Basics of Materials Engineering
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Lecture – 56
Phase Diagrams (Tie Line, Lever Rule, Identification of compositions and weight fractions in two-phase regions)

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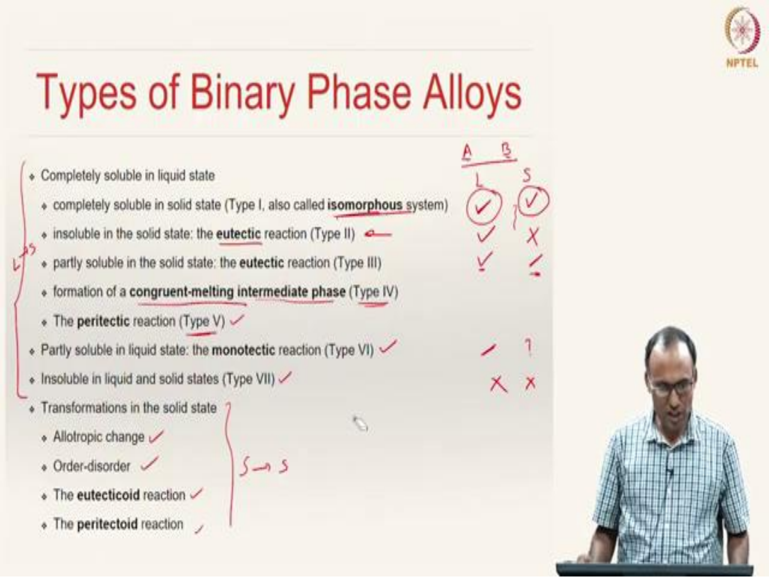

Types of Binary Phase Alloys

- Completely soluble in liquid state
  - completely soluble in solid state (Type I, also called **isomorphous** system)
  - insoluble in the solid state: the **eutectic** reaction (Type II)
  - partly soluble in the solid state: the **eutectic** reaction (Type III)
  - formation of a **congruent-melting intermediate phase** (Type IV)
  - The **peritectic** reaction (Type V)
- Partly soluble in liquid state: the **monotectic** reaction (Type VI)
- Insoluble in liquid and solid states (Type VII)
- Transformations in the solid state
  - Allotropic change
  - Order-disorder
  - The **eutecticoid** reaction
  - The **peritectoid** reaction

Welcome back. In the last class, we have looked at the different types of binary phase alloys that we will be discussing in this course. We have classified them as 7 different types. In this class, we will discuss the types of binary phase alloys, followed by solid-state phase transformation. We will finally spend some time understanding an important phase diagram, called as the iron-iron carbide equilibrium diagram.

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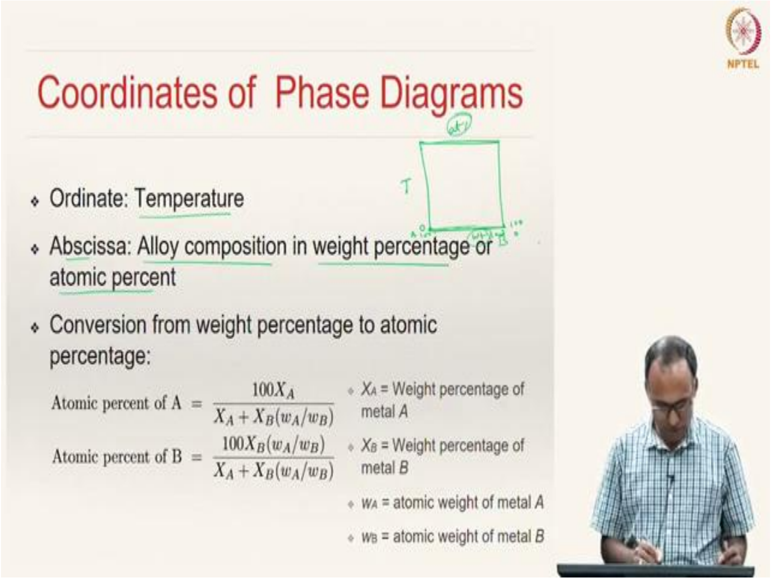

Coordinates of Phase Diagrams

- Ordinate: Temperature
- Abscissa: Alloy composition in weight percentage or atomic percent
- Conversion from weight percentage to atomic percentage:

$$\text{Atomic percent of A} = \frac{100X_A}{X_A + X_B(w_A/w_B)}$$

$$\text{Atomic percent of B} = \frac{100X_B(w_A/w_B)}{X_A + X_B(w_A/w_B)}$$

- X_A = Weight percentage of metal A
- X_B = Weight percentage of metal B
- w_A = atomic weight of metal A
- w_B = atomic weight of metal B

Before we actually start looking at phase diagrams, we need to see how these phase diagrams are drawn. Here, we have two variables, temperature and composition. Temperature and alloy composition are plotted on the y and x axes, respectively. The alloy composition can be written either in weight percentage or atom percentage. We already know how to convert from weight percentage to atom percentage, and vice-versa.

