

Advanced Metallurgical Thermodynamics
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Module #01

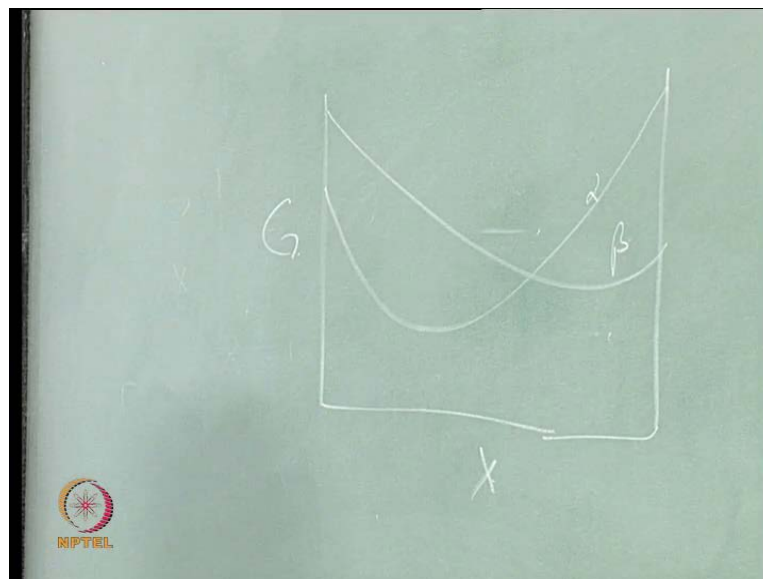
Lecture #09

To concept, Partition less solidification

In the last class, we have talked about how the miscibility gap closes and the thermodynamics behind it. How does the entropy of mixing basically helps as we increase the temperature, **that** the miscibility gap which is created by an inflection in the free energy curve closes. Because at high temperature you have higher $T \Delta X$ mixing term, and which dominates the Δh mixing term and as a result, you will see a free energy of mixing, which is completely negative. And, whenever the free energy of mixing is negative, you will get a curve which will lead you to a single phase state rather than a two phase mixture. This is what we have seen yesterday.

Today, let us take up the free energy composition diagrams again and see an additional feature that this free energy composition diagram gives us; and that gives us a lot of understanding about phase transformations, particularly what we call **it** as polymorphous transitions.

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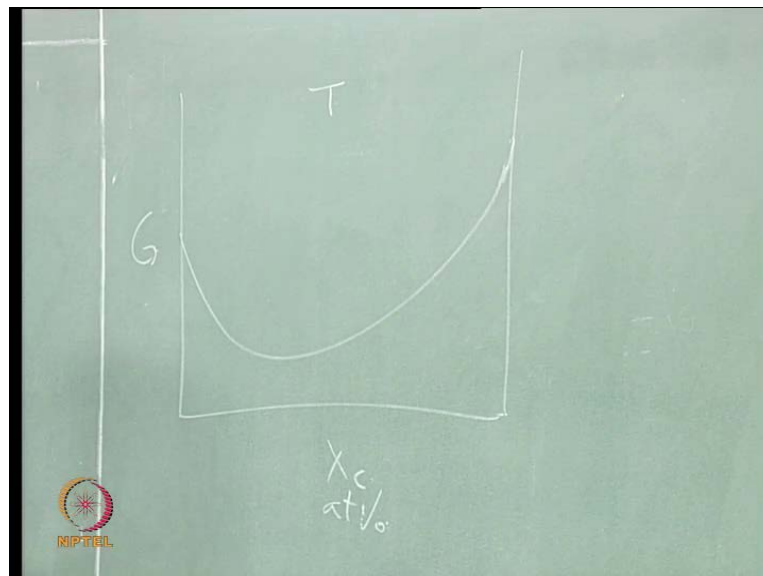


Let us look at that aspect. We are all now aware of this free energy composition diagrams, that you can draw something like this for a particular phase, and if you have another phase, let us call it as a beta phase, you can call something like this.

But one point that all of you should remember is, whenever I draw a free energy curve like this, it basically represents one issue that **that** this particular phase is existing over a wide range of composition. Usually, we use this kind of free energy curves for solid solutions or liquids, for that type of cases, where these phases exist over a range of composition. Whenever, you see a case, such as an intermetallic compound, where it exist over a very short range **particularly** for example, a line compound in principle, the free energy of a line compound in a free energy curve, let us say. I am talking of an iron carbon phase diagram and I have a compound there. What is the compound that we have in iron carbon phase diagram Fe₃C?

Fe₃C has a fixed composition, **isn't it** is it not? What is the composition of carbon content in Fe₃C 6.7, that is, the weight percent atomic percent? How much? 25 percent. So, 25 atomic percent and 6.7 weight percent it is a fixed composition. So, **if** I have to represent that particular phase in a free energy composition diagram.

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Let us say, I am talking about an iron carbon diagram at room temperature and I want to draw the free energy curves for the phases that are present at room temperature. At room

temperature, what are the phases that are present in an iron carbon diagram ferrite and cementite? That is it.

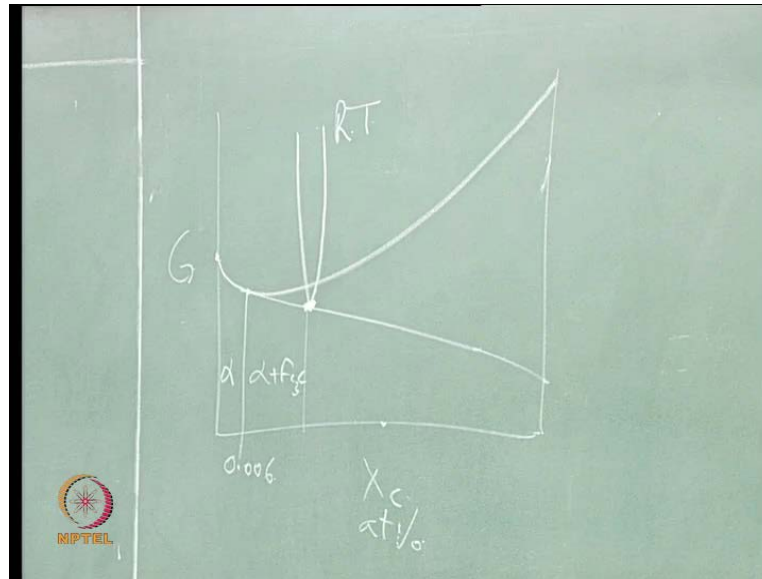
You have only two phases present. Whatever composition that you chose, you have only these two compositions and as a result, the ferrite phase we draw a free energy curve like this, whereas, cementite, what you do for cementite is? at If I am talking in terms of, let us say atomic percent here, when I say X of carbon mole fraction or atomic fraction of carbon. So, in most of our free energy diagrams, we usually use either a mole fraction or the atomic fraction, rather than the weight fraction.

