X-Ray Crystallography
Prof. R. K. Ray
MN Dastur School of Materials Science and Engineering
Indian Institute of Engineering Science and Technology, Shibpur
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture - 19
Phase Diagram Determination

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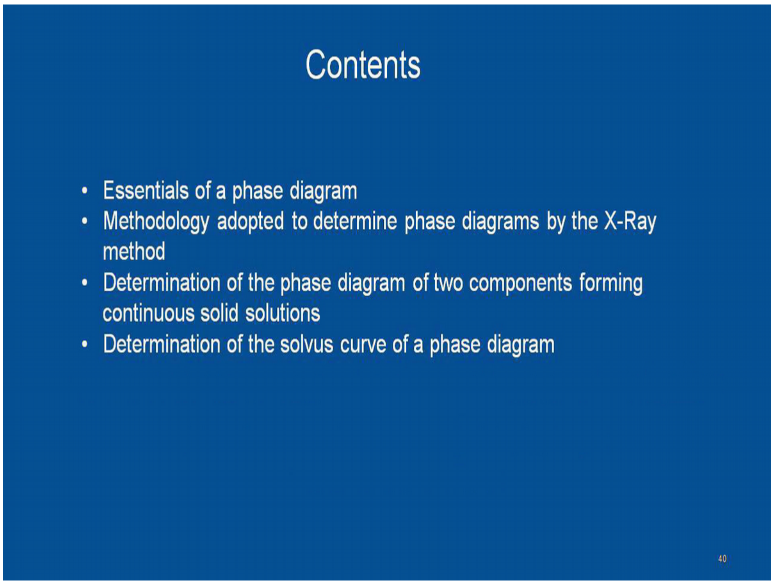

Contents

- Essentials of a phase diagram
- Methodology adopted to determine phase diagrams by the X-Ray method
- Determination of the phase diagram of two components forming continuous solid solutions
- Determination of the solvus curve of a phase diagram

In this lecture I shall deal with a very important application of X-rays, namely phase diagram determination using X-ray diffraction. We already know that for an alloy system a phase diagram or an equilibrium diagram is essentially a plot of temperature versus composition. And this plot is divided in to a number of areas in which a particular phase or a phase mixture is going to be stable. Phase diagrams are of great importance in material science and there are several methods by which phase diagrams can be drawn. Namely: thermal analysis, microscopic measurements and X-ray diffraction.

X ray diffraction has an added advantage over the other 2 methods, because using X-ray diffraction we can not only determine the phase diagrams, but we can also find out the crystal structure and lattice parameter of the phases that are encountered in a phase diagram. Now in this lecture I will concentrate on phase diagram determination by using

X-ray diffraction and I will consider only 2 components or a binary system.

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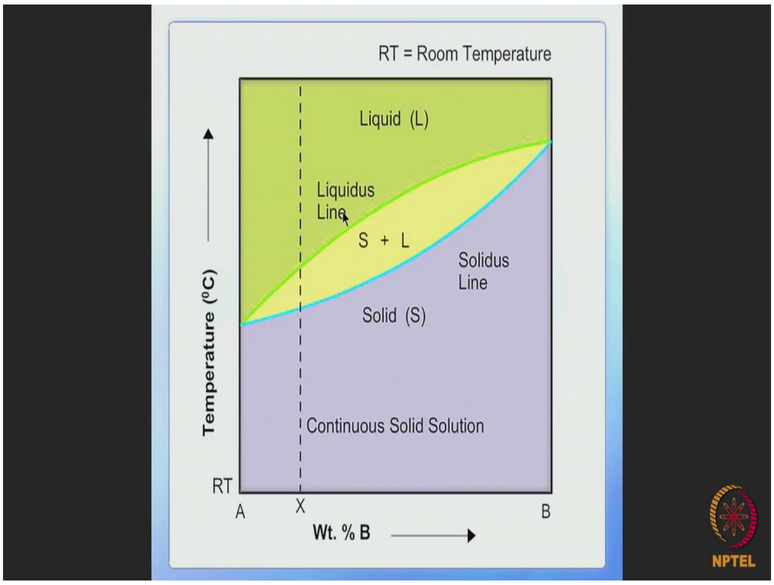

Say for example, this is a typical phase diagram of 2 components A and B. This is a typical phase diagram of 2 components A and B, where the components are totally miscible in the liquid, state and in the solid state they form a continuous solid solution. In the solid state they form a continuous solid solution. That means, even if the composition change takes place this continuous solution has the same crystal structure from there to here although the lattice parameter will change as the composition of the continuous solid solution changes. Now this is the melting point of the component A and this is the melting point of the component B.

Now, if we look at these phase diagram. Above these lines everything is in the liquid state, and below this line everything is in a solid condition. In between these 2 lines we have 2 phases both the solid and the liquid. Now the line above which everything is liquid is known as the liquidus line. And the line below which everything is solid is known as the solidus line.

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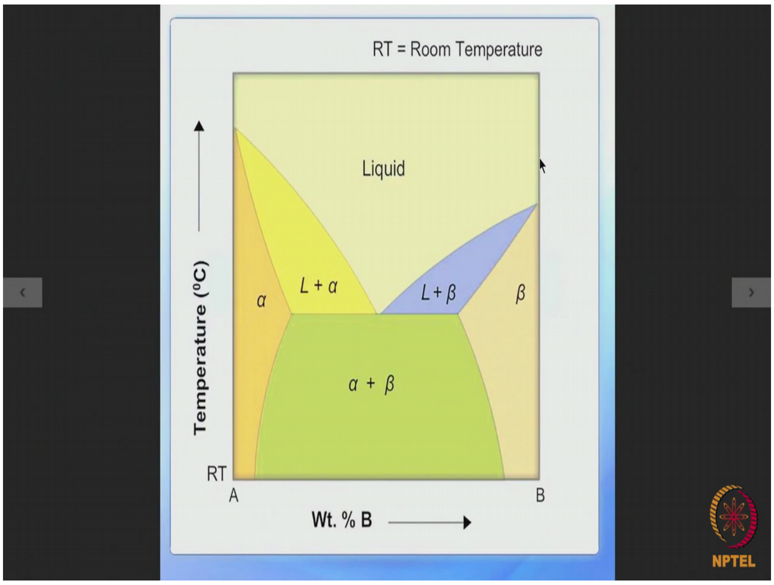

There is another typical phase diagram of a 2 components system here. This is a situation where the 2 components system is such, the 2 terminal solid solutions form which are alpha and beta near A and near B respectively. The liquidus line is this one, and the solidus line is this one. Alpha is a solid beta is a solid and this is the film where both alpha and beta fall in phases co exist. This is the region where we have both liquid and alpha phase, this is the region where we have both liquid and the beta phase.

