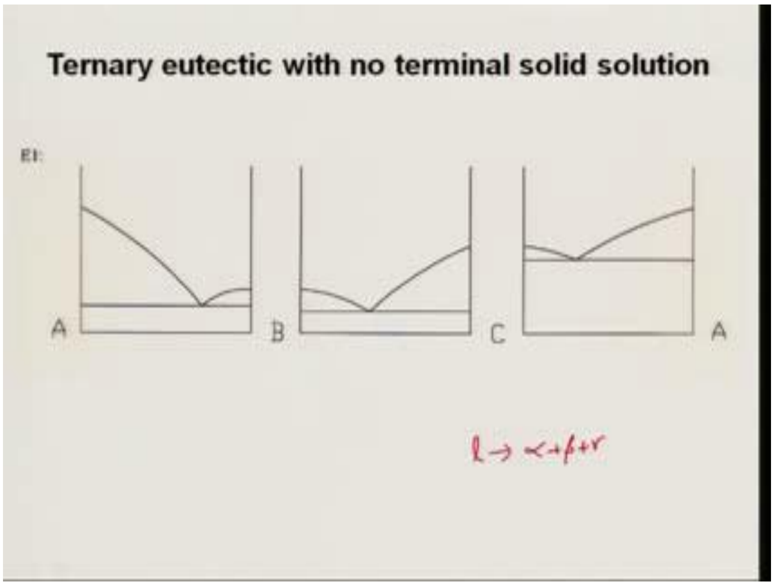
Phase Diagrams in Material Science Engineering
Prof. Krishanu Biswas
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Lecture – 56
Solidification Behaviour of Ternary Eutectic Alloys

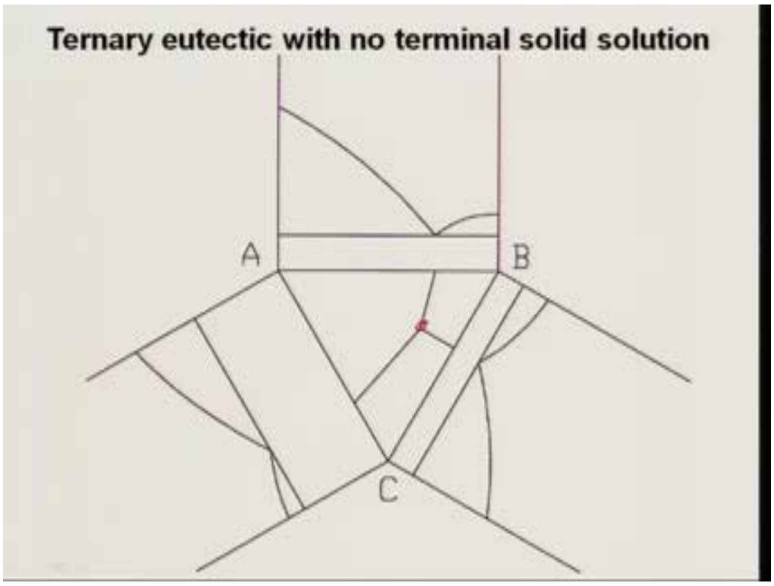
So, in this lecture, I am going to discuss with you about solidification behaviour of the ternary alloys in which a ternary eutectic reaction is present. But, before that, we will do some recap of the previous things. So, we have been discussing of ternary system in which there is a ternary eutectic reaction. And, the reaction – eutectic reaction is like this.