A typical phase diagrams looks something like this. On the y-axis, you have temperature and on the x-axis, you have weight percentage. How is it drawn?

Suppose if you have weight percentage of say element B -- so that means, here element B is 0% i.e., element A is 100% and here element B is 100% i.e., element A is 0%. Usually only one variable is shown, element B or element A, and then we are going from $0 - 100$ weight percent.

Many times, on the same phase diagram, you will use the top x-axis for atom percent. So, the same phase diagram can be read both in weight percentage as well as atom percentage.

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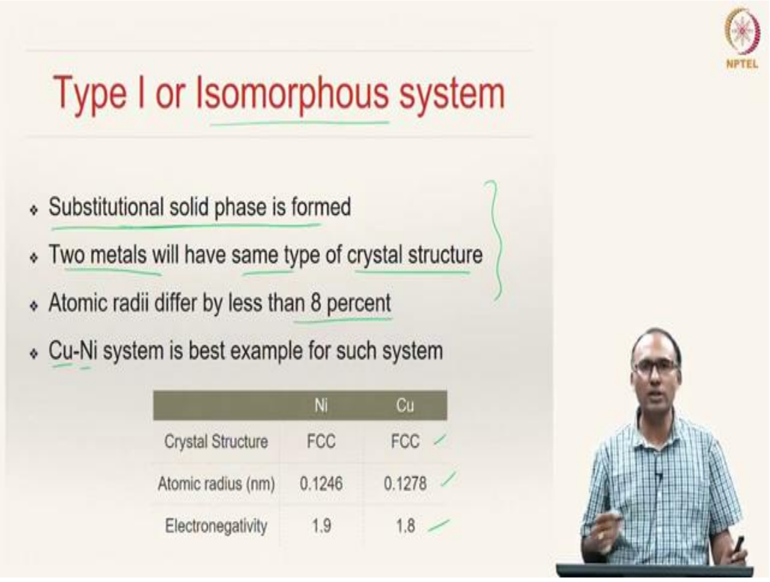

Type I or Isomorphous system

- Substitutional solid phase is formed
- Two metals will have same type of crystal structure
- Atomic radii differ by less than 8 percent
- Cu-Ni system is best example for such system

	Ni	Cu
Crystal Structure	FCC	FCC ✓
Atomic radius (nm)	0.1246	0.1278 ✓
Electronegativity	1.9	1.8 ✓

Now, we will look at Type I or isomorphous alloys. Isomorphous alloys are the ones which have complete solubility in solid state as well as liquid state. As we have looked at the Hume Rothery's rules, 100% solubility is possible only when the atoms are of similar sizes.

When the atoms are of similar sizes, it is more probable to form a substitutional solid solution. Forming an interstitial solid solution is very difficult because we need to create lot of distortion amongst the interstitial location, owing to the larger size of the atom.

Hence, usually, all isomorphous systems are substitutional solid solutions. Because it has 100% solubility, according to Hume Rothery's principles, you should have both the metals with the same crystal structure and atomic radii difference should be less than 8%.

With all these characteristics, a very good example of an isomorphous system is copper-nickel system. Why do copper and nickel form an isomorphous alloy system? Both have an FCC crystal structure, their atomic radii are very close - 0.1246 and 0.1278, i.e., less than 8% difference, and their electronegativity values are also very close; that is also another requirement for having 100% solubility. Hence, copper-nickel system is a very good example or model system for understanding isomorphous alloys.

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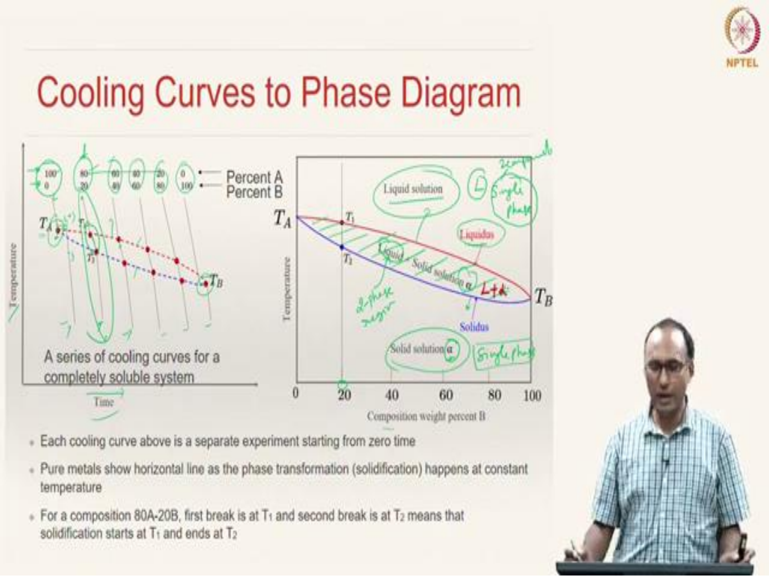

