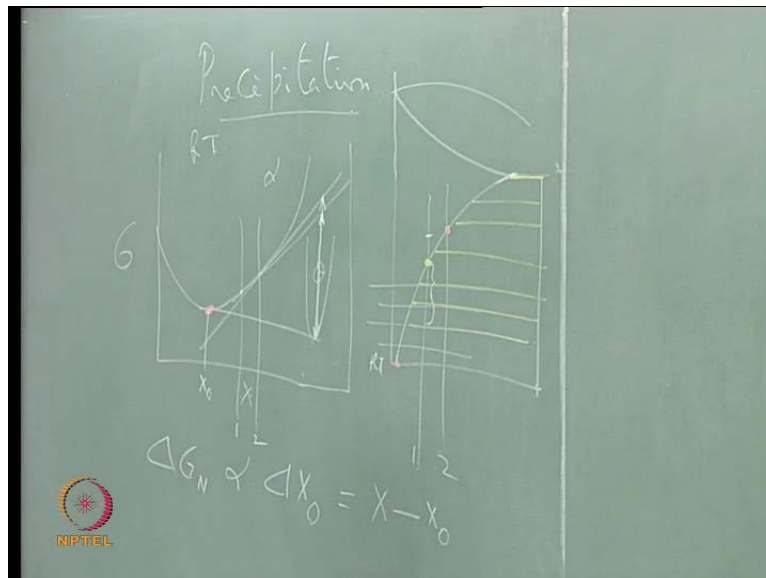


Advanced Metallurgical Thermodynamics
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Module #01
Lecture #19
Precipitation – Quasicrystals

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We will continue where we left in our last class on, “precipitation”. We were talking about one of the solid-state phase transformations - precipitation. When you look at precipitation, and talk about nucleation of a precipitate, we look at the free energy composition diagram; let us say. We talked about an alpha phase, which is nucleating a phase called; let us call it as beta or theta, whatever it is. In an aluminum-copper phase diagram, we call it as theta; let us say.

And if you look at the equilibrium between the two, this is the common tangent, which talks about equilibrium, and the corresponding phase-diagram is somewhere here; let us say, and this is at whatever temperature it is or let just say that we are talking about room temperature. At room temperature, this particular composition that you are seeing here is this composition (Refer Slide Time: 01:15). Am I right? This we know. So, whatever

composition that we are talking about here, is this composition. If you take an alloy of composition like this, which is what is the whole age hardening process that we talk about. So, the alloy is somewhere here; it is on the right side of the equilibrium composition, equilibrium composition of alpha in equilibrium with theta, and that alloy at this temperature; room temperature, this is where we are talking about, at this temperature, if it starts precipitating theta, the driving force for the nucleation of theta, is always given by the line which is a tangent, for the alloy... alpha, at the alloy composition.

At the alloy composition, if I draw a line, which is the tangent to alpha free energy curve, and wherever, it gets extended, at the precipitate phase composition, if you draw a vertical line, this difference indicates the driving force for the nucleation. We call it as ΔG for the nucleation (Refer Slide Time: 02:44). So, anytime you see an alloy, if you want to calculate, what is the driving force for nucleation of a particular phase, any phase it could be; in this particular case, I am just simply taking an example of theta. If I am taking theta, then simply take that alloy composition, it could be 4 percent copper, it could be 2 percent copper, it could be 3 percent copper, whatever alloy composition it is and for that alloy composition draw a tangent.

From the tangent position to the free energy of that particular phase at that temperature, what you get is the driving force for the nucleation. And in such case, if I change my alloy composition and choose another alloy composition here, in principle, if I draw another tangent here, you would see that that tangent would lead you to a different driving force. For the same phase and for the same theta to precipitate out of alpha, alloy 1 and alloy 2 (Refer Slide Time: 03:54) will have different driving force.

The larger the composition of the alloy, with respect to the equilibrium composition, the more away the alloy composition with respect to the equilibrium composition, the greater will be the driving force. So, the ΔG_N is proportional to ΔX_{naught} , we call it, where ΔX_{naught} is $X - X_{\text{naught}}$. What is X_{naught} ? X_{naught} is the equilibrium composition. This is very clearly seen here.

So, if I choose alloys of different compositions and that is the reason why a 2 percent copper alloy, and a 4 percent copper alloy, will have different driving forces at the same temperature. This, I am taking the example of room temperature, I can change the

temperature and if I change the temperature also and choose some other temperature, there also you would see the same thing. You can also see it in terms of the phase diagram. What tells you about the driving force is this (Refer Slide Time: 05:10). This is the actual driving force and I mean, not in terms of ΔG , for that matter.

You are at a temperature, for example; if I am considering the same room temperature for alloy 1 and alloy 2. For alloy 1 you are at a temperature away from the equilibrium transformation temperature. The moment you are below this equilibrium transformation temperature, there is a driving force for the second phase to precipitate. Am I right? If I am at a temperature here (Refer Slide Time: 05:39), obviously there is no driving force for the second phase to precipitate. If you want second phase to precipitate, I have to come below this temperature, which is called as the solvus temperature.

So, the farther away, the temperature is, from the solvus temperature, the higher the driving force, for the precipitation. For any alloy composition, if I am at different temperatures; so the lower the temperature is, the higher the driving force for that alloy. Now, if I am choosing two different compositions and choosing the same temperature, fixing the temperature but changing the alloy composition. You see that by changing the alloy composition, what is changing here, solvus temperature is changing. Whenever I change the alloy composition, for example, alloy 2 has a different solvus temperature. This is the solvus temperature here, and this is the solvus temperature in this particular case (Refer Slide Time: 06:38).

