Advanced Ceramics for Strategic Applications

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Lecture - 41
Magnetic Ceramics

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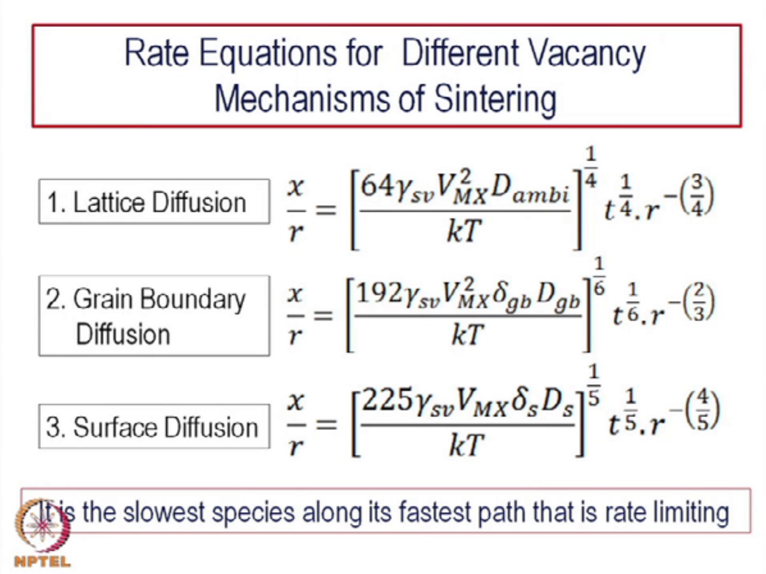

Rate Equations for Different Vacancy Mechanisms of Sintering

1. Lattice Diffusion $\frac{x}{r} = \left[\frac{64\gamma_{sv}V_{MX}^{2}D_{ambi}}{kT}\right]^{\frac{1}{4}} t^{\frac{1}{4}}.r^{-\left(\frac{3}{4}\right)}$

2. Grain Boundary Diffusion $\frac{x}{r} = \left[\frac{192\gamma_{sv}V_{MX}^{2}\delta_{gb}D_{gb}}{kT}\right]^{\frac{1}{6}} t^{\frac{1}{6}}.r^{-\left(\frac{2}{3}\right)}$

3. Surface Diffusion $\frac{x}{r} = \left[\frac{225\gamma_{sv}V_{MX}\delta_{s}D_{s}}{kT}\right]^{\frac{1}{5}} t^{\frac{1}{5}}.r^{-\left(\frac{4}{5}\right)}$

It is the slowest species along its fastest path that is rate limiting

This is the last one in this series of lectures on sintering of ceramics. In our earlier lecture, we had discussed about the different mechanisms of diffusion which are important for most transport during sintering. I will briefly, go through that once again. There are three main mechanisms of diffusion, namely lattice diffusion, grain boundary diffusion and surface diffusion. Each of these mechanisms will have a sintering kinetics. The expression for x by r, in terms of time initial particle size and of course the temperature, they more or less follow the similar pattern, but with some difference, will discuss about two or three important parameters here for example, three diffusion parameters. These diffusion coefficients are obviously different for different mechanisms. For example, d subscript ambi, this is an ambi- polar diffusion coefficient for the material for the compound MX. Then you have grain boundary diffusion D Subscript gb; than surface diffusion coefficient D subscript s.

We will also notice that because this is lattice diffusion volume diffusion so there is absolutely no constraint. So, for this the area of diffusion is concerned or the area of the flux, whereas in these two mechanisms we have the thin surfaces through which the deficient x plus and therefore, the area comes important. This is our grain boundary area. Grain boundary thickness in the cross-section, it comes as an area where as similar is the case of the surface diffusion. We have Trump Delta's service which is the thickness of the surface, through which the definition is taking place and of course, in any kind of process r the limiting one is always the slowest peaces which is a diffusion coefficient of having a low diffusion coefficient and also around its fastest path, so these are some of the concentration which we must keep in mind while we are trying to understand the diffusion mechanisms of a sintering.

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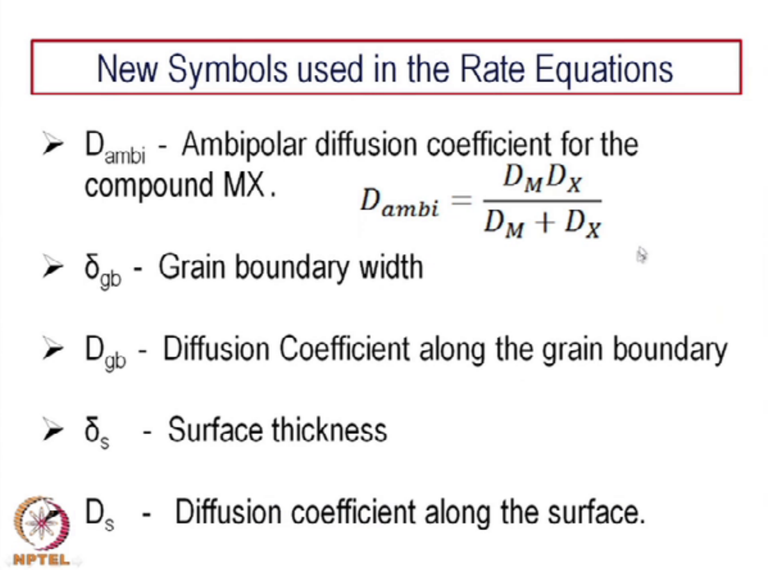

New Symbols used in the Rate Equations

- D_{ambi} - Ambipolar diffusion coefficient for the compound MX. $D_{ambi} = \frac{D_M D_X}{D_M + D_X}$
- δ_{gb} - Grain boundary width
- D_{gb} - Diffusion Coefficient along the grain boundary
- δ_s - Surface thickness
- D_s - Diffusion coefficient along the surface.

This we have already discussed, D subscript ambi means, ambipolar diffusion coefficient for the compound MX and that is defined because it involves both Catalans and to enhance and therefore the average diffusion coefficient is like this, and then grain boundary with diffusion coefficient of grain boundary surface thickness that we have already mentioned.

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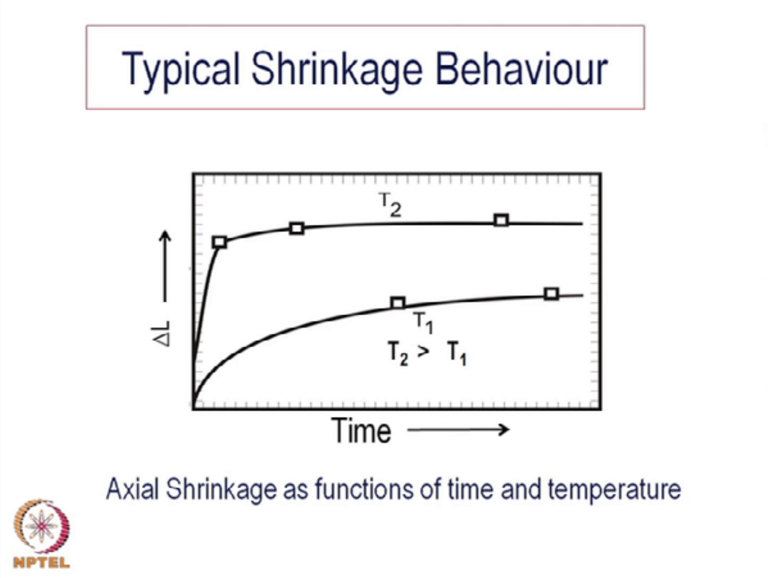

Typical Shrinkage Behaviour

Axial Shrinkage as functions of time and temperature

Now, typical shrinkage behavior we have seen in our very first lecture, on sintering almost applies to almost all the deficient mechanisms, and the kinetics is like this delta L, is the change on the linear thickness of dimension and as a function of time. This is normally analogue scale and have the temperature effect there, and as you have mentioned with time initially the progress of the kinetics is fast and then slows down and the rate becomes almost constant, and that initial rate increases as temperature increases, and the overall shrinkage or the dimensional change is also larger and the temperature is high. So, these are the typical reaction sintering kinetics behavior of almost all the mechanisms, but the coefficients of the exponent is little different.

