Powder Metallurgy
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Lecture – 60
Spark Plasma Sintering (SPS)

Hi everyone and welcome back to another lecture of this series; so, before we proceed let us take a quick recap of the previous class to set the background of this class today.

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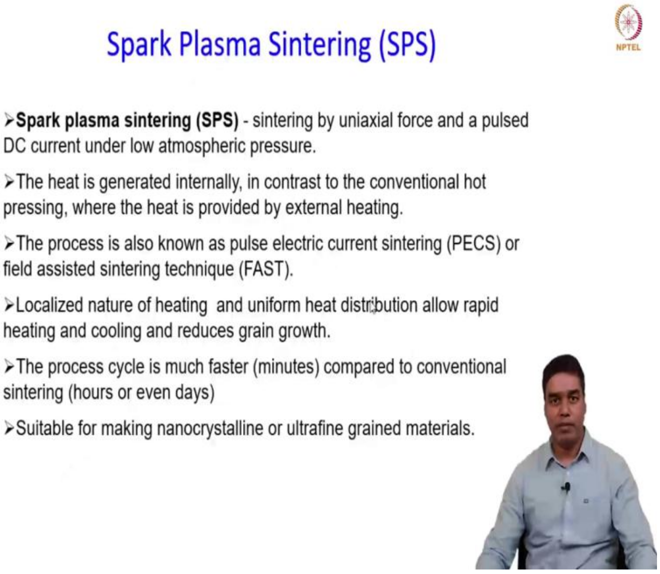

Spark Plasma Sintering (SPS)

- **Spark plasma sintering (SPS)** - sintering by uniaxial force and a pulsed DC current under low atmospheric pressure.
- The heat is generated internally, in contrast to the conventional hot pressing, where the heat is provided by external heating.
- The process is also known as pulse electric current sintering (PECS) or field assisted sintering technique (FAST).
- Localized nature of heating and uniform heat distribution allow rapid heating and cooling and reduces grain growth.
- The process cycle is much faster (minutes) compared to conventional sintering (hours or even days)
- Suitable for making nanocrystalline or ultrafine grained materials.

So, right now we are discussing about the Spark Plasma Sintering process, which is one of the most efficient processes for full density processing. And, in the last class we have discussed about the basic mechanism of this technique.

And, there we have seen that spark plasma sintering is basically a process, which uses the joule heating. Here the heating takes place internally in the compact, unlike the conventional sintering processes in which an external heat source is used to heat the compact.

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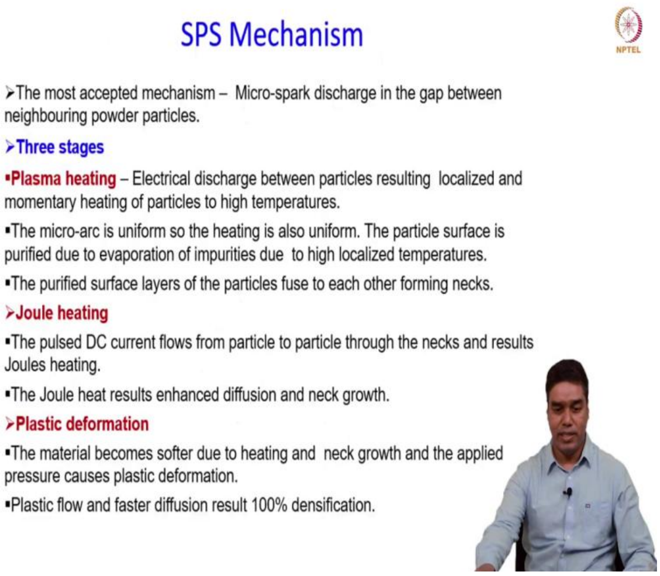

SPS Mechanism

- The most accepted mechanism – Micro-spark discharge in the gap between neighbouring powder particles.
- **Three stages**
- **Plasma heating** – Electrical discharge between particles resulting localized and momentary heating of particles to high temperatures.
- The micro-arc is uniform so the heating is also uniform. The particle surface is purified due to evaporation of impurities due to high localized temperatures.
- The purified surface layers of the particles fuse to each other forming necks.
- **Joule heating**
- The pulsed DC current flows from particle to particle through the necks and results Joules heating.
- The Joule heat results enhanced diffusion and neck growth.
- **Plastic deformation**
- The material becomes softer due to heating and neck growth and the applied pressure causes plastic deformation.
- Plastic flow and faster diffusion result 100% densification.

