Powder Metallurgy
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Lecture – 52
Liquid Phase Sintering – 2

Hi everyone and welcome back. In the last class we have started Liquid Phase Sintering and we have seen the basic driving force for this process in the last class.

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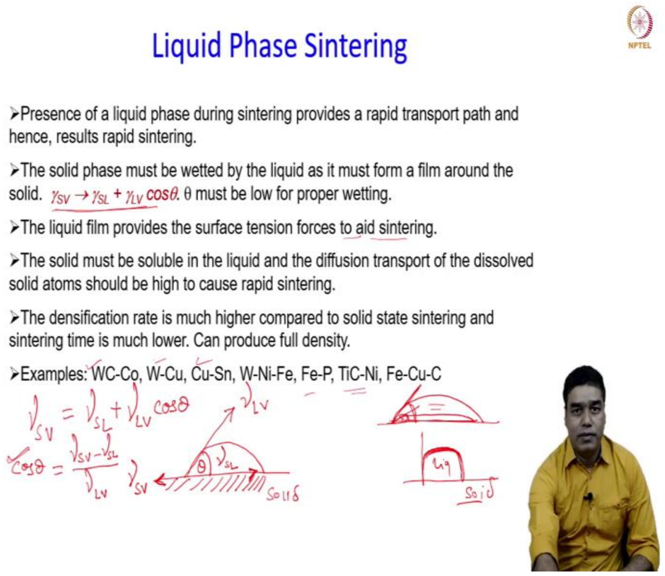

Liquid Phase Sintering

- Presence of a liquid phase during sintering provides a rapid transport path and hence, results rapid sintering.
- The solid phase must be wetted by the liquid as it must form a film around the solid. $\gamma_{SV} \rightarrow \gamma_{SL} + \gamma_{LV} \cos\theta$. θ must be low for proper wetting.
- The liquid film provides the surface tension forces to aid sintering.
- The solid must be soluble in the liquid and the diffusion transport of the dissolved solid atoms should be high to cause rapid sintering.
- The densification rate is much higher compared to solid state sintering and sintering time is much lower. Can produce full density.
- Examples: WC-Co, W-Cu, Cu-Sn, W-Ni-Fe, Fe-P, TiC-Ni, Fe-Cu-C

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

We have learned that the driving force for the liquid phase sintering comes basically from a rapid transport path, which is provided by the liquid once the particle surfaces are wetted by the liquid.

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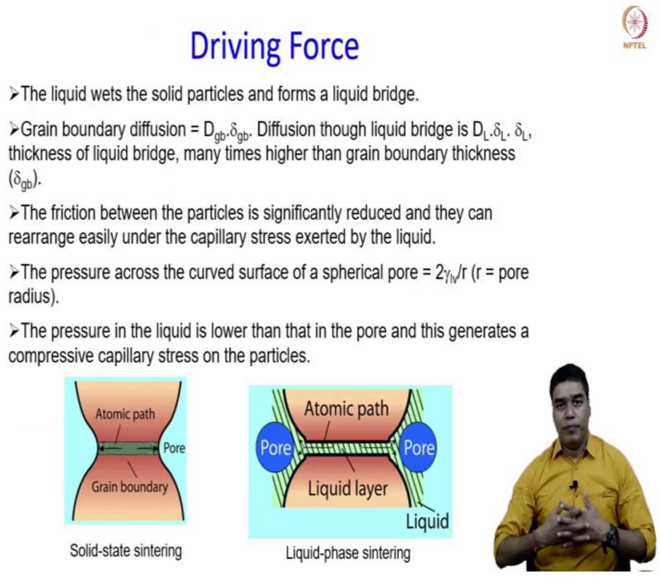

Driving Force

- The liquid wets the solid particles and forms a liquid bridge.
- Grain boundary diffusion = $D_{gb}.\delta_{gb}$. Diffusion though liquid bridge is $D_L.\delta_L$. δ_L, thickness of liquid bridge, many times higher than grain boundary thickness (δ_{gb}).
- The friction between the particles is significantly reduced and they can rearrange easily under the capillary stress exerted by the liquid.
- The pressure across the curved surface of a spherical pore = $2\gamma_{lv}/r$ (r = pore radius).
- The pressure in the liquid is lower than that in the pore and this generates a compressive capillary stress on the particles.

