Basics of Materials Engineering
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Lecture - 64
Kinetics of Phase Transformations (Heterogeneous Nucleation)

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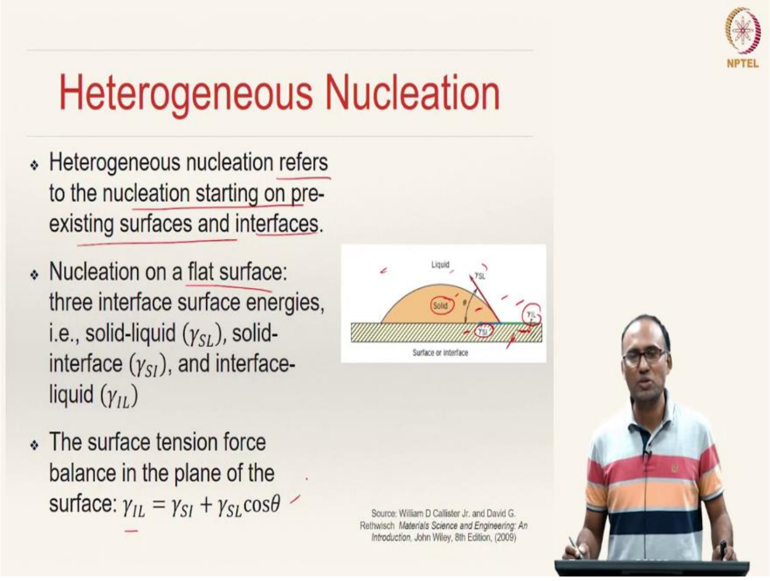

Heterogeneous Nucleation

- Heterogeneous nucleation refers to the nucleation starting on pre-existing surfaces and interfaces.
- Nucleation on a flat surface: three interface surface energies, i.e., solid-liquid (γ_{SL}), solid-interface (γ_{SI}), and interface-liquid (γ_{IL})
- The surface tension force balance in the plane of the surface: $\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta$

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Let us now look at heterogeneous nucleation. Heterogeneous nucleation, as we have already discussed, refers to the nucleation starting on pre-existing surface and interfaces. There will already be some pre-existing surfaces and there the nucleation happens much easily. Here, we are looking at nucleation on the case of a flat surface.

When you have a liquid pool and you are forming a solid nucleus on a flat surface, we can see three different interfaces. The interface between solid and liquid, interface between the liquid and the surface on which the solidification is happening (represented by the green line) and the interface between the solid and the surface on which solidification is happening (represented by the blue line). Each of these interfaces have certain surface energy.

γ_{SL} refers to the surface energy between solid and liquid interface; γ_{IL} refers to the surface energy between liquid phase and the surface on which the solidification is taking place. Here, I refers to the interface of the solid on which the solidification happening;

γ_{SL} indicates the surface energy of the interface between the solid nucleus and the solid surface on which nucleation is taking place.

Let us look at the force balance here. The surface tension force in the plane of the surface is given by

$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta$$

This is something that one can use in order to write the expressions for ΔG. However, we are not going through that derivation of how one would obtain the ΔG^* for heterogeneous nucleation.

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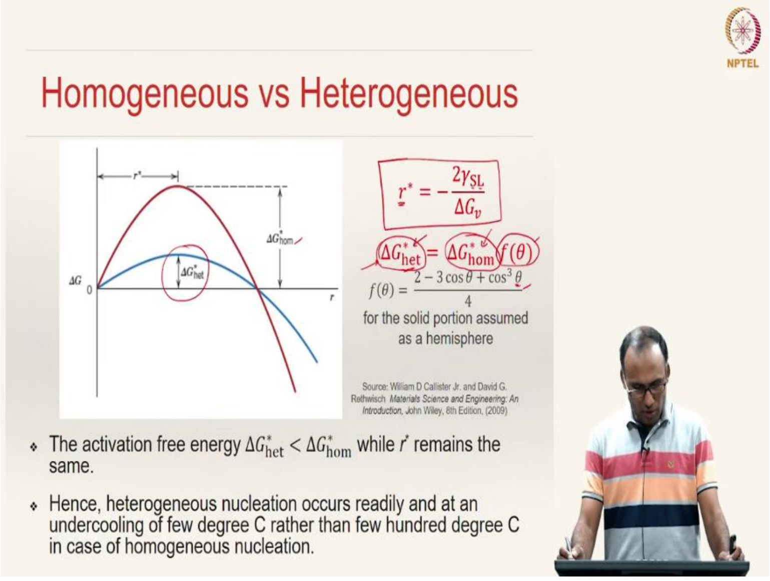

