Powder Metallurgy
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Lecture – 46
Sintering – 6

Hello everyone and welcome back, so we have been discussing about this process called Sintering. And in the last couple of classes we have seen the different stages of sintering. Now as you would have realized by now the main objective of sintering is to densify and this densification is all about the elimination of the pores. So therefore, it calls for a discussion on the pore interaction and the structure of the pores.

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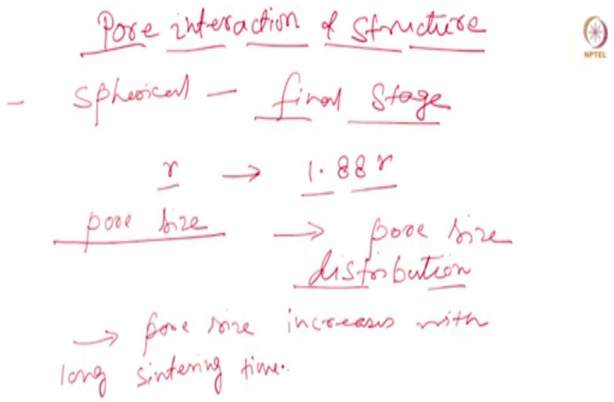

This will be the topic of the our discussion in this lecture. Now, first of all we have seen that the pores become spherical in the beginning of the final stage, the morphology changes from the cylindrical shape that was there in the intermediate stage to the spherical shape in the final stage. And, this shape change to the spherical shape basically occurs through surface transport process. And, when the shape changes from the cylindrical to spherical it is also expected to grow in the radius.

So, a pore with radius r in the intermediate stage will change to a radius of about 1.88 r in the final stage . So now, let us see what happens to the pore size as the sintering process continues. First of all for most of the materials or the powders which we deal with in the powder metallurgy process there is a distribution in the particle size and that also gives rise to a distribution in the packing. And therefore, you can expect a pore size distribution during the final stage of sintering.

Now, what exactly will be the pore size during sintering that depends on a complex combination of interactions, which include coarsening collisions and shrinkage etcetera; the events or the phenomenon which takes place during the densification process.

With long sintering times, the pore size is expected to grow. Since there are both smaller and larger pores as I said there is a distribution in the pore size, the smaller pores will emit more vacancies than the larger once. And therefore will also grow in size because the local vacancy concentration is inversely proportional to the pore radius.

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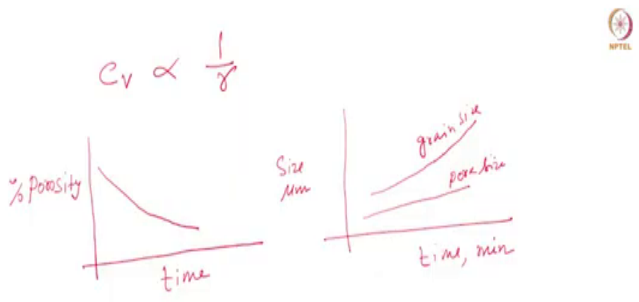

So, if **Cv** is the vacancy concentration, then this is proportional to 1/r . So therefore, the smaller pores will emit more vacancies compare to the larger once and as a result pore closure will happen and the porosity will decrease. But at the same time the size of the pores will also increase as the sintering time is increased. So, if you look at the percent porosity and the pore size with respect to the sintering time it can be illustrated with plot like this.

Let us first see the percent porosity with respect to time for a given material. Let us consider iron as an example; the iron powder was compressed at a particular pressure and then it is being sintered at a given temperature. So, as the sintering time is increased the percentage of porosity of course is supposed to decrease. So, you can expect a plot like this right.

Now, as I said with densification or the reduction in porosity, the size of the pores will also increase with sintering time. And for the iron powder that we have taken as the example this might show a trend like this and grain coarsening will also occur as we have discussed before. So, if we look at the grain size that will also increase with increase in sintering time.

So, coarsening is a phenomenon which is associated with the densification during the sintering process. Now, once the pores have taken this kind of closed pore geometry as we have seen in the final stage of the sintering, the further densification will now depend on the structure of the pores and how they interact with the grain boundaries .

