Nanotechnology Science and Applications
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Lecture - 20
Nanocomposites

Hello, this is a class on Nanocomposites and in this class, we will try to look at issues associated with this area of nanocomposites; it is a very interesting area composite in general is. Itself a very interesting area you have a wide range of composites that are possible and composite materials by definition mean that you have more than one type of material which is being put together and the end product which has this combination of more than one material present in it, typically will have properties that you cannot otherwise individually get in a any of these materials.

So, there is some synergistic effect there and so, the sum is more than the parts put together and therefore, you are having a product that you would otherwise not be able to do or obtain that easily. There are many composites which are natural then we have made many manmade composites and so on. In nanocomposites the composite part of it is still the same, this idea that you are actually having two different or two or more different materials which come together, but importantly one part of it usually is some kind of a reinforcing material that is present there is in the nanoscale maybe one maybe more which could be in the nanoscale.

And this poses challenges, of course, it is interesting because there is something in the nanoscale, but more than that it poses certain challenges to what can be accomplished when you work with nanocomposites and how you would go about trying to handle it.

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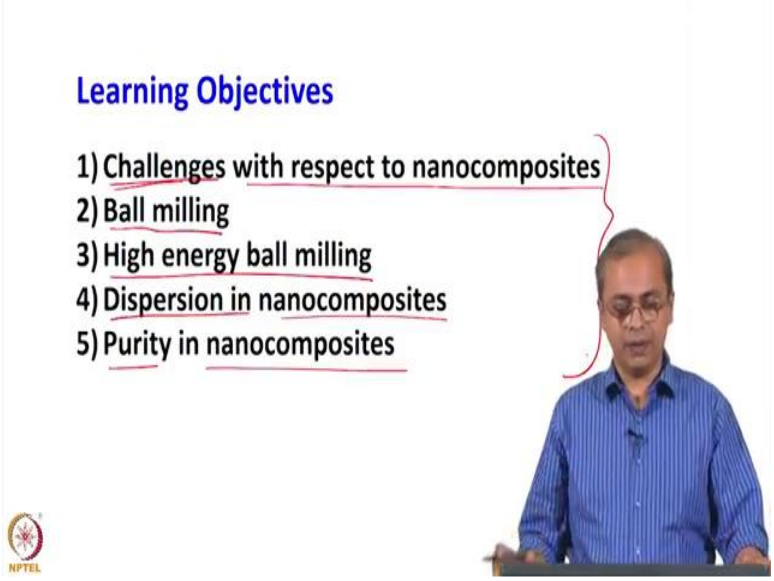

So, our learning objectives for today's class are to look at these challenges with respect to nanocomposites. So, through the class at different parts of the class we are at an underlying theme will be this, without explicitly necessarily focusing on listing them out, but this will be an underlining underlying thin theme.

We will look at something called ball milling which is used to help us which is one of the ways in which you can get a nanocomposite it is not the only way you can get it, but it is an interesting way to get it and through this course we are always looking at both the techniques to get those get us those nanomaterials, what those nanomaterials are and some end-use for those nanometers.

So, all of these ideas and concepts we are touching upon as we go through this course and so, in today's class we will look at ball milling. A version of it is called high energy ball milling. So, that is also something that we will look at and that will give you some a variation on the ball mill, it tells you what I mean that there are certain limitations to what you can do with a ball mill and we will see how by using a high energy ball mill, you can actually overcome those limitations. So, that is one aspect.

The moment you talk of a composite, you have a matrix and you have some kind of a reinforcing agent in it which is present inside it. So, it is very important to know how well that reinforcing agent is dispersed in that matrix. So, the matrix is your major phase and this second phase that is present there, which is reinforcing the matrix in some form needs to be dispersed across that matrix.

So, it is very important for us to know to get a gauge of what we have accomplished in the dispersion process and see if there is a shortcoming there and if so, how you would go about improving it? So, dispersion in nanocomposites is an aspect that we will touch upon through this class. And also, we would look at purity in nanocomposites. So, where is this scope for lack of purity that comes in all scientific activity, we are looking at getting very pure materials and then using them for some application and so on.

So, even here you are going to anyway start with some material that is pure. So, where is this scope for impurity that comes into a nanocomposite and is there something that we can do about it? So, these are some of the ideas that we will look upon through this class and I think you will get some sense of this field of nanocomposites.

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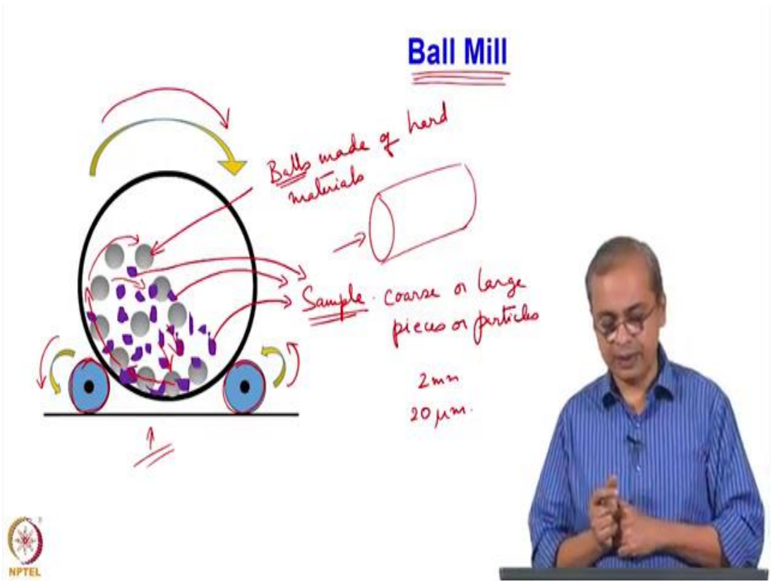

So, we will begin with something called the ball mill. Actually, people who work in chemical engineering, usually have a course on mineral beneficiation and also in metallurgical and materials engineering we have courses in the more traditional form of metallurgical engineering there is usually a course on something called overdressing. But basically those are all courses where you are looking at materials and how you can I know break down the material, how you can convert extract something from the material, what are the processes involved, what are the size scales involved and how would you go from raw material that is at some size scale to some processed material at some other size scale, which is then usable in some application or it can be provided as an input to some industrial process.

So, much of the industry requires this. So, there is always some preprocessing of that material; when you look at the output of the industry, it is all looks very clean it all looks very organized you have this nice say flat sheets of material or some no nice clean glossy product that comes off the end product of an industry, but usually what goes in is far from that.

You are looking at stuff which is broken blocks of material, in all awkward shapes, no specific aspect ratio may be clean may be dirty from different sources may be today it comes from one source which is very clean and organized and tomorrow it comes in another source which is very disorganized and dirty. And so, most industries most large-scale industries have significant processing that happens to the raw material that comes into their doorstep before it gets converted to a product that goes out of their doorstep.

