

Non - Metallic Materials
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Module - 07

Processing of non- metallic materials, sintering microstructure development

Lecture - 37

Solid – State sintering and microstructure development (Continued)

Welcome to my course Non Metallic Materials. And today we are in module number 7, Processing of Non Metallic Materials, Sintering and Microstructure Development. And this is lecture number 37, Solid State sintering and microstructure development. And, I will be continuing from the last lecture wherever I ended.

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Now, we will be talking keep talking on solid state sintering, and we are in the third stage of sintering. Already I have described the initial and intermediate stage of sintering and its relative allied aspects. And we will keep continuing discussion on densification kinetics, and grain growth kinetics.

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Densification kinetics

Bulk diffusion: vacancies eliminated at grain surface

Grain boundary diffusion: vacancies are restricted to diffusing along a GB of width δ_{gb}

- **Pore elimination means:** Atoms diffuse toward the pores, vacancies are transported away from the pores to a sink such as grain boundaries, dislocations, or external surfaces of the crystal
- **Volume diffusion mechanism:** Vacancies are assumed to be eliminated at the grain surface: vacancy source pore surface of radius ρ_p and sink is spherical surface R
- **Grain boundary diffusion mechanism:** Vacancies are restricted to diffusing along a grain boundary of width δ_{gb}

So, we actually described that what happens during bulk diffusion. So, vacancies they are eliminated at the grain surface. So, the pore elimination I meant that atom diffuses towards the pore vacancies are transported away from the pores right. So, it is a counter current kind of situation.

So, vacancy when they are transported away from the pore to a sink, and this sink could be grain boundary or dislocation or external surfaces of the crystal, then we call that the pores are eliminated.

Volume diffusion mechanism, where the vacancies assumed to be eliminated at the grain surface and vacancy source pore surface of radius ρ_p , as you can see here and the sink is the spherical surface of radius R according to this drawing, this already I described in my last class. Grain boundary diffusion mechanism is also operative, vacancies they are restricted to diffusing along the grain boundary of a typical width of say δ_{gb} , this is the width of the grain boundary.

So, here the grain boundary diffusion is operative, you see vacancies are restricted to diffuse along with the grain boundary, which is having a finite width of δ_{gb} .

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Densification kinetics

Pore elimination by volume diffusion mechanism

Vacancy source is the pore surface of radius r_p (ρ_p in last slide Fig.) and sink is the spherical surface of radius R . $R \gg r_p$

$$r_p^3 - r_{p,0}^3 = - (6 \cdot D_{\text{ambi}} \cdot \gamma_{\text{sv}} \cdot V_{\text{aMX}}) / kT \cdot t$$

In tetraaidecahedra of length a_p , we have 24 vertices and each pore is shared by four polyhedra, hence P_c

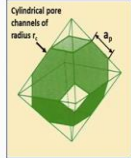
$$P_c = (8\pi r_p^3) / (8 \cdot \sqrt{2} \cdot a_p^3) = (\pi r_p^3) / (\sqrt{2} \cdot a_p^3)$$


combining with earlier Eqn. d scales with a_p

$$P_c = P_0 - (\text{const}) \cdot D_{\text{ambi}} / d^3 \cdot (\gamma_{\text{sv}} \cdot V_{\text{aMX}}) / kT \cdot t$$

P_0 is the porosity at the beginning of the final stage of sintering.

- Porosity during this stage decreases linearly with time
- decreases inversely with grain diameter (scales with a_p), thus smaller grains should result in much faster porosity elimination





Now, the pores need to be eliminated at the final stage of sintering that is by diffusion process, and already I introduced this figure. This is the actual grain which has formed from the particle at initial stage. And through the grain boundary you can see all the pores are eliminated and only at the junction point among the grain you have the porosity left. So, vacancy source is the pore surface of radius r_p , I am assuming now although in the figure it is showing ρ_p , but it is shown r_p .

And the sink is the spherical surface of radius R that I have already shown, and as you can understand the value of R is much larger than r_p . So, one can write this equation that the r_p that is the pore radius which is the final pore radius. And r_{p0} , which is the initial pore radius is given by this relation diffusion coefficient is involved, the surface energy is involved the volume is involved and of course, the time is involved.

Now, in this kind of granular structure, where this is having a length of a_p so, we have 24 such vertices and each pore is shared by 4 polyhedra. So, I can write that the fraction of the porosity P_c by this relation from this geometric consideration. And which turns out to be this which is πr_p^3 divided by root over of 2 into a_p^3 .

