Nanotechnology Science and Applications
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Lecture - 15
An Approach to Prepare Bulk Nanostructures

Hello, in this course we have been looking at different techniques for preparing nanomaterials; usually in the context of some particular application or some particular property that we are trying to investigate So, in the context of that property or that investigation we have highlighted any challenges involved in making those kinds of samples and how those samples can be utilized.

So, in today's class, we are going to do something slightly a different, we are going to focus on An Approach to Prepare Bulk Nanostructures. So, actually, in fact, we did look at one technique earlier which had some capability of this nature. But here we will focus on another technique which is particularly used for in the context of making bulk nanostructures.

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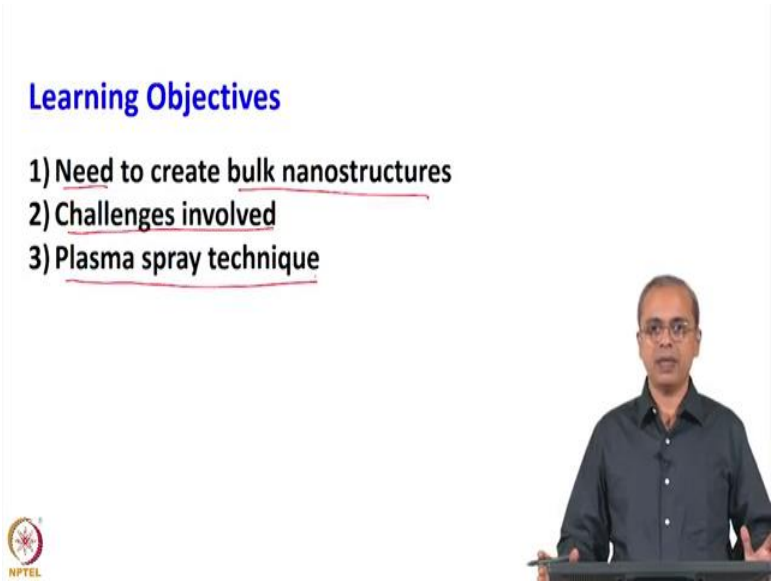

So, our learning objectives are first to understand the need to create bulk nanostructures, again this is something maybe touched upon briefly at a different in different classes. But we will see that for the sake of completeness here, look at some challenges involved in trying to come up with these kinds of bulk nanostructures. And then finally, look at this

particular technique called plasma spray technique. So, that is a particular technique which helps us do this, make nanostructures a sort of in the bulk scale and that is what we are interested in.

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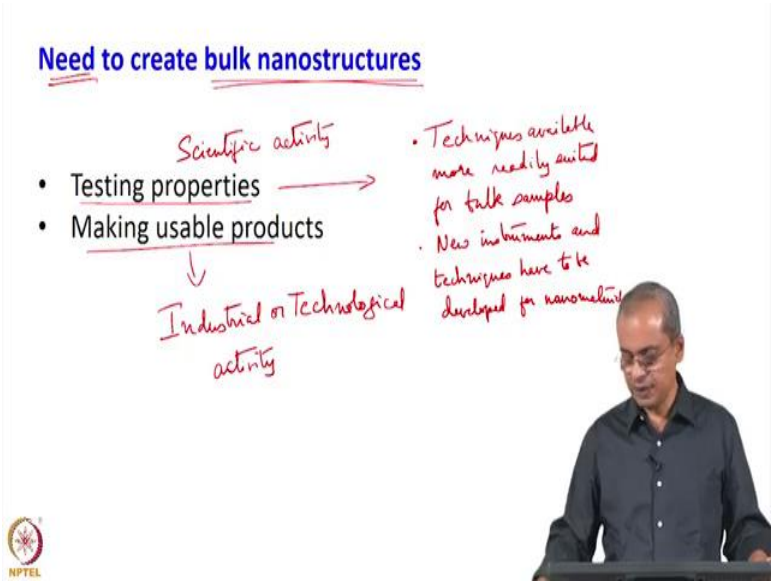

So, what is the need to create bulk nanostructures? Well, first thing is there is like a scientific need and a technological need. So, this is the scientific need; so, the scientific need is that often we want to do material synthesis and processing and then we want to look at the properties of the material. So, we have many techniques that are readily available which help us study particles, I mean sorry study properties of materials. The only issue is that those techniques have evolved over the years and they have typically been used for bulk samples, techniques available, more readily suited for bulk samples.

So, this is the issue here, we have techniques that are readily available in the marketplace or in our labs which are typically intended for bulk samples and it could be any property. It could be a range of properties that we have already seen, some other property that we have probably not looked at in this class so far, but almost always we have this situation. So, if you suddenly say you have made a nanomaterial and you have made a very tiny sample of a nanomaterial, then the chances are that even though you have that technique available in your lab that instrument that you have will know will not be able to probe this particular sample, because the sample size is very small.

