Powder Metallurgy

Prof. Ranjit Bauri

Department of Metallurgical & Materials Engineering

Indian Institute of Technology, Madras

Lecture - 10

Nucleation and Growth

Hello everyone and welcome back again. As I told you in the last class, today I am going to discuss about a very important aspect of the atomization process which is about the Nucleation and Growth as it happens in the atomization process ok.

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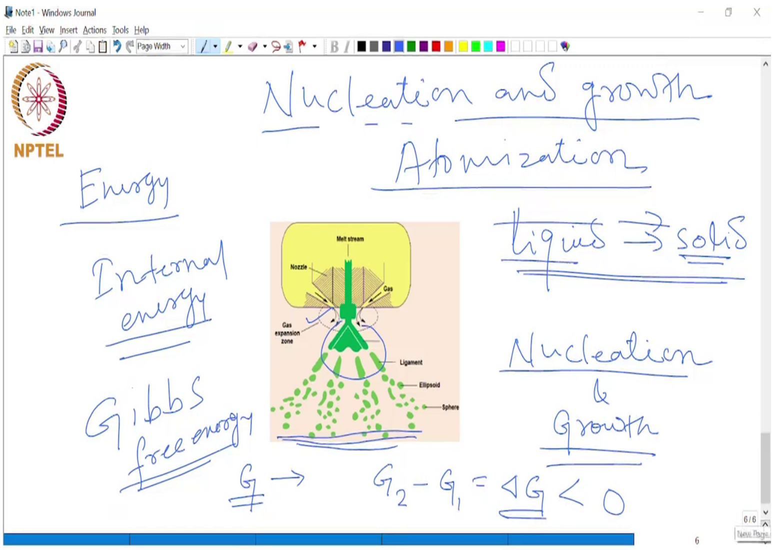

So, if you remember let me quickly bring it back the diagram that we had. So, this is what happens in an atomization process as you can see and as we have discussed before also. You have a molten metal stream over here right in this place which is being broken down into finer fragments by a gas jet ,with the high velocity gas jet as it expands and suddenly impacts the molten metal stream.

It breaks down into smaller fragments and finally, as it travels down this chamber at the end of this, it solidifies as solid metal powder. So, that means this liquid to solid transformation is involved in this process .

And this is a very important aspect that we need to understand as to you know, how these solidification happens in this process and you know what are the different attributes of this and you know what are the details of the atom so on. So, that is what we are going to learn in this class today.

So, solidification or the liquid to solid the transformation can be understood from this concept called nucleation and growth. Nucleation is nothing, but you know the formation of the first solid particles, if you talk about the liquid to solid transformation. For that matter, it is true for any other transformation also.

The product phase the formation of the product phase the first very particle of the product phase that forms from the parent phase is called a nucleus. So, that is the starting of the transformation.

So, in this case when it is transforming from liquid to solid, the nucleus is the first ,the very first tiny particle of the solid that gets transform from the liquid phase as you cool it down below the melting point . So, above the melting point you have the liquid, because the liquid is more stable above the melting point in those kind of temperatures and as you cool it down the solid becomes more stable .

So, the stability of any state of matter that depends on its energy because any matter would like to stay at the minimum energy level . So, when you see a matter in a particular state under particular conditions, it means that under those conditions it is existing in that particular state, because that state will give the material or the system the lowest energy.

For example, if you see water as we all see water it is liquid in room temperature and atmospheric pressure . So, that tells you that the water in liquid condition is the more stable phase in room temperature and atmospheric pressure, because that particular state will give it the minimum energy. So, it will be in the lowest possible energy state in room temperature and atmospheric pressure. And that is why it is the liquid form of water is stable in room temperature and we always see it in the liquid form generally right at room temperature.

So, unless otherwise it is cool down below the melting point ,it is frozen below 0 degree centigrade; you know it is going to remain liquid . And if you want to change the state then you will have to do something to the system; that means, you need to do certain work to the system in terms of either extraction of heat or addition of heat.

So, all these you know boils down to the energy of the system. You can also call it the internal energy of any material or the system. And whether a particulars state of a matter will transform to another state, that would depend on whether the energy is getting reduced or not.

So, for example, any material will go from liquid to solid, if going into the solid reduces the energy of the material . So, whenever you have a transformation like this it will happen only when the energy is reducing. So, that particular aspect is described in terms of a particular energy known as Gibbs free energy or free energy. This is actually related to the internal energy of the system of the material. This is generally denoted as G.

