Chapter 7

Phase Diagrams

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Chemical Engineering Department
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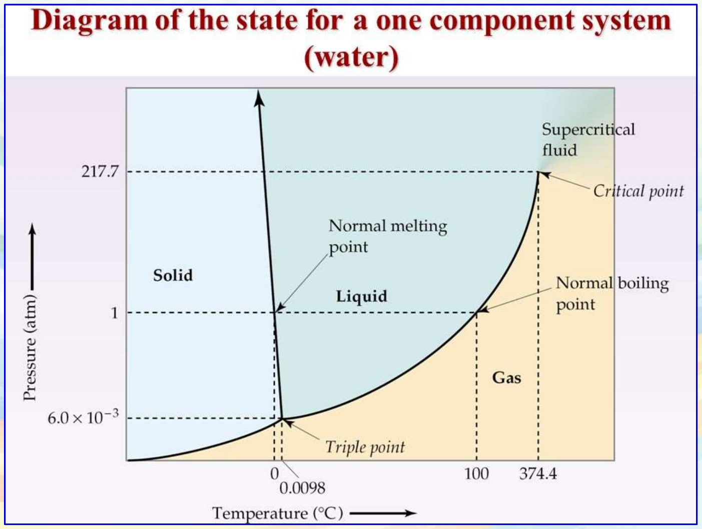
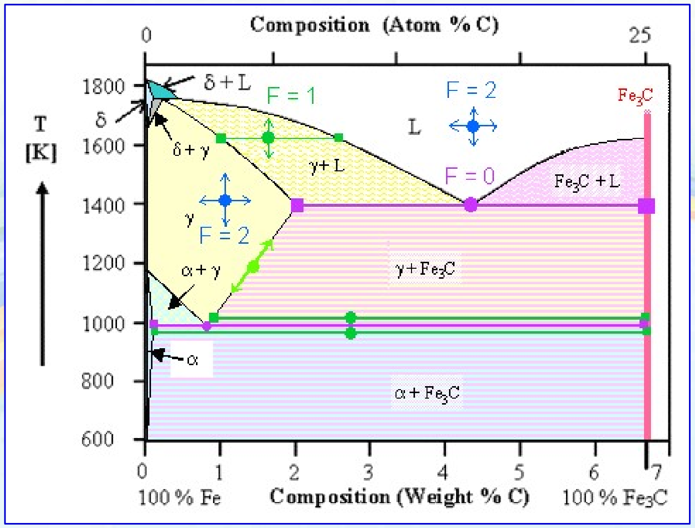
Chapter 7
Phase Diagrams





ISSUES TO ADDRESS...

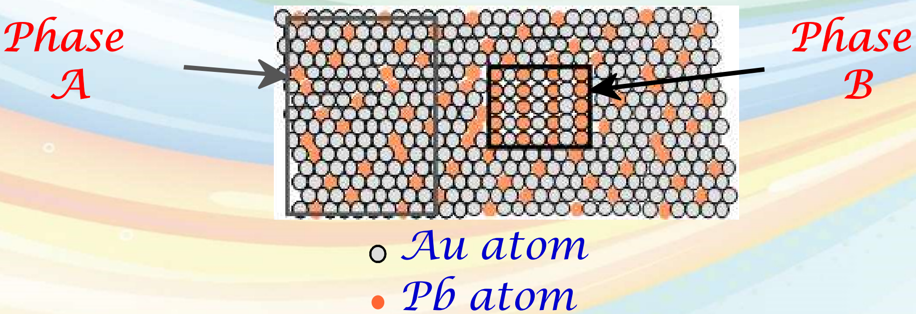
- When we combine two elements...

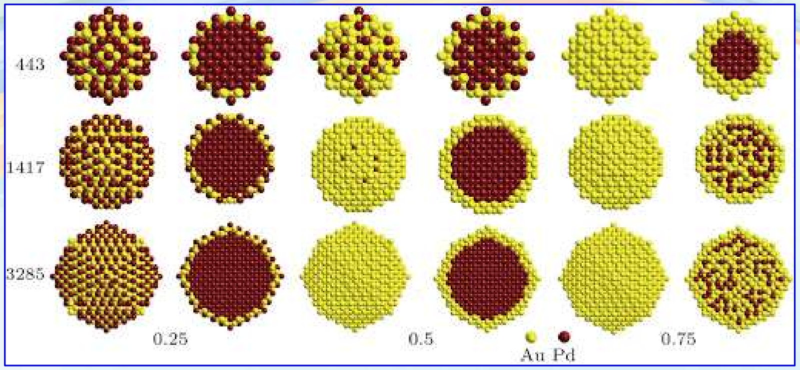
  what is the resulting equilibrium state?

- In particular, if we specify...
  - the composition (e.g., wt% Au - wt% Pb), and
  - the temperature (T)

then...

- How many phases form?
- What is the composition of each phase?
- What is the amount of each phase?





Outline

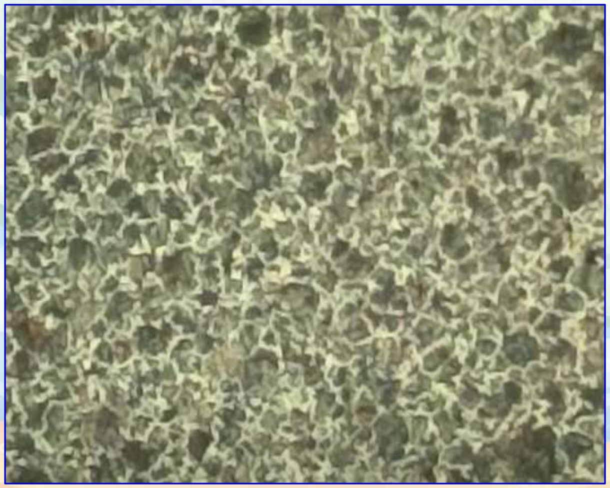
- *Definitions and basic concepts.*
- *Phases and microstructure*
- *Binary isomorphous systems (complete solid solubility)*
- *Binary eutectic systems (limited solid solubility)*
- *Binary systems with intermediate phases/compounds*
- *The iron-carbon system (steel and cast iron)*

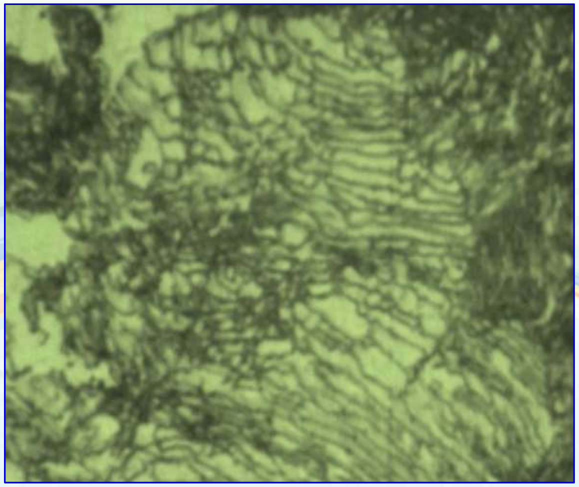
Definitions: Components and Phases

- 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.

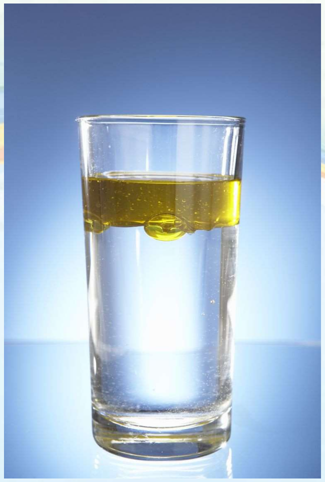




Perlite: ferrite and cementite

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.



Question:

What is the solubility limit for sugar in water at 20ºC?

Answer:

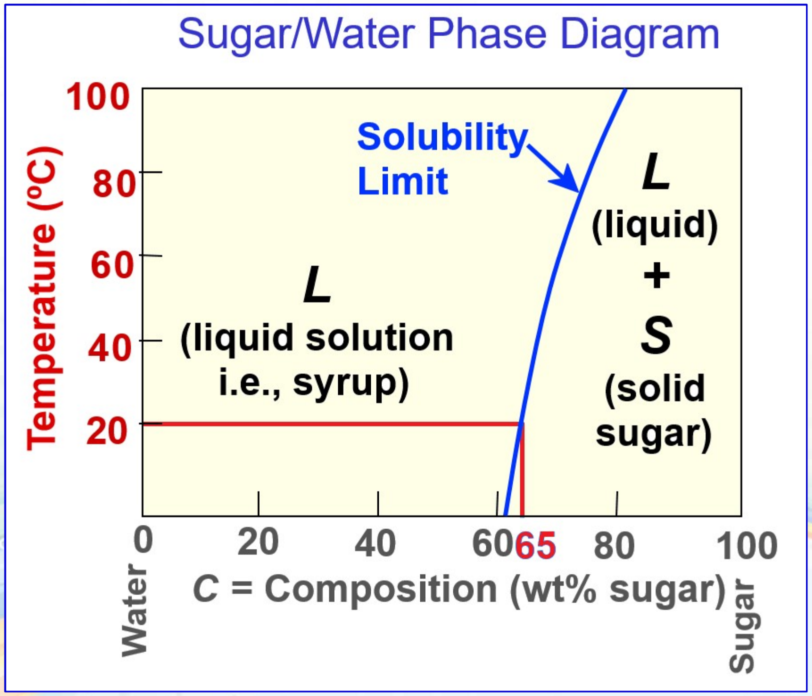
65 wt% sugar.

At 20ºC, if C < 65 wt% sugar:

syrup

At 20ºC, if C > 65 wt% sugar:

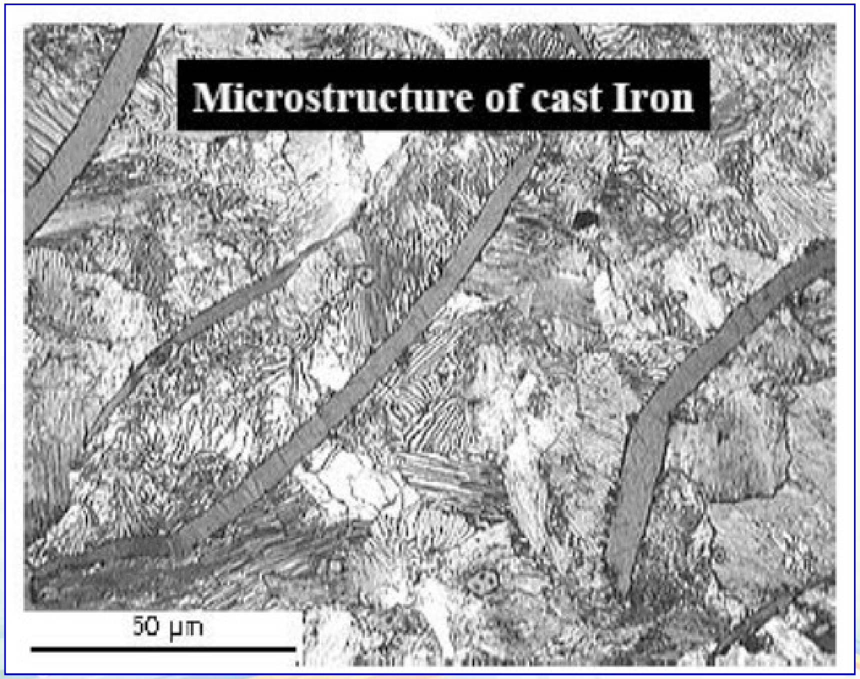
syrup + sugar



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:
  1. The number of phases,
  2. Their proportions,
  3. 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.*

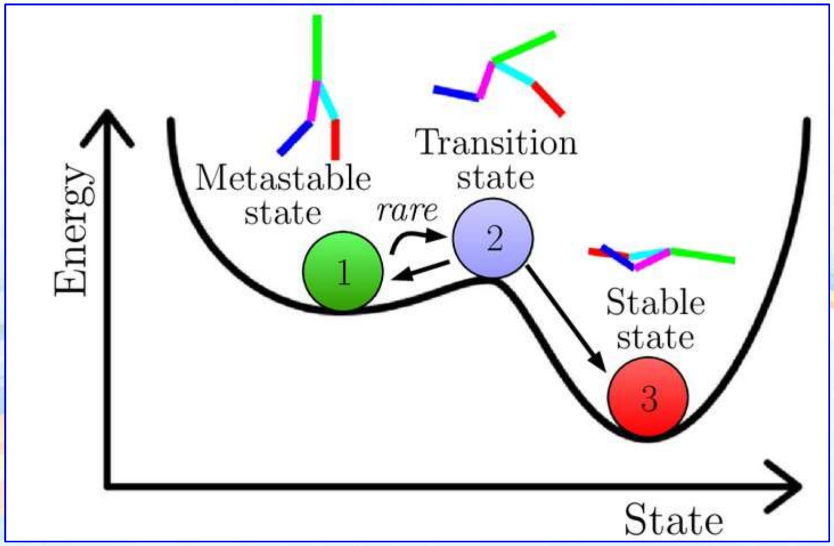
Equilibrium and Metastable States

- *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)*



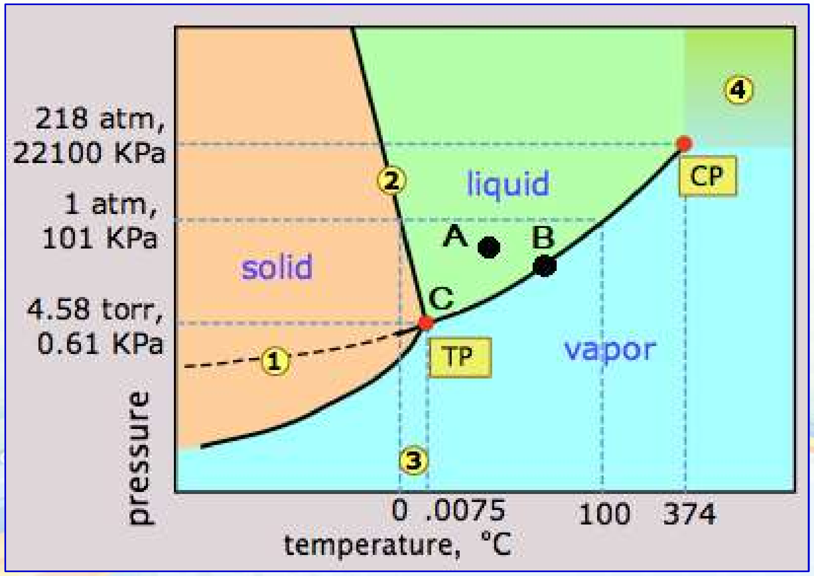
Equilibrium and Metastable States

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.*



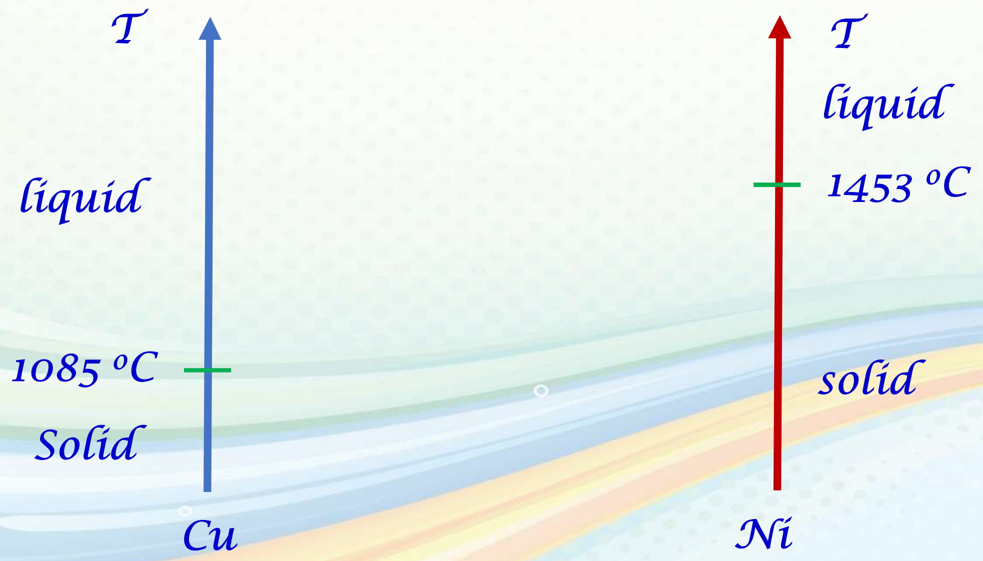
Phase diagram

- 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.

