

Non - Metallic Materials
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Module - 07

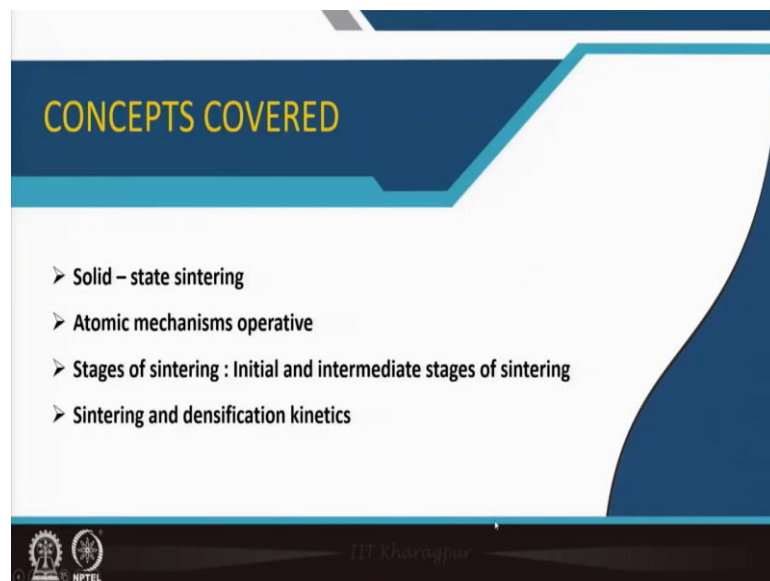
Processing of non - metallic materials, sintering and microstructure development

Lecture - 36

Solid-state sintering and microstructure development

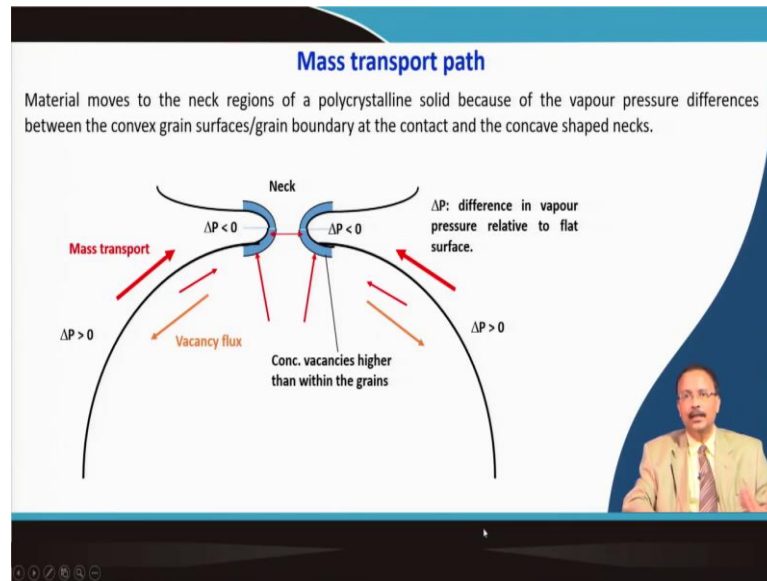
Welcome to my course Non-Metallic Materials and we are in module number 7 Processing of non-metallic materials, Sintering and microstructure development. And this is lecture number 36 where I will introduce Solid-state sintering and microstructure development concept.

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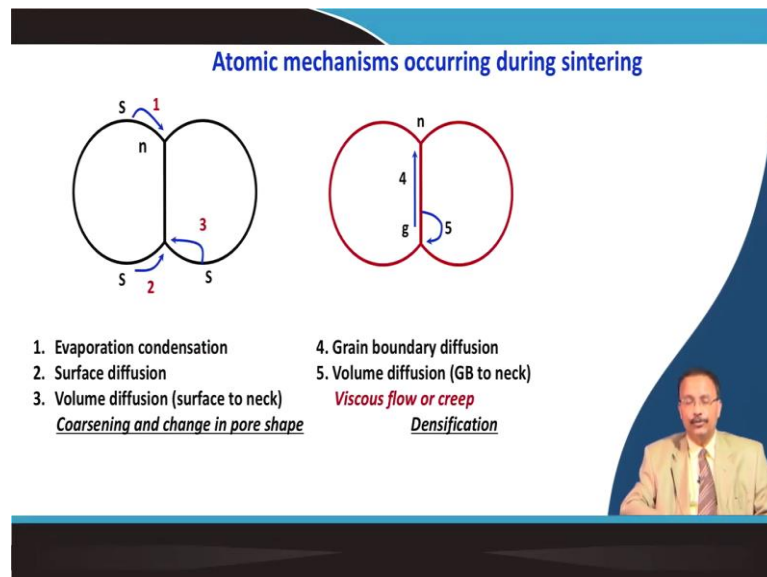
So, the concept that is covered in this particular lecture is the solid-state sintering in details and what are the different mechanisms that is operative and then we will introduce the stages of sintering there are 3 stages. So, initial and intermediate stages of sintering I will describe in this particular lecture and the sintering and densification kinetics will be illustrated the time dependent phenomena.

