**Surface Engineering of Nanomaterials**
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**Lecture - 24**
**Size Effect in Mechanical Properties of Nanostructured Coatings**

Hello, now our next lecture is actually the same topic that size dependency of different nanoparticles, but here only the properties is going to be changed that is in our last lecture we have discussed about that electrode equation techniques or maybe some kind of electrochemical techniques. Now here in this particular case, just we are concentrating on to the mechanical properties of that particular nanoparticle. So, here just we are going to see that if we are changing the size from that micro to nano that how the mechanical properties is going to be changed for these particular nanocomposites.

Size plays the vital role in mechanical properties of nanostructured coatings. So, this is the general idea actually. So, here these lines actually or may be that these statements, we are going to prove in our next subsequent slides. So, when we are reducing our size from micro or macro to nano, the automatically the mechanical properties in terms of tensile strength, elongation at break or maybe the tear properties or maybe some other mechanical properties of that particular nanocomposites is going to be changed.

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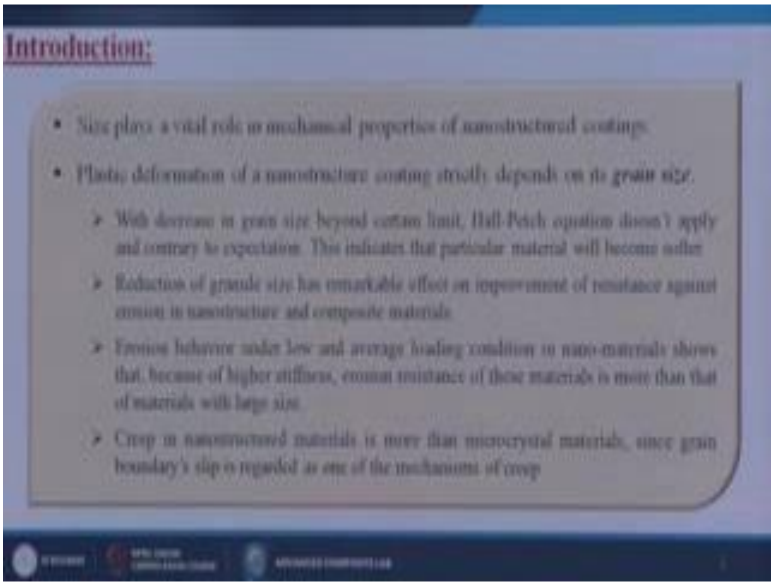

Plastic deformation of a nanostructure coating strictly depends on its grain size; that means, grain size is nothing but that crystallite size of that particular nanoparticles.

With decrease in grain size beyond certain limit, hall patch equation does not apply and contrary to expectations, this indicates that particular materials will become softer. So, this is also one kind of considerations for these particular techniques, reduction of granule size has remarkable effect on improvement of resistance against erosions in nanostructure and composite materials. So that is also one kind of added advantage that when we are using some kind of smaller nanoparticles than the previous one or maybe the then the bulk one so we are getting the best erosion properties in terms of mechanical properties.

Erosion behavior under low and average loading conditions in nanometers shows that because of higher stiffness erosion resistance to these materials is more than that of materials with the large size. So, the erosion property of that particular material is getting enhanced so that the material innocent properties, is going to be decreased when we are decreasing the particle size from micro or macro to nano. Creep in nanostructured materials is more than microcrystal materials since grain boundaries slips are regarded as one of the mechanism of creep. So, here that when we are talking about the micro crystals the creep is more, but when we are talking about some kind of materials which is having the nanoparticles that particles into the nanometer range, the creep of that particular material is going to be reduced.

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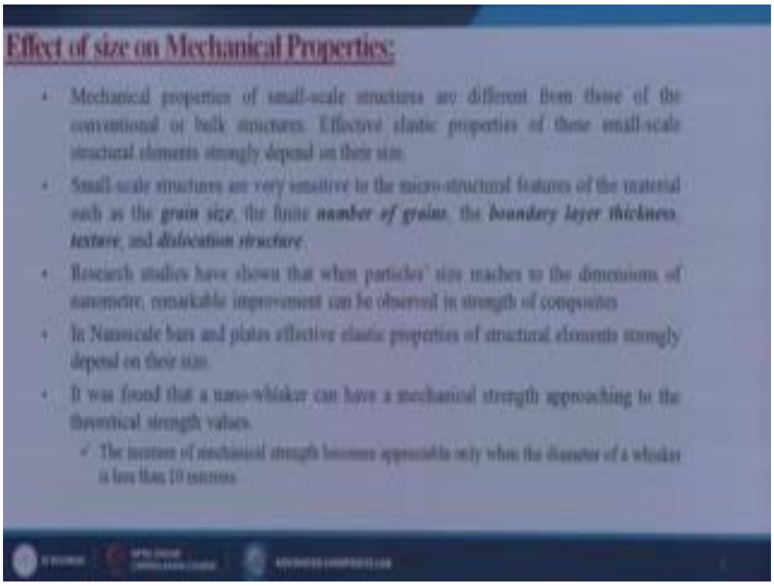


Next, effect of size on mechanical properties; mechanical properties of small scale structures are different from those of the conventional or bulk structures. We have discussed these lines several times, effective elastic properties of these wall scale structural elements, strongly depend on their size, small scale structures are very sensitive to the micro structural features of the material such as grain size, the finite number of grains, the boundary layer, thickness, texture and that dislocation structure; that means, is total properties is totally depend upon that crystallite size that how the material is behaving, what are the average diameter of that particular material, how the grain boundary is forming and then what is the dislocation of this kind of grain boundary? So, all actually depends upon the crystallize size of that particular material.

