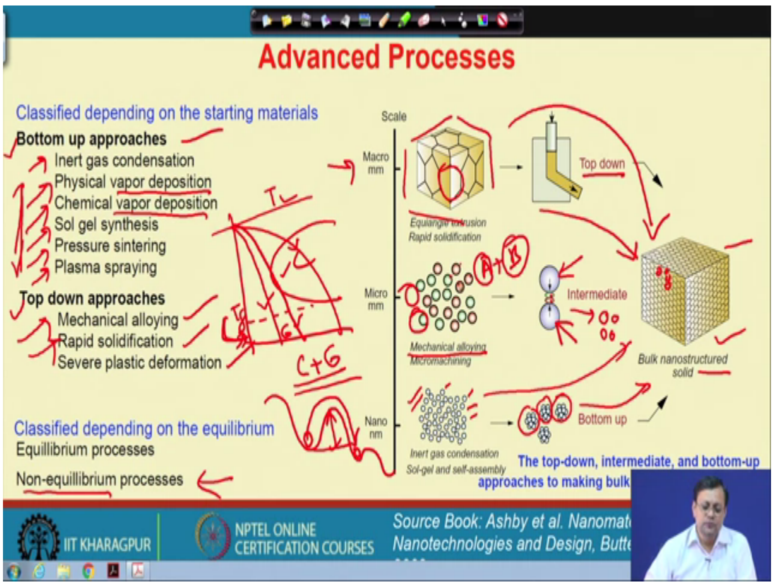
Advanced Materials and Processes
Prof. Jayanta Das
Department of Metallurgical and Materials Science Engineering
Indian Institute of Technology, Kharagpur

Lecture – 51
Advanced Processess

Welcome to NPTEL myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering IIT Kharagpur. I will be teaching you Advanced Materials and Processes. Today, we will discuss Advanced Processes. So, far we have mainly discusses on different materials, they are fundamentals and many of the different aspects and mechanisms involved on the application of those materials. Let us say like one of the very common advanced material like, nickel titanium shape memory alloys. This is also called as a smart material and there are some processes linked with that.

However, on the other hand if we talk about bulk metallic glasses, the processing of bulk metallic glasses required high under cooling, means from the liquid state we have to cool it very fast so, that we can bypass. The crystallization process or avoid the crystallization process and this is one of the such non equilibrium process. So, today we will discuss mainly on those kind of different processes for synthesizing advanced or smart and functional materials.

(Refer Slide Time: 01:49)



So, these all these advanced processes can be classified at depending on the starting materials, what I want to mean that we can start with atoms and those atom can keep on joining together to make and grow to a larger link scale. So, from a atomic scale we go to nano scale, to a ultra-fine scale and then to a micrometer scale and keep on going that. So, that it can reach up to certain length scale of it is application.

On the other hand, we can also start with a very bulk billet or let us say 1 meter cube of a material and then we process those material so, that the structure can be tuned to the scale of a nanometer. If I simply talk about let us say typical nanomaterial's ok so, where the grain size or particle size reaches below 100 nanometer.

So, we can start with atoms or molecule and then we can start from such kind of molecule. And, then by some processing technique, we can make those kind of clusters and then by some other secondary processing we can process some 3 D bulk structure or bulk nano structure. However, definitely it has to go through many different processes. And so, this these processes are mostly concerned with a bottom up approaches. A bottom up approach means, that we start with this molecule or atom and we can reach up to a bulk scale structures.

Now, on the other hand, let us say we can start with such kind of bulk solid, where the grain size is very big maybe 300 400 micrometer or maybe even 1 millimeter. And, then by some processing technique we reach to a very fine nano scale microstructure and these nano scale let us say in the range of 100 nanometer. And, since here we start with a macroscopic sample and then we make these processes or adopt some processes for processing a bulk nano structured solid, we call it as a top down processes.

So, here I basically list these some of these bottom up or top down approaches like, let us say the mechanical alloying, rapid solidification, severe plastic deformation. These are common top down approaches. The question comes here that rapid solidification, we have already know this term during discussion on bulk metallic glasses.

So, here we start with a liquid and then this liquid actually cooled very fast at a certain cooling rate. So, that we can produce those kind of bulk nano structure or metallic glass 2. Now, in case of these bottom up approaches there are several approaches like, inert gas condensation, physical vapor deposition, chemical vapor deposition, these are very common vapor deposition technique and sol gel technique and pressure sintering or plasma sintering or plasma spraying and so on.

So, in case of let us say if we again think about this top down processes; means from a larger scale we can tune these finer structure inside it. So, some of the processes again can be classified on the thermodynamic is aspect during processing condition. What I want to mean, that I can take a liquid and I can cool that liquid infinite smell small. So, very small under cooling can be given to a liquid and we can grow a larger single crystal ok.