(Refer Slide Time: 00:40)



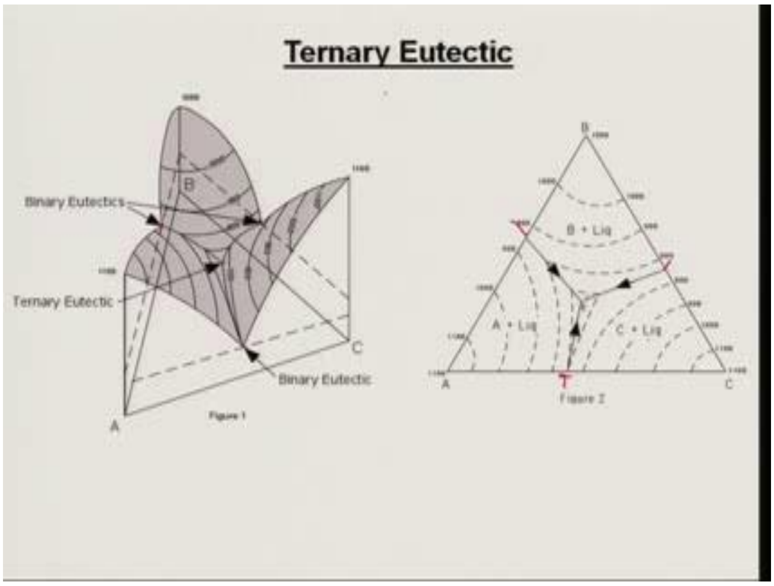
Liquid going to alpha plus beta plus gamma; liquid transforming into three solid phases simultaneously – alpha plus beta plus gamma; and, thought that we need to have binaries in which eutectic is present in all the binaries like between A and B, B and C, C and A, we have eutectics; correct. And, if that is the case; then, ternary eutectic will be present. For very simple reason, I have removed in this lecture the terminal solid solution regions. I have done that in the last lecture, but then I thought that, will complicate the phase diagrams and also analysis. So, that is why I am showing you very simple picture of a ternary eutectic, where all the binaries from the eutectic, but none of the binaries – ternary solid solution exist.

(Refer Slide Time: 01:46)



So, that is what is this ternary system – AB, AC, BC – all of them have ternary eutectics present – binary eutectic present. You can see here there is a eutectic present in all the cases. And, because of that, as I told you in the beginning, because of that, there will be a ternary eutectic present and which will lie inside the Gibbs triangle obviously. That is why it is called a ternary eutectic. And, it is a true ternary eutectic, why? Because not only the composition lies inside the ternary Gibbs triangle, but also the eutectic reaction involves four phase equilibrium; that is why. This is obviously different in contrast to the ternary eutectic in which is extension of the binary eutectic, which we have discussed in the case of three phase equilibrium; correct. So, that is not a true ternary eutectic; where it is a true ternary eutectic.

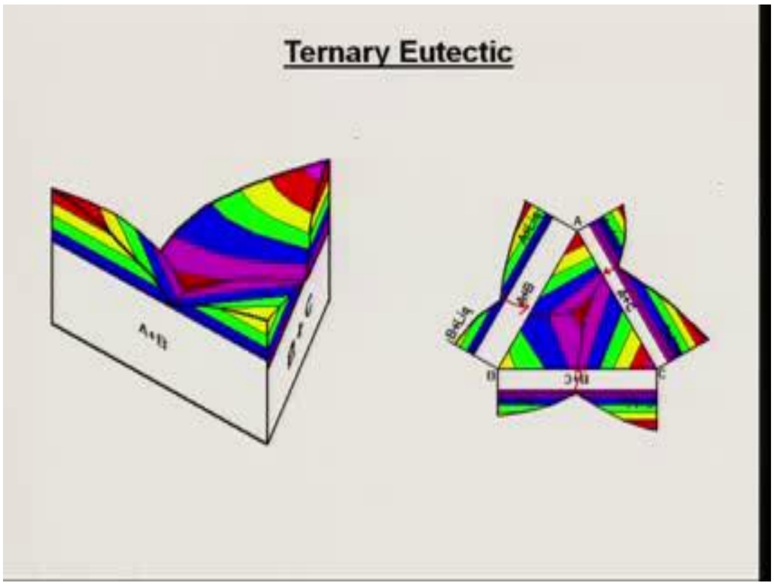
(Refer Slide Time: 02:39)



And, you know the phase diagram will look like this. I have shown you earlier also. You see these are the binary eutectic points – 1, 2, 3. And, the ternary eutectic points are there; it lies well below the three eutectic points in the binaries; correct. And, the liquidus surfaces will look like this, which is shown here; they are actually like going down forming a valley in the three binary eutectic regions. And, one can actually draw this is liquidus surface projections on the Gibbs triangle; they will look like this. You can see this is the binary eutectic; this is a binary eutectic; this is a binary eutectic.

