Advanced Ceramics for Strategic Applications
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Lecture - 38
Sintering Ceramics

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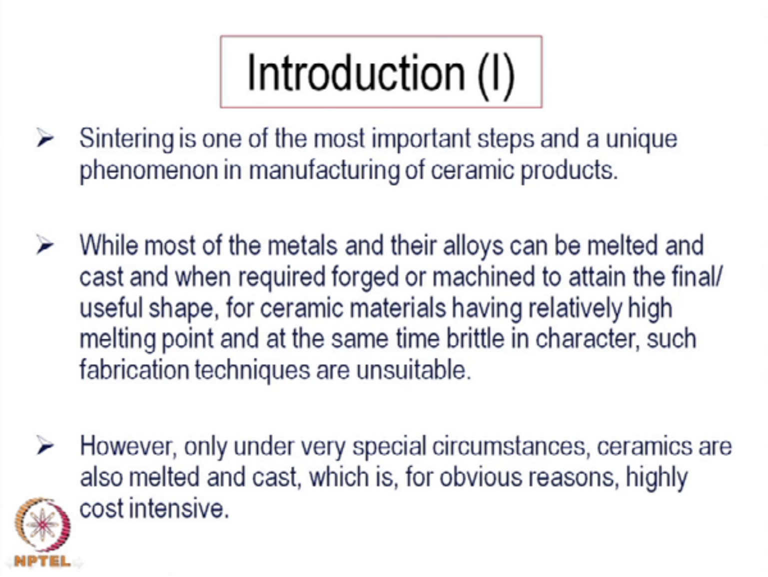

Introduction (I)

- Sintering is one of the most important steps and a unique phenomenon in manufacturing of ceramic products.
- While most of the metals and their alloys can be melted and cast and when required forged or machined to attain the final/ useful shape, for ceramic materials having relatively high melting point and at the same time brittle in character, such fabrication techniques are unsuitable.
- However, only under very special circumstances, ceramics are also melted and cast, which is, for obvious reasons, highly cost intensive.

Today's topic is, sintering of ceramics. Well sintering is one of the most important steps and also unique phenomena in manufacturing of ceramic products. You may be familiar with other production techniques or fabrication techniques for other materials, like metals or alloys. They can be melted and cast when required, forced or machined to attain the final useful shape. However, for ceramic materials which are having a relatively high-temperature or high melting point is difficult to melt. Therefore, it is difficult to cast or give it a shape by molding process, and at the same time the ceramics are also brittle and therefore, it cannot be forced.

So, they do not have in plastic deformation even at a very high temperature and therefore, the normal techniques of fabrications is used in metals and alloys or even plastics as cannot be applied to ceramic materials. So, ceramic materials are also melted and cast only under very special circumstances, and when it is absolutely necessary for some developing certain properties, but obviously they are quite cost intensive and normally avoided.

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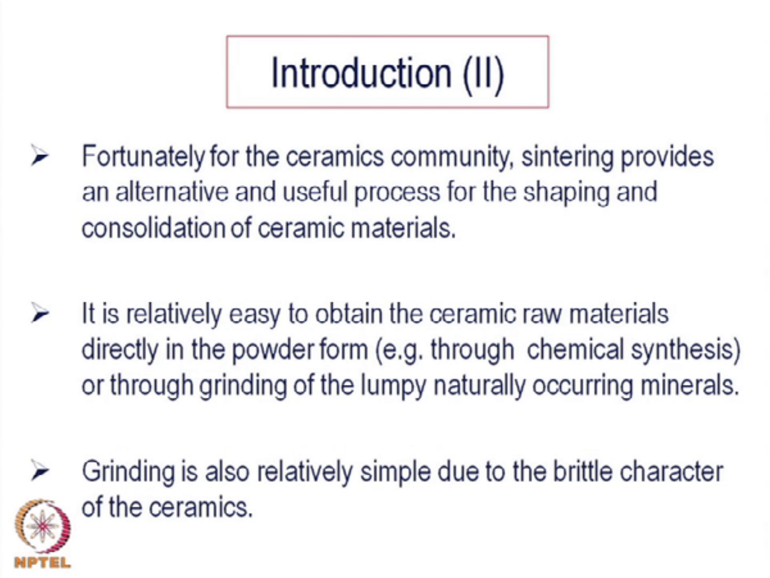

Introduction (II)

- Fortunately for the ceramics community, sintering provides an alternative and useful process for the shaping and consolidation of ceramic materials.
- It is relatively easy to obtain the ceramic raw materials directly in the powder form (e.g. through chemical synthesis) or through grinding of the lumpy naturally occurring minerals.
- Grinding is also relatively simple due to the brittle character of the ceramics.

Fortunately for the ceramics community, sintering provides an alternative and useful process for the shaping and consolidation of ceramic materials. Since, normal melting and casting cannot be done, or forcing cannot be done, rolling cannot be done, so one needs a completely different approach for giving a shape and size, or manufacturing a particular product out of ceramics. The ceramic raw materials are available in powder form.

Well, there are one of the major reasons in ceramics is basically a brittle material. So, it is the naturally occurring materials which are lumpy, and they can be grounded to fineness, and at the same time is called as the advance ceramic products. The compositions are concerned as we have discussed earlier. They are synthesized, they are not naturally occurring, and during chemical synthesis, we do get powders. So, for ceramic material, the raw materials are basically in the powder form and because these materials are brittle, even the lumpy materials are naturally occurring. Lumpy ores can be grounded relatively easily, and they may be the starting powders, or starting raw materials for the ceramic fabrication.

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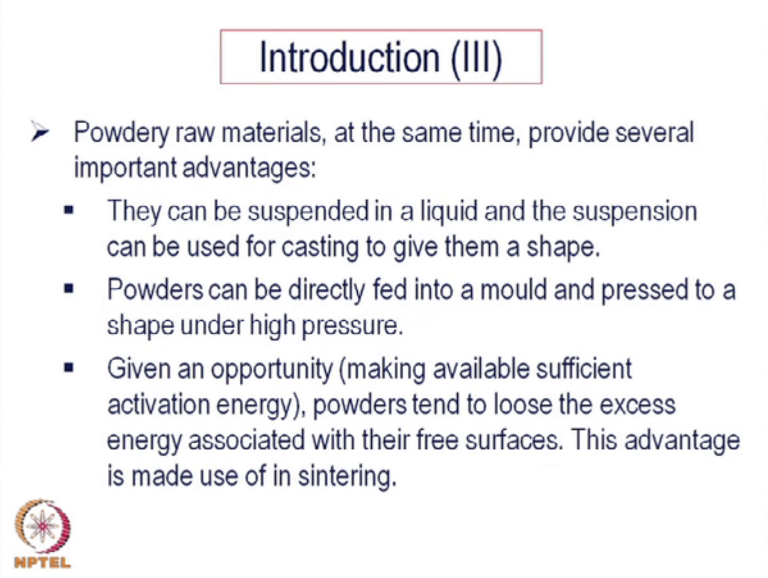

Introduction (III)

- Powdery raw materials, at the same time, provide several important advantages:
  - They can be suspended in a liquid and the suspension can be used for casting to give them a shape.
  - Powders can be directly fed into a mould and pressed to a shape under high pressure.
  - Given an opportunity (making available sufficient activation energy), powders tend to loose the excess energy associated with their free surfaces. This advantage is made use of in sintering.

