Introduction to Biomaterials
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Lecture No. #19
Processing of Bioceramics

In this lecture, we will learn about processing of bioceramics, because in earlier lectures we have seen what kind ceramics do exists what what are the natures in terms of their inertness, bioactivity, bio re-absorptionness. So in this particular lecture, we will learn about the processing of bioceramics.

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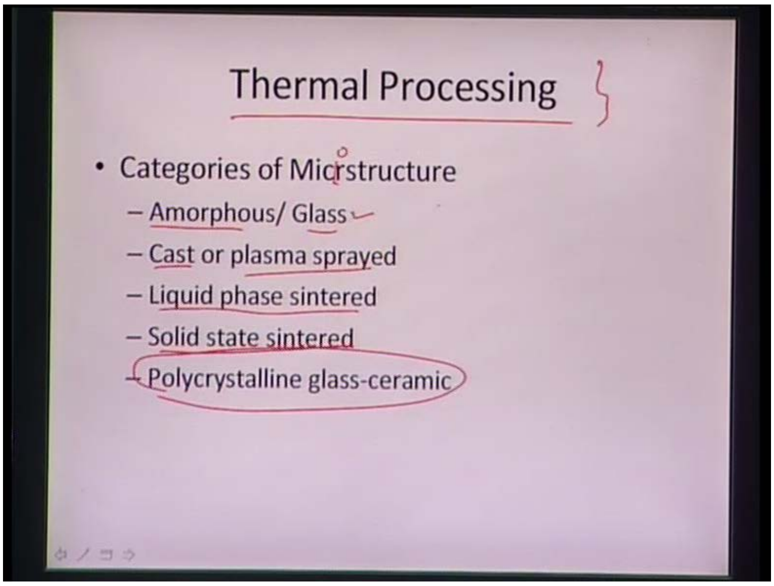

Thermal Processing

- Categories of Microstructure
  - Amorphous/ Glass
  - Cast or plasma sprayed
  - Liquid phase sintered
  - Solid state sintered
  - Polycrystalline glass-ceramic

First is thermal processing, so in thermal processing they are conduct many kind of microstructures which we can really get, so we can see we can either achieve amorphous or glassy kind of a microstructure or it can also be cast or plasma sprayed structure, we can also do this processing via liquid phase sintering, we can also perform solid state sintering. And we can also achieve some times polycrystalline glass ceramics, it can be again glass and glass, and it can be glass to ceramic kind of a microstructure.

So, we can see that via thermal process we can attain different kinds of microstructures, it can be it can range from being structure being very amorphous or glassy, it can also be polycrystalline which can be achieved by a casting or even by plasma sprayed structure, it can also be liquid phase sintered in which we can attain really very high density of materials or it can also be solid state sintered, wherein we do not allow one material to undergo any a liquid phase transition or does not allow to go to liquid phase, and then we attain the we attain the sintering via this particle contract. And then we can also get polycrystalline glass ceramic via certain processing techniques.

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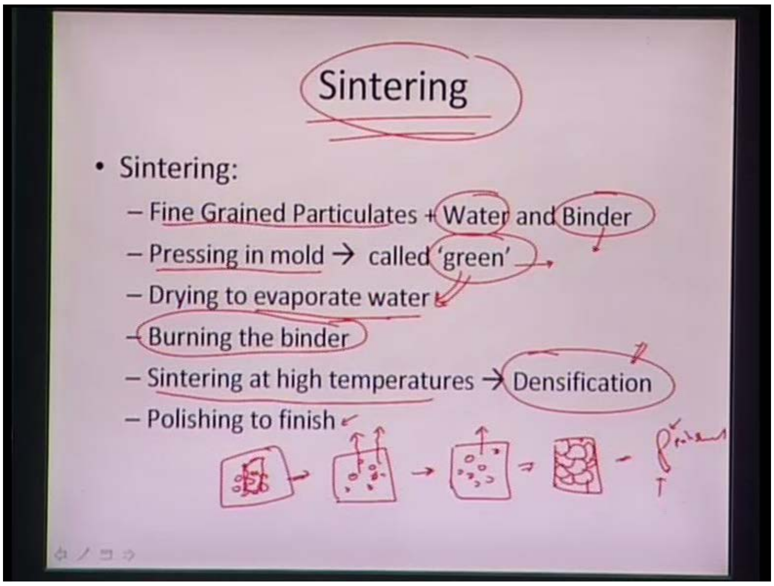

Sintering

- Sintering:
  - Fine Grained Particulates + Water and Binder
  - Pressing in mold → called 'green'
  - Drying to evaporate water
  - Burning the binder
  - Sintering at high temperatures → Densification
  - Polishing to finish

So, first technique of thermal processing is sintering. In sintering what what we are doing? We take fine grained particulates and then we add some water and some binder to it. So, that all the particles which are out there they can get bound together and then we press them in the mold, after pressing we get approximately near net a kind of a shape and then it it is called as green. So, green is attained once we take the takeover particulate material we add water, we add binder and then we press it to approximate near net shape and that is called a green, again it will have certain porosity in it.

And then what we do? We will take this particular green and we heat treated so, that we first, the first step is that we evaporate water from here, so and so evaporating water then we have something still remaining, there is some binder also remaining therein. So, we have a kind of a green green which is called which is being pressed a component which is again we we will also have a certain porosity into it. So, first step we are trying to evaporate the water form there and then we heat it to further higher temperature and that basically burns the binder.

So, now the now our our overall billet or whatever the component is it is free from water, it is free from binder and then we now sinter it very high temperatures, which leads to the densification and once we have attained the particular densified composite, we can polish it to the final requirements.

So, in this particular case of sintering we first step fine granulates, we add certain binder and water so that it can basically bring out all the particulates together, because of capillarity and then first step is that we remove the water, so we will have all the particulates and then water will basically get evaporated and then in the next step we will burn the binder which is still holding the particle. So it is some sort of organic binder and then we burn of the binder which which can burn out at still low temperatures, order of 300 to 500 degree centigrade and then we basically center it at very high temperatures which can be exceeding 0.5 times the melting temperature. So, in that particular case we now start seeing the all the crystallites which are belong to a biocomposite, bioceramics they tend to start sintering together.

And then we can achieve a more densified structure and then once we have a particular components say if we have a particular component it can be polished so, that we can achieve a near net shape with a good surface finish. So, these are all the processing which are required in the sintering process, that first of all we have particulate, we add water, we add binder. So, that now we have a muchwe have particulate which which have basically a kind of accumulate together, because of capillarity and then we remove the we basic then compacted to produce a green, then we remove the water from it and dehydrated, then we we burn of the binder at certain temperature.

Then we basically sinter it at much high temperature exceeding 0.5 times the melting temperature then when after we have consolidated, we have densified it we will basically polish it to or finishing finish size and in second case, we can also achieve something called porous ceramics.