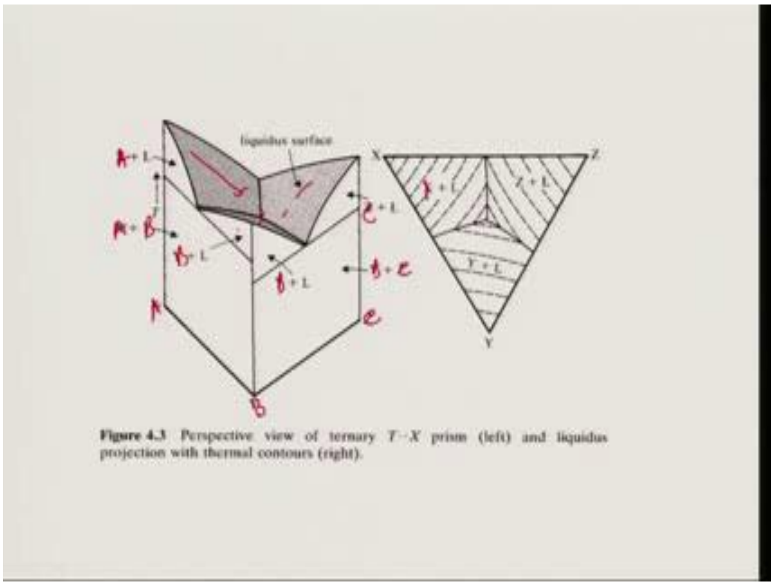
And, ternary one is sitting inside the Gibbs triangle. And, one can also draw actually temperature contours as it is shown on the ternary phase diagram. This is the temperature contours. And, because there is a ternary solid solutions; so, therefore, these regions will be a plus liquid b plus liquid c plus liquid in contrast to alpha plus liquid beta plus liquid and gamma plus liquid. This is much simpler for you to understand and grasp. So, obviously, now, once I know this plot – this projection, it is very easy for me to understand solidification behaviour, which we will discuss in the moments now.

(Refer Slide Time: 03:48)



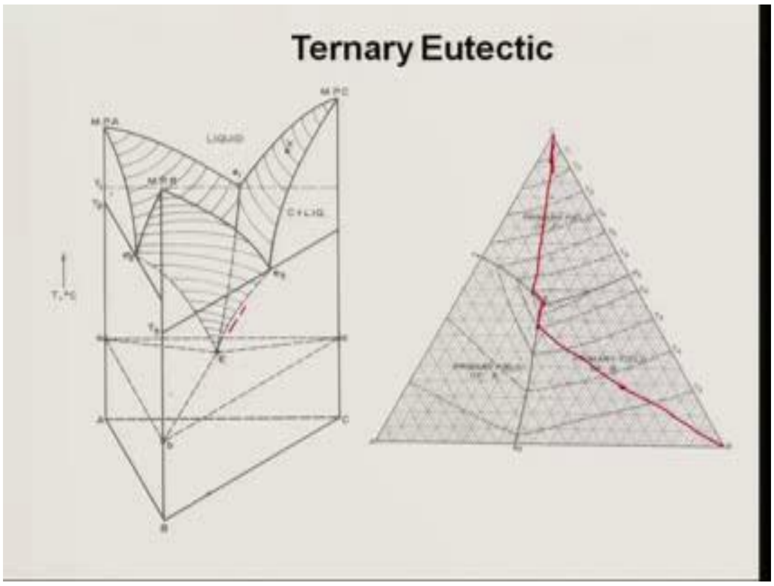
And now, one can actually use gamma plots, which is easy. That is the region actually used the power point projections. And, (Refer Time: 03:59) these are the contours – coloured contours and which is going down just like a tea garden. If you have visited any hill region, tea gardens will look like this, tea gardens going down and all the tea gardens from the three corners of the Gibbs triangle going down and meeting at a point E. And, E will be an invariant point because four phase equilibria will have invariant – it is an invariant in nature – a ternary system because, f is going to be 0 when number of phase is equal to 4. So, on the position side, you have project the whole thing to look like this. This is a ternary eutectic and these are the three binary eutectics. And, they are just extension of these binary eutectics – these binaries ones is obvious. But, ternary one is not; it is a true ternary eutectic.

