Powder Metallurgy

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Lecture – 45
Sintering – 5

Hello everyone and welcome back. So, in the last class, we have seen that the Sintering process happens in stages. And basically there are three stages of sintering – initial stage, intermediate stage and the final stage . In the previous lecture, we have talked about the initial stage of sintering.

And there we have seen that it is basically characterized by the net growth which is measured by the X by D ratio, where X is the radius of the neck and D is the particle diameter.

$$\Delta L/L_0 = (X/D)^2$$

So, we are going to continue on this today and see the other stages of sintering.

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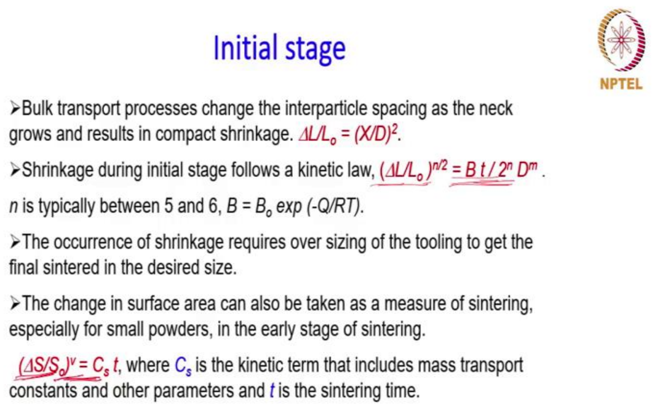

Initial stage

- Bulk transport processes change the interparticle spacing as the neck grows and results in compact shrinkage. $\Delta L/L_o = (X/D)^2$.
- Shrinkage during initial stage follows a kinetic law, $(\Delta L/L_o)^{n/2} = B\,t / 2^n D^m$.

n is typically between 5 and 6, $B = B_o \exp(-Q/RT)$.

- The occurrence of shrinkage requires over sizing of the tooling to get the final sintered in the desired size.
- The change in surface area can also be taken as a measure of sintering, especially for small powders, in the early stage of sintering.

$(\Delta S/S_o)^v = C_s\,t$, where C_s is the kinetic term that includes mass transport constants and other parameters and t is the sintering time.

So, in the initial stage kinetically if you see the densification scales with one-third power of time as you can see from this particular equation over here , and the change in the surface area can be also taken as the measure of sintering and that is given over here by this equation.

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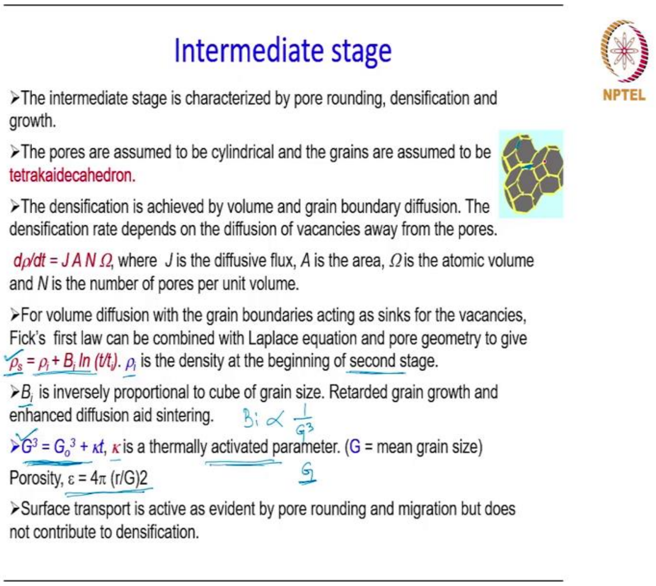

Intermediate stage

- The intermediate stage is characterized by pore rounding, densification and growth.
- The pores are assumed to be cylindrical and the grains are assumed to be tetrakaidecahedron.
- The densification is achieved by volume and grain boundary diffusion. The densification rate depends on the diffusion of vacancies away from the pores.

$d\rho/dt = J\,A\,N\,\Omega$, where J is the diffusive flux, A is the area, Ω is the atomic volume and N is the number of pores per unit volume.

