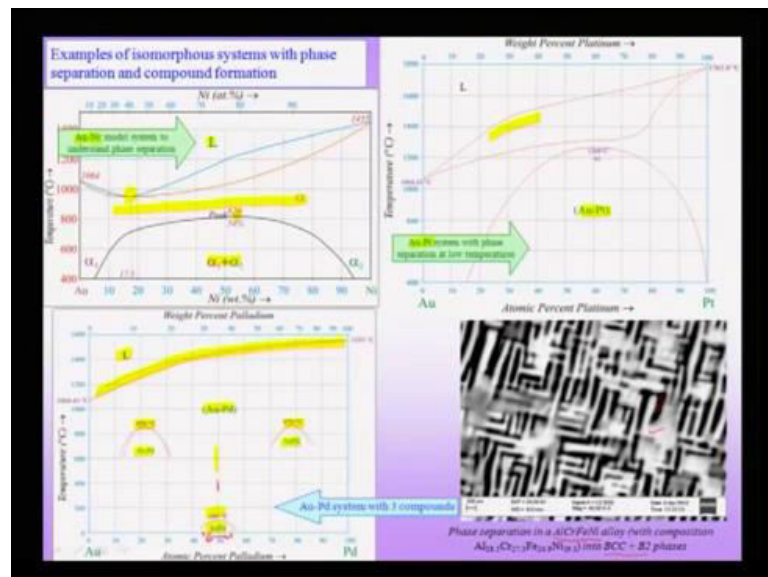


Structure of Materials
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Lecture - 35
Chapter - 07
Phase Diagrams

Let us, now consider some examples of real systems showing ordered compounds and phase separation.

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And these as you can note are isomorphous systems and have either, what you might call a depression in the melting point as in the top left example, which is the nice model system of gold nickel. On the right hand side we have the gold platinum system, which shows phase operation and also we have the gold palladium system in which you can actually see three inter metallic compounds, which form the Au₃Pd, the AuPd₃ and the Au equi-molar, AuPd compound.

Straight away let us start of course, with the first example with the depression in the melting point system, gold nickel system, you notice that at the peak of this splitting occurs. That means, first of all of course, on the liquid phase at high temperatures, at lower temperatures you have a uniform solid solution alpha forming over a range of temperatures.

And if you cool the system even further, it shows the phase separation into alpha 1 and alpha 2, since gold and nickel both have FCC structure, therefore alpha, alpha 1 and alpha 2 all of them are FCC structures. Similarly, in the gold platinum system on the right hand side again you can note that both are noble metals, and having FCC structure you have a phase separation at low temperatures. And you have the isomorphous diagram which is considerable deviation from the ideal kind of a double length system, which we had drawn before.

So, there is as you can see there are considerable non-idealities when you consider real system, on the right hand side bottom you can see actually and this arrow of course, does not point to system here. This is the independent system is a micrograph in which we are able to see a two phase system, this is the aluminum, chromium, iron, nickel alloy with two phases. And which has a composition of aluminum approximately 28 percent, chromium 27, percent iron 24 percent and nickel 19 percent

In which there are two phases which form which separate out which is the BCC and B 2 phases, B 2 being the ordered version of BCC. So, you can actually clearly say there are two phases, the dark phase which has been etched out and the light phase, white phase both of which contain all these four alloying elements, but then they have separated out. The B 2 phase, we expect to be rich in aluminum, because aluminum is an along with nickel is a nice compound former.

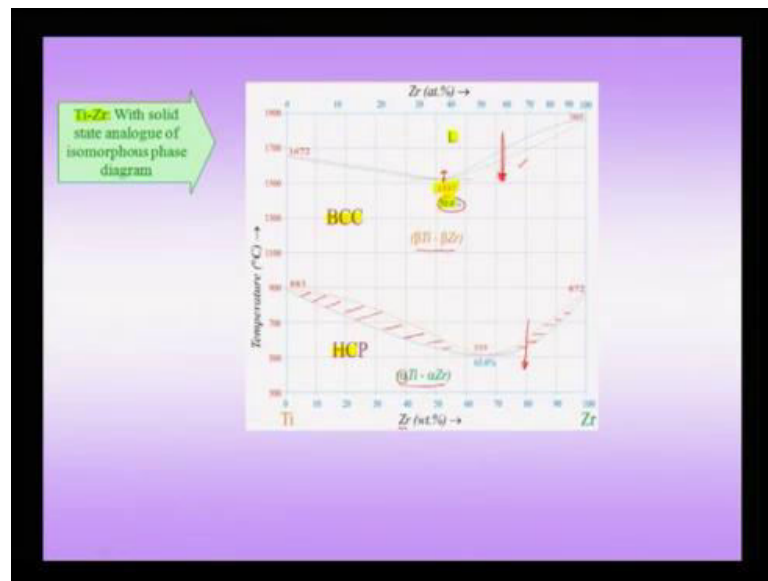
Now, therefore we have a nice micrograph here, in which case there was an uniform solid solution at high temperatures which when cooled actually split into two phases the BCC phase and the B 2 phase. And this kind of a decomposition is called as pinodel decomposition, now coming to the composition system, which we see here on the left hand side, you have a liquid at high temperatures. And you have an isomorphous kind of a system with an elevation in the melting point that means, that such a system will show is excepted to show a tendency for ordering.

And we see three ordered components, one ordering reaction 850 degree Celsius, other at 870 and third is 100 degree Celsius, and there are three compounds forming of gold and palladium. Suppose, I look at an compound which forms closely equi-molar composition of 50-50, the important point to note that unlike what you might call valance compounds, these compounds exist over a range of composition. So, it is not just the palladium gold

50-50 alloy which forms the intermediate compound, but the range of composition as you can see from this diagram, which all show formation of a compound.

Of course, these compounds would imply that to accommodate this off stoichiometry, often either there is a vacancy in one of the sub lattices, or there is an anti site effect which can accommodate this off stoichiometry. So, we have seen three examples of real systems, which now have a tendency for either phase separation or compound formation.

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Now, let us take up another interesting, the example of titanium zirconium and this titanium zirconium system, the interesting point is that, we had mentioned that there are solid state analogs of various reactions. Like if you have the eutectic reaction, we have the eutectoid reaction, now we are talking about the titanium zirconium system here. And in this system both titanium and zirconium both HCP crystal structures, and you notice that at high temperatures there is liquid, at low temperatures there is, when you cool and the liquid you form a BCC phase of beta titanium in solid solution with beta zirconium, both of them being BCC.

But, even lower temperatures you find that you have the natural hexagonal close packed crystal room temperature stable structure is forming; and this transformation at high temperatures is the liquid to... So, this is the liquid to beta structure or the BCC structure phase transformation, which is what you might call the classical isomorphous system. But, at lower temperatures again you see another kind of an isomorphous looking

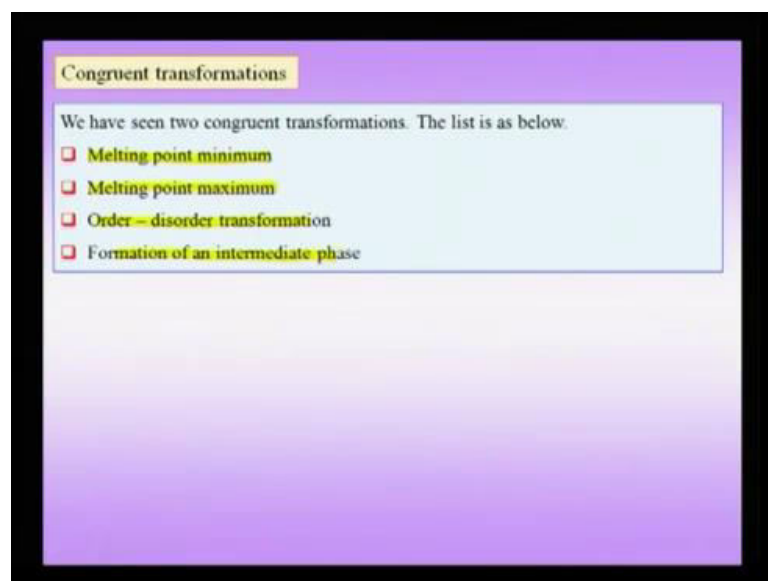
diagram, but now we should note that this is completely a solid state phase transformation.