Research studies have shown that when particles re-size reaches to the dimension of nanometer, remarkable improvement can be observed in strength of composites. In nanoscale bars and plates effective elastic properties of structural elements strongly depend on their size, it was found that a nanowhisker can have a mechanical strength up to the theoretical strength values, the increasing increase of mechanical strength becomes appreciable only when the diameter of a whisker is less than 10 microns. So, from this particular statement we can understand that when the oyster size, we are reducing from the micron level to the nano level so, automatically the mechanical properties is enhancing for that particular composites.

Here is the empirical Hall-Petch model or maybe that well known Hall-Petch model generally by which we are calculating the total grain boundaries of that particular materials.

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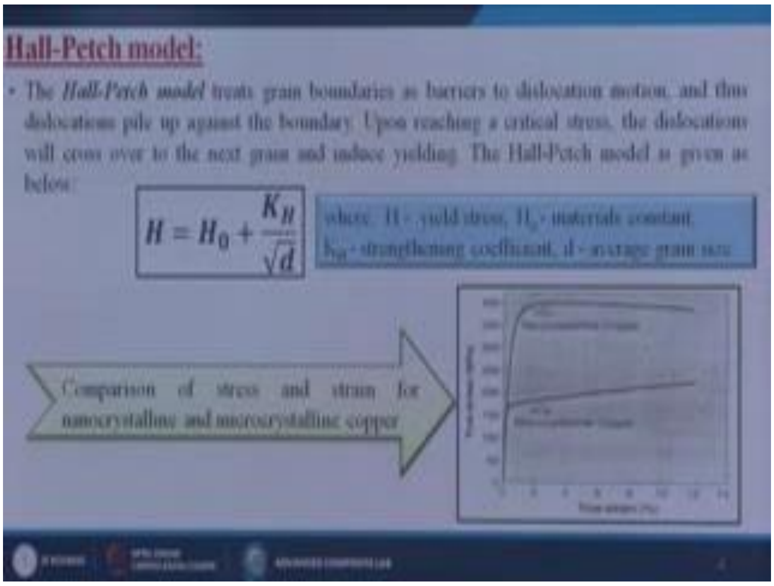


The Hall-Petch model treats the grain boundaries as boundaries to dislocation motions and does dislocation pile up against the boundary upon reaching a critical stress, the dislocations will cross over to the next grain and induce yielding, the Hall-Petch model is given as below because when you are talking about the grain size, the grain size is well distributed inside the composite, if there is some kind of straining or maybe some kind of difficult occurs to a particular grain then after certain time it will induce to the next grain boundaries and that next grain boundaries will be affected by these grain boundaries.

This is the empirical Hall-Patch models which is given below is capital H is equal to H0 plus KH by root over d where H is the yield stress H0 is the material constant we which actually depends upon them that particular material properties, KH is the strengthening coefficient and d is the average grain size of that particular materials.

Here the comparison of stress and strain for nanocrystalline and micros crystalline copper so here this is the 2 stress which is showing into the y axis and the unit of that is mega Pascal and this is the true strain which is into the percentage manner in the x axis. So, when we are talking about some kind of nanocrystalline copper so when it is into the micro crystalline particle size, it is showing the stress up to maybe that 200 mega Pascal, but when the nanocrystalline copper means particle size into the nano scale, the automatic particle size is going around 400 sorry the 2 stress is going around 400 mega Pascal at that particular case; that means, that when we are decreasing the particle size from micro to nano that 2 stress of that particular material is changing or almost the double.

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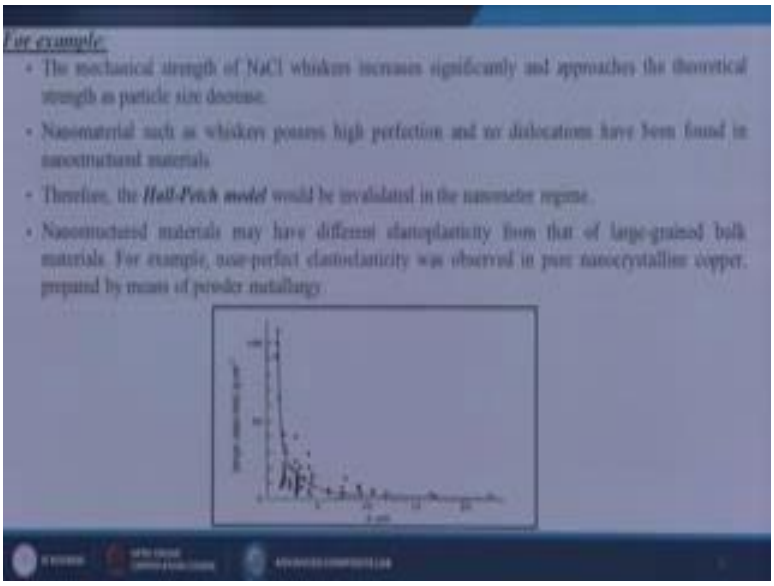


Here is also an example, the mechanical strength of sodium chlorite whiskers increases significantly and approaches the theoretical strength as particle size decrease. Nanomaterial such as whiskers process high perfection and no dislocations have been found in nanostructured materials therefore, the Hall-Petch model should be invalidated in the nanometer regime. So that is also a one aspect of this particular technology.

