Basics of Materials Engineering
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Lecture-59
Phase Diagrams (Type III Alloys with Partial Solubility in Solid State)

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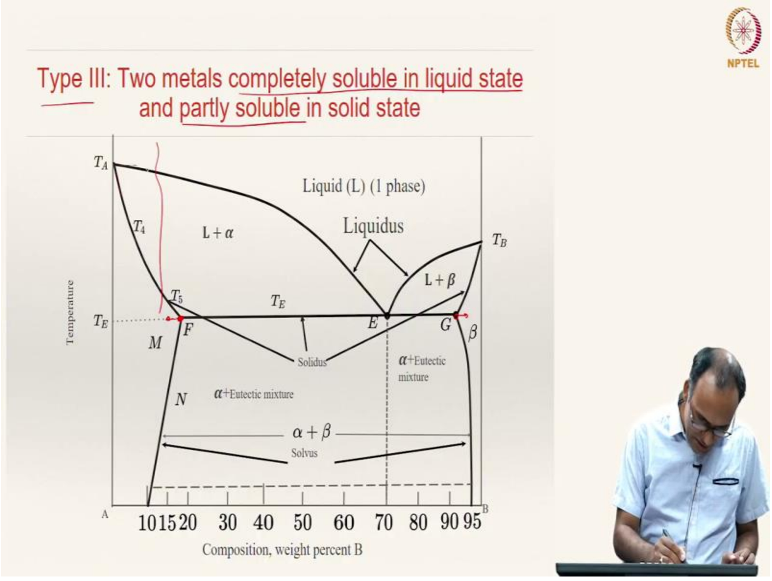

Type III: Two metals completely soluble in liquid state and partly soluble in solid state

Welcome back. In the last class, we have looked at Type II alloys and we introduced a special reaction called eutectic reaction which happens when a liquid of a certain composition reaches the eutectic temperature. Thereafter, the liquid transforms into two new solids, and such a reaction is called eutectic reaction. We also discussed why eutectic reaction cannot be considered as a congruent solidification - it is incongruent in nature.

The way that Type II alloys are classified are based on the solidification in the solid state. In the solid state, they are completely insoluble; that means, two materials A and B are completely insoluble in solid state, while they are completely soluble in liquid state.

Let us relax the constraint on the solubility in the solid state and instead of saying complete insolubility in solid state, let us say, what happens if there is partial solubility in solid state, while complete solubility is there in the liquid state. That is what we are calling as Type III alloys, where the two materials are completely soluble in liquid state and partially soluble in solid state. There is a solubility limit of A in B and B in A.

The phase diagram of such a system looks something like this. This phase diagram is a special case or the Type II alloy is a special case of this phase diagram. In the phase diagram, if you move point G towards right and point F towards left, it looks exactly similar to the phase diagram of Type II alloy.

Otherwise, if you look at the liquidus line and the solidus line, in this region, it looks like the isomorphous alloys where they will meet at some other point. This situation is somewhere in between the Type I and Type II alloys that we are seeing here.

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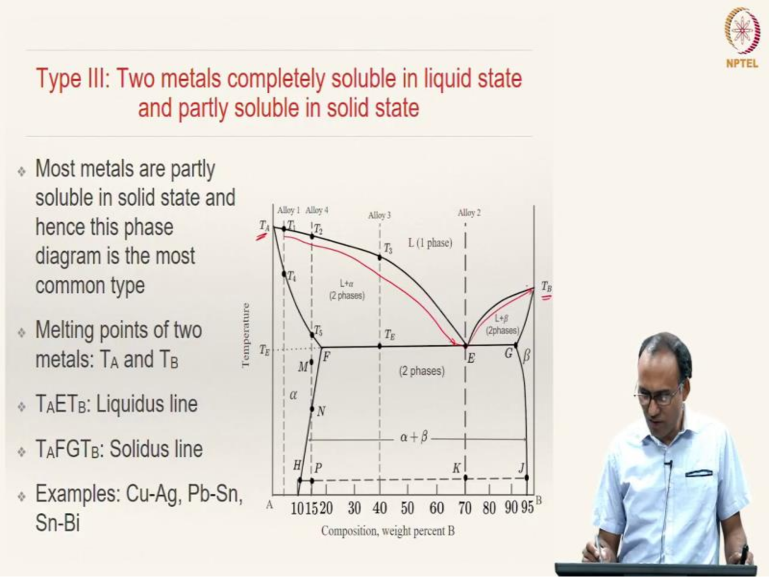

Type III: Two metals completely soluble in liquid state and partly soluble in solid state

- Most metals are partly soluble in solid state and hence this phase diagram is the most common type
- Melting points of two metals: T_A and T_B
- T_AET_B: Liquidus line
- T_AFGT_B: Solidus line
- Examples: Cu-Ag, Pb-Sn, Sn-Bi

This is an important alloy system to look at because most metals are partly soluble in solid state. So, this is the most common type of phase diagrams. It can be seen here that T_A and T_B are the melting points of metals A and B.

$T_\mathrm{A}ET_\mathrm{B}$ is the liquidus line and $T_\mathrm{A}FGT_\mathrm{B}$ is the solidus line. Few examples of such a system which has complete solubility in liquid state and partial solubility in solid state are copper-silver, lead-tin and tin-bismuth.

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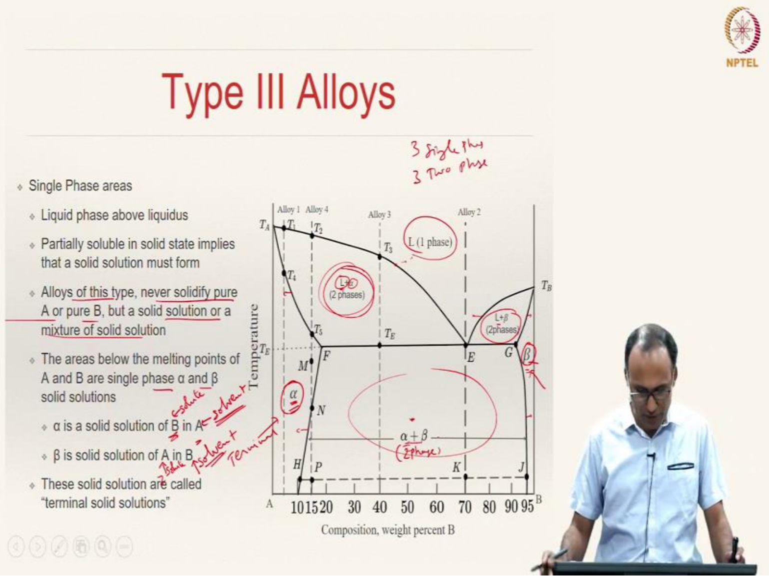

Type III Alloys

- Single Phase areas
  - Liquid phase above liquidus
  - Partially soluble in solid state implies that a solid solution must form
  - Alloys of this type, never solidify pure A or pure B, but a solid solution or a mixture of solid solution
  - The areas below the melting points of A and B are single phase α and β solid solutions
    - α is a solid solution of B in A
    - β is solid solution of A in B
  - These solid solution are called "terminal solid solutions"

Here, we have single-phase areas and two-phase areas. This is a single-phase area and again, you have another single-phase area here, another single-phase area here and here you have a two-phase region, here two-phase region and this is also a two-phase region.

