Biomaterials for Bone Tissue Engineering Applications
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Module 6
Lecture No 29

So in this module we will discuss the some of the fundamentals of the ceramics processing.

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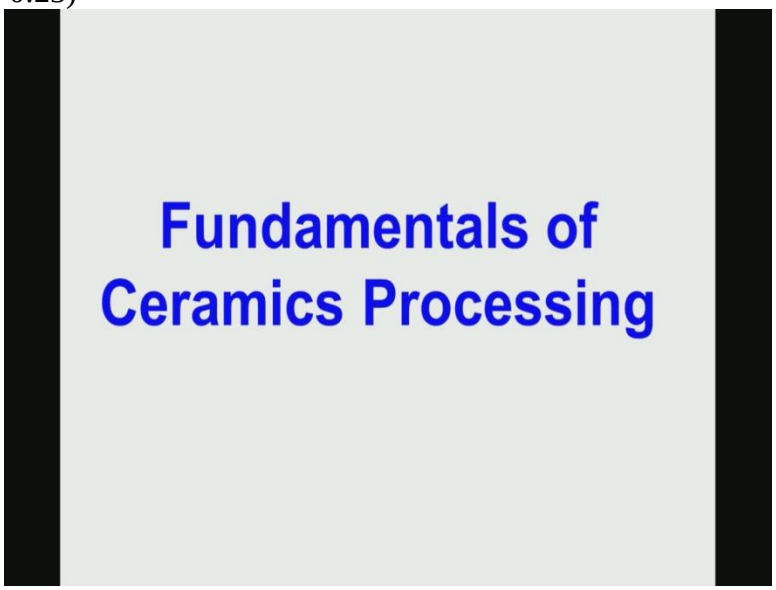

So in one of the earlier modules I have discussed that how metals can be processed particularly metallic bio materials.

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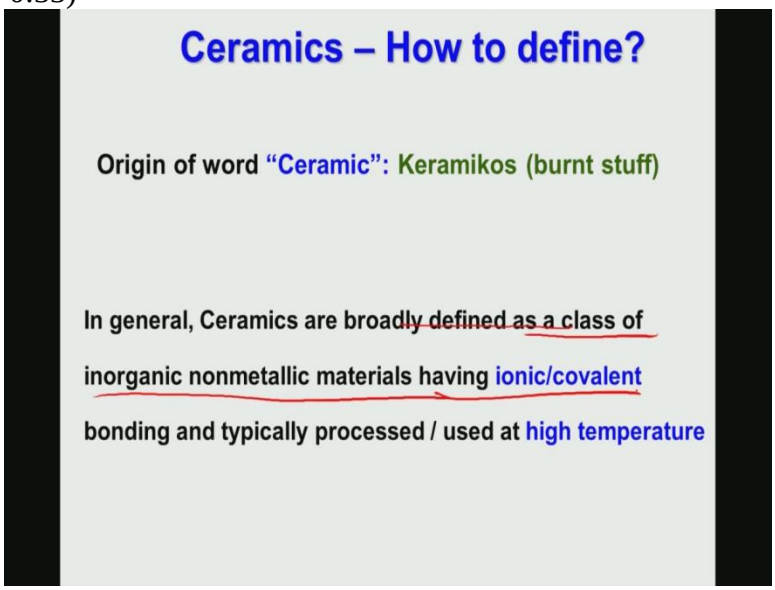

So the word ceramic essentially is derived from the Greek word ceramico that is bond stuff. And in general ceramics are defined as a class of in organic non metallic materials having ironic covalent bonding and typically processed or used at high temperature.

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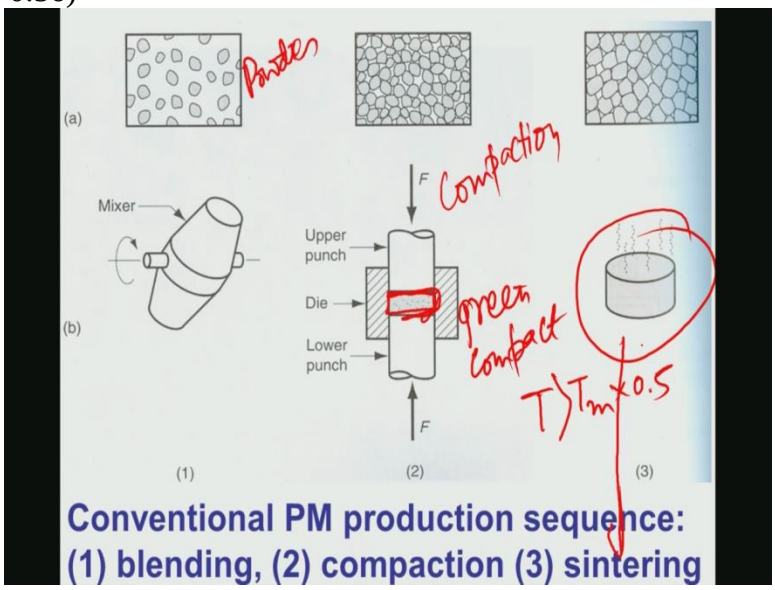

So this is that typical conventional parametrogilcal based processing of the ceramics. So you start with the powder first, so its a powder. Then you mix with some additives or you mix two different kind of powders of two different chemistry. Then you do this is called compaction stage. So this is first is the powder blending , then is the compaction, then you get this kind of small cylindrical shaped green body that is green, this is called green compact.

And this green compact once you put it, once you throw it in the furnace , then you heat it up at high temperature, then green compact , it becomes densified. So this is the process called sintering. Now sintering is always to be done at a temperature where t is greater than .5 tm . So that means t by tm is greater than 1 by 2.

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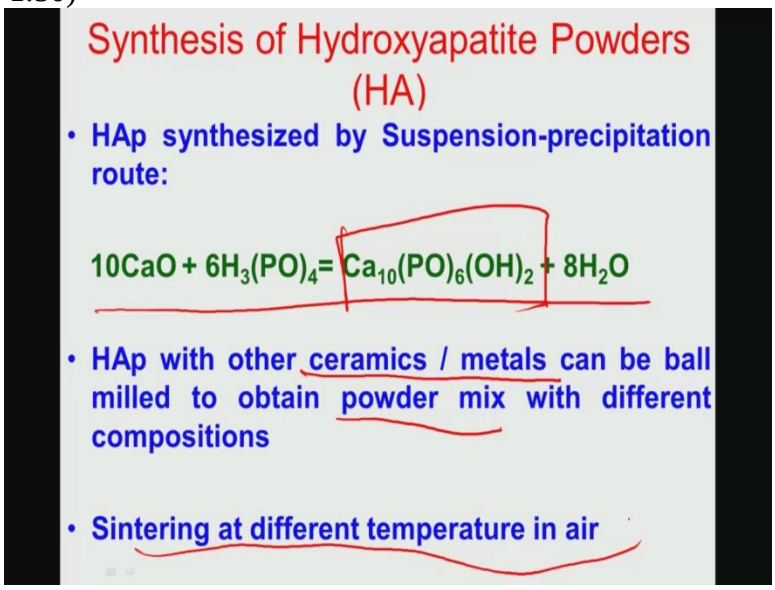

So one of the important process of sintering is that how you can make this powder that is what I said. So I will just give you an example of that hydroxyapatite powders. Because why hydroxyapatite, because hydroxyapatite again I recall that hydroxyapatite is the in organic constituent of the natural bone. So therefore hydroxyapatite powder how it is synthesized I have mentioned.

