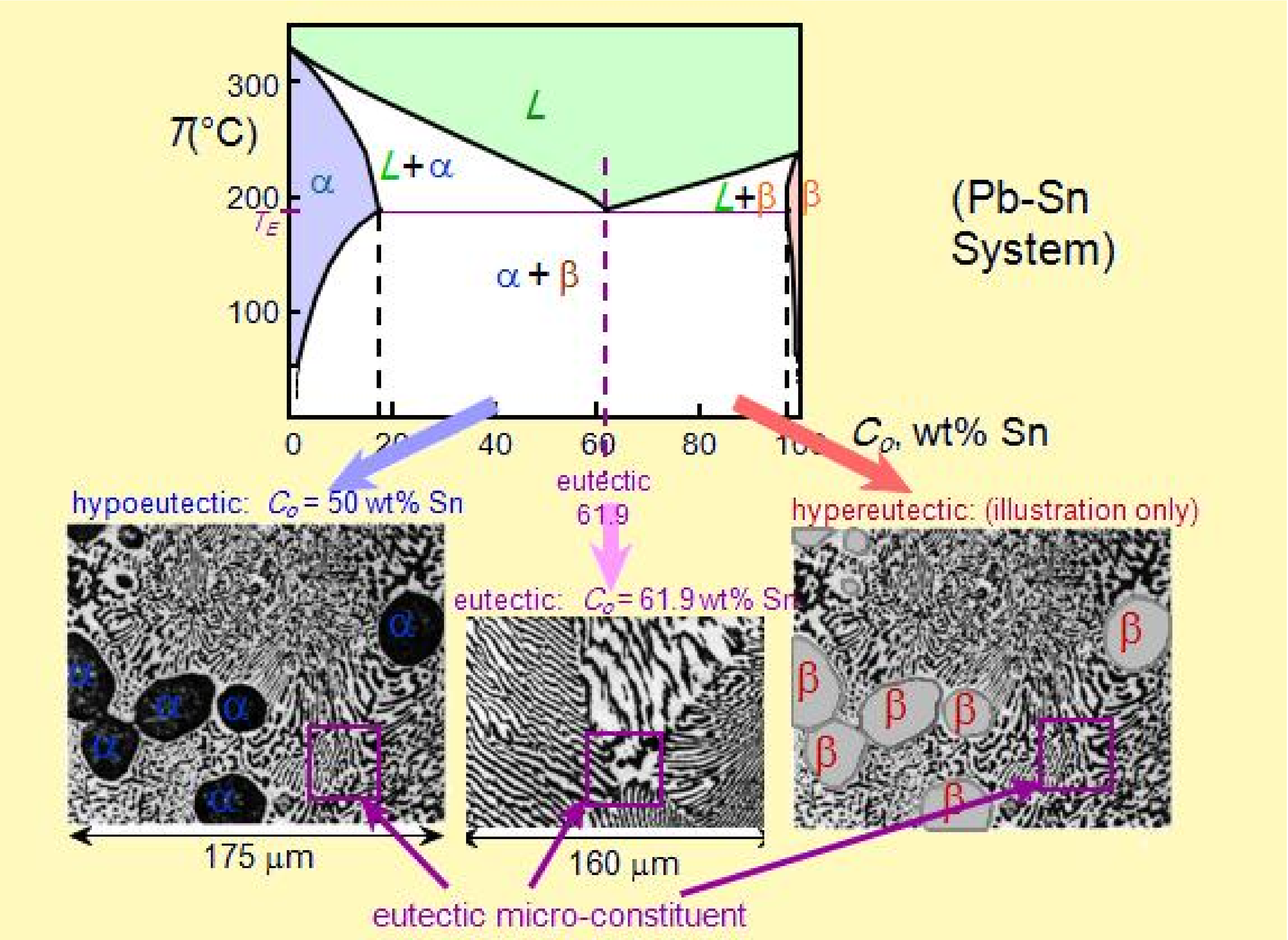
C_α = 18.3 wt% Sn

C_β = 97.8 wt% Sn

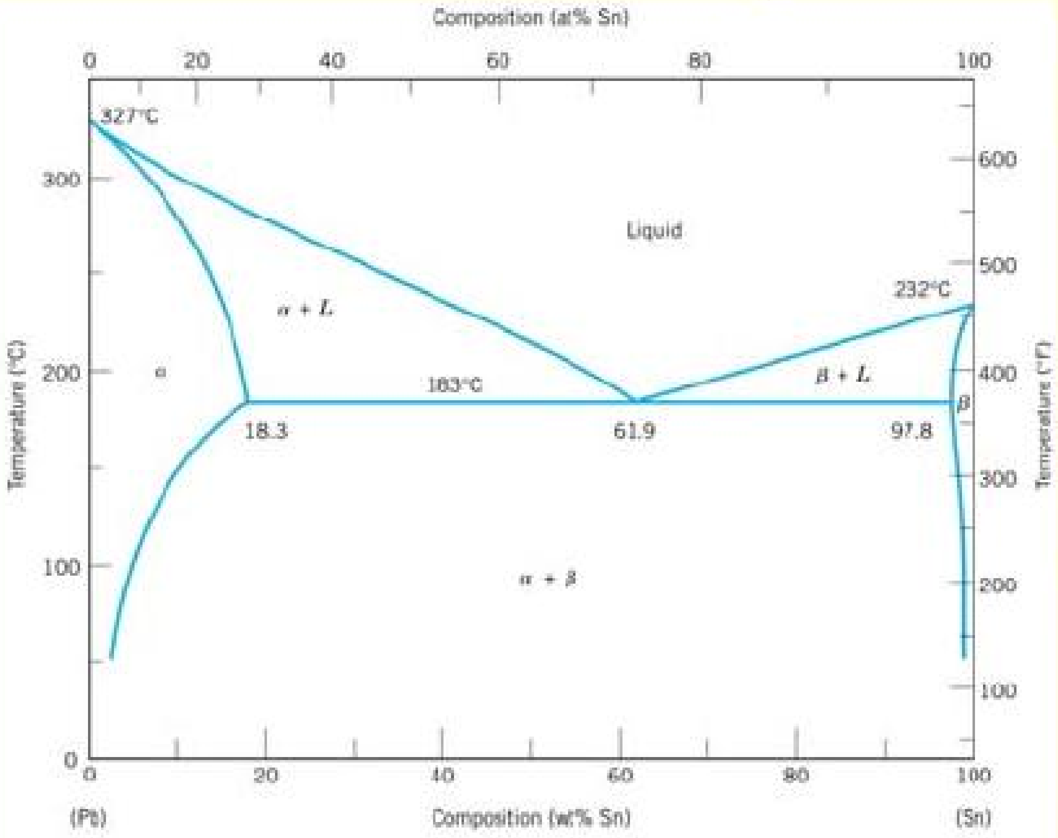
$$W_\alpha = \frac{S}{R+S} = 73 \text{ wt\%}$$

W_β = 27 wt%

Hypoeutectic & Hypereutectic



Eutectic System: Example



Pb-Sn phase diagram

At 150°C for a 40wt% Sn/ 60 wt% Pb alloy:

