Basics of Materials Engineering

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Lecture - 60
Phase Diagrams (Congruent melting alloys, Peritectic Reaction, Monotectic Reaction)

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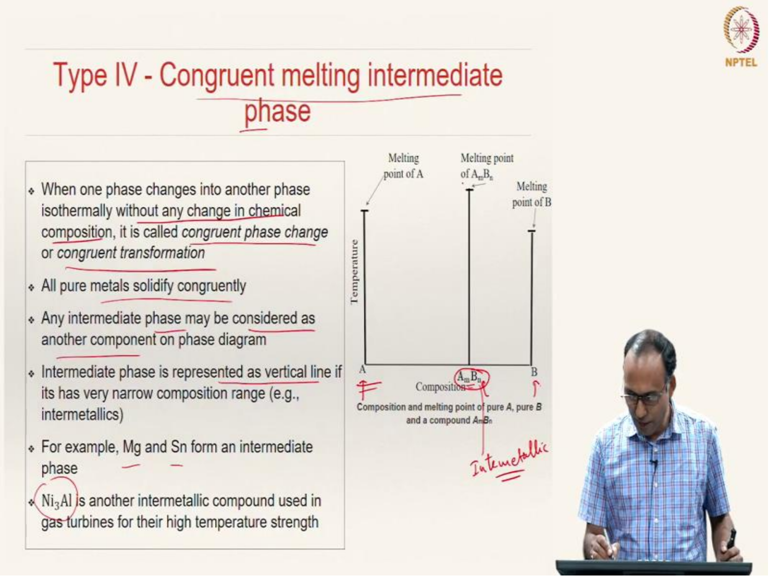

Welcome back. In the last class, we looked at the eutectic alloy types i.e., Type II and Type III alloys, where we have discussed the evolution of microstructure. Today, we will look at Type IV alloys. Basically, in the Type IV alloy, we will look at the formation of congruent melting intermediate phase. What do you mean by a congruent melting alloy?

When one phase changes into another phase isothermally i.e., the solidification is happening at constant temperature from the liquid state to solid state, or any phase change happening at constant temperature, the resulting phase also should be having same composition i.e., without any change in the chemical composition - that is the key.

If the phase change happens isothermally without change in chemical composition, such a phase change is called congruent phase change or congruent transformation. By that argument, all pure metals solidify congruently. Pure metal composition above the melting temperature and below the melting temperature remains the same and it solidifies at a constant temperature.

After solidification, the composition remains the same. Hence, all pure metals can be said as solidifying congruently. In the alloy system, if there is any intermediate phase that is solidifying congruently, that may be considered as another component on phase diagram. The intermediate phase is usually represented as a vertical line.

Such solidification happens for a very narrow composition range or only for a particular composition. For instance, on the right-hand side diagram, you have pure metal A and pure metal B and a for a specific composition A_mB_n, the melting happens at constant temperature. This particular compound can be called as an intermediate compound or intermetallic, because it is between these two metals.

This compound is only possible for a specific whole number combination of A and B. Sometimes this can happen over a range. This solidification happens at constant temperature and the composition remains the same in that range - it goes from one single-phase region to another single-phase region.

For example, magnesium and tin form intermediate phases. Ni_3Al, nickel aluminate is another intermetallic compound that is used in gas turbines because of its high temperature strength. You can see that this particular compound A_mB_n has a higher melting point than A and B.

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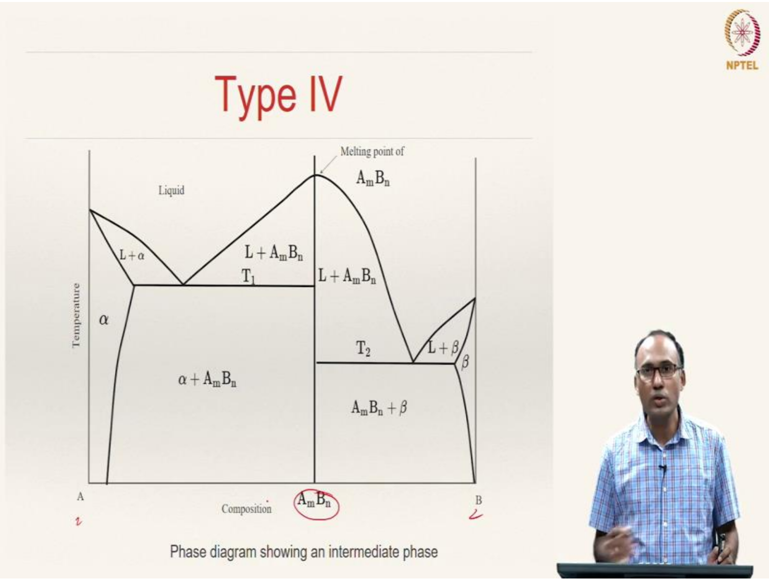

These are A and B and A_mB_n is the intermediate compound which is melting congruently. Then, you can actually see this phase diagram as two different phase diagrams.

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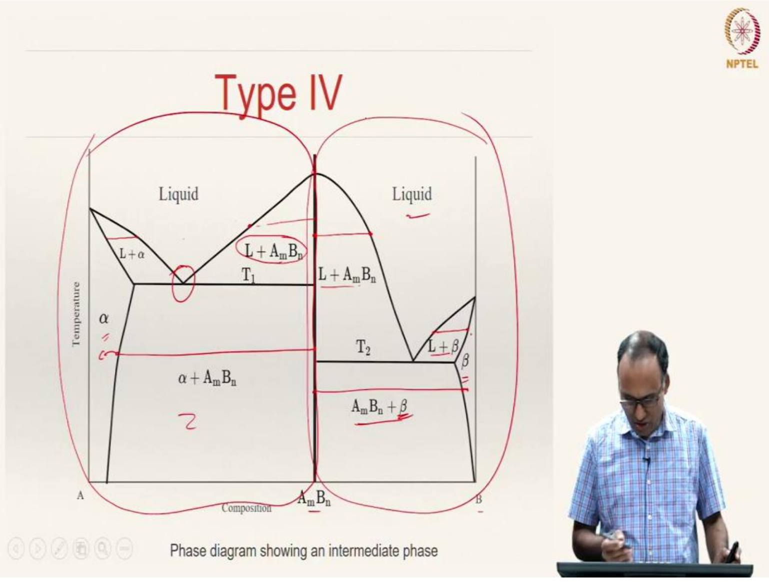

This is a liquid phase and this is also liquid phase. Here, the terminal solid solution is α, here the terminal solid solution is β. Because of the fact that it has higher temperature, it is going up and then at this point, it will solidify into a special compound A_mB_n. If you draw a tie line here, this side you have liquid and this side you have A_mB_n. Hence, the two-phase region will be liquid + A_mB_n. Similarly, tie line hits A_mB_n and hence the two-phase region should be liquid plus A_mB_n.

A tie line drawn here hits the β region and the liquid region. So, this will be liquid plus β. Here also if you draw a tie line, this will be liquid plus α. If you draw a tie line in this two-phase region, on to the left side you have solid solution α and here you have A_mB_n.

