Heat Treatment and Surface Hardening - II
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Lecture – 27
Nucleation rate and it is dependence on T (temp. Of interest), ΔT, ΔGv and ΔG* and, introduction to growth kinetics

So, we the nucleation rate we derived in the last lecture is given by n 0 Number of sides of nucleation n s. The number of atoms in the parent phase surrounding the nucleus nu is the debye frequency which could be taken as 10 to the power 13 per second.

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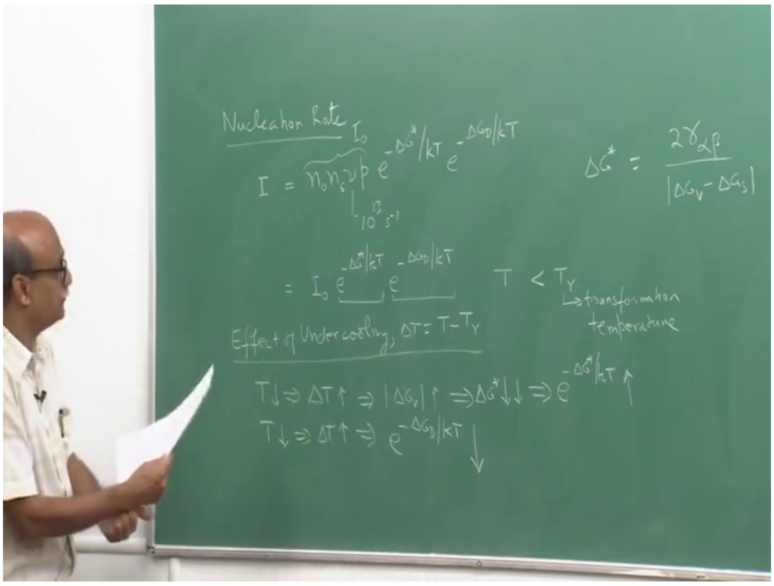

Nucleation Rate

$$I = \overbrace{n_0 n_s \nu p}^{I_0} \, e^{-\Delta G^*/kT} e^{-\Delta G_D/kT} \qquad \Delta G^* = \frac{2\gamma_{\alpha\beta}}{|\Delta G_V - \Delta G_S|}$$

$\nu \to 10^{13}\,s^{-1}$

$$= I_0 \, \underline{e^{-\Delta G^*/kT}} \, \underline{e^{-\Delta G_D/kT}} \qquad T < T_Y$$

T_Y → transformation temperature

Effect of Undercooling, $\Delta T = T - T_Y$

$$T\downarrow \Rightarrow \Delta T\uparrow \Rightarrow |\Delta G_V|\uparrow \Rightarrow \Delta G^*\downarrow\downarrow \Rightarrow e^{-\Delta G^*/kT}\uparrow$$

$$T\downarrow \Rightarrow \Delta T\uparrow \Rightarrow e^{-\Delta G_D/kT}\downarrow$$

P is absorption probability delta G star is the critical free energy and delta G D is the activation energy for the jump from the parent phase to the product phase.

Now, all of these quantities n 0 n s nu p could be lumped into one parameter and let me call that parameter as I 0, and I can write the nucleation rate as I naught e to power minus delta G star divided by k T times e to power minus delta G D divided by k T.

Now, let us understand that the temperature here is temperature less then T r. What is the effect of undercooling? Delta T which is t minus T r, where T r is the transformation temperature. So, yes temperature reduces this implies that the undercooling delta T increases. And as a result delta G v the absolute value of the change in volume free energy increases or delta G v. In fact, becomes more negative which means the driving force for nucleation would increase as temperature goes keeps decreasing below the transformation temperature.

And this you can go back to the part one of the course to understand why delta G v would increase the absolute value of delta G v would increase as your undercooling increases. But as a result we can analyze what is the effect on delta G star where we had already written delta G star to be equal to 2 gamma alpha beta divided by delta G v minus delta Gs. The s the under cooling increases the quantity in the numerator denominator would increase and as a result delta G star would reduce. In fact, delta G star can substantially reduce as a result of increasing undercooling.

