Fundamentals of Materials Processing (Part-I).
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Lecture-40.
Sintering Theory.

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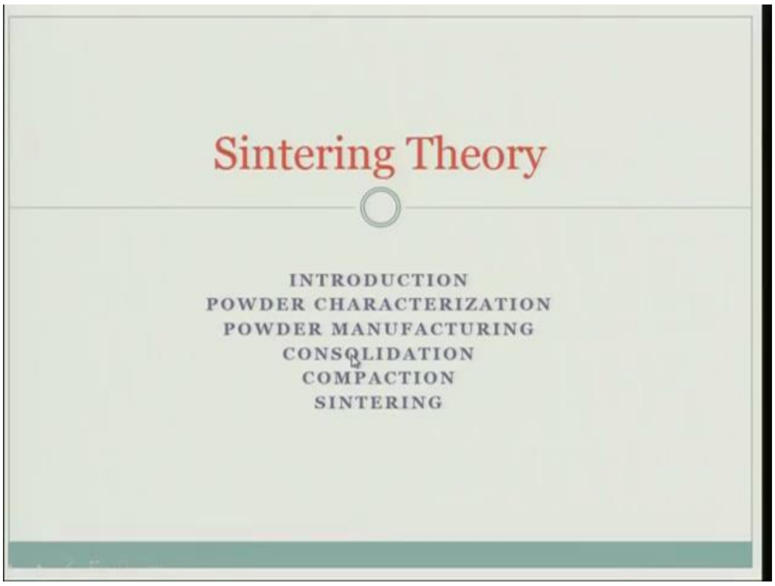

Sintering Theory

INTRODUCTION
POWDER CHARACTERIZATION
POWDER MANUFACTURING
CONSOLIDATION
COMPACTION
SINTERING

Okay, so welcome back students. So this is the last subtopic of the 2nd module. So we have so far gone through the powder introduction, powder characterisation, powder Manufacturing and in the last few lectures we looked at power consolidation and powder compaction. Now the last stage, which is sintering, that is the most important and vital step in the powder processing is what we will discuss today, the theory, the fundamental behind sintering. Now basically if you look at just method or what is happening in sintering is not very difficult to understand, the particle so coalescing together.

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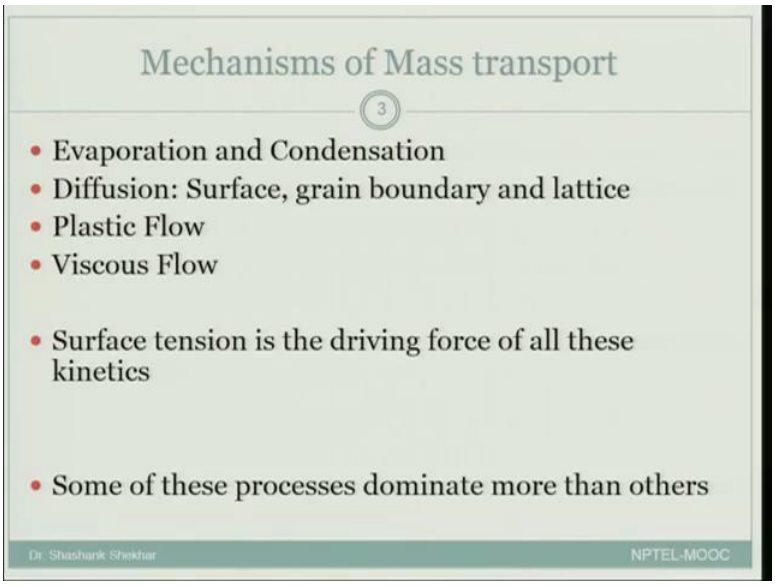

Mechanisms of Mass transport

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- Evaporation and Condensation
- Diffusion: Surface, grain boundary and lattice
- Plastic Flow
- Viscous Flow
- Surface tension is the driving force of all these kinetics
- Some of these processes dominate more than others

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So what is sintering, sintering actually this coalescence of particles and densification is not a necessary requirement, densification may or may not occur. So sintering does not always mean that we are talking about densification, although in the plots that you see, there is the density plot versus time and there you see that sintering is, the densification is occurring when sintering proceeds. But densification is not a necessary requirement, it depends on the configuration and condition. We will see, for example if you have 2 particles and they are in very close contact to each other, now the mask and flow and get deposited over here.

But the centre of gravity of the 2 particular particles, they may remain constant and they may not change, in that case densification is not occurring. And the overall shape of the particle has changed because of the sintering process but the particle centre to centre distance has not reduced. So we will say that densification has not occurred. On the other hand if masses, or the mass moves from the inside of the material to the neck region and finally it reduces the Centre to centre distance, then we will say densification has also occurred.

So sintering, when we say what is sintering, remember sintering is coalescence of particles, densification may or may not occur, effectively it is the joining of particles. There are 2 main classes of sintering, one is liquid phase sintering meaning where one phase is liquid or in amorphous phase and the 2nd is a solid-state sintering. Here both all the phases, not both actually, you can have only single particulates or you can have more than one kind of particulates. Whatever it is, it should be in crystalline or polycrystalline phases.

For example, take an example of mercury droplets. In the thermometers, old thermometers, we used to have Mercury and if sometimes you have broken it, you would have played around with it. So that you remember, if you have couple of droplets, you bring them close together and they suddenly squeeze and form one big drop it. So what was the driving force, think about it, why would they want to coalesce? Was it magnetic or some other force that was driving them together? And does this coalescence implies densification.

So in this case would you say it is densifying, so again you have to look at the centre to centre distance between the 2 original particulates and see the centre, average centre to centre distance has been reduced. If not, then there is no densification, if it has reduced, then densification has occurred along with coalescence. Why do, why does this coalescence take place? The main driving force is surface tension. For example even one droplet you have, how is it able to hold onto it, just member a dropper and you allow one liquid droplet to come out of it.

How it hangs to it, as long as it is not very large in size, if you have droplet, hanging from a dropper, that one piece of droplet will keep Hanging, why is that happening, that is because there is surface tension, something called a surface tension. So what is surface tension? We will look at it in a moment. But that is the driving principle. That ensures that there is or that is what causes the densification of the material. Now that we know what is the driving force, what about the underlying mechanism?

You remember that thermodynamics is one aspect but that does not ensure that the, that something will actually take place because there also has to be some mechanism from kinetics. So what is the mechanics, mechanism, what is the kinetics behind this. That is something we that we need to understand. Now let us look at the 2nd slide which is mechanism of mass transport.

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So here we discuss what are some of the possible mechanisms by which this mass transportation takes place and because of this sintering takes place. One of the most important ones is evaporation and condensation. So in all these examples, just remember you have 2 particles and this is something like this. In fact let me draw it to be, for you to be able to visualize, although we will have, we will see a lot of these diagrams later on. But when we are talking about sintering, it is good to have this in mind.

We have, in general will start with sintering of 2 particulates and this is the same principle that will get extended when you have more than one, more than 2 particulates. So let us say somewhere over here, when you want to coalesce, what is happening is that somewhere these

2 particles should combine and become one. This can happen by particulates or, sorry the material, mass flow taking place by a evaporation and condensation. So evaporation and condensation, something from here will evaporate and where it should get condensed, we want to, we want to coalesce the 2 particles.

So there should be growth in the neck or basically the neck should disappear and therefore it will get deposited over here. And similarly for other mechanisms another kinetics that we will discuss over here, for example diffusion… You know that several kinds of diffusion or basically several parts to diffusion exist. And in the case of particulates, the important ones are surface, grain boundary and lattice. 1st diffusion can take place through surface, it can take place through grain boundary and it can take place through lattice.

All of them in the end should somehow or would in fact somehow can allow the mass transport to move from one particular it to basically the neck region. Once the material gets deposited in the neck region and this process goes on, slowly there will be no neck and in the end you would not be able to see even if there was, just, there were 2 different particles. You would see almost one particulates, unless there is a grain boundary getting formed over there.

Then there is plastic flow, again there is surface tension, it can cause compressive stresses. So there are again these 2 particles you see over here and they remain, and because of the diameter that exists over here and over here, there may be compressive stresses generated and whenever there is compressive stress generated, you can imagine there will be some deformation, only the deformation or the stresses are very high of course.

But let us say the stresses are high enough, so when the stresses are high enough, it can cause plastic deformation at some level and those plastic deformation will cause plastic flow or the material to again the neck region. Similarly there can be viscous flow, because of high-temperature the material will act like a viscous liquid and so material will flow away to the neck region. And the 2 particles will lose their individual identity and become one particle.

In all these you can say, surface tension is the driving force for all these kinetics. However which particular process dominates depends upon the configuration and the particular process or the material that you are looking at or the particular temperature. So not only the material, process parameters, all those things will make a difference and determine which of these mechanisms will actually dominate. However these are the main mechanisms for mass transport, so the overall idea is the mass should get transported.

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Surface tension as driving force

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- Surface Tension is a force per unit length of line in the surface acting normal to the line
- Surface tension leads to compressive forces and hence plastic flow
- ST leads to partial pressure difference and hence evaporation-condensation
- ST leads to lattice/ boundary diffusion

- These mass transport mechanisms lead to the formation of neck and its growth
- Small amount of vapor condensing in neck removes a large amount of surface area
- Sintering ≡ Neck growth occurs, whether or not densification (particle center-to-center approach) occurs, depending on mass transport path
  - For densification to occur, mass must move from between particle centers to the neck region

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However, let me emphasise, that if the mass, if this is your centre of the 2 particles. Now if this centre distance, centre to centre distance, remains constant. So let us say I make up in the end I get something like this, let me use a different chalk over here. So mass has moved from over here to here. But the centre of gravity of the 2, of the 2 particles remains same. So in this case coalescence has taken place, it is no more 2 different particles but the densification has not occurred.

On the other hand, let us say it becomes something like this. So you can say somewhere over here and there may be small amount of grooving that we will discuss, so the centre to centre distance in the 2nd case has reduced and so you can say that densification has also occurred in this particular case. So we see that surface tension can be described as the driving force for most of these phenomena. We will look at some of these particular mechanisms and see what exactly is happening at the particle level.

