Chapter 4. Phase Diagram (Building and Alloys)

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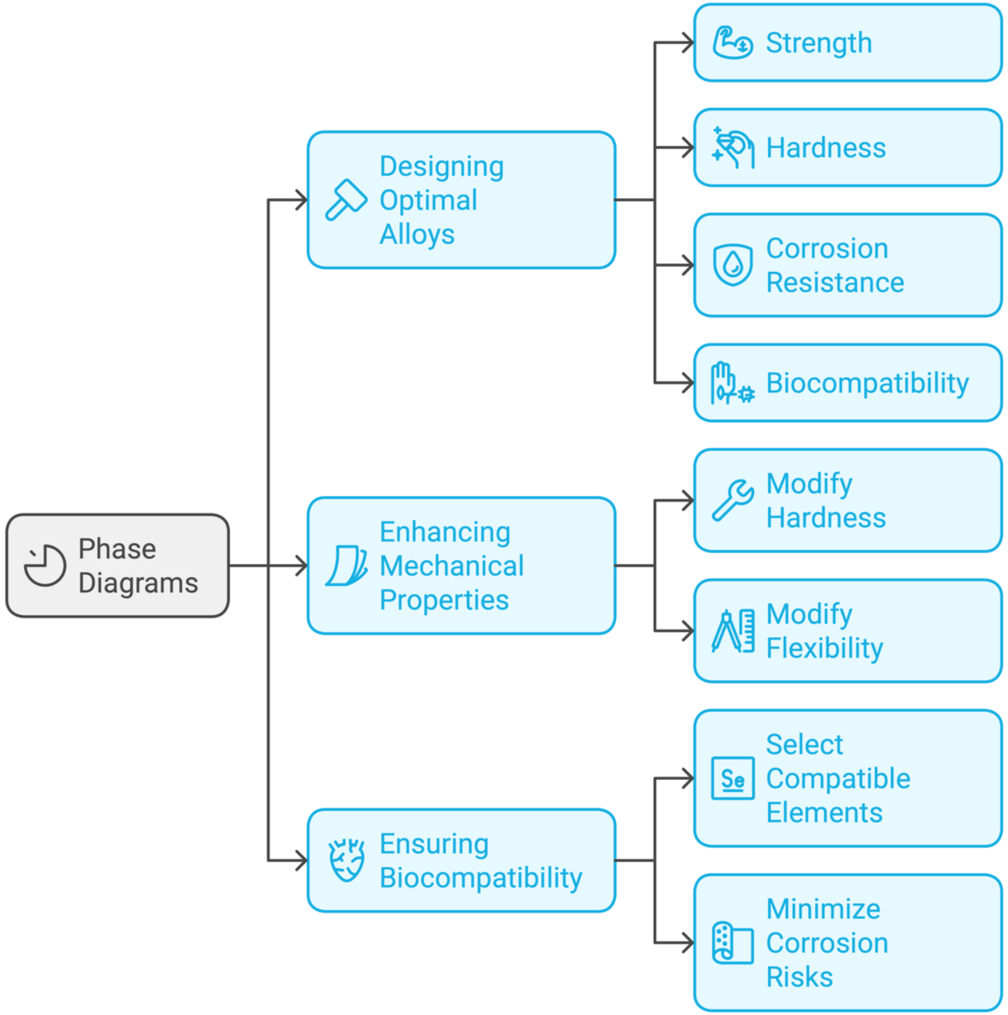
Introduction to Phase Diagrams

- Understanding phase diagrams is a fundamental tool that allows us to analyze and design materials that meet the requirements of medical applications such as bone implants, surgical instruments, and prosthetic devices.
- Phase diagrams are graphical representations of the states of a material (solid, liquid, gas) and its crystalline structure under specific conditions of temperature, pressure, and component composition.
- In biomaterials science, phase diagrams help us determine the optimal ratios of different elements to achieve the desired mechanical and chemical properties.
- **Phase** – a portion of a system that has uniform physical **and** chemical characteristics. Two distinct phases in a system have distinct physical and/or chemical characteristics (e.g. water and ice, water and oil) and are separated from each other by definite **phase boundaries**. 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.

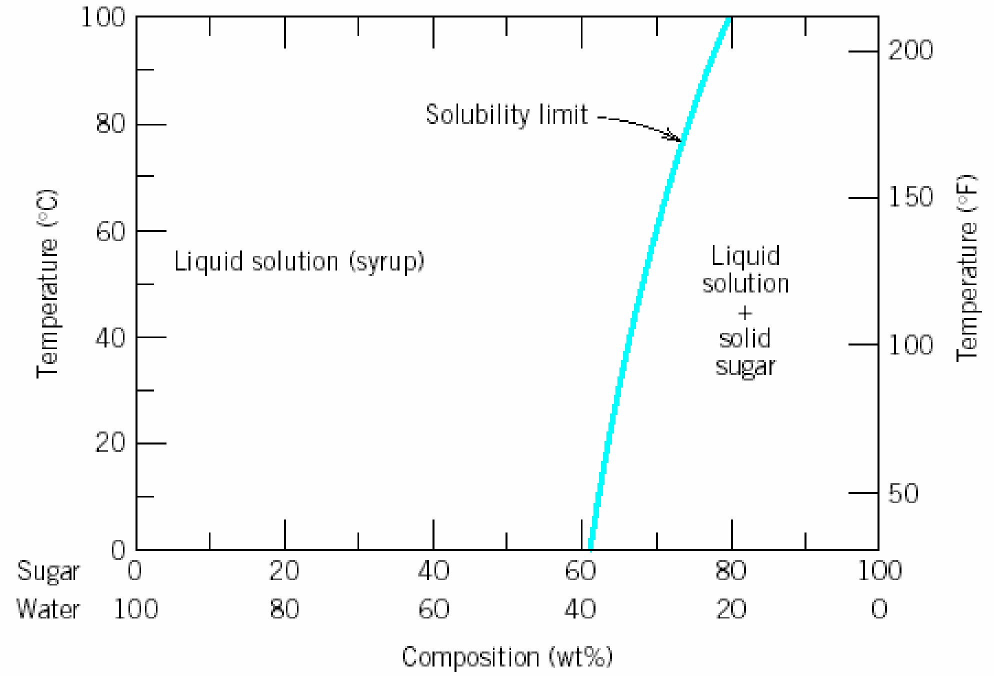
Introduction to Phase Diagrams

- **Relevance to Biomaterials:**
- Many biomaterials used in medical devices, such as titanium alloys for implants or stainless steel for surgical tools, are metallic alloys whose properties can be optimized using phase diagrams.
- These alloys must be biocompatible, corrosion-resistant, and capable of enduring mechanical stresses in the body. The phase composition and transitions within the material significantly affect these properties.
- **Practical Examples:**
- **Titanium Alloys:** Widely used in bone implants due to their high corrosion resistance and lightweight nature. The phase diagram helps determine the appropriate ratios of titanium and other elements like aluminum and vanadium to achieve an optimal balance between strength and flexibility.
- **Stainless Steel:** Employed in surgical instruments and medical devices because of its excellent corrosion resistance and sterilization ability. The phase diagram shows how to balance elements like chromium and nickel to enhance the desired properties.