Now, this would have now what happens if delta G star substantially reduces, look at this term containing delta G star. This would become less negative as a result this exponential term e to power minus delta G star divided by k T would increase. And this would have a positive impact on nucleation; that means, one can expect nucleation rate should go up if my undercooling increases; however, we also need to look at the second term. What happens to this term?

If we assume that delta G D is more or less or constant. Then the effect of reducing temperature or increasing undercooling would result in this term reducing. Because as e to power minus delta G D divided by k T as temperature becomes smaller this becomes more negative, and hence this term would reduce. So, we have 2 opposing factors to nucleation on reducing temperature or increasing undercooling. On increasing undercooling this term increases while this term reduces. And depending on which term dominates the nucleation rate could either increase or decrease.

Now, it has already been shown in the earlier lectures in part one, and as an example that with the taking transformation of water to ice.

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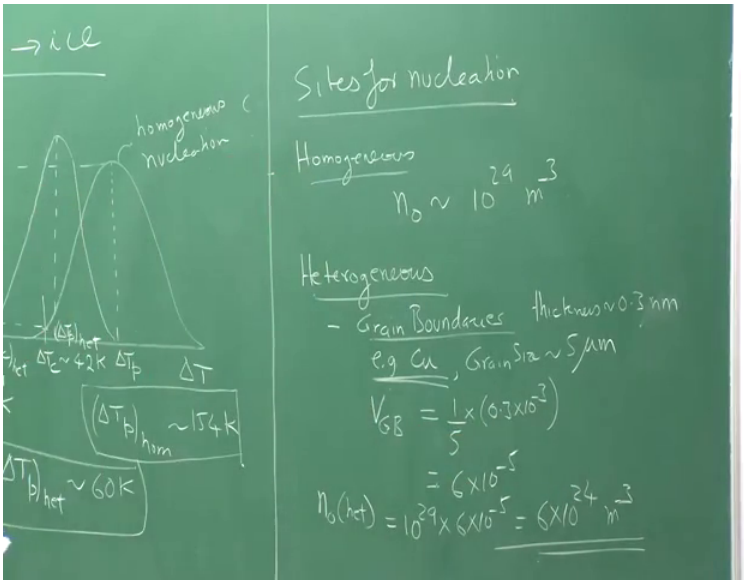

This is this was an example that was taken earlier in part one we found that at small under coolings nucleus nucleation rate is small. For large under coolings the nucleation rate is small while intermediate undercooling gives you larger a nucleation rate and. In fact,. So, if I want to plot I versus delta T I would get a change in the nucleation rate with increasing undercooling in the following manner that initially smaller nucleation rate and as delta T is increasing, the nucleation rate goes up and then it goes through a peak and as the undercooling increases further the nucleation rate starts drop again. So, for small under coolings we has very small nucleation rate for large under coolings we have again very small, nutrition rate for intermediate undercooling we can have reasonably high nucleation rates. In the case of water to ice, we had calculated this curve.

Another important factor that was discussed earlier is what is called as critical undercooling, delta T c. For an undercooling less than the critical undercooling there is no substantial nucleation that takes place and therefore, we cannot expect any significant phase transformation to take place. So, temperature is below that critical undercooling there will be essentially no phase transformation in measurable time. And we are also computed this critical under cooling for different systems including for water to ice. And in that we had assumed that there is a critical nucleation rate.

If the nucleation rate is very, very small then there will be essentially no phase transformation taking place which we can measure. And that undercooling critical under cooling we had taken as 10 to power 6 per meter cube per second. That is formation of 10 to power 6 nuclei in a one meter cube of the material in one second. It is a very small undercooling and it is essentially not even possible to measure.

So, if the nucleation rate is below Ic v say for all practical purposes that no transformation will take place. So, once we put these values into this expression here putting on the left hand side the critical nucleation rate, putting values for the number of sites where nucleation can take place number of atoms surrounding the nuclei the absorption probability calculating delta G star getting data G D the activation energy for jump. And once you do this calculation for the water to ice system then somewhere here let us say is Ic, and this for the water to ice system would give me a delta c which is of the order of 42 kelvin or 42 degree centigrade in this case does not matter. What scale you used because you are looking at the difference in the temperature between the temperature of transformation and the temperature at which nucleation is taking place.

