Surface Engineering of Nanomaterials
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Lecture – 23
Size Effect in Electrochemical Properties of Nanostructured Coatings

Hello. In this particular lecture actually we are going to discuss about the size effect for the electrochemical applications or may be that electrochemical properties of that particular coatings. In our last lecture we have given an a glimpse of different types of applications where the size dependency actually creating some miracles so that means, when you are reducing the size of that particular nanoparticles, we have shown that in terms of mechanical properties, in terms some electrical properties may be optical properties or may be some other properties the properties of those materials has been changed drastically. So, in this particular case actually we are going to discuss that size effect for the electrochemical properties of nanostructured coatings.

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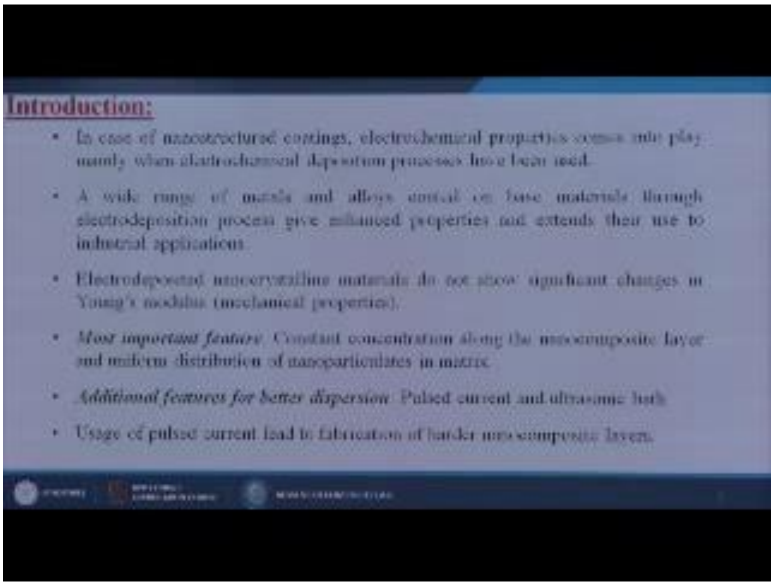

So, when we are talking about the introductions or may be introductory of that particular topic, so in that particular case, the nanostructured coatings electrochemical properties comes into play mainly when electrochemical deposition process have been used.

So, here the main aim of this particular lecture is that we will discuss about the electrochemical depositions or maybe some kind of electrochemical plating, in terms of size dependency of those nanoparticles. A wide range of metals and alloys coated on best materials through electro deposition process give enhanced properties and extend their use of industrial applications. So, this is the main motto of this particular lecture. Then the electrodeposited nanocrystalline materials do not show significant change is in young modulus. So, when you are talking about these kind of electrochemical depositions or may be the electrochemical plating or may be some kind of electrolyzed is or maybe that electrolyses plating, in this particular case the properties will only enhance or maybe change in terms of electrochemical, it will not hamper any kind of material mechanical properties not only that it is not going to increase or decrease the mechanical strength of that particular materials. So, most important feature is that, constant concentrations along the nanocomposites layer and uniform distribution of nanoparticulates in matrix.

Additional features for better dispersion: pulsed current and the ultrasonic bath; usage of pulsed current lead to fabrication of harder nanocomposites layers. So, it depends that what type of synthesis techniques actually we are adapting. So, depending upon that our synthesis techniques, the total nanostructure composites or may be that nanostructure coatings is, may be, can give the different properties.

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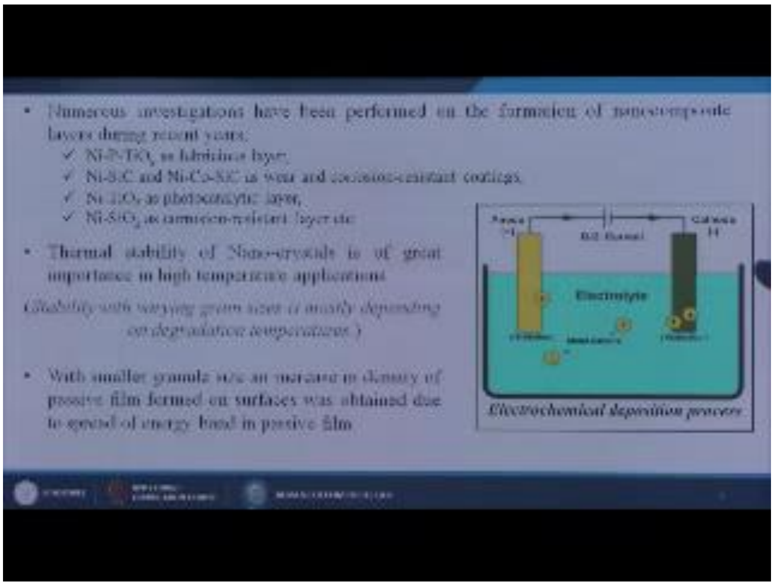

So, there are numerous investigations has been performed or maybe has been done on the formation of nanocomposites layers during recent years like nickel, phosphorus, titanium dioxide as lubricious layer, nickel silicon carbide and nickel cobalt silicon carbide as wear and corrosion resistant coatings, nickel titanium dioxide as photo catalytic layer, nickel silicon dioxide as corrosion resistant layer etcetera.

