Technology of Surface Coating
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Lecture No 19
Sputtere Deposition of Molybdenum Di Sulphide Coating

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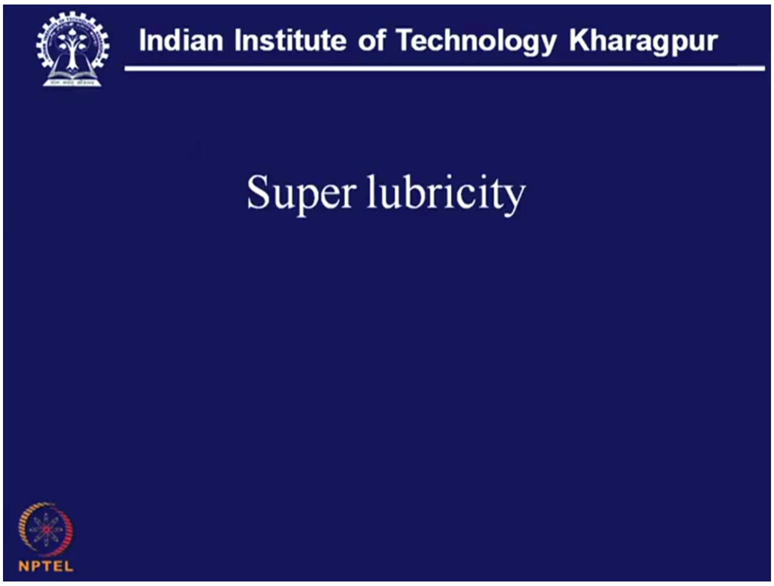

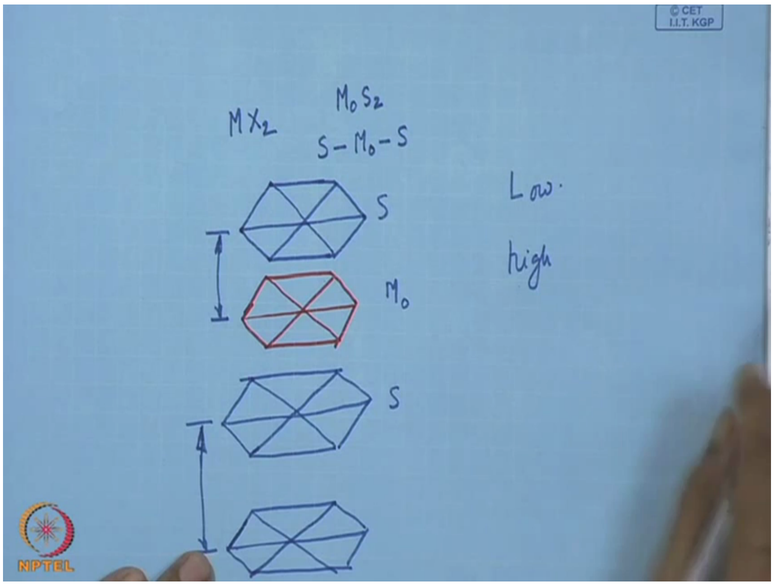

Sputtere deposition of molybdenum disulphide coating, now this molybdenum disulphide or say tungsten disulphide, these are the materials which we can put in the form of this formula MX 2 and where this M stands for one element of this transitional group and this sulphides are known to have very low coefficient of friction or in other words a super lubricity, so this materials are known for their super lubricious property. Now how there is super lubricity is obtained.

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Now to look into this issue what we can see, this is actually M o S 2 that means it is as if it is S M O and S, so when we like to see its structural formation we can see that we have a hexagonal array of the sulphur and molybdenum, so this is actually one plane containing the sulphur in an hexagonal array in an hexagonal arrangement and just with that adjacent to it, we have another plane and this is again is actually the plane containing molybdenum, this is also in hexagonal array, so that means here we can show these lines and finally what we have here another plane that is containing sulphur, so this is one set of M o S 2 and below that what we have further to this we have again here another plane containing sulphur and followed by molybdenum and sulphur, so this is one set, this sulphur, molybdenum, sulphur then also we have sulphur, molybdenum, sulphur.

So what we find normally that the bond between this molybdenum and sulphur that is a covalent bond that is very strong. However, the bond between this sulphur and this adjacent sulphur which is from another M o S 2 that set, this bond is rather weak and also this distance, this inter-atomic distance that is more than the inter-atomic distance here between 2 sulphur planes, so this distance is actually high compared to this distance and this force between these planes that is a very weak force and that is actually Van Der Waal forces of attraction and that is weak force.

So when a force is very much acting on this plane then this sulphur molybdenum bond that does not break but the bond between these 2 being the weak, so this plane can easily slide over this one and that ultimately results in a very low value of friction and it is exactly what we know as super lubricious property of those materials like molybdenum disulphide or tungsten disulphide.

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Now here what we can see 2 planes are there basal plane and edge plane, these are to be taken into consideration because the orientation of this plane is extremely important to have a very low value of friction, low value or high value, good performance or poor performance, these 2 will depend upon the very orientation of this basal plane or this edge plane. Now let us look what is mean by this basal plane and edge plane and how they should be oriented.

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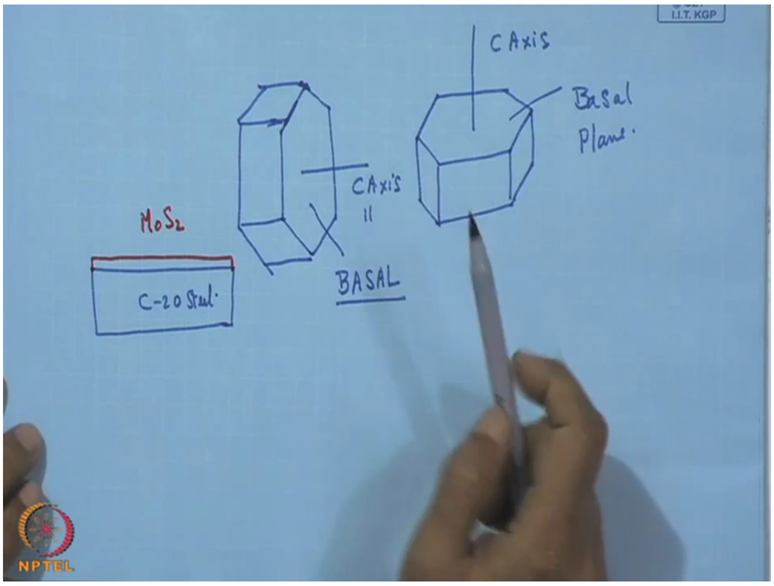

Now what we see in actual field of working say this is one substrate, it may be made of just a low carbon steel C 20 steel and we like to deposit a coating of molybdenum disulphide over this, so it is just not a coating of M o S 2, it is just not M o S 2 but it will be M o S 2 with right orientation and if we cannot get this right orientation, we may not get a very good value of coefficient of friction or a what we call super lubricious property. So this is very important so let us look what does it mean, if we put this hexagonal like this, this is one way of showing, this is one way of showing, so that means your this axis what we call C axis that is perpendicular, C axis is perpendicular to the surface of the substrate, so this is one situation, so this C axis is perpendicular to the substrate what we call it basal plane.

