Surface Engineering of Nanomaterials

Dr. Kaushik Pal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology, Roorkee

Lecture - 19
Characterization of Nano-coatings

Hello. In this particular lecture actually we are going to discuss about the different types of characterization technique by which we can make or maybe we can get that whether our coating is proper or not or maybe how much depth we have achieved whether our coating is uniform or not or whether we are got the overall coating on to the substrate or not.

So, till now we are discussing about the different types of coating techniques that by which we can change the outer surface of that particular material so that we can make the materials from non conductive to conductive or maybe the vice-versa, we can enhance the mechanical properties, we can enhance the thermal properties, we can enhance some kinds of optical properties onto that materials or maybe that so on. So, in these particular techniques we are going to do the characterization of this type of nano-coatings

So, here before going to start first we have to know that why the characterization actually required. So, first of all material structure and properties are proved and measured, next no scientific understanding of engineering materials could be ascertained, study the microscopic structure and properties of materials.

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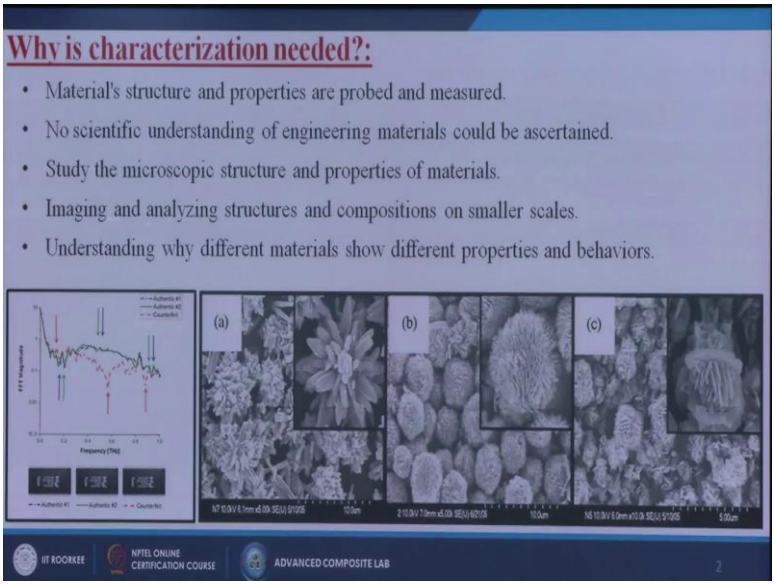

Imaging and analyzing structures and composition on smaller scales. Understanding why different materials so different properties and behaviors. Unless and until we know that what type of materials we are going to use, how they are adhering to the substrate itself, how they are working as a coating materials whether there is any cracks or pores are available or not, with how to rectify these kind of problems we have to go for different kind of characterization techniques.

So, from this particular figure we can see that what is the at different frequency, that what is the magnitude of these nanoparticles on to the substrate itself, and here we have shown some kind of FESAM image; that when we are doing the coating of these kind of materials onto the substrate how the structure is going on, because as we know that nanoparticles the biggest advantage of this one is that they are showing different properties above respective to their alignment; when they are horizontal, when they are perpendicular. So, if it the nanoparticles into the horizontal directions they will give one properties. If it they are into the perpendicular positions they will gives another properties. Or maybe what are the steps of these nanoparticles when they are attaching to that particular substrate depending upon the deposition of that particular nanoparticle onto the substrate itself that it can give different properties.

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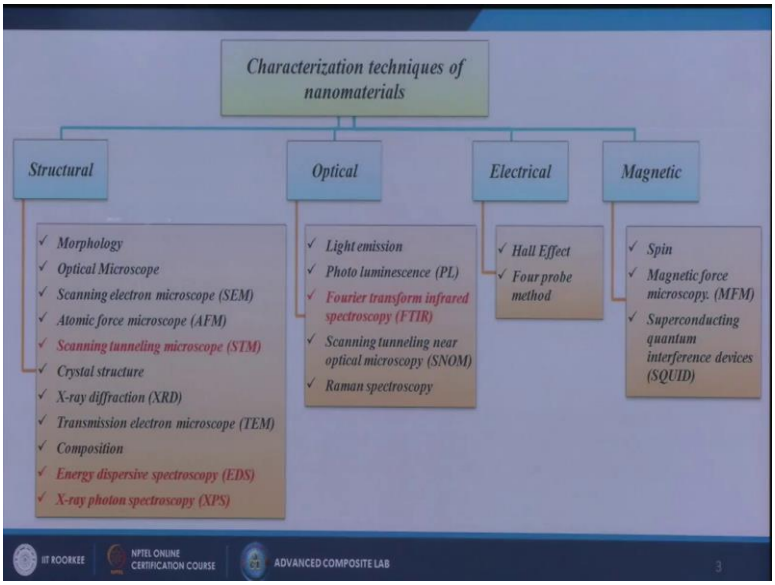

So, here there are several types of characters and techniques are available or maybe in our day to day life. We are doing this kind of characterizations just to check whether our material is good enough to adhere these nanoparticles or maybe that nano-coatings or maybe that nano-coatings is good or bad or maybe there is in cracks or ports are available onto this substrate or not. So, when we are talking about the structural characterizations they are an n number of applications, like morphology, optical microscopes, scanning electron microscope, atomic force microscope, scanning tunneling microscope, crystal structure, x-ray diffraction, transmission electron microscope, compositions, what is the compositions of these particular coating materials, then energy dispersive spectroscopy in short form it is known as the EDS and then x-ray photon spectroscopy in a short form it is known as the x based techniques.

