Technology of Surface Coating
Prof. A. K. Chattopadhyay
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur
Lecture-09
Chemical Vapor Deposition of Aluminum Oxide

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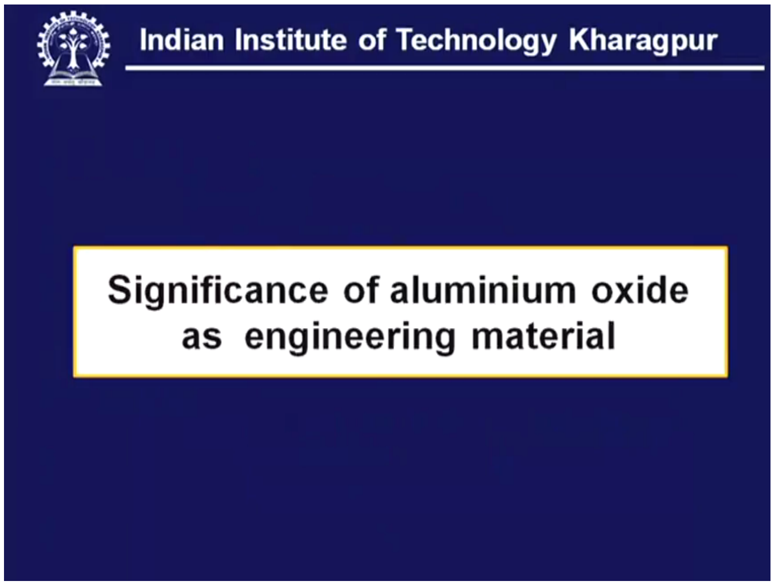

Chemical vapor deposition of aluminum oxide let us look at this aluminum oxide and try to understand and appreciate its significance as engineering material. Now this aluminum oxide is well known for its chemical inertness, high temperature thermal stability retention of hot hardness and very low thermal conductivity.

Now these are the characteristics of aluminum oxide which has made this material an interesting and prospective candidate for many engineering use and one of those is the cutting tool material. Now this cutting tool material requires certain properties which interestingly aluminum oxide does possess. However when it is question of tensile strength or toughness, then this aluminum oxide shows its weakness and that is why though this material has other high temperature properties, but this cannot become universal tool for a general application.

Now we have already understood the very idea of coating the cutting tool so that the required properties can be given on the top surface which becomes the functional surface. But this functional surface having this coating can be also will supported by a core which is having certain other requirements namely tensile strength, bulk hardness, then retention of the geometry, chemical compatibility with the coating material. These are the some required properties.

Now already TiC or titanium nitride and many more similar materials are already in use, and these have augmented the cutting properties of a carbide tool or a high speed steel tool. However when one compares those required properties which are essential at the top working surface of the tool, definitely aluminum oxide can outperform this TiC or TiN or even titanium carbonitride.

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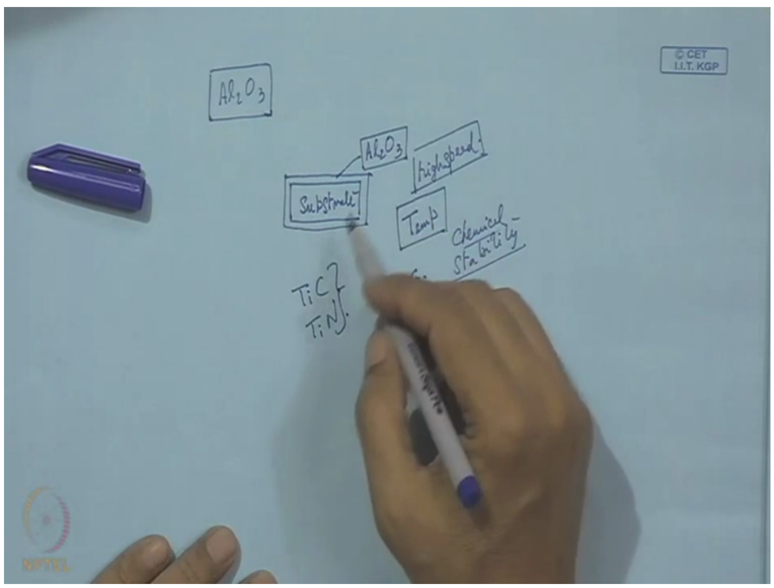

That is why the whole idea here is that if we can have this aluminum oxide which is having all the required property namely chemical, thermal, then if we just put it over this substrate which is made of tungsten carbide cobalt or similar material in the form of a coating, then the whole purpose is served and here we have one of the best candidate in the form of coating which can perform its task very efficiently. That means its use as a cutting tool.

Now application of aluminum oxide as hard coating, that means when we go for high speed operation, then actually this high speed is associated with high temperature and it is actually the wear on the tool which matters most rather than any other mode of failure. And in this respect material which is at the top of the tool surface, it needs some very special characteristics which can enhance its wear rate and that is exactly what we know as chemical stability.

So this chemical stability is very much associated with the free energy of formation of this particular compound and in this case aluminum oxide has a clear edge over TiC or TiN which are already two useful material as coating on the cutting tool. Now this aluminum oxide need to be deposited on this substrate.

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Now here what we can see that CVD can be a very good way of handling this coating technology and coating process. Now in CVD we have a global reaction for deposition of aluminum oxide.

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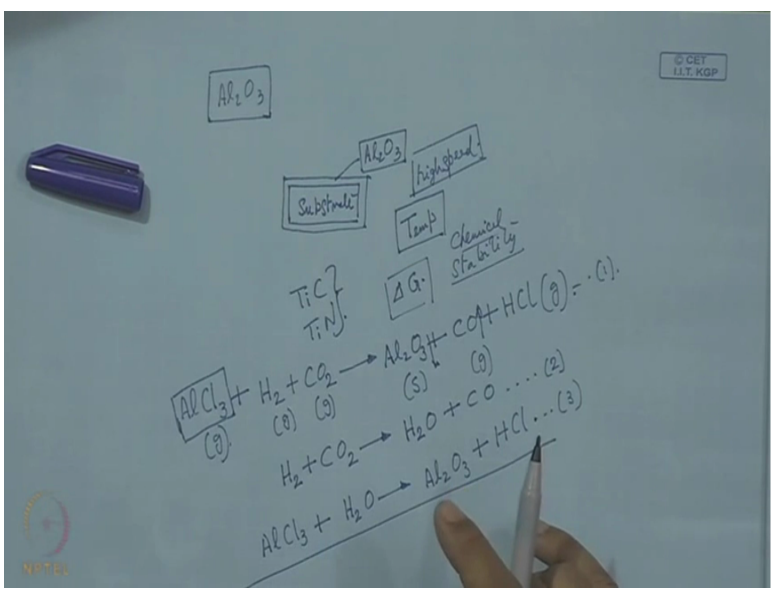

The global reaction is something like this, AlCl3 plus H2 plus CO2, that should give Al2O3 plus CO plus HCL. Now here this is gas, this is also vapor, this is deposited as solid and these two should escape as the gaseous reaction product. Now this is the overall global CVD reaction. Now here the main problem is how to get this aluminum trichloride. Now this aluminum trichloride can be commercially available so easily. So to get this work done, what is done that aluminum trichloride has to be generated during this CVD process.

Now this global reaction can be also splitted into 2 reaction steps. That means first of all what happens, this H2 plus CO2 when admitted in the CVD reactor it will actually transform into water vapor H2O and CO. Now this H2O, AlCl3 plus this H2O, so this aluminum trichloride will undergo hydrolysis and with this hydrolysis Al2O3 will form and at the same time HCL will form.

So if we combine, this is one global, this is one reaction step, this is 3, so when we put 2 and 3 together, then we get AlCl3 plus H2 plus CO2 that actually that moves in the direction of Al2O3, CO and HCL. So these are the basics of this CVD principle for deposition of aluminum oxide.