Now, in order to determine a phase diagram or equilibrium diagram, we must be able to determine the room temperature equilibrium.

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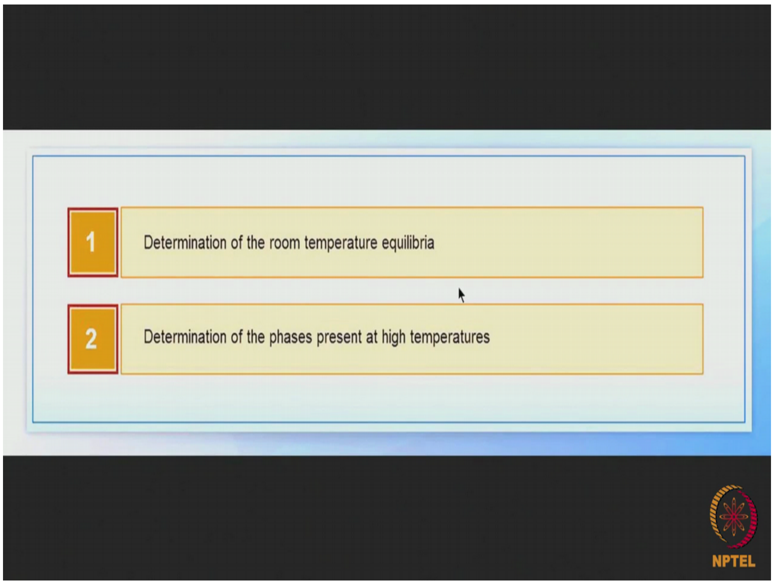

1 Determination of the room temperature equilibria

2 Determination of the phases present at high temperatures

We must be able to determine the equilibrium phases that exist at room temperature and side by side we must be able to determine the phases which are present at higher temperatures, and we must remember these 4 points.

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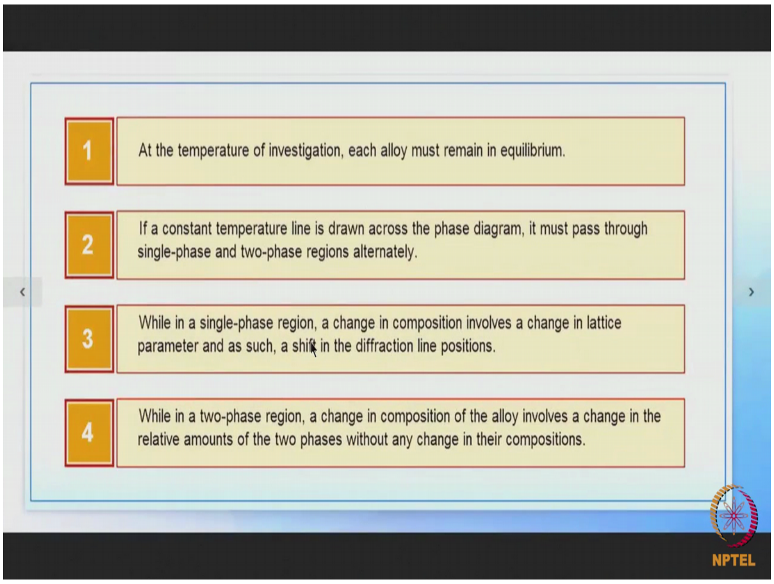

1 At the temperature of investigation, each alloy must remain in equilibrium.

2 If a constant temperature line is drawn across the phase diagram, it must pass through single-phase and two-phase regions alternately.

3 While in a single-phase region, a change in composition involves a change in lattice parameter and as such, a shift in the diffraction line positions.

4 While in a two-phase region, a change in composition of the alloy involves a change in the relative amounts of the two phases without any change in their compositions.

When you deal with the phase diagram, at the temperature of investigation each alloy must remain in equilibrium you see that is the reason why phase diagrams are also known as equilibrium diagrams.

Now, if a constant temperature line is drawn across the phase diagram it must pass through single phase and 2 phase regions alternately. As you can see here, if you draw a line parallel to the composition axis at perpendicular to the temperature axis, what we find? We find up to here this is single phase from here to here another line is a 2 phase, again it is a single, phase again it is 2 phase, again it will be single phase.

So, both single and double phases will do exist alternately. So, if a constant temperature line is drawn across the phase diagram it must pass through single phase and 2 phase regions alternately. So, while in a single phase region a change in composition involves a change in lattice parameter. So, if there is a change in the lattice parameter, what will happen in the diffraction pattern of the material? It will reflect it will reflect as a shift in the diffraction line positions.

So, if we go back to the previous diagram say for example, this is a continuous solid solution. So, within this single phase region if we go for different compositions what will happen because of the different compositions the lattice parameters will be different. Because, if suppose the B atoms are larger than a atoms as we move along these axis the unit cells will contain more and more of B than a and as a result of which the lattice parameters will be higher, and higher larger and larger.

Now, if we take a diffraction pattern of this single phase from different compositions of B, there will be a change in the lattice parameter values and this will be reflected as a shift in the values of shift in the positions of diffraction lines, we will see it very soon. Now thirdly, fourthly now, while in a 2 phase region a change in the composition of the alloy will involve a change in the relative amounts of the 2 phases. Without a change in the lattice parameters there is a error here it will be without any change in their lattice parameters not compositions.

So, this is another important thing to remember, that while in a 2 phase region a change in composition of the alloy will involve a change in the relative amounts of the 2 phases without any change in their lattice parameters. Now let us see what it means. If we look at this particular phase diagram say for example, if we take different alloys made up this much of B, this much of B, this much of B and this much of B, then what will happen? Say at this particular temperature, at this particular temperature here, if we what we find the up to this composition it will be single phase alpha, and at this temperature from there to here it will be 2 phases alpha and beta.

Composition of alpha will be given by this point at this particular temperature. Composition of beta will be given by this point on the same temperature scale, and when we move from here to here you know as the composition changes more and more B it is reduced, the lattice parameter of alpha and lattice parameter of beta here do not change. So, what happens within this 2 phase region although the lattice parameters of alpha and beta do not change and these are fixed by you know the composition as shown here and here, at the particular temperature. The relative weightages of alpha and beta will change. For example, at this particular temperature if we are on a higher side of B then there will be more of beta than while we are on the towards the side of A, while the less of beta more of alpha, we will come to it soon.

