Powder Metallurgy

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Lecture – 41
Sintering – 1

Hi everyone and welcome back to this lecture series on Powder Metallurgy. In last several weeks, we have been discussing about this process of powder metallurgy. And, we have covered almost all the topics related to this process, starting from powder fabrication to the compaction process.

So, far we have discussed fabrication of powders, characterization of powders, then we talked about preparing the powder feedstock by mixing and blending it. And, we have also learned about as to how the powder packing takes place and what are the parameters.

And, then in past few classes, we have been talking about this compaction process with regard to shaping the powder into a particular form. We have seen that the powder can be shaped by different processes, depending on the complexity of the shape. If, it is a simple shape we can use uniaxial pressing for example.

Then, we have talked about other shaping processes also which can deal with more complex shapes. For example, we talked about, the powder injection moulding which can deal with 3D complex shapes.

And, then we have also spoken about the cold isostatic pressing, which is a more uniform pressing technique, which is much effective compared to the uniaxial pressing, because here the pressure can be applied uniformly in all directions and as a result the compact is uniform in terms of the density which is achieved after the compaction process.

Then, we also talked about the slurry techniques to make other kinds of shapes for example, flat thin products or long products. For such kind of shapes slurry techniques are more suitable, we have discussed that also in detail in past couple of classes. So, now, we are in a stage where the green compact is ready for the final product to come out.

So, this is the final stage, where the green compact is to be processed and the porosities left behind are to be closed to finally, come up with a fully dense product. So, this is the final stage, where the ultimate densification will take place. This is what we are going to talk about from now onwards as to how this densification takes place and what are the process details.

The process is called sintering, and this is the final step in the powder metallurgy process to densify the compact and obtain a fully dense product. So, this is one of the most crucial steps simply because of the fact that here, the final densification will take place. And, if something goes wrong in this step then whatever is done before may all go waste.

Therefore, the sintering process is a very crucial step. So, brace yourself for a series of lectures on this particular topic starting from today, but let me tell you that will be worth doing.

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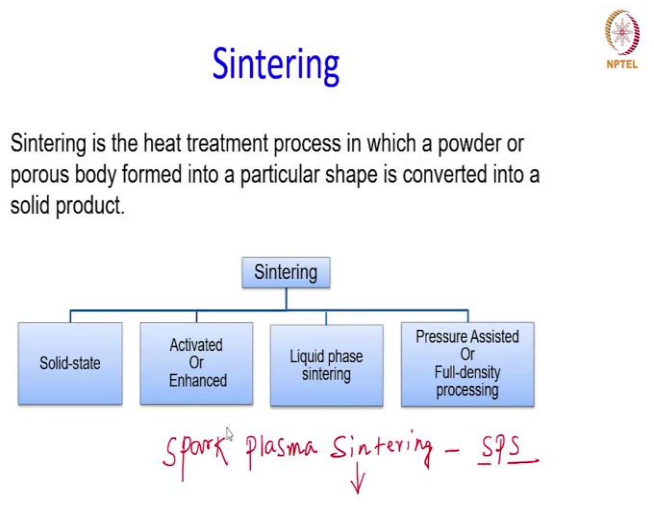

So, sintering can be defined as follows. Sintering is the heat treatment process in which a powder or porous body, already formed into a particular shape is converted into a solid product. In the powder metallurgy process what is done is the lose powder mass is first compacted and a particular shape is given to it. And, then in order to close all the pores and to densify, it is heated at a particular temperature for a certain period of time.

During this heating process the densification occurs and at the end of the heat treatment cycle or the sintering process, a fully dense solid product is obtained. That is what is called as the sintering process.

This process can be divided into different categories. These are as follows, Solid state sintering which is basically sintering a solid mass of powder to densify it and give rise to a solid dense product.

This happens all in the solid state itself. And, you can have some variants of this solid-state process for example, you can have activated or enhanced sintering in which an agent or an activator can be added to enhance the sintering, or there are some other means also to enhance the densification.

For example, a phase transformation can be used to enhance it. So, those kinds of processes are known as enhanced sintering. And, then when a liquid phase is involved that is known as the liquid phase sintering.

