Surface Engineering of Nanomaterials
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Lecture - 21
Need of Advanced Methods for Surface and Coating Testings

Hello, in this particular lecture, we are going to discuss about the different types of characterization techniques, which we need to determine that, whether the coating is proper or not. So, for that reason, we have kept this title of this particular lecture is that need of advanced methods for surface and coating testings. So, in this particular lecture, first we have to discuss that what is the need of surface and coating testing. So, in our last lectures also, you have discussed about several types of methods by which we can determine that whether coating is proper or not, whether the adhesion property of that particular material is proper or not.

But in this particular lecture, we are going to discuss about the measurement of this coating materials on the basis of mechanical testing. So, coatings are used for optical, microelectronics, packaging, biomedical and decorative applications to improve tribological logical properties like lower frictions, mechanical properties, where an abrasion resistance properties, chemical barrier to aggressive gases and optical magnetic and electrical properties of any substrate.

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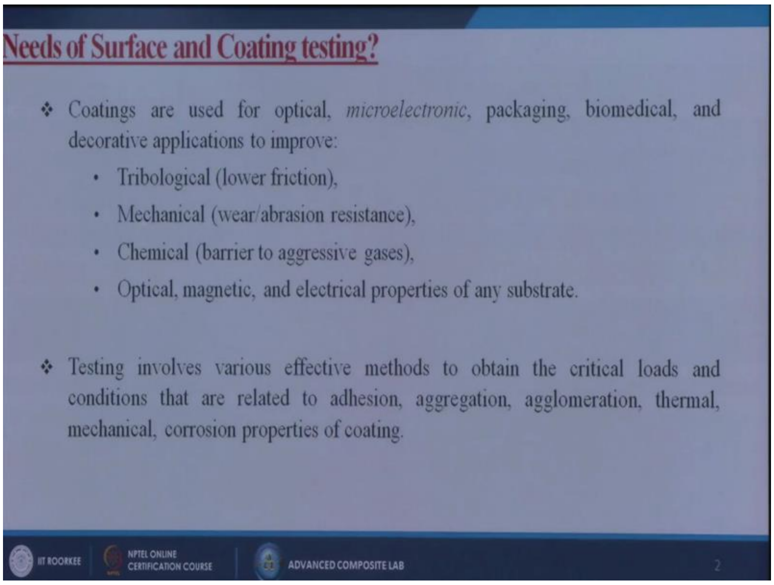

In this particular lecture, we are going to discuss all about these testing methods, how you are going to check that whether our coating is proper or not, how much strength it can carries or what is the additions in between the coating materials and the substrate so that after certain time that coating materials will not come out from the surface itself. Also testing involves various effective methods to obtain the critical loads and conditions that are related to adhesion, aggregation, agglomeration, thermal, mechanical, corrosion properties of coating.

Of course, because when you are using certain kind of materials, when you are doing the coating, then after coating we are using that materials for several purposes, sometimes we are keeping that material in to the higher temperature, sometimes we are keeping that material in to the lower temperature or maybe the minus temperature, sometimes we are applying certain kind of high impact onto that material or maybe that load onto that material or maybe sometimes we are rubbing that materials into against some kind of rough surface. So, while doing the coating we have to check that whether our coating materials can sustain all of these properties or not.

First surface coating and testing characterization methods; so, in this particular lecture or maybe this particular slide we are going to give an over an idea about that different types of characterization techniques that we can do to test the coating properties of that particular substrate is proper or not.

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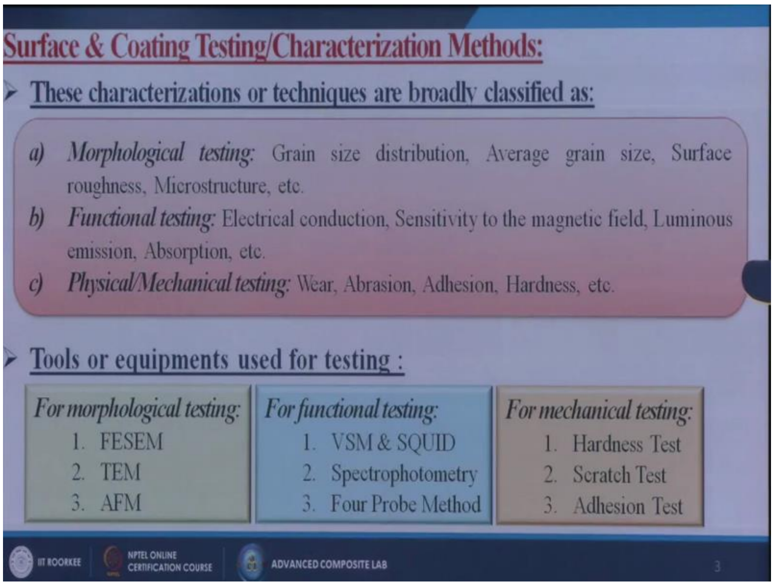

These characterized under techniques are broadly classified as first is that morphological testing; that means, grain size distribution, average grain size, surface roughness and the microstructure. Sometimes in the coating materials, we are putting certain kind of nanoparticles and that nanoparticles is that affinity that it can try to agglomerate in a particular position, they cannot disperse throughout the surface.

