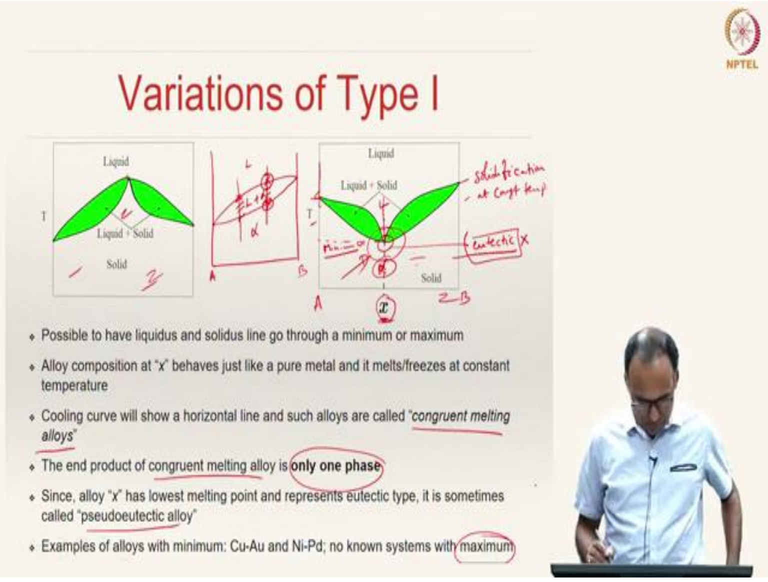
Basics of Materials Engineering
Prof. Ratna Kumar Annabattula
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Lecture - 58
Phase Diagrams (Congruent Melting Alloys, Type II Alloys, Eutectic Reaction)

(Refer Slide Time: 00:13)



Welcome back. In the last class we have looked at Type I alloys called isomorphous alloys; which means both the components are completely soluble in liquid state as well as solid state. Today, here we are going to see few variations of Type I alloy. When we saw the Type I alloys phase diagram, here I am drawing it again on the y-axis, here you have let us say A and B and let us say melting point of A is lower than the melting point of B.

Then, the phase diagram of an isomorphous alloy looks something like that – the kind of isomorphous alloys studies at so far look like that; wherein A and B are completely soluble both in liquid state as well as solid state.

Now, is it possible to have a maxima or a minima for the liquidus and solidus lines? If we have something like that as we have shown here, you can see that this is also isomorphous -- this left side is also an isomorphous alloy, where the liquidus line has a maxima. On the right-hand side here, you have a solidus line showing a minima here.

Alloys of this kind are also possible, but the alloy composition, for instance, if you look at the isomorphous alloy variations with a minima that is shown on the right hand side here, we see that the composition at x -- let us say you are looking at the x composition.

For instance, let us now compare the solidification of the alloy with solidification on A and B. Here when you are solidifying from the liquid state and A solidifies at constant temperature; just above this temperature it is liquid, just below that temperature it is solid.

So, solidification happens at constant temperature for A as well as B. Whereas for any other alloy combination - any isomorphous alloy, the solidification starts at one temperature, ends at another temperature.

Now, if you look at this special case of an alloy with composition x, again if you consider the solidification, the solidification is starting and ending at the same temperature. That means, it is behaving like a pure metal in terms of its solidification, i.e., solidification is happening at constant temperature and such alloys are called congruent melting alloys.

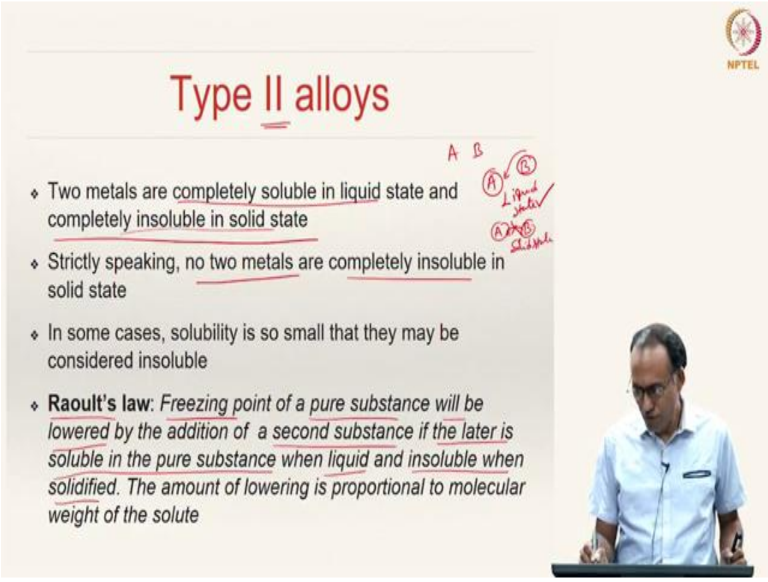
That means, the solidification happens for these materials at constant temperature. The composition of the alloy in the liquid state as well as in the solid state, after the transformation, will not change. So, the end product of a congruent melting alloy is only a single-phase alloy. Here, you have liquid phase and it transformed to solid phase, right? So is the case for pure metals A and B. The melting process or the solidification of pure metals is congruent in nature.

Similarly, if you have any other alloy system which happens at constant temperature, but in addition to that, the end product will be a single-phase system. Here, it is a single-phase solid solution α, right? For instance, if you see this particular alloy composition x, the melting happens -- amongst all the alloy combinations between A and B, the alloy x has the lowest melting temperature.

