Fundamentals of Materials Processing (Part–1)
Professor Shashank Shekhar
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur
Lecture Number 34
Powder Manufacturing Continued…

Will continue from where we left, we were discussing about one of the manufacturing techniques for powder which is precipitation from liquid.

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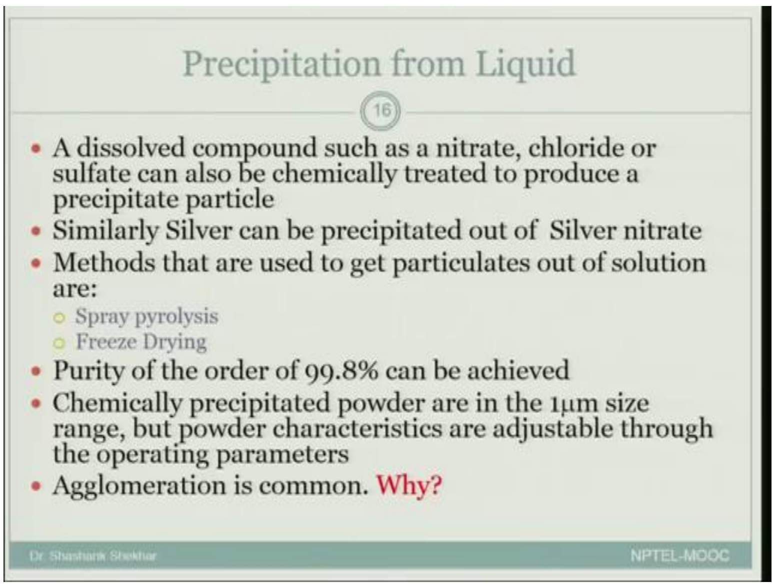

So, we look that some of the methods including (())(0:25) technique which can be included information this and others involved a compound such as nitric, chloride or sulfate form which you can precipitate out product. Now there are some more ways where you can get the precipitations a precipitates out from the liquid two of those methods are spray pyrolysis and freeze drying it will we much better if we explain this draw of schematic of the system using spray pyrolysis.

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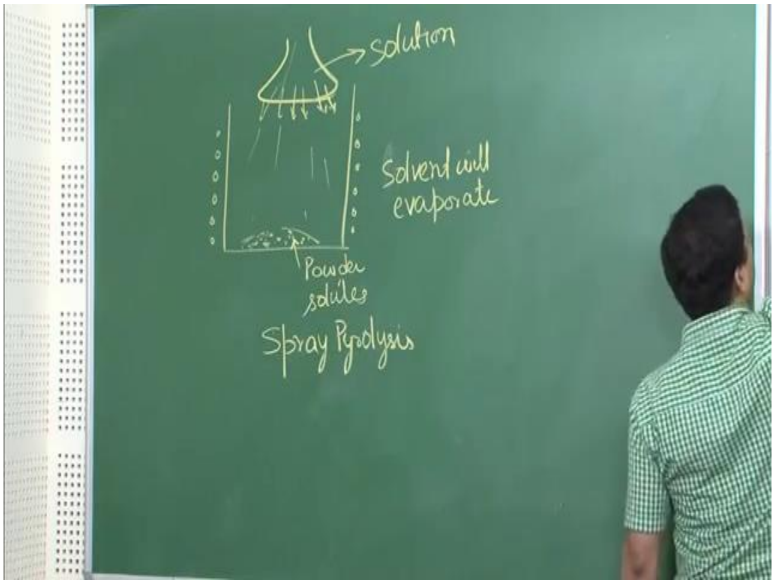

So, let me draw this on the board, so spray pyrolysis is basically what we are mean is you have a liquid in which you have the super saturated solution liquid is basically a super saturated solution and depth use allow to spray to a nozzle acentric. So, this a solution containing the material that we want to precipitate out and what you do is you have a heating zone through which this spread solution would pass through and when get pass through this because of the heated zone the liquid will evaporate liquid or let we call it solvent and what we will get is solid or the powder.

So, since you are spraying a very small droplets, so thus the liquid from that droplet has evaporated water left with is just of solute and then the solute will accumulate somewhere here like this and you will get the powder. So, this is the technique for spray pyrolysis. Another technique which is similar to this but in principal we would see is very different is what is called as freeze drying. Now, here that purpose the aim is that you first freeze it and then decrease the pressure. So, that the liquid which is the solvent is able to sublimate.

