Advanced Materials and Processes
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Lecture – 52
Advanced Processess (Contd.)

Welcome to NPTEL. Myself Dr. Jayanta Das, from Department of Metallurgical and Materials Engineering; IIT, Kharagpur. I will be teaching you Advanced Materials and Processes. Today, we will discuss some of these advanced processes and we specifically try to focus on one of the top down process that we have told the name as ball milling or mechanical alloying.

So, mechanical alloying in this particular case, the term itself says that it has something to do with the alloying of different elements.

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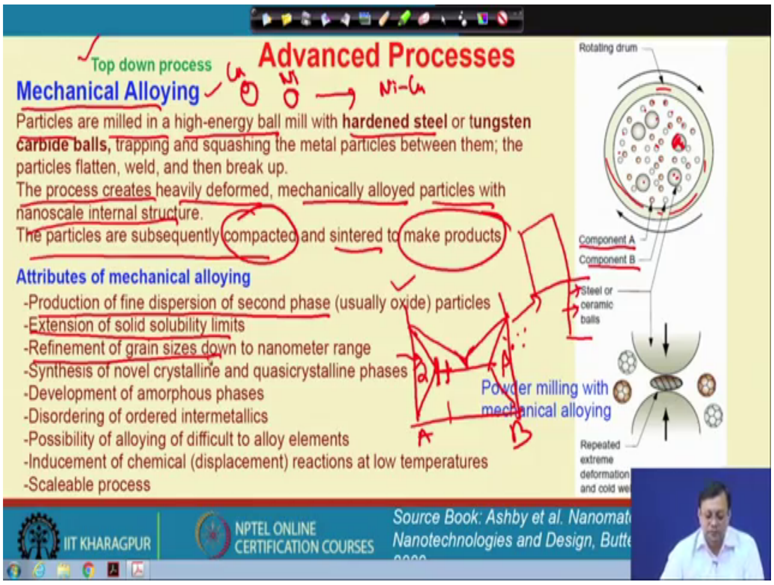

Means I can have copper, I can have nickel individual particles and by this mechanical alloying technique, we can make a alloy of nickel and copper.

However, using the same device means, inside a vial we put these 2 different composition of 2 different particle, we can also put a single composition larger size particle and we can make size reduction, in that case we call it as ball milling ok. So, here balls as a assists for those crushing or it impact on the particles and it basically, refine the size of those particles.

So, in a top down process using this mechanical alloying technique where the particles are milled using some high energy ball mill. So, the ball mill consists of a rotating disc, where some vials or a container is placed. And the initial powders with a larger size are placed in those vials. Here, we also take assistance of some hardened steel or tungsten carbide balls. So, here these are the balls and these are the initial powder particles ok. So, I can think about two different color of 2 different component as I said let us say nickel copper or let us say aluminum or copper or whatever as you preferred.

Now, this process itself has many different parameters to control however, the grinding medium here like the balls that could be made out of a steel or let us say, we can also use some ceramic balls ok. It depends on which material you are going to produce from the initial material ok.

So, let us go through this process, the process creates actually heavily deformed mechanically alloyed particles with nanoscale internal structures. And these particles are subsequently compacted and sintered in order to make the final product. So, ball milling or mechanical alloying produces very fine sized particles, which later on need a secondary process as compaction or consolidation in order to make a ball scale nano structure, by those technique I said like a pressure induced sintering and so on.

Now, a typical attribute of this mechanical alloying process is that, we can produced a very fine dispersion of this solid phase, let us say we can also go for some oxide particles and let us say the oxide particles, that are mixed with some alloyed particles ok. So, here this is like a physical mixing ok. So, oxide is embedded in a metallic alloys alloyed powders.

On the other hand, we can also get extension of the solid solubility. Means what I am talking about that if I take a simple binary phase diagram here this is alpha and this is beta So, in that case actually the extension maximum solid solubility of B in A is here up to here so, the extension of solid solubility can be done. So, I can produce the same alpha phase where, which is become more B reach than the A ok. So, then the conventional equilibrium process alpha so, that is a is possible, we will discuss the thermodynamics of heat later on; however, let us try to go through what are the other attribute of the.