And, it may want a sample to be in a certain geometry, it may expect the sample to be of a certain size. The instrument will have some sensitivity, it will say it applying a load, for example, it will say that it can put in terms of a load so, many Newton's it can put. And, then minimums it will have a minimum value for the load it can put and a maximum value of load it can put. Therefore, it will require your sample to be of a certain size so, that that load will correspond to a certain value of stress and therefore, you can do a mechanical test.

So, now if you say that I do not have a sample that size, I have only a sample that is 1 millimeter by half a millimeter across, then essentially even though you have the sample and you have the technique you cannot make a measurement; so, that is a problem. So, one of the options that people have then is to create to come up with new techniques, new instruments and techniques. So, one approach would be then that you have to create new instruments and new techniques to handle nanomaterials, but then you have a problem here. So, you are going to spend a lot of money and you are going to keep on having multiple versions of the same technique.

So, its hardness tester you will have like two or three different versions of the hardness tester depending on the size scale you are dealing with is a conductivity measurement unit, you will have again multiple sample holders. So, you keep having to keep on building up infrastructure to test a range of sample simply because, the sample quantity is small, the sample size is small and so on.

So, from a scientific perspective, this is an issue that if you work with small amounts of nano samples, nanocrystalline samples it is inconvenient to you. Therefore, if you are able to make a slightly larger sized sample off ah, but that, but a sample that has this nanostructure unit, then you can actually do some scientific testing of that sample using techniques that you already have in the lab.

Now, it is not simply about the need to keep buying new instruments, it is also about repeatability of results, it is also about comparing data. So, I can do a test on a macrocrystalline sample; I can do a test on a microcrystal sample. I would like to do the same test on the same fixture with the same operating condition on a nanocrystalline sample. Then I have greater confidence when I compare the data, when I have when I compare the data I have much greater confidence that there is no instrument effect that

that is hidden from the considerations that I have missed in some sense, that is now clouding the data of the nanocrystalline sample.

So, it really helps for a very thorough scientific study to have samples which are nanocrystalline which can also be tested on instruments that are meant for larger-scale samples. Therefore, there is a need to create bulk nanostructured samples from the perspective of scientific activity. This is an industrial activity, making usable products is an industrial or technological activity. So, this is an industrial or technological activity and again there also it makes sense, you have tested something in the lab and that the nanocrystalline version of that particular composition that particular crystal structure gives you some really interesting property which you will not otherwise get.

And, let say you want to use this in some let say you want to use this in a drill bit, let say you want to use it in some nut and bolt arrangement that you have made. You want to use that for a rim of a spectacle that you are making, any number of things it is supposed to be the heat shield for a spacecraft. Any number of applications they are all macroscopic applications, you have something that you got your holding in your hand, you are bending it, you are putting it on some location, lot of things you are doing which is macroscopic.

So, again it does not help if you have seen some property in the nanoscale, but you cannot make a large-sized structure in the which is a large externally overall dimension size. But, if you look at it in the microscope it is nanostructured internally so, therefore, there is a very strong need to make bulk nanostructures both from a scientific perspective as well as technological applications.

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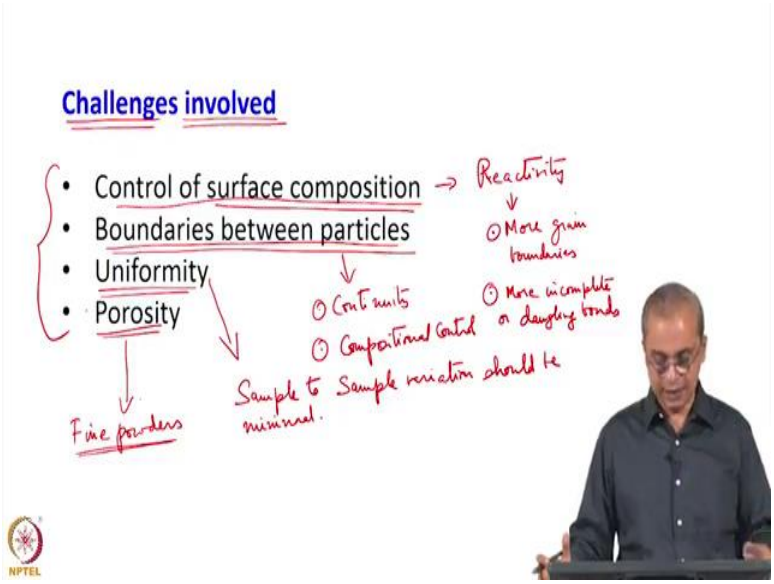

So, what are the challenges involved? Why is this such a big deal? Why should we bother about it? Well, the first thing is the control of surface composition. So, this is what to do with reactivity, as you are aware every time you reduce the crystalline size you are increasing the number of unsaturated bonds at the grain boundaries more grain boundaries; so, more incomplete or dangling bonds.

So, therefore, any nanocrystalline material by nature is very reactive and so, even particularly during the synthesis process, where maybe you are under temperature conditions, where it can more easily react with the various other constituents. You can create a situation where you are trying to make a bulk material of a certain composition, but what is formed is a bulk material of some other composition; maybe it is a got an oxide layer or some other such thing is happening.

