

Non - Metallic Materials
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 07

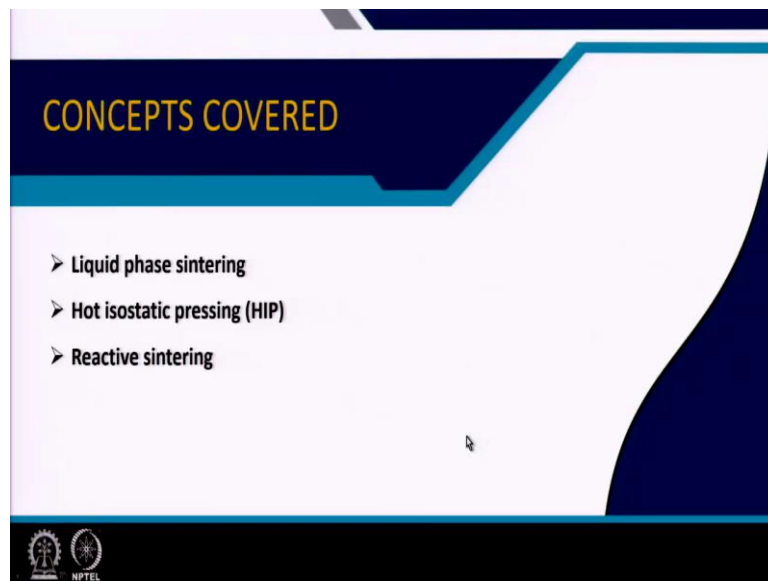
Processing of non - metallic materials, sintering and microstructure development

Lecture - 38

**Liquid phase sintering and microstructure development, speciality sintering,
reactive sintering**

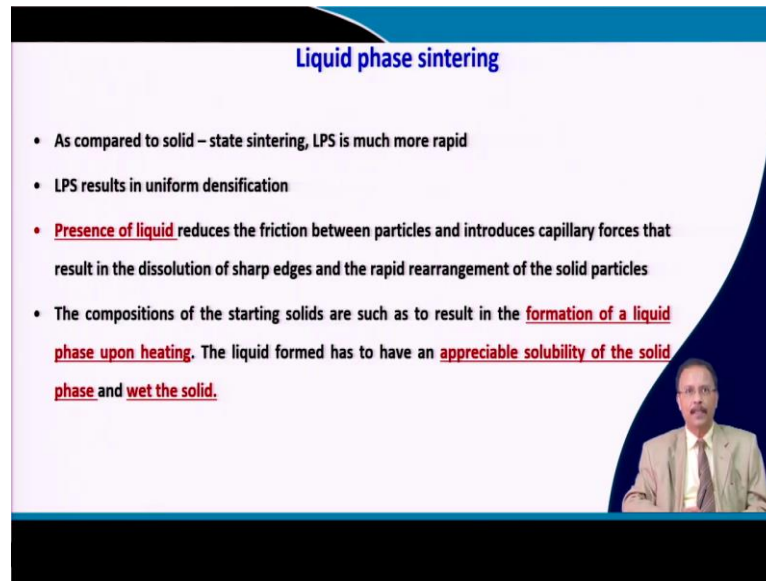
Welcome to my course Non Metallic Materials. And today we are in module number 7, Processing of non-metallic materials, sintering and microstructure development and today, we will be talking about the remaining sinterings that is liquid phase sintering and microstructure development, speciality sintering and reactive sintering, we will just introduce.

(Refer Slide Time: 01:02)




So, in this particular lecture we will be talking about liquid phase sintering and introduce the concept of hot isostatic pressing and reactive sintering without much details.

(Refer Slide Time: 01:18)



Liquid phase sintering

- As compared to solid – state sintering, LPS is much more rapid
- LPS results in uniform densification
- **Presence of liquid** reduces the friction between particles and introduces capillary forces that result in the dissolution of sharp edges and the rapid rearrangement of the solid particles
- The compositions of the starting solids are such as to result in the **formation of a liquid phase upon heating**. The liquid formed has to have an **appreciable solubility of the solid phase and wet the solid**.



