Principles of Casting Technology
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Lecture - 02
Solidification
Cooling curves, concept of nucleation and growth

Welcome to the lecture on Solidification. We will discuss about solidification of castings. Before going to solidification of castings, we will first try to get introduced to the concept of why solidification occurs. Solidification means crystallization, means the liquid state has to convert to the solid state, this process is known as solidification. Now there is a mechanism by which the liquid state step by step converts to a solid state and what is the underlying principle that we will discuss in our this lecture.

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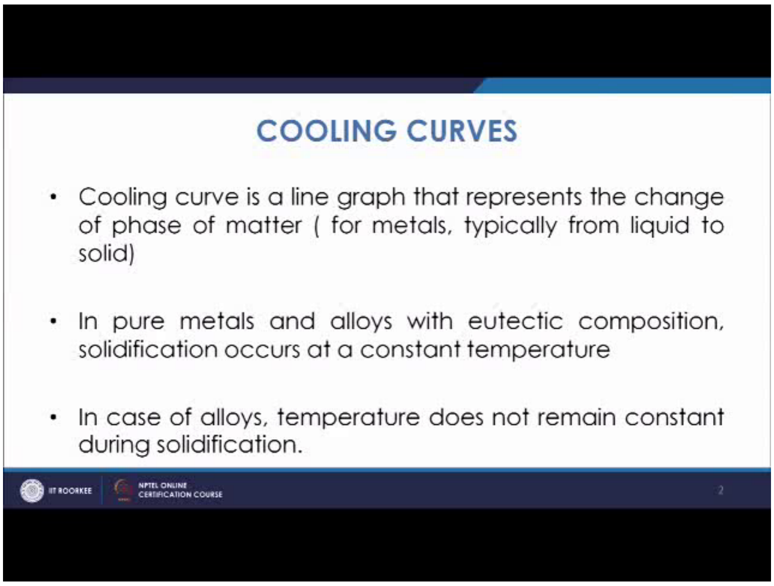

We will first discuss about the cooling curves. Now what do you mean by cooling curves? We have discussed that when a liquid metal is cooled, it has to solidify. Now the liquid metal is attained by heating the solid part because we need to study in casting because of the aspect that a cast metal cannot be shaped to any forms. So, it has to be converted to a liquid a state. Now once it is goes to the liquid state, we have given energy in terms of thermal energy into the solid state and that is why it has attained a liquid state.

Now, from there once you are trying to cool it, the temperature will drop and the behavior of the temperature drop is known as and that can be represented by a line graph and this line graph is known as cooling curve. So, cooling curve basically will be a line graph which represents the change of phase of the matter. It may be from gas to liquid and it may be from liquid to solid. So, when we talk about metals normally we are interested in case of the face transfer from liquid state to solid state and that is why when we talk about the cooling curves of metal, we talk about a curve that is the conversion of the liquid state to the solid state.

Now, it has been seen that in pure metals and alloys with eutectic composition solidification occurs at a constant temperature. So, if you draw the cooling curve of a pure metal or the even alloy with eutectic composition where the solidification at a constant temperature. The cooling curves are represented by such curves.

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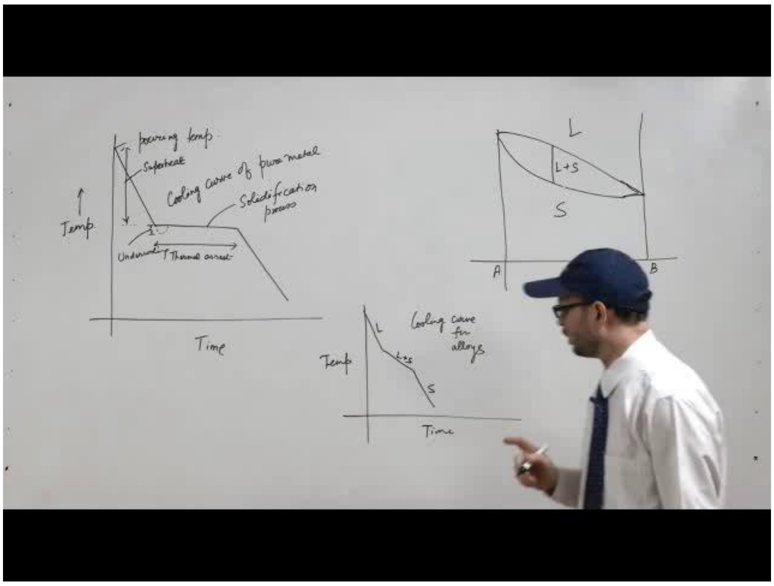

