# Chemical Engineering Principle of CVD Processes
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**Module-5**
**Lecture 30**
## Basics of Nano Structured Materials Synthesis Part 2

Welcome to the 30th lecture in our particle characterization course. In the last lecture we started discussing and particles and in particular there are 3 aspects of Nano particle that we need to be concerned about, the synthesis dispersion and characterization of nano particles. So in the last lecture we started to get into some introductory material on what is nanotechnology? What are the various aspects of nanotechnology? Some applications of nanotechnology and then we started our discussion of synthesis methods of Nano particles and in particular the bottom up methods.

Essentially nano particles and this is methods can be classified as bottom-up and top-down. The bottom up approach is require that we take precursors that are essentially in atomic form and assemble them together to form a narrow dimensional material that is a definition of bottom-up, whereas in the case of top-down which start with materials that are of micron scale and fragment them down to Nano dimensions.

So in terms of bottom up nano particles synthesis methods we again sub classified them based on the nature of the precursors and we discussed several methods where the precursors in the form of solid which must be vaporized to generate the vapor which can then be crystallised to form solid particles. Now let me also started discussing applications where the precursors are in the form of liquid droplets or vapours.

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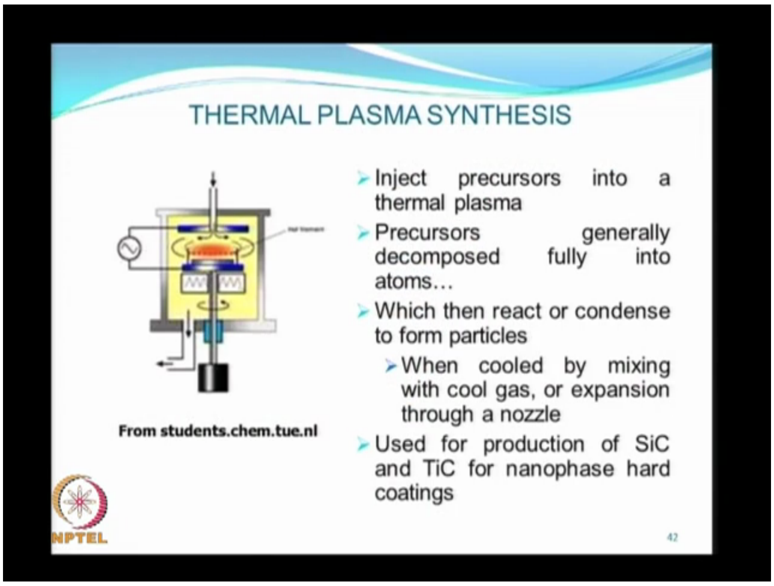

THERMAL PLASMA SYNTHESIS

From students.chem.tue.nl

- Inject precursors into a thermal plasma
- Precursors generally decomposed fully into atoms…
- Which then react or condense to form particles
  - When cooled by mixing with cool gas, or expansion through a nozzle
- Used for production of SiC and TiC for nanophase hard coatings

So we will continue that discussion in this class, there is a method called thermal plasma synthesis which basically requires that you take vapor precursors and introduce them into a thermal plasma and when you do that the plasma supplies additional energy to break down the precursors completely into atoms. So the precursors may be in the form of a high molecule weight molecules which using the plasma irradiation can be broken down into that constituent atoms which then can react or condensed to form particles and this can be accomplished by providing cooling the mixing with the cool Gas or simply expanding the vapor is through a nozzle. This method is used quite wisely for the production of silicon Carbide and titanium Carbide for nano is hard coatings.

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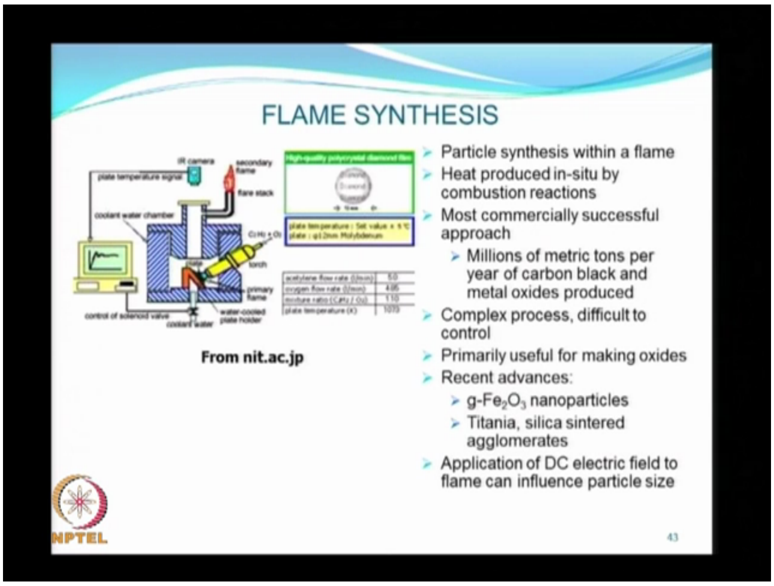

## FLAME SYNTHESIS

From nit.ac.jp

- Particle synthesis within a flame
- Heat produced in-situ by combustion reactions
- Most commercially successful approach
  - Millions of metric tons per year of carbon black and metal oxides produced
- Complex process, difficult to control
- Primarily useful for making oxides
- Recent advances:
  - g-$Fe_2O_3$ nanoparticles
  - Titania, silica sintered agglomerates
- Application of DC electric field to flame can influence particle size

Another technique is flame synthesis. Here the primary difference is that combustion reactions are used to generate the heat that is required. So particle synthesis here occurs literally within a flame. The flame is used to generate the energy or the heat that is required to drive the reaction to completion. It is a very successful commercial process in fact there are millions of tons per year of carbon black and metal oxides being produced using this method.

The drawback to this method is combustion is not an easy process to control so it is a complex process but widely used for making oxides and recently we have been able to make various types of oxide nano particles as well as sintered agglomerates. In terms of control it has been found that if you can apply DC field to the flame that can actually stabilise the combustion reaction and produce a more tightly controlled particle size distribution.

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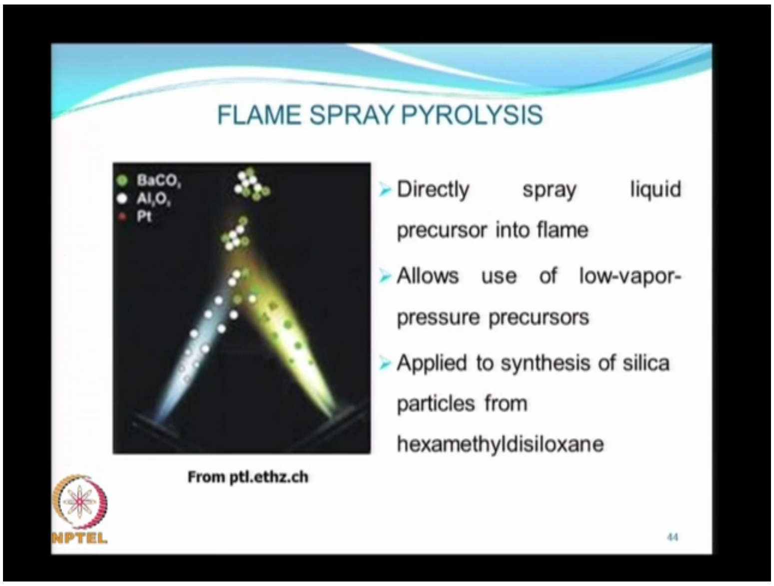

## FLAME SPRAY PYROLYSIS

- Directly spray liquid precursor into flame
- Allows use of low-vapor-pressure precursors
- Applied to synthesis of silica particles from hexamethyldisiloxane

From ptl.ethz.ch

Flame spray pyrolysis is a combination of 2 methods that we have discussed earlier flame pyrolysis and spray pyrolysis. Here the liquid is sprayed directly into the flame so the liquid precursors are injected into the flame. The advantage of this method is that you can use low vapor pressure precursor because the combustion process will supply sufficient heat to vaporise even low pressure precursor materials and this is applied to synthesis of silica particles.

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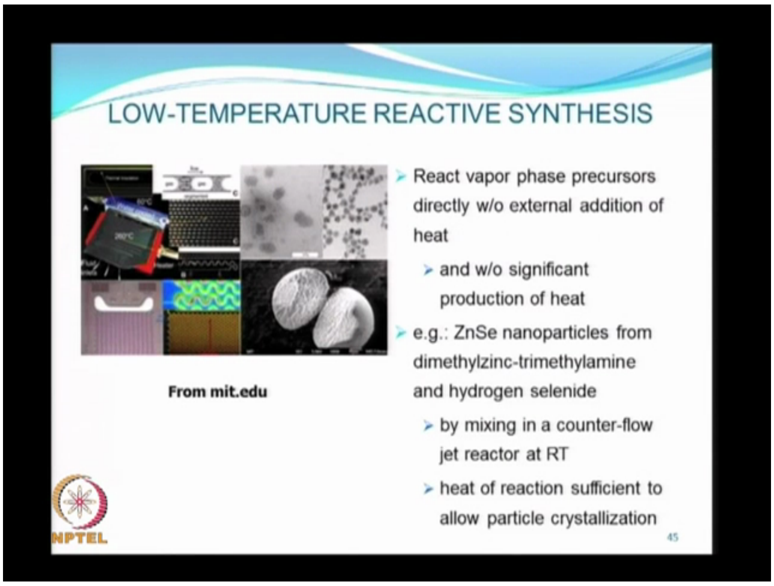

LOW-TEMPERATURE REACTIVE SYNTHESIS

From mit.edu

- React vapor phase precursors directly w/o external addition of heat
  - and w/o significant production of heat
- e.g.: ZnSe nanoparticles from dimethylzinc-trimethylamine and hydrogen selenide
  - by mixing in a counter-flow jet reactor at RT
  - heat of reaction sufficient to allow particle crystallization

Low-temperature reactive synthesis is the name given to Nano particle synthesis methods that do not employ high temperatures. Now in most of the methods that we have talked about earlier energy is being supplied in the form of heat and therefore there is some limitations to such methods if you are trying to make materials that are not compatible with high temperatures then you can actually wind up damaging or changing the composition of the material that you are Manufacturing.

Here we try to bring vapor phase precursors to react without adding heat and without producing heat. For example the sinc selenium nano particles can be made from by dimethylzinc- trimethylamine and hydrogen selenide using this technique; all we do here is provide intimate mixing. Essentially we use a counterflow jet reactor that is kept at room temperature but it provides very intimate mixing of the reactance.

The heat of reaction itself is sufficient to allow particles to crystallise. So it is a very energy efficient process because it can be run at room temperature without external additional heat and the fact that there is no heat generation also means that it can be essentially done in simple equipment designs where do not have to worry about heat generation and heat dissipation and so on.

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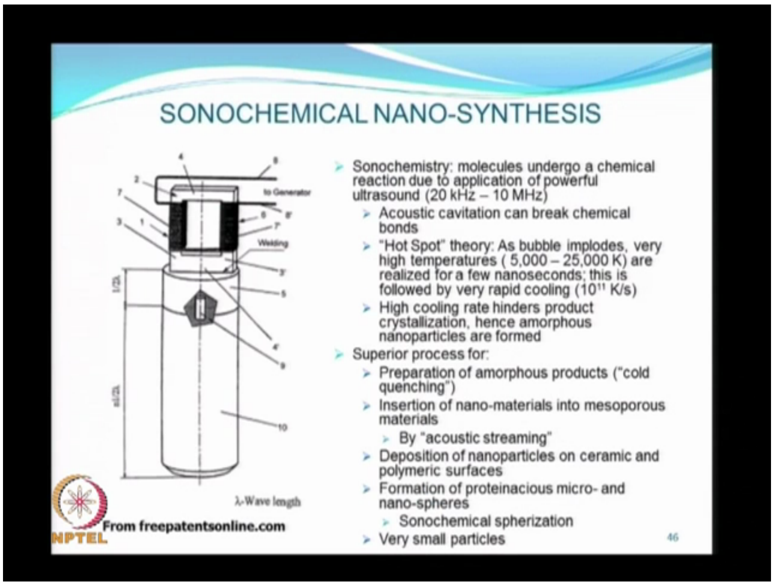

SONOCHEMICAL NANO-SYNTHESIS

- Sonochemistry: molecules undergo a chemical reaction due to application of powerful ultrasound (20 kHz – 10 MHz)
  - Acoustic cavitation can break chemical bonds
  - "Hot Spot" theory: As bubble implodes, very high temperatures ( 5,000 – 25,000 K) are realized for a few nanoseconds; this is followed by very rapid cooling ($10^{11}$ K/s)
  - High cooling rate hinders product crystallization, hence amorphous nanoparticles are formed
- Superior process for:
  - Preparation of amorphous products ("cold quenching")
  - Insertion of nano-materials into mesoporous materials
    - By "acoustic streaming"
  - Deposition of nanoparticles on ceramic and polymeric surfaces
  - Formation of proteinacious micro- and nano-spheres
    - Sonochemical spherization
  - Very small particles

From freepatentsonline.com

Another method that is being widely used in the bottom up side of Manufacturing and particles is Sonochemical nano synthesis. Ultrasound is an interesting technique in the sense that it can be used to synthesise nano particles both from the bottom-up approach as well as top-down approach. Later we will see how Ultrasound can be used to make nano particles in a top-down kind of application but when we apply an acoustic field to a liquid instantaneously extremely high temperatures and pressures can be realized within the liquid as cavitation happens.

So essentially when you apply an oscillating acoustic field you start forming bubbles in the liquid which collapse and as they do their release high amounts of energy and according to the hotspots theory as bubbles implode temperatures of the order of 5000 to 25,000 Kelvin can be realized for a few nanoseconds which is followed by very rapid cooling but during the time when these high temperatures chemical reactions can be driven by several orders of magnitude faster that they would proceed otherwise.

So this acoustic cavitation effect can break chemical bonds and can make chemical reactions run very very fast and therefore it can intensify the process by which nano particles are synthesised using chemical reactions. The high cooling rate can be advantages in some ways because by quenching the reaction which happens naturally in a cavitational field you prevent crystallisation of the product. So you can essentially make amorphous nano particles very easily by using the Sonochemical method. Therefore it is considered a superior process for preparation of amorphous nano particles because of this cold quenching mechanism.