When we are using this kind of nanoparticles, we have to check that nanoparticles is through only dispersed onto the whole surface so that there should not be any agglomerations and we can get a homogeneous property throughout the whole material. If the nanoparticles can segregate and it can agglomerate in a particular position so at the time of applications, the nanoparticle will not give any extra property to that particular system. So, for doing this, we have to check whether the grain size of that particular nanoparticle is well distributed along the system or not, what is the average grain size because as I told already in my last several lectures that grain size distribution and the grain size average diameter is the main factor for this kind of techniques.

Because if we are using certain kind of nanoparticles which is having the micrometer size then that nanoparticle will give you some properties, but if the same nanoparticle is into the nanometer range that will give you some kind of other properties, maybe some enhanced properties in terms of maybe optical, mechanical, thermal, etcetera. So, this is the grain size is the main factor over here, then we can talk about the surface roughness and the microstructure of that particular material. When you are talking about the functional testing, some kind of electrical conduction, sensitivity to the magnetic field, luminous emissions, adsorptions, that means the magnetic properties and the optical properties of that particular material also essential for its applications.

Then some physical and mechanical testing like wear properties, abrasion properties, adhesions and hardness, these also all are the mechanical properties which we have to measure that our material can sustain a certain impact or maybe can sustain up to a certain load so that it will not break or may be that coating will be proper, there should not be any crack or pores will be generated.

Then the tools or equipment used for testings; So, there are N number of characterization techniques by which we can check these properties, but whatever we have mentioned over here, they are the prime characterizations or may be the minimum characterizations which we have to do to check that whether our coating materials or maybe the coating has been done properly. So, for morphological testing, first one is called the FESEM that is not the field emission scanning electron microscopy, second is the TEM that is transmission electron microscopy or nowadays we are using the HRTEM which is called the high resolution transmission electron microscopy and then AFM is atomic force microscopy. Then when you are talking about the functional testing, we are going for the VSM and the SQUID testing, Spectrophotometry, four probe method, when you are going for the mechanical testing, we are doing the hardness test, scratch test and the adhesion test.

One by one, we are going to discuss all these characterizations. So, first equipments used for the morphological testing that is called the field emission scanning electron microscopy or in short form it is known as the FESEM.

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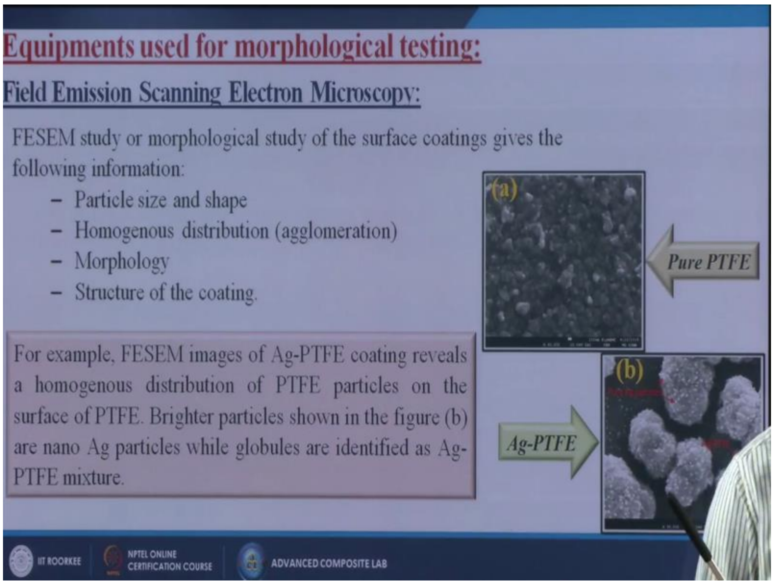

FESEM study or morphological study of the surface coatings gives the following information; particle size and shape, homogeneous distribution, is there is any agglomeration present inside the composites or not, then the morphology of that whole structure and the structure of the coating means after coating how the nanoparticle is behaving on to the material surface. So, for example, FESEM image of silver PTFE, PTFE is nothing but a one kind of polymer that polytetrafluoroethylene coating reveals a homogeneous distribution of polytetrafluoroethylene particles on the surface of the

PTFE, brighter particles shown in the figure b are nanosilver particles while globules are identified as Ag-PTFE micro structure.

Here you can see that small small globules can be seen which is nothing but the Ag-PTFE fiber and the bigger one is the pure Ag particles and the beauty of these techniques is that we can go into the deeper; that means, we can zoom the figure, we can go up to the nanometer size so that we can see the nanoparticles, we can see the any force or cracks are present or not, how these nanoparticles are distributed inside the matrix and then how the matrix is behaving. So, that is the beauty of this FESEM images.

Next is that transmission electron microscopy, the main difference in between FESEM and the TEM is that in FESEM we can go up to certain limit, but for transmission electron microscopy, we can go up to 1 nanometer range, but in FESEM we cannot go up to 1 nanometer range. So, that is the more idealistic photo or maybe the picture we can get from the TEM image.

