Powder Metallurgy

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Lecture - 51
Liquid Phase Sintering – 1

Hello and welcome back. In the past several classes we have been discussing about this solid state sintering process and I hope by now you have developed a good understanding on the sintering process. Briefly, in a solid state sintering process everything happens in solid state, as the name itself suggests. Now, the diffusion process which is the main mechanism of densification during sintering can be quite sluggish in the solid state.

Therefore, it can limit the densification which can be achieved by solid state sintering. And, then we have other factors such as the characteristics of the particle, the surface properties and the morphology of the particles. These factors also influence the solid state sintering process in the sense that the particle to particle contact which is actually needed for the sintering process to initiate will depend on all these factors.

There are materials where it is difficult to form these kind of contacts because of their higher strength. So, if a material has higher strength or higher hardness it is difficult to compact it to form all those particle contacts which are needed to initiate the sintering process. And therefore, solid state sintering process becomes difficult to use for these kind of materials to fully densify them.

Therefore, we need certain other alternatives which can handle such materials which are difficult to compact and sinter. One such approach could be to have another phase in the material in the powder which will melt at the sintering temperature, while the parent material is still in the solid state. Presence of liquid is an advantageous because we know that the diffusion through liquid is much faster compared to that in solid.

So, that is an approach which can be taken up to enhance the densification for materials or for situations where, it is difficult to densify it by conventional solid state sintering process. Due to the presence of the liquid phase, the process is also known as Liquid

Phase Sintering and that is what we are going to discuss in this particular class. Let us start this topic liquid phase sintering. First we will see the basic fundamentals.

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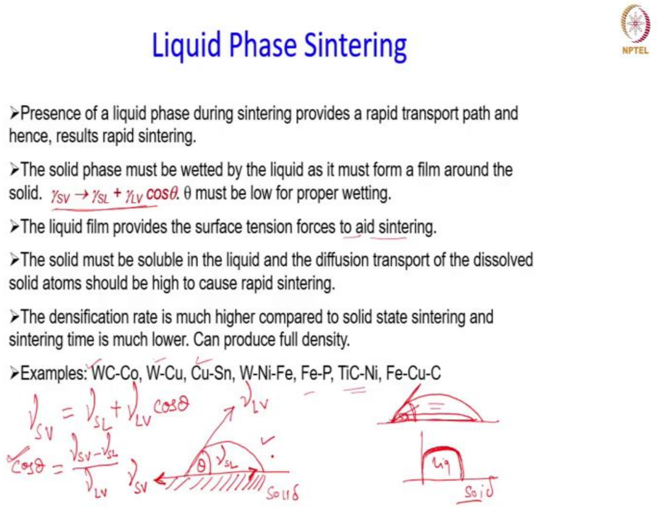

Liquid Phase Sintering

- 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

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

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

As I said presence of liquid phase can provide a rapid transport path or a faster diffusion path and hence, it will result in rapid sintering. That is the objective of having this liquid present during the sintering because, it provides that rapid transport path for the mass to be transported towards the pore for them to be closed. Now, for this to occur the solid phase which is the parent phase has to be completely wetted by the liquid.

The liquid should spread on the solid for this rapid transport path to come into the picture and give you that enhanced sintering which you are looking for in this case. So, for that the surface energies will have to be considered because, that is what actually decides the wetting of the liquid on a solid surface. And, there is one more parameter which is important for this wetting for this wetting phenomena and that is the contact angle.

Contact angle, if it is higher it is not good for spreading or wetting of a liquid on a solid surface. You would have seen lotus leaf and water droplets on a lotus leaf. There the water does not spread over the surface of the lotus leaf because, the contact angle is much higher than 90°. So, for the liquid to spread over the solid surface and wet it, the contact angle must be below 90°.

That we can see from a pictorial like this, if you consider this schematic of a liquid drop on a solid surface and see the surface energies from that you can actually derive this expression for the contact angle. Let us say this is the solid surface and over this we have a droplet of a liquid. Here you have the liquid vapour surface energy acting in this direction. Let us call that γ_{LV}; it stands for Liquid Vapour.

The solid liquid interface is this one (image on the above figure). Here you have the solid liquid interfacial energy γ_{SL} and this is the solid vapor interfacial energy which is acting in this direction. And this is the contact angle θ. So, for this liquid to completely spread over the solid this θ must be very small. If it is close to 0 or just little more than 0 like this, then it is completely spread.

Because, this angle is very small close to almost 0^o; on the other hand, if you have an angle like this, then you can see that the liquid droplet is not spreading on the solid surface. And, if you have less than 90^o then also you will have spreading like this if you have something which is in between 0 and 90^o something like this. Then also the liquid will spread on the solid surface.