1- Unary System

- Consider 2 elemental metals separately:
  - Cu has melting T = 1085 ^oC
  - Ni has melting T = 1453 ^oC

(at standard P = 1 atm)

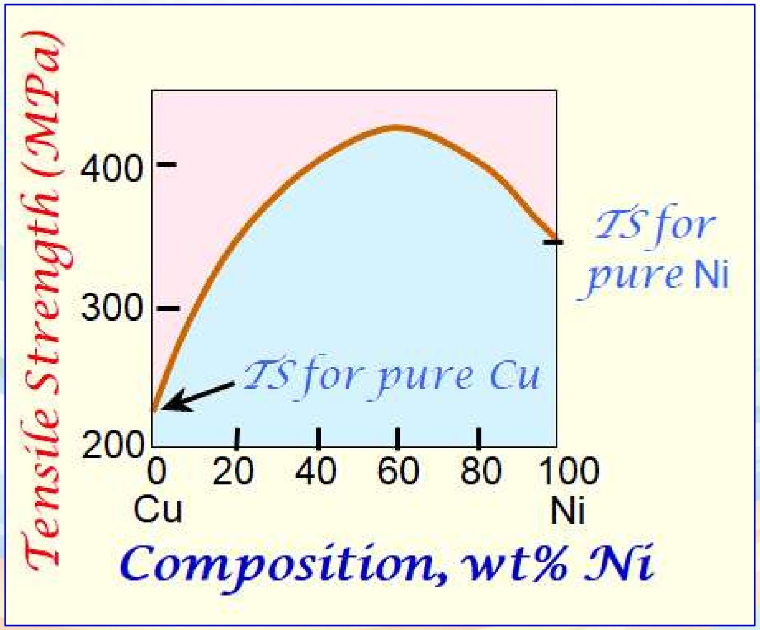


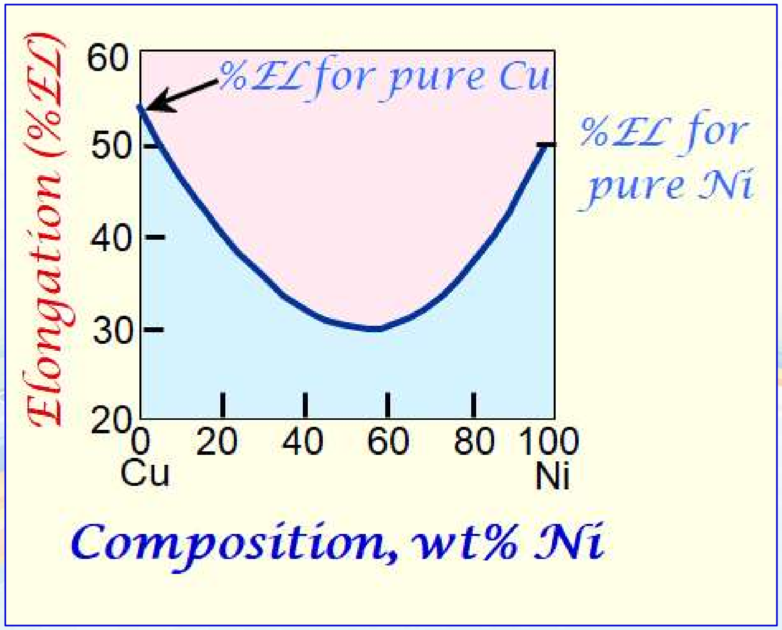
- What happens when Cu and N are mixed?

Why Alloys?

- *Effect of solid solution strengthening on:*

-- Tensile strength (TS) *-- Ductility (%EL)*



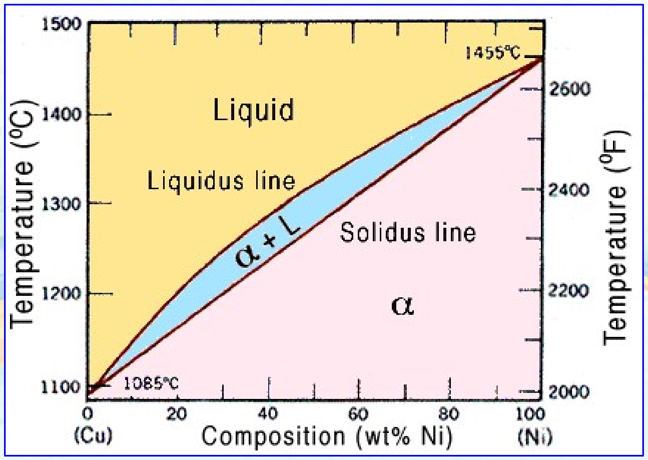


2- Binary Isomorphous Systems

- 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:



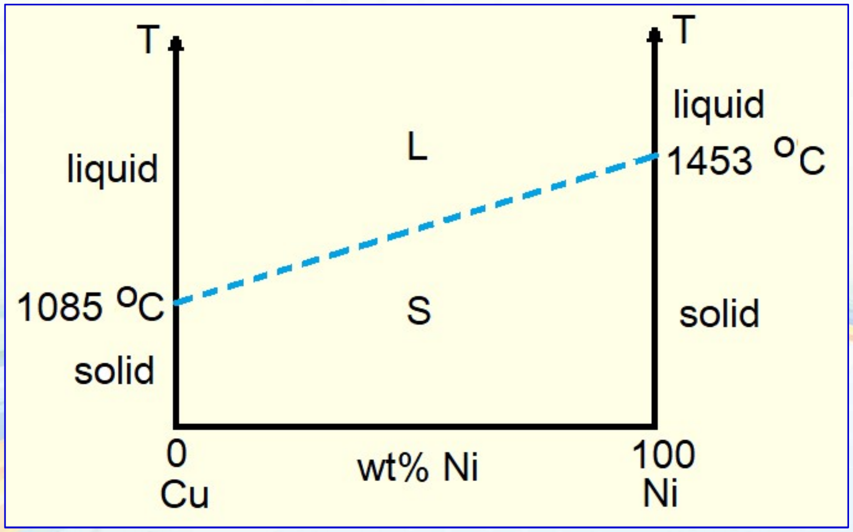
1. Liquid (L) , solid + liquid (α +L), solid (α)
2. Liquidus line separates liquid from liquid + solid
3. Solidus line separates solid from liquid + solid.

Binary Isomorphous Systems

- Binary: 2 components
- Isomorphous: complete liquid and solid solubility

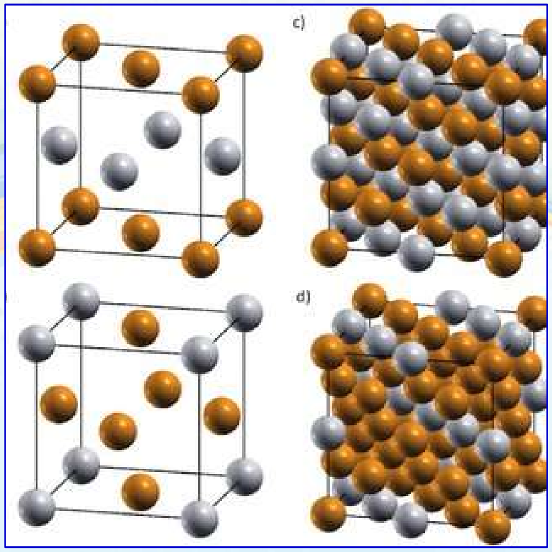
✓ Expect T_m of solution to lie between T_m of two pure components.

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



Binary Isomorphous Systems

- 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



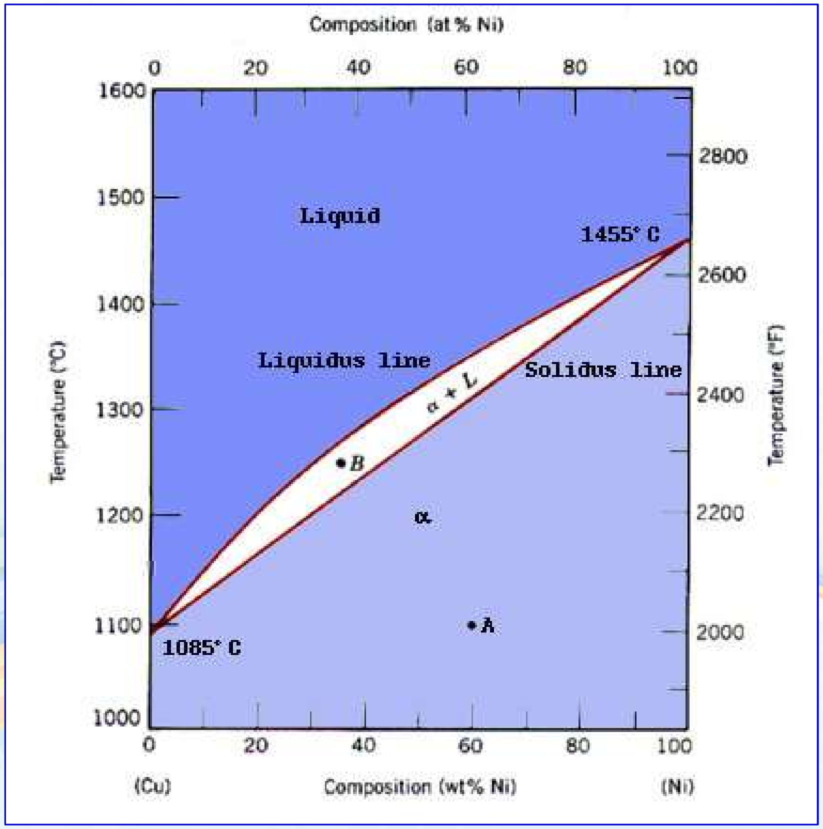
Characteristics of Selected Elements

Element	Symbol	Atomic Number	Atomic Weight (amu)	Density of Solid, 20°C (g/cm^3)	Crystal Structure, 20°C	Atomic Radius (nm)	Ionic Radius (nm)	Most Common Valence
Cobalt	Co	27	58.93	8.9	HCP	0.125	0.072	2+
Copper	Cu	29	63.55	8.94	FCC	0.128	0.096	1+
Fluorine	F	9	19.00	—	—	—	0.133	1−
Gallium	Ga	31	69.72	5.90	Ortho.	0.122	0.062	3+
Neon	Ne	10	20.18	—	—	—	—	Inert
Nickel	Ni	28	58.69	8.90	FCC	0.125	0.069	2+
Niobium	Nb	41	92.91	8.57	BCC	0.143	0.069	5+

Binary Isomorphous Systems

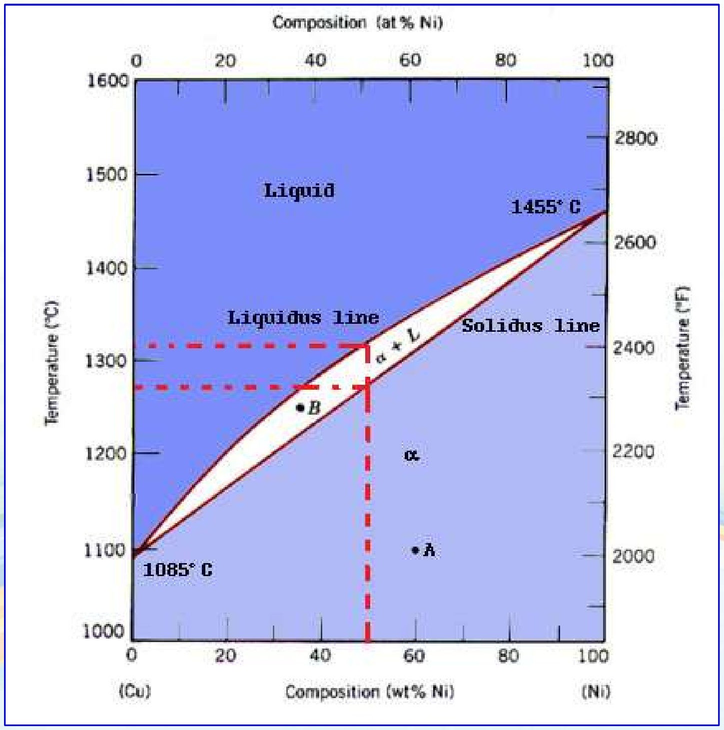
What can we learn from this phase diagram?

