Principles of Physical Metallurgy

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Lecture No. # 19

Solidification of Binary Alloys (Contd.)

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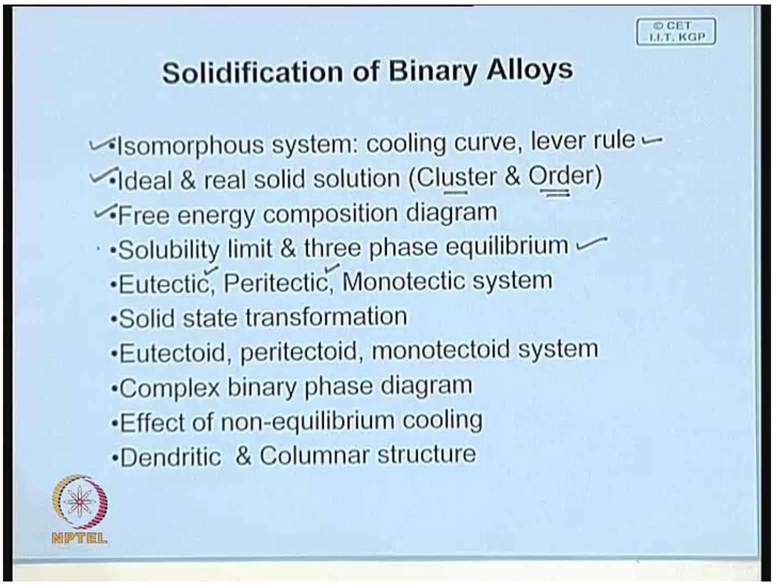

Good morning. We were talking about solidification of binary alloys, and today also will continue the lecture on the same topic. And last class what we looked at is an isomorphous system. We looked at the cooling curve, we also derived an expression for the lever rule. We also looked at free energy composition diagram, and also we have tried to calculate the phase diagram for an ideal solid solution. And we also talked about that most real solid solutions or not ideal, they either form cluster or from an ordered structure. And today, we will talk about the solubility limit and three phase equilibrium. So, today we will cover this, and we will also look at eutectic and peritectic system and evolution of micro structure during solidification in these alloys.

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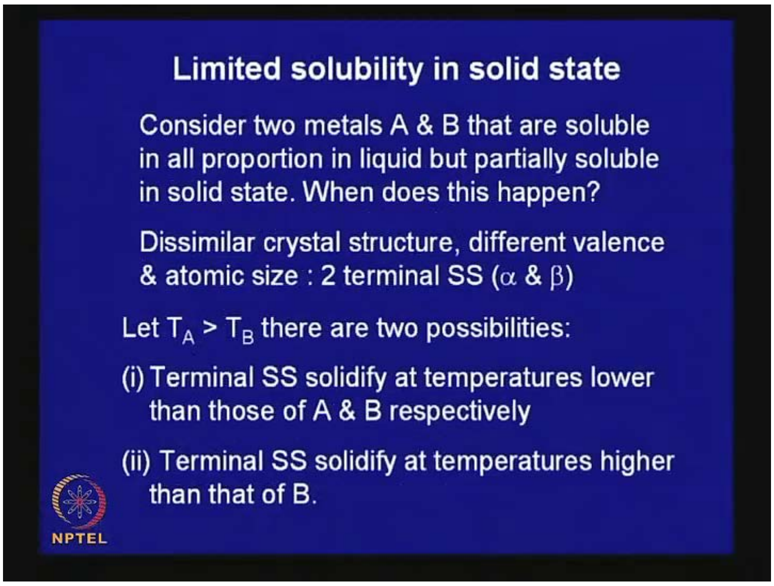

Now, let us look at the case of limited solubility in solid state. We consider two metals; A and B that are soluble in all proportion in liquid, but they are partially soluble in solid state. Now, when does this happen? They can be several cases. It can be due to dissimilar crystal structure, different valence or atomic size and in such cases, we will have terminal solid solutions. In extreme cases, we can have some intermediate phase is also performed. First, let us take up cases where we have two terminal solid solutions and let us consider that melting point of A is greater that of B. Now, in this case there are two clear possibilities. Now, one case one, where terminal solid solutions solidify at temperatures lower than those of both A and B respectively and second case, where the terminal solid solution solidify at temperatures higher than that of B. In that case, we will have several… Let us try and understand what does this mean.

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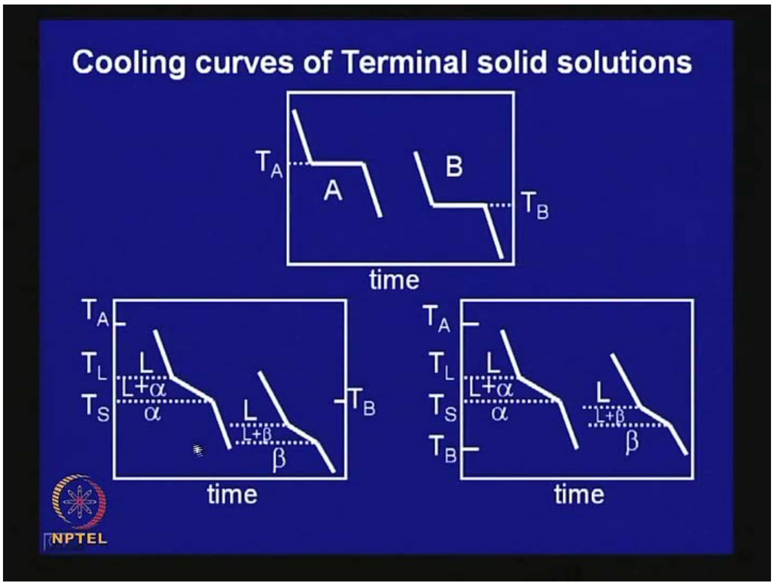

So, if we consider the cooling curve of metal A and B; so pure metal they are solidify; the solidification process can takes place at a fixed temperature; that is T A. And if you draw the ideal cooling curve, it will have the behaviour something like this. In case of B, that is like this and here T A is greater than T B. Now, let us take up cases of terminal solid solutions; one is rich in A; another rich in B and we looked at isomorphous system and solid solution alloys. They have a characteristic cooling curve, which is shown over here. Now, this is the case where you have terminal solid solution; that B in A called alpha and here solidification takes place over a range. So, you do not get any isotherm over here.

