Nanomaterials and their Properties
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Lecture - 15
Synthesis of Nanomaterials

Students as you know the semester has began and we have been interacting for different aspects of the course on nanostructure materials characterization and properties of nanostructure materials. And you know we are going to discuss in this lecture more about the different processes or different techniques rather to prepare nanostructure materials.

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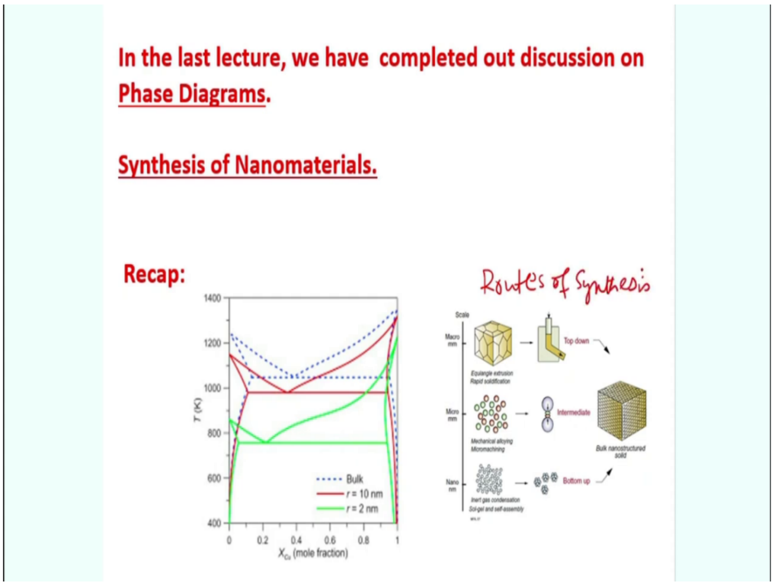

In the last lecture, we have completed out discussion on Phase Diagrams.

Synthesis of Nanomaterials.

Recap:

Routes of Synthesis

But in the last lecture thankfully, we have completed all our discussions on phase diagram that was indeed lot of mathematical expression and it was not easy to understand those things so, you must read carefully. And then at the end, I started discussing about synthesis routes of nanomaterials, right. So, you know that phase diagrams are significantly affected by the size or by the shape size as well as the curvature of nanoparticles.

And we have discussed many facets of that like we have discussed about the chemical composition change, we have discussed about the melting temperature depression and we have also discussed the phase boundaries; how they are going to be change and how we can actually calculate that. And finally, we had also discussed different routes of synthesis right and we will continue discussing on that today.

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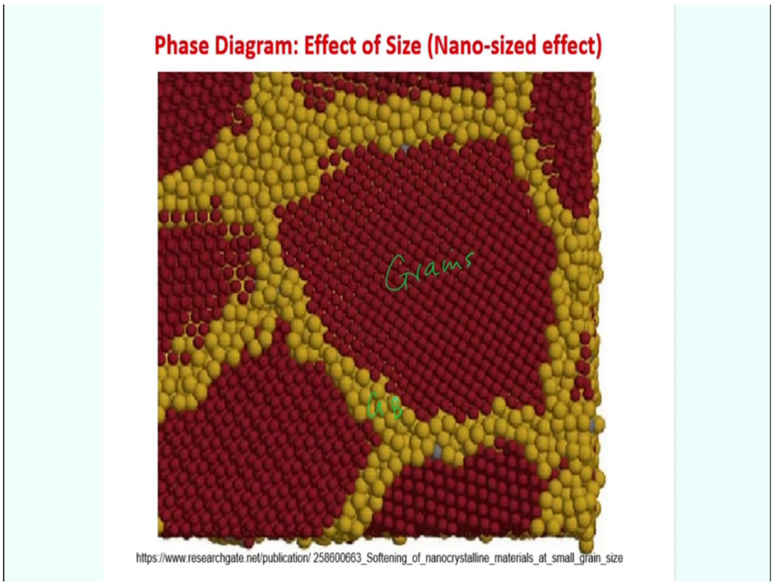

Phase Diagram: Effect of Size (Nano-sized effect)

https://www.researchgate.net/publication/ 258600663_Softening_of_nanocrystalline_materials_at_small_grain_size

So, as you know any bulk nanostructure materials, you have grains and the grain boundaries right. So, grains and grain boundaries are going to be different entities. We need to use as a different entity in case of nanomaterials why? because, grain boundary area is pretty large and they form a significant part of the surface energy or interfacial energy of the system.

Hence, we have to consider grain boundary as a separate phase. That is what we have done at the end of the last lecture I derived, or I rather described an equations which will can be used to calculate the free energy of the whole system consisting of grains and grain boundaries by Weissmuller and others, ok.

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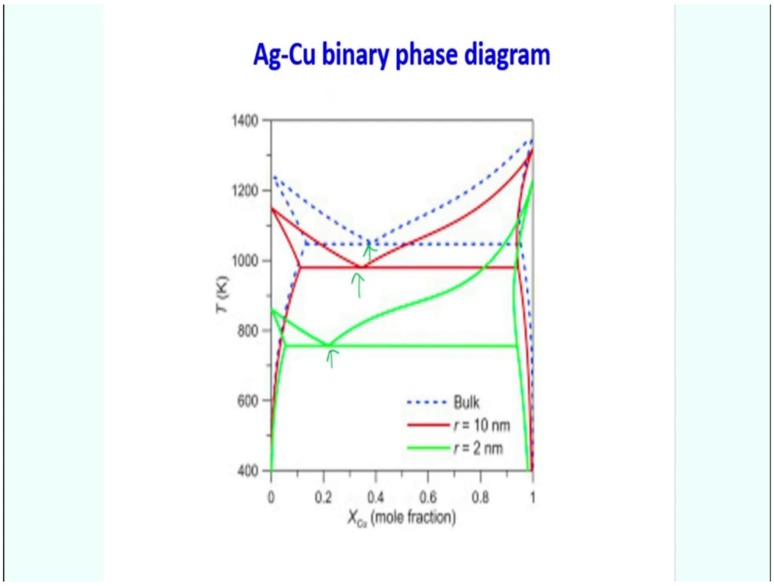

Ag-Cu binary phase diagram

Now, as you know these things when you consider these energetics aspects of that phase boundaries significantly altered ok because of these size effect. As you can see for all silver copper phase diagrams, I have been showing in again the eutectic temperature has shifted down, composition also shift to the left side. And in fact, all the phase boundaries has shifted as compared to the bulk 1. Bulk 1 is shown by dotted blue curve ok.

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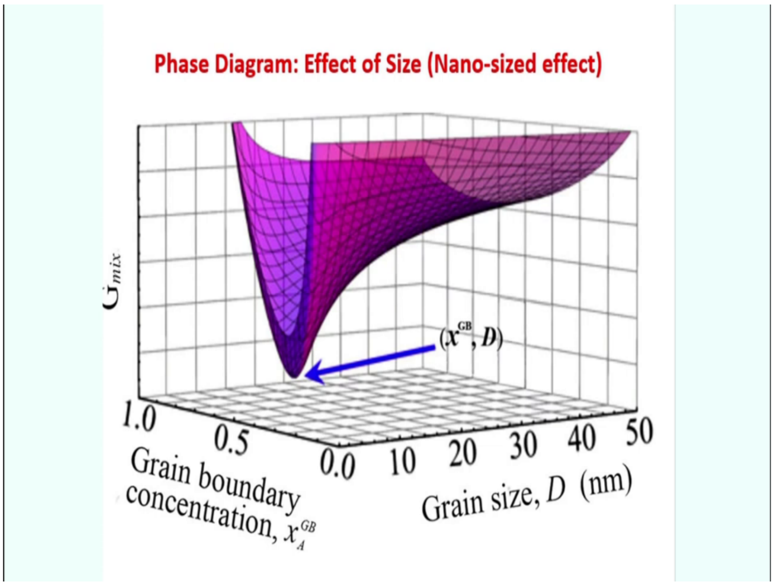

Phase Diagram: Effect of Size (Nano-sized effect)

So, that is what it is. Not only that if you consider the grain and grain boundaries and then if you develop a comprehensive thermo dynamical equation relating the free energy of grain boundaries and the grains separately looking into all aspects like surface energy or interfacial energy and also the entropic contributions, then you can plot that equation and get free energy of mixing as a function of grain size as well as grain boundary concentration ok.