Cooling Curves to Phase Diagram

- Each cooling curve above is a separate experiment starting from zero time
- Pure metals show horizontal line as the phase transformation (solidification) happens at constant temperature
- For a composition 80A-20B, first break is at T_1 and second break is at T_2 means that solidification starts at T_1 and ends at T_2

In this course, we will start trying to understand phase diagrams from cooling curves right away. On the left-hand side in this graph, you have temperature as a function of time. Here, the top line represents weight fraction of A, and bottom line represents weight fraction of B. When the pure metal A, i.e., 100% A is cooled from a very high temperature which is in liquid state, it reaches its solidification temperature T_A. Let us say metal A has higher melting point than metal B.

As soon as it reaches its solidification temperature, it solidifies at a constant temperature, releasing latent heat of solidification. From here to here, it takes this much time for solidification and then after complete solidification occurs, further cooling down takes place in the solid state. So, here you have liquid and here liquid to solid and here you have solid.

Similarly, the same thing happens for pure metal B. The pure metal B when it reaches its solidification temperature T_B, solidifies at constant temperature and then, further cooling down happens in the solid state.

Solidification occurs at a constant temperature only for pure metals. If you take any alloy in between, for example combinations such as 80-20, 60-40, 40-60, 20-80 etc., because it is not a pure material, the solidification starts at a temperature -- because here the solvent is A, and hence the solidification starts at a temperature just below T_A, but close to T_A, say T_1 and then ends at a temperature T_2.

For alloys which are not pure, solidification happens over a range of temperature, rather than happening at constant temperature. For different alloys, the solidification starts at a different temperature and ends at a different temperature and so on. As you move from left to right, the solidification temperature will be going closer to the solidification temperature of B.

Please note that although here we are showing time, each of this cooling curves is an independent experiment and the time for each of them is 0 here. Just to show it on the same graph, we have shown it this way. The red dashed line represents the solidification starting and the blue one represents the solidification ending. We know that for a pure material, solidification starts and ends at same temperature; but for any alloy in between A and B, you will have a solidification happening over a range of temperatures.

Now if you would plot the same thing on temperature-composition diagram -- here we are showing -- because it is time, it is slanted, but let us now assume that there is sufficiently long time that is given for this solidification to happen, so that the solidification is happening such that at each and every instance, equilibrium is maintained.

Let us now remove time from the picture and draw temperature versus composition. At a given composition for 80-20, the solidifications happen over a range of temperature; the composition remains the same - that is why this is a vertical line. This vertical line basically represents this process. Why is it vertical here? Because the composition is fixed. Similarly, if you draw for different ones, then you see that red curve is representing the boundary between liquid state to solid state.

Because above this, it is liquid, below this is solid, right? So, this is the solidification start temperature and solidification end temperature position. This red line is called liquidus; this is the boundary between liquid state and solid state. Above this, everything is a liquid solution, represented as L -- and below this blue line, everything is solid, because the solidification is completed -- and below this everything is solid solution. In phase diagram terminology, all the solid solutions are represented by Greek letters - α, β, γ. Whenever you see a Greek letter on a phase diagram, then it must be a solid solution.

This line red line is called liquidus line, this blue line is called solidus line. Liquidus line is the line above which everything will be in liquid state. Solidus line is the boundary below which all the phases will be in solid state. Here, you have a liquid solution which is completely soluble; that means, A and B are completely soluble in each other; so, this is a single-phase region.

Here you have a single solid solution phase -- please note that this is single phase region, but it may have two components. Here also, it is single phase α-phase; that means, a homogenous phase with two components. So, the solid solution is of A and B.

This region here is a two-phase region because there are liquid and solid solutions.

