Advanced Metallurgical Thermodynamics
Prof. B.S.Murty
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture No. #11
Eutectic Solidification, Glass Formation

Activation energy, that is where you are missing, that any nucleation event and a growth event needs diffusion; this aspect, if you miss out, we will think that the whole nucleation is just driving force related, is it not? That is the reason why the whole of TTT diagrams come. Why do you have a TTT diagram, which has a C shape? The C shape of the TTT diagram comes from the diffusion problem, is it not?

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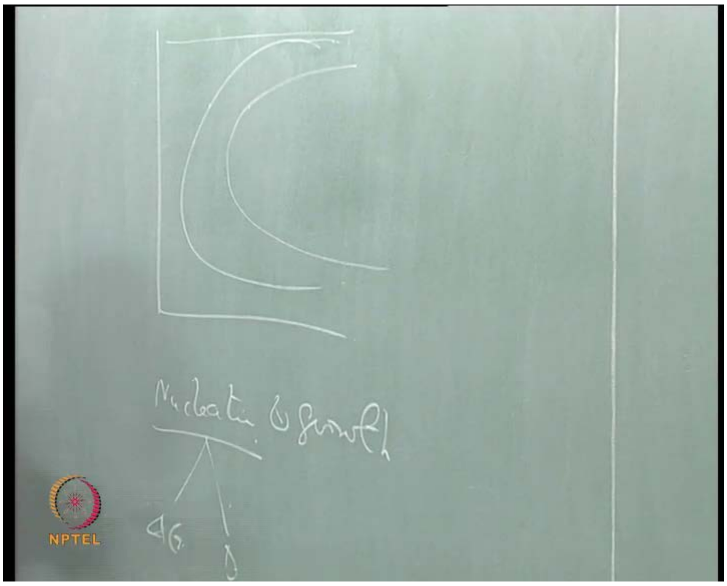

If you remember, this C shape, which for example, we talk about an austenite to pearlite transformation, why is this shape? This is what we call it start of transformation, this is what we call it as an end of transformation; so, that means, this is nucleation; this is the end of growth. Why is this, it has a C shape? Basically, because the nucleation growth, and growth, even for that matter nucleation itself, is a combination of two - one the driving force delta G, the delta G is important and diffusivity D is important.

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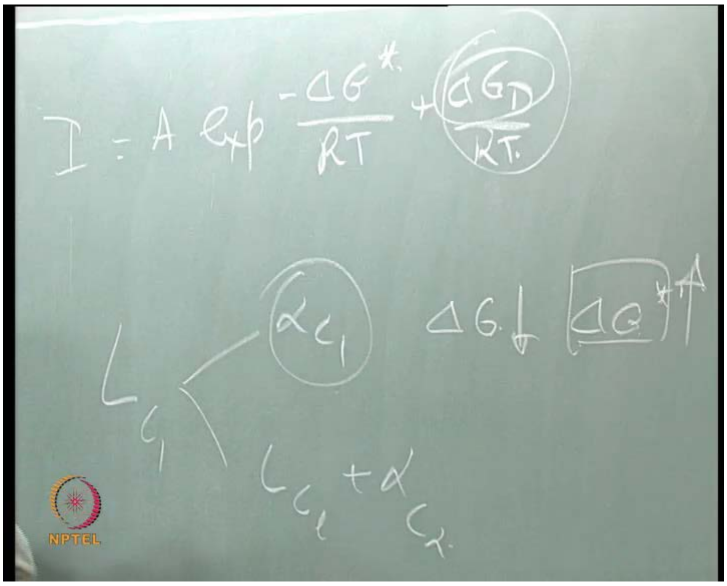

In fact, if you go a little deeper - nucleation kinetics, unfortunately we are not really dealing with nucleation kinetics; you remember, you have an expression like this; you have an expression like that; this part you people are forgetting; that is very very important part (Refer Slide Time: 01:50). Please read Reed Hill, Physical Metallurgy Reed Hill nucleation, there is wonderful chapter in Reed Hill; I thought all of you should have read it at B.Tech level, if not please go through that chapter, and this is very very crucial. And if you look at only this part, then you are right; you are right, that as I keep on going to higher and higher under cooling, I get higher and higher driving force, if the driving force is higher in principle, my activation energy should be lower.

So, as the same thing when we are talking about liquid going to single phase alpha, or liquid going to two phase mixture, we are assuming that diffusion does not play a role. But we know that, if liquid has to go to a two phase mixture it needs long range diffusion, but if liquid goes to a single phase structure of the same composition, then it does not need long range diffusion, it needs only short range diffusion.

And short range diffusion always needs lesser activation barrier; that means this part is smaller for short range diffusion. This part is going to be larger, this particularly this is going to be larger for long range diffusion, and that is the reason why this dominates, you are right, this is go, this is also there, delta G star is going to be higher, if the delta G is going to be lower. If the driving force, so if I look at liquid going, liquid of some particular composition

C 1 going to alpha of C 1, or liquid going to liquid of C L, plus alpha of C, alpha composition. If this delta G is smaller than, if this is smaller, than delta G star is larger here, this is delta G star only for the nucleus that is it. So, this is what is… In fact, if you carefully look at it, what is delta G star? It is delta G for R star, so actually it is speaking, what is the change in free energy, when a liquid goes to a solid, with the solid having a size of R star; that is what we call it as delta G star, but because that it is a higher we call it as an activation energy.

The overall activation energy for nucleation, you have to consider a combination of these two, is this clear? So, as a result, we need to consider that aspect, and definitely this transformation will have a lower activation barrier. This is even true when we come to solid state transformations we will see, why is that when I take a let us say edge hardening, or precipitation hardening, you take a aluminum copper standard example, in an aluminum copper when we are doing precipitation what comes out first, G p zones we say.

We do not, what is the stable state there, theta is the stable state, so definitely the delta G, the driving force for the super saturation to transform to theta must be the highest, because that is the equilibrium state, but it does not happen. Even you see in cases of steels, when you take a steel marten site and temper the marten site, I do not know how many of you remember, what is the phase that comes out during tempering? It is epsilon carbide, it is not the cementite, which comes out, why is that; obviously, epsilon carbide does not stay, if you do the tempering at higher temperature, or for longer times this epsilon carbide vanishes.