So, what we have discussed in the previous class is that, there are basically 3 stages in the spark plasma sintering process. First there is an electrical discharge between the particles when the electric field is applied. And, this leads to an intense localized heating, which leads to purification and cleaning of the particle surface for better bonding to take place between the particles.

This also leads to a melting at the contact points, because of the high localized temperatures and that again is helpful in bonding the particles together for the densification to occur. The heating here basically takes place by the joule heating mechanism, where a pulse DC current flows from particle to particle through the necks and results in heating.

And, this kind of heating also results in enhanced diffusion and neck growth. So, that ultimately leads to a faster densification in this process compared to the conventional sintering processes.

And, finally, when the pressure is applied after the heating has taken place, it will go through the plastic deformation and the densification will occur by the plastic flow. So, this is the basic mechanism of the spark plasma sintering process. Now we will continue on this and we will see the further details of the SPS process.

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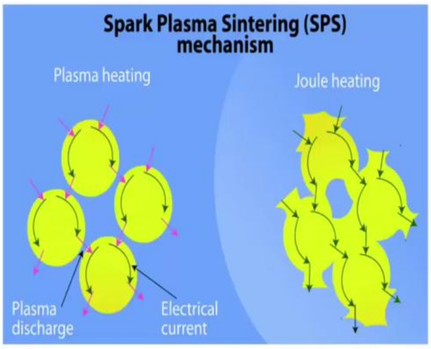
SPS Mechanism



So, when you talk about the SPS mechanism it is basically the plasma heating and the plasma discharge, which is set up in the gap between the particles. And, that ultimately leads to this joule heating, which results in heating up the compact and densification.

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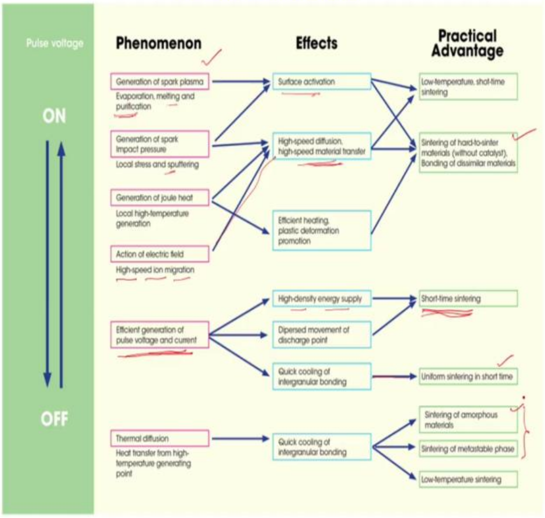
SPS Mechanism



Pulse voltage

ON

OFF

Phenomenon

Generation of spark plasma
Evaporation, melting and purification

Generation of spark impact pressure
Local stress and sputtering

Generation of joule heat
Local high-temperature generation

Action of electric field
High-speed ion migration

Efficient generation of pulse voltage and current

Thermal diffusion
Heat transfer from high-temperature generating point

Effects

Surface activation

High-speed diffusion, high-speed material transfer

Efficient heating, plastic deformation promotion

High-density energy supply

Dipersed movement of discharge point

Quick cooling of intergranular bonding

Quick cooling of intergranular bonding

Practical Advantage

Low-temperature, shot-time sintering

Sintering of hard-to-sinter materials (without catalyst), Bonding of dissimilar materials

Short-time sintering

Uniform sintering in short time

Sintering of amorphous materials

Sintering of metastable phase

Low-temperature sintering

So, here the electric field is applied through a DC pulse, which is on off type. So, during this pulsing of the current there are different phenomena which take place and each of these phenomena have their own effects on the densification process and the densification mechanisms which occur during SPS. So, this is a diagram (slide above), which talks about this phenomena and their effect. And, you can also see the practical advantage that you get due to these effects.

So, when the DC pulse is applied first you have the generation of the spark plasma and this basically leads to surface activation. And, then due to this sparking between the particles intense heat is generated and due to that there is evaporation, melting and purification.

So, due to the intense heat the particles also melt at the contact points and evaporation also takes place and that in turn leads to the purification of the surface of the particles. So, that is about the surface activation and the practical advantage that you get out of this is the low temperature and short time of sintering.