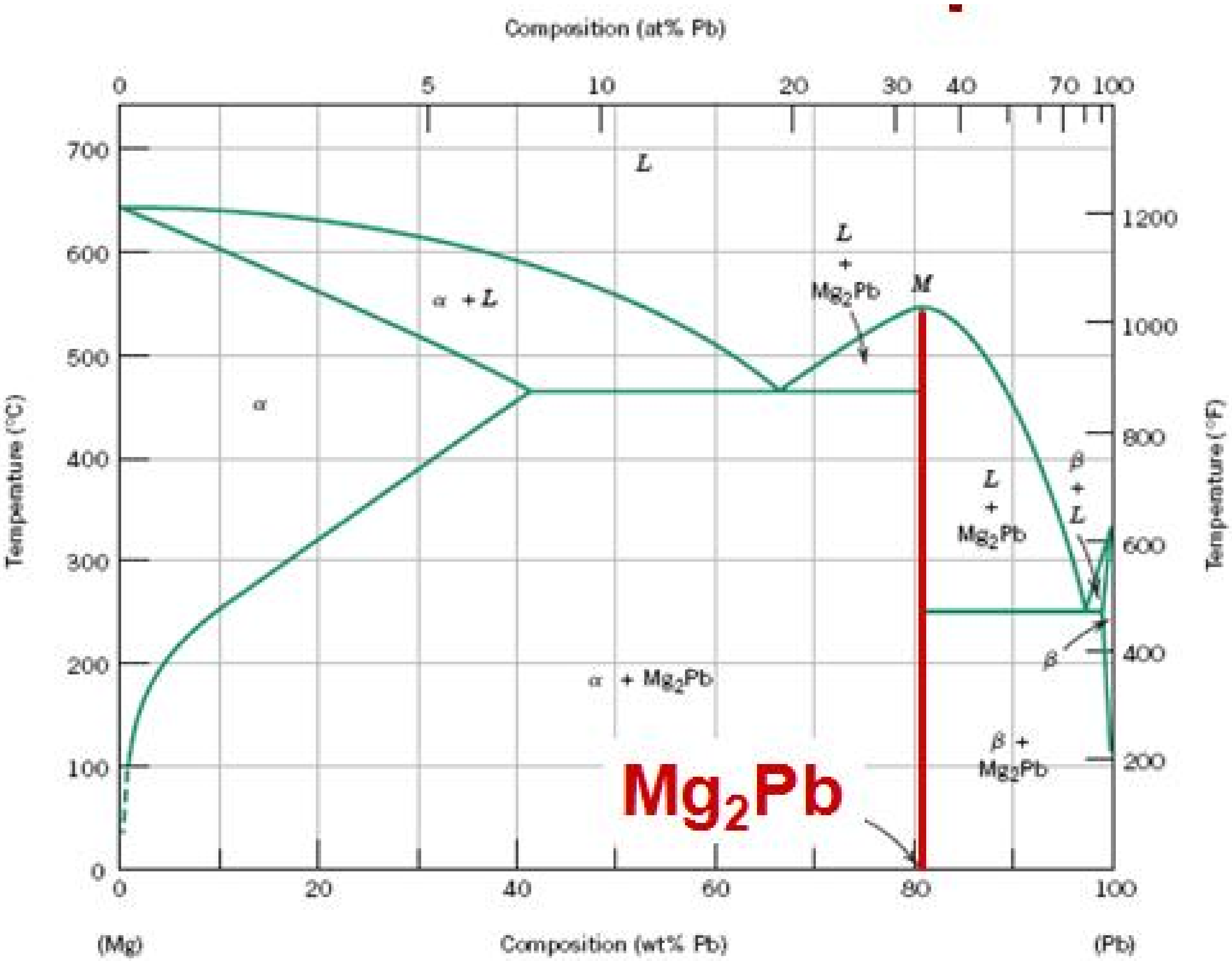
1. What phases are present?
2. What are the compositions of the phases present?
3. What are the mass fractions of the phases?

For a 10wt% Sn/ 90wt% Pb alloy:

1. At what T, can a state with 50% liquid be achieved?
2. At 220°C, how much Sn must be added to achieve the same state (50% liquid)?

Intermetallic Compounds

- Besides solid solutions, intermetallic compounds, that have precise chemical compositions can exist in some systems.
- When using the lever rules, intermetallic compounds are treated like any other phase, except they appear not as a wide region but as a vertical line.
- The phase diagram can be thought of as two joined eutectic diagrams, for Mg-Mg2 Pb and Mg2 Pb-Pb.


Composition (at% Pb)
0
5
10
20
30
40
70
100
700
600
500
400
300
200
100
0
Temperature (°C)
L
α + L
α
L + Mg$_2$Pb
M
L + Mg$_2$Pb
β + L
β
α + Mg$_2$Pb
β + Mg$_2$Pb
Mg$_2$Pb
1200
1000
800
600
400
200
Temperature (°F)
0
20
40
60
80
100
(Mg)
Composition (wt% Pb)
(Pb)

Iron-Carbon (Fe-C) Phase Diagram

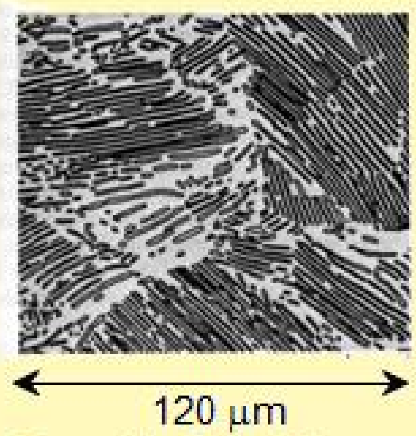
- 2 important points

  -Eutectic (*A*):