Grain boundary concentration is also going to be change that will not be same as the concentrations of the grains, right. Then you can find out the minima of these three-dimensional plot to get an idea what will be that equilibrium at a definite temperature and pressure for the system and it is possible to do that, ok.

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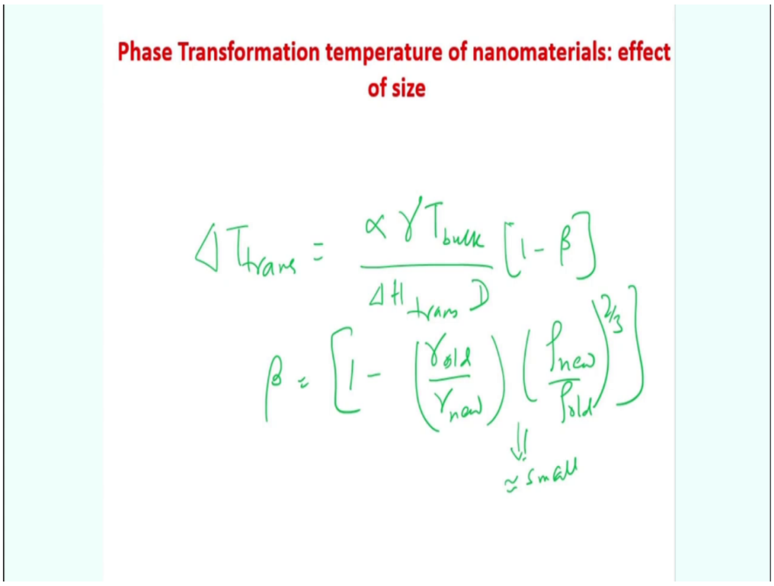

Phase Transformation temperature of nanomaterials: effect of size

$$\Delta T_{trans} = \frac{\alpha \gamma T_{bulk}}{\Delta H_{trans} D}\left[1-\beta\right]$$

$$\beta = \left[1 - \left(\frac{\gamma_{old}}{\gamma_{new}}\right)\left(\frac{\rho_{new}}{\rho_{old}}\right)^{2/3}\right]$$

$$\Downarrow$$

$$\approx \text{small}$$

Well, then we also discussed about how phase transformation temperature can be changed or will be changed because of that and finally, we derive an expression:

$$\Delta T_{trans} = \frac{\alpha\gamma T_{bulk}}{\Delta H_{trans} D}(1 - \beta)$$

where beta was a factor which is given by:

$$\beta = [1 - \left(\frac{\gamma_{old}}{\gamma_{new}}\right)\left(\frac{\rho_{new}}{\rho_{old}}\right)^{\frac{2}{3}}$$

ok. And if this ratio is very close to you know very very small or you can ignore as compared to 1, then you can easily say $\beta = 0$ and then, you can calculate the transformation temperature. What does this equation do? This equation allows you to calculate the change of transformation temperature like melting temperature, change of any eutectic transformation temperature. You can actually calculate straight forward by using this equation if you know the values very well, ok.

Well as you know ΔH_{trans} is available you know from the literature. The bulk transition temperature is also known correct. Only thing which you do not know is the gamma values ok. Density values may be known, but gamma values will not be known and that is why the problem comes. That is why the calculating β is difficult and many cases it is even impossible because surface energies are not available for many systems.

In that case, you can simply ignore it and calculate using $\beta = 0$ that is ok. These are all we discussed for the you know last couple of lectures, ok. So, I am not going to discuss much about that except saying that you know the, this thermodynamic descriptions are very extensive.

You need to study well from the books and the papers which I will provide you as a repository and then, you can read it through and you can ask me questions how it is done.

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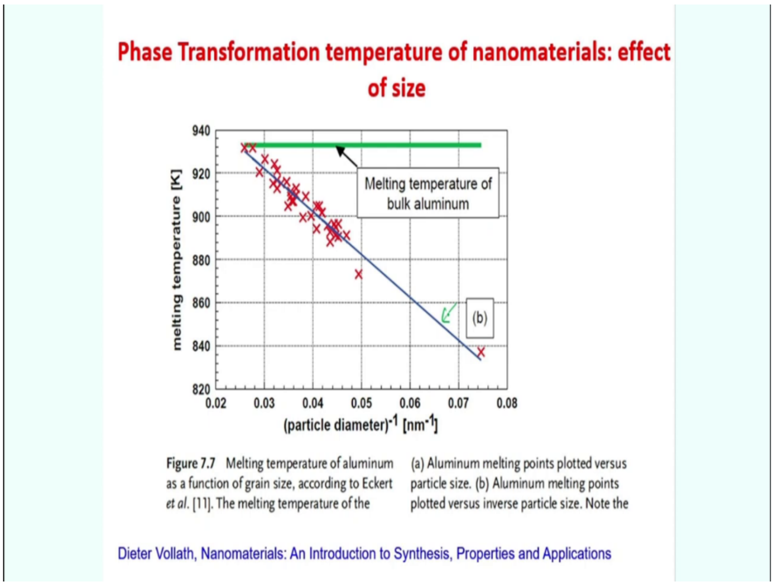

Phase Transformation temperature of nanomaterials: effect of size

Figure 7.7 Melting temperature of aluminum as a function of grain size, according to Eckert *et al.* [11]. The melting temperature of the (a) Aluminum melting points plotted versus particle size. (b) Aluminum melting points plotted versus inverse particle size. Note the

Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications

Well, then this has been used this equation to plot the change of melting temperature as a function of size for or 1 by diameter for aluminum, pure aluminum. You can see that most of the experimental points are actually following the theoretical curve which is given by this, ok and it is very very important that this theory works very well for the experimental values which we have people have obtained in various research, ok.

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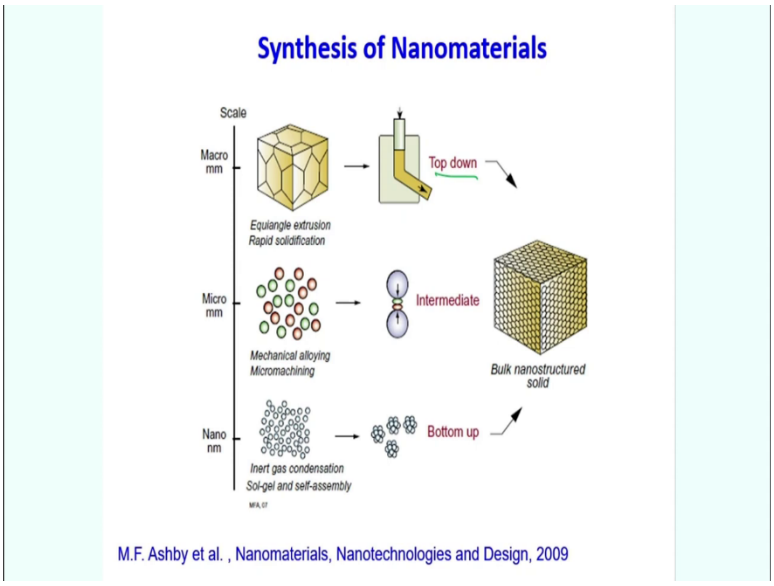

Synthesis of Nanomaterials

M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

Then finally we come to the synthesis of nanomaterials. As I said there are two ways of synthesize nanomaterials. One is called top-down approach. That is why you can take a big size material millimeter size or micron size, then size material and then break it down into pieces and pieces and pieces and finally you arrive at the nano size.

