Technology of Surface Coating
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Lecture-03
Adhesion of CVD Coating

Production of a well adherent coating with adequate and remarkable surface property is the ultimate aim of any CVD operation. A mechanically functional coating, for example with remarkable surface property may fail in a premature manner only because of poor adhesion at the coating surface interface.

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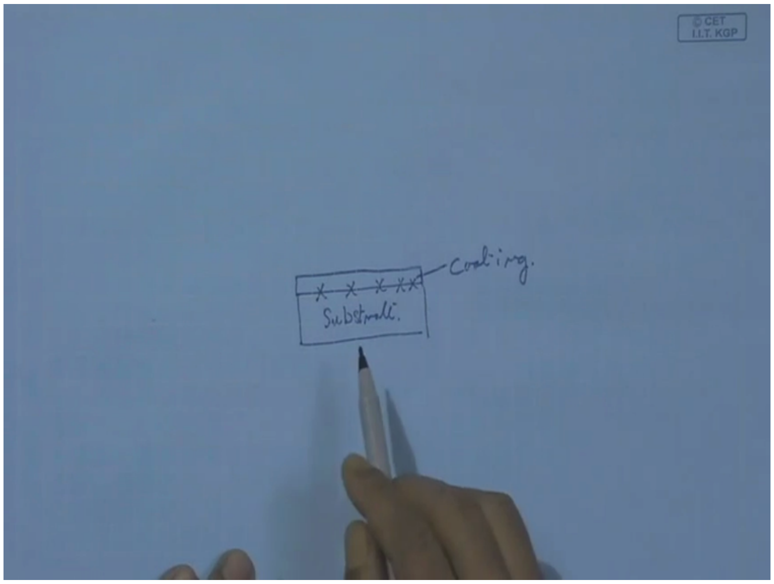

Say for example this is the substrate and the top of this we have a coating. Now this substrate and the coating, they are not independent of each other. They have to behave and perform like an integral piece or component and here each has its own characteristics and the property, but the main problem is how to build up a strong interface in this zone. The coating can have surface hardness, high tribological properties means low coefficient of friction, then chemical stability, high hot hardness and thermal properties.

However, it comes to the point, how to build up this strong interface? So this is said that ultimately it is the interface that determines the overall performance of this integral body comprising this coating and the substrate.

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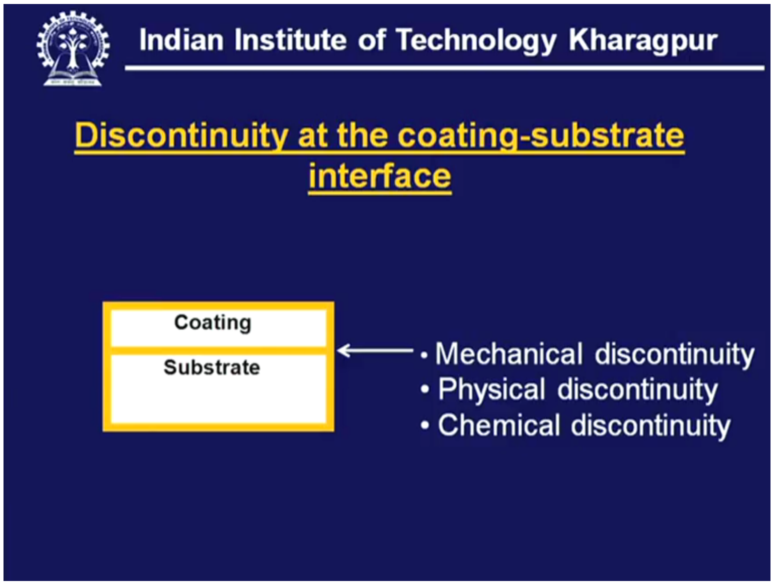

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Discontinuity at the coating-substrate interface

- Mechanical discontinuity
- Physical discontinuity
- Chemical discontinuity

Now if we look in this coating-substrate, this interface, what we can find here, it is actually the discontinuity in this interface and the coating. It can be said mechanical discontinuity, physical discontinuity or the chemical discontinuity.

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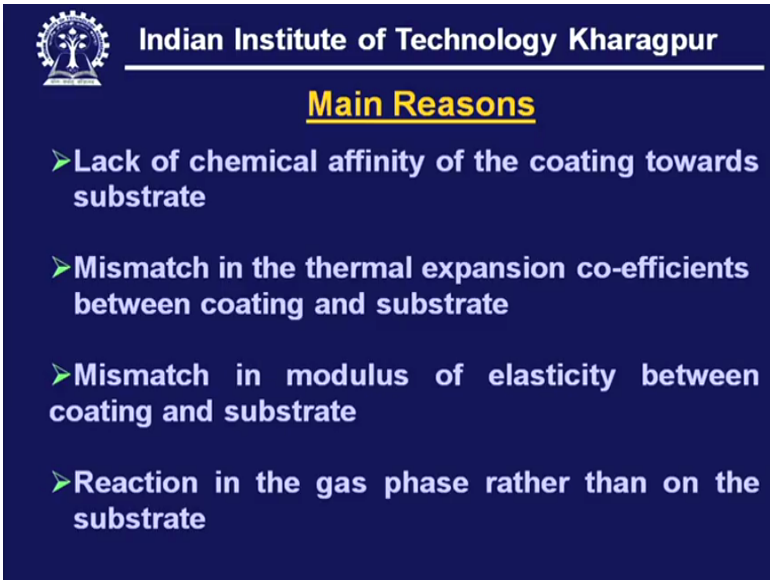

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Main Reasons

- Lack of chemical affinity of the coating towards substrate
- Mismatch in the thermal expansion co-efficients between coating and substrate
- Mismatch in modulus of elasticity between coating and substrate
- Reaction in the gas phase rather than on the substrate

Main reasons it can be the lack of chemical affinity of the coating towards the substrate. It may be the mismatch of thermal expansion coefficient between the coating and the substrate. It is also the mismatch in modulus of elasticity between the coating and the substrate. However we can also see the reaction in the gas phase rather than on the substrate can be one of the determining factor in getting one of the adhesive coating.

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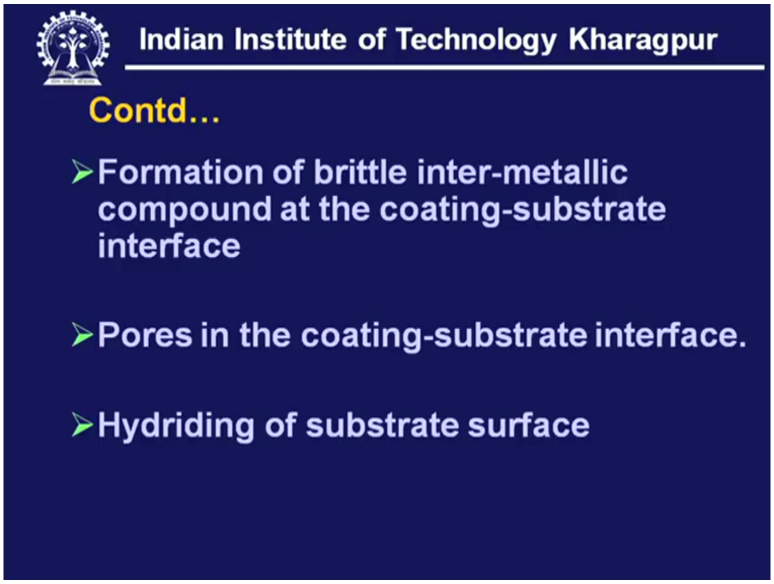

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Contd…

- Formation of brittle inter-metallic compound at the coating-substrate interface
- Pores in the coating-substrate interface.
- Hydriding of substrate surface

Then it can be also formation of brittle interface or inter-metallic compound at the coating-substrate interface. Now pores in the coating-substrate interface may also form and that may also lead to poor coating surface adhesion. We also see that hydrogen plays a very important role in affecting the coating-substrate interface adhesion.

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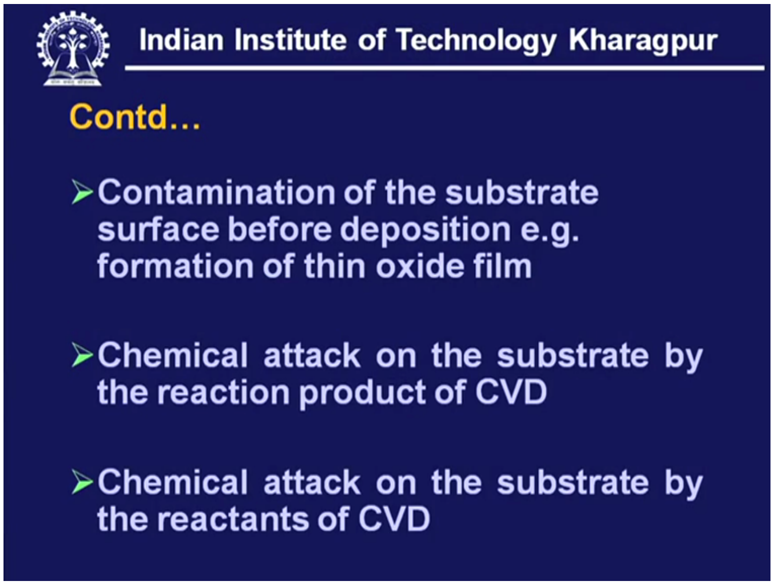

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Contd…

- Contamination of the substrate surface before deposition e.g. formation of thin oxide film
- Chemical attack on the substrate by the reaction product of CVD
- Chemical attack on the substrate by the reactants of CVD

Contamination of the substrate surface before deposition, that is formation of a thin oxide film can also have one overriding influence in this adhesion. It can be also chemical attack on the substrate by the reaction product of CVD. Chemical attack on substrate by the reactants of CVD, this is also not uncommon.