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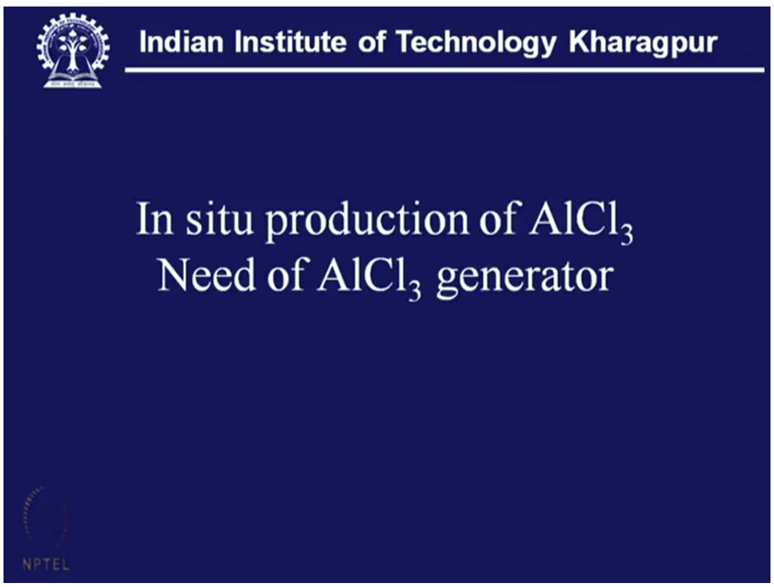

Now here what we have mentioned that production AlCl3 is required, very much required and to have that one has to go for this reaction.

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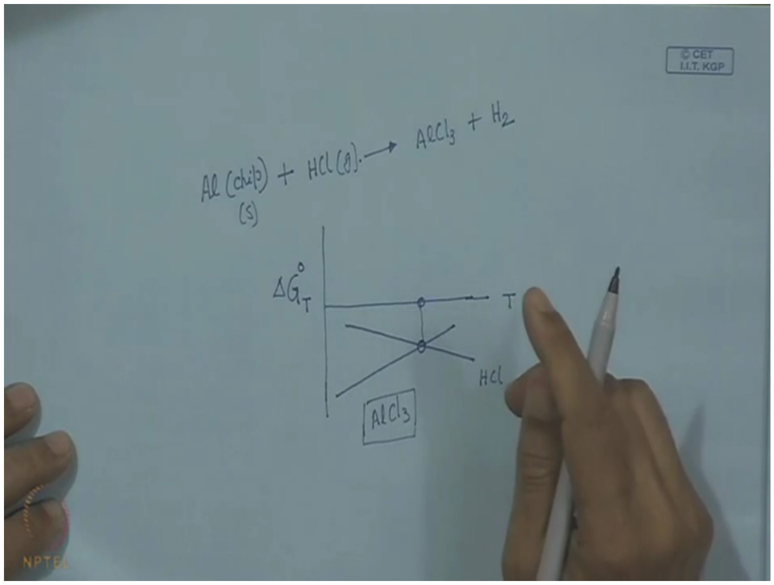

That means this is actually aluminum chip, plus here one has to pass HCL vapor which is in the form of gas. So this is solid and this will lead to AlCl3 plus H2O, H2 hydrogen. And to move this reaction in the forward direction, one can have a look into this Ellingham diagram. So here we have this is delta G0T and this side is the temperature, so here we have to see the equilibrium of AlCl3 with HCL. That means if we find that AlCl3 that is varying in this form and we have the delta G0T curve for HCL like this, this is for AlCl3 and this is for HCL. This becomes the threshold point or crossover point, so on this side of this threshold temperature AlCl3 is very stable and the reaction can move in this direction.

Obviously, it is evident that temperature need not to be very high and as per the practice it is done say in the around of 200 to 250 degree, that generation of AlCl3 vapor in this CVD reactor. This is done at the upstream side of the reactor. So from this, considering this vapor of AlCl3, HCL, one can regulate the vapor pressure of HCL and that of hydrogen to move the reaction in the forward direction. So this is how this AlCl3 vapor is produced.

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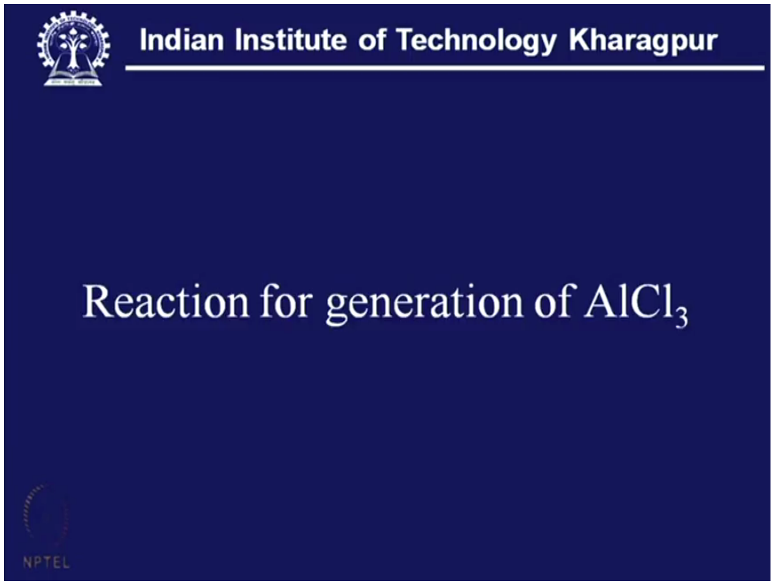

So reaction for generation of AlCl3, that is already shown here.

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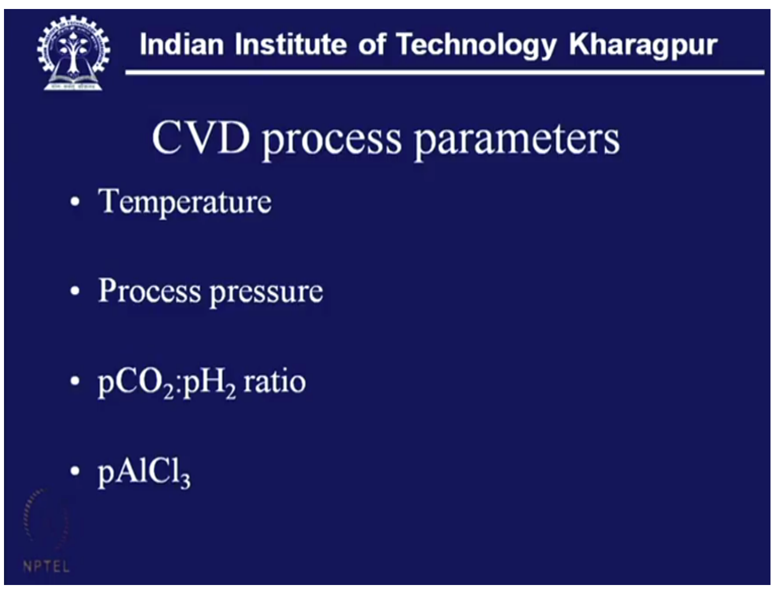

Now what are those process parameters for this CVD of aluminum oxide?

