

Powder Metallurgy
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Lecture – 50
Sintering – 10

Hello and welcome back. So, in the past several classes we have been discussing about this topic Sintering. So, the solid state sintering that we have been discussing is based upon the phenomena of diffusion which takes place during the process leading to densification. And, the main driving force behind this sintering process is surface energy, that is what we have learned so far.

But, surface energy is a very small driving force and therefore, to create a material which is having density and properties comparable to the wrought products sometime it is necessary to enhance the densification. So, in this lecture we are going to learn some of those techniques which can enhance the sintering and lead to better densification.

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Enhanced Sintering



>Phase Stabilization

>Certain phases in a material have better diffusivity. e.g. the volume diffusivity at 910 °C in BCC α -Fe is 300 times more than the FCC γ phase. — Austenite

>Therefore, stabilization of the ferrite phase enhances the sintering. Si, Mo, P are ferrite stabilizer. Hence, Si addition in Fe increases the sintered density.

>The mixed phase microstructure also resists grain growth, especially in the intermediate stage.

>Same concept can be used to sinter stainless steel by using an excess of Cr that provides a second phase helping control the densification and microstructure evolution.

>Adding Ni as powder surface coating enhances sintering by generation of vacancies at the phase interface as homogenization occurs by diffusion.

>Surface contaminants may attack and deplete one of the alloy components and hence, adding excess of C in carbides and Cr in stainless steel is a common practice.

So, to enhance the sintering there are certain external things which can be applied. For example, the sintering can be a pressure assisted sintering where during the sintering process pressure is also applied. But, there are certain things which can take place inside the material

itself and that can also enhance the densification process . For example, if you have a phase which is better in terms of the diffusion of the atoms or having a better diffusivity that phase can be used as a means to enhance the densification, right.

So, we have seen that it is all about diffusion which causes the densification during the sintering process. So, if we have something in the material which has a better diffusivity that will obviously, result in better densification, right. So, here we are talking about a phase which will give a better diffusivity, right. And therefore, this enhanced sintering technique is known as the phase stabilization because here we need to stabilize that particular phase having the better diffusivity.

Apart from temperature, there are certain other factors which can influence the diffusivity and crystal structure is one of them. Now, there are materials which can exist in different crystal structures at different temperatures. So, this phenomena of a material existing in different crystalline forms is known as allotropy. And, this transformation from one crystal structure to another at a particular temperature is known as an allotropic transformation.

For example, iron is BCC at room temperature, but when it is heated above 910 degree Celsius, it transforms to an FCC structure. And, in case of iron the diffusivity in the ferrite phase or the alpha iron as it is called, is much higher compare to that in the FCC gamma phase. This is also known as ferrite the alpha phase and the gamma phase is known as austenite .

For example, if you talk about the volume diffusivity in the BCC ferrite phase at 910 degree Celsius it is 300 times more than that in the FCC in gamma phase. And therefore, in order to enhance the sintering here we are looking to stabilize ferrite phase. So, there are certain alloying elements which can stabilize the ferrite phase in iron and these are silicon, molybdenum, phosphorous this kind of elements can stabilize the ferrite phase.

And, therefore, an addition of this kind of elements for example silicon in iron will increase the sintered density because it will enhance the densification. And, this kind of mixed phase microstructure also resists grain growth specially in the intermediate stage and therefore, it is also good for making materials of finer grain size.

And, the similar concept of the phase stabilization can also be used to sinter stainless steel, where chromium is a major alloying element which is also a ferrite stabilizer. So, by using an excess of chromium, a second phase can be generated and that will help the densification and also the microstructure evolution during the sintering process.

Now, nickel on the other hand, is an austenite stabilizer and therefore, as far as the densification process is concerned, the addition of nickel as an alloying element is not going to help. However, if nickel can be used as a coating on the surface of the powders, that can enhance the sintering by generation of vacancies, right. So, in that case the mechanism of the enhancement is completely different.