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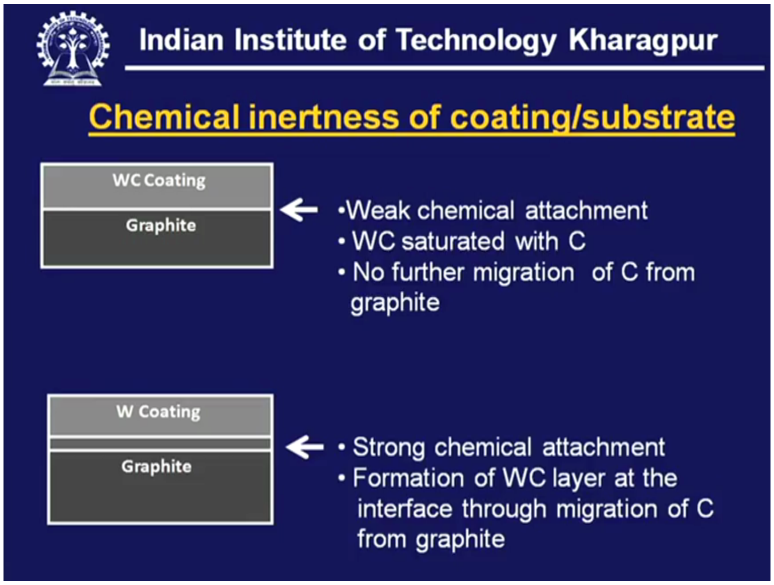

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Chemical inertness of coating/substrate

WC Coating

Graphite

- Weak chemical attachment
- WC saturated with C
- No further migration of C from graphite

W Coating

Graphite

- Strong chemical attachment
- Formation of WC layer at the interface through migration of C from graphite

Let us look what is mean by this chemical inertness of the coating-substrate interface. Say for example, graphite is the substrate and we like to have a deposition of tungsten carbide coating. If we deposit this tungsten carbide coating as one of the overlay coating, then we may not expect a very good adhesion at that interface. The reason is that tungsten carbide is already saturated with carbon and there will not be any further graphite, carbon migration from graphite. So chances are remote. And the result is that those tungsten carbide which comes in the form of a coating, that may deposit just like a mechanical layer and there is no chemical attachment.

But on the other hand, if it is possible to have first a coating of tungsten which is unsaturated with carbon, what is meant here that tungsten is a material, a carbide forming material element and this carbon can, this tungsten, what I mean the tungsten can attract carbon from graphite to have a chemical bridging and chemical attachment, thereby forming a tungsten carbide.

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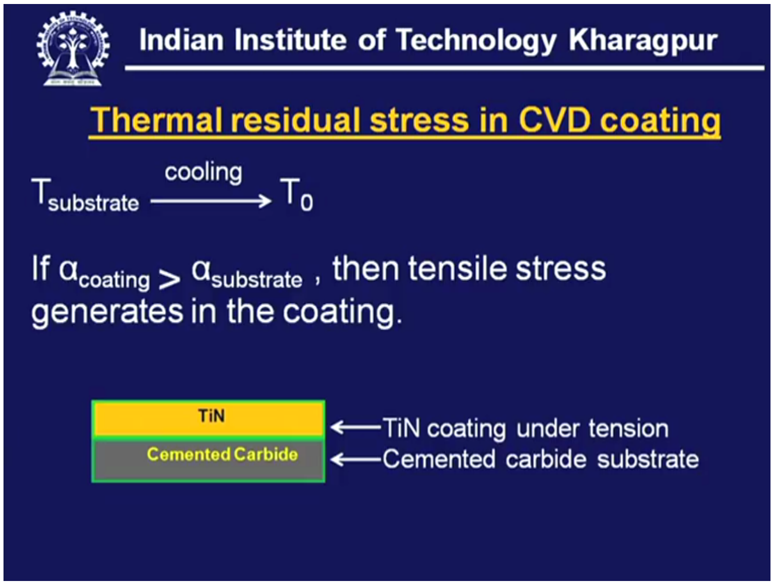

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Thermal residual stress in CVD coating

$T_{substrate} \xrightarrow{cooling} T_0$

If $\alpha_{coating} > \alpha_{substrate}$, then tensile stress generates in the coating.

TiN coating under tension
Cemented carbide substrate

So this thermal residual stress in CVD reaction, this is one of the very important issue to be addressed properly. Now CVD is conducted at a high temperature and when this substrate is cooled to the ambient temperature, then there could be a stress. If coefficient of thermal expansion of the coating is greater than that of the substrate, then a tensile stress generates in the coating. For example, when we have titanium nitride and as the coating and cemented carbide as the substrate, in that case during cooling of this coating from the deposition temperature, because of this differential thermal expansion, the titanium nitride coating could be under tension.

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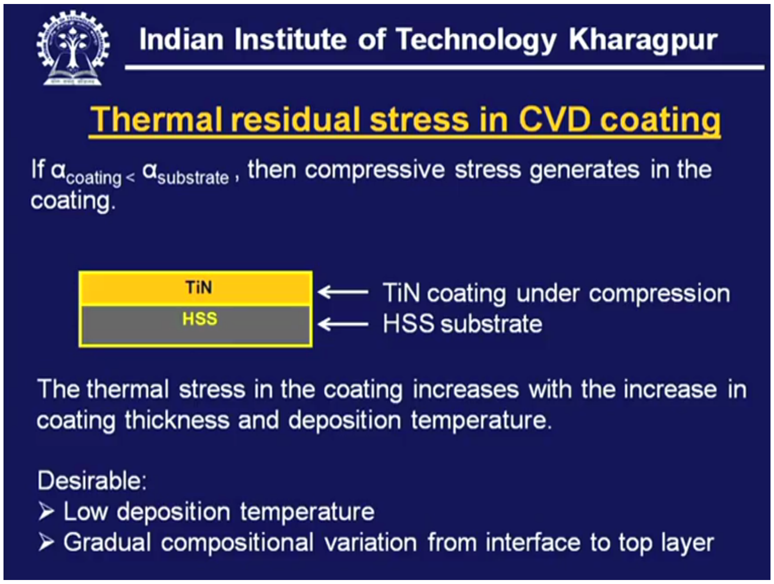

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Thermal residual stress in CVD coating

If $\alpha_{coating} < \alpha_{substrate}$, then compressive stress generates in the coating.

TiN coating under compression
HSS substrate

The thermal stress in the coating increases with the increase in coating thickness and deposition temperature.

Desirable:
- Low deposition temperature
- Gradual compositional variation from interface to top layer

On the other hand, if we have the same deposition, say for example on high speed steel substrate. In this case, the substrate thermal coefficient of expansion is greater than that of the coating and during this cooling down from the deposition temperature to the room temperature, titanium nitride coating will be under compression.

Now this thermal stress, when it is a brittle material, this thermal stress which generates tension, that is, becomes a matter of concern so for as the performance of this hard coating is concerned. So this thermal stress in the coating increases with the increase of coating thickness and deposition temperature. So what is important here, to have a low deposition temperature and a graduation of the composition of the material from the substrate to the top layer so that we can have gradual change in the coefficient of thermal expansion and the stress distribution from the surface, I mean from the substrate to the top layer of the coating is well managed and well monitored.

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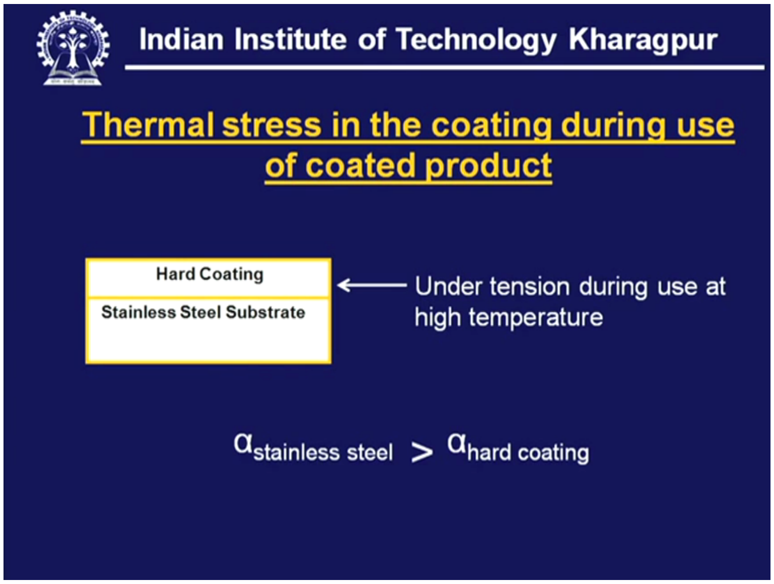

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Thermal stress in the coating during use of coated product

Hard Coating

Stainless Steel Substrate

Under tension during use at high temperature

$\alpha_{\text{stainless steel}} > \alpha_{\text{hard coating}}$

Thermal stress in the coating during use of the coated product here we can see a hard coating is deposited on a stainless steel substrate. Now this is at the room temperature. But when it is put in service which is actually high temperature application, in those case the coating and the substrate because of their difference in thermal coefficient of expansion, the coating will be under tension and there is every risk of fracture of the coating at this high temperature. So this is actually the thermal stress which may generate in the coating during the high temperature application.

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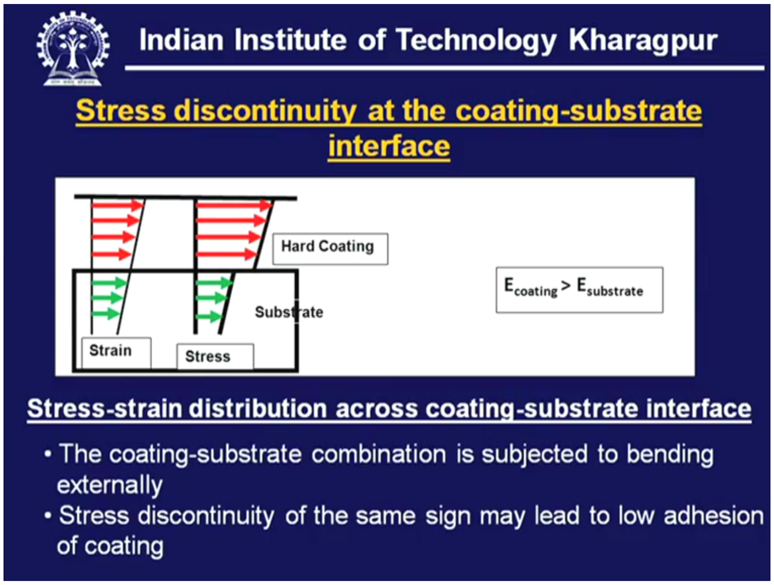

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Stress discontinuity at the coating-substrate interface

Stress-strain distribution across coating-substrate interface

- The coating-substrate combination is subjected to bending externally
- Stress discontinuity of the same sign may lead to low adhesion of coating

Now this is actually the stress discontinuity at the coating-substrate interface. This is actually the coating which is hard coating characterized by high modulus of elasticity. These coatings are known for their high rigidity and the substrate which is a tough material relatively having a lower Young modulus of elasticity. Now if this whole combination, that means this coating-substrate combination is subjected to external bending, then we expect tensile stress on the top layer which will have its gradual change and variation.