So, because the solvus temperature is changing, and is increasing as I increase the solute content. If I am fixing my transformation temperature, where the actual transformation is going on, as a fixed temperature, now you see the difference between the solvus temperature to the temperature at which the transformation is taking place, is larger in case of alloy 2, and is smaller in the case of alloy 1. This means again, alloy 2 has a greater driving force for the precipitation, when compared to alloy 1. So, you can see that by choosing an alloy of appropriate composition, and that is the reason why people want to choose as larger solute content as possible, but that is limited by something. You cannot choose any composition of your choice and is limited by what? (C).

It is decided by what is the maximum solubility, of the solute, in the alloy. That means if I extend this phase diagram somewhere here, I mean, let us not bother about what is on

the other side. Let us only look at this particular composition (Refer Slide Time: 08:06). This is what decides, what the limit to which I can go. That is the maximum and if I go beyond this, then what I have, I have a situation, where I cannot actually solutionize the alloy.

I cannot take it into a **single-phase solid-state** single-phase solid solutions condition. Unless I take the alloy to the single phase there is no age hardening, it does not start. In age hardening process, the first step itself is to take it into a single phase, then quench it, and then you try to do the aging, to precipitate the second phase.

So, in case you cannot get, for example, if I choose an alloy of this composition (Refer Slide Time: 08:49) and this is one of the typical cases of the 6 percent copper alloy; let us say. A commercial alloy-2219; if I take an aluminum-2219 alloy with about 6 percent or 6.5 percent of copper in it. With 6.5 percent of copper, the moment I start heating it, actually in principle as I keep on heating it. What should happen to this alloy? This alloy; this has been solidified, brought to room temperature, now I am heating this in a furnace, to different temperatures. What should happen to this alloy? Theta has to dissolve. Why theta has to dissolve? Because the solvus line, if you carefully observe, the solubility of copper in alpha aluminum, is increasing with increasing temperature and that is what this line tells you.

So, because the solubility is increasing and at each temperature, if I calculate what is the volume fraction or the weight fraction for the second phase, the weight fraction of the second phase keeps on decreasing, if you use the lever rule. Because, what is decreasing is this length is decreasing. Is it not? From that, you can feel that from the lever rule the amount of theta is decreasing, and that amount of theta, where should it go. It gets dissolved into the matrix, in such a way that, the matrix compositions get richer in copper. Because the theta, which is a copper rich phase, is dissolving into the matrix, the matrix becomes, enriched in copper content and that is what you keep seeing, and until the eutectic temperature, you would see that this would keep on happening.

Even at the moment, you reach the eutectic temperature; you will still have some theta and some alpha, alpha at the temperature of eutectic. The moment you reach this eutectic temperature (Refer Slide Time: 10:48), let us say you are just below the eutectic and melting has not yet started. If you are just below the eutectic, then you will see the alpha

composition will be this. You will still have some theta, which is decided by this length of the line, divided by the total from that to the theta phase, wherever theta phase is. That is how we calculate.

So, you can see this tells you that there is still some amount of theta, which means complete solutionizing has not happened. But still, you can take such an alloy, and in such an alloy, where is the theta? Theta is still at the grain boundaries. Though it is dissolved, some amount of theta is still left out at the grain boundaries. This is because during solidification, solidification happens at a slow condition; as a result theta is precipitating at the grain boundaries only. So, you will see that the theta is there at the grain boundaries.

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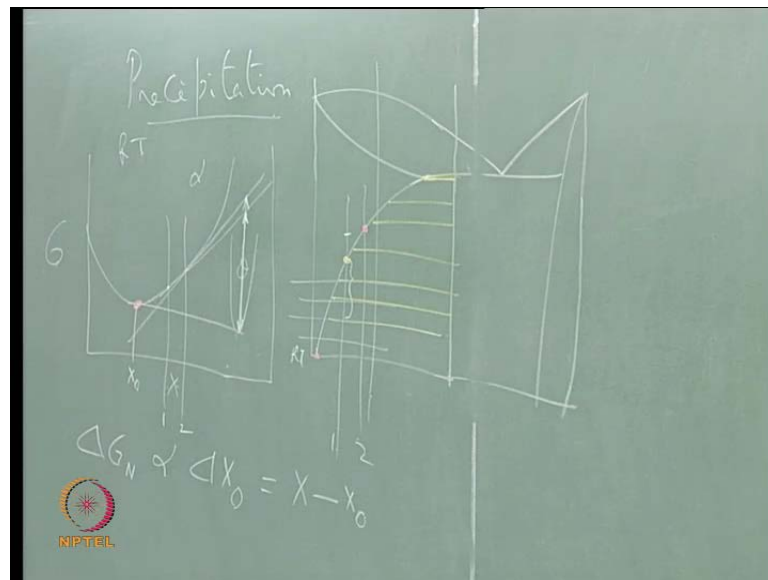


But the matrix, if you look at it, the matrix got enriched, but still you have theta here. **and so this...** If from that temperature, if I quench it, then what should happen? So, alpha which is there here, will remain as super saturated, because I am quenching it, but theta, which is there at the grain boundaries, will remain as theta; depending on what is your alloy composition, some amount of theta will be there, according to the phase diagram.

This alpha, which is now super saturated alpha, and which has formed at the room temperature, when you quenched it, that particular super saturated alpha is the one, which will start precipitating out. So, in such an alloy, you still have age hardening taking place; you will still have precipitation taking place, but in addition to the

precipitate, you will also have the theta, which has been formed during solidification, at the grain boundaries. So, you still have some theta, which is at the grain boundaries. **And in fact this theta...** How does this theta form? Can somebody tell me, during solidification? The theta which you see, it forms from the eutectic reaction.

