Technology of Surface Coating
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Lecture-05
CDV of Tic

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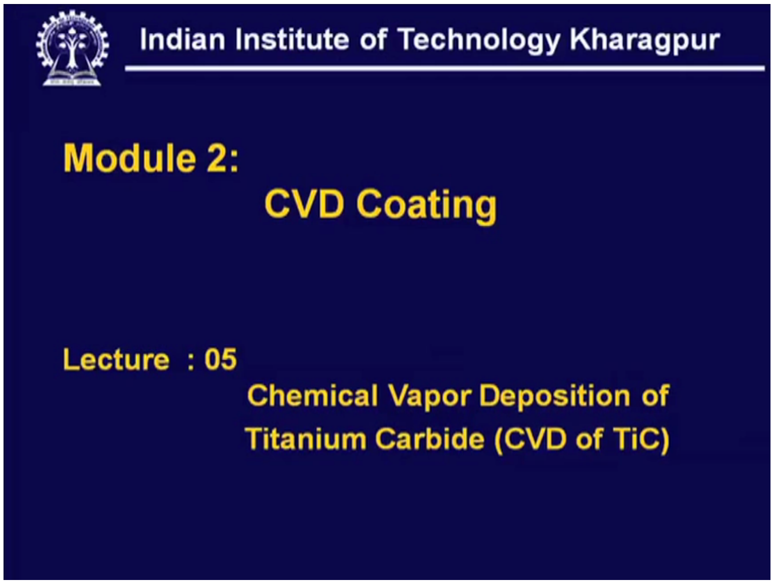

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Module 2:
CVD Coating

Lecture : 05
Chemical Vapor Deposition of Titanium Carbide (CVD of TiC)

Chemical vapor deposition of titanium carbide the basic need of titanium carbide comes mostly from the cutting tool industry.

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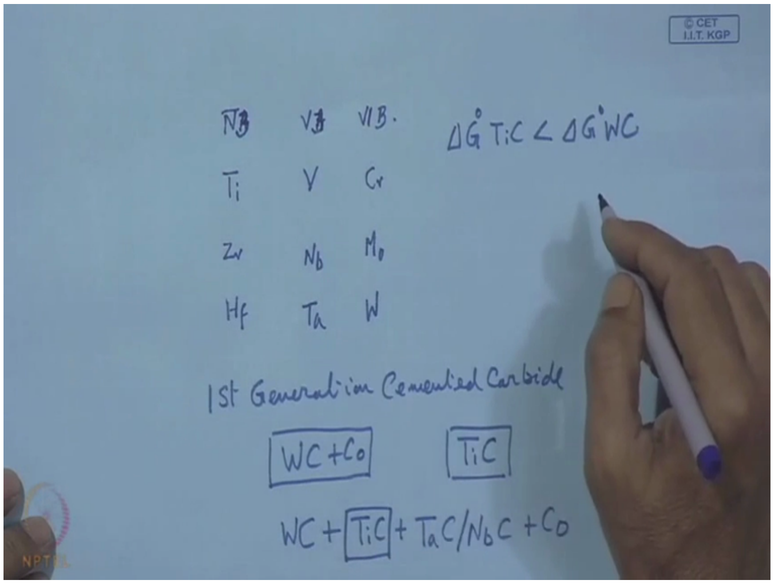

IVB	VB	VIB.
Ti	V	Cr
Zr	Nb	Mo
Hf	Ta	W

$\Delta G^\circ_{TiC} < \Delta G^\circ_{WC}$

1st Generation Cemented Carbide

$\boxed{WC+Co}$ $\boxed{TiC}$

$WC + \boxed{TiC} + TaC/NbC + Co$

Let us look into this portion of the periodic table. That means this transitional element of Group IVA, VA, IVB, VB and VIB. Here we have titanium, zirconium and hafnium. In Group VB, we have here vanadium, niobium and tantalum. In Group VIB, we have chromium, molybdenum and tungsten. This 3 into 3 matrix, that actually constitutes the most of the strategic element which are formed as carbide, nitride, boride or oxide. And they are becoming more and more important to fabricate a high performance cutting tool.

Now here we know that the 1st generation of tungsten carbide, 1st generation cutting tool, that means cemented carbide that was formulated with tungsten carbide and cobalt. However later it was found that this tool though very effective for machining of cast iron, it was not that successful in the machining of steel. And there it has been further revealed that little percentage of this titanium carbide within this tungsten carbide-cobalt matrix can improve the performance of this tool remarkably while machining steel.

Now this becomes the new formulation, titanium carbide and little bit of tantalum carbide or niobium carbide plus cobalt. So this titanium carbide becomes the strategic material when this tool, this cemented carbide tool is engaged in machining steel. The reason is as follows:

TiC happens to be more wear resisting during machining of steel which is a long cheaping material. And here we find that TiC is having an anti-welding character, it has the resistance against possible diffusion across the tool to the chip material and moreover TiC has a improved chemical stability in comparison to tungsten carbide. So if we look into the free energy data, we can find that delta G0 of TiC, it is more negative than that of delta G0 of tungsten carbide. So at least we find some valid reason why this TiC comes in this mixture as one of the very strategic compound to make this cutting tool much more efficient than this one. But this is not just without any problem.

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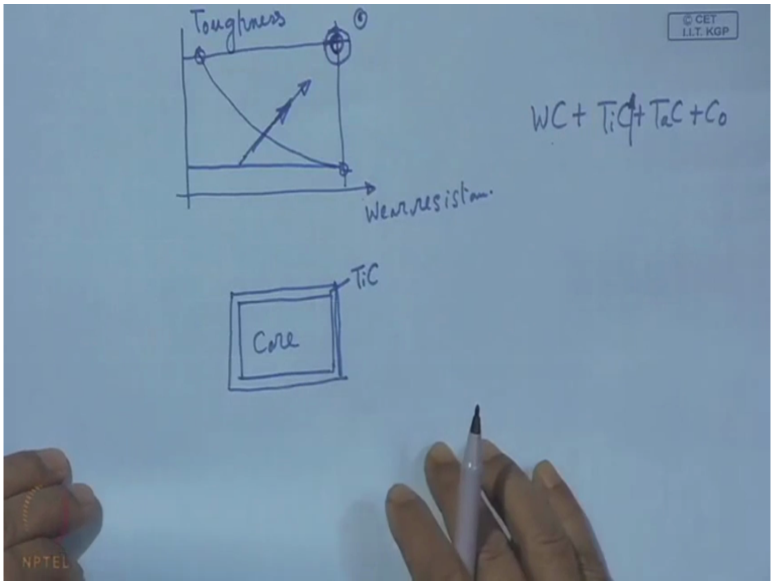

Now when we put titanium carbide, immediately what we find that on a cutting tool we need two requirement. On one side, we have toughness and on one side, we have wear resistance. Now what happens? When we put, we get a graph like this. That means we put more titanium carbide. Then that wear resistance keeps on increasing along this direction but at the cost of toughness.

That means in this mixture, WC, TiC, TaC and cobalt, if we keep on adding TiC, we gain in wear resistance but what is sacrificed that is the toughness. However for a cutting tool, we have this contradiction in the requirement. We need both of them but if we follow this particular two elements and their behavioral pattern, then we can see that these two increases the toughness and this one increases the wear resistance and hardness.

So ideally one would desire to have something which will come over here, that is the point of intersection. That means a strategic material, a tool material or wear part material which can give us both toughness and wear resistance. And that is exactly where we get the concept of a composite material where we have both toughness in the core and a coating at the surface. So that means in this case, if we can put this titanium carbide as a surface layer giving the necessary cutting property or wear resistance, then we can have low content or almost zero content of titanium carbide inside the core.

So we can have the tough grade and at the same time a grade which is known for wear resistance and putting them together the point shifts here and we get one of the ideal tool. So the goal of the research in this direction would be always to push this curve towards this direction and getting more and more points which is higher and higher up. That means this tool would be having remarkable toughness and also wear resistance.

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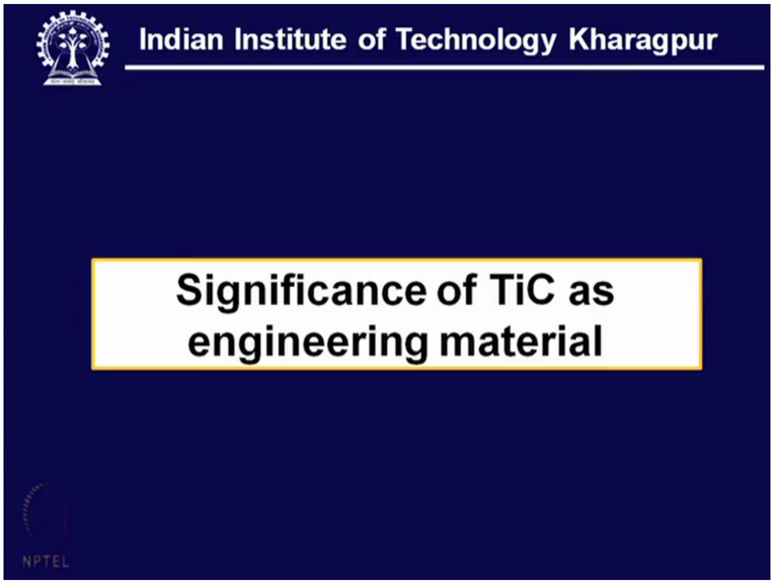

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Significance of TiC as engineering material

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So here we find the significance of titanium carbide as the engineering material.

