Technology of Surface Coating
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Lecture No 20
Influence of Architecture of Sputter Deposited Molybdenum Di Sulphide Coating

Okay influence of architecture of molybdenum disulphide and tungsten disulphide and similar materials, they are known for their super lubricity. However, some additives like titanium, chromium and similar materials could raise or improve these properties remarkably in that, that this type of coatings can be used not just in a very restricted atmosphere like very high vacuum or a atmosphere having a very low value of the relative humidity but with such additives, it is now possible to use this thing in a more pragmatic way that means in the normal working condition and this type of coating has shown marked improvement in their performance.

Now following this idea and this logic there has when several attempts to improve the property of this molybdenum disulphide coating or tungsten disulphide coating along with some hard conventional, hard coating material. Say for example we can use titanium nitride along with molybdenum disulphide and this 2 combination can improve the performance of either of titanium nitride or that of M o S 2.

Now it is in fact it is no longer just molybdenum disulphide coating, it is more or less a composite coating and the whole coating that means the top functional layer that is built on a solid foundation of some hard coating, so this is actually a built structure, well-built structure of this coating and this architecture when properly built is supposed to give one of the best properties in all mechanical, tribological problem. Now this architecture we can have say for example at least we can have 6 architecture which is possible, we can have a quick look to this.

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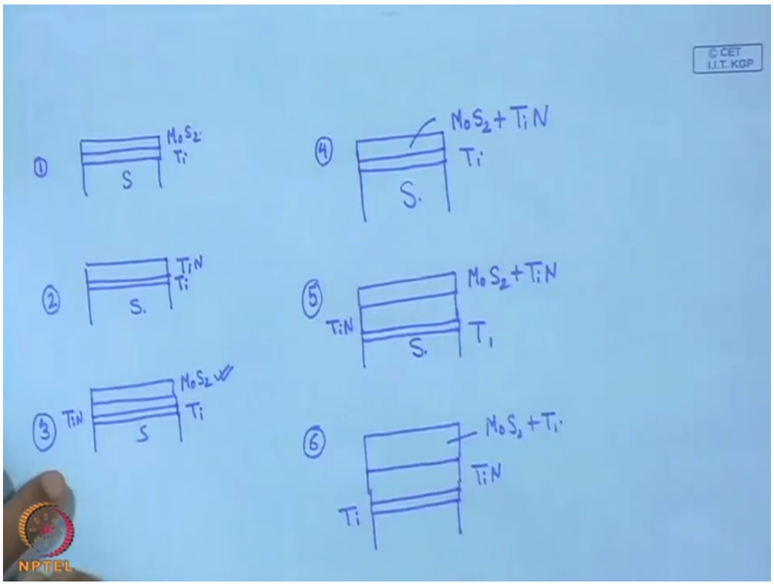

Say we know that M o S 2, this is M o S 2 with a sub-layer of titanium and then it can be substrate this is one possibility this is one extremity super lubricity. However, we can have another extremity where just we have TiN that is well-known for its hardness and wear resistance, so this is just one adhesive layer and S means the substrate, so these are the 2 combinations. Now what can be… so this is one architecture this is number 2, we can have the 3rd one and 3rd one is something like this.

First of all we have the substrate, on that just a thin layer which is called adhesive layer, over that we can have TiN and on the top of that we can have M o S 2, so this is also possible, three. Now we can have 4th option here, now this is actually, it is a now a combination, it is no more a mono phase, this is top mono phase, this is also hard top mono phase, this is also top mono phase but it is a multilayer but this is going to be a code deposited coating that means on this coating we have both. Here we have both M o S 2 and titanium nitride and over this, what we have here just Ti and followed by this substrate. The 5th option what we can have, this would be an architecture, so this is M o S 2 plus TiN followed by the foundation layer of TiN, so this is TiN and then we have here just S.

Similarly we can have another option 6th, so here we have say this is actually one of those development work M o S 2 plus Ti followed by 1 titanium hard layer and then we have here adhesive titanium and substrate, here too we have adhesive titanium, so we can examine all these three 6 and here we have to examine them for their performance and we can judge which one is the best architecture and then following this there can be some process variable of sputtering and just varying those, we can find out which one is the best condition for this sputtering.

Now we know that for sputtering for say A pulse DC keeping that frequency constant what we can do? We can change the cathode current that means cathode current of titanium or cathode current of M o S 2 that is on one side and then also the substrate bias that means the bias voltage for the substrate that is also another process parameter. So these 2 process parameters can be varied and we can look into all those responses in terms of the properties of coating that means when we see the influence of architecture that what we mean the influence of architecture on the final mechanical properties of the coating, now here 2 things we can look into that 1st of all the hardness of the coating.

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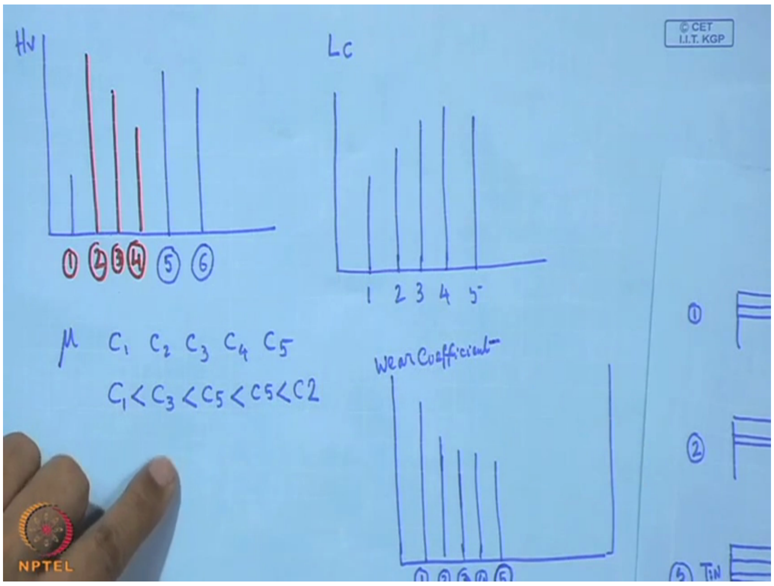