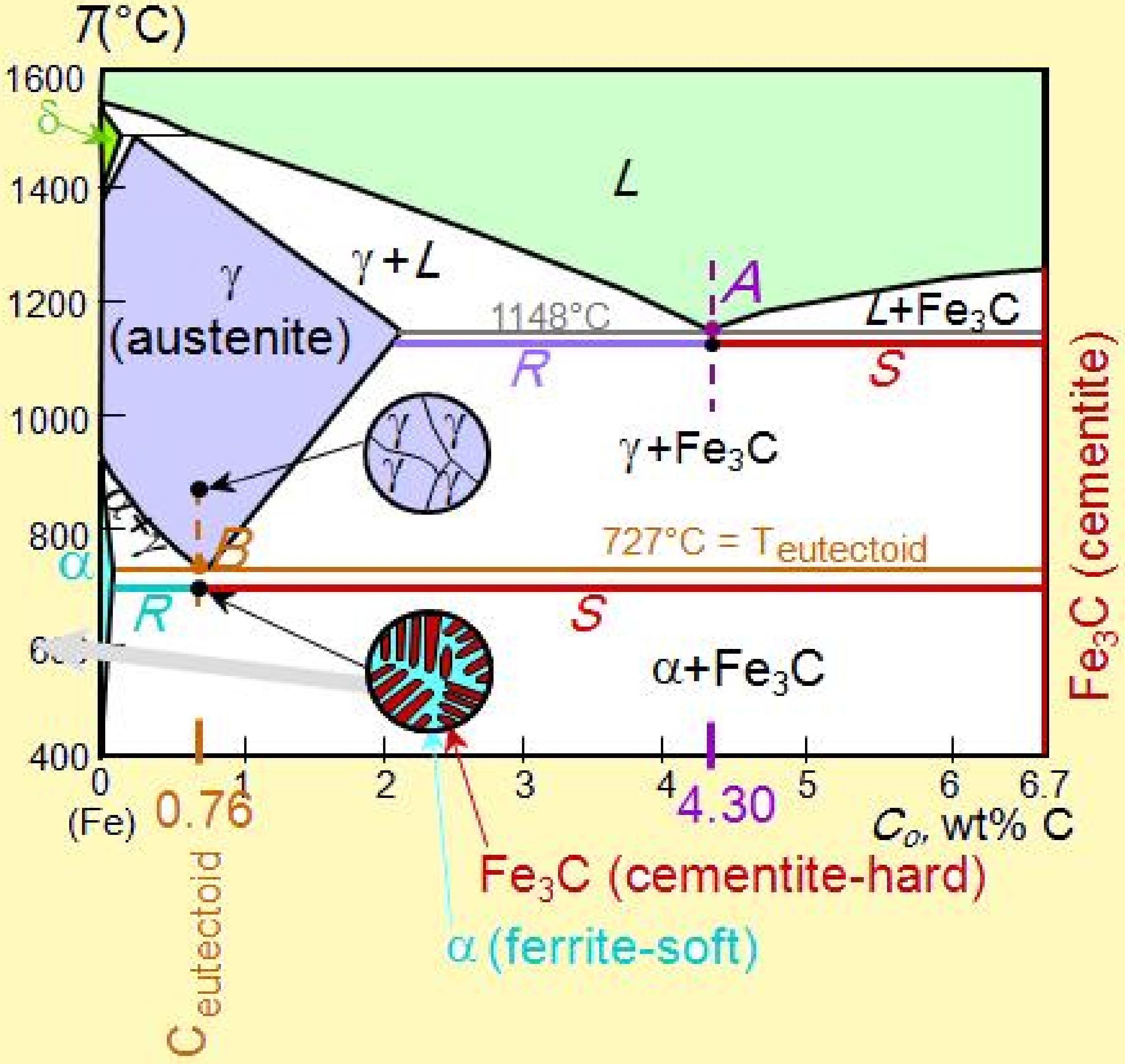
  $L \Rightarrow \gamma + Fe_3C$

  -Eutectoid (*B*):

