Advanced Ceramics for Strategic Applications
Prof. H. S. Maiti
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 40
Sintering of Ceramics (Contd.)

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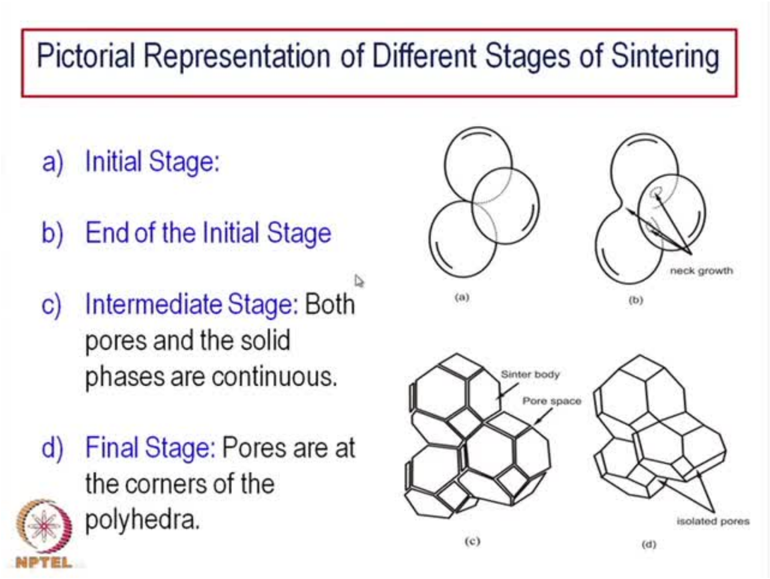

Pictorial Representation of Different Stages of Sintering

a) Initial Stage:

b) End of the Initial Stage

c) Intermediate Stage: Both pores and the solid phases are continuous.

d) Final Stage: Pores are at the corners of the polyhedra.

In this lecture also we will continue our discussion on sintering of ceramics. Earlier we are discussing about the three different stages of sintering; the initial stage of sintering, the intermediate stage of sintering and the final stage of sintering. We have described what actually mean by them and what kind of changes we expect in these three sequential stages. Here is a pictorial representation of the same stages. To start with, this is the initial stage where the particles are just touching each other and the contact is minimum, and there is no deformation of the particle.

They are the original particles, which are put together. So this is we start with and then the second one the b, it is the end of from this to this actually the initial stage. You can say it is the initials not the initials stage the starting point, these are, this this is the starting point and then the changeover which takes place from this to that whatever the time frame is and whatever the physical changes or geometrical changes takes place that includes the initial stage of centering. Here you can see some neck neck growth, it is called the neck growth, that means two particles, which were in point contact.

Now, the contact area has increased from this to this. This is actually a circular contact and the two-dimensional, we are seeing only the line and in addition between these are three particles. So, you have a contact area somewhere there and another conduct area there. So, this third particle is touching this particle and that other particle somewhere here in the form of another neck area. So, there are three different neck areas between one between these two particles another between these two particles, another between these two particles here. So, when as you have mentioned earlier when about 20 percent of neck growth is taking place, then we say the initial phase is over.

Then we go to the intermediate stage when has you can see from this to this. There is a quite significant change in the geometry of the particles, which were spherical in shape. Now, there is a polyhedra large number of polyhedra put together because more and more contact area has increased, a plainer surfaces has created between the two particles and therefore, we have more of polyhedras, different kind of polyhedras has been formed. Some of these polyhedras are actually, these polyhedras are basically grains now having different phase, plainer phase. One can say ideally one can have a dodecahedron kind of configuration, but such kind of ideal situation really not take place.

We do get different forms of polyhedral. Pores, which was in between these particles, interstitial spaces between these particles are now getting distributed along this grain boundaries, mostly along the grain boundaries. These are the pore phases, so this a continuous channel of pores. Once again its quite idealized is not exactly what we get in reality, but something like this happens. So, the pores are still continuous the solid are still continuous. So, that is the kind up to the end of the second the intermediate phase both pores and the solid phases are continuous.

Of course, the solid phases total volume of the solid phases are much larger because 90 percent of is occupied, 90 percent of the total volume is occupied by the solid only 10 percent is actually the pores. These pores are one you want to have a continuous phase naturally that dimensions will be more leaner in shape or cylindrical kind of dimension. So, that is what you get here and the final stages pores are the corner of the polyhedral. Unfortunately these pores are not properly drawn here. Actually these pores are not properly seen. It has been the only difference between here you can see these boundaries are much thicker here.

These boundaries are much thicker. Actually this thickness is basically because of the pores, whereas these boundaries are much thinner. So, those pores have been sunk, the boundaries thickness of the boundary has become less. There are no pores in between, so the boundaries have become sunk and more are less lie in contact now. Whereas the pores are not unfortunate, it is not shown here properly in the drawing the pores. Either will be at the corners, this triple point boundaries like this or like this here. So, most of them pores will be at the triple point boundaries or some of them some of the pores may also within the grains, within the grains that what we discussed earlier, the pores are no discontinuous.

No longer the pores are continuous like this, what happens in the throughout the second stage or the intermediate stage final stages, the pores becomes discontinued phases. The only about less than 10 percent is remaining, and therefore it cannot be continuous anymore. So, but the sides where the force will be there is primarily at the triple point boundaries either here or there or there or somewhere here most of them will be like that. But, few of them may be under certain situations maybe within the grains itself, its again not shown here, but we can imagine some force might be here or some force might be very small force might be there, that is what will call the residual pores.

So, as a result of mass transport and the change in the geometry, the pores or get not only becoming smaller and smaller, the volume becoming smaller the sizes are also become smaller and from a continuous stage up to this intermediate stage. They will be discontinuous at a later stage. Sometimes you will find later, we will discuss that once they become discontinuous the pore removal becomes much tougher and tougher.