So, if I combine it with the earlier equation and noting that the diameter that eventually scales up with the value of a_p . Then this P_c the porosity is equal to P_0 minus some kind of constant you can work it out. So, relating this relation with this relation you get

this final relation, this red colored one. So, here P_0 is the porosity as the beginning of the final stage of sintering.

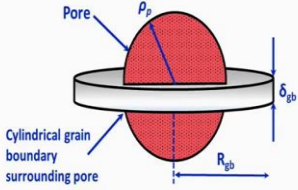
So, it shows that the porosity during this stage decreases linearly with time that is number 1, decreases inversely with the grain diameter, because the D term is coming at the denominator. So, it inversely related to grain diameter which is actually scales up with the a_p value of this schematic.


So, the smaller grains should result much faster porosity elimination. So, therefore that also tell us that one should start with nano crystalline powder for a better sintering behavior.

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Densification kinetics

Pore elimination by grain boundary diffusion mechanism
Following 2nd geometry of the schematic shown

$$r_p^4 - r_{p,0}^4 = - \left(8 \cdot \delta_{gb} \cdot D_{gb} \cdot \gamma_{sv} \cdot V_a \cdot M \right) / kT \cdot \left[1 / \left(\log \left(R_{gb} / r_p \right) \right) \right] \cdot t$$




Pore elimination when it takes place through grain boundary diffusion mechanism, following the 2nd geometry which I have shown that this one. One can write this relation between the radius of the pore and initial and final stage. And this is valid relation for the pore elimination for this kind of geometry.

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Densification kinetics

Final stage of sintering: Pore elimination: Effect of dihedral angle (*Pore removal is not that easy!!!*)

$\gamma_{gb} = 2 \cdot \gamma_{sv} \cdot \cos\phi/2$
 $\cos\phi/2 = \Gamma/\lambda$; now when $\phi = \phi$
 $K = \cos\phi/2 / \cos\phi/2 = 1$
 Driving force for grain boundary migration and pore shrinkage goes to zero, when grains around a pore meet such that
 $\gamma_{gb} = 2 \cdot \gamma_{sv} \cdot \cos\phi/2$ $K = \text{Energy lost/Energy gained} = (2 \cdot \Gamma \cdot \gamma_{sv}) / (\lambda \cdot \gamma_{gb})$

Now, in the final stage of sintering what is eventually happening is the pore is getting shrink right. And, it depends on the grain boundary also grain boundary initially, there were carved grain boundary which is becoming flatter and flatter. So, it turns out to be flat.

Because of the pressure, because of the vacancy concentration we have already seen in the earlier stage of sintering, the first two stages that this thing is straighten up and the pore is getting reduced. So, you see that the consideration here the pore elimination is eventually related to the dihedral angle. So, the final stage pore elimination is not that easy, because all the pore they have now delineated from the grain boundary, and they are at the junction point.

So, that pore elimination or the pore which is residing inside the grain, it is very difficult to get rid of so, we are trying to get rid of in the final stage of sintering. So, here is the concept of the dihedral angle that you can see. And this is the grain boundary energy and these two energy is between solid and vapor phase. So, you can see that if you try to estimate the value of gamma gb, that is 2 into gamma SV into cos of this dihedral angle divided by 2. So, that is from the Young's equation. So, you just split it here and then equate it with this one.

Now, you see this figure. So, here I have shown that original grain boundary are here. So, there are 1, 2, 3, 4 four grains are there right. And initially this was all pore. So,

inside this four grains at the junction point your pores were there right. And, then eventually during the final stage of sintering this porosity shrinkage porosity is shrinking; that means, initially it was here then it is shrinking to this part right.

And this angle is something similar to the dihedral angle not exactly similar, but something similar to the dihedral angle. So, this value and this value is more or less close to each other. Now, what is happening? Because, of this change in the pore. So, energy is lost right, because you are you are just losing this particular length. And due to the creation of this additional grainy area you are gaining energy.

So, you can have a ratio between these two which is energy lost versus energy gain from this geometry. So, this angle is $\phi/2$ so, this angle is also $\phi/2$. So, you can work it on to see that the energy that is lost is $2 \times \text{big pi} \times \text{gamma SV}$. So, that is the energy lost and the energy gain is nothing but this thing is gaining, because your grain boundary is generating. So, this $\lambda \text{ into gb}$ so, this relation is valid.

