Advanced Metallurgical Thermodynamics

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Lecture No. # 13

Eutectic Solidification, Coupled Growth, Heterogeneous Nucleation

In the last few classes, we concentrated on the T naught concept and then its utility for us.

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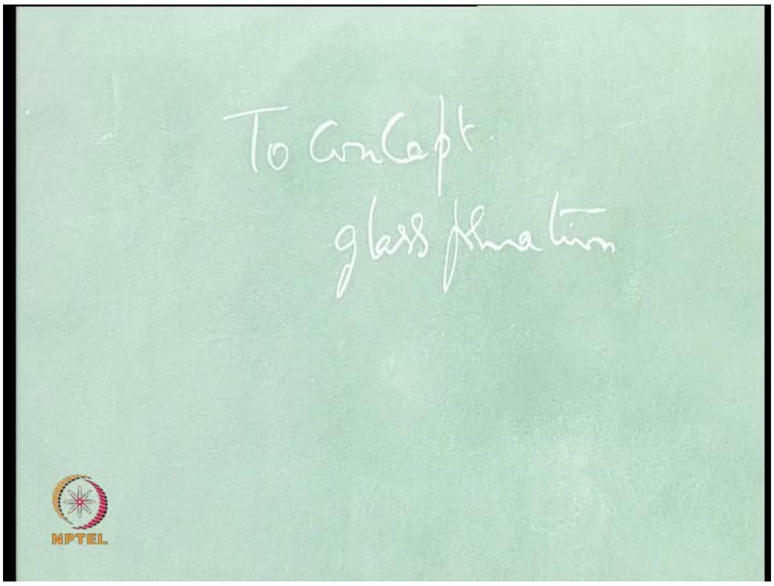

In that connection, we spent sufficient time, quite a significant amount of time on glass formation. And, all of you know glass formation, you have seen with respect to a eutectic phase diagram. Usually, you see glass formation only when there are eutectics. Why? Because eutectic is where the liquid is stable. The meaning of eutectic is the melting point depression. Many of you know, eutectic means low melting. So, with respective to the two pure metal melting points, the eutectic always has a lower melting point. Lower melting point basically means liquid is stable. So, if the liquid is stable, then only you would get a glass; if the solid is stable you would not get a glass. So, in that connection, we talked about glass. Today, let us go a little more detail into the eutectic; not talk about glass formation, but about eutectic itself. So, see how the eutectic solidification occurs.

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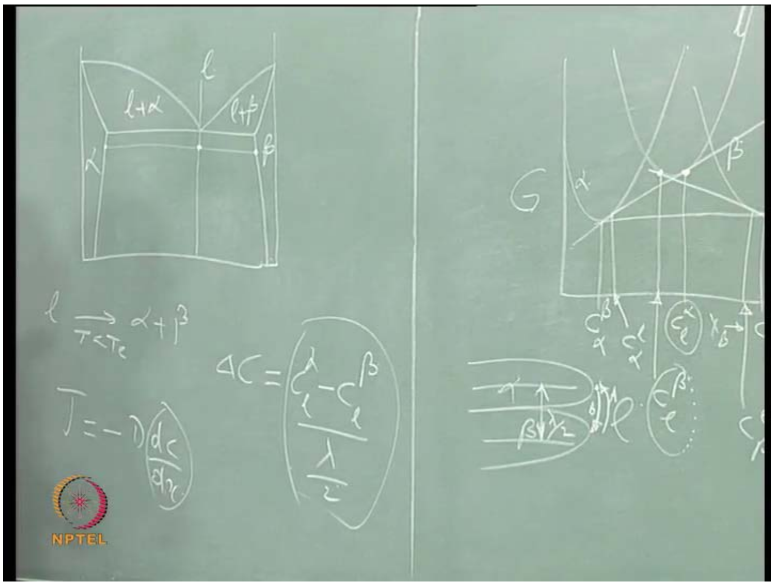

For example, if you take a phase diagram something like this, you take a eutectic composition. And, the moment you come below the melting point, below the eutectic temperature, bring this liquid, hold it at this temperature. What should happen?

Alfa plus beta.

Liquid should give you alpha plus beta. And, this should happen by a nucleation and growth, because the liquid composition is different from the two solid compositions, whatever the two solid compositions are. So, this is liquid; this is alpha; this is beta; this is liquid plus beta; this is liquid plus alpha. All these you people know. So, now, if you take the liquid and bring it to a temperature T; below the T e, this liquid should give you alpha plus beta and this alpha plus beta microstructures. There are varieties of these microstructures. The most common microstructure is what is called as lamellar microstructure. You also might have heard about what is called diverse eutectic. If possible, today’s class itself we will talk about why various types of eutectic come. That is again related to what is called surface energies, which is a part of the thermodynamics; we will look at it. But, if you simply look at this alpha plus beta, which is nucleated inside a reservoir of liquid, you have a liquid here. And this nucleus, a couple, which has nucleated; alpha and beta always nucleate together if it is a lamellar eutectic. If it is not lamellar eutectic, they will not nucleate together that also we will see it later.

But, assuming that they nucleate together, how do they grow? If they want to grow, what you see is that alpha is an A-rich phase beta is a B-rich phase. So, A-rich phase and a B-rich phase, both of them are growing together into the liquid. How do this to grow? They can grow only when the liquid supplies atoms to alpha and beta. Atoms are actually coming from the liquid to alpha and beta; they are joining alpha and beta. And, as a result, the alpha and beta are growing together at the expense of the liquid, so that at the end of the reaction, if I do what is called the cooling curve, temperature verses time, at this particular time, this has nucleated. And, as I grow, by this time, all the liquid should vanish and everything should become alpha plus beta.

Of course, there are a number of such couples nucleated various positions, a number of nuclei; and, all of them together grow, such that they form what are called certain boundaries. What do we call those boundaries as? They are not grain boundaries. In a eutectic, we do not call them as grain boundaries, because it is not a grain boundary is related to one single phase. There is no one single phase here. So, what do you call when the eutectics… This nucleates here; and somewhere else, you have something else nucleating here (Refer Slide Time: 05:07); alpha plus beta both of them come together and meet each other; what do called that boundary? Of course, it is an interphase; even this is also an interphase. So, there is a name, because this is called a eutectic colony. And, what you get them are called eutectic colony boundaries. So, you have a number of such eutectic colonies grow and you will have eutectic colony boundaries coming in like grain boundaries. They are analogous to grain boundaries and you would see in most of such eutectic microstructures, boundaries of different alpha, beta growing in different orientations. Between each colony, the difference is orientation of alpha-beta couple. So, the alpha-beta couple orientations in this and this orientation (Refer Slide Time: 06:02) is going to be different. So, it is similar to grain boundaries, where grain orientations are different at the boundaries.

