**Materials Science and Engineering**
**Dr. Vivek Pancholi**
**Department of Metallurgical & Materials Engineering**
**Indian Institute of Technology Roorkee**

## Lecture – 20
## Nucleation and Growth

Hello friends, today I am starting with a lecture on nucleation and growth till now we discussed all the transformation ok, first we discussed about the phase diagram and then using phase diagram we discussed about the transformation from one phase to another phase; how this transformation is going to take place and so on ok. But we did not discuss anything about the rate at which this transformation is going to take place ok.

So, now the lectures which we are going to have ok, basically we are going to discussed about that how this transformation is going to take place ok. So, this today's course is on nucleation and growth ok. So, you can understand that when for example, you must have seen the formation of ice from water when you keep water in the freezer ok. So, there has to be someplace where the nucleation is started and that nuclei is growing.

So, always whenever you have any kind of transformation there has to be some nuclei which is taking place or some nucleation event has to take place and that nuclei will then grow and then it will take up the whole space. So, from liquid to solid or you can have solid to solid transformation as we saw in case of a steel from austenite to ferrite alternate to pearlite or from solid and that means, from liquid phase to solid phase and during solidification. So, in these are all processes there has to be some formation of a nuclei and then nuclei will grow.

In solidification for example, the vessel in which you are pouring the liquid metal ok, that vessel wall itself act as a site where the nucleation will take place. So, nucleation is starts from the wall and then the growth goes inside the molten metal inside the basically inside that vessel and then the whole liquid metal will solidify and that is what if you do a close examination of formation of ice in your freezer, you will see that it is starting from the walls and it is then going inside the, so central part will be the last 1 to solidify ok.

So, that is what is the nucleation growth process and from that also we will like to bring the time factor in the whole of this transformation process ok. So, just to again bring the idea of if you remember when we were discussing initially That the carbon exist in form of hexagonal graphite as you can see here ok.

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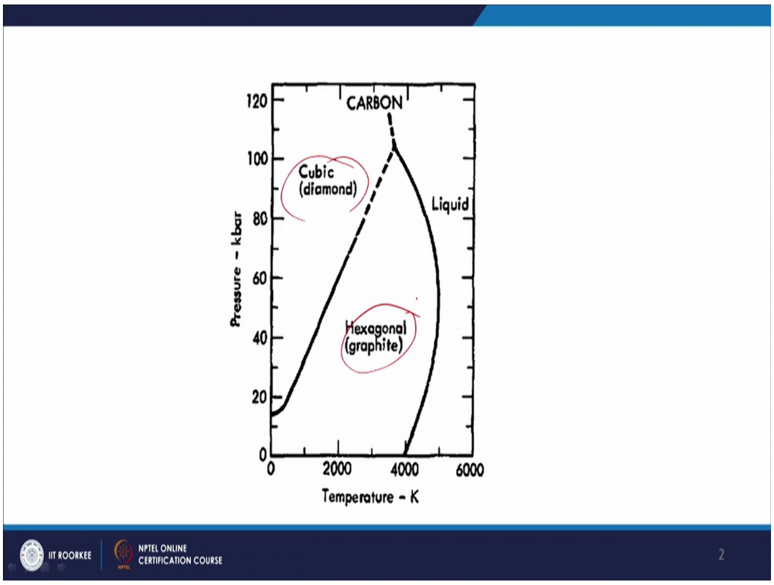

So, you have hexagonal graphite here and you have cubic diamond here. So, if you see this is a pressure temperature scale is temperature and pressure, so at lower temperatures and lower pressures means 1 normal room temperature pressure actually the diamond is not the stable phase, it actually should transform to graphite maybe ok.

So, but we said that it does not happen diamond remains as a diamond for, if a diamond is a was excavated sometime 2000 years back also it still remains a diamond. This Kohinoor still diamond it is not transformed into graphite in so many years ok; that means, it is a still stable form of that and we said that why does not do that is because the rate of changing from this diamond to let say graphite is very slow ok.

So that means, there is a concept of rate here a time factor is here and that is what we will like to understand. So, phase diagram when we see these are based on thermodynamics principles ok. So, there is no mention of time here ok, only it will tell you that at this particular temperature pressure for this composition whether for this particular system which phase is the stable phase.

