# Powder Metallurgy

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

## Lecture – 56

## Full Density Processing - 1

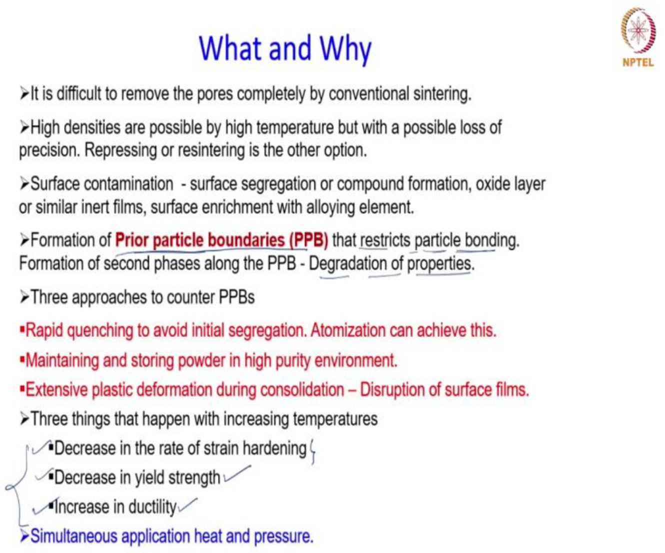
Hello everyone and welcome back again. So, right now we are in the final stage of the Powder Metallurgy process namely, sintering. And so far we have had a great deal of discussions on this process. And we have seen how the densification occurs during the process of sintering and how the pores are eliminated to give rise to a dense compact at the end of the process.

It is difficult to obtain 100 % density in the sintered compact and the primary reason for that is the presence of the residual pores which are difficult to eliminate. Because during prolonged sintering the pores break away from the grain boundaries and the pore structure gets stabilized and therefore, it becomes difficult to remove the residual pores. And if there is any gas trapped in the pores it is difficult to close the pores; because the gas pressure inside the pore will balance the surface energy of the curved surfaces of the pores and therefore the pore closure will be difficult.

So, for all these reasons it is difficult to obtain a full density compact by conventional sintering process. And therefore, we need to look at the processes which can give rise to a fully dense compact which will be having properties that can match the wrought products.

We are going to discuss about the processes which can lead to full density and these processes are known as full density processes.

(Refer Slide Time: 02:35)



## What and Why

- ➤It is difficult to remove the pores completely by conventional sintering.
- ➤High densities are possible by high temperature but with a possible loss of precision. Repressing or resintering is the other option.
- ➤Surface contamination - surface segregation or compound formation, oxide layer or similar inert films, surface enrichment with alloying element.
- ➤Formation of **Prior particle boundaries (PPB)** that restricts particle bonding. Formation of second phases along the PPB - Degradation of properties.
- ➤Three approaches to counter PPBs
- ▪Rapid quenching to avoid initial segregation. Atomization can achieve this.
- ▪Maintaining and storing powder in high purity environment.
- ▪Extensive plastic deformation during consolidation – Disruption of surface films.
- ➤Three things that happen with increasing temperatures
  - ▪Decrease in the rate of strain hardening
  - ▪Decrease in yield strength
  - ▪Increase in ductility
- ➤Simultaneous application heat and pressure.

So, let us first try and understand the meaning of full density. It is difficult to remove the pores completely by the conventional sintering process and there are various reasons for that. And one of the primary reasons for not achieving full density is related to the surface conditions or the surface contamination.

The surface of the particles can have segregation or compound formation including oxide layer or similar inert films. And when this kind of layers are present on the particle surfaces, it will prevent bonding between the particles which is quite obvious.

In pre-alloyed powders there could be possibility of surface enrichment with the alloying element and that again leads to some kind of difficulty as far as the bonding between the particles is concerned. So, this kind of surface contamination leads to the formation of what is known as prior particle boundaries or PPBs.

Since this is a result of the presence of surface layers this will restrict particle bonding. And there are also chances of formation of second phases along the PPBs if there is an enrichment of solute elements which can precipitate out during the heating process.