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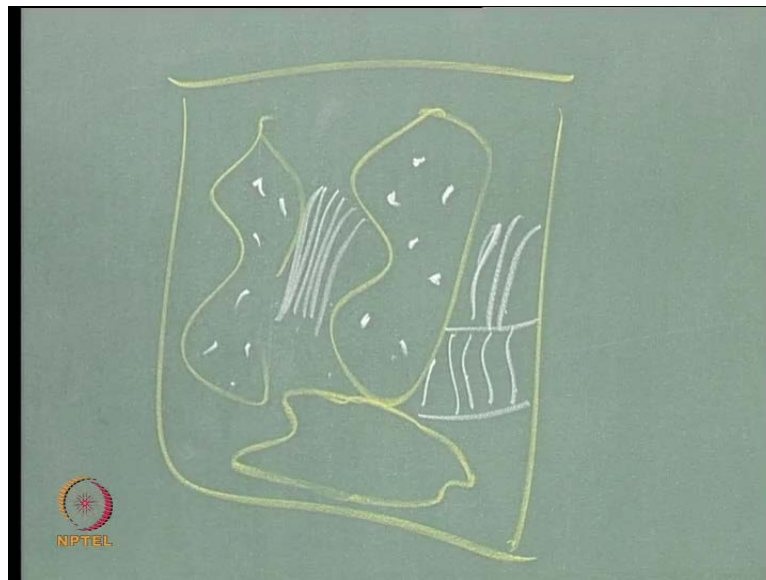
If you look at this alloy, and then extrapolate this phase diagram, let us say that you have theta somewhere here, forget about this, if you have, forget about this line. So, these alloy, if I am solidifying it; how does it solidify first? It is a hypoeutectic alloy, so what comes out first? Alpha; Alpha dendrites come out first. So, you have the alpha dendrites, and once you reach the eutectic temperature, it is the eutectic mixture which comes out of the liquid. What is the eutectic mixture here? It is the alpha plus theta. So, at the dendritic boundaries, these dendrites will get converted into grains, later.

So, at the grain boundaries, where you have actually entered inter dendritic regions and those regions are the ones where you have the theta. So, theta will be present in the form of not as I precipitated. So, if I look at this alloy, this alloy will be a different alloy. This alloy will be entirely different from this alloy in terms of what is the morphology of the theta. In this case, you see that this alloy solidifies completely as single-phase alpha, am I right? Solidification is only single-phase alpha, there is no eutectic there, and this alpha, as I am cooling to room temperature; it starts precipitating the theta and that theta comes out at the grain boundaries. Whereas, in this alloy, the theta that comes out, the theta that

does not come out by precipitation from the alpha, it comes out as a eutectic mixture. But you can still ask me, Sir, “That after the eutectic reaction, when I still cool it from the eutectic temperature to room temperature, what is suppose to happen during solidification?”

After solidification is completed, but that solid is now cooling to room temperature, should anything happen in that alloy. (()) It should increase. Why it should increase? It is because the solubility of copper in alpha is decreasing. Where should that increased theta appear? (()) It cannot nucleate inside. So, in principle it would possibly nucleate on the existing theta, which is there during solidification. Whatever, because already theta is there in the eutectic mixture and that theta gets precipitated over that, because it does not need further nucleating sides.

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So, you would usually see the microstructure, would look like the dendrites and in the inter-dendritic regions, you will have, whatever may be the morphology is, in this particular case, actually you see a lamellar morphology. So, you will see actually a lamellae of, there can be boundaries, which are called eutectic colonies and you will see lamellae where you have that. After the solidification as you, further cool it and if you want to look at where does this form, so that extra theta phase will start forming on the theta, which is already there close to the dendrites. This is because the excess copper is coming out of the dendrites actually. It is dendrites, which are releasing all the copper.

As a result, nearer to these dendrites, the precipitation happens. So, in principle you can also see the theta nucleating either at the grain boundaries, which are the dendrite boundaries or on the cement...theta which is already there; one of the two. (()) That is what I am saying they are alternate layers, the white and the black, white and black, what you see are the alpha, theta; alpha, theta; that is what you are seeing there. On this, for example, if copper that is coming out, will not go and precipitate on this theta, where it has to travel a farther distance. So, in principle if there is a theta, which is already available here, that theta becomes thicker or the theta will form as a layer on the existing alpha.

So, you will have two morphologies of theta, one theta that is already present in the eutectic mixture and second theta which is there at the grain boundaries or the dendrite boundaries if you want to call them so. Whereas, in this case, you have the alpha coming out as the grains here, after the solidification and the theta precipitation is only there. When I am heating this back, now both the thetas start dissolving: the theta at the dendrite boundaries and the theta, which is there within the eutectic mixture.

Both of them start dissolving and as a result, once you reach this temperature (Refer Slide Time: 18:37), you will have some theta that is left out. Now, when you quench it, this particular, and because the theta has dissolved, these dendrites now become richer in copper, to the extent of what it would have had, just after the eutectic reaction. Just after the eutectic reaction, alpha had this composition. So, if you have heated this alloy back to that temperature, you have more or less that particular condition which was just after the eutectic reaction, what was the existing alpha.

And that alpha when you quench it, you will have that alpha, retaining all the copper content and when you start heating it, for the age hardening, then that particular alpha precipitates inside it (Refer Slide Time: 19:22). Some phase which is depending on whether it where what is the under cooling that we are talking about, because in the last class, we talked about, whether GP zones come out or theta double prime comes out, or theta prime comes out, depends on what is the temperature at which we are doing the age hardening, for a given alloy. That is what you have seen different solvus lines, we have drawn and depending on that, we can see that.