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

- *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

Consider C_o = 35 wt% Ni

At T_A = 1320ºC: *Only Liquid (L) present*

$C_L = C_o$ (= 35 wt% Ni)

At T_D = 1190ºC: *Only Solid (α) present*

$C_\alpha = C_o$ (= 35 wt% Ni)

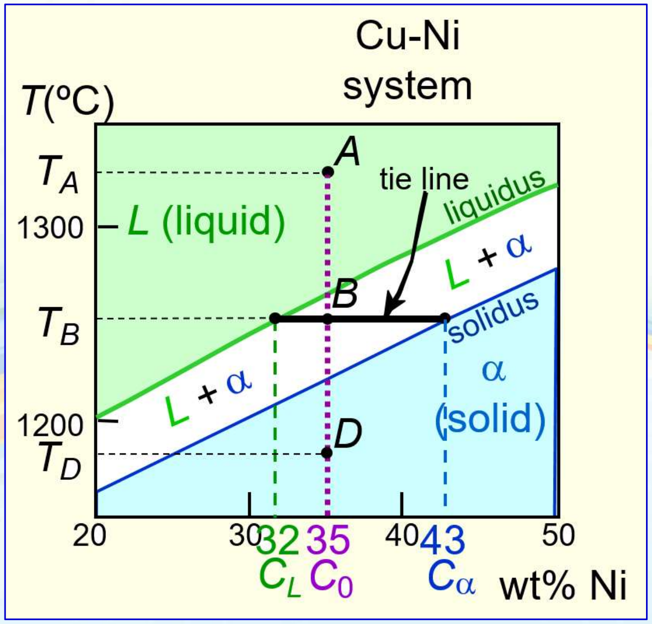
Determining phase composition in 2-phase region

1- *At 1250 ºC, 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 CL amount of Ni (32 et% Ni)*
- ✓ *Solid is composed of Ca amount of Ni (43 wt% Ni)*



Determination of phase weight fractions

- If there is only one phase, then the weight fraction of either solid or liquid will be 100 wt%

- Examples:

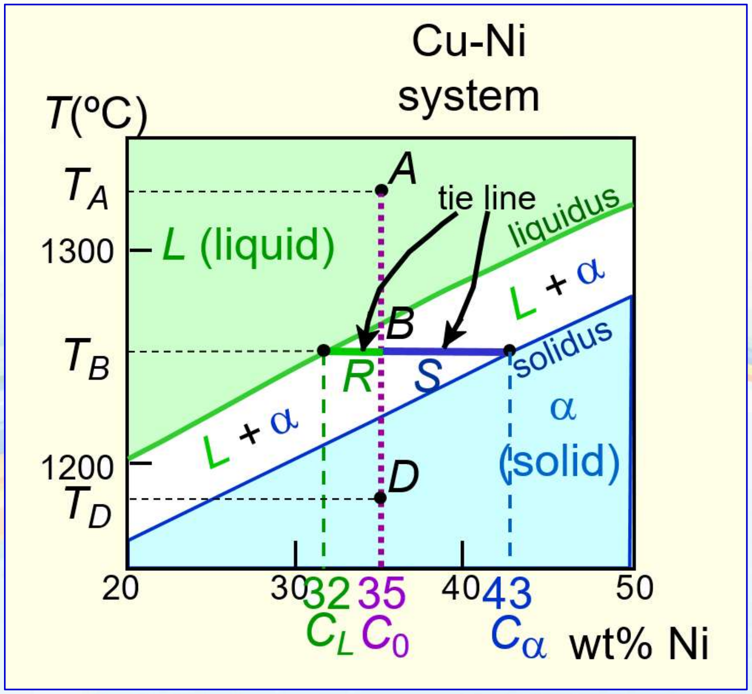
Consider C_0 = 35 wt% Ni

At T_A: Only Liquid (L) present

$W_L = 1.00, \; W_\alpha = 0$

At T_D: Only Solid (α) present

$W_L = 0, \; W_\alpha = 1.00$



Determination of phase weight fractions

- *If there is only one phase, then the weight fraction of either solid or liquid will be 100 wt%,*
- *Example:*

- *Determine phase amount in the 2-phase Region:*

  1- Draw the tie line.

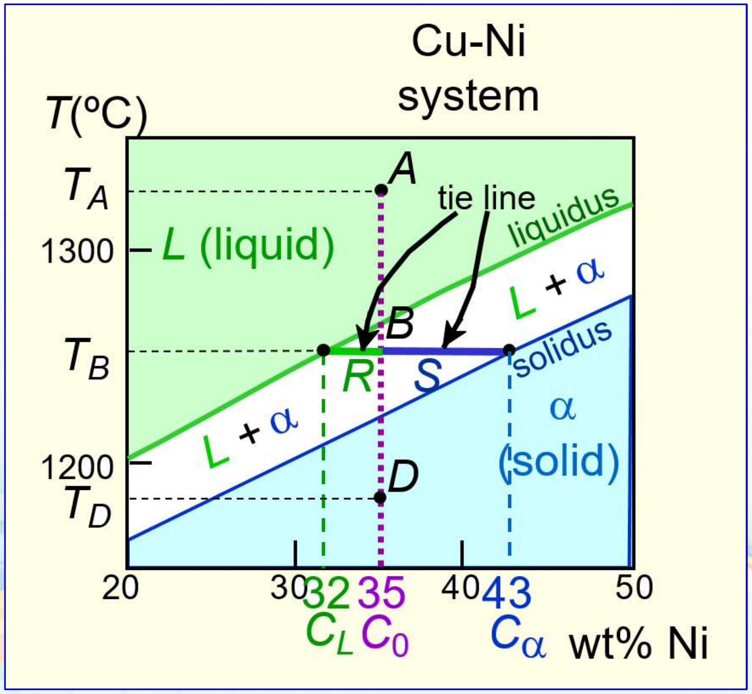
  2- Determine the distance from the point of interest (B) to each of the phase boundaries.

  $R = C_o - C_L$ and $S = C_\alpha - C_o$

  3- Mass fraction (wt%) of each phase:

$$W_L = \frac{S}{R+S} = \frac{C_\propto - C_o}{C_\propto - C_L} = \frac{43-35}{43-32} = 0.73$$

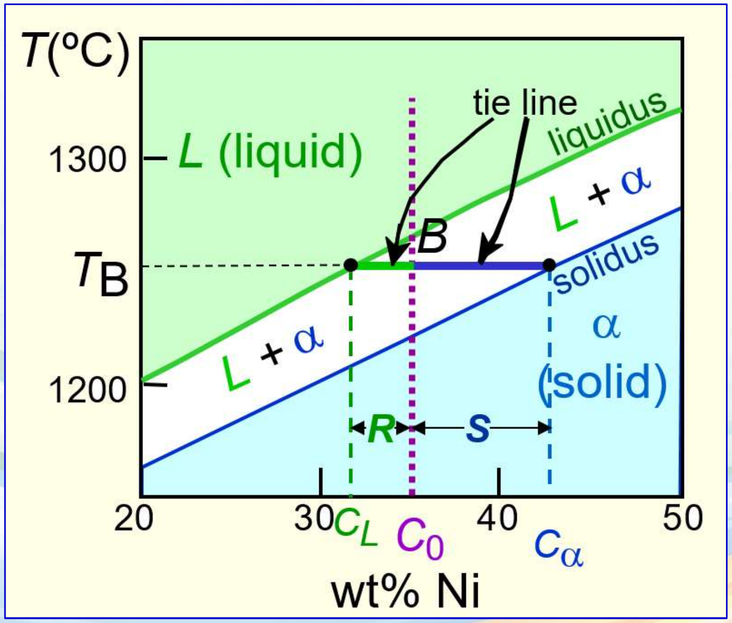
$$W_\propto = \frac{S}{R+S} = \frac{C_o - C_L}{C_\propto - C_L} = \frac{35-32}{43-32} = 0.27$$



i.e. 73% of the mass is liquid and 27% of the mass is solid.

The Lever Rule

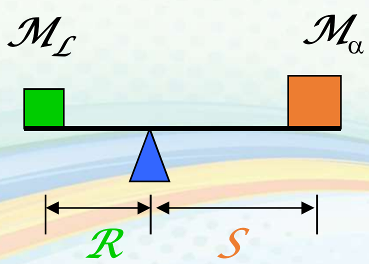
- *Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm*



What fraction of each phase?

Think of the tie line as a lever

(teeter-totter)



$$M_{\alpha} \times S = M_L \times R$$

$$W_L = \frac{M_L}{M_L + M_{\alpha}} = \frac{S}{R+S} = \frac{C_{\alpha} - C_o}{C_{\alpha} - C_L}$$

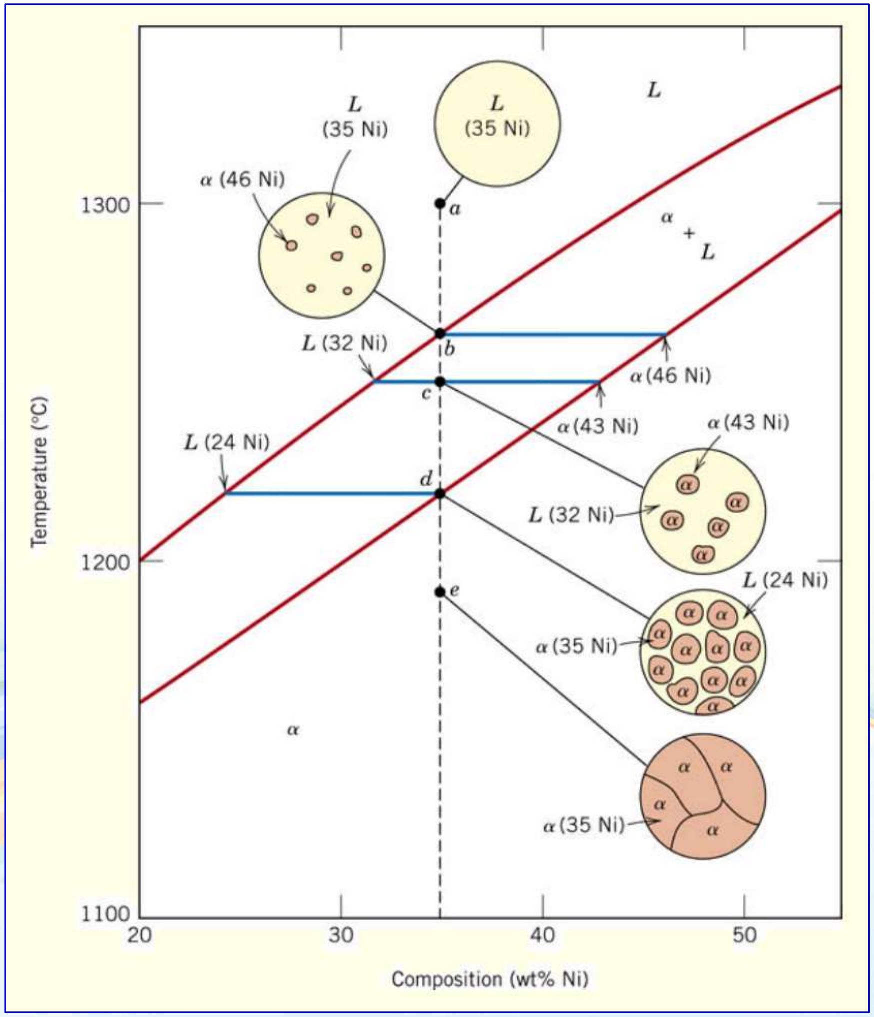
$$W_{\alpha} = \frac{R}{R+S} = \frac{C_o - C_L}{C_{\alpha} - C_L}$$

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>1300 ⁰C): start as homogeneous liquid solution.*
- *B (T ~ 1260 ⁰C): liquidus line reached.* α *phase begins to nucleate.* C_α *= 46 wt% Ni;* C_L *= 35 wt% Ni*
- *C (T= 1250 ⁰C): calculate composition and mass fraction of each phase.*
- *D (T~ 1220 ⁰C): solidus line reached. Nearly complete solidification.* C_α= 35 *wt% Ni;* C_L *= 24 wt% Ni*
- *E (T<1220 ⁰C): homogeneous solid solution with 35 wt% Ni.*



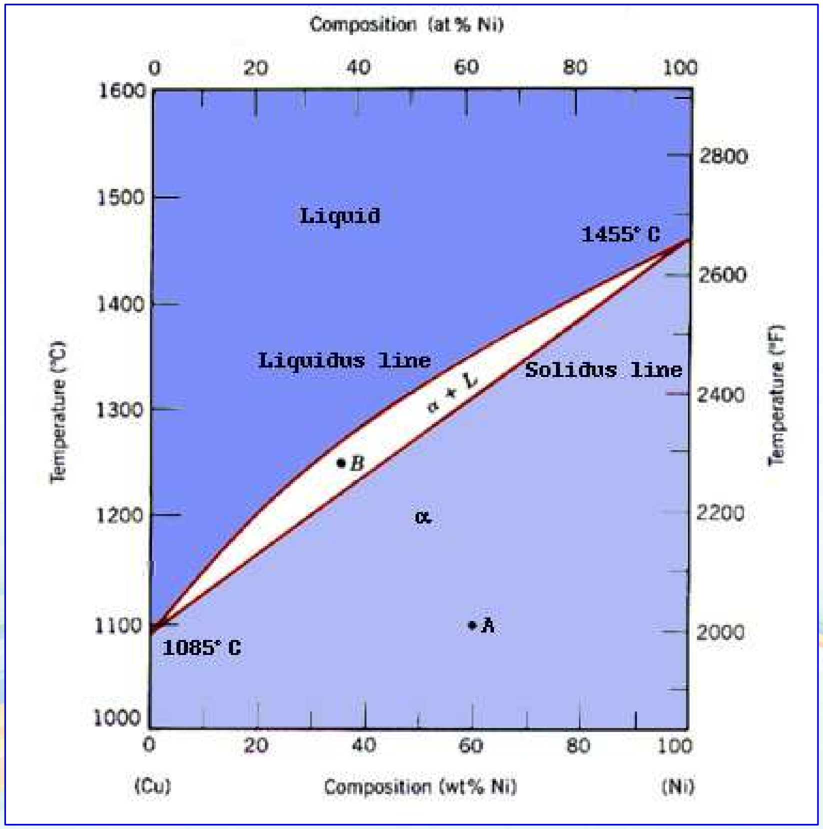
Example problem

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.