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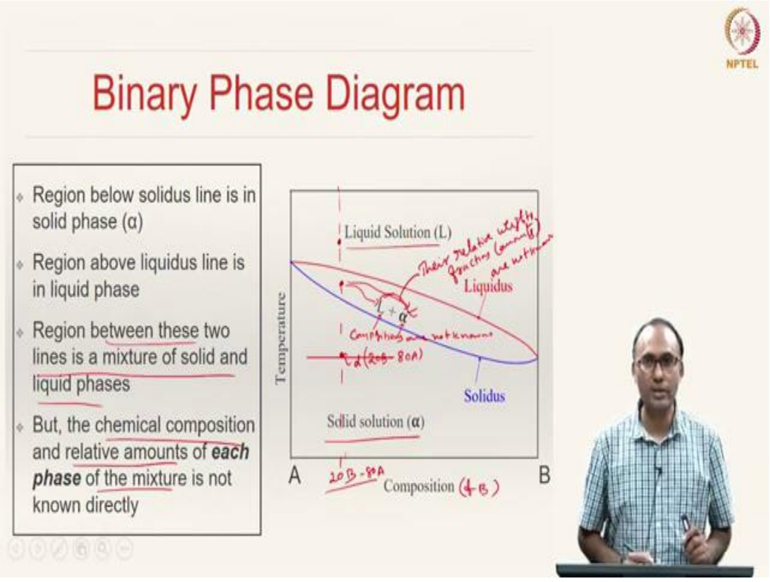

Binary Phase Diagram

- Region below solidus line is in solid phase (α)
- Region above liquidus line is in liquid phase
- Region between these two lines is a mixture of solid and liquid phases
- But, the chemical composition and relative amounts of ***each phase*** of the mixture is not known directly

So, here I am summarizing -- the region below the solidus line is called solid phase, the region above the liquidus line is called liquid phase, and the region between these two lines is a two-phase region, a mixture of liquid solution and a solid solution alpha.

Suppose if you are looking at this particular alloy composition, we know that liquid solution has a composition let us say 20% B and 80 A -- here the composition is known because it is a single liquid solution.

Here also it is a single-phase solid solution α, which has a composition of 20% B – 80% A. But now here, it is a two-phase region; there are several things that we do not know. What is it that we do not know? You have a liquid solution and you have a solid solution. The composition of the liquid solution and the composition of the solid solution are not known. Will they be same or will they be different?

The second thing is the weight fraction of liquid and solid phases, i.e., their relative weight fractions or relative amounts are not known. The region between these two lines is a mixture of solid and liquid phase, but the chemical composition and relative amounts of each phase of the mixture is not known directly – we need to find out.

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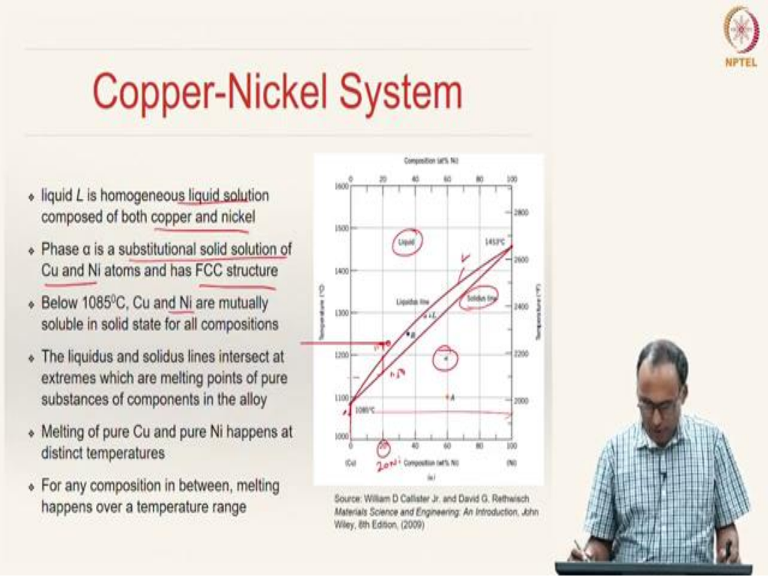

Copper-Nickel System

- liquid *L* is homogeneous liquid solution composed of both copper and nickel
- Phase α is a substitutional solid solution of Cu and Ni atoms and has FCC structure
- Below 1085⁰C, Cu and Ni are mutually soluble in solid state for all compositions
- The liquidus and solidus lines intersect at extremes which are melting points of pure substances of components in the alloy
- Melting of pure Cu and pure Ni happens at distinct temperatures
- For any composition in between, melting happens over a temperature range

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Here, we are showing the phase diagram of copper-nickel system. Copper is a low melting alloy and nickel is a high melting alloy. Previously we have seen the phase diagram this way; instead of plotting the low melting point alloy on the right-hand side, if you plot it on left-hand side, this is how it looks like.

This is copper-nickel alloy system and in this, the liquid L region is a homogenous liquid solution composed of both copper and nickel. α-phase is a substitutional solid solution of copper and nickel atoms and it also has FCC structure. Below $1085°$ C, both copper and nickel are mutually soluble in solid state for all compositions.