So, control of surface composition is a challenge which you face when you have nanocrystalline structure, as supposed to when you have microcrystal in the macrocrystalline structure. Boundaries between particles, again the same issue you have you want continuous boundaries and you want compositional control.

So, you want the bonding between the particles to be very strong. So, that it comes across as like a continuous material, a continuum should be there and you do not want an oxide layer in that boundary so, to speak. So, this is a situation that you have face. Uniformity so, this is uniformity even sample to sample. In any, even in a scientific

activity we normally say that how many samples have you tested, have you do you have 5 samples that you have tested. Do you have an error bar with respect to those 5 samples, what is the mean, what is the standard deviation with respect to the property that you have tested?

So, this is a requirement, this implies a certain uniformity in that sample to sample you have that level of uniformity. And therefore, if you are making tiny quantities of a sample there is a greater chance that this tiny quantity, that you made today is slightly different from the tiny quantity you made tomorrow and so on. And therefore, its uniformity becomes a challenge, the smaller the sample that you make the greater is the influence potential influence of the surroundings on that sample. And therefore, a much higher level of control is required.

So, this is also important from I mean from a scientific perspective as well as a technological perspective. Every time you put, I mean some instrument out the door, you put some component out the door some shaft which is used somewhere in an automobile part; you have to specify that failure rate is this is below a certain percentage and so on. And, that you can do only if your sample to sample variation is very tiny. Then for with greater level of confidence that the sample you are making is similar or identical and you can give that warranty on that sample.

So, uniformity is important again that becomes difficult when you go to the nanoscale, also this issue of porosity. So, if you are making fine powders and many times the nanomaterial synthesis process will help will be easy to do, if you are working with fine powders. If your starting point is fine powders, your finishing point is fine powders things like that then it is actually easier to relatively easier maybe to get yourself something in the nanocrystalline scale.

But the finer the powder you work with when you do the sintering to make this large-scale product all these issues that we already spoke about an oxide formation is an issue. But, more specifically you can also have porosity you will have, I mean you will have to do a fair bit of centering you will never reach 100% theoretical density. You will start approaching it, but you may have some porosity which will act as a stress concentrator and it will affect properties. So, this is another issue. So, these are all issues when you

are trying to make a macroscopic sample which has nano crystalline microstructure, I mean nano crystalline structure inside it ok; so, nano structure.

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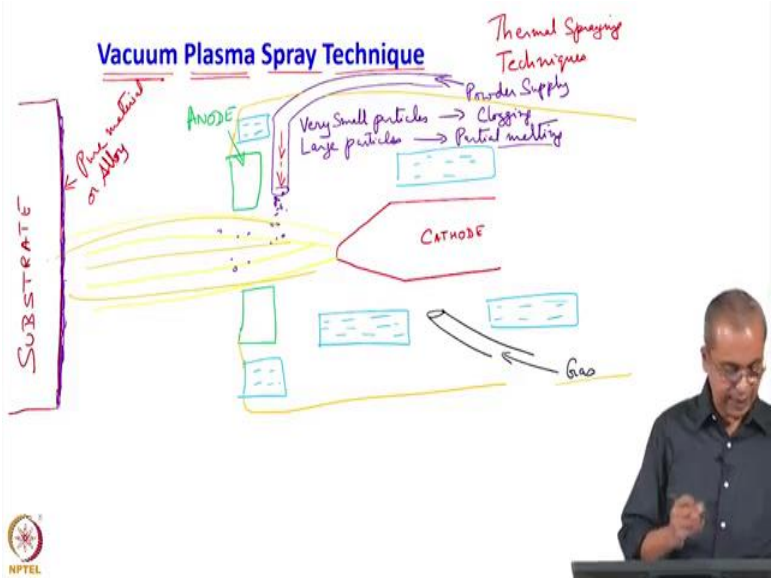

So, one of the techniques that can be used to do this is called a vacuum plasma spray technique. So, it is part of a set of techniques called the thermal spraying techniques. So, thermal spraying technique and it is a technique which basically is very large. So, there are already there are commercially available vendors who give who supply this I mean a machine or instrument that makes does this process called the vacuum plasma spray process or thermal spray process.

So, the chambers are actually kind of large, I mean it is as large as that or is even larger and inside the chamber you can set up the process that you want. And, the samples that you get or samples that you can handle easily you can handle in your hand and so on. So, the general idea is this we are using a plasma and that plasma is generated using a gas and an anode and a cathode and that plasma is created which and there is an opening through which that plasma escapes from that region where it is created.

So, there is a region where the plasma is created and from there it escapes out of that unit through an opening. And, if you provide supply of powder at that opening very close to that opening that plasma pulls that powder along with it and moves forward. And, then you can take and that usually the temperature is reached in the plasma are very high and

then and the velocity is generated are very large; we will see that briefly and then it goes and impinges on some target.

In that target the sample is formed so, this is the basic idea. So, there is a plasma gun which schematically looks something like this. So, you have a system here which is the cathode and there is another electrode which is the anode; so, we have like that. So, there is an opening in the middle which you can see here, then there is a small opening here which is connected externally.