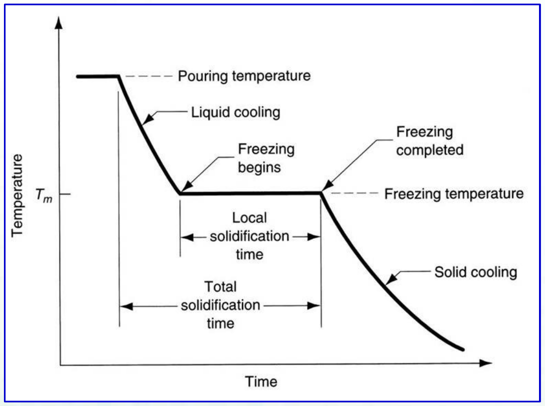


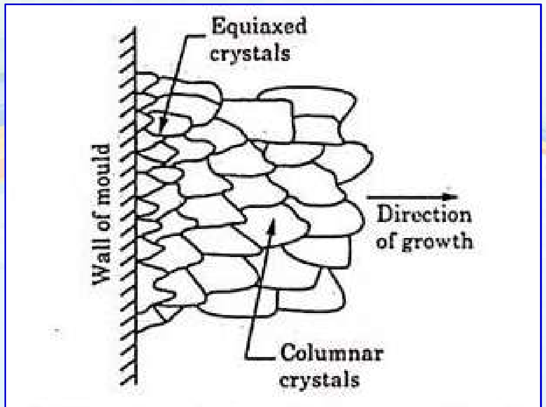
Development of microstructure in isomorphous alloys

- *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)



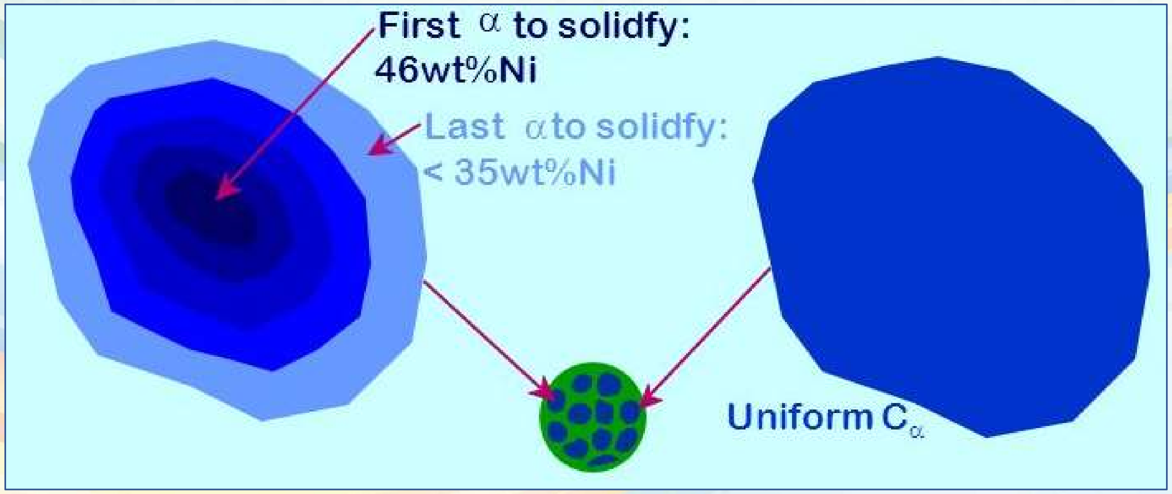


Solidification of pure metal near mould wall.

Cored vs. Equilibrium Phases

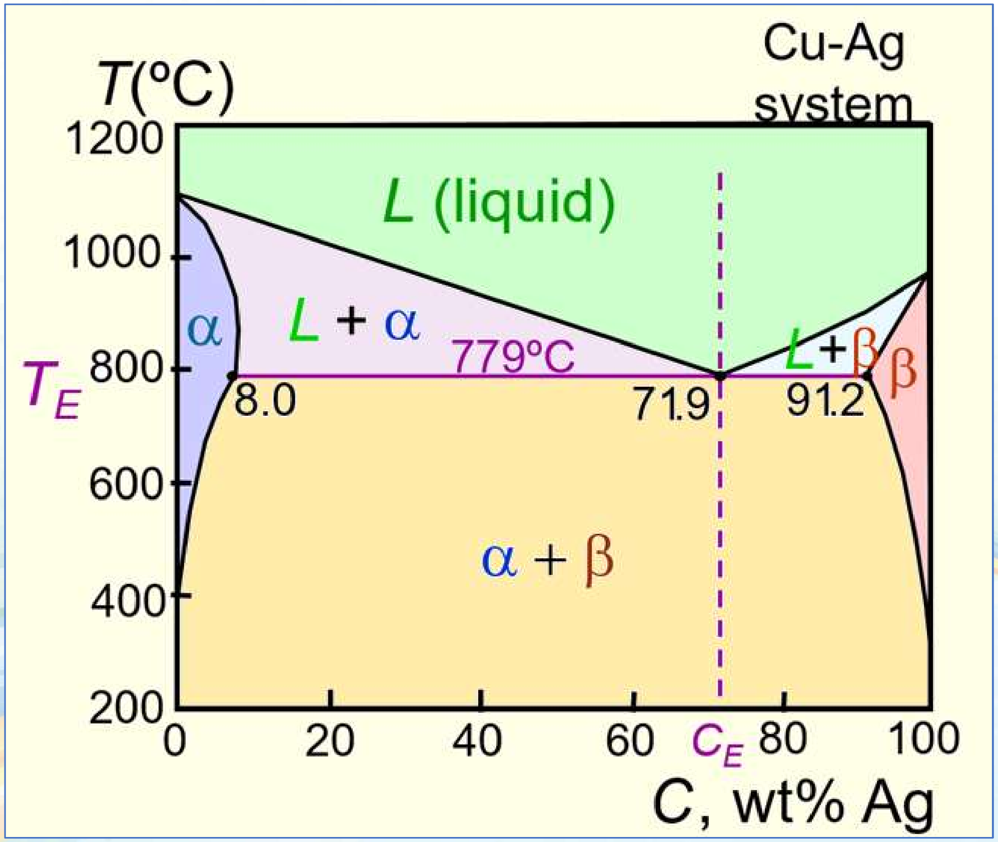
- C_α changes Composition Upon Cooling
  - First α to solidify has C_α = 46 wt% Ni
  - Last α to solidify has C_α = 35 wt% Ni
- Fast Cool Rate — Slow Cool Rate

Cored structure — Equilibrium structure



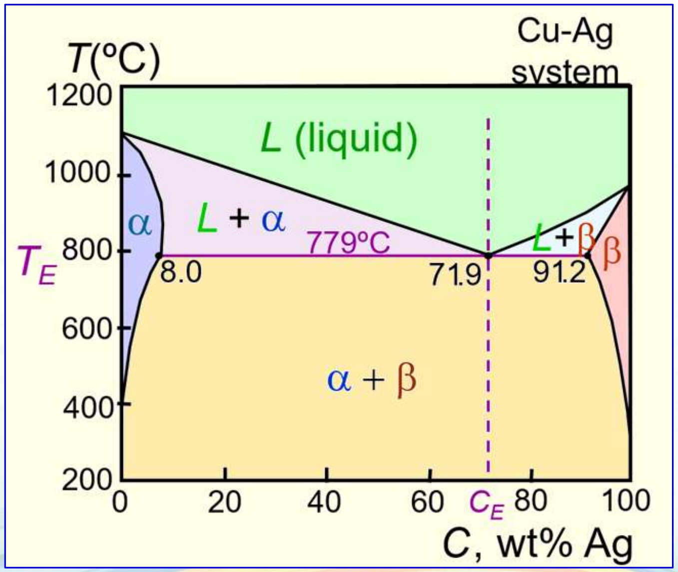
3- Binary Eutectic Systems

- Binary: 2 components.
- Eutectic ⇨ "easily melted, has a special composition with a min. melting T".
- T_m (Cu = 1085 and Ag = 961.8 °C)



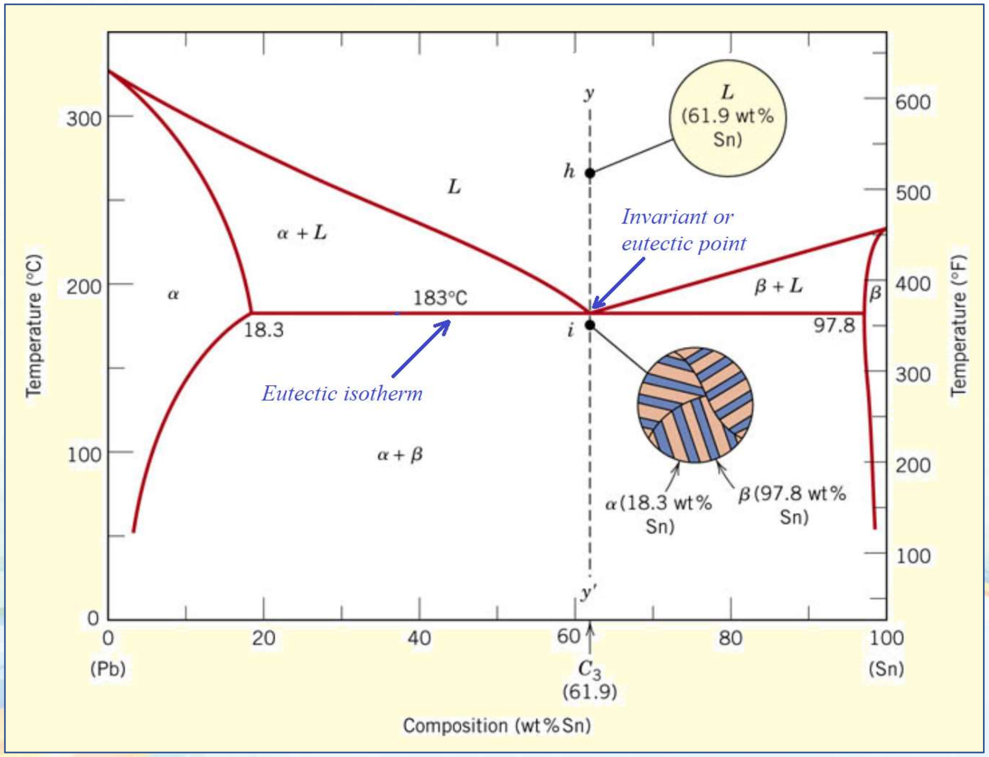
Binary Eutectic Systems

- Single phase regions:
  1. α-phase (solid solution rich in Cu).
  2. β-phase (solid solution rich in Ag).
  3. L-phase (liquid solution).
- Phase coexistence regions:
  1. α + β phases (limited solubility of Ag in Cu and vice versa lead to 2 different solid solution phases).
  2. α + L and β + L phase regions.



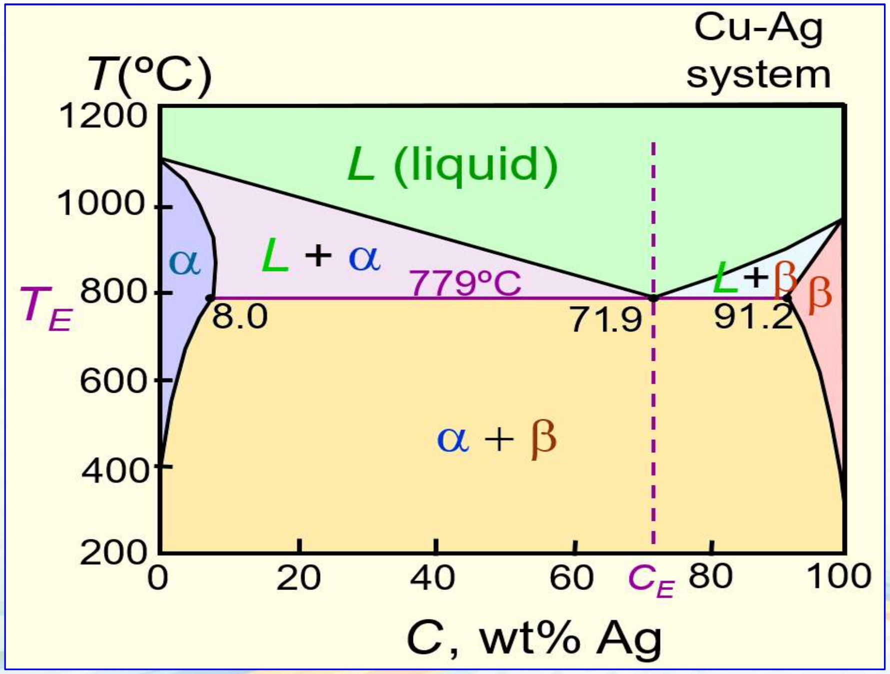
- Tie lines and Lever Rule can be applied in the 2-phase regions.
- Solvus line separates one solid solution from a mixture of solid solutions.

