# Nano structured Materials-Synthesis, Properties, Self-Assembly and Applications

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## Module - 2
## Lecture - 11
## Spray Pyrolysis

Welcome back to this course on nanostructure materials, synthesis, properties, self-assembly and applications. Today we will be having the lecture 9 of module 2. Today lecture would be on spray pyrolysis. In the previous lecture, 2 previous lectures we looked at the template methods of making nanostructured materials. We looked at various templates 3 d templates 2 d templates, then we used like porous alumina. Many different templates, how they can be used to make nanowires and nanorods including materials like DNA on which you can grow nanotubes or nanowires. So, today we will be discussing a very popular method.

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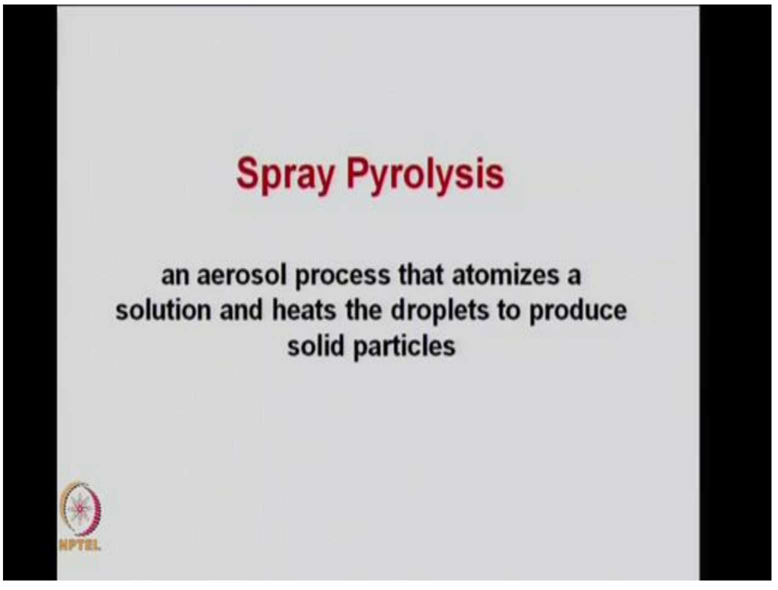


These spray pyrolysis method where which is very important from industrial point of view. Since, it is a simple method it is a scalable method can be applied to large areas and hence you can make lot of materials using this spray pyrolysis technique. From the words spray and pyrolysis you can understand that something will come out as an aerosol and will then be heated to produce the solid particles. So, pyrolysis is the term which is telling you that something is going to be heated and it is going to break down the droplets into particles.

So, typically a spray pyrolysis can be define as an aerosol process that atomizes a solution and heats the droplets which are formed by the atomizer to produce solid particles. So, you can consider 2 steps or you can break down the spray pyrolysis method in 2 basic steps. One you have the atomizer, which creates the droplets and then those droplets are fall of on some sub straight which is heated and gets these solvents evaporates and you gets solid particles. For those who may not have studied what is aerosol or colloid chemistry. Aerosols are typically droplets in a solid particles in liquid. So, you have this kind of an aerosols process which you can use to make droplets and these droplets then will produce solid particles.

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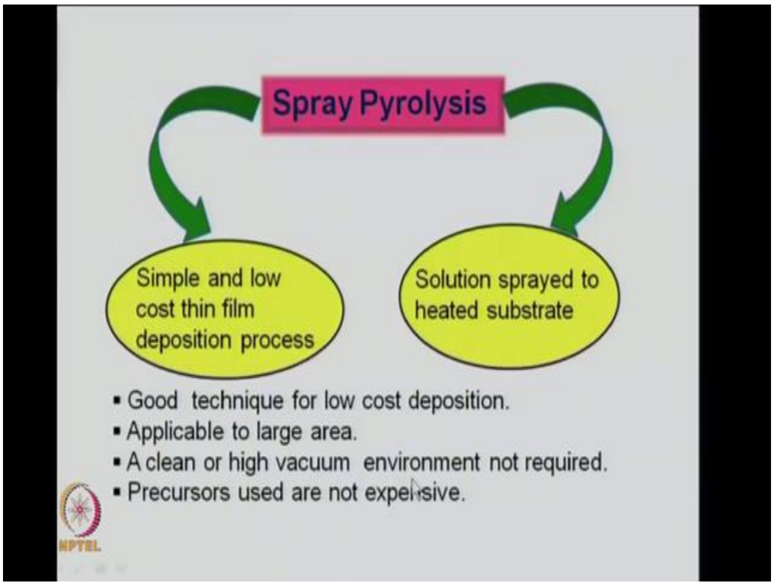


So, it is the basic method or the simple spray pyrolysis method is also called conventional spray pyrolysis method, is very simple and is a low cost process by which you can deposit thin films. So, where what you do is you have this solution and that is solution is sprayed using an atomizer or a nebulizer on to a heated substrate and then you can get particles or films depending on your technique. So, the spray pyrolysis method is a good technique for low cost deposition can be applied to a very large area.

So, you may have applications where you need to make thin films of the size of say 1 square meter by 1 square 1 meter by 1 meter. So, those kind of large area applications are easy to be carried out using spray pyrolysis. More sophisticated techniques is difficult to make large area thin films or coatings, which are easily done by the spray pyrolysis method. You do not need a very complex experimental setup. For example, you do not need very extremely clean rooms or clean environments like is used for certain very a sophisticated techniques.

You do not need a high vacuum for example, to do this kind of spray pyrolysis based thin film deposition. Then the precursors that you used that is the starting materials that you use are not very expensive in this spray pyrolysis method. So, overall we can say this methodology can be applied with very minimal cost in most of the or many of the industries and can give you viable industrial processes which can be scaled to very large sized areas.

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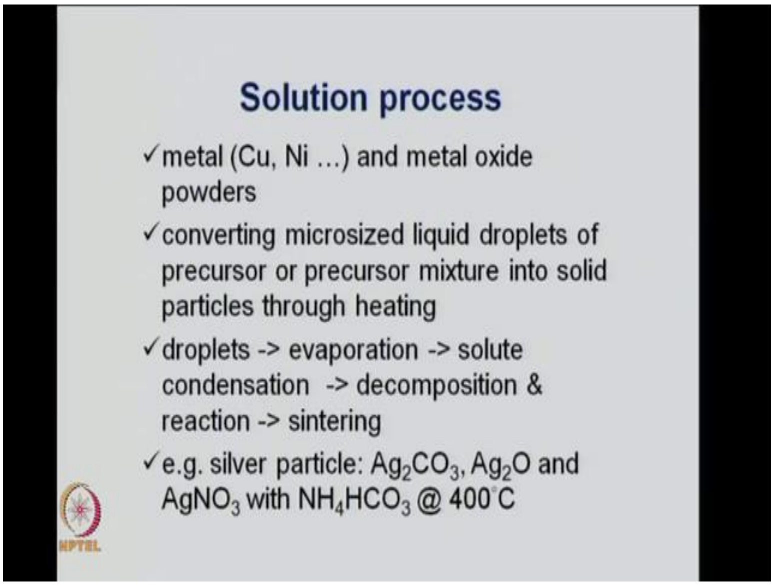


You can get very good films based on the spray pyrolysis technique, using minimal investment. Now, this solution method, it is a solution based process you must first make solution of whatever material you want to deposits. So, you have to take a salt of that in aqueous medium or something. Typically you can make metals metal oxide powders and then you convert these micro sized liquid droplets of the precursor. It may be having one kind of a material or it may have 2 material. So, it is the precursor mixture and then you heat those precursors mixture into solid particles.

So, the process can then be divided into steps like you have droplets liquid droplets in which you have this solid particles which an evaporation give you the solutes which condense. Then after condensation they can decompose and if they are able to decompose they will decompose at higher temperature. Or they can be reacted and then heated at high temperatures to increase the size of the particles which is called sintering.

So, the overall process in steps goes from droplets containing the liquid typically it is water and then which contains the solid particles and then evaporate gives solutes, which condense and then if the solutes are can be decompose they will decompose leaving you behind the oxide or the metal or metals sulfide. Then you further heat them to get particles which is called the sintering step.

So, an example if you want silver particles you can start with silver carbonate silver oxide and silver nitrate and you can make a precursor mixture with ammonium bicarbonate and heat it at 400 degrees. So, you will get droplets initial droplets will be micro sized liquid droplets of these precursor mixture. So, may be silver carbonate or silver oxide with ammonium bicarbonate that will be present in the droplets. Then when you heat them at 400 degrees, then they will leave behind silver particles.

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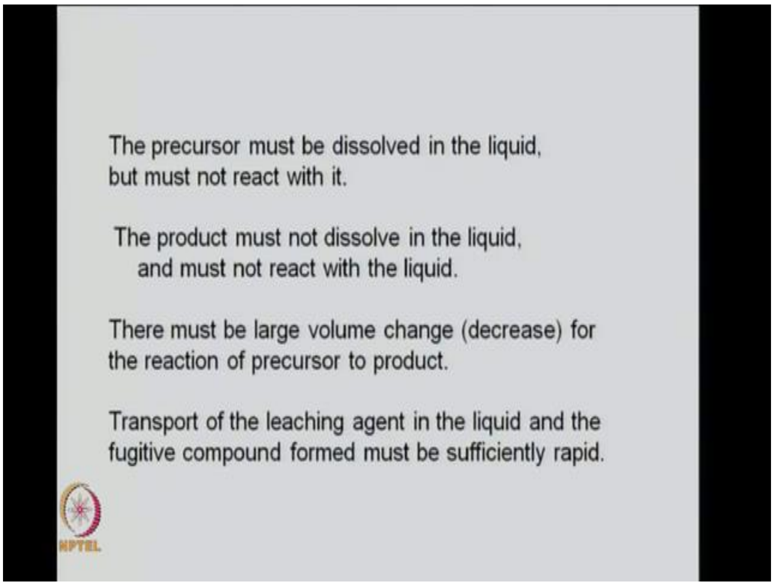


So, this is the solution based process of spray pyrolysis. In this spray pyrolysis method a certain factors need to be considered while during the process. The precursor that you choose must be dissolved in the liquid. Most of the time that is water and must not react with it. This is one of the very important points that whatever you take as your starting or are agent with which you are going to do the spray pyrolysis, they should not react with the liquid in which you are dissolving. The second thing is the product that means what you want to make, the particle that you want to make must not dissolve in the liquid and must not react with the liquid.

So, this is with respect to starting precursor which should be dissolve, but must not react this is with the product which forms at the end should not dissolve in the liquid and neither react with the liquid. These are two very important things. The other factor is there must be a large volume change and typically the volume will decrease because we are going for a droplets to a particle. This volume change should be as large as possible, when you are going from the precursor to the product. That helps in the spray pyrolysis.

The transport of the leaching agent in the liquid and the compound which is formed must be very efficient and rapid. So, the liquid which is remaining when you are having the particles the solvent which is remaining must be removed very fast from the particle. That removal is important. So, these are four criteria which are very carefully chosen while planning a typical spray pyrolysis process. You way in the factor or which precursor you want to choose, what kind of substrate you will use all that has to be taken into account to plan for proper spray pyrolysis process. Such that you have good homogeneous particles of submicron size.

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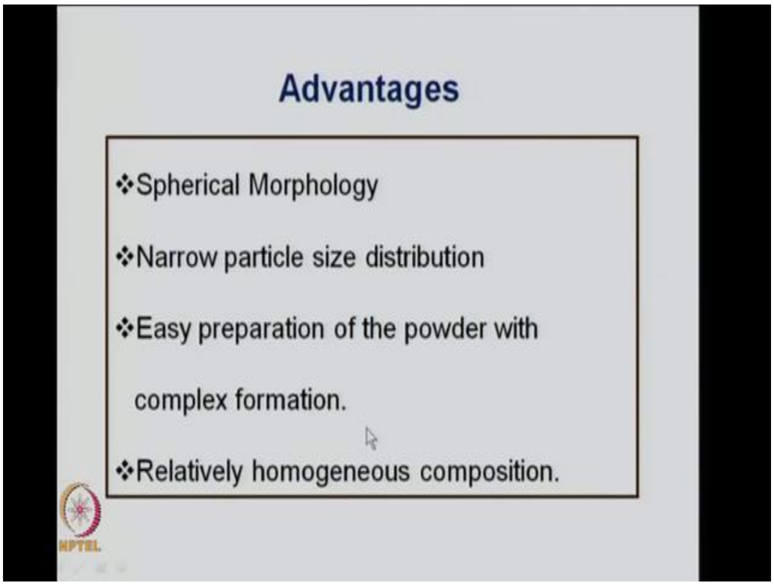

Now, the advantages are most to the time or most other spray pyrolysis processes. If you choose your starting precursors properly and choose you solvent also appropriately then you end of with particles with spherical morphology, with reasonably narrow particle size distribution. The process is quite simple and ultimately it is a good product for minimal investment. So, this has lot of advantages to take this process to the industrial scale.

