CHAPTER 9: PHASE DIAGRAMS

ISSUES TO ADDRESS...

- When we combine two elements...
  what equilibrium state do we get?
- In particular, if we specify...
  --a composition (e.g., wt%Cu - wt%Ni), and
  --a temperature (T)

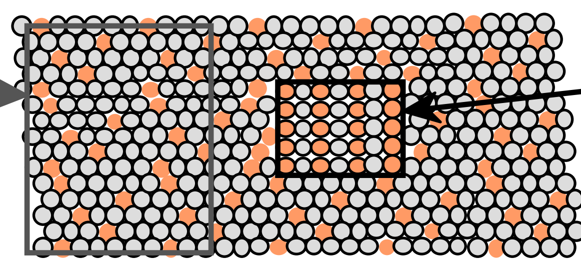
then...

How many phases do we get?

What is the composition of each phase?

How much of each phase do we get?

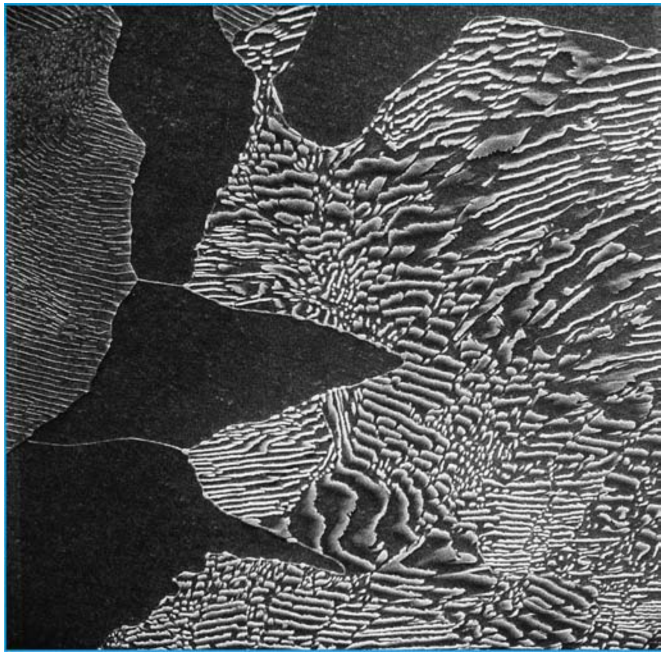
Phase A



Phase B

∘Nickel atom
•Copper atom

Some Definitions



The microstructure of Fe-C alloy

- An **alloy** is a combination, either in solution or compound, of two or more **components** (elements), at least one of which is a metal.

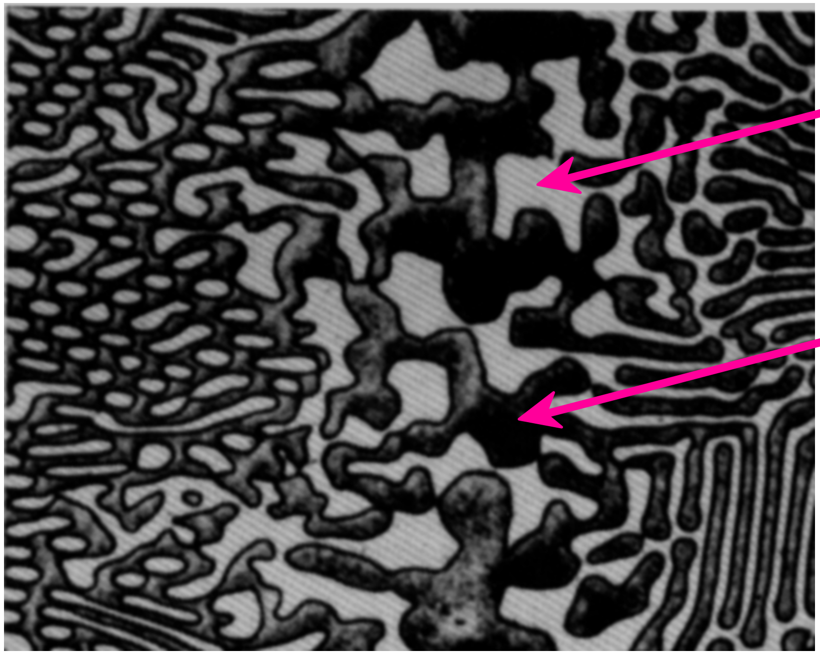
- An alloy with two components is called a **binary** alloy; one with three is a **ternary** alloy; one with four is a **quaternary** alloy.

- The result is a material with ***properties different from*** those of its ***components***.

COMPONENTS AND PHASES

- Components:
  The elements or compounds which are mixed initially (e.g., Al and Cu)
- Phases:
  The physically and chemically distinct material regions that result (e.g., a and b).

Aluminum-Copper Alloy



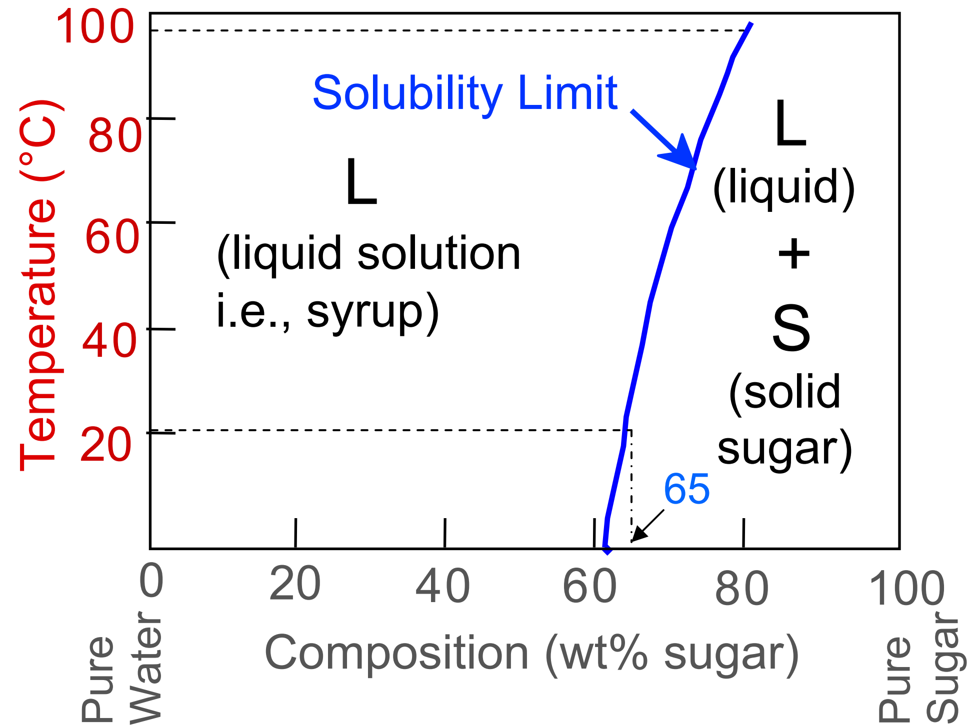
THE SOLUBILITY LIMIT

- Solubility Limit:
  Max concentration for which only a solution occurs (remember ***HUME ROTHERY RULES)***

.

Example: Water – Sugar System

<u>Question:</u>
What is the solubility limit at 20C?
<u>Answer</u>: **65wt% sugar.**
If C_o < 65wt% sugar: syrup
If C_o > 65wt% sugar: syrup + sugar.

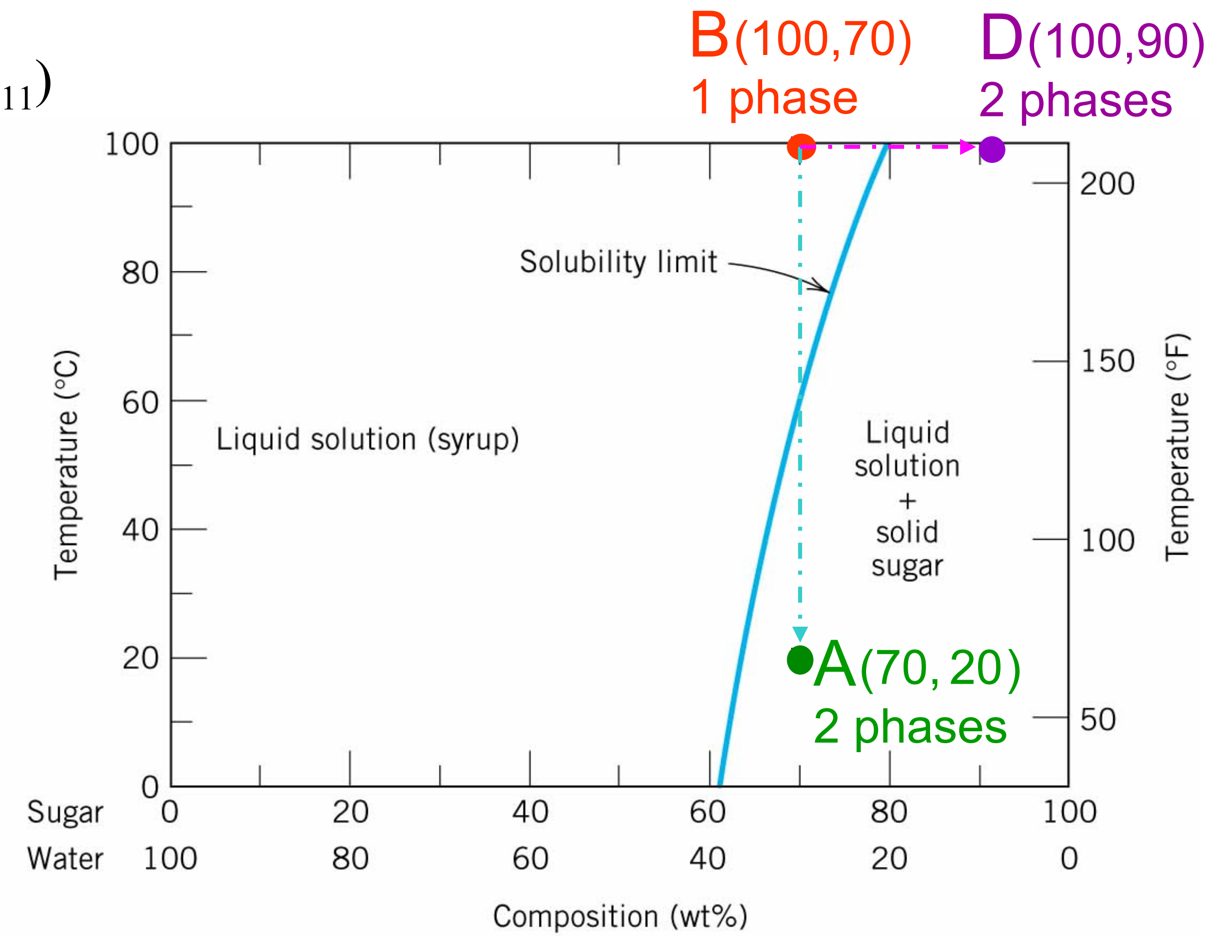


- **Solubility limit increases with T**:
  e.g. at T=99°C, solubility limit is ~ 80wt%

EFFECT of T and COMPOSITION

- Changing T can change number of phases: path A to B.
- Changing C_o can change number of phases: path B to D.

Water-Sugar ($C_{12}H_{22}O_{11}$) system



Phase Diagrams

- A phase diagram shows what ***phases*** are present and where the process ***boundaries*** are within the composition space.

- Equilibrium phase diagrams represents relations between temperature, pressure, ***compositions*** and ***quantities*** of phases at equilibrium.

- Phase diagrams allows to predict phase transformations which occur during ***temperature change*** (e.g. upon cooling).

The following type of ***binary*** (contains only two component) systems will be discussed below:

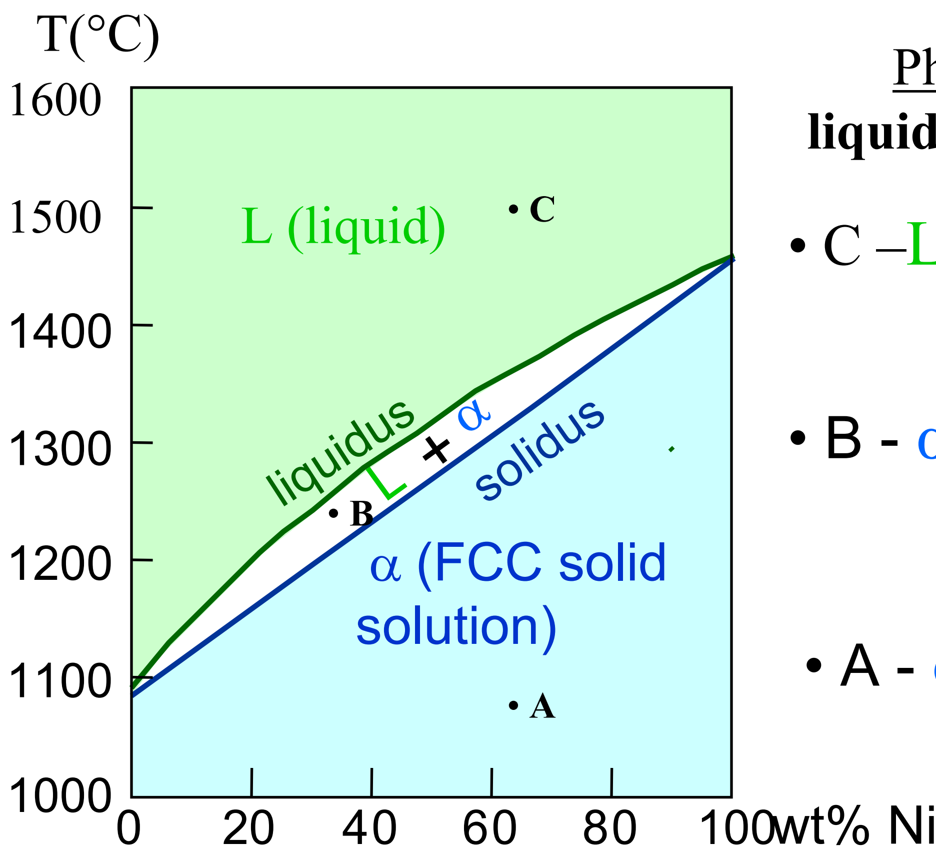
- complete solubility: ***isomorphous***
- ***eutectic***
- with ***intermediate phases*** or compounds
- involving ***eutectoid*** and ***peritectic*** reactions

Special attentions will be paid on the ***iron-iron carbide*** system

Binary Isomorphous Systems

- Isomporhous system is characterized by ***complete*** liquid and solid ***solubility*** of the components
- For this course:
  --binary systems: just 2 components.
  --independent variables: T and C_o (P = 1atm is always used).

- Phase Diagram for Cu-Ni system



Phase boundaries: **liquidus** and **solidus** lines

- C – L (homogeneous liquid solution)
- B - α and L
- A - α (FCC solid solution)

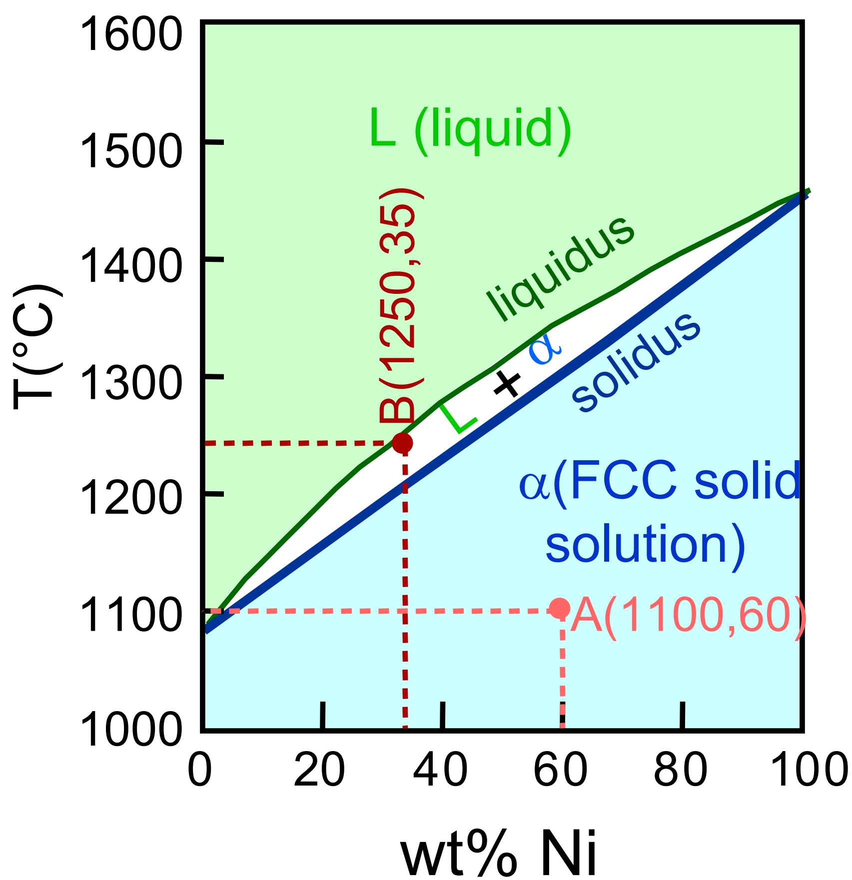
PHASE DIAGRAMS:
Number and Types of Phases Present

- **Rule 1:** If we know T and C_o, then we know:
  -the number and types of phases present.