So, what is the procedure to be adapted to determine the phase diagram of a 2 component system at room temperature?

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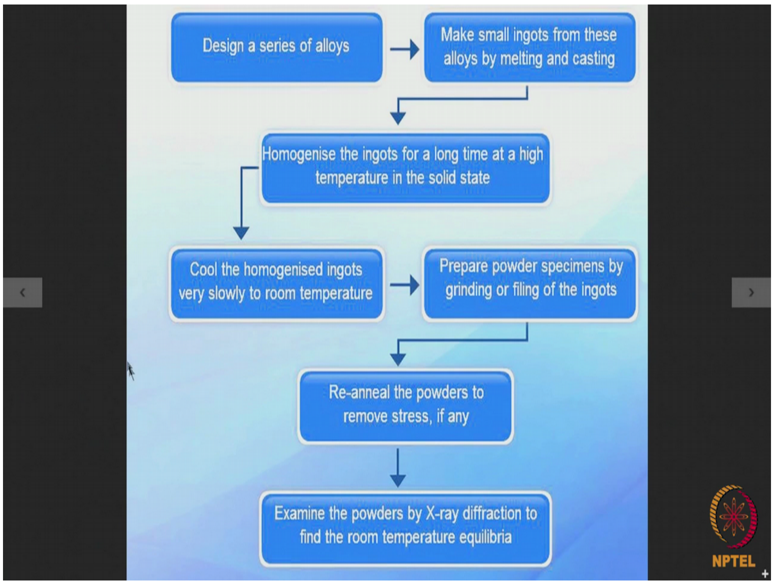

Design a series of alloys

Make small ingots from these alloys by melting and casting

Homogenise the ingots for a long time at a high temperature in the solid state

Cool the homogenised ingots very slowly to room temperature

Prepare powder specimens by grinding or filing of the ingots

Re-anneal the powders to remove stress, if any

Examine the powders by X-ray diffraction to find the room temperature equilibria

So, the first thing is we design a series of alloys; we design a series of alloys. Then make small ingots from these alloys by melting and casting. The third step is, homogenize the ingots for a long time at a high temperature in the solid state. This is very, very important homogenization for a long time is needed so that the phases will be in equilibrium. Cool the homogenized ingots very, very slowly to room temperature. Prepare powder specimens by grinding or filling of the ingots, of the homogenized ingots. We re-anneal the powders in order to remove stress if any.

Finally, we examine the powders by X-ray diffraction to find the room temperature equilibrium. So, this is how we find out the room temperature equilibrium by X-ray diffraction process.

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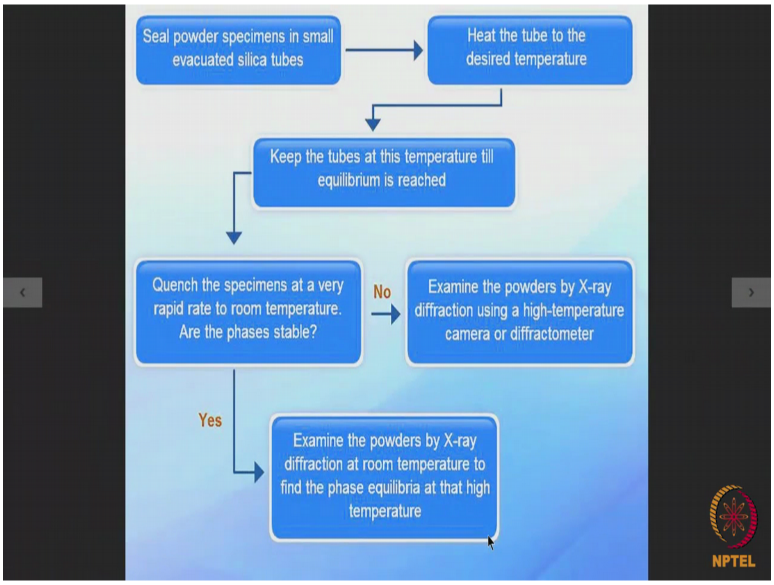

Seal powder specimens in small evacuated silica tubes

Heat the tube to the desired temperature

Keep the tubes at this temperature till equilibrium is reached

Quench the specimens at a very rapid rate to room temperature. Are the phases stable?

No

Examine the powders by X-ray diffraction using a high-temperature camera or diffractometer

Yes

Examine the powders by X-ray diffraction at room temperature to find the phase equilibria at that high temperature

Now, when we deal with the phases and higher temperature, what should we do? The first step is make the powder and the powder specimens in small evacuated silica tubes. Then heat that tube to the desired temperature. We keep the tubes at a particular temperature till equilibrium is reached. Now if it so happens that the high temperature phases can be retained by rapid cooling to room temperature, then that is what we do. Quench or rapidly cool the specimen at a very rapid rate to room temperature. Are the phases stable? If we find s the high temperature phases are stable, then what we do examine the powders by X-ray diffraction at room temperature to find the phase equilibrium at that high temperature.

On the other hand if the high temperature phases cannot be retained by rapid cooling from the high temperature we have to examine the powers by X-ray diffraction using a high temperature camera or a diffractometer, where you can keep the specimen at the desired high temperature for prolonged period of time.

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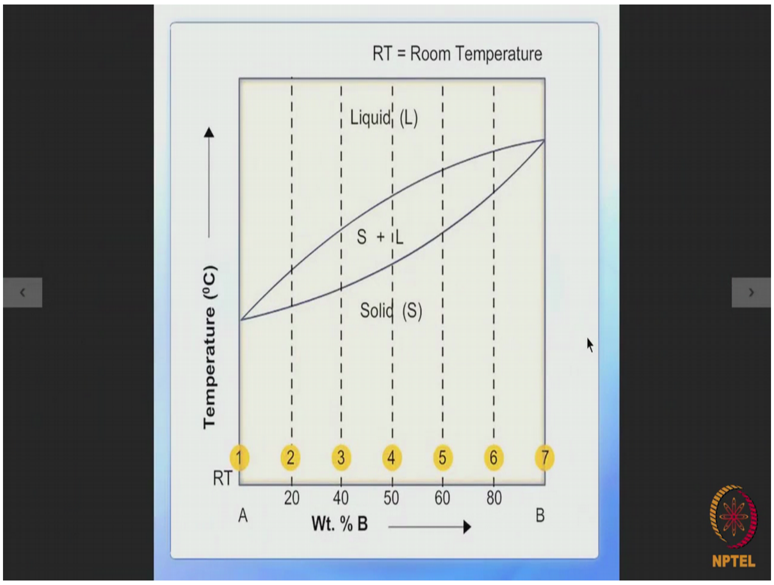

Say for example, when we are dealing with this kind of phase diagram here between 2 components, where you have liquid at high temperature and a solid below the solidus which is continuous solid solution continuous solid solution. Means you can have as much A in B and as much B in A as you want to be without changing the crystal structure.