Now, you consider that this dihedral angle ϕ and this one is same similar type. So, if this is true then you can work it out that this by this ratio this is 1. So, it will it will come to be 1, if you consider this ϕ and this one this angle is same. So, what it tells you that the driving force for the grain boundary migration, and pore shrinkage goes to 0 when the grains around a pore meet. Such a way that the grain boundary energy gamma gb is equal to $2 \text{ into gamma SV into cos of } \phi/2$ exactly the same relation.

So, when this is valid then there is no driving force from this simple geometry. So, if it is a pore is a 4 edges. And if the grain boundary is completely straight, then there is no driving force for the grain boundary movement or the pore removal. So, that is this analysis is showing you.

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Final phase sintering: Stability of pore

Densification kinetics

- When the grains around a pore meet such that $\gamma_{gb} = 2 \cdot \gamma_{sv} \cdot \cos(\phi/2)$, the driving force for grain boundary migration and pore shrinkage goes to zero
- If the pores are to be completely eliminated, their coordination number has to be less than a critical value n_c
- $n_c < 360 / (180 - \phi)$; $\phi = 60^\circ$ (shrink), 90° , and 120° respectively.
- Low ϕ would aid in the prevention of boundary – pore breakaway and thus be beneficial.

So, this is a stable structure and this structure is unstable, because if it is less than the numbers, here it is 4 it is less than this then it will try to shrink. And if it is more than this then it has lot of energy to grow. So, when the grains around the pore meet such that this relation is valid. The driving force for the grain boundary migration and pore shrinkage goes to 0. If the pores are to be completely eliminated, then the coordination number has to be less than the critical value.

So, how this critical value is calculated this is less than 360 degree divided by 180 degree minus phi. So, phi can have 60 degree here. So, that will shrink phi can have 90 degree, it will be stable 180 degree it is possible. So, low value of this phi will aid in the prevention of boundary breakaway and thus be beneficial. So, if you have the pore having less than or three size less than 4 size surrounding grains, then it will shrink and if it is more as has been shown here it will try to grow.

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Coarsening kinetics

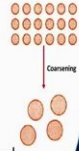
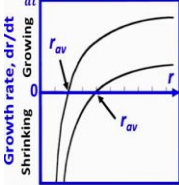
As derived earlier, for particle with average size r_{av} and other size $r \neq r_{av}$

$$P_{av} = P_{flat} (1 + 2 \cdot V_a \cdot M_X \cdot \gamma_{SV} / r_{av} \cdot kT)$$


and

$$P_r = P_{flat} (1 + 2 \cdot V_a \cdot M_X \cdot \gamma_{SV} / r \cdot kT)$$

Now if interface kinetics are rate limiting, velocity (v) (~particle growth) of solid/gas interface is linearly varied with the driving force,

$$v = dr/dt = K_r (P_{av} - P_r) = K_r \cdot P_{flat} \cdot (2 \cdot V_a \cdot M_X \cdot \gamma_{SV} / kT) \cdot [1/r_{av} - 1/r]$$



Plot of the above Eqn. for two different average particle size is shown: smaller grains disappear much faster and larger grain grows



So, already we have derived earlier that the particle with average size r_{av} and other size will be some other value. So, it is more than r_{av} sum will be less than r_{av} . So, this average P value is valid this already, we have established and for P_r for any other value of r , the partial pressure on that particular surface will be given by this relation.

Now, the interface kinetics if they are rate limited, velocity of this particle growth of the solid interface is linearly varied with the driving force. Now, what is this driving force? So, you have the velocity is nothing, but the change increase in the particle size with respect to time.

So, v is dr/dt and then you can have from these two relation you can work it out the value will be a linear function of these two partial pressure on two different particle size. So, this equation is valid. So, if you plot this one it will give you a plot something like this. So, it is a plot of the growth rate dr/dt as a function of the radius of the individual particle. As you can see this is for two different average particle, and if the value of the r this average particle is less than the value of this average.

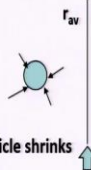
If the particle size is less than the average, they very rapidly shrink which exactly you want, but if it is more than that it starts to grow. So, if you have an average particle size which is relatively larger than the coarsening kinetics is much more favored. If it is less

value if it is less here, then it will actually shrink very fast. So, the coarsening effect will be grossly eliminated.