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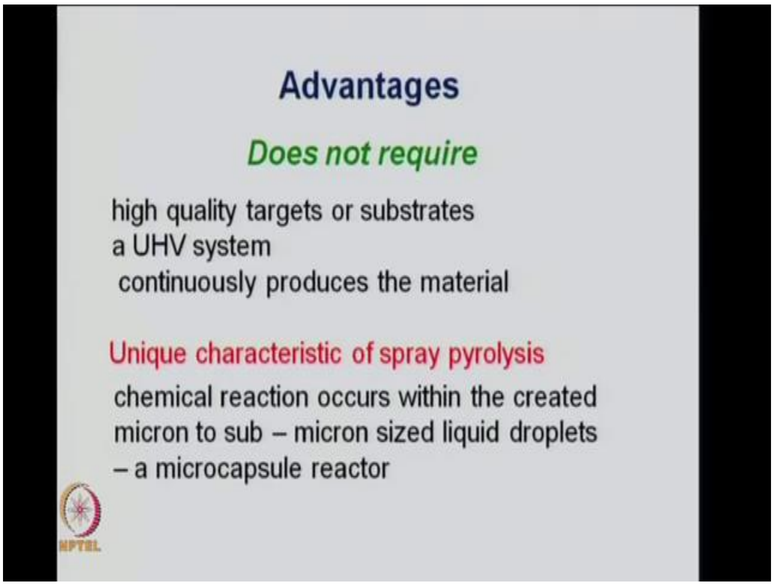


In edition it also has other advantages, like you do not need very expensive ultrahigh vacuum system, that many other processes which prepare particles or films require. This technique can continuously produce the material in a continuous mode. These are added an advantages to the few advantages that we mentioned earlier. The unique characteristic of the spray pyrolysis technique is that, the chemical reaction occurs within those droplets within the created micron to submicron sized liquid droplets. So, which we can call as a microcapsule reactor or a micro reactor.

So, you create a reactor which are those droplets and you are doing reactions within the droplets themselves. So, you have micro scaled reactor and you have to see that whether we can a go to a nano scale reactor using this. So, this is a key characteristic of the spray pyrolysis method.

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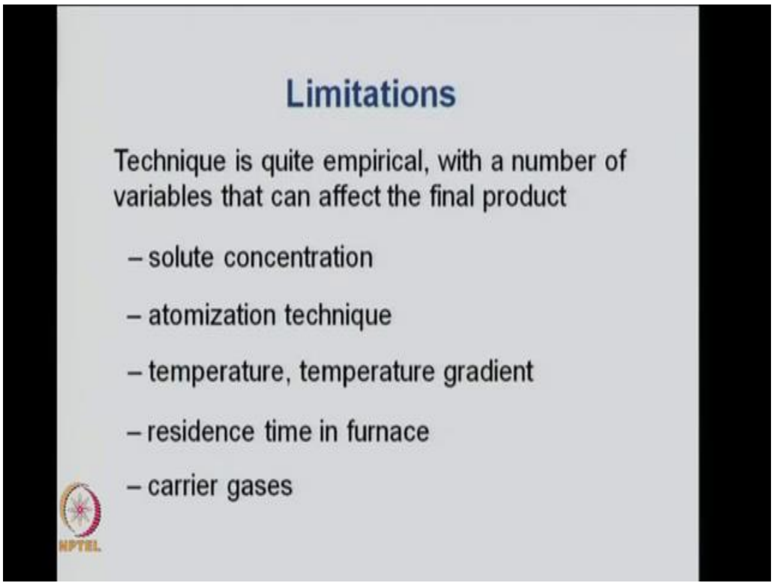


However, as with many most of the processes, there are certain limitations to this process too. The spray pyrolysis method is quite empirical with a large number or variables that can affect a final product. So, you have to optimize these parameters and hence when you move from one setup parameters to another setup parameters you might change the distribution of particle size in the final product, the size of the particles or the nature of the particles.

So, what are these various variables they can be consider to be as follows. The solute concentration that is initially what you take in the precursor, you have some solute which you dissolvent. In the solvent what is the concentration is very important you. What is the process of atomization are you using nebulizer, are you using very high pressure or are you using an ultrasonic atomizer. So, there are various types of atomization techniques which will each will have its own mark on the process.

So, then what is the temperature at which you are drying or sintering. What is a temperature gradient, what is a residence time in the furnace that means how long these droplets are residing or moving in the furnace. So, that will depend on the length of the furnace. So, if you modify the length of the furnace the residence time of the droplets in the furnace will change. That will affect the size of the particles and distribution of particles in the product. Then what kind of carrier gasses you are using because when you are doing these kind of spray pyrolysis, we also add a carrier gas which is a nonreactive gas.

You can vary that carrier gas you can vary whether from argon to pure nitrogen to helium. There are many carrier gases and each of these factors a solute concentration atomization temperature gradient of temperature residence time and the nature of the carrier gases. All of them will affect your ultimate product size and size distribution. We have to a fix our parameters, if you want to fix the product.

So, this is a limitation that they are lots of variables one can play with it is it can be advantages, but it also can be having limitation if a person cannot be produce the process due to the these parameters. However, if one works with a very optimize set of parameters and follows it diligently. Then there is no reason why one cannot reproduce what one has done before.

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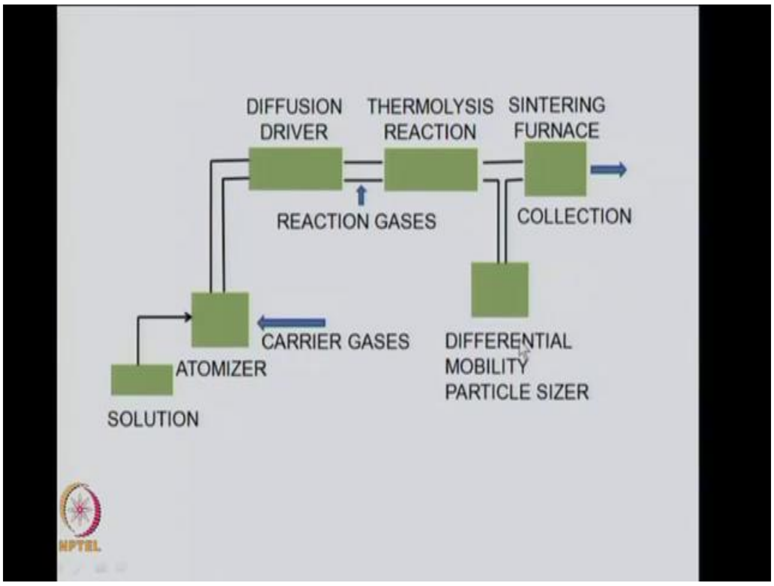


So, as we have to keep in mind not only the advantages of the method, but also the limitations of the method to make this technique a viable and useful for applications. So, this is a typical a semantic flow diagram of what happens in a spray pyrolysis method. So, here you have the solution where you have taken precursor and in a solvent and that goes to the atomizer.

Here you makes the carrier gases the gases which are non-reacting like nitrogen, argon, helium etcetera. This atomizer will then a make droplets out of the solution which is coming here. So, once that droplets are made, this carrier gas will move the droplets in this direction. So, the atomizer makes droplets out of the solution and carrier gases move the droplets. Towards the reaction chamber which is the furnace. So, once the come here you can if you want, you can introduce reaction gas. If you want you are droplets to react with some things.

Say, you want to your droplet to react with hydrogen sulphite. So, you introduce hydrogen sulphite gas here or if you want your droplet which is coming from here to react with chlorine gas. Then you introduce chlorine gas here. So, the droplets are coming along with a carrier gas and then you add your reactive gas or reaction gases. Together then their move into the furnace. So, this is the furnace where thermolysis will occur that means break down of the droplets in the presence of heat.

So, this is a furnace and these droplets then, the solute remains and the solvent evaporates here. Finally, these particles a move into the sintering furnace. So, here the droplets are being broken up and then here you can have a furnace where higher temperature is there. So, this may be a low temperature vessel and there you can have high temperature where the particle which are forming here, after the solvent is evaporated, they become larger in size, they become dens in this sintering furnace. Now, in between this chamber you can find out what is the size of the particles which are coming from the thermolysis chamber to the react sintering furnace because once it is in the sintering furnace, you may have agglomerate of particles before that here you may have individual particles.

So, it is good to find out what is the size of the individual particle when the particles are in this region. So, in this region we attach what is called a differential mobility particle analyzer. The differential mobility particle analyzer is a device which can find out the size of the particles depending on the difference in the speed of the particles. That is another process whole together how each particles can be charged and then the charge particle moves at a certain speed.

That can be evaluated by this device, which is called DMA or differential particle analyzer or differential mobility particle size. So, DMA for differential mobility analyzer of course, you can also call it differential mobility particle sizer. We are not going into this part right now, what we are saying is that once you have droplets coming in and the solvent evaporates you get particles the particles are carried further by the carrier gases into the furnace.

Here the particles can be collect it which are sintered. So, they become either agglomerated or large size depending on the sintering temperature. So, this is a general schematic diagram, however there can be lot of variants for this schematic process depending on a more advanced spray pyrolysis technique. So, this is a very conventional spray pyrolysis technique, which starts from your solution to the atomizer to the thermolysis chamber to the sintering furnace, but you can have many more different types of schematic diagrams where this spray pyrolysis process can be modified based on your application. So, what are these deposition parameters. There are several parameters for example, what is the nozzle to substrate distance. So, that is the nozzle of the atomizer to the substrate. So, if see here that the atomizer nozzle will be somewhere here.

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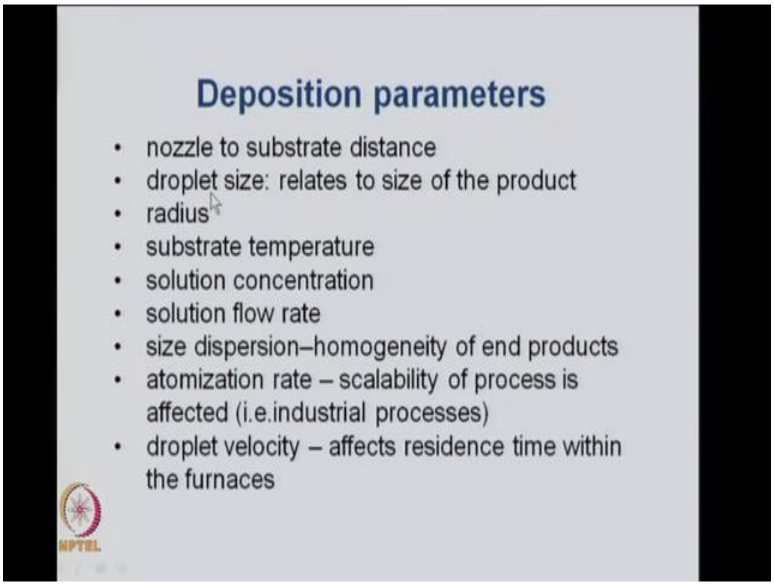


From there to the substrate there will be a certain distance. The droplets size how is the droplets size which is forming here. From here you are getting the droplets and forming here and going here to get the particles, how are these droplets size going to be varied depending on the atomizer, other parameters.

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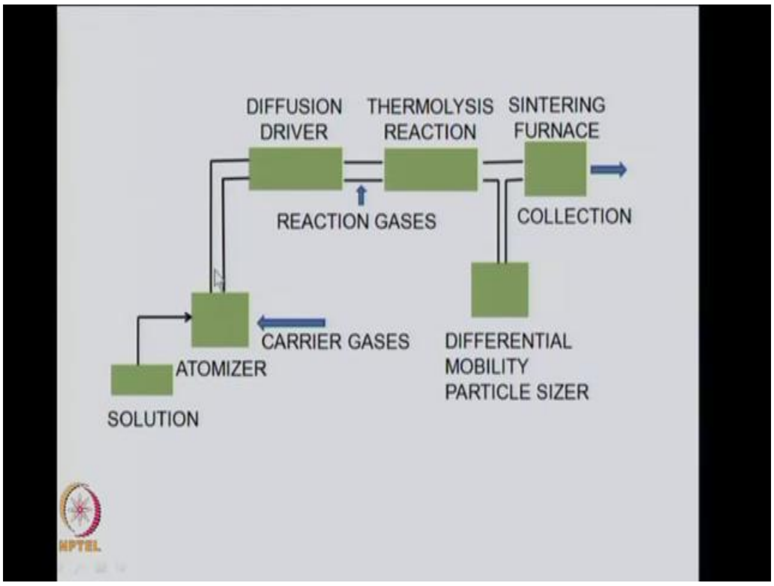


And once you get a particular droplets size how will the droplets size relate to the size of the final product, what is the relation between the droplets size to the product radius.