Similarly, G p zones vanish, if you do aging for a longer time, G p zones turn to theta double prime, then theta prime then finally, the theta, what does that mean; that means, all these initial stages are only transient phases, transient metastable phases, and the stable phase is that theta, similarly in case of steel, it is a cementite which is the stable state, but cementite is not able to come, we will see when we come to solid state.

What are the further complications that you get, for precipitation are future phase transformation in case of liquid to solid, which is what we are now dealing with, in a liquid to solid, there is only one barrier for transformation, what is that barrier? It is the surface energy, and when you talk about solid state you get additional barrier, that is the strain energy we will talk about that, that is when you realize, why you need this to come out, we will talk about precipitation later.

So, you need to understand that, it is just not the driving force that always leads to, so when we come to, for example, we will definitely talk about this later. When we going to talk about solid state transformations, and go in a later little detail on that, at the moment we will continue with our liquid to solid, that we are talking about. Yes, that is what I was telling; delta G star is the activation energy for the nucleus to form, without considering the diffusion, even for the nucleus. What is the nucleus? Nucleus is nothing but, a cluster of atoms with an R star size, I am right; this is what we call it as a nucleus. And for a cluster of atoms of R star size to evolve, from the liquid, you need atoms to move, atoms to come together form the R star, this atoms to come together to form R star, you need some diffusion to required, and that is delta G D, that is what I am telling.

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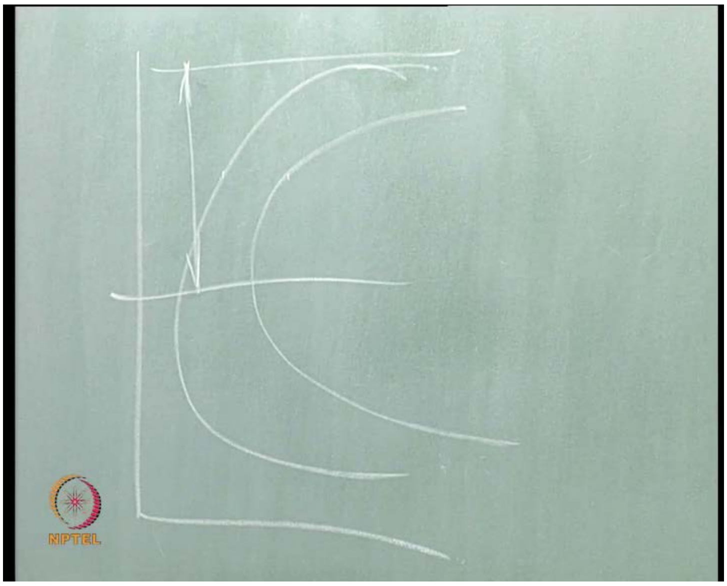

So, when I say delta T is more you get fine grains, we are always making an assumption, that we are in this domain, there is an inherent assumption, which one has to very very careful, that I am in this domain, if I am in this domain as I keep on increasing the delta T; that means cooling rate, if I am increasing the cooling rate, I am increasing the under cooling, if I am increasing the under cooling, I m increasing the delta G.

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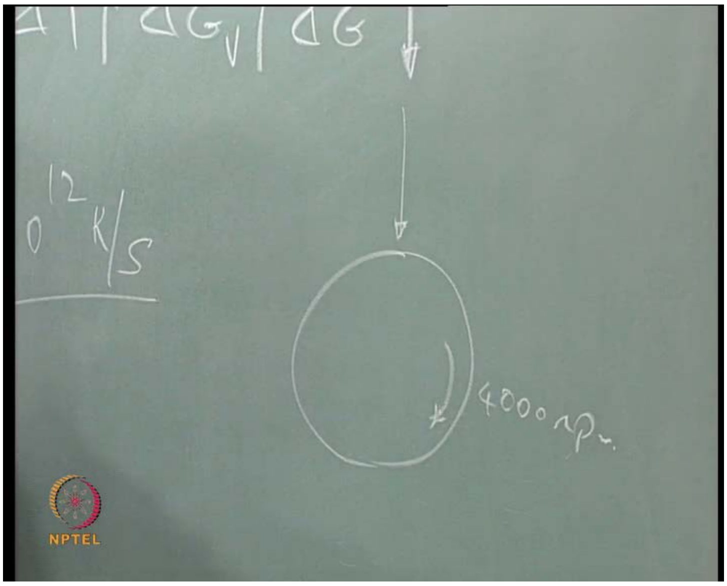

So, you can see, the cooling rate is proportional to delta T, which is proportional to delta G, and as a result delta G star decreases, and the temperature here in this domain is high enough for the delta G D not to be really dominating, so because we are still not in a low temperature domain, for the diffusion to start dominating, so diffusion still can occur because we are at high temperatures.

And as a result, it is this which now decides, what is your nucleation rate, not the delta G D which decide the nucleation rate, but it is delta G star which decides the nucleation rate in this portion. And that is the reason why you will see that finer grain size, and most of the cases the cooling rates that is we adopt in when I talk about sand mould, or a permanent mould, or a water cool copper mould, there the under cooling that we are talking are not really the kind of under cooling that can really bring, they are liquid below this domain. If you really want to get the under cooling below that domain, you need to use much higher cooling rates; that is where you will always see, the diffusion dominates and that is the reason why you will actually see, even glasses forming. The fact that a glass forms from a liquid is an indication that nucleation is not able to happen, the atoms are not able to come together to form that nucleus, and the nucleus is not able to grow, if that can happen then why will glass come out.

In fact, long back turn bull has made a profound statement, that every liquid would like to become a glass, unless crystallization intervenes, it is the crystallization which is coming in the way, otherwise liquid likes to become a glass, because liquid and glass are of similar structure, nothing need to change for a liquid to become a glass, but it is crystal formation which is commonly observed, why? Because in most of the metals and alloys, the crystal structures being is so simple that they can easily nucleate, the atoms coming together forming fcc cluster or a bcc cluster is easy, but if your cooling rate is so high that, even that cluster is not able to come together, performing of a nucleus, even you do not see, pure metals also people have seen glasses formation, pure silicon people have quenched at very high rate, and they have seen it becomes a glass, pure nickel people have shown at has high rates of 10 power 12.

