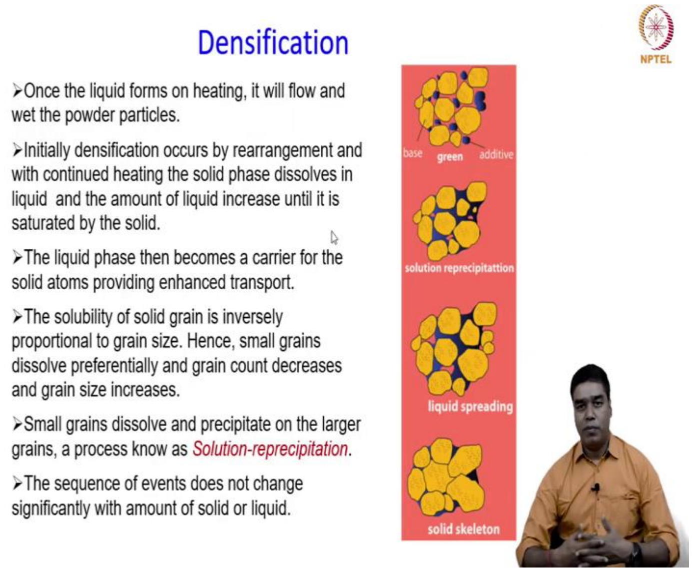
Powder Metallurgy
Prof. Ranjit Bauri
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture – 53
Liquid Phase Sintering – 3

In the previous class we have started discussing about the densification mechanism of the Liquid Phase Sintering process.

(Refer Slide Time: 00:27)



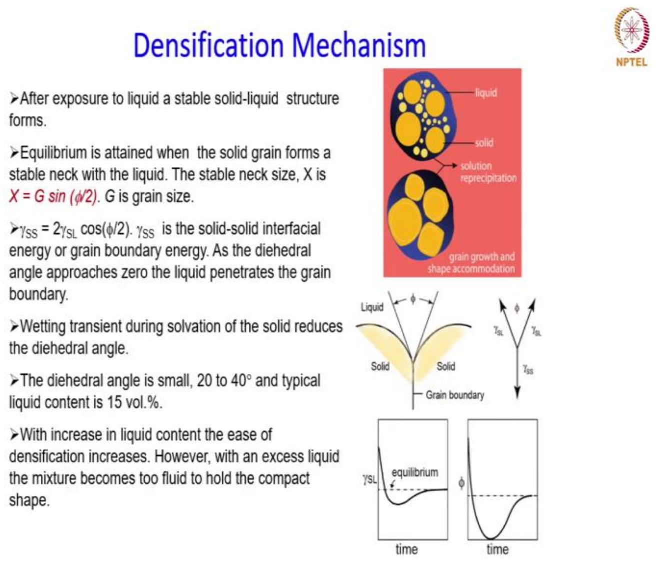
Densification

- 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.

We have seen that it occurs in a sequence starting from the formation of the liquid and the penetration of the liquid leading to rearrangement. And then the rearrangement is followed by the dissolution of the solid particles into the liquid. that is how the liquid then provides a rapid transport path for the solid atoms, which re-precipitate on the surfaces of the larger particles.

First the small particles or the small grains dissolve and then re-precipitate over the larger particles leading to a process called the solution re-precipitation. And in the process the pores also closed and hence the densification is achieved. So, the liquid penetration is the first step towards this densification.

(Refer Slide Time: 01:22)



Densification Mechanism

- After exposure to liquid a stable solid-liquid structure forms.
- Equilibrium is attained when the solid grain forms a stable neck with the liquid. The stable neck size, X is $X = G \sin(\phi/2)$. G is grain size.
- $\gamma_{SS} = 2\gamma_{SL}\cos(\phi/2)$. γ_{SS} is the solid-solid interfacial energy or grain boundary energy. As the diehedral angle approaches zero the liquid penetrates the grain boundary.
- Wetting transient during solvation of the solid reduces the diehedral angle.
- The diehedral angle is small, 20 to 40° and typical liquid content is 15 vol.%.
- With increase in liquid content the ease of densification increases. However, with an excess liquid the mixture becomes too fluid to hold the compact shape.