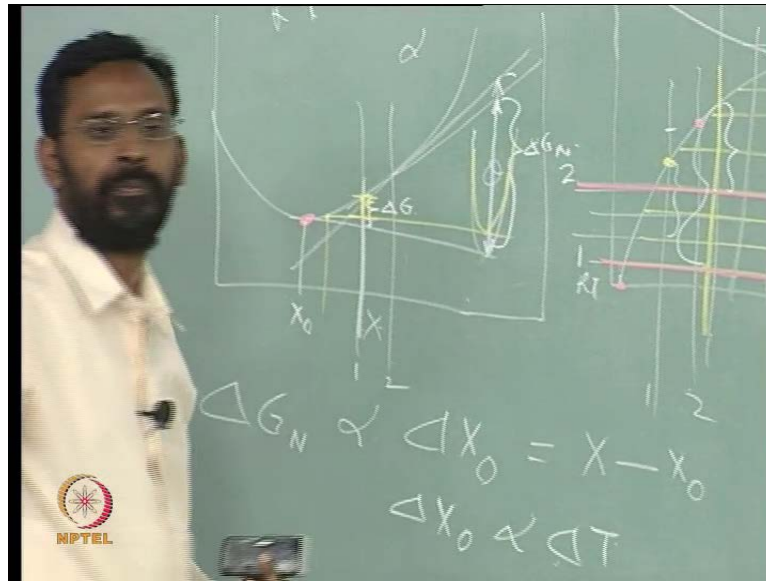
(())... Because again this copper which is there, inside the dendrites, and because we are doing age hardening at this temperature, let us say. So, if it has to nucleate on the theta, which is there, it has to travel a larger, and these are all 100 microns or so, generally grain sizes. So, it has to travel a long distances and at that temperature it is not easy for it to happen, and that is the reason why, it avoids because the time available is shorter.

Otherwise, in principle, if you leave it forever, you will see slowly the diffusion can happen and then some precipitation can happen at the grain boundaries also. But otherwise, because the time availability is shorter, and the temperature is very small and the diffusion is difficult, and at the same time the alpha is super saturated, and it is not stable, because we can see here (Refer Slide Time: 20:54); it is not stable. Alpha single-phase alpha is not stable. It wants to precipitate; it has a higher free energy than a two-phase mixture.

As a result, it wants to come out, bring out the precipitate, and that can happen only by precipitating within the grain. So, this is how you will see, if you have a composition of that sort. But if you are talking of compositions, which are to the left of it and most of the precipitate hardening, we are only talking about those compositions. We actually not talking about this kind of composition (Refer Slide Time: 21:25), because this kind of compositions is not ideally suited for, you know age hardening, because you will somehow have some prior theta, which has been formed during solidification.

As a result, the full advantage of age hardening, which is the combination of ductility and strength, that you want to have, is not possible to be achieved, because of this kind of samples. As a result, you always try to restrict to, let us say, 4 percent, 4.5 percent or 5 percent. In fact, though I say this is the limit, in principle you do not even reach there, because there is another problem associated with it. What is the problem? For example, if I choose this alloy. You may say, this alloy is still to the left of maximum solubility, so why cannot I use that alloy.

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Yes, the range between the solvus and solidus is very small. When that is very small, when you want to do homogenization treatment, what we call in steels as austenization treatment and here we call it, as you know homogenization treatment. So, during that homogenization, if you do not maintain your furnace temperature carefully, you end up into this domain. Once you end up into that domain, some liquid forms, and the liquid usually forms at the grain boundaries.

So, the moment the liquid forms, immediately you will see, the liquid composition will be something of this sort and that liquid when you start quenching it, starts precipitating out some theta, at that grain boundaries. So, you cannot prevent that liquid to solidify. So, that is the reason why, we do not want to go into a liquid state. Because you are not in a single-phase state, you are into a two-phase region and the whole purposes of solutionizing or whole purpose of homogenizing is to get into a single phase state; you do not want to come to a two phase state.

So, that is the reason why you have to have a reasonable margin, considering the furnaces, that are used in the industries, where the temperature ranges, I mean accuracies would not be the order of one degree or so. They could be of the order of 10 degree or 20 degree. So, you need to consider that. So, has to define what the maximum composition to which I can go. So, the reason why I am saying all this is, the higher the composition higher the driving force, and for the same alloy composition, the driving force can be

further changed, by simply changing what? Temperature; once I fix up my composition (Refer Slide Time: 24:08), the only way I can change the driving force is by changing the temperature; a higher temperature or a lower temperature, which is preferable?

A lower temperature will have a higher driving force. So, that means, you can say that the ΔX_{naught} is proportional to ΔT . Am I right? So, the higher the under cooling; instead of choosing a temperature of this sort, if I choose the temperature of this sort (Refer Slide Time: 24:41); so obviously, you see here, this is the ΔT and in this case, this is the ΔT . The higher the ΔT , then the higher is the driving force. The driving force, you can see, the extent of super saturation is larger, and here the extent of super saturation is smaller and you can also see on the free energy diagram. How does the free energy diagram change with respect to this temperature and this temperature? Which will shift up? Which will shift down?

Let us say for example, instead of temperature 1, I have increased to temperature 2, what would happen to free energy curves? Both will go up, and then. (()) Relative moment of theta will be larger, and then. (()) How does it shift the ΔG ? We are all bothered about that. How does the ΔG change? Will the ΔG change? By ΔG , I mean for the moment I fix up my alloy composition. This is my alloy composition and this is the ΔG , I am talking about and this is the overall driving force (Refer Slide Time: 26:04) and whereas this is, let say, I am talking of this alloy. So, this is the ΔG for nucleation.