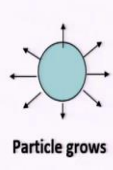
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Coarsening kinetics

Pictographically, the last analyses is like as follows



Particle shrinks



Particle grows


r_{av}

If it is assumed that $dr_{av}/dt = dr/dt$ at $r = 2 \cdot r_{av}$
 integration of the derive equation yields

$$r_{av}^2 - r_{o,av}^2 = \frac{(2 \cdot \gamma_{sv} \cdot V_a \cdot M_X \cdot P_{flat} \cdot K_s)}{kT \cdot T}$$

$r_{o,av}$ is the average particle size at $t = 0$

- Parabolic increase of *average grain size* with time
- Coarsening kinetics are enhanced for solids with *high vapor/surface interface energies* and *high vapor pressure*
- Si_3N_4 , SiC and Si being covalently bonded ceramics coarsen, than densify because they have relatively higher P_{flat}

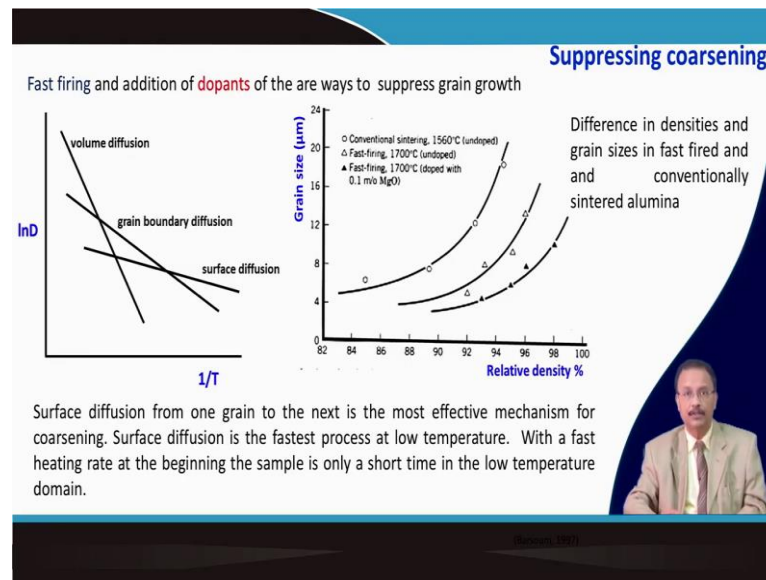


So, if I show you pictographically, then the particle will shrink where it is less than the so called average value and otherwise it will grow.

So, if it is assumed that this dr average by dt at a double particle size. So, r is equal to $2rv$, then if I integrate the relation, then we get this simple equation of r average square final and r average value which is growing from the initial state like this. So, this is a so called parabolic reaction sorry parabolic relation, to increase average size particle with time and coarsening kinetics are enhanced for solids with high vapor or surface interface energy and high vapor pressure.

And for silicon nitride, silicon carbide or silicon being covalently bonded ceramics, they coarsen and densify, because they have relatively high value of the partial pressure on the flat surface.

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So, fast firing is one way that suppresses the grain growth. Now, we are talking about the grain growth. So, as you can see that if I plot this density coefficient the coefficient D as a function of temperature, that at relatively lower temperature the surface diffusion is operative.

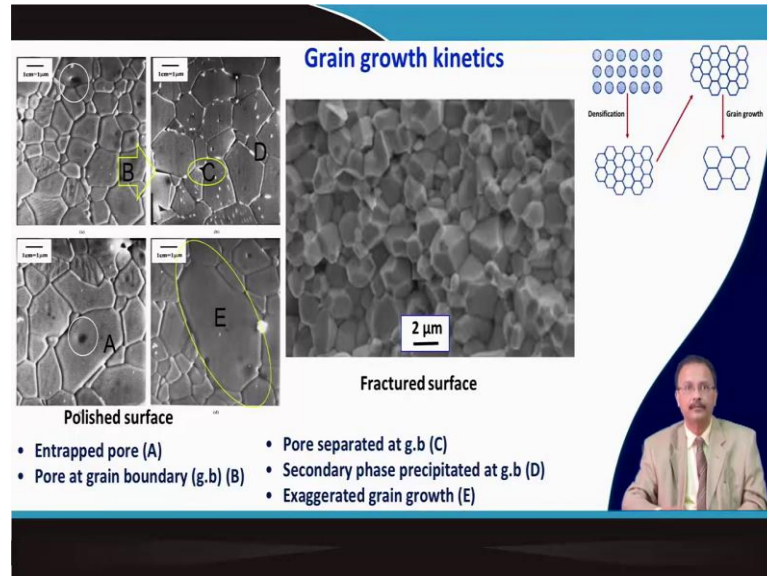
And at relatively higher temperature the surface diffusion is grossly eliminated. And as you can understand, because of the surface diffusion this coarsening effect is more or less, they are dependent on this surface effect. So, surface diffusion on one grain to the other is the most effective mechanism for coarsening, that already we have described. So, surface diffusion is the fastest process at lower temperature with a fast heating rate at the beginning, the sample is only residing at a very short time at low temperature domain.