This represents a special kind of alloy types called eutectic. Although it resembles eutectic, it is not really a eutectic phase, rather it is referred to as pseudoeutectic. We will discuss the definition of eutectic and the salient difference between a congruent melting phase and a eutectic phase.

The materials which show these kinds of variations of Type I isomorphous alloys with a minima or maxima, somewhere in between are not very common. But we do not know many materials which have a maxima like we have shown on the left hand side figure; but there are evidences for alloy systems which show a minima like this, as it is shown in right hand side figure. The copper-aluminum, nickel-palladium systems are known to show this minima and there are no known systems with maximum.

(Refer Slide Time: 05:33)



Having discussed the Type I alloys, now let us discuss the next type of alloys called Type II alloys. How did we define Type II alloys? Type II alloys are characterized by the fact that they are completely soluble in liquid state, but completely insoluble in solid state.

After solidification, they separate out into two different components. They will not make a solution and instead, segregate into A and B separately; that is what you mean by complete insolubility in solid state.

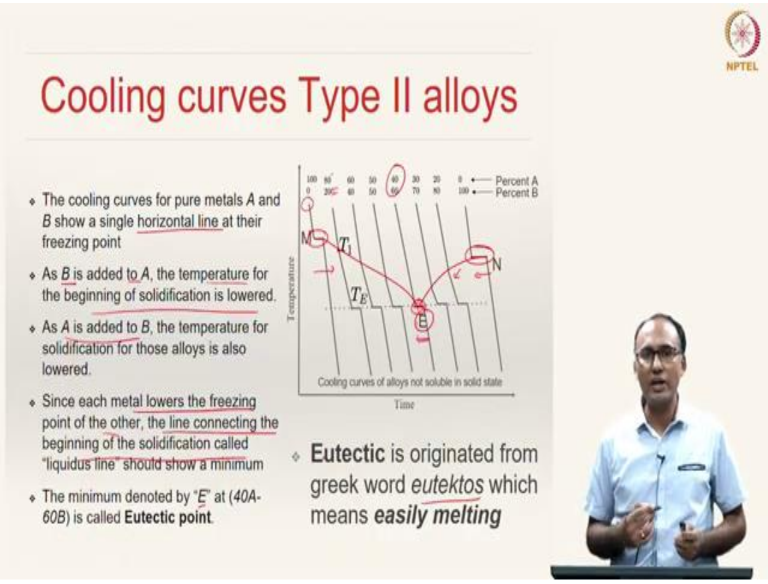
This is a model system that we are choosing to study; because in reality, strictly speaking, no two metals are completely insoluble in solid state. Fractionally tiny amount of solubility may be there.

But if the solubility is very small, then you can idealize that as complete insolubility in solid state. Even if there is a fractional amount of solubility, that will lead to certain differences that we will see at a later stage. Whenever we are saying Type II alloys, we have complete solubility in liquid state and complete insolubility in solid state.

Before we start looking at the phase diagram of these kind of Type II alloys, we will first go through Raoult's law, which states that the freezing point of a pure substance will be lowered by the addition of a second substance, if the latter is soluble in pure substance when liquid, and insoluble when solidified.

That means, if we have two materials A and B, let us say you have A and if you are adding A to B, in the liquid state, they are soluble, but A cannot join B in the solid state.

(Refer Slide Time: 07:58)



If we have a system like that, then Raoult's law says that, the melting point of A will be lowered when you are adding B to that. By how much amount will it be lowered? The amount of lowering is proportional to the molecular weight of the solute; it depends on the molecular weight of the solute.

The bottom line is that, if you have two materials A and B which are completely soluble in liquid state and not soluble in solid state - then, if you take pure substance A and if you add B, then the melting point of A will go down or the combination will go down in solid state. And if you take B and start adding A, then the melting point of B will also go down.

Let us look at the cooling curves. This is pure A which solidifies at temperature M and pure B solidifies at N. Consider a combination of 80 A - 20 B; when you are adding B to A, according to Raoult's law, the freezing point has to reduce. That is why the freezing point has gone down; but it will not solidify at constant temperature, because some liquid solution is present.

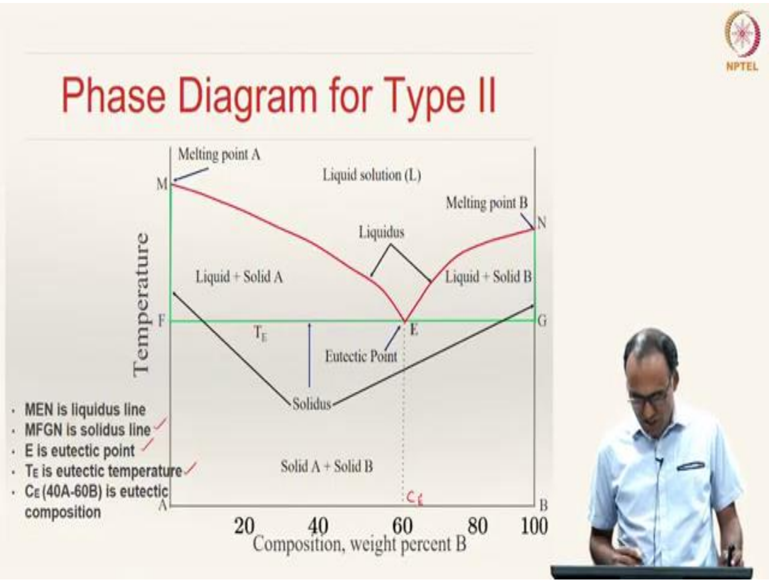
That means, the melting points of the alloys from left to right and the right to left are going to go down, because of the addition of the solute atoms to the solvent cloud. And we see that, there will be one particular alloy composition, in this case 40-60, wherein again the melting happens at a constant temperature. It is like the congruent melting case, as solidification happens at constant temperature, which means it behaves like a pure metal.

