Advanced Metallurgical Thermodynamics

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Module #01

Lecture #17

Solid state phase transformations – Precipitation

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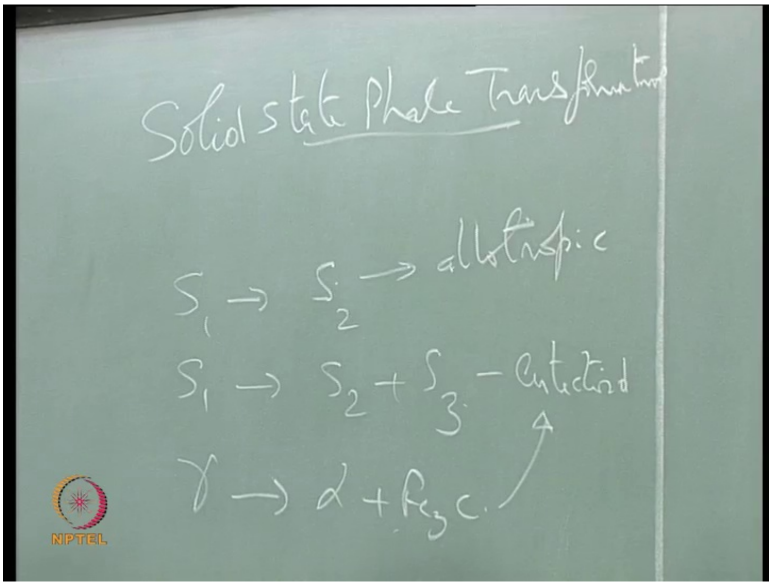

Solid state Phase Transformation

$S_1 \rightarrow S_2 \rightarrow$ allotropic

$S_1 \rightarrow S_2 + S_3$ – Eutectoid

$\gamma \rightarrow \alpha + Fe_3C$

Today, we will start a new chapter, on our topic. The new chapter is - Solid State Phase Transformations. We have been so far, talking about mostly, on liquid to solid. We have seen this so far, as we talked about solidification and melting. We even talked about isomorphous solidification; we talked about eutectic and we talked about peritectic solidification. We even went to an extent of how a liquid becomes a glass, and we also brought in T naught concept, in the meanwhile, and so understood what is called metastable phase diagrams, related to that.

So, today, let us bring in solid state. The moment you talk about solid state; that means, one solid giving you another solid or one solid, S 1 gives you S 2; S 1 gives you S 2 plus S3; variety of transformations. What are the solid-state transformations that you are aware of? Eutectoid is one, and eutectoid is something like this one. You can call this as a eutectoid transformation. So, the well known eutectoid, Aneesha, Which is the Eutectoid that you are aware of? What is the type of transformation? (( )) What gives iron plus cementite? What gives alpha plus? What is the eutectoid reaction in the iron-carbon diagram? (( ))

So, the austenite gives you ferrite plus cementite. This is the eutectoid (Refer Slide Time: 02:04) in the iron-cementite phase diagram. This is we are aware of and any other solid-state transformations that you know? Prerena Solid-state… Where something in the solid state gives you something else in the solid slate. (( ))

Alpha to gamma, gamma to delta, this is something like this. (Refer Slide Time: 02:26).What do you call them as? There is a name given to such transformations, when alpha goes to gamma or let us say alpha-iron becomes gamma-iron, then these are called as - allotropic transitions. If the same thing is happening in alloys, we call them as, polymorphous transformations. Allotropic transition is a term, which we use in case of pure metals or even, for example, in ceramics.

You must have heard of alumina. Alumina exists in different structures, as gamma-alumina, alpha-alumina. These are all allotropic transitions. Even silica; cristobalite, and variety forms of titania, which is Ti O 2. Many people are aware of nano titania, particularly. Do you know what is the particular purpose of nano titania? Self-cleaning; self-cleaning is all nano titania, nowadays. That is just one of the applications. In titania, there are allotropic transitions.

What are the most important allotropic transitions in Ti O 2? Does, anybody knows? Anybody, who is attending any ceramics class? Rutile-to-Anatase, Anatase-to-Rutile, rutile that is another transition. These are all allotropic transitions. There is no compositional change during this, only structure is changing. We call all of them as allotropic transitions, also in some alloys, you can have transitions where the composition does not change, only structure changes. We call them as polymorphous transformations, in general. Usually in practice, we use the term - Massive Transformations.

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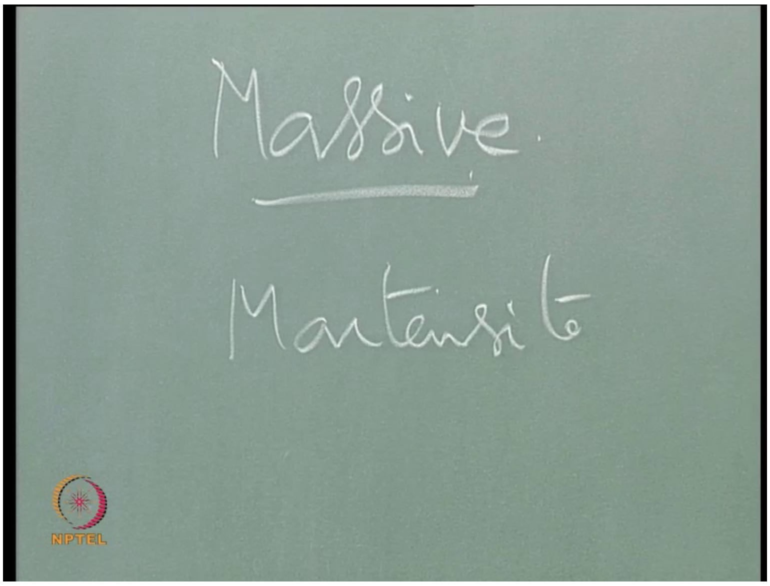

Why we call them as, Massive? It is because such transformations are very fast. Why it is very fast? It is because, it does not involve in long-range diffusion. You cannot say that it does not involve diffusion. Are you aware of any transformation, where it does not involve diffusion? Martensite - so that is the next type of transformation, which is where you have martensite.

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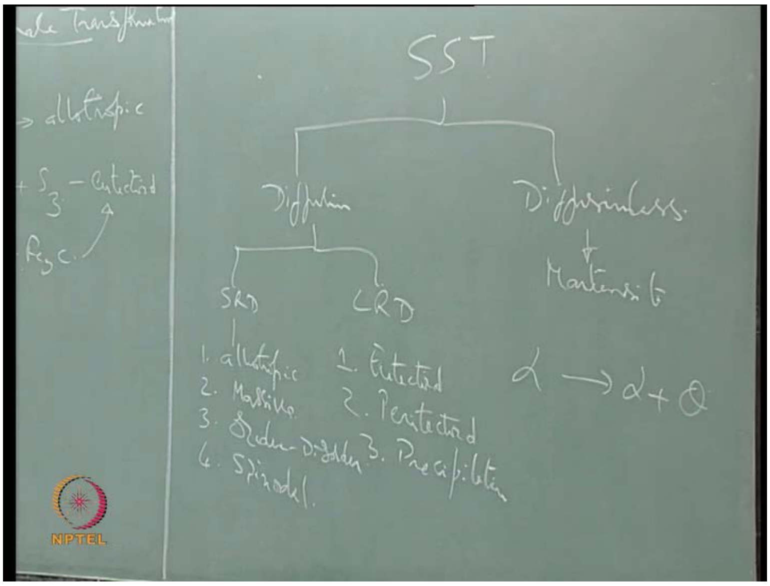

So in fact, if you want to talk more about solid-state transformations, we can; solid-state transformations can be basically divided into, diffusion based and diffusionless. This is a simply one-way of saying it and diffusionless is what is called martensite and in diffusion, you have short-range diffusion and long-range diffusion.