Because, the densification process is all about bonding between the particles and when you have a clean surface, bonding becomes easier and therefore, the sintering can be done at a lower temperature and the sintering time also can be lowered.

Then, once the spark is generated it will also exert some impact pressure on the particles, because it is sparking. You might have seen how sparking comes out with the force. Due to that some kind of impact pressure will be provided when the spark is generated the between the particles.

And, this basically leads to local stress and sputtering. The effect of that is high speed diffusion and high speed material transfer for the neck growth that leads to densification. And, the practical advantage of this is sintering of hard to sinter materials, without any catalysis or any modification to the powder.

And, bonding of dissimilar materials can also be achieved due to this high rate of material transfer. Then, this sparking leads to the joule heating and that leads to local high temperature, and the effect of that is efficient heating and plastic deformation when the pressure is applied.

All these phenomena and their effects are interrelated as you can see from these arrows (slide above). So, joule heating not only leads to efficient heating but it also contributes to high speed diffusion. Similarly, the spark generation contributes to high speed diffusion as well as the surface activation process.

So, there is a cumulative effect of all this phenomena. And, then there is action of the electric field, which leads to high speed ion migration and the effect of that is the high speed diffusion and the practical advantage is sintering of hard to sinter materials.

Efficient generation of pulse voltage and current and its effect can be seen in terms of high density energy supply, dispersed movement of discharge point. And, another effect is quick cooling of inter granular bonding and this quick cooling is good for uniform sintering in a short period of time.

And, then there is a thermal diffusion due to heat transfer from high temperature generating point and this leads to again the same effect, the quick cooling of the inter granular bonding; and the practical advantage of that is the possibility to sinter amorphous material, sintering of meta stable phase and low temperature sintering.

It is suitable for materials where you need to preserve a particular microstructure or a particular phase has to be cooled down quickly. There is not enough time for any phase transformation or any changes that can lead to a change in the microstructure or the structure of the material. Therefore a quick cooling is always helpful for this kind of amorphous materials or materials having meta stable phases.

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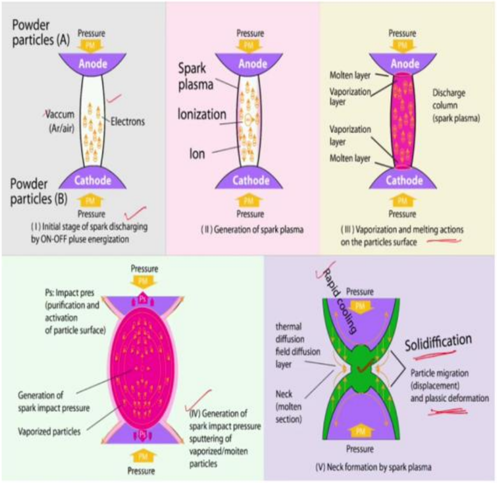
SPS Mechanism



Now, this is a diagram (slide above) which shows the different phenomena that occur during the SPS process from beginning to the end. In the beginning when the electrical field is applied a potential difference is generated between the particles as if they are acting as two electrodes, which can have flow of electrons in between them.

And, therefore, this has to be done in vacuum; otherwise this kind of electron flow cannot happen. So, this is a two particle model which is depicted to demonstrate the phenomena and the mechanisms of the SPS process. So, this is in the initial stage of sintering by that on off pulse energization which occurs as the electric field is applied.

And, then this electric field leads to generation of the plasma between the particles, leading to ionization and the effect of this is basically the melting of the particle contacts and vaporization. So, this ultimately leads to the cleaning of the surface of the particle and also purification. So, vaporization and melting actions of the particle surface are the next step once the spark plasma is generated.

And, the impact pressure which is created by the spark also leads to activation of the particle surface, which is again conducive for the bonding between the particles. So, the phenomena here are generation of spark impact pressure and sputtering of vaporized and molten particles.

And, at the contact points there is also rapid cooling and there is thermal diffusion also due to the intense heating and the temperature gradient that you may have from the contact point towards the core of the particle.

So, this leads to material transport towards the neck and there is localized melting also because of the intense localized heating, and that is again good for the diffusion process at this neck. And, when it is cooled down this molten material will ultimately solidify and as the pressure is applied plastic deformation will happen and the densification will occur by plastic flow. So, these are the different kind of phenomena which occur during the SPS process.