So, from these particular things just we are trying to show that when we are trying to change the material shapes or may be that material composition, the total properties of that particular substrate is going to be changed. So, thermal stability of nanocrystals is of great importance in high temperature applications. Stability with varying grain size is mostly depending on degradation temperature. So, that will come in our next subsequent slides. So, with smaller grain will size and increase in density of passive flame formed on surface was obtained due to spread of energy band in passive film. So, that is one of the vital parameters or maybe that vital logic of these particular techniques.

So, here this is the some kind of schematic illustrations. So, that we have already gone through earlier also, but for your remembrance I am telling you it once again. So, we are taking some kind of electrolyte, that electrolyte should be that what kind of materials we are going to coat, based on that you have to choose the same electrolyte of that particular metal ions. So, suppose I am going to coat our material by the copper, then may be some kind of copper sulphate solutions or may be that some copper related materials we are going to put as electrolyte over there and then we are trying to put our material on to the cathode side. So, what will happen? When we will generate some kind of potential difference in between these two electrodes, the copper sulphate it will divided into two parts one is called the copper, another one is the sulphate and then the copper will go and it will stick or maybe it will deposit on to your cathode or may be on to our substrate materials. So, like this way we can do the coating techniques on to our substrate itself. So, that is known as the electrochemical deposition process or sometimes we are calling it as a electroplating too.

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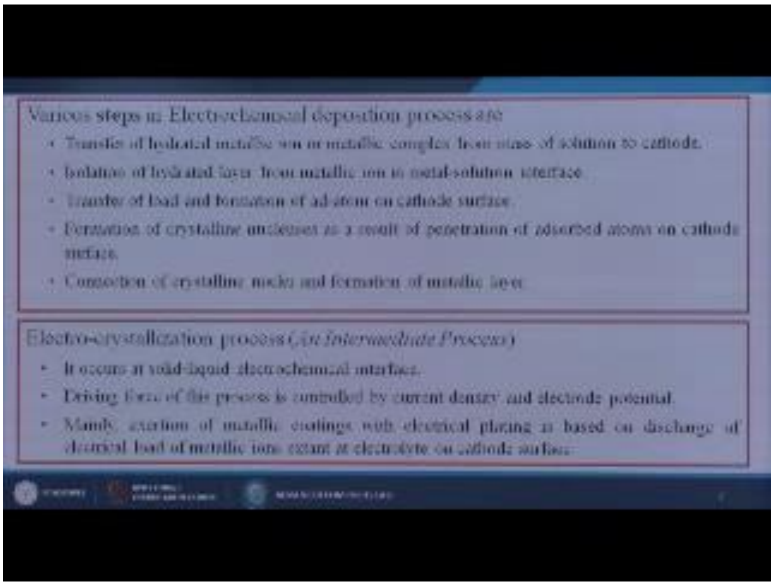

So, there are various steps in electrochemical deposition process which are transfer of hydrated metallic ion or metallic complex form mass of solutions to cathode already I have explained in last slide. Isolation of hydrated layer from metallic ion in metal-solution interface; transfer of load and formation of ad-atoms on cathode surface; formation of crystalline molecules nucleus as a result of penetration of adsorbed atoms on cathode surface; connection of crystalline nuclei and formation of metallic layer. So, these all are the steps actually it is occurring one by one when we are trying to do this kind of electrochemical depositions.

Then that is also a one intermediate process which is going on in between these. So, that is known as the electro crystallization process, it occurs at solid liquid electrochemical interface. So, when we are dipping our substrate into the electrolytic solutions, actually that time this kind of reaction or may be these kinds of techniques is going on.

Next driving force of this process is controlled by current density and electro potentials; mainly exertion of metallic coatings with electrical platting is based on discharge of electrical load of metallic ions extend at electrolyte on cathode surface. So, that is known as the intermediate techniques before finishing the electro depositions, generally this is occurring at the first instance.