And when we are talking about the optical properties of this material we have to check by through this type of characterizations. First one is called the light emissions, then photo luminescence, Fourier transform infrared spectroscopy, scanning tunneling near optical microscopy, Raman spectroscopy. When we are talking about the electrical means electrical properties of that coating materials if we are going to measure we have to go for the Hall Effect method, we have to go for the four probe method. When we are measuring the magnetic properties of this type of coating materials we have to go for the spin, magnetic force microscopy, and superconducting quantum interference devices.

So, these all are at the different properties, based on the applications which applications I need I have to do the proper characterizations so that I can measure these kind of properties from that coating surface or maybe from that substrate itself. So, here some of the applications we have put or maybe we have made into radiant color. So, those characterizations techniques actually now we are going to discuss in this particular lecture and rest of the characterizations we are going to discuss in our subsequent slide in future.

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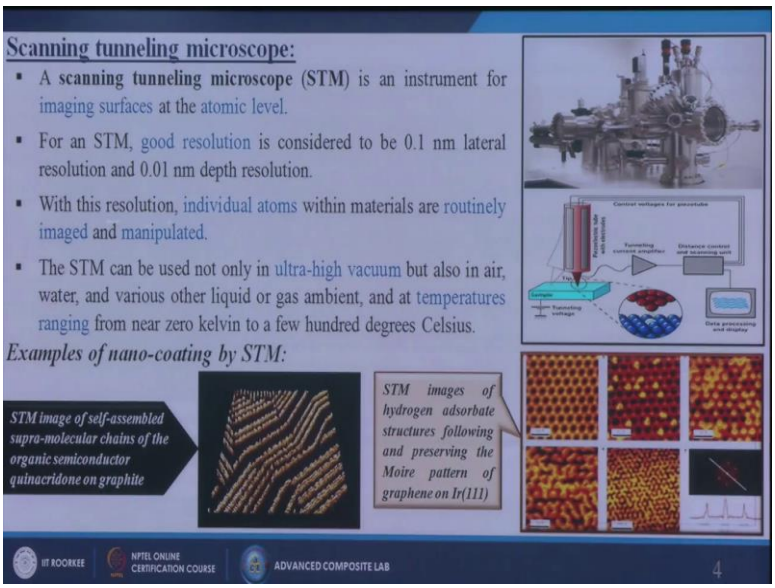

So here, first we are going to discuss about the scanning tunneling microscope, so for in the short form it is known as the STM which is nothing but an instrument for imaging surface at the atomic level. So, you can see in the nano level we can measure this kind of technology; so for measuring the surface morphology in the nanoscale level we can use this scanning tunneling microscope.

For an STM, good resolutions are considered to be 0.1 nanometer lateral resolutions and 0.01 nano meter depth resolutions. With these resolutions individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra high vacuum but also in air, water and various other liquid or gas ambient; and at temperatures ranging from near zero kelvin to a few hundred degree Celsius.

So, there is a wide range, wide environment we can create by which we can measure our material into different atmospheric or maybe environmental conditions. Here we are showing some kind of examples of the nano-coating by the STM technology. So, here the figure is something looking like this which is nothing but the STM image of self assembled supra molecular chains of the organic semiconductor quinacridone on graphite. So, on graphite surface we are doing the coating of these kinds of materials so that we can by this STM technology we are getting this kind of surface structure.

Here is also the example that STM image of hydrogen adsorbate structure following and preserving the more pattern of graphene on 111 plane of iridium. So, on the graphene substrate we are showing that how after coating the material is looking like this, and not only that we can get the surface roughness of that particular material whether the surface roughness of that particular material is smooth or maybe there is some roughness are present. So, here this is the overall image of that equipment which is known as the scanning tunneling microscopy its looks like this, where the principle of this is that here we are having that tip which is actually moving onto the substrate itself which is gathering the image from that particular surface not only that it is giving you the surface roughness of that particular material; it is not actually touching there should be a little bit gap in between your steep of the instrument and your surface.

And here we are getting some kind of tunneling current amplifier the distance control and scanning unit, because we have to because the our surface, surface is not smooth maybe there is some reach point or maybe there is some down point. So, you have to check it out that our tip should not reach the surface substrate otherwise it will hamper. So, in that particular case we are getting the data and displaying that it is giving you the surface structure or maybe that surface structure of that particular coating materials on to the substrate itself.