Do you know, how do we reach this kind of cooling rates, did we talk any time? 10 power 6 is what we get when we do, what is called melt spinning or gun quenching, how do reach this kind of cooling rates? That is what I said spinning is the one, were we talked about it, where you take a wheel, which rotates certain speed like 3000, 4000 rpm and you pour the liquid metal on this, and then the moment droplet falls, because it is spinning, it is like spinning.

So, because this wheel is spinning, it pulls this droplet along with the wheel, so the droplet sticks to the wheel and then gets pulled, as a result the droplets converted into like a sheet of metal, it is like a rolling without a second roll there. So, as a result, you gets flakes every droplet becomes a flake, and if you have a continuous flow of liquid in principle, you can have a continuous sheet of people have produced, even up to almost like a one feet width; I mean almost like a continuous casting, excepting that, in a continuous casting you almost have a two wheels, it comes out as a slab, the liquid metal goes and then it is like rolling, here there is no such kind of rolling because there is no second wheel on top of it, it is the liquid only thing is only you control the flow rate to liquid, and control the speed of this in such a way, that it is comes out as a continuous ribbons. And people have made kilometers of ribbons like this; a particular type of alloy which is hand based metallic glass, where large numbers of people have worked on it. So, here we get cooling rates of order of 10 to power of 6 and 10 to power 12, anybody knows? Laser, if you use laser for example, have you heard of picoseconds laser? No, picoseconds laser, nanosecond laser, pulsed lasers.

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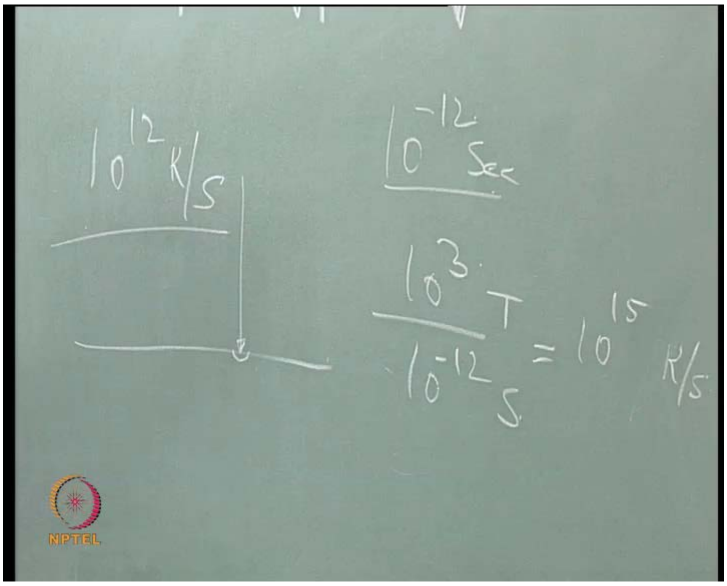

So, in pulsed laser, a picoseconds laser basically means, 10 to the power minus 12 seconds it is active; so, imagine a solid surface on which you have a laser which falls on it, and it is active only for such a short time, within that time the laser will melt that surface very small volume, may be few micro meters of volumes, and then immediately it solidifies. And if you assumes that, this melting and solidification is happening within this particular period, it melts, of course there will be a time lag, so actually it may not happen exactly within the time, but if you assume that, if is melts and take think of aluminum being melted let say, and aluminum if it is melted, what is the temperature to which is goes to approximately let us say 1000 kelvin and then from 1000 kelvin, it cools back within that time.

Because, the laser is active only that period and it is shut off, so that is what a pulsed laser is. So, then within that period again it has to cool back, and how does it cool? The whole metal itself acts as a quenchant, in a in a in a slab of a metal only a few millimeters, few micrometer cubes of a region is getting actually melted, a small pool is melted, so rest of the metals quenches that particular liquid.

So, you get the liquid brought back from 1000 degrees to room temperature within this particular period, and if you consider that, if you think that 10 to the power 3 is the is the temperature change that is taking place, 10 to the power minus 12 is the time, this is the T, and this the time, and you would see the ratio gives you 10 to the power 15 kelvin per second.

In principle in principle, theoretically, one can get this, of course practically it is difficult, that is why I said 10 to the power 12, if you use a picoseconds laser, because there will be a small time difference, it has to heat and then cool. If you consider a small difference, people have been able to achieve this cooling rates, this much temperature difference in this much time, time temperature divided by time is what is the cooling rate.

So, even principle you can get the cooling rates and with that people have shown that even pure nickel can be made into a glass, people have made glasses like that; that means, your temperature, your time available is so short for the atoms to form an R star; it does not mean that clusters do not exist in the liquid, clusters are there, but their size is not equivalent to an R star, they are like an embryos. So, they are not able reach the R star size, and if they do not reach the R star size, obviously you will not have a nucleation, so that is what is the whole concept of the glass formation and in any way we talk about the glass formation later, and this aspect also we will talk about it, when we are going talk about glass formation.

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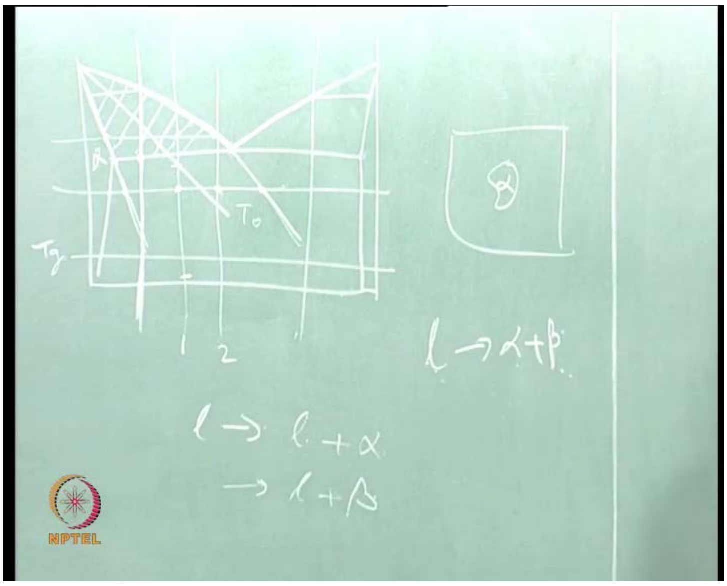

Let us continue where we have left last class; in the last class, we were talking about the T naught curve, and we talk about a curve such as T naught, and we said any alloy that we choose, if you can bring it below that T naught, then we are at a condition, where there is a possibility of partition less solidification, I said there is a possibility of. So, whenever I say you bring it to any under cooling below that, if you are our under cooling is so high, you bring an under cooling up to this level, and you come actually below the T g, there is even a possibility of glass formation, we will talk about it after a while.