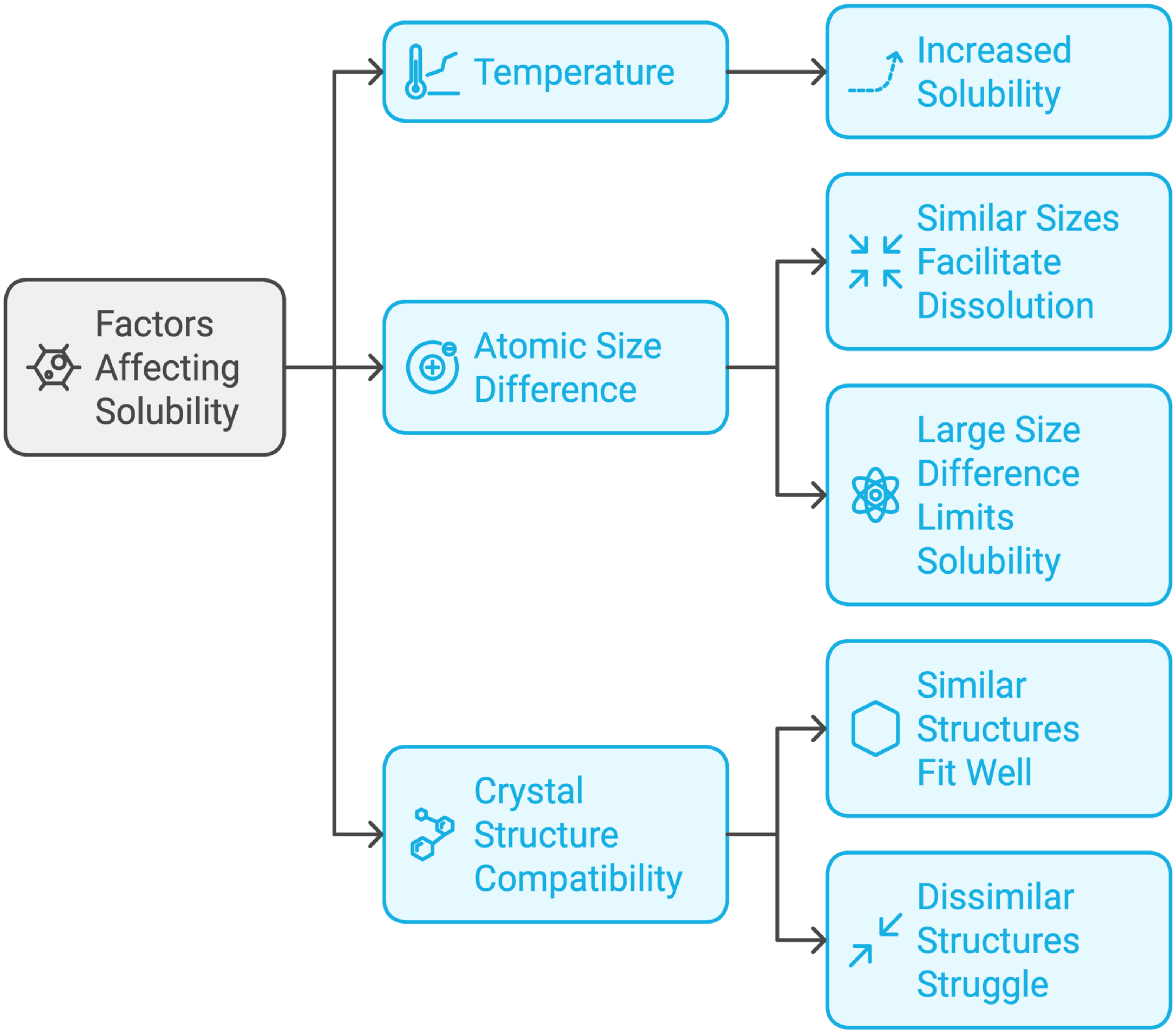
Solubility Limit

- **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).
- In alloys and materials science, the solubility limit is an important concept because it determines how much of one component can be incorporated into the other without forming a separate phase.
- The same concepts apply to solid phases: Titanium and aluminum can form solid solutions. However, titanium can only dissolve about 7% aluminum at room temperature to form a solid solution. After this concentration, the alloy will start to form different phases such as the **alpha** phase (Ti-rich) and the **beta** phase (Al-rich).



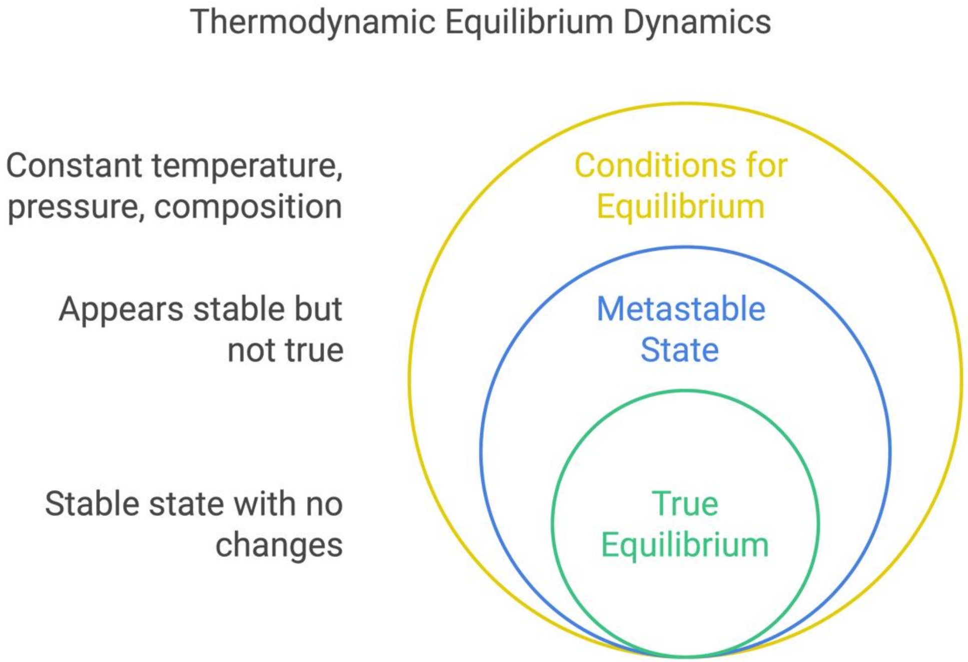
A **solid solution** is a homogeneous crystalline phase that contains two or more species of atoms or ions. In this mixture, the atoms of the solute (minor component) are incorporated into the crystal lattice of the solvent (major component) without altering the overall crystal structure. The resulting material maintains a single-phase structure where the solute atoms are distributed uniformly within the solvent matrix.

Solubility Limit



Equilibrium and Metastable States

- A system is in equilibrium when temperature, pressure, and composition remain constant, resulting in stability over time.
- Equilibrium is the state that is achieved given *sufficient* time. But the time to achieve equilibrium may be very long that a state along the path to the equilibrium may *appear* to be stable. This is called a **metastable state**.
- The equilibrium state of a material is the most stable state it can reach under a given set of conditions (e.g., temperature, pressure, composition). In equilibrium, the material has the lowest possible energy and no net change occurs over time.
- **Phase Equilibrium**: For alloys and materials, the equilibrium phase diagram shows the phases (solid, liquid, etc.) that are stable at different temperatures and compositions.
- **Example:**
- In a **pure substance** like water, at 100°C and 1 atm pressure, the equilibrium state is liquid water. At higher temperatures, water may vaporize to steam, which is also an equilibrium phase under the right conditions.



Types of Phase Diagrams

1- Binary Phase Diagrams:

- These diagrams describe the phase behavior of a system with two components (e.g., an alloy composed of titanium and aluminum).
- They show how the phases (solid, liquid, solid solution) change with temperature and composition.
- Real materials are almost always mixtures of different elements rather than pure substances: in addition to T and P, **composition** is also a variable.

a) Binary Isomorphous Systems (I):