(Refer Slide Time: 04:47)



Space model – I have been showing you many times; space model will look like this – liquidus surface as you shown; it is much clear here. This is the liquidus surface going down and meeting at this point. And, these are the regions of Y plus – basically, I have changed from A B C to X Y; let us do that. So, this is B plus l; this is B plus c; C plus l; this is B plus l, A plus B, A plus l; right? That is all. This is A – A plus l, C plus l, B plus l. And, this is a eutectic point.

(Refer Slide Time: 05:28)

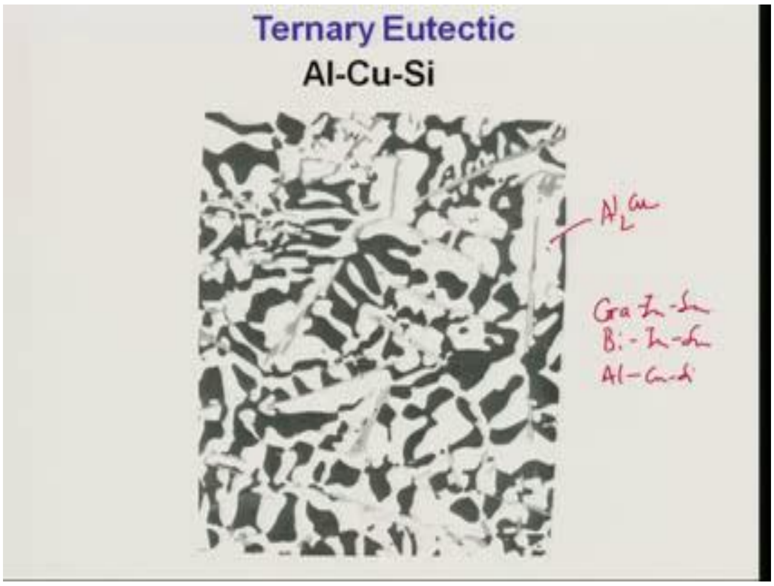


Well, now, I show you the real space model – real space model in terms of the picture. You see here; what is actually happening? If I look at carefully, there are three eutectics e 1, e 2 and e 3 present in the binary side. This is the binary; this is the binary; this is the binary. You can yourself draw; I am going to draw it on the board itself to show you. Now, what happens – actually, the ternary eutectic point is sitting on a – this triangle ABC. This is sitting on the ABC triangle; obviously, this is a four phase equilibria is what? It is consisting of three – three phase equilibria; not three, four.

It is basically alpha – liquid plus B plus C; liquid plus A plus C; liquid plus A plus B – 3 – 3 three phase equilibria. And, each one is a triangle; right? As we have discussed in the previous lectures three phase equilibria will form a triangle; right? That is obvious because that is how we have discussed in the three phase equilibria. So, when the three triangles meet, they form a four phase equilibria point and that is the point, because it is an invariant point. And, in between, you have f c plus l; this is A plus l; this is B plus l; this is also B plus l. These are the regions of I know – solid plus liquid.