All the short-range diffusions are these: allotropic transitions and you have one that you can talk about- massive. Any other transformations that we are aware of, which are short-range diffusion, where the diffusion distances are not more than a few interatomic distances, may be one unit cells, may be few unit cells distance; Order-Disorder. So, these are certain transformations, which are basically short-range diffusion transformations.

Anything else, that you are aware, which is again of short-range; Spinodal transformations, are again of short range, at least at the nucleation stage, and as it progresses, it grows. So, spinodal transformations also more or less, can be at least initially, at the nucleation stage, it is of very short-range.

Then about long-range diffusion, what are the things that you are aware of? One you just now said. What did you say Aneesha, there is a transformation you have talked about, we are talking about, eutectoid. Do not say eutectic, it is eutectoid**.** So, eutectoid and this is the one. Is there anything else of which we are aware? Peritectoid is also fine, and let me take it.

But there is something, of which you are commonly aware, (( )) that is - precipitation, where an alpha, super saturated solid solution, gives an alpha plus a precipitate (Refer Slide Time: 07:54). Let us say, we call it as theta in case of aluminum-copper, and in case of something else; we can talk of something else. We call them in so many types.

Even in steels, we have precipitation. What is the precipitation that you are aware of, in steels? In a plain carbon steels, what is the precipitation that you know in plain carbon steels? Which is regular, I mean all of you in second year B.Tech- Metallurgy, have come across, when you are talking about heat treatment of steels. In heat treatment of steels, lead is not related to that. Yes, somebody murmured some word, just now. Yes, what is the precipitation that you know in steels- plain carbon steels happens during heat treatment, one particular type of heat treatment, it happens and it is not in alloy steels; (( )) Tempering, yes, the epsilon carbide formation in tempering is again that, where martensite with a particular carbon content gives you initially, epsilon carbide and finally, cementite. Is it not?

So, that is also a precipitation where one structure with a certain composition, leads you to a precipitate with a different crystal structure and a different composition. The epsilon carbide is... What is the composition of epsilon carbide? Does anybody know? (( )) Fe 2.2 C, 2.4 or 2.2 C, this is what people talk about.

So, that means, definitely its carbon content is different from that of the steel: martensite, from which you are starting. What is the structure of epsilon carbide? Yes, somebody said. Tell confidently, whatever you say, say confidently. That is important; you are an IIT-ian. Yes, somebody said it. Possibly, you only said it. Somebody said just now and I heard the answer, but he was not confident. Whoever said, has said it right. He has said the right answer, but he is not confident. Can you repeat what you have said? HCP; it is of hexagonal and we will talk about this that why hexagonal should come out.

So, this is all the precipitation. It is a cement Martensite, which is a body-centered tetragonal structure gives you a BCC alpha plus the epsilon carbide, which is hexagonal. Then this epsilon carbide as it grows, slowly it become orthorhombic cementite. Same thing happens in aluminum-copper. We are going to see now that it first gives you GP zones and then slowly it gives you theta double prime, then theta prime, finally, the theta. We will also see that why this kind of sequences has to be maintained.

So, these are all the long-range diffusion, which definitely are in the order of a few nanometers or few microns, depending on the grain sizes that we are talking about. These are all, if you generally want to classify solid-state transformations. We will try to take some of them and then see how we go about it. We will start with precipitation. This is a transformation, which is commercially, also a very important transformation. All age hardening is all due to precipitation hardening via precipitation, of which we are all aware.

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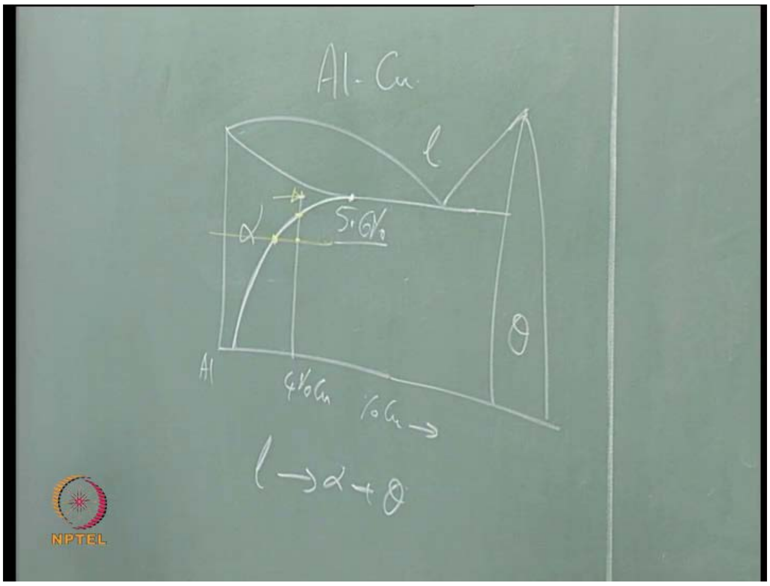

So, let us look at precipitation, and take the example of aluminum-copper itself, the most popular precipitation hardening. If you remember aluminum-copper phase diagram, particularly on the aluminum rich side, if you look at it, it looks something like this curve. This is how it looks like. On this side, there is the theta phase. This is how the aluminum-copper phase diagram looks like.

Of course theta …What is the stoichiometry of theta? What is the composition of theta? Cu Al 2, so it is basically, Al 2 Cu. So, Al 2 Cu basically means, if I am writing the percentage of copper, on this side, then how much is this. How much copper? (( )) 33.3 percent and in terms of what? Is it weight percent or atomic percent? Atomic percent is correct, so it is atomic percent or mole percent. Whatever way you can call it, because Al 2 Cu is of one atom of copper and two atoms of aluminum, and if you convert it into weight percent, actually it comes close to about 50 percent. This is because atomic weight of copper is almost or even more than double of aluminum. Aluminum atomic weight is 27 and 63.5 is that of copper. So, if we consider that, then it comes out to be much higher.

Anyway, this is pure aluminum on this side, and when we are talking about precipitation, what we are talking about is taking an alloy of some composition like this (Refer Slide Time: 13:23), and what is this composition here? Anybody… (( )), I am getting different answers.