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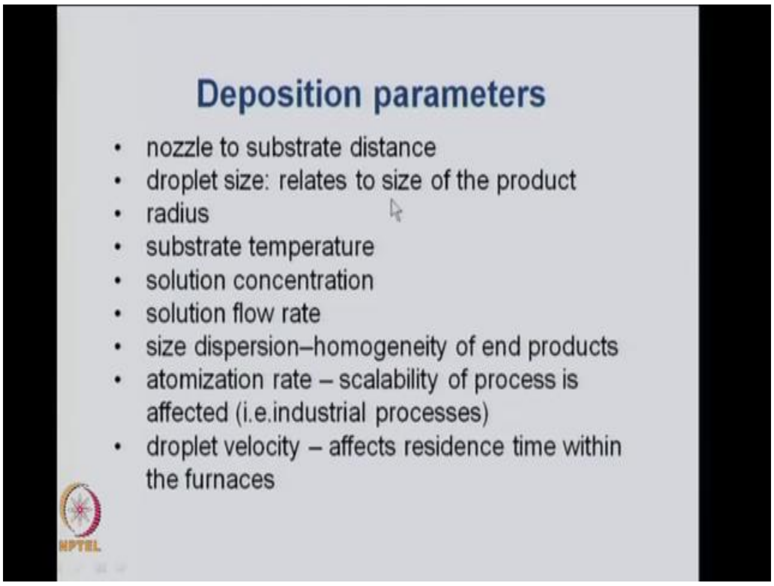


There is a relation if you change the droplet size, the particle size will change. Similarly, if you change the substrate temperature the particle size will change the substrate will be here we are trying to collect the sintered particles.

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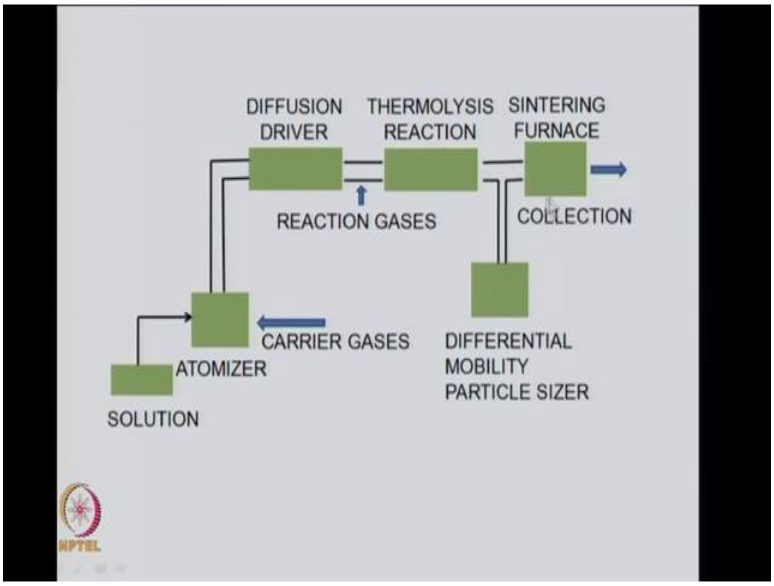


So, here you will keep your substrate they if the particles get sintered and the substrate will be at temperature which is set by this furnace. So, what is the substrate temperature is important.

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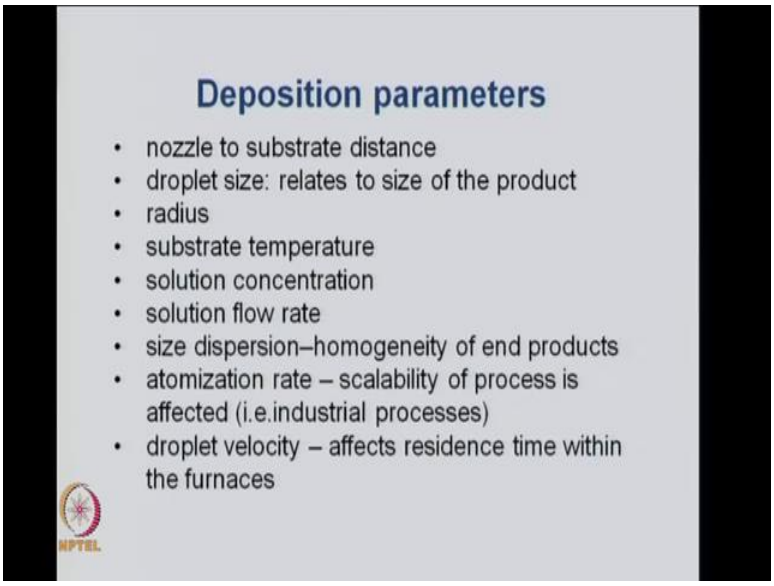


The initial precursor solution has a concentration and you can vary the concentration. So, that again is a parameter which can be varied. The solution flow rate can be varied that means the solution is coming into the atomizer at a certain flow rate say. So, many mile liters per second I can vary that fluoride. Hence I can vary the droplets size and ultimately I can vary the particles which are being collected on the substrate here.

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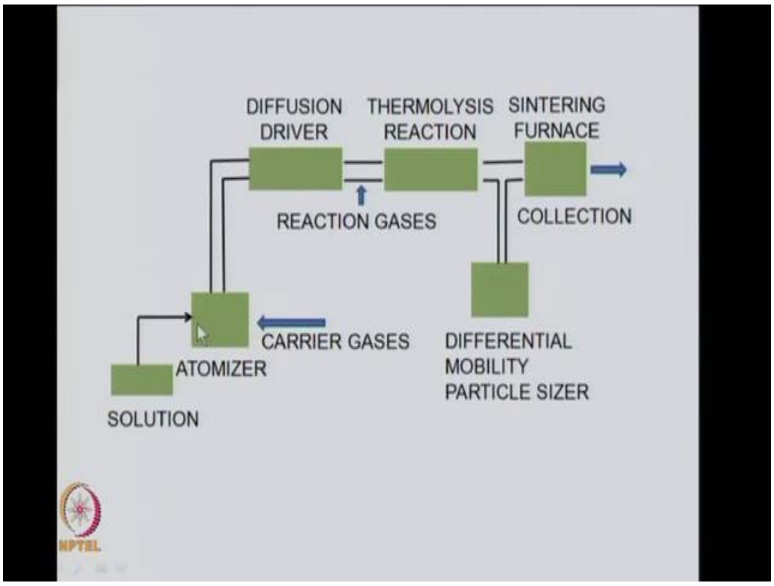


So, it depends on substrate temperature the solution concentration, the solution flow rate the size dispersion, and on which depends the homogeneity of the end products.

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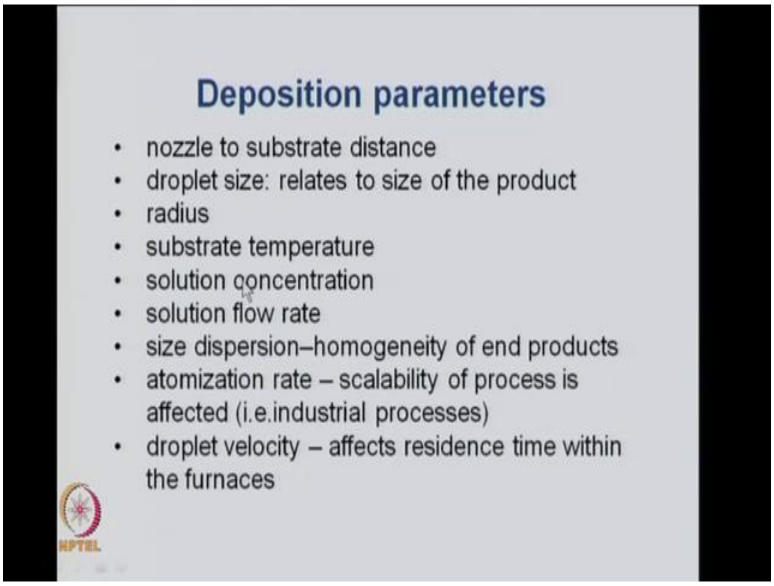


So, all this parameters will affect the size dispersion. That will affect the homogeneity of the final product which you get on the substrate. The atomization rate is very important because if you can do a very fast atomization.

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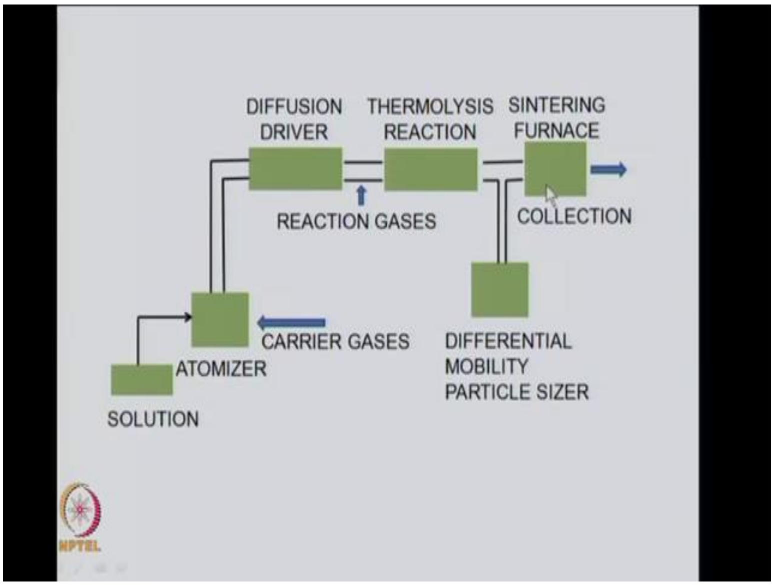


Then you can have a very a very high throughput and you can have very high deposition of particles. So, you can scale the process.

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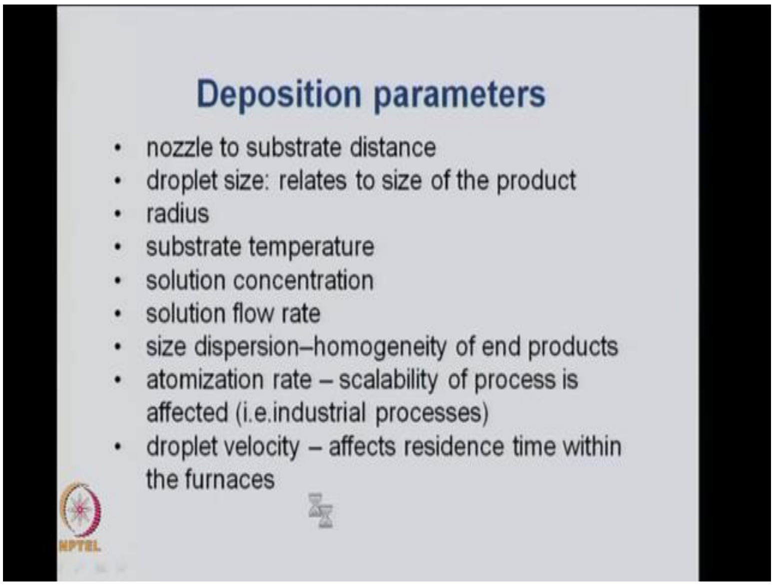


So, for industrial processes you need a very high atomization rate. So, the atomization rate needs to be scaled up for a processes which are going to be used in industry. The droplet velocity affects the residence time within the furnace.

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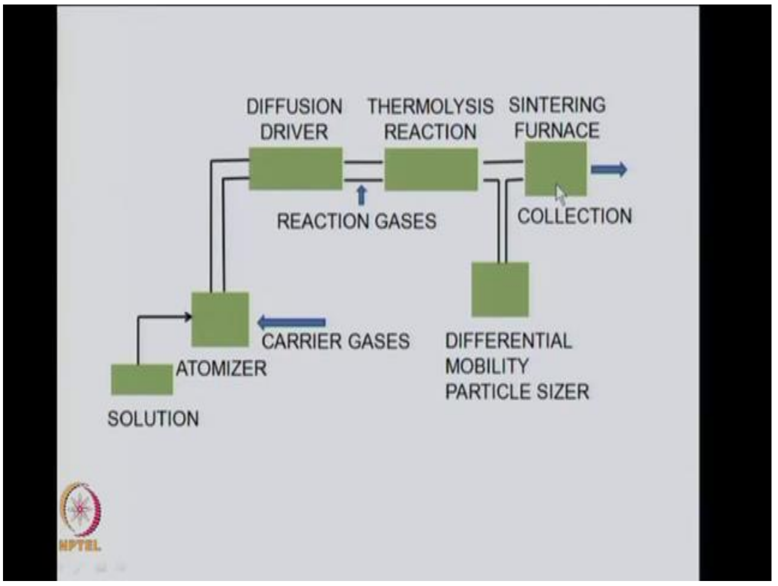


So, if you have these droplets which are coming here at low velocity then they will spend more time in the sintering furnace and the size will go up. However if the droplet velocity is very fast then the size will be small.

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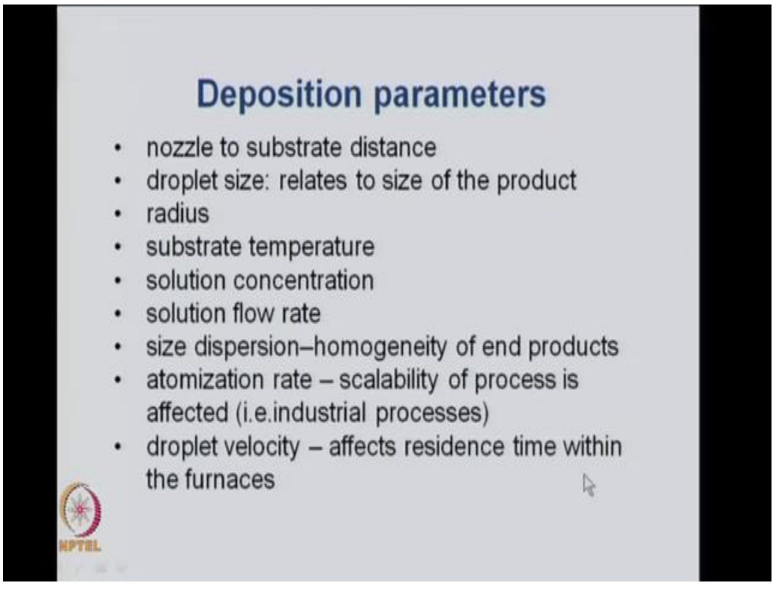


So, the droplet velocity will affect the residence time within the furnace and it will affect the size of the solute particles which will get deposited on the substrate. So, a large number of a parameters are there for 1 2 control and play with. So, that he can get precisely the type of sizes and size distribution of his particles as he wants. So, you have lot of room to play with, but also you need to have good control of these parameters otherwise the processes will not be reproducible.