- Examples:

A(1100°C, 60 wt%):
1 phase: α

B (1250, 35):
2 phases: L + α



Cu-Ni phase diagram

PHASE DIAGRAMS:
Composition of Phases

- **Rule 2:** If we know T and C_o, then we know: **the composition of each phase**

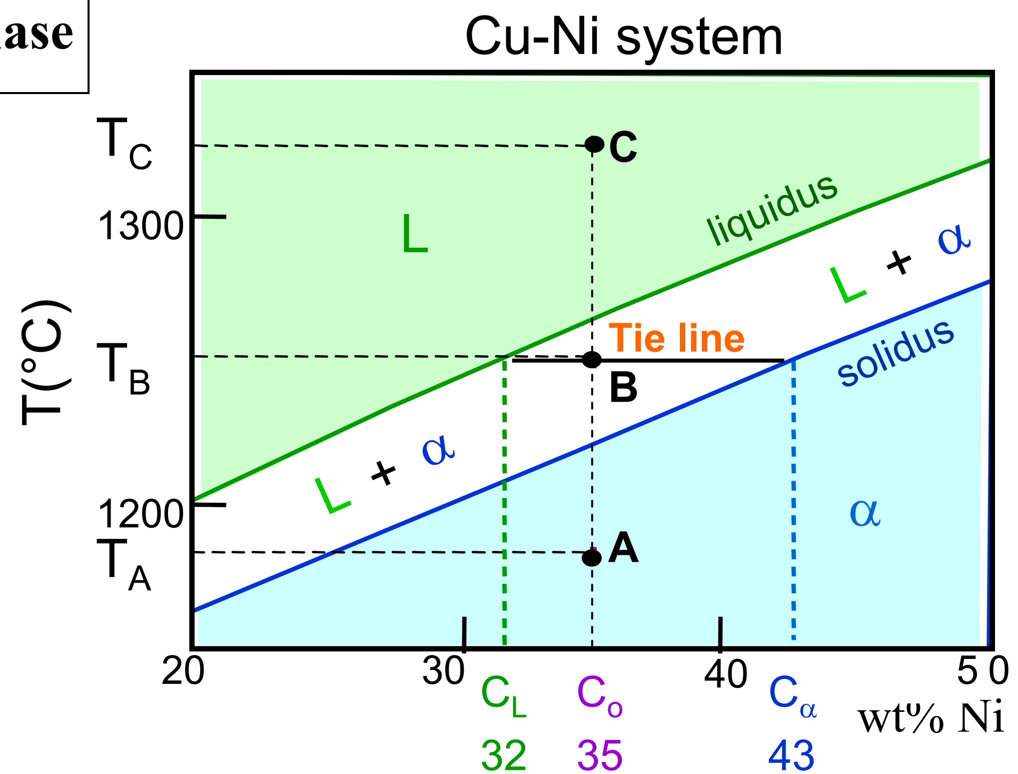
- Examples:

  $C_O == 35$wt%Ni

- at T_C=1350 C, **only one**, Liquid phase exists with composition: 35 wt % Ni – 65 % Cu

- at T_A=1175 C, again **only one**, solid phase exists with composition: 35 wt % Ni – 65 % Cu

- at T_B=1250 C, ***two phase*** (L and α) exist with compositions:
  L – 32 wt% Ni - 68%Cu
  α - 43 wt% Ni - 57%Cu



Tie line is an ***isotherm*** in the two-phase region. Intersects of this line with phase boundary lines (e.g. liquidus and solidus) give the compositions of the corresponding phases (e.g. liquid and solid solutions)

PHASE DIAGRAMS: Weight Fractions of Phases

- **Rule 3:** If we know T and C_o, then we know:
  -the amount of each phase (given in wt%).

- Examples:

  C_O = 35wt%Ni

  At T_C : Only Liquid (L)

  W_L= 100 wt%, W_α=0

  At T_A : Only Solid (α)

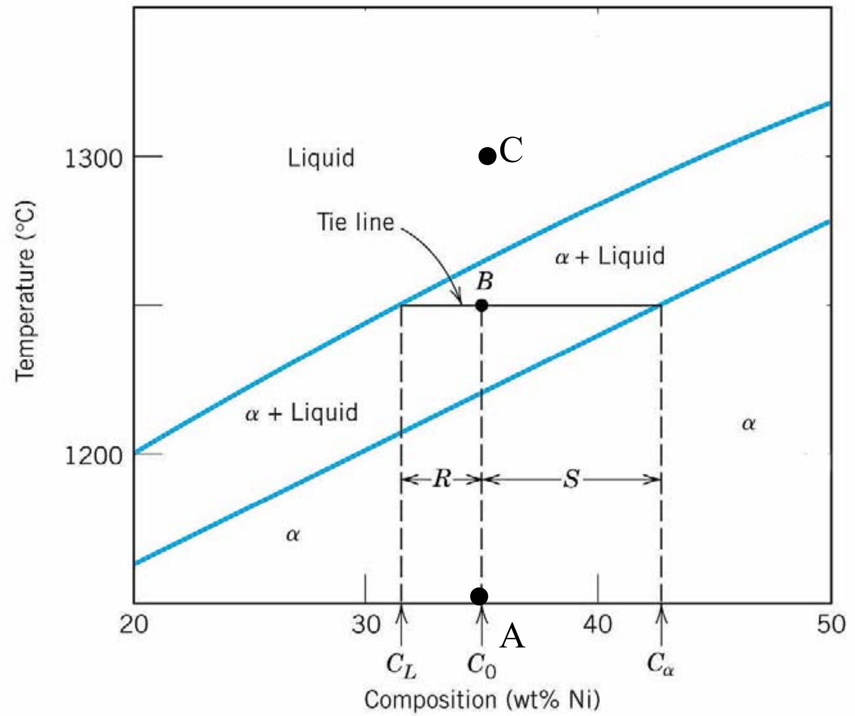
  W_L = 0, W_α= 100%

  At T_B : Both α and L

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 73\text{wt }\%$$

$$W\alpha = \frac{R}{R+S} = 27\text{wt}\%$$

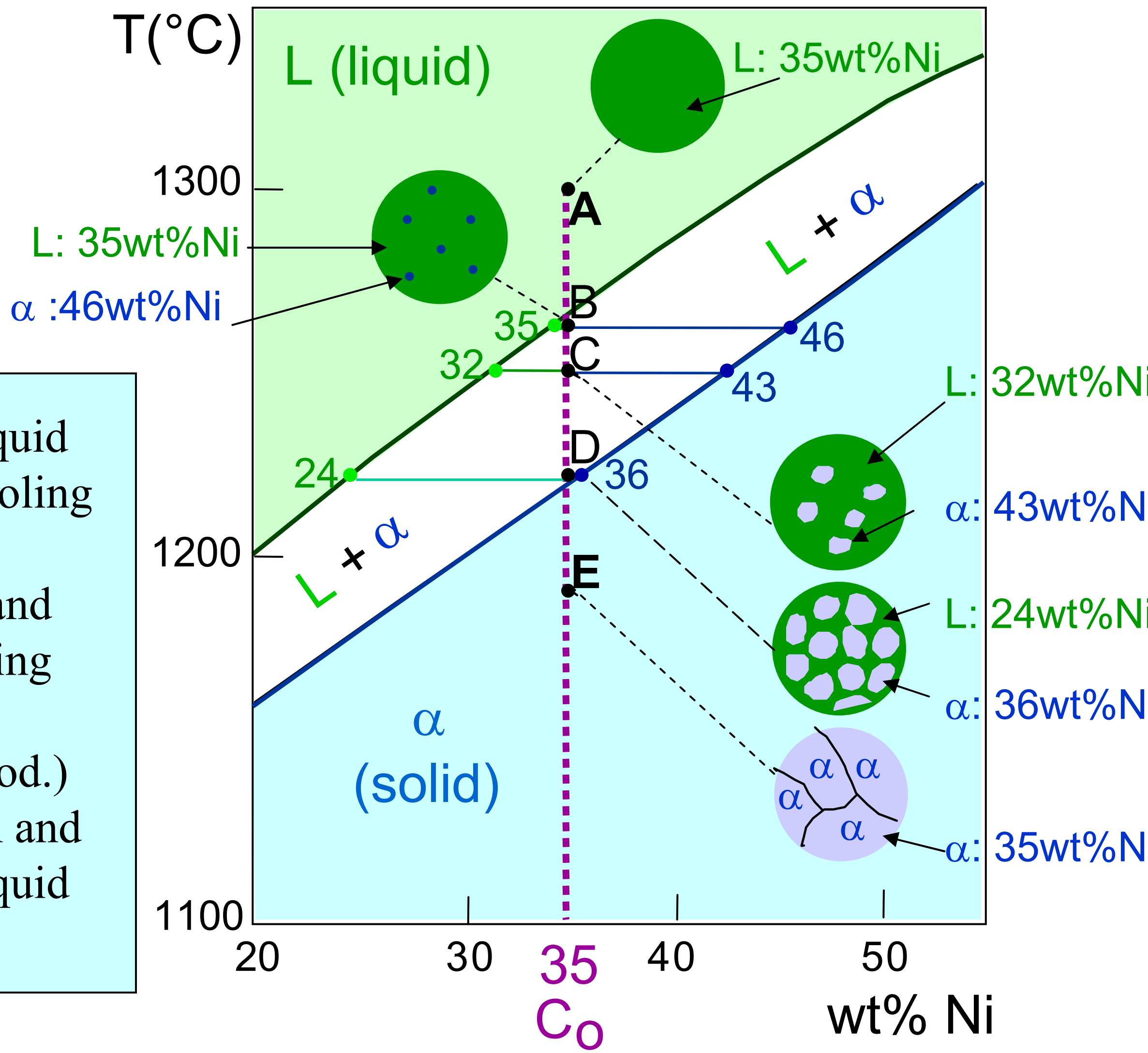
Cu-Ni



Lever rule: The fraction of one phase is computed by taking the length of **tie line** from the overall alloy composition to the phase boundary for ***the other phase,*** and dividing by the total tie line length.

Microstructure Development: Equilibrium Cooling

<u>Example:</u> Cu-Ni system
-slow cooling along the line with C_o = 35wt%Ni.

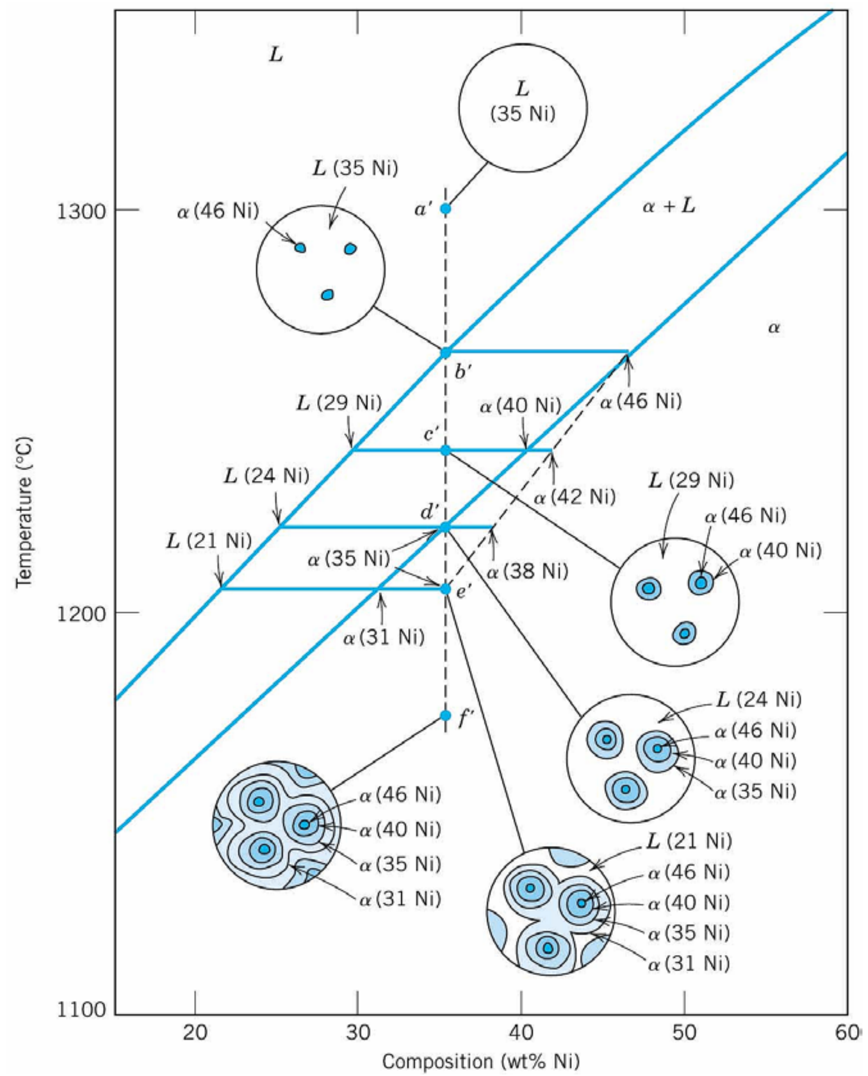


- Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line.
- The composition of the solid and the liquid change gradually during cooling (B→C→D, as can be determined by the tie-line method.)
- Nuclei of the solid phase form and they grow to consume all the liquid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

Microstructure Development:Non-Equilibrium Cooling

<u>Example:</u> Cu-Ni system;
Rapid cooling along the line
with C_o = 35wt%Ni.