Powdery raw materials, at the same time, provide several important advantages, and that is the reason the sintering has come up with the phenomena or technique of sintering which has been developed. They can be suspended in a liquid, and suspension can be used for casting to give them a shape. Well, although they are not plastic materials and they cannot be melted, but these powders which can be suspended in some kind of a medium, liquid medium may be aqua or non-aqua sometimes, and one can form a viscous slip and that act can flow and fill up the cavity of the moulds. Therefore, one can develop casting techniques with the use of molten materials, but with the suspended suspensions of the fine powders and that is a very common technique even starting with this slip casting, to gel casting, and type casting, and so on.

So, powder materials have their own advantages. In that context, powders can be directly fed into a mould and pressed to a shape particularly at high temperature, high-pressure. So, these powders can be free flowing characteristics, or it can be made free flowing by certain additives or some binders can be used. Then a high pressure can be applied into a mould, so that the powders can take the shape of the mould. So, that is another way of using the powders to give it a particular shape, even if these powders are really not plastic, or cannot be melted given an opportunity, which means making available the sufficient activation energy.

So, if sufficient and activation energy is provided to the system, this compact powders tend to lose the excess energy associated with their free surfaces. This advantage is made use of in sintering. So, the powders when that is heated to high temperature, so that certain activation energy is provided to the system. They tend to lose their excess energy because of the high surface area, the surface energy particularly, and this is the technique or this is the process which is taking advantage of sintering. So, in sintering, actually one can provide certain activation energy by heating to high temperature, so that the excess free energy because of the high surface area can be removed, and the particles can be bonded together as a strong bond. We will discuss as that is one of the basic step, or the basic phenomena of sintering.

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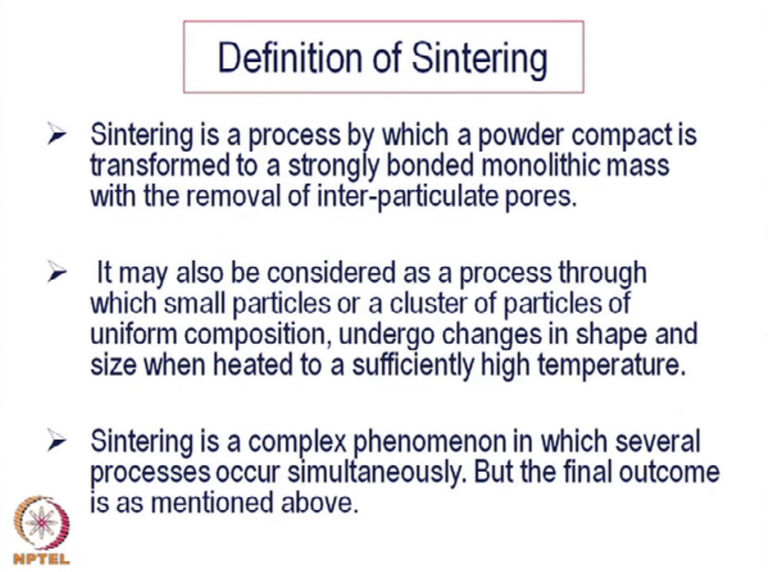

Definition of Sintering

- Sintering is a process by which a powder compact is transformed to a strongly bonded monolithic mass with the removal of inter-particulate pores.
- It may also be considered as a process through which small particles or a cluster of particles of uniform composition, undergo changes in shape and size when heated to a sufficiently high temperature.
- Sintering is a complex phenomenon in which several processes occur simultaneously. But the final outcome is as mentioned above.

So, if you like to have a definition of sintering there is no unique definition. In fact, people have used different kind of approaches to define what is ceramic and what is a sintering. It is a process by which a powder compact is transformed to a strongly bonded monolithic mass with the removal of inter-particulate pores. To start with, obviously the powders when they are compacted, they cannot be completely pores free. There will be some pores and free surfaces available, so is a process of sintering by sintering at a high-temperature.

What we do actually, or what are the changes that take place in the material is, they are strongly bonded to get transformed to a monolithic bond, a monolithic marsh with the removal of inter- particulate pores. So, in the sintering, one way of looking at sintering is basically removing inter-particulate pores, and making a strongly bonded material. They do not longer remain powders, but the powders gets with each other and make some strong chemical bond and that is how the process of sintering can be described. It may also be considered as a process through which small particles or a cluster of particles of uniform composition undergo changes in shape and size when heated to a sufficiently high-temperature is basically the effect. Whatever changes takes place, we have looked into earlier that there is a change in the pore structure. The pores are getting removed. This is also the same thing, but in a different angle.

There are particles or a cluster of particles of uniform composition. What has been added here is a uniform composition; undergoes changes in shape and size when heated to a sufficiently high temperature. So, that is also a process of sintering or can be called as the definition of a sintering. The complex phenomena in which several processes occurs simultaneously is not exactly definition, but what exactly happens, and how it can be described, but the final outcome is as mentioned above. So, it is really from these three points, one can see the exact definition of sintering is really not there various researchers or various engineers have looked at it from a different point of view and described the phenomena in their own ways.

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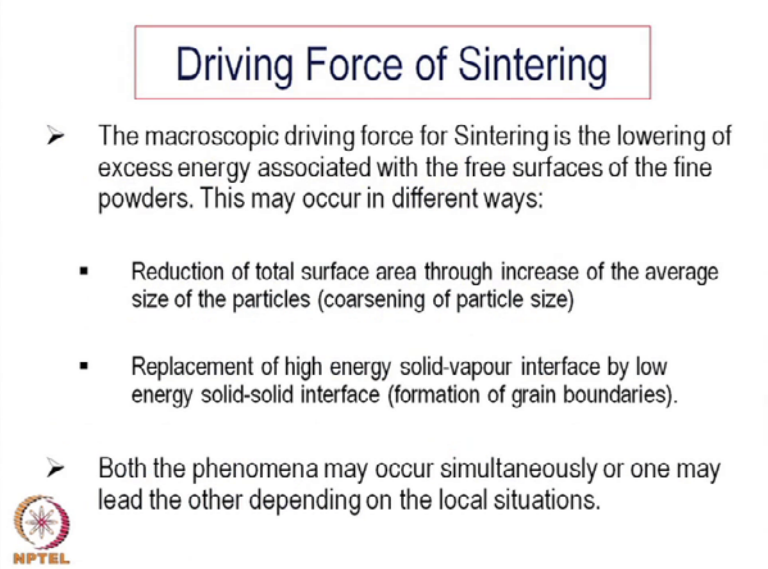

Driving Force of Sintering

- The macroscopic driving force for Sintering is the lowering of excess energy associated with the free surfaces of the fine powders. This may occur in different ways:
  - Reduction of total surface area through increase of the average size of the particles (coarsening of particle size)
  - Replacement of high energy solid-vapour interface by low energy solid-solid interface (formation of grain boundaries).
- Both the phenomena may occur simultaneously or one may lead the other depending on the local situations.

