

Nanostructures and Nanomaterials: Characterization and Properties

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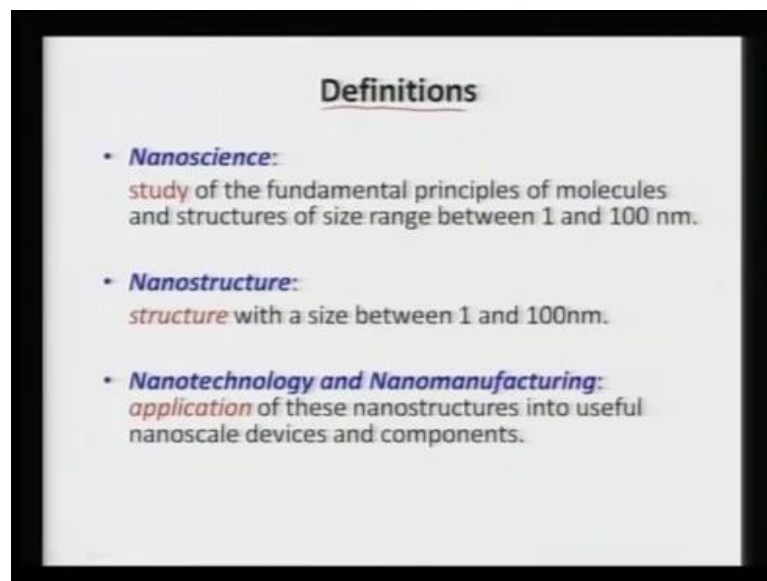
Indian Institute of Technology, Kanpur

Lecture - 34

Nano materials Science and Nano manufacturing

Recently, a very jazzy term of nano materials has come into existence and, because of that all the research and funding has been directed to nanomaterials science and nano manufacturing. So, we will in this lecture we will learn about what is nano material and how the science is dictated by various phenomenon and how we can impart this knowledge into nano manufacturing.

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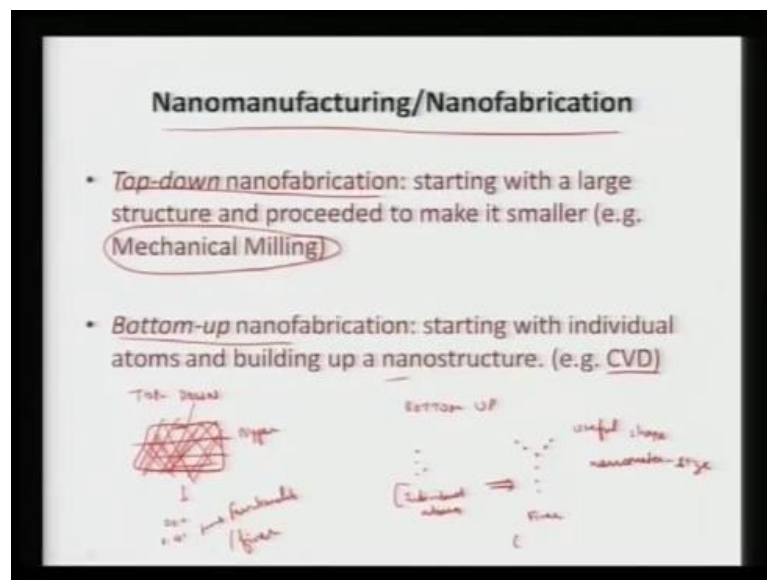
So, there are a couple of definitions, which we need to understand before we progress into nano manufacturing. So, first thing is nano science, nano science is the study science study, so nano science is the study of the fundamental principles of molecules and structure, which lie between size range of 1 to 100 nano meter. Correspondingly, we should not confuse it with nano structure, nano structure is some sort of a structure with some size between 1 to 100 nano meter.

It can possess variety of shapes it can be tubular, it can be quantum dot it can be a sphere it can even be a conical or pyramidal shape. It can be a nano flower any entity, any

structure which is a size range between 1 to 100 nano meter, these comprising what we call nano materials. Then, there comes a term nano technology and nano manufacturing once we have all these nano materials we need to have some sensitive instrument which can track the nanoparticles.

It can over lay them into forming certain bigger entity, so nano technology is an art or application of these nano structures into some useful shapes which can make either components or devices to take advantage of these nano materials So, we learn nanoscience is the study of this materials, which range between 1 to 100 nano meter, nano structure is some sort of a structure which is sized in between 1 to 100 nano meter.

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Nano technology or and nano manufacturing is nothing but the art of applying this nano material into some useful components or devices. Once we have those nano particles, we want to manufacture them into some useful shapes, so there can be two different techniques of nano manufacturing or nano fabrication. It means producing a device or component which is a size range between 1 to 100 nano meter. There is one term called top down nano fabrication, this becomes a necessity when we have a bigger particle available with us, any any bigger entity available with us.

So, we start with a much bigger material it can be a couple of micron meters, it can be it can be millimeters and so on, and then we start breaking it down into certain size range when it comes down to 1 to 100 nano meters. So, we try to make it smaller and smaller if

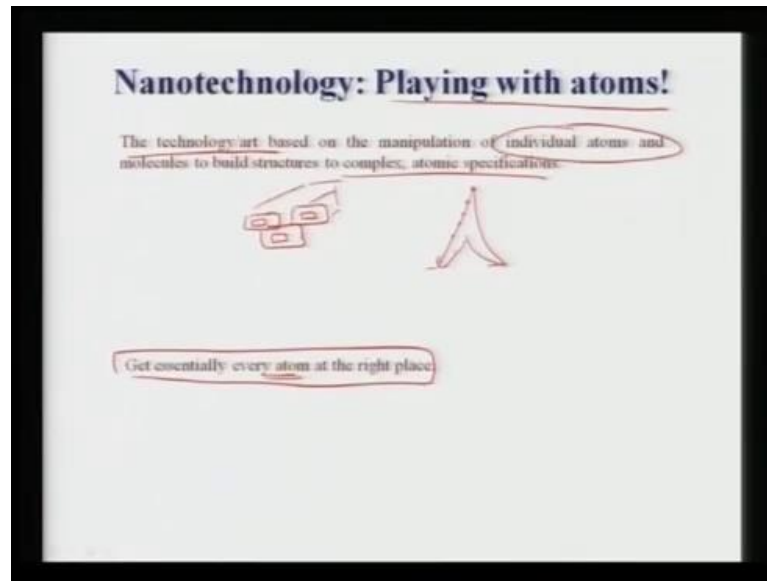
we take a bigger particle, we can start milling it, we can start machining it, we should start impacting it so that it comes into very fine powder particles. Now, we are making it much smaller, so we start with a bigger component and then we start going into making it into much finer.

Second one is the bottom up nano fabrication in this case we start with individual items or molecules, so we have entities which is much smaller than nano, because all the size range of atoms and molecules is angstrom regions angstrom regime. So, we start building up those materials or the atoms individual atoms or molecules into a bigger shape. So, we can see top down we start with a bigger component, we start fracturing it or breaking it down until we get a nano crystallite in the material or nano material out of it. So, this breaking it down some very fine pieces which can again have some function, so we had some bigger chunk.

Now, we have some very finer chunk and that is nothing but top down approach in bottom up approach, we have very fine individual atoms. Then, we can put them into certain structures certain shape to give a functionality to it, so we get much finer, but certain functionality to it. So, in this case we have individual atoms they go into arranging into some useful shape or size. That is what we can see in a nano manufacturing, we have two approaches top down approach, we start with a bigger component. Then, we go into forming a nano material and then bottom up approach in this case utilize individual atoms or molecules to synthesize something which is at nano scale.

