

Introduction to Biomaterials

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Lecture No. # 21

Sintering and Mechanical Properties of ceramics

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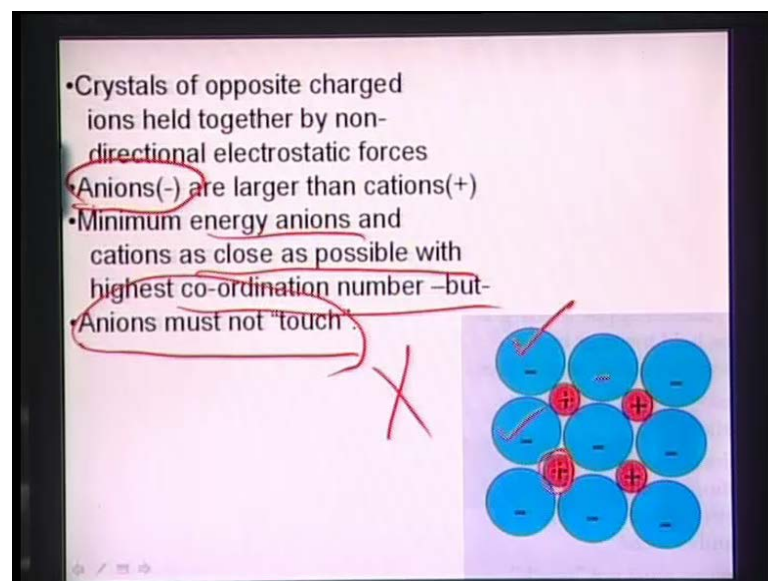


In this lecture, we will discuss mostly the processing structure and properties of ceramic materials, because these ceramics are increasingly been used in biomedical applications; therefore, and in depth knowledge of the how the ceramics are processed to make different shaped components or how the properties of ceramics are different from that of make of a polymers that need to be understood clearly before they are biomedical applications can be realized. So, several things that I will be discussing through a series of slides are as follows, first is that structure and bonding, and then structure and bonding and that basically, how the micro structure they look like and what is the typical bonding of the ceramics that will be discussed. Then it will be discussed about the then processing of the ceramics most to the sintering aspects.

Because each of the materials, they are essentially fabricated or there essentially manufacture by different routes. So far ceramics the sintering is the most commonly used processing routes, which are lastly employed to make different shaped components. Then third one is the ceramic micro structure. So, how the sinter micro structure they look like, how the micro structure is different from that of other material, that will be express upon. One of the major concern of the ceramics is brittleness and for example, in some of the lectures has been categorical mention or it has been repeatedly mention that Hydroxypatite, which has been widely degraded as an important bioceramic materials, because of their good biocompatibility or bioactivity property, they suffer from extreme brittleness.

Because hydroxypatite has a fracture toughness of less than 1, if we square root beta at so, which is around 1.6mpa square root meter. So, why ceramics are brittle and how the brittleness can be overcome or how different toughening mechanism can be invoked in the ceramic material that will be discussed. And expect the fracture toughness or the toughening behavior the mechanical, general mechanical properties of a ceramics like hardness and string properties. How they are experimentally, means that and what are the different formulas, typically used to determine the mechanical properties that also will be discussed.

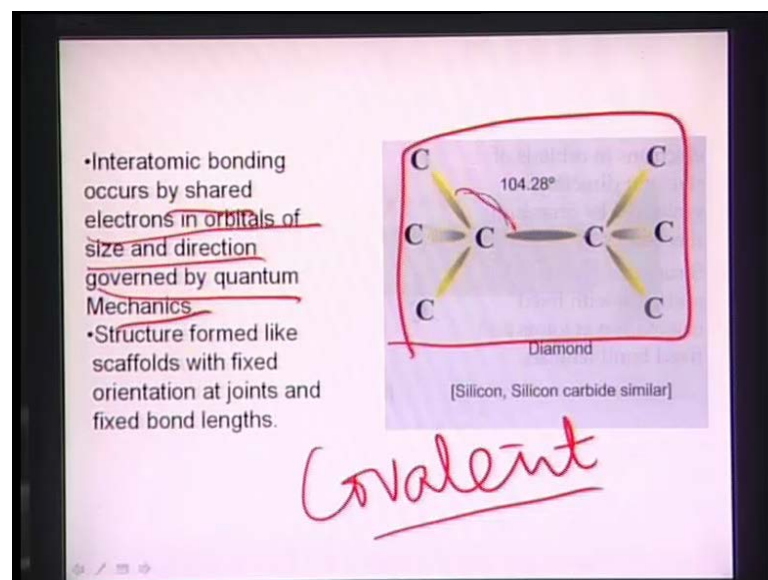
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Now, typically ceramics are defined as a class of inorganic materials **sorry** inorganic solids, which have covalent or ionic bonding. And which are used at high temperature or processed at high temperature either of the two, either it can be processed at high temperature or it can use at high temperature in both the cases, you can fall that class of materials is ceramic material. Now, here in this new graph, you can see these particular ceramics plates X ceramic have largely ionic bonding. Ionic bonding means, like these are cations, positive cations and these are negative anions.

So, positive cations and negative anions, they are ionically bonded to each other. And thereby, they formed ionic bonding the rule of the game is that, anions must not touch each other. Anions means, these one anion and these one anion should not touch each other. So, therefore, the size of the cation will be such that, they will occupy the inter spaces between the anions thereby separating the anions at some physical distance. So, that anions should not touch each others, so you understand what I am saying. So, this is, what is that important thing that anions must not touch each other. And minimum energy anions and cations are as close as possible.

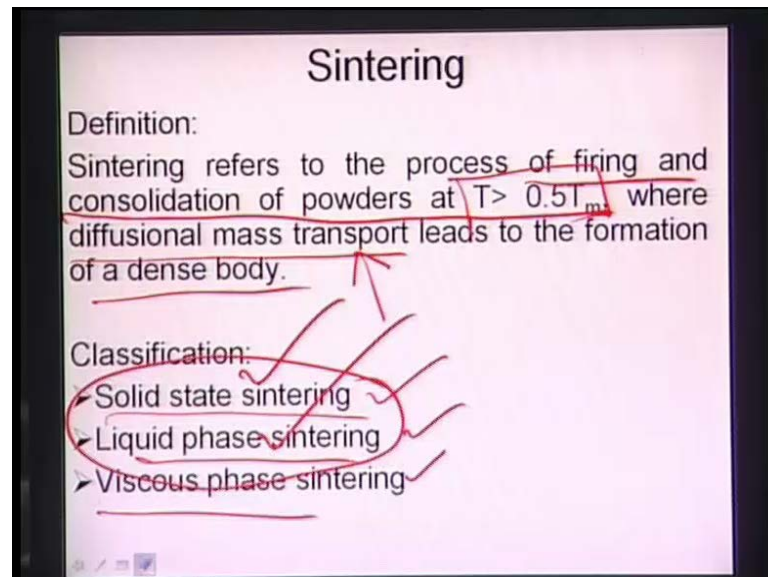
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So, the highest co-ordination number is possible typically, anions are larger than that of the cations. The other bonding is this is called covalent bonding and this is from basic school physics, you know that covalent bonding essentially form by sharing of electrons, in orbitals of size and direction is governed by the quantum mechanics. So, this is the

classical example that has been shown here in case of the diamond. And diamonds is bond it has bond angle is 104.28 degree. So, that is the stable diamond structure, now several material ceramic materials like silicon carbide or silicon they also have a diamond like structure.

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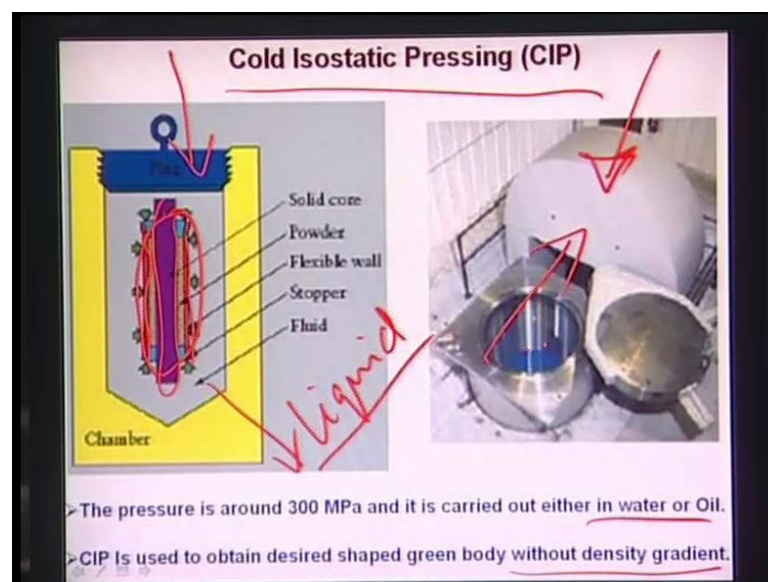
So, now coming to the ceramics like you know this is something about the bonding of the ceramic, that is the ionic and covalent bonds. One point that, I must mention at this point that none of the ceramics, which are used or which are known to the mankind, they do not have 100 percent covalent or 100 percent ionic bond. So, that is simply not possible. So, in other words all the ceramics, they have a mixture of covalent and ionic bonds. So, may be they have 90 percent ionic bonds and 10 percent covalent bonds or vice versa 90 percent ionic bonds and 10 percent covalent bonds. So, therefore, the point that you should bear in mind that all the ceramics, they have a mixture of ionic and covalent bonds. And no ceramic that is known to people, they have a 100 percent ionic or 100 percent covalent bonds.

Now, coming to that how this ceramics are typically process that is the sintering aspects. So, what is meant by sintering? Sintering actually, refers to the process of firing and consolidation of powder at T greater than $0.5T_m$. So, that is the fundamental definition of ceramic and at this temperature region T greater than $0.5T_m$ diffusional mass transport leads to the formation of a dense body. So, essentially, if you know the basic

material science or basic metallurgy, the diffusion is the process, which takes place typically at a temperature region to greater than $0.5T_m$. And therefore, diffusional mass transport process takes place extensively in this process, which typically takes place at this high temperature and that leads to a dense body.

So, what are the different classification of ceramics one is the solid state sintering. One is the liquid phase sintering; third one is the viscous phase sintering. Now, in these lecture we will be mostly, concentrating on these solid state sintering and liquid phase sintering not viscous phase sintering. And we will see as we go, we will see that what are the differences between these two classical sintering mechanism?

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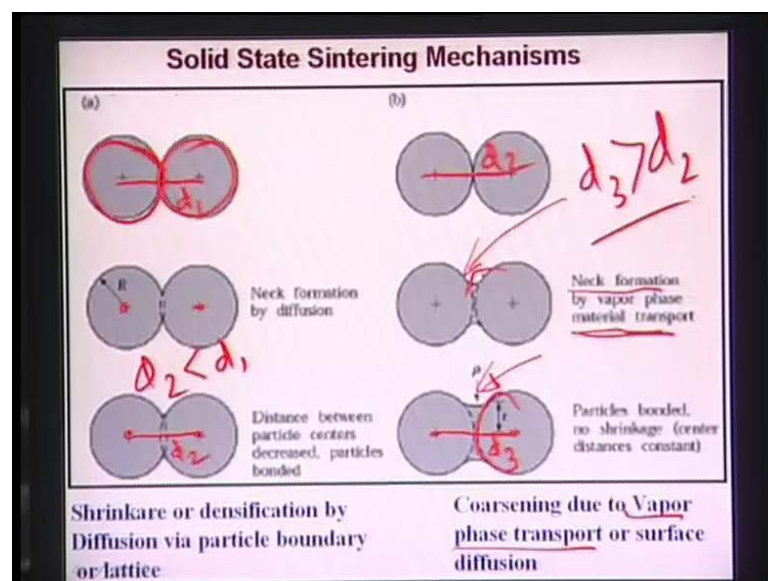
Now, first thing in the sintering process that you have to make the green body or you **you** have to make green compact and then thereafter, you have to do the sintering. So, this green compact can be made by either cold Isostatic Pressing or by simply cold pressing, now how this cold Isostatic pressing they operate. So, you have to put the powder, inside in a balloon or particular cavity. And then you have to immerse this outer body in a liquid and this liquid can be either, highly pressurized water or oil these liquid or once it is put inside this liquids, then from the top, you can apply the pressure and these pressure can be as high as 300 or MPa or it will higher than 300 MPa.