So, the cooling curve for pure metal A and B show a single horizontal line at their freezing point here. As B is added to A, the temperature for beginning of the solidification is lowered. Similarly, as A is added to B, the temperature for solidification is lowered for the alloys coming from the right.

Since each metal lowers the freezing point of the other, the line connecting the beginning of the solidification line, called liquidus - should have a minimum somewhere here. The minimum point is what is denoted by E and that point is called eutectic point; that means of all these combinations of alloys, there is one particular combination, at which the melting or solidification happens at the lowest temperature.

The composition that corresponds to that is called eutectic composition and the temperature at which the solidification happens is the eutectic temperature. What do you mean by eutectic? Eutectic is a Greek word. It actually originated from a Greek word called eutektos, which means easily melting. As you can clearly see here, this is the alloy that has the lowest melting point and hence it is called a eutectic alloy.

(Refer Slide Time: 11:28)



This is something that we see in Type II alloys. From the cooling curves, now let us look at the phase diagram which is temperature-composition.

Let us say this is melting point of A, this is melting point of B and as we said, and this is the solidification starting temperature. This is our liquidus line. M, N are chosen from previous figure. E is the eutectic point and that is our liquid solution above that liquidus line. This green line that we have shown just now, that is MFGN is the solidus line.

That means, below that, everything will be solid; above that you may have liquid plus solid. In between the liquidus line and solidus line, you will have two-phase region. Above the liquidus line, you will have single-phase liquid solution, below the solidus line you will have again a solid phase and it may have two-phases, but here we are only talking about a solid phase.

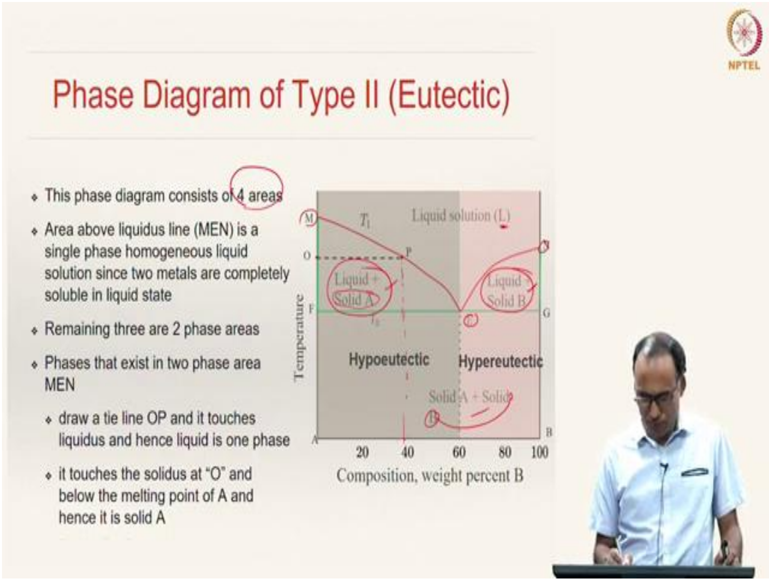
The temperature at which the eutectic alloy solidifies is called eutectic temperature, denoted by T_{E}. This is a liquidus line and the green lines represent solidus lines and here you have liquid solution. Since in the solid state, the materials A and B cannot mix, they cannot be called solid solutions.

In the solid state, we will not have solid solutions, but pure solids. That is why we are not representing the solid phases with Greek letters and instead writing as solid A and solid B; it is not a solid solution, it is pure solid A and pure solid B.

Even though it is a two-phase region in some sense, but then 100 percent will be solid A, 100 percent will be solid B. Their weight fractions are going to be different; that we can get it through our tie line when we draw. This is liquid plus solid A and here you will have liquid plus solid B.

Left to E, you will have liquid plus solid A; because this side, the solid is A, and right to that liquid plus solid B, because this right side you have B. This is our eutectic point at 60 B. So, as we have already discussed, MEN is the liquidus line, MFGN is the solidus line; E is the eutectic point, T_{E} is the eutectic temperature, C_{E} is the eutectic composition, which is 40 A and 60 B.

