Outline

- Introduction
  - Definitions and basic concepts
  - Phases and microstructure
- Binary PD and Gibbs free energy
- Binary isomorphous systems (*complete solid solubility*)
- Eutectic phase diagram
- Interpretation of phase diagram

Definitions and Basic Concepts

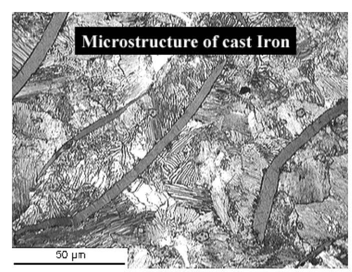
- **Component:** chemically recognizable species (e.g. Fe and C in carbon steel, H_2O and NaCl in salted water).
  - *A binary alloy contains two components, a ternary alloy – three, etc.*
- **Phase**: a chemically homogeneous portion of a microstructure; a region of uniform composition and crystal structure.
  - *Do not confuse phase with grain. A single phase material may contain many grains, however, a single grain consists of only one phase.*
  - *A phase may contain one or ………. components.*
- **System**: a series of possible alloys, compounds, and mixtures resulting from the same components.
  - Examples: the Fe-C system, the water-sugar system, the alumina-silica system.
- **Solvent**: host or major component in solution, **Solute**: minor component *(Chapter 4)*.

Definitions and Basic Concepts

- **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 ………… soluble in any amount (unlimited solid solubility), while C has a ……… solubility in Fe.*
- **Equilibrium:** The stable configuration of a system, when a **sufficient** amount of time has elapsed that …………………… occur.
  - *Equilibrium may take place rapidly (on the order of microseconds), or may require a geological time frame.*
  - *We will talk in this class about equilibrium phase diagrams, that is, the nature of a system at any given temperature after a "………………" long period of time.*
  - *Quenching (extreme cooling rate) can sometimes shift phase boundaries relative to their equilibrium values.*

Definitions and Basic Concepts

- **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, and **(3)** their arrangement in space.

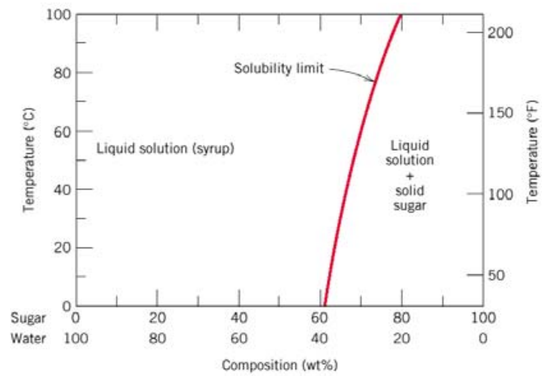


- This is an alloy of Fe with 4 wt.% C.
- There are several phases.
  - The long grey regions are flakes of graphite.
  - The matrix is a fine mixture of BCC Fe and Fe_3C compound.

Phase diagrams will help us to understand and predict the microstructures like the one shown above

Binary Phase Diagrams

Example: sugar – water

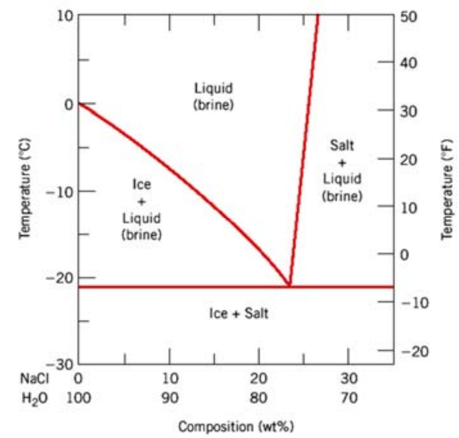


- Composition is plotted on the abscissa
  - *- Usually either weight % or atomic %*
- Temperature is plotted on y axis
- The region to the left of the red line is a single phase region.
- The region to the right of the red line is a two phase region.

Binary Phase Diagrams

Note:

• the components don't need to be elements; they can themselves be alloys or *chemical compounds*, such as NaCl and H_2O.



this is only a portion of the entire NaCl-H_2O phase diagram.

What is a Binary Equilibrium Phase Diagram?

Binary – two components

Equilibrium – stable over time

Phase – a chemically and structurally homogeneous region

Diagram – a map or drawing showing the general scheme of things

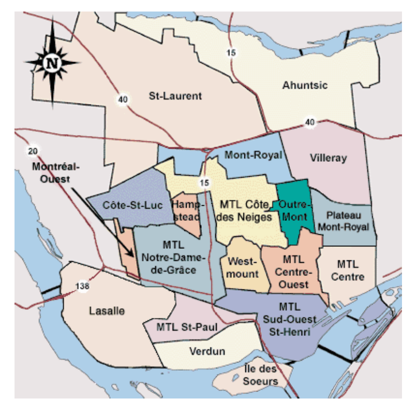
• Phase diagrams are maps of the equilibrium phases associated with various combinations of composition, temperature and **pressure**.