Now, according to Pascal's law, when we applied pressure in a liquid medium, that pressure will be uniformly applied to the dense to the solid, which it is contained in the

liquid. So, from that, basic fundamental principles of applying Pascal's law, what you can immediately realize this powder material or powder based material, they will experience uniform pressure from all the sides. So, therefore, these powder body can be made a green body and this green body which should not have much density gradient, because it will have a uniform density throughout the green body, other things that you have to note here in this slide that first of all it. If this powder need to be mixed with some binder or need to mixed with some second phase, then you have to use these planetary ball milling.

So, you have to put the ball here and the powder here, then you have to close it you have to put it inside this planetary ball mill, then these mill will rotate at a certain speed. And then by mixing these in the liquid medium, then you get a uniform mixture of a plus b or c plus d whatever, powder mixture you want to get.

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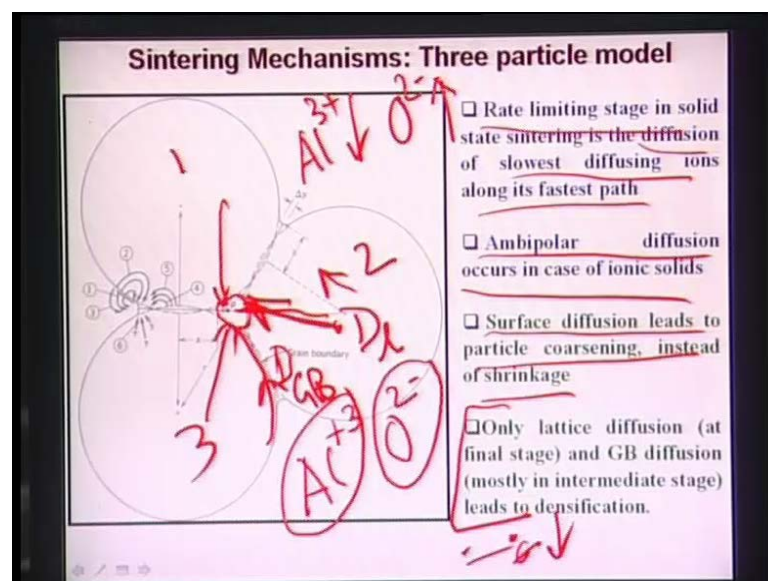
Now, this solid state sintering mechanisms, how do they typically take place in practice? So, these slides tells you that, there are two spherical particle, powder particle, which are coming in contact with each other. Now, if the sintering takes place (takes place) or new formation takes place, then the same center to center distance between these two particles, which time is reduced. So, what I am trying to say here, if this distance is d_1 here and the distance is d_2 here, then d_2 should be less than d_1 . And that means, they

are approaching each other and that is the way that you can experience, that sintering is taking place.

Now, what happens during vapor phase transport which takes place in the initial state of sintering that, if you hold at very initial stage of sintering for longer time. Now, vapor phase transport process cannot encourage, that this neck formation and neck growth to the extend like it, does going to this sintering takes place at the intermediate stage of sintering of final stage of sintering. And in fact, if you hold this powder of article compact at this vapor in the initial stage of sintering, then what will happen material transport takes place by the vapor phase.

And therefore, the grain coarsening will takes place or particle coarsening will take place in other words, these inter particles distance, if it is d_3 and initially it is d_2 , so d_3 is greater than d_2 in this state. So, if the inter particle distance increases, then the sintering certainly does not take place and coarsening takes place.

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Now, these mechanism you can clearly see it in these particular fibrous, where it shown the three particle 1 2 3 all are of same size and there of same shape, spherical shape. Now, three particles are coming in contact and there is a neck formation in the individual particles this is one neck, this is second neck, this is third neck. And then once this neck forms and this is the region in that three particles region, which needs to be filled by the

matter of particles. And these region, how they will to feel by diffusion from the these particle by diffusion from these particles **by diffusion from these particles**.

And therefore, and these diffusion can takes place either by grain boundary region, then it is called grain boundary diffusion or these diffusion can takes place by lattice diffusion; that means, when the mass or atom is transported from within the particles to these neck region, then it is called lattice diffusion. In this case, you have that lattice diffusion constant which is important; in this case it is the grain boundary diffusion coefficient, which is important. This is like you know very brief description, that how simple in takes place in three particle model.

Now, rate limiting stage in the solid state sintering is the diffusion of the slowest diffusion, diffusing ions along it is fastest path. Now, depending on what temperature you are sintering, if your sintering at the intermediate temperature then grain boundary diffusion takes place and then grain boundary is the fastest path. If you are doing at large temperature or highest temperature or the sintering temperature the lattice definition is dominating. And then these sintering takes place by lattice diffusion only.

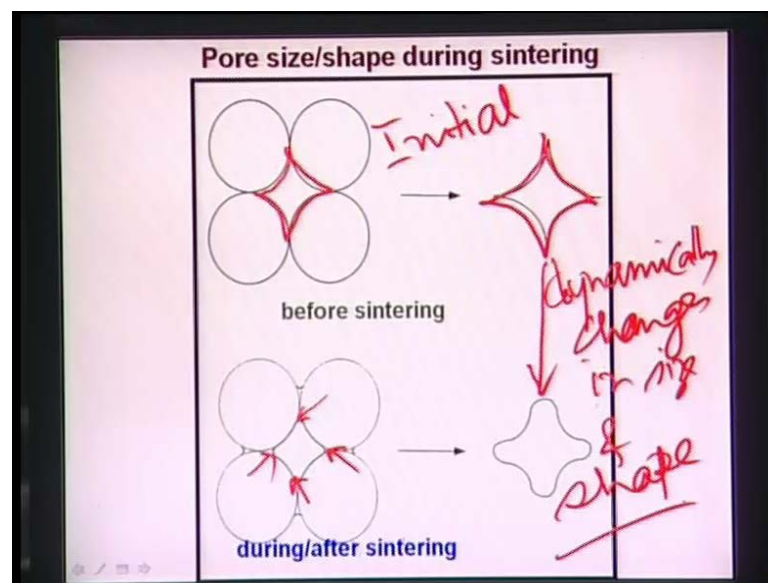
So, accordingly, you can see that you know what is the diffusion of the slowest diffusing ions along it is fastest path, the second one Ambipolar diffusion occurs in case of ionic solids. Ambipolar diffusion means, let us say let us think of aluminum. Aluminum means, this is Al plus 3 ions and oxygen ions. So, when we are discussing about the sintering of alumina, then you have to find out that, what we how this aluminum ions cations will be diffuse and how the oxygen anions will be diffuse. So, now the word is aluminum cations will diffuse, that may be slower compare to the way alumina oxygen ions will diffuse, there diffusion rate may be faster. Accordingly that the heat diffuses faster at a given temperature, that will dominate the diffusion process in the sentry, so you understand.

So, in case of ionic solids there are two ions, cations and anions. Now, depending on whether this cations will move faster or anions will move faster accordingly, you can find out that what is the slowest diffusing ions along it is fastest path, and then you can find out that what is the rate limiting stage. So, from these considerations, now you know that how you can find out that, what is the rate limiting stage in a sintering or diffusion process? Now, second one is that surface diffusion, as I said in the last slide that leads to

particle coarsening instead of shrinkage that is quite straight forward. Because surface diffusion means, like this surface diffusion actually increases the particle to particle distance. And thereby the surface diffusion process encourages the particle portion.

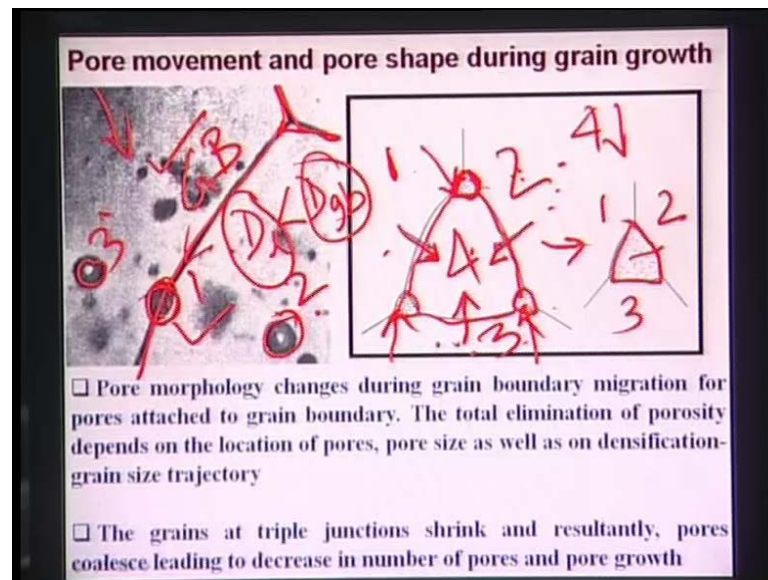
Now, third one that, we have written here that only lattice diffusion and grain boundary diffusion leads to densification that means, in this stage particle to particle distance, that distance decreases as to increase as the density is increased.

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Now, this slide shows that how this pore shape changes, during the sintering process this is the initial stage. In the initial stage your pore party case simply touch each other and the pore shape is pore shape means, that is the inter particle pore shape. This inter particle pore shape, has it is this kind of character restriction. Now, as the sintering proceeds; that means that mass transport takes place from different neighboring particles to the neck region, then what will happen, this pore shape continuously or dynamically changes, it is size and shape. So, important thing in sintering is that pores gets changes, it is size and shape dynamically, during the process and that is what takes place during the process of sintering.

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Now, what happens in the final stage of sintering, when most of the pores are close to the grain boundary and this is the grain boundary region? Now, grain boundary region, that is one forth that is attached to the grain boundary. So, this is let say pore number 1, this is pore number 2, and this is let say pore number 3. Now, this pore 2 and pore 3, they are detached from the grain boundary. So, that means, they are like further away from the grain boundary whereas, pore one is completely attached to the grain boundary. And what exactly, has been shown here now depending on what is the mobility of the grain boundary and what is the mobility of the pore each will determine, whether the pore will be attached to the grain boundary or pore will be detached to the grain boundary.

Now, from the simple consideration of the lattice diffusion and grain boundary diffusion from this particular situation, you can immediately understand that, which pores will be eliminated in the process and which pores will remain. Now, you always know that your lattice diffusion coefficient is less than your grain boundary diffusion coefficient right. Now, this particular pore number one for that your grain boundary diffusion process is much more active. And, if grain boundary diffusion is faster that means, removal of this pore number 1 is much more lightly, compared to pore number 2 and pore number 3, because these two pores pore number 2 and pore number 3 for that your lattice diffusion has to take place. And lattice diffusion is always slower compare to your grain boundary diffusion.

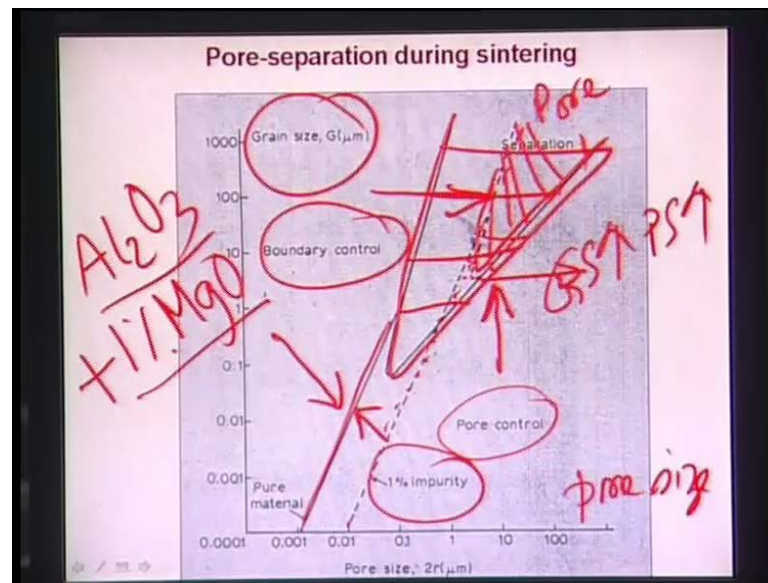
So, from this simple considerations of the diffusional mass transport aspects, you can immediately understand that, why the pores, which are attached to the grain boundaries, those pores will be removed faster compared to the pores, which are away from the grain boundary. Second point from this slide or second message from this slide, this is grain number 1, this is grain number 2, this is grain number 3 and this is grain number 4. And you have this is one pore, this is second pore, this is third pore. So, the way this pores are looks like pores to pores appear here in this particular situation. So, at the interface of the grain 1 and grain 2, these pore at the interface of grain 1 and grain 3, these pore at the interface of grain 2 and grain 4 (()). So, in each case this triple pocket this pores are formed and these triple pocket is 1 2 4, these triple pocket is 1 3 4 and these triple pocket is 2 3 4.