And, it is basically powder supply, they call it the feedstock or things like that it is a powder that is being supplied to this unit. There is a gas being sent in, that is being sent into this region and all around this unit the gas comes in here and all around this unit you have cooling. This is flowing water it is not static water, but you have cooling systems even here you will have, all around you have cooling systems.

So, this is all surrounded; so, we are looking at a cross section. So, the water is actually flowing you are I am just showing you what will be visible, then this whole thing is connected up in some sense; so, that is your plasma gun. So now, what happens is you have this powder that is coming down here and you have this plasma that is being generated and the plasma goes forward.

So, plasma is moving forward and it takes these particles along with it and the particles melt as they come out, they are molten. And, then one molten set of particles are going with that plasma and then you have the you have a target here or substrate, on this the particles that you are sending through the plasma begin to deposit. So, they deposit here so, this is what the deposit is happening.

So, this deposit is happening here and this is the system. So, this is the general system you can look at there are lot of detail images put by various commercial vendors of how their system looks, but in general this is the set of parts that is involved. This is it says here vacuum right on top so, what this means is this whole unit that I have just shown you here which is the substrate, the cathode, the anode all this supply this powder everything is sitting inside a big chamber and the chamber is evacuated.

So, first you begin by pumping down the chamber to very low pressure. So, that you can remove any presence of air, any presence of moisture from that chamber. And, then you

refill with some amount of argon, little bit of argon it is still low pressure it is filled with little bit of argon and it is in that atmosphere that you are doing this plasma-based deposition process.

And, this substrate can slowly rotate; so, usually the substrate is in the form of some kind of cylinder so, you keep rotating it. So, this spray will occur on the surface of that substrate, you can make a reasonably thick spray of a few millimeters thick and from that you can cut out samples. So, this is the few millimeters thick and then a sample that is several centimeters tall, several centimeters tall and a few millimeters thick. So, that is a sample that you can easily handle and you can do something like so, that is what we are looking at.

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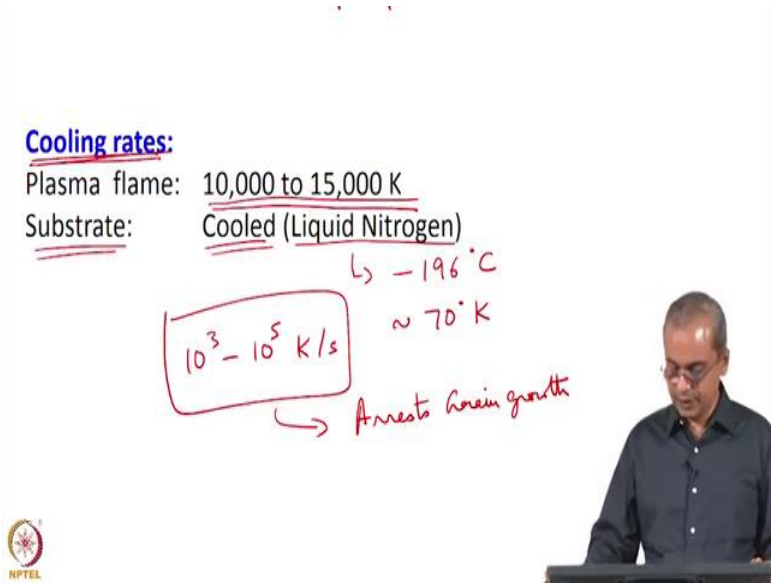

So, now what are the interesting some interesting things are there associated with phenomena, they are associated with this the plasma spray process. So, the first is the cooling rate, the plasma by nature of how it is formed actually attains very high temperatures; you are looking at 10,000 to 15,000K. So, 10,000 to 15,000K is the kind of temperature that is attained at the plasma. So, naturally any powder particle that comes there almost instantaneously melts. So, you will see here that there are some competing phenomena going on and so, we have to be at least conscious of what is going on. So, that we can understand why there are some constraints and how you have to work around this constrain.

The plasma flame is about 10,000 to 15,000K, for your reference surface of the sun. So, surface of the is approximately 6,000ºK, roughly about 6,000K is what you are looking at for the surface of the sun. So therefore, the plasma that you are attaining in your lab is a temperature that is higher than the surface of the sun. So, that is something that you have to understand, then the substrate on which the sample is growing that can also heat up because, you are heating it with something that is at very high temperature. So, in invariably that substrate is cooled. So, you need to cool the substrate, to do that people typically use liquid nitrogen; slowly flowing liquid nitrogen very small amounts you keep flowing to keep the substrate cooled.

So, liquid nitrogen is about we are looking at minus 196ºC or roughly about 70ºK. So, 70ºK is what you're looking at is as the temperature. So, for all practical purposes you are going from 6,000K at the sorry we are going from 10,000K which is more than double the I mean temperature of the surface of the sun from 10,000 to 15,000K. So, roughly double the temperature of the surface of the sun from that temperature to almost 0. I mean in this context I mean it is going to be roughly the same whether you go from 6,000 to 70 or you go I mean you whether you go from 12,000 to 70 or you go to 12,000 to 0 does not make a big difference.