Approximately, anyway, approximately 5.6 percent, different books will talk differently, but remember, whatever we are; talking here is in weight percent. So, this is all now we have to convert it into weight percent, whatever it is. Most of the commercial phase diagrams that we talk about are all in weight percent. Therefore, this is 5.6 percent.

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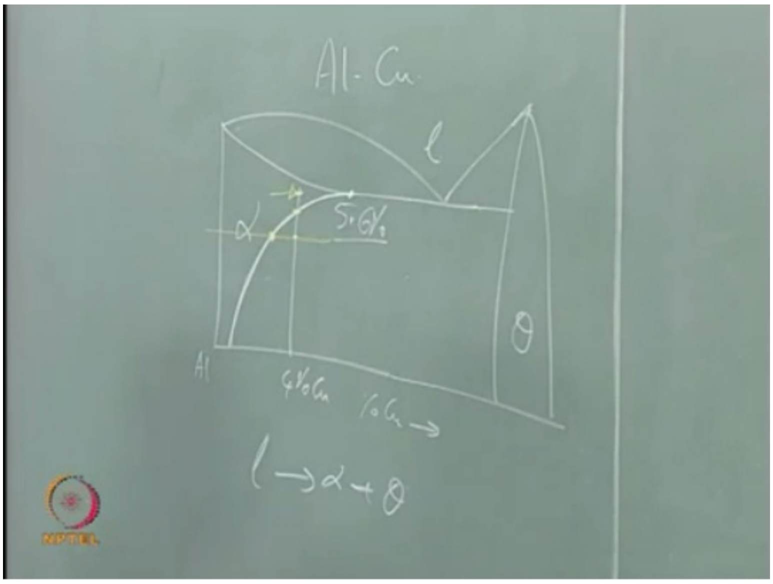

What is this reaction here? Aneesha, can you tell me. What is this reaction here? Eutectic, what gives you what? Liquid gives, what are the two types? (( )) Theta and… little louder, half of the word is only coming out of your mouth. Alpha, so, it is alpha. So, the liquid phase gives alpha plus theta and this is the eutectic reaction there. We are not at the moment bothered about that eutectic reaction, which we had discussed enough in the previous classes. So, let us not bother about eutectic reaction, as such. Incidentally, this particular eutectic is a lamellar eutectic. Aluminum- Copper is a standard lamellar eutectic. Let us not bother about it. We are now looking at the solvus part of it.

So, look at this line, which we call it as a solvus (Refer Slide Time: 14:52), and if I look at this solvus line, and take an alloy of this composition, let us say 4 percent of copper, which is a standard alloy that we talk about. Now, if this alloy is heated to this temperature, what should you get if you heat it, to that temperature? It should be alpha, completely alpha, if I heat it to that temperature. Now if I take it too that temperature and cool it slowly, what should happen? Yes, by the time, you reach this temperature and once you reach a temperature below that, theta should start precipitating out of alpha. Why is it?

Because the moment, I come to a temperature like this (Refer Slide Time: 15:42) and if I come to that temperature, at that temperature the alloy composition is 4 percent, and the solubility of copper in the alpha…. At that temperature if I draw a tie line, solubility of copper in alpha which is this value, and because alloy has more copper content than what it can dissolve, as a solid solution; this excess copper should be rejected out. Is it not? That is the whole principle of precipitation and where does this theta come out? At the grain boundaries, that is what it is.

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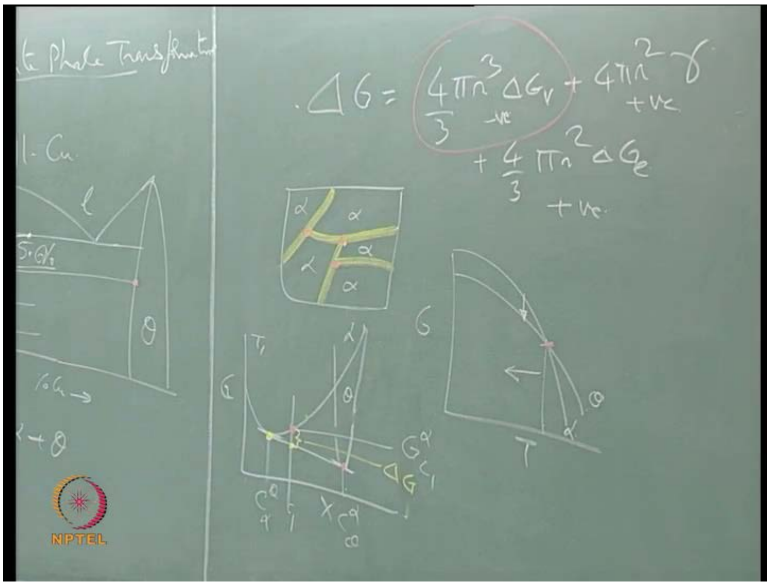

If I look at this microstructure, and say it as alpha, then these are all alpha grains. Then, you will see that, in principle, the theta would come out, at the grain boundaries like this. It will basically nucleate, at the triple junctions, which are at these points. These are the junctions, where the nucleation starts. Again, we will try to understand, why should the nucleation start at these triple junctions? That is where we need to understand, that whenever we are talking about precipitation; alpha giving you a theta phase and this precipitation always should have a certain driving force, and then because any transformation has an activation barrier, it has an activation barrier too. Similar to liquid to solid, it has an activation barrier too.

And in this particular case, whenever we are talking of liquid to solid, the activation barrier that we talked always is called as - the interfacial energy. Is it not? If we remember, we wrote an expression for the delta G for the transformation of liquid to solid, for a spherical nucleus and we wrote it as four-third of pie of r cube of delta G v plus four times of pie of r square times gamma. This is what we have written for the solidification, and we said this is the barrier for nucleation (Refer Slide Time: 18:13), this is the driving force for the nucleation. Am I right? Do you remember all this? Now, when I am talking of solid-state phase transformation, you have another barrier, which comes out, that is called as strain energy.

When a structure, which is different from that of the parent phase, is nucleating inside the parent phase, then there is a structural incompatibility between these two. As a result, certain strain is generated. Even if the structure is exactly same, if the lattice parameter of the precipitate is different from the lattice parameter of the matrix, you will see certain strain and that strain is more of volume in nature, it is volumetric. That is why; you have to add four- third of pie of r square of delta G e to this. (Refer Slide Time: 19:02). People call it as either e or epsilon, because strain is usually represented by elastic energy. So, people put it as either e or epsilon there. In this you see that this is positive, this is also positive, and whereas, this is negative.

