Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 25
Nucleation Rate - 2

Hello everyone, today we will start seventh lecture and seventh lecture would be on Driving Force del G.

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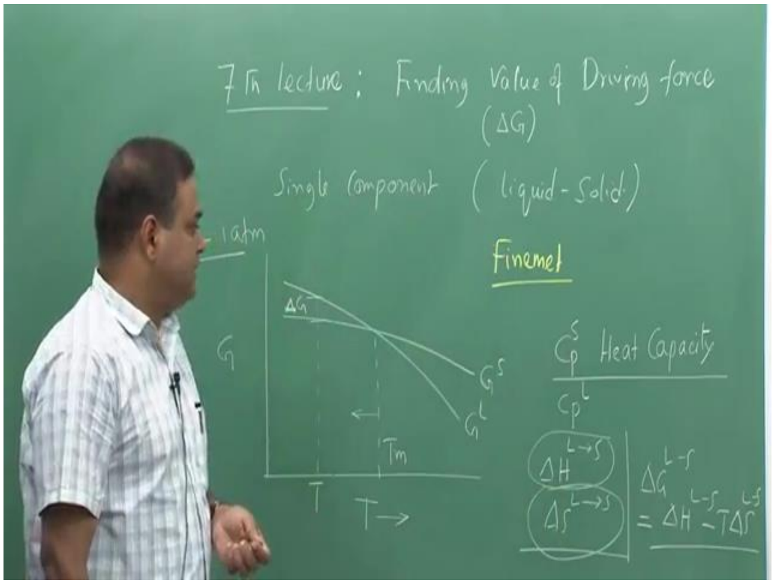

And initially we will consider single component system and that to we will considering liquid to solid transformation. This is very compatibly a simple derivation and later on we will go into the solid solid transformation which will be bit more complicated. And when we try to take the single component, it is also simple compare to the system when we will take binary system where there will be two components and in most of the practical applications we deal with alloys which are binary or ternary or even the alloy might contain a number of elements more than four or five elements.

So but before going into the complications, let us handle a simple condition and where we will take single component. And you must be wondering that though we will be talking about heat treatments of steel as well as aluminum alloys, so then why are we considering liquid to solid transformation. First of all, it gives an idea that what could be the way to find out del G in a very very crude manner I would say, which is I would say very simple manner. But at the same time liquid to solid transformation is useful in one of the structures which is known as a glass.

So glass is a kind of structure which is also in the form of solid, but interestingly the structure is random, that means in three dimension it does not have a long range periodicity. So that kind of structure we call it glass and in many of our practical applications we do use glass, one of the classic examples is window glass. So that does not a have a periodicity, long range periodicity. So there also we get a random structure to a very periodic structure which we call it crystal and that time it is called crystallization of glass and mostly in many of those polymers we do get glassy polymers and at the same time we do get a mixture of crystal and glass for polymer which enhances the properties.

So those cases this will be a very vital transformation mechanism, and at the same time many of those glasses we do get in metals we call them metallic glass, one of the famous metallic glass is finemet this is one of those iron based metallic glass which has fantastic soft magnetic properties. So there also, we try to get glass which is in solid and later on we try to modify its structure by crystalizing so that to improve its magnetic response, soft magnetic response.

So those cases this (pi) particular transformation would be very critical and even in case of cast iron when we do consider casting of liquid metal that time also the solid liquid transformation or liquid to solid transformation are depending on how we carry out that melting, that solidification operation the structure do varies, do vary and that time we do get a difference in properties. So this particular transformation from engineering prospective is very critical, so 1) is it gives a simple expression for del G and that to a single component system and also it has engineering importance.

And that to (whe) later on we will see that heat treatment does play a huge role while looking at this particular transformation. Now we have seen, from our previous lectures that in case of solid liquid transformation, if we try to plot G versus T for a single component system pressure constant and let us consider 1 atmosphere, so we get this kind of graph. So this is my Gs, this is my Gl and this is my Tm and we need to find out at any temperature less than Tm, let us say we try to find out what is my free energy difference if we can quantify this G.