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So, this was the slide from the last lecture where I was describing the mass transport path. Materials move from the neck region of a polycrystalline solid because of the vapour pressure difference between the convex grain surface and grain boundary at the contact and the concave shaped necks. So, that is already illustrated.

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Now, just look at the different atomic mechanism that is occurring during sintering. So, as you can see that these are your initial 2 particle and these two particles they have come into close contact. So, it is forming a region interfacial region which will

eventually be converted into grain boundary and the particle curvature will change and it will lead to the grain.

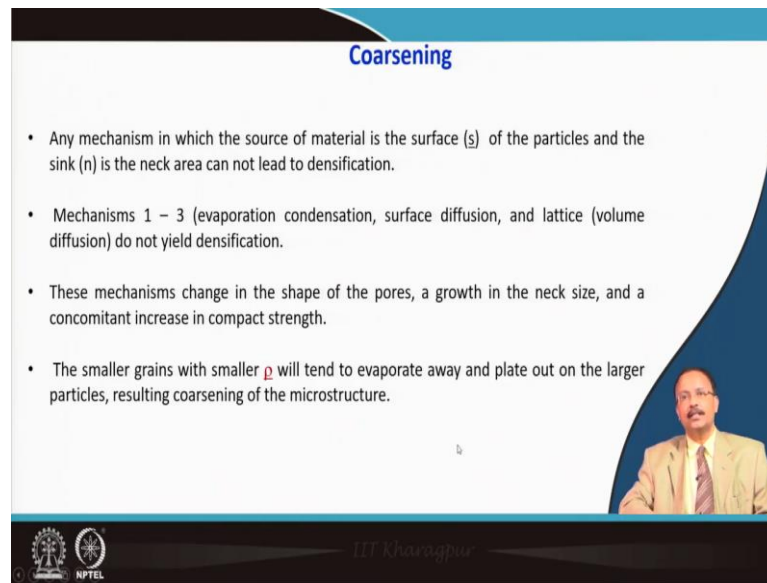
So, you see that the first path which is evaporation and condensation. So, from here material is evaporated because it is a high temperature operation. It is evaporated and it is condensed in the neck region. So, this mechanism is called evaporation condensation mechanism.

Number 2 is a surface diffusion the material is transported it is not going to the gas phase it is transported from this surface to the neck region right from here to here. 3rd one is the volume diffusion that is also from surface to neck, but not through this surface only, but little bit from the volume of the particle. So, this 3 mechanism that only leads to the change in the pore shape and the coarsening of the particle it does not lead to any kind of densification this is first 3 mechanism.

The 4th and 5th mechanism you see that the material is transported through the grain boundary to the neck region. And in this case volume diffusion again from the grain boundary region to this neck region. There is another mechanism which is operative for the glass material we call it is a viscous flow or creep ah, but that I will just introduce I will not go into the details of the sintering for the vitreous material.

So, we will be concentrating only on the solid ceramic particles. So, this 4 and 5 that will lead to the densification of the sintering mass.

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Coarsening

- Any mechanism in which the source of material is the surface (s) of the particles and the sink (n) is the neck area can not lead to densification.
- Mechanisms 1 – 3 (evaporation condensation, surface diffusion, and lattice (volume diffusion) do not yield densification.
- These mechanisms change in the shape of the pores, a growth in the neck size, and a concomitant increase in compact strength.
- The smaller grains with smaller ρ will tend to evaporate away and plate out on the larger particles, resulting coarsening of the microstructure.

Dr. Khuram

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So, first let us concentrate the coarsening mechanism number 1, then 2 and then 3 these 3 will lead you to the coarsening. So, any mechanism in which the source of the material is surface of the particle and the sink is the neck area that will not lead to any kind of densification.