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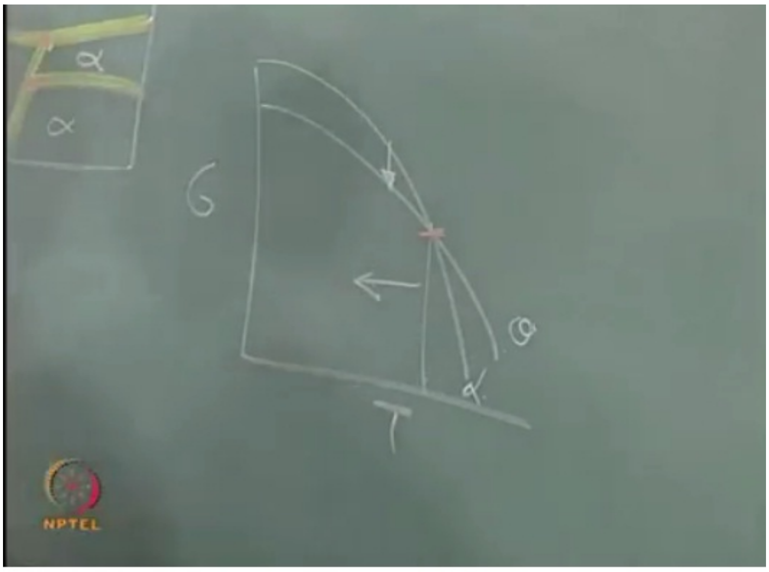

For example, for this particular alloy, if I draw a free energy composition diagram, I can say G versus free energy temperature diagram; let us say if I draw. I can say, this is the alpha phase, and this is the theta phase, let us say. If I say, in principle, theta is at low temperatures, let us say. In principle, if I say, this is theta and this is alpha, below a certain temperature there is a driving force from alpha to theta. For every alloy, there is a particular temperature, that temperature what do we call it as? What do we call that temperature? For every alloy, there is a particular temperature, below which the solid solution, wants to give a precipitate or wants to precipitate out another solid phase. What do you call that temperature? It is called as - solvus temperature. As simple as that, it is a solvus.

This is the solvus temperature for that 4 percent copper, if I am plotting G versus T for both alpha and theta, then that particular temperature is the solvus temperature, which is this temperature, in principle.

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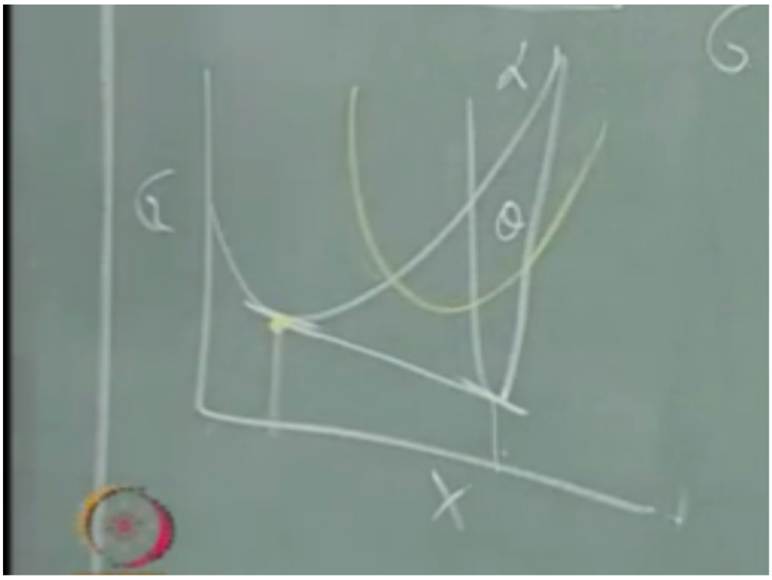

Now, if we write, what is called the free energy composition diagram, which is G versus X diagram. All we have is again two phases: alpha and theta. So, you have an alpha phase, free energy of an alpha phase, and you have a theta phase and theta being an intermetallic compound, it is much narrower in the free energy composition diagram, and it is suppose to be somewhere, at 33. So, let us not bother or consider this as pure end or metal end; let us say this is going towards pure copper.

So, somewhere you can put a theta phase, and if I draw a common tangent between the two, sorry it does not look like a straight line. I will draw it once again for you**.** So, this is one composition and this is another composition. What does this composition corresponds to? What is that composition, this yellow dot! (Refer Slide Time: 22:16). (( )) The composition of alpha in equilibrium with theta, and where is it on the phase diagram? Which point? It is the solvus composition. It is nothing but, one dot on the solvus line, at any temperature, at which I am drawing this.

Before you ask me, what exactly the composition is? You should ask me at what temperature we are talking about first. Depending on it, if I am talking about this particular temperature, this yellow dot is nothing, but corresponds to this yellow dot (Refer Slide Time: 22:51). So, these compositions that you get at various temperatures which are nothing, but the equilibrium between alpha and theta are nothing but this.

In principle, if I can draw alpha and theta free energy composition diagrams at various temperatures, and get these compositions (Refer Slide Time: 23:10), and this composition is not going to change, because this is more or less fixed, because it is like a line compound, its composition is fixed. Though it is not really a line compound, but is of very narrow range composition, it has, you know, I have just expanded for the sake of our easy understanding, otherwise it is not a large composition range, and it is possibly less than or about one percent. So, that is the kind of composition range, we talk about for theta.

So, theta composition does not shift, but alpha composition is going to shift from here at room temperature to here at this temperature. Once I reach this temperature, you will have to talk even about liquid also and until that, temperature is reached. Where is liquid now in our free energy composition diagram? It is above these two, somewhere here. You have liquid also, but that liquid composition is somewhere like this (Refer Slide Time: 24:14), liquid free energy curve is, it is above these two.

So, the stable state is alpha plus theta, and the moment you reach this eutectic temperature, this liquid free energy curve comes and touches the common tangent between the alpha and theta. So that all three of them will have the same common tangent, and this is what is a eutectic temperature. Until you reach that eutectic temperature, you will have liquid curve, always above that of the common tangent between alpha and theta, and the common tangent composition at various temperatures is nothing, but this composition (Refer Slide Time: 24:52).

And, if you draw, what is called the locus of all this compositions, what you generate is the solvus line. What are the other methods of finding out the solvus line? How do you find out solvus line? By XRD, I hope all of you have done it, otherwise some of you are possibly doing this XRD course and there is one separate chapter in Kaliti, please read it, which will talk about on how to find out solvus lines from that, so one of the most common methods is XRD. Of course, there are other methods too which we can talk about and so that is how you talk about it.

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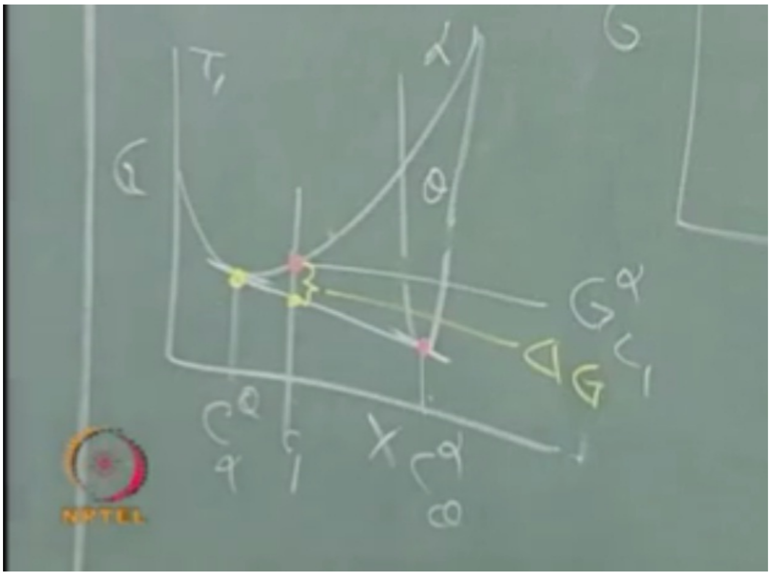

Now, what we are talking about is not this liquid. Forget about this liquid, so we are now talking about an alloy, having a composition in between this and this. This is the composition of alpha in equilibrium with theta, and this is the composition of theta in equilibrium with alpha at, let us say this temperature as, T 1. We call it as T 1 here, let us say.