Insertion of nano materials into mesoporous materials also becomes possible because as we have discussed in one of the earlier lectures on surface cleaning when you couple an acoustic field to a liquid 2 things happen cavitation which is the mechanism of bubble implosion and acoustic streaming which is the high velocity unidirectional flow that is induced with very high frequencies when the bubbles are very very fine but bubble density is very very high.

So the net effect of these bubbles forming and collapsing is that there is no cavitational force that is significant. However the phenomenon of bubble implosion at very very small size scales leads to this (()) (9:13) of acoustic streaming by which the fluid is directed at high velocities in one direction. So if you can harness this acoustic streaming process you can take the nano materials that you have fabricated and actually make them flow into porosities and materials.

So you can actually insert or incorporate nano materials into a porous matrix by taking advantage of acoustic streaming. You can do was it nano particles on ceramic surfaces and polymer surfaces and you can form essentially spherical nano particles. Sonochemical reactions are particularly suited to making spherical nano particles. We will see later that when you use sonofragmentation that also has the effect of making spherical nano particles.

So there are applications which require Sphericity in the nano materials and for that Sonochemistry is a good process to use. It also makes very small particles because of this rapid quenching effect. As the particle starts to form if you can quench the formation process that you do not provide time for the nano particles to grow to larger sizes. So Sonochemistry can be very effectively deployed to control the size.

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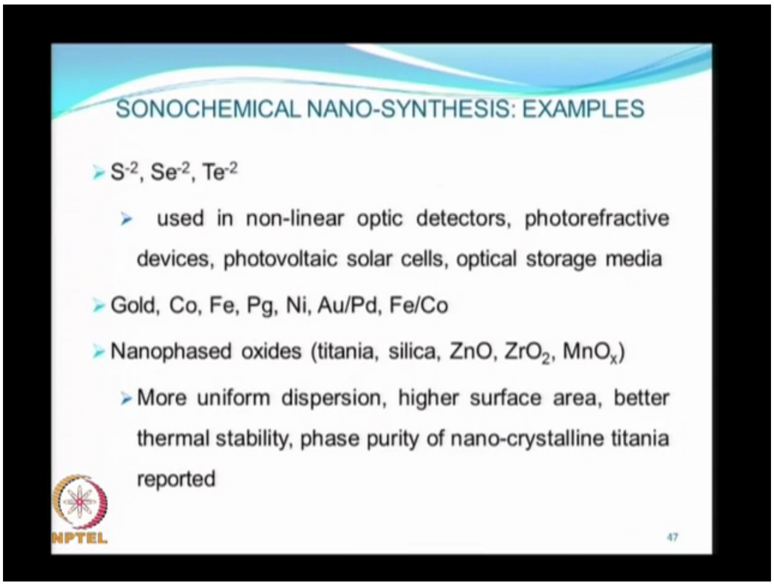

SONOCHEMICAL NANO-SYNTHESIS: EXAMPLES

- $S^{-2}$, $Se^{-2}$, $Te^{-2}$
  - used in non-linear optic detectors, photorefractive devices, photovoltaic solar cells, optical storage media
- Gold, Co, Fe, Pg, Ni, Au/Pd, Fe/Co
- Nanophased oxides (titania, silica, ZnO, $ZrO_2$, $MnO_x$)
  - More uniform dispersion, higher surface area, better thermal stability, phase purity of nano-crystalline titania reported

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Some examples of material that are synthesised using sonochemical methods are shown here.

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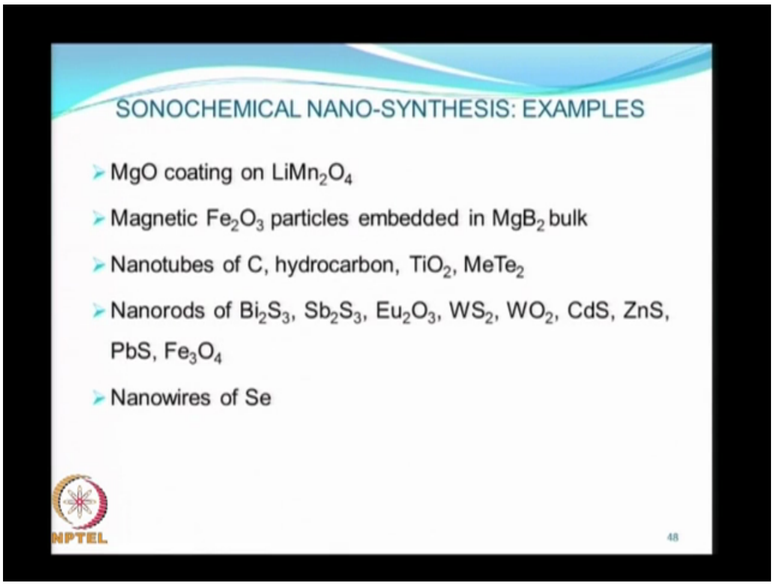

SONOCHEMICAL NANO-SYNTHESIS: EXAMPLES

- MgO coating on $LiMn_2O_4$
- Magnetic $Fe_2O_3$ particles embedded in $MgB_2$ bulk
- Nanotubes of C, hydrocarbon, $TiO_2$, $MeTe_2$
- Nanorods of $Bi_2S_3$, $Sb_2S_3$, $Eu_2O_3$, $WS_2$, $WO_2$, CdS, ZnS, PbS, $Fe_3O_4$
- Nanowires of Se

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And other materials are listed here, so there is a huge variety of a material and compounds that are commercially manufactured using sonochemical nano synthesis techniques.

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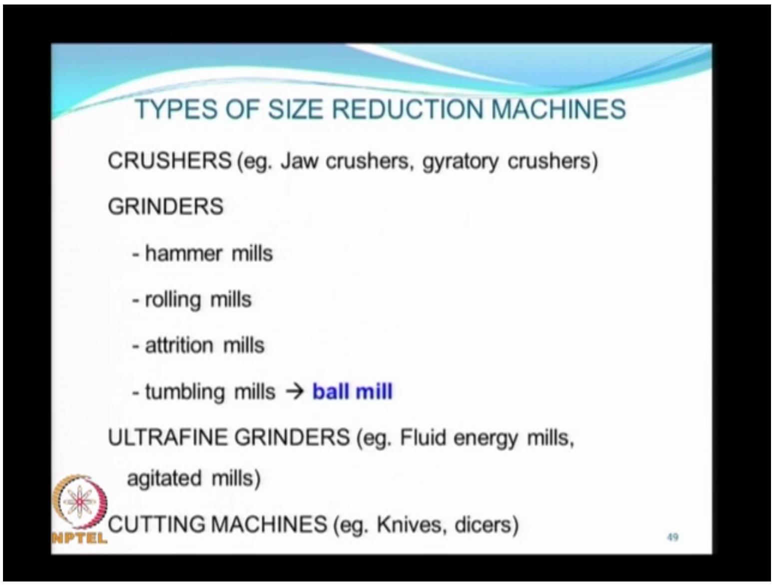

TYPES OF SIZE REDUCTION MACHINES

CRUSHERS (eg. Jaw crushers, gyratory crushers)

GRINDERS

- hammer mills
- rolling mills
- attrition mills
- tumbling mills → **ball mill**

ULTRAFINE GRINDERS (eg. Fluid energy mills, agitated mills)

CUTTING MACHINES (eg. Knives, dicers)

Now moving over to from bottom up to top-down methods of nano particles synthesis, size reduction is the primary mechanism by which we can make nano particles starting from large sized (()) (11:10) material pressures, grinders, ultrafine grinders, cutting machines you are familiar with all of these tools from your courses and labs, in industrial processing mechanical operations they can actually be used quite effectively to do size reduction.

However reaching nano dimensions is very difficult with many of these machines pressures, grinders are only good for reducing particle size from similar meters down to possibly tens or hundreds of microns. A ball mill as well as ultrafine grinders is effective in making particles down to roughly 10 microns but when you try to get the size below 10 microns to 1micorn or less that is a huge energy penalty. Some of these size reduction techniques do not work very well and that has somewhat limited that application to synthesis of nano particles.

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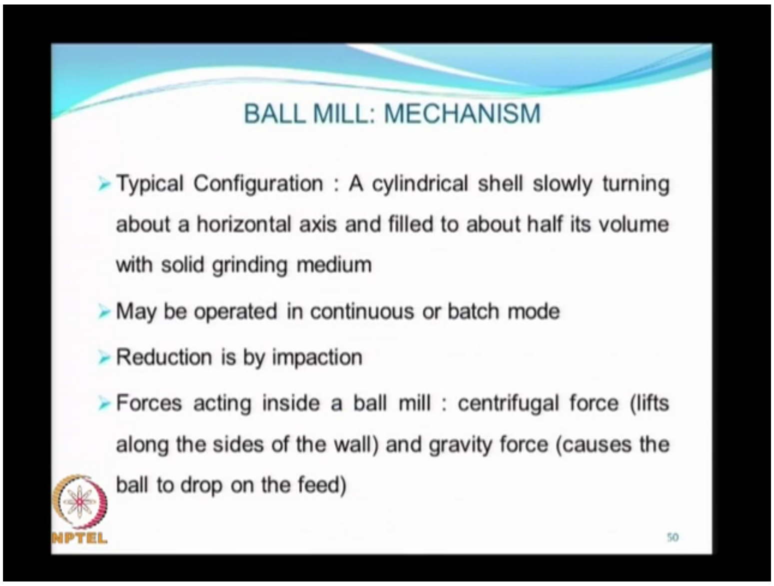

BALL MILL: MECHANISM

- Typical Configuration : A cylindrical shell slowly turning about a horizontal axis and filled to about half its volume with solid grinding medium
- May be operated in continuous or batch mode
- Reduction is by impaction
- Forces acting inside a ball mill : centrifugal force (lifts along the sides of the wall) and gravity force (causes the ball to drop on the feed)

A ball mill which I am sure everyone is familiar with is basically a cylindrical shell that slowly turns about horizontal axis is filled to about half the volume with solid grinding medium and essentially as it rotates the balls that are in the grinding chamber reach a maximum height and then the drop and as they do the impact on the material being size reduced and break it to a smaller size.

The advantage of the ball mill is that it can be operated in continuous mode or batch mode. Size selection happens by a simple impaction process. If you look at the forces acting inside a ball mill you have centrifugal force which is lifting particles along the sides and gravity force which then causes the ball to drop on the feed and crush it.

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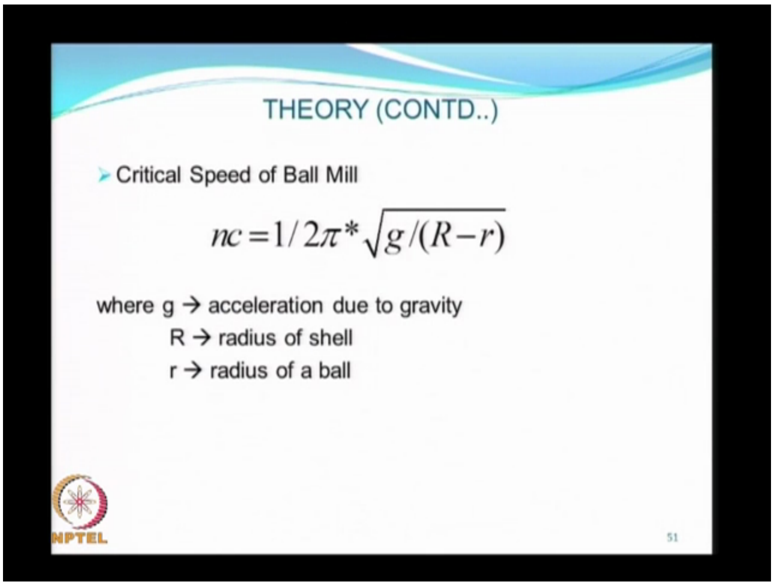

## THEORY (CONTD..)

- Critical Speed of Ball Mill

$$nc = 1/2\pi * \sqrt{g/(R-r)}$$

where g → acceleration due to gravity
R → radius of shell
r → radius of a ball

And you can establish a critical speed of the ball mill nc which is related to the acceleration due to gravity the radius of the shell and the radius of a ball. You want to keep the actual operating speed of the ball mill to know more than 75 to 80 percent of the critical speed otherwise essentially all the ball (()) (13:28) and adjust following the circumferential motion of the grinding chamber rather than dropping on the material to be crushed.

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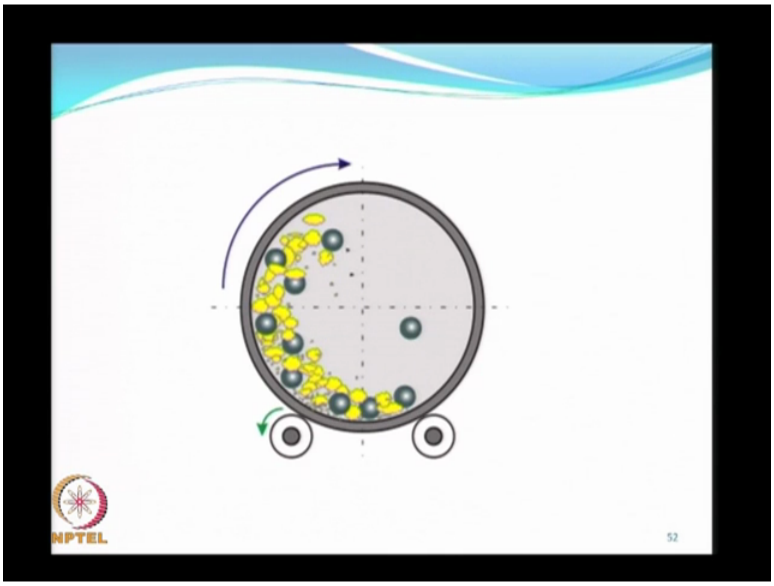

So this is a schematic of how the inside of the grinding chamber looks, the yellow popcorn like things are material that are being crushed and the spherical balls are the grinding media.