So, if you take pure water at room temperature ok, under normal atmospheric pressure it should be the stable phase is water liquid water. If I take this water above 100 degree Celsius then the stable phase is the vapor phase, if I take it again at the atmospheric pressure again I bring it to a temperature below 0 degree Celsius at normal atmospheric pressure the stable phase is the solid phase.

So, thermodynamics tells me that which is going to be the stable phase at a particular temperature pressure condition, but it is not going to tell me about the how much time it is going to take place from for the transformation; for example, from liquid to solid phase. So, it will not give any information about the rate of transformation, so that how fast or slow the transformation will proceed that is the domain of kinetics, so this is the next concept which is called kinetics.

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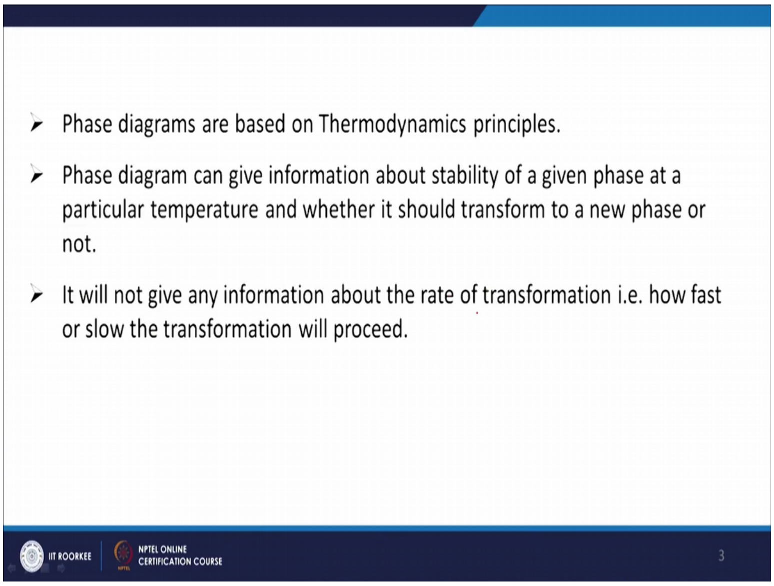

- Phase diagrams are based on Thermodynamics principles.
- Phase diagram can give information about stability of a given phase at a particular temperature and whether it should transform to a new phase or not.
- It will not give any information about the rate of transformation i.e. how fast or slow the transformation will proceed.

So, you have thermodynamics which tells me that which phase should be the stable phase and then there is a kinetics which tells me that how fast or slow this phase will change from this particular state to the another state. So, if you see transformation the transformation involves two processes ok.

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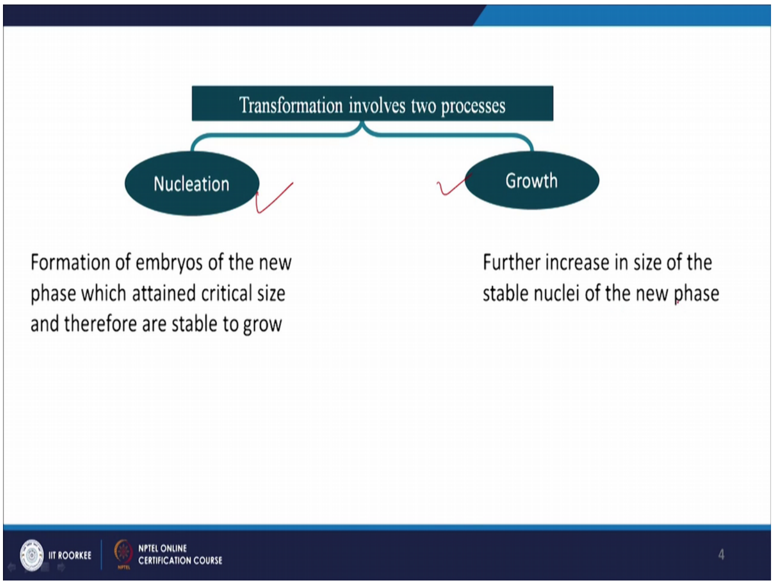
Transformation involves two processes

Nucleation

Growth

Formation of embryos of the new phase which attained critical size and therefore are stable to grow

Further increase in size of the stable nuclei of the new phase

One is nucleation that means, when liquid is transforming into solid or 1 solid is transforming into another solid, there has to be some nucleation at some point there has to be some nucleation and then that nuclei. So, there has to be a formation of embryo of the new phase which attained critical size and therefore are stable to grow and then you have a growth process further increasing the size of a stable nuclei of the new phase.