Similar is the situation with the strain. But at the interface, there the strain is not differing. However because of the change in Young modulus which is quite high in case of this coating, that stress on the coating side will be quite high and the stress on the substrate side will be relatively low. Now if, so this is exactly called a stress discontinuity so if this stress discontinuity is of the same sign, that may lead to low adhesion of the coating.

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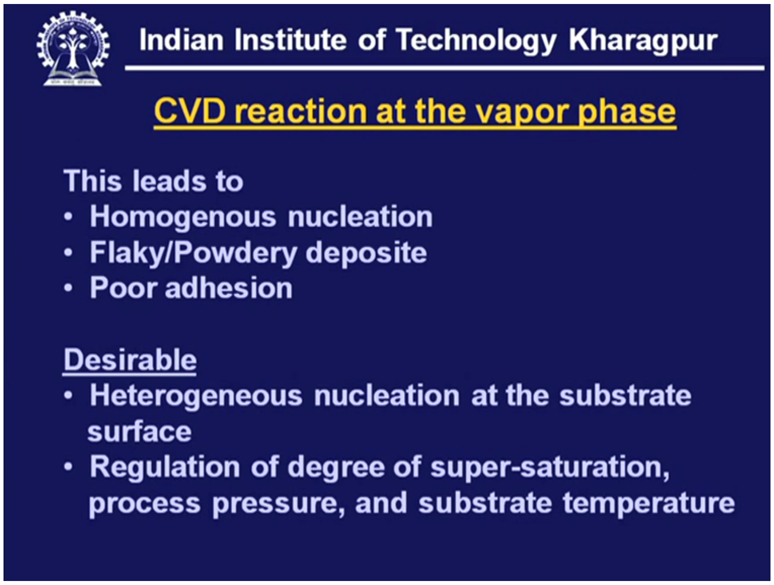

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CVD reaction at the vapor phase

This leads to
- Homogenous nucleation
- Flaky/Powdery deposite
- Poor adhesion

Desirable
- Heterogeneous nucleation at the substrate surface
- Regulation of degree of super-saturation, process pressure, and substrate temperature

Now this is one of the reason of poor adhesion at the vapor phase reaction. This is actually called homogeneous nucleation. That means ideally a CVD reaction is supposed to or expected to occur at the substrate surface. But because of some CVD condition, that means the parametric condition, it may so happen that all those reactants are forced to react in the gas phase and there is a nucleation which may lead to formation of dust, powder and flaky material which may get deposited on the substrate surface.

So under that condition, we cannot expect a well-adherent coating on the substrate. Now what is necessary here that we must have a heterogeneous nucleation at the substrate. That means the nucleation must take place on the solid surface and this can be possible by regulating, proper regulation of the super-saturation. It means that the amount of material which is admitted in the CVD reactor that is in excess of that what is required under the chemical equilibrium.

So this degree of super-saturation must be properly altered or can be reduced. And the process pressure which actually reduced or increase, the main free path before this particles really come into some kind of collision which lead to this nucleation, this one of the parameter which has to be also regulated. And last but not the least, proper substrate temperature should be also chosen so that the reaction desirably takes place at the substrate surface and the nucleation really starts or initiated at that substrate surface.

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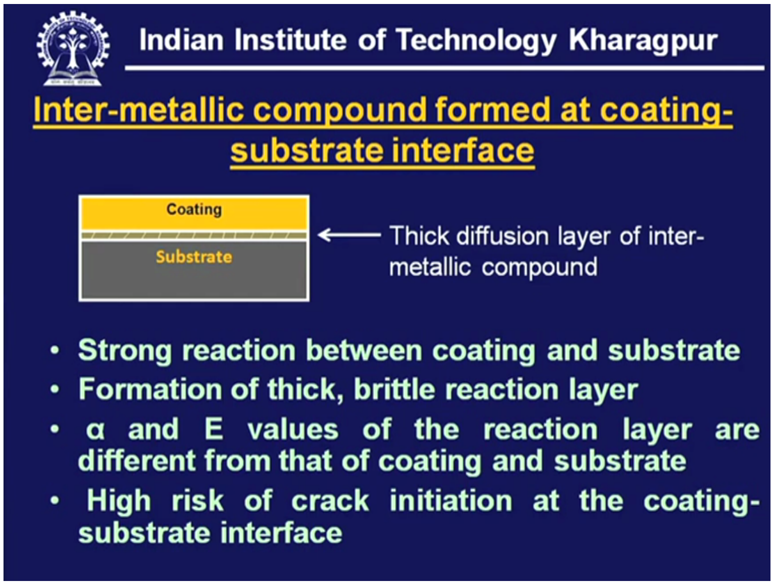

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Inter-metallic compound formed at coating-substrate interface

Thick diffusion layer of inter-metallic compound

- Strong reaction between coating and substrate
- Formation of thick, brittle reaction layer
- α and E values of the reaction layer are different from that of coating and substrate
- High risk of crack initiation at the coating-substrate interface

Inter-metallic compound formed at coating-substrate interface. This is promoted by a strong affinity of the coating towards the substrate surface. Now in this case what happens, a brittle phase may form as a result of dissolution of the coating and the substrate from the two sides. And this layer is quite different in its characteristics with respect to either coating on the substrate. It can be very brittle, its coefficient of thermal expansion may differ widely in comparison to that of the coating and the substrate.

Not only that, the Young modulus that is also quite different from that of coating or the substrate. So under this condition of this formation of thick diffusion layer, there is high risk of crack initiation at the coating-substrate interface during the actual loading of this coated product or during cooling down of this sample or the specimen from the reaction temperature down to the room temperature.

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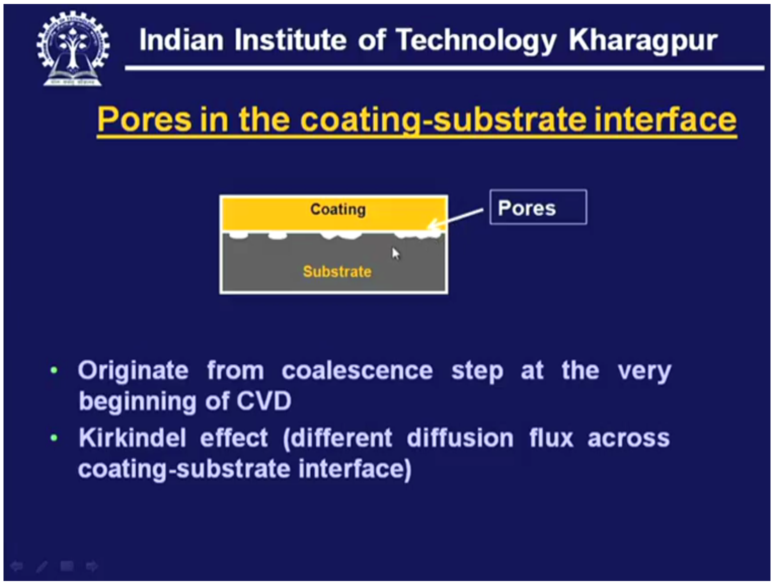

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Pores in the coating-substrate interface

- Originate from coalescence step at the very beginning of CVD
- Kirkindel effect (different diffusion flux across coating-substrate interface)

Pores in the coating-substrate interface so this is also another cause of poor adhesion at the coating-substrate interface what happens in this case, it is because of the difference in diffusion flux which is actually, okay where is the point? This one, okay, so this is actually the coating and the substrate and this is because of the difference in diffusion flux from two ends. Now if the flux from this substrate end is more than that what we have from the coating end, then there will be depletion of the material from the substrate end leaving some pores and voids.

And the whole coating will be supported by some bridge and these are the places where we do not have any material and that is just like a gap. So under this condition, the area of contact between the coating and the substrate is not what should have been reasonable and as a result of that, an external load can cause breakage of this coating, separation of this coating from this weakly jointed interface.

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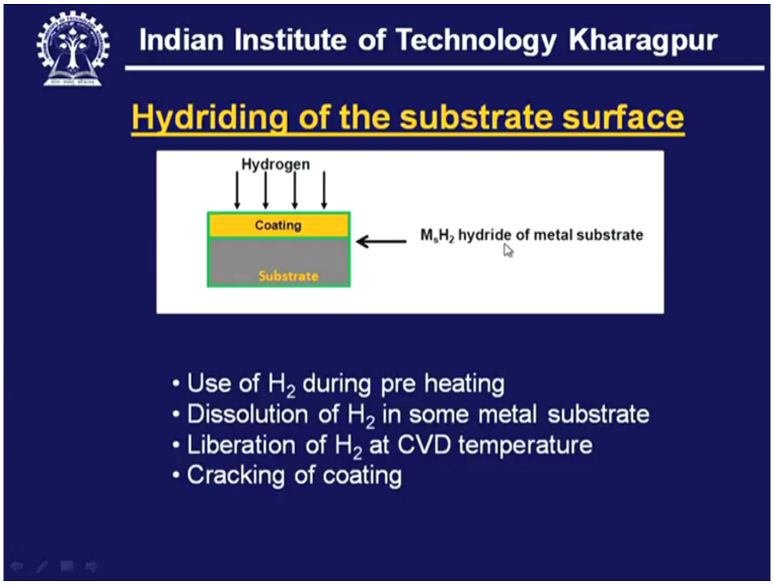

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Hydriding of the substrate surface

- Use of H_2 during pre heating
- Dissolution of H_2 in some metal substrate
- Liberation of H_2 at CVD temperature
- Cracking of coating

Hydrogen has one detrimental effect in influencing the coating-substrate adhesion. There are many substrates which are prone to this hydride formation and we may expect a hydride layer at this substrate surface. Now this may happen during the use of hydrogen during preheating or for cleaning of the surface under hydrogen atmosphere. Now because of this transportation of hydrogen in the substrate side, one hydride in this form MsH2 may form on this metal substrate.

Now during the deposition of the coating at the high temperature, this hydride cannot maintain its chemical stability and it will start liberating this hydrogen. And this liberation of hydrogen, release of hydrogen takes place through the coating and it may lead to cracking the coating. So this is one of the reason why this coating-substrate adhesion may be poor.