Solid-state sintering

Liquid-phase sintering

Once that happens, once the solid particles are wetted by the liquid it forms a liquid bridge, and through that bridge an enhanced diffusion path is provided for the densification to take place.

This diffusion is much higher compared to the grain boundary diffusion, which occurs in case of solid state sintering in the sense that, the diffusion length or the thickness of the boundary across which the diffusion occurs is much larger in case of the liquid bridge compared to the grain boundary thickness, in case of the solid state sintering.

Therefore, if you see the diffusion across a grain boundary and across this liquid film or the liquid bridge that you have, because of the higher thickness of the liquid bridge compared to the grain boundary thickness.

The diffusion is much higher and therefore, you get an enhanced densification in the liquid phase sintering process. So, that is the advantage of having this liquid phase. Therefore, this is a process of choice for sintering materials which are difficult to sinter by conventional solid state sintering.

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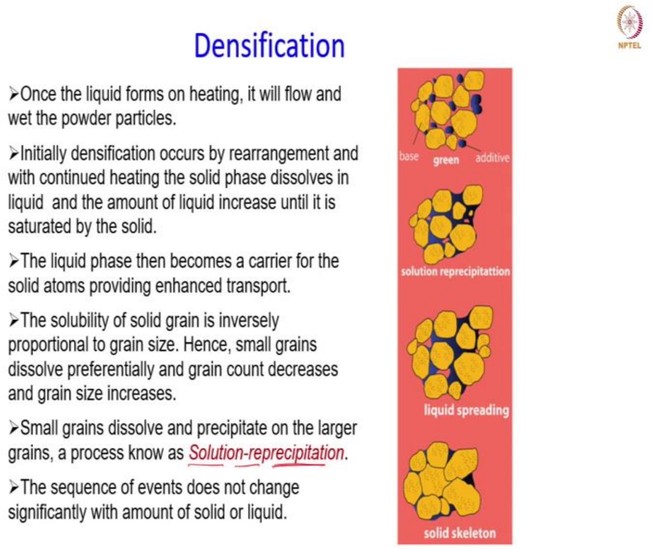

Densification

- ➢Once the liquid forms on heating, it will flow and wet the powder particles.
- ➢Initially densification occurs by rearrangement and with continued heating the solid phase dissolves in liquid and the amount of liquid increase until it is saturated by the solid.
- ➢The liquid phase then becomes a carrier for the solid atoms providing enhanced transport.
- ➢The solubility of solid grain is inversely proportional to grain size. Hence, small grains dissolve preferentially and grain count decreases and grain size increases.
- ➢Small grains dissolve and precipitate on the larger grains, a process know as *Solution-reprecipitation*.
- ➢The sequence of events does not change significantly with amount of solid or liquid.

Now we will have to see the densification mechanism as to what exactly happens during the liquid phase process. And, in the previous class we just started discussing this as to what happens when the liquid forms. And, we had seen that when the liquid forms and it spreads over the solid surfaces, basically it creates a capillary force on the particles and due to that the particles rearrange themselves.

That is the starting of the densification process, when the particles start to rearrange themselves, because of the penetration of the liquid. In this class we are going to continue on that and see how this densification takes place and what are the different stages of liquid phase sintering? This slide shows you the sequence of events which occur during liquid phase sintering. First the liquid forms as it is heated and once the liquid forms, it will flow and wet the powder particles.

Initially densification occurs by rearrangement and with continued heating the solid phase dissolves in the liquid and the amount of liquid increases until it is saturated by the solid. These two thing we have already seen. As we discussed the solid should have some solubility in the liquid for this process to continue and then the liquid phase becomes a carrier for the solid atoms providing enhanced transport.

Once, the solid is dissolved into the liquid, it becomes a faster transport path for the atoms. And, the solubility of the solid grains is inversely proportional to grain size. Therefore, small grains dissolve preferentially, and grain count decreases, and the grain size increases. So, when the small grains dissolve they will actually re-precipitate on the larger grains, and this is a process known as solution-reprecipitation. We are going to talk about this in more detail and this sequence of events does not really change significantly with amount of solid or liquid.

This is how the process goes? But, in order to understand the densification mechanism as to what exactly happens and how the liquid helps in the densification process. We need to first understand as to how and when does the liquid form and how does it penetrate the solid? So, let us first discuss that and then we will come back to this densification mechanism again with regard to the liquid phase sintering process.