So, all this would first of all prevent particle bonding and limit the density which can be achieved and if there is formation of second phases along the PPBs, it will also degrade the properties of the final product.

So, in order to achieve a better densification and also to eliminate the possibility of formation of second phases which are detrimental there are three approaches which can be taken to counter these PPBs. First, rapid quenching can be adopted to avoid the segregation and with regard to that, atomization is a process which can achieve this because the cooling rate in the atomization process is higher compared to many other powder fabrication techniques.

Maintaining and storing the powder in high purity environment will prevent the formation of this kind of surface layers whether it is oxide or any other compound because it is about reacting with the environment around the powder in which it is kept.

So, if the powders are maintained in a high purity environment then it is good for the quality of the surface which in turn will be beneficial for the sintering process. And extensive plastic deformation during consolidation can actually disrupt the surface films and lead to a better bonding between the particles.

When the surface films are no longer present on the surface of the particles it is quite obvious that the bonding between them will be better. And plastic deformation can actually break this kind of surface films and therefore, can lead to enhanced densification by promoting a better bonding between the particles.

Now, high densities can be achieved by high temperature probably with a loss of some precision. And at high temperatures three things that can happen with increasing temperatures are as follows; Decrease in the rate of strain hardening, decrease in the yield strength and increase in ductility.

And all these things are helpful with regard to the compaction and bonding between the particles because a high rate of strain hardening prevents packing of the particles and their compaction.

And then we have also discussed about the effect of the material strength on the compaction process and there we had seen that higher strength materials are difficult to compact. And therefore, when there is a decrease in the strength it becomes easier to compact and densify the powder.

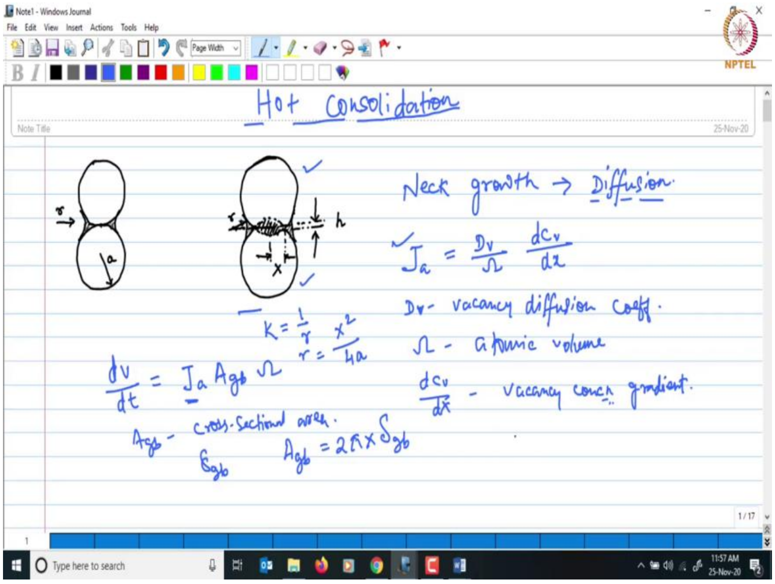
Similarly if the ductility is more, the material can be deformed easily at a particular pressure and therefore, this also would lead to a better densification. Thus high temperature processing can give rise to better densification.

So, in one hand you have pressure which can deform the material and also can disrupt the surface films and on other hand you have high temperature or application of heat which can lead to these three things. And if these two things can happen simultaneously, better densification can occur.

And therefore, when you have simultaneous application of heat and pressure you can expect to achieve a full density compact. So, in the conventional sintering process we have seen that there was no application of any external pressure during the sintering process.

In a pressure assisted sintering, during the sintering process as the compact is heated, simultaneously pressure is also applied. So, this is what the hot consolidation is all about. Here the heat and pressure are applied simultaneously. So, in order to demonstrate the effect of pressure as to how it is different from the conventional sintering, let us talk about one of the densification mechanisms which takes place during the solid state sintering. Grain boundary diffusion is one of the dominant mechanisms of densification during solid state sintering.