You can always convert it into a weight fraction and show it. So, let us say if I am talking of atomic fraction. At 25 percent of atomic percent of carbon, you should have f e 3 C and in principle, the free energy of that f e 3 C if you represent on this G X diagram. G X diagram is always drawn at a fixed temperature, am I right? So, this is at a fixed temperature and of course, pressure is already fixed. So, at a fixed temperature and pressure, we are drawing this.

And at a fixed pressure and temperature, the free energy of f e 3 C is fixed. Because it is a fixed, it is like a pure metal. Like you have 1 point here for a pure a, and another point here for pure B. Similarly, f e 3 C is a single; it is almost treated as a single component. So, it has a fixed free energy at a particular temperature. So, we treat the whole f e 3 C as 1 entity and calculate what is the free energy of this intermetallic compound; as a function of pressure and temperature and at atmosphere pressure. We can calculate as a function of temperature and if you do that, it could turn out to be a nothing but a single dot 1 point on this free energy curve, on the free energy diagram.

So, that point can be above this or below this. But, because we know that, at in this particular phase diagram, that both of them coexist; almost from what level, what composition of carbon they start coexisting, ferrite point 0 0 to 5. Wrong. I am talking of room temperature point 0 0 6 onwards. So, that means, I should have, in fact, this is not a possibly the right way of drawing this.

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If you want to really show that, **and** then you should have at point 2.5. If I call this as a 50/50, and this is somewhere point 2.5, let us say, somewhere here, you should have a dot.

That is a free energy of cementite. It is 1 single point, it is like 1 single point for the pure metal. Pure iron and pure carbon on the other side, you will have 1 point and because showing 1 point is difficult, what we actually do is, we draw a very steep curve like this, just to indicate that at any composition on the left or the right of 25 percent of carbon. The Fe_3C phase is highly unstable; it cannot exist as a single phase.

So, **it is** free energy increases drastically on both **the** sides. That gives you an idea that yes, it is actually a line compound. In principle, this width is very **very** small, just for you to see it, I am showing it. Actually, it is a line compound. So, the width does not exist at all and now, if I draw a common tangent between the 2, between this tip of that curve and the alpha phase, I will be able to see that this is the composition at room temperature. If I am doing it at room temperature, this should correspond to 0.006. Of course, scale wise, it is not showing that way in this particular figure; but we can take it. If you actually calculate it, you would see that this common tangent, the tangent of the Fe_3C curve will touch the alpha curve at room temperature only at 0.006.

Otherwise, thermodynamics is not satisfying the phase diagram. You will see that it will touch at 0.006 and you can say that here is the alpha plus Fe_3C . Of course, we do not

know what is there on the other side because we actually do not talk about iron carbon diagram beyond the $Fe-3C$ because of the **un** instabilities that exist. And to the left of this, I can say you have a single phase alpha. Obviously, at any composition, if you chose less than 0.006, you have actually a single phase alpha.

In fact, we have a number of steels. I do not know how many of you are aware of a new type of steels that are coming up, which have very **very very** small amount of carbon. The first is steel having **the most** 2 point percent carbon. Have you heard of any other steel where you can have almost 30 p p m of carbon? They are called I f steels, interstitial free steels. I mean, **in** though the name is misnomer, it is not interstitial free, but extremely low interstitials. The carbon content and nitrogen content are kept at such a low value that they are 30 to 40 p p m and in fact, people even represent them as the y axis steels.

Because, if you want to locate that particular steel composition on the free energy on the phase diagram, actually, **know** if I draw an iron carbon phase diagram and I want to show point 2 percent carbon, and I can show it. I want to show 2 percent carbon. I show you, draw a vertical line and show it. How do I show a 30 p p m carbon content on the iron carbon diagram, because it actually goes into the vertical line that you have on the left which is nothing, but the pure iron line.

So. So, they are almost, call like that, and why do we make such steels? Can you tell me why should I go to such a low carbon content and in fact, if you want to really go to such low carbon content, what should you do if you remember when, how do we get a iron. All of you should know by now, how do you get iron, from where you get iron, from **from** reduction process, reduction of what to what iron oxide you reduce it in, what in a blast furnace for example, and what you end up in liquid iron. Is it going to be liquid iron simply, of course, with a lot of carbon? With a lot of carbon and what do you call that? We call it as pig iron.

And, that is not steel all of us know. And from there, you have to come to a steel level. And what do we do here? You oxidize the carbon; that carbon which is there in that iron you start as. So, you have to first reduce it and then again oxidize it. That is what you have a Heidi converters, Bessemer converter, all these things. So, you basically oxidize this and if you want to really oxidize from a 3.6 percent level to about 30 p p m level, you can imagine how much of oxidization that you need to do, of this carbon.

And in the process, obviously, when you are trying to oxidize, even some iron also can get oxidized. So, you get a lot of slag. So, you need to really go to, there are what are called special, what is called secondary steel making process, where you can actually reduce the carbon to a very **very** small extent and people are using that. Why do people **go** take all this trouble,, not really that, partly yes, but to have a high formability. This is you know, people want to make automobiles for example, with 1 single sheet so that you can simply stretch it the way you want.

So, the whole body instead of making it different **different** components and welding it. And another problem; while welding steel, you all know that the higher the carbon content, the more the problems is in welding. So, if you have a very low carbon content, even welding of steel also is easier. But more importantly, they want to make in one single go, as much as the body of the automobile. Particularly, these are used for automobiles Japan has come up. Now, even Tata steel is working hard towards that, which are higher steels; lot of work is going on.