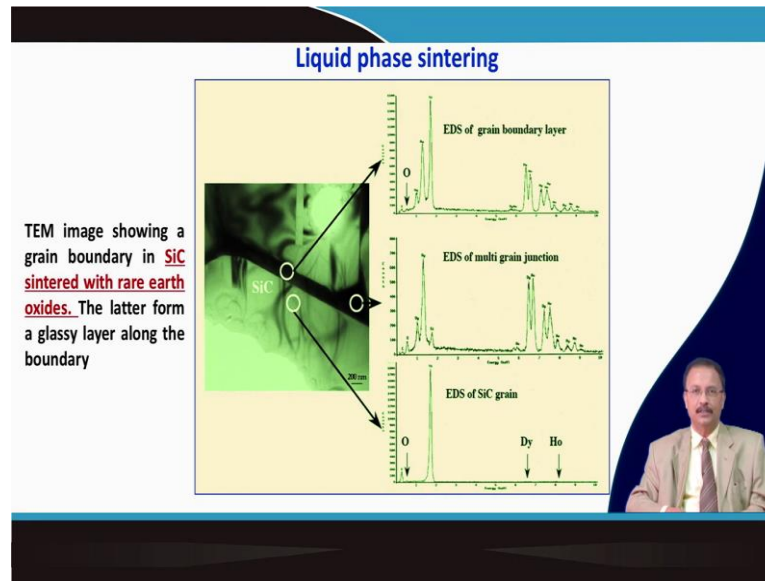
So, in last few lectures I talked about mostly solid state sintering and as compared to that solid state sintering, you will find that this liquid phase sintering they are much more rapid it does not take that much time for sintering to be completed.

Liquid phase sintering has another advantage, because it will give you a uniform kind of densification. It is having a presence of a liquid and therefore, it reduces the friction between the particle and also it introduce the capillary force, that eventually result the dissolution of the sharp edge of the particle which are going to be sintered and rapid rearrangement of the solid particles and that actually leads faster sintering kinetics..

The compositions of the starting solids are such that it results the formation of the liquid phase upon heating. And that can be done by knowing the proper phase diagram already I have told you that if you can control the composition, it is possible for you to generate liquid phase inside the material, and this liquid whatever is formed that should have an appreciable solubility of the solid that is one criteria.

So, that it gets dissolved and then finally, it gets re-precipitated and also you should of course, wet the solid. So, that is the primary requirement of the liquid phase sintering.

(Refer Slide Time: 03:14)



So, this is a typical TEM image of a silicon carbide, which is used mostly for heating element of laboratory furnace and other industrial furnaces. So, that is the grain boundary of silicon carbide and it is sintered with rare earth oxide, which form a glassy layer along with the boundary.

So, three different position I have shown that this is the grain boundary layer. So, at the grain boundary you have seen that the in case of solid state sintering, the pores are basically removed from the grain boundary. So, only the boundary a thin region that is there, but in case of a liquid phase sintered material you have a grain boundary phase which could be glassy and which could be crystalline in nature. So, that is there at the grain boundary.

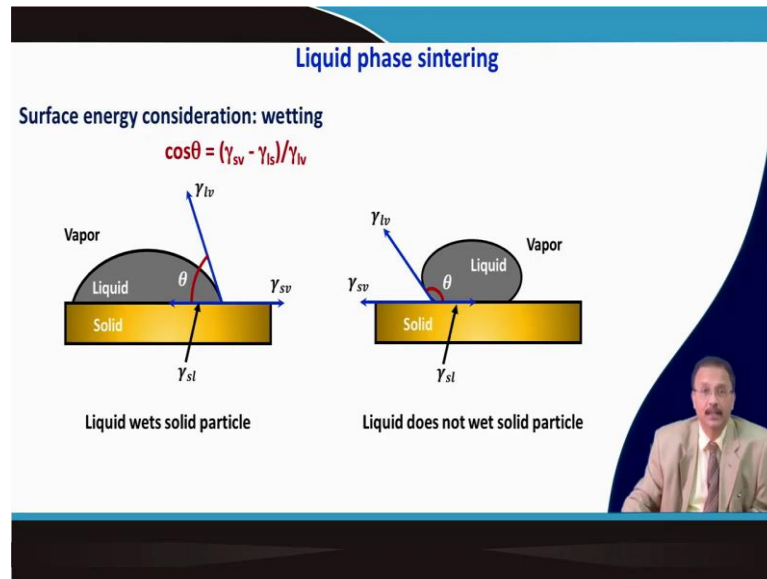
So, here the grain boundary phase it has been identified by EDS Energy Dispersive Spectrometry and it has been compared with the bulk phase which is silicon carbide. So, you see here silicon carbide, here it is additional phases are there. So, composition is different and this is at the triple point, the grain junction where it takes place three grains junction, there also the phase uniformity is no longer silicon carbide.