Now, what will happen during the process of the shrink seems, these grains are growing these grains are growing and these grains are growing and the geometry of the grain boundary such that, the grain boundaries are much more mobile. So, these grain boundary will move these way, this grain boundary will move this way. And these grain boundary will move this way, then what will happen four will collapse. So, four will completely collapse during the process of same field and what will be the result? The result is that this is grain 1, this is grain 2, this is grain 3 and three pores.

Now, will come together and there will be pore growth processes, that will take place. So, what is the net result, that grain growth is also accompanied by the pore growth initially, your pore size here let, if it is 2 micron if it is 2 micron, it is 2 micron, then at the end of the shrinking processes, this pore size would be much larger than 2 micron that is number one point. Number two point is that initially, if your grain size of 1 2 3 same micron, that at the end of the grain growth process your 1 2 3 both the grain feelings will increase in size. So, it will not no more be 10 microns.

So, you understand the physics of the process, that during the shrink spring your grain growth and pore growth both will occur simultaneously, and that is determine by the your geometry or geometrical (()) of grain boundary call. So, this is like you know from the very basic sintering theory, how you can explain the fundamentals of the sintering process.

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Now, based on all these considerations, people have plotted the grain size versus pore size. And this is the grain size here and this is your pore size plotted along the X axis. Now, what you see that, this is the case of pure metal that is not open. Now, this region is the region where there is a pore separation that takes place in this region, where there are pores that will control the boundary motion and this is the region where the grain boundary will control the boundary motion. Now, what is meant by pore-separation, if you go back to this particular slide here, pore separation means that, during the sintering at certain points some scenarios or some situation will come like this. That the pores will be separated from the grain boundaries and they will be isolated pores inside the grain.

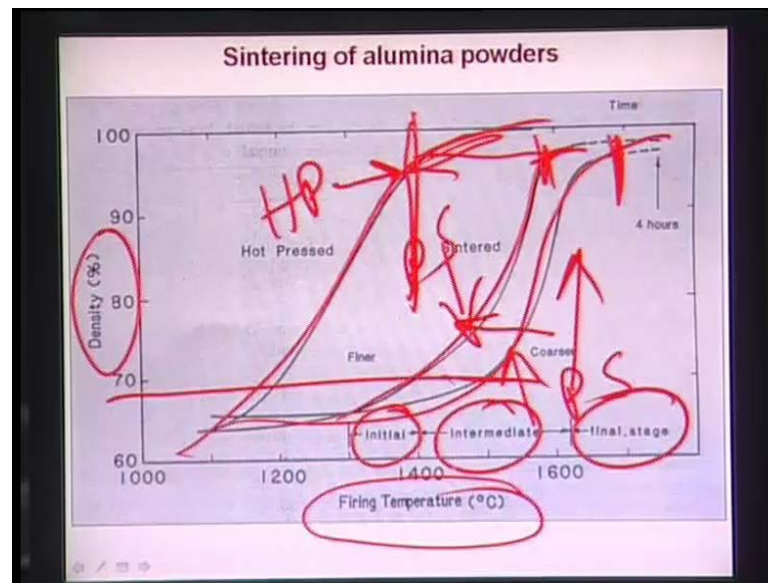
And you do not like that the isolated pores happen in your sintering process, because you know, if the pores become isolated, then what will happen these pores will be very difficult to be eliminated during the sintering process. So, those pores will remain, because your lattice diffusion is always slower compared to your grain boundary diffusion. So, from these considerations, it should be very clear to you that you do not want your pore-separation to take place during at any point or at any stage during the sintering process. And that is what has been shown here, that you know that during your sintering that particularly final stage of sintering, your grain growth for grain size also, increases your pore size also increases.

But if your grain size increases means, you are going these directions, if your pore size increases means you are going this direction. Now, if you by chance that you are entering into these region, during your sintering process or in these hatch region, then what will happen all the pores become, now separated from your grain boundary. And then what about the holding time or what about the time you hold at the sintering temperature, you cannot remove these pores during your densification. And you will get completely, material with much less density then what you have expected otherwise. So, these you can expect from your very basics of sintering process.

Now, what would be strategy that you should adopted? The strategy would be now for example, if you add some impurity. Impurity is like if you (if you) can sinter alumina or in these alumina, you can add let say one percent magnesium oxide, remember alumina is an important bioceramic, because this alumina ball is an used as a femoral ball head in the total hip replacement. Now, if you want to make alumina ceramic and then, if you add this one percent magnesium oxide, then this dotted line essentially indicates, that how this enter the boundary of the pore pore control. And grain boundary control or pore control and boundary control they are shifted towards the right.

And the more important you notice here, now that this pores separation also has been shifted towards much up, these region or these region, you are kind of quite safe as per as your sintering process is concerned. So, that is therefore, that you can choose certain binder content or you can choose the composition of your ceramic, in such a way that your pore-separation area that you can avoid during the sintering process. And, if you can avoid strategically, then you will end up having ceramic with less and less amount of pores and more and more amount of more and more density of the material.

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This is that one of the classical flop, which tells you that how density increases with the temperature. The firing means, it is the sintering temperature firing and sintering, they are like synonymous words. In the many industries, they always use of firing temperature they do not use the sintering. Sintering is more scientific term, firing is more industrial term. Now, what you see in that sintering conditions the density versus firing temperature. Now, if you use the coarse powder then your density, it keeps on increasing and these does not increase in a very linear fashion, but it still increases beyond a certain density values, quite steep manner and then goes to the 100 percent theoretical density.

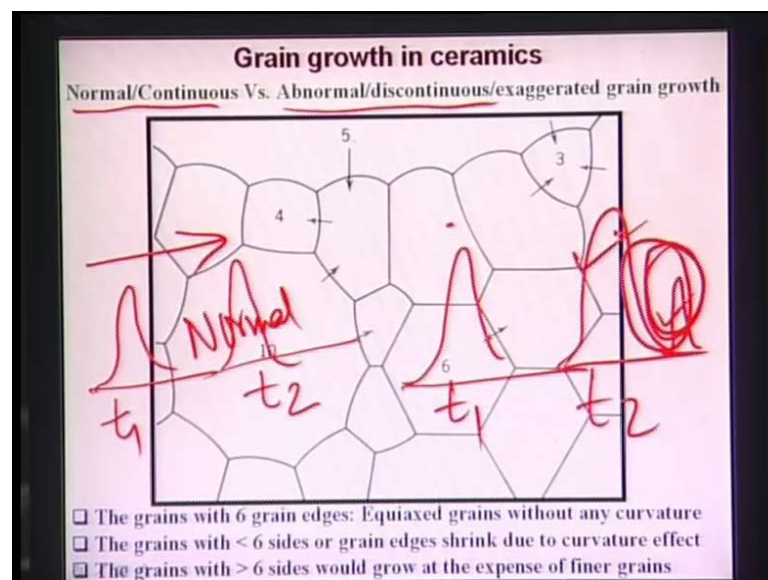
If you use fine powders of the same ceramics, then your curve is shifted towards left and then your actually, completing the densification little bit earlier than coarse of powder. Now, if you go to this hot pressing techniques sound, these two things these is done in the special sintering, this is also done in the special sintering technique. Now, this is your hot pressing route and in your hot pressing, if you see that how these curve look like hot pressing the curve is shifted more towards left and side. And that means, that in the hot pressing route your density increases much more steep. And your hot pressing does not require much longer time period, like the way it requires for the special sintering case.

So, therefore, in the hot pressing, you can quickly densify or you can quickly sinter these materials at a much faster rate of it, because your densification takes place much faster. The other thing, that you notice from these curve is that entire sintering can be

classically, divided into three stages, one is the initial stage, the second one is the intermediate stage and the third one is the final stage. So, initial stage of sintering means, it is just like the net formation takes place. The particles the coming contact with each other, inter particles distance starts decreasing with increasing time. Intermediate stage of sintering means, your grain boundary diffusion process started and intermediate stage of sintering your pores become, they form like a continuous channel is more like a cylindrical channel of pores that forms.

And in the final stage of sintering your pores become isolated and that is the period that your holding, it for longer time. So, that your allowing lattice diffusion to take place and therefore, your are essentially trying to remove these closed porosity from the material.

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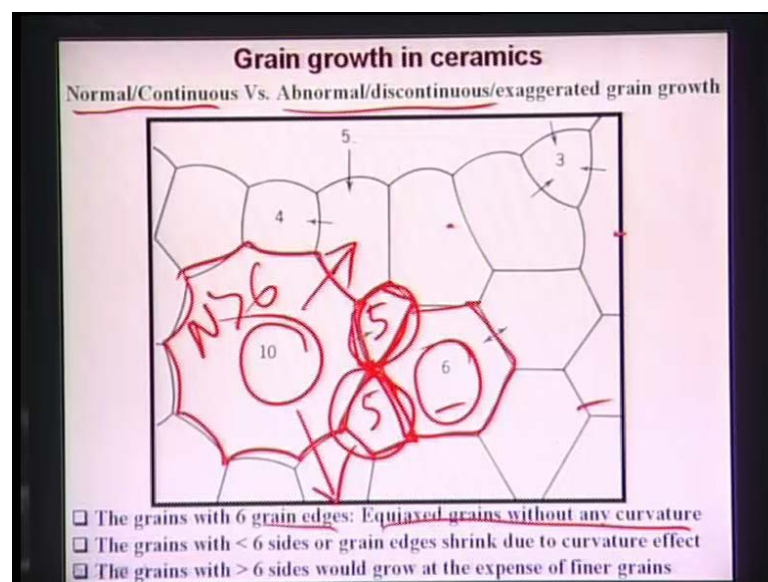
Now, this is the grain growth, which takes place in the ceramics one is the called normal or continuous grain growth, one is called abnormal or discontinuous grain growth. Now, what is normal grain growth? Normal grain growth means, suppose your grain size distribution at any given time t_1 is like these, your grain size distribution changes with at time t_2 , where t_2 greater than t_1 and then it is simply shifted along the X axis to a new distribution time, what it means? That it means, that your mean grain size increases with time, but the overall shape of the grain size distribution remains same.

So, it is called normal grain growth right. Abnormal grain growth means, initially your grain size is like these at time t_1 , at time t_2 your grain size also is giving you two type

of distribution and that is called unimodal distribution, two bimodal distribution, you have one mode here and you have one mode here, what it means? This means, the average grain size not only increases with time, but also there are few number of grains, which is much more coarser size that appears as you sinter, it for longer time period. So, that is the definition of the bimodal grain growth.

The question is that why these grain grow which time and what was the reason for this? The reason is very simple and that is again, comes from the basic geometry. Now, if you look at this slide, you will realize immediately that the grains which, has a grain edges more than 6 grain edges, they will grow at the expense of the smaller grains.

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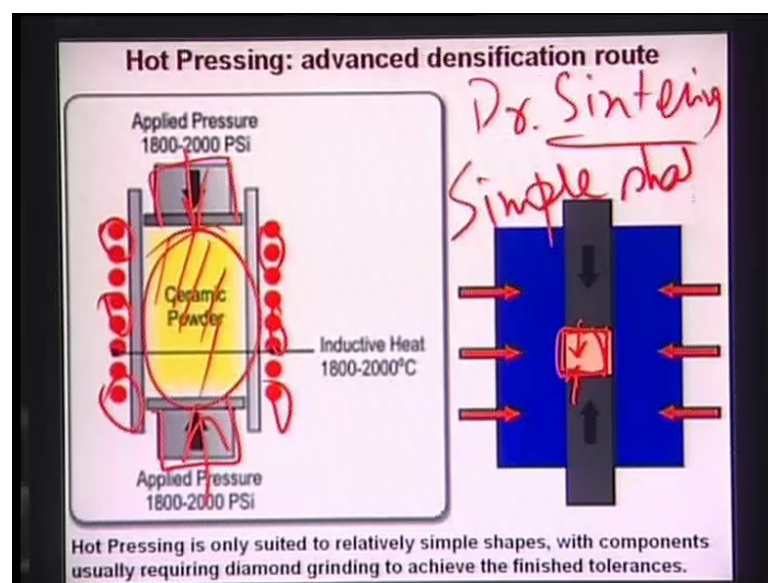
So, here you can see there are few grains, which is 1 2 3 4 5, this is the grain 1 2 3 4 5. So, these has a grains, which has grain edges 5, this is the grain which is the grain edge6; that means, this grains with 6 grains edge, they are equiaxed grains without any curvature. Without any curvature means, the grain edges like, straight they do not have any curvature in the grain boundary. Now, if the grain edge is more than 6 like here for example, 10 like this is 1 grain edge 2 3 4 5 6 7 8 9 10 in this case, your grain growth will takes place, because your grain boundary now is much more curve.