So, therefore you can stop the coarsening if the rate of heating is much faster. So, here you can see the difference in density and grain size in a fast fired ceramics, and its comparison with a conventional fired alumina. So, whatever is fast fired here 1700 degree Celsius the this curve. Then, first fired for undoped one at 1700 degree Celsius and then it is a conventional firing at 1560 degree Celsius, you see the relative density for this case is much higher as compared to the other two.

And, here also doping plays a major role, because of the obvious reason already I have described in my earlier classes. So, if you dope it with magnesium oxide, then the

densification is much better, as compared to the undoped alumina which has been fast fired.

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So, this is the typical grain growth kinetics which will be operative when the densification is almost ended. So, in the polished microstructure it has been shown what are the typical types of pores, that is present the first one is called entrapped pore inside the grain. Second one is pore at the grain boundary.

The third figure, which is C that is pore separated along with the grain boundary. And the D is the secondary phase, which has been precipitated along with the grain boundary and E is exaggerated kind of grain growth. So, this is are all polished microstructure and in the fracture surface actually you cannot estimate the grain size from the fracture surface. So, the fracture surface actually tells you that, what is the extent of porosity, after sintering that you are getting once the sintering is over.

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Grain growth kinetics

Stability of grain boundary: Grains with more than six sides will tend to grow (*Ostwald ripening*), while those with less than six sides will shrink. Grains with flat g.b are stable.

Atoms jump from right to left and grain boundary from left to right.

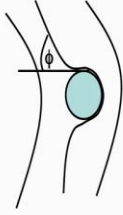
So, the stability of the grain boundary is important and grains with more than six sides will tend to grow. Because, already we were discussing about it, and this is sometimes called Ostwald ripening and whatever is less than 3, they will shrink. And this can be understandable from the concept of the curve surface. So, here you can see that in this area, it will have more vacancy, because this is concave in nature and this will have less vacancy.

So, certainly the vacancy will move in this direction. So, vacancy moves in this direction means atoms jump from right to left and the grain boundary will start to move from left to right. So, by just working out this concepts and thinking it properly, you can understand the concept of pore removal and the grain boundary movement.


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Grain growth kinetics

G.B pinning by solute



- Impurities or dopants are often concentrated at interfaces. When a grain-boundary moves, e.g. during grain growth, the solutes concentrated at the interface have to be carried along.
- The diffusion coefficient of the doping elements such as MgO in Al₂O₃, CaCl₂ in KCl, ThO₂ in Y₂O₃ or Nb in BaTiO₃ are smaller than the diffusion coefficient of the main constituents of the ceramic, thus slowing down the grain boundary mobility called solute drag.
- Pores and second phase inclusions have the same effect.

