Heat Treatment and Surface Hardening - II

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Lecture – 16

ΔG for nucleation and overall transformation, concepts of solid state transformation including precipitation and Quasi-Chemical Model (QCM)

Hello everyone. Let us come to lecture number 16.

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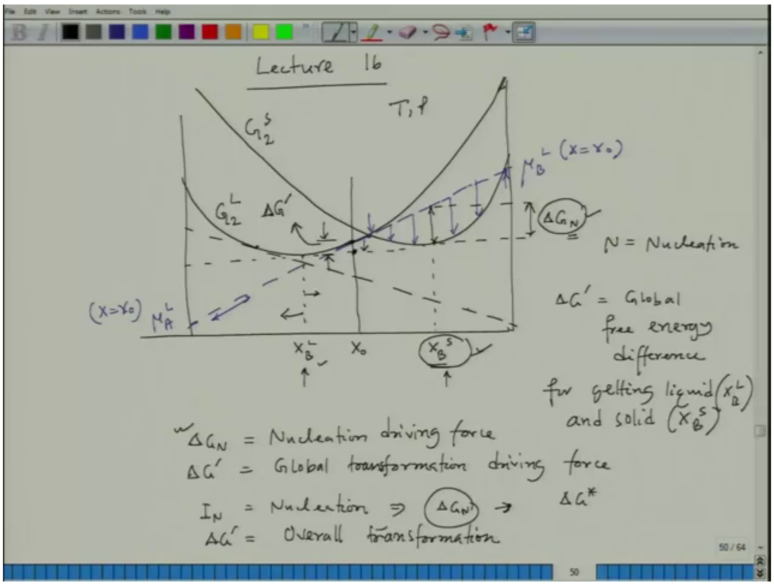

Lecture 16

ΔG_N = Nucleation driving force
$\Delta G'$ = Global transformation driving force
I_N = Nucleation $\Rightarrow \boxed{\Delta G_N} \rightarrow$ ΔG^*
$\Delta G'$ = Overall transformation

N = Nucleation

$\Delta G'$ = Global free energy difference for getting liquid (X_B^L) and solid (X_B^S)

In our previous lectures we have been discussing on the possibility of formation of second phase, and in our situation what we have considered that is a solid formation from a liquid composition. What we have observed that whenever we consider a particular composition of liquid at that particular composition on that G 2 line up that liquid we have to draw a tangent. And then we have to see that the part of the tangent whether that part would be higher off than the solid G 2 line. And then only there is a decrease in free energy for the formation of solid from that particular composition of liquid.

And in why we are drawing that common tangent, this common tangent is indicating that any composition can be reversibly form from the base composition of the liquid. And then we are getting equilibrium transmission from that particular composition to some other solids.

So, what we have seen if we draw the free energy composition graph. So, if this is my liquid line this is G 2 of liquid and if we consider this is to be my G 2 of solid, and at it is have a particular temperature T and pressure the equilibrium compositions can be seen from common tangent on both the free energy lines. And this is my equilibrium X B liquid and this is X B solid. I mean our last lecture what we have seen that if we take composition left to this particular composition, then no solid would come out. Because every time if I draw a tangent let us say here, if we draw the tangent these tangent would be always below the G 2 lineup solid.

So, in order to form solid we have increase the free energy which is not thermodynamically possible. But if we take any composition in the right side of it of the liquid because initially everything was liquid; so let us say if I take a composition this one this is X 0. When we get this composition then as per our concept we have to draw a common tangent, if we draw it with blue color so then the common tangent would pass through this. So, this is my mu B of liquid this is mu A of liquid. And that time composition equal to X 0 and this is also composition equal to X 0.

BF picture place real crystal train thing is up to draw slightly this and these two angles should be And then we are saying that from this composition along this particular free energy line which is drawn at the intersection point of X 0 and G 2 of liquid I can transform reversibly. That means, every time I will maintain the equilibrium, this if I follow through this particular line. Now while doing that I could see that this point and this point between these 2 intersection point, I see that every time I could get a solid because, free energy difference is negative for the liquid line this is basically the liquid line this tangent and solid line which is G 2 of solid. So, solid nucleation is possible.

Now, if I try to see what should be my free energy difference for the equilibrium that is if this particular composition has to come out from that particular liquid. So, my free energy difference is this one. So, this I can give a name which is called delta G N. And this N I am mentioning this N indicating nucleation. We are saying that if I have to get this solid of this composition they should be my free energy difference which will be driving that particular transformation.

