Friction and Wear of Materials: Principles and Case Studies
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Lecture – 16
Processing Concepts of Ceramics

Hello welcome back, so today in this lecture, we will see major concepts of ceramic processing. As you know the ceramic materials are different in their characteristics of bonding so it makes them different in properties as well as the processing. So, as you know the ceramics are inherently different in their characteristics of bonding so that makes them.

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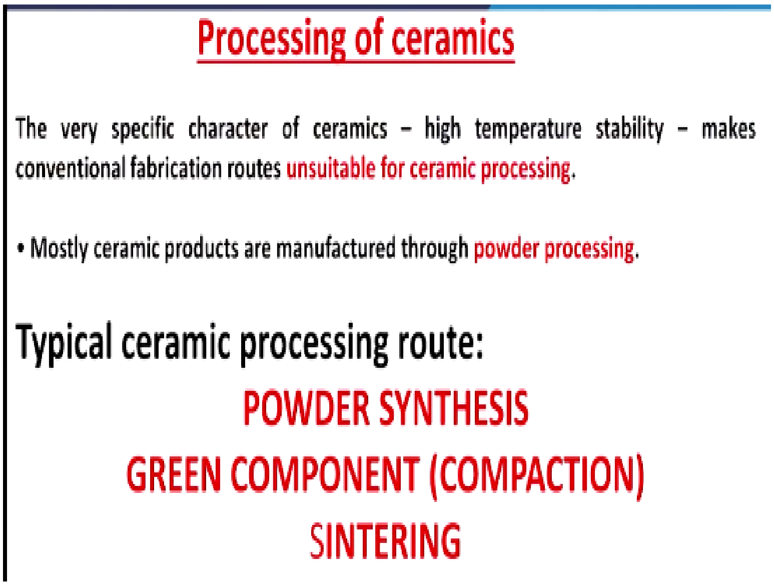

Stable at high temperature but the same characteristic of high temperature stability makes them unsuitable to process a ceramic material by conventional routes. So, conventional roots of processing for example this solidification right it is very difficult because high temperature stability means that comes from the bonding. So you have ceramics with higher melting point so high melting points ceramic material cannot be melted easily.

So, you require high temperatures so maintaining high temperatures in furnaces for long time for the production point of view is itself a difficult. So, it is very difficult to process these ceramic materials so through conventional fabrication root so the reason behind this is the very specific characteristic of ceramics that is high temperature stability right. But how they are manufactured they are manufactured generally through powder processing.

That means you have a folder of the ceramic material right and then the ceramic powders are compacted to give a shape component. So, for an engineering application you need to have a ceramic component with the definite shape and good properties. So, mostly ceramic products are manufactured through powder processing right that you start with powder of that material and then make it a component.

So, typically ceramic processing roots involved with powder synthesis step followed by the compaction step followed by the most important step that is sintering today in this class so we learn about these very important steps in the ceramic processing particularly we will focus on the last part sintering because that gives larger difference in the micro structure as well as the result and the properties.

So, the micro structure and result in properties differences make them suitable are unsuitable for the given tribal optical applications. That means the sintering influences the micro structure the micro structure results in a mechanical property variation that will lead to a different performance in the given tribological conditions. So, ceramic materials processing must be studied thoroughly so if you look at the overall chart of these ceramic processing.

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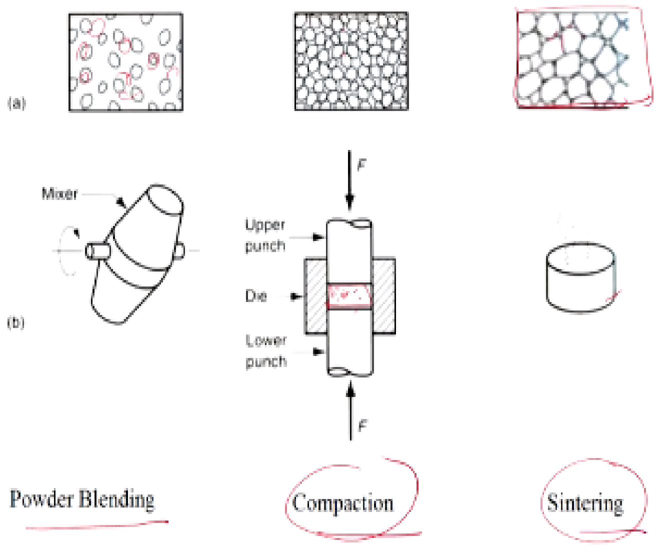

So, first we take these powders right powders of the ceramic materials and then we will mix it so we will mix it after mixing, We will keep it in a die cavity and then close this upper and lower punch and give certain pressure that we call compaction. So, compaction generally done in a unidirectional way so this upper punch and lower punch are given a pressure so that the powder loose powder is compacted.