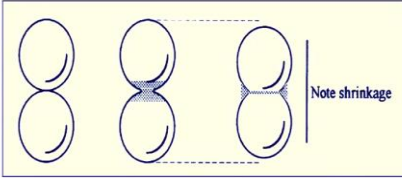
So, mechanism 1 to 3 evaporation condensation, surface diffusion, and lattice or volume diffusion in the periphery of the surface that do not yield any kind of densification. These mechanism change the shape of the pores, a growth in the neck size, and the concomitant increase in the compact strength. It is just being attached to the particle it is not leading to the shrinkage the centre to centre distance does not change much.

Sometimes it is useful for example, in gas sensing research we extensively use it this kind of low temperature sintering. So, that the porosity is maintained in the material. So, not always it is bad for catalysts research is also important. Porous ceramics development it is important these 3 initial mechanism.


So, the small grains with small radius of curvature will tend to evaporate away from the surface and plate out on the larger particles, resulting the coarsening of the microstructure. So, that mechanism is also important as far as the coarsening is concerned.

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Densification



- Mechanisms, apart from viscous or plastic flow, that can lead to densification are grain boundary diffusion and bulk (volume) diffusion.
- For both the driving force is curvature – induced vacancy concentration. Because there are more vacancies in the neck area than in the region between the grains, a vacancy flux develops away from the pore surface into the grain boundary area, where the vacancies are eventually annihilated. Equal atomic flux will diffuse in the opposite direction filling the pores.



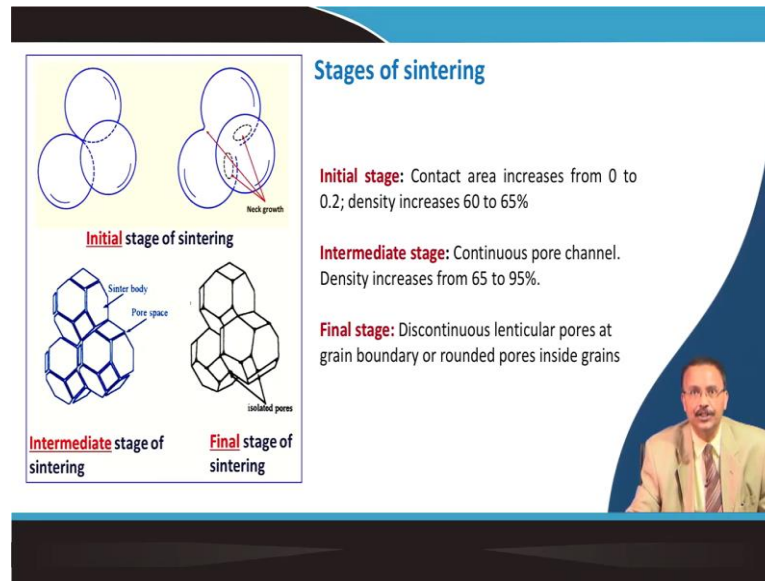
So, mechanisms apart from the viscous or plastic flow, that can lead to the densification or the grain boundary diffusion and bulk or volume diffusion. So, viscous flow is also that gives you sintering the shrinkage, but here you can see that in case of this grain boundary diffusion and bulk diffusion there is a notable shrinkage of the particle that is taking place.

So, initially it is in just the contact then the neck formation is taking place and the grain boundaries just begin to appear and then finally, this thing grows and you get a proper grain boundary.

So, for both this both the driving force is the curvature and induced vacancy concentration. So, that is. In fact, the driving force that I have already covered in the last lecture.

There are more vacancy in the neck area than the region between the grains a vacancy flux will develop away from the pore surface into the grain boundary area where the vacancies are eventually annihilated. So, equal atomic flux will diffuse in the opposite direction to fill up the pore. So, that is the basic mechanism where the densification is important.

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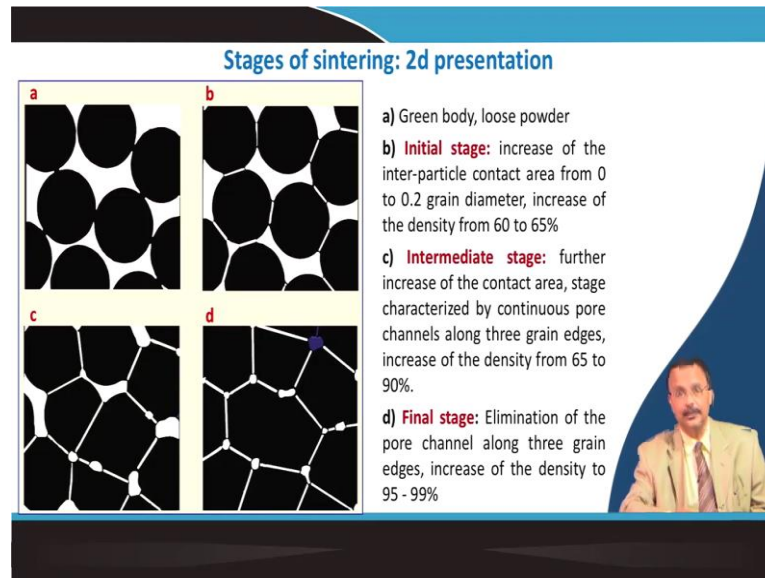