- For volume diffusion with the grain boundaries acting as sinks for the vacancies, Fick's first law can be combined with Laplace equation and pore geometry to give $\rho_s = \rho_i + B_i \ln (t/t_i)$. ρ_i is the density at the beginning of second stage.
- B_i is inversely proportional to cube of grain size. Retarded grain growth and enhanced diffusion aid sintering. $B_i \propto \frac{1}{G^3}$
- $G^3 = G_o^3 + \kappa t$, κ is a thermally activated parameter. (G = mean grain size)

G

Porosity, $\varepsilon = 4\pi$ (r/G)2

- Surface transport is active as evident by pore rounding and migration but does not contribute to densification.

So, now, let us see as we progress to the next stage of sintering what happens in that, so that is the intermediate stage, which is basically characterized by pore rounding densification and growth . So, here the pores are assumed to be cylindrical and the grains are assumed to be tetrakaidecahedron in shape . So, tetrakaidecahedron is a polyhedron with 14 faces.

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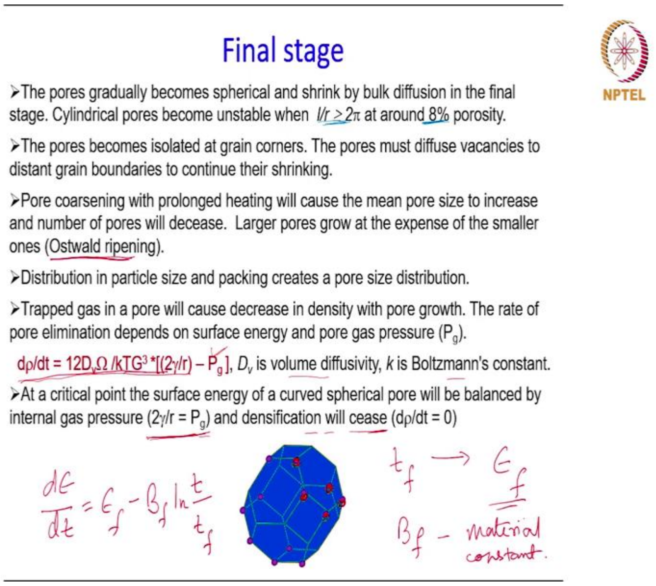

Final stage

- The pores gradually becomes spherical and shrink by bulk diffusion in the final stage. Cylindrical pores become unstable when $l/r \geq 2\pi$ at around 8% porosity.
- The pores becomes isolated at grain corners. The pores must diffuse vacancies to distant grain boundaries to continue their shrinking.
- Pore coarsening with prolonged heating will cause the mean pore size to increase and number of pores will decease. Larger pores grow at the expense of the smaller ones (Ostwald ripening).
- Distribution in particle size and packing creates a pore size distribution.
- Trapped gas in a pore will cause decrease in density with pore growth. The rate of pore elimination depends on surface energy and pore gas pressure (P_g).

$d\rho/dt = 12 D_v \Omega / kTG^3 * [(2\gamma/r) - P_g]$, D_v is volume diffusivity, k is Boltzmann's constant.

- At a critical point the surface energy of a curved spherical pore will be balanced by internal gas pressure ($2\gamma/r = P_g$) and densification will cease ($d\rho/dt = 0$)

$$\frac{d\epsilon}{dt} = \epsilon_f - B_f \ln \frac{t}{t_f}$$

$t_f \rightarrow \epsilon_f$

B_f - material constant.

A polyhedron like this or this image if you see over here, this is how a tetrakaidecahedron appears. So, in the beginning, the pores were basically growing at the contact points. So, if you look at the contact points and the pore filling as to how it happens during the densification- in the beginning as the sintering process starts, the pores will have a triangular kind of geometry in the initial stage.