(Refer Slide Time: 14:40)



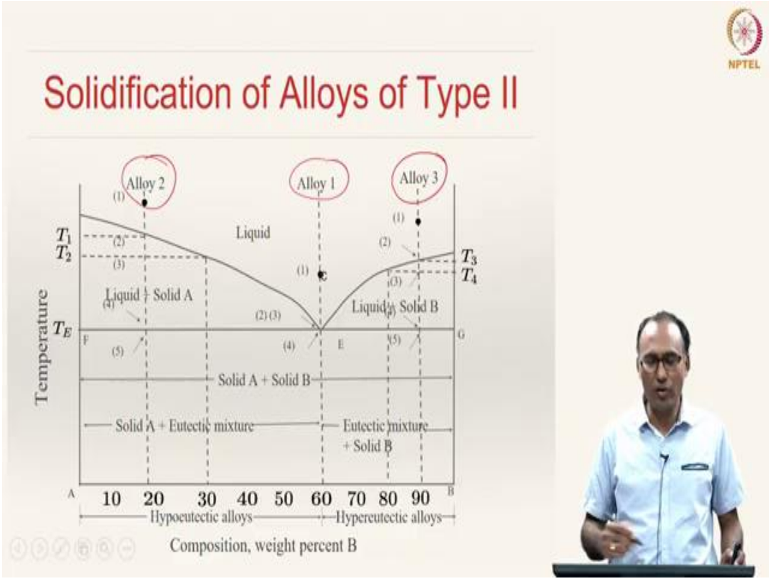
This is our phase diagram for Type II alloys and this is our eutectic composition. All the alloys left to this eutectic point are called hypoeutectic alloys; this particular alloy at composition C_{E} is called eutectic alloy. All the alloy compositions left to that eutectic point are called hypoeutectic alloys, and all the alloy compositions right to the eutectic point are called hypereutectic alloys; that is the convention that we use in the rest of the module.

Here, we can clearly see that the phase diagram has four areas to be identified; the area above the liquidus line MEN, this red line is a single-phase homogenous liquid solution, L.

This is the single-phase region, which is actually a liquid solution of two metals A and B, which are soluble completely in liquid state. The remaining three areas are two-phase areas; liquid plus solid A is one area, liquid plus solid B is another area, solid A plus solid B is another area. This is a two-phase region. So, this should be solid B.

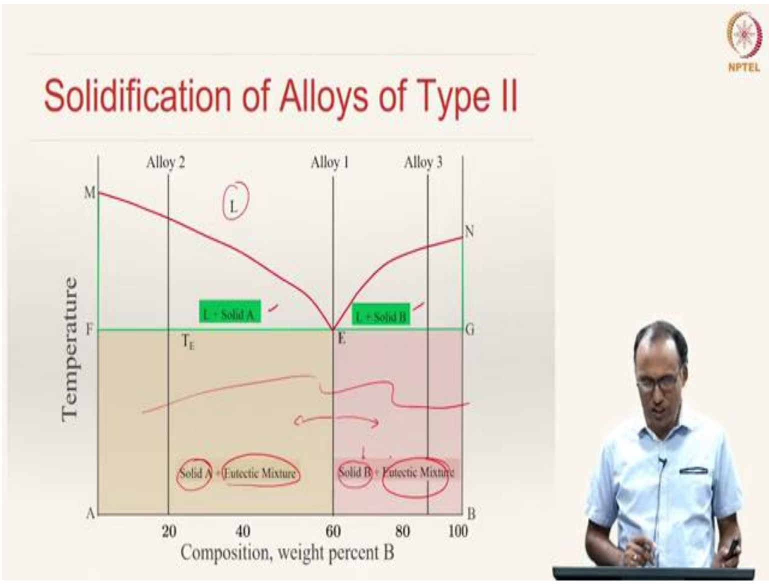
This is liquid plus solid A; this region is liquid plus solid B and here you have solid A plus solid B - all three are three two-phase regions. If you want to find the phases that exist in two-phase region, for instance if you take this, you draw a tie line OP and it touches the liquidus line at P and the solidus line at O - which means, the solid composition will be solid A 100 percent A and liquid composition will be corresponding to this vertical, that is about 40.

(Refer Slide Time: 16:50)



Let us look at the microstructure evolution of the three different alloys of Type II. Alloy 1 is having eutectic composition exactly, alloy 2 is a hypoeutectic alloy, and alloy 3 is a hypereutectic alloy. Let us look at how the microstructures look like for these three different kinds of alloys.

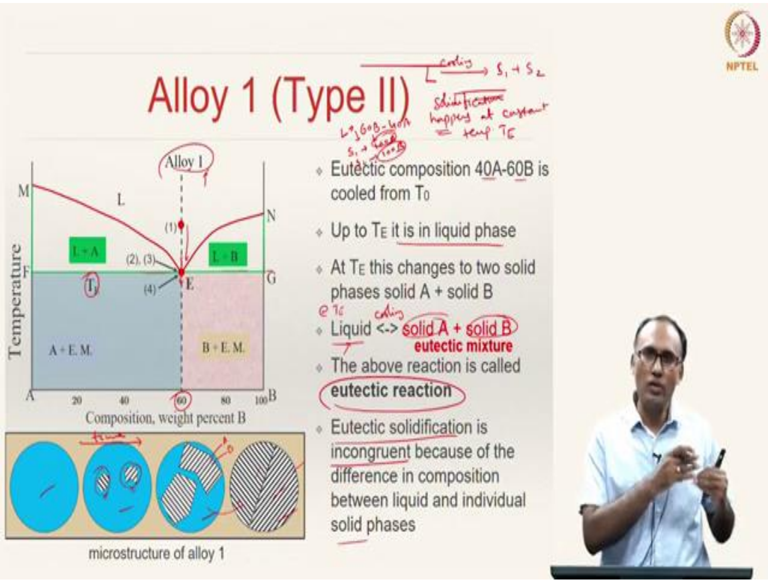
(Refer Slide Time: 17:23)



As we have already mentioned, above the MEN liquidus line, everything is liquid solution of A and B. You have three two-phase regions; that is liquid plus solid A, liquid plus solid B, this entire region is solid A plus solid B. But here, we are showing hypoeutectic alloy region and hypereutectic alloy region. Left to the eutectic composition is hypoeutectic, right to the eutectic composition is hypereutectic; both are two-phase regions.