So, there are 3 prominent stage of sintering. The initial stage you see that the particles are something like this then they are coming into contact and in initial stage the contact area increases from 0 to about 20 percent and the density is also increased 60 to 65 percent so, that we call initial stage of sintering. In case of intermediate sintering you see that this curvature is gone.

So, it is replaced by the flat kind of vein boundary region and also it is faceted right. So, it is a 2d kind of defect 2d defect you know that 2-dimensional defect this grain boundary that is appearing. And pores are now continuous along with the grain boundary. So, the black regions are force and the density it increases from 65 percent from the initial stage up to 95 percent. So, up to 95 percent densification is possible in intermediate stage of sintering.

Then in final stage of sintering you see that this pores they are detached from the grain boundary and it is actually at the junction of the grain boundary. So, it is a discontinuous lenticular pores at the grain boundary. So, either in the grain boundary or sometimes inside the grain also this rounded force can recite. So, this is very difficult to drive out this kind of force eventually.

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So, if you do it 2d presentation of the same phenomena which is which I just described. So, this is a green body is a loose powder in initial stage, inter particular contacts area increases from 0 to 20 percent grain diameter, increases the density about 60 to 65 percent.

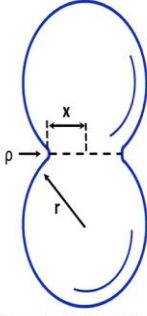
In intermediate stage which is see further increase of the contact area is taking place, stage characterised by a continuous pores channels along with the 3 grain edges, right and then the density increases from 65 to 90 percent 90 to 95 percent. And final stage of sintering elimination of the pore channels these are all eliminated and along with this 3 grain edges the pores are still remains almost it is gone the porosity is almost gone and the density increases to 95 to 99 percent.

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Sintering kinetics


For each of these stages *sintering kinetics* will be different. In addition, kinetics will depend on the *specific atomic mechanisms* operative. However, all sintering models have the following points common:

- A representative particle shape is assumed
- Surface curvature is calculated as a function of geometry.
- A flux equation (depending on the rate limiting step) is chosen.
- The equation is integrated to predict the rate of geometry change (x/r).



The diagram shows two overlapping circles representing particles. A horizontal dashed line indicates the neck width, labeled 'x'. A vertical dashed line indicates the radius of the particles, labeled 'r'. A small 'p' is also visible near the neck.

Growth of x/r is estimated



A small inset image of a man in a suit and glasses, likely the speaker, is positioned in the bottom right corner of the slide.

So, now we will talk about the kinetics of the sintering. So, for each of these stages of sintering the kinetics will be different. Kinetics will depend on the specific atomic mechanism operative. However, all this mechanism whatever I have just described they have something common in them.

So, first a representative particle shape is assumed and mostly it is spherical in nature. Then surface curvature is calculated as a function of the geometry of the packed material. Then third step a flux equation depending on what is the rate limiting step is chosen and this equation is integrated to predict the rate of the geometric change.

So, eventually what is happening initial contact is here a point contact and then finally, you will grow this region. So, this is called the neck region growth which is given by x by r , where x is this dimension and r is the radius of the particle. So, we will just see that how it works.

