University of Anbar/ Faculty of Engineering

Department of Mechanical Engineering

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Subject: Engineering of Metallurgy

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Stage: 2nd Year

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Lecture # 11

CHAPTER FIVE/PHASE DIAGRAMS

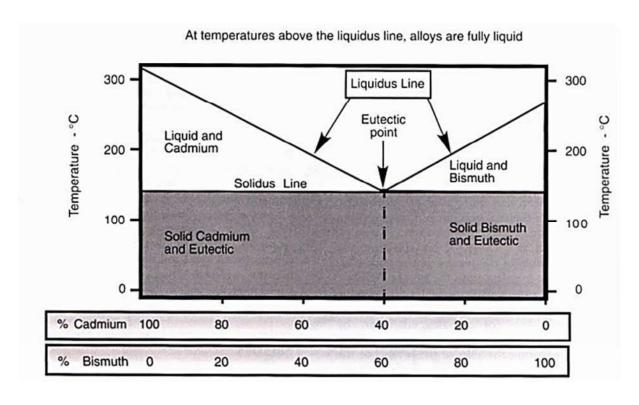
2) Eutectic Phase diagrams

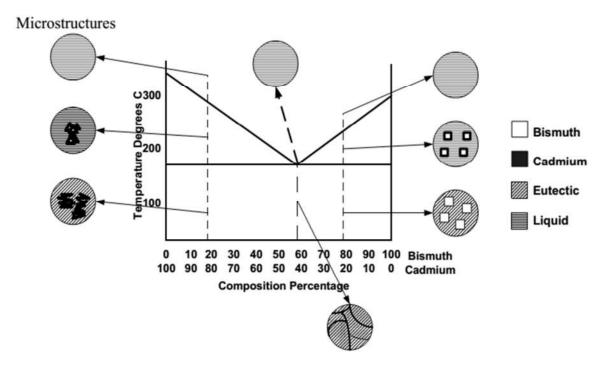
- ➤ **Eutectic** is a homogeneous mixture of substances that melts or solidifies at a single temperature that is lower than the melting point of either of the components. **OR**: it is the particular composition of two substances which freeze simultaneously at the same temperature.
- ➤ Eutectic temperature; It is the melting temperature of any alloy with the eutectic composition . OR: The temperature at which the liquid and the solid are in equilibrium.
- Eutectic equilibrium diagram results when the two metals are soluble in the liquid state but insoluble in the solid state. In the liquid state the two metals are soluble in each other but when cooling is complete, the grain of the solid alloy consist of two distinguishable metals which can be seen under

- a microscope to be like a layer of one metal on top of a layer of the other metal.
- ➤ In practice, few metal alloys form simple eutectic type phase diagrams.

 As an example of eutectic are carbon steels.
- Example: Tin/Zinc and Cadmium/ Bismuth eutectic thermal equilibrium diagram. Cadmium and Bismuth are completely soluble in the liquid state, but are completely insoluble in the solid state.
- ➤ The eutectic point (140°C) is the lowest melting point of the alloy. The alloy changes directly from a liquid to a solid without going through a pasty stage at this point. The eutectic composition (40% Cadmium).
- ➤ **Eutectic Reaction** in Cadmium/ Bismuth eutectic thermal equilibrium diagram:

L (
$$40\%$$
 Cd -60% Bi) $\stackrel{\text{cooling}}{\longleftrightarrow}$ (40% Cd -60% Bi) (at140°C).





Cadmium/ Bismuth eutectic thermal equilibrium diagram

An examination: at 80% Cadmium and 20% Bismuth. Above Liquidus line phase is full liquid as the temperature falls at 250°C (solidification start temperature) crystal nuclei of pure cadmium begin to form. Crystal nuclei continue in growth with the temperature decreases to 140°C (Eutectic Temperature) and the remaining liquid transforms to eutectic. At temperature below eutectic temperature, the microstructure is (Cd + Eutectic).

By the same manner, we can follow the cooling of alloy (20%Cd + 80%Bi)

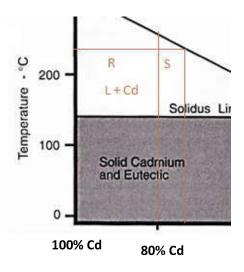
 \triangleright The amount of the phases at point Co = 80%Cd, 240°C:

CL % Cd

$$WL = (100 - 80) / (100 - CL)$$

$$WL = (20) / (100 - CL) = ? \%$$

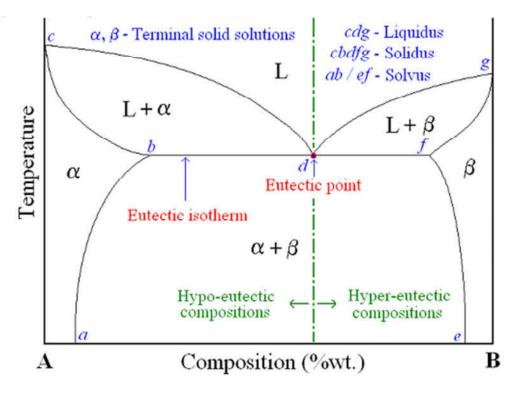
$$WCd = (80 - CL) (100 - CL)$$



3) Combination Type, Limited (partially) solubility Phase diagram

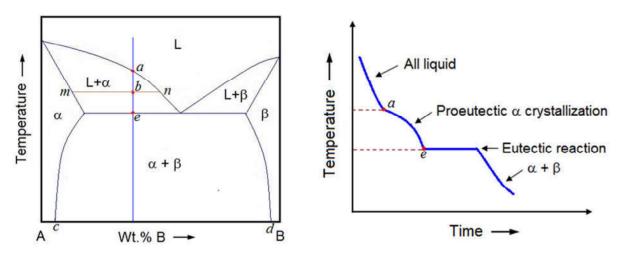
There are:

- (i) Eutectic and (ii) Peritectic.
- ➤ Many of the binary systems with limited solubility are of eutectic type eutectic alloy of eutectic composition solidifies at the end of solidification at eutectic temperature. **E.g.:** Cu-Ag, Pb-Sn
 - \triangleright In the eutectic system between two metals A and B, two solid solutions, one rich in A (α) and another rich in B (β) form.
 - ➤ In addition to liquidus and solidus lines there are two more lines on A and B rich ends which define the solubility limits B in A and A in B respectively. These are called **solvus lines**.



- Three phases $(L+\alpha+\beta)$ exist at point d. This point is called eutectic point or composition. Left of d is called hypoeutectic whereas right of d is called hypereutectic.
- A eutectic composition solidifies as a eutectic mixture of α and β phases. The microstructure at room temperature (RT) may consist of alternate layers or lamellae of α and β .
- In **hypoeutectic alloys** the α phase solidifies first and the microstructure at RT consists of $[\alpha]$ phase (called proeutectic α) + eutectic $(\alpha+\beta)$]. Similarly **hypereutectic** alloys consist of [proeutectic β and the eutectic $(\alpha+\beta)$].
- The melting point at the eutectic point is minimum. That's why Pb-Sn eutectic alloys are used as solders. Other eutectic systems are Ag-Cu, Al Si, Al-Cu.

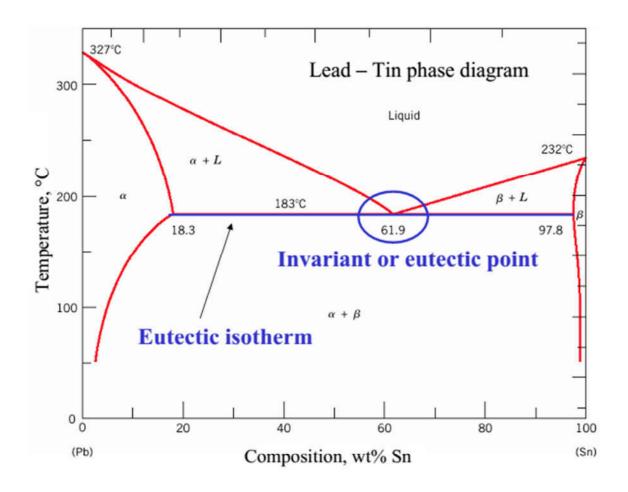
Cooling Curve: while cooling a hypoeutectic alloy from the liquid state, the temp. drops continuously till liquidus point, a, at which crystals of (proeutectic α) begins to form. On further cooling the fraction of α increases. At any point, b, in the two-phase region the α fraction is given by the lever rule as bn/mn. Solidification of proeutectic α continues till the eutectic temperature is reached. The variation in the cooling curve between points a and e is due to evolution of the latent heat. At the eutectic point (e) the solidification of eutectic mixture ($\alpha+\beta$) begins through the eutectic reaction and proceeds at a constant temperature



Cooling curve of a hypoeutectic Pb-Sn eutectic alloy

Question: What is the difference between hypoeutectic and hypereutectic Sn-Pb alloy (Solder)? **Ans.**: A hypoeutectic has a Sn (tin) less than eutectic (CE=61.9%Sn) with microstructure [primary α + eutectic (α + β)]; A hypereutectic has a Sn (tin) greater than eutectic with microstructure [primary β + eutectic (α + β)].

Example: limited solubility phase diagram (e.g. Pb-Sn):



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 .