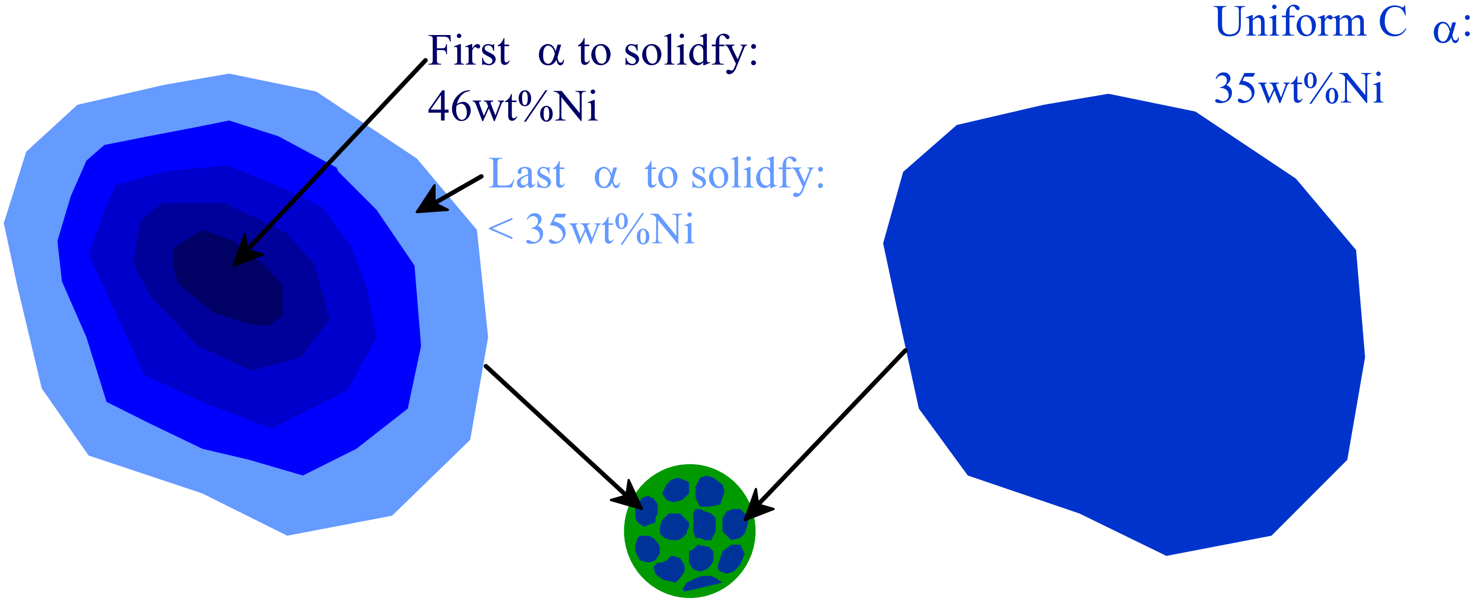
• Solidification in the solid + liquid phase still occurs gradually.
•The composition of the liquid phase evolves by **relatively fast** diffusion, following the equilibrium values that can be derived from the tie-line method.
• However, diffusion in the solid state is **slow**. Hence, the new layers that solidify on top of the grains have the equilibrium composition at that temperature but once they are solid their composition essentially does not change. This lead to the formation of layered (cored) grains and to the **invalidity of the tie-line method** to determine the composition of the solid phase.



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.

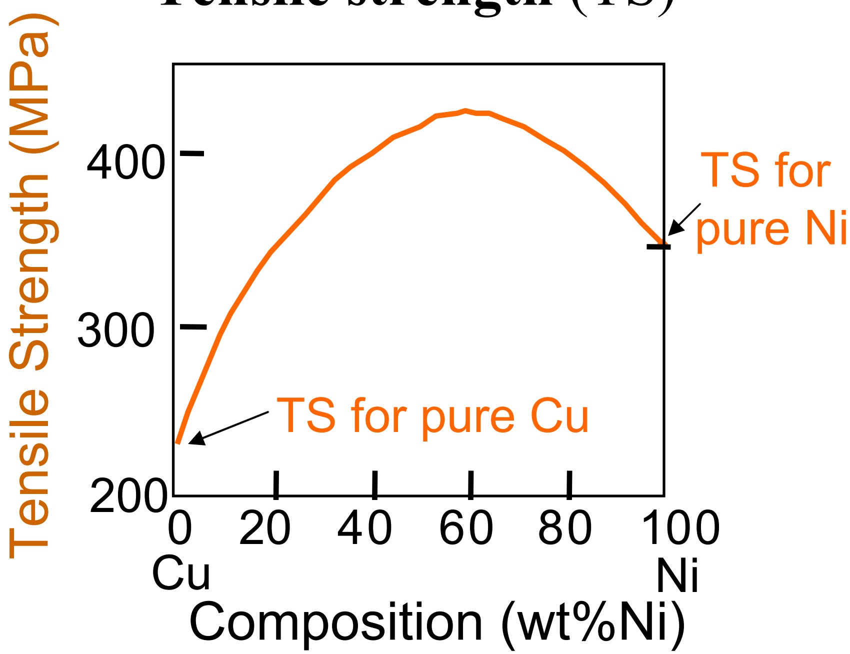
- Fast rate of cooling:
  Cored structure
- Slow rate of cooling:
  Equilibrium structure



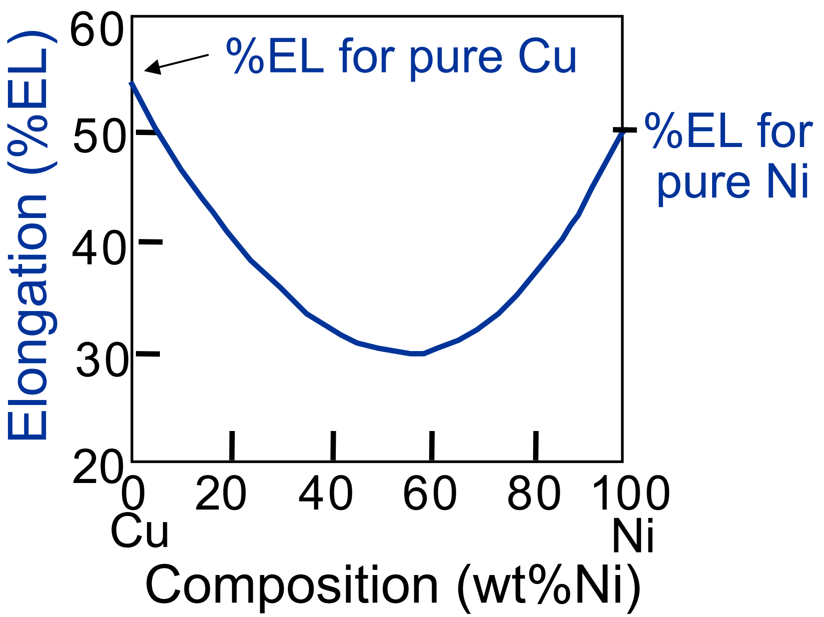
MECHANICAL PROPERTIES: Cu-Ni System

- Effect of solid solution strengthening on:

-Tensile strength (TS)



-Ductility (% EL)



Tensile Strength exhibits a **maximum**!!

Opposite behavior for Elongation

BINARY-EUTECTIC SYSTEMS (1)

Such systems are characterized by **limiting components solubility** and existing of a special composition (eutectic) with a **minimum melting point**, T_E (eutectic means easily melted) .

Example I: Cu-Ag system

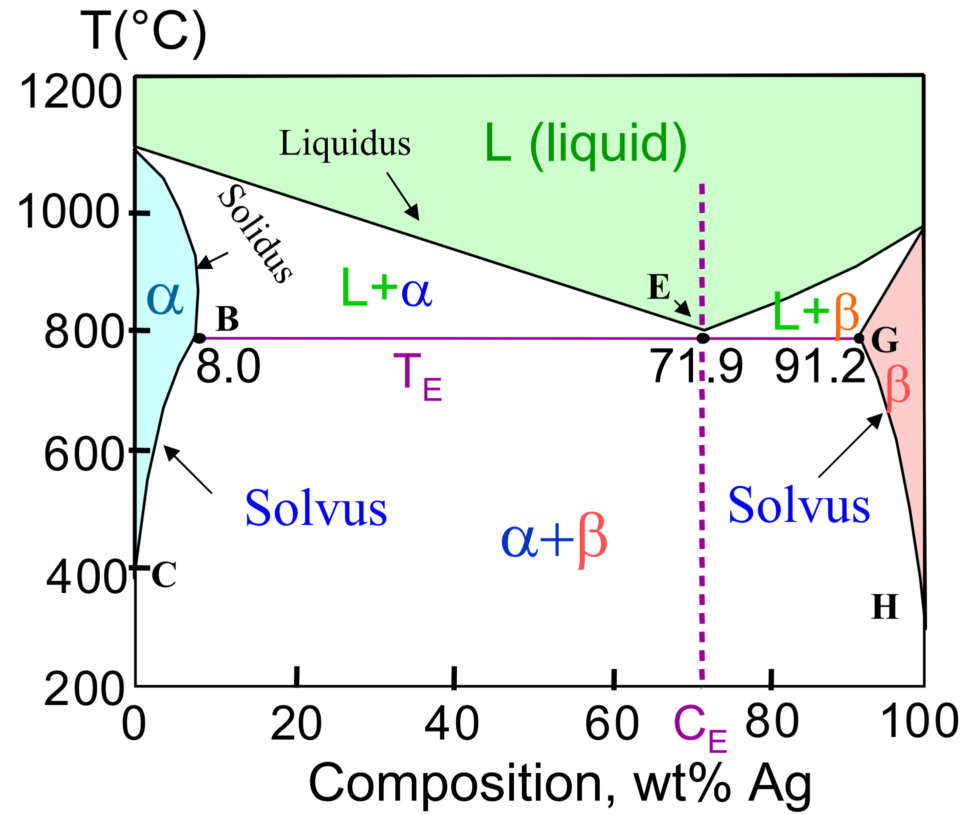
The specific features are:

- ***3 single phase regions***: L, α and β
- ***Limited solubility***:

  α: mostly Cu

  β: mostly Ni

- **Solvus** lines, **BC** and **GH,** separates one solid solution from a mixture of solid solutions.
- **Solvus lines show limit of solubility**



BINARY-EUTECTIC SYSTEMS (2)

Such systems are characterized by **limiting components solubility** and existing of a special composition (eutectic) with a **minimum melting point**, T_E (eutectic means easily melted) .

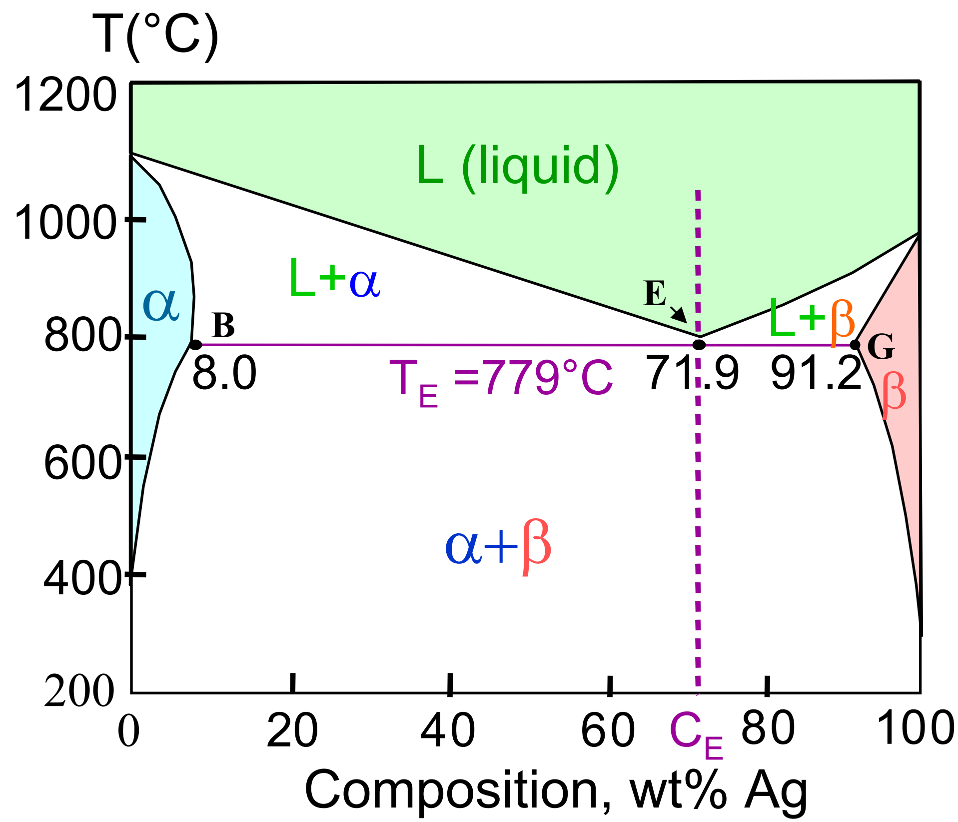
Example I: Cu-Ag system

- Point E is an ***invariant point***
- T_E : No liquid below T_E
- C_E : Composition with ***minimum melting*** T_E

- ***Eutectic reaction:***

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

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



- line **BEG** is the ***eutectic isotherm:*** ***3 phases*** can be ***in equilibrium*** along eutectic isotherm

EXAMPLE II: Pb-Sn SYSTEM (1)

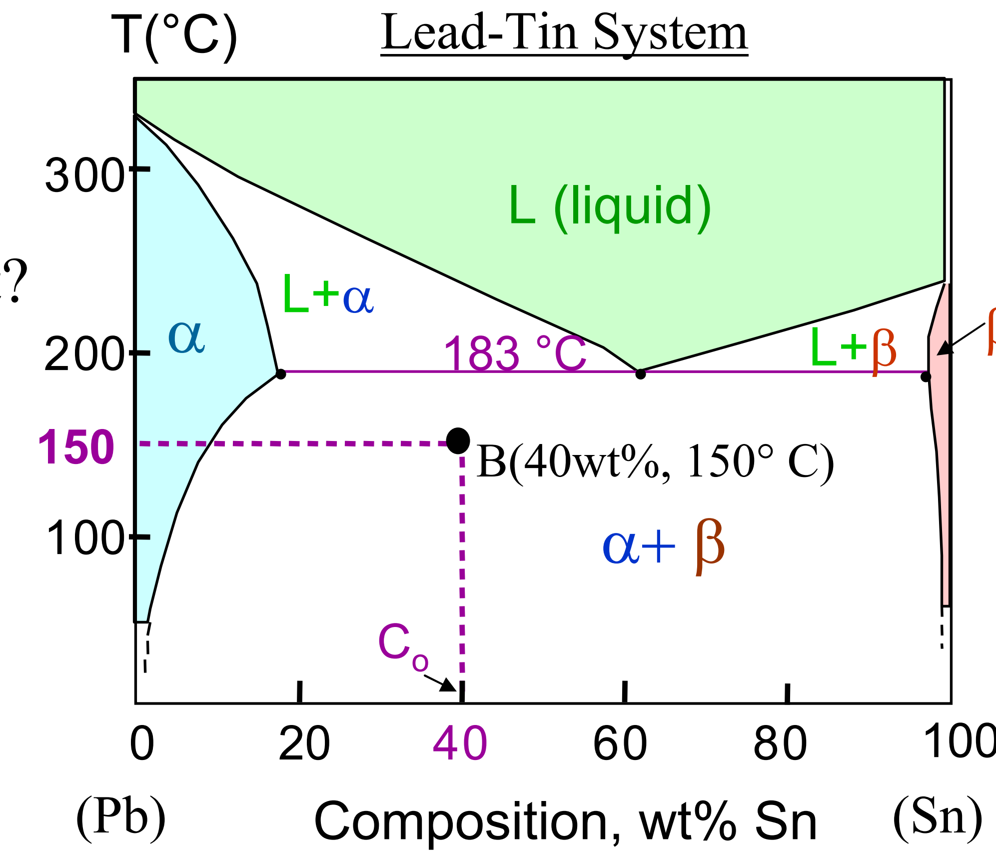
- For point B,

i.e. alloy 40%Sn-60t%Pb at 150°C,

find...

-What phase(s) is (are) present?

- <u>Answer</u>: α and β coexist



Pb-Sn EUTECTIC SYSTEM (2)

- For point **B**,

i.e. alloy 40%Sn-60t%Pb at 150°C, ***find...***

-What are the compositions of the phases?