And there are many industrial processes which help them break down those materials and purify those materials separate them into different fractions and then use them. So, one important such technique is this technique called a ball mill. It is an operation that you can use on for breaking down material, it can be used for more than that, but typically it gets the initial motivation is to break down materials.

So, the setup is quite simple you have a cylinder. So, a cylinder of some nature like that and you are seeing the cylinder side on here in this image that you see here. So, this image is side on that you are seeing and therefore, you see the circular cross-section, it is sitting on two rollers. So, you have a roller here and you have a roller here. So, that cylinder is sitting on those two rollers and those rollers rotate. So, that is what we have here the rollers rotate naturally because the rollers rotate this way the cylinder itself rotates in the opposite direction right.

So, the rollers here are rotating counterclockwise and therefore, the cylinder is rotating clockwise with respect to us. Now inside the cylinder you have balls specific balls these are hard balls made of hard material these are balls made of hard materials and what happens is, as the cylinder rotates you have material inside this you also have some sample this material that you see here is the sample all the stuff that you see here is the sample.

So, typically what you do in a ball mill is it is a jar, it is a cylindrical jar. So, you open the jar and inside the jar you fill some number of these balls of made of hard material, that hard material could say a tungsten carbide for example. So, tungsten carbide balls you can put in there which are extremely hard materials, they do not break easily and they very hard that sense. So, you fill some number of balls, you also put in some amount of the sample that you are interested in breaking down.

So, that sample will usually be in the form of some coarse particles some course coarse or no coarse or lumpy or largish particles large pieces or particles. So, this is how the sample will be. So, that is what you put in along with the balls sometimes we also if the sample that you are putting in is already somewhat in a fine powder, then we also may have to add a liquid I will talk about that in a little bit, but basically you first we are just having these balls inside and this sample inside.

Now, when the ball mill is started and the roller starts rotating, the jar also begins to rotate. When the jars rotate when the jar rotates, the ball, as well as the material, get dragged along due to friction they get dragged along the wall of that cylinder. So, they get dragged along for some distance and then eventually they fall off like that they fall like that right. So, they begin to fall and that is what happens. So, both the this is happening both to the balls as well as to the material that is present there that sample. So, it all comes and falls back down here.

So, when that happens, you have your sample materials fall and then these hard balls come and hit it. So, it is and, in the process, it breaks this breaks those sample particles. So, in a sense, it is sort of a continuous process of hammering. So, it is like you take this piece and you break it hit it with a hammer you break it etcetera, but you are not doing a single place you are repeatedly doing that activity, here you have a more continuous process and because it is balls they all roll and they come and fall automatically and they keep on breaking this material.

So, what is basically happening is, you are essentially using gravity to assist you in this hammering process. So, the ball goes up and because of gravity it falls down first of all because of friction it is getting dragged up, it is getting dragged up the ball mill because of friction and then because of gravity, it falls down. So, it falls down and then in the process it hits that material which is also present inside that ball mill and breaks that material into finer particles.

So, this is the idea of a typical ball mill and like I said it is an interplay of gravity and frictional forces and also, in fact, the centrifugal force. So, this is basically what a ball mill does and you can use it to break down particles. As the particle size comes down when it becomes finer and finer particles. So, you have you are already you have already run you started with particles which were all say 2 millimeter in size approximately average radius was 2 millimeter in size of various sample particles that you put in, you start ball milling. And maybe a half an hour or 1 hour down the road when you of ball milling you stop it and you take the sample out take a piece of the sample out and you check it is particle size.

Maybe what started off as 2-millimetre size may suddenly have dropped to say 20 microns. So, something you started with at 2 millimeter becomes say 20 microns and so, the finest. So, as you continue with progressively with time the particle size keeps going down, but what also happens is when you get to extremely fine particle size especially if it is dry powder that is in there that particles will start floating in the ball mill just like dust particles float in the air they start floating in the ball mill.

So, when they float in the ball mill, the balls which are hitting which are going through this impacting process are unable to impact that floating powder. So, the effectiveness which; so, even though the ball mill is running and these balls are just rolling up and hitting and hammering and hammering, they are not actually hammering the powder is just floating around they just hammering each other. So, the effectiveness the efficiency with which they are able to break down the particles keeps coming down with time.

So in fact, what they do is, once you find that the particles are becoming fine in size or if your target is extremely fine particles then we also add a liquid in the system which acts like a medium which holds the particles down and so, they do not just keep floating in there and then you are more effectively able to hit those particles and therefore, continue this break down process. So, this is a way in which you can start with large particles and come down to small particles. So, this is an important technique.

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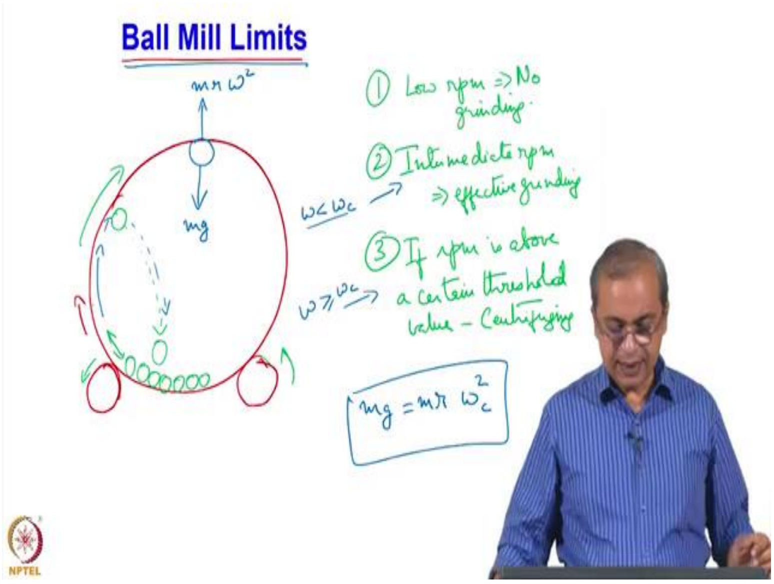

Now, what are some limits here? So, we need to understand something here on what is the limit here. So, basically, if you take the cylinder if you switch on the rollers and make them rotate it extremely small rpm. So, the rollers are operating at low rpm and. So, a cylinder rotates that way. So, if the rollers roll in at low rpm; then the balls that are present inside they also just keep rolling. So, they roll up a little bit they are all down they roll up a little bit and then they roll down. So, this is basically all that they are doing.