Now, why the materials get sintered? That means why the pores get removed and a loosely bonded compact what sometimes referred to as green compact, without heating to high-temperature. So, they have a very low mechanical strength, and not useful for all practical purposes, but when you heat them at a high-temperature, you do get a very sound material, a mechanically strong material, a non-porous material, and it is as good as any other materials like metals or plastics. So, it becomes a very sound material instead of a porous material. It loses its porosity, and the particles get bonded together, and a strong bond gets developed.

So, there must be some driving force, and this everything happens just by heating the material to a high-temperature. Something must be happening and there must be some processes taking place for which there must be a driving force or there must be a thermodynamic tendency for changeover to take place. So, if you like to look at what is the driving force of sintering, it can be mentioned in this manner. The macro macroscopic driving force for sintering is a lowering of excess energy associated with the free surfaces of the fine powders, any fine powder whether fine or cores does not matter. The powders have a high specific surface area. That means the area; surface area per unit weight is much larger than a solid material of the same mass or same weight. So, it has a very high surface area and all surfaces have certain amount of surface energy.

So, it is obvious that fine particles or fine powder do have a very high surface area, and surface energy term. So, when you compute or try to look at what will be the overall free energy of the system, the free energy of the system is dominated by the surface area. The surface energy term compared to a solid material powders or do have an extra energy in the form of surface energy. So, if an opportunity is given to the system, it will try to lower its surface energy and also the free energy of the system and therefore, the macroscopic driving force for sintering is nothing, but the lowering of the excess energy associated with the free surfaces of the fine powders.

Now, this may occur in different ways. This lowering of surface energy, the reduction of the total surface area, though increase the average size of the particles, nothing happens, no bonding takes place, but some materials become finer materials, gets quaver with each other, or the average particle size increases, but a strong bond does not develop. So, by that process also it can reduce the surface area and surface energy. So, this is one of the way to look at the system where the particle size is just growing about inter particulate bonding is not really taking place. So, this kind of a process if it happens, so if somebody takes just to lose powders, not compacted powders, or strongly bonded at the green condition, before firing we have said earlier that normally the powders are consolidated by applying pressure, or by some casting techniques. So, if that is not done, just the loose powders getting heated together there may be a particle coarsening, but though no mechanical strength really get developed.

So, that is one way by which the surface energy term can be reduced. The other possibility is the replacement of high energy solid vapor interface, by low-energy solid interface formation and that is nothing, but what we call the formation of grain boundaries. That means the particles are the fine powders when they are free. They have a surface area and that surface is nothing, but the solid to vapor interface. That means with air in this case. So, one can say solid gas interface. So, that is one kind of surface which has certain amount of surface energy no doubt and if that is replaced by a solid interface, that means the gas, the intervening gas is removed and the two solid particles comes in contact with each other, and form a strong chemical bond between them. Then the gas interface is no longer there.

So, there is no solid vapor interface. Instead, a new interface has been formed by way of formation of grain boundary. So, the solid two particles by some mean impact that is called the process of sintering. They come closer to each other and slowly there is an inter-particulate transfer of certain atoms, and we do get a chemical bond. So, that kind of bonding give rise to what we call the grain boundaries. So, the two crystals, in fact the particles can be considered as two different crystals. So, they will come close to each other and form the bond, so that the intervening vapor phase is not there.

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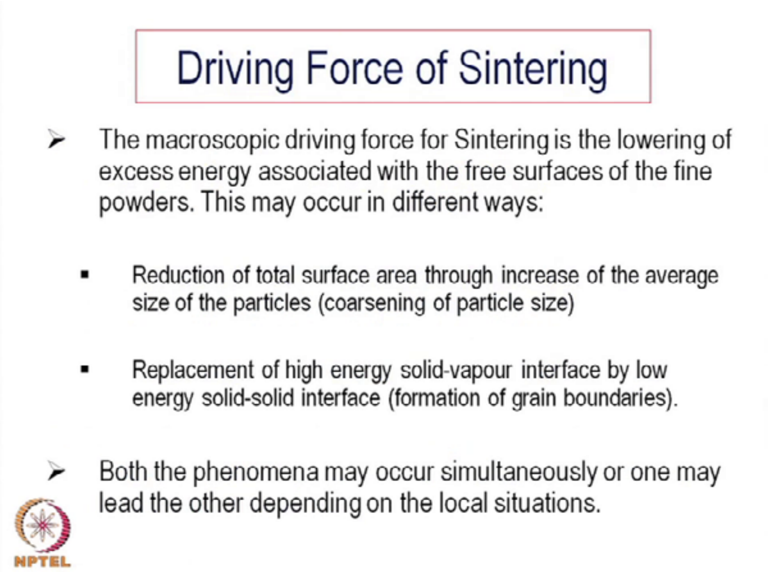

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So, the vapor, instead of a solid-vapor interface, we are creating solid interface. So, that is a grain boundary. It is also an interface. It also is associated with some kind of surface energy because the surface is very much there, but this energy term, the surface energy for the solid interface is lower than the solid-vapor interface. That is also the driving force. So, there is also a tendency to lower the overall free energy or the overall surface energy. The term and that surface energy term can be reduced by replacing the solid vapor interfaces, but with solid interfaces. So, that is another driving force for the sintering. Both, the phenomenon may occur simultaneously, or one may lead the other depending on the local situations.

So, locally whatever the situations are there, what kind of experimental parameters are there, depending on that, both of them can do then can proceed simultaneously, or one can proceed, one can precede the other, one can lead the others, but these are two primary driving forces why the sintering should take place in a powder compact of ceramic materials.

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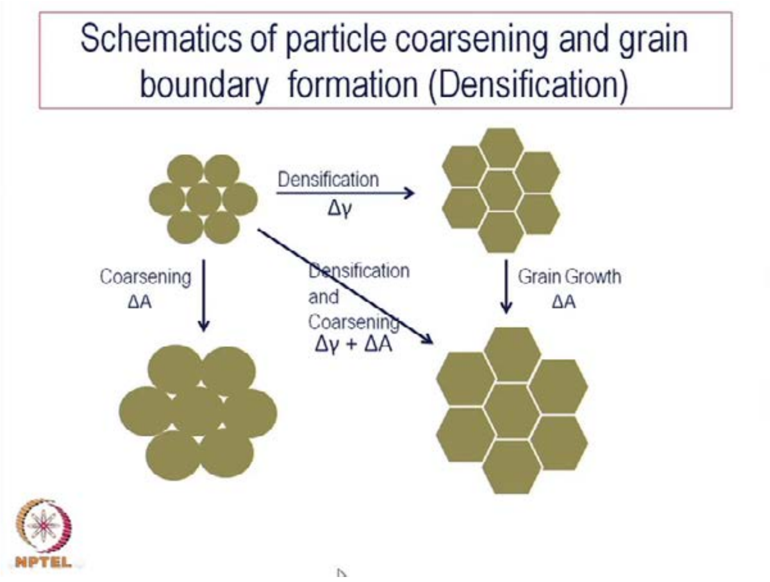

Schematics of particle coarsening and grain boundary formation (Densification)

Now, these are the pictorial representation of what we have just discussed. What is the driving force, what is coarsening, what is grain boundary and what is the overall process of sintering? Here this shows the particulate compact, their agglomeration of particles or the compacted particles. They are loosely bonded at those interfaces and this one can say that there is a solid-solid interface, but this amount of solid-solid interface is very low, very small compared to the solid-vapor interfaces. These pores or the boundaries of the pores actually provide the solid-vapor interface areas. Now, if this is the initial particulate compact, there are three ways of what can happen. If we heat to high temperature, one is very simple, one which we have described earlier that is the particle coarsening if we look back.