So, in this case certain examples of nano approach can be nano mechanical milling, we start milling a bigger component and bottom up approach can be chemical vapor deposition or physical vapor deposition. In this case, we utilize individual atoms to start depositing on a substrate to form a nano coating.

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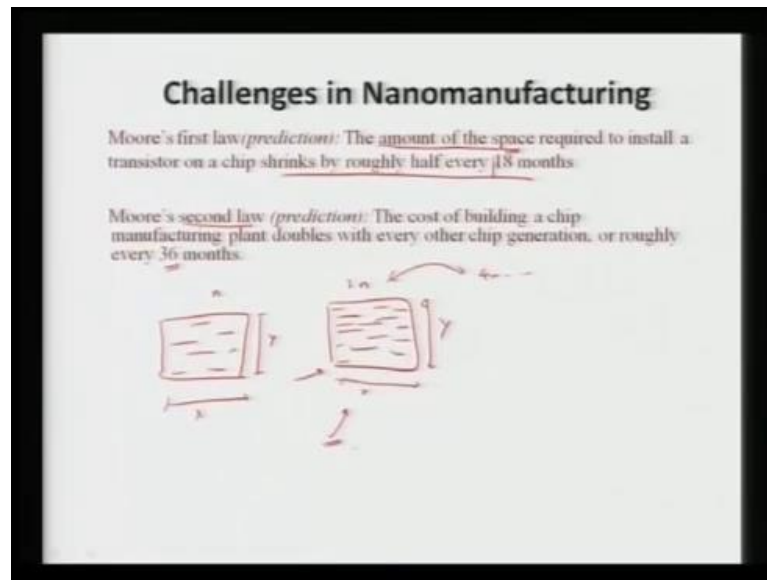


Again, nano technology or playing nano technology or synthesizing nano materials into something useful shape is nothing but playing with atoms. Many of us have played with legos, in that case we take each and every block and start constructing it, so we get either buildings or dolls or some useful shape. So, the similar way this technology or art is based on manipulating individual atoms or molecules and then go onto making some very complex shapes or structures with defined atomic specifications. So, we have certain blocks we can go on to making certain cards out of it or certain structures out of it by placing each and every block into a specified locations to make a bigger or complicated structure. In a similar way, we start playing with lego, we take individual blocks either to make individual cars robots dolls any bridges or something like that, so it is nothing but getting essentially every item at the right place.

So, we need to take and be able to manipulate each and every atom and that creates a difficulty, because there is very hard to manipulate each and every atom or a molecule. So, we need to have very sensitive instrument which can first of all see those nano particles or these atoms individually be able to pick them and then place them into a right location. So, that again provides as a challenge in order to see those nano particles or those individual atoms manipulate it have a manipulator sort of a sub nano manipulator to pick up these individual atoms and molecules and place them at the right place.

Again, because of the instability of atoms, because as soon as they are putting a individual atom that may not be stable, so again the stability of atom may come into picture in nano technology.

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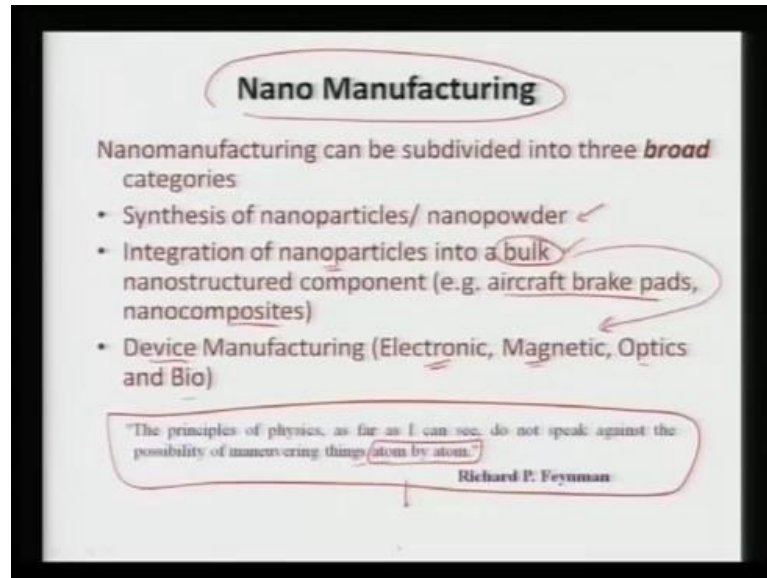
There are certain challenges in nano manufacturing like Moore's first law, it has predicted that the amount of the space, which is required to install a transistor on a chip will shrink roughly by half every 18 months. It means that we need to double the electronic components which is resistors transistors capacitors everything on a smaller chip, we need to double its density every 18 months.

So, that that is what is says the amount of space required to install a transistor on a chip has to shrink by roughly half every 18 months, so the density has to increase dramatically over time. Correspondingly, there is a converse or a Moore's second law, which says the cost of building such a chip will also double every 36 months, because if you are if you are making a certain chip and it has transistors capacitors everything and this density has to double. We need to somehow enhance the capability of being able to install so many components in the certain limited dimension of the chip.

So, if you have a dimension of x and y and we had a density of n in this case it has to increase by twice at least, because the density has to increase, so if you are increasing the density we have to have at least $2n$ and that keeps going to $4n$ and so on. So, that is if I need to synthesize or manufacture this one, so the cost also will start enhancing

dramatically, because we are increasing the overall density the overall technology has to change. So, more number of transistors and such components can be installed in a similar dimension chip and thereby it also increases the cost of the particular chip.

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Again, the nano manufacturing it can again be sub divided into couple of broad categories, first thing is if you want to manufacture something say if you want to manufacture nano component the thing is we need to have nano particles available to us. This can be consolidated later on, so first challenge, first thing is for synthesizing a nano material or a nano device or a nano component. First thing is we need to have a pure nano particle or a nano powder and then we need to integrate these nano particles or nano powder into some bulk nano structured component. So, from nano particles we go onto making certain components which can be such as aircraft brake pads or other some nano composites. So, there can be individual components, which should be made from these nano particles and third stage is we consolidated all the components into certain device.

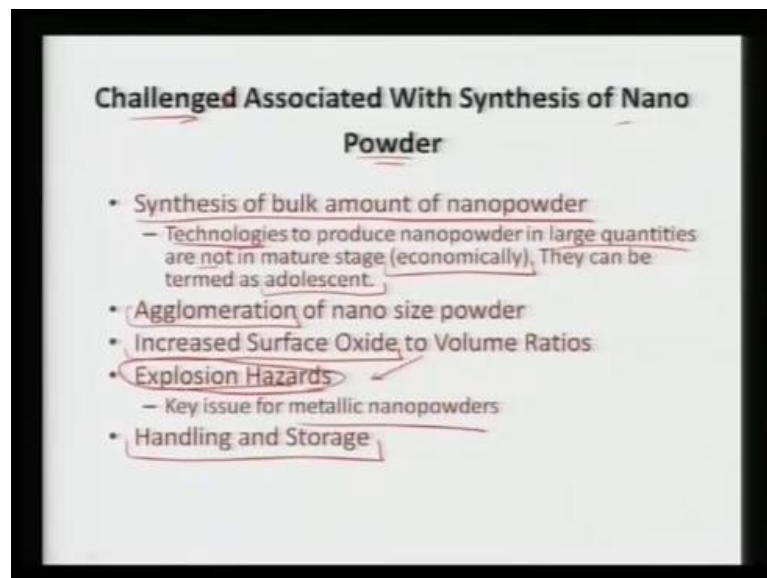
Those can be electronic devices magnetic devices optics or even biological devices bio medical devices. So, we can see nano manufacturing it is not a single step process, but it requires first the processing or synthesis of nano particles and again their purity their size their distribution may be also of concern. Then, integration of these nano particles into bulk nano structures there are always some problems which are being imposed by these

nano particles, because of their size, because of their high surface area. Even their handling there can be certain problem in synthesizing them into some bulk components and again after they have been composed as a bulk component making them into certain device.

