

Powder Metallurgy
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Lecture – 55
Liquid Phase Sintering – 5

In the last class we were discussing about this densification mechanism during the Liquid Phase Sintering process. And, we have seen that the densification occurs by two stages here; one is the rearrangement process and the other is through the solution precipitation route.

During the solution precipitation route there are two modes; one is through contact flattening and that is what we have discussed in the previous class. And, the other mode is through Ostwald ripening; so, that is what we are going to discuss in this particular class.

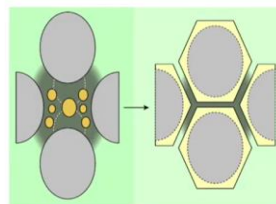
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Solution-Precipitation



Densification by Ostwald Ripening:

- The smaller grains dissolve and re-precipitate on larger grains away from the contact points.
- Larger grains grow at the expense of the smaller ones (Ostwald ripening), center-to-center distance decreases and the resulting polyhedra (due to shape change) fill the space effectively.
- This shape change induced efficient packing is known as *Grain shape accommodation*.



In the Ostwald ripening mode what happens is the smaller grains dissolve and re-precipitate on the larger grains away from the contact points. So, we have seen before that the mass transport occurs away from the contact points due to a difference in the chemical potential which results from a higher solubility at the contact point compared to any other point on the surface of the particles.

Larger grains will grow at the expense of the smaller ones and this is what is known as the Ostwald ripening. The center to center distance will decrease as we have seen before also as the contact point dissolves away and the mass is transported away from the contact points. And, this will result in the formation of a polyhedra because this will lead to a shape change; so, that the space between the particles can be filled effectively.

This will only happen when these kind of shapes will form rather than the more regular spherical kind of shapes. Because, what happens is this Ostwald ripening process is favored by a situation where the volume fraction of the liquid is low. And therefore, when you talk about the normal conditions like how we have discussed before having particles of spherical regular shapes; in those kind of conditions the liquid will find it difficult to fill the spaces between the particles.

Because, the amount of liquid is low and therefore, in order to fill the space between the particles effectively the shape of the grains has to change to a polyhedral; where you have this kind of flat contact surfaces. And, this kind of shape is more effective in filling the space between the particles.

And therefore, this shape change induced efficient packing is also known as grain shape accommodation. Because, this happens due to the change of the shape which results in a better packing leading to densification. So, this was all about solution precipitation and we have seen how the densification occurs in this case through these two modes; the contact flattening and Ostwald ripening.

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Coarsening



- The solid phase coarsens at a rate such that average grain size, G , changes with one-half or one-third power of time.
- Rounded shape grains that grow by solution-precipitation with $1/3$ kinetics.
- Angular grains, such as in WC-Co, develop in $1/2$ rate kinetics. In that case the coarsening rate is limited by the availability of surface reaction sites.
- In solution-precipitation, the coarsening rate increases as the amount of liquid decreases due to smaller diffusion distance (thinner liquid layer).
- The growth law is same as solid-state sintering.
 $k = 0.9 \gamma_{SL} \Omega S D_L / [KT(1 - V_s^{1/3})(1 - \sqrt{C})]$. S - solubility, V_s - solid volume fraction, C , contiguity, is the fraction of solid grain surface in contact with other grains.
- Many of the parameters are thermally activated and hence, grain growth is more at high temperature.

Image

Now, this densification during the liquid phase is also associated with the coarsening. The solid phase coarsens at a rate such that the average grain size, G , changes with one-half or one-third power of time. And, this will depend on the shape of the grains as to whether it will be a one-half power or one-third power with respect to the time.

The rounded shape grains for example, will grow by solution re-precipitation with one-third kinetics. And, this is what we have already seen before that the densification is proportional to the one-third power of the sintering time t . And, angular grains on the other hand such as in the tungsten carbide cobalt system will take up one-half rate kinetics and in that case the coarsening rate is limited by the availability of surface reactions sites.