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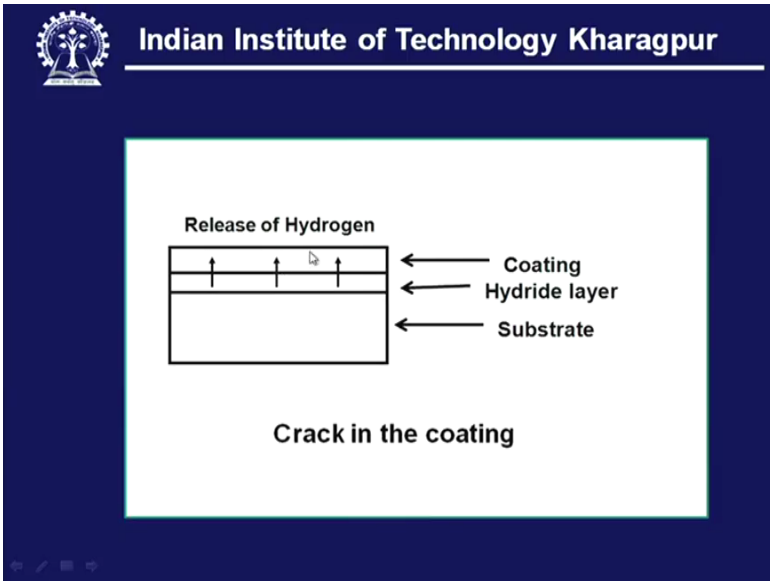

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Release of Hydrogen

Coating

Hydride layer

Substrate

Crack in the coating

So this slide shows the release of hydrogen through the coating and then there is a risk of release of this hydrogen resulting in release of cracks in the coating.

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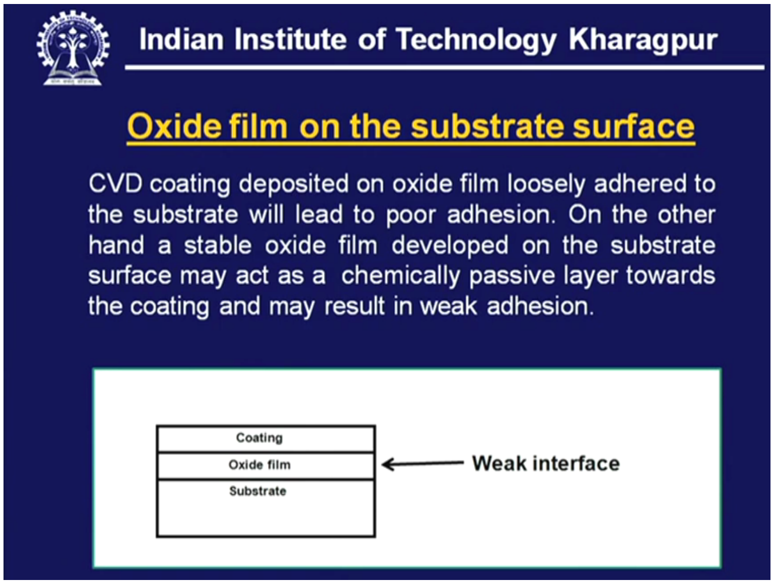

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Oxide film on the substrate surface

CVD coating deposited on oxide film loosely adhered to the substrate will lead to poor adhesion. On the other hand a stable oxide film developed on the substrate surface may act as a chemically passive layer towards the coating and may result in weak adhesion.

Coating

Oxide film

Substrate

Weak interface

Oxide film on the substrate surface now this CVD coating deposited on the oxide film loosely adhered to the substrate, it may lead to poor adhesion. Now this oxide film may be of two types. It is just an oxide scale which may not be continuous and which may not be well-adherent. So this is just a oxide scale which is spreaded over the surface and which is in discrete location. However if the coating is deposited over the substrate, it comes in contact with these oxide scales which are scattered over this substrate surface. And as a result of that, this coating cannot have a direct contact with the substrate which will lead to poor adhesion.

There can be, however there can be also a very stable oxide on this substrate. Now these substrates are oxygen getter and immediately a oxide, stable oxide formed on the substrate and which may not be cleaned by normal cleaning methods. So as a result, this oxide layer which is the oxide of the metal, this oxide layer will form as a passive layer for the coating. So this oxide layer will be chemically inert towards this coating and this coating cannot have a good chemical attachment with the substrate, the result is weak interface.

So at least we find that these are the few possible reasons which may lead to poor adhesion of the coating on the substrate.

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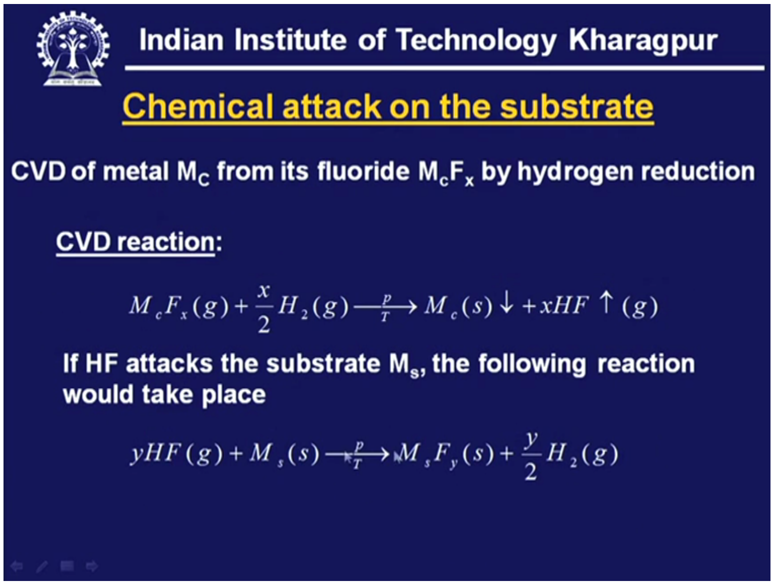

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Chemical attack on the substrate

CVD of metal M_C from its fluoride M_cF_x by hydrogen reduction

CVD reaction:

$$M_cF_x(g)+\frac{x}{2}H_2(g)\xrightarrow[T]{p}M_c(s)\downarrow+xHF\uparrow(g)$$

If HF attacks the substrate M_s, the following reaction would take place

$$yHF(g)+M_s(s)\xrightarrow[T]{p}M_sF_y(s)+\frac{y}{2}H_2(g)$$

Now comes very important issue of this chemical attack on the substrate. Now this chemical attack on the substrate may be caused by the reaction product of the CVD reaction or even by the CVD reactants directly on the substrate surface. Now here we can illustrate this point through this example. Now we like to have CVD of a metal. That means a coating of the metal, Mc from its fluoride by hydrogen reduction.

And that is illustrated by this reaction. This is the metal fluoride of this material to be coated which will be reduced by hydrogen under a particular set of pressure and temperature leading to free metal which will be deposited in the form of coating and releasing hydrogen fluoride as the gas. In normal operation, this hydrogen fluoride is expected to leave this CVD reactor and it should be inert towards this substrate surface.

But in the event, if this hydrogen fluoride attacks the substrate, the following reaction would take place. Here we can find that this hydrogen fluoride in the form of vapor, it is reacting with the substrate surface and this happens at the very early stage of the CVD reaction. And here also we have a pressure-temperature combination and we are left with the fluoride of the substrate material liberating hydrogen.

So this reaction, this is called the CVD attack reaction for the substrate and as a result we get this fluoride of the metal substrate and which, on which this coating Mc has to deposit. Now since this is non-adherent, naturally a adherent coating of this Mc cannot be expected.

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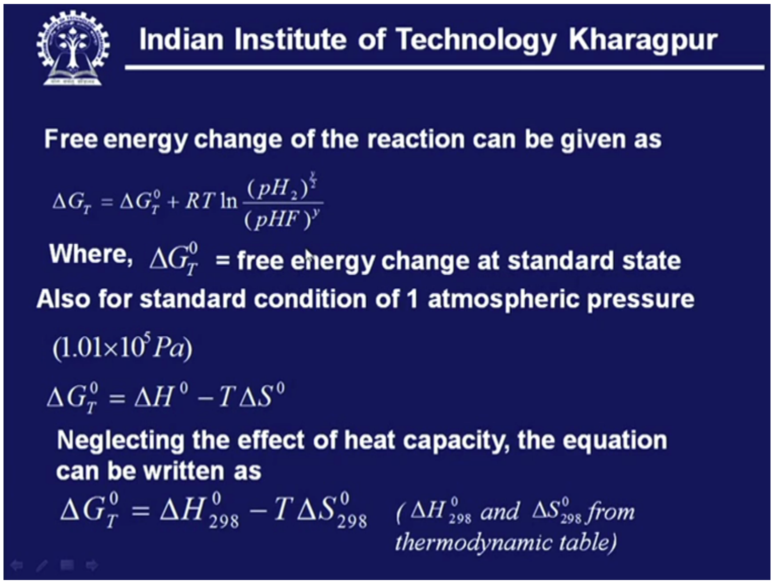

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Free energy change of the reaction can be given as

$$\Delta G_T = \Delta G_T^0 + RT \ln \frac{(pH_2)^{y/2}}{(pHF)^y}$$

Where, ΔG_T^0 = free energy change at standard state

Also for standard condition of 1 atmospheric pressure

$(1.01 \times 10^5 Pa)$

$$\Delta G_T^0 = \Delta H^0 - T \Delta S^0$$

Neglecting the effect of heat capacity, the equation can be written as

$$\Delta G_T^0 = \Delta H_{298}^0 - T \Delta S_{298}^0$$

(ΔH_{298}^0 *and* ΔS_{298}^0 *from thermodynamic table)*

Now here we can look into this free energy change of the reaction and which can give us some kind of guidance. This equation is illustrated by this change in free energy of any reaction. Here of course, this CVD attack reaction and this is the free energy of formation or free energy of the reaction at the standard state and at that prevalent temperature. Plus, the effect of partial pressure of hydrogen and partial pressure of hydrogen fluoride, that effect is clearly visible.

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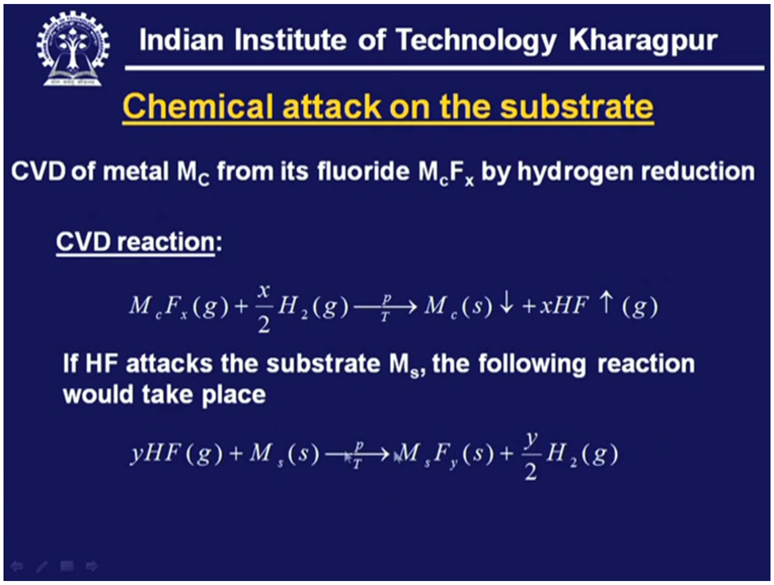

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If HF attacks the substrate M_s, the following reaction would take place

$$yHF(g) + M_s(s) \xrightarrow[T]{p} M_sF_y(s) + \frac{y}{2}H_2(g)$$

And if we go to this slide, from this, this effect of hydrogen fluoride and effect of hydrogen that can be clearly visible here.