Now, forgetting about that, basically, these alpha beta grow at the expenses of the liquid; that means, what? For alpha beta to grow together, you need liquid to supply more A atoms to alpha and more B atoms to beta. This is a very tricky problem. How is that the liquid, which is there in front of it is selectively able to supply more A atoms to alpha and more B atoms to beta, such that they grow together. It is it is one single liquid. One single liquid is able to supply more A atoms to alpha and more B atoms to beta. Unless you do that… If only certain atoms, let us say, A atoms are coming uniformly to both the things, only alpha will grow; beta will not grow. Then, it will not be a coupled growth. So, if you want a coupled growth to happen, this has to (Refer Slide Time: 07:03). So, that means, selective supply of atoms to alpha and beta should take place. And, how does this happen? It happens if you understand the thermodynamics a little bit.

Let us try to see what happens when we draw a free energy composition diagram at a temperature like this (Refer Slide Time: 07:22). I have taken a liquid of eutectic composition; brought it to this particular temperature. At that temperature, this whole thing is happening and I am trying to look at what is happening. So, if I draw the free energy composition diagram at that temperature, how will it look like? What is stable at that temperature? Can you tell me? Alpha plus beta. So, that means alpha and beta curves, free energy curves should be below that of the liquid. By now, all these should be clear to you.

If that is the case, I can easily draw (Refer Slide Time: 07:53). So, I can draw a liquid and I can draw an alpha and a beta and draw a common tangent between them. So, this is the alpha curve; this is the beta curve; this is the liquid curve. And, these two compositions, where you have the common tangent of alpha and beta, should correspond to these two compositions in our phase diagram, because there has to be a one to one correspondence between free energy compositions diagram and the phase diagram. And, this is the G x diagram, free energy compositions diagram.

Now, if I look at again our couple once again, alpha and beta, you have a liquid here. So, this alpha is in equilibrium with liquid; this beta is also in equilibrium with liquid. Now, let us look at, in this free energy composition diagram, what represents the equilibrium between alpha and liquid and beta and liquid? Whenever I say equilibrium, it is represented by what? It is a common tangent. So, when I say equilibrium between alpha and liquid, I should draw a common tangent between alpha and liquid. So, how do I draw a common tangent between alpha and liquid? See something like this (Refer Slide Time: 09:15). So, you have this composition and this composition. And let us first give certain notation for the first two compositions that we have already drawn. What is this? This is (Refer Slide Time: 09:58) the composition of alpha in equilibrium with beta; this is the compositions of beta in equilibrium with alpha. And, what is this composition now? C alpha liquid. And, this is C liquid; this is C liquid alpha.

Now, similarly, let us do the same thing for the beta. So, if I do this, some two compositions again you get (Refer Slide Time: 10:10). We are getting totally some six compositions now. And, this composition is if I put it, this is C liquid beta; and, if I identify this composition, this is C beta liquid. What am I getting out of all these? Simply certain six compositions we have got. But, if I carefully observe these six compositions; forgetting above the first two compositions which are between the alpha and beta, look at these four compositions. If I compare the composition of liquid in equilibrium with alpha and the composition of liquid in equilibrium with beta, I get some information.

What is the composition of liquid in equilibrium with alpha? It is this (Refer Slide Time: 11:00). This is the composition of liquid in equilibrium with alpha; this is composition of liquid in equilibrium with beta. What does that tell you? That tells you that the liquid, which is in equilibrium with alpha has a higher b content when compared to the liquid, which is in equilibrium with beta. This is the liquid, which is equilibrium with alpha; that means, the liquid, which is just in front of the alpha and the liquid, which is just in front of the beta if I look at the compositions of those two liquids, there are not the same. And, not only that they are not the same, the common tangent generation itself makes it such a way that the composition of liquid in equilibrium with alpha has more b content; the composition of liquid in equilibrium with beta, that is, this quantity and this quantity; these are the two we are looking at. This quantity (Refer Slide Time: 12:05) is higher than this quantity in terms percentage b; that means, what? Just in front of alpha, you have more B atoms; and in front of beta, you have more A atoms. And, this means that liquid is not having the same composition everywhere.

If I go for away from this alpha plus beta (Refer Slide Time: 12:30) interphase, what is the composition of the liquid? It is same as that of the eutectic composition. It is only because of the local equilibrium that has to be maintained for this alpha. If this composition is not maintained, then alpha and beta cannot exist in equilibrium with liquid. They will not lie; they will possibly dissolve back into the liquid. If alpha and beta have to exist with the liquid, the only way that is possible at this temperature; at this temperature we are talking about. Remember, if I am talking of at this temperature, situation would be different. At this temperature, it is same, because it is a common tangent between all the three. But, we are talking of a temperature below the eutectic. I have brought the liquid below the eutectic and now, looking at what would happen. If I am looking at that, you would see because of this, here at this position, you have more B atoms than this. Then, what you see is that B atoms will start travelling in this direction and A atoms will start travelling in this direction.

And, the gradient is decided by what is called this. What do we call it as? Inter lamellar distance. Actually, this distance; can you tell me what is this distance? Between the half of the alpha and half of the beta; between the center of the alpha lamellae and center of the beta lamellae (Refer Slide Time: 14:06). Will it be the inter lamellar distance? Or, what do you mean by inter lamellar distance? In a eutectic, you must have heard of this word inter lamellar distance. When I say inter lamellar distance, what distance I am talking about? From where to where? Between two lamellae of what?

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Correct.

