Technology of Surface Coating

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Lecture-06

Chemical Vapor Deposition of Nitride Coating

Chemical vapor deposition of nitride coating, by this we mean mainly the deposition of nitride of transitional metals which are known for their hardness, anti-welding property and also anti-diffusion property. So these materials are extremely suitable for those parts which are mechanically functional and if we consider the transitional elements of Group IVB, VB and VIB, we can have a matrix here.

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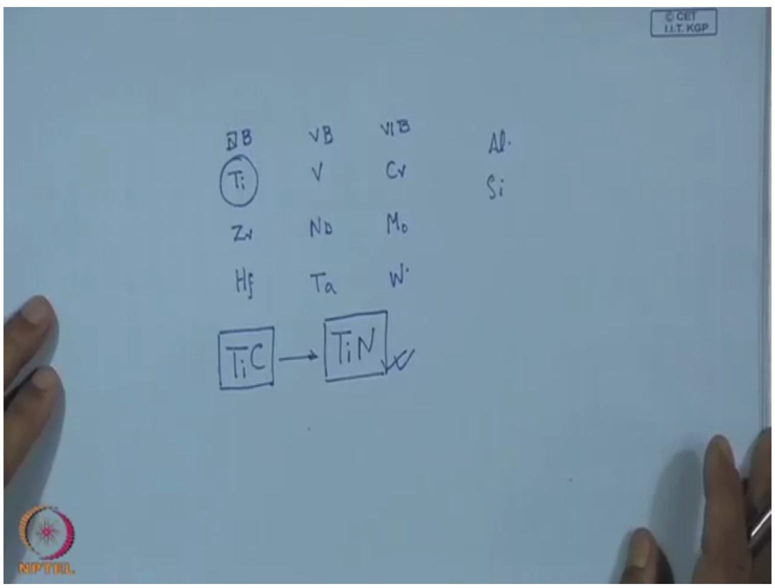

This is titanium, zirconium, hafnium. This is IVB, then comes VB. Here we have vanadium, niobium and tantalum and finally in the Group VIB, we have here chromium, molybdenum and tungsten. Now all those strategic materials which are used for those high-end application requiring extremely high wear resistance, hardness, anti-welding property, chemical stability, now their carbides, nitrides, borides and oxides can give us this type of properties.

And in addition to this, 9 element we can also add here, aluminum and silicon because their carbide, boride, or nitride can also give us such kind of property. Now here we find that this titanium is so popular and so important in that this titanium carbide has a tremendous success in offering such kind of property particularly in all forming tools or tool of production just like forming tool or cutting tool.

And this TiC at the top of the tool, this works so successfully that it can raise the lifetime of the tool by few times or even the cutting speed can be increased quite substantially. Now this TiC is indeed an effective solution to those problems where we have the wear on the tool that becomes a great problem and a challenge. Now if we consider TiN against this TiC, then we find that this has an improved property in comparison to TiC. Because of the simple reason this is more chemically stable than TiC, its anti-welding property is better and diffusion of carbon say for example in steel will be more than diffusion of nitrogen.

Or we can say in this way that this titanium nitride is more stable against steel than titanium carbide and we can identify many more application where we can see even this TiN is found to be much more effective, high performing than TiC. So this TiN can be used in the form of a coating over this tool substrate to give this surface property so that we can get a high performing product. Now this TiN, how we can put it on this surface?

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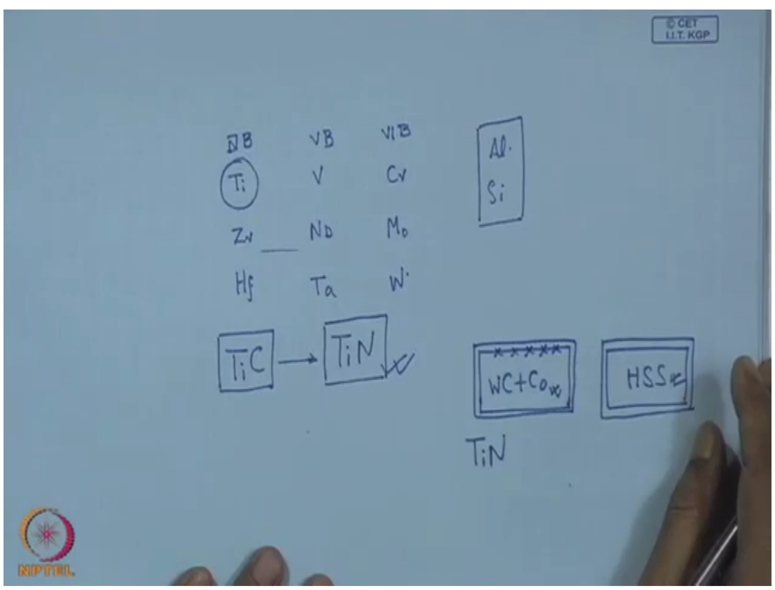

Now here we can see, so here we can see this is a substrate and say it is made of tungsten carbide and cobalt or it can be even HSS or say die steel, tool steel, bearing steel and many more, alloyed steel where we need to augment the surface property or to enhance the surface property. Now by this what we can put here, a TiN coating which can give us this kind of augmentation of the property. However the question here, it is just not the TiN alone, this material alone.

First of all, we have to find out the process which is compatible to this substrate HSS or tungsten carbide, number one. Number two, we can have proper nucleation, growth rate and high nucleation density. These are the essential requirements to be fulfilled in order to have one effective coating because it is just not the coating, there are various issues are to be addressed. For example, smoothness of the coating, density of the coating, obviously comes the hardness of the coating and last but not the least the adhesion of the coating.

That means this is going to be the interface and how this interface is strongly established between this coating and this substrate. Now here we can mention that we have this 3 into 3 matrix. And apart from that, this aluminum nitride or silicon nitride, these also appear to be extremely successful in offering this surface property which are useful for application requiring high wear resistance and hardness and sometimes anti-welding property.

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Now here we see that nitride of transitional element, nitride of aluminum, nitride of silicon, their significance can be felt and understood by those who are using this mechanical component or mechanically functional component which are going to be used in those application.

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Now it comes to the question of CVD, chemical vapor deposition of nitride. And here we focus our attention to titanium nitride because of the simple reason that the success story of TiC is well known. And following the same path if we can also deposit effectively titanium nitride, that will be one degree ahead in the in terms of coating technology and the coating material and that product will be much more useful and effective in comparison to TiC.

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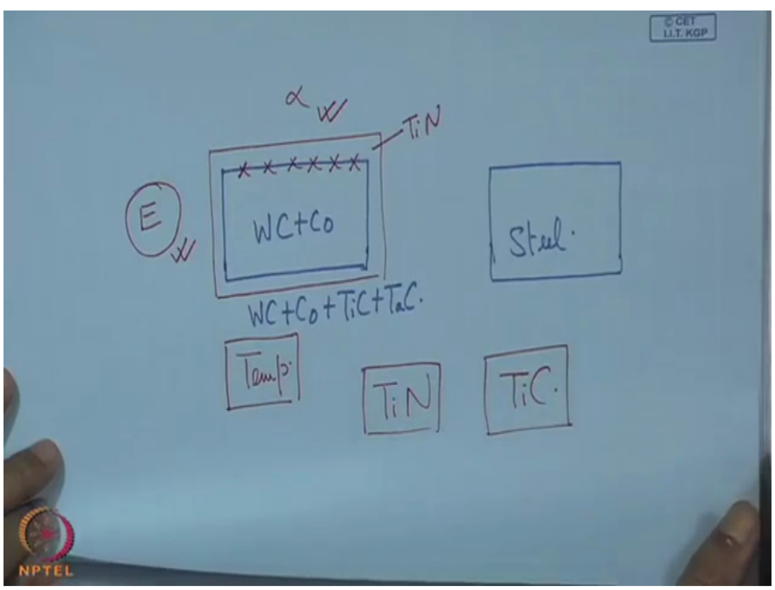

Now here comes the most important issue, that if we have such a block which is made of tungsten carbide and cobalt, it can be also tungsten carbide cobalt plus TiC plus TaC. These are routinely used. Or on the one side, we have all sort of steel families, steel, which includes HSS, high speed steel, die steel, then tool steel, bearing steel and those are the, few are the steel materials which are alloyed steel consisting of molybdenum, cobalt and similar materials, chromium, vanadium to enhance the bulk property.

Now here comes the question, this CVD coating already known for its versatility, (())(9:31) power, ability to coat a complex geometry that is well known. But how to put this TiN here, becomes the question. Already it has been discussed that the substrate and the coating, so that is actually the zone of discontinuity. So that is the zone of discontinuity. We can see here, this is the strong interface we need here, but at the same time one has to understand that is the zone of discontinuity.

This is the coating and that is the substrate. So their alpha value, coefficient of thermal expansion that varies widely. The value of E, that means this Young modulus. And then comes the deposition temperature, that is the deposition temperature, that is also very important. So when it is used and I mean when it undergoes such kind of treatment requiring high temperature, and then it has to be cooled down to the room temperature, lot of stress develop over this surface.