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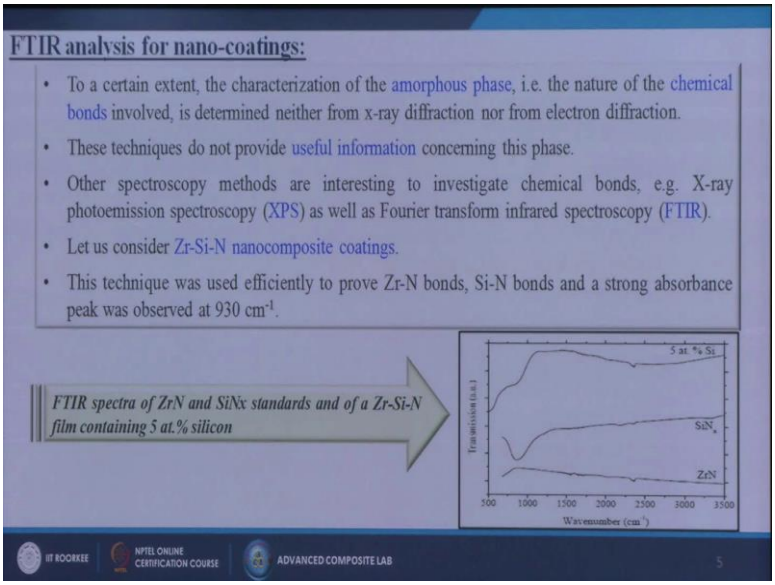

Next we are going to discuss is the FTIR techniques, so FTIR is nothing but the Fourier Transformed Infrared Spectroscopy or maybe that sometimes we are calling it as a FTIR technology. So, to a certain extent the characterization of the amorphous phase that is the nature of the chemical bonds involved is determined neither from x-ray diffraction nor from the electron diffraction. So, suppose generally for the maximum polymeric or rubber cases we are going to do these kind of FTIR testing. So, from the FTIR testing actually it is giving you the what kind of bonding is taking place in between the substrate and the coating materials, not only that sometimes it is giving that what type of bonding is taking place in between here nanoparticles or maybe the nano composites.

So, here these techniques do not provide useful information concerning this phase. Other secondary methods are interesting to investigate chemical bonds like x-ray photo emission spectroscopy as well as Fourier transform infrared spectroscopy or maybe the FTIR which can give you the structure of your particular materials, not only that what is the chemical bonding formations is taking place inside your material. Let us consider the zirconium silicon nitrogen nano composite coatings these techniques was used efficiently to prove zirconium nitrogen bonds silicon nitrogen bonds and a strong absorbance peak was observed at 930 per centimeter.

So here, this is the FTIR spectra of zirconium nitride and silicon nitrogen compound standards and of a zirconium silicon nitride film containing 5 atomic percent of silicon.

So, here from this FTIR spectrum we can get the wave number in the translation mode generally, two modes we can get this kind of results one is called the adsorptions another one is the transmission mode, and generally it will give you the a wave number. So, by getting this reach or maybe that pattern we can match with our database that whether this is for the carboxyl group or maybe this is for the hydroxyl group or maybe this is for the other methyl group.

So, by this we can get that what type of material of coating is we are depositing not only that what is the chemical structure of that final composite on onto the substrate itself. So, it will give you a one kind of element analysis also it will give you a one kind of chemical structure of your particular material.

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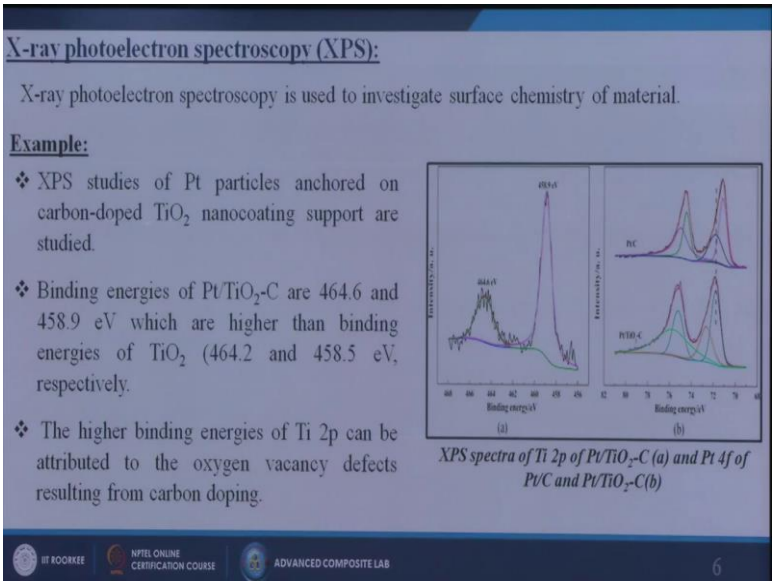

Next is called the XPS, which is nothing but the X-ray Photoelectron Spectroscopy. This is also a one kind of blood test technology by which we can get more detailed information about the chemical structure of that particular nano composite. So, x-ray photoelectron spectroscopy is used to investigate surface chemistry of a material, so what type of materials we are going to coat onto the surface the total chemical structure of that particular material we can get by these techniques.

So, here we have given some kind of examples: XPS studies of platinum particles anchored on carbon doped TiO 2 nano-coating supports are studied in this particular

case. So, here the binding energy of platinum and titanium dioxide carbon doped are 464.6 and 458.9 electron volt which are higher than binding energies of TiO 2, 464.2 and 458.5 electron volt respectively. The higher binding energies of titanium 2p can be attributed to the oxygen vacancy defects resulting from carbon doping.

Actually, before going to do this kind of coatings we can do the expressed studies and after coating we can do the express expressed studies and then from the two results we can compare that before coatings what was the chemical structure of that particular material, and after that what was the chemical structures of these coating materials so that we can compare easily the results in between these two. Not only that it will give you the information's about the carbon, it will give you the information's about the oxygen, it will give you the information's about the nitrogen and the other materials too.