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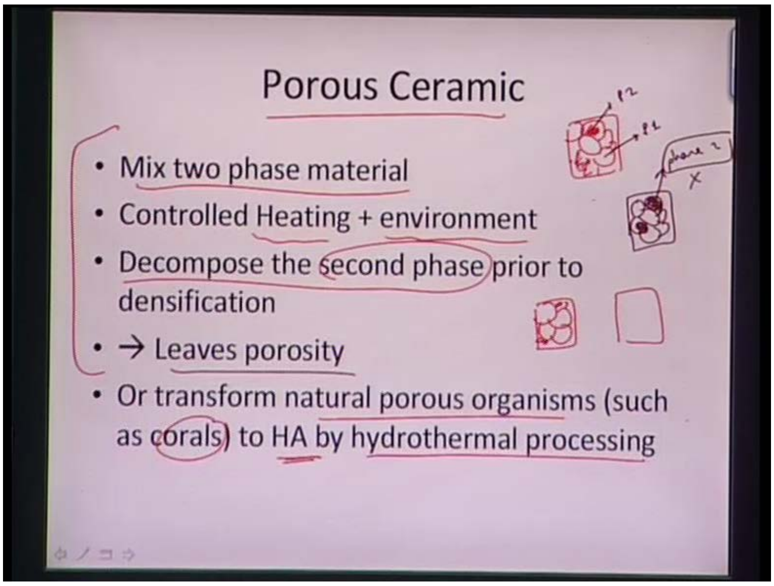

Porous Ceramic

- Mix two phase material
- Controlled Heating + environment
- Decompose the second phase prior to densification
- → Leaves porosity
- Or transform natural porous organisms (such as corals) to HA by hydrothermal processing

And in porous ceramics how do we get it first of all we will mix two phase material and we provide a controlled heating and with a control environment. So, we have initially two phases: one phase and second phase out here. So, we will have one phase, we have second phase which is basically being embedded into the two phase material.

And we provide control heating with control environment so, what happens we allow the decomposition of the second phase before densification. So, what we are doing is we are basically removing the one of the one of the components so, what we are doing like this more like this, that we take a particular component in second case what we are doing we basically burn of the second phase, we remain with only first phase material whereas, second second phase material has been decomposed. So, it will leave of certain porosity at its place. So, this was phase 2 which is now basically burned off.

So this was phase 2, this is phase 1 and now the phase 2 is basically being removed or it decomposed so, we have overall composite with certain porosity in it. So, that that is what that leaves the porosity behind or we can also do we can have phase 1 and we can have phase 2, but in in case of this in this particular case we can let the second phase transform to hydroxyapatite. So, what we what we are doing we are taking some natural porous organisms such as which can be coral, it already has certain porosity into it.

So, corals will have definite some porosity inside them which can it can vary from size or to it can vary from the size of the porosity to their connectivity, but they have very

very good porosity interconnect porosity which certain pore size and the our our objective in the second case is that we convert that particular coral to certain hydroxyapatite by certain hydrothermal processing.

So it is we have we take particular calcium carbonate or any phase of calcium phosphate and then we make it react with water or certain chemicals so that that particular phase converts to hydroxyapatite and that will produce eventually a porous ceramics. So, here we are basically trying out two methodologies: In first case we are mixing two phase material and then overall what we are trying to do we are try with the control heating in the providing particular environment, we are letting one of the phases get decomposed and once since one of the phases get get decomposed, the second phase remains continuous and the phase one which was decomposed leaves porosity behind behind itself.

So, we are getting overall a control porosity which which equals to the amount of phase 1 which has present and then phase 2 forms the continuous network of the required implant so implant materials. So, that is what we are doing in first first case and in second case we can take a porous organism itself just which can be coral and then basically a hydrothermal process to hydroxyapatite to leave again a porous biocompatible material.

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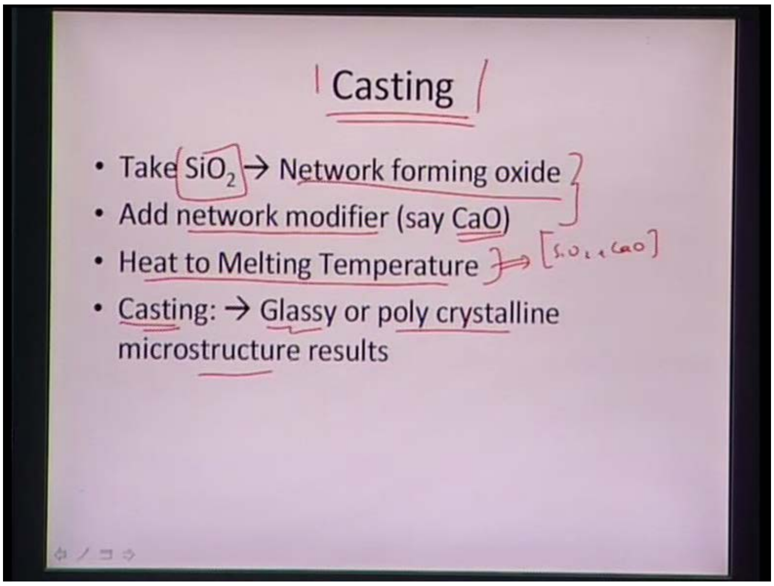

Casting

- Take SiO_2 → Network forming oxide
- Add network modifier (say CaO)
- Heat to Melting Temperature ⇒ [SiO_2 + CaO]
- Casting: → Glassy or poly crystalline microstructure results

And third process can also be casting, and in this particular case we can take silica which is S i O 2; and S i O 2 is the network forming oxide. So, silicon oxide it basically tends to form network whether itself, so it may not lead to a very all under the crystalline structure it will basically start forming networks.

So, network means it will just link on to the other silicon oxide and it will keep growing in that particular manner without any particular type of arrangement to it and what we can do we can add also, some some something network modifier which can basically associate itself to the network and get attach to it so that can be calcium oxide, so we will get a kind of mixture between the silicon oxide and the calcium oxide and in this process we heat them to the melting temperature. So, in this particular case we are heating them to melt melt temperature so, we get a kind of homogenous mixture which can be one one liquid or two liquid depending on range we are in and it will form a combination of S i O 2 plus calcium oxide and it will form certain liquid and we can cast it, to form a glassy or polycrystalline microstructure.

So, depending upon how we are casting it we can produce either totally amorphous structure which is totally glassy in nature or we can also induce some sort of a crystalline crystalline to it by by allowing certain nuclear to initiate before it really solidifies. So depending on how we are cooling it and what is the composition which is being involved out here, we can alter how the casting can result either amorphous structure or a totally crystalline structure. So, that is the overall strategy with the casting and again there is one more processfor deposit for deposition basically coatings and that is called plasma spraying.

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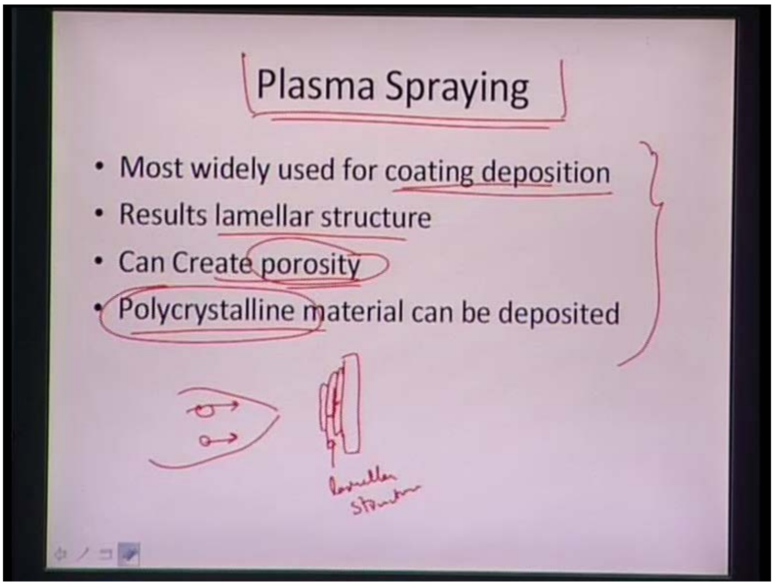

Plasma Spraying

- Most widely used for coating deposition
- Results lamellar structure
- Can Create porosity
- Polycrystalline material can be deposited

And plasma as we know as the four state of matter here in it is used utilizedto basically let the powder through it and it will melt it and it will accelerate the powder particles so, that they get imparted on to a substrate.