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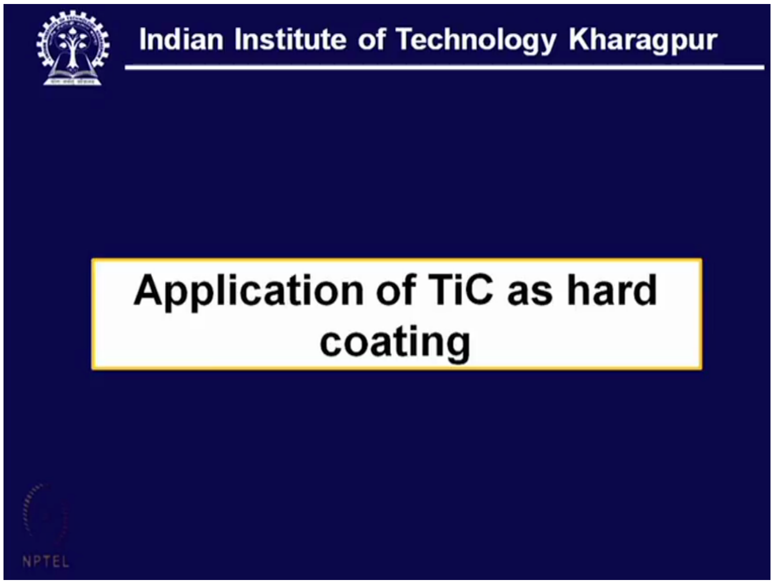

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Application of TiC as hard coating

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So application of TiC as hard coating, that means the demand mostly comes from the cutting tool industry. There are other areas, metal forming tool, bearing particularly the balls of the ball bearing. These are also coated with TiC to improve their wear resistance.

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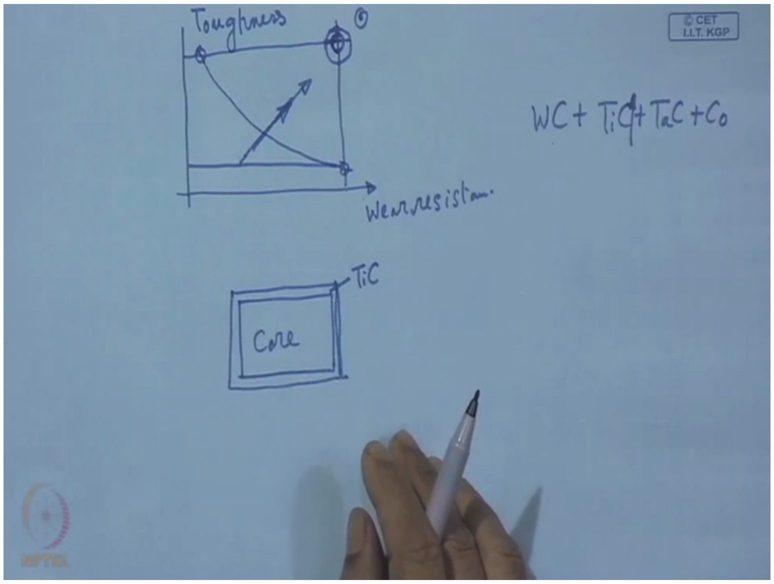

So this is the coating which enhances the performance of the whole composite consisting of this tough core and a wear resisting surface.

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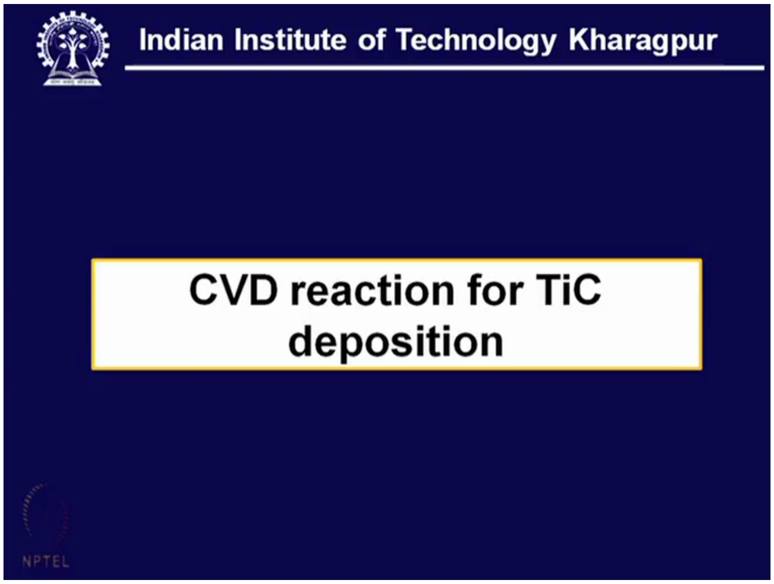

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CVD reaction for TiC deposition

Now the CVD reaction for TiC deposition.

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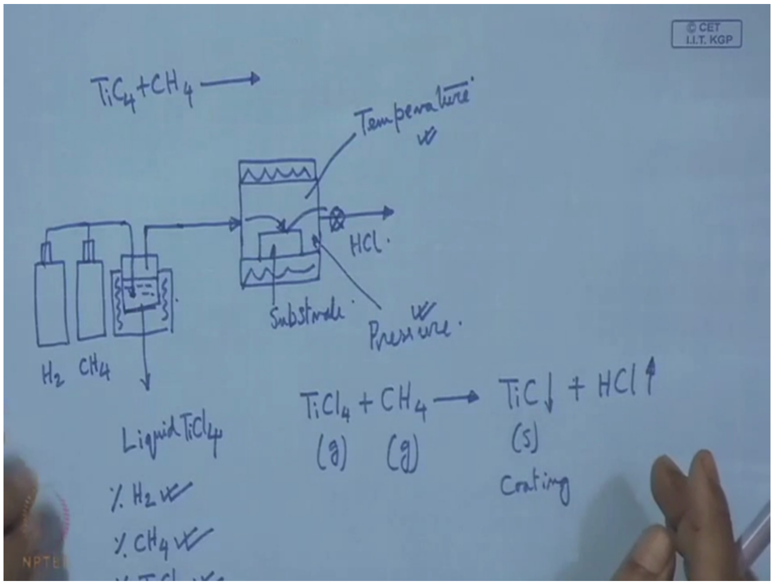

Now what is done normally, if we consider one CVD reactor schematically, and here we put the substrate. This is the substrate and this is a reactor which is heated. That means this is the hot wall reactor. So it has one incoming line, that means the upstream and that is the downstream side. So on this side, we can show schematically, at least we need two sources. One is hydrogen and another is methane. Now these two are mixed and these two are passed through a bottle or a container containing this liquid TiCl4.

So this one will be dipped into this liquid, that means hydrogen and methane will be bubbled through this. And then you have here this nozzle which is leading to this furnace. And here we have to keep the temperature, a controlled temperature. That means in this zone, evaporation of this titanium tetrachloride that takes place. And hydrogen and methane, those are passed through this vapor, that means hydrogen is actually saturated with TiCl4.

In one, this H2 has one role of as a transporter of this TiCl4 vapor and at the same time it has the purpose of reducing this TiCl4. Now here what we have to do, you have controlled flow. That means this H2 and CH4 are to be metered and at the same time controlling this temperature of this TiCl4, we can properly meter the percentage of H2, percentage of CH4 and percentage of TiCl4 in this gas mixture.

So CVD means the gaseous reactants that will be admitted here, so it is basically now TiCl4 and CH4 and then comes the reaction inside this reactor. We control the temperature, and also the system pressure what we call process pressure. So here we have proper throttling at the downstream side which will be connected to some vacuum system, vacuum pump. And by this proper throttling, we can control the system pressure.

So here the global reaction is TiCl4 plus CH4 which are in the form of gas that will lead to TiC as a synthesized material which will deposit as solid which is the coating and HCL vapor which should leave this reactor. That is the downstream side. So this is actually HCL. Now here the process parameters are percentage of or concentration of H2, concentration of methane and concentration of TiCl4. At the same time temperature of the substrate, system pressure, these are also two important parameter. Now with this parametric control, we can carry the reaction in this forward direction with this end result.

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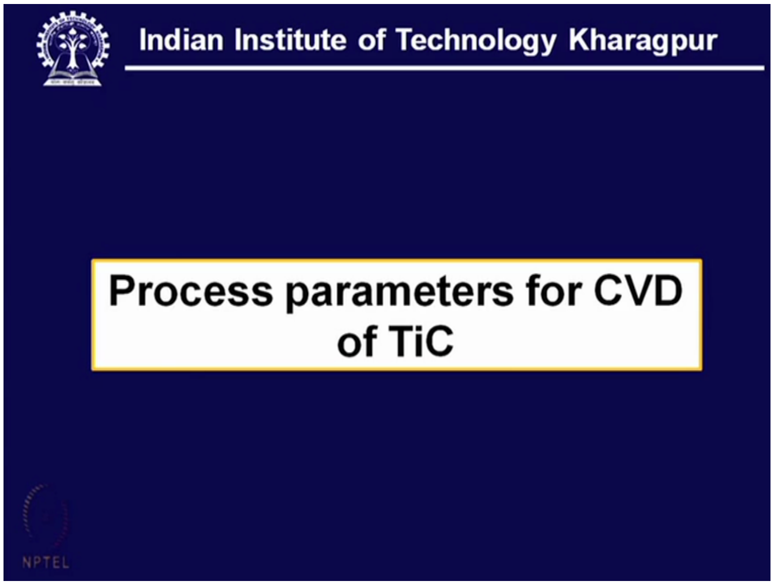

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Process parameters for CVD of TiC

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So these process parameters for CVD of TiC that has been mentioned here.

