



University of
South Australia

ENR116 Engineering Materials

Module 3 Metals

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- My name is Drew Evans, and welcome to Module 3 – Metals



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ENR116 – Mod. 3- Slide No. 2

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Binary phase diagrams

- This presentation will cover Binary Phase Diagrams



Intended Learning Outcomes

At the end of this section, students will be able to:-

- Understand how a **phase diagram** is used to describe the mixing of two elements
- Recognise what a **phase** is and how many are present under any particular set of conditions.
- Calculate the relative amount of the **phases** present, and the **composition** of those **phases**.

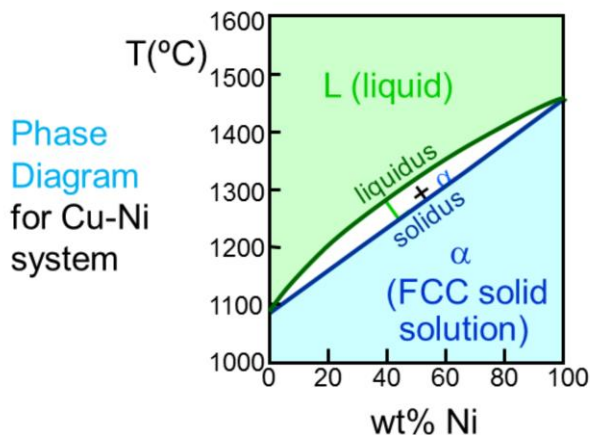
By the end of this presentation, you should be able to,

- Understand how a Phase Diagram is used to describe what happens when two elements are mixed
- Recognise what a Phase is, and how many Phases are present under any particular set of conditions
- Calculate the relative amount of the Phases present, and the Composition within those Phase



Phase diagrams

- Indicate phases as a function of **T**, **C**, and **P**.
- For this course: Binary systems (just 2 components) and only **T** and **C** as independent variables ($P = 1$ atm almost always).



- 2 phases:
 - L** (liquid)
 - α** (FCC solid solution)
- 3 different phase fields:
 - L**
 - L + α**
 - α**

Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

- While a Phase Diagram is presented as a function of Temperature and Composition, it is also a function of Pressure
- In this course only binary (2 component) systems will be explored, and the Pressure is almost always assumed to be 1 atmosphere
- An example of a simple binary system is the Cu-Ni system
 - In this system there are two Phases observed, L and α
 - In the Phase Diagram there are three Phase Fields (L only, L + α, and α only)
- A Phase Field is a region of the Phase Diagram where the observed Phase or Phases don't change in type, but may in Composition
- The boundary lines between neighbouring Phase Fields are defined as,
 - Liquidus at the boundary of the liquid Phase Field, above which a single L phase is observed
 - Solidus at the boundary of the solid Phase Field, below which a single solid (α in this example) phase is observed

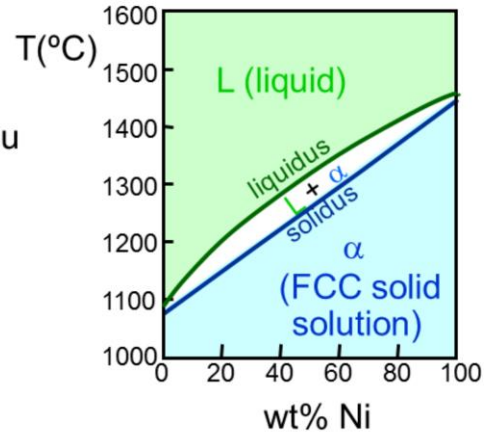


Isomorphous binary phase diagrams

Phase diagram: Cu-Ni system

System is:

1. **Binary** i.e., 2 components: Cu and Ni.
2. **Isomorphous** i.e., complete solubility of one component in another; α phase field extends from 0 to 100 wt% Ni.



Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

- The example of the Cu-Ni system has as a Phase Diagram described as an Isomorphous Binary Phase Diagram
- The term Binary refers to the presence of two components in the system
- The term Isomorphous refers to the complete liquid and solid solubility of the two components
 - That is, in the solid and liquid regions only one Phase is observed across all Compositions



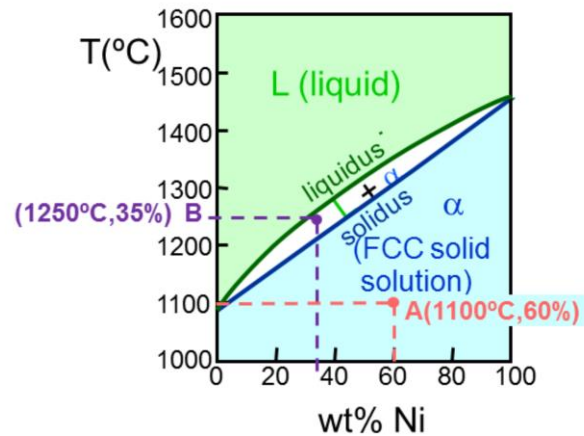
Phase diagrams: Determination of phase(s) present

Rule 1: If we know T and C_o , then we know the phase(s) that is (are) present.

Examples:

A (1100°C , 60 wt% Ni):
1 phase, α

B (1250°C , 35 wt% Ni):
2 phases, L + α



Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

- When using a Phase Diagram, if the Temperature and the Composition is known, it is possible to determine the Phase or Phases which are present
- Let's use the Cu-Ni system as an example
- To find the Phase or Phases present at 1100°C and 60 wt% Ni, horizontal and vertical lines are drawn, and the point where they intersect is noted
 - At this point, A, there is one Phase present (α)
- A similar approach can be made for 1250°C and 35 wt% Ni, with the intersection point residing in the L + α Phase Field, hence two Phases are present



Phase diagrams: Determination of phase compositions

Rule 2: If we know T and C_0 , then we can determine the composition of each phase.

Examples:

Consider $C_0 = 35 \text{ wt\% Ni}$

At $T_A = 1320^\circ\text{C}$:

Only Liquid (L) present

$C_L = C_0 (= 35 \text{ wt\% Ni})$

At $T_C = 1190^\circ\text{C}$:

Only Solid (α) present

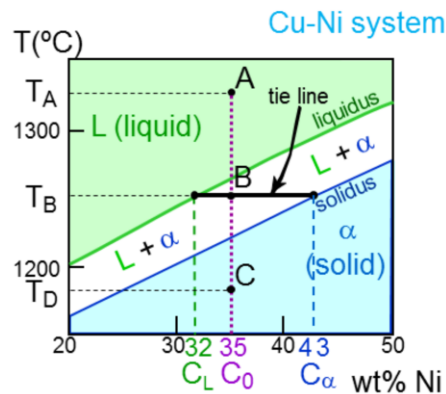
$C_\alpha = C_0 (= 35 \text{ wt\% Ni})$

At $T_B = 1250^\circ\text{C}$:

Both α and L present

$C_L = C_{\text{liquidus}} (= 32 \text{ wt\% Ni})$

$C_\alpha = C_{\text{solidus}} (= 43 \text{ wt\% Ni})$



Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

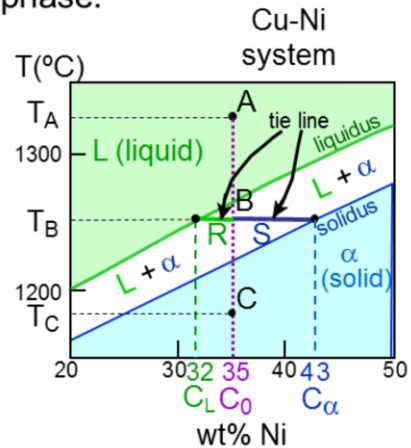
- Once the number and type of Phases have been determined, it is possible to then calculate the Composition of each of the respective Phases
- For example, consider 1320°C and 35 wt\% Ni ; Point A on the Phase Diagram
 - Only one phase is present, the L phase, with the Composition of the liquid being 35 wt\% Ni
- Similarly, consider 1190°C and 35 wt\% Ni , Point C on the Phase Diagram
 - Again, only one phase is present, the α phase, with the Composition of the solid being 35 wt\% Ni
- Now consider an intermediate point, Point B, in the $L + \alpha$ Phase Field at 1250°C and 35 wt\% Ni
 - Obviously there are two Phases present, $L + \alpha$
 - To determine the Composition of each of these phases an additional step is required
 - A tie-line is drawn at the given temperature linking the edges of the Phase Field
 - At the intersection of the tie-line with the edges of the Phase Field, vertical lines are drawn to determine the Composition of the respective Phases
 - The intersection with the liquid Phase at the Phase Field boundary gives the Composition of the L Phase, 32 wt\% Ni in this example
 - The intersection with the solid Phase at the Phase Field boundary gives the Composition of the α Phase, 43 wt\% Ni in this example
- Hence, in the two Phase region, a tie-line is used to determine the Composition of the two Phases