This is different from the conventional solid-state sintering in the sense that apart from the main solid phase which is to be sintered. There is a second phase which will melt at the sintering temperature and therefore, a liquid phase is also involved in this case.

And, then depending on the material at times the sintering is also done under the application of an external pressure. So, those are the pressure assisted sintering in which a full density is obtained. And, therefore, these processes are also known as full density processing.

So, which method of sintering will be used that primarily depends on the material which is to be sintered. For example, if you have a material which can be easily compacted and sintered, then the conventional solid state sintering itself will be enough. On the other hand you might have materials, which are difficult to sinter and you may not be able to get full density by conventional solid state sintering.

In those cases you may have to use the other kind of sintering processes such as the liquid phase sintering or pressure assisted sintering. Then, we also have another advanced sintering process known as spark plasma sintering. This is quite different from all the other sintering processes that we have described in this particular diagram over here.

In the sense that the heating mechanism in case of spark plasma sintering or SPS is quite different from all other sintering processes right. And, due to that this sintering process is also very effective in sintering hard to sinter materials and the sintering time is also much lower compared to the conventional sintering processes.

So, we are going to take up all of these one by one and discuss about them in detail as to what are the fundamental mechanisms, how it is done and so on. So, let us start with the fundamentals first where we learn about the basic principle behind sintering. And, as we progress we will also discuss about the underlying mechanisms involved in the process of sintering.

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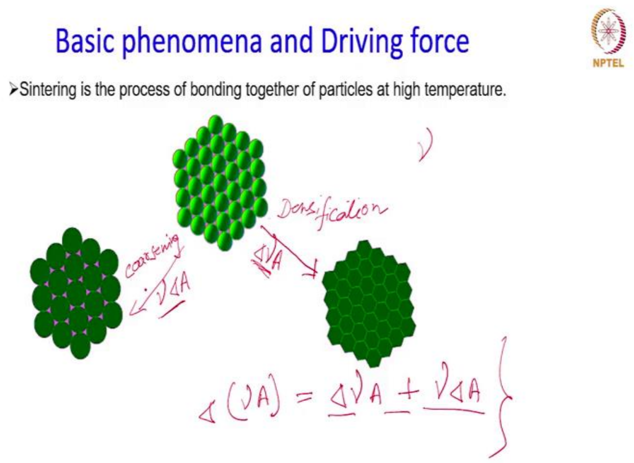

So, sintering basically is the process of bonding together of particles at high temperature. If you need to close the pores, the green compact has to be heated to a particular temperature, depending on the material, because for these pores to be filled there has to be diffusion occurring.

And, that will occur only at higher temperature, where the atomic diffusion can happen, and the mass can be transported towards the pores for them to be filled and the densification to take place.

First of all when you heat the compact to higher temperature, there could be two things which can happen. So, let us say this is the green compact and the arrangement of the particles, here you can see that after the compaction process the particle-to-particle contacts are formed.

But still there are pores between the particles and this is what we have discussed before, we discussed the fractional porosity. As it occurs in the green compact and it is correlation with the compacts and pressure and so on.

The pores which are to be closed for the compact to fully densify. So, now, when you heat it to high temperature two things can happen. One it will densify, where this pores in between the particles will be completely eliminated and the particle contacts will grow and form these kinds of boundaries or form the grain boundaries between the particles.

On the other hand, it can also lead to coarsening of the particles. Because at high temperature there is a driving force for the growth of the particles as well. As it decreases the total energy of the system, because as grain growth occurs, number of grains will decrease. And, hence the number of interfaces will also decrease or in other words the total grain boundary area will decrease as the grain size increases.

Since the interfacial area is decreased, the total interfacial energy will also decrease and that would lead to a decrease in the total energy of the system. So, that is why there is a driving force for the grain growth or coarsening during the sintering process. And, when you talk about sintering a porous compact the pores will also play a role in the grain growth process.

While talking about the growth during sintering, the pore interactions will also have to be considered. Because depending on the locations of the pores, whether they are located along the grain boundaries or inside the grains the grain growth behaviour will change.