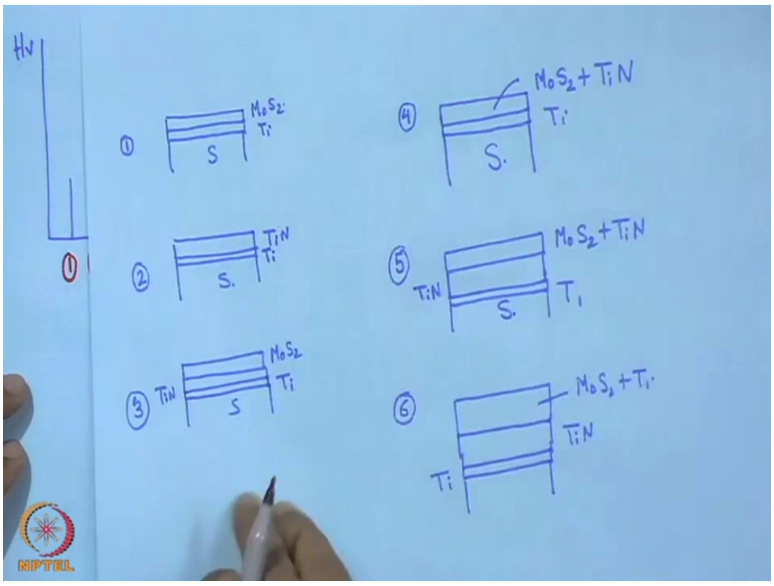

Now when we have such architecture, we can find out here that means first of all this is hardness this is Hv and on this Hv we can have a hardness something like this and then we can have…this is number 1 and then number 2 will be very high for obvious reasons cost this is number 2 means here just we have titanium nitride and since titanium nitride is known for its hardness, so we expect a higher hardness followed by number 3 and this number 3 is actually M o S 2 and which is supported by this TiN, so its hardness will fall but we can see the bulk hardness of these 3 will be more than that of 1 because here we have a support of TiN, so that will be somewhere little below this one and then we have number 4.

In number 4 what we can see here that it is a composite coating but with no support layer of TiN, so it will give a bulk value which will be more than M o S 2 but it will be less than of TiN. So naturally when we see that this value of TiN then definitely this will be less than that one, so we have something somewhere here and this is going to be 3 and that is going to be 4 and then we have number 5 and this number 5 we can have a quick look here that this number 5 distinguishes itself from rest of the thing because in this case we have a composite architecture the top but we have a supporting layer of TiN.

So this is one of the very hard coating and in this case we have TiN and at the same time at the top M o S 2 plus TiN, so with this we expect a hardness which will definitely exceed or more than that of 3 and 4 but it cannot be more than 2 because it is top TiN and it is just a composite, so it has its own effect and as a result we have this hardness which will be somewhere here, so this is 5, so architecture 5 will give a hardness more than 3 and 4 but less than 2 and then we have this M o S 2 plus Ti plus TiN and this is going to be one which will give a hardness somewhere little more than this and so it will be 6, so it will be here less than 5 but more than 4, so it will be less than 5 but more than 4, so this is the distribution of hardness.

So this is one way we can find the hardness distribution but one thing of immediate interest next will be that this what we call adhesion that means this critical load, critical normal load which causes the 1st failure of the coating and in this case it is also the observation that if we put the bar diagram we can find that for all this 1, 2, 3, 4 and this is actually here what we find this one, so this is something like that, this is 1, 2, 3, 4, 5 and this coating that means the coating with this architecture of M o S 2 TiN at the top that one and with a coating interlayer of TiN and that gives a good adhesion and this is actually the value what we can see here.

Now comes very important thing, so for 1, 2, 3, 4 and 5, so what we see here the adhesion of this one is not so good.

Now in this case what happens with this combination actually the resistance to fracture and resistance to crack of TiN which is rather micro-grain, which is coarse-grain here and which becomes little bit micro-grain, so resistance to cracking and resistance to fracture, that becomes more and because of this grain refinement and that is why we expect a better adhesion in this case. Now comes what is important that coefficient of friction, coefficient of friction that means this is actually the coefficient of friction one can find out in the ball whack test that means it is a tribometer and when the pin on disk what is also our observation that means this samples, this C 1, C 2, C 3, C 4 and C 5.

Now here obviously since one is having just pure M o S 2 obviously from stands point of lubricity that is going to be the best one. However, that is short lift that means life of this coating is very short, it is a short lift coating. However, when it is mixed with when we when it is number 3 with the support of TiN the life is actually more compared to that of this one, so it gives a greater support, so what we find also compared to this 4, 5 is a better one and this is because of this support of TiN, so what we can put in this case that this C 1 that means in here what we can show that C 1 coefficient of friction that is less then we have C 3 that is the 2nd lowest followed by C 5 and then we have, we have C 5 and finally C 2.

So coefficient of friction in that scale, C 1 happens to be the one which gives the lowest value of coefficient of friction because of this M o S 2 and TiN, it is not that lubricating coating though it is one wear resistances coating and in this respect what we find that in between C 3 and C 5 that means this one with M o S 2 with a TiN support that gives that is the 2nd best and then we have this M o S 2 with TiN and with a TiN support that is the 3rd one in that ranking. Now apart from that what is also important for us also to know that is called wear coefficient. Wear coefficient is actually the wear on the track that means on the disk which is coated, on that disk we have a wear channel and the depth of that channel from that we can determine wear coefficient we have already discussed that means the volume of the wear on that circular wear channel, wear track divided by the normal load which is which is applied into the distance travelled by this normal load.

So from that point of view what we can find here, we can just show this thing. This is wear coefficient, so here what we find this wear coefficient of this coating number 1 that means this is not that wear resisting though friction value is quite low but that is only for a small period of time and then we have here 2, 3, 4…1, 2, 3 and then we have here 4, this is the number 4 that is a composite coating without any support and finally what we have, we have here this 5 and this 5 means it is composite coating with a support of titanium nitride and that give also quite low value of this coating.

So from this point of you were, what we find that this 5th one that means an architecture with this value with this architecture with M o S 2 plus TiN with a support of TiN that gives one of the best value in consideration of hardness number 1, number 2 that means this adhesion with the substrate this is number 2 and number 3 that is the coefficient of friction and number 4 that is the wear coefficient that means the how much is the wear. So with all this consideration what we find that this number 4.

