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

Continuing from the previous lecture, our discussion on nucleation rate, in this lecture we will try to bring in and describe the nucleation rate in a quantitative manner. So in order to determine the nucleation rate, we need to be concerned about, at what rate we would be forming stable nuclei, and what are stable nuclei? Stable nuclei are those which have a size greater than the critical size of the nucleus at a given temperature.

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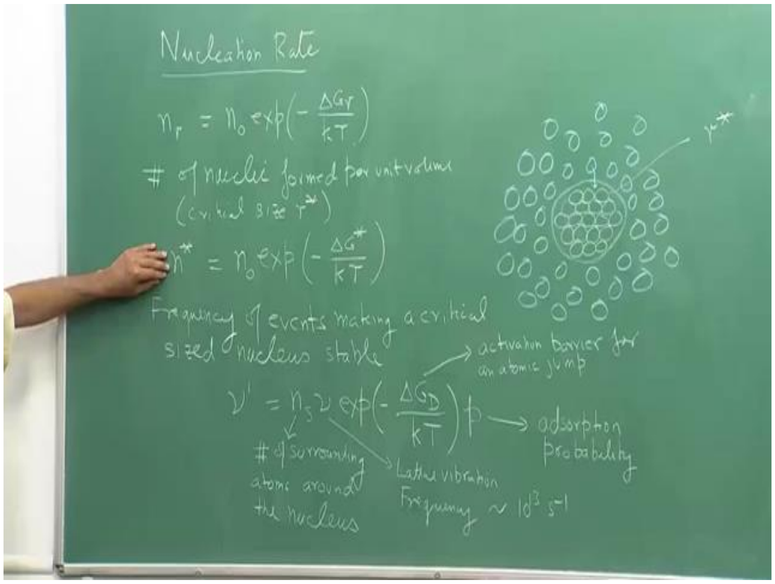

Nucleation Rate

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

# of nuclei formed per unit volume (critical size r^*)

$$n^* = n_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

Frequency of events making a critical sized nucleus stable

$$\nu' = \underbrace{n_s}_{\text{\# of surrounding atoms around the nucleus}} \underbrace{\nu}_{\text{Lattice vibration Frequency} \sim 10^3\ s^{-1}} \exp\left(-\frac{\overbrace{\Delta G_D}^{\text{activation barrier for an atomic jump}}}{kT}\right) \underbrace{p}_{\text{adsorption probability}}$$

In the earlier lecture, I had written that for a given size, the number of nuclei formed per unit volume is given by n0 exponential minus delta Gr divided by KT. For in order to estimate the number of nuclei of critical size that will be formed per unit volume, so would be given by an analogous equation; so number of nuclei formed per unit volume and these are nuclei of critical size. Critical size r star, that I will write as n star, which is related to n0, the potential site where a nuclei can form in a unit volume multiplied by exponential and instead of having delta Gr, I will replace this by delta G star, the critical free energy associated with the critical size nucleus divided by KT.

A critical size nucleus as was told earlier also is in a state of unstable equilibrium. So either it can fall back into the liquid, or it can move on by adding some atoms to become a stable solid. So imagine the following situation, that I have a critical size nucleus that is formed. So this is my critical size nucleus of size r star, and surrounding this are liquid atoms; and this is the interface between the nucleus and the liquid. Even if one atom were to jump and join the nucleus, this nucleus would become stable.

So what we have here is that we can estimate the number of such stable rather this critical size nuclei; out of this some of them would become the stable solid while others will dissolve back in the liquid. Combining these two that how many such nuclei would become stable, we would be able to determine at what rate nucleation would occur. So let us continue further, that what are the frequency of events, frequency of events making a critical size, critical size nucleus stable. Let that frequency be denoted as nu prime.