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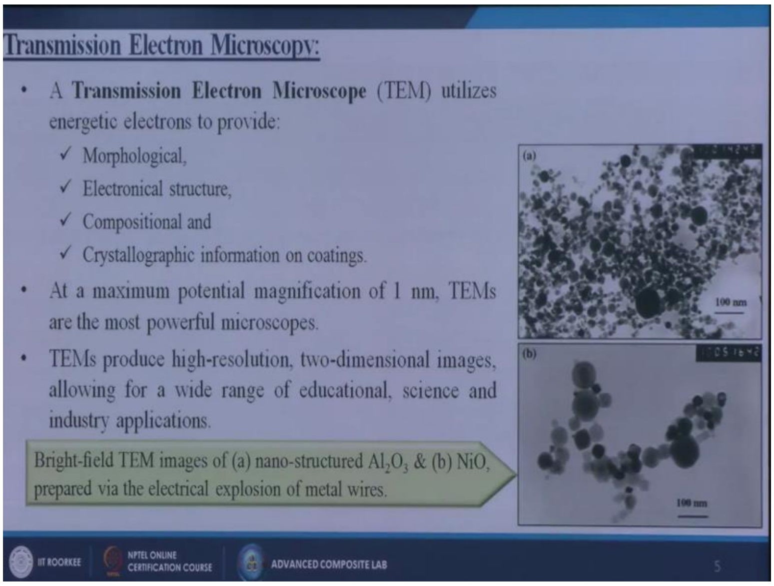

A transmission electron microscopy utilizes energetic electron to provide morphological, electronic structure, compositional and crystallographic information on coating.

Sometimes it can give you that what kind of materials also or maybe the elements are present inside the matrix or composites. So, at a maximum potential magnification of 1 nanometer, TEM are the most powerful microscopes. So, if I am using any nanoparticles that size up to 1 nanometer, easily I can detect those nanoparticles by the TEM microscopy, TEM produce high resolution, 2 dimensional images allowing for a wide range of educational science and industry applications. So, nowadays those who are working with these nanocomposites or maybe that nanomaterials this TEM, FESEM, XRD, XPS, these all are the common techniques by which we can detect about our nanoparticles, we can detect the characteristics of those nanoparticles and without these techniques or maybe without this experiments we cannot prove that we are working with the nanoparticles or maybe any kind of nanofillers.

Here this is also the example of some samples, bright field TEM images of an, a is the nanostructured alumina and b is that nickel oxide prepared via the electrical explosions of the metal waves and from this particular figure you can see that there is 100 nanometer has been written in both the figure; that means, in the 100 nanometer range, we are taking this kind of image. So, any tiny particles, whatever the particles I am using for making these composites, easily I can detect this kind of nanoparticles over there.

Next is called the atomic force microscopy, in the short form it is known as the AFM. So, AFM is mainly used to analyze the morphology and structure of the coatings.

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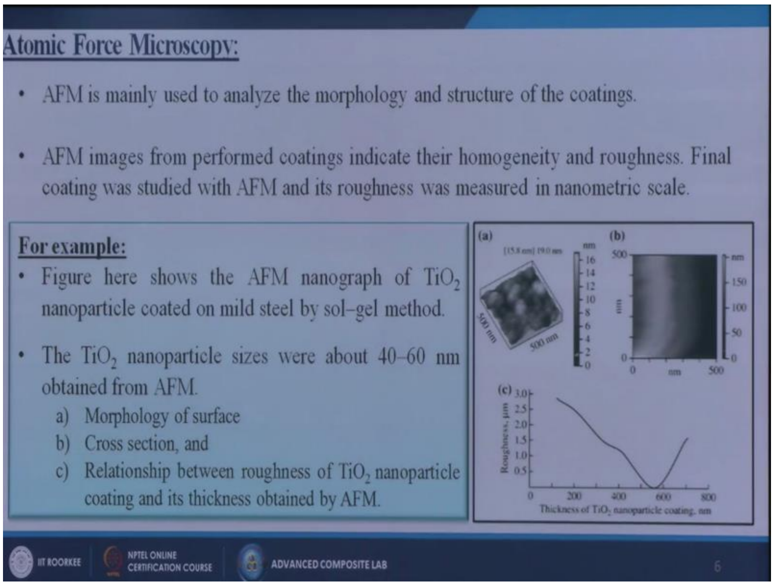

Just AFM is a good tool to measure the surface roughness or maybe that surface morphology of that particular nanocomposites because when we are making any kind of coating by simply this thing, we are thinking that, that is so smooth, but when we see it is the same materials or maybe the same components under AFM, we can see that there is some noise or maybe some there is some OAV surface is present at that particular point. So, AFM is a good tool to see the surface roughness of that particular material, not only that sometimes it can gives you that homogeneity that whether your nanoparticles is well dispersed onto your substrate or be the base that information also can be observed by this AFM study.

Here also we have given one example that is figure here shows the AFM nanograph of titanium dioxide nanoparticles coated with mild steel by the sol-gel method. So, this one is the preparation techniques, the TiO2 nanoparticles sizes were about 40 to 60 nanometer obtained from the AFM. So, in the AFM also, we can measure the diameter of that particular nanoparticle. So, by getting all the diameter we can get the average diameter of these nanoparticles that what we are going to use for our compo coating purposes. So, here it can give you the morphology of the surface, cross sections and relationship between the roughness of TiO2 nanoparticles coating and its thickness obtained by the AFM. So, these all kinds of properties, we can get from the AFM study.