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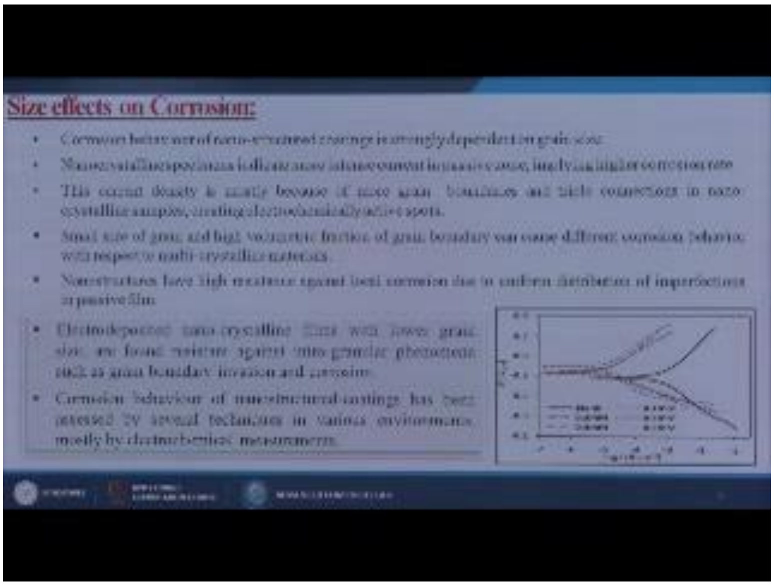

Then we are going to show you that when we are talking about the size then when we are reducing the size of our crystallites, how it is affecting the corrosion properties. So, corrosion behavior of nano-structured coatings is strongly dependent on grain size. Nano crystalline specimens indicate more intense current in passive zone, implying higher corrosion rate. So, that is the principle behind this technology. This current density is mostly because of more grain boundaries and triple connections in nano crystalline samples, creating electrochemically active spots. Small size of grain and high volumetric fraction of grain boundary can cause different corrosion behavior with respect to multi-crystalline materials. Nanostructures have high resistance again against local corrosions due to any form distribution of imperfection in passive film. So, this is the actually the main logic or main technology behind this techniques.

So, here we are given one examples. So, electrodeposited nano crystalline films with lower grain size, are found resistant against intra-granular phenomena such as grain boundary invasion and corrosion properties; corrosion behavior of nanostructured-coatings has been assessed by several techniques in various environments mostly by the electrochemical measurements. So, the empirical testing is that when we are trying to check the corrosion properties simply we are putting that material into some electrolyte solutions, we are seeing that how the chemical reaction is taking place, how much material in a single time or may be into some stipulated time how much material is removing from the surface itself by doing this kind of techniques, by doing this kind experiments we can check whether our material is corrosion proof or not.

Here also one empirical examples that here we have used different sizes of this particles, then we have measured the voltage verses current and then we have shown that the how the corrosion properties is changing when we are trying to change the particle size of that particular nanoparticles.

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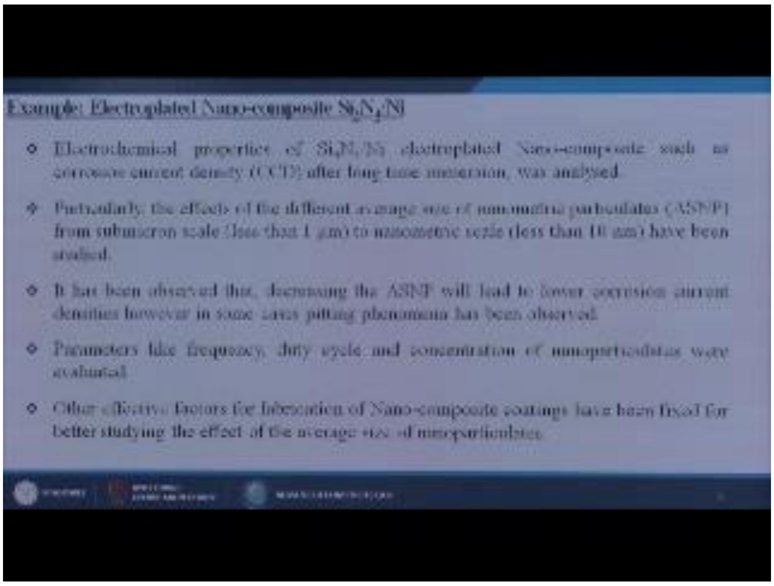

Then here we have given one examples that electroplated nano composites of silicon nitride and nickel composite. So, electrical properties of silicon nitride and nickel electroplated nano-composite such as corrosion current density after long time immersions, was analyzed.

So, as I told already in my last lecture the or may be the last slide that when we are dipping that material into the electrolyte just we are giving some time to react our substrate with the electrolyte, then we are trying to measure the reaction time then how much material actually it is removing from the substrate itself so by doing taking this value, then we are having the calculations or may be the empirical formula where we have putting those values and simply we are calculating that how much material is corroding at that particular environment. Particularly the effects of the different average size of nanometric particles particulates ASNP, from submicron scale less than 1 micro meters and nanometric scale, less than 10 nano meters have been studied. It has been observed the decreasing the ASNP will lead to lower corrosion current densities however, in some cases pitting phenomena has been observed.