However, there is a slight difference. Left to the eutectic composition that is hypoeutectic alloy will be a two-phase mixture of solid A and a eutectic mixture. We will see what do we mean by eutectic mixture. To the right, you will have solid B and eutectic mixture. In order to understand this carefully, let us pay attention to each and every alloy.

(Refer Slide Time: 18:21)



Let us look at the microstructure evolution alloy 1. Alloy 1 is having a composition of 60 B - 40 A. Let us say it is cooled from a temperature T_0 from point 1.

As you are cooling down from point 1, the liquid will be giving away sensible heat. As a result, the temperature of the liquid goes down, until it reaches temperature T_{E}. Up to T_{E}, it is liquid phase.

What happens at the eutectic temperature, T_{E}? There is a reaction that is taking place - all the liquid will transform to solid A and solid B; above this it is liquid solution, below that it is transforming to two solids, solid A and solid B.

If you have a liquid solution, with 60 B and when that composition is brought down to a temperature T_{E} - that is this line called eutectic line, and at that point, the transformation happens from liquid state to two solid states - solid A and solid B. This mixture of solid A and solid B is called eutectic mixture, because it is going through a eutectic reaction.

In a eutectic reaction, a liquid upon cooling will transform to two solids, solid 1 and solid 2; that is the definition of a eutectic reaction. Please note that, this eutectic reaction is happening at constant temperature; that means this solidification happens at constant temperature T_{E}.

In the previous module when we said pure metals solidify congruently, that means they solidify at constant temperature. Now, can we call this solidification also to be congruent? We cannot call eutectic solidification congruent. It is incongruent, because of the difference in composition between liquid and individual solid phases.

For instance, the liquid solution has 60 B, 40 A that is the composition of liquid solution. But when it is solidified, solid 1 has 100 A, solid 2 has 100 B. It solidified, but it did not retain the compositions - the compositions have changed.

Hence, it is not a single-phase, it is two-phase. What happened in the congruent melting alloys? An alloy solidifies, but it will remain in one phase; but here it is solidified into two-phases and their compositions have completely changed. Hence, a eutectic solidification cannot be termed as congruent solidification. It is incongruent in nature.

Let us now look at the microstructures. When you are cooling down, just at this point, we are showing the microstructure as an evolution in time. At point T_{E}, initially you have liquid and as you are cooling it down, at that particular temperature, nuclei start forming. As you are providing more and more time, the nuclei start growing and complete solidification happens from liquid state to solid state.

However, when it is solidifying through eutectic reaction, it will form alternate layers of A and B. For instance, in this picture, you have the black region and the white region.

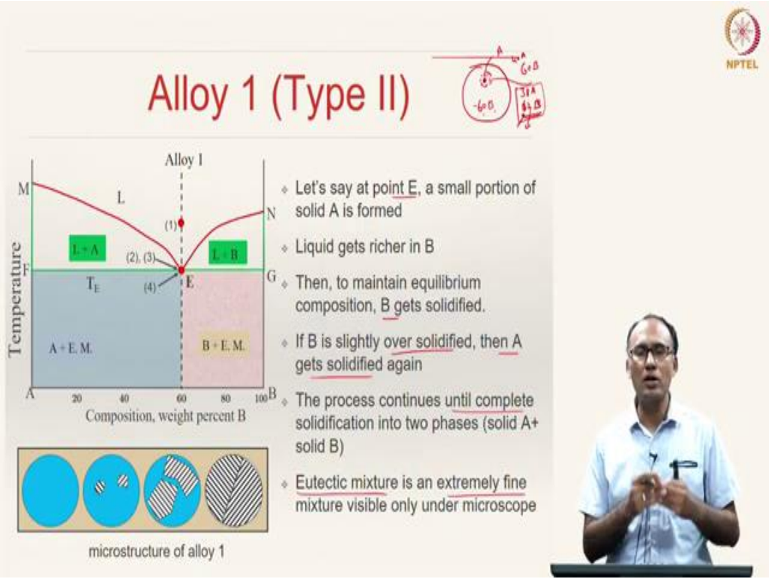
Let us say that the black region is A and white region is B. The solidification microstructure looks like alternate layers of solid A and solid B. Such a mixture is called eutectic mixture. A typical nature of a solid that is formed through eutectic reaction will have this alternate layer microstructure.

That is what is usually represented here. Please note that the microstructures that we are showing in these four graphs are only representative, i.e., they are schematics and not the real microstructures. The real microstructures when looked under the microscope, may have an alternate layer structure which may similar but not identical. Moreover, the initial shape of the nuclei or grains can be very different.

Here, I have only shown two grains; it does not mean that in reality, you will have two grains; you can have several grains. To summarize, in Type II alloys, the solidification of alloy 1, which has a eutectic composition, occurs at a constant temperature called eutectic temperature.

When it solidifies, it transforms into two solids - solid A and solid B and the microstructure will be alternate layers of solid A and solid B.

(Refer Slide Time: 24:26)



Let us see how this eutectic reaction is taking place. Let us say at point E, from the liquid a small portion of solid A is formed, because in the solid state, they cannot be mixed.