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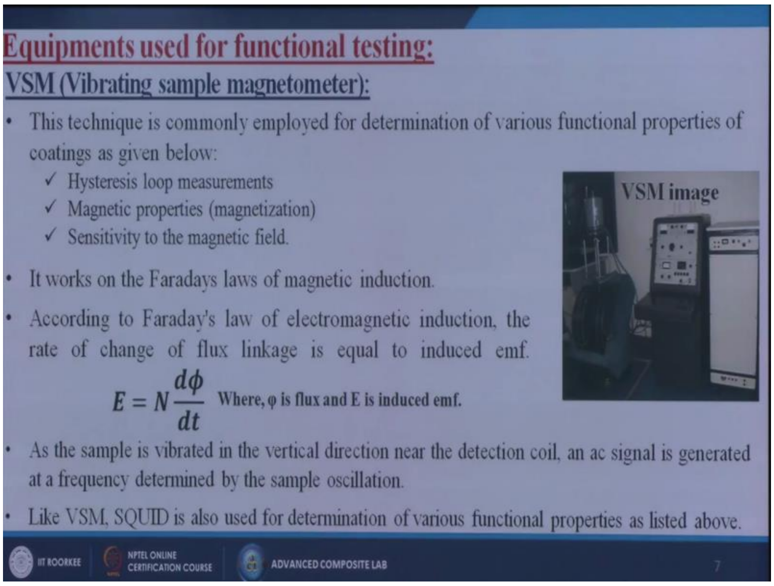

Next we are going to use some kind of functional testings. So, from functional testings the first testing is comes or may be known as VSM which is nothing, but the vibrating sample magnetometer. So, in this particular case, we are trying to measure that whether our material is magnetic or non magnetic or maybe when I am doing some kind of coating, whether it will show you some magnetic properties or not. So, by testing this one, it is commonly employed for determinations of various functional properties of coatings as given below - first one is that hysteresis loop measurements, magnetic properties or maybe the magnetization and sensitivity to the magnetic field. So, all magnet related properties, we can get it from these particular equipment.

Then it works on the Faraday's lots of magnetic induction, according to the Faraday's law, this is the very well known law. So, which is tells us that electromagnetic inductions, the rate of change of flux linkage is equal to the induced EMF. So, simple the equation is looks like this, where we have to measure the E that is nothing but the induced EMF, phi is the flux and N is the constant. So, as the sample is vibrated in the vertical direction near the detection coil and AC signal is generated at a frequency determined by the sample oscillation. Like VSM, SQUID is also used for determination of various and functional properties as listed above. So, SQUID is also the advanced versions of the VSM properties.

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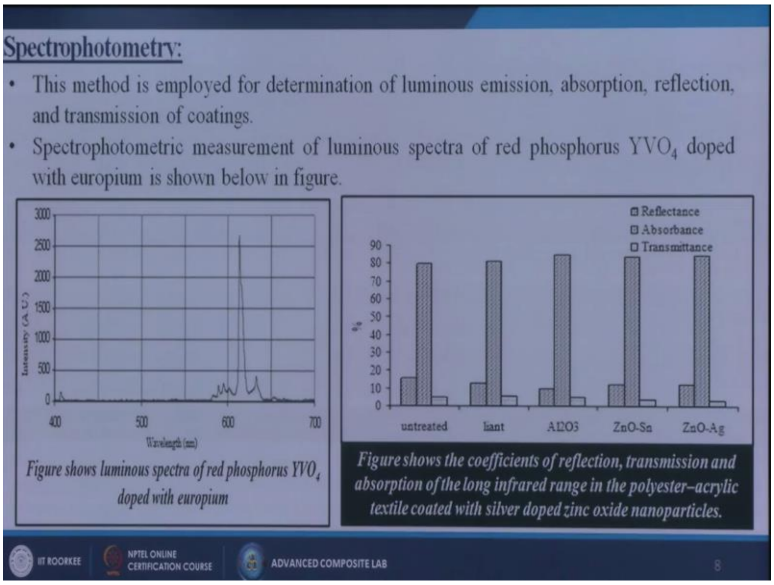

Next we are talking about the spectrophotometry. So, spectrophotometry this is also one kind of method which is employed for determination of luminous emissions absorptions reflections and transmissions of the coating. So, spectrophotometry; by using these techniques we can measure that luminous emissions, absorptions, reflections and transmissions of that particular coating materials. Spectrophotometric measurement of luminous spectra of red phosphorus yttrium vanadate doped with europium is shown below means it has been shown here.

In this particular case, we can see that in the y axis, it is having the intensity and x axis it is having the wavelength. So, this figure shows luminous spectra red phosphorus yttrium vanadate doped with europium. So, in this particular case, it is showing some kind of visible peak over there by which we can measure its luminous spectra, not only that this figure also shows some kind of coefficient of reflections, transmissions and absorption of the long infrared range in the polyester acrylic textile coated with silver doped zinc oxide nanoparticles. So, when it is untreated, when it is treated with liant, when alumina has been added, when zinc oxides and tin has been added and when zinc oxide and silver has been added. So, here the 3 bars is reflecting, one is called the reflections, one is called the absorbance and one is called that transmissions. So, it is giving the value in the percentage.

Then we are trying to use the four probe method, four probe is nothing but that we are having the 4 pin which will touch the material and last 2 pin from both the end, it will give you some kind of voltage inside your materials, but; that means, it will give you the potential difference and the middle 2 needles will measure the current. So, in that particular case simply we can measure the electrical conductivity of that particular material.