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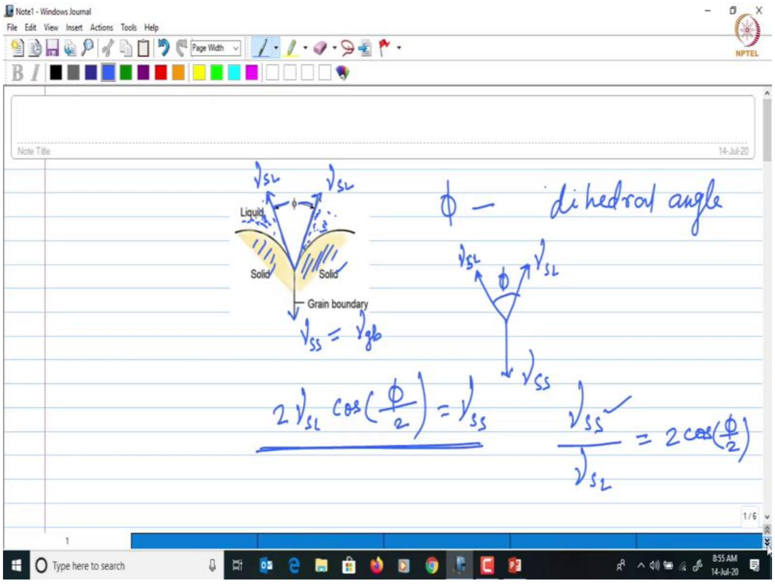

$$2\gamma_{SL}\cos\left(\frac{\phi}{2}\right) = \gamma_{SS}$$

$$\frac{\gamma_{SS}}{\gamma_{SL}} = 2\cos\left(\frac{\phi}{2}\right)$$

Consider two solid grains in contact with the liquid, like this these are the solid grains (first image in the above slide) here and the liquid is around it. So, it has made a contact at the corners of the solid grains and due to the surface energies the liquid will form a group or a neck like this with a particular angle. So, this angle is known as dihedral angle (ϕ). This is an angle between the solid liquid surface energies and the solid-solid surface energy, which is actually the grain boundary energy.

So, it is like this (second image). Now, if you take the balance of forces here, we will get,

$$2\gamma_{SL}\cos(\phi/2) = \gamma_{SS} \quad \text{-----------------------} (1)$$

From here you can see that, the ratio γ_{ss} that is the ratio between the solid-solid interfacial energy (γ_{SS}) and the solid liquid interfacial energy (γ_{SL}) is equal to $2\cos(\phi/2)$. If you take a plot between the dihedral angle and this ratio then it will appear like this (first image in the below slide).

$$\gamma_{SS} / \gamma_{SL} = 2\cos(\phi/2)$$

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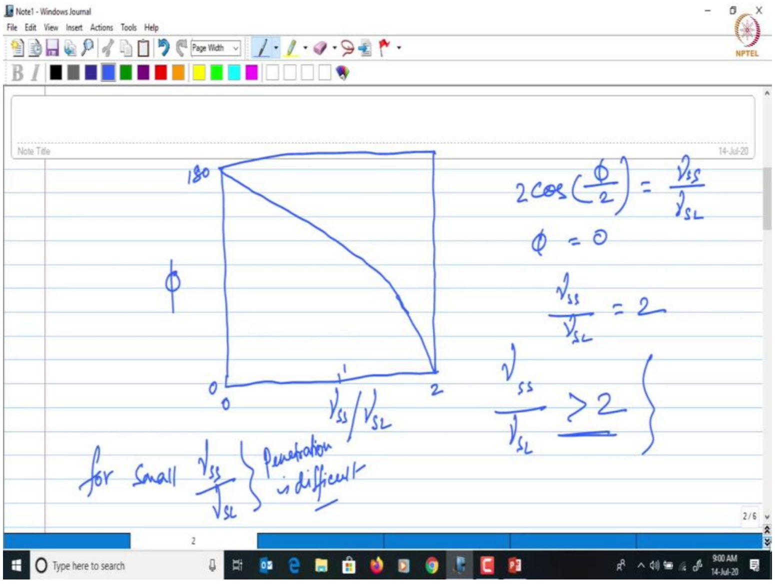

$2\cos\left(\frac{\phi}{2}\right) = \frac{\gamma_{ss}}{\gamma_{SL}}$

$\phi = 0$

$\frac{\gamma_{ss}}{\gamma_{SL}} = 2$

$\left.\frac{\gamma_{ss}}{\gamma_{SL}} > 2\right\}$

for small $\frac{\gamma_{ss}}{\gamma_{SL}}$ } Penetration is difficult

From here you can see that, when ϕ is equal to 0, this ratio is equal to 2, which means that when ϕ becomes 0 the solid-solid surface energy will just balance the solid liquid surface energies. Ttherefore, when this becomes greater than 2, this ratio becomes greater than 2; the liquid will penetrate the grain boundary.