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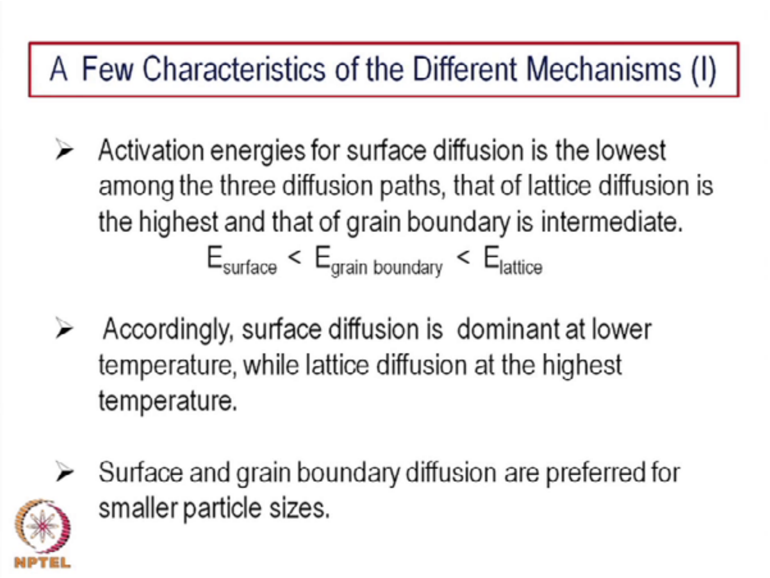

A Few Characteristics of the Different Mechanisms (I)

- Activation energies for surface diffusion is the lowest among the three diffusion paths, that of lattice diffusion is the highest and that of grain boundary is intermediate.

$$E_{surface} < E_{grain\ boundary} < E_{lattice}$$

- Accordingly, surface diffusion is dominant at lower temperature, while lattice diffusion at the highest temperature.
- Surface and grain boundary diffusion are preferred for smaller particle sizes.

While talking about the diffusion mechanisms, we should also remember that all the deficient producer activation, their activity process, thermally activated processes and they have thermal activation energies. So, the activation energy for three different mechanisms to surface diffusion, grain boundary diffusion, lattice diffusion is slightly different in that context. The activation energy for the surface is the lowest. The grain boundaries are intermediate and the lattice surface energy, the activation energy is the greatest. So, this becomes operative at a high-temperature and heat particle size also. This is intermediate temperature and this is at lower temperature. Surface diffusion is dominant at that sort; mention the surface deficient is dominant at lower temperature, while lattice diffusion at the highest temperature as which surface and grain boundary diffusion are preferred, for smaller particles sizes. So, this is also another because smaller particle size means we have a higher surface energy and the surfaces are available in larger quantity, and therefore the small particle size prefers surface r grain boundary diffusion. The larger particle always dominates the lattice diffusion dominant and larger particles.

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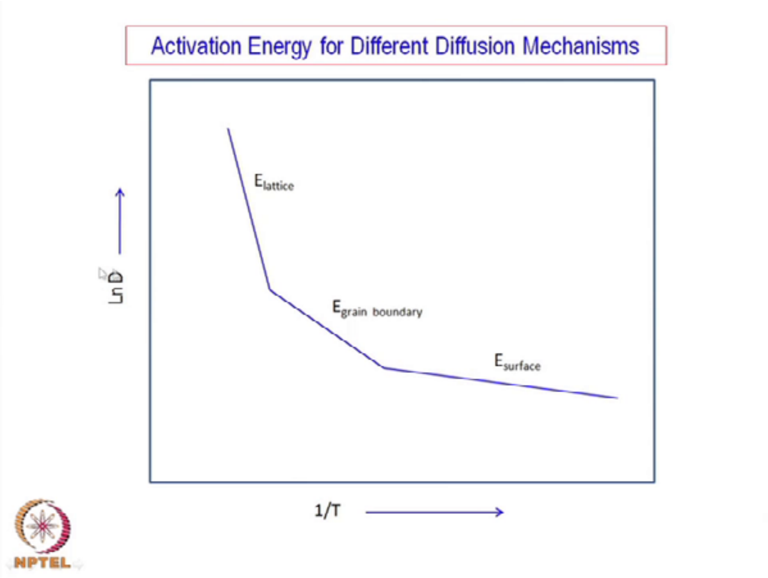

Activation Energy for Different Diffusion Mechanisms

Now, this is what it means, particularly the comparison of the activation energies for the three mechanisms. If you plot an LnD versus one by T, then you have straight-line plots. These slopes are surface energies, so at low-temperature because of one by T. So, you can see that, this is the activation energy for the surface diffusion, were as intermediate one is grain boundary diffusion, then lattice diffusion the highest and the activation energy. The slope is also highest; this slope is lower when this is intermediate.

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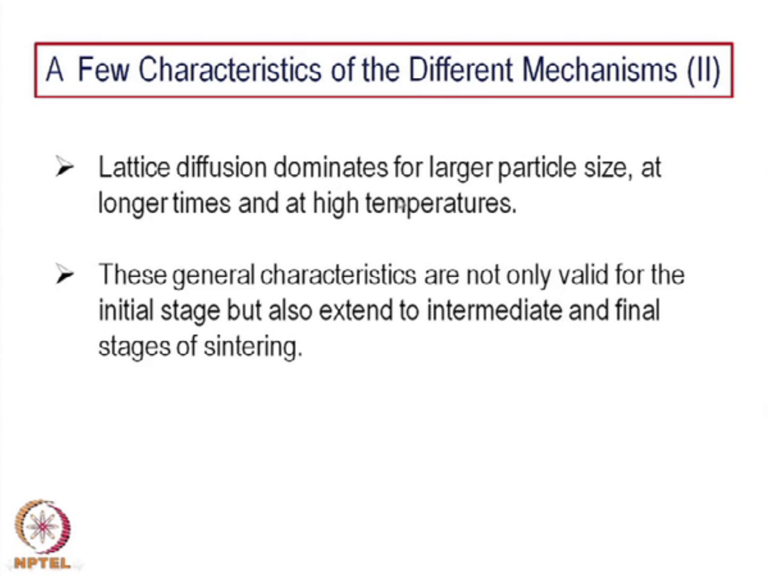

A Few Characteristics of the Different Mechanisms (II)

- Lattice diffusion dominates for larger particle size, at longer times and at high temperatures.
- These general characteristics are not only valid for the initial stage but also extend to intermediate and final stages of sintering.

Few more characteristics of lattice diffusion dominate for larger particles size. Also that I mention this now a longer times and at high-temperatures, so that is also another characteristic of this lattice deficient. The general characteristics are not only valid for the initial stage, but also extend to the intermediate and final stage sintering. Although we have not analyzed those processes at the intermediate, as well as the final stage of sintering. What we have discussed so far, is applies primarily to the initial stages of sintering, so the calculations and the mathematical analysis, what has been carried out, are primarily based on the initial stages of sintering. However, phenomena or mathematical analysis applies to the other two stages. The intermediate stage and the final stage, however will not be during under the scores.

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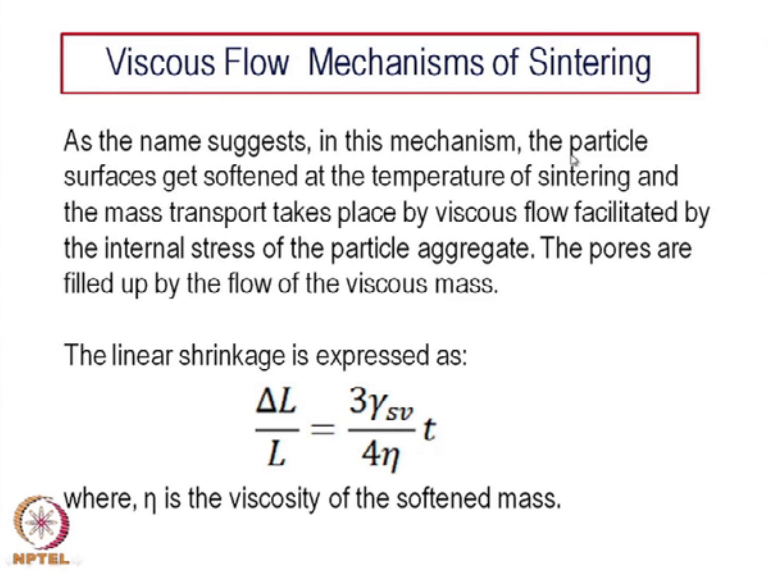

Viscous Flow Mechanisms of Sintering

As the name suggests, in this mechanism, the particle surfaces get softened at the temperature of sintering and the mass transport takes place by viscous flow facilitated by the internal stress of the particle aggregate. The pores are filled up by the flow of the viscous mass.

The linear shrinkage is expressed as:

$$\frac{\Delta L}{L} = \frac{3\gamma_{sv}}{4\eta} t$$

where, η is the viscosity of the softened mass.

Now, we had discussed are two different mechanisms. Already one is the vabortion condensation and the other one is just discussed about the diffusion bheggancy mechanism of deficient. They both are serviced sintering process and there is one more in that is called the viscous flow mechanism sintering, that we have mentioned earlier. So, let us try to look at it in slightly difficult details, as the name suggests in this mechanism also the particle surfaces, that softened at the temperature of sintering and the transport must take place by viscous flow are facilitated by the internal stress of the particle. Aggregate, whenever you consolidate particles, their praste either praste or there is capillary action of the feed which makes them entangled to each other.