Homogeneous vs Heterogeneous

$$\boxed{r^* = -\frac{2\gamma_{SL}}{\Delta G_v}}$$

$$\Delta G^*_{\text{het}} = \Delta G^*_{\text{hom}} f(\theta)$$

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

for the solid portion assumed as a hemisphere

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

- The activation free energy $\Delta G^*_{\text{het}} < \Delta G^*_{\text{hom}}$ while r^* remains the same.
- Hence, heterogeneous nucleation occurs readily and at an undercooling of few degree C rather than few hundred degree C in case of homogeneous nucleation.

So, if you are interested, I encourage you to go through the textbook of Reed-Hill on Physical Metallurgy. There you have the derivation for finding ΔG^* for heterogeneous nucleation. You will see that the activation energy for heterogeneous nucleation is related to activation energy for homogeneous nucleation times some function of θ. θ is what we call wetting angle as we have shown in this figure.

$$\Delta G^*_{\text{het}} = \Delta G^*_{\text{hom}} f(\theta)$$

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

$f(\theta)$ is given by the above expression for a spherical particle and you can see that the value will always be less than 1. The free activation energy for heterogeneous nucleation is always going to be less than the activation energy required for homogeneous nucleation. However, r^* remains same.

$$r^* = -\frac{2\gamma_{SL}}{\Delta G_v}$$

This is γ between solid and liquid interfaces. γ_{SL} is going to be same for homogeneous and heterogeneous nucleation scenarios and hence r^* is not going to change.

For the same critical radius, you need much lower activation free energy for heterogeneous nucleation compared to homogeneous nucleation; that is why it is much easier to have heterogeneous nucleation. Heterogeneous nucleation happens much more readily than homogeneous nucleation.

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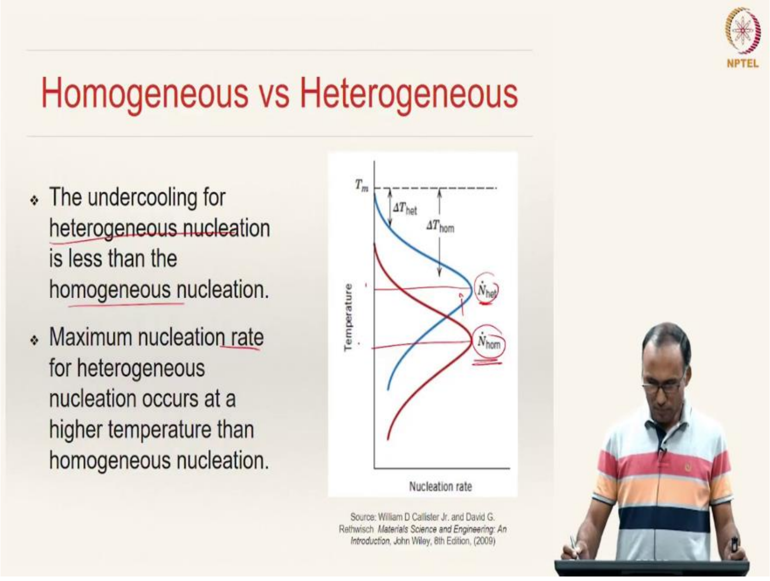

Homogeneous vs Heterogeneous

- The undercooling for heterogeneous nucleation is less than the homogeneous nucleation.
- Maximum nucleation rate for heterogeneous nucleation occurs at a higher temperature than homogeneous nucleation.

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

If you see the degree of undercooling required for heterogeneous nucleation and homogeneous nucleation, this graph clearly shows that $\dot{N}$ for homogeneous nucleation curve is little lower than heterogeneous nucleation. We have studied the red curve before i.e., the homogeneous nucleation case.

The degree of undercooling required for heterogeneous nucleation is only few degrees Celsius - not few hundreds of degrees Celsius like homogeneous nucleation. That means, the heterogeneous nucleation can actually happen at much higher temperatures than homogeneous nucleation. And as a result, the curve shifts upwards alright.