We have two ΔG 's. One is the overall driving force for the precipitation. This is the driving force for the nucleation, just for the nucleus to form, at the start of the nucleation. But this is for the complete transformation. What is the ΔG ? And this ΔG , how will it change? By changing the temperature it will decrease. Why it will decrease? (()) Yes, the moment you see that this goes up (Refer Slide Time: 26:42), with respect to alpha, what should happen. So, for example, let us assume that this theta has shifted this time to this.

Now, alloy composition is fixed, your alloy has not changed. What has changed is this common tangent composition; that means, the composition of alpha in equilibrium with theta has shifted and that is shifted to a higher copper content. Once that is shifted to a higher copper content, this value (Refer Slide Time: 27:26) decreases and that is how

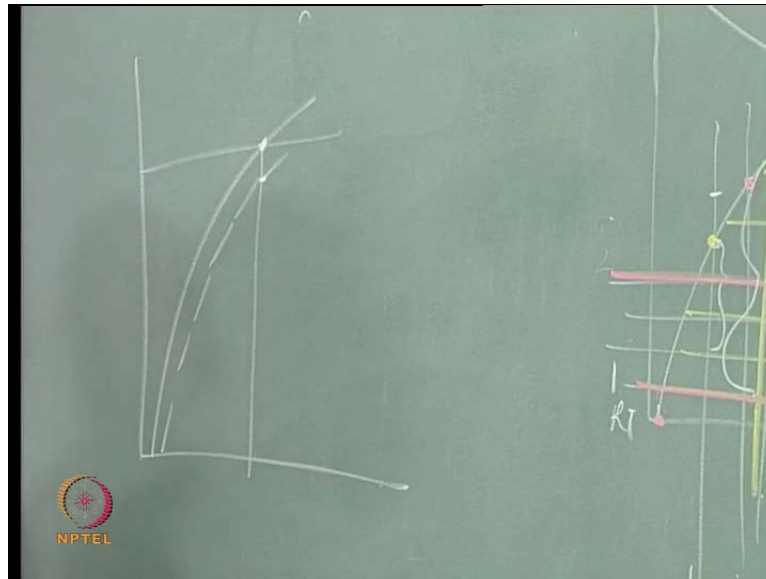
because this is a positive term (Refer Slide Time: 29:36). And as a result, the activation barrier that you are going to get is going to be higher activation barrier.

So, the moment, I consider a strain energy term in a solid-state transformation, so this activation barrier, which is the ΔG^* that you get, if you again calculate using the ΔG , which is a summation of the overall energies plus γ ; $A\gamma$ and V (Refer Slide Time: 30:10), and the way we do is put this values V and A , in terms of the r , and then differentiate free energy with respect to r and then equate that differential to zero and that is how you get these values, r^* and ΔG^* , and if you try to look at this ΔG^* , the ΔG^* value is going to be larger here, because this ΔG has got decreased.

So, in principle if you write r^* expression, you remember this, you get this ΔG , 2γ minus 2γ by ΔG , here you have to consider this (Refer Slide Time: 30:51). So, wherever ΔG is there, you will see that ΔG becomes ΔG minus $\Delta G \epsilon$, because both are volume terms.

So, as a result, the r^* is going to be larger, because this is decreased. So, you will have a bigger nucleus and then if you again put this back into the ΔG^* term and calculate the ΔG^* . ΔG^* is again $\frac{16\pi}{3} \gamma^3$ by $\Delta G v$ square. So, you will see $\Delta G v$ minus $\Delta G \epsilon$ square; again, because this value is decreased (Refer Slide Time: 31:35), this value will be higher. So, you will see the moment we talk about solid-state transformations, you need to consider these things, the strain energy particularly, which the new term, that is coming up is and that new term will decrease everything.

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And because of that, in principle, **if you even consider...** if I take an alloy of this composition, this is the actual transformation temperature for that particular composition, which is what we call it as solvus line. This is assuming that there is no strain energy term. All phase diagrams when you draw, we do not consider any strain energy term. We do not even consider surface energy term also.

So, in principle now, the moment you consider the strain energy term, you will see the transformation temperature comes down. Transformation does not happen there, it happens at a lower temperature, because only when you come to a lower temperature, you have sufficient driving force, which can overcome the strain energy term. So, that you have the actual transformation taking place.

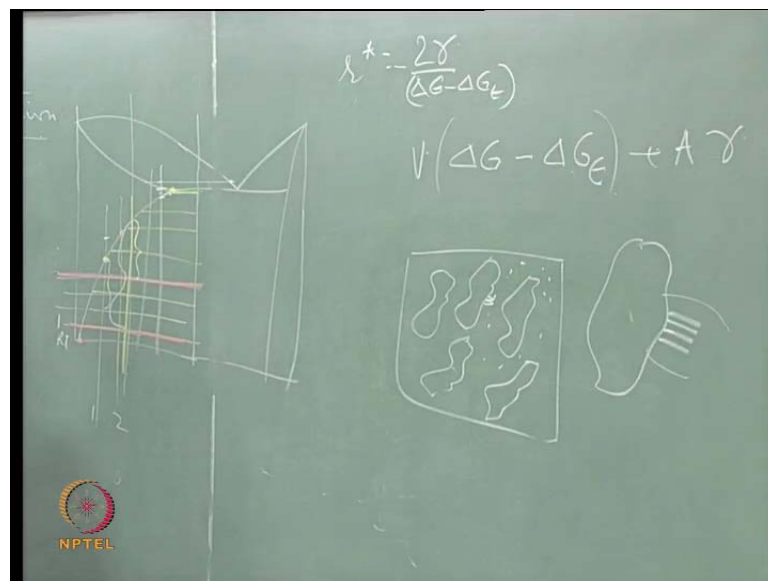
So, if you now, consider the solvus line, considering the strain energy, you would see a new solvus line coming up. This has nothing to do, with the theta double prime solvus or theta prime solvus that we have talked about it. Simply, just whatever may be the phase that is coming out, as long as this (Refer Slide Time: 33:22) is a non-zero term. When we will this be non-zero and when this will be a zero. When you have perfect coherence and when the misfit is zero, whenever the misfit is zero, and misfit being zero is a too idealistic situation.