So, change in the Gibbs free energy will decide whether the transformation will proceed or not; that means, when it is changing from the parent phase to the product phase or from the parent state to the product state, whether this energy is reducing or not. In other words, the change from going from state 1 to state 2, this delta G whether it is negative or not ok. So, a transformation will happen or will proceed in the forward direction only when the delta G is negative.

So, as far as the liquid to solid transformation is concerned, this free energy change can be explained with the help of a diagram like this; where you have the free energy on the y axis and temperature on the x axis.

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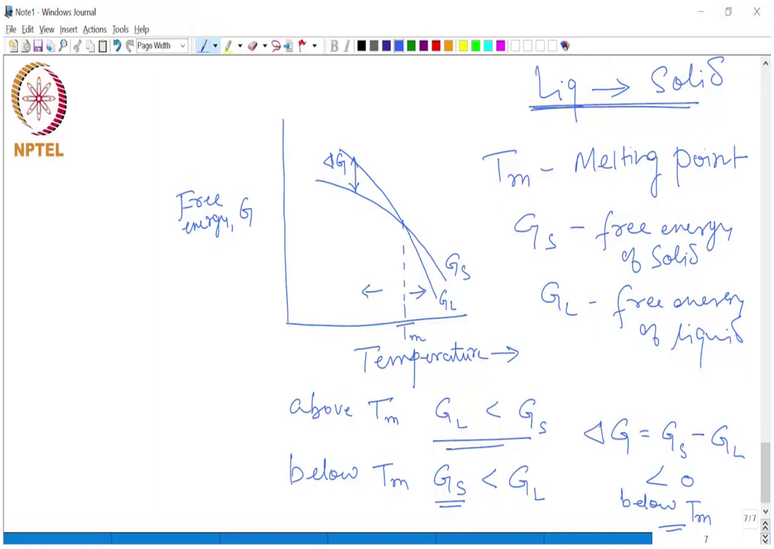

Now, again taking the same transformation liquid to solid this is the melting point that we denote as T_m.

So, here you can see these two curves that you have. They represent the free energy of the solid and the liquid as a function of temperature. This one is for the solid, G_S that is free energy of the solid and this one is the free energy for the liquid denoted as G_L. So, now you can look at this curves on the left and right of the melting point T_m; that means, if you come to this or that side, what do you see in the free energies?.

So, above the melting point you can see the free energy of the liquid is lower than that of the solid. And therefore, the liquid is more stable above the melting point and that is why it melts as you cross the melting temperature and becomes liquid.

Similarly, below T_m, the free energy of the solid is less than that of the liquid and therefore, the solid is more stable below the melting point. And that is why when you reduce the temperature below the melting point the liquid transforms into the solid .

So, therefore, you need to see this change in the free energy ΔG and below the T_m you see that G_S is less than G_L. So, if you take the ΔG that becomes negative below the melting point ok. As we reduce the temperature and bring it down, the solid will have lower free energy compare to liquid as a result ΔG is negative and therefore, when you cool it down below the melting point, this liquid to solid transformation takes place. So, that you can see with the help of this particular diagram.

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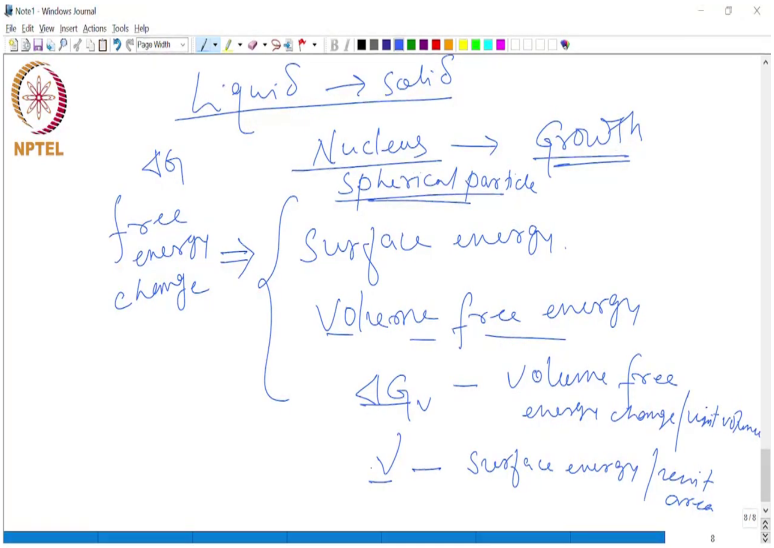

Now, when the solid forms, it does not form at once. The solidification or the formation of the solid particles it starts with a very small tiny particle. As I said before the very first particle that forms as you cool it down below the melting point. So, that is known as the nucleus.