$$F = 2\pi\gamma r \sin\phi \cos\phi$$


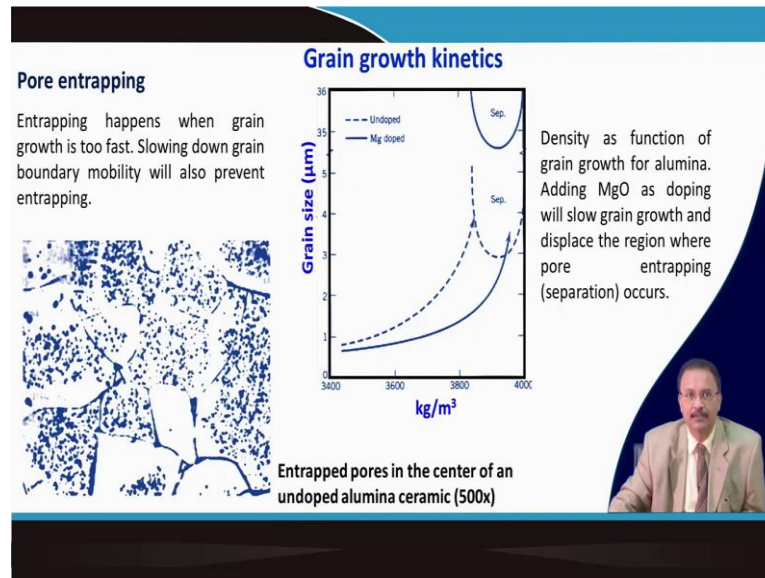
Now, if the grain boundary movement is related to the grain growth. And, if you want to stop it then the grain growth kinetics is grossly stopped by grain boundary pinning. So, you can put impurity atoms inside the material, they are often concentrated at the interface when the grain boundary moves during grain growth.

The solute concentration at the interface have to be carried along. So, there is a force involved and the force can also be estimated from this simple relation, where phi is this angle and gamma is the relevant surface energy and R is the radius of this solution.

So, this diffusion coefficient of the doping elements such as magnesium in alumina, calcium oxide in KCl, thorium oxide in yttrium, or niobium in barium titanate, they are smaller in size and diffusion coefficient of the main constituents of the ceramic.

They actually slow down the grain boundary and this phenomena is called the solute drag. And pores and second phase inclusion also they act in the same way to retard the grain boundary movement.

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So, this is one example of the pore entrapping inside the grain. So, entrapping usually happens when the grain growth is too fast. So, when the grain mobility is too fast, then it will acquire the pores very fast within the grain structure while the grain growth takes place. And slowing down the grain boundaries of utmost importance, otherwise it will have a almost a very porous entrapped microstructure.

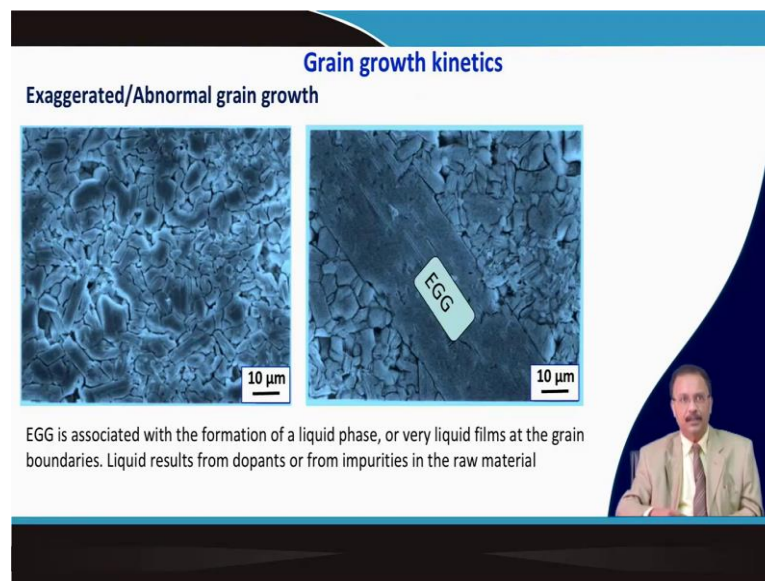
So, this is in alumina a sintered undoped alumina. So, you have the situation something like this. Now, if you see the relation between the grain size and the densification. So, the situation is something like that densification of course, will with the densification grain growth will take place. So, remember that the z curve I talked about. So, your grain size will start to increase theoretically, when your densification is almost completed.

Now, simultaneously this pore delineation from the grain boundary is also taking place. Now, if this kind of densification is crossing this pore separation this region, then that is not good for sintering will not achieve a good sinter able product. So, here in this view graph, we have shown that the density as a function of grain growth and that is for alumina ceramics.

Now, in alumina ceramics this trajectory of the grain growth versus densification that is intersecting in the pore separation region and this sintering is not good for conventional alumina.