This is simply like you take a chalk, break it into smaller small pieces, then get a dust of the chalk, still grinding it again and again to get a nanoparticles of the calcium carbonate ok. That is the ingredient, measure ingredient in the chalk right. Same thing is can be done here. There are many routes of many kinds of processes available for this kind this route, ok.

But second one is which is routinely done by the chemicals. Synthesis technique is to use a bottom-up approach. Bottom-up approach means you start in the molecule or start with atoms, then allow these atoms and molecules to come from micro molecules and finally, they can self-assembly and form a nanostructure material ok. That is possible actually, but you know in this process you may not get a bulk nanostructure material or it will get a powder a nanomaterial in the form of powder.

So, that can be again centered to obtain a bulk nanostructured material. We are going to discuss about those aspects later. So, now there is also intermediate way right. You can always use micro machining and also mechanical alloying to mix particles, mix different kinds of elements together and form nanomaterials, ok.

Again, that will come as in the form of surface layers getting nano crystallized or powders getting nano crystallized that those things needs to be centered to obtain a bulk nanomaterials. But in a very routine way top down and bottom up the main approaches, main two approaches to produce nanomaterials. This you must not forget this. You must keep in mind when you are understanding the different synthesis routes of preparation of nanomaterials, ok.

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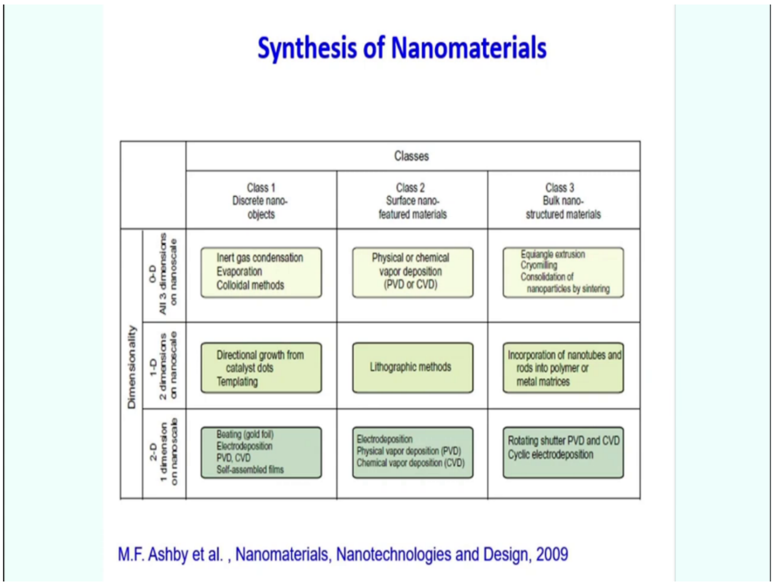

Synthesis of Nanomaterials

		Classes		
		Class 1 Discrete nano-objects	Class 2 Surface nano-featured materials	Class 3 Bulk nano-structured materials
Dimensionality	0-D All 3 dimensions on nanoscale	Inert gas condensation Evaporation Colloidal methods	Physical or chemical vapor deposition (PVD or CVD)	Equiangle extrusion Cryomilling Consolidation of nanoparticles by sintering
	1-D 2 dimensions on nanoscale	Directional growth from catalyst dots Templating	Lithographic methods	Incorporation of nanotubes and rods into polymer or metal matrices
	2-D 1 dimension on nanoscale	Beating (gold foil) Electrodeposition PVD, CVD Self-assembled films	Electrodeposition Physical vapor deposition (PVD) Chemical vapor deposition (CVD)	Rotating shutter PVD and CVD Cyclic electrodeposition

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And these things I am not going to discuss again. There are various ways of preparing 0D 1D 2D. We are going to discuss one by one that and also 3D nanomaterials or bulk nanomaterials correct.

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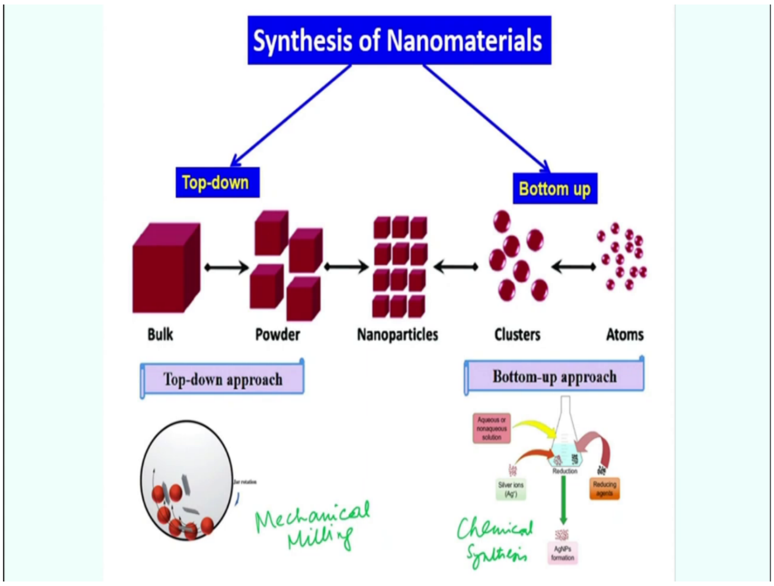

Synthesis of Nanomaterials

So, you know top-down approach I have just discussed you take a bulk material big grain size, break it down and the ball milling is one such or mechanical milling is one such technique which we discussed mechanical milling. All the chemical synthesis routes actually falls under bottom up approach ok all of them.

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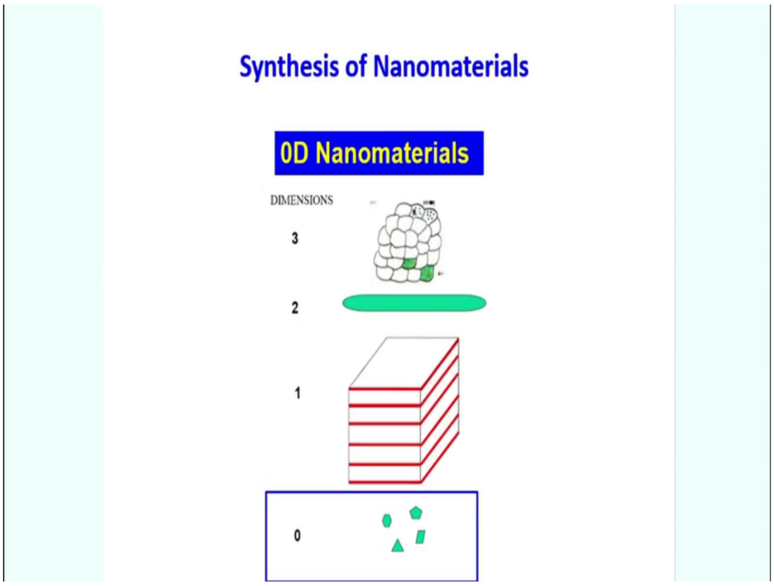

Synthesis of Nanomaterials

0D Nanomaterials

Well, so we are going to discuss you know like we can divide our discussion based like how to produce zero-dimension nanomaterials, then 1 and 2 and finally 3.

Let us first talk about how to produce zero-dimension nanomaterial. Zero dimension you know right in which all the directions x y z, the size of the nanomaterial. So, there is a grain size or particle size, all three directions is must be less than 100 nanometers. That means, all the sizes in all the directions will be a nanometric domain. That is what is defined as a 1 to 100 nanometer. This is the you know important aspect about zero dimension nanomaterials.