At this temperature T 1, if I extrapolate this line: tie line, wherever this tie line intersects here, that particular composition; this composition is this composition, am I right, and this composition, this yellow dot is this yellow dot, and my alloy composition is somewhere between these two. So, that means, I am talking about a composition like this, a composition between C alpha theta and C theta alpha. So, this particular composition, the moment I look at it, this composition, if it exists as a single-phase alpha, at that temperature, what would be its free energy?

How do I know it? If this alloy exists as a single-phase alpha at that temperature T 1, what would be its free energy? How do you get that? Can I get it from the free energy composition diagram? The intersection point of this vertical line on the alpha curve will give you the free energy of alpha, having that composition, and what is that point. That point is this (Refer Slide Time: 27:18), that is the free energy of alpha of whatever composition, say 4 percent of copper and I will call it as a c naught or c 1 composition, let us say, for our benefit. So, we call this as c 1 composition and so that is the free energy of alpha. I can call it as G of alpha of c 1 composition.

Now, if you carefully look at it, that value is higher than the free energy of the two-phase mixture, which is given by this point. (Refer Slide Time: 27:59).What is that? The line joining the common tangent line, which is the straight line, at any composition between the two compositions, always gives you the free energy of the two-phase mixture.

The free energy of the alpha is this and the free energy of theta is that, and a line joining these two is something follows like the rule of mixtures. (Refer Slide Time: 28:21).This is what you do in composites for example, I know the strength of the matrix and the strength of the precipitate or the second phase and if I want to know the strength of the composite, then we simply draw a line joining the two, call it as a rule of mixtures, and find it out.

Similarly, we can use the rule of mixtures and this point on this line at any given composition will tell you what will be the free energy of that alloy containing two-phase mixture. (Refer Slide Time: 28:48).So, this is the two-phase mixture free energy and so this value is lower than that value. That means, there is a driving force for the alpha to precipitate alpha plus theta. Now, what is that driving force? That driving force is this driving force.

This is what I call it as delta G, and the same delta G, I showed you just a while ago in the form of G versus T diagram. This is a G-T diagram and this is a G-C diagram or G-X diagram. So, in a G-X diagram, you can see if this is the alloy and you can see that if I increase the alloy composition and take it more and more towards theta composition, what you will see is larger and larger driving force. That is what you see here, that I come to and if I keep on increasing the alloy composition, I would see more and more driving force or for the same alloy, if I change the temperature, instead of this temperature, I come to this temperature or this temperature. The lower the temperature, the more the theta is stable.

You would see that this point (Refer Slide Time: 30:11), what is called as the equilibrium composition of alpha in equilibrium with theta, shifts to the left as you can see here. It shifts to left to such an extent such that this difference will keep on increasing, the difference between your alloy composition and the composition of alpha; if that increases, then you will see the driving force will increase.

So, you have a driving force and which is what is this (Refer Slide Time: 30:38). This is all the driving force that you have. So, at any given temperature, I can talk about what is the driving force. But though you have a driving force, you have a barrier. The barrier in this case is the surface that has to be created, the new surface that has to be created and the strain that the sample has the new phase that is coming out. Depending on which phase that is coming out, you have different strain, depending on what is the structural difference between the parent phase and the product phase; the strain is going to depend on.

That is the reason why the actual choices of various structures, come into picture. This is the reason why, the system chooses the triple junctions, and the grain boundaries for the nucleation is because the triple junctions are the region, which are in a high-energy state. First and foremost, there in a high-energy state, as a result the system can easily relax to a low energy state, if the nucleation can occur there. Second is that, these are the regions which have more random structure. As a result, the strain can be accommodated much more easily, at those grain boundaries.

On the grain boundaries and triple junctions, because of the randomness that is available and because of the open structure that is available, the strain can be easily accommodated. As a result, you will see most of the nucleation occurs at the grain boundaries are at the triple junctions. In fact, when you go by the hierarchy of nucleation or hierarchy of the energy, you will always say the triple junctions are the highest, and then come the grain boundaries, but of course, the surface comes first.

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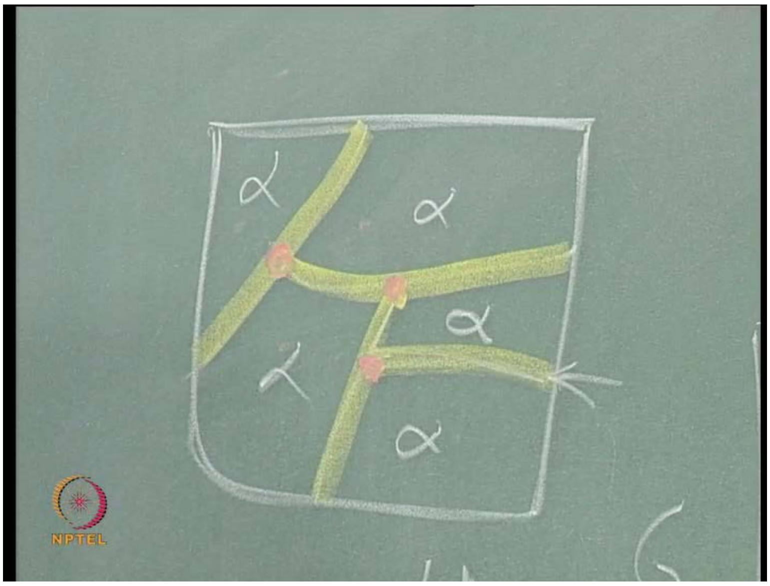

This surface is the first and this is where the first nucleation will occur; surface is the first, and then numbers two will be at the triple junction, and number three will be the grain boundaries. Grain boundaries are those where two grains meet, triple junctions are where three grains or more than three grains meet. This is the triple junction where this, this and this are meeting. Whereas, at this line, two grains are meeting and that is what we call it as a grain boundary.

So, that is how, these are the regions where the nucleation taking place, but the problem we have is: it is fine that the nucleation is occurring but because of the nature of this theta phase, once it nucleates, it grows along the grain boundaries. Once it grows along the grain boundaries; it forms a thin network at the grain boundaries; it is like imagining the grain to be something like spherical where you would see a kind of a layer forming on the sphere.

