Heat Treatment and Surface Hardening - II
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Lecture – 26
Recap of homogeneous and heterogeneous nucleation for solid to solid transformation

So, in this particular course on heat treatment and surface hardening, I will be talking about time temperature transformation diagrams and continuously cold transformation diagrams. But before that let us briefly review the kinetics of phase transformation that was done in part one of this course, and the phase transformations that we are looking at in this particular part of the course is diffusional type of phase transformation. And you can refer to the lectures in part one of this course then particularly the lectures under week 5 to week 7 of the part one of the course.

So, in order to understand what are the transformation diagrams we need to have a good idea about how diffusional phase transformations take place and in this review of what we have already done?

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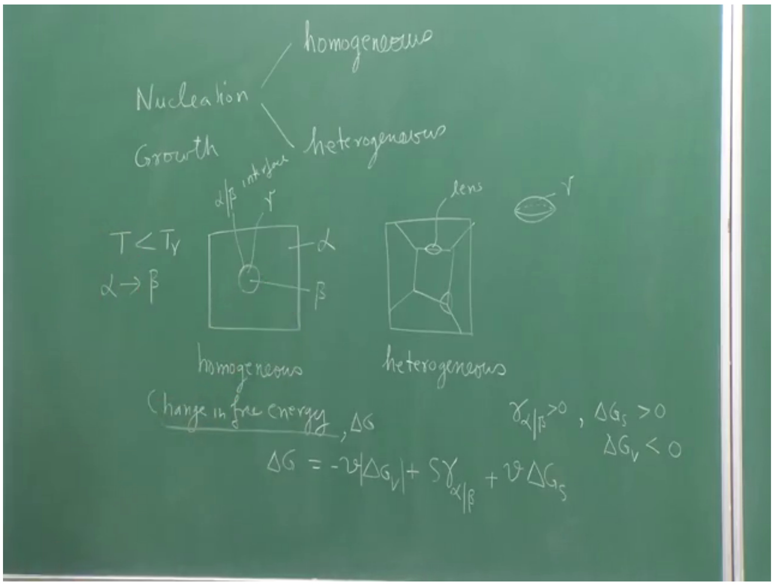

Phase transformations take place through 2 steps nucleation followed by growth. And let us first quickly review nucleation and kinetics of nucleation, then we will follow it off with growth and kinetics of growth of the formed nuclei. Now nucleation could take place in 2 different ways.

One way is homogenous nucleation. And an alternative way of nucleation is heterogeneous. So, what happens? Suppose we have to start with we have the alpha phase everywhere and as we have cooling down the material to a temperature less than the transformation temperature, where the transformation temperature is the transformation of alpha to beta. So, beta starts to form inside alpha, and for it is formation to occur first nuclei of a certain size beta precipitate will form. If this beta precipitate occurs anywhere we will call that as homogenous nucleation; that means, it can take place over the entire bulk of the material. And alternative way that a beta precipitate may form could be for example, on an existing surface particularly grain boundary.

So, if I have a polycrystalline alpha phase beta precipitate way form on the grain boundary. It could form on a grain boundary it can form were 3 grains meet that is on a triple point it. Could also form on other defects in the material such as this locations. This way of nucleation is what is called as heterogeneous nucleation. And in this route of nucleation this is known as homogenous nucleation. So, we will assume that in the homogenous case spherical nuclei of a certain size given by it is radius.

In the case of heterogeneous nucleation this lens shaped nuclei which is actually nothing but 2 spherical caps that may form. And the radius of this spherical caps is r. And let us now understand what is the change in free energy that is involved when a beta precipitate forms either homogenously, or heterogeneously what are the various terms that would go into the overall change in free energy. For so, let us try and write an expression for change in free energy delta G in the formation of a nuclei of a certain size. So, this change could be looked at as in different components

For example, there is a volume free energy involved, where alpha to beta transformation results in the reduction in the free energy. Let us call that as delta G v multiply it by the volume of the nuclei that is formed. This is resulting change which would be negative. Then there is the change in free energy as a result of the formation of and alpha beta inter phase. This would result in a positive change in free energy, and it can be written as the surface area of the nucleus multiplied by the surface energy per unit area of the alpha beta inter phase termed as gamma sub alpha beta. Thirdly there may be a volume change that is involved in the formation of beta.

For example if you consider a transformation of phase centered cubic iron to body centered cubic iron at temperatures below 910 degree centigrade, x there may volume expansion going from phase centered cubic structure to body centered cubic structure, as a result there would be a expansion producing a defamation in the surrounding alpha matrix and that would resist the change. So, this would produce another change in free energy which would also be positive and we would call that as delta G sub s the strain energy the strain that is resulting into the alpha matrix results in a change in free energy delta G sub s multiplied by what is the volume of the nucleus.