So, now if you project the whole thing on the triangle much easier, this is just projected here. e 2 is here; e 2 is here between A and B; e 3 is here between B and C; and, e 1 is here between A and C; right? And, these lines – this one – e 3 E – e 3 E is this one; you can see here – e 3 E; u 1 u 1 E is this one; and, e 2 E is this one. They are just projected simply from three dimensions to two dimensional projections; correct. Now, what will happen? Now, these are the temperature contours – T 3, T 4, T 5, T 6. It goes from T 1 to T 6 (Refer Time: 07:25). Basically, this is the way the temperature is going down. See if I take alloy composition like this, it is very easy. What will happen for solidification?

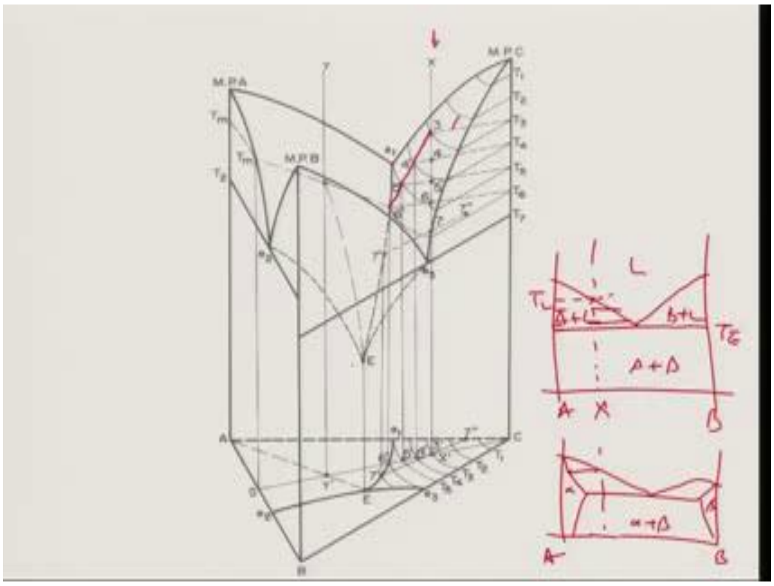
(Refer Slide Time: 07:38)



Let us carry forward and discuss. Let me slowly show you that, there are many systems, which from ternary eutectics. Aluminium copper silicate is one such. Then, you have a system – gallium – gallium, indium, tin – bismuth, indium, tin. Then, this one is aluminium, copper, silicon. They – which these are the systems which form two ternary eutectics. How do you know these are two ternary eutectics? Obviously, that will be three phases. You see here there are three phases here. Aluminium is white; I will tell you why also. Silicon – aluminium is black – aluminium is black; then, silicon is needles; these are the needles of silicon. And, this is Al to Cu. This one is Al to Cu. This is (Refer Time: 08:27) image.

So, therefore, the phase which has the highest atomic number will be shown as the brighter. Aluminium has the lowest atomic number out of these three phases. It is basically not aluminium; it is alpha aluminium, because it will contain copper and silicon both; where, silicon will be pure. That is why silicon comes in needles. So, therefore, three phases, who exists in the microstructure. That is why it is called a two ternary eutectic.

(Refer Slide Time: 08:52)



So, now, this is what we are going to spend lot of time. How the solidification will happen? You know in this case, in this system, where there is no terminal solid solution, obviously, alloys – there are many alloys, which will undergo ternary eutectic reactions. Not only the alloy, which will exile the ternary eutectic composition; composition corresponds to E. But, a corresponding component is corresponding to X, Y; even composition corresponding to X and Y; they will all actually, because they are falling on the – you know what is called the regions of A plus liquid or B plus liquid or C plus liquid – these are falling on the – falling on these cups of the – of the liquidus, these cups – any of these cups; on these cups – this one or this one or this one. They will be basically solidifying as a ternary eutectic.

Not only that, alloys which actually forms – which are actually forming suppose this one, one will also form this ternary eutectic. So, let us now discuss general case. I will take an alloy composition X X X prime denoted by this line X X prime becomes; we can see. So, what will happen? As it cools down, remember that binary; let me just tell you the binary; binary is easy. And, I am just drawing simplest possible binary phase diagram between A and B. And, if I take an alloy composition x, what will happen? Nothing will happen; this is a liquid; this is A plus B; this is B A plus l; this is B plus l; right? What will happen? If I cool it down, nothing will happen above this temperature. This is the temperature T 1 or T l; nothing will happen; this is even liquid. Only if you cool it down below the temperature T l, it will start forming A – pure A obviously, because there is no terminal solutions here. Remember this is in the opposition to this phase diagram; correct?