Correct, which curve, this one?

Yes, that is what I am saying, when you say L plus alpha region for example, if I take this liquid, and under cool to this temperature, what should happen to that liquid? Under normal conditions, if the liquid is simply cooled, it would have first formed alpha, and then by time you reach this temperature, eutectic reaction should have occurred. Now, you have brought this liquid to that temperature, and your T g for that alloy is some where here let say, you are above T g, but below T naught, so liquid has no chance for yet to become a glass, you have not yet reached the temperature where glass can form, I will talk about glass formation possibly in next class, we will know a little more about this T g concept. But, at the moment if you understand that this is above that, so liquid has to, and at the same time liquid is not stable at this temperature, according phase diagram, what is stable? In principality, the alpha plus beta that is stable at that temperature, so liquid is no way, it has a chance to be stable there, so liquid wants to transform now. So, how do you does it, what it will transform is, what we are looking at.

Again the same concept if because, we are at this temperature, if I extrapolate the T naught curve, I will see that my composition at this temperature is to the left of the T naught, so there is a possibility that, that liquid which is staying there at temperature has a chance to become a solid by partitionless solidification. But, if the same liquid is somewhere here no, or if I choose another alloy, and bring it to the same temperature, this alloy has no chance for it to become a partitionless solidification, because now it is on the right side of the T naught curve at the same temperature, and whenever we at the right side, there is no driving force for partitionless solidification.

So, alloy number 1 has chance for becoming a single phase alpha by partition less solidification, and that is what it happens, and now if you look at compositions like alloy 2 what should happen to this compositions? It has no driving force for partition less solidification, at the same time at a temperature, where the liquid is not suppose to be stable, because we have brought it to this temperature, at this temperature liquid cannot remain as a liquid, so the only chance for it is and at the same time, it is also above the T G.

So, liquid has only one solution, that it has to become a solid by partitioning, the only difference would be the solid that comes out at that temperature, may not be the solid at this temperature when the liquid is taken, the liquid should give you liquid plus solid. At this temperature once I bring this liquid, it has to give you liquid plus solid, either liquid plus alpha or liquid plus beta, depending on the situation, and depending on which side of phase diagram you are.

And now which will be composition of that alpha, which will be composition of liquid, how will I know at that temperature? I have brought this to liquid to this temperature, at this temperature it has no solution, that too undergo partitioning, and it should have a solidification along with partitioning, and such a partitioning when it is taking place, what will be the composition of liquid, what will be the composition of alpha? How will I get? Let say, if I, if this alloy is this temperature, this alloy alloy 1 is that temperature, at that temperature also it is above the T naught, is it not? Above the T naught and if I draw a line at that temperature horizontal line, it is on the right side on the T naught, so that means, partitionless solidification is again ruled out.

So, that alloy will now undergo solidification by partitioning, what will be composition of liquid, what will be composition of alpha at that temperature? How do you see? By not the leave a rule, it is only amounts of liquid, amounts of alpha, it is that tie line and wherever the tie line intersect the alpha and the liquid, that would be the composition of alpha, the composition of the liquid.

So, alpha of this composition will come out of the liquid at that temperature and the remaining liquid will get this particular composition, and that is how you will have a two phase mixture of alpha and liquid. Now, if I am considering another alloy, alloy 2 and I am saying that this alloy 2 his brought to this temperature, again the situation of this alloy 2 at this temperature is similar to the situation of alloy 1 at this temperature, there is no difference. Now, what will be the composition of liquid and alpha? The only difference is, I am now below the eutectic temperature, earlier I was above the eutectic temperature. Now, what will be the free the composition of the liquid and the composition of alpha? Why? Liquid is not eutectic, liquid composition is this, eutectic composition is this, again draw a tie line; yes, how do you do? Now, I drew the tie line now, now this tie line, when I extent the tie line, it is intersecting alpha here beta here, so but I am talking of liquid and alpha, liquid is giving me liquid and alpha, liquid is not giving me alpha plus beta.

So, how do find out the composition of alpha and liquid now? To find out you need to look at whenever I am talking of liquid and alpha, I need to look out, what indicates the equilibrium between the liquid and alpha? What is that particular composition which talks about liquid alpha equilibrium, liquid alpha equilibrium is decided by this line, and this line, these are the two which talk about liquid and alpha equilibrium; this is the liquids, this is the solidus, and this gives you the alpha composition, this gives the liquid composition. If you want to know, what the composition of alpha is, and what the composition of liquid at any temperature is, what you need to do is, you need to extrapolate those curves; so you extrapolate the liquids, you extrapolate the solidus, and the compositions. Because what I meaning to say is, at this temperature, at this temperature, if alpha has to come out of liquid, imagine there is a liquid, inside that alpha is coming out, if this liquid has to be in equilibrium with alpha, it can be in equilibrium with alpha only by this, this is the only line which tells me what is the composition of alpha that can be in equilibrium with liquid, no other alpha composition can be in equilibrium with liquid.

So, this whole domain talks about liquid alpha equilibrium and so if I want to know, what is the composition of alpha that can be in equilibrium with liquid, it is only this composition. Because if I draw that free energy curves, common tangent between alpha and liquid, if I draw it, this tells me the composition of the common tangent for the alpha, and this tells me the composition of the common tangent for the liquid. And so at some other temperatures, at a lower temperature if you want to look out it basically I extrapolate that, and these extrapolations will tell me, what will be the composition of alpha, what will be the composition.