Nanostructured materials may have different olestra plasticity from that a large gain bulk mod material for example, near perfect elastoelasticity was observed in pure nanocrystalline copper prepared by means of powder metallurgy. So, in that particular case, for a single material when we are changing the diameter size or of that particular particulate, we can see that the strength of that particular material is drastically changing, it is directly coming from the 100 to almost 0 then when we are actually increasing the diameter into the micrometer level. So, from small particle to bigger particle when we are changing our composite particulate size, the strength is totally decreasing at that particular point.

Then we are going to discuss about the size effect on hardness and strength of nanostructures. So, following mechanical properties were significantly affected by the grain size.

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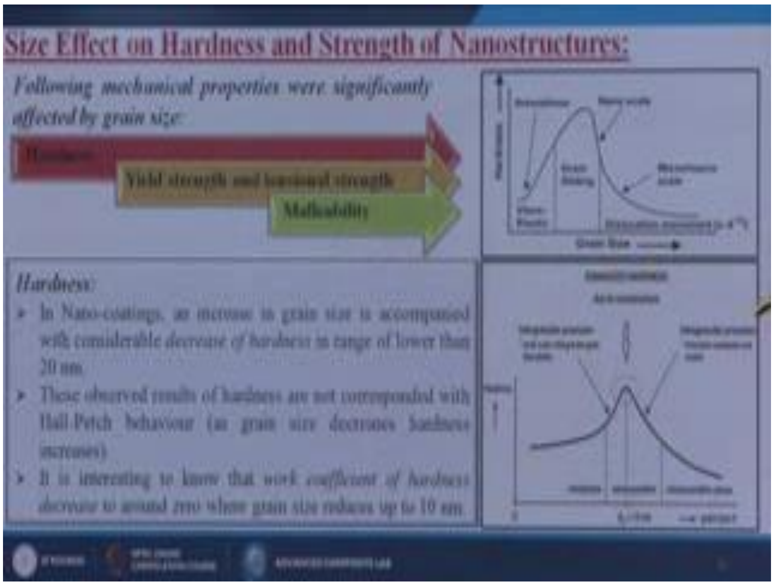


One is called the hardness another one is called the yield strength and tensile and tensional strength and third one is called the malleability. So, these all 3 are the materials inherent property which is going to be changed when we are using the particular size from micro to nano.

Here this is an examples that if we are putting the grain size into the x axis and we are putting the hardness into the y axis we can see that hardness; simple, it is starting from the low value then sudden it is going to the higher value then it is almost the same when we are increasing the grain size so; that means, when the particles into the amorphous regions, its hardness is little bit low, but when the particle size is going into the nanoscale size or maybe the nanometer range then suddenly the hardness is increasing tremendously, but when the particle again we are going into the micro sizes, so automatically the hardness is going drastically decreased. So, what is the hardness in nanocoatings and increase in grain size is accompanied with considerable decrease of hardness in range of lower than 20 nanometers.

These observed results of hardness are not correspondent with Hall-Petch behavior as grain size decreases, hardness increases. So, we have already told in to the nanometer range the Hall-Petch relations is actually not working properly, it is interesting to know that what coefficient of hardness decreased to around zero when the grain size reduces up to 10 nanometer . So, here also the same thing, so when you are having the in the amorphous regions the hardness is moderate, but when we are going to the nanocrystalline regions that hardness is tremendously increasing. So that is due to the inter granular processes small scale sliding in the grain boundaries and then due to the enhanced hardness is occurring due to the nanostructure in that particular zone then intergrangler processes is starting; that means, dislocation nucleation and motion is taking place that is why when the size is going from nano to the micro then automatically the hardness is getting to be reduced.

Then in terms of ill strength and tensile strength, yield strength and tensile strength tensional strength increase with grain size decreases well as considerable increase in hardness.

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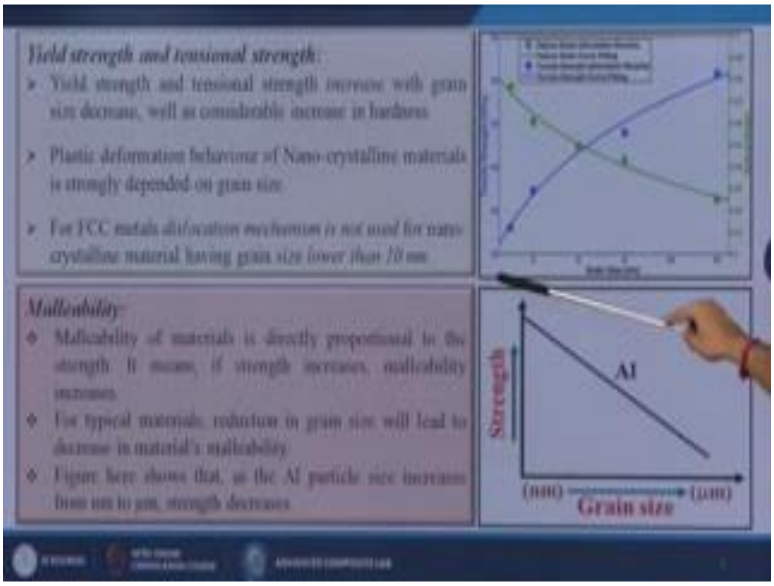

When we are saying the grain size then in terms of tensile strength, it is changing very very rapidly, it is increasing in a very rapid manner and also the vice versa is taking place when we are talking about the failure strain. So, when the grain size is increasing then the failure strain is also decreasing in that manner. So, yield strength and tensile strength increase with grain size decreases well as considerable increase in hardness, plastic deformation behavior of nanocrystalline materials is strongly dependent on grain size. For FCC metals dislocation mechanism is not used for nanocrystalline materials having grain size lower than 10 nanometers.