So, you are basically dropping about 12,000º of temperature almost instantaneously. So, the cooling rates they get are huge, the cooling rates we are looking at is off the order of 10^3 to 10^5 K/s. So, you are going from the from a temperature twice that of the temperature of the sun to room temperature in less than 1 second. So, that is some phenomenal cooling rate. So, this is very important because it is it arrests grain growth and that is very important, because only if you arrest the grain growth then correspondingly your nanostructure is maintained. So, whatever nanostructure you want you maintain. So, it is always a competition between nucleation and growth.

So, we want to create a situation here whether there is very large amount of nucleation ah, but very extremely tiny amount of growth. So, that is the combination that we want to create and that is what we are doing with this kind of high temperature initially followed by very fast cooling to very low temperatures.

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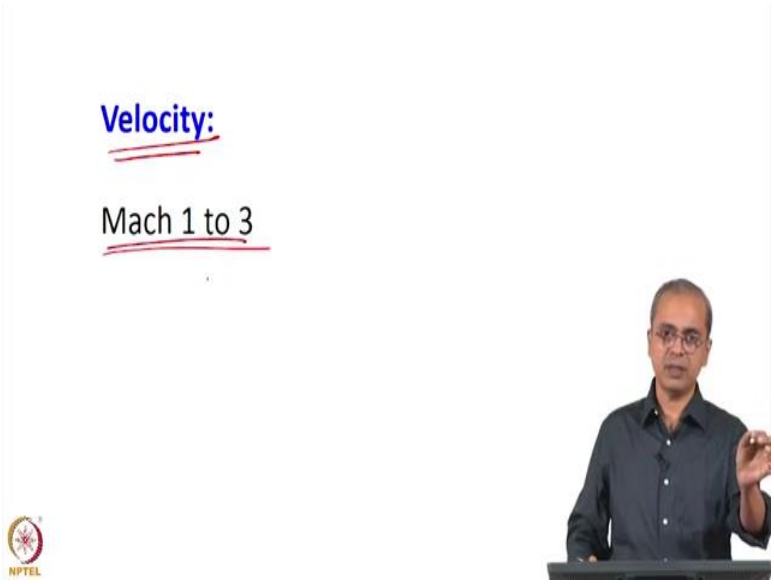

What is the velocity that is attained? Because this plasma is formed so, there is like its very high temperature. So, significant expansion is happening and then there is vacuum outside. So, it is being pushed out rapidly, it is also being sucked out rapidly because there is vacuum on the outside. So, taking these two into combination you are heating usually heating velocities which are Mach 1 to Mach 3.

So, that is higher than the speed of sound, you are going at velocities very high very high velocities. So, that again shortens the time between where the plasma is formed and that cooling substrate the cooled substrate, the time taken for particles to traverse this distance is extremely tiny because, of this high velocity.

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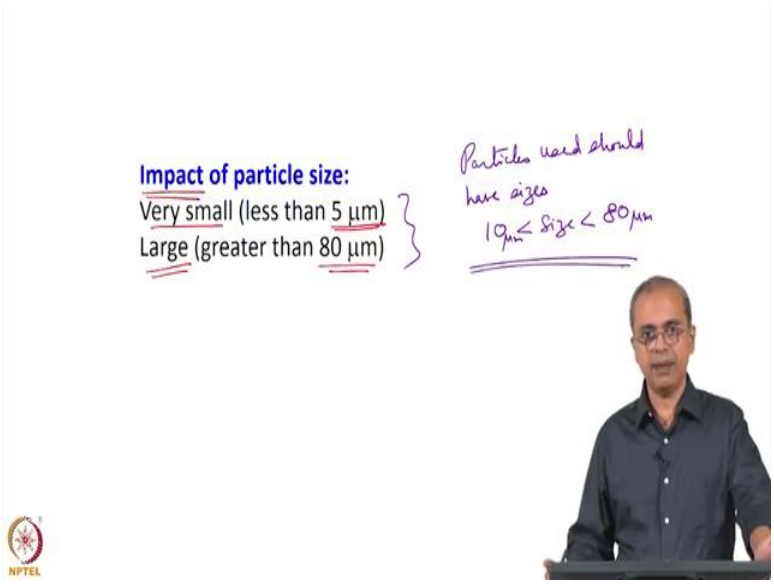

So, one issue that we have is the impact of particle size. So, if you look at so, you can see here that I have indicated that there are very this particle size, that we can consider as very small which is less than 5 microns, less than 5 or 10 microns and then very large which is greater than about say 80 microns. So, there are two issues with this I mean so, corresponding to this there are some issues. So, this is where the particles are coming. So, this is where they are coming out. So now, very small particles; so, we will just put here very small; very small particles implies clogging.

The gun get can get clogged, the location where those particles are coming can get clogged if because the very fine particles which stick to each other and then just clog the gun; so, it may not necessarily work. Large particles partial melting so, in other words if you have large particles, the particles that are coming out of that gun have not completely melted. Even though you have because this is where you have to understand the fact that you have now competing processes going on. So, yes on the one hand you have 10,000K, on the other hand you have an 80-micron particle which is now moving at around the speed of sound or maybe even more than the speed of sound and racing towards a target.