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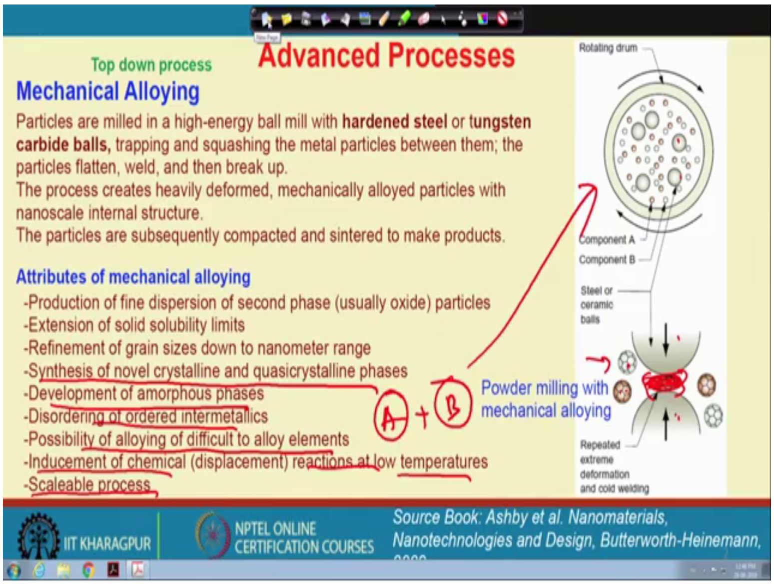

So, let us say we can definitely refine the grain sizes down to the nanometer range, on the other hand, we can synthesize Novel crystalline or quasi crystalline phases or we can also produce some amorphous phases ok. And disordered intermetallics by keep on putting high energy ordered metallic inter metallic, we can produce some disordered of ordered inter metallic or in some cases, where alloying is not possible in the liquid state I may have a component of A and B and that does not mix in the liquid state.

So, I can simply take A and B in the solid state and put it inside in a mechanical alloying device and then we can alloy those powders. And inducement of the chemical or displacement reactions at a low temperature, so means during milling itself some mechanochemical synthesis can be done. On the other hand it is a scalable process means, we can go for a industrial scale in order to make a very large scale.

So, here this is a typical schematic is shown here that if, we repeatedly heat let us say 2 different such kind of composition and then it is heated by 2 of these balls like such a ball very hard balls then, we deform the structures and these both of this particle can be welded together and there will be some diffusion and it will alloyed. It will be alloyed; because of surface atom keep on increases of the solubility limit also increases. So, we will go into detail of those things in the next slides.

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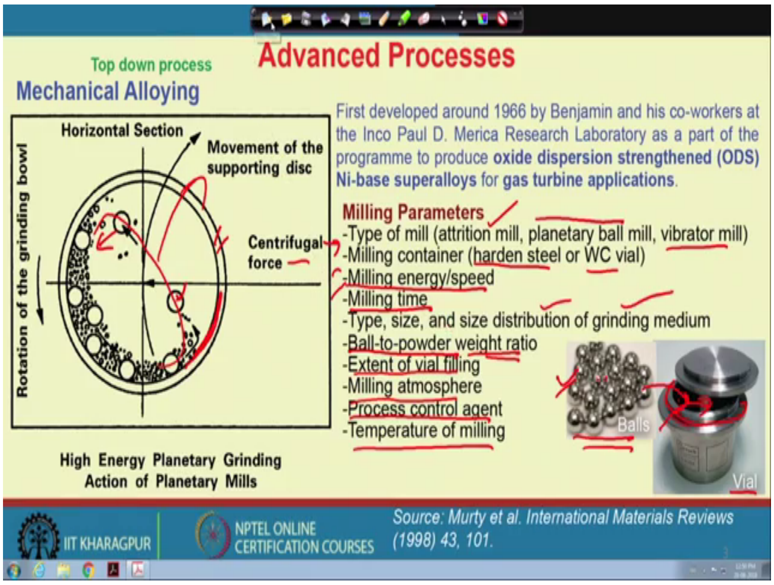

Now, these typical a mechanical alloying process it was discovered while processing of oxide dispersion strengthened nickel based super alloys for gas turbine application in 1966. So, this is not a very old technique, so in that case actually, people think about such kind of introduction of very high energy, using some planetary motion. So, here you see that this is a vial where, we place those powdered initial powders and the media some very hard spheres of steel stainless steel or hardened steel or tungsten carbide and they are basically rotate the vials rotate along this direction ok.

On the other hand in its axis on the other hand the whole vial on a bigger disc it rotate along this direction. So, this is like a simple planetary motion. So, we call it as a planetary ball mill ok. So, both the centrifuge force, that work along this direction and there is a movement of the supporting disc, so it basically goes into such a way and we can we can we can get these powder particle that crust by heating that medium during the rotation of the grinding bowel.

So, in that particular milling process, we have many different parameters that can control and to optimize the process parameter. So, here it depends on what are the mill we choose. So, there may be a planetary type of motion, in a mill we call it as planetary ball mill or maybe it can be a vibrator type of mill or it could be a attrition type of mill, we will discuss what are those mills name means and how the process goes on.

However, these container means I am talking about the vial that could be made of hardened steel tungsten carbide or maybe some ceramic ok. However, one should prefer that the grinding medium as well as the vial should be made of the same material that will increase the efficiency also.