Sometimes it becomes almost impossible to remove last traces of the pores and show getting a theoretical density is becomes almost impossible. But more than 99 percent or even 9 between 95 to 99 percent both removal is possible. It does not take lot of difficulties or difficult steps, okay? So this is kind of pictorial view of the progress of sintering, what happens in the total phenomena and how they can be subdivided into three different stages, having discussed all these things.

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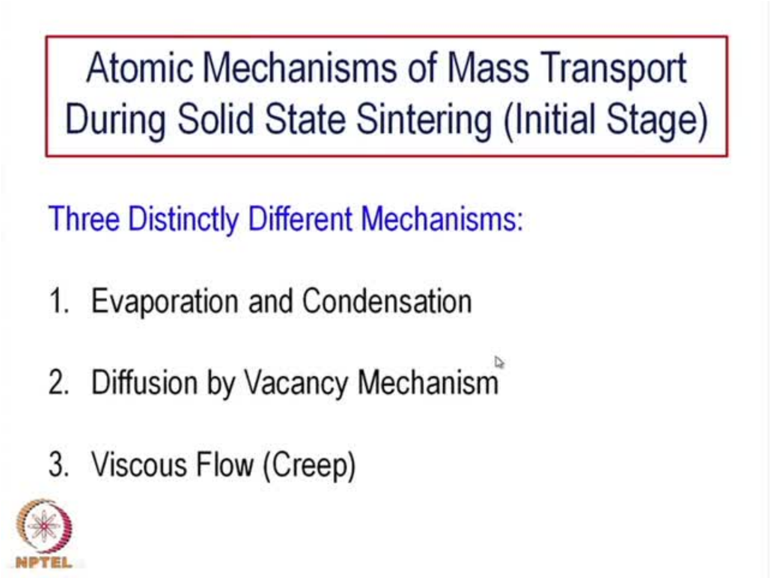

Atomic Mechanisms of Mass Transport During Solid State Sintering (Initial Stage)

Three Distinctly Different Mechanisms:

1. Evaporation and Condensation
2. Diffusion by Vacancy Mechanism
3. Viscous Flow (Creep)

Now, we go to little more details the atomistic or atomic mechanisms of mass transport during the solid state sintering. We have earlier seen that there are basically two types of sintering; one is the solid state sintering where there is no presence of liquid and another is the liquid phase sintering where there is a major quantity of liquid is produced to enhance or to facilitate the sintering process. Here we are talking about the solid state sintering.

Now, in the solid state sintering of course, the mass transport has to be there and we have seen there are two major mechanisms by which the mass transport can happen. One is the evaporation condensation that is when the vapour pressure of the solid is quite high. The vapour pressure of the solid is quite higher, it is very close to its melting point. The vapour pressure of course, increases quite substantially and in such cases evaporation condensation mechanism is predominant or is the dominant mechanism.

Whereas in the most of the cases most of the oxides have a diffusion mechanism or diffusion by vacancy mechanism, mass transport express not by evaporation condensation, but by diffusion and that again the diffusion can take place many way by many different mechanisms. Out of that vacancy mechanisms is normally the predominant mechanism by which a sintering takes place. Third one of course, is a viscous flow. This is not a in presence of liquid, but the solid itself becomes little bit viscous. In nature and particularly the grain boundaries and that also facilitates the mass transport along the grain boundaries. So that is also another mechanism we will discuss briefly about that.

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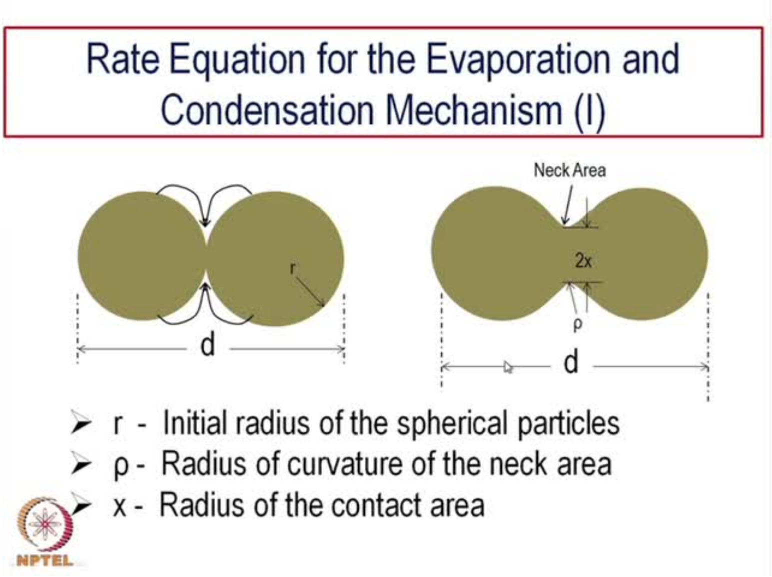

Rate Equation for the Evaporation and Condensation Mechanism (I)

- r - Initial radius of the spherical particles
- ρ - Radius of curvature of the neck area
- x - Radius of the contact area

Our main discussion will be on these two what exactly happens in atomistic scale by this mechanism. To start with we will first take up the evaluation condensation mechanism what exactly takes place at the atomic level, how the mass getting transported and what is the phenomena which takes place in such situations? What is the driving force evaporation condensation? We have already seen that there is a difference between vapour pressure difference of vapour pressure between the convex and the concave surfaces. So, just because the change of curvature sets up a driving force, now here what it happens?

If you we are just taking a two spherical spherical particles of course, this case there are uniform in size same size of spherical particles. That is how when they are compressed or they come together the condensation particles. So, this is the contact area or the conduct. In theoretically it is actually a point contact, but the otherwise reality there were be a slight finite volume or finite area. Now, once this contact is made there are two types surfaces created. This is the convex surface, this is a spherical surface, spherical convex surface. But at the point contact, at the point contact a very small convex, a concave surface is also formed.