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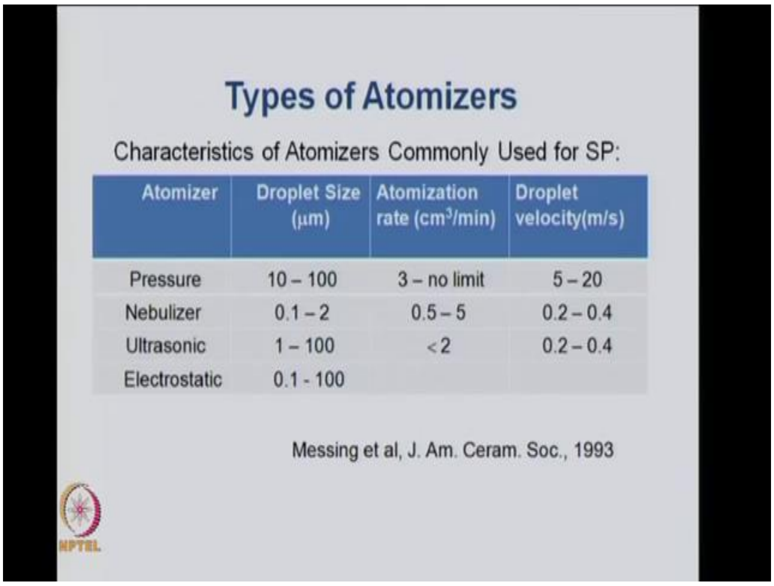


Now, coming to types of atomizers. So, where is the atomizer, the atomizer is here which basically changes the solution which is coming at the continuous flow of liquid, into droplets that is the atomizer. That atomizer can be of various kinds the commonly used atomizer for spray pyrolysis are these 4 kinds. You have pressure based atomizer then you have nebulizer based atomizer. Then you have ultrasonic based atomizers and electrostatic based atomizers. So, as you can see depending on the atomizer that you used or the kind atomizer you can have a certain range of droplet size.

So, in some cases you can have very high droplet size like 10 to 100 microns or micro meters, where as if you use an aerosol based atomizer that is a nebulizer it use an aerosol. There you can see the droplet size is can be very small from 0.1 micron to around 2 micron. So, it is like 100 nanometers to 2 micron, that is the size you can generate of the droplets from the liquid which is coming into the atomizer.

So, you have various ranges depending on the type of size you want you choose your atomizer the atomization rate also is of fixed by the type of atomizer that you are going to get. For example, you can get a pressure type atomizers which can go to very high atomization rate.

So, from 3 centimeter cube per minute to practically no limit, you can go as high as possible in the atomization rate using a pressure type atomizer. However both nebulizer and electro ultrasonic means which are using acoustic waves that is sound waves to create the droplets. So, these kind of ultrasonic atomizers create an atomization rate of less than 2 c c per minute. Based on these kind of droplet size and atomization rates you will have a particular droplet velocity. So, the droplet velocity as you see in a pressure type of atomizer can be very high from 5 to 20 meters per second where as for the other atomizers they are quite small on 0.2 to 0.4 meters per second. So, you have a variety atomizers which give you a variety of droplet sizes. Ultimately these matter when you choose what kind of atomizer you want to create a particular deposition with the particular size distribution.

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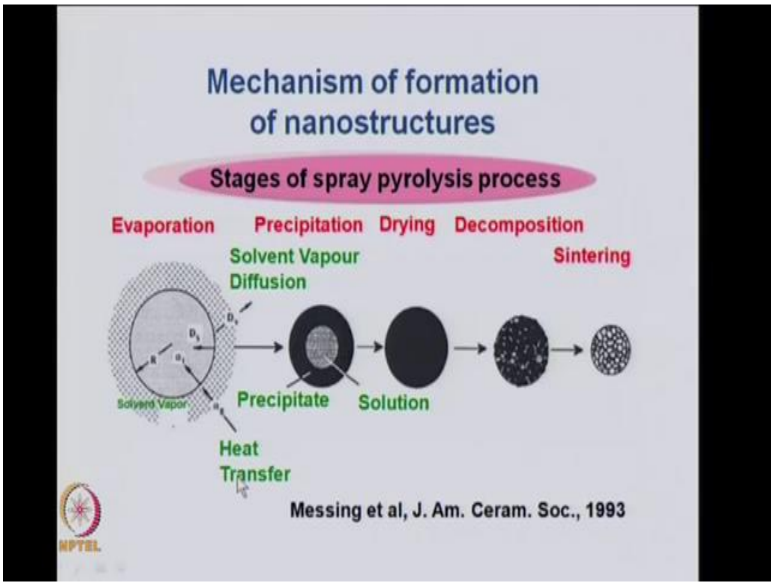


Now, the mechanism of forming nanostructures, suppose you want to make particles then what happens during the spray pyrolysis process. So, there are various stages in this spray pyrolysis process. So, when you start with suppose you have this droplet which has the solute in the solvent. Then you are bringing to the chamber where there is heat transfer. So, the there is a higher temperature, then what will happen the solvent will try to migrate out. So, heat it will try to go inside or there is a heat transfer in this direction.

There is a solvent vapor diffusion towards the out periphery. So, what will happen first the solvent will go away from the periphery and then the solvent from the interior will go out in that case you will first have a precipitate that means there is no solvent here only the solute, but inside you have still a solution. So, you have this kind of ring structure or what we call core shell type of structure, where you have the solid part or the precipitate outside from where the solvent has been removed due to the heat. Inside still there is some solution has time goes on even the solvent from the interior goes out or diffuses out and. So, this becomes a dense particle.

So, now we can say that the particle has dried once the particle has dried that means all the solvent has left then this particle, if it decomposes at the temperature that you have kept in that means, if the temperature here is sufficient to decompose. The precursor which is there then you decomposition will take place and you will have smaller particles found from decomposition of this and certain gases will be evolved.

So, this will be the type of structure of the particle which has undergone decomposition after drying. Now, when you sinter this further that means this particle becomes heated for long time or at higher temperature then it becomes more dense. So, here you had some particles with some whites from where the gases have a gone out, where there was solvent molecules. So, this structure is not fully dense

Once you sintered that is you go to higher temperature or you change increase the time of heating then you get a solid particle, all the grains these small things, which you see are each independent grains and these grains are touching each other. There is no porosity no gap between 2 particles and that is called a very well sintered sample. Higher the sintering or better the sintering the density will become very high. So, this will be a very dense particle.

So, you start from your droplet the solvent starts evaporating first from the outside and then from the inside, you get this kind our core shell structure with solid outside or precipitate outside and liquid inside. Then the whole thing becomes a solid, it is now dried up no solvent then it decomposes to give you particles with some words and then you sinter the particles become all condensed close to each other with barely any voids. So, this is the process which is happening when the droplet has come into the sintering furnace.

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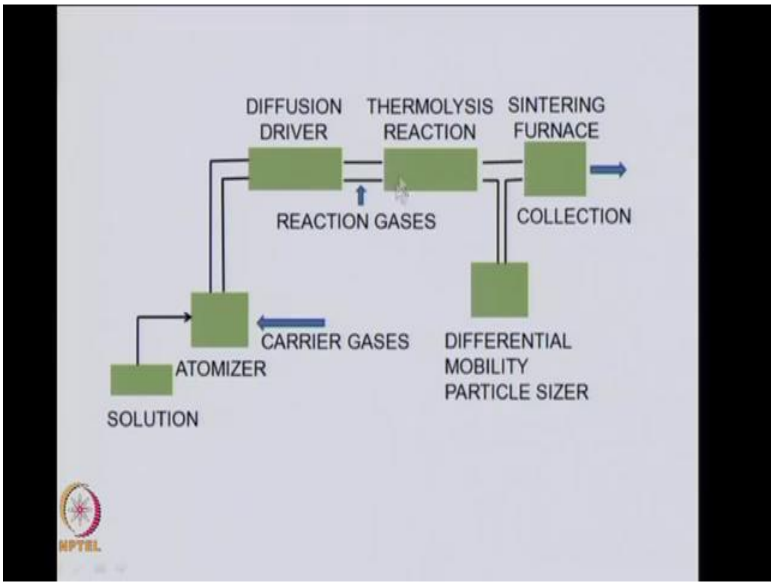


So, that is the overall mechanism how you go from the initial droplets used in spray pyrolysis when the droplets has generated by the atomizer to the final particle which is being deposited on the substrate.

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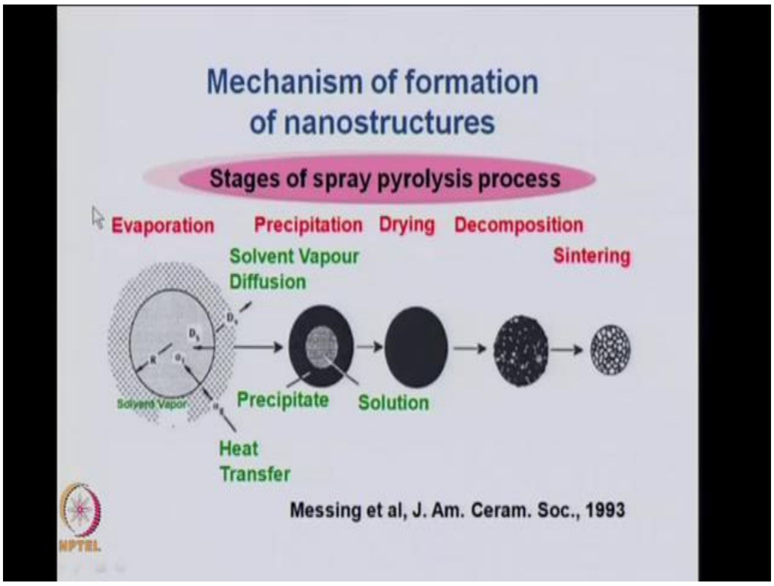

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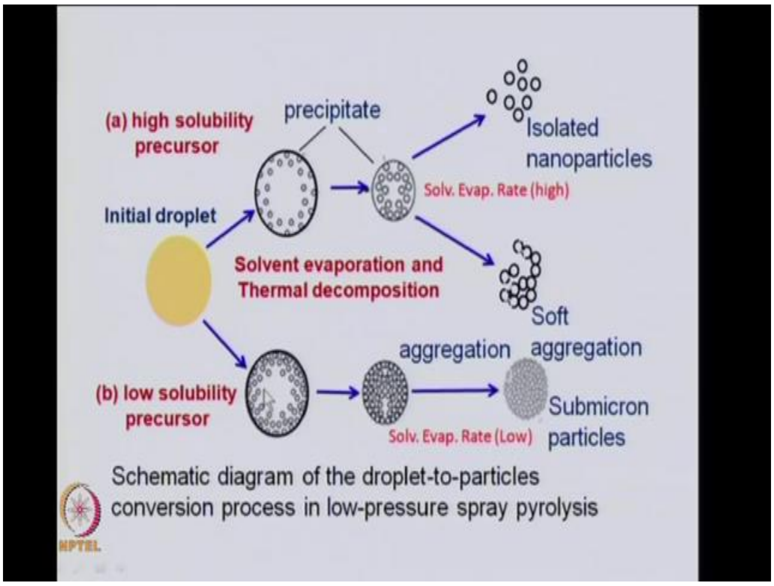


Now, depending on the starting precursor, you can have isolated nanoparticles or soft aggregation that means loosely held particles or very dense particles. That depends on the starting precursor. So, here if you have a very high solubility precursor, you see that you can initially the precipitate will have this kind of very fine particles which are separated well separated. So, you have an initial droplet which has very high solubility precursor that means solute is very well dispersed.

Then once this precipitates occur then there you start evaporating and the solvent evaporation rate is very high because the concentration of solution is low. So, the solvent evaporation rate is very high which leads to isolated nanoparticles or it might lead to some aggregation, but still the particles as you see are very loosely connected. So, this is soft aggregation. However, if you have a very low solubility precursor. So, you have a solution where the solubility is not very high and then you will see that the precipitate stands to agglomerate in the droplet.

So, when the solvent is drying the particles start agglomerating because many of them form together and this aggregation continues and the evaporation of the solvent is very low. The rate of evaporation of the solvent is very low and hence the particles can stick together instead of being separate where it will remain separate if the solvent evaporates very quickly. Here the solvent evaporates very slowly.