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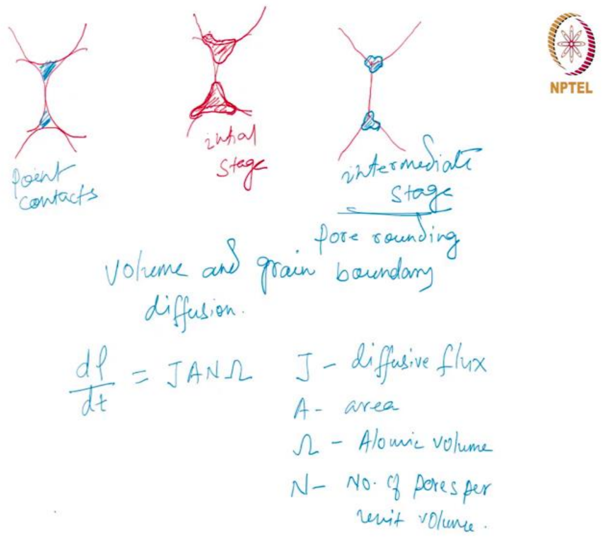

pore rounding

volume and grain boundary diffusion.

$$\frac{d\rho}{dt} = JAN\Omega$$

J - diffusive flux

A - area

Ω - Atomic volume

N - No. of pores per unit volume.

So, these are the point contacts between the particles after compaction. And this is the kind of pores that you have in the green compact. Now, as the sintering starts, the neck will grow and then these pores will get filled.

So, the pore geometry will be kind of this one; it is still close to the triangular geometry, but some rounding you can observe due to the matter transport towards the pores right. And as you proceed to the intermediate stage, then you can observe more rounding to happen for these pores here.

So, in the intermediate stage, you can observe the pore rounding to occur . So, the vacancies diffuse away from the pores, and therefore, the atomic flux is towards the pore. And that atomic diffusion in this case takes place by volume and grain boundary diffusion.

So, these are the dominant mass transfer mechanisms in the intermediate stage. And the densification rate d rho by dt is given by this equation, where J is the diffusion flux that is mass transport per unit time per unit area, A is the area, and **Ω** is the atomic volume, and N here is the number of pores per unit volume .

$$d\rho / dt = JAN\Omega$$

And for the volume diffusion that occurs , the grain boundaries act as the sinks for the vacancies and Fick's first law can be combined with the Young Laplace equation and the pore geometry to come up with an expression for the density which is given over here, where **ρi** is the density at the beginning of the second stage, and **ρs** is the final density or the sintered density .

$$\rho s = \rho i + B_i \ln(t/t_i)$$

And the parameter Bi that you see over here that is inversely proportional to the cube of grain size .

$$B_i \alpha 1 / G^3$$

And the grain size is expressed with an equation like this which also includes the temperature effect because kappa is a thermally activated parameter here, and G_0 in this equation is the initial grain size .

$$G^3 = G_0^3 + \kappa t$$

So, the final grain size G which is obtained after sintering will depend on temperature as I said. And from this equation, you can see that with increase in temperature the grain size G will increase, and therefore, you can expect some grain coarsening to occur .

And this is what we have seen in the beginning also when we discussed about the driving force for the sintering process. We have seen in one hand the densification takes place and on the other hand the coarsening also occurs right. So, that coarsening part, you can observe from here also from this particular equation. And the relationship between the porosity and the grain size is given by an expression like this one.

$$\varepsilon = 4\pi (r/G)^2$$

Now, the cylindrical pores that you have in the intermediate stage lie at the grain edges as you could see from this image over here . So, this kind of cylindrical pores are mainly confined along the edges of the grains. And for that geometry, the pore radius are the grain size and the porosity epsilon are related by an equation like this right, where G is the grain size and r is the radius of the pores.

And the occurrence of the pore rounding in the intermediate stage is an indication of the surface transport mechanism of mass flow to be active. And as I said grain boundary diffusion in one of the main mechanisms of densification in the intermediate stage, and therefore, the pores which are located on the grain boundaries will be eliminated more rapidly compared to isolated pores because along the grain boundaries first of all the diffusion is happening.