Now, this milling speed or energy can also be controlled and milling time can also be controlled. I will show you later on what is the effect of milling time and milling speed the energy input into the system depends on these parameters actually. So, the type size and size distribution of such grinding medium or balls is also important. So, this is a typical image of a vial ok. So, like a bowel inside we pour these balls and the powder particles.

Now, another important aspect that the ball, that is the grinding media and the powder that we want to mechanically alloy or simply size reduction want to make the weight ratio is also important. Now, the extent of vial filling, milling atmosphere this could be done in a inert atmosphere or some different temperatures. So, we can also make some cryogenic temperature milling that is called cryo milling. Now the there are some process controlling agent ok, if there is some sort of reaction goes on here and also the temperature these are some of the very important aspect of a mechanical alloying processes.

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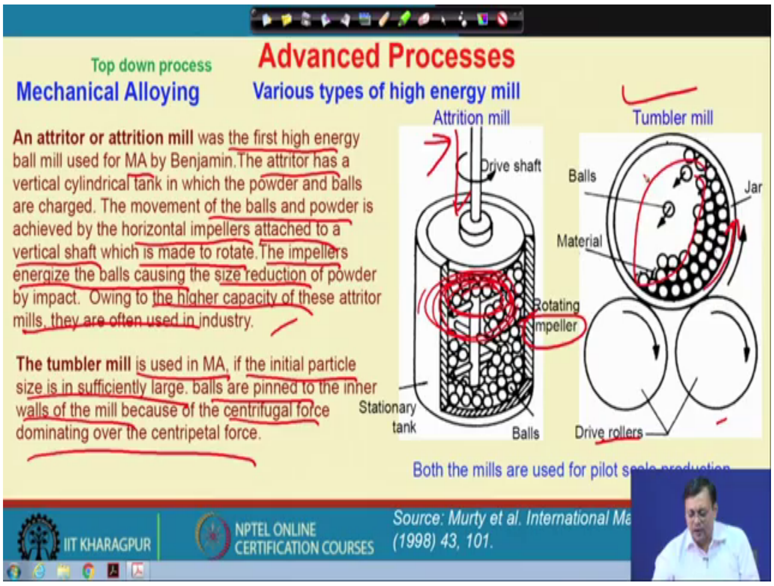

Now, the two other mill that I told about that is a attrition mill and a tumbler mill and these are typical different types of high energy mill that are adapted for some industry purpose and for pilot scale production process. So, here you see, these are some rotating pillar here that rotate a in a grinding medium that is the balls are present here and this is a stationary tank and this is rotated using a drive shaft and this is a typical attrition mill whereas, in case of a tumbler mill actually, the inside a jar we place those balls and those balls goes up and then it basically, falls down.

So, the rotation p speed should be chosen in such a way so that, all the balls should not be centrifuged. So, the balls will go up and then it should fall and make impact on the bottom balls including those powder particle, that has to be mechanically alloyed or the size to be reduced, that is very much important. So, the speed, it means that we cannot choose any speed if the speed is too less then, the ball will go maximum up to such a height and then it will again fall here if it the speed is too high the hole all the balls will be centrifuge.

So, a optimum speed has to be chosen, so that the ball can go up to the higher distance or higher height and then it will fall so that, it will cause impact. And these are some of the very important parameters or let us say the milling parameters that should be chosen.

So, these are simple drive role which basically, assist the jar to move. And an attritor mill actually was a the very first in this case, it was one of the very high energy ball mill, that is used for this mechanical alloying purpose. And the attritor has a vertical cylindrical tank and which the powder and balls are charged. And the movement of these balls and powder is achieved by horizontal impellers so these are the impellers here and which is attached to a vertical shaft and which is made to rotate. And these impellers energizes the ball to cause is size reduction of the powders.

So, in this basically, assists the ball not to segregate, but the ball has to rotate along this way so that, they cause impact with each other and when the powder particle comes in between 2 balls then, the particle will be alloyed or let us say the size will be reduced, so, both will causes So, higher capacity of this a attritor mill are often used for the industry in case of a tumbler mill this is also used for mechanical alloying purpose and if the initial particle size is sufficiently large the balls are pinned in the inner wall and the mill because of the centrifugal force dominating over the centripetal force actually. So, so this is a typical schematic of such a tumbler mill.