- *Since most materials engineering work involves atmospheric pressure, we are usually most interested in composition – temperature diagrams.*

• Binary phase diagrams are two component maps widely used by engineers.

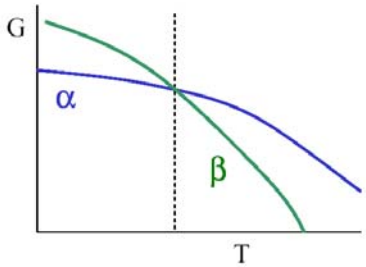
• They are helpful in predicting phase transformations and the resulting microstructures

Phase Diagrams



Binary phase diagram and Gibbs free energy

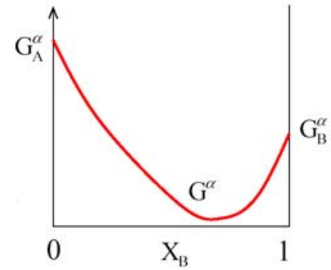
The equilibrium state can be found from the Gibbs free energy dependence on temperature and composition.



$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_P}{T}$$

We have also discussed the dependency of the Gibbs free energy on composition at a given T:

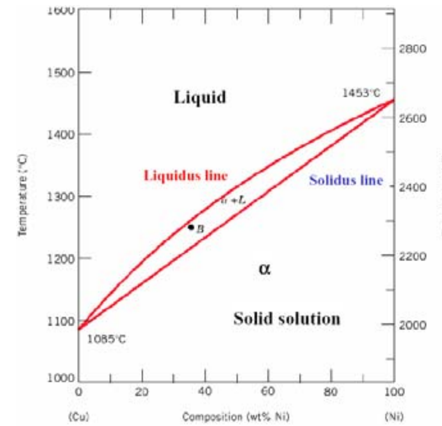


$$G = X_A G_A + X_B G_B + \Delta H_{mix} - T\Delta S_{mix}$$

Binary solutions with unlimited solubility

Let us construct a binary phase diagram for the simplest case: A and B components are mutually soluble in any amounts in both solid (*isomorphous system*) and liquid phases, and form ideal solutions.

But let us review the isomorphous system first.

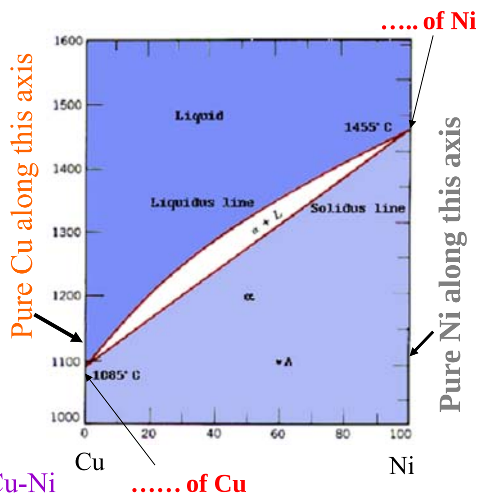


Binary Isomorphous Systems

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

❖ Three distinct regions can be identified on the phase diagram: Liquid *(L)* , solid + liquid *(α +L)*, solid *(α)*

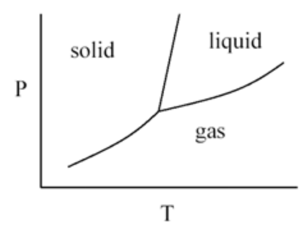
- **Liquidus** line separates liquid from liquid + solid
- **Solidus** line separates solid from liquid + solid



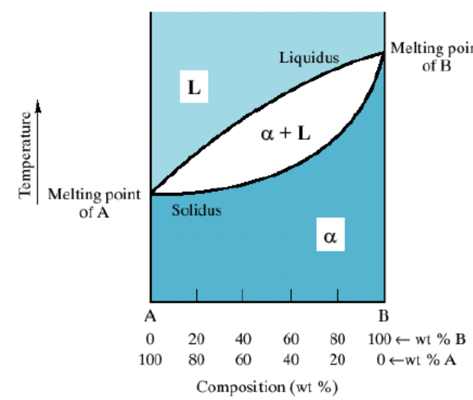
<u>Example of isomorphous system</u>: Cu-Ni

Recall: the complete solubility occurs because both Cu and Ni have the same ……….…………….., ……..……., ……………….. and ………