And from basic geometry, it needs to be curved it cannot be simple straight line, because with a grain edge of 10, your grain boundary is also will be curved. And what you see here, in both these cases and both these cases, the grain boundary will be now dragging

towards diagonally, this way and this way. So, that this grains will now grow, now enter volume will remain constant. So, these grain growth can take place only when whatever, smaller grains it has in the neighborhood that will be consume, it is just like in a society, where rich people live and poor people live.

So, rich peoples property will only increase at the expense of the poor people. So, similarly, the grains which have a grain number is more than 6, they will grow at the expense of consuming the smaller size grains, which has a grain edge of less than 6.

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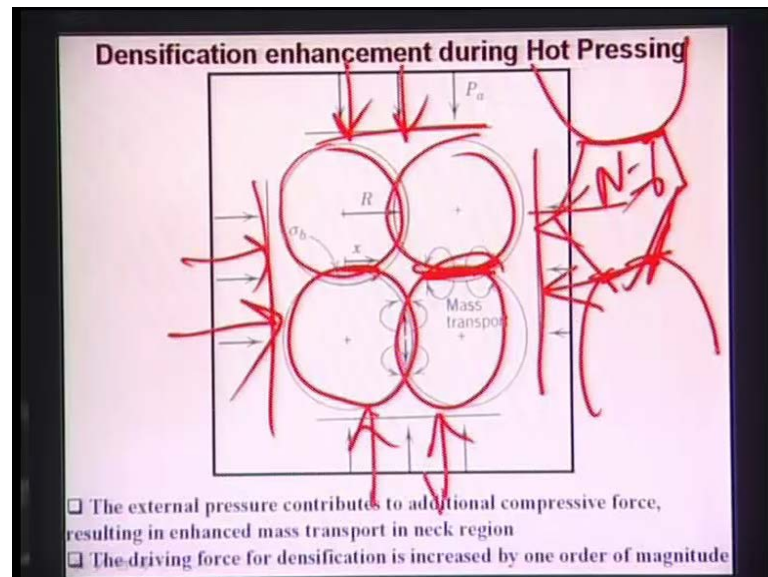


Now, typically the sintering process, they can be classified again from the technological point of view, one is called pressure less sintering. Pressure less sintering means, your sintering without any pressure and another one is the hot pressing technique. Hot pressing means as the name suggest you press, it when it is hot and how this process takes place in practice, you have this ceramic powders here, which you feel these mold here graphite mold. And in these from these graphite mold from the bottom and top, you start pressurizing. And from these resistance sitting here, your actually also hitting it from externally.

So, this ceramic powders will keep on experience more and more temperature. And you push the pressure going ceramic reaching at high temperature, as a result what will happen there, will be shrinkage from both the directions and this entire powder compact is contained in these graphite di wall assembly. So, side walls there is limitation, that is

restriction and the temperature in the hot pressing, can go very high as high as 1800 to 2000 degrees celsius. And this is how the hot pressing takes place in practice. However, the basic thing in the hot pressing is that, you can only make very simple separate material, not very complexure.

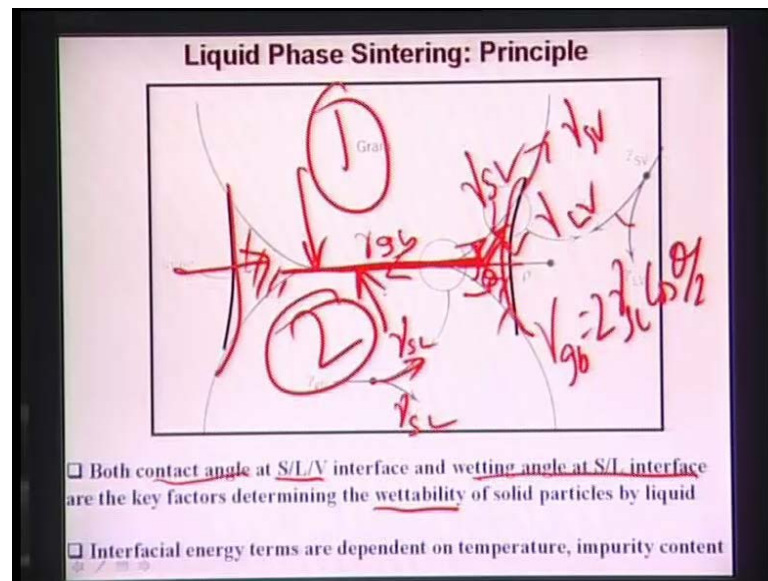
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Now, what is the mechanism of hot pressing? Mechanism of hot pressing means, you have these four particles model. So, four particles they are coming in contact with each other and they are touching each other. And then you are pressurized, you are applying pressures from both the ends and this is your graphite die wall. So, this way there is no expansion possible; that means, there is a lateral constraint here, these constraint and that constraint, And then this particles, now they have the only way that these shrinkage can take place, if these center to center distance keeps on decreasing. That means, these particle **particle** boundary should become more and more flat.

And that leads to the material, which has an equiaxed type of grains, equiaxed means that is any pick up to 6 as I have explained few slides back. Now, how these frames form now, you can understand that these, h must be this is a part of this one particle, this h must be part of the another particle. But due to the external pressure application and due to the fact that only longitudinal displacement is possible not the transverse way, that these particle **(particle)** distance becomes more flat. And that is how these entire grain structure, they involve mode like an equivalence type of grain morphology.

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Now, coming to the liquid phase sintering, liquid phase sintering means, the way this sintering takes place in the presence of the liquid phase. And these liquid phase then name suggest, that you **you** form some liquid during the sintering process. And then you in the presence of the liquid your shrinkage takes place. So, again here is grain number 1 and this is grain number 2 and this is your liquid phase here, this is your liquid phase there. So, this is your liquid, now this liquid in the presence of this liquid, it has some surface tension and surface energy this is like say γ_{SL} this is also γ_{SL} .

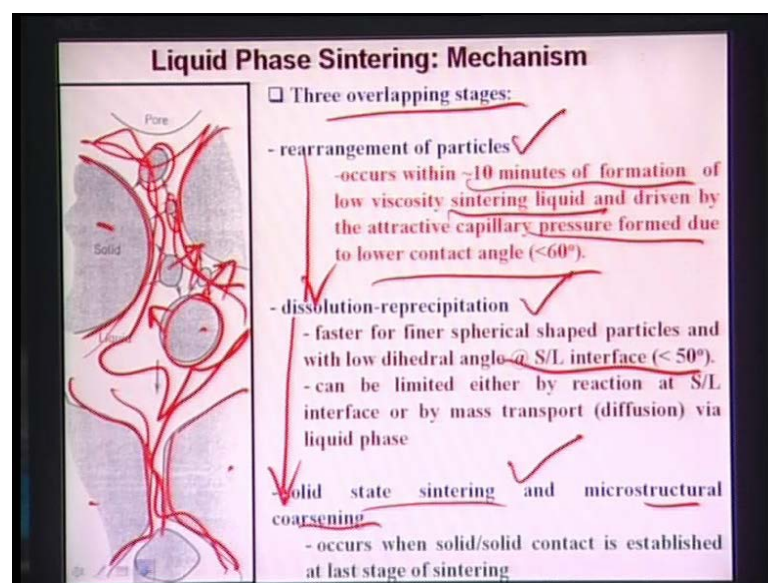
So, this way it is γ_{SL} , this way is γ_{SL} and this way, it is γ_{gb} . And, if you know this angle θ , the entire angle θ then this half of the angle would be $\theta/2$. So, from the basic physics, then you can find out that γ_{gb} should be equal to $2\gamma_{SL}\cos(\theta/2)$, that comes from your basic equilibrium. And from that you can find out θ value, if you know that γ_{gb} and γ_{SL} value right. Now, similarly, there is also another angle here and here again, you have γ_{SV} that is solid vapor interface, you have γ_{LV} that is liquid vapor interface and this is your γ_{SL} that is solid liquid interface.

Now, from your basic geometry again, you can find out the relationship between the three interfacial energies. And both the contact angle at the solid liquid vapor interface or wetting angle solid liquid, they actually determine whether, this liquid phase is wet will wet the solid particles or not. So, even if you have the liquid phase, if it does not wet the

solid particles, it will not serve the purpose of liquid phase sintering. Only in places, when it will wait **wait** means, this liquid phase has to flow in between this grain boundary region.

And once it flows, then these has to dissolve in this liquid phase **this has to dissolve in this liquid phase**. And there by the diffusional mass transport process will take place faster and accordingly, you can get more and more diffusional mass transport and fast and faster diffusion and that will actually, increase that shrinkage.

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Now, what happens in case of the liquid phase sintering that heat in mechanisms and these are like three overlapping stages; that means, you cannot essentially, say that these will take place first, this will take place second, this will take place third. That means, overlapping means, these and these can overlap these and these can overlap. The first stage is that rearrangement of the particles. So, this is your liquid entire stage is liquid, that liquid has formed. Now, in the powder compact, you have some smaller particles and you have some bigger particles also.

Now, what will happen the smaller particles will dissolve here in this liquid phase and then they will go and reprecipitate on the pores are solid particles. And then as a result this pores of particles will actually increase in size. So, that means, there will be grain growth of this course of particles are the expense of the smaller particles, that is what

exactly happens, during the grain growth of the solid state sinter particles. If you go back here also, I have shown you that course of particles will grow at the expense of the smaller particles here, also in the liquid phase sinter materials; I am showing you again, that you have this course of particles and you have this smaller particles.

And these smaller particles will dissolve in the liquid phase, and then thereby, they will reprecipitate on the solids particle surface. And the solid particle now will grow and this grain growth will take place at the expense of the finer particles. So, liquid phase sintering essentially, take place by three overlapping stages. The first one is the rearrangement of particles. Rearrangement of particles means, that once a liquid phase forms as the inter particle regions, then all the smaller particles then course of particles, they rearrange themselves.

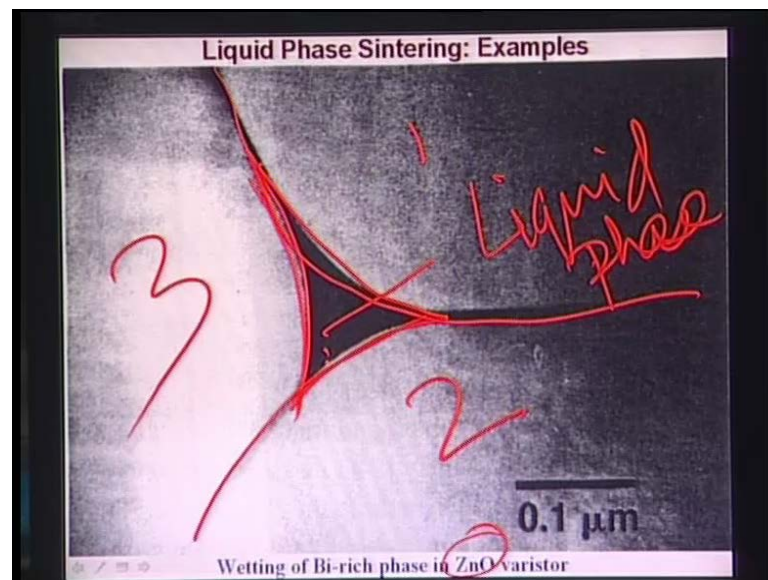
So that means, they can float and they can rearrange themselves. And that offers within around 10 minutes of the formation of low viscosity sintering liquid. Remember that sintering liquid, what it forms as the inter particle region, it should have a low viscosity, it is a high viscosity or if it is a very highly viscous liquid, then what will happen, the diffusion process will be much larger, you just seen you think of water and you think of a some polymeric gel or something. Now, in the water anything can diffuse faster, because it is a low viscosity liquid, but it is a polymeric gel, which is the very thick and viscous, then that mass transport or diffusional mass transport will be much more sluggish.