That means, now the solid solution of beta titanium and beta zirconium, transforming to alpha titanium and alpha zirconium, therefore like you are looking at the two phase field here, what exists is not a mixture of liquid and solid phases. But, a mixture of the high temperature form of titanium and zirconium coexisting with the low temperature form of a solid solution of titanium and zirconium, which is label the alpha titanium and zirconium.

So, in this single diagram which is a nice illustrative example, not only do you see depression in freezing point as you would expect, but at lower temperature, you see the solid state analog of the isomorphous transformation. So, this is a nice example to be considered, when you are talking about examples of phase isomorphous systems.

And if we had noted that if you look at a composition say for instance in this example of about 50 percent of zirconium composition at 1537 degree Celsius, we noted that such a composition will melt at a single temperature working into a pure metal. That means, we call this a congruent melting composition, so there is 50 percent zirconium alloy is a congruent melting composition. And we have noted the degrees of freedom for at this composition on this temperature is 0, and such a system would melt like a pure metal.

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Congruent transformations

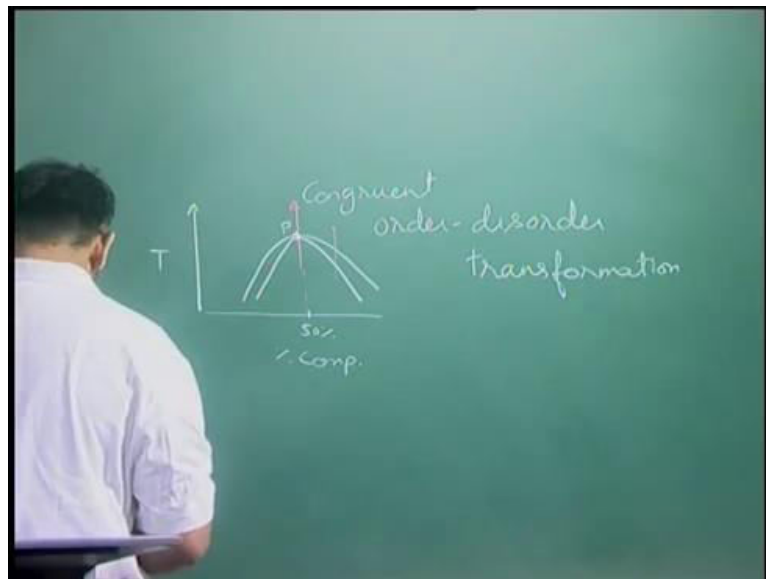
We have seen two congruent transformations. The list is as below.

- Melting point minimum
- Melting point maximum
- Order – disorder transformation
- Formation of an intermediate phase

What are the other congruent transformations we list here, we already seen two of them the melting point maximum, the melting point minimum. And we will we also seen the order disorder transformation which, if you look carefully which will go back to the previous side and notice one more, is also can occur take place at a single temperature and also the formation of an intermediate phase.

So, now suppose we are talking about an order disorder transformation, then you would note that this transformation for compositions which are of 50-50 take place for instance over a range of temperatures here. But, for this composition it takes place at a single temperature, so let me draw this on the board, so you have an ordering reaction taking place.

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Say for instance now this is my composition axis and this is my temperature axis, and say now let me arbitrarily take this to 50 percent of an element and I take... So, if you see take any composition to the right or left of this 50 percent, then the order disorder transformation will take place over a range of temperatures. But, suppose I take this precise composition will lies at the maximum, then this composition would show a congruent order disorder transformation.

So, this is precise composition and we can label this point P, which shows an order disorder congruent transformation. Next we consider a special kind of a phase diagram, the the eutectic phase diagram.

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Eutectic Phase Diagram

- ❑ Very few systems exhibit an isomorphous phase diagram (usually the solid solubility of one component in another is limited).
- ❑ Often the solid solubility is severely limited, though the solid solubility is never zero (due to entropic reasons).
- ❑ In a simple eutectic system (binary), there is one composition at which the liquid freezes to two solids at a single temperature. This is in some sense similar to a pure solid which freezes at a single temperature (unlike a pure substance the freezing produces two solid phases- both of which contain both the components).
- ❑ The term EUTECTIC means *Easy Melting* → The alloy of eutectic composition freezes at a lower temperature than the melting points of the constituent components.
 - This has important implications → e.g. the Pb-Sn eutectic alloy melts at 183°C, which is lower than the melting points of both Pb (327°C) and Sn (232°C) ⇒ can be used for soldering purposes (as we want to input least amount of heat to solder two materials).
- ❑ In the next page we consider the Pb-Sn eutectic phase diagram.
- ❑ As noted before the components need not be only elements. E.g. in the Al-Cu system a eutectic reaction is seen between α (Solid solution of Cu in Al) and θ (Al_2Cu compound).

* Actually in Pb-Sn alloy (or Pb-Sn eutectic alloy)

In the eutectic phase diagram, we will note that there is something known as the eutectic reaction and we need to consider this, because very few systems actually exhibit the isomorphous phase diagram. And usually the solid solubility of one component in other is limited that means, we are not in the regime of Hume-Rothery and therefore, we typically see that there are other kind of phase diagrams which exist.

And often this solid solubility could be severely limited, and we will take up some examples of these also, those truly speaking the solid solubility is never 0. Sometimes when you look at phase diagrams, when the solid solubility is very small, they will not show it in the phase diagram, it will be seem as if the solid solubility or the terminal solid solubility is 0. But, due to entropic reasons we know that it can never truly be 0 and there will be some small amount of solubility, which exists typically.

In a simple eutectic system and we consider now binary eutectics for now, there is one composition at which the liquid freezes to two solids at a single temperature, this is another congruent, what you might call melting temperature. Or the eutectic reaction is another congruent kind of a reaction, in some sense this is similar to a pure solid which freezes a single temperature.

Of course, unlike like a pure substance the freezing produces two solids phases both of which contain both the components, if you talk about a pure element melting, for instance or a pure component melting. Then this will take place at a single temperature

cooling, the liquid produce a single solid of a single composition. But, now when we are talking about this eutectic reaction, here though the solidification takes place at a single temperature, two compositions of the solid or produced which we will see from the phase diagram.

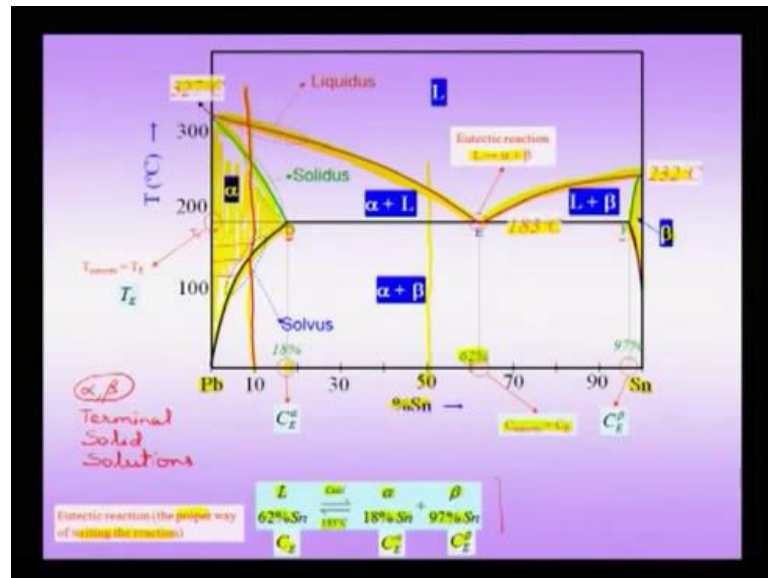
The term eutectic is used to tell us that it means easy melting that means, and we will see this from the phase diagram, that if the melting point of the solid is typically lower than both the components. And this can be used advantage for instance, in the lead tin system and when you say lead in system, actually we are talking about not pure lead and pure tin, but solid solutions of tin in lead and lead in tin. If you talk about this eutectic alloy it melts at 183 degree Celsius, which is lower than the melting points of both lead.