So, this is a typical crystal growth phenomena, on the other hand I can simply take the same liquid and cool it very fast. So, that I can avoid crystallization ok or maybe I cooled in such a way that it simply touches the noose of the TT curve and so, I get Nano clustered crystalline clusters inside a glassy matrix.

So, what I would like to depict here with this diagram, that this is a crystal and let us say if I cool very slowly then I can enter into the crystalline phase. Whereas, from the T L that is the liquidus temperature if I cool very fast and glass transition temperature is somewhere here, then I can get a glass.

But, I am talking about processing of some nano structure, where the cooling rate has been adapted in such a way, that part of the microstructure transformed into very fine nano crystal where the crystal we do not allow them to grow, because of the rapid solidification and very low temperature, where diffusion of atoms are be less whereas, the part of the microstructure solidified into glass. So, I will get a crystal glass in that case.

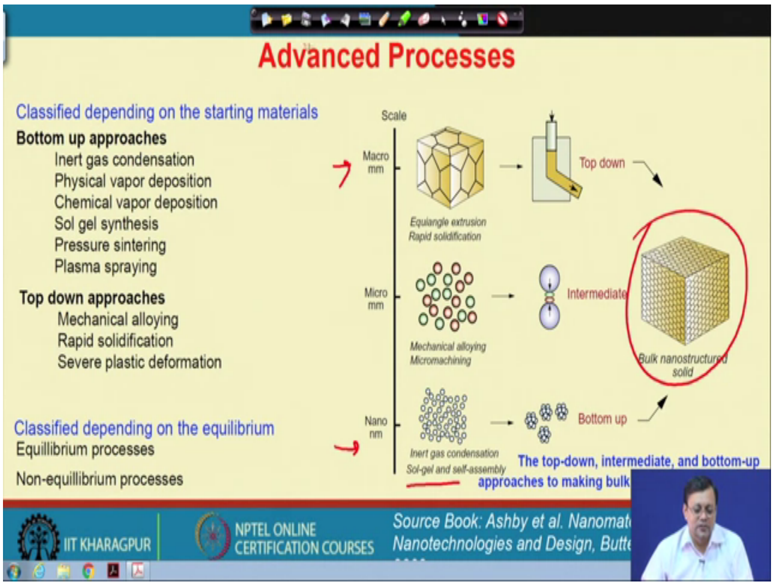
So, I am talking about such a process. So, there are enough opportunities of these processes. However, the thermodynamic condition has to be satisfied. So, in that case, if that very faster cooling can be given, we usually call them as a non-equilibrium process ok. Where, we somehow try to reach to a microstructure or a thermodynamic state of the material that is in a metastable condition.

So, let us say we have already discussed about different metastability. So, from 1 metastable state we can reach to another metastable state by passing some of these activation energy. So, these are some of the important aspect so, these are the bottom up approaches all these they are also the non-equilibrium processes and also rapid solidification mechanical alloying these are also the non-equilibrium processes, to achieve let us say the bulk finer structures.

Now, another aspect of a mechanical alloying, that we start with a let us say micrometer or millimeter sized particles. And then we take a grinding medium which let us say very hard spheres or balls and then we simply tried to make a finer size of those particles, that is a typical wall milling. However, we can also start with A or B element together of 2 different composition and, try to allow them together to make a bulk very fine nano powder, which are already alloying by A and B ok.

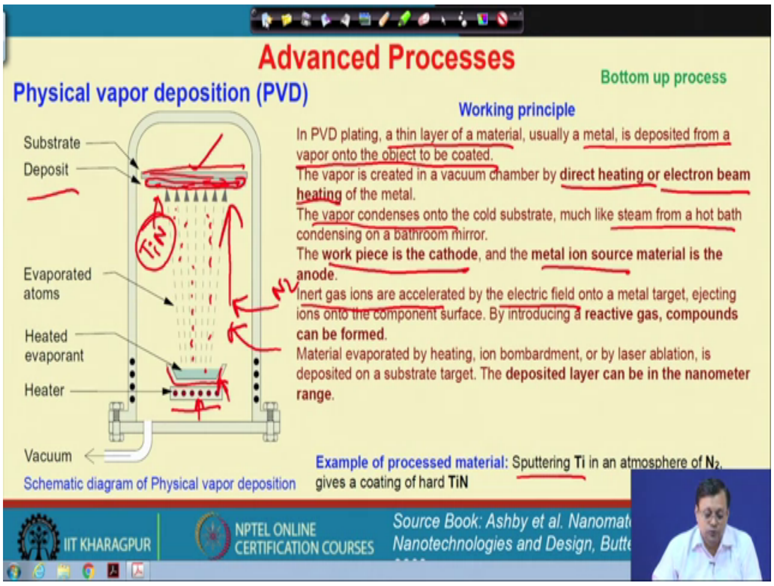
So, I am talking about solid state alloying. So, both are in the solid state and both have different composition may be one is the pure element like, nickel another one is let us say the copper. So, I took these two and then two different particle with one is nickel another one is copper. I mix them physically and using a grinding media and by introducing very high energy impact, we alloyed those powder it is also possible so, in the solid state. However, all these process has some benefit positive and negative side and so one has to consider all these aspects.