So, this is temperature and this is time. So, this is the typical cooling curve of pure metal. We are pouring at this point, this is the pouring point, so pouring temperature we are pouring into the mould at this temperature, the liquid is poured always at somewhat higher temperature than it is melting point. This temperature differential from it is melting temperature to this point, this point the temperature difference is this and this is known as superheat, degree of superheat.

Now, once you are cooling the material. So, with time the temperature of the metal will come down steadily at one point of time, this temperature does not decrease for some time. So, this reason is a reason of thermal arrest. Now what happens during this reason? Once it comes here the liquid tries to lose the latent heat and the liquid is converting to the solid crystals slowly and this process is basically represented by this straight line. This is the reason of thermal arrest. It means that the amount of free heat which is extracted because of the mould conditions that is compensated by the amount of heat released because of the latent heat released and in that process this temperature during this whole solidification process. So, this is a process of solidification going on. So, this is solidification process.

At this point the solidification is complete. After the solidification is complete, then now again further by further cooling the temperature goes on decreasing. So, this is the cooling curve for a pure metal. In fact, this is the idolized cooling curves, but the thing is that once you have conversion of the liquid state to solid state, once the solid crystals are coming out of the liquid state, it does not occur at this temperature itself. So for that, slight amount of under cooling is required.

Initially this so far it start for the solidification to start initially, there has to do some decrease in the temperature and this is known as under cooling. So, this decrease in temperature below its melting temperature is known as under cooling and the amount by which decreases that is known as degree of under cooling. So, degree of under cooling is a must for the solidification to start with and this is typically for a pure metal or even in case of eutectic composition like may be for aluminum silicon alloys or may be for iron carbon with carbon composition of 4.3 percent. In that case, you have a point where it melts at a constant temperature. So, there also similar type of cooling curve is being faced.

What happens in case of alloys? In case of alloys as we know alloys are having certain phase diagram. So, you may have, this is A and this is B, A 100 percent and B 100 percent or so, in that case, what we see is this is the process this is the arranged which is characterized while liquid plus solid and this is liquid and this is solid. Now in this case the alloys are characterized by the property like it does not solidify at a constant temperature because it is a mixture of 2 components. So, the crystallization is in different way. In this case, the even during the solidification process also there is decrease of temperature, it does not occur at a constant temperature.

So, for alloys it goes like this. So, this is the cooling curve for alloys. So, this is the pouring temperature, it has come to it is liquidus point, after that it has come to a solidus point, but between that this is the liquid plus solid reason, this is liquid reason and this is solid reason. So, during this solidification process also there is decrease of temperature and this is the typical character state of an alloy now the slope of these lines depends upon the freezing range of the alloys and accordingly it will vary for different materials different alloys.

Similarly, the slope of this line or this line also will be depending upon the how fast you are cooling or how slow you are cooling. So, that way the slopes will vary, but the characteristic of the lines or the nature of the lines will be similar and these are known as the cooling curves for metals and alloys. In case of alloys temperature does not remain constant during solidification.

Now we will discuss about the concept of nucleation and growth. What happens when the solidification starts at this point and why it is basically converting to the solid state? We are going to discuss about it.

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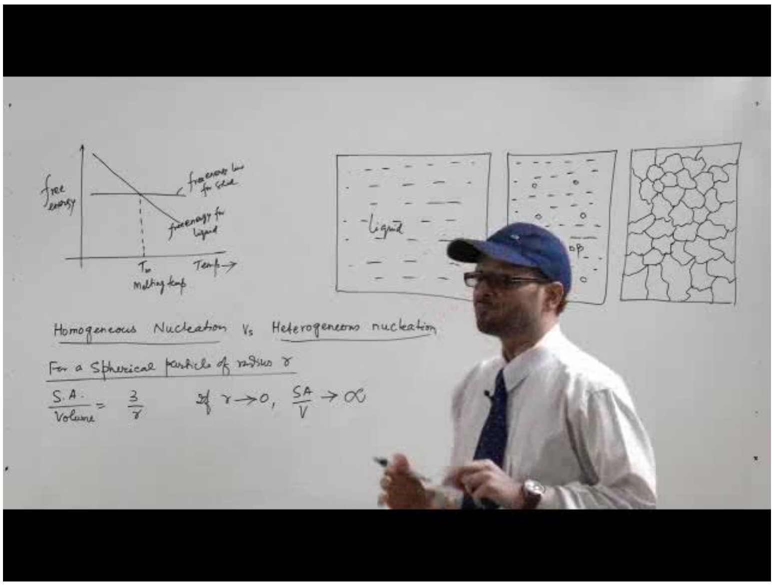

