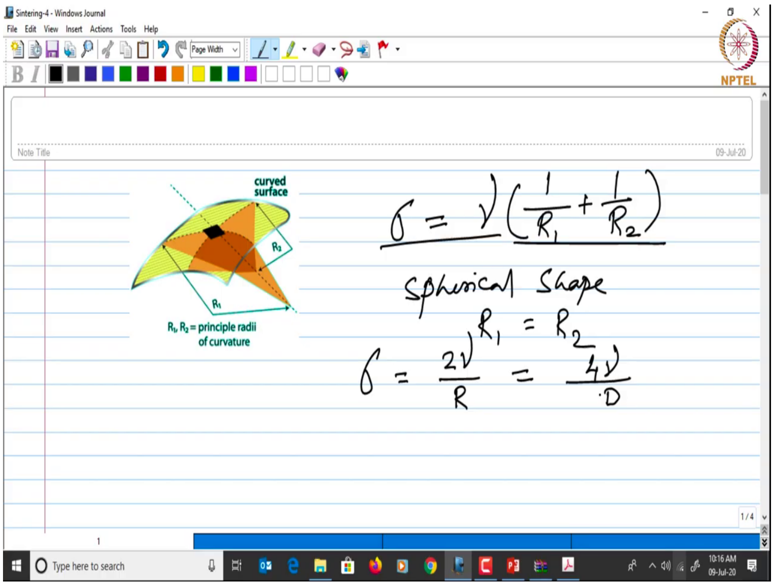
Powder Metallurgy
Prof. Ranjit Bauri
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture – 44
Sintering – 4

Hello and welcome back again to this lecture series on Powder Metallurgy. Right now we are on this topic Sintering and in the previous lecture, we discussed about the surface curvature and its role in the sintering process and we also derived the stress on a curved surface. So, in this class, we are going to continue on that and we will see how this curvature is related to the densification which happens in the sintering process.

(Refer Slide Time: 00:47)



$$\sigma = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Spherical Shape

$$R_1 = R_2$$

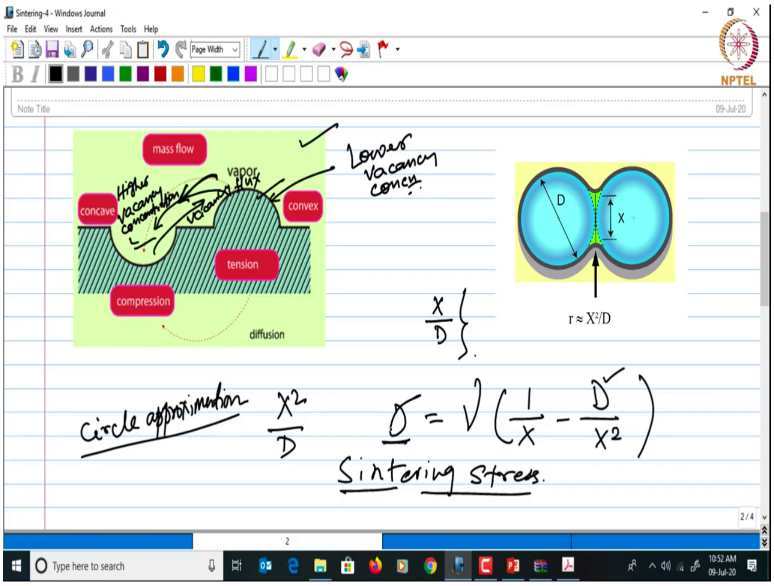
$$\sigma = \frac{2\gamma}{R} = \frac{4\gamma}{D}$$

So, we derived this Young-Laplace equation which basically talks about the stress on a curved surface the stress, sigma on a curved surface is related to the radii of curvature and the surface energy in this manner . And, for a spherical shape R 1 is equal to R 2 and therefore, the stress sigma becomes

$$\boldsymbol{\sigma = 2\gamma / R = 4\gamma / D}$$

, where R is the radius of the sphere and if D is the diameter then this can be written as 4 gamma by D.

(Refer Slide Time: 02:46)



$\frac{X}{D}$

Circle approximation $\frac{X^2}{D}$

$\sigma = \nu\left(\frac{1}{X} - \frac{D}{X^2}\right)$

Sintering stress.

Now, coming back to this densification that we are talking about we had seen that it basically happens through the formation of the neck and then the transportation of mass towards the neck for it to grow and the densification to proceed.

So, the mass transport which happens during the densification will also be affected by this stress which is generated due to the curvature . So, this is something that can be depicted with the help of this picture over here where you have this kind of curvature both convex and concave.