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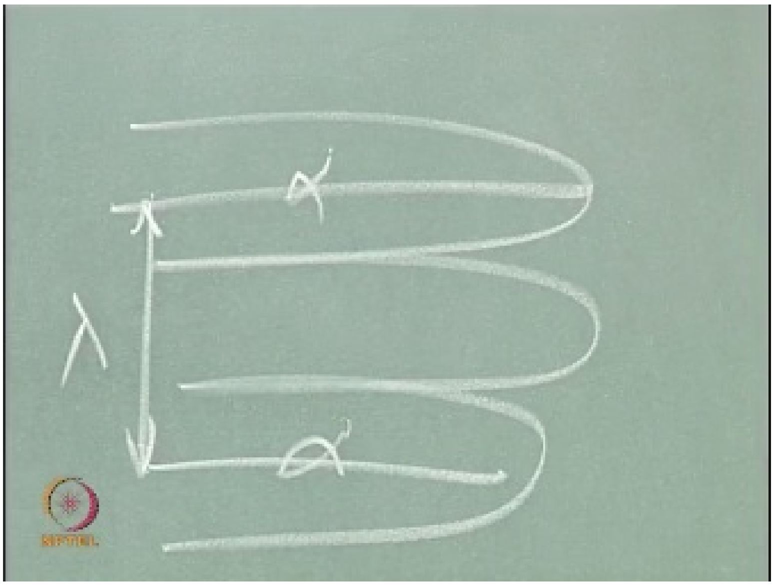

So, when I say if I have an alpha here, beta here, another alpha here, this to this; this is the inter lamellar distance lambda. So, basically, this is lambda by 2 we are talking about (Refer Slide Time: 14:53). And, this movement of atoms B atoms going towards the beta and the A atoms going towards the alpha will make sure that the alpha will get more A atoms and the beta will get more B atoms, so that both of them grow together. And, this is driven by what? It is driven by the distance between the composition of this and this, which is what we call it as delta C, which is nothing but C liquid alpha minus C liquid beta. This (Refer Slide Time: 15:31) and the concentration gradient can be written as this by 2; this by lambda by 2. This is the actual concentration gradient. And, if you say diffusion J is minus d c by d x, the d c by d x for the flow of atoms comes from here. Once the nucleation has taken place, the growth is decided only by diffusion. And, the diffusion – you need a gradient. If there is no gradient, if the gradient is 0, there is no diffusion. So, this gradient is provided by this. And, how do I see this in the phase diagram? Can I see these two points in the phase diagram?

Now, C liquid alpha and C liquid beta – where are they in the phase diagram? Extrapolate what? Yes. So, you have two liquidus here: one is called the alpha liquidus, another is called the beta liquidus. And, what does alpha liquidus tell you? Alpha liquidus tells you, at all temperatures, what is the composition of liquid in equilibrium with alpha. And, the beta liquidus tells you the composition of liquid in equilibrium with beta at various temperatures. So, I want to know at this temperature T, what is that?

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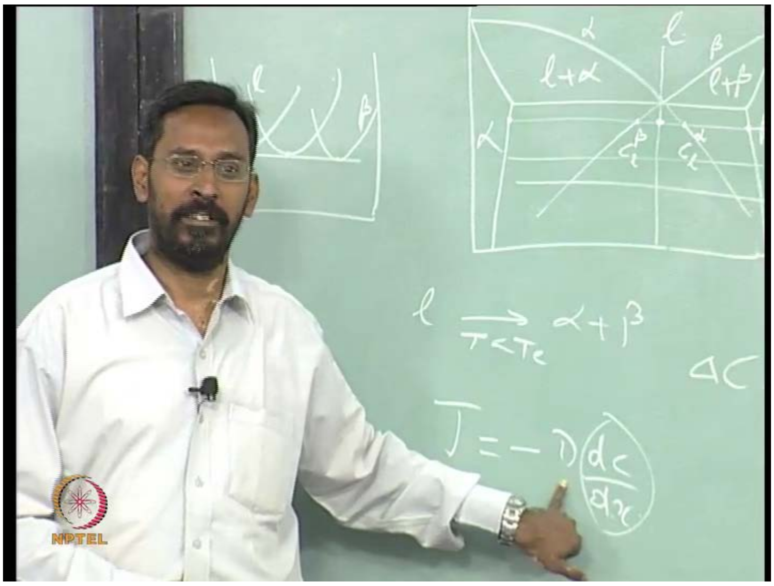

So, if I want to know what is the composition of liquid in equilibrium with alpha and liquid in equilibrium beta at that temperature, the only way I can find out is by extrapolating the two liquidus. So, if I extrapolate the two liquidus, I get this. And, this composition is nothing but C l what? Alpha. This is nothing but C l beta. And, the difference between these two is actually the driving force for the growth of eutectic. If you want the eutectic to grow and that is the reason why, if you carefully observe, at the eutectic temperature, this difference is 0. C l alpha is equal to C l beta, because if I draw at the eutectic, it is actually a common tangent. If you remember, I can draw it for you once again if you want. So, this is alpha; this is liquid; this is alpha and this is beta; let us say liquid, alpha, beta. So, if I am trying to look at what is the composition of liquid in equilibrium with alpha, what is the composition of liquid in equilibrium with beta, they are the same at the eutectic.

Once they are the same, this delta C is 0 (Refer Slide Time: 18:28). And, if delta C is 0, the gradient is 0. If the gradient is 0, the flux is 0. So, in principle, at the eutectic, you cannot have a growth; you need at least a small under cooling. It can be very small if there is a heterogeneous nucleation available; otherwise, it can be a slightly large. But, you need a small under cooling, so that you have a driving force. And, that is why you can again see that if extrapolate this to lower temperatures, the lower the temperature, the larger the delta C. And, that means the larger the gradient. And, as a result, in principle, you can see the growth rate has to be higher. But, there is a catch here. What is the catch? The catch is the D there. So, we are forgetting the D there also. And, this D incidentally… See if you carefully look at these two curves, if I assume that these are linear, then I can assume that the delta C is linearly dependent on the temperature, because these difference can linearly increase with temperature if these two are linear.

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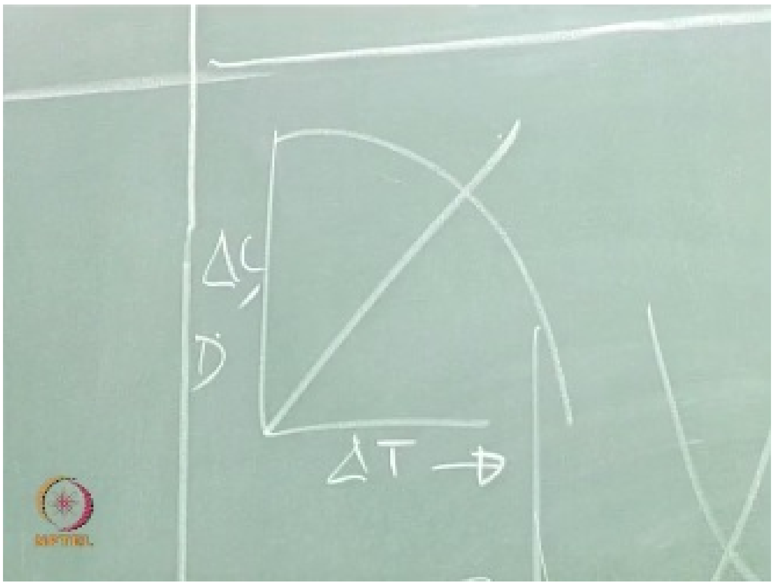

If these two are straight lines, not curved line, if I assume them to be straight lines, then you will see if I plot delta C verses delta t; delta t is under cooling, I will see that this will be linear. And, at delta t being 0, delta C has to be 0. Now, as a function of under cooling if I look at the d, how does it change? How does the diffusivity change with temperature? It decreases of course; in what fashion? Exponential. Be confident whatever you want to say; you are an IITian. Tell me how does diffusivity change with temperature? That is what we are questioning. All of you have read from your B. Tech levels, at various stages, how does diffusivity change the temperature; there is a particular expression, which we always (( )) What is that expression called?