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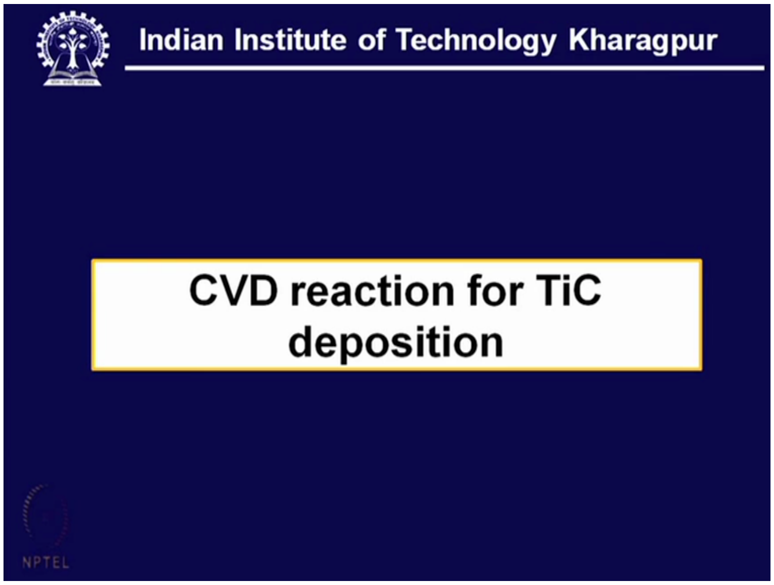

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CVD reaction for TiC deposition

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Now what about the CVD reactions? What we have already mentioned.

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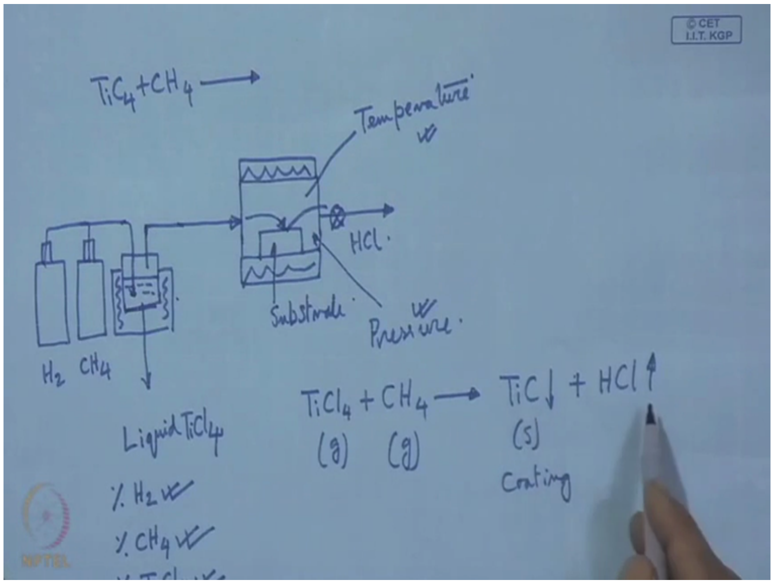

Now what happens in this case exactly, this we have shown a global reaction, TiCl4 plus CH4, that is proceeding or moving in the forward direction with the product TiC and a byproduct HCL.

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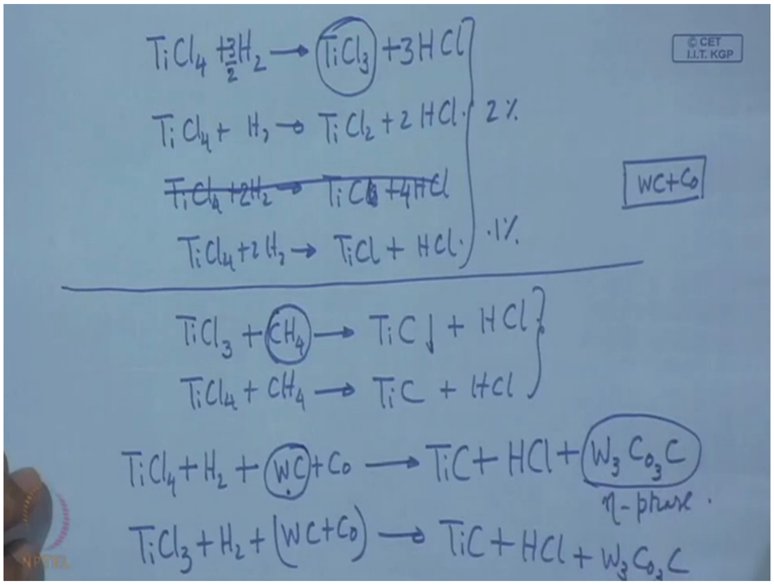

$TiCl_4 + \frac{3}{2}H_2 \rightarrow TiCl_3 + 3HCl$

$TiCl_4 + H_2 \rightarrow TiCl_2 + 2HCl$ 2%

~~$TiCl_4 + 2H_2 \rightarrow TiC + 4HCl$~~

$TiCl_4 + 2H_2 \rightarrow TiCl + HCl$ .1%

$\boxed{WC + Co}$

$TiCl_3 + CH_4 \rightarrow TiC\downarrow + HCl$

$TiCl_4 + CH_4 \rightarrow TiC + HCl$

$TiCl_4 + H_2 + WC + Co \rightarrow TiC + HCl + W_3Co_3C$

η-phase.

$TiCl_3 + H_2 + (WC + Co) \rightarrow TiC + HCl + W_3Co_3C$

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But during this process, we have also because of the local equilibrium, it can also happen because of this very existence of hydrogen which is the carrier gas for this methane and TiCl4, so here also we have pressure and temperature. So here we can have TiCl3 which is a sub-chloride plus HCL. That means it will be actually 3 by 2 and as a result of that, we get here 3 HCL and TiCl3. So this is actually 3 HCL. We can have also another reaction which happens to be TiCl2 plus 2 HCL, this is also possible. Further to this, another reaction cannot be also ruled out, TiCl plus HCL.

So with this, what we can get, TiC and here 2 H2 that means it is 4 HCL. So it is TiCl4 plus 2 H2, that gives actually TiCl plus HCL. Okay, so these are also some possibilities but it has been found during the experimentation that mostly it is TiCl3 that forms and it is only 2 percent and it is about 0.1 percent. So this can happen during the transportation of TiCl4 and hydrogen and there can be some effect, influence of hydrogen to convert this TiCl4 into some sub-chloride.

But one reaction also we should consider, that means what happens with this incoming reactants over the substrate. So here we can have another reaction, TiCl3 plus CH4, that may also lead to titanium carbide and HCL. So formally what we have shown, TiCl4 and CH4, that gives us TiC plus HCL. So these are the two reactions which can also occur. But most importantly, what can also happen, let us look into that.

TiCl4 plus hydrogen plus now it is the participation of the substrate, this is the substrate which is just tungsten carbide plus cobalt and this is going to now participate in this CVD reaction with the result we have here TiC, we also have HCL. But at the same time, we do have another phase which is having this formulation, and this is actually called eta phase. This can also happen with TiCl3 plus H2 plus this participation of the substrate, which can give us the same result.

Now this reaction is one way it is very important and at the same time it can be also harmful if it is not properly controlled. So this is actually the formation of eta phase. Why does it happen? When the substrate has some source of carbon, then this carbon in the substrate that becomes more active. That means this carbon which is in the substrate, that becomes more active than the carbon which is present in the gas phase. So naturally this reaction is promoted by the very presence of carbon in the substrate. And this becomes a carbide deficient in carbon.

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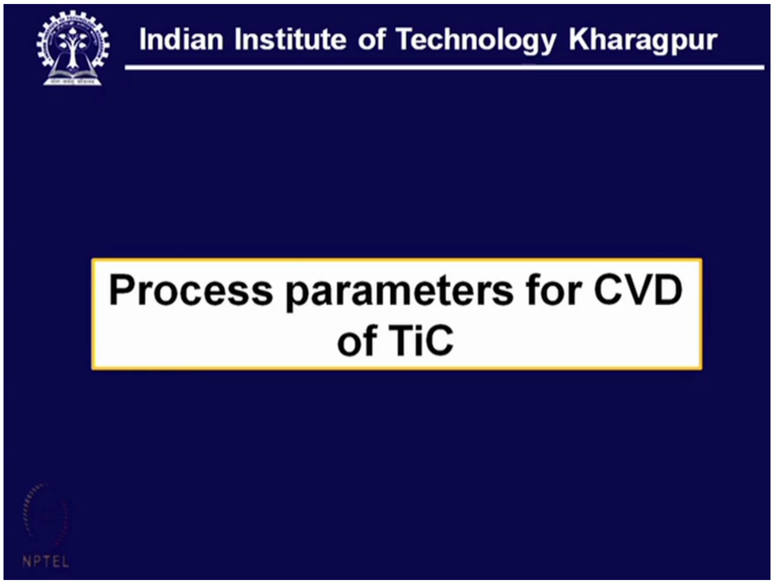

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Process parameters for CVD of TiC