So, by just getting the intensity of these particular materials and what is the binding energy we are achieving simply we can calculate that what is the percentage of materiality has been attached, what is the structure chemical structure it is forming inside the materials.

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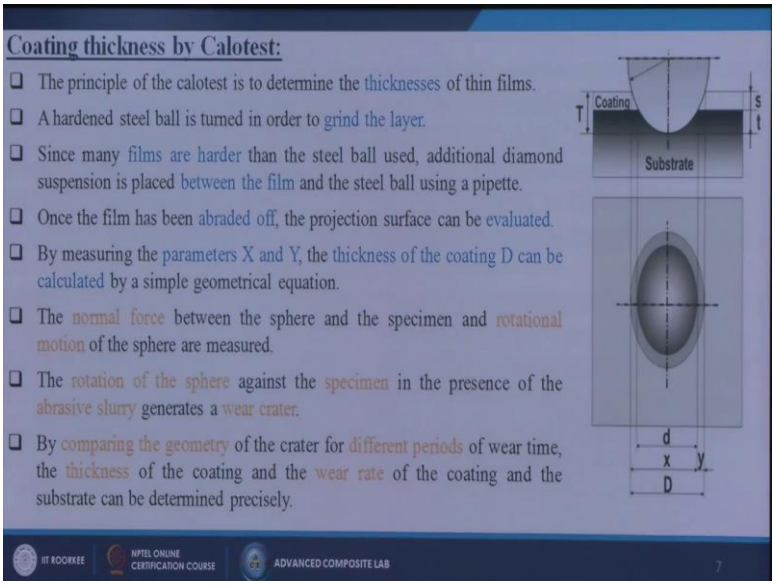

Next we are trying to measure that what is the coating thickness of these particular coatings onto the substrate itself. So, till now we are discussing about the coating, we are discussing about the different layer formations onto the substrate itself, but in this

particular case we are trying to measure the coating thickness; whether that coating is uniform or not, how much materials are present onto that substrate or not, and what is the thickness whether the thickness is uniform towards the surface of that materials or not.

So, the principle of the calotest is to determine the thickness of the thin films. A hardened steel ball is turned in order to grind the layer. Actually this is the surface there is one ball it is like a ball, like a ball bearing or maybe small ball which we are putting onto the substrate then we are rotating in a high pressure onto that substrate so that the ball is giving impact onto that substrate itself, so that easily we can measure the thickness of that particular coating on to the substrate itself.

Since many films are harder than the steel ball used additional diamond suspension is placed between the films and the steel ball using a pipette. Sometimes we are putting some kind of diamonds; that means some kind of imprinted diamonds in that particular region so that the impact will be more, maybe sometimes the ball is not good enough to give a load on to that coating surface.

Once the film has been abraded off the projection surface can be evaluated. By measuring the parameters x and y the thickness of the coating d can be calculated by simple geometrical conditions. The normal force between the sphere and the specimen and the rotational motion of the spheres are measured. The rotation of the sphere against the specimen in the presence of the abrasive slurry generates a wear crater. Sometimes we are using some kind of abrasive particles; sometimes we are using some kind of diamond particles over there.

By comparing the geometry of the crater for different periods of wear time the thickness of the coating and the wear rate of the coating and the substrate can be determined precisely. So, by the calotest method we can easily determine the coating thickness of our materials onto the substrate itself.

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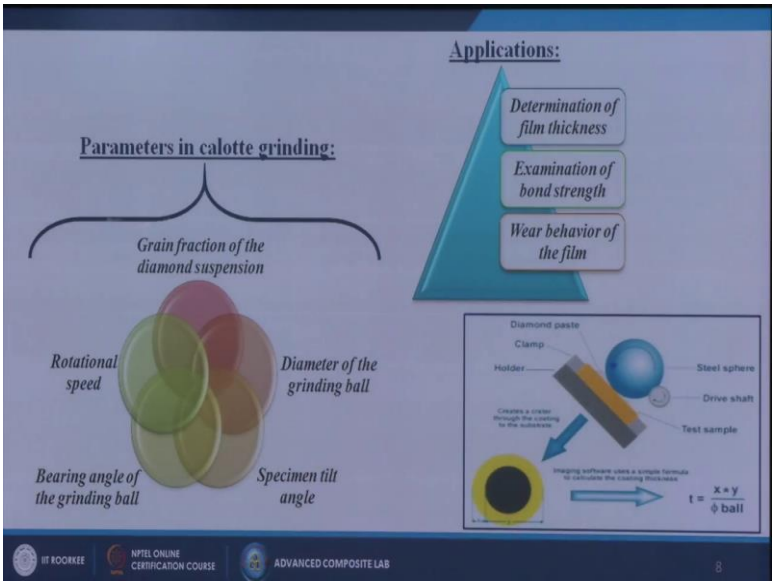

So, here are the different parameters actually which is influencing the calotest or maybe that calotte grinding; what are those? First one is called the rotational speed. What are the rotational speed of that ball that which is rotating onto our coating surface. Second is that grain fractions of the diamond suspensions. Then diameters of the grinding ball whether it is too small or whether it is too big. Specimen tilt angle whether the ball directly heating onto the substrate or maybe it is putting certain kind of angle onto the substrate or not, then bearing angle of the grinding ball.