And you have also seen before that the grain boundary diffusion is actually faster than volume or lattice diffusion. And therefore, if you have pores like this which are along the grain boundaries, so the diffusion which happens along the boundaries will actually result in the filling of these pores first compared to isolated pores which may be located somewhere else in the lattice.

And although surface transport is active as indicated by the pore rounding but this surface transport mechanism so do not really contribute to the shrinkage or densification. So, this is something that we have discussed before also that surface transport mechanisms are actually non densifying mechanisms.

So, now, let us move to the final stage. Here the pores gradually becomes spherical and also shrink by bulk diffusion. The cylindrical pores that you had in the intermediates stage will become unstable, then the l by r ratio is greater than or equal to 2 pi ok. So, that particular ratio when it reaches this kind of size, the cylindrical pores become unstable and they will break down.

And for geometry where the pores are lying at the edges of the grains, this corresponds to a porosity of about 8 percent when the cylindrical pores lie along the edges of the grains. So, as the densification process continues, the pores become isolated at grain corners like how you see over here.

All these pores are now concentrated along the corners of the grains ok. And for the pore closure or the shrinkage of the pores to continue, the atoms must continue to flow towards the pores, and therefore, the vacancy diffusion should be away from the pores towards the distant grain boundaries. Now, pore coarsening can also take place on prolonged heating. And this will cause the mean pore size to increase and number of pores will decrease .

So, here the larger pores will grow at the expense of the smaller ones – a phenomena known as Ostwald ripening which is basically a result of the differences in the pore curvature. Now, if there is trapped gas in a pore that will cause a decrease in the density with pore growth . The rate of pore elements depends on the surface energy and the pressure of the gas which is trapped .

And this is given by an equation like this what you can see over here

$$\mathbf{d\rho / dt = 12D_v\Omega / \kappa TG^3 * [(2\gamma/r) - P_g]}$$

where d rho by dt is the densification rate and D v is the volume diffusivity and k is Boltzmann’s constant . So, here you can see that it is dependent on the gas pressure of the trapped gas . So, because of this, there is a limitation on the final densification which can be achieved in conventional sintering which is done in air atmosphere without any evacuation or any vacuum.

So, it from here we can see that at a critical point when the surface energy of a curved spherical pore becomes equal to the gas pressure or in other words when the internal gas pressure balances the surface energy of the pore, that means, these two are equal then from this equation we can see that d rho by dt becomes equal to 0 which means that densification ceases .

So, therefore, for full 100 percent densification to take place, vacuum has to be used, so that this kind of trapped gases can be eliminated. And therefore, this effect of the gas pressure that you see on the densification rate will not be there . So, when vacuum is used the generalized sintering equation for that is given by an expression like this.

So, t is sintering time. And t_f corresponds to a point where the pores become closed indicating the end on the intermediate stage . And the corresponding porosity is ε_f, and B_f is a combination of material constants.

$$\mathbf{d\varepsilon / dt = \varepsilon_f - B_f \ln(t/t_f)}$$

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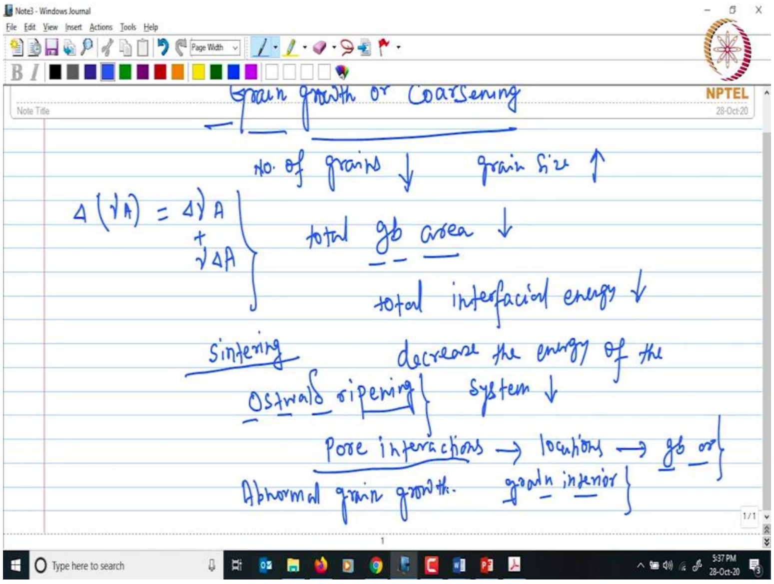