So this is called suspension precipitation route, so calcium oxide is added to this orthophosphoric acid solution. And this orthophosphoric acid then it is precipitated, what is precipitate is the c8 and po for whole 6ho2 that is the stoic metrichydroxyapatite. I may like to mention here also that

in the bone that is the calcium phosphate or calcium apatite that is there it may not be having all the places that stoic metric hydroxyapatite in most cases that hydroxyapatite is present in the natural bone in non stoic metric hydroxyapatite.

Now once you make this hydroxyapatitethen you can make this hydroxyapatite, you can sinter them with added with certain other metals it ceramics and then you get a powder mix and then this powder mix you make a compaction. And then you sinter them in high temperature, different temperature in here.

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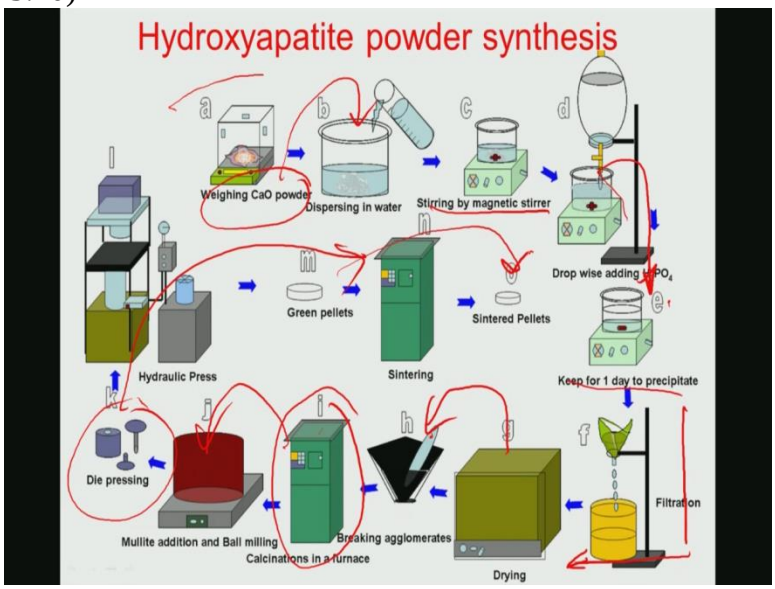

So this is that entire thing that has been mentioned. So hydroxy powder synthesis, so this is just you start with the calcium oxide powder, then you disperse them in water, then you stir it in a magnetic starter, then you drop by drop just add this hydroxyapatite. So and after that you keep at least one day for precipitation, filtration , after that you dry this hydroxyapatite powders, after you dry, you break their agglomerate, then you calcine it in a furnace, after you furnace it, then you add certain second phase. Then you make the compaction dye pressing and after the dye pressing it goes to the sintering furnace again.

So this total circle of the making, of synthesizing the hydroxyapatite powder to go to a sintered pallets, this it is a quite a lengthy process but at each step one has to do additional characterization . Like one has to see that what is the particle size and shape using scanning

under micro scope. One has to also quantify that what is the size distribution using that particle size distribution like laser particle size analyzer and so on.

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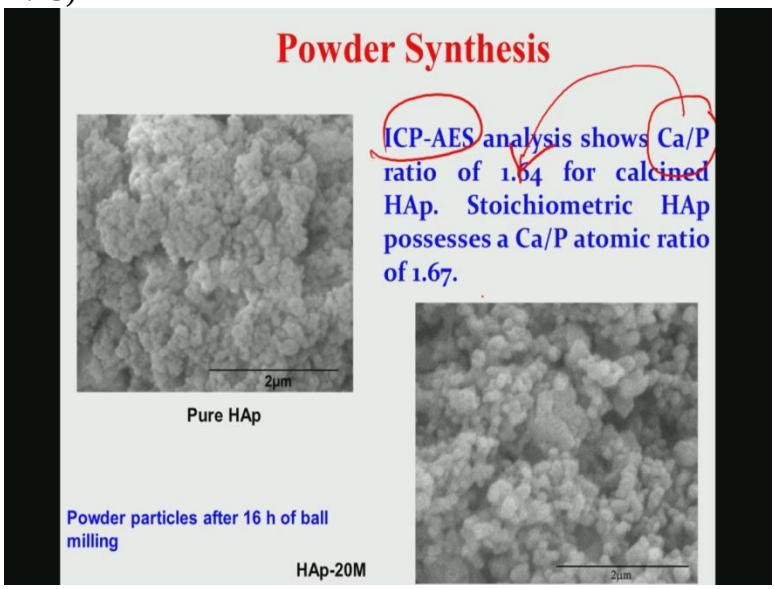

So this is that scanning electron microscope picture of the hydroxyapatite powders and what you see this is the spherical shaped powders and this spherical shaped powders in that inductively coupled plasma ((()))(04:28) electroscopic analysis can also be performed just to see what is the ca by p ratio. And this ca by p ratio is very important in case of hydroxyapatite because that actually influences biomenalization property of many of this hydroxyapatite based composites. Now in the stoichiometric hydroxyapatite with the composition ca10po4 whole 6 to h whole 2 their ca by p ratio is 1.67.

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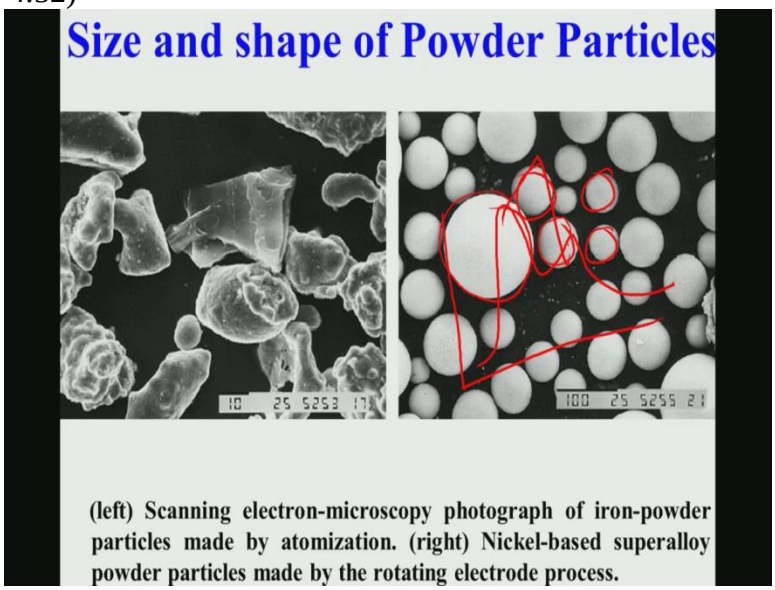

So some of the typical shape of the other powders like you can see the spherical shaped powders so you can see that this sphere but it shows more like a bio moral type of distribution. Some of the sphere powder particles is larger size and some of the particle powder size is relatively much smaller size. So if you plot this particles size distribution then there can be two kind of a peak. So and this kind of peaks is called bi modal type of distribution.

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So once you do this powder particles then you have to mix with other phases, other ceramics or metals. And then you can use this ball mill. And this mill, there the powder to ball ratio is

typically maintained as 1 is to 4 or more or higher. Or to it can go up to 1 is to 10. So that means if you want to Mill 50 gram powder you must add 200 grams of the ball so that you can ensure efficient milling of the powders.

So the powder milling has two purposes, one is to reduce the particle size that means you start with the micron size powder you expect that at the end of the ball milling you get sub micron size powders that is the number 1. Number 2 is that in case of for example you are adding hydroxyapatite and you are adding to titanium so essentially addition of titanium you have to ensure that titanium is homogenously mixed with hydroxyapatite. So that homogeneous mixing also needs to be accomplished and that places the second importance in case of the powder milling.