So, when these loose powders they are compacted they just to come in contact nothing else will happen so this is just a sufficient to handle this material this powder material in your definite shape. But the bonding is not formed but it is very poorly bonded so this particular powder compact is ejected from the compaction die and then after that we will do the sintering that is a heating this material in a controlled atmosphere and the controlled processing way.

So their happens at time metallurgical bonding between this powder particles too. So, you get a ceramic component of this shape with a strong bonding between these grains right so mainly the blending compaction and sintering. There are three major steps in the processing of a ceramic component so powder syntheses generally done by an either chemical way or a mechanical way. Important chemical synthesis methods for the powders of ceramics are chemical vapour deposition.

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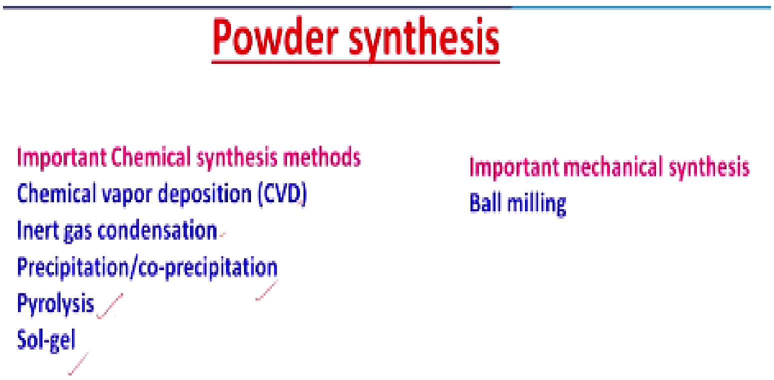

Inert gas condensation precipitation process and then pyrolysis or sol- gel so we are not going into details of these all chemical synthesis routes but considering the importance we will just go through the mechanical synthesis to that is by ball milling. The major synthesis of powders of ceramics is by ball milling so we will just to see the principal of this ball milling so ball milling is generally done.

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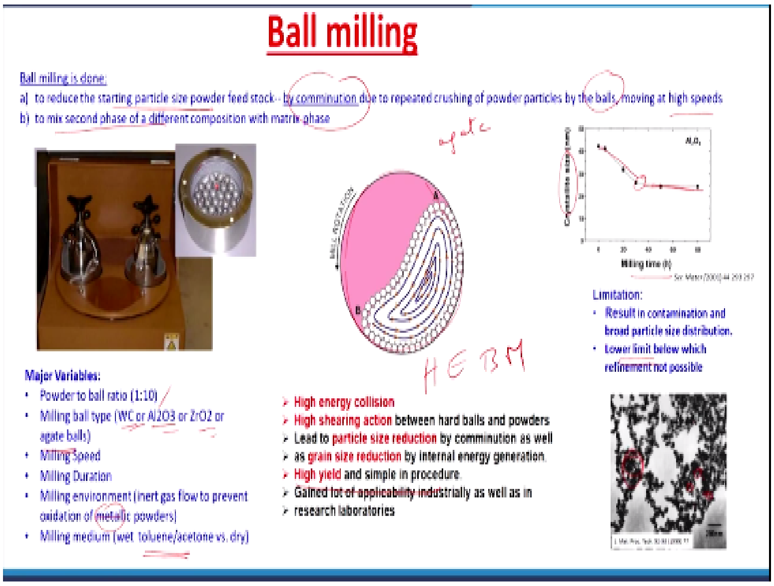

To reduce the starting particle size of the powder or to mix different powders, right? So, ball milling is done to reduce the starting powder particle size by a process called comminution this comminution happens because of the repeated crushing of the powder particles by the balls. So, we use certain balls and these balls move at a high speed in a container. So, in this container this balls and powders are placed and they are rotated at a particular speed.

Because of these there is a high energy collision happening and the high shearing action between this hard balls on the powders that lead to size reduction by comminution. Then as well as the grain size reduction by internal energy generation. So, this type particular syntheses gives very high yield and the procedure is very simple then the other process of any other synthesis so because of that this ball milling has gained wide applicability in the industries as well as in research laboratories.

So as I told, we use the balls, the balls of certain material which always have a hardness which is more than the hardness of the ceramic powders you are mixing right. So, you generally balls of type agate or the tungsten carbide aluminium oxide are agate or zirconium oxide balls are used for the ceramic powders synthesis. Energy for metallic powders synthesis by ball milling we use stainless steel walls in a stainless steel vial.

So, this vial for ceramics generally we go for you know the harder while that mean at least the surface inside the vial is soft tungsten carbide or aluminium oxide silicon oxide like this. So, we use a combination of a vial and the balls and a particular powder material to ball material ratio Generally 1:4 and 1:10 are used and milling is done in a particular speed for a particular duration.