The principle behind the transformation from this liquid to solid state is the free energy basically the free energy curve if it is drawn for the 2 states, liquid state and solid state we get such free energy.

If it is free energy, what you see is this is the melting temperature. So, this is the temperature line. Now what we see is this is basically the free energy line for liquid and this is free energy line for solid. Now we need to know why a state is there at any temperature. Any material as a solid state or a liquid state at a particular temperature, this is governed by this free energy value. Now in that particular condition or at that particular temperature, whichever state will have the lower free energy the material will try to have that phase itself. Now if you look at the free energy for liquid, it is seen that above this melting temperature the liquid state has a lower free energy.

Basically any material would like to be in a state which as the lower value of free energy. So, above this melting temperature you have the liquid state which as a lower free energy that is why when you heat the material above a certain temperature, it is converted into a liquid state.

Similarly once you are cooling it and going at a temperature lower than the melting temperature, what we see is that the solid state as lower free energy. That is why when we are decreasing the temperature the material has to be converted to a solid state which as lower free energy. At this temperature this is known as the melting temperature or even equilibrium temperature. At this type temperature it is seen that the solid state and the liquid state both have equal amount of free energy, it means at this point solid and liquid co exist they have. So, you have both solid as well as liquid state once you go below this temperature then only the conversion of liquid to solid starts.

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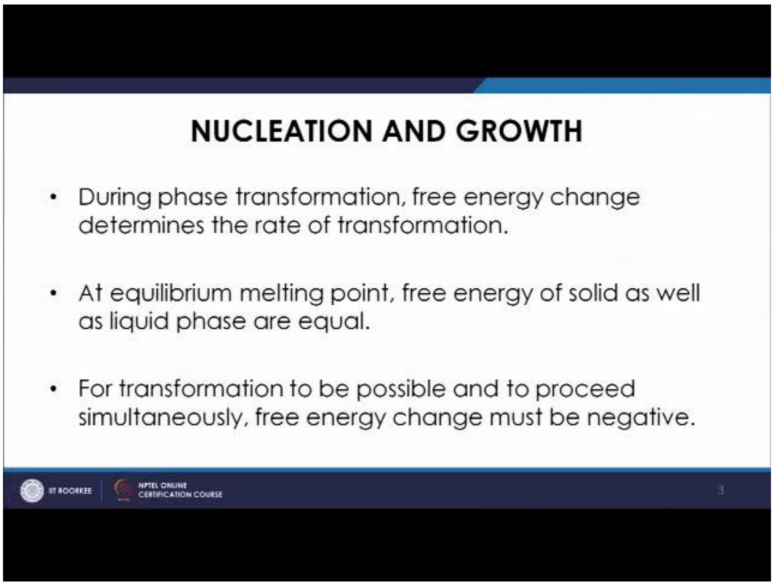

What we see here that for phases can transformation free energy change, now the change of this free energy will determine the rate of transformation how the liquid is going to be transformed to the solid state and it is rate of transformation is basically governed by the free energy change. At equilibrium melting point we have the already discussed that the free energy of liquid as well as solid is same for transformation to be possible and to proceed simultaneously free energy change must be negative. So, for any transformation to take place and then further to continue it, the free energy change must be negative. So, this is 1 criteria which must be satisfied so that you have any transformation in this case from liquid to solid state to be possible your free energy change has to be negative.