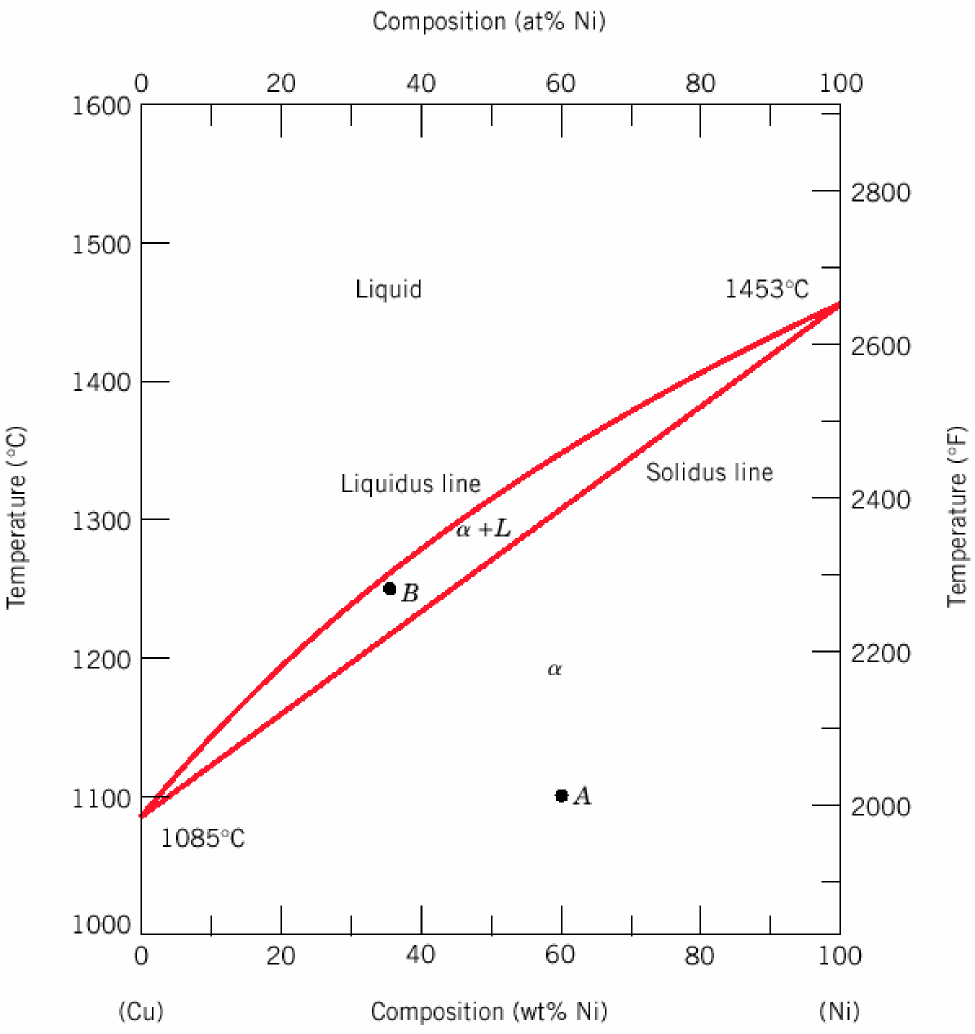
- Isomorphous system - complete solid solubility of the two components (both in the liquid and solid phases).

➢ **Three phase regions can be identified on the phase diagram:**

- Liquid (L) , solid + liquid (α +L), solid (α)
- **The Liquidus** line separates liquid from liquid + solid
- **Solidus** line separates solid from liquid + solid

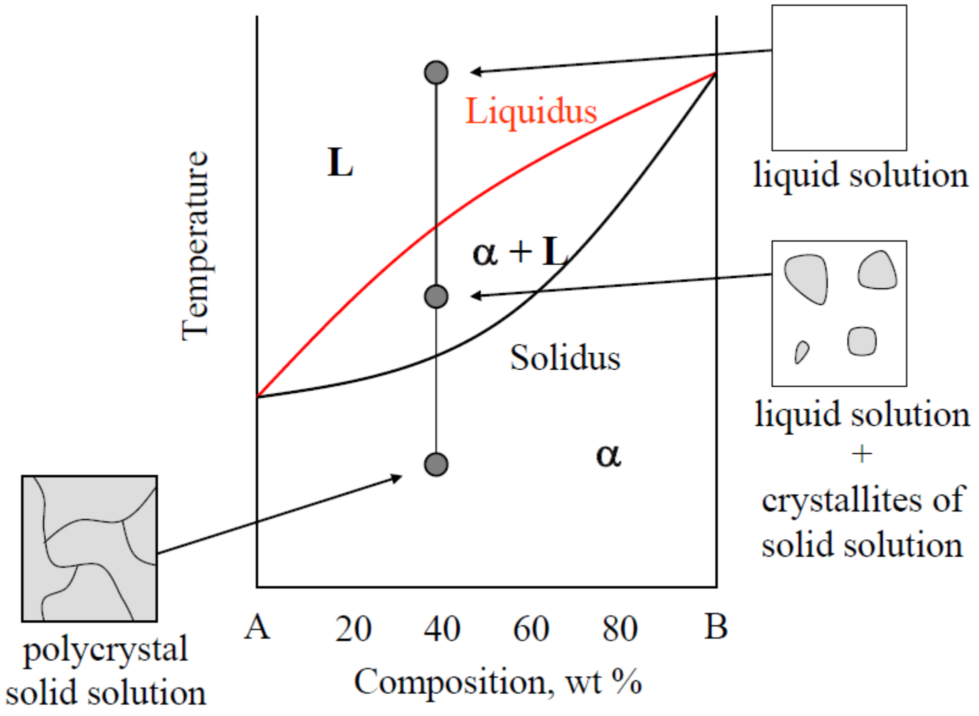
❖ In a one-component system, melting occurs at a well-defined melting temperature.

❖ In multi-component systems, melting occurs over the range of temperatures between the solidus and liquidus lines.



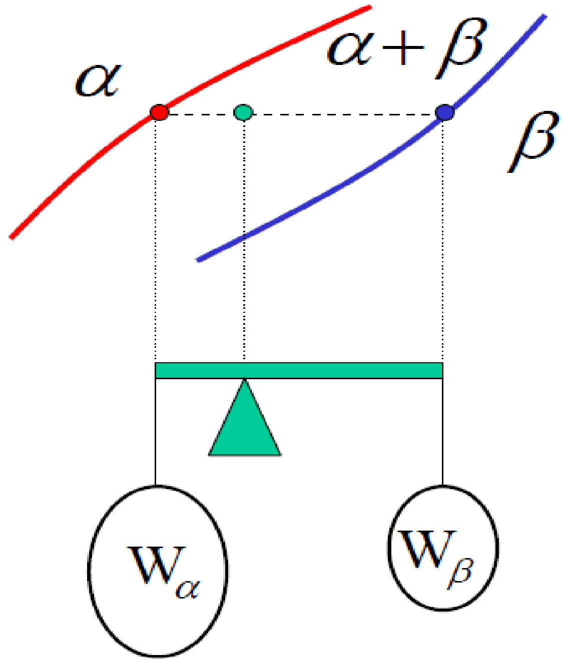
Types of Phase Diagrams

- 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



The lever rule:

- *Finding the amounts of phases in a two-phase region:*
- 1. Locate composition and temperature in diagram
- 2. In two-phase region draw the tie line or isotherm
- 3. Fraction of a phase is determined by taking the length of the tie line to the phase boundary for the other phase and dividing it by the total length of the tie line



Derivation of the lever rule:

1) All material must be in one phase or the other:

$W\alpha + WL = 1$

2) Mass of a component that is present in both phases equal to the mass of the component in one phase + mass of the component in the second phase:

$W\alpha C\alpha + WLCL = Co$

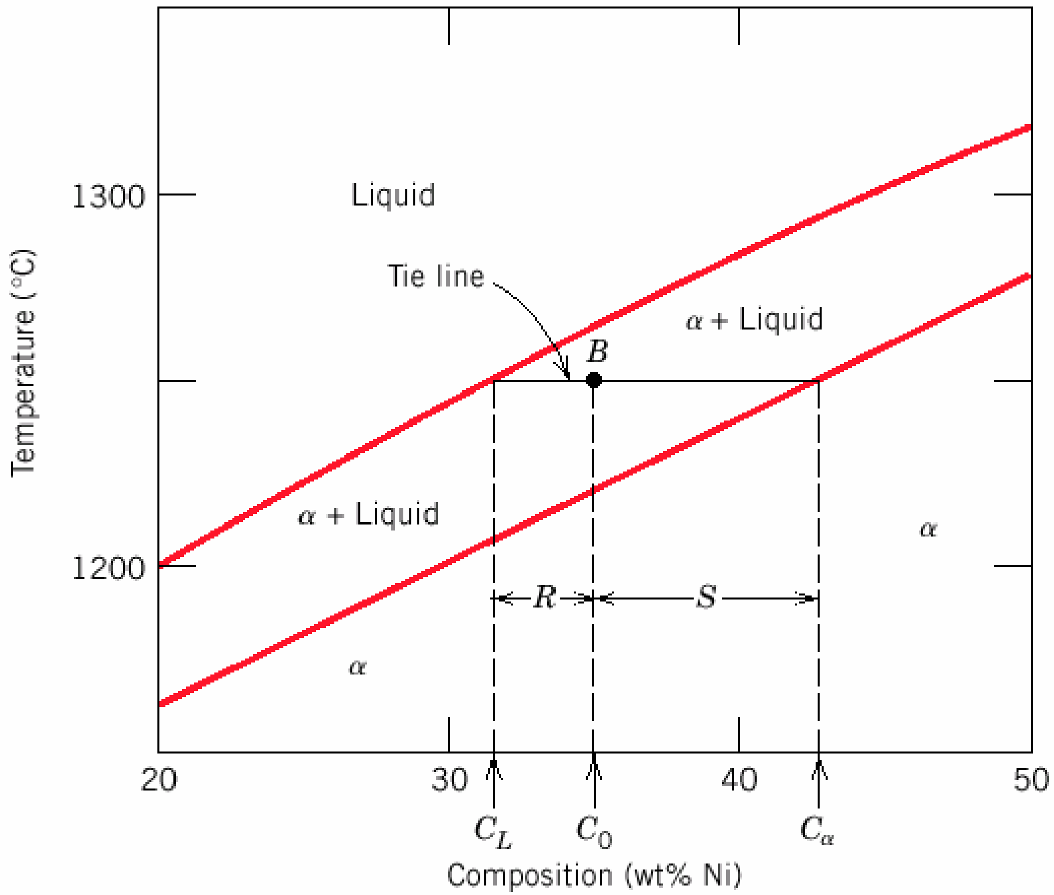
3) Solution of these equations gives us the lever rule.