Now, alpha beta is greater than 0 delta G s is greater than 0, while delta G v is less than 0. Let me write this is slightly differently let me take the positive or the absolute value of delta G v and put a negative sign to make things very clear that this is a negative term while these 2 terms are positive. Now we are done a detailed analysis in the part one of this cores as to what would be the critical size of the nucleus beyond which the change in free energy would start to reduce, because when you plot this change In free energy delta G v versus the size of the nucleus whether it is homogenously nucleated or heterogeneously nucleated, that change can be shown or illustrated in a graph like this.

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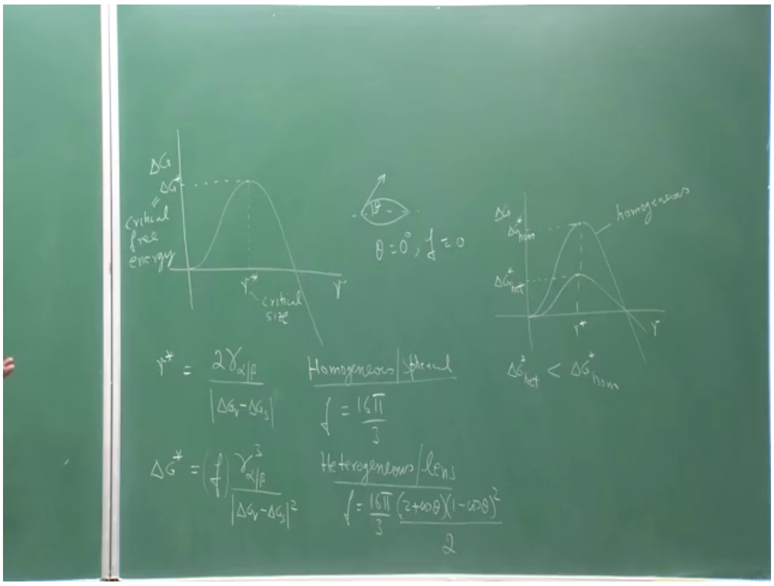

So, initially at small sizes the change in free energy is positive and it goes through a peak beyond which it starts to reduce and eventually there is an overall negative change in free energy. This peak in free energy it occurs at a size which is been called as the critical size r star. And corresponding to this critical size there is a critical change in free energy delta G star, critical free energy. We have analyzed this curve in detail in the part one of this course and the critical size of the nucleus is given by 2 times gamma alpha beta this surface energy of th alpha beta inter phase, divided by delta G v minus delta G s squared.

So, from this it is very clear that if your surface energy of the alpha beta interfaces high your critical size is going to be high; similarly if you are strain energy is large. Then also delta G v minus delta G s will reduce and as a result the critical size would increase. Let me see this peak would shift to higher critical sizes. Corresponding to the critical size of the nucleus the critical free energy delta G star was derived as some constant f times gamma alpha beta cube divided by delta G v minus delta G s square. I made a small mistake in the critical size of the nucleus there is no square here. So, it is simply 2 gamma alpha beta divided by the absolute value of delta G v minus delta G s.

Now, what is this constant f? That is there that constant f depends on what is the shape of the nucleus. In the homogenous case if we assume a spherical nucleus. So, homogenous and spherical shape f is simply 16 phi by 3. In the case of heterogeneous nucleation, and lens shape as I have shown here in this figure f is 16 pi by 3 multiplied by 2 plus cos theta times 1 minus cos theta square divided by 2, where theta is the contact angle that the nucleus makes with the substrate.

So, in this case for instance this was earlier grain boundary, this triangle is theta. And what it means is that theta decides the wettability of beta on alpha. So, if theta is 0 degrees beta completely wits the substrate. If theta is one 80 degrees it does not wet the surface at all. So, if theta is 0 degrees if we substitute in this expression f becomes 0. So, if theta is 0 degrees f is 0 and what it simply means is delta G star goes to 0. So, there is no barrier to nucleation for in such a situation. While for other values of theta they would be sub barrier; however, that barrier would be less than in the case of homogenous nucleation.

If we were to compare the barrier tot nucleation versus size of the nucleus if this represents the homogenous nucleation case, then the barrier to nucleation is delta G star homogenous. In the case of heterogeneous nucleation the shape would be something like this. With the same critical radius r while the barrier to nucleation delta G star heterogeneous is less than delta G star homogenous. And for very small contact angles delta G star heterogeneous becomes very, very small. So, in systems where homogenous nucleation could be very difficult in those systems heterogeneous nucleation maybe the only choice for the material to transform.

Now, this was a brief summary of just the nucleation process, now in order to understand the kinetics of phase transformation, we would need to look at how what would be the rate at which nucleation would take place. Now to look at that let us let us first understand that for phase transformations to proceed we must form stable nucleolus. For radios less than r star the nucleus formed is unstable and therefore, it will 10 to dissolve back to the left of this curve. For size is greater than r star the nucleus would become stable, because it can simply keep adding more atoms and increase in size and eventually the free energy change would become negative. So, it can. So, we would need to produce a stable nucleus in order for the phase transformation to proceed.