So, when the misfit is zero, in principle, this is zero (Refer Slide Time: 33:44), and when that is zero, everything changes. This becomes equal to this; these values will be similar

to a liquid to solid transformation. We need not have to bother about it, and then this solvus line gets shifted to that. So, you can see that all these things are shifted just because of one term called strain energy term, which comes in and that is why all the solid-state transformations are somehow trying to see how to minimize this strain energy and the surface energy.

This is what we talked in the last class also, where the system tries to minimize the strain energy by choosing that particular phase, which can be coherent. So, that the surface energy is minimum, and at the same time that particular shape, which can have the minimum strain energy. This is how we have seen. (()) Now, there is no precipitation there. Where is the grain there, when you still have a liquid there, why do you talk about grain?

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Let us say, how is the solidification? This is all the liquid, and then inside the liquid, you have the alpha dendrites, which have come out. These are all the dendrites; of course, you can have side branches and things like that. So, now the liquid that is left out, is somewhere between these regions. This is all the liquid; there is no grain boundary still here. We can only talk of regions which are inter dendritic regions, between the dendrites, and the liquid that is left out, between the dendrites is the one, which is undergoing the thing. Then the question is, where does the eutectic nucleate, and in fact

another question, also people always bothered for quite some time, is what nucleates in the eutectic.

If you have an alpha plus theta in a typical eutectic phase diagram, **this was...** and in the eutectoid, lot of people studied eutectoid in much more detail, because it is the solid-solid, you can easily study, because you can have a XRD, going to the temperature and also you can quench that, after just precipitation has started, reaction has started eutectoid reaction, and you can quench it, then see what is the phase that is coming out.

But from a liquid to solid, is not easy to find out, what actually is the first one to nucleate in a eutectic mixture. Because whenever you say there are two phases, which are nucleating simultaneously, but how do they nucleate simultaneously, because both of them have two different structures. One is alpha; another is theta, in this particular case, let us say. How do alpha which is a FCC structure, theta which is an orthorhombic structure, nucleate simultaneously. It is not an easy thing. That is where people have seen, that if is a hypoeutectic or a hypereutectic, life is very easy, because if it is a hypoeutectic, you already have an alpha dendrites.

So, in eutectic mixture, when the eutectic mixture is forming, you can have the nucleation that can occur (Refer Slide Time: 37:04) on the alpha which is already there. And it is because it is alpha is already there, it will be the alpha of the eutectic mixture, which will nucleate first, and the moment alpha forms, because alpha is a pure aluminum kind of a composition, and the regions which are next to it, become rich in copper. So, theta comes out. So, it is like one follows the other, the theta follows the alpha.

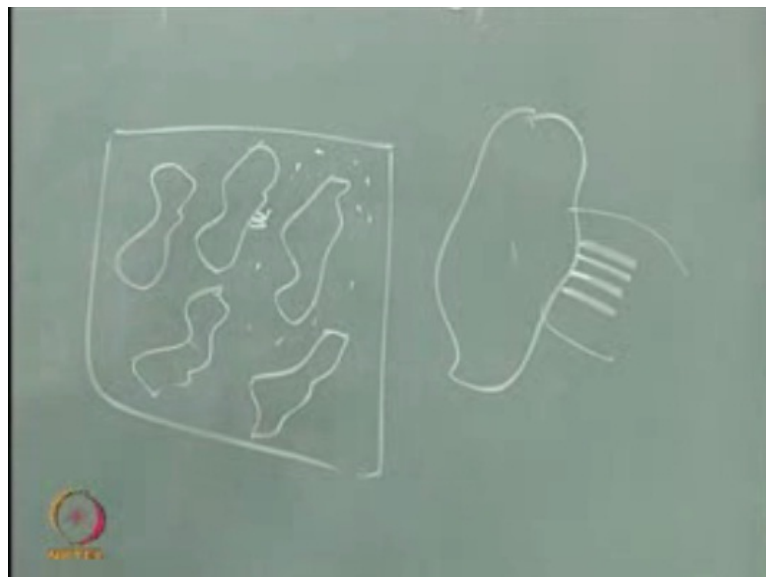
Though nobody has actually seen the nucleation and is not easy to see, because that happens in such a fraction of second and in such a small scale, a few nanometer scale, so you really need very high resolution microscope to be able to catch that nucleation event, and also catch in situ; if you can keep a liquid, at that temperature, in a high resolution electron microscope, let say, and then cool it and then see the solidification happening, you can really see it at a high resolution state, but it is not so easy.

So, that is easy to understand on a hypo, on the hyper we already know, it is a theta that has already come out. So, you can say the theta of the eutectic mixture nucleates, on the theta which already existing, but, if you are exactly the eutectic composition, it is very difficult to say. That is where people say, the phase which is easier to nucleate, which

has the lower activation barrier, whose structure is similar to that of the liquid structure, is what nucleates first. So, that is where people always say FCC kind of phases, are more easy to nucleate than orthorhombic kind of phases and that to it is inter metallic compound.