Phase diagrams: determination of phase weight fractions

Rule 3: If we know T and C_0 , then we can determine the phase fraction or percentage of each phase.

Examples: Consider $C_0 = 35 \text{ wt\% Ni}$



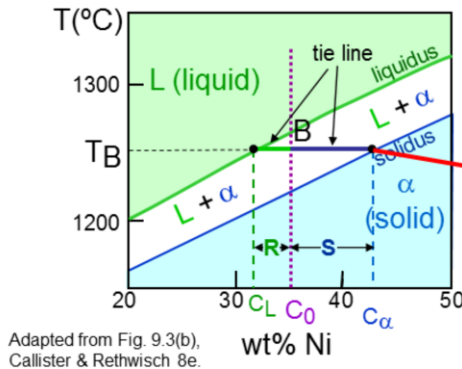
Adapted from Fig. 9.3(a), Callister & Rethwisch 8e. (Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

- Once the number, type and Composition of the Phases have been determined, it is also possible to calculate the phase fraction or percentage of the Phases present
- Again, let's examine the Cu-Ni system, at a Composition of 35 wt% Ni
- At 1320 $^{\circ}\text{C}$, Point A, there is only one Phase present and therefore a phase fraction of 1.0 is L and 0.0 is α
- At 1190 $^{\circ}\text{C}$, Point C, there is only one Phase present and therefore a phase fraction of 1.0 is α and 0.0 is L
- Now consider the two Phase region of the Phase Diagram, at 1250 $^{\circ}\text{C}$ (Point B)
 - Firstly, a tie-line is drawn to connect the edges of the Phase Field
 - Next, vertical lines are drawn through the intersection of the tie-line and the Phase Field boundary
 - The Composition of the L Phase is 32 wt% Ni, and of the α Phase is 43 wt% Ni
 - Finally, to determine the phase fraction of L and α a procedure called the Lever Rule is applied
- The Lever Rule requires the tie-line to be divided into two, from the point of interest (in this case Point B) to the Phase Field boundary
- In the example here, the tie-line for the liquid is labelled as R and for the solid as S
- The phase fraction for one Phase is calculated by taking the length of the tie-line for the other Phase and dividing by the length of the total combined tie-line
- Hence for this example, the phase fraction of the liquid Phase is determined to be 0.73 (or 73%)
- Similarly, the phase fraction of the solid Phase is determined to be 0.27 (or 27%)

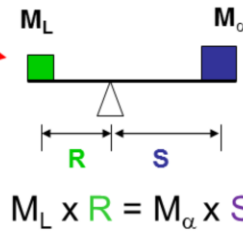


The lever rule

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 (seesaw)



$$W_L = \frac{M_L}{M_L + M_\alpha} = \frac{S}{R + S} = \frac{C_\alpha - C_0}{C_\alpha - C_L} \quad W_\alpha = \frac{R}{R + S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

- The tie-line spans the Phase Field from each boundary through the point of interest
- An alternate definition is that the tie-line connects the phases that are in equilibrium with each other
- Because the tie-line connects the phases at a constant temperature, it is sometimes called an isotherm
- The Lever Rule uses the tie-line and is an important procedure to determine the fraction of each phase present
- The term Lever Rule refers to the type of calculation used to determine the phase fractions
- The tie-line can be considered as a Lever, with a mass balanced on each end to represent the two phases
- The pivot point is placed such that its distance from the masses represent the length from the Phase Field boundary to the point of interest on the Phase Diagram
- To balance the lever, the Mass times Length is equal on both sides of the pivot point
- The phase fraction of one phase can be thought of as the mass fraction of that phase as a function of the combined mass
- Using the Mass times Length is equivalent equation, this mass fraction can be written in terms of the Length (R and S)