So, one of the thing in the liquid phase sintering, that your sintering liquid must have a low viscosity, otherwise this diffusional mass transport that entire purpose of having the sintering liquid will not be fulfilled or will not be solved. Now, that is given by the attractive capillary pressure from due to the lower contact angle that is less than 60 degree. This lower contact angle means, we are talking about this angle or this angle, which is less than sixty degree. So, there is some requirement of the geometric angle. And this geometric angle that takes place solid liquid vapor that is less than sixty degree.

Now, what happens to these contact angle, that is at the solid and liquid. Now, if you go back to the slide, it says that the solid liquid interface angle should be less than 50 degree. So, roughly in both this angle should be around less than 60 degree. So, this one specifically around 60 degree, this one less than 50 degree and, if this angle or this geometric criteria is fulfilled then that essentially, these combination of parameters will

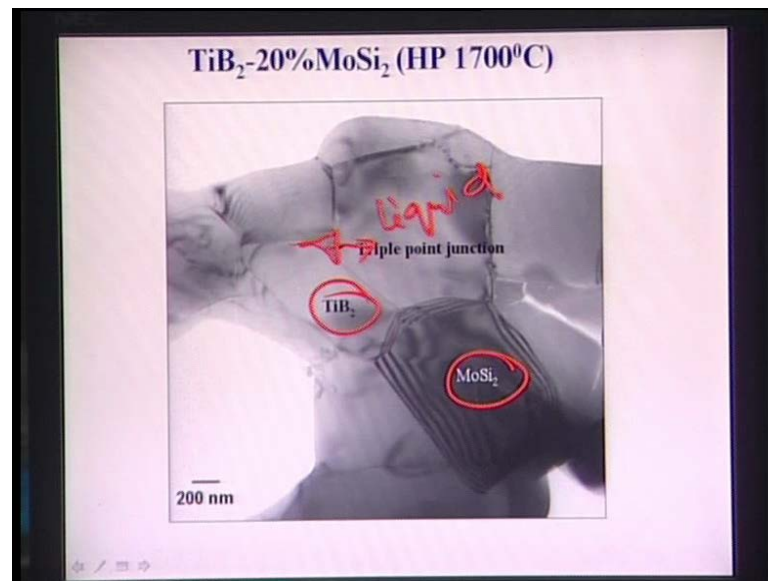
influence, the liquid phase sintering to take place more effectively. So, third one is that once this liquid phase becomes very smaller in volume fraction, then solid state sintering. And micro structural coarsening occurs and that typically take place at the last stage of sintering.

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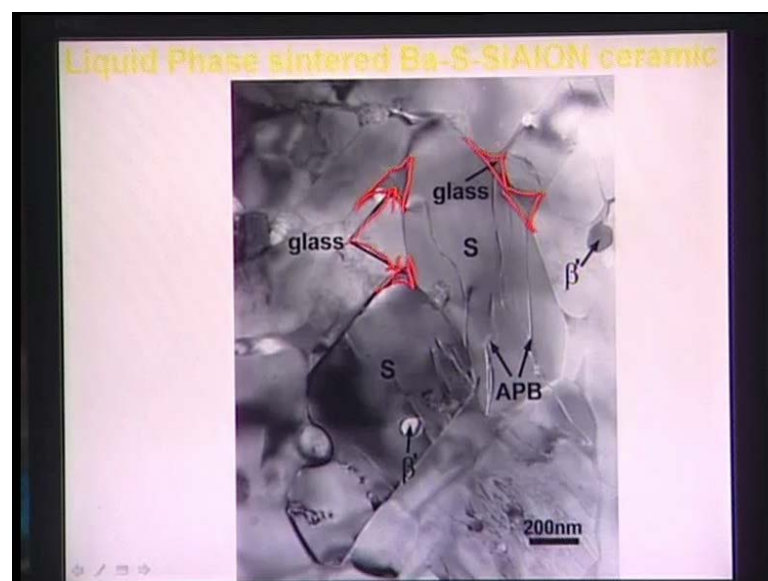
Now, this is an example of the liquid phase sinter materials although, it is not a bioceramiczinc oxide, but it is a vary state applications. But zinc oxide can also be added as a second phase, in this hydroxypatite to improve the anti microbial property, this is grain 1, this is grain 2, this is grain 3. In this grain 1 to grain 2 grain 3 this triple pockets this is the phase, where liquid phase respond and after sintering this liquid phase actually, remain there as a residue. And that is the evidence, that liquid phase sintering has taken place. And lead to the densification of the zinc oxide material.

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Now, this is like you know some other examples of the ceramics basically structure ceramics now what you see here, that liquid phase which was form in the TiB_2 and molysilicide. So, this is the triple pocket where the liquid phase form and this liquid phase has completely different composition compare to this to TiB_2 and molysilicide phase.

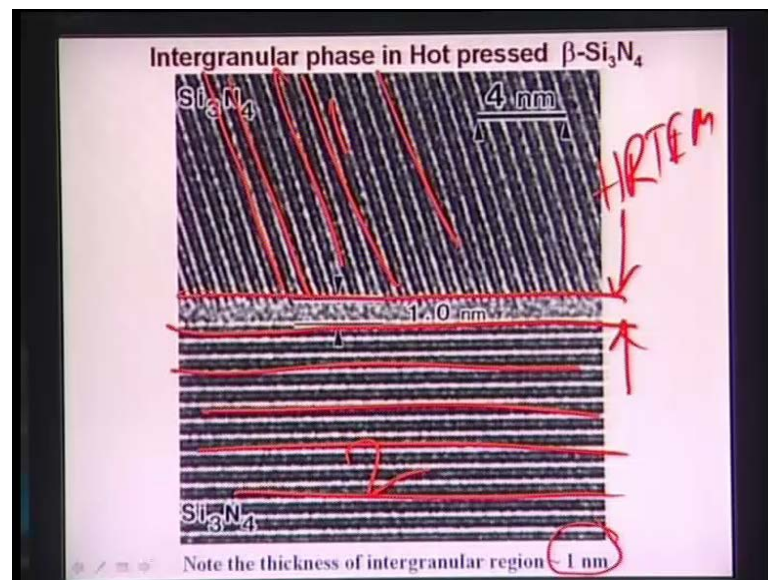
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Another examples, of the liquid phase in the silicon nitrate or another ceramic materials, where you can see this liquid phases formed at the triple pocket that is the glass phase.

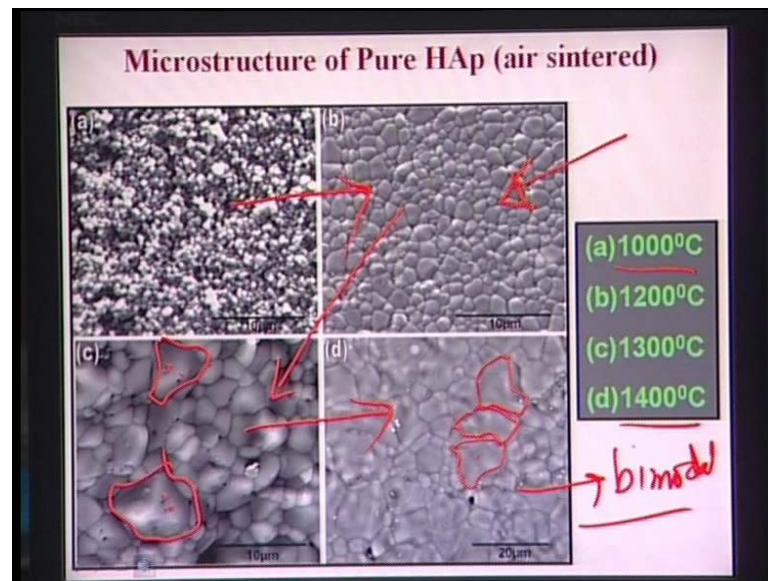
This is one liquid phase, this is another liquid phase in this transmission of a microscope pictures you can clearly see that, they are several phases the liquid phase that has formed. And this leads to the good liquid phase sintering property of this Silicon Nitrate based materials.

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Now, this is like very high resolution t e m that is high resolution transmission electron micrograph and what you see that this is part of grain 1 this is part of grain 2. In the grain 1 your atoms are aligned in this particular region, in grain 2 your atoms are aligned in this particular region. So, therefore, there is a orientation difference and this is the region, where is disordered region and in this disordered region your liquid phases formed and this is the amorphous of glassy phases formed, because you do not see any crystallinity in this phase. And that is the again, they evidence that liquid phase sinter materials that formed over a where in order range one two three and (()) nanometer thickness.

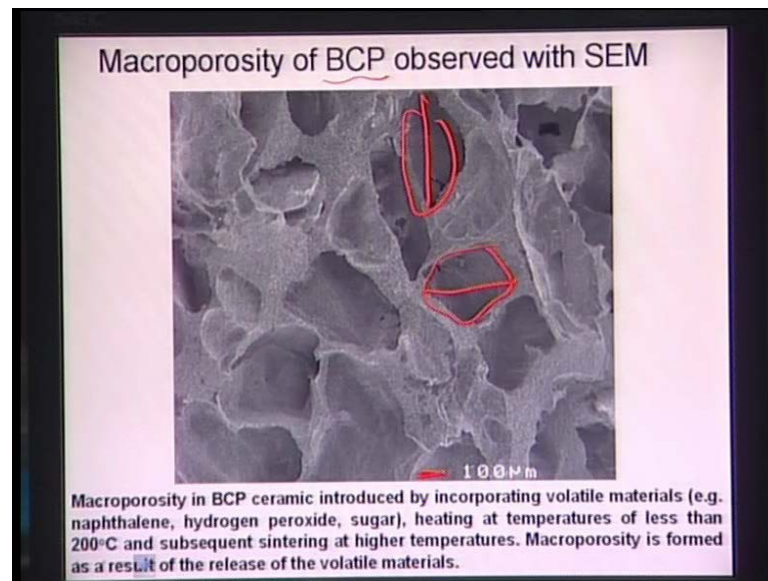
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Now, I will give you some examples, from the bio ceramic materials. Now, how these solid state sintered and liquid phase sinter materials they look like or how, do their micro structure they look like in this bio ceramics materials. Now, it is the examples, from pure Hydroxypatite now pure Hydroxypatite they have very good biocompatibility property, if you sinter them at thousand degree Celsius to fourteen hundred degree Celsius, what you see that grain size they increase at twelve hundred degree Celsius it further increase with thirty nine degree Celsius. And also it further increases to fourteen hundred degree Celsius. At fourteen hundred you can see really fairly coarse grain structure in the material and this coarse grain structure essentially indicate that you have large number of coarse grains and very few number of fine grains.

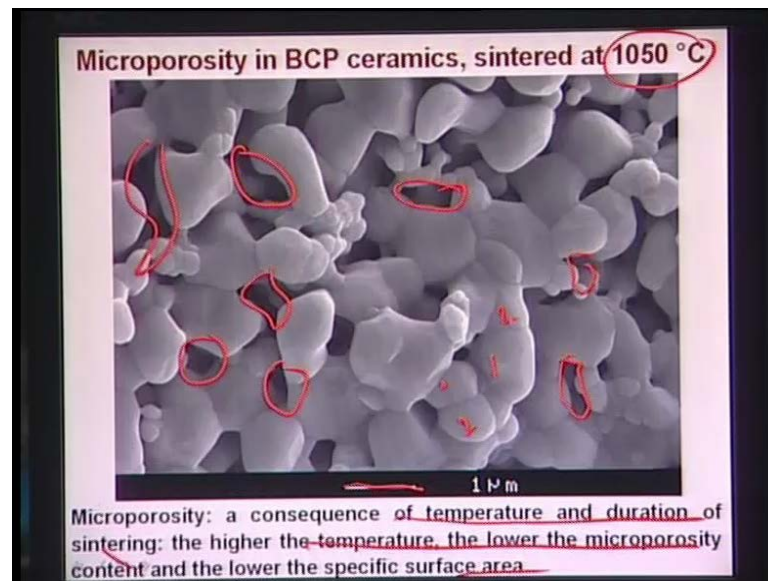
So, therefore, it will have a bimodal grain size distribution. So, number of coarse, grains and there are number of solid few small grains such bimodal grain size distribution is not that evident in this particular microstructure. However, here there are some bimodal grains are formed interesting things that you observe here that in this bimodal coarse grains they have some kind of porosity and which are really coarse pores, which are present at inside the grain.