Once this happens and because this an intermetallic phase, which is a brittle phase, any crack that is nucleating at this place (Refer Slide Time: 33:41) can easily grow through the intermetallic phase. As a result, what you get is an intergranular cracking. This makes the alloy very brittle, this is what we do not want, and that is the reason why in high carbon steels, you see the presence of cementite, at the grain boundaries of the austenite, makes the high carbon steel very brittle. This is the reason why we do certain kind treatment.

What is the treatment we do? We do sparadisation or even we do another treatment. Other than sparadisation, any other treatment, which does not take as long as sparadisation, in high carbon steels, plain carbon high carbon steels, what is the treatment that we do to take care of this problem, of continuous networking of cementite, at the grain boundaries. Normalizing, as simple as normalizing, where you simply heat the steel to the austenitizing temperature and cool it rapidly.

So, that there is no time available, for all the cementite, which can come under the equilibrium conditions, which can come according to the lever rule. You do not have sufficient time for all the cementite to come and it nucleates, there is no sufficient time for this nucleated cementite to grow and cover the whole grain boundaries. So, what you get is a discontinuous network of cementite rather than the continuous network.

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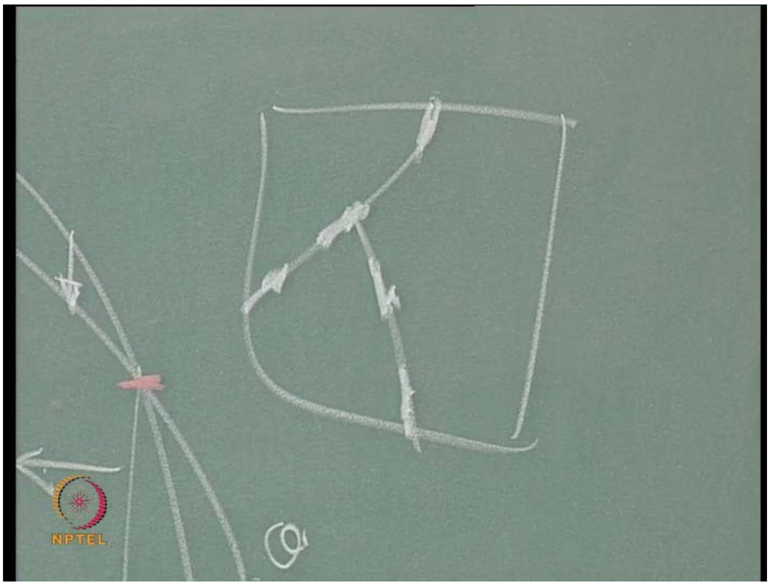

And that discontinuous network, which is what, looks something like this. You have discontinuous network of cementite of something like this. Once you have that kind of things, there is no continuity of the brittle phase at the grain boundaries. So, intergranular fracture can be controlled. This is one way, we can control that. The other way to do is, if I can somehow prevent the precipitation at the grain boundary, at all. That is the whole crux of precipitation hardening.

I somehow try to avoid precipitating at the grain boundaries. How do I avoid this? The only way I can avoid is to allow precipitation to occur, not near to the solvus line, but at temperatures much below the solvus line. How does precipitation does not occur at if I am if the precipitation is occurring at much below.

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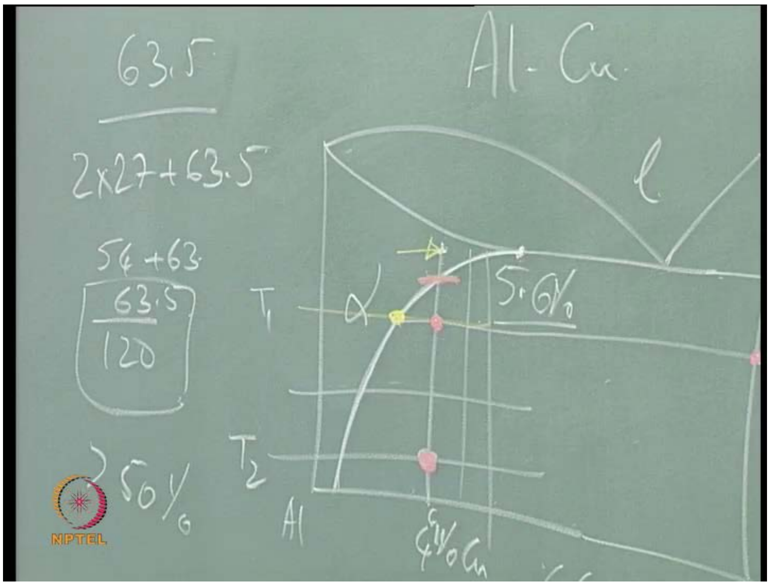

For example, if the precipitation is occurring at this temperature, let us say instead of this temperature. Let us say I call this as T 2. Instead of T 1, the precipitation is occurring at T 2. What is the difference between the two? Ultimately, the phase diagram shows only theta phase. Theta has to nucleate, but theta nucleation at the grain boundaries at temperature T 2 is not easy. Why is it so? Because if you want nucleation at the grain boundary to happen, the copper atoms… because you remember what alpha phase is, alpha phase has 4 percent copper. What is theta phase? Theta phase, if I talk in term of weight percent it is approximately 55 percent or so. Is it not?

Basically, if you want to convert it into atomic percent, it is 63.5 divided by 2 multiplied by 27 plus 63.5; one atom of copper, two atoms of aluminum. So, if you, anybody has a calculator, you can simple do this, this is something like this… and that turns out to be more than 50 percent. Whatever it is, approximately 55 that is what I said. That is the composition.

So, that means, you need copper atoms to move from the centre of the grains, to the grain boundary, such that the copper gets enriched at the grain boundary to the level of the 55 percent, so that the theta can nucleate. That means, from the centre of grains you need the carbon copper atoms and copper atoms are substitution elements; they are not interstitial elements. So, their diffusion rates are not very high and you are talking of temperature, which is very low, and because of this, you see that the diffusion of copper atoms to those particular grain boundaries is not**.**

Because we are talking of grain sizes of the order, let us say a few microns. While most of the alloys, whenever you do solutionizing, and cool back, they are of the order of 100 microns. So, if you think 100 microns as a grain size, 50 microns as diffusion distance; 50 microns is very large diffusion distance for the atomic diffusion. If that is the case then you see at this temperature (Refer Slide Time: 38:49), there is no problem, because the temperature is high enough, where the diffusion rates are high enough.

Whereas, at this temperature, it is difficult, and because it is difficult for the atoms to diffuse up to the grain boundary to nucleate at the grain boundary, but at the same time, there is a driving force. Alpha does not want to remain as an alpha. For example, if I take this alloy and heat it to this temperature, make it a single-phase solid solution, bring that single-phase solid solution to this temperature and I am holding it, let us say.