- <u>Answer</u>:

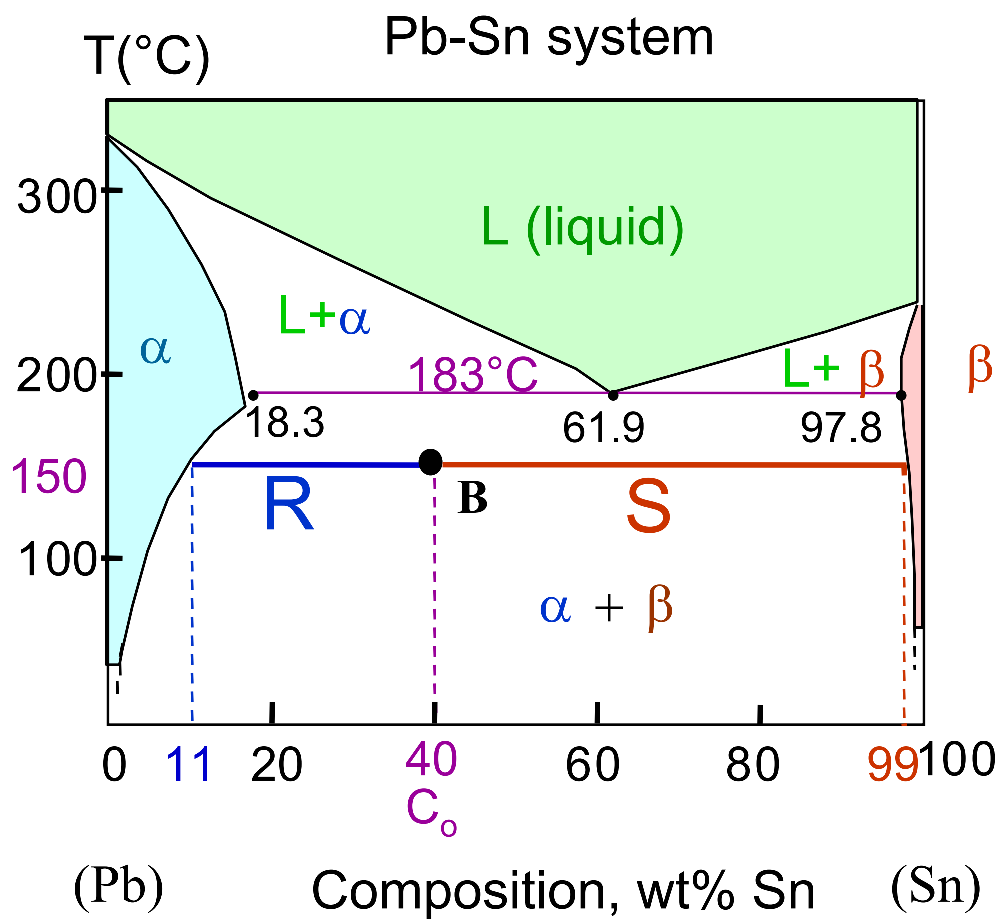
C_α = 11% Sn – 89wt% Pb
C_β = 99% Sn – 1wt% Pb

-What are the relative amounts of each phase?

<u>-Answer:</u>

$$W_\alpha = \frac{59}{88} = 67 \text{ wt }\%$$

$$W_\beta = \frac{29}{88} = 33 \text{ wt }\%$$



MICROSTRUCTURES IN EUTECTIC SYSTEMS: Equilibrium Cooling (1)

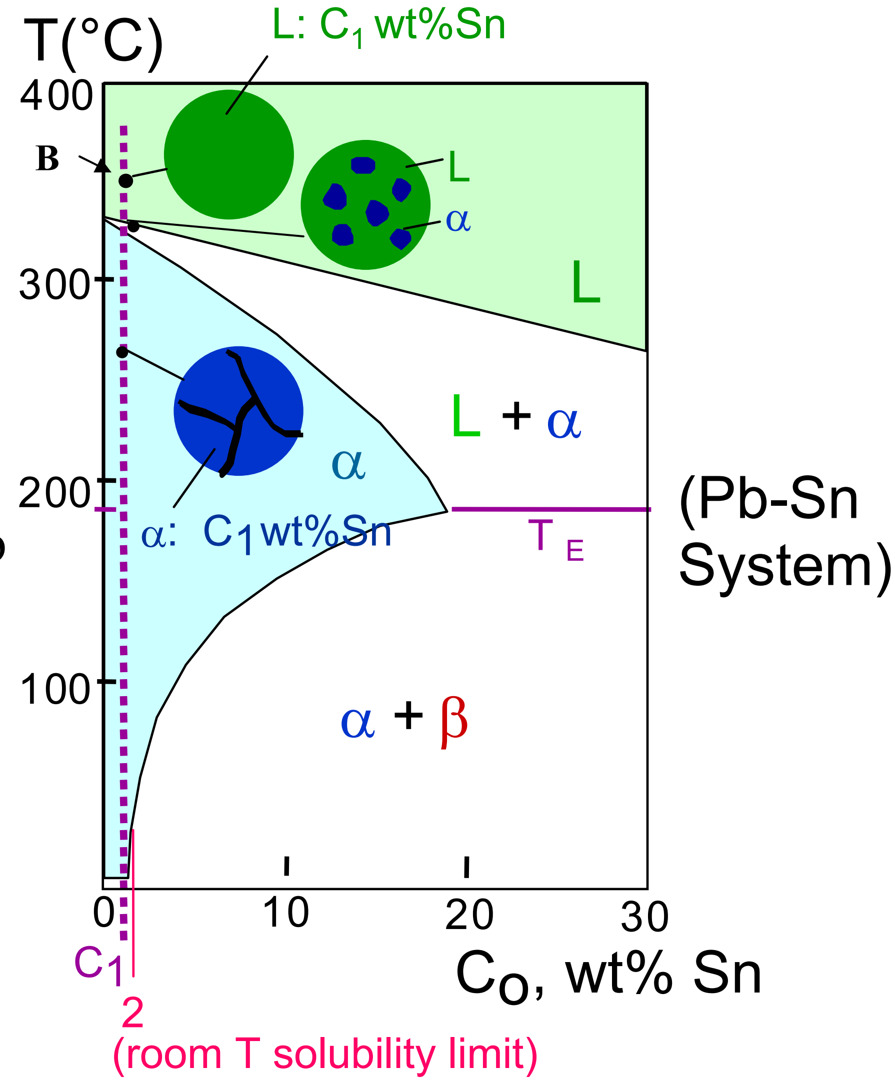
• Composition range: a pure component (e.g. Pb) - its maximum solid solubility at ***room*** (20°C) temperature (e.g. point B with C_B=C_1< 2wt%)

• Result:

T>T_L=330 °C – ***liquid alloy*** with C_1comp

T_S< T<T_L – very narrow region: ***solid*** a phase in ***liquid*** (L) and compositions of phases are defined by **tie-line method;**

T<T_S - ***polycrystal*** of α ***grains*** with uniform composition of C_1.

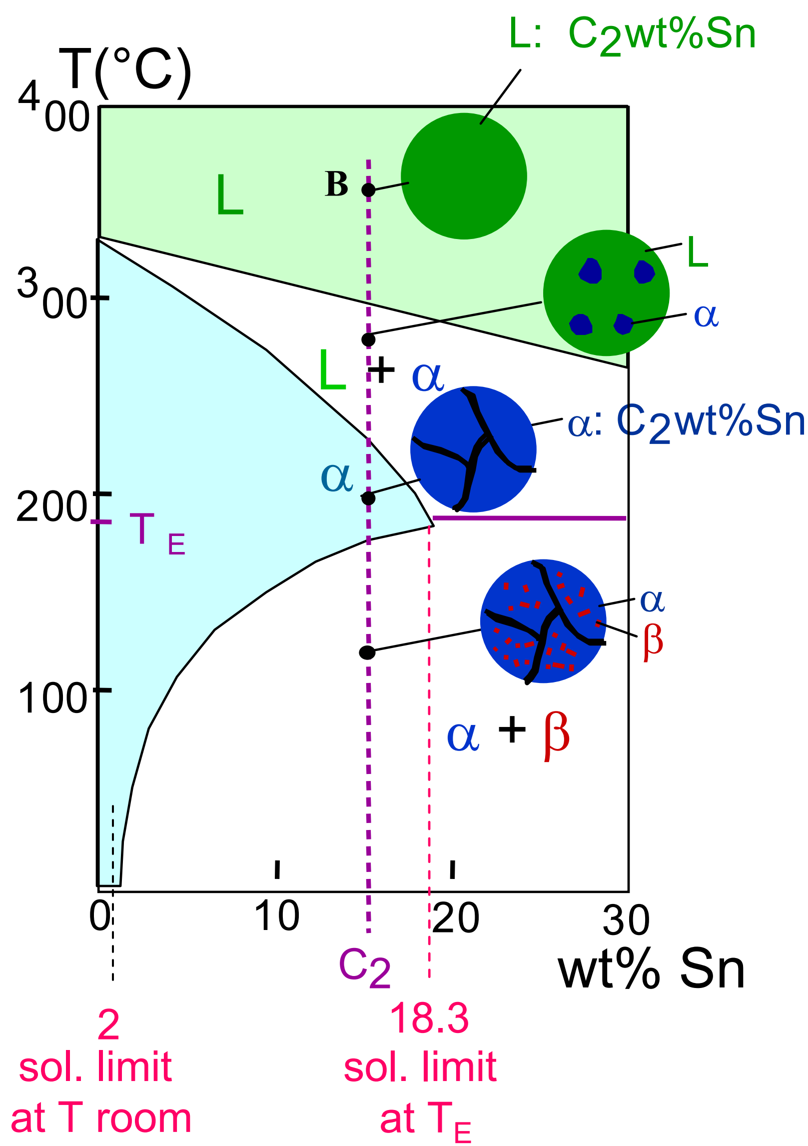


MICROSTRUCTURES IN EUTECTIC SYSTEMS: Equilibrium Cooling (2)

• <u>Composition range</u>: maximum solid solubility at ***room*** (20°C) temperature (C = 2wt%) and maximum solid solubility at ***eutectic*** temperature, T_E=183°C (C=18.3%)
(e.g. point B with 2wt%<C_B=C_2< 18.3 wt%)

• <u>Result:</u>

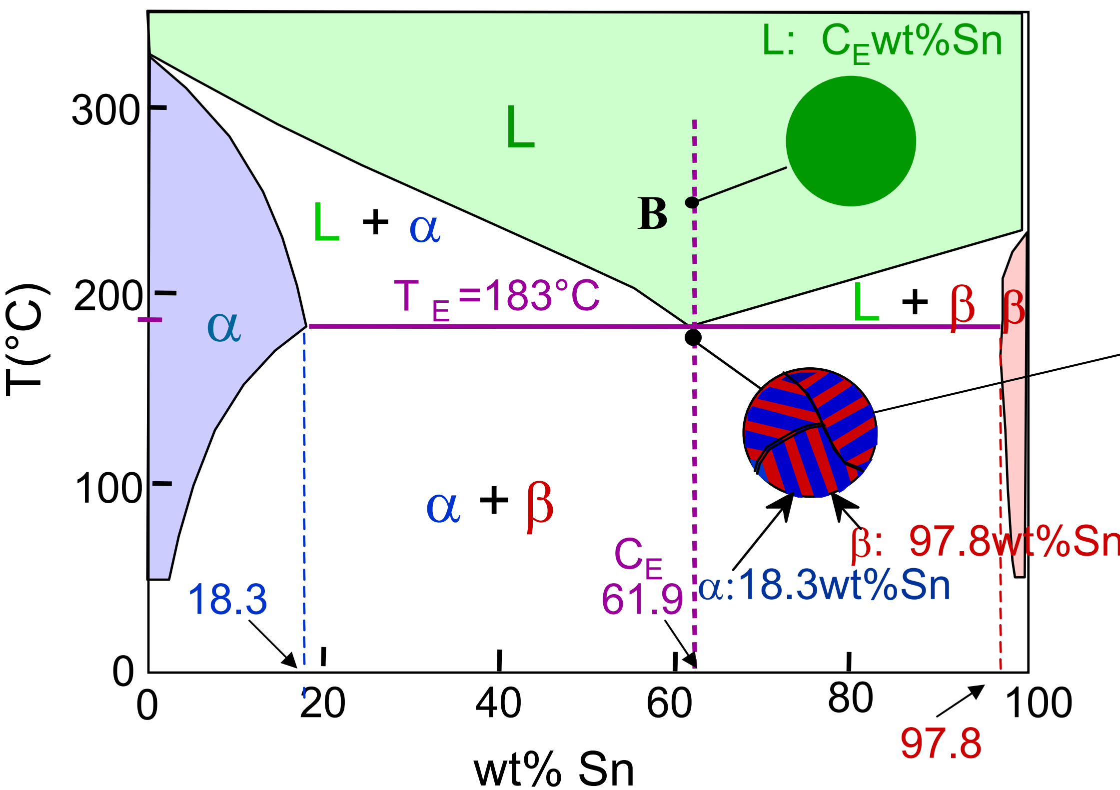
- T>T_L – ***liquid alloy*** with C_2comp.;
- $T_{solidus}$<T<T_L – ***solid*** α phase in ***liquid*** (L) and compositions of phases are defined by tie-line method;
- $T_{solvus} < T < T_{solidus}$ - ***polycrystal*** of α ***grains*** with uniform composition of C_2.
- T< T_{solvus} - α ***polycrystal*** with fine β ***crystals;*** the compositions of phases are defined by tie-line method and the amount of each phase by Level rule.



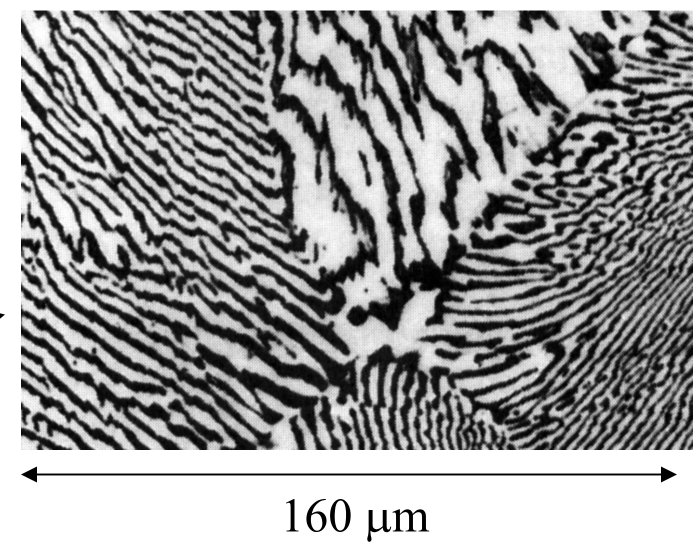
MICROSTRUCTURES IN EUTECTIC SYSTEMS: Equilibrium Cooling (3)

- **Composition range**: $C = C_E$

- Result:
  - $T>T_E$: ***liquid*** with $C = C_E = 61.9$ wt% Sn
  - $T<T_E$: ***alternating layers of α and β crystals***.



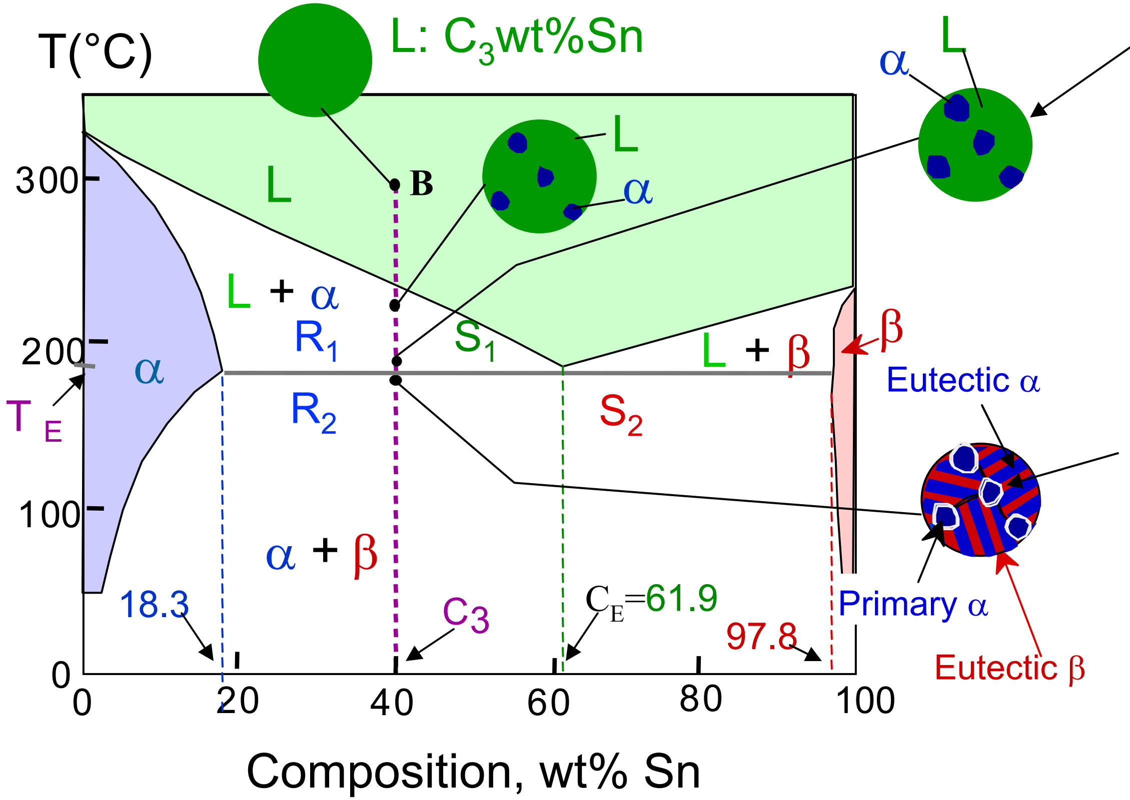
Microstructure of Pb-Sn eutectic lamellae



$$L(61.9wt\%Sn) \underset{heating}{\overset{cooling}{\rightleftharpoons}} \alpha(18.3wt.\%Sn)+\beta(97.8wt\%Sn)$$