So, this is what is the process of transformation nucleation and growth. Now if we come to nucleation the formation of new phase from parent phase ok.

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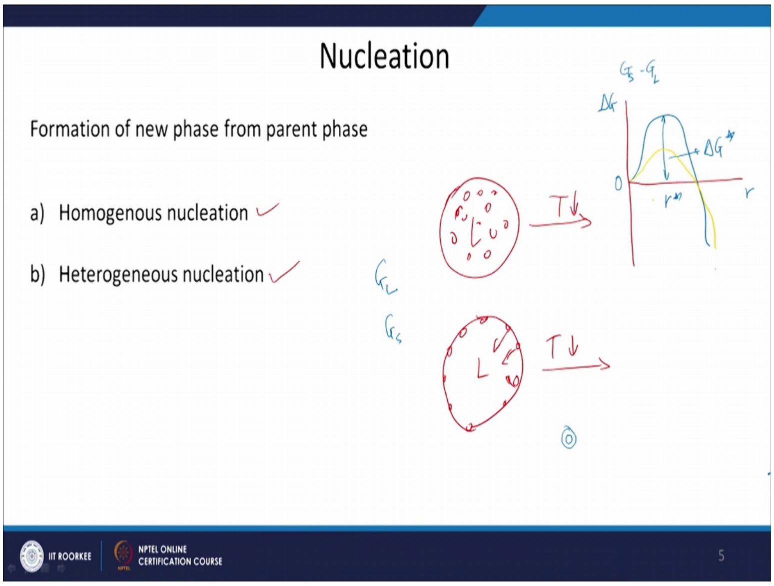
Nucleation

Formation of new phase from parent phase

a) Homogenous nucleation ✓

b) Heterogeneous nucleation ✓

So, suppose I start with the liquid now the question is where the when I am bringing down the temperature. So, I am bringing down the temperature here. So, in this liquid in this system here this is my system boundary and there is a liquid inside. So, where this nucleation is going to take place is it going to be homogeneous nucleation; that means, that the whole liquid everywhere as soon as I have bring down the temperature at every point there will be some nuclei which is forming of solid is it going to be like this or it is going to be heterogeneous nucleation ok. That means, if this is my system contains the liquid the nucleation will takes place for example, at the surface of this system it can be a vessel or whatever.

So, when I bring down the temperature here the nucleation is starting from here then it will grow inside and later on the whole liquid will transform. So, it can be either homogeneous nucleation means, at throughout the system the nucleation is taking place or it can be heterogeneous nucleation ok; that means, only at few location the nucleation will takes place and actually what decides this whole process and you will see that in general the heterogeneous nucleation is the one which is going to be dominating ok.

To achieve a homogenous nucleation actually you have to have very specific conditions only then you will have homogeneous nucleation. In fact, it is a very difficult process to do to have homogeneous nucleation and the reason is ok.

So, suppose let us say I draw a free energy curve here 1 of the plane here, for example so suppose you have 2 axis here 1 axis I am saying is axis y axis is delta G axis and the x axis is the radius of the nuclei. So, delta G is suppose my liquid is not the stable phase. So, my system want to go into solid phase. So, the there is a free energy of the liquid phase and then there is a free energy of the solid phase delta G will be equal to let us say it will be GS minus GL.

So, what is the change in free energy and if you remember earlier also that we said that the transformation will takes place only when the free energy change is negative. So, this is at this point it is 0 and then the transformation will takes place when the free energy is negative, but the problem is that when you want to have a new phase coming ok, what will happen you will have a new interfaces there between solid and liquid ok.

So, some change is there because of the stable phases solid now ok. So, there is a decrease in free energy, but there will be also an increase in free energy because of the formation of the interface. So, all this will what it does is that it actually increases the free energy initially and then the free energy decreases as the solid is growing ok.

So, as a function of radius if I want to see by I can have a small nuclei which is forming and then it grows and become a bigger nuclei. So, I can draw a free energy diagram like this my drawing is not very good here ok, but it will have some curve like this ok. So, you can see that initially when the transformation is taking place the free energy is becoming positive and then after some time it is becoming negative. So, this increase in the free energy and reaching the maximum this will I will call it as this is known as delta G star and at the radius at which you have delta G star is called r star.