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Initial stage sintering

Evaporation condensation

The evaporation rate (/sq.m.s) is given by (Langmuir equation)

$$j = (\alpha \cdot \Delta P) / (2 \cdot \pi \cdot m_{MX} \cdot kT)^{1/2} = K_r \cdot \Delta P; \alpha \text{ Ev. coeff. } m_{MX} \text{ mass of gas molecule}$$

$$\Delta P = P_{\text{flat}} \cdot V_{aMX} \cdot \gamma_{sv} \cdot \rho / kT$$

From geometry: $(r + \rho)^2 = (x + \rho)^2 + r^2$ for $r \gg x$;

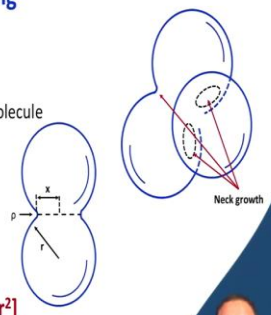

$$\rho = x^2 / [2 \cdot (r-x)] \approx x^2 / 2r$$

Now $dx/dt = j \cdot V_{aMX}$

Combining above Eqn.s and integrating it can be derived that

$$(x/r)^3 = t \cdot (6 \cdot \alpha \cdot \gamma_{sv} \cdot V_{aMX}^2 \cdot P_{\text{flat}}) / [(2 \cdot \pi \cdot m_{MX} \cdot kT)^{1/2} \cdot kT \cdot r^2]$$

- The rate of growth of the neck (x/r) is initially quite rapid but then flatten out
- x/r is a strong function of initial particle size (r)
- x/r is a function of the partial pressure P_{flat} of the compound, which in turn depends exponentially on temperature

So, first let us consider the evaporation condensation mechanism. So, first I will choose a rate equation evaporate rate equation and usually the Langmuir equation is adopted. So, where the flux is j , which is equated with the evaporation coefficient which is α , ΔP is the pressure difference and m_{MX} is the mass of the gas molecule because as I said it is going from the surface to the gaseous region and then it is deposited in the neck.

So, I know that the ΔP is given by this relation this I have already derived earlier. Now if you see this simple geometry. So, here tentatively Pythagoras theorem is applicable. So, I can write r plus ρ square ρ is the radius of curvature, x is this length of the neck region and r this r is the radius. So, this equation is valid, but as you can see this radius of the particle it is much much larger than this neck region x .

So, I have just simplified it. If you do this and ρ square will be a very small term and then we will find that this equation is valid. So, radius of curvature is almost equivalent to x square by $2r$. Now it is the rate of the neck growth. So, dx by dt that is nothing, but j that atomic flux into the molar volume atomic molar volume $V \times V_{aMX}$.

So, if you combine this equation then you can have this relation with the neck growth which is to the power 3 and this equation is valid you can just derive it derive this equation. So, as you can see that from the flux equation eventually dx by dt type of relation I have gotten then I will have to integrate this and finally I will get this relation.

Then why this reaction relation tells you? The rate of neck growth is initially quite rapid but then it flattens out. So, that is number 1 observation, x by r the neck growth is a strong function of the initial particle size right. So, smaller particle size more surface energy and the neck growth will be tremendous high.

So, that is why that is one implication to get small particles to start your sintering. This x by r is a function of the partial pressure. So, it is a function of P flat of the compound which in turns depend exponential on the temperature.

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Initial stage sintering

Lattice diffusion model: material diffuses away from g.b area through bulk and deposit in neck (densification)

$$(x/r)^4 = [(64 D_{ambi} \cdot \gamma_{sv} \cdot V_a M_X^2)/(kTr^3)]. t$$


Lattice diffusion model: material diffuses away from g.b area radially along the g.b of width δ_{gb} and deposit in neck (densification)

$$(x/r)^6 = [(192 \cdot \delta_{gb} D_{gb} \cdot \gamma_{sv} \cdot V_a M_X^2)/(kT \cdot r^4)]. t$$

Shrinkage is

$$(\Delta L/L)^3 = [(3 \cdot \delta_{gb} D_{gb} \cdot \gamma_{sv} \cdot V_a M_X)/(kTr^4)]. t$$

Surface diffusion model (coarsening, no densification): atoms diffuse along the surface (thickness δ_s) towards neck area

$$(x/r)^5 = [(225 \cdot \delta_s D_s \cdot \gamma_{sv} \cdot V_a M_X)/(kTr^4)]. t$$


So, that is part of the initial stage sintering. Now if you do similar kind of calculation for other models like Lattice diffusion model. Then you will come up with all different types of relation and what you will have to see that how this x by r varies with the time as well as the particle size because this is miserable quantity right, time is measurable that is a sintering time and the initial particle size you know.

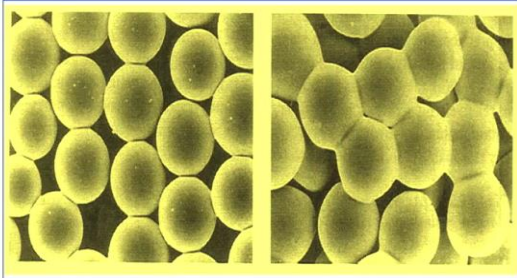
And diffusion coefficient surface energy solid and vapour surface energy atomic volume it is dependent on this. So, lattice diffusion model; lattice diffusion model where densification takes place that kind of relation you can develop. And for the densification mechanism where the densification takes place, the shrinkage is given by this type of relation.