So, they can be sensitive into some stimuli or serve as a structural material with exposure to certain temperature or mechanical strength or overall properties of nano particle can themselves change. So, overall functionality of this nano material or nano components can also change once they are composed as a device. So, again these are also certain concerns in nano manufacturing, but as Richard Feynman has said basically for the electronic chips that principle of physics does not speak against the possibility of maneuvering things atom by atom.

So, if we can manipulate atom by atom, then we can definitely achieve the class which we call nano material, we can achieve any functionality by somehow manipulating atoms on a individual scale and then making them into certain devices or components. So, let us now try to tackle each and every challenge, which is being faced at individual level.

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So, the first let us start with the challenges which are challenges with are associated synthesis of nano powder, so first thing is synthesis of bulk amount of nano powder if we are trying to pick atom by atom and then try to make another powder out of it. So, even to make couple of grams to make nano powder, we require months, because the process

is very slow. So, first thing is synthesizing nano powder in bulk scale itself is a challenge, so we require certain technologies which can produce these powders in bulk. So, they can synthesize in large quantities and also it has to be economic, otherwise if it becomes highly costly, the cost may not be supporting its commercial viability.

So, that is what is required some technologies which can produce this nano powder or nano particles in bulk and right now these technologies are still in adolescent stage, they still need maturity. Even when we have manufactured those nano powders, they have a tendency to agglomerate, so because of their high surface area to volume ratio, they have a tendency to agglomerate, because of their high surface area they tend to minimize their surface energy. So, they come in contact with the nearby nano particles and in turn they tend to agglomerate, so agglomeration is the inherent tendency of these powder particles, if we take a metallic nano powder particle, they also have a very high tendency to oxidize.

So, they can form increase surface oxidation, because of the high surface now exposed to the environment or the atmosphere so they come in contact with oxygen and they tend to oxidize very easily. So, it is very hard to even produce a pure metallic powder, because they tend to form oxides concurrently if the nano particles are metallic in nature. If they are tendency to oxidize so rapidly, because of their high surface area, it can be even very explosive. So, there it can create even explosion hazards, probably you might be aware that the aluminum is used as a fuel in the rocket engines, because of its inherent oxidation tendency and nano aluminum powder particles. They can create so much energy that it can impulse provide an impulse to the rocket so that it can achieve very high speed.

So, they can again have explosion hazards, so the high surface area which is associated with the nano particles and that becomes the key issue for the metallic nano powders. If you want to make a component out of metallic nano particles, first thing is they then to oxidize and the second thing is they can be highly explosive, if they come in contact with the atmosphere. So, for handling all this, we need an inert atmosphere where we can handle them as well as we can start synthesizing them.

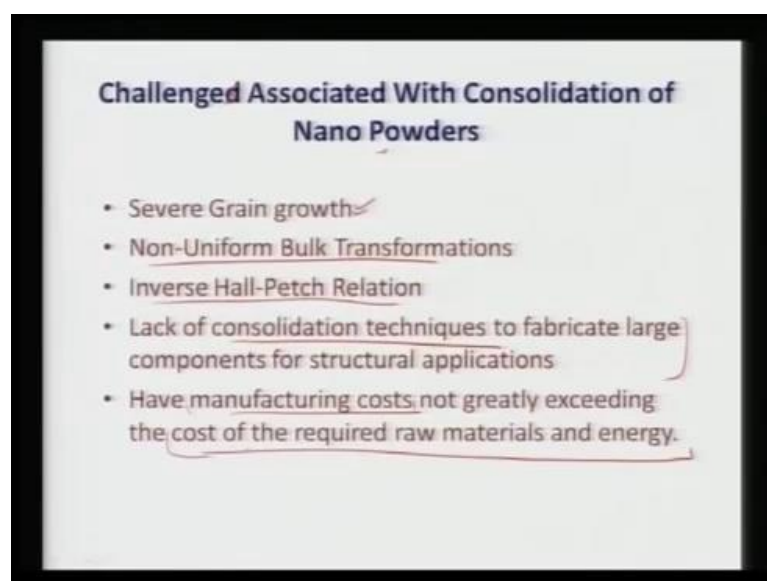
Then comes the problem of handling and storage, because again these nano particles, we need some space for storing them. If we had to create an inert atmosphere powder

particle powder used powder bulk, then it required much space. Then, it also becomes costly to store and handle these materials even while handling, if you are exposing them to atmosphere, it is creating surface oxides it also poses a threat of explosion, so we need to take care of all these concerns.

So, there are many challenges which are associated with the synthesis of nano powder, first thing is being able to produce bulk quantity and then avoiding the agglomeration of these nano sized powders and somehow try to limit the surface oxidization. This is inherently there in the nano powder particles, it can also create explosion hazards and also we need to minimize the cost and the handling and storing issues, which are there with the nano powders. Again, one more concern with the nano powders is the bio safety, because the nano powder particles, if they go in our lungs it is very hard for them to come out.

So, we need proper safety protocols which are required like the person has to be in the proper safety protocols wearing safety gadgets all the mask, which will not allow nano particles to seep through the filters or respiratory filters at the same time they should not get in touch with our skin something like that to avoid any irritation or their inducing. Oxidation affects to our body, so there are many challenges which are associated with nano powder particles and all of these are listed here.

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Now, coming to the second stage in terms of processing them, so once we have the nano powder particles and we want to consolidate them into certain device or components. So, there are certain challenges, it is again challenges associated with the consolidation of the nano powders. The first thing is as soon as we expose these nano powder particles to a high temperatures, it undergoes severe grain growth overall identity of the nano particles is lost. If it starts growing it becomes enhanced the size of the nano particle enhances, it has lost the characteristic of the nano particle.

So, we need we want to avoid the severe grain growth which is now inherited in the nano particles via conventional processing. Second thing is it also can undergo very non uniform bulk transformation, but the surface is highly active, it might be much more prone to surface reconstruction as well as transformation.

So, it can render very non uniform bulk transformation, apparently the mechanical properties of the nano powder particles will vary drastically up to a certain size range. If you start reducing the grain size, you will enhance the overall hardness and the strength of the material, but after a certain size range say below 10 to 15 nanometer. If we go much below the grain size of 10 to 15 nano meter there is not enough grain area to support the pile up of dislocations.

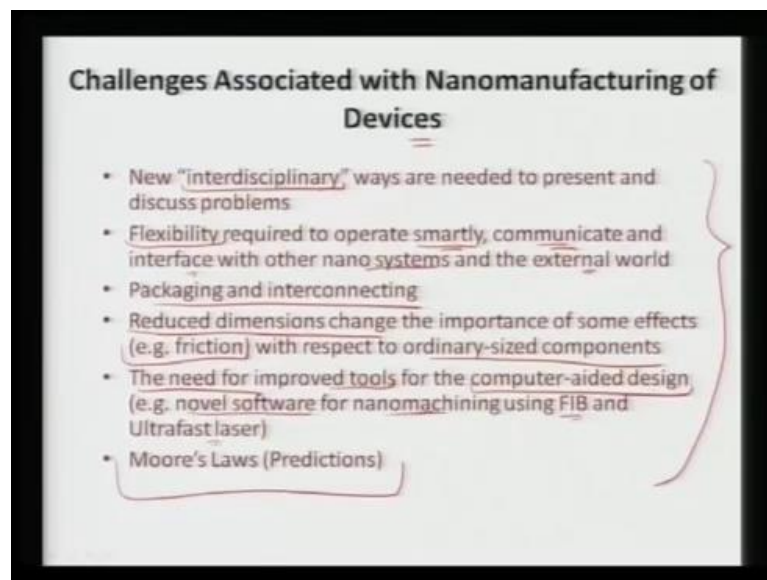
So, in turn it starts reducing the overall strength of the material that is called inverse hall petch relationship, we still know conventional reducing the grain size and enhances the strength of the material. In nano material, the problem can be inverse hall petch relationship, which means the strength of the material overall starts degrading with the decrease in the grain size. So, again that may not be good for the longevity of the nano device or the nano component.