Pitting phenomena is nothing but the it is one kind of empirical phenomena, suppose I am having a several balls and if I release those balls one by one, the balls will simple from a certain height it will fall on to that substrate or may be onto the floor and it will hit; that kinetic energy whatever that ball will achieve simple that kinetic energy will directly go on to the floor itself. So, like this way when we are realizing that electron that electron bombardment is directly coming and it is hitting our substrate material continuously. So, that is known as the one kind of pitting phenomena over here. Parameters like frequency duty cycle and concentration of nanoparticulates were evaluated; other effective factors for fabrication of nano composite coatings have been fixed for better studying the effect of the average size of the nanoparticulates.

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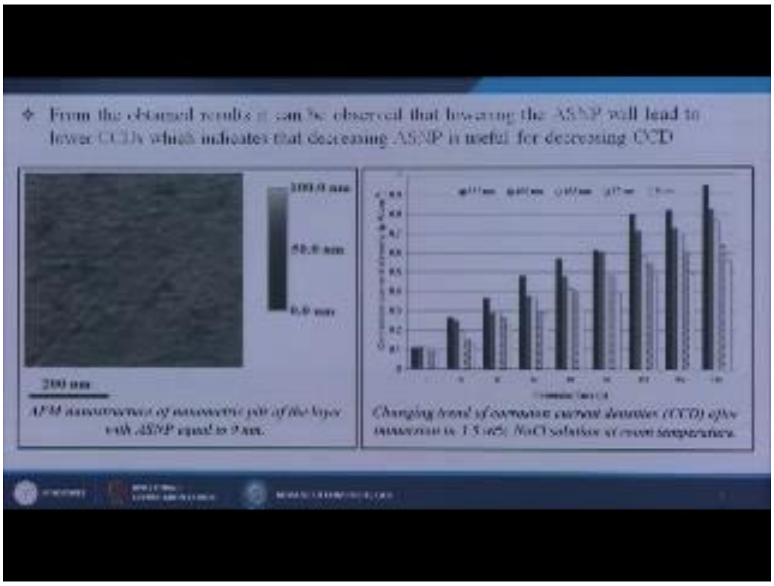

So, here we have given several examples that how that size factor is affecting our corrosion properties; from the obtained results it can be absolved that lowering the ASNP will lead to lower CCDs, which indicates the decreasing ASNP in useful for decreasing the CCD.

So, here we have shown one kind of AFM atomic force microscopic image that nanometric pits of the layer with ASNP equal to 9 nanometer, from these particular figure you can see that there is some kind of penetrating zone or may be some kind of regious also some kind of small small block holes, which actually has been occurred due to their pitting phenomena by the electrons or may be by that particular ions. And the right hand side we have shown that if we increase that immersion time, then what will be the corrosion current density actually taking place and not only that we are changing the particular size also. So, first we are going for a smaller size then slowly, slowly we are increasing the particle size also; like that black one is giving you the 832 nanometer, then the 499 nanometer, 168 nanometer, 72 nanometer, 9 nanometer. So, when we are seeing into the high immersion time, we can see that corrosion current for a smaller particle size is much lower than the bigger one that is 832 nanometer particle sizes.

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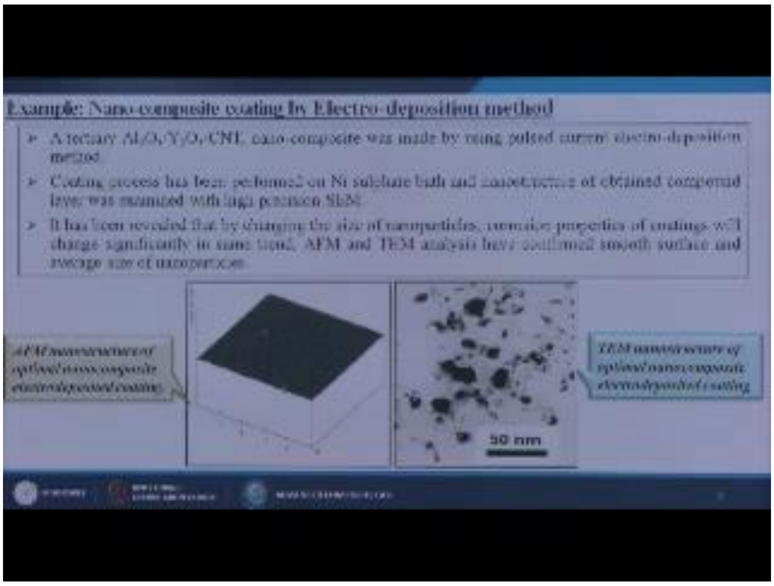

Here is also an example that nano composite coating by electro deposition method. So, a tertiary alumina, yttrium oxide and carbon nano tube nano composite was made by using pulsed current electro deposition method. Coating process has been performed on nickel sulphate bath and nanostructure of obtained compound layer was examined with the high precession atomic force microscopy. So, in that particular case here we have done transmission electron microscopy and the atomic force microscopy together. So, in the atomic force microscopy it has been given what is the surface (Refer Time: 13:25) of that particular coating materials and the transmission electron microscopy has been given that the actual morphology of that particular nano particles on to the substrate itself.