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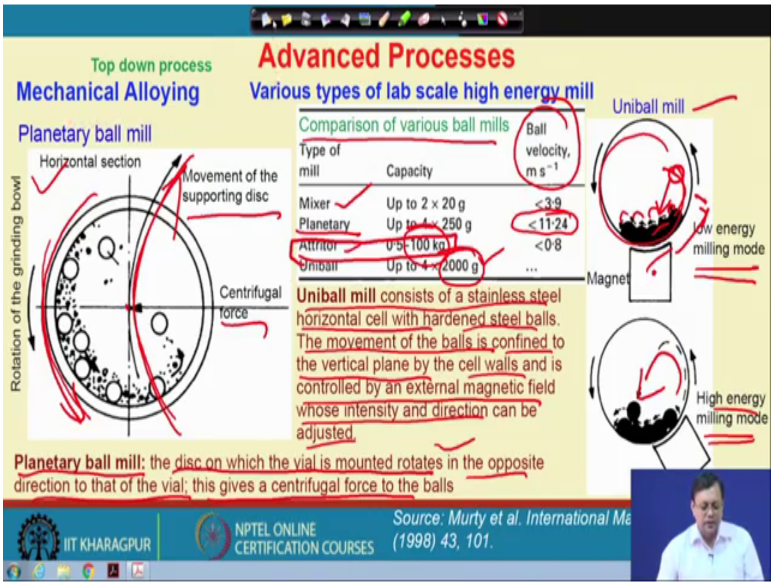

Now, initially I have shown you one of the image of a planetary ball mill where, we causes a planetary motion of the vials, so like the vial rotate in its own axis in the direction and then in the opposite direction in a clockwise direction it rotate on a bigger wheel base. So, we get basically effect or both the motion. So, the initiate the vial itself rotate in the counterclockwise direction and in the clockwise direction on its base.

So, the movement of the supporting disc is also important in this case and the centrifugal force is also very much important. Now if you compare between these various types of mill the comparison basically says that the ball velocity that could be very high in case of a planetary mill. So, you see this is like a velocity where a simple mixer mill or attritor mill cannot go up to such a case.

However, for a smaller scale we can take assistance of this uniball mill what is this a causes sometimes giving higher energy to the system make the make the complex processes very odds. So, in that case if very low energy input when it is required then, uniball mill here it simply rotate and the ball actually goes to the next process and very very small amount of energy can be given. However, we can place a magnet and move this magnet to upward sidem, in order to control that the ball will go up to certain height and then it will fall ok.

So, this is for let us say a higher energy milling mode. So, we can choose the mode by using some sort of magnetic action or with the interaction between the balls and the magnet. So, uniball mill actually consists of stainless steel horizontal cell, with a hardened steel balls and this movement of these balls are confined in a vertical plane of the cell wall and it is controlled by a external magnetic field whose intensity and direction can be adjusted.

So, this is a very so slow process and also the energy input is a relatively high; however, we can go for let us say a higher amount of the mass. The attritor mill is used for let us say the industry purpose where, we can reach up to 100 kilogram So, compare to a planetary motion we can scale up the process in a industry scale So, all these processes can produces very fine nanoscale structure or amorphous structures and so on or let us say very bulk scale which can be consolidated to make a fine product.

On the other hand, that disc on which the vial is mounted it be rotated in the opposite direction and so that, the vial it gives a centrifugal force to this case of a planetary ball mill. So, we have a compared with a various types of mechanical alloying devices and all of them have their own benefit advantage depending on the ball velocity the process parameter you choose in order to alter the energy input into the system.

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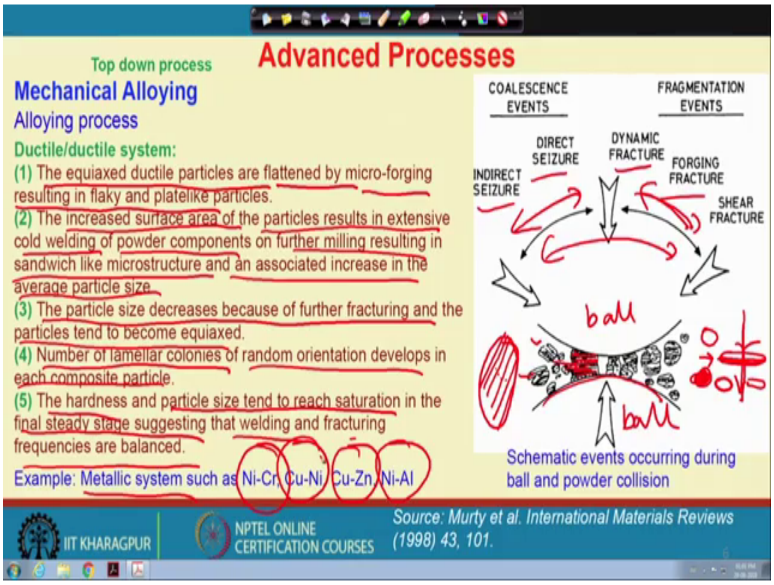

Now, if we look at the mechanism of the process that controls this mechanical alloying we must consider some of these systems. So, let us consider that I have a ductile, ductile system, here I am not at all talking about the milling media as ductile, I am talking about the powder particle are ductile. So, I have a 2 particle of 2 different chemistry which are let us say ductile in nature. So, what could be the sequence of operation that goes on?