Again, there exists a lack of consolidation techniques to fabricate large components till now the research has been directed to very small pieces or discs of these nano components which can go as may be couple of millimeters or centimeters in that. That scale, the research has been directed and there is no commercial technique available to make bulk nano structures. Only, a limited of such techniques is available, but there is a overall limitation of synthesizing this nano particles into some bigger entities and again.

So, that again is a challenge associated with the processing and for that the manufacturing cost should also not basically exceed the cost of the required raw material

and energy. So, in order to maintain a balance and so that it can be easily commercialized later on, so manufacturing cost also be limited and it should be well below the cost of the raw material itself that is again a challenge for the processing of nano material.

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The challenges associated with the nano manufacturing of devices, if we want to create a device or a or a nano device first thing we need is interdisciplinary approach, because it requires knowledge of materials knowledge of processing. Also, it is going to be used electronic industry it is a bio medical industry or electrical industry, so we need to have a interdisciplinary approach in terms of the material itself, what are the physics which is governing the overall functionality and materials processing. Again, the exact point where we are going to use this particular device, so we need a combination of knowledge of these all areas to be able to make such a device.

It also requires flexibility to operate smartly and also communicate and interphase with other nano systems, because once the device itself is nano, it definitely needs to has some sensors or some connectors which are again nano in size. Then only, it makes sense to make this use this nano devices, so it requires a very good connectivity with those systems so that it can communicate and interphase with them and it can send the required information to the external world.

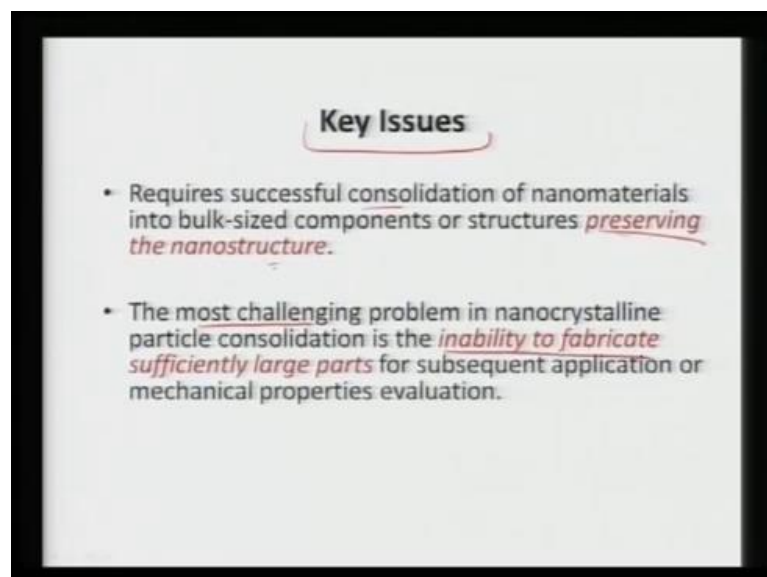
So, in terms of packaging and interconnecting again it becomes a challenge then the reduced dimension also induce some different sort of responses with respect to the ordinary sized components.

In this case, reduced dimensions result enhanced friction in the nano devices, because their low very low size. Once they come in contact with other devices, the overall surface area is so high that the overall friction among the devices or the moving part becomes extremely large. Then, it requires the need for improved tooling or computer aided design for their design. So, we utilize novel software for nano machining and focused iron beam and ultrafast laser for certain machining as well and again the Moore's law, they to maintain with the Moore's law or the prediction.

There is always a thrust which is always there to go into miniaturizing all these components so there is again certain pressure to be able to reach this particular level to be created by the Moore's law. So, we can see there are certain challenges that we want to go for very lighter and lighter devices and components

So, we need to keep the pace with it in terms of manufacturing it, so require interdisciplinary ways we require much more flexibility. We require that they can communicate or interphase with the adjoining external world, be able to reduce the dimension and come up with some improved tooling such as focused iron beam or even laser ultrafast laser to be able to keep pace with the technology.

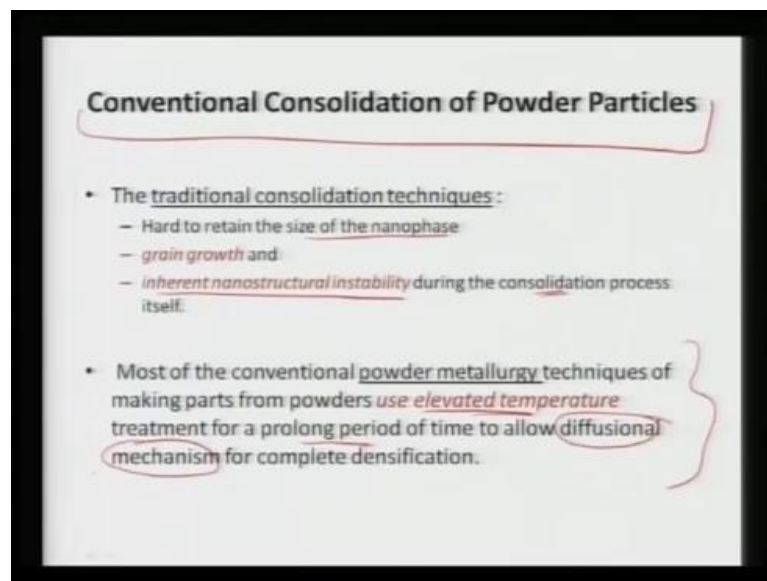
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So, there are certain key issues Which are existing in this nano materials first thing is the preservation of nano structures for successful consolidation of nano materials into bulk sized components. We need to preserve nano structures, so the properties of nano materials can be retained and secondly the most challenging problem in the nano crystalline particle consolidation is the inability to fabricate sufficiently large part.

So, we need a technique to make these nano particles into bigger components bigger or bulk or large components which can be of usable size. So, now we can make small small particles or devices which are functional, but it is very hard to create a functional bulk material or a bigger functional component such as chair or such as elevator. This can be made entirely of this nano particles, so the challenges in terms of enhancing the scale at which the nano materials are being synthesized into useful components.