And it tends to form basically coatings and it is most widely used coating deposition technique for the depositing hydroxyapatite and it tends to develop some something called lamellar structure. So, we have powder which basically passes through some plasma clave and then this particles are accelerated to certain velocity so that they get they get emptied on to a substrate to forms splat and consecutive layers basically tend to form layers over it and this is called a splat structure or the lamellar structure.

And it can also create certain porosity into it, because all the lamellars which are which we find here they may not be interact homogenous chemically to one another they might be just mechanically integrated. So, it can also create porosity if we can defines certain way what is the overall initial powder particle size which we are trying to utilize or even the kind of kind of distance from the plasma plume to the substrate. So there is certain certain parameter which we can really control and play around to to render it a certain porosity on the coating material.

And again here we can also have polycrystalline material which can be deposited using plasma spraying. So, plasma spraying is (()) very important techniques which is most fairly used for producing coatings on to implant materials and it generate tends to results lamellar structure, it can also lead to producing some sort of a porosity on to the implant surface, because we can really control the powder size, we can control the heat basically via controlling the overall power which is being supplied to the plasma spraying unit and that will eventually control the overall melting of the powder particles and the and the impact of the powder particles on to the substrate will lead to the overall porosity in the microstructure.

So, in this particular manner again we can control the cooling rate. So the cooling is typically very fast and plasma spraying which is to the order of 10 the power of 6 kelvins per second. So with by controlling the cooling as well, we we can limit the solidification or we can ease the solidification by preheating it. So those all are the things we can play around in terms of rendering very dense structure or rendering a very porous structure, but ideally this plasma sprayed techniques are utilized for developing porous coatings for on the implants and those coatings can be either polycrystalline and they can even create porosity out here. So that is the overall strategy strategy behind using the plasma spraying for the coating deposition.

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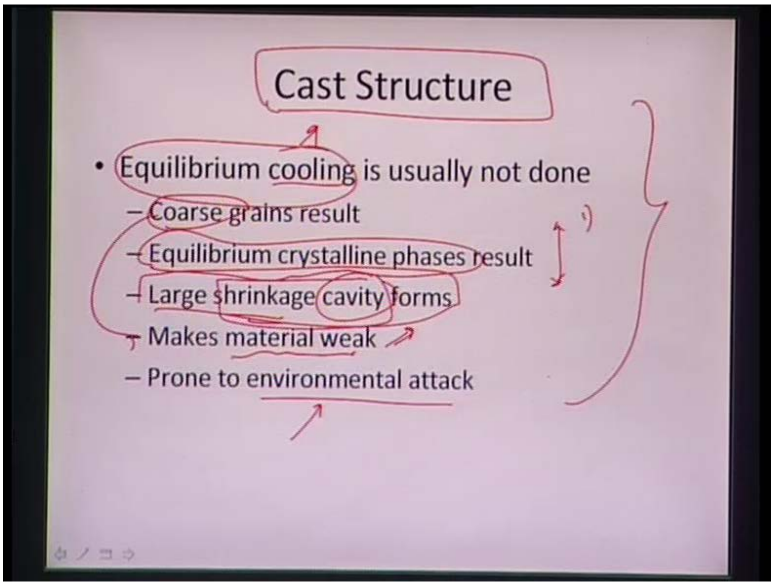

Cast Structure

- Equilibrium cooling is usually not done
  - Coarse grains result
  - Equilibrium crystalline phases result
  - Large shrinkage cavity forms
  - Makes material weak
  - Prone to environmental attack

As we had seen earlier that there is we can also provide some casting to get a particular shape and the problem is that the casting is once we are trying to cool the particular material in equilibrium, we get a very coarse material, the grains structure becomes very coarse, though we will get some equilibrium crystalline phases, but the problem will be it lead to large shrinkage cavity and once we have large shrinkage cavity once we have a very coarse grains it will make the material very weak.

And once the material is gone very weak, it will basically yield to the environmental attack. So, that is the problem with that is the reason we does not does not we do not want to really go with casting structure all the time, those can produce good good amount of we can really get a very good shape very good shape can be cast from it, but it the equilibrium cooling is not really preferable for the cast structures, because first of all it will have a very coarse grains, it will once we are heating it to very high temperatures and we letting it cool according to the phase diagrams so that the all the phases which are in equilibrium that tend to equilibrate, but that equilibration will lead to much more cautioning of the grain though we will get equilibrium phases which have been which which should be present out there, but it will holding it for such long time at such high temperatures will basically make the structure very coarse.

So once structure, microstructure is very coarse it will lead to very huge grains sizes and it will make the material very weak, because of because of all such relationship and again this particular cooling will allow the phase transitions to occur and also what will happen is, that it will yield out to a very it will provide a very large shrinkage cavity in the center, because once the material is cooling down it will has it has so basically assuring and that creates certain cavity in that cavity generally is not acceptable, because it will make the material very weak.

And again once those once we have very huge grains or once the material is very weak, it will obviously we prone to the environmental attack. So, those are the all the all are the limitations of the cast structure that first of all it will make the coarse grains very coarse which will eventually germinate out of the equilibrium cooling. Once we have very coarse grain it will lead to basically it will make the material very weak.

Casting can also induce shrinkage cavities and over all these things will make the material very prone for environmental attack. So, those are the problems with the cast structure as such

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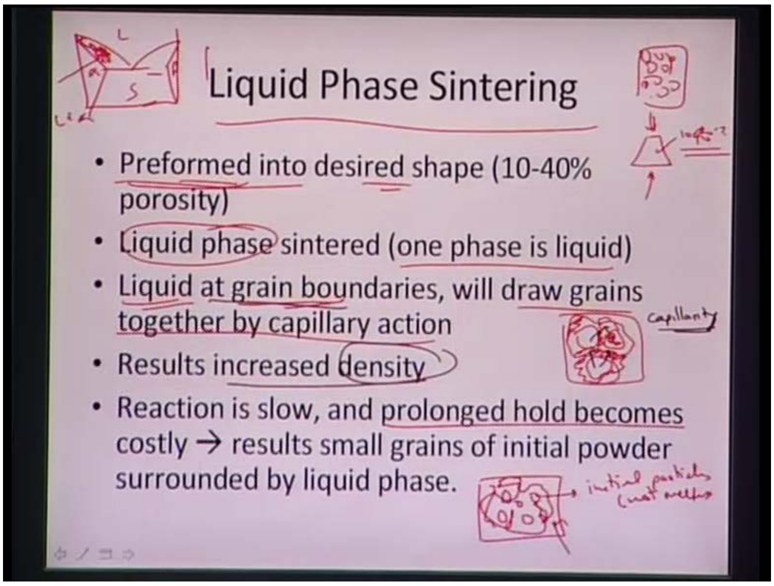

Liquid Phase Sintering

- Preformed into desired shape (10-40% porosity)
- Liquid phase sintered (one phase is liquid)
- Liquid at grain boundaries, will draw grains together by capillary action
- Results increased density
- Reaction is slow, and prolonged hold becomes costly → results small grains of initial powder surrounded by liquid phase.

So, solution to that aswe can go with something called liquid phase sintering and in the liquid phase sintering what we are doing here is, first of all we make a particular component and that component is a green and that is preformed into a desired shape. So, we take a particular a particular structure and then we preformed it to whatever kind of a shape in it say if we want to have certain kind of a shape, we basically preformed into certain shape.