Nu prime, and let me write down a relationship for nu prime first; ns times nu times exponential minus delta GD, divided by KT, and let me explain the individual terms. Nu prime is a frequency of events which will lead to critical nucleus becoming super critical which means an atom comes and joins the new critical sized nucleus. This frequency would be dependent on how many atoms are surrounding the nucleus, and that is what this term ns denotes, number of surrounding atoms around the critical size nucleus. Nu is the latest vibration frequency; the atoms are constantly vibrating at this frequency can be kept, can be assumed to be of a fixed value which is 10 to power 13 per second.

If I look at delta GD, this is the activation barrier for for an atomic jump from the liquid across the interface and the atom joins the nucleus. This is like a similar barrier that we have which is delta G star for formation of a stable nucleus, this is another barrier that is present; and then there is one more term that not all jumps are going to be successful. For example, an H2O molecule jumps, but let us say if it is not on the right orientation, then it will not be able to join the nucleus and that jump would be unsuccessful; so therefore, there is a certain probability of success of the jump, that is denoted as p and which we will call it as the adsorption probability. So very clearly then, this is the number of stable nuclei that are formed and nu prime denotes the frequency with which these nuclei would become super critical and subsequently stable.

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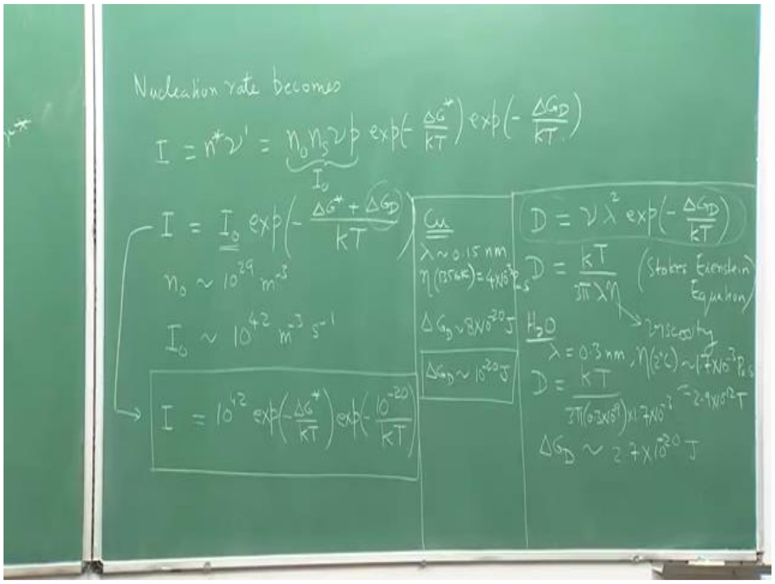

And hence, the nucleation rate can be written as; the nucleation rate becomes, denote it as I, which is nothing but number of critical size nuclei divided by frequency at which with which these nuclei will become stable. So n star times nu prime. If I take the product of all of these; so I will have n0, ns, nu, p exponential minus delta G star divided by KT times exponential minus delta GD divided by KT. If we look at these terms, this could be logged into one constant, I0 and hence the nucleation rate could be written as I0 exponential minus delta G star; along with this I can also put delta GD divided by KT. So this becomes the nucleation rate.

But we have to have some estimates for the various terms and words, then only we would be able to estimate what is the rate of nucleation for a given system at a given temperature. So let us first look at delta GD, which is the activation barrier for a liquid atom to jump across a interface and join the nucleus. The this comes from, if we have to estimate this, this comes from the theory of diffusion. And I can write some relationships in trying to estimate what is delta GD.

The diffusion co-efficient D and by the way I will be talking about this diffusion co-efficient in detail later; right now I am going to write down an expression for the diffusion co-efficient D; this is diffusion of atoms or molecules in a liquid, but if this equation is equally well true for solids as well, which is the latest vibration multiplied by lambda square where lambda is what is the jump distance for an atom or a molecule to go from the liquid to the solid in this case times exponential minus delta GD divided by KT.

So if higher the delta GD, smaller is gong to be the diffusion co-efficient or more difficult it is for diffusion to take place; and there is another relationship for D which comes from what is called the Stokes'-Einstein equation, and which is that D is equal to KT divided by 3 pi lambda eta, this is what is called as a Stokes'-Einstein equation, where lambda again is a jump distance and this is the viscosity of the liquid.