So, it is that the alpha that comes out at this temperature will be having that composition, and the moment alpha of that composition comes out the liquid which is remaining, will tend to have this composition. And once that happens now you see the liquid composition is beyond that of eutectic composition actually, it is not? So, because the liquid composition is beyond that of the eutectic composition, there is a possibility that, the remaining liquid which has a richer in B atoms, can start a nucleating the beta, and there is a possibility that the remaining liquid gets converted to beta, because we are on the B side now, the liquid composition is on the B side now, so because it is rich in B, the liquid is rich in B, it can easily nucleate beta, which is the beta be rich phase.

So, you you will see that in all these cases, though the alpha that comes out initially will be of this composition, at some stage you will see the remaining liquid gets converted to beta, so you will have a situation of beta matrix, and alpha phase. And as the as you hold for a longer time as you cool to lower and lower temperature, this alpha slowly changes to the equilibrium composition of alpha, because the moment beta comes out, alpha of this composition cannot be in equilibrium with beta; if alpha has to be in with equilibrium beta, only alpha of this composition can be in equilibrium with beta.

So, as a result, the alpha composition shifts from here to here, so that it can be in equilibrium with beta, and you will see let slowly and because of the composition is becoming lower in B content, so that excess B atoms which are available in in in alpha, will be rejected out of alpha, and we will go join the beta, so that the beta quantity will increase and then alpha composition will get shifted towards richer a and that is how the whole process happens. This is all assuming that partitionless solidification is not taking place, if you have a situation where partitionless solidification is not taking place, and you are at temperature below the eutectic.

If you are above eutectic, all this problem does not happen, here at this temperature you will at the alpha, and as you cool to lower and lower the liquid composition changes, and then finally, it reaches eutectic and that liquid will give you a eutectic mixture like an like any other solidification. But, if I have under cool the liquid to a temperature below the eutectic, and solidification is now about to start, what should happen to this liquid? It cannot straight away give you the eutectic mixture, because the liquid composition is not a eutectic composition, you know, please remember eutectic reaction is an invariant reaction.

What is the meaning of invariant reaction? Invariant reaction means everything is fixed, the composition of liquid that can undergo a eutectic reaction is fixed, every liquid cannot undergo; you may say, sir this alloy also will have a eutectic reaction, this alloy also will have a eutectic reaction, why do you say that liquid should have this composition only? This alloy is undergoing eutectic reaction, but the liquid of this alloy which is undergoing eutectic reaction always has only that composition, please remember that.

If I take this alloy, this is the alloy I am choosing, if I slowly cool under normal condition you will have the alpha coming out, and as I come to lower and lower temperature, more and more alpha comes out, and the remaining liquid, its composition shifts towards this, and then comes to this particular composition, so the moment I reach this temperature the liquid that is remaining inside the liquid plus alpha mixture will always have that composition, and it is that liquid which is undergoing a eutectic reaction, not the liquid with which you have started. So, the eutectic reaction always the liquid which under goes the eutectic reaction will have this composition, because it is A rich phase that is coming out liquid becomes richer in B, if you are on this side, it is beta that comes out first of this composition, and as you comes to lower and lower temperature, more and more beta comes and beta, because beta is B rich the liquid gets depleted in B.

All that B in liquid goes in to that beta as a result the liquid composition changes, and then once you reach eutectic, the liquid composition is always that, so that if you choose this alloy or this alloy or any alloy within the eutectic domain, the eutectic reaction always happens between the liquid of a fixed composition, and that composition is the eutectic composition. So, that is the meaning of an invariant reaction, you cannot have any liquid giving you a eutectic reaction, so because we are not talking about this liquid… yes, it is again the free energies.

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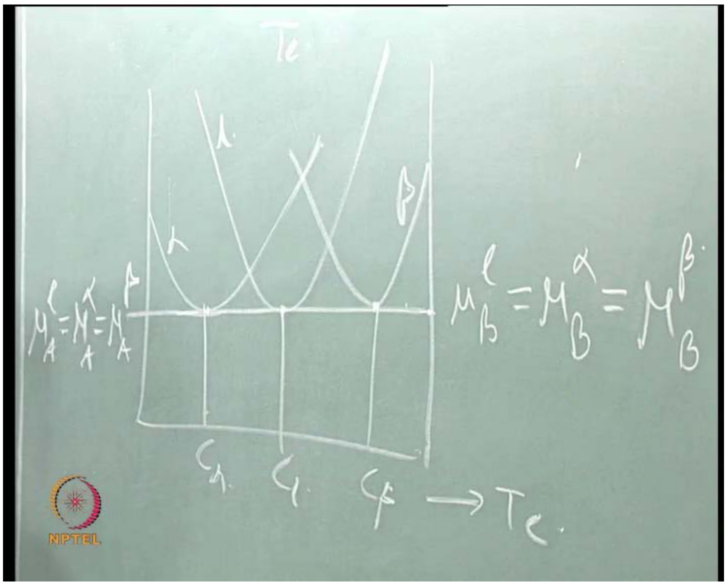

If you draw for example, if I draw if I draw, what is the meaning of eutectic? Liquid giving you alpha plus beta, that means, once a phase is giving you two phases, there are three phases in equilibrium, it is not? So, if at that temperature eutectic temperature, if I draw a free energy composition diagram, I will see that you will have one liquid curve, one alpha curve, and if I draw a common tangent, you will see this; this is the liquid, this is the alpha, this is the beta, you will see at that temperature, if I draw at eutectic temperature T e, if I draw the free energy composition diagram, I will see a free energy composition diagram like this, where all of them having the same common tangent, and what does that mean? It means that, where ever this tangent intersects here, on the y axis I can call this as mu of B in liquid is equal to mu of B in alpha is equal to mu of B in the beta.

Similarly, on this side, I can say mu of A in liquid is equal to the mu of A in alpha is equal to the mu of A in beta, that is what is the definition of equilibrium here, the chemical potential of A in alpha, beta and in liquid all of them are equal, similarly chemical potential of B in all the three phases is equal. And now, what decides the composition? It is this composition, where ever this common tangent is taking place, the composition corresponding to that common tangent will be the composition of the liquid.

So, if you draw this free energy curves at that temperature, draw a common tangent whatever composition corresponds to a liquid composition of that common tangent will be this composition, and this composition and this composition, this will be alpha composition, this will be the beta composition, this will be the C liquid composition at the eutectic temperature; that means, this three compositions.

