

**Powder Metallurgy**  
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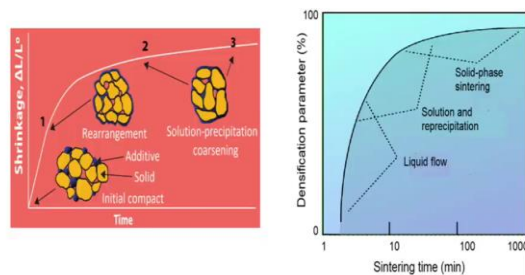
**Lecture – 54**  
**Liquid Phase Sintering – 4**

Hello everyone and welcome back to this lecture series on Powder Metallurgy. Right now, we are on this topic Liquid Phase Sintering and so, far we have discussed about the basic mechanisms. And then we started discussing about the different stages and the different mechanisms which are operative in these stages.

In the previous class we talked about the first stage of the densification in this process and it was through particle rearrangement, which happens due to the capillary force which is exerted by the liquid. Once the liquid forms and the particle surface is wetted by the liquid a capillary force is developed and due to that the particles rearrange themselves.

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**Sintering Stages**



So, this is what we have seen in the previous class. That is the first stage or the initial stage of densification in the liquid phase sintering process.

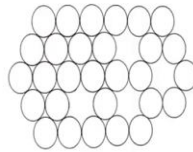
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## Rearrangement



### Liquid redistribution

- At small volume fraction liquid fills the isolated necks.
- Increasing the vol. fraction – 3-fold coordinated pores will be filled by liquid.
- When all of the 3-fold pores are filled, the liquid redistribution will happen by filling the necks around 6-fold coordinated pores - Third stage
- Finally in the fourth stage 6-fold coordinated pore are filled.



And then we also talked about the liquid redistribution as to how it happens during this rearrangement process and how does it lead to the rearrangement of the particles that also we have discussed. We have discussed about different types of pores and how they get filled by the liquid as it is redistributed.

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## Particle Rearrangement

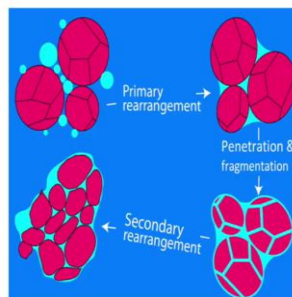


### Primary rearrangement:

- Rapid rearrangement soon after formation of the liquid.

### Secondary rearrangement:

- When  $\gamma_{sl}/\gamma_{sl} > 2$ , liquid penetrates the grain boundaries and particles fragment. Rearrangement of these fragments is the *secondary rearrangement*.



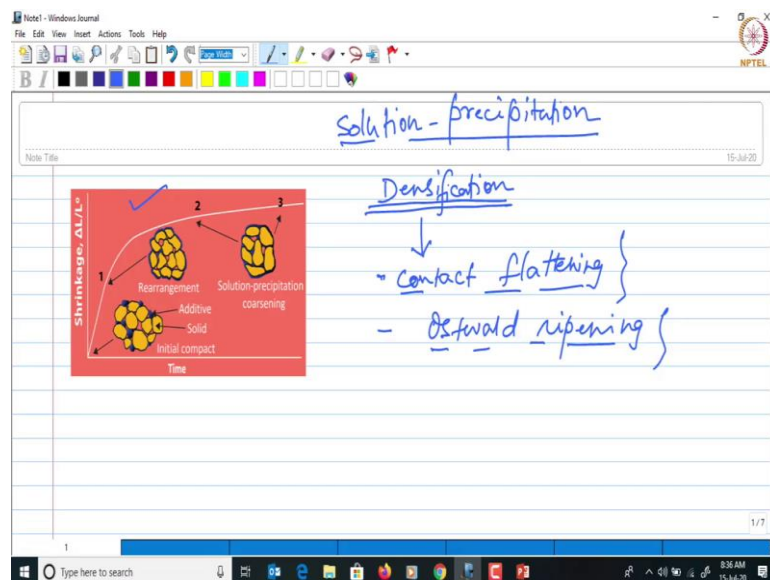
And then finally, we talked about two types of rearrangement. One is primary rearrangement and the other one is secondary rearrangement. The primary rearrangement is due to the rearrangement of the main constituent particles due to the capillary action of

the liquid, while the secondary rearrangement is because of the penetration of the liquid into the grain boundaries of the particles.