$WL = (C\alpha - Co) / (C\alpha - CL)$

$W\alpha = (Co - CL) / (C\alpha - CL)$

Phase compositions and amounts. An example:

- C_o = 35 wt. %, C_L = 31.5 wt. %, C_α = 42.5 wt. %
- *Mass fractions:*
- $W_L = S / (R+S) = (C_\alpha - C_o) / (C_\alpha - C_L) = 0.68$
- $W_\alpha = R / (R+S) = (C_o - C_L) / (C_\alpha - C_L) = 0.32$

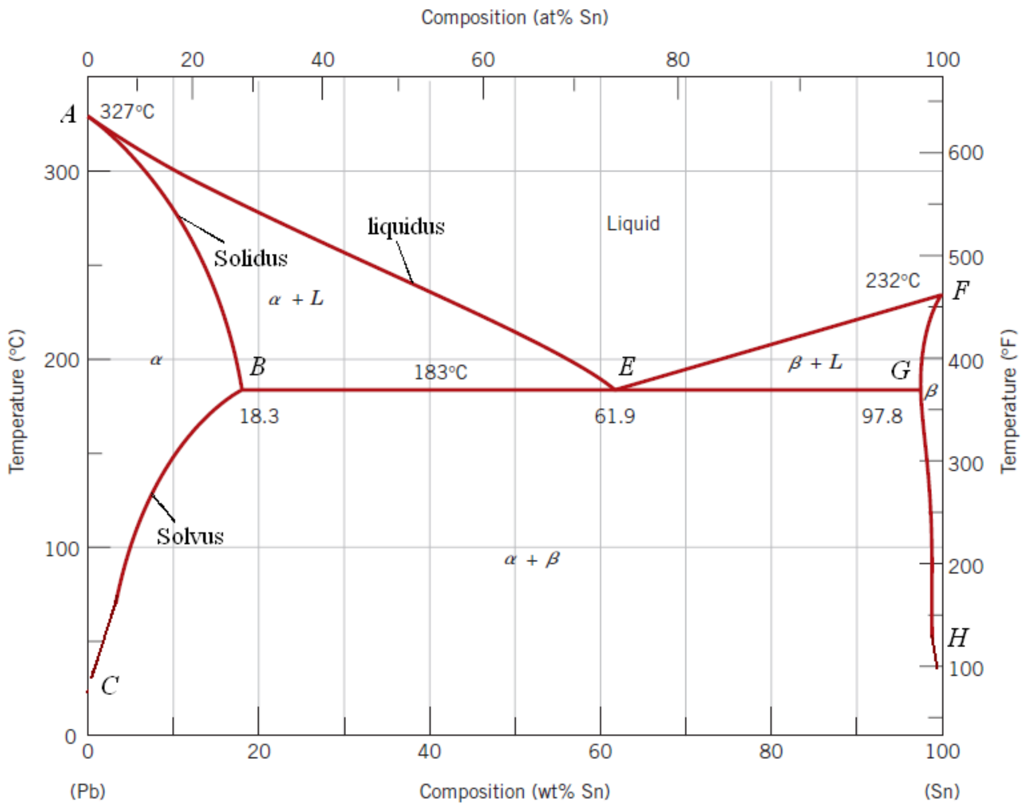


Binary Eutectic Systems with limited solubility:

- Three single-phase regions (α - solid solution of Sn in Pb matrix, β = solid solution of Pb in Sn matrix, L - liquid)
- Three two-phase regions (α + L, β +L, α + β)
- **The Solvus** line separates one solid solution from a mixture of solid solutions.
- **The Solvus line shows a limit of solubility**
- **Eutectic or invariant point** - Point E is called the **eutectic point, and the composition of** 61.9 wt% Sn with 38.1 wt% Pb is the eutectic mixture. Point E is designated by the composition CE and temperature TE .
- The reaction

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

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



A **eutectic point** is point in a binary phase diagram (a diagram with two components) where a liquid phase transforms into two solid phases upon cooling.

Binary Eutectic Systems with limited solubility:

- **Example 1:** For a 40 wt% Sn–60 wt% Pb alloy at 150C, **(a)** what phase(s) is (are) present? **(b)** What is (are) the composition(s) of the phase(s)? **(c)** What is (are) the relative amount of the phase(s) in terms of mass fraction?

Solution

(a) point B in Figure within the region $\alpha + \beta$, both α and β phases will coexist.

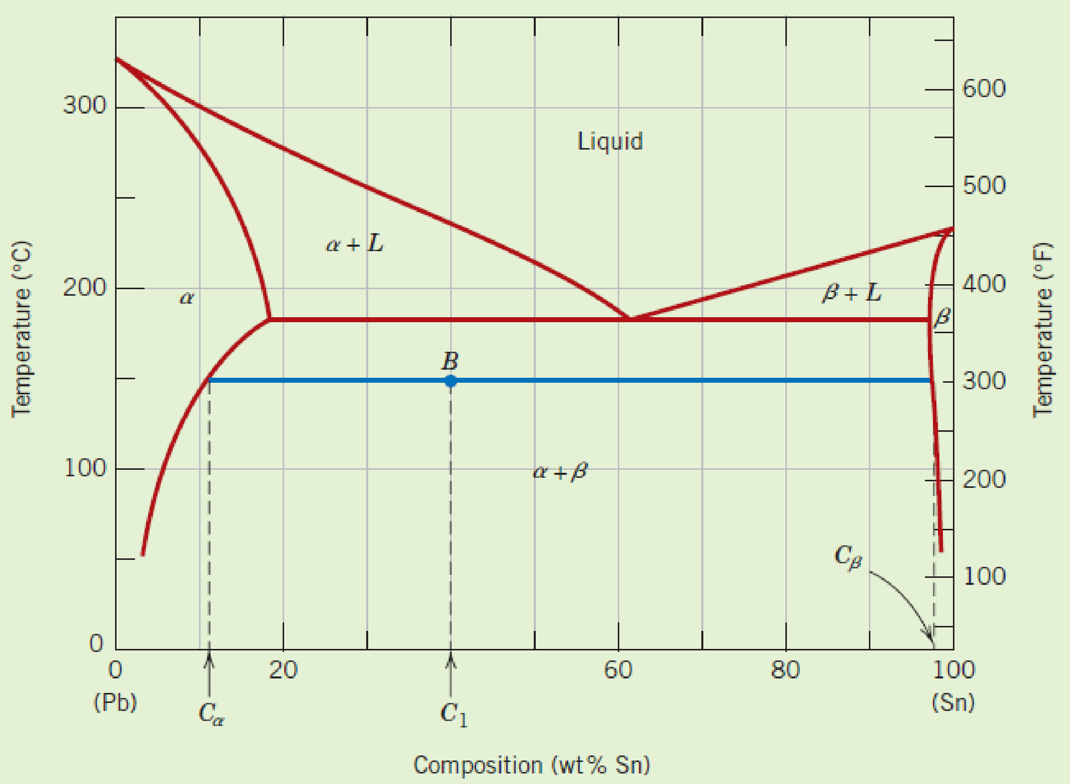
(b) C_α: 11 wt% Sn–89 wt% Pb

C_β: 98 wt% Sn–2 wt% Pb

(c) Employ the lever rule. If C_1 denotes the overall alloy composition:

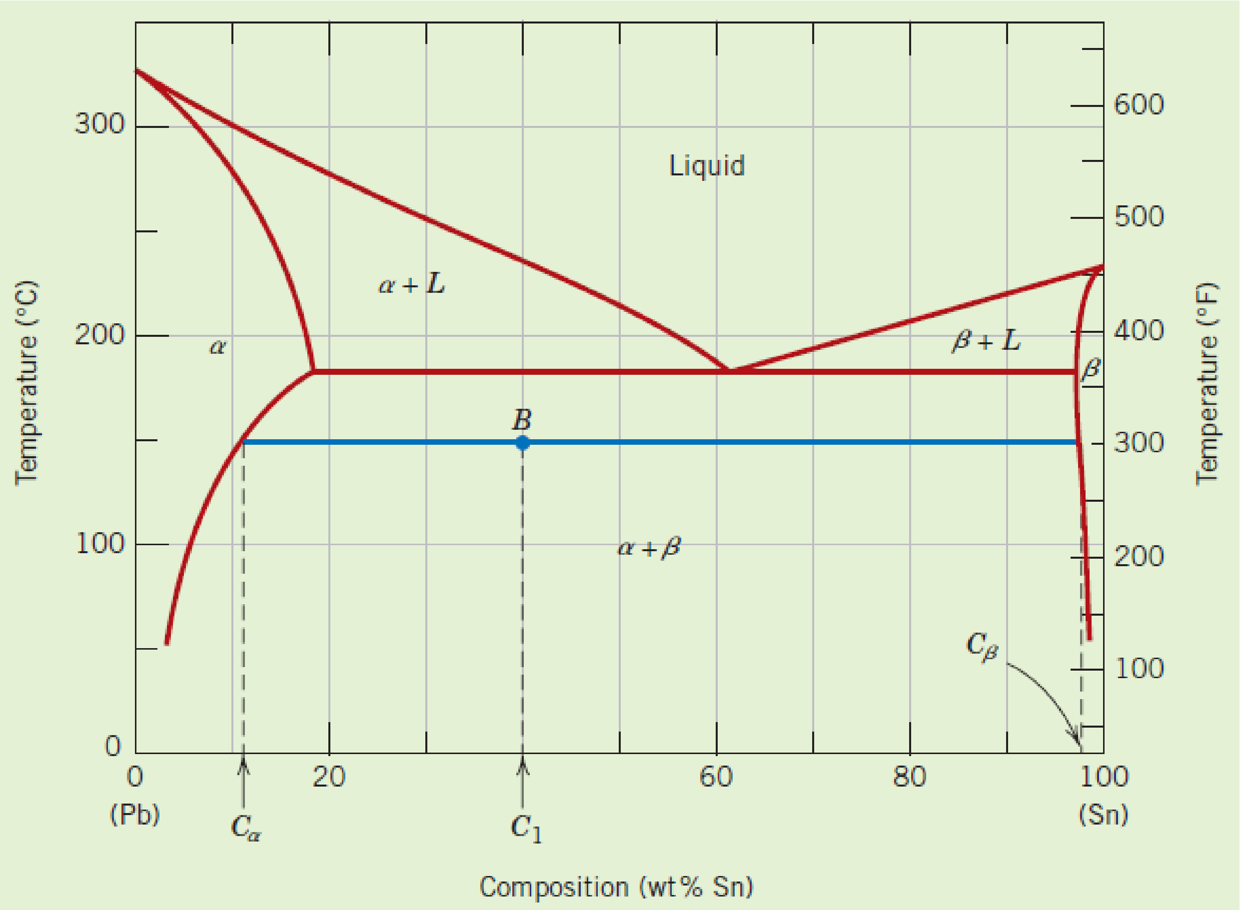
$$W_\alpha = \frac{C_\beta - C_1}{C_\beta - C_\alpha} = \frac{98 - 40}{98 - 11} = 0.67$$

$$W_\beta = \frac{C_1 - C_\alpha}{C_\beta - C_\alpha} = \frac{40 - 11}{98 - 11} = 0.33$$



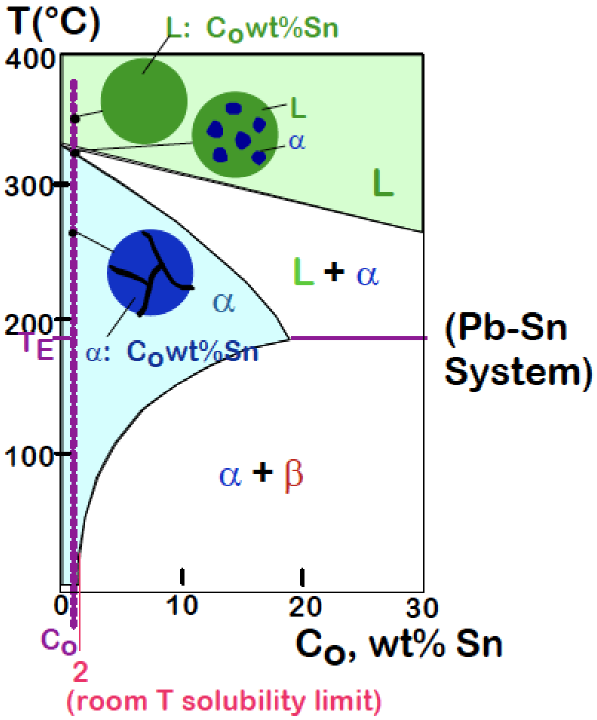
Binary Eutectic Systems with limited solubility:

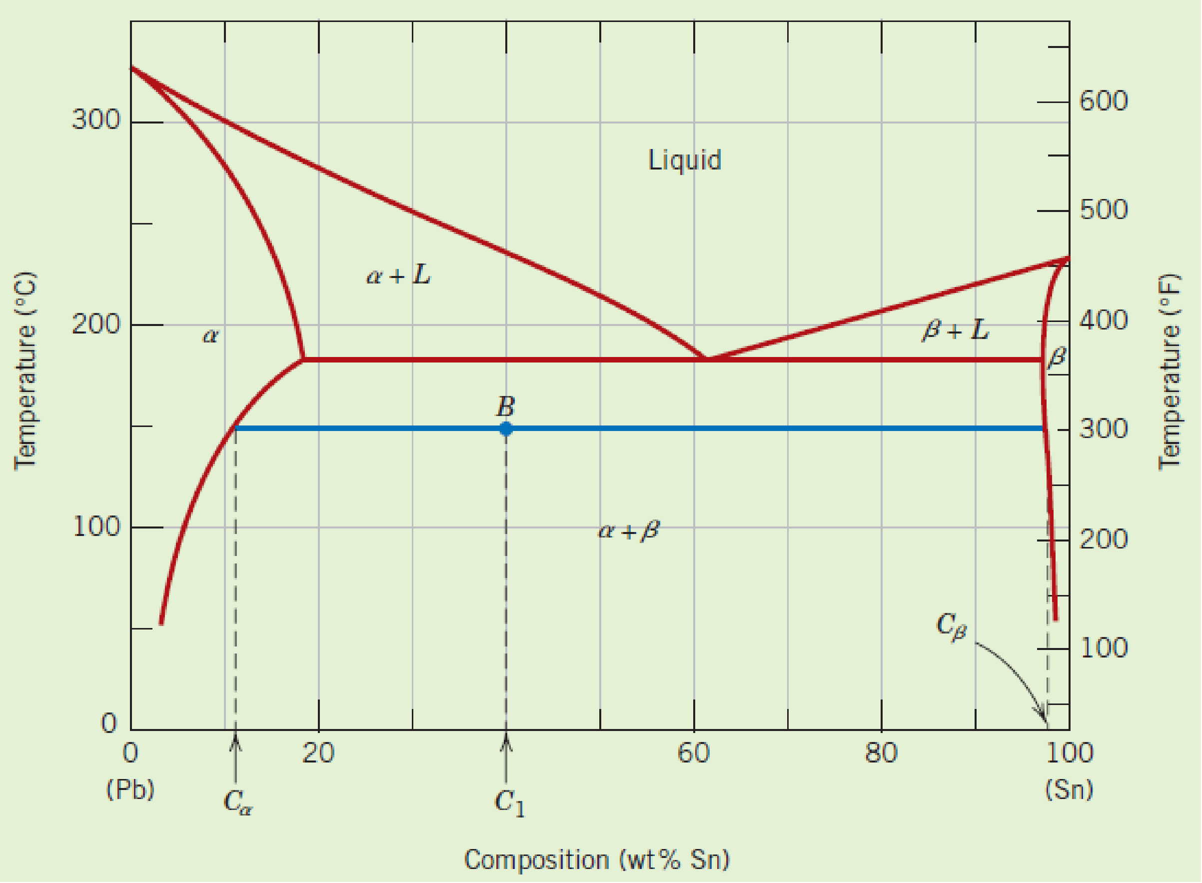
Example 2 : For a Pb-30 wt% Sn alloy, determine the phases present, their amounts, and their compositions at 300C, 200C, 184C, 182C, and 0C.