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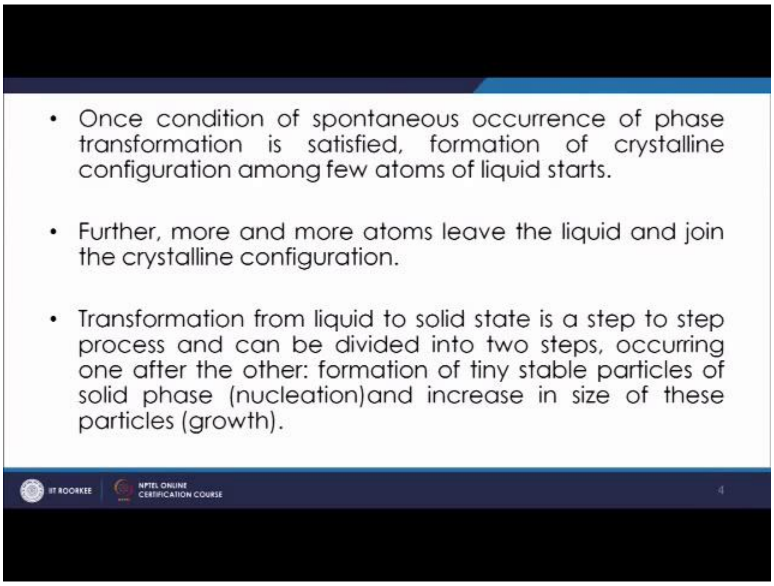

Once condition of a spontaneous of occurrence of phase transformation is satisfied transformation of crystalline configuration among few atoms of liquid starts, it means that when you feel that there is change of energy and at that point the free energy were equal now the free energy of solid state is small. So, there has to conversion from liquid to solid state and basically solid being the crystalline material in general. So, basically the atoms will try to rearrange themselves in the crystalline way, but this is not possible or this is not particle that whole of the domain is converting to a crystalline state at one point of time.

Basically it is a step by step process now what happens that from the liquid few atoms will come and among them there will be a solid crystal formed. This solid crystal formation will be based upon the theory of it is existence. So, there are principles behind how they will exists, they will be able to have their existence in the liquid phase as a solid particle. Further once they are meeting the condition of maintaining their existence in the liquid then at one point of time in they are in position to basically further invite to more of the liquid atoms to come and join and they have the further opportunity to grow. So, that is how it goes in a step by step manner.

Transformation from liquid to solid state is a step to step process and basically there are 2 steps, 2 discrete steps this transformation goes on. First is formation of tiny stable particles of solid phase and then increase in size of these particles. So, formation of the tiny stable particles of solid phase, this process is known as nucleation. So, from the liquid phase, the small tiny particles have nucleated, they have taken the birth that is known as nucleation and further in course of time when they are growing by taking more and more atoms from the neighborhood that is a process of growth.

Let us see how it goes. So, basically you have initially all liquid. So, this is a liquid phase once you are cooling at one point of time, you will have at some point you have some crystallization of certain solid phases, otherwise you have liquid. So, these are the beta phases, these are the solid crystal of beta page phase which has come out at certain locations and once they are able to sustain themselves, then slowly they will grow and after sometime once they grow then you will have the formation of such structures and these are the phases and this is how the macro structure looks like. So, they become the whole solid phase from the liquid phase. So, that is how the whole certification process is carried out.

So, this small tiny particle or crystals of solid appearance of them and sustenance of them is known as nucleation and before that they are may be because of the conditions because of the fluctuations or because of the unavailability of under cooling, these crystallization are not possible. But with that favorable condition at one point of time these crystals are able to sustain themselves and after that once they are over to sustain themselves with further under cooling and with further passage of time, your structure becomes like this, whole a solid state a microstructure which is looks like this they are the different crystals of solid phase. This is how you have the nucleation and growth and giving you the whole solid matrix, now how it goes.

So, basically when we talk about nucleation. Nucleation is nothing, but the presence of solid crystals or the birth of solid nuclei into the liquid stream now if you look at. When we talk about nucleation, there are 2 types of nucleation, homogeneous nucleation and heterogeneous nucleation. So, homogeneous nucleation is that type of nucleation in which, in whole the domain the probability of having nucleation at any point in the domain is constant throughout, whereas in case of heterogeneous nucleation, in heterogeneous nucleation basically the probability at certain preferred sites is more. So, in case of heterogeneous nucleation the nucleation will be more preferred at certain points because of certain requirements that you may discuss in brief later and this is basically because of the formation of because of the presence of certain foreign particles or may be on the walls or other reasons, that we will discuss.