You ultimately end up with the very dense solid with all the particles very close to each other. So, there are 2 basic types of precursors that you can use. A high solubility precursor, which will give you a very high solvent evaporation rate and ultimately give you isolated nanoparticles. On the other hand if you choose a low solubility precursor then the solvent evaporation will be very slow and you will get dense particles and you will not get nanoparticles, you will get submicron particle something like 200 300 or may be larger sized particles 200 300 nanometers or even larger may be 1 micron sized particles. So, this is the process how droplets can convert themselves to particles in a low pressure spray pyrolysis technique. So, the 2 things that can happen as you are moving the droplets to the product, one is evaporation.

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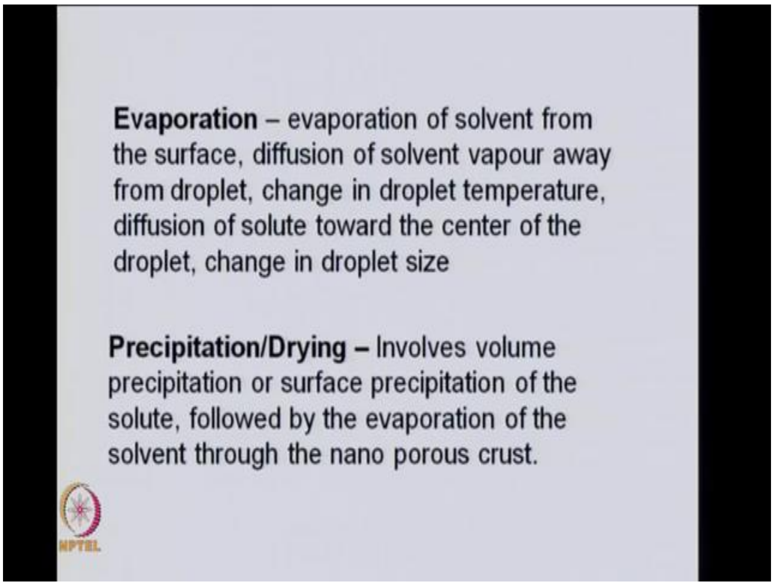


The solvent has to evaporates from the surface and the solvent has to diffuse the solvent vapour the gases that are forming due to the evaporation of the solvent have to move away from the droplet. This will cause a change in the droplet temperature and also diffusion of solute towards the center of the droplet. Ultimately this will bring about a change in the droplet size.

So, that is basically in words explaining what this process is explaining in figure. It can be through evaporation it can also be in the precipitation drying which involves volume precipitation or surface precipitation followed by evaporation of the solvent through the nanoporous crust. So, in the precipitation drying you can have precipitation on the surface, and you can get a crust formation. And this crust formation will lead to solid particles on the outside in the solvent inside.

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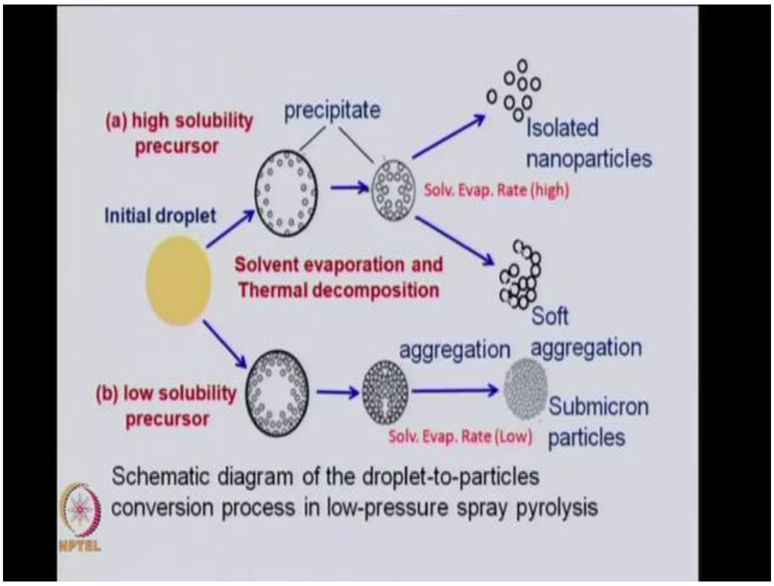


Of course, it will be nanoporous in structure and then the solvent can go through this nanoporous crust.

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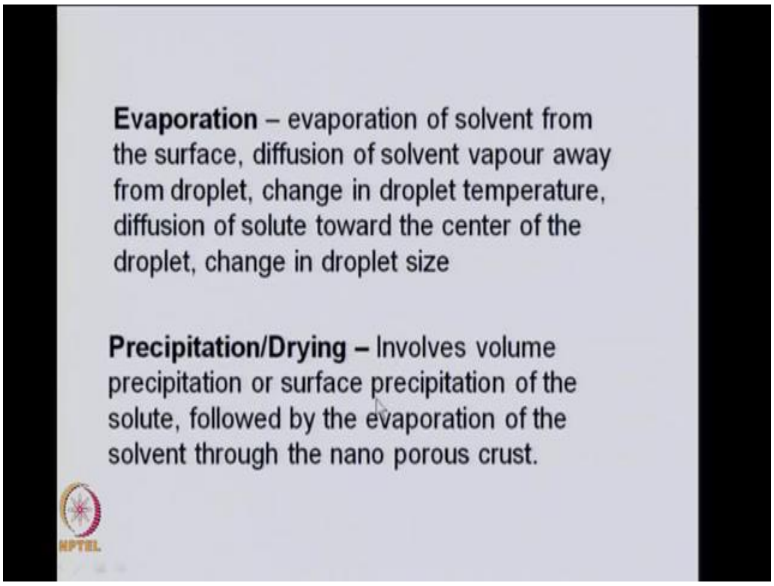


So, this mechanism of removal of solvent goes through these particular step. Through evaporation or precipitation drying ultimately leading to the submicron or nano particle.

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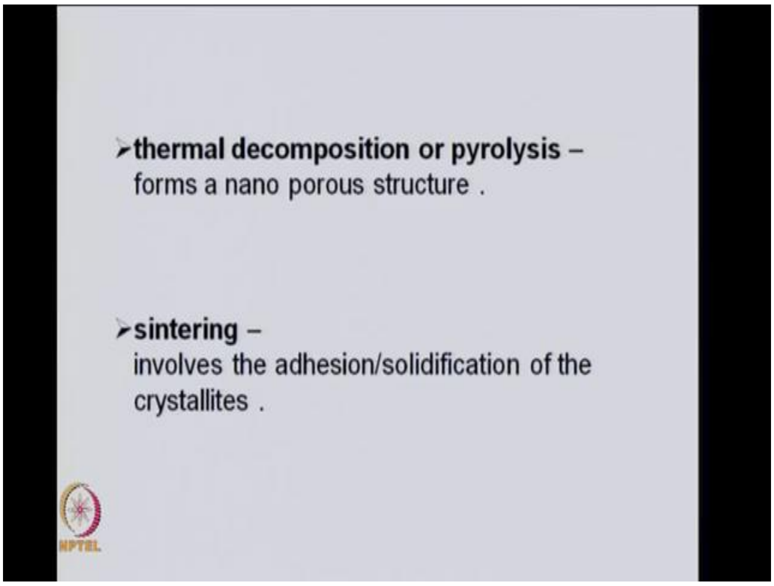


So, again the thermal decomposition or pyrolysis leads to a nanoporous structure and a sintering will cause adhesion of the particles and solidification of the crystallites. So, that is this step that you have the sintering where the particles become a combined and you get a solid particle, then the density becomes very high. So, these are the two things; one is thermal decomposition or pyrolysis to form the nanoporous structure and then sintering which involves the adhesion and solidification of the crystallites to form the dense particle.

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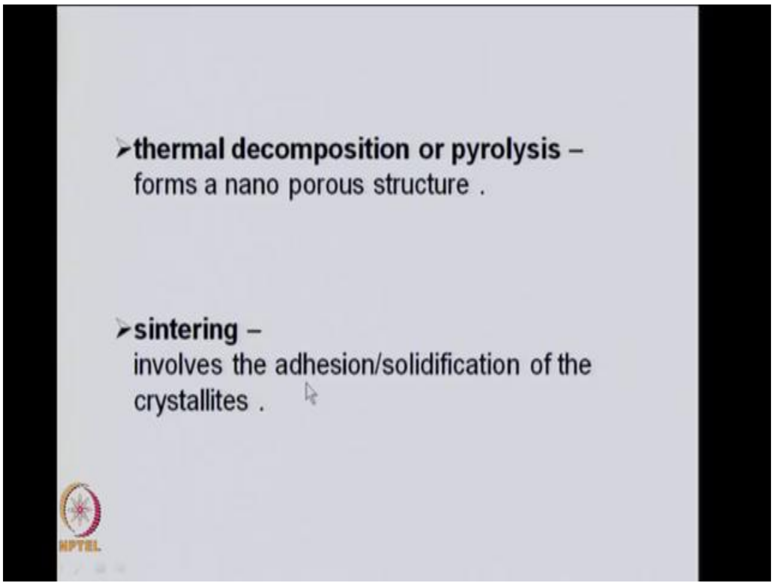

How do you control the precipitation. So, you have the droplet.

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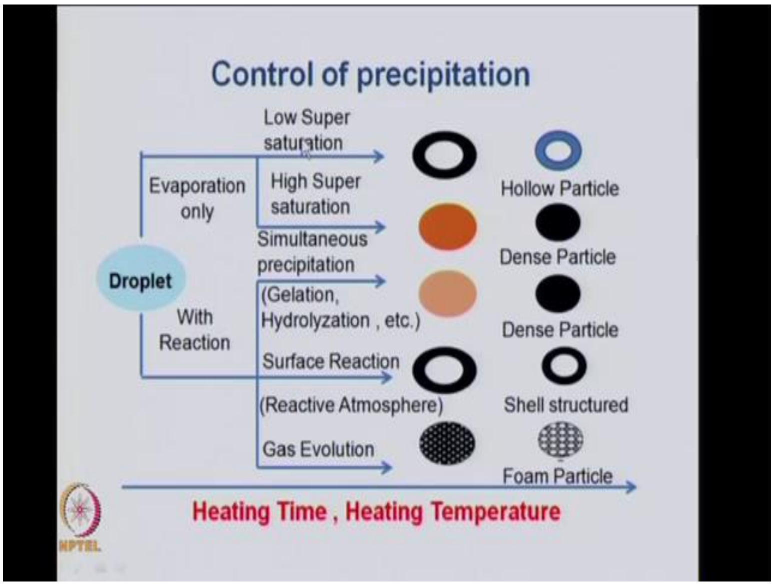


You can make the droplet go to the particle or either via evaporation route that means just remove the solvent or you can do this by some reaction with you are reacting some reaction is occurring on the surface etcetera. So, if you look at the 2 different processes the evaporation process can again be broken down into 2 parts. You can have a process with low super saturation and you can have a process with high super saturation. If it leads, if you go through this low super saturation that means the concentration is very low of the solute then you tend to get a shell type of particle, where the surface gets solidified and the solvent evaporates.

Ultimately you get a hollow particle as time is increasing or temperature is increasing. So, you start from a droplet you have evaporation process in precursor which has low super saturation. Then you get this hollow particle towards the end. If you have high super saturation then you get a solid particle as we discussed here in the previous case. You have high concentration that means low solubility and you get a dense particles same thing is being shown here. If you have high super saturation you end up with the particle which then on sintering gives you a dense particle.

So, this is using the evaporation only no reaction. However if there is a reaction say there is surface hydroxyl groups which bond to each other. So, in that case if you have surface reaction then again you form a shell on the surface. If you sinter it, you get the particle with a shell structure. If there is gelation or hydrolyzation something happens to the whole particle, then you will get a solid particle, which on sintering will give you a dense particle.

So, if there is only a surface reaction then you get this kind of a shell structure, but if you have a gelation or a hydrolysis hydrolyzation then you get a dense particle. If you use a reactive atmosphere that is you incorporate some reaction takes place with gas evolution. Then you will get a particle with some force in it because the gas comes out of those force.

So, during the reaction when gases come out this force are formed. So, when you sinter them further they form this very high surface area porous structure which is also called like a foam particle. So, in a foam you will have lot of force inside. So, this is possible when a some reaction leads to evolution of gases and those gases when they come out make these porous structures which forms like a foam. So, depending on how you control the precipitation from the droplet you can get shell type of structures or dense particles or particles with porosity which are 3 dimensional in nature. Hence these are called foams. So, all these can be done by properly controlling the precipitation.