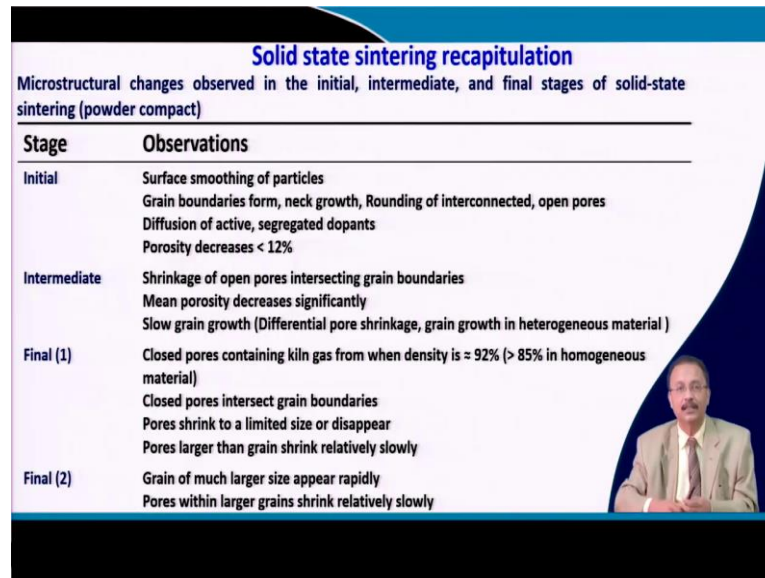
And you will not achieve a good densification for pure alumina, but in case of a magnesium dope, it will slow the grain growth right. The grain growth has been slower down but the densification is more, you see that each point it has slow down the grain growth, but densification is continuously increase. And the pore separation here this pore separation is far apart it. So, pore separation is far apart it so, in this case you will get a very good sintering characteristics for this material.

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So, this is the example of a exaggerated grain growth. So, this exaggerated grain growth is associated with the formation of sometimes a liquid phase or a very liquid film at the grain boundaries and liquid results from maybe the dopant or from some impurity. And grain boundary mobility is very much enhanced and some of the grain, they are of abnormal size range that you can think of.

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Stage	Observations
Initial	Surface smoothing of particles Grain boundaries form, neck growth, Rounding of interconnected, open pores Diffusion of active, segregated dopants Porosity decreases < 12%
Intermediate	Shrinkage of open pores intersecting grain boundaries Mean porosity decreases significantly Slow grain growth (Differential pore shrinkage, grain growth in heterogeneous material)
Final (1)	Closed pores containing kiln gas from when density is = 92% (> 85% in homogeneous material) Closed pores intersect grain boundaries Pores shrink to a limited size or disappear Pores larger than grain shrink relatively slowly
Final (2)	Grain of much larger size appear rapidly Pores within larger grains shrink relatively slowly

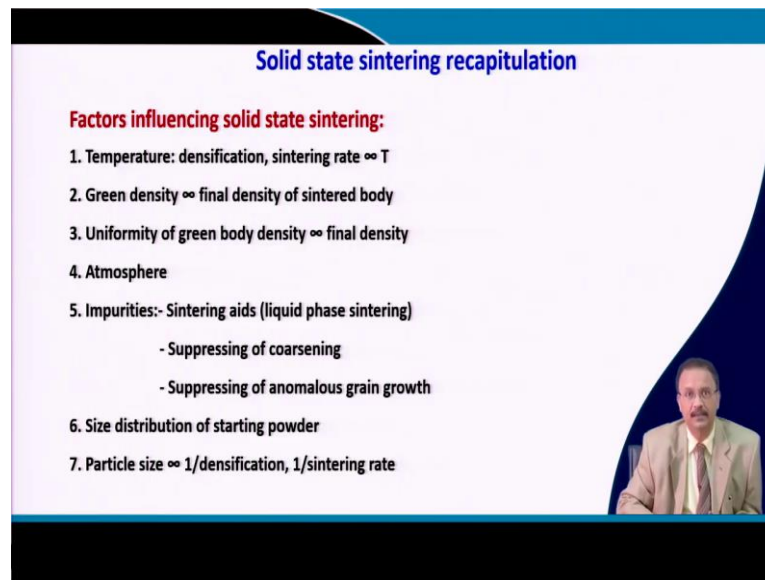
So, now I will just tabulate or summarize that different stages of sintering, because I have been talking about sintering for quite long duration. So, let us see what are the important point as far as the microstructural change occurring in these three phase of sintering solid state sintering.