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Correct. What is that expression called? It is an Arrhenius equation. So, this tells you that the D is exponentially related to the T. You can see, the D is D naught exponential minus Q by RT (Refer Slide Time: 21:39). So, you will see that the actual, if I plot D… On the same plot, if I plot D, you would see D would decrease. I have actually drawn parabolic; it is not actually parabolic, it is exponential. So, it decreases very rapidly as you increase the delta T or decrease the temperature. Increase the delta T basically means decreasing the temperature. So, our delta T is increasing in this direction. So, that means there is a particular temperature, critical temperature beyond which you will see the diffusivity plays a major role. So, that is where you will see… In fact, we are not really talking kinetics here; otherwise, I can even talk about the whole growth rate, how does it change.

In fact, lambda itself changes as a function of temperature. You cannot have the same lambda as a function of temperature; all these things. When you study any kinetics course, you will know more about it. So, you can see, until certain temperature, we can always say growth rate is proportional to this under cooling (Refer Slide Time: 23:00) because the under cooling is what decides the delta C. And, the delta C decides the dc by dx. And, as a result, I can say at temperatures closer to the eutectic temperature, the growth rate is always decided by the delta T under cooling. So, the higher the under cooling, the better… That is the reason why any eutectic mixture… If I pore the liquid metal into a metallic mode are to a sand mode, you would see the growth rates are different.

In fact, you will also see not only growth rates, the lambda is also different. You will get a finer lambda. Again basically because the nucleation rate is higher, the r star is smaller. So, all those things become important and you will see this. So, you can see that this problem of how liquid is able to supply atoms to alpha and beta; we are able to see simply understand it just if you understand this diagram (Refer Slide Time: 24:02). So, you can see, from thermodynamics, very easily we can explain how does this come.

Now, let us go to the second concept of what should be the nature of the eutectic. It does not always give you lamellar eutectic. Can you tell me what is the type of eutectic in a cast iron? We should not say steel; you do not have eutectic in steel. In fact, that is what differentiated is steel and cast iron. Have you ever known what is the difference between the steel and a cast iron? When do you call a (( )) carbon alloy as steel; when do you call it as a cast iron?

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Less than 2; why? what is so sacrosanct about this 2 percent?

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The cast iron – that name suggests they are easily castable. And, easy castability basically related to eutectic. So, cast irons are all those where you have a eutectic reaction. And, in the phase diagram, if you look at it, below 2 percent, there is no eutectic reaction. So, remember the iron-carbon diagram, iron-cementite diagram; you would see that it is only beyond 2 percent you start seeing the eutectic reaction. And, that is the reason why we call beyond 2 percent. It is not just a magic number; it is basically the phase diagram; the eutectic reaction wherever it starts, we call them as cast irons; below that, we actually call them as steels anyway. So, coming back to that…

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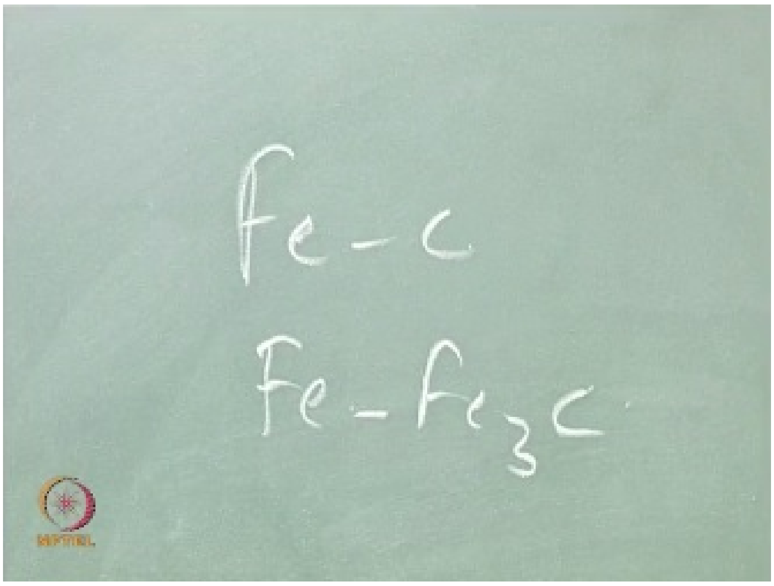

And, that also reminds me that we should also try to understand why an iron-carbon diagram and an iron-cemented diagram are different. Today, we will try to understand that also before that also. Before that, we will try to see, there are different types of eutectics we said. For example, we are coming back to our first question – the iron, carbon, cast irons; what is the type of eutectic you have? Lamellar? You people have not seen microstructures. You have what is called a second year physical metallurgy lab. Many of you B. Tech. should have.

What is the eutectic? If I take a white cast iron… White cast iron is a typical cast iron; the other cast iron, where you get graphite is not actually decided by the iron carbon; it is a graphite, which comes from the iron carbon; whereas, the iron cemented diagram, which we look at it, the actual eutectic reaction is liquid giving the gamma plus Fe 3 c. That is the eutectic. And, where do you see that eutectic? You see that eutectic only in the white cast iron; you do not see that eutectic in any other cast iron. Whether you take a grey cast iron or regular cast iron, you see the graphite there, which is not the gamma plus cementite eutectic. Gamma plus cementite eutectic, which is called the ledeburite is seen only in the white cast iron. So, what is the morphology of this gamma plus ledeburite? What is the morphology of the ledeburite? Is it lamellar? It is not lamellar. It is you have cementite networks you see; microstructures here.