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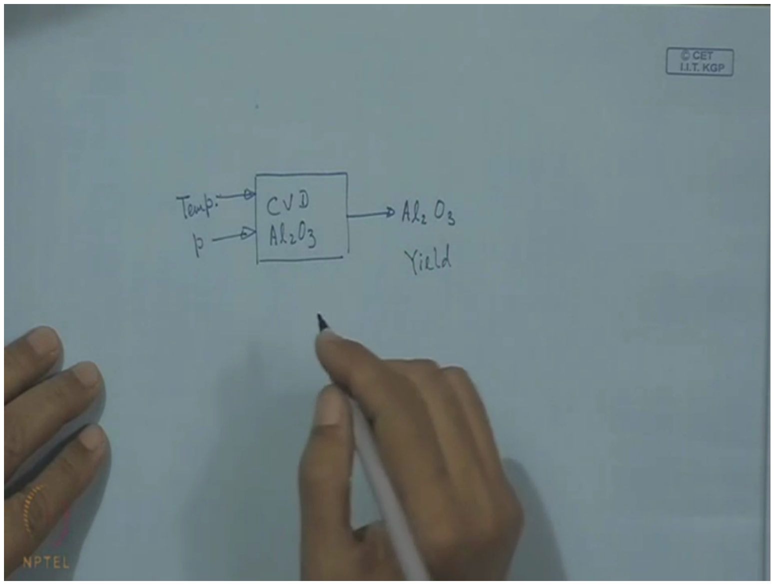

Now when it is the CVD of Al2O3, so this side we want Al2O3, that means the yield of Al2O3, that means the growth in milligram per hour or micron per hour, that is one of the criteria which is an index of production rate and this is the outcome with of course the morphology of the coating. That means whether it is a coarse coating or a fine grain structure with a smooth surface or rough textured, then the density of the coating, these are the issues to be addressed.

And this is very much associated with this Al2O3 coating. But on this side the process parameters one can look, this is as the temperature, then process pressure. So these are the two thing one should look in.

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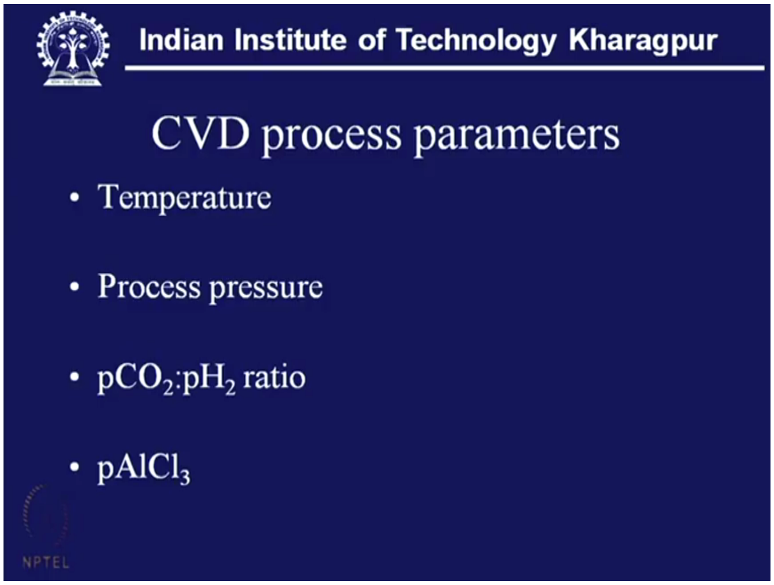

However in addition to that, since we have already noticed that it is carbon dioxide CO2, hydrogen, these are admitted in the reactor maintaining certain temperature and pressure plus at the same time we have aluminum trichloride vapor which is continuously generated and admitted. So these are, all 6 are the process parameters which can have a dictating term in producing or in providing the final outcome that means Al2O3 coating yield.

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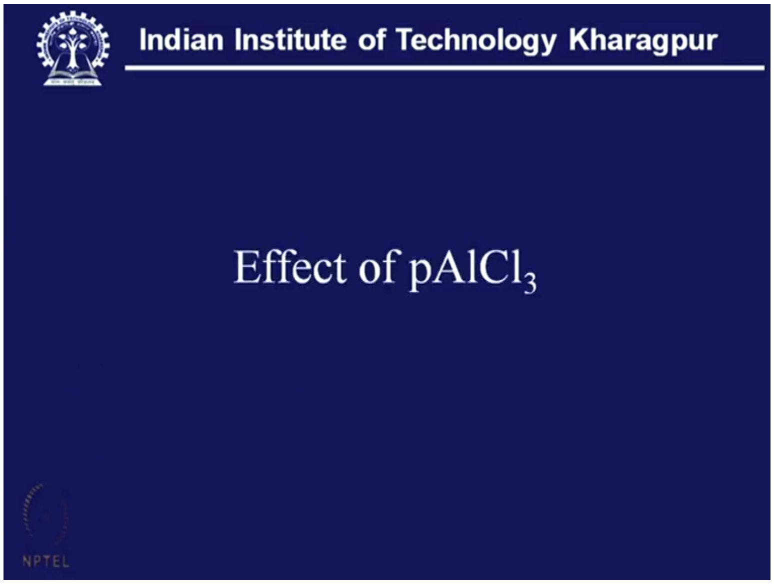

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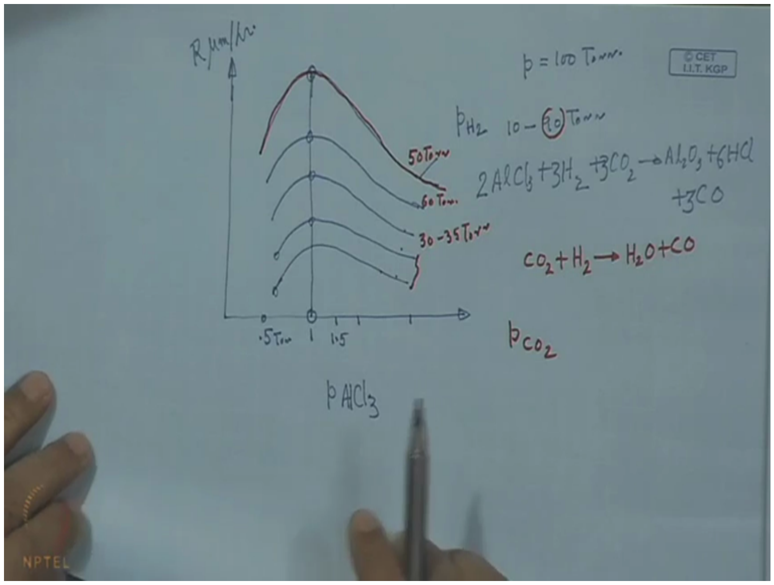

Effect of partial pressure of aluminum trichloride, now this can be represented by this graph. This side we have partial pressure of AlCl3 and on this side that is called R, that is the growth rate in micron per hour. Now here the nature will be more or less like this, and this curve that is applicable or valid for a particular value of partial pressure of hydrogen. And by changing this partial pressure of hydrogen, we can have different location of this curve and it may also little bit changes its shape. For example, it can be something like this, it can change its peak position and say these are 5 such condition. And 5 such condition means pH2, partial pressure of hydrogen is varied.

Say for example, the total pressure if it is 100 torque for example, this pressure can be varied say between say 10 to 90 torque. Now the question is, which one will be applicable for 10 torque or 90 torque? One thing we can look here that this particular growth rate which is expressed in micron per hour that will be given at a particular value of partial pressure of aluminum trichloride. And this is a very low value, it may start with say 0.5 torque, it can be 1, 2 and 3, something like that. So it is 1.5.

So it is also an experience that at a particular value of pAlCl3, this growth rate assumes very highest value and on the two sides we have a very low value. Now this can be explained by fact that on this low side, concentration of aluminum trichloride is quite low which may lead to the low yield of aluminum oxide which is given by micron per hour. And on this side what happens?

Because of this reaction which already we have seen, AlCl3 plus H2 plus CO2, which gives Al2O3 plus HCL.

Now if one can balance this equation, one can look into this how the thing can be balanced, so this is going to be 3, so this is going to be 6 HCL and here we have CO also. And this is actually 3 CO and here we have 3 CO. So what we find that for two units of AlCl3, we get 6 unit of HCL. So that means the volume of the reaction product is increasing and that can push the reaction in this direction.