(Refer Slide Time: 10:15)



So, this is a very simple schematic to show that from a macro scale to a nano or atomic scale we can start building those blocks in order to achieve a bulk structure so that is possible and tune the microstructure. So, let us start with one of these vapor deposition technique and how this processes actually help to develop some advanced materials.

(Refer Slide Time: 10:41)



So, like the first one is the physical vapor deposition. So, the name itself says that there is a need of vaporizing the species which has to be deposited in a preferred place. So, we need a heater and the evaporate material are kept on a crucible and then we allow some heat to pass and then those evaporated atoms goes towards the preferred place, where it has to be deposited and then it finally, deposit on a substrate. So, this is the after deposition this material atom goes and preferentially deposited on a substrate.

So, for this you can see that if we need to develop a functional nanostructured coating, then we can adopt such a process where the atoms are molecule, which will be evaporated from the place and then depo goes to a place where it has to make the coating. And a thin layer of such material can be deposited from a vapor species on the object to be coated.

So, the vapor is created maybe in a high vacuum chamber where there will be no interaction with some other species or molecule or some other air molecule that should not interact with them. And a direct heating or let us say electron beam heating we can provide to these vaporizing species. And, the vapor basically condense on the cold substrate until it act as a sink of the heat it will never be possible.

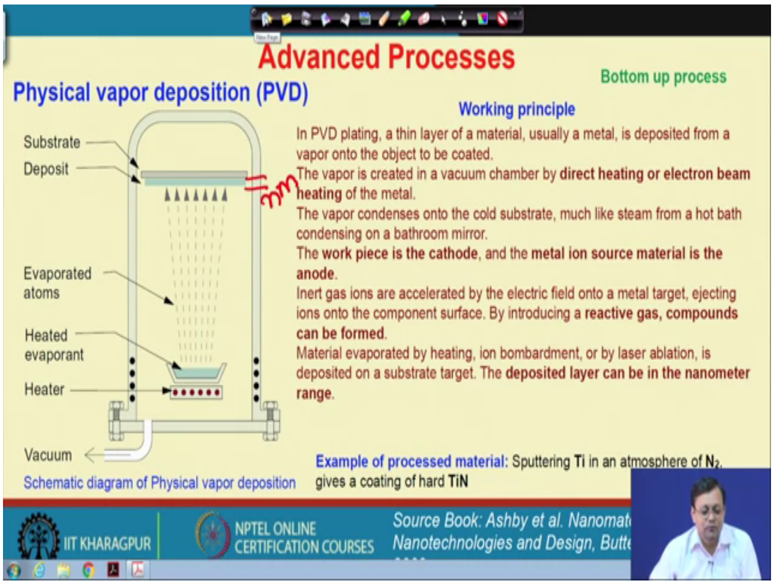
So, we can deposit on those substrate and the steam from a hot bath condensing like a bathroom mirror that is simply example, when we go to any for in a bathroom actually you can see that the vaporizing water molecule that simply goes on the mirror and deposited there yes. So, this is a simple example of that.

So, the work piece here act as a cathode and the metal ion as a source material is like an anode. And so, inert gas ion are accelerated maybe accelerated using some electric field on these target material to be deposited and the ejecting ions onto the component surface. And, by introducing we can also introduce some reactive gas into the media or let us say that compound can be formed.

So, I can give you 1 example of such very interesting vapor deposition technique, like we can simply take a sputtering of titanium. So, titanium will be vaporize and then we incorporate nitrogen into it ok and so, this nitrogen and titanium they goes together and make a titanium nitride coating on a substrate and this is something very interesting phenomena actually.

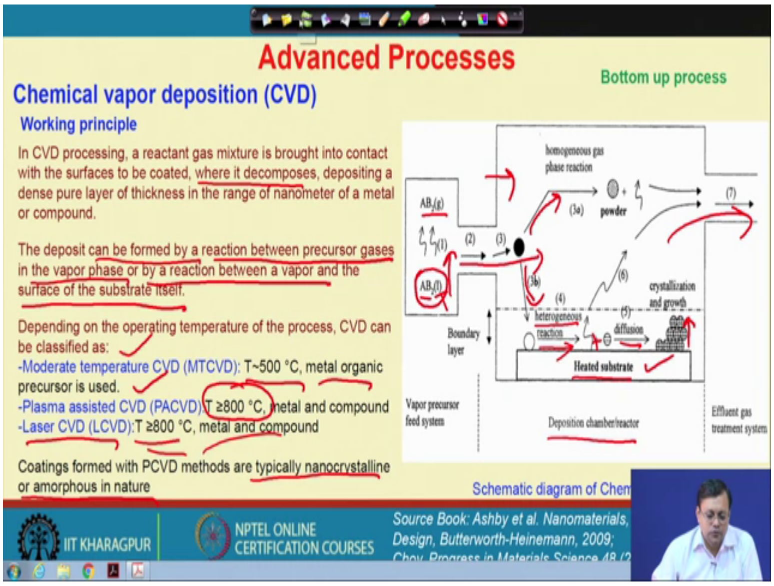
So, metal evaporated by heating or maybe it can go for some sort of ion bombardment by you can use some laser aberration to goes into the substrate. And these deposited layer, we can choose that depends on the time of deposition and, we can make something like few nanometer length scale thickness.