So, in a definite environment if you do in an uncontrolled environment there is a chance for the oxidation to happen for non-oxide ceramic materials so control atmospheres are generally preferred to prevent such type of oxidation of powders either it is metallic or the ceramic. It is to prevent the oxidation of the powders generally milling is done in a controlled atmosphere control and environments that is inner to gases.

And milling is done either in a dry condition or we use the medium to lean or acetone these are filled this vial is filled with this. And then you get a you insert this ball and the powder mixture. So, at least half of the vial volume is filled with this milling medium and the ball and powder mixture and they are rotated. So, here is an example to show you two jar so they are rotated in this rotation.

Planetary rotation is more efficient to reduce the particle size as well as the mix. It mix a different powders of different composition so this planetary ball mill gives a high energy collision so it is usually called high energy ball mill. So, high energy ball mill is generally used for the ceramic powders but the high energy ball milling has certain limitation so because we use the balls and vials.

So, there is a chance for the contaminations from the balls are while material into the powder mixture so and this may also result into your broad particle size distribution right. And if you look at this the size of the crystallite has as a function of milling time so there is a decrease in the size of this crystallite initially. So, after obtaining some crystallite size there is no much difference in the crystallite size.

So, generally what happens because of this tiny g collision so there is a fracture of this material right so initially deformation and then fracture happens and the cold weld each other. And then form an almost a spherical particle so they find size remit powder will become more agglomerated and then there is no much influence of prolonging the milling on the size of the particle so there is no much difference after a certain time.

So, you need to identify the lower limit below which the refinement is not possible so for every material there is a lower limit below which the refinement is not possible. So, for those studies which you require a size reduction to a larger extent this becomes a major point so you can see one example of these powders of almost Nano size right. But you can see because of the reduced the particle size they tend to agglomerate each other.

Those so finer particle size 10 to agglomerate it very easily so there happen certain pores happening in an interim agglomerates as well. This ball milling is much useful even in industries because of its simplicity so after these ball milling we will go to the next stage. We will go to the next step of this process processing of ceramics.

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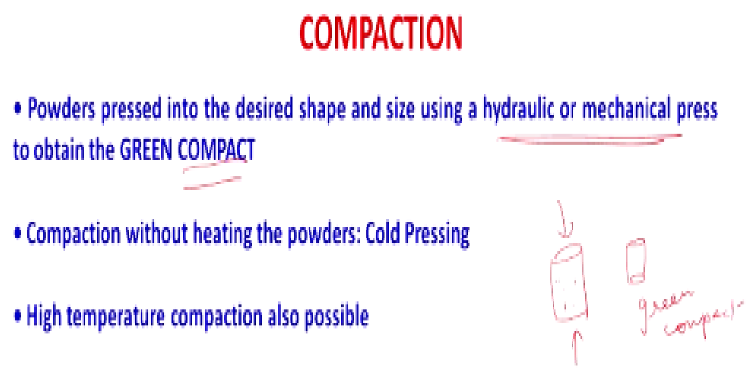

So, powders that are synthesized so after the synthesis the powders are pressed into the desired shape and size using a hydraulic or mechanical press to obtain a compact so all these powders after keeping in a die and pressing right either by hydraulic or mechanical press. So, this will lead to a compact and it is named as green compact so green means it is not heated right so the powders are loosely contacted with each other.

The compaction without heating the powders is usually called cold pressing or there are certain compactions where the high temperatures can also be applied.

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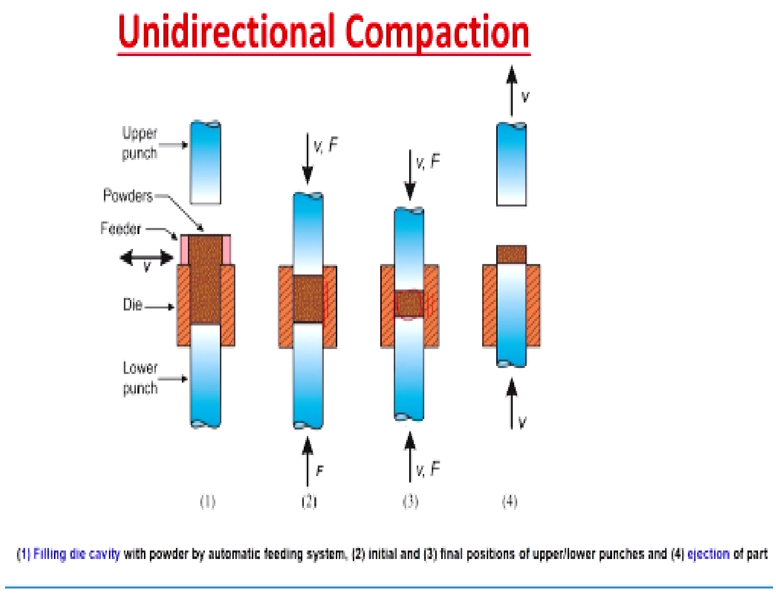

So, but cold pressing is much more useful and the pressing can be a unidirectional or iso static one right so unidirectional compaction is much widely used. So, you can see the different steps in the unidirectional compaction. You fill this die cavity with the powder and then close these punch upper punch so you have a upper punch lower punch and a die. And this die has a cavity which is filled with the powder.