So, it is two phases, liquid and alpha; here (( )) coexistive coexist together over a range of temperature and this is the temperature where solidification is completed. So, you have two distinct temperature; T L which is the liquidus temperature; this is the solidus temperature. Similarly, the B rich solid solution; that is beta; so, its solidification behaviour is given by this type of plot. Now, both of these cases here; this solidification is complete; see in this case this is takes place lower than… Solidification is completed at temperatures say here it starts lower than higher than T B; but it is completed before T B. In this case, T B is somewhere intermediate here. Now, we have another case which is like this.

Here, the melting point of B is somewhere here; melting point of B is somewhere here. So, in this case this solidifies at a temperature above the melting point of B; whereas, this solidifies this also solidifies (( )) above the melting point of B. So, in this case the terminal solid solutions; they solidify this one; A rich solidifies at temperature lower than A. The B rich one solidifies at temperature lower than that of B; whereas, in this case A solidifies A rich solid solution solidifies at temperature lower than T A. But B rich solid solution beta solidifies above T B. So, these are the two cases and let us try and understand what will be... How can be construct the phase diagram in these two cases. Let us first consider this one.

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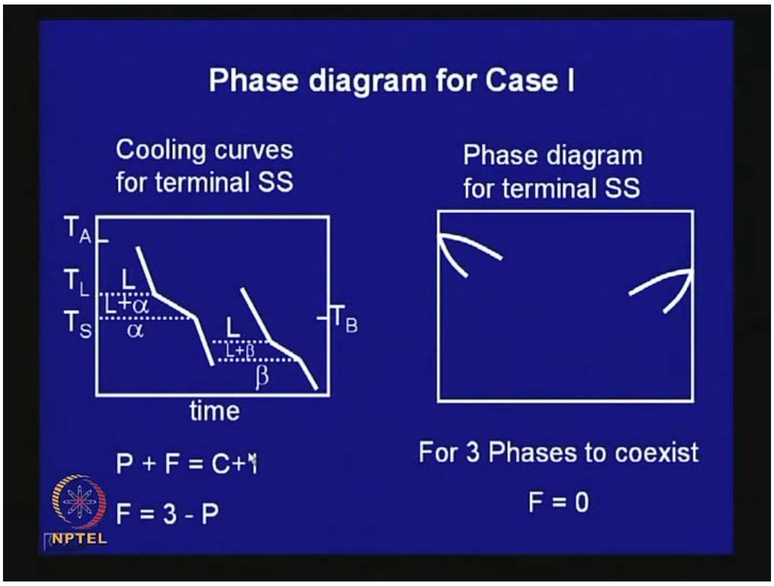

Phase diagram for the case I: Here cooling curve of terminal solid solutions alike this. Now, here you can draw on the phase diagram; here you have temperature on this axis; composition here. Now, take up several alloys; find out liquidus and solidus temperature. And let us consider this A rich portion; here this is the solidus; this is the liquidus. Similarly, terminal solid solution beta; this is the liquidus; this is the solidus.

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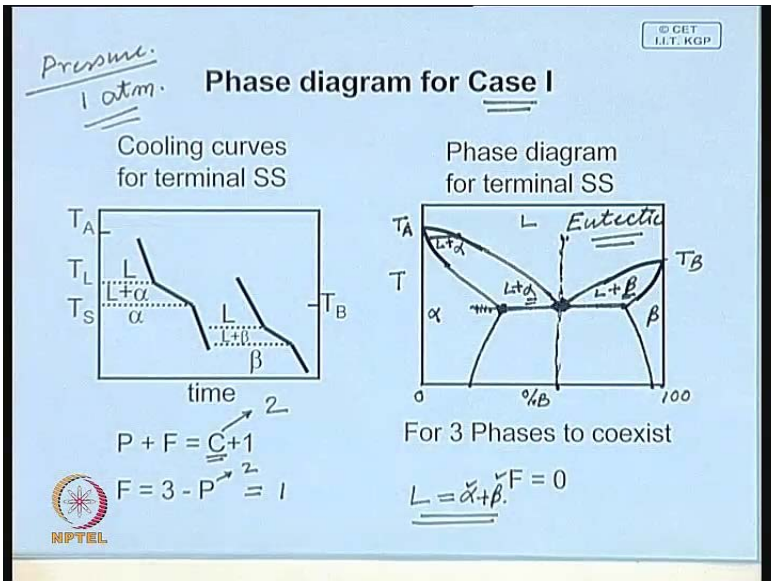

Now, so if you look at here; so this is the temperature; this is composition. Let us say percentage B. So, this is zero B; this is 100 B. Now, this part above this; it is liquid and in liquid, they are miscible in all proportion. Now, this part it is terminal solid solution, alpha; this part it is beta. Now, if you apply the phase rule; let us go back to the phase rule; the gives phase rule states that number of phases plus degree of freedom P plus F equal to C plus 1. Now, this is the binary solid solution. So, binary it is a binary alloy; here number of C is equal to 2; the C this is 2. So, therefore degree of freedom is 3 minus P. Now, if the number of phase is 2; if this is 2, then this is equal to 1.

So, that means at this particular case where you have liquid plus alpha coexisting; you can define one of the variable. So, that means you can have the temperature is variable. If you say this is the temperature, then the composition of liquid as well as solid they are fixed; this is no longer variable. So, you have one degree of freedom. Now, what happens if there will be some alloy where it is possible that 3 phase can coexist? So, that means liquid is in equilibrium with alpha and beta and when thus these happen, then the degree of freedom is 0. So, that means this can take place 3 phases can coexist at a definite temperature and definite set of composition for definite composition of alpha and beta.