MICROSTRUCTURES IN EUTECTIC SYSTEMS: Equilibrium Cooling (4)

- **<u>Composition range</u>**:
  18.3wt%Sn < C_3 < 61.9wt%Sn
  (e.g. point B with $C_B = C_3$ 40wt% Sn)



<u>Results:</u>

- <u>Just above T_E:</u>

solid primary α phase in liquid

$C_\alpha \approx$ 18.3wt%Sn

$C_L \approx$ 61.9wt%Sn

$$W_\alpha = \frac{S_1}{R_1 + S_1} \approx 50\text{wt\%}$$

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

- <u>Just below T_E:</u>

α ***crystals and*** α ***eutectic microstructure***

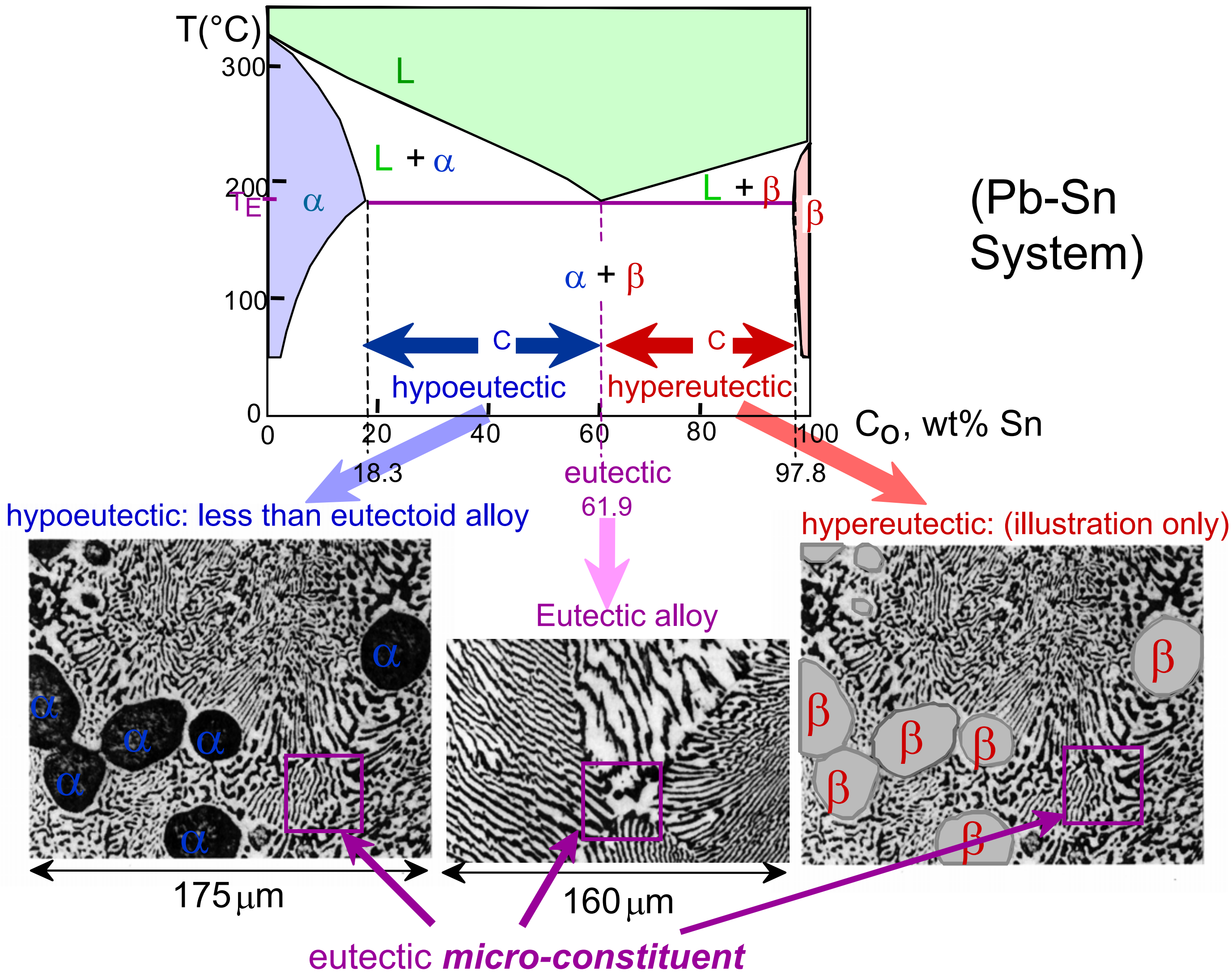
$C_\alpha \approx$ 18.3wt%Sn

$C_\beta \approx$ 97.8wt%Sn

$$W_\alpha = \frac{S_2}{R_2 + S_2} \approx 73\text{wt\%}$$

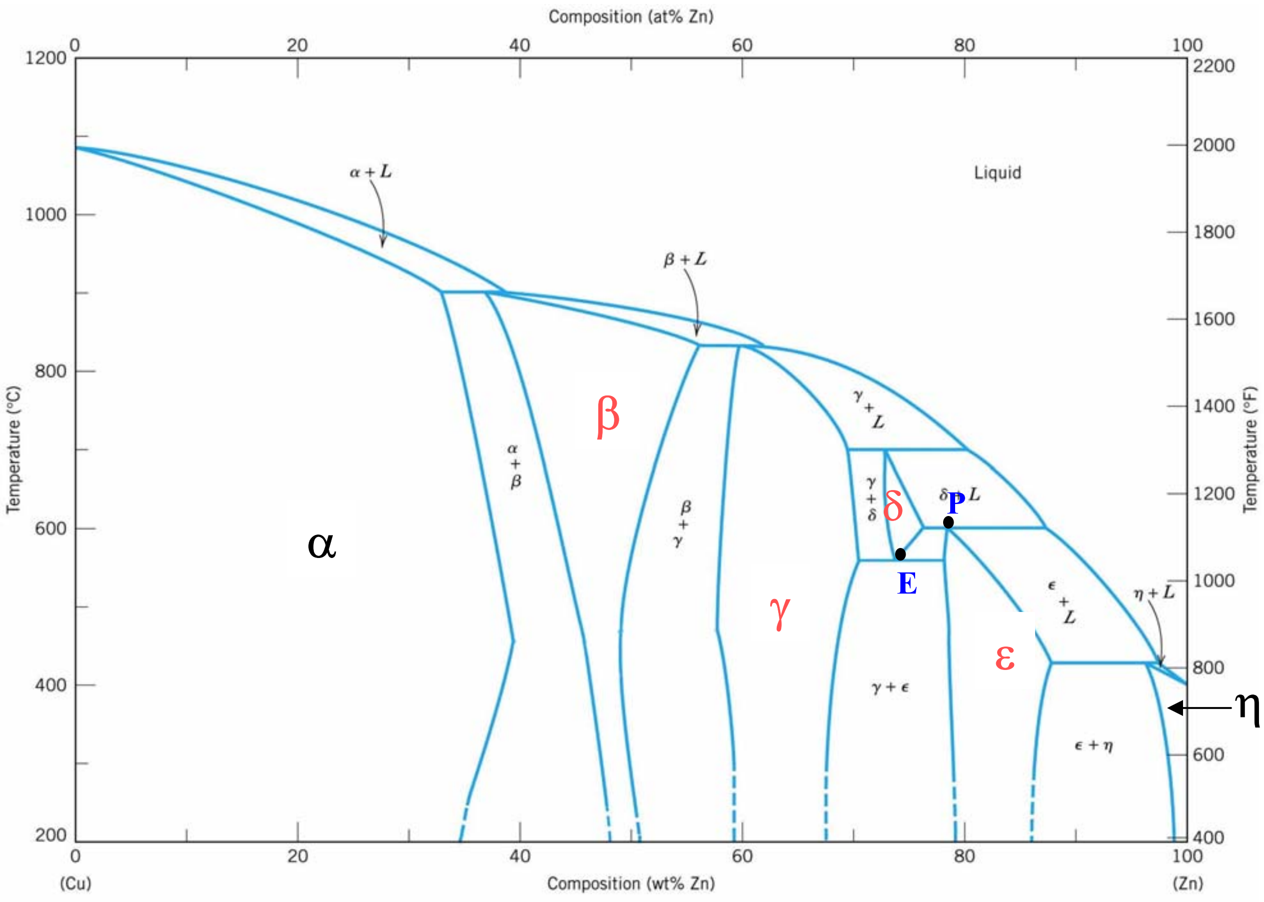
$W_\beta \approx$ 27wt%

HYPOEUTECTIC & HYPEREUTECTIC



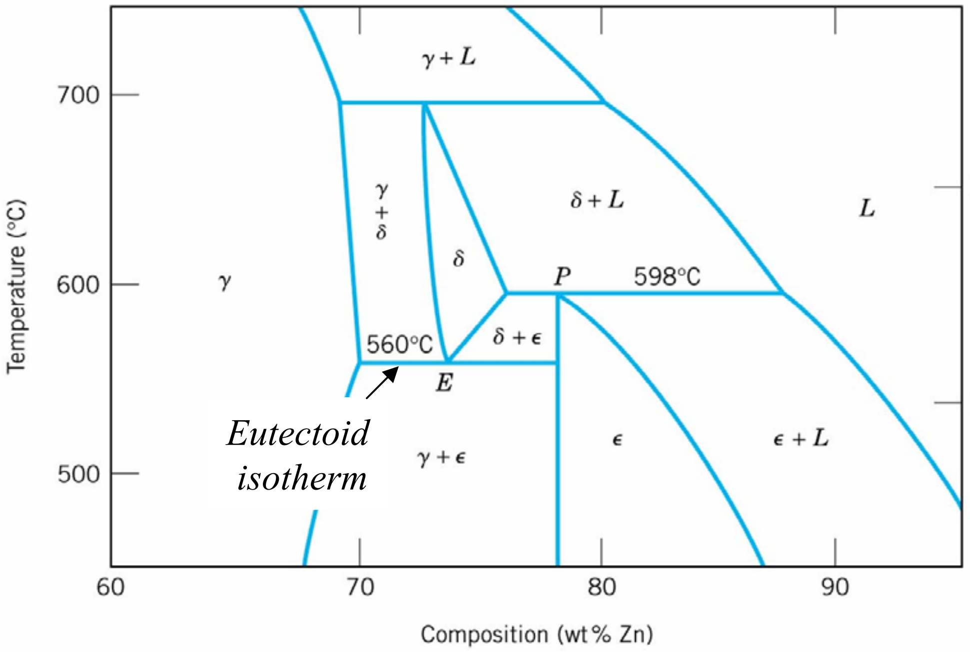
Equilibrium Diagrams with Intermediate Phases

<u>Example:</u> The Copper-Zinc System



- α and η are **terminal solid solutions**: exist near the concentration *extremities* of the phase diagram
- β,γ,ε,δ are **intermediate solid solutions** (or *intermediate phases*)
- new types (not eutectic) of ***invariant points*** (e.g. **E, P**) and corresponding reactions are shown below

Eutectoid and Peritectic Reactions



• **point E** (74 wt%Zn at 560°C): again (as in eutectic) ***three phases*** are in ***equilibrium*** (δ,γ,ε)

• but in this case upon cooling a ***solid*** phase transforms to ***two solid*** phases, so-called a ***eutectoid reaction***:

$$\delta\ (74\text{wt\%Zn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma\ (69.5\text{wt.\%Zn}) + \varepsilon\ (78.6\text{wt\%Zn})$$

•**point P** (78.6 wt%Zn at 598°C): ***three phases*** are in ***equilibrium*** (δ,L,ε)

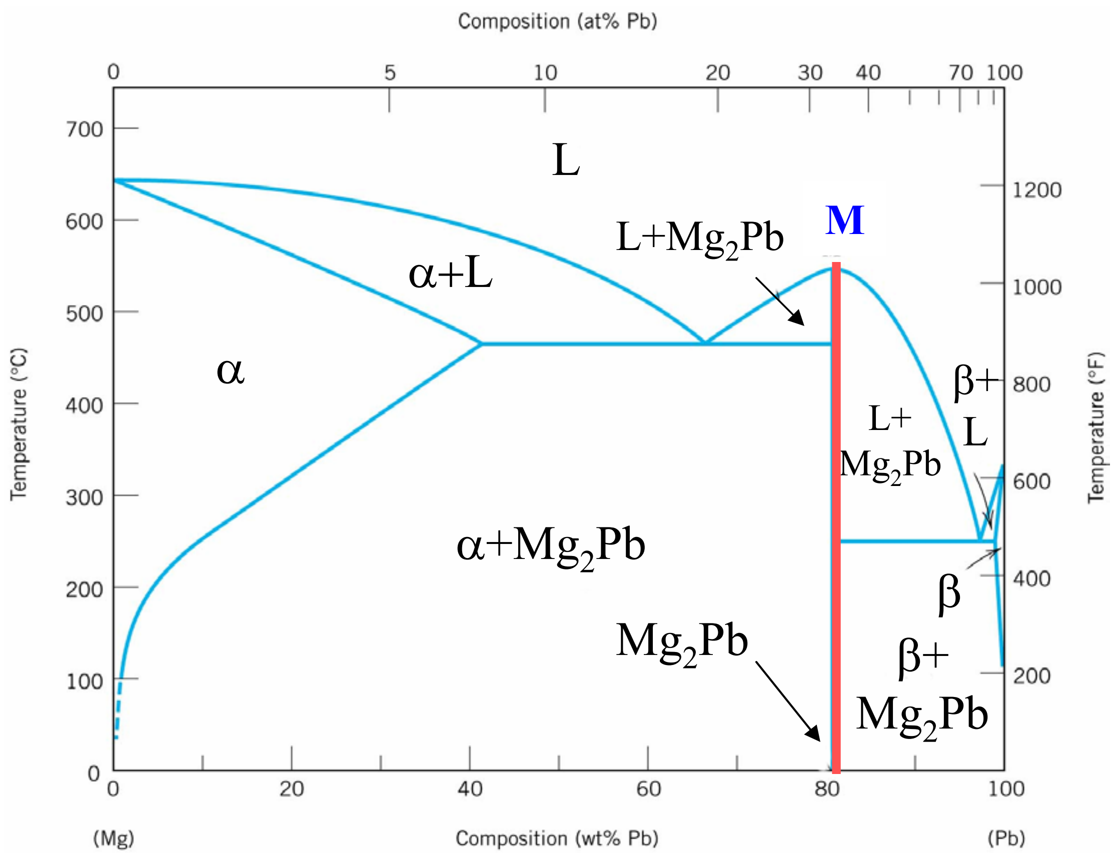
• in this case upon **heating** a ***solid*** phase transforms to liquid and another ***solid*** phases: a ***peritectic reaction***:

$$\delta\ (76\text{wt\%Zn}) + L(88\text{wt\%Zn}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \varepsilon\ (78.6\text{wt\%Zn})$$

How many peritectics do we have for copper-zinc system?