Lead melts at 327 degrees Celsius and tin melts at 232, but the eutectic composition melts at 183 degree which is lower than both the components lead and tin, this is very nice because now, we can make a solder alloy of the eutectic composition. And therefore, we will have to input least amount of heat to melt the solder material and therefore, we can use it for soldering, using an temperature which is smaller and therefore, heating the electronic components need not to worry about it.

So, we want input least amount of heat into the into the solder of the two materials and this eutectic composition helps us in doing so. And we will take up a few examples of this eutectic system and we will see what is the importance of this. And we have already noted that the components not only need elements like in the previous example, in the lead tin system both the components were elements, but it there can be other kind of eutectic reactions.

For instance, in the Al-Cu system the alpha that is copper solid solution of aluminum, shows a eutectic reaction with the theta phase which is the Al₂Cu phase that means, one side is a solid solution alpha, or essentially aluminum. And the other side is a theta phase which is Al₂Cu and between these this compound and this solid solution, we have an eutectic reaction.

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So, let us start with a simple example of an lead tin eutectic system, so on the left hand side lead melts at 327 degrees Celsius, on the right hand side tin melts at 232 degrees Celsius. But, there is a specific composition which we call C eutectic, C subscript E with 62 percent of tin which melts at 183 degrees Celsius. And you can see that, on the right hand side the melting point or which we call the liquidus line, the liquidus line slopes downwards towards the eutectic temperature of 183.

On the right hand side, similarly the liquidus line slopes from 232, 180 degree Celsius and similarly, the liquidus line also slopes downward and at 183 degrees Celsius. We have a reaction known as the eutectic reaction, in which case a liquid of a certain composition gives rise to two solids alpha and beta. This alpha on the left hand side and beta on the right hand side are what are called terminal solid solutions, they are both terminal solid solutions.

And we will later on take up examples, where the terminal solid solubility is actually very very limited, so now we have an for 62 percent of tin a reaction of a liquid giving two solids alpha and beta, and all this happening at a single temperature. Of course, we will have to ask ourselves this question, suppose I am working on off eutectic composition, for instance I am working at a composition with 50 percent of tin. Or I am working at a composition which is below having a composition of tin below the point d, so d is 18 percent.

So, if I am working at a composition with 10 percent of tin how will be the solidification behavior of such an alloy, so these kind of questions we will ask ourselves; and we will try to address these. That what kind of typical microstructures are produced when you are talking about these of eutectic compositions, suppose I am taking an off eutectic composition here.

I would like to know what is the solidification behavior of eutectic composition, now if you want to write down this eutectic reaction, which now I pointed out takes place for compositions between the point d with 18 percent of tin. And f which is what you might call the terminal point till which I would see an eutectic reaction, I would observe an eutectic reaction. And the point where the reaction is completely dominating the whole transformation is the point with 62 percent of tin.

So, I can write down the eutectic reaction in complete form as and this is the proper way to write the reaction as shown in the equation below, that a liquid with 62 percent tin when cooled and this double headed arrow means at 183 degrees Celsius, there is actually in equilibrium. And if the cooling direction I would produce alpha and beta two phases, alpha as is a solid solution of tin and lead and this alpha contains 18 percent tin, beta is also a solid solution of tin and lead.

And this contains 97 percent tin and I have label these as C alpha eutectic and c eutectic and this reaction occurs at 183 degrees Celsius. So, when I am writing eutectic reaction, the proper way of writing this reaction is that, I would include the cooling direction, I would include the temperature at which the transformation is taking place. I would include all the compositions that means, that composition of the liquid and the compositions of the alpha and beta, which rise from this eutectic reaction.

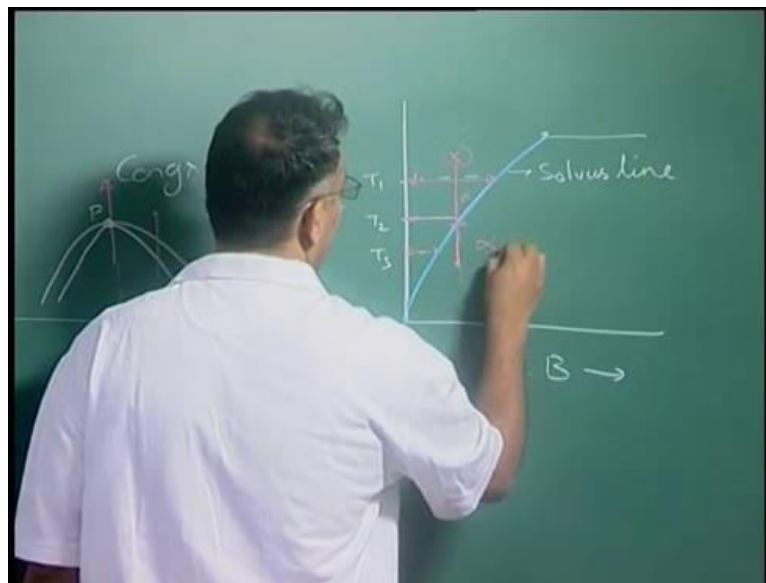
So, I have these two terminal solid solutions which I can mark on the right hand, left hand side here ((Refer Time: 17:22)), so this is my terminal solid solution on both side the alpha and beta; and beyond this you have the eutectic reaction. The bounding line on the lower side, the blue line is called the solvus line, and the solvus line this separates the alpha phase from the alpha plus beta phase on the left hand side, and on the right hand side the solvus line, so this F tin line the line here, so which I will highlight once more.

So, this line starting from F and going downwards is also another solvus line, and this solvus line separates the beta phase from the alpha plus beta phases, this kind of a solvus

line is called as sloping solvus line, that implies... If you look at the solubility possible of for instant tin in lead at high temperature for instance, suppose I am here in this temperature and I call this temperature T_1 . I would notice that there is a large amount of solubility of tin in lead possible.

Suppose, I go down to lower temperatures I will see that the solubility keeps falling, so let us let me show this solvus line in a little more detail on the board, so what I am going to draw here is what is called the sloping solvus line.

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So, I have a percentage of B on the x axis and I have temperature on the y axis and I have a line which is called the sloping solvus line and this sloping solvus line, so I have the solvus line. And now of course, it could be could terminated in what we may call a eutectic reaction there, but suppose I am tracking my solubility at a temperature T_1 and at a lower temperature for instance T_2 and even lower temperature T_3 . You would notice that at T_1 this much amount of solid solubility is possible of B in A, so this is my a at lower temperature the solubility keeps falling.