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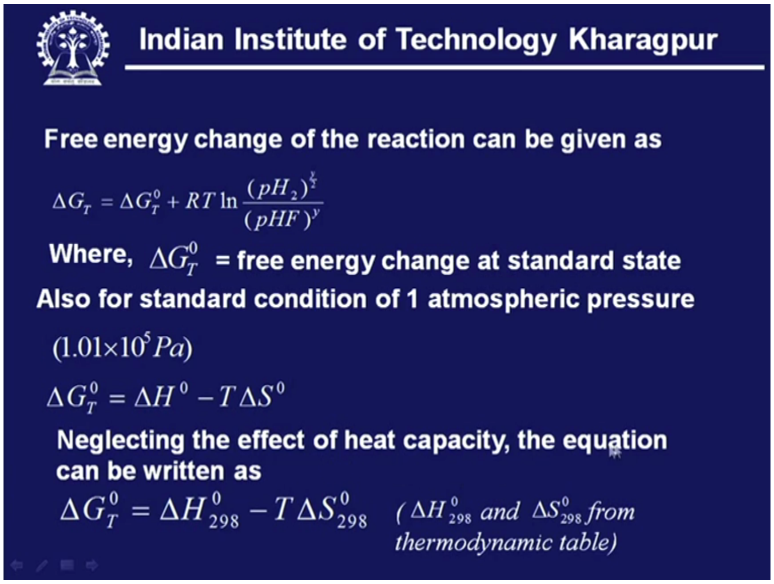

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Neglecting the effect of heat capacity, the equation can be written as

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0$$

$(\Delta H_{298}^0$ *and* ΔS_{298}^0 *from thermodynamic table)*

And as we have said this is the free energy change at the standard state. And we can further see that this delta G0T that means free energy change at the standard state is again related by enthalpy change and also entropy change. So this is the basic equation, so neglecting as a first approximation the effect of heat capacity, we can reasonably reduce this reaction in this following form.

And this following form facilitates us to find out the value of delta G0T using the value of these two property from the thermodynamic table. So this is one of the criteria or the guide, guiding parameter to judge how, whether the coating will be adherent or coating is non-adherent.

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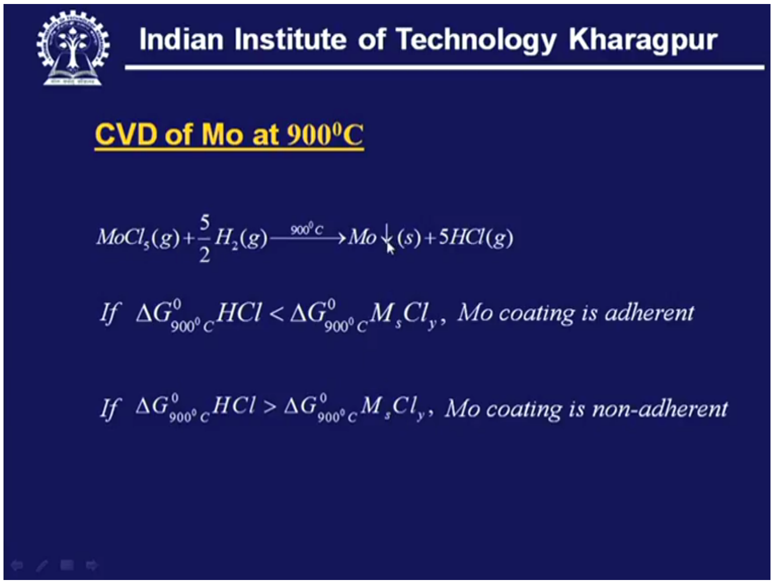

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CVD of Mo at 900⁰C

$$MoCl_5(g)+\frac{5}{2}H_2(g)\xrightarrow{900^0C}Mo\downarrow(s)+5HCl(g)$$

If $\Delta G^0_{900^0C}HCl < \Delta G^0_{900^0C}M_sCl_y$, Mo coating is adherent

If $\Delta G^0_{900^0C}HCl > \Delta G^0_{900^0C}M_sCl_y$, Mo coating is non-adherent

Now coming to the next section, say let us take one example, chemical vapor deposition of molybdenum at 900 degree centigrade. This 900 degree centigrade facilitates deposition of molybdenum through reduction, hydrogen reduction. Here we get through this reduction, deposition of molybdenum film and also hydrogen chloride as the reaction product of this CVD.

One thing, we have to be extremely careful to see this delta G0, that means free energy of formation of HCL and free energy of formation of the respective chloride at that point. Now if this hydrogen chloride is more negative, that means which is, which means more chemically stable, then formation of this, chances are remote. So this is less stable and this is more stable. So in that case, we reasonably expect the coating to be adherent.

But if it happens contrary to this, that means in this case this chloride of this metal substrate, this free energy of formation that is more negative than that of hydrogen chloride, in that case this will become more stable than HCL and as a result a well-adherent stable chemical compound is, can be seen on the substrate surface so over this, if this molybdenum is deposited, that we cannot expect to be a well-adherent coating.

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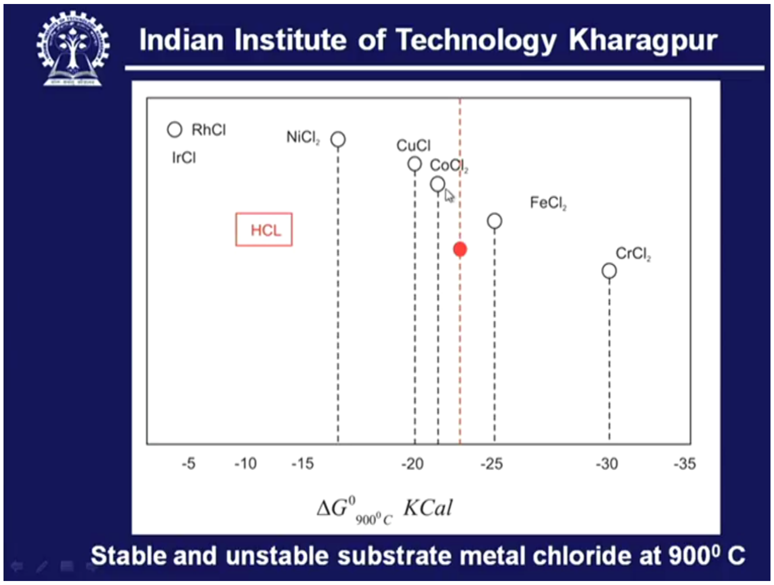

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Stable and unstable substrate metal chloride at 900^0 C

This can be illustrated by this diagram which is very, very significant, which shows the stable and unstable substrate metal chloride at 900 degree centigrade. So these figures are actually free energy of formation of different chloride expressed in kilocalorie at standard state and at 900 degree centigrade. So here we have to find out this border line which we have shown by this red border, and this shows the free energy of formation of hydrogen chloride.

So looking at this figure, one can find out few chlorides are on the right hand side and many of those are on the left hand side. It means simply that chlorides which are on the right hand side, that means say for example this ferrous chloride and chromium chloride, this chloride of iron and chromium, chloride of chromium which are going to be more stable than that of HCL. Whereas chloride of cobalt, chloride of copper, chloride of nickel and all these elements which are on the right hand side having less negative value for this delta G0 at 900.

So from this, it appears these are all less stable. So from this diagram which give us a clear indication and we may expect that if we like to deposit molybdenum on steel or some (com) some alloy containing chromium, then we may not expect well-adherent molybdenum coating. On the other side, on the other hand, if we find a metal or alloy mostly which is containing cobalt or having some copper or it is a nickel, in that case we, these are of immediate common engineering use.

And these metals can form a chloride which are unstable, more unstable than that of HCL. And if we deposit molybdenum following that CVD technique, CVD chemistry, then we expect at least this adherent coating so far as chemical attack is concerned.

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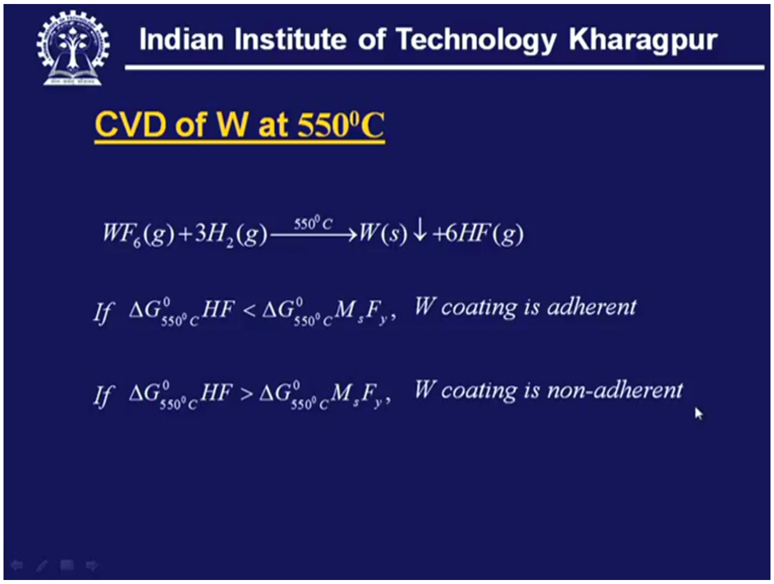

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CVD of W at 550^0C

$$WF_6(g)+3H_2(g)\xrightarrow{550^0C}W(s)\downarrow+6HF(g)$$

If $\Delta G^0_{550^0C}HF < \Delta G^0_{550^0C}M_sF_y$, *W coating is adherent*

If $\Delta G^0_{550^0C}HF > \Delta G^0_{550^0C}M_sF_y$, *W coating is non-adherent*

We take another example where tungsten is to be deposited by the same chemical vapor deposition and this can be conducted at 500 degree centigrade. Here of course, we use or what is commonly used, it is tungsten hexafluoride and this is also hydrogen reduction at 550 degree centigrade. So this leads to deposition of tungsten in the form of a coating and hydrogen fluoride as the reaction product.