Then we can see that malleability property which is also one kind of mechanical properties of that particular metals or maybe that some metals then malleability of materials is directly proportional to the strength, it means if strength increases malleability increases, that is the standard thinking in our mind. So, for typical materials, reduction in grain size you lead to decrease in materials, malleability figure here shows that as aluminum particle size increases from nanometers to micrometers the strength is totally decreasing, when the strength is totally decreasing; that means, the malleability is also totally decreasing because strength is directly proportional to the malleability. So, if the strength will increase, the malleability will also increase and if the strength will decrease the malleability will also decrease. So, when the strength is decreasing simultaneously the malleability will be also decreasing.

Then how to enhance the strain strength into the nanostructure systems? The emerging areas of micro and nanotechnologies exhibit important strength differences.

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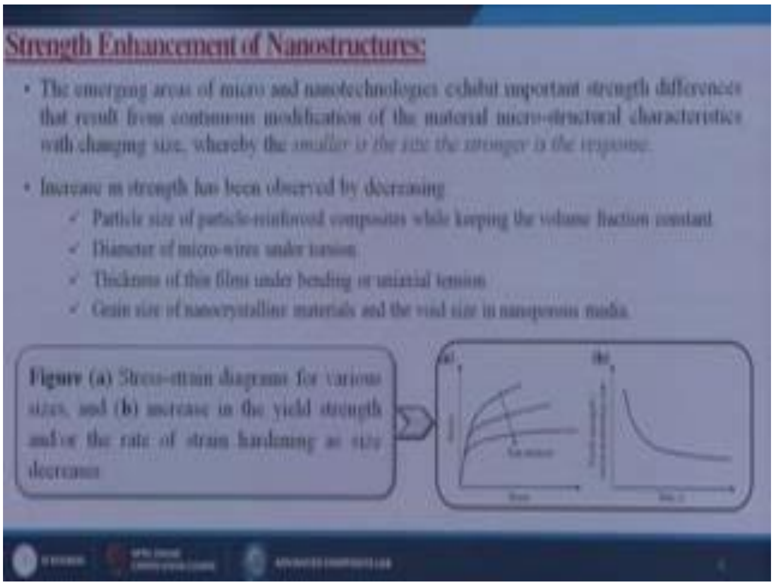


The result from continuous modification of the material micro structural characteristics which changing size, where the smaller is the site the stronger is the response. So, increase in strength has been observed by decrease in particle size of particle and force composites while keeping the volume fraction constant, diameter of micro wires under torsions, thickness of thin flames under bending or uniaxial tensions, grain size of nanocrystalline materials and a void size in nanoporous media.

When we are increasing the strength or our maybe has been observed by decreasing. So, this can be occurred inside the material itself or maybe these properties we can see from that materials point of view. So, here is the figure which is a is showing the size strain diagrams for various sizes then when we are changing the size how the stress is varying in terms of strain and not only that the right hand side figure it is showing the change in yield strength or the rate of strain hardening as the size decreases. So, how this mechanical properties is changing depending upon the crystallized size of that particular nanocomposites or maybe the coating?

Then mechanisms of the strength enhancement 2 possible mechanisms actually are available depending upon that there are 2 schools those who are thinking these 2 different mechanisms. So, 2 possible mechanisms have been proposed to explain the enhanced strength of whiskers.

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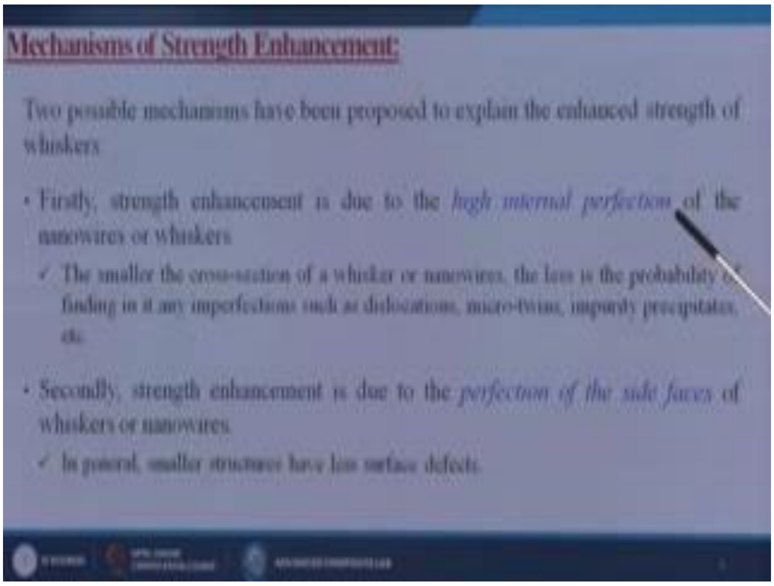


Firstly, strength enhancement is due to the high internal perfections of the nanowires or whiskers. So, this is one vital parameter is high internal perfections the smaller the cross section of a whisker or nanowires the less is the probability of finding it in any imperfection such as dislocations, micro twins, impurity, precipitates, etcetera. So, automatically if the crystallized size will be smaller than the chance of impurities or maybe that imperfection will be getting low. Secondly, the strength enhancement is due to the perfection of the side phases, this is also the another thinking that perfection of the side phases of whiskers on nanowires in general smaller structures have less surface defects. So, if we see at the end of the day maybe these 2 theories are almost same, but still there are 2 different thinking by the scientist itself.