Ledeburite – I am not asking you what is the cementite network you will all actually see. When you come to the cementite being precipitated from austenite, hypo-eutectoid, hyper-eutectoid steels is what you are talking about. We are talking about cast iron and the eutectic mixture in the cast iron; not what is the microstructure at room temperature. I am not asking you what is the microstructure at the room temperature. After the eutectic reaction is over, if you see the microstructure, how should the microstructure be? You have basically cementite particles in an austenite matrix. That is why if you see white cast iron, you see chunks of cementite particles; go back and look at atlas of microstructures (( )) hand book; you will get all these.

Similarly, if you look at aluminum silicon eutectic – aluminum silicon again a popular eutectic; why is it popular aluminum silicon? where do you use the aluminum silicon? automotive systems particularly? So, there again you would see aluminum silicon eutectic; you have silicon needles in an alpha aluminum matrix. So, you do not see it as alternate lamellae of alpha and silicon. Can you tell me which eutectic has actually a lamellar eutectic? Now, I have given two examples of non-lamellar eutectics. Give me any one of the lamellar eutectic that you know.

[Not audible] (Refer Slide Time: 29:21)

That is not eutectic madam.

You are talking of eutectoid. I am asking eutectic. Which eutectic is lamellar? You have never come across? All of you are metallurgies; at least majority of you. Aluminum copper is one; lead-tin is another. These are all lamellar eutectics. If you take aluminum silicon and if you take iron-carbon, these eutectics are non-lamellar and people call them as divorce eutectics. Divorce in the sense, they are not together; the alpha and beta are not together; they are kind of separate. Why does that happen? To understand this, we need to understand the interfacial energies.

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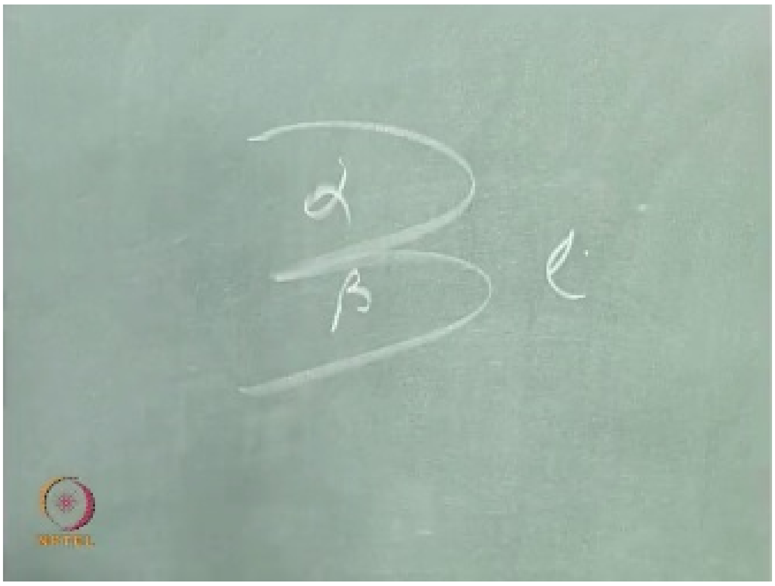

Whenever I talk about alpha, beta and liquid, I have three interphases. What are the three interphases?

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Correct. Liquid to alpha, liquid to beta and alpha-beta.

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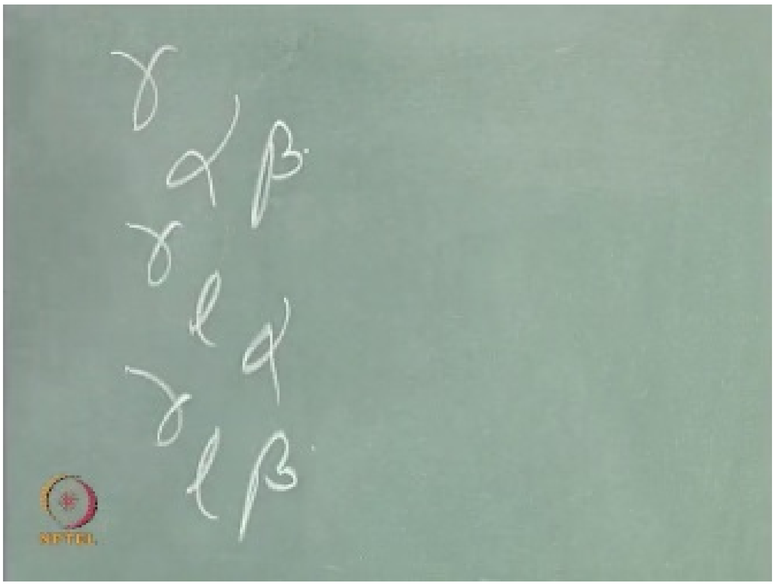

So, if you look at these three interphases, alpha-beta interphase, liquid-alpha interphase, liquid-beta interphase, all of them are associated with certain interfacial energies. There is an alpha-beta interfacial energy; there is a liquid-alpha interfacial energy; there is a liquid-beta interfacial energy. And, we have always seen that whenever you talk about a liquid to solid transformation, the barrier for the transformation is always the interfacial energy. Whenever I bring the liquid below the melting point, it wants to become a solid, because there is a driving force in terms of the volume free energy. Thus, liquid has a higher free energy than the solid below the melting point. As a result, solid wants to form. But, why solid does not form is because of the interfacial energy.

So, as a result, whenever we have this kind of three interphases, the system would choose the one which has the lowest interfacial energy. If a particular system has alpha-beta interfacial energy as the lowest, the system would like to have that particular interphases maximized, so that the overall interfacial energy. Overall interfacial energy is what?

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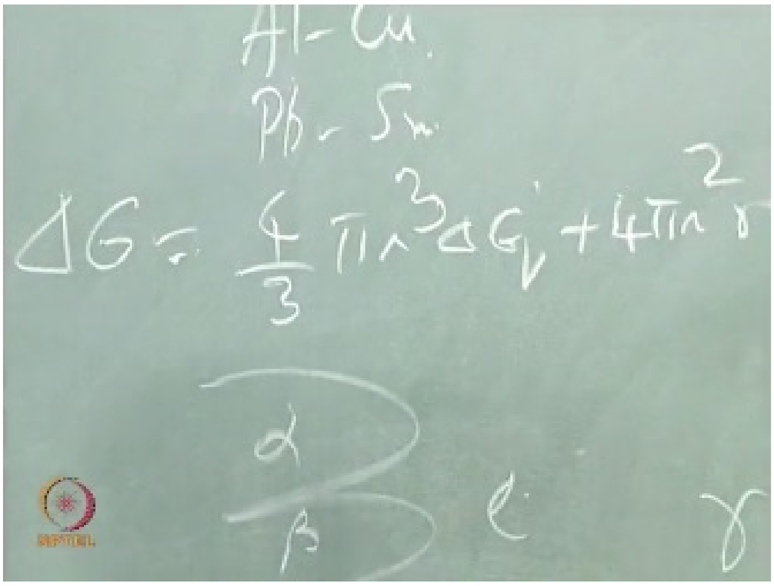