So, for water to transform to ice you require an undercooling of 42 k, and this calculation was done for the case of homogeneous nucleation. So, if heterogeneous nucleation would not cannot take place if it has there is no possibility of a heterogeneous nucleation in where you do not do not have any substrate on which an ice nuclear can form, then freezing of water could become very difficult. You would have to go down to minus 42 degree centigrade in order for solidification to take place.

We had also computed the peak the highest nucleation rate at what temperature that takes place. Let us call that as delta T p the peak in nucleation at what undercooling that are does we found that delta T p for homogeneous one of the order of 154 kelvin. Then we compared this for the heterogeneous, in the heterogeneous case if there are substantial amount of sites where ice can nuclei heterogeneously, then one finds that nucleation of ice can take place quite easily.

And In fact, if you look at the rate of nucleation in this case one might get a curve which is shifted to the left, and this is my delta T c heterogeneous. And this is of the order of only 6 k. So, you just have to go few degrees below 0 in order for water to freeze you know that is what we normally observed in our refrigerators. And that it is because in our refrigerators water is solidify through heterogeneous route. And the peak temperature, So let me call that as delta T p heterogeneous. So, delta T p heterogeneous is of the order of only 60 k as compare to delta T p homogeneous.

So, this was a quick summary and before we leave this topic of nucleation rate. Just also summaries what we discussed regarding sites for nucleation. Because in this expression for nucleation rate if I now look at I 0 term. The I 0 term corresponds to as several terms and 0 n s nu and p in which n 0 which is the number of sites where nucleation can take place. What is the density of such sites? How many sites per unit volume are present? Let us just quickly have a brief idea of this number as well sites for nucleation.

In the case of homogeneous nucleation all possible atomic sites in the parents phase nucleation can take place. That in the case of metals n 0 is of the order of 10 to power 29 per meter cube all possible atomic sites for a site homogeneous nucleation.

Now, in the case of heterogeneous. In the case of heterogeneous nucleation, consider for example, grade boundaries. The number of sites for nucleation and grade boundaries that always depend on what is the density of grain boundaries, which could be related to the grain size of the material. For large grain size material the density of grain boundary is small, hence the site for heterogeneous nucleation would be small. For verify materials the heterogeneous sites would be much larger. For example, consider case of copper. Let us say the grain size is about 5 micrometers. Then first figure out what is the total volume of grain boundaries present.

So, volume of grain boundaries that would you present in a unit volume of the material would be inversely proportional to grain size. So, in this case 5 microns. So, it is 1 upon 5 multiplied by what is the thickness of the boundary which we assume the thickness, thickness of the boundary to be of the order of 0.3, 0.3 nanometers then we multiplied this by 0.3 and convert this into microns by multiplying it by 10 to power minus 3. And this gives me basically the volume fraction of grain boundaries pressure as 6 into 10 to power minus 5.

And hence n 0 in the heterogeneous case put simply this volume fraction multiplied by so many sites that are available for the homogeneous nucleation. So, that would give me the heterogeneous nucleation site. And that would be 10 to power 29 into 6 into 10 to power minus 5, and that gives me 6 into 10 to power 24 per meter cube. So, it is all of the order of the 10 to the power 24, here if I have a grain size of 5 microns versus the number of sites assisted 10, 29 if I have the homogeneous nucleation. So, the sites for heterogeneous nucleation can be substantially small. In fact, for a very large grain size material like let us say 50 micrometers, the number of heterogeneous I will further reduce by another order of magnitude.

Similarly, dislocations similarly if we consider dislocations.