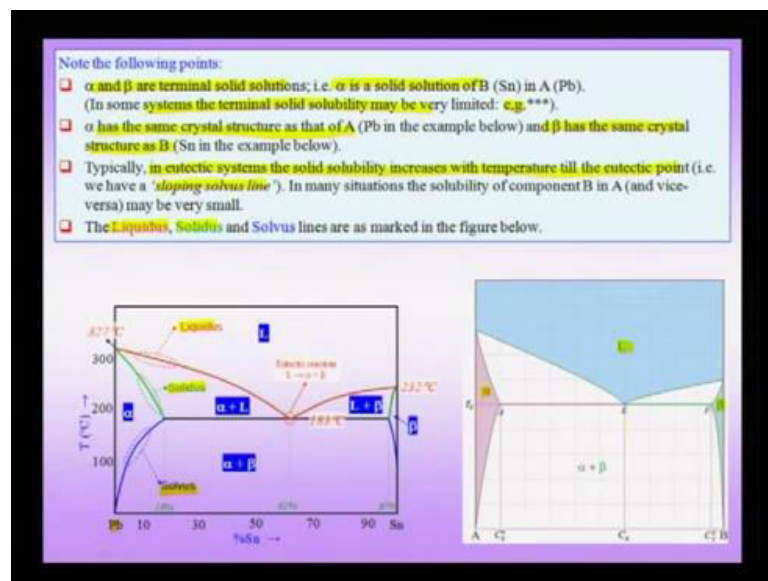
And this is why I call this a sloping solvus line; that means, suppose I were at a I take a composition like this here which I label for instance C_1 . And I slow cool from here, I would note when I cross this line here this intersection to this line, this uniform solid solution of say A and B, say for instance the alpha solid solution would breakdown into

an alpha plus beta. So that means, an alpha here would breakdown into an alpha plus beta mixture, this is because of the reducing solubility with decreasing temperature.

So, in addition to the previously lines, the liquidus and the solidus lines which we encountered, while we talked about the isomorphous system, we have an additional line to talk about here, in the phase diagram which is called the solvus line. And to summarize the most important point in this diagram, that there is liquid at high temperatures, but then that breaks down into two phases alpha and beta at low temperatures.

And for a fixed composition 62 percent in this example at point E which I label the eutectic point, this whole transformation takes place at a single temperature. And between all the single phase regions the liquid region, the alpha region and the beta region you have all the two phase regions, the liquid plus beta region, the alpha plus liquid region and the alpha plus beta region.

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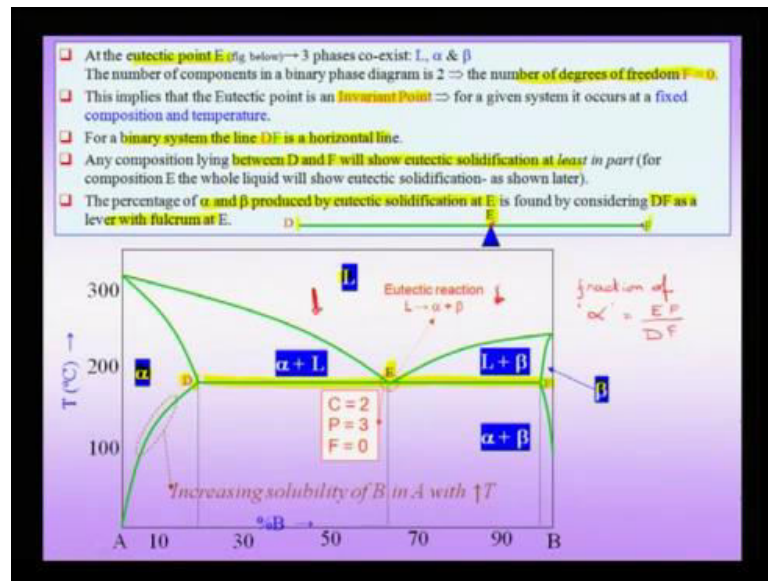
And as I pointed out before, we need to note the following points when we are talking about an isomorphous phase diagrams, that alpha and beta terminal solid solutions that means, that alpha is a solution of B in A, and similarly beta is A in B. And in some systems the terminal solid solubility may be very very limited and we will consider these examples in the coming slides. Alpha has the same crystal structure as a, for instance the

crystal structure of lead in the left hand side, beta has the same crystal structure as B tin in the right hand side.

Typically in eutectic systems, the solid solubility increases the temperature till the eutectic points that means, that we have the sloping solvus line about which we talked a little bit. And we have to note that in the case of a eutectic phase diagram, we have to note that there are three important lines, the liquidus marked in red, the solidus marked in green, and this solvus line which is marked in blue.

And there are three such lines to the left of the eutectic, we have the liquidus solidus and the solvus and similarly to the right we have the, of the eutectic point also we have the liquidus solidus and the solvus lines. And in the diagram in the right hand side, we can note that the single phase regions are all marked the liquid region, the alpha region and the beta region and all the other regions in white, are the two phase mixture regions.

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Now, we have already noted that at the eutectic point, there are three phases coexisting, the liquid phase, the alpha phase and the beta phase, all three of them coexist at the, what we might call the eutectic point. And this implies according to the phase rule that the number of degrees of freedom is 0, and since that automatically implies that the temperature and composition, at which the eutectic reaction occurs for a given system.

Of course, the actual composition and temperature will be dependent on the system, for instance in the lead tin system this may occur at a certain composition, in certain other system it will occur at a different temperature and composition. But, for a given system the temperature and composition at which the eutectic point occurs is absolutely fixed, that means it is an invariant of the phase diagram.

And we have to additionally note that in a binary system, the DF line, the line D joining F the temperature of the eutectic reaction is an horizontal line that means, you cannot allow this line to tilt, because the degrees of freedom along this line is fixed. Any composition between D and F will show at least impart an eutectic solidification, this aspect we will consider in detail in the coming slide. What we have to note though we have a very particular composition E. at which the entire liquid shows an eutectic reaction.

But, this does not imply that there are, not other compositions which are at least show eutectic reaction in part. And what we are saying is that, if you take a composition between D and E or between E and F such compositions will also show eutectic reaction, but that will be only part of the liquid which will show the eutectic reaction. The entire liquid will not undergo the eutectic reaction, and we will see the reason for that very soon.

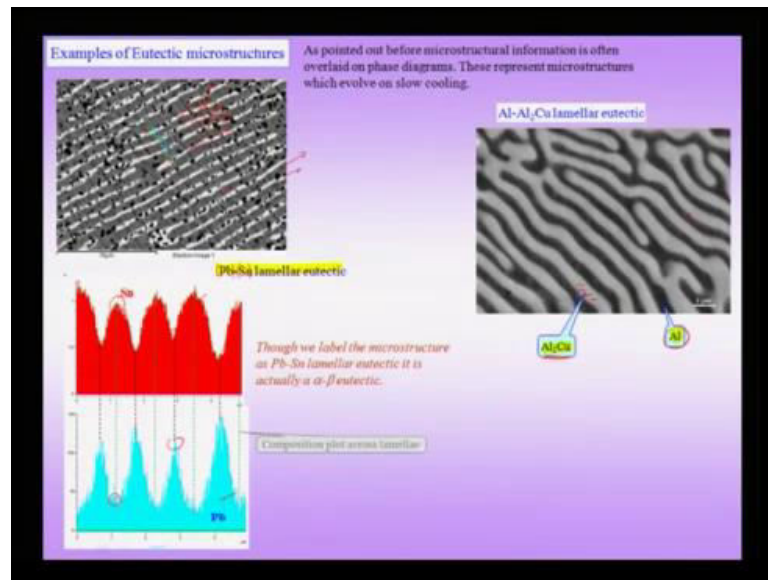
Now, the percentage of alpha and beta produced by the eutectic solidification at E can be found out by considering DF as a lever with fulcrum at E that means, I can put my fulcrum at E. And now I have two sections to this lever D E and E F and I can use my lever rule to actually calculate the phase fractions that means, suppose I want to know the amount of the alpha phase in this reaction.

Then, I will take the section E F and divide it by the total length of the lever DF, so the fraction of the alpha phase is equal to the arm of the E F divided, the opposite arm of the lever divided by DF. Of course, I will have to express this in terms of the compositions as we have done previously, so I can similarly find a fraction of the beta phase in this eutectic mixture. So, to summarize this slide the important point being that DF is an horizontal line, this horizontal line can be considered as a lever with fulcrum at E.