A into gamma. This is what is actually preventing. That is why if you remember delta G, we always write this four-third phi r cube delta G v plus 4 phi r square gamma. Do you remember this? Of course, there we are assumed as spherical nucleus; we are not talking about eutectics there. But, if you talk about eutectics, the same things holds good except that these geometric factors will change. Basically, I can write delta G as V into delta G V plus A into gamma (Refer Slide Time: 32:28). So, it is this A into gamma to be minimized, so that even at a smaller under cooling, the liquid can become a solid. The liquid wants to become a solid at r small under cooling as possible. So, it will choose whenever it has… For example, if it is having let us say as pure metal solidifying, it has no choices of interfacial energies. It is one single solid nucleating out of that. There also, it will search for if there are any heterogeneous nucleating sites. The moment there are heterogeneous nucleating sites, the liquid is very happy, because the gamma is very small there, because that is what is the meaning of a heterogeneous nucleation site.

A heterogeneous site is that site, where the interfacial energy between the solid that is nucleating and the particle that is available is very small. And, that is the reason why you see heterogeneous nucleation occurring. If you just add any type of particle to a liquid, it does not give you heterogeneous nucleation. Simply take let us say aluminum; add some sand particles to it; it does not give you though you may say sir there are particles available. That particle that you are adding should have a structural compatibility with the solid that is nucleating such that the interfacial energy between the solid and the particle that is available should be very small, so that this is minimized (Refer Slide Time: 34:05). And, that is why if you remember, again, I will take you back to heterogeneous nucleation.

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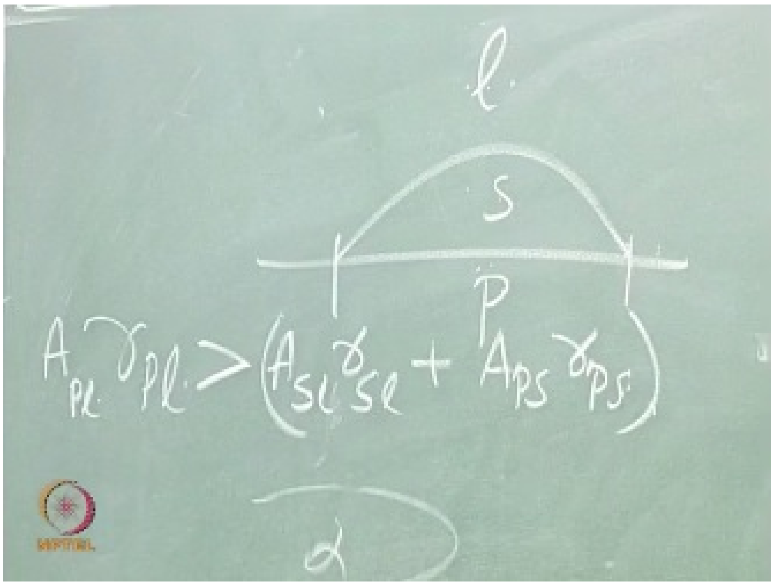

Think of a particle here and a solid nucleating and there is a liquid. So, you should know that when the solidification has not taken place if the solid has not formed, then what you have is only particle liquid interphase. You have a particle; you have a liquid; solid has not formed on it. So, you have a gamma p l. The moment solid has formed on it and this gamma p l has some surface area; so, you have A into gamma p l, will decide what is the total interfacial energy of that particular system. There is a particle inside a liquid. Now, the moment there is a solid that nucleates on the particle, now you have different interphases; you have a particle solid interphase; you have a solid liquid interphase also. So, a particle liquid interphase, which was in this area, has been now replaced with particle solid interphase and solid-liquid interphase. So, you will have A of Sl into gamma of Sl plus A of PS into gamma of PS.

These two are replacing A of Pl into gamma of Pl. If this is smaller than (Refer Slide Time: 35:56) this, if this combination smaller than this, then only the heterogeneous nucleation will take place, because you can see here this interphase is replaced with two interphases. There is a particle liquid interphase and particle solid interphase, which is actually a circular interphase, because it is a plain surface on which you have a hill forming; a bubble kind of solid forming let us say. So, this interphase is circular; whereas, this is like a spherical cap. The solid-liquid interphase is a spherical cap. Geometrically, you can calculate what is the area of that. You calculate the area; multiply with the gamma of that particular thing. Similarly, calculate this PS area, which is this (Refer Slide Time: 36:50). So, actually, A PS is equal to A Pl. Before the solid has nucleated, these two surfaces are the same.

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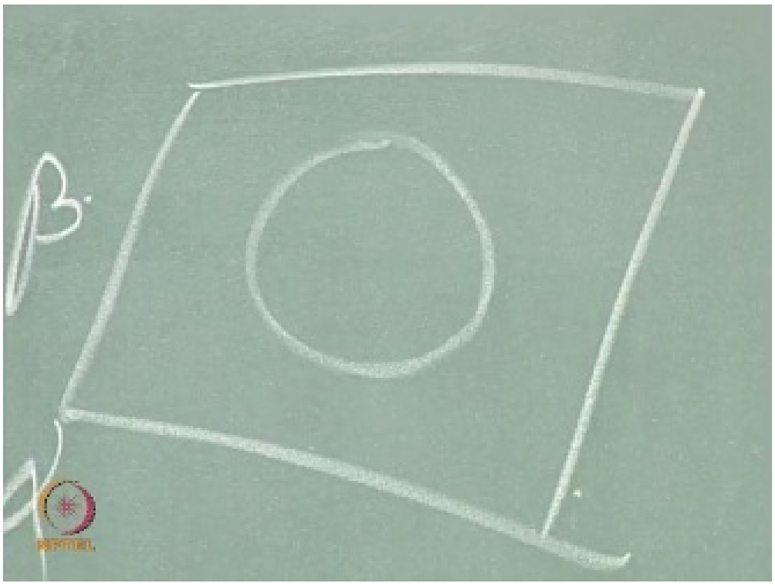

It is something like a flat surface. And, in that circular area, the solid has nucleated. And, solid has formed like a like a balloon. And so, this area before the solid has nucleated, it was actually a particle liquid interphase. So, I can say that this is equal to this (Refer Slide Time: 37:22). So, considering these two total surface energies, this overall surface energy has to be smaller than that. Then only, you would have heterogeneous nucleation. So, whenever I say heterogeneous nucleation is taking place, when does that happen? It happens when this is very small (Refer Slide Time: 37:40). When gamma PS is very (( )) because gamma Sl does not depend on what particle I am adding. Gamma Sl is between liquid and solid. That has nothing to do with which particle I have added. But, it is gamma PS, is decided by actually the structural compatibility between the solid and particle.