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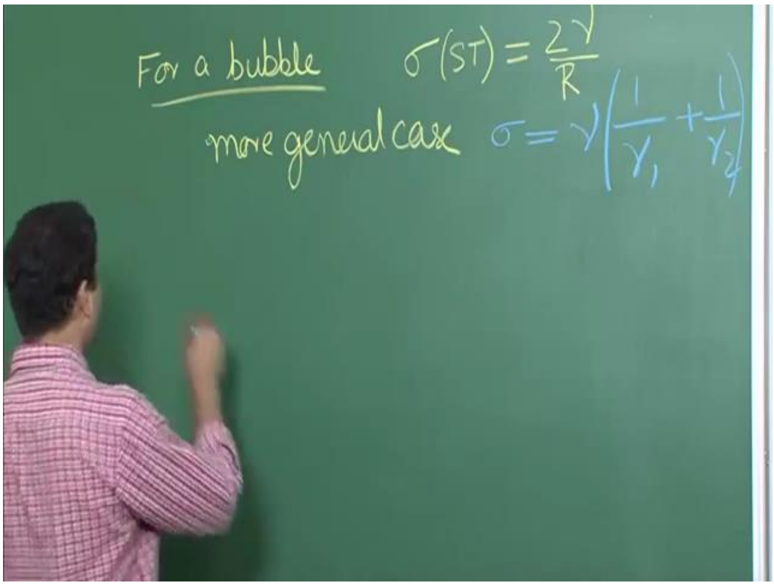

So for example, surface tension is a force per unit length, we know for a droplet, we can imagine what will be, we have the equation of what is a surface tension for a small droplet. And from there we will see that they can also derive relation for the surface tension that leads to compressive forces and hence a plastic flow. So let us get down to some equations over here. So we will start with what is the surface tension for a simple, for a bubble. For a bubble, we know the surface tension denoted by Sigma is given by 2 gamma by R. Where R is the radius and gamma is the surface energy.

Now, we are not talking about the simple bubble but a complex surface where 2 different diameters exist. In a bubble, the 2 diameters, the perpendicular diameters are equal and therefore you get a much more simpler equation. But if you have a complex surface like the neck over there, then there are 2 different diameters and then for a more general case, we have and what are these R1 and R2, these are 2 perpendicular radius for that particular point where you are trying to find the surface tension.

Over there you will find radius of curvature in 2 perpendicular directions and that will define the surface tension like this. So in a much more, in a more complex shape you can have only 2 different radius in 2 perpendicular directions and here this is how you will get. Again, gamma is a surface energy, R1 and R2 are the 2 radii. Now we will again go back to our particulates, so there, let us say, let me rewrite over here for sake of completion.

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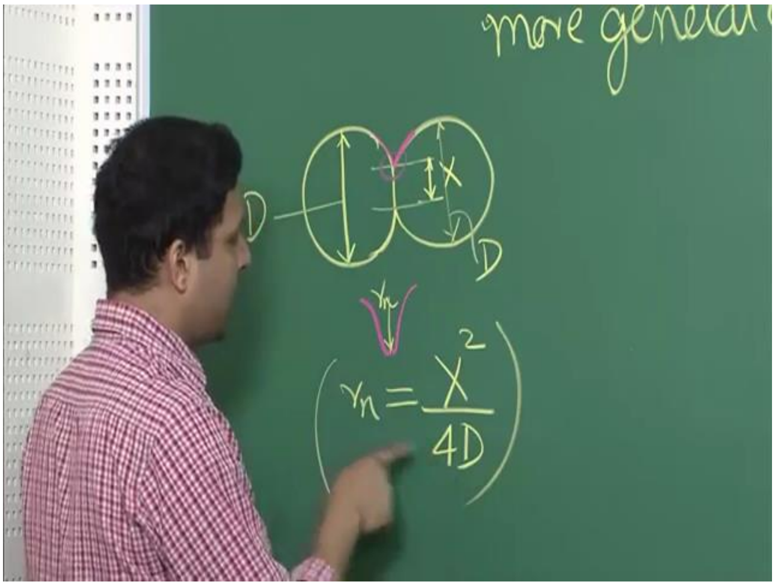

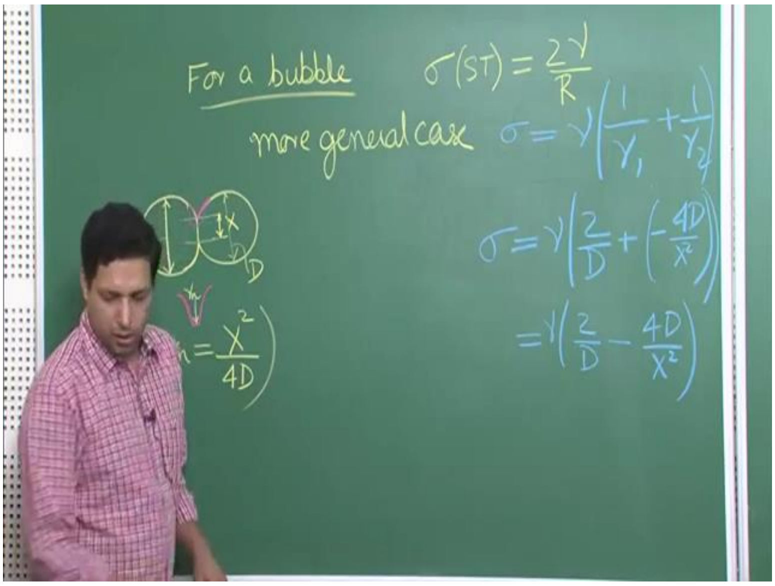

So let us say, this is something like this, what has happened and this is the neck that is already formed. So let us say this is the distance X after the neck has formed initially instead of radius, here just the way the convention is followed, I will follow the same conventions. And let us say this is the diameter, and we are assuming similar diameter for the 2 particles. So this is the 2 diameters, D, this is the X and if we are looking at this region, there is a radius of curvature in this small area also.

So we are looking at the very neck region, at the very point where neck is formed. There is a small radius over there. So it will look, in fact if you were to look at it. And it has been found that this radius, radius neck, let us say RN, R subscript N, so R subscript N is usually given by X square by 4 D. Meaning, larger your particle size, smaller is this neck radius. Larger is the X, smaller is the radius. So this basically X also represents the growth of neck.

If it is large, meaning your particles have coalesced much, to much larger extent and therefore radius of curvature will be much smaller, the radius of curvature over here. Now let us put that over here and what is the Sigma that you will get. Okay, so here, what we will have to do, you see this radius is convex in shape and this radius is concave in shape. And that would be, in that we will have to put a different sign for this. Although we are putting a + sign, so here we will get a - 4 D by X square is equal to gamma times 2 over D - 4 D by X square.

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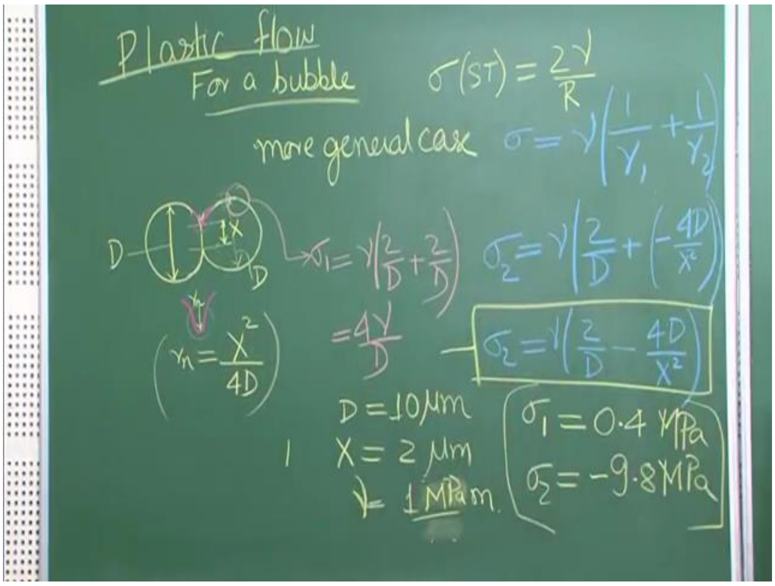

In comparison, let us see what will be the, what will be the surface tension at some other point far away from the neck, over here. So let me call this Sigma 1 and let me call this Sigma 2. So over here, let us see what will be the question for Sigma 1 which will, it will be equal to, our same old equation but with R1 equal to D by 2. So this becomes gamma 2 by D +2 by D because we are looking at this particular region where both diameters, perpendicular diameters are, radius are basically the radius of the particle. So this will be like this.

Which will be 4 gamma by D. Now at this point, let us take some typical values, so let us say we have particle size D equal to 10, let us say 10 micrometre and neck dia or basically X, let us say X is equal to 2 micrometre. So we are saying this is 2 micrometre and this diameter is 10 micrometre and gamma, let us take gamma equal to some, what value should we take? Let it be some 1 mega Pascals. So it will be per metre because surface tension is per unit length.

So this will be, not mega Pascal, it will be mega Newton per metre. So when you Divide it by, so this surface, there is a surface energy divided by D, will get the surface tension. So let us say we have over here, mega, mega Pascals times meter actually. So this will be 1 mega Pascal times meter, that is our surface energy. If you put these values, what is Sigma 1 and Sigma 2 you will get. You will get Sigma 1 of the order of and Sigma 2 of the order of - 9.8 mega Pascal.

Why, why do we, why are we trying to do these calculations, it becomes clear when you look at the relation or relative values. What is the Sigma 1 value, it is a comparatively very small number, 0.4 mega Pascal. What is the Sigma 2 value? This has 2 things, one, it has magnitude very large and it is negative. So there is a compressive stress that is going on over here. So in this particular neck region, you would see some compressive stresses. And that compressive stress is very large.

And the magnitude as you see is large, that would mean that there will be large plastic flow. So what we will get over here is what we were trying to, we wanted to derive for this kinetics which is plastic flow. So this is what we wanted to emphasise that because of the surface tension, you will have plastic flow and therefore material will flow from near the neck region into this region. And another thing is that there is a big gradient from here to here, sorry, it is this gradient that is driving the material from over here into the neck region. Now if you had X equal to, X much larger, let us say if you increase X 2 times then radius, the radius of curvature will increase 4 times.

Which would mean that this value would become much smaller. If this becomes much smaller, that would mean that you will have less compressive stresses. So again what it is saying that as your neck grows, the driving force decreases, the total amount of compressive stress, that is acting or the total gradient, this is gradient that exist over here will reduce as the, as the neck grows. So that is one thing that we understand from this. 2nd is, when we have particle size which is smaller, so for a small particle size, the compressive stresses will be much larger for larger, for larger particle size, compressive stress will be smaller.

So again you cannot in that from this relation. So we have 2 things, like I said, one that once that for larger particle says, you have smaller compressive stresses and 2nd that when the neck is smaller in size, you have larger growth. So these are the 2 things that we are able to understand from this particular equation. So this is one of the mechanisms for plastic, for the particle coalescence or the mechanism of sintering. Then next look at, still another process, this time we will look at evaporation-condensation.