So, then the impact action is not there. So, then the breakdown of the particles is not happening. So, if you pick up the rpm a little bit more and you start increasing the speed with which of rotation, the rate at which these rollers are rotating then what you will see is, you will see these balls beginning to go up further. So, they will go up somewhere up here and then from here, they will begin to fall.

So, from here when they fall, they will fall like this they will not roll they will fall like this. So, this is when the grinding action begins to happen. So, as long as they are rolling it is not very effective, it is not really doing any grinding may be extremely minuscule grinding it might be doing not very effective, then when it when you pick up the rpm enough that the ball climbs up the cylinder or some distance and then falls down that is when you actually start having a fair bit of grinding.

So, therefore, by increasing the rpm you are improving the grinding; however. So, low rpm no grinding intermediate rpm you have effective grinding if you go to very high rpm. So, the temptation will be to keep on increasing the rpm. So, that you can actually have more and more grinding the ball will go even higher and hammer down etcetera. If you go to very high rpm if rpm is high is above value is above a certain threshold value, then we reach a very different situation when is as the rpm increases as I said the ball goes higher and higher and then comes down and hammers down on the powder. But if you go to very high rpm then what happens is, the centrifugal force keeps the ball attached to the wall of that ball mill it does not allow the ball to fall down at all. So, that is called centrifuging, so, it is called centrifuging.

So, this happens. So, it is no different then you have a string and you have a ball you just swing it along, if it will go to some height and keep following, but if I mean no rotate it faster and faster and faster you will find that it makes the complete circle, it does not fall down in the middle it does not flop down in the middle right. For the ball mill the intermediate action is what is useful. If you go at high enough rpm it stays in the air it makes a perfect circle and never falls down and that action is not useful for this.

So, the reason that happens is basically because the ball mill depends on the interplay of gravity versus centrifugal force. So, if you at any point you go to the topmost part of the ball mill when the ball is up here, the force that is acting down is the gravitational pull mg the mass times the gravitational pull mg is the force that is acting down. What is pushing it out centrifugally is $mr\omega^2$ that is the centrifugal force.

So, if your ω as long as your ω is less than some threshold value you will have. So, for example, this intermediate rpm your ω is. So, let us say; so, there will be a threshold value, let me just say let us consider one particular ω where

$$mg=mr\omega_c^2$$

this ω square is some critical value cmω critical value at which point this these two mg matches $mr\omega^2$ or other g matches $r\omega^2$ they match exactly.

So, when your ω is less than ωc, when ω is less than ωc then you have a situation that you will have this process happening. That means you do not centrifuge before you reach the top of the cylinder, the ball falls down and therefore, it comes and impacts the powder. One the moment you cross this value which is ω greater than or equal to ωc, then at that point the centrifugal force is higher than the gravitational force. So, when you reach the top part of the ball mill, there is enough force still pushing the ball outward then there is pushing it inward and therefore, the ball does not come down and hit the powder and therefore, no grinding happens.

So, therefore, the ball mill has that limit the typical ball mill has this limit and that limit essentially is because of the gravitational force. So, the gravity we have a certain gravity in on earth. So, with this gravity, this is all we can do because the gravity can only pull it down so, much. So, if you go to higher rpm, you are not going to pull it down right. So, you are limited to this and within the scope of this you have to do the ball milling.

Initially, you do need some centrifugal some ω because that is what is the causing the I mean it is helping along with gravity when it is below, it is helping along with gravity to give you the frictional force to drag the ball up and then eventually it falls down. So, all these things are in interplay here and there is a critical value of ω which below which you have to stay for you to have this grinding.

So, naturally if you want to do extensive grinding, you want to make nanomaterial, you want to do a nanocomposite, where you have to do significant amount of grinding then a ball mill limits you the ball mill the way I have shown you here limits you there is only so, much you can do with it or you will have to keep grinding indefinitely for you to start going below a certain size scale and that is not really a very time effective manner of going about things and it has many other attendant issues. So, therefore, this is not sufficient for us.

Then people came up with some interesting ideas to actually overcome this limitation that gravity imposes on us and that is this idea of a planetary ball mill.

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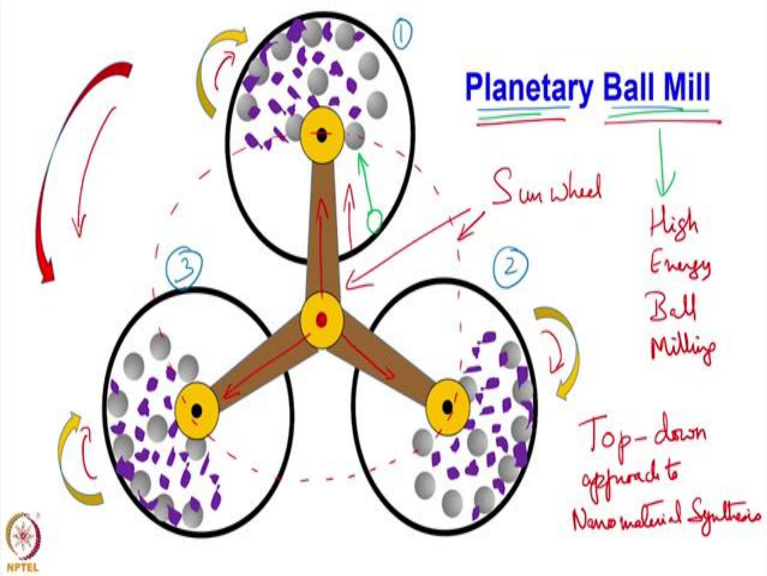

So, in a planetary ball mill as the name suggests you actually have more than one ball will in fact, here. So, right now here we have 1 2 and 3 ball mills. So, 3 ball mills are here you can have more also these are all commercially available you can purchase them and there is a central wheel which is referred to as the sun wheel or the sun circle. So, this one is the sun kind of. So, you can think of it as one orbit it is an orbit that the. So, this is like a sun wheel, on which these planet planetary ball mills are seated.

Now, one important difference between the planetary ball mill, there are a few differences, but one important difference between a planetary ball mill and what we just saw as the regular ball mill is that this is oriented such that the axis the central axis here the central axis is vertical. So, whereas, previously the central axis was horizontal, so, this is kept vertical. So, the cylinders are sitting vertically standing vertically and then the whole sun wheel rotates. So, here, for example, we have pointed out that the sun wheel is rotating like this.

So, the ball mills are now held on this at this radius from the center and the entire cylinder itself is now roaming around like this. So, the cylinder keeps roaming around in that direction. So, there are three cylinders here to balance the way and you can similarly have other cylinders and you can put samples in all of them and they are all rotating around like that. So, there is a certain rpm with which they are rotating that sun wheel is rotating and then each of the individual cylinders is also rotating usually in a direction typically in a direction that is opposite that of the sun wheel.