And then if this the small particle ,the tiny particles if it attends a size which is stable under those conditions when it is solidifying from the liquid to the solid in that particular atmosphere in the liquid, if this small particle is stable then it will grow up.

So, that is what is the growth process when more and more atoms will join this tiny nucleus and it will continue to grow and finally, you know this solid material will grow from the liquid the solid crystals as we call them the solid crystals will form from the liquid.

So, whether this nucleus will be stable or not that depends on the two different kind of energies. First of all, when you are forming a solid particle, you are actually creating a new surface ,a new surface . So, that surface energy therefore, has to be considered. And then you are also creating a new volume of material a solid material which will grow ultimately from the liquid and therefore, the volume free energy also has to be consider.

So, the free energy change that we talked about the ΔG-It will have two components, one coming from the surface energy and another from the volume free energy. So, if ΔG_V is the volume free energy per unit volume and γ be the surface energy per unit area then, considering this nucleus as a spherical particle, we can write this ΔG in terms of ΔG_V and the γ.

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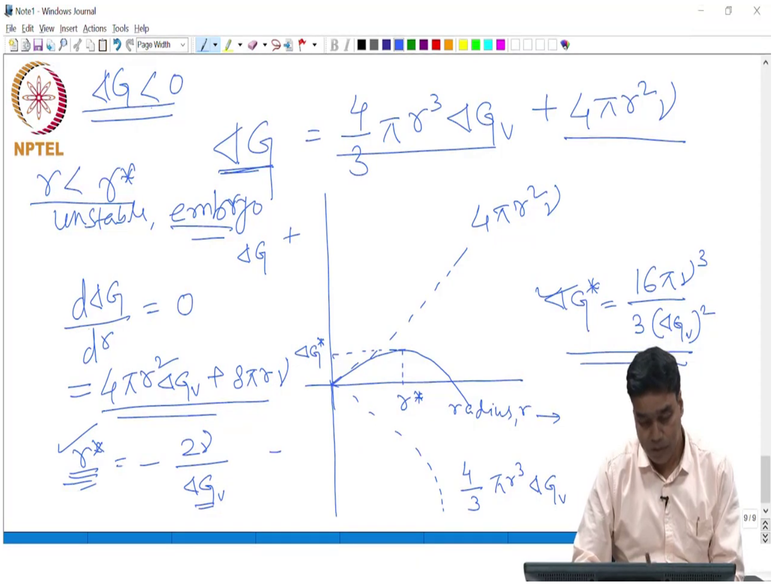

So, if you consider the nucleus to be spherical, the volume will be this if you take the radius as r. So, therefore, this will be the total volume free energy change and the surface energy would be this; where $4\pi r^2$ is the surface area . And these two components of ΔG; that means, this one and this can also be represented graphically where you plot it in terms of the size or the radius.

This is ΔG positive and this is negative. This is the surface area contribution and this is the volume free energy contribution, which is negative. And the summation of these two is ΔG which can be shown here as the sum of these two is like this.

So, if you take this maxima here the maximum, this is the critical size of the nucleus. So, if the size of the nucleus does not attain this size it will dissolve back into the liquid L and will not grow as a solid . So, the nucleus has to attain these critical radius then only it is going to grow .

So, since it happens at the maximum. This $d\Delta G/dr$ is 0 . So, if you differentiate this you get this is equal to 0. And from here, you can derive the critical size of the nucleus which will come out as

$$-2\gamma/\Delta Gv.$$

So, the negative sign here indicates that this ΔG_V is negative; that means, the free energy, the volume free energy will reduce once it attains this a critical size . So, that is what the negative sign indicates. And similarly, the corresponding ΔG value will be given as given as this. So, these are the critical values one for the size of the nucleus and one for the free energy change.

So, as the nucleus attains the size it will become stable in the liquid and more and more atom will diffuse to the nucleus and it will grow ok. So, just remember this thing. This is a very critical parameter if the size is if r is below r*, it will be unstable and then the nucleus is called as an embryo and only when it is more than the critical size r* this nucleus will grow as a solid particle. So, that would depend on the local conditions during the solidification process .

So, this is about the free energy change , like how you can see it from here. It has two different contributions. And only when this ΔG becomes negative, this transformation will take place and the solid will grow from the liquid.

Then you will also have to see as to, what are the effect of different process parameters as you cool the liquid from liquid to solid on the solidification phenomena as such .

So, those are the other things that we need to consider to understand this whole process of solidification as it happens during the atomization process. So, you know that has to be discussed again in more detail so that we will take up in the next class. So, for today I am going to stop here.

Thank you for your attention.