While it retains around 10 to 40 percent of the porosity, so in this particular case we have first preforming it we are preforming it into desired shape. So, this is the desired shape and this will still have 10 to 40 percent of porosity in it and then we heated to certain temperature so that one phase remains liquid, so if we see go to a phase diagram if we have particular material and we see a phase diagram for a binary system then we will see in this one of the regions we have liquid, we have solid, we have alpha, we have beta, in this particular regime this particular regime we will have liquid plus alpha.

So, we we will take the material to that particular regime where we have at least one phase which is liquid and then we let it sinter. So, what is happening out here that we get all the particulates where one phase is liquid, that liquid will tend to at the grain boundaries and will draw to it will basically draw the grains together by capillary action. So we had say one grain, second grain, third grain like this and I do not think it will filled with certain liquid and since liquid is filled all all along a side it it will basically tend to bring all the grains together. So, this grain will try to go near to the other grains so it will more like this that we have we have one grain it will try to go towards the near second grain this grain will also try to come closer to it, this grain will try to come closer to it and this grain also will try to come to one and another.

So overall this effect arises, because of the capillarity action. Because of capillarity everything will tend to come closer and they will get basically consolidated and it will lead to increase density among in this structure so this is what is happening out here that it will lead increase density, because of the capillarity action, because liquid is present at the grain boundaries which will tend to draw the all the grains together and that will basically make the structure highly dense or it will increase the dense density out here.

So, but what what happens in the liquid phase sintering is that since reaction is little very slow, because in this particular case one phase is still solid so it has to undergo much diffusion and the prolong holding at very high temperatures that will basically lead that the overall structure because much more closer. So, in this particular case we have this particles which are still there so we will in this particular case we had small grains which are present initially and then one phase becomes more liquid, so we in the overall structure microstructure looks like that we have initial particles if we are not melted at all initial particles of one phase which are not melted they remain as such and again it all the structure now the all the particles that they are not enclosed in a liquid phase.

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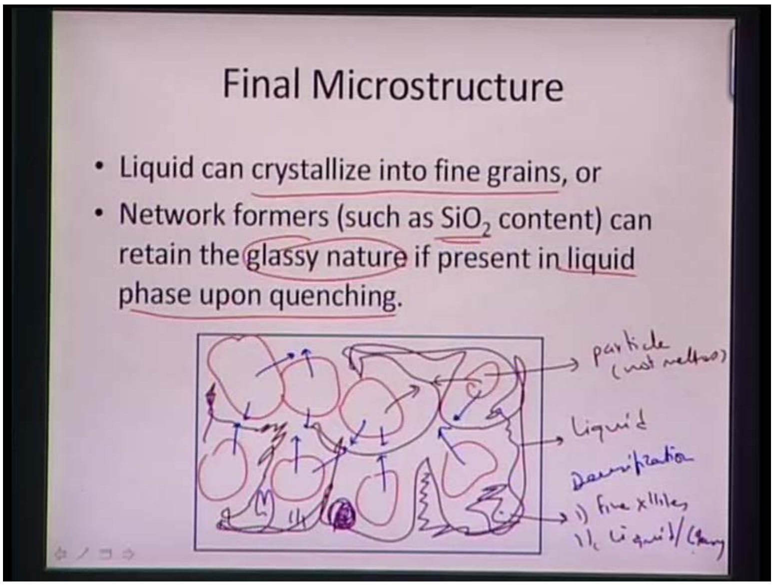

Final Microstructure

- Liquid can crystallize into fine grains, or
- Network formers (such as SiO_2 content) can retain the glassy nature if present in liquid phase upon quenching.

So, that is that is what is happening out here that everything is now enclose in a all these particles are now enclosed in a liquid phase. So liquid phase sintering we are first of all we are taking the particular material or the component in the desired shape which still has certain porosity, then we start the liquid phase sintering in which we are taking a material to to a temperature where we have at least one phase liquid. So, that liquid tends to draw all the grains nearby itself, because of the capillarity action and once we have all the grains we allow the cooling to happen and because of that overall structure looks like that we have all the smaller grains which were nothing but the initial particles which which did not melt at all, those are grain basically cover with liquid region.

And upon solidification, we see that kind of a microstructure which is kind of generated out here. So, what happens that now all the liquids which is surrounding the particles that can basically crystallized either into fine grains or it can also if in case we have some network formers which are present in the liquid regime and those network formers generally silica, they can retain the glassy nature.

So, we had liquid which are surrounding smaller finer particles and if have much more of network formers which are present in a liquid regime they can retain that particular structure, they can remain amorphous. So, it will retain the liquid as nature of itself and it can basically be again amorphous and that process can occur when the liquid phase is basically quenched.

So, we we see we see that the overall microstructure looks more like this, we have all the grains which are basically stated out here and there and then over that we have something all the liquid which is basically covering it, covering all the grains which are basically made the grains come much closer to one and another. So all this is basically liquid and all these are the particles or finer grains which were not melted and during the processing all the particles they all the grains they have tried to come closer to one and another.

So, in this particular case so we can see that all the particles all the grains they have tried to come closer to one and another as much as they could so, what is happening out here is that they have come as closer as possible. So, in this particular case it has result densification, so we achieve the densification by the capillarity action, because of the liquid as liquid which is surrounding the particles it has try to bring all the grains to one and another and what happens in the next stages that then happens that all those liquid is basically being surrounding this all those grains or the particles which are which are unmelted. We can start shrink crystallization even in this regime, in the liquid regimes or we can also see that the glassy nature or the liquid nature of this particular liquid remains as such.

So, from this liquid we can either get fine crystallites either we can get fine crystallites or we can have an again liquid or a glassy structure. So, that is what is happening in this liquids state sintering that we are first of all we are we are heating it to a temperature we have one of the phases liquid and then we are letting it cool and the depending on the cooling or a kind of a composition of the liquid phase, we can allow the crystals to either nucleate or we can also allow it to retain the liquid structure or the glassy structure at the room temperature.

So that is what the overall microstructure comes out to be that we have retention of the initial particles which were not melted or the grains which were not melted, which is again surrounded by glassy phase or again a very fine crystallite crystallite phase which basically (( )) from the liquid which was surrounding the all those particles and the next next methodology of sintering is solid state sintering.

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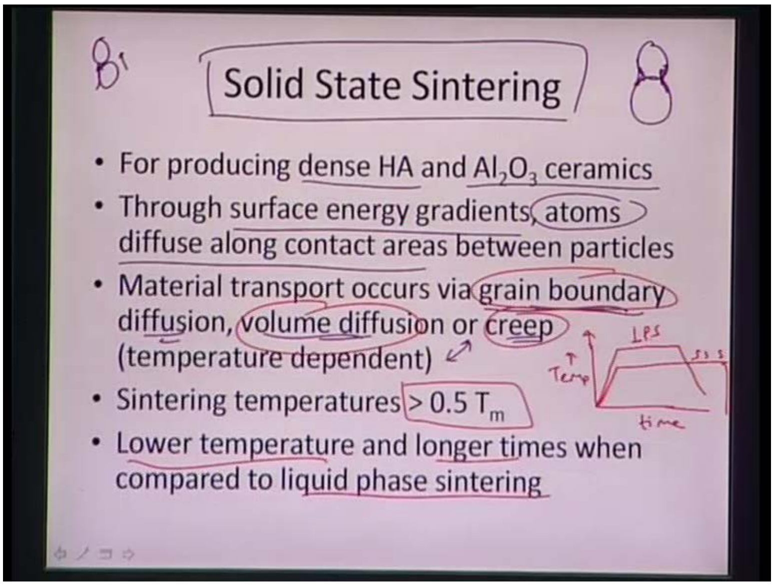

Solid State Sintering

- For producing dense HA and Al_2O_3 ceramics
- Through surface energy gradients, atoms diffuse along contact areas between particles
- Material transport occurs via grain boundary diffusion, volume diffusion or creep (temperature dependent)
- Sintering temperatures > 0.5 T_m
- Lower temperature and longer times when compared to liquid phase sintering

So, in this particular case we can it can be used utilize for producing very dense hydroxyapatite or aluminium oxide ceramics and basically it this solid state sintering happen, because of the surface energy gradients and in this particular case everything is in solid so atoms they are basically diffused along the contact areas which happen between the particles. So, we take certain particles and atomic diffusion along this particular regime on the surface as well as the latest along the along the latest it occurs, because of the surface energy gradients. So, they will tend to minimize this surface area so we will see first of all a kind of a necking which can occur between the two particles as the diffusion go goes along it high temperatures.