And we had seen that it basically depends on this dihedral angle which forms between the liquid and the solid grains. And when the conditions are such that the dihedral angle is very small close to 0^o, then the solid-liquid surface energy that you have becomes smaller compared to the solid-solid surface energy.

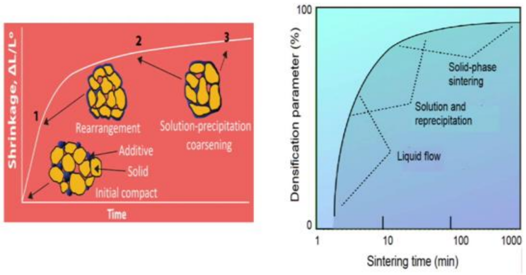
Therefore, there is a driving force for the liquid to penetrate this solid-solid interface or the grain boundary in order to reduce the overall energy of the system. That is when the liquid penetration happens and that is defined by this condition. If you take the ratio between γ_{SS}, which is the solid-solid interfacial energy to γ_{SL}, which is the solid-liquid interfacial energy and that becomes more than 2, which you can derive from this.

This is the condition where the solid-solid interfacial energy is just balancing the solid-liquid interfacial energies. And if you go beyond that if the dihedral angle falls below this then the solid-solid surface energy becomes greater than the solid-liquid surface energy by a factor of more than 2. Or in other words $\gamma_{SS} / \gamma_{SL}$ is greater than 2, in that situation the liquid penetrates the grain boundary.

So, this is where the rearrangement process starts and this is followed by rest of the stages that we are going to discuss in this class. So, this sequence of events that you have for the densification process over here can be also illustrated with the help of diagrams like this.

(Refer Slide Time: 03:26)

Sintering Stages



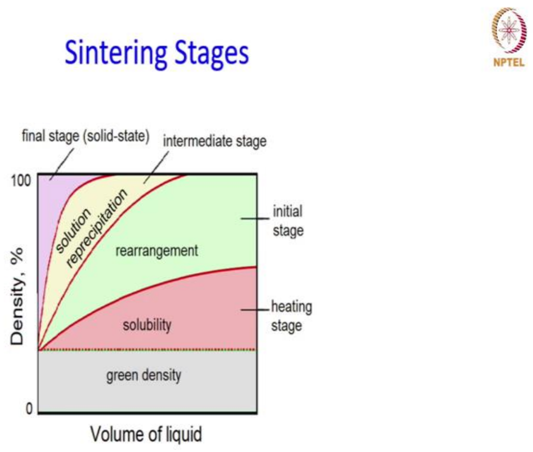
This is the shrinkage (first image in the above slide) which represents the densification and if you see that as a function of time you can see the sequence of events leading to the densification. As we discussed it first starts with the rearrangement. Here in the powder feedstock you have the parent material. It is the solid and the additive which melts when it is heated.

Once the liquid melts and it penetrates the solid boundaries then due to the capillary force exerted by the liquid, the particles rearrange. And as you progress the pores are filled by the liquid and the particles ultimately starts to dissolve in the liquid and the solution precipitation phenomena begins. And beyond that solid particles are again re-precipitated and therefore, beyond this stage you can also expect solid state sintering to take place.

Something that you can see over here also (second image), first the liquid flow leading to the rearrangement and then as the particles dissolve in the liquid and then precipitate that is when this says solution and re-precipitation stage starts.

When the re-precipitation is completed you have all the solid particles back, but with much less porosity between them. Then it is in solid phase because now that all the dissolved particles are re-precipitated, you can also expect solid phase sintering to occur for the closure of the rest of the pores.

(Refer Slide Time: 05:28)



Sintering Stages

And these are the events (above image) which are again described with the help of a plot like this which shows the density as a function of the volume of liquid. As we increase the volume of liquid there are certain changes with regard to the interfaces of the particles. And as you increase the volume, there are different stages of the sintering process which will come into play with different phenomena leading to the densification.