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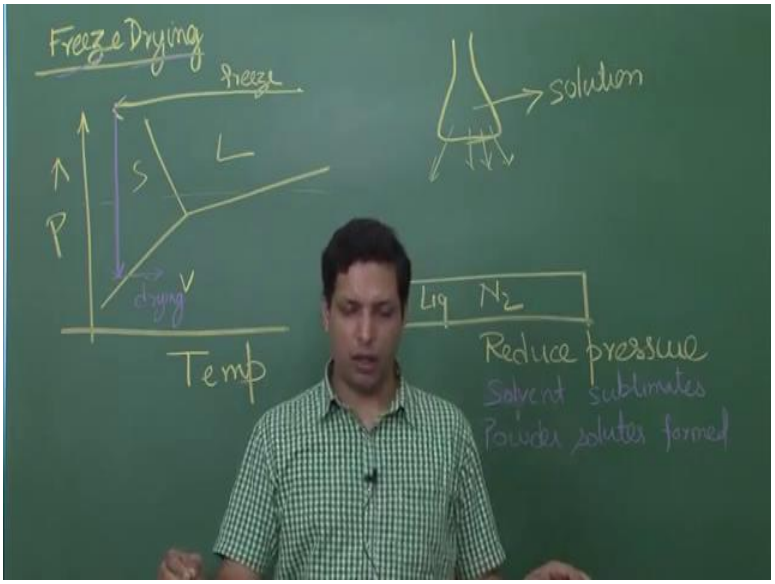

So, instead of evaporating it sublimate it is sublimating and therefore you are able to get the solute. So, if you were to first let me draw what the pressure temperature plot would look like because this is what makes this process different from the previous one which is spray pyrolysis. So, here if you if your solvent had a phase diagram like this, so this is a solid it is a liquid, in a vapor phase, usually you will be somewhere in this pressure range where it will go from solid to liquid and then to vapor but if you decrease the pressure enough. So, that you are somewhere over here then solid gets transferred transformed directly to vapor phase.

So, this is what you are doing, you take the solution to decrease the temperature. So, initially your temperature will be somewhere on the higher range, so you first freeze it. So, this is the freeze step of the freeze drying and then let me take a different chalk, and then you suddenly dropp the pressure. Now when you suddenly dropp the pressure and allow the temperature to reach the normal value then what will happen is that here the solute will start to sublimate.

So, this is that drying state and therefore it is called freeze drying. So, you are first decreasing the temperature and then decreasing the pressure and when you are at this very low pressure where the liquid thus directly sublimate instead of going from solid to liquid to vapor it goes from solid to vapor and leaves behind the particles of the solute and so you are that is the way you get this powder precipitates.

And now let me schematically draw what, now you can imagine the schematic would not be very different here again you have the solution which is being spread through this and to decrease the temperature we will have liquid nitrogen.

So, this takes care of the first step where we decrease the temperature freeze it and once it is at low temperature you reduced the pressure and that the low pressure when solute the solvent is sublimide a sublimates and one left with only the powder particles. So, you are after the pressure, so you will, after freezing you will reduced the pressure when the pressure reduces liquid sublimates or let will write precise solvent sublimates and powder solutes formed.

So, these are some of the ways for review and getting precipitation from the liquid. Now the purity that you will get using this method is known to be of the order of 99.8% this is decent purity but not very high very high purity will be something like 5 9 purity, or 6 9 purity, that will be 99.999 that will be 5 9 purity and so on. Chemically precipitated powder are in the one micron size range but provide characteristics by that the powder characteristics are adjustable through the operating parameter.

So, now here you see what is something very different from the other processes that you have seen, the powder particle size, we are getting much smaller powder particle size than we have been able to get through other methods. So, here we are able to get one of the smaller powder size although not very very very high purity likely get in say electrolysis method that we are able to get very smaller powder size . So, that is one you get to about it.

Now agglomeration is common in such precipitate and the question you should ask yourself is why then again remember what we talk about that agglomeration it is proportional to inversely proportional to diameter. Now if I diameter is smaller than agglomeration will be larger.

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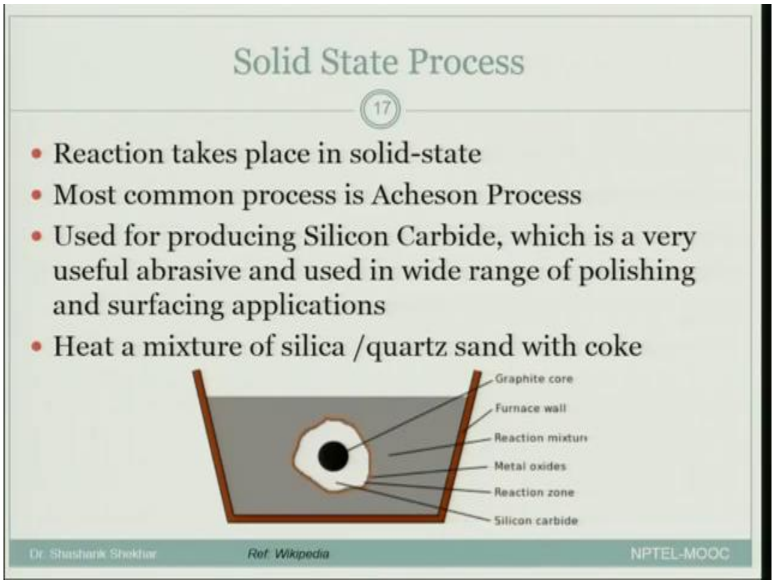

Let us look at you still another process or process for manufacturing which is solid state process, meaning the reactance are in the solid state and the product is also in the solid state. In some ways even the our oxide reduction was somewhere solid state but there we were using hydrogen gas and the product was moisture. So, other than that the reactant, the starting material or the origin material was oxide which was in solid state and the oxy reduced metal or the element was in the solid state.