See if I take an alloy like this, it will precipitate alpha. But, here because there is no permanent solid solution region, there is terminal solid solution. So, therefore, it should precipitate A and B, whichever; it is a hypo and hyper eutectic alloys. So, as we consider hypo, it will precipitate – keep on precipitating A. And, as it precipitates A, liquid will reach in P and B – more (Refer Time: 11:17) when temperature goes down, you can see here; there is the tie lines.

So, finally, when the eutectic temperature will reach, whatever liquid will remain, that will form the binary eutectic between A and B. Exactly same thing will happen here; exactly same thing. But, in a ternary space model, it will be shown in that way. So, if I take an alloy X, I pull it down; only when it touches the liquidus surface at point 3, this will precipitate C; remember. This will precipitate C; correct. So, that is happens at T 3 – at temperature T 3. Please try to look carefully; at temperature T 3, the alloy composition line hits the liquidus surface. As it hits, obviously, below that temperature, C will precipitate – start precipitating.

What will happen if C starts precipitating? Liquid will be reach A and B. So, that is why the liquid composition will follow along this curve; got it? So, what will happen if liquid composition is falling? 3 to 4 prime to 5 prime to 6 prime; 6 prime something else happens. What is that? 6 prime is the point, which is lying on the line or intersection line between e 1 and capital E; e 1 is the binary eutectic between the A and C; and, E is the ternary eutectic point inside the Gibbs triangle. So, what will happen? Because it is lying on this on this valley between e 1 and E – small e 1 and E; so, still the temperature T 6 – this is going to precipitate only C.

But, as it reach the temperature below T 6; that means what? As it touches this line, this valley – e 1 and capital E, this will also start precipitating A. Why? Because this is the curves or this is the valley, which is sitting on A and C; am I clear? So, the title will be very clear. Do not look at the bottom; just try to see what is happening at the – what is happening on the space model in the three dimensional picture. So, as I cool it down, only at temperature T 3, some crystallization will happen. And, this crystallization will be of C. So, and, as the temperature is going down from T 3 to T 4 to T 5, more and more (Refer Time: 13:45) And, as and when the temperature reaches T 6, this liquidus curve or liquidus surface is going to meet the valley small e 1 to capital E – this valley. And, once it touches that, this will precipitate A also. This will precipitate A.

Now, further on, as the temperature is going down, the liquidus composition will follow 6 prime to 7 prime precipitating more amount of – more amount of A. And finally, it will arrive at E, where all the three A plus B plus 3 eutectic will (Refer Time: 14:27) out. That is what is going to happen. Now, one has to carefully look at this ternary space diagram. This is exactly the same way as I have discussed the binary one. And, binary – first, it is like this primary A; then the liquid composition become rich and B – as the temperature, it goes down.

And, when the liquid temperature reaches the eutectic isotherm, it undergoes eutectic reaction between A and B; liquid transform A and B. But, in ternary, you have three phases A plus B plus C here in this case. So, therefore, before that ternary eutectic reaction happens, crystallization of both C and A should happen. Now, remember as eutectic composition is more rich in B; so, therefore, in order to reach the eutectic composition in order for the liquid to reach the eutectic composition, A and B should get out from the liquid as the primary solid or primary (Refer Time: 15:31) phase as you may call. And then, it will reach point E and form the eutectic. That is very easy.