So, once a small contact area is developed, you have a mostly it is a convex surface like this, but at this point of contact you have a concave surface also. This is the concave surface and because of that there will be a difference in vapour pressure. So, more amount of vapour will be generated on the convex surface the vapour pressure on the convex surface is more. Therefore, more and more amount of material will get evaporated from these surfaces. All these convex surfaces free surfaces. Of course, there should not be any other contact there may be other particle coming in contact then there will be another concave surface and so on.

So, whenever there is a contact there will be a concave surface and that concave surface and this convex surface makes all the difference. So, the vapour pressure will be much lower here because of the convex character. Whereas, or the convex surface the vapour pressure will be high. So, there will be pressure vapour pressure gradient and obviously from the higher pressure material will try to flow to the lower pressure to the equalize them, So, the material transport will go to the gas phase, it will not to the solid phase, but it will evaporate here at different points of course. Then there will be some vapours of the same material in the gas phase and because there is a concentration gradient much lower pressure vapour pressure is there, so they will try to condense, that the vapours will evaporate the material will evaporate here and try to go to the conduct vapour phase the gas phase.

Finally, condense at this convex, concave surface surrounding in the form of a circle actually from all the surfaces material will come in deposit here. So, it is not because by temperature gradient. Normally, if you heat to high temperature and then there is a cold zone in the material will be normally deposited at the cold zone. But this is not because of the temperature gradient it is because of the curvature change. Even at both both the points at the same temperature, this material will be transported from here to there and that is a very simple mechanism of evaporation and condensation mechanism.

So, from the concave surface, the materials will get evaporated and at the conclave area, the material will condense and because of this condensation the convex a concave area will slowly grow and that is what happens more and more material has deposited and this area increased. This area theoretically point contact area has gone to a circular area and this radius of curvature. Now, have changed now is changing also, which was more convex now becomes more flatter.

So, these will be more flatter, so more material will be evaporated and come here and this will grow a contact area will grow automatically and this will be a flatter and flatter. Till the pore shape is also getting changes you can see the corners are getting reduced, it is more become mean less concave, more and more radius of curvature you also going to change. So, in this process the center center of this particle to or the distance between the two centers is not going to change. This particle will not come closer to each other. This total distance in fact one should have drawn from the centre to centre and this centre to this centre. So, it is about same size is there, it is about the diameter of the distance is about the diameter of the sphere, so there is no change in dimension.

The overall dimension is not going to change by this kind of a mechanism. If this is the mechanism by which sintering is taking place the result is, there will be no change in dimension. There will be no shrinkage, no densification that is also another very important. Although by definition sintering do give rise to densification and that is one of the major effect of sintering. But in this particular ha mechanism evaporation condensation there is no densification, what does it mean? There is no densification, but even then there is a sintering.

Now densification is not a necessary condition for sintering more important condition is the mechanical strength. It is whether the particles the agglomerated particles or consolidated particles do have a better strength after sintering or not? That is a more essential condition. So, in that context there is a bond area, increase of bond area because there is a point contact originally. Now, we have much larger contact larger area, area of contact here and therefore, there is a increase in the bond area. So, there will be enhancement of strength.

So, this is more essential parameter or essential property after sintering or as a result of sintering. This may or may not happen; particularly in this case it is not happening. That does not mean that it is not getting sinter, it is getting sinter because the bond area or the contact area is increasing and consequently there is a enhancement of mechanical strength. So, that is an important concentration. So, I think it is very clear now that material is getting transported from the convex area through the gas phase to the concave area. That is how the concave area or or the contact area is slowly increased.

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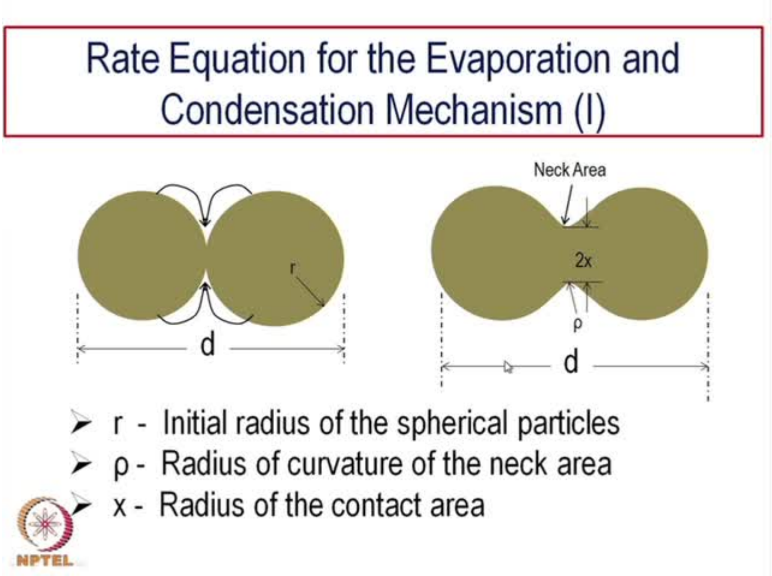

Rate Equation for the Evaporation and Condensation Mechanism (I)

- r - Initial radius of the spherical particles
- ρ - Radius of curvature of the neck area
- x - Radius of the contact area

So this is what we know about the basic physical process which is taking place in in evaporation and condensation mechanism well with this physical concept. Let us try to look at the rate equations whether we can write some equations relating the different parameters, the time, the temperature, how the growth is taking place and what rate it is taking place? What is the time dependence, temperature dependence, even is there any particle size dependence of this rate? This is for that we once again take the same example, same pictures.

Here we have introduced few parameters; we have introduced r the initial radius of the spherical particles. So, once again our assumption is we are having uniform size spherical particles not of different sizes, all of same size and they have a radius of r. Rho we also define a radius of curvature rho at the neck area. So, this is a concave surface and the radius of curvature is rho that is what we define. Another term or another parameter we also like to define is the x, the x is the actually half radius of the contact area. Here it is half the length, here in one two dimension or one dimension.