So here 2 things we must notice of those 2 things one is basal plane is parallel to the substrate surface and obviously C axis is a perpendicular but we can have another extremity, so another extremity means this way, so let us have a quick look here at this is another situation, okay so this is here, what we see? This basal plane this plane, now this is no more parallel to the substrate surface but it is perpendicular that means the C axis, C axis is now parallel to the substrate surface and this is actually the edge plane and that is now parallel to the surface, so this is one of the extreme worst situation under which condition, what we can have? We can have very a poor performance of this coating.

Now this can so here we can summarise one thing that even to have this coating whether it is PVD or any other process, 1st and foremost thing is that whether this basal plane is parallel to the substrate surface because only in this direction as it slides, as it slides here in this direction then only we can expect good coefficient of friction and if it is perpendicular like this, then this sliding will not be easy rather sliding will be difficult and with result of high value of friction, high sliding force and removal of the coating.

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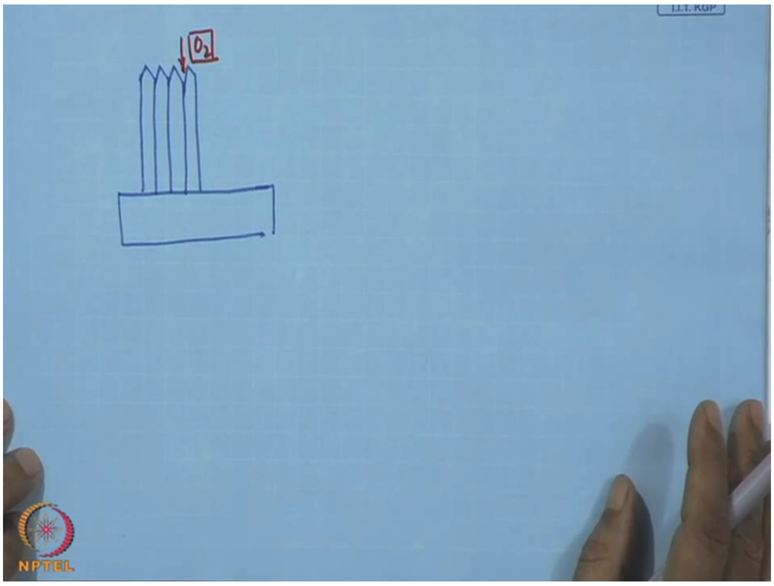

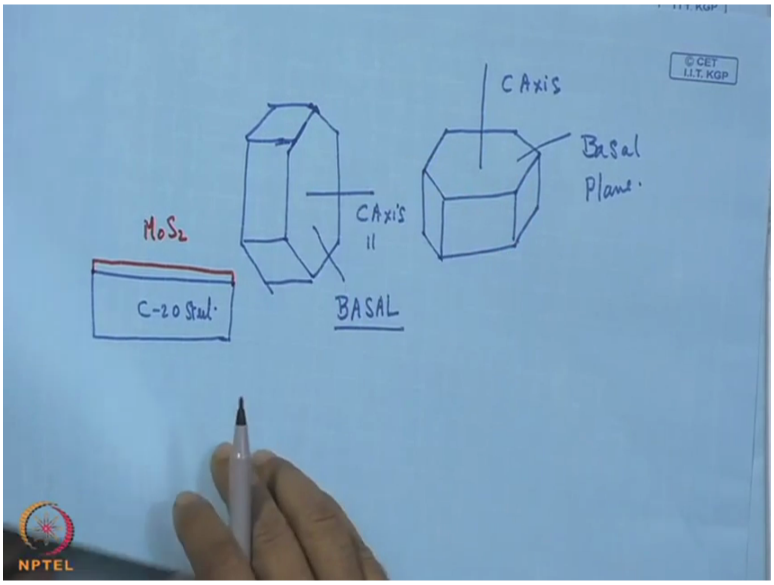

Another thing also we can look here that this normal orientation say we have the substrate here and these are the this is just the arrays of coating, so if this is the orientation and then these are the basal plane is like this, so then there is also attacked from the atmospheric oxygen and that can also damage the coating, so when this edge plane that is parallel to this substrate surface, in that case also we can have oxygen attacked in this way that means here the attack will be difficult but here it will be attacked will be rather easy and in this way the atmospheric oxygen or humid in humid atmosphere, the moisture can get in and then it may cause deterioration of the quality of the coating, so then under the action of this force this coating will immediately break and that will lead to high value of friction, so this is what we call basal plane and edge plane.

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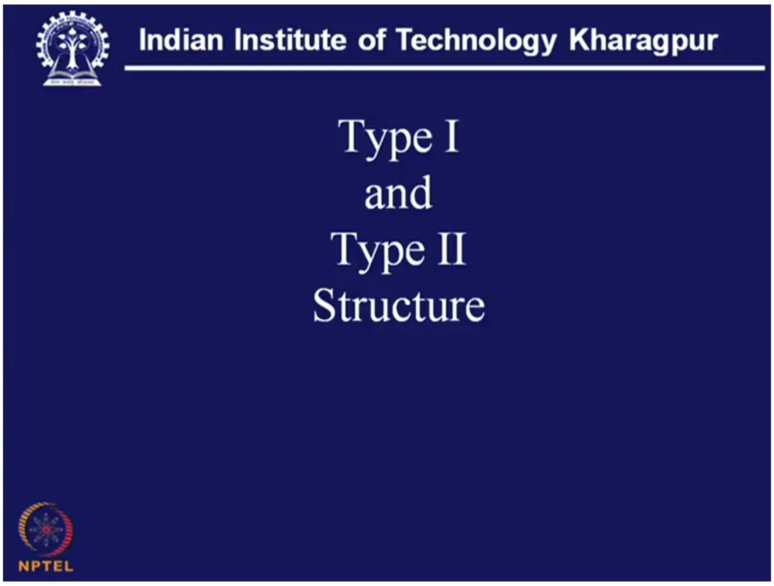