And even if we have some chemical bonding, that advantage will be offset because of this wide variation in value of E and L which actually leads to residual thermal stress. And here we have breakage because of this stress development. So at any cost, this has to be stopped. So that is why when it is a CVD coating, though we know that TiN in every respect it is better than TiC but we have no other choice but also to bring TiC as the buffer between the coating and the substrate and thereby we get this kind of grading, graduation of the property.

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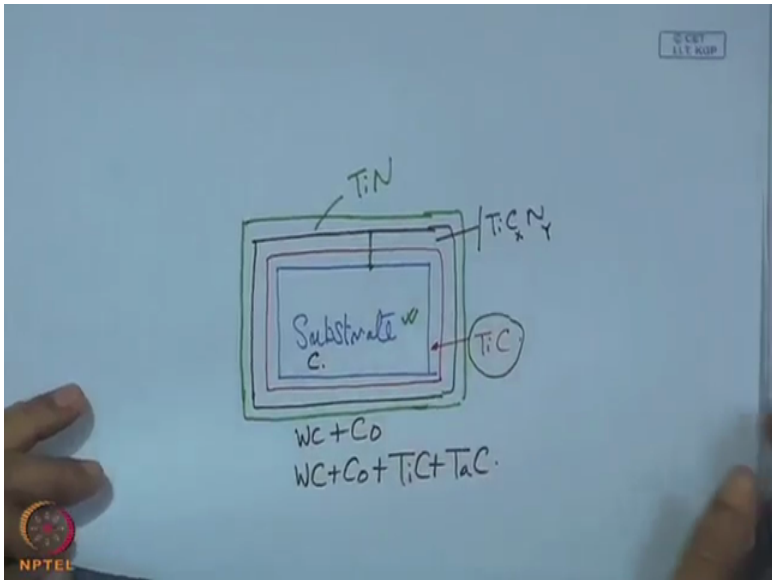

So for all practical purpose, what we have to have here, this is the substrate and then what we have here, we have here the TiC coating. This is not exactly the way we mean, it is not exactly the tough functional coating in classical term but it is, it helps in graduating the property. And on the top, we have say this TiN coating. But before that, what has to be attained gradually, that means here you have exactly a transition layer, this one. This is in fact TiCN with value of x and n.

So this TiC has a very good compatibility with cemented carbide substrate which is Co or plus TiC plus TaC. This is a formulation and with that TiC has a good compatibility. And then to bring that compatibility over TiC, one has to go for titanium carbo-nitride having carbon and nitrogen in that lattice and varying in the value of x and y. So x plus y is equal to 1, so x and y can be varied and when it comes to the top of this transition, there the value of y may be quite high and x may be small.

And at the beginning, x value is high compared to the value of n. So this transition keep on going and finally what we get at the top, we have this TiN and TiN is actually the functional coating. So though it is TiN coating CVD, CVD of TiN coating but to have one of the effective high performing coating, one has to do this preparation starting from substrate, getting TiC, then transitional coating and finally this TiN coating. So this way, one can get a well-adherent integral coating with this substrate surface.

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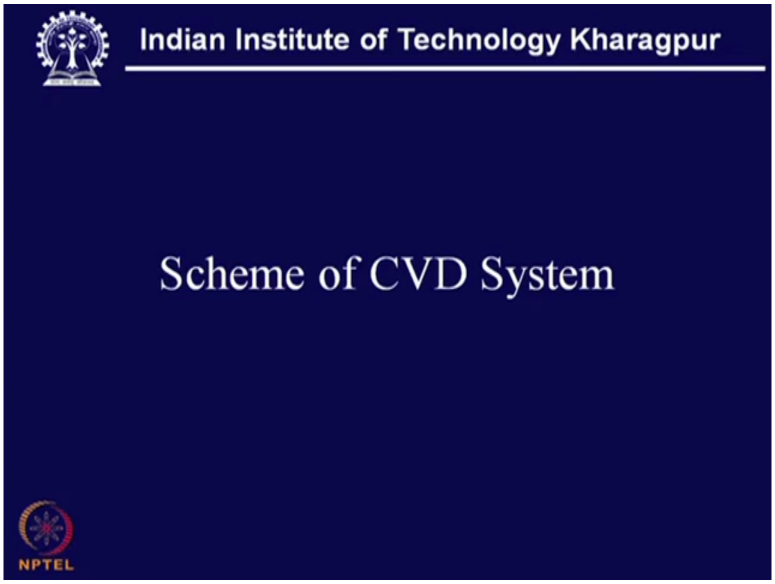

Now this TiN coating can be carried out by following a CVD reaction, scheme of CVD.

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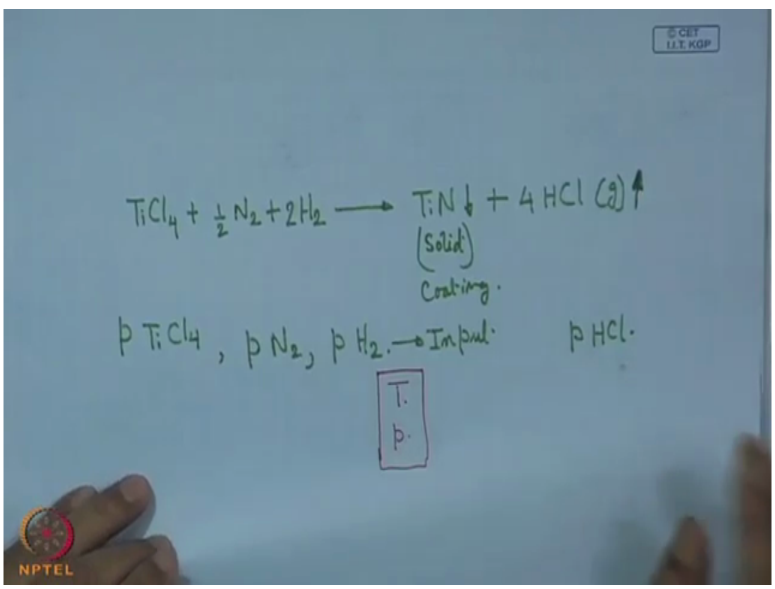

Now here what we have, we have here titanium tetrachloride plus nitrogen plus hydrogen which will reasonably give TiN which comes as the coating. That means it is solid, plus HCL. And here what we get, something in this form, 4 HCL and which is gas which should escape this CVD reactor or CVD system.

Now here what are those thing necessary as we find CVD process variables, now these CVD process variables are actually partial pressure of TiCl4, partial pressure of nitrogen, partial pressure of hydrogen. These are on the input side, these are on the input and as a result of this CVD what we get, in the form of gas, here it is solid which comes like a coating. This is the coating, so here also in the output we get pHCL.

Now these are the operational parameters, that means the concentration of various reactants. And this is automatically the concentration of the reaction product. And here what we have to have, we have to have the process temperature and the system pressure. That means inside the CVD reactor, one has to maintain this temperature and pressure and to have the reaction goes in the forward direction. That means what we like to have here, it is actually a product favored reaction. And this reaction should take place under a condition of temperature and pressure with certain parametric combination, so it can move in this direction.

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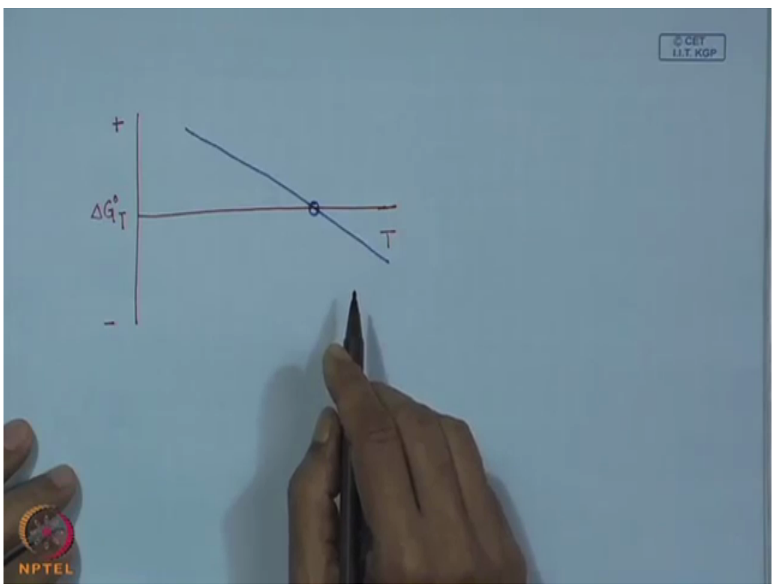

Now here one can see that to make it happen, this is delta G0T, this is plus, this is minus and that is the temperature. And here according to this, it is just like showing Ellingham diagram and we may have a plot like this and that is the crossover point. So this is, this line is showing actually the change in free energy of the reaction which just now we have stated here.