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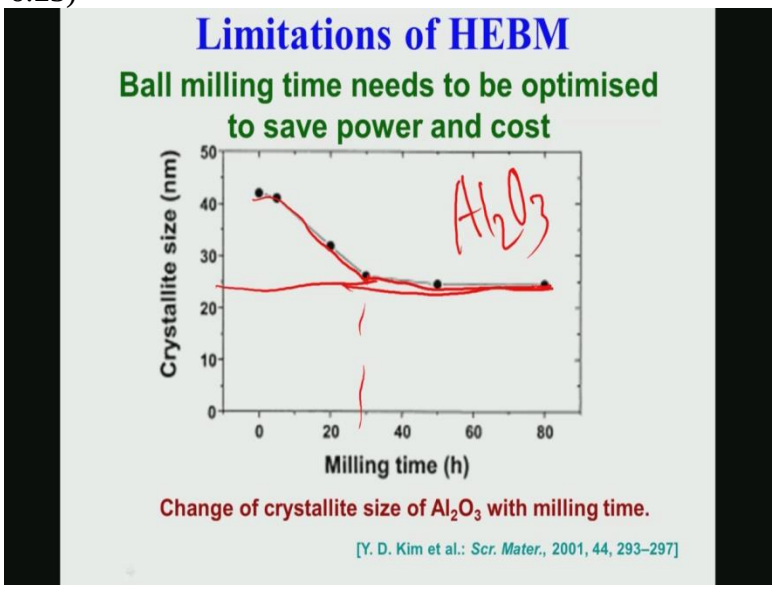

Now there is certain thing called limitations . So as far as the first aspect is concerned when that crystallite size or powder particle size is reduced but there is a limit to which it can be reduced to a maximum level, beyond that there is not much reduction and that has been shown here in the case of the alumina particles as a model system. What you see at the end of 24 hours, the particle size is around 20-30 nano meter and then it remains constant towards the rest of the milling time.

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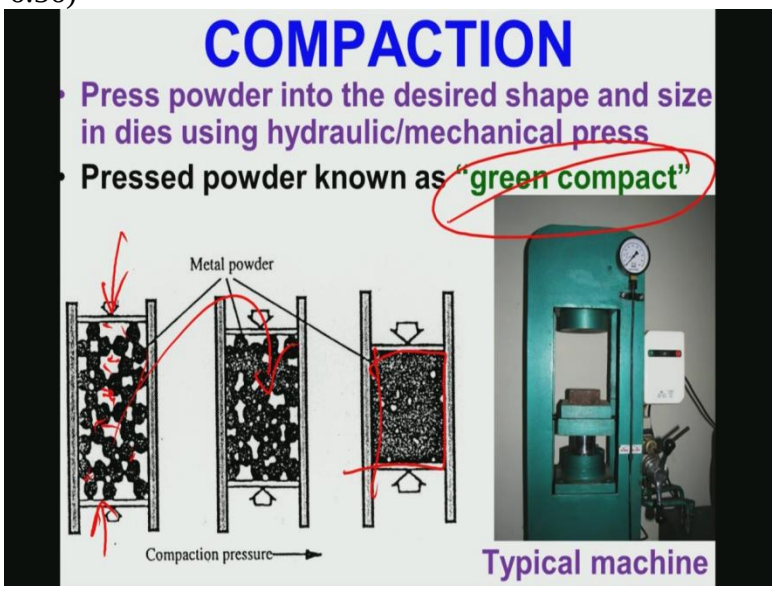

Now after the milling is over then you have to do the compaction. The wings you have to take the powders and after that the powders then you have to press the compressive force and this powder particles of this void spaces here, this void spaces is squeezed and then you get a solid compact. And this solid compact you get and then you call it as a green compact, why its called green compact, because you have not sintered that compact that means you have not fired them at high temperature. Or in other words you have not heat treated them at high temperature, at the room temperature it is called green compact.

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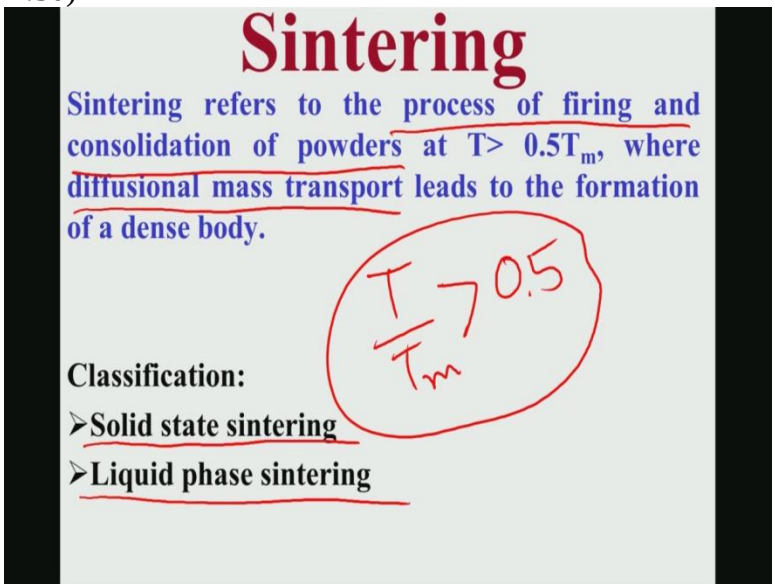

After the green compact you need to consolidate this compact and that process is called sintering. So sintering is the process of firing and consolidation of powders at a temperature t greater than .5 tm stop so somehow you can see that t by tm greater than .5 is something kind of unique temperature where the earlier bulk deformation processes like rolling, forging, extrusion all these processes is much more effective at hot working condition like when temperature actual temperature of operations, actual temperature of processing is greater than .5 tm.

Here again in the context of the ceramics densification, here again you can see that sintering takes place normally y greater than .5 tm, so therefore this is called homologues temperature like ratio of the application temperature to the melting temperature. So homologues temperature .5 is kind of very unique and this has been used in many metal processing, many materials processing techniques. Now why t greater than .5 tm?

Here diffusional mass transport, that means here diffusion processes becomes much more effective or much more extensive and that leads to the formation of a dense solid. Now what is the two different types of classification? One is called solid state sintering and one is called liquid state sintering.

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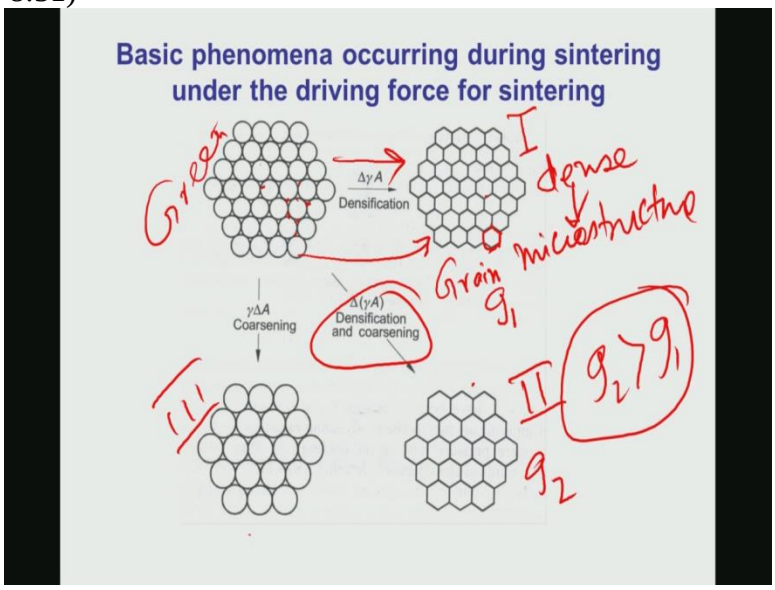

Now in case of basic phenomenon which occurs during the sintering is essentially what I have shown here. This is the spherical powder particles, now this spherical powder particles which,

this is in the green compact, so this is the powder particles, and this powder particles, this is the spherical shaped powders, this spherical shaped powders which will undergo densification, then it is gets a hexagonal array of the grains.