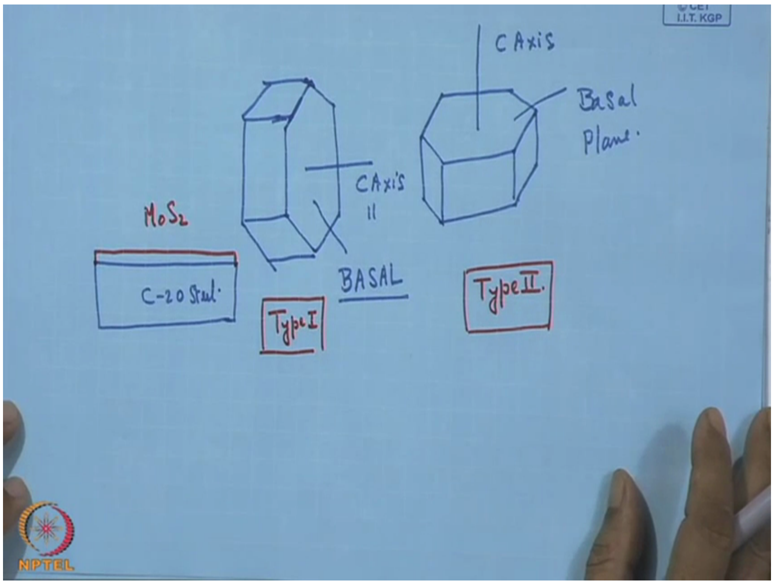

Now we have type I and type II structure, so type I structure what we can call…we can refer to this previous figure that means if we have the basal plane parallel to the substrate surface then we call this is as type II structure, type II and when the basal plane is perpendicular to the substrate surface, we call it type I structure, so obviously our choice will be type II structure considering that low value of friction is most desired and this is for the purpose of having the best performance of any component or wear part.

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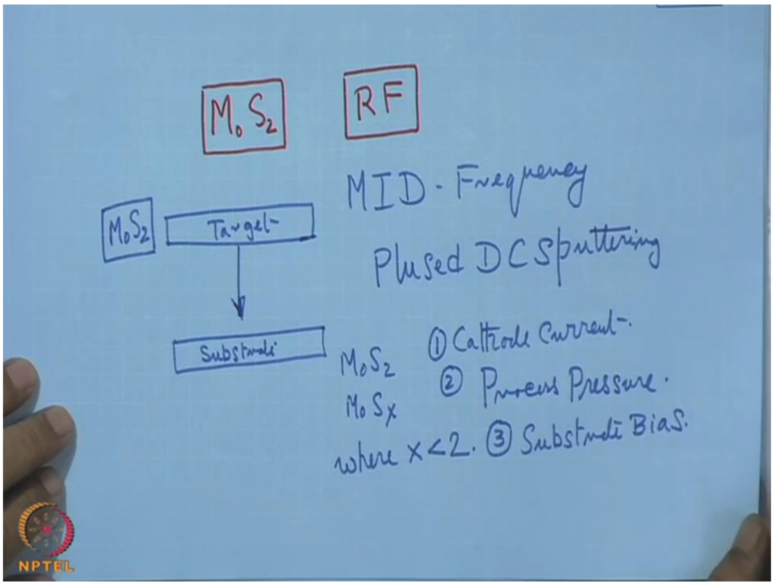

Now what we can see further to this sputtering of molybdenum disulphide, now this M o S 2 what we have written M o S 2, this sputtering is possible by at least 2 processes because this is not a very good conductor of electricity that is why earlier this DC sputtering, that was not very popular and what we had it is mostly RF sputtering, RF radio-frequency sputtering and we know that with this RF it is possible to use a non-conductor or a poor conductor as one of the target material, so it was a RF but RF has a complexity that is also noted that it is the complexity of matching the capacitance with an external capacitor and it is also the impedance matching.

So that is why later on came into being what we know as mid-frequency pulsed DC. It is actually mid-frequency pulsed DC sputtering, so both are very useful in having a coating of molybdenum disulphide on the substrate and in this case it is mostly for all mechanical application it is going to be a steal substrate which can be coated with this molybdenum disulphide to have better performance in all tribological activities. Now here the sputtering of molybdenum disulphide, we can take a solid target of M o S 2.

However, the question is that during sputtering when this material is coming like a flux and intercepted on this side by the substrate, so this is actually the substrate and this is target, so the question is whether we get here also M o S 2 or it is M O S x where x is less than 2 and if it is less than 2, is there any problem associated with the value of friction, so these are the few things can be also noted for this sputtering operation and at the same time there is another way of doing, so this is applicable whether it is RF or mid frequency pulsed DC sputtering and in this case definitely the parameters which are going to influence this value of x that is on one hand, we have the cathode current.

So it is actually the cathode current that is the said value of cathode current, this is number 1, number 2 is also be process pressure, process pressure that is also another parameter and number 3 what also appears to be quite important and it can also influence that is substrate bias voltage, substrate bias. So these 3, this combination is very important their selection of this and they are combined effect and lead to a particular value of x and not only that, it can be also is formation of this basal plane or edge plane, so this is what we can mention here.

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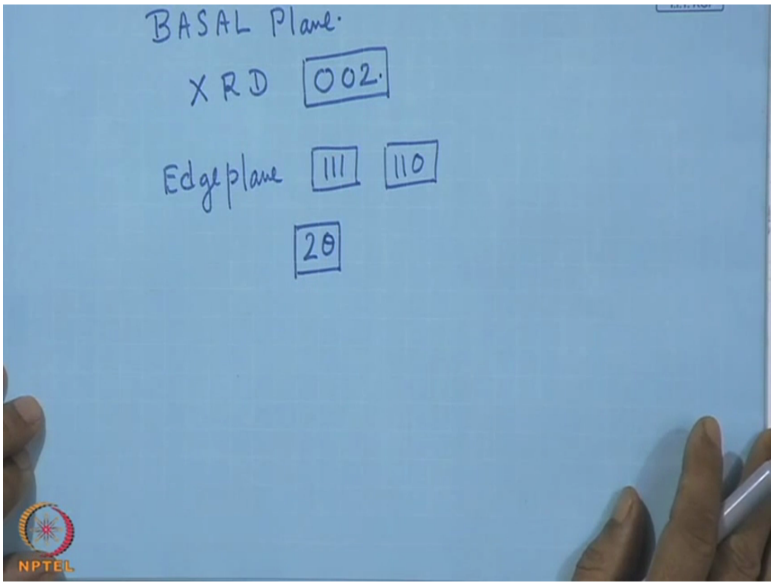