(Refer Slide Time: 10:39)



Hot Consolidation

Neck growth → Diffusion.

$J_a = \frac{D_v}{\Omega} \frac{dC_v}{dx}$

$D_v$ - vacancy diffusion coeff.

$\Omega$ - atomic volume

$\frac{dC_v}{dx}$ - vacancy concn gradient.

$K = \frac{1}{r}$

$r = \frac{x^2}{4a}$

$\frac{dV}{dt} = J_a A_{gb} \Omega$

$A_{gb}$ - cross-sectional area.

$\delta_{gb}$

$A_{gb} = 2\pi x \delta_{gb}$

With the help of that particular mechanism we will try and understand the effect of the pressure which is applied simultaneously in case of hot consolidation or pressure assisted sintering. So, let us consider the two sphere model of sintering.

As the compact is heated, a neck is formed between the particles at the contact points and as the neck grows, densification occurs what you could see from the second image (above slide). So, densification is all about the neck growth and we have seen that neck growth occurs by diffusion.

So, the diffusional transport of matter can be described in terms of the flux of atoms or equivalently in terms of the vacancy flux in the opposite direction because when the diffusion occurs atoms move in a particular direction and the vacancies move in the opposite direction. So, the flux of atoms at the neck can be given by the equation,

$$J_a = \frac{D_v}{\Omega}\frac{dC_v}{dx}$$

where $D_v$ is the vacancy diffusion coefficient, Ω is the atomic volume and $\frac{dC_v}{dx}$ is the vacancy concentration gradient.

And the volume of matter transported into the neck per unit time, that is, dv/dt is given as:

$$\frac{dv}{dt} = J_a A_{gb} \Omega$$

where $A_{gb}$ is the cross sectional area over which diffusion occurs. And now if you consider the grain boundary diffusion, (which is one of the dominant mechanisms of mass transport during sintering) it occurs over a constant thickness of the grain boundary given by this $\delta_{gb}$ term.

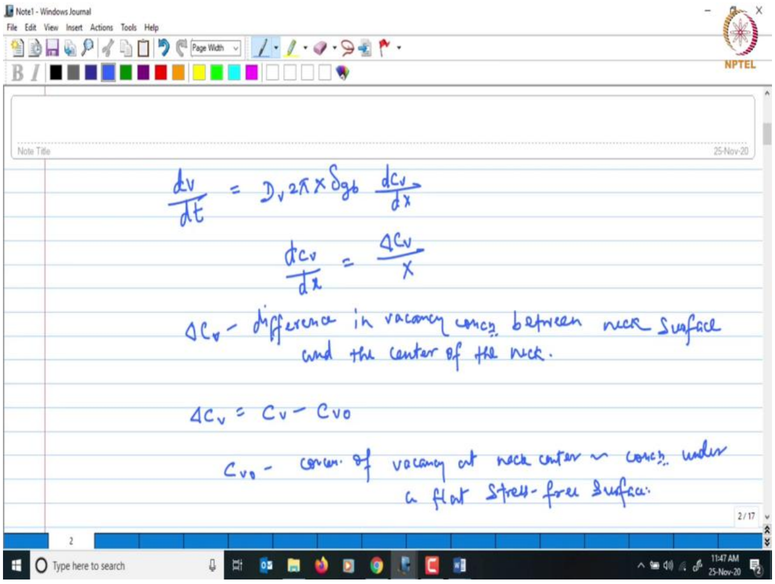
The cross sectional area will be given as

$$A_{gb} = 2\pi x \delta_{gb}$$

where x is the radius of the necks (slide above). So, now, if we replace $J_a$ then we would get this expression:

$$\frac{dv}{dt} = D_v 2\pi x \delta_{gb}\, \frac{dC_v}{dx}$$

(Refer Slide Time: 15:21)



$$\frac{dv}{dt} = D_v 2\pi x \delta_{gb} \frac{dc_v}{dx}$$

$$\frac{dc_v}{dx} = \frac{\Delta c_v}{x}$$

$\Delta C_v$ - difference in vacancy concn. between neck surface and the center of the neck.

$$\Delta C_v = C_v - C_{v0}$$

$C_{v0}$ - concn. of vacancy at neck center ~ concn. under a flat stress-free surface.