If, the pores are located along the grain boundaries during the final stage of the sintering process, then it is expected that they will retard the grain growth and the grain growth will not be very significant it will be a normal kind of grain growth.

On the other hand, if the pores are located inside the grains, then there is a chance for abnormal grain growth, because now there are no more pores along the boundaries to pin them and as a result of that the grains can grow abnormally. So, the occurrence of grain growth or coarsening during sintering is quite normal.

Therefore, apart from densification coarsening will also occur simultaneously in the compact. So, as more interfaces are generated because of the densification process, the interfacial energy will change. So, if gamma is the specific interfacial energy, then the change in the surface energy or interfacial energy due to densification will be this.

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

And, due to the coarsening the area is going to change and due to that the change in the surface energy will be gamma into delta A, as opposed to delta gamma into A for the densification process.

So, the total change in the surface energy will be coming from these two contributions, one from the densification and the other from the coarsening. This process of densification and coarsening will essentially lead to a decrease in the total surface energy of the system.

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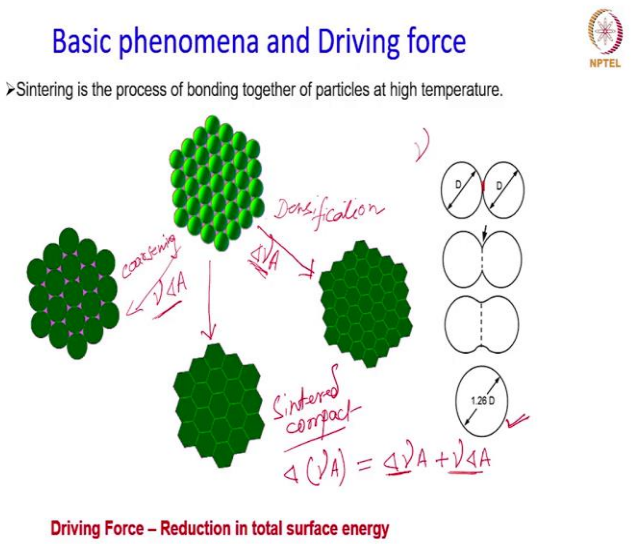

So, when sintering finally, occurs in the sintered compact both of these phenomena will take place. And that can be seen from this diagram as well; here this is demonstrated with just two particles both having equal diameter D.

So, this is the contact which is formed during compaction and as the compact is sintered a neck will form in this contact points and as the sintering proceeds, this neck will grow and as it grows the solid vapour interface will be replaced by the solid, solid interface, which means that the grain boundaries will replace the solid vapour interfaces.

And this final picture of a bigger particle that you see over here that depicts the coarsening process, wherein if sufficient time is allowed these two particles of diameter D can coalesce into one particle with a bigger diameter. So, that is the coarsening process.

So, the sintering process involves both densification as well as grain coarsening. Therefore, the total change in the surface energy, delta gamma A will be given by these two contributions, one from densification and the other from coarsening.

This phenomenon that takes place during the sintering process, it basically leads to a decrease in the total surface energy of the system and that is what drives the process. Therefore, we can say that the driving force for the sintering process is the reduction in total surface energy.

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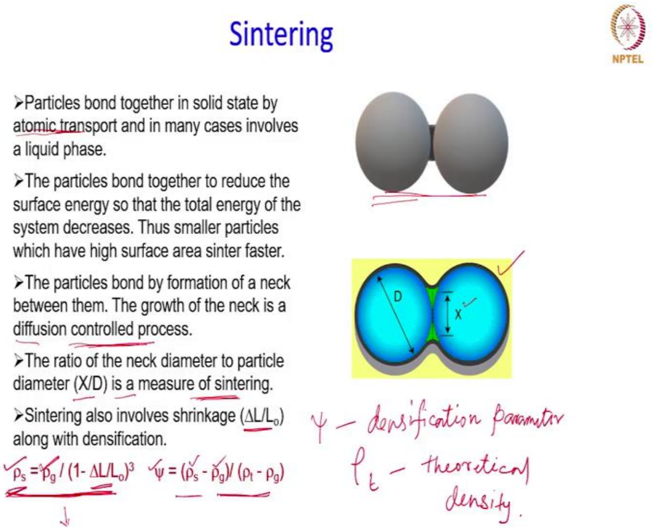

Now, if you look at the process as to how it happens you know first you can just see two particles as to how do they bond, when they are heated to a particular temperature for the sintering process.