So, there is certain amount of internal stress generated, so if there is plasticity available on the surface of these particles, set high-temperature, then this stress is good enough for the flow of the materials, particularly on the surface. The posts are filled up by the flow of the viscous mass and are more or less, somewhere in between the solid state diffusion and the order solid-state, must transport the liquid state sintering, which will discuss briefly after sometimes. It is somewhere in between to viscous flow, somewhere in between the solid-state must transport or solid-state mechanism of solid-state sintering and liquid states sintering and the linear shrinkage is expressed. As in this manner once again there is a temperature dependent, time-dependent and it is in fact linearly dependent on time. In this case and the tarp which is very important here, is the viscosity. So far, we have not talked about viscosity of the solid because it is basically solid state diffusion or evaporation kind of coping mechanism. Here, first time there is liquid where, viscoelastic material is involved, and therefore we have viscocity term curving for its flow of characteristics.

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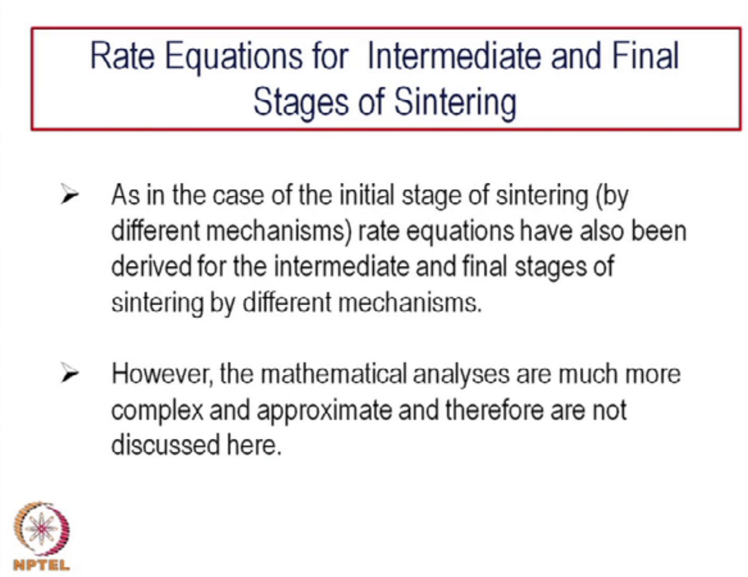

Rate Equations for Intermediate and Final Stages of Sintering

- As in the case of the initial stage of sintering (by different mechanisms) rate equations have also been derived for the intermediate and final stages of sintering by different mechanisms.
- However, the mathematical analyses are much more complex and approximate and therefore are not discussed here.

That is another pointer which I mentioned just now. As in the case of the initial stage of sintering by different mechanisms, rate equations have also been derived for the intermediate, in the final stage of sintering by different mechanisms. However, the mathematical analyses are much more complex and more approximate. The exact necromancy is still unavailable.

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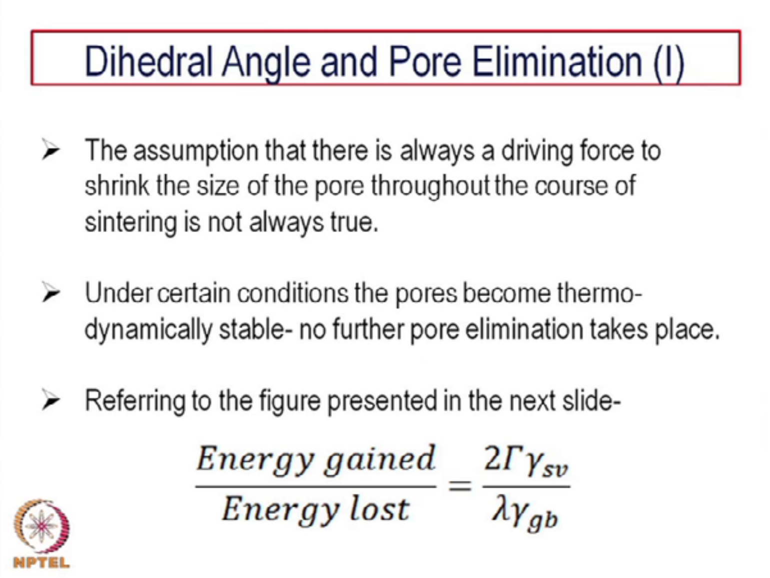

Dihedral Angle and Pore Elimination (I)

- The assumption that there is always a driving force to shrink the size of the pore throughout the course of sintering is not always true.
- Under certain conditions the pores become thermo-dynamically stable- no further pore elimination takes place.
- Referring to the figure presented in the next slide-

$$\frac{Energy\ gained}{Energy\ lost} = \frac{2\Gamma\gamma_{sv}}{\lambda\gamma_{gb}}$$

And therefore, we are not discussing it under the Scores. As discussed, depend mechanisms, are at least three different mechanisms of solid state diffusion, a solid-state sintering evaporation, condensation vacancy mechanism and a very briefly in the viscous flow mechanism. Latest try to look at what happens, when towards the final stage of sintering. How the poor elimination takes place and what are the different driving forces are for pore elimination, of course takes place because of the surface energy change, but then at the local level, what are the tune things happening to a letter stripe, let us look at it little more carefully. The assumption, that there is always a driving force to shrink the size of the pore throughout the course of the sintering is not always true. We have assumed that there is a extra energy because of the extra surface available and the removal of surface, will certainly lower down the energy to energy of the system, and therefore there will be a continuous removal of the pores because pore removal reduces the surface energy, and therefore there will be a continuous removal of a pore or densification, but sometimes under certain situations, it really does not happen.

Under certain situations, fold becomes more stable. They do not even get eliminated, even if we heat it to high-temperature, and because there are some other energy terms, which comes seem to play. So, that is what it means, that assumption is always a driving force for a shrink forced to synthesize the pore throughout the course of this sintering is not always true. Always certain circumstances, pore elimination really does not place under certain conditions. The pore become thermodynamically stable, and the pore elimination takes place, that is the same statement more or less in different way, referring to the figure presented in the next light, will come to that. The energy gained by the energy lost is equal to this much. A comeback this in the moment, but let me go to the figure.

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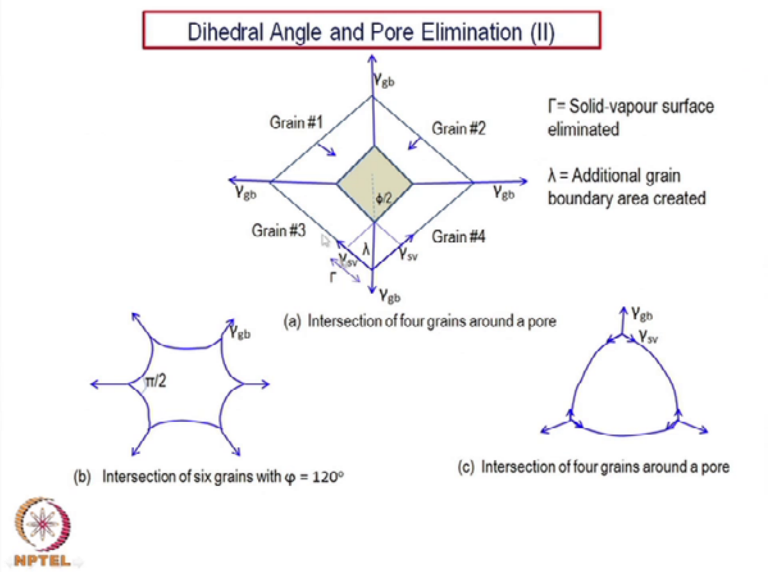

Dihedral Angle and Pore Elimination (II)

Γ= Solid-vapour surface eliminated

λ = Additional grain boundary area created

(a) Intersection of four grains around a pore

(b) Intersection of six grains with φ = 120°

(c) Intersection of four grains around a pore

This is a concept of a dihedral angel. We have already introduced earlier is basically the anobide in the tangent of the surface and the tangent on the surface. Tangents to tangents of the two different surfaces are where, is meeting at a particular point and particular surface, so that is called dihedral angle. Now, here what we do have considered as, if this is a pore, a kind of for simplicity, we have considered it as a rectangular pore. Initially this was the size of the pore, the larger Square actually not rectangle, which is square. So, larger square is the initial size of the pore and then these are the surface on the boundary, between the paper and the solid, so this is another grain, so there are four different grains forming a pore. Initially this was the largest Square, representing the pore and because the pore is shrinking, so it takes some time before it gets shrunk. This system, this size, so it is still uniform, once again is an ideal situation as still it is uniformly shrinking has from the boundary and has move from this to this boundary. Similarly, this one now during this thing, there is some energy lost and some energy gain. These are gamma is in solid vapor solid, the surface energy throughout. We have solid vapor surface energy and depending on the area, the total energy should be surface energy multiplied by the vaporous surface area, so while the pore was this much. This was considering that, there is unit thickness of the surface.