These vacancies that the nickel helps generate will actually assist the mass flow as we have seen before and that will in turn lead to a better densification. So, vacancies are generated at the phase interfaces as the homogenization occurs by diffusion. And, when you talk about stabilizing the phase by addition of alloying elements, it is always good to have little more excess of these elements because there could be some surface contaminants which may attack and deplete the alloy concentration.

And, therefore, if you have some excess of this it will be better to adjust the chemical composition to the range where it is needed for the phase stabilization to happen.

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Activated Sintering

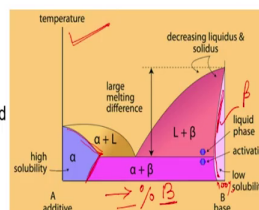


> Chemical additions, external electric field or mixed phase sintering that lower the activation energy, sintering temperature or time.

> W powder treated with Ni, Pd or Pt to form powder surface coating gives rise to activated sintering and shows higher shrinkage.

> The amount of activator is often less than 0.3%. It must meet certain criteria.

- It must be a metal or compound which forms a low-melting phase,
- it must have a large solubility for base metal but the base metal should have low solubility for the activator.
- It should stay segregated to the interparticle interfaces during sintering to provide a high diffusivity path.



α - Solid solution of B into A
 β - Solid solution of A into B

Now, another technique which is used to enhance the densification is known as activated sintering. This is basically through some external additions which can enhance the densification. For example, it can be chemical additions or application of some external electric field or some kind of mixed phase sintering that will lower the activation energy and sintering temperature or time. So, that way it will enhance the densification and give rise to a better sintered density.

So, in order to understand as to how these kind of additions enhance the densification, we will have to understand a little bit about these kind of phase diagrams between the additive and the material which is being densified. The additive which is enhancing the sintering is also known as the activator. So, the activator must be a material or compound which forms a low melting phase with the parent material in which it is being added and it must have a large solubility for the base metal, but the base metals would have low solubility for the activator.

And, this is what you can see in this phase diagram over here. So, phase diagram basically is a diagram which is a representation of different phases existing at different temperatures and concentration of a particular alloying element. So, here A is the additive and B is the base material. So, this is the phase diagram for addition of A into B or B into A. So, the condition is A should have a large solubility for the base material.

So, here you can see this is increasing percentage of B that is the base material which is being sintered. So, at this end it is 100 percent B on the right hand side here and on the left hand side here it is 100 percent A. So, as you go from left to right the amount of B increases. So, here this field, that you have that alpha field over here that shows the solubility of B into A. So, here you can see a large amount of solubility of B into A and that is what is needed, but the base metal should have low solubility and that is what we can see over here.

This phase field is much narrower compare to this. So, this is basically the beta phase which is a solid solution of A into B, whereas alpha is a solid solution or an alloy of B into A right. So, here you can see that the solubility of B into A is more than that of A into B, ok. So, that is why this alpha phase field is much larger compare to the beta phase field.

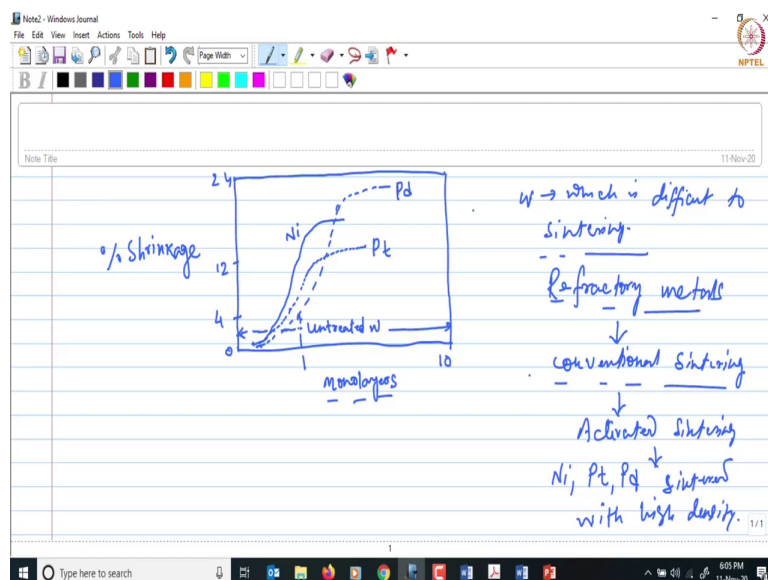
So, in this case A is the solvent and B is the solute and for the beta phase, B is the solvent which is dissolving the solute A. And, the next condition to be satisfied by the activator is that