Similarly, if you draw a tie line here, this side it is β and this side it is A_mB_n. So, this is a two-phase region β + A_mB_n. There are two eutectic points between A, A_mB_n and A_mB_n, B. One can treat A and A_mB_n as one system, and A_mB_n and B as another system. So, this is one phase diagram; that is another phase diagram.

Let me erase this part so that we can discuss. As we have shown before, this is our complete phase diagram. Now, let me blank the right-hand side part. If I blank that, this is how it looks like. It is very similar to the Type III alloy on this side, but on this side, it is actually having zero solubility; that means, it is like a pure solid.

You can think of this as a system which has some α solid solution, but this side there is no solubility of A in A_mB_n. That is how you can see this as a one phase diagram. And if you blank this left-hand side part, then you will have this phase diagram. You will have one terminal solid solution β and on the left-hand side, you will have pure solid A_mB_n. It is a compound, but it can be thought of as pure solid because it is congruently melting.

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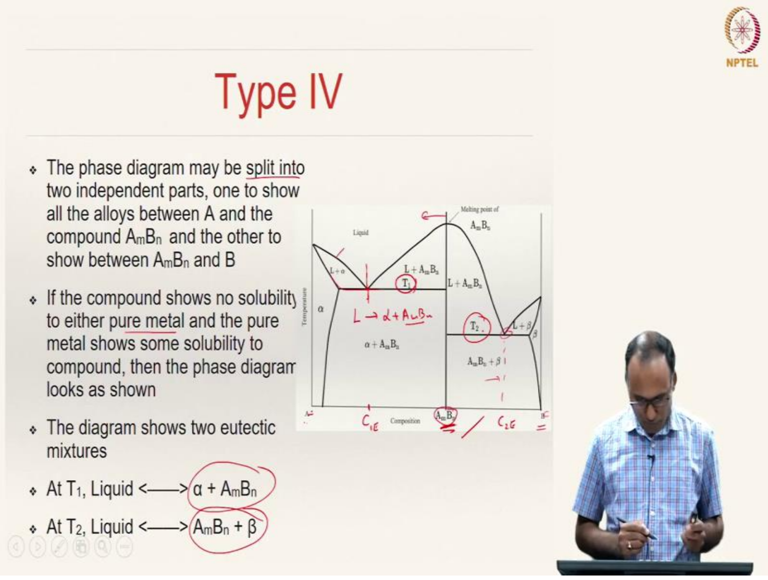

As I have discussed, the phase diagram can be split into two independent parts - one to show all the alloys between A and A_mB_n and another to show all the alloys between A_mB_n and B. If the compound A_mB_n has no solubility to A or B and pure metal of course, shows some solubility to compound, then the phase diagram looks like this.

However, if there is some solubility, this phase diagram may look little different. At temperature T_1, you have the liquid. Corresponding to a composition of C_{1E}, if the liquid is cooled until this point, it will transform to two solids, α and A_mB_n.

This is the liquidus line and this is the solidus line, and hence, this must be the eutectic reaction at temperature T_1. Similarly, at temperature T_2, there is another eutectic reaction. If you look at only the left-hand side portion between A and A_mB_n, you have one eutectic temperature. If you see the right-hand side portion between A_mB_n and B, you have another eutectic temperature.

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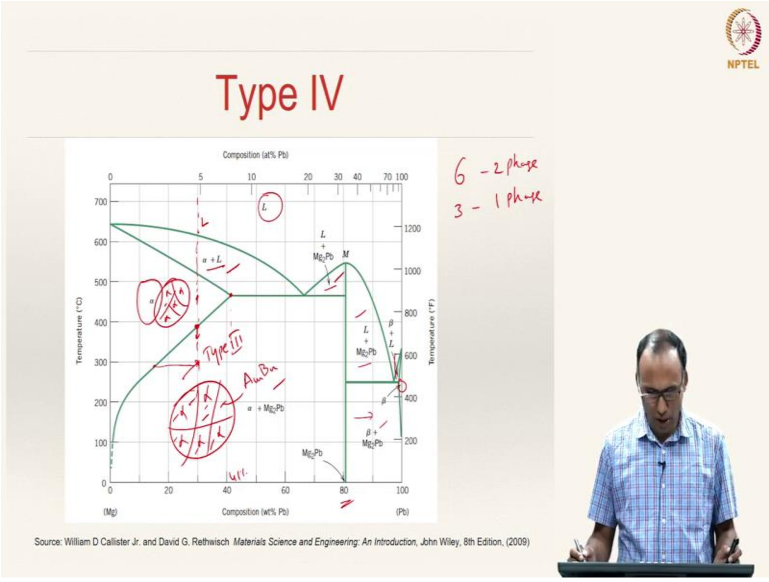

Such systems do exist, for instance, magnesium-lead system. You can clearly see $\mathrm{Mg_2Pb}$ is an intermetallic. Left to that is what we have seen and right to that is between $\mathrm{Mg_2Pb}$ and β solid solution. You can clearly identify all the two-phase regions - this is α + L, this is L + $\mathrm{Mg_2Pb}$, etc. So, how many single-phase and two-phase regions are there?

There are six two-phase regions and three single-phase regions. Again, as you can see, the solubility of B in A is maximum at temperature T_1 - that is about 41%. As you are reducing the temperature, solubility reduces.

You can actually draw the microstructures of different alloys. If you take a microstructure of this alloy, this is something that we have seen in Type III alloys. In Type III systems, we have seen the evolution of the microstructure, here it will be liquid and here liquid + solid and in this region, you will only have the solid α. By the time it comes here, it is undersaturated, whereas here, it is perfectly saturated in terms of solid solution.

But when you come down, the additional B present in this α will come out as $\mathrm{A_mB_n}$, as it cannot come out as B. If you look at the microstructure, you will have α everywhere. However, there is limited solubility and hence this is showing additional B. This additional B comes out as $\mathrm{A_mB_n}$ which will be distributed throughout like that. This is $\mathrm{A_mB_n}$ phase.

We have seen already this kind of microstructure; you should be able to draw the microstructures for any alloy composition within this phase diagram.

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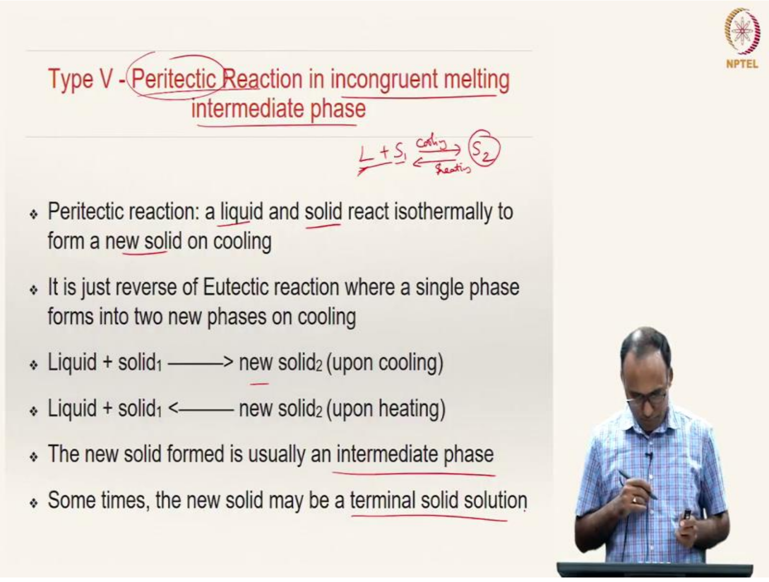

Let us now look at next type i.e., Type V which shows peritectic reaction in an incongruent melting intermediate phase. Here you have an intermediate phase, but it is not a congruent melting intermediate phase. It is an incongruent melting intermediate phase, in which we will see a special reaction called the peritectic reaction. We have seen already one special reaction called eutectic reaction.