So when it is the basal plane, so from this XRD, it is a diffraction diagram we get a peak of 002 and that is a conformation and that is a conformation of the existential of this basal plane which is given by this 002 orientation and that is parallel to the substrate surface. It can be edge plane and in that case the peak comes from this 111 or 110 and for that we have definite angle 2 theta and from this from the standard XRD corresponding to this M o S 2, we can find out the value of theta which correspond to this 002 or 111 or 110 and from that concerning the quality of the coating we can have fair idea and whether it is the effect of high cathode current or wrong choice of process pressure or the substrate bias selection all these things can be known just by looking at here that whether on the XRD diagram which peak is coming up and depending upon the sharpness of the peak or the little widening of the peak, from there also we can have fair idea impression about the size of the grain, fineness of the structure apart from this scanning microscopy.

So these are the few things one has to look while going for this M o S 2 coating deposition because ultimately it is going to be 1M that it is the best possible technically functional coating, so from this XRD we can get a fast information and the very preliminary information but it is very useful. In that, that whether we are in the right track or right direction in the whole deposition process or deposition activity and whether the process parameter selections are proper which may finally lead to one of the best performing coating. So this is one thing, one has to look but apart from this it is also possible just instead of using a target which is made of M o S 2 what we can also do? It is also called reactive sputtering.

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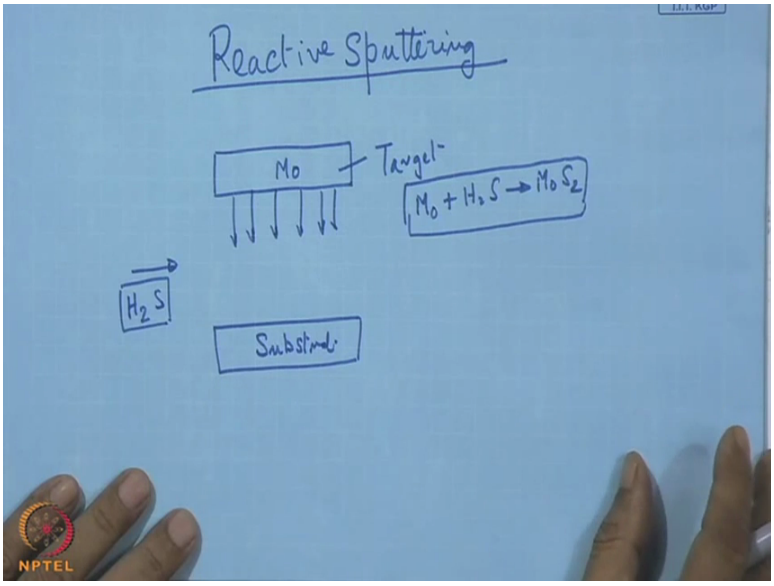

Reactive sputtering, so in that case we have one, we have one molybdenum target and then we have one substrate facing this molybdenum target and here just like reactive deposition by sputtering, say for example titanium nitride deposition or aluminium nitride or chromium nitride or even it is molybdenum nitride but in this case it is going to be molybdenum disulphide, so M O flux, sputtered flux come in this side, it will on its flight towards the substrate and then we, what we have? We have here incoming instead of nitrogen it will be there H 2 S that is the source of sulphur and then there is a M O from this target and this H 2, from H 2 S from this external source that can also make this finally M o S 2, this is also possible and in that case perhaps this problem of less sulphur in the coating here, so this is on the on the substrate that means less sulphur deficiency in sulphur that can be eliminated by this reactive sputtering, so that is also possible.

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Now comes coating architecture, what we want? We want a stable coating and this stable coating means it should be stable not only in a very restricted atmosphere that by that what we mean? That it should be high vacuum.

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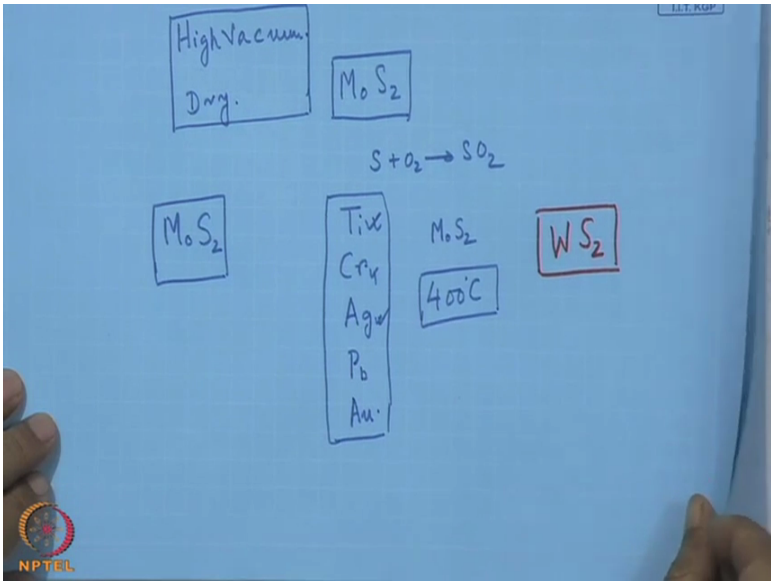

This is a restricted atmosphere, high vacuum, it is a dry environment no moisture content and we know that from our experience that this high vacuum dry environment here M o S 2 it is one of the best materials for giving one the lowest value of friction but when it comes to the question of practical use, normal use and filtered use where we cannot maintain this lower value of humility, it is normal atmosphere, in that case this M o S 2 can show its weakness that means it will simply absorb moisture and then from that oxygen will be active and this sulphur will be attacked and it will be actually S and O 2 it will lead to sulphur oxide, so oxygen will convert the sulphur into sulphur oxide or it can go inside, it can also make molybdenum oxide.

So there are lots of investigation, there are a lot of documentation in this particular subject whatever may be the thing, ultimately it is the total failure of the coating, so what we like to say here that just M o S 2 alone that can be a good candidate for such high vacuum or dry environment but for mass scale use in numerous mechanical application, this alone M o S 2 cannot just serve as a good candidate and a good coating material, so that is why there has been lots of effort to formulate, to have a new formulation of this M o S 2 and that is done by doping with some other material.