In fact it is actually a 2 dimensional circular contact area between the two particles and the radius of that circle is actually x, the radius of that circle is x. So, this distance from here to there is actually the diameter, this is the diameter of the circle and so it is 2 x, okay? So, actually it is x is a radius of the contact area the flat circular contact area.

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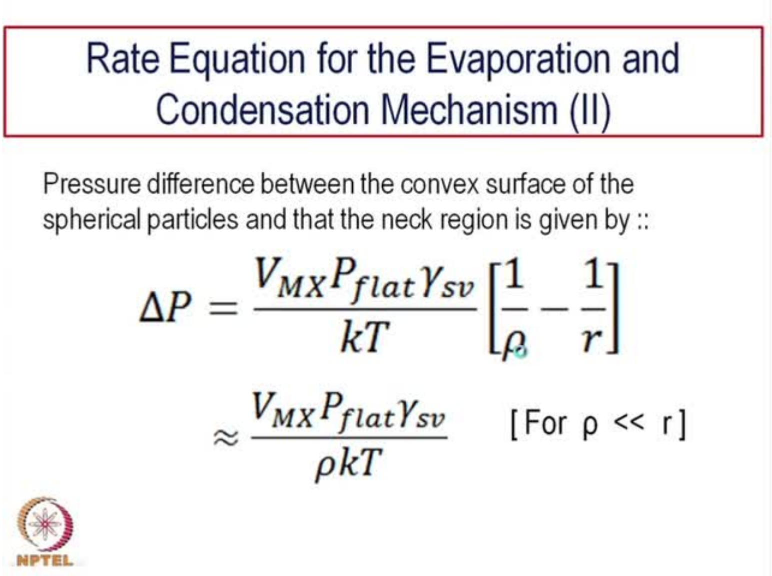

Rate Equation for the Evaporation and Condensation Mechanism (II)

Pressure difference between the convex surface of the spherical particles and that the neck region is given by ::

$$\Delta P = \frac{V_{MX} P_{flat} \gamma_{sv}}{kT} \left[\frac{1}{\rho} - \frac{1}{r}\right]$$

$$\approx \frac{V_{MX} P_{flat} \gamma_{sv}}{\rho kT} \qquad [\text{For } \rho << r]$$

If we define these parameters or take into consideration, these parameters, then we can write an equation of this form the pressure difference between the convex surface of the spherical particles. Then neck region, that the concave surface actually neck region is given by this formula, which can be derived, but this has not been derived here. We have just taken the dealt V dealt P the pressure difference. Once again this is related to the V M X that is the volume of the one following formula unit M X provided M X is a compound of which the particles are made of.

Then P flat, P flat peace of flat is actually that the vapour pressure or sometimes is also called the partial pressure, vapour pressure of the flat surface that the reference reference surface. Then gamma V is the solid to vapour surface energy solid to vapour surface energy, k T is the Boltzmann constant. Temperature time at is temperature and here there are 2 radius of curvature, actually one is 1 over rho, another is 1 over r, r is the radius of the sphere of the initial particle size of the sphere spherical particle size and rho is the radius of curvature of the concave surface or the neck region, that we have defined earlier this is rho.

This is X and this is r. X has not come so far, X will come later. This can be since rho is much much smaller than r compare to radius of the initial spherical particle, the rho the neck region the radius of curvature of the rho is much smaller. Because it is very very sharp peak, a sharp sharp radius there is although concave. But, it is a very sharp change in radius change in curvature. So the radius of curvature is much of smaller than r, so if that the… So, this becomes 1 by rho only 1 over r can be neglected and that becomes equal to this term multiplied by 1 over rho that is what you get here.

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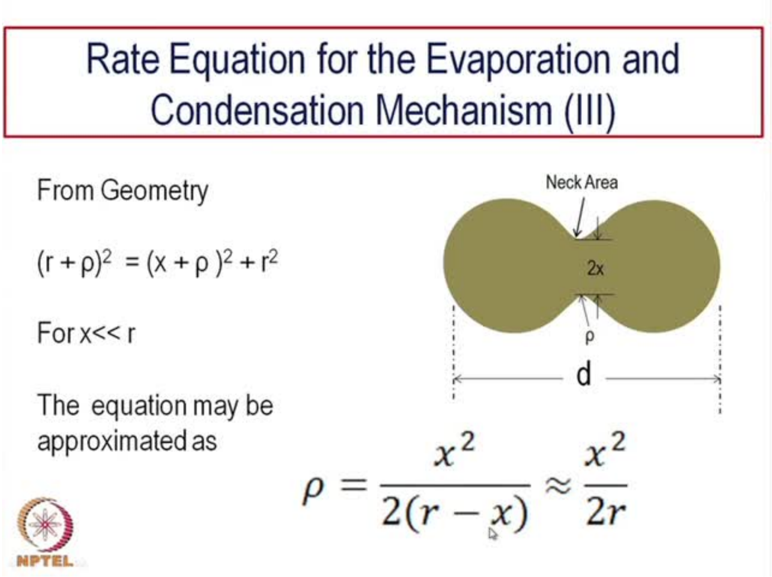

Rate Equation for the Evaporation and Condensation Mechanism (III)

From Geometry

$(r + \rho)^2 = (x + \rho)^2 + r^2$

For $x << r$

The equation may be approximated as

$$\rho = \frac{x^2}{2(r - x)} \approx \frac{x^2}{2r}$$

Then from the geometry one can also co relate this two terms on these two parameters, these three parameter. In fact, both are rho as well as X here again. It is shown what is rho? What is X? r is not shown here, r was shown in the earlier pictures. So, one can write r plus rho square whole square equal to X plus rho whole square plus r square. So, that is another sphere. Simply from geometry one can write that and once again if X is equal to X is also less than r, that means earlier we have seen rho is very less than the r this value.