What is peritectic reaction? A peritectic reaction is one in which a liquid and solid react together isothermally to give a new solid. Liquid plus solid 1 upon cooling will give you a new solid 2. You can also interpret peritectic reaction as - a solid upon heating gives a liquid and solid 1 that is also peritectic reaction, when we are coming from solid state to liquid state.

We are primarily focusing on solidification, so we are always coming from liquid state to solid state. Upon cooling, liquid plus solid should give you another new solid; that is what we call a peritectic reaction. Here, two phases are giving you one single phase, whereas in eutectic reaction, you have one phase giving you two phases. This is opposite in terms of number of phases before reaction and after reaction - it is exactly opposite to eutectic reaction.

The new solid that is formed is usually an intermediate phase. Here, a liquid and a solid upon cooling give a new solid and then the composition will not remain the same because the solid 1 and liquid 1 will have different compositions. The resulting solid 2 will have a different composition. Hence, this solidification cannot be called a congruent solidification and hence it should be an incongruent solidification.

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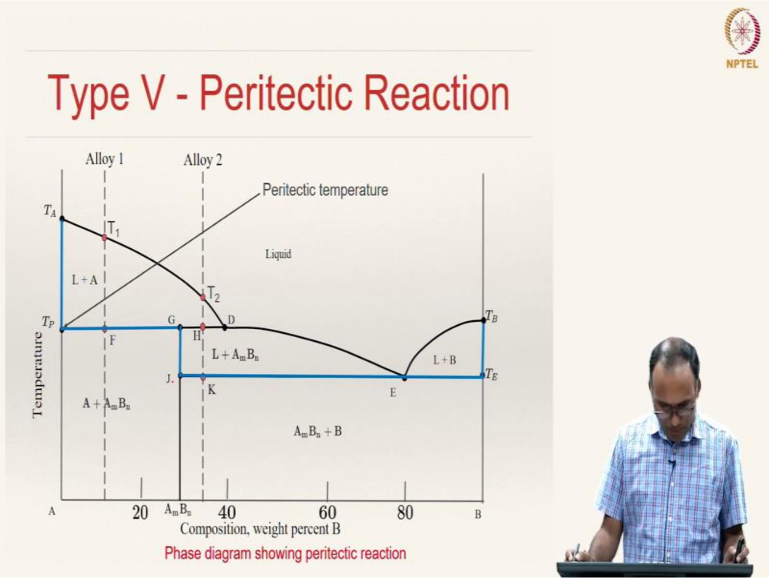

Sometimes, a new solid that is formed can also be a terminal solid solution. This is a model system where we have not looked at any terminal solid solution, because here, we are dealing with a system which has complete insolubility in solid state. Let us now look at the phase diagram here. T_P is the peritectic temperature.

At G, when you are cooling down, liquid + A is transforming to a new intermediate phase called A_mB_n. Let us look at the microstructure evolution in these systems. $T_A T_P G J T_E T_B$ is the solidus line.

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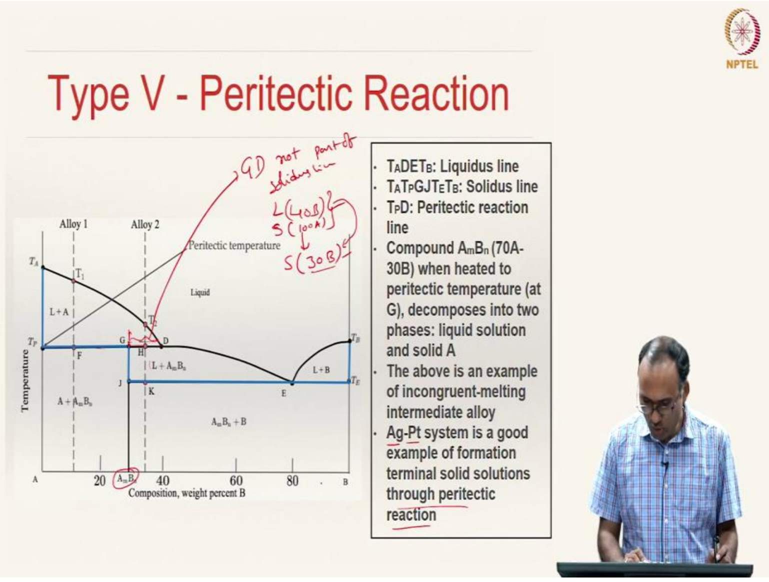

$T_A D E T_B$ is the liquidus line and $T_P D$ is the peritectic reaction line. The solidus line is not up to here, i.e., GD is not part of the solidus line - please note that. If it happens to be solidus line, then you will not have liquid here.

If you are heating the compound $A_m B_n$, when it reaches the peritectic temperature, that is when it becomes liquid + solid A; that is our peritectic reaction. Or a liquid plus solid A when it is cooled down of this particular composition, when it reaches G, then it will transform to $A_m B_n$.

This is a clear example of incongruent melting. At G, if you draw a tie line, you see that the liquid composition is 40 B, and solid composition is 100 A. But when you have solidified, the solid composition in $A_m B_n$ is 70 A - 30 B.

The composition has changed. So, it is a two-phase region changing to single-phase region and hence, this transformation is incongruent. One of the examples for such a system which shows peritectic reaction is gold-platinum system.

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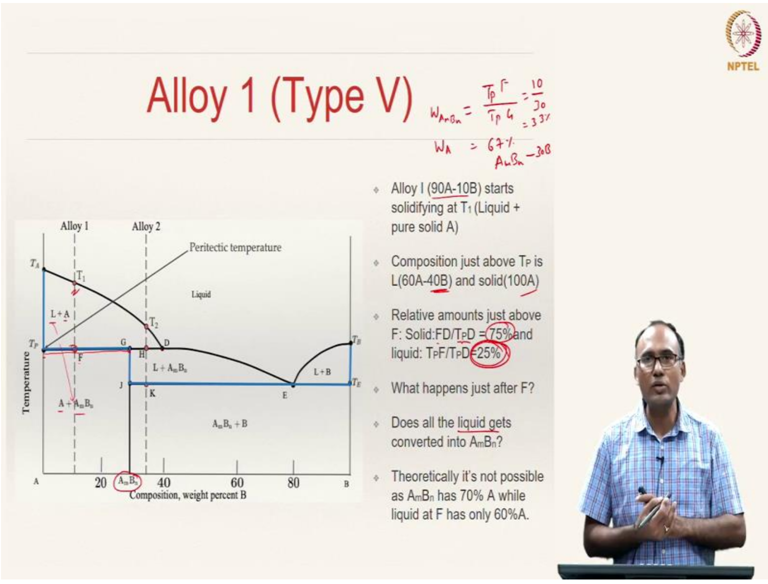

This gold-platinum system forms terminal solid solutions through peritectic reaction. Now, let us look at alloy 1. Alloy 1 is actually 90 A - 10B. It starts solidifying at temperature T_1, as we have seen here. It solidifies to liquid + pure solid A - it is like our Type II alloy. The moment it reaches the position F - the composition just above T_P, the liquid will be 40 B and solid will be 100 A; it reaches the peritectic reaction temperature.