- Further to this, the values of R and S could be replaced with the Composition values for the mixture, C_0 , and the respective phases, C_L and C_α

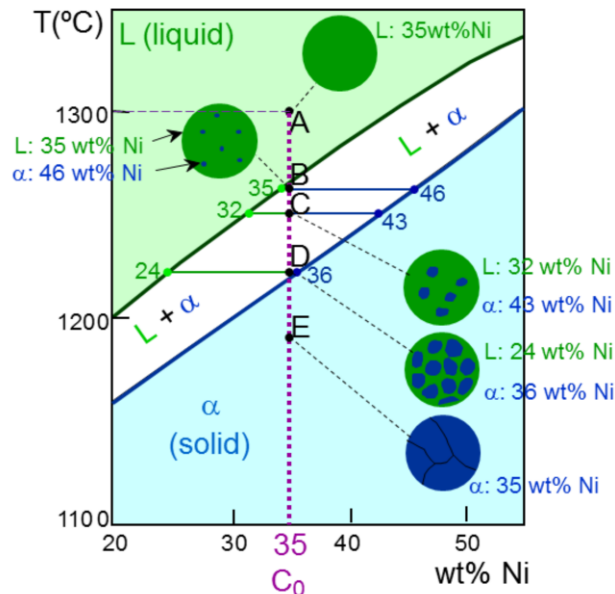


Example: Cooling of a Cu-Ni alloy

Phase diagram: Cu-Ni system

Consider microstructural changes that accompany the cooling of a

$C_0 = 35 \text{ wt\% Ni alloy}$



Adapted from Fig. 9.4, Callister & Rethwisch 8e.

- A practical example of where the tie-line is useful is examining the change in microstructure as an alloy is cooled
- Again, at 35 wt% Ni, the alloy is first examined at 1300°C, at which point it is a liquid at 35 wt% Ni
- This alloy is then cooled until it just transitions through the Phase Field boundary into the L + α region at Point B
- Using a tie-line the L and α Phases are determined to be 35 and 46 wt% Ni respectively, with the phase fraction of L being approximately 1.0
- This alloy is then cooled to Point C, and the tie-line reveals that the L and α Phases are 32 and 43 wt% Ni respectively, with the phase fraction of L being 0.73
- At point D the tie-line shows the L and α Phases to be 24 and 36 wt% Ni respectively, with the phase fraction of L now only 0.08
- Further cooling results in the alloy transitioning through the Phase Field boundary into the single solid Phase region, and a 35 wt% Ni α Phase is observed



Cored vs. equilibrium structures

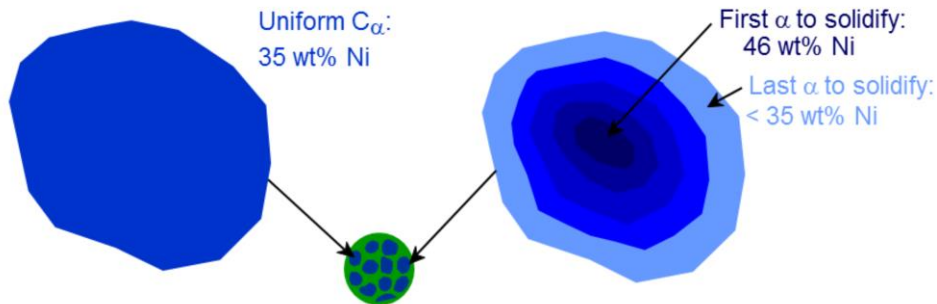
C_α changes as we solidify. Cu-Ni case:

First α to solidify has $C_\alpha = 46$ wt% Ni.

Last α to solidify has $C_\alpha = 35$ wt% Ni.