First as you heat it the liquid forms and there is a solubility for the liquid into the solid and for the solid into the liquid. It is always better to have a small liquid solubility and a higher solid solubility for better densification to happen in this case without any swelling or other issues.

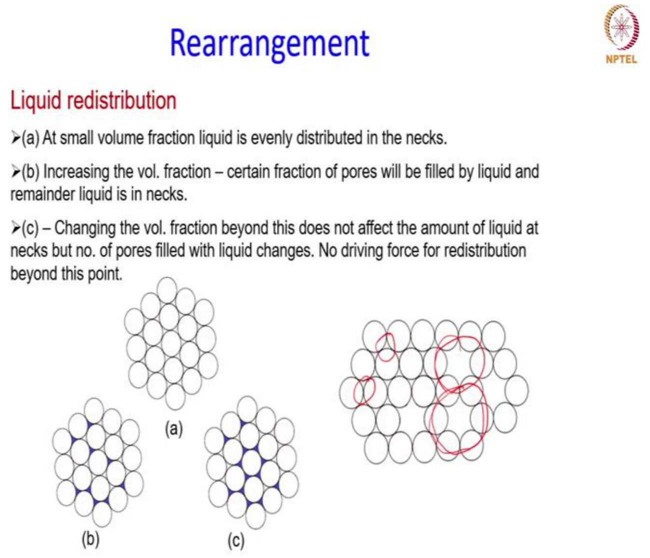
And then as the liquid penetrates rearrangement happens as the volume fraction of the liquid increases. Beyond that when all the neck regions and the pores are filled by the liquid then the solid particles start to dissolve. Here you have seen the solubility of the smaller particles are higher compared to the larger particles.

Therefore, the smaller particles will dissolve in the liquid and then re-precipitate on the larger ones. So, solution re-precipitation phenomena then starts to happen leading to not only the dissolution of these particles, but also the densification because this process will also lead to growth of these particles and closer of the pores.

And ultimately on the re-precipitation stage ends then you have all the solid particles back together with smaller fraction of pores or with the higher density. Then you can expect the solid state sintering to also take place, so during the later stage of the process.

So, we will take this of a one by one to understand in a greater depth. So, we will discuss each of these phenomena in detail. We have already discussed about the solubility and the penetration of the liquid as to how it happens and what are the conditions for the liquid to penetrate to the solid boundaries.

(Refer Slide Time: 08:13)



Rearrangement

Liquid redistribution

- (a) At small volume fraction liquid is evenly distributed in the necks.
- (b) Increasing the vol. fraction – certain fraction of pores will be filled by liquid and remainder liquid is in necks.
- (c) – Changing the vol. fraction beyond this does not affect the amount of liquid at necks but no. of pores filled with liquid changes. No driving force for redistribution beyond this point.

Now let us talk about the next stage which is the rearrangement of the particles rearrangement occurs when the liquid penetrates into the solid. Here the liquid has to be spread over the compact. So, the liquid distribution has to be considered in order to see what is actually happening during this rearrangement process to understand how this rearrangement occurs as a result of the liquid penetration.

So, liquid redistribution also kind of happens in a sequence because here it depends on the volume fraction of the liquid. As you heat it the liquid forms first and then with continued heating the volume fraction of the liquid increases.

As the volume fraction changes the filling of the solid surfaces or the void spaces between the solid particles will also start to occur and this fraction of pores filling will also start to change as you increase the volume fraction of the liquid. This is what is depicted here in this picture (first image in the above slide or left hand side image).

When the liquid volume fraction is small, it will be evenly distributed in the neck region that have formed by the liquid and the solid particles at the contact points (Image a), liquid will be distributed mainly along those necks. Now, as you increase the volume fraction this extra liquid that you have after the necks are filled that will now go to the pores and certain fraction of the pores will be filled and the rest of the liquid will remain in the necks.