So, in that case, the equiaxed ductile particle are flattened by some micro forging process resulting, a flaky plate like particle. What I want to mean, I have 2 ductile particle that goes on these are the balls ok. So, this is just a curvature of that ball is shown here and they goes between the balls and when the ball causes impaction then they are getting welded actually ok.

And, this causes some flaky shape of particles; now we increase the surface area of the particle, so initially I have some spherical particle after welding of this two particle, let us say I have one particle which is like here. So, this is the one particle and it is welded together because, it is a ductile, ductile system and because of the surface area has increased during the impaction with the ball, it causes extensive cold welding with the powder components and further milling resulting sandwiched like micro structure which is a associated increase in the average particle size. So, if basically, keep on welding things then the particle size actually increases.

Now, the particle size decreases because further fracturing of the particle, that tend to become more equiaxed. Now upon again further mechanical alloying or ball milling operation this particle will get fragmented ok. So, we again fragment this particle together, so this so this process is like a like a dynamic fracture or some sort of forging fracture type of process.

Now, the number of the lamellar colonies of random orientation develop inside each of this composite particle. So, if there is a 2 different component I may get such kind of lamellar structure inside a particle, where I have two different chemistry of this particle actually or composition of this particle. And the hardness and the particle size came to reach to a saturation at the final stage suggesting that these welding and fracturing frequencies need to be balanced. So, since the particle a ductile system, so there is a competition between the fracturing of the particles and the welding of this particle. So, these two process when it optimizes then we can achieve a optimized condition or the frequencies of a particular particle size.

So, this is one of the very important aspect. So, starting from a indirect seizure or let us say the welding we have a fracture process and both these welding process and fracturing process has to be optimized in some case. So, typical example for such kind of ductile system I can choose nickel chromium, I can choose copper nickel, I can choose copper zinc or let ius say nickel aluminum system ok.

So, here we will go for such kind of ductile system mechanism.

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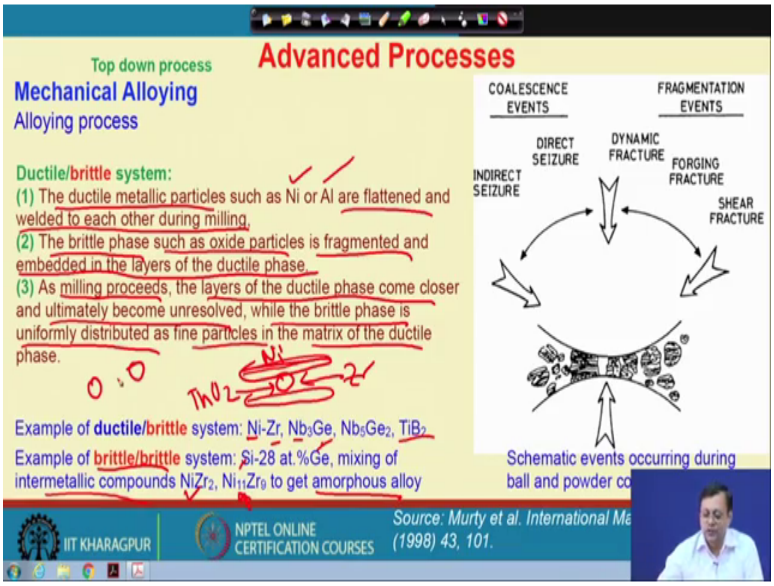

However, the system mechanism may altered when we consider a ductile brittle system means, one of the initial particle is very hard and another one is relatively soft.

In that case actually, the ductile particle like nickel or aluminum which is a FCC structure and very ductile they are flattened and welded to each other during milling whereas, the brittle phase like zirconium such as like it can be a oxide particle they are fragmented and embedded in the layers of the ductile phase.

So, let us say I have a flattened nickel and inside here I have a zirconium particle. So, this is a nickel, and let us say this is a zirconium or maybe it could be a oxide phase like td nickel or like a thoria dispersed. So, this is like a thoria or an inside a nickel phase So, they basically sandwich between 2 nickel layers.

And as the milling proceeds, the layer of the ductile phase become closer and ultimately become undissolved, while the brittle phase is uniformly distributed in the fine particle of the matrix of this ductile phase. So, example of such kind of ductile brittle system like nickel zirconium or a niobium germanium and titanium titanium diboride system. However, we may also have a brittle brittle system means, both of them are very brittle ok. So, here we can think about silicon and germanium. So, we can mix this 2 inter metallic compound like nickel germanium intermetallic and Ni 11 zirconium 9 in order to produce a amorphous alloy.

So, we can start with two different brittle phase and then we allow them to join together both in terms of alloying as well as the size reduction. So, both process can be chosen and definitely the mechanism of such processes are also a little bit different.