Now we apply the pressure so you can see while applying the pressure you can see there is shrinkage of this powder bed so after this application of the pressure so you can eject it. So, there is a feeling of the powder initial and final positions of upper and lower punches while pressing and then this is after ejection so now we come to the very important step in the processing of ceramics the sintering right.

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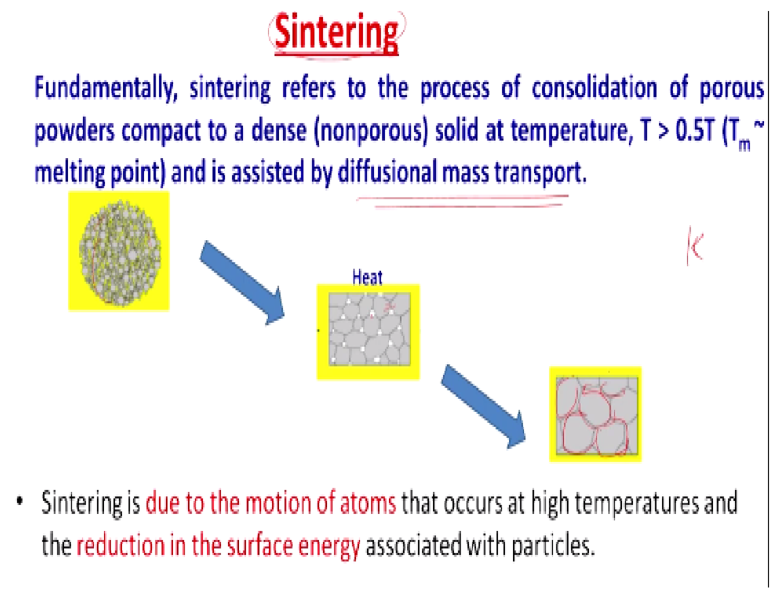

Sintering fundamentally sintering refers to the process of heating sintering is nothing but heating so fundamentally sintering refers to the process of consolidation of a porous to a dense solid. But you can you can have by definition sintering is a process of firing off a loosely contacted powder bed at a temperature more than half of the melting point. And the melting point is generally in absolute scale so because of the heating at a temperature more than the half of the melting point.

There is a considerable diffusion mass transport the diffusional mass transport leads to consolidation of this loose powder compact. We are dense component right so sintering refers to the process of consolidation of porous powders compact to the dense solid at a temperature usually more than the half of the melting point and is assisted by the diffusion mass transport so you heat it.

At a temperature where diffusion is possible because of the diffusion the atoms move from one location to the other location. So, there is a bonding happening at the grain boundaries level. So, there is a strong metallurgical bonding happening because of this heating that leads to a dense body so you can see the loose powder particles. They are heated and you can see this white portion is nothing but the porosity.

So, while heating actually the diffusion mass transport leads to the consolidation and leads to elimination of such a porosity. And then you have a strongly bonded grains of this ceramic compact so we call it as sintered ceramic so we understand that sintering is because of the movement of atoms that occur at high temperatures and the reduction in the surface energy associated with the particles.

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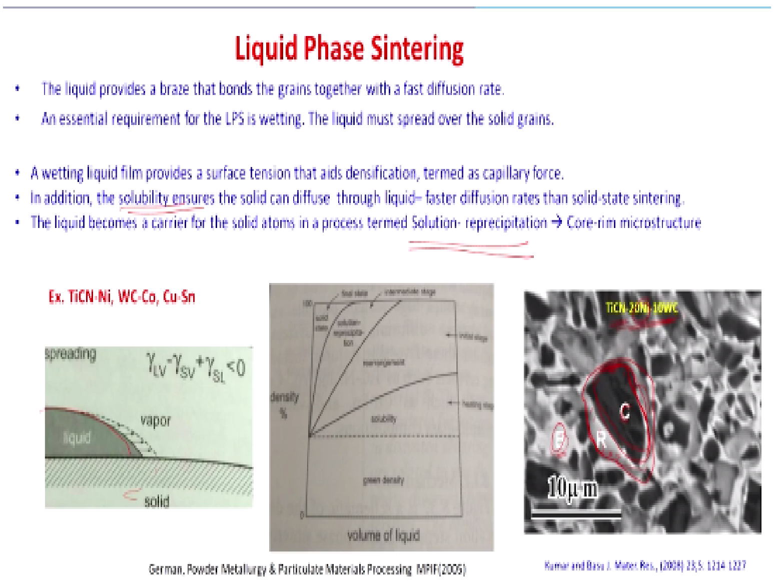

We will see for the liquid phase sintering major catastrophic liquid face sintering if you have a material with the lower melting point than powder material which we you want to centre. So, this low melting point material will be melted before you reach the peak temperature for the sintering. So, at lower temperatures this liquid melt is formed so this liquid melt will penetrate in the solid particle a mixture.