So, in that sense it was still a solid state process but we used hydrogen gas over there. But in here everything is in the solid state. So, reaction takes place in solid state and one of the most common process is what is known as Acheson process. This is used for producing silicon carbide and what is much more surprising is that this came in to being this method came into being more about a century ago somewhere around 1930s.

So, since then it is, this process is being used for the producing silicon carbide, which is as we know is a very useful abrasive and used in wide range of polishing and surfacing application. So, if you have ever done polishing of the samples you know that there are silicon carbide particulates on the lapping paper. So, those silicon carbide are most likely produced by this Acheson process.

What you do here is that at the core of this there is a graphite of carbon and then on the outside you have a reaction mixture and therefore and then you heat it and when you heat it then this there is this silicon carbide on the outside this one sorry silicon dioxide. So, we use the mixture of silicon it is SiO2 and quartz sand are in this like a said in their core is your coke and you heat it. So, the coke will react with SiO2 to give you silicon carbide.

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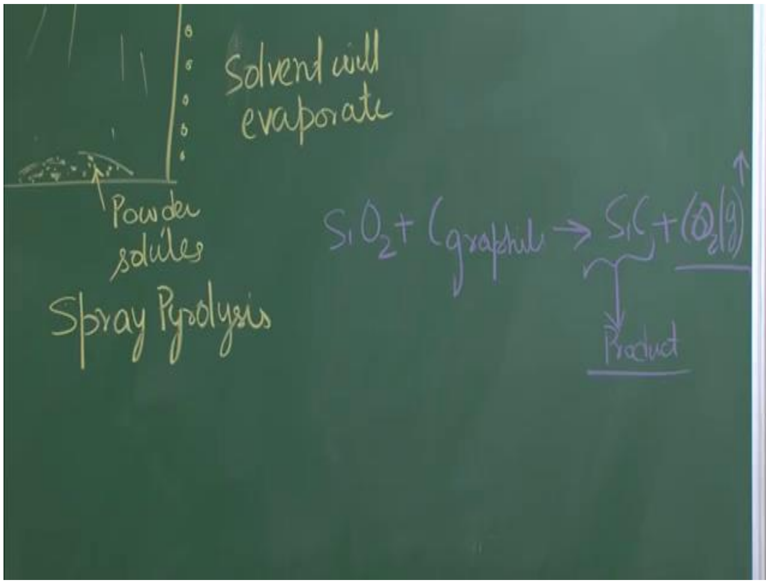

So the reaction would be from would you like this it is not a very complicated reaction it is SiO2 let us see graphite which is at the core this silicon carbide plus CO2 gas. So, again we have something getting in the gaseous state but it is no were related to the process or it is not even being used for controlling the process parameter like in the oxide reduction.

So, this is also you can see it is in a way to oxide reduction but the overall process parameters that we control are very different we over there we controlling the moisture and the hydrogen ratio to insure that the reaction goes to completion over here the reaction is taking place inside the solid state graphite. So, the graphite is at the core SiO2 is all around it and at the interface you start getting silicon carbide and then CO2 because at the porosity of theSiO2 able to escape through to the gaseous, escape through the reactants and products. So, this is the mixture and this is the you know this the product that we are looking at. So, this is the simple reaction that takes place over there.

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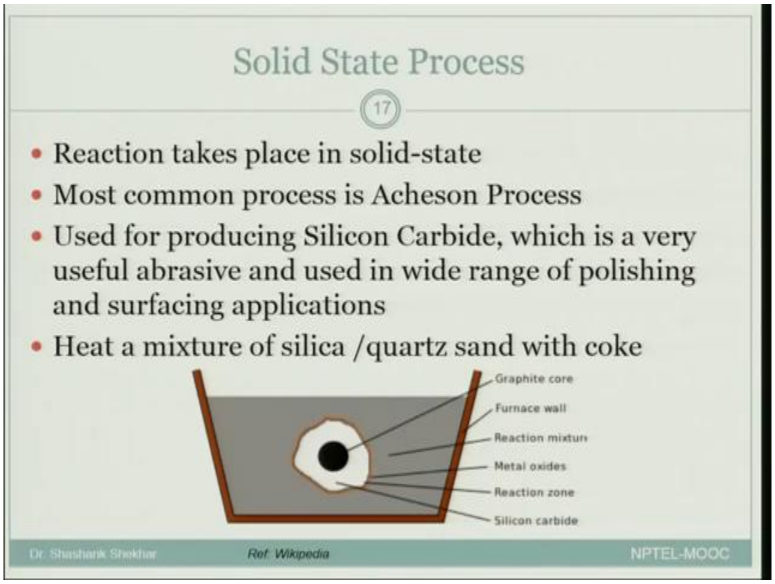

So, let us get back to our slide and you see, so this is the carbon which is used in the graphite form which is the at the core and here the grey region represents our SiO2 and the white region represent what has already been reactant or which has already been formed as final product which is silicon carbide and this layer we can say is the reaction layer.