But, the problem is, we know that when I reduce the carbon, I lose something. What is that, is lose the strength, that is the major sacrifice I am doing. So, how do I overcome that problem? That is where people are coming up with what are nano steels now. So, they are adding some elements into the iron which precipitate inside the iron. For example, copper. When you add to iron, copper does not dissolve. In iron copper **iron** **iron** copper phase diagram, if you see, copper does not dissolve into iron. In fact, though there is a peritectic, there is actually a submerge miscibility gap in that particular phase diagram.

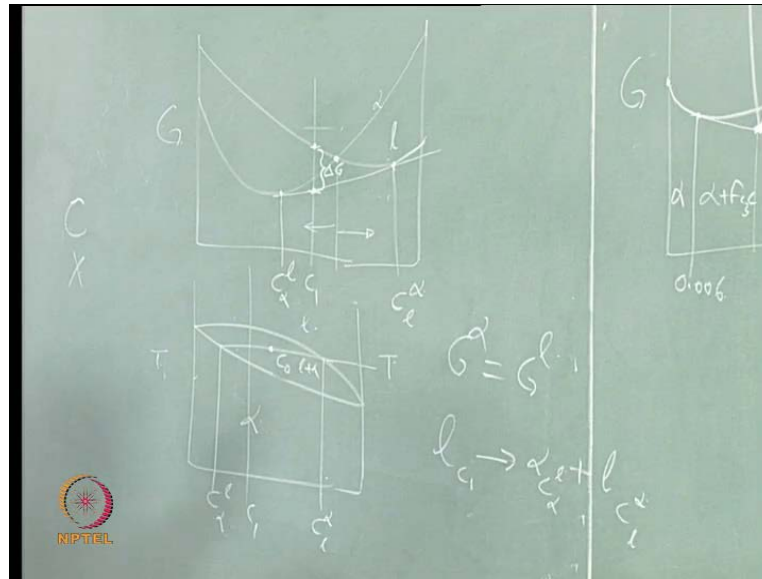
So, copper does not dissolve into iron so easily. So, copper actually precipitates as nano particles in iron and that gives you a high strength. A lot of people are working on that. In fact, **a such** a similar precipitation of a metal which is **a** dissimilar with iron, which does not dissolve with iron. People have been doing it very regularly earlier. Have you ever heard of any such element which is added to iron specifically to precipitate out as a pure metal and give you something, some good property? Have you ever read this? They add an element which does not dissolve, then pretty well know that it does not dissolve into iron.

But, they know that this precipitates out and gives you a good property. This is known for 30-40 years. No, that is all h s l a you are talking there; h s l a does not come niobium, does not come out as pure niobium. It forms carbide. We are talking of some element which comes out as a pure element. It does not form any carbides. It is the led. Have you heard of free cutting steels? If you have heard of free cutting steels; led is added to basically improve the machine ability. It acts almost like a solid lubricant. It is like graphite in **in** cast irons which acts as a kind of a lubricant. That is why, cast irons are with graphite, are easily machinable.

So, similarly, here led is basically added because you do not have graphite in steels. So, what is the equivalent of it? So the thought. Let us take a low melting metal and **in** interestingly, iron and led are immiscible. They do not mix with each other. So, this is where you know the alloy design we talk about. The excitements in metalogy come in that **of a** way; that how to really play with the phase diagrams and get what we want. So, similarly, people are using copper and we ourselves have done a lot of work where we had small amounts of copper which precipitates as nano particles and gives you extremely high strength; hardness levels of as high as 5 gigapascal. We have seen in this kind of materials, very high strength.

Anyway, so, that is what you do on a low carbon. It is an off shoot of **a** what we have been talking on the free energy, though, it has nothing to do with the free energy. Now, let us come back to this kind of a phase diagram and talk about instead of putting a beta there, put a liquid there.

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So, I am talking of a liquid and solid and when you see a free energy composition diagram like that, I can always talk about a common tangent, and talk about these two compositions. What are these two compositions? There is no, by nodal term, you have to use only when there is a miscibility gap. Please remember, there is no miscibility gap. Here, we are talking of a liquid and a solid and remember that we are drawing two free energy curves. Because there two different phases, two different structures, whenever you see, there is 1 single structure.

Have you ever seen, did we talk about pure iron phase diagram? For example, I **i** want you to take this as an assignment. Please, I want you to draw the free energy curves as a function of temperature for pure iron. What are the solid phases that you have? **alpha** delta and gamma iron; 3 irons you have. So, I want you to draw the free energy curves to show the transitions between alpha to gamma **gamma** to delta and delta to liquid.

So, that means, also draw the free energy curve for liquid and see what happens and that is where something which I just now mentioned, that structure should play a role there, and you will see that it becomes very important. Of course, we will also talk possibly in the next class; just to check those who have not been able to do. We will try to correct that, but I want you to work on this, this week end.

So, draw the free energy versus temperature for alpha iron, for gamma iron, for delta iron and for liquid iron and then see where they are intersecting of course, schematic though, and show these temperatures; where we see this phase stabilities changing from 1 phase to the other; and see if there is any difficulty that you find there; and you would find some difficulty, let us see how you will overcome that difficulty. Coming back to here, let us say a simple case as a **a** simple isomorphism. I should draw the other way because, this liquid is on this side.

So, let us say, we are talking at this temperature. At this temperature, if I draw this free energy composition diagram, these two points are nothing but the equilibrium composition of alpha and the equilibrium composition of liquid at that temperature. So, **we, in fact,** we say this is a C of alpha in equilibrium with liquid. This is how we write composition of alpha in equilibrium with liquid and this is C of liquid in equilibrium with alpha.

These terminologies have to be clear, so that we understand them well. As we go to eutectic and peritectic, you will see more interesting things coming up. So, you can see that I can talk about this as composition of alpha in equilibrium with liquid, composition of alpha in equilibrium, liquid in equilibrium with alpha and those compositions are these two compositions. This is the composition of, because, this is alpha, this is liquid, this is the composition of alpha in equilibrium with liquid, this is the composition of liquid in equilibrium with alpha.