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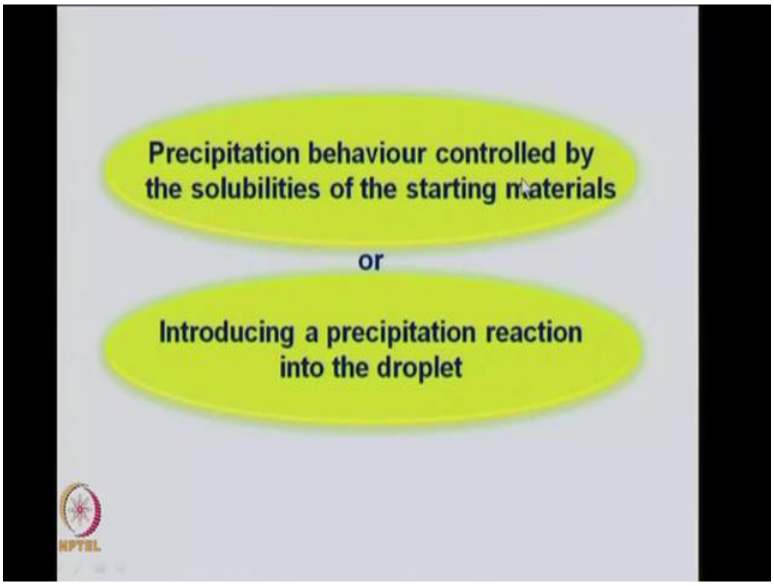


Now, as we said the precipitation behavior is very important and is controlled by the solubilities.

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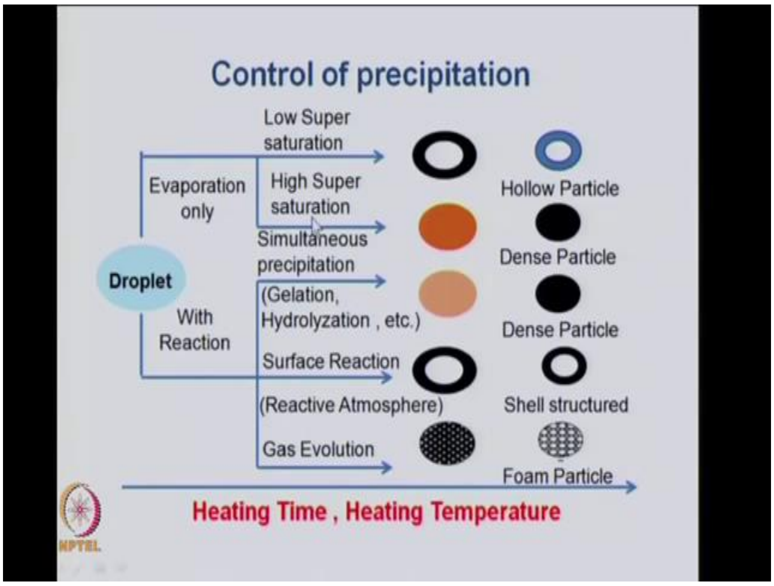


Of the starting materials because depends whether there is low super saturation that is high solubility or high super saturation that is low solubility. So, depends on the precipitation behavior by controlling the solubility or you can introduce a precipitation reaction into the droplet which is the second part.

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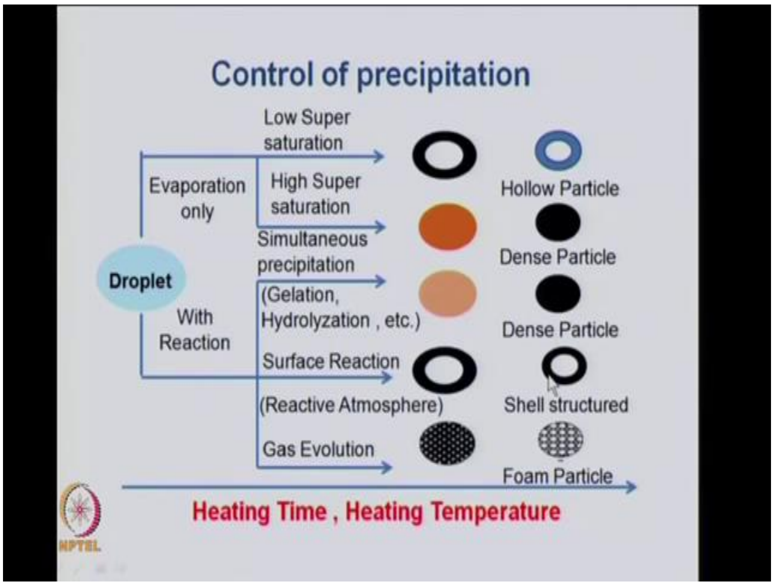


Can you introduce a reaction, and then you can get either dense particle or shell type of particle or a foam type of particle. So, by both these you can control the morphology or the nature of the particle from the droplet.

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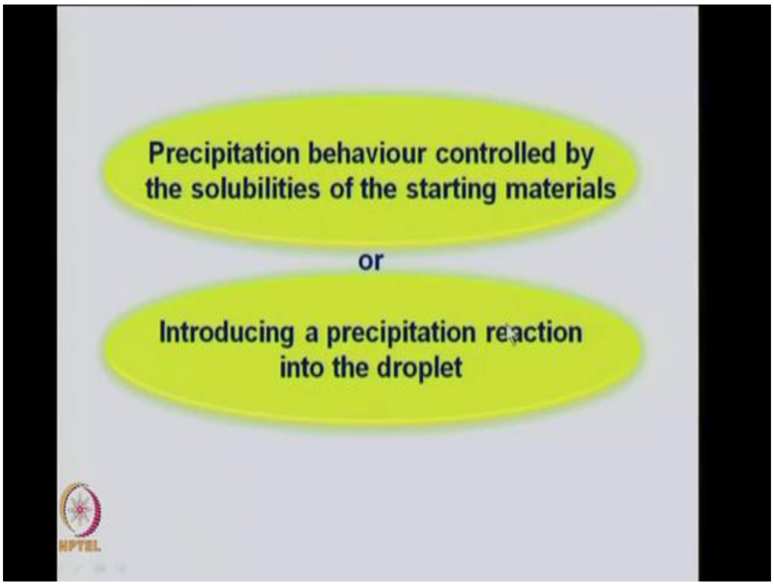


Now, these are the some examples of some particles of oxides. These are zirconium oxide and both are zirconium oxide a and b, but you see here the concentration of the staring material has been change. So, concentration or the saturation is low.

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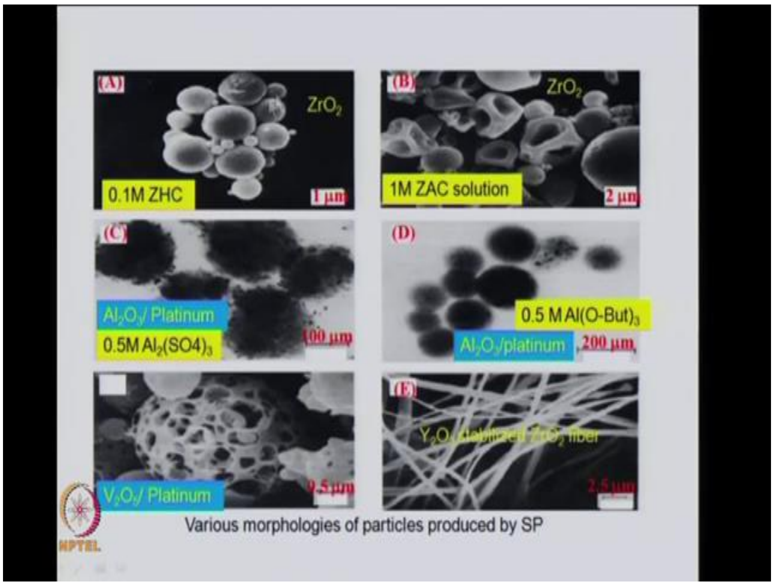


Very high there and you can see the type of a morphology is very different here. You have got spherical kind of structures, here you have a very irregular structures. So, the concentration and the type of agent that you are using is also different and that affects the morphology of these particles which you can see of the order of a micron or more.

So, these are large particles which are grown through the spray pyrolysis method. These 2 examples c and d are of alumina platinum and the 2 are quite different as you see the morphology because again we have modified the concentrations, here it is point 5 molar aluminum sulfate. Here it is point 5 molar of another reagent aluminum utoxide. Now these 2 materials have different solubilities and all though the concentration as such appears to be the same. Since the solubilities are different.

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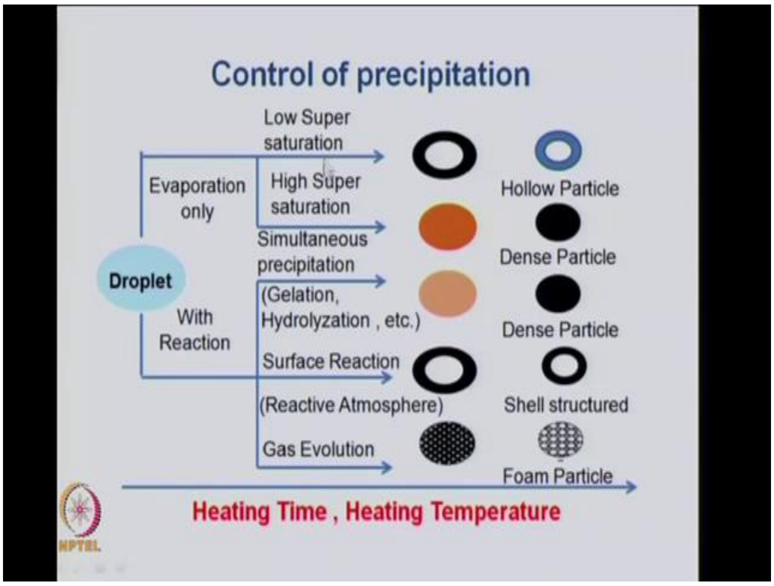


Hence you have a different level of saturation. So, one has a slightly lower level of super saturation then the other one.

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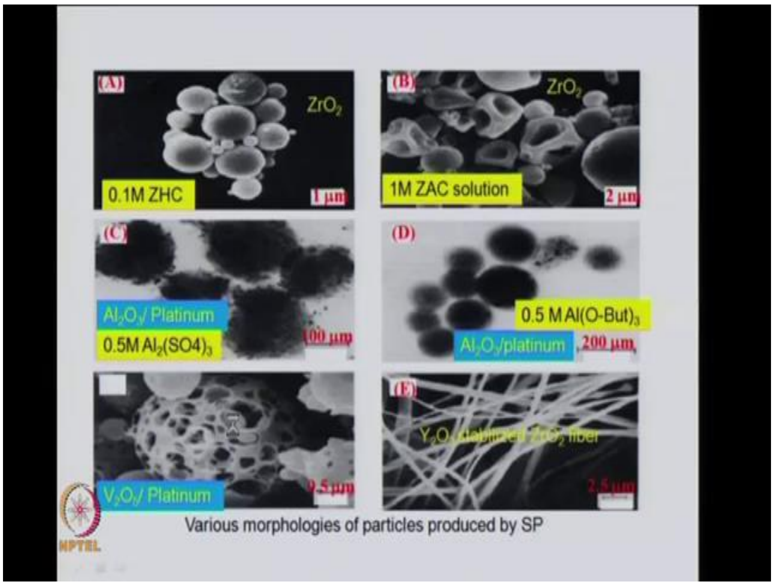


Hence the nature a morphology of these particle are very different from the morphology of the particles, both form the same compound or composites of alumina in platinum, but because of the different reagent having different solubilities in the solvent, you are getting different morphology. Then these are some other examples of how you can get very different morphology. Here very porous structured just like in this case this foaming type particle and that you can see in this case which is an example of penedium pentoxide in platinum. You get this kind of 3 d porous network connected porous networks in this case all the particle looks spherical, but it is highly porous.

In this case you have this fiber like or rod like structures. So, you can imagine very wide variety of structures and porosity are possible by this spray pyrolysis method by choosing different solvents, choosing different precursors, choosing different concentrations.

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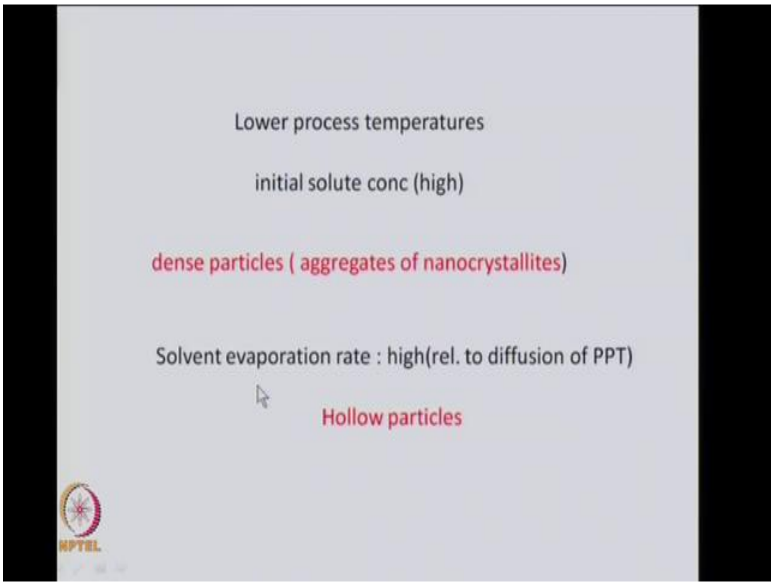


Now, in general if you want to make some conclusions of what we discussed just now. You can see that lower process temperatures and initial concentration is high. So, if you have low temperature and high concentration you will get dense particles. That means the nano crystallites will aggregate. If the it is just the other way that means you have very high solvent evaporation rate, then you will get hollow particles. So, you will dense particles if you lower process temperatures and high initial solution a solute concentration. Whereas you get hollow particles if you have high temperatures and which will lead to high solvent evaporation rate and that will lead to hollow particles.