(Refer Slide Time: 14:03)



So, we can simply tune the surface properties of steel or any other substances by some coating. So, deposition technique or physical vapor deposition technique is one of the very interesting technique and for such kind of advanced processes.

(Refer Slide Time: 14:31)



Now, a very similar vapor deposition technique; however, a reaction is involved here, the reaction could be with the substrate itself. So, in that case this is called as a chemical vapor deposition technique. So, the basic working principle here is the CVD technique that a reactant gas mixture, that brought very close contact with the surface to be deposited or coated.

So, I can give you one example like A B 2 this is a composition. Let us say A B 2 is a composition and I take it as in the liquid state ok and then let us say the liquid goes into the gas phase by using some heating source ok. And, since this deposit need to be formed on a substrate and so, in this case these decomposes and deposited on a dense pure layer of thickness in the range of nanometer scale, but the deposit can be formed by a reaction between the precursors gases, in the vapor phase or by reaction with the vapor and the surface of the substrate.

So, these are the two possibilities so, I first from liquid it goes to a gaseous state and then it entered into a chamber. So, I have two different possibilities; one possibility that it react with the environment itself and then deposited or it can go and make a reaction with the substrate. So, you basically need a heterogeneous reaction and where, it has to react and then the diffusion will occur and then we can simply build up a particular as thickness on the deposited surface.

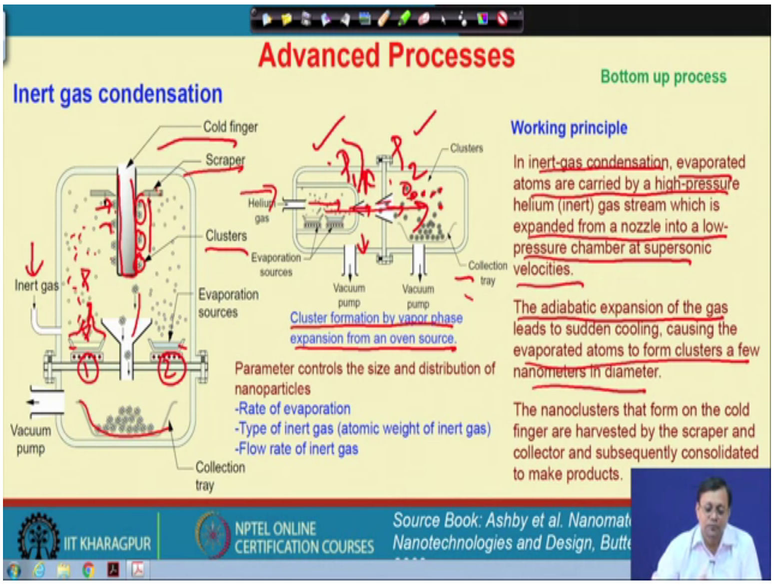
So, here you can see the processing parameters are must be very much important, because you have to control many of these aspects here. So, let us say the temperature of the substrate that may be one very important and the gas you want to incorporate in the chamber. So, the temperature somewhat in the close off let us say 500 degree centigrade for a metal organic precursor so, that it can be evaporated.

So, moderate temperature CVD can be done or let us say the plasma assisted CVD, in case of a plasma we can go walk to higher temperature, metal and compound can be used here for deposition or we can simply take a leisure for this vapor deposition technique, where we can reach to much higher temperature for again for the metals and compounds.

So, coatings are formed by these kind of PCVD that is the plasma assisted CVD technique and here the method typically produces some nano crystalline or amorphous microstructure. So, I show you here one of these reactor part where the deposition are taking place.

Now, definitely some a fluent gases will be created and that gas will go out of the chamber with some after the reaction has occurred and some deposition has been take place. So, these are the two very important vapor deposition technique for let us say producing some coating on the surface and very hard coatings. If the coating is amorphous in nature and if you diffuses into the surface, then the interface strain to definitely increase.