So, that means you do not have any degree of freedom; only variable is pressure. Because when we talk about this phase diagram, we assume that pressure is 1 atmosphere; this construction of pressure; this is 1 atmosphere. Now, here let us try and extend this. If you extend here, extend this (No audio from 11:20 to 11:29) then this is a case where the two meeting… Then this is where you have liquid plus alpha; you have liquid plus beta. So, you have; so this is a point when three phases alpha, beta and liquid are coexisting. So, this is where the composition of alpha and beta should be fixed. So, infact if you extend this, this meets here; if you extend this, this meets here. So, your diagram; it looks like this.

So, this is a case. So, that means here is an alloy; here which solidifies, whose cooling curve will be exactly same as that of pure A. So, that means T A and T B. Cooling curve of this alloy will be exactly similar to that of pure A or pure B. We call this alloy, eutectic and what happens if you go lower down? Hence, if you lower the temperature what happens? Now there can be two cases; one, if the usually the solubility decreases of B and A decreases with temperature; that case in course like this. Similarly, if the solubility of A in B decreases, it goes like this. So, this is a typical diagram. One of the case; that is case I with three phases can coexist and the final structure that forms is called an eutectic alloy here the three phases and which has a specific fixed composition.

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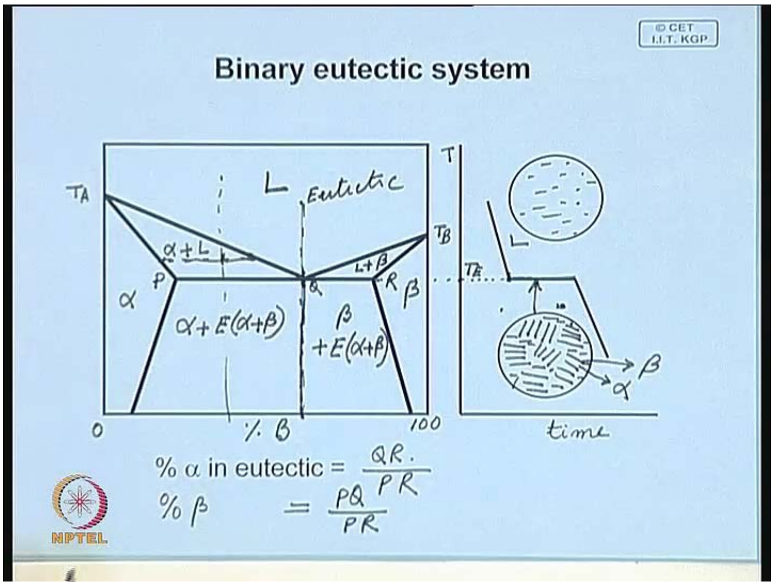

Now, let us look at this diagram once again. So, here this is the percentage beta, percentage B; here this is 0 B; this is 100 percent B. This is the melting point of A; this is melting point of B. And if you can level the diagram here, the phase that is (( )) stable phase is liquid; here the stable phase is alpha; here it is beta and this region, it is alpha plus liquid and this region, it is liquid plus beta. So, here your structure will be in this case, this is the eutectic; this line represents eutectic alloy. So, this is I will draw it by dotted line. This is an eutectic alloy and the micro structure of this part will be alpha plus eutectic, eutectic which is actually we will come it later, which consist of both alpha and beta; mixture of alpha and beta.

And this part you will have beta primary beta plus you will have eutectic consisting of alpha and beta. Now, let us look at the solidification behaviour of the eutectic. Now, this is the cooling curve of an eutectic alloy; this is time; this axis is the temperature. You have heated the alloy to a temperature; where it is molten and here it is liquid here it is liquid. So, this portion it is liquid and the solidification starts here. After certain time, when you cool to a temperature, this temperature is called the eutectic temperature; this is this temperature, eutectic temperature. And when the solidification starts, it actually the temperature does not go down; it remains constant. And once the solidification is completed, then the temperature drops down.

Now, how does this process take place? Now, here imagine say suppose we represent beta by a dark line. So, what happens? Suppose, here once the solidification starts, the beta crystal forms; then surrounding it will be alpha; then again beta. So, this way; so it will be a mixture. So, that means one colony of this eutectic forms here. Similarly, there may be another eutectic region another eutectic. So, this is how it will look like; there will be intimate mixtures. So, that means this dark line, I am representing this is beta and this white region, this is alpha. So, the entire structure will be an intimate mixture of two phases alpha and beta and this amount, you can find out from the phase diagram using lever rule.

Say, suppose we say that at this eutectic point, at this point what is the amount of alpha? How will you find out? Let us mean this point; say let us say. This is P; this eutectic point is Q; this point is R. Then percentage alpha in eutectic; we apply lever rule; this is the composition of the alloy and this is the eutectic temperature. Now, here percentage alpha will be proportional to… (No audio from 18:32 to 18:44) Say, you will apply the lever rule in the same way as over here. We did it last class for that isomorphous system. Lever rule percentage alpha is proportional to this part; this over whole. You extend the same thing here; this amount of alpha is equal to Q R over total P R. Similarly, percentage beta in eutectic will be equal to P Q over P R.

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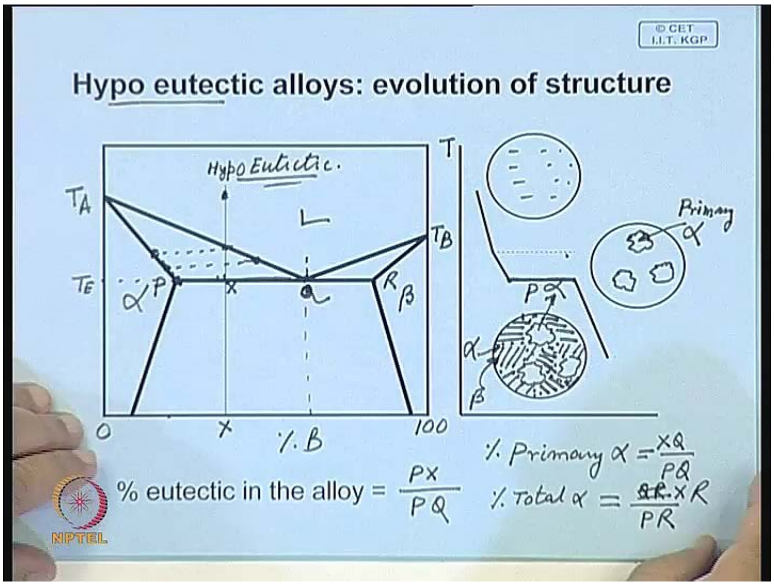

Now, let us look at the solidification of a behaviour of an alloy, which is in between this region and we call this region; this type of alloy we call hypo eutectic alloy hypo eutectic alloy. This is hypo eutectic alloy; anything which is from here to here that eutectic. Now, here that solidification will proceed like this; this is the temperature. And say suppose we have heated up to this, here it is totally liquid. And when solidification starts, it is the first; the alpha will start precipitating out from here. From this temperature, alpha will start precipitating out. So, you will have some primary (( )) of alpha form.