Now, I said there is also a composition here, where there is an intersection. What does this intersection basically mean and what kind of **an** information that it gives you? We said that at this intersection, G of alpha is equal to G of liquid, am I right? And if that is the case, what is it going to happen if I am on either this side or on this side of the phase diagram? For example, at this temperature, on this phase diagram, this is a G X diagram and the phase diagram. If I want to locate this particular point, I think in 1 of the classes, we have seen that it usually falls between these 2 compositions, because, obviously, it has to fall between these compositions.

So, let us identify a particular composition, **call it as that we** call it as X naught or C naught, **call it as** because, we are talking in terms of composition as C. See, composition can be talked either as C or X; **sorry** I will keep on interchanging in this class may be

once in a while, but please forgive, you can either use X which is a mole fraction or C as a composition; but both are both are equally accepted in all the books. In different different books, people use different different terminologies.

So, if call this as C naught point, now what is it if I chose a composition on the left of this? What I am saying is, I am taking a liquid heated it to a high temperature, where it is completely liquid. Now, taking this liquid of that particular composition which I will call it as a C_1 composition, brought it to that particular temperature where we are talking about it, this is the temperature we are talking. Now, I have brought it to that temperature, what should happen to this liquid at that temperature? What does the phase diagram tell you? The phase diagram tells you that, that is the temperature, which is a two phase mixture.

It is a liquid plus alpha mixture; at this particular temperature, this whole region is liquid plus alpha. So, if I am taking a composition like this, is the C_1 composition for me, which is on the left side of the C naught and I have heated to this temperature, brought it to this temperature. At that temperature, in principle, liquid is not stable as a single phase liquid and you can easily see it in the free energy composition diagram. Also, if I look at this particular, what is the free energy of the liquid? Free energy of the liquid, of that composition is given by this point, am I right? Because, this is the liquid free energy curve.

So, at any composition, I can get the free energy of that particular liquid by choosing that particular point. So, free energy of liquid of C_1 composition is this, is not stable because the two phase mixture having a two phase free energy, as that is more stable than the liquid. So, there is a driving force for the liquid to become a two phase mixture. So, liquid having C_1 composition would split to alpha, having C_{α} liquid composition plus liquid having C liquid alpha composition, which are these two compositions and for that, you have a driving force, which is given by this particular quantity. This is what the Δg is.

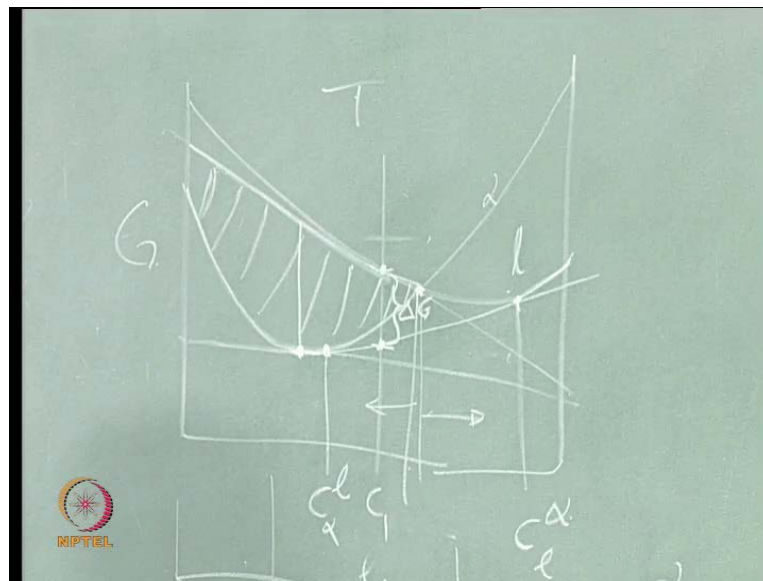
That is why, liquid does not remain as liquid. The moment I bring the liquid to that temperature, it will split into alpha plus liquid. But if you carefully observe, for this split to happen, you need something to happen; why because, here, this is a liquid of C_1 composition, this is alpha C_{α} composition, this is the liquid of C liquid composition.

All the three are three different compositions; that means, from a liquid of C_1 composition, now you have a solid with some other composition and a liquid with some other composition **to** has to come out.

This means, you can see from this alloy, this composition and this composition should come out. That means, you need a lot of diffusion to happen, you need alpha to first nucleate of it and the nucleate **the** alpha will have some other composition. Again, how do I know alpha will nucleate? I simply draw a tangent. The moment I draw a tangent, I can easily see **that** what is the alpha that can nucleate out of this liquid; I can easily. Wherever this tangent intersects the alpha curve, it is intersecting somewhere here, let us say, very close to C_{naught} . Let us not bother about it.

So, it is intersecting somewhere here. On the right side of this, the free energy of alpha is higher than this tangent. So, no alpha of that composition can nucleate out of this liquid because, the free energy is higher on the right side of this intersection

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If I look at it, the whole alpha curve is below the tangent. So, as a result, all this compositions in principle, this whole domain can, any composition can nucleate. But, the composition that nucleates will be the one which has the highest driving force usually. So that, **they** it has a greater tendency to form and as a result, you would see some composition will come out of it.