So if we increase AlCl3 on this side, then it will become counterproductive and there could be a fall in this yield of the coating. Now one thing we can also look into that these graphs what we have mentioned, this 1, 2, 3, 4, 5 graphs that we got for different values of partial pressure of hydrogen. Now say if it is a 100 torque, in that case for example and if we keep the partial pressure during this CVD around 1 torque, then obviously considering this reaction, that means this CO2 plus H2 which gives H2O plus CO. That means here one thing is also extremely important that this production of water vapor.

So what we find that this growth or production of water vapor that would be highest when we take 1 is to 1 ratio of hydrogen to carbon dioxide, CO2 and H2, 1 is to 1. So naturally what happens, if we keep the pressure around 50 torque, then we can get this curve, this curve we may expect. It is not unreasonable to expect such curve around 50, 60, so this can be also quite high which is around 60.

However when we go either on a very high value of pH2, say for example 90, in that case this curve will shift its position and it can take up this position. Or when we take pH2 as 10, then also we get a low value of this one because in this case the yield of H2O will be less because it is not 1 is to 1. So if we increase pH2, that means keeping the same pressure, CO2, pCO2 has to be automatically adjusted.

So whether it is pH2 is high means pCO2 is less. Then this 1 is to 1 condition cannot be maintained. Again when we have partial pressure of H2 as 10, then pCO2 becomes quite high, that can also, cannot also give us 1 is to 1 ratio. And those, in those condition, the process is not at all efficient and it leads to low yield. So these are the two curves where the pH2 value will be either too low or too high. And this is more or less in the central position about 50 percent of the total pressure and it may be somewhere around 30-35 torque. So this is a curve one would expect during CVD of aluminum oxide, just growth rate of aluminum oxide versus partial pressure of aluminum oxide.

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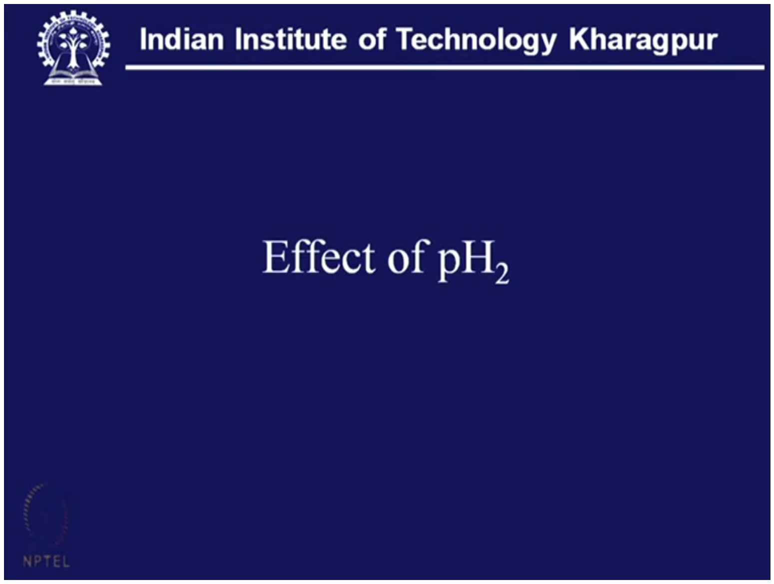

Effect of pH2 and that effect already we have shown here.

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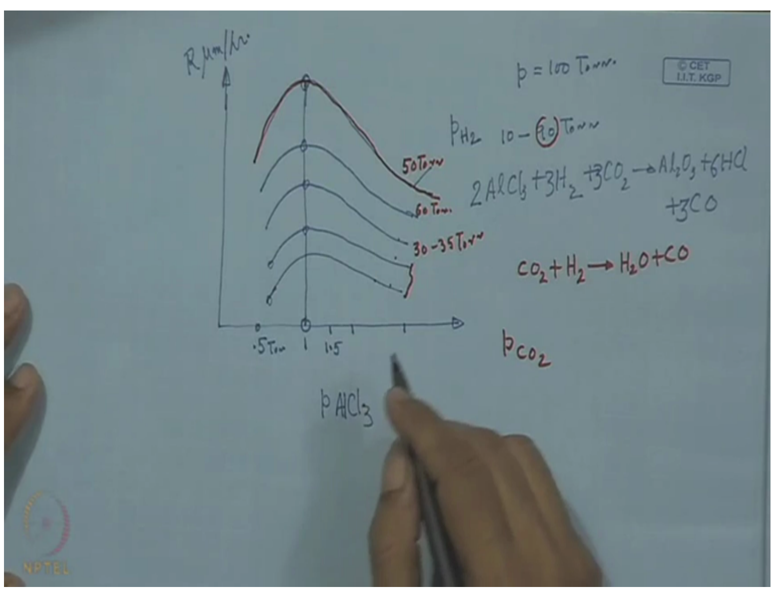

That this effect that means this graph actually shows the combined effect of pAlCl3 with that of hydrogen and this can be also drawn in another way.

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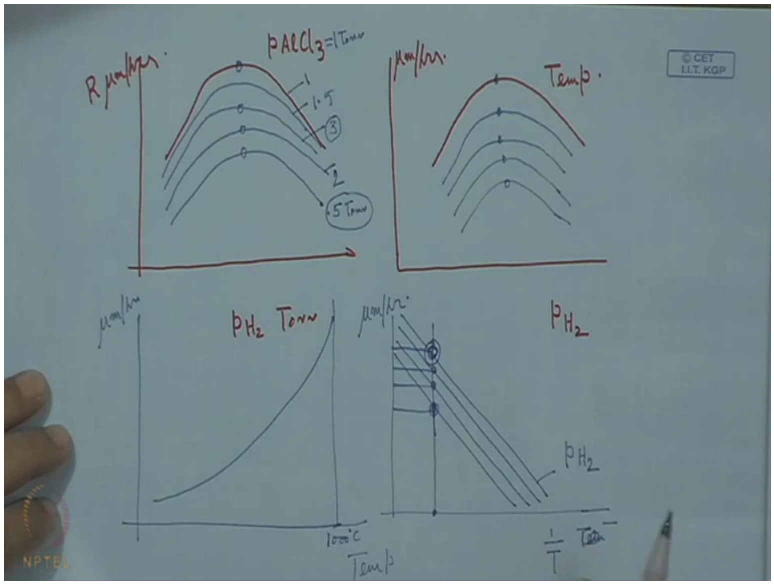

That means in this case what we can show here, that means this is the growth rate which is in micron per hour and this gives us partial pressure of pH2 that is in torque. We can have another one side by side showing this growth rate of aluminum oxide coating which is given in micron per hour. This axis is pH2 and here also we can draw but only the difference is that in this case this graph is drawn for a particular pAlCl3 and this is for the temperature.

That means in this case what we see, if we have, say for example this is around 1 torque, we can have variation which can be something like this. This is maybe 0.5 torque of aluminum chloride, then we can also have with 1 point, with 2, with 3 and with 1.5. So what we can see here that this is with 1 torque of pAlCl3, this is with 2, this is with 0.5, this one with 1.5 and this one with 3.

That means as we increase or decrease the partial pressure of AlCl3, definitely the pick point gets shifted and it is also the same fact that highest yield can be obtained at an intermediate value. And at the low end of this pCl3 or the very high value of pAlCl3, then we can have a low value of the yield. Now for the temperature what we see here that with this pressure, higher the temperature, higher is the growth rate. And this is actually the activation and with this activation it is a temperature dominated reaction. So naturally higher the temperature, the reaction rate increases and as a result the growth rate is also, that is also increasing.

So this way we can also show that growth rate versus temperature which is micron per hour, and this can be shown something like that which goes exponentially. And here this temperature is in the order of about 1,000 degree plus, maybe around 1,100 degree centigrade. And in this case the rate of yield of this coating or the growth rate attains a very high rate and it goes at a very faster rate. Another illustration can be also shown here, micron per hour on one side and in this case this is the temperature, this is actually 1 upon T.