And because of these penetrations it goes and wets the surface of the solid particles based on the wet ability there is a larger capillary forces and this capillary forces bring this solid particle closer. And there is a chance for the making so the liquid provides a braze that bonds the grains together with the faster diffusion rates. An essential requirement for the liquid phase sintering is wetting the liquid faster spread over the solid grains.

So, if you see this contact angle is much more important in the liquid phase sintering there is a liquid and it has interfaced with the vapour and the solid the liquid faster spread over the solid grains. So, contact angle is very much critical to have effective liquid phase sintering. A wetting liquid film provides a surface tension that aids densification termed as a capillary force. So in addition the solubility also ensures the solid can diffuse it through the liquid.

So, because it is defusing through the liquid the diffusion rates are much higher than compared to solid state centric so the liquid becomes a carrier for the solid atoms in a process termed as solution and reprecipitation. So, what happens while leak this liquid phase sintering. So, the liquid penetrates into the solid particle gaps. The liquid penetrates into the gaps right and it dissolves the solid material right.

And on this dissolved material will be precipitated in the other stages of the sintering there is a certain fraction of the material which is dissolved and it is not precipitated back. So, after sintering we will find material which is not precipitated so after sintering we will find a micro structure with a core and rim phases. The core phase is the retained phase and the precipitated phase is the rim phase.

You see this rim phase right and this is actually the binder for the given material here nickel so this is a nickel rich binder. So because of the lower melting point the liquid of the nickel penetrates and then because of the good wettability with the ceramic particles they are dissolved the ceramics ceramic particles are dissolved in the liquid and forms under precipitates back.

So there is always a solution and the reprecipitation happening that will lead to a core and the rim micro structure right. So the amount of liquid formed is very important in achieving a proper density. So you see these as the this is amount of liquid and this is density schematically shown here. So finally the solution and reprecipitation which is happening in intermediate stage it results in to larger densification right.

First of all this is solubility soluble for the liquid dissolves the material solid and then and then rearrangement is happening after that the solution reprecipitation then when completely the liquid is consumed you will have only solid right. So that becomes solid state sintering in the final stage it is nothing but a solid state sintering. So dissolution and resolution rearrangement of this particle solution reprecipitation and then again solid state sintering. so these are the major stages in the liquid phase sintering.

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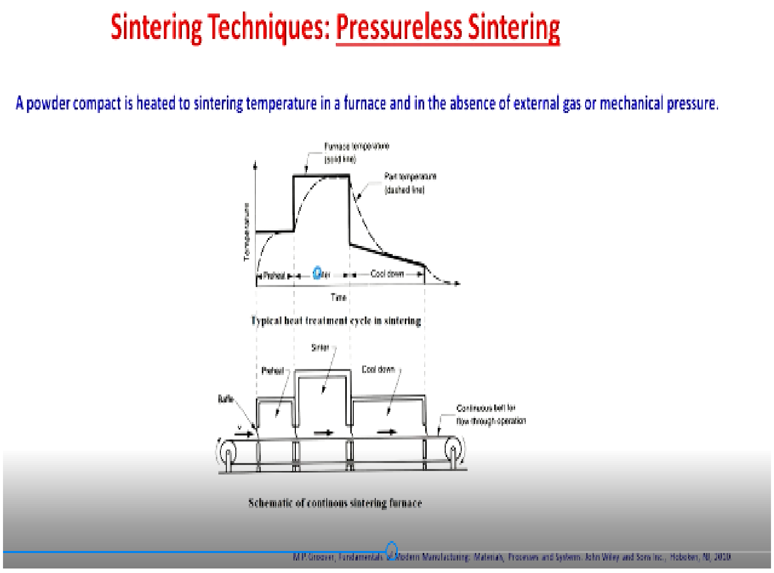

Let us now see the major techniques of this sintering conventionally the sintering is called pressure less sintering what do you mean by that. Sintering is possible only by heating the powder mixture right you do not apply any external gas or mechanical pressure so a powder compact is heated to a sintering temperature in a furnace without application of any pressure right.

So and this is the most inexpensive sintering technique and this is the most widely used sintering technique but because of only the effect of the sintering temperature you need to give larger temperatures for the sintering to happen that means to have it diffusion to happen to give a consult considerable mass flow right that result into the consolidation. So far the consolidation to happen you need to give higher temperatures.