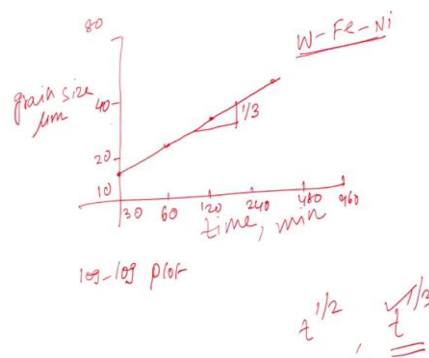
When it takes up the t to the power half kinetics kind of densification and during the solution re-precipitation the coarsening rate increases as the amount of liquid decreases. And, this is due to the smaller diffusion distance because the liquid layer becomes thinner. Therefore, the diffusion can occur rapidly leading to growth of the grains which have already formed contact between them.

The growth law is same as the solid state sintering and it is given by an equation like this,

$$k = 0.9 \gamma_{SL} \Omega S D_L / [KT(1 - V_s^{1/3})(1 - \sqrt{C})]$$

where S is the solubility, V_s is the solid volume fraction, C is known as contiguity that is the fraction of solid grain surface in contact with other grains. And many of these parameters are thermally activated for example, the diffusion coefficient through the liquid D_L that is a temperature dependent parameter; it increases with increase in temperature. And therefore, the grain growth will be more at high temperature; higher the temperature, higher will be the coarsening.

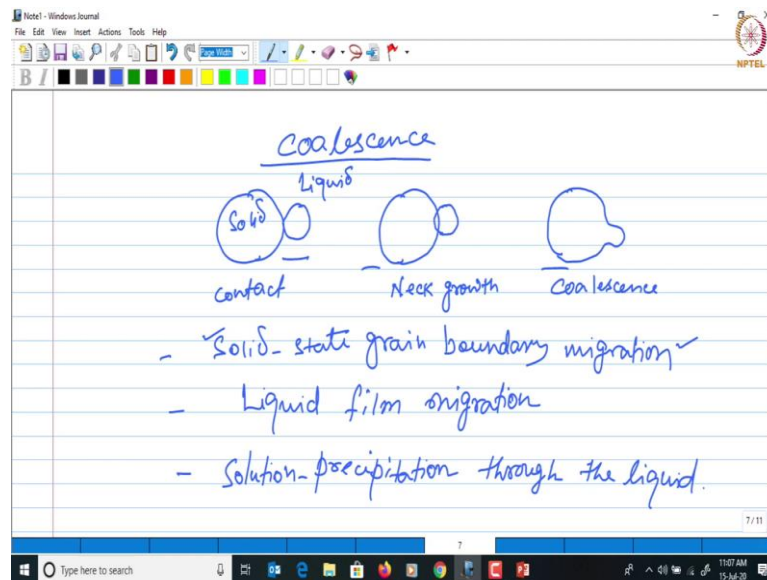
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If you look at the grain coarsening rate (above image) or the various grain size with respect to time, it might vary with $t^{1/2}$ or $t^{1/3}$; depending on the shape of the grains. And, it might also depend on what kind of material system. Let us say we are talking about an alloy of tungsten iron nickel (W-Fe-Ni) in this case, just to demonstrate how the grain size varies with time.

This is on a log-log plot between grain size and sintering time. This will give rise to a straight line, as the time increases the grain size will also increase. If you see the slope in this particular case it is one-third; so, this varies with one third power of time t . So, this is what we have seen before, this is basically the case for this kind of rounded shape grains.

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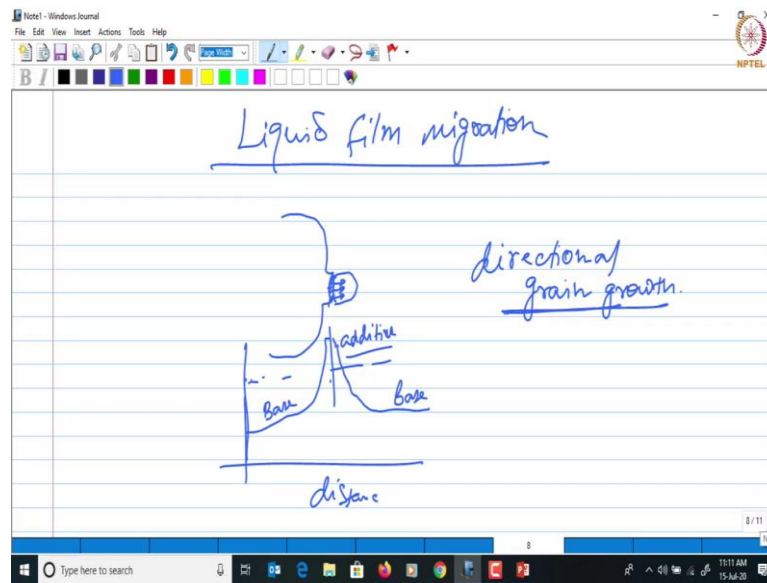