And solid state sintering may not allowing any phase to reach a liquid regime so, that holding temperature for solid state sintering are much lower than the liquid phase sintering. So, that is one of the difference between the solid state sintering and a liquid state sintering and this particular case we only see atomic diffusion which is happening to cause the densification and here in the material transport from one particle to another particle it occurs via grain boundary diffusion, it can also be volume diffusion or it can also be creep diffusion, depending on the a kind of temperature this particular material is undergoing. So, that is what the that is what the strategy out here is that depending on the temperature we can either achieve a grain boundary diffusion, it can also be volume diffusion or it can again be creep which can occur to move the material from one location to another location for the mass transport.

So, again here in that sintering temperatures are in excess of 0.5 times the melting temperature, but again here in the low temperatures and longer times are basically used when compare to the liquid state liquid phase sintering.

So if we have use the particular cycle in which we have liquid phase sintering the temperature usually very high, but in this particular case this is for liquid phase sintering, but for solid state sintering we can go to very low temperatures, but we can keep it for prolonged heating. So, we have solid state sintering which will progress like this so that is this is respect to time; this is respect to the temperature. So this is a kind of difference we will see in terms of liquid phase sintering L P S or the solid state sintering which is S SS so in this particular case we can make very dense structures, but we do not allow the any of the phase to basically become liquid and because of the surface energy energy gradients we can first of all allow a contact particle to particle contact it will start creating create a net and once we have the surface diffusion then the volume diffusion can also occur and depending on the temperature we can also have creep coming into the play for the overall mass transport of the material.

And sintering temperature general in the order of 0.5 T m more than 0.5 T m, but this temperatures are lesser than that of a liquid phase sintering, because depending on the phase diagram we are not allowing the structure to undergo undergo to form a liquid phase and in this particular case we are holding them for much lower temperatures, but for much longer times and when compare to that that of a liquid state sintered region. So one more difference which comes out eventually is, because if we have a liquid present in the material it will tend to draw the all the grains closer to itself, that will lead to much more densification as well. So, overall density is in the solid state sintering are much lower as come to that of a liquid phase sintering as well so that there are certain differences which can arise in the solid states sintering and the liquid phase sintering.

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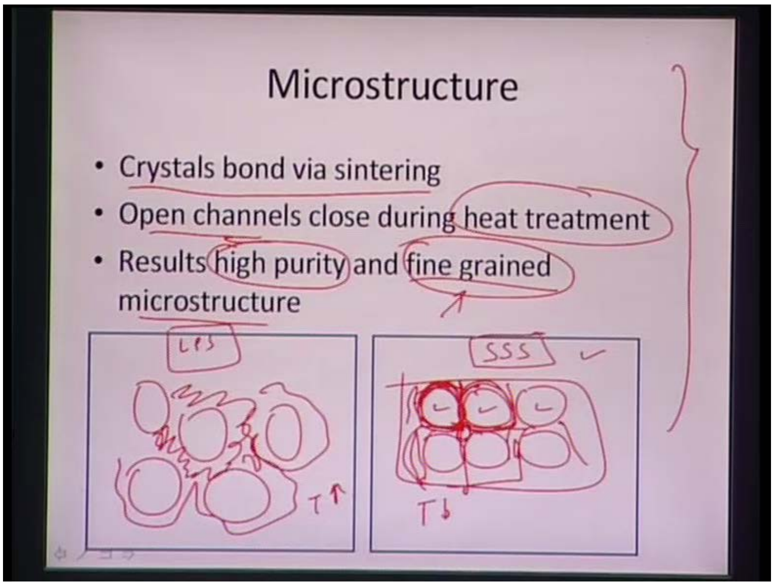

Microstructure

- Crystals bond via sintering
- Open channels close during heat treatment
- Results high purity and fine grained microstructure

So in this particular we see that the crystals they are bonded via sintering and it can also tend to close the channels which were open earlier during when a heat treatment is being given to it, but in this case we are holding therefore, much lower temperatures, that can lead to very fine grain microstructure and one more thing important here is it can also result high purity, because we are not allowing a solid to become liquid and since liquid have much more higher capability to to dissolve certain impurities into it and those impurities basically are now entrap into the into the material in case of liquid phase sintering.

But since we are not allowing any liquid to form, the material times to be much more pure than as compare to the liquid phase sintering, at the same time since the temperature is much lower we can also get very fine grain microstructure. So, in in case of liquid phase sintering we will see kind of a microstructure which is very very dense which is very very dense and it has entrapped liquid and between out here, but in the solid state sintering will see all the particles which are basically which have come together, because of the near contact difference in the surface energy and the contact between the particles. So, we will get a dense structure, but not as denser as asas liquid phase sinter region.

So, in this case case of solid state sintering we will see all the particles which have come closer and also they will have sort of a surface melting, because of those surface contours of the kind of curvature surface can melt to a certain extent, but not it will very marginal and then it will basically contact with the nearby particle and then volume diffusion and surface diffusion, because of those it will create the bond with the nearby a particles.

But it cannot eliminate all the porosity the solid state sintering, because we need very high pressures, at very high temperatures to eliminate that porosity. So, material as to deform the material as to yield to be able to result that kind of a densification, which is so easily possible in the liquid phase sinter region, because liquid for liquid is it is very easy for them to flow through the channel, through the porous to create that kind of a densification so liquid tend to take all the empty spaces directly and, but it becomes very difficult in case of solid state sintering.

So, that that is also difference between the macro structures of liquid phase sintered structure and the solid state sintered region, but assesses on the solid sinter material that tend to be much more purer and it tend to be much more fine grain, because the temperatures are very very low as compare to the liquid phase sintered sintered structures.