Phase Diagrams



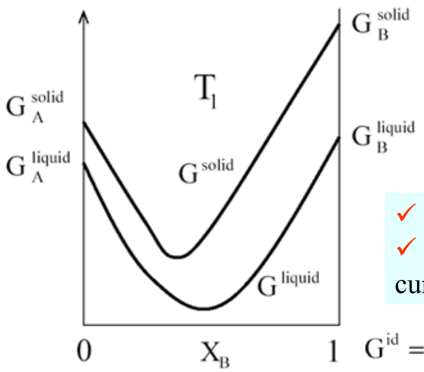
A typical phase diagram for a pure material

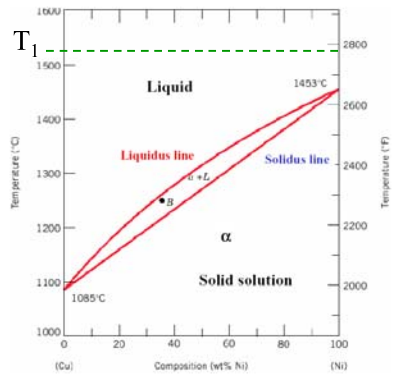


- In one-component system melting occurs at a well-defined melting temperature.
- In multi-component systems melting occurs over the range of temperatures, between the solidus and liquidus lines.
  - *Solid and liquid phases are in equilibrium in this temperature range.*

Gibbs Free Energy of Isomorphous Binary System

T_1 is above the equilibrium melting temperatures of both pure components: $T_1 > T_m(A) > T_m(B) \rightarrow$ the liquid phase will be the stable phase for any composition.





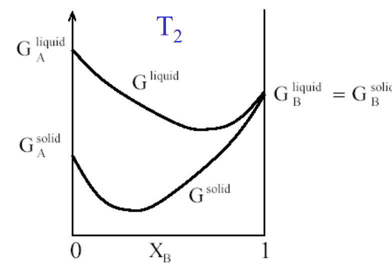
✓ We have 2 phases: liquid and solid.
✓ Let's consider Gibbs free energy curves for the two phases at different T

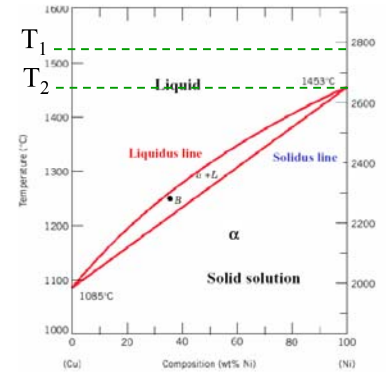
$$G^{id} = X_A G_A + X_B G_B + RT[X_A \ln X_A + X_B \ln X_B]$$

Gibbs Free Energy of Isomorphous Binary System

Decreasing the temperature below T_1 will have two effects:

- G_A^{liquid} and G_B^{liquid} will increase more rapidly than G_A^{solid} and G_B^{solid} Why?
- The curvature of the $G(X_B)$ curves will decrease.



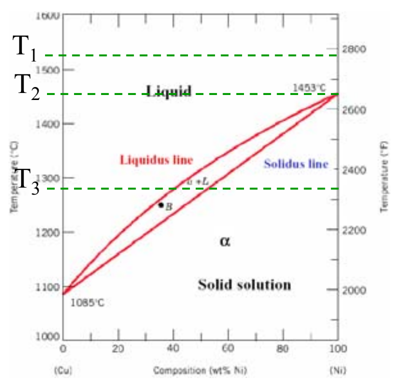


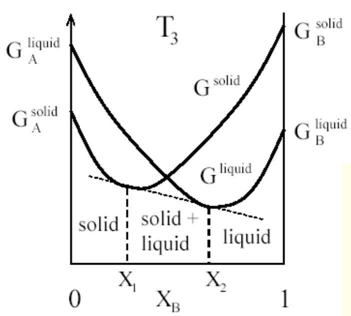
Eventually we will reach T_2 melting point of pure component A, where

$$G_{\mathbf{B}}^{liquid} = G_{\mathbf{B}}^{solid}$$

Gibbs Free Energy of Isomorphous Binary System

For even lower temperature $T_3 < T_2 = T_m(A)$ the Gibbs free energy curves for the liquid and solid phases will cross.



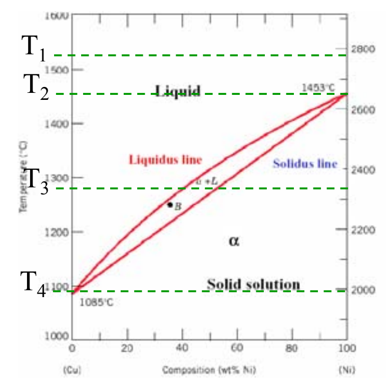


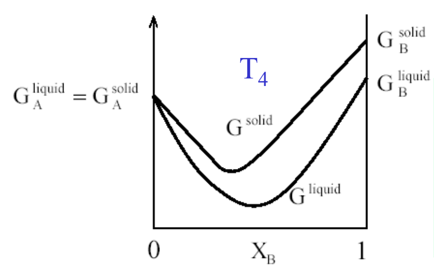
As we discussed before, the common tangent construction can be used to show that for compositions near cross-over of G_{solid} and G_{liquid}, the total Gibbs free energy can be minimized by separation into two phases.