Totally, there are 3 single-phase regions and 3 two-phase regions. Please note that you do not have pure solids, you have solid solution α and solid solution β. There is a partial solubility of A in B and B in A, and hence, they do not solidify pure solids. Alloys of this type never solidify pure A or pure B, but a solid solution or a mixture of solid solution will be formed.

The areas below the melting points of A and B are single-phase α and single-phase β - usually they are called terminal solid solutions because they are towards the end. In between other compositions also you may have new phases, but the phases that form towards the end and are closer to the pure solids are called terminal solid solutions.

Here, α is a solid solution which is rich in A; so that means, A is the solvent and B is the solute in α. What is β? β is a solid solution of A in B; that means, B is the solvent i.e., host and A is the solute i.e., guest, whereas in α, A is host and B is guest. In between, you have $\alpha + \beta$, this is two-phase region. So, you can easily see how the two-phase regions are identified in this phase diagram.

So, for instance, if you see this is a two-phase region. What are the two-phases? You draw a tie-line, you see that it is hitting this line. Right to that you have liquid phase and hence, liquid phase is one of them and left to this boundary, you have α and hence, these are the two phases. Similarly, here, right to this boundary, you have β, left to that boundary you have a liquid so, liquid + β. Here in this region, left to this boundary, you have α, right to that boundary you have β and hence, it is $\alpha + \beta$.

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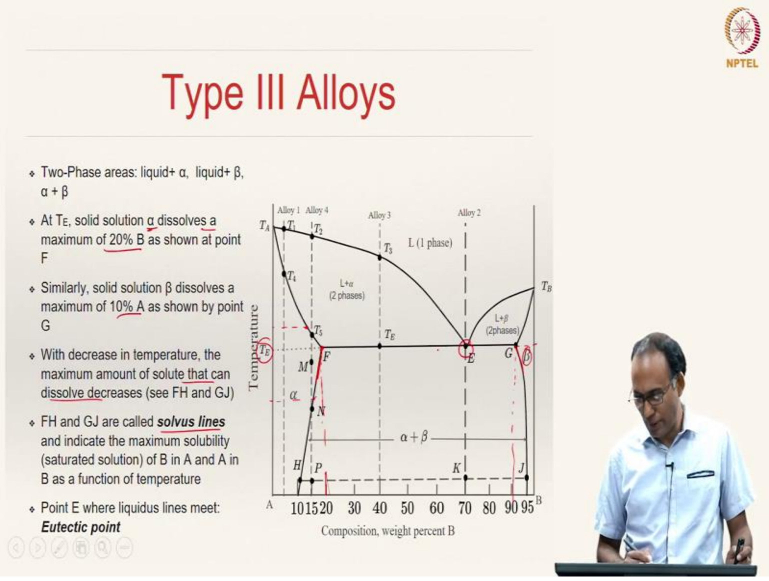

Type III Alloys

- Two-Phase areas: liquid+ α, liquid+ β, α + β
- At T_E, solid solution α dissolves a maximum of 20% B as shown at point F
- Similarly, solid solution β dissolves a maximum of 10% A as shown by point G
- With decrease in temperature, the maximum amount of solute that can dissolve decreases (see FH and GJ)
- FH and GJ are called ***solvus lines*** and indicate the maximum solubility (saturated solution) of B in A and A in B as a function of temperature
- Point E where liquidus lines meet: ***Eutectic point***

The two-phase areas as we have already discussed are liquid + α, liquid + β and α plus β. At temperature T_{E}, there is a maximum solubility for α. The solid solution α dissolves a maximum of 20% B; beyond that it cannot dissolve.

So, α has a maximum solubility of 20% B in A; that happens only at temperature T_{E}. At any other temperature, it will have a much lower solubility. For instance, at this temperature, the solubility is only this much. At this temperature, the solubility is only this much. So, the solubility limit changes as a function of temperature, as we have already seen in the sugar-water syrup example that we have discussed in the very beginning of this module.

Similarly, if you take β at the same temperature T_{E}, it has the maximum solubility of 10% of A; that means, you have 10% A in B which is described by point G. And the maximum solubility of B in A is described by point F. With further decrease in temperature, the maximum amount of solute that can dissolve decreases, because the solubility is decreasing with decreasing temperature in both the cases.

The lines FH and GJ represent decrease in the solubility of the solute atoms as you decrease the temperatures and these two lines are called solvus lines; they indicate the maximum solubility of B in A and A in B as a function of temperature. Point E is the eutectic temperature or eutectic point.

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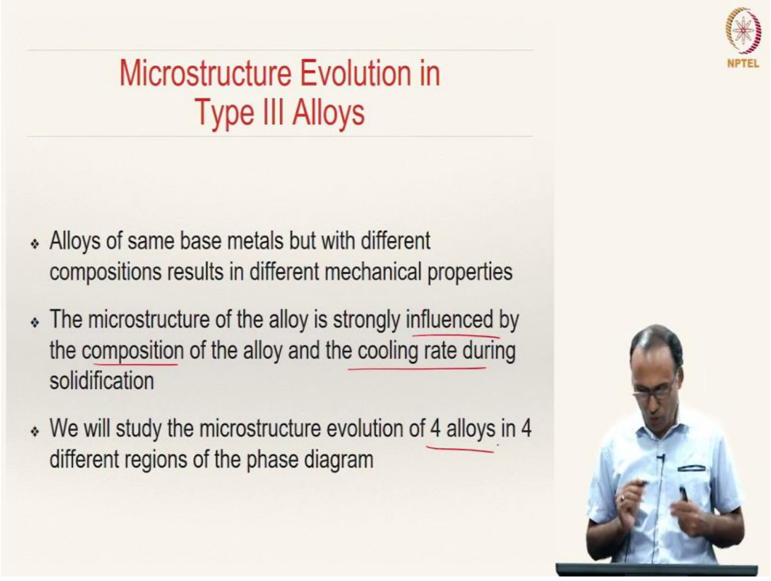

Microstructure Evolution in Type III Alloys

- Alloys of same base metals but with different compositions results in different mechanical properties
- The microstructure of the alloy is strongly influenced by the composition of the alloy and the cooling rate during solidification
- We will study the microstructure evolution of 4 alloys in 4 different regions of the phase diagram

How does this microstructure look like is something that we will see. Alloys of same base metals, but with different compositions - A and B are the same, but different compositions will result in different mechanical properties. That is one of the reasons why we need to study their microstructures, which is going to be strongly influenced by the composition of the alloy and the cooling rate during the solidification.