Because, in second case the two solid liquid surface energies that you have will be less than the solid-solid surface energy or the grain boundary energy and as a result of that, when the liquid penetrates the grain boundary, the energy of the system will decrease.

That is why there is a driving force for the liquid to penetrate when this becomes greater than two. That is how, the situation is created for the liquid to penetrate the grains of the solid. And, it all depends on the surface energies, on the other hand when this ratio is small, the liquid will simply spread over the solid surface and it becomes difficult for the liquid to penetrate.

So, only when the solid-solid surface energy exceeds the solid liquid surface energies by more than a factor of 2, then only the liquid penetrates the grain boundaries. So you need a very small dihedral angle for the liquid penetration to happen.

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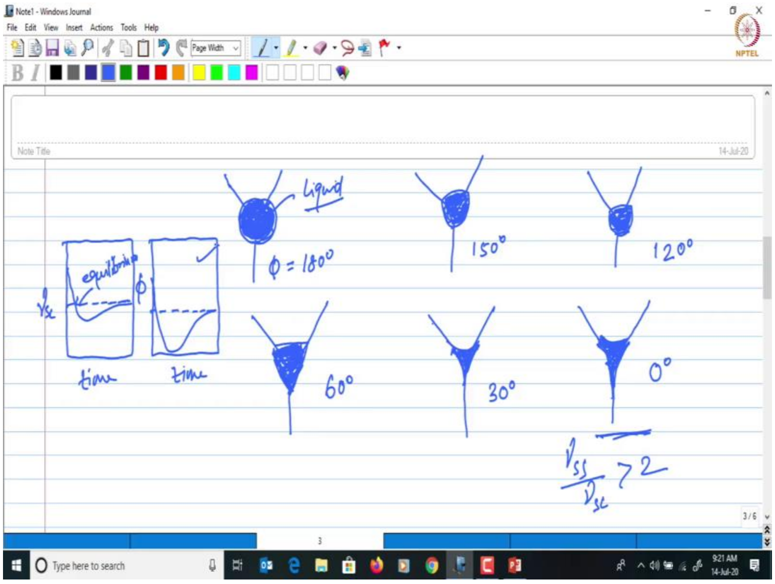

And, the scenario for different values of the dihedral angle as to how the liquid shape will be that can be depicted through a diagram like this. This is when the dihedral angle is equal to 180° (first image in the above slide). The liquid will simply spread over and as the angle is reduced, this spreading will also reduce (second one) and the shape of the liquid will change.

For example, this kind of shape is obtained for phi equal to 150°, this is for 120° (third one), then as you decrease it below 90°, then it kind of becomes like penetrating towards the grain boundary. For example, this is for 60° (fourth one) and then as it is decreased further down (30°-fifth one), then it starts to penetrate the solid grains and when it becomes 0 (sixth one).

This is when the solid liquid surface energies are just balanced by the solid-solid surface energy. And, beyond this a complete penetration will take place, when this ratio becomes more than 2. So, for the liquid penetration to happen, the solid liquid surface energy has to decrease and one of the driving forces for that is the waiting transient, which happens during the salvation process as the solid dissolves in the liquid.

The solid liquid surface energy kind of fluctuates as you could see from here (left hand side image in the above slide), this dash line that you have that shows the equilibrium value, for the solid liquid surface energy. But, as that salvation happens as the solid dissolves this kind of fluctuates and goes below the equilibrium value and due to that, the dihedral angle also decreases. So, this kind of waiting transient as it is called leads to a significant decrease in the solid liquid surface energy leading to a decrease in the dihedral angle and creating the conditions for penetration.