Now, if you see the mechanism of the grain coarsening it basically occurs through a coalescence kind of process. As the grains make contact through a wetting liquid, they can coalesce and make a bigger grain as depicted by this diagram (above image in the slide). So, after making contact they actually penetrate into one another and as a result of that coalescence will happen, leading to a bigger particle.

Now, there are different mechanisms of coalescence such as solid state grain boundary migration, liquid film migration and solution precipitation through the liquid. Although, the coarsening by solid state grain boundary migration can occur but, the probability of occurring this particular mechanism is low.

So, in cases where there are no contacts like this between the solid grains then the coalescence can occur by liquid film migration. Let us see that mechanism as to how it occurs.

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There is a liquid film in this case which separates the grains. And the coalescence therefore; will have to happen by the migration of this liquid film rather than the migration of the boundary. And, this kind of coalescence process in metallic system is also known as directional grain growth, where the grain is growing in a particular direction as the liquid film moves.

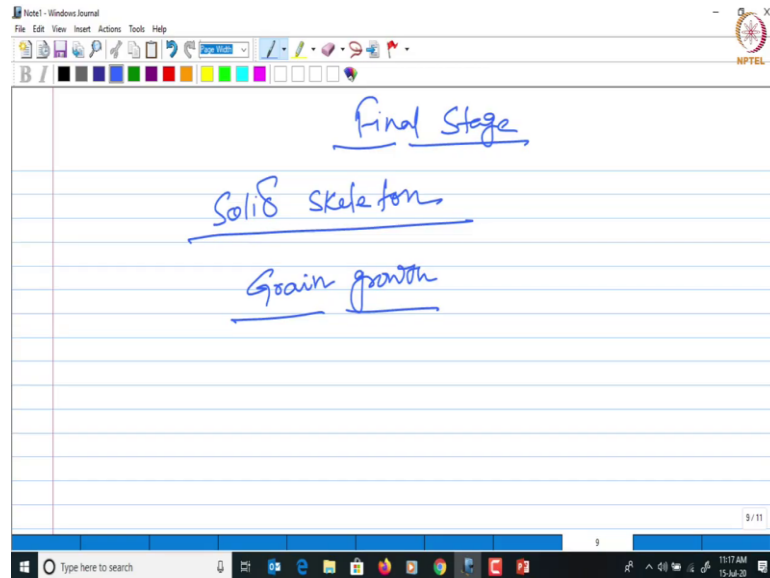
And, if you see that particular portion where the liquid film is there and the grain is growing, that growing part will be different from the rest of the particle in terms of the chemical energy. Due to the formation of this part which is basically a combination of two materials, the base material and the additive; there is a driving force due to a reduction on the chemical energy part.

This process is driven by a reduction in the chemical energy rather than a reduction in the interfacial energy. In fact, the increase in the interfacial energy due to the creation of this interface is actually overcome by this reduction in the chemical energy. So, this portion if you see, the portion at which the particle is actually growing there you would find a higher concentration for the additives compared to the other regions.

If you see it as a function of distance in this region (above image), where the liquid film is growing you would find that the concentration of the additive is high. And, the rest of the region is basically the base material which does not contain any additive. So, this

creation of this region having both the materials will actually lead to a reduction in the chemical energy.

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Now, once the contacts between the solid grains form and a stable neck grows between them; then the final stage densification occurs through the solid skeleton which forms. In this case it is basically driven by the pore-filling rather than solution precipitation or contract flattening. So, here whatever the leftover pores are there those have to be filled through a diffusion across this solid skeleton which has already formed now; as the solid grains have already made contacts and stable necks have grown between them.