However, in this module, we are assuming that the cooling is done at a sufficiently small rate; which means equilibrium cooling is done. The effect of cooling rate will not to be discussed in this module. It will be discussed at a later stage.

The key to the properties of different alloys is the microstructure and hence, we will study the evolution of the microstructure for four different compositions in four different regions of the phase diagram.

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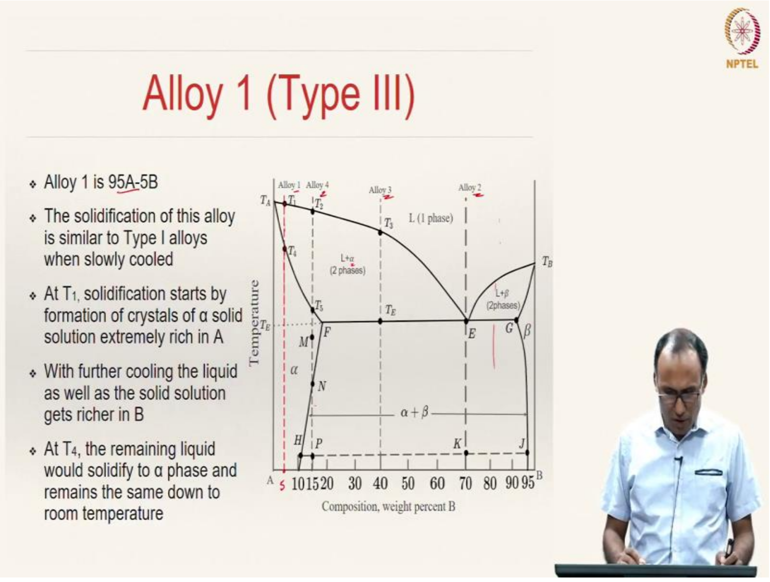

Alloy 1 (Type III)

- Alloy 1 is 95A-5B
- The solidification of this alloy is similar to Type I alloys when slowly cooled
- At T_1, solidification starts by formation of crystals of α solid solution extremely rich in A
- With further cooling the liquid as well as the solid solution gets richer in B
- At T_4, the remaining liquid would solidify to α phase and remains the same down to room temperature

So, this is alloy 1, alloy 2, alloy 3, alloy 4. We could also have another alloy in this region, but it will be similar to alloy 1 or alloy 4. That is why we are studying these four classifications. Now, let us look at alloy 1. Alloy 1 is 5% B and 95% A.

The solidification of this alloy starts at temperature T_1 and ends at temperature T_4. In the two-phase region, you will have liquid plus solid; that solid will be α solid solution and when it comes down, it again enters from the two-phase region - all the liquid would have transformed to α.

This alloy microstructure is very much similar to the case of isomorphous alloys that we have looked at, wherein the liquid starts solidifying at a temperature and then, ends at another temperature when all the liquid would have transformed to another solid phase. So, this is very similar to our isomorphous alloy microstructure.

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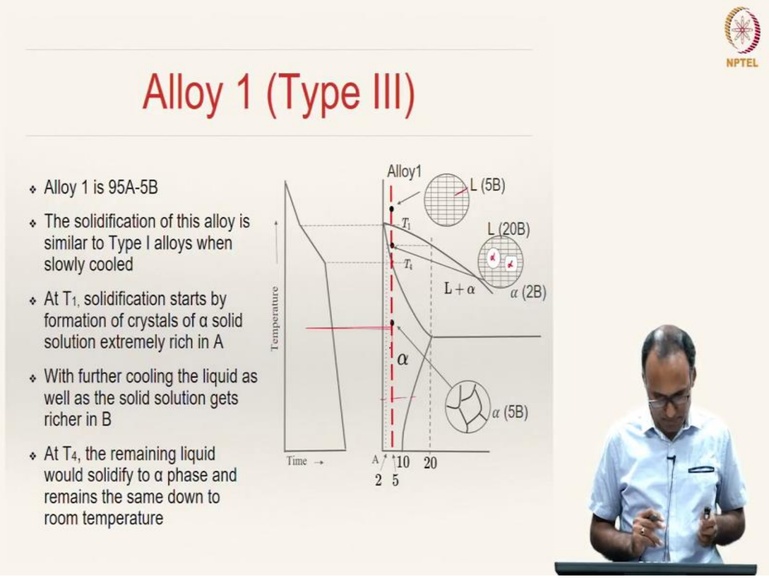

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You have a liquid and then somewhere in between, you will have solidification happening. These are α grains. By the time it reaches T_4, entire solidification would have finished. As you are coming down, the alloy composition is 5 B, but everywhere the solubility is much larger i.e., it is actually under saturated and hence, nothing will happen.

Basically, the temperature of the solid reduces, nothing else happens as far as the microstructure change is concerned. So, it is very similar to our isomorphous alloy system.

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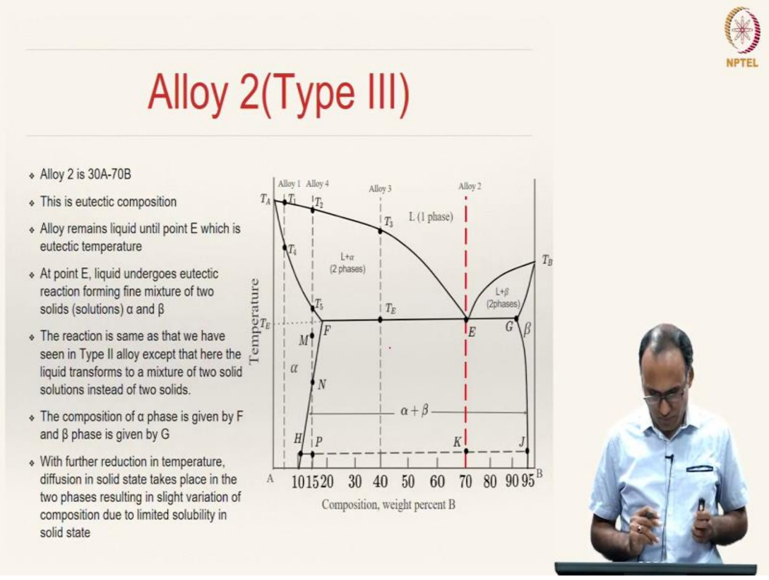

Alloy 2(Type III)

- Alloy 2 is 30A-70B
- This is eutectic composition
- Alloy remains liquid until point E which is eutectic temperature
- At point E, liquid undergoes eutectic reaction forming fine mixture of two solids (solutions) α and β
- The reaction is same as that we have seen in Type II alloy except that here the liquid transforms to a mixture of two solid solutions instead of two solids.
- The composition of α phase is given by F and β phase is given by G
- With further reduction in temperature, diffusion in solid state takes place in the two phases resulting in slight variation of composition due to limited solubility in solid state

Let us look at alloy 2. Again, alloy 2 is our eutectic alloy because it is a eutectic composition.