So, the sun wheel rotates one way the individual ball mills rotate the other way and they have their own rpm and in fact, usually, you will have a higher rpm for those ball mills relative to the rpm of that sun wheel. And this situation actually frees us up from the force of gravity, because here essentially the force that is pushing the ball from here back is because of the centrifugal force of the sun from the sun wheel. So, due to the rotation of the centrifugal due to the rotation of the sun wheel, you are having a centrifugal force which is going from the center of that from this center here outwards.

So, that is your force which is now substituting what gravity was previously doing and therefore, since you can control the rpm of the sun wheel you can control that. So, it is like having variable gravity, except that that is not what we are having here, but it is similar to that in the context of the ball mill. And then within that context, therefore, you are changing the limits that you can actually access with respect to the rpm of the ball mill of the individual ball mills this 1 2 and 3 ball mill and therefore, you can change the energy with which the ball that comes at some location here falls back.

So, the ball is going to fall back with an energy that you can control and can actually be much higher than what you will accomplish with a regular ball mill. So, the planetary ball mill is also actually because you can you enable the balls to hit or strike the material with much higher energy, it is also referred to as high energy ball milling this kind of ball milling is also referred to as high energy ball milling.

So, in the use of a ball mill to create nanoscale materials particularly and in fact, also not necessarily within the context of it is not restricted to the context of nanocomposites alone, but certainly also in the context of nanocomposites in the use of a ball mill to help you reach those kinds of scales, typically they are working with planetary ball mills. So, there are groups which specialize in this they work with planetary ball mill there are no research groups, which work with planetary ball mill and they do typically break down materials or all sorts of different materials can be broken down to very fine particles and into the nanoscale and then you can use that to carry out a wide range of studies ah.

By definition here you are actually breaking down a large-scale material. So, this is a top-down approach. So, this is a top-down approach to nanomaterial synthesis and that is the way the typical ball mill operates and so, if you actually have this kind of a planetary ball mill in your lap, you can actually I mean you can convert a wide range of materials into nanomaterials that is essentially what you can do. With a single technique you can start creating nanomaterials so if almost any sample that you can throw into it based on certain sample characteristics. If the sample is too soft then it may not fracture easily it may just become a flatter flake kind of thing.

So, those are certain aspects that you need to look at, but in principle you can take any material throw it in there and it will get you will get a nanomaterial and not just a nanomaterial, you can actually control sizes of the nanomaterial and so, make there are many things that you can do with it. So, it is a very useful kind of technique to have and there are groups which specialize in this where the primary technique they use in the lab is this high energy ball milling and they use it they are able to work in a very wide range of experimental areas by simply using this single technique. So, therefore, it is a very nice technique to work with.

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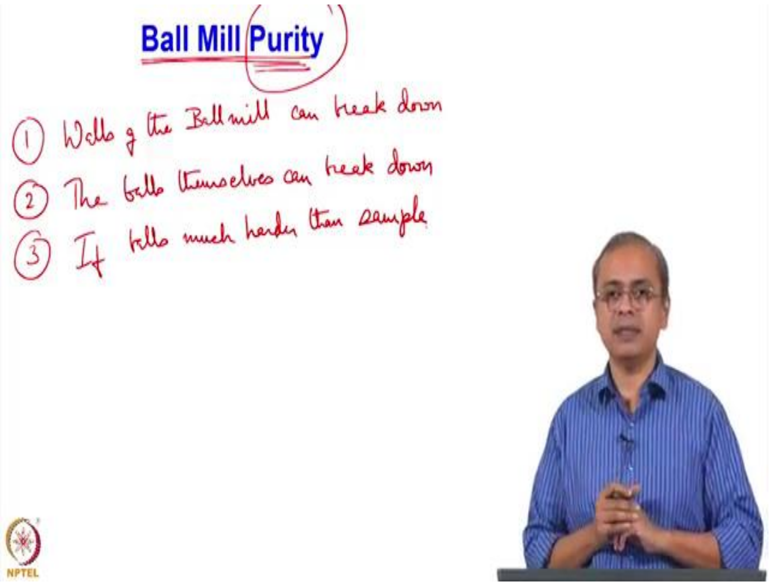

Having said that ball milling has certain aspects associated with it, that you have to pay attention to you cannot I mean I told showed you the bright side of it which is that I anything you can throw in there you can get a nanomaterial out of it and therefore, if you are working in the area of nanomaterials, it is a great technique to have at your disposal you can do many things with it. But the problem is one of purity. So, this is an issue that you have to always be careful about.

So, anytime you use a balm mill the, for example, the walls of the ball mill can also break down can break down meaning as you use the ball mill with as time progresses, you do 1 hour of ball milling you do 2 hours of ball milling etcetera if you do that kind of ball milling a tiny amount of the wall of that ball mill may also break into fine particles and enter your sample.

So, the walls of the ball mill can break down, the balls themselves can break down. So, the walls then ball stem cells can break down and this is always happening. So, it is not that it is not happening it is actually a fairly accepted part of the ball mill process that at some rate the balls will break down. So in fact, in industrial setting we are talking of I am showing you a high energy ball mill in a lab setting where you are throwing in say 5 grams of a sample and then you do something with it or 1 gram of a sample and do something with it and then you take it and you do considerable amount of analysis with 1 gram of sample. So, that is a different setting.

In an industry or setting, you may have tons of material coming in and then there is some particular step requires a ball mill. So, those ball mills may be running continuously they may be running continuously and breaking something down for hours 24 hours a day it may be running and so on. So, in fact, in such settings the balls actually get consumed and the, in fact, they use their experience and expert I mean the accumulated data of the ball mill to know the rate at which the balls get consumed.

So, what they actually do is they know that by the time if you continue ball milling using this ball milling ball mill and then after 3 days if you inspect many of the balls might have shrunken in size because they have also lost material and then I after about 1 week you may actually do loose the balls completely. So, you may actually be just rotating material without any ball in it.

So, what they actually do is, they will set up a schedule. So, every this is just an example in terms of numbers every 48 hours they will add 3 more balls or 4 more words into the ball mill. So, that as the old balls get consumed new balls are continuously being added into that system. And they will also look at some material compatibility so, that this material that is breaking down is not completely making your sample useless. So, your sample is of a certain material and if this is an allied material, which will assist the sample in some way in it is final application it helps you may not always have that combination, but it helps. So, that is the kind of thought process that goes into operating a ball mill over any prolonged period of time.

And therefore, if you go to the other extreme of it where you are trying to synthesize high purity samples extremely high purity samples where you want to know what is that high purity sample doing in some particular and application if purity is a very major concern for you then ball mill does give you a challenge it is prone to adding impurity that is what it is prone to adding impurity even there you may actually know if the balls are really hard. So, if the balls are much harder than the sample then you may be able to get away with it you may actually not have much impurity coming into it, but it is a concern you should at least be aware of.