So, these all are the input parameters for these calotest results. What are the applications? Determination of film thickness, examination of the bond strength, wear behavior of the frame; because when this ball is heating on a high pressure on to the surface itself whether your coating is coming out from the surface of your materials or not or maybe that the coating materials is changing its properties or not, we can easily measure all these kind of techniques.

Not only that, this is the tilt angle actually what I am talking about the specimen tilt angle; so whether that ball will give a heat like this or maybe it will heat your substrate in a perpendicular motions you can change all these things. Here the yellow color is into the color of that coating materials and the black is that hold whichever that crater is formed by this ball. So, here this one is the holder then we are having the clamp by which we are holding our specimens or maybe that substrate, and then we are putting

some kind of diamond paste or maybe that diamond slurry and that ball is rotating in a high velocity and not only that it is giving a normal load to the substrate by which a hole is creating onto the surface.

Then from this image software uses a simple formula to calculate the coating thickness is t is equal to x into y by phi ball means ball diameter of that particular ball. By applying this we can measure what is the coating thickness on to the substrate itself.

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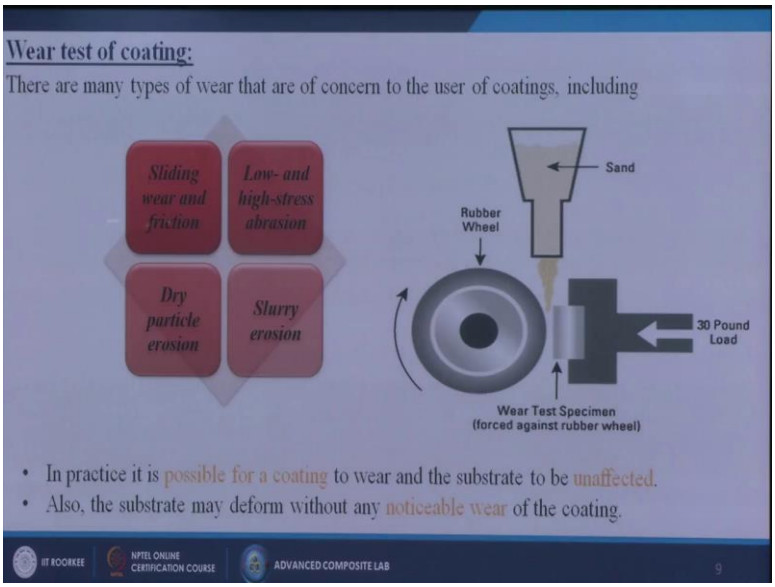

Next is that the wear test of coating. There are many types of wear test that are of concern of the user of coating including sliding wear and frictions, low and high stress abrasions, slurry erosion dry particle erosion. So, there are several types of frictional test can be achieved by this kind of methods. So, in this particular case actually we are having one grinding wheel or maybe that rubber wheel which sometimes it is embedded with some kind of abrasive particles or maybe sometimes it is totally merging, in between our test specimens or maybe the substrate we are putting some kind of sand or maybe some kind of abrasive particle so that the rubber is getting stick with that sand particles and then continuously it is rubbing our test specimens.

After finishing these results before weight and after weight if you decrease this to weight, sorry if we minus this to weight will get that how much mass loss is taking place in the form of a mass fractions or maybe sometimes we can calculate the volume of that

particular wear by this kind of methods. Here also we are using some kind of normal load so that that specimen is giving a continuous load onto our rubber wheel.

In practice it is possible for a coating to wear and the substrate to be unaffected. Also the substrate may deform without any noticeable wear of the coating. So, how much mass actually it is losing depending upon that we can calculate that how much wear is taking place onto our coating surface.

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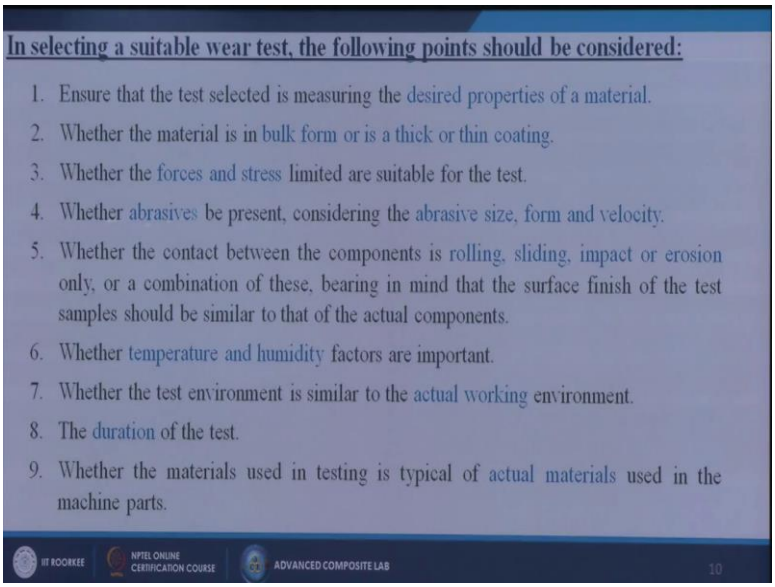

Next is that in selecting a suitable wear test the following point should be considered. So, first one is that; ensured that the test selected is measuring the desired properties of a material. Second whether the material is in bulk form or is a thick or thin coating, Whether the forces and stress limited are suitable for the test or not, whether abrasive be present considering the abrasive size form and velocity. These all are the input parameters for measuring this kind of wear test.