Microstructures in binary systems

- C_o < 2wt%Sn
- Result:
  --polycrystal of α grains.

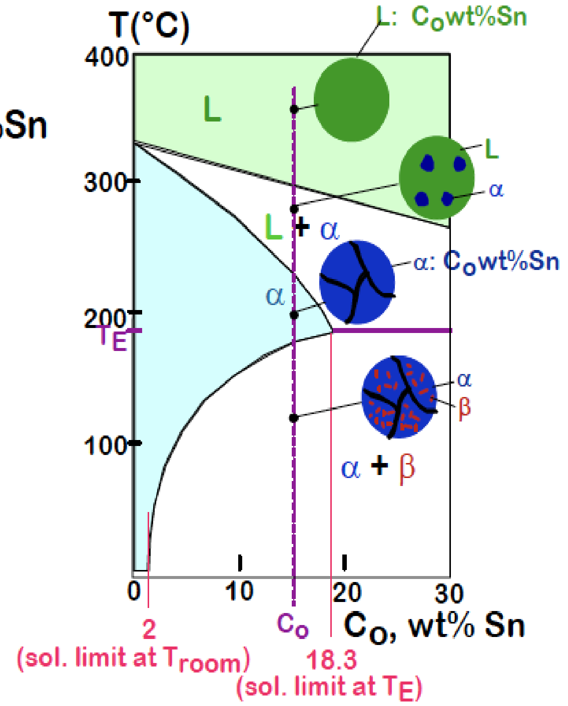


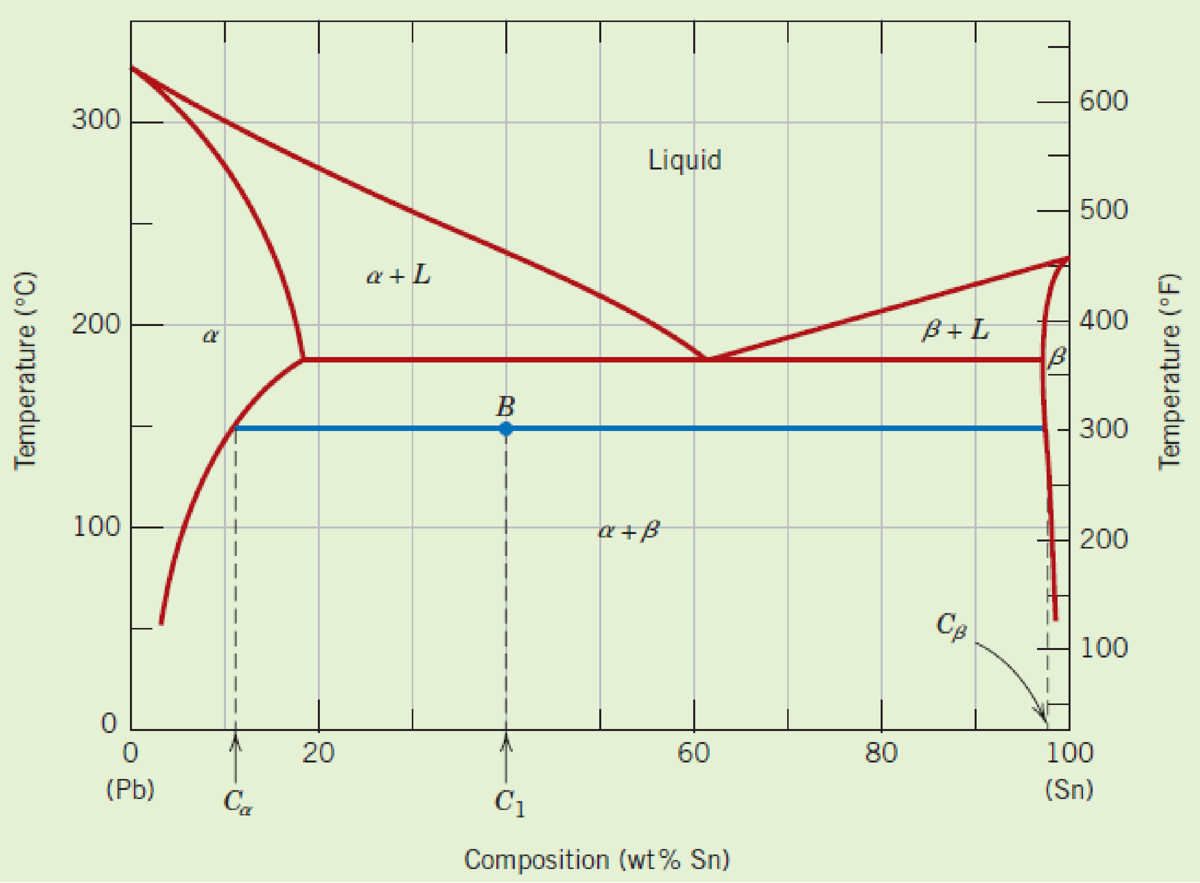


Microstructures in binary systems

- 2wt%Sn < C_o < 18.3wt%Sn
- Result:

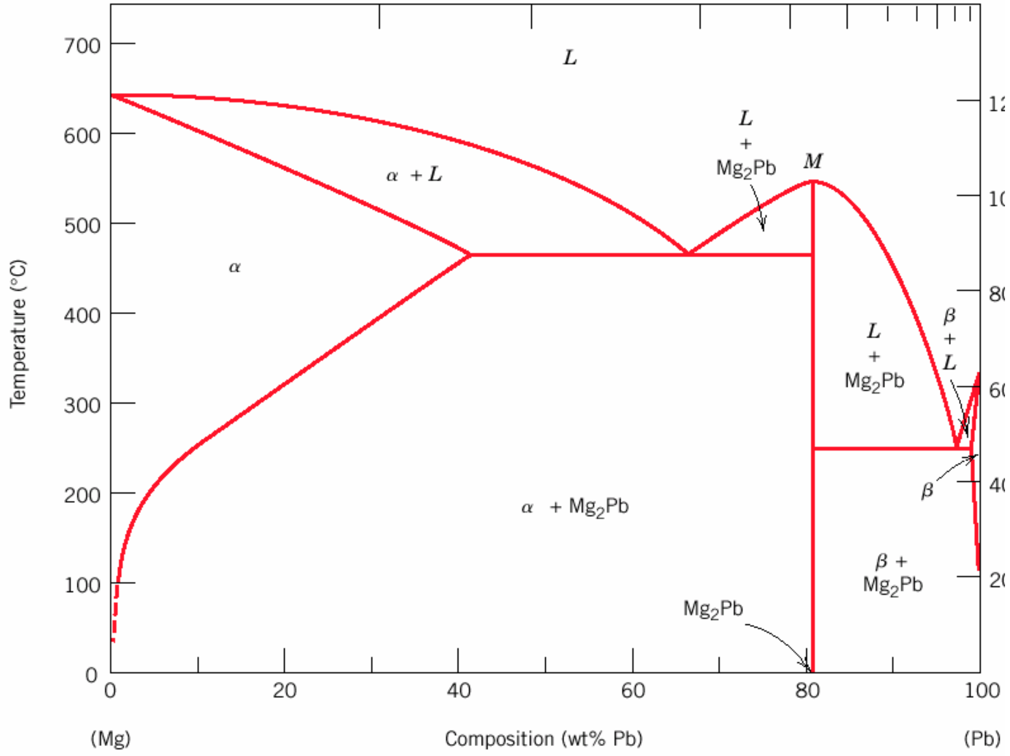
  --α polycrystal with fine β crystals.