So, here in this particular case we have done the SEM, we have done the TEM also, but here only we have shown the transmission electron microscopy image of that particular sample. It has been revealed that by changing the size of nanoparticles, corrosion properties of coating will change significantly in same trend. AFM and TEM analysis have confirmed smooth surface and average size of the nanoparticles itself.

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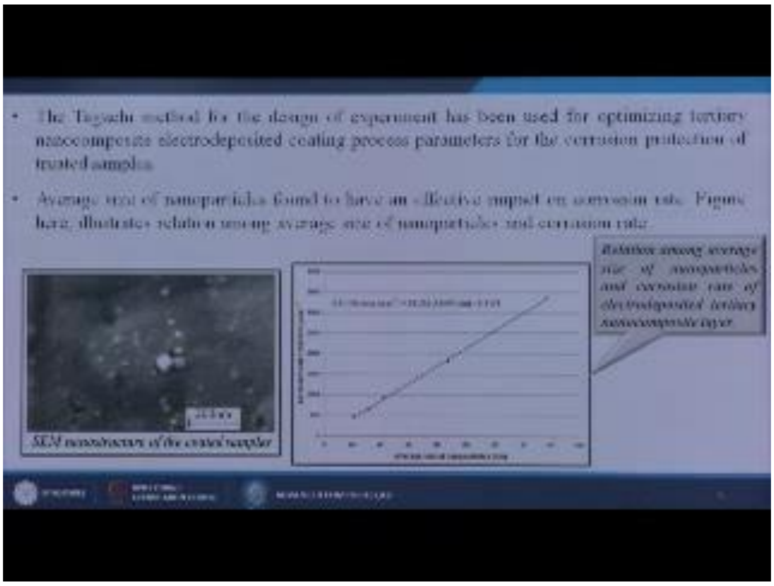

Then the Taguchi method for the designing of experiment has been used for optimization tertiary nano composite electro deposited coating process parameter, for the corrosion protection of treated samples; because we are having several nanoparticles average nanoparticles size. So, we are trying to use the Taguchi method by which we can optimize the particle size diameter or may be all the input parameters, so that we can uniformly use all the particles size diameter or maybe we can rather we can put all the input parameters over there. Average size of nanoparticles found to have effective impact on corrosion rate.

Figure here illustrates relation among average size of nanoparticles and the corrosion rate. So, in this particular figure we are seeing that there is some kind of scanning electron microscopy nanostructure of the coated samples. So, from that particular figure we can easily measure the particle size of that particular composites and not only that here in that particular graph we are showing into the x axis the average size of the nanoparticles and the y axis it is showing the corrosion rate. So, here we are trying to show you that how we are trying to increase the nano particle size and how the corrosion rate is increasing; that means, if we are going to reduce the particle size of that particular nano composites or may be the nano fillers automatically the corrosion rate will be decreased.

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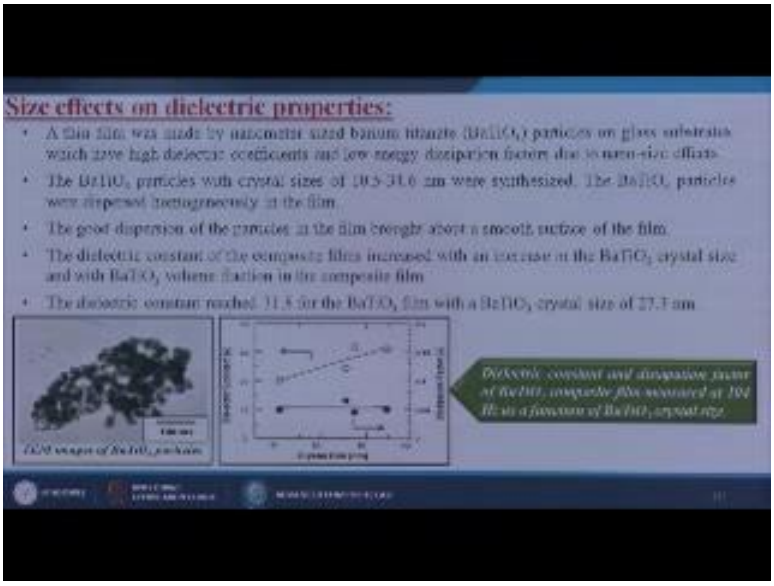