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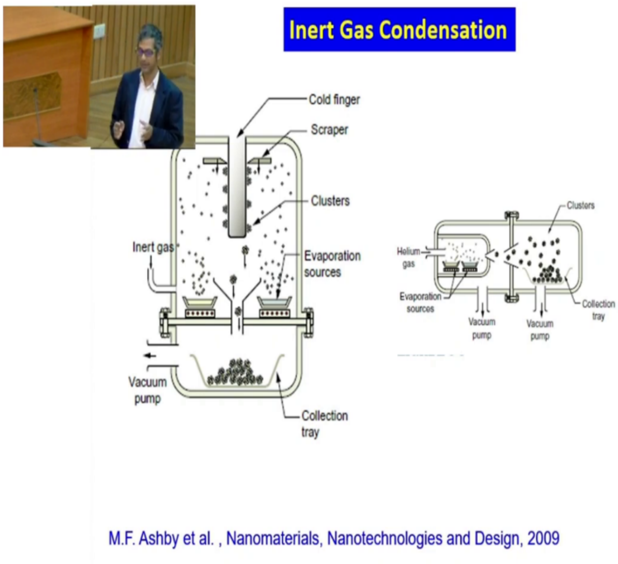

Inert Gas Condensation

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So, how do you make that? And I discussed one of them the inert gas concentration. I am not going to go back to again this is this route which was used by a Hubert Glider in his you know starting carrier in 1960s and 1970s, ok.

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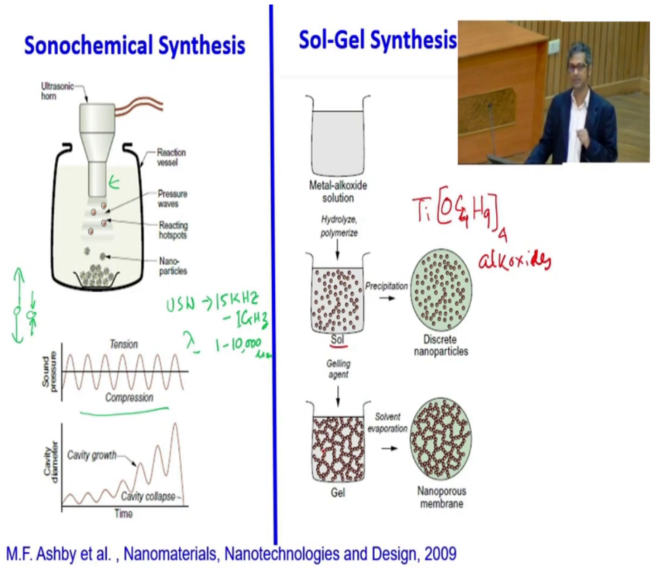

Sonochemical Synthesis

Sol-Gel Synthesis

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The next technique which is important is for you it is sonochemical. What is this technique? Well, sonochemical means using ultrasonic. What is that? What is known as it is known as use of ultrasonics waves? Actually, you know ultrasonic waves span in the frequency range of watt from 15 kilohertz to 1 gigahertz ok. These are called ultrasonic waves. They range 15 to below 15 kilohertz to 1 gigahertz, right. That is what it is that it is a very large span, ok.

Now you can produce this ultrasonic wave by using magnetostriction. What is magnetostrictions ok? There are a lot of materials in which you if you apply magnetic field, their length increases. So, by increasing lengths, they can be used to produce a force ok. Basically, you can produce to make an ultrasonic wave right or you can do it by using piezoelectric transducers ok. That is also possible.

So, basically it is like a horn ok. You can see there this is a horn, this is what is called as long as a horn, ultrasonic horn. It is moving you know back and forth that is how it is creating ultrasonic waves, right. So, the wavelength of the ultrasonic waves are very large ok. What are the wavelengths?

Wavelengths will be from 1 to 10,000 microns. So, you must be wondering why if it is micron, then how can ultrasonic waves used for preparation of nanomaterials. Well, that is what the cracks of the matter is ultrasonic waves. Wavelengths does not make any effect as far as the size of nanoparticle is concerned. Well, so these are not molecular dimensions and so, therefore there is no direct coupling of acoustic field is the ultrasonic is the acoustic field with the chemical species.

So, reaction actually happens because of a cavitation phenomenon. What is cavitation phenomena? Well, you know let us discuss about it. As this horn is moving up and down ok. It is creating tensile and compressive force inside. Basically, it is a waves as the waves moves, it creates a tensile and compression right.

You can see that actually this is the wave, sound wave, which is shown here, this one correct. So, the top side is under tension and bottom side is under compression ok. You can easily read of any sound waves books of any sound wave, you will find out that when the sound wave moves, there is a compressive component. There is another is a tensile component.

Now, the tensile part of the wave is an intense wave, wave 1. It will pull the liquid apart as it pulls the liquid apart. This will create a cavity, right. The compressive part of the wave what will happen this will compress it, but before it compresses that cavity, it is a cavity form. Its tensile force is going to create a cavity right. It is just like a small cavity in the water. So, now this again then the compressive force comes the compressive direction the compressive part of the wave, this will try to close it up.

But before it close it up, some reactants will vaporize inside these bubble ok. That is what will happen. This is a bubble or it is a tiny cavity. The next tensile wave then they expand the bubble and this oscillation happens expansion, contraction, expansion, contraction happens, correct. So, when because of these bubble size will change. As the bubble size changes, bubble size will reach a critical size and after which it will basically undergo a collapse or so, what we call as a bubble burst, correct.

So, when it reaches a critical size, this bubble will undergo a collapse and because of this collapse basically collapse is very rapid. It happens in a very very small time scale ok nanometric time scale level, people have done bubble dynamics. They found that these bubbles collapse in the nano secondary time and because of that the heat transfer is adiabatic.

What is the meaning of adiabatic? That is from the bubble to the surrounding water. Heat transfer will be adiabatic. There will be no heat transfer at all because of the fast collapse of the bubble in the nanosecond design. And this can lead to huge increase of temperature and you won't believe in these bubbles. That is what the reaction centers of these sonochemical synthesis temperate can reach 5000 k.

Yes 5000 k almost close to temperature of the sun, but because it is a big mass of solution, you do not feel it is happening in a tiny small bubble and this is happening in adiabatic manner, ok. You may ask if thousands of bubbles happens, then what will happen. Yes, then it will lead to explosion, but normally we do not allow that things to happen ok and pressure inside will be also pretty high. Pressure can be as high as 2000 atmospheric pressure.

So, such a high pressure and temperature ok it will react or it will trigger chemical reactions in this shaded bubbles for the species or for the chemical things which you have already put in, ok. Now the size of this chemical size of this part will determine the size of the nanoparticle.

So, that means size is very important size of the bubble very important critical size of bubble and this can be altered by using different frequencies of the this horn or ultrasonic horn. Actually, you can do that. So, by using different frequency, you can easily create that ok.

So, you know by using organometallic precursors ceramics metallic particles anything can be prepared and it has been found as small as 2 nanometer size particles can be also produced and most importantly, you can use this for large scale production of nanomaterial. It means large volume of nanomaterials can be produced.

You understand that at the bottom, the cavity diameter function of time is shown you know I think initially the cavity will be small because of a tensile and compression compressive part of the wave pulling up and pulling pushing down and that is why the cavity will not grow much.

But after some time because of this reversible process, the cavity will start growing little bit and then, finally it will be a critical size. Then, it will collapse any cavity, any bubble. Actually, once it is a critical size, it collapses, it bursts. Actually, you seen yourself you can create those kind of bubbles by using you know various ways like these two children play with bubble creators, ok.

Device you can also see these bubbles actually fly in the air when after going somewhere. The size increases, then it undergoes a collapse. Same thing happens here. These liquid bubbles will collapse and collapse means temperature and pressure increase. That is what can lead to very high what is called temperature pressure and reaction ok. That is about the all so no chemical. This is also used to produce zero-dimension nanomaterial because nanoparticles are very small size.