So, I will have a stable nuclei only when I have cross this hill and this is what I call is activation barrier earlier also we use this term ok. So, this is the activation barrier for formation of new phase from the old phase ok. So, this much activation barrier you have to cross to go into the next phase or to have the transformation and at this point the radius of the your nuclei will be equal to r star.

So, if I my radius of the nuclei is below r star then I will call it as embryo; that means, it is not a stable nuclei it can again go back into liquid phase, If it crosses this critical radius r star then it will become a stable nuclei and then the free energy will start coming down and then it will become negative later on. So, this is the how the change in the free energy is there when we transform from 1 solid to another solid a 1 phase to another phase.

Now, how homogeneous and heterogeneous nucleation will come into picture in this, suppose this is a curve for homogeneous nucleation then for the heterogeneous nucleation for the heterogeneous nucleation the curve will look something like this; that means, the r stars remain the same, but my activation barrier has come down ok. So, when I provide heterogeneous nucleation site ok, what I am trying to do is I am trying to bring the activation barrier down. So, I now require a small driving force for changing from 1 phase to another phase and that is why heterogeneous nucleation is the dominant nucleation mechanism when you have phase transformation.

Of course, these curves you look into in the books because I have, I am not able to draw it very nicely here. So, if we will want to look at heterogeneous nucleation sites of course, I am not talking about solidification now, I am talking about in transformation in solid phase. When you talk about the transformation from liquid to solid the vessel wall is a very good nucleation site if there are some foreign impurity particles are there, then they connect as a nucleation site when you have transformation.

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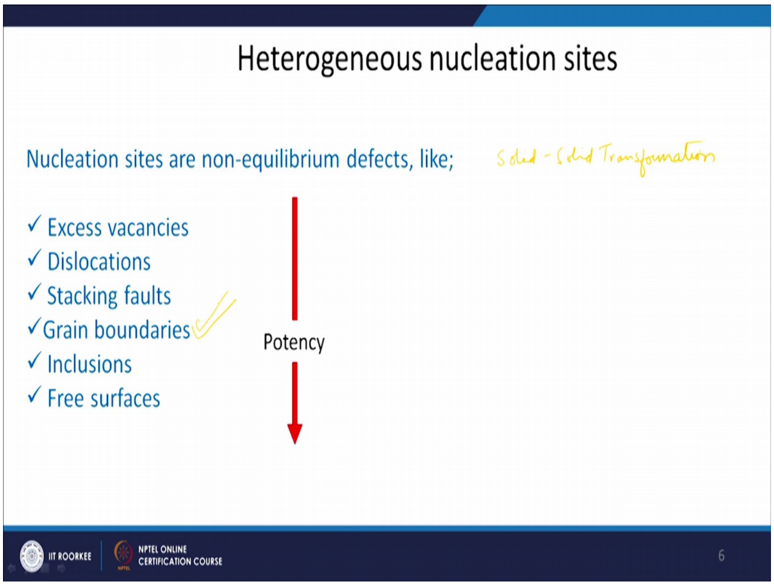

Heterogeneous nucleation sites

Nucleation sites are non-equilibrium defects, like;

Solid - Solid Transformation

- ✓ Excess vacancies
- ✓ Dislocations
- ✓ Stacking faults
- ✓ Grain boundaries ✓
- ✓ Inclusions
- ✓ Free surfaces

So, if this is solid to solid transformation ok. So, in this case we are talking about solid to solid transformation. So, nucleation sites are the non equilibrium defects. So, the you have a either excess vacancies are equilibrium defects, but when you have excess vacancies more than the equilibrium vacancy concentration. So, of course, that is not a equilibrium condition, so then we will call it as non equilibrium defects otherwise equilibrium vacancies defect are the equilibrium defect that is thermodynamically it is a vacancies have to be there.

So, excess if you have excess vacancies they can they that can act as a heterogeneous nucleation site, dislocation can act as heterogeneous nucleation site staking faults are there grain boundaries are there, inclusions are there already inclusions are present on which you can have another phase forming or you can have free surfaces on which the nucleation can take place.