it should stay segregated to the inter particle interfaces during sintering to provide a high diffusivity path right. So, we have seen that the contact points formed at the interfaces between the particles.

So, that is where the neck grows and the densification is all about transport of matter towards the neck right for it to grow leading to the densification. So, therefore, this interface should have an activated path for the diffusion to take place and therefore, this activator which is being added to enhance this diffusion should be segregated along that path that is along the interfaces. So, the amount of the activator which is typically added is often less than 0.3 percent.

So, this will probably satisfy both of these conditions particularly the second one, right. It should be only along the inter particle interfaces and not distributed all over the place in the compact otherwise you know this activation will not happen effectively as we discussed. So, let me give you an example of activated sintering to demonstrate its utility. Activated sintering of a tungsten treated with some metals such as nickel, palladium or platinum is a perfect example of this activated sintering.

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And, it can be shown with the help of a plot like this in which the amount of the activator is plotted against shrinkage. The activator concentration is expressed in terms of atomic

monolayers on the tungsten powder. So, the activators in terms of these metals are applied on the tungsten surface as coatings and the concentration is expressed as monolayer of that particular coating.

So, if you look at the percent shrinkage which represents the densification during sintering, the untreated tungsten will lie somewhere around here. So, you can see without the addition of the activators, the shrinkage or densification of tungsten is quite low, but when the activator is added in certain amount you could see that the shrinkage will increase significantly as demonstrated by these plots.

This one is for tungsten treated with platinum, this is for nickel treated tungsten and the top one is for tungsten treated with palladium. So, you can see that when an activator is added, the densification increases quite significantly and therefore, it becomes easier to sinter a material like tungsten which is otherwise difficult to sinter by conventional sintering processes because of its high melting point. And, because of its melting point, tungsten is one of those refractory metals as they are called.

So, materials like this having very high melting points may be difficult to sinter by conventional solid state sintering process and that is where the activator sintering comes into picture. And, with the help of such activators like nickel, platinum or palladium, even these kind of metals can also be sintered with high density.

This is how we can see the utility of the activated sintering process as to how it helps, particularly for materials which may be difficult to sinter by conventional sintering process.

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Activated Sintering contd..



- >The kinetics of activated sintering depends on the rate of diffusion through the activator.
- >Thick activator layers provide significant diffusion flux. However, concentrations above the minimum required do not make a difference.
- >The activation energy for shrinkage is closer to that of self-diffusion in the activator. Due to low activation energy for diffusion, temperature is the important parameter.
- >The process resembles grain boundary diffusion, initial **shrinkage** $\propto t^3$.
- >Densification results in loss of pores that can result in rapid grain growth and consequent degradation of properties.
- >Chemical additions are most successful for activating sintering. Radiation treatments have shown success but its use is limited.
- >All of the activation sintering treatments either alter the kinetics or the driving force for sintering.
- >Radiation alters the kinetics by generating excess vacancies. Heating cycle through polymorphic transformation like $\alpha \rightarrow \gamma$ generates internal stresses that increases the driving force.