Here you need to see how the pores are actually being filled for the final stage densification to take place. We have seen before that the pore-filling happens in a sequential manner; first the smaller pores get filled and then comes the bigger ones and so on. So, these isolated pores which remain unfilled we will have to be filled now in the final stage through this solid skeleton.

And, this is basically accompanied by the grain growth, as the grains grow it will lead to a more favorable condition for the liquid to flow into these isolated pores and fill them. And, that is how the final stage densification is going to occur.

This is basically determined by the curvature of the liquid vapor meniscus. In the final stage four filling driven by grain growth is a dominant densification mechanism. So,

fully dense compact will be achieved only when all the pores are filled in the final stage. And therefore, here also you need to consider if there are any gases trapped inside the pores.

We have seen before that during solid state sintering if there is a gas trapped inside the pores, that will limit the final densification. Because, pore closure will not happen due to the gas pressure inside the pores and that will lead to a lower density in the sintered component. So, here also if there is a gas which is not soluble in the liquid, it will be trapped in the pores and will limit the densification that can be achieved in the final compact.

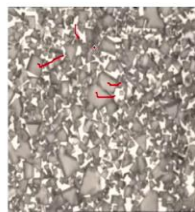
So, the gas trapping concerns that we had for the solid state sintering has to be considered here also. And, it has to be made sure that all the pores are filled during the final stage for a fully dense compact to come out at the end of the sintering process. In order to make sure that this kind of gases are not trapped and the densification in the final stage is not limited, the sintering can be either done in vacuum or in a gaseous atmosphere that is soluble in the liquid.

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Microstructure



- The final structure consists of solid grains connected by a network of the solidified liquid phase. If the solid is etched out it will leave behind a skeleton of the liquid.
- Different grain-liquid structure can develop depending on the dihedral angle. A typical structure that develops in WC-Co cemented carbide is solid grains dispersed in the solidified liquid.
- Residual pores can also be found. In some cases pores are retained to serve purposes like lubrication, filtering.



WC-Co

Now if you look at the final structure of the material at the end of the liquid phase sintering process, you will find solid grains connected by a network of the solidified liquid phase. If you polish the sample and etch it and observe it under a microscope, this

is how the microstructure will look like (above image). The gray regions that you see these angular grains over here these are the solid grains.

The white region in between is actually the solidified liquid. So, that is what is holding these solid grains together as if they are kind of cemented by the solidified liquid. And, you have a final solid microstructure like this where, the grains are held together by a network of the solidified liquid. This micrograph that you see over here for example, belongs to this material tungsten carbide.

In this case you can see the presence of cobalt which is basically the additive, the low melting material which is added to sinter the tungsten carbide material which is difficult to sinter by conventional solid state sintering process. So, here the grains that you see these grains, this blocky type of grains that you see these are the tungsten carbide grains. And, the white phase that you see around these grains that is the cobalt which has now solidified.

And, now we can see that these tungsten carbide grains are being held together by this solidified cobalt, as if these grains are cemented together by the cobalt phase. That is how perhaps the name has been given as cemented carbide for these kind of carbide materials, which are sintered by the liquid phase sintering process with the help of an additive which is in this case cobalt.


That is what actually helps in sintering this material and you get a fully dense material at the end of the liquid phase sintering process. This is also an example of how the liquid phase sintering process is useful in terms of processing materials which are very hard and are difficult to process by conventional processing routes. This kind of carbides such as tungsten carbide and there are a few more like tantalum carbide, titanium carbide and so on.

These materials are very hard and that is why they are used for tool materials where you need a very high wear resistance. So, that the tool can easily cut other materials and the tool wear and tear can be minimized. These kind of materials are used for cutting tools and similar applications where you need a very high hardness. So, being a very hard material tungsten carbide or similar other carbides are difficult to sintered by conventional solid state sintering route.

That is where the liquid phase sintering comes into rescue and you can easily process this material to full density with the help of an additive which melts at the sintering temperature. That is how with the help of the liquid phase sintering process, one can obtain a fully dense material even if it is a material which is difficult to compact and sinter by conventional processes.