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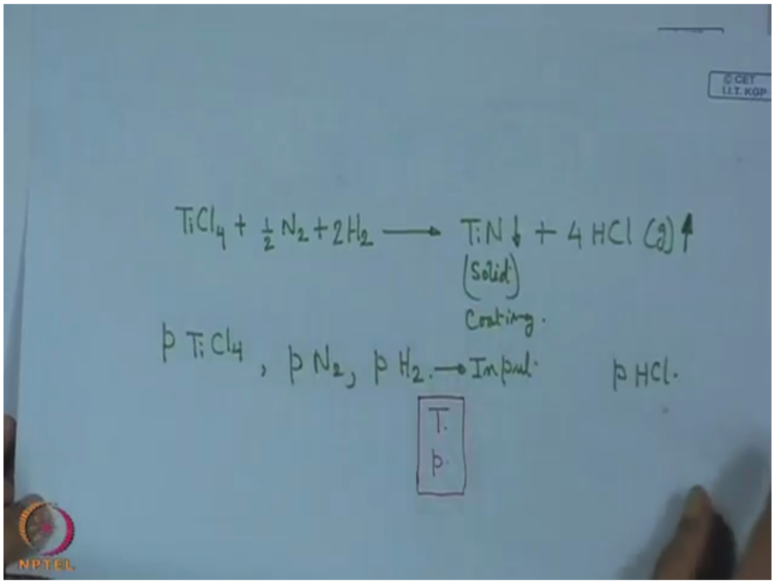

This is the CVD reaction and the change of free energy of this reaction. Now here what we can find that this is the crossover point, that means here these reactants and the products are in equilibrium and at that temperature it is a proper balance between the reactants and products.

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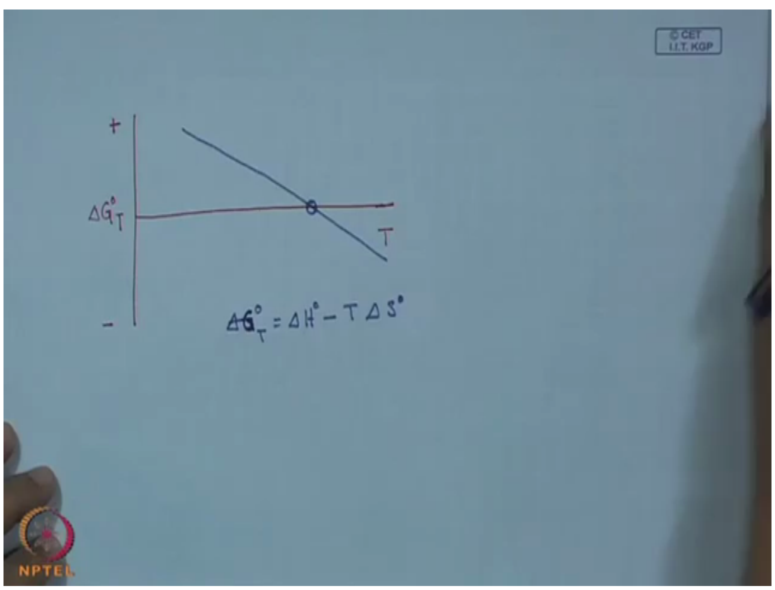

Now this temperature we can reasonably find just by putting this way. Delta G0T is equal to delta H minus T delta S. So these are in the standard state.

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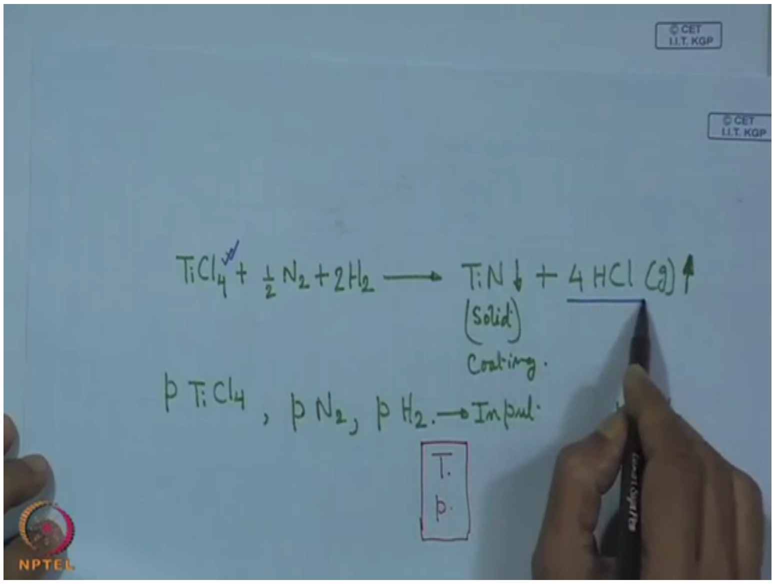

Naturally, this delta G0T and delta H that we can find from for titanium tetrachloride, nitrogen and hydrogen so these are on the product side and then sorry, these are on the reactant side and this is on the product side.

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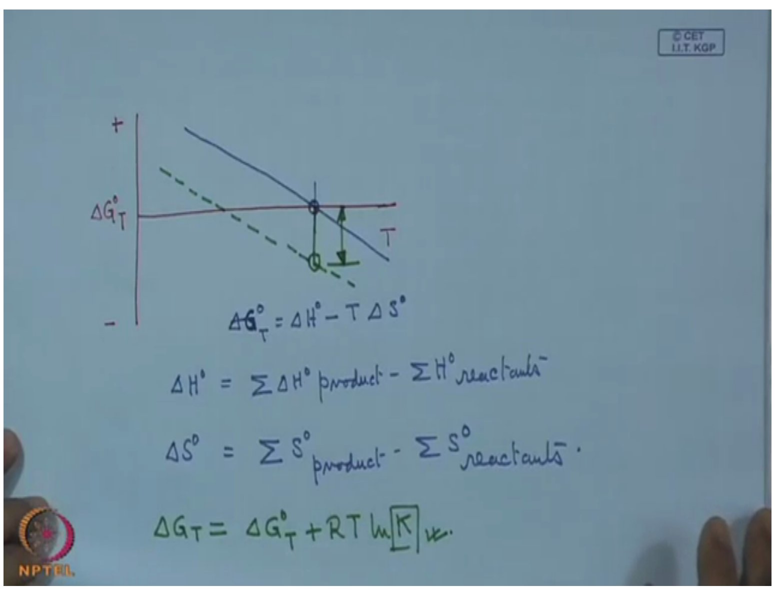

So here we can have this delta H0 means actually this is delta H0 of the product minus delta H0 of reactants. Similarly, we can find this one as of product minus sigma S0 of reactants. So with this, these values we can get from thermodynamic table. So from there one can find out just by putting the value of this delta G0T corresponding to this point, one can be able to find out the value of T. However it is also of our interest to shift this curve, say for example like this if it is possible, say what we have shown by this dotted line and to see that is the net shift.

That means this is also a value of delta G0T and which will be quite negative not 0. That means here we can write further to this, delta GT is equal to delta G0T plus RT into ln K which is actually the equilibrium constant.

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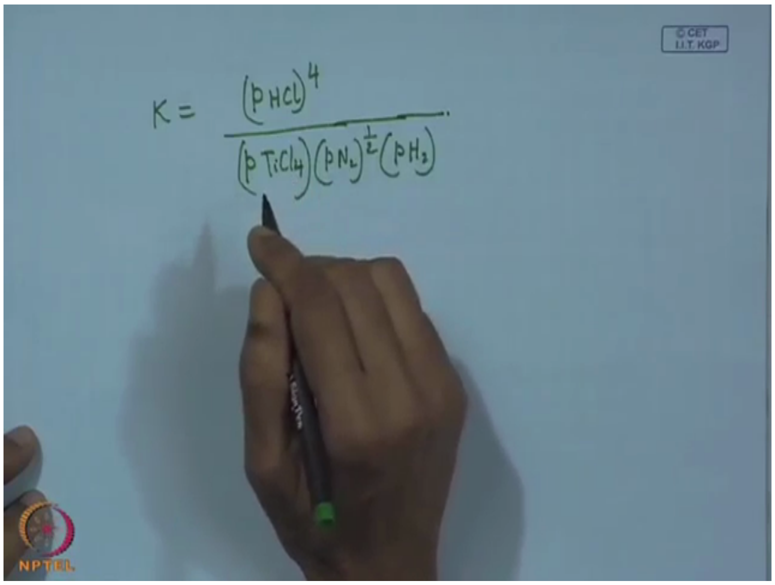

And this equilibrium constant we can find out from this relation that K is equal to, from there we can write that pHCL to the power 4 minus divided by pTiCl4 into partial pressure of nitrogen that is to the power half and pH2. So this is another relation we get.