Now this your grain micro structure ok? So in the grain micro structure whatever you see the size of this grains, the size of this hexagonal grains, has some correlation with the powdered particles, but essentially what you see that whatever the void spaces the way I'm sketching in between the inter particle region these void spaces are lost, that means this void spaces are removed leading to a very dense grain micro structure.

Now this dense micro structure is characterized by certain geometric shapes and sizes of the grains. So this is one of the scenario that is scenario number 1. Another scenario is that scenario number 2 that I have highlighted here, here densification also takes place. At the same time coarsening also, particle coarsening also takes place. So if you compare grain number 1 and grain number 2, if the grain size here is g1, if the grain size here is g2, so g2 is essentially greater than g1.

So this simply because that here sintering is not done in correct manner or in the correct temperature for the correct time, so if it is inappropriate selection of sintering conditions can lead to grain coarsening/ so this one I have emphasized in this slide. Third scenario is that, that if you do not if you have a very poor understanding of the overall sintering process then you arbitrarily select the temperature of the sintering, then this particle size, this simply will undergo coarsening, and then your particle size will increase but there will be no grain structure formation. So this is also another important thing in this sintering process.

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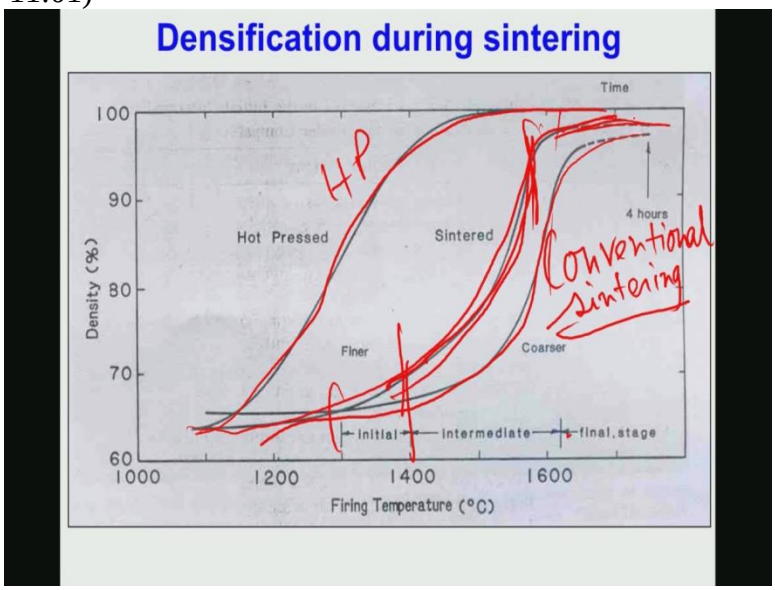

This is a typical sintering curve like how the density changes with the sintering temperature. Now what you notice here that all this curve has a similar qualitative description. Like this is a finer particle powder, this is a coarser particle powders and this is the hot pressing. What is hot pressing I will come to this in after 5-10 minutes. So hot pressing is a unique technique where you are applying uni axel compression pressure when you are heating the powder compact.

Now this is the curve for the conventional sintering. Conventional sintering means you do not apply any pressure but you are simply heating the powder compact at higher temperature so that diffusional mass transport process can take place. So conventional sintering and hot pressing. In case of hot pressing you are essentially adding additional external pressure to accomplish the densification process. Now what you what I would like you to notice here is that during the initial phase of the sintering the density increase.

Then after the intermediate phase of sintering there is the largest increase in the density. That means maximum densification takes place or maximum removal of the pores from the powder compact takes place, that is intermediate densification. And the final stage of sintering then it reaches almost at the final end and there sintering, that consolidation or density change takes place to a much smaller extent.

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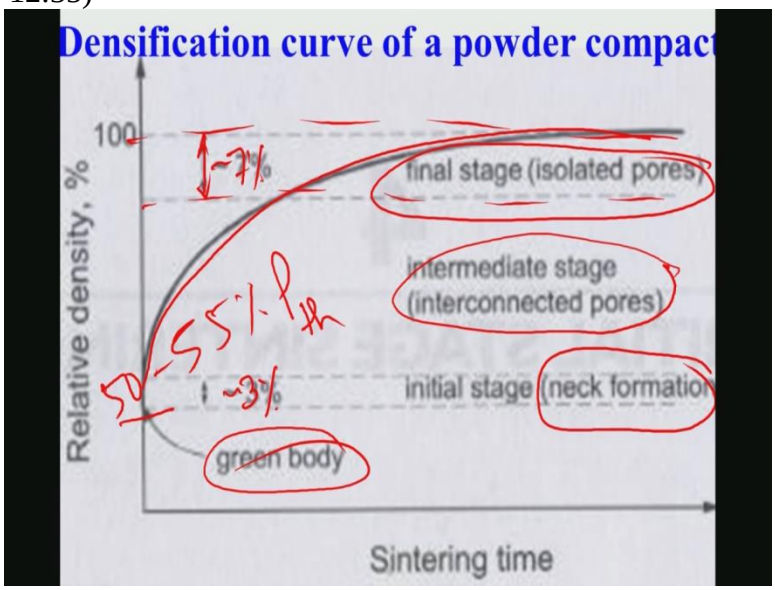

So this is what has been taken place that is the initial stage there is the neck formation. Intermediate stage that is the interconnected pore formation. And the final stage of densification that is the closed pore formation. So initial stage that is density changes almost 3 percent and your start with a green body which has the density something around 50-55% of the theoretical density.

Theoretical density typically in ceramics literature is known as Rho TH. Rho is the typical way density is denoted the subscript th essentially stands for theoretical density. How it increases in the final stage and goes to the isolated pores, then in that isolated pores, essentially this one is only 7% change in the density.

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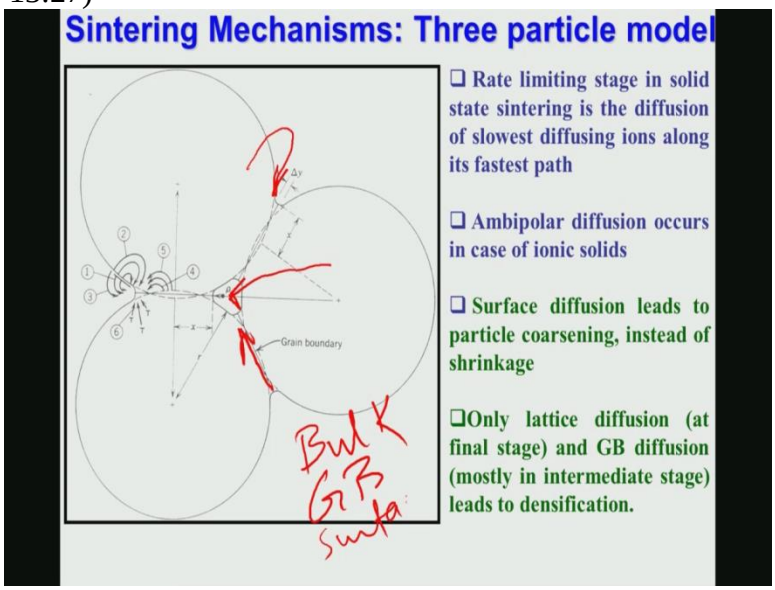

So as far as the mechanism of density is concerned people use three particle model or four particle model. In all the theoretical description of the mechanism I must mention to you uprightly is that all the particles are considered as spherical because spherical particles the geometry is very regular and then one can also derive certain equation because you have the spherical geometry. And second thing is that in three particle or four particle model or two particle model, in all these cases the size of the individual powder particle is considered as identical or considered as equal or same.