Once, it hits the target it is going to cool to liquid nitrogen temperature. So, you have a very tiny amount of time during which this particle has to melt and stay molten till it hits the target. So, it is extremely tiny amount of time and even though you are putting

10,000K temperature at that region heat transfer takes some finite amount of time. So, the larger the particle, heat takes certain amount of time to go from the surface of the particle to the center of the particle. So, the larger the particle, the greater is going to be the time required for the heat to reach the center. And so, you may not completely melt the particle and even before that you will hit the target.

And so, if you want to do if you want to change the crystal size, you will not accomplish that if you only have a partially melted particle. If you take an 80-micron particle it is a single I mean they are all crystals, maybe just a 1 or 2 grains inside that 80-micron particle, then you are looking at say 40-micron 80-micron crystal size. If it does not melt then you will still have a residual say 20-micron crystal size which does not help us, maybe 20 microns melts 20 micron and becomes nanostructure because of the sudden cooling, but the other 20 microns has not melted. So, that does not help so therefore, partial melting does not help us.

Therefore, if you see here, we actually have a range, you have to stay within this range. So, particles used should have sizes say between 10 and 80 microns, 10 micrometers to 80 micrometers. So, this is a size range that we need to have for us to effectively do this process, effectively melt the particle and create these nanostructures.

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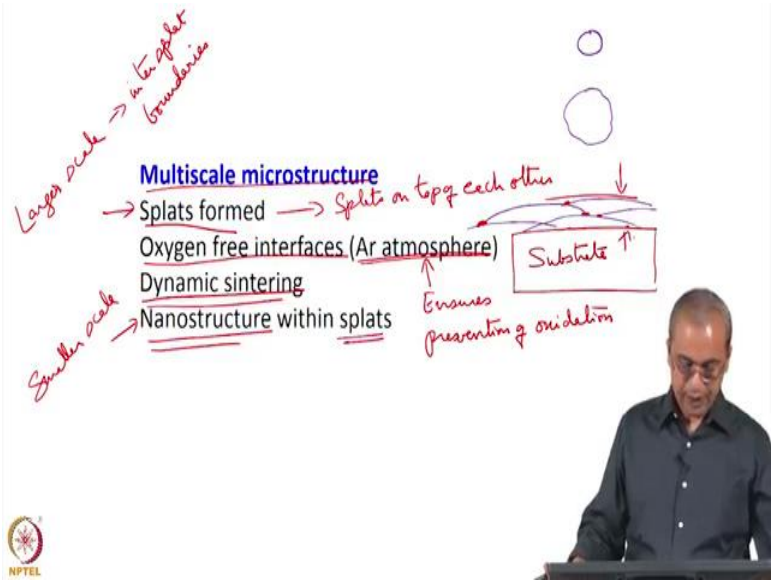

Now, this technique is very interesting because, you the microstructure that you create in the sample it sorts of has a multi scale dimension to it, I mean aspect to it. And so, we

would like to see what this multi scale time microstructure is, we say multi scale because first there are something called a splat that is formed. So, as splat is, I mean it just conveys the idea that something splattered and that is really what is happening; you are taking a particle, you are taking a particle. So, you have around particle and then you have melted it. So, you have some I mean liquidish material with maybe little lower density than the solid.

So, it is having little higher space and then you have a surface on which it is going to be impacting; so, that is your substrate. So, when this particle impacts that surface you essentially have a splat, it just splats splatters on that surface it is called a splat. So, now every drop that is coming forms a splat. So, you have a splat there, you have a splat here, you have a splat on top of it, we have a splat like that that and so on. So, you have a splat after splat after splat forming on it and so, you usually will have multiple splats. I mean in fact; you have the whole processes full of splats and those splats are pressed against each other.

So, when this is done, if you look carefully in the microscope you may be able to identify those boundaries. This boundary here, this boundary here, this boundary here depending on what is visible on from the top surface you may be able to see faintly you may be able to see boundaries the nice thing is so, that is one level of the microstructure; so, that may be a largish. So, you are looking at a few microns sized splat with a very faint boundary between those splats, but that splat is consisting of nano crystalline microstructure. So, we will get to that the in between it is very important that the interface between the splats be oxygen free, only then it forms nice proper bond between one splat and the other splat. This is accomplished by the fact that we have an argon atmosphere.

So, the argon atmosphere helps us ensures prevention of oxidation. The thing that is happening there is also that you have this molten particle that is coming at very high velocities like, I said Mach 1 to Mach 3 and then goes and hits. So, when once platforms even as it is cooling the next splat comes and hits it. So, you have sort of a sintering going on between splat to splat to splat, that is why you do not have a gap between the splats. They just for hit one on top of the other, they sinter with respect to each other and this is sort of a dynamic sintering that is happening; one is solidifying the other hits it that is also solidifying. So, the third one hits it so, there is it is partially molten, partially solid and it is all coming together in one place.