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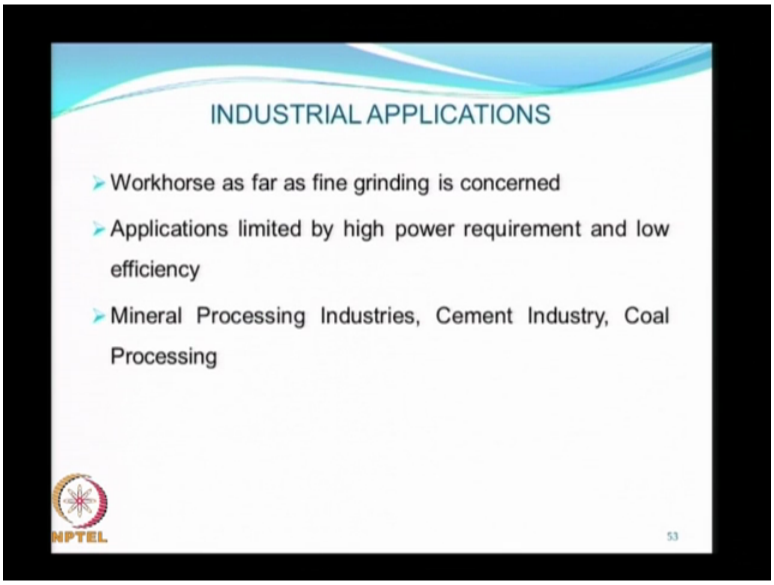

## INDUSTRIAL APPLICATIONS

- Workhorse as far as fine grinding is concerned
- Applications limited by high power requirement and low efficiency
- Mineral Processing Industries, Cement Industry, Coal Processing

The ball mill is the workhorse and industry as well as fine grinding is concerned. Applications are limited by high-power requirement and low efficiency I am sure you all recall the lab experiments you have done which demonstrate that as the effective particle size decreases you have to keep supplying more and more energy to produce new surface area, so it is essentially a self-limiting process. As the surface becomes finer becomes more and more difficult to reduce its size further. However it is widely used in many mineral processing industries cement industry, coal processing and so on.

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INDUSTRIAL BALL MILLS

Here are some examples of industrial ball mills, you can see the scale of the equipment these are you chamber that are used to make thousands of tons of materials on a weekly basis. So it is difficult to think of these machines in the context of nanotechnology where our production rates are much more modest and so many of these industrial ball mills really do not lend themselves to making nano particles.

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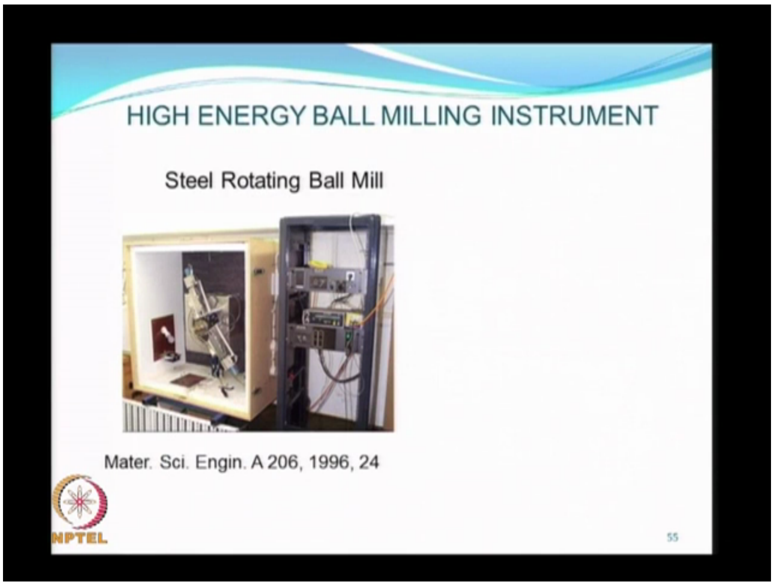

## HIGH ENERGY BALL MILLING INSTRUMENT

Steel Rotating Ball Mill

Mater. Sci. Engin. A 206, 1996, 24

However more recently there have been advances in ball milling technology in particular the high-energy ball mill which is an improvement over the conventional ball mill in the sense that it is a more controlled operating environment. Say can actually control the temperature inside the milling chamber, you can control the pressure, you can even control the chemistry of the ball milling chamber in order to produce the product that you need.

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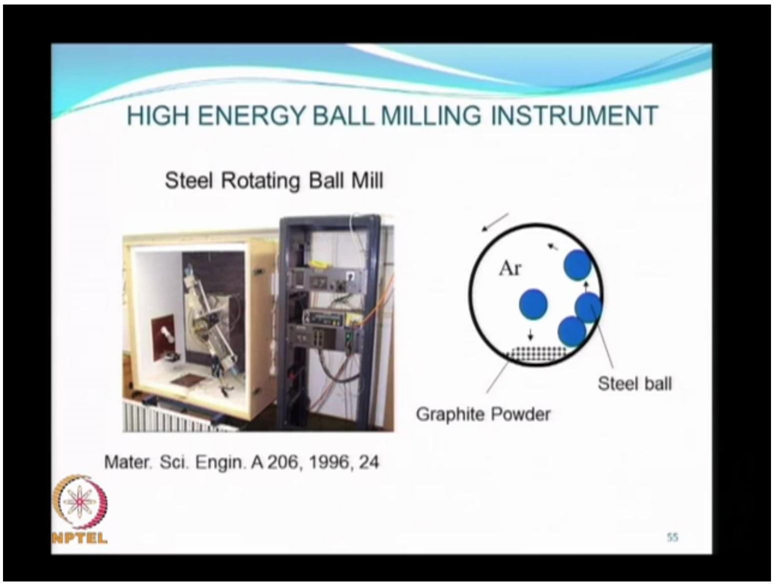

HIGH ENERGY BALL MILLING INSTRUMENT

Steel Rotating Ball Mill

Mater. Sci. Engin. A 206, 1996, 24

This is again a schematic of how a high-energy ball mill might look, essentially the mechanism remains the same you are still taking material to be size reduced putting it in a chamber and allowing the grinding media to impact on the material with some force which causes the size reduction to happen. However in this example you can see that the inside of the chamber is filled with argon and inert material to prevent oxidation.

So for example if you have aluminium or copper that you are trying to produce, if you do this in the ambient environment air itself is sufficient to cause aluminium and copper to oxidise. So if you want to make sure that you synthesise the metal nano particle without any oxide being taken up then you have to provide an inert environment.

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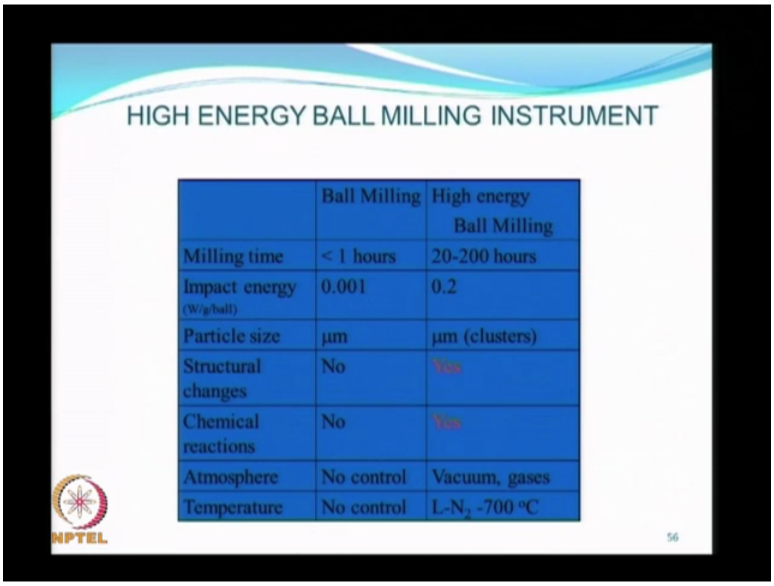

HIGH ENERGY BALL MILLING INSTRUMENT

| | Ball Milling | High energy Ball Milling |
|---|---|---|
| Milling time | < 1 hours | 20-200 hours |
| Impact energy (W/g/ball) | 0.001 | 0.2 |
| Particle size | µm | µm (clusters) |
| Structural changes | No | Yes |
| Chemical reactions | No | Yes |
| Atmosphere | No control | Vacuum, gases |
| Temperature | No control | L-$N_2$ -700 °C |

This table shows the differences between ball milling and high-energy ball milling. One of the key differences is in a high-energy ball mill you run-of-the-mill for much longer. Essentially the mean size will keep decreasing as you run-of-the-mill longer and longer, so while in our ball mill with the milling time of one hour or less you can achieve particles that are say 10 micron mean size.

In a high-energy ball mill just by running it much longer you can achieve much smaller sizes. Also the impact energy is designed to be much higher in a high-energy ball mill. The particle size that is produced, well actually if you take a look at it the output from the high-energy ball mill looks not very different from the output from a conventional ball mill that is because even though you may be size reducing to much smaller sizes because you are running the process for so long, agglomeration set in.

So the final product that you get from a high-energy ball mill is a kind of a powdery substance that has agglomeration clusters that are micron in size. Now it is possible to take these clusters and then disperse them, so that extra step is required after high-energy ball milling to take the material that you have produced and disperse it into the sub micron sized individual particles.

In a high-energy ball mill structural changes and chemical reactions can be induced. The atmosphere can be vacuumed or it can be gas filled in our high-energy ball mill and the temperature can be controlled all the way from subzero temperature that are achieved using cryogenic fluids to 700 degrees centigrade. So a very wide temperature range is possible in a high-energy ball mill.

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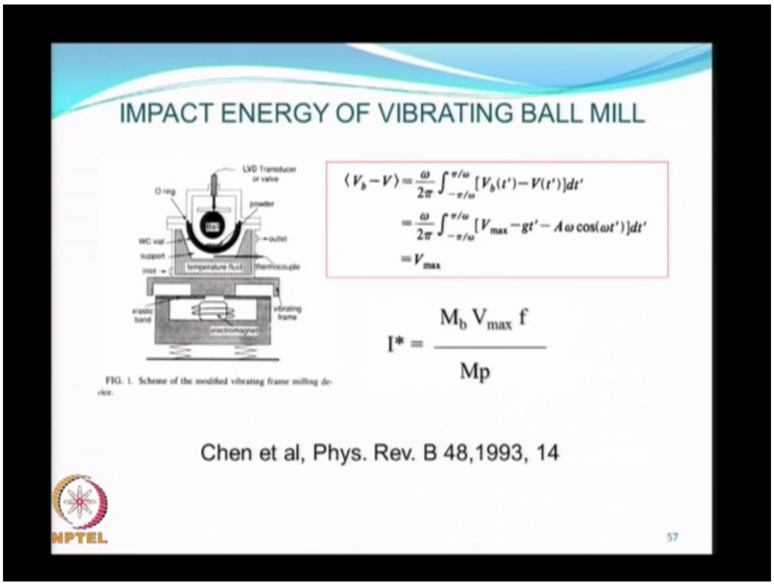

IMPACT ENERGY OF VIBRATING BALL MILL

FIG. 1. Scheme of the modified vibrating frame milling device.

$$\begin{aligned}\langle V_b - V\rangle &= \frac{\omega}{2\pi}\int_{-\pi/\omega}^{\pi/\omega}[V_b(t') - V(t')]dt'\\ &= \frac{\omega}{2\pi}\int_{-\pi/\omega}^{\pi/\omega}[V_{max} - gt' - A\omega\cos(\omega t')]dt'\\ &= V_{max}\end{aligned}$$

$$I^* = \frac{M_b\, V_{max}\, f}{Mp}$$

Chen et al, Phys. Rev. B 48,1993, 14

The impact energy of a vibrating ball mill can be calculated based on the operating conditions in particular the frequency of the vibrating ball mill. The vibrating ball mill is an alternative to the impact ball mill where the balls drop by the force of gravity and it is another method for making fine particles from course of feed. However vibrating ball mills are not widely used in industry comeback to the impact based ball mills that are more conventionally used.

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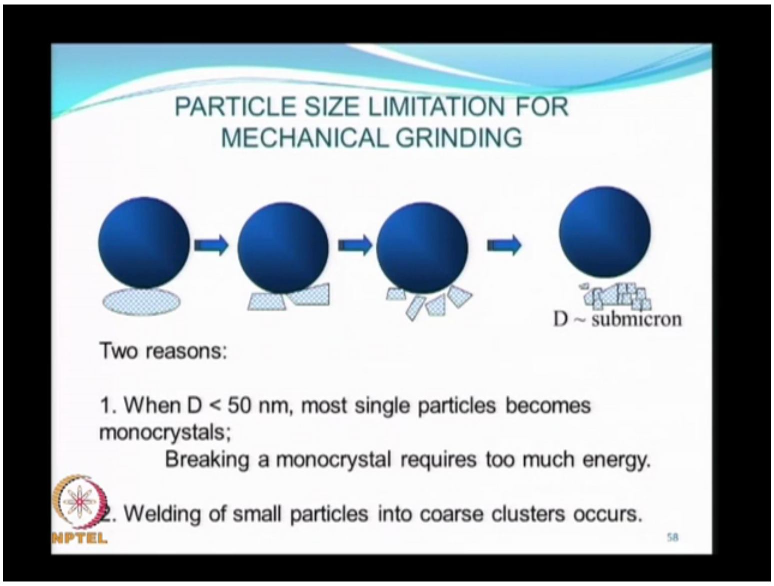

PARTICLE SIZE LIMITATION FOR MECHANICAL GRINDING

Two reasons:

1. When D < 50 nm, most single particles becomes monocrystals;
Breaking a monocrystal requires too much energy.

2. Welding of small particles into coarse clusters occurs.

Now why is there a size limit in mechanical grinding? There are really 2 reasons, one is that as the size decreases particles become monocrystalline in nature and as they do the energy requirement to break the particle keeps increasing, so essentially the particle itself becomes more and more unbreakable as it gets smaller.

In addition agglomeration begins to happen welding of small particles into clusters begins to happen and again the longer you run it the stronger are this inter particle cohesive forces and essentially sintering begins to happen after some period of time and these clusters that form over long period of operation can be very very difficult to break down into their component materials.