So, here when the solid-solid surface energy becomes more than the solid-liquid surface energy the liquid penetrates the grain boundaries as we have discussed before. And, as the liquid penetrates the particles fragment into smaller pieces as we could see from this particular figure over here (above image).

And, the secondary rearrangement is all about the rearrangement of these fragmented particles. So, today we are going to continue on this and see the next stage of the liquid phase sintering process in this particular class.

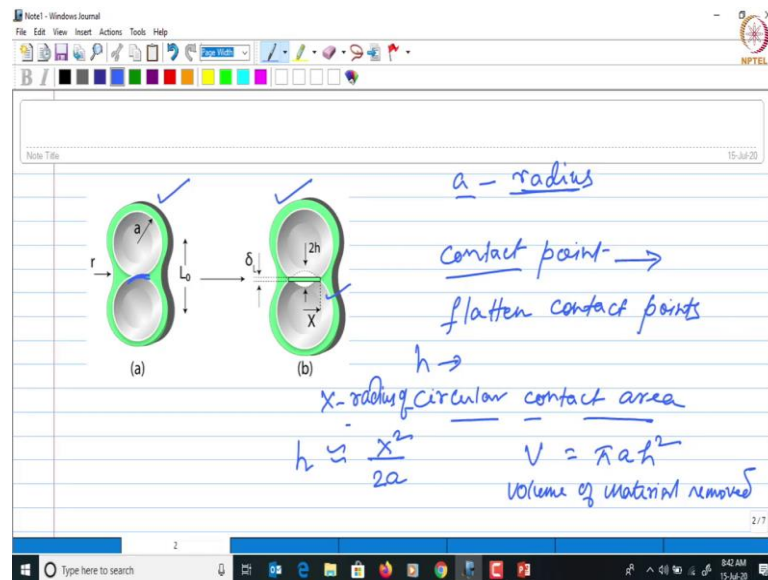
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The next stage of the densification process is solution precipitation as you can see from this figure once again (above image). As I was discussed before the small grains dissolve in the liquid and then re-precipitate over the larger grains.

The densification in this stage can occur through two modes. One is by contact flattening and the other mode is through Ostwald ripening which is accompanied by the grain coarsening because in this case the bigger grains grow at the expense of the smaller ones. Let us first talk about the contact flattening mechanism.

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Here the model which is proposed for the densification mechanism through contact flattening considers two spheres of similar size as you could see in this figure here (image in the above slide). Let us say the radius of the sphere is  $a$  and these two are in contact. So, the initial center to center distance is  $L_x$ . Now, the solubility at the contact points is higher compared to other places on the surface of the particles.

Therefore, the mass will be transported away from the contact points and as a result of that these two particles will move to each other as the contact points dissolve along the line, which connects the center of these two spheres. As that happens, the contact points will get flatten which you can see from figure b. So, let us say due to this center to center approach of these two particles due to the dissolution of the contact points, let us say each sphere is moved by a distance  $h$  and let us say  $X$  is the radius of the circular contact area.

As you can see from figure b,  $h$  and  $X$  are related to each other by this equation.