Say for example, we choose this 7 compositions 1 and 7 are the pure components A and B and 1, 3, 4, 5, 6 these are 5 different alloys of A and B. 2 containing 20 weight percent of B, 3 containing forty weight percent of B, 4 containing fifty weight percent of B; the fifth one containing sixty weight percent of B; and the sixth one containing 80 weight percent of B.

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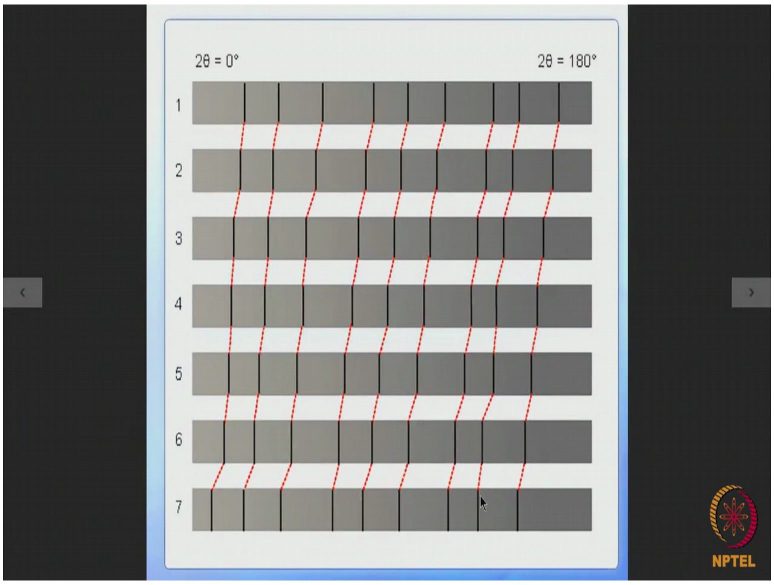

Now, at room temperature when we make specimens from those 7 samples and take the diffraction pattern, say this is the kind of diffraction pattern that we get. This side is 2 theta is equal to 0; that means, low theta side this is 2 theta is equal to 180; that means, the high theta side. Now what we find here, say for example, for the pure the component one A this is the diffraction pattern. So, we get diffraction lines for the component A.

What will happen to this pattern when you go to the alloy 2? If you will remember the alloy 2 is made up of pure component A with 20 percent of B and if the B atoms are larger than A what will happen to this particular composition? The lattice parameter will be higher than the case of this. Although the crystal structure everywhere is the same, but this one is have a higher lattice parameter. This one will have a still higher lattice parameter because more of the large atom B is present.

This one is still has larger value of the lattice parameter the will have larger value of lattice parameter etc. Now when there is an increase in the value of the lattice parameter it means there will be an increase in the d values also.

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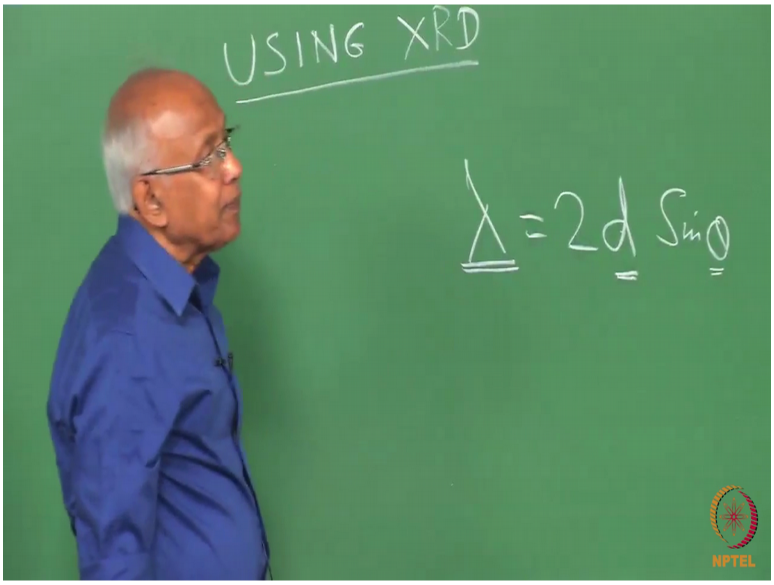

So, when we look at the brag reflection lambda is equal to 2 d sine theta. Lambda is fixed quantity because that this is the radiation, we are using for doing the experiment. So, if d is large automatically theta will be lower. So, you see that due to the addition of the component B in a when B atom size is higher than the a atom size the lattice parameter and d values of the lines will increase, as a result of which they will shift to lower and lower theta values, they will shift to lower and lower theta values. And this is what we observe in the diffraction patterns. Say this particular pattern is for component A this particular pattern is for component B and what we find that although the crystal structures are not different.

But look at the line positions these lines are present much towards the shorter values of theta and here the lines are shift you know towards the higher values of theta. This is bound to happen because B atom size is bigger, B lattice parameter is bigger, B d values are bigger than of A. Automatically these will be shifted more towards lower theta values and these will be shifted more towards higher theta values. Now when you go to the sample 2 you know an alloy we find that yes these lines are present in the pattern because as I told you the crystal structure does not change when we have a continuous solid solution, but only thing that happens is the lines will be shifted slightly, but the lower theta side and for that reason you know for the alloy 3, alloy 4, alloy 5 and alloy 6 there will be a continuous shift of the lines towards lower theta values and finally, this will be the pattern for the component, pure component B.

