# Heat Treatment and Surface Hardening (Part–1)

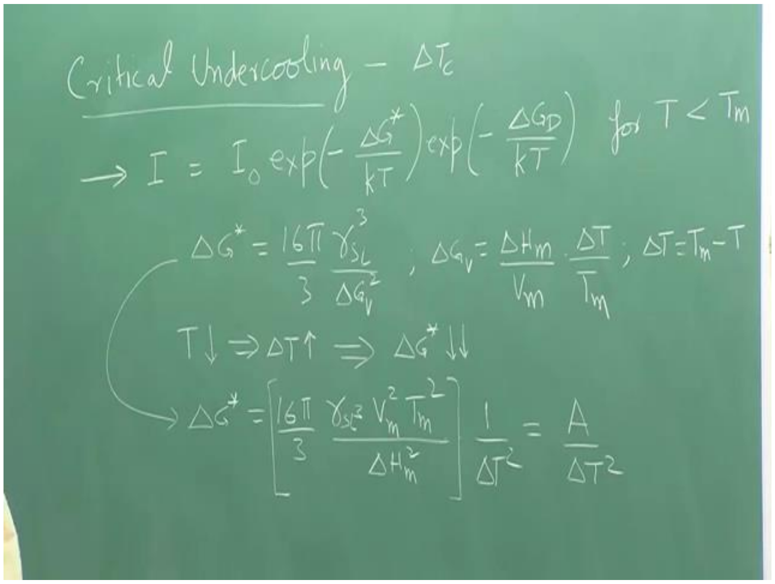
**Professor Kallol Mondal**
**Professor Sandeep Sangal**
**Department of Materials Science and Engineering**
**Indian Institute of Technology, Kanpur**

## Lecture Number 26

## Critical Undercooling

Continuing our discussion on nucleation rate, today we are going to talk about critical undercooling.

(Refer Slide Time: 00:35)



Critical Undercooling – $\Delta T_c$

$$\rightarrow I = I_0 \exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{\Delta G_D}{kT}\right) \quad \text{for } T < T_m$$

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma_{SL}^3}{\Delta G_V^2}, \quad \Delta G_V = \frac{\Delta H_m}{V_m}\cdot\frac{\Delta T}{T_m}; \quad \Delta T = T_m - T$$

$$T\downarrow \Rightarrow \Delta T\uparrow \Rightarrow \Delta G^*\downarrow\downarrow$$

$$\Delta G^* = \left[\frac{16\pi}{3}\frac{\gamma_{SL}^3 V_m^2 T_m^2}{\Delta H_m^2}\right]\frac{1}{\Delta T^2} = \frac{A}{\Delta T^2}$$

Critical undercooling delta Tc, now what do we mean by this is that and again we are going to continue in the context of homogenous nucleation that there is a certain critical undercooling is required before any nucleation can take place. So if the undercooling is less than the critical undercooling , then there will be no nucleation of the solid in the liquid and the liquid would remain in the super cooled state.

Let us let me just write down the equation for the nucleation rate which I had already written in the last lecture and which is I is equal to I not exponential minus delta G star the critical free energy for nucleation divided by kT multiplied by exponential minus delta Gd upon kT, where delta Gd is the barrier for an atom to jump across the liquid solid interface to make the critical nucleus super critical. And of course this equation is for temperature T less than Tm the melting point.