The undercooling for heterogeneous nucleation is less than the homogeneous nucleation and the maximum nucleation rate $\dot{N}$ for heterogeneous nucleation occurs at higher temperature than for homogeneous nucleation rate.

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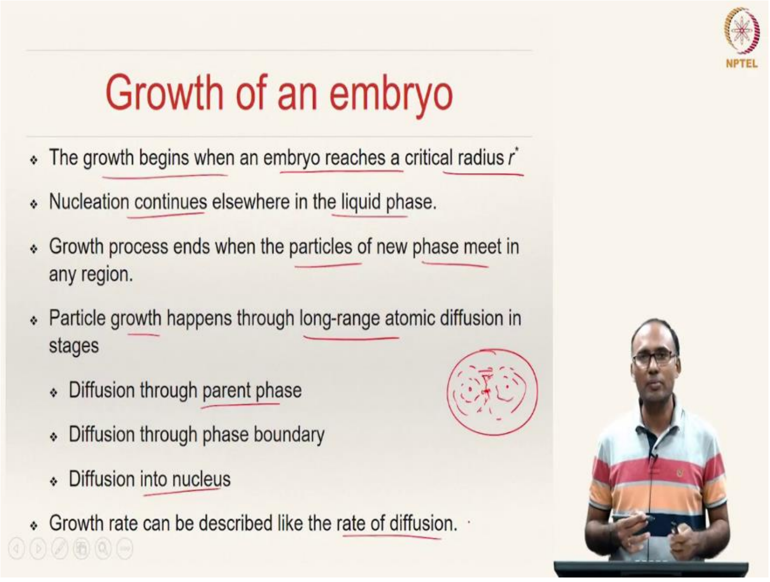

Growth of an embryo

- The growth begins when an embryo reaches a critical radius r^*
- Nucleation continues elsewhere in the liquid phase.
- Growth process ends when the particles of new phase meet in any region.
- Particle growth happens through long-range atomic diffusion in stages
  - Diffusion through parent phase
  - Diffusion through phase boundary
  - Diffusion into nucleus
- Growth rate can be described like the rate of diffusion.

We have looked at the concept of nucleation and the two different types of nucleation - homogeneous nucleation and heterogeneous nucleation and the nucleation rate (rate at which the nuclei are forming in these two different types of nucleation).

Once you have certain nuclei formed, the next step is growth of this nucleus; that means, more liquid has to come through diffusion and join the solid phase in order to increase the size of the solid phase. As we have discussed, growth begins when embryo reaches a critical radius r^*. Below that radius, it again dissolves. Only when the embryo reaches r^*, that is when it is called nucleus and is ready for growth.

Once you have certain nuclei formed at one place in the liquid solution, while this is growing, it is still possible that the nuclei can still continue to form at other locations. So, they can happen simultaneously. The nucleation continues elsewhere in the liquid phase. However, this growth process ends.

If you have one nucleus here and another nucleus here, when these two nuclei which are growing meet, the growth process ends. The growth here stops and then it continues in this region and so on.

We can see that the particle growth happens through long-range atomic diffusion in different stages. What are these long-range atomic diffusions? You can have diffusion through the parent phase - parent phase is for instance the liquid phase; diffusion through the phase boundary from the liquid phase to the solid phase; diffusion within the solid phase i.e., diffusion into the nucleus.

The growth rate can be described like the rate of diffusion which is pretty similar because the growth is a diffusion process.

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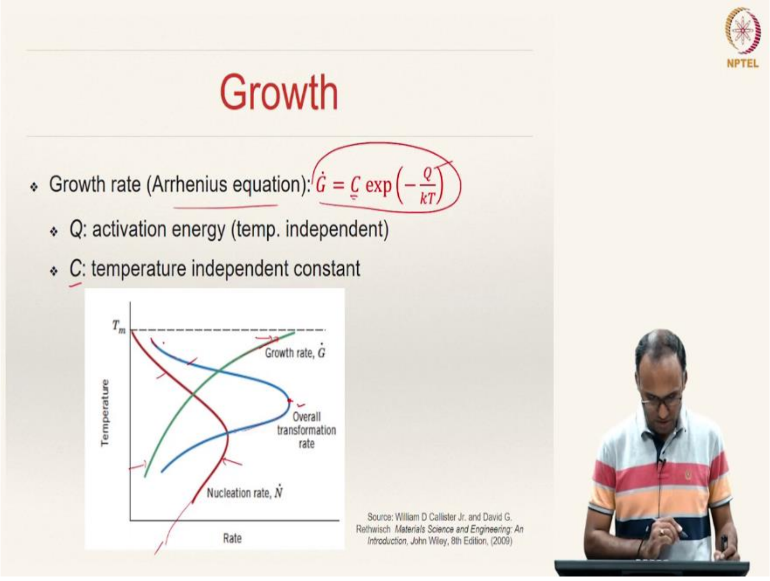

