Powder Metallurgy
Prof. Ranjit Bauri
Department of Metallurgical & Materials Engineering
Indian Institute of Technology, Madras

Lecture – 11
Thermodynamics and Kinetic of Solidification

Hello and welcome back again. So, we have been talking about this nucleation and growth mechanism as it happens in the process of atomization.

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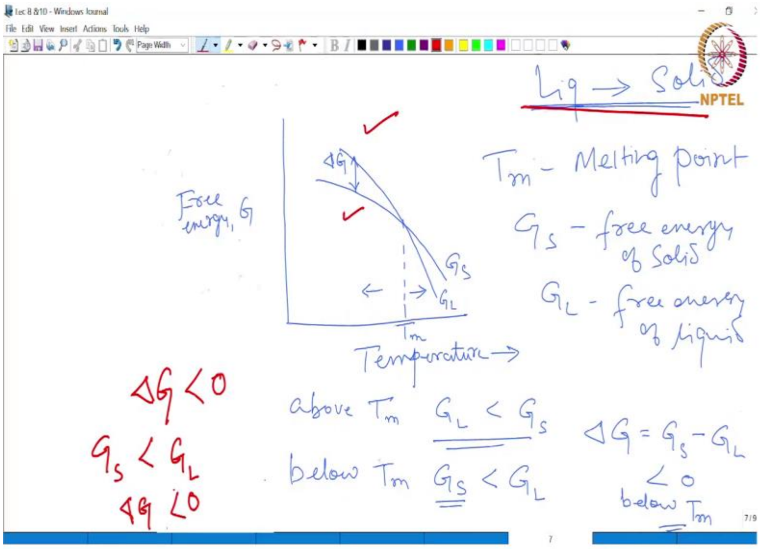

In the previous class we talked about how the nucleus of the solid forms and how it grows. Basically, it involves this free energy change as we discussed with the help of the above diagram.

Whenever there is a transformation from liquid to solid or any transformation going from one state to another state, one should look at the energy change from a thermodynamics perspective whether that energy change is negative or positive.

Any transformation will occur spontaneously whenever the change of free energy is negative. For example, when there is a transformation between liquid and solid, the liquid goes to solid as the temperature is lowered below the melting point and the ΔG becomes negative.

Because below the melting point the free energy of the solid that is G_S is less than that of the liquid which is G_L and because of that ΔG becomes negative. Hence, the liquid transforms to solid.

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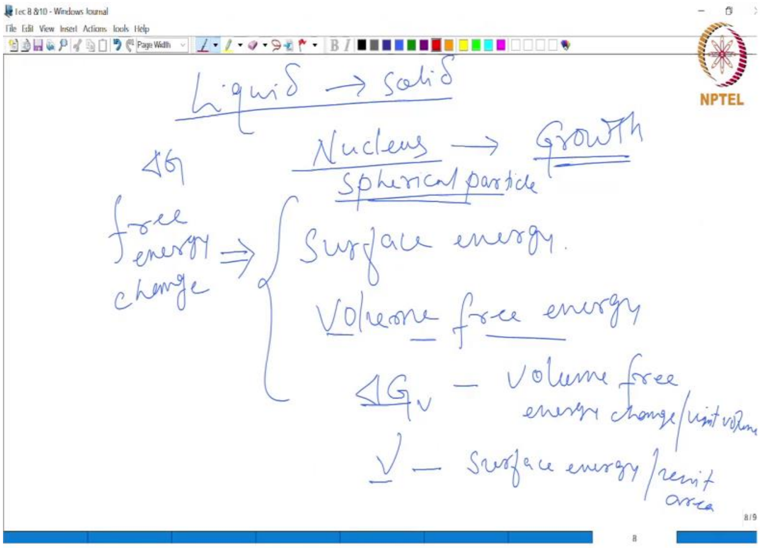

So, that is when the first particles of the solid forms and these very small or tiny particles of the solid or the first few particles of the solid are known as the nuclei or the nucleus.

Depending on whether this nucleus is attaining a critical size or not, it will grow or dissolve back into the liquid.

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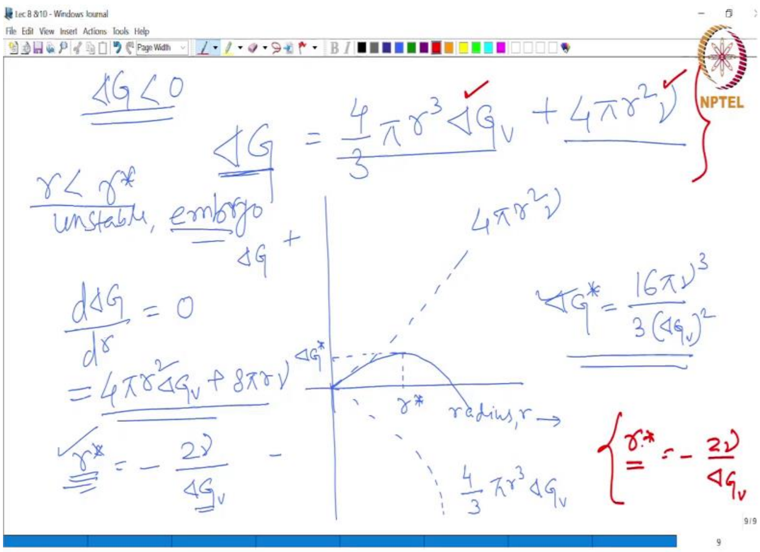