So this is my temperature where we like to find out, this is my temperature axis this is the temperature where I would like to find out what is my free energy difference. And as we know that in order to calculate the difference in state function in thermodynamics like G, S or H, we have one experimentally determine value which is Cp, which is heat capacity, heat capacity.

Now if we can find out the Cp of solid as well as Cp of liquid we can easily determine what could be the value of del H liquid to solid del S, liquid to solid and finally we can get del G liquid to solid equal to del H liquid to solid minus T del S liquid to solid. So this simple formula we can use, and here now we have to find out how we can get this value as well as this value. Let us assume that we do have calculated values of these two parameters, so now if we try to see as a function of temperature, as a function of temperature if we try to find H enthalpy value for solid and liquid.

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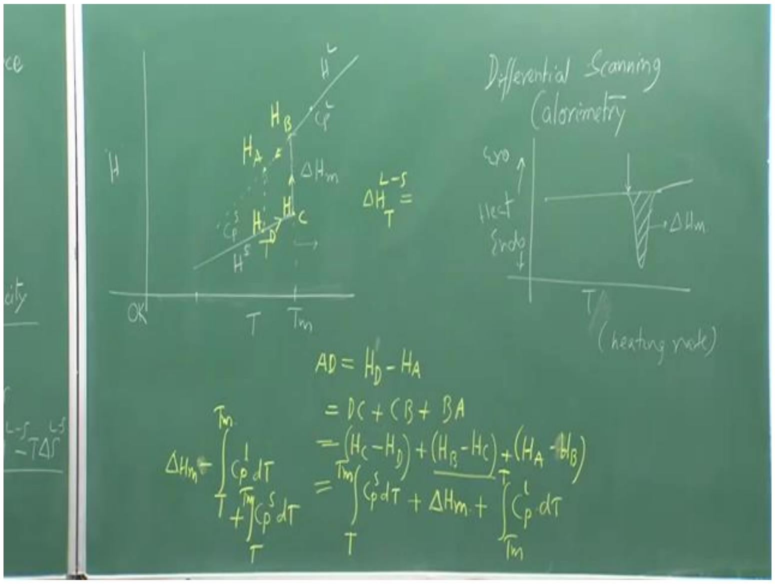

Now at temperature less than let us say this is my Tm at less than Tm and this is zero k, let us say at this some temperature I can easily find out the Cp of solid and accordingly I can find out CpdT equal to dH. So now there, I can have H plot, now at Tm, beyond Tm, I will get liquid and that liquid is stable so I can calculate the Cp of liquid and then I can find out the H of liquid and this is H of solid. And as we know the melting is first degree transformation, first order transformation and that time there would be a sharp drop which we call it as enthalpy of melting.

Now this Cp, from this we can get Cp information liquid this is Cp of solid. Now if we extend this line assuming that this is following this track and somehow because of some mechanism if we can find out the experimental Cp, so then at any temperature let us say at this temperature I simply find out del H which is the difference between liquid and solid, so that means this is let us say A, this is B, this is C, this is D and this is my enthalpy line, then this I can easily calculate at T.

Now when we try to calculate this value, since we know this value this we can calculate from DSC, simple DSC root which is called Differential Scanning Calorimetry which actually plots heat as a function of temperature or time, here we are considering temperature and that time we are heating at a particular heating rate and if we try to see a pure metal DSC pattern, DSC trace, we would see that DSC trace would look like when it melts that time it actually is endothermic reaction see would get a plot like this, it absorbs heat.

Now if this is my Xo heat and this is endo heat, so at lower side and this would be my melting point and the area under this graph is nothing but del Hm, fine. So this is a DSC graph we can easily calculate this. Now since we know this value, can we make use of this particular value while calculating del Ht liquid to solid transformation at any temperature below Tm. So that means, at this point from this point if we start, it will be all liquid and then gradually it is following this path and if we take the temperature below keeping liquid as liquid without solidification or crystallization, then I can reach to this point and if we hold that particular liquid at this temperature, then there is a possibility that it can go back because I see that at that temperature I have a lowering in free energy.