So, this distance becomes this distance multiplied by this, becomes total area and when it comes to this; the area has decreased considerably, so this energy tumbled. Introduced on the other hand, we have created these grain mountains. This was original because they are of four grains. This is because the pore was so much, so there is no question of this grain boundary neither this nor that, so we have reduced the solid-vapor area, but we have increased the solid-solid area, that is the grain boundary energy, so this is the increase in energy and this on the site are the reduction in energy. So, that is what has been mentioned. This distance is gamma capital and this distance is lambda, so this increases the energy grain boundary and this energy has been reduced, so that is what has been mentioned in earlier expression. So, gamma is the solid-vapor surface, eliminated. This one is eliminated particularly for this corner. Similarly, these corners are also there four corners and lambda, the additional grain boundary area created, this is the grain boundary area and this has been eliminated, so this is for each lambda to gamma area which has been produced. So, this is increasing and this is reduced. This also is reduce, same is the case in the four pores.

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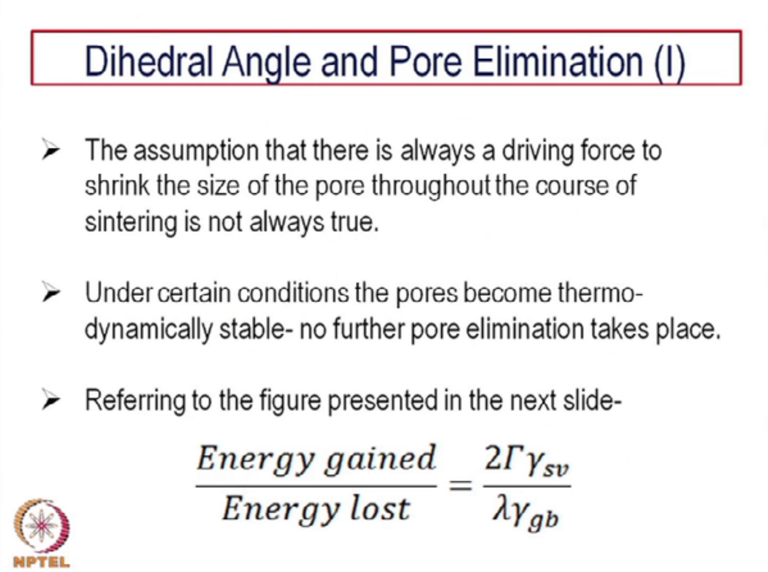

Dihedral Angle and Pore Elimination (I)

- The assumption that there is always a driving force to shrink the size of the pore throughout the course of sintering is not always true.
- Under certain conditions the pores become thermo-dynamically stable- no further pore elimination takes place.
- Referring to the figure presented in the next slide-

$$\frac{Energy\ gained}{Energy\ lost} = \frac{2\Gamma\gamma_{sv}}{\lambda\gamma_{gb}}$$

So, if you take the that is what is called the referring to the figure presented the next slide, the energy gained is twice gamma into gamma is band the energy lost to lambda to gamma gb, so this is the ratio of the energy gained the energy lost

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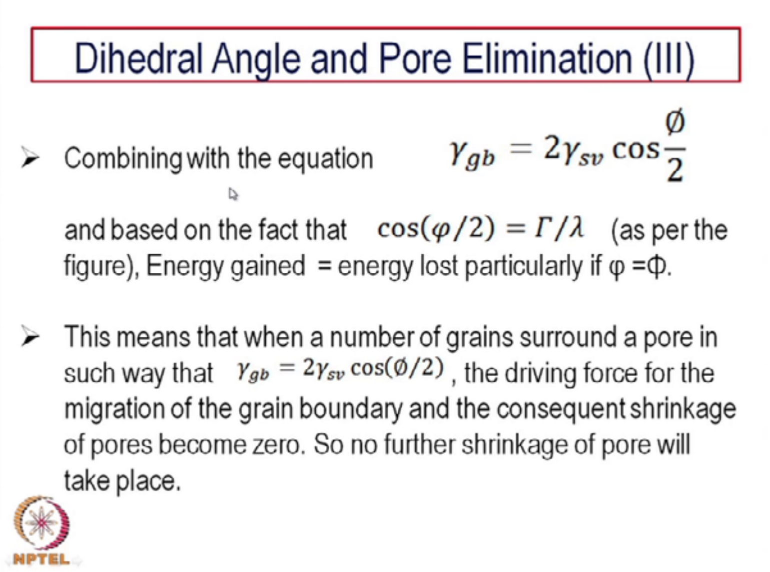

Dihedral Angle and Pore Elimination (III)

- Combining with the equation $\gamma_{gb} = 2\gamma_{sv}\cos\frac{\emptyset}{2}$

  and based on the fact that $\cos(\varphi/2) = \Gamma/\lambda$ (as per the figure), Energy gained = energy lost particularly if φ =Φ.

- This means that when a number of grains surround a pore in such way that $\gamma_{gb} = 2\gamma_{sv}\cos(\emptyset/2)$, the driving force for the migration of the grain boundary and the consequent shrinkage of pores become zero. So no further shrinkage of pore will take place.

So, the combination with this equation, the dihedral angle is given by, while five the title dihedral angle between these two surfaces, this grain boundary surface and the solid-vapor surface, that is the relationship of the dihedral angel and based on the fact that costs five by two equal to gamma by lambda from this geometry.

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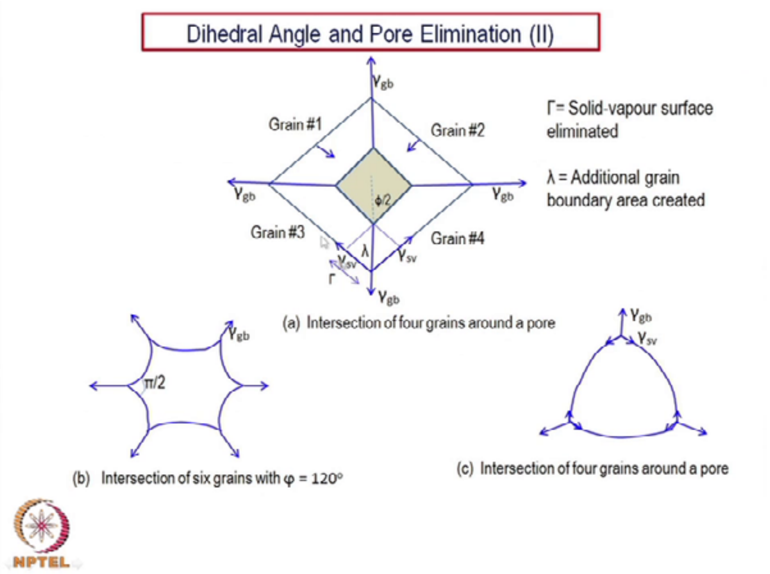

Dihedral Angle and Pore Elimination (II)

Γ= Solid-vapour surface eliminated

λ = Additional grain boundary area created

(a) Intersection of four grains around a pore

(b) Intersection of six grains with φ = 120°

(c) Intersection of four grains around a pore

This is the distance, these distances are not the angles or energy terms, is a distances basically geometric terms. This is the lambda and this is gamma, this one from this, so this is five by two, so from that this is also five by two. So, cos five by two actually gamma by lambda as per the figure, so the energy gained is equal to energy lost, particularly if the five is equal to five. The capital five and small five are equal, so this is a five equals five the other one is here.

So, if this kind of situation happens, then the energy to energy is balanced and energy gained is equal to energy lost particularly, if this is this. This means that, when a number of grains surrounding a pore in such a way that lambda gb, the grain boundary energy equal to two lambda, is the solid- vapor energy, cos five by two to the driving force for the migration of the grain boundary and the consequent shrinkages of pores become a zero, so no further shrinkage of pore will take place. So, that is another concentration, although it is a flat surface energy reduction. In surface energy, gain certain energy and therefore there will always be a driving force for shrinkage of the pores, but that is not always the case. It all depends on the two terms, what are the value of gamma, a correspondent grain boundary and gamma to the solid solid-vapor. So, depending on that the dihedral angle changes and that will change control, whether the pore will shrink or it will be stable.

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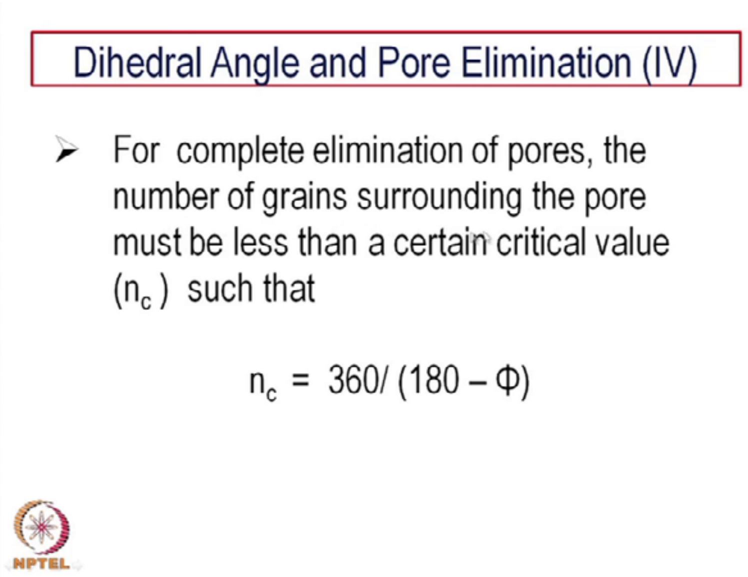

Dihedral Angle and Pore Elimination (IV)

- For complete elimination of pores, the number of grains surrounding the pore must be less than a certain critical value (n_c) such that

$$n_c = 360/(180 - \Phi)$$

For the complete elimination of pores, the number of grains surrounding the pore, must be less than a certain critical value nc, such that nc is equal to 360 by 180 minus psi, so this is also important how many number of sites, how many grains surrounding a particular pore, that is also an important factor, so for complete elimination of pores, the number of grains surrounding the pore, must be less than a certain critical value. If too many grains are surrounding a particular pore, then there is a less possibility of pore elimination, so that also is an important issue while we are trying to see the sintering kinetics or trying to get a theoretical density. I also look yes.