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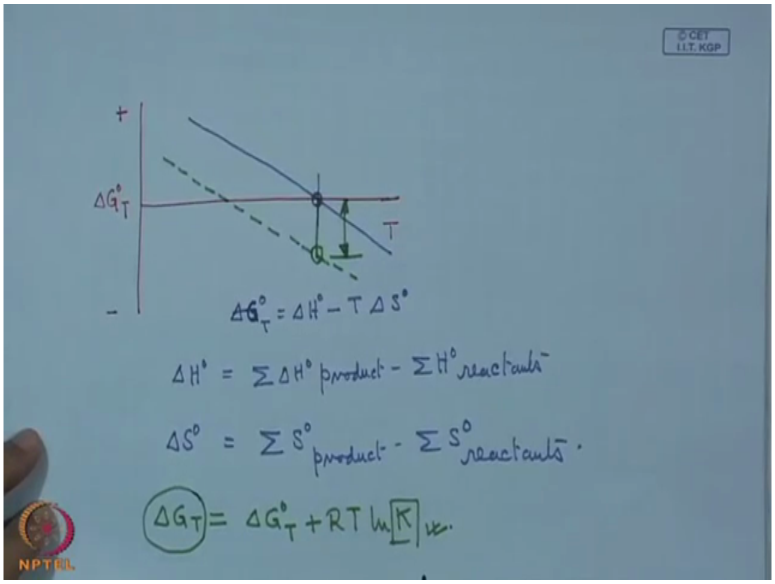

And it is obvious that if we follow this relation to, our idea is to make this more negative and to make this more negative, what we can do?

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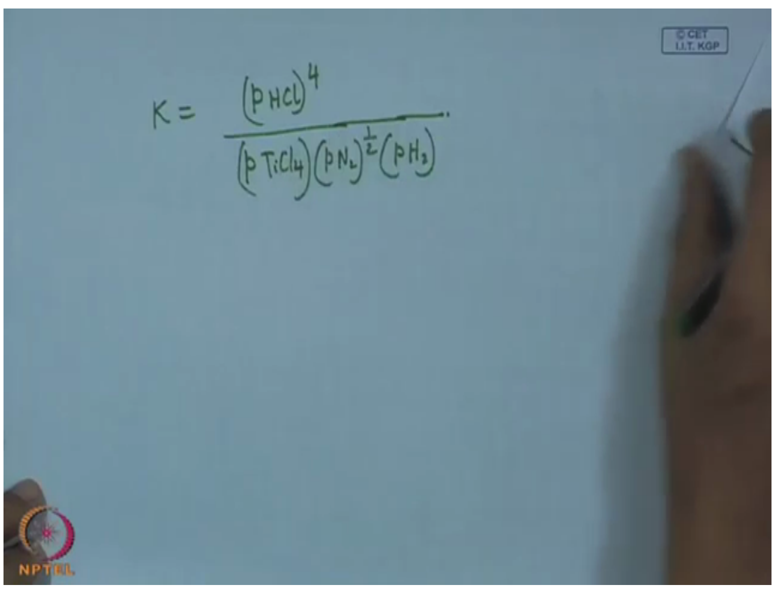

We can check the partial pressure of hydrogen chloride which comes like a value to the power 4 and which is in the numerator. And in the denominator, it is TiCl4, it is nitrogen to the, I mean partial pressure to the power half and partial pressure of hydrogen. So the goal should be to make this as negative as possible so that this....

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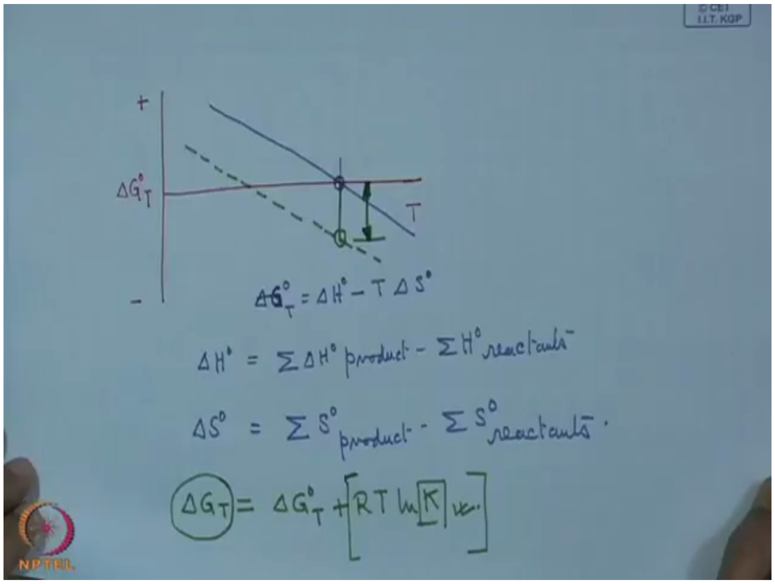

This part in the, in this relation on the right hand side, second part in the right hand side becomes highly negative so that we can get a net negative value here and that means that this is actually a driving potential for this reaction to push or to drive in the product direction and or the reaction becomes product favored. So this is one way one can look into this problem and determining the respective concentration of respective elements and the reactants and also the system pressure and also the temperature.

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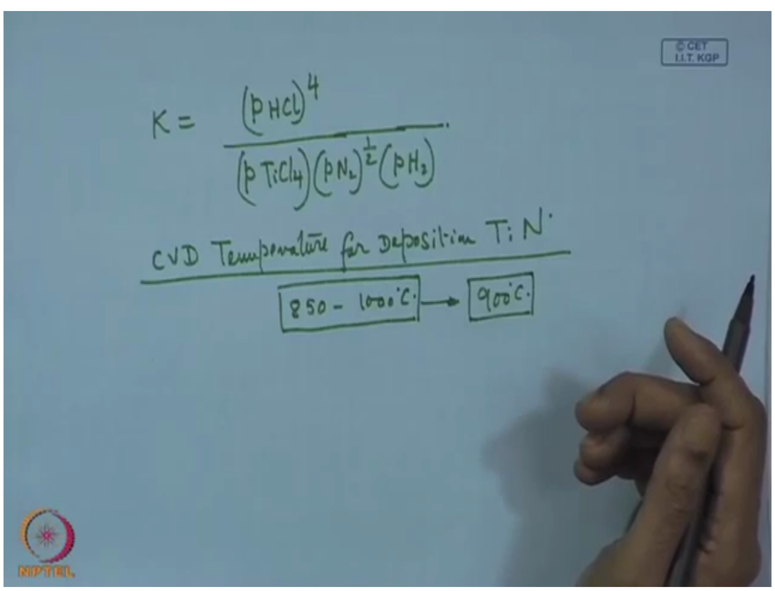

Now from the experience, it is known that this CVD temperature for deposition of TiN that ranges around 850 to 1,000 degree centigrade. It can be done pretty well. And industrial CVD, in many application it is around 900 degree centigrade which is carried out in the commercial scale.

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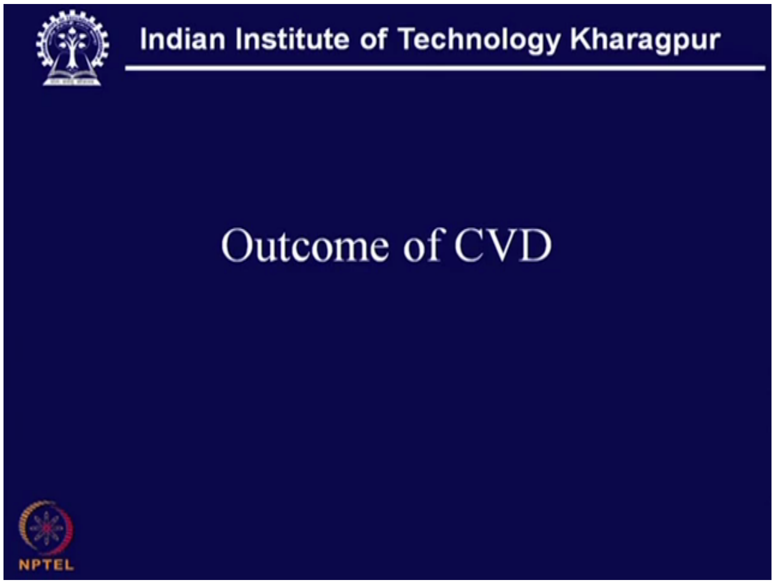

Now what are the outcome of CVD?