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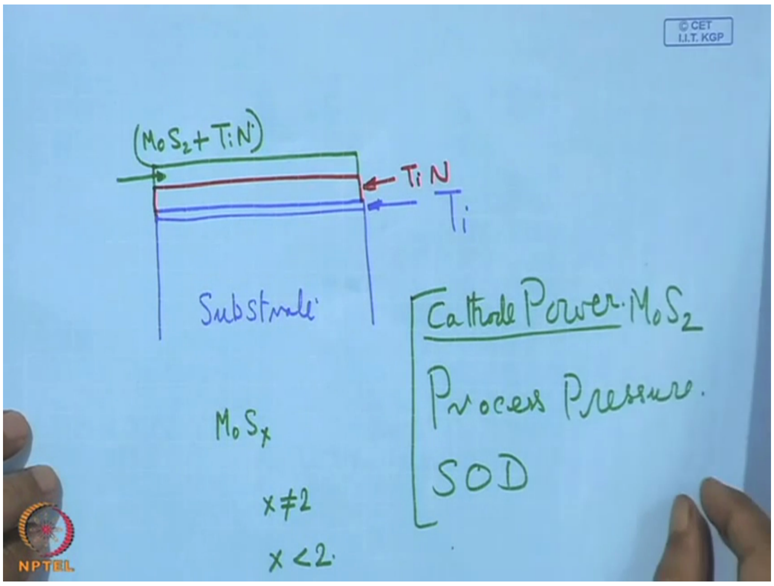

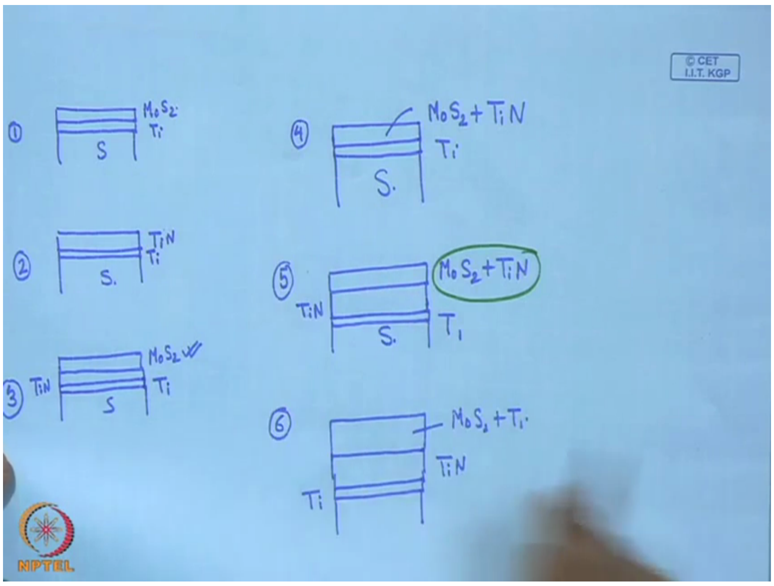

This particular architecture that means the architecture which consist of this architecture, this is the substrate. Here we have a Ti coating, this is Ti and on that top it is TiN and finally the functional coating, this one this one is actually, it is M o S 2 plus TiN, so this is architecture so out of this what has been found that this particular architecture, this particular architecture with the support of TiN that is found to be one overall performance of this architecture is found to be the best considering the overall performance.

Now here one thing we also should look in, now during sputtering of M o S 2 what happens that it is also the cathode current or say cathode power, cathode power of M o S 2 and also the process pressure these 2 and the stand-off distance SOD that means the stand-off distance between the cathode and the substrate from this there is a relation and if the cathode power and process pressure considering SOD if they are not properly chosen then instead of this 2, we may end up with something as S x where x is not equal 2 and most likeness that is less than 2.

However, it is also our observation that with even less value of 2, we can get a good coating with the desired basal plane which is parallel to the substrate surface and also a tribological coating which can give offer a low value of coefficient of friction, so it is actually instead of M o S 2 most reasonable would be to write M o S x where this x value depends upon this cathode power, process pressure and SOD under a given set of condition. So this is M o S x coating that the present in in the general form M o S x.

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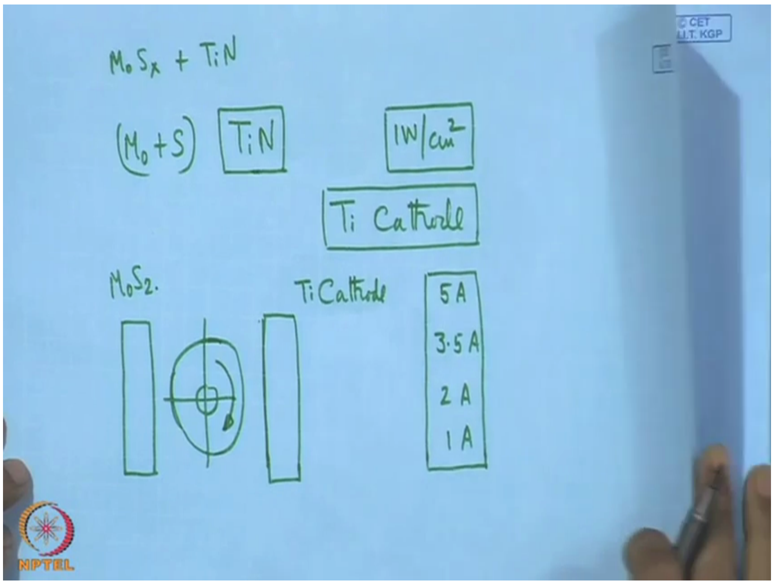

Now this M o S x and with TiN most important thing here is that, what will be this proportion atomic percentage that means M o S x plus TiN, so one would be interested to know what will be this M o plus S within this TiN, so TiN is on one side and this M o plus S, so this is something quite important and interesting to know and for that what can be done in this case there is some restrictions in the operational restriction with this cathode power of M o S 2 target say about 1 watt per centimetre square and with this it may not be that easy to vary this cathode current for M o S 2 target that means molybdenum disulphide cathode current cannot be that conveniently varied.