So, these are alpha and this will nucleus of alpha will form and grow like this. So, here right at this temperature amount will be very less; as you go down, amount of alpha will increase, and when it reaches that eutectic temperature, you will have maximum amount of primary alpha. This is called primary alpha primary alpha and now, what happens at this temperature? You have this primary alpha; these are primary alpha. Now, here both alpha and beta start precipitating out together. So, this is alpha; this portion is beta; this is melting point of A. Now, in this particular case when alpha precipitates out; first alpha that precipitate out will have composition this.

But as it goes down, composition of both alpha and liquid keeps on changing; alpha changes along this line; liquid changes along this line. And when it reaches the eutectic temperature, composition of alpha is given by this point P; composition of the eutectic is given by eutectic point is Q; this point is R; P Q R. So, the liquid now attains the composition of that of eutectic. Now, here when the solidification starts, temperature will remain constant eutectic temperature remains constant until this entire amount of liquid changes or become solid. So, this is where it will… This portion inter these are the boundary; this area they will be totally converted into eutectic.

The structure will look something like this. So, here you will have primary primary alpha. These are primary alpha and these are eutectic and in eutectic, this white region is alpha. Let us see the black region; this is beta. Now, one way of representing eutectic is its structure as it looks under micro scope is something like this; a lamellar structure. But there are other possible ways also. It may be some cases; they may be particulate and an intimate mixture consisting of particulate beta like this. Nevertheless, eutectic is an intimate mixture of the two phase alpha and beta in binary alloy. Now, here if you want to find out, what is the amount of primary alpha at temperature eutectic temperature?

This is the eutectic temperature. You can also apply the lever rule here. The eutectic composition is given by this point Q and this alloy composition is let us say is given by point X; X is this point; this composition X. So, what you need to do? You read the coordinate P from this composition axis percentage B; that is 0; this is 100 and this is the composition of the eutectic. The amount of eutectic in the alloy will be proportional to this arm of the lever. The opposite one, this is the eutectic composition; the P X is the amount of eutectic. So, this is P X by P Q and if you want to find out primary alpha, then percentage primary alpha this will be equal to… Primary alpha is proportional to P X.

Primary alpha is proportional to the opposite arm of the lever that is X Q; X Q over P Q. Now, look at this. You have alpha in two places; one as a primary alpha; you also have alpha within the eutectic and if you want to find out percentage total alpha percentage, total alpha which will be proportional to… So, this is the composition of alpha; this is the composition of beta. So, therefore total alpha will be proportional to Q R over sorry this is total alpha is proportional to X R. X is the composition; X R, this is the arm over P R; P R is the total. This is the amount of beta. Amount of beta is proportional to P X; amount of alpha is proportional to X R.

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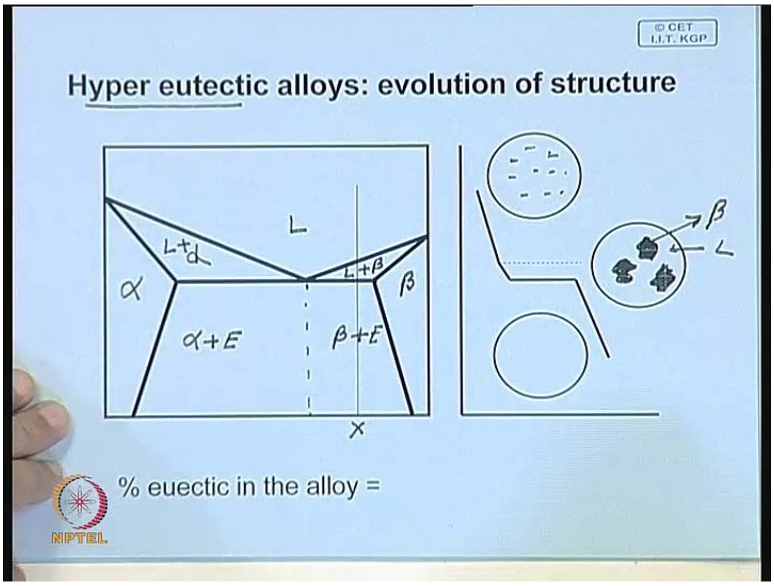

Now, exactly in the same way you will be able to find out or you have you will be able to explain the solidification behaviour of an alloy having a composition X, which lies on the right hand side of this eutectic point; that is between this eutectic and this point, which is the maximum solubility of A in B. So, this and this alloy is called hyper eutectic alloy and here also, you can level the diagram. This is alpha; this is beta; this is liquid plus alpha; this is liquid plus beta and here it is alpha plus eutectic; here you have primary beta plus eutectic. Now, I will leave it to you to complete that evolution of the structures over here.

Only thing is here from the liquid here in the liquid, you will have beta precipitating out. So, beta I will draw it like this. The beta is the primary (( )) beta; this is beta in primary phase; this is still liquid. And once that eutectic temperature is crossed, the entire liquid will transform into eutectic and here also, you try and find out. Take a composition; try and find out; apply lever rule. Find out amount of primary beta, amount of eutectic and amount of total beta. Now, what happens as the temperature goes lower than eutectic? Here, what will happen is if you go back here (Refer Slide Time: 19:48) this case, you have a certain amount of alpha here.