So, that is what you see in this picture in figure b here. You can see these pores are now filled in certain fraction of pores are filled and the rest of the liquid will be now in this neck regions. And changing the volume fraction and at this stage does not really affect the amount of liquid at the necks, but of course, it will alter the fraction of force that will be filled by the liquid. And once this happens there is no driving force beyond that.

The driving force for this pore-filling is the reduction in the surface energy. Once the pores start to fill the liquid will always tend to redistribute itself due to the reduction in the surface energy. And it does not really matter which pores are filled as long as a certain fraction of force are filled with the excess liquid that is there after filling the neck that is enough to redistribute the liquid.

Therefore, beyond that point when a certain fraction of force is already filled there is no driving force for the redistribution to take place and this is what is shown over here in this particular figure (figure c). Figure c here you can see that a certain fraction of pores is filled with the liquid as you can see and beyond this point as I said there is no driving force for the redistribution to occur.

So, pore filling also happens in sequence. First it starts with the neck and then only it goes through their pores. So, this picture this diagram that you have over here this is more like an idealized situation where the powder particles are homogeneously packed and there are only 3-fold coordinated or triangular pores in between them. And there is no other type of pore or pore size distribution and all that.

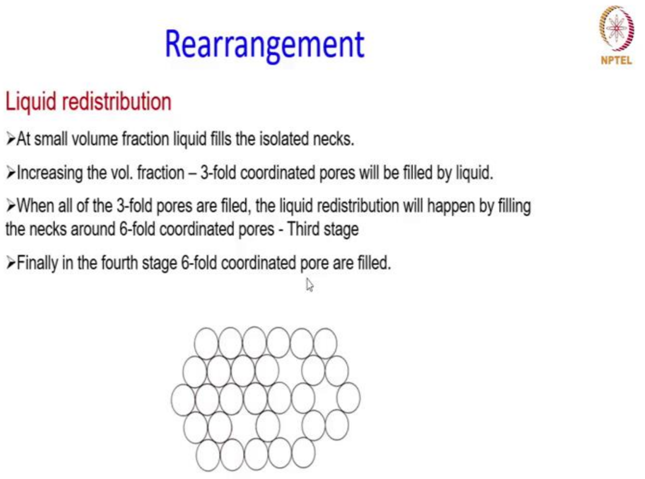
Therefore, this is the ideal scenario, but practically apart from this 3-fold coordinated force there will be other type of pores also. For example, you can have these kind of 6-

fold coordinated pores (right hand side image in the above slide) as you can see from this particular diagram apart from 3-fold pores that you have in these regions. You can also have 6-fold coordinated pores like these ones.

This is a more practical scenario because a little bit of in homogeneity is always expected when the powder is being pressed and therefore, you can expect presence of different types of pores in the green compact. When you have a practical scenario like this when you have different types of pores having different coordination then you need to see how the redistribution of the liquid occurs.

So, let us take this scenario when you have certain numbers of 6-fold coordinated pores also present along with the 3-fold coordinated pores.

(Refer Slide Time: 13:48)



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 filed, 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.

In this case again it will happen in a sequence like how it happened in the case of this idealized situation at small volume fraction of the liquid. It will only stay in the isolated necks. The liquid will be distributed only along the necks when the volume fraction of the liquid is small. As you increase the volume fraction first the 3-fold coordinated pores will be filled by the liquid.

Like what happened in this case the certain fraction of the 3-fold coordinator pores will be filled. The same thing is going to happen in this case also. And now once all the 3-

fold pores are filled then only the liquid can redistribute itself by filling the necks between the 6-fold coordinated pores now.

Here neck filling happens twice unlike in this case (idealized case) where the neck filling happened in the beginning itself and after that only the pores were filled, but here since you have two types of pores; one 3-fold and another 6-fold coordinated you have the necks also distributed around them around both of these kind of pores. Therefore, after the smaller pores have filled the necks which around 6-fold coordinated larger pores will be filled by the liquid.