Out of this the grain boundary is one of the most important nucleation site because, first thing is that it has very good potency you can see the potency of the nucleation site is increasing. So, free surface is the most potent site and excess vacancies are the least potent site. So, grain boundaries are highly potent and the second thing is the that in the material there la in number of grain boundary.

So, the if you want to see the concentration of the sites, the grain boundary sites are will be in very high concentration inclusion and free surface free surface can be only on the outside. So, for a given volume the amount of free surface will be very less, inclusion also if your material has impurities only then inclusions will be there. So, the grain boundary is actually 1 of the most important heterogeneous nucleation site ok.

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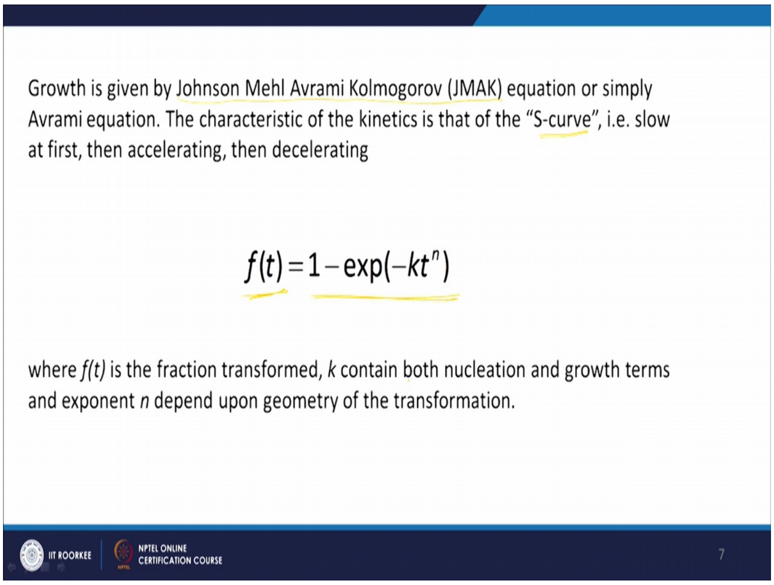

Growth is given by Johnson Mehl Avrami Kolmogorov (JMAK) equation or simply Avrami equation. The characteristic of the kinetics is that of the "S-curve", i.e. slow at first, then accelerating, then decelerating

$$f(t)=1-\exp(-kt^n)$$

where *f(t)* is the fraction transformed, *k* contain both nucleation and growth terms and exponent *n* depend upon geometry of the transformation.

Now, come to coming to growth the growth is given by equation called Johnson Mehl Avrami Kolmogorov equation, JMAK equation or simply we called is a Avrami equation and the characteristic of this is the that it gives you a typical S-curve. Which what it shows is that the growth kinetics are slow initially at first and then it accelerates and then at the end it dissolute. So, this is the typical growth kinetics you will find out in large number of systems for example, if you want to see a bacterial growth then also you will have similar S-curve ok. So, S-curve you will see in large number of different systems.

So, it is a very common system or common characteristic and it is given by an Avrami equation and the friction as a function of time will be given by an exponential expression like this where ft is the fraction transform k contain both nucleation and growth terms and exponent n depend upon geometry of the transformation ok.

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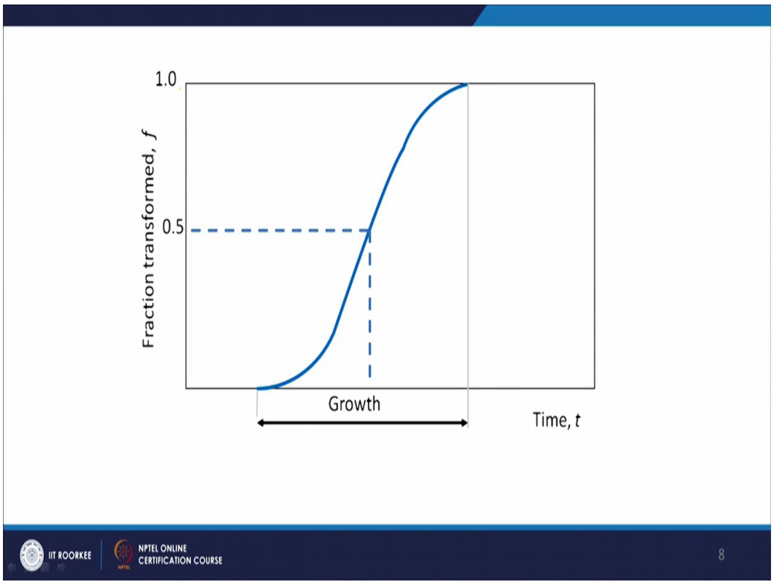