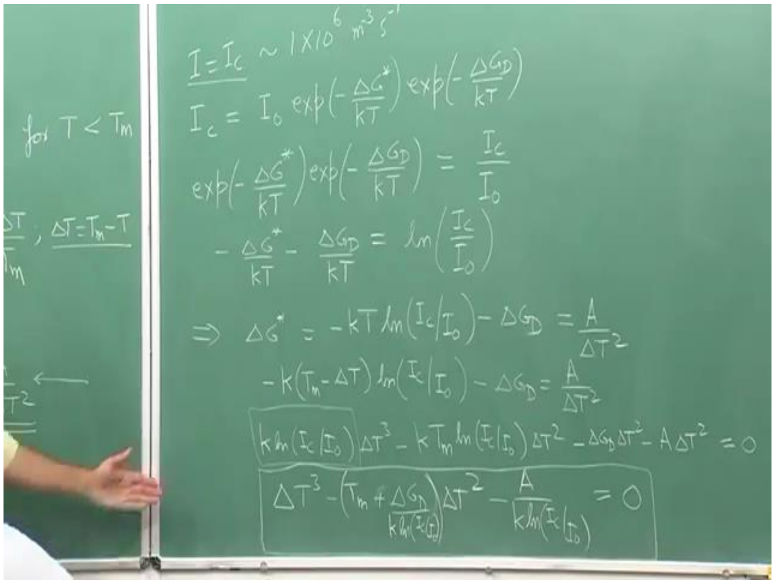
Just to recall delta G star is 16 pi by 3 cube of the solid liquid interface upon delta Gv square where delta Gv is the bulk free energy or the volume free energy change and delta Gv is given by if in terms of the molar enthalpy delta Hm upon the molar volume Vm times delta T upon Tm and of course delta T is the undercooling which is Tm minus T. So we are looking at a system which is at temperature T below Tm, so you can very clearly see that if I increase the undercooling, that means I go down to a lower temperature as the temperature is reduced.

So the undercooling in increased delta T goes up and this would lead to a rapid reduction in the barrier to nucleation or the critical free energy for nucleation delta G star. If I look at this expression, I substitute delta Gv into this, so then I can write this equation in a more compact form, so I substitute for delta Gv into this so delta G star is equal to 16 pi by 3 gamma Sl cube Vm square Tm square upon delta Hm square and then we also have the term delta T which is one upon delta T square, so if I take all of these quantities in square brackets all these quantities in our present case is a constant.

Gamma Sl is constant, Vm is constant, Tm is constant and we are assuming that delta Hm is also constant independent of temperature. So I can write for delta G star as a constant A upon delta T square, so clearly as I reduced the temperature, the undercooling goes up delta T goes up and since in this relation delta T is coming as a inversely delta G star is inversely related to delta T square, so delta G star will rapidly reduce as the undercooling is increased.

Now let us go back to the nucleation rate and let us say that there is a critical nucleation rate I is equal to Ic below this critical rate there is very low probability of nucleation, very small amount of nucleation would take place. And hence, below this nucleation rate we do not expect any substantial nucleation would take place and the liquid actually remains in the super cool state without solidifying.

(Refer Slide Time: 05:32)



So I will rewrite this equation now in terms of critical rate as Ic is equal to I not exponential minus delta G star upon kT times exponential minus delta Gd upon kT. What I want to do is for a given critical rate and in fact very often this critical rate is taken to be 1 into 10 to power 6 (new) nuclei of form in a meter cube per second. So in 1 meter cube per second 10 to power 6 nuclei would be forming.

Below this, this rate is too small and we can expect that no solidification is going to take place. So only at this critical rate or beyond we would get solidification, in fact critical rates beyond this we will see that rapid solidification would take place which means nucleation and growth. So going with this, what we want to find out is that for the given critical rate, what should be the critical undercooling?

Now in order to determine this we would need to find out what is the required delta G star. Then we can go back to this equation once we know what is delta G star, we would be able to determine what is the critical cooling rate. So let me write this expression rearrange the terms as exponential minus delta G star upon kT times exponential minus delta Gd upon kT equal to the critical cooling rate upon I not, taking logs on both sides, this will become minus delta G star upon kT minus delta Gd upon kT is equal to natural log of Ic upon I not.

Then clearly from this, we can write down now an expression for the critical free energy that is required to obtain the critical nucleation rate. And so delta G star becomes by rearranging the terms again minus kT ln Ic upon I not minus delta Gd. So this gives me an expression for delta G star in terms of the critical cooling rate. But we already have a expression for delta G star in terms of the undercooling from here, so I can equate these two relationships. So this I can put it to A upon delta T square.