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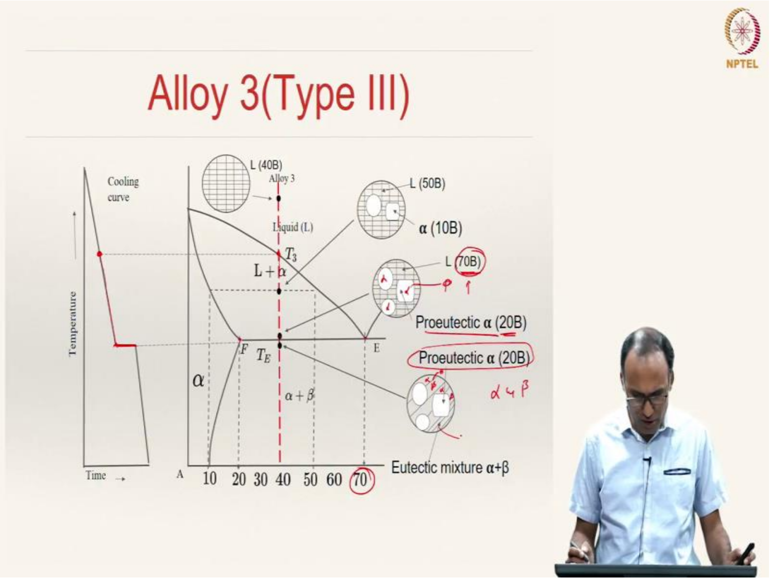

Alloy 3(Type III)

Let us look at the microstructure. At this position, everything is liquid. At T_3, the solidification starts and on the left-hand side, we are showing the cooling curve. Here, the solidification starts at this point. As we are cooling down, the liquid starts becoming richer in B and the liquid solidifies into not pure A, but into a solid solution of type α, which means solid solution of B in A. So, α is a solid solution which is rich in A. The α crystals will be formed, and they grow over the time.

By the time you are here, you have some amount of liquid and remaining is pro-eutectic α. So, it is called primary α or pro-eutectic α. From the tie line, we see 20 B is the composition of pro-eutectic α and the remaining liquid solution composition is equal to eutectic composition. 70B is the liquid eutectic composition in this particular system.

Since, the remaining liquid has reached the eutectic composition and the temperature is eutectic temperature, what should happen? The remaining liquid should go through a eutectic reaction. The eutectic reaction, that happens at a constant temperature; that is why you see a constant line. Up to here, the liquid is crystalizing solid α and then at this point, the remaining liquid has reached the eutectic composition and eutectic temperature.

And hence, at constant temperature, the solidification happens and that solidification results in formation of two solids. Here, the two solids will be two solid solutions and alternate layers of α and β form.

The final microstructure will be a pro-eutectic α which has been crystallized from the liquid solution before the eutectic reaction took place and the remaining liquid transforming to alternate layers of α and β. Here, we are forming α and β because pure solid A and solid B cannot form due to partial solubility. You can also calculate all the weight fractions based on the discussions that we had so far, on different other systems.

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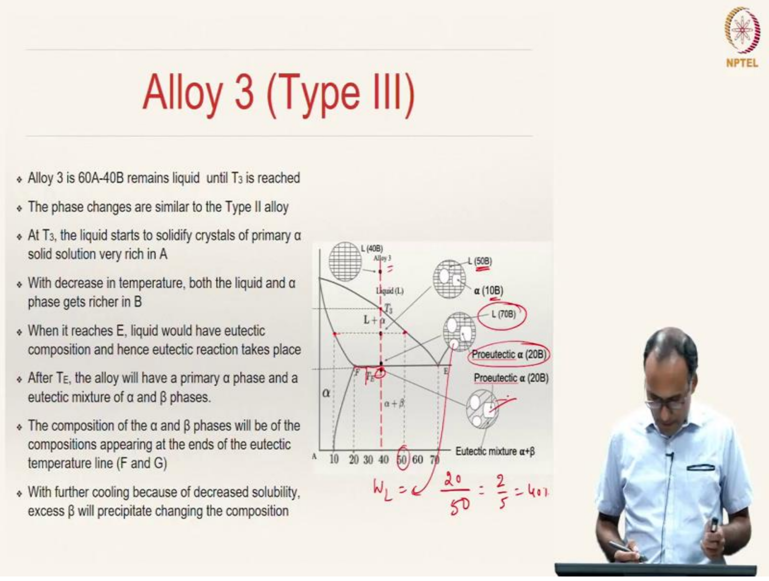

Alloy 3 (Type III)

- Alloy 3 is 60A-40B remains liquid until T_3 is reached
- The phase changes are similar to the Type II alloy
- At T_3, the liquid starts to solidify crystals of primary α solid solution very rich in A
- With decrease in temperature, both the liquid and α phase gets richer in B
- When it reaches E, liquid would have eutectic composition and hence eutectic reaction takes place
- After T_E, the alloy will have a primary α phase and a eutectic mixture of α and β phases.
- The composition of the α and β phases will be of the compositions appearing at the ends of the eutectic temperature line (F and G)
- With further cooling because of decreased solubility, excess β will precipitate changing the composition

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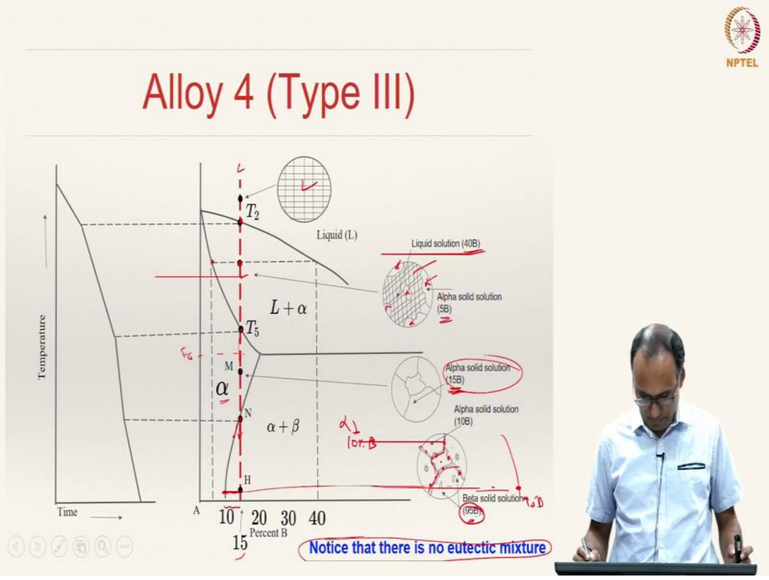

Alloy 4 (Type III)

Notice that there is no eutectic mixture

Let us now look at alloy 3 which is also quite straightforward. You have a complete liquid solution at temperature T_3, small grains of α start solidifying. You draw a tie line and you see that it is 50 B. The liquid composition will be 50 B and solid i.e., α composition will be 10 B.