If we take heat pure copper, melting happens at constant temperature. Same applies for pure nickel. However, for any alloy, melting happens over a range of temperatures. For instance, this particular alloy which is 20% nickel, melting occurs approximately over the range of temperatures $1150° - 1190°$ C.

This is the liquidus and this is the solidus line; they intersect at extremes which are the melting points of the components/pure substances.

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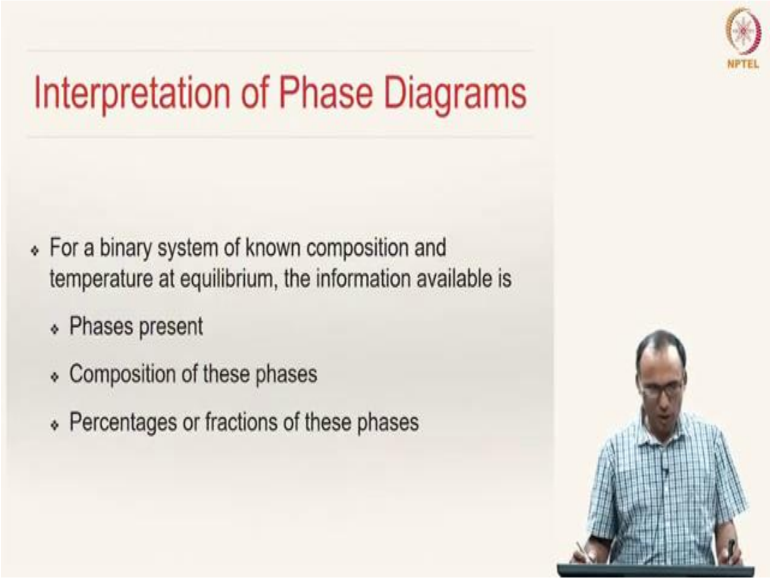

Interpretation of Phase Diagrams

- For a binary system of known composition and temperature at equilibrium, the information available is
  - Phases present
  - Composition of these phases
  - Percentages or fractions of these phases

How do we go about the interpreting the phase diagrams? For a binary system of known composition and temperature at equilibrium, we have the following information. What is the information that we have? For a given composition and a temperature, we know what are the phases present - whether it is a single phases region - if it is a single phases region, whether it is liquid phase or solid phase or is it a two-phase region.

If it is single phase region, the composition of the phases is known; but if it is a two-phase region, of course we need to find out what are the compositions of these individual phases and what are the percentage or fractions or amounts of the individual phases.

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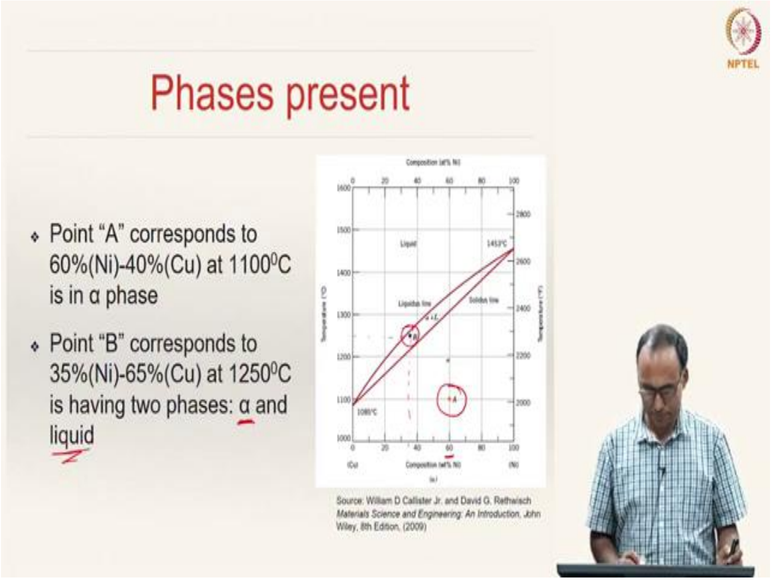

Phases present

- Point "A" corresponds to 60%(Ni)-40%(Cu) at 1100^{0}C is in α phase
- Point "B" corresponds to 35%(Ni)-65%(Cu) at 1250^{0}C is having two phases: α and liquid

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

For instance, in this phase diagram, you see the point A which corresponds to 60% nickel, 40% copper at $1100°$ C, and is in α-phase -- it is a single-phase region. However, point B here, corresponds to about 35% nickel, 65% copper at $1250°$ C, but having two phases - alpha and liquid solution.

Again, liquid refers to the liquid solution -- it is not pure copper or pure nickel -- it is the solution of copper and nickel. So, you have α-phase and liquid phase. There are two phases that are present at B.