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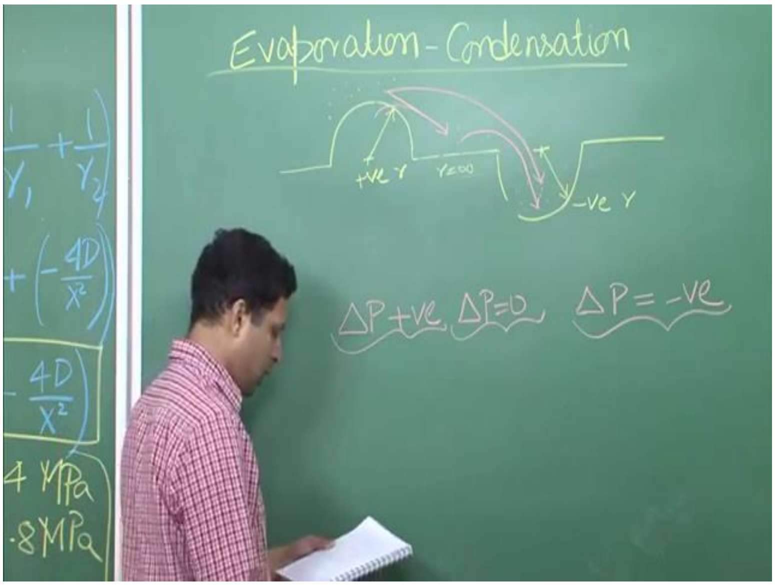

So evaporation condensation is what, when the material is getting evaporated from one region and getting condensed into another region. So let me draw a simple, basically what I am trying to show over here, how the radius curvature difference will lead to evaporation at one region and condensation at other region. So we have to draw a typical plot where we have R is equal to positive, so this is positive radius of curvature, R is equal to infinity and over here we have negative radius of curvature.

So let me write it as positive radius of curvature. So what, what is their implication, now when you have R greater than 0 then Sigma is also actually proportional to radius. And with that we can say that Delta Sigma will also be positive. In fact we do not even need to look at the Delta Sigma, we can look at the more, much better term which is Delta P over here which is a portal to Sigma and Sigma is, sorry this will be having proportionality sign. So this is your Sigma is proportional to radius and Delta P is proportional to Sigma, therefore if your radius is positive, Delta P will be positive.

Over here, we have Delta P equal to 0, Delta P is negative over here. We are looking at Delta P with respect to a flat region. So basically when we say Delta P is positive, what we mean is the partial pressure, if you look at the particles over here, they will have a higher partial pressure with respect to what you have in this flat region and compared to much, even higher compared to this negative radius of curvature.

So there is a much higher partial pressure over here, there is almost, because we are comparing it with the flat region, so here with respect to that region, this Delta P is equal to 0 and with respect to the flat region, in the negative radius of curvature you have negative or the Delta P is negative. So Delta P is lower than what you will see over here. So this is, we are comparing that Delta P which is the partial pressure with respect to the flat plate. And from here what we see, that if Delta P is positive, it means the amount of that particular particle is very large in a region just over this.

In fact we can forget about this region, we can just at this point, it will be better, if we just look at Delta P, how the P varies with the radius. So Delta P is positive, then you have positive radius, Delta P is 0 because we are comparing with the flat region and Delta P is negative when you have a negative radius of curvature. What would that mean? That would mean that the material will have a tendency to flow from or when it evaporates from over here, so let me draw it from over here. It will also be have a tendency to evaporate over here and then condense over there.

Evaporates over here and then condense over here, similarly this is still negative compared to this, therefore again the particles will have tendency to flow or evaporate from this region and then condense over this region. So this is the driving force behind, behind your evaporation condensation and as you can see that Delta P is what is driving this and Delta P is again related to the radius of curvature. So we have positive radius of curvature, we have positive Delta P, that is higher partial pressure, here somewhat lower partial pressure and here even lower partial pressure. And therefore you get this evaporation condensation mechanism that we see over here.

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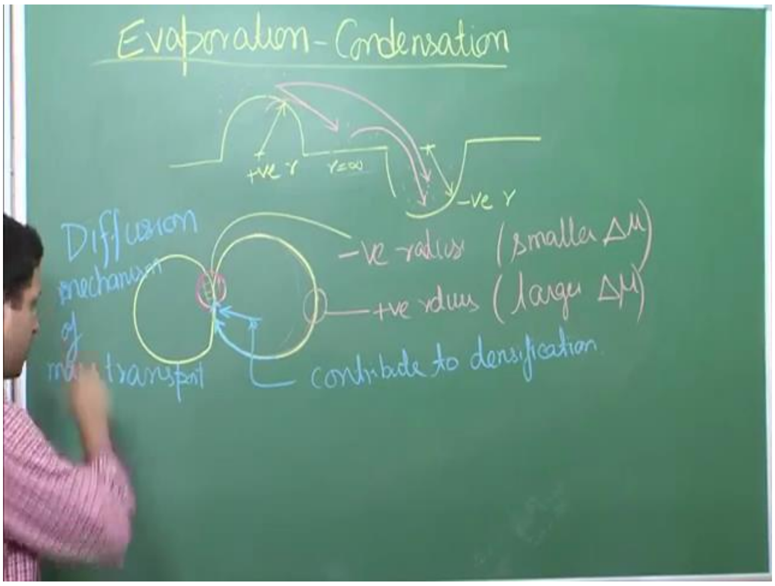

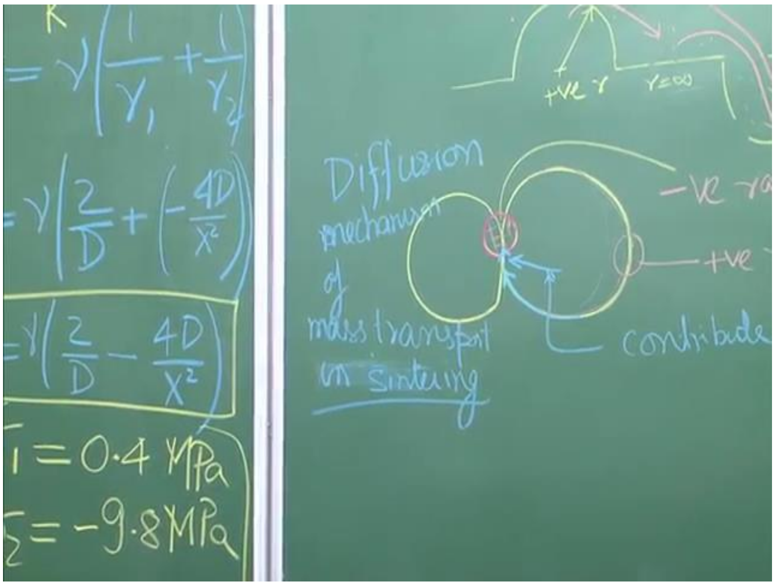

Now similar argument can be applied, when we are looking at the diffusion process. So here, again we have negative radius of curvature, so you have smaller Delta mu compared to this region, here you have positive radius of curvature. The Delta mu is nothing but chemical potential. So the chemical potential is higher over here, in this region and lower in this particular region.

From diffusion, we know what will happen, from diffusion we know that material will have the tendency to flow or to use a more appropriate word, to diffuse from this region, all this region where you have a higher positive, higher chemical potential flow into this region of smaller or lower chemical potential. So this is the region where it will come and move towards this region. And this diffusion can be of different types, it can be through the surface, it can move through the grain boundaries, I can move through the lattice.

So there are several kinds of diffusion that can take place and the one where you have lattice of diffusion taking place, particularly from the Centre or from the inside of the mass into the neck region, this is the one that will contribute most to the densification. So this one is diffusion or, diffusion mechanism of mass transport. And you know that this will be temperature dependent at higher temperature, it will be faster. Diffusion mechanism, mass transport, sintering.

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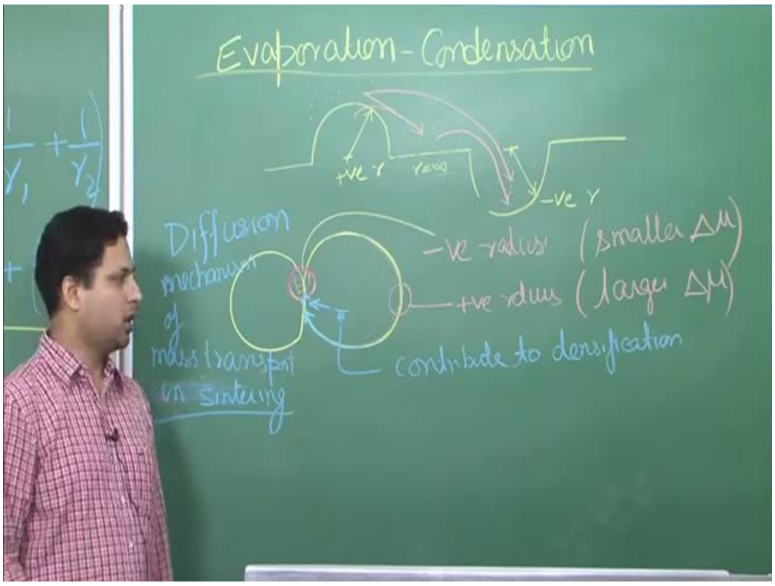

So we have seen 3 different mechanisms, one is the plastic flow, 2nd is the evaporation condensation and 3rd is the diffusion mechanism of passport in sintering. And we see that all of them will contribute to coalescence of the particle by mass transport of material from other regions into the neck region. However densification is limited to only certain particular cases and that will depend from configuration to configuration, one, in one particular case we know for example when diffusion is taking place from lattice into the, from inside the powder particles to the neck, at that point, in that particular case will get lattice diffusion, in that particular case we will get densification.

So we should not confuse that whenever sintering is taking place, densification will also take place. Densification and sintering maybe independent. However when we are looking at much larger picture, where you have a whole, a large, a lot of particles, then over there, no matter what kind of diffusion is taking, or no matter what mechanism is taking place. Just because some pore regions in between are getting disappeared, the material will have the tendency to shrink. And so overall you will always get out of densification, no matter what is the mode of mechanism of sintering.

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Surface tension as driving force

- Surface Tension is a force per unit length of line in the surface acting normal to the line
- Surface tension leads to compressive forces and hence plastic flow
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- ST leads to lattice/ boundary diffusion

- These mass transport mechanisms lead to the formation of neck and its growth
- Small amount of vapor condensing in neck removes a large amount of surface area
- Sintering ≡ Neck growth occurs, whether or not densification (particle center-to-center approach) occurs, depending on mass transport path
  - For densification to occur, mass must move from between particle centers to the neck region

So what we saw, let us get back to our slides. So what we saw that these mass transport mechanisms lead to the formation of neck and its growth. We also so that small amount of vapour condensing or in fact any other mechanism where a small amount of neck is removed a large amount of surface area, when you just increase the neck size my small amount, so initially we have just one point contact. And then you have some, little bit additional amount of material over there.

So the neck size is increased by just a small amount. At the surface area decreases by large, very large fraction. So that means that initially you will have a much higher rate of sintering. Sintering is equal to neck growth, when the neck growth occurs, it is sintering, whether or not densification occurred. And what is densification, it is particle centre to centre approach. However we and I am also seeing in the overall big picture, when we, when you look at much larger number of particles, you will always, the sintering will always accompany with some amount of densification.

You will know when we look from the definition of centre to centre approach, there may not be densification. For densification to occur, mass must move from between particle centres to the neck region which is what we saw when we have lattice diffusion taking place. Here are some more information about sintering rate, we said, the particle size will make a difference, we also said that at, what a, what stage you are, it will also make a difference on what is the sintering rate.