So, everything is fixed, like we have we drew a unary phase diagram for H 2 O, we saw that the pressure and temperature at which all the three phases can exist is fixed, is not in your hands, similarly the compositions of alpha liquid beta is fixed and it is not in your hands, it is decided only by the temperature. Now if I come to lower temperature, at a lower temperature in principle liquid is not stable.

What should happen I, when I decrease the temperature what should happen to this free energy curves? They will go up, which one will go up, alpha and beta will not go up, everything will go up, this has to be remembered, it is not that liquid only goes up, alpha beta do not go up, it is only the rate at which they move up that matters for us. Yes, correct, see the question is whenever we talk of equilibrium there is always something called local equilibrium which has to be maintained, unless you are a at such a highly non equilibrium states, that where atoms cannot move at all like a like a molten state transformation, diffusion less transformation that is taking place, or a liquid giving you a glass, that you are a such a temperatures, where no diffusions can occur, atoms cannot move, then local equilibrium fails at all other temperatures liquid tend to have, that is why the moment the alpha forms what happens is a thin, may be it can be even a mono atomic layer, it can be a two atomic layer thickness, but that thickness within that thickness of liquid around it will have a composition which is decided by that tie line.

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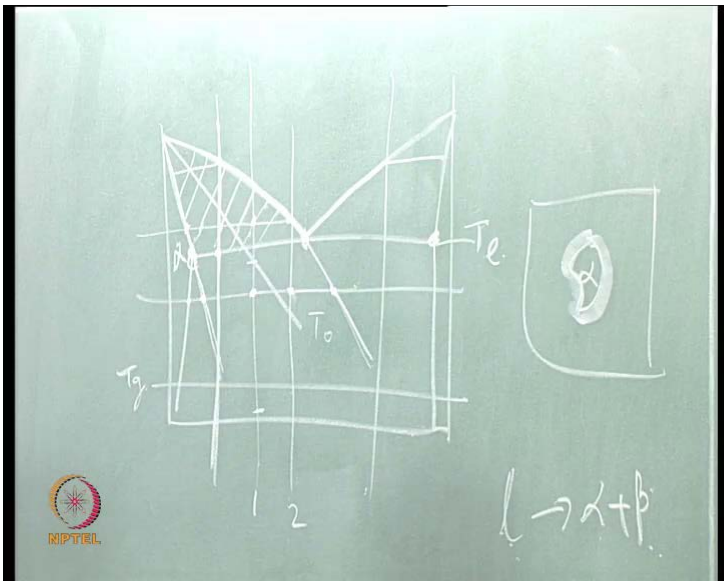

And if you think that the temperature is like very very small like absolute 0, or very close to room temperature, even room temperature whenever we talk of temperature, we should remember, what that we are talking about. For example, you many of you know that deformation at room temperature for lead we call it as high temperature deformation or deformation.

So, with respect to what we are talking; that means, with respective which material were diffusion is easier or faster or not easier; that means, with respect to the melting point of that metal we are talking about. Similarly, if we are talking about a material which has a sufficiently high melting point and if we are talking about a temperature, which are close to room temperature, where this also cannot happen;. inside the liquid, inside liquid atoms cannot able to move, to be able to come to that temperature, that composition decided by the local equilibrium, then what would happen is liquid will not give you that alpha.

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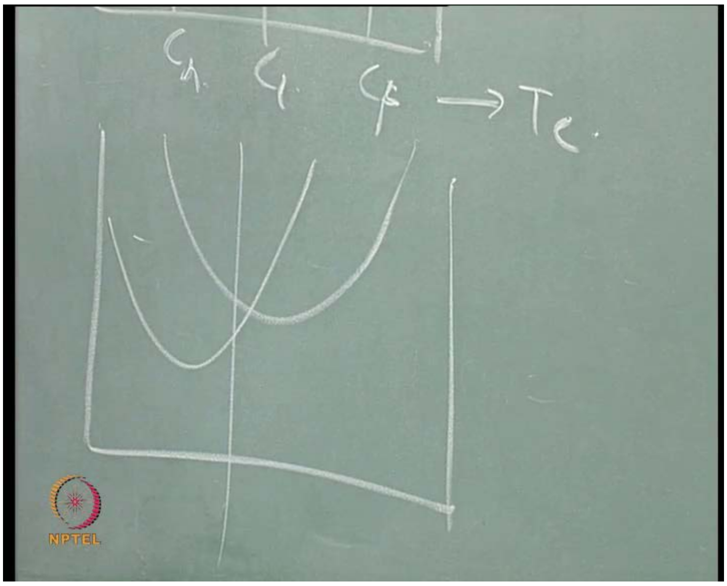

Even for liquid to give you that alpha atoms have to come together, and form a structure which is an fcc or bcc structure having this composition, because now at this temperature, if I simply draw the free energy composition diagram, I have liquid, now this is a liquid of certain composition that I am choosing, this liquid what should happen to it, if I look at it? Then I should look at what all the other phases that are possible, can I draw the free energy composition diagram for them? And if I draw the free energy composition diagram for alpha let us say, I may see that yes there is a deriving force now. Just because there is a deriving force will it form or not is decided by that structure of that particular phase, how complicated or how easy it is, whether it is able to nucleate or not. If it can nucleate, that means, the diffusion is able to take place, even if it is localized diffusion and if localized diffusion can happen, then local equilibrium has to be established.

If local diffusion also is difficult; that means, short range diffusion is also difficult, then there is no chance of even local equilibrium. Yes, coring definitely happen, you see, but the thing is the coring we are assuming, that you know you have a alpha at each temperature as you go below of different different composition nucleating, this is assuming that our temperature is such that, we are above the T naught, if you are below the T naught there is no question of coring; the alpha that comes out will be same composition as that of liquid, absolutely there is no coring, clear.

So, coming back to this problem, if we are at a lower temperature, then you would see that all of them are going up, only thing is liquid will go up faster, why should it go up faster? Yes remember G verses T curve, G verses T curve the slope of it is entropy and as a result, so if you change the temperature by 1 degree, how much the G will go up is decided by the slope. So, you will see that, if I decrease the temperature by 1 degree, the liquid will go up faster when compare to solid because both the solid has a shallower free energy curves, free energy verses temperature curves, so because the entropy are lower, so they will not raise at a same level as a liquid; so, as a result when I decrease the temperature, this starts going up.