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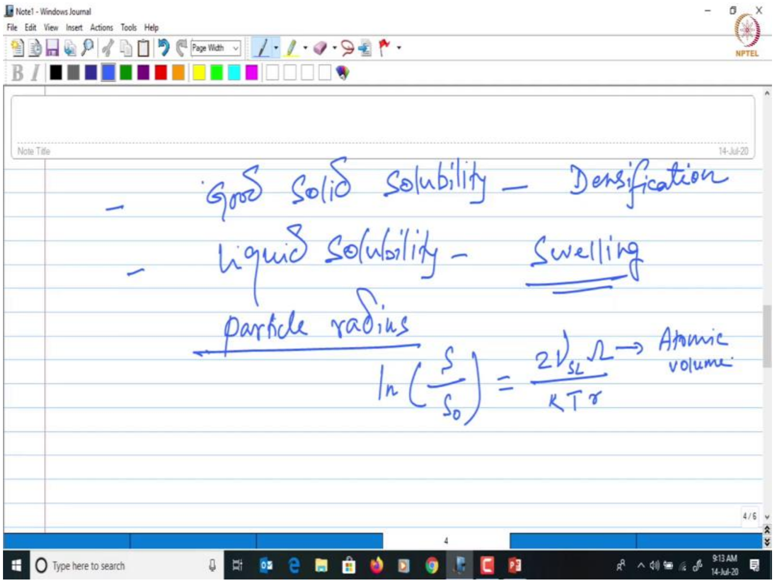

- Good Solid Solubility – Densification
- Liquid Solubility – Swelling

particle radius

$$\ln\left(\frac{S}{S_0}\right) = \frac{2\gamma_{SL}\Omega}{kTr}$$

$\Omega \rightarrow$ Atomic volume

Now, the other condition for this liquid penetration to happen and a better densification path to come into picture. The other condition is that the solids should be having some solubility in the liquid. Therefore, we need to also see the effect of the solubility. If you consider both the solubilities that is the solubility of the solid and that of the liquid good solubility product solid leads to densification. So, let us take an example to understand the effect of the solubility on the densification.

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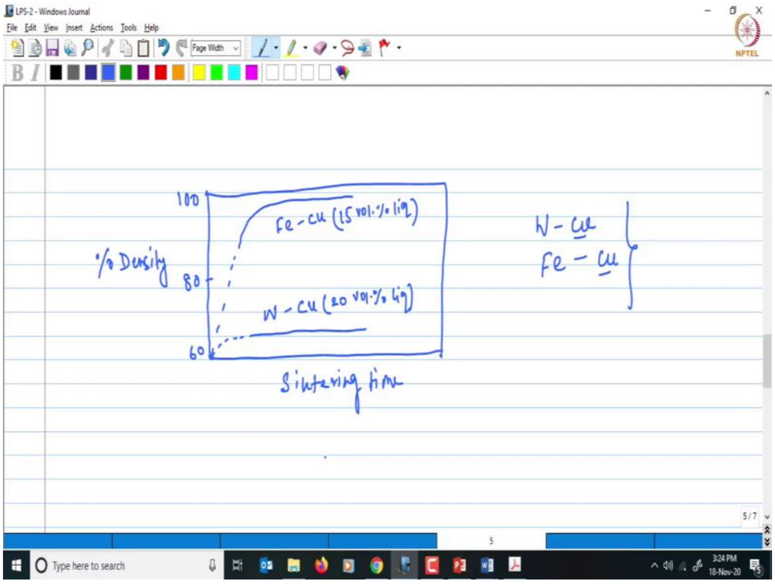

We will take the example of two systems one is tungsten copper (W-Cu) and another is iron copper (Fe-Cu) (image in the above slide). Iron is soluble in copper, but tungsten is not and that is going to make a difference in the density, when they are sintered by liquid phase sintering. This one is for tungsten copper (below one), which is having 20 volume percent of the liquid and the upper one is for iron copper having 15 volume percent of liquid.

So, you can see due to the solubility difference although the tungsten copper system has a higher liquid fraction, the density is much higher in the iron copper system, even after having a lower liquid content. This is because of the fact as I said iron has solubility in copper, but tungsten does not have solubility in copper. And, that is what is making the difference in terms of the densification of these two material systems.

So, the solubility of the solid in the liquid is good for densification in liquid phase sintering. However, if you have liquid solubility, that may lead to some difficulties such as swelling which is not desirable. Therefore, a high liquid solubility in the solid should be avoided.