So, what happens if you have a curvature like this -concave and convex surfaces will try to become flat and hence will result in mass flow. So, you can expect the mass flow to occur from the convex region to the concave region so that the convex portion will become flat and the concave portion will be filled with more mass and that will also tend to become flat.

These kinds of mass flow can be also shown in terms of the vacancy flow. We have seen before while discussing the diffusion process that the vacancy flux is in the opposite direction to the direction of the mass flow or the atomic flux. So, in this case where you have both concave and convex surfaces the vacancy concentration here in the concave region is higher compared to the convex region right.

So, as a result of that the vacancy flux will be from the concave to the convex region and as a result of that the atoms will flow in the opposite direction as we talked about. So, this will be the mass flow direction .

So, with that kind of mass flow it will help the densification process which occurs during sintering and now, we have also seen that the sintering process essentially starts with the formation of a neck at the contact point between the particles and as this kind of mass flow by different paths happens the neck grows for the densification to occur.

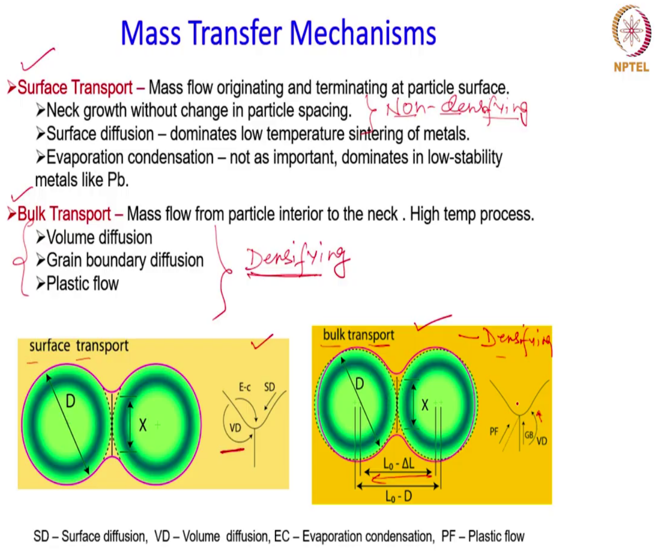
And, we have also seen that the neck has a particular radius. The neck radius is X and X by D is the ratio which is related to the densification. Now, if we use a; circle approximation of the neck shape with the radius X^{2}/D, the stress can be written as

$$\sigma = \gamma (1/X - D/X^{2)}$$

this is the sintering stress which helps the particles bond and therefore, is a driving force for densification.

And, from here you can also see that when the diameter is small then the σ is high . So, that means, that smaller particles will have higher sintering stress or greater driving force for densification.

(Refer Slide Time: 07:55)



Mass Transfer Mechanisms

- **Surface Transport** – Mass flow originating and terminating at particle surface.
  - Neck growth without change in particle spacing. } Non-densifying
  - 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 } Densifying
  - Plastic flow

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

Now, let us come back to this the mass transfer mechanisms of sintering. So, here we have seen there are distinct paths across which the matter is transported towards the neck. So, these mechanisms in terms of the path can be basically categorized in to two broad categories: one is surface transport and the other is bulk transport.

So, under the surface transport category you basically have the surface diffusion which dominates at low temperatures sintering of metals, and evaporation condensation . And, on the other side for the bulk transport which is basically the mass flow from particle interior to the neck includes volume diffusion, grain boundary diffusion and plastic flow. So, all of these mechanisms lead to neck growth and bonding between the particles; however, only some of them will lead to shrinkage or densification.

Therefore, a distinction can be made between a densifying and a non-densifying mechanism. Grain boundary diffusion, volume diffusion and plastic flow all these mechanisms lead to shrinkage. So, these are densifying mechanisms; on the other hand surface diffusion and evaporation condensation does not lead to shrinkage .