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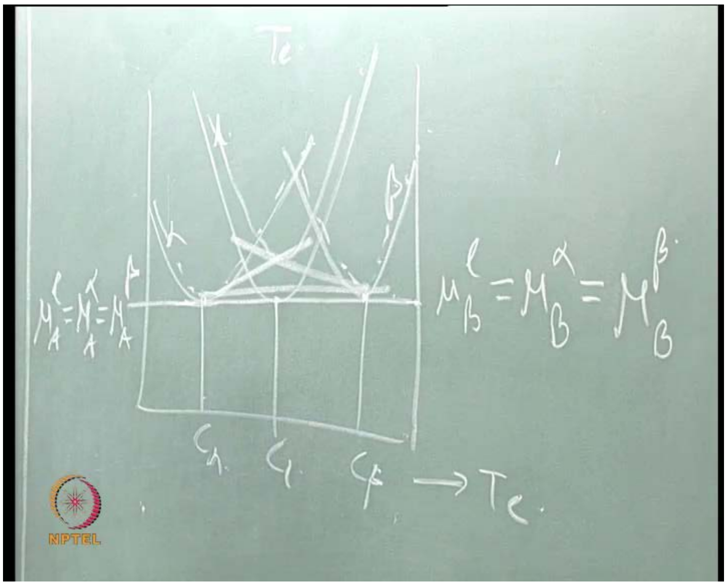

So, that means, and all of that are going up, let us say they go up like this, but this goes up faster. If this goes up faster, then you will see a situation, now I cannot maintain a commonly equilibrium between all the three, common tangent between the all the three is not possible, the only tangent that is possible, of course you can have three tangents; you can have a tangents between alpha and liquid, you can have a tangent between beta and liquid, you can also have a tangent between alpha and beta, and if you look at which of the tangent is the lowest, which tangent has a lower free energy? You would see, the alpha and liquid, the alpha to liquid will be like this, the beta to liquid will be like this, and alpha to beta will be like this, and because alpha and beta free energy I mean, common tangent is below that of the other two, we say that alpha beta is most stable state. That is why when I come to a lower temperature below this, at this temperature it is alpha and beta which is stable, and that is what you will see; come back, you see we our interest is not this, our interest is to see what happens?

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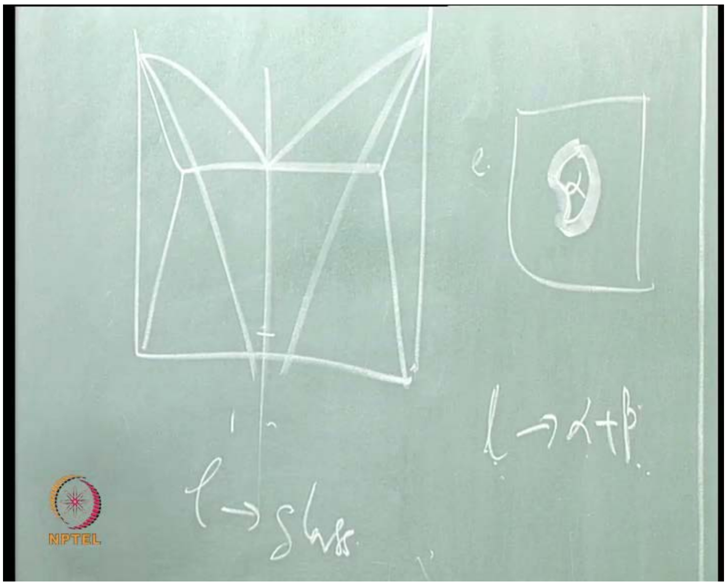

If I take a case of if I take a case of, if I take an alloy of this composition, I have under cooled it to a very low temperatures, and to an extent that as I keep on under cooling it, the T naught curves of the alpha and beta are such that there slope of such that, this composition is not intersecting any of them, if that is the case when you reach a low temperatures, at that stage where we are just now talking about it, even local equilibrium cannot be maintain because atoms are not able to move, and at such stage, this liquid will have a tendency to form a glass. And there is a temperature below which this will happen and that temperature is what is called glass transition temperature.

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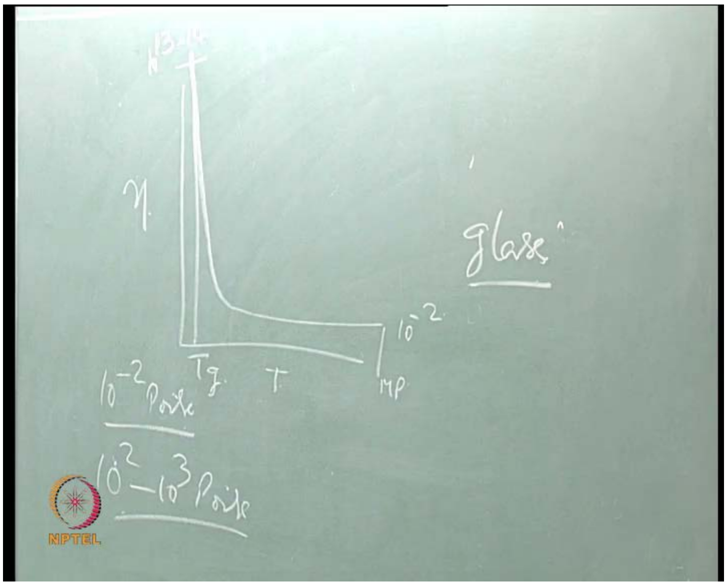

And that comes from a concept of if you draw the viscosity as the function of temperature, viscosity of the liquid, you will see that liquid viscosity above the melting point is usually of the order of around centipoises. Most of the metal liquids metallic liquids just above the melting points, if you measure there viscosity, they are all of the order of centipoise where as if you take silicate glass liquid above its melting points, take any silicate glass type of materials any silicates, and take them above the melting point and measure there viscosities, the viscosities of them will be the order of 10 to the power 2 to 10 to the power 3 poise. We are all talking of above the melting point, whatever may be melting point, so that what does it tell you?