And in this case what we see, we can get a series of curve something like this and all these curves, these are actually meant for a particular value of partial pressure of hydrogen. As we have seen here that a particular partial pressure of hydrogen which is around middle of the total pressure and there we see the highest possible production of water vapor which can be quite effective in pushing the reaction in the forward direction. So this would be, so for this particular situation if we consider one point here, we can get in the vertical line four points showing the different growth rate.

Naturally one can conclude that this is one of the pressure of, partial pressure of hydrogen which facilitates high rate of production of H2O. And in all other condition, that is not that efficient. So this pressure, partial pressure of hydrogen it is situated somewhere about 50 percent of the total partial pressure if we consider the partial pressure of aluminum chloride quite negligible and insignificant. So this is, this can be concluded that the partial pressure of hydrogen should be around 50 percent of the total pressure so the remaining partial pressure that should be of that of CO2.

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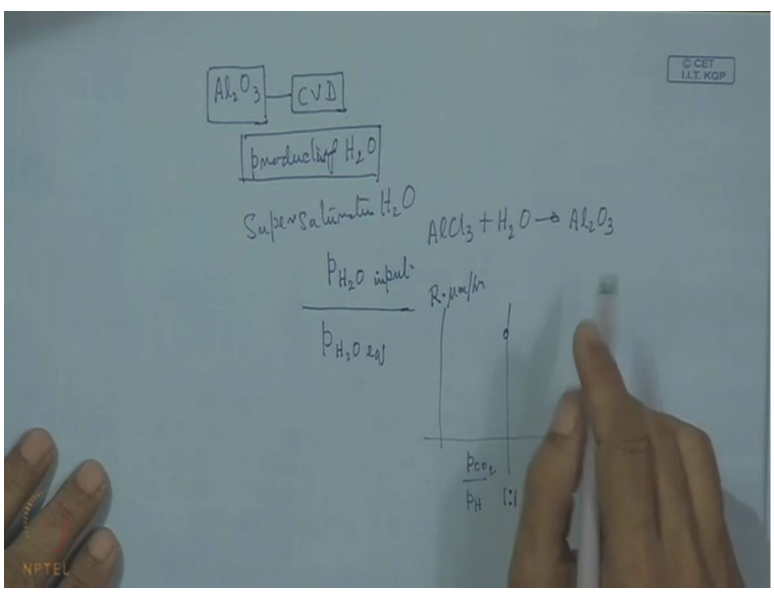

Now here one thing is also important that aluminum oxide, that is the CVD product, here this coating is a CVD product. Now in this case what happens that fineness of the structure to get a finer structure of this is very important. Now in this issue that generation or production of water vapor, production of H_2O that has decisive role, production of H_2O. And that is given by what we call super-saturation, super-saturation of H_2O and this super-saturation of H_2O means that partial pressure of H_2O which is the input, partial pressure divided by pH_2O in the equilibrium.

So objective of CVD should be to make this ratio which is the index of super-saturation as high as possible in order that this reaction, that means $AlCl_3$ plus H_2O which is nothing but hydrolysis of $AlCl_3$ and that will go at a faster rate in this direction with the result of Al_2O_3. So if we move this reaction at a very fast rate, then we can have rapid growth of this Al_2O_3 and in that case nucleation rate that will be also quite high and as a result of that we may expect a finer grain size and a smoother coating on this carbide tool substrate. So in principle, one should attempt to make this super-saturation of H_2O as high as possible.

Now this is actually effect of pCO_2 and pH_2 ratio. This is shown but this can be also shown this way that this is the yield R which is in micron per hour. And here we have this is pH_2 by pCO_2 and on this side we have say pCO_2 by pH_2O. So obviously here we have when it is 1 is to 1, there we have the very high value and on both the sides we can have a decreasing trend on this growth rate. So that we can see as the effect of this ratio so this ratio should be ideally 1 is to 1, partial pressure ratio, to have highest production of H_2O and this will lead to faster growth rate of Al_2O_3.

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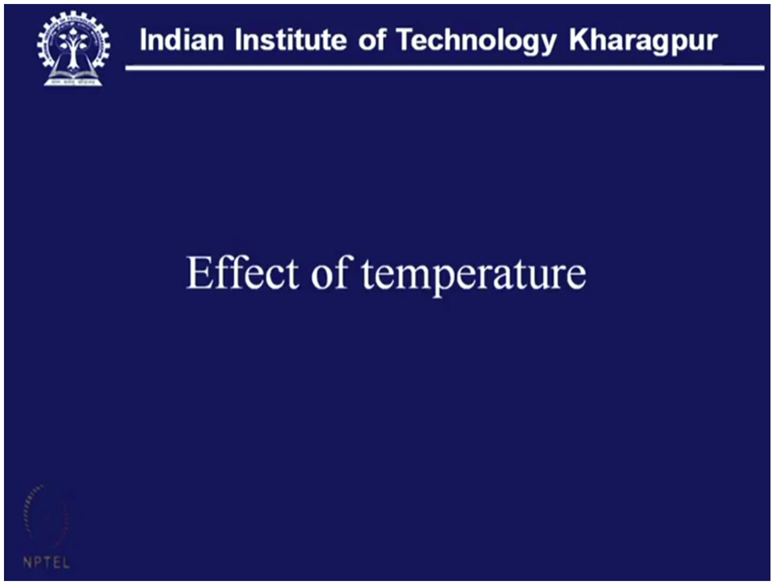

Effect of temperature, so effect of temperature we have mentioned that this is actually activated by temperature. Naturally the growth rate will be quite high at higher temperature. However one thing should be also taken into consideration that it is the limit of the CVD reactor and also the substrate of choice which should not be affected by this high temperature.

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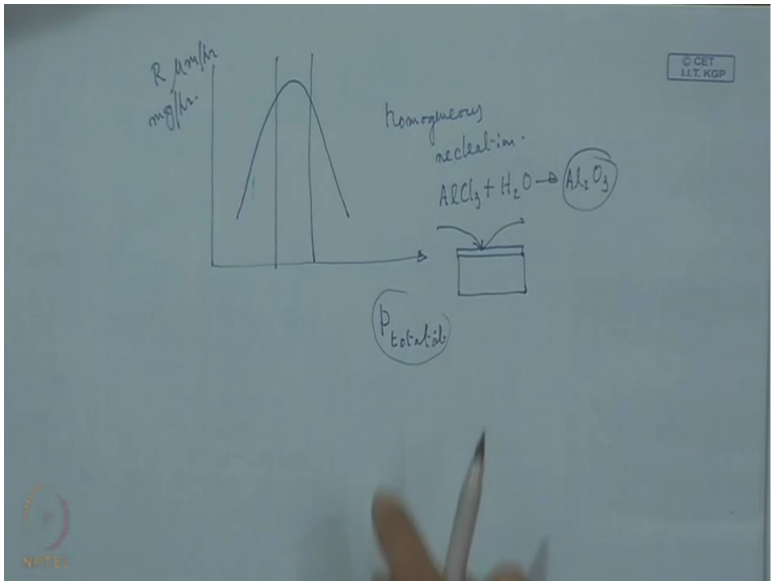

This is effect of total process pressure. Effect of total process pressure say this side, it is the growth rate which we can express as micron per hour or it can be just increase in weight of the substrate in terms of milligram per hour. And this side, that is the total pressure inside the CVD chamber, the total pressure. And here we may expect a curve something like this. Now this curve, we can interpret this curve in this form, say this is a zone, interesting zone for conducting the CVD operation. Now why it is so?

If we are on the higher side, we can see growth rate is falling drastically. And even with a low partial pressure, total pressure, growth rate is also not adequate. Now when we are on the higher side, what happens? With this high rate of deposition, high rate of total pressure, we can have homogeneous nucleation. Homogeneous nucleation, that means this reaction is occurring in the gas phase. So AlCl3 plus H2O and if we have a very high pressure, then this Al2O3 that may form in the gas phase but ideally it is supposed to form, condense and synthesize on this carbide substrate.