So, this is dynamic sintering that is going on and as I said this is at the at the larger scale you have the splat. So, largest scale you have these inter splat boundaries, at the smaller scale you have a nanostructure within those splats, you have a nanostructure within those splats. So, this is very useful for us. So, we have now got substrate here; so, this is the substrate that we had and on top of this you have got a layer, this layer here which is of this thickness. So, that is the layer that you have got, that layer has a splat structure, it has inter splat boundaries which are oxygen oxide free continuous without any porosity and it is having a nanostructure.

Now, as I said that the substrate can be a fairly large substrate, you can have a pretty large sample as a substrate because, this is a gun which is sitting here and then spraying stuff on it. It is sort of like a sophisticated version of spray-painting ah, but basically you are doing this and in a plasma with very high temperatures and some molten material that is coming and you make the sample.

So, the sample is like a is like a thick layer which you can form on top of this substrate and to the extent that you can maintain the thermal gradient. In other words, to the extent that you can keep cooling this sample and you can keep heating it with this thick with this plasma, you can make thicker and thicker layers. So, like I said you can make several millimeter-thick layers and once you have done that, you can carefully machine and remove that layer and you can remove that layer and you can do various things with that layer.

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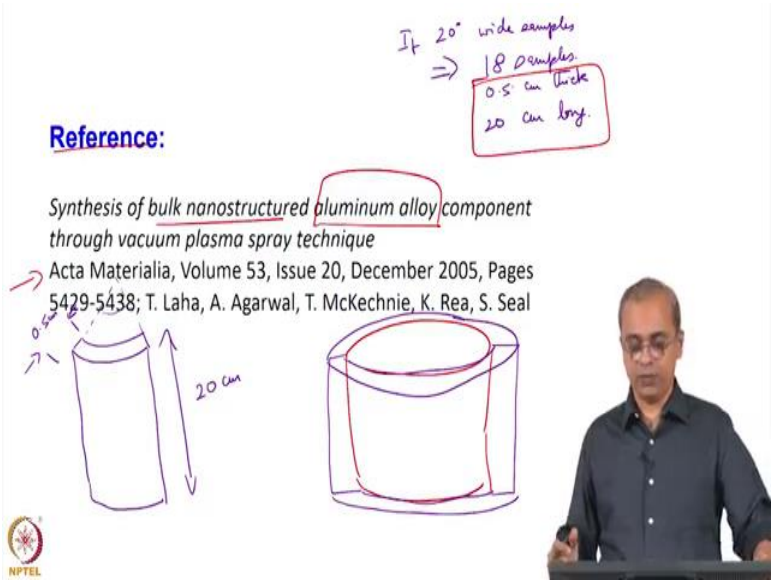

So, if you see here there is what we spoke about is the general idea of what you can do with this particular kind of technique and the kind of conditions that are required for using it. I am giving you a reference here; it says synthesis of bulk nanostructured aluminum alloy component through vacuum plasma spray technique. This is an Acta mate paper so; it is a very good journal and the details are given here. So, you can see here they have actually worked with an aluminum alloy.

So, they have worked with an aluminum alloy which means what? They actually have powder which is now having more than one component so, you can mix components, you can create the alloy in situ; you do not have to start with an alloy. So, you want aluminum with some percentage or some other component, you take aluminium powder, you take a proportional weight with respect to weight, you take a proportional amount of the other powder and then you mix them. And so, in the powder supply that you do here, you can actually put the mixed powder; so, the mixed powder can come this way.

So, the mixed powder can come this way so, that will melt and it will go and form melt it will melt, it will go and hit the substrate and so, you here you will have the alloy. So, you can have a pure material or alloy; so, this can form here. So, what they have done is they have up with an aluminium alloy and they are able to get bulk Nanos structured samples out of it. So, in fact, in their case they actually take a hollow cylinder. So, they take a large hollow cylinder and on the surface of this they make the sample. So, that is how

like I said you have this cylinder on which you can paint it and that is why that is how you can flow the liquid nitrogen etcetera. So, you get your sample of a certain thickness.

So, you get this sample of a certain thickness. So, you're getting like a cylindrical sample on top of a cylinder cylindrical substrate then you can machine it out. So, once you machine it out you can get various pieces out of it; so, you can radially machine out a whole bunch of pieces. So, you will get sample pieces which look like that. So, this is a fairly large sample and then you can get radially how many ever based on what you are how many^{o} you have got here based on the number of^{o} that you have here, you can have some sample some number of samples So, whatever it is, if you say it is 20^{o} angular dispersion that you have then potentially you can get about 18 samples out of it.

So, 18 samples so, that is the nice thing. So, I am if 20^{o} wide samples then you have 18 samples. So, please remember now we have 18 samples made at the same time and those dimensions could be say anything. So, this dimension I like I said this is I do not know to give you an example this could say 20 centimeters, this could be 0.5 centimeters so, something like that. So, you have 18 samples which are 0.5 centimeter thick. So, that is 5-millimeter-thick and 20 centimeters long, all of which have been prepared at the same time under the same conditions with the same atmosphere and so on.