Now, alpha the solubility decreases; solubility of B in alpha decreases. So, therefore as you go down from alpha, some amount of beta will precipitate out. So, this is what some amount of beta will precipitate out. So, beta will precipitate out; lightly area is the grain boundary. So, grain boundary is some amount of beta will precipitate out; an amount of alpha will decrease. Similarly, here also there will be a readjustment. Some alpha some amount of beta will precipitate out. Similarly, from beta some amount of alpha will precipitate out.

And therefore, the percentage of the phases what you determine will be a function of temperature. So, at this (( )) case say may be this is P prime; this is Q prime; this is R prime. Let us say this is at room temperature; in that case, you have to find out… if you have to find out percentage eutectic in the alloy at room temperature, that you should consider these points. And I will leave it up to you to do this and find out what is the change that takes place from here to here and same thing will be applicable here as well. From beta, as you go down some amount of alpha will precipitate out.

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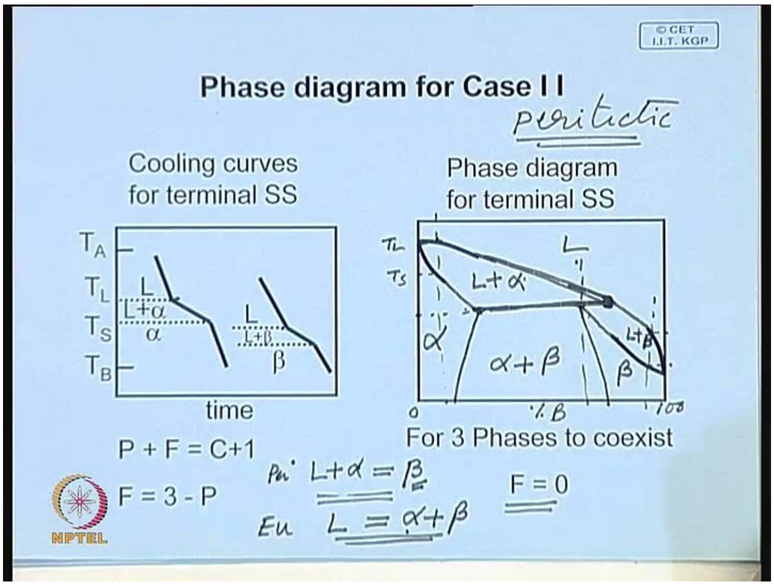

Now, let us take up the case II. In this case, the B rich solid solution here it solidifies at temperature higher than the melting point of B. And here let us say, this is the solidification curve for that terminal solid solution alpha. This is solidification curve for terminal solid solution beta and in this case, you draw this liquidus T L. Say suppose this is the composition; so, this is this is T L; this is T S. Similarly, here also this is the liquidus; this is the solidus and this part, it is liquid and this is the composition B; this is 0 B; this is 100 percent B. Now, in this case what happens?

I mean these liquid line they will join somewhere. So, that if you extend this, they join somewhere. Now, when this liquid line they joined, you will get the condition something like this; here you have liquid plus alpha; here you have liquid plus beta. So, there will be some temperature in between where three phases will coexist and your phase diagram will look like this. So, this part is alpha; this is beta; this portion is liquid; here you have alpha; here you have beta. So, here as well you can see the three phases when they coexist, degree of freedom is 0. So, that means three phases can coexist at a fix temperature and this is called a peritectic system.

This type of diagram is called peritectic system; this type of three phase equilibrium. So, what is happening here? You have liquid plus alpha you have liquid plus alpha and at this point, the liquid plus alpha they combine, they react, and they give the solid solution beta. So, that means when this transformation is complete, the entire amount of alpha disappears and is replaced as beta. So, this is called is type of… So, look at the difference in eutectic; this is peritectic. And eutectic, it is a liquid breaks down simultaneously into a mixture of two phase, alpha and beta; this is eutectic; whereas, peritectic that liquid reacts with primary alpha and gives beta.

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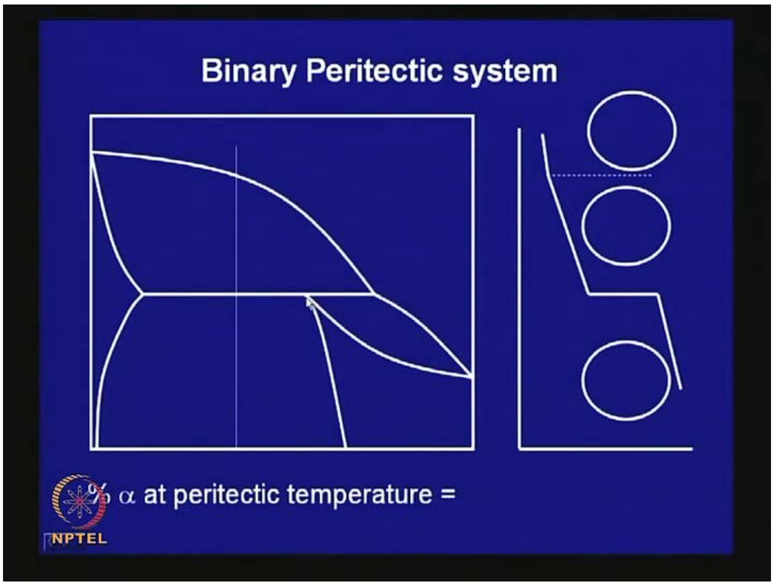

Now, let us look at the binary peritectic diagram, which is shown over here. Now, here this is a typical binary peritectic system phase diagram. And here also at the same way, if you want to understand evolution of micro structure, you have to proceed at the same way the level the different phase field. So, this is the terminal solid solution. So, this portion is exactly same as that eutectic; this is alpha and solubility of alpha; B in alpha is a function of temperature solubility decreases with the temperature; that is why you have a plot like this. If the solubility was independent of temperature, it would have been a vertical line drawn like this and here you have alpha and liquid coexisting. And this is the peritectic point and here also, you can in this exactly in the same manner you can apply phase rule.