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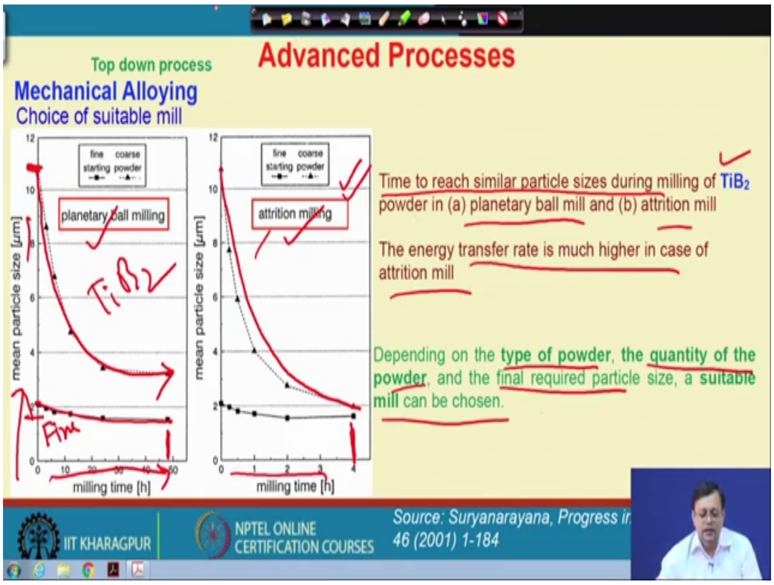

Now, as I said the choice of a mill is also important because, each and every mills and their parameter control the net energy input. However, choice of the mill is very much essential in order to achieve your final product. Let us say a particular mill where, I am talking about let u s say the planetary ball mill. So, where planetary motion is involved and the attritor mill where I can produce a very high amount of yield of powders ok, which can be possible in a industry scale.

Now, which also considered a very high energy input. Now in a planetary motion, here let us say, I may start with a very fine powder and the fine powder reduction cannot go to a very high fineness, it is almost less. Let us say, this is like a micrometer, I have started with 2 micrometer, now I can also start with 12 or 11 micrometer and keep on doing some milling here the x axis is the milling time and here is the mean particle diameter. So, the mean particle diameter keep on decreases, it reaches to something like three micrometer using a planetary mill, but taking the same powder and putting in a attritor mill the size reduction can be much finer.

So, it reaches to 2 micrometer particle size and so with increase of the milling time, only 4 hour of milling instead of 50 hour of milling using a attritor mill so we can reach to very final fineness. So, there is a benefit of each and every milling processs.

So, the time to reach is similar particle size during milling of let us say, titanium diboride powder in a planetary ball mill or attritor mill So, this was a titanium diboride powder that was chosen and the energy transfer is much higher in case of a attrition mill. So, depending on the type of the powder, quantity of the powder and the final required particle, size a suitable mill can be chosen. So, this is just a case I have shown you with an with an a suitable example.

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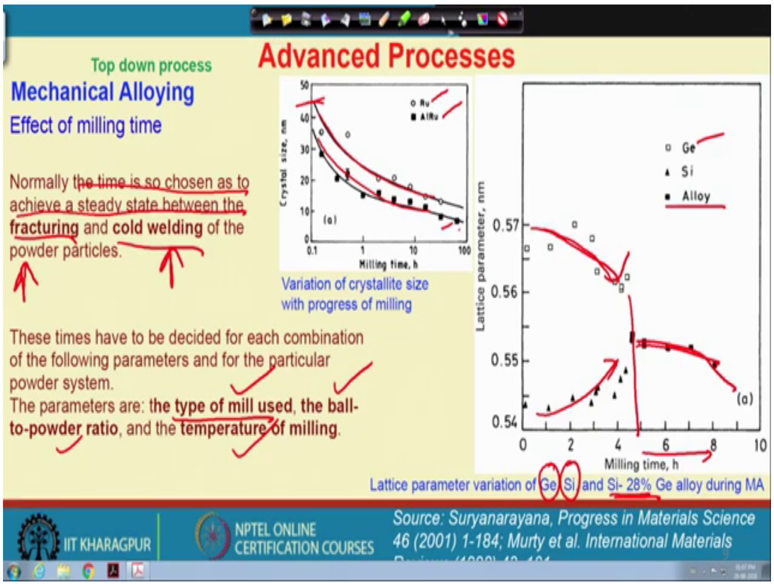

Now, the time is also very much important ok. So, how much time you will allow for a milling purpose. So, like a crystal size here I am talking about the in maybe the particle is self is one micrometer, but inside a particle there are many crystals ok. So, those crystals size can be easily measured using X ray diffraction and we call it not as a crystal, it is a crystallite size ok. So, means the individual domain, that contribute to the diffraction.

So, in that case that crystallite size can easily reach within let us say, 100 hour from a 50 nanometer to 10 nanometer. So, in 2 different chemistry it shows a two different trend let us say. So, normally the time is chosen so that, it achieve a steady state between the fracturing process and cold welding process. If we allow more and more time then maybe it may get cold weld and or maybe the fracture and it need to as sum optimize situation, so that this two process should be in a same frequency level.