Now, the kinetics of the activated sintering depends on the rate of diffusion through the activator because that is the diffusion path as we discussed just now. So, a thick activator layer provides significant diffusion flux. However, concentrations above the minimum required do not make a difference right because as we have seen it has to be only along the inter particle interfaces, where the activator is actually needed right.

So, if you have concentrations higher than that which will lead to spread of these activator beyond the inter particle contacts, then it is not going to make much of a difference right because the other areas of the activators apart from the inter particle interfaces are not going to be the active diffusion paths. The activation energy for shrinkage is closer to that of self diffusion in the activator and due to the low activation energy for diffusion; temperature is the important parameter here.

The process is quite similar to grain boundary diffusion. In grain boundary diffusion also it happens along those interfaces between the grains. So, this grain boundaries are nothing but the interfaces between the grains and the mass transport happens along these boundaries. So, here also we are talking about scenario where the inter particle interfaces are actually coated with this activator, and the mass is flowing predominantly along these paths.

So, this is very similar to the grain boundary diffusion that you have as span of the densification mechanisms of sintering. And, here the densification results in loss of pores and that can result in rapid grain growth and consequent degradation of properties. So, there are many properties for example, the strength and the hardness which depends on the grain size, a finer grain size will give rise to a higher hardness and strength. So, if there is grain coarsening this kind of properties will degrade .

Now, chemical additions are most successful for activating sintering, but there are certain other ways of activating the sintering process. For example, radius and treatments have also shown success with regard to that, but their use is limited because of various other reasons. For example, if you talk about this radius and it has its own safety hazards and all that.

And, if you talk about the activation mechanisms it is primarily either by altering the kinetics or the driving force for the sintering process or all of the activating agents which are generally used, right. So, this is what we in fact discussed in the beginning also that it can actually reduce the activation energy for sintering leading to a better densification or it can even lower the sintering temperature or time.

So, when you talk about the sintering time that is altering the kinetics of the process right , it can be either through altering the activation energy or the kinetics of the process in terms of the sintering time. Radius and treatment for example, alters the kinetics by generating excess vacancies and heating cycles for the phase stabilization like this allotropic or polymorphic transformation, like ferrite to austenite generates internal stresses that increases the driving force right.

So, you can see the example of both of these phase by which the activation takes place: one is through kinetics, so that happens for the radiation treatment. And, another is through the driving force which happens in this kind of phase stabilization which is generally done by a heat treatment cycle.

Alright, so, it is time for us to summarize this lecture. So, to summarize this lecture we can say that the solid state sintering process can be enhanced by certain means and ways. For example, if there is a phase which is having higher diffusivity, that phase can be stabilized in

the material by some alloying additions and it will lead to a better densification because of the higher diffusivity.

Iron is an example which exists in different crystalline forms at different temperatures and one of these phases the ferrite phase, has a much higher diffusivity compare to the high temperature gamma phase. So, if the ferrite phase can be stabilized it will give you better diffusivity and higher densification.

So, additions like silicon, molybdenum, phosphorous will stabilize the ferrite phase and lead to a better sintered density, ok. And, the other way of doing it is through addition of some activating agents and these activators which are added have to satisfy certain requirements such as solubility and also the concentration. These are some example of activators nickel, palladium or platinum which are used for sintering tungsten powder.

Then we have also discussed what kind of a mechanism is responsible for this activation that occurs during this kind of activated sintering. So, the mechanism is similar to grain boundary diffusion because here the diffusion path is the inter particle interfaces like how you have the inter-grain interfaces which are basically the grain boundaries in a crystalline material.

So, since the activator predominantly lie along these inter particle interfaces the diffusion happens across this interfaces and therefore, it resembles grain boundary diffusion and this activation occurs either by alteration of the kinetics or the driving force for sintering. In some cases for example, if radiation is used as an activating agent, it will alter the kinetics and in some cases like the phase stabilization process, it will actually alter the driving force.

And, with that we come to the end of this class.

Thank you for your attention.