But this does not happen. So the growth rate is obviously, it is falling in nature. And when the pressure is too low, in that case the residence time of this gas which are incoming gas on this substrate, so this must not, this is not getting enough time, dwell time to reside and to get adsorbed on this surface. So this is also a function of this total pressure. So when it is too low, it is actually the problem with dwell time or residence time and the problem associated with adsorption.

And when it is the high pressure, then it is homogeneous nucleation, that means this formation of Al2O3 that is taking place in the gas phase and this substrate does not yield, receive much of this vapor which could have condensed and synthesized over this surface.

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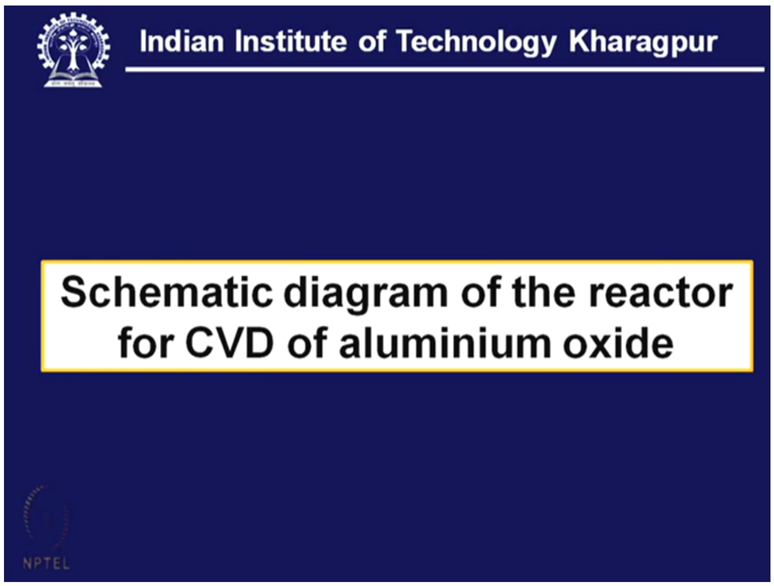

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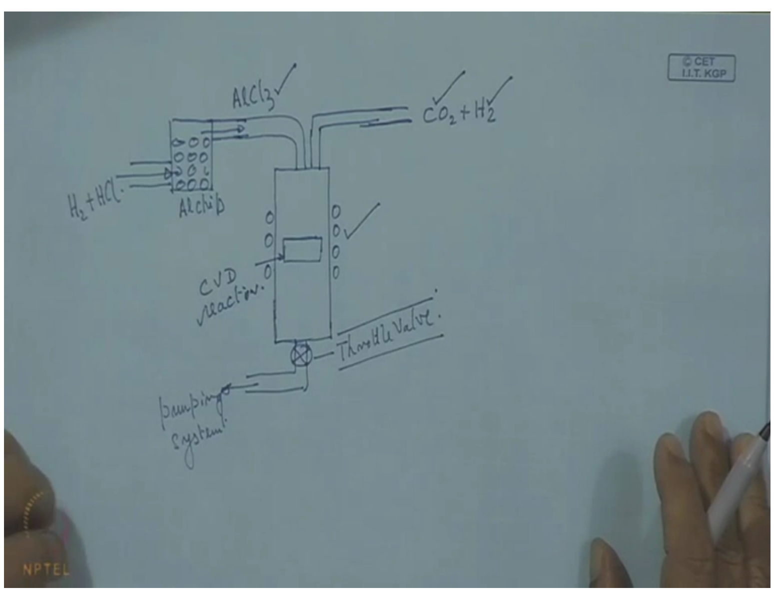

Now there how this CVD is conducted? So here if we try to see this thing, what we should have, here actually we have what we call the Al_2 generator. This is actually aluminum chip. Aluminum chips are placed here, that means this vessel is filled with aluminum chip and from this side it is H_2 plus HCL, that mixture that is being fed. And here we expect $AlCl_3$ to form. And this will be fed in the CVD reactor.

And this is actually the CVD reactor. Now on this, from this side also we have another stream which are all metered and this is actually CO_2 plus H_2. So these should be mixed and there should be metered quantity and we have all the provisions for getting the right temperature. We have the substrate here. And on the downstream side, we must have the pumping system which may lead to the vent. Here also we have vent before the gases are fed into the reactor.

So all these features must be provided in the CVD system so this is actually the pumping system and here and the downstream side there is a throttle valve for controlling the system pressure. So partial pressure of hydrogen, partial pressure of CO_2, partial pressure of $AlCl_3$ which is saturated with hydrogen, then the temperature here inside the CVD reactor and the total pressure prevailing inside the chamber, that is controlled by this throttle valve. So this is in basic, basically a CVD principle which is practiced in this particular CVD chamber.

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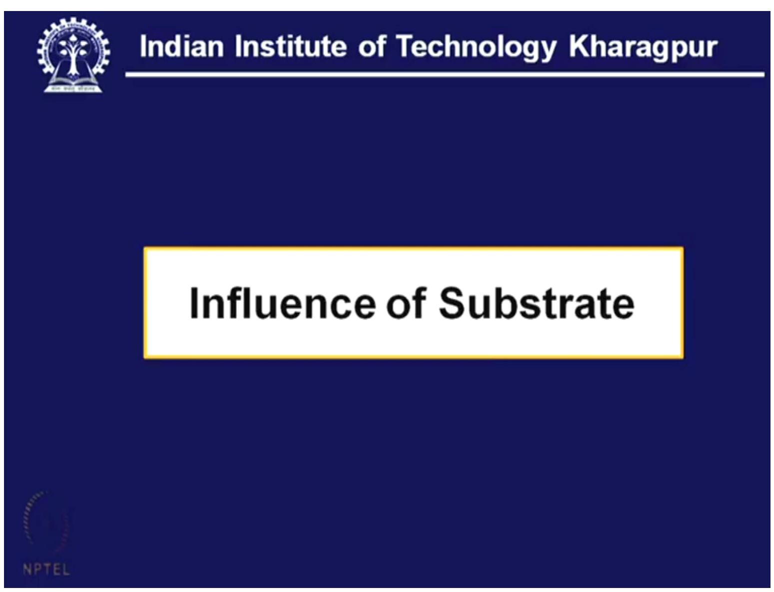

Now comes very important issue. That means influence of the substrate. Now we see that this aluminum oxide coating happens to be one of the very prospective candidate to be used with tungsten carbide substrate.

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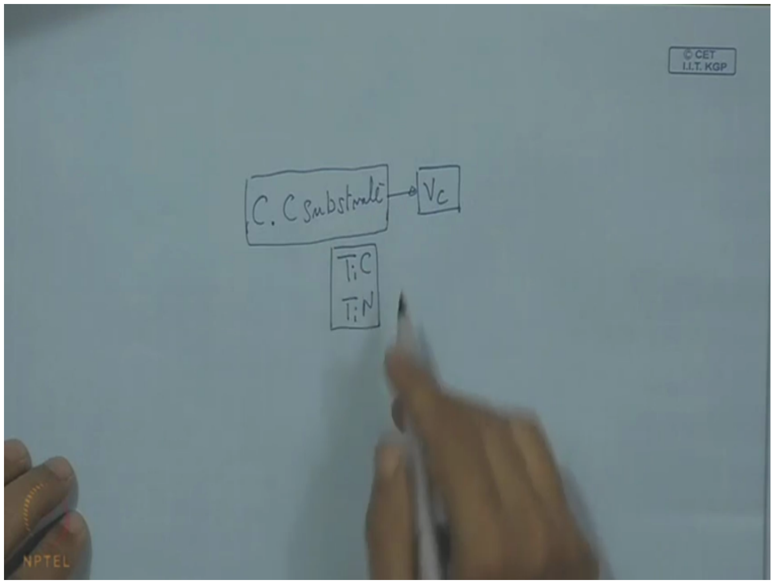

That means what we call cemented carbide substrate. And this is going to be straight in a cutting tool and which can be used with a higher process parameter, that means higher cutting velocity. So that is the aim of the whole work to have this coating on cemented carbide substrate. Now this cemented carbide substrate is a very successful substrate when it is TiC or TiN. For that, this is a very good candidate. But when it comes to deposition of aluminum oxide on this cemented carbide substrate, we find lot of difficulties. Now what are those difficulties? Let us look into detail.