So, on the other hand I can also take, let us say a germanium whose lattice parameter decreases this is the lattice parameter of germanium and silicon whereas, my intention is to make an alloy out of it and then after allowing has began let us say something like 5 hour and then the final lattice parameter is changing with time ok. So, as the alloys alloying is caused.

So, this is from a germanium silicon we are producing, let us say silicon germanium during mechanical alloying. So, the parameters here are the type of the mill that we use, the ball to powder ratio and the temperature of milling, this could be also varied. So, the ball to powder ratio will simply allow to get a higher impact.

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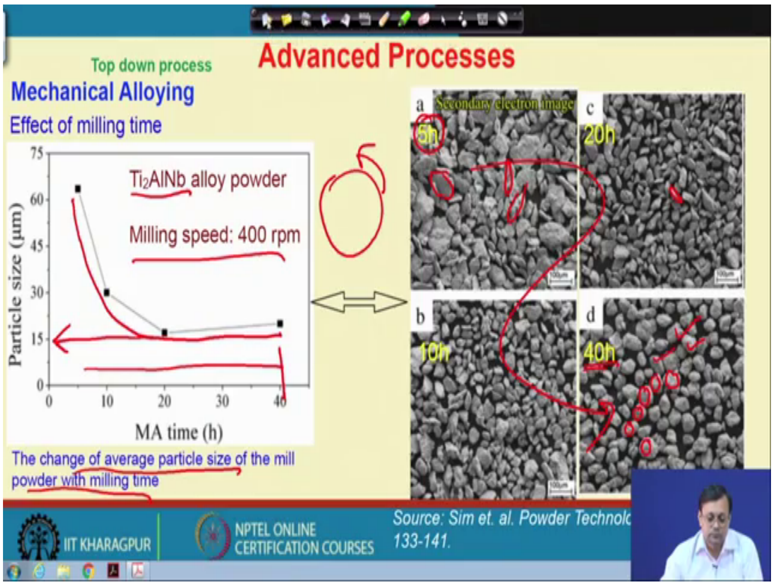

Now, the milling time, as I said is also important and the rotation speed that can also be controlled because, the whole centrifugal force can be controlled by the milling speed because, if I have such a mill and the speed it is rotating at a certain RPM So, you can see here, this is a titanium to aluminum niobium alloy powder ok.

And let us say for 5 hour you can see some flaky shape of particles right, some flaky shape of the particles. After 20 hour, the size has been reduced, but the aspect ratio has not changed too much. However, if you go up to 40 hour you can reach to a spherical shaped particles ok. So, this is one of the benefit, so particle size in that case does not reduce below 15 micrometer but the shape of the particle can be controlled with a suitable choice of the milling time. So, the change of the average particle size of the milling powder with the milling time is shown here where, if the shape is more preferred then we have to definitely go through all these different mechanisms that play a crucial role.

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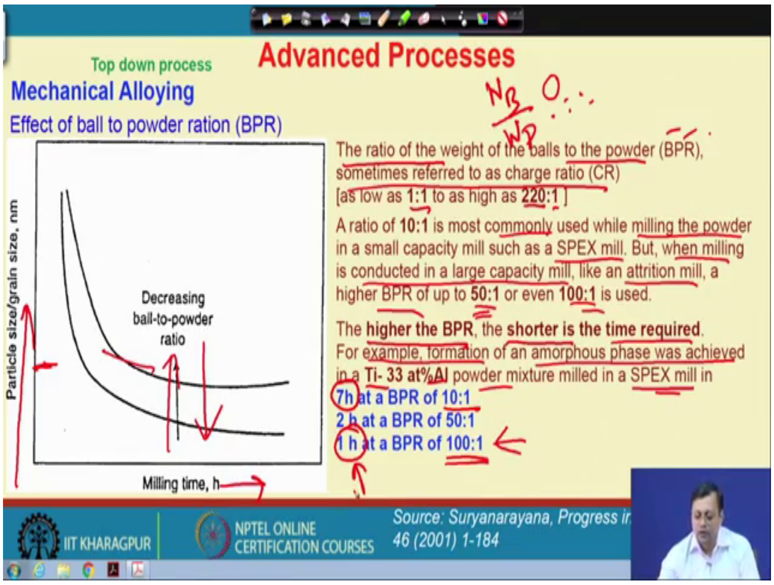

And now as I said the ball to powder ratio control the net energy input into the system. So, the ball to powder ratio hereby, is very much important So, I show you a plot here this is a milling time versus particle size or grain size in nanometer just a schematic. So, if you increase the ball to powder ratio, it is easier to go to a nano scale. However, if you decrease ball to powder ratio the size of the final particle size will be higher. So, the ratio of let us say, these ball and the powder particle, the ratio means this is a ratio of the weight, in terms of the weight of the ball by the weight of the particles or the powders.