Therefore if I have a liquid completely showing an eutectic reaction, I can find the phase fractions using the lever rule, and I have to know also note that any liquid which is of the

eutectic composition. Suppose, I consider for instance a liquid which is solidified here, which is of the eutectic composition or a liquid which is here, with this composition. However, I have to keep the region between D and F such kind of liquids between D and F will show at least in part the eutectic reaction, so this is an important point to note.

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Before, we go and consider some actual some more examples and what will happen if we solidify, for instance a eutectic mixture and off eutectic measure in detail. Let us see some eutectic microstructures, as I pointed out when we did the equilibrium phase diagrams, that this information of microstructures is typically overlaid on top of phase diagrams to enhance the utility of phase diagrams.

And we should not think that this is a natural product of the phase diagrams, so let us look at these phases here and we have two examples of eutectic reactions. The one on the right hand side is between a pure component aluminum of course, a solid solution of aluminum with copper. And Al_2Cu , so it is a one of the components A is a solid solution of aluminum and copper, and the other is Al_2Cu a compound, on the left hand side is our familiar lead tin are eutectic, again noting that when you saying lead actually lamellar what we mean is lead drawn within brackets.

That means, it is a solid solution which actually shows the eutectic reaction, and suppose I have that means, I have now a two phase mixture and this type of a microstructure is called a lamellar eutectic. Of course, all eutectic reactions need not show the lamellar

morphology, there are other kinds eutectic like Chinese script eutectic, and sometimes even get what is known as degenerate eutectics. So, we are not considering examples of those in this particular slide, what we are seeing here is the, what you may call the standard lamellar eutectic.

Of course, we have to note that these in three dimensions are actually like plates, and in three dimension these are plates, when you take a metallographic section, then you see them as these bands which arise here. So, here for instance in this microstructure, you have two bands one dark and one light, and if I draw a straight line across this microstructure and then, note the composition. I would note that, if you can see here the white is actually a lead rich phase, the white phase and the dark phase which is seen here is actually a tin rich phase.

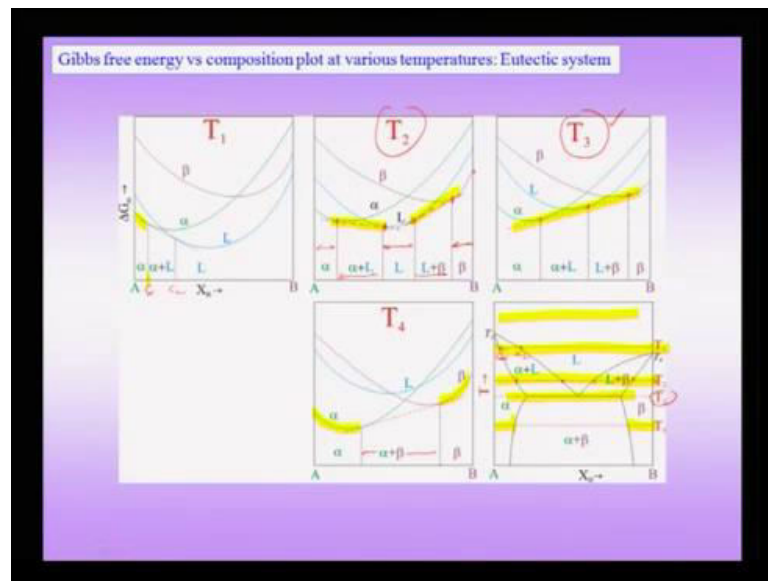
So, you have the tin rich phase and the lead rich phase in forming a lamellar eutectic and as I pointed out this is actually in three dimensions, they are something like plates. And when you take out what you might call the alternating plates, and when you take a cross section through these alternating plates, then you get a microstructure which looks like this. And when you take a composition across these plates, you can see that wherever you have the tin rich phase here, there is a paucity of lead.

So, there is a lead poor is where the tin riches, and wherever it is lead rich and lead rich, we noted that is the white phase as seen in the micrograph, the scanning electron micrograph is where the tin is poor. Therefore, you have this tin rich phase and the lead rich phase which of course, we have already noted are the two terminal solid solutions alpha and beta. Alpha being the, ((Refer Time: 29:04)) let us go back here to the lead tin diagram, alpha being the lead rich phase and beta being the tin rich phase.

So, the lead rich phase and the tin rich phase are coexisting in the form of a lamellar eutectic, similarly in the micrograph on the right which is an aluminum A 1 2 C u lamellar eutectic you note that the dark phase and the white phase coexist. One of them is of course, as I you can see at the dark phase is the aluminum phase, and the light phase is the A 1 2 C u inter metallic compound. And since, it is an intermediate compound the ideal composition would be consisting of 33 percent of copper and 66 percent of aluminum.

And so in this diagram we have taken up some examples of lamellar eutectics, noting that there are other kinds of eutectics like Chinese script eutectics, which are also possible. But, here we have taken the particular example of a lamellar eutectic, and we note that that these microstructures are typically overlaid on phase diagrams, assuming that we have to doing a slow cooling, and to enhance the utility of these phase diagrams. But, by no means this particular information is a direct product of the phase diagram.

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Now, let us try to correlate the Gibbs free energy composition plots with the eutectic phase diagram. And typically we would like to start with this what you might call the Gibbs free energy composition plots and may be theoretically calculated and then, try to actually arrive at the eutectic phase diagram. But, here we just trying to correlate that how does the Gibbs free energy temperature plot look for various temperatures.

Exactly I thing the similar way we did for an isomorphous system previously right here ((Refer Time: 30:42)), so we did this for an isomorphous system, where we plotted the Gibbs free energy composition diagrams and try to correlate it with the phase diagrams. Similarly, we will try to do the same thing for the eutectics system, so at very high temperatures of course, we have the liquid. And the if you draw the Gibbs free energy temperature plot, we will note that the liquid line will lie below both the alpha line and the beta line.

But, suppose I start with the interesting part of the diagram which is at T_1 , at T_1 you would notice that the alpha phase has the lower value between say the pure A and a certain composition here, so I can mark this composition say S_C alpha. Then beyond say C liquid, you notice that the liquid has a lower Gibbs free energy here, so this is my C alpha and this is my C liquid, so it has a lower free energy. And between the $2 C$ alpha and C liquid I have to draw a tie line to construct and that means, that there is a coexistence of alpha.

I have to make a common tangent construction to show that the alpha and the liquid phases coexist, throughout this whole composition range, you can notice that the beta curve lies above the liquid line. And therefore, you find that there is no region where the beta is stable, suppose I cool down to a lower temperature, say to a temperature T_2 , then I would notice that there is a regime here on the left hand side. Wherein, the alpha phase is stable in other words till here, then there is a regime in which the liquid phase is stable that means, the liquid free energy is the lowest.

Then to the right there is a temperature composition regime, where the beta phase has the lower Gibbs free energy, so the role of these three phases the region in which these three curves lie at the lowest keep switching to the left here it is the alpha phase, which is the lowest. Then it is a liquid phase in this intermediate compositions and at towards the right is the beta phase, and between any two of these single phase regions, you can notice that I can make a common tangent construction by this line.