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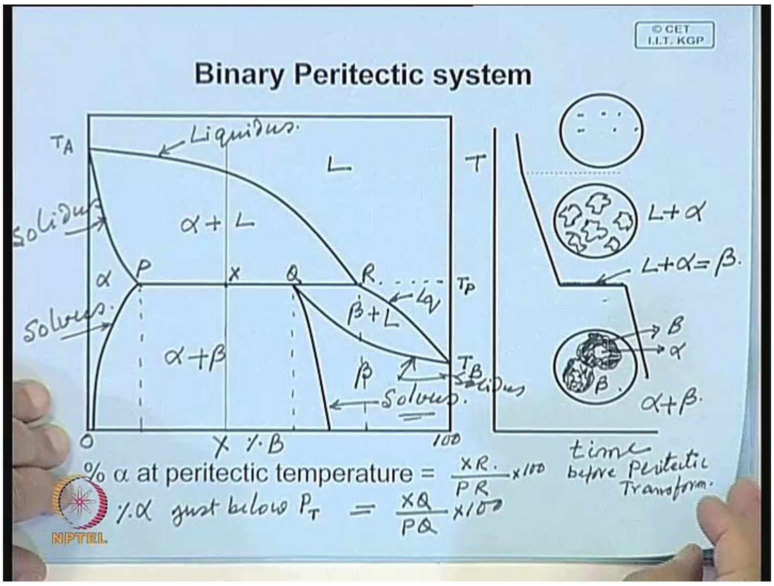

You can apply lever rule and find out phase percentages. Now, here let us say this is liquid; this is alpha; this is beta; this is percentage B; here it is percentage is a 0 B; this is 100 percent B. This is melting point of A; this is melting of B; this is the peritectic temperature this is the peritectic temperature and peritectic temperature, degree of freedom is 0. So, that means three phases can coexist. Here, you do not have any freedom. The alpha composition is fixed; this is the composition of alpha; this is the composition of beta that forms and this is the composition of liquid and here you have alpha and liquid coexisting. Here you have a micro structure alpha plus beta; here you have beta plus liquid.

And these are the liquidus liquidus temperature; this temperature this is called solidus and these lines, which shows that solubility is changing with temperature. This line is called solvus line. So, this is solvus line; this is solidus; this is liquidus. Now, here you it will be interesting to follow the solidification process. Here it is totally liquid; this is temperature; this is the time and the cooling curve will look like this. It cools at a particular rate. Once alpha starts precipitating out, cooling rate decreases; goes like this and at peritectic temperature, you get an isotherm. Temperature remains constant until solidification process is complete and then from here onwards, it starts decreasing again.

So, in between what you have? Here, you will have liquid plus alpha. So, you will have some primary alpha primary alpha. Now, here what will happen is and here you will have this reaction taking place; liquid plus alpha and it will give raise to beta. So, that means beta will start forming here. So, you have (( )) this alpha and what will happen? So, part of it this will react with a liquid and it will form beta. So, that means you will have this alpha area; this will become smaller and rest is this is be beta. And I am just representing beta as a dark area; this is beta; this is alpha and the process will continued you know and then this will be beta.

And ultimately, it will be made up of two phase, alpha and beta and here you can try and find out exactly in the same way what is the amount of alpha and beta here and the alloy. So, here if this composition is X and here if you say P; this point is X; this point is Q; let us say this point is R. Then here percentage alpha at peritectic temperature percentage alpha at peritectic temperature just before solidification; just before solidification, amount of liquid is proportional to P X; amount of alpha is proportional to X R. So, this is X R over P R. So, this is percentage; so this into 100 will be percentage. So, this will be the percentage alpha at peritectic temperature; X R over P R and this is before peritectic before peritectic transformation.

And after peritectic transformation, amount of alpha will be… Because once this is completed, then your percentage alpha just below peritectic temperature just below peritectic temperature this will be proportional to… Because here you will only have alpha and beta. So, here this will be X Q over P Q times 100. And peritectic, so what happens here? The amount of liquid whichever is whatever is present that is P X over P R. This reacts with reacts with alpha which has precipitated out and gives beta. And here since amount of alpha is quite large, it is not able to consume that entire amount of alpha and some amount of alpha remains.

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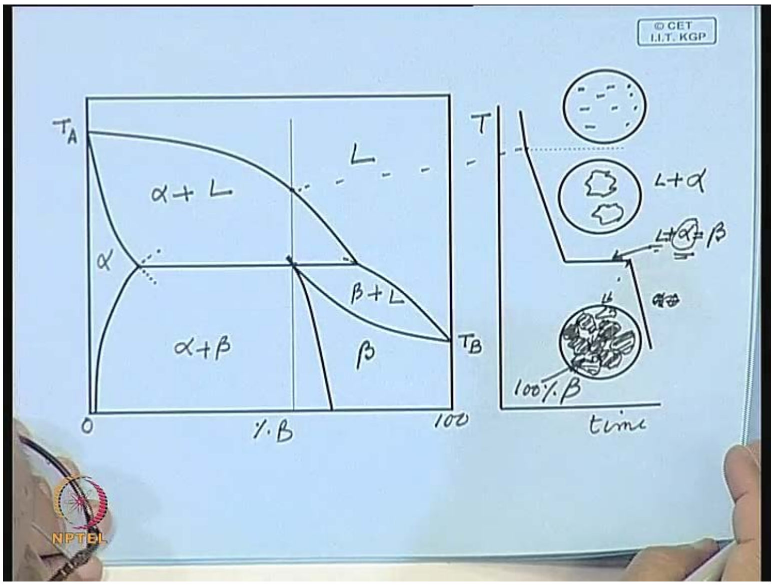

Now, what will happen if the situation is like this? This is again this is percentage B; this is 0; this is 100 percent B; this is alpha; this is liquid; this is the beta field; this is the two phase field. And look at carefully this diagram, if you extend this one, these points to the two phase region. If you extend this, this points here; if you extend this, if you extend this, they point to the two phase region and each single phase region between two single phase region, if you have a you have a two phase region. Here you have alpha plus beta; here you have beta plus liquid; this is the melting point of A; this is melting point of B.