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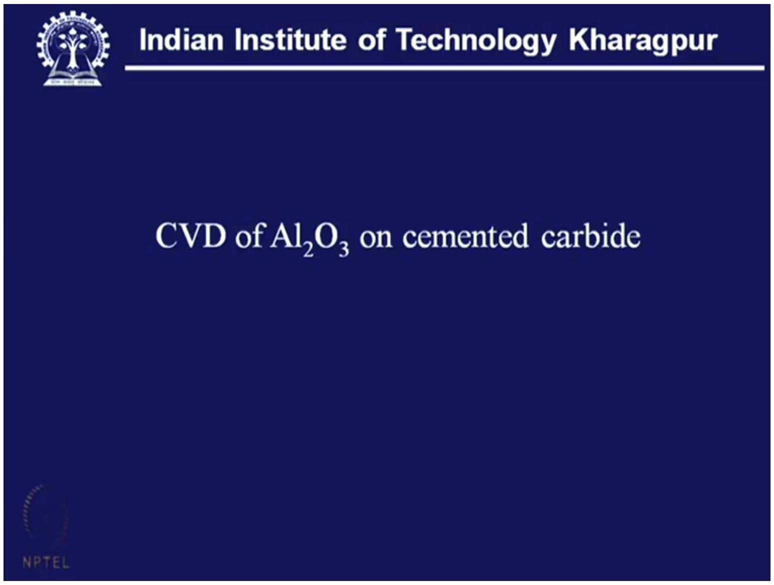

So it is actually CVD of aluminum oxide on this cemented carbide substrate.

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Now before we go to this intermediate layer, let us try to understand the basic problem with this cemented carbide.

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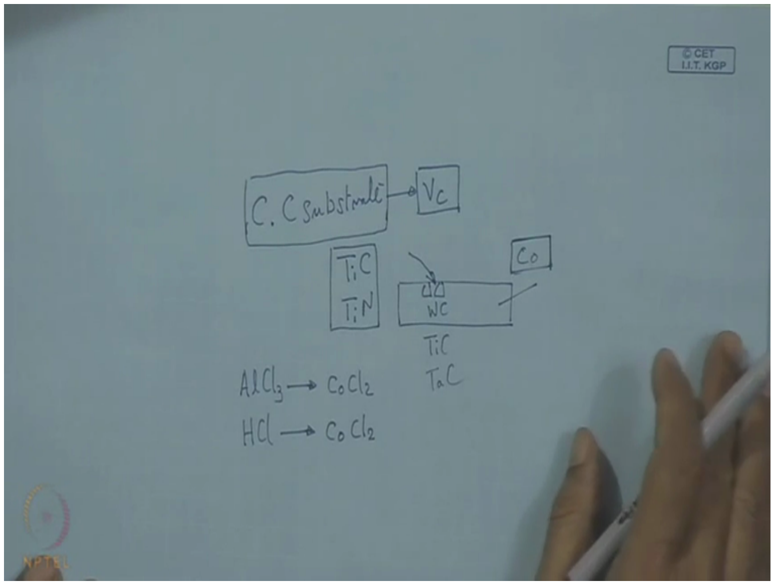

It is actually a composite structure consist of cobalt and without this cobalt it will be extremely difficult to put, to hold this carbide grains, whether it is WC or TiC, TaC together. So existence of cobalt that is a, that is a must for this carbide to give the adequate toughness. However when it comes the question of AlCl3 or HCL which are fed and which will be deposited, which will adsorb on this surface, there is every chance that this AlCl3 attacks the surface cobalt leading to cobalt chloride.

In some extreme situation, this HCL can also chemically dissolve cobalt leading to this cobalt chloride. And when this, whether it is a reaction product of CVD or the reactants of CVD, if they really attack the substrate surface, then the whole purpose is lost. So the thing what one should go or do is how to suppress this cobalt. And if one try to deposit aluminum oxide, then what happens?

That we have a non-uniform coating, the coating is not uniformly covered, you have discrete some island which are certain favorable sites where the coating may grow. But it is unpredictable, unreliable. So one comes to an immediate conclusion that with such an existing substrate, this deposition of aluminum oxide we have great difficulty apart from the mismatch with alpha value, E value and other issues. So it is just the interference of the chemical reactants with the substrate surface that creates, that becomes the root of the problem.

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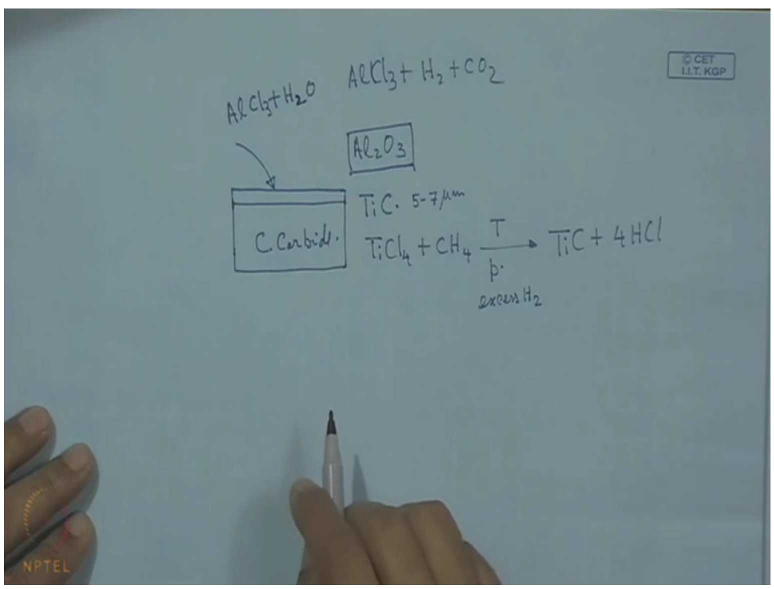

So what is done in this case, it is an intermediate layer of TiC that is put over this surface. So that means in this case, this is the cemented carbide and over that one layer of TiC is grown. It is also CVD TiC and this thickness is around 5 to 7 micron. And this TiC can be deposited by this reaction, TiCl4, CH4 and with excess, then you have the temperature, then pressure, excess H2 and that will lead to TiC and that can go pretty well with this one.

And over that a, over this, this AlCl3 plus H2O, that vapor that will come and if we follow the global reaction, that means all these thing AlCl3 plus H2 plus CO2, the whole mass that arrives here and that is on TiC coating. So this Al2O3 which is formed, that is actually condensing, so it is adsorption. Then this condensation of Al2O3, nucleation of Al2O3 and growth of Al2O3 so this way actually the substrate cobalt is suppressed in this case and we can expect a good coating with much better uniformity, better smoothness, even improved adhesion.

And that will be reflected in its performance during actual machining task. So this is one way of handling the problem, just by depositing one layer of TiC, it is by CVD. However further investigation has also been made to look for something even better than TiC.