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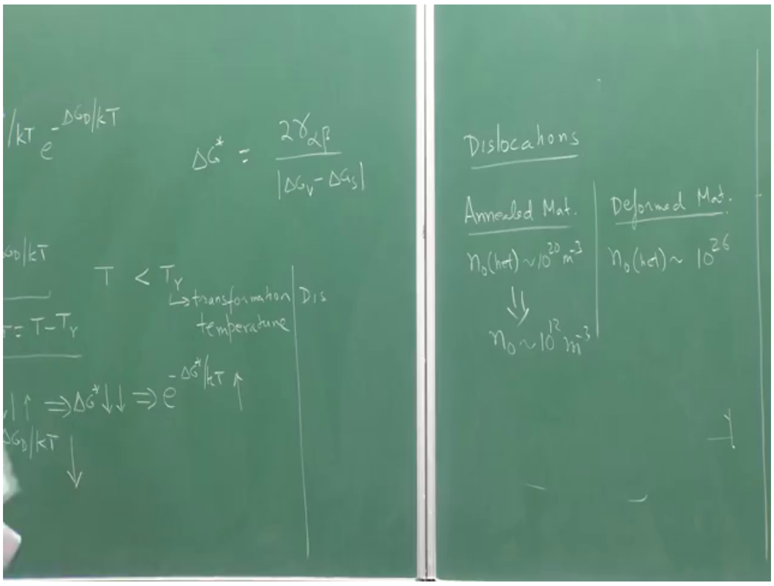

In the case of dislocations the number of sites of nucleation will depend on what is the density of nucleation. In case of unveiled material n 0 heterogeneous can be of the order of even smaller 10 to the power 20 per meter cube, in the case of deformed material the heterogeneous site would be much higher because deformation increases the density of dislocations. And hence n 0 heterogeneous can be of the order of 10 to power 26.

For materials which are specially prepared and have very low dislocation density, the heterogeneous sites could even go down to as low as 10 to power 12 per meter cube. So, even though heterogeneous nucleation will be a easier process as compared to homogeneous nucleation, but if there are no sites of very few very low density of sites are available then also the heterogeneous nucleation may become difficult.

So, this summaries what we have done regarding nucleation, if you wish you can go back to the old lectures of part one where over large number of lectures all of these topics for discussed in great detail. Now this is one aspect of phase transformation that is nucleation once a nuclei forms, how fast it grows will also determine what will be the rate of overall phase transformation. So, phase transformation is going to big a 1 by both kinetics of nucleation as well as kinetics of growth. So, let us also now look at a brief review of the growth kinetics of the stable nucleus v that gets formed.

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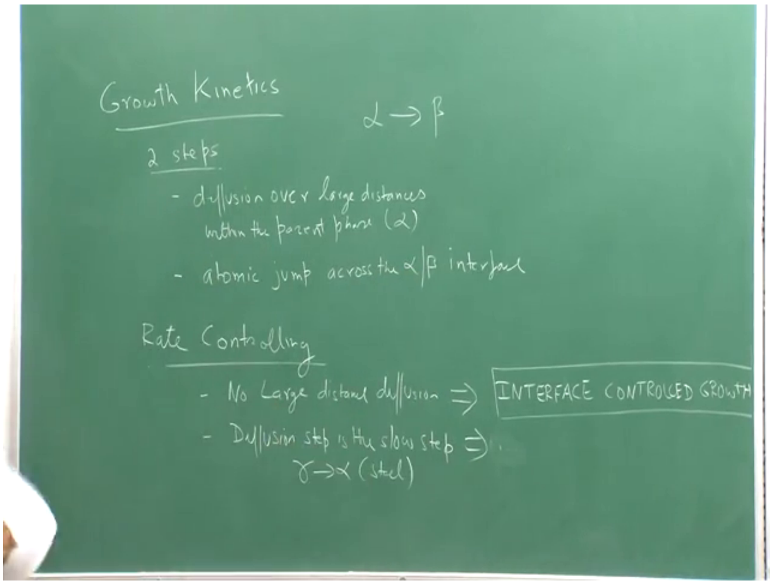

Growth Kinetics

$\alpha \rightarrow \beta$

2 steps

- diffusion over large distances within the parent phase (α)
- atomic jump across the α/β interface

Rate Controlling

- No Large distance diffusion $\Rightarrow$ INTERFACE CONTROLLED GROWTH
- Diffusion step is the slow step $\Rightarrow$
  $\gamma \rightarrow \alpha$ (steel)

So, reviewing Growth kinetics we can look at growth kinetics as in the form of 2 steps that are involved. Once a stable nucleus forms, the first step may involve diffusion over large distances within the parents phase this parent phase is what we have been calling as a alpha we are looking at alpha to beta transformation. So, beta precipitates out has a nucleus and then it starts to grow. So, there could be first diffusion within the parents phase over fairly large distances. And the second step would be atomic jump across the alpha beta interface. So, an atom has to jump from the parent alpha phase to the beta nucleus in order for the beta to grow.