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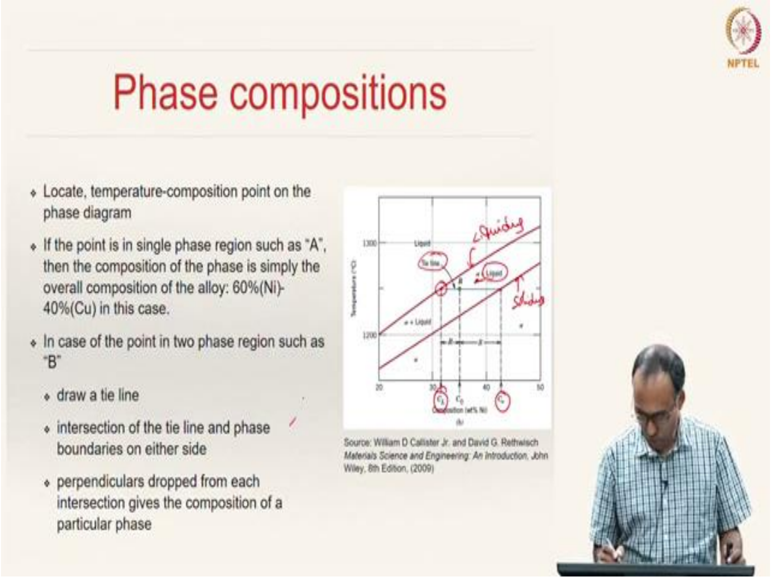

Phase compositions

- Locate, temperature-composition point on the phase diagram
- If the point is in single phase region such as "A", then the composition of the phase is simply the overall composition of the alloy: 60%(Ni)-40%(Cu) in this case.
- In case of the point in two phase region such as "B"
  - draw a tie line
  - intersection of the tie line and phase boundaries on either side
  - perpendiculars dropped from each intersection gives the composition of a particular phase

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009) And now, what are the compositions of these phases? So, in the two-phase region at B you have alpha and liquid - what is the composition? The way that one needs to find the composition is, at 1250° C, you draw a horizontal line that represents the constant temperature line, called as the tie line - the horizontal line that is drawn in the two-phase region is the tie line and wherever this tie line hits the liquidus, you drop a vertical and that represents composition of the liquid phase that is present.

Wherever this tie line hits the solidus, drop a vertical - that represents the solid phase -- composition of the alpha phase present. That is how we can find out the compositions of the phases; that is what we have clearly written here. So, you can go through the text later.

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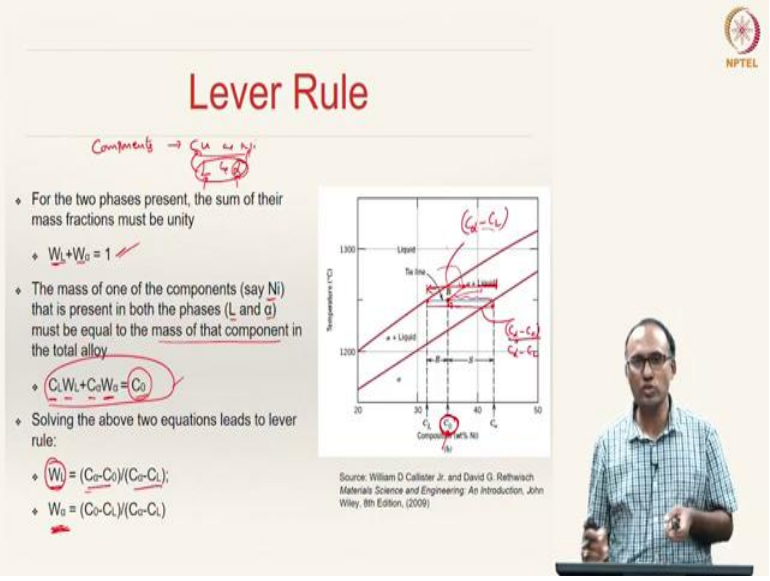

Lever Rule

Components → Cu & Ni
L & α

- For the two phases present, the sum of their mass fractions must be unity
  - $W_L+W_\alpha = 1$
- The mass of one of the components (say Ni) that is present in both the phases (L and α) must be equal to the mass of that component in the total alloy
  - $C_LW_L+C_\alpha W_\alpha = C_0$
- Solving the above two equations leads to lever rule:
  - $W_L = (C_\alpha-C_0)/(C_\alpha-C_L)$;
  - $W_\alpha = (C_0-C_L)/(C_\alpha-C_L)$

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

We know the compositions, but how do we find out the fraction of liquid that is present, what is the fraction of the solid that is present? For that, we use something called lever rule. So, what is that lever rule?