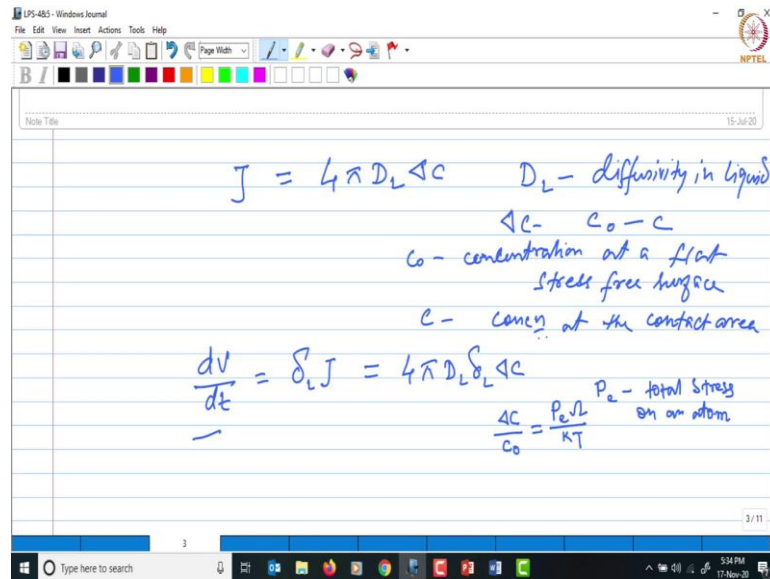
$$h \sim X^2/2a$$

The volume of material which is removed due to this center to center approach is given as

$$V = \pi a h^2$$

Now, let us see what is the diffusion rate through this liquid in this stage.

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The flux from the boundary per unit thickness  $J$  is given as,

$$J = 4\pi D_L \Delta C$$

Where  $D_L$  is the diffusivity in the liquid and  $\Delta C$  is the concentration difference, where  $C_0$  is the concentration at a flat stress free surface and  $C$  is the concentration of the solute atoms at the contact area. And the rate of material removal  $dv/dt$  that is given as,

$$dv/dt = \delta_L J$$

Where  $\delta_L$  is the thickness of the liquid bridge. And replacing  $J$  over here we will get  $dv/dt$  equal to,

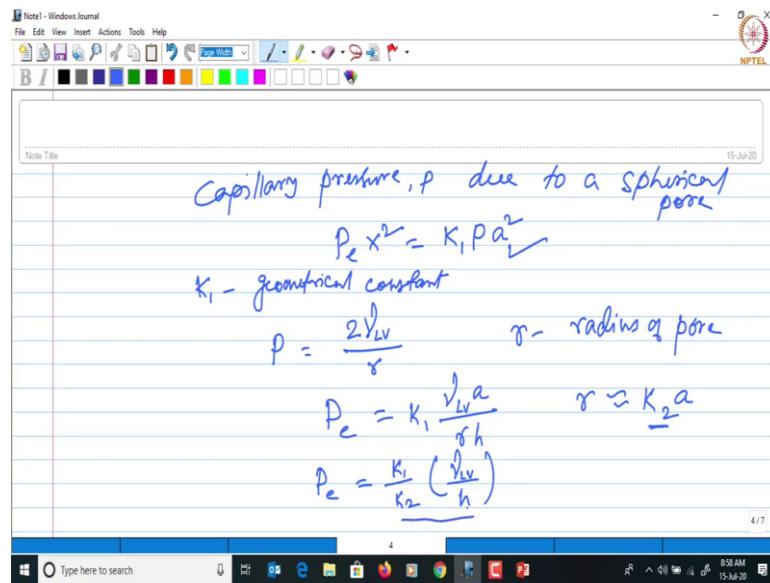
$$dv/dt = 4\pi D_L \delta_L \Delta C$$

$\Delta C$  is small and can be written as this,

$$\Delta C / C_0 = P_e \Omega / KT$$

where  $P_e$  is the total stress on an atom,  $\Omega$  is the atomic volume and the other terms have their own meanings their usual meanings.

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Now, if the capillary pressure is P, a force balance would give this equation,

$$P_e X^2 = K_1 P a^2$$

where  $K_1$  is a geometrical constant. And we have seen before that the capillary force P is given as,

$$P = 2\gamma_{LV}/r$$

Where r is the radius of the pore. This capillary pressure is actually due to a spherical pore in the liquid. So, now if you substitute P in this equation then we get  $P_e$  as this.