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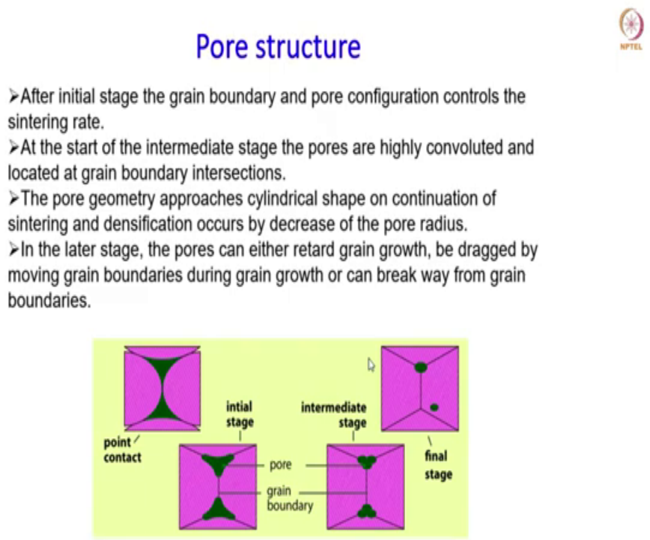

So, let us talk about that. So, as I said after the initial stage the grain boundary and the pore configuration will control the sintering rate. So, we have seen that at the start of the intermediate stage the pores are highly convoluted and located at the grain boundary intersections right.

So, this is what you see first in the initial stage and then as the sintering progresses, the pores kind of takes up more rounded kind of geometry and becomes more convoluted and they are primarily located along the grain boundary intersection points .

And, now as the sintering process progresses the pore geometry approaches cylindrical shape as we have seen while discussing about the different stages of sintering. So, this is the intermediate stage where the pores takes up this kind of cylindrical morphology and densification in that case occurs by the decrease of the pore radius .

So, as more mass flows towards the pores this pores get filled and their size of the radius will continue to decrease and that would lead to densification . And in the later stage as we approach the final stage of the sintering, then the pores can either retard the grain growth or be dragged by the moving grain boundaries . So, that would depend on how the pores are oriented with respect to the grain boundaries .

So, the possibilities that exist with regard to interactions of the pores with the grain boundaries are as follows, the pores can be dragged by the moving grain boundaries during the grain growth process or they can break away from the grain boundaries or if they keep attached to the boundaries all along they can actually retard the grain growth by peeling the grain boundaries .

So, these are the possibilities which exist depending on how the pores interact with the grain boundaries and in this diagram again as we have discussed you can see the different morphologies that the pores take in the different stages of sintering . So, starting from a triangular kind of geometry in the beginning it goes all the way to a spherical morphology during the final stage.

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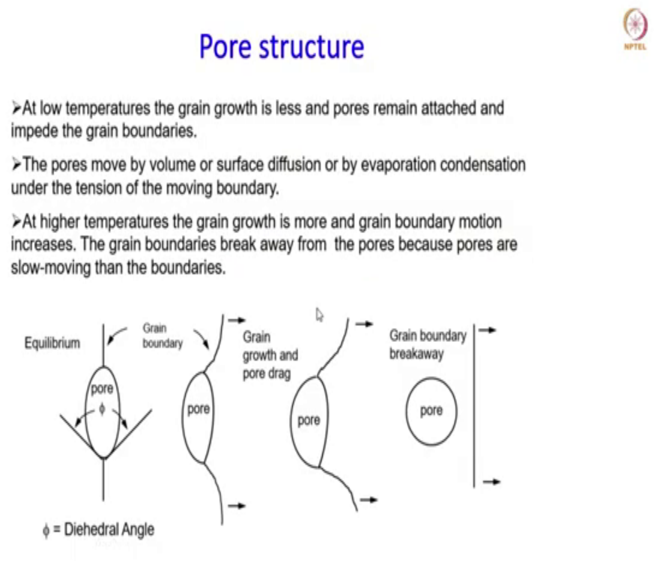

So, talking about this interaction between the grain boundaries and the pores, we can depict it with a diagram like this. So, for a pore sitting on a grain boundary the equilibrium between the grain boundary energy and the solid vapor surface energy will cause a group to form as you could see from here and the angle of this group is known as the Dihedral angle . So, that is how the interaction between the pores and the grain boundaries will start.

And now you know as we have discussed just now there could be two things happening one the pore will get dragged along with the grain boundary as the grains grow during the process of sintering or they might break away . So, this what you can see the pore is sitting in the grain boundary right and as the grain growth occurs basically it occurs through the migration of the grain boundaries.

So, as the grain boundaries move when the pore is sitting on the grain boundaries they will also move, but they may get attached to it or simply break free from it . So, at low temperature the grain growth is less and the pores will remain attached and consequently will impede the grain boundaries basically and restrict the grain growth .