For the two phases present - the liquid and alpha, sum of their mass fraction or weight fractions should be equal to 1. The weight fraction of liquid plus weight fraction of alpha solid solution must be equal to 1. In both phases you have both the components; the components are copper and nickel. This copper and nickel are present in both liquid and alpha phase.

$$W_L + W_\alpha = 1$$

Now, we are saying that the mass fraction or the mass of the component B or component A for instance in this case nickel present in both the phases must be equal to the mass of that component in the alloy, isn't it? In this alloy C_0 is the weight fraction of alloy. Then this is amount of nickel that is present in this alloy and that should have been distributed into alpha and liquid.

Then, the composition of nickel in liquid phase times weight fraction of liquid plus composition of nickel in solid phase times weight fraction of solid should be equal to the weight fraction of the nickel alloy; that is the total weight fraction of the nickel in that alloy, now that is distributed into liquid phase and solid phase.

$$\mathrm{C_L W_L + C_\alpha W_\alpha = 1}$$

Using these two equations, we can find out the weight fractions of liquid and solid.

$$\mathrm{W_L = (C_\alpha - C_0)/(C_\alpha - C_0)}$$

$$\mathrm{W_\alpha = (C_0 - C_L)/(C_\alpha - C_L)}$$

Note that $(\mathrm{C_\alpha - C_L})$ is the length of the tie line. Weight fraction of the solid will be the length of the tie line from the point where we are looking at the composition to the liquidus line. So, that is this length divided by the total length; that will give us weight fraction of the solid.

This is the methodology that one needs to adopt in the two-phase region, because there are two phases present and hence, we need to know what is the weight fraction of solid and what is the weight fraction of liquid whereas, in the single-phase region 100% will be that particular phase.

There is no reason for us to use the tie line or lever rule because there is only one phase that is present and hence all the weight fraction will be of that one and the alloy composition will be the composition of the single-phase region.

The reason why we need to do that in a two-phase region is because there are two different phases and each phase how much weight fraction is present and each phase what is the composition is something that one needs to find out.

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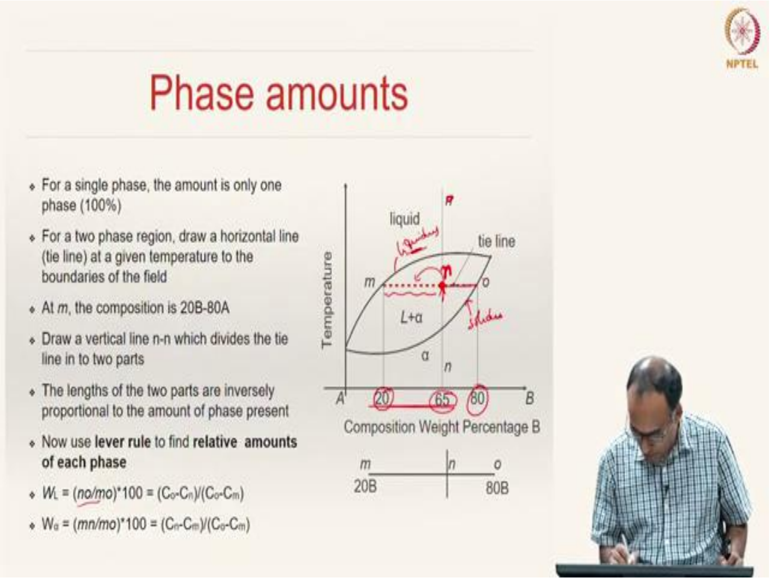

Phase amounts

- For a single phase, the amount is only one phase (100%)
- For a two phase region, draw a horizontal line (tie line) at a given temperature to the boundaries of the field
- At *m*, the composition is 20B-80A
- Draw a vertical line n-n which divides the tie line in to two parts
- The lengths of the two parts are inversely proportional to the amount of phase present
- Now use **lever rule** to find **relative amounts of each phase**
- $W_L = (no/mo)*100 = (C_o - C_n)/(C_o - C_m)$
- $W_\alpha = (mn/mo)*100 = (C_n - C_m)/(C_o - C_m)$

For example, if we are looking at 65% B situation, let us say you are interested in this point; all that you need is draw a horizontal line *mo* -- this is our liquidus line, this is our solidus line. So, the composition of liquid will be 20% B, composition of solid will be 80% B. Let us say this point is n. This is liquidus line and hence we need to take the other point. This is lever because it is like fulcrum about which it is oscillating.