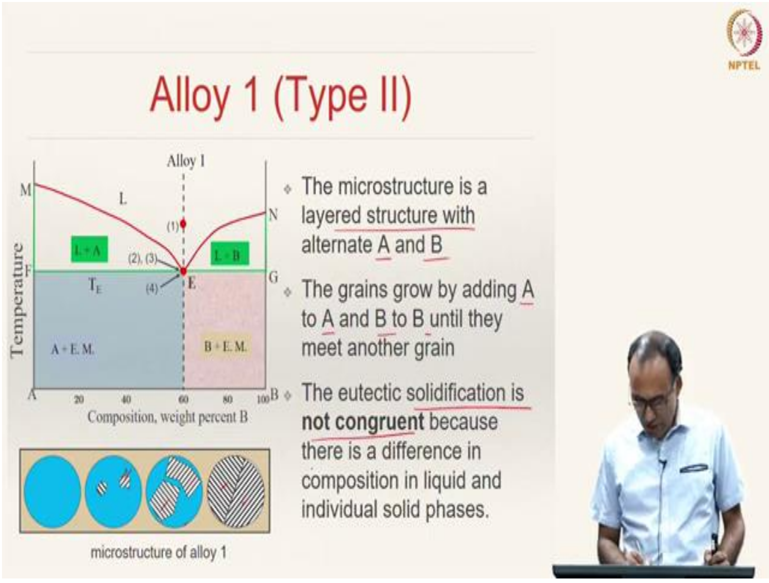
The surrounding liquid would become richer in B, because some amount of A has gone away from that liquid. Let us say now this is 40 A - 60 B. Since a small amount of solid A has formed, the surrounding liquids composition might have changed to 38 A - 62 B.

Everywhere else it is still 60 B; but only the liquid that is surrounding the initial nucleus of A has become rich in B. That means, this is not in equilibrium, because we have started with the composition of liquid having 60 B.

Now, it has become 62. To maintain equilibrium, it will give away this 2%, i.e., some amount of B gets solidified. It is possible it might not exactly give away 2%, it might give a little more.

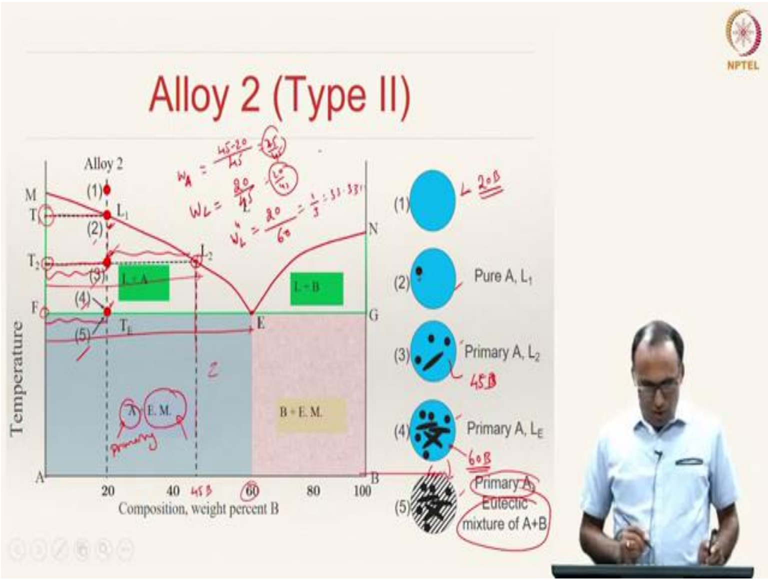
If B is slightly over solidified, then what happens? From that liquid, A gets solidified again; A and B try to solidify one after the other in order to maintain equilibrium. The process is continued until complete solidification happens into two-phases, that is solid A and solid B. Under the microscope, the eutectic mixture looks like an extremely fine mixture of two substances.

(Refer Slide Time: 26:57)



As I have already mentioned, the microstructure is a layered structure with alternate A and B. These grains that we have seen here, grow by adding A to A and B to B, until they meet one another. Here, you will start adding A to A and B to B, and then they grow. As we have already discussed, the eutectic solidification is not congruent, because there is a difference in composition in liquid and individual solid phases.

(Refer Slide Time: 27:28)



Let us look at the solidification of alloy 2 and its microstructure. Here 1, 2, 3, 4, 5 states and the corresponding microstructures are schematics - please keep that in mind. Blue colored regions represent liquid phase. At 1 it is in liquid state. At point 2, on this liquidus line, you would be entering two-phase region.

In the two-phase region, when you draw a tie line like this at temperature T_1 – let's denote this as L_1 state -- then the tie line hits the solidus line here and that is what represents pure solid A. That is the reason why you would form pure A. What will be the liquid? Because A is very small, liquid composition will be almost same, i.e., 20 B.

Upon further cooling it down, we reach point 3 i.e., at temperature T_2. Then you draw a tie line. The tie line hits the solidus line at this position and the liquidus line at L_2. That means, the solid composition is again 100 A, because it has hit at 100 A.

So, there is 100 A, and what is the liquid composition? That is coming out to be something like 45 B, right? Initially the liquid was 20 B. By the time it came here, it has become 45 B. What happened? The liquid became richer in B, because some amount of solid A is getting out of liquid.

As you are cooling down, solid A is segregating out and the liquid is becoming richer in B. Let consider the situation at point 4 here. You draw a tie line -- FE will be the tie line in some sense.