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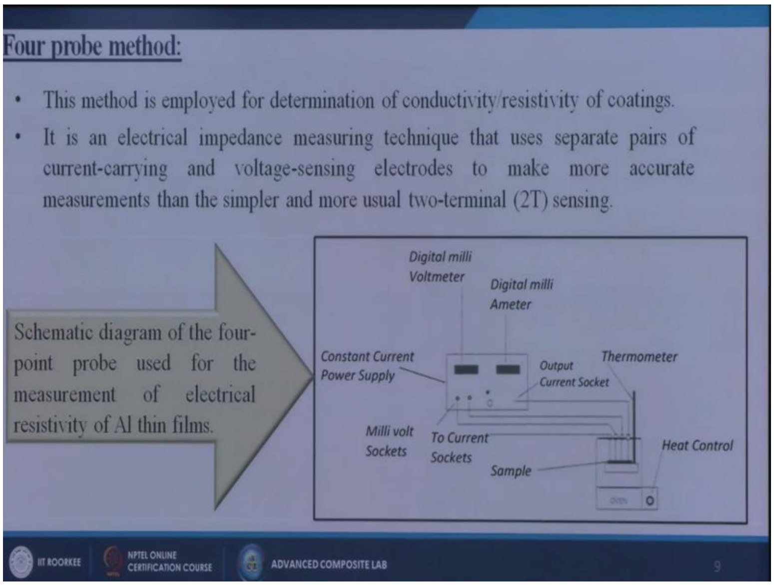

This method is employed for determination of conductivity or resistivity of the coatings. So, if I am doing some kind of coatings onto some materials and maybe that materials is non conductive, but I want to make that material conductive. So, what I will do? I will do a coating of some conducting material onto it so that the outer surface of that particular material will become like a conductive one, then why that coating is properly conductive or not, for checking that one, I can do this kind of test which is known as the four probe method. So, it is an electrical impedance measuring techniques that uses separate pairs of current carrying and voltage sensing electrodes to make more accurate measurements than the simpler and more usual 2 terminal sensing 2T. So, here is the schematic diagram of the four point probe used for the measurement of electrical resistivity of aluminum thin film. So, here we are keeping the sample over here, four pin are coming in 2 pins, we are giving the currents and 2 pins just we are measuring the volt potential difference or maybe the V.

Here, this is the circuit or maybe that this is the instrument where we are having, it will show you the voltmeter, it will show you the current or maybe the ammeter, then we are having some constant current power supply from the back, then we are having 1 milli volt socket and 1 where we are having some current sockets. So, we are keep the sample over here, not only that the total sample we can keep into some oven so that we can raise the temperature of that particular sample so that we can measure the conductivity or resistivity of that sample in particular some temperature say like 50 degree centigrade, 100 degree centigrade. So, we are having that heating arrangement over there also, not only that we are keeping the thermometer to measure the exact temperature of that particular sample.

Here, next we are going to measure the hardness. So, this comes under the physical and mechanical testing. So, whatever the coatings I have been done. So, generally this kind of techniques is required suppose I am making any kind of machine tool or maybe the cutting tool. So, where that cutting material will cut some kind of metals or maybe we are using these materials for some aerospace applications or maybe some automotive applications. So, I have to make that material more harder, but if I use that harder material as a whole maybe the weight will be more high or more weight will be more and cost will be high. Just to reduce the cost and just to reduce the weight what we are doing? We are taking any kind of light material and then from outside, we are coating by some hard material so that it can give the same results or maybe that same properties like the bulk materials. So, for the testing of hardness we are doing some tests what are those?

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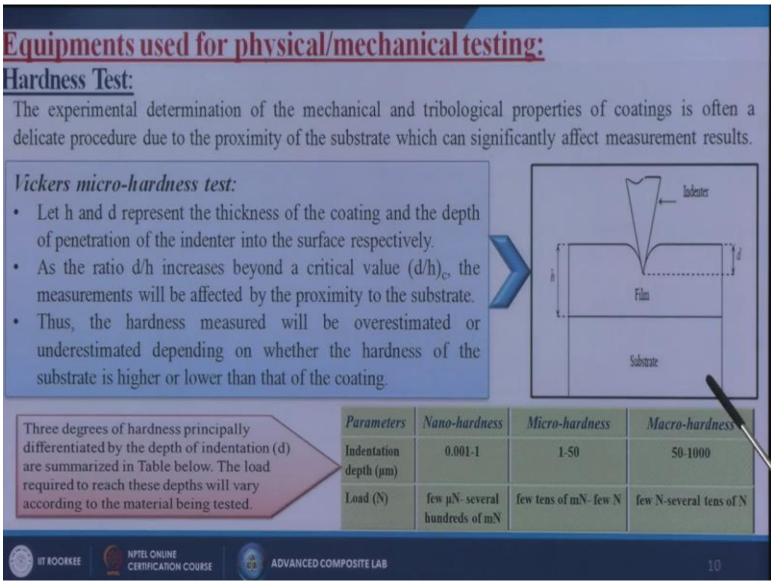

First one is called the Vickers micro-hardness test. So, here in this particular case, we are having that substrate; then we are putting certain kind of film over there. So, let h and d represent the thickness of the coating and the depth of penetration of the indenter into the surface respectively. So, here this is the coating thickness, this is our substrate. So, we are having some indenter. So, now, the total thickness of the film is small h, then I am giving a constant load onto the indenter so that the indenter can goes into the thin film so suppose it goes up to small d.

Next, as the ratio d by h increases beyond a critical value, d h whole c the measurement will be affected by the proximity of the substrate thus the hardness measured will be overestimated or underestimated depending on whether the hardness of the substrate is higher or lower than that of the coating. So, from these particular techniques, we can measure that how much my indenter is going inside the coating material. So, by calculating this value, we can easily say that what is the hardness of our particular coating materials? So, 3 degree of hardness principally differentiated by the depth indentation d are summarized in table, the load requires to reach these depths will vary according to the material being tested.