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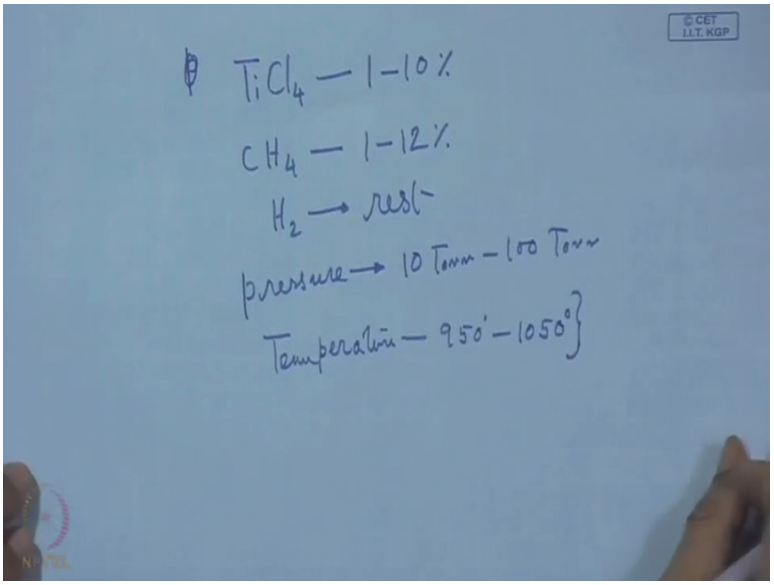

$TiCl_4$ — 1-10%

CH_4 — 1-12%

H_2 → rest

pressure → 10 Torr – 100 Torr

Temperature — 950° – 1050° }

So the process parameter which normally we consider here, that means say TiCl4, these are certain indicative values. 1 to 10 percent, that is the normal operation range. CH4, that is also around 1 to 12 percent and rest is hydrogen. Process pressure, that one can keep between 10 torque to 100 torque, this is the normal operation range. One can also deviate from this range and can have further investigation on the final outcome of this reaction.

And temperature, it is around 1,000, that means maybe from 950 to 1,050 that could be an interesting operational range. And these are the some indicative values. This is the rest for the CVD of TiC.

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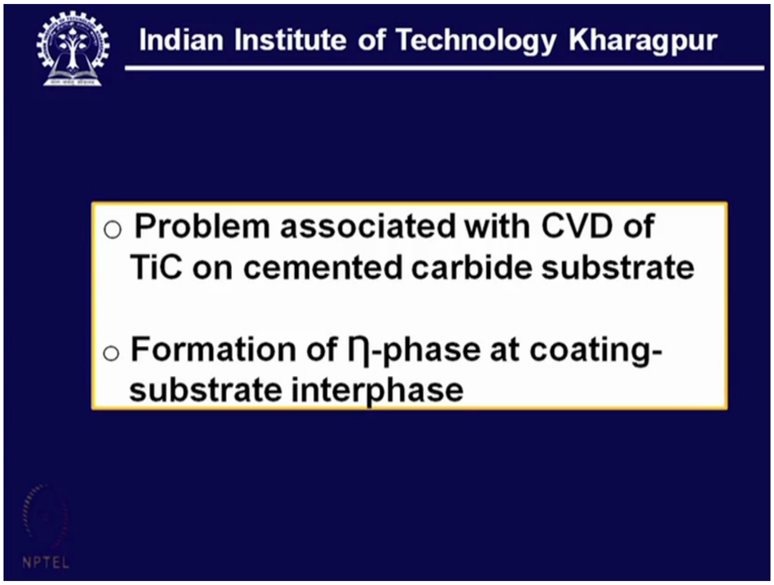

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○ Problem associated with CVD of TiC on cemented carbide substrate

○ Formation of η-phase at coating-substrate interphase

Now comes an important issue one should pay attention. Problem associated with CVD of TiC on cemented carbide substrate. Why we put much emphasis on cemented carbide substrate? Because it is the more, mostly demanded TiC on cemented carbide substrate to make one high performance, high capable tool of production. And that is the sole goal why this cemented carbide becomes one of the strategic substrate for this TiC deposition.

So here we have already highlighted the formation of eta phase, that we have illustrated by this reaction product on the downstream side and which deposits on the substrate surface interface. So this eta phase, how does it form?

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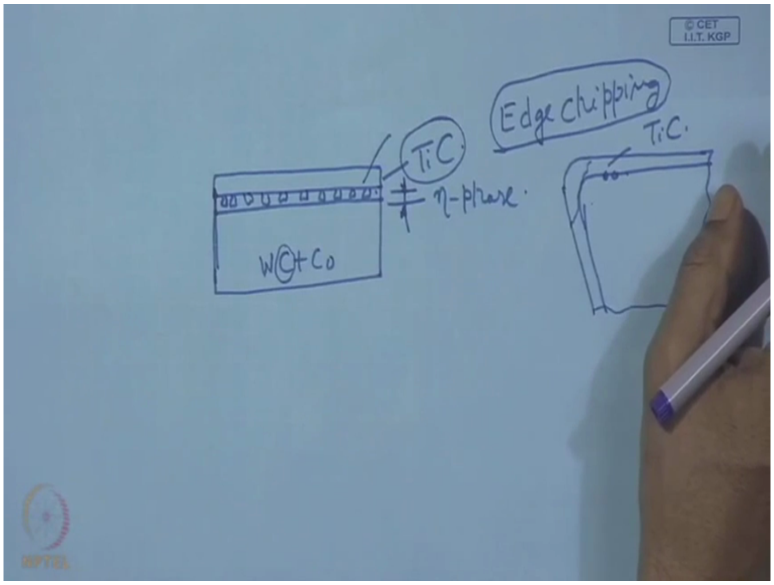

It is something, this is tungsten carbide cobalt and on that we have this TiC. And this carbon comes from the very source of, that means tungsten carbide here is the supplier of carbon and what happens? Just beneath this coating, we have a layer which we call eta phase. Now this eta phase is having a deficiencies of carbon, sorry, and it is characterized by pores and voids in this zone. So this interface which is known as eta phase, that is characterized by the very presence of pores and voids and that becomes the weakest link between the top functional coating and the substrate.

We have one of the very best coating and one of the toughest grade but this interface is weak and that is why this coating cannot survive for long and there can be a detachment on this surface. One of the requirement of the cutting tool is the edge strength, cutting edge strength. So if we see the cross-section of this tool, so this is just a sectional view of the coating, (coat) sectional view of the tool and on the top, we have the coating and here is the substrate and this is actually the interface where we have full of voids and pores.

And as a result, when this comes in contact with the workpiece during machining, then immediately this edge gets damaged, there is called edge chipping. So that means this edge chipping becomes one of the problem, major problem with this very existence of eta phase. And this has to be solved in order that this tool become one of the high performance tool.

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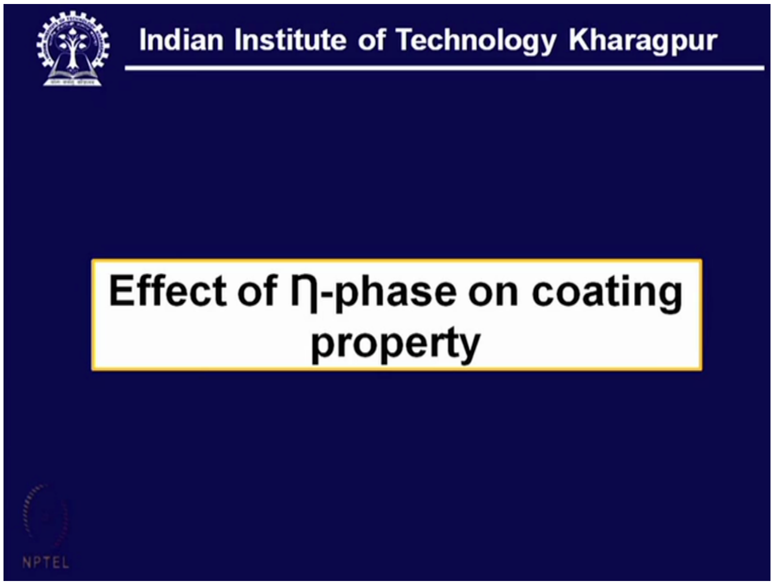

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Effect of η-phase on coating property

So here what we can find, effect of eta phase on coating property.

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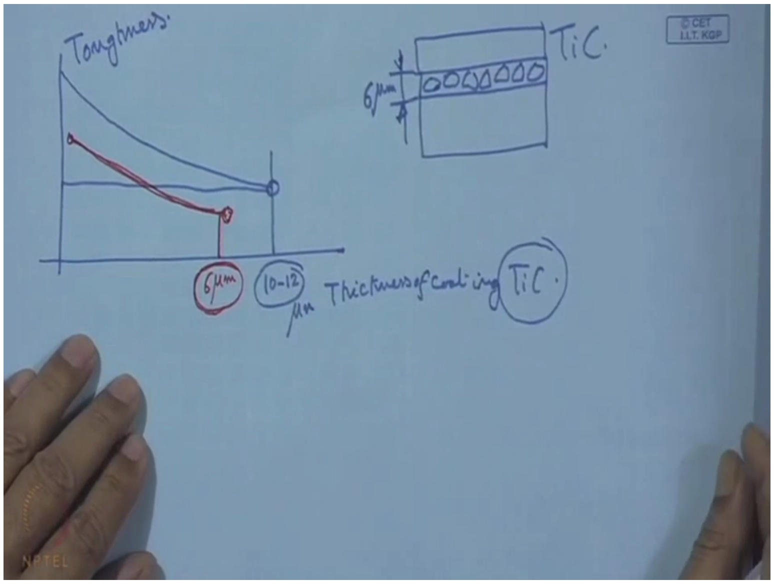

Normally what we see, if we look into this toughness of the cutting edge and on this side thickness of the coating, so this is TiC, then we can get a curve which is almost like this. This shows that with the increase of this tough coating, edge toughness is falling. And this is about, the research reveals that this is about 10 to 12 micron which is very, very alarming in that, that this toughness has fallen substantially. So a tool with a thicker coating perhaps cannot be used at all though we understand the importance of coating or the utility of the coating.