Here also we see that if this fluoride is more stable, that means if this delta G0 of this hydrogen fluoride at 550 degrees is highly negative than that of this fluoride of the substrate, coating is going to be adherent. If it is contrary to that, that means in this case it simply points to the fact that in this case this delta G0, that means free energy of formation of this fluoride of the substrate element that is more stable and that is going to be more negative, then this tungsten which will form on this stable chloride cannot be an well-adherent coating.

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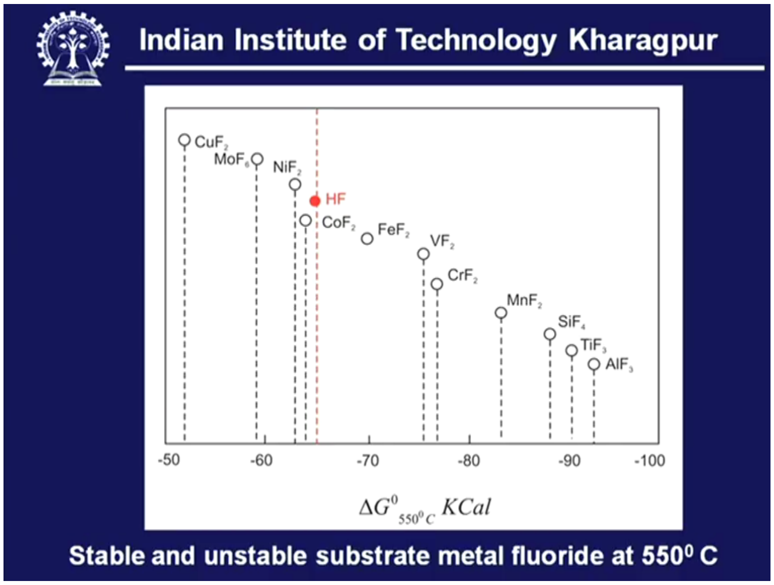

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Stable and unstable substrate metal fluoride at 550^0 C

Now getting back to this example, what we see, very interesting figure that this also shows the free energy of formation of various fluoride, copper, molybdenum, nickel. We have cobalt, it is the free energy of formation of hydrogen fluoride. On the right hand side, we have all those elements starting from iron, vanadium, chromium, manganese, silicon, titanium and aluminum. So for some reason, if for some reason someone wants to have a CVD of tungsten on all these elements which is in the form of some metal or alloy, one would expectedly get a non-adherent coating.

However, if we choose some of those metal, that means cobalt, nickel or molybdenum or even copper which are on the right, which are on the left hand side, that means where we have less negative free energy of formation, that means here chances of HF formation is more than that of formation of this. Then if we deposit tungsten on that, then at least this attack reaction is not going to take place and this will not anyway affect the adhesion of this tungsten coating on the substrate.

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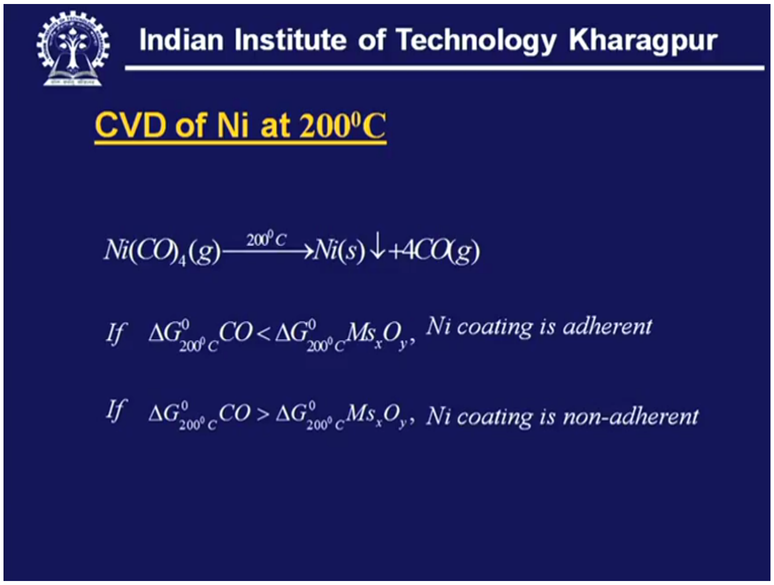

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CVD of Ni at 200^0C

$$Ni(CO)_4(g) \xrightarrow{200^0 C} Ni(s)\downarrow + 4CO(g)$$

If $\Delta G^0_{200^0 C} CO < \Delta G^0_{200^0 C} Ms_xO_y$, *Ni coating is adherent*

If $\Delta G^0_{200^0 C} CO > \Delta G^0_{200^0 C} Ms_xO_y$, *Ni coating is non-adherent*

This is chemical vapor deposition of nickel at 200 degree centigrade. This particular compound, nickel carbonyl that facilitates or allows the nickel deposition leaving this CO and this can be possible just at 200 degree centigrade. So this material undergoes thermal decomposition leaving nickel which can be deposited on a particular substrate.

Here too, we have to see that this nickel coating will be adherent when we have a compound of oxygen which is less stable than that of carbon monoxide. And we find here that this is less stable and we get a nickel coating which is adherent. But if we find the situation, a different situation if we see it that in this case this carbon monoxide, this free energy of formation is greater than that of this oxide of this material, in that case what we see that this is going to be a very, very stable oxide and (in) on that oxide, nickel cannot be deposited because we have already mentioned that few of those oxides can become very, very passive, thus preventing the bond formation between nickel and the substrate material.

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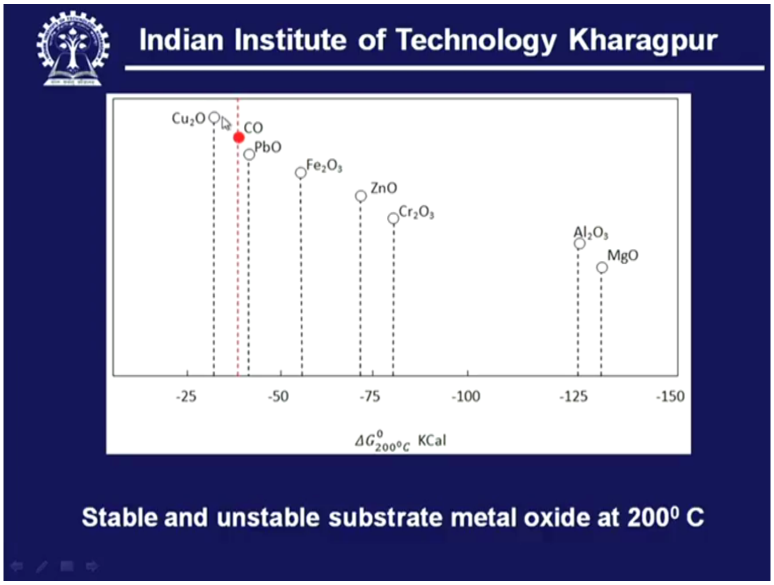

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Stable and unstable substrate metal oxide at 200^0 C

So this is also another diagram showing the location of various oxides of different elements with respect to the location of carbon monoxide. And we find that this iron, say chromium, aluminum oxide or other oxides which are very, very stable with respect to carbon monoxide, in that case it is reasonable to say that nickel coating cannot be very adherent in this side. Whereas if we can have this nickel coating on copper, chances are fair to have a well-adherent coating because this copper oxide, by this looking at this respective position we can say that this copper oxide will be less stable than that of carbon monoxide and we can have a fair chance of getting a well-adherent nickel coating.

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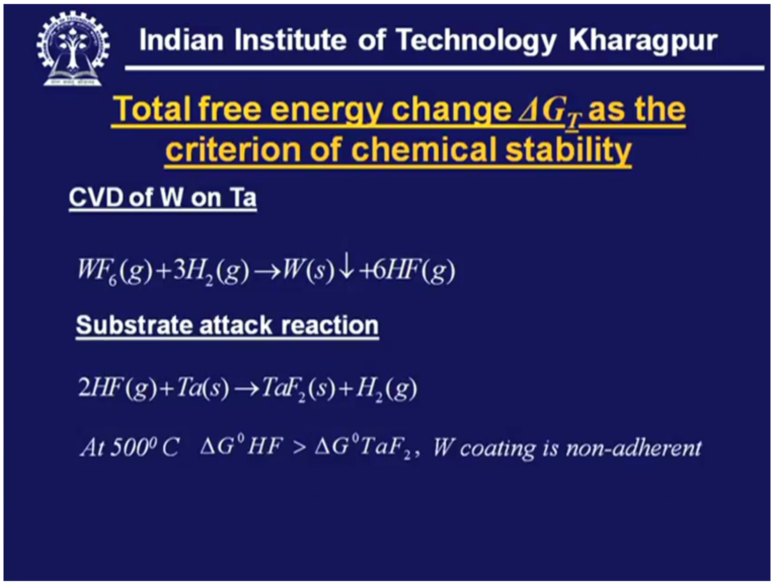

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Total free energy change ΔG_T as the criterion of chemical stability

CVD of W on Ta

$$WF_6(g)+3H_2(g)\rightarrow W(s)\downarrow+6HF(g)$$

Substrate attack reaction

$$2HF(g)+Ta(s)\rightarrow TaF_2(s)+H_2(g)$$

At 500^0 C $\Delta G^0 HF > \Delta G^0 TaF_2$, W coating is non-adherent

Now this is one issue one must consider. So far what have considered, it is actually the free energy of formation of a particular reaction product at the standard state. And we have shown that this free energy of formation of the reaction product at standard state if it is less negative than in, I mean than hydrogen fluoride, hydrogen chloride or carbon monoxide, in that event, the coating is going to be an adherent.

But if it is not the case, that means that this reaction product has free energy which is more negative than that this hydrogen fluoride, hydrogen chloride or carbon monoxide, in that case the coating will be non-adherent. But we can now see that there is a scope of manipulating the whole reaction to our advantage just by considering not delta G0T but it is the total free energy change as the criteria of chemical stability of one compound.

Let us consider CVD of tungsten on tantalum. So as usual, we can get tungsten in the form of coating and hydrogen fluoride will form as the reaction product. Now in this substrate attack reaction, obviously hydrogen fluoride is going to attack tantalum forming tantalum fluoride and liberating hydrogen. And as we see, at 500 degree, delta G0HF is greater than that of delta G0 of tantalum fluoride. That means this is more negative and more stable. And as we have discussed, then this tantalum fluoride is going to be a stable compound deposited adhering the, on the substrate.

So this tungsten cannot have a direct contact with the substrate and it is being deposited on this. So coating will be non-adherent. This part is understandable.