$$W_L = (no/mo) * 100 = (\mathrm{C_o} - \mathrm{C_n})/(\mathrm{C_o} - \mathrm{C_m})$$

$$W_\alpha = (mn/mo) * 100 = (\mathrm{C_n} - \mathrm{C_m})/(\mathrm{C_o} - \mathrm{C_m})$$

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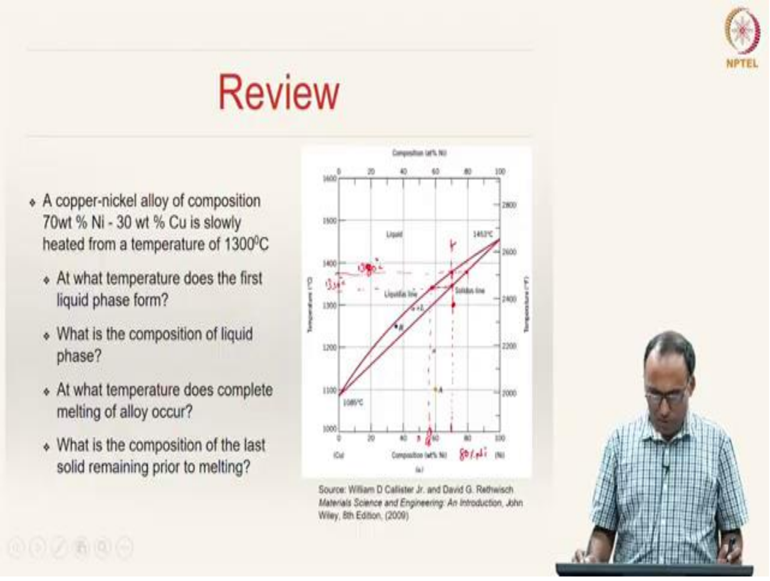

Review

- A copper-nickel alloy of composition 70wt % Ni - 30 wt % Cu is slowly heated from a temperature of 1300⁰C
  - At what temperature does the first liquid phase form?
  - What is the composition of liquid phase?
  - At what temperature does complete melting of alloy occur?
  - What is the composition of the last solid remaining prior to melting?

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009) So, let us review once again. You have a copper-nickel alloy of composition 70 weight percent nickel and 30 weight percent copper. Where is 70 weight percent nickel - that is this point. It is slowly heated from a temperature of 1300° C. Initially it is at this temperature. From that temperature, it is slowly heated.

The question is at what temperature does the first liquid phase form? Here, it is a solid state and when you are entering here, at this temperature the first liquid phase starts forming, right? So, that is about so 1330° C approximately; that is the temperature at which the liquid phase starts forming.

What is the composition of liquid phase? If you are in this region, if you draw a small tie line there, that will be the composition of the small liquid phase that is forming initially. So, that will be about 58% nickel. At what temperature does complete melting of alloy occur? If you continue to heat it up at 1380° C, the complete melting of alloy occurs and then it will be in complete liquid state. What is the composition of the last solid remaining? Just below this line will be the last solid remaining. In the two-phase region, you have to draw a tie line. So, that will be the composition of the last solid remaining which is 80% nickel.

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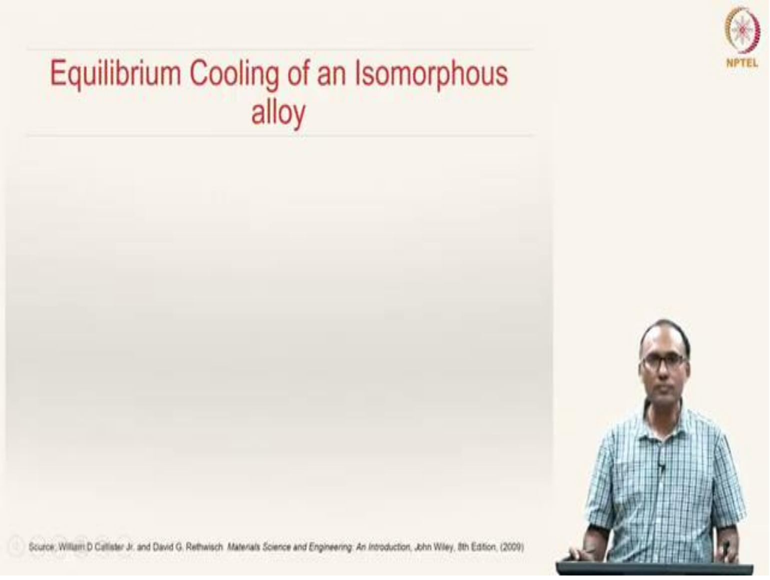

Equilibrium Cooling of an Isomorphous alloy

Source: William D Callister Jr. and David G. Rethwisch. *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

With that you can find out all the weight fractions and then compositions of an alloy.