Grain growth or Coarsening

No. of grains ↓ grain size ↑

$\Delta(\gamma A) = \Delta\gamma A + \gamma\Delta A$

total gb area ↓

total interfacial energy ↓

Sintering

decrease the energy of the system ↓

Ostwald ripening

Pore interactions → locations → gb or grain interior

Abnormal grain growth.

Now, apart from densification, grain growth also occurs concomitantly in sintering. This is because there is a driving force for the grain growth also to occur because when the grains grow in size the number of grains will decrease. And therefore, the total grain boundary area will also decrease right. So, since the interfacial area is decreased, the interfacial area or the grain boundary area, the total interfacial energy will also decrease.

And this will in turn decrease the total energy of the system, and that is our driving force for the grain growth . So, that is what we have seen in the beginning also if you remember the change in the total surface energy of the system during sintering has two components, one coming from the densification that is delta gamma into A, and the other coming from the coarsening effect that is gamma into delta A.

$$\Delta(\gamma A) = \Delta\gamma A + \gamma\Delta A$$

So, as I said grain growth occurs concomitantly with densification during sintering. And it might also involve a mechanism of growth such as Ostwald ripening in which the larger grains will grow at the expense of the smaller ones. And as a result of that, the total interfacial area will decrease leading to a decrease in the interfacial energy as I said before.

The pores also play a role in the grain growth. So, the interaction between the pores and the grain boundaries will have a influence on the movement of the grain boundaries involved in the grain growth process. And therefore, depending on the locations of the pores whether they are along the grain boundaries or in grain interiors, the degree of grain growth can change when they are along the grain boundaries, then they can retard the grain growth by filling down the grain boundaries.

So, the extent of grain growth will be lower. On the other hand, if the grain boundaries break away from the pores and if the pores are left behind in the grain interiors, then there will be a significant grain growth and in fact under those conditions abnormal grain growth can also take place.

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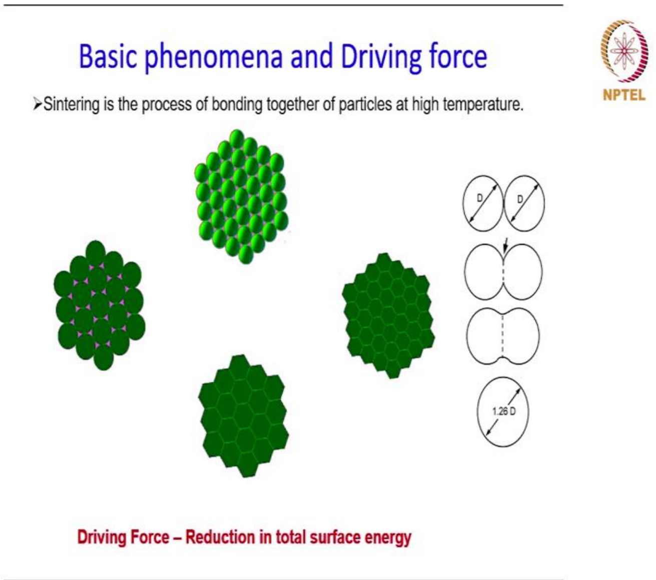

Basic phenomena and Driving force

➢Sintering is the process of bonding together of particles at high temperature.

Driving Force – Reduction in total surface energy

Now, that we have learned about all the three stages of the sintering process. Let us take a moment to summarize it. So, sintering is the heat treatment process which leads to densification of a porous compact giving rise to a fully densed solid product . And the driving force behind the sintering process is the reduction in total surface energy.

So, the process starts with the formation of the neck had the contact points between the particles. And as this neck goes, densification occurs. So, densification leads to closure of the pores, and as a result the density of the compact increases.