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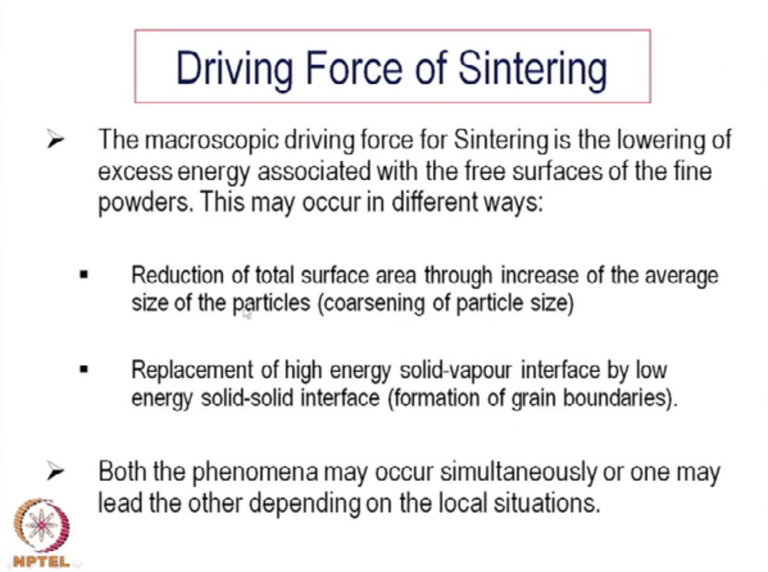

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This was reduction of the total surface area through increase of the average size of the particles. So, that is called the coarsening of the particles and this is given here.

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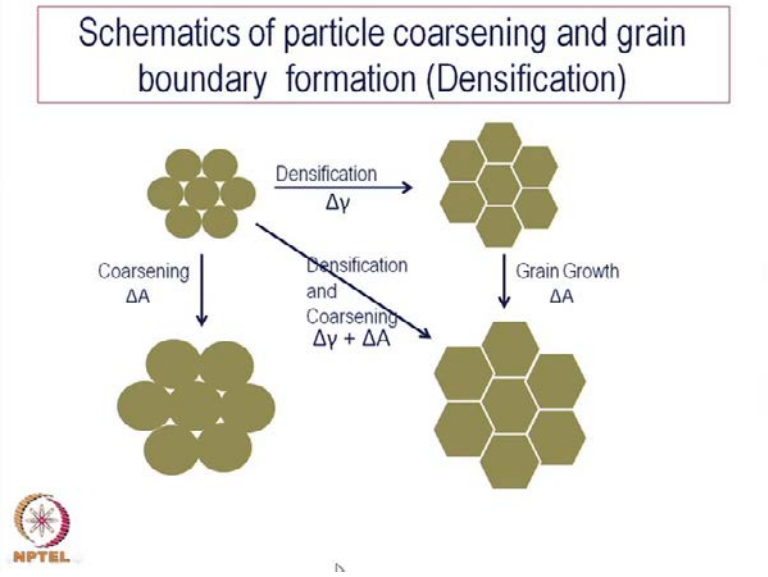

Schematics of particle coarsening and grain boundary formation (Densification)

So, the particles are there and each of these particles grows of course. In reality, although it has been shown that all the seven particles here have grown, but in reality that does not happen. Some of the particles grow at the expense of the others because the overall mass remains constant. We are not adding any mass to the system. So, the overall masses remain constant. So, obviously from mass balance, some of the particles will grow at the expense of the other, some others will dissolve. So, that is not shown here unfortunately, but basically what we are showing here is that particle size grows, but the contact area does not change much and there is no mechanical bond, chemical bond taking place. So, the overall surface area reduces because of the larger or the coarser particles. That is why the surface energy term reduces, but the strength of the material does not change.

So, this is what we call coarsening and delta A means, basically A is the area. So, there is a change in area, but there is no change in the surface energy term or whatever surface energy term we reduce is because of the area. There is no qualitative change in A in the types of the surface. The other alternative is what we call the densification. That means this kind of a loose powder changes configuration and makes a strongly bonded powder. So, they are now strongly bonded, the size and shape have changed and their greater surface to a particle to particle contact, or solid to solid contacts. So, these white lines are actually called the grain boundaries and the larger pores have gone out. So, this is more compact and dense material compared to this aggregate.

So, as a result of this we call it densification. That means pores have been removed. Because the pores have been removed, the average density has increased. So, the material become more dense and once the density increases and grain boundary are formed, a mechanical strength also is developed, so in this case, actually the quality of the surface changes. So, there is a change in gamma, the surface energy term, surface area or the specific surface energy changes because the nature of the surface are changed from primarily from solid to solid-vapor surface. Now, it is a solid- solid surface. So, this contact is actually solid-solid contact. So, this surface energy term is different. It is a lower energy term, a lower energy surface and that is a driving force for that. It may also happen, so happened that both coarsening and densification proceeds simultaneously.

So, densification and coarsening can proceed simultaneously and finally, you will see the size of the grains have increased. The size of each particle has increased from their size to the size, and also the contact area has changed the contact area from kind of point contact. Here, we have quite large surface contacts and these are once again grain boundaries had in this previous one here. So, here it was only one process happening, here another process is happening and diagonally, you have simultaneous processes of coarsening and densification.

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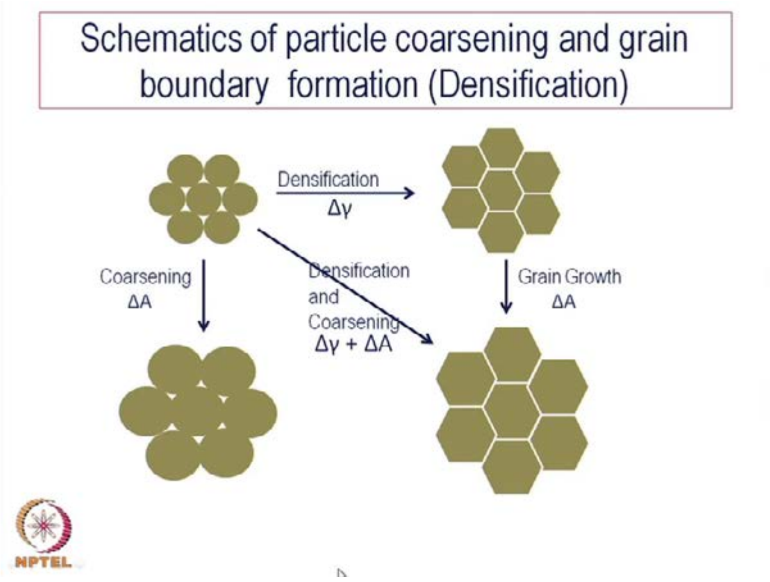

Schematics of particle coarsening and grain boundary formation (Densification)

Now, under certain circumstances, this can also happen. It can follow first step. In a step by step, it goes to the densification first, but without much grain growth. The grains are relatively small. It is almost like this the grain size or the individual particle size. Although, their shapes are changed, but their sizes, average sizes are more or less same, but afterwards if you continue to hit or provide sufficient activation energy to the system, these smaller particles may grow to the larger particles and that is what we call the grain growth.