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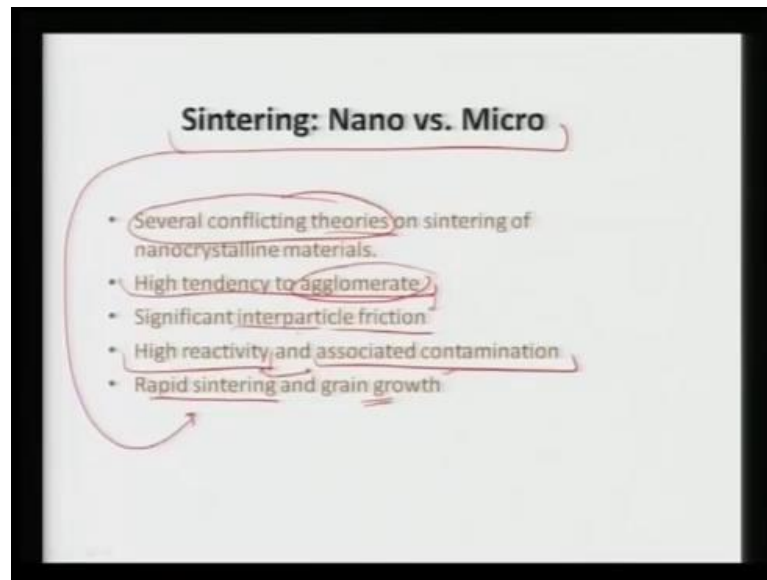


The conventional consolidation of powder particles has not been that lurid, because in traditional consolidation technique it is hard to retain the size of nano phase. The nano phase or the nano particles inherently undergo grain growth and again it can also lead inherent nano structural instability. So, nano structure may not remain stable even if there are certain processing techniques through which we can produce them, but they still remain instable during the consolidation process.

Even powder metallurgy it utilizes high temperatures or elevated temperatures for prolonged duration of time and that creates a diffusion mechanism. So, the overall

distribution of these nano particles, it becomes much more homogenous or it can also be it can basically go through or diffuse through the nearby phase. They lead to the non homogenous part can be basically not be retained at the interphase, so that is a problem with the powder metallurgy type.

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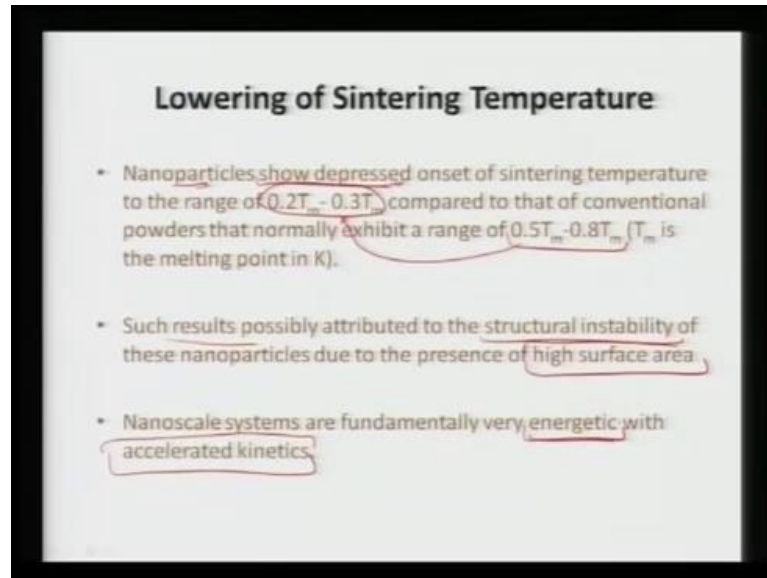
Again, the sintering of nano versus micro, so there are very conflicting theories how these nano crystalline materials sinter the conventional knowledge on sintering is very different. When it comes to nano, the overall sintering itself is very rapid and very different than what is being suggested for the bulk or the macro materials. Nano particles again they have very high tendency to agglomerate and there is one more problem with the nano particle is that they have very high inter particle friction. So, it is very hard to obtain enhanced density again there is very high reactivity, so because of that they nano particles also undergo high contamination.

The surface oxidation or grabbing of certain impurities from atmosphere or even from the overall nearby container, it can also react and grab some impurity and it gets contaminated on the sintering part, because of their high surface area. It also can undergo rapid sintering and it also occurs, it also incurs rapid grain growth, so these are certain problems associated with the nano and micro sintering.

There are various conflicting theories that there is sintering of nano particles, they have tendency to agglomerate, they render very high inter particle friction they have tendency

to get contaminated, because of their high reactivity. They also undergo very rapid sintering and they undergo rapid grain growth which may not be required to acquire their useful properties.

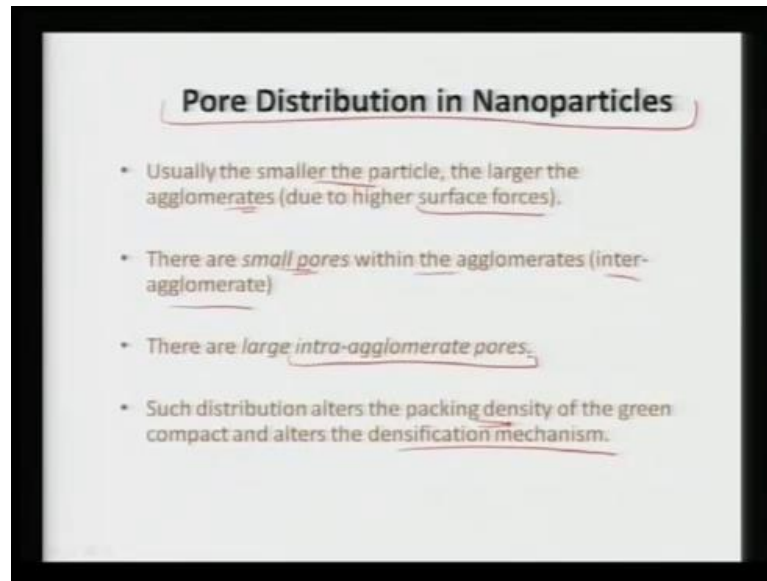
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The nano particles they generally show a very depressed onset of sintering temperature they occurs at as low as 0.2 to 0.3 T_m or the melting 0.2 or 0.3 times that of a melting temperature. Here, for conventional materials for conventional powders the sintering starts at 0.5 to 0.8 of the melting temperature. So, that is the key role of nano materials that they tend to sinter at even very low temperatures. So, they can start, so they can start consolidating at very lower temperatures, the sintering starts at very in the initial stages itself.

Such results is attributed to the structural instability of these nano particles, because of their high surface area, because of their high surface area. They come in contact with the nearby particles and they incur various phenomenon, which we will be discussing in a few later on in a few slides. Because of that, it can initiate or actuate these processes of solidification of densification as early as 0.2 to 0.3 times the melting temperature and this occurs, because they are fundamentally very energetic. They also render accelerated kinetics, so because of their high surface area and their structural instability this is basically provides accelerated kinetics or very high energetic to undergo filtering or consolidation or even grain growth.

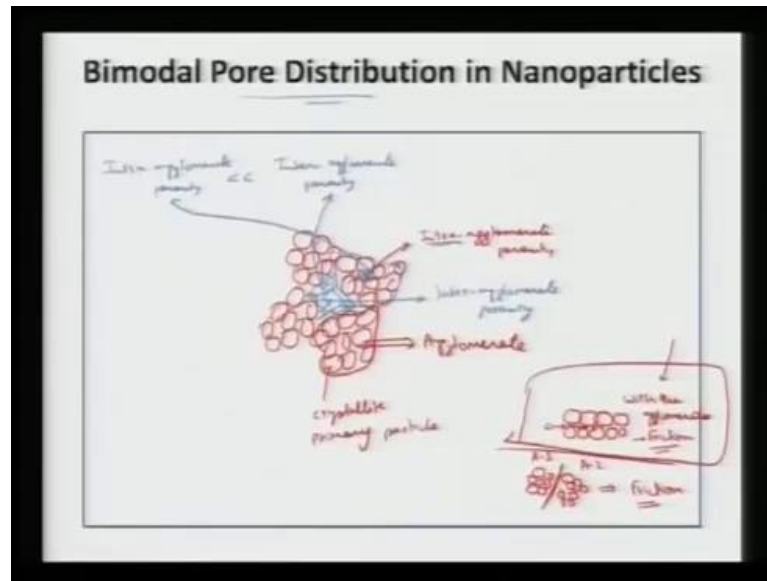
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Again, when the nano particles are getting agglomerated, there is overall the overall pore distribution of nano particle also is of very high concern. Generally the smaller the particle the Larger the agglomerate, because if the particle size is very small, they have very high surface area. They tend to render very high surface forces and in turn they form a very bigger chunk of the material or the bigger agglomerate. Again, they are very small pores within the agglomerate these are called inter agglomerate pores and again there are some pores which are very large in size.