That is the growth criteria of this nucleus which forms and this depends on these free energy terms or these two contributions to the free energy change; one is the volume free energy change ΔG_V and another is the surface free energy.

From this we could derive the critical size r* which is given as,

$$r^* = -(2\gamma/\Delta G_V)$$

Only when the size of the nucleus reaches its critical size i.e., r* then only it can become stable and grow further. So, now in today’s class we are going to see, what is that criteria for the growth of this nucleus and how the solid ultimately grows.

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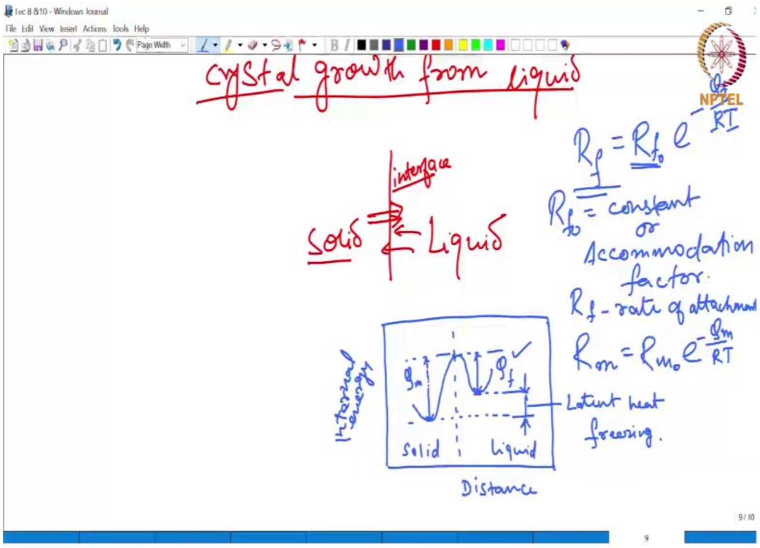

If you look at this crystal growth from liquid, it is basically the growth of that nucleus which forms and then attains the critical size. So, when that happens, there is an interface which develops between the liquid and the solid which is growing. Also, how this solid will grow that would depend on how atoms are coming from the liquid and joining the solid.

So, there is a movement of atoms from the liquid phase to the solid phase for the solid to grow. When the solid cannot grow; that means, nucleus is in the process of attaining the critical size, in such case it can dissolve back into the solid and then there are movement of atoms from the solid to the liquid.

So, we can see here that across the interface there is two-way movement of atoms either from liquid to the solid or from solid to the liquid. From an energy perspective, this for the solid to grow there is a energy barrier to it or there is an activation energy which is needed for the solid to grow from the liquid phase.

Let us say y-axis is internal energy (graph in above figure) and this is where our interface is the right of which is liquid and at left you have solid. The energy is plotted as a function of distance from the interface. When you look at it from an energy perspective where there is an energy barrier. So, that can be represented with a above mentioned plot.

So, for the solid to grow or for the atoms to transfer from the liquid to the solid, the energy barrier which is given by the distance between the well and the peak must be overcome. Similarly, for the movement of atoms in the other direction the energy barrier that has to be overcome.

Because the growth of the solid is dependent on the attachment of atoms from the liquid phase i.e., the atoms have to move from the liquid and go to the solid and attach to it for the solid to grow.

So, that rate of attachment can be written as,

$$R_f = Rf_0 \, e^{-(Qf/RT)}$$

Where Rf_0 is a constant which basically is related to how these atoms which are coming from the liquid to the solid, how those atoms are being accommodated in the sites inside the solid.

That accommodation or the ease of these atoms to be attached to the solid that is given by Rf_0 and this is also known as an accommodation factor. And Q_f is the activation energy, and the other two terms have their usual meaning that is R is the gas constant and T is the absolute temperature.

Similarly, for the solid to get dissolved back into the liquid, there has to be detachment of atoms from the solid and going into the liquid. So, that rate of detachment can also be given by a similar relationship like how the rate of attachment is given.

$$R_m = Rm_0\, e^{-(Qf/RT)}$$

So, there is an activation energy which is required for the solid to grow and the difference between these two points that means, these two potential wells, i.e., potential well for the liquid and potential well for the solid, the difference between those two is obviously, the latent heat of freezing. Because here we are talking about freezing of a solid; that means, solidification from the liquid phase.