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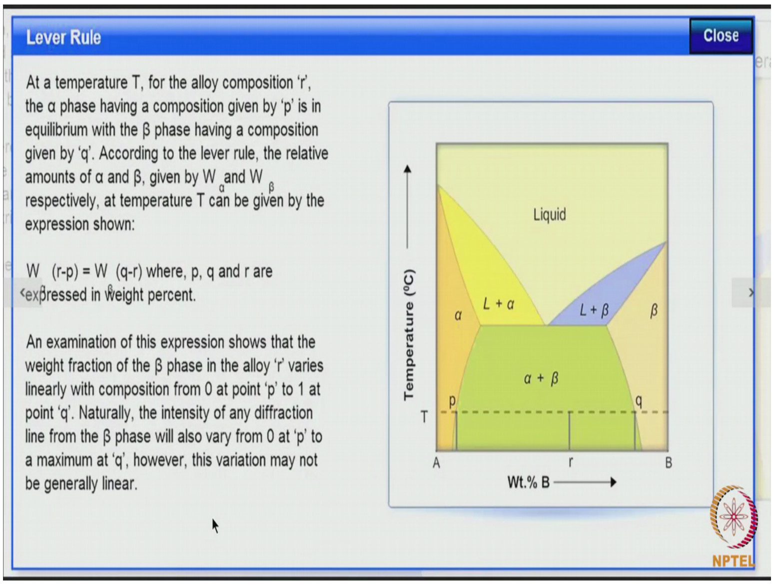

Lever Rule

At a temperature T, for the alloy composition ‘r’, the α phase having a composition given by ‘p’ is in equilibrium with the β phase having a composition given by ‘q’. According to the lever rule, the relative amounts of α and β, given by W_α and W_β respectively, at temperature T can be given by the expression shown:

$W_\alpha (r-p) = W_\beta (q-r)$ where, p, q and r are expressed in weight percent.

An examination of this expression shows that the weight fraction of the β phase in the alloy ‘r’ varies linearly with composition from 0 at point ‘p’ to 1 at point ‘q’. Naturally, the intensity of any diffraction line from the β phase will also vary from 0 at ‘p’ to a maximum at ‘q’, however, this variation may not be generally linear.

Now, we will deal with what is known as the lever rule. Say for example, when we deal with this 2 phase region here, when we deal with the 2 phase region here we have both the phases alpha and beta present. Now if we take any temperature here and if the temperature line cuts this 2 phase region at p and at q. Say, if I am dealing with an alloy of composition r say then alpha and beta, these 2 phases will be in equilibrium in this region and at this temperature value the composition of alpha will given by this point. So, you can read out the composition from the composition axis. In a similar manner the composition of the beta phase you can read out from the point q. So, this will be the composition of the beta phase.

Now, these are the composition of alpha these are the composition of beta. So, what happens when we have an alloy having the composition given by r? So, this alloy will have 2 phases alpha, having a composition given by this and beta having a composition given by this. But how much will be the weight fraction of alpha in this alloy? That will be given by this length divided by the entire length. So, the weight fraction of the alpha phase at this temperature will be given by this length divided by the entire length. And what will be the weight fraction of the beta phase, it will be this length divided by the entire length.

So, we can simply write it down W into r minus p for beta, sorry for alpha is equal to W into q minus r for beta. So, you say that here the alpha it is for alpha phase, W alpha r minus p is equal to W beta q minus r. So, how much will be weight fraction of alpha by beta? It will be q minus r divided by r minus p. So, it will be q minus r divided by r minus p. So, what will happen if we take an alloy of composition r then at this particular temperature say, if we draw a line parallel to the composition line p will be the composition of alpha, and q will be the composition of beta. Within the entire range and this particular temperature there will be no change in the composition of alpha and no change in the composition of beta.

But what about the weight fractions of alpha and beta; they keep on changing as we move along these line. And at this particular temperature we find that the weight fraction of alpha divided by the weight fraction of beta will be equal to q minus r that is this length divided by r minus p; that means this length. So, this rule is known as the lever rule, and that will give us an idea of how much of the 2 phases will be present in an alloy within the 2 phase region. So, one thing we have to remember that at any particular temperature when and beta phases are in equilibrium. The composition of alpha and beta will be unchanging for example, at this temperature composition of alpha will always be given by that and composition of beta will be always given by that.

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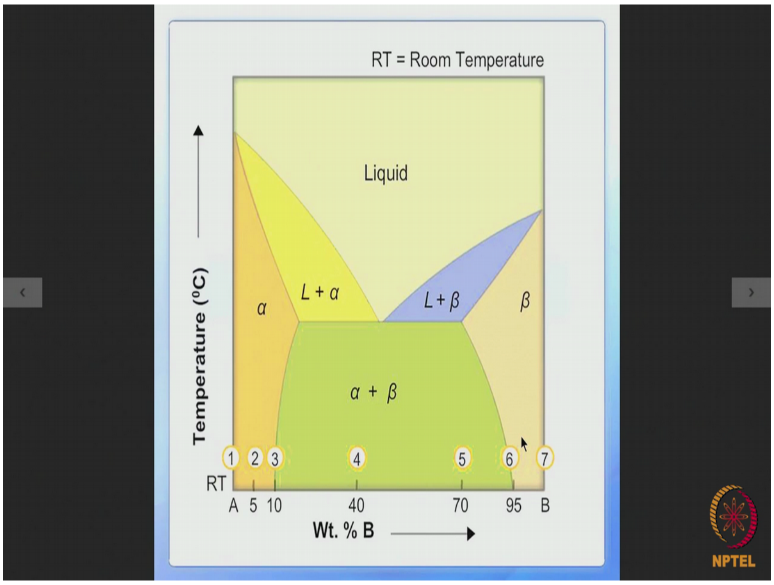

So, what will happen if we take different compositions of the alloy is that the relative weight fractions of alpha and beta will change only. Now if suppose we want to find out the room temperature equilibrium for this kind of a system. So, what we do as before we take a sample for the pure A sample for pure B and we choose several samples in between and make X-ray diffraction specimens out of which in the usual manner.