(Refer Slide Time: 18:23)



On the other hand, let us say in a inert atmosphere and we can also condense, these this molecule on and collect those molecule which deposit on a some surface by using some scrapers. What I want mean that I took a liquid and then I vaporize us in the liquid. The liquid goes and deposit on a finger or cold finger means, there is a need of a sink heat sink actually, because the deposition can took place only when the atoms will release the energy and the energy will be absorbed by that cold finger right.

And, then after a some amount of deposition we can simply take a scrapper and take out all these clusters or nano scale clusters and collect together. So, this is a typical inert gas condensation process and, I show you here that how it really took place.

So, first we take let us say evaporation sources, these evaporation sources we can take let us say 1 and 2 of 2 different species ok. Because, we want to make a composition which should be a mixture of these 2 different pieces, that is also possible or maybe the single species. And so, the evaporation will take place from those pieces and goes and deposit on the cold finger.

So, this is a cold finger, which is a heat sink and after some amount of deposition with a regular periodic interval, I can uses scrapper which take away all these clusters of particle and simply it is collected at the bottom.

And, this can be done in a inert condition and we can introduce some inert gas during this whole process. So, cluster of those atoms that can be done in that case. We can also modify this kind of inert gas condensation technique, where we can pass through very small orifice and here the pressure is less than the pressure here.

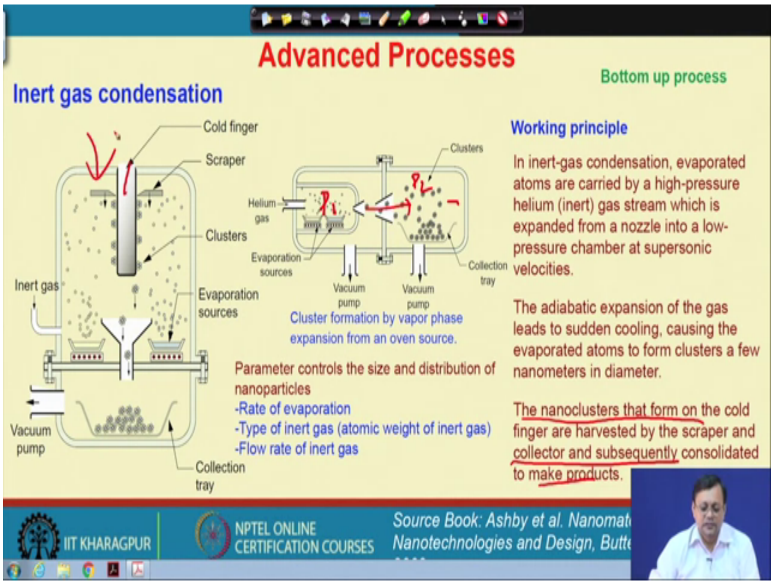
So, when the pressure it goes to a lower pressure region then it will expand right. So, from high pressure to a low pressure and it will expand and then we will get individual particle in a much better form. So, that is also a possibility so, like here these are the 2 different chamber and let us say helium inert gas we will carry all these vaporized species. After evaporation it goes through a small orifice and it deposited here as cluster and this is like a collection tray. So, these are the cluster that formation by the vapor phase expansion from a oven.

So, here the pressure is basically higher than the pressure here. So, this is P 1 P 2 P 1 is higher than the P 2s. So, I have 2 different chamber and by maintaining these difference in the pressure, we can simply make form those clusters. So, in a inert gas condensation technique the evaporated atoms are carried by a high pressure helium or inert gas, which expand from a nozzle into a low pressure chamber at a supersonic velocity.

Because, whenever we passed these helium gas then from a higher pressure to a lower pressure it goes very fast. Without condensing in any of the localized places, because, we want the maximum efficiency of the process that all that atoms or molecules that is going to be vaporized should be deposited in the chamber and that will simply yield the process.

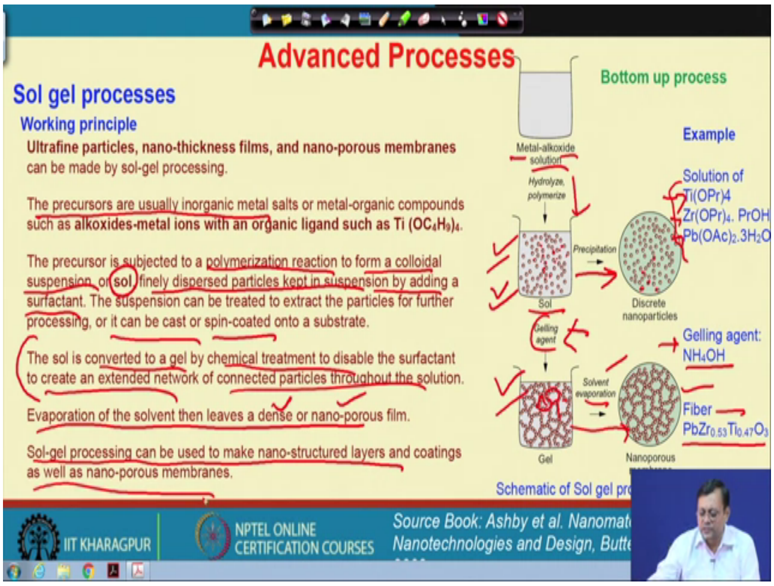
So, the adiabatic expansion here of the gas has another help or assist that once the gas expand by volume, then temperature will automatically decrease right. So, causing that evaporated atoms of cluster to a to form a nanometer scale clustered you are in the environment itself actually right. So, it does not need to be deposited on a cold finger. So, they form cluster inside during going to the next chamber so, that is one of the very benefit of the process.