In this particular conventional sintering technique because of the simplicity in the technique and this pressure less sintering is widely used in industries as well. So you can see one schematic of a continuous so sintering furnace so where you see the powder bed will come and this is preheated and then this is subjected to the sintering and then cooling is happening and then after that component is taken back.

So there is a continuous process of preheating sintering cooling down and all these things. So you need to decide the temperature and the time right if you heat it to a temperature lesser than the required temperature for the sintering the densification is not complete right so sometimes you know you need to do these type of lower temperature sintering to produce a porous ceramics right porous materials right.

Whereas usually the tribological applications we require dense ceramics so always our aim is to achieve the density as maximum as possible right. So fully dense ceramic components are generally preferred for the tribological applications so that means the temperature needed for the sintering is to be selected such that the densification happens to a larger extent and also if you give a higher temperatures the diffusion happens more.

And then you do not have a control on the sintering and there is no need for the for giving such a high temperature if you get a same densification happening at a much lower temperatures right. So the optimum temperature is very important to get the densification easily for the ceramic powders right and also the time needed for the sintering is also to be selected the optimum time required to sintering is to be selected.

If you prolong the sintering at high temperatures that will lead to coarsening right so generally speaking if you have a larger sized the grains the strength of the material is decreased Hall page relation right. So if you if you have a finer sized of the grains you have a higher strength as per the Hall page relation. So generally we do not prefer to have the coarsening happened at a larger extent.

Unless it is required we do not go for the coarsening to happen to a larger extent so if you give a lesser time if you give lesser time so you do not have the know the density densification happening to a larger extents. So the selection of optimum temperature and time for the sintering is much important so generally is cycle called sintering cycle is designed the time and temperature.

So initially this is heated at a rate and then you have heated to a higher temperature and then allow it for a night and then cool it right. So the rate of this heating and the rate of the cooling is are also very important in a conventional pressure less sintering furnaces generally we go 2 to 10 degrees per minute right. This type of heating or cooling are possible and the temperature required.

As I told, it is at least more than half of the melting point and melting point in absolute scale. T in absolute scale right melting point so you need for a given material you have to select the proper temperature and the proper time for the sintering and because of these conventional pressure less sintering the densification maybe less.

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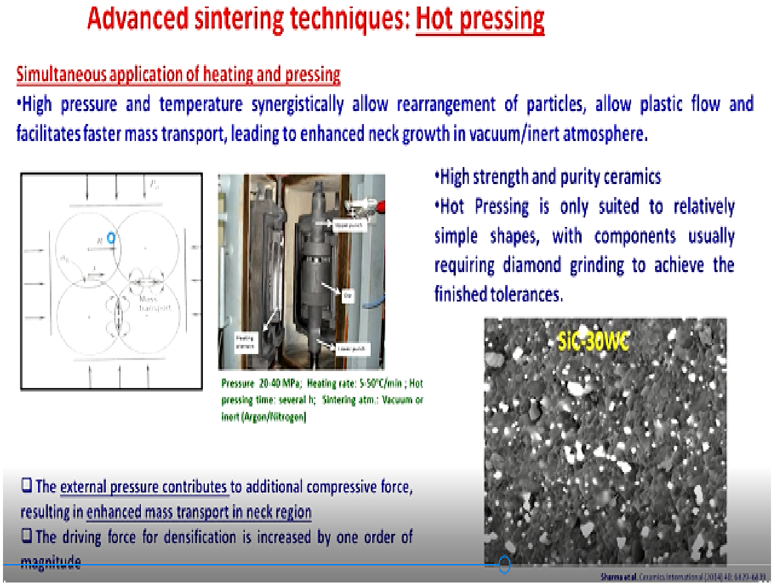

Hot pressing is one advanced sintering technique which is being used for preparing a ceramic component with high density and good mechanical properties. In this hot pressing we apply the pressing as well as heating simultaneously so the high pressure and temperature synergetically allow rearrangement of particles, allow plastic flow and facilitates faster mass transport leading to enhanced neck growth in vacuum or inert atmosphere.

So because of this pressing these are the powder particles right so you apply the pressure at high temperatures right the pressure can be applied again in a unidirectionally or in all directions. In that if you apply in all directions it is called isostatic pressing right because of the application of external pressure you will have a compressive forces that result in to enhanced mass transport in the neck region.

So you can see lot of mass transport happening in the neck region so because of this increase in mass transport the diffusion rates are higher and you get the densification easily what do you mean by that at a temperature lesser than what you require in a conventional sintering process generally speaking 100 Celsius to 150 Celsius lesser temperatures are sufficient to give a same densified body of ceramic.

When you compare with the conventional pressure less sintering technique. So generally high pressures of around 20 to 40 MPa are applied at high temperatures and the temperatures are reached at a heating rate of more than 10 degrees Celsius usually 50 degree Celsius per minute and on you do this hot pressing for several hours right and the sintering atmosphere can be inert or vacuum.