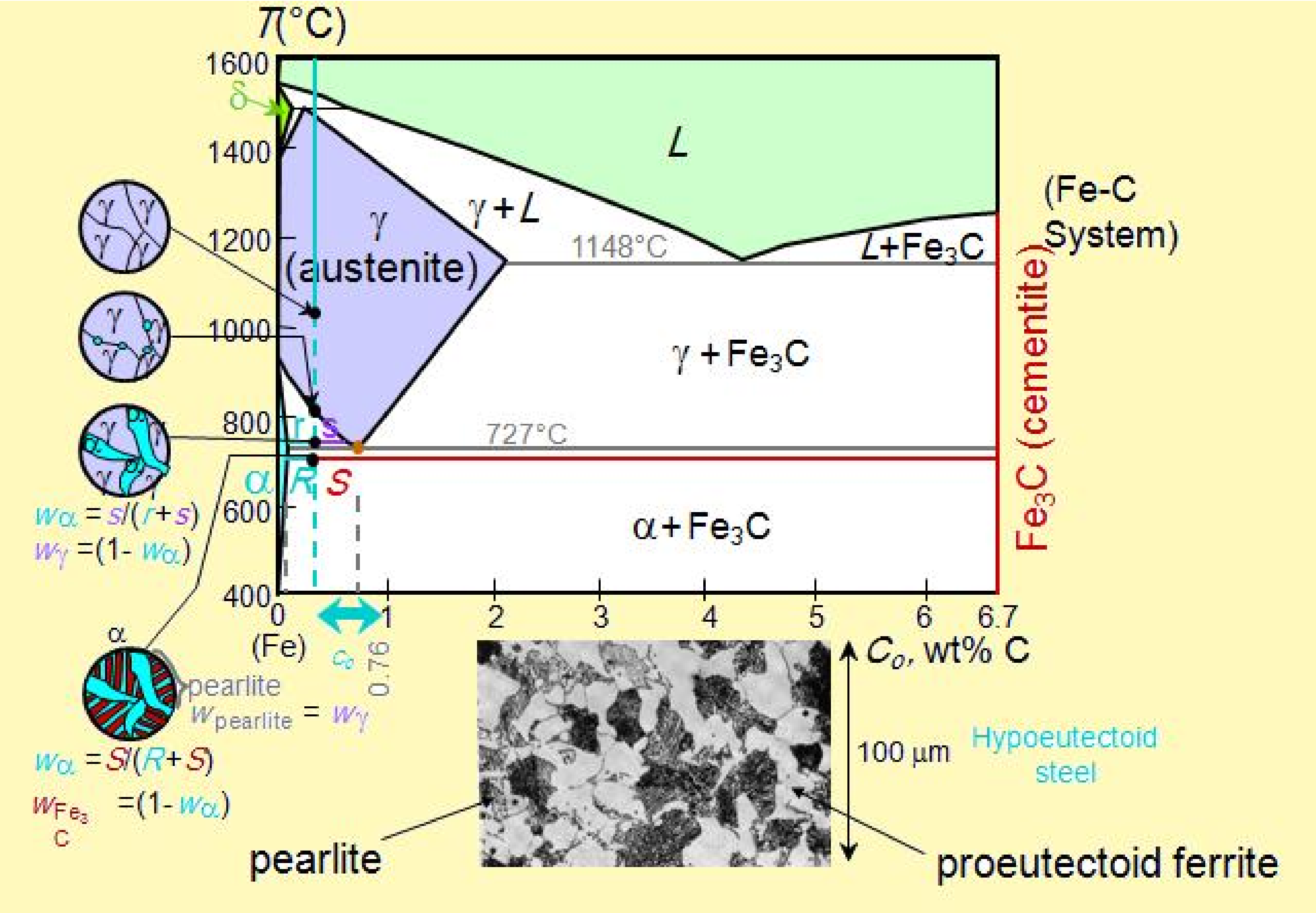
  $\gamma \Rightarrow \alpha + Fe_3C$



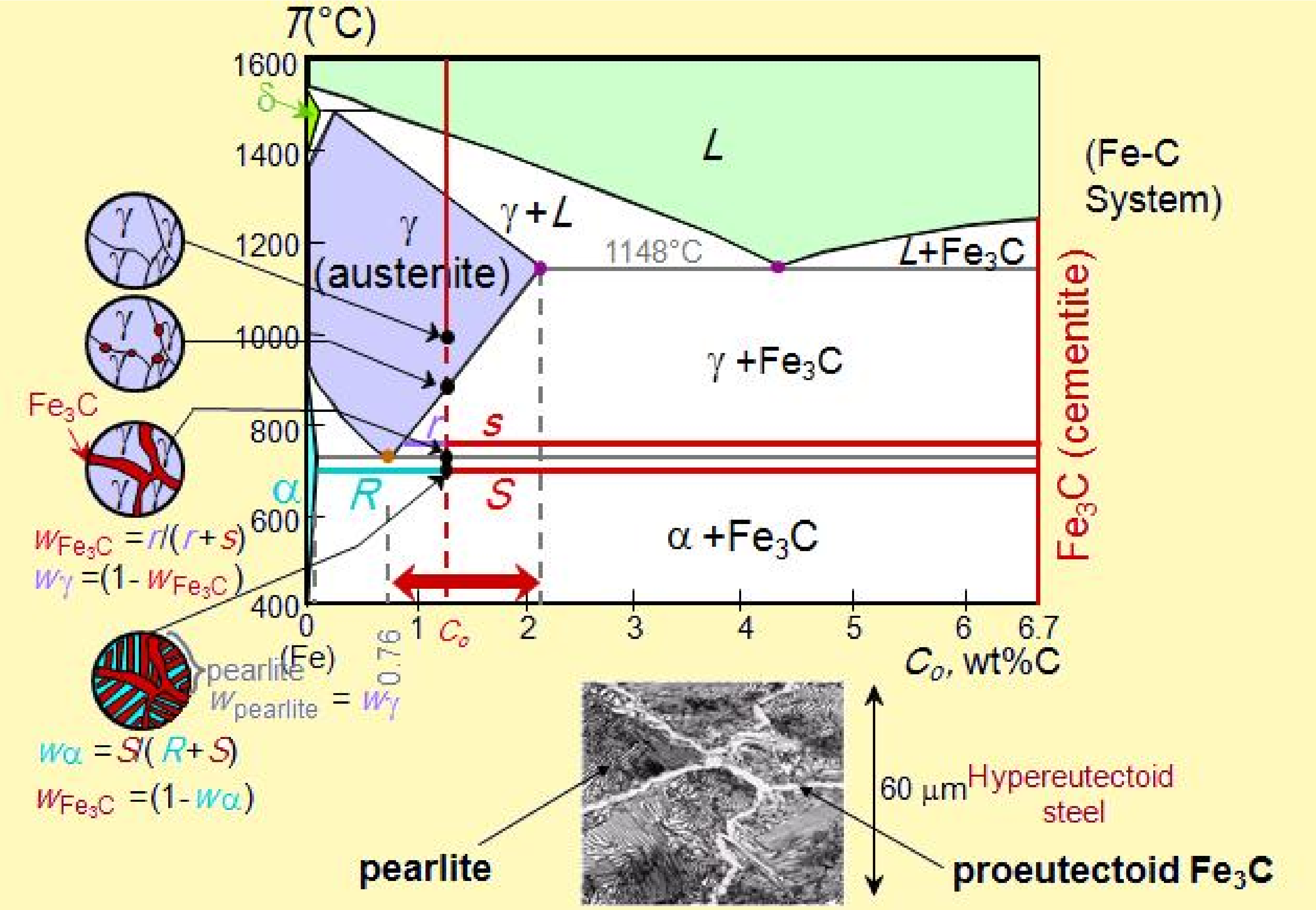
Result: Pearlite = alternating layers of α and Fe_3C phases



Hypoeutectoid Steel



Hypoeutectoid Steel



Phases in Fe–Fe3 C Phase Diagram

1. α-ferrite - solid solution of C in BCC Fe
   - Stable form of iron at room temperature.
   - The maximum solubility of C is 0.022 wt%
   - Transforms to FCC γ-austenite at 912 °C
2. γ-austenite - solid solution of C in FCC Fe
   - The maximum solubility of C is 2.14 wt %.
   - Transforms to BCC δ-ferrite at 1395 °C
   - Is not stable below the eutectic temperature (727 ° C) unless cooled rapidly

Phases in Fe–Fe3 C Phase Diagram

3. δ-ferrite solid solution of C in BCC Fe
   - The same structure as α-ferrite
   - Stable only at high T, above 1394 °C
   - Melts at 1538 °C
4. Fe3 C (iron carbide or cementite)
   - This intermetallic compound is metastable, it remains as a compound indefinitely at room T, but decomposes (very slowly, within several years) into α-Fe and C (graphite) at 650 - 700 °C
5. Fe-C liquid solution

A few comments on Fe–Fe3 C 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 limited (max. 0.022 wt % at 727 °C) - BCC has relatively small interstitial positions.
- Maximum solubility in FCC austenite is 2.14 wt % at 1147 °C - FCC has larger interstitial positions
- Mechanical properties: Cementite is very hard and brittle - can strengthen steels.

A few comments on Fe–Fe3 C system

- Mechanical properties also depend on the microstructure, that is, 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: less than 0.008 wt % C in α−ferrite at room T.
- Steels: 0.008 - 2.14 wt % C (usually < 1 wt %) α-ferrite + Fe3 C at room T.
- Cast iron: 2.14 - 6.7 wt % (usually < 4.5 wt %).

Example: Phase Equilibria

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

a) composition of Fe_3C and ferrite (α)

b) the amount of carbide (cementite) in grams that forms per 100 g of steel

c) the amount of pearlite and proeutectoid ferrite (α)

Solution: a) composition of Fe_3C and ferrite (α)

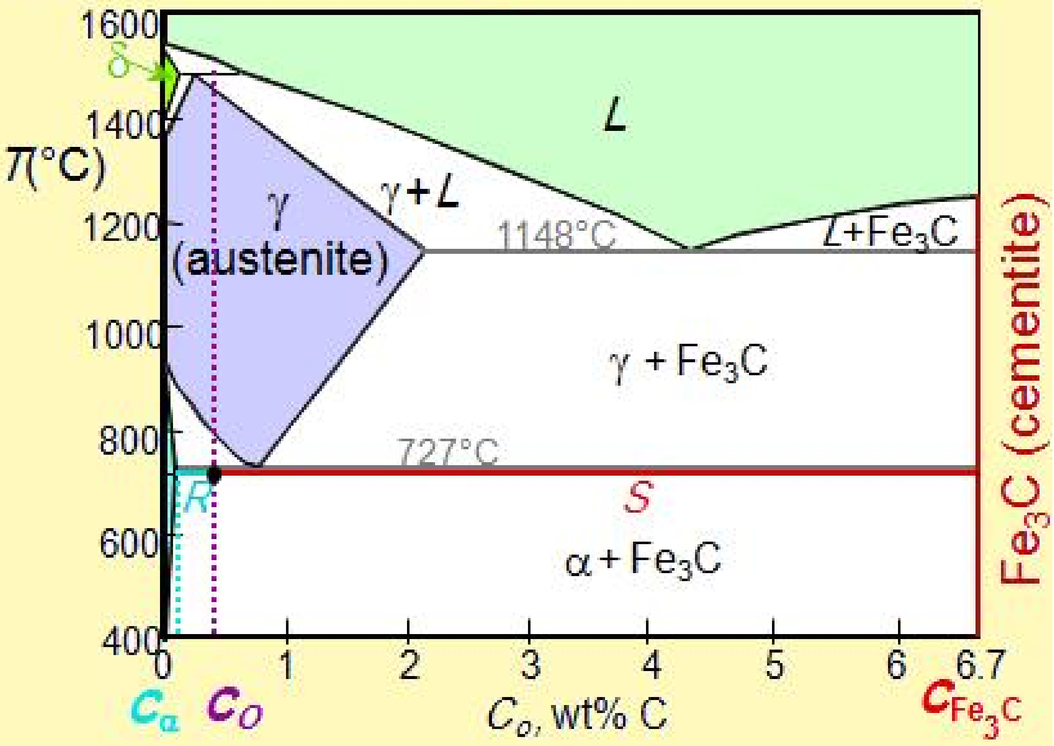
b) the amount of carbide (cementite) in grams that forms per 100 g of steel