Whether the contact between the components is rolling sliding impact or erosions only or a combination of these bearing in mind that the surface finish of the test sample should be similar to that of the actual components, whether the temperature and humidity factors are important, whether the test environment is similar to the actual working environment, the duration of the test where the materials used in testing is typical of actual materials

used in the machine parts. So, these all are the different input parameters, different conditions which we have to keep in mind before going to start this kind of experiment.

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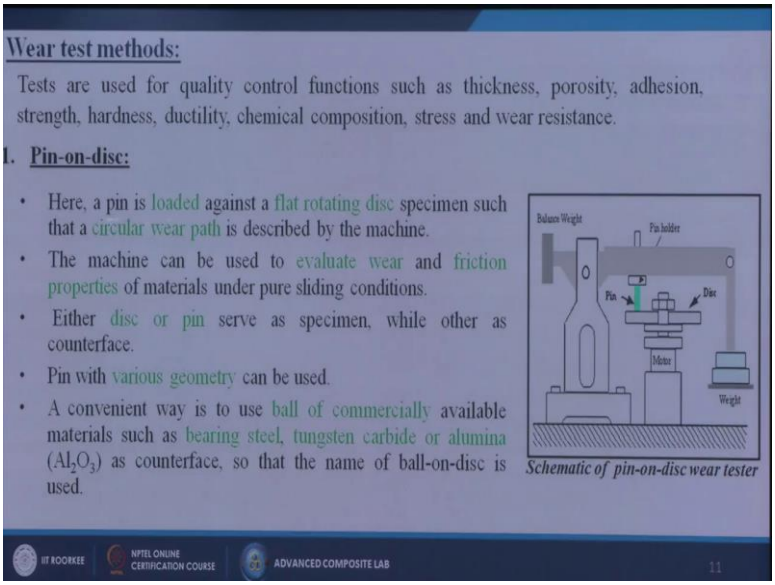

So, now we are going to do the wear test methods. There are several methods are available which first one is known as the pin-on-disc methods. So, in pin-on-disc methods we are making our sample in a pin formation. So, there is one pin holder which is holding our materials in a pin form and then we are having a disc that disc is made by some kind of abrasive particles. So, our team or maybe our substrate materials is giving a continuous load onto that disc, and this disc is rotating by a mortar in two different rpm; we can change the rotational speed of our particular abrasive disc.

Here a pin is loaded against a flat rotating disc specimen such that a circular wear path is described by the machines. The machines can be used to evaluate wear and friction properties of materials under pure sliding conditions. Either disc or pin service specimens while other as counter face. Pin with various geometry can be used. A convenient ways to use ball of commercially available material such as bearing steel, tungsten, carbide or alumina Al 2 O 3 as counter face so that the name of the ball on disc is used.

Sometimes we are using these materials in a pin or maybe sometimes we are using these materials in a ball safe. So, here the schematic diagram of that disc wear tester, here we

are putting some kind of weight that is actually acting as a normal load of pin to the disc itself.

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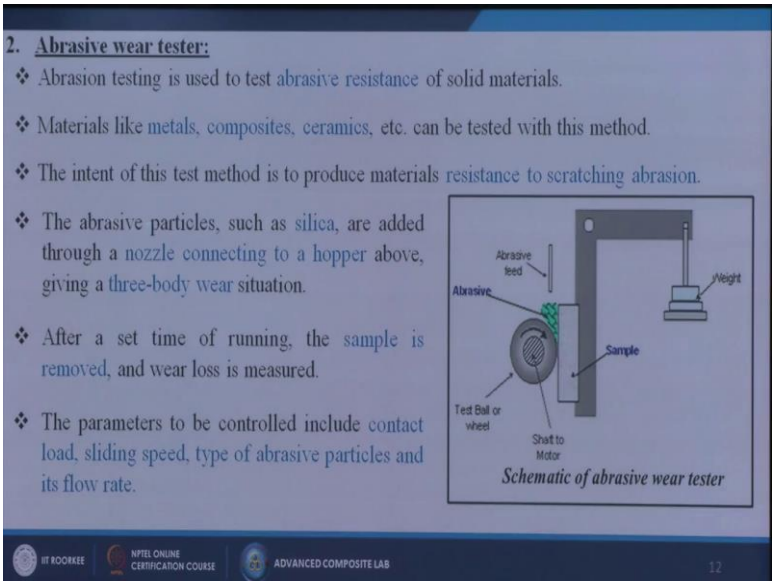

Next one is called the abrasive wear tester. So, in the abrasive wear tester; so here the example is that in abrasion testing is used to taste abrasive resistance of solid materials. So, materials like metals, composite, ceramics, etcetera can be tested with in this method. The intent of this test method is to produce material resistance to scratching abrasions. The abrasive particle such as: silica are added through a nozzle connecting to a hopper above given a three body wear situations.