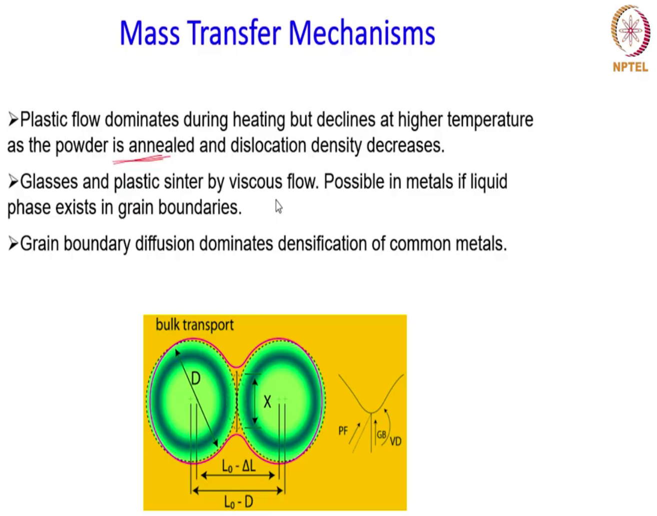
So, this can be categorized as non-densifying, but this does not mean these non-densifying mechanisms can be ignored because they also lead to the neck growth and therefore, reduce the curvature of the neck and hence will affect the densification rate.

Now, let us talk about these mechanisms in little more details. So, these two pictures that you have over here, they depict these two kinds of mechanisms – one is the surface transport process which basically falls into this non-densifying category here as we have seen you have surface diffusion, evaporation condensation. And, also lattice diffusion or volume diffusion that happens from the surface of the particles towards the neck.

So, these are the surface transport mechanisms and these are non-densifying as I said and in this picture over here you can see the densifying mechanisms which are basically all these bulk transport that takes place. So, here you can see it is associated with the shrinkage as shown over here right. So, whenever shrinkage occurs it means that densification is occurring. So, therefore, all these processes of bulk transport can be categorized as densifying mechanisms.

And, here you can see their paths also as to how do they lead to material flow towards the neck volume diffusion or lattice diffusion as it happens in the bulk it is actually leading the atomic diffusion from the bulk or the lattice of the material towards the neck region as we can see from here. Grain boundary as the name suggests it occurs across the grain boundary and the material flows through the grain boundary towards the neck for the neck to grow.

(Refer Slide Time: 13:18)



Mass Transfer Mechanisms

- Plastic flow dominates during heating but declines at higher temperature as the powder is annealed and dislocation density decreases.
- Glasses and plastic sinter by viscous flow. Possible in metals if liquid phase exists in grain boundaries.
- Grain boundary diffusion dominates densification of common metals.

And, plastic flow dominates during heating, but it declines at higher temperature as the powder is annealed and the dislocation density decreases. Now, this is a dominant mechanism in metals and in case of metals the plastic deformation is primarily controlled by the dislocation motion . So, plastic flow will occur as long as the dislocations are there to move and cause plastic deformation.

Now, when you increase the temperature, this dislocations will be annihilated as the powder is annealed at high temperature and as a result the dislocation density will decrease right.

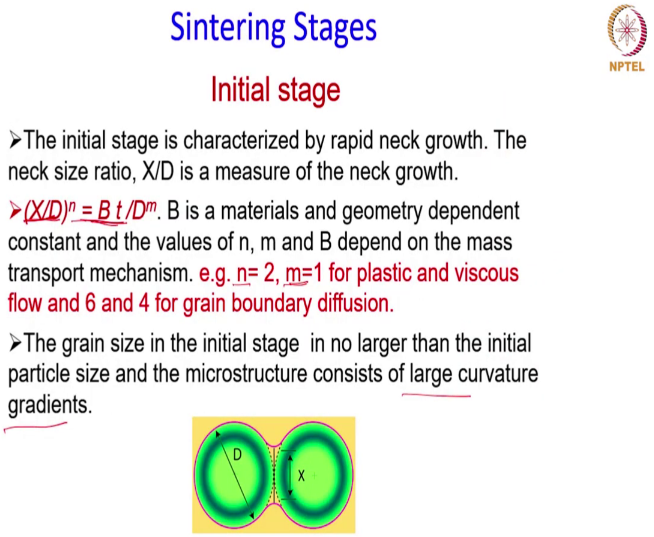
So, since this plastic flow is controlled by the dislocation motion when the dislocation density decreases, the domination of the plastic flow will also decrease. So, that is why at high temperature the plastic flow is no longer a dominant mechanism for densification.

Now, there is also something called viscous flow, but that is more likely to occur in glasses and plastics and it might happen in metals if there is a liquid phase along the grain boundaries.

And, grain boundary diffusion dominates densification of most of the common metals because as we have seen before also the densification rate or the diffusion coefficient for grain boundary diffusion is much higher compared to lattice diffusion.

And, that is why the mass flow rate along the grain boundary is much higher compared to that in the lattice and therefore, the grain boundary diffusion becomes dominant for densification of most of the common metals.

(Refer Slide Time: 15:37)



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 in no larger than the initial particle size and the microstructure consists of large curvature gradients.