Now, let us talk our let us discuss the homogeneous nucleation part. Now if we think of the nucleation of a spherical particle. Now what happens once in a spherical particle tries to have a birth in the liquid domain now what we see is that when any birth as to take place it is nothing, but the creation of a surface and the surface as a positive energy. Now this energy has to be supplied during the transformation process. So, what happens that during the initial birth many a times if the under cooling is less or so, the surface all though appears, but because of the thermal fluctuations or because of unfavorable birth conditions, this basically is further suppressed, but then at one point of time it comes into it is assistance.

For example, if you take for as spherical particle for a spherical particle of radius r, now what happens? When this r is very small, so for that surface area upon volume this is if you take the surface area of by volume of for spherical particle of radius r, it is comes as 3 by r. So, what happens if r is very very small tending towards 0, this surface area by volume is tending towards infinity. This requirement is very high and that is why they are not able to sustain themselves. So, they are basically going into the melt every time they try to come up they collies further and they go into the melt, but then as this r increases, you have 2 terms basically and due to that term this they are able to sustain themselves that we will see how they are going to do.

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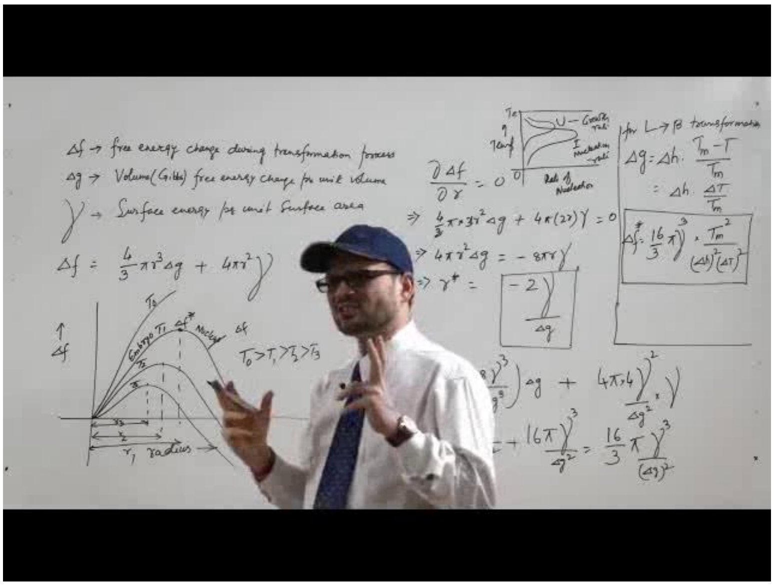

If we talk about certain terminologies, one is delta f that is free energy change during transformation process then we take delta g as volume or gives free energy change per unit volume and this gamma, this is nothing but the surface energy term, this is surface energy per unit surface area. So, for any spherical particle, delta f can be taken as volume times the free energy per unit volume. So, that will be 4 by 3 pi r cube and delta g plus surface times, surface energy per unit surface area. So, surface area is 4 pi r square times gamma. So, this is the free energy change for the transformation to take place.

Now, if you look at the graph of the free energy, the surface energy term is always positive and when the radius is very small or at the equilibrium temperature, you have only surface energy term and this volume free energy term that can be positive or negative and for any volume to form this free energy term as to be negative. So, initially with higher temperature goes through the melting temperature at t 0, the graph goes like this now once we decrease the temperature and once the radius.

What happens, once you have for negative value of this volume free energy term this graph will have a maximum at certain point. So, what happens with that value, the graph will have this shape when this delta g terms becomes negative, slowly it starts dominating as r becomes more if you look at this term if the r becomes more and more this term starts dominating and since this is negative this graph curve will have a maximum point and after that it will try to go on reducing. So, at this point, this is the maximum point and this graph is nothing but the same line delta f. So, this is expression for delta f and this is basically a point where you have maximum value of delta f. At this point you have dou delta f by dou r as to be 0, this is your change in free energy and this is radius.

This is r for this r this becomes the value of free energy change in free energy now this as to be 0 at this point. So, if you differentiate this term this becomes 4 by 3 pi r cubes. So, it will be 4 by 3 pi into 3 r square delta g plus 4 pi r square gamma. So, it will be 4 pi into 2 r into gamma that has to be equal to 0. So, basically this if you look at that you will have r. So, this is 3 and 3 will cut. So, 4 pi r square delta g will be equal to minus 8 pi r gamma and r will be equal to minus 2 gamma by delta g. So, this is and this r is known as the critical radius.