Let us see the relative amounts of solid and liquid. What is the amount of solid? Solid fraction will be FD/T_PD = 75% and liquid fraction will be 25%. So, what should happen just after F?

Normally, if you do not pay attention to the fact that there should be a peritectic reaction, what you could expect is that here you have liquid + A and below that you have A + A_mB_n. Then, is all the liquid transforming to A_mB_n because A is already formed, or something else is happening? Let us pay a careful attention to that.

Just below F, what are the weight fractions of A and A_mB_n? The question is: does all the liquid get converted to A_mB_n? We have to see whether it is theoretically possible. Just below F, if you draw a tie line, it is also two-phase region. The weight fraction of A_mB_n is found as,

$$W_{A_mB_n} = \frac{T_PF}{T_PG} = \frac{10}{30} \approx 33\%$$

The remaining weight fraction will be of solid A i.e., 67%. How much B is present in A_mB_n? A_mB_n has 30 B. If all the liquid is transforming to A_mB_n, the liquid should also be 30 B. But what is liquid composition? Liquid composition is 40 B.

A 40 B liquid cannot transform to 30 B in A_mB_n, if all the liquid is transforming to A_mB_n. Theoretically it is not possible. Moreover, it is not possible from the weight perspective.

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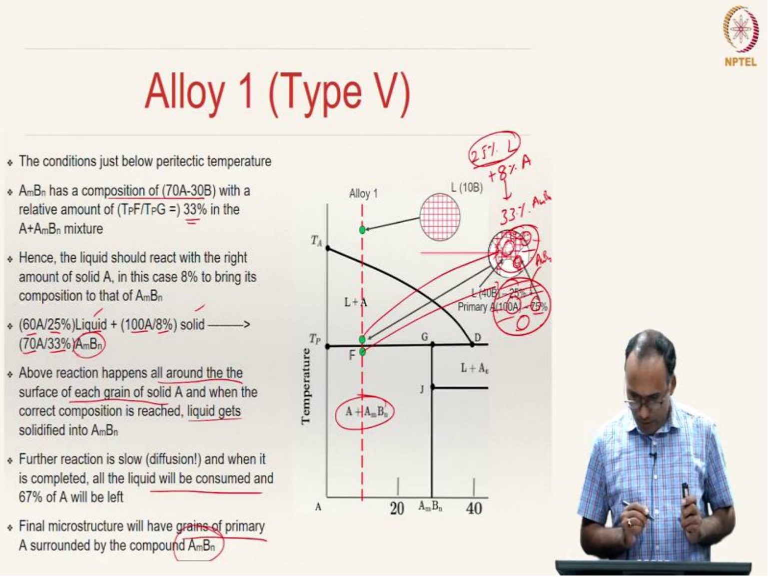

So, A_mB_n is having a composition 30 B and the relative amount will be 33% in the A + A_mB_n mixture. But you know that you only have 25% liquid - weight fraction of the liquid is only

25%, as we have calculated before. So, a 25% weight fraction liquid cannot give you 33% A_mB_n if liquid is completely transforming to A_mB_n.

The 25% liquid should interact with 8% A and give 33% A_mB_n. The only possibility is that liquid should interact with A to give a new solid A_mB_n.

A liquid which is 60 A – 40 B of 25% percent weight should be interacting with 100A of 8% weight of the solid, to give you 70A and 33% A_mB_n. That means, here a liquid and a pure solid A are giving a new solid A_mB_n. This reaction happens all around the surface of each grain of A.

Let us say this is the microstructure. All around A, this reaction takes place. Hence, the weight fraction of A reduces and the remaining will be A_mB_n. The above reaction that we have discussed happens all around the surface of each grain of solid A. When the correct composition is reached, the liquid gets solidified into A_mB_n.

The further reaction will be slow because of the diffusion and when it is completed, all the liquid would be consumed and eventually, 67% percent of A will be left. The final microstructure will have grains of primary A surrounded by compound A_mB_n. So, all that will be A_mB_n. So, just to show you the microstructure let me erase this part.

The hashed region is the liquid and the white region is primary A. On the surface, primary A interacts with the liquid, such that the liquid + solid A changes to intermediate compound A_mB_n. So, this is A_mB_n region and this is primary A.

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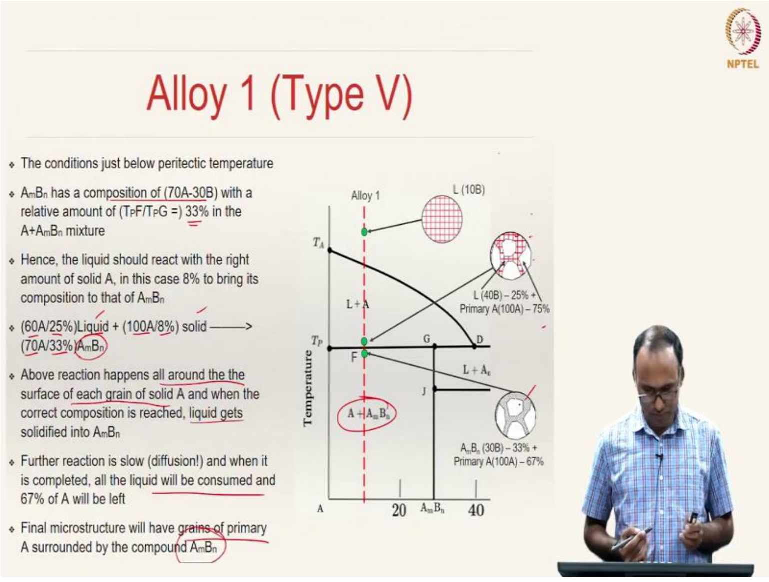

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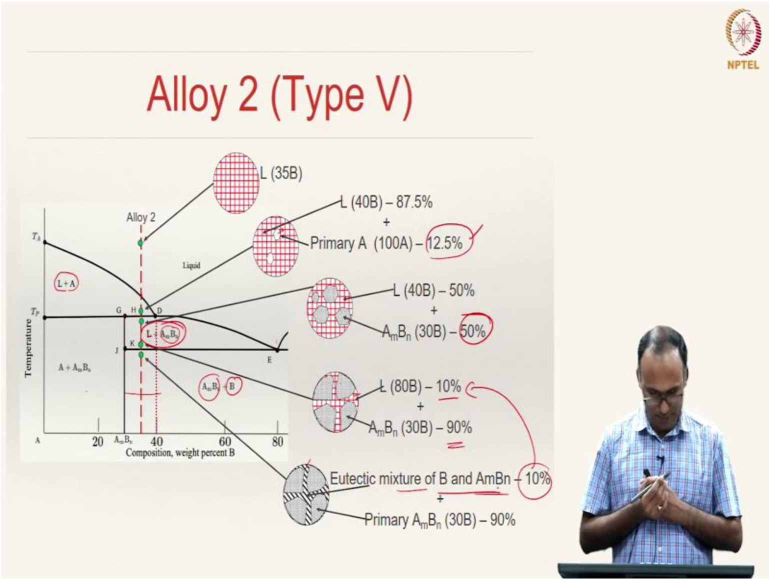

That will be the microstructure of this alloy. Let us now look at alloy 2 which is in this region. It is a little bit more complicated than this one. Alloy 2, when it is solidified, here it will be pure liquid and from the liquid, crystals of A start solidifying. At H, you will have liquid + A -- so, that is liquid and -- liquid + primary A will be there.