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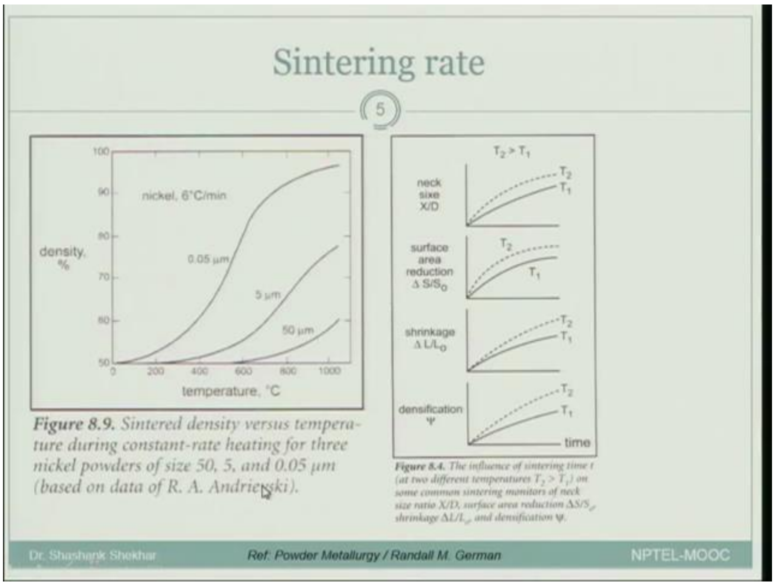

Sintering rate

Figure 8.9. *Sintered density versus temperature during constant-rate heating for three nickel powders of size 50, 5, and 0.05 µm (based on data of R. A. Andrievski).*

Figure 8.4. *The influence of sintering time t (at two different temperatures $T_2 > T_1$) on some common sintering monitors of neck size ratio X/D, surface area reduction $\Delta S/S_0$, shrinkage $\Delta L/L_0$, and densification Ψ.*

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Ref: Powder Metallurgy / Randall M. German

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So here we see one plot that describes this. On the Y axis, you have density and again we see that whenever we are talking about sintering rate, you would see that in the end we talk about density. So densification is taking place at the broad, at the macro scale. Only when we look at the definition of particle to particle distance, then we differentiate that all the sintering, all different kinds of mechanism of sintering will not lead to densification. But when we are looking at the big picture, when we are looking at the whole compact, then whenever you are doing sintering, there will be densification occurring and that is why on the y-axis you see over here we have density, percentage density and on the X axis we have temperature.

So in this particular case, nickel particulates were needed at a rate of 6 degree Celsius per minute and 3 different sizes of nickel were taken 0.05 microns, that is 50 nanometres, 5 micrometre and 50 micrometre. So what you see at very low temperature, 50 nanometre nickel particulates start to densify. And it reaches very close to 100 percent, in fact by the time it reaches 800. On the other hand if you keep increasing the particle size, this amount of growth, the one that the growth takes place at a later temperature, something like here in the 5 micrometre, it is starting somewhere at 400 or 350.

And by the time it reaches 800 degrees Celsius, it is only 65 percent densified. And for 50 micrometre region, it has not even started by temperature of 600 and at 800, it is just 55 percent densification close to 55 percent densification. So when the particle size changes, densification starts earlier and it gets to completion into a much larger saturation value. Another thing you see over here is that initial, at the initial stage, if we call this the initial stage, there densification or the rate of change of density with temperature is much larger.

And with time, it becomes, it decreases. Again that is related to neck growth. Here initial neck must have formed, most of the particles have initial necks, so the neck radius is very small and therefore we see a much larger growth. And at the neck size becomes larger and larger, then growth rate or the sintering rate reduces. So particle size makes a difference, what is the stage at which you are looking at, that makes a difference, temperature makes a difference. And of course what is the material that will also make a difference.

Here the same thing is explained in schematic. So here is the next size, X over D, remember X is the size of the neck, X is equal to 0, it means just a particle, the particles are in point contact, D is the diameter. And on the X axis you have the time. So this for 2 different temperature, it is shown how the X over D is changing. So for lower temperature you have lower X by D, for higher temperature you get higher X by D. That is one thing, again but what you see is that initial time period, the rate of change of X by D is large and with time it gets saturated.

So again our concept that this rate is higher at initial stages is still holds true. Surface area reduction, so now that was the most important driving force, surface area reduction. So that is also shown here on the Y axis, Delta S by S0, so this is the amount of surface area that has changed and this is the initial, the surface area and again it is shown with time. So at higher temperature, it will reduce faster and reach to a much larger saturation value, at low temperature it will, it will reduce at a lower rate at which a lower saturation value and again we see that initial rate is higher than during the later stages.

This is shrinkage, so this is the more you can say appropriate or more easily measurable quantity when it comes to densification, the overall shrinkage between 2 particulates Delta L by L0 and again we see similar kind of behaviour and the final overall densification if you will measure the density and then again measure it with as a function of time, this is the kind of plot that we will see.

So overall that we have seen, that sintering rate depends on particle size, smaller the particle size, higher the sintering rate, it depends on what stage you are, initial rate is much higher, it depends upon the temperature, higher the temperature, higher is the sintering rate, even in the initial stage and you reach a much larger saturation values. So sintering is faster during initial stages when the curvature is very large.

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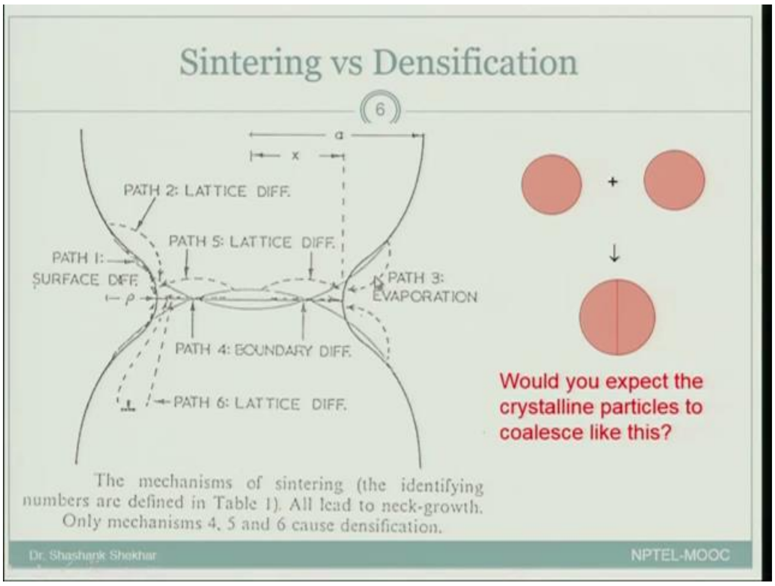

Sintering vs Densification

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The mechanisms of sintering (the identifying numbers are defined in Table 1). All lead to neck-growth. Only mechanisms 4, 5 and 6 cause densification.

Would you expect the crystalline particles to coalesce like this?

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Now again to reemphasise the point about sintering versus densification, another plot is shown here. Here your show the 2 particulates, so these were the original 2 particulates, now you see there is a small amount of overlap. And why is that overlap taking place? Because the centre to centre distance has come closer and that centre to centre distance as it defines, there are some of these mechanisms shown over here. And in the caption you can see that only mechanism 4, 5 and 6 cause densification.

So you see mechanism 4 is grain boundary diffusion, so basically the particles are getting diffused into the neck region by grain boundary mechanism, in part 5 lattice diffusion which is from over here from somewhere over the centre, the material is going to the neck region and in part 6, you have lattice diffusion which is from the Centre to somewhere under the neck region, the material is flowing. So some of these methods, like I said will lead to densification and again we have, this densification we are talking about is centre to centre distance.

Now having talked about sintering and densification, let us say we sinter these 2 particles, so we started with this. So do you think after completion of sintering, will it look like this? This is how it should look like, that is you have the 2 particles now completely coalesced and there is a boundary between these 2. Is that the right concept? Well, let us look at it, we will look at the equation to be able to, not the equation but just a simple schematic to understand if this is the right process, right figure to represent 2 coalesced images, sorry the 2 coalesced particulates.

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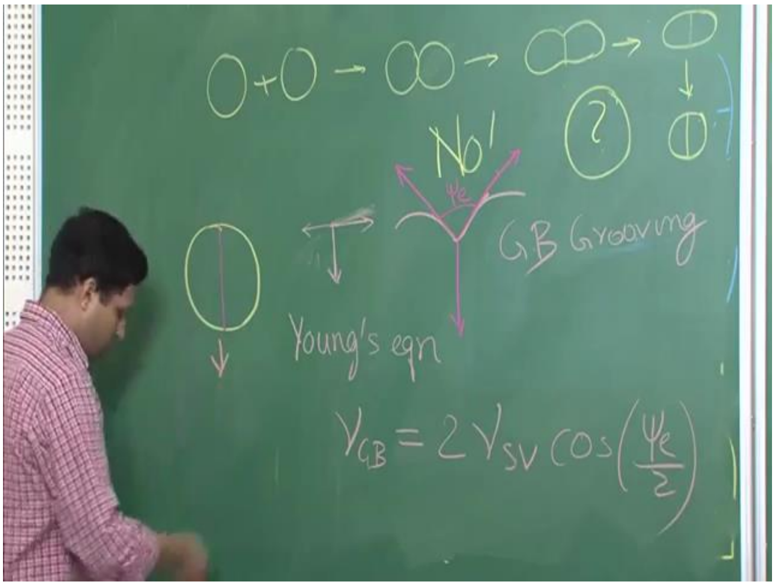

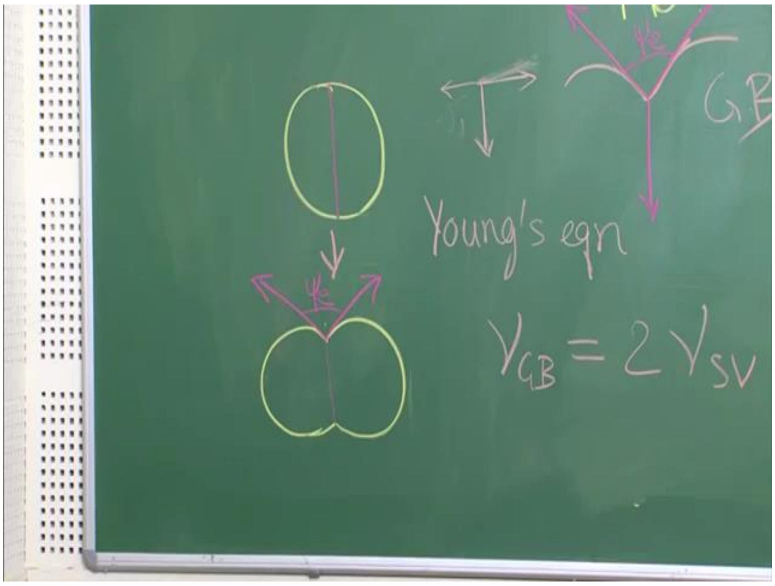

So what we are saying is, we started with like this. So if this, the question is, is this a right representation, or this the right final stage for the 2 particulates. The answer is no. Why? We will see in a moment. Let us say we have something like this. And let me use…, So there is an interface over here which has energy and there are 2 interfaces over here which also have energy. So we can say that there will be energy, there has to be energy balance over here. Now you see, if this was the configuration, these 2 would have been like this. And therefore this energy is not getting balanced.