That means on one side we have M o S 2 but another thing it can be say titanium, chromium, so these are the good candidates as per the literature research literature, there had been also silver for example then lead also used which may not be encourage much than gold, so these are the candidates which has been tested and here as per the literature such it is found that this titanium, chromium and also silver they appear to be quite effective in that now this M o S 2 with little addition of titanium, chromium or silver become more stable in high humidity and also when little rise of temperature. We know that from research document that M o S 2 that is in open atmosphere that is stable up to 400 degrees centigrade, so when it is the requirement is about 400 degrees centigrade for any application of that component or part then we have seen that this frictional coefficient it rise is quite fast and that means that is the end of the service life of the coating, so this coating is no more useful.

However, the whole idea here is also to have this titanium, chromium or silver with M o S 2 to increase its capability to work at a higher temperature and in that in this respect we can mention here that we have on one side M o S 2 but also we have W S 2. That is an addition, later addition tungsten disulphide, so this has a capability of holding its stability, it is chemically stable still up to 700 degrees centigrade that can be also another good candidate but it is truly also seen whether by adding such material in this site whether we can also augment its property for various field of application where still we have to work with a higher temperature or with a higher level of humidity, whatever may be the case. Now this coatings routine practice is to not just M o S 2 but to have this doping of titanium with M o S 2.

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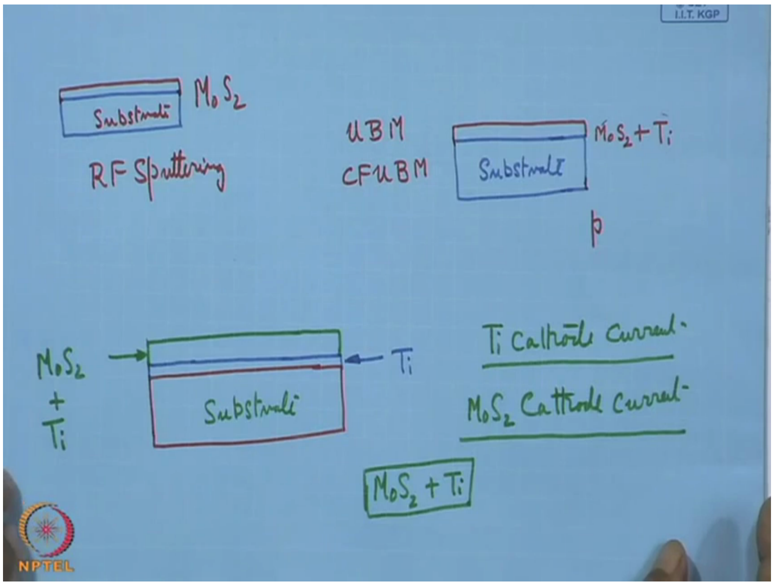

So the basic structure of architecture of the coating which was used with RF. That was just M o S 2 and it is mostly a columnar structure, so it is the substrate, this is the substrate and on that we have M o S 2 coating and it is mostly RF sputtering with just conventional magnetron RF sputtering but with the advent of this unbalanced UBM and CFUBM it has open up new opportunities and new scope of working with this M o S 2 and in this case we can have a better architecture and we can blend this M o S 2 with 1 material say for example titanium, so with this addition the architecture looks like and here we have M o S 2 plus titanium.

So this titanium addition increases the capability of this coating that has been also established that with this addition of titanium, this coating can work in an environment which is rich in moisture water content and the coefficient of friction is quite low or even if we increase the temperature of the coating still this one is better than this one, so here also the pressure that means the source pressure that can be brought down compared to what is needed here because it is now unbalanced magnetron or close field unbalanced magnetron, so with that we can bring high ion current on the side and that is actually is the case where we can work with still lower value of the pressure and according to this new actual diagram for this coating architecture, we can see that even with low-pressure and low-temperature, we can get a very good architecture of this coating and then we have widened the scope of activity of this coating.

So this is one of the structure but when we like to use this thing, we can also have the architecture like this. This is the substrate and then obviously we have to have a sub layer of titanium which is a adhesion layer, so this is of titanium and over that what we get, we get actually this M o S 2 and titanium. This is actually M o S 2 plus titanium, now during the sputtering what one has to do? Just to have a transition first of all the routine process route has to be followed that means first of all cleaning the surface with titanium then this titanium is used as the ion for cleaning this one then changing the condition of sputtering, this titanium now should not be just used as for iron etching but now this titanium should get deposited over the surface.

So the 1st step is cleaning the substrate surface with titanium followed by deposition of titanium and process parameter has to be monitored properly and then according to the requirement when we get this titanium sub-layer that means that is called the adhesion layer then obviously the target for M o S 2 that should be switched on that should be activated and here obviously it is the titanium cathode and M o S 2 cathode. These other 2 cathodes and for the reasons, so this is you have titanium cathode current and M o S 2 cathode current, so this cathode current should be adjusted and there should be…

So we have proper intermixing between titanium and M o S 2 in this transition, so it is gradually the titanium percentage is getting down and M o S 2 percentage is going up and finally what is required in the coating that is actually M o S 2 plus titanium and that is the final content in titanium, so once the transition is done then we have a steady state deposition and where keeping there is titanium cathode current constant and M o S 2 cathode current constant this deposition can be continued for several hours to have a consistent bulk value of M o S 2 and the bulk value of the Ti content in this composite coating. So this way one architecture can be built up.

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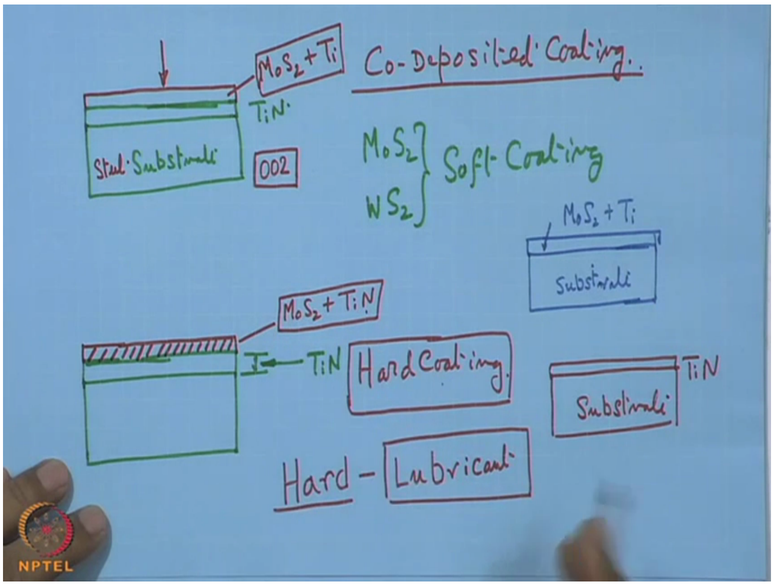