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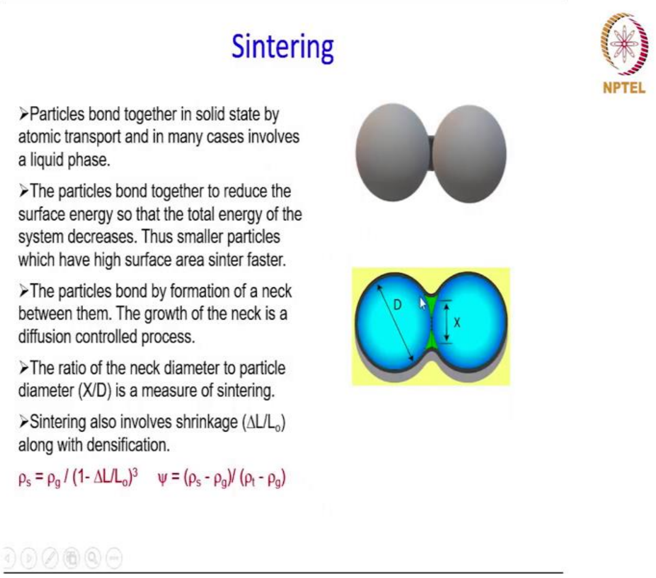

Sintering

- Particles bond together in solid state by atomic transport and in many cases involves a liquid phase.
- The particles bond together to reduce the surface energy so that the total energy of the system decreases. Thus smaller particles which have high surface area sinter faster.
- The particles bond by formation of a neck between them. The growth of the neck is a diffusion controlled process.
- The ratio of the neck diameter to particle diameter (X/D) is a measure of sintering.
- Sintering also involves shrinkage ($\Delta L/L_o$) along with densification.

$\rho_s = \rho_g / (1 - \Delta L/L_o)^3 \quad \psi = (\rho_s - \rho_g)/(\rho_t - \rho_g)$

So, this neck growth occurs through mass transport along different paths. And the extent of sintering can be measured with the help of the neck size ratio .

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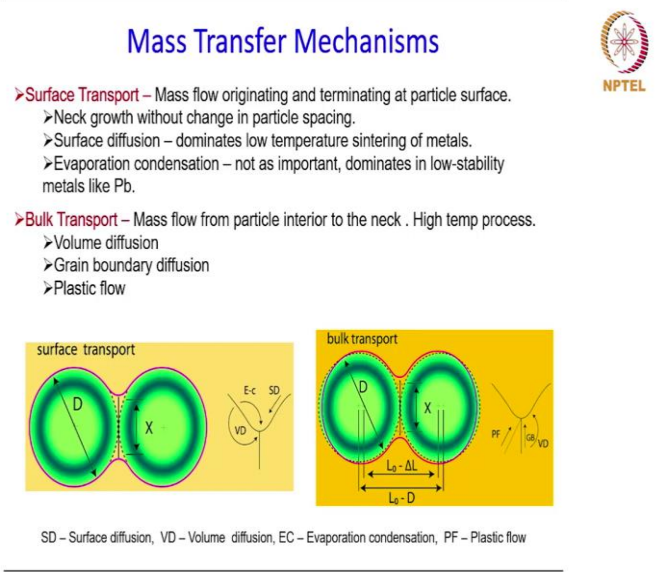

Mass Transfer Mechanisms

- **Surface Transport** – Mass flow originating and terminating at particle surface.
  - Neck growth without change in particle spacing.
  - Surface diffusion – dominates low temperature sintering of metals.
  - Evaporation condensation – not as important, dominates in low-stability metals like Pb.
- **Bulk Transport** – Mass flow from particle interior to the neck . High temp process.
  - Volume diffusion
  - Grain boundary diffusion
  - Plastic flow

SD – Surface diffusion, VD – Volume diffusion, EC – Evaporation condensation, PF – Plastic flow

Now, the neck grows by mass transport along well defined paths. So, basically there are two types of mass transport involved in the sintering process. One is the surface transport which includes surface diffusion and evaporation condensation, and the other one is the bulk transport which includes volume diffusion grain boundary diffusion and plastic flow.