So, may this is the reaction is going out boundary the invisible reaction boundary where the all the reaction are taking place and here also you can say that diffusion will play an important role again because we are talking about a solid state process and where original particles of SiO2 will have to get converted to silicon carbide. So, here also this diffusion process will play a important role. So, that is one of the most well known solid state process.

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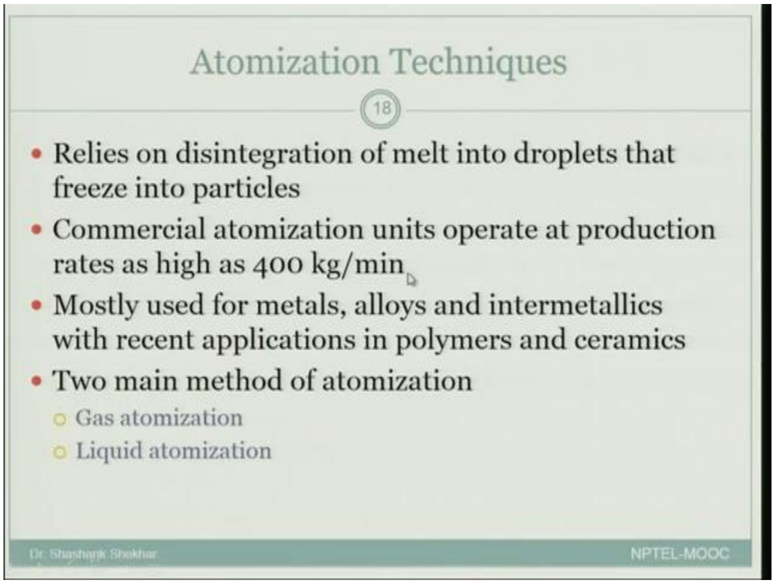

Let us get to some more fabrication techniques and the one of the most you can say well known particle is the atomization technique. What it does is that in this you disintegrate or melt, you melt the material and then disintegrate that particulate into very very fine droplets and once you have those fine droplets you freeze those droplets and then we will be able to get very small particulates.

So, using this method people have been even able to get Nano size to powders because this is you can say a (())(12:11) force method, you are melting the liquid and then disintegrating by apply by applying some form of energy that form of energy could be apply through gaseous state or through liquid state and therefore you have gas atomization technique or the liquid atomization technique and overall principle is not very different, only some of the process parameters are very or different that will see in just a few minutes.

This is mostly used for metals alloys and intermetallic with recent applications in polymers and ceramics. So, the most important application for there is metal alloys and intermetallic you can realize that we have to heat it all the way to the melting temperature and therefore only material with not very high melting point would be suitable for this and that is why it has so far will mostly use for metals, alloys and to some extend intermetallic with low melting points. Ceramics will people are now trying to use up to use atomization techniques to get for the powder particles or ceramics. And like I said the way that you are applying the energy it can be through gas or through liquid and therefore you have gas atomization or liquid atomization.

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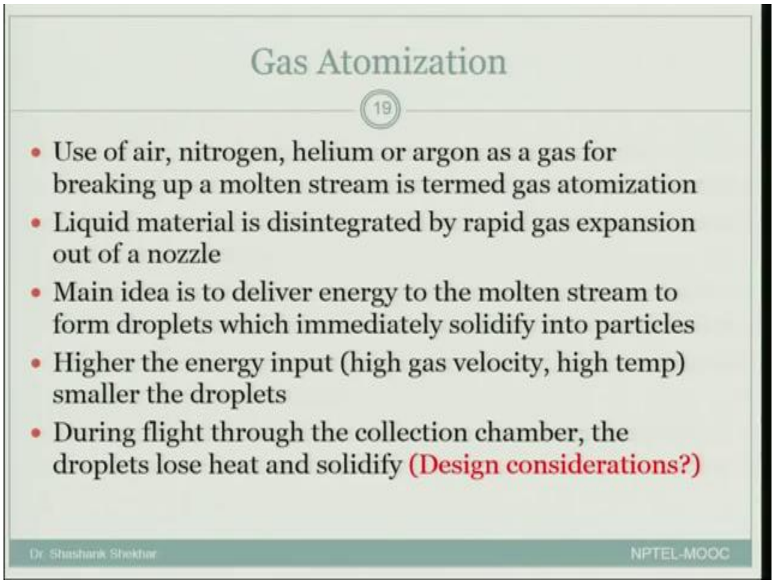

Let us look at gas atomization and being spend more time when gas atomization and may be just one slide on liquid atomization because the overall understanding or the overall fundamentals will grain the same only that some of the parameters which determine the final product size was particle size are different at therefore at the end of a we atomization technique will look at the empathical relation which defines the particle size that you will obtained.

So, what you use that we do is use care nitrogen helium or organ which is a gas for breaking up molten stream and this is termed as gas atomization. So, you are using some gas like nitrogen, helium, organ to break down and so the energy is coming through this gases, you are putting flowing the gaseous at very high velocity and therefore the molecule have very large very high energy and that energy goes into disintegrating the melt stream.