Whenever you see the particle as a very similar structure, that is a reason why when I take an aluminum alloy, I add a TiB2 particle; it acts as a good nucleating site. Why? Because the TiB2 has a structure, which is hexagonal. And, whenever you have a hexagonal structure, there is some similarity between hexagonal structure and aluminum. What is the structure of aluminum? FCC. What is the similarity between these two?

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Yes. Some plane of FCC has a similar packing to that of another plane in HCP; the basal plane of HCP and the 1 1 1 plane of FCC have exactly similarity. So, on the basal plane of TiB2 particle, actually an aluminum can grow. And, that is how the actual nucleation takes place. And, just because structures are same; I mean there is a compatibility that is not sufficient. What you have to also look is what is the interatomic distance in the basal plane and what is the interatomic distance in the 1 1 1 plane is also important; otherwise, there is strain during this nucleation. So, that is why actually when we talk about different particles being added, we look at whether first of all there is a structural compatibility.

For example, if I add a cubic particle into a an aluminum; for example, titanium carbide is a wonderful nucleating site for aluminum, because it is cubic. If I add a cubic particle because aluminum is cubic, it has easy compatibility. But, if I keep on adding different cubic particles, but with the different lattice parameters; and at some stage, you see that lattice parameters of this cubic particle that I am adding is entirely different from that of the aluminum lattice parameter. Though it is cubic, it may not nucleate. So, all that is reflected in terms of one single parameter called gamma P S. So, that is why, we talk in terms of what is called coherent interphases, semi-coherent interphases; all that comes from here (Refer Slide Time: 40:14). Then, there is a lattice parameter compatibility. And, you can see that when this is much smaller, so that this is satisfied, then only you have nucleation.

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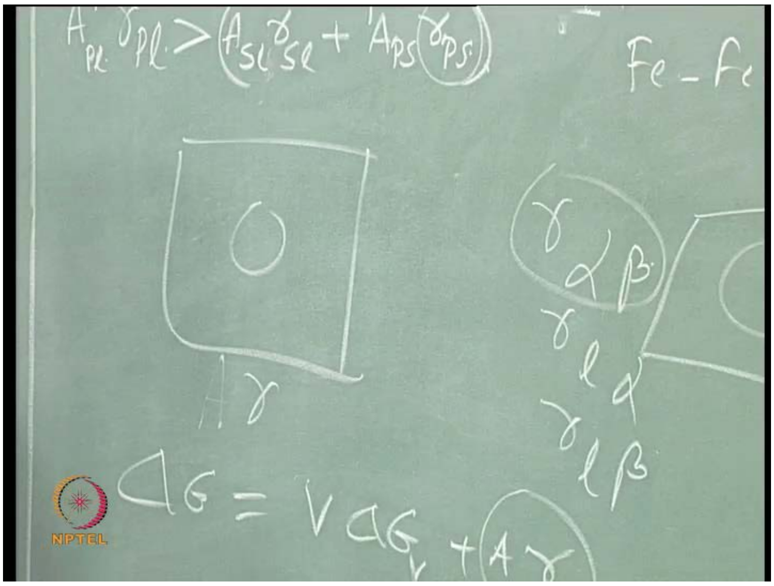

Similarly, here when you have these three interphases, the interphase, which has the lowest… In fact, when I want to talk in terms of this; for example, in case of eutectic, I have to split this A gamma into three parts. I have to say A of alpha beta into gamma of alpha beta plus A of alpha liquid into gamma of alpha liquid; and, A of beta liquid into gamma of beta liquid, because these all three are together. So, I have to spilt this into three parts. And, out of the three parts, whichever is the lowest, the system would like to choose that. And, that is the reason why wherever you see lamellar eutectic, it means actually the alpha-beta interphase energy is the lowest. You can actually calculate it or see a hand book, where the interfacial energies are available. And, you would see that this is true.

Whenever this is smallest, you will see that happening. And, if one of these two is (Refer Slide Time: 41:32) smaller, then what should happen? When one of these two is smaller, for example, if I assumed alpha liquid interfacial energy is the smallest, then you see inside the liquid alpha will nucleate first. The moment liquid-alpha interfacial energy is smaller than alpha plus beta, alpha plus beta will never look together as a couple. You will see alpha nucleating first. And then, the remaining liquid slowly converts to the beta, so that you will have a beta matrix and alpha particles; it can be alpha particles, it can be alpha needles, it can be alpha plates depending on growth conditions. Depending on what is the structure of alpha, for example, if you look at cementite, cementite is a particle in a ledeburite; whereas, aluminum silicon eutectic if I look at it, the silicon are needles. Why? Because the diamond cubic structure of silicon is such that some directions can grow much faster than the other directions.

Maybe if you have read about solidification, the growth directions are different, because in all the directions the growth rates are not the same. Have you ever heard about it? For example, if I take a cubic structure, if I take aluminum nucleating inside, we always say it is spherical nucleus. Actually, first and foremost is never spherical. Never a nucleus is spherical, excepting a situation where a liquid is nucleating out of a gas, because there is no crystal structure there. The moment you are talking of solid nucleating out of a liquid or a solid nucleating out of another solid, you can never ever have a spherical, because solid nucleus is composed of unit cells. It would tend to minimize the surface energy; not tend to become spherical. It would tend to minimize the surface energy by choosing such a shape, which has the lowest surface energy. That which you think is sphere, but it is actually not.

Coming back to that point; here (Refer Slide Time: 43:54) you understand this that it would be alpha that nucleates and grows and then rest will be beta. And, in other case where liquid beta interfacial energy is lower, you will see beta nucleating and then growing. So, depending on what is the situation, you will have either different morphologies of alpha, but you will always see that there is no lamellar nature there. You will always see something growing inside the other one. So, when the eutectic reaction is finished, when you look at the microstructure, you will see one phase embedded in the other phase. The moment you see embedding of one phase in the other phase, you can easily understand for example, silicon inside aluminum are cementite inside austenite. It clearly tells you that the cementite has nucleated first.