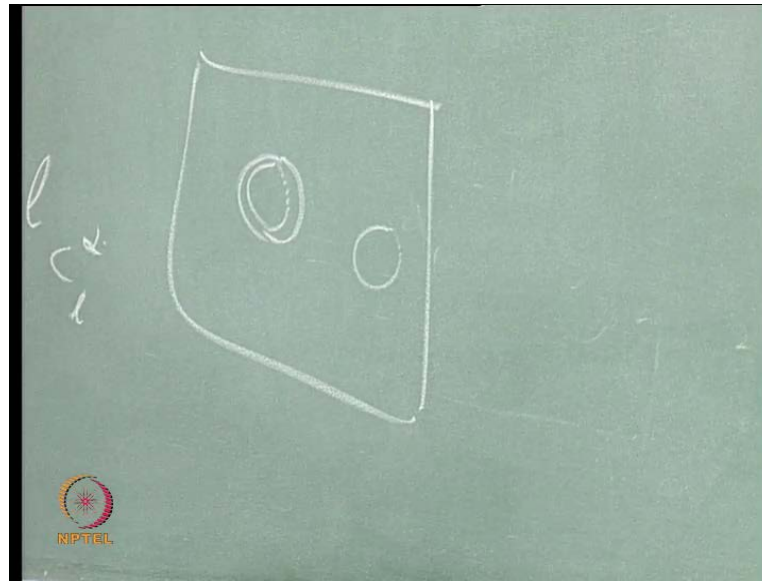
Let us not bother which composition comes out of it. Usually, whatever composition that comes out it shifts again to the equilibrium composition which is possible. For example, that is also interesting, now that I am saying, let us say, a case that this particular composition has the highest driving force. But interestingly, that alpha cannot be in equilibrium with the liquid, with any liquid because this composition, if I take it, I cannot draw a common tangent between this alpha composition, with any liquid. Because, if I draw a tangent, that tangent will be, you know, below the liquid curve; you can see that.

It is not possible for that, I can draw. So, what happens is, this alpha which is coming out of the liquid, because it is not stable, because it has to remain in the liquid environment and because it cannot remain stable in the liquid environment, it changes its composition slightly such that comes to a composition which can coexist with the liquid of some other composition; whatever is possible under equilibrium conditions at that temperature. That is why there will be a small change in the alpha composition that would occur.

So that now a new alpha composition will come out of the initial nucleus, initial nucleation will be this. But, that nucleation cannot be in equilibrium with **with** the liquid. So, some more rearrangement of atoms will occur so that the nucleus composition will change to this value so that, that particular alpha can be in equilibrium with liquid. But now, with what composition it can be in equilibrium? It cannot be in equilibrium with the C 1 with which I have started. So, it will have **a** some other composition. **So, this is what**. In the last class also, we have seen that when an alpha having a lower B content comes out of the liquid, there we talked about alpha and alpha one, the same argument you can give here.

From a liquid, when an alpha of a lower B content comes out of it, the surrounding liquid composition will change.

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So, for example, if I take this kind of a liquid reservoir and a small alpha is coming out of it, and because this alpha has lower B content, then the liquid which is surrounding that will have, obviously, more B content. And that is why, you will see the equilibrium will be with that liquid; not with the liquid which is far away from it. There is no equilibrium between this alpha and the liquid which is far away; but **with the** this is what we call **it** as local equilibrium.

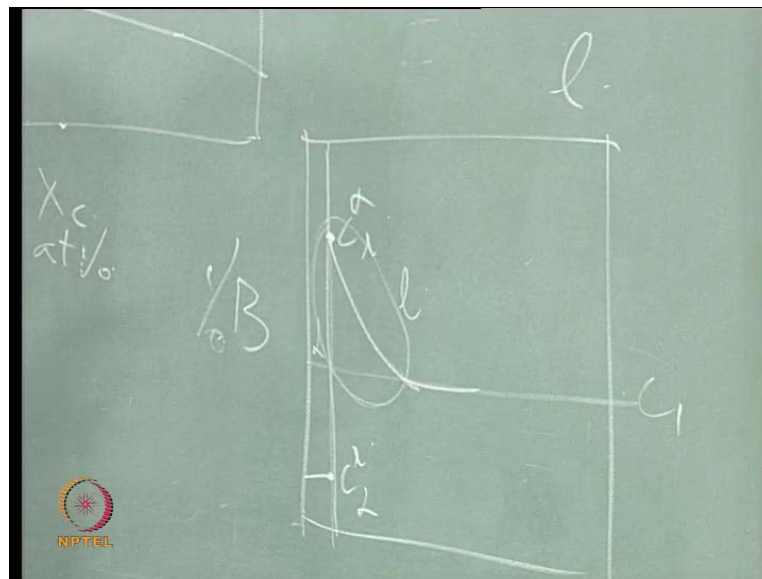
So, whenever a nucleation occurs, there **will** has to be a local equilibrium to be established. If there is no local equilibrium, **they** that particular phase, that nucleating out of any phase, any parent phase cannot be stable. For it to be stable, it has to establish a local equilibrium with the parent phase and the way it can establish, is by changing **a** the compositions locally **domain**. It can be a even a monatomic layer; very thin 1 nano meter or even **a** less than **a** 1 nano meter layer of liquid **changes its**. And in a 1 nano meter thin layer of liquid, atomic **the** composition change can **be** easily happen at that temperature. Temperatures are high enough; we are not talking of absolute 0 or anything like that.

So, because of which, you will see that there will be an equilibrium. Yeah, **the** now **now** the remaining liquid that is there, has a different composition and **this is** this is happening at the beginning of the nucleation. And that liquid, because it cannot remain, because C liquid of C 1 composition cannot remain at that temperature, you see at this temperature, if I bring this liquid as C1 composition to this temperature, liquid cannot remain as single

phase liquid. So, what happens is, slowly now like what we have seen in the last class, there will be a diffusion of B atoms from this liquid towards that and you would see that because of the diffusion, slowly liquid composition starts changing and becomes that of this composition.

And amount of alpha will slowly increase from the initial stage such that finally, you will have alpha of this composition of certain volume fraction, certain weight fraction. Similarly, liquid of that composition, if you draw the same composition profile like what we have done in the last class, I can draw that composition profile for you once again if you want.