And the pores as far as their movement is concerned, the pore movement happens by volume or surface diffusion or by the evaporation condensation mechanism under the tension of the moving boundary . So, as the boundary moves the pore is kind of you know stationery, so it will takes out some stress on that pore and due to that the pore will also tend to move. Now at higher temperature the grain growth is more and therefore the grain boundary motion also increases.

And as a result of that, it will be difficult for the pores to keep pace with the moving boundary, because now the boundaries are moving faster and therefore, there are chances that the boundaries will break away from the pores. Because as I said the pores are slow moving and they find it difficult to keep pace with the fast moving boundaries. So, it leads to breaking away of boundaries from the pores as you could see from here .

So, this is how you know depending on how the pore is interacting with the boundaries and how the grain boundaries are behaving during the densification and the coarsening process, the structure or the interaction of the pores will change .

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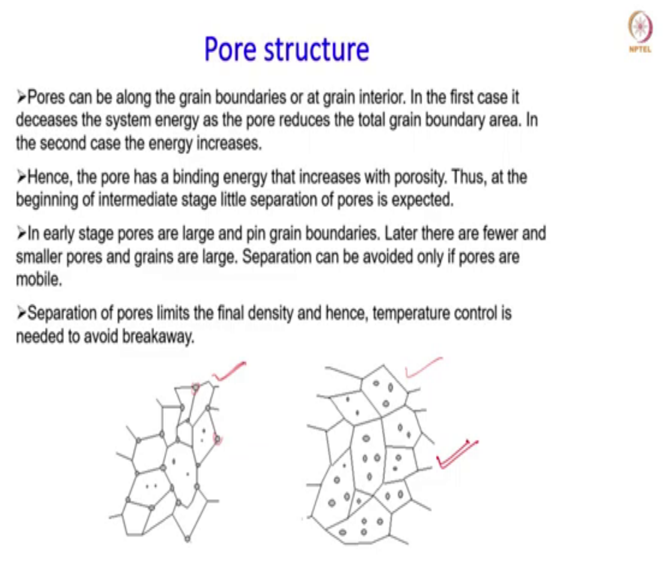

So, when the pores will finally, you know distributed in the material they can be either along the grain boundaries or at the grain interiors. So this is one picture which shows that the pores are the primarily along the grain boundaries right and here the second one shows the pores to be primarily located in the grain interiors .

So, in the first case it will decrease the system energy, because pores are taking some of the grain boundary area and therefore the energy associated with this surface, this boundary will decrease. So, it will ultimately lead to a decrease in the energy of the system. And in the second case for this one it will lead to an increase in the energy of the system and therefore the pore has a binding energy that increases with porosity.

So, at the beginning of the intermediate stage there is little separation of pore and in the early stage the pores are actually larger and pin the grain boundaries, later there are fewer and smaller pores as more and more pore filling happens and the pores shrink. And the grains are larger during the final stage and therefore a separation can be avoided only if pores are mobile .

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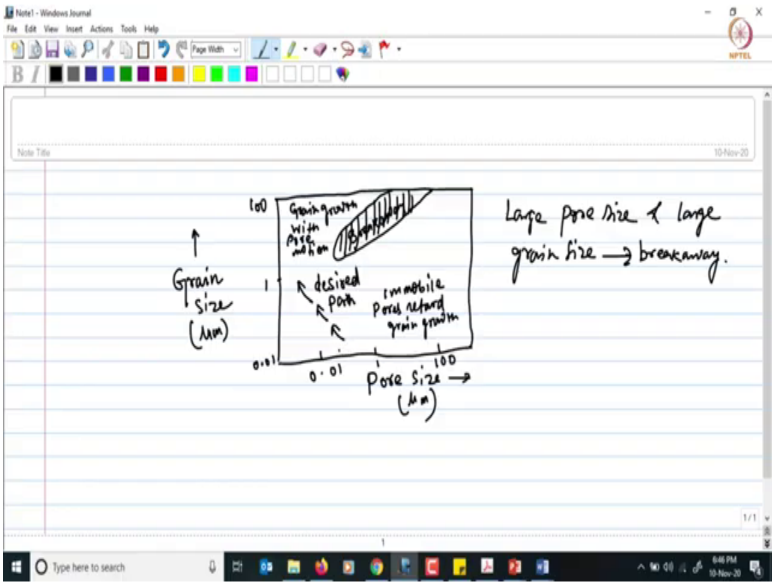

It can also be shown by a plot between grain size and pore size. So, if the grain size is plotted against the pore size then it will look something like this, it will basically help us identify the region in which the breakaway of the pores will take place.