This is also stabilized system, while there is six grains; inter-section of six grains with psi is equal to 120 degrees. This is also a very stable configuration and whenever, there is a convex configuration this is also important and although we are considering, here is a planar configuration, but this convex of the concave nature is also important. This is a pore surrounding that, you have a convex surface of the game that becomes more stable than this kind of situation. So, this is a more stable situation than this and this kind of pores will not be eliminated.

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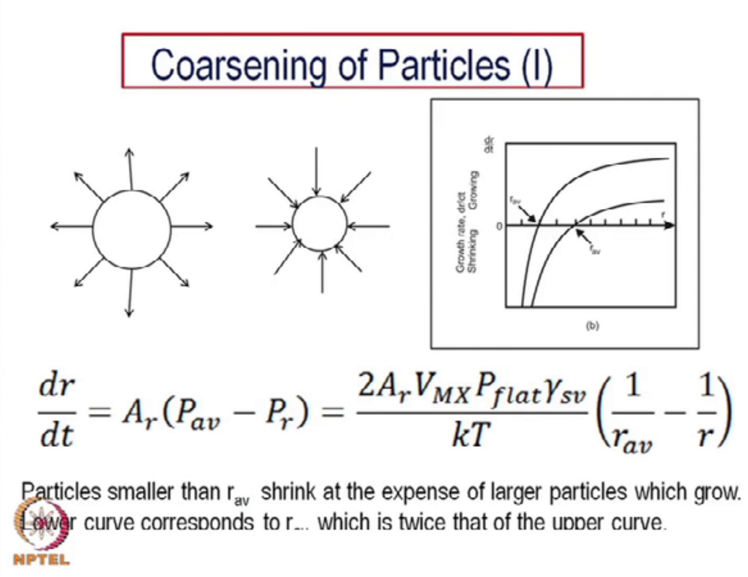

Coarsening of Particles (I)

$$\frac{dr}{dt} = A_r(P_{av} - P_r) = \frac{2A_r V_{MX} P_{flat} \gamma_{sv}}{kT}\left(\frac{1}{r_{av}} - \frac{1}{r}\right)$$

Particles smaller than r_{av} shrink at the expense of larger particles which grow. Lower curve corresponds to r... which is twice that of the upper curve.

So, visually we have considered earlier the coarsening of the particles in the very first lecture. There is a possibility of coarsening of particles to take place at a very low temperature or at initial stage of the sintering. Then the densification becomes difficult. The grain growth takes place quite fast and full densification is not possible most of the time, so let us try to see how the coarsening of the particles takes place; because this has some analogy with the grain growth phenomena, which takes place towards the end of the sintering process. After the intermediate states, sintering over that is a possibility of grain growth, sometimes called abnormal grain growth, very fast rate of grain growth of certain, not all the grain grow, of course only few grains grow abnormally and their sizes becomes order of magnitude, larger than the other grains and that is not a very rare accepted situation or satisfactory situation. Because if there is a difference in grain sizes, then may the particular mechanical properties gets deteriorated and therefore, whenever we are trying to center particular material, we need to process the material in such a way or both the particle size. The agglomeration and also the temperature rise and all that must be controlled in such a way that, there is no abnormal grain anyway, so the mechanism of course in the particles and the grain growth have certain amount of similarities.

So, latest try to look from that point of view, this is the rate equation dr dt that means, the radius of the particle here, these are not pores, but the solid particles, so the rate of change of the radius at a function of temperature of the particle is equal to this kind of expression rp average p is a partial pressure or vapor pressure and then the vapor pressure of the actual particles with a radius of part and this kind of particles surface which can be again represented like this and one b y the similar kind of equation. We have considered earlier as well as 1 by r average, which maybe a reference and this is 1 by r, actually which is given here. The particles smaller than r average, shrink at the expense of the larger particles which group corresponds to there is a plot here the dr dt as a function of r. What is the rate of change temperature, so this rate is positive here, the rate is negative there.

So, if you plot this dr that is the function of r. So, we get a card like this and this is what we call r average, which is the intersection of this scarp of the x-axis. This x-axis is zero are this is positive that means the particles will grow here and the particles will shrink in this. The basic essence of this particular question is any particle having a radius more than this particular value is a positive dr dt, that means it will grow. So, any particle having value more than this value, has a positive dr dt, whether less than this is negative dr dt, that is very critical, so this is either you can call it a average particle size or a critical particles size.

So, this is what happens, if this diameter at this radius and this is a radius, the average somewhere here, then this will slowly collapse and the material will get transported to the other one and this will group, so that is the phenomena of particle coarsening and also a phenomena of grain growth. This of course has, depending on what is the average particle size which is a critical particle size, in this case the critical particle size is almost double than this value, so that depends on the different parameters. Here what is this value? What is this vapor pressure on the flat surface and what is the exact compound so on.

So, if for any particular system there is always a critical value, below which the particles will collapse, will dissolve and the material for that solution which go to the other particles having the particle size greater than the critical size, so that is always a phenomena which also happens in case of phase transformation like nucleus and growth phenomena. Wire that is always a critical embroil are critical nuclear size, below which the nuclear gets dissolve and call embraispariahs. About this critical size phase transformation takes place of the nuclear grow and then the phase transformation take place, so that is a normal phenomena in this kind of a system.

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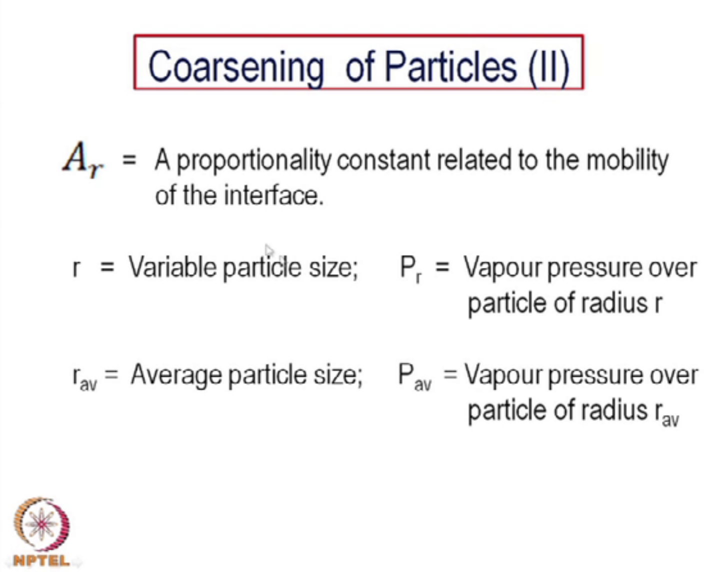

Coarsening of Particles (II)

A_r = A proportionality constant related to the mobility of the interface.

r = Variable particle size; P_r = Vapour pressure over particle of radius r

r_{av} = Average particle size; P_{av} = Vapour pressure over particle of radius r_{av}

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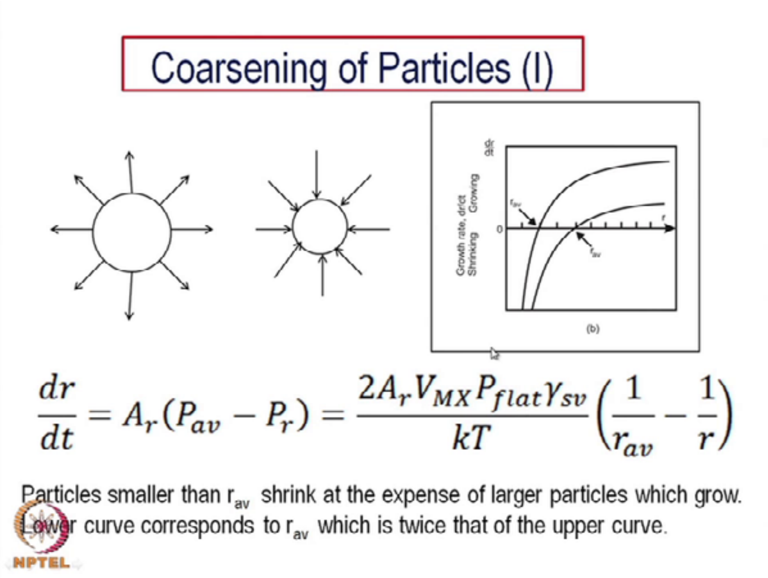

Coarsening of Particles (I)

$$\frac{dr}{dt} = A_r(P_{av} - P_r) = \frac{2A_r V_{MX} P_{flat} \gamma_{sv}}{kT}\left(\frac{1}{r_{av}} - \frac{1}{r}\right)$$

Particles smaller than r_{av} shrink at the expense of larger particles which grow. Lower curve corresponds to r_{av} which is twice that of the upper curve.