Now, grain growth here once again the driving force is basically changing surface area. Not the surface energy term, but the surface area. Here, it is surface energy and surface area both are changing. So, this is also another possibility, but in principle, this is not so feasible because once these larger particles are there, the sintering itself becomes difficult and it may not reduce its pores so easily. So, until now less one goes to a very - very high temperature. So, once that coarsening takes place, the pore removal becomes quite difficult. That is the reason from this step is not really quite feasible, although it can come via this step to this step or directly from this step to a diagonal root. So, these are the different possibilities what exactly happens. We have considered two different phenomenons here. I mean, both of them are constituents of the overall sintering process. One is the coarsening particle process; another is the densification process with our interest to have more densification than coarsening.

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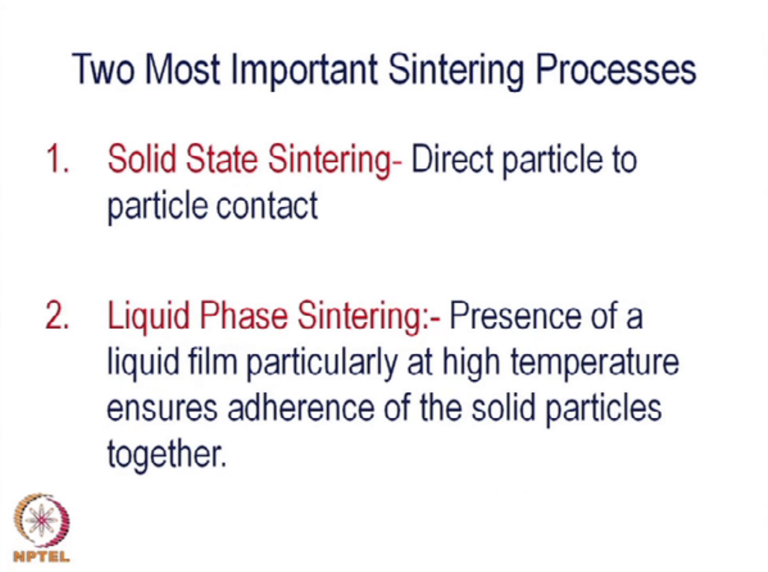

Two Most Important Sintering Processes

1. Solid State Sintering- Direct particle to particle contact
2. Liquid Phase Sintering:- Presence of a liquid film particularly at high temperature ensures adherence of the solid particles together.

The two most important sintering processes. Normally, we look at it from this point of view is solid state sintering. That means the direct particle to particle contact. There is no intervening of other phase except of course there is a vapor phase all the time present. Whenever there is a pore, there will be some vapor phase or gases space there, either air or something else. So, the very important mechanism or the sintering process is a solid state sintering, and that is really prevalent in most of the materials, of course not in traditional ceramics.

In traditional ceramics, of course the solid state sintering is not so prevalent, but in advance ceramics, it is quite prevalent, whereas there is a liquid phase sintering also. That means, in addition to the solid particles, we are talking about basically solid particle making bonds with each other, but we may take help of a liquid phase. Just like an adhesive, we do stick two different materials by an adhesive. So, here also a liquid phase can be used as a kind of adhesive. So, the presence of the liquid film particularly at high temperature ensures adherence of the solid particles together. So, that is we normally call a liquid phase sintering.

So, we take advantage of a liquid and normally more adherent, and they have good weight ability with the other solid surfaces and by choosing the liquid composition, one can have a good bonding. So, that is another a very simple or a common technique of sintering, and both the things of course both in both the cases, there is bonding between solid and solid because this liquid whatever we are taking advantage of at the high-temperature ultimately becomes a solid and the room temperature. So, that is another way of taking care of the sintering process. Basically, we want to strengthen the material and remove the pores.

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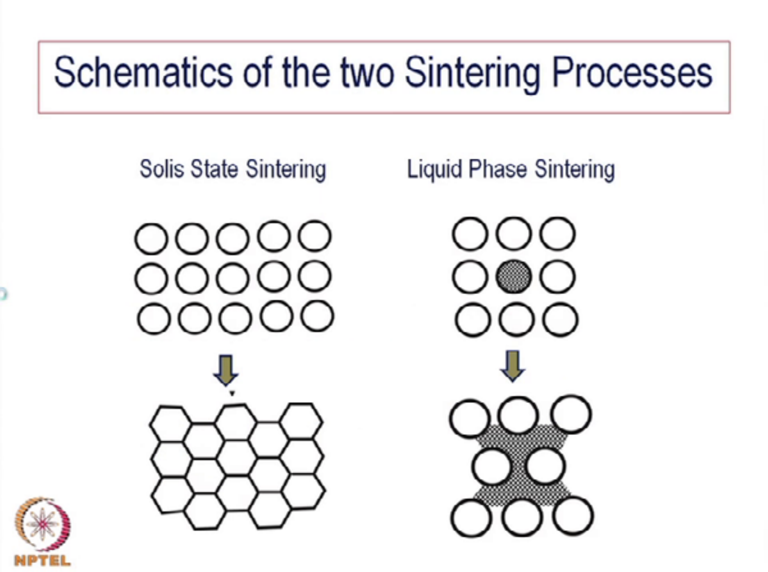

Schematics of the two Sintering Processes

Now, this is a pictorial representation of what happens in case of solid state sintering and liquid phase sintering. This kind of representation we have already seen. We have grain boundary formation. So, in a solid state sintering, basically the loosely constructed powder directly goes to grain boundary formation. We are not talking about any coarsening or anything like that. Coarsening may take place or may not take place, but finally the final structure should be like this. That means, there is a direct grain to grain contact or solid to solid contact, and overall area of the contact area should increase. So, that is the solid state sintering.

Here is a liquid phase sintering. That means we are taking some material within the green compact, some material which can form a liquid at a relatively high temperature. At room temperature, of course it is solid and it behaves like any other rest of the particles, but so far as this consistency is concerned, but at high temperature, this will melt first and this will not melt. This will still remain solid, but this will melt and form a liquid. So, a full of liquid forms in between the solid particles, and the pores get filled up with the liquid and also because of the high weight ability factor of this liquid, this bond is formed.

So, there is no direct grain to grain contact or solid to solid contact. There is an intervening film which actually takes care of the bonding and strengthen mechanically provides the mechanical strength. So, the mechanical strength in this case will of course depend on the mechanical behavior of this bond phase. It is a kind of bond between the solid particles. So, that is basic difference between a solid state sintering and a liquid phase sintering.