Then size effect in mechanical properties of 2D nanofilms. So, when you are talking about the nanofilms, it is 2D in structure.

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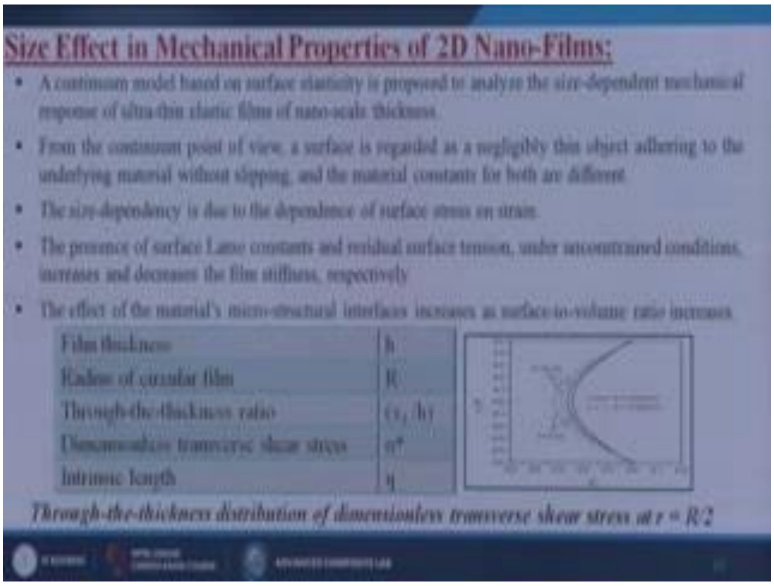


How the mechanical properties are affecting on based on the size of that particular particle, a continuum model based on surface elasticity is proposed to analyze the size dependent mechanical response of ultra thin elastic films of nanoscale thickness, from the continuum point of view a surface is regarded as a negligibly thin object adhering to the underlying material without slipping and the materials constant for both are different, the size dependency is due to the dependence of surface stress on strain, the presence of surface name constants and residual surface tensions under unconstraint conditions increases and decreases the flame stiffness respectively.

Here is the example the effect of the materials micro structural interface increases at surface to volume ratio increases. So, this is the main message of this particular lecture. So, here the film thickness is h; small h, radius of circular flame is capital R, through the thickness ratio is x3 by h, dimensionless transverse shear stress is sigma and the intrinsic length is eta. So, though the thickness distribution of dimensionless transverse shear stress at are smaller is equal to capital R by 2 then size dependency on tensile and fatigue strength on ultra thin films, then fatigue strength as a function of film thickness was measured under the constant load constant total strain range control at a frequency of 10 harsh.

The experimental results exhibit that both yield strength and fatigue lifetime are dependent on film thickness.

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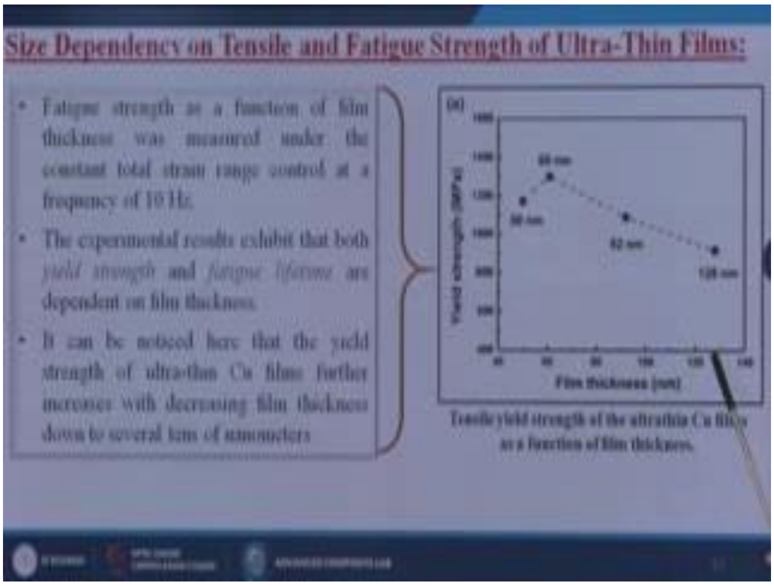


It can be notice here that the yield strength of ultra thin copper films further increases with decreasing film thickness down to several 10s of nanometers. So, here we can see that when we are changing the crystallite size, how the yield strength is changing, still the film thickness is also increasing. So, film thickness is increasing from 40 to 140 nanometer, yield strength is changing it from 400 to 1600 mega Pascal. So, at 50 nanometer, whatever the yield strength is occurring, when you are applying the 16 nanometer crystallized size though the film thickness is also increasing, but it is showing the maximum in strength at that particular point.

Fatigue damage behavior in 100 nanometer thick copper films having nanometer sized grains is different from that in micrometer thick copper films having large grains, fatigue of thin metal frames is a key issue for the long term service of micro devices, investigations of fatigue of thin metal foils show a tremendously tendency of improved fatigue strength with decreasing foil thickness.