So, the melt gets basically broker into a several thousand of small droplets. So, the liquid material is disintegrated by rapid gas expansion out of the nozzle main idea is to deliver energy to the molten stream to fall droplets which immediately solidify into particles. So, the temperature is kept low enough during the process of flight itself the particulates solidify. Higher the energy input smaller the droplets. So, you can imagine that the each droplets have some surface area and that surface area is related with energy.

So, if you want to have smaller droplets larger number of larger amount of surface area will be generated and therefore the larger amount of energy has to be invested into this. During the flight through the collection chamber the droplets lose heat and solidify. This should also give you some hint about that designed consideration, you want a powder particulates to solidify before reaching the end zone where the particulates are being collected and therefore the length should be large enough that it loses it heat before it reaches there and at that the same time it should not be small enough that the droplets have not becomes spherical or of uniform size, will see about that when shown and here is a schematic that that it explains how this powder particles are produced.

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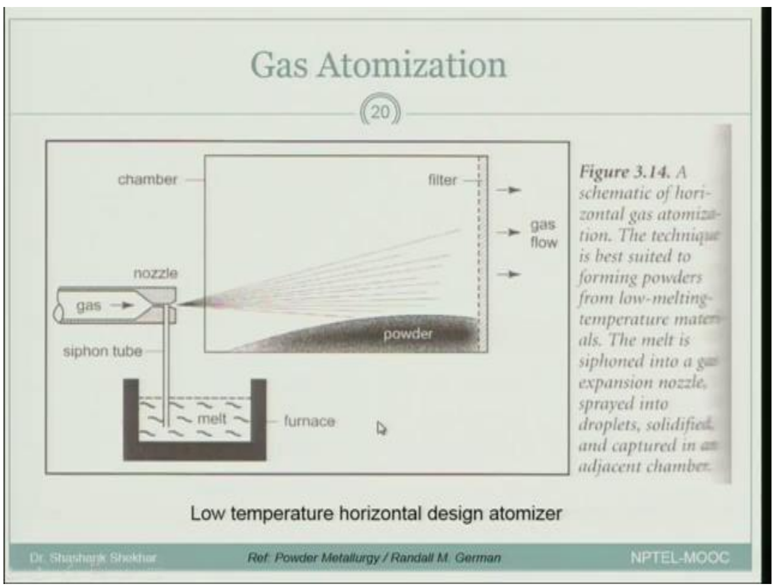

So, in this particular process this is the liquid melt and it is being stubbed in over through here by capillary action and also because of the because the gas is flowing over here therefore it is allowing or causing the liquid liquid level to rise up over here. So, the liquid rises through this tube and the gas that is coming through over here it is being spent at very high velocity. So, that high velocity means high energy so high energy is being given to the liquid melt and it breaks down into several thousand small droplets and so it falls like this and during the drop during the flight itself somewhere here over hear over hear it should or it does solidifies and by the time it reaches this heat it is already in solid state and there is a filter over here because in a gas coming is also coming in over here and it needs a state.

So, the gas eventually leaves the chamber and you are only left with powder and the gas comes out from this. So, this is the designed for a gas atomization one of that designed of gas atomization chamber you can this is called the horizontal gas atomization, you can also get what is called as vertical gas chamber.

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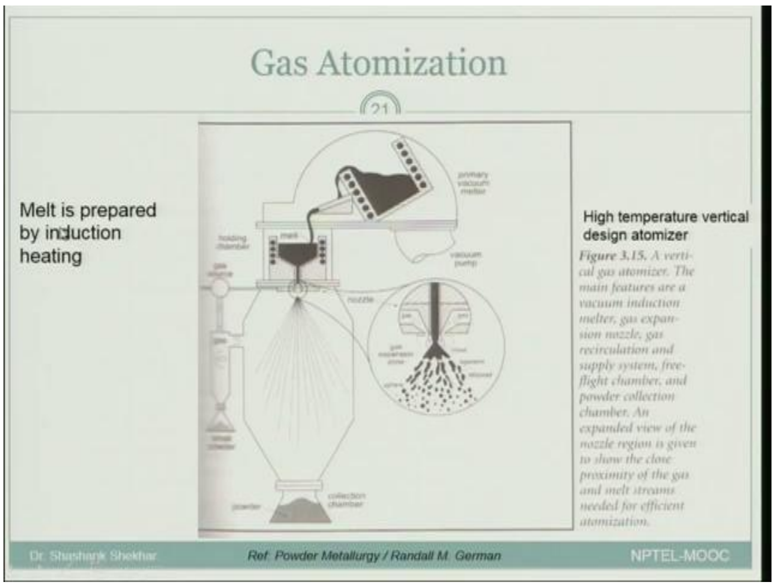

So, here is that diagram for a vertical gas chamber, so here also you can see the principle remains the same here we are pouring the liquid. So, here is the liquid metal that has been poured and to keep the temperature a little (())(17:13) that the metals remains in the liquid state you can even have heaters over here and then here you all allowing the gas or pushing, the gas through this into at just at the point where the liquid exists. So, the liquid through here the gas is coming out at very high velocity and it is shown in a much more you can say expanded or zoomed in view is given over here.