We are also assuming that the X is much smaller than r, then the equation will approximated as rho equal to X square 2 by r minus X, which is approximately equal to X square by 2 r. Once again x is neglected. So, it becomes 2 r and X square remains there. So, rho becomes X square by 2 r. Now, that was the geometric relationship.

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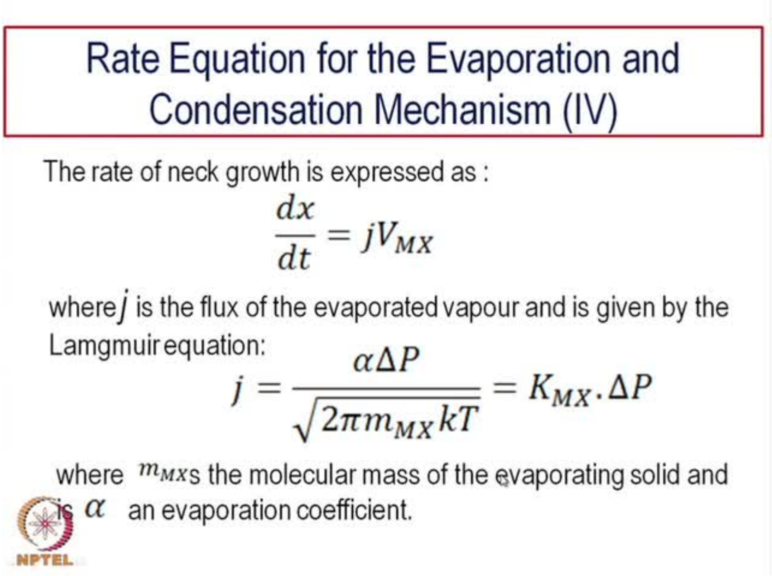

Rate Equation for the Evaporation and Condensation Mechanism (IV)

The rate of neck growth is expressed as :

$$\frac{dx}{dt} = jV_{MX}$$

where j is the flux of the evaporated vapour and is given by the Lamgmuir equation:

$$j = \frac{\alpha \Delta P}{\sqrt{2\pi m_{MX} kT}} = K_{MX}.\Delta P$$

where m_{MX}s the molecular mass of the evaporating solid and is α an evaporation coefficient.

Then we have earlier seen the delta P, which is the driving force, delta P we have equated. We have got some equation relating delta P and the radius of curvature. Then we have also seen how the radius of curvature is related to the other geometric parameters X and r? This is another both rho X and r is all the three geometric parameters are also related. Then we find what is the rate of neck growth at what rate material is getting deposited driving force is delta P? So, the delta P is the term, which basically determines at what rate the material is getting deposited.

So, the d x d t here that means the rate of growth more the material get transfers sorry, more the material gets transferred from here to here, the X grows, okay? So that is also a measure of the the rate of change of X or rate of growth of X is actually measure of the sintering rate, so that is also basically the sintering rate. That is how we have defined the sintering rate here. So, this is the sintering rate or the rate of change of X has a function of time and that will be equal to j, j is the basically the flux, the flux of the evaporated vapour and is given by the Langmuir equation, which will discuss later. But before that it is a flux into the atomic volume of the compound or the molecular form volume to compound.

So, and j is the amount of the material flowing in per unit per section. So, that is the flux, so and that flux again depend on the delta P. What is the pressure difference? So, the pressure difference in the flux is of course, proportional, but with some other terms. If you want the exact numerical or quantative equation or quantative equality, so that actually j can be this is called the Langmuir equation, which is a relates the flux and the vapour pressure difference between the two sites.

So, this becomes alpha and root over 2 by M X k t here again there are some terms has been introduced where M X is the, is I think there is a mistake here. When script M X is the molecular mass, it is mass know not the volume molecular mass evaporating solid and alpha is an evaporation coefficient. Once again the alpha has been wrongly placed, sorry I need to change.

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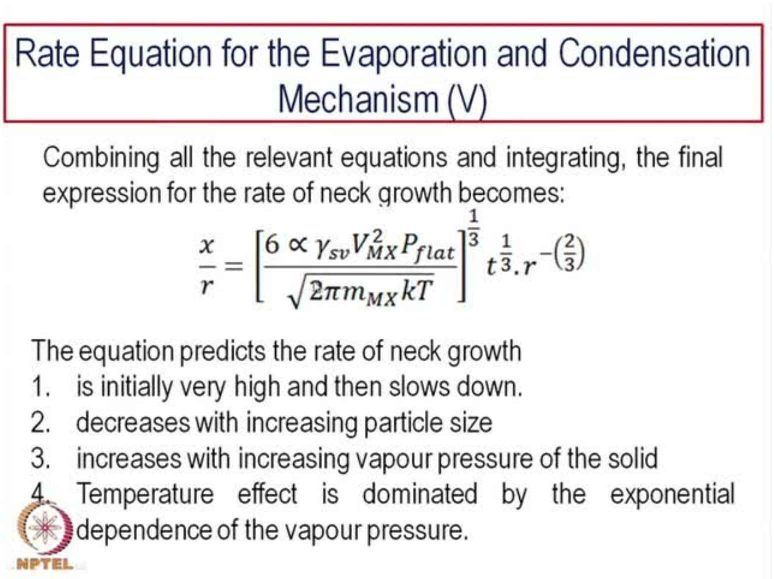

Rate Equation for the Evaporation and Condensation Mechanism (V)

Combining all the relevant equations and integrating, the final expression for the rate of neck growth becomes:

$$\frac{x}{r} = \left[\frac{6 \propto \gamma_{sv} V_{MX}^{2} P_{flat}}{\sqrt{2\pi m_{MX} kT}}\right]^{\frac{1}{3}} t^{\frac{1}{3}} . r^{-\left(\frac{2}{3}\right)}$$

The equation predicts the rate of neck growth

1. is initially very high and then slows down.
2. decreases with increasing particle size
3. increases with increasing vapour pressure of the solid
4. Temperature effect is dominated by the exponential dependence of the vapour pressure.