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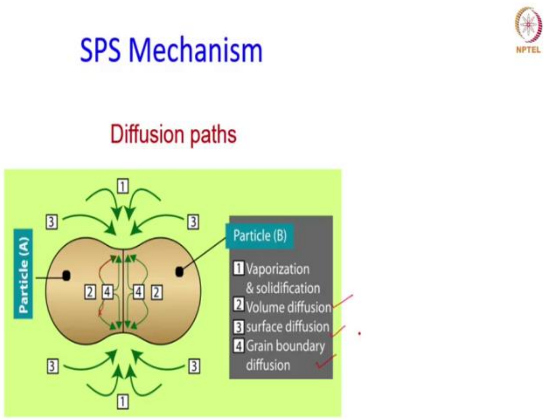

SPS Mechanism

Diffusion paths

1 Vaporization & solidification
2 Volume diffusion
3 surface diffusion
4 Grain boundary diffusion

And, this (slide above) is a two particle model showing the different diffusion paths, which exist during the SPS process. These mechanisms of diffusion are not very different from what we have in case of solid state sintering except probably this vaporization and solidification which occur due to the intense localized heating as a result of the spark.

And, apart from that you have similar mechanisms like volume diffusion, which occurs from the bulk of the particles towards the neck region, surface diffusion that occurs from the particle surface towards the neck; and, of course, grain boundary diffusion which occur along the grain boundary between the solid particles.

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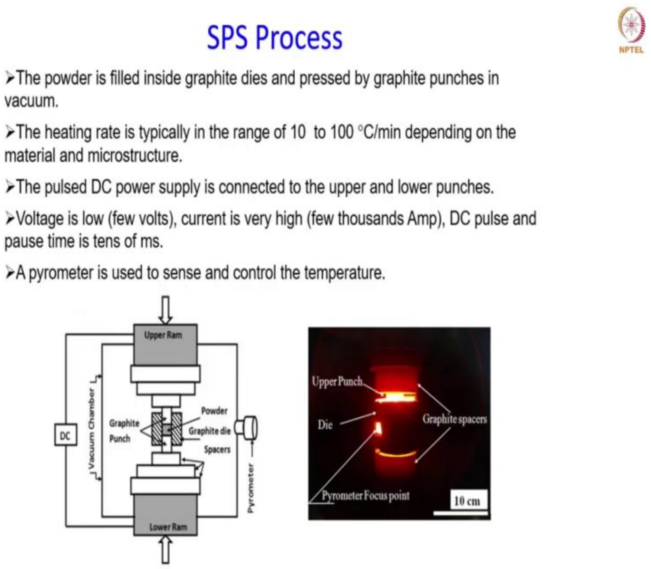

SPS Process

- The powder is filled inside graphite dies and pressed by graphite punches in vacuum.
- The heating rate is typically in the range of 10 to 100 °C/min depending on the material and microstructure.
- The pulsed DC power supply is connected to the upper and lower punches.
- Voltage is low (few volts), current is very high (few thousands Amp), DC pulse and pause time is tens of ms.
- A pyrometer is used to sense and control the temperature.

Now, let us see the process and the instrument of SPS. The powder is filled inside graphite dies, because graphite is conductive and through the die, the electrical current can be conducted to the powder. And, the powder is pressed by the graphite punches. The use of graphite here is basically to ensure that the current can be easily conducted to the powder particles.

The heating rate is typically in the range of 10 to 100 degree Celsius per minute, but it can be higher also depending on the material and the microstructure which is desired. And, a DC pulse is used as the power supply and the DC power supply is connected to the upper and lower punches.

And, through this graphite punches the current is conducted to the powder which is in the die. Here, the current levels are very high to the tunes of few 1000s of amperes, but the voltage is low. So, it is a low voltage high current process. And, DC pulse and pulse time is of the order of tens of milliseconds.

And, a pyrometer is used to measure the temperature. So, here is the schematic of the basic setup (slide above) that is used for SPS. So, as I said you have graphite die and punch sets, which are used to pressurize the powder and also to carry the electrical current to the powder. And, then you have this upper and lower ram through which the powder is pressurized and this upper and lower rams are connected to the DC supply.

And, here you have the pyrometer to monitor the temperature. And, this is how it would look like (right image in the above slide) if you have a look at the SPS chamber when it is in operation.