Growth

- Growth rate (Arrhenius equation): $\dot{G} = C \exp\left(-\frac{Q}{kT}\right)$
  - Q: activation energy (temp. independent)
  - C: temperature independent constant

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

The growth rate can be described by Arrhenius type of equation as shown below,

$$\dot{G} = C \exp\left(-\frac{Q}{kT}\right)$$

In the above expression, Q is the activation energy and it is temperature independent, and C is the temperature independent constant.

If you would plot the growth rate $\dot{G}$, it looks like this green curve - this is our growth rate. We know that the diffusion is faster at higher temperature and as a result, you will have higher growth rate. At low temperatures the growth rate is low. The red curve is only a part of the nucleation rate -- there is also somewhere here, but we have not shown that.

Now, you have certain nucleation rate and some growth rate and you can plot the overall transformation rate using these two quantities. The overall transformation rate looks something like this.

The overall transformation rate increases as you reduce the temperature and reaches a maximum value and then it starts decreasing again. At this point, although nucleation rate is increasing, diffusion is decreasing significantly and hence the overall transformation rate reduces.

At the top, we have low nucleation rate; that means, stable nuclei will be less at high temperature, but the growth rate is large. The rate at which the particle grows is very large here; that means, the diffusion can happen over long distances at high temperatures.

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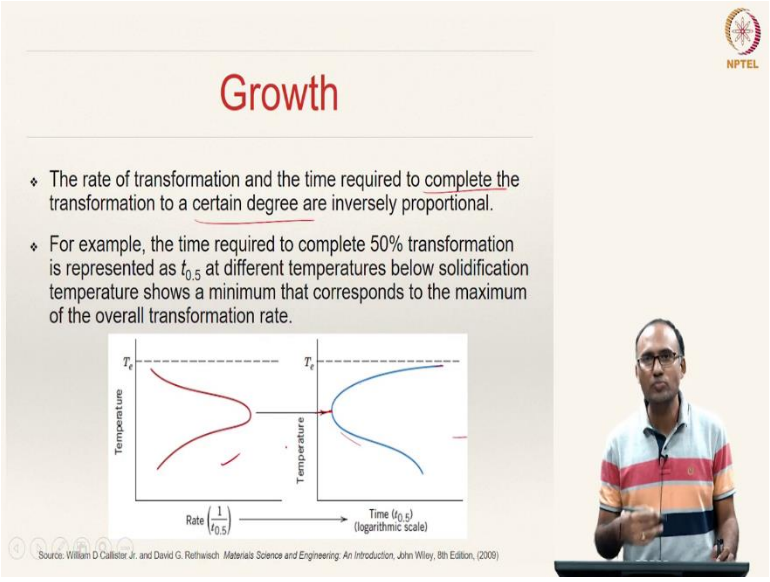

Growth

- The rate of transformation and the time required to complete the transformation to a certain degree are inversely proportional.
- For example, the time required to complete 50% transformation is represented as $t_{0.5}$ at different temperatures below solidification temperature shows a minimum that corresponds to the maximum of the overall transformation rate.

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

The rate of transformation; that means, the rate at which this transformation takes place and the time required for the completion of the transformation to certain degree should be inversely proportional, right? Because if you are having a faster rate, then the time required for transformation will be less.

Here, we are showing this is the rate of transformation as a function of temperature - rate of transformation to say for instance, 50% transformation. Because these two are inversely proportional, you can see on the right-hand side, here this is the time required for transformation to finish 50% quantity; that means, if the transformation from liquid state to solid state is happening and if 50% of liquid is converted to solid state - what is the time required for such a thing at different temperatures? If you would do that then you will get curve like that.