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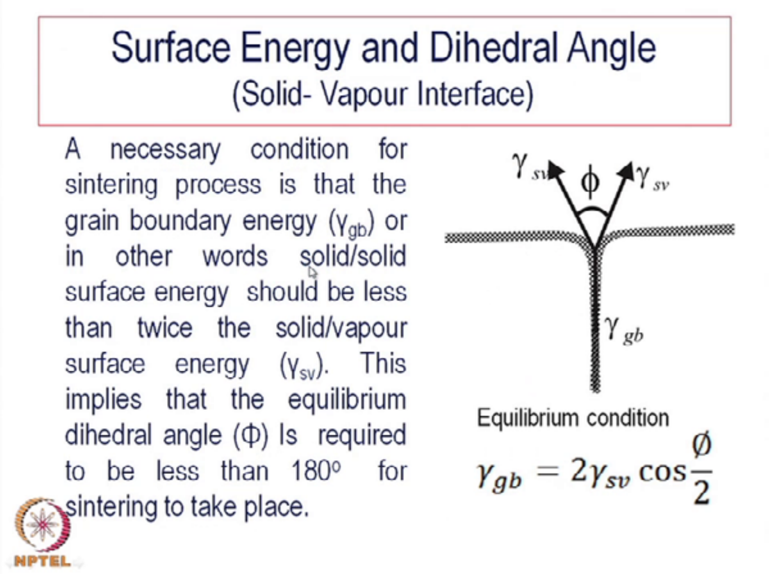

Surface Energy and Dihedral Angle
(Solid- Vapour Interface)

A necessary condition for sintering process is that the grain boundary energy (γ_{gb}) or in other words solid/solid surface energy should be less than twice the solid/vapour surface energy (γ_{sv}). This implies that the equilibrium dihedral angle (Φ) Is required to be less than 180° for sintering to take place.

Equilibrium condition

$$\gamma_{gb} = 2\gamma_{sv}\cos\frac{\emptyset}{2}$$

Now, we have talked about the surface energy term, and we have talked about both the solid vapor surface energy and solid liquid surface energy. Now, there is a concept of what we call the dihedral angel the surface energy and dihedral angel. Whenever there is a surface energy term and two surfaces coming in contact with each other, there is a dihedral angle. So, we will discuss just now a necessary condition for sintering process is that the grain boundary energy that is the solid -solid energy surface or in other words, the solid-solid surface energy should be less than twice the solid-vapor surface energy. It comes out from that particular geometry. This implies that the equilibrium dihedral angle which is five is required to be less than 180 degrees for the sintering to take place.

Now, what does it really means? We have A from this diagram. One can see this is a solid surface of course is not circular. It is not been taken as circular. Here is of course a curvature or radius of curvature, and there also another radius of curvature. Here, now this is in the midway of let us say the sintering process.When it is on, this surface is air are some vapor. So, this part of the solid, if we consider this is one particulate or one surface, originally everything was exposed to the vapor phase and slowly the part of the surface is coming or growing in such a way that the vapor phase is eliminated, and a direct solid to solid contact develops. So, this becomes our grain boundary.

Then, this is solid to vapor surface. Sea is still exposed to the vapor or the air and here also the same thing. So, this is one particle and this is another particle and slowly, this grain boundary gets developed, so that the vapor phase is eliminated from that region. So, if you look at the surface energy terms, this is the grain boundary. So, the surface energy term is gamma gb grain boundary and these are the two tangents. These are the two tangents at the interface or at the point of inter-section and the type of radius it has formed here. So, this is one tangent and that is another tangent, and along these two tangents, actually the solid vapor tension, vapor phases and the surface tension terms acts.

So, this is one tangent, this is another tangent and the angle between them is the ~~o~~ and that is called the trihedral angel. So, if you have two pair of tangents on the two surfaces at the point of contact or point of formation of the grain boundary, then that particular angle is called the dihedral angle, and one can see this kind of equilibrium. This is downwards, whereas these two are upwards, and this gamma gb is equilibrated with the two tensile forces term, and this is O by 2. So, the component along the perpendicular direction is actually gamma s v (cos) 5 by 2, so twice because there are two surfaces.

So, twice of that must be equal to the gamma gb. So, the angle will be determined by these two terms. The ratio of these two terms and as per definition, this grain boundary must increase and the other two must decrease in the sintering process and therefore says that it should be less than 180 degrees. O must be less than 180 degrees, so that this becomes around O by 2 is 90 degrees. It must be less. Normally, if material is around 120 degrees, so that is one precondition from the surface energy points of view. So, this values of the gamma gb grain boundary surface energy and the solid vapor surface energy, these two terms are certainly important to determine, whether the sintering process will proceed or it would not sinter at all. So, that is purely from the surface energy point of view. Some surface energy has a very important role to play in sintering process.

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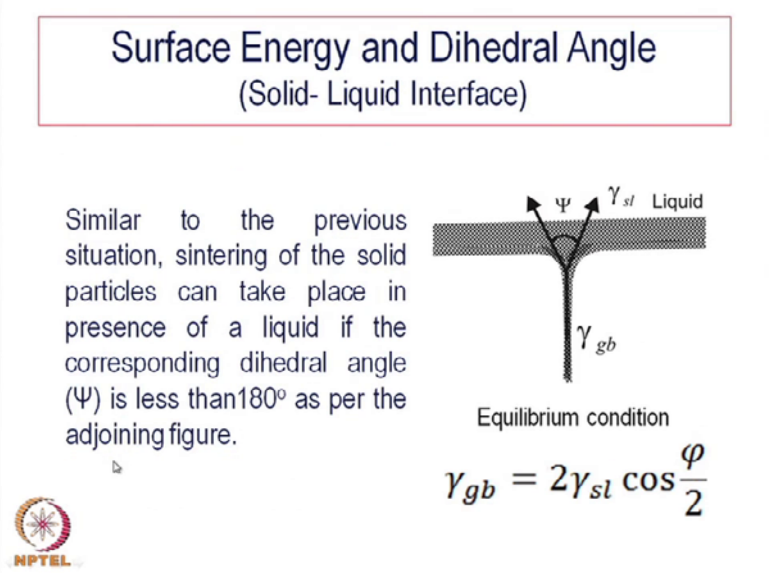

Surface Energy and Dihedral Angle
(Solid- Liquid Interface)

Similar to the previous situation, sintering of the solid particles can take place in presence of a liquid if the corresponding dihedral angle (Ψ) is less than180° as per the adjoining figure.

Equilibrium condition

$$\gamma_{gb} = 2\gamma_{sl}\cos\frac{\varphi}{2}$$

That was for solid state sintering. If you have a liquid phase sintering, then it is actually the surface is not solid to vapor, but there is a solid to liquid interface because there is full of liquid present and that liquid in contact with vapor, but the vapor is not directly in contact with the solid of our concern or interest. So, here also is the same kind of conditions applied and instead of psi, we call it (( )) is again the same condition applies here. Only thing the surface energy term here is gamma s l. The gamma gb is the boundary. Once again, once the grain boundary has formed, here we are still assuming that although the liquid is there, but in this case, it is not liquid forming the grain boundary phase or there is no film of liquid along the grain boundary.