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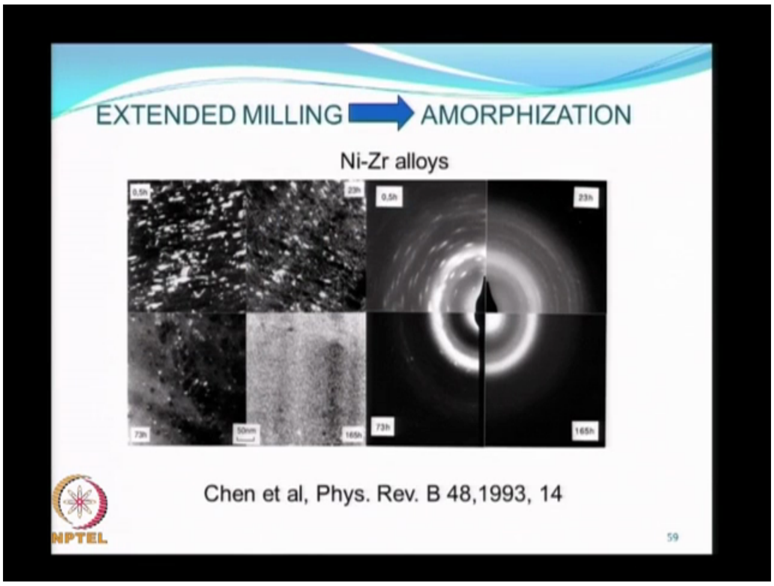

EXTENDED MILLING → AMORPHIZATION

Ni-Zr alloys

Chen et al, Phys. Rev. B 48,1993, 14

Extended milling also leads to Amorphization this is shown here in a series of graphs that are taken at various time intervals ranging from 23 hours to 73 hours to 165 hours and you can see that what started out as very crystalline material where the structure can be easily identified soon reaches an amorphous form where it is very difficult to really identify the shape of the individual particles.

Essentially you get an amorphous powder which you know if we were to test it using x-ray diffraction would basically tell you that it is a highly non-crystalline material. So one of the problems with the extended time high-energy ball milling to make nano particles is that it is very difficult to get crystalline materials using this process that is overtime and Amorphization that happens which is very difficult to avoid.

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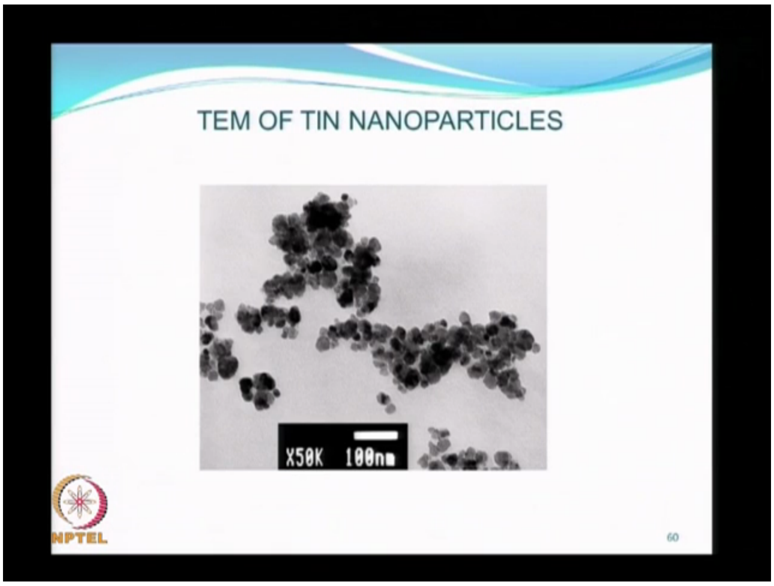

TEM OF TIN NANOPARTICLES

This TEM pictures of titanium nitride nano particles that are produced by high-energy ball milling and here you can see the clustering that is happening this is a good example of characterization of the nano particles using tunnelling electron microscopy. You can see that the resolution is fantastic you can actually see particles that are nanometres in size and you can actually result particles that are nearby which are about a nanometre apart.

The primary advantage of the TEM over scanning electron microscopy is its ability to sensitively detect as well as resolve particles that are in the nano size range and the clustering is very apparent in this picture.

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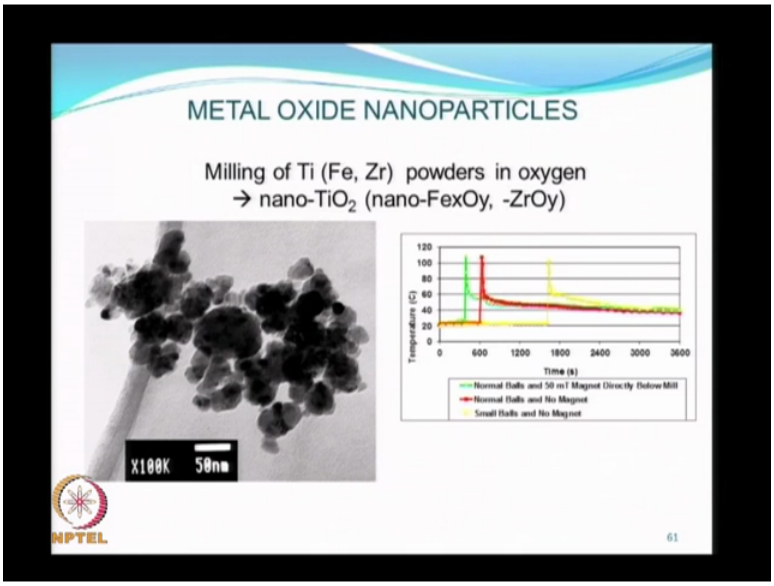

METAL OXIDE NANOPARTICLES

Milling of Ti (Fe, Zr) powders in oxygen
→ nano-$TiO_2$ (nano-FexOy, -ZrOy)

Now these are examples of metal oxide nano particles that are produced by milling of various powders titanium, iron, Zirconium in an oxygen environment. Again this is done in a high-energy ball mill where the interior of the mill can be made to be oxygen rich and what produces nano titania, nano-FexOy and nano ZrOy and here again when you look at the TEM picture at the bottom you can see the extent of clustering that is happening.

Clearly nano particles are being produced but by the time you take them out of the mill they have essentially clustered into agglomerate that is of the order of several hundred nanometres in dimension. So they have to be broken up somehow before you can employ them for further processing.

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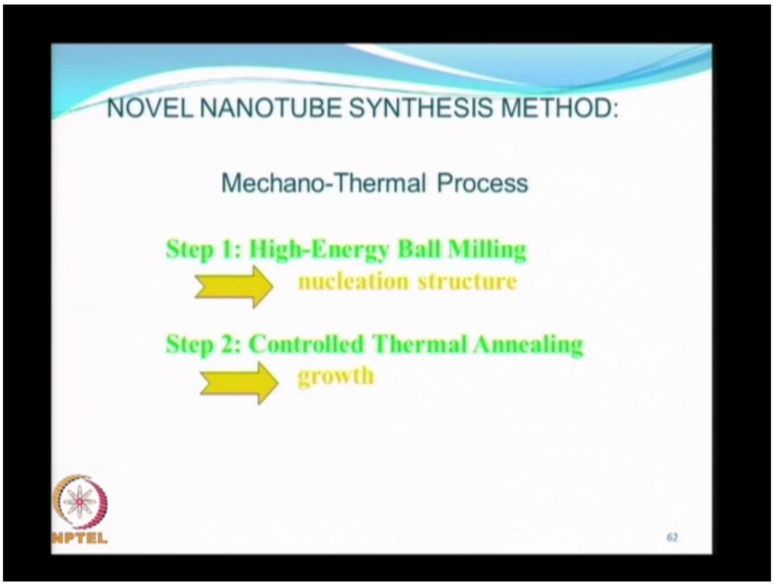

NOVEL NANOTUBE SYNTHESIS METHOD:

Mechano-Thermal Process

**Step 1: High-Energy Ball Milling**

nucleation structure

**Step 2: Controlled Thermal Annealing**

growth

So there is this process that is labelled as Mechano-thermal process which involves a two-stage procedure. In step one you use high-energy ball milling to produce a structure that is a nucleate structure, step 2 is to then produce a controlled thermal annealing process which leads to growth. Now thermal annealing is essentially taking a nano material that you have produced and exposing it to high temperatures in a controlled manner in order to obtain a certain structure and size that you are interested in.

Typically thermal annealing is done to get a more sintered a harder structure compared to the amorphous structure at a high-energy ball mill would normally produce. So if you want to take the output from a high-energy ball mill and give it more of a crystalline structure than thermal annealing is a process that is highly recommended.

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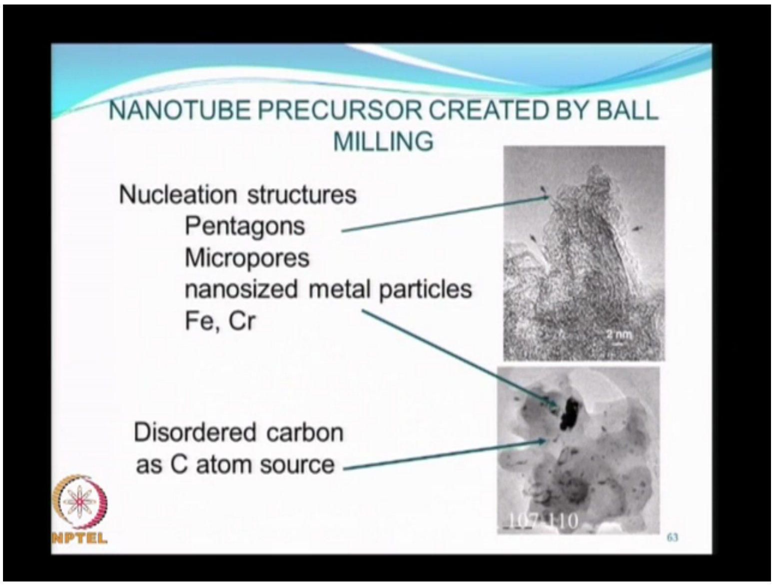

## NANOTUBE PRECURSOR CREATED BY BALL MILLING

Nucleation structures
- Pentagons
- Micropores
- nanosized metal particles Fe, Cr

Disordered carbon as C atom source

These are examples of nano tubes that are produced by ball milling. Here you can see that ball milling is been able to produce the precursors of nano tubes. So the nucleation structures are there went Pentagon, micropores as well as the nano sized metal particles and you can see that carbon is being incorporated as the source of carbon atoms.

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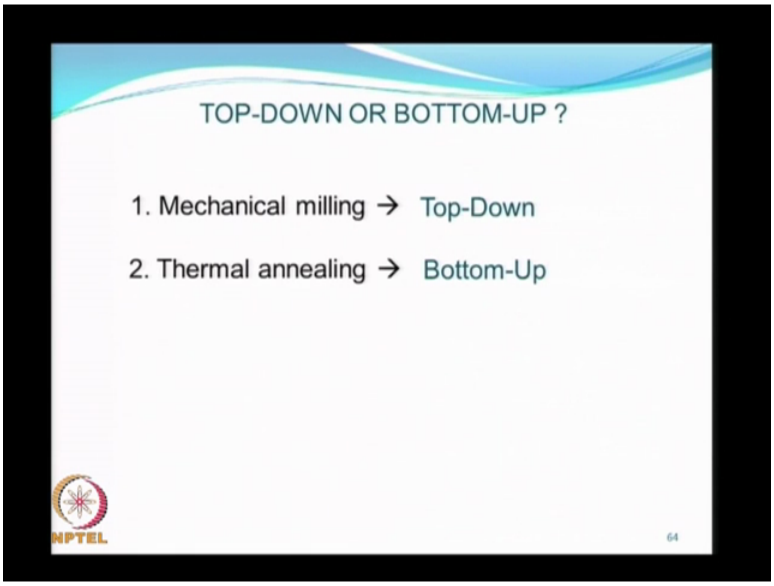

## TOP-DOWN OR BOTTOM-UP ?

1. Mechanical milling → Top-Down
2. Thermal annealing → Bottom-Up

Now when you look at this process that combines mechanical milling and thermal annealing it is actually difficult to decide whether you should label it as a top-down process or a bottom-up process because the mechanical milling itself is a top-down process obviously but thermal annealing is where you are essentially taking loose fragments that we have generated by the mechanical milling and bonding them together to produce a crystalline structure. So it is kind of combination of top-down and bottom-up methodologies just like the liquid gel technique was that we talked about earlier.

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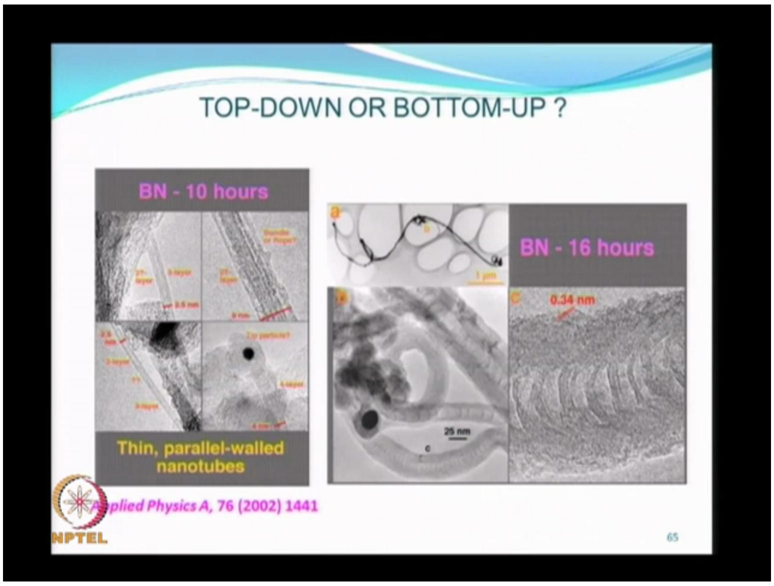

TOP-DOWN OR BOTTOM-UP ?

BN - 10 hours

Thin, parallel-walled nanotubes

BN - 16 hours

Applied Physics A, 76 (2002) 1441

So here is some output from this combined process boron nitride, nano tubes can be produced using this process and you can see structure of the nano material at results after 10 hours and after 16 hours.

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## THE FIRST COMMERCIAL SOURCE FOR BN NANOTUBES

http://www.anutech.com.au/TD
http://www.rsphysse.anu.edu.au/nanotube/
http://www.pa.msu.edu/cmp/csc/nanotube.html

**PRICE LIST**

| Quantity | Price US$/gram |
|---|---|
| 1g | US$400/g |
| 2g - 5g | US$350/g |
| 6g - 10g | US$300/g |

In fact a high-energy ball milling combined with thermal annealing was the first commercial process to be used for the production of boron nitride nano tubes and cost wise actually this is very competitive with bottom-up approaches. You can see some prices listed here for grams of material, in comparison if you are trying to make the same materials using a bottom-up process it would cost you at least 3 to 4 times as much.

