Technology of Surface Coating
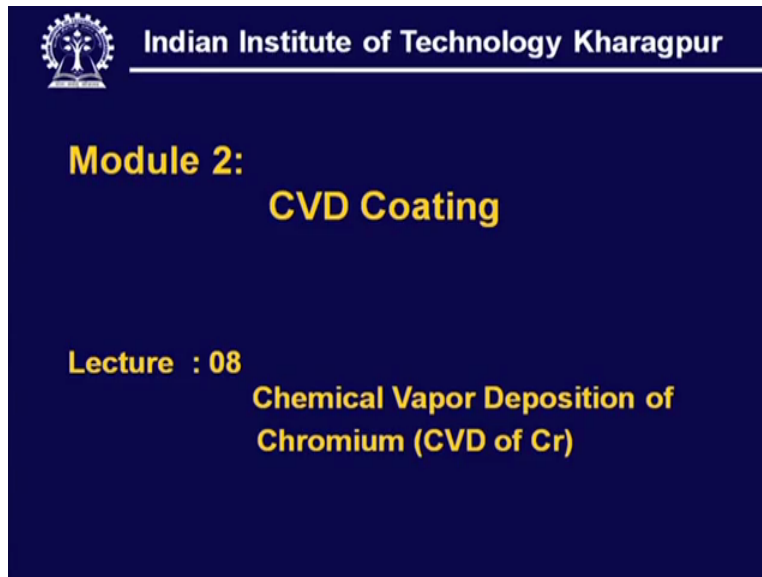**Professor A K Chattopadhyay**
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur
Lecture-08
Chemical Vapor Deposition of Chromium

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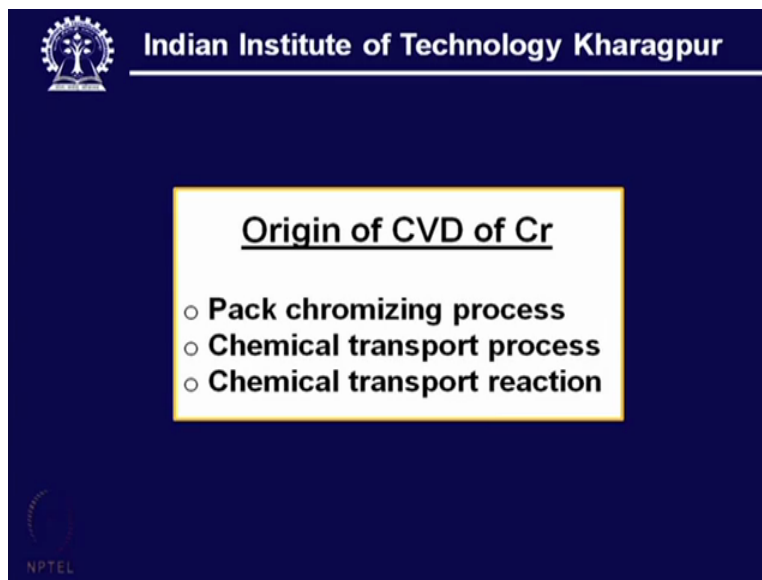Chemical vapor deposition of chromium that means it is CVD of chromium.

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Now let us see what is the significance of chromium coating in engineering application. Now this use of chromium is already well established in reducing oxidation or corrosion of various machine component and part. Say for example the turbine blade and vanes of aircraft engine or turbine and also in tubes and fittings. This is also used as a oxidation preventing layer or corrosion resistant layer.

It is also used for graduating the property from the surface of the substrate to the top functional coating. That means the top functional coating has a different Young modulus and coefficient of thermal expansion which is quite different from that of the substrate and herein particular a steel substrate. So this chromium deposited on this steel substrate serves as a buffer in between the top functional layer and this substrate.

It can have further to this one very important function. It is mostly used for metallization of various ceramic material for enhancing its wettability towards some metal binder. Normally these ceramic materials are inert to metal binder. So when we can deposit a thin layer of chromium on this surface of this ceramic, then it attains certain wettability which means it can improve the bond with the metal matrix. So these are actually the three areas where one can find the significant use of this chromium coating.
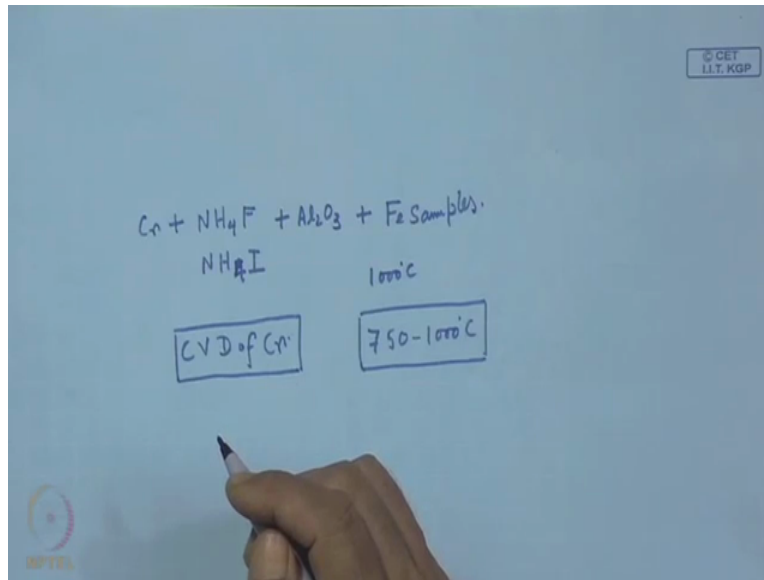
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Now CVD of chromium has its origin. In fact, CVD of chromium finds its principle from the very chromizing process or pack-chromizing process.
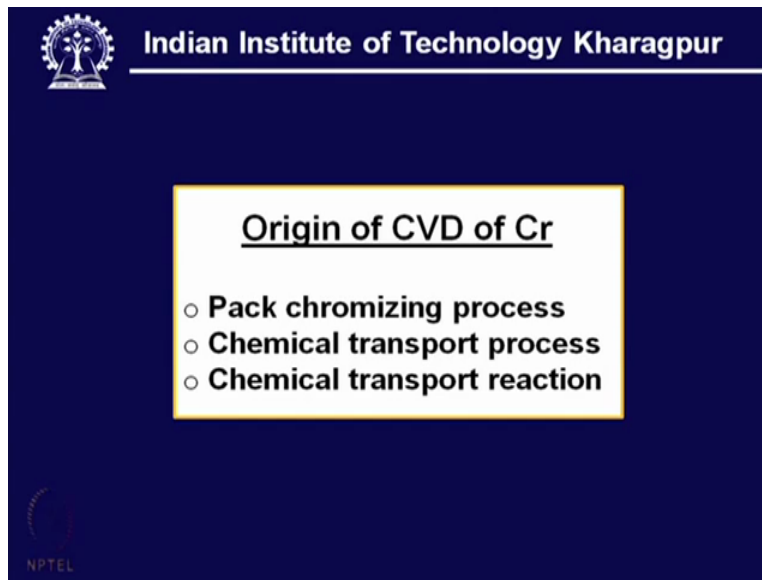
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Now in this pack-chromizing process, what happens? It is the chromium powder plus one activator like NH4F or it can be NH4I which can be used as an activator plus powder of aluminum oxide which is inert material. However it provides the necessary porosity in that mixture of this mass of chromium powder, this ammonium fluoride or iodide and aluminum oxide. Plus it is the steel based specimen samples.