Gibbs Free Energy of Isomorphous Binary System

As temperature decreases below T_3 G_A^{liquid} and G_B^{liquid} continues to increase more rapidly than G_A^{solid} and G_B^{solid}

Therefore, the intersection of the Gibbs free energy curves, as well as points X_1 and X_2 are shifting to the right, until, at $T_4 = T_m(B)$ the curves will intersect at $X_1 = X_2 = 1$





At T_4 and below this temp. the Gibbs free energy of the solid is lower than that of the liquid in the whole range of compositions ⇒ the solid phase is the only stable phase.

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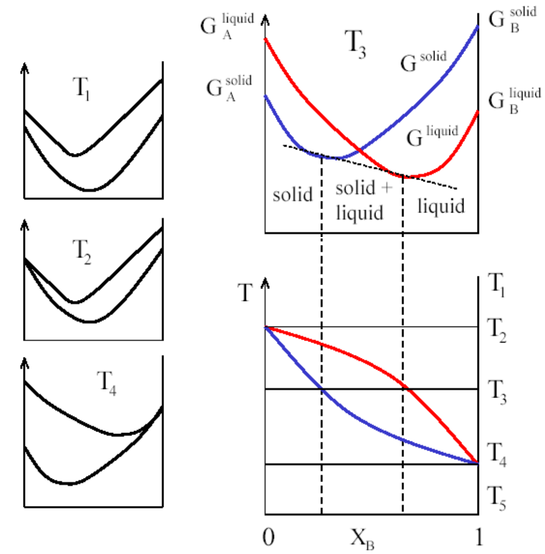
Gibbs Free Energy of Isomorphous Binary System

Based on the Gibbs free energy curves we can now construct a phase diagram for a binary isomorphous systems



Interpretation of Phase Diagrams

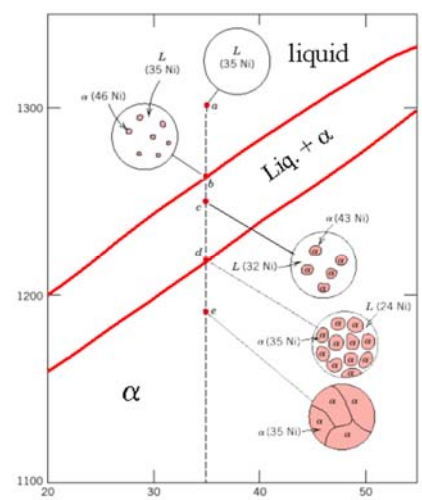
For a given temperature and composition we can use phase diagram to determine:

1) The phases that are present

2) Compositions of the phases

3) The relative fractions of the phases

Microstructure Development



Schematic representation of the development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy.

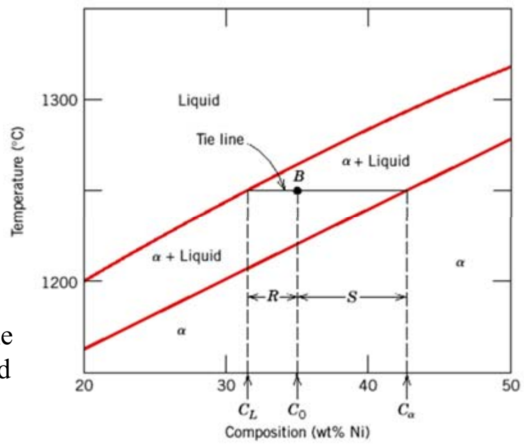
Finding the composition in a two phase region:

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.

4. Intersections with the liquidus and solidus determine the compositions of liquid and solid phases, respectively.

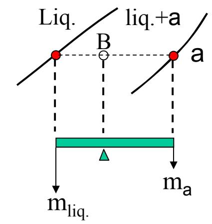


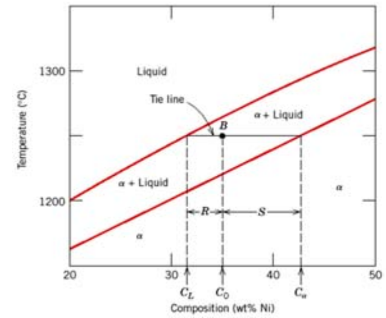
Example: What are the phases and their composition at point B?

Liquid: (………………) and a: (……………..)