It is been explained that Ar, a proportionality constant related to the mobility of the interface are the variable particle size Pr. Whatever terms we have used in the expression, they are actually explained here, vapor pressure over the particle of radius r average either equal average, critical servers particle size. One can say critical particle sizes, so the P average is also the vapour pressure over particle size of radius r av are particles.

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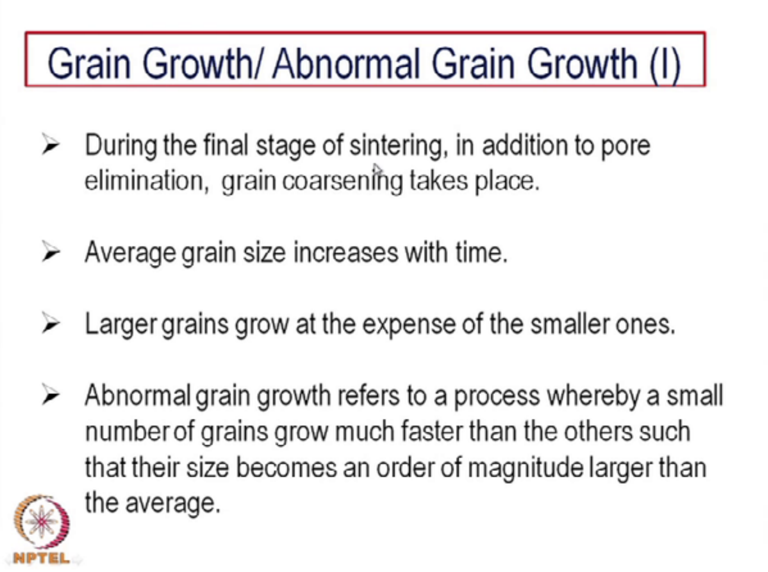

Grain Growth/ Abnormal Grain Growth (I)

- During the final stage of sintering, in addition to pore elimination, grain coarsening takes place.
- Average grain size increases with time.
- Larger grains grow at the expense of the smaller ones.
- Abnormal grain growth refers to a process whereby a small number of grains grow much faster than the others such that their size becomes an order of magnitude larger than the average.

Having discussed that, just consider the so-called grain growth than abnormal grain growth phenomena in all sintering process you have estates, where there is a possibility of grain growth particularly at the final stages of sintering or it did not say all the time the grain growth take place. Abnormal grain growth takes place in some cases, it takes place depending on the system, depending on different other parameters, so during the final stage of sintering in addition to pore elimination grain coarsening takes place, so that needs to consider this average grain size as it increases with time. Larger grains grow at the expense of the smaller ones, thus is very similar phenomena is particle coarsening abnormal grain growth refers to a process, whereby a small number of grains grow much faster than the other, such that their sizes becomes an order of magnitude larger than the average, so are few grains grow much faster than the other ones and as a result their sizes becomes order of magnitude larger than the average grain size, so that is what we call the abnormal grain growth.

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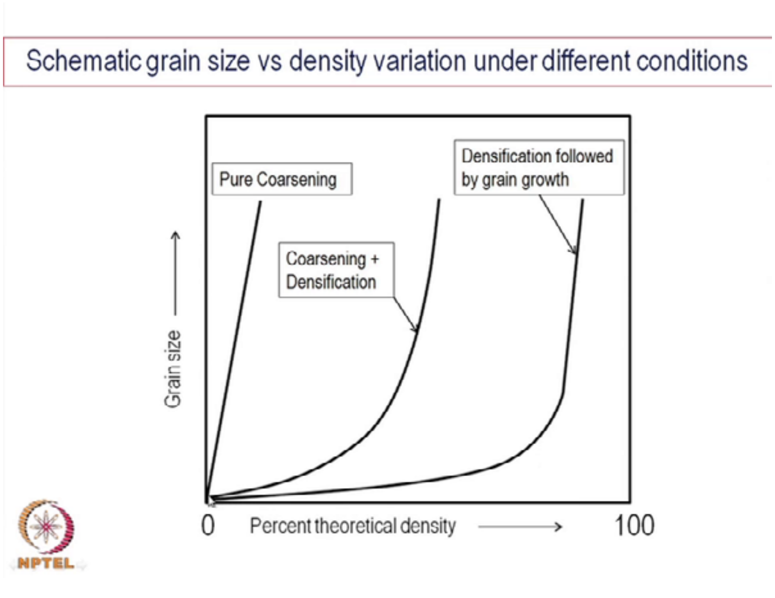
Schematic grain size vs density variation under different conditions

This we have seen again earlier a typical thing in context of the abnormal grain growth. This is what happens in a situation, where densification is being extended almost towards the theoretical density and more than 90 percent and then there is a sudden rise in grain size, so that is what we really call the abnormal growth in some cases, but in general there is a tendency of grain growth, obviously this is coarsening plus densification show. These are some of the situation; we do not need this as we have mentioned earlier there is hardly any grain growth without densification, which is not a desire situation. There should be a line like this somewhere here in the intermediate grain size. The theoretical density is achieved here. Theoretical density is not cheap, but deviance is increasing, so that this is somewhere in between all ceramic systems which receive less than 90 percent density is never used or is not very useful product, if it is less than 90 percent density, it is actually pores ceramics.

There are some pores ceramics as membranes, so there poor sizes is the criteria, it is not the densification which is important or the mechanical strength, but one is to balance how much pores is needed for the material to be used as membrane as it receives as a micro fine pores material. So, they need larger pores or finer pores in large numbers, but at the same time you need strength also, so you have to make a compromise between the densification and the mechanical strength, so that material can be used as a high strength membrane or pores material. So, 100 percent density densification is not always the preferred thing, particularly for remembrance, but otherwise a very close to 100 percent densification is suddenly a preferred situation. Then also these large grains may move away from the pores which are trapped within the grains and thereby do not allow reaching the theoretical density of the solid within a definite. Now, this is the problem of the abnormal grain growth.

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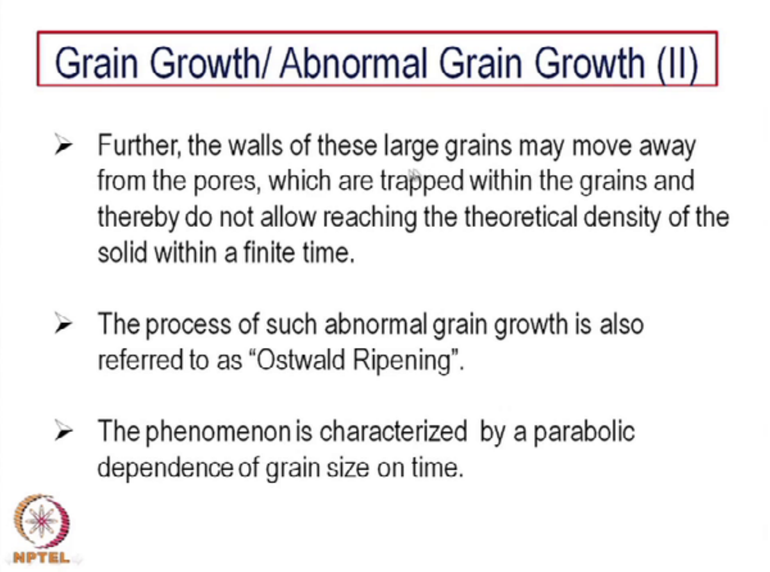

Grain Growth/ Abnormal Grain Growth (II)

- Further, the walls of these large grains may move away from the pores, which are trapped within the grains and thereby do not allow reaching the theoretical density of the solid within a finite time.
- The process of such abnormal grain growth is also referred to as “Ostwald Ripening”.
- The phenomenon is characterized by a parabolic dependence of grain size on time.

When there is a abnormal grain growth, the walls of these larger grains move away from the pores, so the pores interact within the grains. Normally the pores are supposed to be at the grain boundaries, then the pore elimination is easier or pore removal becomes easier, so the pores are the grain boundaries, than the pore removal is possible and one can reach the theoretical density is some definite within some definite time. However, if we entrap some of the pores and as you mentioned earlier, they are no longer perpendicular in shape rather becomes more spherical in shape. Once they become spherical in shape that may increase the number of grains actually phasing that particular pore and there is a possibility that they get stabilized. So, there is a possibility that no further pore removal takes place, so abnormal grain growth also has that kind of problem that, the pores do not getting entrapped and do not get the chance to be removed. The process of such abnormal grain growth is also referring as Ostwald ripening.