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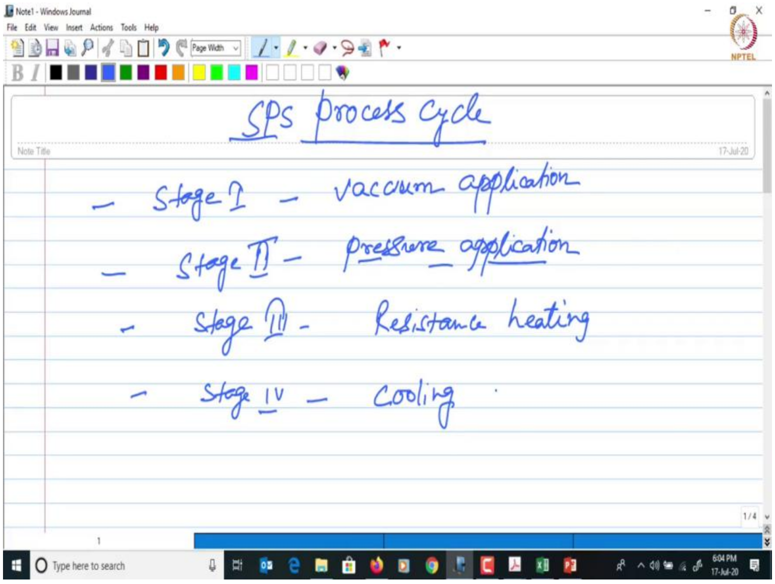

SPS process cycle

- Stage I – vaccum application
- Stage II – pressure application
- Stage III – Resistance heating
- Stage IV – cooling

So, if you look at the SPS process cycle it is basically a 4 stage process. In stage I, the SPS chamber is evacuated till the desired level of vacuum is reached. So, it is vacuum application stage. Then, in stage II the pressure is applied. Stage III is all about heating, where the joules heating or resistance heating takes place and the densification occurs under pressure.

And, finally, stage IV is the cooling stage. This is also important because how fast or how slow, the compact is cooled depending on that the microstructure can change. So, SPS is a process which is quite often used for preserving a particular type of microstructure, because of the rapid sintering which occurs here and the short sintering times.

A particular type of microstructure can be easily preserved, which may not be possible in conventional sintering processes as the sintering cycle is quite long. So, therefore, the cooling rate or the cooling stage is also important in this case.

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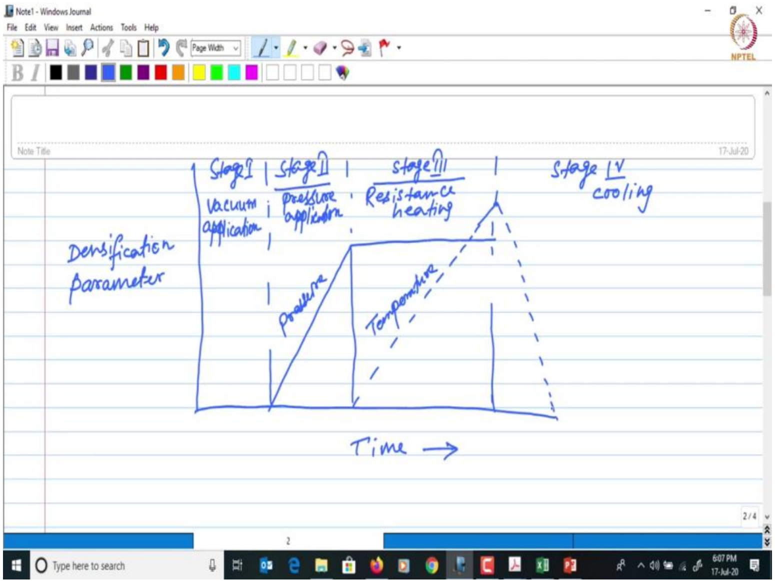

And, stage IV is all about that. It can be also illustrated with the help of a diagram like this (slide above), stage I is vacuum application, then once the vacuum is reached, the pressure is applied, that is stage II; and in stage III, the resistance heating takes place. And, finally, once it is held at the sintering temperature for a particular period of time it is cooled down. So, that is stage IV.

So, pressure is increased continuously and the compact is then held at a particular pressure as the sintering temperature is reached. And, as the heating takes place the temperature increases continuously all the way to the sintering temperature and once the sintering is accomplished it is cool down. So, these are the 4 stages of the SPS sintering process.