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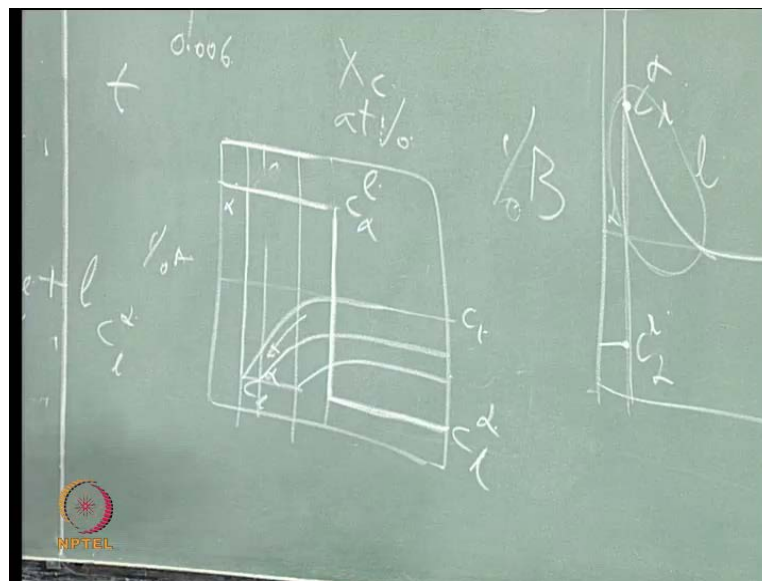
For example, I am starting a situation like this. Initially, everything is liquid. You have let us say, a small alpha that is nucleated. I am talking of alpha, initially everything is liquid, that is, this is the composition C_1 .

Now, the alpha that is nucleated has what composition; has a much lower composition than C_1 . You can see alpha has a lower composition than C_1 . So, as a result, the liquid in equilibrium with the alpha will have a higher composition. So, that is why, at the interphase, this is the interphase between alpha, and liquid at the interphase, you will have two compositions. 1, the composition of alpha, another, the compositions of liquid. This is what we call **it** as C alpha liquid. This is what we call **it** as C liquid alpha and this is C_1 .

Now, you see that there is a gradient and in fact, this is what we call **it is** as a diffusion zone. The chemical potential **of** at this particular, the chemical potential of alpha of this composition, chemical potential of liquid of that composition, will be equal. That is **what** is the meaning of common tangent. So, that is why they are in equilibrium, other, they will not be. So, alpha of this composition cannot be in equilibrium with this because, chemical potentials are not the same; but alpha can be in equilibrium with liquid of that composition because, chemical potentials are equal.

So, now, they will be in equilibrium. Now, the only way it can happen is the C1 composition has to slowly change. The only way the C 1 composition changes is, it keeps on giving more and more atoms to the alpha. How does it give this is in terms of B percentage B. If I draw the same thing in terms of percentage, **a** you would see that it is a reverse kind of a trend. So, a atoms **in the** in the C 1 are higher than the a atoms here. So, I will actually see that there is a gradient from **the** this one. Let me draw that also for you.

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If I draw as a function of a, now you see again, I draw this. Now you see that this is the situation, this is the C 1 composition and you see this percentage a in alpha is higher. C alpha liquid has a higher a content than C liquid alpha.

And the C 1 composition. You see C 1 composition is here and C liquid composition is this side. So, it has very less amount of a, when compared to C liquid **C liquid**. So, you

can see a atoms will start diffusing from here to here. So, more and more alpha **alpha** needs a atoms, because, alpha is a rich phase. For it to grow, you need a atoms. In fact, you will see this becomes a problem, when you are talking of eutectic. We will talk about it; very interesting problem. For example, here in a eutectic, a liquid gives alpha plus beta liquid is in contact with alpha and beta.

Alpha is a rich phase, beta is a B rich phase. How is that liquid **is** able to separately give a atoms to alpha and B atoms to beta so that both of them can go grow together? That is **what is** a lamellar growth. If both of them have to grow together, you need to see some mechanism by which liquid is a know. Somehow, a **care** carefully giving a atoms to alpha and B atoms to beta, **is again**. This can be understood from the thermodynamics. We will see it when we come to eutectics. At the moment, we are only talking about isomorphous; let us stick to that. So, you can see that a atoms, though B atoms, there is a gradient in this direction, a atoms there is a gradient in this direction.

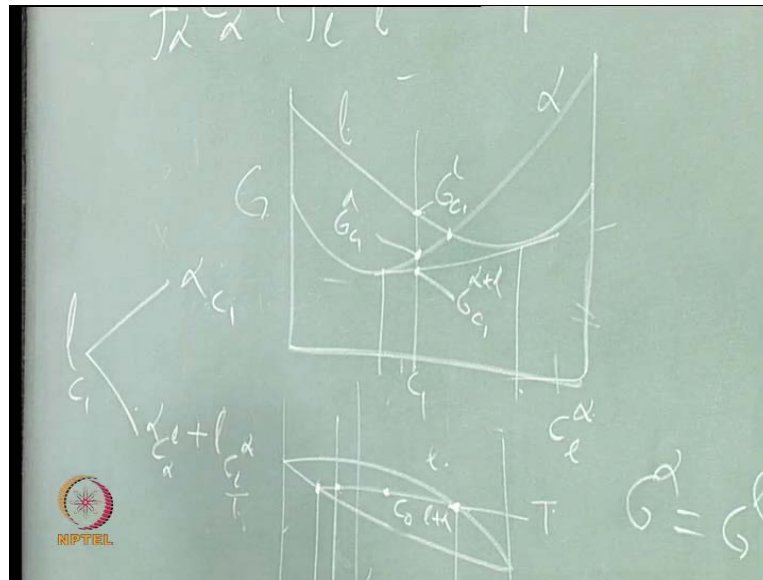
So, a atoms gets supplied from C 1 and in the process, what happens, the **the** a atoms in the liquid comes down. So, you will see **at** as this grows to next level like this, you would see that composition shifts like this. As alpha grows much more, then, you would see this composition remains the same. This is the C 1 alpha that is fixed at that temperature. Here, we are talking only as a function of time. Now, temperature is fixed, I have brought the liquid to that temperature, and now as a function of time, what is happening as a function of time, alpha will grow. And in the process, the composition of liquid which is far away from that of the alpha also starts coming down, because, it is supplying more and more a atoms.

As it supplies a atoms, a atoms have to come down inside that. So, it is like a reservoir supplying the a atoms. So, slowing the a content in the liquid comes down to an extent, at that some stage, it will it will come to, like that. So, you will have a **chem**. The composition profile exactly becoming like that, then, you will see that the remaining liquid, all the liquid will have that composition, and the remaining alpha will have this composition, which is what is decided like this. I am sorry, here I should call it as this **composition**. This is **the** what we have called **it** as C alpha liquid.