They are intra agglomerate pores, these are porosity between certain agglomerates and such a distribution will be the overall packing density, because they are now bimodal size of distribution of the porosity. Again, because of their high friction which is associated with the nano particles, it can alter the densification mechanism. So, we can see the smaller the particle larger the forces, because of that it gives very bigger agglomerate. Then, there are smaller pores within the agglomerate there are larger pores between the agglomerates and smaller pores within the agglomerate. This distribution will lead to change in the densification mechanism and it will alter their packing density of these nano particles.

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So, you can see the bimodal pore distribution of nano particles it can be like this if we have an agglomerate. We have an agglomerate then we can also have a second agglomerate, which is our which comes in contact. Then, we might have third agglomerate, which is basically comes in contact like this we have fourth agglomerate which comes in contact like this. So, we can see that we have some porosity within the agglomerate which is called intra agglomerate porosity. This entire thing is nothing but the agglomerate and then these are nothing individually, they are called either crystallite or primary particle.

Once we have this agglomerate, there is a there is so much space which is available, so much space which is available out here this space this is nothing but inter agglomerate porosity inter agglomerate porosity. So, we can there is some porosity between the powder particles between the particles and the crystallite which is called intra agglomerate, because this is the agglomerate. Then, we have between the agglomerates, it is called inter agglomerate porosity. So, we can see and there is a bimodal pore distribution, because the size of this particular porosity, the intra agglomerate porosity is much smaller is very smaller than inter agglomerate porosity.

So, we can see there is much difference in the size range of this porosity which is intra agglomerate porosity and then inter agglomerate porosity. So, that in turn provides the distribution of pores which is one is within the agglomerate, so within the agglomerate,

because of the porosity, because of the intra agglomerate porosity these particles will undergo certain shift. It will lead to friction and second friction that arises is, because of the link between the different agglomerates.

So, there can be again friction along this side agglomerate one and agglomerate two again we will see we observe some friction between them and that arises, because of inter agglomerate porosity. So, there is a gap between agglomerate that gives out the intra agglomerate porosity and that again and that gives out friction. Now, friction, because of this entity will might be much higher the movement of individual powder particles, it can render very high frictional forces and that will make the flow of these particles very small.

It will basically stop the movement between the powder particles and that creates a problem in the flow of particles. If you want to fill a cavity for compression or hot pressing or something like that it will it would not be that uniform. So, that is the reason the nano particles they need to have they need to be treated, so they can be agglomerate spherical agglomerate and somehow they can reduce the overall friction between the particles. Out here as well, they have a very high tendency to remain in touch with the other particles so the movement between those particles can be very limited.

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Consolidation of Nanoparticles

- The **density of the green compact** depends on the **frictional forces** of the powder particles that are originated from electrostatic, **Van der Waals and surface adsorption phenomena**.
- These **frictional forces** are **significantly high** in nanoparticles forming **hard agglomerates** and **inter-agglomerate** which are relatively large.

The diagram shows a rectangular container on the left containing several small circles representing particles. A downward arrow is positioned above the container, and an upward arrow is below it. To the right of the container is a small rectangular block with diagonal hatching, representing a compacted state.

Now, from the consolidation of nano particles and as we said, because of this porosity and the overall surface forces it becomes very hard to move the particles in the direction

of each other. So, that gives a very high frictional forces and since the density of the green component green compact depends on the frictional forces. It becomes very hard to compress them to very high density and that basically originates from the electrostatic or Van der waals forces and the surface adsorption phenomena and this crystal forces are extremely high in the nanoparticles. They form very hard agglomerate and inter agglomerate porosity which is basically very large.

So, in turn it is very hard to move those particles and then result is a very dense compact out of it. So, we require very additional pressures to make them move and consolidate to a very high dense palette or a components of consolidation of nano particles. It is of a bigger concern, because the overall frictional forces are very high and in turn it requires very high forces to consolidate into dense particles.

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Thermodynamic Consideration for Pore Consolidation

- Based on the thermodynamic treatment of the shrinkage of the pore, the finest pore size usually yields the highest densification rate.
- Large pores require not only higher temperature but also prolong sintering times for their successful elimination; consequently, it becomes difficult to retain the grain size in the nanometer domain.

grain size (nanometer scale)
pore size

Coming to the thermodynamic consideration for the pore consolidation, so based on the overall size of the pore, so we can see that the thermodynamic treatment can provide the shrinkage of pore occurs. It requires very high pressure, so the finer the pore size usually is the highest densification rate, so we can see that if the pore size is very fine. It can easily get consumed by the surrounding and the larger pores require not only high temperature, but also prolong sintering times for their complete engulfment. So, consequently it becomes very difficult to retain the grain size in the nano meter regime.

So, we can see first of all that the nano particles that if you have the nano particles the final grain are present within the agglomerate. It very easy to eliminate these nano pores and make them densified very quickly, so these porosities will go first, so in turn the nano nature of this this is a nano particle and this is a nano porosity. So, these will get consumed first, so these can get a agglomerate a densified agglomerate and then we have second densified agglomerate. The third densified agglomerate, so the overall grain size is now increased and in turn it has become difficult to retain the nano particles or nano grains.

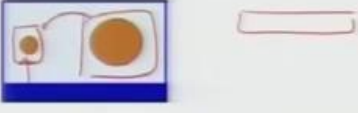
So, the consolidation of nano particles or reduction or retention of the grain size is very difficult in the nano meter regime and this forms a bigger pore. It becomes very hard to consume it and densify the material, so in the process we are not only consuming the final grains or final particles, but also being able to induce certain porosity in the material, which is very hard to eliminate.

So, that is the requirement of pore consolidation, so we need to have very uniform size of pore throughout the material to retain the nano meter grain size, while achieving a rapid sintering. So, rapid sintering becomes of key issue that we can achieve densification in very short duration of time while retaining the nano grains in the structure.

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Vapor pressures of nanoparticles

Why should the vapor pressure increase?



- Flat surface remains in equilibrium with the vapor
- The small ball has higher free energy so,
- The vapor around the smaller ball must increase

for the gas: $d\mu = RTd\ln p$

for particle: $d\mu = V^m dP = 2\gamma/V^m dx$

$P \propto 2\gamma/R$

→ Higher Vapor for smaller

Again, why the vapor pressure of nano particles basically increases that occurs, because of your smaller particle and a bigger particle first of all the flat surface will remain in

equilibrium with the vapor. As soon as the size is changing, the free energy also keeps changing the smaller the ball the higher the free energy which is associated with the final particle. So, the vapor pressure around the smaller ball has to increase and this pressure whether for gas or for particle the overall pressure, basically is the overall function of the inverse of the radius. So, smaller the radius higher will be the vapor pressure, so in turn this entity the smaller entity will render much more vapor pressure.