- *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.*



Ex.: Cu-Ag 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*
- $L(C_E) \longrightarrow \alpha(C_{\alpha E}) + \beta(C_{\beta E})$

$$L(71.9\ wt\%\ Ag) \leftrightarrow \alpha(8.0\ wt\%\ Ag) + \beta(91.2\ wt\%\ Ag)$$

↓ *Cooling* ↑ *Heating*

EX 1: Pb-Sn Eutectic System

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

  1- The phases present

  Answer: α + β

  2- The phase compositions

  Answer: C_α = 11 wt% Sn

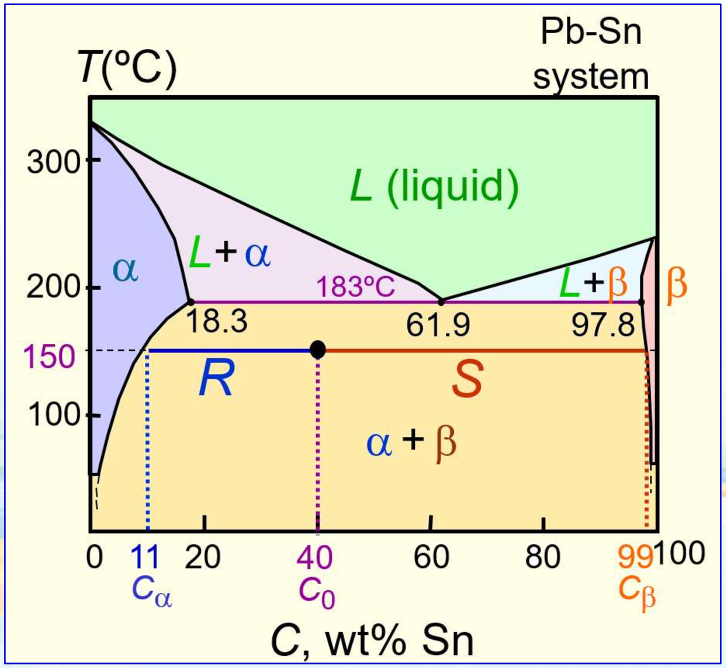
  C_β = 99 wt% Sn

  3- The relative amount of each phase

  Answer:

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_o}{C_\beta - C_\alpha} = \frac{99-40}{99-11} = \frac{59}{88} = 0.67$$

$$W_\beta = \frac{R}{R+S} = \frac{C_o - C_\alpha}{C_\beta - C_\alpha} = \frac{40-11}{99-11} = \frac{29}{88} = 0.33$$



EX 2: Pb-Sn Eutectic System

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

1- The phases present:

Answer: $\alpha + L$

2- The phase compositions

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

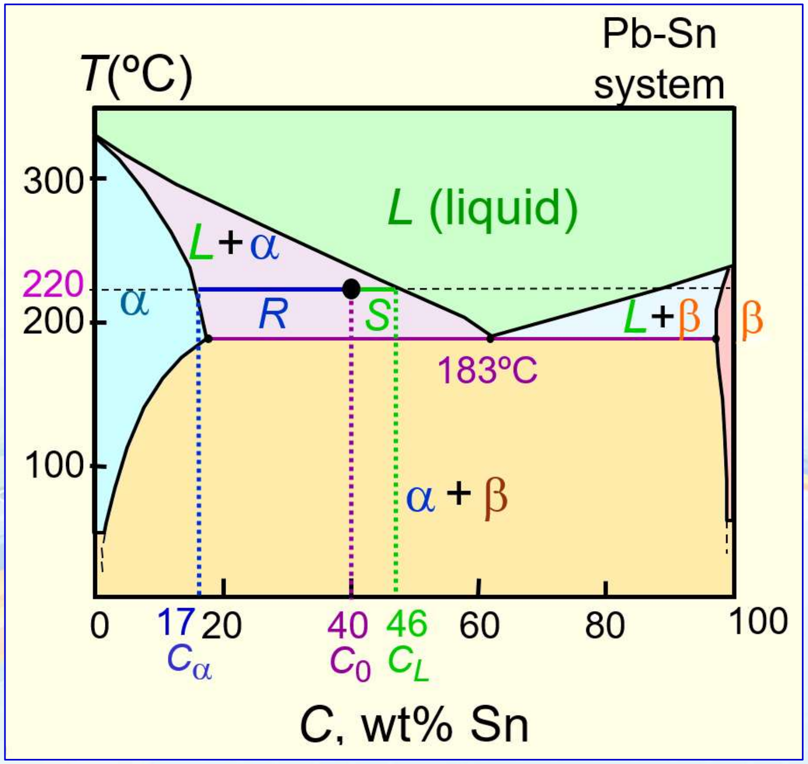
$C_L = 46$ wt% Sn

3- The relative amount of each phase

Answer:

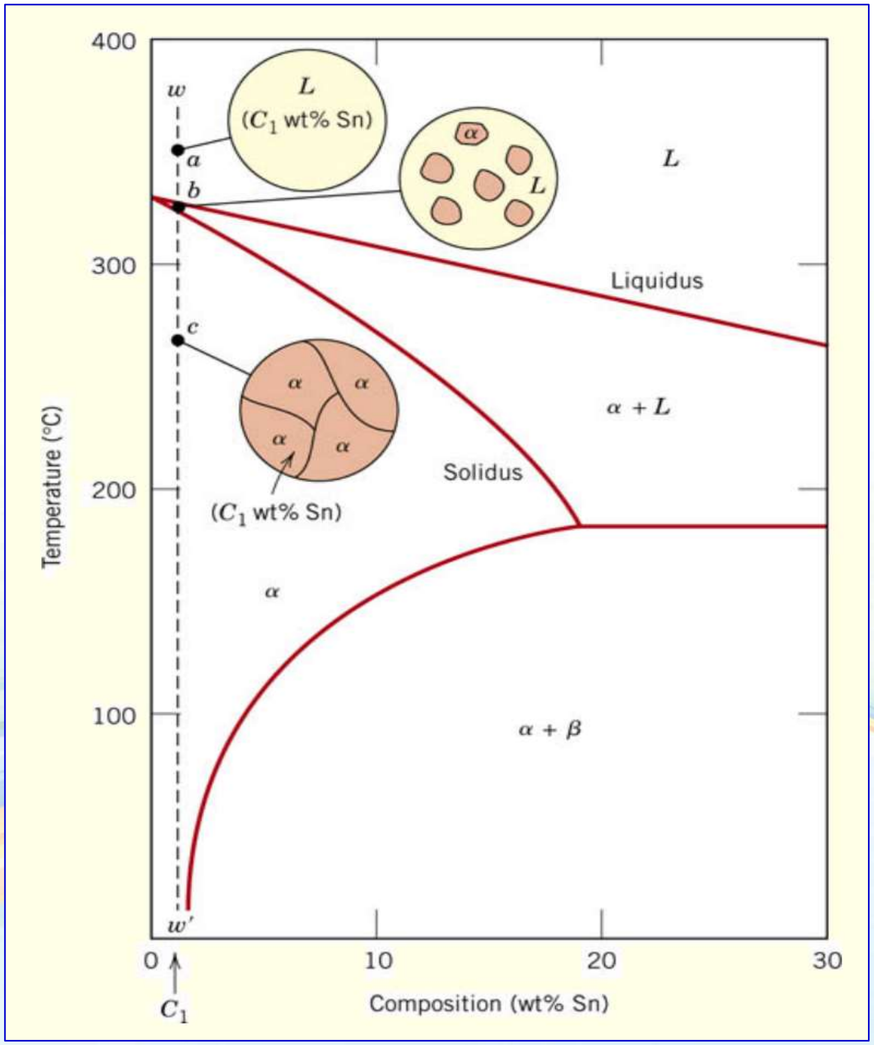
$$W_\alpha = \frac{C_L - C_o}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 0.21$$

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



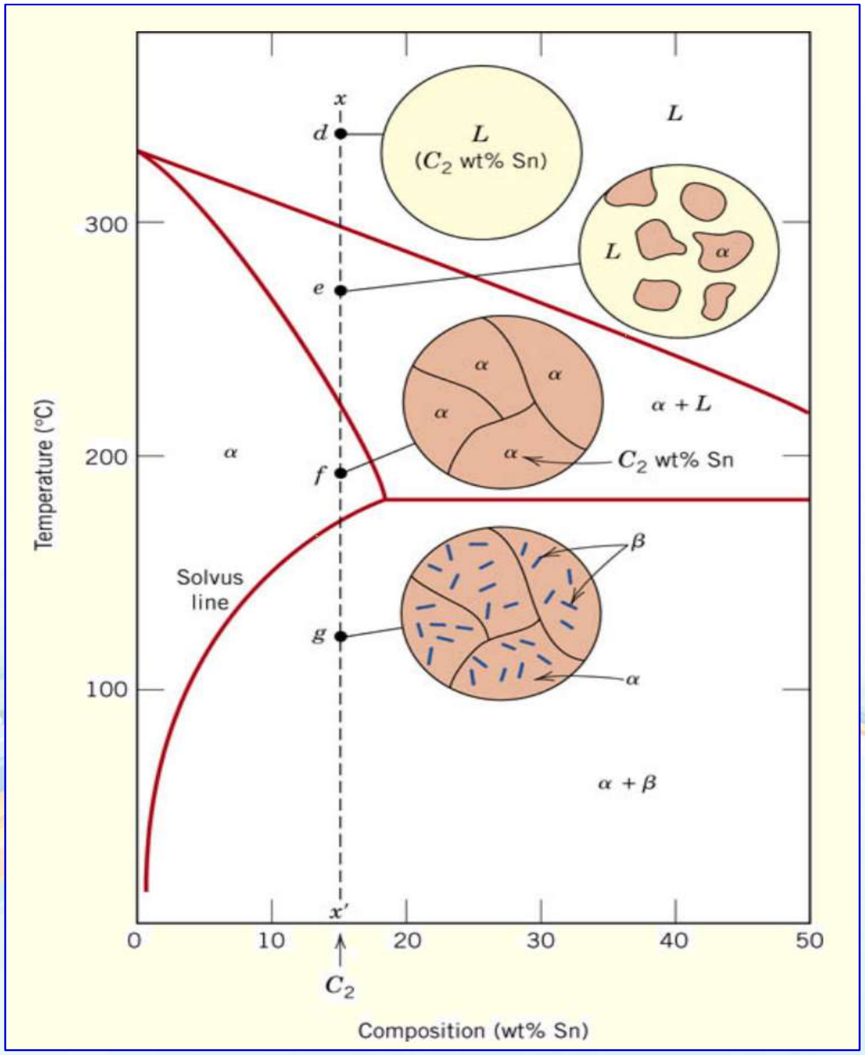
Microstructural Developments in Eutectic Systems I

- *For alloys for which C_o < 2 wt% Sn*
- *Result: at room temperature*
  - ✓ *Polycrystalline with grains of a phase having composition C_o*



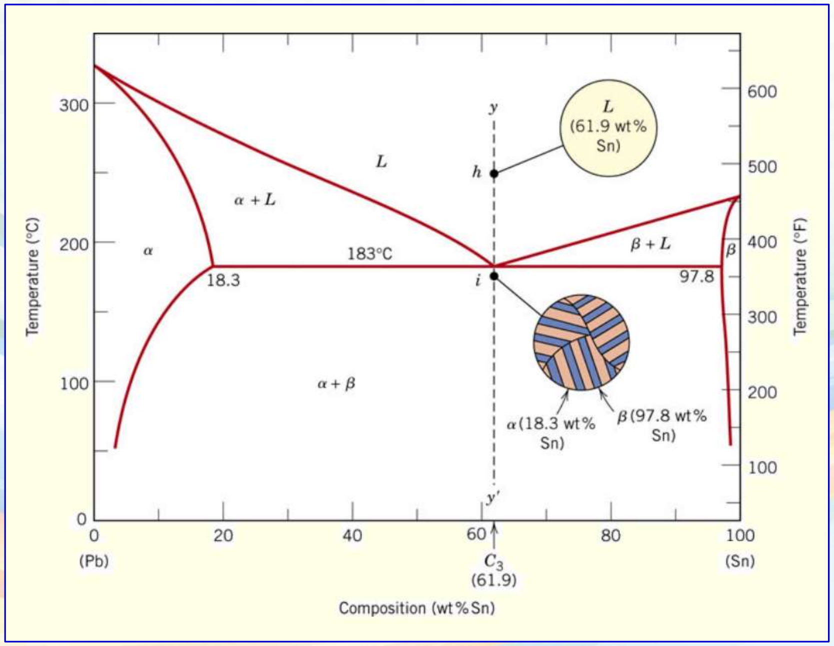
Microstructural Developments in Eutectic Systems II

- For alloys for which 2 wt% Sn < C_o < 18.3 wt% Sn
- Result:
  - ✓ Initially liquid + α
  - ✓ Then α alone
  - ✓ Finally at temperatures in α + β range: Polycrystalline with α grains and small β-phase particles

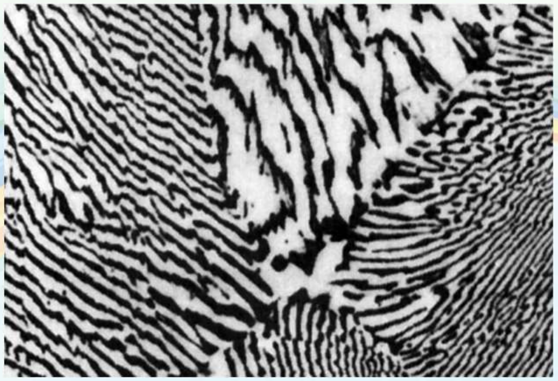


Microstructural Developments in Eutectic Systems III

- For alloy of composition $C_o = C_E$
- **Result:** Eutectic microstructure (lamellar structure)
  - ✓ Alternating layers (lamellae) of α and β phases.

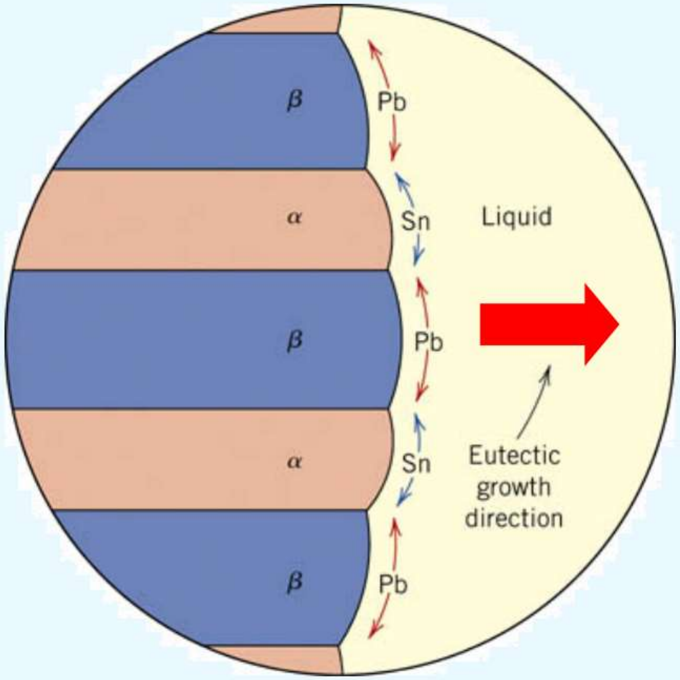


Micrograph of Pb-Sn
Eutectic microstructure



160 μm

Microstructural Developments in Eutectic Systems III



Microstructural Developments in Eutectic Systems IV

- *For alloys for which 18.3 wt% Sn < C_o < 61.9 wt% Sn*
- *Result:* α *phase particles and* α *eutectic micro-constituent*
  - ✓ *Just above T_E:*

C_α = 18.3 wt% Sn C_L = 61.9 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.5$$