Slow rate of cooling:
Equilibrium structure

Fast rate of cooling:
Cored structure

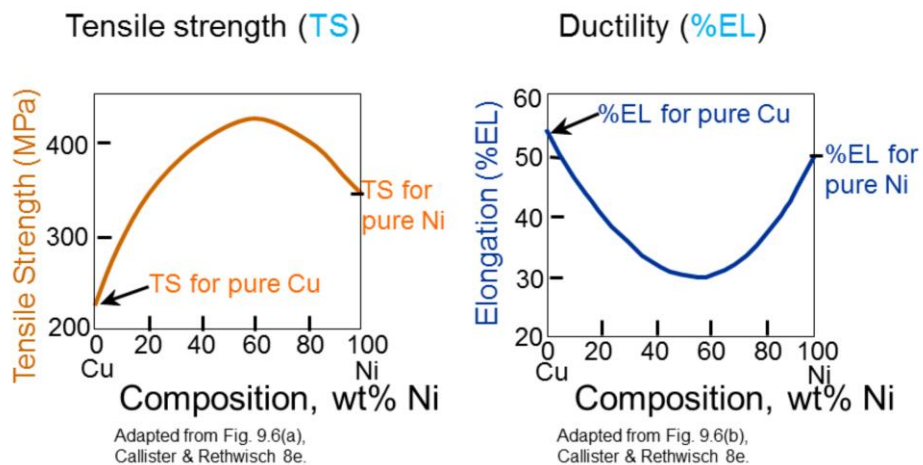


- An interesting point to note with the Compositions of the α or L Phases as the alloy was cooled was that it changed as the alloy progressed through the different points
- As the alloy transitioned through the Liquidus line, the Composition of the α Phase was 46 wt% Ni
- Once the alloy transitioned through the Solidus line, the Composition of the α Phase was 35 wt% Ni
- As the alloy cools, grains or particles of the solid α Phase begin to form
- Under slow cooling rates, the grains or particles equilibrate in Composition such that the whole grain or particle has a uniform Composition
- What happens if the cooling rate is increased?
- Because the alloy is rapidly cooled, there is not enough time for the grains or particles to reach an equilibrium Composition
- Each grain or particle has a gradient in Composition from its core to its outer shell



Mechanical properties: Cu-Ni system

Effect of **solid solution strengthening** on:



- A feature of Isomorphous Binary alloys is that their mechanical properties can change as a function of Composition, even though only one solid Phase is observed (for the Cu-Ni system this is the α Phase)
- Represented here are the Tensile Strength and Ductility of the Cu-Ni alloys with changing Composition, at temperatures below the Solidus line
- Increasing the wt% Ni in the alloy from low values to around 60 wt% yields almost a doubling in tensile strength and over 20% elongation reduction
- This increase in strength of the alloy is known as Solid Solution Strengthening
- The strength of the solid solution is increased by controlling the alloy's Composition



Binary-eutectic systems

2 components

has a special composition with a min. melting T.

Example: Cu-Ag system

3 single phase regions: (L, α , β)

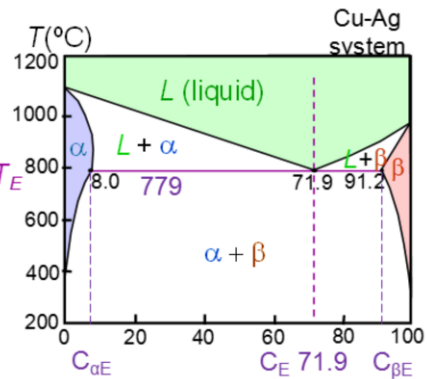
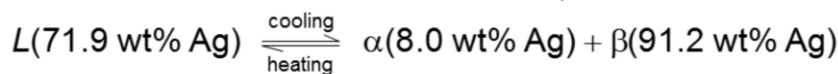
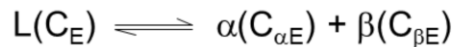
C_E : Composition at temperature T_E

Limited solubility:

α : mostly Cu

β : mostly Ag

Eutectic reaction



Adapted from Fig. 9.7, Callister & Rethwisch 8e.