Now this problem is compounded, so this is just a characteristic curve with a coated tool but now the problem will be compounded by the very presence of this eta phase. If we have eta phase along with this one, maybe here the thickness, now I draw this line, so with this what is going to happen? This red line shows actually the resultant curve, because of the eta phase now we do not follow this curve. This is actually the curve, toughness versus thickness.

And here when this thickness of the eta phase comes about 6 micron, this is quite not at all acceptable and here we have to be extremely careful. That means this thick layer which we have already seen, this 6 micron means here this is the coating and this is the substrate, so this is a TiC coating and this is actually the eta phase full of voids, pores. And this is actually what I mean by this 6 micron, so this 6 micron by any cost has to be reduced substantially much below 1 micron in order that tool can be put back in operation. So this we have to see. So we can see here that the effect of eta phase is just directly to reduce the toughness of the cutting edge and this tool is not at all suitable for machining operation.

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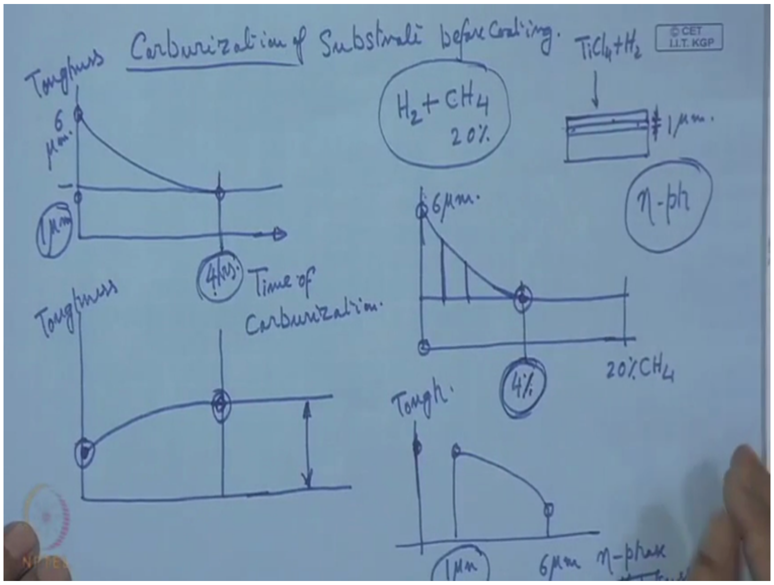

So there are ways how to control this eta phase, at least one has been suggested and that technology has been experimented with considerable success and this is called carburization of the substrate, carburization of this cemented carbide substrate before coating. Carburization of the substrate before coating so if we see here that this is a toughness number, indicative toughness number and this shows the time of carburization.

Now how this carburization is done? It is actually the same CVD chamber, we do not need any extra attachment or extra accessories. So in this case, in this pre-coating process, we have only hydrogen and methane and this is about 20 percent in concentration with hydrogen. That has to be admitted keeping that temperature and certain pressure level so that this carbon can enrich the top surface of the carbide.

And here you have to allow some dwell time or residence time to have this carburization takes place, so that is actually the time of carburization. So what is seen here that when we have the coating without carburization, here we have a 6 micron thick eta phase coating. Now this thing will be brought down just to 1 micron here. So this is about 4 hours and in 4 hours what we can see that the substrate is carburized for certain period of time, then it is admitted for CVD operation and then we measure if there is any eta phase present.

And that we can plot against this, so here the thickness of this eta phase is falling and when it is about 4 hours, it has become almost constant. And this thickness is just 1 micron or it is little less than 1 micron that means it is actually the time, critical time up to which the carburization process has to be continued. And by this thick layer of carbon which is already here, enrichment of the layer and now on that if we have this CVD, that means using $TiCl_4$ and H_2, then this carbon will be used from the substrate to make this TiC and we do not have too much of take-up of carbon from the substrate.

So in this case, only eta phase though it is formed it is only limited to a thickness even less than a 1 micron. And that we can achieve just by pre-carburizing, enriching the top layer and this carbon will be supplied during CVD of this TiC. Now immediately that result is found here if we draw another graph. And on this graph, what we can see, this is actually the thickness of the eta phase which is decreasing with increasing time of carburization.

And here we see directly the effect that means toughness value. Now this toughness we have something here which is extremely low and what we can see here with time of carburization, that means when we have 4 hours time of carburization, then we find toughness attains a very steady state and which is adequate for the normal operation of the cutting tool. So this carburization helps in reducing this thickness of the eta phase.

Another thing we can also look here, that means amount of methane and the thickness of the carburized layer. That means in this case, if we have percentage of methane, then this falls like anything, this falls like this curve and this is about 4 percent methane and we can go up to 20 percent methane. But in this case, what we see, that means it starts with 6 micron with no methane treatment. That means if we just take a substrate and carry out the CVD operation, we end up with eta phase which is 6 micron.

Now what we do, without going directly for CVD, we treat this surface with this carburization and this carburization can be done either with 4 percent or another extreme is 20 percent. So what we find that with 4 percent for 4 hours, we reach almost a saturation point. And if it is less than that, then we have little dipper or little thicker (carbo) thicker eta phase. So this experiment or this research clearly suggest that there is a critical concentration of methane which is around 4 percent and at the same time there is a time duration for this carburization process to conduct.

So this 4 percent methane and 4 hours of treatment, that bring down the eta phase layer to a very narrow value, well within 1 micron. And that is why now what we can see that this tool can go for a high toughness which is quite high when it is just 1 micron and which falls like anything here as 6 micron. So it is actually the eta phase thickness. So all these four graphs give a clear indication that 6 micron means it is a weak tool and when we limit it with a value less than 1 micron, it is one of the high performing tool and the coating on the top of this is supposed to work just like a remarkable coating.

And this coating is supported throughout the service life only because of the close control of this eta phase within a limit of 1 micron and that is possible just by this treatment of 4 hours with at least 4 percent methane mixed with hydrogen. So this is pre-carburization.

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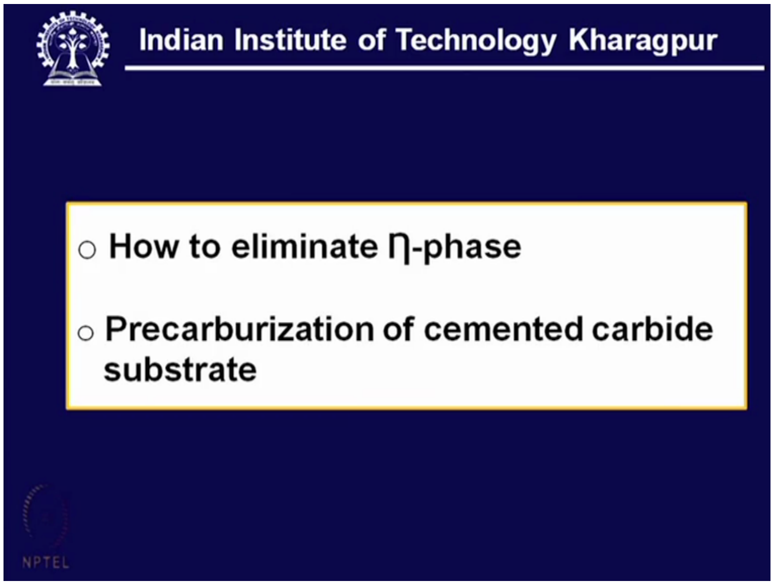

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○ How to eliminate η-phase

○ Precarburization of cemented carbide substrate

So this point we have already discussed, how to eliminate this eta phase and pre-carburization of the cemented carbide. And this is one of the way that this eta phase is restricted.

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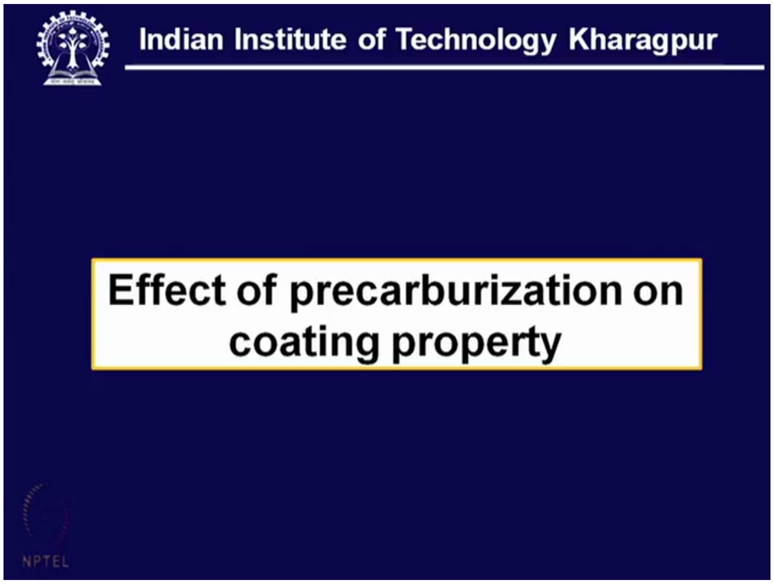

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Effect of precarburization on coating property

So effect of pre-carburization on coating property that has been already also narrated that, by pre-carburization what is very demanding. That means the toughness of this coating at the cutting edge which has been already illustrated. How this effect of pre-carburization can recover the toughness of the cutting edge that also we can see.