So, this is slightly different concept than the liquid phase sintering which we have used earlier or we have defined earlier. The liquid phase sintering you have a film of liquid, but here in the pool of liquid, ultimately the liquid is not along the grain boundaries. Grain boundaries form on own. It is a solid-solid interface and it is not a solid-liquid-solid interface. So, it is basically a solid-solid interface, but growing out of the solid-liquid interface. Solid- liquid interface gets eliminated, and solid-solid interface are getting created just like in case of solid state sintering, where solid vapor phase interface is getting eliminated and solid-solid interface are created.

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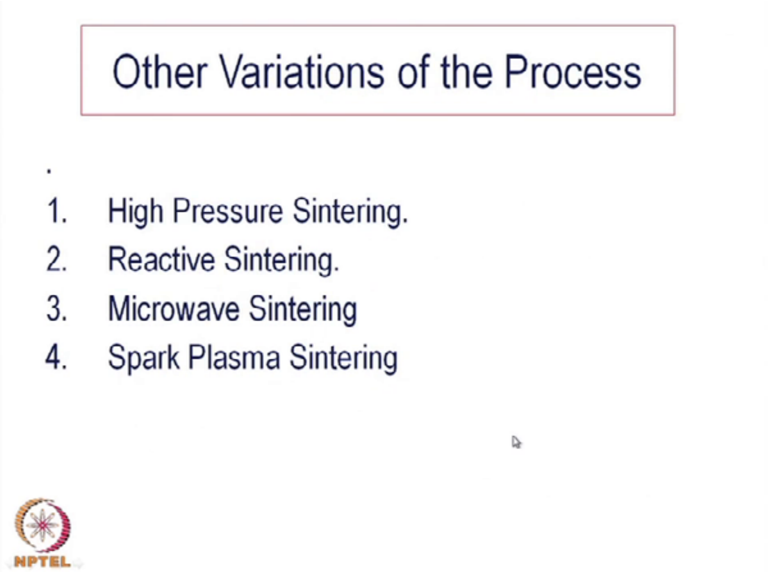

Other Variations of the Process

1. High Pressure Sintering.
2. Reactive Sintering.
3. Microwave Sintering
4. Spark Plasma Sintering

We have just discussed two different techniques, two most important techniques which normally occur in different materials. One is solid state sintering, the other is liquid phase sintering in presence of a liquid, and of course there are different variations in addition of the liquid phase sintering. Also, we may discuss later on what are those variations, what kind of liquidity is it, a liquid it is not so reactive liquid and so on. In addition, you have few more types of sintering, where some of the parameters are slightly different. For example, high pressure sintering.

Well, what we have discussed earlier is basically an atmospheric sintering. Although there is a presence of vapor, but the vapor is present in atmospheric condition. So, it is not really one can say it is a pressure. Sometimes, it is called pressure less sintering, but one can also use high pressure, gas pressures at high-temperature, so the reaction or the sintering process can take place under high pressure of gas pressure. So, that is called high pressure sintering. We will discuss briefly later on, just mentioning here what are the other variable variations possible, and reactive sintering. Primarily this is not a pure sintering, but a combination of chemical reaction and sintering. Sometimes in presence of a liquid phase, it may not be in the presence of liquid phase.

So, there are chemical reactions between the reactants, between the different powders. So, it is not exactly the normal sintering. In normal sintering, we have assumed that the chemical compositions of all the powders are identical, but it may not happen. So, in some cases, we do have different powders of different compositions and that those different composition may have some chemical affinity towards each other, and that is not only sintering, but a chemical reaction is also taking place simultaneously and therefore, that kind of sintering process sometimes are referred to as reactive sintering. In addition, we have microwave sintering. The only difference here, of course is the mechanism of heating. The heating are different, the way the product or the compact is heated to high-temperature is completely different. This we will discuss later on.

What is the advantage or disadvantage of microwave sintering? Every material cannot be heated by a technique of microwave by applying or exposing it to microwave. There are certain dielectric characteristics required for microwave sintering. So, if those characteristics are met, microwave sintering is one of the very good sintering heating processes. So, by that heating process, one can get sintering because the heating is one of the pre requisites of sintering spark plasma sintering when it is a relatively new technique, where you apply certain pressure and also, at the same time apply a very high dc voltage, so that at the local level, there are minor sparks generated. So, the temperature goes very high, particularly at the surface of the particles because of the high surface energy. These sparks are basically generated at the surfaces and therefore, one can have a different kind of sintering or the surface reactions at those interfaces we will discuss briefly at a later stage.

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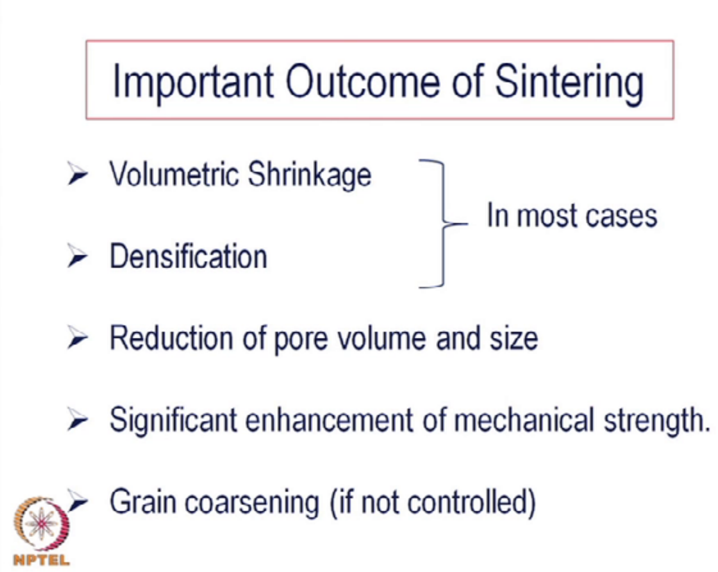

Important Outcome of Sintering

- Volumetric Shrinkage
- Densification

In most cases

- Reduction of pore volume and size
- Significant enhancement of mechanical strength.
- Grain coarsening (if not controlled)

Well, having looked at what are the different preliminary mechanisms or preliminary variations of the sintering process and what the driving force are, let us look at what is the ultimate outcome of the sintering process at the end of the sintering process, or at the end of exposure to high-temperature. What do you end up with these are few things which actually happened as a result of sintering two things of course are very common. One is the volumetric shrinkage, another is densification. So, volumetric shrinkage means the pores getting reduced. So, the particles becoming coming closer to each other as a result, there will be a volumetric shrinkage. Whatever the compact volume was there to start with, after sintering the size, certainly should be smaller and consequently, the volume gets decreased. So, the mass remaining same. We have a densification process. So, these are the two most important things happening.

In most of the sintering processes associated with that, there are few others reduction of pore, volume and size. Once again the volume gets shrunk. So, the pores are actually reduced, not only the overall pore, volume, but also the size and that also has an important consequence as far as the physical properties of the ceramics are concerned. So, you have a reduction in the pore volume as well as size of pore. Average size of the pore decreases, and that is very significant enhancement in mechanical strength. That is another very important in fact one of the basic purposes of sintering. The material is to enhance the mechanical properties, otherwise the powder compacts are very weak and they cannot be used for any practical purposes. So, that is another thing we expect at the end of the sintering process.