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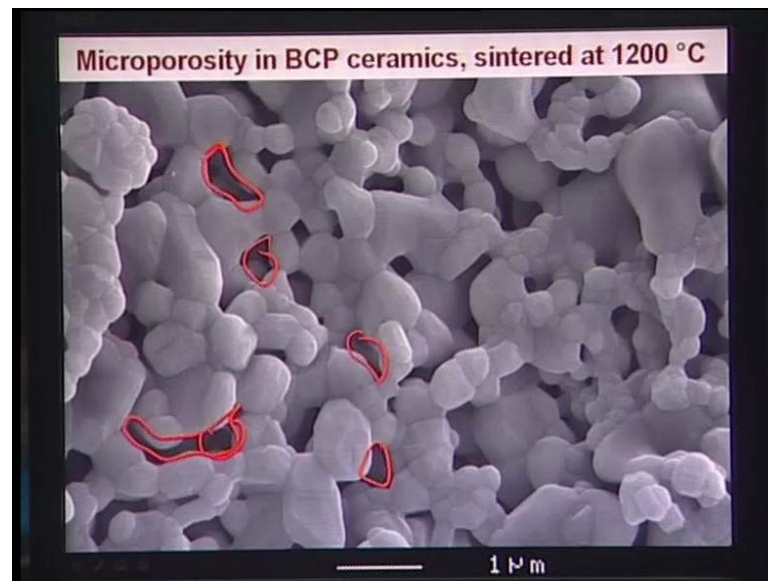
So, these actually shows that although it is ninety nine point more than ninety nine percent theoretical residue they are still some pores, which are left to be sinter or sinter to be closed. One of the material that has been recently attracted attention is the B C P, B C P is the biphasic calcium phosphate materials and biphasic calcium phosphate means, it has a mixture of Tricalcium Phosphate as well as the Hydroxyapatite. And Tricalcium Phosphate and Hydroxyapatite these mixture, when they sinter after the sintering what you can see you it leads to a very coarse porosity. Now, if you look at the microstructure this is a hundred micron. So, they may be a three hundred micron or this may be a two hundred micron pores these are commonly of that in this biphasic calcium phosphate materials.

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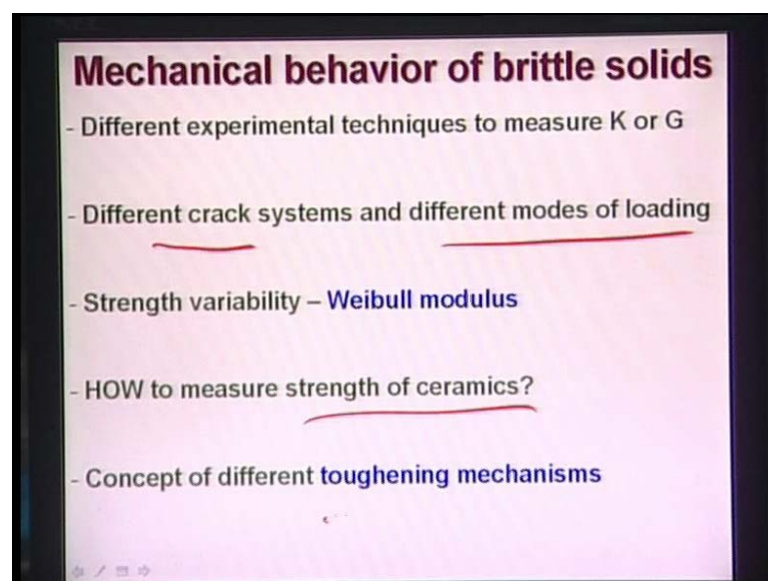
Also it has a microporosity in this biphasic calcium phosphate ceramics, which are sintered at thousand fifty degree celsius and this microporous materials it is a consequence of temperature and duration of sintering. So, higher the temperature lower is the microporosity that is very evident from your basics of sintering, what you observe here, this is one micron size. And sometimes this pores they may not be inter connected and they may not be very coarse. And the size of the pores is somewhat between one micron to five micron around that range and they are most of the cases that two neighboring grains they are joined together at various places.

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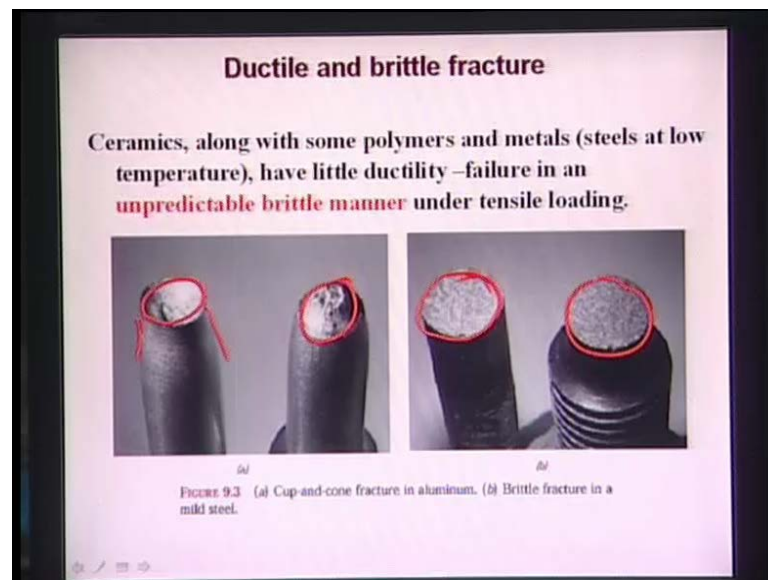
This is more clear picture of the microporous B C P ceramics, which are sintered at even **thousand** twelve hundred degree celsius. So, volume passion of the porosity in this particular case, should be less than, when it is sintered at thousand fifty degree Celsius. And here, you can see that these are the porosity and there is the long channel of pores here and these are the porosity here and they have different places. Coming to the mechanical behavior of brittle materials like ceramics, first I will show you that how you can measure the stress intensity factor or fracture toughness of this ceramic materials.

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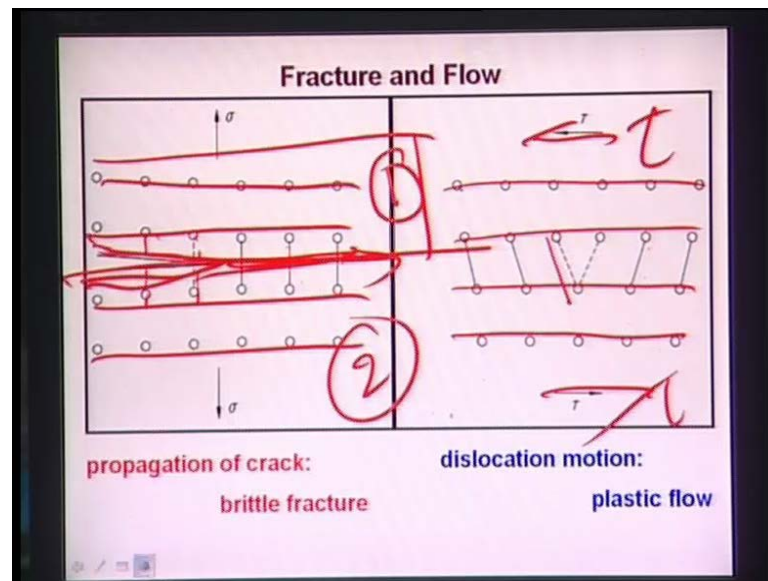
For other different crack systems and different modes of loading in these materials and why, the strength is variable in nature in case of ceramics. And how to measure strength of ceramics and what are the different concepts of toughening mechanism. Now, first let us understand, what is meant by ductile fracture and what is meant by brittle fracture?

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Ductile fracture means, that prior to the fracture material undergoes extensive deformation and that has been shown here and it is typically cup and cone type of fracture. Brittle fracture means, that the material is fracture to two completely two surfaces without much deformation prior to the fracture.

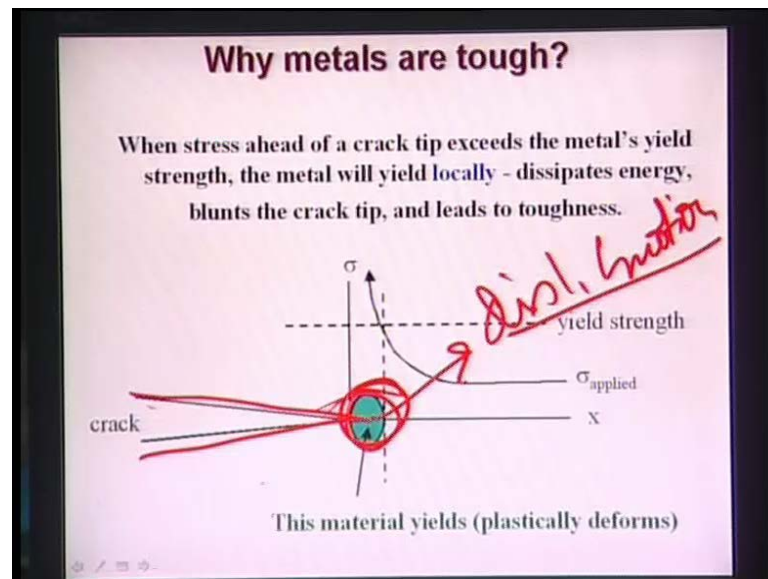
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Now, this brittle fracture takes place in a very unpredictable brittle manner. Now, what is the difference between fracture and plastic flow? Now you have this atomic plane here now, because of the crack propagation crack is nothing but the region of the microstructure, which is essentially from by the breakage of the inter atomic bonds. So, this is the inter atomic bonds here, this is the inter atomic bonds here and in both the cases inter atomic bonds have broken now, if this cracks will propagate further then subsequently all the inter atomic bonds will be broken. And then entire material will be simply made into two half this is part one and this will be part two and that is taking place under the action of the tensile force.

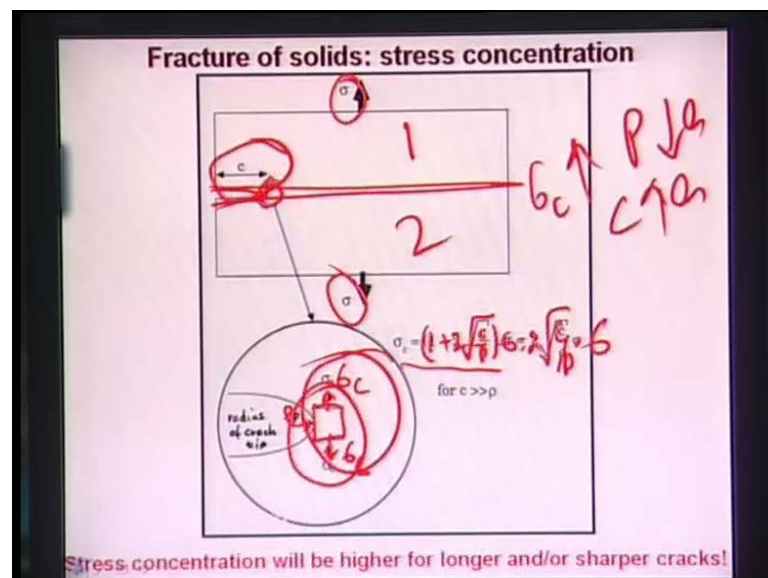
Now, this is called the fracture now what will happen, when that the plastic flow of the materials? Plastic flow means, you have a dislocation in this fracture and this dislocations are present in varying number. Now, when you apply the shear stress tau here is tau shear stress then subsequently all the interactive bonds are shear they are broken and remain (they are broken and remain).

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So, essentially the dislocation motion will take place and why metals are tough? Metals are tough, because ahead of the crack tip in these region you have the material they yields and they are plastically deforms and these region is actually the dislocation motion which takes place.