Now, if we assume that the vacancy concentration between the neck surface and the center of the neck is constant, then

$$\frac{dC_v}{dx} = \frac{\Delta C_v}{x}$$

wherein $\Delta C_v$ is the difference in vacancy concentration between the neck surface and the center of the neck. And this is given as $\Delta C_v = C_v - C_{v0}$ where $C_{v0}$ is the vacancy concentration at the center, which is assumed to be equal to the concentration under a flat stress free surface.

Now, considering the surface curvature, $\Delta C_v$ can be written as

$$\Delta C_v = C_v - C_{v0} = \frac{C_{v0}\gamma_{sv}\Omega}{kT}(\frac{1}{r_1} + \frac{1}{r_2})$$

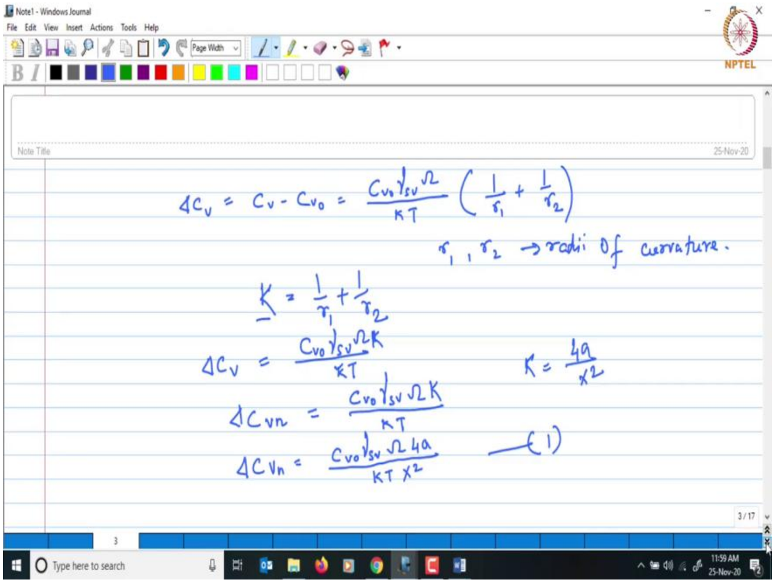
where r1 and r2 are the radii of curvature. If K is the curvature then it is given as

$$K = \frac{1}{r_1} + \frac{1}{r_2}$$

and therefore, $\Delta C_v$ can be written as this.

$$\Delta C_v = \frac{C_{v0}\gamma_{sv}\Omega K}{kT}$$

(Refer Slide Time: 18:11)



$$\Delta C_v = C_v - C_{v0} = \frac{C_{v0}\gamma_{sv}\Omega}{KT}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$$

$r_1, r_2 \rightarrow$ radii of curvature.

$$K = \frac{1}{r_1}+\frac{1}{r_2}$$

$$\Delta C_v = \frac{C_{v0}\gamma_{sv}\Omega K}{KT} \qquad K = \frac{4a}{x^2}$$

$$\Delta C_{vn} = \frac{C_{v0}\gamma_{sv}\Omega K}{KT}$$

$$\Delta C_{vn} = \frac{C_{v0}\gamma_{sv}\Omega 4a}{KT\,x^2} \quad \text{---}(1)$$

Here the small k is the Boltzmann constant and the capital K is the curvature. Now when you apply pressure during hot consolidation the vacancy concentration under the neck surface is not affected and therefore, following a similar approach we can write this expression for the vacancy concentration difference in this case.

$$\Delta C_{vn} = \frac{C_{v0}\gamma_{sv}\Omega K}{kT} \; and \; K = \frac{4a}{x^2}$$

$$\Delta C_{vn} = \frac{C_{v0}\gamma_{sv}\Omega 4a}{kTx^2} \quad (1)$$

where $C_{vn}$ is the vacancy concentration at the neck surface.