Now, you do not need to do all these stuffs. Let me show what I have. You do not need to do all these stuffs. This is little bit, I know cumbersome, because one has to draw the three dimensional diagram and discuss this. If you have a binary, if you have a position of these surfaces, liquidus surfaces on to the Gibbs triangle; then, even things are much easy. Let us see what happens. I have the position of this. Now, I concentrate only on the bottom Gibbs triangle ABC and these are my projection e - e 2 to capital E; e 1 to capital E; e 3 to capital E. These are my liquidus surfaces projections; correct? And, my alloy compositions lie on this point. Now, what is this phase field? u and e – e 3. See this is phase field of primary C plus liquid obviously. Similarly, this is the phase field e 2 E and e 3. This is the phase or B; this is the phase field of primary B plus liquid. And, this one A e 2 E – capital E and e 1 is a primary phase field of A plus liquid.

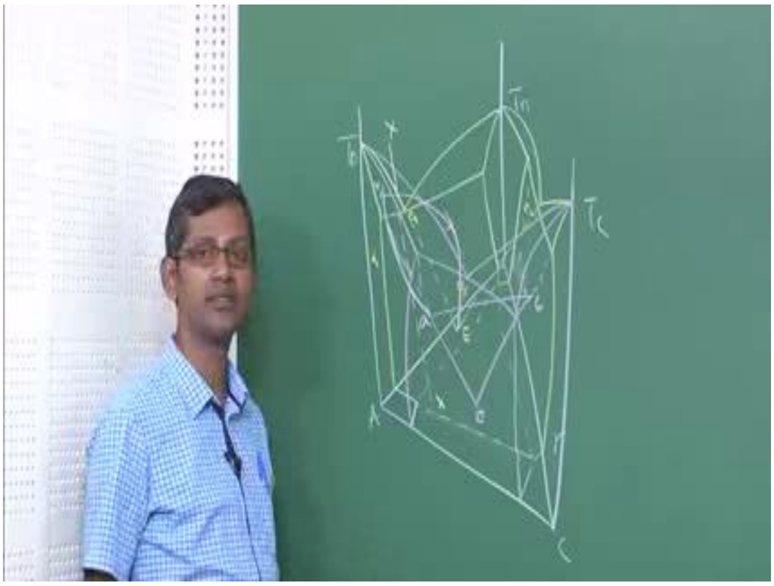
So, as the composition lies on the primary phase field of C plus liquid, the fast crystallization product will be seen. So, how do you do that? Very simple, I join this point X prime with C and extend this line on this side. So, what will happen? If I extend this on line, it will keep on going like this – 3 prime, 4 prime, 5 prime into 6 prime. 6 prime – it is hitting the liquidus surface of or the valley of e 1 small e 1 E. Remember this is the connection of binary eutectic e 1 with the ternary eutectic capital E. So, therefore, if the alloy composition – liquid composition is sitting on this curve, it must precipitate A and C both, because that is basically a binary eutectic reaction; it will crystallize both A and C.

So, three point, one point before 6 prime or temperature little bit above 6 – T 6, this will crystallize C only. Once it reaches 6 prime or temperature T 6, this has to crystallize both C and A, because the point is lying on the surface of e 1 E. And, that is basically connects the binary eutectic between AC and the ternary eutectic point. Now onwards, it is very easy. This is going to follow 6 prime to 7 prime to E; and, E is the lowest melting temperature point in the phase diagram. So, everything will solidify at point capital E.

So, now, I go back here. Now, you see it is very easy. Suppose this is my alloy – the composition; and, I want to know what will happen to solidification of this alloy. What I will do? First thing I will do; (Refer Time: 18:34) follow me. I connect this point with C – with B here because this is the primary phase field of B; B is basically (Refer Time: 18:42) with the liquid. So, as the temperature goes down, this must precipitate B, not anything else. Now, I connect, I extend this line. Just I will draw a line. Basically you take a slide ruler and just draw a line between B and this point extended to that. So, as you see here from this point onwards, temperature is going down – T 3, T 4, T 5, T 6. So, till T 6, it is going to precipitate B; right? It is going to precipitate B only.