So, out of all this diffusion mechanisms which are involved in the sintering process some are called densify mechanisms and some are non-densifying. So, the mechanisms which lead to shrinkage are the densifying mechanisms.

And all the bulk transport mechanisms such as volume diffusion, grain boundary diffusion, and plastic flow will come under this category because all this lead to a shrinkage of the compact and results in densification. The other mechanisms that is the surface transport mechanisms are nondensifying, although they take active part in the sintering process.

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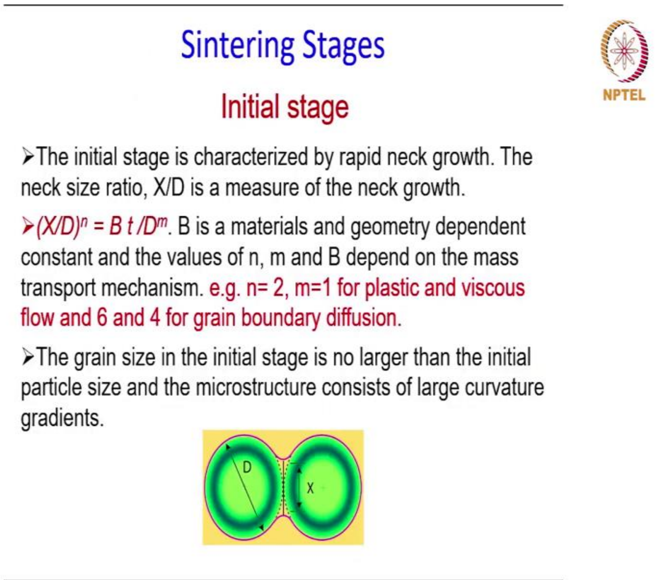

Sintering Stages

Initial stage

- The initial stage is characterized by rapid neck growth. The neck size ratio, X/D is a measure of the neck growth.
- $(X/D)^n = B\, t / D^m$. B is a materials and geometry dependent constant and the values of n, m and B depend on the mass transport mechanism. e.g. n= 2, m=1 for plastic and viscous flow and 6 and 4 for grain boundary diffusion.
- The grain size in the initial stage is no larger than the initial particle size and the microstructure consists of large curvature gradients.

Sintering occurs in three different stages – the initial stage, the intermediate stage and the final stage. The initial stage is characterized by rapid neck growth. The neck which forms at the particle contacts will grow in this stage, but there is no grain growth involved in this particular stage of the sintering process.

The intermediate stage is characterized by pore rounding which basically occurs by surface transport. Here the pores take up cylindrical shape and the grains take up a tetrakaidecahedron kind of shape.

And the main mechanisms of densification are volume and grain boundary diffusion. And here the grain size is dependent on the temperature with an increase in the temperature and increase in the grain size is expected which leads to coarsening.

Now, the final stage of sintering starts when the cylindrical pores become unstable. And for a geometry like the one that we had here where the cylindrical pores are lying along the grain edges that corresponds to a remaining porosity of about 8 percent.

So, in this stage the pores tend to become more spherical which happens due to surface transport processes. And the pores in this stage are mainly located on the grain boundaries. And pores can also get coarsened with prolonged heating.

The larger pores grow at the expense of the smaller ones due to the difference in the curvature. And finally, we had seen that the densification rate depends mainly on two parameters; one is the surface energy gamma and the other one is the pore gas pressure if there is a trap gas inside the pore.

So, this trapped gas pressure puts a limitation on the densification that can be achieved in conventional sintering processes where no vacuum is used, and where it is susceptible for this kind of gas to be trapped in the pores right. So, therefore, for full densification to take place, this trapped gas has to be eliminated, this has to be removed and that is why at times vacuum is used.

So, that this kind of gasses can be eliminated and full densification can be achieved in the compact at the end of the sintering process . So, with that we come to the end of this particular lecture, but there is more to come on this particular topic, keep watching.