Next we are talking about the size effects on the dielectric properties. So, when you are using this kind of material for the semiconductor purpose or may be the electronic purpose, these dielectric properties are the most vital parameters that we have to check whether our material can be electrical conducive or not. So, a thin film was made by nanometer sized barium titanate, particles on glass substrates which have high dielectric coefficient and low energy dissipation factors due to nano size effects. The barium titanate particles with crystal size of 10.5 to 34.6 nanometers were synthesized. The barium titanate particles were dispersed homogenously in the film. So, from the tem image we can see that barriers titanate has been homogenously dispersed among the matrix itself.

Then when the good dispersion we have achieved in the film brought about a smooth surface of the film. The dielectric constant of the composite film increased with an increase in the barium titanate crystal size and with barium titanate volume fraction in the composite film. The dielectric constant reached from 31.8 for the barium titanate film with a barium titanate crystal size of 27.3 nanometer; in this particular case we can see that when we are increasing the crystal size, the dissipation factor is not changing or may be changing in a particular case in a very minimal value, but when we are talking about the dielectric current, the dielectric current is rapidly changing with the increasing of the crystal size, when the crystal size was around 10, the dielectric constant was almost 20, but when it has reached up to 35, it values also goes up to the 30, so that means, the particle size here the increasing in particle size here clearly reflect that the dielectric constant of that particular material is changing.

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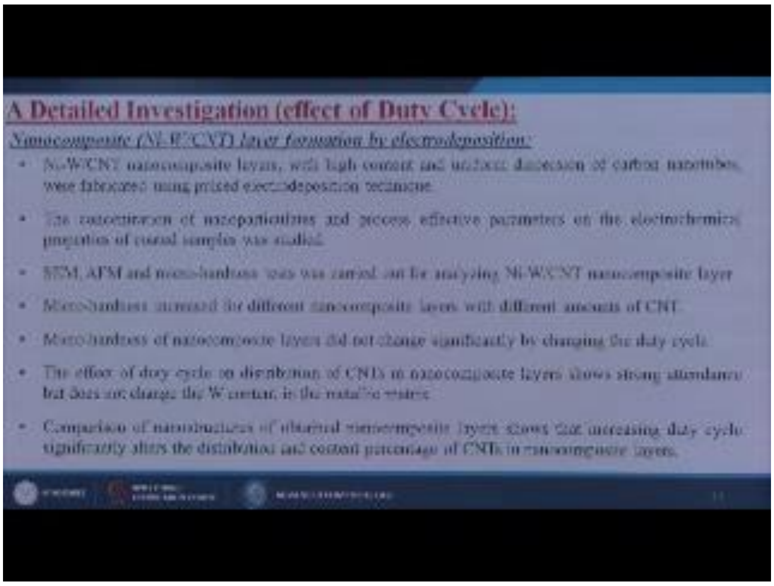

Then also we have done some kind of detailed investigation about the duty cycle; duty cycle is a process parameter and electrochemical deposition process by which we can change that our material can store some kind of energy or not or may be how it can react that when I am applying certain kind of voltage or current to that particular material. So, nanocomposites here we have prepared that nickel with tungsten and CNT composite layer formations by electrodeposition techniques.

So, nickel tungsten CNT nano composite layers with high content and uniform dispersion of carbon nano tubes were fabricated using pulsed electro deposition techniques, this is also a one kind of advanced deposition techniques, that deposition techniques already we have discussed in our previous lectures. The concentration of nano particulates and process effective parameters on the electrochemical properties of coated samples was studied.

SEM, AFM and micro hardness test was carried out for analyzing the nickel tungsten carbon nanotube, nano composite layer. Micro-hardness increased for different nanocomposites layers with different amount of CNT. So, here actually we are changing the loading of the CNT, into this composite system. Micro-hardness of nanocomposites layers did not change significantly by changing the duty cycle. The effect of duty cycle on distribution of CNTs in nano composite layer shows strong attendance, but does not change the tungsten content in the metallic matrix. Comparison of nanostructures of obtained nanocomposites layer shows the increasing duty cycle significantly alters the distribution and content percentages of CNTs in nanocomposites layers. So, these all are the obtained results which we have received by doing this kind of testing or may be by making these kind of materials.