$$P_e = K_1 (\gamma_{LV} a / r h)$$

Now, assuming that the radius of the pore is proportional to the sphere radius that is r is proportional to a or if you introduce this constant r equals to,

$$r \sim K_2 a$$

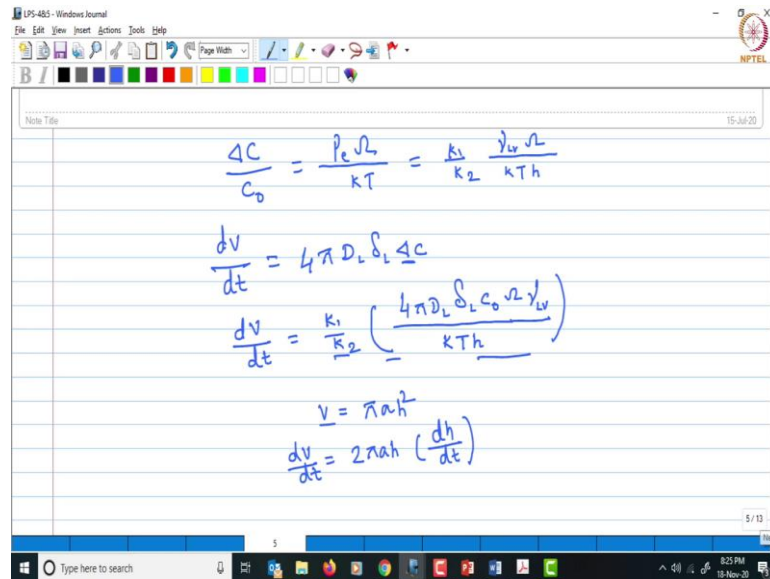
From there we get  $P_e$  as this.

$$P_e = K_1 / K_2 (\gamma_{LV} / h)$$

So, from here  $\Delta C$  by  $C_0$  can be written in terms of  $P_e$ . So, if we replace  $P_e$  from here into the  $\Delta C$  by  $C_0$  equation then we will get the following equation.

$$(\Delta C / C_0) = P_e \Omega / KT = K_1/K_2 (\gamma_{LV} \Omega / KT h)$$

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And now, if we take  $dv/dt$  from here,

$$dv/dt = 4\pi D_L \delta_L \Delta C$$

and replace  $\Delta C$  over here then we would get  $dv/dt$  as follows.

$$dv/dt = K_1/K_2 (4\pi D_L \delta_L C_0 \Omega \gamma_{LV} / KTh)$$

And we have also seen before that the volume  $V$  is given by,

$$V = \pi a h^2$$

So, from here we would get  $dv/dt$  as this.

$$dv/dt = 2\pi a h (dh/dt)$$

So, now, if we replace  $dv/dt$  over here then we would get the following expression.

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$$h^2 dh = \frac{2K_1 D_L \delta_L C_0 \Omega \gamma_{LV}}{K_2 a K T} dt$$

Integrating with boundary  $h = 0$  at  $t = 0$  conditions

$$h = \left( \frac{6K_1 D_L \delta_L C_0 \Omega \gamma_{LV}}{K_2 a K T} \right)^{1/3} t^{1/3}$$

$$h^2 dh = (2K_1 D_L \delta_L C_0 \Omega \gamma_{LV} / K_2 a K T) dt$$

And now, if we integrate this with the boundary conditions  $h = 0$  at  $t = 0$ . Then we will get an expression for  $h$ .

$$h = (6K_1 D_L \delta_L C_0 \Omega \gamma_{LV} / K_2 a K T)^{1/3} t^{1/3}$$

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$$\frac{\Delta L}{L_0} = \frac{h}{a} = \frac{1}{3} \frac{4V}{V_0}$$

$$\frac{\Delta L}{L_0} = \left( \frac{6K_1 D_L \delta_L C_0 \Omega \gamma_{LV}}{K_2 a^4 K T} \right)^{1/3} t^{1/3}$$

$a^{4/3}$   
 $\delta_L^{1/3}$

And now, the shrinkage  $\Delta L$  by  $L_0$  is given as,



$$\Delta L / L_0 = h/a$$

Which is also equal to this, one-third  $\Delta V / V_0$ . And therefore, the shrinkage is equal to if we put the value h from here if we substitute h which we derived just now then the shrinkage becomes this.

$$\Delta L / L_0 = (6K_1 D_L \delta_L C_0 \Omega \gamma_{LV} / K_2 a^4 K T)^{1/3} t^{1/3}$$

So, shrinkage varies with one-third power of time. That is the densification which is basically given by shrinkage. Densification in this mechanism varies with one-third power of the sintering time.