Let us say we are having these two particles, which are formed a point contact during the compaction process. And, as it is heated now for the sintering process, this contact will grow in the form of a neck.

A neck will first form between the particles at the contact points and this neck will grow by diffusional transport of matter or atomic transport and in some cases, it can also involve liquid phase. So, this bonding of particles will reduce the surface energy so that the total energy of the system decreases.

And, therefore, we can also say that smaller particles which have higher specific surface area will sinter faster compared to larger particles, because if the surface area is higher it will also have higher driving force for the sintering process.

So, the particles will bond by formation of a neck between them as you see over here this is the starting of the formation of the neck and it will form in a manner like this as it is shown schematically in this particular picture over here.

And the growth of the neck is a diffusion controlled process. So, the mass transport has to happen towards the neck for it to grow and the pores to be closed and that ultimately will lead to densification.

Here there is a neck radius as you could see which is written as X. And the ratio of the neck diameter to the particle diameter *X/D* is a measure of the sintering. As to what extent the particles have sintered that can be gauged by looking at this *X/D* ratio. And, in sintering as you would have already understood by now, the pores are closing. So; that means, you know the particles are coming closer and closer.

And, therefore, the process of sintering or the densification that happens during sintering will also lead to some shrinkage in the compact, which is given by,

$$\text{Shrinkage in the compact} = \Delta L/L_0$$

Where delta *L* is the change in the dimension and L_0 is the initial dimension.

This can be one of those dimensional parameters. For example, the length and this shrinkage is related to the sinter density ρ_s, and the green density ρ_g with this equation.

$$\rho_s = \rho_g / (1 - \Delta L/L_0)^3$$

From this relation we can say that the compact densifies from the green density ρ_g to the sinter density ρ_s which is higher compared to ρ_g, due to the shrinkage which takes place during the sintering process.

So, densification will be always accompanied by shrinkage. And the densification parameters ψ is given by relationship like this.

$$\Psi = (\rho_s - \rho_g) / (\rho_t - \rho_g)$$

So, this is basically the ratio of the change in the density; that means $\rho_s - \rho_g$, the density of the sintered compact and the green compact the difference of that divided by the change needed to attain a pore free solid.

ρ_t here in the denominator is the theoretical density of the material. So, that is how the densification parameter Ψ defined. Densification is all about elimination of the pores and the final density the neck size surface area and shrinkage these are all related to the measures of the pore elimination process, which takes place during sintering.

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Sintering is a high temperature process for all these phenomena that leads to elimination of the pore a higher temperature is needed, because the atomic diffusion that happens that is a thermally activated process.

And, therefore, for the densification to occur the compact has to be heated to higher temperature. And, through these plots the effect of temperature can be seen here T_2 is greater than T_1, T is the temperature.

So, this is depicted in terms of the densification parameters or the parameters which can be related to the densification such as the neck size. The surface area reduction $\Delta S/\Delta S_0$, the shrinkage and the densification parameter that we defined just now.

Here you can see that as the temperature is increased the densification is also increased, because all these parameters which define densification, increases with increasing temperature.

Because the processes which lead to pore closer are all thermally activated processes and therefore, an increase in the temperature will lead to a higher densification. In sintering process as such the two important parameters are the temperature and the time.

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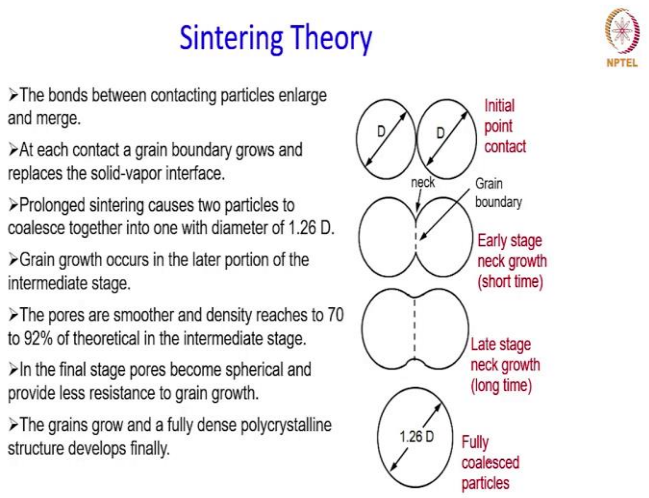