Which would only happen if there was low energy in this but that was not true, there is some energy associated with grain boundary and therefore the actual surface must have a shape like this. And therefore if we, so let us call this angle Psi E. And this is what is called as grooving, grain boundary grooving. So if you heat, whenever we have polyester sample, the grain boundaries are always exactly perpendicular to the surface. That if you allow or heat the sample little bit, the grooving is bound to occur, because the grain boundary energy must be balanced through the other 2 surface energy.

And therefore the Young’s equation you can write, you can even find out what is the grain boundary energy flow the surface volume energy of these 2, the surface, surface to volume. So this can be written as gamma SV cos, so gamma GB can be given in terms of gamma S V and you can measure Psi E experimentally. Or in other words, if you know grain boundary energy, you can calculate gamma S V and if you know Psi value which you can measure easily.

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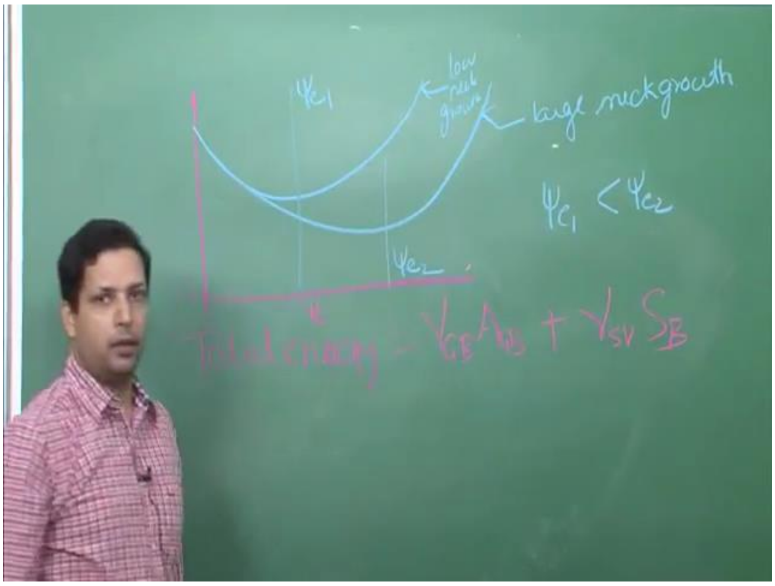

So this is, so this is the Psi angle and that would mean that the final shape should look like, something like this. Here we are sintering 2 particles, remember we are talking about only 2 particles. And therefore and there will be an equilibrium Psi E. So no matter how long you sinter, this shape will be the final shape, it will not change beyond this if there were only 2 particles. And that means that if we have to, so if we were to look at the total energy, we can write, we can write like this. Gamma GB times area GB, for the 2 particulates we are talking about, gamma SV times surface of the particulates.

So this is the total area of grain boundary and this is the energy, grain body energy per unit area. So this is the total energy, similarly this is a surface volume per unit area and this is the area of the surface. So this will be the total energy and if you were to plot this with Psi E angle, you would get, so there will be a minima and this will be the Psi that will be, that will be your equilibrium Psi. So this is the angle at which it will get become equilibriated. In some other cases, for example if the material was different, you may get a different Psi E.

And what does this mean, so let us say this is Psi E1 and this is Psi E2, so this is Psi E1 less than Psi E2, it means that in here the neck growth is lower neck growth. And in this one, large neck growth. So this is how your plot will look like, the higher the Psi E value, higher is the neck growth. Now let us ask ourselves that, here we have taken that the 2 particles are of same size, what if one of the particles is much smaller than the other one?

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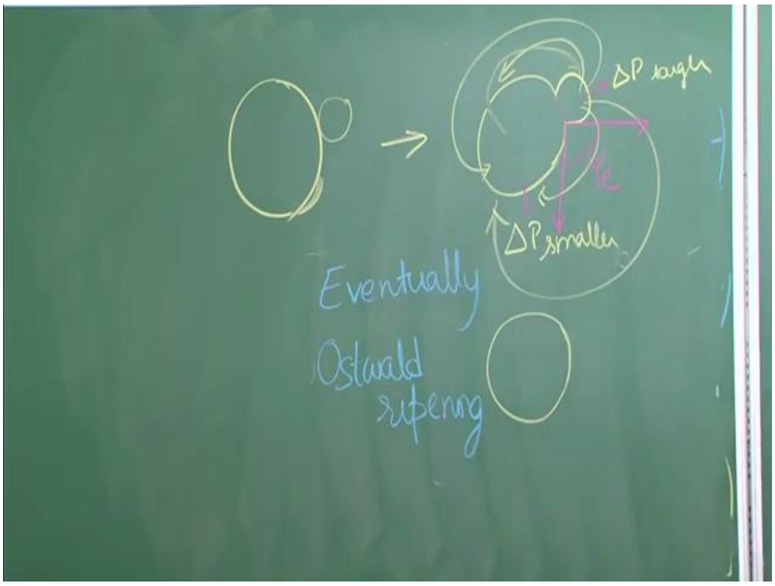

So let us say this time I have this + a small particle. Now if we follow the logic that we described earlier, we would get a Psi, I can give Psi, so this is some Psi value, the equilibrium Psi value. However now note that the particle radius is smaller over there and the particle radius is larger over here. So the vapour pressure over here is much smaller and vapour pressure is much larger over here. And therefore the particles will, sorry the material will have the tendency to condense, I am sorry the other way round actually. It is the vapour pressure is larger here, Delta P is larger and here it is smaller.

Because Delta P, when the radius becomes infinitely, Delta P is 0, so smaller the radius, Delta P is larger and therefore the particle, here will evaporate, it condense. So eventually what will happen? We will have a larger particle and this will be what we can call Ostwald’s ripening. So in sintering, you may even have particles going are basically larger grain forming from the smaller particles, from the combination of smaller and larger particles.

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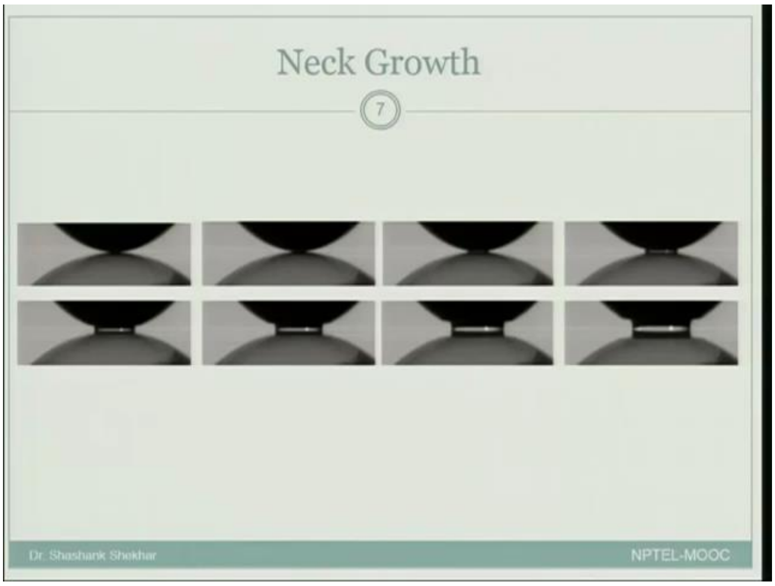

Neck Growth

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So let us move ahead and let us take a look, we have always been saying that in the neck region, just a small amount of addition of the mass will change a surface area by a large margin. Let us look at these 2 particles, these are in the liquid state, now when these 2 particles come together, you will see a very small neck has formed. So the amount of material that has gone over here is very very small. But how much has a surface area reduce?

Now the overall surface area would initially would have included the whole curvature but now just a small amount of addition has reduced the surface area in both the spheres up to this length X. So a large amount of surface area has been reduced and slowly you see initially if you were to, you were to compare it with sintering, there is a very large sintering rate over here and the neck is growing, X is growing, X is growing even further by addition of small amount of particles at the neck region.

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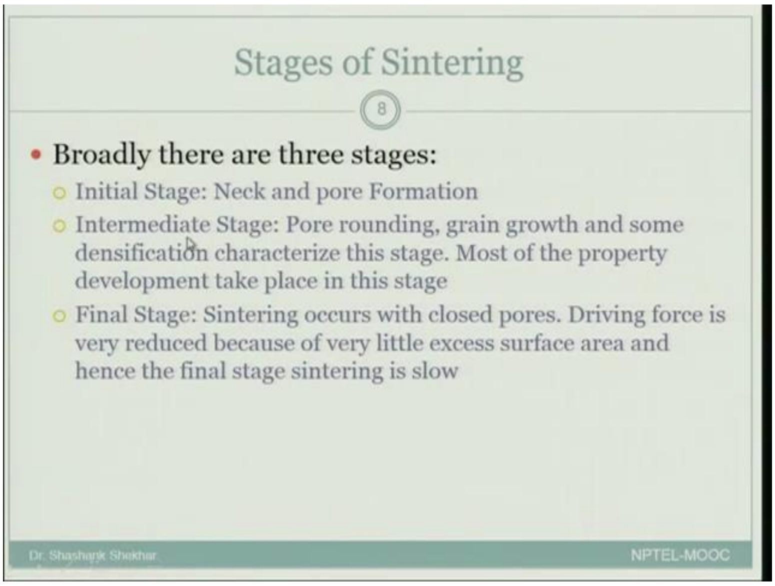

Stages of Sintering

- Broadly there are three stages:
  - Initial Stage: Neck and pore Formation
  - Intermediate Stage: Pore rounding, grain growth and some densification characterize this stage. Most of the property development take place in this stage
  - Final Stage: Sintering occurs with closed pores. Driving force is very reduced because of very little excess surface area and hence the final stage sintering is slow

And when this neck becomes large enough, and the radius of curvature reduces, then the sintering rate reduces. So that is how in general neck growth takes place. Now let us, it is time for us to take a look at stages of sintering. Broadly there are 3 stages of sintering. In the initial stage, you have neck and pore formation. So the particles will stick to each other, they will form neck and hence there will be a very large, there will be very large network of pores.

In the intermediate stage, pore rounding, grain growth and some densification take place. So you will have the pores which are now very very large and interconnected all throughout, they will become, start to round off, they will become rounded in characteristics. Most of the property development of the material takes place during this stage. And in the final stage where initially now, in the end of 2nd stage, you had network of pores, cylindrical pores joining from here to there. In the final stage, sintering occurs with closed pores. So now the, the cylindrical regions get closed and only, at the nodes you will have spherical pores remaining.