So, the gas is coming over here and the liquid metal is coming out from here and because of the energy of the gas but droplets or the stream gets disintegrated and you can see that it gets disintegrated into very small ligaments and in fact there are stages of formation of these droplets. So, first it forms ligament that enough side the fleck and the finally the spherical part you will see about that are very soon. What we need to focus here is that these powder particles would not sot yet the powder particles but the stream which has been disintegrated and now flowing in different direction and again the size should be such that the powder particulates lose heat and freeze even before the reach the boundary of this cylinder.

So, why and why do we want that why do we want that it should not hit the wall before it is freezes, there are two reasons one we want that it it solidifies homogeneously and second if it hits the wall then it will be it will be squeezed and it will be have a flat surface or a flat shape but what we are what we desire in atomization are spherical particulates. The spherical particulates have some advantages you are able to get good flowability good amount of even (compact) compatibility and also very high compressibility.

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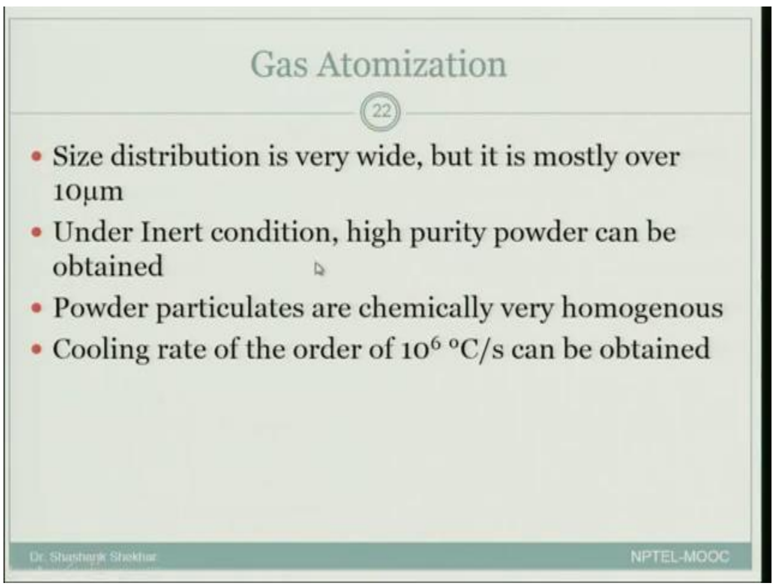

So, that is the reason you want uniform shape and back to spherical shape and for that to happen the liquid must freeze on it is path before it hits some walls. Now the size distribution is very wide okay when you are using gas atomization technique the size distribution you will obtained is very wide but it is mostly avoid 10 micrometer and again you will see that the size that you will obtained are usually greater than 10 micrometer if you want submicron and manometer range or particulates you we have to apply some additional technique we will see in the one of the last slides when you want to produce Nano precipitates or Nano powders. Under inert condition high purity powder can be obtained.

So, if you insure that inside the chamber there is no contaminant it is inert it does not react with anything then the powder you can obtain can be very high purity. So, that is one another advantage of gas atomization technique you can get very high purity particulates. Powder particulates are also very chemically very homogeneous, because you have obtained with using homogeneous nucleation and that there was low at the particulates also small information size they are chemically very homogeneous. You can get cooling rate of the order of ten to the power of 6 degree Celsius per second during gas atomization.

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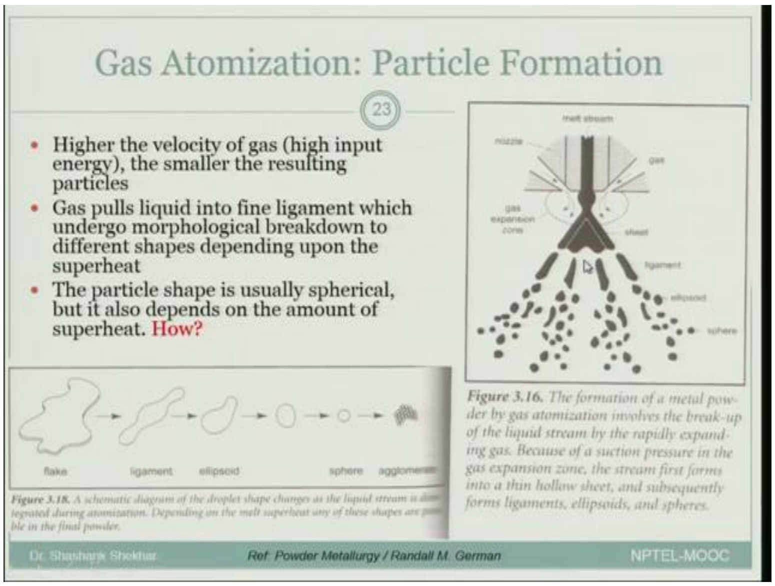

Now that we are looking at the gas atomization let us also look at small amount of let spend some time on the particulate formation. So, you can see what is the different kind of shapes that forms, so first the liquid comes out as a stream and because there is a high velocity gas also exiting at that point which impacts a lot of energy it breaks into ligaments and these ligament eventually turn into sphere.