Here that, parameters is indentation depth micrometer and whatever the load we are giving that is capital N. So, for nanohardness generally indentation depth is 0.001 to 1 micrometer and load will be few micro Newton to several 100s of mega Newton then micro hardness is 1 to 50, few 10s of milli Newton to few Newton and macro hardness is 50 to 1000, few Newton to several 10s of Newton. So, this is the standard parameter of these particular techniques.

Then we can taste the scratch; that means, as I told in our earlier lecture also, then when you are using these kinds of coatings we are using into the environment. So, may be some dust particles or may be some while doing some other applications or may be some kind of usage that may be some materials can rub onto that coating material. So, what is the property of that particular coating material in terms of scratching we can do this kind of scratch test.

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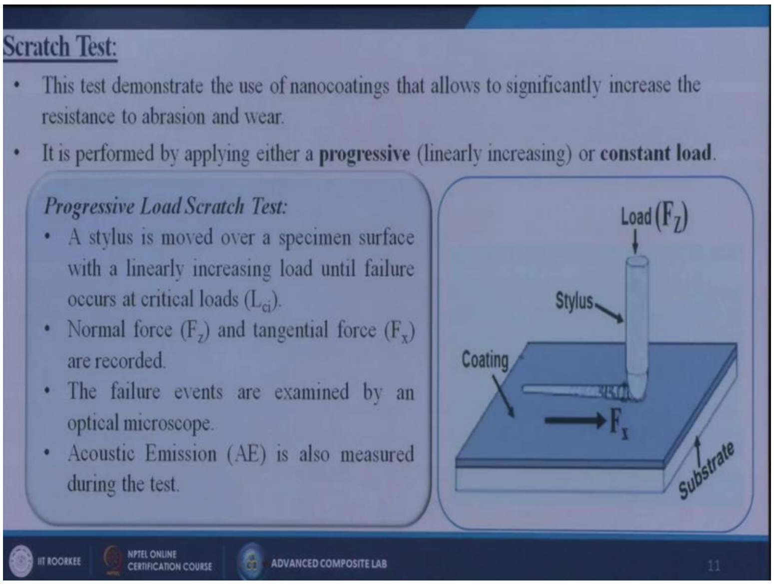

These tests demonstrate the use of nanocoatings that allows to significantly increase the resistance to abrasions and wear, it is performed by applying either a progressive, linearly increasing or a constant load.

Here, we are trying to do that I am having some needle, I am having the substrates, either I can put a constant load then do the scratching or maybe slowly slowly with time I can increase the load. So, first one is known as the constant load and the second one is known as the linearly increasing. So, progressive load scratch test is stylus is moved over a specimen surface within linearly increasing load until failure occurs at critical loads. Normal force and the tangential force are recorded. The failure events are examined by an optical microscope. So, whatever the scratch it is forming by seeing into the optical microscope, we can easily check that whether my pin, how much depth it has been gone, whether the virgin surface of our substrate has come out or not.

Then Acoustic Emission is also measured during this test. So, this is about the scratch test, then we are trying to make or measure the testing of additions because I am telling you several times that when we are doing the coating of particular nanocomposites on to the substrate so there should be a affinity of that particular substrate that it can pull the nanocoatings towards it otherwise what will happen the nanocoatings at a certain time, it will go up that pulling is nothing but the additions in between your coating materials and your substrate.

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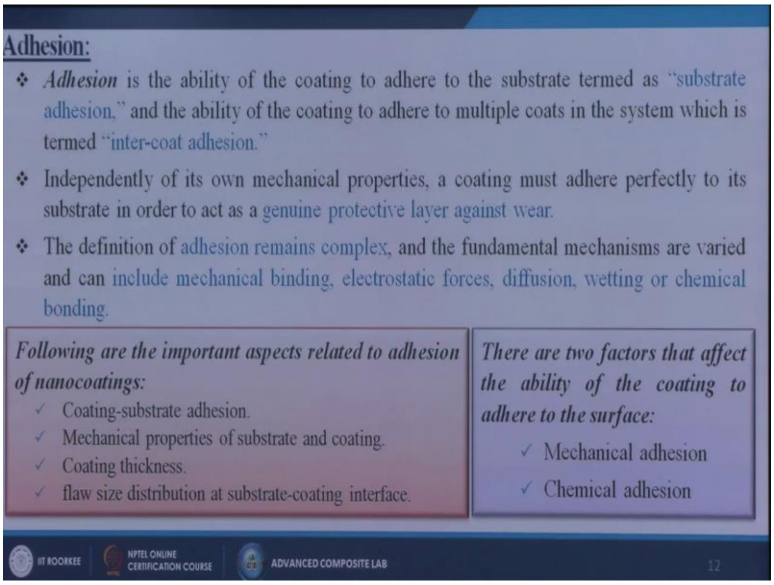

Here adhesion is the ability of the coating to adhere to the substrate termed as substrate adhesion and the ability of the coating to adhere to multiple courses in the system which is termed as the intercoat additions. So, simple I am having the substrate, if I go for a 1 pass or maybe the 1 layer coating so that is known as the additions or maybe that substrate additions and if I go for 2 layer, 3 layer, then in between the layer, whatever the additions it will known as intercoat additions, independently of its own mechanical properties a coating must adhere perfectly to its substrate in order to act as a genuine protective layer against wear.