So, for a high purity device, if it is required then one should think whether he or she will adopt the liquid phase sintering, because your composition is changing. Think about a good capacitor or a piezoelectric sensor material and if you can afford the change in

composition at the grain boundary particularly at the grain boundary, then it is fine. Otherwise, densification will be there, but the phase uniformity will not be that good.

But for certain electronic components like varistor, we do need a different types of grain boundary composition in those cases this is a good option.

(Refer Slide Time: 05:41)

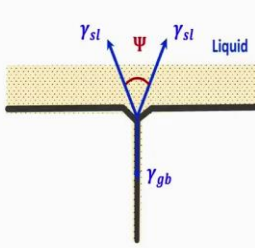


So, wettability is one criteria I have already described it in my earlier lectures as well. So, surface energy consideration that will actually allow whether this will form a good wettability or it is this angle this wetting angle is more than 90 degree.

So, it behaves like a hydro I should not call it hydrophobic, but that liquid phobic kind of structure if that is something similar to this, when the liquid does not wet to the solid particle. So, that those kind of liquid is not very one will not appreciate those kind of liquid for liquid phase sintering. But on the other hand if the liquid uniformly wets the solid particle, then it is good for liquid phase sintering.


(Refer Slide Time: 06:35)

Liquid phase sintering



- Complete penetration of grain boundaries with a liquid is also important (breakup of soft agglomerates is possible).
- $\gamma_{gb} = 2 \cdot \gamma_{sl} \cdot \cos \psi / 2$; ($\psi = 0$ preferable);

$\gamma_{gb} > 2 \cdot \gamma_{sl}$ high value of γ_{gb} and low γ_{sl} are desirable.



Now, we already introduce the concept of the dihedral angle. So, now as you can see that you have the grains here and earlier it was here right, in case of solid state sintering it was there. Now, this has been replaced by the liquid, which has formed during sintering and this liquid eventually it will have a capillary action that I will show, it should have a good wettability.

So, that it is completely wet and this complete penetration of this liquid of the grain boundary is important and that eventually also will break up the soft agglomerate. During the processing the liquid forms and it has soft agglomerate due to capillary pressure liquid is going in. So, soft agglomerate you know that the pore distribution will be very different in soft agglomerate. So, that part will be broken.

So, from energy criteria you can have this grain boundary energy with solid liquid into \cos of this dihedral angle divided by 2. So, certainly 0 is preferable, if it is 0 then the grains will be pulled to the close proximity for a better sinter ability. So, eventually this γ_{gb} of this grain boundary that should be twice of γ_{sl} that liquid solid interfacial energy.

So, high value of this grain boundary and low value of this are actually desirable for efficient liquid phase sintering.

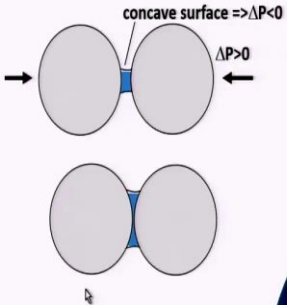
(Refer Slide Time: 08:26)


Liquid phase sintering

Capillary action

With the distributed liquid, grains will be pulled together due to the negative curvature of the liquid-solid surface and the associated pressure difference (capillary effect). This pressure difference will assist the compaction during sintering.

Example: ZnO varistors are sintered with the addition of Bi_2O_3 , which is only slightly soluble in ZnO and forms an eutectic liquid at the sintering temperature of ZnO.