Driving force is very reduced because of very little excess surface area. And hence the final stage sintering is slow. So here the stage, the sintering becomes even slower, because the overall driving force has reduced, surface area has reduced.

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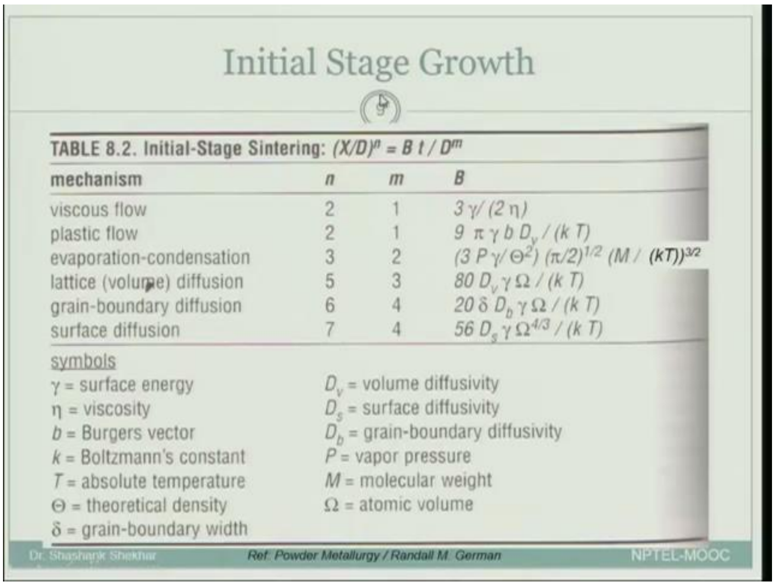

Initial Stage Growth

TABLE 8.2. Initial-Stage Sintering: $(X/D)^n = B\,t/D^m$

mechanism	n	m	B
viscous flow	2	1	$3\gamma/(2\eta)$
plastic flow	2	1	$9\pi\gamma b D_v/(kT)$
evaporation-condensation	3	2	$(3P\gamma/\Theta^2)(\pi/2)^{1/2}(M/(kT))^{3/2}$
lattice (volume) diffusion	5	3	$80 D_v \gamma \Omega/(kT)$
grain-boundary diffusion	6	4	$20\delta D_b \gamma \Omega/(kT)$
surface diffusion	7	4	$56 D_s \gamma \Omega^{4/3}/(kT)$

symbols

γ = surface energy
η = viscosity
b = Burgers vector
k = Boltzmann's constant
T = absolute temperature
Θ = theoretical density
δ = grain-boundary width
D_v = volume diffusivity
D_s = surface diffusivity
D_b = grain-boundary diffusivity
P = vapor pressure
M = molecular weight
Ω = atomic volume

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If you were to look at the equation, it will look like this. In the initial stage growth, you will have X over D, X is the neck size, D the diameter and B is some constant which carries the process parameter, it also carries some of the material characteristics and it will be given depending on what is the mechanism. So different mechanisms are described over here and for them, N, within the exponential factored over there and M which is the exponential factor over here are given.

So for different mechanisms like viscous flow, plastic flow, evaporation, condensation, lattice diffusion, grain boundary diffusion, and so on, it is given over here along with definition of these different property. Now this B itself is actually a temperature dependent parameter. So if you were to write it in terms of temperature, then will look like this.

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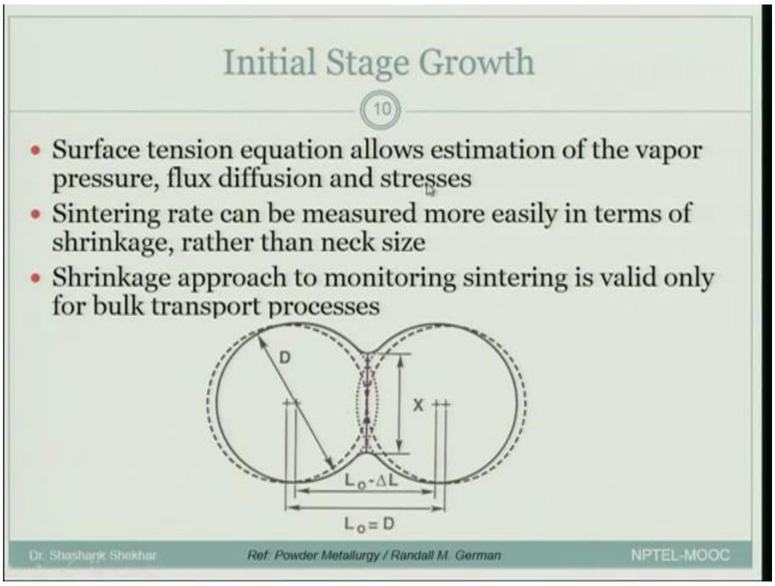
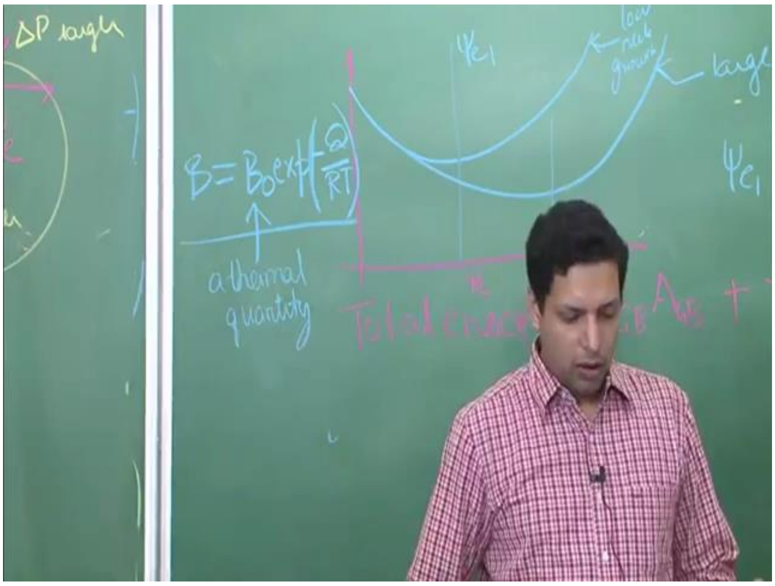


Initial Stage Growth

- Surface tension equation allows estimation of the vapor pressure, flux diffusion and stresses
- Sintering rate can be measured more easily in terms of shrinkage, rather than neck size
- Shrinkage approach to monitoring sintering is valid only for bulk transport processes



Where Q is the activation energy of the, for the process further which this diffusion is or this process is taking place, this densification is taking place. And here B0 will be your, a thermal quantity. This particular equation in general holds for values of X over D less than equal to 0.3. When the X over D value reaches 0.3, then we will say that initial stage growth has come to an end and we move onto the intermediate stage.

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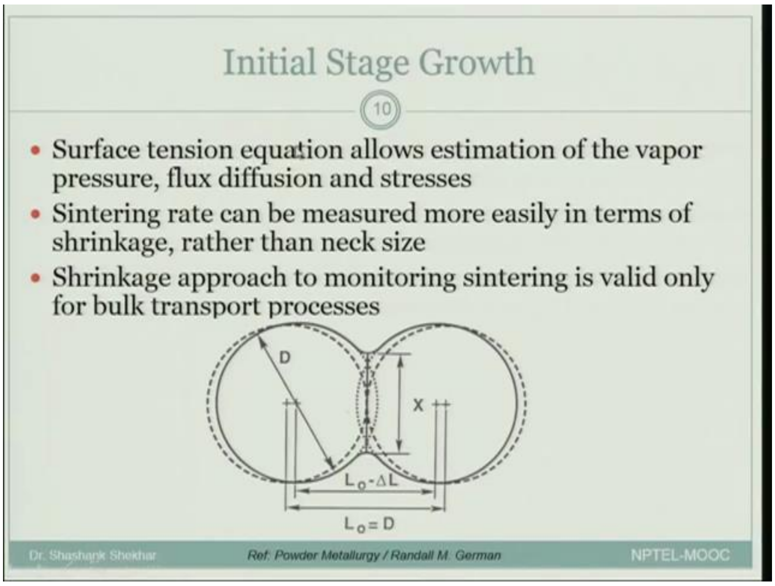

Initial Stage Growth

- Surface tension equation allows estimation of the vapor pressure, flux diffusion and stresses
- Sintering rate can be measured more easily in terms of shrinkage, rather than neck size
- Shrinkage approach to monitoring sintering is valid only for bulk transport processes

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So but before we get over there, let us look at some more facts about initial stage growth, surface tension equation allows estimation of the vapour pressure, + diffusion and stresses. You can use surface tension equation that we solved for one of the cases and estimate the vapour pressure or flux diffusion and stresses. We saw an example of calculating compressive stresses. Sintering rate can be measured more easily in terms of shrinkage rather than neck size. So neck size is a parameter which we use for densification but that is not so easy to calculate, you will have to take with the accurate micrograph, on the other hand the parameter which is the inter particle distance, that can be much more easily calculated.

For example, start with your L0 and after sintering, the centre to centre distance is L0 - Delta L. So this Delta L represents the shrinkage in terms of distance, centre to centre distance. Shrinkage approach to monitoring sintering is valid only for bulk transport processes.

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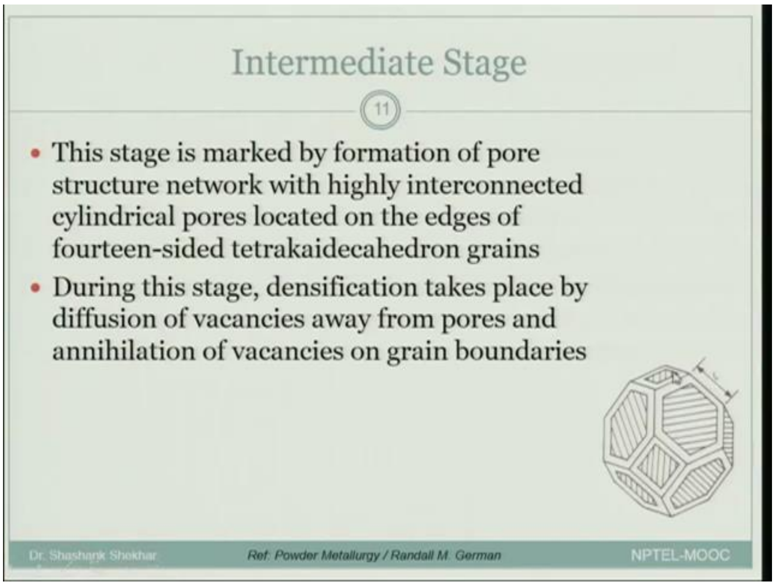

Intermediate Stage

11

- This stage is marked by formation of pore structure network with highly interconnected cylindrical pores located on the edges of fourteen-sided tetrakaidecahedron grains
- During this stage, densification takes place by diffusion of vacancies away from pores and annihilation of vacancies on grain boundaries

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Next we get to the intimate it stage and this is characterised by this kind of shape. So there are grains, this is a grain or particle which has stuck to the other particle and in between the particulates that it is attached to, there will be network of pores. So these are long cylindrical pores that are forming a network. In a much, you can say simplified way, we can say it is a 14 sided, Tetrakaihedron grain, in the much more ideal or simplified form. During this stage, densification takes place by diffusion of vacancies away from pores. So the vacancies move away from the pores and get annihilated at the grain boundaries.