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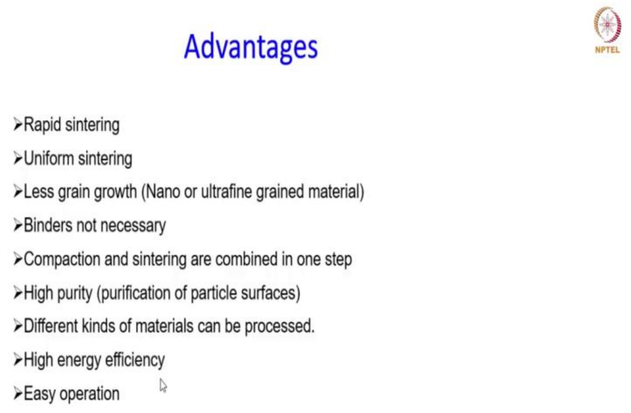

Advantages

- Rapid sintering
- Uniform sintering
- Less grain growth (Nano or ultrafine grained material)
- Binders not necessary
- Compaction and sintering are combined in one step
- High purity (purification of particle surfaces)
- Different kinds of materials can be processed.
- High energy efficiency
- Easy operation

Now, let us also have a look at the advantages of this process. You can achieve the rapid sintering and the sintering is also uniform because of the uniform heating that takes place; less grain growth because of the short sintering time and faster cooling. And, therefore, nano or ultra fine grained materials can be easily processed by the SPS technique.

Here binders are not necessary unlike many of the conventional sintering processes, where a binder is added to the compact to aid the packing of the powder particles. And, compaction and sintering are combined in one step, as the pressurization and heating occur simultaneously.

And, a high purity can be maintained here because of the purification of the particle surfaces, when the spark is generated and there is local intense heating. It also leads to the purification of the particle surfaces by evaporation and melting. And, all kinds of materials can be processed no matter what whether it is a softer material or a stronger material, even difficult to process materials can also be easily processed by this technique.

And, it also offers high energy efficiency and as far as the operation of the sintering equipment is concerned, it is also easy to operate. So, because of all these advantages in recent times SPS has become a quite attractive process to fabricate a large variety of materials for different applications.

So, we have been discussing about the different hot consolidation processes and their mechanisms in past few classes, including today's class. So, now, that we have learned about different techniques of full density processing or hot consolidation, it is time for us to have a quick recap and try and summarize these techniques.

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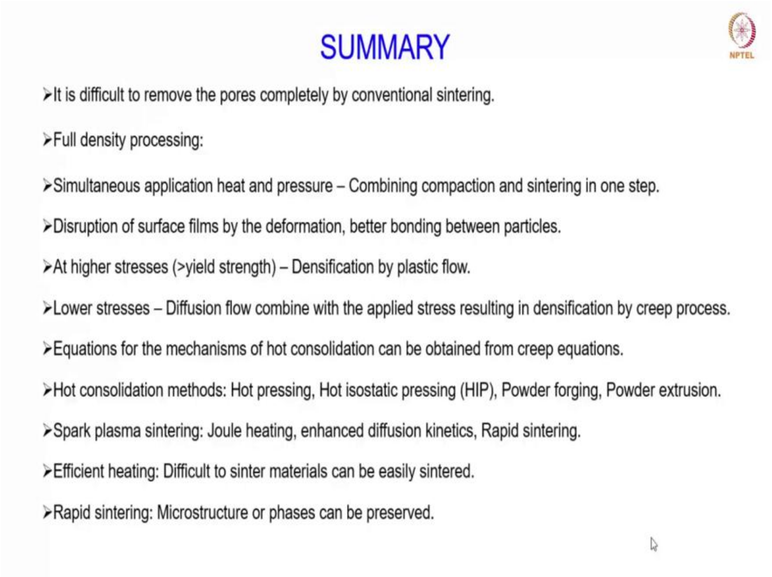

SUMMARY

- ➢It is difficult to remove the pores completely by conventional sintering.
- ➢Full density processing:
- ➢Simultaneous application heat and pressure – Combining compaction and sintering in one step.
- ➢Disruption of surface films by the deformation, better bonding between particles.
- ➢At higher stresses (>yield strength) – Densification by plastic flow.
- ➢Lower stresses – Diffusion flow combine with the applied stress resulting in densification by creep process.
- ➢Equations for the mechanisms of hot consolidation can be obtained from creep equations.
- ➢Hot consolidation methods: Hot pressing, Hot isostatic pressing (HIP), Powder forging, Powder extrusion.
- ➢Spark plasma sintering: Joule heating, enhanced diffusion kinetics, Rapid sintering.
- ➢Efficient heating: Difficult to sinter materials can be easily sintered.
- ➢Rapid sintering: Microstructure or phases can be preserved.