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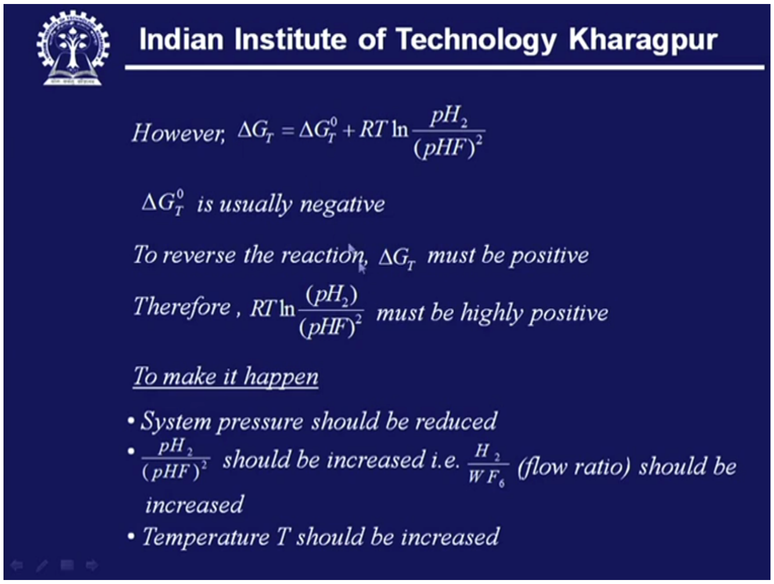

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However, $\Delta G_T = \Delta G_T^0 + RT\ln\frac{pH_2}{(pHF)^2}$

ΔG_T^0 is usually negative

To reverse the reaction, ΔG_T must be positive

Therefore, $RT\ln\frac{(pH_2)}{(pHF)^2}$ must be highly positive

<u>To make it happen</u>

- System pressure should be reduced
- $\frac{pH_2}{(pHF)^2}$ should be increased i.e. $\frac{H_2}{WF_6}$ (flow ratio) should be increased
- Temperature T should be increased

But if we take a broader view, that means this one, delta GT is equal to delta G0T plus RT into ln pH2 divided by, this is actually partial pressure of hydrogen and this is the partial pressure of hydrogen to the power 2. Now here the reaction can be adjusted or regulated to the advantage of stable adherent coating. What can be done?

This is going to be negative as usual. But if we can make this as positive, then perhaps this highly positive value and this negative part, their resultant effect may be positive and in that case we can say that delta GT of the reaction is positive, means this reaction cannot go in that direction. And we can protect the substrate against the chemical attack by this hydrogen fluoride.

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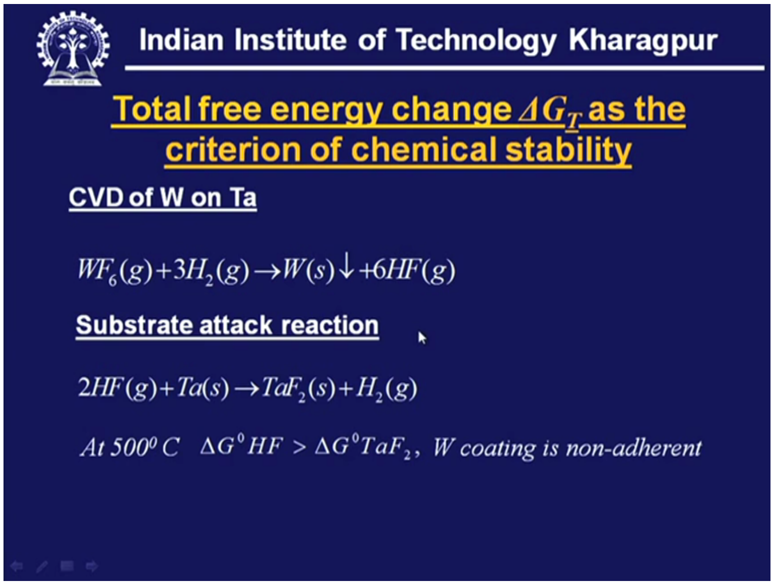

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Total free energy change ΔG_T as the criterion of chemical stability

CVD of W on Ta

$WF_6(g) + 3H_2(g) \rightarrow W(s)\downarrow + 6HF(g)$

Substrate attack reaction

$2HF(g) + Ta(s) \rightarrow TaF_2(s) + H_2(g)$

At $500^0 C$ $\Delta G^0 HF > \Delta G^0 TaF_2$, W coating is non-adherent

This hydrogen fluoride.

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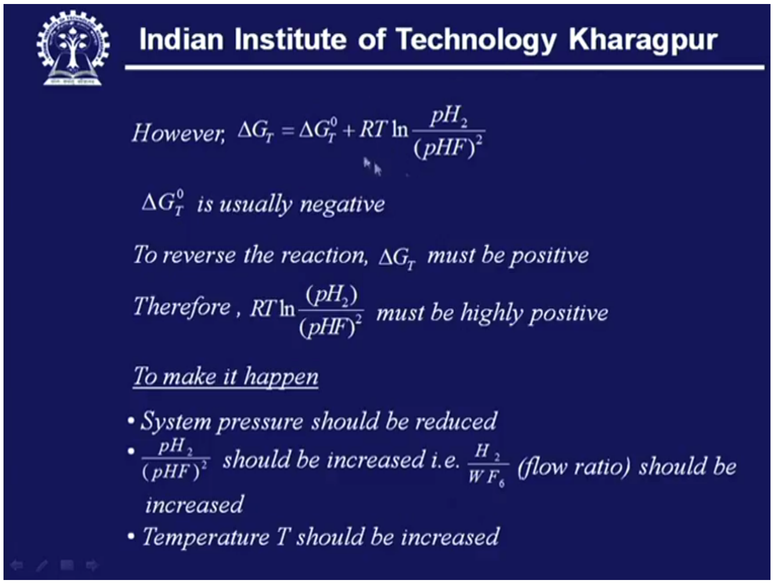

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To make it happen

- System pressure should be reduced
- $\frac{pH_2}{(pHF)^2}$ should be increased i.e. $\frac{H_2}{WF_6}$ (flow ratio) should be increased
- Temperature T should be increased

So this can be prevented reasonably by, though it is negative, by making this highly positive, the whole thing becomes positive. And to make it happen, what we have to do during the CVD operation? That means this should be increased adequately, this thing, which means that flow ratio at the upstream side of the CVD reactor, hydrogen, quantity of hydrogen should be in excess than what is required in the equilibrium condition. So this flow ratio should be highly, should be adequately increased and at the same time the temperature T, that should be also increased so that the whole thing becomes highly positive.

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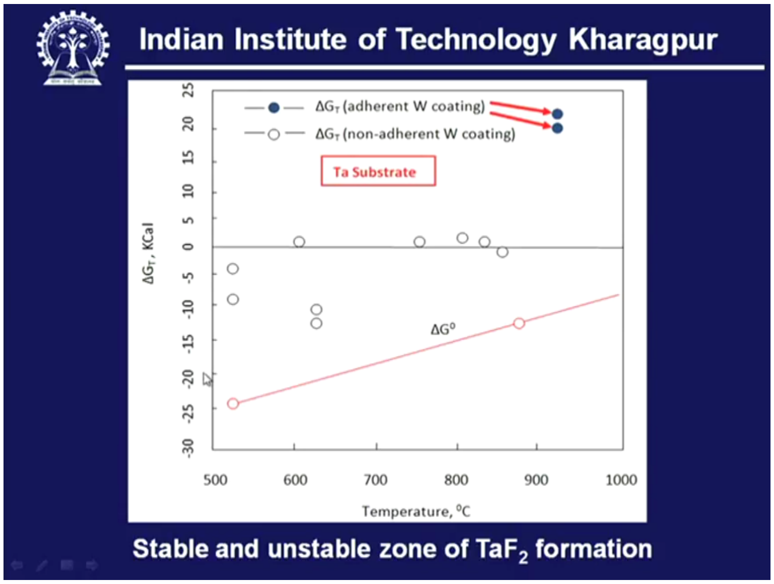

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Stable and unstable zone of TaF_2 formation

And this has been illustrated, well illustrated in this diagram. We can look into that, this one shows it is the total delta GT. And how this delta GT value can be adjusted?

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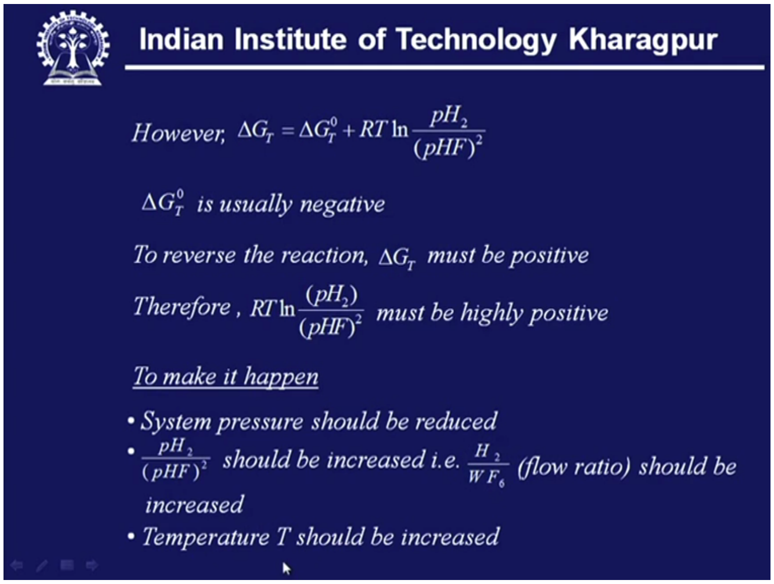

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ΔG_T^0 *is usually negative*

To reverse the reaction, ΔG_T *must be positive*

Therefore , $RT\ln\frac{(pH_2)}{(pHF)^2}$ *must be highly positive*

To make it happen

- *System pressure should be reduced*
- $\frac{pH_2}{(pHF)^2}$ *should be increased i.e.* $\frac{H_2}{WF_6}$ *(flow ratio) should be increased*
- *Temperature T should be increased*

Just by adjusting this flow ratio, hydrogen to this hydrogen fluoride that means at the very upstream side, one has to monitor this flow ratio and the deposition temperature.