That means you will have a minimum time required for transformation to 50% at a certain temperature. Above that and below that you need to spend more time.

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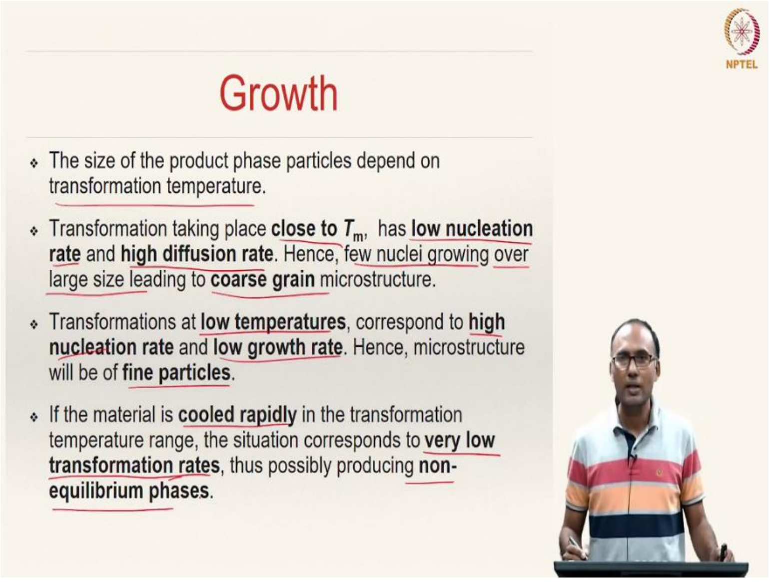

Growth

- The size of the product phase particles depend on transformation temperature.
- Transformation taking place **close to T_m**, has **low nucleation rate** and **high diffusion rate**. Hence, few nuclei growing over large size leading to **coarse grain** microstructure.
- Transformations at **low temperatures**, correspond to **high nucleation rate** and **low growth rate**. Hence, microstructure will be of **fine particles**.
- If the material is **cooled rapidly** in the transformation temperature range, the situation corresponds to **very low transformation rates**, thus possibly producing **non-equilibrium phases**.

The size of the product phase particles depends on the transformation temperature. If the transformation is taking place close to the T_m, which is considerably high, the nucleation rate will be low, the number of stable nuclei will be less, but diffusion rate will be high.

Consequently, we have few nuclei growing over large size to coarse grain microstructure due to high diffusion rate. Hence, the resulting microstructure will be a coarse grain microstructure.

However, if the transformation is happening at a lower temperature, which corresponds to high nucleation rate; that means, there are several nuclei, but the growth rate will be low as the diffusion is very low. So, there are several nuclei, but their growth rate is small and hence they cannot increase their size significantly. As a result, you have a fine-grained microstructure.

If the material is cooled rapidly, the situation basically corresponds to very low transformation rates. As you can see, the transformation rate first increases and then decreases.

So, when it is cooling down rapidly, you are actually hitting very low transformation rates. As a result, you would be producing non-equilibrium phases. And that is what happens when you have non equilibrium phase, we have seen how the microstructure changes and we will see in detail how the microstructure is going to change.

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Kinetics of Solid-State Transformation

- Kinetics discusses the time dependence of the rate of transformation.
- Usually, the fraction of transformation (or reaction) occurred is described as a function of time at a given temperature.
- The progress of the transformation is monitored through microscopic examination or by measuring a physical property such as conductivity.
- The fraction of the transformed product is plotted against time (on logarithmic scale) at a given temperature.

The kinetics of solid-state transformation is something that we will discuss. So far, we have looked from liquid state to solid state, now we shall see how the solid-state transformation happens. Here again the kinetics discusses the time dependence of the rate of transformation and usually the fraction of transformation or reaction occurred is described as function of time at a given temperature.

That is how we describe this fraction of transformation. And how do we monitor the transformation? Usually, the progress of transformation is monitored through microscopic examination or measuring a physical property such as conductivity. So, you measure the conductivity and then based on that you will be able to predict what fraction of the material has been transformed. Then, the fraction of the transformed product is plotted against time on a logarithmic scale at a given temperature.