Finding the Amounts of Phases in a Two Phase Region

The Lever Rule





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 by the total length of tie line.

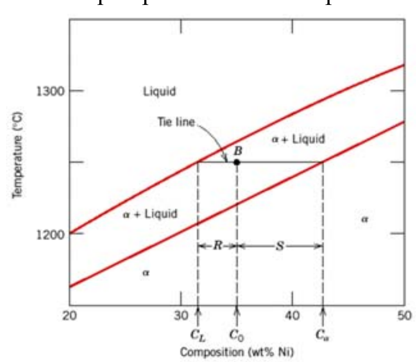
Example

Again using the Cu-Ni phase diagram, suppose the overall composition of an alloy is 35 wt. % Ni and the alloy is at a temperature of 1250°C (i.e., point “B” in the figure). What are the mass fractions of solid and liquid phases at that temperature?

Mass fractions:

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

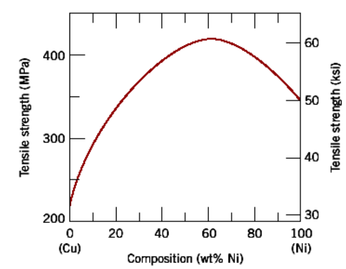
$$W_\alpha = \frac{R}{R+S} = \frac{C_o - C_L}{C_\alpha - C_L}$$

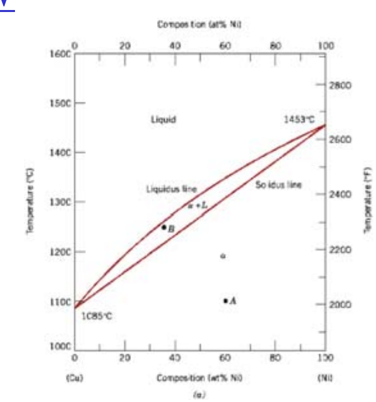


Solution:

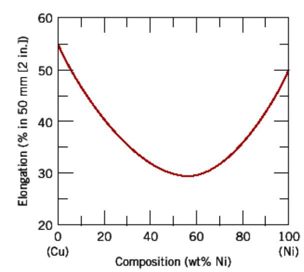
REVIEW

Mechanical properties of isomorphous alloys





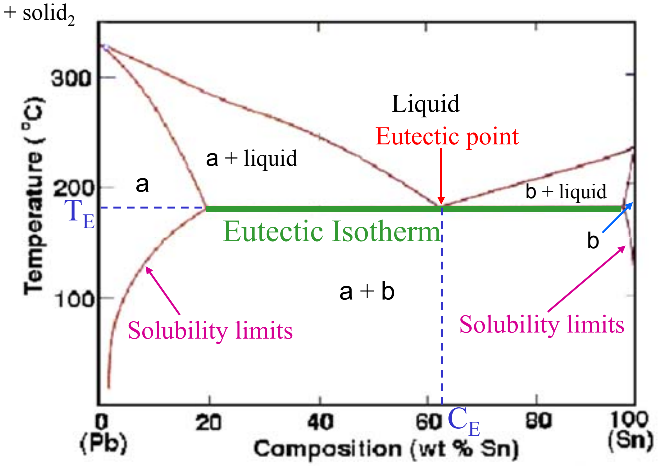
Solid solution strengthening



By making appropriate choices of compositions and alloy elements, we can engineer materials to have specific properties needed for certain applications (mechanical, electrical, thermal, optical).

Eutectic Phase Diagram

Eutectic reaction:
Liquid □ $solid_1 + solid_2$

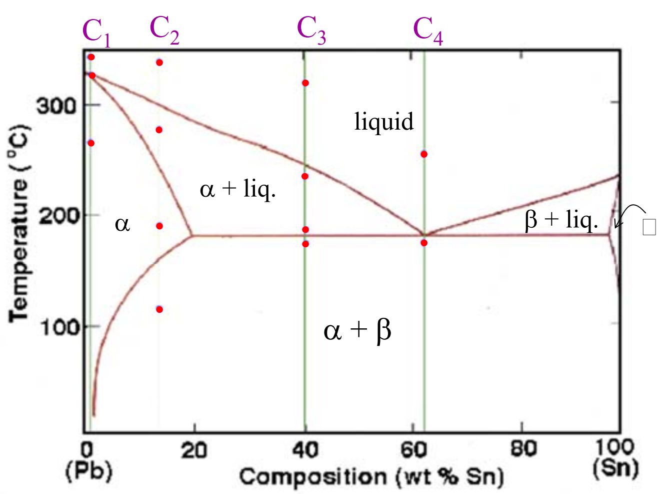


What Information can we read from a phase diagram?