(Refer Slide Time: 23:17)



So, we really never need any assistance of such a cool finger here, because it is going from a higher pressure region to a lower pressure region and there is a expansion of the gas actually, because the metals will filled cooled. So, the nano cluster that formed from a cold finger and harvested by the scraper or collector that is a typical process for a typical inert gas condensation technique. So, these are the 3 very important process like the vapor deposition or inert gas condensation for producing such kind of bulk structures, including coating and so on.

(Refer Slide Time: 23:53)



Now, the sol gel process is another technique for producing very bulk skill powders or nano scale particles. So, that the n product can also be tuned it could be also a network like nano structures. So, we not only produces powder of such a scale, but we can also produce using sol gel process.

So, here the working principle that we need a metal-alkoxide solution and then we polymerized it or hydrolyzed it and so, we create that sol and then if we allow precipitation of the precipitation process then we will get these discreet nanoparticles in the solution. However, we can also add some gelling agent and then these suspended a nano particle, they will basically from some network like structure. And, if we evaporate those solvent then the residue product will be like that kind of nano porous membrane or network like structures.

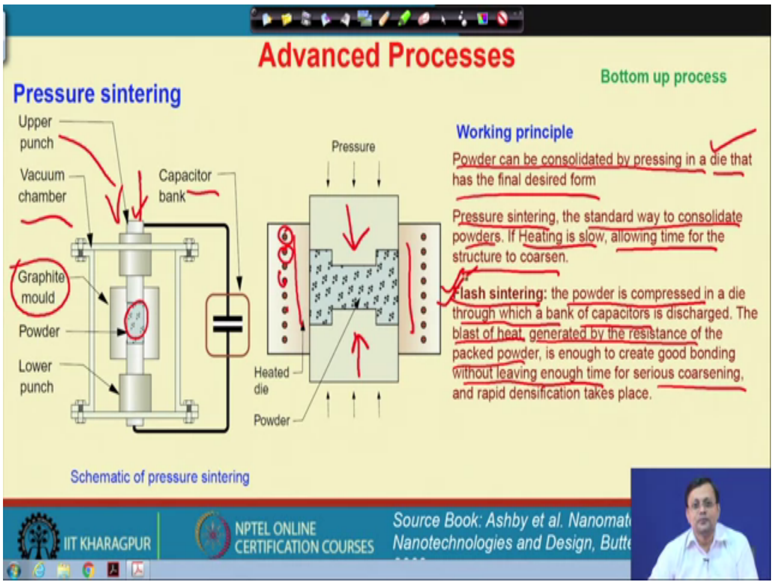
So, in that case actually the precursors are usually the inorganic metal or salt like here we have procedenium and titanium compounds with zirconium or led. So, we can take all these 3 together and then we can add some gelling agent NH 4 OH. And, ultimately after this solvate evaporation we will get such kind of fiber compounds so, this is a very typical sol and gel process.

However, if you need let us say only this has the discrete nanoparticle which may be consolidated later on you can you really do not need any gelling agent here. So, the precursors here they are subjected to polymerization reaction that I am repeating again, this polymerization reaction is very important to form a colloidal suspension, this is actually called as a sol. So, after polymerization and finely disperse particle that kept suspended by adding some surfactants.

So, that the particle should not may form any cluster together right. So, they should be individual suspended particle in a sol. So, suspension agent should be a added or let us say some spin coating on a substrate can also be done. So, the sol is converted to a gel by some chemical treatment to disable the surfactant and to create a extended network of connected particle throughout the solution.

Whereas, the evaporation of the solvent in the next day when we need such kind of network that can form a dense or nano porous film. So, sol gel processing technique can be used to make nano structure layer or coating as well as nano porous membranes.

(Refer Slide Time: 27:13)



So, these are the very useful technique for direct synthesis of the nano particle. Now, this pressure sintering is also another advanced process however, this is a process linked to it let us say scaling up process. Means, I can start with some powder of precursor powder and then I can scale up the length scale of the product final product.

So, here usually we can also use some graphite mold or any other material we can also use and then we have a vacuum chamber. So, we take this powder and using some pressure we assist some sintering process with the assistance of some temperature actually.