On the other hand what can be handled rather easily that titanium target titanium cathode current and that has been done that means in this process in fact what has been done if we consider it is actually a dual cathode machine, in this dual cathode machine this is the rotary table and here we have this titanium cathode and M o S 2 cathode. So what can be done? In this dual cathode system that titanium cathode current that could have been varied say from 5 ampere, 3.5 ampere this is just by way of illustration any other combination is also possible and with that we can also see the effect of this thing on the overall performance.

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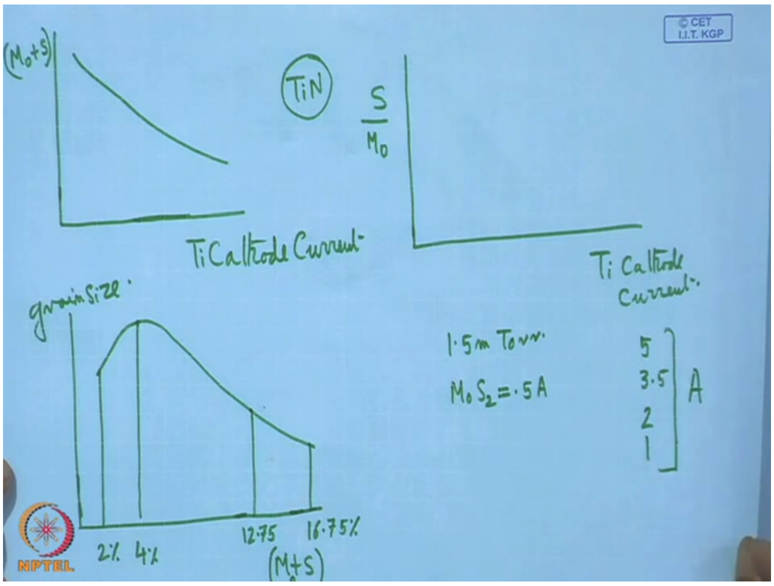

Now with this, what we can find that this percentage of M o S 2 that means this is actually… so what we get it is something like this, so it is titanium cathode current, so percentage of M o S O when we have higher value of titanium naturally we have higher percentage of titanium nitride in the coating, so this is actually a reactive sputtering.

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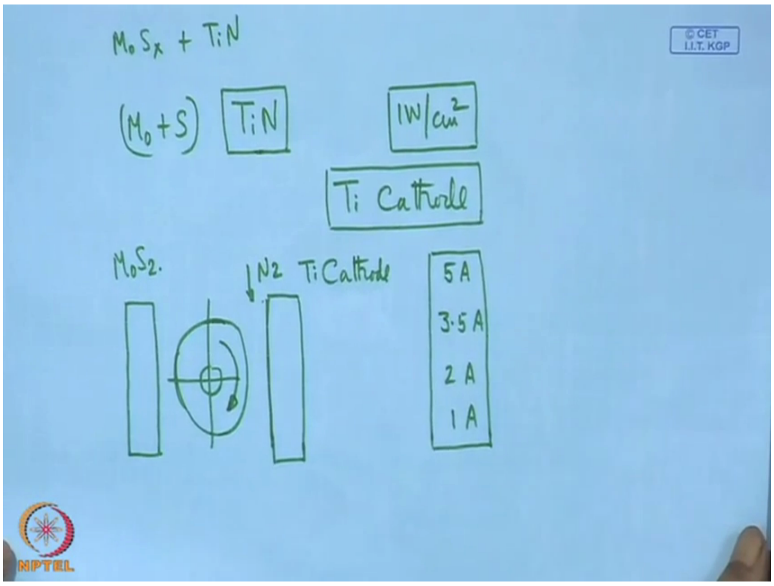

So where titanium and nitrogen admission that means titanium nitride and then M o S 2 as a whole that is deposited, so it is a reactive sputtering of titanium nitride and direct sputtering of M o S 2 using a pulse DC system and we have another observation in this case that is actually S by M o ratio.

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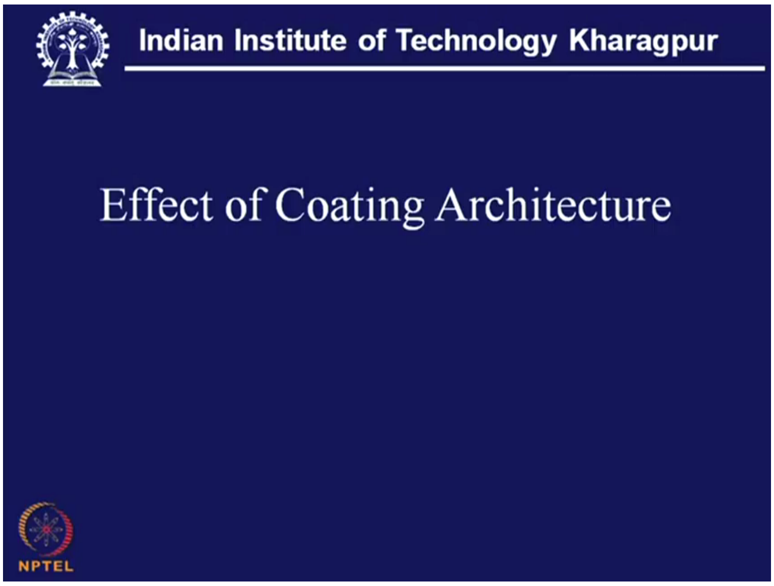

Adhesion of the Coating

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Hardness

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Frictional Characteristics

So what we have seen so far the effect of coating architecture that we have just discussed with this coating architecture we found that this M o S x plus titanium nitride coating architecture that gives the best overall performance and then this adhesion, hardness, fictional characteristics, wear coefficient. So considering all these we saw that this is the overall performance that is the best one.

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Now what we can find here that this is now TiN M o S x coating, so influence of M o S M o and S content, so that what we have seen here also it is Ti cathode current, so what we can see here that grain size, grain size that is also one thing. Now with this formation of this variation of cathode current say from 5, 3.5, 2 and 1 those in ampere what we can see the grain size that is the grain size and this may be cathode current or Mo plus S content, so what we find here it is something like this, it is falling and here it is about 2 atomic percent, here it is about 4 atomic percent and this is about 12.75 and this is about 16.75, so this is a condition of deposition where the process pressure was 1.5 millitorr M o S 2 cathode current that was restricted to 0.5 ampere and then the cathode current of this titanium that actually that was varied, so with this we can get grain size of this order and then comes very important thing that is actually the surface that means that adhesion.