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

➤ *Compositions and relative amounts of phases are determined from the same tie lines and lever rule, as for* ***isomorphous*** *phase diagram*

Development of microstructure

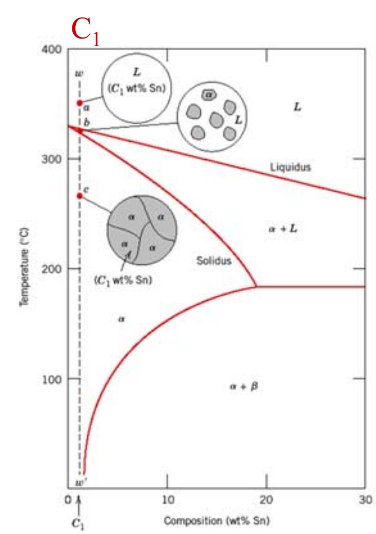


Lead-Tin Binary Phase Diagram

- *Schematic Representations of the* ***equilibrium microstructures*** *for lead–tin alloys as they are cooled from the liquid-phase region.*

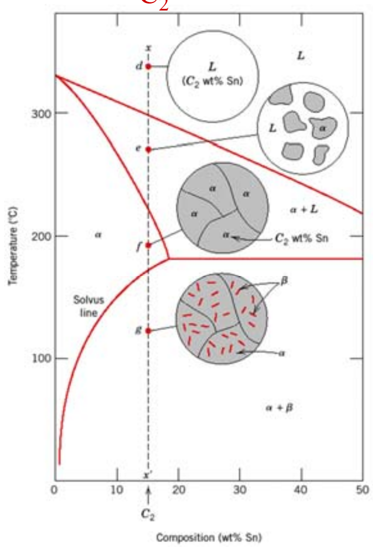
Lead-Tin Binary Phase Diagram

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

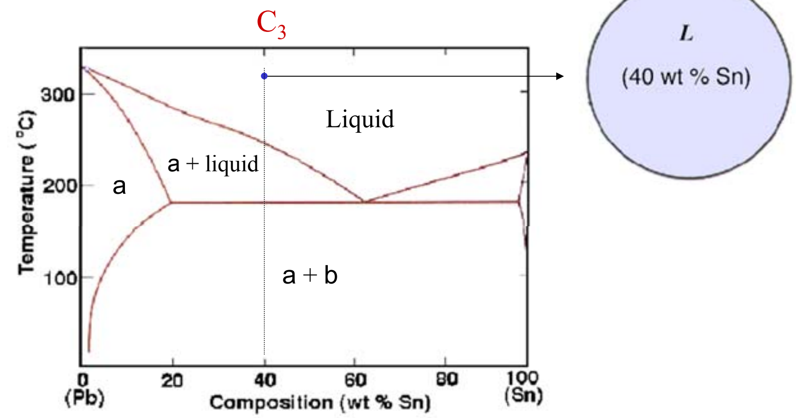


Lead-Tin Binary Phase Diagram

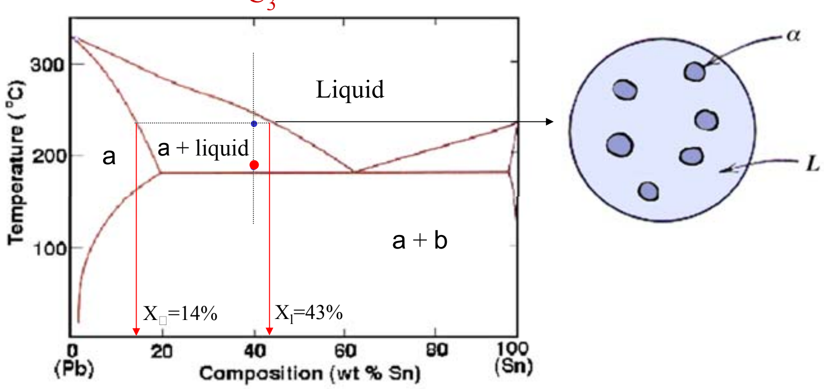
L
$\Downarrow$
$\alpha + L$
$\Downarrow$
α
$\Downarrow$
$\alpha + \beta$