The deflection of adhesion remains complex and the fundamental mechanisms are varied and can include mechanical binding, electrostatic forces, diffusion, wetting or chemical bonding. So, these all are the properties by these all are the main addition properties by which we can measure or for which we can measure this kind of testing. So, following are the important aspects related to adhesion of nanocoatings are coating substrate additions, mechanical properties of substrate and coating, coating thickness and flow size distribution at substrate coating interface.

Now, there are a 2 factors that affect the ability of the coatings to adhere to the surface, one is called the mechanical adhesions, another one is called the chemical adhesions. So, the adhesions when you are doing, it is subdivided or maybe divided into 2 parts, one is called the mechanical adhesions and other one is called the chemical adhesions and these all are the parameters or may be that important aspects that why we are doing the testing of adhesions for nanocomposite coating.

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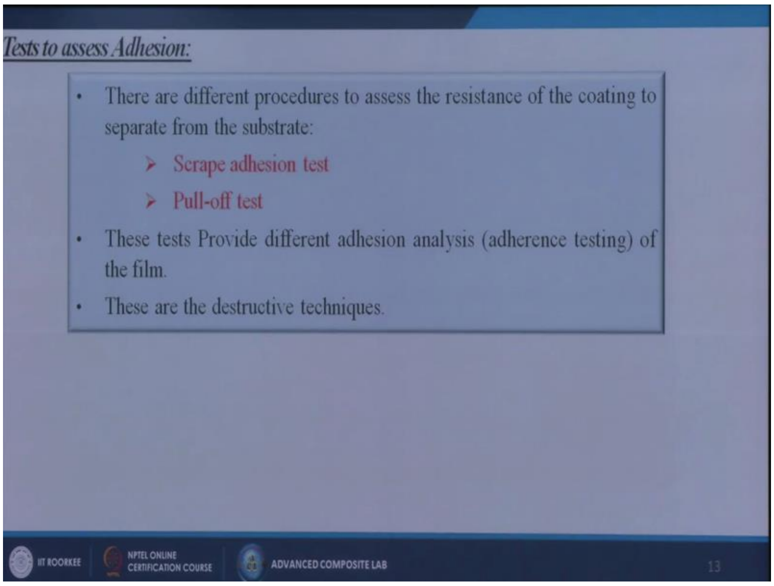

Test to assess adhesions; now we know that what is adhesions, then now is that how to measure these properties when we are doing the coating. So, these there are different procedures to assess the resistance of the coating to separate from the substrate, first one is known as the scrap adhesion test and next one is called the pool of tests. These 2 are the most versatile experiments or characterizations by which we can check whether the adhesions in between the substrate and in between the composites, in nanocomposites or maybe the nanocoatings are good or not.

These tests provide different adhesion analysis, adherence testing of the film, these are the destructive techniques; that means, when we are doing this kind of testing, either we have to destroy our coating materials. So, due to that we have to break our coating materials or maybe we have to destroy our coating thickness or maybe that coating lines so that we can check whether that material is easily come out from the substrate or maybe it can stick with the substrate itself.

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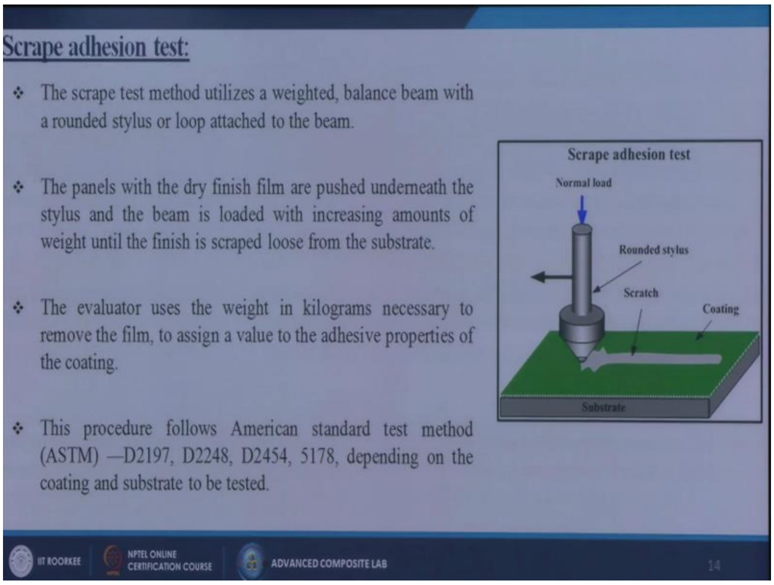

First one is called the scrap adhesion test; in the scrap test method utilizes a weighted balance beam with a round stylus or loop attached to the beams. So, it is known as the stylus in which we are putting a constant normal load either that load may be constant or may be it can be progressive and here so, we are starting the experiment from here then we are giving motions into these directions so, what will happen? This stylus or maybe that tip will rub onto the coating materials.

Then the panels with the dry finished films are pushed underneath the stylus and the beam is loaded with increasing amounts of weight until the finish is scrapped loose from the substrate. So, we have to take out some coating materials from our substrate itself that is our main motto or maybe that is the main motto of this particular testing. The evaluator uses the weight in kilograms necessary to remove the film to assign a value to the adhesive properties of the coating, this procedure follows American standard test method like ASTM D2197, D2248, D2454, 5178 depending of the coating and the substrate to be tested; that means, when I am using this stylus, continuously I am increasing the load or maybe that N onto that substrate. So, that slowly slowly it can increase its load and it can rub the substrate so that at the ultimate that coating materials can come out from the substrate itself. So, this is known as the scrap addition test.