So spontaneity is there. Now then, this value I have to calculate, I can simply calculate by difference on Cp of liquid and solid and then get the value here. But since it is a state function, we can also calculate using this particular value into our consideration, how we can do it? So if I try to give a notation, so this is Ha, this is Hd, this is Hc, this is Hb let us say, so at those points I have those enthalpy values. Now if I try to find out the difference between these, so actually I am trying to find out AD. So that means I am trying to find out Hd – Ha.

So when I try to find out Hd – Ha, so that means I am taking this path but since the state functions are path independent. So I can also get this, get this difference if I start moving this way, so let us say I start moving this way, so now if I go from here to there, from there to there and then from B to A and then I see the difference, it will give me the same difference. So if I do this particular route, so then it would be DC + CB + BA. Now if I put it in terms of H values, so (Hc – Hd) + (Hb – Hc) + (Ha – Hb). Now this is related to Cp we will solve it, so I can also write so that means from T1, this is my T to Tm, T to Tm Cp solid dT plus this is nothing but del Hm, then plus Tm to T, so that means Tm to T Cp l dT, I can write this way also.

So then, if I take this particular term, this particular term I can put it this way del Hm plus minus T Tm Cp l I reverse this position of temperature dT plus Cp s dT T Tm, I can just make little adjustment, I will get this.

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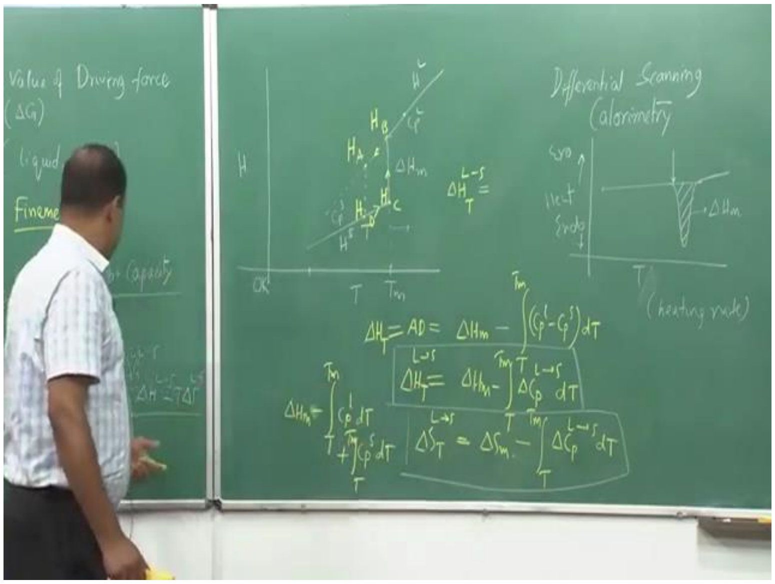

Now this one we can I just remove this part then this becomes del Hm minus T Tm Cp l Cp s dT and this is nothing but if this difference is del Ht, so this becomes del Hm minus Cp l minus Cp s dT. So this finally I can write del Hm minus T Tm del Cp since it is a solid to liquid, so I can put liquid to solid, okay, dT.

So I get this information, fine. So now del Ht, so it is basically liquid to solid transformation, fine. So now, if I get the expression like this, now there is one more term which is del s liquid to solid I should, if I follow the same procedure, I would get dT. So now I do get the information of del s liquid to solid and T del s liquid to solid and I get two expression this is one expression, this is another expression since I know del Hm, I also would know del Sm from experiment and this is experimental quantity so I do get this two parameters and I have to only do this particular thing, so this here I just replace those del s ls del Hm del s term and T I know where I would like to do my experiment.