Lead-Tin Binary Phase Diagram

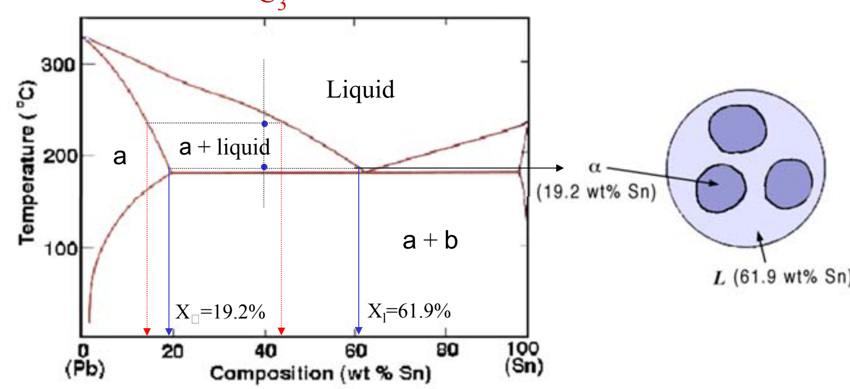


Lead-Tin Binary Phase Diagram



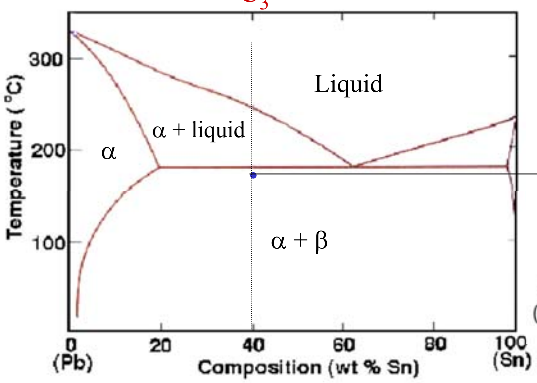
Liquid composition is: 43 wt% Sn
 composition is: 14 wt% Sn

Lead-Tin Binary Phase Diagram

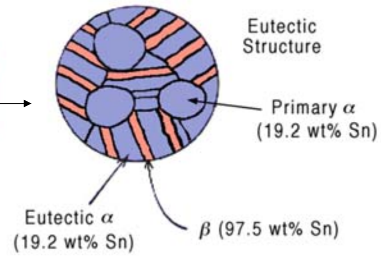


Liquid composition is: 61.9 wt% Sn
 composition is: 19.2 wt% Sn

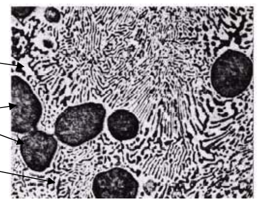
Lead-Tin Binary Phase Diagram



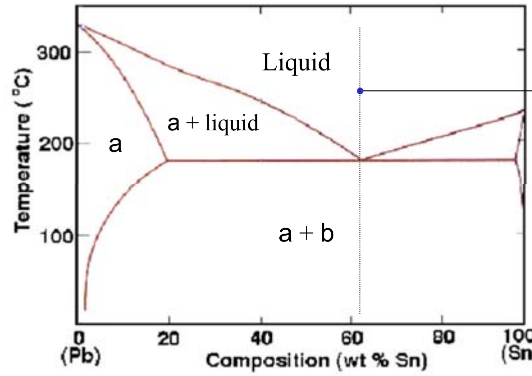
Primary α phase is formed in the α + L region,

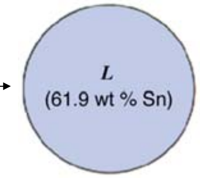


The eutectic structure that includes layers of α and β (called **eutectic** α and eutectic β) is formed upon crossing the eutectic isotherm.