So, simple we are having that sample in a square formation, then we are having one test ball or wheel which is continuously rotating onto our substrate, and in between the test ball and our samples we are having some kind of abrasive feeder through which the abrasive particles is coming and it is going in between the interface of your abrasive wheels and the test samples.

So, here also we are applying some kind of deadweight or maybe some kind of weight that the sample can give a continuous normal load onto the abrasive wheel. After a set time of running the sample is removed and wear loss is measured. The parameters to be controlled include contact notes sliding speed types of abrasive particles and its flow rate. So, our abrasive test specimens or maybe the abrasive wear tester these all are the

input parameters by which we can measure that our mat material is totally abrasive particle resistant or not.

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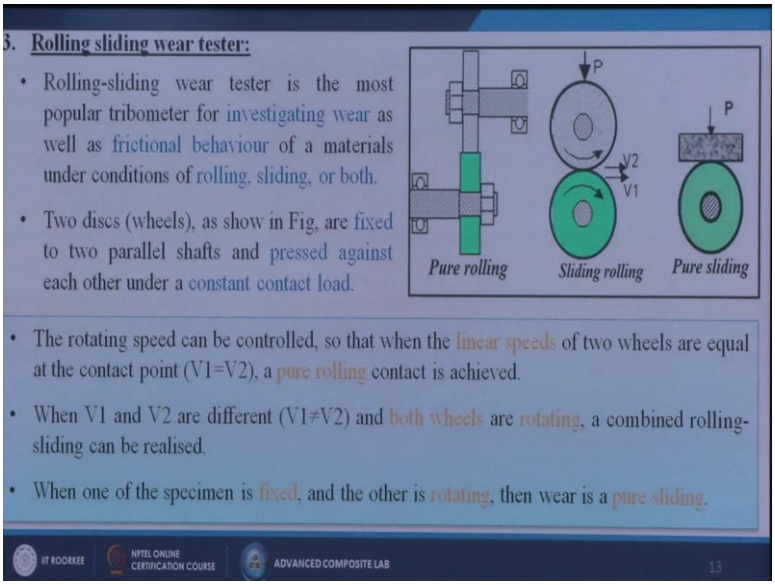

Next one is called the rolling sliding wear tester. So, here the rolling sliding wear tester is the most popular tribometer for investigating wear as well as frictional behavior of materials under conditions of rolling sliding or both. So, two disc wheels as shown in figure are fixed to 2 parallel shafts and pressed against each other under a constant contact load. Here you can see that both are rolling both are rotating so that is known as the pure rolling. Here both are sliding on one another into different velocity. And here this one is the pure sliding; one is into the static conditions just giving a normal load onto that wheel and the pure sliding is taking place. So, we can do the pure rolling, sliding rolling, and pure sliding by this particular method.

The rotating speed can be controlled so that when the linear speeds of two wheels are equal at the contact point like V1 is equal to V2 a pure rolling contact is achieved in this particular case. When V1 and V2 are different and both the wheels are rotating a combined rolling sliding can be realized. And when one of the specimens is fixed and the other is rotating then the wear is a pure sliding method. So, in that particular case one case V1 is equal to V2, another case V1 is not equal to V2, and another case the specimen one is fixed and other is rotating.

So, in this particular case generally one case V1 is equal to V2, one case V1 are not equal to V2, another case one is totally stopped and another one is rotating. So, this will give you the pure sliding mechanism.

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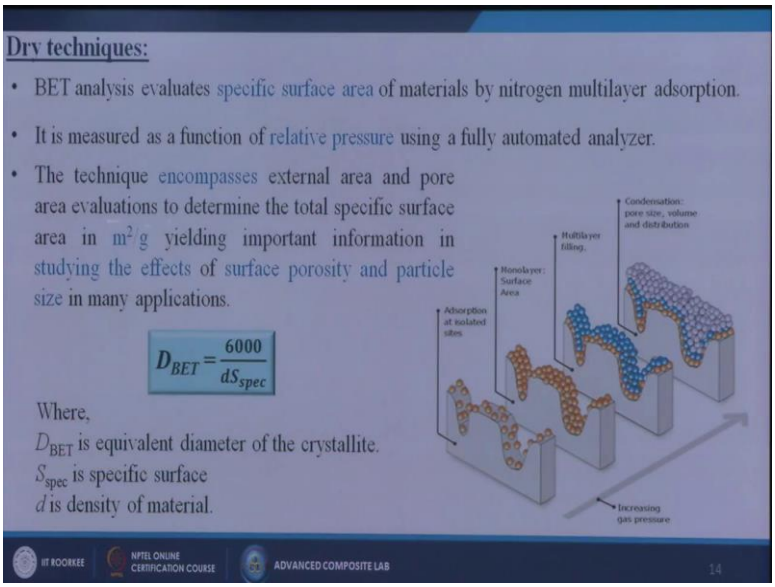

Next one is called dry techniques. In that particular dry techniques BET analysis evaluate specific surface area of materials by nitrogen multilayer adsorptions. It is measured as a function of relative pressure using a fully automated analyzer. The technique encompasses external area and poor area evolutions to determine the total specific surface area in meter square per gram. So, meter square per gram yielding important information's in studying the effects of surface porosity and particle size in many applications.