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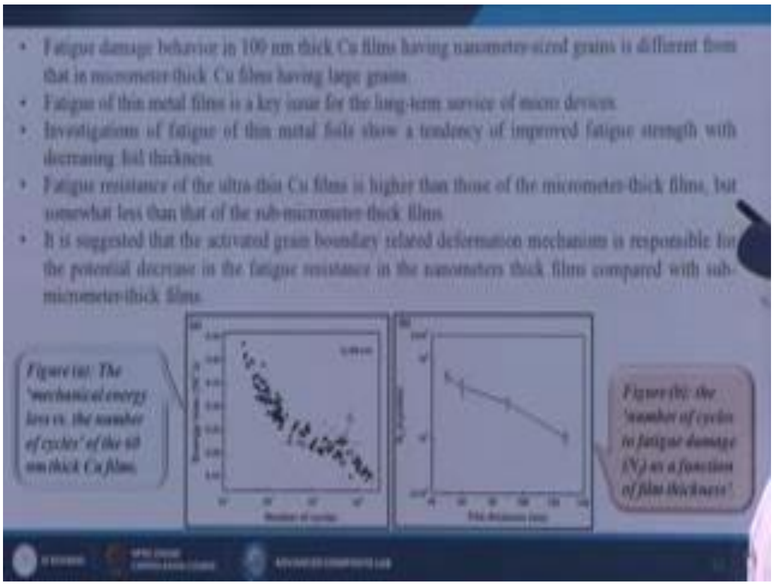

Fatigue resistance of the ultra thin copper films is higher than those of the micrometer thick films, but somewhat less than that of sub micrometer thick films, it is suggested that the activated grain boundary related deformation mechanisms is responsible for the potential decrease in the fatigue resistance in the nanometer thick films compared with the sub micrometer thick films. These all are the obtained result from this particular slide. So, here, figure a, the mechanical energy loss versus the number of cycles of the 60 nanometer thick copper films, it is showing like this and the right hand side figure which is giving the number of cycles of fatigue damage as a function of flame thickness.

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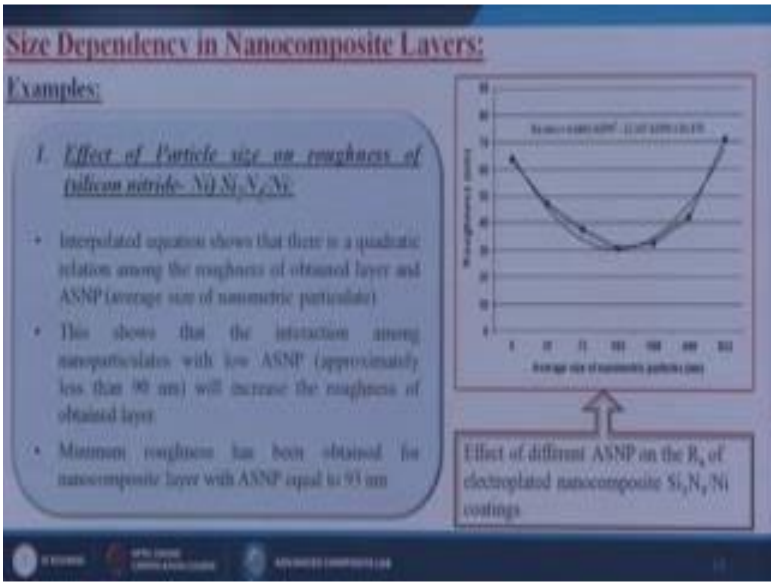


Then the size dependency in nanocomposite layers; so in this particular case, we are going to see that how the particle size is affecting the surface roughness of that particular materials or maybe of that equal nanocomposites or maybe that coatings. So, effective particle size on roughness of silicon nitride, then silicon and oblique nickel composites so, here it is a hybrid kind of composites in where the interpolated equation shows that there is a quadratic relation among the roughness of obtained layer and ASNP; average size of nanometric particulate.

This shows that the interaction among nanoparticulates with low ASNP approximately less than 90 nanometers will increase the roughness of obtained layer, minimum roughness has been obtained for nanocomposite layer with ASNP equal to 93 nanometers. So, here this is the roughness generally we are giving in nanometer range here is the average size of nanometric particles from this particular case, you can see that when we are increasing the particle size up to certain time, the roughness is reducing, but after that the agglomeration for particles is taking place when you are increasing the more particles that is why certainly the roughness is again increasing. So, effect of different ASNP on the surface roughness value which is known as the Ra of electroplated nanocomposites silicon nitride nickel coatings.

Then effect of particle size on roughness of tungsten carbide nanoparticles; here the tungsten carbide nanoparticles probably act as new sites for gram stain; grain growth and hence decreases the final size of the grains, Ra values of the nanocomposites layers were of observed aprox between 1.6 to 4.9 micrometer Ra is nothing but the surface roughness of that particular material.