So, now coming back to this bonding process, so, this again you know depicts the sintering process as it proceeds starting from the development of the neck at the contact points. During the early stage of sintering and then as the process continues this neck grows in the later stages.

When more time is allowed during the sintering at a particular temperature and if it happens for a prolonged period of time, then the particles can also coalesce to bigger size. Now, for all this to happen the matter has to be transported to the neck for it to grow and for the pores to close.

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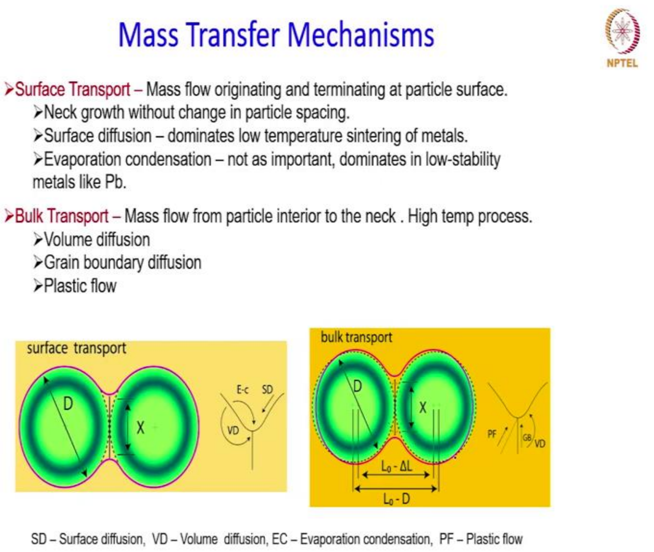

So, this atomic diffusion occurs through well defined paths. Those diffusional paths are depicted in the above diagram. These are basically the surface diffusion, the volume diffusion, which is one of the bulk transport processes.

Then, you also have grain boundary diffusion where the transport of the matter occurs along the grain boundaries and then you have plastic flow ok. And there is one more type of mechanism known as evaporation condensation that can also happen for the matter transport towards the neck.

Here you can see diffusion plays a very important role for the densification to occur during the sintering process. And, therefore, at this point it will be good to have a little bit of discussion about the diffusion phenomena as such, but for this particular lecture this is all I have, but before we close let us take a moment to summarise the lecture.

So, today we talked about the basic principle of the sintering process. And, we have learned that the main driving force for the sintering is the reduction in the total surface energy that leads to an ultimate reduction in the total energy of the system. And, the sintering process basically starts with the formation of a neck at the contact points of the particles and as it proceeds the neck grows which ultimately leads to pore closer.

So, therefore, the neck ratio which is the ratio of the diameter of the neck to the diameter of the particle is taken as the measure of the sintering and sintering is always associated with shrinkage. So, whenever densification occurs shrinkage will be accompanied.

And, therefore, the shrinkage also is an indication of the densification which occurs in the sintering process. And, therefore, the sinter density and the green density; that means, the transformation of this compact from the green density towards the higher sinter density is related to the shrinkage; through this particular relationship over here.

And, then we defined a parameter called the densification parameter, which is related to the final density, which has to be achieved at the end of the sintering process. So, this is the densification parameter written as ψ.

And, then we talked about the effect of temperature on the sintering the phenomena, which happens during the sintering process is thermally activated. And, therefore, any increase in the temperature will lead to a higher densification during the sintering process.

Then, we started talking about the diffusion mechanisms or different paths of mass transport that you have in case of the sintering process. So, these are basically categorised into two different categories one is the surface transport and other is the bulk transport.

And this mass transport through all these different paths ultimately leads to the densification, which takes place during the sintering process ok. So, with that we come to the end of this class.

Thank you for your attention.