It tells you that these are highly viscous when compare to metallic liquids, the reason is the 3-dimensional network kind of clusters that are there in those liquids, the silicates clusters that are there in the liquids will make this liquids very viscous, and that the reason why we always say glass formation in these liquids easier, because for them to nucleate a silicate solid, crystalline solid is more difficult when compare two metals. Atoms can easily move because there are less viscous, atoms can move because this is more viscous, atoms are not able to move, and now if I plot how this viscosity changes with temperature, you will see the viscosity changes almost like this, this is starting from about melting point, 10 to the power minus 2 to is goes a temperature level of around 10 to the power 13 to 10 to the power 14 poise. And these 10 to power 13 poise he is a he is a kind of viscosity of solids, any solids that we talk about, whenever we talk solids the mechanical definitions, the mechanical definitions of a liquid is that liquid, which are shear modulus 0 is what we call it as a liquid, it can easily flow if shear modulus is 0. So, a solid is the one which shows some shear modulus, so that is actually related to the viscosity, so the movement the viscosity reaches that value, then immediately this liquid has to become solid. So, it is a mechanically a solid, it as a shear modulus now, but its structurally is a liquid, because you are at a temperature were there are no atomic arrangement can take place, atomic rearrangement, so atoms remain were they are, that is why we called it as a configurationally frozen liquid. So, glass is what we call it as configurationally frozen super cooled liquid, so the movement you bring the liquid to this temperature, which is what we call it as T g, if suddenly see that the liquid freezes into a solid, but into a solid which has structure similar to that of a liquid, and that new type of solid which we do not have not seen before, because of the most of the solids that we know are all crystalline solids, now you have a solids which is non crystalline, which has a structure similar to that of a liquid, we call that as a glass. This is what is one way of looking at glass formation, we will also possibly look at the other way of looking at how the glass forms, and I can achieve this particular thing by basically very a fast cooling, if I cool because we are all talking of under cooling the liquid, please remember I am not simply cooling the liquid, I am under cooling.

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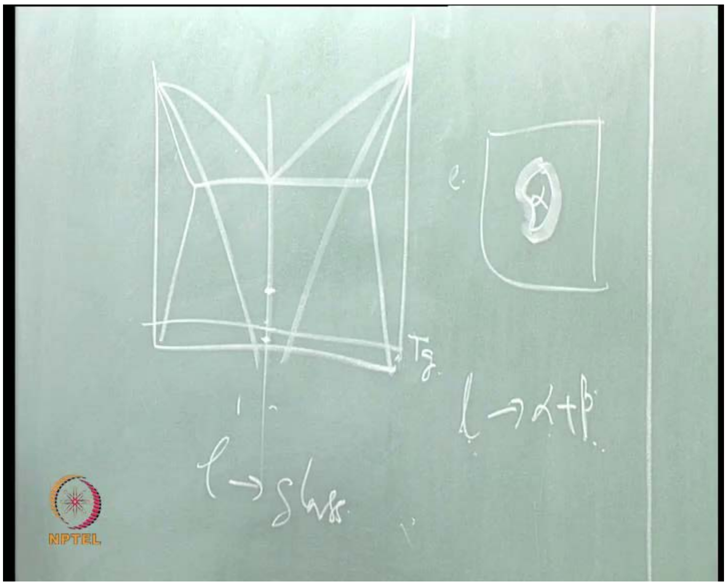

So; that means, I am able to achieve, if this is the T g for this phase diagram, if I can under cool the liquid below this T g and at the same time, not being able to intersect the 2 T naught curves, then I will see that particular liquid will because at this temperature, partition less solidification cannot occur, because I am above the T naught for both alpha and beta.

So, the liquid is able to remain as a liquid, it is not able to become a partial solidification to single phase alpha or single phase beta, now what should liquid can happen? The liquid can only undergo solidification by partitioning, or for that to happen if diffusion is difficult the only choice for it is to becoming a glass. And because we are at temperatures were fusion is not able to take place, because liquid has already configurationally frozen, because atoms are not able to move, so as a result that particular liquid at that temperature would become a glass. If I am any temperature here, if I have under cooled liquid to that temperature it can still become a solid by partitioning, it can start the giving alpha or beta whichever has a lower activation barrier for nucleation, it will start forming that and then it will it will continue, but the moment I bring it below the T g, this liquid has no chance, but to become a glass.

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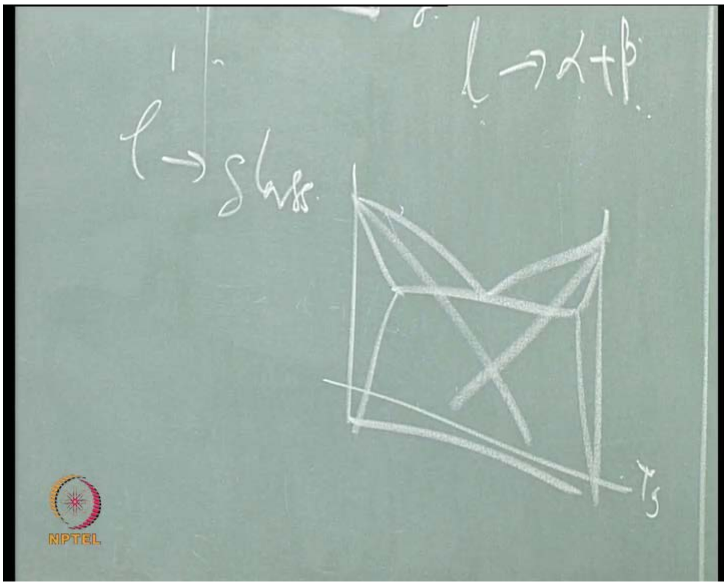

And that is where we start defining what are called deep eutectics and shallow eutectics. There are some phase diagrams which are like this lets say, were the T naught curves look like this, they intersect with each other, and if the T g is somewhere here by the time the liquid eutectic liquid is brought below the T g it already intersects the T naught, either the alpha T naught or beta T naught, and once that happens, we will see either alpha or beta comes out, we will continue this later and see more of how to understand the glass formation.