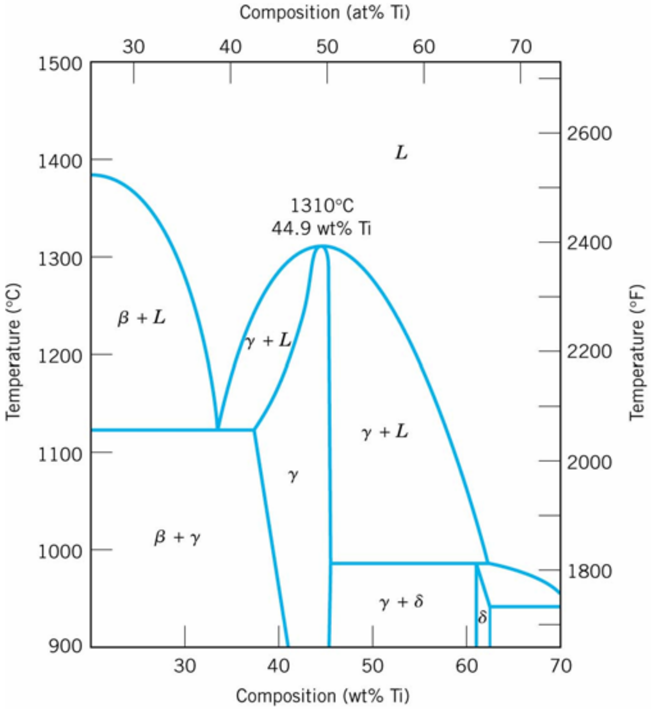
Equilibrium Diagrams with Intermediate Compounds

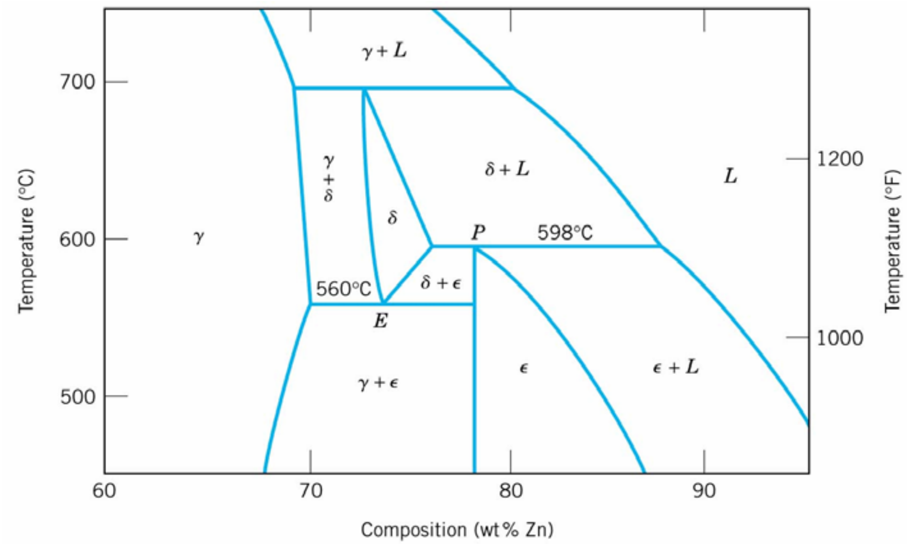
Example: Magnesium-Lead System



- Mg_2Pb is a ***intermetallic compound*** with a distinct chemical formula (not a solution)
- for this specific example, the intermediate compound exists by itself only at this precise composition (region of its existence has ***infinite width-just a line***!!)
- the phase diagram in Mg-Pb system can be thought of a ***two simple eutectic diagrams*** joined back to back, one for Mg- Mg_2Pb system and other Mg_2Pb-Pb system

Types of Phase Transformations





• γ ***solid solution*** at 1310°C and C = 44.9 wt% Ti melts without changing of the composition – ***congruent transformation***

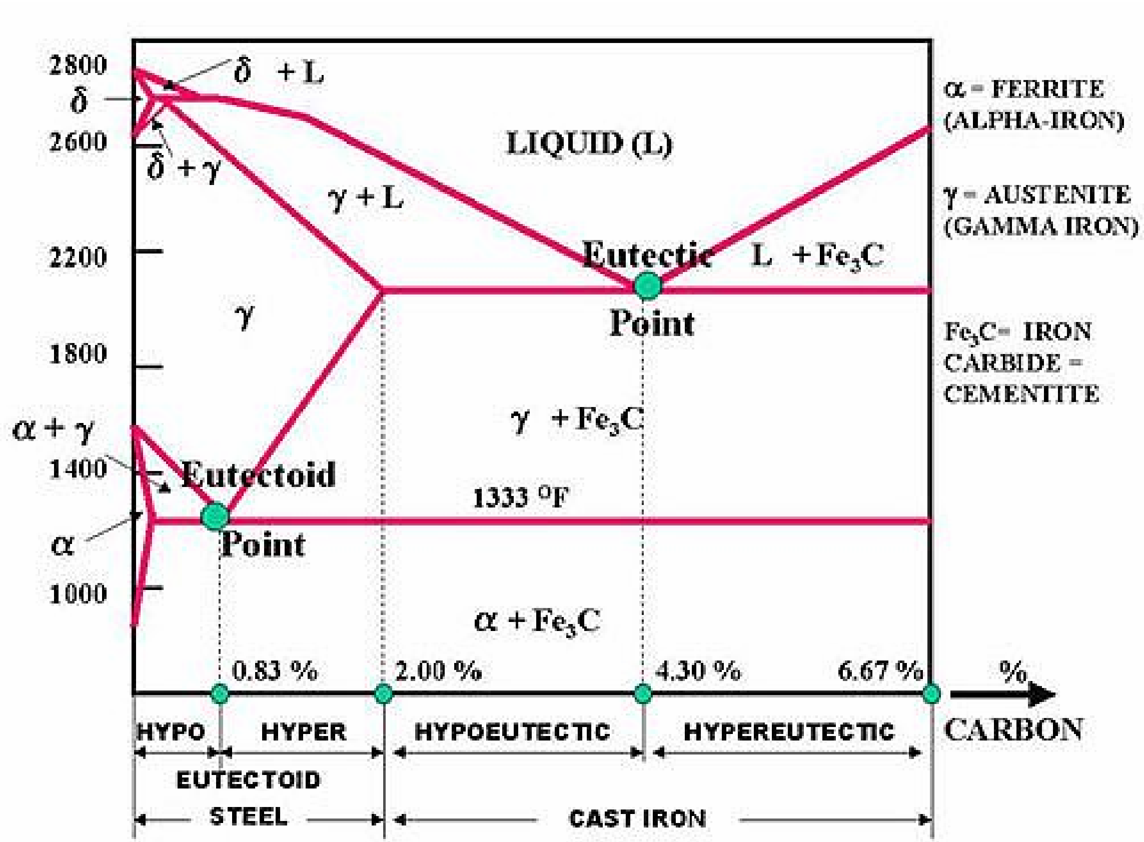
• melting of pure metals, allotropic transformations are ***congruent***

• P melting at 598°C: $\varepsilon \Rightarrow \delta + L$ (peritectic reaction) occurs with ***changing of phase*** composition – ***incongruent phase transformation***

• Eutectic, eutectoid and peritectic reactions are examples of incongruent transformations

IRON-CARBON
(Fe-C) System

IRON-CARBON (Fe-C) PHASE DIAGRAM



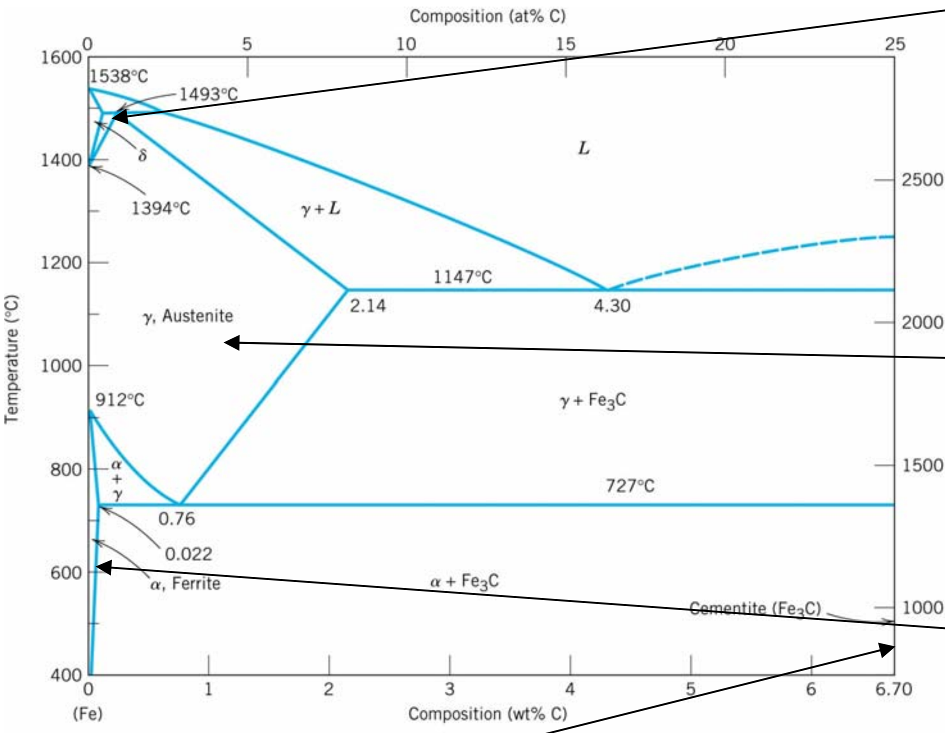
- ***Iron*** are alloys with less than 0.008 wt% of carbon
- ***Steels*** are carbon-iron alloys with carbon in the range 0.008 wt.% to2.14%.
- ***Cast irons*** contain 2.14 – 6.7wt% of carbon
- Iron and carbons combined to form ***Fe-Fe$_3$C*** at the 6.67 % C end of the diagram.
- **Eutectoid**: 0.76 wt%C, 727°C

$$\gamma \Leftrightarrow \alpha(\mathbf{0.022wt\%C}) + \mathbf{Fe_3C}$$

- **Eutectic**: 4.30 wt%C, 1147°C

$$\mathbf{L} \Leftrightarrow \gamma\ (\mathbf{2.14\ wt\%C}) + \mathbf{Fe_3C}$$

PHASES in Fe-C SYSTEM



• **δ–iron** exists between 1394°C and 1538 °C It may exist in combination with the melt to ~ 0.5 %wt C, with austenite to ~ 0.18 %wt C and in a single phase state to ~0.10 %wt C. Delta iron has the B.C.C crystal structure and is magnetic

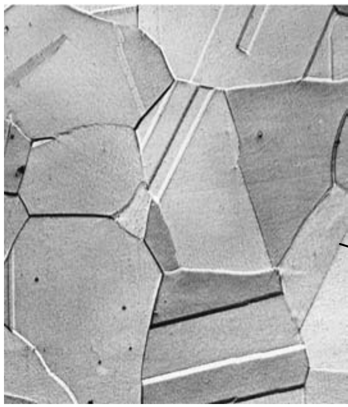
• **Austenite-** (γ) **gamma-iron:** interstitial solid solution of carbon (up to 2.14wt%) dissolved in iron with a (F.C.C) structure. Stable up to 1394 °C. Non-magnetic phase.

• **Ferrite** - (α) ***alpha -iron***, which is an interstitial solid solution of a small amount (up to 0.022wt%) of carbon dissolved in iron with a B.C.C.crystal structure. Possesses polymorphic transformation to γ–iron at 912C It is the softest structure on the iron-iron carbide diagram. Magnetic below 768°C

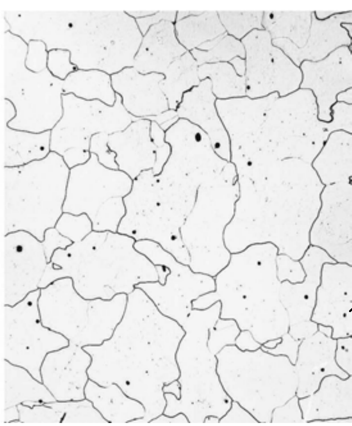
Cementite - ***iron carbide:*** chemical formula, $\boldsymbol{Fe_3C}$, contains 6.67 % wt C. It is a typical hard and brittle interstitial compound of low tensile but high compressive strength. Its crystal structure is orthorhombic. Metastable phase: at~700 °C slowly (several years) decomposes to α-iron and carbon

Steel Microstructure

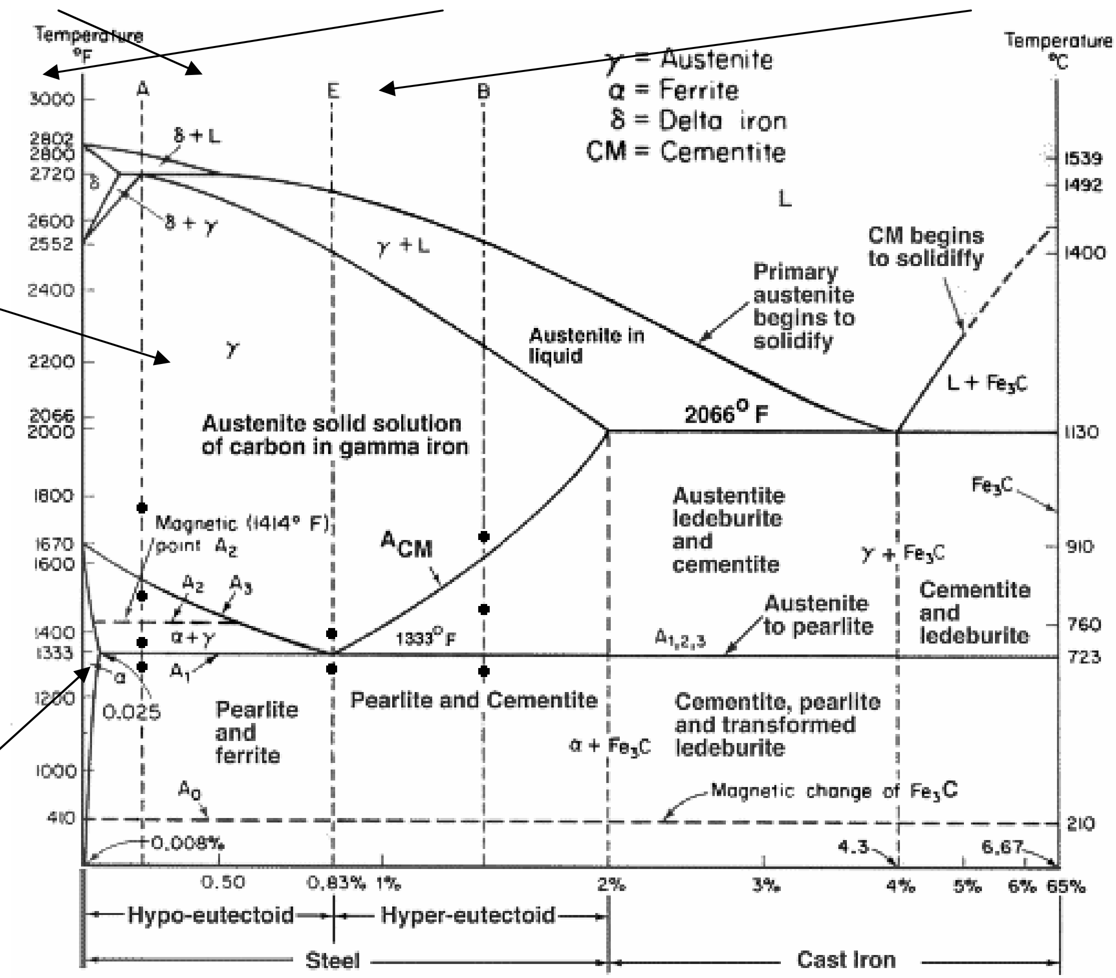
Three significant regions can be made relative to the steel portion of the diagram: the **eutectoid** E, the **hypoeutectoid** A, and the **hypereutectoid** B.