If you further cool it down just above, at this point on this line, then the liquid composition will be 70 B so that means eutectic composition and pro-eutectic α will be 20 B. What is the weight fraction of this liquid?

The weight fraction of the liquid will be this distance divided by the total distance.

$$\mathrm{W_L} = \frac{70 - 50}{50} = \frac{20}{50}$$

The 40% liquid would transform to a eutectic mixture of α and β. So, somewhere here, if you look at microstructure, you have pro-eutectic α which is 20 B and eutectic mixture of α and β.

Let us look at alloy 4 which is an interesting alloy. At this position, everything is liquid and at temperature T_2, the liquid starts solidifying; so that means, initial α phase starts happening. At some intermediate temperature, we are seeing the α solid solution -- and the remaining liquid and here if you see, the composition of α is 5 B and the remaining liquid will be 40 B.

The moment you reach temperature T_5, all the liquid would have transformed to solid α; so that is like our isomorphous alloys. So, at this position, you will have complete α. Here, we have started with 15% B so, all the α would have transformed to 15 B.

And if you further cool it down, what happens at N? When you are further cooling it down, the moment it reaches point N, the solubility limit has reached saturation. At N, it can have 15 B so, we already have 15 B, and hence that is saturated. If you cool it down below this temperature point N, what happens? The solubility limit is only this much, but your composition has 15 B.

Let us say you are looking at point H. Your composition is having 15 B, but your solubility limit says that it can only have 10 B - α can only hold 10 B; that means, the α has become rich in B, richer than what it could hold and hence, what should happen? The additional B that is sitting in the solid solution should come out because it is over saturated.

However, the B cannot come out as pure solid B because there is some partial solubility of B in A and A in B. Hence, it comes out as solid solution β. This solid solution β is actually dispersed everywhere throughout the α matrix. So, what will be the weight fraction of that β?

The tie line, which is in the two-phase region, hits the GJ line at 95 B. Hence, the composition of β solid solution will be 95 B and the weight fraction will be very small - only this much is the weight fraction of β.

The additional B that is present in α comes out as β solid solution and that is randomly distributed throughout the matrix, preferentially along the grain boundaries. These are α grain boundaries, you may have β dispersed throughout the grain boundaries and also in the matrix.

Because of the limited solubility, as you are cooling down, there is something more happening to the microstructure. There is some event taking place because of the limited solubility and hence, the position of the solvus line is also an important aspect to be paid attention to.

Please note that, in this particular system, after T_5, you are entering a single-phase region. Since, we are in a single-phase region, you do not have a tie line concept, although you are crossing through the temperature T_E, there is no liquid anymore, everything is solid first of all. And there is no reaction taking place; so that means, you do not see eutectic mixture in this particular microstructure.

Although there are several alloys which will form eutectic mixture, this particular composition is not going to give any eutectic mixture. In that sense, alloy 4's microstructure is very different from alloy 2 and alloy 3 and also from alloy 1. Alloy 1 is like isomorphous alloys but alloy 4 is really interesting. Please note that here it is again going from a single-phase region to two-phase region without actually going through any reaction, but just by giving out B.

Because of the over saturation of α solid solution with B, the additional B has to come out and that comes out as β solid solution which will be dispersed uniformly within the matrix. We are actually going from a liquid solution single-phase region into a two-phase region liquid + α into another single-phase region α and again entering a two-phase region α + β. So, that is about alloy 4.

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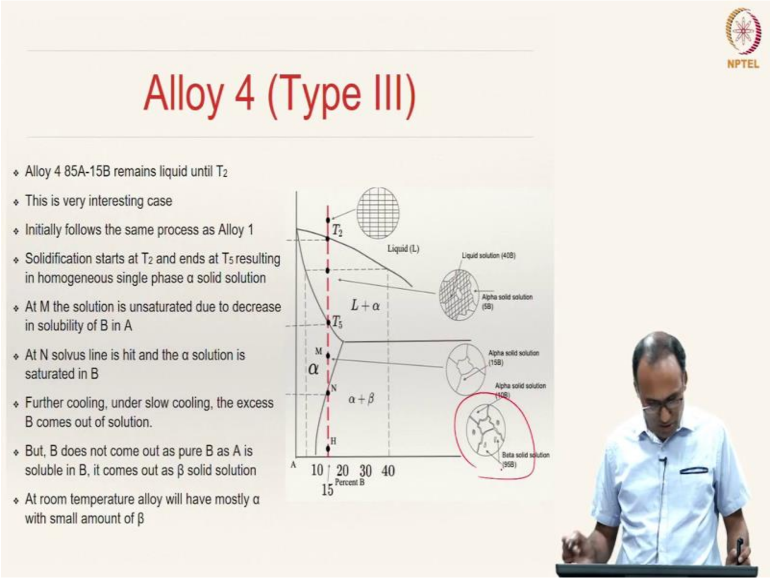

Alloy 4 (Type III)

- Alloy 4 85A-15B remains liquid until T_2
- This is very interesting case
- Initially follows the same process as Alloy 1
- Solidification starts at T_2 and ends at T_5 resulting in homogeneous single phase α solid solution
- At M the solution is unsaturated due to decrease in solubility of B in A
- At N solvus line is hit and the α solution is saturated in B
- Further cooling, under slow cooling, the excess B comes out of solution.
- But, B does not come out as pure B as A is soluble in B, it comes out as β solid solution
- At room temperature alloy will have mostly α with small amount of β

So, the microstructure looks something like this.