So, you dot have to worry about that right now all these things will come into the overall growth kinetics. So, this is what your typical S-curve will look like. So, this is on the x axis you have fraction transform ok. So, one means it is fully transformed 100 percent transformed, there is some gap up to which time you would not have any transformation. So, this is you can understand as a nucleation gap then this is the first it is slow as we told you then it accelerates ok, then it becomes goes into a steady state condition and then it desolates and be become very slow at the end also.

So, initially also it is slow and at the last stage also it is slow and it has maximum growth kinetics in the in the this central part ok. So, it is a typical S-curve you will usually see in lot of transformation 1 of and you will see it in the our phase transformation also. So, is a function of time what is the friction transform is what is shown here.

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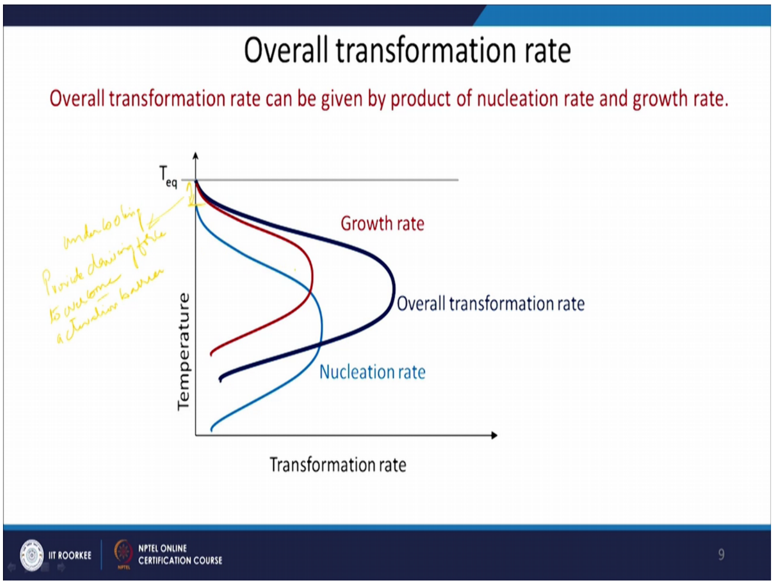

## Overall transformation rate

Overall transformation rate can be given by product of nucleation rate and growth rate.

From that from the idea of nucleation and from idea of growth I we can say that you will have some rate of nucleation. So, this is the equilibrium temperature ok, below which the phase transformation it will start ok. So, nucleation will start after you do a some amount of under cooling ok, so I use this word during solidification also. So, some amount of under cooling will be required under cooling, why we have to have under cooling to provide driving force for nucleation, why we need driving force to overcome activation barrier.

So, there is always going to be some under cooling is required to start the transformation, that under cooling will give you the driving force for transformation and their driving forces required to overcome the activation barrier as we just discussed. So, this is your nucleation kinetics, so initially it will be there will be some under cooling, as you bring down the temperature the nucleation rate will increase because now you are giving more driving force; as you keep on being decreasing the temperature that driving force will increase, but it will saturate at certain temperature and then it again the nucleation rate will start decreasing because, the diffusion of atoms which is required to make the nuclei stable the diffusion becomes very slow, so again it will come down.

Similarly, you will have in the growth the growth rate will also increase as you bring down the temperature then it saturates and again as the diffusion becomes slower the growth rate will also decrease and if you combine both the nucleation and growth you will have a overall transformation rate ok. So, it is a function of temperature ok, as you bring down the temperature the transformation rate will increase become maximum at some intermediate temperature and then it start decreasing as you bring down the temperature.

So, this is the overall transformation rate combining both the nucleation rate and the growth rate to give you that how the transformation will show how the transformation rate will change as a function of temperature.

With that I would like to say thank you and now using this formation rate in the next lecture we will come to a very important topic which is on time temperature transformation curves and continuous cooling transformation curves, one of the two very important topics in the transformation phase transformation ok. Especially when you go to steels ok. So, using this idea of the overall transformation rate we will try to understand the TTT and CCT curves.

Thank you.