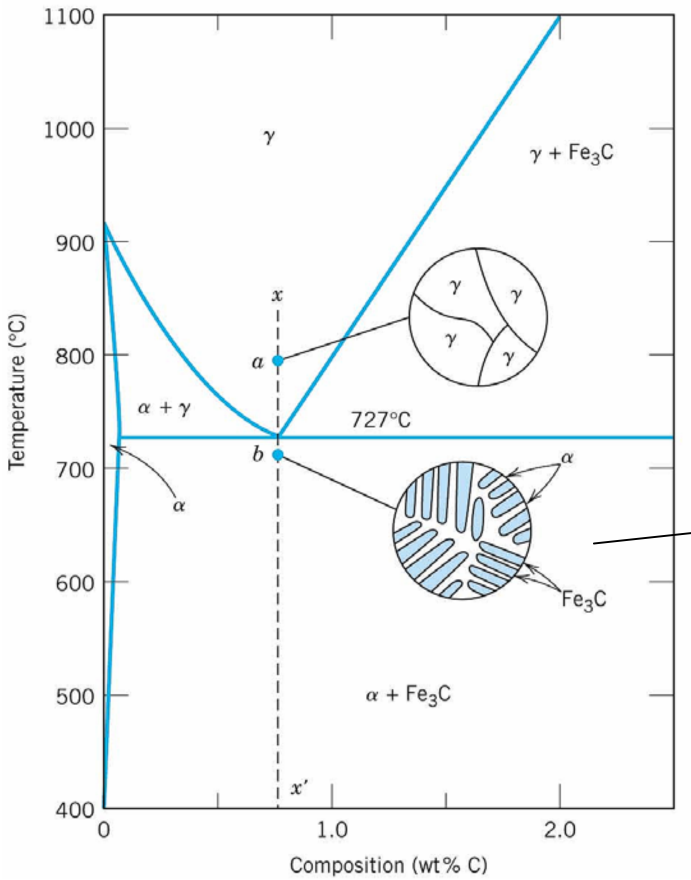
austenite



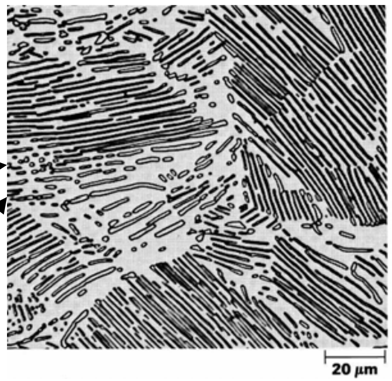
α-ferrite



Iron-Carbon Alloy:Eutectoid Composition

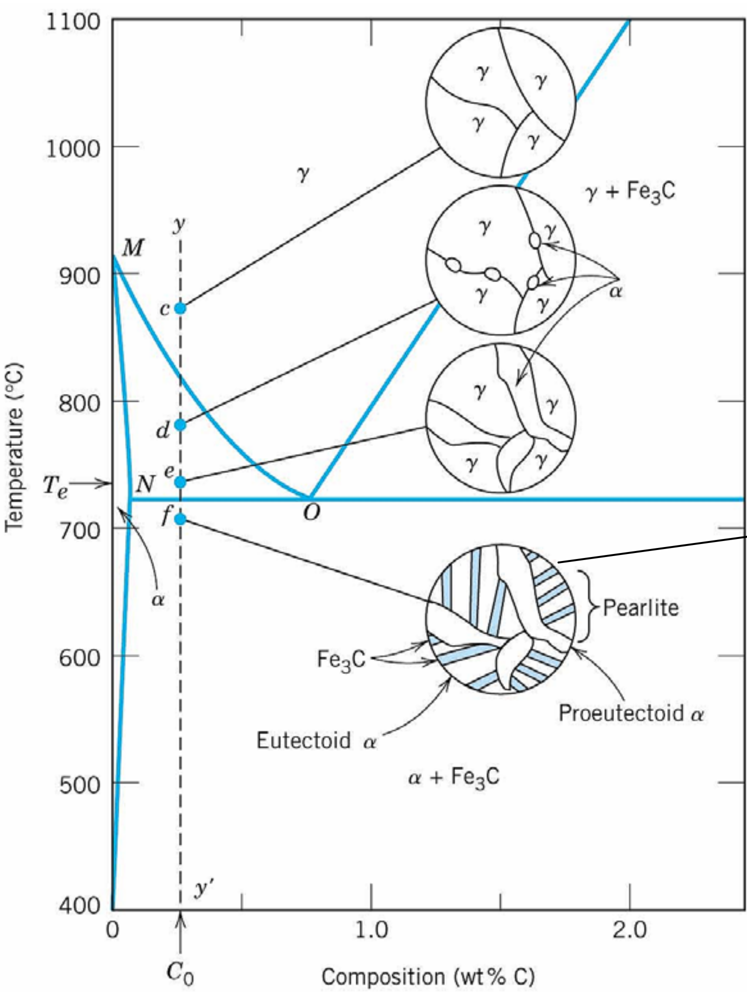


- **Eutectoid invariant point**: 0.76 wt%C, 727°C
  Eutectoid Reaction:
  γ ⇔ α(0.022wt%C)+Fe_3C



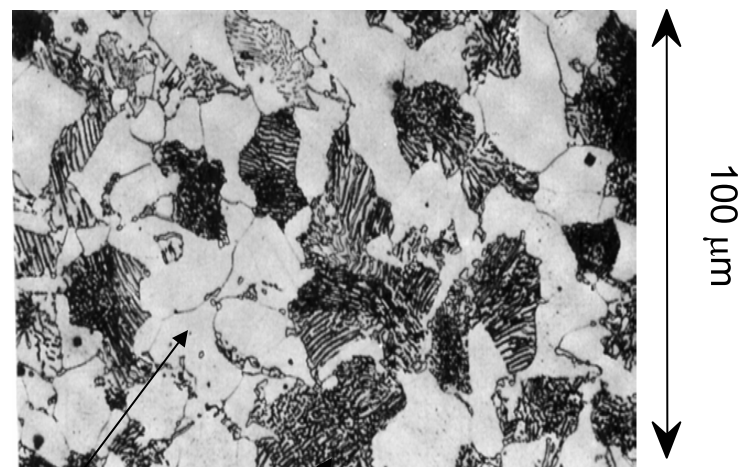
- **Pearlite (<u>α + Fe_3C</u>):** eutectoid mixture containing 0.76 %wt C and is formed at 727 C under slow cooling. It is very fine plate-like or lamellar mixture of ferrite (0.022 wt%C) and cementite (6.7 wt% C). The structure of pearlite includes a white matrix (ferritic background) which includes thin plates of cementite.

Iron-Carbon Alloy: Hypo-eutectoid Composition



•Hypo-eutectoid compositions:
0.022-0.76 wt% C
(less than eutectoid)

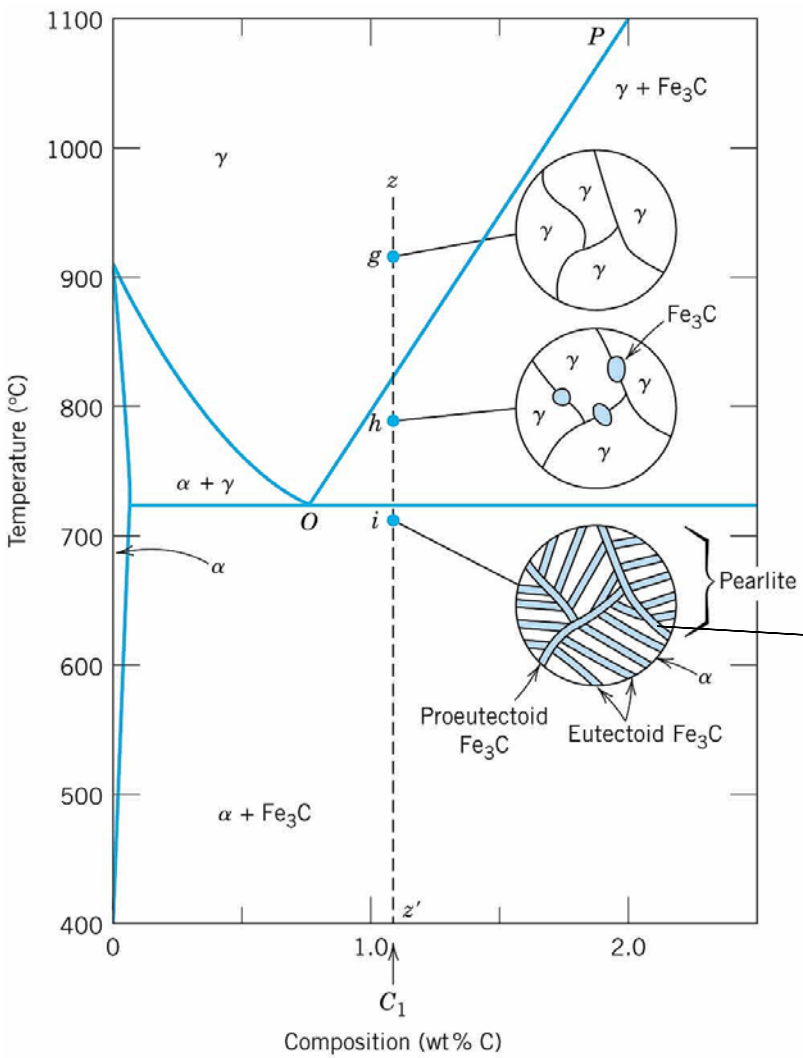
<u>Hypo-eutectoid Steel</u>



Pro-eutectoid α
(before eutectoid)

Pearlite

Iron-Carbon Alloy: Hyper-eutectoid Composition



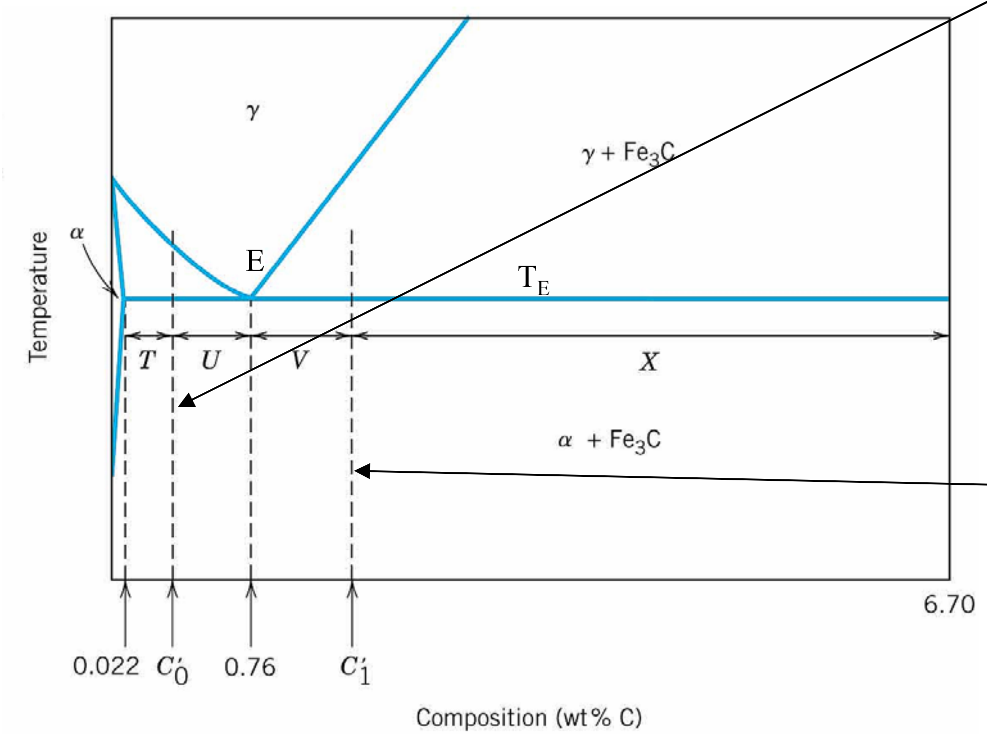
•**Hypo-eutectoid compositions**: 0.76 – 2.14 wt% C (more than eutectoid)

<u>Hyper-eutectoid Steel</u>

Pro-eutectoid Fe_3C (before eutectoid)

Pearlite

Computation of the Relative Amounts of Different Phases in $Fe\text{-}Fe_3C$ System



- **<u>Hypo-eutectoid</u>** <u>composition</u>:

  $C'_o \,;\, T < T_E$

- Phases: **α-Fe** and **pearlite**
- The fraction of pro-eutectoid **α-Fe**:

$$W_\alpha = \frac{U}{T+U} \approx \frac{0.76 - C_o'}{0.76 - 0.02} = \frac{0.76 - C_o'}{0.74}$$

- The fraction of pearlite:

$$W_\alpha = \frac{T}{T+U} \approx \frac{C_o' - 0.02}{0.76 - 0.02} = \frac{C_o' - 0.02}{0.74}$$

- **<u>Hyper-eutectoid</u>** <u>composition</u>:

  $C'_1 \,;\, T < T_E$

- Phases: **Fe_3C** and **pearlite**
- The fraction of pro-eutectoid **Fe_3C**:

$$W_{Fe3C} = \frac{V}{V+X} = \frac{C_1' - 0.76}{6.7 - 0.76} = \frac{C_1' - 0.76}{5.94}$$

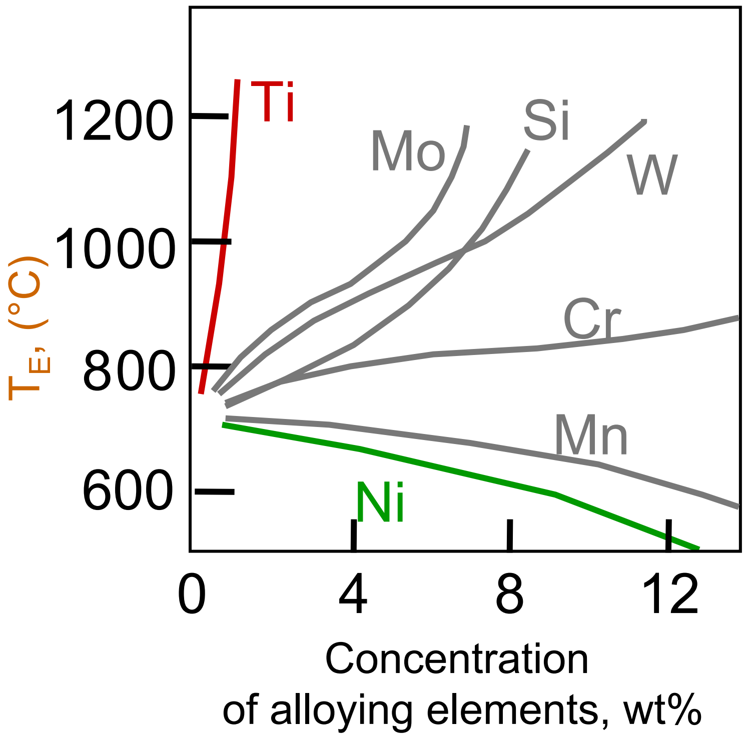
- The fraction of pearlite:

$$W_{Fe3C} = \frac{X}{V+X} = \frac{6.70 - C_1'}{6.7 - 0.76} = \frac{6.70 - C_1'}{5.94}$$

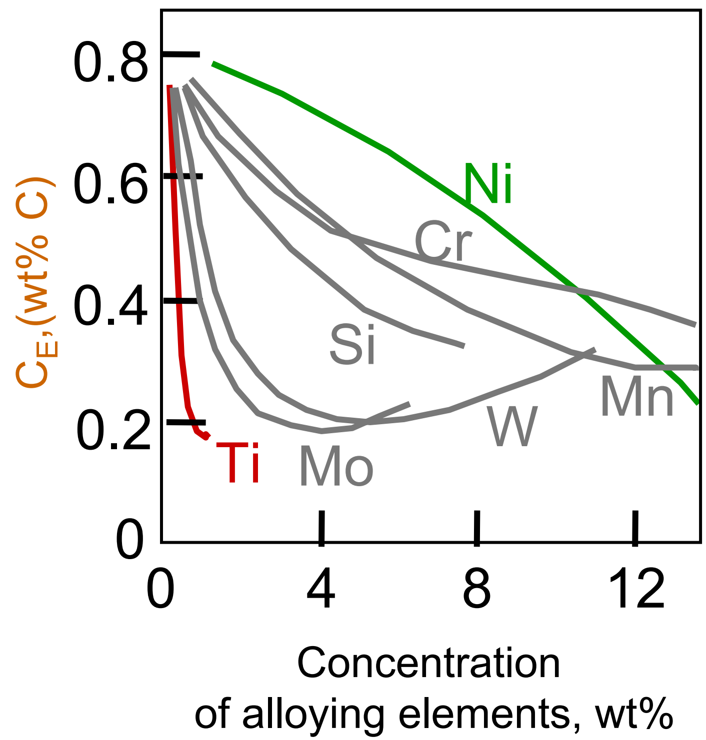
ALLOYING STEEL WITH MORE ELEMENTS

In general, alloying elements that added to improve some specific steel properties, also ***effect*** the positions of ***phase boundaries*** and regions shape on the phase diagram

- $T_{eutectoid}$ changes:



- $C_{eutectoid}$ changes:



Example:addition of ~1 wt% of Ti increases T_E almost twice!!