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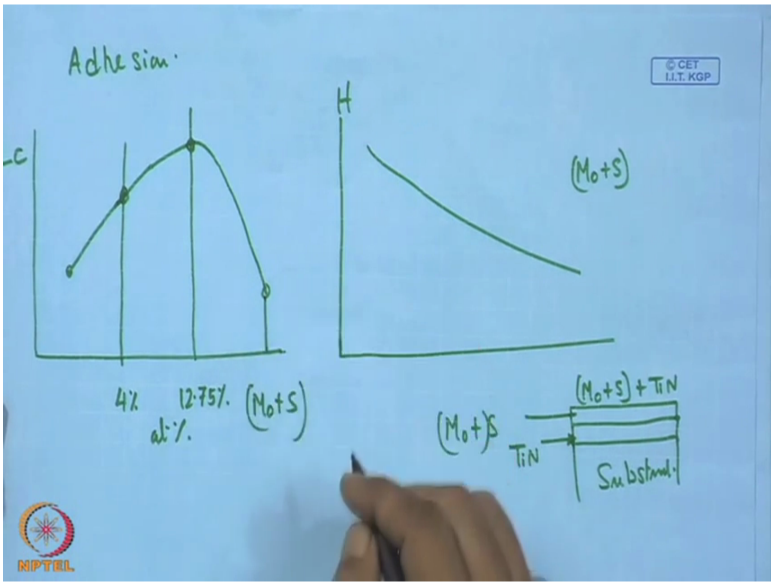

Adhesion, so with this, what we can see here that this is just L c critical normal load and this critical normal load what we can found that this is actually a…it is just like a rising and a falling curve, so this is actually is zone that means where we have a good result that means the good result means it is somewhere around 4 to 12.75 atomic percent atomic percent of M o S, M o plus S where we can get a good value of L c that means the addition but when it is below that it was dripping sharply and here also it has a very sharp fall, so this is can this can be considered a zone where it is expected to give a good result.

However, hardness wise it is continuously falling, so it is a continuously falling the reason is as follows that higher the percentage of M o S. Naturally this is going to be a soft phase and with this soft phase what we have seen that this compound hardness or say the average hardness of this composite structure because this is going to be a composite structure here what we have. This is going to be the structure, so that this is actually M o plus S and this is titanium nitride, so when we measure this hardness the influence of the substrate definitely this coating comes in picture and here we have M o S plus also, so here we have M o plus S which is in the form of M o S x plus TiN, so higher the percentage of this one naturally when we measure the hardness it has its own influence that is why it has a dripping curve. Now when it is a coefficient of friction, so if we put this way the coating with the highest value that is going to give the…I mean that means here this coating.

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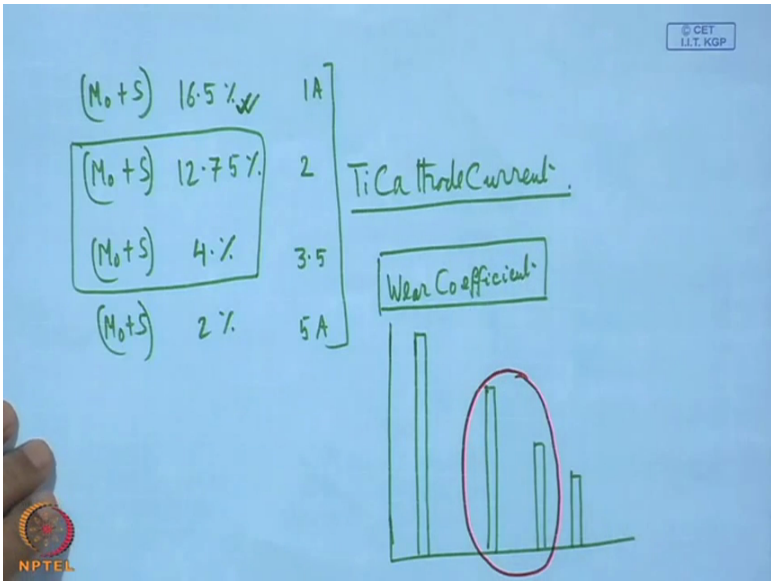

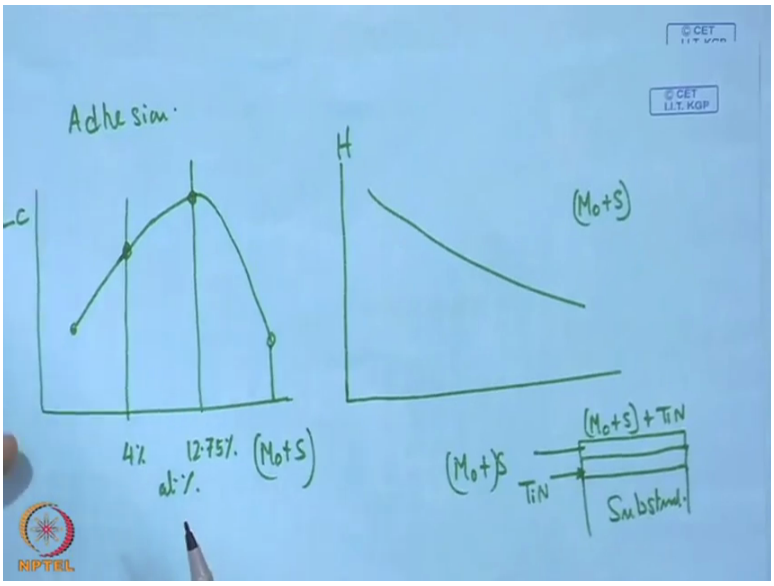

This coating that means a coating with M o S 16.5 percent and then we have one with 12.75 and then we have one with 4 percent and then this one with around 2 percent and this is corresponding to 1 ampere cathode current, this is 2, this is 3.5 and this is 5 of titanium cathode current, titanium cathode current. So with this what we see that the fiction coefficient for this one that is going to be the lowest followed by this composition, so lower the value of M o S higher will be the coefficient of friction.