The second thing is you may have some medium that you are throwing in there is you put acetone in there or some others dispersing medium in there which will hold the powder particles together down they may also react. So, you are increasing the chances of some reaction happening. So, you have to always be aware of it and you are doing this in some atmosphere. So, if the finer the particles that you create you may have some oxide formation occurring.

So, these are all aspects that you have to be aware of it does not mean that the system is useless, but what I am saying is you when you run the experiment, these things should be in the background of your mind. So, that you accomplish first you want to see whether you are getting nanoscale. So, you are getting great; you also want to see are you getting any other problems from it, which you did not want and the potential source for those problems is some of the things that I am highlighting here.

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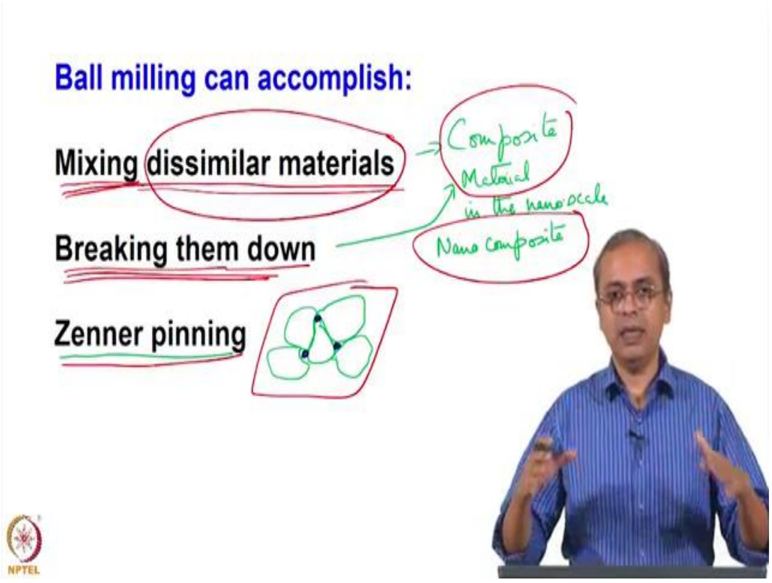

So, what can the ball milling accomplish ok? So, why are we using ball milling and what can it accomplish for us? So, we already spoke about breaking materials down, but we can go one step earlier than that it can first of all help you mix dissimilar materials. So, we spoke only about breaking something down. So, we said you can start with particles which are 2 millimeter in size on average and you can use a ball mill to break those particles down to say a 20 micron sets or less you can start determining to from 20 micron, you continue the ball milling you can go into the nanometer scale also some 100s of nanometers you can accomplish it right.

So, that is always possible, but you can you also use the ball means simply to mix different materials. So, you have a powder of one material and you have a powder of another material you can mix them. Of course, if you take 2 powders you can also mix them with using a spatula. So, that you can always do, but usually a ball mill does a much more effective job of mixing them in a much more intimate way they get mixed as supposed to your hand mixing it using a spatula or some such process, there is a much better job of mixing it. And in what it will also do for you is that it will do this while also breaking them down. So, it can mix dissemble dissimilar materials while also breaking them down. So, that is a very useful thing to have.

So, you may have one hard material, one somewhat relatively softer material and you can put it all together in a ball mill and then do the milling. So, you will find first of all that the hard material mixes with the soft material, then on top of it the soft material also breaks down the hard material also breaks down and if you do that then when you have these two different materials sitting there one hard and one soft and so on you are actually creating a nanomaterial right. I am sorry you are creating a composite material; you are creating a composite material because these are dissimilar materials because they are dissimilar materials what you are creating is a composite material. So, you creating a composite material and on top of it you are breaking it down.

So, what you are now creating is a composite material in the nanoscale that is a nanocomposite. So, this is what we have accomplished by doing ball milling with dissimilar materials. So, why is this important to us? Why is it of interest to us to mix dissimilar materials? Well one of the reasons you may want to do that there may be many reasons why you want to do it one of the reasons why you may want to do it is to make use of this concept called Zenner pinning; Zenner pinning which basically does the following that if you have a grain structure, where you have a lot of grains and then in between the grains you also have one hard material.

So, there is some hard material here, there is some hard material here, some hard material here like that you have a lot of hard materials and then you have these grains also sitting around then when you try to do plastic deformation these hard materials pin those grains down.

So, the grain is trying to change it is shape because you have dislocations moving through it and so on. So, the grain is trying to change it is shape because you are now trying to know you have applied stress on it and that stress is more than it is yield point. So, it is trying to change it is shape, but these hard materials which are sitting on those grain boundaries pin those grain boundaries down that is called Zenner pinning. They hold the grain boundaries in position they are not allowing the grain boundary to move forward because they are holding in place.

So, the grain boundary now has to twist around it and go and only then it is able to. So, essentially the grain boundary has to change shape before it can move forward and that increases the amount of work that you can do to the material before it will change it is shape, essentially it makes the material harder and stronger. So, that is what it is a doing. So, you can create a stronger material and a harder material by making taking advantage of this concept called Zenner pinning, by simply introducing a second phase which is hard.

And usually in like in most other cases, the finer these materials this for the same weight fraction you put whatever you put 5-8% of the solder material into this soft material, the finer they are dispersed and the finer they are and the more evenly dispersed they are, the more effective they are in holding those grains down and preventing them from moving.

And therefore, this all these things of being able to mix them, mix the dissimilar materials and to break them down is all very effective in creating a composite material which is a nanocomposite and is very strong. So, it is a very a number of things you are accomplishing here by simply using a ball mill a high energy ball mill and then very in a very appropriate choice of materials.

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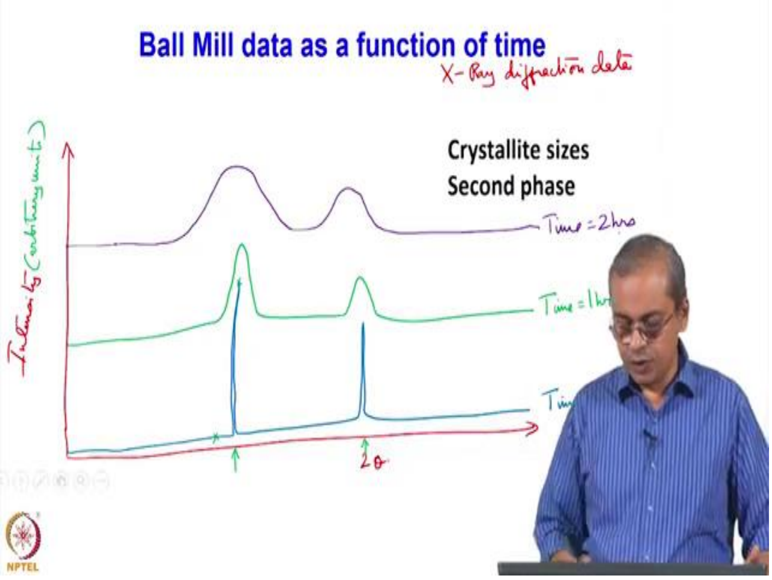

So, how does ball milling data look as a function of time? First of all, what data we are interested in of course, whatever property you are investigating you are going to look for that property. If you are looking for hardness then you are going to check for hardness, be looking for electrical conductivity you may look for electric that measurement you may make. But one of the standard things that techniques that people use for following the progress of ball milling is XRD which is X-ray diffraction.