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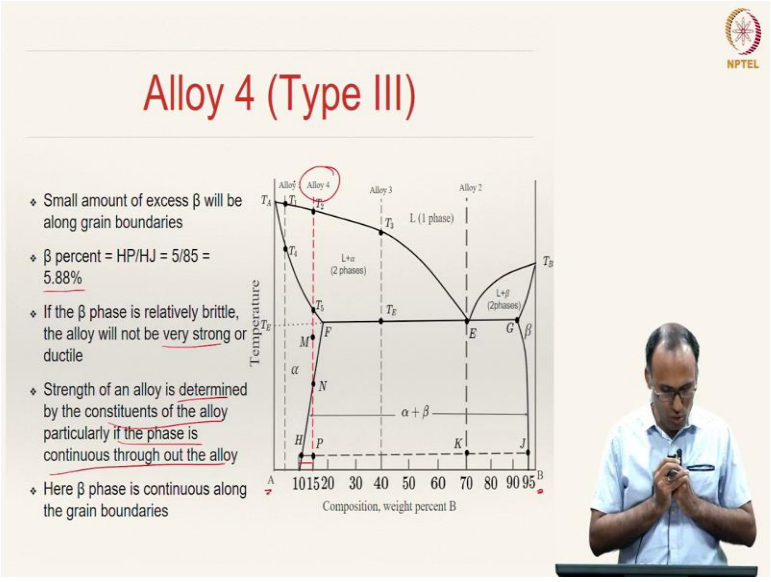

Alloy 4 (Type III)

- Small amount of excess β will be along grain boundaries
- β percent = HP/HJ = 5/85 = 5.88%
- If the β phase is relatively brittle, the alloy will not be very strong or ductile
- Strength of an alloy is determined by the constituents of the alloy particularly if the phase is continuous through out the alloy
- Here β phase is continuous along the grain boundaries

In the two-phase region, we can calculate the weight fraction of β. So, we can see that if you are drawing this line, the weight fraction of β will be,

$$W_\beta = \frac{HP}{HJ} = \frac{5}{85} = 5.88\%$$

Please note that, if the β phase happens to be a relatively brittle phase -- let us say that the element A and B are there, let us say A is a soft version and B is a brittle phase. If the β phase is relatively brittle, then what happens is because of the distribution of this β phase throughout the microstructure, this β brittle phase can actually make the material vulnerable for failure. Because of its brittleness, it may not be very strong or ductile.

From this particular alloy composition, we can understand that the microstructure plays a critical role in understanding the strength of an alloy. The strength of an alloy, as we have discussed is determined by constituents of the alloy, particularly if the phase is continuous throughout the alloy. That is what happens particularly for alloy 4 because the β phase will be continuous throughout, as the α phase everywhere has additional B and that B comes out as β, and then it gets segregated there as β phase and it is continuously distributed throughout the alloy.

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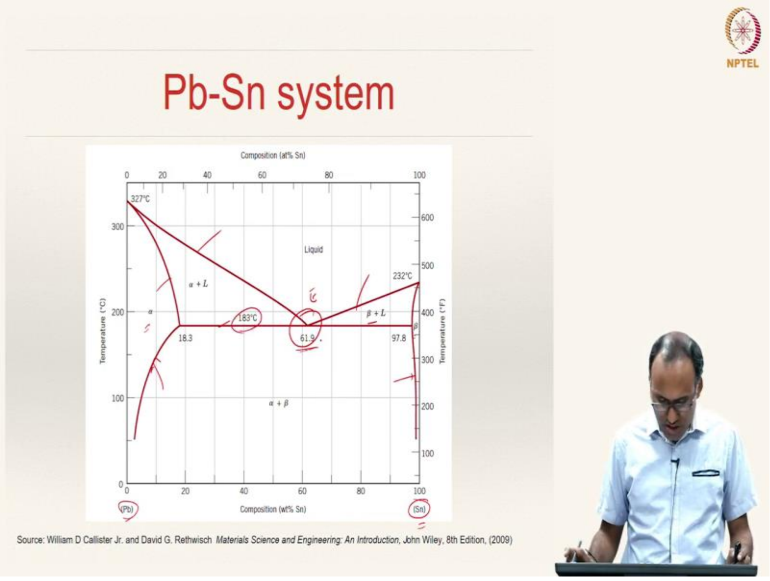

Pb-Sn system

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

A real system that has such an alloy phase diagram that we have discussed so far -- three type of phase diagram is lead-tin system which is very well known to us as solder which is used for solder joints. So, here, lead is on the left-hand side, tin is on the right-hand side.

Lead is soft and tin is known to be relatively harder compared to lead. You have α solid solution and this our β solid solution and this is our solvus line -- these two are solvus lines and this is liquidus line and this is solidus line and that is our eutectic point. So, eutectic temperature is 183° C and eutectic composition is 61.9% tin.

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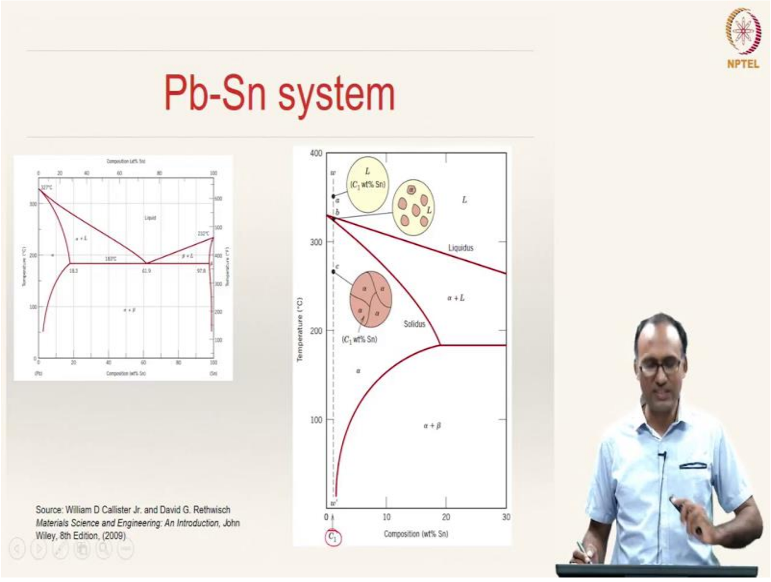

Pb-Sn system

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

If you look at the microstructures, it is like alloy 1 that we have discussed. In this two-phase region, you will have α and liquid and by the time it comes here, you will have complete α. And the composition will be C_1- it is a single-phase region; it is exactly like our isomorphous system that we have looked at.