C_O = 0.40 wt% C
C_α = 0.022 wt% C
C_{Fe_3C} = 6.70 wt% C

$$\frac{Fe_3C}{Fe_3C+\alpha} = \frac{C_o - C_\alpha}{C_{Fe_3C} - C_\alpha} \times 100$$

$$= \frac{0.4-0.022}{6.7-0.022} \times 100 = 5.7\text{g}$$

$$\boxed{\begin{array}{l} Fe_3C = 5.7\text{ g} \\ \alpha = 94.3\text{ g} \end{array}}$$



c. the amount of pearlite and proeutectoid ferrite (α)

note: amount of pearlite = amount of γ just above T_E

$C_o = 0.40$ wt% C

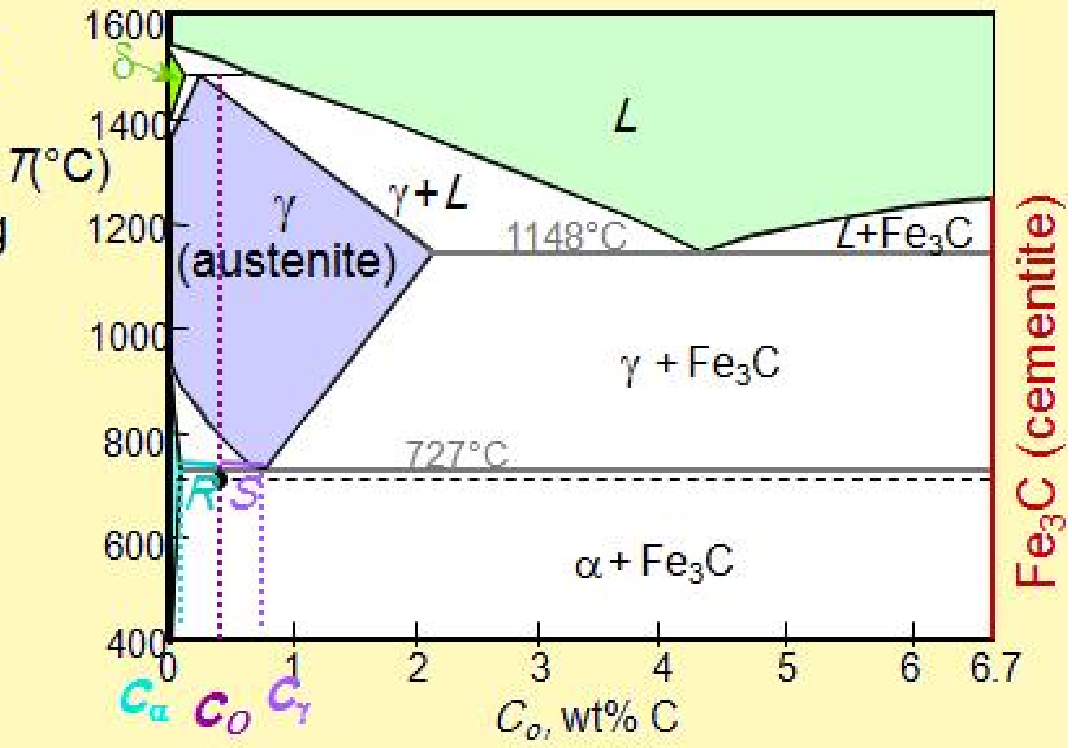
$C_\alpha = 0.022$ wt% C

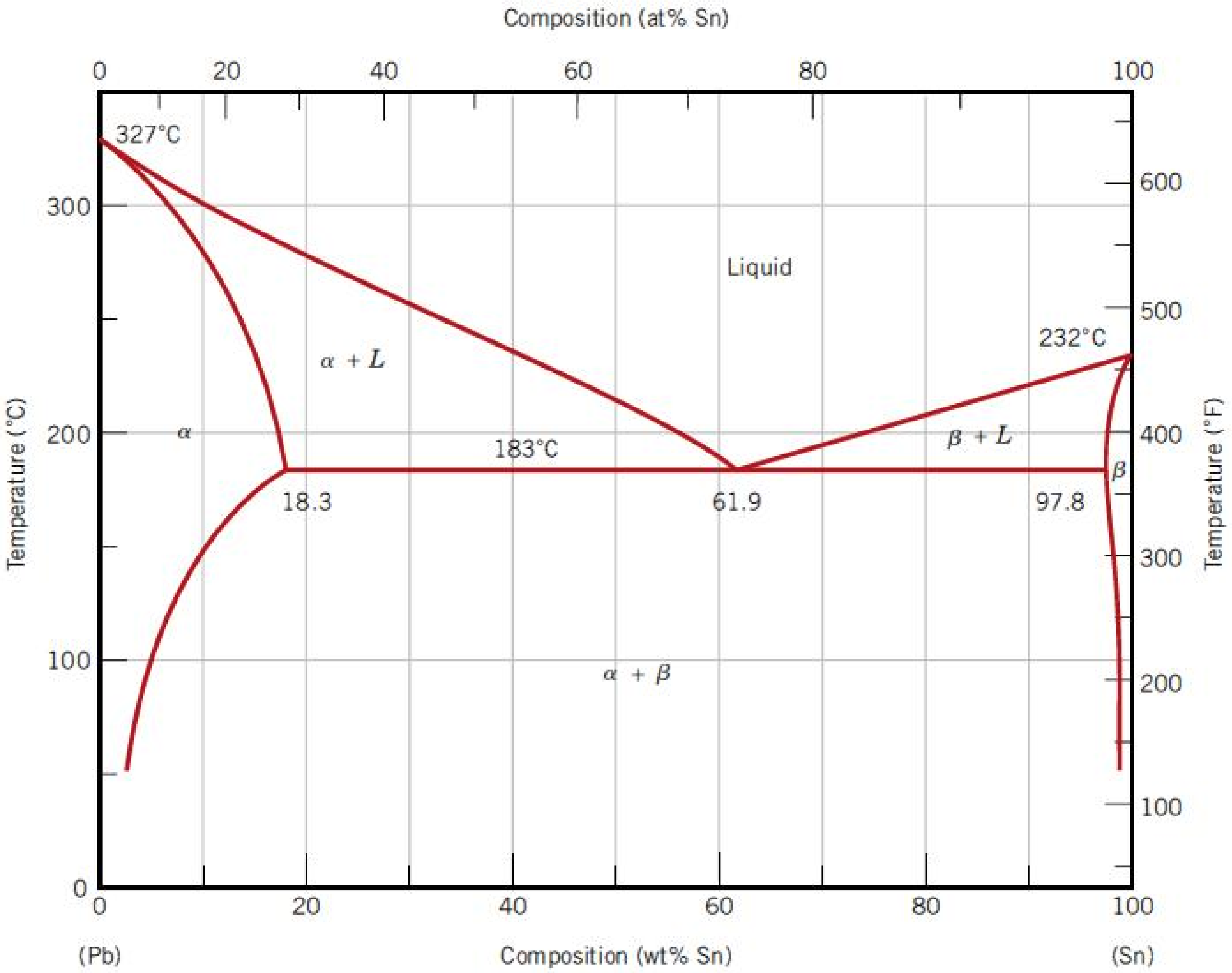
$C_{\text{pearlite}} = C_\gamma = 0.76$ wt% C