So, the overall flow is overall change of morphology is actually given over here. So, you in the very beginning thus even before it has come out from the just stream it is more like a flake sheet and by the time it comes out it is in ligament shape and slowly it is starts to convert and slowly starts to convert into more symmetric shape which is ellipsoid unless of the ellipsoid with less asymmetry and finally spherical shape.

So, this is the usual particle change in the size or the shape which is in the morphology, another thing is that it is not that just one particle of flake will get one particle of sphere, this also will breakdown into legal several ligaments, ligament will breakdown into even several ellipsoid and so on. So, each at each stage it is still disintegrating because of the energy been imparted by the gaseous particles. And if you allow this sphere particle which are very small in size to stick to each other they have a very high tendency to agglomerate again because of the driving force of reducing the surface energy.

At this point now that we have seen that the the particulates particle morphology moves from ligament to sphere in a position to say something about the size or constraint on the ligament and the sphere. So, let us look at one of these equations that defined the size relation between ligaments and and sphere. So, how we know that initially you get ligament (())(22:34) and we can roughly equate it with a cylinder.

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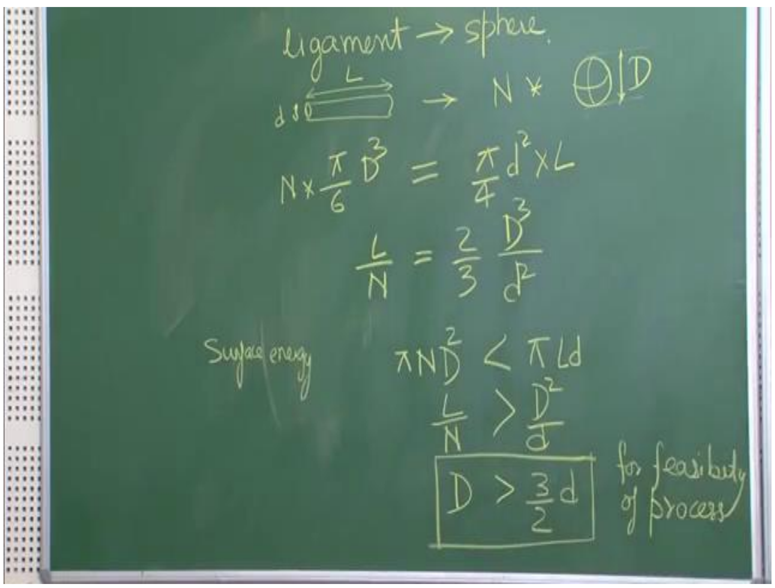

So, we are looking at ligament it gets transformed it is spherical particle, ligament let say is more let us cylinder and let say this is L in diameter length and small d is the diameter and by the end by the time it get translated transform to sphere, n number of sphere has from let say and let say this is a sphere of diameter D.

This one ligament has broking into n spherical diameter so volume has to be (cons) volume has to be maintained and therefore we can say the volume of sphere times n number of sphere is equal to volume of one ligament area of the cross section times for length like this or you can say L what n is equal to 2 by 3, D cube by d square.

Now let us look at the surface energy times, since this is forming from this the total surface energy for the n spheres must be less than the total surface energy that we have for the ligament and therefore we can write, what we are doing is we are just calculating the surface area over here and surface area over here.

Since the surface energy term per unit area is constant on both side it get cancelled out we are just we should be able to get the total surface area for this it should be less than the total surface area for this and therefore from here we will get but we know L over N is equal to 2 over 3 D cube by d square and therefore we should, when you put this over here and you will get D should be greater then. So, we can get a relation between the size of the sphere and the ligament and we this will also allow us to designed the atomizer according to the size that we want to obtained.

So, what it is saying that diameter of the spherical particle must be greater than 3 by 2 times the diameter of the ligament for this for feasibility of this process in this is not greater than this what will happened it will say that the surface area for this is larger than the surface area for this, which may it is not really feasible. So, now that we have this, we let us look at what it means towards in terms of design.

So, if you want to get a smaller particle size if you look at this if you want to get a smaller particle size that is a small d if you want to get this sorry capital D to be smaller than tour this d must also reduce or that the diameter of the ligament must also reduce.

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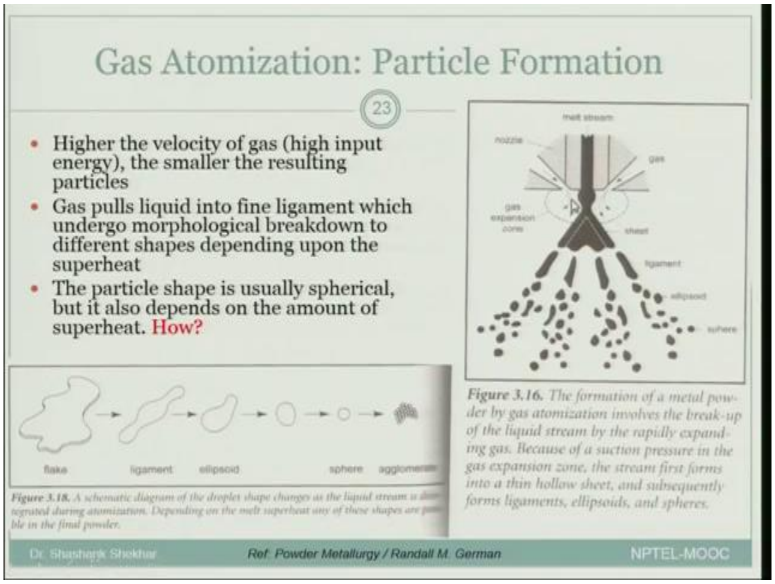