We can have another architecture that is say for example it is also known that if this is the substrate then over the substrate we can build a titanium nitride coating. There is no difficulty in getting a titanium nitride coating, so titanium nitride by reactive sputtering by using a DC or RF or pulsed DC that can be very well used. However, the whole idea here is to improve the performance of M o S 2, we know that we call them super lubricious coating but at the same time this M o S 2 or W S 2, we also call them soft coating, soft coating. So we have actually 2 extremities ultra-hard coating, hard coating and this is soft coating, so that is a wide range on one side we have diamond CBN those are ultra-hard material, in between we have all hard material that means conventional hard material say for example all Carbide, nitride, boride of transitional element, we have aluminium, silicon their nitride or oxides that can be also mentioned.

However, on this side on this extremity, we have a soft coating of M o S 2 and tungsten disulphide. Now this is going to be used on a steel whose surface property has to be improved a lot and this surface property means increased the tribological surface property. So this obviously our choice will be a super lubricious coating which we have already mentioned. However, it is found that this coating can be also improved further, what we mean, its performance. If we put a coating of titanium and if the deposition is done on titanium that means this should be now the architecture, so this is now the architecture, this is M o S 2 plus titanium, so it has been also seen that established from research documents that a coating of M o S 2 plus titanium directly deposited on a steel substrate, on a steel substrate and a coating deposited on an intermediate layer of TiN, so this architecture is better than an architecture only containing M o S 2 and titanium.

So this way one can also design the architecture of the coating just to improve the performance and here it is said that the load-bearing capability of this coating is better and higher when it is put over a hard coating, so a soft coating is well supported, well boned by 1 hard coating and here the resistance to deformation is more because when the load is applied on this side there will be a tendency of deformation. Since the substrate is of lower hardness, so naturally whole thing will get deformed along with M o S 2 but if we have a properly chosen architecture of a hard layer, hard metal like TiN then it is expected at this coating will improve its performance. Now this is one architecture but it can be extended to this one, say we have again are steel substrate.

However, on this we can have titanium coating, this is a titanium nitride coating and on this what we have it is just not M o S 2, it is just not M o S 2 but here as we see here say for example this situation. Here it is actually co-deposition, so this we should say it is a composite, it is a co-deposition co-deposited coating. Similarly, now what we can do instead of titanium we change this titanium to titanium nitride, so this top player now this top player is going to be a M o S 2 plus titanium nitride. So in this case what has been done, it is in principle M o S 2 on which titanium is added to improve its property to stabilise this M o S 2 coating, to stabilise 002 plane and so on.

In this case what we like to have TiN that is one hard coating, so on that we have put M o S 2 TiN coating, so if we consider alone how will this performance will differ? Say this is just one TiN coating and substrate, so we have now 3 architectures, one just with TiN, another with TiN on the top of that we have M o S 2 Ti coating and in another case we have TiN on the top of that we have M o S 2 plus TiN and what we have already discussed, this is actually a coating which is having just what we have mentioned this is actually M o S 2 plus Ti, so whole idea here to maintain this lubricity, this remarkable lubricity of M o S 2 over a longer period of time and in any atmosphere, in any practical environment, so for that a lot of architecture can be proposed and can be tested.

Now here what is the difference between these? So here it is just on the substrate, so compared to this we have a better load-bearing capacity here. However, TiN is a better choice when it is the wear resistance and hardness is concern, so just to improve its lubricity or say coefficient of friction, in that case we are adding a top player but what is done here in this case, it is actually a TiN coating plus M o S 2 plus TiN. Now whether it is complementary to each other or supplementary each other that is the big question, here because it is something comes in support of the other whether it is M o S 2 that is going to help out TiN or it is rather it is the other way round. What we have to see here? The whole idea here to have what we call a hard coating and also lubricant and also having this lubricious property.

So it is also hard coating or also it is serving like a lubricant, of course it is solid lubricant. Now all this M o S 2, W S 2 these are going to be a substitute for all sort of grease, oil type of lubricant and in most of the parts of machine, heavy machine tools the parts are going to be coated with this M o S 2 or similar material and we must have suitable process to coat large part, so that those machines can become also dry machine, so dry machine means without having any application of oil or grease or any blend of that but however, it will be just a dry part, so there is no question of oil drop or grease coating, so it is a solid lubrication. So here what we find that we want both hardness and lubricant because of the simple reason that when it is the question of wear resistance and with high sliding speed, high temperature and high load.

In that case this coating from family of hard coating that means the material from the family of hard coating, they are found to be very effective. In that the wear resistance is excellent and remarkable but when it is come it comes to the question of various stable friction coefficient even at a very low speed and at a higher load, say for micro-moments and other places then it comes the question of super lubricious material which can maintain that condition of very smooth movement without any jerk, without any stick slip and for that this M o S 2 and similar materials are so useful and so effective but here the idea would be, the whole idea would be not to just keep this use restricted only to host slide guides because mechanical component means it can be slider mechanism, slide guides, screw nut, it can be cam and follower, it can be the bush and the bearing, it can be gear and pinion and so on.

Wherever we find any sort of rubbing, it is only where we can pay attention and just by putting this solid lubricant in the form of M o S 2 and similar material but say when it is the tool of productions, say metal forming tool or metal cutting tools in those cases also this material having this super lubricious property that can be also have that can also have one use, effective use and that can also be attractive for those and that is the idea behind here to have this blending of this hard coating and lubricious coating and that is why one can also call it as hard lube coating.