Generally this is the standard parameters where D BET is equal to 6000 divided by dS spec. Where, D BET is equivalent diameter of the crystallite, S spec is the specific surface; d is the density of that particular material. So, here absorption is isolated site from this particular case when we are increasing the gas pressure, so mono layer surface area can be seen like this. When we are giving it by the multilayer filling its looks like this, when the condensation and pore size and volume and distribution is happening then its looks like this, when we are increasing the gas pressure from lower value to the higher value.

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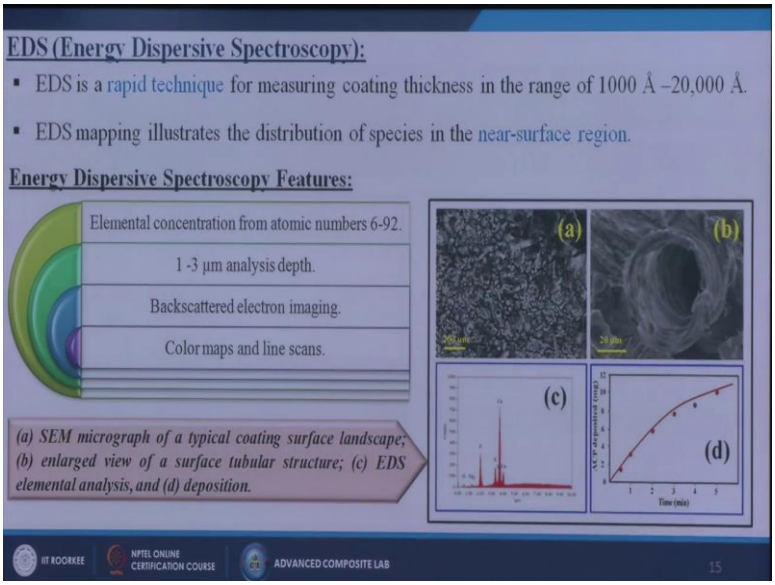

Next is called the EDS or maybe that Energy Dispersive Spectroscopy. So, in energy dispersive spectroscopy is a rapid technique for measuring the coating thickness in the range of 1000 angstrom to 20000 angstrom. EDS mapping illustrates the distribution of species in the near surface region, mainly the EDS will give you the elemental analysis of your coating materials onto the surface itself. So, energy dispersive spectroscopy features: elemental concentration from atomic number 6 to 92, 1 to 3 micrometer analysis depth backscattered electron imaging color maps and line scans.

So, here it is giving you the FESAM image also it is giving you the elemental analysis that what is the percentage of different materials are present into the coating materials. Suppose, I am giving a coating of any copper or aluminum coating then what is the percentage of aluminum as present, what is the percentage of magnesium are present, what is the percentage of oxygen may be carbon may be nitrogen are present in to the species it will give you the total elemental mapping of that particular coating materials. So, SEM micrograph of a typical coating surface landscapes, b is the enlarged view of a surface tubular structure, c is the EDS elemental analysis, and d is the deposition rate of that particular materials on to the substrate itself.

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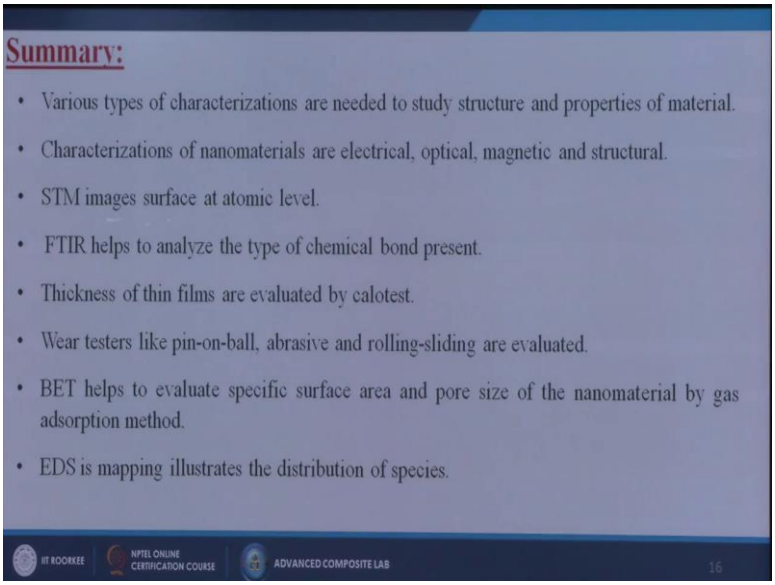

So now, we have reached up to our last slides which are nothing but summarize of this particular lecture. So, various types of characterizations are needed to study structure and properties of materials. Characterization of nanomaterials are electrical optical magnetic and structural. STM images surface at atomic level. FTIR helps to analyze the type of chemical bond present; that means, the chemical structure of that particular materials.

Thickness of thin films is evaluated by the calotest. Wear testers like pin on ball abrasive and rolling and sliding are evaluated. BET helps to evaluate specific surface area and pore size of the nanomaterials by gas adsorption methods. Simple it will absorb the gas inside the materials, by calculating that how much gas has been adsorbed inside the material we can easily measure that what is the pore size of that particular material so that we can modify or maybe we can easily measure that what is the surface roughness or may be that pore size on that particular material. EDF is mapping illustrates the distribution of the species; simple it will give you the elemental analysis of that particular coating materials.

Thank you.