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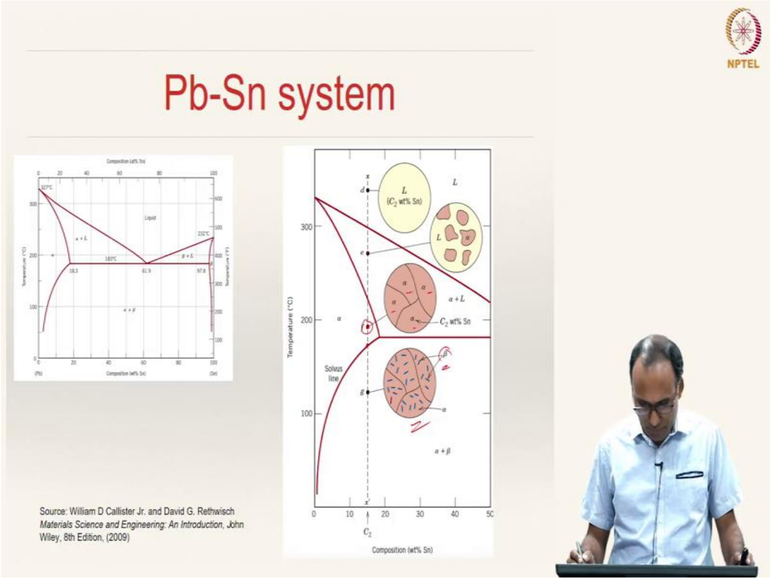

Pb-Sn system

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

This is the alloy 4 type that we have just now discussed. So, you have complete liquid and then, you are entering two-phase region liquid plus solid, again you are entering pure solid -- sorry -- not pure solid, a single-phase α -- all are α grains. And by the time you cross this line, you have over saturated -- the over saturated α will have to give out B, but it cannot give B as pure B, but it gives out as β. And hence, this β phase is continuously distributed throughout the matrix.

If this β phase happens to be a brittle phase, that can be detrimental for applications in which we are using this component. Depending upon the nature of this β, the mechanical properties can be significantly engineered.

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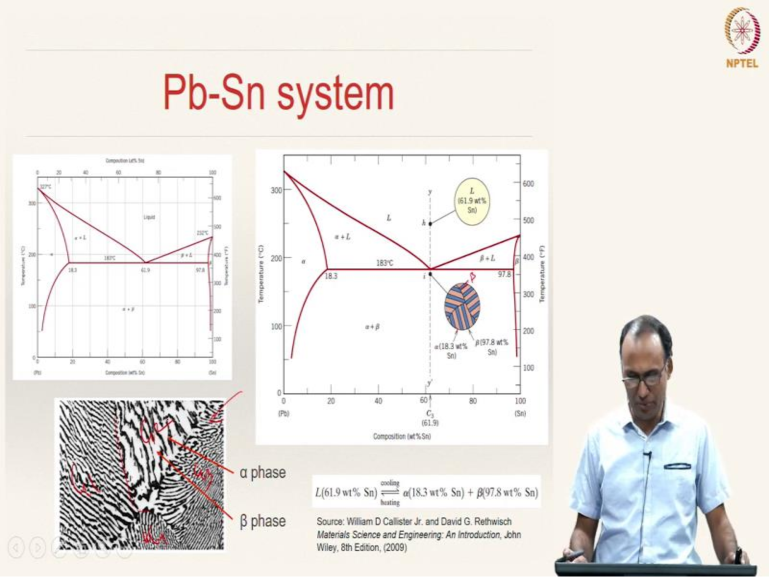

Pb-Sn system

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

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

If you look at the eutectic alloy, you have liquid and at this position, you will have formation of alternate layers of α and β. Let us say blue region represents β and pink region represents α. So, you have formation of alternate layers of α and β.

If you observe such a system under microscope, you will see these alternate layers of α and β. Here, we can see different grains and the respective boundaries where they meet.

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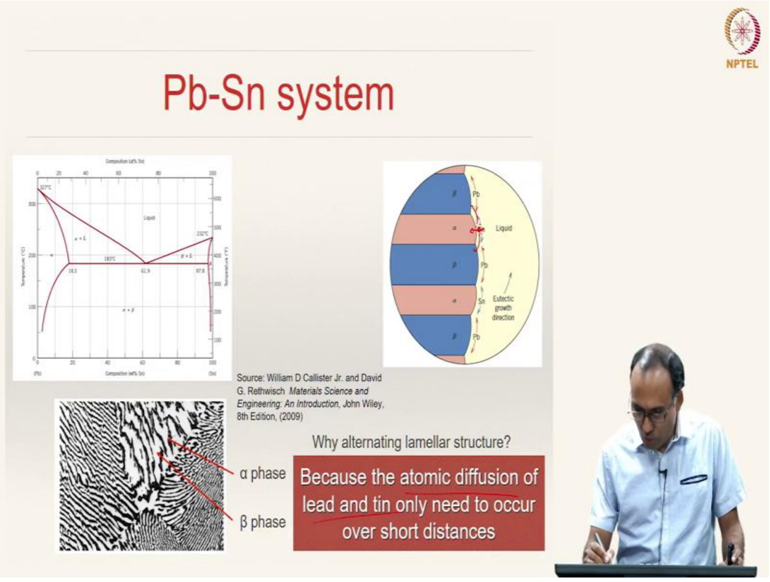

Pb-Sn system

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

Why alternating lamellar structure?

Because the atomic diffusion of lead and tin only need to occur over short distances

Why do alternate layers of α and β form? The liquid here is having a certain composition and then, that is solidifying α. The surrounding liquid becomes richer in β or richer in B and instead of forming B elsewhere, it is much easier for B to travel to the neighboring grains.

If you are forming alternate layers, the atomic diffusion needs to take place only over a shorter distance, rather than forming individual grains further way from each other. The reason for this alternating laminar structure is because the atomic diffusion of lead and tin only need to occur over small distances.

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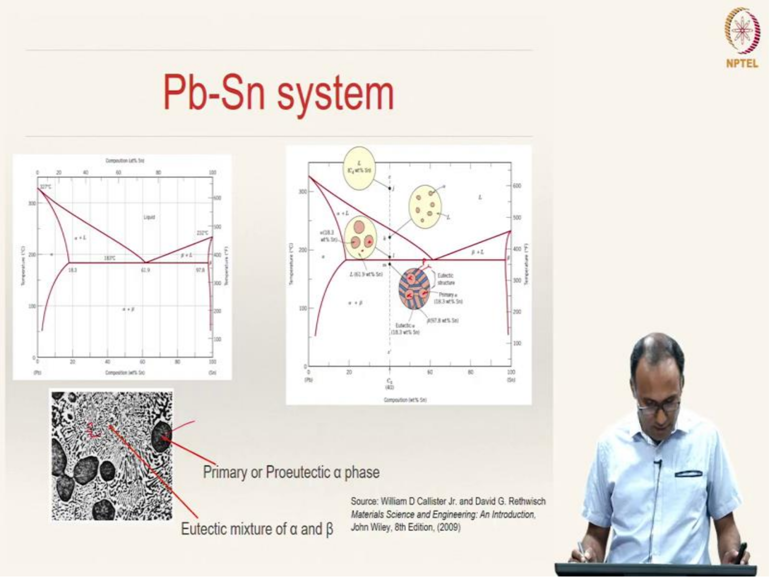

Pb-Sn system

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009) This is like our alloy Type II that we have discussed so far. There is pro-eutectoid α here and at this position, the remaining liquid -- the yellow portion will form alternate layers of β and α. If you observe under a microscope, you see the pro-eutectoid α and eutectic mixture of α and β. Again, all the weight fractions can be calculated by drawing the tie line and using the lever rule.