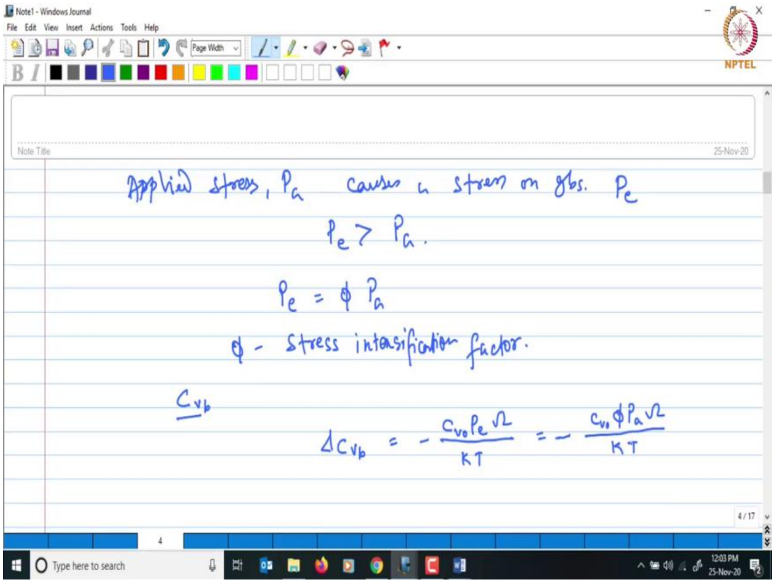
Now, the applied stress will cause a stress on the grain boundary. So, let us say the stress on the grain boundaries is $P_e$. So, $P_e$ is going to be greater than $P_a$ due to the presence of the pores. So, we can write that $P_e = \Phi P_a$

where $\Phi$ is known as the stress intensification factor that comes into play due to presence of porosity.

So, the vacancy concentration in the grain boundaries $C_{vb}$ will be less compared to that on a flat stress free boundary due to the presence of a compressive stress on the grain boundaries. And now this vacancy concentration in the boundary is given by this expression.

$$\Delta C_{vb} = -\frac{C_{v0} P_e \Omega}{kT} = -\frac{C_{v0} \Phi P_a \Omega}{kT}$$

(Refer Slide Time: 22:25)



Applied stress, $P_a$ causes a stress on gbs. $P_e$

$P_e > P_a$.

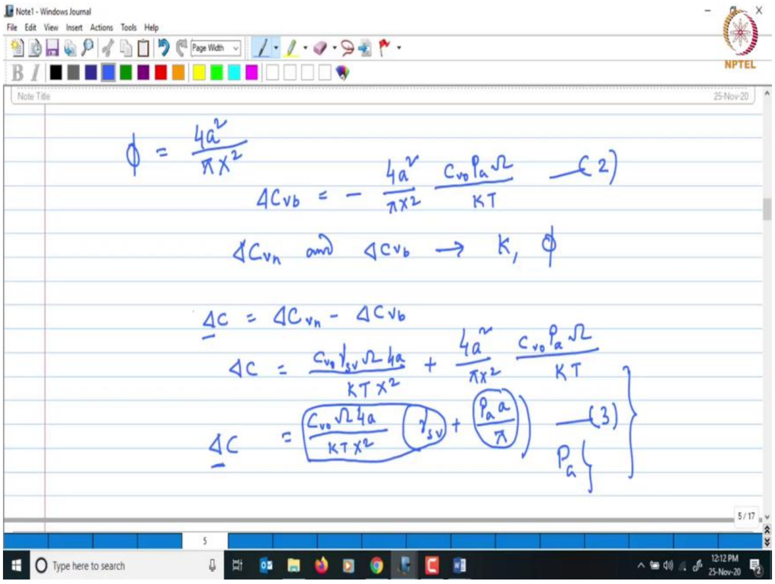
$P_e = \phi P_a$

$\phi$ - stress intensification factor.