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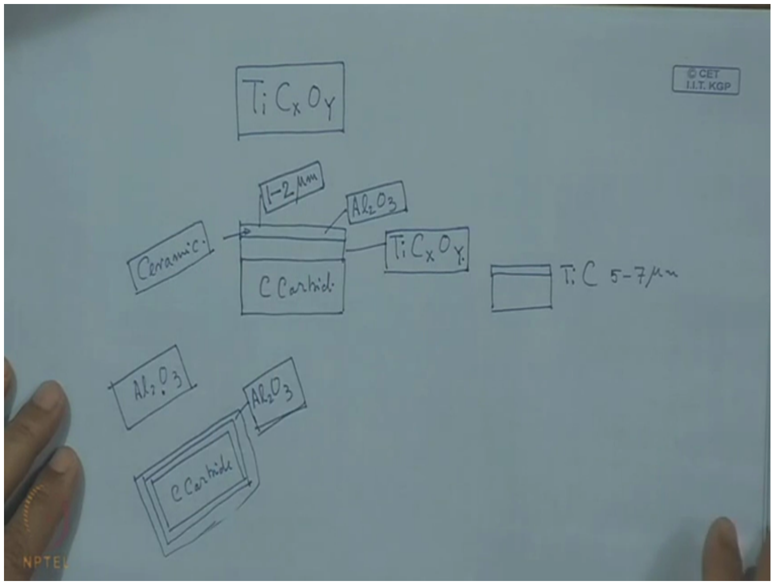

So this is actually an intermediate layer of titanium oxycarbide. Titanium oxycarbide, so this titanium oxycarbide if one puts on this surface, this is cemented carbide and this is a layer of titanium oxycarbide and this x and y can vary, one can vary this value of x, y. But there is an optimum value of x and y which leads to one of the best deposition of aluminum oxide over this surface and it has to be, it must be mentioned that this aluminum oxide that is just in the order of 1 to 2 micron and with this 1 to 2 micron the performance of the tool can be remarkably increased in comparison to a monolayer coating of TiC.

So it we have here TiC and if we have which is also say 5 to 7 micron thick but over that, instead of that if one can put this titanium oxycarbide and that is the intermediate layer and over that if we have 1 to 2 micron thick aluminum oxide coating, then this coating material it is now behaving like one ceramic tool. It is not exactly the ceramic tool where we have aluminum oxide as the solid piece, but here we have the tool basically it is cemented carbide. But over that we have the intermediate layer and followed by one aluminum oxide layer. So this aluminum oxide ceramic has low toughness.

But this carbide can compensate for that and it has this less tensile strength which can be also well taken care by this carbide. And at the top, we have aluminum oxide, so it becomes the functional surface, behaves almost like the surface of a ceramic tool and that is why its capability is enhanced in, with a, in a few order of magnitude. And that is why this becomes one of the high performance cutting tool. So this aluminum oxide coating can be put on this titanium oxycarbide. Now how this titanium oxycarbide is given on this surface?

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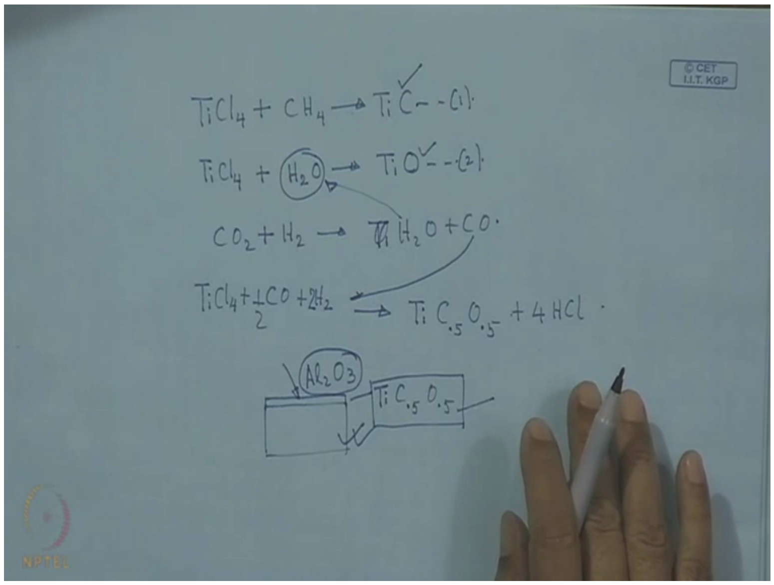

Now we can see that how titanium carbide is formed. Titanium carbide is formed by TiCl4 and CH4, that gives us TiC. Now when we have TiCl4 and this here to get this TiCl4 if we have H2O, that can give us TiO. And this H2O is, can be obtained from this reaction. So this is 1 and this is 2. But to get this H2O, one has to also conduct this reaction, that means CO2 plus H2, that gives us H2O plus CO.

And this H2O can be used here but this gives us TiO. But one is interested to have not TiO but a oxycarbide. This gives 100 percent TiC and this gives 100 percent TiO through this hydrolysis. But if one can take this CO here that means TiCl4 plus CO plus H2 and if we have this kind of thing, one can also go for Ti, it is actually 0.5 and O 0.5. And here we have 4 Cl plus 2 and that can give us 4 HCL.

So instead of using this CO2 if one uses CO in this reaction, in that case this Ti oxycarbide with 0.5 ratio fraction of that, atomic percent of 0.5 to 0.5, so this is 1 is to 1, that can be formed. So it is a 50-50 oxycarbide. And that can be put here over this surface as 0.5, O 0.5, this is an oxycarbide. And on that, Al2 can be easily deposited. And what is more important here, to have high density of nucleation.

So with this subsurface or intermediate layer, immediately one can get with ease aluminum oxide coating with high nucleation density, smoother coating and well-adherent coating. And this coating in comparison to a coating which is deposited on TiC, they can show their difference in performance and it is mostly the resistance to wear. That means with a high degree of adhesion and with a high degree of density, and with a high fineness of the coating, all the required qualities of the coating can be obtained just by putting intermediate layer of titanium oxycarbide.

So this is one of the step in synthesizing aluminum oxide on tungsten carbide, cemented carbide because the deposition of aluminum oxide by CVD that interest mostly comes from the use as a hard coating and that is mostly that is, that comes from the manufacturing industry.

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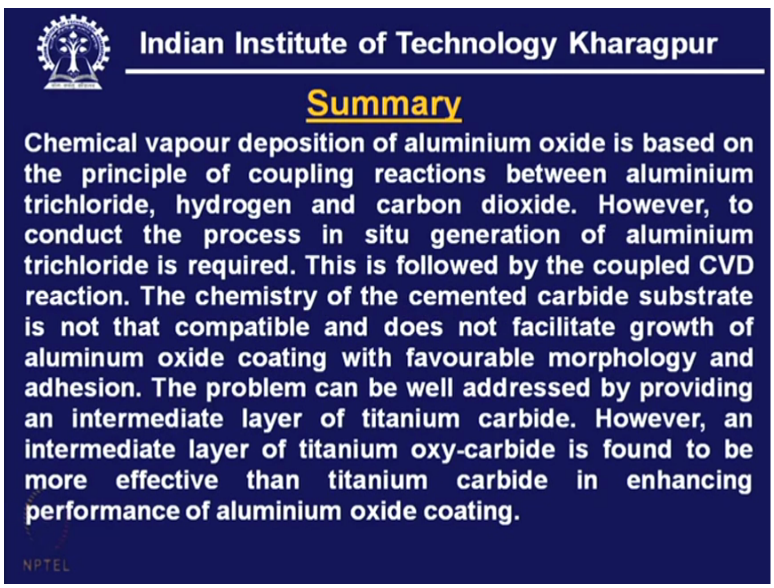

So with that, we can summarize the whole topic like this: chemical vapor deposition of aluminum oxide is based on the principle of coupling reactions between aluminum trichloride, hydrogen and carbon dioxide. However, to conduct the process in situ generation of aluminum trichloride is required. This is followed by the coupled CVD reaction. The chemistry of the cemented carbide substrate is not that compatible and does not facilitate growth of aluminum oxide coating with favorable morphology and adhesion.

The problem can be well addressed by providing an intermediate layer of titanium carbide. However intermediate layer of titanium oxycarbide is found to be more effective than titanium carbide in enhancing the performance of aluminum oxide coating.