So, the need for full density processing arises from the fact that it is difficult to remove the pores completely by conventional sintering. And, therefore, we need methods which can overcome such limitations of conventional sintering and give rise to a fully dense compact at the end of the sintering process.

So, full density processing basically is a method, which applies the heat and the pressure simultaneously. So, this is kind of combining the compaction and the sintering process in one step, unlike the conventional sintering process in which the powder is first compacted. And, then the green compact is separately sintered to achieve densification.

But, in this case the powder can be directly sintered with the simultaneous application of heat and pressure to fully densifying it. And, the process which basically leads to this enhanced densification is the disruption of the surface films, by the deformation that takes place at high temperature.

So, this will ensure that when the particles come in contact a fresh surface is there for them to bond together. So, the fresh surface will essentially give rise to a more effective mass transfer and therefore, the particles can bond together more effectively giving rise to better densification.

And, if you look at the mechanism of this hot consolidation, where the heat and pressure are applied simultaneously; it basically resembles the creep phenomena, which is a high temperature deformation process that occurs at a constant stress. So, at higher stress levels the densification can take place simply by plastic flow as the yield strength of the material is exceeded, it will start to deform and the densification can occur through plastic flow along the necks which develop between the particles.

And, at lower stresses the diffusional flow will combine with the applied stress resulting in densification by the creep process. And, therefore, the equations for the mechanism of this hot consolidation process can be obtained by suitably modifying these creep equations taking into account the porosity which is present in the compact.

So, once we understood these mechanisms, we went ahead to talk about the different hot consolidation methods. And, we have covered these processes with regard to full density processing, hot pressing, which is basically uniaxial pressing in a die with the simultaneous application of heat and pressure.

We also talked about hot isostatic pressing in which the pressure can be applied from all direction uniformly unlike the die pressing in which the pressure is applied along a particular direction, which is basically along the axis of the die. So, this leads to a better densification when the pressure is applied uniformly through all directions. And, then we talked about other two hot consolidation processes and these were powder forging and powder extrusion.

So, this is basically you know deforming the powder inside dies to achieve the densification during this hard deformation. And, then we talked about a process called spark plasma sintering, which is quite different from all other sintering processes that we discussed before it; because in this case the heating mechanism is completely different.

So, unlike the conventional sintering process or the hot pressing process, here in case of spark plasma sintering the heating occurs internally by joule heating. So, here what is done is an electrical current is passed in the form of a DC pulse and the heating is achieved with the heating effect of that particular current.

So, that is basically the joule heating which is the heating effect of electrical current. And, this happens across the particle to particle contacts when a spark results due to the application of a very high current. And, therefore, the heating is quite intense and also uniform across the entire compact.

So, this results in enhanced diffusion kinetics and as a result of that a much rapid sintering compared to any other sintering process. And, because of this enhanced densification the process offers several advantages. For example, the efficient heating that you have in this technique will enable sintering of difficult to sinter materials.

So, there are certain materials which are difficult to sinter by other processes, but due to this enhanced diffusion kinetics and an efficient heating the spark plasma sintering can easily sinter those materials as well. And, the rapid sintering which occurs in this case will also allow us to preserve a particular microstructure, which may be desired in the final product or a particular phase, which may be needed for achieving certain properties.

That can also be preserved with the help of this particular technique called spark plasma sintering, because the sintering time in this case is much lower, it is in the range of few minutes to maybe couple of hours at max compared to several hours or even days for the conventional sintering process.

So, due to this kind of rapid sintering kinetics, a microstructure can be easily preserved, because there is no time for the microstructure to grow or change as the sintering and the heating and the cooling processes occur rapidly. Similarly, if a particular phase has to be preserved that can also be done since, there is no time for any phase transformation to take place.

So, these are the different advantages which can be achieved with the help of this spark plasma sintering, because of its efficient heating and the enhanced diffusion kinetics which results from the uniform heating that occurs through the generation of sparks between the particles.

With this lecture we have come to the end of this particular course.

Thank you one and all.