- In addition to the Isomorphous Binary System, another simple system is the Binary Eutectic System
- Again, the term Binary refers to the system being made from two components or elements
- The term Eutectic refers to the system having a special Composition where a minimum melting Temperature is observed
- This point is interesting because slightly more complex microstructural change is observed compared to the simple Isomorphous Binary System
- The complex microstructural change occurs because the two elements being mixed have limited solubility in each other
- An example of this system is the Cu-Ag system
- Three single Phases are observed, a liquid Phase, a Cu rich Phase (α) and a Ag rich Phase (β)
- The point of minimum melting Temperature on the Phase Diagram is known as the Eutectic point
- Where the word Eutectic means “easily melted”
- This point exists at a fixed Composition
- In the example here this is at 71.9 wt% Ag and a Temperature of 779°C
- A transition through this Eutectic Point is described by the Eutectic Reaction
- The Eutectic Reaction is defined as a Liquid transforming into a two Phase solid, and vice versa
- The Composition of the Liquid Phase at the Eutectic Point is labeled as C_E
- The Composition of the α Phase at the Eutectic Point is labeled as $C_{\alpha E}$
- The Composition of the β Phase at the Eutectic Point is labeled as $C_{\beta E}$
- These Compositions are determined by using a tie-line, just like in the Isomorphous Binary System
- For the Cu-Ag system, this yields C_E of 71.9 wt% Ag, $C_{\alpha E}$ of 8.0 wt% Ag and $C_{\beta E}$ of 91.2 wt% Ag
- This highlights how the single Phase Liquid at 71.9 wt% Ag can be cooled to form a two Phase Solid having both Cu-rich and Ag-rich phases
- These two solid phases exist because of the limited solubility of the two elements in each other

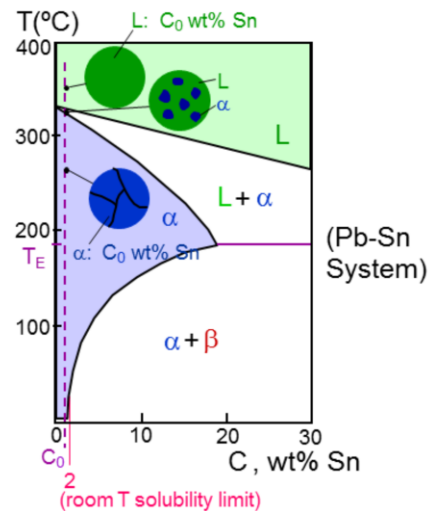


Microstructural developments in eutectic systems I

For alloys for which

$$C_0 < 2 \text{ wt\% Sn}$$

Result: at room temperature
alloy is polycrystalline with
grains of α phase having
composition C_0



Adapted from Fig. 9.11,
Callister & Rethwisch 8e.

- In the Binary Eutectic System interesting microstructural change can be observed at other Compositions than the Eutectic Composition
- To highlight this, another Binary Eutectic System will be used, the Pb-Sn system
- In this system, at Compositions less than 2 wt% Sn, cooling the alloy from the Liquid Phase transitions into the L + α Phase (α particles in L) and then into the α only Phase at the same Composition as the Liquid
- This is because at such low Compositions of Sn, the alloy is below the solubility limit of the Sn in Pb at room Temperature

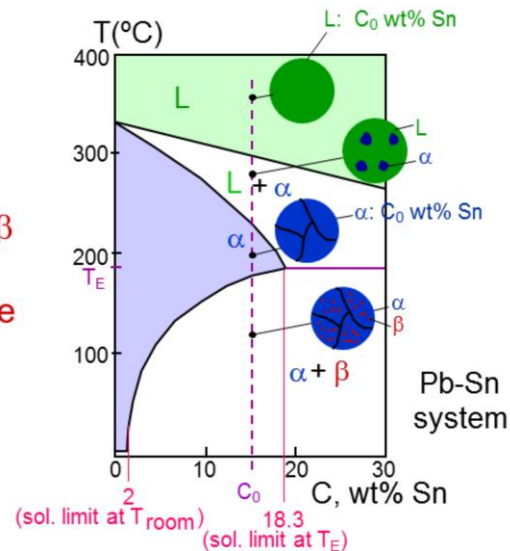


Microstructural developments in eutectic systems II

For alloys for which

$$2 \text{ wt\% Sn} < C_0 < 18.3 \text{ wt\% Sn}$$

Result: at temperatures in $\alpha + \beta$ range alloy is polycrystalline with α grains and small β -phase particles.