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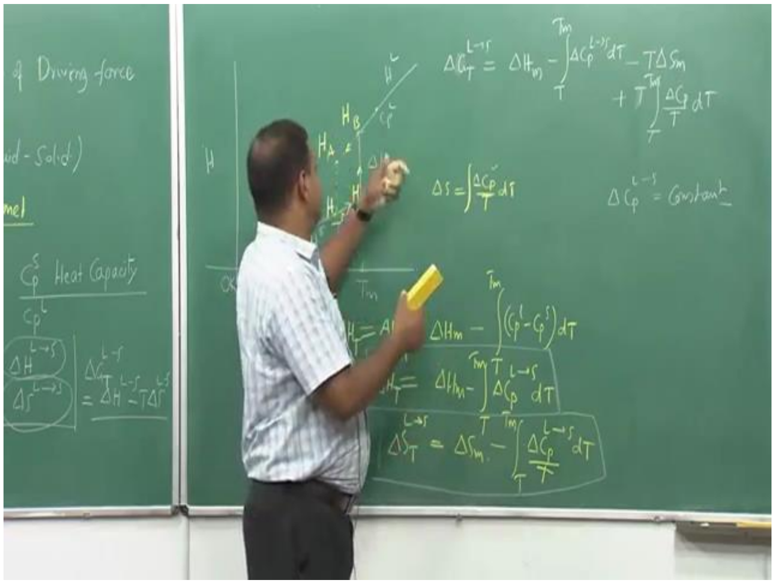

And rather where I would like to find out the driving force which is free energy difference. Now if I take that particular thing and put it there, so I just remove this part here let me remove this part so I will get del G liquid to solid T equal to del Hm minus T Tm del Cp liquid to solid dT minus T del sm plus T, sorry there is a small change here, there should be a temperature here, okay because del s is this, so I have I just forgot to put this temperature term. So this is this into dT. Now since this is very easy to find out from experiment which is DSC, this is also easy to find out from DSC.

But the difficulty is to find out this value. Now we assume that the liquid remains liquid below melting point, but this is against to our actual experimental leviness, we have seen that once the liquid is taken below melting point, it solidifies that means it becomes solid. But though you will later come to know that this liquid can (main) remain liquid over a entire temperature below over a very large temperature below Tm and the reason for that would be simple homogeneous nucleation we will talk about the nucleation term later, but for, for your information let me tell you the liquid water, okay we have seen that once we take it to zero degree Celsius its solidifies.

But actually the liquid water can be maintain liquid even below minus 40 degree below the zero degree Celsius. So that particular undercooling we call it undercooling is possible if we can allow homogeneous nucleation in liquid. So that time we can maintain liquid as liquid below melting point and we can easily find out what is the Cp people do calculate Cp of liquid like that. But since those experiments would be very expensive as well as very elaborate experiments.

Before we try to find out Cp, let us see whether we can have little bit of assumption which will be little a kind of unjustified assumptions, but initially let us take that those unjustified assumptions and later on we will take more justified assumptions and we will see k what is the difference that justified assumption would create over the unjustified assumptions. I would simply consider those assumptions those crude assumptions, for example the simplest assumption could be if we do not have del Cp value, it is very easy to find out Cp of solid but it is very difficult to find out Cp of liquid below melting point. So we have to take some value of this particular del Cp, so if I assume let us say let us assume a very simplistic value to this let us assign some value. So one assumption could be if del Cp liquid to solid is constant.

Now we take constant value, that means it does not change over the entire temperature gamete temperature range below melting point. But then next question is what would be that value? Okay, so then it is a problem. Now the next crude assumption could be if we can take it to be zero which is let me tell you this is a very crude assumption, okay. But still let us see whether this assumption would create any problem for our further calculations, okay. So now if we take this to be zero, then this term as well as this term goes to zero.