I under cool it; I quench this alloy to this temperature and hold it there, like what we talked about under cooling during liquid to solid transformation. Similarly, if we under cool that alpha to this temperature, now the precipitation must happen. At that temperature (Refer Slide Time: 39:37), there is a large driving force, for the precipitation. According to this, there is a driving force and this is at T 1, now if we draw it at T 2, the same free energy composition diagram, you would see the driving force is still larger. There is driving force, so alpha cannot remain as alpha, but the problem is the diffusion is slow.

Then the only solution for the alloy is that precipitation should occur inside the grain. That is the only solution and if precipitation has to occur inside the grain, then you need to consider this and this very carefully (Refer Slide Time: 40:17).

Strain energy becomes very important; surface energy also becomes very important. If the precipitation has to occur inside the grain, a new inter-phase has to be created at the grain boundary. You can say that the grain boundaries are already of high-energy regions, therefore, nucleation can occur, so this energy can be reduced, but, if it is within the grain, the nucleation has to occur somewhere here or somewhere here. Imagine then, we need to create a new surface and that is where the system will choose that particular structure, which has a lower interfacial energy and lower strain energy.

That is where; you would see that instead of alpha giving you theta, where the theta crystal structure is orthorhombic, am I right? The theta is orthorhombic and theta has to come out of alpha, which is a FCC. From a FCC an orthorhombic structure should come out and that is not easy.

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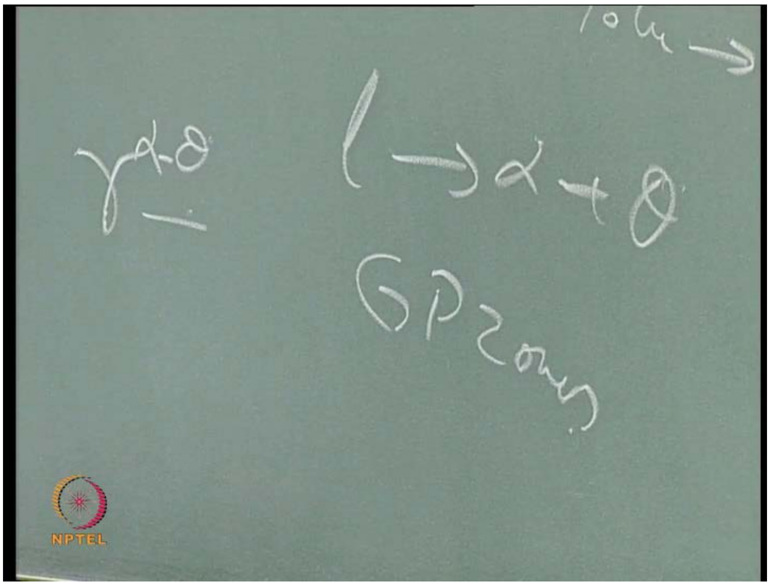

So, the system will choose and that is not easy, because the interfacial energy for such transformation between alpha to theta; interfacial energy is very large. For that interfacial energy being very large, the system will try to choose, is there any alternative for me, or there any possible transient phases, which can have a lower interfacial energy.

Hence, it starts looking for transient phases, which are metastable phases, of course, but looks for those, which have a lower interfacial energy, and that is where you come across something called GP zones. So, the alpha precipitates, which are called as GP zones, inside the grains at different regions. Are these the only heterogenic nucleating sides or what? Yes, dislocations, anything else?

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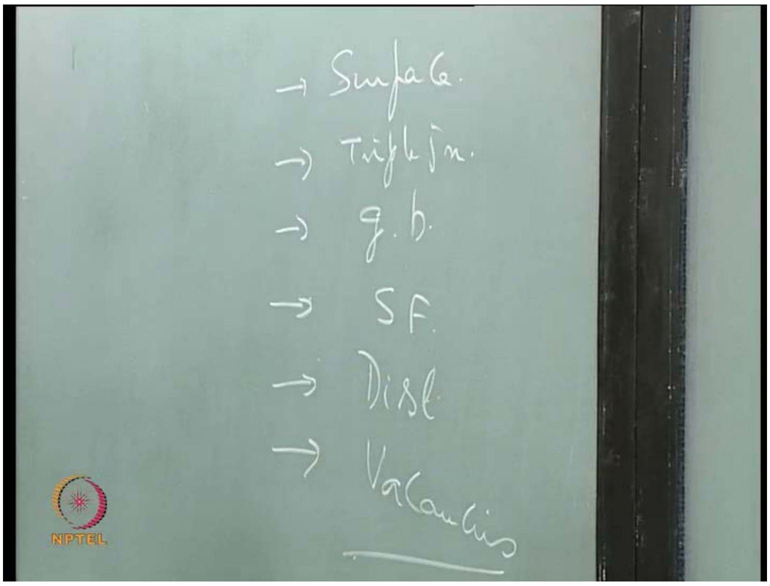

I was talking to you earlier on the hierarchy of nucleation, I said - surface is first, second is the triple junction, then the grain boundary, and then comes the staking faults, which you have just said. After that comes, your, what is the previous answer that you gave? Dislocations, after that comes what? (( )) Vacancies, perfect; these all are the hierarchy of nucleation and the surface energies actually decrease in this order.

That is why, in fact, if your sample has lot of quenched in vacancies; vacancies can themselves act as nucleating sides, for such nucleation to occur or dislocations can be there, or staking falls can be nucleating sides. So, this is how you see a GP zones come out. The reason GP zones come out is GP zones are nothing, but, copper rich clusters. They are copper rich cluster and copper rich clusters have… What structure copper has? FCC.

So, that means, inside an FCC matrix another FCC phase is nucleating. When a FCC nucleates inside another FCC, then obviously, the surface energy is very low. The only problem now, is the strain energy. Why? Is because, the lattice parameter of copper is different from the lattice parameter of aluminum. There will be definitely some strain. So, it will choose that particular shape, which has the lowest strain energy; so shape determines to a large extent to the strain.

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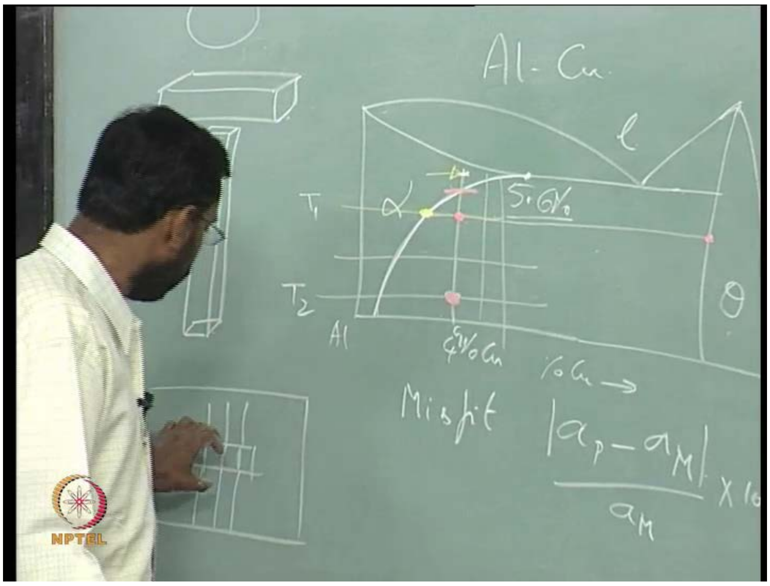

I do not know, whether you have come across. For example, if I look at different shapes, like if I take a spherical shape, if I take like a plate like shape, and if I take a needle like shape. Either this could be something like this or it could have a cylindrical shape, whatever it is.