And for surface diffusion model where no coarsening takes place sorry coarsening only takes place, but no densification takes place. There attempt diffuses along with the surface of thickness I have assumed as δ towards the neck region there the x by a r relation is something like this. So, following the same concept which I have derived for evaporation condensation this equations can also be derived.


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Initial stage sintering

Viscous sintering



The shrinkage of glass spheres during the initial stage is given by

$$\Delta L / L = (3 \cdot \gamma_{sv} / 4 \cdot \eta \cdot r) \cdot t$$


In case of viscous sintering this shrinkage law that is valid. So, shrinkage is given by this relation where as you can see it is a function of the viscosity of this glass sphere. Its radius as well as the time of sintering.

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Porosity of sintered bodies

Pores are important and unwanted elements of a ceramic microstructure. The final pore space in an sintered ceramic is mainly a function of the pore volume in the greenbody. Source of pores

Inter-granular pore space.
Ordered packing of monodispersed spherical particles minimizes initial pore volume.

Intragranular pore space

Extra pore space due to hard, disordered agglomerates

Extra pore space due to poly-dispersed powders.

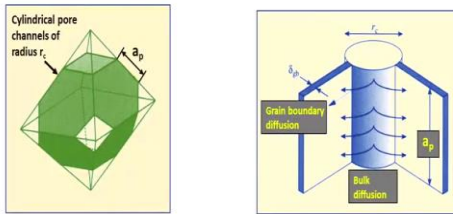
So, porosity in the sintered body is important as I have shown you that ultimately it is the porous region this porous region will have to be eliminated. So, what kind of pores that you can have? So, once you pack the particle press it and the initially if the particle size are all uniform then the pore that is still remaining that is called the intergranular pore size and as you can know that if it is the FCC kind of packing then maximum you can pack it up to 74 percent and a CP also 74 percent.

So, you cannot the twenty 6 percent void will be there. So, that is this 26 percent void space. Sometimes intragranular pore space is there. So, inside the particle itself the pores are there. Sometimes this extra pore space that occurs due to the hard disordered agglomerate which is detrimental for sintering.


So, they are hard agglomerate if it is present in the material then also pores come. An extra pores was due to poly disperse powder you have different size of particles than the pore region is much larger as compared to the uniform particle size as far as the packing of this particular is concerned while you press it.

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Intermediate stage of sintering: Densification; Coble's model Densification kinetics



- Compact is composed of ideally packed tetraidecahedra of length a_p , isolated by long porous channels of radius r_c .
- Densification occurs by the bulk diffusion of vacancies away from the cylindrical pore channels towards grain boundaries.
- A linear, steady state profile of the vacancy concentration is established between the source and the sink.
- Vacancies (C_v) are annihilated at the grain boundaries.



So, now we will talk about the intermediate stage of sintering and initial stage of sintering is over then it is more about densification and we will talk about the densification kinetics. In case of the initial stage of sintering we were worried about the neck growth x by r . So, kinetics was related to x by r .

Now, the densification kinetics is important. So, here is a bit model that has been adopted. So, initially we have assumed that when the particle is changing into grain, it is composed of ideally packed tetraidecahedra kind of thing. So, this is the faceted type structured grain. You have seen in case of aluminium doped with magnesium oxide it is a faceted type of granular structure takes place.

So, this is having a length of a_p of one of these site and this is isolated by the long pores channel. So, these are the grain boundary region the pores are there and eventually after the intermediate sintering the pores are detached from this grain boundary region to form a porous region at the junction of the grains something like this white kind of thing.

So, densification actually occurs by bulk diffusion of vacancy away from the cylindrical pores. So, initially the grain boundaries they are cylindrical. So, cylindrical pore bulk diffusion of vacancy that takes place that goes away from the cylindrical pore. And a linear steady state profile of the vacancy concentration is established between the source and sink. And vacancies are annihilated at the grain boundary.

So, here it is the porous region this is the grain boundary. So, I have defined the thickness of this grain boundary is δ_{gb} and this is the value of r_c cylindrical pore channel radius and this one is the a_p . So, called this part is modelled like this and bug diffusion is operative here.