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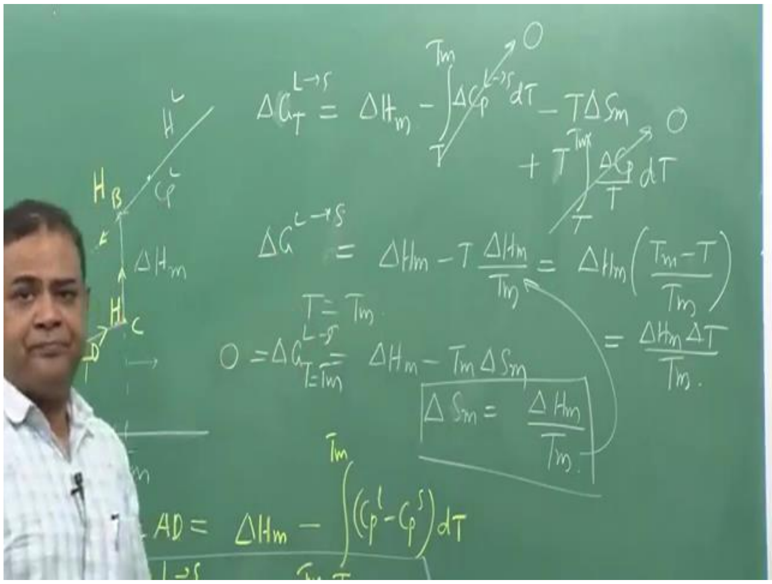

So we are left with this term and this term, so now if we try to take the del G liquid to solid, then it is going to be del Hm minus T del Sm. Now if we see this particular diagram, we see that at melting point, this value is zero. So if that is zero if we take T to be Tm, then del G liquid to solid is basically del Hm minus Tm del Sm and this is at T equal Tm which is nothing but zero. If that becomes zero, so then I can write del Sm equal to del Hm by Tm. So I convert everything in terms of enthalpy of melting or latent heat of melting or solidification.

So now if I know this particular expression and if I replace that here, what do we get? So I replace it, now if I replace it then it becomes, it becomes del Hm Tm minus T by Tm which I can simplify as del Hm del T Tm, fine.

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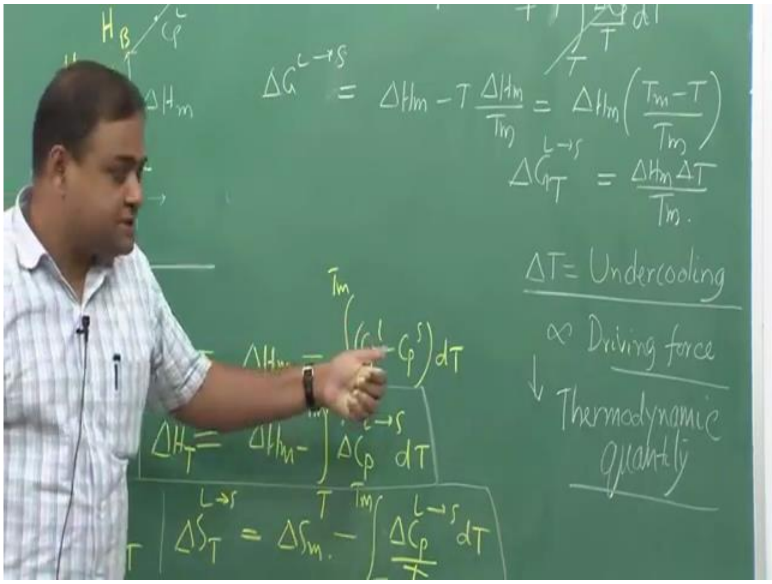

So now final expression is this, where this is nothing but undercooling, this is nothing but undercooling, okay. See this undercooling term if we see that undercooling is directly proportional to the driving force because these two terms are constant for a particular method.

So that means, this is proportional to driving force, what does it mean? This is a thermodynamic quantity, so that means if this is proportional to driving force then this becomes also a kind of thermodynamic quantity. I think let us stop here, we will continue in our next lecture. Thank you very much.