At the critical size a nuclei that is formed is under what we can call as unstable equilibrium. At this unstable equilibrium the nucleus would either role back and dissolve or it could go forward and become stable.

Let us understand this process of how critical size nucleus could become stable.

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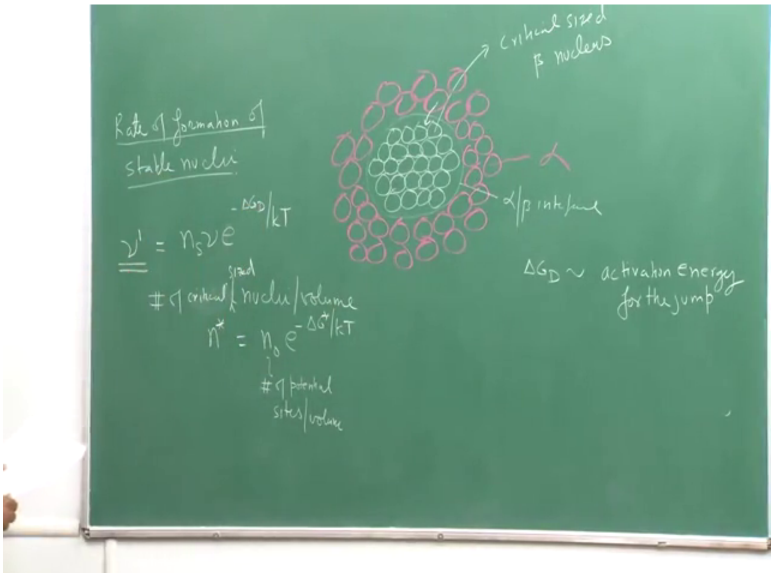

Rate of formation of stable nuclei

$$\underline{\underline{\nu'}} = n_s \nu e^{-\Delta G_D/kT}$$

# of critical sized nuclei/volume

$$n^* = n_0 e^{-\Delta G^*/kT}$$

# of potential sites/volume

$\Delta G_D \sim$ activation energy for the jump

So, for example, we have created a stable nucleus not us stable nucleus are critical size nucleolus. So, let us say this is a critical size nucleolus consisting of some number of atoms. So, critical sized beta nucleolus. Surrounding this is alpha so, the alpha phases surrounding it. So, all of this is alpha and for this nucleolus to become stable even if one of the atom from the parent phase alpha jumps across the alpha beta interface. So, this is your alpha beta interface.

So, even if one atom jumps the size of the nucleus would become greater than the critical size and the nucleus would become stable. So now, we would like to explore rate of formation of stable nuclei. That is what is going to governed the kinetics of phase transformation. So, rate of formation of stable nuclei, you know could be understood in the following manner. It will depend on number of atoms that our surrounding the nucleus the critical size nucleus number of atoms in the alpha phase. Let that be n s. All of these atoms are vibrating with a certain frequency called the debey frequency multiplied by that frequency multiplied by an activation barrier across which atom from the alpha phase needs to go across the alpha beta interface to the beta nucleus. And that activation barrier is delta G d the activation energy for the jump.

In therefore, the probability of a jump is related to e to power minus delta G d divided by k T were k is the boltzmann constant and t is the temperature. All of this put together gives me the rate new prime at which I would be forming stable nuclei.

Now, number of stable nuclei per unit volume no not for the stable number of critical size critical sized nuclei per unit volume would be given by n star. And that is equal to n 0 e to power minus delta G star divided by k T. So, n star is a number of critical size nuclei in a unit volume n 0 is the number of potential sites then new critical size nuclei I can form per unit volume and delta G star of course, is the critical free energy for the critical sized nucleus.

So, at any given time I can expect to find so many critical size nuclei per unit volume. Out of which some of them would roll forward and become stable while many others would rollback become unstable and dissolved back. So, not all of these critical size nuclei I will form stable nuclei. At what rate this is going to happen this is going to happen at a rate of new prime, and hence the nucleation rate I will call this with the symbol I number of nuclei number of stable nuclei per unit time per unit. So, volume of the material this is simply equal to n star times new prime. And if I just multiply both of these quantities together I will end up getting n 0 n s new e to power minus delta G star by k T multiplied by e to power minus delta G d by k T.

There will be another quantity that I have to introduce and let me introduce that quantity called p. P is the absorption probability. That even if an atom jumps it may not get absorbed in the nucleus and the jump actually may end up in a failure. Now this expression gives me the rate of nucleation whether the nucleation is occurring homogenously or heterogeneously.

Now, in the next lecture we will briefly analyze the nucleation rate, in terms of temperature. How it varies with temperature below the transformation temperature how I varies as a function of under cooling, under cooling is under cooling delta T which is defined as the temperature at which the nucleation is taking place minus the transformation temperature. So, as the undercoating increases which means the temperature transformation reduces, how the nucleation kinetics changes we will analyze in the next lecture.