In fact, this was primarily taken from the metallurgical term mettle. They use this particular term quite often in the process. This is Ostwald ripening of the large grains and this grain growth is normally avoided, if you want to have better mechanical strength with a better plasticity of the material and to improve move to avoid brittleness. Normally higher is the grain size or abnormal grain particularly abnormal grain growth of few grains give rise to more brittleness. The phenomenon is characterized by a parabolic dependence of the grain size on time, so that is the analyst mathematical analysis which gives rise to parabolic dependence of grain size as a function of time.

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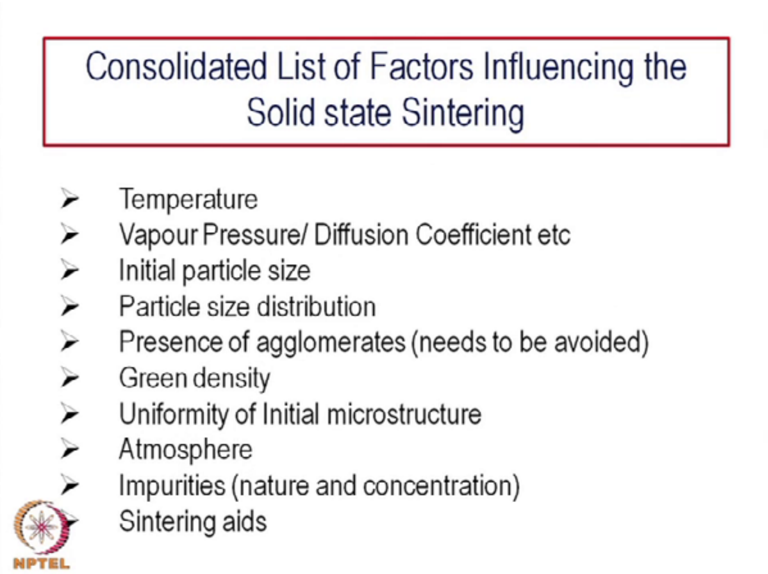

Consolidated List of Factors Influencing the Solid state Sintering

- Temperature
- Vapour Pressure/ Diffusion Coefficient etc
- Initial particle size
- Particle size distribution
- Presence of agglomerates (needs to be avoided)
- Green density
- Uniformity of Initial microstructure
- Atmosphere
- Impurities (nature and concentration)
- Sintering aids

Well, we have discussed quite a bit on different mechanisms of sintering. Different parameters, how they affect the sintering process of the grain growth, how they affect the densification? Whether there is a possibility of stabilization of certain pores under certain conditions? Many different things have been discussed and let me just go through a kind of summary, a consolidated list of factors influencing the solid-state sintering. There is large number of parameters, which actually affects the sintering process, impact to as mentioned earlier; the sintering is always very complex process.

There are many different micro processors which proceed simultaneously and they affect each other, so there is large number of factors which actually controls the phenomenon. The most important factor of course is the temperature as mentioned, we have discussing the rate equations, the temperature although it is normally in the denominator, but the numerator is a term either the pressure or the diffusion coefficient. These are actually exponential terms with temp exponential function of temperature and therefore, those parameters actually dominate. So, for this the temperature affect is concerned and in the central temperature, the whole sintering process is a thermally activated process and therefore, without temperature sintering, it just cannot take place.

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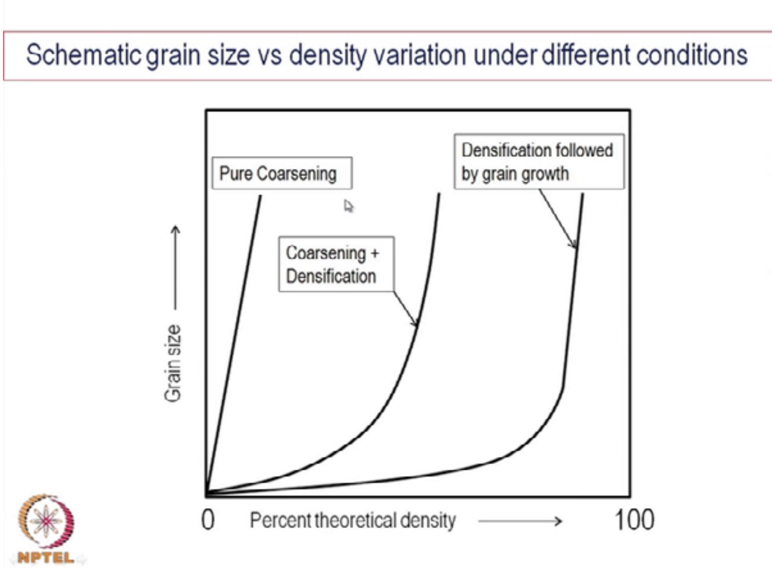

Schematic grain size vs density variation under different conditions

We need thermal activation energy to be supplied through the thermal process and therefore, temperature has a very important role to play. However, one also should mention the rate of heating is another very important issue, because it increase the temperature so fast that there may be a coalition of particles, but we have seen here coarsening of the particles and that may hinder the sintering process, so rate of temperature rise is also another very important issue during central vapour pressure on diffusion coefficient. We have already discussed, as we they have also an indirect effect of temperature. The vaporous pressure dependent temperature diffusion coefficient is also dependent on temperature and because our sintering is in the forms must transport to show, these parameters are also part of most important in diffusion coefficient in the sintering process.

The initial particle size we have seen in almost all the mechanisms, just like there is a temperature term. There is a vapour pressure on diffusion coefficient term, there is also incredibly the initial particle size term and always there, and it is a sparsely related to the rate of progress of the sintering process or the x by r, that are the area and the neck area growth of the neck area is related to the initial particle size and generally finer is the particle, a greater is the rate or faster is the process, so you need less time and also there is more possibility of getting the theoretical density, so almost all the pores can be eliminated and therefore, ceramics were particularly in advance ceramics. When you are talking about different kind of advance ceramics, not the conventional ceramics in advance ceramics particle size or particle preparation powder is a very important parameter or step in getting the dense materials, so there are many different techniques.

The powder preparation, mostly by a solution chemistry wrote a hydrothermal route and many different other routes cumbersome synthesis route show the idea to make a finer particle from micro fine to nano sized particles. These nano sized particles obviously has a faster rate of sintering and you can get better theoretical weightier density are densification by a sintering process. If you use it since we are talking about advance ceramics. This particle size is one parameter which can be controlled and that is normally done knowingly by better property, whether it is a mechanical properties or optical property or even electrical and magnetic properties, particle size distribution not only the average particle size, but the particle size distribution also has very important role as almost all ceramics know that the particle size distribution has an important bearing on the initial green strength or green density of the material pack particle packing. The particle packing can be optimized only through better particle size distribution, how much fraction is finer and how much is the action. Of course, the intermediate that determines the packing density and better is the packing density, larger is the initial density.

The initial poor faction is less and if you dense the room temperature to larger fractional to a larger extent, one can certainly get a better density option as presence of agglomerates need to be avoided. If you have agglomerates that mean the cluster particles, so if you have a non uniform density of the particles or agglomerates, of course soft agglomerate as well as harsh agglomerates. The soft agglomerates normally break under pressure whenever trying to either drive press or do it by other suspended particle technique and so on. The slip casting and the tape casting technique distribution or the particle distribution is very important particle suspension uniformity. The particle suspension is extremely important, if you do not have a uniformity of particle suspension, you and non uniform distribution of particles and that will immediately lead to non uniform sintering at different places at different sites and ultimately some pores will be trapped.

So, pore removal will be extremely difficult, if you do not have a uniform particle list dispersion in the step of a dry pressing or cold pressing or even cold isocratic pressing, which shows not only the particle size distribution is important. The agglomerates must remove, particularly the agglomerates shock tolerates can be broken during pressing or during suspension, but hard agglomerates, obviously have to be perfect. The density is also related to the particle size distribution as well as the agglomerates, so if you can have a higher green density before sintering at room temperature, obviously there is a possibility of achieving a better density after sintering uniformity of initial microstructure.

Once again it is related to some extent the particle agglomerates which must be avoided, otherwise any initial microstructure, the pore size distribution, initial forces distribution will be non uniform and that it will lead to non uniform pore structure and removal of a pore is difficult in that atmosphere. Of course, as an influence because it controls the defect structure of the material as the defect structure is also important, because ultimately the solid state definition is taking place by vacancy mechanism. Most of the time in vacancy mechanism, the atmosphere also has a very important role to control the concentration of vacancy at different places and therefore, their mobility also that atmosphere from that point of view is important, but it depends on the particular nature of the material. If it is an on stoichiometric material, atmosphere has a much greater importance or greater influence. If it is a stable material, it is not so stoichiometric material, more of mostly stoichiometric material, also their atmosphere may have a much less sense imperatives control which defect the properties and therefore, the point defects in particular and therefore by impurities you can control the sintering process. The impurities many times added intentionally.