What happens the moment you hit this $T_P D$ line? You have reached the peritectic point and hence you need to see whether the peritectic reaction takes place. Some amount of liquid plus A is transforming to $\mathrm{A_m B_n}$ and some amount of liquid is remaining here. After this, all primary

A which you have, is interacting with the liquid and converting to A_mB_n.

In this region, you do not have A anymore. All material has been converted to liquid + A_mB_n. So, all the primary A; that means, 12.5% A interacts with some liquid in order to give A_mB_n. The amount of liquid it needs to interact with, will depend on the weight fraction of A_mB_n. Here you can see, if you draw the tie line GD, H is exactly in between GD, and hence, below this, the weight fraction of A_mB_n should be 50% and the liquid should be 50%.

Hence, 12.5% A should be interacting with 37.5% liquid in order to give 50% A_mB_n, right? There is a peritectic reaction taking place, and you have liquid + A_mB_n. The moment you are reaching line JE, here this is again your eutectic point.

A_mB_n grains are growing in size because the A_mB_n weight fraction is increasing. Just above that line, you will have 10% liquid and 90% A_mB_n. So, this is your primary A_mB_n. Now across this horizontal line JE, you should have eutectic reaction taking place; that means, all the liquid present there should be transforming to eutectic mixture of A_mB_n and B, because the other side you have B; it is a two-phase region of A_mB_n and B.

All the remaining liquid has transformed to a eutectic mixture of B and A_mB_n; that is actually having same weight fraction as the liquid that was present. So, you have primary A_mB_n and a eutectic mixture of B and A_mB_n. Here, both peritectic reaction and eutectic reaction are taking place, giving a primary A_mB_n and eutectic mixture of B and A_mB_n.

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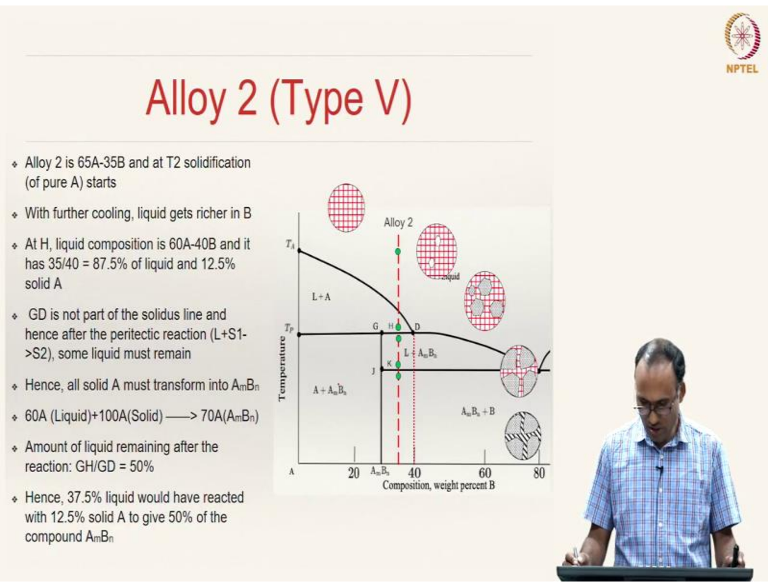

You can also calculate all the weight fractions. Whatever I have discussed so far, I have put them in the text here. You can carefully go through that and then understand how this microstructure is evolving.

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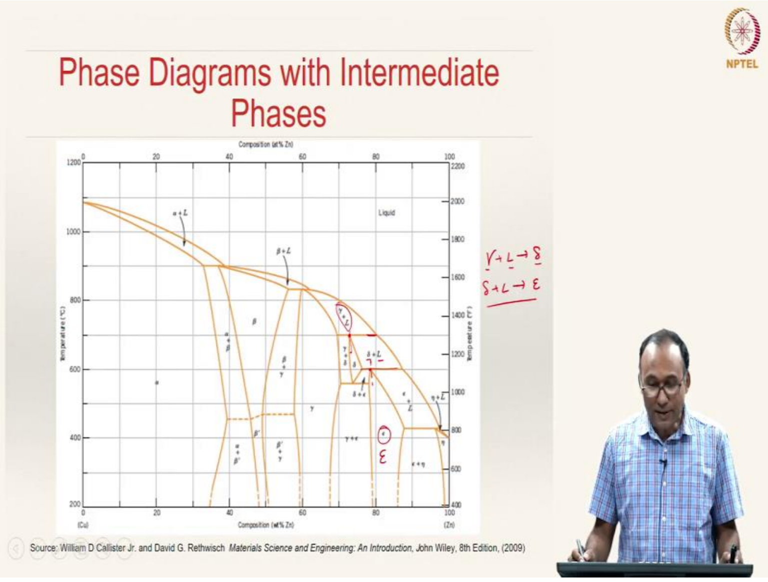

Here you are showing copper-zinc system, wherein you have different reactions taking place. And you will be able to identify various positions where peritectic reaction and eutectic reactions are also possible. You need to verify whether there are any eutectic reactions taking place and so on. For instance, if you see this point here you have solid solution γ + liquid solution L.

And then if you are cooling down, you are entering a single-phase region. At that temperature γ plus L is transforming to δ. One solid and a liquid giving you a new solid; so, this is a peritectic point. This is one point where the peritectic reaction takes place and this is another point. If you are cooling down here, then δ + L is transforming to ϵ.

You can identify other reactions in this region and you should be able to mark all the two-phase regions and so on.