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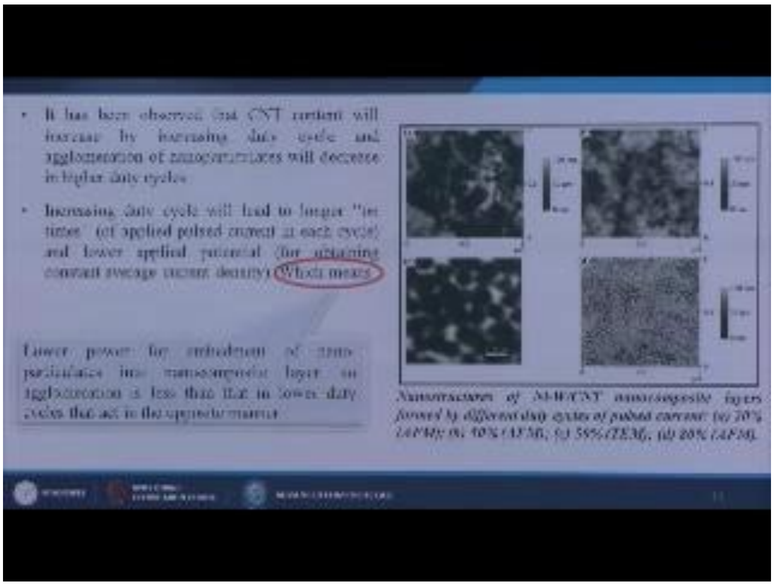

So, here we are trying to show you some results. So, it has been observed that carbon nano tube content will increase by increasing duty cycle and agglomeration of nanoparticles will decrease in higher duty cycles. So, that is the added advantage for this particular case. Increasing duty cycle will lead to longer ‘on times” of applied pulsed current in each cycle and lower applied potential for obtaining constant average current density; which means that lower power for embedment of nanoparticulates into nanocomposites layer so agglomeration is less than that in lower duty cycles that act in the opposite manner.

So, actually what should be happened, but it is not happening that vice versa case is happening over here; then here we have given some figures like nanostructure of nickel tungsten CNT nanocomposite layers formed by different duty cycles of pulse current: a is the 20 percent and b is the 50 percent duty cycle, c is the 50 percent that is the TEM image. So, this is the AFM image and this is the transmission electron microscopic image and d is also the 80 percent, but this is also the atomic force microscopy image of those particular samples.

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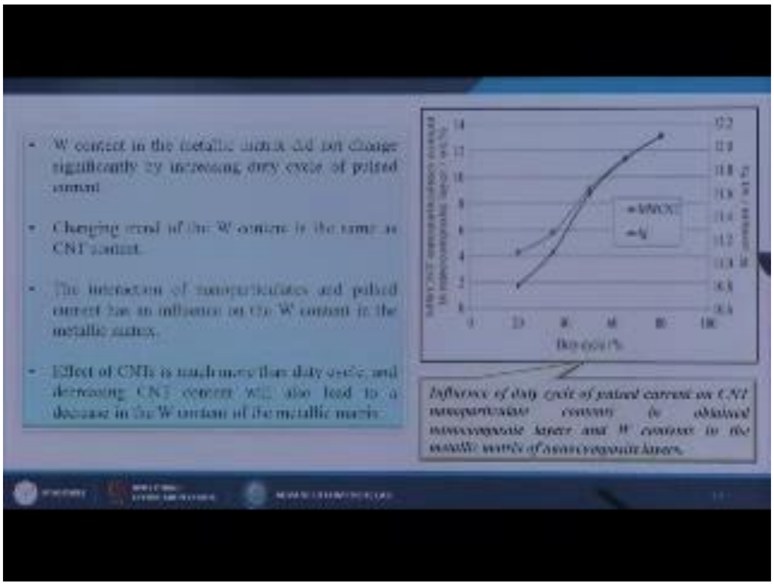

So, here we are also showing the duty cycle percentage how it is changing when we are applying that multiple carbon nanotubes into different percentage, when we are using the tungsten content into the different percentage and where we are using the both. So, tungsten content in the metallic matrix did not change significantly by increasing duty cycle of pulsed current, changing trend of the tungsten content is the same as CNT content in this particular case, the interaction of nanoparticulates and pulsed current has an influence of on the tungsten content in metallic matrix.

Effect of carbon nanotubes is much more than duty cycle and decreasing carbon nanotube is much more than duty cycle and decreasing in carbon nanotubes content also decrease in tungsten content of the metallic matrix. So, from this particular figure we can get that influence to the duty cycle of pulsed current on carbon nanotube nanoparticulate contents in obtained nanocomposite layers and tungsten constant in the metallic matrix of the nanocomposite layers. So, that is the mixture or maybe that is the hybrid composites kind of thing.