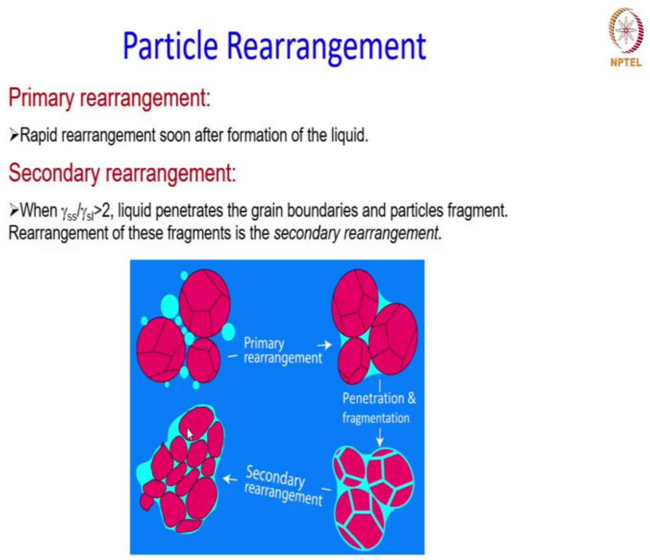
So, that is the third stage. First stage is only filling the isolated necks between the particles. Second stage is filling up the 3-fold coordinated pores. And then once this happens in the third stage the necks which are there around the 6-fold coordinated pores will start to get filled. And finally, in the fourth stage when these necks around the 6-fold coordinated pores are filled, the 6-fold pores will be filled. So, here you have four stages of pore-filling in a sequence.

Apart from this even if you have a little more complex situation where you have a distribution of the pore size and presence of different kind of pores then also this sequential filling of the pores will still be valid. First the smaller pores will be filled because of their high surface area to volume ratio and then it will continue in a sequence to fill the other kinds of pores. The larger pores will be filled in the later stage of the liquid redistribution process.

But, in a scenario like that when you have a pore size distribution there are chances that the liquid might find it difficult to reach some of the small pores and therefore, they may remain unfilled. On the other hand, the larger pores are the last ones to be filled and therefore, in those regions there are chances of in homogeneities like segregation and things like that because that is the last liquid to solidify where this kind of phenomena can happen.

Therefore, the powder compact which is being sintered by the liquid phase sintering process should be a homogeneous one. The powder particles should be packed homogeneously, so that there is a narrow pore size distribution which will prevent this kind of inhomogeneous redistribution of the liquid.

(Refer Slide Time: 17:42)



Particle Rearrangement

Primary rearrangement:

- ➢Rapid rearrangement soon after formation of the liquid.

Secondary rearrangement:

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

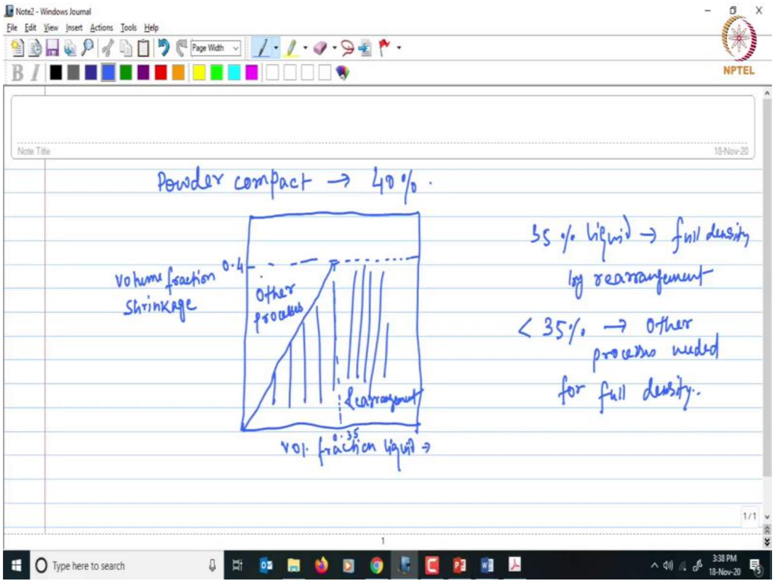
Now, this redistribution can happen in two ways. One is the primary rearrangement that is basically the rapid rearrangement of the particles soon after the liquid forms. This is basically due to that capillary force which the liquid exerts on the particles once the particle surface is wetted by the liquid. And the secondary rearrangement is basically the invading of the grain boundaries of the solid particles by the liquid phase. This is something that we have already discussed.