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This is the yielded region. Now, another region that is why fracture takes place in brittle solids more easily than the fracture takes place in metals. Now, in the brittle solid let us take an example of the rectangular block, which as a h crack. And in this h crack region

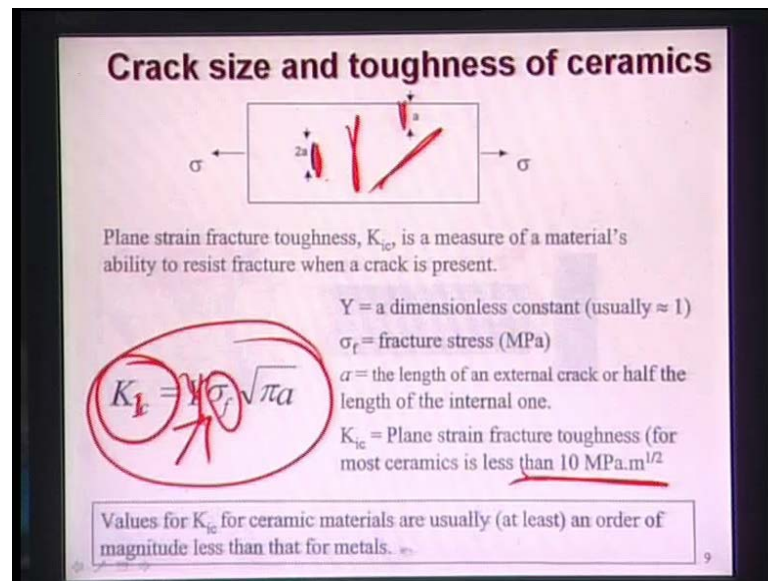
ahead of the h crack you have the region, where the material any volume element let say this is a volume element, this volume element will experience a stress, which is σ_c . And this σ_c stress will be much larger than you are actually applying externally, which is a nominal stress σ . Then, how larger it can be how it can be mathematically described the σ_c would be $1 + 2\sqrt{c/\rho}$ into σ , what it means? This means that it can be approximated as $2\sqrt{c/\rho}$ multiplied by σ .

So, what is c ? c is the half crack length here and what is ρ ? ρ is the radius of curvature. Now, you think of the situation, if a crack they look like this and if c is larger that means, this length increases and ρ is smaller, ρ smaller means, it is sharper and sharper crack. And if it is a sharper and sharper crack then ρ is less means σ_c will increase, because σ_c will increase if ρ decreases or c increases. So, as I give you showing you the example that, if you consider this is a crack phase.

Now, if crack length increases that means, c increases, c increases means σ_c will increase and if crack becomes sharper that means, radius of curvature also decreases and also then that σ_c will increase. So, essentially what you see here, that with increase at in so, you do not need to change the external stress at a given stress. When σ is constant by changing the length of the crack or by reducing the radius of curvature of the crack you can experience more amount of stress at this particular localized area. Now, if this stress is much larger than, the inter atomic bond strength, then what will happen in bonds will be rupture. And if the bonds are rupture or bonds are broken then, this cracks will completely go through the material leading to the fracture of the two surfaces and this is one and this is two.

So, that is how this brittle fracture they takes place in the materials like ceramics. Now, the question is these kind of things also happens in metals that why metals they do not fracture so easily like ceramic? Answer is that at this growing crack tip area there is dislocation motion and that dislocation motion leads to the yielding of the material yielding means that means material will be plastically deforming. But in the ceramic that plastic deformation is not possible and as a result ceramics can be easily fracture into two pieces by simply the crack propagation. Now, from these examples previous examples, it must be clear to you it is not the external stress alone which will be responsible only for the fracture of the material.

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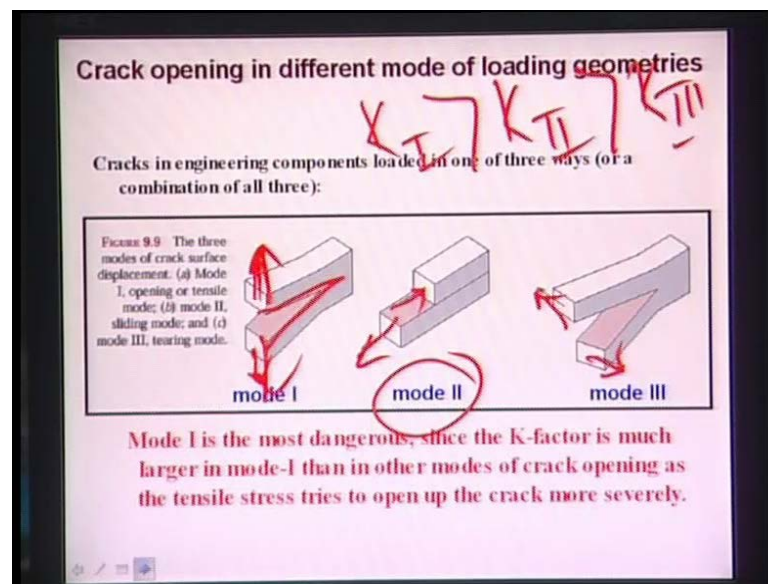
It is the external stress coupled with the crack length both will contribute to the fracture of the ceramic materials. Therefore, a parameter, which is known as K_{Ic} that is the critical stress intensity factor under mode one loading has been defined and this definition is as follows K_{Ic} is equal to $Y \sigma_f \sqrt{\pi a}$. And what is a ? a is the half crack length, if the crack are present within the volume of the material or inside the material then a is the half crack length. Now, if the cracks, which are present at the surface then it is called then you have to take the full value of the crack. So, for surface crack the a is the full crack length, if it is the in the within the volume of the material then a is the half of the total crack length.

Now, if it is cooled in tension then what will happen, K_{Ic} actually increases and this K_{Ic} is the material property. So, once this K_{Ic} is fixed; that means, it is like that, if your strength is fixed and strength is nothing but maximum load divided by the cross sectional area. Now, if your strength is fixed your cross sectional area of the specimen is fixed then you can find out, what is the maximum load the material can react without fracture. Similarly, it to come to the description of the fracture toughness, if your fracture toughness value is fixed let say $10 \text{ MPa}\cdot\text{m}^{1/2}$ and if I tell you this material has a fracture strength of certain MPa let say 100 and 200 MPa.

Then you can immediately find out, what is the minimum crack length or what is the maximum crack length that this material **can be tolerate**, can tolerate without going to

fracture from this particular expression. Now, the question is that what does Y signify? Now, Y is the constant which depends on the mode of loading like how you are loading whether it is a uniaxial tension, whether it is a biaxial tension and so on. At the same time Y depends on what is the orientation of the crack? Whether the crack is oriented at an angle to the loading axis, whether crack is oriented transverse to the loading axis all those things that will contribute to the value of Y .

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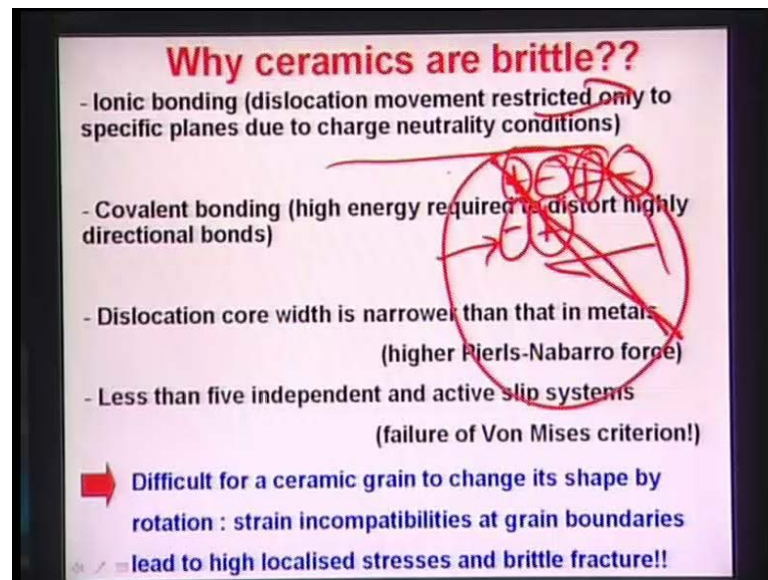


Now, as I said that K_{Ic} essentially means, that is the critical stress intensity factor under mode one loading then there should be mode two and mode three. Now, the question is that how this three different modes they are characterized by that term. Now, this particular slide tells you that there are mode one loading means that is the typical pooled tensile mode opening. So, this is the crack and it is pooled intension now cracks will grow fast and that leads to fracture, mode two loading means, it is a shear type of loading, mode three loading means it is a tearing type of loading.

So, mode one, mode two, mode three most dangerous mode is mode one. Therefore, K_1 is greater than K_2 greater than K_3 , what I am saying is that stress intensity factor under mode one is always greater then mode two gets stress intensity factor or mode three stress **stress** intensity factor. Therefore, if you want to really understand that, what is the maximum fracture toughness that a material can have then, you can find out that only

mode one loading and that is why people always are interested to find out that what is mode one loading.

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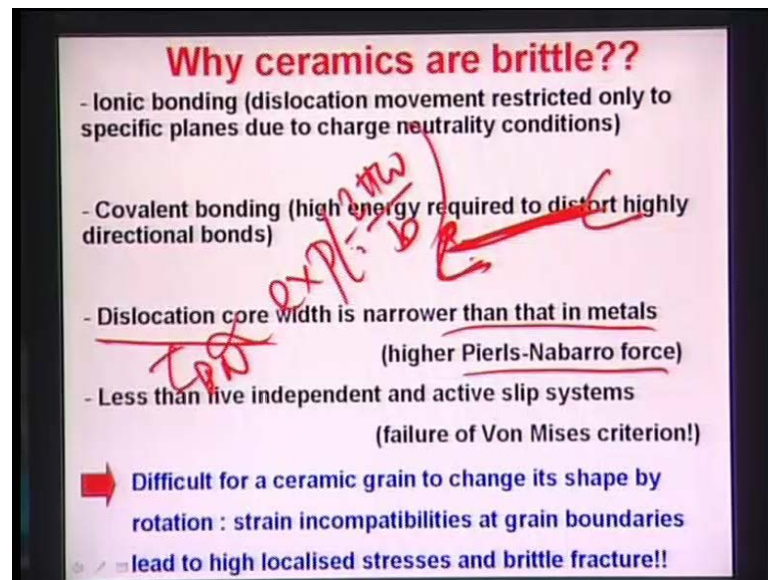


Now, question is that, why ceramics are brittle? Now, ceramics are ionic bonding as I said that ceramics have ionic bonding and covalent bonding. Now, ionic bonding means that distribution movement only can take place on certain specific angles, because you have the positive ion cation you have the negative ion anion, positive ion cation you have the negative ion. Now, one anion will be placed at the just below the positive ion and one cation will be placed just below the negative ion. Now, if you simply stress them apply the shear stress what will happen, the second row this anion will be displaced by one moment then what will happen, this anion will be just below the second anion and that is not possible. Because two anions cannot touch each other do you understand, what I am saying?

So, therefore, this kind of dislocation movement simply is not possible in the ionic solid. But how, this ionic solids can then dislocation will move, if the dislocation can move at a plane at an angle forty five degree to the stress at the then the dislocation movement is possible. Because then this positive cation will displace another positive cation and this will displace another positive cation. So, the total neighborhood in this ionic arrangement will not change. So, from the consideration of the basic ionic arrangement you can

immediately notice that dislocation movement is not easy in ionic salts so, that is number one.

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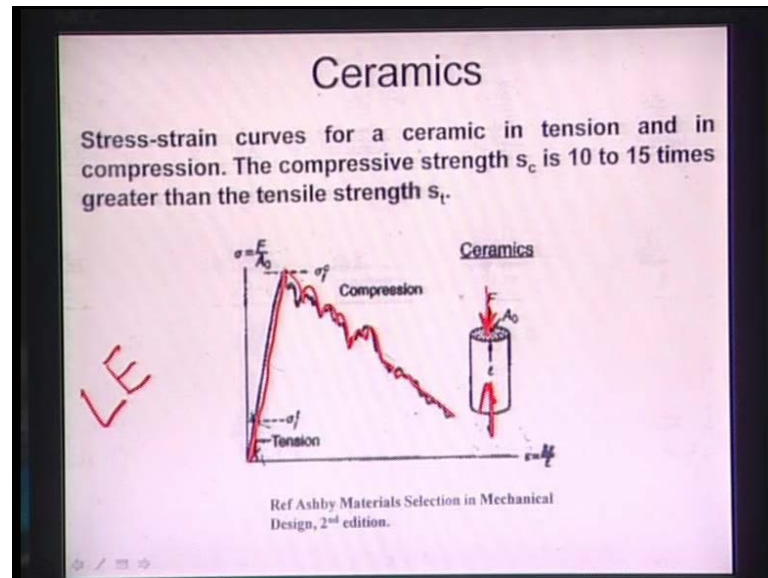


Number two is that covalent bonding and in this covalent bonding what will happen, that these two bonds let say it is a carbon bond and two carbon bonds are directionally they have a very directional type of bond. And you require really large amount of energy to break this directional bonding and therefore, the ceramic they have a much they are really strong and they do not have this good fracture toughness. Third one is that dislocation core width in ceramics are much more narrower than the solids and the dislocation core width means, how it is related to τ_{PN} . τ_{PN} is the pierls-nabarro force and it is related to some exponential minus 2 by w by b whereas, w is the core weight and b is the $(\)$ vector.