However, what is very important here to know that in this case we have also another term what we call wear coefficient, wear coefficient. So when we consider the wear coefficient definitely we found out that this wear coefficient of this 2 that means this percentage wise this is much better compared to that with higher value of percentage of M o plus S that means this is a zone, this is a zone where we can have a lower value of wear coefficient though we can have a high value of wear coefficient with higher percentage of M o S that means a range within this 12.75 atomic percent to 4 percent that is going to be a good condition for deposition of this composite coating and in this case we can get a good value of wear coefficient and this is just a balance between titanium nitride content and that of M o S content and at the same time the coefficient of friction that can be also obtained with a rather favorable value.

So this is actually on one side the coefficient of friction and at the on the other side this is also the wear coefficient. Now considering this to what we find that this value in fact wear coefficient will be quite high on this side, now in this case this is actually the percentage of this 16.5, 12.5 or 4. However, what we can find considering the coefficient of friction and wear coefficient, we can find that this zone this is this is not to be compared to this one, so this is actually a zone where we can find one of the good performing coating considering this value of this critical adhesion load, critical adhesion normal load and also the coefficient of friction which has been also explained and at the same time the wear coefficient. So this is a percentage, atomic percentage of molybdenum plus sulphur inside the top functional layer which can give a favorable value of wear coefficient considering other 2 properties that means the coefficient of friction and also the critical load of adhesion.

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Now comes the effect of substrate bias, now we understand that this effect of substrate bias is to improve the hardness of the coating, to improve the density of the coating, to neutralise any stress which can built because of temperature high temperature and a wide difference in coefficient of thermal expansion and also the modulus of elasticity, so the role of bias is well understood. However, what is the best value of this substrate bias that also one to look because of the simple reason that too much of substrate bias can also cause re-sputtering of the coating and then the growth rate will also can fall.

Not only that, in addition to that too much of energy of impeachment that means this impinging ion can also cause too much of interaction at the interface promoting a diffusion across the interface and as a result of that of formation of the diffusion layer in not be ruled out and this can also be counter-productive in that, that the adhesion strength that means the article value may also be affected and hardness value may also be affected that means with a low with a high value of substrate bias, hardness value also even fall, so these are the 2 things one can immediately look in apart from this coefficient of friction and also the wear coefficients, so we can look into this effect of substrate bias.

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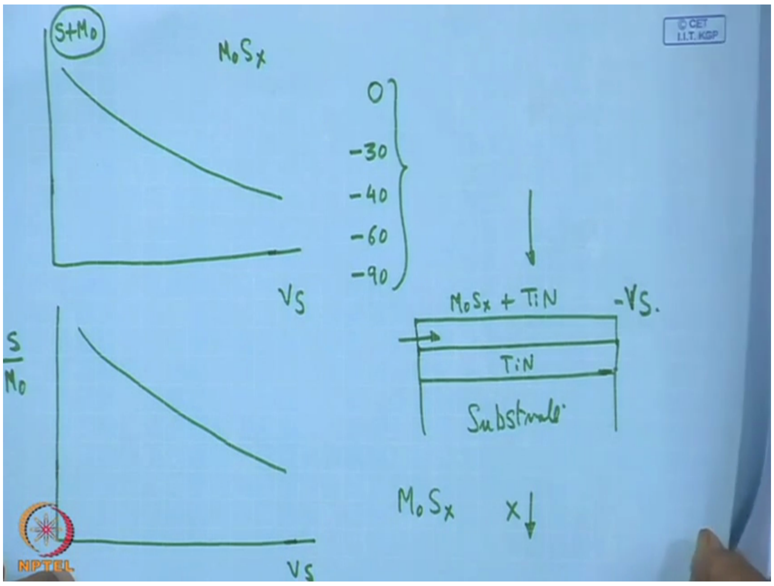

Now with this increased of substrate bias what we can see that this SM content that means what we are interested in sulphur plus molybdenum in the coating and with this increase of bias voltage what we can see? We can also have a falling curve and this is because of the sputtering re-sputtering of molybdenum M o S x, so M o S x actually gets re-sputtered from this coating that means the coating is somewhere here.

This is titanium nitride, this is going to be the substrate and on the top of that we have 2 have we are supposed to have M o S x plus TiN, so when we have this high value of this VS which is the substrate bias, now this energy incoming ion that will impinge that will bombard the surface and it will lead to re-sputtering of this preferentially in comparison to titanium nitride, so as a result of that what would be the outcome? In this coating we can have less amount of M o S x and relatively more amount of TiN, so this is 1 point should be also taken in consideration.

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Then another thing, this is S M o ratio, this is also very important issue if we consider the tribological property of this coating, so it is actually S M o ratio with this VS, so this is also not only S plus M keep on falling but within this S plus M which remains inside the coating in that also the ratio of S and M that is also falling that means in clear terms if we increase VS then in this M o S x the value of S x will keep on falling and with that fall we may arrive at a situation in that case this M o S that combination that means molybdenum and sulphur that combination in certain sulphide form, stoichiometric sulphide that will not be in a position to give any tribological property and the whole purpose will be just lost or defeated.

So this has to be also taken into consideration, so normally say bias voltage if one consider to increase bias starting from 0 say it is minus 30, minus 40, minus 60 and minus 90 this is a range, so if one try to examine the effect of the substrate bias voltage, so one should have such kind of variation with increase of bias voltage.

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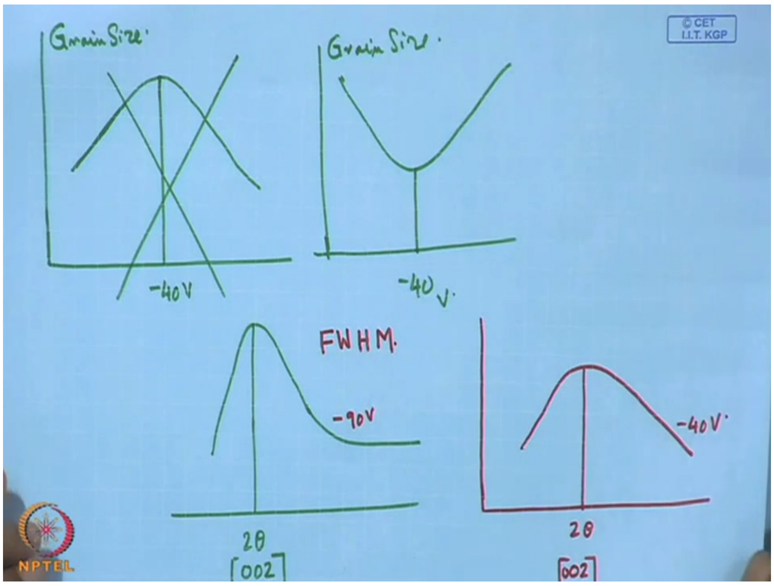

Now comes grain size, now this grain size this is also important considering the refinement of the coating, surface roughness of the coating, so grain size, so here what we can find that grain size is having such a variation and it is around say with that condition around minus 40 volt, we got one of the…this is actually sorry this is actually it should be like this, grain size, so it is actually somewhere like this, so it is the grain size here, so this is around minus 40, so this is the grain size and that can be also looked into from XRD. Now when we have this XRD diagram it is typically of this shape, so and this is actually angle which gives a 2 theta value corresponding to 002 plane and this one from the shape of this XRD diagram one can also have fair assessment about the grain fineness, so this is one so what we called full width at half maximum.