So essentially all the three particles have the identical particle size. Now coming to this one there are three ways this densification takes place, one is this densification along the grain boundaries, one is from bulk and then this diffusion process goes to in the neck region. So this is called bulk diffusion, that is called grain boundary diffusion. And another one is surface diffusion like it evaporates something and then it goes, it comes back to the neck region here.

So this is the three type of diffusion processes. One is called bulk diffusion process. The second one is the grain boundary diffusion process, gb. And third one is the surface diffusion process.

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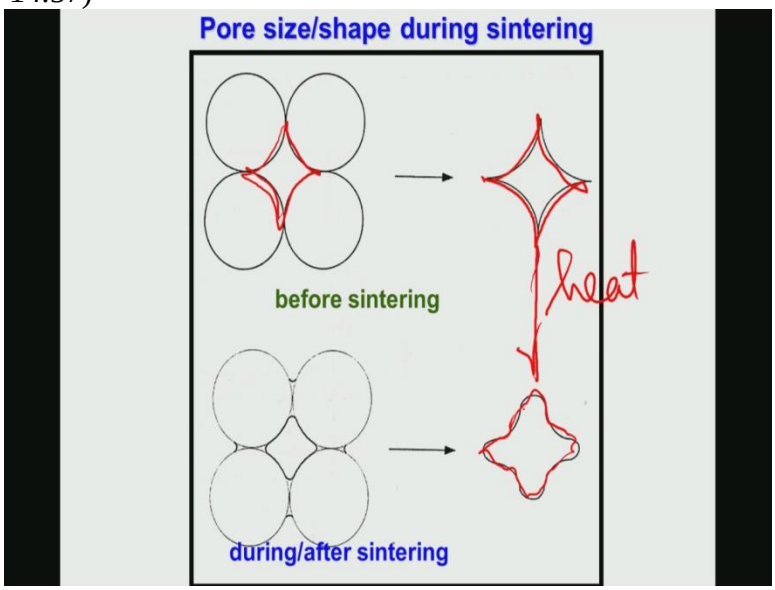

Ok. This is that one more very simplistic description of the process of sintering. You have a four particle model, you have this kind or pore space ok? And this type of pore space you see, and then after sintering now you heat it up and then what is happening during heating this pore shape is dynamically changing, it becomes more like off symmetric and it doesn't have any uniform geometrical features and so on and then that will be squeezed slowly after it is squeezed then it is completely disappeared.

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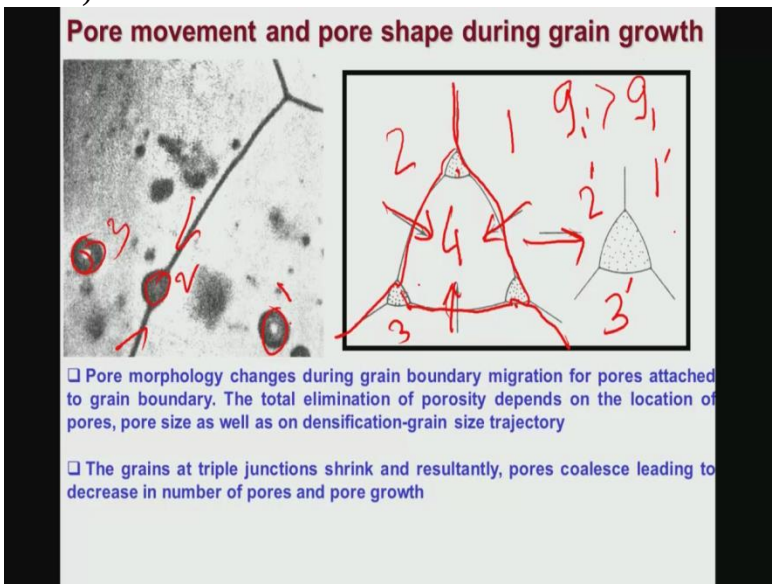

So as the sintering process advances, what happens is that when the pores will not be any more connected to each other they become isolated. Then that particular case it is very difficult to remove the pores. Because I will just give you the three examples one is the pore number 1, one is another pore number 2 and third one is pore number 3. Here pore number 1 and pore number 3 are located well within the grain. Pore number 2 are located at the grain boundary region.

So when the pores which are located in the grain boundary region, those pores are can be removed very easily simply because grain boundary diffusion process is much faster than the lattice diffusion process. The pores which are marked as number 1 and number 3, that will be very difficult to be removed simply because bulk diffusion process is extremely slow. The same has been shown here in this particular figure here.

So this is your one grain, this is your another grain and this is your third grain. And this is your fourth grain. So this is one grain, grain number 2, grain number 3, grain number 4. What will happen ? Because of the curvature effect grain number 4 will disappear completely and that will lead to the collisions of the pores which are located at the grain 1,2,4 grain 2, 3, 4 or grain 1, 4, 3 and this pores become larger pores. So then this will become the new grain number 1 1 dash, this will become this grain number 2 dash and this will become new grain number 3 dash. So certainly the size of grain number 1 dash, if I may write it like this, is greater than grain number 1, before the final stage of densification.

The same is true for grain number 2 dash, size is greater than grain number 2. So essentially what you see during the sintering process is that both the grain growth takes place at the same time pore growth takes place. So grain growth and pore growth they simultaneously take place during the process of sintering.

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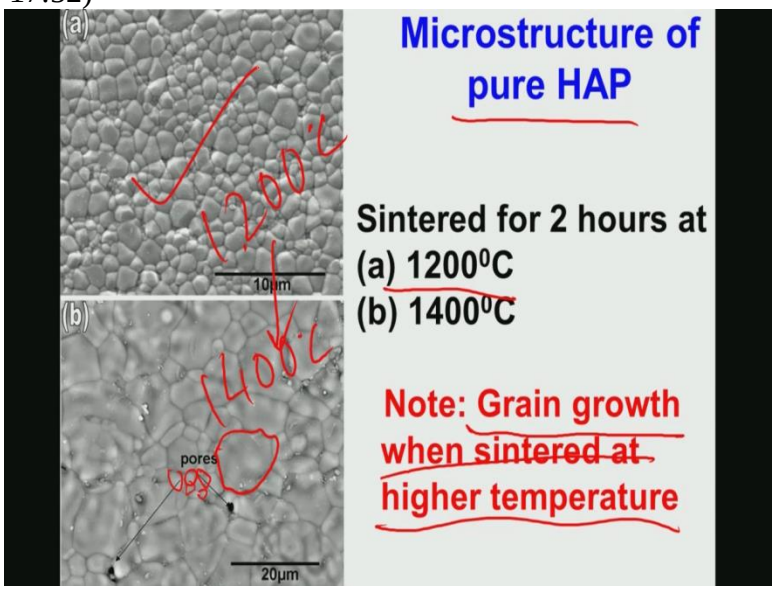

This is the classic example of hydroxyapatite micro structure and what you see is a very fine scale micro structure which is sintered at 1200 degree Celsius. Now what I'm showing here this is 1200 degree Celsius sample. And this is 1400 degree Celsius if you compare immediately between this and this, what you see there is a large grain size and there is a small number of grains also here. So this is the smaller grain size and this is a much larger grain size.