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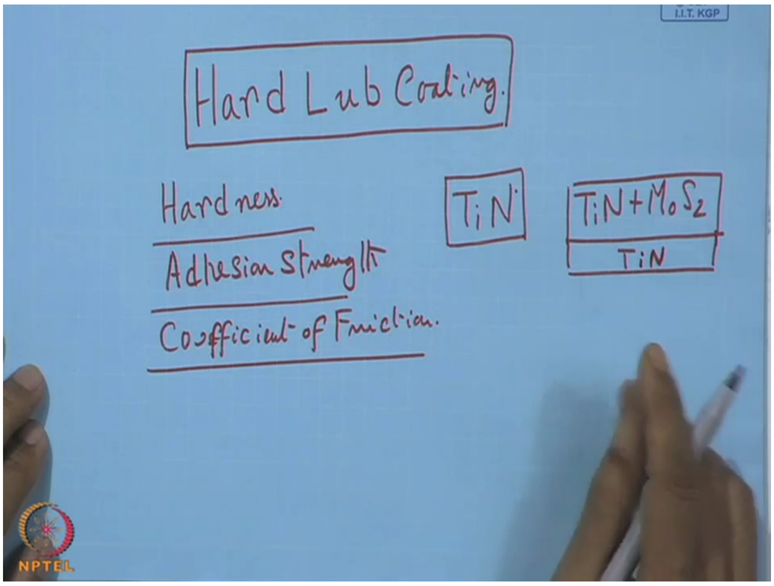

So it is actually hard coating at the same time lubricating coating, so this coating can be used for all sort of applications like machining as a cutting tool, in all metal forming die punches and similar areas, this can find extensive use.

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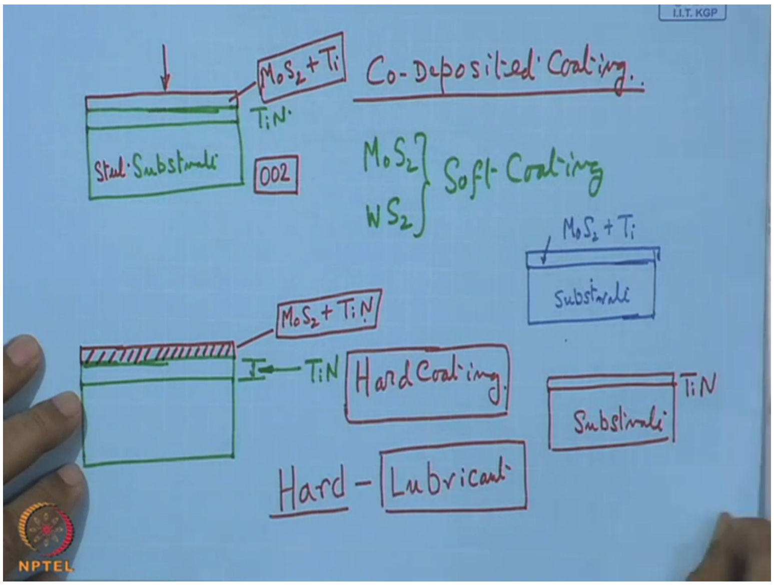

Now the question that these are the architecture, now how we can rank this coating architecture, now for ranking this coating architecture we have to find out some ways or means that means this coating as to undergo some kind of characterisation and it is going to be a mechanical sort of characterisation that means the coating whatever we have mentioned here at means just molybdenum disulphide without any support of TiN we have a hard coating, a conventional hard coating TiN and we have M o S 2 with TiN support and we have also M o S 2 with a TiN support and this is a composite coating.

So with that what we can find here this hard lube coating for ranking, what we have to see here this, say hardness of the coating, hardness of this coating, then adhesion strength of and then coefficient of friction. Okay, so against this what we can see that when it is the hardness, obviously that hardness of titanium that will be the best out of that family, so titanium will be the best and it is also our experience that this titanium nitride plus M o S 2 with a support of titanium nitride at the just beneath it, so that beneath it is also another thing, so that is actually the support that is the second-best, so this is one thing.

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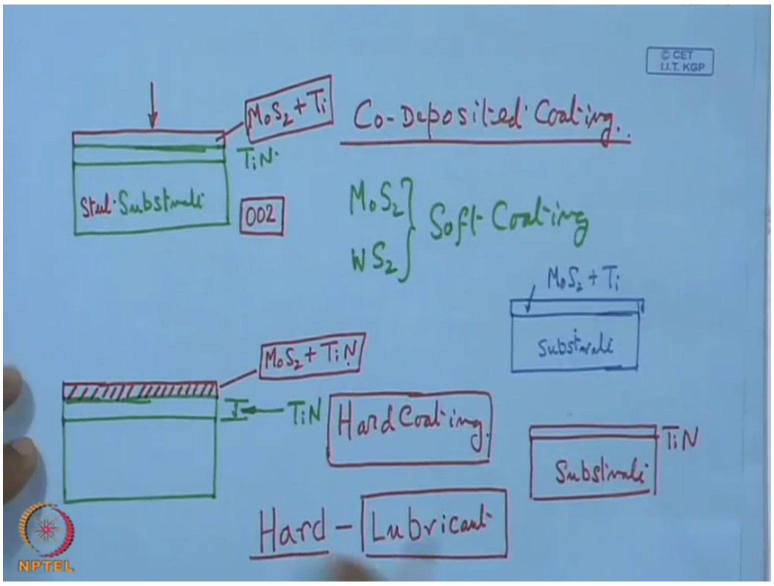

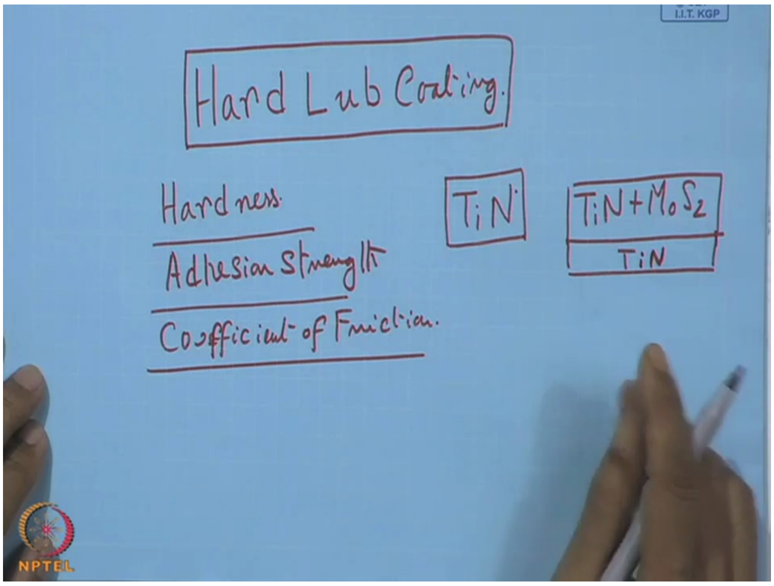

Now when it is the coefficient of friction and then what are the other coating what we have mentioned hardness wise, this M o S 2 titanium or M o S 2 over this these are not showing the same characteristics as that of this titanium nitride and M o S 2 supported by this TiN but when it is the coefficient of friction.