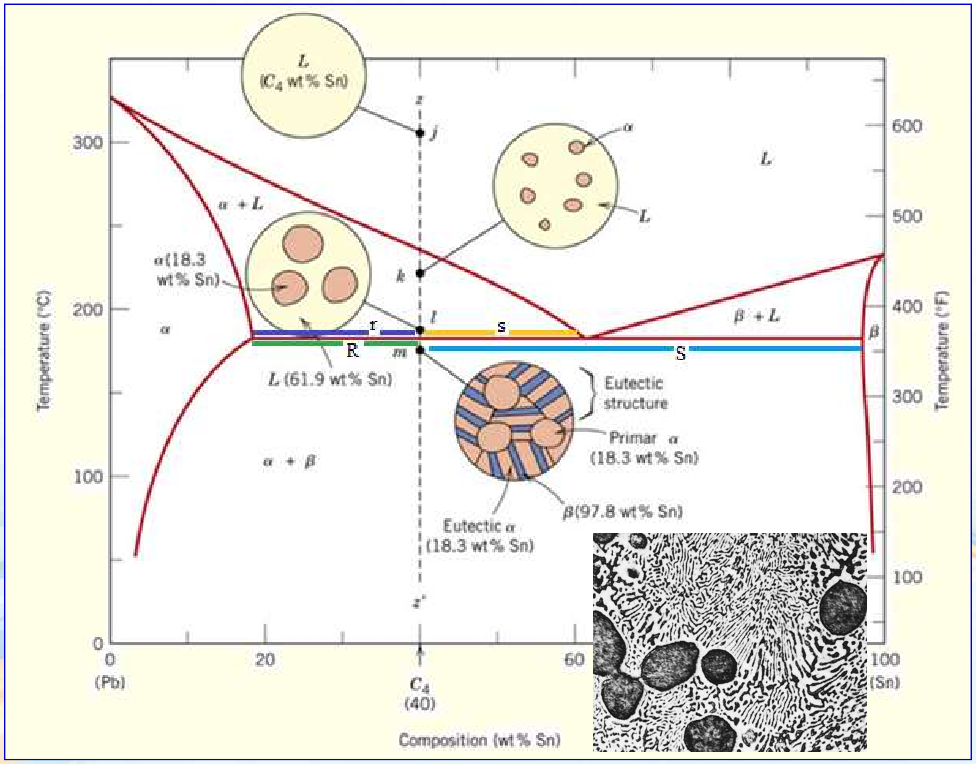
$$W_L = (1 - W_\alpha) = 0.5$$

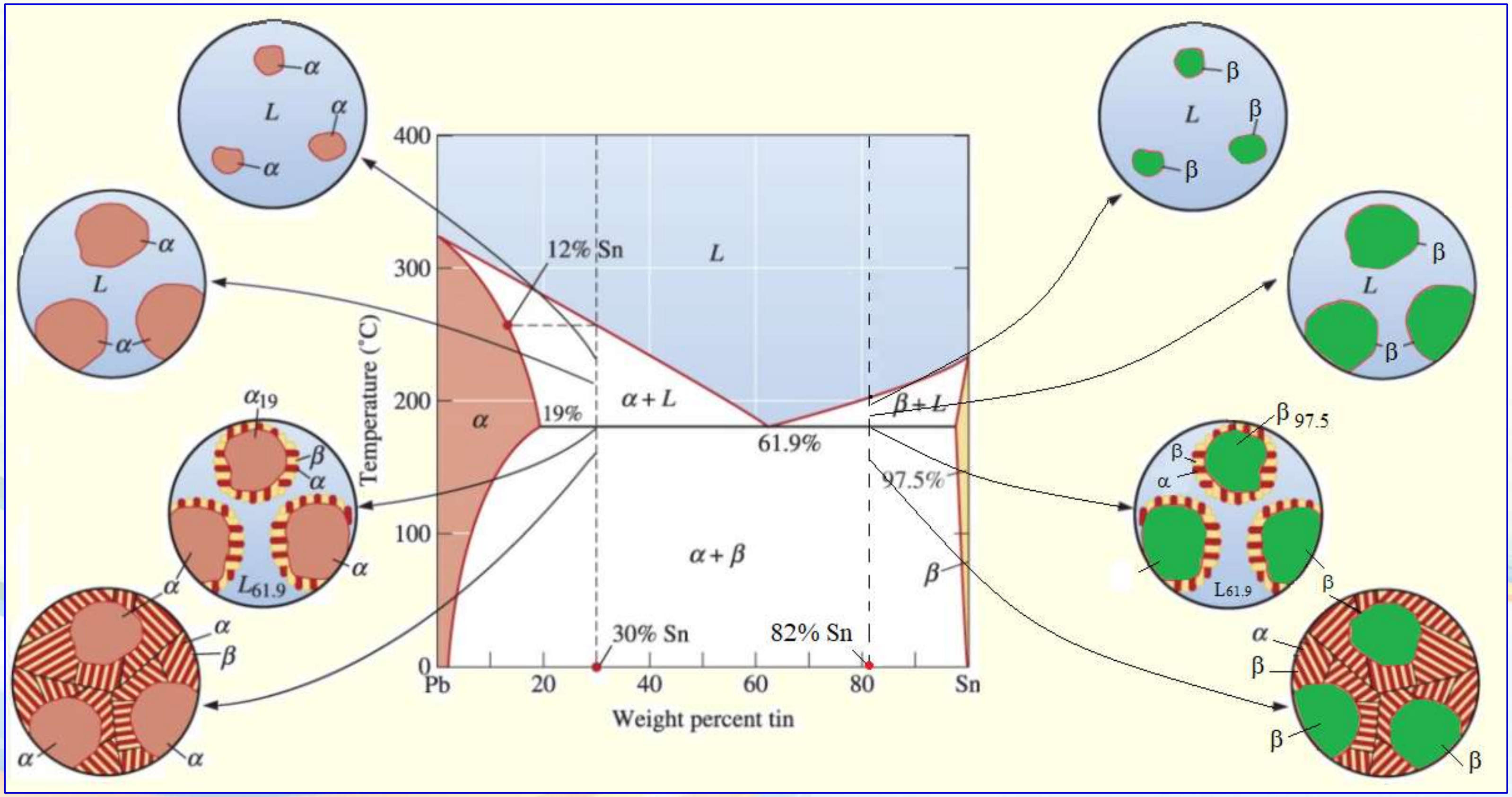
  - ✓ *Just below T_E:*

C_α = 18.3 wt% Sn C_β = 97.8 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.73$$

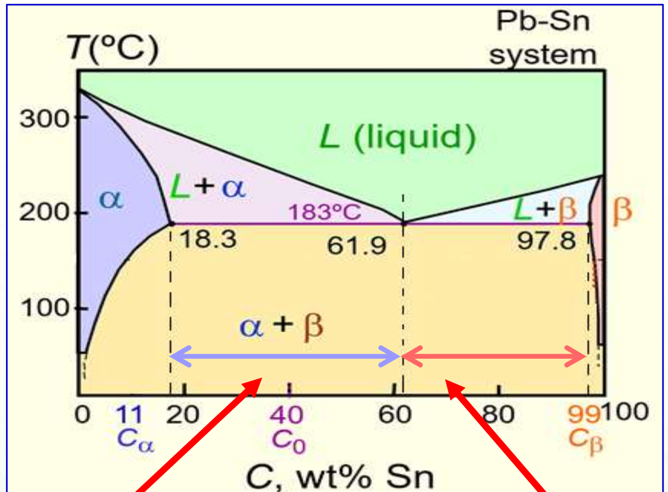
$$W_\beta = (1 - W_\alpha) = 0.27$$





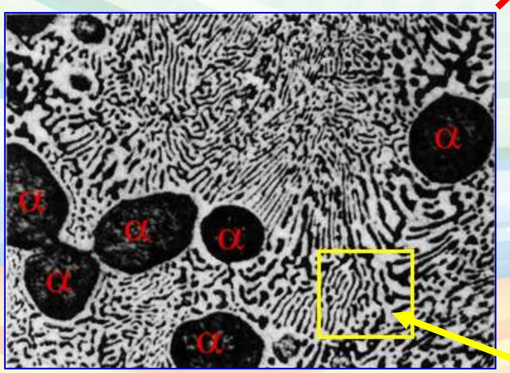
Hypoeutectic *Hypereutectic*

Hypoeutectic & Hypereutectic

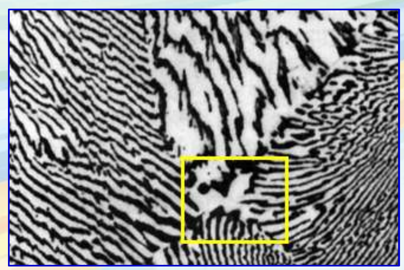


Eutectic 61.9

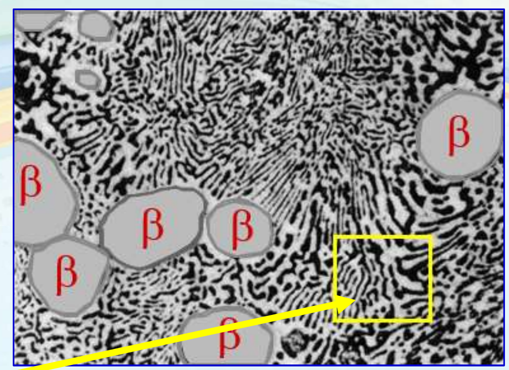
hypoeutectic: C_0 = 50 wt% Sn



eutectic: C_0 = 61.9 wt% Sn



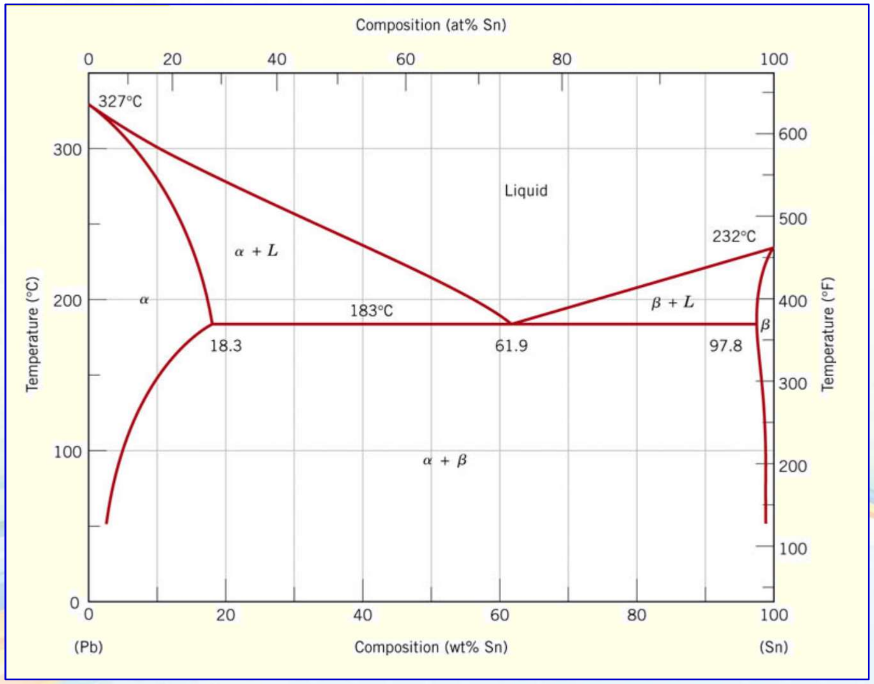
hypereutectic: (illustration only)



eutectic micro-constituent

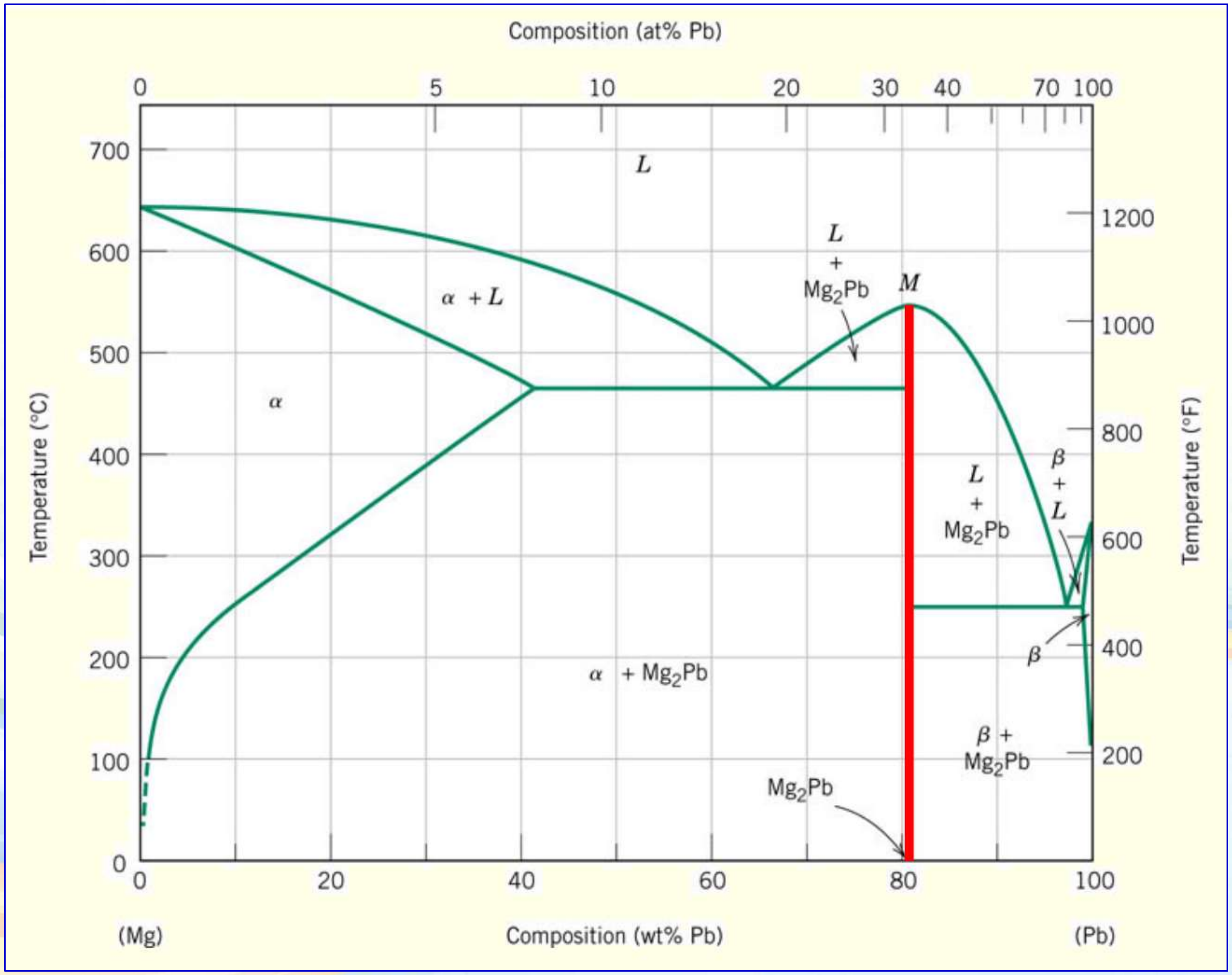
Exercise:

- At 150 °C for a 40 wt% 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 10 wt% Sn / 90 wt% 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)?