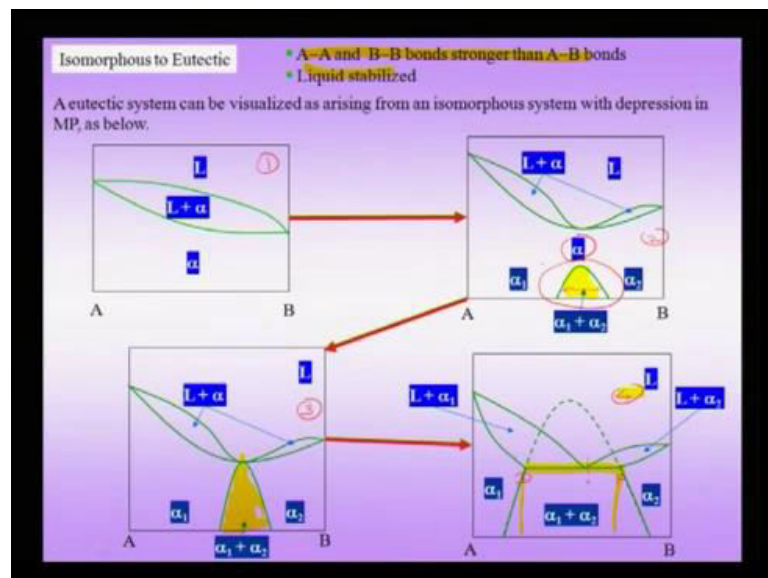
And therefore, using these common tangent constructions I can find out that there is liquid plus alpha, which is coexisting in the left hand side and liquid plus beta on the right hand side. Of course, at the eutectic temperature also I can draw which is T_3 shown here right here, so I have a T_3 wherein I see the eutectic reaction and I would notice that, I can make a single common tangent construction going through the alpha, the liquid and the beta compositions.

That means, that at this temperature the alpha, the liquid and the beta all three phases can coexist, they have not two common tangent constructions like we had in the temperature T_2 . Wherein I have to draw a common tangent between, for instance the alpha phase in the liquid phase, and on the right hand side I had between liquid phase and the beta phase curves. But, here I have a single common tangent covering the entire three phases the

alpha liquid and beta phases and therefore, at the eutectic temperature all three of them coexist.

Now, we go down to even lower temperatures, you would notice that there is an alpha region which is stable here and then, there is a beta region which is stable to the right and between the two you can have a common tangent construction giving us, a alpha plus beta region of stability. So, this is trying to correlate the Gibbs free energy composition curves and of course, the most important new thing which we have noted here is the temperature T 3 at which you notice that, we can have a single common tangent to three curves, three composition. Gibbs free energy plots for the alpha liquid and the beta phases, and that is an important variation as compared to the isomorphous system.

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Now, I can visualized this isomorphous system turning into an eutectic system, based on the stability of what you might call the strength of the A-A and B-B bonds and also the liquid stability. So, I can start and of course, this is not as a single system will show all these things, a single system of course, will either B for instance the diagram 1 here. There may be some systems which will look have a phase diagram which looks like 2, there may be of course, yet other phase diagram which is the classic eutectic diagram, which is the diagram 4. It is unlikely of course, you may land up with the diagram which is some like 3 which is something just to visualize our, what we might call a limiting situation. So, suppose I start with the classic double lens isomorphous system A in 1 I

shown and then, I assume that there is a depression in melting point, as we have seen which also means that there is a phase separation α_1 plus α_2 at low temperatures here.

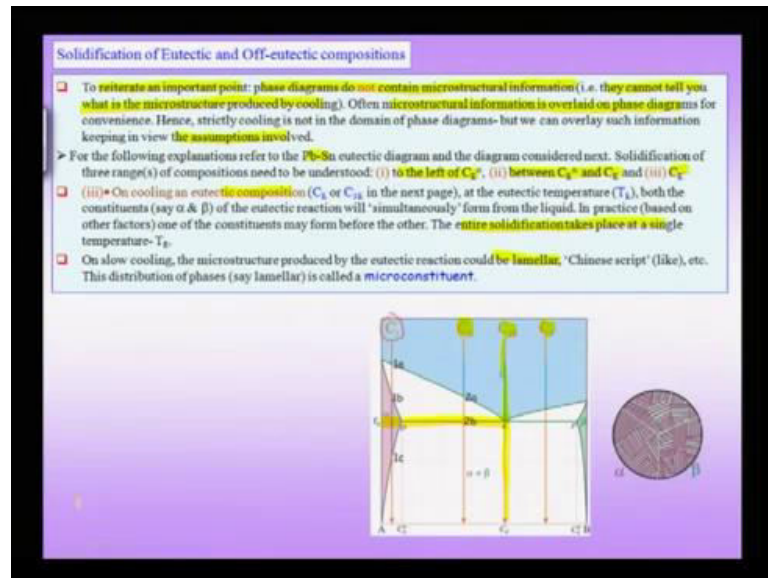
Now, of course, if we are talking theoretically these might be thought of as the variations in interaction parameters, but we are not going to that detail at this point of time. We are just trying to get a heuristic or an intuitive feel of how we can go from an, what we might call an isomorphous phase diagram to what we might call a eutectic phase diagram with what we might call decreasing solid solubility. So, you may consider situation where you have a double lens, but then the region of stability of the two phases just almost touches my...

That means, the moment the liquid is cooled below this congruent transformation temperature it tends to split into α_1 and α_2 , now in the case 4 which is the eutectic case, you can think of this liquid solubility curve extending beyond the eutectic temperature. That means, now for a range of temperatures or for a range of compositions starting from what we had considered here, and we had label these two range of compositions as D and F, so you have a D and F here.

Between D and F compositions you notice that the moment the liquid transforms, it transforms into a mixture of α_1 α_2 that means, you never get a pure solid solution like α or a unmixed solid solution, single disordered solid solution like α . And therefore, I can now visualize my isomorphous system slowly turning into an eutectic system, based on the stabilization of the liquid that means, looking at the two phase mixture which is getting the region of which is getting more and more pronounced.

And therefore, I can think of an isomorphous system turning into an eutectic system as we go from 1, 2, 3 and 4. Once again to emphasize this does not mean that all these kind of phase diagrams are obtained from a single system, they are all different systems and you may find examples of some of these as you have encountered.

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Now, let us consider solidification of eutectic and off eutectic compositions, now this is as I pointed out we would like to enhance the utility of phase diagrams by drawing what we might call the slow cooling curves. And these cooling curves are at various compositions, so when I want to talk about cooling curves, some representative cooling curves are as shown having a composition C 1, which passes through the alpha region, the alpha single phase field.

Then, I have the cooling curve C 2 which is not at the eutectic composition, but is off eutectic, then I have C 3 which is also a subscript E to it indicate that it is an actually the eutectic composition which I am solidifying. And C 4 which is also an off eutectic composition, but lying to the right of E the difference of course, between C 4 and C 2 is just the kind of phases which produced and not in the, they are very similar in terms of the overall solidification which is taking place.

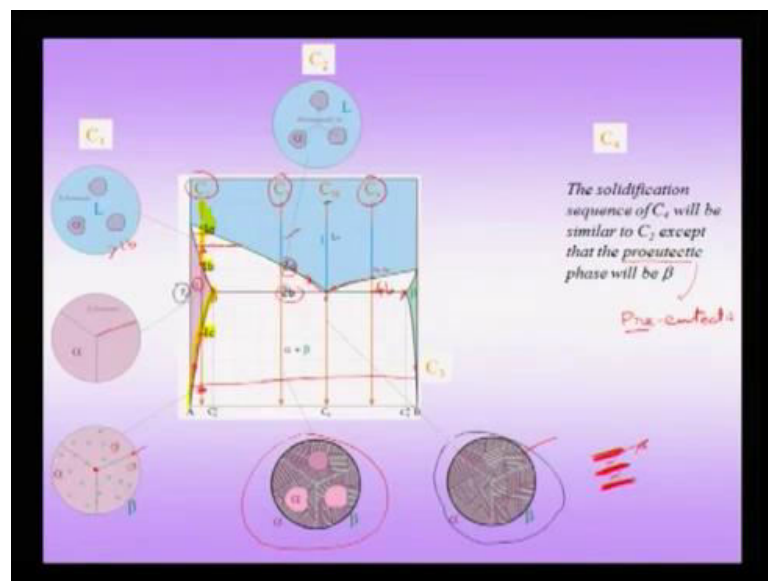
Now, in the case of you would notice that in all these cases, if you talk about a cooled C 1, C 2, C 3 E or C 4, I would actually obtain a mixture of alpha plus beta at room temperature. However, the way these phases are distributed are going to be very very different and that is what we are interested in knowing, to reiterate an important point, phase diagrams do not contain micro structural information. That is they cannot tell you what is the microstructure produced by cooling, often experimental micro structural information is overlaid on these phase diagrams for convenience.