IRON-CARBON (Fe-C) PHASE DIAGRAM

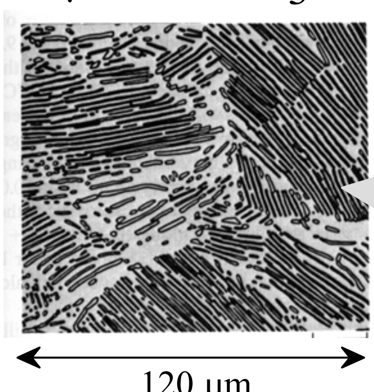
- 2 important points

  -Eutectic (A):

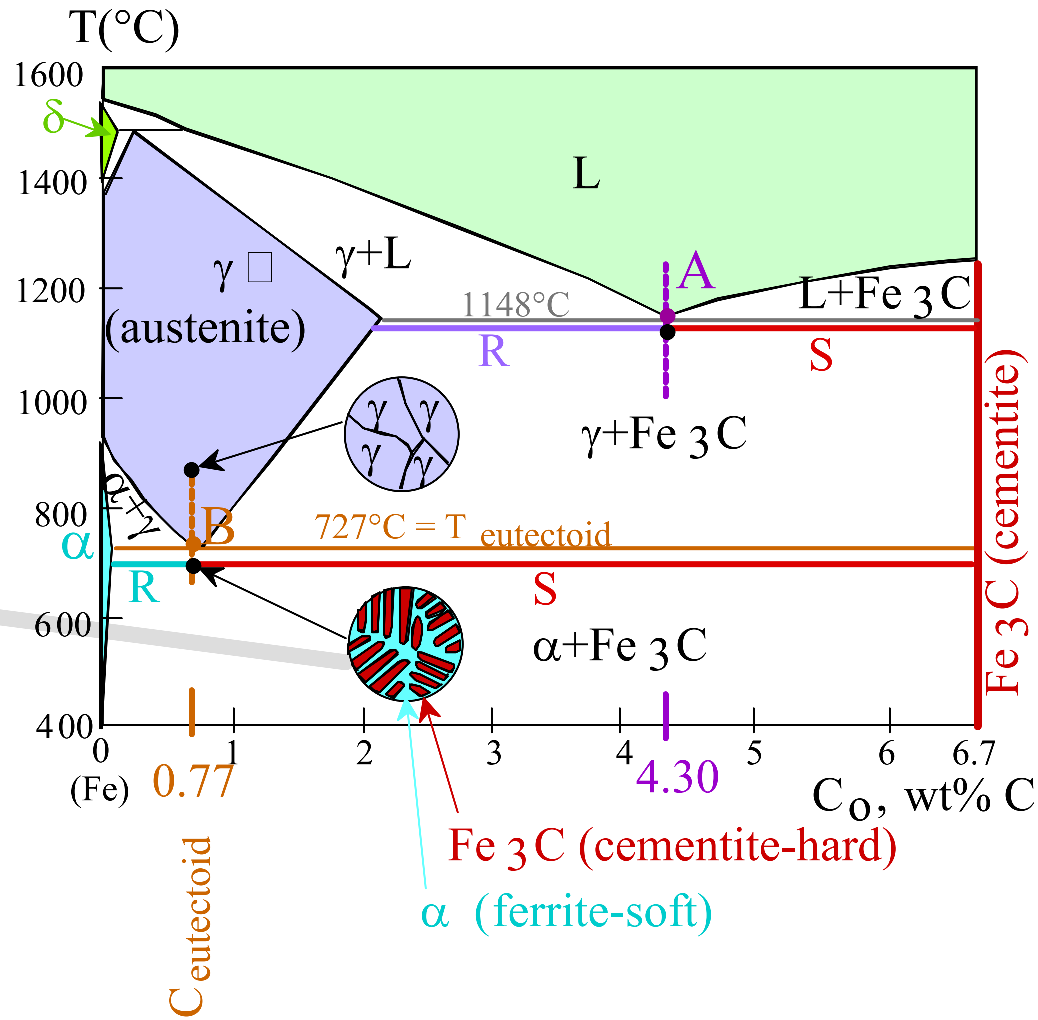
  $L \Rightarrow \gamma + Fe_3C$

  -Eutectoid (B):

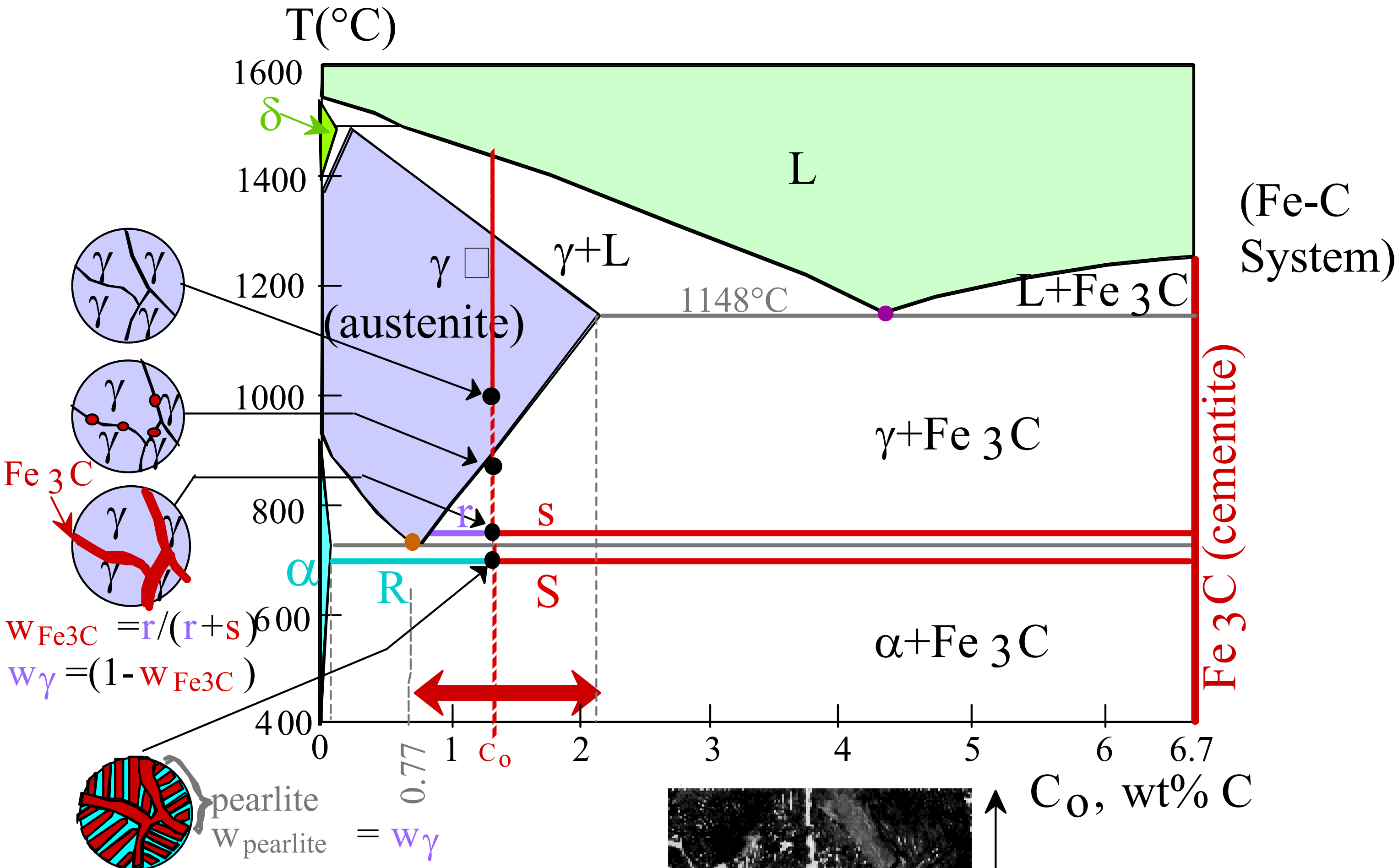
  $\gamma \Rightarrow \alpha + Fe_3C$



Result: Pearlite = alternating layers of α and Fe_3C phases.



HYPEREUTECTOID STEEL



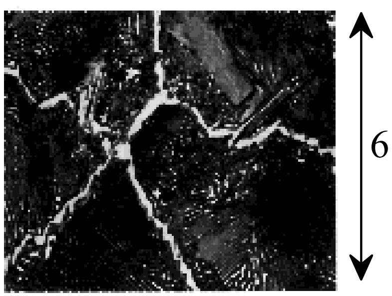
$w_{Fe3C} = r/(r+s)$

$w_{\gamma} = (1 - w_{Fe3C})$

$w_{pearlite} = w_{\gamma}$

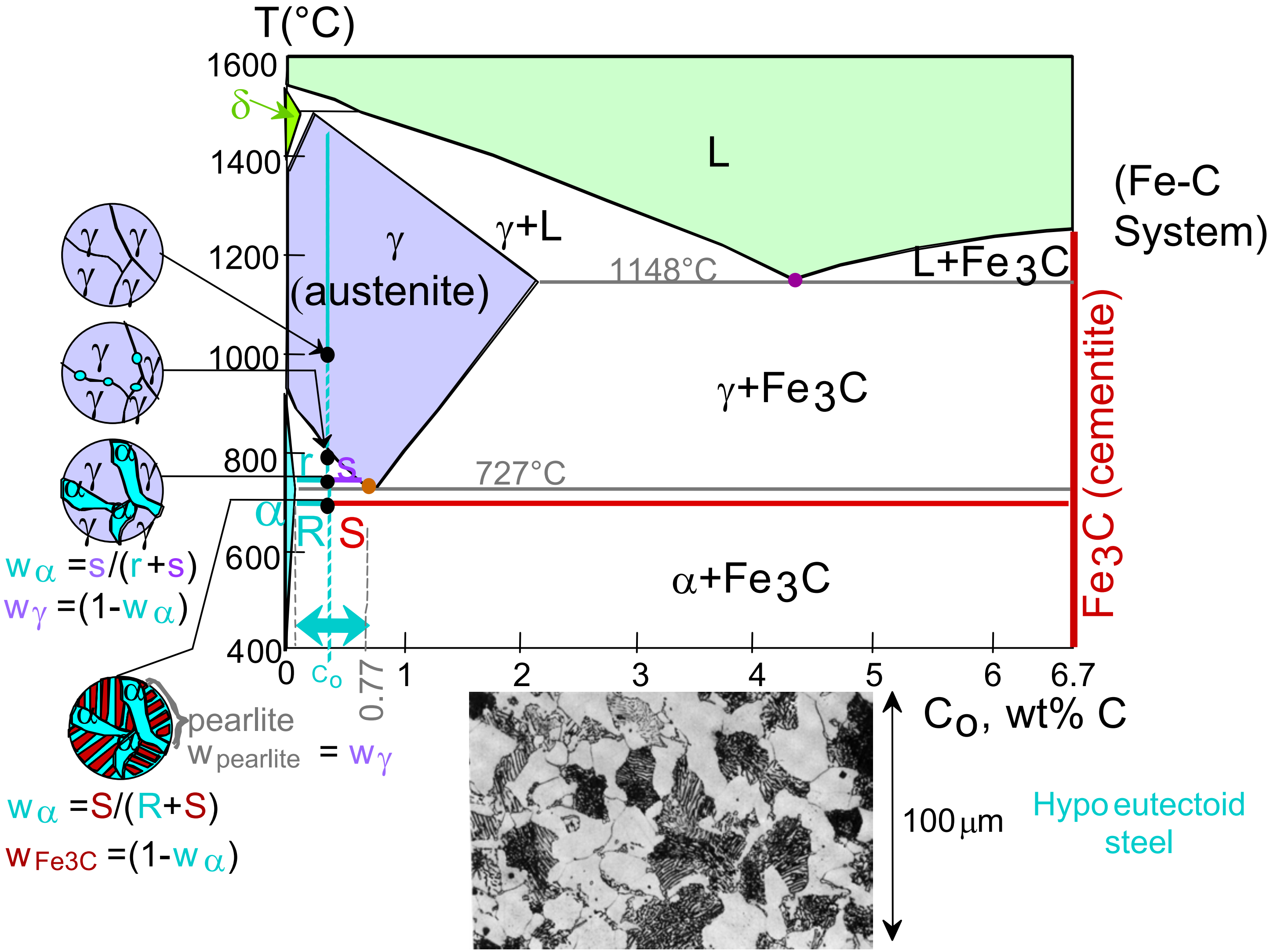
$w_{\alpha} = S/(R+S)$

$w_{Fe3C} = (1 - w_{\alpha})$

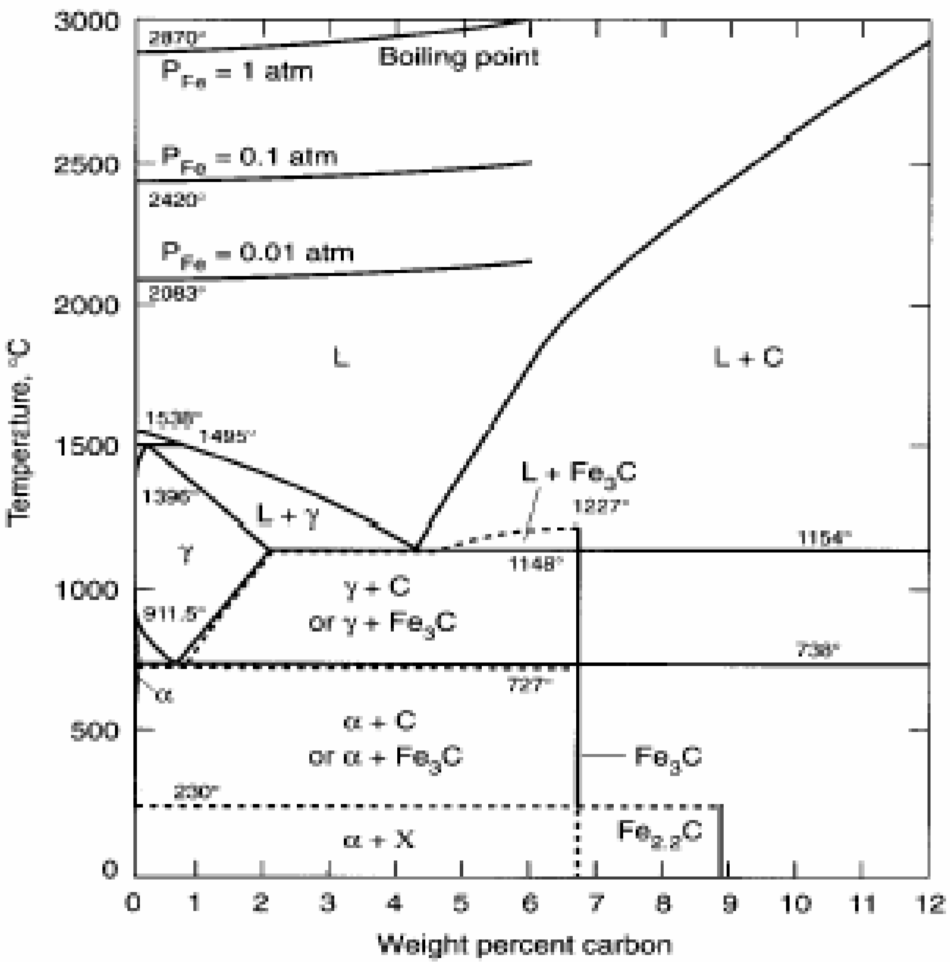


Hypereutectoid steel

HYPOEUTECTOID STEEL



IRON-CARBON (Fe-C) PHASE DIAGRAM



• Note that this diagram has both stable and metastable features. For example, the stable phase in equilibrium with iron is carbon, but since it is easier to nucleate Fe_3C, it is the phase that is usually found in equilibrium with iron.

• The $Fe_{2.2}C$ phase, or Hagg carbide is found in purified iron which has been carburized below 350°C.

SUMMARY

- Phase diagrams are useful tools to determine:

  --the number and types of phases,
  --the wt% of each phase,
  --and the composition of each phase

  for a given T and composition of the system.

- Binary eutectics and binary eutectoids allow for a range of microstructures with different properties