Then, it will have very high energetic in terms of its growth or consolidation, so that is the problem associated with the nano particles, but then in turn it also yields very rapid kinetics for sintering. So, we can see the smaller the smaller particle it has a direct dependence on the radius inverse relationship with the radius. So, higher the r , lower will be the vapor pressure, so flat surfaces will be in equilibrium with the vapor, whereas smaller entities smaller particles they have very small radius, so in turn it will tend to increase the vapor pressure.

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Sintering Mechanism

- It occurs in early stage of sintering. (0.2-0.3 T_m)
- Typically, lower activation energy are needed than conventional diffusion.
 - E.g. For W powder of size 40 nm, activation energy is 134 kJ/mole much lower than its lattice diffusion (580 kJ/mole) or surface diffusion (300 kJ/mole).
- High diffusivity path like surface diffusion also fails to explain, "extremely fast sintering".
- Other diffusion mechanisms have been suggested.

Sintering mechanism, this sintering starts in the even in the earlier stage of sintering even starts at the temperature around 0.2 to 0.3 times the melting temperature. So, overall lower activation energy is needed, because of their higher vapor pressure and overall it is even lower than that is required for the conventional diffusion.

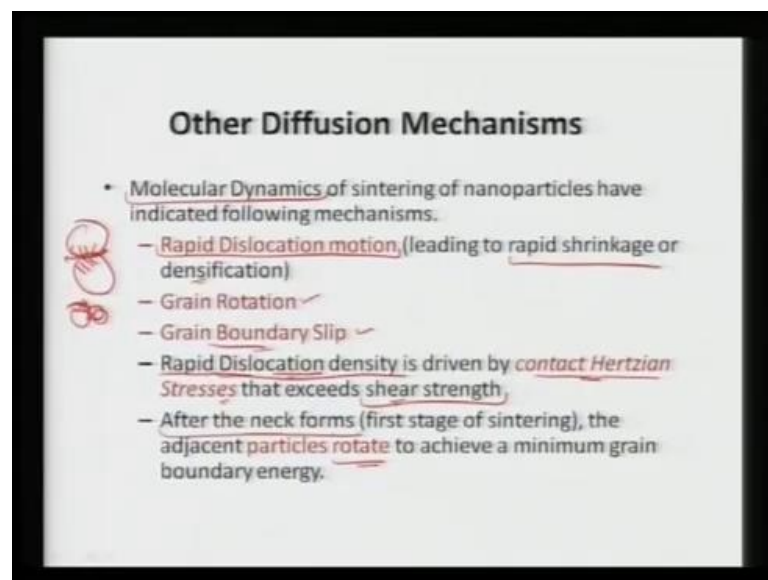
So, for example, tungsten powder of size 40 nano meter, the activation energy is approximately 134 kilo joules per mole and that is very low. Even when you compare it

with the lattice diffusion or even when you consider with the surface diffusion, so that is the kind of energy which is even lesser than the half of surface diffusion. So, even surface diffusion cannot explain the overall, which is occurring in the nano tungsten powder.

So, even diffusivity of this tungsten powder particle cannot be explained by the surface diffusion, because of the high energetic associated with the nanoparticles, even when we are able to achieve very fast sintering in the tungsten particle. We cannot explain it using conventional wisdom of either lattice diffusion or even by surface diffusion. So, that requires that we explain these phenomenon of sintering via some additional diffusion mechanisms.

So, we can see the sintering mechanisms it starts occurring at the early stages as early as 0.2 to 0,3 times at melting temperature and requires activation energy, which are much smaller than that required for either for surface diffusion or even for the lattice diffusion. So, these phenomenon becomes stable via conventional cognizance, so we require to explain them with some other diffusion mechanisms.

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So, we can see that other diffusion mechanisms of this nano particles, they have been explained via certain molecular dynamics, which we can see what is happening in the material. So, first thing is the rapid dislocation motion, so once the dislocation is generated in the material via the inter phasing in these particles. The dislocation created

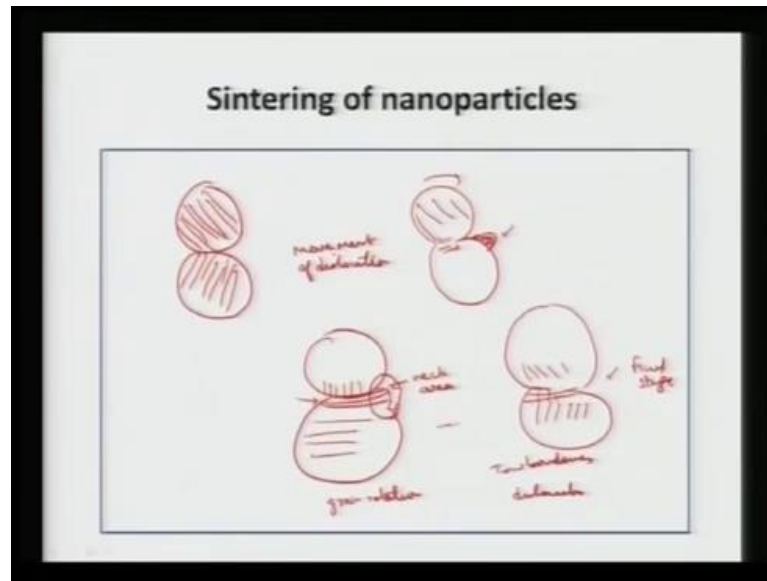
at the interphase starts moving very rapidly and that leads to rapid shrinkage or densification.

Second thing is the grain itself can start rotating the first rapid dislocation, the grain itself can start rotating the grain can slip and again dislocation density is again driven by contact hertz Ian stresses that exceed the shear strength. So, before the shear strength starts dominating the hertz Ian strength itself is now available for deformation of the material and then yield to lead the dislocation density change the structure of the material itself and lead to densification. After the neck forms the adjacent powder particles can also rotate to achieve a minimum grain boundary energy.

So, let us see the min point by point the rapid dislocation movement, so as soon as you have a contact of two powder particles, the dislocation which is created at the interphase the different orientation the dislocation itself can move very rapidly. The grains themselves can now rotate, so once you have some deformation achieved at the necking this entire grain can rotate and result a much denser interphase grain boundary slip. The grain boundary, because of the temperature the grain boundary can also start slipping and the overall trace can also be obtained using this the moment of the two different powder particles and rapid dislocation density is driven by the hertz Ian stresses.

It is no more by the shear, shear it is no more by limited by the shear strength of the material. It exceed the shear strength of the material, it exceeds the shear strength of the material, because of contact hertz Ian stresses, which are developed at the interphase. They lead the moment of rapid dislocation density and again once the crack has formed the neck has formed the particles can also rotate to achieve a minimum grain boundary energy.

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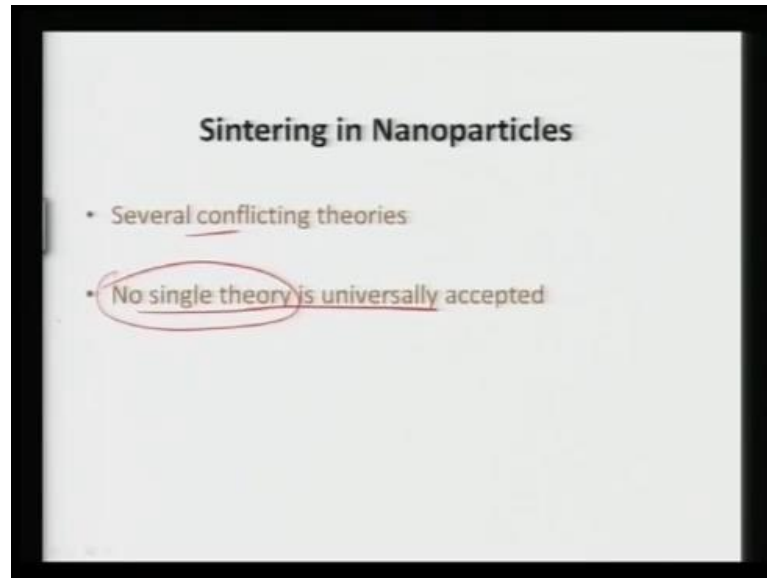
So, we can see initially when we have two powder particles they might have different orientation of grains and the first thing is there is overall movement of this density itself. So, they come in contact they start forming neck and then this dislocation, now start moving to some location so that you have some development of extra material. That extra material now can allow it slipping so the grain rotation can also occur to come and join the interphase now in turn you have prolonged neck area.