So, to continue with that related equation combining all the relevant equations and integrating the final expression for the rate of neck growth that is how normally this x by r, this is by a ratio is actually term has the neck growth or the x as a relative to the particle size, initial particle size. So, that is a kind of kinetics or the growth of the sintering process. That is the how the x is increasing, x is increasing from 0 to some value and with respect to r. So, this becomes this kind of an equation, we are not going to details this is the final equation, but it gives us a lot of clue, how this reaction is changing and what are the different parameters which controls this behavior, which controls this phenomena?

6 alpha gamma is v ha V M X square and P flat piece of flat means the vapour pressure in the flat surface. Then in the denominator you have root over 2 phi M X that is the

mass of the formula unit and k and T temperature. This is to the power of one-third and then there are two other terms, two other parameters which is time, T is the time and then r is the initial radius, initial radius of the particle. That is raised to the power minus two-third. So, this is a quite a complex relationship, but it gives us very important information.

So, for as the dependence of this process on different experimental parameters are concerned, so this if this equation predicts the rate of neck growth, how at what rate with particular the respect to time, how it is growing and how it will grow? Obviously, there are different material parameter as well as extremental parameters which, which determines this rate. The neck growth is initially very high and then slows down, because with time the exponential, the exponent is about is one-third.

It is suddenly non-linear, it is a carved relationship and initially with lower values of T it grows quite fast, but as we increase the time it slows down it becomes more or less constant sometime and almost at it at it as it reaches the 100 percent density or 100 percent growth, the rate becomes very slow or almost nil. That is one information we get from this equation, than the number 2 information is it decreases with increasing in particle size because r is here, r is the initial particle size. Now, this is inverse, this is a r this is negative. Therefore, larger r means the rate is slow, higher is the r the rate will be slow x by r will be less.

So, it decreases with increase in particle size, so higher is the particle size, the sintering process will be slower and slower. That is the reason when you are talking about to getting a very 100 percent dense material; you have to have very fine particle size to start with. A millimeter size material may not centre at all whereas; a micron size or a nano meter size particle will centre much faster. So, that is the reason particle size is very very important, particle size very very important in the sintering process. So, it is not only the temperature, temperature effect of course, will come later just now in a minute, it is time of course, is the anyway in the determining factor. Larger the time the densification will be more.

Of course, in this particular case there is now densification, but the sintering will take place, the neck growth will take place. So, even if there is a neck growth there is no densification that we have seen earlier. So, both time and the initial particle size are the two most important parameters, which actually determines the sintering process, but another very important parameter is the temperature. Now, temperature has a little tricky effect here. For example, temperature here in the denominator, so as if increasing the temperature will decreases the rate, but it is not so.

It is not? So, the temperature here is the temperature is there, but more important temperature effect is here. This will not change too much with temperature, there will be slight changing in gamma of course, but not much. But the more important effect is here in the vapour pressure. Now, the vapour pressure it is not been shown, that the vapour pressures is an exponential exponential depends on the temperature. So, higher is the temperature vapour pressure increases exponentially. Whereas, this is a denominator in the route to the per half.

So, the temperature actually comes in the form of the vapour pressure. So, increases with increases in increases in vapour pressure of the solid. That is quite obvious. Vapour pressure means this one is increasing as it increases directly, almost direct is not directly proportional is the one-third exponent is there. So, but it is proportional to this directly proportional actually it is not linearly proportional. The temperature effect is dominated by the exponential dependence of the vapour pressure not by this denominated term.

It is dominated by this term, so the vapour pressure increases exponentially temperate and therefore, the x by r also will increases quite significantly with temperature. So, there are three different parameters, which actually determines the rate; one is of course, the time, then the initial particle size and temperature. These are the three things which one is to take to control the sintering process for evaporation condensation mechanism. Of course, this has been derived for evaporation and condensation mechanism although, but very similar things are also valid or very situation very similar situations are also valid for the other mechanisms as you will see in few minutes.

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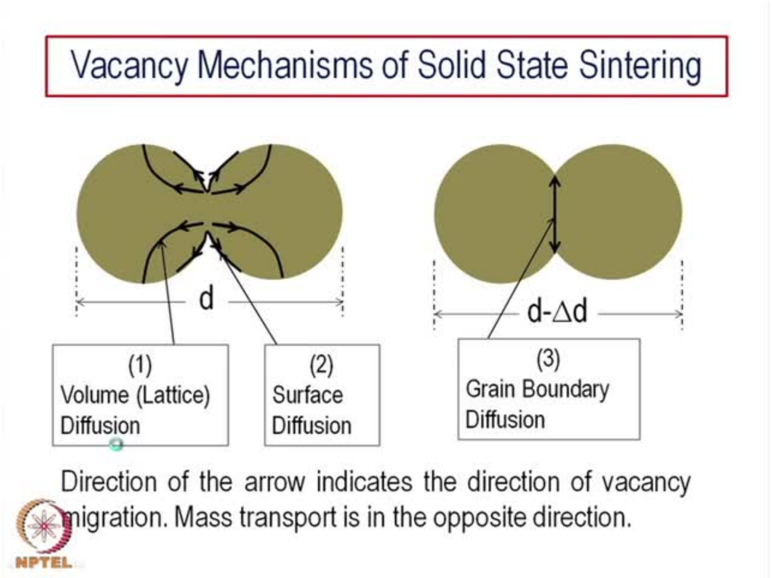

Vacancy Mechanisms of Solid State Sintering

(1) Volume (Lattice) Diffusion

(2) Surface Diffusion

(3) Grain Boundary Diffusion

Direction of the arrow indicates the direction of vacancy migration. Mass transport is in the opposite direction.