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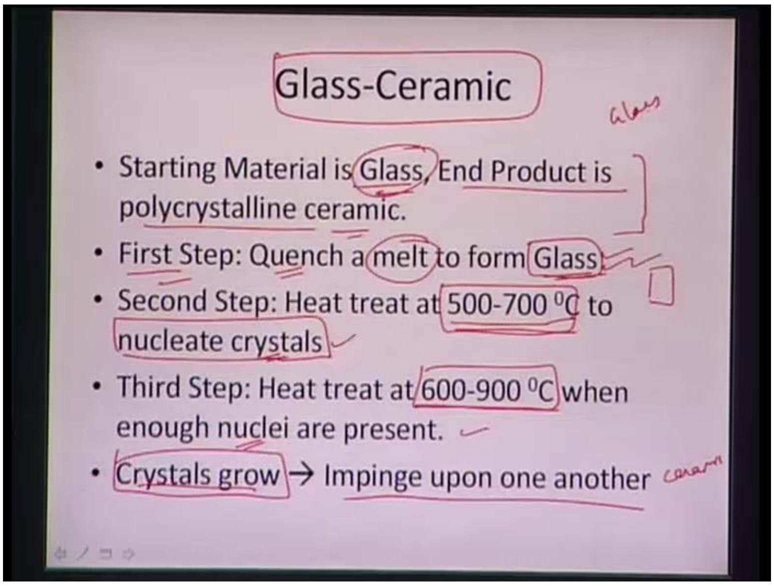

Glass-Ceramic

Glass

- Starting Material is Glass, End Product is polycrystalline ceramic.
- First Step: Quench a melt to form Glass
- Second Step: Heat treat at 500-700 ^{0}C to nucleate crystals
- Third Step: Heat treat at 600-900 ^{0}C when enough nuclei are present.
- Crystals grow → Impinge upon one another

ceramic

And also we can see that they can be some formation of glass ceramic. So, this type of material can form once we can have initial material which is glassy, but the end product which comes out is more of more or less ceramic phase. So, how we can produce that particular structure is that in the first step we make a total melt. Melt, it means we make it a glassy. So, first of all with taking the material to a high temperature then we are quenching it to form a glass. So, first step is that we form a glass and a second step becomes that we heat treat them at around 500 to 700 degree centigrade to nucleate certain crystals.

So, first step we make a glass, then we take it to a temperature where it can nucleates certain crystals, one said as a initial some number of crystals then we can basically heated at much higher temperature. So, that all those nucleus which are present they can basically grow and once they start growing they will start a impinging upon one another. So, now we have a got and a composite which is a glass ceramic. So, in this particular case we are starting with a glass and then first of all we are melting everything and then we are quenching it to result a glass.

So, once we have a glass then we basically are heating it to up to around 500 to 700 degree centigrade to nucleates certain crystals and we are allow into grow at much higher temperatures 600 to 900 degree centigrade and once once the crystal start growing they will tend to impinge upon one on the another, to form a ceramic.

So, that is what we can see that in our initial condition we had a glass, so glass was was basically found by melting and followed by consequent quenching then we then we let the glass to start nucleating certain crystals. So, we heat it up to may be 500 to 700 degree centigrade, so that nuclear can basically form and those nuclear tend to become crystals and then crystals starts to become a become a little bigger grains. Once we again heated to a much higher temperature which can range from 600 to 900 degree centigrade and once enough nuclear present they will eventually grow to impinge upon one another to form a polycrystalline material which is again nothing but a ceramic.

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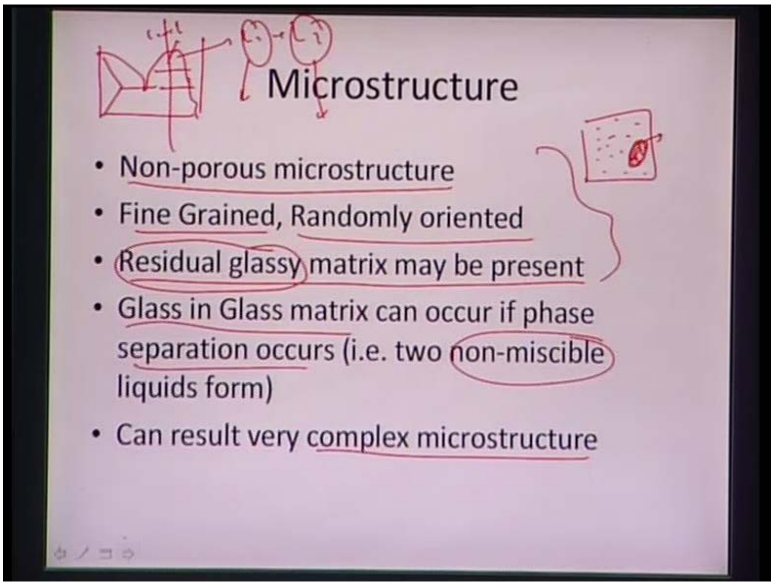

Microstructure

- Non-porous microstructure
- Fine Grained, Randomly oriented
- Residual glassy matrix may be present
- Glass in Glass matrix can occur if phase separation occurs (i.e. two non-miscible liquids form)
- Can result very complex microstructure

So, in this particular case we can get non-porous macrostructure and in this particular case we can get grains which are very fine, at the same time they are randomly oriented, because in this particular case we had a liquid and there has no particular location whether grains will basically nuclei, they tend to get nucleated a random locations and that is the reason they are also randomly oriented as well and then what we get that the residual glassy matrix can also present, because it might lead to that certain regime they do not get chance to nuclear at all and even raising them to very high temperatures we may not see any formation of any crystals or nuclear those certain locations so we can have we can we can also see retention of a glassy matrix in the microstructure.

So, this can also result that we have we have a so this some residual phases of glass inside the microstructure, eventually we can also form glass in glass matrix as well. If we can find some there is some phase separation which can occur at much high temperature So, let us go back to the phase diagram, that in the phase diagram if we have kind of a two phase material. So, which can lead to formation of certain glassy phases or immiscibility gap between the material so if we had say liquid 1 plus liquid 2, say in this case we had liquid1 plus liquid 2 and if we have basically cooling it down from that particular location where we had liquid 1 and liquid 2.

So we can see that liquid 1 will tend to remain liquid 1(( )) will be able to remain liquid 2, because we will have basically if you can coincides such faster rates that liquid 1 does not gets time to equilibrate with liquid 2 and they do not really tend to form one one homogenous liquid. So, in that particular case we can get a glass in glass matrix as well. When we have a non miscible liquid which can form at much higher temperature, but again this can lead to very complex microstructures, because if we once we try heat treat them or something like that, it can even lead to very complex microstructure. So, I will basically take a break here.

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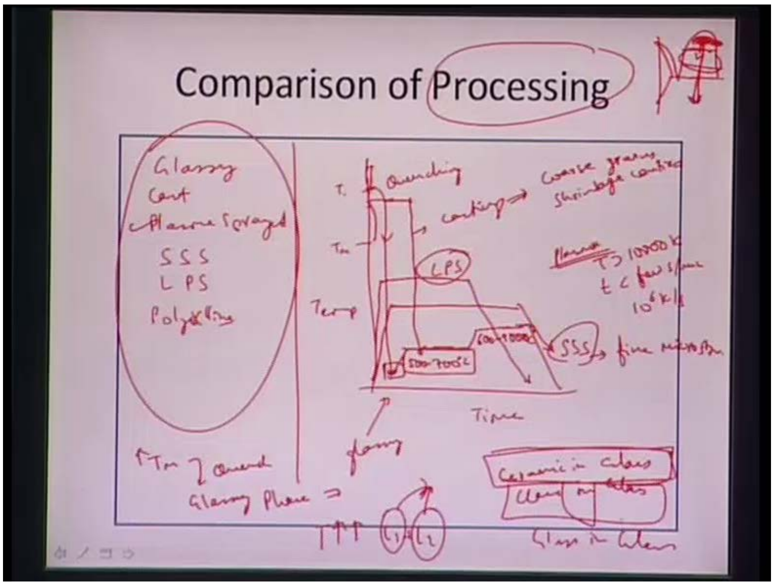

Comparison of Processing

We can see that, we can have a variety of microstructure which which can generate depending on the processing technique. So, we can either of a glass glass glassy kind of a structure, we can also have a kind of a cast structure, we can also have plasma sprayed structure, we can also have a kind of solid state sintered ceramic, we can also have liquids liquids liquid phase sintered ceramic, we can also have a kind of a polycrystalline

polycrystalline matrix which can be again ceramic and ceramic in glass or it can be also in glass in glass.