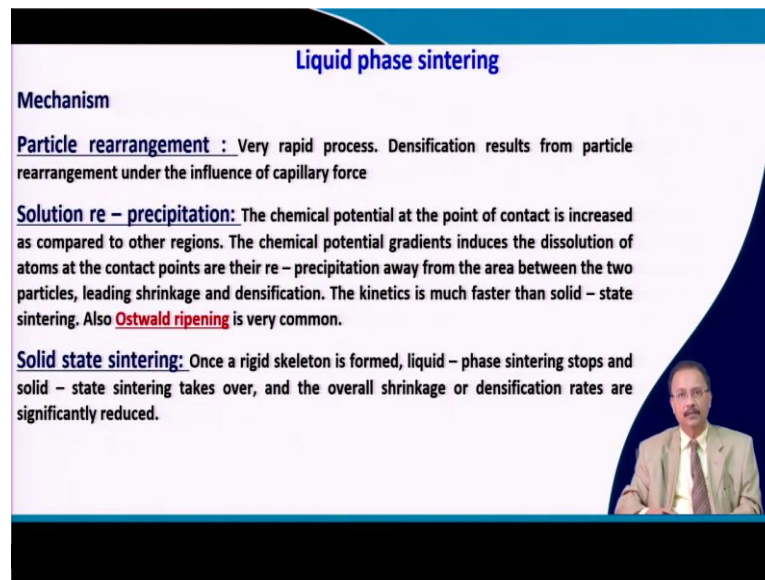


So, capillary action is important here. So, with the distributed liquid, so, liquid will penetrate between the particles and particle will have their usual curvature, I already talked about the curvature. Here the pressure is positive in the convex region and in the concave region this is less than 0 in fact.

So, this will introduce a compressive kind of force as you can see and this liquid inside will get penetrated. So, with the distributed liquid grains will be pulled together due to the negative curvature of liquid solid surface interface. The associated pressure difference that is known as the capillary effect and this capillary effect assist the compaction during sintering.

And example can be given zinc oxide I just mentioned a few minutes back, that zinc oxide varistor are sintered with addition of bismuth oxide, which is slightly soluble in zinc oxide and this eventually forms a eutectic liquid at the sintering temperature and this actually does this purpose of this capillary action.

(Refer Slide Time: 09:55)



Liquid phase sintering

Mechanism

Particle rearrangement : Very rapid process. Densification results from particle rearrangement under the influence of capillary force

Solution re – precipitation: The chemical potential at the point of contact is increased as compared to other regions. The chemical potential gradients induces the dissolution of atoms at the contact points and their re – precipitation away from the area between the two particles, leading shrinkage and densification. The kinetics is much faster than solid – state sintering. Also **Ostwald ripening** is very common.

Solid state sintering: Once a rigid skeleton is formed, liquid – phase sintering stops and solid – state sintering takes over, and the overall shrinkage or densification rates are significantly reduced.

So, if you want to know about the mechanism of the liquid phase sintering, it has distinct three phase. The first phase is the particle rearrangement, it is a very rapid process and as you can understand that part of this particle rearrangement that actually is under the capillary force, which I just talked about. And in normal solid state sintering, it is difficult right, because if you have different types of particle and basically packing is either by uniaxial pressing or biaxial pressing that is taking place.

Now, inside I mean during the liquid phase sintering you know the particles are there, but liquid is also penetrating. So, liquid is doing some kind of rearrangement of the particles. So, that is good for the grain density right. So, if a pore is something like this you have a huge pore, then only in case of solid state sintering, diffusion, mass transport, vacancy transport etcetera will have to take place.

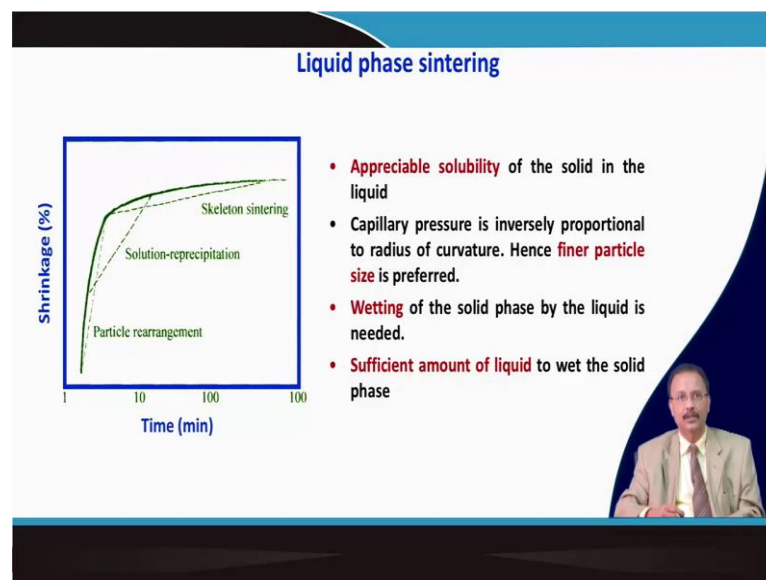
But, if you have a liquid inside it is going and due to the capillary action it is giving you some kind of movement so, that particle rearrangement is taking place. So, densification is a bit expedite. Then what happens there is a solution re-precipitation. The chemical potential at a point of contact is increased as compared to the other regions, this chemical potential gradient induces the dissolution of the atoms in contact points and they are re-precipitated,