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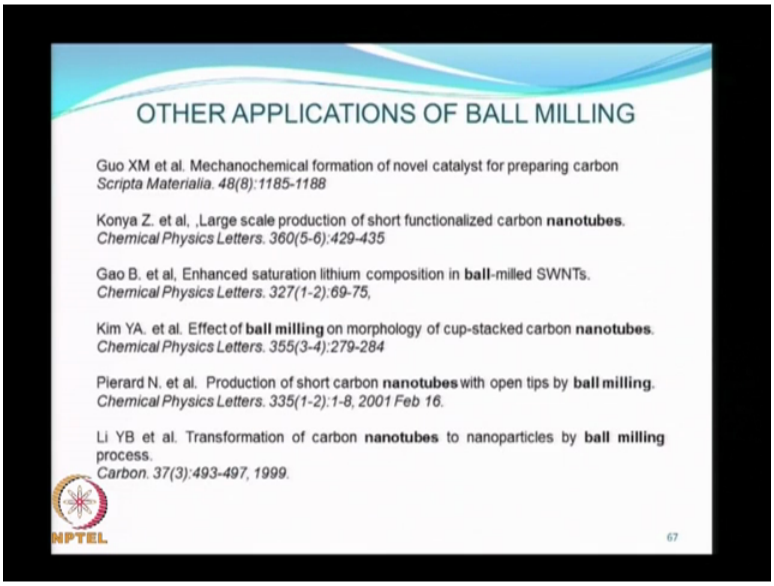

### OTHER APPLICATIONS OF BALL MILLING

Guo XM et al. Mechanochemical formation of novel catalyst for preparing carbon
*Scripta Materialia. 48(8):1185-1188*

Konya Z. et al, ,Large scale production of short functionalized carbon **nanotubes**.
*Chemical Physics Letters. 360(5-6):429-435*

Gao B. et al, Enhanced saturation lithium composition in **ball**-milled SWNTs.
*Chemical Physics Letters. 327(1-2):69-75,*

Kim YA. et al. Effect of **ball milling** on morphology of cup-stacked carbon **nanotubes**.
*Chemical Physics Letters. 355(3-4):279-284*

Pierard N. et al. Production of short carbon **nanotubes** with open tips by **ball milling**.
*Chemical Physics Letters. 335(1-2):1-8, 2001 Feb 16.*

Li YB et al. Transformation of carbon **nanotubes** to nanoparticles by **ball milling** process.
*Carbon. 37(3):493-497, 1999.*

There is in literature many many applications of ball milling for the synthesis of nano particles and you can see that there is a large variety of materials that are made using the ball milling process particularly popular for making nano tubes.

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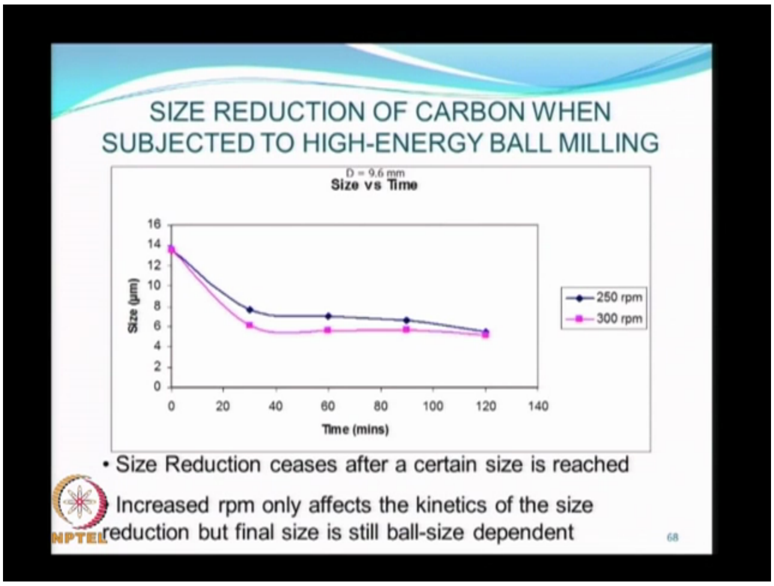

### SIZE REDUCTION OF CARBON WHEN SUBJECTED TO HIGH-ENERGY BALL MILLING

- Size Reduction ceases after a certain size is reached
- Increased rpm only affects the kinetics of the size reduction but final size is still ball-size dependent

Now these are some results from our laboratory where we have taken carbon and try to do size reduction using various techniques. So when we do this in a high-energy ball mill and you plot the (()) (26:20) size as a function of time you can see that there is a levelling off effect or an asymptotic effect which in this case is reached in about 6 microns or so. And the size reduction stops happening after this meeting size is reached.

When you increase the rpm of the ball mill it really does not affect the asymptotic size there is reached what it does affect is the rate at which the size is approached. So by increasing the rpm you can increase the kinetics of the size reduction process but you really cannot do anything about the final size which is more dependent on the dynamics of the mill itself suggest the size of the ball, the size of the chamber and ultimately the size reduction process itself will stop after a certain minimum size is reached.

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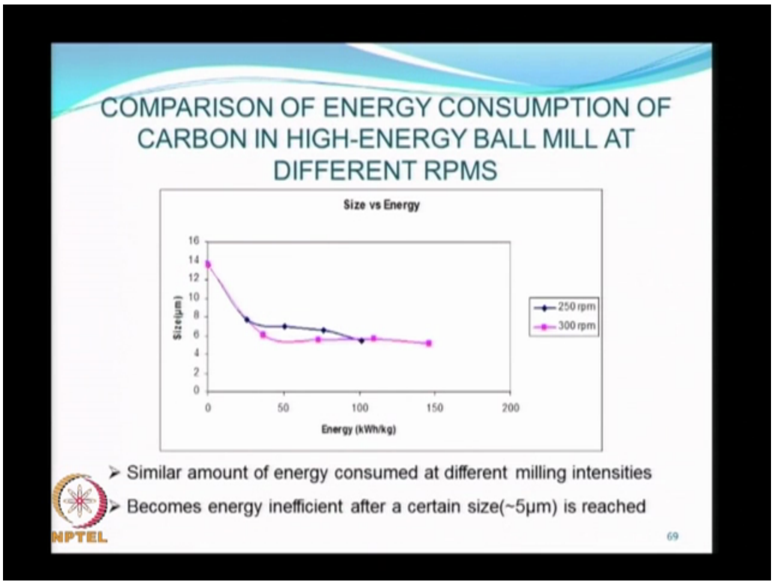

COMPARISON OF ENERGY CONSUMPTION OF CARBON IN HIGH-ENERGY BALL MILL AT DIFFERENT RPMS

- Similar amount of energy consumed at different milling intensities
- Becomes energy inefficient after a certain size(~5µm) is reached

This is a comparison by size versus energy. So if you look at energy that is being input and the size that is achieved as a result of the energy input you can see that there is a similar amount of energy being consumed at various milling intensities. In other words even if we change the RPM long as the input energy remains the same the final size that is achieved also remains the same and again you can see that the process of size reduction by ball milling essentially becomes energy inefficient after about 5 microns is reached because you can keep increasing the amount of energy that you input without causing any change in the mean size after roughly in this case about 50 kilowatt-hours per kilogram.

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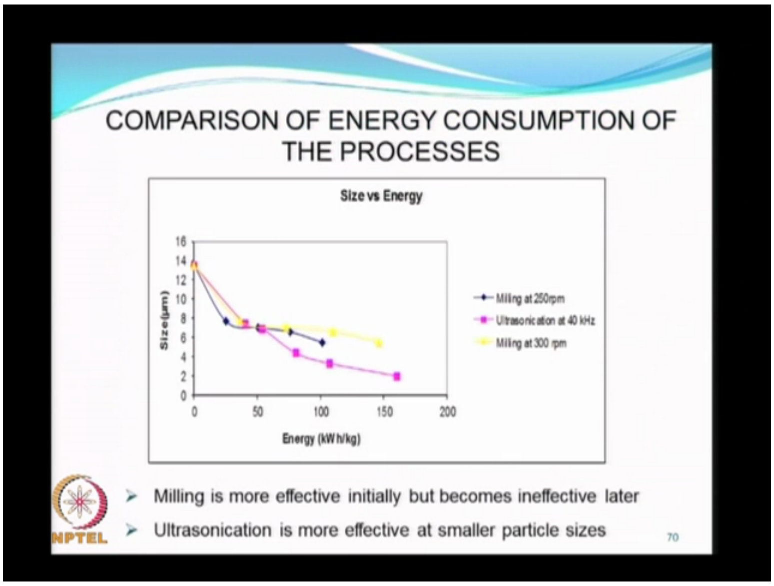

## COMPARISON OF ENERGY CONSUMPTION OF THE PROCESSES

- Milling is more effective initially but becomes ineffective later
- Ultrasonication is more effective at smaller particle sizes

Here we compare the ball milling processes with ultrasonication to look at the energy efficiency of these processes. As we have seen in the previous pictures milling at various rpms starts to show a levelling of tendency around 6 microns whereas if you did the size reduction using sonofragmentation as the technology in this case at 40 kilohertz you can keep driving the size much lower than you can with conventional size reduction processes such as ball milling.

In fact if you look at this figure more closely you can see that actually milling is a more energy-efficient process until a size of roughly 5 microns has reached after which son equation becomes more energy-efficient process. So if you are trying to do in a particles synthesis by size reduction then you are probably better off using a combination of techniques. So to get from an initial size that is let say around 70 to 100 microns to about 5microns you should use ball mill to reach that size and after that you start sonicating the particles to do further size reduction.

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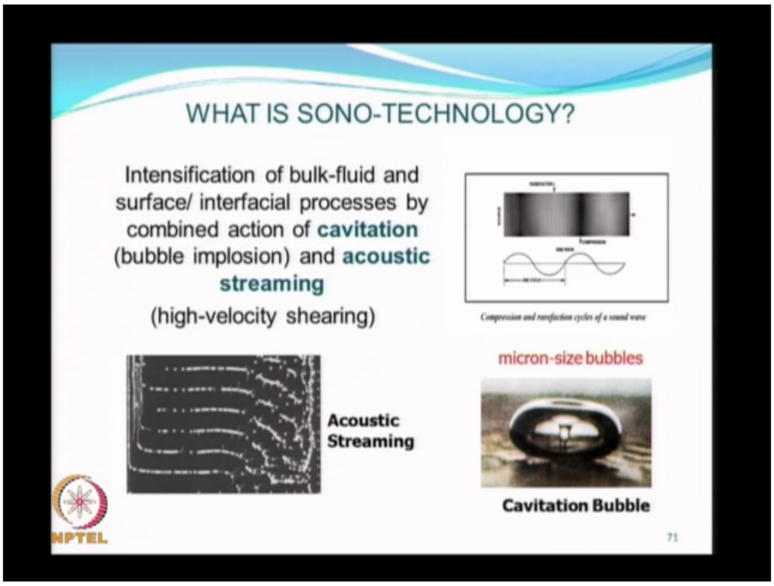

## WHAT IS SONO-TECHNOLOGY?

Intensification of bulk-fluid and surface/ interfacial processes by combined action of **cavitation** (bubble implosion) and **acoustic streaming** (high-velocity shearing)

*Compression and rarefaction cycles of a sound wave*

micron-size bubbles

**Acoustic Streaming**

**Cavitation Bubble**

So let us quickly recap what is Sono-technology? We have discussed this in the context of surface cleaning earlier. Sonotechnology refers to an intensification of bulk fluid as well as surface and interfacial processes by the combined action of cavitation and acoustic streaming and here we see schematics of what a cavitation bubble looks like just before it implodes? We see a typical acoustic streaming pattern which is essentially unidirectional in nature and at the top we see the typical compression and rarefaction cycles of a sound wave. Here of course the bubbles will be forming during the rarefaction cycle and they will be collapsing during the compression cycle.

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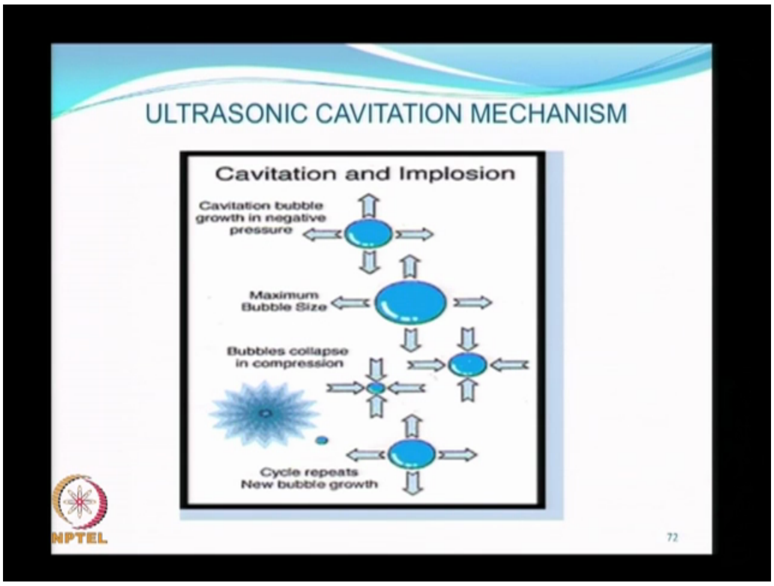

ULTRASONIC CAVITATION MECHANISM

Cavitation and Implosion

Cavitation bubble growth in negative pressure

Maximum Bubble Size

Bubbles collapse in compression

Cycle repeats New bubble growth

This is how the cavitation actually happens there is a bubble growth which leads to a maximum bubble size at which point the bubbles collapse in the compression cycle releases energy as a shockwave that propagates through the liquid medium and either impacts on particles that are suspended in the liquid or it impacts on a surface that the liquid is adjacent to and energy that is transferred due to this shockwave impaction causes physical changes of chemical changes to happen and then the cycle keeps repeating itself as new bubbles form and implode.