$\underline{C_{vb}}$

$$\Delta C_{vb} = -\frac{C_{v0} P_e \Omega}{KT} = -\frac{C_{v0} \phi P_a \Omega}{KT}$$

(Refer Slide Time: 24:41)



$$\phi = \frac{4a^2}{\pi x^2}$$

$$\Delta C_{vb} = -\frac{4a^2}{\pi x^2} \frac{C_{v0} P_a \Omega}{KT} \quad \text{—} (2)$$

$\Delta C_{vn}$ and $\Delta C_{vb} \rightarrow K, \phi$

$$\underline{\Delta C} = \Delta C_{vn} - \Delta C_{vb}$$

$$\Delta C = \frac{C_{v0} \gamma_{sv} \Omega 4a}{KT x^2} + \frac{4a^2}{\pi x^2} \frac{C_{v0} P_a \Omega}{KT}$$

$$\underline{\Delta C} = \frac{C_{v0} \Omega 4a}{KT x^2} \left( \gamma_{sv} + \frac{P_a a}{\pi} \right) \quad \text{—} (3)$$

$P_a \{$

So, now $\Phi$ is taken as equal to the area of the sphere projected onto the punch of the hard pressing die divided by the cross sectional area of the neck that $\Phi = \frac{4a^2}{\pi x^2}$. So, therefore, $\Delta C_{vb}$ can be written as:

$$\Delta C_{vb} = -\frac{4a^2}{\pi x^2}\frac{C_{v0}P_a\Omega}{kT} \; (2)$$

So, $\Delta C_{vn}$ and $\Delta C_{vb}$ will depend on these two parameters K and $\Phi$. And now we can write the vacancy concentration difference. So, $\Delta C$ is nothing but the vacancy concentration difference between the neck surface and the grain boundary.

So, now using equation 1 and 2 which give the expression for $\Delta C_{vn}$ and $\Delta C_{vb}$ respectively we can write the expression for $\Delta C$ as: $\Delta C = \Delta C_{vn} - \Delta C_{vb}$.

$$\Delta C = \frac{C_{v0}\gamma_{sv}\Omega 4a}{kTx^2} + \frac{4a^2}{\pi x^2}\frac{C_{v0}P_a\Omega}{kT} = \frac{C_{v0}\Omega 4a}{kTx^2}\left(\gamma_{sv} + \frac{aP_a}{\pi}\right)$$

So, from here you can see this additional term $\frac{aP_a}{\pi}$ which has come above and over the normal sintering equation.

So, this is due to the fact that now the sintering is being done under the applied pressure $P_a$ and that is what is making a difference over here in terms of bringing an additional contribution to this vacancy concentration and therefore, an additional driving force is there when the sintering is done under pressure. And that is how the densification is enhanced in case of hot consolidation which is done under the application of an external pressure.

So, the other parameter here in case of the hot consolidation is the temperature because temperature and pressure are applied simultaneously in this case. So, the effect of pressure can be seen with the help of the vacancy concentration.

Now, we will have to look at the temperature because it is a combined effect of both of this. So, we will have to understand when the pressure is applied at a higher temperature what happens to the material as such.

So, that is the other aspect that we need to discuss and understand in order to understand the mechanism of hot consolidation, but that is something we are going to take up in the next class.

So, before we wind up this class let us take a quick summary of today's learning. So, to quickly summarize this class we have seen today that in conventional solid state sintering process it is difficult to achieve full densification. And therefore, we need alternative sintering techniques which can achieve full density and the reason behind not achieving full density in conventional solid state sintering are many.

One of the main reasons which prevent the bonding between the particles is the presence of the prior particle boundaries and the consequent formation of second phases on this kind of boundaries.

So, in order to get a full density this kind of boundaries or the surface layers which lead to this kind of boundaries are to be removed. And that is where the hot consolidation comes into picture where during the sintering process an external stress is applied and due to that stress this surface layer on the particles can be disrupted and the prior particle boundaries can be prevented.

And apart from that the high temperature also leads to decrease in the rate of strain hardening and the strength of the material and it also increases the ductility which is again helpful in densifying the material. And therefore, when there is simultaneous application of heat and pressure you can expect a much better densification and a full density compact can be obtained. And with that we come to the end of this class.