Now, in this case this is the peritectic alloy. Now, peritectic alloy what happens? Here also, the solidification starts from here. So, this temperature is this temperature; this is temperature; this is time; here alpha starts precipitating out; here it is liquid above the liquidus; here it is liquid plus alpha. So, you will have some amount of alpha precipitating out. And here when this reaction takes place, here this is the case where you have liquid plus alpha giving raise to beta and here you have alpha. So, here just over here, you will have that entire that liquid you know it will react and produce all data.

So, I will leave it (( )); they will all appear dark. But they will have different (( )) depending on orientation. So, this will be full of beta. So, at this temperature that what happens; the amount of liquid is sufficient to consume entire amount of alpha to form beta. So, you will have hundred percent. saw Just after solidification, you will have hundred percent beta over here. But as you go down, the solubility decreases; from beta, some amount of alpha will precipitate out and I will leave it to you to find out phase percentages in respective alloys. (No audio from 47:44 to 47:54)

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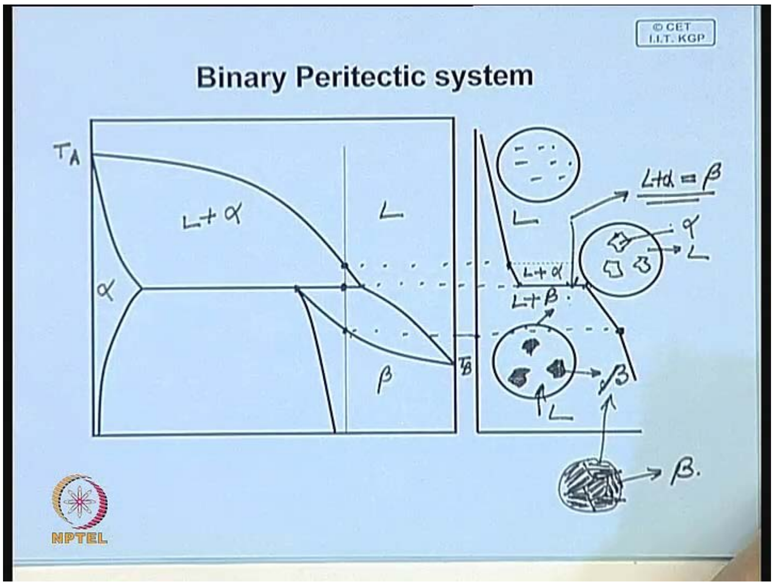

Now, similarly you can also consider a case here, which is beyond this peritectic point. This is alpha; this is beta; this is liquid; this is melting point of A; this is melting point of B. Now, here the solidification proceeds from here; this this is the temperature. When it reaches peritectic point, you get an isotherm on the cooling curve and here after the peritectic reaction, solidification is not complete. So, you still have some liquid and solidification is completed at this temperature. So, you will get one in point 2, 3, 4; these four points. From the cooling curve, these four points represents one; then this is start; this is the end and this is the third temperature.

Now, here also here you have liquid; here you have liquid plus alpha and at this particular point line, you have liquid plus alpha; they reacting and forming beta. Now, here whatever alpha is there; say this is alpha. Now, here what happens if you try and draw the structure in this particular zone where you have liquid plus beta? So, that means entire amount of this this reacts and forms beta; this is beta; the entire amount here it is alpha primary alpha; this is liquid; here primary alpha, the entire amount is converted into beta and you still have liquid here. And as the temperature goes down here; that means down here, you will have the entirely the beta structure. So, that means you will have beta grains. So, they will all be this is beta; this will be hundred percent beta.

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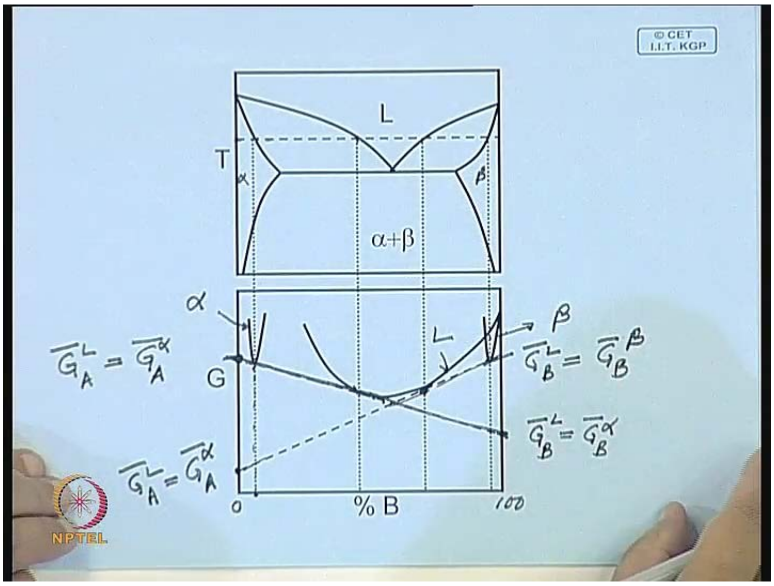

So, we have just considered three phase equilibrium. There are two distinct cases. One is the peritectic; another eutectic system. Now, last class we talked about the concept of free energy and free energy of solid solutions and we know that free energy is an indicator of a stability. Now, it will be good to look at what will be the nature of free energy composition diagram to alloys belonging to such systems, where you have three phase equilibrium. Say let us take up a case; look at that eutectic system. This is the eutectic phase diagram; this part is alpha; this is beta. Let us try and construct the free energy composition diagram for a particular temperature, which is shown over here for this temperature.

Now, here from here to here, the terminal solid solutions you have that alpha region here. So, this is the free energy composition. It is a schematic diagram. So, here this is the free energy diagram of alpha; this is the free energy diagram for beta and this is the free energy diagram for liquid. Now, here you look at when you draw, I mean it is possible to draw a common tangent like this. Now, this common tangent this gives; this is the composition of alpha, which is in equilibrium with this liquid here and this point is known as partial molal free energy. Sometime, it is written as G bar partial molal free energy of… This is the A axis; this is 0 B; this is 100 percent B.