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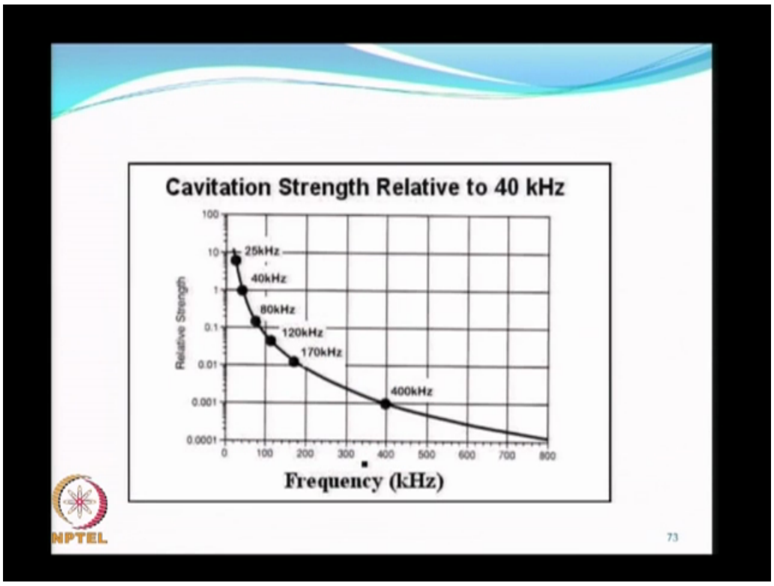

Cavitation Strength Relative to 40 kHz

Frequency is the major player in this. As you increase the frequency the acoustic field the cavitation intensity drops quickly. Actually there is 1 over F cube dependence cavitation strength decreases with frequency as 1 over the cube of the frequency. So you can see here that as you approach 400 kilohertz, 800 kilohertz or close to 1 megahertz cavitation is virtually absent and at its most significant levels for ultrasonic frequencies that are less than 100 microns. The 25 kilohertz to 100 kilohertz range is where you get the most intense cavitation.

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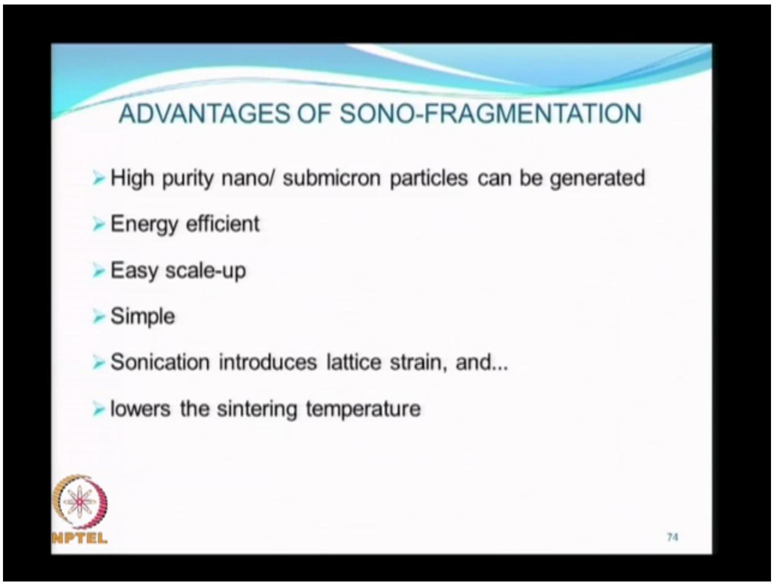

ADVANTAGES OF SONO-FRAGMENTATION

- High purity nano/ submicron particles can be generated
- Energy efficient
- Easy scale-up
- Simple
- Sonication introduces lattice strain, and...
- lowers the sintering temperature

Some of the advantages of Sonofragmentation for synthesising nano particles are high purity because essentially you are taking the base material, if you are trying to make nano alumina you are taking micron sized alumina, so there is no additional chemicals involved and all you use is high purity water typically. So you must have the micron sized particle in high purity water turn on the acoustic field and you start fragmenting the particles. So it is a very simple process it is energy-efficient, easy to scale up and also it the some interesting things to the crystalline structure of the material.

The sonication introduces what is known as lattice strain. So the crystallinity of the particle is maintained it does not become amorphous with extended exposure like high-energy ball milling does but there are certain changes in the crystallinity. Effectively from a physical viewpoint what you see is a rounding off of the corners. So that material or a particle that is subjected to long term sonication becomes increasingly spherical with the passage of time.

It also lowers a sintering temperature, now that is an advantage when you are using these particles in an application that requires them to be sintered and the ability to use lower temperature is advantages from an energy-efficient viewpoint. Of course the reason that the sintering temperatures are lower is because the process of sonication increases the surface energy of the particle.

So the natural adhesiveness of cohesiveness of the particle is greatly increased by the process of sonication this is actually true for all top-down methods but in particular ultrasound because it imparts such high energy to the particles to fragment them leaves behind a residue of the energy which is much higher comeback to for example high-energy ball milling. So the nano particles that are synthesised using sonofragmentation have much more reactive much more adhesive and much more confirmable to your process compared to nano materials that are made by other techniques.

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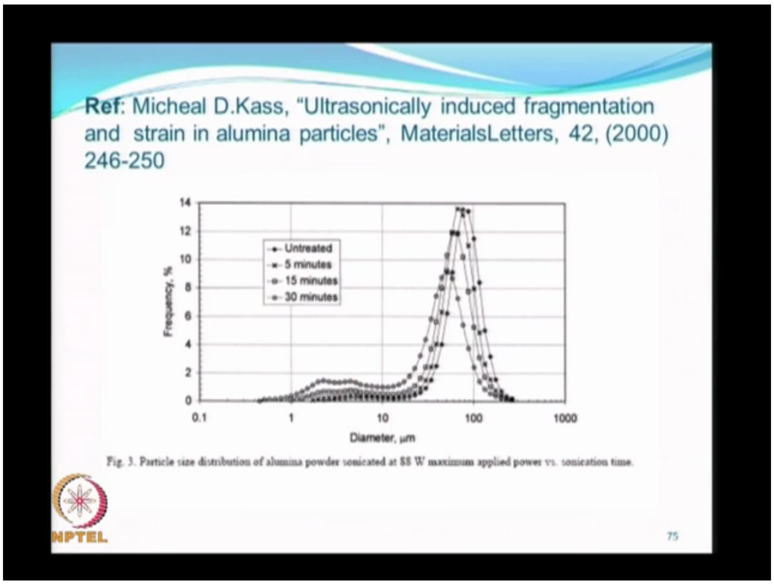

**Ref**: Micheal D.Kass, "Ultrasonically induced fragmentation and strain in alumina particles", MaterialsLetters, 42, (2000) 246-250

Fig. 3. Particle size distribution of alumina powder sonicated at 88 W maximum applied power vs. sonication time.

Here are some examples of particles that are produced using sonofragmentation and again form a particle characterization viewpoint what you see here are data that are produced using a particle size analyser. In the chart you can see that come back to the untreated alumina particles as you expose them to sonication for various spades of time and this is using fairly low-power ultrasound 88 watts you can see that the mean size keeps shifting to a smaller size range.

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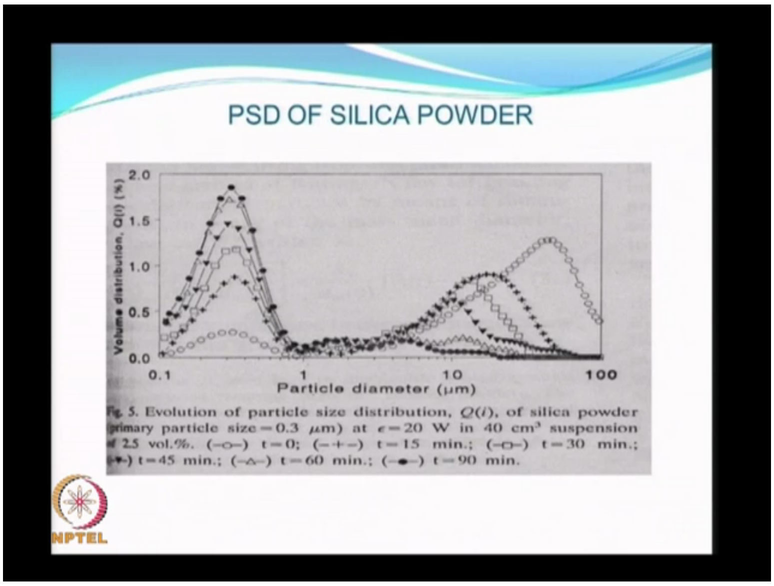

PSD OF SILICA POWDER

Fig. 5. Evolution of particle size distribution, $Q(i)$, of silica powder (primary particle size = 0.3 μm) at $\epsilon = 20$ W in 40 $cm^3$ suspension of 2.5 vol.%. (–○–) t = 0; (–+–) t = 15 min.; (–□–) t = 30 min.; (–▼–) t = 45 min.; (–△–) t = 60 min.; (–●–) t = 90 min.

This is an illustration of a silica powder that has been exposed to ultrasound and you can see here that very characteristic (()) (34:57) model simulation develops over time and here again what you see is a reduction in the mean size of particles and also an increase in the volume fraction of particles in the finer size range.

So you can say that there is a significant enrichment of particles in their sub 1 micron size range as you subject a powder to sonication over an extended period of time. This is a sample of Zirconia powder that has been subjected to ultrasound and again you show you see the same trend. The volume fraction of particles in the larger size range decreases with increasing sonication time and the volume fraction of particles in the submicron size range increase with increase in sonication time. So the mean size decreases as well.

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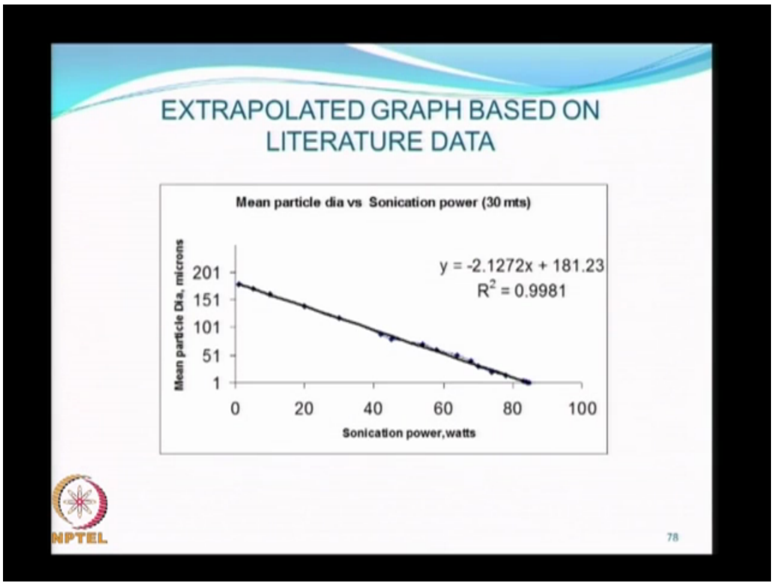

EXTRAPOLATED GRAPH BASED ON LITERATURE DATA

So if we actually took all the data that is in literature and plot at it as mean particle diameter versus sonication power in watts you see very interesting trend that with increasing sonication power you can drive the mean particle diameter after 30 minutes of sonication down to 1 micron. However if you look at the literature data that is not much work reported particles that are smaller than 1 micron.

It is reasonable to expect that this line cannot simply be extrapolated to submicron sizes there will be a levelling off effect even with sonofragmentation. However based on this it is reasonable to expect that sonication will remain a viable technology even for particles that are smaller than a micron.

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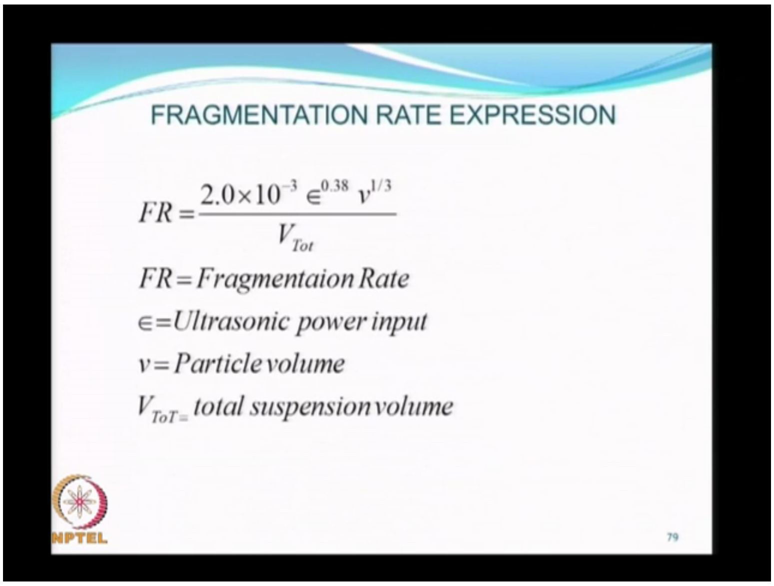

## FRAGMENTATION RATE EXPRESSION

$$FR = \frac{2.0\times10^{-3} \in^{0.38} v^{1/3}}{V_{Tot}}$$

$FR = \text{Fragmentaion Rate}$

$\in = \text{Ultrasonic power input}$

$v = \text{Particle volume}$

$V_{ToT=}$ total suspension volume

If you look at the fragmentation rate expression reported in literature, the fragmentation rate in sonofragmentation is related to the ultrasonic power input with exponent of 0.38, particle volume with an exponent of 1 3rd and the total suspension volume which is in the denominator. This is an interesting expression but what it implies is that as the total suspension volume increases the fragmentation rate will increase reciprocal.

The reason for that is sonofragmentation is a volumetric affect; you are supplying a constant power if you increase the volume of a liquid then the power per unit volume decreases and that result in reduced fragmentation. It is reasonable to expect that power input will be in the numerator but an interesting finding is that particle volume is in the numerator, what that implies is, as the concentration of the particle in the suspension increases sonofragmentation efficiency will increase and that is somehow counterintuitive because what that says is that if we process more material the process will be more efficient that is usually the reverse of what happens with most chemical processes as you try to pump in more material your efficiency will decrease.

The fact that in this particular case the particle volume or concentration is in the numerator gives us a lot of home that scale up would not be that difficult because in scaling up what you are trying to do is essentially process more material at least this expression would indicate that fragmentation rate will not decrease when you do that. If anything it will increase as the particle volume to the power 1 3rd.