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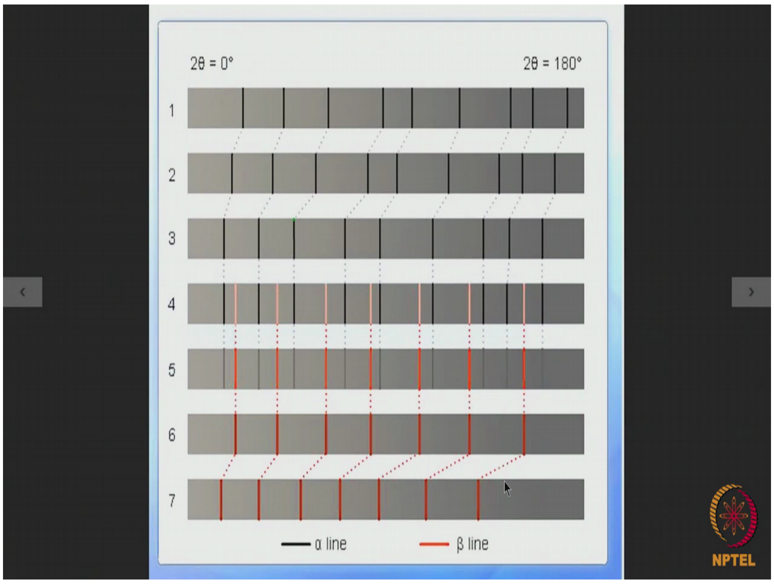

And then when we examine the diffraction patterns, what we find you see this is for the pure component A sample number 1 and these are the diffraction lines for the pure component B. You see one thing we have to remember in these corrections that, a particular phase whether an element or a compound will give rise to a particular diffraction pattern. You know, and a particular diffraction pattern what we mean by that? The diffraction lines at specific values of theta and relative intensities of a specific type. So, when we talk about a diffraction pattern we talk about both the positions of the lines corresponding to the theta values as well as the relative intensities of the lines.

So, an X-ray diffraction pattern of any element or compound; that means, for any particular phase is unique you know just as the finger print of individuals is unique by you know examining the finger prints of 2 different persons you can identify them as different persons. In a similar way just by examining the X-ray diffraction pattern when I call X-ray diffraction pattern 2 things must be kept in mind. The positions of the lines as well as the relative intensities as, when we talk about an X-ray diffraction pattern it is unique for a particular phase an element or a compound. So, this is the way by which we recognise one phase from another.

So, if we look at the diffraction pattern taken from the component A this is given by 1 and diffraction pattern taken from the component B which is 7 over here. Then as we move you know what happens in this place say for example, when we move from this composition to these and these, we are in the alpha phase. And if we assume that beta accounts a larger than the alpha phase since the weight percent of beta is increasing we will have here and here the alpha phase in the same phase, but the lattice parameters will be larger, or the d values will be larger; that means, the lines will be shifting towards lower theta as we have already seen. So, you will see that when we are alloying with B for the phase alpha how these lines are shifting to lower theta and this goes on till the alloy three.

Then what happens when we take say alloy 4 and 5, what will happen? You will have lines for both alpha and beta present simultaneously in the diffraction pattern. And as we can see here the alloy 5 has a higher amount of B compared to the alloy 4. So, naturally the diffraction pattern of alloy 5 will show stronger lines or of beta and this one will show weaker lines of beta, because in this case in the alpha beta mixture amount of beta will be much higher than over here.

So, the beta lines will be much stronger here that over here and this is what we see here. Say in case of 4 again the dark lines are for the alpha you see and these weak lines are for beta. So, as we go to alloy number 5 what we find the amount of beta increases in alloy 5 from alloy 4. As a result of which the beta lines are much stronger here and what about the alpha? alpha lines are much weaker in this particular case. So, you say that when we reach the alloy number 6 practically alpha has fully vanished. So, we will have only the beta lines. So, these are only the beta lines for alloy number 6.

Now, if we go back to the phase diagram, what we find 6 to 7 you know as we go from alloy 6 to alloy 7, then the beta will be more enriched in the B component. So, what will happen the lattice parameter or the d values will shift to shorter theta values and that is exactly what happens here. You see, it is you know this is beta and this is the B component and you see the lattice parameter shifts to the theta lower theta values. So, in this way at any particular temperature say at room temperature we can figure out you know where the whole thing changes from alpha to alpha plus beta to beta and if it. So, happens that we can have equilibrium at higher temperatures also. And if by quenching from the higher temperature the phrases can be preserved there by doing X-ray diffraction at room temperature also we can figure out what the phase distribution is going to be like.

Now, if we go back to this diagram we observe there are 2 important lines in the phase diagram this is these and this. These are known as the solvus curves or solvus lines.

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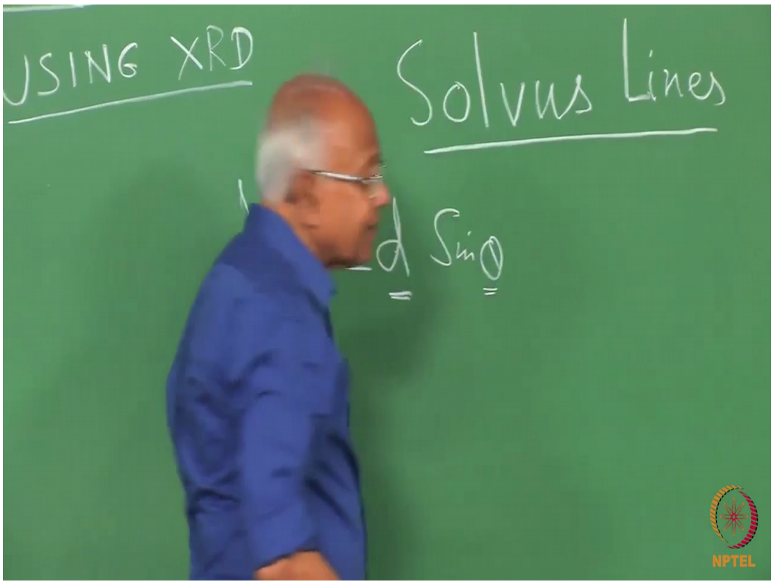

Just as this line over here, is known as a liquidus this line over here is known as the solidus these 2 lines are known as the solvus lines. And there are 2 methods, X-ray diffraction methods by which we can determine the location of the solvus lines as a function of temperature. So, the locations of the solvus curves as a function of temperature can be easily done using the X-ray diffraction method. Now let us see how the whole thing is done.