Similarly, there also, silicon has nucleated first than the alpha aluminum. So, by looking at microstructure we can know which has nucleated first. And, that gives you an idea whose interfacial energy. Not only the interfacial energy, I have to also caution you here, interfacial energy is one aspect. The second aspect that decides which will nucleate first is a structure. It is also the structure that decides, because it is some structure of… One of the two phases has a very complicated structure let say; its nucleation is more difficult. So, the kinetics will force that one of the phase nucleates first rather than the other phase. So, that is also another point.

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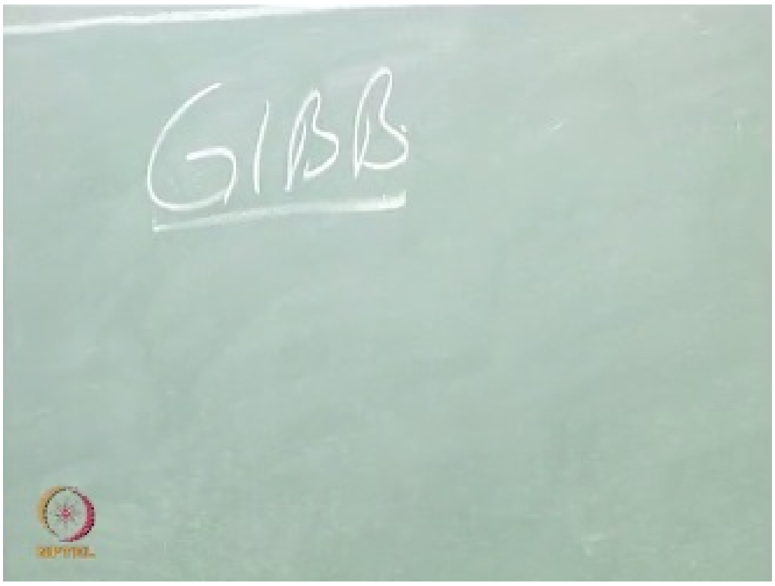

Now, coming back to this point of shape of the nucleus; lot of people have worked on it; many. Have you heard of this gentleman by name this? Of course, the whole thermodynamics that we talk about; the free energy that we talk about is Gibbs. Gibbs has worked on it for quite some time to understand what is the shape of the nucleus.

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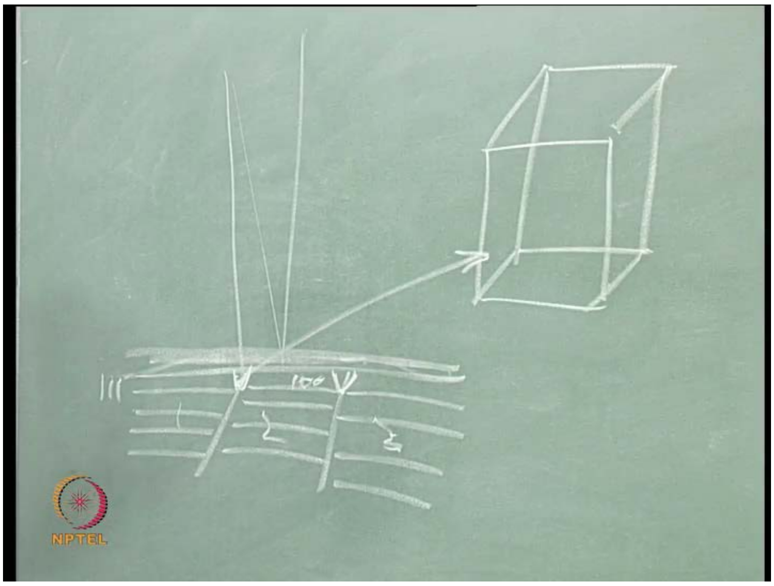

And, that is when he has realized that when I look at a particular a cube let say; in a cube, there are different phases; different planes in a cube. You have the 1 0 0 type, 1 0 type, 1 1 type; verity of phases. Each of them has a different surface energy. Do you accept this? The 1 0 0 plane will not have the same surface energy as 1 1 1 plane. In fact, that is the reason why when you take a polycrystalline metal and put an (( )) on it and then see it in a microscope, you will see different shades; some grains look black, some grains look bright, some grains look some grayish. You must have seen this. And, what is the reason that we say?

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Yes, if you simply look at a sample with different grains let us say; and, let this is (Refer Slide Time: 47:04) grain 1, grain 2, grain 3. And, if the light falls on it and goes back; and, you are seeing the light, which is coming through the eye piece; and, depending on what is… And, this happens only when I have a (( )) there; I put an (( )) And, what is this (( )) doing? It is selectively dissolving different regions. Whichever regions are more reactive, it dissolves more; whichever regions are less reactive, it does not (( )) And, this reaction depends on the surface energy. That is the reason why we start seeing the grain boundaries first. Why? Because grain boundaries are high energy regions. So, they get attacked first. So, you see a pit formed there at the grain boundary. Once a pit is formed, the moment light enters there, it does not get reflected back towards the objective; it goes out. So, the light that is coming through, it goes out like that. Once it goes out, it does not reach the objective. And, if it does not reach the objective, you see it as black. That is why grain boundaries look black for you.

Now, similarly, looking at these grains, these (Refer Slide Time: 48:14) grains also dissolve in a different fashion. Why? Because if I look at the planes that are parallel to this surface, for grain 1, grain 2, grain 3 are not the same; the atomic planes I am talking about. So, for example, in grain 1, maybe the plane that is parallel to the surface may be 1 1 1 plane; in grain 2, it is impossible to have 1 1 1 plane parallel to the surface; why? It is a different orientation. If the same 1 1 1 plane is parallel to the surface, then I do not call it as grain 2; both of them are same grain. So, as a result, you will see some other grain, some other plane; maybe 1 0 0 is parallel. And, maybe here 1 1 0 is parallel.

Now, if you look at these, each plane has a different surface energy. And, what does that surface energy depend on? It depends on actually the number of broken bonds. If you think of a plain like (Refer Slide Time: 49:20) this, there are atoms below it, but there are no atoms above it. Per unit area, how many number of atoms are not there decides the surface energy of it. The closest packed plane will always have a higher surface energy that way, because in a given area, you have more number of atoms supposed to be there; or, above it, there are no atoms; below it you have atoms. So, that is why, you see different planes have different surface energy. And, as a result, you will see the (( )) reacts.

Now, what Gibbs has done is he tried to look at these surface energies and tried to form a shape of what is called the nucleus based on the surface energies. And, I think we will look at that possibly in the next class.