So, inter metallic compound nucleation is more difficult, than a solid solution nucleating. This is because in solid solution, it is all random. Chemically, it is random. Structurally, it is not random, but chemically it is random, whereas, in inter metallic compound you have an ordered structure. So, you have fixed positions for the copper and aluminum sitting there. That is why it is more difficult to nucleate. Anyway those are the issues. So, here there is no grain boundary that we talk about.

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So, the nucleation starts, let us say here. If I enlarge it, let us say this is the thing. So, you will have things like that. So, the moment a small nucleus, let us say, alpha nucleates, next to it becomes the theta, and on both sides the theta. Once the theta comes, the region next to it again, becomes poorer in copper. So, alpha comes out and that is how a small colony forms, and the colony starts growing, and there will be another colony somewhere else; another nucleation event.

You see the whole nucleation is actually on the alpha, and then grows into the liquid. This is how it happens. (()) Inside the liquid, all aluminum and copper (())... What is the short range order of aluminum and copper will correspond to FCC and

orthorhombic? (()) So, this is the interesting thing, when you say short range order, so inside the liquid, when aluminum and copper are there, it is not that all aluminum, copper atoms are segregated somewhere, all copper atoms are segregated somewhere else. It is all a mixture; it is a liquid solution, where inside the liquid, copper atoms are statistically there, whatever is the percentage.

So, the probability of finding a copper atom at any particular point will be, let us say 0.4, because of 4 percent of copper; let us say. So, that is how you should look at it. (()) Yes, because... there are..., you see the question is the phase is stable.

So, the moment alpha comes out, the remaining copper atoms that are there; because the phase that is most stable there has a lowest free energy is the orthorhombic; no other structure has a lower free energy. The atoms get to rearrange themselves to that particular structure. (()) Because it is not stable as simple as that; It is not stable.

According to the phase diagram if you look at it, for that alloy composition, this is the stable (Refer Slide Time: 41:20). You cannot get anything else, the question is why, for example, for aluminum, why FCC? Why not BCC? The same arguments holds good here, though copper atoms are there, the copper atoms could, in sometimes, you can get what are called metastable phases. For example, we have seen in number of cases where, when you are cooling, even in precipitation hardening also, we are seeing the GP zones, theta double prime, and theta prime. These are all metastable phases. They are not stable phases. The ultimate stable phases is the theta phase, am I right?

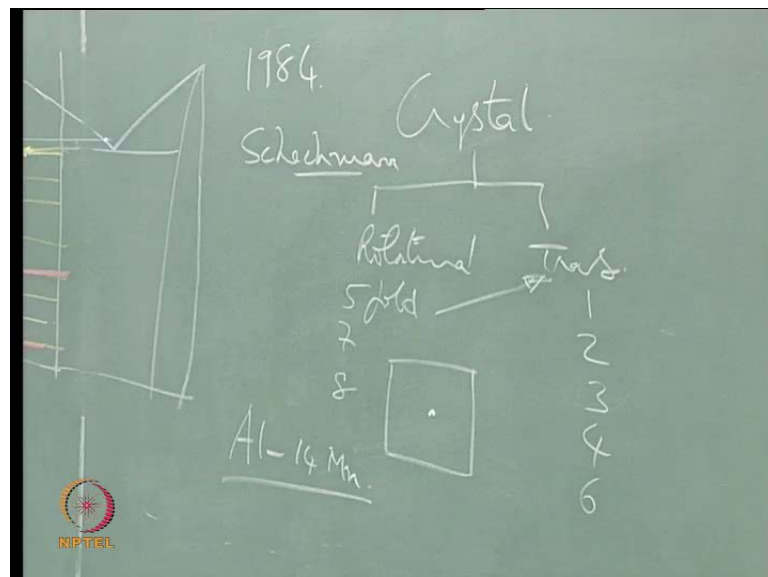
Similarly, also during liquid to solid transformation, sometimes you may get particularly, when you are cooling it rapidly. For example, assume that this alloy is being cooled very rapidly, then the theta phase which is orthorhombic you said it is more difficult to nucleate. So, it is very difficult for it to nucleate. So, the system will try to choose that particular phase, which can easily nucleate, if there is a metastable phase, but that would be remain always as the metastable phase, provided you heat it, it will come back to the theta phase.

There are quasi-crystalline phases also, which form generally, when you cool it, quench it. Many alloys people have seen, particularly aluminum alloys: aluminum iron, aluminum vanadium, aluminum manganese, a number of cases, people have seen quasi crystals form, when you take the liquid and quench it, because in the quasi-crystalline

structure, the clusters, the short range order inside the liquid is similar to that of the arrangement in the quasi-crystalline structure.

So, as a result you will see the liquid prefers to give you this, rather than the equilibrium inter-metallic compounds; but these phases are metastable. Obviously, when you heat the quasi-crystal, it gives back the equilibrium phase. (()) Yes correct, the difference between the two is it has a structure. The quasi-crystal, as the name suggests, it is a crystal. It is one type of a crystal. The only thing that is missing in a quasi-crystal is the translation periodicity. I do not know, how many of you read about crystal.

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Any Crystal, I mean we are deviating, but maybe, we will talk at some other time. Any Crystal has two types of symmetry, one is called rotational symmetry, and another is called translation symmetry. Have you heard of this? A translation symmetry means that if you take an atom here and go in a particular direction by a particular unit distance x ; let us say, you find another atom, and in the same direction, you move by another x , you should find the third atom. The moment you find it, you say, yes there is a translation symmetry, that is what we call it as periodicity. What is this rotational symmetry? That means, around a particular atom, if I rotate the unit cell, in a particular angle, that unit cell you would see, would merge into itself.