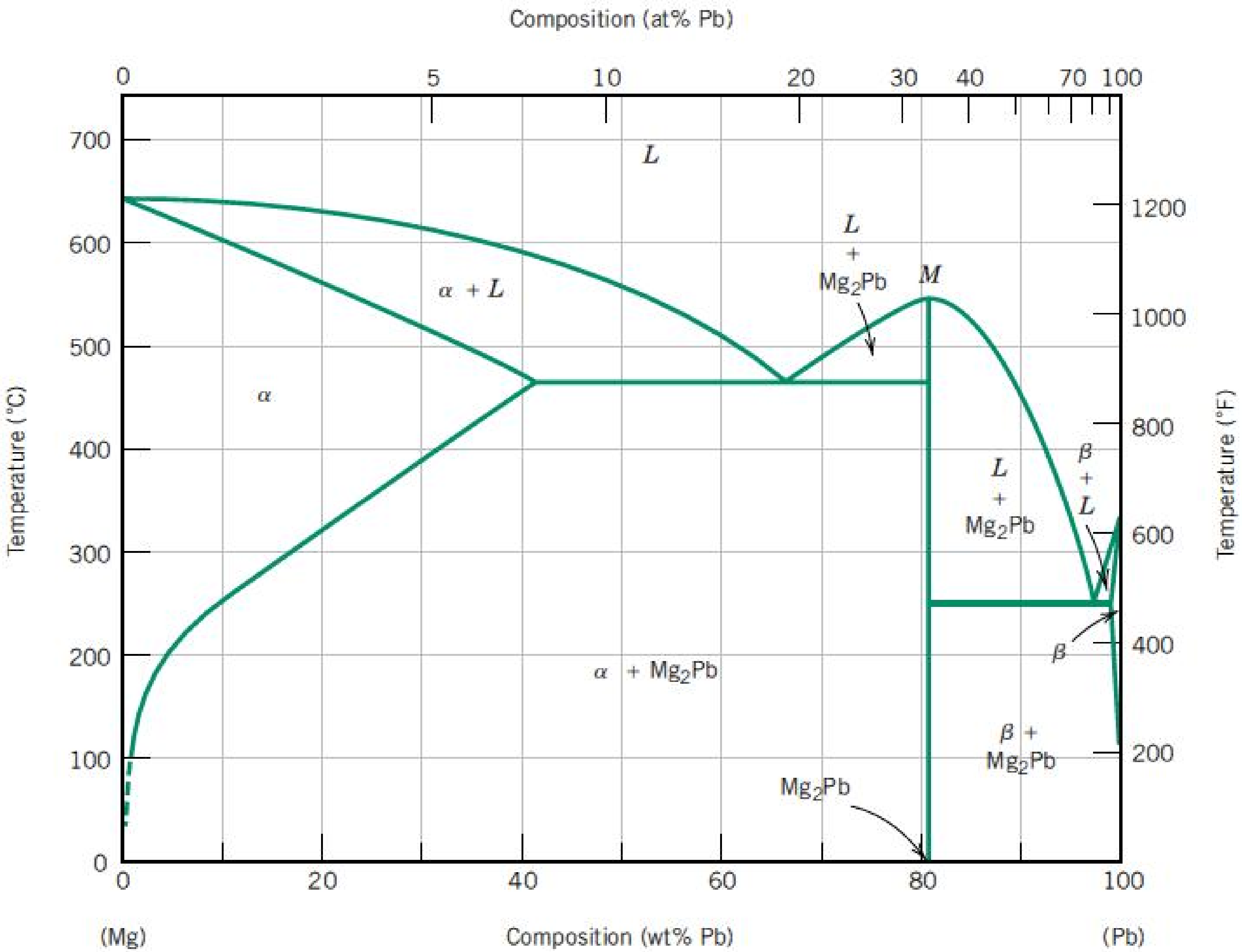
$$\frac{\gamma}{\gamma+\alpha} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha} \times 100 = 51.2 \text{ g}$$