First there is a dissolution takes place and then they are re-precipitated away from the region of the two particles and that actually leads to the shrinkage and densification is a

fast process as I have said as compared to the solid state sintering process. The kinetics is really faster and Ostwald ripening is also very common, because it is basically a solution re-precipitation process. So, there is a lot of rearrangement particle of the particle first takes place then there is a solution inside the liquid of the solid particle,

Then they are transported because anyway it is being done at high temperature. So, by all this process when it is done then a rigid skeleton is formed and the liquid phase sintering basically stops and then finally, it is solid state sintering that takes over and the overall shrinkage and densification rates are significantly reduce as compared to the liquid phase, liquid phase was much more faster, but as the skeleton forms for the solid state sintering, it actually is appreciably slowed down.

(Refer Slide Time: 13:14)



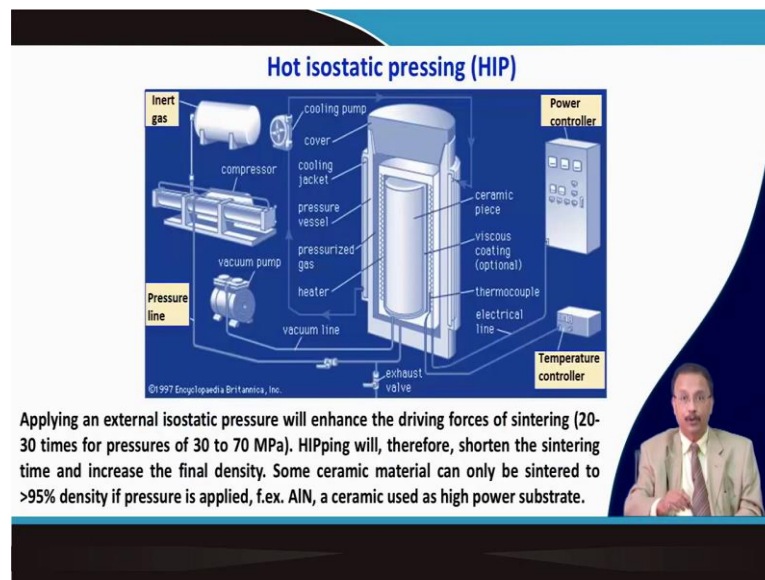
So, if you see the shrinkage versus time profile. So, appreciable solubility of the solid phase in the liquid, then particle rearrangement it takes place, then capillary pressure that is inversely proportional to the radius of the curvature, finer particle of course, is preferable for this purpose. Wetting is also another thing; wetting of the solid phase with the liquid is welcome and sufficient amount of liquid to wet the solid phase.

So, these are the primary requirement and if you see the shrinkage, it is very fast initially and after the time passes, when it is a skeleton sintering due to solid state the rate actually they are pretty slow as compared to the initial rate of densification. Now, liquid

phase sintering is having one problem, because we will have to control the liquid phase. Because, if the liquid is too much then in its own weight the heavy article.

If you are sintering and if you have too much liquid formation during sintering, then in its own weight the material can form a defect which we called warping. So, that needs to be avoided, particularly white ware type of particles including tile, commode etcetera. They are getting sintered by liquid phase sintering. So, this is extremely important to judiciously control the liquid volume.

(Refer Slide Time: 14:59)



So, liquid phase sintering is otherwise good. It does not have the problem of solid stress sintering as far as the pore removal is considered or the densification is concerned, but at the same time the compositional uniformity, the defect like warp age and those kind of stuff are associated with it. There are other sintering mechanism which by intuition you can say that it will be more effective as compared to pressure less sintering.

So, here I have considered the hot pressing that is one important type of sintering that is usually used for near zero porosity material. In fact, the lead, lanthanum, zirconium, titanate is a good electro optic material. It is of course, ferroelectric and as you know if it is ferroelectric; that means, it is pyroelectric, it is piezoelectric material, it is a good electric material and apart from that it is electro optic in nature.