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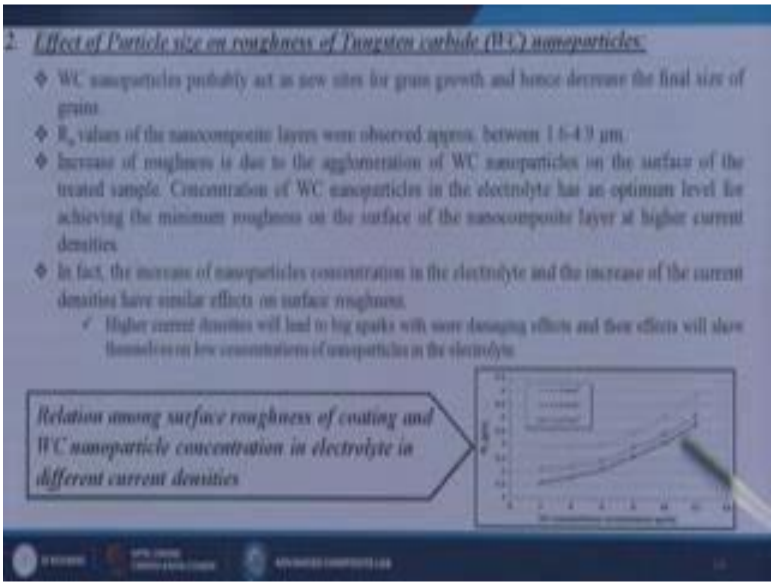


Increase of roughness is due to the agglomeration of tungsten carbide nanoparticles on the surface of the treated samples. As I told already sometimes the agglomeration is taking place, concentration of tungsten carbide nanoparticles in the electrolyte has an optimum level for achieving the minimum roughness on the surface of the nanocomposite layer at higher current densities. In fact, the increase of nanoparticle concentration in the electrolyte and the increase of the current densities have similar effects on surface roughness, higher current densities will lead to big sparks with more damaging effects and their effects will show themselves on no concentration of nanoparticles in the electrolyte.

Here we are showing that how the material is changing in terms of nanoparticles concentration of tungsten carbide and here is the surface roughness value, so relations among surface roughness of coating and tungsten carbide nanoparticle concentration in electrolyte in different current densities. So, first one is 1.2 and ampere per centimeter square the next is that 0.8 ampere per centimeter square and the next 1 is 0.2 ampere per centimeter square. So, different current densities, how the tungsten carbide nanoparticles concentration is totally changing and how the roughness is totally changing.

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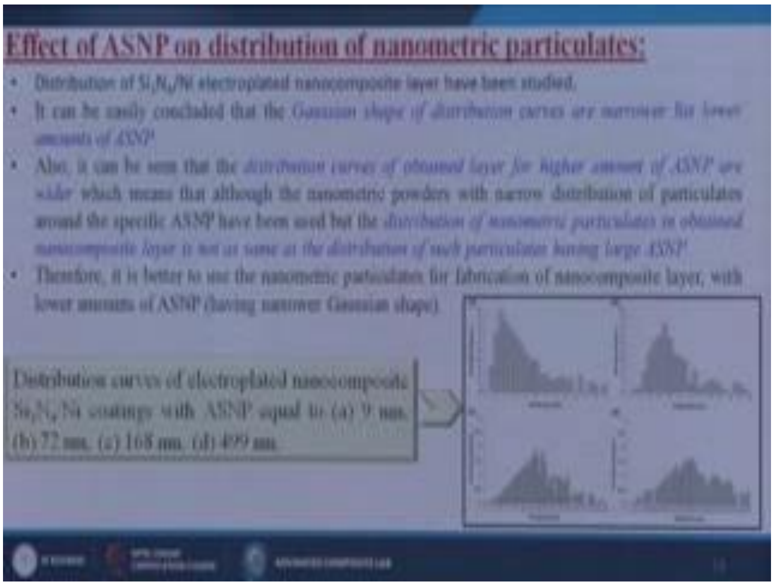


Then effect of ASNP on distribution of nanometric particulates; so distribution of silicon nitride and nickel electroplated nanocomposite layer have been studied, we have shown so many results in our last slide also. So, it can be easily conclude that the Gaussian shape of distribution curves are narrower for lower amounts of ASNP, but if we increase the percentage of that ASNP so we can see the Gaussian curve will be more broader. So, also it can be seen that the distribution curves are obtained layer for higher amount of ASNP are wider which means that although the nanometric powders with narrower distributions of particulates around the specific ASNP have been used, but the distribution of nanometric particulates is obtained and a composite layer is not as same as the distribution of such particulates having large ASNP.

If average diameter of that particle will be increased then it will cover the large area and also some kind of small small particle will fill up the gap, but if the average diameter size will be less then there will be very uncovered area so that is why the Gaussian curve is not the wider one. So, therefore, it is better to use the nanometric particulates for fabrication of nanocomposite layer with lower amounts of ASNP having narrower Gaussian shapes. So, distribution curves are electroplated nanocomposite silicon nitride and nickel coatings with ASNP equal to 9 nanometers is a then 72 nanometers then 168 nanometers and the 499 nanometers where you are getting a broader spectrum of Gaussian curve.

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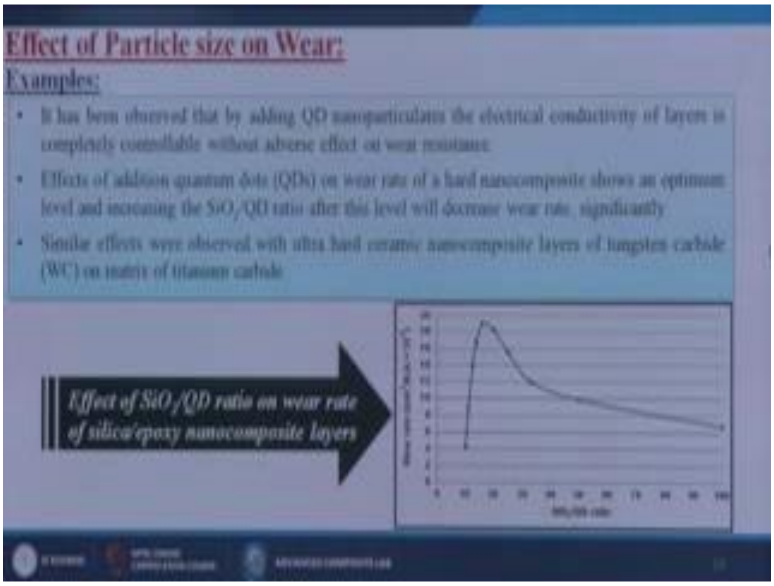