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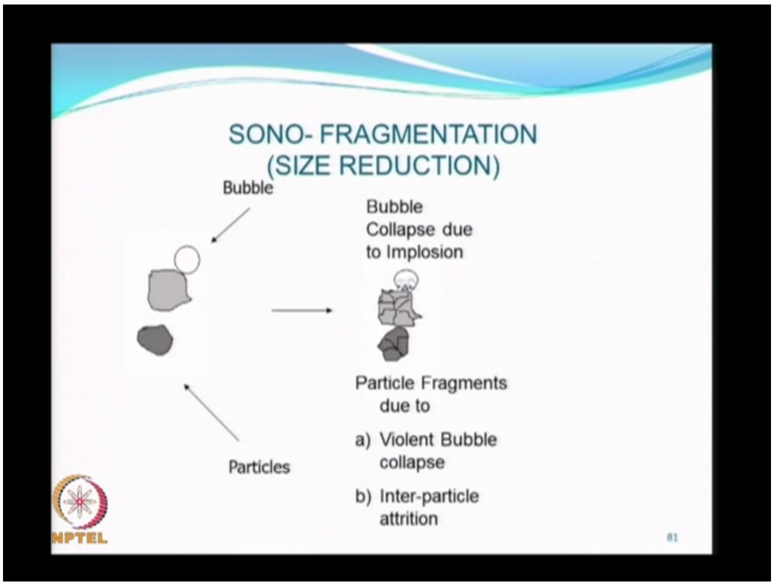

## SONO- FRAGMENTATION (SIZE REDUCTION)

Particle Fragments due to

a) Violent Bubble collapse

b) Inter-particle attrition

Now if you look at the mechanism of sonofragmentation there are actually 2 mechanisms by which particle fragmentation happens. There is direct interaction of the bubble with the particle and also interaction between 2 adjacent particles that are being accelerated by the bubble explosion. So the bubble collapse due to implosion is one of the mechanisms but the other mechanism is simple but particle to particle impact.

So particle fragmentation here occurs due to the violent bubble collapse as well as being the particle collisions and the resulting attrition the particles. So this is basically what happens the bubbles impact on the particle, particles impact on each other and the net result is a fragmented population of particles.

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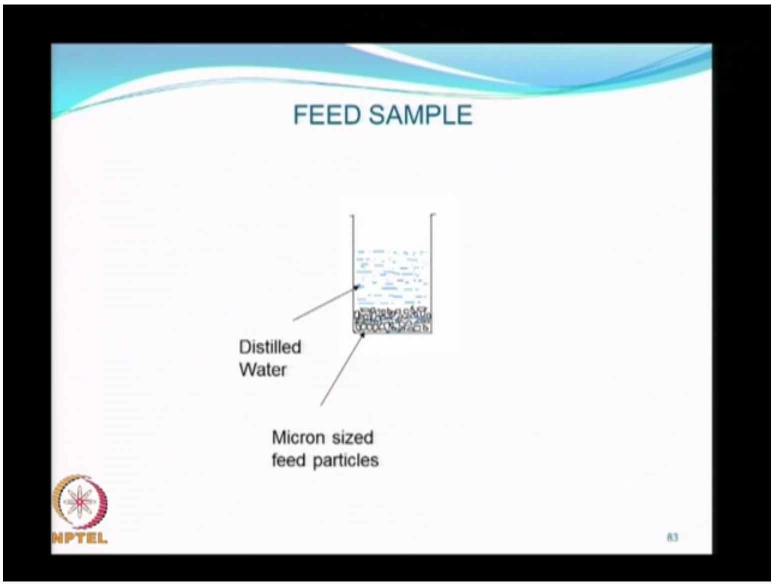
FEED SAMPLE

So in a laboratory setting this can be easily simulated by taking a beaker with distilled water. Put some micron sized feed particles into it and subject it to ultrasound which can be in the form of a tank with bottom mounted transducers or it can be in the form of a horn or nozzle through which the ultrasonic energy is transmitted.

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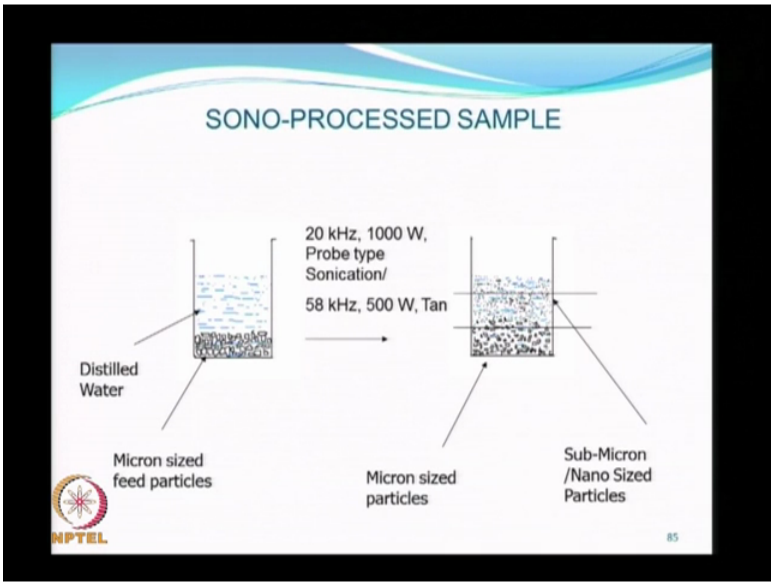
SONO-PROCESSED SAMPLE

And if you look at what happens in the beaker now, you will see that you have essentially 3 layers that show up the bottommost layer will contain the unfragmented particles, mostly the feed particles that have escaped the process of Sonofragmentation. The topmost layer will show the fragmented particles that have been reduced from microns size to nano sized because of the Sonofragmentation mechanism.

Then there will be a middle layer which is a mix of both it will have a fraction of the particles being the size reduced nano-dimensional particles and it will have a fraction of the particles being the original micron sized particles. So this gives us a clue that if you were to combine this solo process with kind of decantation process you cannot only make nano particles but you can also quickly collect them by a process that is based upon the sedimentation characteristics of the various sized fragments. If you have a beaker decantation type of setup you can simply take the top layer of and drain it into a collector and that will be enriched in nano particles whereas the bottommost layer can be recycled, so that it can be size reduced further.

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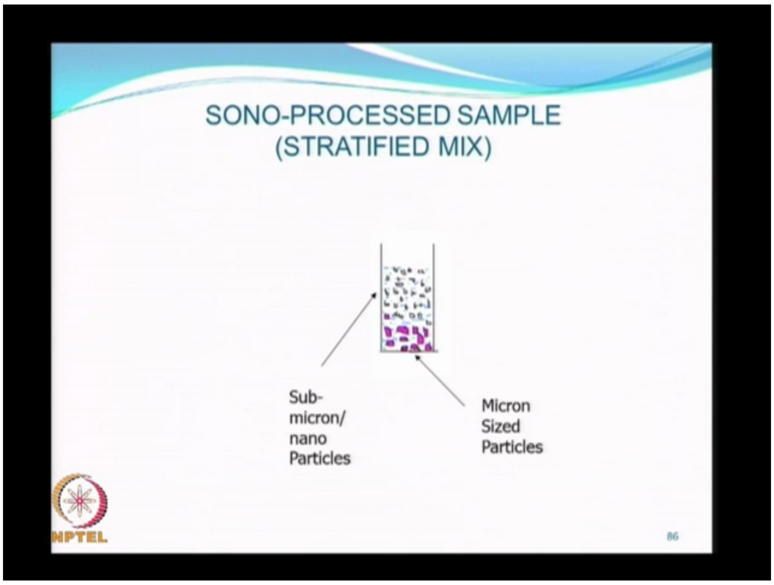

SONO-PROCESSED SAMPLE
(STRATIFIED MIX)

What you can also do is take this sample which is stratified, you know with 3 different size distributions and you can actually mix them up again. Now that may be important in some applications where you need a range of particle sizes rather than a particle size in a particular size range. So it is really easy to take the stratified layer of submicron, micron and nano sized particles and remix them to produce a homogeneous suspension.

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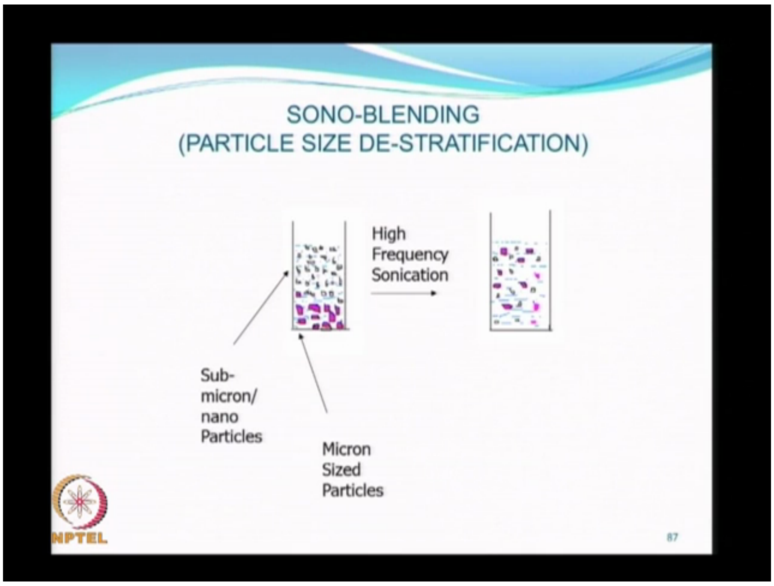

SONO-BLENDING
(PARTICLE SIZE DE-STRATIFICATION)

High Frequency Sonication

Sub-micron/ nano Particles

Micron Sized Particles

So in this particular case it is possible to take particles that have been produced by sono-blending as this is called and essentially make a uniform composition of nano sized, submicron sized and micron sized particles which can then be used  to be composites.

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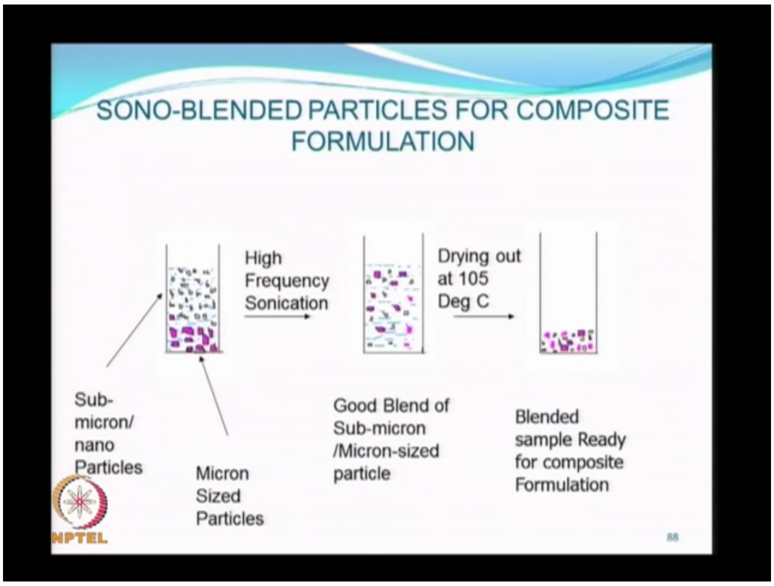

SONO-BLENDED PARTICLES FOR COMPOSITE FORMULATION

One of the major applications of Sono-technology is not only to synthesise nano particles but also to incorporate them into polymers and other materials to make composite materials so the way that works is you take this blend of various sized particles dry them out and keep the blended sample ready to make into composites.

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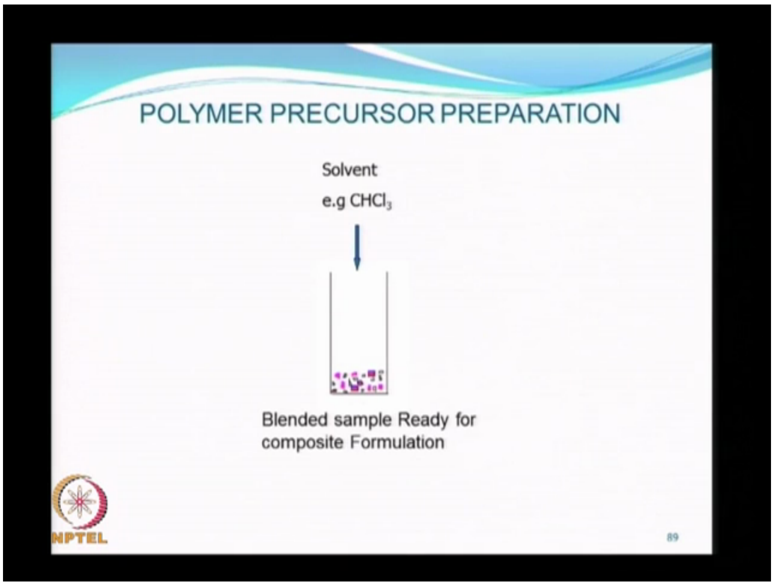

POLYMER PRECURSOR PREPARATION

The polymer precursor itself has to be prepared by dissolving it in a solvent and then you take the nano materials that you have to (()) (42:45) your Sonofragmentation process and blend them into the polymer that you have prepared by dissolving in a solvent and then you can again use sonication to uniformly mix the particles into the polymer.

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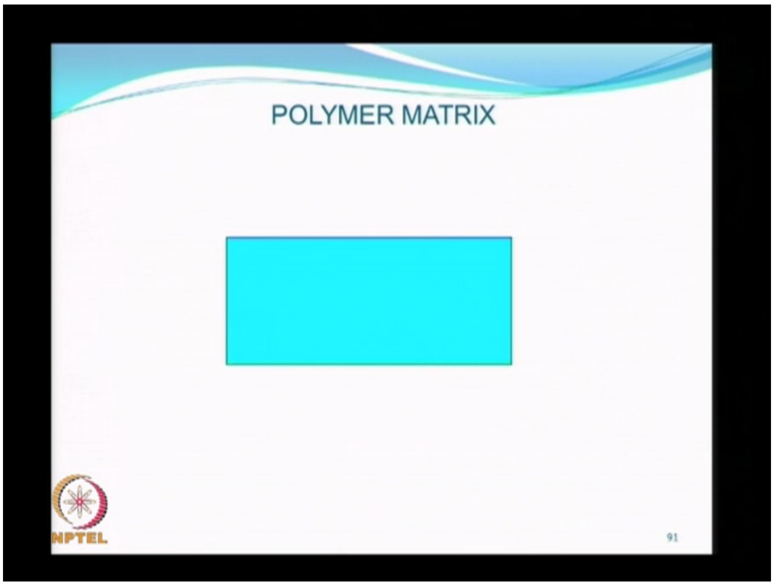

POLYMER MATRIX

And the polymer matrix that you have prepared in this fashion.