Generally in a argon and nitrogen atmosphere silicon carbide silicon nitrate or any other ceramic material. So the driving force for the is increased by one order of magnitude so the temperature required for the sintering to happen is reduced and generally speaking 100 to 150 Celsius lesser temperatures are sufficient to produce a ceramic of a decent to density right for the same density the conventional sintering requires higher temperature.

So by hot pressing we can produce ceramics of high purity and high strength. Hot pressing is only suited to relatively simple shapes right as I told the application of both pressure and heat simultaneously so there is a limitation in the mechanism of this machine. So hot pressing is generally suited to relatively simple shapes with components usually required in diamond grinding to achieve the finished tolerances.

But if you go for a complicated shapes the distribution of the load at high temperatures becomes difficult right. So generally hot pressing is preferred for the simple shapes relatively simple shapes so you can see here it is upper punch and the lower punch here you have a die inside these there is a die and the die is filled with the powder right. Die cavity and then cavities filled with the powder.

So generally these die are made up of graphite dies and there is a heating element in the chamber so you have a heating by this heating element and pressing by these mechanical pressing. So you have the pressing and heating simultaneously happening that leads to enhanced mass transport in the neck region that leads to easy densification.

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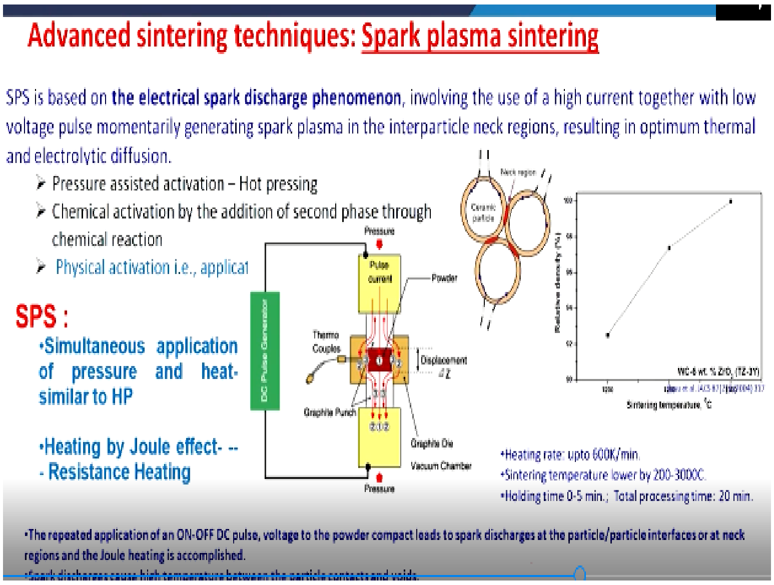

Coming to the other technique which is very important and very much famous nowadays advanced sintering technique called spark plasma sintering technique. So spark plasma sintering is generally based on the electrical spark could discharge phenomenon right that involves the use of high current together with the low voltage pulse momentarily generating a spark plasma in the inter particle neck regions in the intro particle neck regions.

And that results in an optimal thermal or electrolyte diffusion so generally three driving forces are applicable in the spark plasma sintering. The pressure activated hot pressing right so same pressure is used and chemical activation by the addition of second phase through chemical reaction and the physical activation by a placation of this current. So in general the spark plasma sintering involves the simultaneous application of pressure and heat.

That is similar to hot pressing no difference what is the difference here the difference is because of the heating by joule effect called resistance heating. So the repeated application of an on and off DC pulse voltage to the powder compact leads to spark discharge at the particle and the particle interfaces or at the neck region some the joule heating is accomplished.

The spark discharges cause high temperatures between the particle contacts and voids. So because of this such a high temperatures at the contact they happens the easy necking so the necking is easy because of this spark right and then plasma. So this is a schematic representation of the SPS technique of the generator of the DC pulse and you can see this policy current is being applied from 1 electrode to the other electrode.

Here these are nothing but the punches so the electric current the policy current goes through this punch the die and to the punch right and if the material has a good conductivity then the current also passes through this material as well. So because of this there happens a particle to particle there happens the joule heating and this joule heating results into high temperatures.

And the diffusion happens very fast you do not require higher temperatures for the sintering a generally high heating rates up to 600 kelvin per minutes are possible in this SPS technique and the sintering temperatures are lowered by 200 to 300 Celsius and the holding time is only 5 minutes right. So the total processing time of heating and holding and then cooling this is almost like 20 to 30 minutes time right.

The temperatures are reached at a very faster rates heating rates of around 600 kelvin per minute right and sintering temperatures are lowered by 200 to 300 Celsius and the holding time is also 0 to 5 minutes. So in some cases you do not need to even hold just going to the peak temperature and then immediately decrease the temperature cool it. So the total processing time is reduced to a larger extent.