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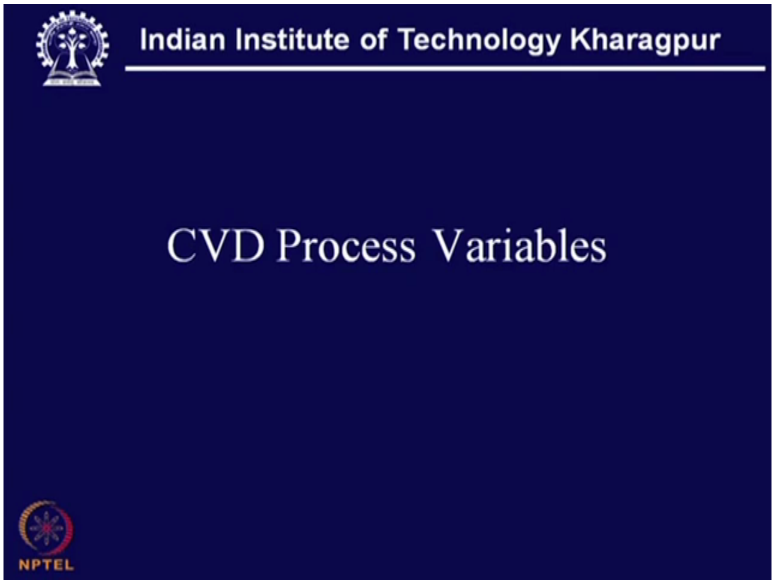

Now here we can have CVD process variables, we have discussed.

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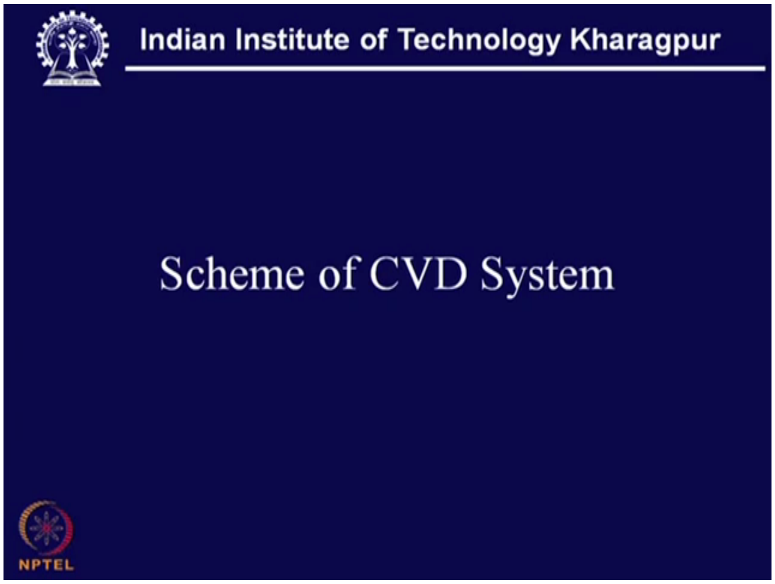

Now what is the CVD, scheme of CVD? That means what are the component or the element the system should have for successful operation of this chemical vapor deposition of titanium nitride.

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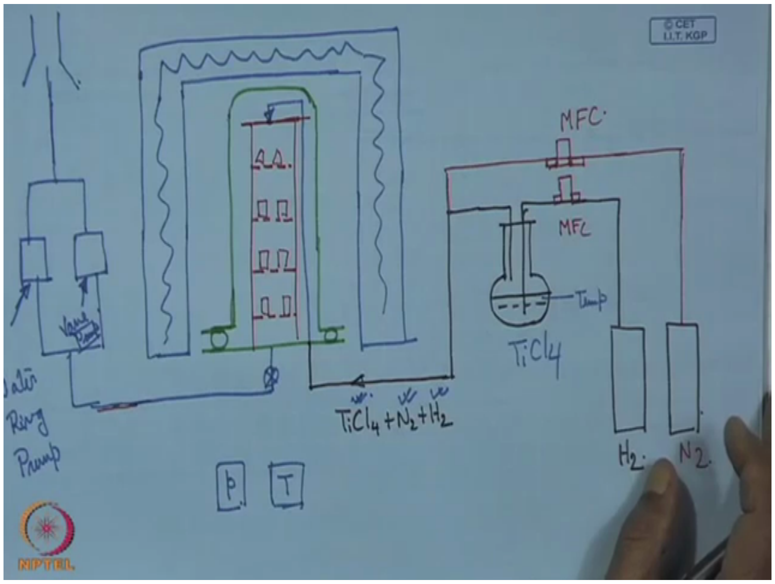

Basically what we need? We need one reactor. So this is one reactor. And then within this, we have one tower and there we have the different stages so that the substrate can be kept over this. These are the substrates which we can put over this. And externally it is a hot wall reactor, obviously there must be a heating element. It looks like a resistance heater and this is placed, schematically we can see it. So this is actually the furnace.

Now there must be two lines, one is the exhaust. Another is incoming, so incoming line it is like this. It is the incoming line and through this what gets in, TiCl4 plus N2 plus hydrogen. And here we have the storage for this TiCl4, it is a flux. And hydrogen should be bubbled through this, so this is one such thing. And here we have bottles for hydrogen that goes inside. So it is something in this form. So this is hydrogen and then we have one for nitrogen.

So this is the basic scheme. Of course, here we have the mass flow controller. So these are the MFC. Plus, we have many peripherals like the pressure gauge, these valves and other thing. Here also we have, I mean inlet valve. And this side, of course we have two pumps. One is, and this goes to the ventilation, so this is actually water ring pump. And this one and this one, that is the vane pump. So these are the basically the CVD setup what we can see here.

And this is TiCl4, so these are admitted and this will go over this surface and it will be showered. And as the outcome, we have HCL. So during the CVD operation, this vane pump does not work, it is actually the water ring pump where this HCL is neutralized. And any residual gas will escape through this ventilation. So this water ring pump actually or the liquid ring pump, it contains sodium hydroxide which is used for neutralizing this HCL.

So here the system pressure, here we have a valve. With this valve by throttling, we control the pressure. That means the process pressure which we have already mentioned. And through this furnace, we control the temperature at different zone if it is so necessary. So this P and T plus here we have hydrogen and this is a saturated with TiCl4. So at a particular temperature, if we can maintain a particular temperature, so at that temperature hydrogen will be saturated and one can also determine what is the percentage of TiCl4 which saturates hydrogen.

So these amounts are known, pressure-temperature known. Naturally from this temperature, one should be able to find out the rate of reaction or the conversion. And finally one would be able to determine that growth rate or the thickness of the coating which will grow per hour and that is also one of the outcome of this whole operation. Now comes, so this is basically a summary of the CVD system. We have the reactor, hot wall reactor, the furnace, the gas dispensing system and also the gas disposal. So these are the few things just we have summarized.

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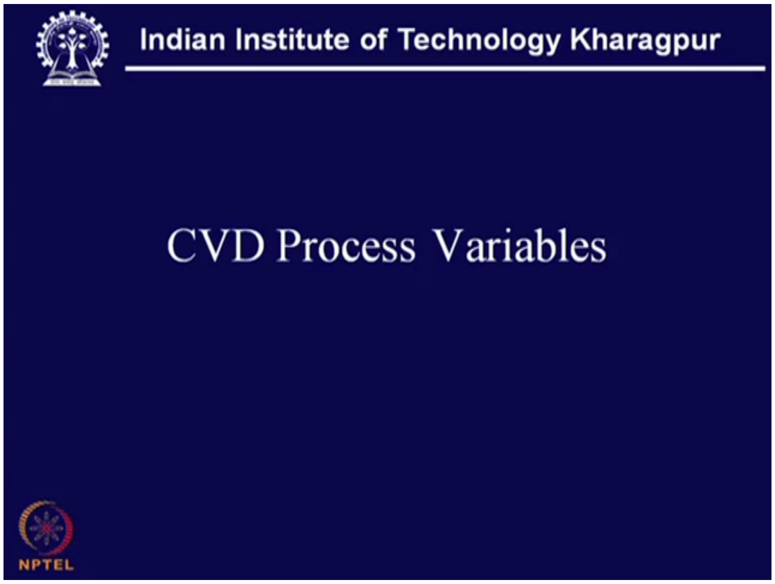

And now comes the CVD variables. We have already mentioned, it is the process pressure, process temperature, concentration of TiCl4, concentration of nitrogen and concentration of hydrogen.

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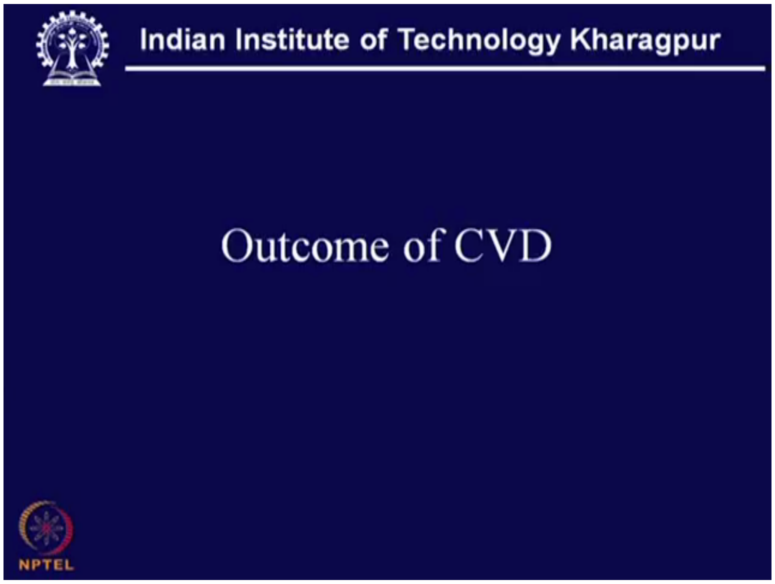

Now comes the outcome of this CVD. Now outcome of this CVD is, outcome of this CVD, one outcome is the deposition parameter.