Significant enhancement of mechanical strength, other thing particularly at looking at the microstructure or what happens to the powders. The grain coarsening if not controlled. Grain coarsening and particle coarsening is slightly different. We have seen particle coarsening without sintering. Here, the grain coarsening is basically grain growth. So, the grain growth takes place at a high temperature after the basic sintering process is over. So, the particle-particle contact has already taken place. So, the contact area have increased, but even after that if you allow it to expose it to high thermal energy, there is further reduction in the surface area. Even the solid-solid interfaces gets reduce. The area of the solid-solid interfaces has reduced. That means, each individual crystals grow to large extent and that is called grain growth. Sometimes, the grain growth is good for certain purposes, but for many, particularly for mechanical properties, grain growth may not be always good. So, you need to control that size, also that aspect. So, these are important outcome of the sintering process.

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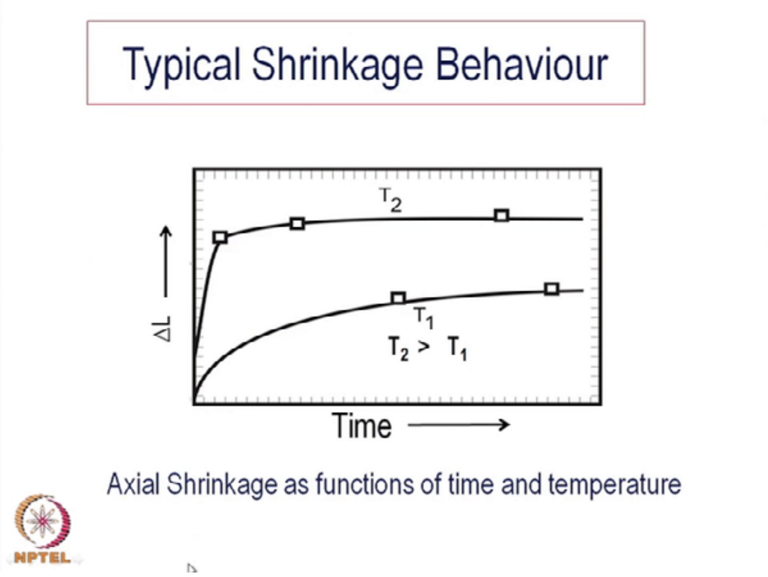

Typical Shrinkage Behaviour

Axial Shrinkage as functions of time and temperature

Oh, that we have already considered. I am sorry. These are something again a schematic representation of what kind we have already mentioned that there is a volumetric shrinkage, and this is just a time verses shrinkage curve or the shrinkage verses time curve. It is an axial shrinkage. Linear shrinkage is not volumetric shrinkage and two are related quite obviously. So, this is a linear shrinkage which is normally measured. Volumetric shrinkage is basically computed from the linear shrinkage data. So, one can see, initially there is a little sharper rise. That means, the slope is little large. So, there is a first shrinkage took place initially, but then slowly with time, it taper soft and becomes almost constant. So, after some time, this shrinkage is no longer taking place further and it comes to a constant few value.

So, if you increase the temperature, there are two different temperatures. One is relative low temperature, another is high temperature, and the curve itself says that at high temperature, the initial rate is very fast and then taper soft and becomes almost constant over independent of time after sometime, but if you take a low temperature, then it continues for a longer time, and then finally, of course it comes to a constant value. So, this is normal behavior of any ceramics and how the typical shrinkage proceeds with time and temperature.

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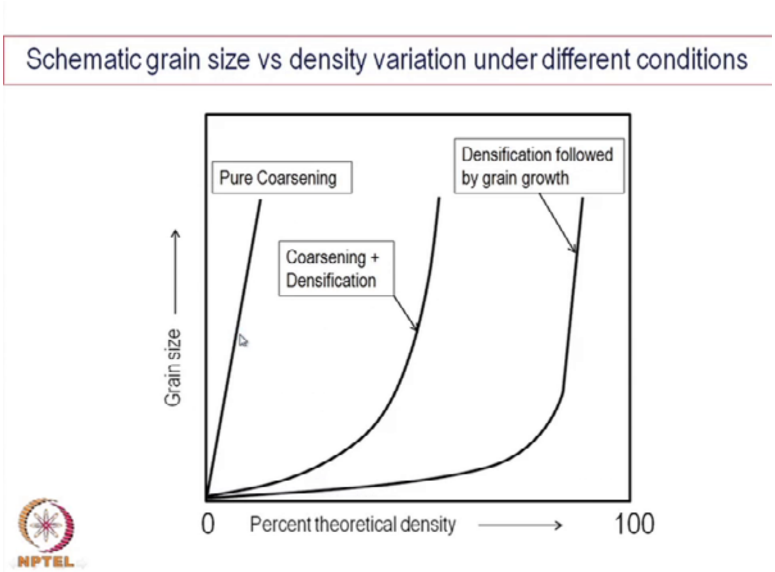
Schematic grain size vs density variation under different conditions

This is a schematic grain size versus density variation that was with time. Here, it is not time, but as a function of the percentage shrinkage which has taken place. Percentage shrinkage takes place and how the grain size changes? Now in this case, of course there may be three different possibilities. We have discussed earlier in the very beginning pictorially what happens to the powders, either it may coarsen. That means the powders can grow themselves without any sintering. The powder can get sintered grain boundaries formed, and then later on grain growth can take place. Here, this is something little intermediate. That means, coarsening and densification proceeds more or less simultaneously. In that case, we have three different curves or three different effects you can get where the grain sizes is concerned.

Now, grain size initially is a starting material is relatively fine grain or there is hardly any grains to form, but as the theoretical density increases, that means more and more sintering takes place, theoretical density means you are eliminating the pores. So, you were increasing mechanical strength also which is normally directly proportional to each other. So, the percent theoretical density means initially 0 percent to about 100 percent densities, may be 100 percent dense materials.

So, you have three different situations as I mentioned coarse, coarsening plus densification. So, there is a gradual growth of grain size as we move, as the density increases, as the pores get removed more and grains also grow simultaneously. So, this is more or less a preferred situation, where both the things should be controlled in a manner that they grow with each other. This is not a very good situation, where theoretical density has not grown, but the grain size has grown very fast and as a result what will get is a very poor mechanical strength here. So, this is not preferred, nor this one neither this one because high grain growth leads to many different problems. Primarily more brittleness and we will see later on how the mechanical behavior changes as a function of grain growth.

So, normally grain growths are not a very preferred situation except under certain situation if you are talking about a transparent ceramics and so on. Sometimes, grain growth is preferred, but their mechanical properties are not that important. It is more optical properties which are of interest to us. So, there one can allow grain growth, but normally for most of the purposes, this is a preferred situation where coarsening and densification grows simultaneously. Well, so that is more or less a half of the sintering lecture we have completed. Rest half will take it up in the next class.

Thank you.