No new parts are generated. For example, if you take a cube and I rotate it along, around its axis, which is the z axis, let us say by 90 degrees. You will see this in that unit cell,

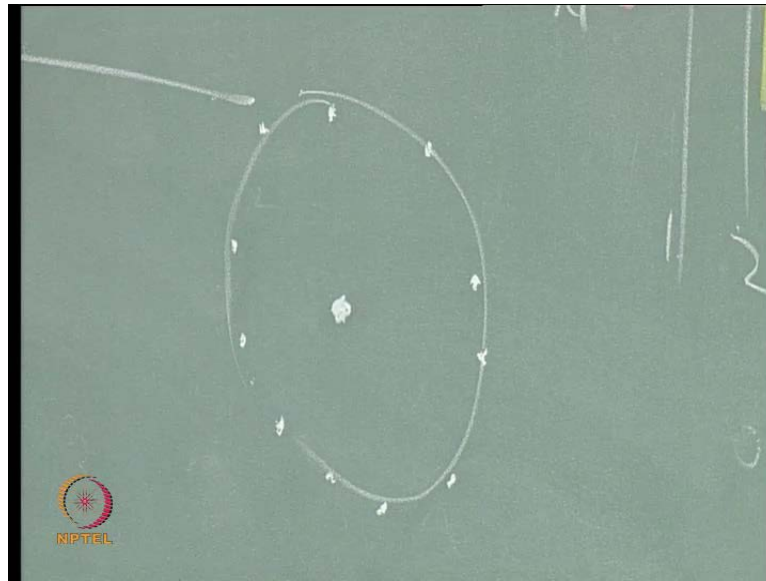
the new positions that you are creating, you are not going to differentiate from the old positions. Take any square rotate around this, you will see this part goes here, this part goes here, this part goes here; 90 degrees, and that is what we talk about rotational symmetry.

A quasi-crystal has rotational symmetry, but does not have translation symmetry. A crystal has both; an amorphous does not have both. So, it only has a short-range order. It does not have a long-range order, but a quasi-crystal has a long-range order, long-range crystalline order, in terms of its rotational symmetry. Only thing is it has special rotational symmetries. What are those special? For example, a normal crystal has a twofold, a threefold, fourfold and a six fold. You cannot have any other symmetry other than these. Of course, you can also have the one fold symmetry, which is what we call it as trivial symmetry in a crystallography.

So, these are the possible symmetries, everything else, we call is called forbidden symmetry. For example, fivefold symmetry cannot exist in a crystal. Many of you want to know why then you should go to solid state physics by Kittel. He tries to prove it. I can also prove it in a minute, and basically that such a rotational symmetry, fivefold symmetry does not guarantee translation symmetry. That is the problem, the moment you have the fivefold symmetry, you cannot have a translation symmetry, whereas, all these symmetries, you can simultaneously have a translation symmetry. You can just go back to any crystallography book and try to see the proof of it.

So, that is the reason why fivefold, sevenfold, eightfold, any other things, other than these, are all forbidden. For the first time in 1984, a person by name Schechman saw in an alloy of aluminum 14 percent manganese, when he prepared this alloy by fast cooling, the technique that (()) used- rapid solidification, and took that the foil that came out of it, and put it into a TEM, and he observed a diffraction pattern, which has the fivefold symmetry. That was the first time anybody has actually seen fivefold symmetry in a diffraction pattern.

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So, the diffraction patterns look like this: a central spot with some 10 spots, around it, at equidistant. 3 plus 3, whatever it is... equidistance. So, 10 spots on a circular ring, let us say, which actually looks like a tenfold and if you know little bit about crystallography, then you can know, how to differentiate between a tenfold and fivefold. There is something called Fridel's Law.

If you read, the electron microscopy then you will come across that, where we can differentiate between how to see a fivefold and a tenfold. But basically, even if it is considered as tenfold, still tenfold, it is not possible under normal conditions. So, the moment he saw that, then he tried to repeat it a number of times and every time he got the same thing and that is when people started accepting it, and saying that this can possibly exist. Hence, they said that we cannot call them as crystals. So, let us call them as quasi-crystals.

The only difference between this alloy and amorphous alloy is when you do an x-ray diffraction. In amorphous alloy, what do you see during x- ray diffraction? (()) You see a broad peak whereas, in quasi-crystal, you see sharp peaks, exactly the same way as in a crystal. So, you get sharp peaks and that is where recently around 1990s, people, till then the definition of a crystal is that which has both rotational and translation symmetries; they use to define. Now, they say a crystal is that, which shows a sharp diffraction pattern.

After people have discovered quasi-crystals, people have to change the definition of a crystal of which we were use to. If you ever remember in the B.Tech second year, when you start knowing crystal structures, you said crystal is that which has periodicity. Something, which is periodic, is a crystal. This is not periodic, but this is also one type of a crystal. Hence, people really had to change the definition, and the crystallographers had to accept that there are alloys like this, materials like this, which can give you rotational symmetries, which is forbidden under normal conditions,.

But if you try to... It is simple, you imagine if I have to show you in a 2d, a pentagon and if I keep on putting pentagons next to each other, then you will always have some gaps left out and there you will see some difference. But if you take a square, you can keep on joining squares. You take rectangles. You can do that. You can take an equilateral triangle. So, you can keep on. This is what we call them as tiles for example, you can see a square tiles there. You cannot have pentagonal tiles and still have no gaps left out, that is where the problem comes.

So, if you take such a quasi-crystalline unit cell, and keep joining them, you will always have some voids left out, which we call it as a frustration in crystallography. So, you will always have such voids left out. That is why people say these alloys have these phases have a high energy state, they are at a high energy state, because of those voids that are available, they are at a higher energy state, and that is why they are more metastable when compare to a stable structures. We will stop now.