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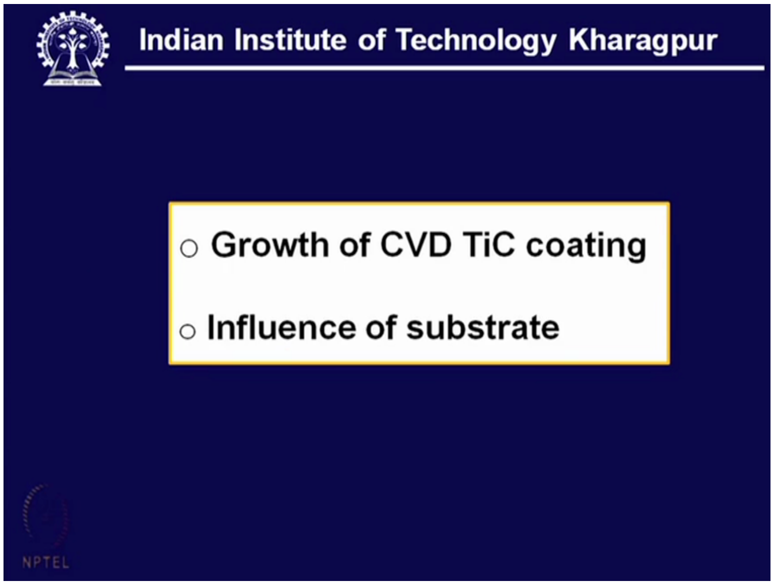

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- ○ Growth of CVD TiC coating
- ○ Influence of substrate

Now here we see the growth of CVD TiC coating, influence of the substrate.

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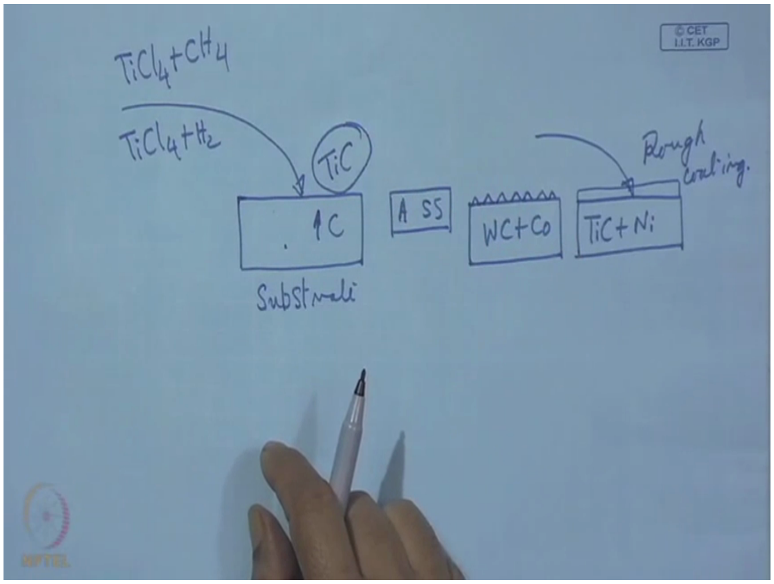

So it is very important that this substrate, it is actually the receptor surface. This is actually the receptor surface. So whatever is incoming in the form of vapor, TiCl4, CH4 or TiCl4 just H2, whatever may be, this surface should be able to receive, it should not bounce back. There should not be any repulsion. So for that, it is also our experience that the steel or any substrate which is having low percentage of carbon is not at all a good candidate as a substrate for this TiC coating.

So in that case, TiC cannot grow with high nucleation density. So for that, what is necessary that say for example austenitic stainless steel which is having very low percentage of carbon, it is extremely difficult to get a coating of TiC because of the simple reason that here we have no participation of carbon from this side. So as such, this steel if it is used, then it cannot be a prospective candidate for this CVD of TiC.

It is also very interesting experience if we have tungsten carbide plus cobalt, we have high nucleation density of this TiC, high nucleation density and ultimately the coating appears to be rather smooth with a fine grain structure. So here this happens to be a very good receptor. On the other hand, attempt has been also made to have such a composite, TiC powder with nickel just like tungsten carbide cobalt.

And this is another composite having TiC as the hard material and nickel as the binder. And when this process has been attempted, result was not that successful. In that, here you have a rough textured surface, the coating was extremely rough. It has a dendritic structure. You have columnar grain, columnar growth. So in this surface, it is a very rough coating. Larger grain size and on this side, we have a finer structure and a smooth coating.

Naturally from cutting point of view, one would like to have a coating with fine structure, fine grain smoothness and not with a rough coating. It is actually seen that at the very initial stage, the nucleation centers or the nucleation density is extremely poor on this surface and as a result we have large grain growth which are joining together to make a rough textured surface. So here one should also look into the compatibility of the substrate with this particular incoming reactants which are supposed to do the necessary reaction giving the required, much required TiC as the coating.

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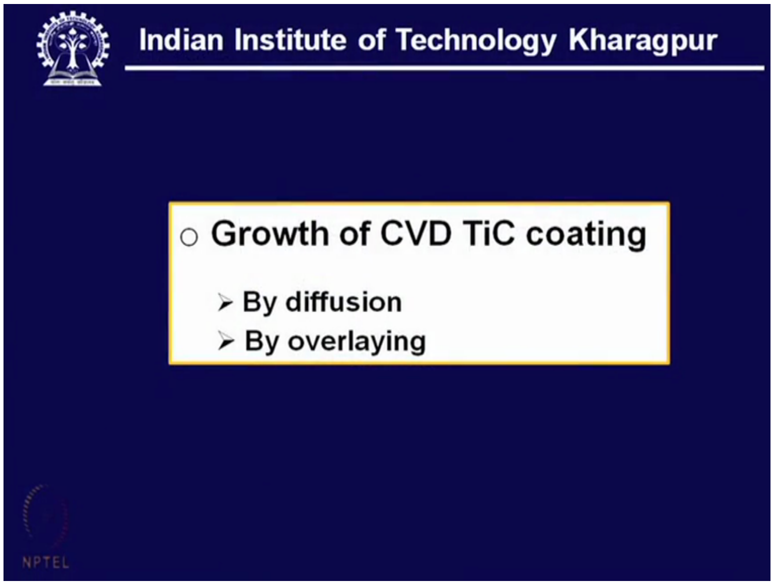

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- Growth of CVD TiC coating
  - By diffusion
  - By overlaying

Growth of CVD coating either by diffusion or by overlaying.

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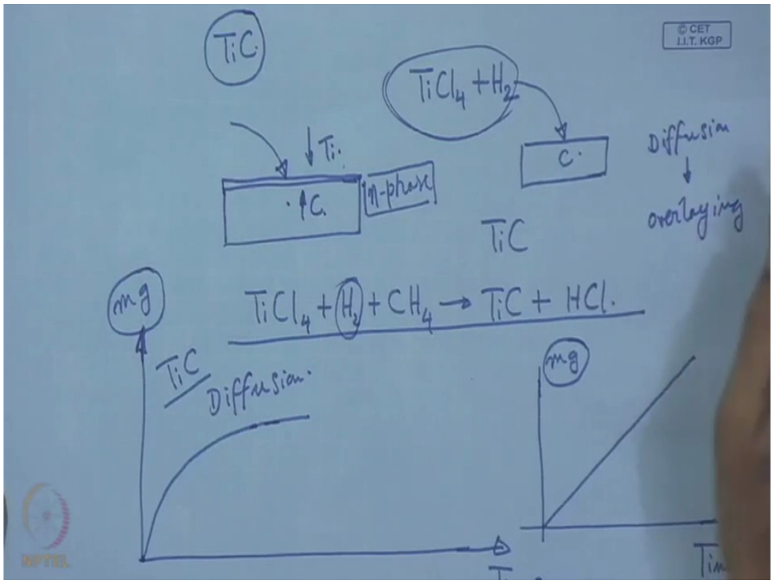

As we have mentioned here that coating of TiC, now to have good adhesion on the substrate, there must be a participation of the substrate by sharing its carbon with the Ti from the vapor phase and as a result, a chemical bridge is established by carbon participation and by titanium participation from both sides across this interface. And this phase is actually called the coating by diffusion. But here as we have already discussed, there is a high risk of this eta phase formation. So the requirements are contradictory.

We want participation of carbon from the substrate but this participation in a very restricted way. It should not be a continuous flow of carbon from this side. So once a layer of TiC, well-adherent, well-bonded layer is formed through this participation of Ti from both sides across this boundary, then it can be switched over to this overlay process. That means at the beginning, the process should be something like H2 with no CH4 and this will be here and on the carbon-rich substrate so that this carbon and titanium make TiC.

And after having successful completion of that period, the CVD process will go to the second stage. That means now it is going to be TiCl4, H2, and CH4. And now here, we see that this TiC is coming from this methane. This H2 is necessary as a carrier for this TiCl4. So this H2 is no more that important in the reaction. However this is used as a carrier gas and this saturation is important.

So here graphically we can see that the growth of this TiC coating may be say the increase in weight of the substrate over a period of time, say coating deposition. So what we find, when it is a diffusion, one would expect such nature of variation. That means this increase of weight by milligram, that means the weight increase, that will almost come to a saturation because of this formation of TiC and that may inhibit further migration of carbon.