Certainly the sample sintered at 1400 Celsius would exhibit bi modal size of distribution where as sample which is sintered at 1200, degree Celsius should show more uniform, uni modal grain size distribution. And this bi modal grain size distribution is certainly because of the grain growth when the sample is sintered at higher sintering temperature.

So this places the importance of correctly or appropriately selecting the sintering conditions in terms of both temperature and pressure. If you do not have sufficient understanding of the sintering process and if you arbitrarily or by heat and trial method if you use the sintering conditions then what will happen you may get a dense micro structure but at the expense of the grain growth. In other words if your sintering temperature is higher then certain grains will show exaggerated grain growth or abnormal grain growth.

Essentially then you get a mixed type of population of larger grains together with the smaller grains, and that is not good for the mechanical properties. For mechanical properties your typical

micro structure that is required uniform grain size distribution not like bi modal size of distribution and also the finer grain size. In the material it is well know that the finer is the grain size better is the mechanical properties. Better mechanical properties meaning hardness or strength properties ok? Fracture toughness depends upon various other parameters depending on what kind of material you are considering.

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Now having given sufficient background of the conventional sintering processes and the sintering mechanisms, let me now spend time on the advanced sintering processes and some of this advanced sintering processes has been used to develop many material both in the lab scale as well as the commercial scale production of the ceramic based materials. And some of this results also will be shown in the subsequent modules when I discuss the development of specific materials or specific composites based on hydroxyapatite and so on.

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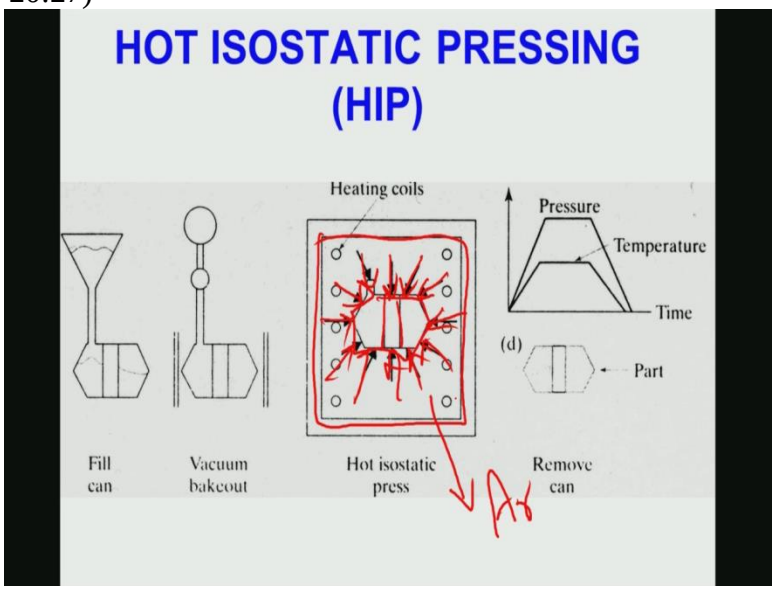

So one of the most advanced sintering processes is called hot isostatic pressing. As the name suggest hot isostatic pressing means you are applying equal pressure from all directions. Now the classic example is that, this is a typical hot isostatic pressing chamber. So we fill it up with some high pressurized gas let is say argon, so argon then you pressurize it like 300 mega Pascal and so on. And then you put your sample somewhere here, in a glass container.

What will happen when you create this pressure there and according to Pascal is law, pressure what will be transferred in the fluid will be equal from all directions right? And if you follow this Pascal is law, then what will happen, that this material will experience equal pressure from all directions. So therefore isostatic that one is the result. Hot means this argon gas firing in the you are firing in the argon gas environment that takes place at high temperature. That is why it is called hot isostatic pressing.

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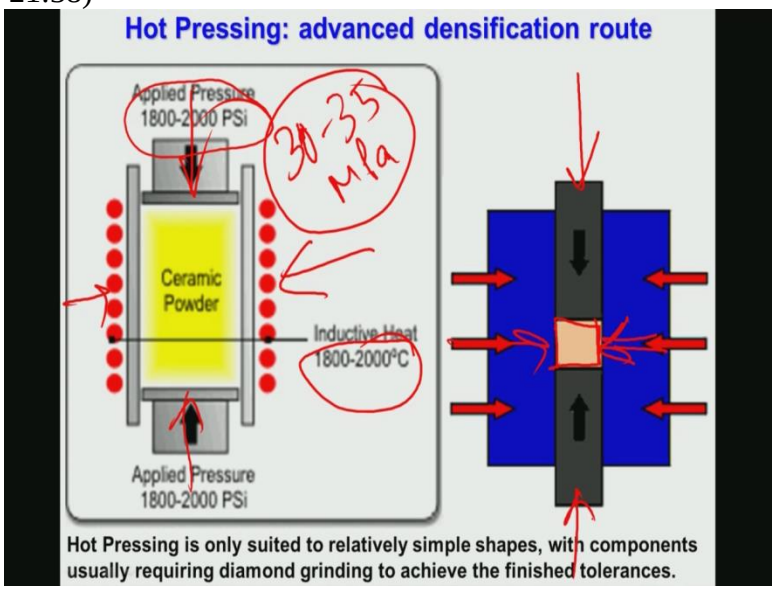

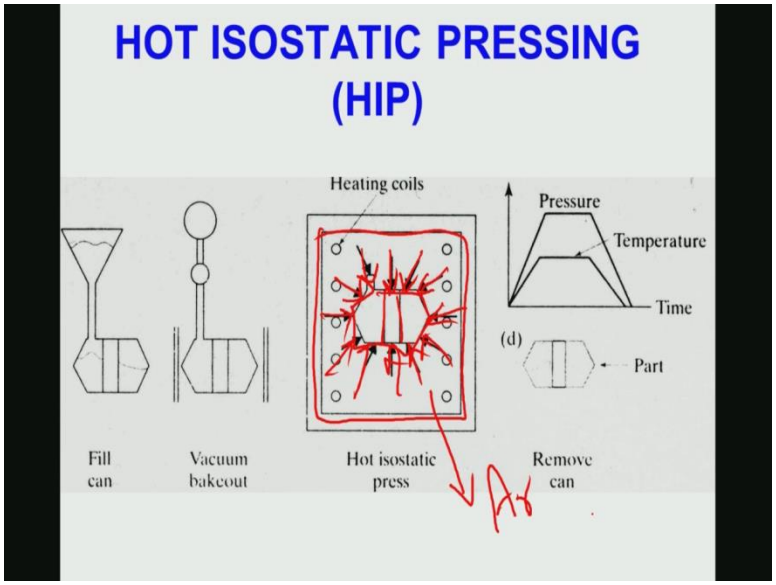

What is the advantage between, of hot Isostatic pressing over hot pressing? Now if you look at hot pressing technique which I will come to here, so in the hot pressing, you put the ceramic powder or for that matter of fact any powder particles. Then it is a external heating process. So the heat is coming from outside through inductive heating coil and that temperature can go up to 1800-2000 degree Celsius. And then when it becomes red hot then you also apply compressive presser here.

And when you apply the compressive pressure it is known as it is mentioned here as 1800-2000 psi that is pounds per square inch. But typically in the commercial hot pressing machine you can go up to 30-35, mega Pascal ok? That is the typical commercial hot pressing machine.

Now in the commercial hit pressing machine you know when you put in the dye and it is contained, then this, because of the constraint that you know that your material will get densified. But here you are applying the pressure only from the, in the compression, uni axel compression mode. If you go back to the hot isostatic pressing mode you are applying the pressure from all the direction and in equal amount so that uniform densification of the sample is possible in case hot isostatic pressing which is otherwise not possible in case of hot pressing technique.