So, the it has birefringence and with the application of external electric field, this refractive index can be changed. So, this is used for optical switch. So, for that sintering you need almost a zero porosity, because that is a transparent ceramics. So, during the fabrication of this PLZT component way back in 1970s I guess, in sandier national laboratory, that people used to do this kind of hot isostatic pressing.

So, applying an external isostatic pressure will enhance the driving force of sintering. So, it is roughly 20 to 30 times for pressures of 30 to 70 mega Pascal's and heaping therefore, will shorten the sintering time and increase the final density. Some ceramic material can only be sintered more than 95 percent density if pressure is applied.

Example is aluminum nitrite a ceramic that is used for power electronic substrate, because it is having extremely high thermal conductivity, that is centered by this way simultaneously application of pressure and temperature and pressure is in a hot isostatic pressure. So, this is a complicated arrangement your sample is here. So, you have a compressor you need to put isostatic pressure across the sample, there is some kind of viscous coating which is of course, optional.

But that is also in the around the ceramic particle and you have a power necessary power controller and temperature controller to control the ambient as well as the heating condition in this furnace. So, hot isostatic pressing an expensive equipment and that is used for developing almost zero porous ceramic materials


(Refer Slide Time: 18:36)

Hipping of Si_3N_4

sinter mode S: normal HP: hipping	sinter aid appearance of a liquid	% of theoretical density reached	mechanical strength	
			RT [MPa]	1350 °C [MPa]
Si_3N_4 (HP)	5% MgO	> 98	587	173
Si_3N_4 (S)	5% MgO	90	483	138
Si_3N_4 (HP)	1% MgO	> 99	952	414
Si_3N_4 (S)	BeSiN ₂ + SiO ₂	> 99	560	-
Si_3N_4 (S)	6% Y ₂ O ₃	98	587	414
Si_3N_4 (HP)	13% Y ₂ O ₃	> 99	897	669

(HP) Heissgepresst, (S) gesintert

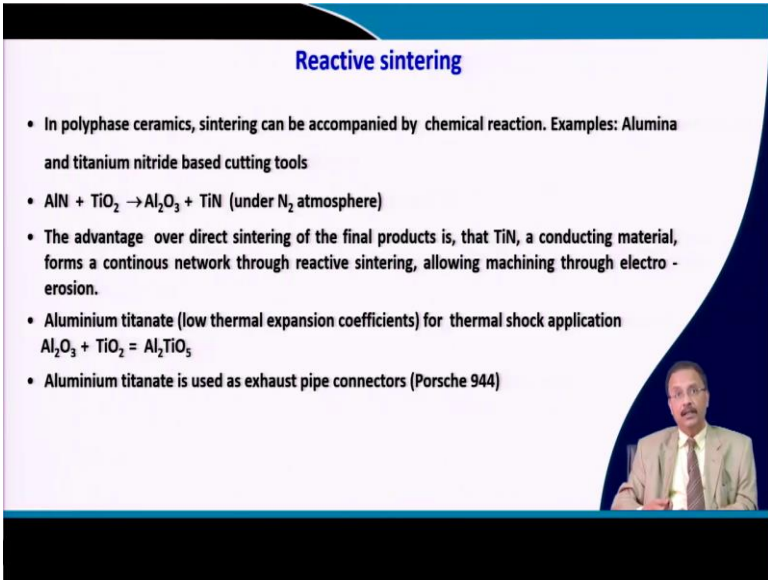
Hipping of silicon nitride improves the final density and as a consequence the mechanical strength. An improvement of almost 100% is possible.



So, if you see the effect of this hot pressing with normal kind of sintering. As you can see here the densification and the related mechanical strength and by comparing with the normal sintering and the hot isostatic pressing, particularly for silicon nitride material you can see that much more improvement that you get densification more than 99 percent it is possible,

It is possible to achieve room temperature as well as high temperature strength, probably this was a flexural strength that you can achieve out of this material. So, it is indeed very effective to have the hot isostatic pressing.

(Refer Slide Time: 19:31)



Reactive sintering

- In polyphase ceramics, sintering can be accompanied by chemical reaction. Examples: Alumina and titanium nitride based cutting tools
- $\text{AlN} + \text{TiO}_2 \rightarrow \text{Al}_2\text{O}_3 + \text{TiN}$ (under N_2 atmosphere)
- The advantage over direct sintering of the final products is, that TiN, a conducting material, forms a continuous network through reactive sintering, allowing machining through electro-erosion.
- Aluminium titanate (low thermal expansion coefficients) for thermal shock application
 $\text{Al}_2\text{O}_3 + \text{TiO}_2 = \text{Al}_2\text{TiO}_5$
- Aluminium titanate is used as exhaust pipe connectors (Porsche 944)

Video inset: A man in a suit and glasses speaking.