The solid composition is 100 A as expected. What is the liquid composition? Liquid composition is equal to eutectic composition; that means the remaining liquid has reached eutectic composition - it has become 60 B.

What is the temperature? Eutectic temperature. Whenever you have a liquid solution at eutectic temperature and having a eutectic composition, what should happen? The liquid solution should undergo eutectic reaction; that means all the liquid solution should transform into two solids at constant temperature.

So, you have some primary A that is formed until point 4 and between 4 and 5, there is sufficient amount of time which we are not showing on the phase diagram; but remaining liquid solution would transform into eutectic mixture of A and B. That is why you see alternate layers of A and B here.

If you look at the microstructure, you have primary A and a eutectic mixture of A and B. That is the reason why in this blue region hypoeutectic alloy, the microstructure is primary A and eutectic mixture of A and B.

Please note that there is A in the eutectic mixture and there is primary A. If you take the total weight fraction of A, there will be some amount of weight fraction that is formed through primary A and some amount will be in the form of eutectic mixture of A and B.

Another thing that I would like to point out - when we are going from point 2 to point 3, what is the weight fraction of liquid? It is almost 100 percent. Only a tiny amount of solid has formed. Now, come to point 3; what is the weight fraction of solid or weight fraction of A?

$$W_A = \frac{T_{23}}{T_2L_2} = \frac{45-20}{45} = \frac{25}{45}$$

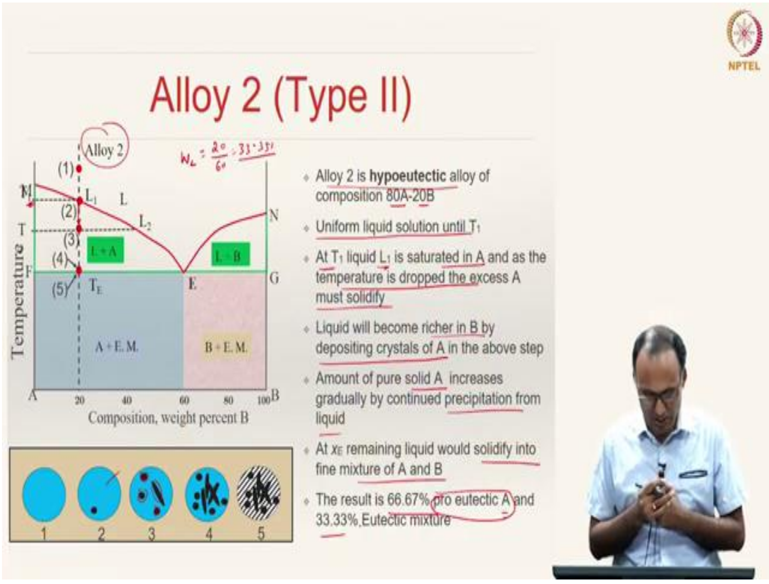
The weight fraction of liquid is,

$$W_L = \frac{20}{45}$$

So, the weight fraction of the liquid has come down and the weight fraction of solid has increased compared to point 2. And by the time you come to point 4, what is the weight fraction of the liquid?

$$W_L^4 = \frac{20}{60} = \frac{1}{3}$$

(Refer Slide Time: 33:59)



Let us carefully look at it now and go through it once again. Alloy 2 is hypoeutectic alloy of composition 80 A and 20 B. Until temperature T_1, uniform liquid solution exists. At T_1, liquid L_1 is saturated in A as the temperature is dropped, the excess A must solidify.

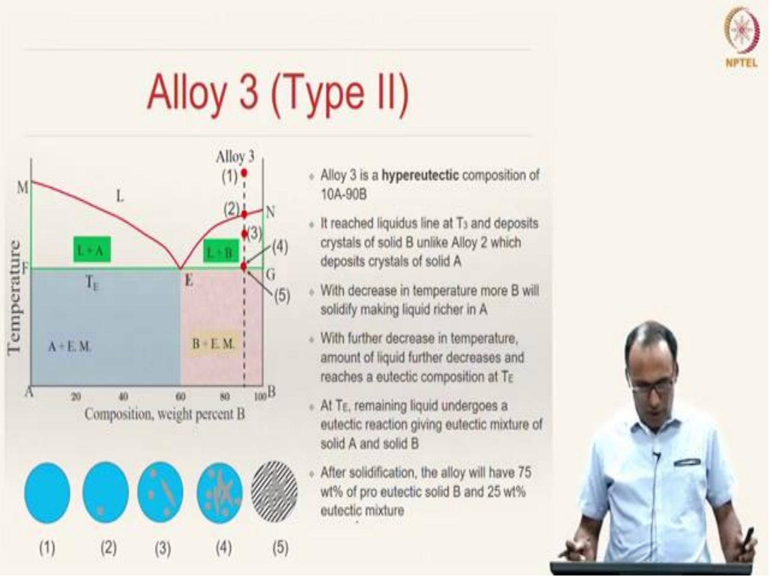
As you are coming down, the excess A must solidify and the liquid becomes richer in B by depositing crystals of A in the above step. As you are going from 1 to 4, the amount of pure solid A increases gradually by continued precipitation of solid A from liquid.

At X_E, that means at this position, by the time you reach here, the remaining liquid will would have reached the eutectic composition. That would go through a eutectic reaction and solidify into mixture of A and B. What is the weight fraction of the liquid just above this point? It is 33.33%.