So that was all about the evaporation and condensation mechanism. Once again I just try to recapitulate that going back to the particular picture or the figure here. One of the things the we have concluded that there is no shrinkage. There is no shrinkage because the material is not getting removed from here. The shrinkage has to take place these two particle has to come closer, but it is not happening on the some extra material is getting deposited. That is how the neck growth is taking place, so there is no dimensional change. Overall dimensional change is not there, only the shape of, shape of the pores are changing.

Shape of the pores is changing, which was a very sharp corners here in the pore, where this part is the pore. This part is the pore, so which there is asharp corner which has been a a slightly less sharp corner. So, the shape of the particles will shape of the pores are changing, but there is no change in the overall pore fraction or percentage of the pores. So, that is a very important thing one must remember where this is in comparison to the next mechanism, which is the vacancy mechanism. This is the vacancy mechanism of solid state sintering and there as you have seen the concentration differences is in opposite direction.

That means at the concave surface here, once again there is a neck growth here same thing. At this point there is a concave surface and away from that point is there is a convex surface. So, this convex surface the vacancy concentration is low, where as the concave surface the vacancy concentration is high. So, the vacancies will move from this concave surface to the convex surface. So, the movement will be opposite, so far has the vacancy are concerned compared to what we saw in case of vapour deposition or vapour transport. So, from this region the vacancies has to move out. Now, vacancy moving out means there is a there is a void desecrated and that void will be filled up by the materials or the atoms from the surroundings.

So, if vacancy concentration the vacancies are moving out there is a high vacancies concentration the vacancies are moving out, which means material is getting filled up here. So, that is the situation, so that is what is happening here. The vacancies are going out and the material is getting deposited from this to that or the from this to this end. So, the ultimately it forms neck in the form of a grain boundary, what we call a grain boundary region. This is this is one crystal, this is another crystal and boundary is basically a grain boundary. So, from the grain boundary region the vacancies are moving out towards the convex surfaces. Now, this movement can take place again by three different paths. Three movement of the vacancies can take place in three different ways or three different paths, can be followed by this movement. Now, for this movement one is these are the three different paths, which is been designated here are shown here also.

The vacancies are moving on this through the lattice, through the solid through the bulk of solid. So, this is called volume diffusion or lattice diffusion that means the vacancies, that is the point defects, which being created here or generated here because of the high concave surface or very strong concave surface or one can say very small radius of curvature of the concave surface is a negative curvature. So, large concentration of vacancies are already generated because of this curvature and that has to go out to equilibrate. So, if the sufficient thermal energy or the artificial energy is provided, this high concentration of vacancies will tend to distribute redistribute itself and it will go towards the convex surfaces.

So, it can go it can come here it can go there it can go there and so on. So, every where it will get distributed and this distribution can take place either by this path through the bulk of the volume a bulk of the solid, which is called the volume diffusion or the lattice diffusion. It can go through the surface, it can just very near to the surface. It will not go to the bulk of the solid, but the vacancies will move along more or less along the surface just near the surface and that is called the surface diffusion. This can go like this, the vacancies which is generated here or the vacancies which are generated there will go inside, go inside because this becomes a flat surface. This becomes a concave surface, a convex surface.

So, there is a gradient between this point and that point, same thing there is a gradient between this to that also. Although the gradient is less, but the compared to the flat surface this is also more. So, the vacancies can go along the grain boundaries. So, basically at this point the vacancy is the highest vacancy concentration is highest here. The vacancy concentration is less here and also relatively less there. So, the vacancies can move from this to this towards that or from this towards that. Then here from this along the surface or along the bulk, so there are three different paths, which the vacancy can follow. Accordingly there are three different mechanisms and the rates are also will be slightly different.

So, the direction of the arrow indicates the direction of the vacancy migration. Of course, here it is slightly misleading may be actually it is vacancy is moving from this point to that point or from this point to that point that possibly has not been drawn well. So, but the vacancies are moving along this line, which is a basically a flat flat surface. So, the mass transport is in the opposite direction, so when vacancy are moving out materials are moving in are in fact because of the vacancies the materials are slowly coming in.

There will be a collapse, there will be a collapse of this surface or they will come closer. So, as a result of this vacancy mechanism unlike evaporation and condensation will have a change in dimention, this d this distance will be less d minus delta D. So, after the growth of the neck there will be a change in dimension. So, that is one of the most important effect of vacancy mechanism as compared to evaporation condensation.

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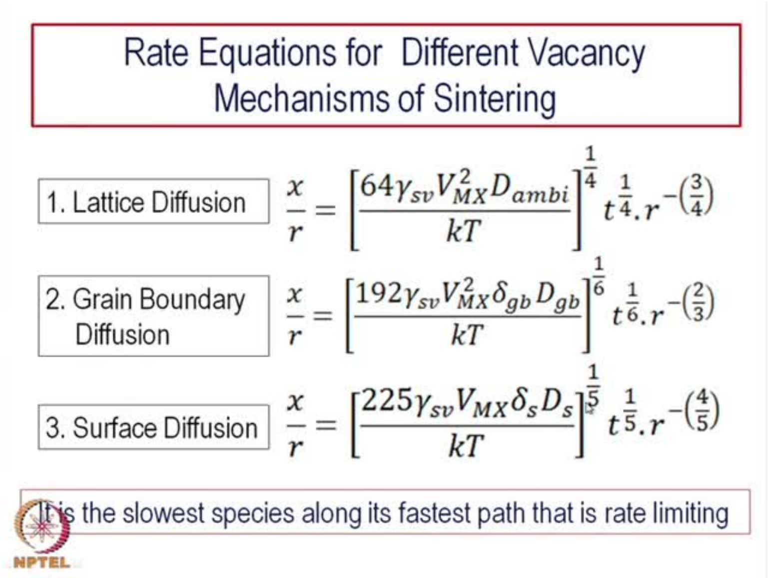

Rate Equations for Different Vacancy Mechanisms of Sintering

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

Now, there are three different mechanism or different paths, the vacancy can follow and that is why the three different names have been given, as mentioned earlier also. The lattice diffusion, the grain boundary diffusion and the surface diffusion and the equations for the rate equations are also different. We are not go into the details of that, but more or less in the same manner, which we have done in case of evaporation condensation one can go through that kind of analysis, mathematical analysis and find out this kind of a a rate equations here.