Now the whole thing is put inside a reactor and which must have a temperature 1,000 degree plus, greater than 1,000 degree. And during this process, actually chromium transformed into some halide of this which can be fluorine or iodine or even chlorine and then it gets deposited over this iron sample to produce a layer of chromium. And this is exactly what we know as pack-chromizing process.

However CVD process, that means chemical vapor deposition of chromium has a distinct advantage over this pack-chromizing process. Number one, very important point one should look in, that means here the chromium coating has better uniformity than that can be achieved by this pack-chromizing process, number one. And number two is also the advantage in terms of temperature. We can have a temperature ranging between 750 to 1000 to conduct this CVD of chromium, this process. So we can immediately recognize the two very advantage or strength of this CVD process.
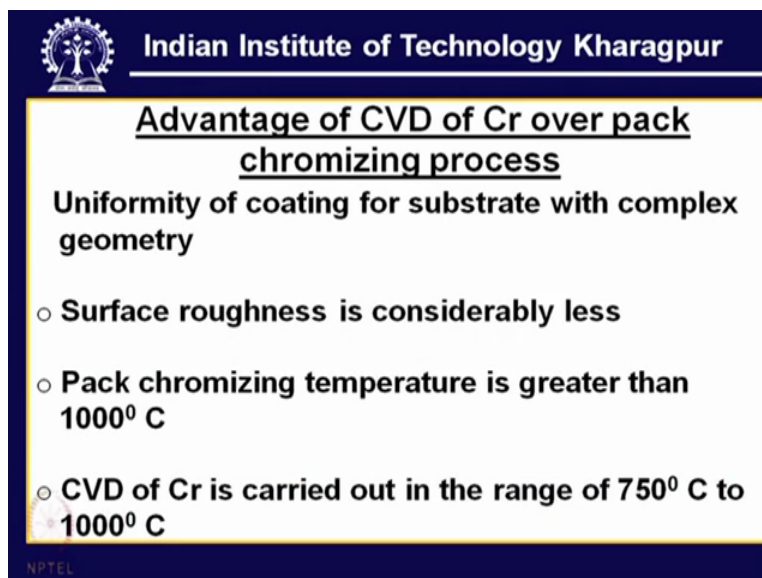
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Now here we understand this chromizing process, it is actually chemical transport process and chemical transport reaction. That means the material will be transported to the, onto the surface of the substrate where the necessary reaction will take place releasing chromium vapor and which will condense in the form of a solid film.

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So these are the advantages which is already mentioned. And this uniformity is very much important when the geometry of the substrate is complex in nature.

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Now difficulty of CVD of chromium Now one can look into all conventional CVD process. What is very important? To have the metal donor.

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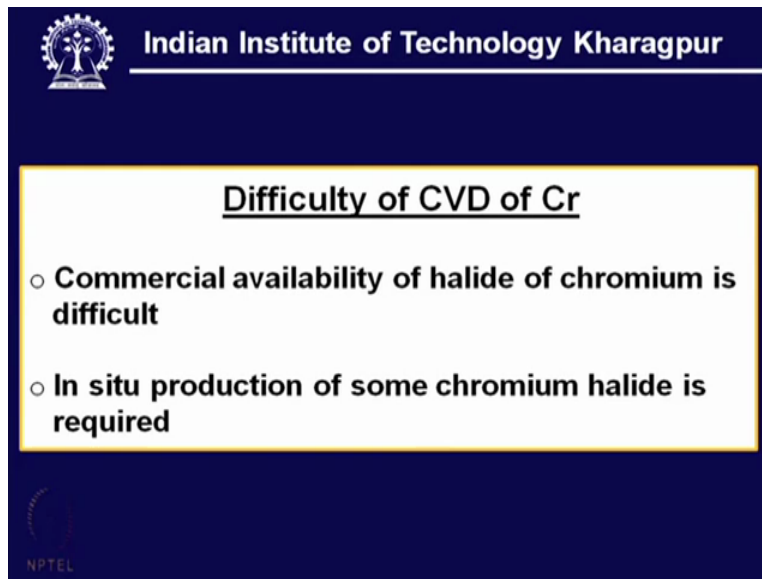
Metal donor means here it is in most cases it is one halide of the metal. Say for example, we have tungsten hexafluoride or molybdenum pentachloride, tantalum pentachloride or even titanium tetrachloride, so we find that these are all metal donors. The advantage here is that these materials are available in the form of liquid commercially. So to handle this liquid which is available commercially, that gives a clear advantage in the use of this metal donor which can be

evaporated, which can be transported near or on the substrate surface to do the necessary CVD reaction. However in case of chromium, this is just, this just does not happen.

So what commercially, what is commercially available? We find that this is actually $CrCl_2 \cdot 6H_2O$. So this is a material which is available commercially. However it needs complete drying, number one. And this material has to be fed in a metered quantity through this reactor near the substrate surface to have a close control on the growth and deposition rate. So unless one has a sophisticated system for doing this thing, this will not be very interesting way of conducting the CVD of chromium by using this commercial product.

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So what is preferred? It is in situ production of some chromium halide and which can be an iodide, fluoride, bromide or even chloride. So the necessity of in situ production of this halide is an important step in the CVD of chromium.

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So what exactly we need here, just in the upstream side of the reactor we want, we must have one chromium halide generator.