Another standard rule to preparation nano material is a sol gel technique and the way it says there is a sol and there is a gel, right. Gel all of you know because many of you use, I know whenever in the morning you are in hurry and then, making a breakfast.

And you can use bread and then you can apply various kinds of jelly like mango jelly or you know these different fruits are available, jellies are available in the market ok. We call them jam, actually fruit jam, but they are nothing, but a jellified thing.

If you look at it, they are very high viscous jellified thing. You have to really you know apply it properly on the surface of the bread and to make it nice and tasty right and, but they are jelly actually. So, jelly actually, but you know gels can be prepared by many ways that, but you require a sol first to make that.

So, ultra fine nanomaterials in this way, even nano thickness streams that is very thin films or nanoporous materials can be prepared. By this way the starting point is a solution precursor, ok and most of the cases precursor are basically organometallic compounds like alkoxides.

What is alkoxides ok? Let me give one example like a for titanium. It is ok let me write it properly for titanium it is ok. What is that? Titanium alkoxide; TiOC4H94; that is titanium alkoxides. What is again let me tell you alko these are actually this is a precursor of titanium, correct?

So, now the precursor is subjected to polymerization reaction. You can add some polymerizing species into it and make it polymerize. So, once in polymerize you will form a long chain molecule correct. So, once it is polymerize, then basically it will form a colloidal suspension. Obviously for polymerizing, it will lead to long chain molecule production that will lead to colloids and this is what is known as a sol you can see that, correct.

So, this precursor is then mixed with a polymerization of agent and hydrolyzed and polymerized, so that a sol forms then what happened you keep this sol for some time at some elevated temperature. This will lead to precipitation of these nanoparticles like titanium nanoparticles from this alkoxides will be precipitates, ok. And then once they precipitate then you can actually invert to.

So, they are precipitate and then they will now grow, they will come and join together and grow you know to stop this growth of these precipitates. What you can do? You can produce a gel, you can add a jellified gelling agent ok. There are many gelling agents are available ok. This is basically nothing, but a surfactant correct.

So, this surfactant will lead to you know three-dimensional network of gel and three dimensional network of gels will have a you know you can see that actually they have a very nice structure. And these structures will allow nanoparticles to be embedded inside this gel, so that they cannot come in contact each other and cannot grow correct.

That is the idea. So, sol is produced first is made to get the nanoparticles formed. But then once the nanoparticle forms? They can come in contact each other and grow and to stop that you have to form a gel. So, after you have discrete nanoparticle formation, then only jelly gelling agent has to be added ok. Do not ask me about the gelling agents ok. You can ask your mother who is knows how to make gel jams.

They will tell you easily what they add to make this gelling agent. So, this is an exercise for you to learn from your you know kitchen because you are at home and you can always ask your mother or your maybe if your father is also knows ok unlike me, then you can ask how they make the jams. So, jams that will tell you how what is the gel, how gel can be formed ok.

So, idea is to form an open 3D network ok and that network will allow basically the nanoporous basically formation of nanoporous thin films and in that nanoparticles can get and embedded. Then once you heat it up, this membrane will be gone and you can collect the nanoparticles very easily. So, you can understand that this is a very very classic process and very interesting process to produce zero-dimension nanoparticles.

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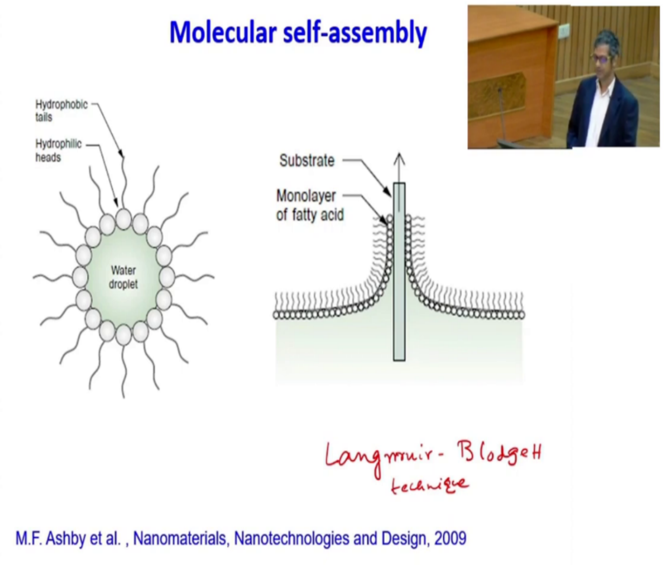

Molecular self-assembly

Langmuir- Blodgett technique

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Well, these also allow us that we can always do molecular self-assembly. What is molecular self-assembly? This is nothing, but a self-organization of organic molecules ok. What is that? Ok, you know as you know what is self-organization start with the liquid atoms are random right because of thermal energy atoms will to will like to be moving here and there.

So, once we cool it down and crystallize, the liquid atoms will come in together and form a crystallized network. Crystallization means what? Atoms will be forming a regular interval in the crystal lattice. That is nothing, but self-assembly atoms are getting self-assembled in a fixed positions in the lattice.

So, that exactly same thing and nature uses extensively for that crystallization is a natural process. It can happen in volcanic rocks, it can happen in even water when mixed with salt or something. So, nature uses everything. You might perhaps the most remarkable one is the self-assembly of DNA right and once the cell divides every cell has a lifespan before it dies, it has to divide.

So, once it divides, the DNA carries the information from the you know parent cell to the product cell and that is actually had happens by again by what self-assembling. So, and basically recently this thing has come into big way and people are trying to realize how to exploit the potential of this technique, ok. Idea is to create actually conditions in molecules or atoms will self-organize into useful structures.

Again, this is driven by minimization of the energy, minimization of the free energy plus surface energy, right. So, advantage is that when the system is converged to very specific configuration without need of further control because it is self-assembling. So, energy has to minimize.

So, you do not want need to control. It will be, it will be self-control itself typically aggregate forms by self-assembly and they tend to bond each other very weak energy. Normally this will be not larger than thermal energy as kt, ok and these molecules actually self-assemly molecules are called as a micelles ok.

You can see that these are all called micelles and every micelles will have two parts; hydrophobic part and hydrophilic part. Hydrophobic part means they do not like water. That is why it is called phobic phobia ok claustrophobia. If inside the lift, you feel claustrophobic. Same thing hydrophobic means they do not like water that is why they will have higher form water and hydrophilic heads they will be they like water.

So, they will be self-assembling, they will come together and form such a kind of a cavity. You can see that with inside there is a water, correct. Now you can have a reaction in this in the water media or maybe in some other media.

Sometimes you can form such can micelle structures using polymer as organic media also like from alcohol or some kind of other compounds liquid organic molecules. It is also possible, but finally is basically a cavity forming by this hydrophilic heads of the micelles.

So, then center of the micelles can act as a reaction chamber in which you can have reaction possible and that can lead to production of nanoparticles, right and you know that to give you perspectives of that you can also have self-assembly of 2 D nano films, right and that is what is done by Langmuir.

Most of you know Langmuir Blodgett technique right. What is that done in this case well a monolayer of fatty acid is formed on the surface of water. If you put a fatty acid, this will spread uniformly on the surface of water. It is basically because of Vander Waal interactions and then you can simply because it has a hydrophilic part and hydrophobic part.

So, all the hydrophilic part will be touching the water surface, hydrophobic parts will be away from the water surface ok. So, the fatty acid self-assembled the across the water surface as a monolayer, correct and any other measurements is not allowed then you can put a substrate.

Substrate is nothing, but a surface on which this can be formed into the deep into the water and then take it out. So, then you can form a nice two-dimension thin films on the surface of that. The thickness of the thin films will be very small. That is that is what is called a 2 D thin films.