So, A in alpha and this is the partial molal free energy and infact, this is also is equal to partial molal free energy of A in liquid; because both are intersecting. This is the common tangent. So, these intercepts are common. So, in this case this part is the partial molal free energy of B in liquid and is also equal to partial molal free energy of B in alpha. In the same way, you have this equilibrium for the beta and alpha. So, this is the partial molal free energy of A in liquid is equal to partial molal free energy of A in alpha. Similarly, here this is the partial molal free energy of liquid B in liquid is equal to partial molal free energy of B in beta; this is the beta phase.

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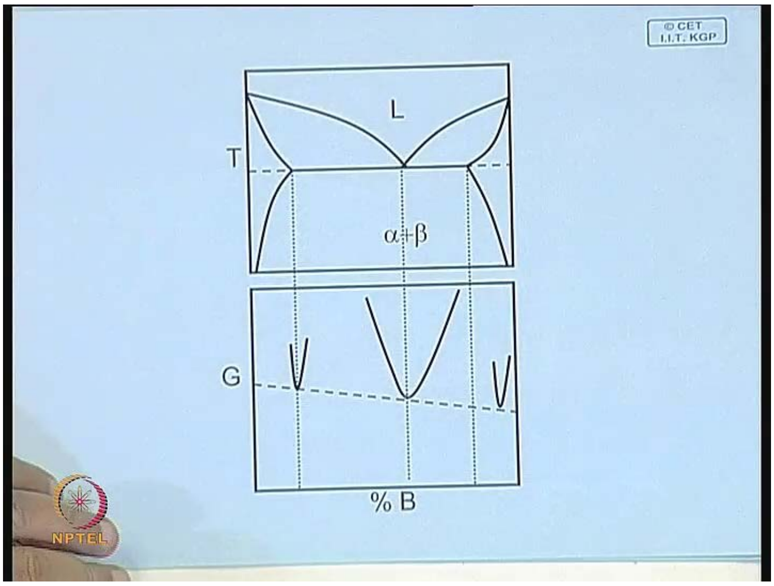

Now, I leave it to you to draw the same thing, which is shown over here and level these points. So, in thus this particular temperature you have three phases coexisting. So, with this concept it also possible to find out I mean from the thermodynamics; it is possible to calculate the phase diagram, where we did it for isomorphous system. It is also possible to draw I mean both ways either you infer the thermodynamic information from the phase diagram or from the thermodynamic properties; you can construct the phase diagram.

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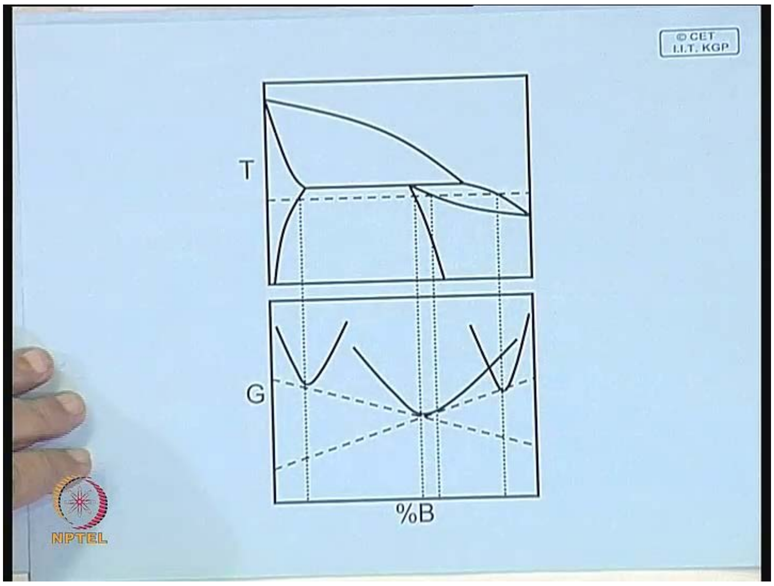

Same thing is possible in case of peritectic system, which is shown over here.

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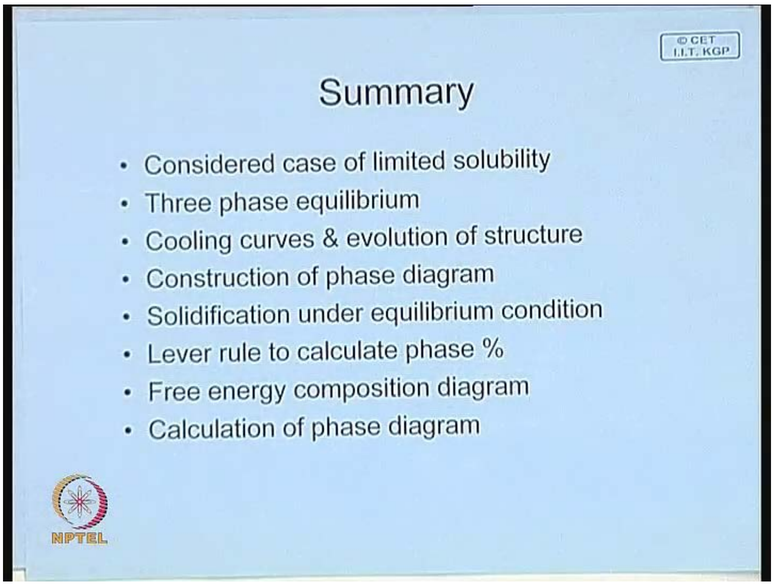

So, with this today what we have done? I think let us look at the summary. We considered the case of limited solubility. Limited solubility occurs in material when there is a difference in crystal structure or there is a difference in atomic size or there is a difference in valance. We considered three phase equilibrium. We considered two cases peritectic, and eutectic system. We looked at the cooling curve evolution of micro structure, we looked at construction of phase diagrams and solidification, we also considered the evolution of structure, when the alloy is cooled at a very slow rate that is under equilibrium condition. We also applied phase rule to calculate phase percentages at different temperatures. And just now, we also saw the free energy composition diagram and which is possible, and it is possible to estimate or calculate wherever I mean from thermodynamic properties, it is possible to calculate the phase diagram,and the principle has just been illustrated. Thank you.