So, we have already spoken quite a bit about X-ray diffraction, particularly I spoke about peak broadening as a result of the nanoscale formation. So, that background is there in one of the earlier classes you can take a look at it. So, we are just simply going to use it here, many groups which work with ball milling as the way in which they go about reducing the crystal sizes our grain sizes for accomplishing nanoscale materials what they do is, in fact, they start the ball milling. So, a very standard part of their study is that they will start the ball milling and ever so often. every half an hour interval or 1-hour interval they will take a small sample from the of that powder from the ball mill and they will do an X-ray diffraction scan on a in XRD scan.

So, a typical XRD scan has intensity on your y-axis and you have 2θ on the x-axis. So, what they typically do is as he said you they take the sample every 1 hour and I will just say we have like 3 hours of data we have got as received after 1 hour after 2 hours this is what we have let us say; that is the data that we have and I will just draw some schematic of it and then we will discuss what that might represent.

So, this is how and I just say that we are seeing only 2 peaks in the 2θ range that we are investigating, this is how your initial. So, this is then they will mark this as time 0. So, at 0; so, as received material, this is as received material this is what you are saying as your X-ray data then we will have data after 1 hour of ball milling and in usually in the X-ray data the y-axis which is intensity is usually set at an arbitrary scale.

The reason it is set at an arbitrary scale is simply because you it is based on how long you take the data. So, that is all it is. It is counting the number of X-ray photons that are arriving at the detector. So, the most slowly you take that for the exact same sample you the more slowly you take the data you will have more X-ray photons coming for the faster you take the data you will have less X-ray photons coming, but the relative amounts of photons that are coming will not be disturbed.

So, at the peak if you are getting 1000 times the number of photons at the base this place you get 1000 times more photons then you are getting here that ratio will remain roughly at 1000 it will be roughly 1000, but whether you get say 1 versus 1000 or you get 10 versus 10,000 really depends on how many I mean how many seconds you are counting the data. So, that is, therefore, this intensity is usually marked as arbitrary units.

So, by that they usually mean that let us not worry too much about the exact value of the intensity, we are more worried about relative values of the intensity that is essentially what they mean. So, this is how the data looked when you did at time 0 and then the data are maybe after 1 hour of ball milling look something like this. So, what do you see here?

So, this is time 1 hour this is after 1 hour of ball milling what you see is that the peak positions have not necessarily changed and that is some, we want to see this what has happened to the peak position. Assuming the peak position has not changed, it means your sample composition is still safe it has not changed their will be some variation because of strains in the sample, but generally it if the peak position is not shifted, it means you have not got any strains in the sample you will also see so, that what is that peak position that is this angle 2θ.

So, that 2θ value of both the peaks has not changed. What you will see is the peaks have become little broader which means you have broken the material down and you are getting nanoscale materials, you are getting smaller particle size materials using that to full width at half maximum you can figure out whether or not you have got the nanoscale material or you have got something larger, but that is the second part of it and you can also see that the relative heights of the 2 peaks is a ratio of the heights of the 2 peaks is largely unchanged.

Now, we can consider we have gone to the third time stamp and therefore, what you will see is something that looks like that. I am exaggerating here, but this is just to give us an idea of what you can expect. So, you can see here from a sharp peak it becomes broader and broader peak and in and the broader the peak it is the smaller the crystal sizes that you have accomplished the past particle size.

So, normally you will see anybody who is doing this kind of ball milling work to create nanomaterials, present a data that looks like this they will have series of X-ray scans overlaid one on top of the other and usually these are the things that they will be highlighting they will try to tell you what has happened with respect to the peak position has it shifted, not shifted and they would interpret that to say what is happening with respect to the purity of the material and then they will look at the full width at half maximum or the width of that peak and tell you something about the crystal size.

And there again they may do much more sophisticated analysis they will like I said typically ball milling means you are hammering the material again and again and again. So, there will be some strain in that material. So, they will try to accommodate for the strain they will there are no techniques which help them remove the strain from the data and then on that basis, they can tell you what is only related to the crystal size broadening and then give you that data.

So, using this they can make a plot of crystal size as a function of ball milling time. So, you have crystal size as a function of ball milling time and that they may use for some other application. So, they can tell you roughly how much time of ball milling you have to do, for you to get both the software material as well as the harder material both in the nanoscale and in some size range that is of interest to you. So, this is what we are trying to do and this is what typically ball mill data will look like.

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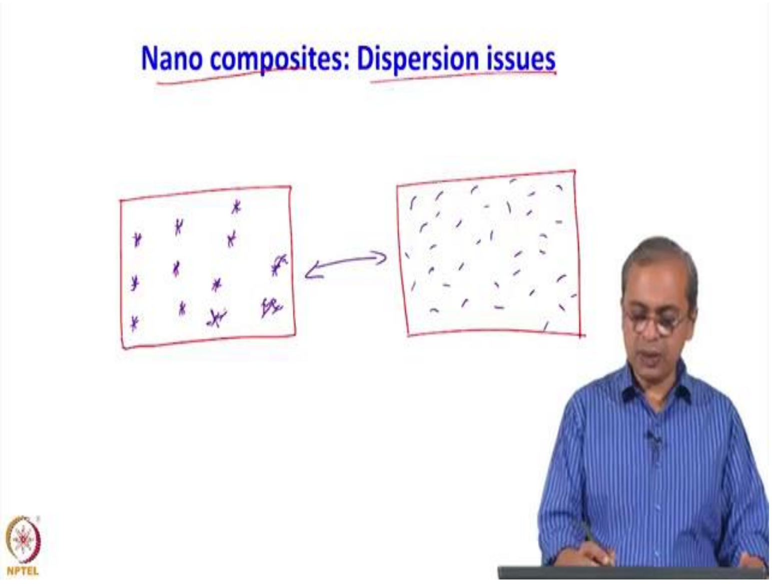

So, when you look at nanocomposites one major issue is that of dispersion. So, nanocomposite typically has one major issue that is a dispersion what do we mean by that? So, this is the matrix that we have and another matrix that I have here another sample of that matrix and I have fine particles that are present. So, in one case they are not that dispersed. So, I have them like this they are all like that.