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Densification kinetics

The fractional porosity P_c decreases linearly with time

$$P_c = (\text{const}) D_{\text{ambil}}/d^3 \cdot (\gamma_{SV} \cdot V_a \cdot M_X) / kT \cdot (t_f - t) \quad (\text{diffusion from cylindrical pore})$$

where, t_f is the time required to vanish the cylindrical pore channel, d is the diameter of the grain

$$P_c = (\text{const}) \cdot [D_{gb} \cdot \delta_{gb}/d^4 \cdot (\gamma_{SV} \cdot V_a \cdot M_X) / kT \cdot (t_f - t)]^{2/3} \quad (\text{G.B diffusion is operative})$$

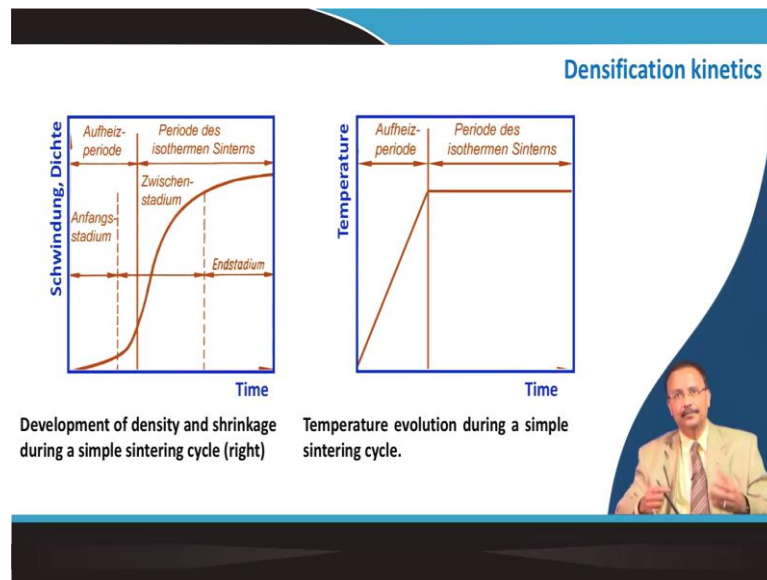
Initial powder packing is very important to yield a pore-free microstructure after sintering.

So, the fractional porosity decreases linearly with time. So, I can write the equation of fractional pore is related with the diffusion is involved and actually the a is scaled down with the d diameter of the so called particles and this is the diffusion from the cylindrical force which was that curved arrow. So, those kind of situation the fractional porosity reduction is given by this relation.

So, here the t_f is the final time required to vanish the cylindrical pore channel and d is the diameter of the grain right. And if you consider the grain boundary diffusion is operative then this relation is valid. This relation can be derived so it is valid and this is the straight line path in the last slide.

So, the implication is the percent of theoretical density if you now estimate with the sintering temperature. So, if it is having an agglomerated free powder then you can see it is possible for you to densify it more because the starting pore fraction is much less in this situation. But if it is having a pore you can see that the densification initially is pretty small with rise in temperature it density is increased, but it does not achieve this value. So, it is always good to have a agglomerated free material.

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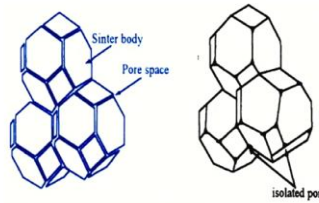


Now, the stage of sintering pardon for the language it is taken from a German slide. So, still the German things are there. So, initial stage it is here and then it intermediate stage this increases. The density and it is the final stage the it is almost asymptotic about 96, 97 percent. And corresponding heat treatment schedule is given here.


So, once you are initially ramping the temperature up to this maximum sintering temperature you are basically in this region in this region and then during soaking the densification actually taking place. So, it is a function of time rather than the temperature where the actual sintering takes place.

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Densification kinetics



- Cylinder gets smaller in diameter, its curvature increases and vacancy concentration gradient also increases.
- As cylindrical pore get longer and thinner, at some point they become unstable and break up into smaller spherical pores along the grain boundary and/or at the triple points between grains (isolated pores).
- This initiates **final – stage sintering** where annihilation of remaining porosity and grain growth occur simultaneously



So, the situation is something like that the cylindrical cylinder gets smaller in diameter, here. So, as compared to this it is getting smaller here its curvature increases and vacancy concentration gradient also increases. Cylindrical pores get longer and thinner, at some point they become unstable and break up to smaller spherical pores along with the grain boundary or specifically at the triple point between the grains.