The particle radius has an effect on the solubility and the relationship between the radius and the solubility is given by the following equation,

$$\ln (S/S_0) = 2\gamma SL\ \Omega / KTr$$

where S is the solubility and r is the radius of the particle and S_0 is the equilibrium solubility of the solid in the liquid. And, other terms are there usual meaning like k is the Boltzmann constant and T is the absolute temperature and Ω is the atomic volume.

This equation tells you that smaller radius particles will have higher solubility and this is what I have already said before also that these smaller particles have higher solubility and they will dissolve first. And, this is what ultimately leads to that solution re-precipitation mechanism and Ostwald ripening which comes into play, because these smaller particles will dissolve and the bigger ones will grow at the expense of the smaller particles.

That is a phenomena known as Ostwald ripening which ultimately leads to grain coarsening in this process. And, in addition to dissolution of the smaller particles surface features like, asperities will also dissolve, because asperities have small radius of curvature. On the other hand, a pits, crevices and necks between the particles have negative radii of curvature and therefore, there solubility is low.

And, hence the precipitation is enhanced in these regions. This kind of surface features like pits, crevices and necks will act as the sites for the precipitation to take place, when that solution precipitation mechanism comes into play. So, before we finish this lecture let us take a moment to summarize it.

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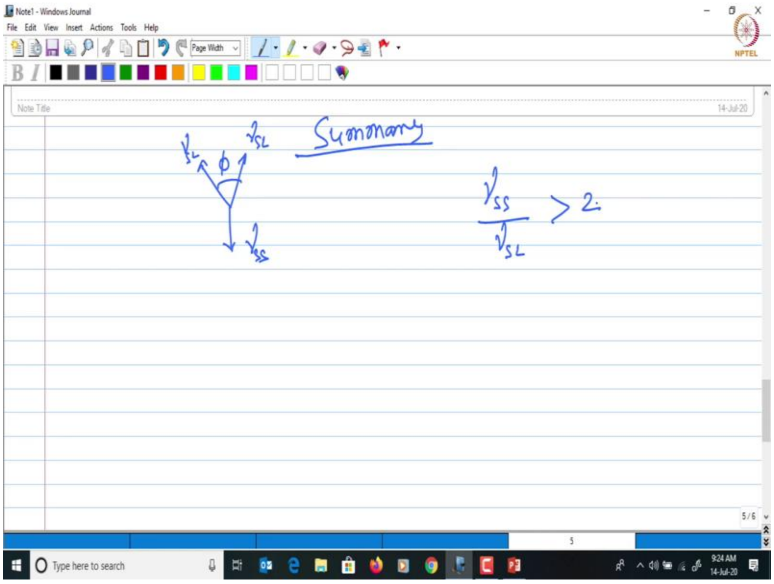

Summary

$$\frac{\gamma_{SS}}{\gamma_{SL}} > 2$$

So, to summarize we can say that, the solid liquid surface energies and the grain boundary energy from an angle and the liquid comes in contact with the solid grains. And, this angle is known as the dihedral angle (ϕ). And, it is the value of the dihedral angle which decides the penetration; you need a small enough value for the ϕ for the penetration to happen.

Because, this condition has to be satisfied for the penetration, this ratio γ_{SS}/γ_{SL}, must be greater than 2 for the liquid to completely penetrate the solid. Then, we have also discussed about the role of the solubility. The liquid and the solid both can have solubility, while the solid solubility is good for the densification; the liquid solubility is not good.

Because if you have a high solubility for the liquid, it will lead to swelling of the compact and that is not good for the sintering process and for the integrity of the green compact. And, therefore, the solubility for the liquid should be minimum. On the other hand, a good solubility for the solid gives rise to a good densification by providing a faster diffusion path through the liquid bridges which form as the liquid penetrates the solid.

And, once the liquid penetrates all these mechanisms will come into play that is particle rearrangement, and then the liquid spreading through the solid and the solid particles dissolving into the liquid. And, we have also seen that the solubility depends inversely with the radius of the particles. And, therefore, the smaller grains will have the smaller particles will have higher solubility. So, the small grains will dissolve and the larger ones will grow at the expense of that.

Once, the small grains dissolve and these mass transport happens they will ultimately re precipitate on the larger grains, a process known as solution re-precipitation. And, surface features like the crevices and pits and necks on the surface, which have low solubility will actually act as the sites for this re-precipitation to occur and will enhance the precipitation of the solid grains.

And, with that we come to the end of this lecture, but I will see you again soon for the rest of the things that we have on this particular topic; until then goodbye.