And we have to keep the assumptions involved, when we are talking about such kind of micro structural information. Now, if you are talking about a diagram for instance, the lead tin eutectic diagram solidification we can consider in three ranges, one to the left of C eutectic, second between C eutectic and C, and third at C E. So, these are three important ranges we need to talk about that is to the left of D, between D and E and at E.

These are three important ranges and of course, to the right hand side you can clearly see it is just nothing but, everything wherever there was alpha, now it will become beta. Now, if you talking about an eutectic composition and that means, now the C 3 which is the simplest to consider now, and you are cooling along this line here from high temperature to low temperature.

We will note that the entire solidification will take place at the single temperature T and you would what we had seen before in the example that we will produce a lamellar kind of an eutectic, in typical cases like in the case of the lead tin eutectic.

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And this eutectic microstructure will look something like as shown in the diagram on the right, so here we have the lamellar eutectic produced, when we take a eutectic composition and solidify. That means, now at high temperatures till we have liquid region and at temperature T E, what happens is that the liquid which is present solidifies at a single temperature producing both the micro constituents alpha and beta.

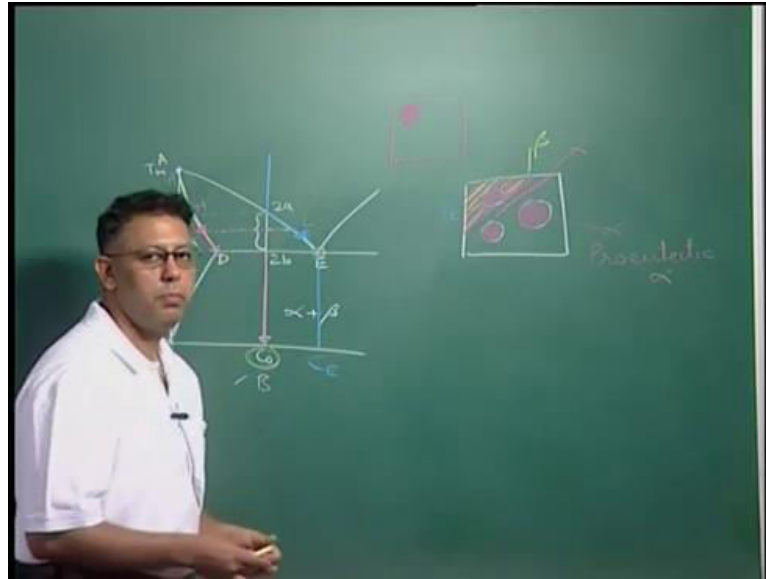
And typically this happens in a way such that, suppose I can consider for instance, that in a certain region you have the say the beta phase being produced, next to it is an region which is deprived in component B. And therefore, you will have the alpha phase, suppose this is my beta phase coming out, then you will have the alpha phase, then you will have a beta phase coming out then there will be an alpha phase and so forth. Such that, the overall composition is as given by the lever rule construction at the eutectic temperature, and that is what we note as the eutectic composition.

Now, suppose I take a composition which is for instance, ((refer Time: 42:14)) to the left of the eutectic composition like C 2 or C 4 which is to the right of the eutectic composition. An important point to note would be that between temperature, for instance suppose I am considering C 2 initially of course, there will be liquid at high temperatures, then between temperatures which is marked by labels two A and 2 B, you will have the alpha phase coming out of the liquid.

This alpha phase is called the pro-eutectic phase which is indicative of the fact that this is actually a pre-eutectic phase, so this is called the pro-eutectic, but it what is actually implied it is the pre-eutectic phase. So, this pre-eutectic phase is called a pro-eutectic phase, and this comes out from the liquid in the temperature regime labeled by 2 A and 2 B. Now, we had already noted that when we did the isomorphous phase diagram that as you are cooling from the point two label, 2 A to 2 B.

What will happen to the composition of the liquid, the liquid will move along this line, the composition of the liquid and the composition of the solid will move along this line, so let us examine this fact a little more in the table.

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So, I have a portion of my eutectic phase diagram wherein of course, I have the component B here, pure component A here, I have my liquidus line here which is say for instance T_m A to E point E and maybe I can call this point A if you want and then, I have the solidus line here. And of course, I have the solvus line from D E to this point here x, now what I want to consider is the solidification of a composition which is labeled as C 0 above this label 2 A which is occurs at a temperature 2 A, I find that its entirely liquid.

Now, at low temperatures we known finally, we will get an alpha plus beta mixture between 2 A and 2 B I would note that, I should get what is called a precipitation or a formation of alpha from the liquid. So, initially I have a liquid mixture here and from this I will have the alpha phase coming out and this alpha is called the pro-eutectic alpha. Now, the important point to note is that as this alpha is coming out, this alpha which is coming out at any temperature for instance, suppose I have here, I draw a temperature line here in between.

So, the liquid in composition with an alpha say at a temperature T_3 the alpha composition is changing, similarly the liquids composition is also changing, as we are going down from 2 A to 2 B point. The composition of the alpha as we have noted before would go along the solidus line from this point which I say for instance call it M to D and the composition of the liquid will go along this line which I call from 2 A to E. So,

this is my composition of liquid as you are cooling and this is my composition of the alpha phase as I am cooling.

So, the composition of the liquid and alpha which is in equilibrium with it is constantly changing that means, if I talk about the first alpha which came out at, this temperature T_A its composition could be different. Suppose, I started with a small amount of then it grew a little more, but then this larger alpha would have a different composition which would be richer in B. Then it grew even further, then I or more of this alpha form then its composition would change with respect to what was the original alpha which came out, so the alpha is constantly changing.

Now, this and the fact that the liquid is now getting richer and richer in B, and when you reach this temperature for instance the T_E eutectic temperature, suppose I now consider this is my snap shot at T_E eutectic is my snap shot at eutectic. Whereas, certain amount of alpha has already come out from the liquid, now what is the composition of the liquid, the composition of liquid is not the original nominal composition C_0 . But, is actually the composition which is C_E eutectic, because now the liquidus travels along this line and therefore, has reached this point E.

And now that implies that the solidification of the remaining liquid here is going to take place, as if now the liquid is an eutectic liquid and therefore, I would get an eutectic kind of a micro constituent and that will look like this. So, I will have an alternating lamella of, so this is my alpha and now you have an alternating lamella of alpha and beta, so suppose I have my beta which is say for instance I label it in yellow color. So, this will be my beta in between the alphas, this is my beta, so the final solidified microstructure will have an eutectic component which is consisting of alpha and beta lamella.

But, also have the pro-eutectic alpha that means, alpha is present in two places as is big what we may call approximately spiral lumps and section looking circular the alpha; and the alpha present in the eutectic mixture. So, this is an important point to note that when you are doing in solidification of an half eutectic composition like C_0 here, that the composition of the solid and liquid is constantly changing, as we noted for the isomorphous system.

And their liquid composition when you reach this temperature T_E has reached this point E and that implies that, that liquid is ready to undergo eutectic transformation; and we

already know that the eutectic transformation will produce alternating lamella of alpha and beta phases. And the end product microstructure will constant of an pro-eutectic alpha and also in eutectic mixture consisting of alpha plus beta.