Once this activation barrier is overcome more and more atoms will attach to the solid. This rate of attachment is going to increase as more and more atoms attached to the solid and it grows. And, as a result of that growth this interface is also going to attain a particular growth velocity because the interface is also going to move when the solid grows that interface will move towards the liquid so that solid will grow more and more.

Once this happens there will be a growth velocity which can be assigned to the interface. So, this is how you know from a thermodynamic point of view you can see how the solid will grow from the liquid phase.

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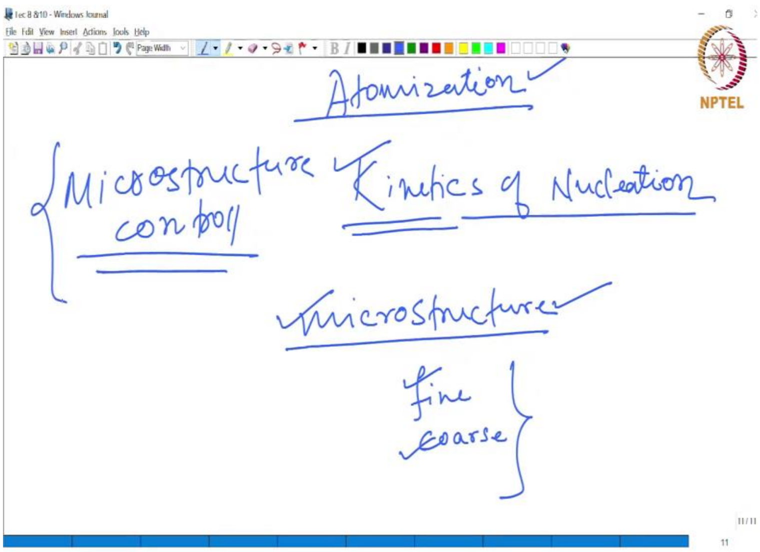

And, from here when we come back to the process of atomization, you are actually forming the solid powders from a stream of liquid metal and that is how this nucleus and growth aspect is coming into picture. So, here you can see you know the powder is forming from the liquid phase and considering these thermodynamics we saw that how or what is the criteria for the solid to crystallize or for the solid to form from the liquid phase.

Now, if you also want to know what is going to be the structure of this powder which is forming from the liquid phase, then you will have you will also have to consider the kinetics aspect of this solidification process. That means, you will have to see what is the rate of nucleation and at what rate it grows that will decide the structure of the solid which is forming in terms of whether it will be a finer or a coarser particle.

Or whether the microstructure as we call it microstructure is nothing but the internal structure of any material whether the microstructure is going to be fine or coarse that would depend on the kinetics of the process. So, let us try and understand that as well because ultimately we will have to correlate the process to the structure that we get inside the material including these powders.

That is what we call as structure property correlation because the structure will finally, decide the properties of the materials.

So, let us see what are the kinetics aspect of this atomization process or the solidification that happens in atomization.

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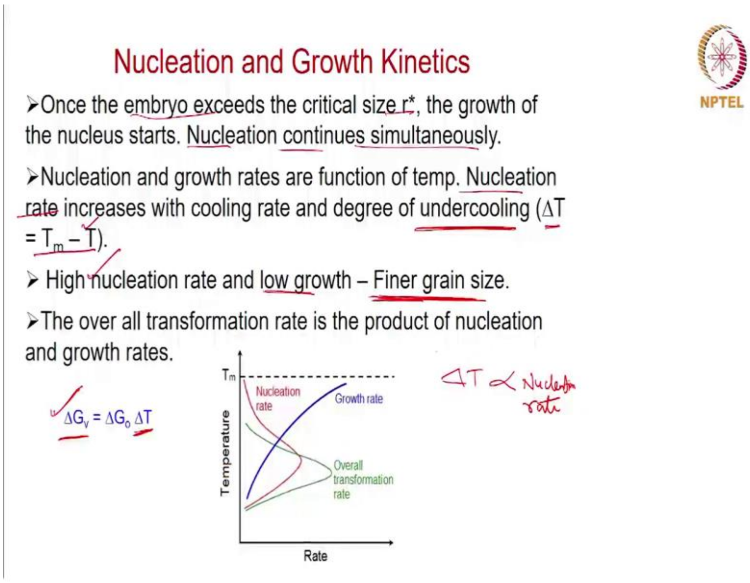

As we understood by now once the embryo reaches that critical size *r**, the growth process will start and on the other hand, nucleation continues simultaneously; that means, at these critical size nucleus starts to grow more and more and smaller nuclei will also form simultaneously. As and when these nuclei also attain that critical size they will also start to grow.