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So therefore little bit more details of the hot Isostatic pressing. This is the American isostatic press, this is aip, stands for American isostatic press, who manufacturers this kind of isostatic pressing.

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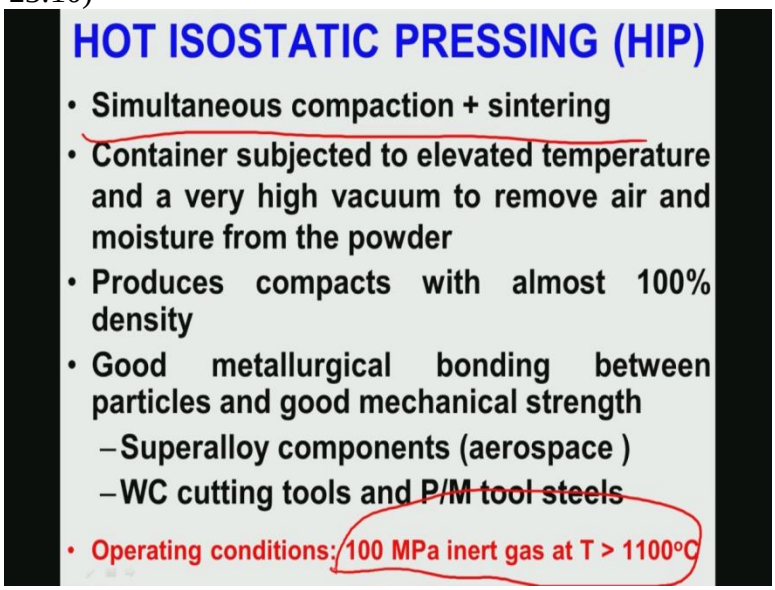

So essentially the concept that is used is simultaneous compactions and sintering and here container is subjected to elevated temperature and very high vacuum to remove air and moisture from the powder. And operating conditions like 100-200, mpa, inert gas like argon and temperature is more than 1100 degree Celsius.

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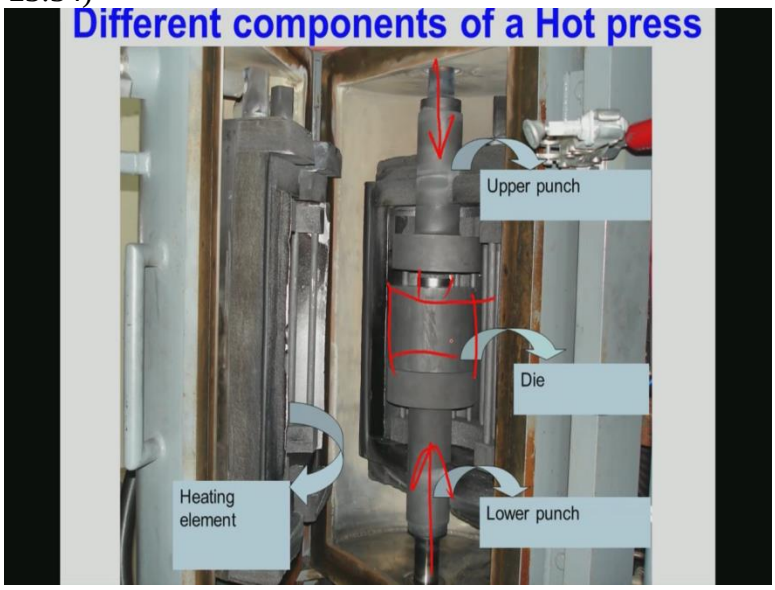

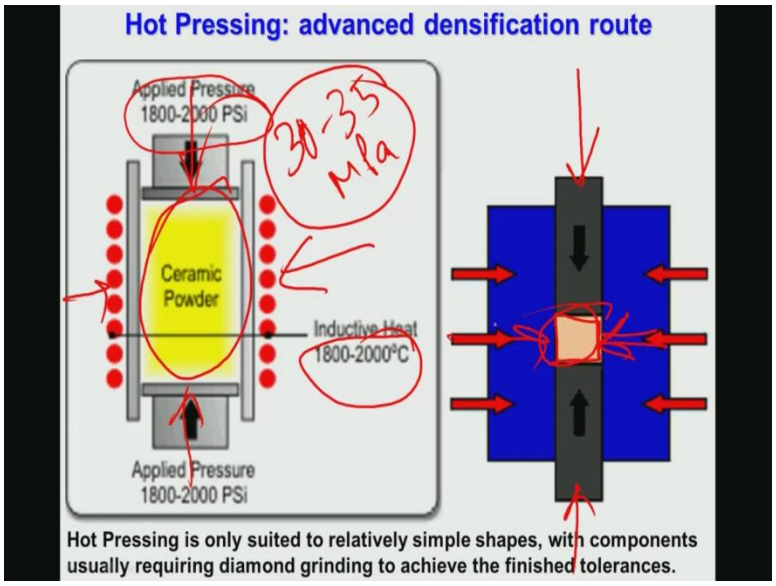

This is the classical hot pressing unit. So you can see this is the ramp here, you apply this compressive force, this is your graphite dye punch assembly. And you can see this is your punch here which is exposed outside, and inside the dye you have dye cavity and there the dye cavity, this powder is now filled up in the dye cavity and this is your dye cavity and then whole assembly is now put it under two upper punch and lower lunch then you apply, then compression pressure and then the material gets densified.

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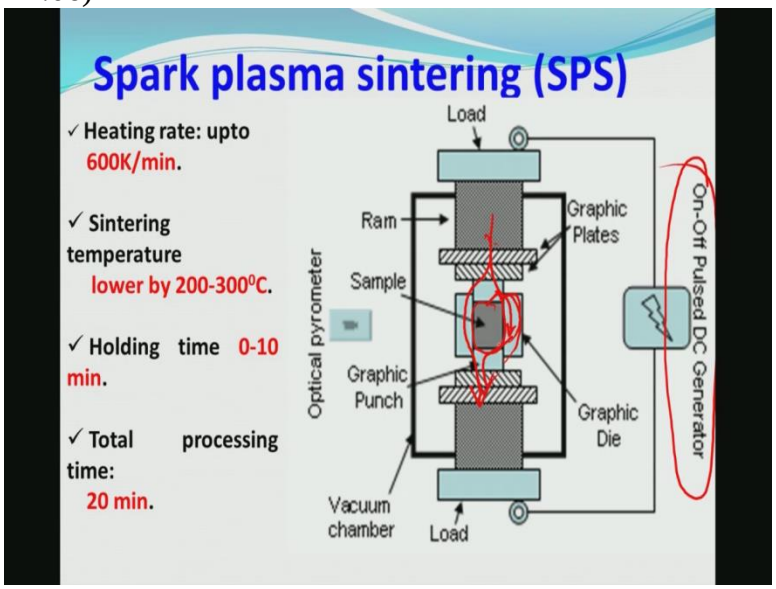

The last technique before the end of this module is the spark plasma sintering. Now spark plasma sintering is very similar to that of the hot pressing but the fundamental difference between spark plasma sintering and hot pressing is that, instead of the hot pressing what you have seen there is external heating in the spark plasma sintering that is, that you allow the large amount of current to slow through that graphite dye punch assembly and then it goes there and this is a on off pulsed DC generator.