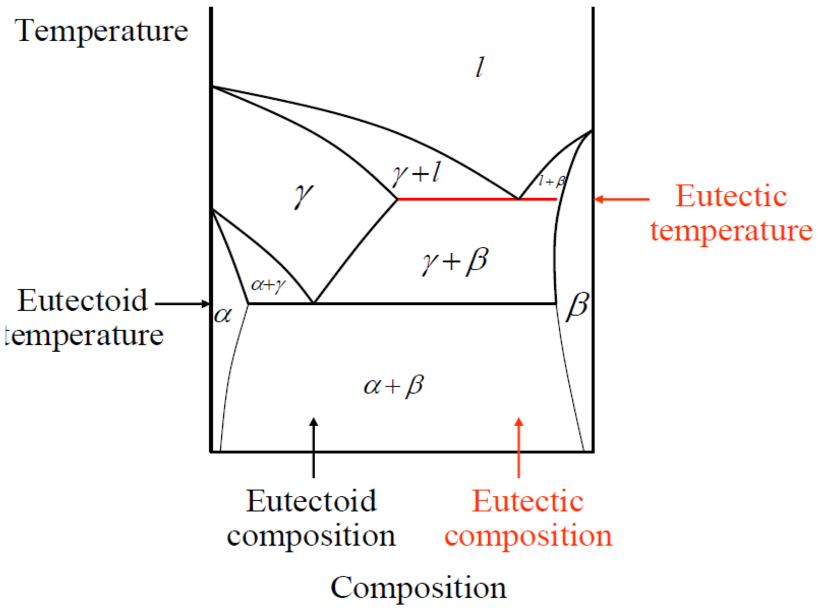
Phase diagrams with intermetallic compounds:

- Besides solid solutions, **intermetallic compounds** that have specific 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.
- This diagram can be considered two joined eutectic diagrams, for Mg-Mg2Pb and Mg2Pb-Pb. In this case, compound Mg2Pb can be considered a component.



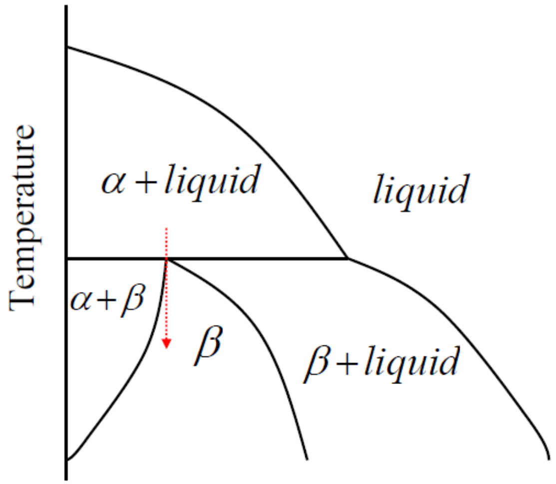
Eutectoid Reactions (I)

- The **eutectoid** (*eutectic-like* in Greek) reaction is similar to the eutectic reaction but occurs from one solid phase to two new solid phases.
- Invariant point (the eutectoid) – three **solid** phases are in equilibrium.
- Upon cooling, a solid phase transforms into two other solid phases ($\delta \leftrightarrow \gamma + \varepsilon$ in the example below)



Peritectic Reactions:

- A **peritectic** reaction - solid phase and liquid phase will together form a second solid phase at a particular temperature and composition upon cooling, e.g. $L + \alpha \leftrightarrow \beta$
- These reactions are relatively slow as the product phase will form at the boundary between the two reacting phases, thus separating them and slowing down any further response.



Fe-C system

Phases in Fe–Fe3C Phase Diagram:

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.

γ -austenite - solid solution of C in FCC Fe

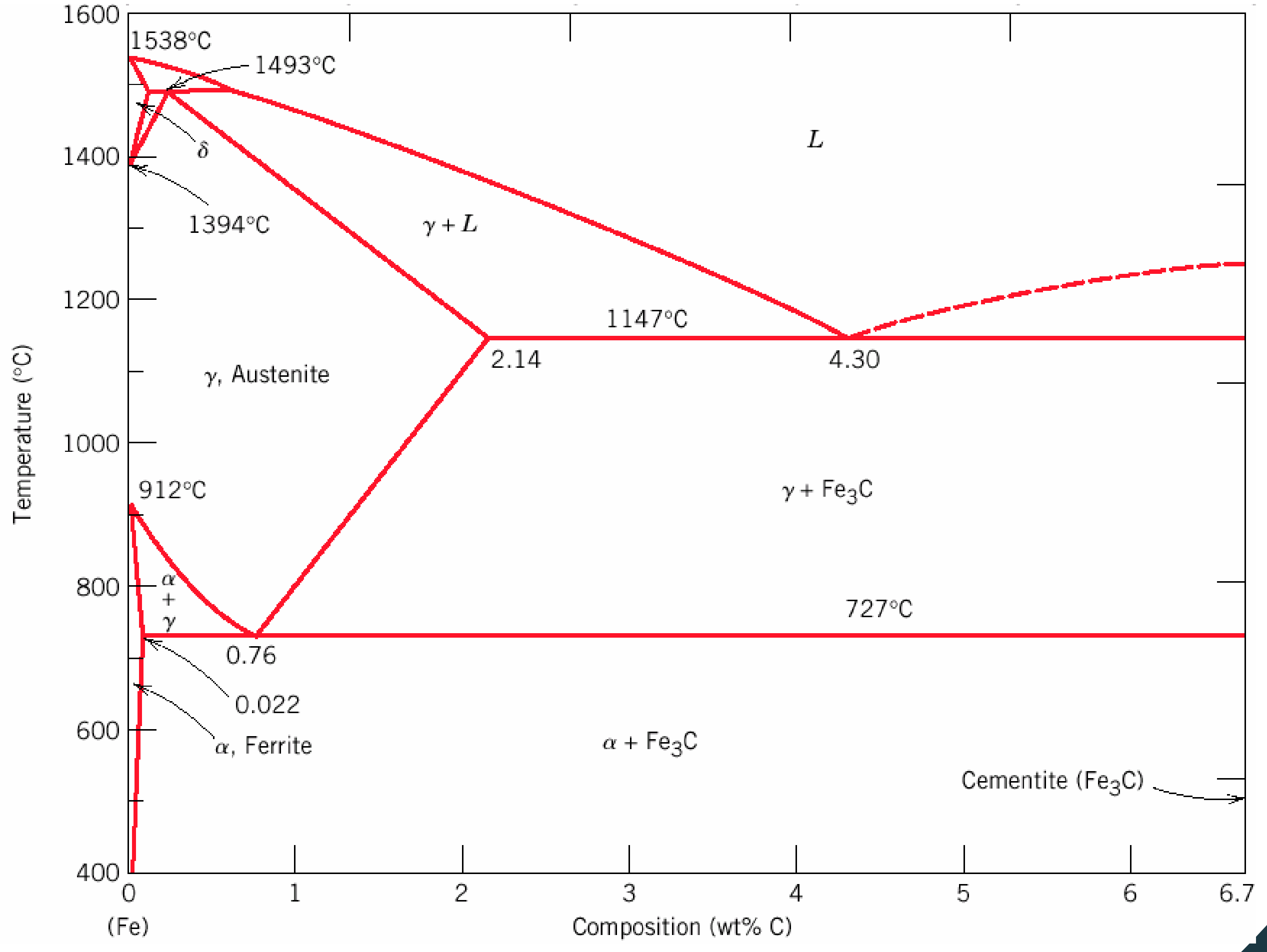
- The maximum solubility of C is 2.14 wt %.
- Transforms to BCC δ -ferrite at 1395 ° C
- Is not stable below the eutectoid temperature (727 C) unless cooled rapidly.