So, the capacitor bank is here and the upper punch is here. So, pressure improves the sintering process so, powder can be consolidated using this kind of process inside a die. So, the die can be from different metal it could be a tool steel, it could be a graphite mold and so on. So, the in a pressure sintering process the standard way to consolidate powder this is a very common technique, and like another technique you may have heard that is the hot isostatic pressing.

So, there the temperature is also used so, alloying the time for the structure to coarsen. So, we need a heated die here so, these are the induction coil and the powder is simply consolidated during application of the pressure so, the why we need application of pressure in that case?

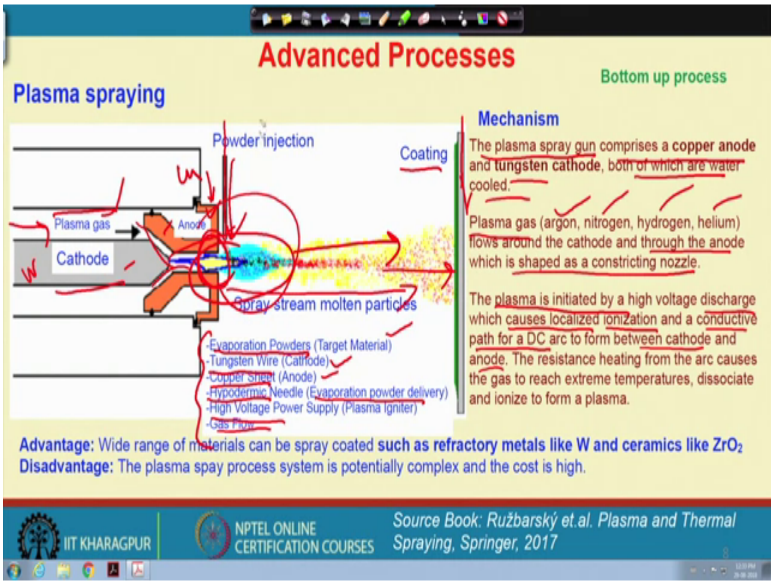
So, if you apply only temperature for sintering then that the density of the sintered product will very less. So, maybe 80 percent, but if we apply pressure during sintering then not only the mass can be transported, but the atomic diffusion can also be enhanced at a higher temperature.

So, with that process we can reach to near theoretical density depending on the material and the parameters of the experiment you have chosen. However, there is also another additional technique with that we call it as flash sintering process. So, during this process the powder is basically compressed in a die through which a bank of such capacitors are discharged and the blast of heat is given at a flash and it generate actually a resistance to these back powder is good enough to create a good bonding, what without leaving enough time for serious course any.

So, one of the very important aspect of consolidation of the nanostructured powder, that they always prefer to have a grain growth. So, if a nanostructure causes grain growth that it does not remain as nano so, it become basically microscopic scale. So, from 10 Nanometer, we can easily get basically a 100 micrometers. So, that is not our intention of sintering, our intention of sintering that we need to reach to a theoretical density by maintaining the structural unit or the grains to be in the nano scale.

So, far doing that this flash sintering process is very important process, that at a flash we at a very sudden instant we provide the heat, which causes immediate packing of those powder without any grain growth. Because, grain growth is a diffusion control process and if you get some time so, we do not allow that time to cause (Refer Time: 30:54) process.

(Refer Slide Time: 30:57)



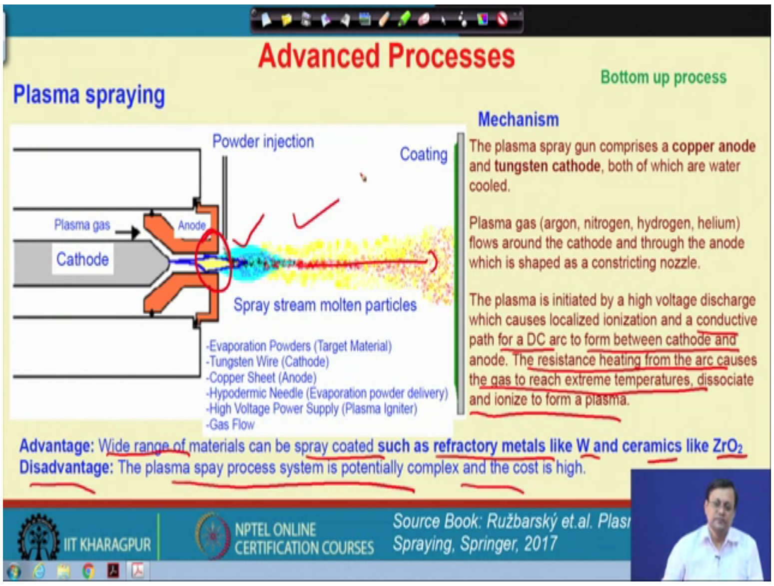
Now, these are all these process we are talking about basically some from a very fine particle or cluster to go up to the higher side. So, now, another process is the plasma spraying, in this process here a plasma means basically a vaporized iron or atom that is a force to go in on a substrate ok. So, for coating purpose let us say so, there are many different coating thermal barrier coating many of these are plasma spray coating we have discussed, for improving the surface properties of super alloys for higher temperature you may recall those discussion.