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So this is actually this generator which will generate the vapor of chromium halide. That is in simple term we understand. Now if we have a close look in the Ellingham diagram, we can immediately find, this is the Ellingham diagram, X axis is T and this is the 0 level, and this is delta G0 at certain temperature. This side plus, and this is minus. So here one would like to represent the free energy change in a reaction.

And if we like to see that chromium iodide or chromium bromide, their location is somewhere here. And these materials can be decomposed by thermal process, thermal activation and through this thermal decomposition reaction one can have this chromium vapor which can be condensed on the surface of the substrate. That means here these are the points which suggest that this is the threshold temperature for a halide to have decomposition into its metal and that halogen. So if one can attain this temperature and this side is this, on the minor side where this halide is very stable.

But what we can understand from this Ellingham diagram that this iodide and bromide of chromium are not so stable like fluoride or chloride of chromium. So the advantage which can be immediately exploited is that, that chromium iodide which is in this form if it is heated, we can get, so this is actually gas or vapor, so we get chromium as a film solid and leaving this iodine. Similarly we can also have for bromine also. These are less stable halide. Now how to put this thing in practice?

So to do this thing, one can have either a horizontal type reactor or a vertical type reactor. In principle, this thing can be put in a practice, so this one tower of a CVD reactor. This is the base and here we have one flux that means the cover. So it is supported by this O-ring and just outside that we have a shell like furnace like this which is like a shell. So what we can do here, this top part that means this upper stage of this vertical reactor here we can put chromium powder or chromium particle, chromium nugget, chromium chip.

And in the downstream side, for example this is a stage where the substrates can be held, placed. Now this is actually the flow line for this halogen, it can be iodine or it can be bromine. So this will pass through this stage, the topmost stage where we have chromium nuggets or chromium chips and it is placed. This temperature, controlling of this temperature is very important. So this is the temperature and here also you have another temperature.

So this temperature gradient that helps to take the reaction in the forward direction. That means first of all here this part we call the generator, that chromium iodide generator, so here actually this chromium iodide is formed. And then this chromium iodide is transported, you can have also hydrogen as the transporter. However this is called a closed tube process. We can use it in a closed loop form, closed tube. It is a closed tube, means these are the substrate and because of

this temperature differential what we can find that on this side if we look at this diagram, this chromium iodide will form on this side where chromium iodide is more stable.

However on this side which is above the 0 line, where obviously chromium iodide, since it is delta GT0 that is in the standard state which is plus, it cannot be stable, so it will decompose into chromium and iodine. So to this have this CVD, one has to take the temperature above this, little greater than that and which is shown here. So these two temperature will be somehow different and then leaving this chromium coating and release of iodine.

Now this iodine can be recycled and this becomes a closed loop system. So there can be some arrangement for circulating this iodine, so this iodine will be again fed back over this chromium granules making chromium iodide and the process will keep on repeating itself. So what are those two important things to move the thing in the forward direction? What we can find here that delta GT at a particular pressure, that we can write as delta G0T plus RT into ln.

If this reaction goes in this forward direction, we can write this is actually ratio of partial pressure of iodine divided by the partial pressure of chromium iodide. Now from this, this is one of the governing equations, so we can fix the temperature, we can also adjust the partial pressure of this one, quick evacuation of iodine and with that we can take the reaction in the forward direction. That means here it should be, we can write this step that at this stage in the generator it should be chromium plus iodine that should lead to chromium iodide.

However in the downstream side, it should be chromium iodide to chromium plus iodine. So this way a process can be conducted and this can be well used for CVD of chromium.

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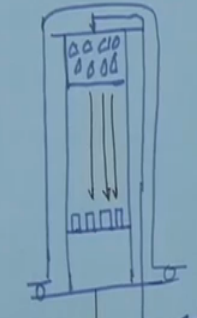
Now here also we can use chromium chloride as the source of chromium and in this case what happens? That this chromium chloride has to be also produced in the similar way as it is the case with chromium iodide formation.

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So here it is not a closed tube process but we can call it one open tube process. So here also we have a tower and this tower is encased in a flux and at this top stage here we have the chromium granules and in this case what is passed, here it is actually HCL vapor. This is HCL vapor and we can also have H2 or argon also, so these are the some of those gases which can be passed through

these chromium granules. And later in this area where the substrates are placed, on that the necessary CVD reaction can take place. Now this generation of chromium chloride or chromium trichloride that can be possible by various ways. Let us have a closer look this chromium and HCL that can give chromium chloride and hydrogen.

We can still further, we use titanium tetrachloride for generation of chromium chloride, this is also possible. So here this titanium tetrachloride instead of HCL vapor, we can also have a provision for passing TiCl4. So this will be the passage for passing TiCl4. And as a result, we have chromium chloride plus TiCl2. So this is another way of getting this thing. It is further possible by directly used chlorine.

In this case we have this chromium CrCl3 and with further addition of chromium with CrCl3 it becomes CrCl2. So at least we find four ways, four chemical reactions leading to formation of chromium chloride. Now in this case what happens? Now comes how to reduce it. So this is actually formation of chromium chloride and which will now travel this distance. So this is actually vapor of chromium chloride. So this is the chromium chloride generator. Now in here what is to be done?
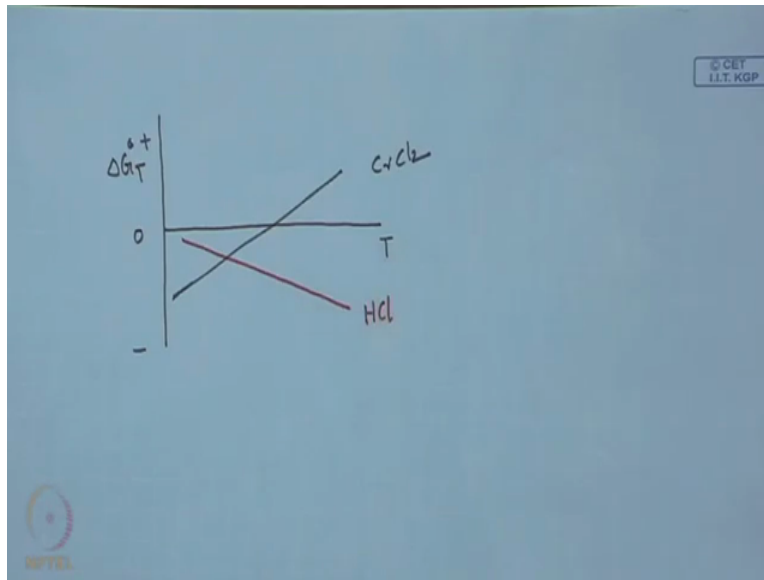
Here actually this chromium chloride has to be reduced to film chromium and a byproduct. So it can be possible if it is a steel substrate, say for example in a steel substrate and here we can have the byproduct which we must show. So this is upstream side and that is the downstream side. It is an open tube process. So in chromium chloride it will adsorb on steel substrate giving such kind of possibility, it is condensed chromium, however Fe transformed to FeCl2. This is one way. It can be possible further to this just by hydrogen reduction. So this is actually chromium plus 2 HCL.