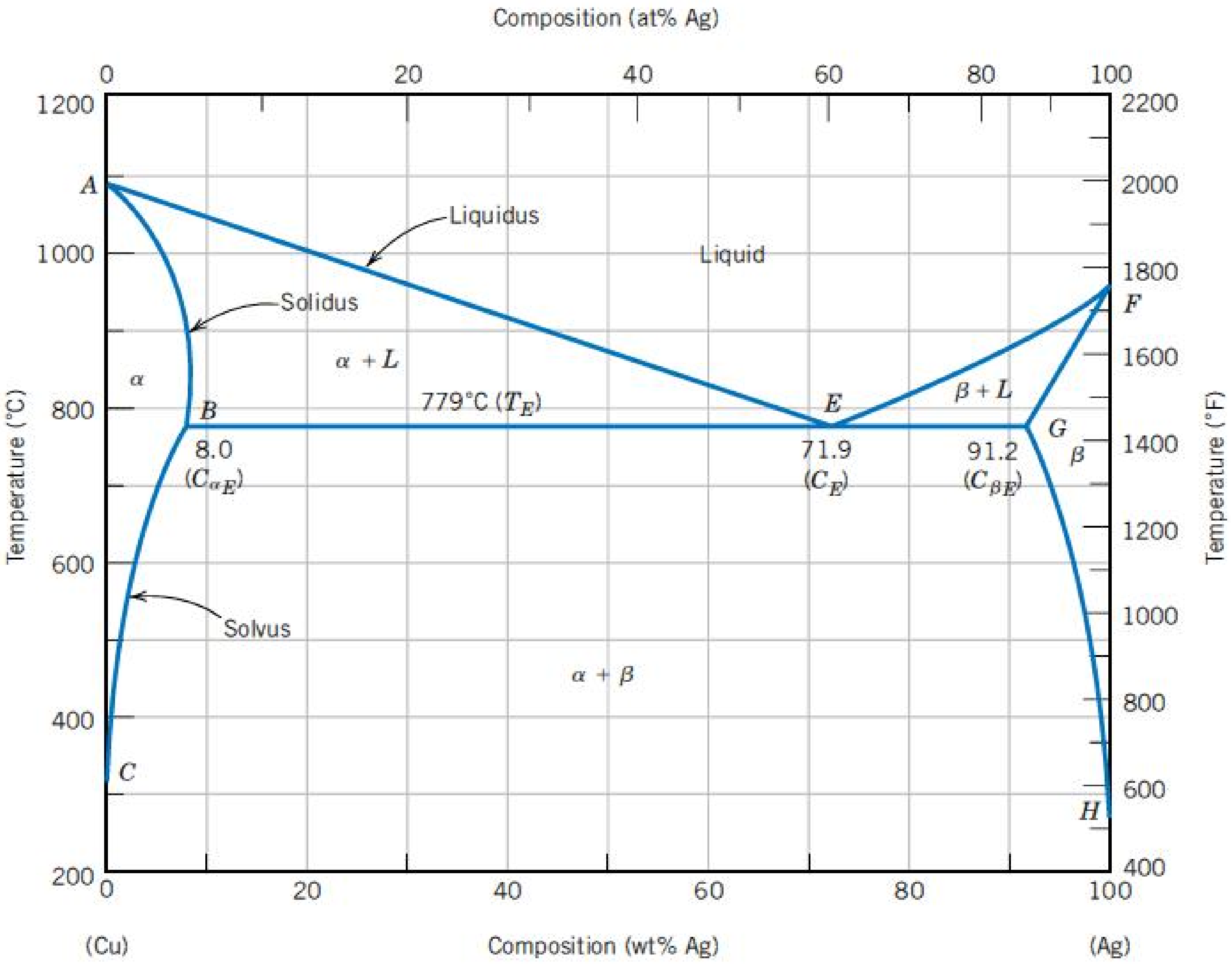
pearlite = 51.2 g

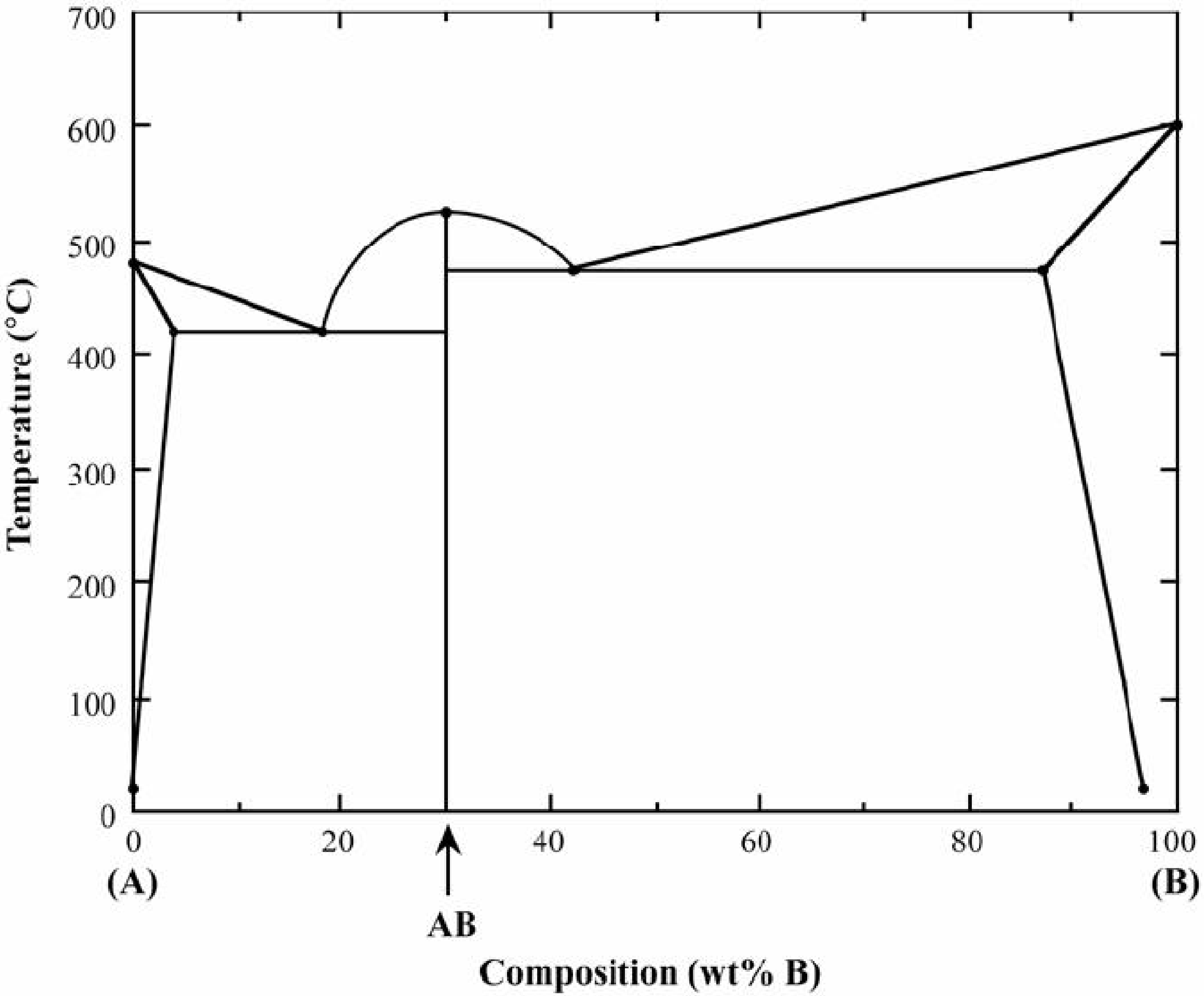
proeutectoid α = 48.8 g

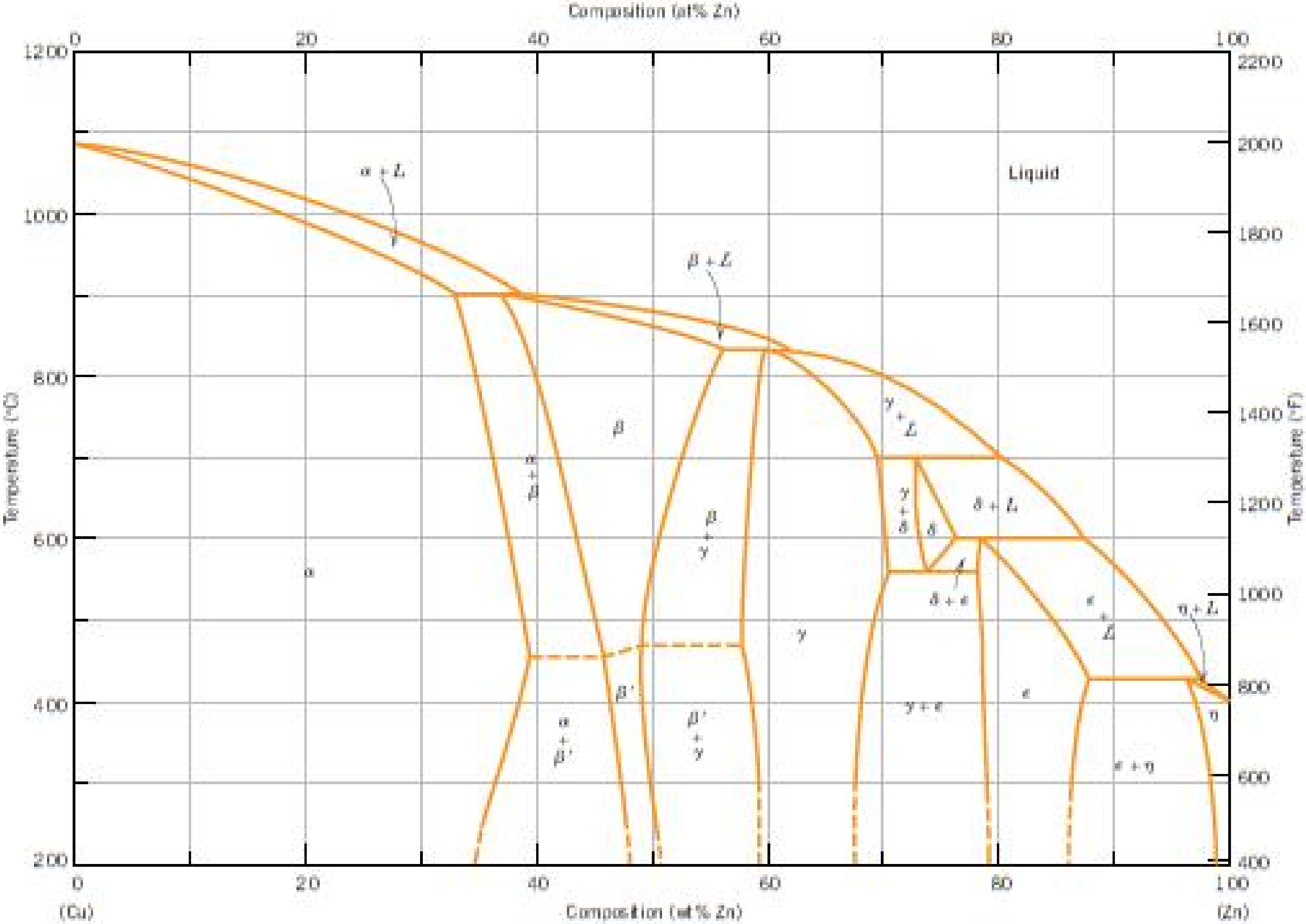


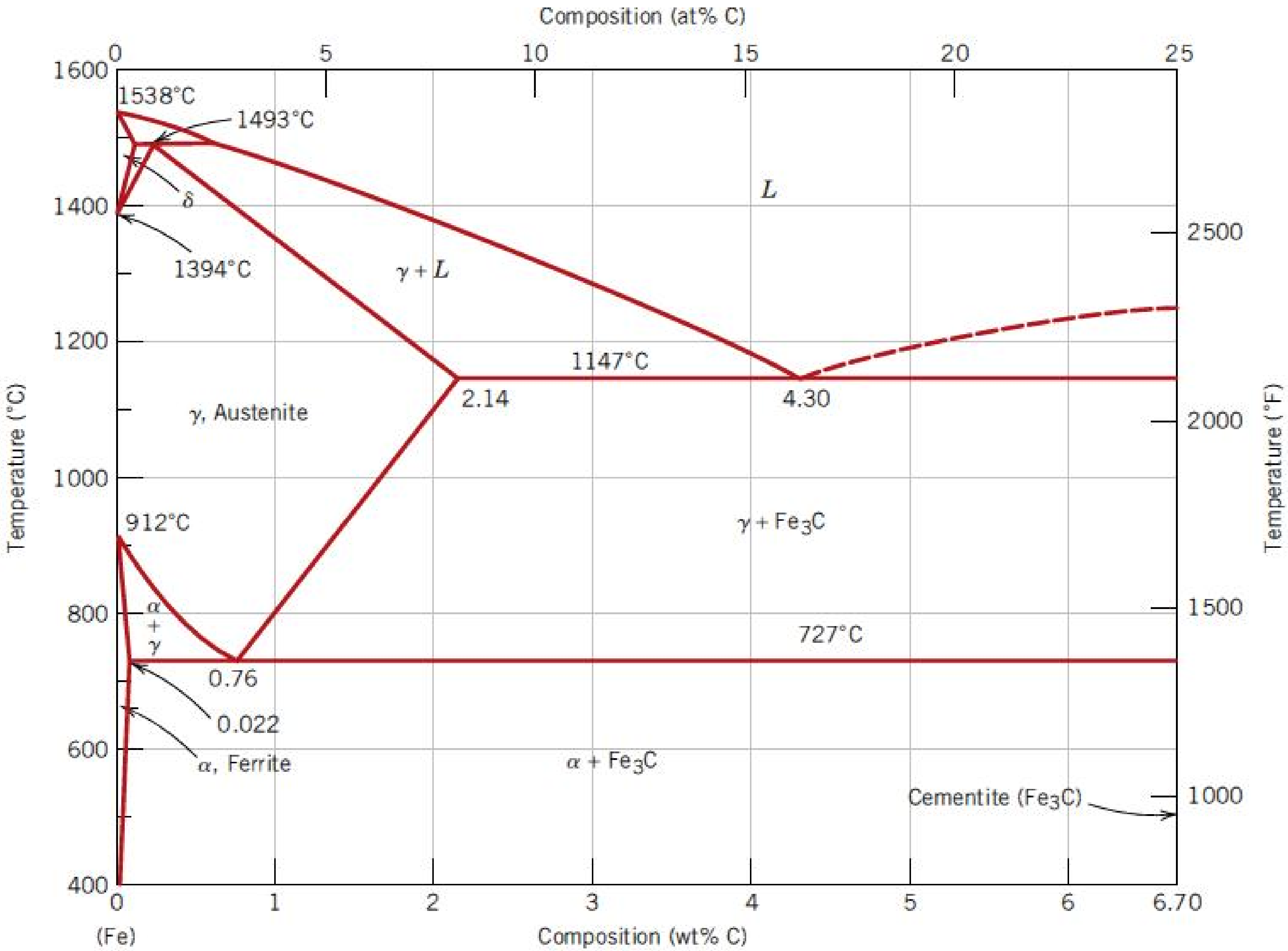

Composition (at% Sn)
0
20
40
60
80
100
327°C
300
Liquid
600
500
232°C
α + L
200
α
183°C
β + L
400
18.3
61.9
97.8
β
300
Temperature (°C)
Temperature (°F)
100
α + β
200
100
0
0
20
40
60
80
100
(Pb)
Composition (wt% Sn)
(Sn)


Composition (at% Pb)
0
5
10
20
30
40
70
100
700
600
500
400
300
200
100
0
Temperature (°C)
1200
1000
800
600
400
200
Temperature (°F)
L
α + L
L + Mg2Pb
M
α
L + Mg2Pb
β + L
β
α + Mg2Pb
β + Mg2Pb
Mg2Pb
0
20
40
60
80
100
(Mg)
Composition (wt% Pb)
(Pb)


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
B
779°C (T_E)
E
β + L
G
β
8.0
($C_{\alpha E}$)
71.9
(C_E)
91.2
($C_{\beta E}$)