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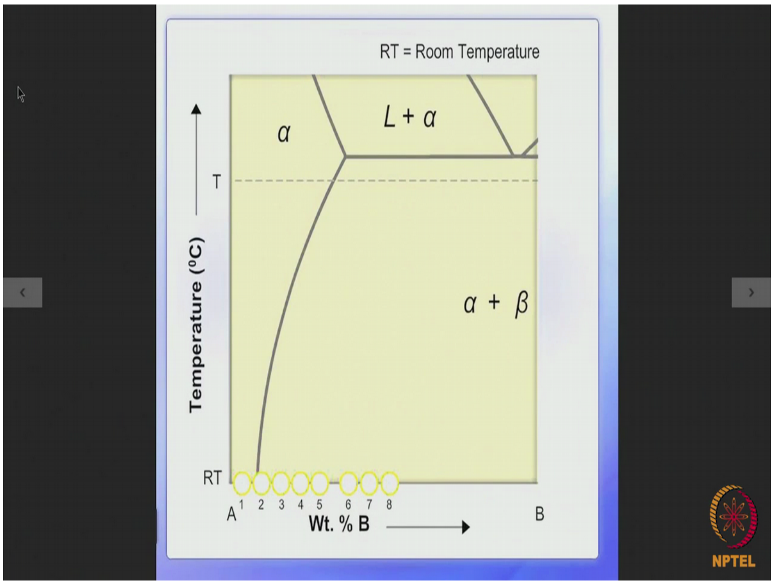

There are 2 x r d methods for determining the solvus curves, at these r number one, disappearing phase method and the second method is the parametric method.

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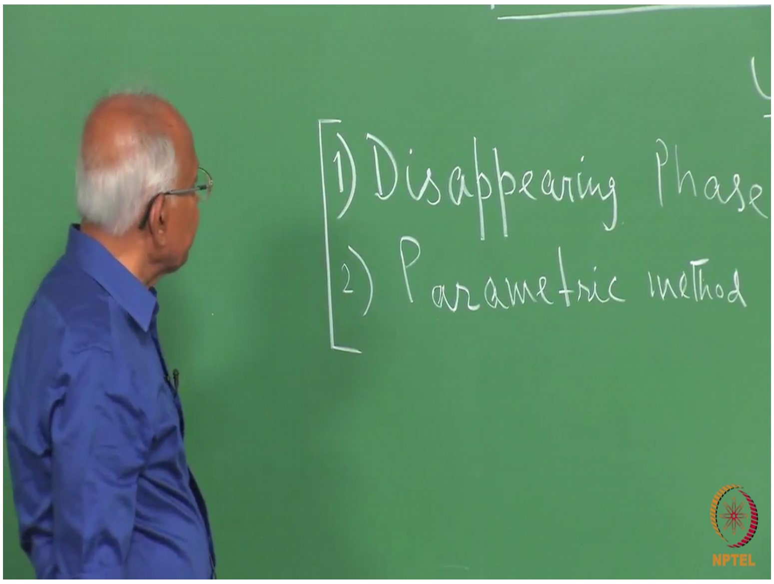

So, there are 2 different X-ray diffraction methods to determine the solvus curves in a phase diagram. These are number one the disappearing phase method and the parametric method.

Now, we will describe both these methods separately. Say for example, we make a number of alloys having the compositions shown over here. Say, 1, 2, 3, 4, 5, 6, 7, 8 alloys you make having different weight percent of B.

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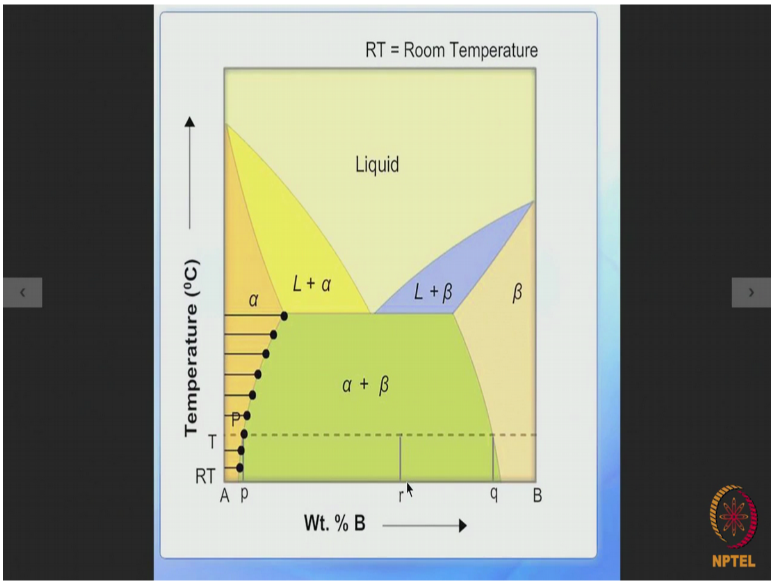

Now, using the disappearing phase method and the parametric method it is possible to find out the points where alpha changes in to alpha plus beta. And therefore, once this point or these compositions are marked we can have a smooth line through them and that will give us the solvus line. Similarly we can find out the solvus line on this side also. You see, the weight is done is very simple.

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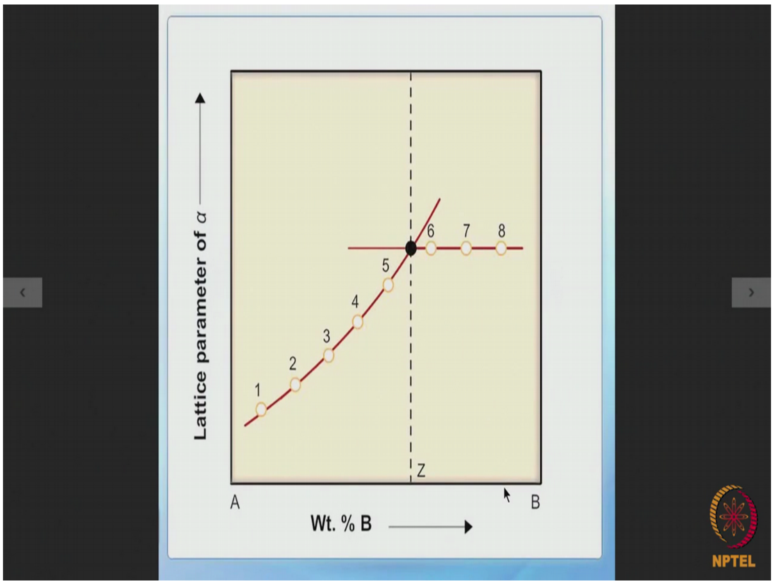

Say for example, if we consider say a temperature given by a temperature given by this. So, if we make an alloy over here of this composition. If we have an alloy of this composition, at this temperature it will be the alpha phase totally. If on the other hand we take an alloy of this composition on the other side here it will be the alpha and beta phases both. Now when you take a composition given by this point at this temperature it will have alpha and beta both, but here the amount of beta will be much less compared to the amount of alpha.