If you look at these three shapes, each of them has different strain energies. Strain energy basically is the compatibility of the precipitate with respect to the matrix, that what determines the... Whenever you have a spherical shape, spherical precipitate sitting inside a matrix, the strain energy is always the maximum. This is because the unit cells of the matrix cannot have compatibility and because they cannot have the continuity. For example, whenever you look at a matrix, inside which you have a precipitate, if the lattice planes inside the precipitate and those inside the matrix; if there is continuity, then we will see the strain energy is the minimum.

When do you have this? You have this, when the lattice parameter of the precipitate, and the lattice parameter and the matrix are exactly, the same. Whenever you see the lattice parameter of the matrix and the precipitate exactly, the same, and this is what we call it as - misfit. It is called as - misfit, and this is given as a lattices parameter of the precipitate minus, the lattice parameter of the matrix, divided by the lattice parameter of the matrix and in terms of percentage, then multiply by hundred.

Obviously, we look at the absolute value of it. It can be negative or it can be positive, we always look at absolute value and when this is very small, you see that there is continuity. Even if it is a sphere, and whenever you have a misfit very small, strain energy is also very small, and when the strain energy is very small, the system will choose that particular shape, which will reduce the surface energy. What is the shape that will have the lowest surface energy? Sphere and that is the reason why in some of the systems, you get spherical precipitates. Are you aware of any system where you have spherical precipitate?

Any solid-state transformations where you get spherical precipitates? Gamma-gamma prime; Ni 3 Al, when it nucleates inside the nickel base matrix, you always see spherical precipitates initially, and when they grow, they become cuboidal. Initially they are. Similarly, in aluminum-lithium phase diagram, if you look at it, in Al 3 Li, precipitates inside the aluminum, again in a spherical. In aluminum-silver phase diagram, you have a phase called Al 2 Ag, which is again spherical. It is all because of their interfacial the strain energy is minimum, so it chooses that particular shape which can minimize that. If the strain energy is large, then what it chooses is it chooses that particular shape, which has the minimum strain energy, by choosing the shape and that particular shape is…

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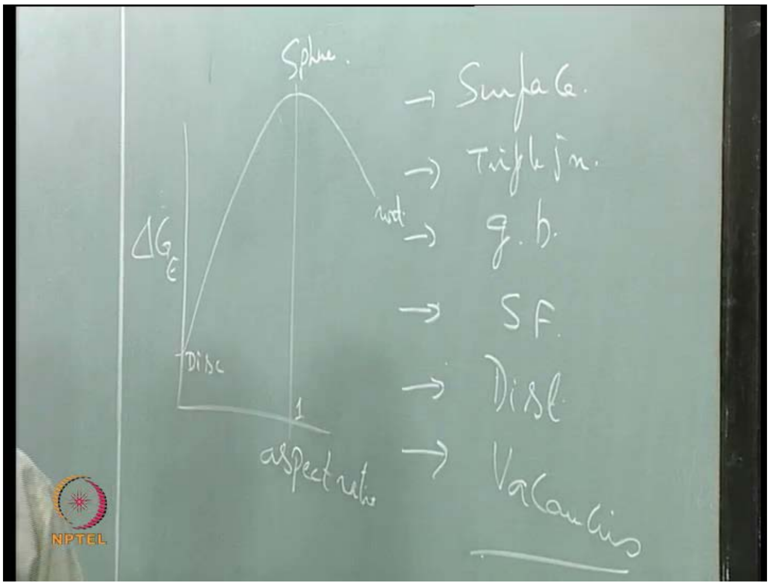

If you plot the strain energy delta G epsilon as the function of shape aspect ratio, if you plot, you will see that, you get something like this. This is where the aspect ratio is one;

this aspect ratio is very large, and here the aspect ratio is very small. This is what we called it as disk, this is what is sphere, and this is what is called a rod. Aspect ratio means the length verses the width of it. If I look at it, sphere obviously will have one, and in disk, the length the height is very small whereas, the length is very large. So, it is less than one.

So, you will always see wherever the strain energy is more, the system will choose a disk shape precipitate and that is what GP zones are. All the precipitates in aluminum-copper system like the theta double prime, theta prime; all of them are disk shaped or plate like. So, plate can have a best kind of compatibility, when compared to either a sphere or a rod. That is the reason why you see this happening, so the shapes of the precipitates depend on these two, because ultimately this has to be minimized (Refer Slide Time: 49:15). The system wants to minimize this over all things, because both are positive; this has to be somehow minimized.

If you can minimize this, then this, driving force that is available, can be utilized for the precipitation. As long as, this is larger than this, you can never have precipitation. This is how you see the GP zones come out from first in the aluminum copper, and this GP zones as they grow, and because the final equilibrium is theta, and these GP zones are nothing but, copper rich and copper rich precipitates are on this end of the phase diagram. We are only up to 55 atomic percent here. We have to go up to 100 percent to get to copper, and this copper rich precipitates slowly change their composition and their structure towards the structure of the theta in steps, and that is how you see the GP zones.

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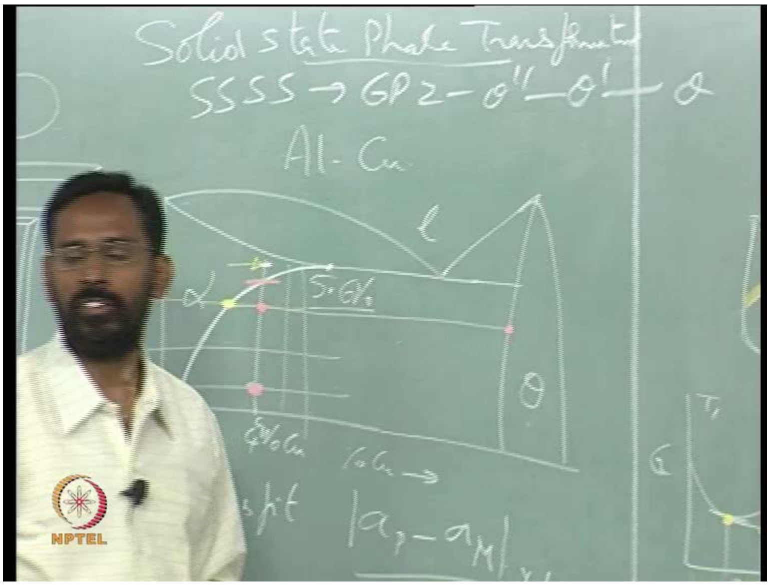

The super saturated solid solution becomes GP zones then theta double prime, then theta prime then finally, theta. We will stop here and take up later.