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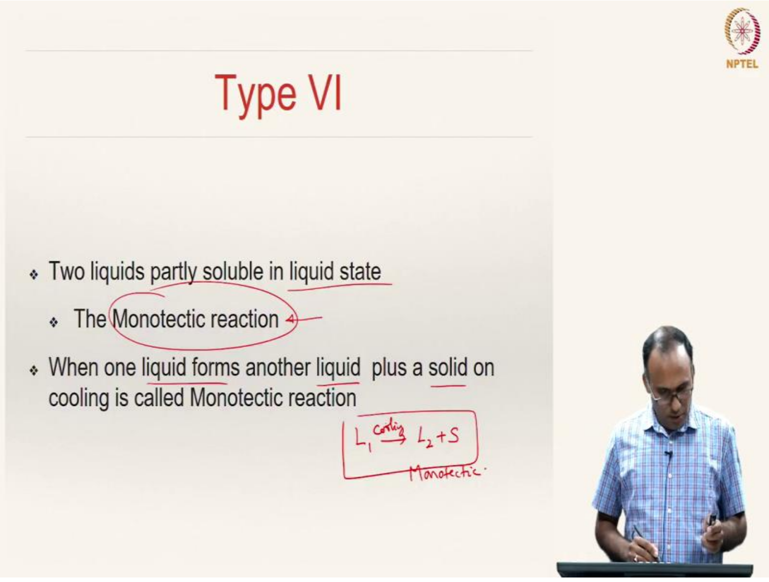

So, that is about Type V alloys, where we have discussed the peritectic reaction. In the Type VI alloys, we will look at another important reaction called monotectic reaction. So, the Type VI alloys are classified by having partial solubility in the liquid state. Until Type V alloys, we have complete solubility in liquid state.

The Type VI alloys give an example of a system wherein you have partial solubility in the liquid state. Two liquids are partially soluble in the liquid state and that gives us an example of a special reaction called monotectic reaction, which we will see in the phase diagram. What is monotectic reaction? When one liquid forms another liquid plus a solid; so, a liquid 1 transforming to a liquid 2 plus a solid upon cooling is called monotectic reaction.

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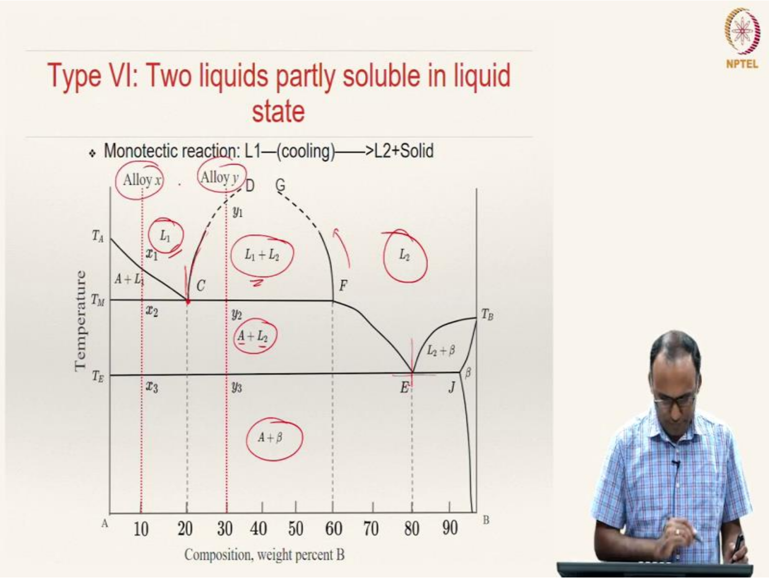

So here, this is a typical phase diagram that actually shows the monotectic reaction. We will see where it is happening. It actually shows a partial solubility in the liquid state. And hence, like in the case of solid state, if you have partial solubility, you will have two solid solutions that are forming.

Similarly, in the liquid state, if you have partial solubility, you will have two liquid solutions. Liquid solution 1 is the liquid solution in which A is the solvent and liquid solution 2 is the one in which B is the solvent. So, here you have a liquid solution 1 and liquid solution 2 and in between liquid solution 1 + 2. So, this boundary represents the boundary between single-phase region and two-phase region.

Up to a certain point, the lines CD and FG are drawn as solid lines, after that they are shown as dashed lines. In a phase diagram, if a boundary is shown as a dashed line, it means that the position of that boundary is not very well known until now.

And another important thing to keep in mind - if you have a horizontal line on a phase diagram, there is some special reaction taking place at that position. By looking at the phases above and below the horizontal line, you can figure out what sort of a special reaction is taking place.

If you look at this point C and if you are cooling down, you have liquid solution L_1 and below that you have A + L_2. This is a clear case of monotectic reaction - a liquid is transforming to a solid and a new liquid solution. This line $T_M F$ is sort of representing the monotectic reaction line. The horizontal line $T_E E$ represents a liquid transforming to two solids and hence it is eutectic reaction.

Now it is much easier for us to identify where the eutectic reaction is taking place or a special reaction taking place. And by looking above and below that horizontal line, we will be able to identify what sort of a special reaction is going to take place around that region. Here, we will look at the microstructure evolution for two alloys - alloy x and alloy y.

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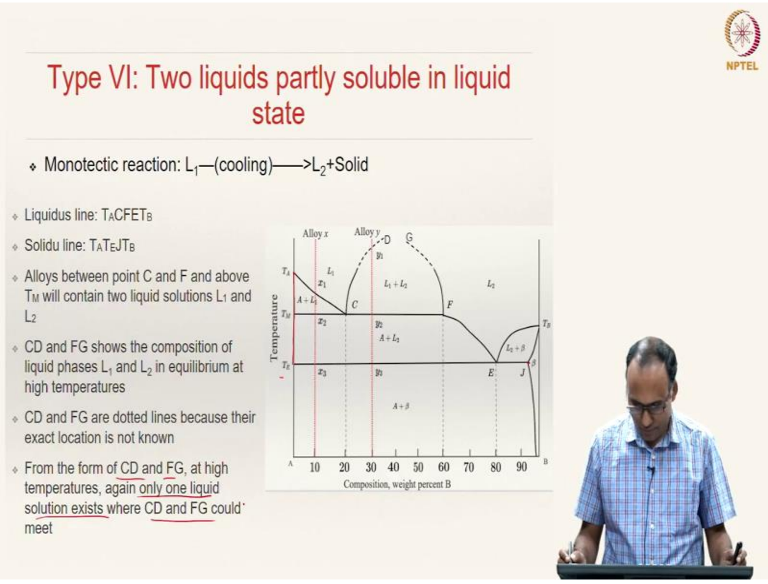

Let us identify the liquidus line. The liquidus line is $T_A CFET_B$ and solidus line is $T_A T_E JTB$. CD and FG show the composition of liquid phase L_1 and L_2 in equilibrium at high temperatures.

What is the composition of the liquid phase at high temperatures? You know that after certain time, CD and FG are dotted lines because their exact location is not known. Hypothetically, if you imagine CD and FG lines are extended to high temperatures, at much higher temperatures, these two may actually join together, such that at much higher temperatures, you may still have one liquid solution.

As you are coming down, you may have two liquid solutions; that means, the liquid solubility might improve at high temperatures; that is what we are saying. From the form of CD and FG, at high temperatures, again only one liquid solution exists where CD and FG would meet.