It is also possible to have this CrCl2 as Cr plus CrCl3. Of course, everywhere we have temperature-pressure combination and in certain case we have the reducer. However this temperature and pressure, they, these are the governing parameters directing a, giving the clear idea in which direction the reaction should move. Now if we look into this first chemical reaction by following which we get chromium coating, we can have another step where this FeCl2 can be reduced by hydrogen releasing iron and HCL. Now this is the basic principle of chromium deposition by hydrogen reduction.

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Now here one thing we can look in this Ellingham diagram. Ellingham diagram, it is one which can guide us. Say this is the free energy variation with temperature for chromium chloride. And we can also find this is actually the free energy change for HCL.

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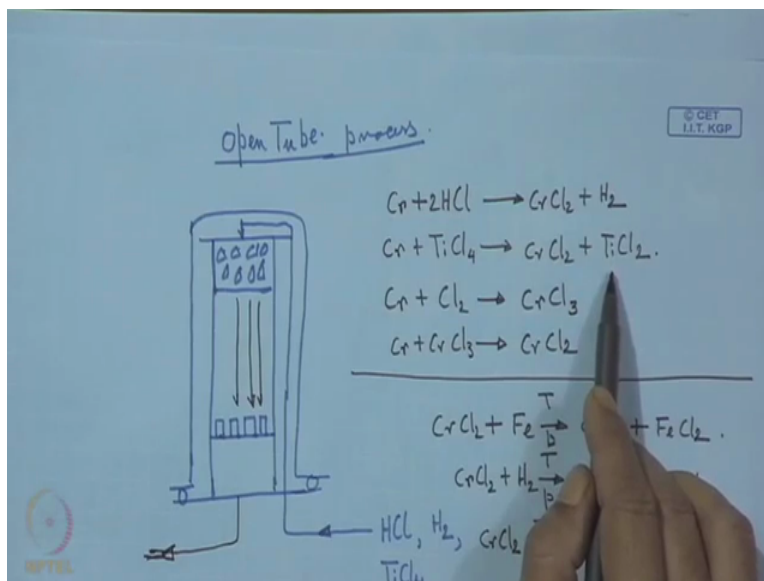
We are following this equation that means reduction of chromium chloride by hydrogen which happens to be the most interesting in this case. One thing if we look into this, chromium chloride deposition is possible. However deposition of some compound of titanium cannot be ruled out because of the very presence of titanium chloride.

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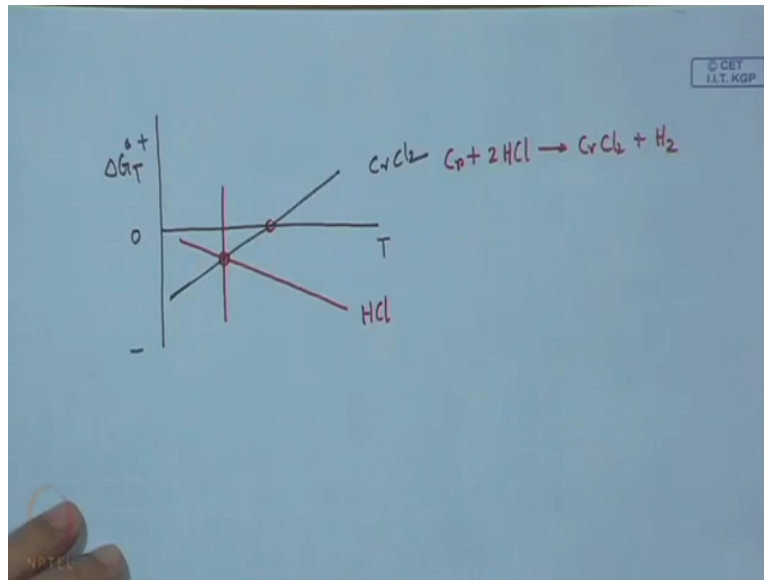
So this graph is important in that, that the location of this temperature, location of this temperature that is the threshold point. And what we can see, if we go on the left hand side, CrCl2 is more stable than HCL. But when you go on the right hand side, we find HCL is more stable than CrCl2. And this is the point where CrCl2 is no more stable and it may split up into chromium and chlorine by just thermal decomposition. But we are interested in this curve, so naturally for the equation, for the chemical reaction, that means here chromium plus 2 HCL which will give us CrCl2 plus H2.

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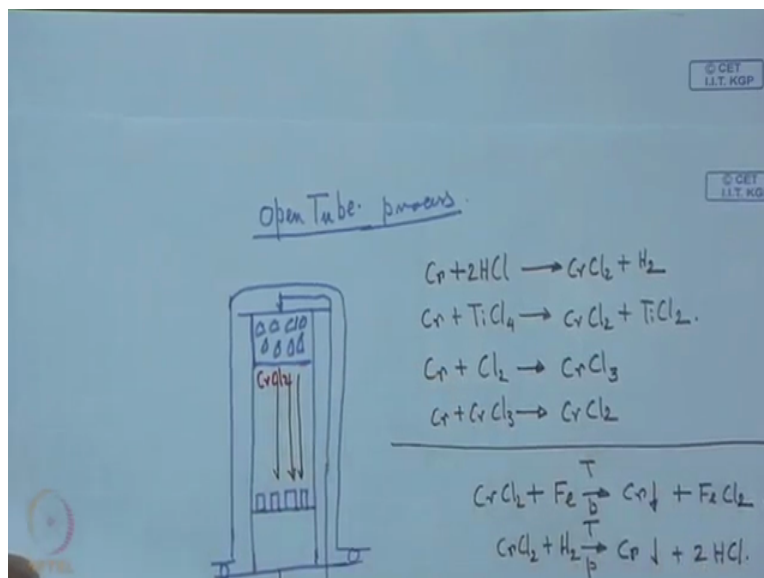
So this one, we can take the help of this diagram. Here actually we have formation of CrCl2 and that will be transported here.