We have seen that when this surface energy ratio $\gamma_{SS} / \gamma_{SL}$, where the γ_{SS} is the solid-solid or the grain boundary surface energy and the γ_{SL} is the solid-liquid surface energy. When that ratio is greater than 2, the dihedral angle is very small and that is when the liquid penetrates the grain boundaries and as a result of that the particles fragment.

The secondary rearrangement is about the rearrangement of these fragments which are generated due to the penetration of the liquid phase into the grain boundaries of the solid particles. These are the two types of particle rearrangement. One is primary rearrangement and another is secondary rearrangement.

The densification by rearrangement depends on the relative amounts of solid and liquid present in the compact during sintering. So, let us consider an example in order to understand the affect of the volume fraction of the liquid which is present on the densification by the rearrangement process.

(Refer Slide Time: 19:53)



Powder compact → 40% .

35 % liquid → full density by rearrangement

< 35% → Other process needed for full density.

Let us say we are talking about a powder compact with the porosity of 40%. So, this compact is sintered by liquid phase sintering. All these pores have to be closed and if this has to happen by the rearrangement process it would require a considerable amount of liquid to be present during sintering. That can be shown with a plot like this (image in the above slide). Here, the volume fraction of the liquid is plotted against volume fraction of shrinkage.

The example that you considered for this powder compact having 40% porosity. It has been shown that a full density can be achieved only by the rearrangement process with 35% liquid. So, this half of this plot belongs to the rearrangement process and the other half is for other processes.

If the liquid fraction is less than 35% then for full density to occur other processes have to come into play and this other processes include mechanisms such as solution re-precipitation. In principle, it is possible to achieve the full density by rearrangement with a small amount of liquid, but in reality it is generally observed that rearrangement is difficult when the liquid content is small. If it is say less than 2 to 3 volume percent particularly, when the solid particles have irregular shapes.

So, that is why practically a considerable amount of liquid is required to achieve full density in liquid phase sintering. So, to summarize this lecture we can say that the densification in the liquid phase sintering process occurs in a particular sequence of events. It starts with the rearrangement of particles and that is what we have discussed in this particular class today.

When the liquid is formed and the solid particle surface is wetted by the liquid then the liquid redistribution takes place which involves a sequential kind of filling. First the neck between the particles will be filled by the liquid followed by the pores. As the volume fraction of the liquid is increased, a certain fraction of the pores will be filled and the driving force behind that is the reduction of the surface energy as the pores are filled by the liquid.

That means, as the solid-solid surface energy is replaced by the solid-liquid surface energy which is lower, it will basically reduce the surface energy and that is what drives the liquid into the pores. Once the pores are filled, then we have seen the liquid is redistributed and once a certain number of pores are filled there is no driving force for the redistribution beyond that point.

And we have also seen that in a practical scenario there could be different types of pore and different sizes of pore. So, we have discussed a scenario where you have 6-fold and 3-fold coordinated pores. So, first the 3-fold coordinated pores will be filled as the liquid redistribution takes place.

In that case there are basically four stages starting from the filling of the isolated necks followed by the filling of the 3-fold coordinated pores which will be followed by filling up the necks which is around the 6-fold coordinated pores and finally, the 6-fold coordinated pores themselves will be filled by the liquid.

So, when you have different types of pores sequence of filling that will take place when the liquid is being redistributed. And then finally, we talked about the two types of particles rearrangement. One is primary rearrangement, which is basically the rearrangement of the particles soon after the liquid forms. And the other one is secondary arrangement, which is induced by the invading of the liquid phase into the grain boundaries of the solid particles. And when that happens, the particles fragment and the secondary rearrangement process is basically the rearrangement of these fragmented particles. So, with that we come to the end of this lecture.

Thank you for your attention.