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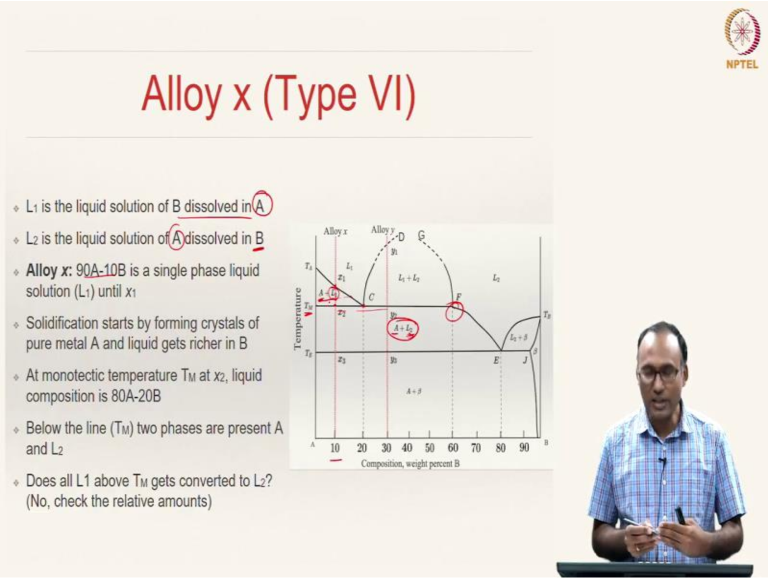

In alloy x, L_1 is the liquid solution of B dissolved in A; that means, A is our host and L_2 is the liquid solution of A dissolved in B; that means B is the host. Alloy x comprising 90 A – 10 B is a single-phase liquid solution (L_1) until this position x_1. Solidification starts the moment it hits this line and then the liquid starts giving out crystals of A - A + L_1, it is a two-phase region.

As you are coming down, the liquid starts getting richer in B, because the liquid composition is increasing.

The moment it reaches the monotectic temperature here, the composition reaches the monotectic composition; so that means, whatever -- the liquid composition you can see is 20B 80A. And at that point, the remaining liquid L_1 will undergo a monotectic reaction to give L_2 + A; that means, the weight fraction of A increases and the L_1 will become L_2.

L_2 is a liquid solution in which B is more whereas, you can see that as you are coming down the weight fraction of B is increasing. Just below T_M, the composition of B will be more than 50% as you can see here. Below the line T_M, it is a two-phase region. The two phases present are A and L_2.

The question is, without paying attention to any reactions, if we see here A + L_1 has become A + L_2 which means, can we simply say that all L_1 is becoming L_2? No. Again, you can look at the composition of L_1 and the composition of L_2 and weight fractions of L_1 and L_2. And then, you will see that L_1 cannot completely transform to L_2, but L_1 + A should transform to L_2. That is the only thing that is feasible, if you look at the weight fractions.

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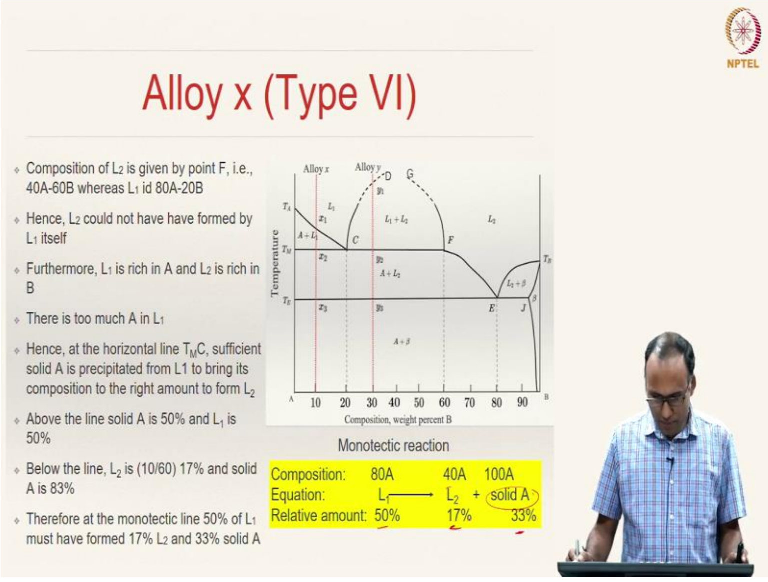

So, the L_1 which is 50% here will transform to L_2 + solid A. So, solid A will be 33% and L_2 will be 17% out of that.

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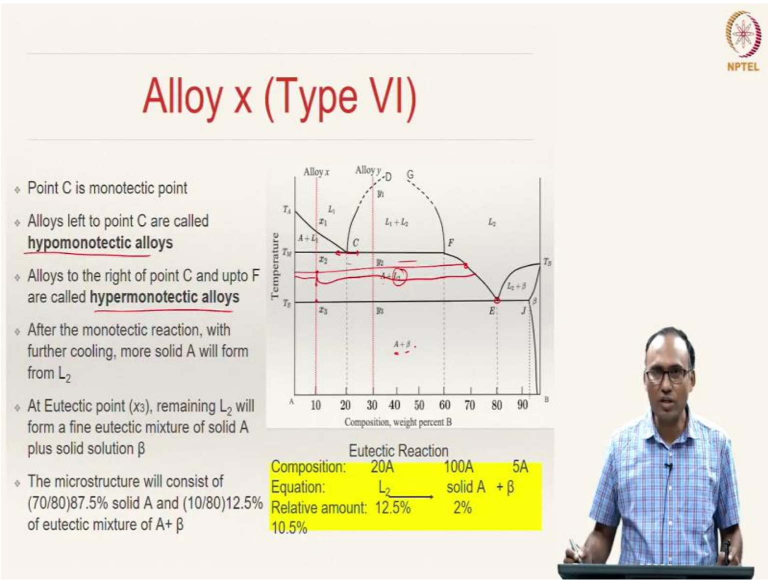

This is the monotectic point. All the alloy compositions left to the monotectic point are called hypomonotectic alloys. All the compositions right to that are called hypermonotectic alloys. After monotectic reaction, with further cooling what happens? The weight fraction of solids keeps increasing, because this line's length is going to increase.

If you draw a tie line, as you are going down, the length of this region keeps on increasing - that is the weight fraction of solid. And this portion is remaining the same, but the total length is increasing and hence weight fraction of solid keeps on increasing and weight fraction of L_2 keeps on reducing.

At T_E, the remaining L_2 will reach the composition equal to eutectic composition. And then, that remaining liquid has to transform to two solids that are A and β; but that will transform as a eutectic mixture of A and β. Eventually, you will have some primary A and eutectic mixture of A and β - that will be the final microstructure that you would see.