Now, at this temperature, this is sitting on the curve of e 2 E – capital E. And, e 2 is what? e 2 is the eutectic between A and B. So, therefore, if it is sitting on it, it must crystallize both A and B together. And, then onwards, it will follows this (Refer Time: 19:34) and it will (Refer Time: 19:35) the ternary eutectic reaction happen; is it clear? That is very easy to understand. Similarly, if I have alloy composition like this; I can draw a line between these two – and join and goes. That is very easy, right? Not be very difficult. Now, after giving you this you know concept clearly understandable way, I would just like to you know touch upon little bit on the complex diagram. That is what I have to draw it on the board and show you how things possible. Let me try; it is not an easy diagram to do, but I will try; otherwise, I will show you on the slides in the next lecture.

(Refer Slide Time: 20:24)



So, there are three binaries. I think I have three coloured chalks. But, remember I am here; I am going to draw the primary phase field of A, B and C; and, this is going to be a little bit complex that is why. It will look like a – so, this is my C; this is my B and C. So, this has to be drawn in an angular way; otherwise, you will not realise it. I have a red colour chalk here and this one. So, these are the three eutectic points. Between A and B let us say this is e 1; between B and C, e 2; and this is B and C, e 3.

And, if I connect these three, I get into ternary eutectic point E, right? So, it will sit on a triangle. So, let us do that. This is one point of the triangle and then; correct. So, E is sitting inside the triangle A, B, C. And, we can also draw this one. I will draw by a white chalk. It is better to draw by a dotted line. That is how the ternary space model will look like. Now, if I want to know solidification of an alloy, that is what I told you; it is going to be little bit cumbersome like this. How it is going to happen? Just I will like to tell you that I am teaching from this book of (Refer Time: 23:41) where figure number 181 is nicely shown things.

So; obviously, as it goes down, it is going to touch liquidus surface here. And, from then, this is going to follow this route and solidification will be over like this; correct. What does it mean? This is the track of solidification path trace. What does it mean? This means that, as the alloy composition goes down this way, it will start precipitating alpha. Remember this is alpha right; alpha phase field solid solution between A and C is or A and B – both. This is alpha phase field (Refer Time: 24:24) connect these two. This particular phase field here is alpha. So, it is going to precipitate alpha here. And, this is be the alpha; this is the way alpha. And, alpha will have a composition of alpha 1, which you can obtain from that. Then, this will follow – the solidification solid will follow this way. And, to reach this point – this will reach point A – point A; correct? And, this is the solid composition variation; how this way? But, if you look at carefully, as this will first thing it will precipitate is alpha 1.

And, as it goes down, it is going down and slowly reaching the e 3 and E – e 3 – it is reaching – no, it is reaching not e 3 here. Here it is reaching e 3 and E. So, e 3 and E is eutectic between A and C. So, therefore, as it reaches e 3 and E curve or the valley, it is going to precipitate both A and C; so, alpha and gamma. This is gamma; alpha and gamma. It is going to precipitate. And, because of that, what it will going to happen? Because of that, liquid will become breach and reach in B more. And finally, it will reach the eutectic composition and it will solidify as a – full three phase alpha plus beta plus gamma. That is what is going to happen.

So, same thing will happen in any of the other composite sitting suppose this side or this side or this side of this phase. That is why you have to draw yourself and try to understand. And, this is the reason I have (Refer Time: 26:19) touched upon the basic thing of the eutectic; where, there is no primary phase freely alpha, beta, or gamma; only pure A, pure B, pure C exist. And whenever another important thing I should tell you that, whenever this precipitates both alpha and gamma. There will be three phase equilibria between the alpha, gamma and the liquid.

And, that will look like a triangle inside this. I am not drawing it; this will make the picture very complicated and we are not going to appreciate that. So, it is not a difficult for you to understand. Again this is going to follow – liquid composition follow like the way I have drawn in the case of shown in the case of A plus B plus C. So, in the next lecture, I am going to take a some sort of this scan and show you and try to make you believe; try to understand that, from the position of the liquidus surface, just how it is possible to discuss the phase formation.