Once again the ultimate parameter, which you would like determine is the x by r in each case as also in the case of evaporation condensation. Only thing we have introduced few more terms like diffusion, D is the diffusion coefficient here, instead of vapour pressure earlier we have use vapour pressure, here it is diffusion coefficient. All through it is diffusion coefficient one type or the other, this is one kind of diffusion coefficient, this is another kind of diffusion coefficient, this is another kind of diffusion coefficient, but they are all diffusion coefficient of the vacancy movement.

These are D subscript (( )), will define that what is that actually. It is ambivalent D ambivalent or the ambivalent diffusion coefficient and then g b is the grain boundary diffusion coefficient of the same vacancy. Then the surface diffusion coefficient, we have introduced three different paths, three different paths all of them are diffusion coefficient controlled by the diffusion coefficient. But the values of diffusion coefficient their activation energies will be different.

That is why different terms have been used here. Then of course, this numerical values of course, again different one is 64 or there are 192 and another 125, but everywhere you have the gamma, the surface energy surface to solid paper. Sorry, solid vapour surface energy term everyone it is there, this term is also there M square X a V V V M X square is also V M X square, but here it is only V M X, it is linear not the square. Then you have an another two terms here which is delta g b and delta s. That term is not there, the first one that is not there.

And k T of course, denominator k T is all the time present. So, delta g b delta g b is actually thickness of the grand boundary, thickness of the grain boundary and delta s is the thickness of this surface, through which the vacancies are moving that is the path which is falling. Then these exponents are different. One case is one-fourth, one-sixth and one-fifth. So, it is not too difficult to remember, but once again they are not that significant, but the exponents are suddenly there. Then these two terms are as usual there, the time term and the radius of of the initials spheres or the spherical particles. Spherical particles are there and then these exponents are also different. One is three-fourth another is two-third and four-fifth.

So, obviously there dependence on the particle size are slightly different, but they have all negative exponent which means higher is the radius of course, sorry the higher is the particle size lower will be the rate, lower will be the neck growth here. Again as time increases the neck growth increases obviously, but at different rates and even the slopes will be different and one would be reaching the flat too faster than the other. In all of this it is the slowest species along its fastest path that is the rate limiting. Well there are different, we are talking about the vacancy mechanism, but we have not talked about which particular vacancy?

Is it the metal vacancy? It is a oxygen vacancy? If it is a more complex oxide, there may 2 or 3 different cations, there may be 1 cations or 2 cations. So, all of them have different rates of diffusion. All of them may follow the vacancy mechanism for diffusion, but the rates will be different, which we have not talked about here in this particular case. In fact the so called ambivalent and diffusion coefficient takes care to some extent of that particular situation.

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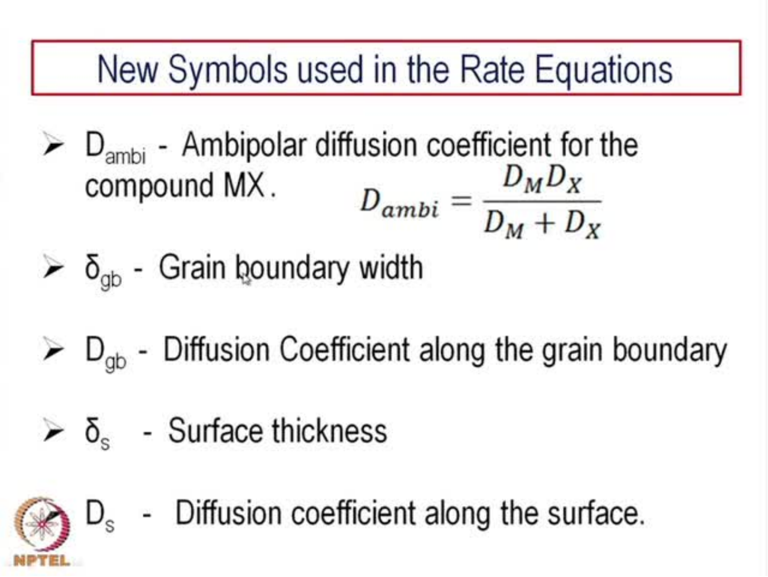

New Symbols used in the Rate Equations

- 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 is a, which we have already told you that this are the different parameters, but this is ambivalent diffusion coefficient for the compound itself because it is the compound, which is defusing or moving. So, but when you talk about diffusion coefficient the compound as such is not moving, is moving by either throw a vacancy of this or a vacancy of that. One of them will be predominant, so the diffusion coefficient of the compound is something like this.

This is a diffusion coefficient of the metal to diffusion coefficient of the anion or the cation and the anion, then diffusion coefficient of the cation and anion. So, this D subscript ambi, that is the ambivalent ambipolar not the valent sorry, ambipolar, ambipolar diffusion coefficient.

I may give important this is ambipolar, I might be telling ambivalent, it is not ambivalent it is ambipolar, ambipolar diffusion coefficient for the two different ions or the cations. One is the cation and the anion is related like this. So, I think the time is up, so you have two complete this discussion here or close this discussion here for the time being. But we have some more things to discuss so far as the sintering is concerned and we will do that in the next class.

Thank you and thank you for your attention.