Initial stage of sintering surface smoothening of particles takes place; grain boundaries form neck growth forms, rounding of the interconnected pores, that takes place open pores they form, diffusion of active segregated dopants, and porosity decreases to only 12 percent. Intermediate sintering shrinkage of open pores, interacts with the grain boundaries mean porosity decreases significantly, slow grain growth, differential pore shrinkage, grain growth in heterogeneous material.

Then final stage of sintering part 1 is closed pores containing some of the kiln gas from when the density 92 percent in homogeneous material. Closed pore intersects with the grain boundary pore shrinks to a limited size or it disappears, and pores larger than the grain shrinks relatively slow.

Final stage of sintering grain of much larger size, I mean grains of much larger size appear very rapidly, pores within the larger grains shrink relatively slowly, because these are entrapped pore.

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Solid state sintering recapitulation

Factors influencing solid state sintering:

1. Temperature: densification, sintering rate $\propto T$
2. Green density \propto final density of sintered body
3. Uniformity of green body density \propto final density
4. Atmosphere
5. Impurities:- Sintering aids (liquid phase sintering)
 - Suppressing of coarsening
 - Suppressing of anomalous grain growth
6. Size distribution of starting powder
7. Particle size $\propto 1/\text{densification}, 1/\text{sintering rate}$

So, finally in solid state sintering factors that influence the solid state sintering is temperature, that densification and sintering rate that is proportional to the temperature that we are using. Green density is important that is proportional to the final density of the centered body. Uniformity of the green body density that is proportional to the final density.

Atmosphere plays a major role, impurities also play a major role, sometimes it is I mean added intentionally that is called sintering aid, it can lead to liquid phase sintering also, but that can also lead to exaggerated grain growth. So, one should be cautious about it. Impurities can suppress the coarsening we talked about the dragging effect in the in the grain boundary.

So, that the grain size is not beyond a certain limit and of course, it suppress the anomalous grain growth, size distribution of the starting powder is important if it is not properly packed. Then, as I have shown it can lead to initial porosity. So, size distribution sometimes it is actually invited, if you can control the packing efficiency. It can lead to a better packing efficiency than the mono size particle.

In mono size particle you cannot go beyond 74 percent of packing. So, if you have correctly chosen particle size, then it is possible for you to have a better grain density that is welcome, but otherwise if it is not it is haphazard, then that will lead to large

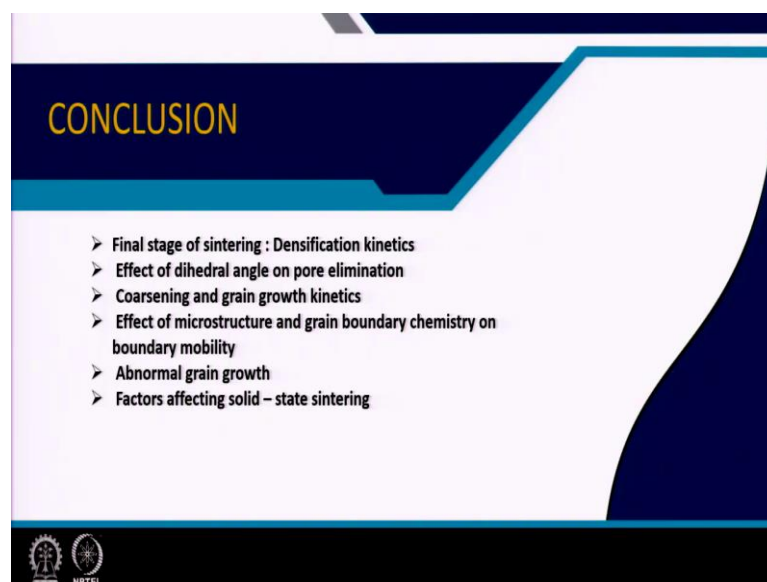
porosity. And particle size is having a large effect, this is densification increases. If the particle size is less and sintering rate is also favorably increased with lower particle size.

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So, Bersoum chapter number 10, the remaining part of the solid state sintering. And apart from that the other two literatures, what already I have described that can be read.

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So, in this lecture final stage of sintering particularly densification kinetics, they are described effect of dihedral angle on pore elimination, that has been illustrated coarsening and grain growth kinetics have been introduced, effect of microstructure and

grain boundary chemistry, on the boundary mobility that has been illustrated. Abnormal grain growth why it happens that has been explained, and factors affecting the solid state sintering we have covered.

Thank you so much for your attention.