This 33.33% liquid is at eutectic composition at eutectic temperature and hence it solidifies at that particular instance. So, if you have alloy 2, 33.33% of that alloy when it is solidified, will be in the form of eutectic mixture of A and B. The remaining 66.67% would have already precipitated as A. So, the result is 66.67% primary A, which is also known as pro eutectic A.

That means, this A has formed before the eutectic reaction has taken place; that is why it is called pro eutectic A. The remaining 33.33% will form eutectic mixture due to the eutectic reaction of the remaining liquid which is 33.33% in weight. And that transforms to alternate layers of solid A and solid B; that we are calling as eutectic mixture.

(Refer Slide Time: 36:35)



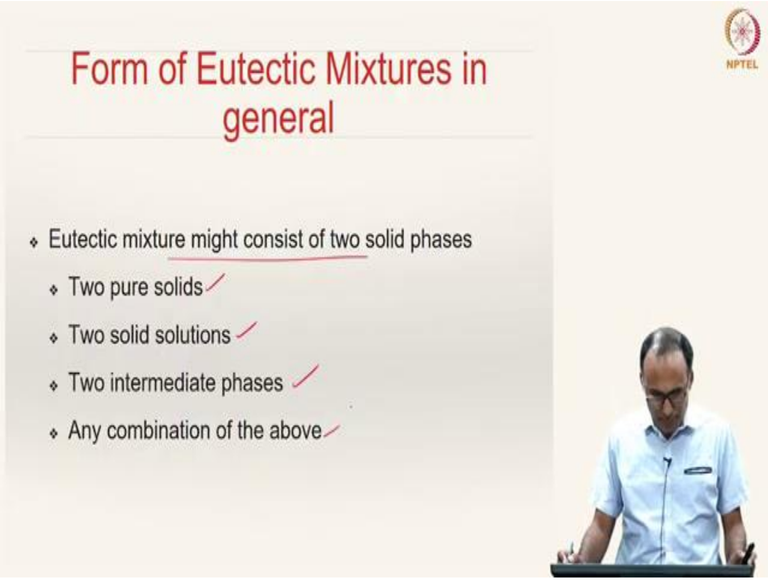
Let us now look at alloy 3 which is exactly similar, except that if you draw a tie line at point 3, this tie line hits the solidus at pure solid A (**correction**: pure solid B). And hence the solid phase that is precipitating from the liquid should be pure B.

Now, you understand why we have written liquid + A here; because when you draw a tie line in this region, it will hit the solidus line at pure solid A and hence it has to form pure solid A. Here it will hit the pure solid B line and hence it has to form pure solid B.

All the alloys here will have pro eutectic B; this grey region is what you call pro eutectic B. By the time you reach point G, again your liquid solution will have the composition of eutectic solution. The remaining liquid solution will transform to eutectic mixture of A and B.

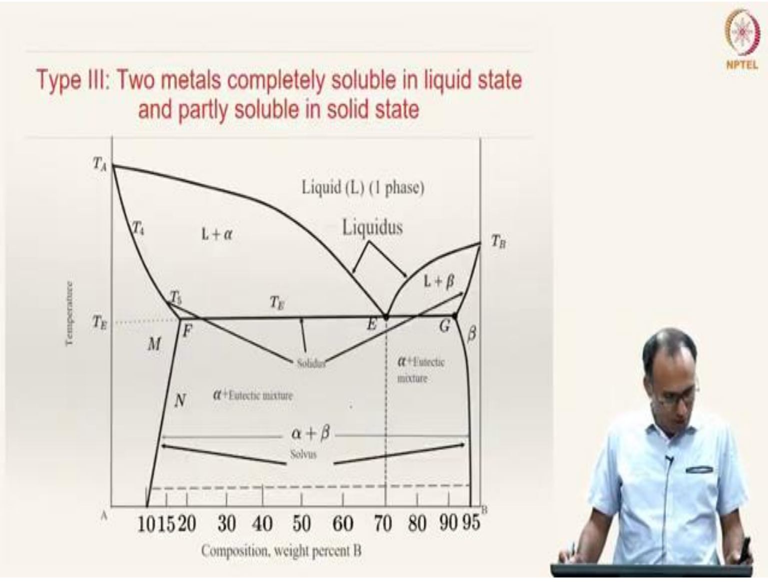
When we have a liquid solution which is reaching eutectic composition, at the eutectic temperature, it has to go through this eutectic reaction and the liquid should transform to two solids.

(Refer Slide Time: 37:57)



The eutectic mixtures in general -- not for only Type II alloys; you can also have eutectic mixtures where you have partial solubility in solid state and so on. So, in general, the eutectic mixture might consist of two solid phases and those two solid phases that we are talking about can be two pure solids like in the case of Type II alloy that we have looked at or two solid solutions or two intermediate phases or any combination of the above. You can have one solid - one solid solution, one solid - one intermediate phase, one solid solution - one intermediate phase; the only requirement is that the liquid solution transforms to two solid phases.

(Refer Slide Time: 38:37)



We have looked at an important reaction called eutectic reaction which happens at constant temperature, but it is not congruent; because after the transformation, the liquid transforming into two solids, the compositions of the solids and the liquids are not the same, and hence it cannot be called as a congruent solidification process.

So, with that, we have understood the Type II alloys. In the next class, we look at Type III alloys.

Thank you.