Full width at half maximum that means if we consider this full width at half maximum of this XRD then we can find out a graph this is one graph, we can also have a graph which is quite wider compared to this one, so when we see from the same 2 theta at the same place a wider XRD then this one actually gives a fine grain size, so this may be a graph with minus 40 volt and this may be a graph with minus 90 volt or minus 60 volt or 0 volt without any bias. So from this XRD x-ray diffraction diagram one would be able to also locate the condition where or around which grain as the finest size or the smallest size, so this grain size refinement that is also the result of this substrate biasing.

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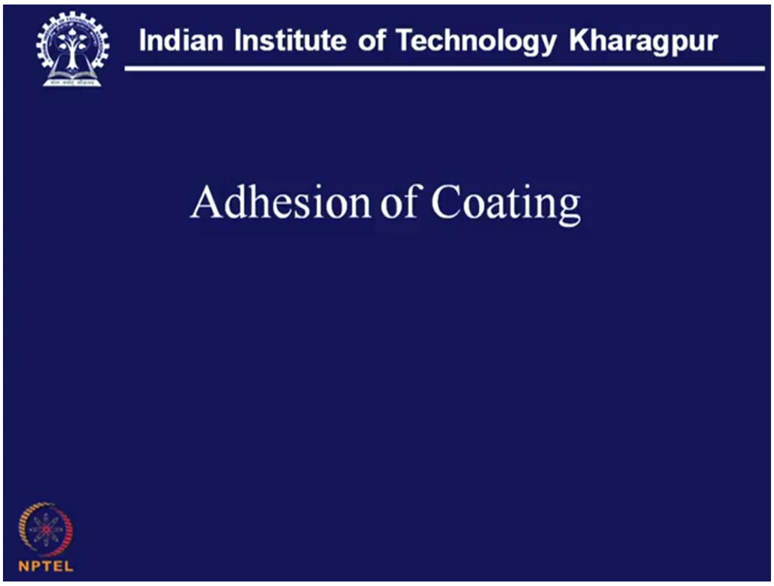

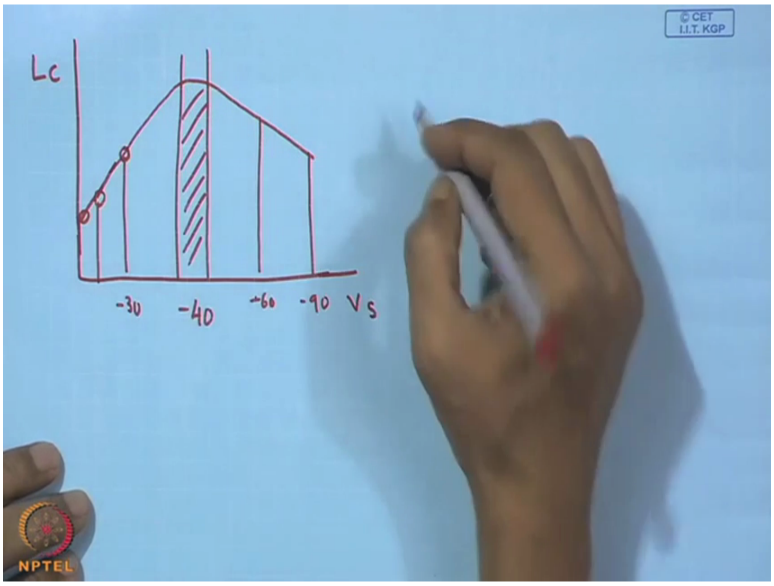

Similarly what we can do, adhesion of the coating, now adhesion of the coating that is also important that is the most important property one should look for, so this is L c and this is also bias, so here also we see that this is going to be a graph of this nature and this may be a zone which will be of immediate interest and it is around minus 40 volt this is actually 0 volt, so this is about 0 volt where we have one of the lowest L c value that means the critical adhesion strength and this is may be around 30 but on this side it is actually minus 60 and this is going to be minus 90, so what happens in this case too much of stressing and at the interface and also if we have because of very high energy availability too much of diffusion or a (())(51:10) layer and on this side there is no diffusions, so no diffusion or too much of diffusions both are counter-productive, so value in between that could give one of the very best result so far as adhesion is concern.

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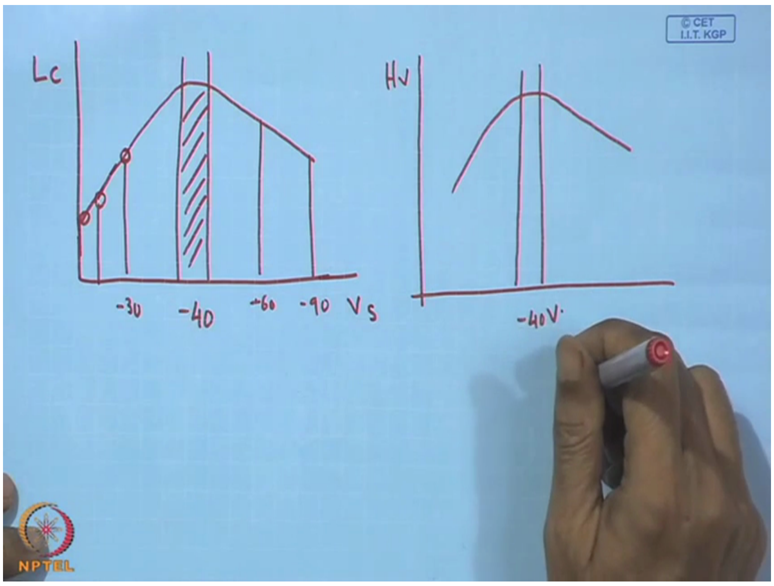

Hardness, now this hardness this also can have a curve like this with substrate bias and here also is zone we may come across around minus 40 and this is where we have densification of the coating that closing all the pores (())(52:03). However, if we go further to this then what is happening that too much of compressive stress will be frozen inside the coating and the material becomes too brittle on this side and when that indenter comes on this coating and try to penetrate instead of having any plastic deformation, very localise plastic deformation this this penetration this loading of the indenter that actually leads to crack propagation because the material cannot undergo even the smallest possible plastic deformation and as a result the material shows crack propagation and that means it has a lower surface hardness.