So, remember this particular value is value required for driving nucleation of solid of this composition. But if I try to see the overall transformation free energy change, because finally we would get this composition and this composition because this particular composition distribute between X B solid X B liquid these are the equilibrium composition at that particular temperature. Finally, we will get this composition and this composition of liquid and solid that is fine. So, if I try to see what will be the global free energy difference the global free energy difference is coming So, this difference is the global free energy difference. So, I can term it as delta G I can say delta G prime.

So, delta G prime is global free energy difference for getting liquid of composition X B L and solid of composition X B S. And here also you see that actually we are reducing the free energy because from the liquid line to this point I am reducing the free energy. So, that transformation is also thermo dynamically feasible.

So, we have 2 free energy term: one is delta G N another one is delta G prime; this is nucleation driving force and this is the global transformation driving force. These term will be applicable while considering the nucleation phenomena or nucleation rate. This is nucleation rate that time we have to consider delta G N. And these term will a part of delta G star which is activation energy for nucleation. Nucleation before the delta G prime will be effective for overall transformation. So, we will see that

Now, coming to the discussion what we have done in our last phase of lectures.

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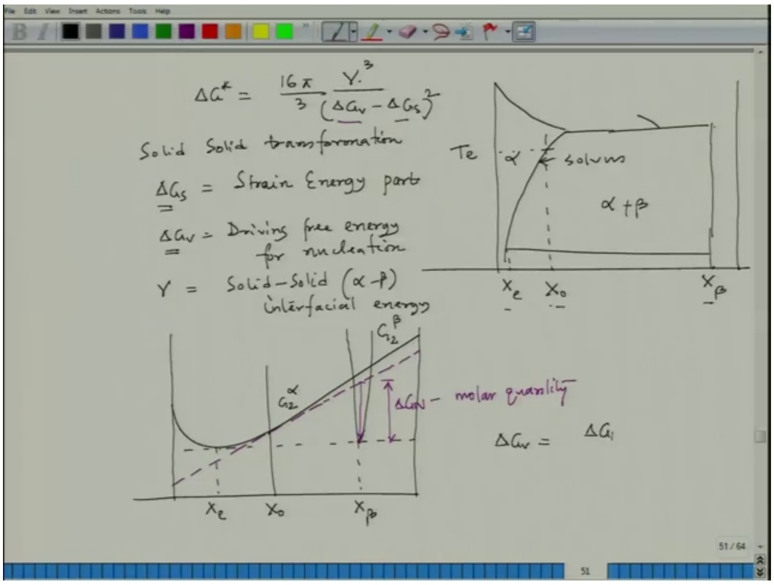

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma^3}{(\Delta G_v - \Delta G_s)^2}$$

Solid Solid transformation

ΔG_s = Strain Energy part

ΔG_v = Driving free energy for nucleation

γ = Solid-Solid (α-β) interfacial energy

ΔG_N - molar quantity

$\Delta G_v = \Delta G_1$

So, there we have seen that delta G star can be indicated with this particular formula gamma 3 divided by delta G V minus delta G S square. And remember that time we have considered precipitation of beta phase we are going little away from the solid liquid transformation, the solid liquid transformation actually is indicating that when we would have nucleation of solid similar phenomena can be active by solid equation form another solid. So, now, in this case I have diagram phase diagram was. So, this is let us say I am considering beta phase formation.

So, this is solvus this is this line is solvus solvus line and this is x beta and if you start with a composition X 0 and at this temperature my composition should be x e and this would be my x beta and this is my alpha and alpha plus beta. So, this is my equilibrium temperature T e if you go back to previous lectures of phase 1 you would see this phase diagram was considered while considering precipitation of beta phase in alpha and that time since it is a solid solid transformation then delta G s is strain energy part and strain energy is coming because there will be always some sort of lattice mismatch between the parent phase and the product phase; that means, the precipitated which is coming out of alpha phase.

So, this term is a positive quantity delta G V is the driving free energy for nucleation gamma is solid solid or alpha beta interfacial energy and in this case if I try to see the delta G V then you have to draw free energy composition diagram of alpha and beta. So, if I see the free energy composition diagram of alpha and beta since beta is almost about a single composition that is not much of variation of beta line with change in temperature. So, it would be a very narrow change in free energy this is G 2 beta and if I try to see alpha line is this one this is G 2 alpha now equilibrium composition at that particular temperature. So, this was my X 0 that the initial competition this is x e and this is X B which is corroborating to this competitions as per the phase diagram.