But, for a better wetting to take place the θ should be as small as possible. And, you can also see that from this if you take the balance of forces from here γ_{SV} is balanced by γ_{SL} and the cos component of γ_{LV}.

$$\gamma_{sv} = \gamma_{SL} + \gamma_{LV} \cos\theta \text{ ---------------- } (1)$$

And, from here you can derive the θ.

$$\cos\theta = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} \text{ ------------------------------ } (2)$$

So, it is basically the surface energies which will decide the contact angle θ and as I said for a better wetting to take place theta should be as small as possible.

Now, once this liquid is spread on the solid surface, the solid particles that you have it will form a kind of liquid film. And, the surface tension forces or the surface energies that you have from this liquid film will actually aid the sintering process. Now, the solid material that you have, the parent material that is actually being sintered, that should have enough solubility in the liquid.

And, the diffusion transport of the dissolved solid atoms should be high to cause this rapid sintering which you are looking for in this case. Now, this diagram that you see over here for the wetting does not really take into account the solubility to avoid complications. But, when the solid has some solubility in the liquid this scenario can change and you might have a different kind of wetting geometry.

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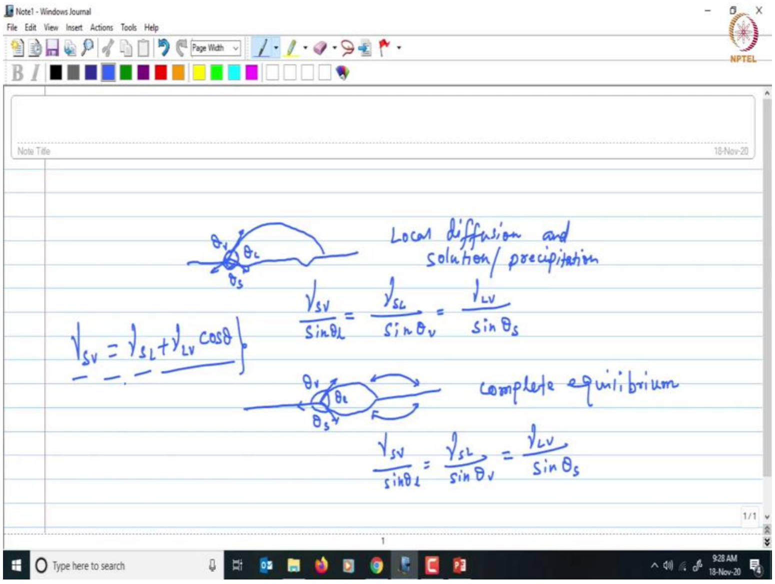

Local diffusion and solution/ precipitation

$$\frac{\gamma_{SV}}{\sin\theta_L} = \frac{\gamma_{SL}}{\sin\theta_V} = \frac{\gamma_{LV}}{\sin\theta_S}$$

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

complete equilibrium

$$\frac{\gamma_{SV}}{\sin\theta_L} = \frac{\gamma_{SL}}{\sin\theta_V} = \frac{\gamma_{LV}}{\sin\theta_S}$$

For example, if you consider some local diffusion and solution or precipitation, then it might look like this and a complete equilibrium must have forced balance as well as attainment of constant surface curvatures. The Young's equation that is this equation, that we had for the case when no solubility is considered has to be modified accordingly when the solubility comes into picture.

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

This is the well-known Young's equation for wetting up the solid surface by a liquid. This does not really take into account the solubility.

When the solubility comes into play, this equation may have to be modified. So, solubility will have some effect in case of liquid phase sintering because, the solid has some solubility in the liquid. It is not about only the presence of the liquid, but we also need to consider how the solid will interact with the liquid. And, then you will also have to see whether that kind of interaction will give rise to a rapid diffusion path or not.

Furthermore, when that happens, this kind of interaction leading to a better diffusion path; when that happens then only you can expect the better densification to take place. And, the densification rate in this case is much higher compared to solid state sintering because, of the presence of a rapid transport path for the matter to flow. And therefore, the sintering times are much lower in the case of liquid phase sintering compared to solid state sintering.

Since the densification is enhanced in this case; one can also achieve full density or 100% density at the end of the sintering process. These are some examples where this liquid phase sintering process is quite useful. This cemented carbide or tungsten carbide materials, these are quite hard. And, as I was mentioning earlier this kind of materials which are actually difficult to compact and sinter by conventional processes.