Next is known as the pool of taste. So, in that first case we have done the scratching onto that material, in that particular case we are doing something different.

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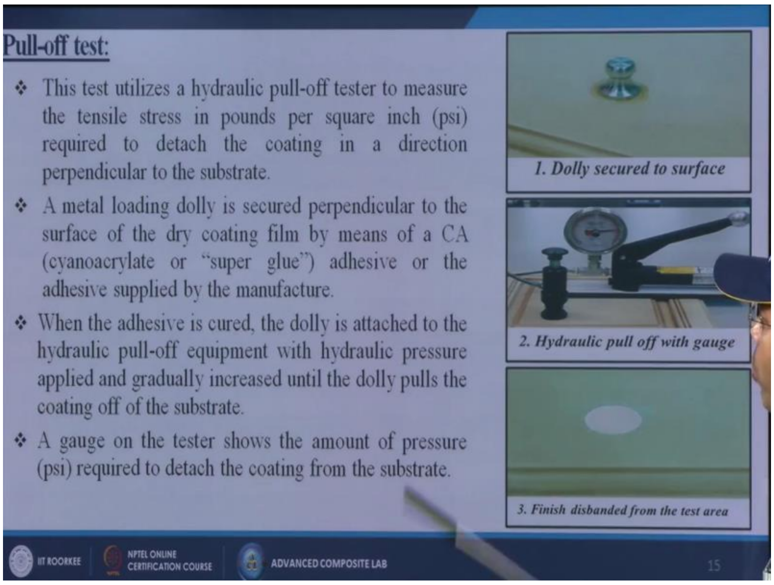

What is this? This test utilizes a hydraulic pool-off tester to measure the tensile stress in pounds per square inch psi required to detach the coating in a direction perpendicular to the substrate. A metal loading dolly is secured perpendicular to the surface of the dry coating film by means of CA, CA is nothing but the cyanoacrylate or maybe the super glue adhesives or the adhesive supplied by the manufacture.

Simple, on the surface itself we are putting one dolly or maybe one kind of small materials so that it can stick with the coating materials and then we are applying certain kind of glue over there so that it should not easily come out then we are pulling this dolly by some kind of hydraulic machines or maybe that hydraulic pull so that while pulling it can take out some kind of coating materials from the substrate itself.

When the adhesive is cured the dolly is attached to the hydraulic pull up equipment with hydraulic pressure applied and gradually increased until the dolly pulls the coating of the substrate. A gauge on the tester shows the amount of pressure required to detect the coating from the substrate. So, this is the gauge which will give you the value that how much pressure is required to take out the dolly from the substrate itself. So, by just getting that value, we can see that what is the tensile test in between the coating materials and in between the substrate itself?

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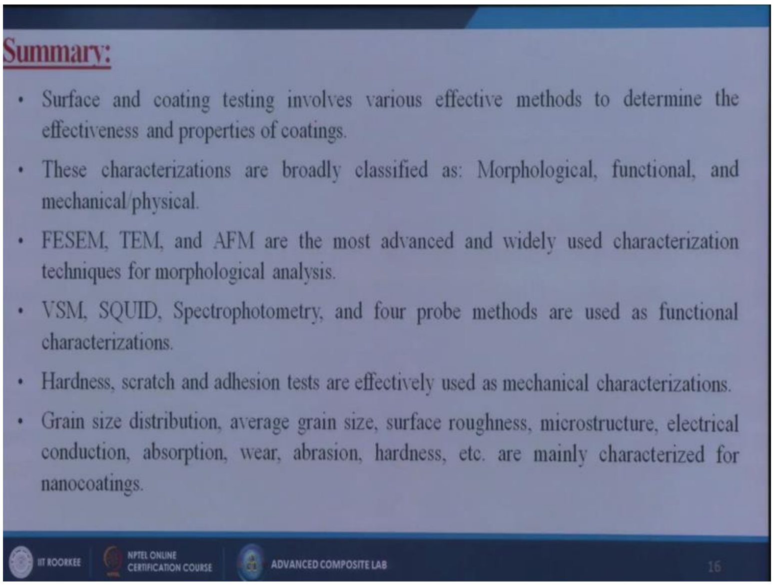

Now we have come to the last slide of this particular lecture is called a summary. So, in summary we have discussed about the surface and coating testing involves various effective methods to determine the effectiveness and properties of coatings, these characterizations are broadly classified as morphological, functional and mechanical or physical we have discussed about. So, many types of testing like FESEM, TEM, AFM and not most advanced are widely used characterization techniques for morphological analysis, we have discussed about the VSM, SQUID, Spectrophotometry and the four probe method for the functional characterization, we have discussed about the hardness scratch and addition tests that are effectively used as mechanical characterizations.

Then we have also discussed about the grain size distribution, average grain size, surface roughness, microstructure, electrical conduction, absorptions, wear, abrasion, hardness etcetera are mainly characterized for nanocoating. So, these all are the techniques are widely used to check whether our coating is proper onto our surface or not, if the coating is not proper then it can give the lower properties. So, by checking this one, we can see that whether the coating and the substrate is sticking together or not and how much that coating is giving the better properties and whether these properties or maybe these coating materials can sustain for a longer time.

Thank you.