Now, if it is proportional to the exponential minus 2 ϕw by t and if the core weight is small then what will happen, since it is exponential minus so that will increase. So, the τ_{PN} value will increase and then in either τ_{PN} value will increase that means, you have to really apply large pierls-nabarro stress to move the dislocations in the ceramics and that is why ceramics are also brittle. Fourth point is that you have less than five independent and active slip system. Slip system means, it is the combination of slip direction and slip plane. Now, if any material, which has the less than five independent slip systems then that material as per the Von Mises criteria they are not ductile at all.

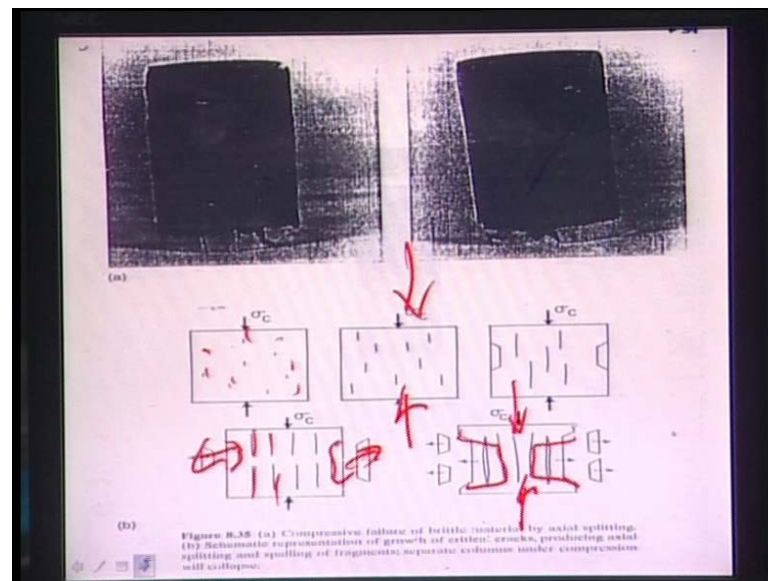
And that is the result that for a given ceramic grain it is very difficult to change its shape by rotation and that leads to the strain incompatibilities leading to fracture of the material.

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How does the ceramic behave in compression? Now, compression means, you are actually pushing at the ceramics from two ends. So, tension you have a very small fracture strength. So, it is straight to fracture that is why, it is called linear elasticity or linear elastic solid, because ceramics they do not have any non-linear elasticity. In case of compression it has a much larger strength and this strength is eight times than the strength in tension. And this compression, if you notice that each time the ceramics break during compression it will be reflected in kind of some jags in the compression stress-strain curve.

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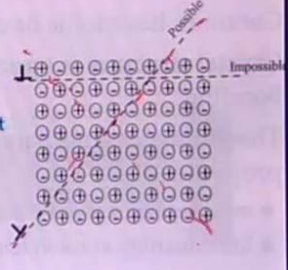
And that is what is explained here now, if there are multiply cracks in the ceramics, because it is a brittle material, when you are pushing compressive forces from two ends this cracks will increase in size **right**. And if certain point this cracks will lead to the squalling of the material from both the ends leading to the fracture. Now, each time this squalling occur that leads to certain jerk in this compressive torque. After sometime what will happen, that at certain point of time this amount of the material that will remain to bear the stress that will be very less and entire material will be shuttered into pieces. And that piece, if reflected in this compressive stress-strain behavior of this material.

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Dislocations In Ionic Solids

- Ionic structures are usually fairly close packed
- Slip direction and slip plane are constrained by charge e.g. cannot bring like charged ions in contact
- Dislocation motion is possible but difficult because slip is not on the most close packed planes
- Often only a limited number of slip systems due to low symmetry of crystal structures
 - need 5 for full plasticity in polycrystals
- Dislocation motion can be easier at high temperatures
 - easier flow on "normal" slip systems, new systems may begin to operate.

Introduction to Ceramics: 3: Bonding, structure and strength



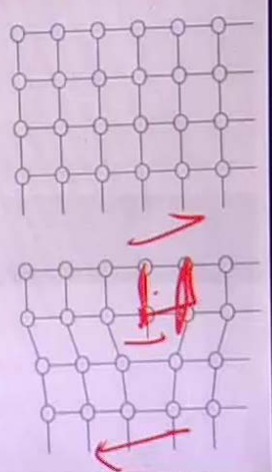
The diagram illustrates a 2D ionic crystal lattice with alternating positive (+) and negative (-) ions. A dislocation line is shown as a vertical step. Two potential slip directions are indicated by red arrows. One direction, labeled 'Possible', shows the dislocation moving by shifting ions such that no like-charged ions are brought into contact. The other direction, labeled 'Impossible', shows a path where like-charged ions would be forced into contact, which is energetically unfavorable.

This is what I have been telling you, that you know ceramics they can only the dislocation can only takes place at the forty five degree angle not in other angle. And this shows the covalent bonding in case of covalent bonding, if we have a dislocations.

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Dislocations In Covalent Solids

- The rigid bond network in covalent solids is very resistant to deformation
- Dislocations have very high energies
- Dislocation motion is difficult as bonds must be broken and remade, and bond angle distorted.
- Very low dislocation mobilities - except at very high temperatures ($> 0.5 T_m$ or higher)



The diagram shows a 2D covalent crystal lattice where atoms are connected by a network of strong, directional bonds. A dislocation is represented by a line of atoms with a missing bond. Red arrows indicate the movement of the dislocation, which requires the breaking and subsequent reforming of covalent bonds and the distortion of bond angles. This process is shown to be highly resistant to deformation.

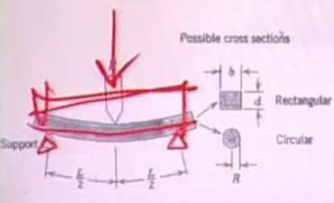
Now, each time the dislocation has to move on the application of the shear stress this bonds has to be broken and this review. And this bond breaking and remaking it is not very easy in case of ceramics and that is why coherent ceramics also are very weak in tension.

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Strength measurement for brittle solids

- Recall in the case of metals, mechanical properties were determined from tensile tests, in which a stress-strain curve is generated.
- Ceramics are not normally tested in tension because:
 - it is difficult to machine to the required geometry
 - it is difficult to grip brittle materials without inducing fracture
 - ceramics typically fail after only $\sim 0.1\%$ strain

For these reasons, the mechanical properties are determined using a different approach, the three point bend test:



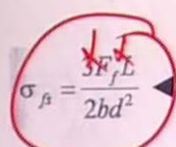
- specimen geometry is circular or rectangular cross section
- during the test, the top surface is under compression while the bottom surface is under tension
- maximum tensile stress occurs on the bottom surface, just below the top loading point

Now, how you can measure the strength in ceramics now, strength traditionally for metals you can measure it by tensile force. Now, tensile specimen for ceramics is very difficult to make. So, what you do? You can make the flexure specimen and you can put two rolls on the flexure you can **you can** place the samples and this samples you can break it by pull it by pushing it from one end. And when you make this tension sample you put it on the two support **(())** from the top roll you can place a force P and according to the equilibrium of forces these two support rolls will carry the load P by 2 **P by 2** . And then this is your tensile phase, and this is your compression phase. And then fracture will take place from the tensile phase and then cracks will be propagating from the tensile phase to the compression phase leading to the fracture of the material.

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Strength measurement for ceramics

The stress at fracture, σ_f , (flexural strength, modulus of rupture, fracture strength, or bend strength) is given by:


$$\sigma_f = \frac{3F_f L}{2bd^2}$$

Or

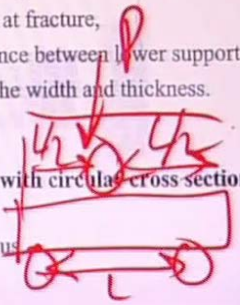
$$\sigma_f = \frac{F_f L}{\pi R^3}$$

for samples with rectangular cross sections, where,

F_f is the load at fracture,
 L is the distance between lower supports,
 b and d are the width and thickness.

for samples with circular cross sections, where,

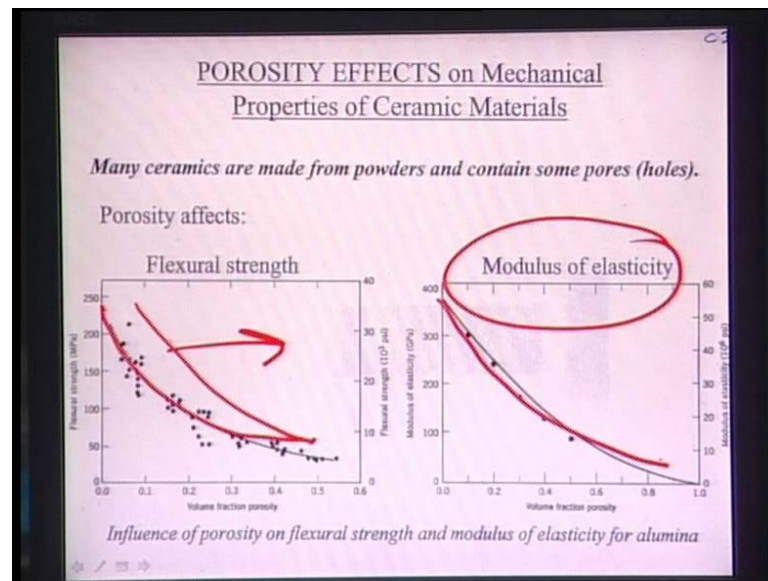
R is the radius.



Now, that how this three point flexural strength that can be measured. Now, three point flexural strength that is measured by three times multiplied by force. Multiplied by span length and these are the 2 b and d are the width and the thickness directions. So, essentially what you mean by that is roll is that this distance between two support rolling is called span length that is L you put a top roll and you put a pore c by 3. Now, this length is your L by 2 and this length also is your L by 2. So, the top roll is placed exactly at the center of the span length, and then your other things is that this is your height age and you have the other dimension **right**. In this rectangular cross section sample so that dimension is your b.

So, you have the width, you have the height, you have the span length everything has been there in this strength curve. So, you measure that what is the load at which the fracture takes place and then you know the geometry of the sample from that you can calculate immediately what is the flexural strength. Flexure means, bending. So, this strength essentially measures that what is the maximum strength that a ceramic can carry, what is the maximum stress ceramic can carry without failure under bending. And bending is one of the mechanism for the bone fracture also.

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So, whenever, you put the ceramic material it is important that you determine that, what is the strength in bending. Now, I have spent quite some time on describing the sintering mechanisms and trying to tell you that why porosity needs to be removed by adopting a particular sintering mechanism. Now, the reason why the porosity removal is important you can realize now from this particular two graphs that is how the strength flexural strength will decrease with increasing the porosity. So, as we increase the porosity in this direction your flexural strength also goes down systematically. Similarly, your modulus of elasticity also goes down systematically as you increase the porosity.

So, if you have a porous ceramic that will have a much lower elastic modulus much lower strength value that is the reason you remember cortical bone and cancellous bone. Cortical bone is a much more compact shape less porosity. So, it has a much better strength, much better elastic modulus. Cancellous bone is a much porous material much spongy bone. So, that is why you have a poor elastic modulus and poor strength value. So, for a given ceramic material whenever you are talking about macro porous ceramic, micro porous ceramic the thing that you need to bear in mind that in this kind of porous ceramic your strength that elastic modulus will be very low. So, I think I will stop here in the next class, I will teach more about the ceramics mechanical properties.