Solvus
α + β
C
H
Temperature (°C)
Temperature (°F)
0
20
40
60
80
100
(Cu)
Composition (wt% Ag)
(Ag)


Temperature (°C)
700
600
500
400
300
200
100
0
0
20
40
60
80
100
(A)
(B)
AB
Composition (wt% B)


Composition (at% Zn)
0
20
40
60
80
100
1200
1000
800
600
400
200
Temperature (°C)
2200
2000
1800
1600
1400
1200
1000
800
600
400
Temperature (°F)
α + L
Liquid
β + L
β
β + α
β + γ
γ + L
γ + δ
δ
δ + L
δ + ε
ε
α
γ
ε + L
η + L
β'
α + β'
β' + γ
γ + ε
ε
η
ε + η
0
(Cu)
20
40
60
80
100
(Zn)
Composition (wt% Zn)


Composition (at% C)
0
5
10
15
20
25
1600
1538°C
1493°C
L
δ
1400
2500
1394°C
γ + L
1200
1147°C
2.14
4.30
2000
γ, Austenite
1000
912°C
γ + Fe3C
800
α
+
γ
1500
727°C
0.76
0.022
600
α, Ferrite
α + Fe3C
Cementite (Fe3C)
1000
400
0
1
2
3
4
5
6
6.70
(Fe)
Composition (wt% C)
Temperature (°C)
Temperature (°F)