And you can also see that the densification is inversely proportional to the four-third power of the particle size. So, each again means that the shrinkage is higher for lower particle sizes or the densification is higher for lower particle sizes and the densification also increases with one-third power of the thickness of the liquid boundary. This is when the diffusion through the liquid is the rate controlling mechanism.

These are the parameters which affect the densification in this particular mechanism of solution precipitation. But, the mass transport rate can also be controlled by the interface reaction which leads to dissolution of the solid into the liquid if it is slower.

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Interface reaction controlled

$$\frac{\Delta L}{L_0} = \left( \frac{2k_1 k_3 C_0 \Omega V_{LV}}{k_2 a^2 k T} \right)^{1/2} t^{1/2}$$

$k_3$  - reaction rate constant

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So, for the interface controlled mechanism following a similar approach it can be shown that the  $\Delta L/L_0$  that is the shrinkage is given by the following equation.

$$\Delta L/L_0 = (2K_1K_3C_0\Omega\gamma_{LV}/K_2a^2KT)^{1/2} t^{1/2}$$

Where  $K_3$  is the reaction rate constant for the interface reaction. Here you can see that shrinkage scales with square root of time unlike the previous case when it was proportional to one-third power of time.

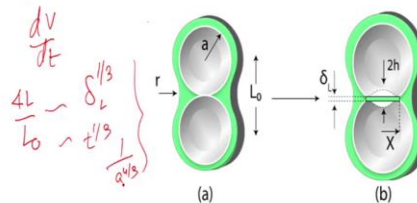
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## Solution-Precipitation



### Densification by Contact Flattening:

- Solubility at contact points is higher due to the capillary force of the liquid.
- This difference in solubility (chemical potential) leads to mass transport away from the contact points and the center-to-center distance decreases (shrinkage and densification).
- Each particle (spherical, radius =  $a$ ) dissolves giving rise to flattened contact area of circular profile of radius  $X$ .
- Center-to-center movement  $h = X^2/2a$ . Volume of materials removed from each sphere  $\approx \pi X^2h/2 \approx \pi ah^2$



So, that was the contact flattening mechanism of densification during the solution precipitation stage of liquid phase sintering. Let us take a moment to summarize this lecture. So, to summarize we can say that there are two modes of densification during the solution precipitation stage. One is by contact flattening and the other one is by Ostwald ripening. Today we have discussed the contact flattening mechanism of densification. Here the particles approach each other along the center line as the contact point between them dissolves due to a compressive capillary stress that works at the contact points.

And, since the solubility at the contact point is higher compared to that in any other portion of the particle there is a chemical potential difference and due to that the mass is transported away from the contact points. And as a result of that the contact points become flatten and the center of the particles approach each other along the line which joins the centers of the two particles like what you can see over here.

So, this center to center approach as a result of the dissolution of the contact points leads to a flattened contact area between the particles. And this center to center movement or the extent of movement  $h$  is given by the radius of the contact area and the radius of the particle through this particular equation. And then we talked about the rate of material removal  $dv/dt$  and we have seen it basically depends on the diffusivity, the thickness of the boundary layer or the thickness of the liquid bridge  $\Delta L$  and of course, the concentration.

And, using these two particle model the kinetics of the process that is the time dependence of the densification was derived. And as by now densification is manifested by the shrinkage;  $\Delta L$  by  $L_0$  which is given by  $h/a$  in this particular case, where  $h$  is the center to center movement of the particles due to the dissolution of the contact points between the particles and  $a$  is the radius of the particles.

So, first  $h$  was derived from the material removal rate  $dv/dt$  with an expression like this. And from that the shrinkage  $\Delta L$  by  $L_0$  was derived as  $h/a$ , which will ultimately give rise to an expression like this. So, first  $dv/dt$  was derived and from that we derived the shrinkage of the densification.

And here we have seen that it varies with one-third power of the thickness of the liquid bridge, one-third power of the sintering time  $t$  and inversely varies with the four-third power of the particle size. So, as the contacts flatten and the material is transported away shrinkage takes place and that is how the densification occurs in this case. So, that is all I have for this class today, but I will see you soon again.

Thank you for your attention.