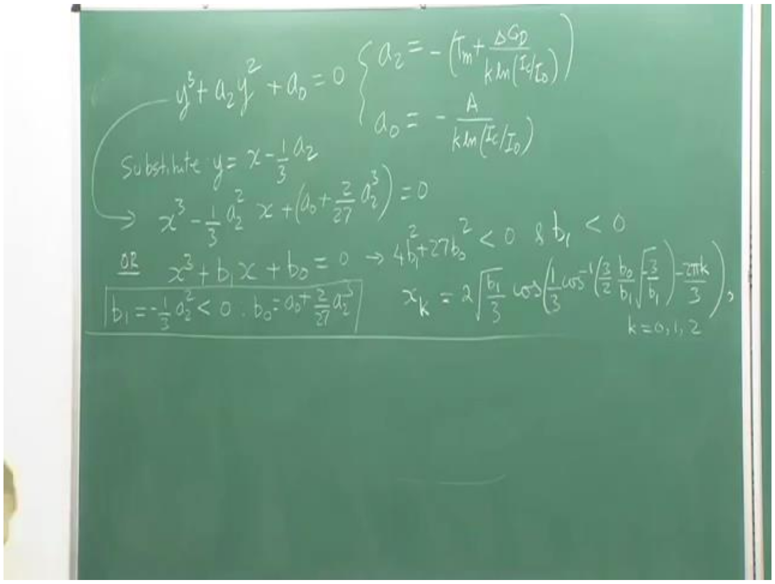
So now I should be able to setup a relationship for the undercooling that is required to obtain a particular critical nucleation rate. So let me just do a little bit more rearrangements here is let instead of minus k and instead of writing T let me write this temperature T in terms of the undercooling delta T, which of course this is my undercooling delta T so I can write the temperature T in terms of Tm and delta T. So I can write it as Tm minus delta T natural log Ic upon I not minus delta Gd is equal to A upon delta T square.

So let us try to do some more rearrangement and one will get k ln Ic upon I not delta T cube minus kTm ln Ic upon I not times delta T square, then I will have minus delta Gd times delta t square minus A the constant times delta T square equal to zero, let me divide this entire relationship with k ln Ic upon I not if I do this I will get a relationship delta T cube minus Tm, in fact this will be Tm plus delta Gd upon kln Ic upon I not minus A upon kln Ic upon I not and over here just a I made a little mistake here, let me correct this, delta T square here minus A upon kln Ic upon I not equal to 0.

So we have a relationship of this kind, if I look at it, I know everything in this expression putting and assume critical nucleation rate like 10 to power 6 per meter cube per second. From the last lecture, we had made a estimation for delta Gd for many systems it is the order of 10 to power minus 20 joules A can be determine from here and therefore in principle, I should be able to solve this relationship and get the value for the critical cooling rate critical undercooling.

So what kind of an equation is this? This (eq) you can see it is a cubic equation in delta T. So we need to solve this cubic equation and let us see how we solve this cubic equation.

(Refer Slide Time: 15:40)



$$y^3 + a_2 y^2 + a_0 = 0 \quad \begin{cases} a_2 = -\left(T_m + \dfrac{\Delta G_D}{k \ln(I_c/I_0)}\right) \\ a_0 = -\dfrac{A}{k \ln(I_c/I_0)} \end{cases}$$

Substitute $y = x - \frac{1}{3} a_2$

$$\rightarrow x^3 - \frac{1}{3} a_2^2 \, x + \left(a_0 + \frac{2}{27} a_2^3\right) = 0$$

OR $x^3 + b_1 x + b_0 = 0 \rightarrow 4 b_1^2 + 27 b_0^2 < 0$ & $b_1 < 0$

$$\boxed{b_1 = -\frac{1}{3} a_2^2 < 0 \, . \; b_0 = a_0 + \frac{2}{27} a_2^3}$$

$$x_k = 2\sqrt{\frac{b_1}{3}} \cos\left(\frac{1}{3}\cos^{-1}\left(\frac{3}{2}\frac{b_0}{b_1}\sqrt{\frac{-3}{b_1}}\right) - \frac{2\pi k}{3}\right), \quad k = 0, 1, 2$$

So let me write for delta T let me write I use the term y and hence I can write this cubic equation as y cube minus plus a2 y square plus a0 is equal to zero, so this is a cubic equation where very clearly a2 is equal to minus Tm plus delta Gd upon k ln Ic upon I not. Similarly, a0 is minus A upon k ln Ic upon I not.