So, this powder to ball ratio or a ball to powder ratio sometimes, referred as a change ratio or CR. So, it could be 1 is to 1 to a 220 to 1, this is a very high ball to powder ratio actually. Usually, 10 to 1 is a convention for using this kind of mechanical alloying purpose, that are commonly used for let us say any planetary ball mill or specs mill that is also a high energy ball mill. But when milling is conducted in a large capacity mill like attritor mill or let us say higher ball to powder ratio something like 50 to 1 or 100 to 1 is typically used in a larger scale.

So, that the probability of the impact with the particle and the powder particle as well as the milling medium that is the balls are increased. So, the higher the ball to powder ratio will basically shorten the time required for the whole mechanical alloying purpose because, we are putting more energy into the system. As an example, the amorphous phase can be achieved in a titanium aluminum system by a powder mixture in a specs mill let us say, it will take 7 hour if you use 10 is to 1. It will take 1 hour, if you use 100 is to 1. So, energy input is very high and you can achieve to the amorphous state within 1 hour of milling only So, this is one of the very common example of let us say choice of the proper milling parameter.

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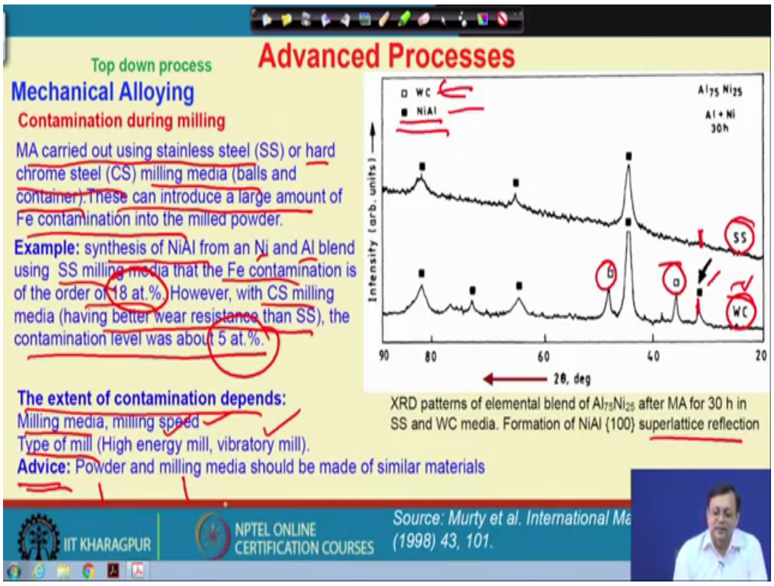

Now, besides all these processing parameter, one important aspect one has to keep in mind on processing these advanced materials using these non equilibrium processes like mechanical alloying that is basically, the contamination. You are milling or we are milling in a medium using a vial and the ball. So, the vial and the ball they may also add some contamination and change the purity level of the powders that you are going to produce.

So, in that case let us say, a choice of proper vial and the and the media is also important. What I want to mean let us say, a mechanical alloying that has been carried out using stainless steel or let us say hard chrome steel hardened steel and a milling media is the ball and the container, that can introduce a large amount of iron contamination in the powder.

Let us say I take a example or I want to produce nickel aluminum intermetallics or some solid solution phases and here if I use a stainless steel then I do not contaminate too much, but if I use a tungsten carbide vial and ball then I will introduce let us say, the some other contamination of the tungsten carbide peaks are coming here. So, this is tungsten carbide peak here.

Whereas, if I use a stainless steel then, I do not get the get these 1 0 0 reflection that is the superlattice reflection of nickel aluminide but in case of tungsten carbide I am getting this peak actually. So, I have reached to a process where, I can produce some ordered structure. So, optimization of the milling media time so they play a strong role. So, the synthesis of nickel aluminum we using nickel aluminum blend using a stainless steel media that causes some iron contamination in order let us say to of the range of 18 atomic percent; however, using a hardened steel or let us say the chrome steel milling media having a better wear resistance than the stainless steel.

So, the contamination level is 5 percent only. So, we can simply bring down the contamination level from 18 to 5 percent. So, the extent of the contamination depends on the milling media, milling speed, the type of mill whether it is a high energy mill, vibratory mill and so the advice here that the powder and milling media should be in the same material but this is impossible. Let us say if I want to mill a nickel aluminum, then I have to create a vial of nickel aluminum and that is not really possible, but at least we should choose the hardness level in such a scale or let us say if I want to produce some zirconium oxide then zirconium oxide vials are possible to make.

So, that kind of consideration has to be taken for using any of these non equilibrium processes or let us say the top down process such as mechanical alloying. With this we finish our discussion today, we will continue with different other non equilibrium and equilibrium advanced processes in the next class.

Thank you.