Now, at this point if I draw a tangent, So, in order to form this particular composition my free energy gradient would be this much which is nothing but delta G N as per our previous concept now if we consider this is basically the molar quantity that is free energy in joule per unit mole in order to we have to convert everything into volumetric term because this terms are considered with reference to volume per unit volume. So, then delta G V can be written as delta G N divided by v m and this b m we are assuming that solid or liquid solid both the solids of the almost similar molar volume this is an assumption which may not be true this is done just to make calculation simple.

So, these delta G V term is coming we could do the calculation by considering the free energy line equation of alpha free energy line equation of beta and then finding the equilibrium composition from the concept of chemical potential which is at this point mu A of alpha equal to mu A of beta and here mu B of alpha equal to mu B of beta. So, these, concept we can follow up and we have done the calculations while doing isomorphism phase diagram from thermo dynamic principal.

So, we can easily get those 2 points by solving these 2 equations and then at this point we can also draw a tangent and then that tangent we can get the cross section of the tangent with the free energy line of beta and then measurement of this particular value delta gm and then dividing it by molar volume we can get delta G V which can be used up in this particular equation.

Delta G S term how do we calculate it we will show it in next few lectures, but for the time being we are bothered about this particular value and these value will be used up for calculation of n and if we see our previous discussions we could get I n which is the nucleation rate graph from this semantics.

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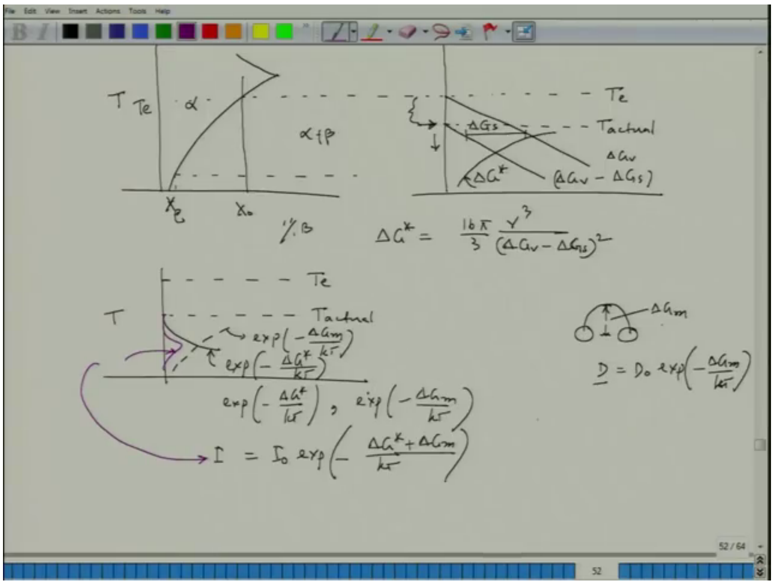

So, we if we this is my T versus percentage of b this is the composition we are talking about X 0 and at this point we are getting this is my x e equilibrium composition of alpha this is alpha plus beta . So, this is my T e this is equilibrium temperature

Now, since there is a contribution from strained free energy So, that is what we will not experience the total free energy change to be this the total free energy change will be actually coming from this difference this difference gives me the total free energy change and since delta G s term is positive in nature. So, it will actually reduce the driving force and if we if this strain energy term reduces the driving force then we have to go further in the further under cooling in order to get solid formation; that means, a second phase formation in this case it is beta.

So, that case the this is my T actually delta G V varies this way and there is a positive contribution from delta G s term which actually reduces the free energy term and if we consider the delta G s term is constant over the entire temperature range. So, I would get another line which is my effective free energy driving force.

So, this difference is delta G s and if we try to measure delta G star which is 16 pi by 3 gamma q delta G V minus delta G s square. So, now, actual transformation start temperature would be this one which is T actual this is T e equilibrium. So, delta G star would follow this particular line

From that so; that means, any transmission which would take place which would be between this point to bellow point. So, till this range we will not get anything because that time I am seeing that the total driving force is not sufficient for any transformation because that time delta G s term is more than delta G V term. So, actually we are not getting any driving force for transformation.