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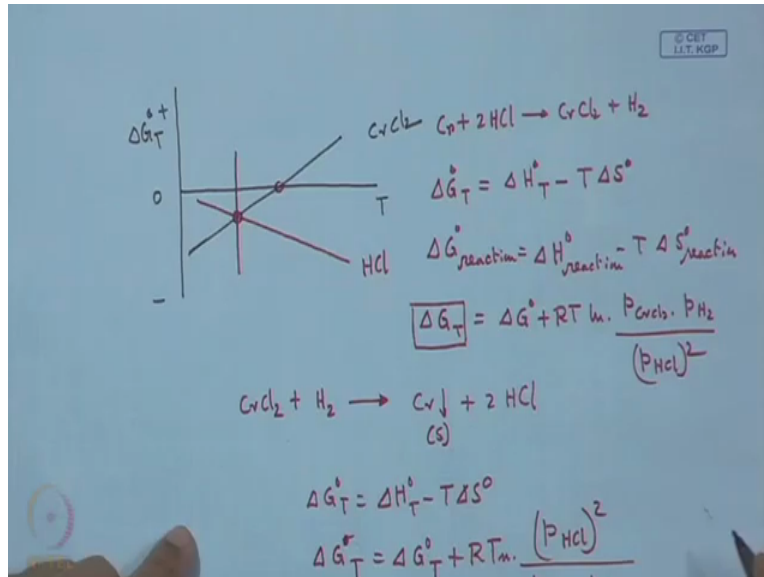
And in the process, we must choose a temperature which favors CrCl2 formation. That means in this case we can write, for this reaction to happen this is given by this delta H0T minus T into delta S0. Now this we actually, this is actually the free energy change of the reaction. So we can put this symbol for this reaction at that particular temperature in question. So this is actually the reaction. So this way we can find out where it is negative that means the reaction will be spontaneous.

However to aid the reaction we can write further to this as RT into ln, and from this we can write it is in terms of partial pressure CrCl2 into partial pressure of hydrogen divided by this pHCL to the power 2. So this part which is with a plus sign, so here one can regulate or manipulate the respective partial pressure of CrCl2, H2, HCL to move the reaction in the forward direction. And that would, can be a driving force.

Now when it is so this is generation of CrCl2, so this is on this side, so we can shift this point and get a very stable value of delta GT which is highly negative so that the reaction move in the forward direction now when it comes to reduction of this CrCl2 and that happens with H2 that means now the reaction should be reversed. So this will give us Cr which is solid film and HCL. So we can see that this is just reversed. So how to make it happen?

So to do this thing, again the same equation we have to write but in a different form. So in this case delta GT is equal to delta H0T minus T delta S0. And one can find out that both the reactions are actually exothermic because of their negative delta H. However what we can find that when we increase the temperature on this side, in that case HCL become more stable. That means CrCl2 will be less stable and HCL will be more stable. That means it promotes formation of or reduction of metallic chromium.

And for this, we can write delta GT is equal to delta G0T plus RT ln, however in this case we have to write pHCL which will be now in the numerator divided by pCrCl2 into pH2. So we can compare these two and accordingly in the CVD reactor that condition must prevail.

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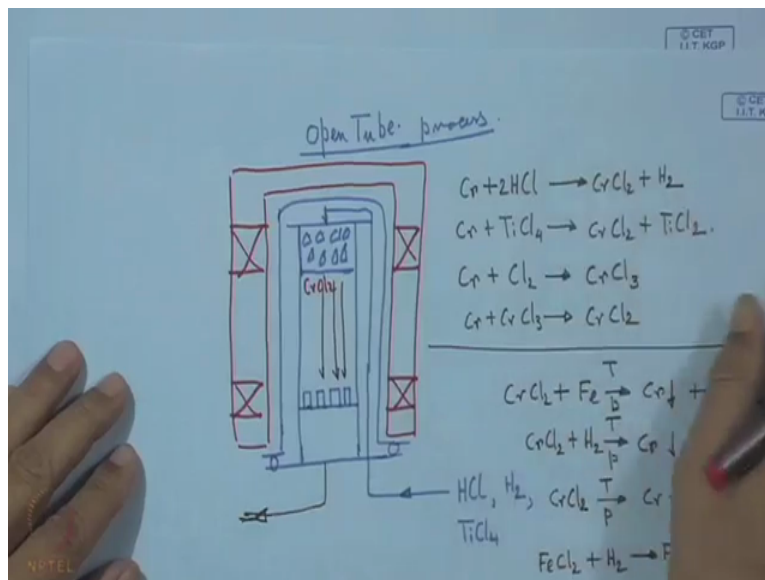
That means number one that though this thing can be also handled at the same temperature but one would expect that if we have a furnace with a hot wall furnace, then we can control this temperature in this zone and we have various zones in the furnace. And this is another zone, so we can control this temperature of these two.

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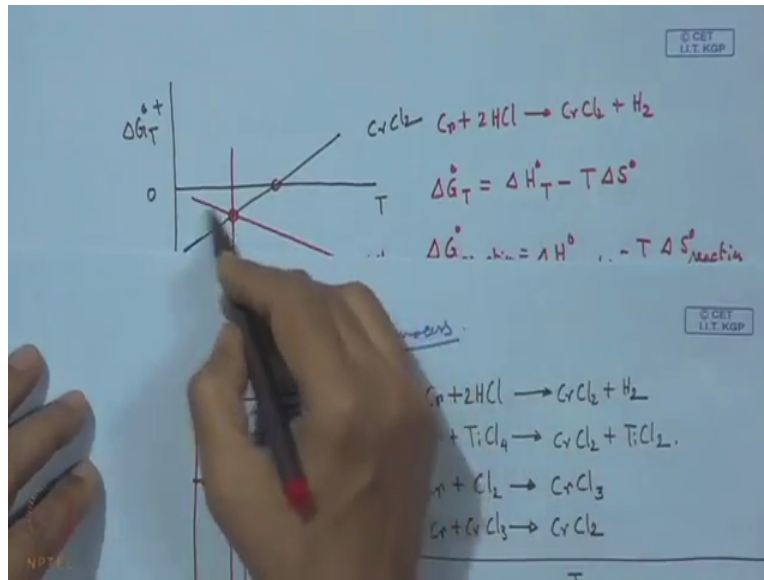
Thereby we can work for generation of CrCl2. We can work in this zone.