So, as you can see a large pole size and a large grain size can lead to break away during grain growth. So, in this region of the break away, the densification will be limited and therefore for better densification the sintering path should be something like this, in which this breakaway region can be avoided. So, this should be the desired path of sintering for better densification.

Now, the separation of the pores will limit the final density and hence the temperature has to be controlled to avoid this break away . Because once the pores break away from the grain boundaries then the mass flow which is occurring along the boundaries for the pores to be filled get closed will stop .

And therefore it is necessary that this separation is prevented and the parameter which can be controlled in order to do that is the temperature right. So, from that perspective you can see that the temperature is a very important parameter in the whole sintering process and that is why for every material there is a optimum temperature which will give rise to high sintered density .

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Process Variable

Table: Variables affecting sinterability and microstructure

Variables related to raw materials (Material variables)	Powder: shape, size, size distribution, agglomeration, mixing, etc. Chemistry: composition, impurity, non-stoichiometry, homogeneity, etc.
Variables related to sintering conditions (Process variables)	Temperature, time, pressure, atmosphere, heating and cooling rate, etc.

So, talking about the process variable of this sintering process, there are two kinds of the variables - first the variable is related to raw materials and the second kind are the variables related to the sintering conditions . So, as for as the sintering process variables are concerned, these are the parameters - temperature is one of the most important parameter here as I was mentioning. And then apart from that time also plays a crucial role a very important role in the sintering process.

So, it is not only about temperature, but the sintering time also has to looked at because we have seen how the time of sintering affects various phenomenon including the grain size as well as the pore size. And, therefore the sintering as a whole has to be looked in the window of temperature and time both right. So, it is basically a temperature time cycle which has to be looked at when we talk about the sintering process as a whole .

And apart from that, the other variables which might have their own influences on the sintering and the densification process are pressure, the sintering atmosphere, heating and cooling rates .

Sintering atmosphere we have discussed about these as to you know how the presence of air can limit the final density which can be achieved, because the gas or air which is present around the compact can be trapped inside the pores and that will prevent the densification.

And therefore, if the atmosphere is changed from air to vacuum, then a better densification is expected to occur right. The variables related to the raw materials are either connected to the powder for example, the shape, size, distribution, agglomeration, mixing of powder etcetera or the chemistry which relates to composition impurity, non stoichiometry, homogeneity etcetera.

For example, if you talk about the powder characteristics we have seen before how the powder share affects packing and packing in turn will affect the compaction and the densification right. So, apart from the variables related to the sintering conditions the material variables will also affect the sintering process and densification which occurs during sintering.

So, before we finish this class today let us take a moment to summarize it. So, to summarize this class we have seen that the pore structure and the pore interactions have a lot to do with the densification process. The pore first of all change their morphology as the sintering process goes through different stages.

What you can see from here in this diagram; it changes from this kind of triangular pores to more convoluted and rounded pores, which then takes up cylindrical kind of morphology in the intermediate stage. And, as it enters the final stage the pores become spherical .

And then we have also seen how the pore growth takes place with respect to the sintering time, apart from the densification or pore elimination the size of the pores also increase with the increased sintering time. And then we discussed about the interaction of the pore and their orientation with respect to the grain boundaries.

So, these grain boundary pore interaction will actually have a lot of bearing on the densification process and also on the grain growth which occurs during the sintering process. So, the pores can either remain attached to the grain boundaries , if they can keep pace with the moving boundaries as the grains grow or the grains can break away from these pores, when the pores will no longer be able to keep pace with the moving boundaries .

So, basis that whether they are breaking away or not the densification will also depend on that, because the separation of the pores limits the final density. And therefore, to have a higher final density this separation process has to be controlled and the external parameter which can control that is the temperature.

So therefore, temperature control is needed to avoid this break away and achieve a higher final density in the sintered compact. And, then we talked about the process variables which fall in to two categories, one is related to the raw materials like the powder shape, size and size distribution and also whether the powder has any agglomeration whether the mixing is done properly and all that.

And the chemistry might also play a role on the sintering process with regard to the composition, the impurity content and also the ratio between the terms that is the stoichiometry, the homogeneity of the chemical composition etcetera will also have their own influence on the densification process. And the variables related to the sintering process as such are this temperature and time; these are the two most important parameters.

And in fact these are the two parameters which are actually controlled to control the sintering process and other parameters are the pressure, atmosphere, heating rate and cooling rate. And, with that we come to the end of this particular class.

Thank you for your attention.