So, there are small fibrous particles, for example, say carbon nanotubes or something like that and you may have like this. So, what this means is, you have put in say whatever 3-4% of this nanomaterial and rest of it is all matrix those 3-4% are not uniformly distributed across this matrix, we will compare that to a situation where you have it like this.

So, you can see clearly the dispersion is very different between these two cases the extent to which you have managed to disperse the nanoscale material in your matrix is dramatically different and this is always a challenge whenever you are making a composite material, where at is one of the phases is in the nanoscale. And even if both the phases are in the nanoscale either if you are doing it you may have a situation where one of the phases tends to agglomerate more than the others phase and therefore, you have to do something about dispersion. So, dispersion is a challenge that you typically have and so, one of the techniques that is always used is ultrasonication.

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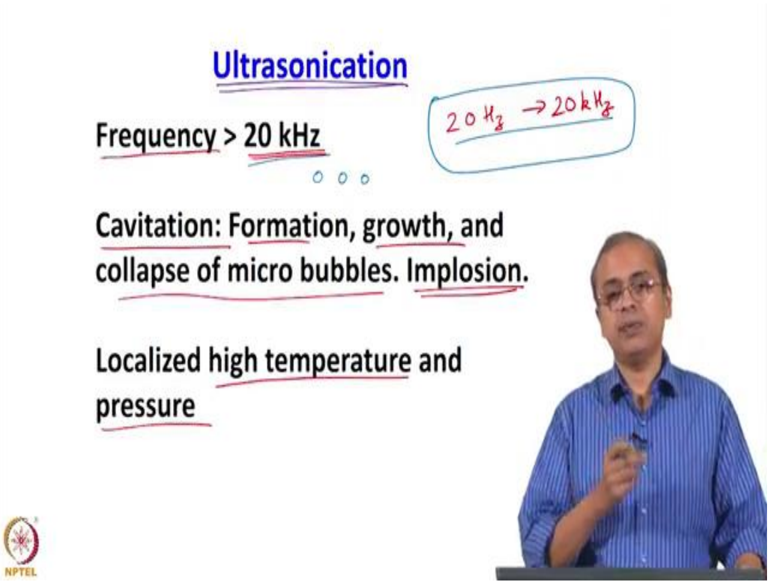

So, ultrasonication is a standard technique by which we disperse various substances in each other for example and the main idea there is to use this ultrasonic frequency. So, it is basically a sound wave with a frequency greater than 20 kiloHertz. So, our hearing I mean as capacity is usually between 20 Hertz and 20 kiloHertz this is the frequency range that human ear can hear.

So, in fact, if you look at if you want to buy a high quality audio speaker, then this is the range of frequencies over which that speaker would have been tested they would have actually done some tests and they will even give you plots. If you really if you are really serious about buying a speaker you can go and look up those kinds of data audio speaker if you are really interested in music and how it sounds etcetera this is the kind of information that many of the speaker manufacturers will provide about their speaker. This is only one of the things that you should look at when you are looking at the speaker, but this is an important aspect.

So, this is and usually, they will expect a flat performance across this entire frequency range, which is not colored by that speaker. But this is anyway the range that we use in our is the range that are ear can handle and can actually give us a signal that we are processing that we have heard something. If you go to frequencies higher than that is called ultrasonic frequencies and 20 kiloHertz is the threshold can go to much higher frequencies also.

So, what does ultrasound do? So, ultrasound is sending a set of pulses through that you have a liquid, you send it sends pulses through that liquid and essentially those pulses are compressive pulse and an expansion pulse compressive expansion, compressive expansion and that frequency with which it is sending is this 20 kiloHertz frequency.

So, now the material you have water, the water is being pulled apart and is being pushed together pulled apart push together that is what is going on in that water. Generally, when that happens small bubbles are formed. So, small bubbles get formed because of this especially in this expand expansion mode, it forms a bubble. Now those bubbles will during this repeated compression expansion they actually start growing; they grow for some small duration they grow and at some point they implode because basically, it is it has grown to some point and then this compressive force and make it implode it will just implode down at that point a lot of energy gets released.

So, locally this say this is called cavitation. So, this cavitation is this thing that this idea that it builds this bubble and then it just collapses. So, it is the formation growth and then collapses of a microbubble by in a process that is that as opposed to a no exploding outwards, this is falling inwards. So, that is implosion and this is how that happens this is microbubbles it is happening through that entire medium. So, especially a liquid once you put a liquid and this is what is happening that liquid.

So, this cavitation at that instant because of this collapse, very locally I mean you are looking at some extremely micro-regions very locally high temperatures and pressures are created. You are looking at few hundred bars of pressure and maybe even a few thousand degrees of centigrade of temperature. It is happening instantaneously I mean at that instant you can see it so in fact, if you do ultrasonication over a slightly prolonged period of time you can feel that sample becoming bomb. So, that is essentially what is going to happen.

In fact, more than that even more specifically you can actually do certain things with ultrasonication which is for example, because of this energy that is being released you can even do welding with it; there are ultrasonication waste welding processes which essentially do this I mean very locally they are now focusing that energy and enabling you to do the welding, but anyway this is what is happening. And so, when this implosion happens and the sudden release of energy happens, it puts pushes material around all the fine material that is around locally it gets pushed apart and so, this is a very effective technique in dispersing some nanomaterials.

So, nanomaterials because of their high surface energy may tend to agglomerate with respect to each other, but by putting ultrasonic frequencies you may actually push them apart. But again, a lot of studies have shown that you have to do this in some good controlled manner or with some level of moderation. If you do it excessively because this energy is getting released and you have this high temperature very locally formed you may even actually end up doing welding locally you may end up doing welding and so, you may in fact, of instead of breaking the agglomeration you may actually propagate the agglomeration in some sense.

So, but generally, this is a good way of dispersing nanomaterials usually if you have a matrix and you have this nanomaterial in it you can do this and you can disperse it and that helps you. So, that is something that is useful.