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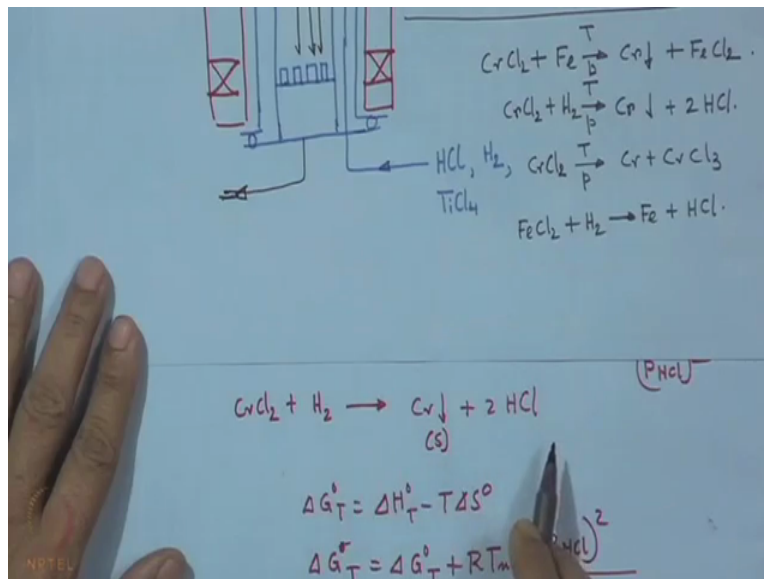
However when we are interested in deposition of chromium which is shown by this reverse direction, then we must have a temperature which favors the reaction to proceed in this direction.

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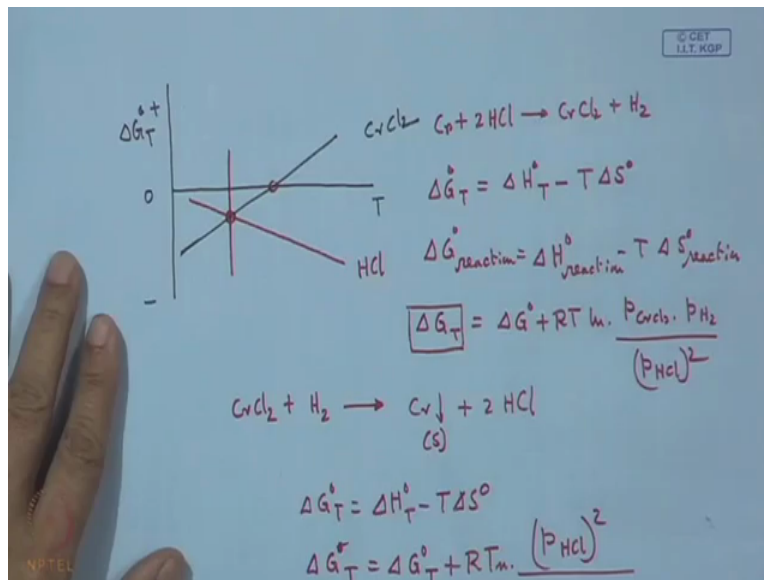
Similarly one can also have an interesting look here that means here pHCL that has to be increased. But in this case what we have to see that, here pH2 that means hydrogen has to be increased. That means to generate chromium chloride we must have less concentration of hydrogen here but more of HCL.

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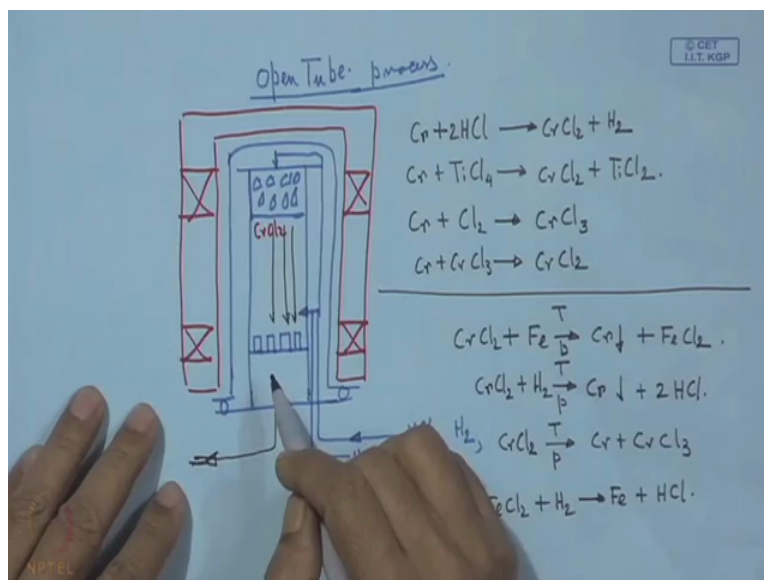
But in this zone what we have, higher concentration of hydrogen and less HCL. So in principle one would expect to have a better result or a driving force by increasing the quantity of hydrogen on the downstream side near the substrate. So if some arrangement can be made to have some

kind of arrangement and source, so that would be hydrogen which will have a higher concentration near the substrate. Then possibly the reaction can be moved also in the forward direction.

So these are the some specialties of CVD of chromium and here we are using mostly the reduction reaction and in this reduction reaction we are using HCL for generation of chromium chloride vapor. However in the downstream side, what we are using, we are using excess hydrogen so that the reduction can take place and this increase of hydrogen acts like a driving force.

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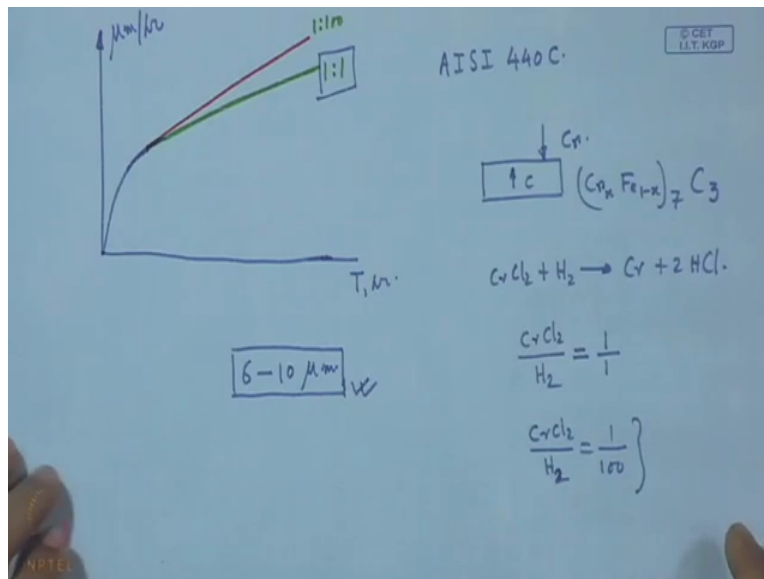
So here one would be interested in the growth rate of the coating. As we have said one of the important role of this chromium coating would be to graduate the property of the coating from the steel substrate to the top functional coating. So here we find that this chromium when deposited say for example AISI 440C martensitic steel. In this case, on this substrate when chromium gets deposited, chromium actually becomes partially converted into a carbide.