So, whatever you have generated you have now got for all practical purposes 18 identical samples of this size of this fairly large size that I am mentioning here which is a very significant accomplishment for you to do work, where you are doing reproducible samples, where you can study sample behavior with much greater confidence.

So, you can make say tensile test samples with this or any other sample that you want to make out of it, you can even make a tool out of it. You want to convert this into some kind of a drill bit, I am just giving you an example of a drill bit, you can make something else out of it. But this is large enough this is something that you can hold in your hand, you can make a screwdriver out of it, you can make a knife out of it.

Any number of things which can be made directly out of this sample that you have received, you just have to take it to any industrial production process and you can make this kind of sample, I mean to make this make the product out of it. And, as I said you got this all those problems, that I originally mentioned; all the challenges that I originally mentioned are negated in this particular process here. So, surface composition reactivity

is not an issue you have an argon atmosphere, boundary between particles is not an issue because you have got very high velocities. And so, that splat that forms a very nice boundary between the particles, uniformity sample to sample variation should be minimal.

Yes, you have got 18 samples here with virtually no variation between samples, porosity is also known a virtually non-existent because again you are hitting molten material on top of molten material. And so, some kind of dynamic sintering at very high velocities, it's not only you do not have to put pressure like you would do in the nominal sintering process, where you take powder put pressure. And, then you do the heating, it is not like that here, it is arriving hot, it is arriving molten and the pressure is happening because of the impact, impact of one splat on another splat. So, virtually all these conditions, all the conditions that I mentioned as challenges have been taken care of in this technique.

So, they do this with an aluminium alloy and then they study some mechanical properties and they are able to show some interesting results based on that. So, if you get a chance take a look at this reference.

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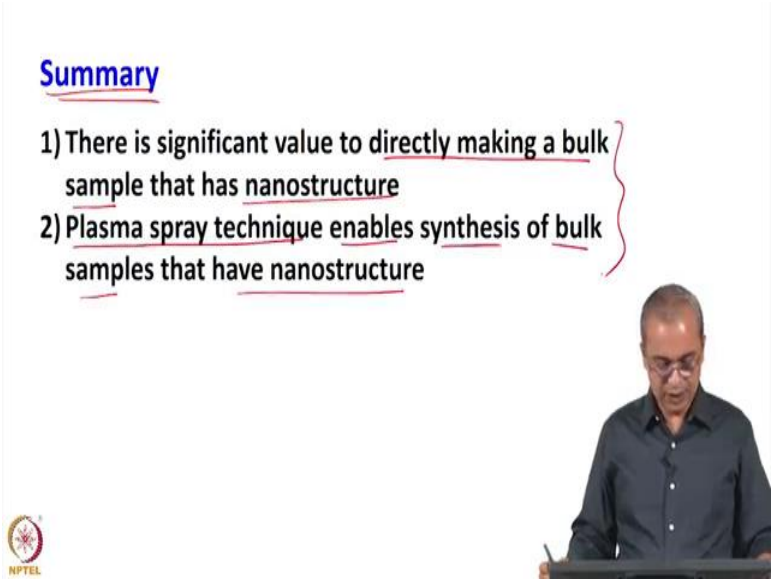

So, in summary, there is significant value to directly making a bulk sample that has a nanostructure. We establish this very clearly there is a lot of value both scientifically as well as technologically to making a bulk sample, that has nanostructure. The plasma spray technique which is a part of a type of thermal spray technique enables you to do

this. It enables your synthesis of bulk samples that have nanostructure and it overcomes many of the challenges associated with other techniques which are starting off with tiny quantities of a nanostructure and then trying to put it together.

We spoke of other techniques, we spoke of severe plastic deformation, now severe plastic deformation by nature of the fact that you have to deform that sample in multiple times, it is not a sample that can be large scale. I cannot take a big cylinder and keep on trying to deform it in multiple times, the amount of energy that is required to deform that sample is going to be very huge and I am I may not have the machinery to do that. So, that is also relatively macroscopic sample, it is not a microscopic sample as supposed to say having a powder sample. But, there also I am sort of restricted to thinner dimensions, I maybe have to work with say 2-millimetre-thick sample.

So, some restrictions would be there on what I can do with it and also the size of the sample in addition to the thickness. And, even high-pressure torsion it will be a small sample which has to be held on two sides and then twisted in several different ways. So, you cannot again have 20-centimeter samples, 50-centimeter samples those samples you are not going to be able to make in that situation. Even though in many other ways they will meet these requirements that we are talking of, there is no boundaries there, that you have better control on the surface, there is no porosity and all that. So, that maybe you can think of it as an intermediate way of in terms of the size scale. And, intermediate size scale which you can address by using severe plastic deformation kind of techniques.

But I mentioned when we spoke about severe plastic deformation that it does have this limitation, making macroscopic samples, making industrial-sized samples is a problem with that. Here you do not have that problem in with vacuum plasma spray technique, you can actually make this large-scale sample; so, that is a very nice aspect of it. So, those are our highlights for this technique and I have given you a reference. So, please take a look at it and that is our class for today. We will look at something else in our next class.

Thank you.