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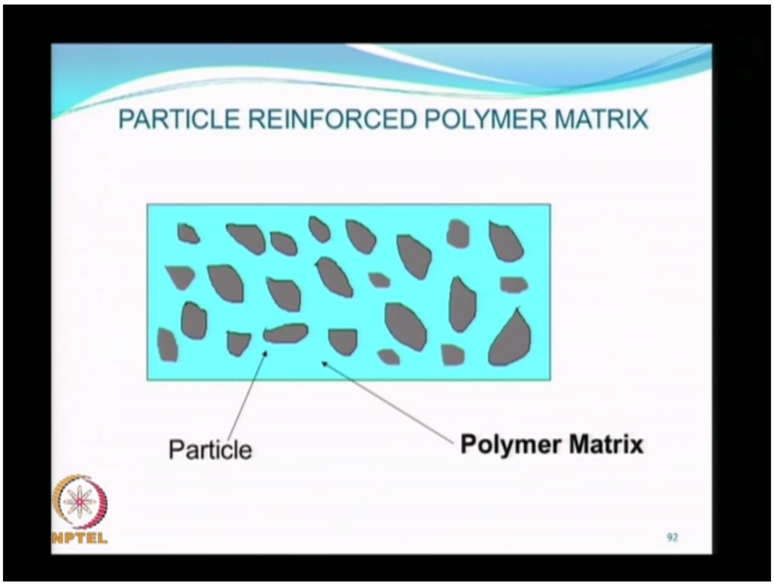

PARTICLE REINFORCED POLYMER MATRIX

Will essentially look like this, you will have the polymer material within which the nano particles are incorporated. Now there are 2 important things here the particles should be non-agglomerated, so they should be dispersed very well they should also be distributed. we will see later on when we talk about nano particle dispersion that these are 2 different characteristics dispersion and distribution. They are both very important in preparing a high-quality polymer composite material.

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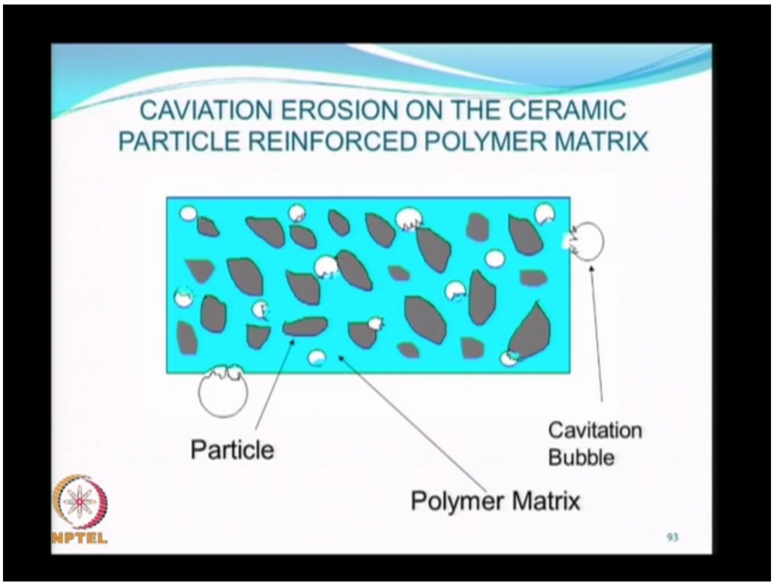

CAVIATION EROSION ON THE CERAMIC PARTICLE REINFORCED POLYMER MATRIX

The strength of these nano composites can also be tested by subjecting them to cavitation erosion. For example you can take this composite material that we have prepared and expose it to hang ultrasonic field and look for (()) (44:02) and as material becomes stronger there will be less weight loss due to cavitation erosion. So ultrasonic processing can be used very effectively to synthesise nano particles, to prepare nano composites and also to test the cavitation resistance or strength of the nano composites.

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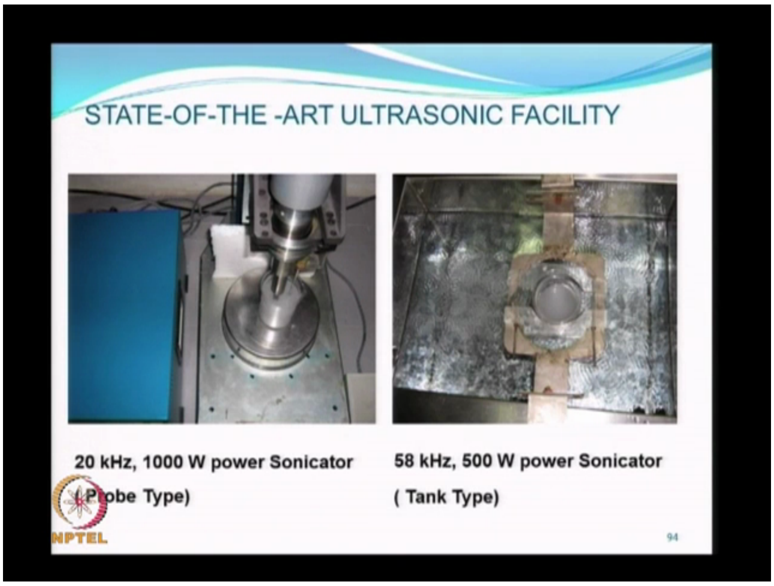

STATE-OF-THE -ART ULTRASONIC FACILITY

20 kHz, 1000 W power Sonicator
( Probe Type)

58 kHz, 500 W power Sonicator
( Tank Type)

In a laboratory we have some state-of-the-art ultrasonic facilities that we used to make nano particles as well as the nano composites. You can see over 20 kilohertz probe type sonicator here on the left inside and the 58 kilohertz tank type sonicator underwriter inside. On the right-hand side if you look down on the water you can see that the ultrasonic field is very very uniform over the entire surface.

That is in fact the primary advantage of the tank type Sonofragmentation process that you produce very uniform cavitation patterns over the entire liquid whereas in the probe type sonicator the acoustic field is highly localised. So you get very very high intensities in the immediate vicinity of the probe but as you move further away from the probe the energy intensity drops off very rapidly.

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ANALYZERS USED

Some of the analyses that are used for testing particle compositions and sizes and counts are shown here. The left inside top picture shows a turbidity meter, may recall that we discuss this in the context of measuring particle concentration since suspensions. Turbidity is a measure of the total scattering intensity of particles in suspension. So it can be used as a qualitative measure of particle size as well as particle concentration in liquids.

The top picture on the right-hand side shows a laser particle counter which works by principle of laser scattering which we also discussed in one of the earlier lectures. This particular laser particle counter can count particles in liquids down to 1 micron and at the bottom you have a particle size analyser which works by the principle of acoustics attenuation spectroscopy which we also discussed earlier in one of the lectures. So these are the 3 instruments which are very widely used in our laboratory as well as many other laboratories to characterize particle sizes and particle counts in liquid suspensions.

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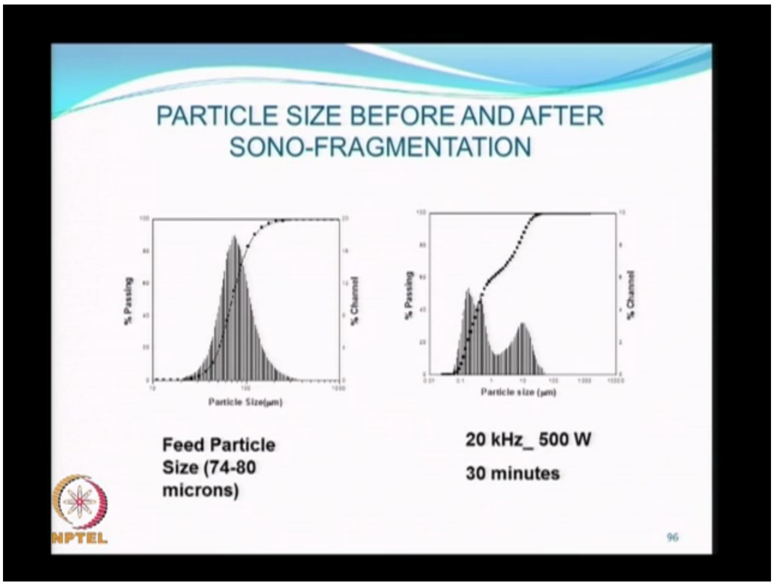

PARTICLE SIZE BEFORE AND AFTER SONO-FRAGMENTATION

**Feed Particle Size (74-80 microns)**

**20 kHz_ 500 W**

**30 minutes**

The data that we will be reviewing here are taken from one or the other of these instruments. So here we see what happens to feed particles are alumina that are subjected to Sonofragmentation. So the peak size shown on the left hand side is 74 to 80 microns when you expose it to 20 kilohertz ultrasonic at 500 watts for 30 minutes you can see that there is a substantial reduction in size and the particle mean size is now close to 1 micron and you can see there are substantial fraction of the particles are less than a micron. So even a fairly short duration sonication is sufficient to make a sizeable number of submicron particles.

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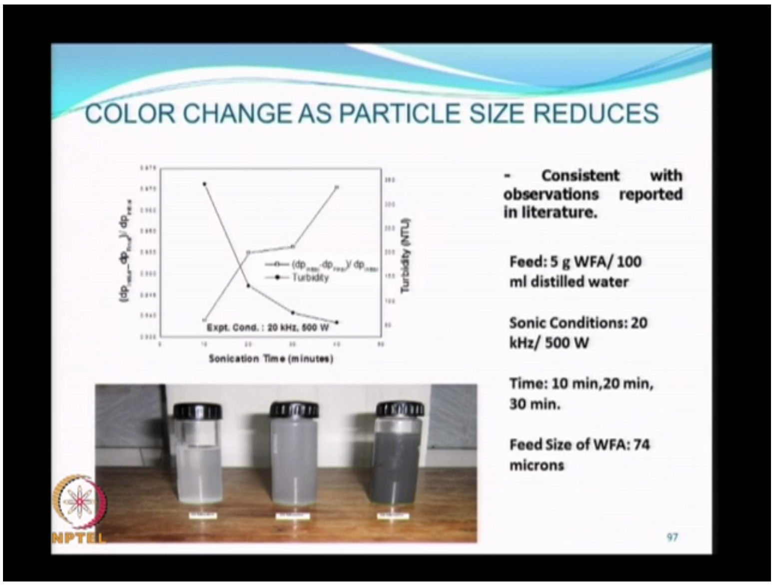

COLOR CHANGE AS PARTICLE SIZE REDUCES

- Consistent with observations reported in literature.

Feed: 5 g WFA/ 100 ml distilled water

Sonic Conditions: 20 kHz/ 500 W

Time: 10 min,20 min, 30 min.

Feed Size of WFA: 74 microns

Another indicator size reduction physical change. You will find that for the same material in this case white fused alumina which is being size reduced the colour of the suspension changes as particle size decreases which actually gives us an idea that if you can monitor the turbidity or the colour of the suspension quantitatively that can actually be used to track size reduction without having to use more sophisticated techniques such as particle size analyser.

So the graph shows sonication time in minutes and on the left hand side vertical axis we see the particle size that results after Sonofragmentation and you can see that decreases to a very low value. On the right-hand side vertical axis the data plotted in terms of turbidity which is a measure of particle suspension in the liquid and also the colour of the suspension and you can see that with sonication time that colour essentially becomes darker and darker which is an indication that we have many many more particles now in suspension but of smaller sizes. So this is an interesting part that says that colour change can actually be correlated to size reduction when you subject a suspension to sonication in order to achieve size reduction.

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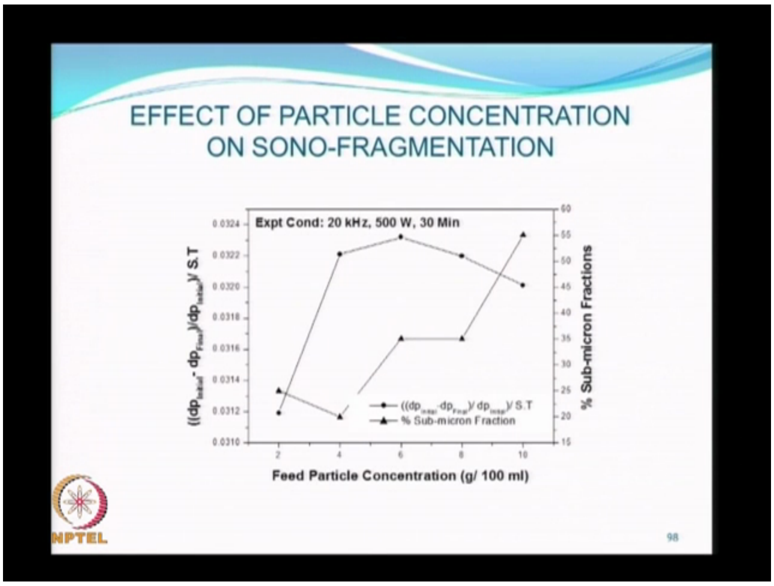

EFFECT OF PARTICLE CONCENTRATION ON SONO-FRAGMENTATION

Here we are showing the effect of feed particle concentration on size reduction. The interesting theorem here is that it is actually not a monotonic relationship. The fragmentation rate expressions that I showed earlier seem to suggest that as particle concentration increased the size reduction efficiency will keep increasing. However you will see from this figure that is not necessarily the case, there is actually an optimum value of particle concentration at which you have the best size reduction efficiency but if the concentration increases beyond that the size reduction efficiency actually starts to drop.

And the reasons for that are interesting and we will pick up the discussion from this point on the next lecture and we will highlight the influence of P particle concentration on size reduction efficiency. Are there any questions on what we have talked about today? Okay, so see you at the next lecture.