And here we have high amount of carbon, so this actually becomes one complex carbide in this form. So it is actually a complex carbide of chromium and iron with 7 suffix and C3. So this is actually one interlayer that forms immediately on this substrate. And if one is interested to see the growth rate, say this is micron per hour and this is time in hour, so what we can find it is something like that, this growth is quite fast and then it slows down.

So this fast growth rate actually it is the, it can be explained by the rapid pickup of this carbon from the substrate and thereby this chromium becomes a part of this complex carbide. And later on what we can see, so here chromium and carbon from the substrate they are participating to make a chromium carbide along with iron. But later on this hydrogen become very active in the later part of the process that means $CrCl_2$ plus hydrogen that gives chromium plus HCL.

And here this ratio of $CrCl_2$ by hydrogen that indeed matters to have nucleation and growth rate of the coating on a substrate, on a given substrate. If we fix the chemistry of the substrate, then obviously this $CrCl_2$ by hydrogen, that partial pressure ratio, concentration ratio or flow ratio, that will definitely matter in the growth nucleation of the coating over that substrate. So it can be even 1 is to 1 or it can be as high as 1 is to 100.

Now here we understand the role of hydrogen, it is only to move the reaction in the forward direction and not to have too much of HCL which can also push the reaction in this direction. So this is 1 is to 100 and if we now see the influence of both, one can find that 1 is to 100 that gives a higher value whereas 1 is to 1 that gives a lower value of this coating growth. So this is actually 1 is to 100, $CrCl_2$ by hydrogen 1 is to 100 and this is something like 1 is to 1.

Here also we can have a smoother coating as it has been seen through some investigation carried out that with this high flow ratio of hydrogen in relation to chromium chloride, one can get a smoother coating. That means we have a higher nucleation density on the substrate surface than what we can see with a ratio of 1 is to 1. Now this thickness of the coating for this steel substrate where graduating the layer thickness is very important, there at least the coating thickness kept is, it is kept in the order of 6 to 10 micron. That is the order of the thickness. So this is the thickness which is necessary to graduate the property of the coating.

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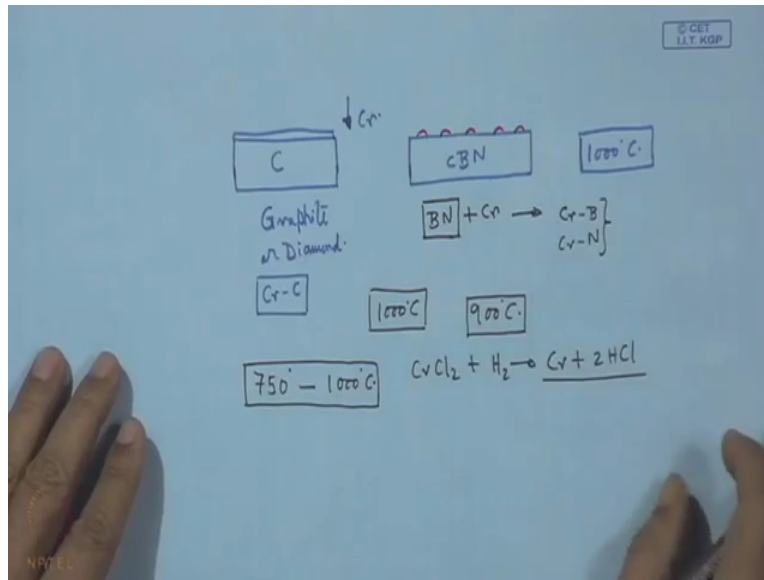
Now this coating nucleation and further growth, that is also affected by the chemistry of the substrate surface. If we have higher percentage of carbon in the substrate, it is a source of carbon, then immediately the coating grows at a faster rate because of the affinity of chromium towards carbon and it is a very good receptor surface. So chromium carbide grows at a very faster rate. However if we have a substrate where the chemistry is such that chromium cannot very easily participate in any reaction at the interface, then this nucleation growth that will be having some difficulty and some limitations too.

Say for example, we have seen that this chromium is used say for example for metallization of ceramic and it has been investigated that when it is a graphite or diamond, chromium can grow very easily over the surface. It is because of the simple reason that chromium carbide has a higher chemical stability than that of carbon and as a result immediately chromium carbide forms. However when it comes to this deposition of chromium in the range of 1,000 degree centigrade, that is a range which is of technical interest for any industrial CVD, then we found that this chromium could not have a uniform coating.

Here we had a uniform coating but here we did not have any uniform coating, few globule like thing in the form of some island which shows typical of a non-wetting substrate on this surface and this is not a very good sign of chromium coating on cBN. Now this can be explained by the fact that in this case this chromium though deposited but the substrate participation was not that

encouraging. Because it is BN and when it comes chromium which is deposited, one would expect that it should result in either chromium boride or chromium nitride.

These are the two thing should form, however what we find from the thermodynamic data that this boron nitride is much more chemically stable than that of chromium boride or chromium nitride. And as a result, this 1,000 degree was not enough under that condition to have a continuous coating of this chromium on this boron nitride substrate.

Here also one thing one should also look in that this deposition of chromium is necessary on this graphite or diamond as we have mentioned at the beginning of this lecture to enhance the wettability of a metal. Say for example nickel, wetting of nickel on graphite or diamond that would have been extremely difficult but when we have a chromium deposition, then this chromium which is either in the form of chromium or chromium carbide that will be wetted immediately by this nickel.

However here one point should be looked in to that this temperature of the deposition, if it is conducted at 1,000 degree, cracking the coating is not unexpected. However because of this driving force of carbon which facilitates deposition of this chromium at even 900 degree centigrade, so at 900 we could reduce chromium chloride by hydrogen and releasing chromium and this chromium could have immediately chemisorption. It can be said chemisorption on this surface because even at 900 degrees chromium could form a carbide of chromium over diamond surface with a good adhesion.