This is C alpha liquid and this is C liquid alpha, and at that particular condition, when this whole process has been finished, we say now, the whole equilibrium has been

established at that composition, at that condition, after whatever time T that it takes for that particular process. After that time T , if I now look at what is the volume fraction of alpha and the volume fraction of liquid or weight fraction of alpha and weight fraction of liquid.

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And if do this, the weight fraction of alpha multiplied by C_{α} plus weight fraction of liquid multiplied by C_{β} should become equal to C_1 . It will be equal to C_1 .

So, you will have some amount of alpha, some amount of liquid in such a way that this multiplication will give me this. And if I change this C_1 , what would happen? The amounts of these two will change; but these two will not change. If I take instead of this alloy, if I take this alloy, **this alloy** bring it to the same temperature. These two compositions are fixed for that temperature, what will happen is only these two will change such that, this mass balance is maintained and this is how the whole solidification takes place.

Now, we are actually not looking at this, **is** something which is very easily known. We are trying to see something which is not that easily known. That is what is a new field that has emerged, that is what we are going to see. **as** If I now draw this once again these 2 compositions, now we are talking of this. Now again, I draw your C_1 composition for you. Look at this C_1 composition once again. What is said just now is that, this is the

free energy of the liquid of C₁ composition, and because it is higher than that of the free energy of the two phase mixture, which is this, that there is a driving force for the liquid to become a two phase mixture.

But, at the same time if you carefully observe the free energy composition diagram, there is something else there, that there is an alpha. If I look at what is the free energy of alpha of C₁ composition, where do I locate it? Alpha, this is alpha of curve, this is a liquid curve. If I look at what is the free energy of alpha having C₁ composition, where does that fall? Between those two which is this point. That is the free energy of alpha, having the same composition as C₁.

So, this is, I call it as G_{liquid} of C₁. This, I can call it as G_{alpha} C₁. What is this then? This is G_{alpha} plus liquid, having an overall composition of C₁, am I **right**? So, there are, you see, three points there and what is the meaning of this? It means, the liquid has a chance to, liquid has two choices now. 1 liquid of C₁ composition can become alpha of C₁ composition, or it can become alpha of C_{alpha} liquid plus liquid of C_{liquid} alpha. Why because, liquid of C₁ composition has a higher free energy than both of them, am I right? It is higher free energy than this and also this.

So, this liquid has two choices now, either to do this, to go from this level to this level by which it is decreasing its free energy, or it goes from here to here. Now, which path the liquid will choose **which path the liquid chooses** depends on your process. If I am cooling a liquid very fast, let us say, a non equilibrium processing and in that condition, the time available is very small. Let us say then, this process, for it to take place, that is a second path for it to occur. You need a lot of diffusion, you need a long range diffusion. In fact, diffusion, there are two types of diffusion, some of you might have heard of. For example, if pure metal, liquid **liquid** aluminum changes to solid aluminum or take an example of pure iron changing from an fcc structure to a bcc structure.

When I am cooling from gamma iron becoming an alpha iron, all these transformations **are all** need short range diffusion. Why, it is only 1 structure changing to another structure. So, structural changes from 1 structure to another structure, 1 unit cell changes to another, fcc unit cell becomes a bcc unit cell. That means, atoms which are sitting now at the moment, at the phase centered positions, will simply move to body centered

positions. That means, what is the distance by which the atoms are moving? They are moving within a unit cell distance.

The actual distance by which atoms move does not actually cross more than 1 or 2 unit cells. This is what we call **it** as short range diffusion **the** wherever there is a compositional change. For example, precipitation super saturated solid solution of aluminum copper alloy, precipitating, what is called a theta phase or a G p zones, where the composition of the precipitate is entirely different from that of that. So, that needs long range diffusion, both the nucleation and growth of this. I am talking of the whole process, both of them need, actually nucleation process does not need a long range diffusion.

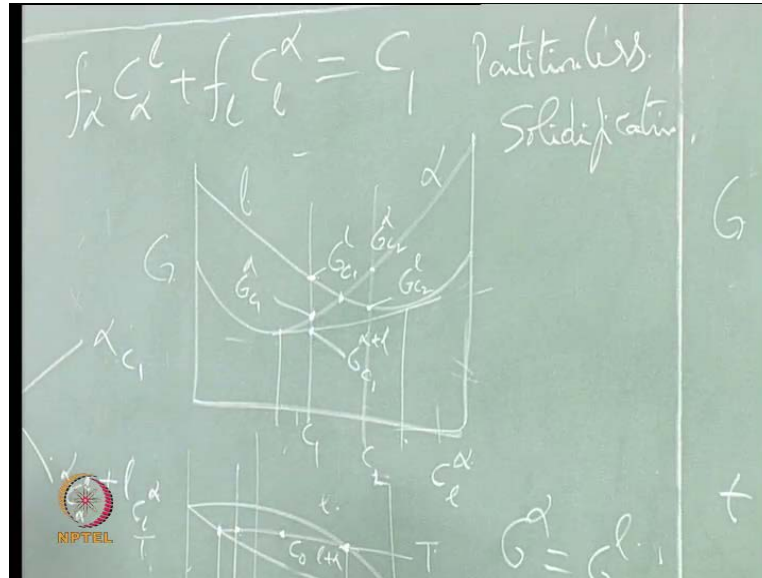
Nucleation process occurs in a very small range though. Of course, they are also many times the nucleus size, **I is** at least about hundred atoms size. There, you need diffusion over the whole thing. So, this is what we call **it** as long range diffusion and when you have a long range diffusion, it needs more time, a short range diffusion does not. You also have **a** another type of process. For example, think of the case as a austenite giving you martensite. What is that type? We call it as diffusion less. There is no diffusion there, neither short range nor long range and interestingly, **there** also what is happening is only structural change. One structure is becoming another structure; whether it is B C T or B C c, that is the another problem.