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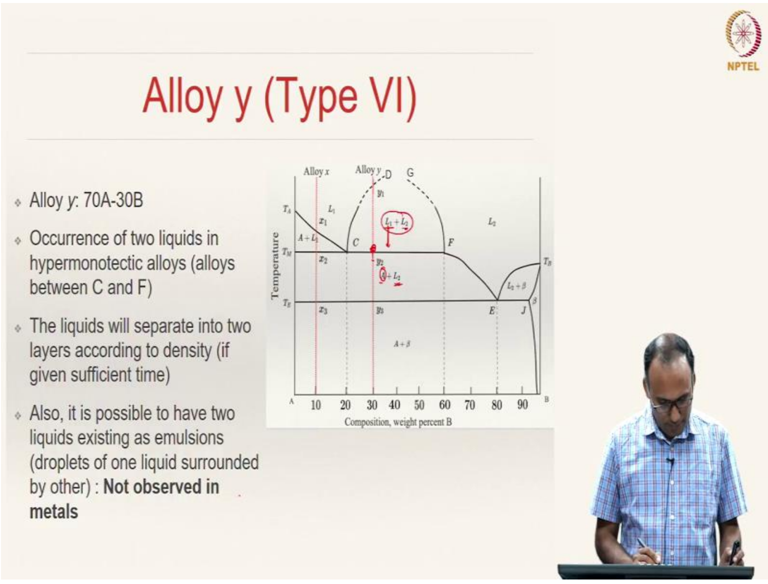

And if you look at alloy y -- let us say, this is one liquid solution and then it enters two-phase region, liquid solution 1 plus liquid solution 2. And here, at this point, you will have the liquid solution L_1 transforming to A + L_2. So, can we say that L_1 is simply transforming to A or $L_1$is actually giving A and L_2?

So, that we can see by looking at the weight fraction of L_2 above this point and below that point. You see that the weight fraction of L_2 increases; that means, some L_1 is also responsible for transforming to A.

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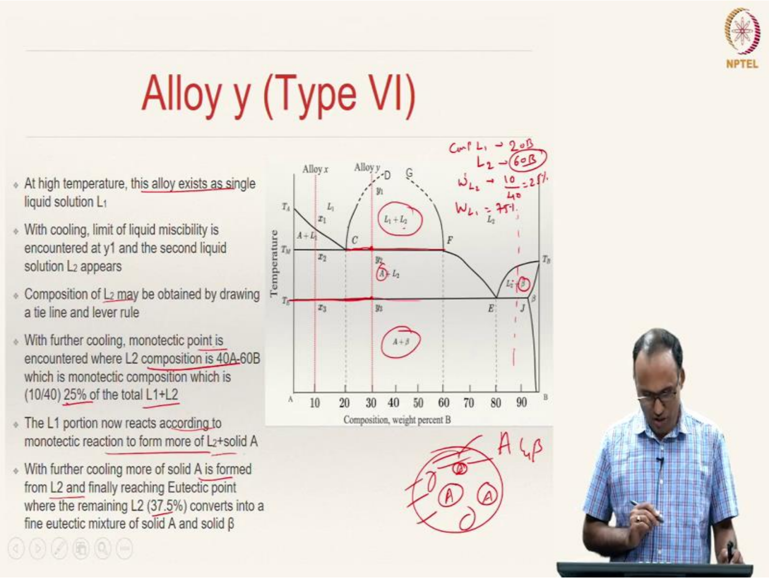

We can actually look at the weight fractions here. At high temperature, this alloy exists as a single L_1. With cooling it will enter $L_1 + L_2$, so, L_2 starts appearing. And composition of L_2 may be obtained by drawing a tie line, right? So, if you are somewhere here, then if you draw a tie line, at this point just above y_2, the composition of L_1 will be 20 B and composition of L_2 will be 60 B.

Weight fraction of L_2 will be 25% and weight fraction of L_1 will be 75%.

With further cooling, monotectic point is encountered where L_2 composition is 40 A - 60 B, which is monotectic composition - weight fraction is 25% of the $L_1 + L_2$. So, the L_1 portion now reacts according to monotectic reaction to form more of L_2 + solid A. So, that is what happens. So, with further cooling, more of solid A is formed from L_2, finally reaching eutectic point.

Here, you can see the weight fractions of L_2 and primary A formed until now. We can find out that weight fraction of L_2 as 37.5%. That 37.5% L_2 would have transformed to eutectic mixture of A and β.

The final microstructure will have primary A and remaining will be eutectic mixture of β and primary A.

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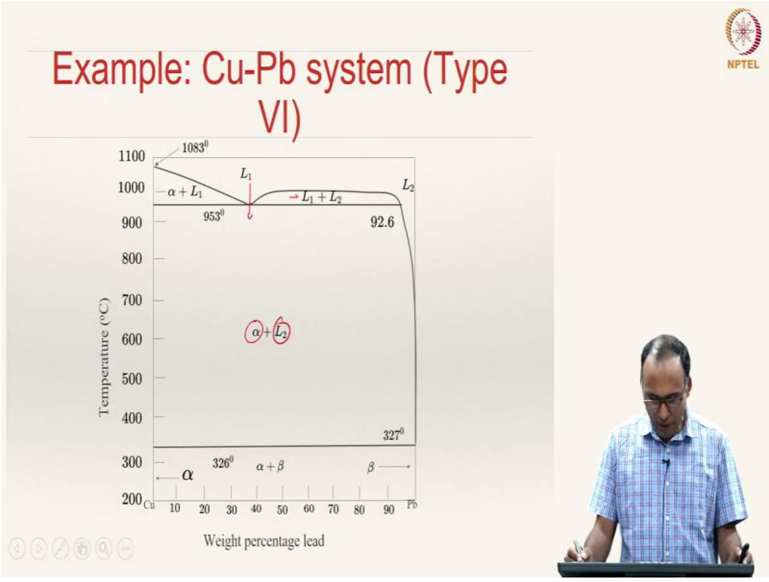

This is a typical example of a system which has monotectic reaction, that is copper lead system. Here you can see the two liquid solutions and then this is L_1, this is our monotectic reaction. L_1 transforms to $\alpha + L_2$. Since the weight fraction of lead in copper is very small, we have not shown this line; but it is not pure solid copper, but it will be a solid solution of copper and lead.

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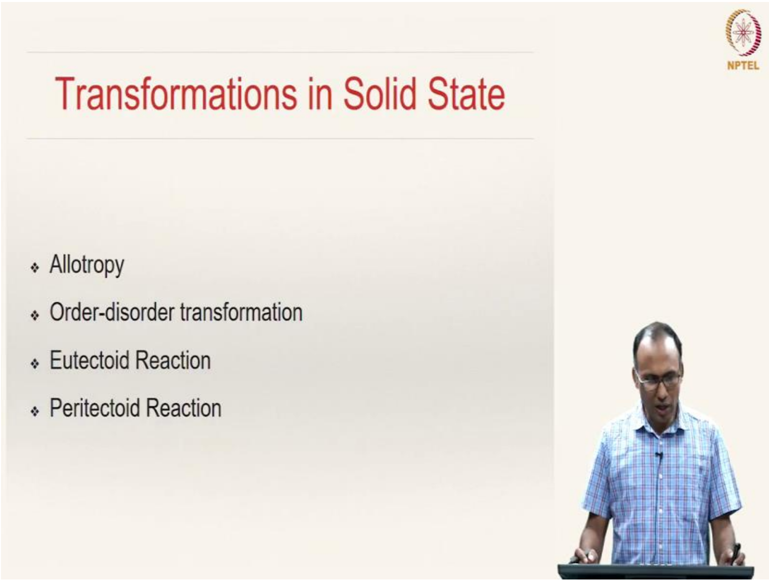

So far, we have looked at the transformations where a liquid phase is always involved and the next sort of transformation that we need to look at are transformations in the solid state, which we will discuss in the next class. Thank you very much.