Also, other materials like tungsten copper, copper tin, tungsten nickel, iron phosphorus, titanium carbide nickel and so on. In all these cases one of the materials that you have will actually melt at the sintering temperature and it will give rise to all this enhanced densification mechanism.

That is how with the help of a material which is a lower melting material compared to the parent material which is being sintered, the densification can be enhanced. But, as I said the condition should be such that the contact angle is low and the solid surface is wetted by the liquid.

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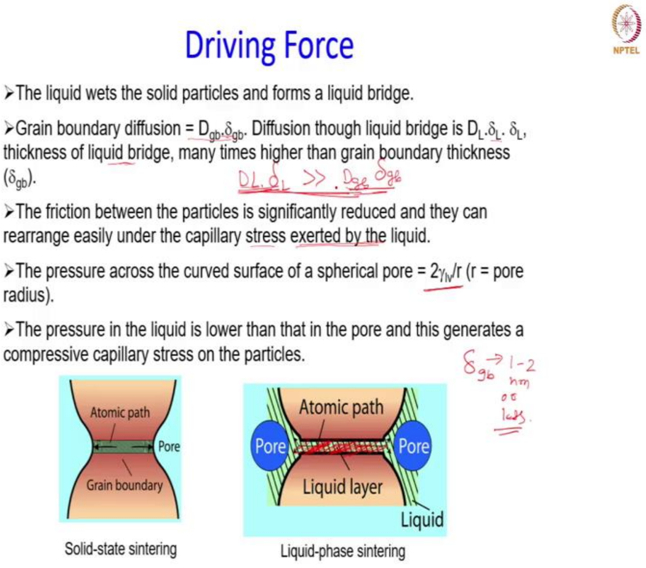

Driving Force

- 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}).

  $D_L.\delta_L >> . D_{gb}\,\delta_{gb}$
- 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.

$\delta_{gb} \rightarrow$ 1-2 nm or less.

Solid-state sintering

Liquid-phase sintering

Now let us have a look at the driving force behind this process. When the liquid wets the solid particles it forms a liquid bridge which you can see from here; a liquid layer is formed between the particles, over here you can see that. This is essential for the enhanced densification to take place. And the way it happens as to why it gives a better densification rate, that we can see if you look at the diffusivity; that you have for a solid state sintering case versus the liquid phase sintering.

Grain boundary diffusion is one of the paths which gives faster diffusion in case of solid state sintering. And, that diffusion can be given as this,

$$\text{Grain boundary diffusion} = D_{gb} \,.\, \delta_{gb}$$

Where, D_{gb} is the grain boundary diffusivity and δ_{gb} is the thickness or width of the grain boundary. Similarly,

The diffusion through the liquid bridge is given as, $D_L.\delta_L$

where, D_L is the diffusivity in the liquid and δ is the thickness of this liquid bridge.

So, now, this δ_{gb} is much smaller compared to δ_L, if you look at the values of this, this is within 1 or 2 nanometer or even less than that. This is such a small thickness such a small distance, that we are talking about here. On the other hand, if you talk about this thickness of the liquid bridge this is physically present on the external surface of the particle. Obviously, this is going to be much larger, δ_L is going to be much larger compared to δ_{gb} which is on atomic scale.

Therefore, from here itself you can see that the diffusion is much higher because, this quantity is much higher compared to grain boundary diffusion.

i.e. $D_L.\ \delta_L >> D_{gb}\ \delta_{gb}$

The diffusion through the liquid bridge is this and this is the grain boundary diffusion. This is what actually leads to that enhancement and better densification in this case. And, the other factor which aids the sintering is the reduction in the friction between the particles due to the presence of this liquid film again.

Therefore, they can rearrange under the capillary stress which is exerted by the liquid. Once the particle surface is wetted by the liquid phase, it will first of all reduce the friction. And, then the particles now can rearrange themselves for better packing or better densification. This is something that you cannot expect in the solid state sintering process because; there once it is packed during the compression process that remains while it is being sintered.

During sintering there is no rearrangement as such because, we are not applying anything externally during that conventional solid state sintering. So, there it is all about how the pores are being filled and eliminated by the mass transport that takes place in the green compact when it is being heated at a particular temperature. And, the other factors which again leads to mass transport towards the pores is the pressure across the curved surface.

And, for a spherical pore this will be given by the surface energy and the radius of the pore as to $2\delta_{lv}/r$. And, the stress due to curved surface we have already discussed before and we have seen that if it is a spherical shape, then it is simply $2\gamma/r$, where r is the radius. And, here in this case of liquid phase sintering the pressure in the liquid is lower than that in the pore. And therefore, it generates a compressive capillary stress on the particle.