2; why 2D? Because two dimensions are in a micron scale and thickness is in the nanometric scales. So, this is very easily done. There are many such kind of systems available in the world where you can actually produce such a kind of a nice structures, ok self-assemble structures. So, that is all for all the zero-dimension nanoparticles.

Now, we are going to talk about two and three dimension, two and one dimension nanoparticles ok. So, two let me write down this is 1D or 2D, ok nanoparticles ok.

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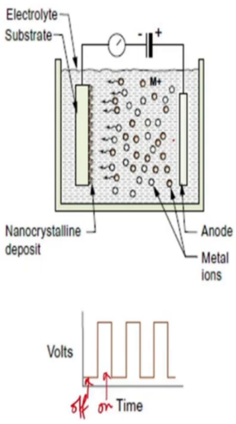
Electro-deposition



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So, that means how to create that, right. Well one of the way we have to creating this is to what is known as a electro deposition. You know it is a standard technique in which you can create large area thin films ok and these thin films will have thickness of nanometric scale and xy dimensions can be very large ok because you are putting a substrate. But then what is electro deposition?

Electro deposition is nothing, but if you have a cell electrolytic cell in which you have a solution, this is a solution inside it. You can see and you have two electrodes, one anode, one cathode ok. Then if you apply current through this circuit, what will happen is things will dissolve from anode and then get deposited on the cathode. That is what happens.

Now, how to create nanocrystalline deposits? Well, that is can be done by putting a various way by putting a pulse current, ok or pulse voltage basically because you are applying a voltage instead of applying a constant voltage. You can have pulsing and this you know pulsing can be on and off.

You can see this is off cycle voltage is off, this is on cycle right. And the thickness of this width for the on cycle would be nanoseconds like 10 to 20 nanoseconds. Off cycle can be large ok. It can be as large even microsecond also.

So, when you are making the cycle on, that means when the voltage is on ok crystallization happens. That means, the material get dissolved from the anode and then they reduced and get deposited on the cathode correct. So, then the off cycle nothing happens because you are not applying voltage. So, what will happen? Nothing will happen. So, idea is to nucleate these grains of the material from the anode whatever dissolving and do not allow them to grow.

So, if you put a constant voltage, nucleation will happen one step, then final growth will happen extensively, and you will not be able to retain a crystalline grains. So, in order to do that, you need to do a pulsing operation ok and this pulsing is very very important. You know you can have on and off pulses to create that otherwise you can have you can combine this thing with high current density. If you make a high current density, current density is what current per unit area of the cathode.

So, if you apply a high current density ok, then what will happen is, nucleation rate will be high. That means, at a particular time many many nuclei will form and this nuclei will can cover the whole surface and they will come in contact with each other. So, they cannot grow any further. They can only grow when they center, but temperature is not very large in this kind of electro depositions. So, it will happen normal like room temperature. So, therefore you can always get nanostructure 2 d thin films very easily.

So, you know this is a classic process and this has been widely used many many in fact long time I can say and pulsing actually requires a device to do that you know all the potentio stats available can do pulsing operations that is easily done ok. So, that is one other way of creating thin films, right. Very easily one can do.

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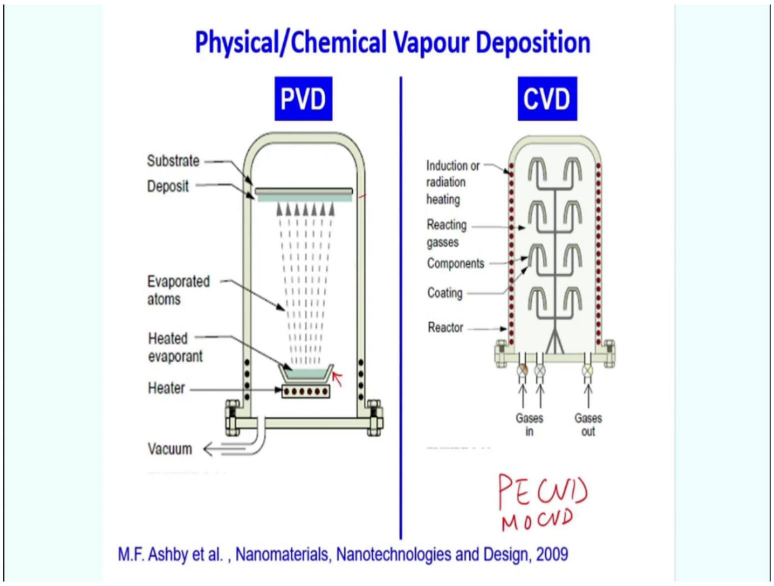

Physical/Chemical Vapour Deposition

PVD

CVD

PECVD
MOCVD

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Then you can do obviously PVD and CVD. PVD is what physical vapour deposition. Physical vapour deposition you know there are many such techniques. I am not going to discuss in details about that. Well, the easiest one technique is to create a vacuum chamber and in which you can put a things which you want to deposit right like a metal or a polymer or a ceramic and then, heat it up. You can keep you put it in a boat, you can see that this is put it in a boat, right.

And then what you do? Then, you basically heat it up. Once you heat it up, this will evaporate inside this vacuum chamber. So, once it evaporates, it will create vapour. Then if you put a substrate little further away from it, you can see that these vapours will deposit in the substrate and create a thin film.

This is the simplest one, but you may not need to do heat always because some metals may not be operating at all at normal temperatures or maybe they will take you to high temperatures. So, you can do a sputtering ok using argon ion or you can do even magnetic magneto sputtering. There are many ways of doing that, ok.

So, this PVD allows you to create again 2d nanomaterials, ok. By proper control of the whole process, your grain size of this thin film can be very small nanometric domain and thin film can also be nanometric thickness.

Both are possible. Well, you know many everything cannot be deposited by PVD. So, that is why CVD used what is known as a chemical vapour deposition, ok. Chemical vapour deposition is a route in which a reactant gas mixture in come in contact with a surface on which it has to be coated correct.

And then on come in contact with that substrate or surface on which is to be coated. The reaction happens basically gas decomposes like a methane. If you put it on a heat it up and put it on a surface like nickel or something, it will decompose into carbon and water in presence of a oxygen and this carbon then can deposit as a thin film of graphene whatever nano tubes or even pure amorphous carbon also. All kinds of things can be prepared and you know.

So, deposit can be formed by reactions between the precursor gas in the vapour phase or by reaction between vapour and the surface of the substrate. So, you can also have a reaction in the gas phase also like you can put two gases, they will react each other and produce the things which can be deposited on the substrate.

So, there are many ways of doing that. Easiest one is to have put a gas inside the chamber and then allow the gas to come in contact with a surface at high temperature and the gas will decompose and produce a thin films.

Other way of doing is that you can have a reaction between two gases or three gases in the gas phase and reaction will lead to production of a deposit on a substrate. So, both are possible. One, the variation of these is called you know by a moderate CVD that is called MTCVD or you know best one is called as Metal Organic Precursor, CVD ok or MOCVD, ok. As the decomposer relatively lower temperature because decomposed temperature can be high also then it is very difficult to maintain.

So, you need to have a precursor which can decompose very easily at a lower temperature. That is what is a metal organic precursor can do, that it was a relatively low temperature reaction temperature is typically around 600 to 700 or even some cases 500.

The chemical reaction in the vapour phase are activated by creation of plasma. Also, you can have a plasma CVD, ok. If you create a if you put a plasma on the surface of that, it can lead to rapid reactions ok or decomposition possible and that is also PV CVD plasma enhanced PE CVD, ok. PE CVD is plasma enhanced CVD or MO CVD metal organic compound CVD, both are basically mean to reduce the decomposition temperature or you can also have you know laser induced CVD also LCVD.