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That means the deposition rate. So deposition rate, one would be interested to know what is the deposition rate.

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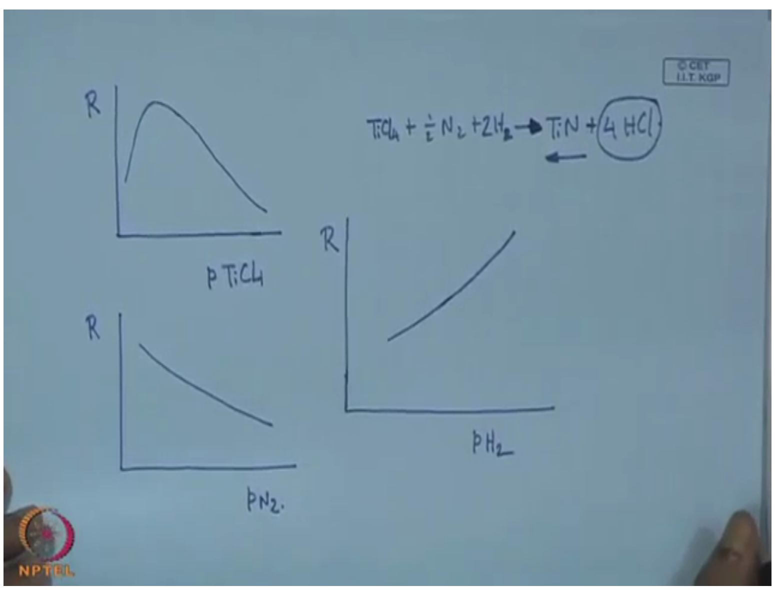

So if this is the deposition rate and this is the concentration or partial pressure of TiCl4, so it comes like this and it falls drastically. The deposition rate with, for a, what does it mean? That means for a given condition if one keep on increasing titanium tetrachloride, then it is found that deposition rate starts falling and almost comes to 0. This is because of the reason that one can look into this reaction, that means here TiCl4 plus half N2 plus H2, so for one molecule of TiN what we get? We get actually 4 HCL.

So if without increase of H2 or other parameter if we keep on increasing this pTiCl4, partial pressure of titanium tetrachloride, then what is going to happen, that there will be too much of formation of HCL and it will revert the reaction in this direction. And this reaction in the forward direction, it will be seriously affected. So this pTiCl4 if it is increased without touching hydrogen or temperature or any other parameter, then we can see such a trend.

Similarly what we find, this is also the case with nitrogen. Also, it has a falling curve, that pN2. However this is also a falling curve. However if we increase hydrogen under a same condition, then what we can find out, this growth rate which is may be so many milligrams per hour per unit area of the substrate or simply micron per hour, that is the thickness of the coating. So if we specify the growth rate, this way we can see the nature of the curve and here we can see it is a rising trend. It is simply because of the reason that here it has a better reducing effect. And if we have excess hydrogen, then this reaction is going to move in the forward direction and as a result we have a rising tendency.

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Now comes the lattice parameter. Now this lattice parameter, that is influenced by these parameters and here what we find that this lattice parameter that is the function of temperature. So when temperature is increased and this what you mean that the temperature of interest is around 800 to 1,100 and in this zone, it is found that this lattice parameter keeps on falling with this value of nitrogen, with the value of temperature and with increase of nitrogen it also keeps on increasing.

So this actually the partial pressure of N2, so it goes like this so this is a lattice parameter which is an index of the stress inside the unit cell and by refining this we can also refine structure of the coating.

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Now comes the grain size. Now this grain size is one of the parameter of interest because one would like to have finer grain size for various reason. Number one, the toughness of the coating at the edge can be improved a lot, number one. Then if we have a fineness of the grain, then roughness of the coating can be also significantly reduced. And these are the two things at least one should have an attention at this point.

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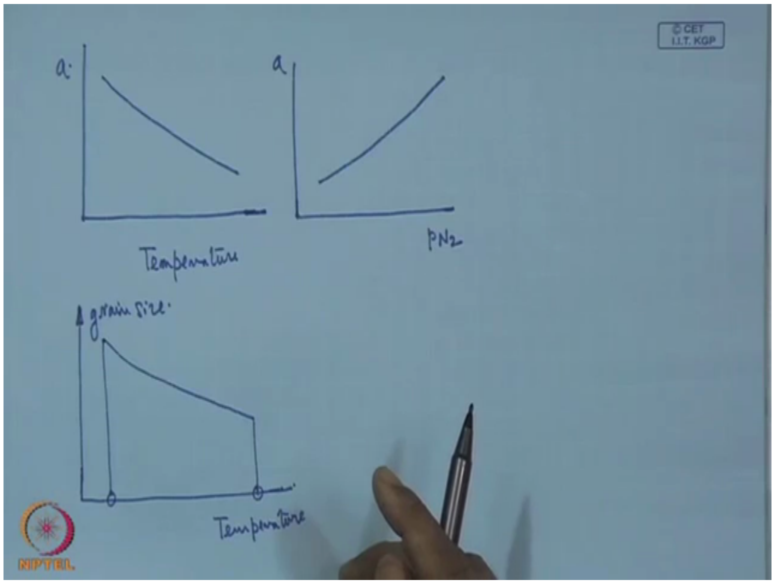

So here if we see the grain size, so it comes like this. By increasing the temperature, we can see fineness of the grain. Now this happens because of the simple reason that when the molecules are formed on this surface because of the low mobility of the adatom, there is less diffusion on this surface. So because of this less mobility of the adatom, they cannot join together and become an integral unit.

And there remains lot of void space, porosity and gap. And this can be (full) I mean filled in if we have better mobility of this adatom. And this can be enhanced by simply increasing the temperature. So within this condition of experiment, that means within this 800 to 1,100 when this temperature is increased, there is a marked improvement in the grain size of the coating. And one can note that out of these three parameters, that means where we are considering this partial pressure of hydrogen, partial pressure of nitrogen and temperature, it is mostly the temperature that has a very strong influence on the final grain size.

And here we see that by increasing the temperature, we can have a finer structure. And it is because of the simple reason that this porosity or the void can be significantly reduced and we can have a grain structure and thereby we can increase the density of the coating.

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Surface morphology in fact what we can see here that surface morphology, this is one of the criteria. That means what is the structure, whether it is just like a broomstick or equiaxed, that means it is spreading in every direction. Or it is just like a dome like top or it is, have a crystallographic plane just like a 1:1 plane, preferential 1:1 plane and it becomes just like one face of a pyramid. So these are the few things one has to look in, so it is also one observation that when the temperature is less, there is less amount mobility of this adatom and they cannot move a lateral shift and thereby we can get a structure which is not so dense and it is porous.

But when we have a high temperature, then there is diffusion across these atoms which are, which arrived on this surface of this substrate and which makes this TiN and by this rise of temperature, we get a favorable morphology which is finer in size and also there is less amount of dome like structure, less amount of porosity and we have more of a densified structure. So this amount of, that means the temperature has one effect and if we increase the temperature, definitely a compact structure can be expected.

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Now comes the coating hardness.

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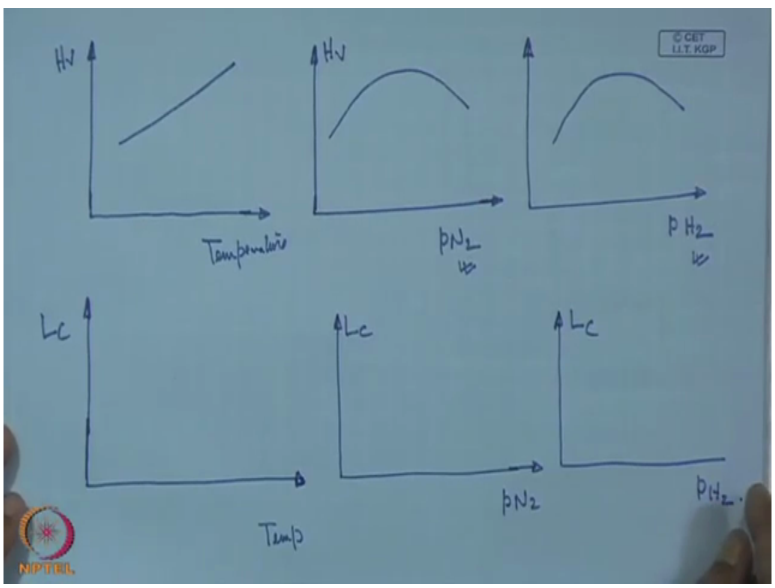

Now this coating hardness means here resistance to penetration. That means this structure should not have much of residual stress, that means which is very highly compressive stress and the coating becomes very, very brittle. But this is, this hardly be the case with a CVD coating where the coating is mostly having a stress which is tensile in nature. So it is a tensile stress, so the coating is not, may not be that brittle. However what one can see that if the coating is porous and having voids, imperfection, in that case the indenter can have an easy penetration indicating less hardness.