At this critical radius for this condition, this is the critical radius value for which the maximum point is achieved and this is basically the condition which tells that it may be now in a position to further grow and once further atoms go to this then it becomes super critical. So, that is the condition for critical and that is why you have this is also known as delta f star, at this point this value is known as delta f star that is known as critical barrier. So, once it has crossed this point, it means it is likely that it will be sustained and there will be further growth of the particle which as nucleated.

Before this, it is known as embryo, before this since it is not able to sustain itself it is known as embryo and after that it is known as a nucleus. So, once it as attained that then it is known as nucleus now with this is at t 3 temperature if you go for t 2 temperature, the curve goes like this and if you go for t 3 temperature, the curve will goes like this where t 0 is more than t 1, t 2 and t 3. So, what we see is as you go for lower temperatures, the radius which is required critical radius, its value is going on decreasing. So, this will be r 1, if this is r 1 this will be r 2 and this will be r 3. So, like that the radius will be varying.

So, this is the concept of having that particular critical radius above after which this nucleation will sustain. If you put this r star value into this you let us see what happens then in that case delta f star will be 4 by 3 pi into r cube. So, it will be r star cube and that will be minus 8 gamma cube by delta g cube into delta g plus four pi r square gamma r square will be 4 gamma square by delta g square.

What we see is minus 32 by 3 pi gamma cube by delta g square plus 16 pi and here further you have gamma. So, gamma cube by delta g square and that comes out to be 16 by 3 pi gamma cube by delta g square. So, what we see is the critical value or this barrier comes out to be 16 by 3 pi gamma cube by delta g square. Now further this value of delta g can be taken as, for liquid to crystal formation to take place the delta g value can be taken as delta h into t m minus t by t m.

What happens, this can be taken as delta t that is under cooling t m minus the temperature. So, that will be delta h into delta t by t m. So, further, this is for liquid to beta transformation. So, once you put this delta g value, here you can have the value of delta f as you have 16 by 3 pi gamma cubes upon delta g square. So, into t m square upon delta h square into delta t square, this is what you get the value of delta f the critical barrier in terms of delta t.

Now, what you see is that when this delta t is 0 when this delta t is 0 your delta f star value is infinite and once this value is infinite in that case no nucleation will take place. So, that is why at equilibrium temperature where delta t is 0, there will be no nucleation taking place similarly at a temperature of absolute 0. This value may be 0 and in that case again delta f will be infinite and in that case further the nucleation will seize. So, basically nucleation starts below the equilibrium temperature and it stops when the temperature achieved is the absolute 0 between that there is a variation of the nucleation rate.

Now, further nucleation rate is basically dependent upon also the rate by which or the frequency by which the atoms are joining into the product phase from the parent phase. So, that way the rate of nucleation is referred that is further another topic which can be further considered in detail, but what we mean to say is that nucleation starts at that particular point below the equilibrium temperature and it stops at absolute 0 and in between it comes through in maximum because this value is infinite at the equilibrium temperature, but it becomes finite as the temperature is lowered.

So, in that process the rate of nucleation is increased and it comes to a maximum value. So, if you look at the nucleation graph it if this is the equilibrium temperature then the rate of nucleation goes like this. So, this is the 0 temperature rate of nucleation. So, the rate of nucleation goes like this and this way, the maximum nucleation rate is that this is basically the degree of under cooling in this direction and this temperature is there. This is the degree of under cooling in the opposite direction. So, these will maximum nucleation here and this is how the nucleation starts.

Now, once nucleation has been done, there will be further growth and basically growth curve is also like this. So, this is nucleation rate of nucleation and this is growth. So, this is rate of growth, growth rate, this is nucleation rate. So, nucleation rate as well as growth rate both are having the similar shape and they basically start below the equilibrium temperature and growth is dominant in the upper temperature reason where as nucleation is dominant in the lower temperature zone of under cooling. So, that is how nucleation and growth because of this you will have the crystallization of solid particles from the liquid particles. In the next lecture, we will discuss how they are (Refer Time: 39:14) in case of metals and alloys.

Thank you.