Possible you can put a laser beam to decompose some gas. Basically, idea is to decompose some gas to produce some deposit on the substrate. That is the idea in CVD. In CVD in PVD, you are evaporating something or sputtering something that will lead to generation of the molecules or vapour and this can deposit on the substrate ok. So, there are many variations of that you know you can read it thoroughly different books also possible.

So, what we discussed, I discussed that you can create electro depositions, you can create 2 nanomaterials by electro deposition or PVD or CVD. You can also do it by you know a technique known as a thin film formation by sol gel, ok. Sol gel can also allow you to form thin films, fine.

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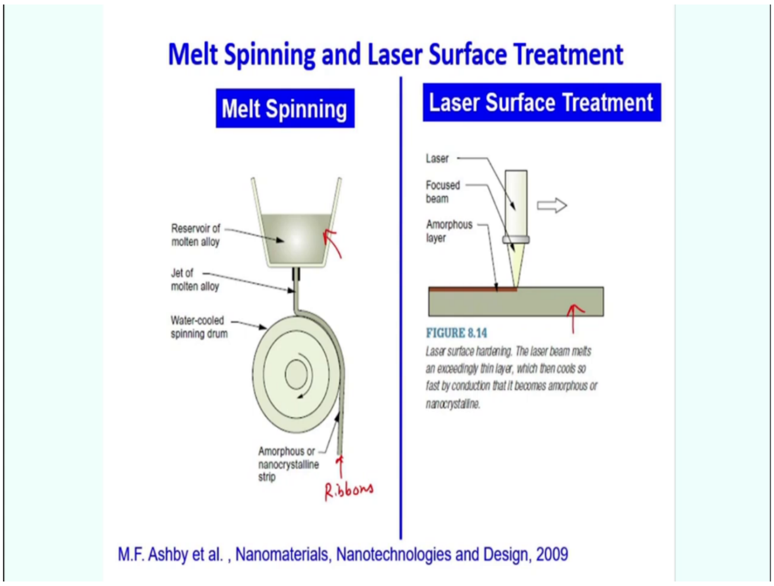

Melt Spinning and Laser Surface Treatment

Melt Spinning

Laser Surface Treatment

FIGURE 8.14

Laser surface hardening. The laser beam melts an exceedingly thin layer, which then cools so fast by conduction that it becomes amorphous or nanocrystalline.

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So, now let us come to the 3D, ok. I will just discuss few of them and so, that you understand it you know making 3D bulk nanomaterials is not easy. That means, it will have a large grains with grain boundaries, that is what is bulk actually.

And you know but these are important from the perspectives of applications because you can produce, you can induce huge strength or you can induce many other properties like you can create high strength low alloy steels, you can create aluminium alloys, you can create magnesium alloys, titanium alloys, right.

Many many such kind of things are possible correct. That is possible. Even an aluminium alloys you can I have told you that you can have precipitates. So, basically these are used for structural applications unlike all the others thin films and nanoparticles mostly they are used for functional applications, but these are used for structural applications.

And the grain size should be between normally 10 to 100 if not 1 to 100, ok and they are basically made by top-down approach which we have discussed already. Top-down approach means starting with the big one and then to that, but you know need not always you know start with the big one, big grain size. You can start with liquid also.

So, materials ok would be rather crystals than glasses. You know this is what is as we said and many other people have said. Why? Because it orders all atoms will sit exactly the same distance from each other and they can satisfy the inter atomic bonds very easily, disorder. You disturb these comfortable sitting arrangements, you can see that when you are in a class if you all are sitting in all the you know every chair, that means distance from each other is constant and your bonding is strong.

But if you are sitting disorderly, some people here some people there, then what will happen there will be stretching of bonds and there may be squeezing of others. Also if you are sitting very close by and this leads to you know energy of the system to be increased.

Liquids are only this order because the heat actually a leads to violent movement of the atoms and they can sprung these low energy crystalline bonds very easily, but solids are not that they are from at lower temperature therefore, this can do that but you know if you cool it rapidly, you can produce nano crystals right.

How? Because if you cool it rapidly, the crystals will not get time to grow and if you cool rapidly you can have large nucleation also. As the nucleation rate increases, you are going to form many many many nuclei and then they freezes rapidly. Then you can have a small grain size and that is what is done in a melt-spinning technique ok.

What is done in melt-spinning technique? Very simple, you can take a reservoir of liquid or a molten alloy or liquid molten pure metal also possible in this is a reservoir, ok and then you can allow this liquid to fall onto a water cooled spinning copper drum, ok. I will talk about why copper drum. As it is falling on this water-cooled spinning at a very high speed 2000 to 3000 rpm rotations per revolution per minute ok; because is rotating a high speed.

It is water cooled this thin liquid jet or stream actually which is falling on this copper drum immediately solidifies in a microsecond time, not even a millisecond, microseconds time because it is cooling at a very rapid rate.

Most likely, it will lead to formation of amorphous space or if you can control this cooling rate little bit by controlling the spinning, you know revolution per minute or you can control the cooling of this copper drum, then you can form nano crystal instead amorphous, ok.

So, this is the way you can basically form a thin ribbon. This actually ribbons actually you can see ribbons in which nano crystals are present. This is known as a melt-spinning. You are spinning the ribbons out of the only melting, ok. So, now why we are using copper? Because copper can extract heat very fast. It has a high thermal conductivity.

So, as soon as the liquids jet falls on this copper wheel, it can extract very fast and if you cool it by water, you can even cool it. You can even remove very fast. So, that is why in all this the rapid solidification experiments, copper is used as a mould or as a drum or something right that ok. This is one way of creating nanostructure materials. Basically, you are from a thin strips by rapidly solidifying.

Other way I have doing is to basically you know using a surface molten layer. You can put a laser beam on the surface of this material. You can see that correct and as you put the laser beam and pass the laser beam is passed on the surface of these solid a thin layer is molten and now, you imagine a thin liquid layer is a contact with a large solid layer.

Heat transport will be massive very fast from the liquid to the solid. Because of the very rapid heat transport from the liquid to the solid, the solid liquid on the surface of these because of laser melting will solidify at a very fast rate, ok. So, you can see that you can so you can cool it very fast by using melt-spinning using copper drum. You can also cool it very fast by first melting a thin layer on the surface of the material by using a laser beam or you can do electron beam also.

So, only difference in electron beam and laser beam is that electron beam requires vacuum system. Laser beam requires nothing. It can be done in normal air, ok. Obviously, if you do a normal air oxidation is high. So, you could you have to put some argon gas or something near the molten zone ok. That is ok. These are all can be done.

So, that means what you can always create nanostructure surface layers by using laser surface treatments, this is routinely done. Nowadays in various applications if you want to create a surface layer which is a nanostructures, this can be easily used as a technique correct.

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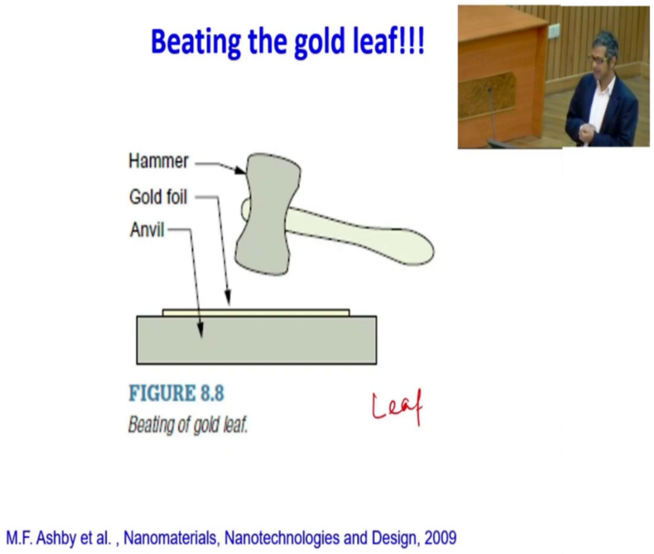

Beating the gold leaf!!!