And that could be something which becomes, here the growth is almost insignificant. So what is done? But if we have this process, the second process, here it is carbon participation. So this is actually diffusion, deposition of TiC that is by diffusion and it follows such kind of curve. However if we allow this process from the very beginning, that means here also increase in weight in milligram and this is actually time, then we can find it is something like this. From the very beginning it is growing and it is a uniform increase with time linearly varying.

So what would be the resultant effect if it is diffusion, first diffusion coating followed by overlaying?

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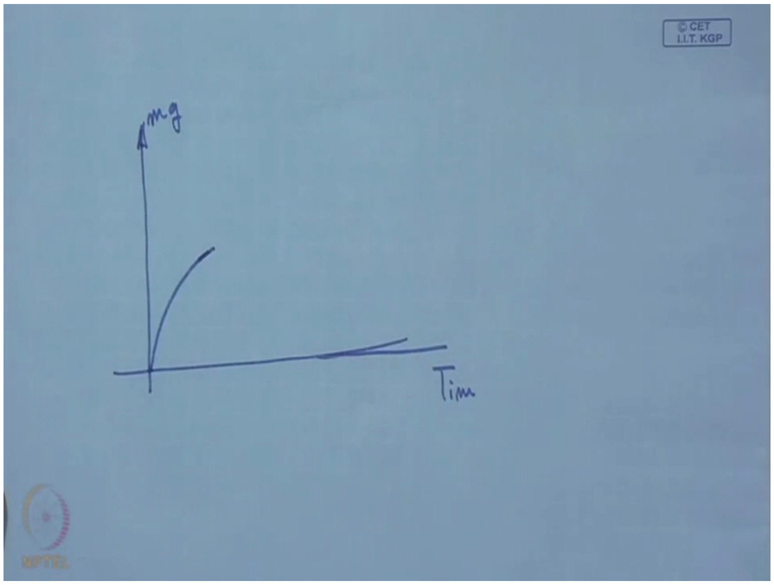

Then we can expect a curve something like this. Weight increase, this is time. So it will be something like that the growth is changing and at this point, we can go to this.

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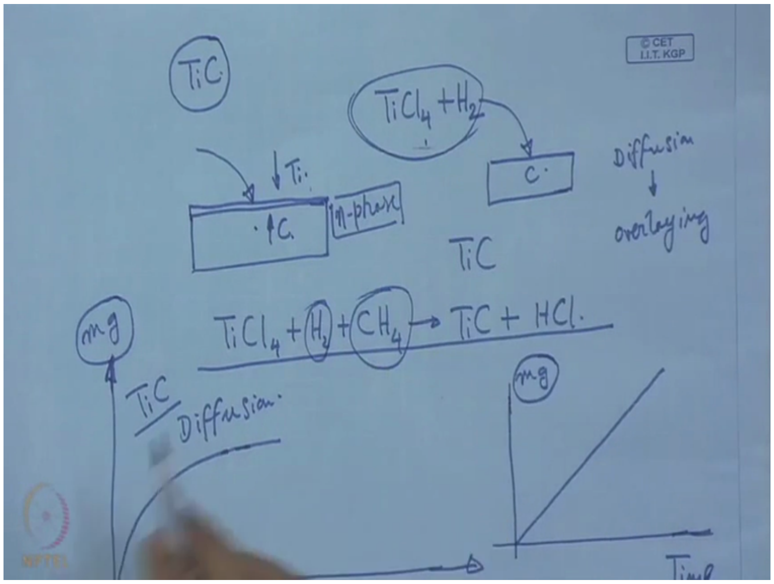

We can go to this second step, that means overlay process, switching on methane, allowing this flow of methane and here flow of methane is restricted.

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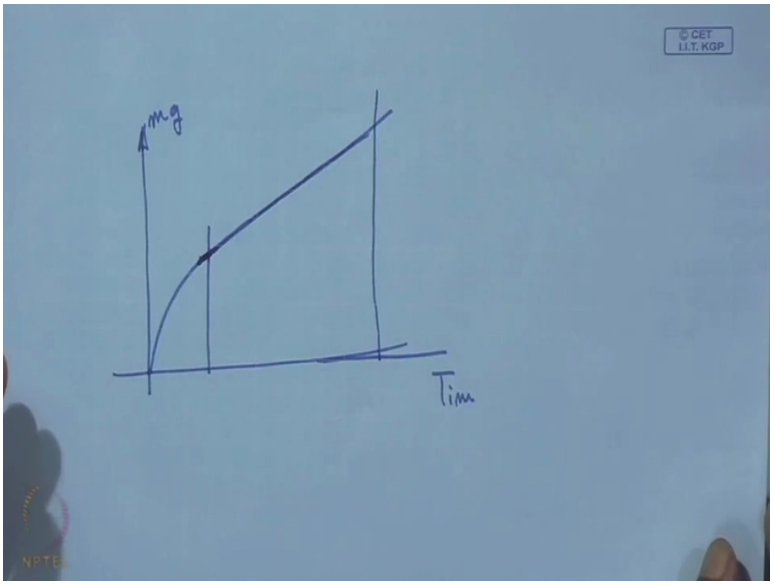

So if we allow this methane to flow, get admitted, then this curve will take this shape. So up to this point, it is diffusion and then we have this overlay process. So this is exactly what we see as diffusion and overlaying, both are important.

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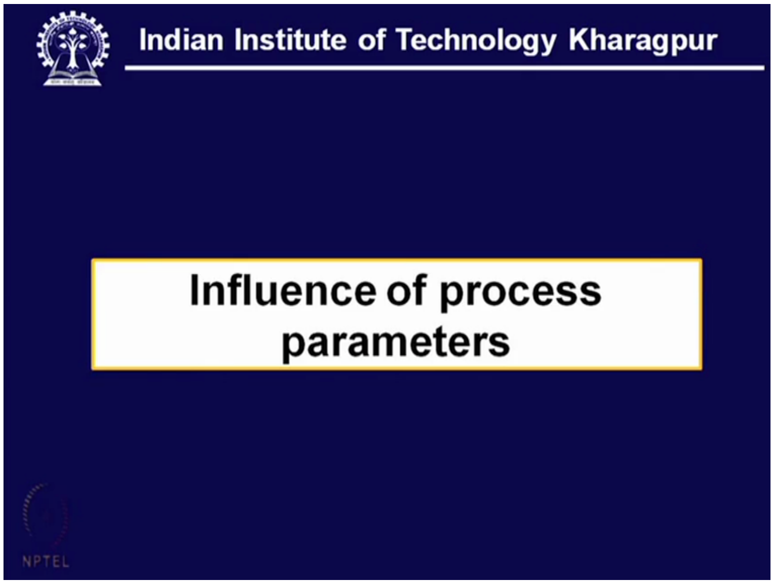
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Influence of process parameters

Influence of process parameters, very important consideration.

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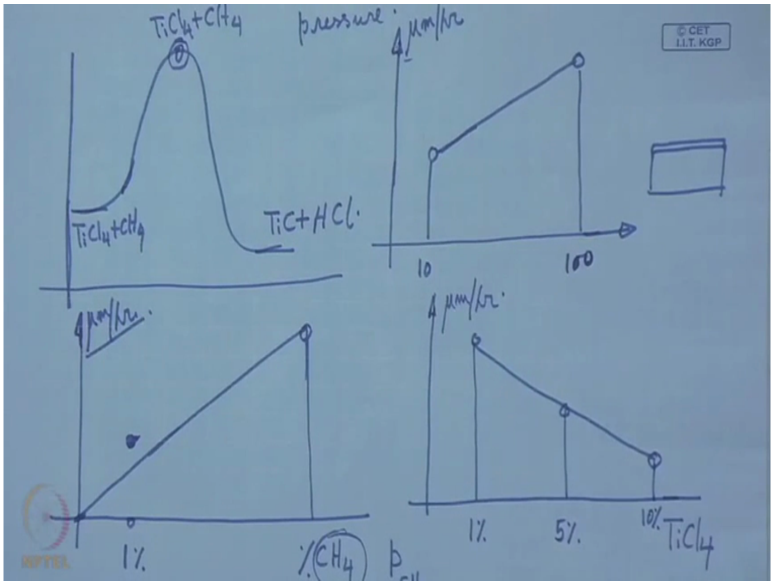

In that here, say process pressure. Now temperature is also one because of the simple reason, if we see the activation of this process, we can illustrate it like this. So on this side, it is the reactants, so here we have TiCl4 and CH4 and this will go here at this process TiCl4 and CH4, it will be activated here. And finally what we expect that this is as the product of this CVD it should be HCL.

So TiCl4 and CH4 activated at this activated complex, here we have an equilibrium between these two, so this will be rest here and finally we have, naturally here the effect of temperature is strongly felt. So higher the temperature, more will be the rate of reaction or rate of formation of TiC. Now comes the influence of pressure. It has been seen that when this is carried between a wide range of pressure starting from say 10 to 100 torque, that is one range, there is a steady increase of growth rate.

That means say it can be expressed in micron per hour. That means the coating thickness on the substrate is increasing in certain micron per hour. So increase of pressure definitely beneficial considering the growth rate. Now comes important consideration for this methane concentration. Now here either we can say it is methane concentration, since it is in the gas phase, we can also consider partial pressure of methane.

So with that, what we can see? If it is say from 1 percent to 10 percent, here also we see a growth of this thing with this methane. That means it comes like this with 0, that means it is also linearly varying with this. So effect of increase of methane is to only increase this growth rate, micron per hour growth of TiC.