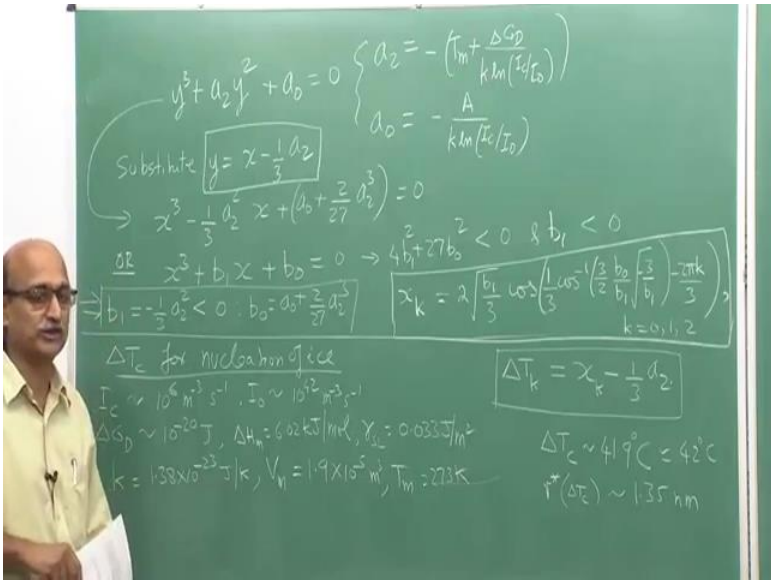
If I make a substitution substitute for y as y equals x minus one third a2 if I make this substitution in this cubic equation, this equation will then reduce to or it will become of the form x cube minus one third a2 square x plus a0 plus 2 upon 27 a2 cube equal to 0 or I can write this as x cube plus b1 x plus b0 equal to zero, where b1 is equal to minus one third a2 square and very clearly this quantity will always be less than zero, b0 is a not plus 2 upon 27 a2 cube. This kind of a polynomial equation is also called as a depressed polynomial because it does not have this square term.

And the solution for this, there are in fact several solutions depending on the sign of b1 depending on what this quantity is which is 4 b1 square plus 27 b not square if this quantity is less than zero, in fact for just about every system whatever values we put for the critical cooling rate the Boltzmann constant whatever value we get for A and so on from there you will get A2 and A0 and from here you will get b1 and b0 this quantity is less than zero and at the same time b1 is also less than zero, then this polynomial has three real roots and those real roots are given by the following relation.

Xk where is the kth root is equal to 2 square root b1 upon 3 cosine one third cos inverse 3 by 2 b0 upon b1 square root of minus 3 upon b1, so this is cos inverse of this quantity minus 2 pi k upon 3 and brackets close so you are taking cosine of this entire quantity. If this relationship was not valid, then you would not be able to take the cosine inverse of this, so in fact cosine inverse would not exist. So for this to be true, you get this as a solution, and what is k? K is simply k equals 0, 1 or 2, so the three roots k is equal to 0 corresponds to the first root, k is equal to 1 corresponds to the second root, k is equal to 2 corresponds to the third root.

So what do we do with this? So first we determine for a given system, so let us say suppose I were to calculate the critical undercooling for nucleation of ice.