So, both the steps would then cover the growth kinetics, but whenever you have more than one step involved in a process there can be systems where one of the steps is a rate controlling and the rate controlling step is the one which is the slow step. So, let us look at some scenarios of rate controlling step. There could be a situation where there is no large distance diffuse. And this would typically occur in pure component systems and in single component system for example, water to ice. Another example gamma FCC phase of iron transforming to beta body centered cubic phase of iron. Again there is no large distance diffusion of iron atoms within the gamma phase. So, no large distance diffusion. So, really the controlling step is the atomic jump over the alpha beta interface.

Such a process where it is the atomic jump across the alpha beta interface that controls the growth kinetics is called as interface controlled growth. So, this is one scenario that may be there. A second scenario is that the diffusion step is the slow step, and that can occur in many lay systems. For example, it could take place in austenite phase of steel transforming to the ferrite phase of steel. So, gamma to alpha in still. Here large scale diffusion of carbon atoms would be involved. Such a growth kinetics where only the diffusion over large distances in the parent phase is involved in growth is called As diffusion controlled growth.

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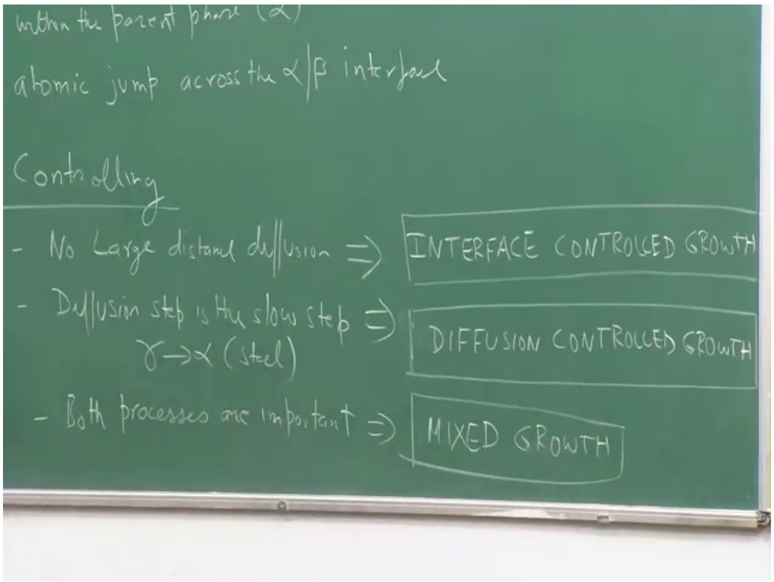

within the parent phase (α)

atomic jump across the $\alpha | \beta$ interface

Controlling

- No Large distance diffusion $\Rightarrow$ INTERFACE CONTROLLED GROWTH
- Diffusion step is the slow step $\Rightarrow$ DIFFUSION CONTROLLED GROWTH
  $\gamma \rightarrow \alpha$ (steel)
- Both processes are important $\Rightarrow$ MIXED GROWTH

Finally, there can be systems where both processes are important. Neither one is essentially dominating, this we will call this as mixed growth.

Now, why is it important to understand growth like this is because once we understand let us say that interface control growth then we can work out the kinetics for such a process. If you know what is that it is diffusion controlled growth then we can work out what is the kinetics. And both cases the kinetics going to be quite different. And all of this we have already discussed it quite detail and I am simply quickly basically reviewing the whole growth kinetics that we have done in a number of a lectures in part one.

So, what I will so, is in the next lecture, I will review individually the interface control growth and diffusion control growth. Look at how the 2 kinetics are different, and then we will combine the nucleation and kinetics and the growth kinetics, together to obtain the kinetics of overall phase transformation. So, I will stop here.