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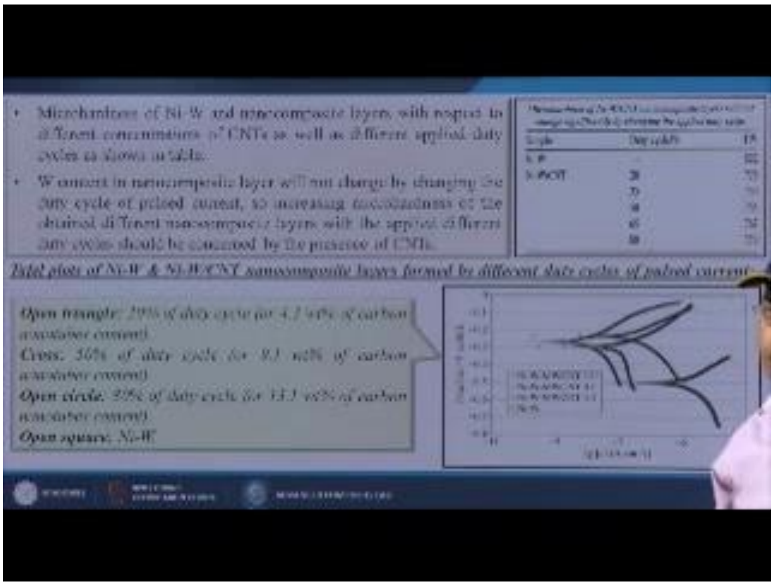

Then we have measure the micro hardness also in terms of the duty cycle for these particular samples. So, micro hardness of nickel tungsten and nanocomposite layers with respect to different concentration of different carbon nanotubes as well as different applied duty cycle as shown in this step particular table.

So, in this case the tungsten content in nano composite layer will not change by changing the duty cycle of pulsed current. So, here the thing is that when you are only using the nickel and tungsten current the hardness value is coming around 522, but when we are introducing the carbon nanotube into the systems at the 20 percent duty cycle, the hardness value is going around 725 and if we increase the duty cycle up to 80 percent, the hardness value is going up to 779, so that means, the. So, increasing the micro hardness the obtained different nanocomposites layers with the applied different duty cycle should be concerned by the presence of CNTs. So, in this particular case the carbon nanotube place a vital role to these particular systems.

Here also we are showing certain kind of tackle plots of nickel tungsten and nickel tungsten CNT nano composites layer formed by different duty cycles of the pulsed current. So, here we can when we are talking about the open triangles, open triangles the 20 percent of duty cycle or 4.38 percent of the carbon nanotubes content. So, here we have shown 4 different graphs or may be that 4 different samples, but here it is not easily or may be visible shown that is why you have return that cross, that cross means that it is the 50 percent of the duty cycle or may be the 9.1 weight percent of carbon nanotubes content when you are talking about the open circle 80 percent duty cycle; that means, 13.1 weight percent of carbon nanotube content and open square is only the simple nickel and tungsten composites except the carbon nanotubes.

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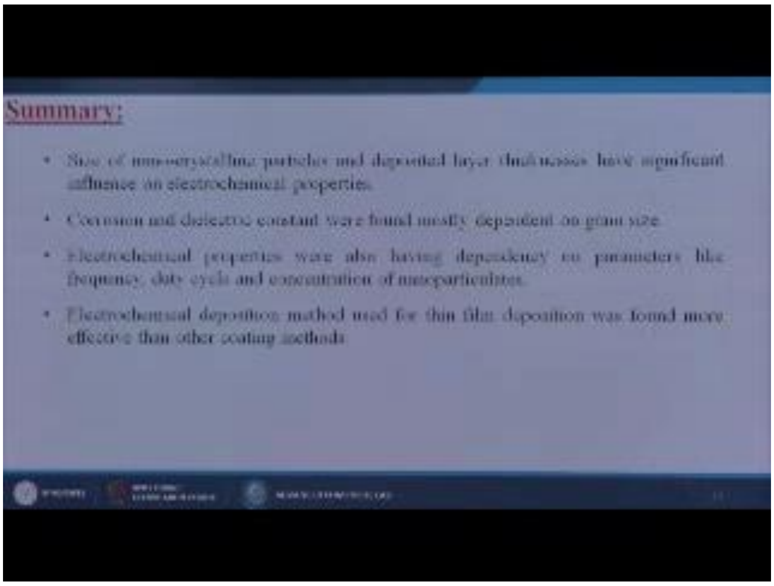

Then we are coming to the summary of this particular lecture, that size of nano crystalline particles and deposited layer thickness has significant influence on electrochemical properties; corrosion and dielectric constant were found mostly dependent on grain size.

Electrochemical properties were also having dependency on parameters like frequency, duty cycle and concentration of nano particulates. Electrochemical deposition method used for thin film deposition was found more effective than other coating methods. Actually this lecture is only dealing with the particle size which is effecting the electrochemical depositions or may be the electroplating techniques. Just here we have gathered some examples from some literature review and also we have given some kind of results what we are doing in our lab that we are presented, but there are n number of applications, there are there are n number of materials which we are going to use and which can give the better electrode deposition properties or may be that better electroplating properties.

Thank you.