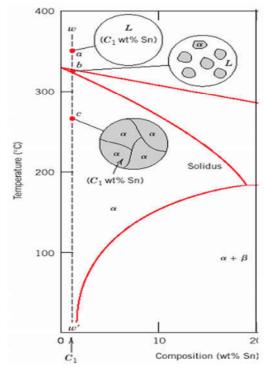
Eutectic reaction – transition between liquid and mixture of two solid phases, (α + β) at eutectic concentration C_E .

Microstructure obtained with different compositions (Pb-Sn diagram)

In this case: Co < 2 wt% Sn

ightharpoonup Microstructure obtained: (only one solid phase α) all liquid transform to solid solution α .

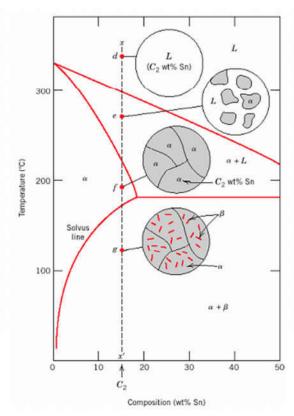
$$L \rightarrow \alpha + L \rightarrow \alpha$$



At 2 wt% Sn < Co < 18.3 wt% Sn

- > Microstructure obtained:
- Initially liquid $+ \alpha$
- then α alone
- finally two phases:
 α crystals and β precipitates

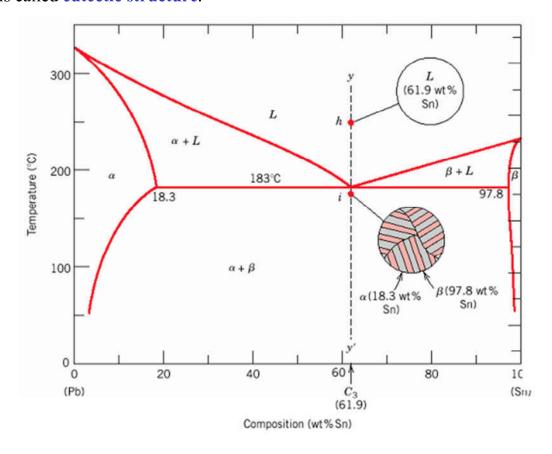
$$L \rightarrow \alpha + L \rightarrow \alpha \rightarrow \alpha + \beta$$



At (Co = CE = 61.9 wt%Sn) and T_E (183°C), the liquid transforms to α and β phases (eutectic reaction);

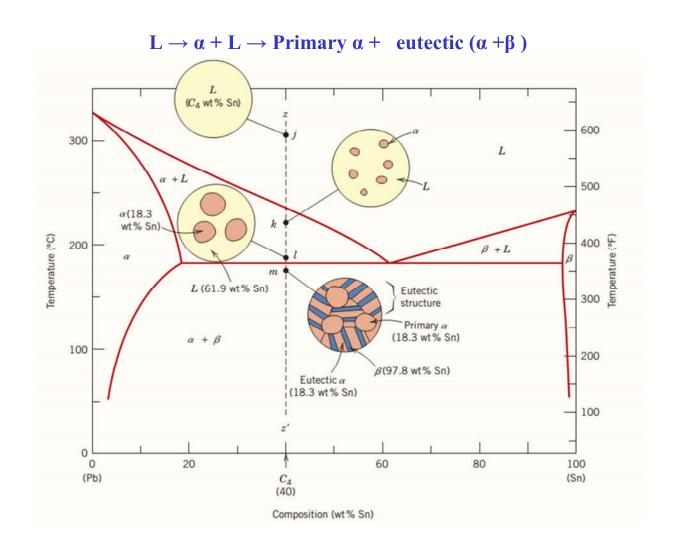
$$L(61.9 \text{ wt\% Sn}) \stackrel{\text{cooling}}{\rightleftharpoons} \alpha(18.3 \text{ wt\% Sn}) + \beta(97.8 \text{ wt\% Sn})$$

eutectic reaction involves redistribution of Pb and Sn atoms by atomic diffusion. This simultaneous formation of α and β phases result in a layered (lamellar) microstructure that is called **eutectic structure**.



At 18.3 wt% Sn < Co < 61.9 wt% Sn:

Primary (or proeutectic) α phase is formed in the α + L region, and the eutectic structure that includes layers of α and β phases (called **eutectic** α and **eutectic** β phases) is formed upon crossing the eutectic isotherm.



Question: In a hypoeutectic Sn-Pb alloy (Solder), both eutectic and proeutectic (α) exist. Explain the difference between them. What will be the Sn (tin) concentration in each? **Ans.**: proeutectic or (primary) α phase is formed above eutectic temperature (TE=183°C), eutectic (α) is formed below eutectic temperature. The concentration of Sn for both is 18.3% Sn.