Now compared to the conventional pressure less sintering the time the heating rates or the cooling rates in conventional pressure less sintering are very much low right as I told less than 10 degrees Celsius per minute. So heating to a temperature high temperature of 1500 or so it requires several hours right and then holding is also of several hours like 2 hours 3 hours and then again cooling with such a slow heating rates.

So the total processing time for a conventional pressure less sintering is like a 20 to 22 hours right in a hot pressing so you can still go at a relatively faster heating rates 50 degrees Celsius per minute the required temperature also lower. So once you go to the peak temperature hold it for several hours and come back so generally speaking the hot pressing processing time is like 10 to 15 hours.

Now you compare with this one processing time with this time of 20 to 30 minutes so it will have such a benefit if you use the spark plasma sintering and this is one example to show the tungsten carbide 6% zirconium oxide ceramic powder mixture was sintered by spark plasma sintering method so it you see the density of almost a 100% relative density is achieved for the sintering at around 1300 Celsius.

So just for the compassion the conventional and pressure loss sintering the same powder mixture required 1700 Celsius right. So you have like 400 degrees Celsius lower temperatures needed for the sintering to 100% densification in spark plasma sintering compared to conventional pressure less. So we will more about the spark plasma sintering when we see certain case studies.

And then one more important point in spark plasma sintering our these are because of the foster heating rates the grain growth is also restricted. So because of the faster growth actually there is a relation called this G if you see the grain growth at a particular temperature there is a grain size initially and there happens a heating rate and if you see the temperature difference temperature difference.

So there happens one okay activation energy required for the grain growth that is Q and then you have the Boltzmann's constant K and T. So if you look at this relation the grain size is larger if the heating rates are lower. In other words in spark plasma sintering or micro sintering where few 100s of Celsius per minute heating rates are possible. So faster the heating less studies the grain growth.

So these type of techniques are used for restricting the grain growth and we will see in another lecture where these type of sintering techniques are used to prepare a ceramic with a Nano crystalline material. For Nano crystalline ceramic preparation you require such a faster heating rates we will see in certain case studies in other lectures the use of such techniques of the spark plasma sintering microwave sintering.

Where heating rates have more than 100 Celsius per minutes can be possible. So this use of such an advanced sintering techniques will result into a ceramic of a restricted grain growth. The grain growth can be restricted even we are Nano size range if you start with a small powder particle size of Nano right. So particularly for the Nano ceramic materials or Nano ceramic composites.

These advance sintering techniques with a faster heating rates are much useful. We will see in other classes how these are useful okay. So summarizing todays class we understood the processing of ceramics is different than the processing of other materials like metals this difference is mainly because of their high temperature stability. The high temperature stability makes it difficult to use a conventional routes of fabrication.

Mostly ceramic components are manufactured by powder processing. So in which the powder synthesis they are mixing.

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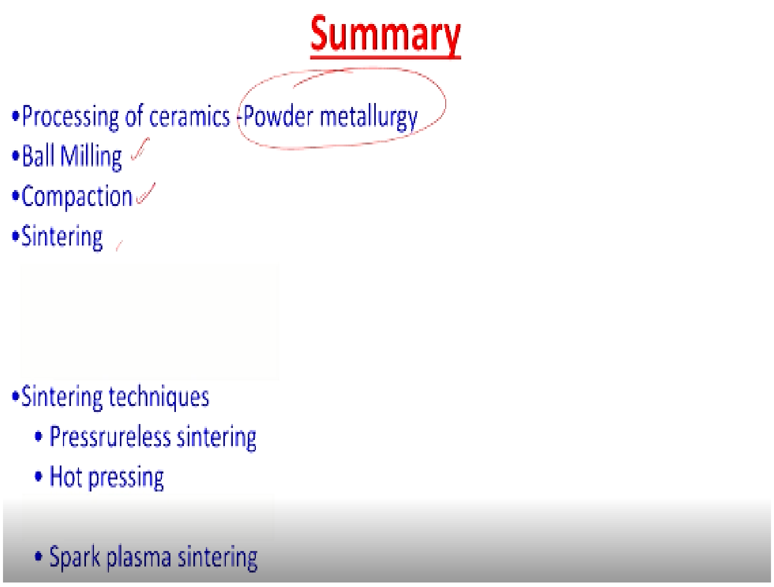

And compaction and sintering so these three are the major steps in the powder processing. So we have seen the principal and the limitation of ball milling which is a mechanical syntheses of powders and for the mixing also and then compaction of this powder cold pressing then the sintering we have learnt important points of pressure less sintering hot pressing on spark plasma sintering.

And these the later techniques are called advanced sintering techniques, these techniques are generally used to prepare a dense ceramic with the restricted grain growth and we will see this in the other class, thank you.