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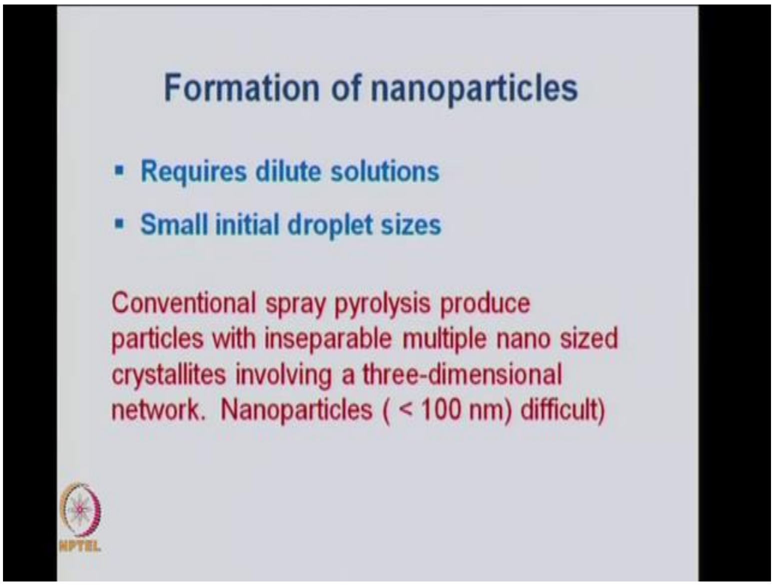

Now, these most of these conventional methods lead to formation of a submicron particles. As I said it may be 200 nanometers 300 nanometers 500 Nano maters etcetera, but if have to make nanoparticles less than 100 nanometers. So, 20 nanometers 50 nanometers using the spray pyrolysis method.

Then we have to modify our conventional spray pyrolysis technique. This the formation of nanoparticles using the spray pyrolysis technique would lead to, we would require very dilute solutions and very small initial droplet sizes. Since, if you want to makes small particles at the end you have to start with small initial droplets sizes and you need very dilute solution.

Conventional spray pyrolysis what we discussed just now, produces particles with a large number of connected nanoparticles and crystallites and they are always this aggregated and they give you sizes much bigger than 100 nanometers. So, less than 100 nanometers is difficult in the conventional spray pyrolysis method.

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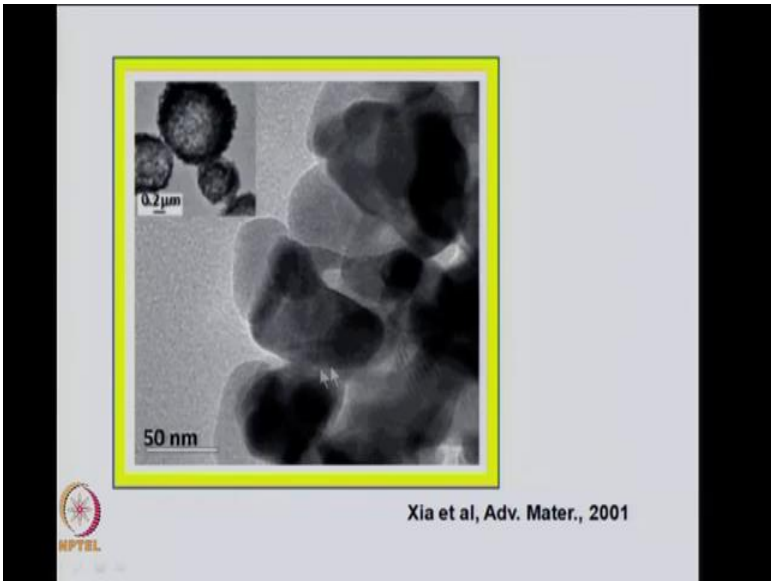


But we want to make a nanoparticles using spray pyrolysis method. So, what one can do. This is a typical conventional spray pyrolysis method what I discussed where you get large particles, because the small particles are all aggregated together and these particles are of the size of 50 60 nanometers, but the whole thing is all aggregated.

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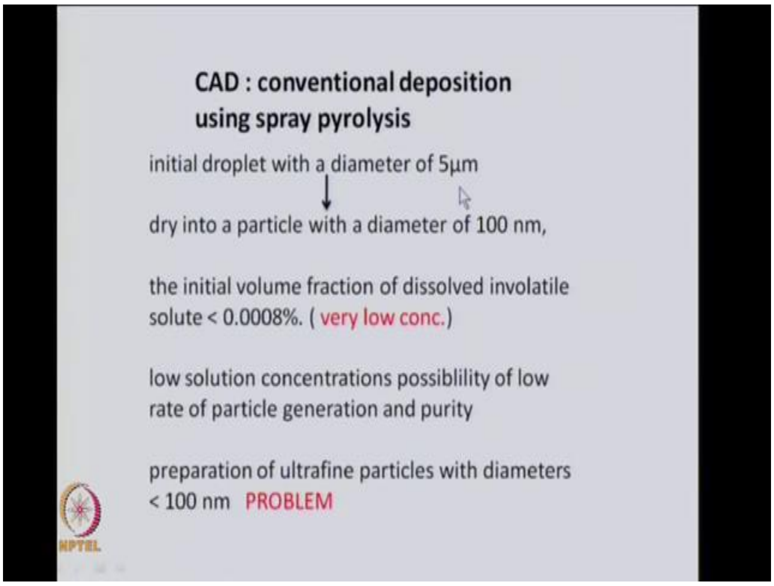


So, conventional deposition using spray pyrolysis has certain limitations because the initial droplet in a conventional spray pyrolysis has a diameter of around 5 micron. where has to make nanoparticles we need to have droplets a much smaller size.

Then we dry it into a particle with a diameter of 100 nanometers. If we have to do that from 5 micron to 100 nanometer from 5 micron droplet to 100 nanometer particle, the initial concentration has to be very, very low. Then you can do this change and this working at this very low concentration is very difficult plus it generates impurities because at this level of concentration something else can also be present or likely to be present. So, taking such small amount of concentration is not very good idea. So, preparation of ultrafine particles with diameters less than 100 nanometers becomes a problem in the conventional deposition processes using spray pyrolysis. So, there are other techniques.

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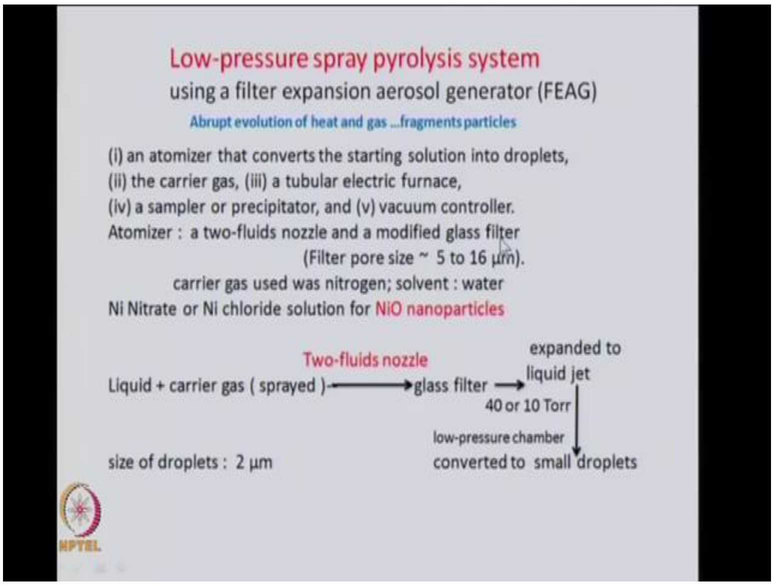


For example, you have the low pressure spray pyrolysis. In the low pressure spray pyrolysis system where there is a filter expansion aerosol generator, it is called FEAG. That allows an abrupt evolution of heat and gas and fragments the particles. So, this is a technique which has been develop is called the low pressure spray pyrolysis system with FEAG.

It allows us to make nanoparticles small particles much smaller than the conventional spray pyrolysis technique. So, here you have an atomizer as we studied earlier. It has carrier gas it has furnace, it has precipitator and a vacuum controller. The atomizer normally used is a 2 fluid nozzle that means we can pass say one liquid and one gas through that nozzle.

Apart from this 2 fluids nozzle it has a modified glass filter. This glass filter has pores and these pores have diameter of the order of 5 to around 16 micron. In the particular study the carrier gas chosen was nitrogen and the solvent was water. The salts which were dissolved in water where nickel nitrate or nickel chloride to make ultimately by this method nickel oxide nanoparticles where made.

So, this process which has been a published in a journal of materials such in bulletin will have the reference soon. Uses this liquid where which is water and the carrier gas and in the water you have nickel irons because nickel nitrate is dissolved in this liquid and then it is sprayed through the 2 fluids nozzle. Then this this spray forms a small film on the glass filter and which has pores and when it goes through the pores then it is expanded to a liquid jet.

Since, the pressure of the chamber, which is connected to the glass filter is very low. So, hence this expands and then is converted to small droplets. So, because of the low pressure after the glass filter you get a droplets and the size of the droplets are 2 micron. In the conventional method as we said the size of the droplets were of the order of 5 microns. Now, with this low pressure spray pyrolysis system along with the filter you can achieve small droplets which are present in this low pressure chamber.

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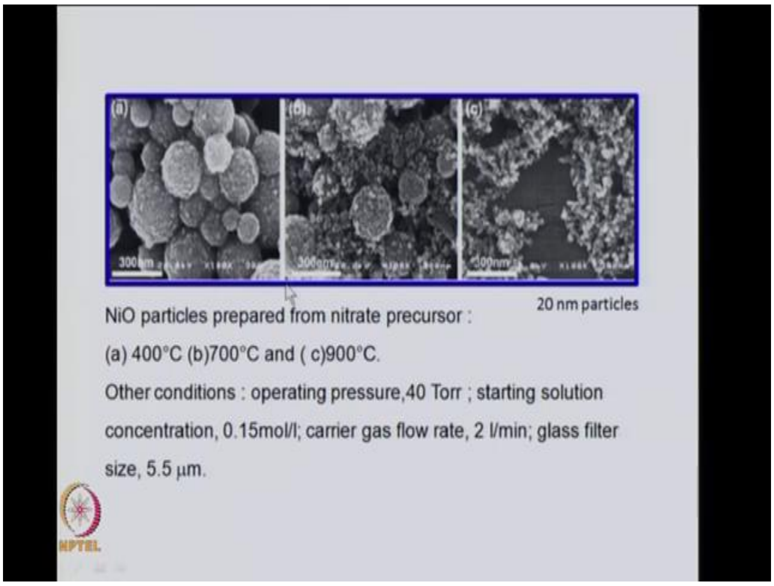


Based on that you can now put those droplets on to a substrate and you can get the particles. The substrate is heated at different temperatures 400 700 900 and you get particles of nickel oxide. So, you can see if this at 400 700 900, the 900 particles are very small and nanoparticles of the order of 20 nano meters. So, why does this happen normally, the size of the particles should increase when you increase the temperature, but in this case a 900 you are getting small particles. So, the reason is this that when you are using 900 degrees you are greeting a nanoparticles. Most of the nanoparticles are formed at a higher temperatures.

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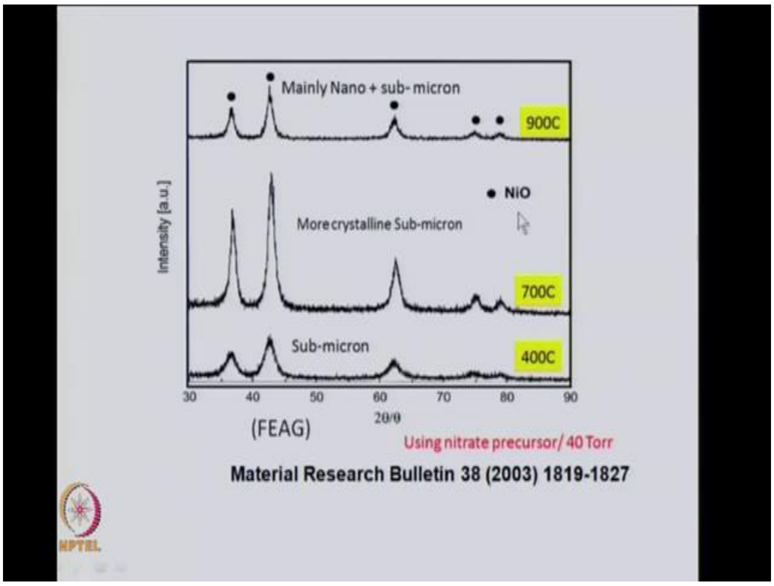


Whereas, at lower temperature you get the sub micron which particle, which are normally formed in any spray pyrolysis method. Then when you heat at 700 these sub micron particles crystallites, but when you are doing reaction at 900 then because the temperature is high.