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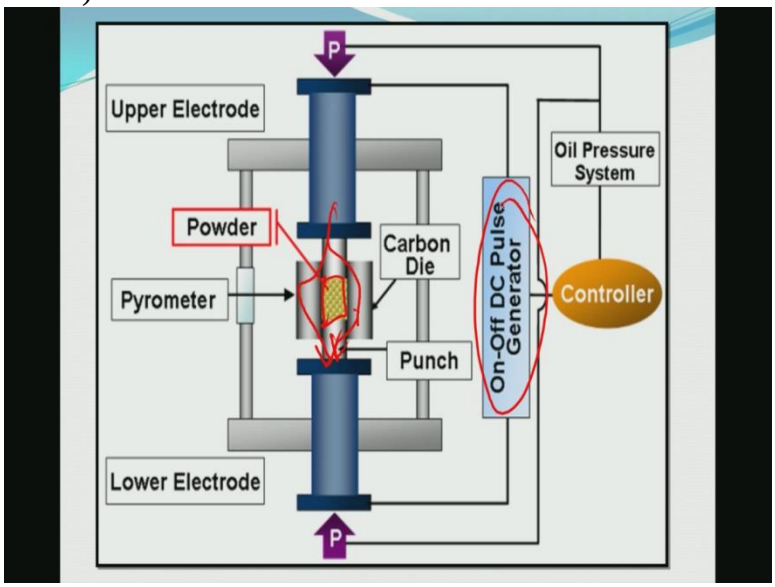

And in this graphite plates that this depending on the conductivity of the sample powder and depending on the conductivity of the graphite dye punch assembly, some fraction of the current will go through and this is a very clear picture. Like you can see that powder particles here and this is the fraction of the current will go through like this. And this fraction of the current will go through and this is the DC pulse generator and then after that what will happen?

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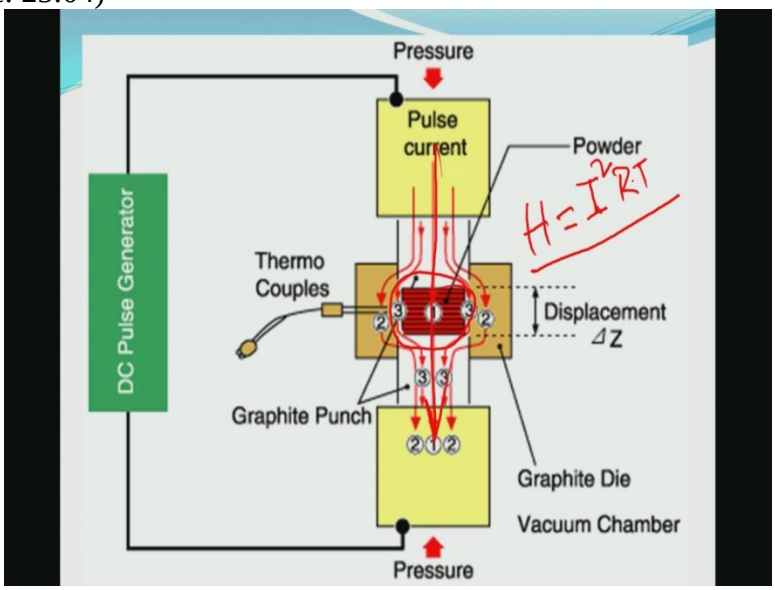

Depending on how much current is passing through the powder compact, powder compact will be heated up. So this T is heating is typically done by the Joule is heating where h is equal to I square rt. I is the current that is flowing through the sample, r is the resistance, that is conductor resistance and t is the time through which this current is passing through the material.

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So because of this high pulse current, now you can see through this window that how this temperature is going, shooting up, this is a commercial spark plasma sintering machine, where hydroxyapatite based material can be routinely consolidated and densitfed and then you can do this sintering process and you can sinter it even at higher temperature to consolidate the material.

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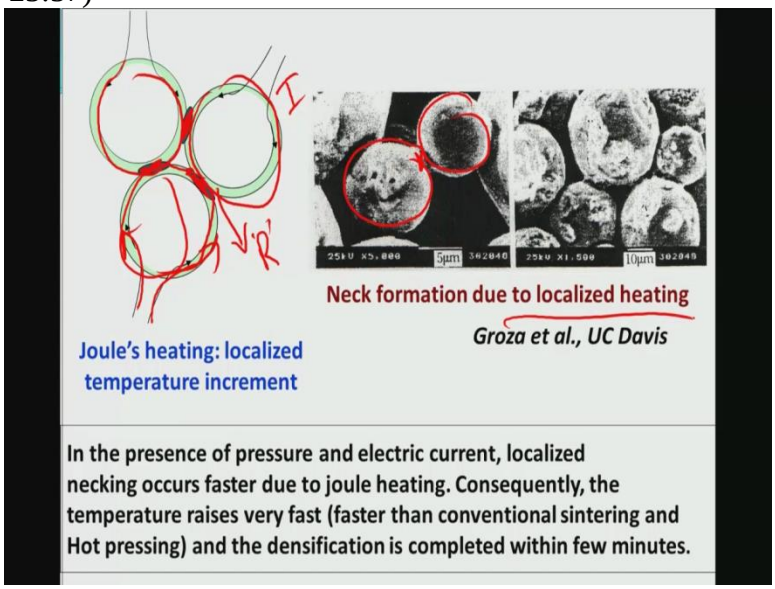

So one of the technique here is the is this Joule is heating and in the Joule is heating essentially what you see that, so this is the schematic this is the schematic. It shows that this is the three particle model. This is particle one, this is the particle 2 and this is the particle 3. This is a particle 1, particle 2 and particle 3, and this is the contact resistance here. In the contact resistance here, when the current will pass through this particles, this particles will experience certain resistance to the current path.

Now this contact-contact resistance will essentially give it as a resistance r, and this current which is going through that is current I, so therefore the total temperature that will be generated, the heat that will be generated is nothing but I square rt and this is the neck formation that will take place here, and this shows that how this neck formation is taking place and this neck formation due to localized heating is possible.

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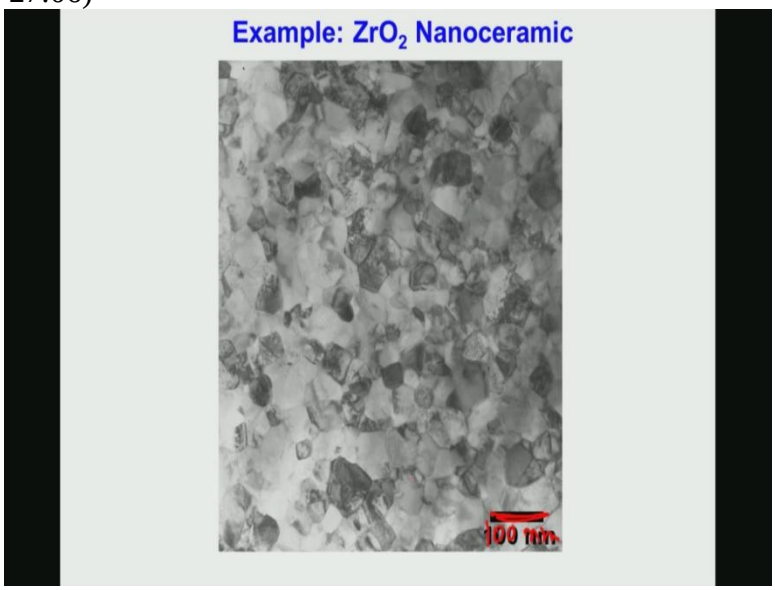

This is the examples that how fine the grain size be. You can see this aron bar, this micron bar here, 100 nano meter. So 100 nano meter means essentially this nano structure materials can be very easily sintered using the spark plasma sintering machine. So I think I have now competed that ceramics processing and this will be followed by some description of the different ceramics of relevance to bio medical applications in one of the future modules. So that you can understand that how different sintering conditions are to be tailored to develop some materials.