Then effective particle size on wear; so, example is that it has been observed that by adding quantum dots nanoparticulates the electrical conductivity of layers is completely controllable without adverse effect on wear resistance, effect of addition quantum dots on wear rate of hard nanocomposite shows an optimum level and increase in the silicon dioxide quantum dot ratio after this level will decrease wear rate significantly, similar effects were abroad with ultra hard ceramic nanocomposite layers of tungsten carbide on matrix of titanium carbide.

Here we are showing that effect of silicon dioxide quantum dot ratio on wear rate of silica epoxy nanocomposites layer. So, when we are changing the ratio of silicon dioxide and quantum dots we can see that wear rate suddenly it is increasing, but simultaneously the ratio when it is increasing then automatically it is going down so; that means, it depends upon the particle size of silicon dioxide and quantum dots which is affecting the wear properties in this particular system.

The next is that effect of particle size on wear of alumina, yttrium oxide and carbon nanotube nanocomposites layer.

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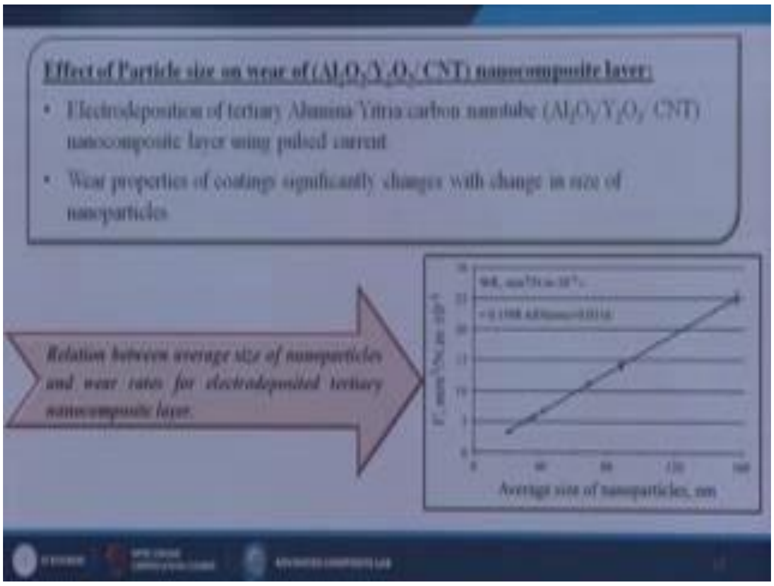


Electro deposition of tertiary alumina, yitria, carbon nanotube, nanocomposite layer using pulsed current; wear properties of coating significantly changes with change in size of the nanoparticles. So, from this particular figure, we can understand that there is a relation in between the wear rate and the average size of nanoparticles. So, automatically it is going in a standard manner. So, relation between average size of nanoparticles and wear rates for electrodeposited tertiary nanocomposites layer is showing an increasing in a standard manner.

Then we are coming to our last slides which will give a glimpse of this lecture which we are now discussing actually.

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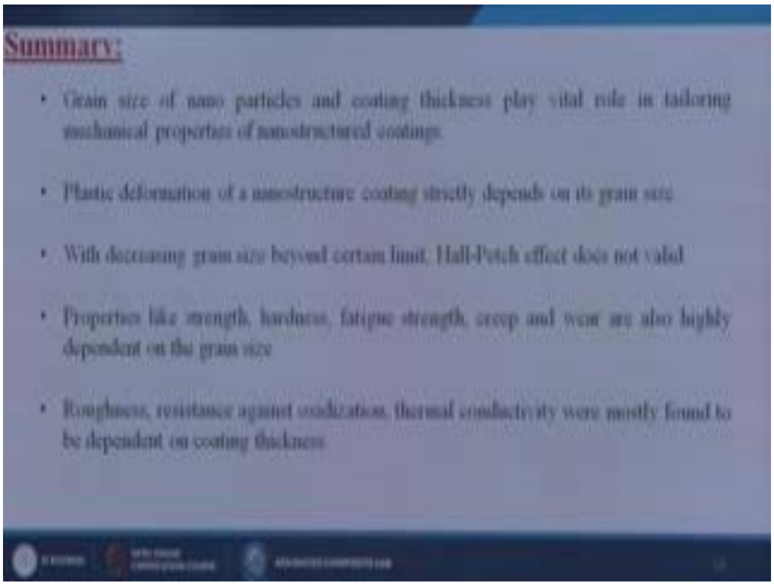


Grain size of nanoparticles and coating thickness play vital role in tailoring mechanical properties of nanostructured coatings. Plastic deformation of nanostructure coating strictly depends on its grain size, with decreasing grain size beyond certain limit Hall-Petch effect does not valid, properties like strength hardness fatigue strength creep and wear are also highly dependent on the grain size, roughness, resistance and oxidization thermal conductivity were mostly found to be dependent on coating thickness.

These all are the points we have extensively discussed in this particular lecture.

Thank you.