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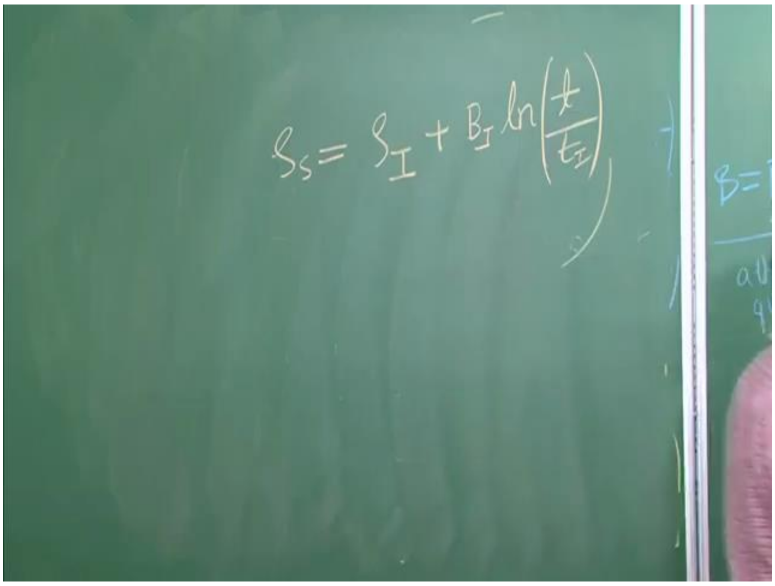

$$\rho_S = \rho_I + B_I \ln\left(\frac{t}{t_I}\right)$$

So this is what describes the intermediate stage and let me quickly write down the equation which describes this. So this is fractional density after sintering, this is fractional density at the start of intermediate stage, meaning at the end of initial stage. BI is a constant, that varies inversely with grain size and TI is again the time at the start of the intermediate stage. Meaning if you are calculating the time from the beginning, then TI is the time at which initial stage ends and intermediates stage starts.

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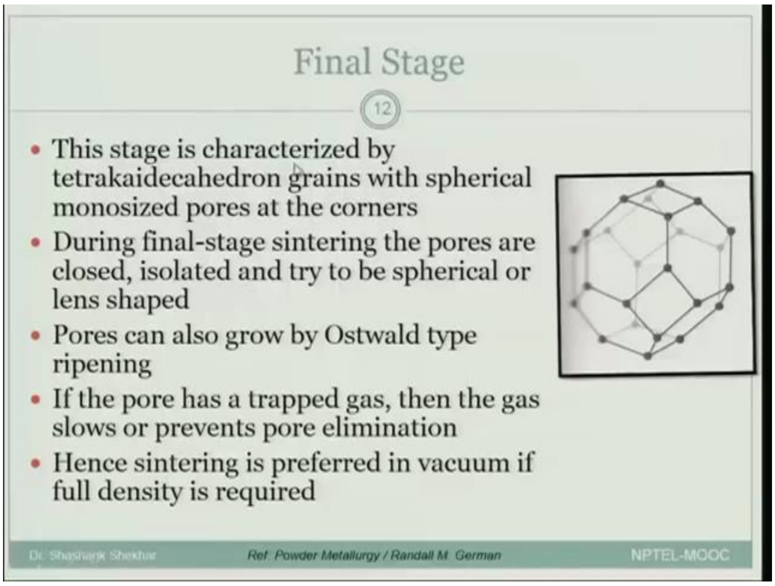

Final Stage

12

- This stage is characterized by tetrakaidecahedron grains with spherical monosized pores at the corners
- During final-stage sintering the pores are closed, isolated and try to be spherical or lens shaped
- Pores can also grow by Ostwald type ripening
- If the pore has a trapped gas, then the gas slows or prevents pore elimination
- Hence sintering is preferred in vacuum if full density is required

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So at a particular time T rho S will be given by this equation. Now let us move onto the final stage. This stage is characterised by Tetrakaihedron grains with spherical monosized pores at the corners. Now in the previous stage we had long pores are all around like a square but here those regions are have also been filled and you are only left with pores at the corner and these are not isolated pores, that is the characteristic of the final stage. In final stage sintering, the pores are close, isolated and try to be spherical.

And because of the service energy term, they will try to reduce and that will happen the best when it is spherical in shape. Pores can also grow by Ostwald’s type ripening. So like the particle ripens by Ostwald’s ripening, similarly pores can also grow. If the pores have a trap gas, now we are doing it in some atmosphere, so inside this, there is still some of the gas remaining inside it. So that gas is now trapped inside, then the gas slows or prevents pore elimination.

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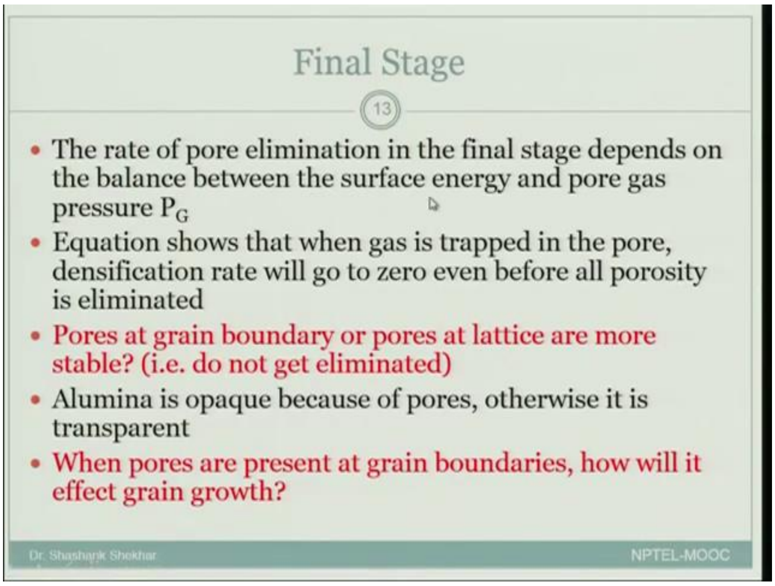

Final Stage

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- The rate of pore elimination in the final stage depends on the balance between the surface energy and pore gas pressure P_G
- Equation shows that when gas is trapped in the pore, densification rate will go to zero even before all porosity is eliminated
- Pores at grain boundary or pores at lattice are more stable? (i.e. do not get eliminated)
- Alumina is opaque because of pores, otherwise it is transparent
- When pores are present at grain boundaries, how will it effect grain growth?

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Now that gas is remaining there, it will not escape, now disclose, it is isolated, no matter how much pressure you apply, you cannot get rid of those gases. Hence sintering is preferred in vacuum. If you want to get very high-density, get rid of all the pores, then you have to do that sintering in vacuum. The rate of pore elimination in the final stage depends on the balance between surface energy and pore gas pressure PG, we will see at the equation in a moment.

So this describes that the, rate of pore elimination will depend on the balance between surface energy and pore gas pressure. Equations show that when gas is trapped in the pore, densification rate will go to 0 even before porosity is eliminated. We see that in this particular case, we will not be able to get rid of all the porosity. There is a possibility that porosity, not, not just a possibility in most of the cases, if you are doing in some atmosphere, the pores will not be removed.

Pores and grain boundaries or pores at lattice are more stable. So you have to, this is the question that you should ask yourself that which of them are more stable, which of these do not get eliminated. And high will give you an answer but you must think about it, the pores in the lattice are more stable, that is they will not get eliminated. And pore has a very strong role to play, for example in alumina, it is opaque, you seen it is very opaque, it is white coloured almost.

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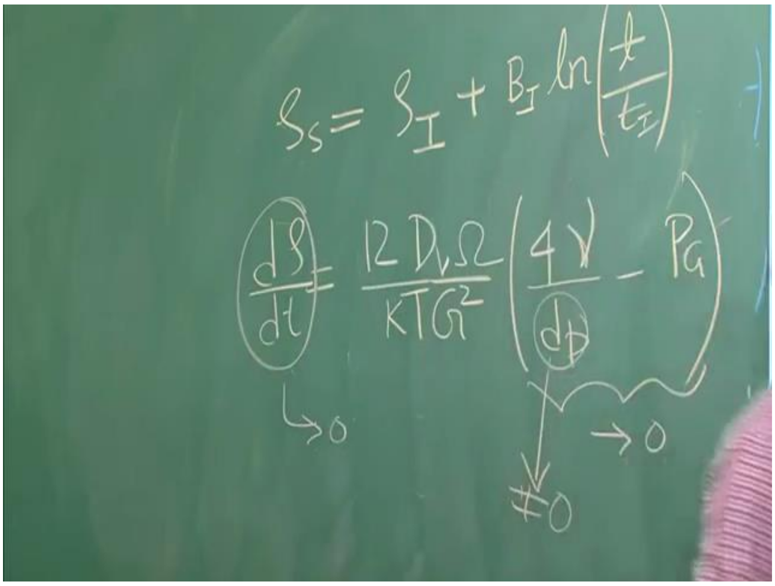
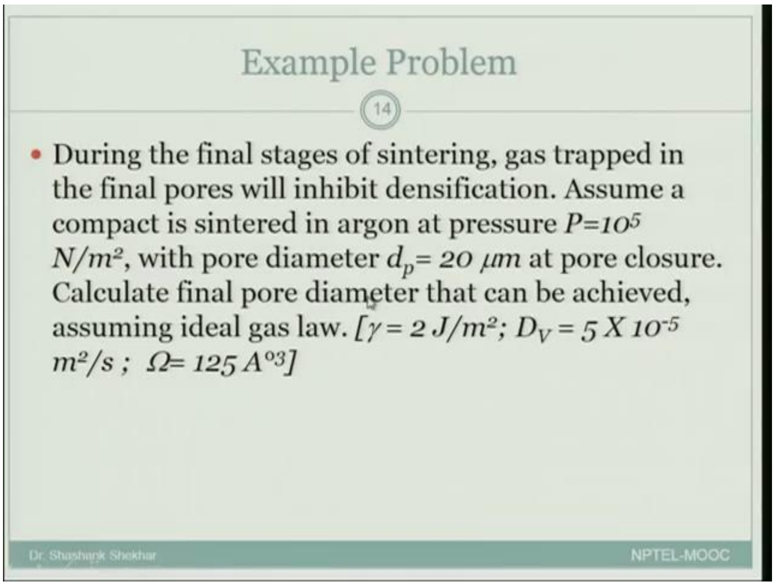


$$\rho_s = \rho_I + B_I \ln\left(\frac{t}{t_I}\right)$$

$$\frac{d\rho}{dt} = \frac{12 D_v \Omega}{KTG^2}\left(\frac{4\gamma}{d_p} - P_G\right)$$



Example Problem

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- During the final stages of sintering, gas trapped in the final pores will inhibit densification. Assume a compact is sintered in argon at pressure $P=10^5\ N/m^2$, with pore diameter $d_p= 20\ \mu m$ at pore closure. Calculate final pore diameter that can be achieved, assuming ideal gas law. $[\gamma = 2\ J/m^2;\ D_V = 5 X 10^{-5}\ m^2/s\ ;\ \Omega= 125\ A^{o3}]$

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It is mainly because of the pores, otherwise alumina, which is Al2O3, it is transparent. So let us, now that we have described the final stage, again let us describe the equation that describes this final stage. So if we were to look at d rho by DT which is the rate of change in the factual density, then it will be given by 12 DV, where DV is the volume which diffusibility, omega is the tonic volume, K is the Boltzmann constant, T is the temperature and G is the grain size times pore gamma, where gamma is the solid vapour surface energy, DP the pore radius - PG.