So if I want to estimate what is delta GD for let us say the water-ice system? So lambda is the intermolecular distance, this is of the order of 0 point 3 nanometers; the viscosity of water at 2 degree centigrade is 1 point 7 into 10 to power minus 3 Pascal-second. If I put down these values in this equation, so D is KT divided by 3 pi into 0 point 3 into 10 to power minus 9, convert that to meters, into 1 point 7 into 10 to power minus 3; solve this putting the Boltzmann constant value, you get 2 point 9 into 10 to power minus 12T.

We put this value of D in this equation, take nu to be 10 to power 13, again take lambda to be point 3 so on, and find what is delta GD, we get an expression for delta GD or an approximate value of delta GD to be of the order of 2 point 7 into 10 to power minus 20 Joules. Now, same estimate, suppose I make for copper; then in the case of copper, lambda is of the order of point 15 nanometers, viscosity measured at the melting point 1356 degrees Kelvin is 4 into 10 to power minus 3 Pascal-second, and you can repeat the calculation as it is done here, and one would get a value of delta GD to be of the order of 8 into 10 to power minus 20 Joules. In fact, if we do this calculation for different metals, we can assume that the value of delta GD can be taken as a order of magnitude estimate to be 10 to power minus 20 Joules.

And for all practical purposes, we can consider this value of delta GD to be a constant and independent of temperature for our calculation of the nucleation rate. So in this case if I look at this equation, now I know what is delta GD and I can calculate delta G star, I already know how to compute delta G star; now I should look in some detail into I0. Now this term I0 is not that straight forward; as you can see it involves n0, ns, nu and p; and we are not sure of let us say for example, what p I should take and so on that involves much more involved analysis.

But if you consider, in the previous lecture, n0 was of the order of 10 to power 28 or 10 to power 29. So we can assume n0 to be of the order of 10 to power 29 per meter cube. If we calculate it for other metals as well, one would find a value very close to this; so in order of magnitude estimate of 10 to power 29 is fairly okay. Nu, we already know can be taken as 10 to power 13 per second; if I take all of these terms together, I can estimate or a good enough estimate for I0 is 10 to power 42 per meter cube per second.

Hence, I can write the nucleation rate now for for the simple case of a nucleation taking place in a pure component system where liquid to solid transformation is taking place, the rate of nucleation per unit volume per second can be taken as 10 to power 42 exponential minus delta G star upon KT multiplied by exponential minus, instead of delta GD, I just split this again, and instead of writing delta GD, I can write this as 10 to power minus 20 from this estimate upon KT. If I look at this expression, I can see that now for a given system, I will be in a position to estimate the nucleation rate because I would know everything and I would be able to calculate delta G star.

Another thing about this expression is that while here the temperature dependence is only in the denominator of the exponential, in this first exponential, exponential of minus delta G star upon KT, the temperature dependence is not just in the denominator, but that delta G star itself depends on temperature; so this would be a much more complicated variation with temperature. This will not be a simple increase or decrease in the in this term, in fact it will be shown that the nucleation rate would first increase as the temperature goes down, goes below TM, or as the undercooling increases, it will go through a peak, and then the nucleation rate will start to go down as we go and keep increasing the undercooling.

So initially, at high temperature also one would find the nucleation rate is going to be small because at high temperature delta G star is going to be large; and since it is in the exponential, this value would become quite small making the nucleation rate low, and then the nucleation rate will increase, reach a peak, but then as the temperature keeps going up, then again one will find that the nucleation rate goes down. So as that, we will see in the next lecture, we will start the next lecture will start from where we ended here, and we will then try and analyze this equation on specific system.

Again we will take the example of nucleation of ice and water as example, and look at how the nucleation rate changes in that case, we will determine what is called as the critical undercooling that is required before homogeneous nucleation can actually take place and we will look at what kind of an undercooling is required, let us say for nucleation of ice homogeneously in water. With this I close this lecture. Thank you.