δ -ferrite solid solution of C in BCC Fe

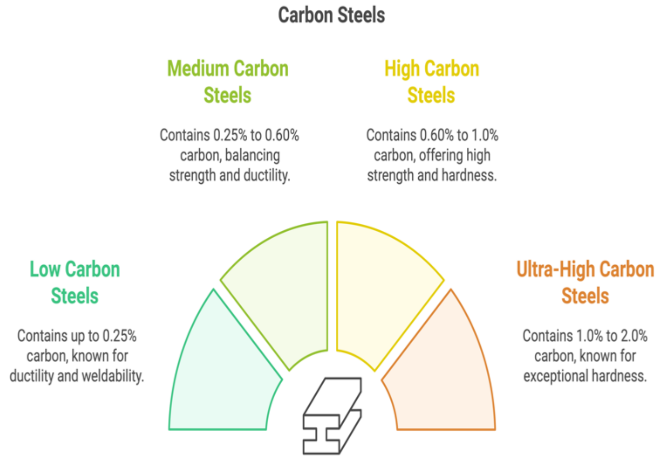
- The same structure as α -ferrite
- Stable only at high T, above 1394 ° C
- Melts at 1538 ° C

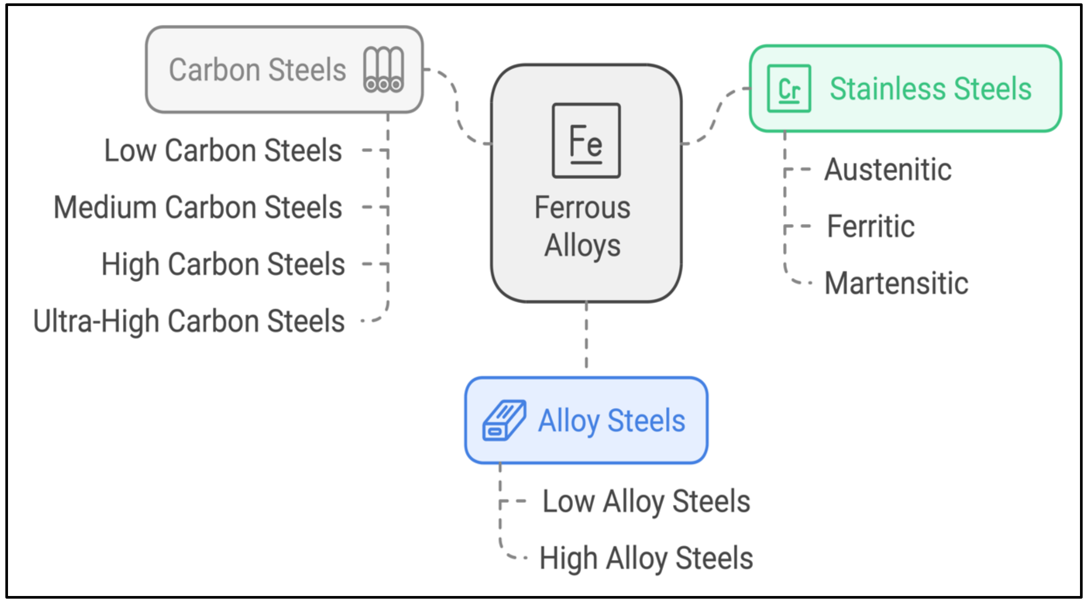
Fe3C (iron carbide or cementite)

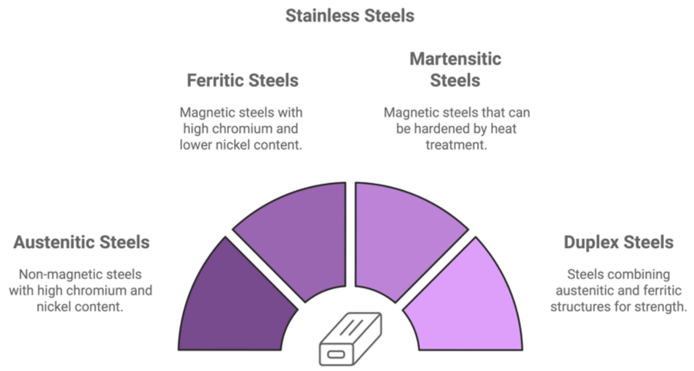
This intermetallic compound is metastable, it remains as a compound at room T, but decomposes (very slowly, within several years) into α -Fe and C (graphite) at 650 - 700C

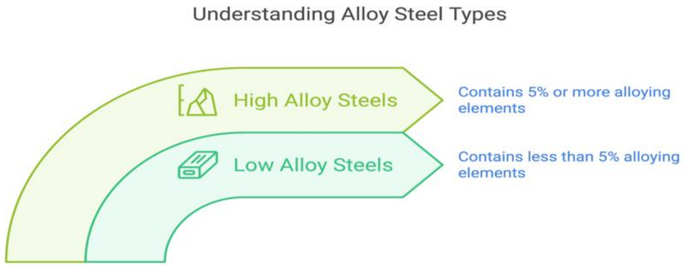


Classification. Three types of ferrous alloys









H.w

Metal (A) melts at (1400ºC), Metal (B) melts at (600ºC). Thermal arrest data is obtained from cooling curves for the alloy of (AB) is shown below.

%A	0	10	20	30	50	60	80	90	100
1st Arrest Point	600	700	860	960	1140	1220	1320	1370	1400
2nd Arrest Point	600	630	690	760	910	1000	1160	1280	1400

1. Plot and label the equilibrium diagram.
2. For an alloy containing (**40%**) **A** and (**60%) B** state:
(a) Solidification beginning temperature.
(b) Solidification ending temperature.
(c) Composition of phases at (**900ºC**).
(d) The ratio of phases.

H.w

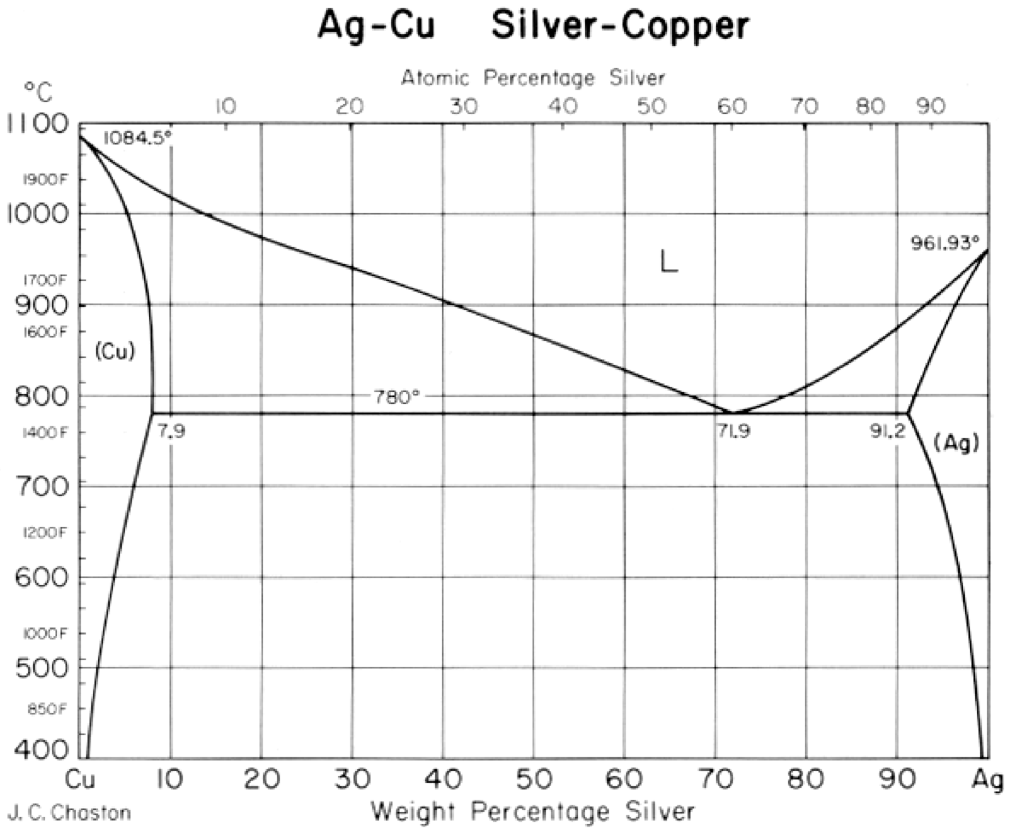
Use the silver-copper phase diagram shown

1. What are the solubility limits of Ag in (Cu) and Cu in (Ag)? The (Cu) and (Ag) phases are the same as α and β, respectively (just different naming methods).

2. For equilibrium solidification of a Cu-Ag alloy containing 40 weight percent Ag,

a. State the temperature at which solidification begins.

b. State the temperature at which solidification is complete.



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