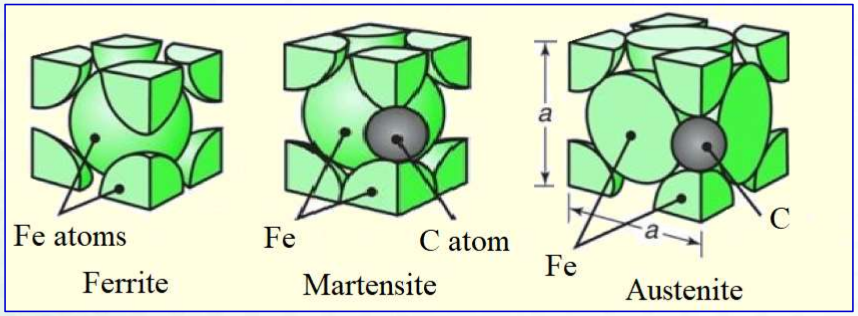


4- Intermetallic Compounds

- Besides solid solutions, intermetallic compounds, that have precise chemical compositions can exist in some systems.
- Intermetallic compound exists as a line on the diagram - not an area - because of stoichiometry (i.e. composition of a compound is a fixed value).
- 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 - Mg_2Pb and Mg_2Pb - Pb.


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
L
+
Mg2Pb
M
α + L
α
L
+
Mg2Pb
β
+
L
β
α + Mg2Pb
β +
Mg2Pb
Mg2Pb
0
20
40
60
80
100
(Mg)
Composition (wt% Pb)
(Pb)

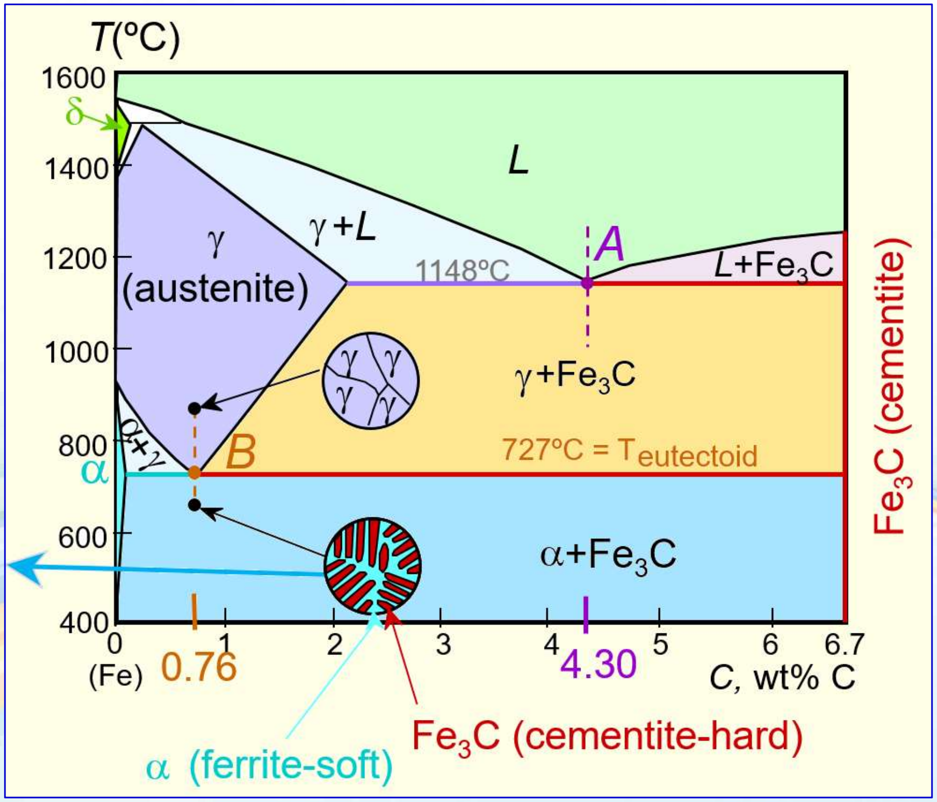
5- Iron-Carbon (Fe-C) Phase Diagram



- Two important points

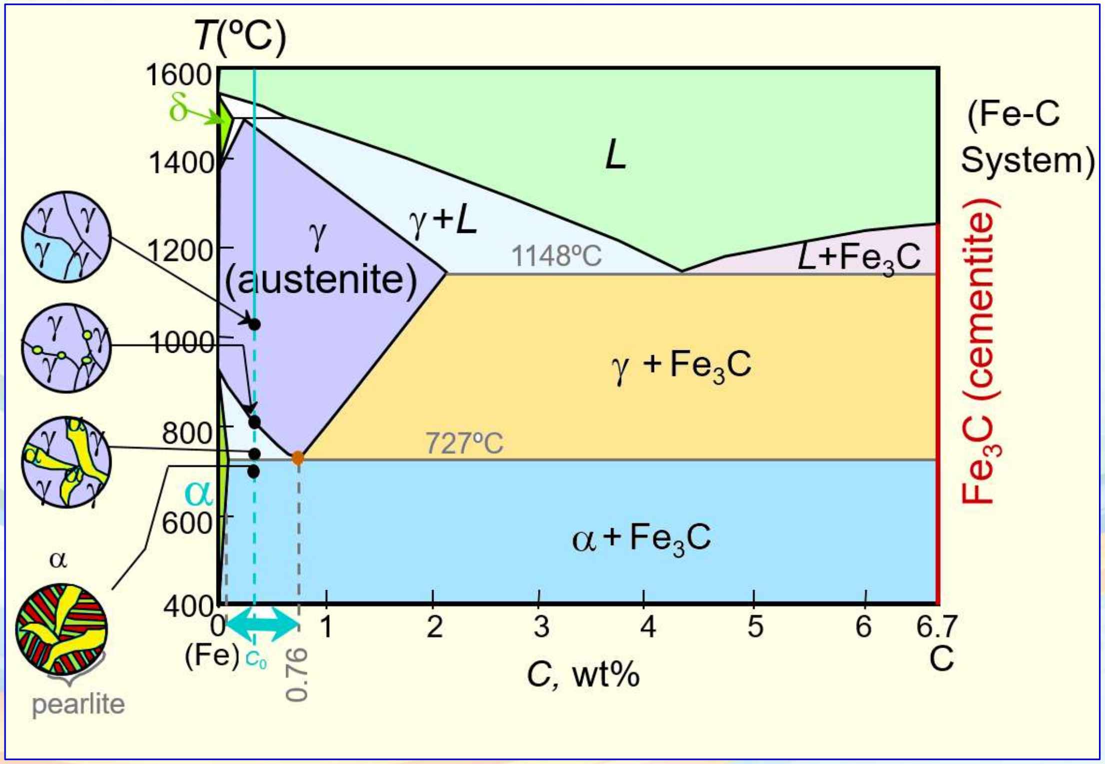
✓ Eutectic (A): $L \longrightarrow \gamma + Fe_3C$

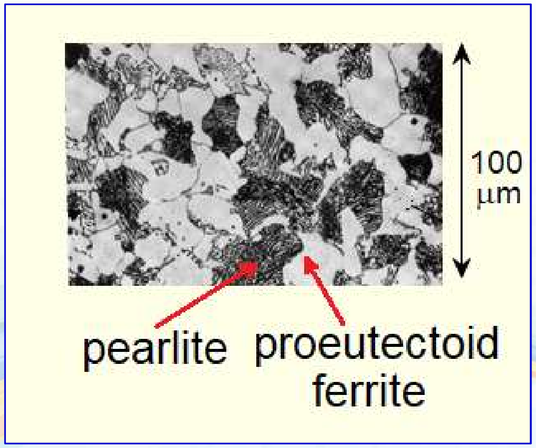
✓ Eutectoid (B): $\gamma \longrightarrow \alpha + Fe_3C$



<u>Result:</u>
Pearlite = alternating layers of α and Fe_3C phases

Hypoeutectoid Steel





Hypoeutectoid Steel

Hypoeutectoid Steel

- *Just above the eutectoid line*

$$W_{\acute{\alpha}} = \frac{s}{r+s}$$

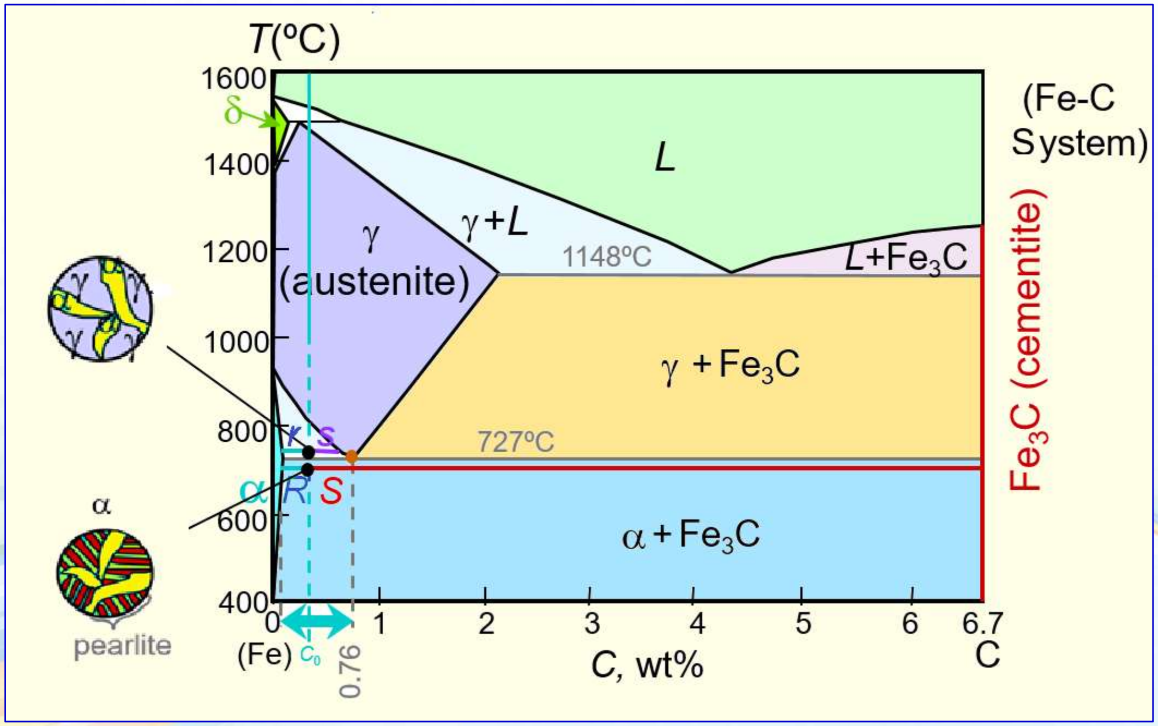
$$W_{\gamma} = (1 - W_{\acute{\alpha}})$$