Adapted from Fig. 9.12,
Callister & Rethwisch 8e.

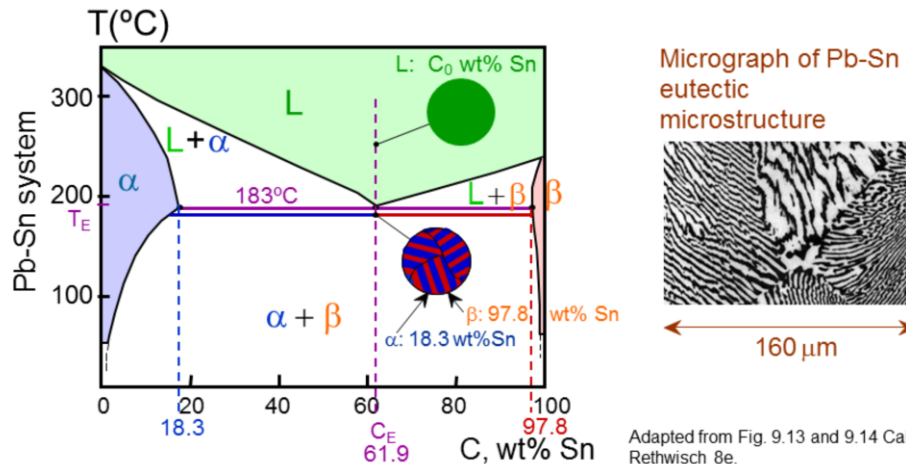
- Let's now look at the microstructural change at Compositions above the room Temperature solubility limit of Sn in Pb, but below the Composition of α at the Eutectic Point
- Cooling from the Liquid yields the same $L + \alpha$ Phase Field, and then to the α only Phase
- However, further cooling reduces the solubility of the Sn in the Pb, and therefore grains rich in Sn begin to precipitate
- This then yields a majority Phase of α (Pb-rich) with grains of β (Sn-rich)
- The microstructure observed here is due to the limited solubility of the two elements in each other



Microstructural developments in eutectic systems III

For alloy of composition $C_0 = C_E$

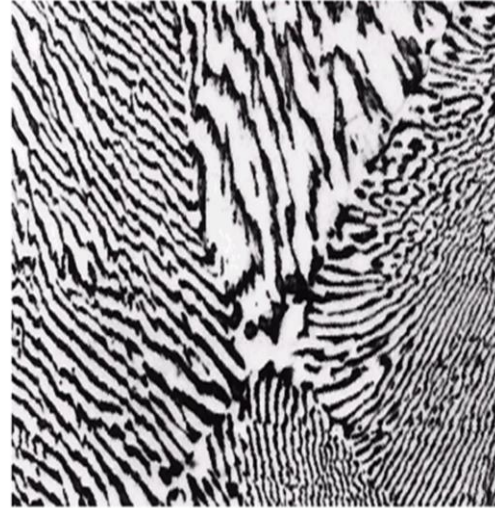
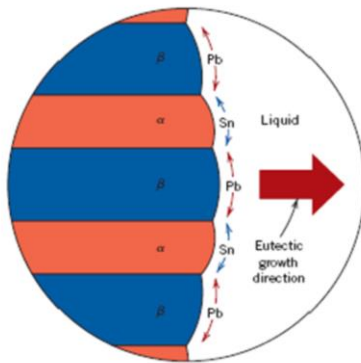
Result: Eutectic microstructure (**lamellar structure**), alternating layers (**lamellae**) of α and β phases.