Now if I make an alloy you know further down the percent weight percent of beta a less beta say we come we have an alloy of this composition. So, when we take the diffraction pattern at this temperature from the sample. Again I will find lines alpha and beta. And at this case the beta lines will be much weaker because the amount of beta in the sample is much less. A time will come when say if you come to this point this position if we make an alloy of this particular composition. Then the beta lines will be so weak that, those lines will not be visible in the diffraction pattern at all. That means the lines will disappear from the pattern.

So, in the disappearing phase method what we do? We take series of compositions say if we want to find out the solvus point at the temperature t. We will make a large number of alloys and then say for example, we have an alloy over here find out the X-ray diffraction pattern it will give you alpha lines as well as beta lines, but if I move down this line and make an alloy with less weight percent of B, then also I will get the alpha lines and the beta lines, but what will happen to the beta lines here corresponding to the previous case beta lines will become little weaker. Because in this point for an alloy of this composition the amount of beta will be much less than say for example, of this composition.

So, as we were going down towards the a composition the amount of beta in the alloy will become less and less and then a time will come when we have an alloy of say this particular composition which will show lines of alpha only no beta lines will be there will be almost disappearing. So, that is the point which will be lying on this solvus curve at this particular temperature. And if we follow the same method for each and every temperature for several temperatures it is possible to find out by joining these points the solvus curve.

Similar thing, similarly you can do by you know taking a large number of alloys on this side and getting that x r d patterns and figuring out when the alpha phase completely disappears. And those points can be joined by a simple curve to show the solvus line. So, this is all about the disappearing phase method. But you see, sometimes you have a problem say for example, if we are dealing with a 2 components one has a very high atomic number the other has a very low atomic number.

Then what will happen? Say A is very high atomic number element and B is a very low atomic number element. You see, higher atomic number will mean higher value of small f the atomic scattering factor and small capital f the crystal structure factor, for a higher atomic number I am sorry for a higher atomic number element, both small f the atomic scattering factor and big f the crystal structure factor will be large. And for a small atomic number element both small f the atomic scattering factor and capital f the crystal structure factor those will be smaller.

As a result of which the diffraction lines from a will be much stronger compared to the diffraction lines of coming from B. So, the beta phase will have much weaker diffraction lines compared to alpha phase. So, it may. So, happen that when the beta phase is present it is very small amount, but the corresponding diffraction pattern may show no beta lines at all. Because, beta has got much lower value of small f the atomic scattering factor and big f the crystal structure factor.

So, you see that this is the source of error; that means, say for example, even when beta is present to the extent of 5 weight percent, but since you know the beta phase produces a much weaker diffraction pattern those lines will not be visible with respect to the alpha lines in the pattern. So, although the beta amount is present to extend of a 5 or 10 percent you know we may miss that. So, this is a source of error in the disappearing phase method when the components have widely different values of crystal structure factor f; that means widely different value of the atomic number.

Now, we come to the second method the parametric method. So, what we do in the parametric method? You see, if we look at if we look at any temperature t over here an if we look at here we have got the alpha phase. So, if we look at the you the diffraction pattern or the of a and find out the lattice parameter and if we go to a an alloy of A and B here we are still in alpha phase and if B atoms are bigger than the a atoms, what will happen? We will be still in the same phase, but the lattice parameter will more.

So, a time will come as go from you know this place to this place and make a number of alloys we will see that the lattice parameter will be different. As we are adding more and weight percent of B in the alloys the lattice parameter will increase. So, we will have a situation that you know as you are adding weight percent of B this is the lattice parameter of theta alpha phase so they are increasing. Again, if we go back to this diagram and if we take alloys on A on this side it will the alpha and beta, but remember you know at this temperature alpha lattice parameter is fixed given by this beta lattice parameter is fixed given by this at this temperature.

So, if we make a number of alloys and measure the lattice parameter of alpha for each and every one of those alloys and plot them and extrapolate them; so what we find that we will have a situation it will be a line straight line because all the lattice parameter are the same and you can extrapolate this line. And extrapolate this line they will meet their intersect at this point and the weight percent of B given by the point z is the corresponding point on the solvus curve. So, this is what is known as the parametric method. And here also there may be a problem if it so happens that a and B atoms are of almost similar size then what will happen the change of lattice parameter of alpha will be minimum.

So, in that case we have to find out the solvus point by the intersection of 2 very similar and flat curves. This is perfectly flat and here if the B atoms and a atoms are not much different in size then you know the increase in the lattice parameter value of alpha will be minimal. So, in that case this line instead of having this position it way much flatter line. And you see, when we find out the point of intersection of 2 flatter lines you know it is difficult to pin point where they are intersected. So, you say that in such cases you know the parametric method may not be very useful and we must find out other methods to determine the phase diagram for example, the microscopic method will be a good method to do so.

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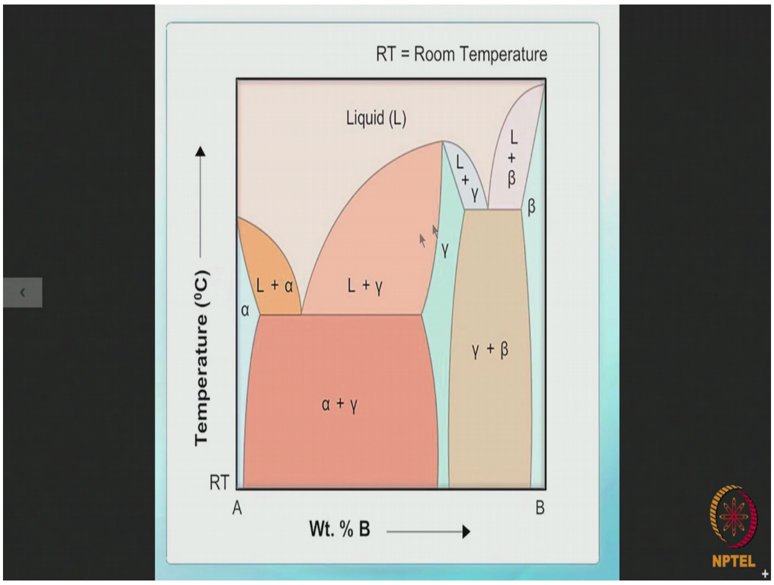

Now, there are complicated phase diagrams I will just give you a one example. So, here we have got the alpha and beta tanual solid solutions and we also have a compound you know it which is got extended solid solubility if it were a pure compound if gamma were a pure compound in the phase diagram it should have been the single line, but the very fact that it is extended over an area. That means it shows that gamma has much wider solid solubility. Otherwise this diagram is not much different from the phase diagram which I have shown you before.