We call these are isolated pores has been shown in this figure. This initiate the final-stage of sintering. So, once you are delineated the pores from the grain boundary region to the junction of the grain boundary then the intermediate sintering stops and that is going to be the final stage of sintering.

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Densification kinetics

- **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
- **Grain boundary diffusion mechanism:** Vacancies are restricted to diffusing along a grain boundary of width δ_{gb}

So, here you have a situation something like this. So, you have a porous region and then you have the granular region right. So, here it is your grain boundary this grains and it has this pores region in between right. So, the pore elimination means attempt diffuses towards the pore so covered the pore region. Vacancy is a transported away from the pore to a sink such as grain boundary dislocation or external surface of the crystal and then the pores are eliminated.

So, the pores along the grain boundaries they are eliminated and this is one measure mechanism of the sintering that how these pores are eliminated through the grain boundary. Volume diffusion mechanism here we are assuming vacancies are assumed to be eliminated at the grain surface. So, that is the volume diffusion mechanism and third one is the grain boundary diffusion mechanism vacancies are restricted to diffusing along with the grain boundary.

Remember the atomistic model which I had described earlier and this grain boundary with is having a finite weight like δ_{gb} value. So, this things are illustrated here.

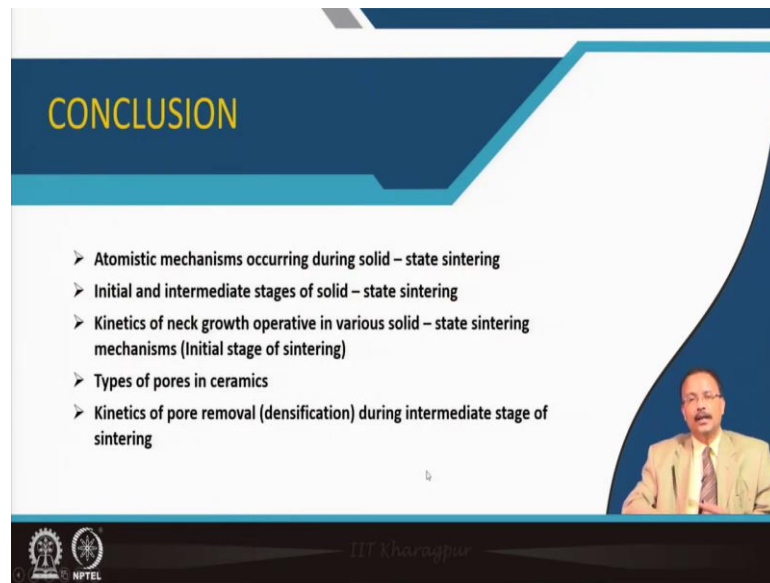
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So, here the pore radius is I have identify as row of P and sometimes I just use the radius in different terminology. In the next lecture you will see that while I will talk about final stage of sintering where, I will describe it in more details that what exactly is happening where this pores are delineated from the grain boundary region and it is entrapped into the isolated grain structure.

So, the study material is a continuation of chapter 10 of the book by Bersoum and also the book by Reed and the chapter by professor A R Das is important for you to cover for this particular lecture.

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The slide features a dark blue header with the word 'CONCLUSION' in yellow. Below the header is a white area containing a bulleted list of topics. On the right side of the slide, there is a small inset image of a man in a suit and glasses, presumably the lecturer. At the bottom left, there are logos for IIT Madras and NPTEL. The text 'IIT Madras' is faintly visible in the bottom center.

CONCLUSION

- Atomistic mechanisms occurring during solid – state sintering
- Initial and intermediate stages of solid – state sintering
- Kinetics of neck growth operative in various solid – state sintering mechanisms (Initial stage of sintering)
- Types of pores in ceramics
- Kinetics of pore removal (densification) during intermediate stage of sintering

IIT Madras

So, in this lecture I have introduced the atomistic mechanisms occurring during sintering the solid-state sintering process. Initial and intermediate stages of solid sintering I have explained. Kinetics of the neck growth operative in various solid-state sintering mechanism that is the initial stage of sintering that has been described the how x r varies with t and the radius of the particle.

Types of different pores in ceramics that have illustrated intragranular, intergranular kind of pores due to hard agglomerate, pores due to the difference in particle, initial particle size so that have been described. And finally, the kinetics of pore removal that is the densification during intermediate stage has been covered. So, next lecture I will cover the final stage of sintering where the densification occurs.

Thank you for your attention.