So, you can it is not saying anything about the length, so we can our very long lengths of ligaments that the diameter must be smaller and therefore if you want to get a smaller particle size let say you are earlier getting 25 micron but you want to get now just ten, twenty microns or ten microns then in that case what to you to do is reduced or set the parameter such that the ligaments that you are getting have smaller diameter and one of the ways to do that is we can reduced and we can set the gas parameter such that the overall that critical diameter that you are getting over here gets reduced. So, that so these are some of the means that you will be able to understand and you are able to relate once you see a relation between the ligament and that particle diameter.

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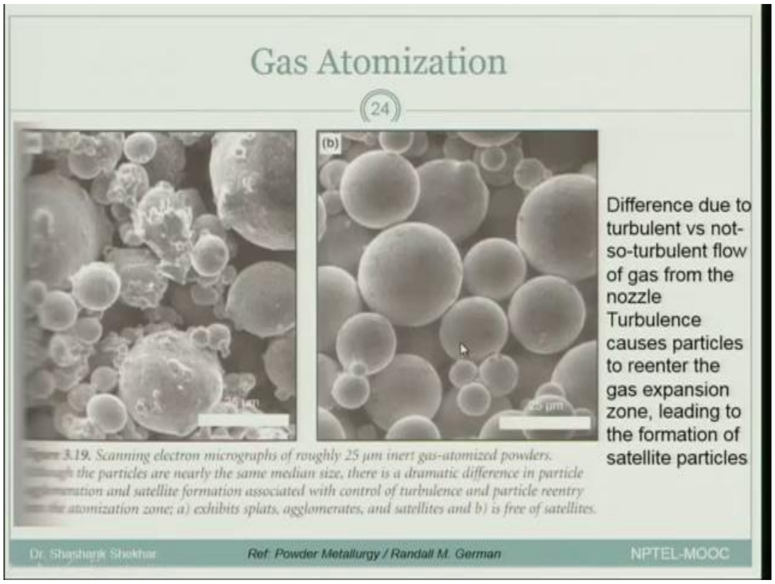

And this is a micrograph a see a micrograph showing particulates that you has been obtained using gas atomization technique and the other are two different condition parameters the used for that you this particulates will one of them what do you seen is very clean and very perfect spherical particles on the other hand here also an spherical particle but on tap of that there are some spherical satellite particle.

So, these are light satellite particles seeping on to the main particles and the reason the main reason while this one got some satellite particle is because during the flow of the stream at the ejection there were there must having some turbulence and that turbulence can one of the particles to come back and seat on to the top of the particulates that have already formed and that you one will starts to see this satellite formation. So, if you want to avoid the satellite formation by best and easiest way is to get rid of turbulence.

So the difference is because of the turbulent and this is not so turbulence flow. Turbulent causes turbulence causes particles to reenter the gas expansion zone leading to the formation of satellite particles.

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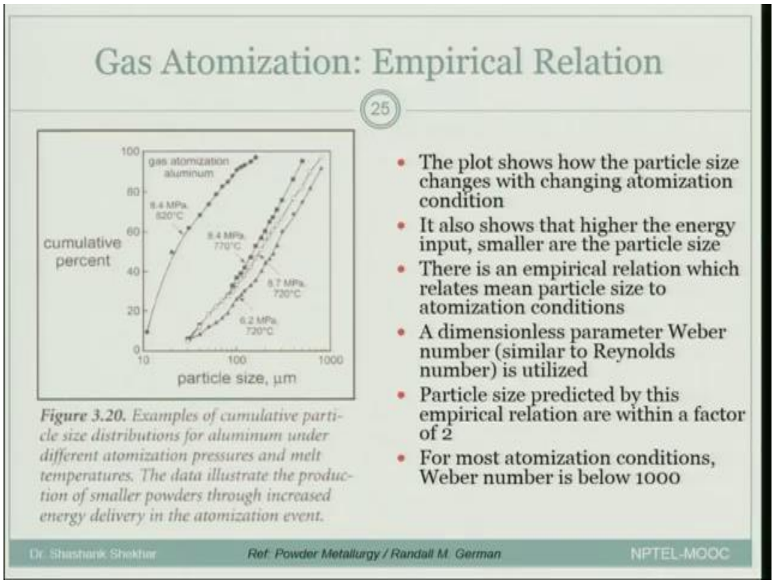

So, this is the a little bit about gas atomization technique will come back and will start discussion about some of that empirical relation not some but one empirical relation that relates the particle size to the parameters used in gas atomization, so will come back on to this slide. Thanks.