Now the 1st thing and the most important thing that you will see here is that if you keep increasing the pressure which is, if you are doing it in a very large high-pressure condition, sintering is being carried out at high-pressure, then PG will increase, keep increasing and at certain point, this whole quantity may reduce to 0. And what will happen, when it reduces to 0? D Rho by DT becomes 0. Meaning there will be no more change in the density shrinkage, shrinkage rate will not be, will not move any further.

And the density will remain constant at that point, although DP may not be 0. DP may not be 0, meaning the pore diameter will still be some finite value and your rate of densification may come to 0. So that is what something can happen or in particular, actually I should not say may happen, it does happen when you are doing in some atmosphere because there is a pressure and that, there is some gas that you have used and that gas gets trapped inside those pores and that, because of that there is a pressure.

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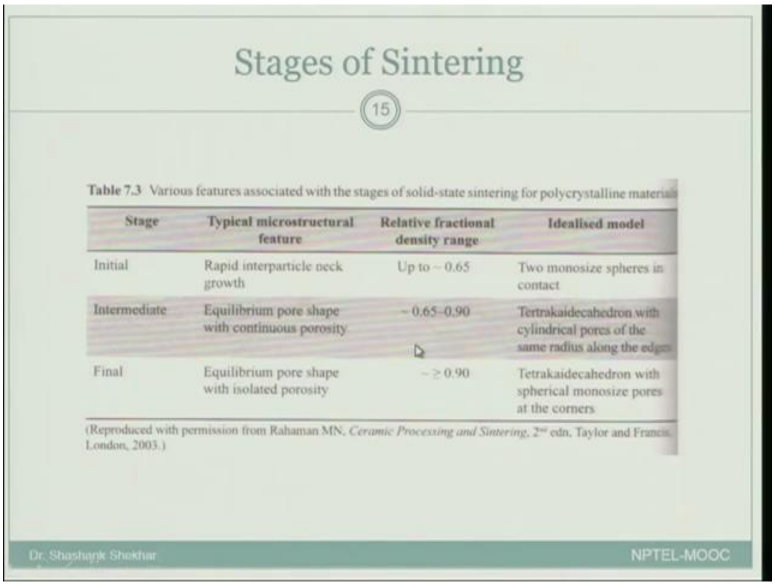

Stages of Sintering

Table 7.3 Various features associated with the stages of solid-state sintering for polycrystalline materia

Stage	Typical microstructural feature	Relative fractional density range	Idealised model
Initial	Rapid interparticle neck growth	Up to ~ 0.65	Two monosize spheres in contact
Intermediate	Equilibrium pore shape with continuous porosity	~ 0.65–0.90	Tetrakaidecahedron with cylindrical pores of the same radius along the edg
Final	Equilibrium pore shape with isolated porosity	~ ≥ 0.90	Tetrakaidecahedron with spherical monosize pores at the corners

(Reproduced with permission from Rahaman MN, *Ceramic Processing and Sintering*, 2nd edn, Taylor and Franc London, 2003.)

And the pressure and the surface energy term, they balance each other and therefore the densification, they come to 0 even before DP, which is the particle pores size, it may come down to 0. So there is an example problem you should try and we will, you can discuss it with the TS and try to solve it on your own. We will just summarise the 3 differences of sintering, initial there is rapid inter particle neck growth, relative fractal density in a reach of 0.65, 2 monosized spheres in contact, this is our idealised model.

In the intermediate equilibrium, pore shape will, with continuous porosity, so you have network of porosity and your fractional density may reach 0.65 to 0.90, the Tetrakaihedron with cylindrical pores of same radius along that is, pores are of that kind of form. In the final stage, it can be pore shape with isolated porosity are formed and you may get fractional density greater than equal to 0.90. Tetrakaihedron grains are made with spherical monosized spheres at the corner easy idealised form, idealised shape.

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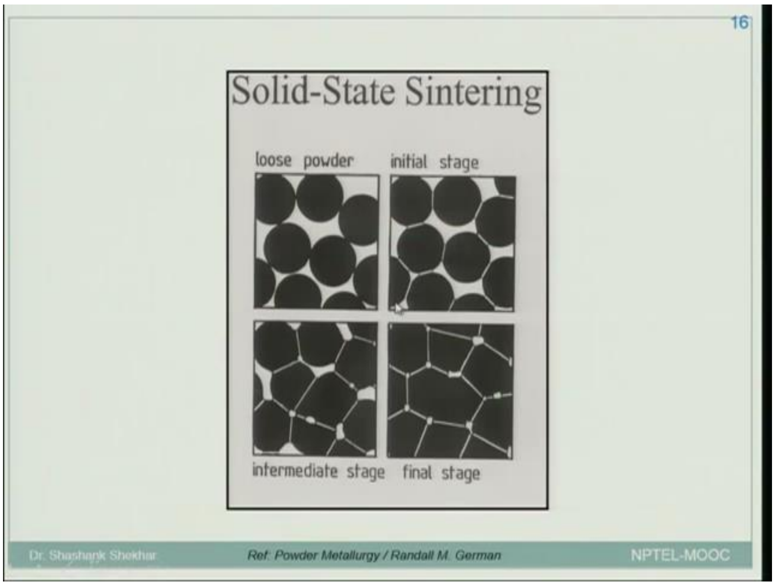

Solid-State Sintering

Ref: Powder Metallurgy / Randall M. German

So this is the schematic of what is happening in the different stages, you have loose powder, then you have initial stage where you have neck growing and in the intermediate stage you have network of pores, so these are network. And in the final stage is, these are the pores at the corner of the grains.

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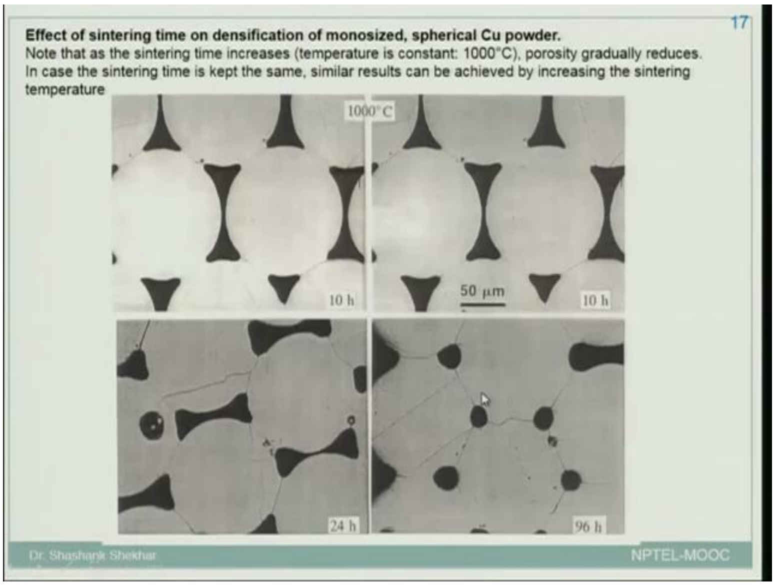

Effect of sintering time on densification of monosized, spherical Cu powder.
Note that as the sintering time increases (temperature is constant: 1000°C), porosity gradually reduces. In case the sintering time is kept the same, similar results can be achieved by increasing the sintering temperature

And these are some of the real micrographs that you see. So here you have copper spheres and here are different stages, so at particular temperature which is 1000 degrees Celsius at different times you see like this. And even at the end, you see some pores, even after 96 hours. So this is how it will look like.

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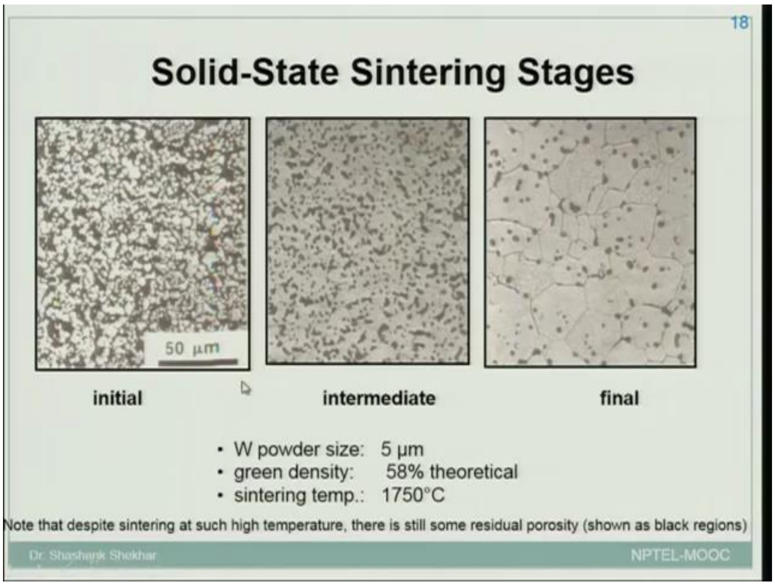

Solid-State Sintering Stages

- W powder size: 5 μm
- green density: 58% theoretical
- sintering temp.: 1750°C

Note that despite sintering at such high temperature, there is still some residual porosity (shown as black regions)

And we will, and this with slide, here again we have tungsten powder which has very very high melting point. And you see that at the, the grain density you get is 58 percent which is very low and at the end of the final stage of sintering at 7, 1750 degrees Celsius, you still get some pores. So there are still large number of pores because the sintering temperature is relatively low for tungsten which has very high melting point. And these are, these are the different stages of sintering.

So this covers the sintering concept that about the powder processing. So now we have looked at all the different stages of powder processing starting from powder characterisation to compaction, to consolidation, to compaction and finally to the sintering. So sintering like we said is the most important and vital stage and understanding sintering theory is very important. You would, if you have any doubts about this, or if you want any clarification, please do get in touch with us and you can ask questions as usual to the TS and to us and we will answer as soon, as soon as possible. So that brings us to the end of this course and hope that you have had good opportunity to learn and I wish you all the luck for your final examinations. Thank you.