So, so there are various kinds of microstructures we which we can really attain just by varying the processing technique and all these are basically thermally spread thermally thermal spread techniques. So, depending on what kind of a structure we are looking at whether it is glassy or whether it is a cast structure, whether it is a plasma sprayed structure. We have to play along with the temperature in time cycle of the processing in which we can alter the various properties which can germinate out of the particular processing technique.

So, in this particular case we can draw a kind of a time temperature graph so if we have time out here and we have temperature out here. So, in in case of if you want to attain a glassy structure is basically heat them to very high temperatures much above the melting temperature. So, if we have a melting temperature somewhere here we we let take the particular material at very high temperatures and will basically quenching.

So, that quenching will lead to retain the glassy phases or the oral structure will remain amorphous. So, will attain something called a glassy structure out here and second case we can also have a cast structure. So cast structure also we basically take it to very high temperatures will put it in the mold and then will let it basically cool in the mold.

So, that kind of a thing will it comes eventually via via homogenization so we take it to the high temperatures let it homogenize it sometime and then basically we cool it down to room temperature. In this case of casting we can also get some sort of a microstructure, but the problem with that casting is we can get very coarse grains and once you have a very coarse grains we can also get determination in the properties all the mechanical properties, we can also see sorts of sometimes shrinkage shrink shrinkage cavities which will be again detoriate the properties of material and it will lead to the environment degradation and third case we can also get something called a plasma sprayed structure.

So, in this particular case we can see that the structure is much more polycrystalline in nature. So, in this particular case we are taking the powder particles we are getting them heated through plasma which is nothing but an ionize gas and we let the particles flow through that particular plasma and there accelerated to very high temperature very high so very high velocities and while the experiencing very high temperatures which can exceed even 10000 Kelvin, they are basically impacting the substrate material and depending on on the power size, depending on thepower which we utilizing for plasma spraying we can attain different kind of porosity as well.

So, plasma spraying is basically utilize for depositing a some sort of a ceramic coating onto an implant surface, that is the overall idea behind it and in the (( )) that particular case we are able to reach very high temperatures and the cooling rates are very very drastic, they can in plasma spraying temperatures can be as I as 10000 Kelvin 10000 Kelvin and time can be less than less than couple of minutes to cooling rate can be as high as 10 to power 6 Kelvins per second.

So, few seconds can few seconds to minutes will will be able to complete the plasma deposition process and coming onto third third property, let us say liquid phase sintering were taking the material to below the melting point, but it temperature where we can have formation of at least one phase which is liquid.

So, we take it to a certain temperature which is again a liquid and then we hold it for certain duration and then we let it basically cool this is a liquid phase sintering and a liquid phase sintering what is happening is where allowing one phase to reach, one phase to become solid, one phase to become liquid and because capillarity now that liquid tends to basically bring out or draw all the grains together and that basically is consolidating the material.

So, what we are seeing will have some locations or some grains which are unmelted and those are now being clocked by liquid phase and the liquid phase again we can have depending on the kind of a composition we can either have get a crystallite matrix or we can also get a glassy matrix depending on what kind of a structure we want.

So, if we cool it very rapidly and if you have network network former such as silica they can basically make the overall matrix very glassy in nature. That is that is the liquid phase sintering again we can also go to solid state sintering in which we can hold it to much lower temperature as compare to liquid state a liquid phase sintering, but for very longer times.

So, we can get again a very dense structure, but now in this case when we have solid state sintering, we basically get very fine microstructure, because the temperature is very very low as compare to liquid phase sintering. So, solid state sintered regions they are much denser in nature also we avoiding the formation of a liquid phase and liquid phase as I have the tendency to absorb some impurities which are which can be which can arise from either the mold volar or somewhere else.

So, ideally the solid state sintered products are much more purer than the liquid phase sintered products. At the same time, they had the solid state sinter sintered component will have much porosity also as compare to the liquid phase porosity, because there is no more liquid which can flow into the crevices or any cavities to draw the grains closer.

So, here we need to apply certain sort of a pressure or some sort of a hydrostatic pressure to basically consolidate the overall structure and in this case we all we have solid state a movement of the solid state diffusion process is which can arise from either surface diffusion or volume diffusion or the lattice diffusion or it can also be creep depending on the temperature where we are utilizing out here. So, that is that again advantage with the solid state sintering process so, sometimes even getting porosity also becomes much more advantages in case of solid state sintering.

Because, we really need the porosity so that cells can come and they can attach themselves on to the particular porous surface. So, sometimes this solid state sintering is much more preferred technique to make a particular component and finally, we can also make particular material which can have much more of a ceramic in ceramic in glass or glass in glass. So we can have ceramic in glass, or we can also have glass in glass structure. So, coming to the first ceramic in glass we can we can first of all we can quench the material, so first of all we have particular material we take it to melting point and then we basically quenched, so once we quenched we will get a glassy phase.

So once we had a glassy phase now we increase the temperature to certain regime. So first of all we do a quenching so once we attain the glass out here then we basically heated again to certain temperature which can range from 500 to 700 degree centigrade and then once we have this particular temperature the nucleus starts forming out here.

And once the nuclear have already formed, we can make the crystals growth by heating at even much higher temperature so 600 to 900 degree centigrade, we can let the nuclear grow at much higher temperatures and then basically if we coincide if we can let it cool down then basically what we have gotten is ceramic in glass.

Because, the overall material can again still be glassy depending on the way we cool it, but most of the nucleus already formed if the nucleus formed completely we can get a polycrystalline matrix and so we get all the grains which are very fine and everything is much more crystalline or ceramic, but it can again be glass in glass. So, once we have cooled it depending on the way we are cooling it you can again retain the glassy phase itself, once we have much more of a network former in the liquid regime, we can retain the glassy structure itself, once we have two liquid which are forming at much higher temperatures.

So, for glass in glass we need to have a phase diagram where we can see two regimes which are forming liquid 1 and liquid 2 at very high temperature so we have immiscible liquids at higher temperatures so whereas, temperature is very very high, but much below the melting point the overall total melting point, we will see liquid 1 plus liquid 2. So, that will locates we are saying a phase diagram which will have liquid 1 plus liquid 2 in this particular regime and then they basically come to homogenize at much lower temperatures.

But we do not let them homogenize at lower temperatures, we basically quench them from the immiscible regime. So, in this particular temperature we basically tend to quench them. So, we can get two liquids as it is as they are in the liquid phase. So, we do not let them to homogenize at lower temperatures and we basically retain the structure of liquid 1 and liquid 2 which are which were immiscible at much higher temperatures and then we get glass in glass.

So, these are the various comparison of the various thermal processing techniques to get very different microstructures which can be glassy, which can be cast structure, which can be again a plasma sprayed structure, which can be solid state sintered region, which can be again liquid phase sintered type of microstructure, it can be again polycrystalline, it can be ceramic in glass, it can be glass in glass. So, this is the overall mixture or a blend of different techniques and which which can really help us provide a very different paradigm of properties S H or different type of applicability in terms of the microstructure which we can get out of it.