That is how the capillary stress is exerted by the liquid on the particles leading to their rearrangement. And, this rearrangement process as we are going to discuss later is quite helpful in achieving better densification. This was all about the driving force behind the liquid phase sintering.

Before we wind up this lecture, let us take a moment to summarize it. Today we have started this liquid phase sintering. This is one of the enhanced sintering processes for achieving better densification and higher sinter density; particularly for materials which are difficult to sinter by conventional sintering process.

Here we have seen that the presence of a liquid phase provides a rapid transport path and that is how it enhances the sintering process. Here what is done is apart from the parent material which is being sintered, there is another phase or another material which is added to it. And that material is going to melt at the sintering temperature, while the parent material will still be in the solid state. It is not that everything is going to melt and become liquid here then there is no sintering, then it will become simply solidification.

So, it is done in a manner that only one of the phases that is the minor phase that you have here that will melt. And, it will kind of provide simply a rapid diffusion path for a better densification to happen. And, here we have seen that for this to occur, for this liquid to act as a better or faster diffusion path; first of all, it should wet the surface of the solid particles because, as I said the parent materials is still in the solid state.

So, when the liquid forms, it should first spread over the surfaces of these solid particles; then only you can expect this rapid transport path to come into picture. And, the condition for that is having a contact angle which is much lower than 90^o. And, this will be decided by the surface conditions because surface energies will decide the contact angle as you can see from this particular equation (equation 2).

So, it is all about the interplay of the surface energies that you have over here which will decide the contact angle between the liquid and the solid surface. So, once this solid surface, the solid particles are wetted by the liquid, a liquid film will form and that will also create a surface tension which will actually aid the sintering process. The solid also must be soluble in the liquid for this faster diffusion to take place.

Here these are some of the examples that we have where this liquid phase sintering process is quite useful. And, then we also talked about the driving force behind this process, it is basically the diffusivity and the thickness of the diffusion layer that you have here which is much larger compared to the grain boundary thickness. So, grain boundary diffusion is one of the dominant mechanisms in solid state sintering.

But, if you look at the diffusivity or the diffusion in terms of the diffusivity and the thickness of the boundary or the interface across which this diffusion takes place. Then, we will see that the diffusion across the liquid film which forms in case of the liquid phase sintering is much larger compared to that through grain boundaries. Because, the thickness of the liquid layer or the liquid film which has formed here is much larger compared to the thickness of the grain boundary.

This is what actually drives the liquid phase sintering towards better densification. Then we also talked about this capillary stress which is induced by the liquid on the surface of the particles. And this is something which is quite helpful in this case; in the sense that it helps in rearrangement of the particles. How that happens and what exactly are the phenomena, that is something we are going to discuss later on. So, we will see how the rearrangement takes place.

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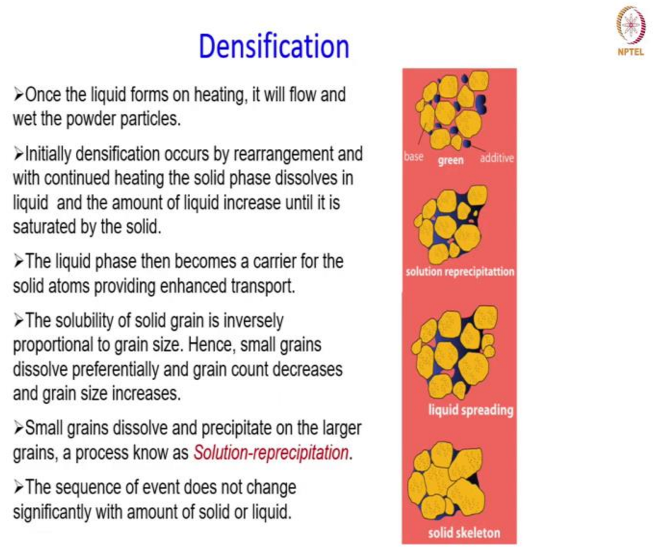

Densification

- ➢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 event does not change significantly with amount of solid or liquid.

And, what are the other stages of the liquid phase sintering process, what kind of phenomenon happens during each of the sintering process. All these things we are going to discuss when we take this up again. So, today we have seen that this rearrangement will occur due to the presence of the liquid film which creates some kind of stress on the particles for their rearrangement to occur.

With that we come to the end of this class, but there is more to come. So, I will see you again soon with the rest of the things, that we have on this topic.

Thank you for your attention.