The final one is reactive sintering. So, in reactive sintering basically two powders they are used, they form the desired compound and simultaneously gets sintered. So, the idea of separately calcine it and then sintered it, that is that is gone for this reactive type of sintering.

So, in polyphase ceramics, this kind of sintering with a chemical reaction that is possible and one example is alumina and titanium nitride based cutting tools. So, here aluminum nitride and titanium oxide is used to form aluminum oxide and titanium nitride and this is done under nitrogen ambient. So, the advantage of direct sintering of the final product, this is in the fact that titanium nitride is a conducting material and forms a continuous network structure, through reactive sintering inside the material.

So, these are used for machining as cutting tool. So, you have a thermally conducting network inside the hard matrix. So, this allows machining through electro erosion process. So, that is advantageous. Aluminum titanate it is having a very low thermal expansion coefficient, this is especially good for thermal shock related application, when the temperature changes and it yields thermal shock. So, for those kind of application this is important.

Aluminum titanate for your for example, is used for the exhaust pipe of pipe connector for high end cars. So, that is one of the examples.

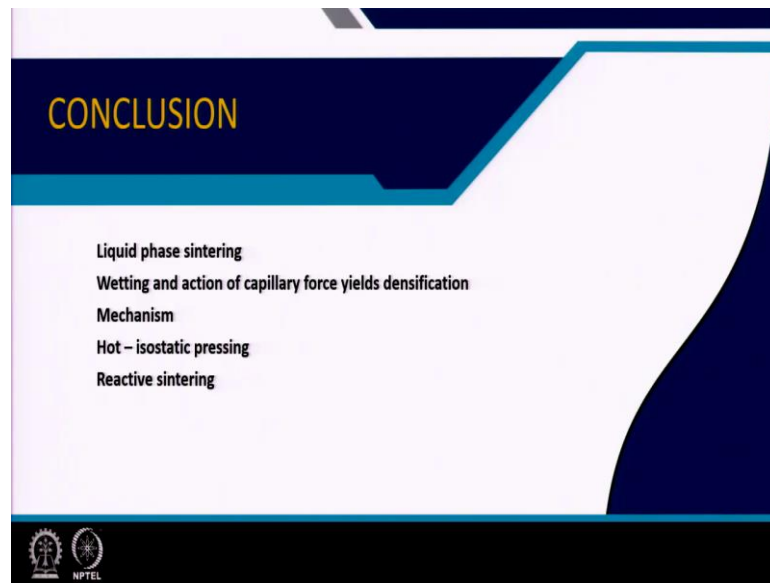
(Refer Slide Time: 22:01)



So, the study material for this particular lecture is Barsom and chapter number 10 and along with this the other books that I referred, this is also one can look at. There are speciality books on specifically on ceramics by Professor Rayman that also can be consulted for advanced level advanced knowledge about the sintering.

What I have covered is exactly a fundamentals aspect of the prominent type sintering mechanisms, namely solid state sintering and also liquid phase sintering and specially this sintering is not part of this lecture, but two more popular things or the concept of reactive sintering I thought, that I should introduce through my lecture. So, therefore, I have just touched upon it, but they are subject by themselves it is no way a exhaustive coverage of those two aspect of sintering.

(Refer Slide Time: 23:19)



So, in this particular lecture we introduce liquid phase sintering and here you have seen that the wetting of the liquid on the solid particle is of at most importance. And capillary forces which is again related to the surface curvature of the initial particle, that plays a major role. So, therefore that that curvature particle curvature in controlling the pressure and also the vacancy that plays a major role.

But here the mechanism is a bit different, because here initially the solution leads to the rearrangement of the particles. So, that yield to very fast densification and then solution reprecipitation that occurs and the strength. Of course, it will be dependent on that when you cool it down whether the liquid will form a crystalline phase or a glassy phase.

A very fast slide I showed that it forms a glassy phase in case of silicon carbide, it might have good grip resistance, but its mechanical property will not be that good. Then finally, hot isostatic pressing and the concept of reactive sintering is introduced.

Thank you for your attention.