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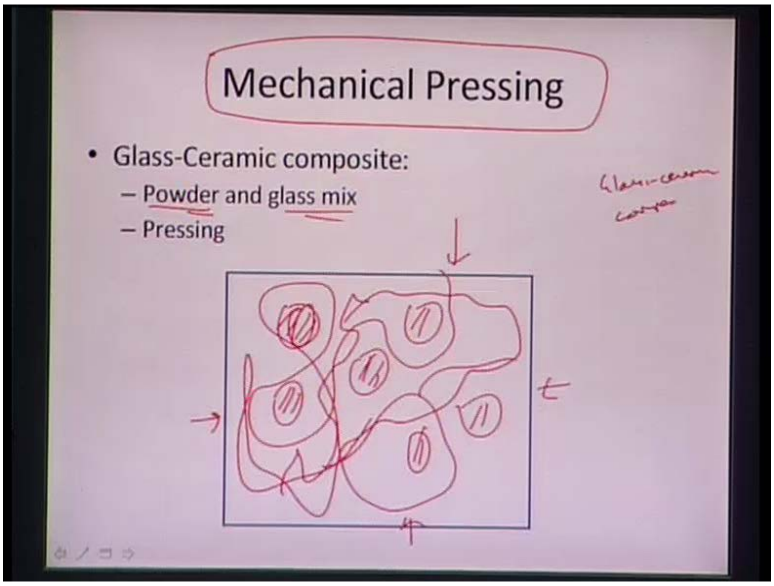

Mechanical Pressing

- Glass-Ceramic composite:
  - Powder and glass mix
  - Pressing

Glass-ceramic
compo

So, they can also be mechanical process apart from thermal loads we can also have mechanical routs to basically produce a glass ceramic kind of a composite. In this particular case, we take a ceramic powder and we take a glass mix and then we basically compress them altogether. So, we see all the powder particles which are basically thrown here and there and then the glassy phase will basically flows over those over those particulates to form a matrix. So, we have so in this particular case we have all the particles solid solid ceramic particles and then we have a glassy phase which is basically covering which is covering the entire regime and then we basically compress it or mechanically press it, so that we can get a structure something like this, that it has a particulates which has a surrounding liquid or a glassy mode phase. So, that produces a glass ceramic composite.

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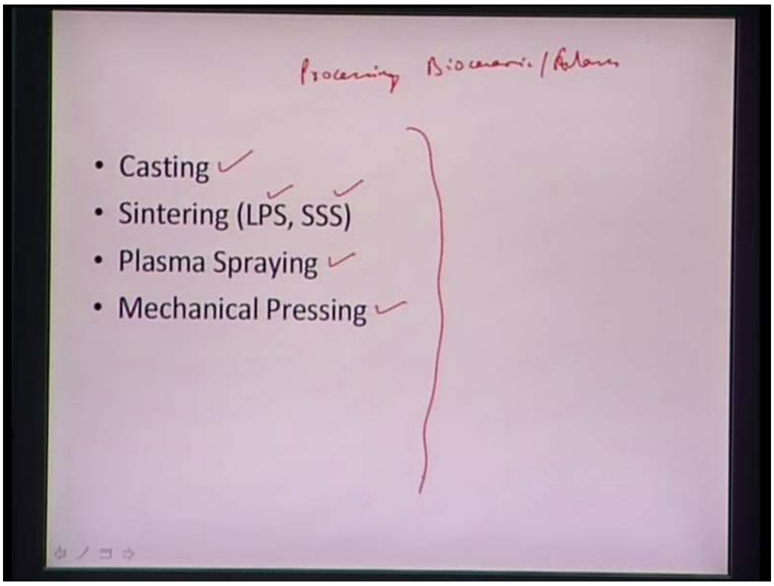

Processing Bioceramic/Bioglass

- Casting ✓
- Sintering (LPS ✓, SSS ✓)
- Plasma Spraying ✓
- Mechanical Pressing ✓

So, that is what we are able to see out here that we can get various kind of techniques for processing the ceramic, bioceramic or a bioglass or a glass kind of a composition either via casting or via sintering which can be liquid phase sintering or can be solid state sintering, it can be again plasma spraying, it so basically thermal treatments are utilized in this particular case and it can again be more mechanical pressing as well to revealed the certain microstructure.

So, overall what we basically see in this particular what we see in this particular lecture is that we can utilize that the either thermal spraying problem the thermal techniques or a mechanical techniques to form a bioceramic or a glass kind of a microstructure. So, in thermal techniques we can get various types of microstructure which can which can be resulted they can range from either cast structure, which can be plasma split structure, which can be glassy structure, glass in ceramic structure, liquid phase sintered structures, solid state sintered structures so there is the variety of all the structures can be resulted from a different type of techniques which are utilized here. So, attain a glassy structure we take the melt to a very high temperature and we cool it very rapidly or we can also induce some sort of a network formers and network modifiers.

So we can get a combination of silica which is a network former and we can have network modifier of calcium oxide to result overall a glassy structure, we can also get a we can also get a cast structure by taking a melt high temperature letting it cool in a cast

cast product, but here the problem is the to produce the equilibrium structure the overall grain growth really occurs during this particular time. And because of that there is there is much detonation of the properties the mechanical properties and also it can lead to detonation of the corrosion properties, because now the overall structure is very weak.

It can also lead to some cavity formation which can arise from the strengthen of the material. So, there is a problem with the cast structure we can also go with a liquid phase sintered structure in which we take the take the temperature to to such that that, we have one phase which which forms a liquid and second phase remains as such unmelted. So, we have the liquid phase basically collecting or the drawing all the other grains closer to itself and it forms a very dense structure, but the the overall temperature is very higher as compare to the solid state sintering.

Where in we do not make even one phase go to a liquid regime, so we have solid and solid and then we basically are sintering them and there is transformation of transformation of material via solid state diffusion processes which can be either grain boundary diffusion or the lattice diffusion or it can beeventually creep as well depending on the temperature we utilize it, but here in we see that since everything is solid there is no much impurity concern in cooperation out here, because the liquid tends to a track or dissolve much more impurities, it can be in the gaseous form, it can be arises from the from the surface of of the overall cavity.

So, it can arise from there as well so in this solid state sintered structure such a we can see the grains are much more finer, because here we are here we are keeping the material to be much at lower temperatures as compared to the liquid phase sintered regime, I will again we can also process the material via plasma spray where we are taken the material to very high temperatures and we have we have very high cooling rates so they basically forms as as splits or lamellates on to a substrate implant substrate. So, we can get a polycrystalline matrix as well or eventually we can also form something called glass in ceramic, ceramic in glass or glass in glass kind of composites. So, here we first form a glass, so in this particular case we take the material to a very high temperature we quench it, so that we get a glass and now we have to crystallize this particular glass to achieve ceramic in the glassy phase.

So, we take it to high temperatures where we can may be around 500 to 700 degree centigrade where we can led the crystallites gets nucleate get nucleated out here. Once once the nucleated within increase into the further higher temperatures order of 700 into 900 degree centigrade, when all this crystallize tend to grow and must they are growing they will starting bending one another and depending on cooling we can either achieve a polycrystalline matrix or we can also achieve a glassy matrix. So, that becomes a ceramic in glass.

We can also get glass in glass, by basically having microstructure where we have two immiscible liquids at higher temperatures. So, we have liquid 1 and liquid 2 which are immiscible once we take them to low temperature temperature that tend to get miscible much at low temperature, but but what we do we take them to the temperature regime where we have liquid 1 plus liquid 2 and we cool it very rapidly, so what happens that liquid 1 remains as such at the room temperature, liquid 2 also remains as such at the room temperature and we get glass in glass matrix.

Those are all the thermal techniques and coming to the mechanical techniques we can take a ceramic material and we can get a glassy phase we just basically mechanically press them together. So, what we are getting eventually is we get solid particles where ceramic and those are basically doing compress via glassy matrix, because glass for glassy phase it is easier for them flow around and consolidate the overall material. So this is what basically completes the overall processing of bioceramics or glasses in this particular lecture. Thanks a lot.