- *Just below the eutectoid line*

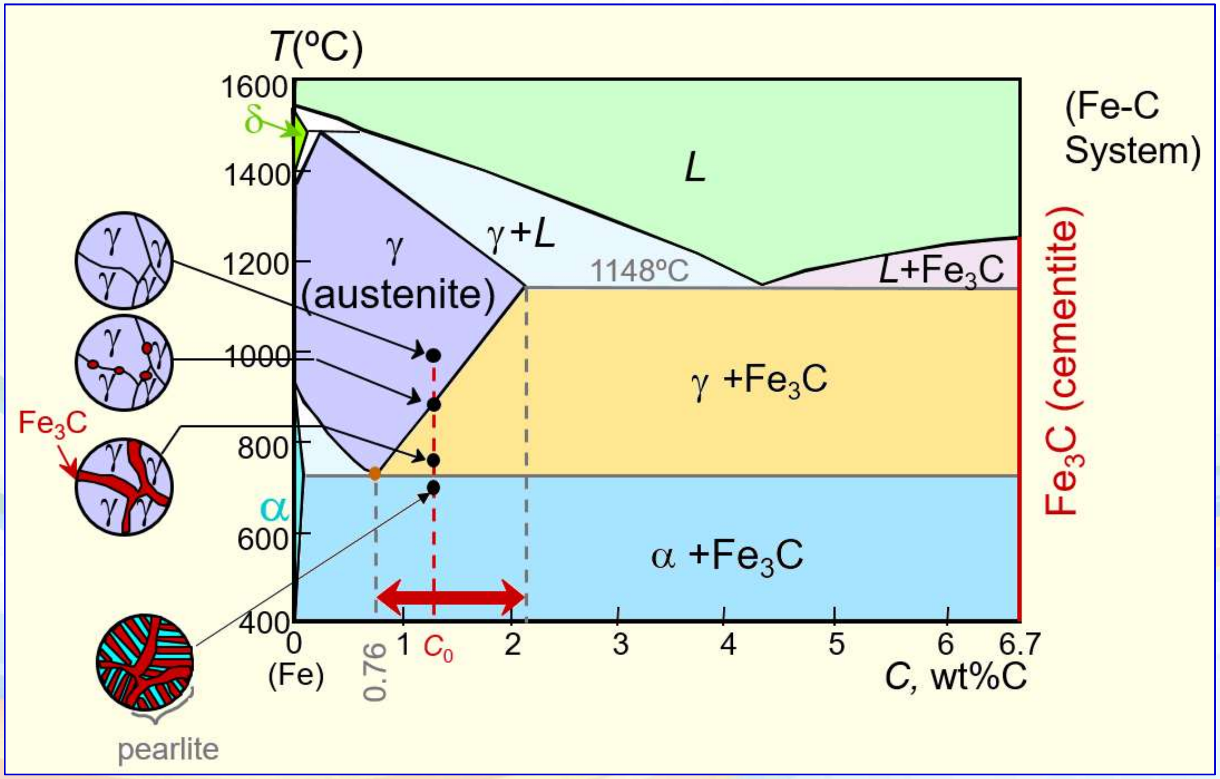
$$W_{pearlite} = W_{\gamma}$$

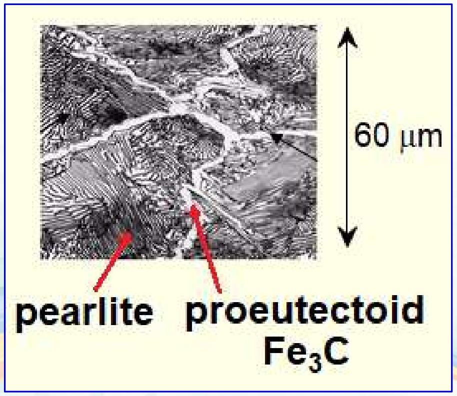
$$W_{\alpha} = \frac{S}{R+S}$$

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



Hypereutectoid Steel





Hyperoeutectoid Steel

Hypereutectoid Steel

- *Just above the eutectoid line*

$$W_{\gamma} = \frac{x}{v + x}$$

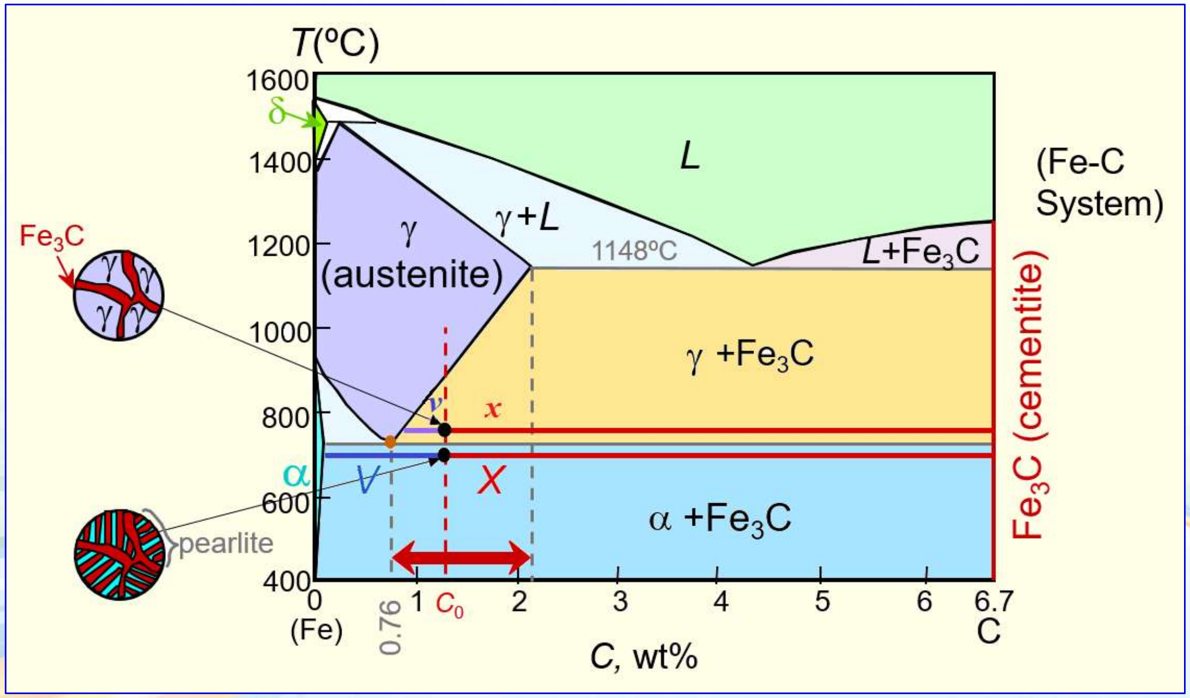
$$W_{Fé_eC} = (1 - W_{\gamma})$$

- *Just below the eutectoid line*

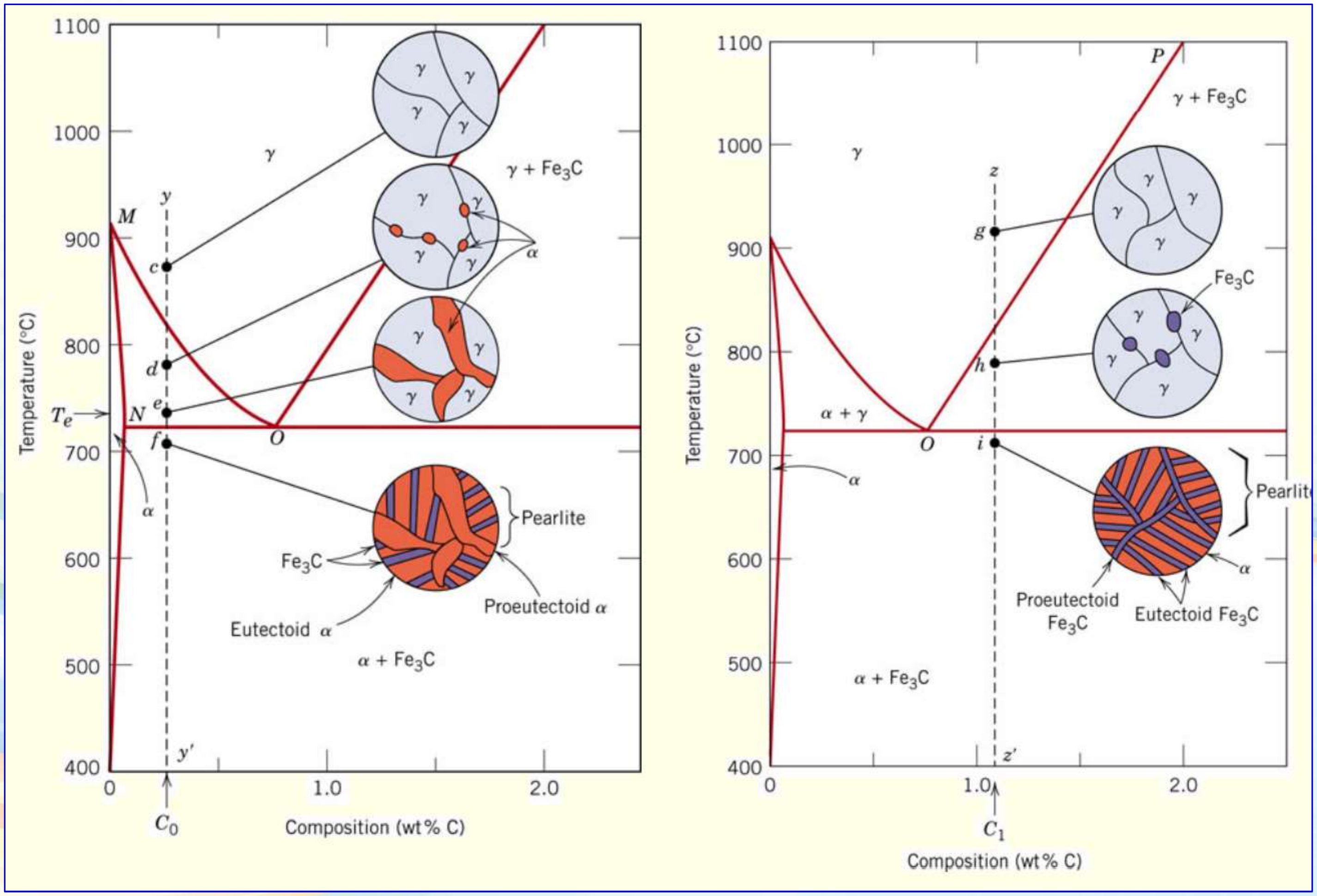
$$W_{pearlite} = W_{\gamma}$$

$$W_{\alpha} = \frac{X}{V + X}$$

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



Hypoeutectoid & Hypereutectoid



Phases in Fe–Fe_3C 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 eutectoid temperature (727 ° C) unless cooled rapidly

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. Fe_3C (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

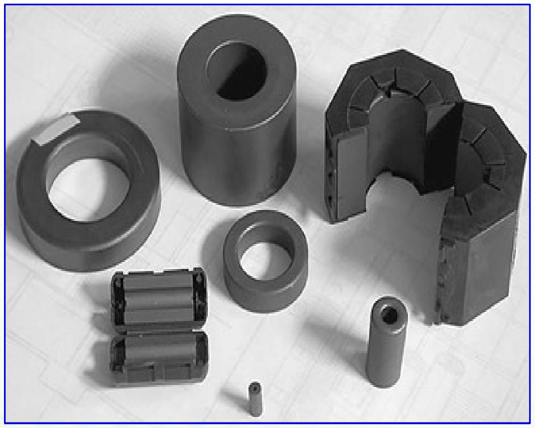
A few comments on Fe–Fe3 C system

- *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.*
- *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 of Iron

- Three types of ferrous alloys:

1. **Iron:** less than 0.008 wt % C in α−ferrite at room T.
2. **Steels:** 0.008 - 2.14 wt % C (usually < 1 wt%) α-ferrite + Fe_3C at room T.
3. **Cast iron:** 2.14 - 6.7 wt % (usually < 4.5 wt 50 %).



Example:

For a 99.6 wt% Fe and 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

a) Using the RS tie line just below the eutectoid

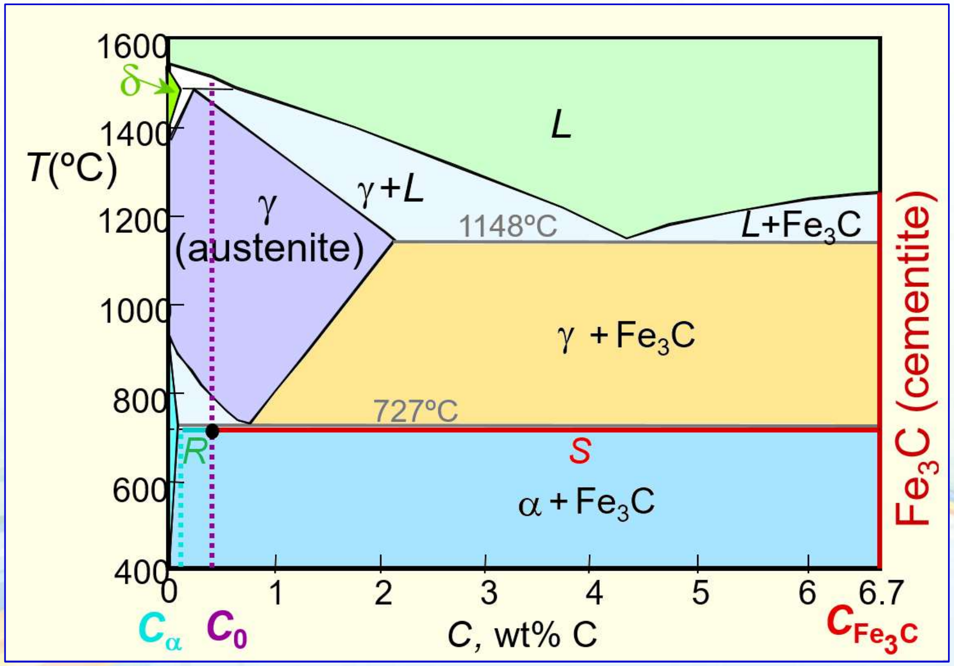
C_α = 0.022 wt% C

C_{Fe_3C} = 6.70 wt% C

b) Using the lever rule with the tie line shown

$$W_{Fe_3C} = \frac{R}{R+S} = \frac{C_L - C_\alpha}{C_{Fe_3C} - C_\alpha}$$

$$= \frac{0.4 - 0.022}{6.7 - 0.022} = 0.057$$



Amount of Fe_3C (eutectoid) in 100 g

= (100 g)W_{Fe_3C} = (100 g)(0.057) = 5.7 g

Amount of total ferrite in 100 g = 100 - 5.7 = 94.3 g

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

$C_o = 0.40$ *wt% C*

$C_\alpha = 0.022$ *wt% C*

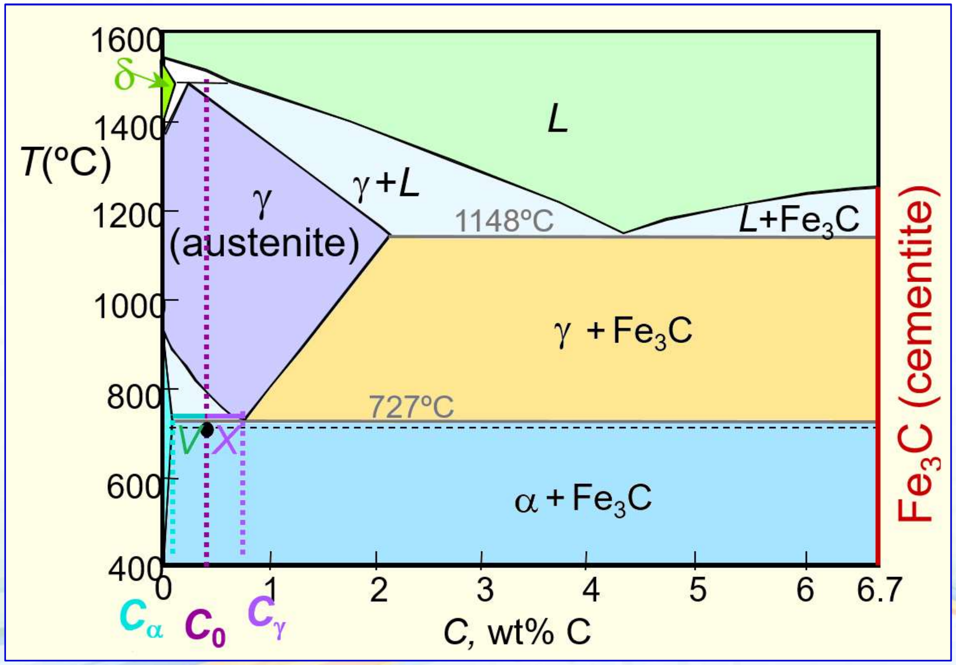
$C_{austenite} = C_\gamma = 0.76$ *wt% C*

$$W_{Austenite} = \frac{V}{V+X} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha}$$

$$= \frac{0.4 - 0.022}{0.76 - 0.022} = 0.512$$

Amount of austenite in 100 g

= (100 g)(0.512) = 51.2 g



Amount of proeutectoid ferrite in 100 g = 100-51.2 = 48.8 g

Then The amount of perlite ferrite (eutectoid) = 94.3 – 48.8 = 45.5 g

The Influence of Other Alloying Elements

- *Adding alloying elements (Cr, Ni, Ti, ….) yields dramatic changes in the binary iron-iron carbide phase diagram.*
- *Alterations of the positions of the phase boundaries and the shapes of the phase regions depend on the alloying element and its concentration.*