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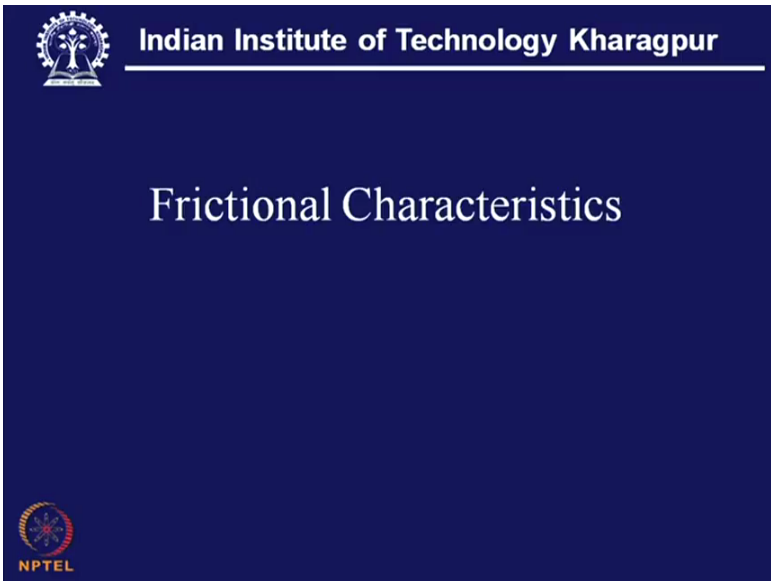

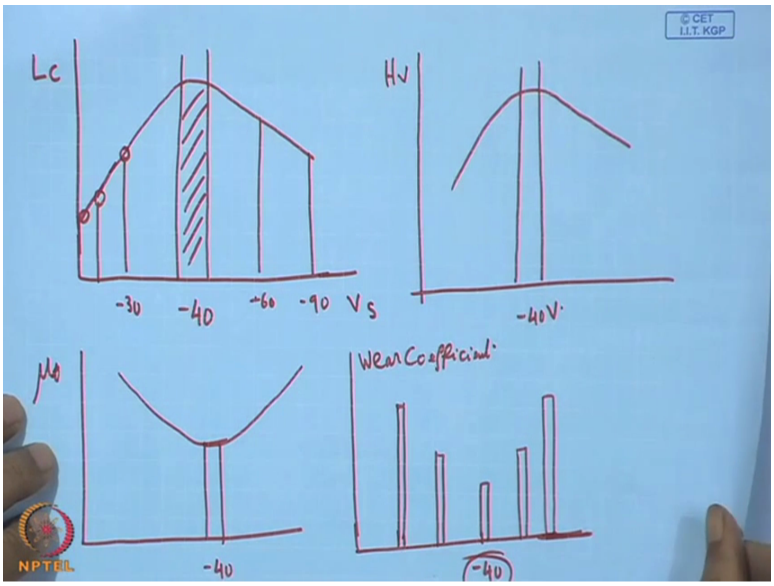

Frictional characteristics, now with this also what is what we have seen, coefficient of friction. Coefficient of friction that has been also seen in in between here, so this is actually given by a particular morphology of the coating and which we could get around this value and on the 2 sides the coefficient of friction is rather high and this will also lead to another graph which we call wear coefficient, so this is a measure of wear on the ball or also on the disc, so here also we find that with this we have high value with low bias but somewhere around intermediate value of minus 40 we get one of the lowest wear lowest wear amount of wear is the lowest around this value and that is because of the hardness of the coating, lower value of the friction and with this the coating can give one of the best possible performance in actual practice.

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So what we find as a summary what we can summarise that we have examined various type of coating architecture one may be just molybdenum disulphide. However, it is known that this molybdenum disulphide alone cannot work so effectively in all for all practical purpose in normal atmosphere that is why this molybdenum disulphide always come with material like titanium, chromium and similar material of transition group to improve its property that means protecting against moisture, oxidation and holding that basal plane that means the 002 plane parallel to the substrate surface. So these are the major role of this type of element which are added in small quantity and they are atomic percentage hardly exceeds 10 - 15 percent and with that this coating capability, capability or performance of the coating could have been raised remarkably.

However, it has been found that this coating performance of this coating can be augmented further just by putting a hard surface layer beneath this top functional tribological coating to have better and much improved bearing surface that means the load bearing capability of this top functional coating can be also improved and that is why there has been a lot of attempts to put some transitional element metal nitrides and one of those is titanium nitride, so with this titanium nitride as the intermediate supporting layer and the top titanium layer with M o S 2 that results shows a much promise. However, the most remarkable thing is that that this TiN which is just beneath M o S 2 that can be also brought on the top surface and it can also play as one of the contributor in the top functional coating that means the top functional coating is just not M o S 2 or M o S 2 with small addition of titanium.

However, this is going to be rather major part will be this hard material like titanium nitride and with this titanium nitride and with addition of M o S 2 we can see that this properties of structure, properties of titanium nitride could have been improved a lot and with that M o S 2 addition with right amount which has been controlled by controlling the cathode current of titanium and then also by holding substrate, suitable substrate bias value, we can find out one of the best condition which not only holds the hardness, high adhesion strength and then low very low coefficient of friction but at the same time grain refinement and a low wear coefficient that can be also achieved, so what we can see that this titanium nitride plus M o S x type coating which can be termed like a hard look coating that can have a very balanced property in terms of wear resistance and lubrication.