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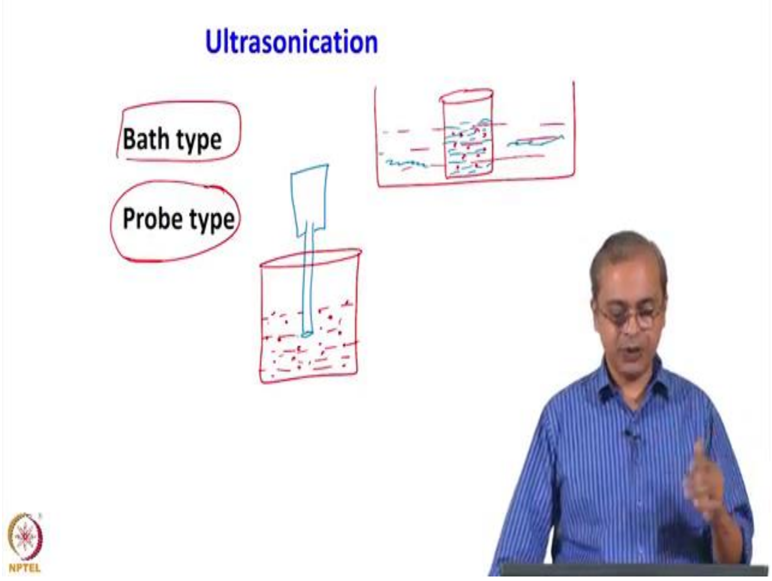

You actually also have this in 2 different varieties you have something called the bath type. So, in this you usually will have a big tub which we can filled with say water and then in this you can keep a beaker and in that beaker you can have your particles whatever it is that you are trying to disperse in some other liquid that maybe even the same liquid, but some other liquid also you can have inside the beaker and usually that will have even the matrix material if necessary, that depends on what you are trying to do and with this vibration going through it you will have this dispersion of those particles happening.

So, this is the bath type you also have probe type which means it is just like it is like a rod, the tip of it which has that vibration being released and therefore, in this you can actually have you can dip this in that beaker and whatever liquid you have here. So, if those are your particles and you have some liquid in which you are keeping it. So, the particles will get dispersed in that liquid.

Now, the main difference is the amount of in a concentration of energy that is happening here, in the probe type ultrasonic gating process you are able to concentrate the energy much further and so, this is what helps us accomplish this no dispersion. So, that is the way we would have to handle dispersion and these are some techniques that help us do it.

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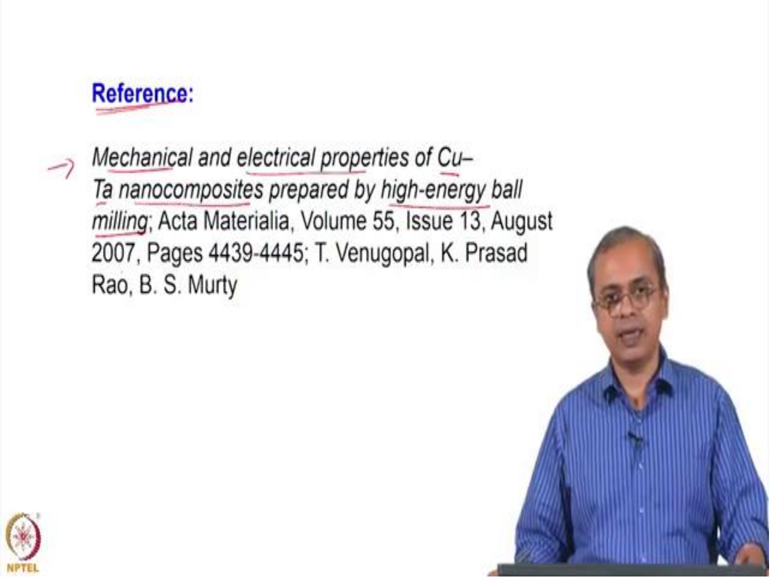

So, I close this class by showing you a reference or directing you to a reference where, we have seen in this class something about nanocomposites how they come about and the fact that you have to there is a technique such as ball milling through which you can make it what are the challenges associated with it what are some ways to handle those challenges such as dispersion and so on.

So, all that we saw through this class, what I would like to draw your attention to is this reference which is actually looking at mechanical and electrical properties of copper tantalum nanocomposites prepared by high energy ball milling. So, they look at they are actually looking at some for example, materials for electrical switches and so, on where you want good conductivity as well as you want good hardness because the switch is going to keep being switched on and off and therefore, you do not want it to wear easily (Refer Time: 24:00).

And they have done a very systematic work in terms of bringing showing how they are improving one property while not losing the other property and nice ways of presenting the data etcetera are theirs. So, if when you get a chance to take a look at it is a paper which very nicely showcases how you create a nanocomposite and what benefits you can get from it.

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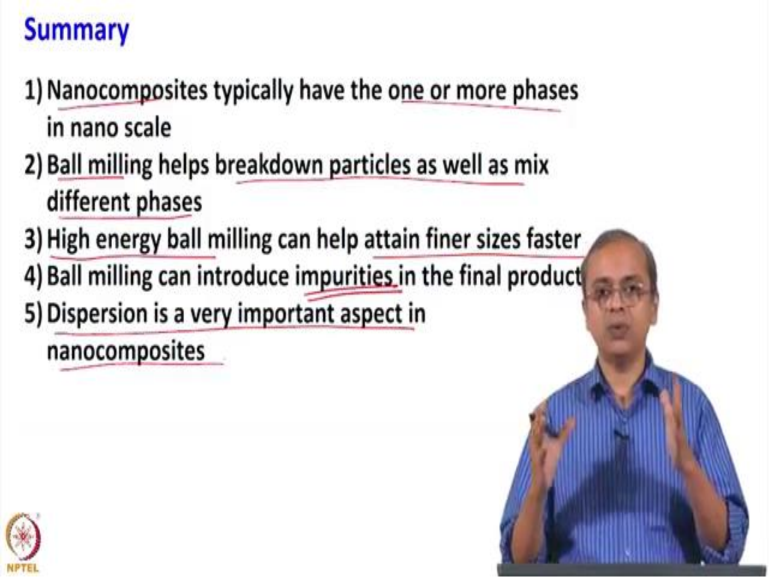

So, we will close with this summary nanocomposites typically have one or more phases in the nanoscale ball milling will help you break down the particles as well as mix different phases and that is how you can create the nanocomposite first of all with the ball mill. In this more than the regular balm in the high energy ball mill can help you attain much finer sizes faster because you are no longer limited by just the pull of gravity you are sort of creating much higher impact on those particles. However, the thing that you have to be cautious about is both with respect to ball milling and high energy ball milling is that you very likely you can introduce impurities in your final product.

So, when you are doing the X-ray diffraction that is another thing that you want to look for you want to make sure that, there are no new peaks appearing in that sample which would imply that you have introduced an impurity into that sample. So, that is something that you want to look at and then in any of these nanocomposite materials because you have 2 different phases there a dispersion is a very important aspect, you have to handle it, you have to do something about it and you should be ultrasonication is a way in which you do that. So, that is the summary of what we were we would like to discuss today and we will look at some other aspects in our next class.

Thank you.