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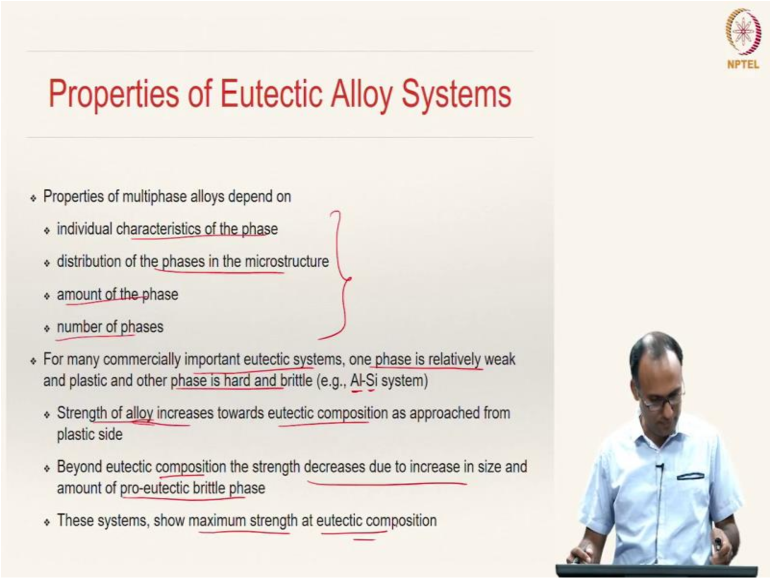

Properties of Eutectic Alloy Systems

- Properties of multiphase alloys depend on
  - individual characteristics of the phase
  - distribution of the phases in the microstructure
  - amount of the phase
  - number of phases
- For many commercially important eutectic systems, one phase is relatively weak and plastic and other phase is hard and brittle (e.g., Al-Si system)
  - Strength of alloy increases towards eutectic composition as approached from plastic side
  - Beyond eutectic composition the strength decreases due to increase in size and amount of pro-eutectic brittle phase
  - These systems, show maximum strength at eutectic composition

What are the properties of these eutectic alloy systems? The properties of multiphase alloys in general, depend on the individual characteristics of the phase, the distribution of the phases in the microstructure i.e., whether they are continuously distributed or not, the amount of the phase and the number of phases that are present. These factors are going to determine the mechanical properties or in general the properties of the alloy system.

For several commercially important eutectic systems, one phase is known to be relatively weak and plastic (ductile), and other phase is hard and brittle. A typical example for that is aluminum-silicon system. When we are dealing with eutectic systems, the strength of the alloys increases towards the eutectic composition.

The strength of the alloy increases towards eutectic composition, as we are approaching from the plastic side, not necessarily from the brittle side.

Beyond the eutectic composition, the strength decreases due to increase in the size and amount of pro-eutectic brittle phase. Because the brittle phase is increasing, you will have reduction in the strength. The eutectic system shows a maximum strength at eutectic composition because after the eutectic composition, if you have a brittle phase, that is going to be detrimental for fracture.

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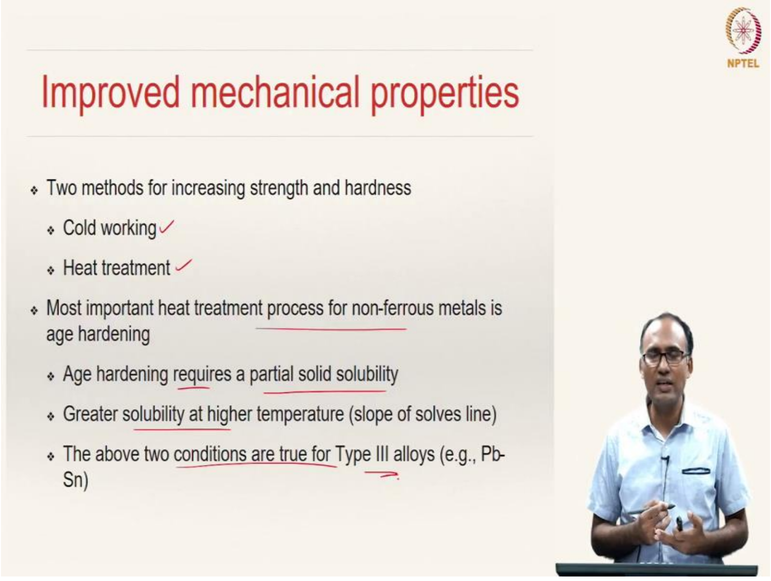

Improved mechanical properties

- Two methods for increasing strength and hardness
  - Cold working ✓
  - Heat treatment ✓
- Most important heat treatment process for non-ferrous metals is age hardening
  - Age hardening requires a partial solid solubility
  - Greater solubility at higher temperature (slope of solves line)
  - The above two conditions are true for Type III alloys (e.g., Pb-Sn)

If you have these continuous phases distributed throughout the system and are going to be detrimental to the mechanical behavior, we need to improving the mechanical properties. Let us see how.

There are typically two methods. We can use cold working wherein you apply deformation to the material at room temperature. Heat treatment is one of the most popular ways to enhance the mechanical properties, after the solidification of an alloy. The most important heat treatment process for nonferrous metals is age hardening, a special kind heat treatment.

So, the details about age hardening can be read from the textbook of Sidney H Avner or from the Callister's text book on Material Science and Engineering.

Age hardening primarily requires partial solid solubility which is the case for Type III alloys. It needs to also have greater solubility at higher temperatures. These two conditions are true for Type III alloys. They have a higher solubility at higher temperature, and they have partial solubility, and hence, age hardening can be used in order to enhance the mechanical properties.

We will look at other important heat treatment process in the module that we are going to discuss after the phase diagrams. If you want to understand more about age hardening, I encourage you to go through the text book of Sidney H Avner's Physical Metallurgy or you can also refer to the other text books that are mentioned in the references of this module.

So, with that, we will stop here and we will look at Type IV, V and VI alloys in the next class.

Thank you very much.