And, the grains can have different kind of shape and structure depending on the dihedral angle. If the pores are not completely filled during the final stage, some residual pores can also be found in the microstructure. This was all about liquid phase sintering.

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Pros and Cons of Liquid phase sintering

Advantages:

- Enhanced kinetics, faster atomic diffusion and hence, faster densification.
- Lower melting additive enables sintering at lower temperatures.
- Processing difficult to sinter materials like WC, SiN is possible.

Disadvantages:

- Proper control is necessary. Too much liquid may cause collapse of the compact.
- Enhanced kinetics can lead to grain growth.
- Possibility of grain boundary segregation.
- High temperature properties of the material are compromised due to presence of the liquid phase at the grain boundaries.

Now, every process will have its own pros and cons. Let us look at the advantages and disadvantages for this process as well. The advantages are enhanced kinetics, faster atomic diffusion and hence, faster densification as we have already discussed. A lower melting additive enables sintering at lower temperatures. And, the processing of difficult to sinter materials like tungsten carbide, silicon nitride is possible with the help of this liquid phase sintering.

The disadvantages are it needs a proper control. If there is too much of a liquid, it might cause collapse of the compact and it may even disintegrate. Enhanced kinetic can lead to grain growth. And possibility of grain boundary segregation is also there, because of the presence of liquid which solidifies at the end of the process.

High temperature properties of the material are compromised due to presence of the liquid phase at the grain boundaries. So, as we have seen the micro structures of the final solid consists of a network of this solidified liquid. Therefore, you cannot use the material at a temperature where this solidified liquid can melt again. And therefore, the high temperature applications of such materials are limited.

So, we have been discussing about this particular technique liquid phase sintering over the past few classes. So now, that we have learned about the technique in detail, it is time for us to have a recap of the entire process and try and summarize it.

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Summary of LPS



- High diffusivity in liquid provides rapid transport path and enhance the densification.
- Liquid penetrates the grain boundaries when $\gamma_{ss}/\gamma_{sl} > 2$.
- Mechanism: Rearrangement, Solution-precipitation.
- Rearrangement: Primary – due to capillary force, Secondary: due to liquid penetration into the grain boundaries.
- Densification: Contact flattening, Ostwald ripening and grain shape accommodation.
- Final stage: Sintering of the solid skeleton.
- Microstructure: solid grains connected by a network of the solidified liquid phase.

Here goes the summary of the liquid phase sintering process. Here we are talking about sintering a material which is having another phase known as the additive which will melt at the sintering temperature and will provide a rapid transport path. And, hence will lead to enhanced densification. So, when the liquid forms it basically penetrates the grain boundaries when this ratio γ_{ss}/γ_{sl} becomes greater than 2.

And, once the solid grains are wetted by the liquid the densification starts. As far as the mechanism of densification is concerned, there are basically two types of mechanisms. One is the rearrangement and other is the solution precipitation. In the rearrangement process as the liquid forms the particle will rearrange themselves due to the capillary force exerted by the liquid. And, the rearrangement process can be of two types.

Primary which is essentially due to the capillary force exerted by the liquid and the secondary rearrangement is because, of the penetration of the liquid into the grain boundaries leading to the fragmentation of the solid particles and, when these fragments rearrange themselves that is known as the secondary rearrangement. Now, densification occurs through primarily two modes.

One is through contact flattening and another mode of densification is Ostwald ripening in which the densification is also associated with grain growth. So, contact flattening is basically due to the dissolution of the contact points and creation of a flat surface along these contact points across which the mass transport takes place and the densification occurs.

In the final stage sintering, once the solid grains make contact and a stable neck forms between them then the final stage sintering takes place through the solid skeleton. And, here it is basically through the pore-filling, the remaining pores which were unfilled gets filled in this stage.

That is how a full densification can be achieved when all the pores are completely filled in the final stage. The microstructure of this kind of material will basically consist of solid grains connected by a network of the solidified liquid phase. And, with that we come to the end of this particular lecture. I will see you soon again.

Thank you for your attention.