- At the lower Compositions, the microstructure has evolved from a Liquid, to a Liquid plus Solid, and then a mixed solid Phase of two different solids
- At the Eutectic Point, the microstructural change upon cooling goes straight from the Liquid to the mixed solid Phase
- The microstructure is not observed as grains of one Phase dispersed within another, but lamellar structure
- The lamellar structure has alternating layers, known as lamellae, of each of the different solid Phases
- Using the tie-line, the Composition of each of the Phases within the lamellae can be determined
 - In this case, α at 18.3 wt% Sn and β at 97.8 wt% Sn
- An example micrograph shows what this lamellar structure looks like, where boundaries between grains are still observed, though within each grain the lamellae are clearly visible



Lamellar eutectic structure



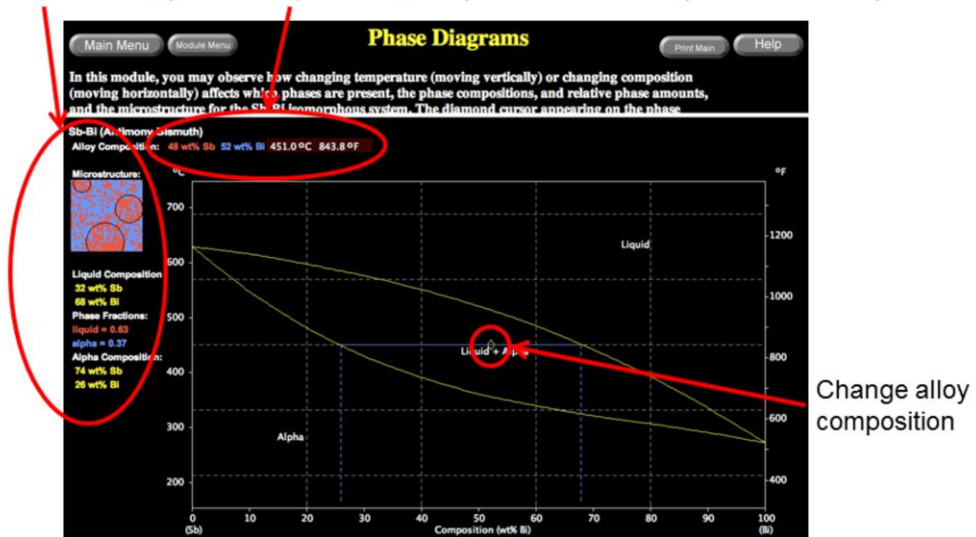
Adapted from Figs. 9.14 & 9.15, Callister & Rethwisch 8e.

- The growth of the lamellar structure occurs parallel to the originally formed lamellae, which propagates the sheet like structure
- The atoms required to form the lamellae are supplied from the liquid at the liquid-eutectic interface
- In the liquid close to this interface, the appropriate elements diffuse towards the matching lamellae, as indicated by the arrows in the schematic
- The reason for the layer structure is because this configuration requires the atoms to diffuse over very short distances



VMSE: Interactive phase diagrams

Microstructure, phase compositions, and phase fractions respond interactively



- Rather than manually “handling” a Phase Diagram by drawing in the appropriate tie-lines and measuring the lengths for the Lever Rule, it is possible to use Interactive Phase Diagrams
- An Interactive Phase Diagram has all the Phase Field information incorporated into an interactive piece of software
- The user then only needs to enter in the appropriate Composition and Temperature, and the software then calculates the Compositions of each Phase, and their phase fraction
- Microstructural changes can be observed by varying the Temperature and/or Composition



Summary

- Phase diagrams can identify; the **phases**, their **composition** and **weight fraction** given the temperature and composition.
 - The **microstructure** of an alloy depends on its **composition**, and whether or not the **cooling rate** allows for maintenance of equilibrium.
-
- In summary,
 - From a Phase Diagram, knowing the Composition and Temperature, it is possible to determine the Phases present, their Composition and their Phase Fraction
 - The microstructure of the alloy not only depends on the Composition, but also on the rate of cooling to room temperature
 - Slow cooling rates allow for the alloy to equilibrate in Composition
 - Fast cooling rates yield gradients in Composition within the microstructure



Thank you

- This concludes the presentation on binary phase diagrams
- If you have any questions or desire further clarification please post a question or comment on the ENR116 Discussion Forum
- For further reading, please consult the course text, specifically chapter 9