So, here we have a cathode and there is a anode and the powder is injected we create a plasma and this plasma is shown on a surface. So, here the evaporation of the powders, that is basically the target material and the tungsten where that act as a cathode and the copper sheet that act as the anode. So, here what we are talking about and then hypodermic needle that is a evaporation of the powder delivery that basically lends this powder. And on the other hand the high voltage power supply is required and the gas flow these are let us say some of the parameters that you can choose and these are very much needful.

So, on the other hand this plasma sprayed gone that comprises of a copper anode and tungsten cathode. So, this is basically tungsten and here we have a copper and both of which are basically water cooled near the plasma actually. So, this plasma require a gas and that gas has to be passes through that anode, which will carry those plasma particles actually.

So, here we have argon, nitrogen, hydrogen or helium, that flows around the cathode and through it passes through a nozzle and goes and heat on the surface where the coating has to be done. So, the plasma is only created when a very high voltage is applied so, that basically due to some voltage discharge that all causes localized ionization and a conductive path for the DC are to form between the cathode and the anode so, this plasma is created in this place.

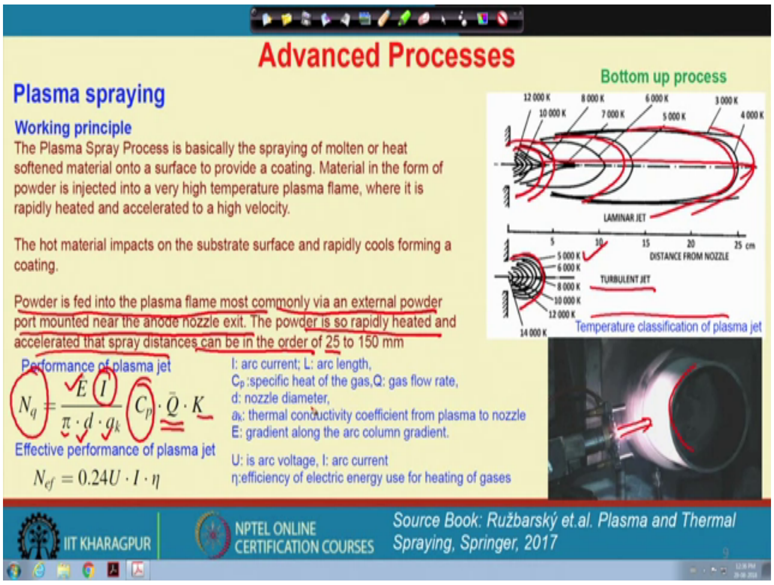
(Refer Slide Time: 33:15)



And, the conductive path for the DC arc to form this cathode and anode. The resistance heating of these arc causes the gas to reach to extreme temperature and dissociate an ionize in order to form this plasma, which basically goes and on a cold substrate it basically deposited.

So, advantage is a definitely the wide range of material can be sprayed or coated as a refractory metal like tungsten ceramic zirconia, we can use that for the thermal barrier coating and these advantage that the plasma sprays process is potentially rather complex and the cost is definitely high. However, we can create highly sophisticated advanced coating on the material.

(Refer Slide Time: 34:03)



So, if you just have a look at the temperature scale then you can realize that how much temperature we can reach here. So, something like 5000 K 2, 6000 K with a turbulent jet. So, this is something like a temperature classification on it is plasmas grade and the temperature basically falls as the plasma, if you are away from this plasma process.

So, here I show you on a turbine engine how this plasma are sprayed on a material. So, the working principle or the efficiency that N q that is the performance of a plasma jet are linked with the gradient along the arc column, divided by the pi multiplied by the arc current that we applied and d is the nozzle diameter, and a is basically the thermal conductivity, C is the C p is the specific heat of the gas that is conducting and at the glass flow rate and so, the gradient along the arc column current and so on.

So, there is some constant with that so, here all these a process parameter and variable has to be optimized so, that we can get a effective condition for plasma spraying. So, this powder is basically fed in on the plasma frame that most commonly on a external powder port that is mounted near the nozzle to exist. And, at the powder is so rapidly heated and accelerated that the spray distance can be formed let us say something in the range of 25 to 150 millimeter.

So, these are also some of these advanced technique or advanced processes for processing some coating techniques. So, with this we finish our discussion today, we will continue the discussion of different top down and bottom up approaches in the next class.

Thank you.