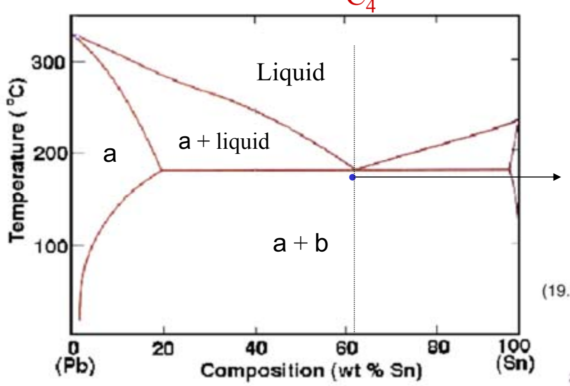


Lead-Tin Binary Phase Diagram

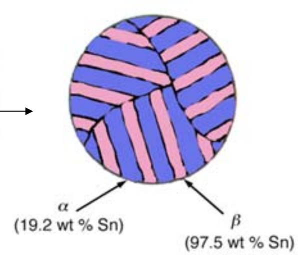




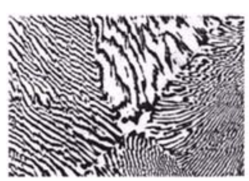
Lead-Tin Binary Phase Diagram



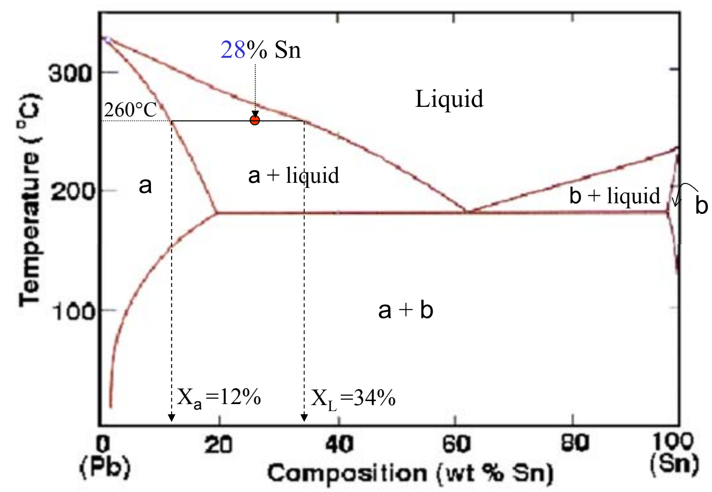
$L \rightarrow \alpha + \beta$



The microstructure of a Pb–Sn alloy of eutectic composition. *a-phase (dark layers), and* *b-phase (light layers). 375X.*



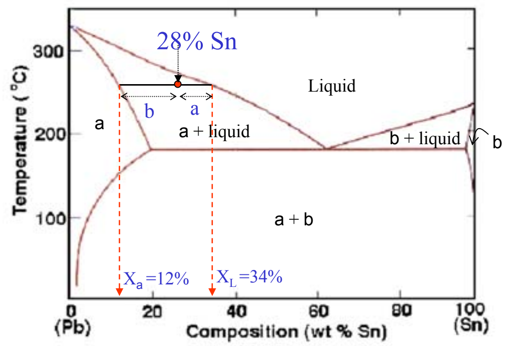
How much of each phase exists at the given temperature?



Lever Rule

$$Fraction\ of\ \alpha = \frac{a}{a+b}$$

$$Fraction\ of\ liquid = \frac{b}{a+b}$$



$$\text{wt\% of } \alpha = \frac{34-28}{34-12}\times 100\% = 27.27\%$$

$$\text{wt\% of liquid} = 100 - 27.27 = 72.73\%$$

How to calculate the total amount of α phase?

Question:

At T_1, find the total amount of α phase (*both eutectic and primary*) in alloy C?

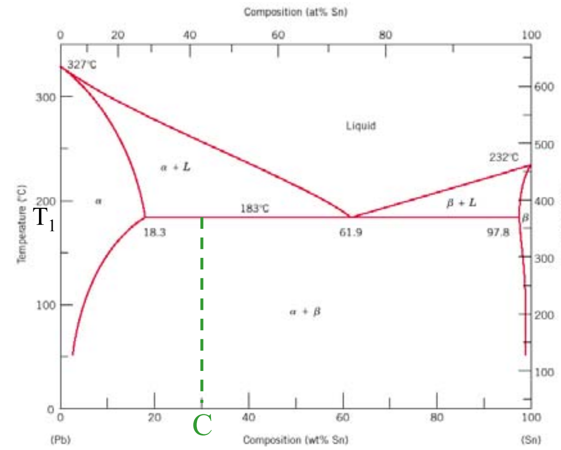
$$W_\alpha = \frac{Q}{Q+P}$$

$$= \frac{97.8 - 30}{97.8 - 18.3}\times 100\%$$

$= \ldots\ldots\ wt\%$

$W_\beta = 100 - 85.3$

$= \ldots\ldots\ wt\%$



How to calculate relative amounts of microconstituents?

Question:

For alloy C, find the weight percentage of (1) primary α (2) eutectic phase and (3) eutectic α, at T_1?

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

$$= \frac{61.9 - 30}{61.9 - 18.3}\times 100\%$$

$= \ldots\ldots\ wt\%$ Primary α

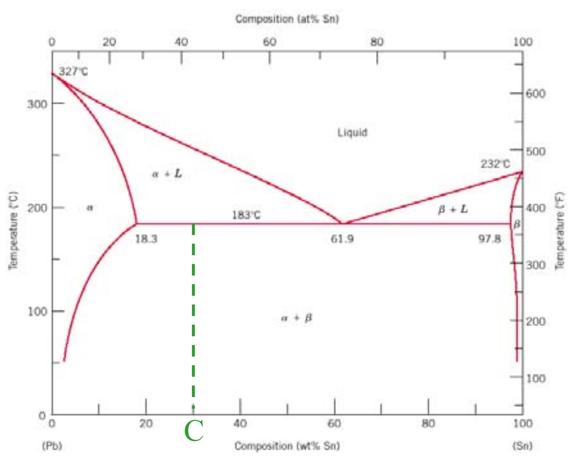
$W_e = 100 - 73.2$

$= \ldots\ldots\ wt\%$ Eutectic phase

$W_{\alpha'}$ = total α – primary α

= 85.3 – 73.2

$= \ldots\ldots\ wt\%$ Eutectic α



Next time:

Continue Binary Phase Diagrams