So, that is what is schematically shown in the diagram here ((Refer Time: 49:26)), which is the diagram shown at the bottom. Now, suppose I take a mirror reflection composition of this of course, I do not mean a real mirror, I mean a mirror conceptual mirror, wherein instead of working with C 2 composition, I work with a C 4 composition. The only difference I would see compared to this diagram would be that the microstructure would be, that I would get pro-eutectic beta coming out for this composition between these labels.

For instance I consider say 4 A and 4 B, but in 4 A and 4 B temperatures I would get, what you might call pro-eutectic beta coming out the composition of the liquid will travel along this line and reach E. And therefore, at T eutectic I would get the standard eutectic microstructure and therefore, the only difference would be that the pro-eutectic phase instead of the alpha phase would be the beta phase.

Now, we also need to talk about an composition which does not lie in the section of between D and F, so at E we already seen it is a eutectic micro constituent I would produce between D and E or E and F I would get a pro-eutectic component. First coming out followed by an eutectic solidification, but suppose I take a composition to the left of D, for instance a composition like C 1. So, what would happen to such a composition let us try to understand.

So, above the point labeled 1 A I would notice that I have the liquid phase between 1 A and 2 B I would expect that the alpha phase starts to come out and slowly as you go down to lower and lower temperature, I would notice that the fraction of the alpha would increase. Because, now I can construct what I may call a tie line, at any temperature in this regime and I know I have to have my fulcrum here and therefore, you can see that this arm of the lever is suppose, you draw a fulcrum at higher temperature.

You would notice that, this arm of the lever is small, but then this arm of the lever increases as you go down to lower and lower temperatures, and like in the case of an isomorphous system. Once I cross this temperature 1 B below that I go, I get a pure alpha phase, so this is similar so far to an isomorphous system in which you start with the

liquid and then, land up with a pure alpha phase at lower temperatures. So, this is very very similar to an isomorphous system, but this system is not completely what I call done with yet, because at even lower temperatures you intersect the point 1 C.

At 1 C you notice that the solubility of the alpha phase has fallen that means, to be more precise the solubility of B in A is falling along the sloping solvus line as we had pointed out the D A curve. And because of this sloping solvus line, when the cooling curve intersects this point 1 C you would expect that the beta phase would precipitate out from the alpha phase. So, initially you at high temperatures you had liquid, then when you at 1 B for instance, so at 1 B you could have a picture something like this, wherein or just above 1 B, so this is slightly above 1 B.

So, you would notice that there is alpha phase and the liquid phase in coexistence with it, I mean you cross the 1 B line and get into phase field between 1 B, and 1 C and just above 1 C, you would notice that the entire alpha would look like this. That means, there is a polycrystalline alpha and these can be considered as grain boundaries, now when you go down below 1 C, then you would notice that the second phase beta would try to precipitate out from the alpha.

Because, there is a sloping solvus line and of course, given the composition I can find out at any temperature for instance, I can draw a line like this horizontal line of course, not looking toward on this, but this is my fulcrum. And now the amount of beta phase is proportional to the small arm of the lever that means, a small amount of beta would have precipitate out. And of course, the composition of the beta would travel along this line here which I can draw, so the composition of the beta would travel along this line.

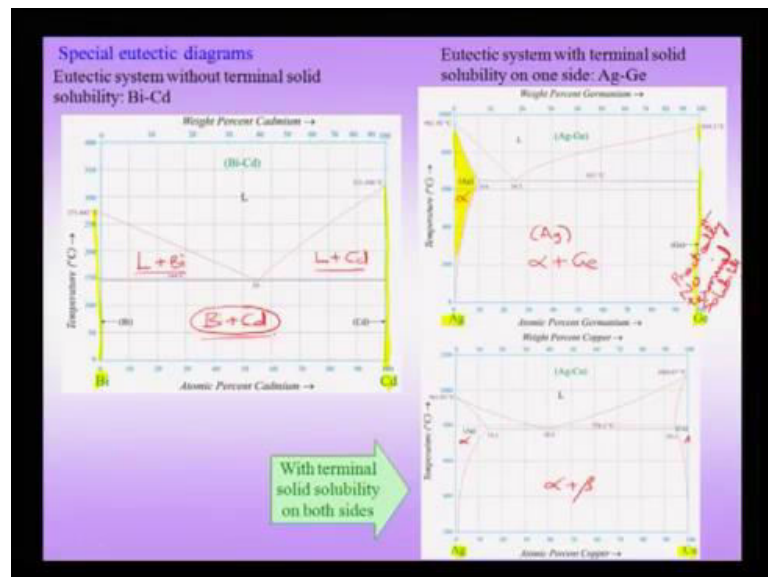
And the composition of the alpha would travel correspondingly on the other line, the corresponding line on the right hand side and the end microstructure would be consisting of alpha essentially alpha phase, but then there will also to be beta phase. In this schematic I have shown two kinds of beta phases, one which is heterogeneously nucleated at the grain boundary; and the others which is nucleated homogeneously at inside the grains. These terms heterogenous and homogenous nucleation, we will consider in detail in the chapter on phase transformations.

But, for now we will not that if there is some aid to the phase transformation, the nucleation part of the phase transformation, then for instance the form of grain

boundaries or dislocations. Then such a thing is called heterogeneous nucleation, the other of course, occurring uniformly over the material is called homogenous nucleation. But, essentially we note that, the beta phase can be present along the grain boundaries, may be even along the triple junctions or triple lines here or they could be present within the grains of alpha.

So, you have the final micro constituent which consist of the alpha phase which came out between the temperatures labeled with 1 B and 1 C, and also the beta phase which came out from below the 1 C temperature.

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So, this is the brief summary of the what you might call the solidification sequence, when we consider what you may call eutectic compositions, off eutectic compositions, showing eutectic reactions and off eutectic compositions which are beyond the D F region of the phase diagram. And therefore, they are producing a two phase mixture which does not have any eutectic component in it, before we leave this topic let us consider some special eutectic diagrams.

Like we pointed out a typical eutectic phase diagram is like the one we have seen so far, which is like this lead tin eutectic and the right hand bottom shows such a similar diagram for the silver copper. In which case silver and copper both are FCC, but then they do not have complete solubility in each other and therefore, I have an eutectic phase diagram and this is standard kind of phase diagrams which we have been seeing so far.

But, I could also have phase diagrams in which case like for instance, the silver germanium system, silver is FCC, germanium is diamond cubic

And you notice that practically no amount of silver dissolves in germanium, so there is no terminal solid solubility on the germanium side however, on the silver side I can see that there is some amount of terminal solid solubility. So, on the germanium side there is no terminal solid solubility, so we have no practically known terminal solid solubility in the right hand side, while on the left hand side, the silver side there is some amount of germanium thus dissolve in silver. Now, but if you look at the bismuth cadmium, you would notice that there is practically no terminal solid solubility, either on the bismuth side or on the cadmium side.

And therefore, this system has no terminal solid solubility and therefore, if I want to label the two phase fields, I will have to label it as liquid plus bismuth here, and highlight label it as liquid plus cadmium here. And this is not an alpha plus beta mixture in this region, in this region I will have to label it as bismuth plus cadmium, and in this case of course, I will have the alpha solid solution of silver which I could label as either A_g like this or as alpha.

So, we will have alpha plus germanium here, in this case of course, if I label this alpha and I label this beta, then I would have an alpha plus beta mixture. So, often when phase diagrams like the one of bismuth cadmium drawn, students get a little confuse that how come there is no terminal solid solubility, this is because and how do I label the phases. So, you have to note that this phase is now liquid plus beta, on the right hand side it is liquid plus cadmium, on the two phase field, the solid field is bismuth plus cadmium.