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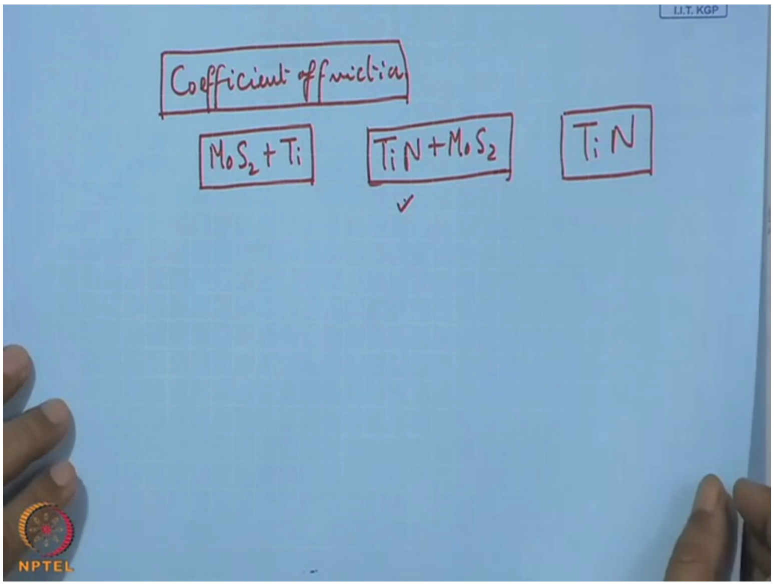

Obviously when it is the coefficient of friction, obviously a coating with M o S 2 plus titanium that will be the best one because it is having high percentage of M o S 2 and that gives the super lubricity and it is better than this than this titanium M o S 2 and titanium nitride is on the other side. However, if we like to consider both wear resistance and coefficient of friction then the blend of this one with right blending between titanium nitride and M o S 2 that would be one of the right choice in that direction and accordingly that coating can be ranked as number 1 in this family which can give a hard look property and this means the hardness of the titanium nitride and also the lubricity of molybdenum disulphide. Another thing is also found out that this particular M o S 2, this M o S 2 is also assisting in refining the this grain structure which is otherwise quite course and that grain structure can be refined by this M o S 2 and this way it is also playing another role that refinement of this titanium nitride structure and thereby improving its property.

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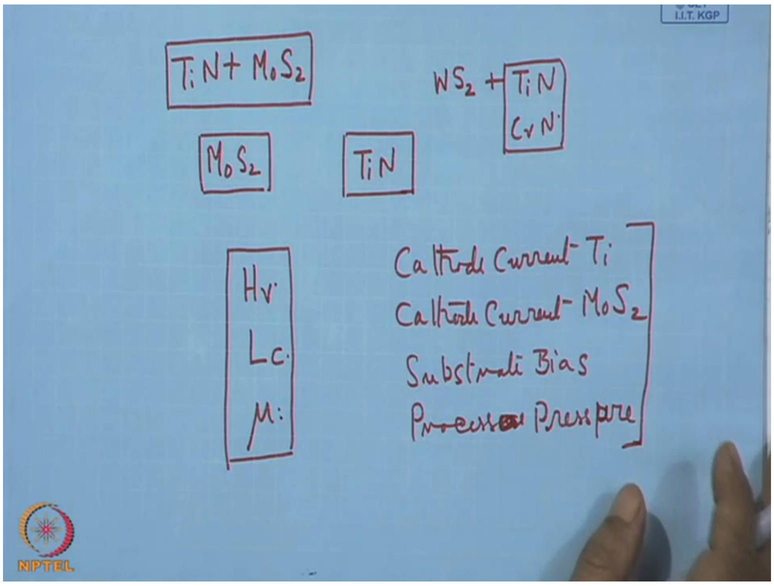

So from this we can see that is titanium nitride and M o S 2 that can be one of the good candidate for all sort of applications of coating which require both wear resistance and also lubricity and at the same time we have to also evaluate how good it is in terms of coefficient of friction or wear resistance or hardness in comparison to M o S 2 on one side and another side is that titanium nitride, okay titanium nitride. So these are the few things one to look, so one has to look to this and by this also what we can see that it is M o S 2 buttons similar effort and be also made with other coating materials say for example WS 2 with some of the hard coating from this hard coating family and it can be titanium nitride or chromium nitride or some of this.

So that can be also useful to augment this property that means it is the hardness at on one side and also the wear resistance on the other side, so these are the coating architecture which are of immediate interest and immediate use and these are the materials also need proper evaluation that means here comes the question of once we are resolved that it is actually titanium nitride and M o S 2 that is the combination then we have to also find out what will be the percentage of this titanium nitride and molybdenum disulphide will get the best value of hardness, best value of grain size, best value of critical load for adhesion and also the best value of coefficient of friction.

Now for this, what we need to have here actually the process parameter for depositing M o S 2 and the process parameter for deposition of titanium nitride and for that what we need? The cathode current, cathode current for titanium, cathode current for M o S 2 then the substrate bias and process pressure, keeping other things constant, process pressure, keeping other things constant means if it is a pulsed DC then pulse frequency for the target and the substrate that is not altered, so with this one can find out the best combination of these 2 things to get one of the best value of hardness of the coating, adhesion of the coating and lower value of coefficient of friction.

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So with this we can make a summary of our today's discussion that M o S 2 and tungsten disulphide, these are the materials which are called super lubricious arterial because of their architecture and this hexagonal array of this one set of molybdenum that is in between 2 layers of sulphur. Now molybdenum sulphur has a good bonding between the sulphur of adjacent layer, the bond is weak and that leads to a lower value of friction because the Van Der Waals force of friction, force of attraction is prevailing there. Now what we have also seen that M o S 2 coating and be augmented, its property can be improved just by use it alone but by a blending with the material like titanium, chromium and sometimes also it has been found that material like silver gold can also help in getting lower value of friction.

The most important thing in the whole architecture is to have the basal plane orientation that means the 002 plane of this whole structure that should be parallel to the substrate surface have the lowest value of friction. It has been also seen that instead of this M o S 2 or titanium there can be a good blending of one hard component and one soft component and with right blending and when the sputtering process by controlling the process parameter one can make a good composite coating giving one of the very best value of coefficient of friction and one of the highest wear resistance.