Now what is very interesting to see that in contrast to what happens here, if we also try to follow the growth rate behavior with percentage of TiCl4 under a given condition, we are now changing the percentage of titanium tetrachloride say from, 1 percent, this is 5 percent and this is 10 percent. And we find that it is in contrast, this is falling. However it is a normal expectation that with this TiCl4 increase, we can also inject, admit more number of Ti atom but that does not mean that growth rate is increasing. It is in contrary that is falling.

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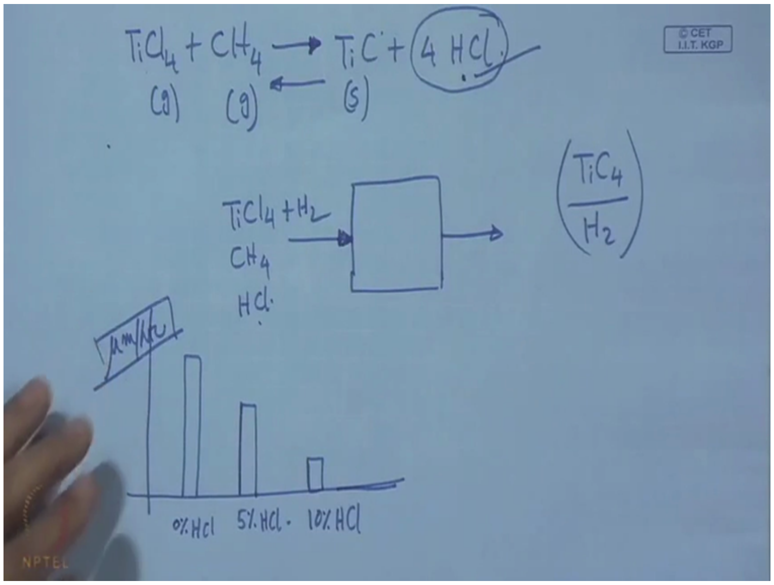

Now this can be, an attempt can be made to give an explanation, acceptable explanation. This, what we can see here that TiCl4 and CH4, that gives TiC which comes like a solid. This is gas and this is gas, and that gives 4 molecules of HCL. That means 1 molecule of TiCl4 gives actually 4 molecules of HCL and as a result that the number is increasing. So unless this number is decreased, there will be a tendency to reverse this reaction and as a result of that, this reaction which is now directed in this direction, it can change its course and it can reverse the whole process with formation of, less formation of TiC and more formation of TiCl4.

That means if we increase this HCL through this reaction, then it becomes less and less product favored. It will not be product favored, rather it becomes actually reactant favored so here we have to pay attention and for thus we can see the role of hydrogen and methane and tetrachloride.

So this can be well demonstrated by another experimental result. Now here what we see that in the reactor, this is incoming, this is outgoing. Now at each point, here we have TiCl4, CH4 and then HCL, hydrogen is also there as the carrier gas.

But if we put HCL on the upstream side, what we see that this percentage of HCL actually reduces. If we have HCL admittance, that means one with 0 HCL, that means 0 percentage HCL, we have a growth rate like this. And when we have an HCL, okay, thank you, and when we have 5 percent HCL, then growth rate falling. When we have 10 percent HCL, growth rate of TiC is further down.

That means if we inject HCL on the upstream side, immediately we understand the influence of this hydrogen chloride on this growth rate which is in micron per hour. Micron per hour, that means just by increase of HCL that growth rate of TiC is reduced. So what should be logically done in this case, that means this HCL should be removed as fast as possible just by rapid evacuation so that partial pressure of HCL can be reduced and the reaction can be moved in the forward direction. And that is one of the reason why this TiCl4 by H2, that flow ratio is taken as high as possible only to move the reaction in the forward direction.

Now this one we can write this way:

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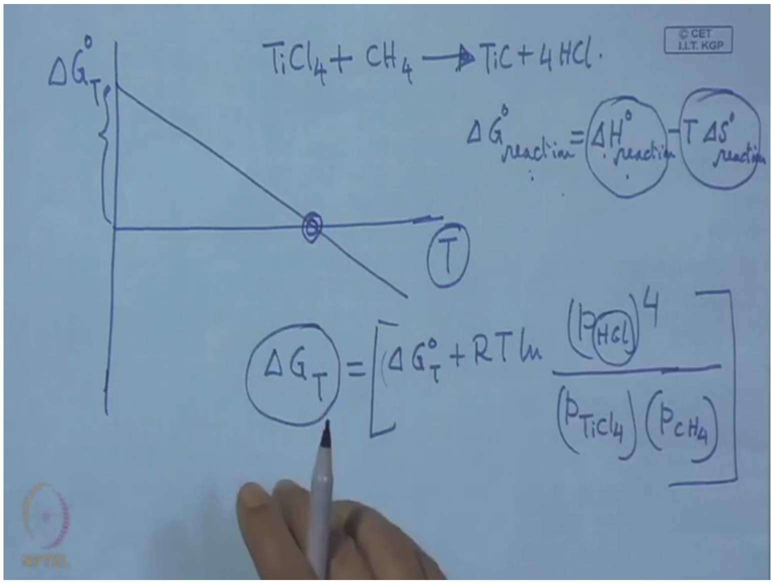

$TiCl_4 + CH_4 \rightarrow TiC + 4HCl$

$$\Delta G^{\circ}_{reaction} = \Delta H^{\circ}_{reaction} - T\Delta S^{\circ}_{reaction}$$

$$\Delta G_T = \left[\Delta G^{\circ}_T + RT\ln\frac{(P_{HCl})^4}{(P_{TiCl_4})(P_{CH_4})}\right]$$

Say for example Ellingham diagram showing variation of this delta G0T for TiC with temperature. And this is something like this. So this is actually the change in free energy of this reaction, that means TiCl4 plus CH4 is equal to TiC plus 4 HCL. Now here what we can see that delta GT is equal to delta G0T plus RT into ln into partial pressure of HCL to the power 4 divided by partial pressure of TiCl4 into partial pressure of CH4. Now this is a clue for this reaction.

So our job would be to reduce this value as much as possible to make this thing more and more negative so that finally this becomes more negative and if it is more and more negative, then the reaction will be also more and more product favored. That means it will move in this direction. And here from this graph, what we can see that this delta 0 of this reaction is equal to actually delta H0 reaction minus T into delta S0 reaction. So this would be a governing equation.

So this is the change of free energy in this reaction. So this is actually the most critical point, that curve must attain this point and this corresponds to a temperature. So that means to carry forward the reaction in the product direction, we have to attain this temperature. And this temperature finally it comes to this G0 reaction which is also here we find and this can be find out, okay, this can be written as this one.

So here we see that if this HCL partial pressure is brought down drastically, then the whole thing becomes more negative and that will contribute to this delta G0T and the whole thing as a whole will be the driving force for the reaction to move in this direction. Now here what we find that this delta H0 reaction that is positive, so it is one endothermic reaction. So in order to move the reaction in the forward direction, this is actually plus positive change in entropy with increase in molecules compared to the reactant.

So we see this has to be negative, highly negative so that it can neutralize this positive effect of enthalpy of reaction and finally the change of free energy of reaction becomes negative. So here one is the temperature that we understand. Another is also the role of this partial pressure of this HCL which has to be brought down for a given condition and for that, we have to increase the flow ratio or say flow rate of hydrogen so that this reaction can be moved in the forward direction. So with this, we can come to the summary.

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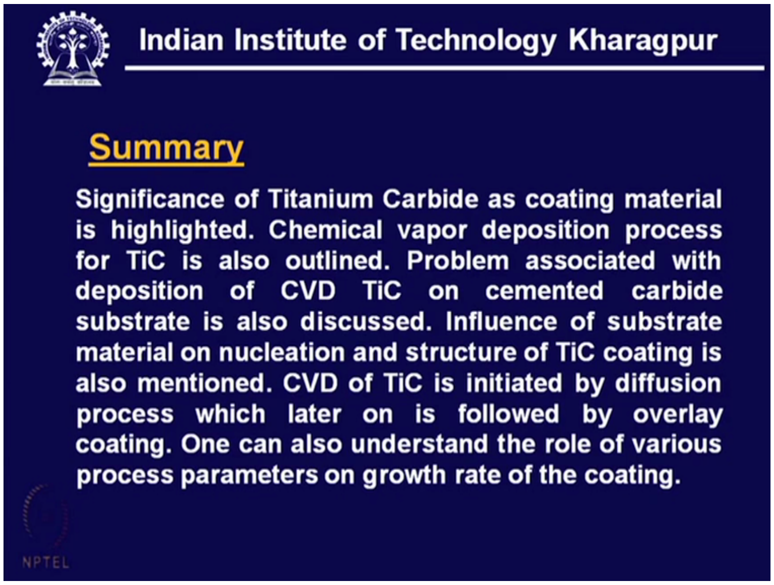

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Summary

Significance of Titanium Carbide as coating material is highlighted. Chemical vapor deposition process for TiC is also outlined. Problem associated with deposition of CVD TiC on cemented carbide substrate is also discussed. Influence of substrate material on nucleation and structure of TiC coating is also mentioned. CVD of TiC is initiated by diffusion process which later on is followed by overlay coating. One can also understand the role of various process parameters on growth rate of the coating.

And summary is like this: significance of titanium carbide as a coating material is highlighted. Chemical vapor deposition process for TiC is also outlined problems associated with deposition of CVD TiC on cemented carbide substrate is also discussed. Influence of substrate material on nucleation and structure of TiC coating is also mentioned. CVD of TiC is initiated by this diffusion process which is later on is followed by overlay coating.