So in that case what is understandable that when we have a finer grain, that means finer grain means obviously a denser structure. So with the same volume if we have larger grain and if we have finer grain, obviously with a finer grain we get a (densi) densified structure and which is much more compact in nature. So with this compact structure, one would expect increase in hardness. So as a corollary we can say that if we increase the temperature, the hardness of the coating is also increasing.

However what happens with flow of hydrogen and nitrogen, that one has to look in. This is partial pressure of N2 and this is partial pressure of H2, it can be also expressed in terms of flow rate of the reactive gases. And here one can find that this is having a trend like this and this one is also having a trend like this. And this happens, one would expect here that if we have less amount of nitrogen, what we get, we get a porous structure.

And here similarly is the case with less amount of hydrogen but when we have increased quantity of nitrogen or hydrogen which favors a reaction of titanium nitride, then we get a densification of the coating. But if we increase this value of nitrogen or hydrogen excessively, then we can also have a shoot-like structure which is like a shoot and which has less compaction and less hardness.

So in that case, we have what we call, it is like a dust formation and it is homogenous reaction which can takes place in the gaseous phase. And as a result of that, what is going to happen? This is not exactly happening on the substrate surface and as a result of this the structure is not so densified and this will be translated into a low value of hardness. So we can summarize that with excessive nitrogen and excessive hydrogen, there could be a fall of the hardness.

Now comes coating adhesion. Now adhesion of the coating, say this is Lc and this is temperature. This is also critical load, pN2. This is Lc and pH2. Now what is, what exactly happens at the interface?

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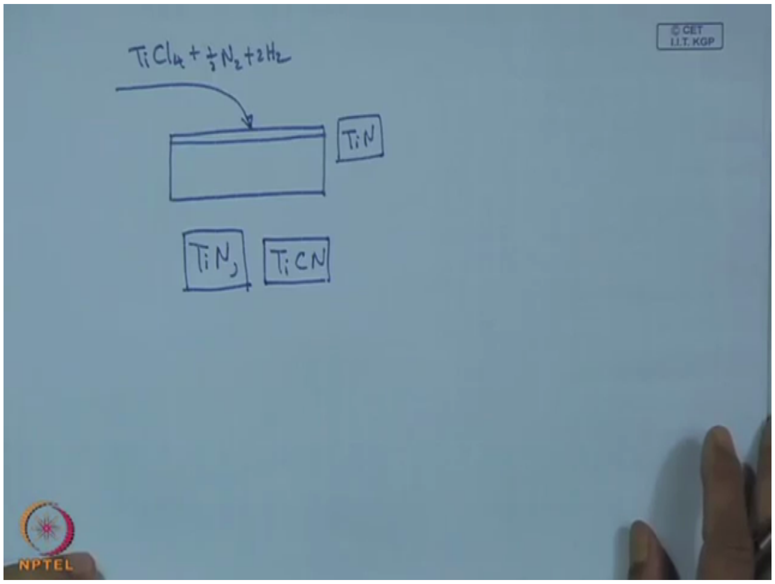

We can try to follow this way. This is the substrate and TiCl4 plus half N2 plus 2 H2. And as a result of that, we like to have TiN and that should grow on this surface. And this definitely, this will be promoted by temperature because it is the, okay, this is actually the interface where one would like to have the reaction on the substrate and not in the space between the shower and the substrate surface. So what we like to have here that this reaction should take place on this surface.

And for that, definitely temperature will be a promoter of this reaction. So this reaction and right temperature on this substrate, then this reaction will take place on the surface and then this TiN will have a good attachment with TiCN and there will be a perfect transition between this carbonitride and nitride. Now here temperature has a very big role to play. Now what is going to happen?

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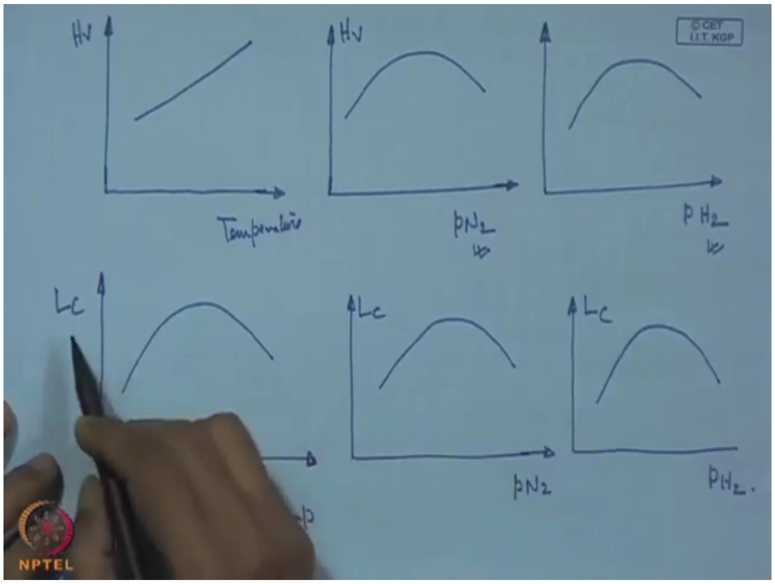

We can see that this curve is actually going like this and then falls. This is also a curve what we see on this side and also with pHydrogen. That means for all the cases, what is seen that this critical load.

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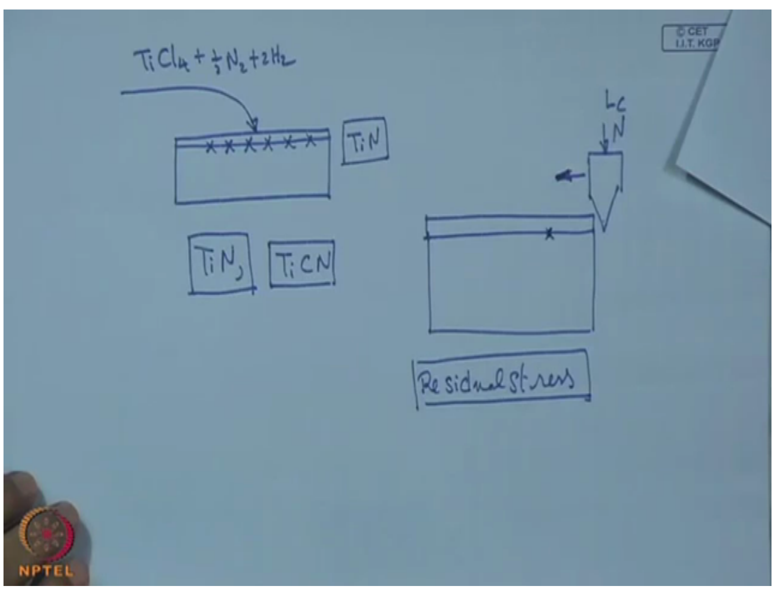

This critical load means if it comes like this, this is the coating and there is one the scratching tool which moves on this side and it has a penetration and it is actually the load at which the first detachment is detected. And for that, we have the dedicated instrument, that adhesion scratch tester. So this adhesion scratch tester detects the point corresponding to a normal load at which this fast separation takes place and that is known as the critical load which is the normal load here.

So this critical load, so this critical load has a rise because of this reaction, very strong adhesion, chemical attachment. But because of this high temperature, finally that is going to be offset or neutralized by the residual stress at this point. So this one, one has to also look in while setting the temperature.

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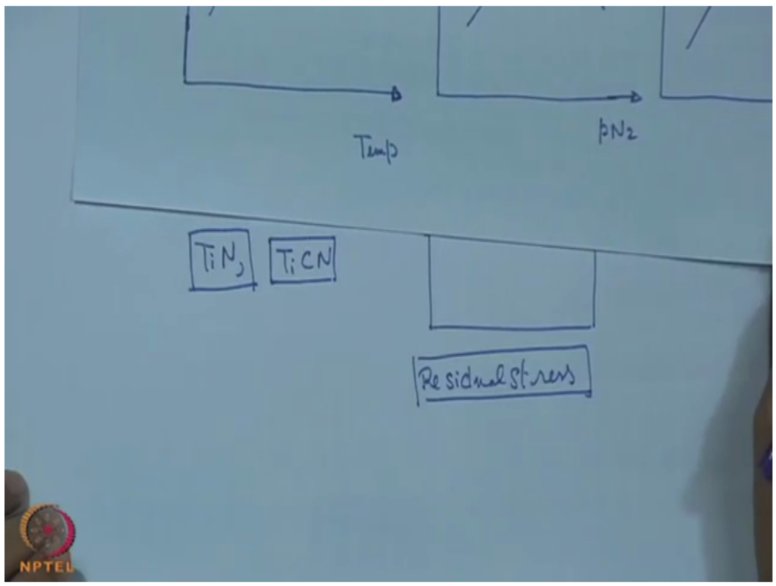

Similarly pN2 and pH2, there are also the partial pressure and with this partial pressure exactly what happens?