FIGURE 8.8
Beating of gold leaf.

Leaf

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Well yeah so this is something I should discuss. I thought I should have discussed, but you know you can always do a use a technique what is known as a the beating the foil, beating the gold leaf. All of you know that gilding. Gilding you do not know? Well, you have seen probably many people use the gliding as it is nothing, but applying gold leaf thin layer of gold on a surface.

Suppose you have a ring made up of stainless steel and you want to make it looking yellow color, ok. So, you can put a gold leaf on this ring or even on the bracelet ok. Many people do it.

Then it will be cheaper because it is not fully made of a gold ok. The bracelet is very heavy if you make fully made of gold, then it will be very expensive right. Instead you can you can put a layer of gold, but you know in olden days, there is no way of depositing gold by electro deposition. The technique was not known.

So, what the artisans used to do? They used to take a gold and hammer it. Hammer hard and hard and hard and as they hammer it, gold will become thinner and thinner and it will form a leaf ok. Remember that this word leaf. Leaf means very thin as thin as like a tea leaves ok.

So, you can make that, then this one can be wrapped around your objects whatever you want to cover it up and this is known as a gold gilding. It is very old technique. It was available in you know mesopotamian times also ok many people know it but this is a labor intensive method, much labor intensive.

You can create 2d layers by this way. Instead of depositing thin films, you can easily do a 2d layer, but if you nowadays obviously it is expensive. That is why people wanted to make as thin as possible, but if you make a very thin, it will may break and it may not have sufficient strength to withstand during volunteer because you are wearing a bracelet and you are hitting it on surface, it will break.

So, that is why you need it will be always 1d. Actually, not even 1 d do, the 3 d only the grains of gold will be nano crystalline, ok. Because of this heavy deformation, you are hitting hard and hard and hard because of heavy deformation this will happen correct. So, that is something which is a always to happen that.

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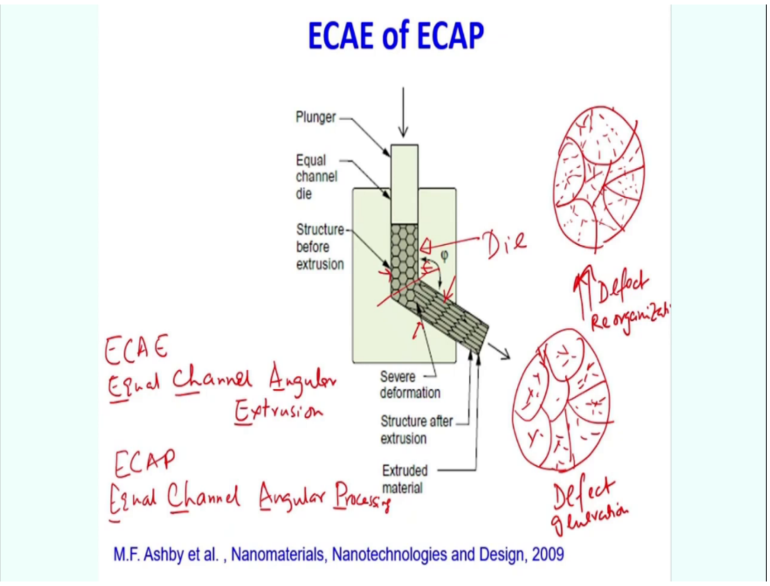

ECAE of ECAP

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So, one of the technique which is the which is done which can used to create some nano nanostructure grains is known as a ECAE or it is same as like gold leaf or ECAP? What is that technique ECAE or ECAP? Ok this is nothing, but equal angle extrusion ECAP means equal channel angular processing.

So, you can see that how the ECAP comes or what is ECAE again equal channel angular extrusion; because extrusion is a word which is peculiar to metallurgy. That is why people use p angular processing, what is done here ok. Very simple thing you can have a die, you can see this die this is the die, correct. Sorry, this is the plunger, this is not die. Die is inside. This is the die correct and this is written ok.

Now you can this die is made such way that angle between entry and exit is higher than 90 degrees. You can do 90 degrees also, but it should be at least 90 degrees higher is better, ok. So, now you put a material, you can always heat it up many cases you may not need to heat, but some material you need to heat it up and then after it is hot, you can use a plunger at to push it down or push it down to pass through this channel, pass through this die.

Because it is a channel and that is why I had given the equal channels. You see that thickness of this channel is same. That is why it is called equal channel and it is an angle like entry and exit. That is why it is called angular and because you are pushing is down that is why it is known as extrusion, ok.

Those of you know extrusion will understand that extrusion is a process in which you can push a metal through a die. Normally when you are pushing is to the die, the entry and the exit dimensions are different. Normally entry thickness will be larger, exit thickness will be lower, but here it is opposite. Your entry and exit thickness is same. The diameter of this die, they are same.

So, because of that because you are pushing it high, so what will happen at this position where there is a direction change ok here and this one is plane basically grains have to really reorient themselves.

So, when they are reorienting themselves, they elongated ok. It was nicely hexagonal grains become elongated and in the whole process because you are pushing it hard, the grains also get deformed and deformed extensively. Deformation means it kill lot of dislocation and twin structures and then, this can lead to nano crystallization ok. That is what is done.

How it is done? Well, suppose you have a large grains in this material. Now, I deformed it. Once I deform, I will create defects and I dislocations inside the grain you can create twins also. So, as you create more and more dislocations. They will entangle, then interact each other correct because they are entangle randomly forming energy of system will increase. So, what they would like to, they would like to arrange themselves nicely.

So, that is why what they can do is, they can arrange nicely inside these grains. Easily they can arrange inside this grain. How they can form small angle grain boundary like these they can arrange. So, what you are doing? You are forming additional grain boundaries and when they do that, the dislocations can easily reduce their energy and that is the way they can form new grains. So, these big grains then become disintegrated to small grains, ok.

So, you can start this big grain and then, you can divide these grains into small grains because of defect generation dislocation is a defect right in solid material. So, these defects will lead to reorganizations of the defects because as you create more and more defects, that is what happened if you are hitting a gold leaf hitting hitting hitting hitting, you will generate keep on generate dislocations right, but then once it will be filled with dislocation density will be so high, then dislocations will be interacting each other.

They will cut each other energy of this. Whole thing will increase, mechanical energy and to reduce it this dislocation will like to rearrange themselves. One of the way of rearranging themselves is what one of the way of rearranging themselves is by following the small angle grain boundaries because any small angle grain boundary will be nothing, but a combination of dislocations arrange nicely one after the another one below. The other correct that is why they can do such a kind of a nice crystallization crystallized grains or recrystallized grains whatever you say or recovered grains it can form.

So, this is what happens. In this case also not only the grains are getting elongated, but also grains are becoming finer because of these aspects. So, just now I discussed correct defect generation, defect generation here and defect reorganization here correct. These are the two ways things happens.

So, I will stop here. I think I have discussed a lot, ok. So, what I discussed? I started with zero-dimension nanomaterials. Remember in the last lecture, I have discussed about the inert gas condensations and in this case I have discussed about sonochemical techniques sol gel techniques, right.

And then I discussed about what else sonochemical sol gel. Let me go back molecular assembly, self assembly like Langmuir Blodgett techniques, then I discussed about 2 D or 1 D nanomaterials like electro depositions PVD CVD, Ok. And obviously, then I started discussing about the three-dimension nanomaterials like liquid root melt-spinning or laser surface treatments or deformation rules.

So, we will continue discussing about these things in the next lecture also. I will try to complete in the next lecture that whole process of synthesis of nanomaterials and then, I will move forward for the properties.

Thank you