But if we go to very high temperature, then and if it is a thicker coating, then what is going to happen? That because of large variation in thermal coefficient of expansion or Young modulus, there is a risk of coating, cracking of the coating and the whole purpose may be seriously affected and the whole purpose may be lost. So the question is that a temperature as low as possible, as we have said that this deposition can be done between 750 to 1,000 degree centigrade, so one can look into this temperature, low-end of the temperature which will be quite suitable for deposition of this chromium over this graphite or diamond.

Now when it comes to the question of oxidation resistance or corrosion resistance, it is chromium which readily gets oxidized and form a fine layer of chromium oxide and which can

serves as a buffer layer or a passivating layer which prevents further oxidation or corrosion. Now comes the question of graduating the layer.

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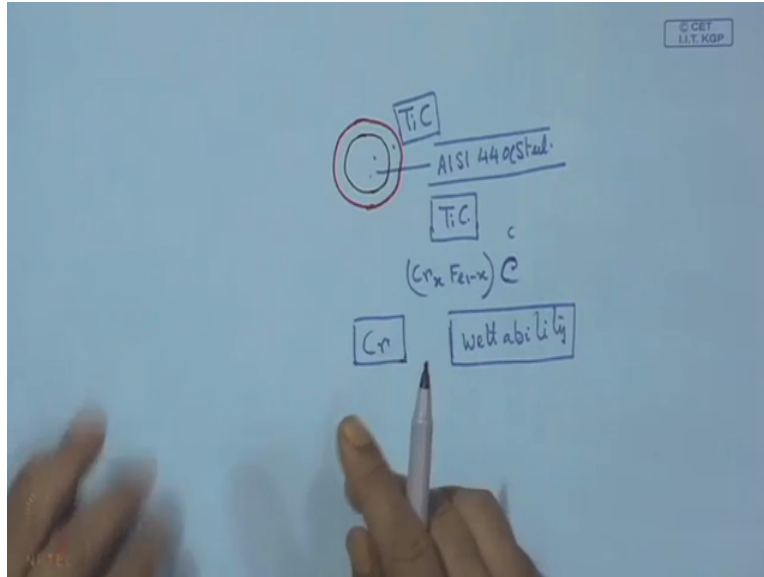
Now this is particularly important when one like to coat the ball of a, steel ball of a ball bearing or the roller or the inner race of a antifriction bearing. Now the topmost, outermost layer is actually TiC. Outermost layer is TiC and the core area that is the material which is AISI 440C steel. 440C steel and in this case if one deposit TiC on this, deposition, because of the high carbon content perhaps deposition of TiC is not a difficult task.

But what would be important here? To have a good adhesion of the coating and also proper matching of Young modulus and coefficient of thermal expansion that means mechanical continuity, physical continuity and thermal continuity, all those things should be properly maintained. And that is why we need here this chromium coating and this chromium coating will form a chromium like carbide on this steel. And over that, a coating of TiC can be deposited.
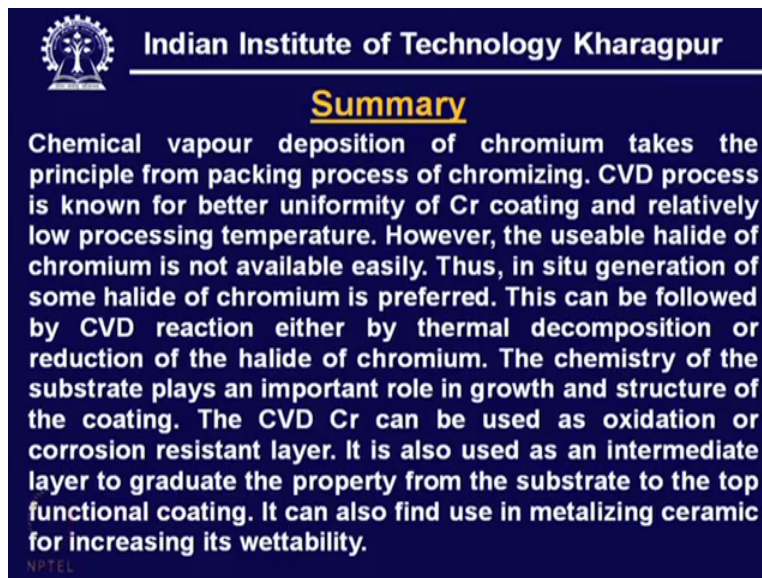
So this way one can deposit chromium carbide over the surface and can have one of the end-product which is high performing. Now concerning the chromium coating, in particular what we have mentioned in case of wettability enhancement? In this case what we have seen that the chromium coating for passivation and chromium coating for graduating the surface layer from the core area to this top layer and chromium coating for oxidation prevention, requirements are not same.

Okay, requirements are not same. In one case we want a inert surface, that means no further oxidation or attack of the substrate is possible, that is totally ruled out. So that is the role of this chromium while providing this passivating layer or anti-oxidation or anticorrosion. Now when it is the top TiC coating on the steel ball, this is the ball of a bearing, in that case it is not directly functioning but it is actually a buffer layer and the top layer is TiC.

But when it is the question of wettability, it is just changing the surface chemistry of the ceramic which is otherwise inert towards a liquid metal. So when it is the question of wettability, 1 to 2 micron thick layer is sufficient but when it is the question of passivation it is a pore free dense coating is necessary. And when it is a buffer layer which graduates the property, it should come like a bridge between the core area and the top.

So the three functions which can be done by this chromium coating but the layer thickness, then the chemical or physical characteristics, mechanical adhesion characteristics, these requirements may not be the same. So with this, we come to, we have discussed all those issues.

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Indian Institute of Technology Kharagpur

Summary

Chemical vapour deposition of chromium takes the principle from packing process of chromizing. CVD process is known for better uniformity of Cr coating and relatively low processing temperature. However, the useable halide of chromium is not available easily. Thus, in situ generation of some halide of chromium is preferred. This can be followed by CVD reaction either by thermal decomposition or reduction of the halide of chromium. The chemistry of the substrate plays an important role in growth and structure of the coating. The CVD Cr can be used as oxidation or corrosion resistant layer. It is also used as an intermediate layer to graduate the property from the substrate to the top functional coating. It can also find use in metalizing ceramic for increasing its wettability.

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