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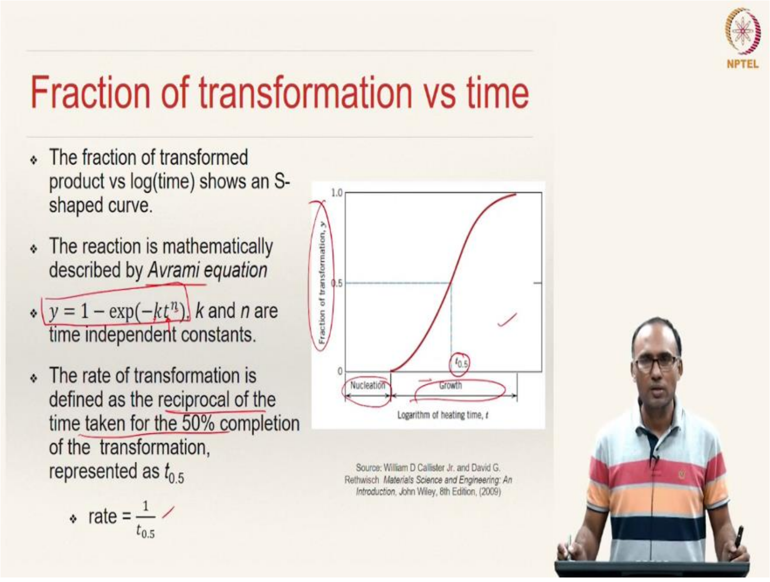

Fraction of transformation vs time

- The fraction of transformed product vs log(time) shows an S-shaped curve.
- The reaction is mathematically described by *Avrami equation*
- $y = 1 - \exp(-kt^n)$, k and n are time independent constants.
- The rate of transformation is defined as the reciprocal of the time taken for the 50% completion of the transformation, represented as $t_{0.5}$
    - rate $= \frac{1}{t_{0.5}}$

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Let us look at the fraction of transformation as a function of time. It is known that it takes sufficiently long time depending upon the temperature at which you are actually doing this transformation. It takes some time for nucleation. Up to certain time there will not be any growth, because the system is nucleating particles or nuclei and after nucleation is finished, that is when the growth begins.

On the y-axis, we are showing fraction of the transformed product – here, up to growth beginning there is no transformation. As you are increasing the temperature from that stage, the fraction of the transformation increases asymptotically to 1.

This state is our growth state. This curve which looks like an S-shaped curve can be mathematically described by Avrami equation given by,

$$y = 1 - \exp(-kt^n)$$

In the above expression, t is the time, k and n are time independent constants which depend on temperature at which this transformation is taking place.

Here, the rate of transformation is defined as the reciprocal of the time taken for 50% completion of the transformation, represented by $t_{0.5}$.

You can see that here, this is the time taken for 50% completion of the transformation, and the rate is described as $\frac{1}{t_{0.5}}$. So, with that, we have understood how nucleation happens under different conditions - homogeneous and heterogeneous nucleation.

We have discussed the concept of activation free energy and critical radius r^* and then how activation free energy changes as a function of temperature - both r^* and activation free energy change as a function of temperature. We discussed at low temperatures, the activation free energy is low and hence nucleation occurs readily at low temperatures compared to high temperatures.

We have discussed the difference between heterogeneous nucleation and homogeneous nucleation and we looked at the fact that the heterogeneous nucleation has lower activation energy compared to homogeneous nucleation. Then we have discussed the concept of nucleation rate and we have shown that the nucleation rate is going to have a maximum at a certain temperature.

The heterogeneous nucleation rate occurs at a higher temperature - maximum value of heterogeneous nucleation rate occurs at a higher temperature compared to homogeneous nucleation. The degree of undercooling required for heterogeneous nucleation is less than the degree of undercooling required for homogeneous nucleation.

We have discussed the growth process and how the growth process is described by a diffusion like phenomena and we have shown that the growth is higher at high temperatures and reduces at low temperatures, because at low temperatures the diffusion is low. The overall transformation rate is shown to have a maximum at certain temperature below T_m. We have also looked at the transformation rate as a function of time at different temperatures.

Finally, we looked at the fraction of transformation as a function of time. So, as a function of time, how much amount of material has been transformed from parent phase to product phase and that is described by Avrami equation wherein the fraction of transformation when plotted against time looks like an S-shaped curve as shown here.

In the next class, we will use this knowledge in order to understand an important concept called isothermal transformation and diagrams particularly for steels. Thank you very much.