So, now similarly, I can get the plot between exponential minus delta G star by k T as well as exponential minus delta gm term k t. So, this delta gm term is coming because if we have 2 atoms. So, then when there is a jump between one atom to another atom. So, we are going via barrier this barrier is delta G m which can be obtained from diffusion cause constant d equal to d 0 exponential minus delta gm by k T . So, this way we can get this is diffusivity of that second element; that means, a solute element which is nothing but the b

So, we will get to see this see this is my T this is my T actual from where nucleation is possible because then from that point onwards we are getting effective driving force which is negative. So, we will get. So, this is my exponential minus delta G m by k T and this is exponential minus delta G star by k t. So, my m would be we also I would be I 0 exponential minus delta G star by k T plus delta G m we all we have already seen this particular equation. So, this would be lying between this line. So, this line is nothing but this through we are getting nucleation rate and remember while calculating nucleation rate apart from gamma and delta G s term delta G V term is also very important. So, we see that nucleation rate can only be quantified if we know gamma delta G V and delta G S.

Now, let us see what would be the effect of this free energy driving force for the growth rate we can also have an impact on growth rate we have already seen from our previous discussion that if we have a slab.

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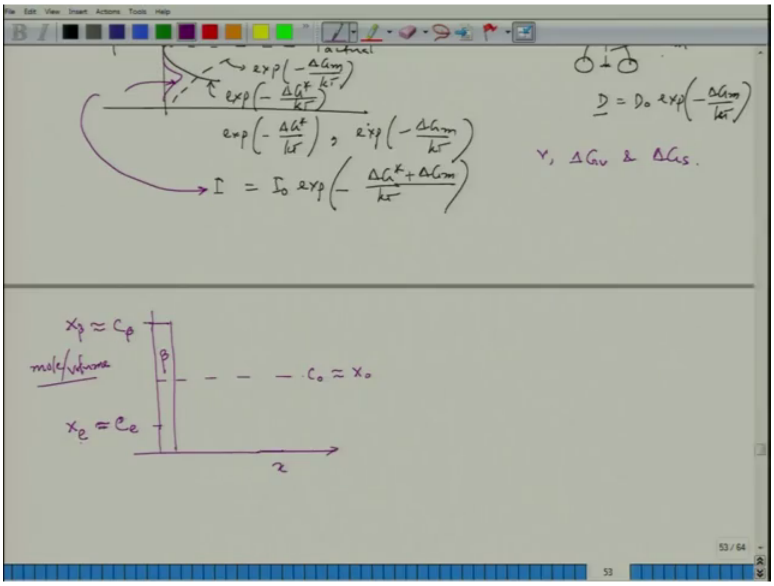

$\exp\left(-\frac{\Delta G_m}{kT}\right)$

$\exp\left(-\frac{\Delta G^*}{kT}\right)$

$\exp\left(-\frac{\Delta G^*}{kT}\right), \exp\left(-\frac{\Delta G_m}{kT}\right)$

$I = I_0 \exp\left(-\frac{\Delta G^* + \Delta G_m}{kT}\right)$

$D = D_0 \exp\left(-\frac{\Delta G_m}{kT}\right)$

γ, ΔG_v & ΔG_s.

So, this is x. So, this slab is forming which is beta phase and this is my composition of c beta and I am considering all the composition in terms of c which is molar composition so; that means, mole per unit volume mole per meter cube. So, then this composition is c e and the base composition is c 0 which is equivalent to X 0 this is equivalent to x beta and this is equivalent to x e as per the phase diagram what we have drawn.

And then the diffusion takes place on the bulk composition X 0 b goes to the surface of the beta phase which is nucleating from alpha phase of composition X 0. Then we can get an equation for v which is the growth rate equal to d del c 0 square 2 c beta minus c e c beta minus c 0 x this is a distance and that time if we consider that the molar volume does not change and molar volume of alpha and beta both are similar.

Then we can write mole fraction would be equal to molar composition into molar volume. So, then I can replace this with v equal to d del X 0 square 2 c beta minus c e c beta minus c 0 x sorry now everything would be converted into composition of mole fraction. So, this is x mole fraction. So, finally, we get v equal to after doing little bit of reshuffling then we get X 0 x beta minus x e root over d by T del X 0 divided by 2 x beta minus x e root over d T and that time we are assuming X B minus x c is equal to x beta minus X 0 . So, then only this particular thing is possible

So, now here also if we could see from this diagram del X 0 is nothing but X 0 minus x e and also we can prove that particular part delta G N is proportional to delta X 0 or delta G V proportional to del X 0 here also we are seeing that free energy term for nucleation is proportional to the composition difference between the base composition where we have started and the equilibrium composition of alpha phase at a temperature where we are doing the transformation of beta phase from alpha phase. So, that proves that this particular term is extremely important in order to get an idea of growth rate and nucleation rate.

Let us stop here. We will continue our discussion in our next lecture.

Thank you.