Now, the sintering process occurs in stages. This densification that you have during the process of sintering does not really takes place at once. There are stages at which different phenomena can take place leading to growth of the neck and pore closure and ultimately when all the stages are completed you will get a fully dense product .

So, primarily there are three stages of sintering – initial stage, intermediate stage and the final stage. So, let us go ahead and talk about this sintering stages and find out what exactly happens during each of these stages. So, we start with the initial stage the initial stage is characterized by rapid neck growth.

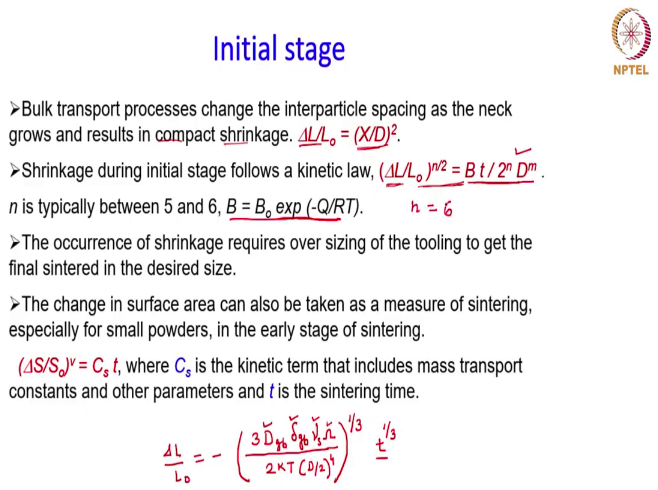
The neck size ratio X by D is a measure of the neck growth as we have discussed before and also the sintering model which deals with the initial stage considers isothermal neck growth as measured by the neck size ratio X by D and the values for n, m and B depend on the mass transport mechanism.

$$(X/D)^n = Bt / D^m$$

For example, n is equal to 2 and m is equal to 1 for plastic and viscous flow and these are 6 and 4 for grain boundary diffusion right. So, depending on the mechanism of the mass flow, the value of these two parameters will change and as a result the neck growth rate will also differ depending on the mechanism of mass transport.

The grain size in the initial stage is no larger than the initial particle size because this is just the beginning of the sintering. So, there is no coarsening and all that. So, the microstructure consists of large curvature gradients.

(Refer Slide Time: 18:09)



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, $B = B_o \exp(-Q/RT)$. $n = 6$

- 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.

$$\frac{\Delta L}{L_o} = -\left(\frac{3\check{D}_{gb}\check{\delta}_{gb}\check{\gamma}_s\check{\Omega}}{2kT(D/2)^4}\right)^{1/3} \underline{t}^{1/3}$$

So, as the mass flow occurs , the particles bond and the inter particle spacing changes as the neck grows and this results in the compact shrinkage or densification which is related to the neck size ratio X by D . And, the shrinkage during initial stage follows a kinetic law through this equation.

$$(\Delta L / Lo)^{n/2} = Bt / 2^n D^m$$

So, if you look at the rate of densification or the kinetic of the process during the initial stage, it will follow a relationship like this with respect to the sintering time t. n is typically between 5 and 6 and B is an exponential function of temperature as we could see from this equation over here . So, you can see that as the temperature increases, B also increases exponentially and this again tells you that the densification rate will increase as the temperature is increased.

$$B = Bo \exp(-Q/RT)$$

In terms of the diffusion coefficient and other relevant parameters the actual form of this kinetic equation can be given by this particular expression,

$$(\Delta L / Lo) = [(3\ Dgb\ \delta gb\ \gamma s\ \Omega) / (2kT(D/2)^4)]^{1/3} t^{1/3}$$

where Dgb is the grain boundary diffusion coefficient, δgb is the grain boundary thickness over which the diffusion occurs, γs is the surface energy and Ω is the atomic volume and rest of the terms have their usual meanings.

So, from here you can see that shrinkage scales with one third power of time that is what you will get from this equation also if n is taken as 6. The occurrence of shrinkage will require over sizing of the tooling in order to maintain the dimensional tolerances of the final product; shrinkage means the dimensions are actually reducing and therefore, initially you have to start with little bit bigger size so that when the shrinkage happens it comes back to the actual size which is required in the final product, right.