So, the overall neck area enhances, because of the movement of the grain rotation itself, so in first case you have moment of dislocation and second case you can also have grain rotation. It can turn it can also lead to the twin boundaries or even dislocations in the final material, but now it has come to a much denser state. In this case again we can see much more the overall grain orientation or the grain size can also be very different than the starting material.

So, we can see that in this case we can again have some sort of an orientation resemblance in the final stage. So, in this case initial grain orientation was very different the overall was very different. In this case we see the moment of dislocations and even the even the grain rotation has occurred in once case, so that we can achieve a certain similarity near the neck region.

Also this neck area which was basically being promoted by the movement of dislocation and that comes in contact with grain, and in turn we can achieve very rapid densification via sintering of nano particles.

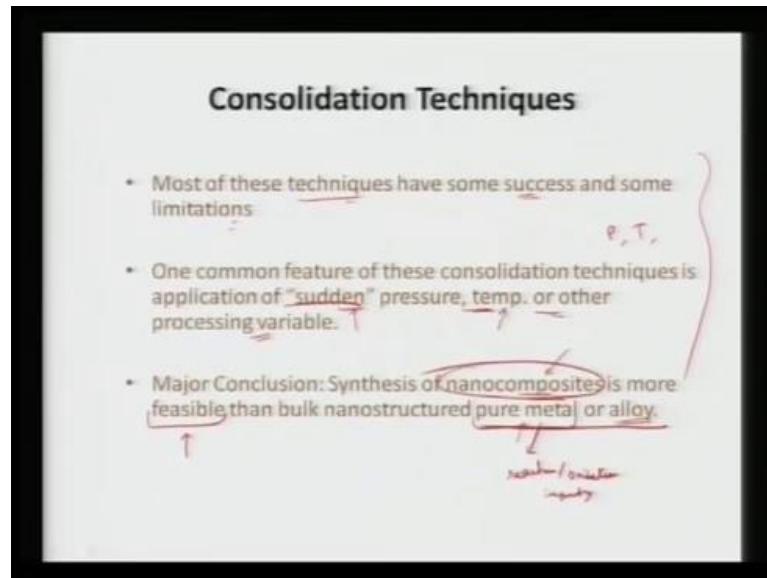
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Again, in the sintering of nano particles, there are very conflicting stories and there is no single theory which is available to universally explain what is happening in the nano materials. So, there are a variety of phenomenon which are dominant in the nano materials, they can range from the moment of dislocations to what is happening at the grain. Either, it is by surface diffusion or by the rotation of grain or it is by the hertzian contact, which enhances the movement of these dislocations.

There are many conflicting theories which describe the sintering in nano particles and any one of them might be much more dominant in one set of system in comparison to the other set of systems. So, there is no single theory which is able to explain the overall densification or grain growth and even the sintering of the nano particles.

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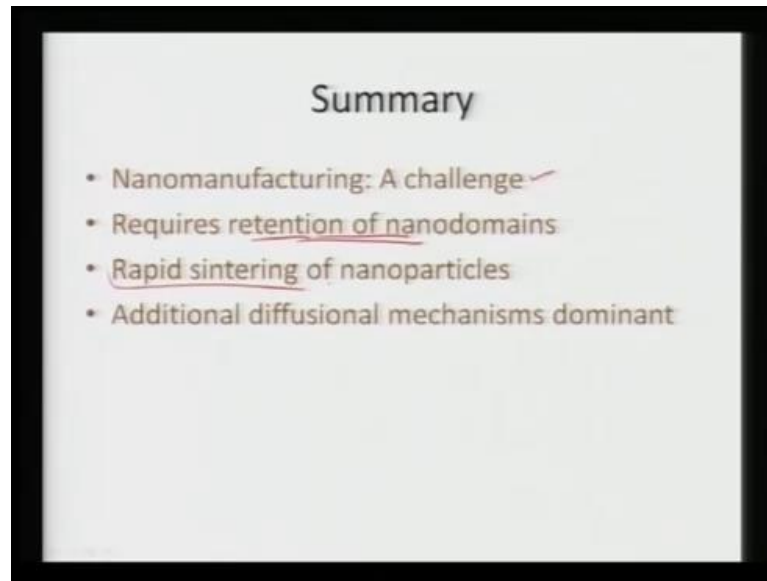


Most of these techniques have some success as well as certain limitations, but one common feature of these techniques is the application of sudden pressure temperature or other processing variables. So, in the consolidation we can apply a sudden pressure a sudden temperature or the cooling rates are very sharper, very high or any other processing variable. So, either the time is very short, the pressure is very short or the temperature is attained in a very short duration of time.

So, these sudden jerks can allow the retention of these nano particles in the sintered component, but again the major conclusion which can come out of this is that the synthesis on nano composites is much more feasible than that of a pure metal or an alloy. Because of the high surface reactivity, metal always undergoes certain reactions oxidation and also it starts getting some impurity whereas, in case of nano composites we always already inducing sudden change in the systems.

So, in that case it becomes much more feasible for the component to attach itself to a different species and then reject with it and again get densified. So, the overall Nano composites is much more feasible and also it renders enhanced mechanical properties or enhanced surface properties in comparison to that of a pure metal or alloy. So, in in this case the consolidation we are applying a rapid rate of pressure or temperature or even the deformation or any time which is associated with this processing.

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So, in summary we can see that the nano manufacturing is a challenge, because we need to incorporate first of all we need to make those nano particles then be able to process them and then make them into a shape which is much bigger in size. So, it can be used effectively, so it requires the attention of nano domains and again there are certain challenges with each and every stage of this nano manufacturing. They are in terms of either handling the powders being able to manufacture them the oxidation the surface reactivity.

Then when it comes to devices again, there might be certain challenges of inter connects and the kind of getting signals out of them making them into certain useful shape. Then, again components it can again be challenge, because the overall pressure temperature or the working environment can also induce certain effects and it might become very hard to merge those nano components into a bulk or a useful shape.

Then, comes the rapid sintering of nano particles this can also create certain challenge, because retention of nano particles is very difficult since the nano pores which are present between the nano particles. They are very easy to get consumed, whereas the porosity between the agglomerates it is very hard to eliminate. So, in turn the rapid sintering or the rapid jerk which can be applied via pressure temperature or even by consolidation it requires a jerk or short pulse. So, they can be retained and the process can get completed in a short duration of time and nano particles, additional diffusion

mechanism can also become predominant such as dislocation movement which becomes very rapid.

The hertzian contact which can enhance the overall movement between the dislocation density and again there can be grain rotation to yield to enhanced densification of these nano particles. So, we can see the overall nano manufacturing is totally dependent on the nano materials synthesizing them into certain devices becomes again a very big challenge. That requires understanding of the mechanisms or the sintering mechanisms, which are dominant in terms of creating these functional devices with this I end my lecture.

Thank you.