Calculating amount of the phases

Example (1): **Pb-Sn Eutectic System**; For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find:

- 1. The phases present.
- 2. Compositions of phases
- 3. The relative amount of each phase

Solution:

The phases present:

$$\alpha + \beta$$

Compositions of phases:

$$C_0 = 40 \text{ wt}\% \text{ Sn}$$

$$C\alpha = 11 \text{ wt}\% \text{ Sn}$$

$$C\beta = 99 \text{ wt}\% \text{ Sn}$$

The relative amount of each phase:

$$W\alpha = S / (R+S)$$

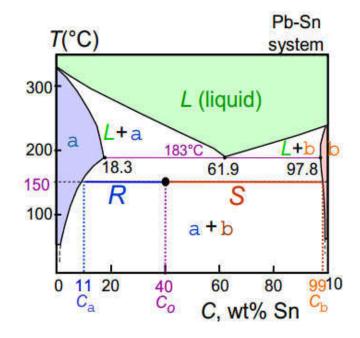
$$W\alpha = (C\beta - Co) / (C\beta - C\alpha)$$

$$W\alpha = (99 - 40) / (99 - 11) = 67\% \text{ wt}$$

 $W\beta = R / (R+S)$

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

$$W\beta = (40 - 11) / (99 - 11) = 33\% wt$$



Example (2): **Pb-Sn Eutectic System**; For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find:

- 1. The phases present.
- 2. Compositions of phases
- 3. The relative amount of each phase

Solution:

The phases present:

$$L + \alpha$$

Compositions of phases:

$$C_0 = 40 \text{ wt}\% \text{ Sn}$$

$$C\alpha = 17 \text{ wt}\% \text{ Sn}$$

$$C_L = 46 \text{ wt}\% \text{ Sn}$$

The relative amount of each phase:

$$W\alpha = S / (R+S)$$

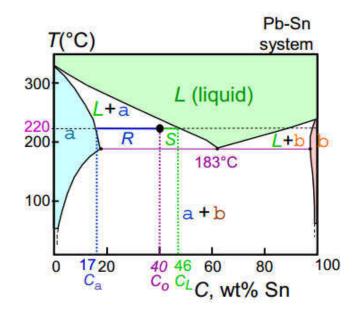
$$W\alpha = (C_L - C_O) / (C_L - C_\alpha)$$

$$W\alpha = (46 - 40) / (46 - 17) = 21\%$$
 wt

$$W_L = R / (R+S)$$

$$W_L = (Co - C\alpha) / (C_L - C\alpha)$$

$$W_L = (40 - 17) / (46 - 17) = 79\% \text{ wt}$$



Amounts Just above T_E:

Example: 40%Sn

$$C\alpha = 18.3 \text{ wt}\% \text{ Sn}$$

$$CL = 61.9 \text{ wt}\% \text{ Sn}$$

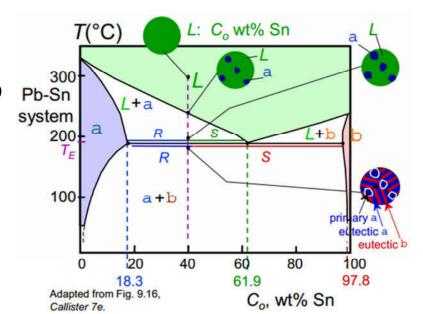
$$W\alpha = S/(R+S)$$

$$W\alpha = (C_L - C_O) / (C_L - C\alpha)$$

$$W\alpha = (61.9 - 40) / (61.9 -$$

$$18.3) = 50\%$$

$$WL = 1 - W\alpha = 50\%$$



Amounts Just below T_E:

$$C\alpha = 18.3 \text{ wt}\% \text{ Sn}$$

$$C\beta = 97.8 \text{ wt}\% \text{ Sn}$$

$$W\alpha = S/(R+S)$$

$$W\alpha = (C_{\beta} - C_{O}) / (C_{\beta} - C_{\alpha})$$

$$W\alpha = (97.8 - 40) / (97.8 -$$

$$18.3) = 73\%$$

$$W\beta = 1$$
- $W\alpha = 27\%$

Example: You start with 10 kg solution of 10 wt% Sn - 90 wt% Pb at 200 $^{\circ}C$ a)How many phases do you have?

1, α phase

b)You continue to heat. At which temp will the first liquid appear? What is the wt% of Pb in this first liquid?

Around 280 °C. 78 wt% Pb

c)You start to cool your solution. At which temp the first β phase appears?

Around 150 °C

d)At 100 °C what is the amount in kg of the α phase? What is the amount of the β phase?

Using the lever rule to find the amount of β :

$$W\beta = (10 - 5) / (98 - 5) = 5\% \times 10 \text{ kg} = 0.5 \text{ kg}$$

e) What is the wt% Pb of the α and β phase at 100°C?

95% and 2% respectively

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,

$$L + \alpha \leftrightarrow \beta$$