These impurities lead to some liquid phase formation and the liquid phase facilitates sintering are just briefly discussed liquid phase sintering. The time is not much there, so I will just mention about what liquid phase is sintering. eight it is also kind of impurities going to solid solution of the form, and interacts with the basic material and they may form a liquid phase that helps it for sintering acts as both impurities sintering acts more or less have the similar characteristics, either they enhance the diffusion coefficient or increases the vapour pressure or reduces the vapour pressure or sometimes forms liquids.

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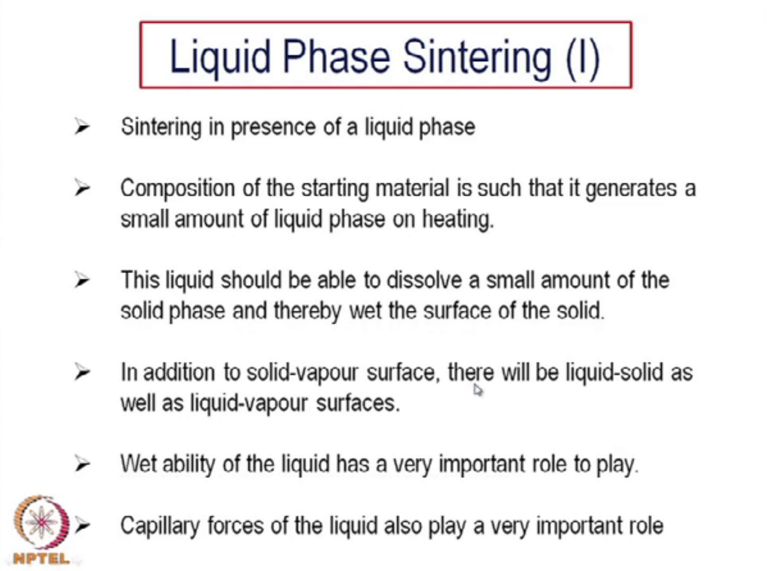

Liquid Phase Sintering (I)

- Sintering in presence of a liquid phase
- Composition of the starting material is such that it generates a small amount of liquid phase on heating.
- This liquid should be able to dissolve a small amount of the solid phase and thereby wet the surface of the solid.
- In addition to solid-vapour surface, there will be liquid-solid as well as liquid-vapour surfaces.
- Wet ability of the liquid has a very important role to play.
- Capillary forces of the liquid also play a very important role

So, all of them do have a significant effect on the Central process. What is highly unjust, briefly mention about the little. So far, have discussed about the solid-state sintering, the liquid phase sintering also important in many places. Many cases these are the different characteristics, let me go rad out sintering in presence of liquid face that is what we call the liquid phase sintering. The composition of the starting materials is such that, it generates a small amount of liquid phase on heating, so the composition has chosen for sometimes impurities to be added or some sintering eight subs to be added which forms liquid face and of course, the viscosity of the liquid phase is also very important. The viscosity surface tension and the surface energy, all of them are very important and also the activity the solid. All of them, normally the liquid is produced in a very small quantities, not even in 1 percent or maybe within 1 percent and then it reacts normally. It has a very low viscosity and a kind of high capillary action through which the liquid phase moves along the grain boundaries or along the particles interfaces and forms the bond liquid should be able to dissolve the small amount of the solid phase and thereby, with the surface of solid, so weight ability is another very important ability of that liquid with respect to the solid as is very important for the liquid phase sintering.

So, without weight ability the liquid is of no use. If a notable liquid is formed, that liquid certainly will not help sintering in addition to solid vapour surfaces because you have a additional phase liquid phase, so there will be liquid-solid as well as liquid- paper surfaces and those energy terms are also considered by while talking about the liquid phase sintering. Wet ability of this liquid phase, as I mention just now, liquid has a very important role to play in capillary forces of the liquid, also play a very important role because in between the grains, we have some kind of a capillary, the size of the pores or the openings of the capillary force also helps in the distribution of the liquid throughout the metrics.

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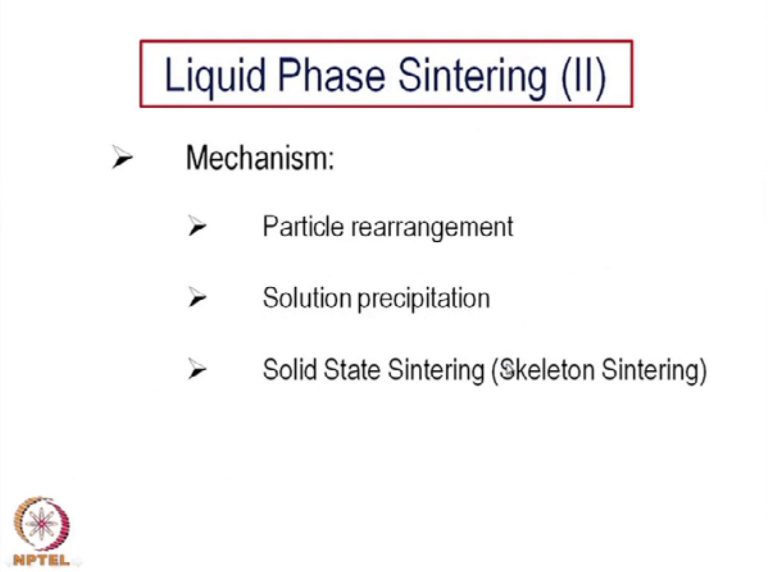

Liquid Phase Sintering (II)

- Mechanism:
  - Particle rearrangement
  - Solution precipitation
  - Solid State Sintering (Skeleton Sintering)

In case of liquid phase sintering, the three main stages or main mechanisms which help in sintering or bonding or removing the pores are particle rearrangement, solution precipitation and imper solution. The precipitation, re-precipitation and solid state sintering towards the end, while the temperature is relatively again in solid state sintering or some time called skeleton sintering which takes place. So, initially particle re arrangement because in presence of the particles with it, may be easier with loose particle to get rearrange and entangle which other and some densification takes place almost immediately, so that is a very fast process and then depending on the composition of liquid the dissolved part of the very fine layer of the solid surfaces gets dissolved and then it re-precipitates, they within the pores show that is another mechanism solution and precipitation is another mechanism and finally, the solid-state sintering also takes place, porous with later stage of the sintering process, by the time the densification has already taken place in presence of the liquid and because of the re-precipitation, the liquid should get a solidify and then solid-state sintering takes it over.

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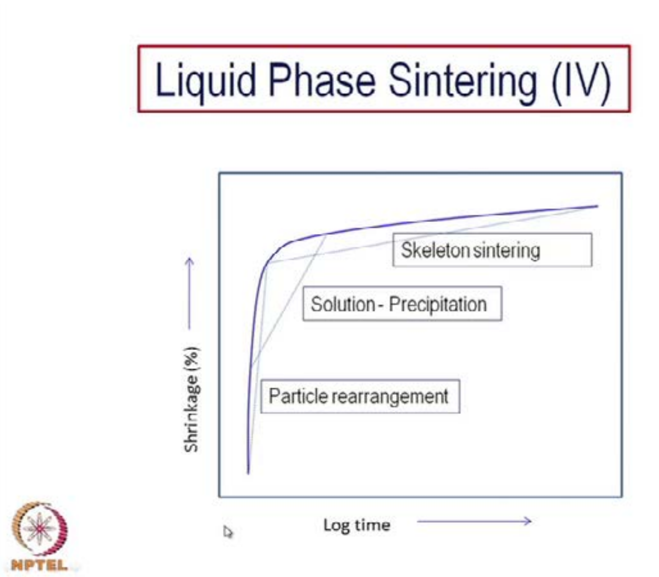

Liquid Phase Sintering (IV)

I think this is the site of liquid phase sintering, so if you plot log time against shrinkage which is a major of the extent of the densification or extent of sintering, you get a very steep price first and then guess flatten out. This is slightly different than the other mechanisms, so this first price takes place because of the particle rearrangement, then the solution and precipitation takes over it, goes together the particle rearrangement and solution precipitation overlaps and before this solution precipitation is complete, skeleton sintering also takes place in a kind of solid-state sintering. So, all this theme mechanisms actually a hawker one after the other in some cases take place simultaneously and that is out the liquid phase sintering is a very fast process and better densification.

Sometimes it is obtained with liquid precipitation, so there are many different examples of liquid sintering, particularly in advance ceramic. Some of them an actual materials, will discuss that in a class, so with this will come to the conclusion of the discussion on sintering and I hope we have been unable to give you some idea, what exactly the sintering means, how it can be performed? What is the basic purpose of sintering and what are the different mechanisms of sintering to take place and what is the importance of sintering in ceramics.

Thank you for your attention.