All martensites are not B C T, all steel martensite are not B C T. For example, there can be iron base alloys martensites which are not B C T, do you know this? For example, pure iron also become martensite and pure iron martensite is not B C T, it is B C c when we come to martensite; we will talk about it. If you take iron nickel alloy **iron nickel alloy** also, you go to austenite quenching. It becomes martensite, is again a B C c. B C T comes because of something else; because of the presence of carbon. **presence of carbon** We will see it later, when we talk about martensite any way. So, that is where you have to mix up thermodynamics with something else. **When, I teach you all this things.**

So, the interesting thing is, because this is difficult whenever I do a non equilibrium processing, the liquid will tend to do this. In this process, what is happening? Liquid is changing to alpha of the same composition. So, it does not need any long range diffusion. Only a structure has to change; from the liquid structure to whatever is the

alpha structure, it may be f C c, it may be B C c, whatever it is. **and** This is what is called polymorphous transformation or partition less solidification.

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We call it as partition less solidification. Solidification is occurring, but there is not partitioning of atoms. Partitioning means, the atoms being distributed to 2 phases; that is not happening. So, the compositions are remaining the same and the general term for this is called polymorphous transformation, because, such a transformation can occur in even solid state. Just now I told you, if it is happening in pure metals, we call it as allotropic transition. For example, pure iron going from f C c to B C c, we do not call it as polymorphous transition; but, if it is happening in alloys, for example, if you have heard of beta brass are **in** there, **are** you know alpha beta brasses, where if you take a alpha beta brass mixture and cool it very rapidly.

This phase, which is a high temperature phase, is a beta phase transforms to a low temperature phase, which is alpha phase, without any change in the composition and at the same time, not by a martensitic transformation. **and** That kind of transformations are called massive transformations. **This** We will also possibly come across that later, as we talk about more and more phase transformations.

So, these are what are called polymorphous transformation. That means, only structure is changing, composition is not changing. You can also have cases where the composition and structure both change or only composition changes, structure does not change. Can

you tell me that case where composition changes, but structure does not change? Any example where structure does not change, but compositions change? Yes? Answer. We have done this, to just give you a clue, we have done it yesterday. A transformation that we talked yesterday is that spinodal or even a miscibility gap. A simple bimodal 1 alpha having a **some** structure, changes to alpha 1 plus alpha 2, with two different compositions, but the structure remaining the same.

So, this kind of binodal transition miscibility gap, whatever decomposition we call, that is why we call such things as decomposition. It is simple; 1 thing decomposing into 2 with two different decompositions. Anyway, come back. So, this is what is called polymorphous. Why this becomes important is, because, on this side of the phase diagram, what I have said just now cannot happen. Why because, now on this side of the free energy composition diagram on the right side of the C naught point, if I look at it, liquid has this free energy.

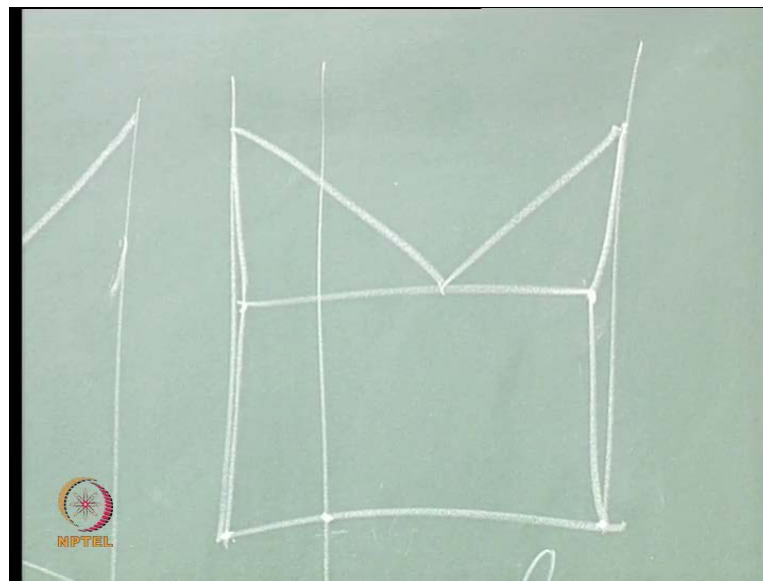
Alpha having **the** this, if I call it as C 2 composition liquid of C 2, this is the G of liquid of C 2 composition, this is the G of alpha of C 2 composition. G of alpha of C 2 composition is higher than that of G of alpha liquid of C 2 composition. There is no chance for the liquid to transform to alpha of the same composition because, there is an increase in the free energy there whereas, it can split into 2 phase structure, which is this. The two phase structure still has a lower free energy.

So, that means, on the right side of this thing, polymorphous transformation is not possible, or partition less solidification is not possible. That means, if I draw this particular point, I call this as now, a C naught point on the **right** side. If I chose any alloy of this composition, I cannot have a partition less solidification. You may say, Sir, what is the advantage of a partition less solidification? You just hold on for **a** 1 or 2 days. When we are going to talk about eutectics, I will show you **what is** the advantage of it.

One thing is, you can produce alloys with compositions which are much more than solute content. Then, what is by equilibrium allowed? For example, under the normal conditions, if I take a liquid, I will solidify under slow cooling conditions, what you see is that liquid will split into two phases, and finally, you would see the alpha would have this composition, liquid will have that composition and if I cool it very rapidly, I can retain whatever is solute content that is there inside the liquid.

Of course, in isomorphous, that is not important because, finally, when the solidification is taking place, the alpha will have the same composition as that of the liquid. Of course, it is. You will have what is called a non equilibrium cooling coring; all these things are going to be there. So, considering the coring is going to be there, you have actually compositional differences in any dendrite you have that coring. But, here, we are talking of a solidification where, absolutely there is no coring and you have a composition of the same as that of the liquid coming out, and particularly if I look at compositions like this, in eutectic kind of cases.

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Let us take a case of, like this. If I take this alloy in a normal condition, this alloy when it is solidified and brought to room temperature, you will have the alpha of this composition; beta has this composition is it not? And similarly, if I just come out of the eutectic, at the end of eutectic, alpha will have this composition, beta will have this composition. Now, if I do partition less solidification, what I have is the liquid, the alpha that comes out. The liquid will have the same composition **of that** of this.

So that, now at room temperature, I have alpha having this much of B content than what I can have under normal equilibrium conditions. That can give you an advantage that you can do precipitation. **Later, things like that,** we will talk about it in the next class.