Now, depending on what is this rate of nucleation and what is the rate of growth depending on that your microstructure will be decided. So, whether you would get a finer grain size; that means, a finer microstructure or not that is going to be decided by the nucleation and the growth rate or the competition between these nucleation and growth rate.

And, here you should also understand another parameter known as under cooling because what happens when you solidify a solid from the liquid phase you know the liquid has to be cooled below the melting point, then only this solid will grow continuously and ultimately all the liquid will transform into the solid phase.

This cooling below the melting point without starting the nucleation of the solid crystal is what is known as the under cooling. Which is given by,

$$\Delta T = T_m - T$$

This T for example, is the temperature to freeze the liquid is cooled below the melting point when it is still in liquid condition. That means, it that the formation of solid is yet to start, but the temperature is still below the melting point.

So, that under cooling or $T_m - T$ or this ΔT that is what is needed for the solidification process to start and this free energy change the volume free energy change ΔG is a function of this under cooling and ΔG_0 is the standard free energy change. And, therefore, you can see what will be the effect of the under cooling from this simple equation itself.

As ΔT or under cooling increases ΔG_V would also increase.

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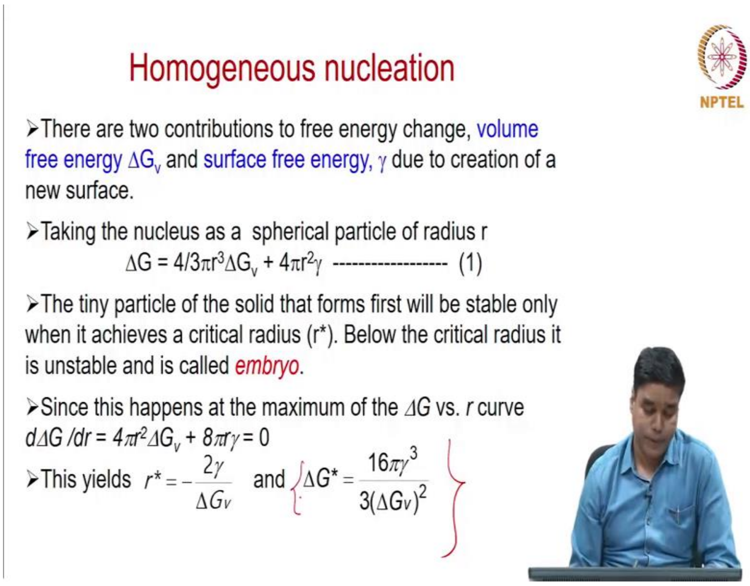

And, from this relationship you can see that as ΔG_V increases it becomes easier to form more and more nucleus because the critical size needed for the nucleus to be stable decreases and the critical free energy change also decreases.

As ΔG_V increases it becomes easier for more of these solid particles or more of these nuclei of the solid phase to form and as a result you can expect the nucleus and rate to increase as the under cooling increases. So, ΔT will then equate proportionality to the nucleation rate. As ΔT increases the nucleation rate will also increase.

If that happens if the nucleus growth rate overtakes the growth rate; that means, if the nucleation rate is higher than the growth rate then the microstructure is going to be finer because in that case as the nucleation rate is higher you can expect more and more nucleus to form in a given period of time. Therefore, the growth or the rate of growth will be much lower compared to the nucleation rate and on the other hand there will be more number of nucleus.

These two factors; that means, the formation of more number of nuclei in a given period of time and you know less growth will ensure that the microstructure does not grow microstructure can be characterized by different aspects or by different kind of features, grain size is one of them. So, that will lead to the finer microstructure or finer grain size.

You can also say that a high nucleation rate in the case of the atomization process would also lead to finer particles. Because the nucleation rate is given as a function of temperature; this is the nucleation rate and this is the growth rate, (graph in the above slide) and you know overall transformation rate is just the sum of these two.

This micro microstructure would depend on which is prevailing over the other whether nucleation rate is prevailing over the growth rate and in that case you are going to end up with finer microstructure.

And, on the other hand, if the growth rate prevails over the nucleation rate; that means, if the growth of this nuclei which form is high then you can also expect these grains to grow right if you talk about the grain size.

And, as a result the size of the grains will be high, what is known as what can be called as coarse grain microstructure or a coarse microstructure. This is how the kinetics of the nucleation process which relates to nucleation rate would decide the microstructure whether it is going to be a fine or a coarse kind of microstructure.

So, that will give us an opportunity of controlling the microstructure in the atomization process and this is an important aspect because as I said the properties that we are going to get from a powder or for that matter for any material, that is going to depend on this microstructure.

So, how that will be controlled you know that is what will be our next topic or that is what we are going to discuss next. So, with this I am going to end today’s class and I will see you again in the next class.

Till then, goodbye.