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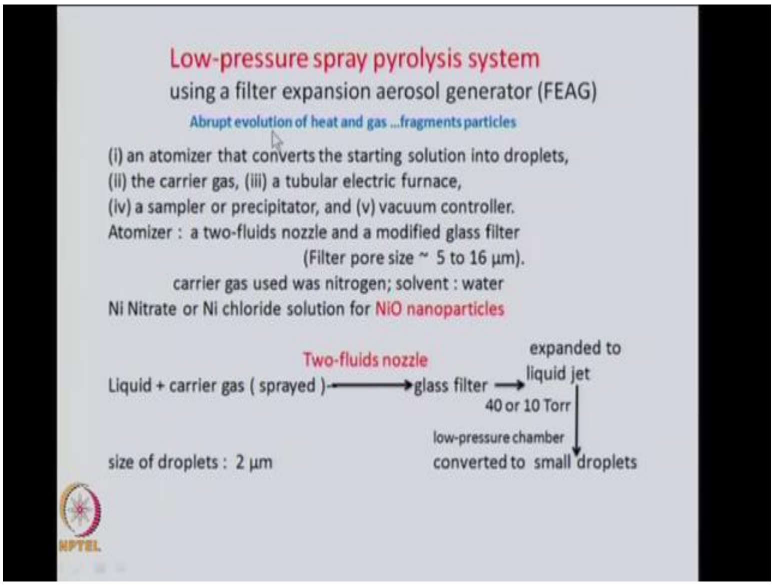


You are using there is abrupt evolution of heat and gas in this low pressure chamber, the particles becomes very small and you get this 20 nanometer particles.

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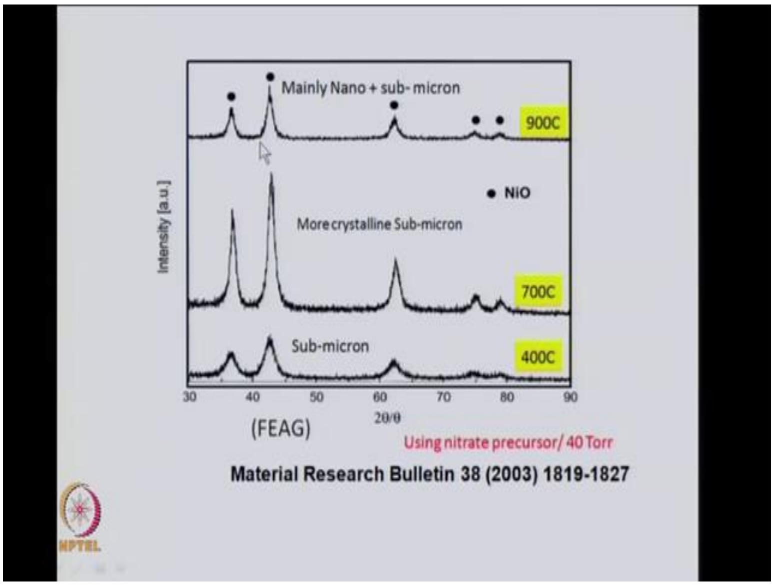


That is what is seen in the X ray also. The more broad the line it tells you that you are more the particles are small size. So, if you see these are more crystalline because the more sharp that is at 700 whereas, here they become broader and that is because you have more nanoparticles here and less sub micron particles. So, this is one method you using low pressure method.

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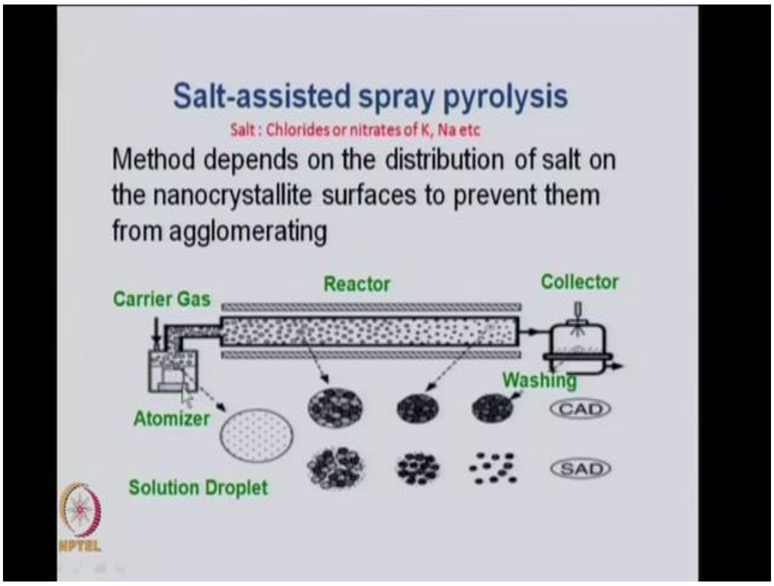


Then another method is the salt assisted spray pyrolysis this method is very simple. The same atomizer is there and carrier gas is there and you come to the furnace which is the reactor, but you adds some salts in the atomizer. Along with your solution you add some potassium chlorides sodium chlorides of these kind of salts. So, when the salt is in the solution along with your precursor particles they come to the reactor that means some temperature is there.

So, you get these kind of particles which has got salt particles around it and as you go through this chamber this particles as you see in which no salt is there tend to get aggregated. These particles after washing give raise to this kind of sintered particles. Whereas the particles in which salt was added since salt was around it does not allow the particles to agglomerate. When you wash this then the all the salt will go away leading behind this small particles and this is the salt assisted deposition.

So, you have the salt assisted spray pyrolysis and then here we did the low pressure method published. In this 1 example published in material research bulletin on deposition on nickel oxide where you can get nanoparticles using the spray pyrolysis method. This is a salt assisted spray pyrolysis, where the salt is preventing the agglomeration of the particles around it and when you wash away the salt this is after the washing after you collect you wash you get small particles where there is no salt and there are nanoparticles.

So, this is the conventional method you get this particles agglomerated this is the salt assisted method you get the nanoparticles and this is a clearer picture. So, this is the conventional method this is the salt assisted method.

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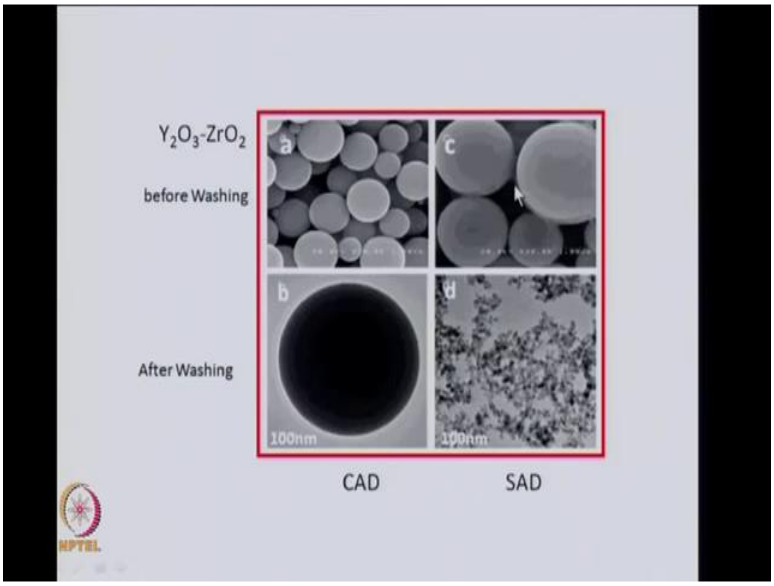


In the conventional method, this is the initial particle you get before washing. When you wash them you get these individual particles. In the salt assisted method; these are the initial particles that you get after washing you see you get very small particles, because all these particles now get a from here the salt gets removed and they break away into the small particles.

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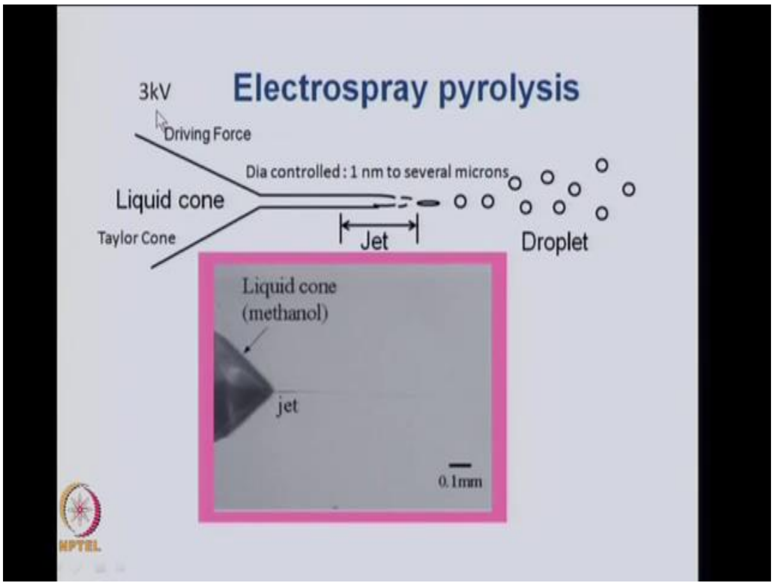


So, this is a method by which you can make very small nanoparticles using spray pyrolysis by the salt assisted method. The last method that I will discuss here today is the electrospray pyrolysis. Where you apply to a liquid suppose a liquid is coming out of a tube here you apply and electric field of around 3 kilo volts because of the electric field the liquid becomes conical in shape. So, it was a like flowing in a tube which is like cylindrical and then it becomes conical because you are applied an electric field. Once you apply this electric field then this conical shape is gives the driving force for the liquid to come out as a jet.

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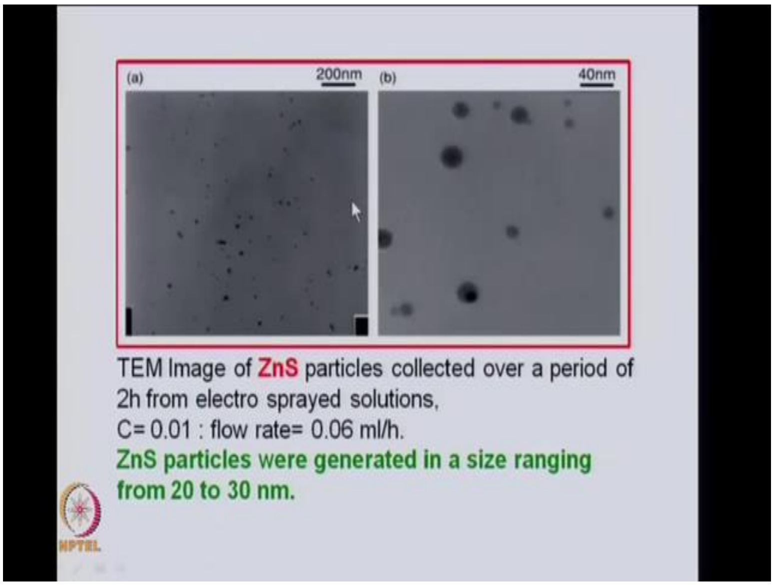


So, because of the electric field that you apply a cone is form and because of the cone the liquid comes out as a jet. This jet can be control to make particles of from 1 nanometer to several microns and these droplets when they are put on a substrate will gives you small particles like shown here.

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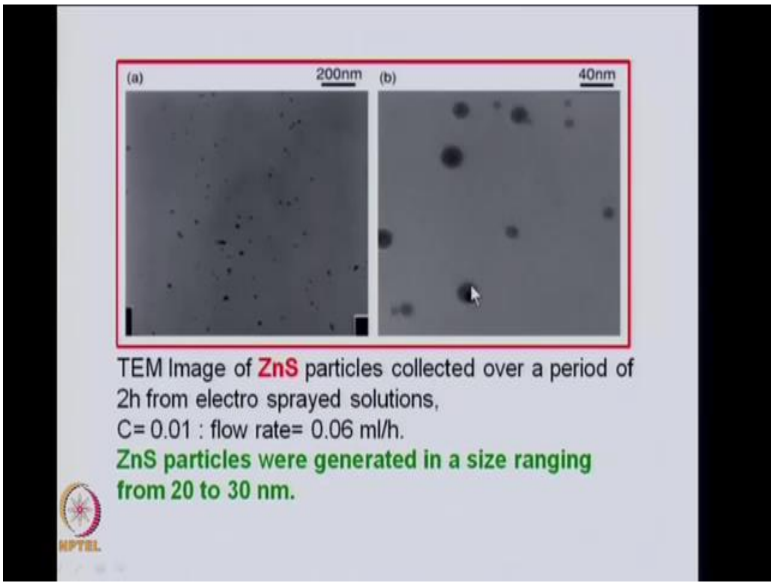


So, this is an example of zinc sulfide particles of the order of some 20 30 nanometers which have been used in a electro sprayed system for 2 hours, the electric field was the applied and the solution was passed through this electric field and you get this particles. So, you can make nanoparticles also by modifying the conventional spray pyrolysis method and which we discussed 3 methods, how you can control the spray pyrolysis method. Such that, to makes smaller particles much smaller than the conventional method gives and you can now get 20 30 nanometer particles. So, you come to the end of the today's lecture. We meet again for the next lecture to continue and that would be our last lecture of module 2.

Thank you and good bye.