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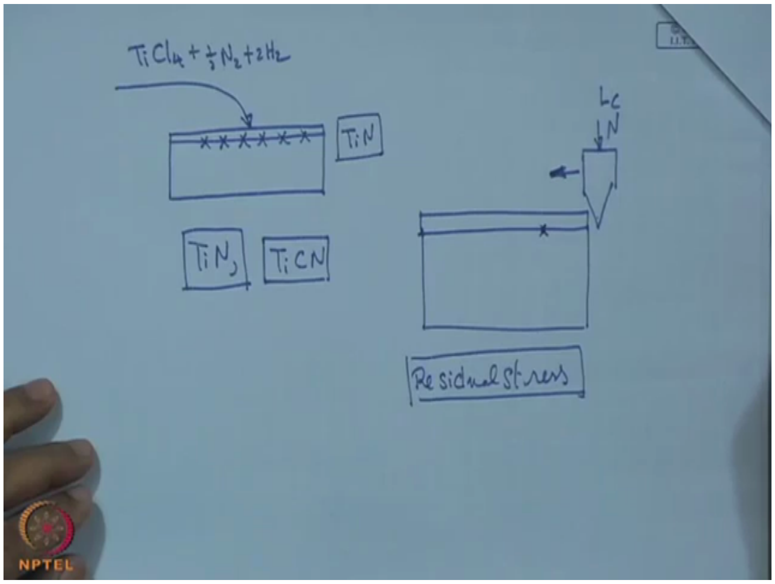

The reaction we want to have the reaction here, but because of the high pressure of nitrogen or hydrogen this can be promoted in the gas phase before the reactants reaches the surface. So if that be the case, then we can have some flake formation, some void may form, some dust may form which is less adherent and as a result this kind of fall of the critical load may be observed.

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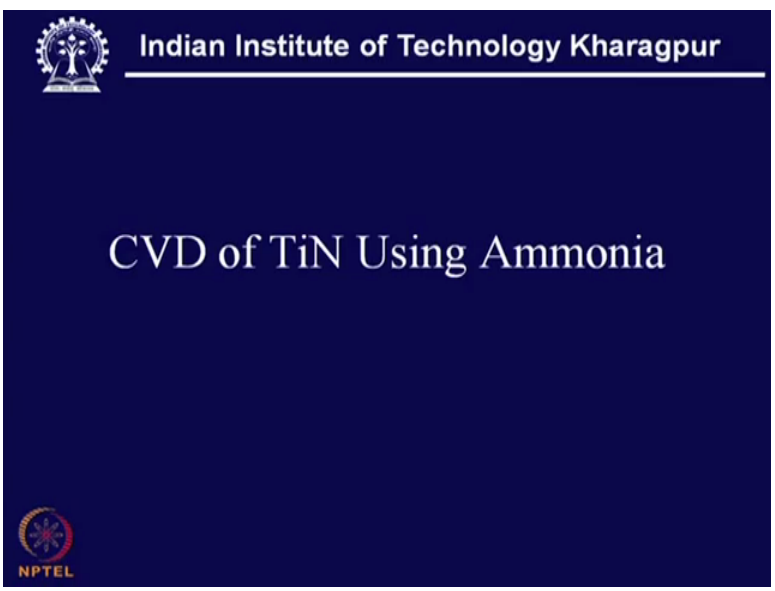

So it is actually CVD of titanium nitride using ammonia. And what we have seen at the very beginning that if it is the delta G0T, so this is the temperature and this is minus, plus. So when it is the reaction using TiCl4, hydrogen and nitrogen, then we have a temperature here which is around 900 degree centigrade for this reaction to occur.

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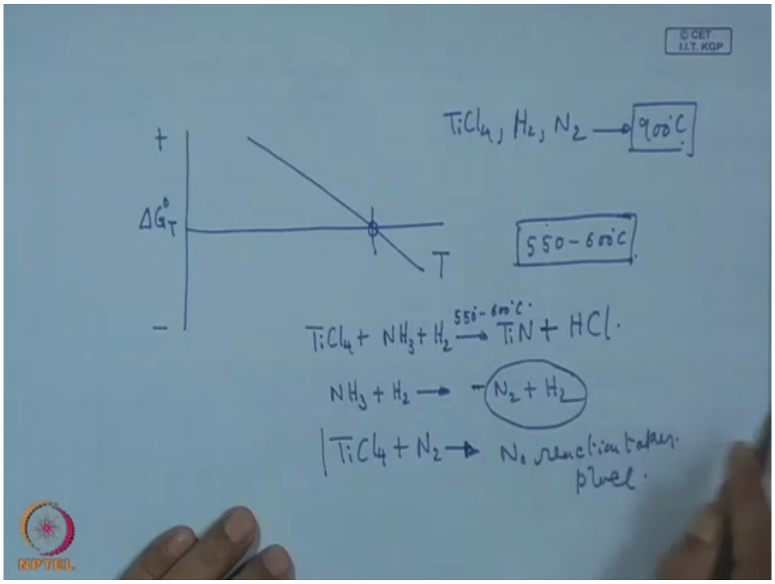

But if one is interested in having a low temperature CVD, so this is in the order of at least 900 degree centigrade temperature. But if one is interested in the CVD around 550 to 600, then some attempt can also be made with instead of nitrogen using ammonia. And in this case, it is something like that, NH3 plus H2, that gives TiN plus HCL. And this can happen at this temperature of 500 degree to 600 degree centigrade.

However here we have this breakup. So that means it is actually NH3 plus N, so this gives actually N2 plus H2. So that will be split here, so this is also another reaction which may occur. And when we put this TiCl4 plus this N2 at this, no reaction takes place so one has to also look into this type of reaction that this dissociation does not occur. So in that case, this N2 cannot come in as an effective means for converting this TiCl4 into TiN.

However with this use of ammonia and hydrogen and taking appropriate measure if one can make this ammonia to react with hydrogen and then this reaction can move in the right direction. And in that case, we get a TiN at low temperature. And this TiN can be used for those application where this high temperature can be little delicate and where this high temperature can also damage the metallurgical property or the mechanical characteristics of the material.

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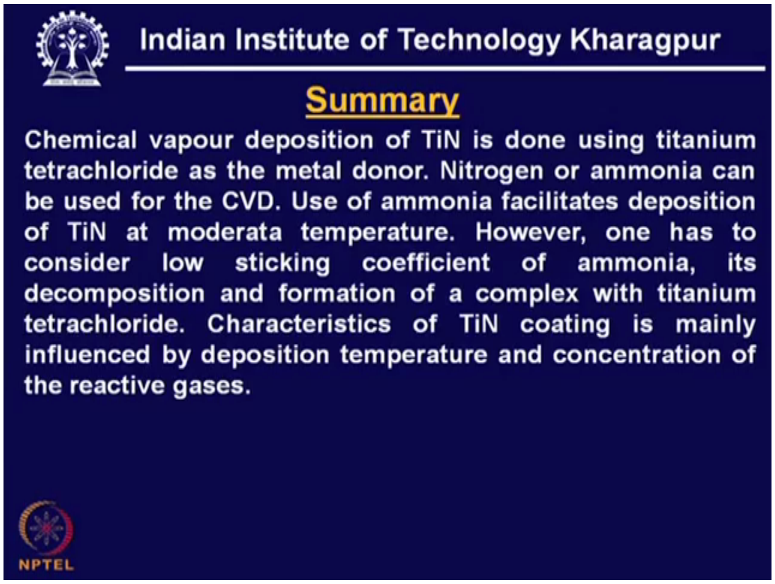

So with this, we can summarize the thing. That means chemical vapor deposition of titanium can be done using titanium tetrachloride as the resource material. And this is actually the donor of titanium and what we can see further to this, as a source for nitrogen we have two options, either nitrogen or ammonia. Nitrogen with hydrogen as the carrier gas can be rather conveniently used and this particular reaction requires at least a temperature above 800 or 850 degree to happen.

And this reaction can be quite useful for those substrates which are unaffected. Say for example, cemented titanium carbide which can be one of the best candidate for such thing. However in this case, we need to have a transition from TiC to titanium carbonitride and followed by TiN. However for HSS and other materials if we like to carry out this reaction at a high temperature, a special heat treatment after coating is necessary.

Alternatively ammonia and hydrogen can be used and in this case the reaction can be, reaction can be made to happen around a temperature of 550 to 600. But there one have to be careful that ammonia and hydrogen can split into nitrogen and hydrogen. And in this case this nitrogen will not be effective for conducting this CVD at this 500 to 600 degree centigrade.