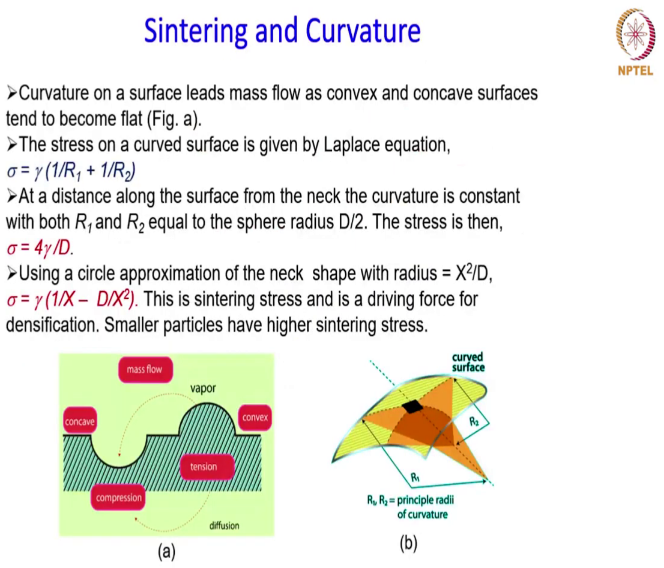
So, therefore, the tooling has to be little bit over sized to take care of the shrinkage. And, the surface area also changes during the process and therefore, the change in the surface area can be also taken as a measure of sintering especially for small powders which have high surface area.

So, in the early stage of sintering, the sintering rate or the densification in terms of the surface area change can be described by an equation like this

$$(\Delta S / So)^v = Cs\ t$$

where ΔS is the change in the surface area and So is the initial surface area and Cs is a kinetic term that includes mass transport constants and other parameters and t of course, is the sintering time right. So, this is how the initial stage goes through as far as the mass transport is concerned.

(Refer Slide Time: 24:02)



Sintering and Curvature

- Curvature on a surface leads mass flow as convex and concave surfaces tend to become flat (Fig. a).
- The stress on a curved surface is given by Laplace equation, $\sigma = \gamma(1/R_1 + 1/R_2)$
- At a distance along the surface from the neck the curvature is constant with both R_1 and R_2 equal to the sphere radius D/2. The stress is then, $\sigma = 4\gamma/D$.
- Using a circle approximation of the neck shape with radius = X^2/D, $\sigma = \gamma(1/X - D/X^2)$. This is sintering stress and is a driving force for densification. Smaller particles have higher sintering stress.

(a)

(b)

So before we finish this class let us take a moment to summarize it. So, to summarize we can say that the curvature on a surface leads to mass flow as the convex and concave surfaces tend to become flat so that tendency for the surfaces to become flat is a driving force for the mass flow. And, the stress on a curved surface is given by the young Laplace equation that we have derived before right.

So, this is the equation which relates the radii of curvature to the stress on a curved surface and for spherical particles R 1 becomes equal to R 2 and therefore, sigma becomes this 4 gamma by D. And, if we use a circle approximation for the neck shape then the stress can be expressed with the neck size x through an equation like this. So, this is the sintering stress which aids the densification process.

Then we talked about the different mass transfer mechanisms. These are basically categorized in to surface transport and bulk transport. The surface transport mechanisms are non-densifying. They lead to neck growth and bonding between the particles, but do not really need to shrinkage . The bulk transport mechanisms on the other hand lead to shrinkage and therefore, they are the densifying mechanisms.

And, this can be seen from these two diagrams also the flow path for the surface transport processes and the flow path for the bulk transport processes and also the sintering that this bulk mechanisms lead to . And, we have seen that plastic flow dominates during heating, but declines at higher temperature as the dislocation density decreases at higher temperature. And, grain boundary diffusion is a dominant densification mechanism for most of the metals.

Then we started talking about the stages of sintering. The sintering process occurs in three stages the initial stage, the intermediate stage and the final stage. In this class today we have talked about the initial stage which is basically characterized by the neck size ratio X by D and it considers an isothermal growth of the neck which can be seen through an equation like this.

The growth with respect to the sintering time and then we also talked about the shrinkage which takes place during the initial stage of sintering and this again is related to the neck size ratio X by D. And, in terms of the kinetic of the process if you see this follows a kinetic law through an equation like this where n is between 5 and 6 and B is an exponential function of temperature.

And, we have also seen that the change in the surface area can also be taken as a measure for sintering giving the initial stage and the relationship between the sintering and the surface area change can be seen from this equation over here.

And, since this shrinkage occurs during the sintering process the tooling has to be over sized so that the dimensional tolerances of the final product can be taken care. And, at the end of the sintering process it should come out with the size which is actually needed ok. So, with this we come to the end of this class.

Thank you for your attention.