(Refer Slide Time: 21:50)



$$y^3 + a_2 y^2 + a_0 = 0 \quad \begin{cases} a_2 = -\left(T_m + \dfrac{\Delta G_D}{k \ln(I_c/I_0)}\right) \\ a_0 = -\dfrac{A}{k \ln(I_c/I_0)} \end{cases}$$

Substitute $\boxed{y = x - \frac{1}{3} a_2}$

$$\rightarrow x^3 - \frac{1}{3} a_2^2 \, x + \left(a_0 + \frac{2}{27} a_2^3\right) = 0$$

OR $x^3 + b_1 x + b_0 = 0 \rightarrow 4b_1^2 + 27b_0^2 < 0$ & $b_1 < 0$

$\Rightarrow \boxed{b_1 = -\frac{1}{3} a_2^2 < 0 \; . \; b_0 = a_0 + \frac{2}{27} a_2^3}$

$$\boxed{x_k = 2\sqrt{\frac{b_1}{3}} \cos\left(\frac{1}{3}\cos^{-1}\left(\frac{3}{2}\frac{b_0}{b_1}\sqrt{\frac{-3}{b_1}}\right) - \frac{2\pi k}{3}\right), \quad k = 0, 1, 2}$$

$\Delta T_c$ for nucleation of ice

$I_c \sim 10^6 \, m^{-3} s^{-1}$ . $I_0 \sim 10^{42} \, m^{-3} s^{-1}$

$\Delta G_D \sim 10^{-20} J$, $\Delta H_m = 6.02 \, kJ/mol$, $\gamma_{SL} = 0.033 \, J/m^2$

$k = 1.38 \times 10^{-23} J/K$, $V_m = 1.9 \times 10^{-5} m^3$, $T_m = 273K$

$$\boxed{\Delta T_k = x_k - \frac{1}{3} a_2}$$

$\Delta T_c \sim 41.9°C \simeq 42°C$

$r^*(\Delta T_c) \sim 1.35 \, nm$

So I can take the critical cooling rate I see to be 10 to power plus 6 per meter cube per second, from the last lecture I not we have estimated to be 10 to power 42 per meter cube per second, delta Gd for this system and for many other systems is of the order of 10 to power of minus 20 joules, delta Hm as we are taken earlier for this system, is 6.02 kilo joules per mole, the solid liquid interface energy is 0.033 joules per meter square, Boltzmann constant 1.38 into 10 to power minus 23 joules per kelvin, molar volume Vm is equal to 1.9 into 10 to power minus 5 meter cube.

And of course the melting point is 273 kelvin. So I take this values and I plug them in find out what is a2, in fact I will have to first find out what is A from the expression that I have already given, find the small a2 a0 find out what is b1 and b0 from b set of relationships once I know what is a2 and a0, then b1 and b0 are straight forward. Once I have this, plug this into this relationship on what which gives you the roots of the cubic polynomial and I will get three values for x from there then I calculate the undercooling and what is the undercooling? Well we have done this substitution y is remember was what I has used for delta T the undercooling.

So y is the undercooling, hence the undercooling delta T and let me also put this as k because I will get three different values of undercooling. So delta T k is equal to xk minus one third a2. So from here for three different values of k 0, 1 and 2 I will get three different values of undercooling. But out of which we have to select one and you would find that two of the undercoolings are actually a negative number. Now we are talking about temperatures below Tm and the undercooling is Tm minus T hence the undercooling has to be positive.

So out of the three roots of the cubic polynomial, I will have only one root which is which has physical validity or which is valid for the physical system. If I do this calculation for this nucleation of ice I get an undercooling delta Tc as 41.9 degrees centigrade or kelvin whichever we whatever you wish to write here or essentially around 42 degrees centigrade. Therefore for ice to nucleate homogenously, I have to go down 42 degrees below the melting point 42 degrees below 0 degrees centigrade for it to nucleate homogenously, so you have to have a huge undercooling for homogenous nucleation of ice in water.

One can also calculate what is the critical size of the nucleus for the given undercooling and that you would get and this I leave it to you to calculate 1.35 nanometers. And now what I want you to do is for this given size of the critical nucleus which is for this particular undercooling estimate how many H2O molecules will make up this nucleus. So this is a kind of a homework problem of estimating the number of H2O molecules in this nucleus. So finally the conclusion of this analysis that we have done is that for homogenous nucleation of ice you (req req) you need quite a large undercooling before homogenous nucleation can take place.

And in fact this will be true for many systems, the undercooling required for homogenous nucleation is very large. So with this I will conclude this particular lecture and we will continue forward with further aspects of the rate of nucleation, thank you.