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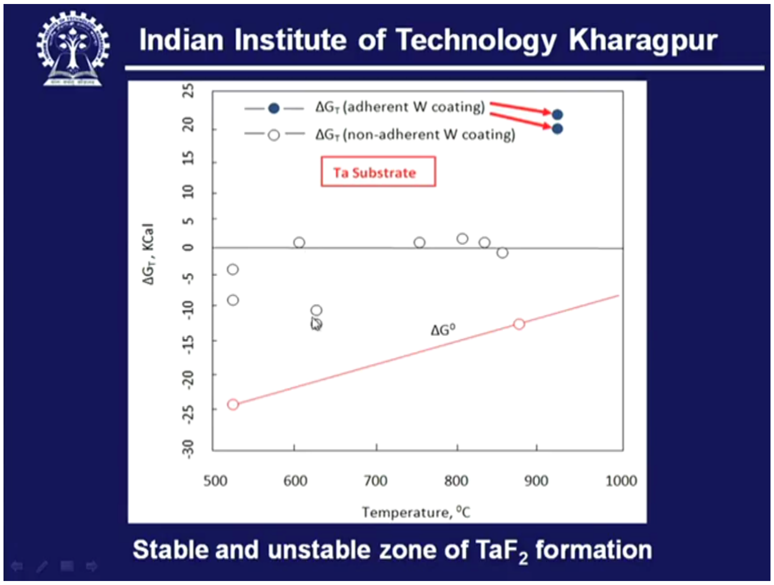

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Stable and unstable zone of TaF_2 formation

And immediately you can raise this point, location of this point. This is actually delta G0. However delta GT that can be raised at any different level and this can be.

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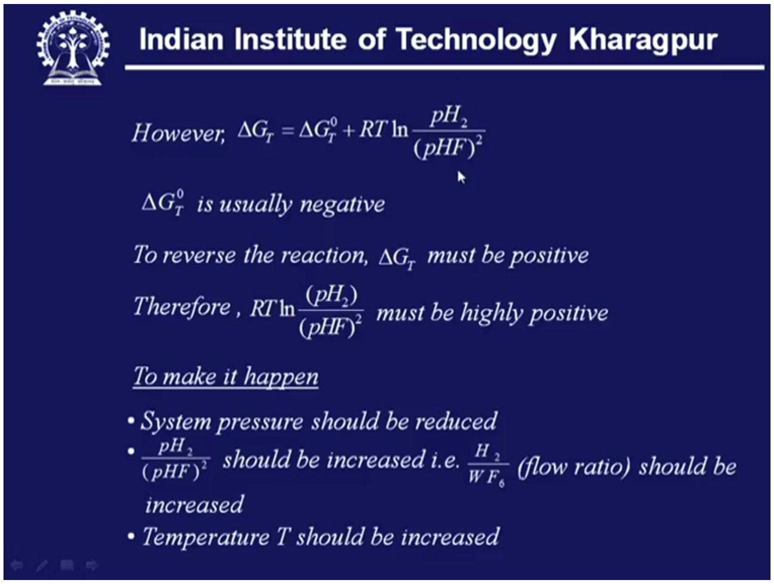

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However, $\Delta G_T = \Delta G_T^0 + RT \ln \frac{pH_2}{(pHF)^2}$

ΔG_T^0 *is usually negative*

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Therefore , $RT \ln \frac{(pH_2)}{(pHF)^2}$ *must be highly positive*

To make it happen

- *System pressure should be reduced*
- $\frac{pH_2}{(pHF)^2}$ *should be increased i.e.* $\frac{H_2}{WF_6}$ *(flow ratio) should be increased*
- *Temperature T should be increased*

As I have said that this can be done by just adjusting this.

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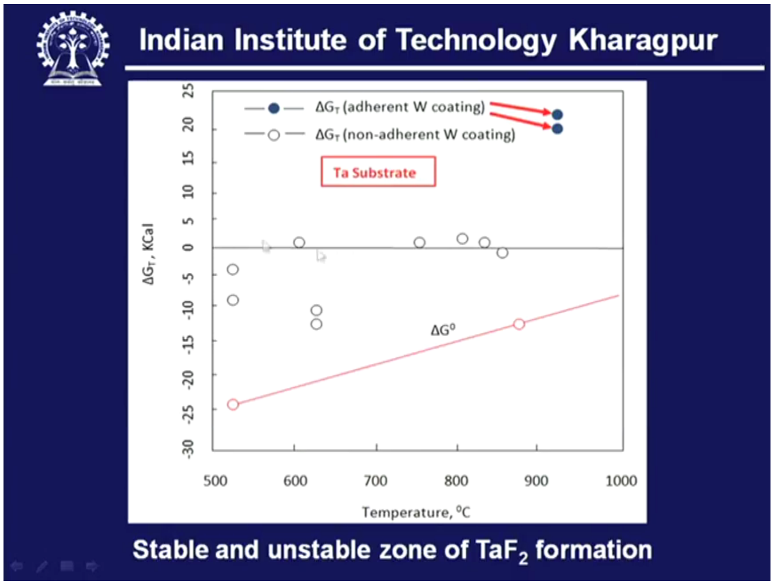

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Stable and unstable zone of TaF_2 formation

So we are here. This is actually the limit. At least, it should attend a value at the 0 level. But to be very pragmatic, we must take this, push this thing to a very high positive value. That means at 900, we find that this point can be raised here by just adjusting this flow ratio of the incoming reactants in the upstream side. And as a result, we can find out a very highly positive delta GT. And by this value, we can ensure that this non-adherence caused by this substrate attack reaction can be totally stopped. And this has been achieved by this particular action.

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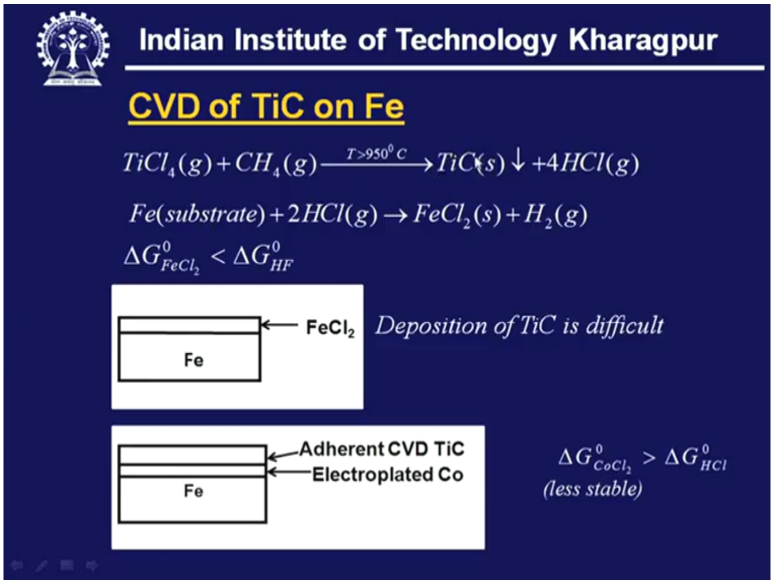

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CVD of TiC on Fe

$$TiCl_4(g)+CH_4(g)\xrightarrow{T>950^0C}TiC(s)\downarrow+4HCl(g)$$

$$Fe(substrate)+2HCl(g)\rightarrow FeCl_2(s)+H_2(g)$$

$$\Delta G^0_{FeCl_2}<\Delta G^0_{HF}$$

Deposition of TiC is difficult

$$\Delta G^0_{CoCl_2}>\Delta G^0_{HCl}$$

(less stable)

This is another example. How this adherence can be maintained, though by normal process of CVD there could be non-adherence of the coating. This is illustrated by this example, titanium tetrachloride and CH4, this will give reasonably titanium carbide. And if one is interested to get titanium carbide on the substrate surface which is steel to augment the surface property, then we can see this HCL is also simultaneously active on this substrate surface.

So the titanium carbide deposition and its adhesion will be hindered by this participation of this HCL in a chemical attack reaction. And we can see the formation of FeCl2 and we have already seen that delta G0 of this FeCl2 is more negative than that of HCL. And then deposition of this TiC will be rather a difficult task. However the problem can be solved if we can have an electroplated pre-deposition of cobalt over this steel.

And this cobalt will prevent this HCL from attacking the substrate because of the simple reason what we have seen that chloride of cobalt is less stable than that of HCL. That means HCL will remain as it is and it will not participate in any chemical reaction forming chloride of cobalt. And as a result the situation is, can be well handled, steel is well protected and we can have a TiC coating on this surface of iron which is actually pre-coated by cobalt.

It has to be of course pointed out that this attack or the reaction product which is actually affecting the adherence of the coating, that happens at the very initial period. So once this is protected, this steel is protected and we get a complete layer of TiC however small it is in terms of thickness, then this HCL cannot attack the substrate surface which is already covered with TiC.

That means in all CVD reaction, the process parameters at the beginning has to be chosen in such a manner that this HCL or the reaction product is more stable than that of the reaction product of the attack reaction. And once, but one thing we can say that if we like to follow that reaction, efficiency of the process falls drastically. But this is only for a small period of time and once through this change of the parameter if we can protect the substrate and we get one layer of the top coating, then we can switch over to this particular surface. And then we can have this coating without any problem.

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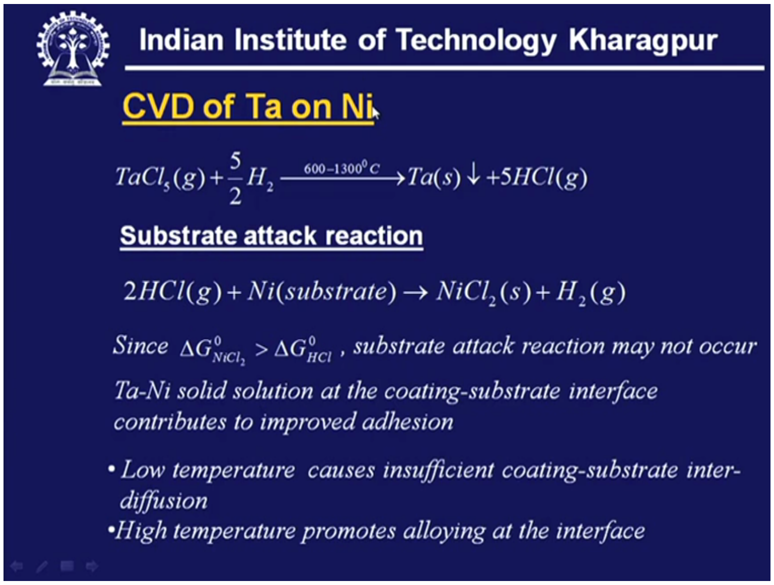

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CVD of Ta on Ni

$$TaCl_5(g)+\frac{5}{2}H_2 \xrightarrow{600-1300^0C} Ta(s)\downarrow +5HCl(g)$$

Substrate attack reaction

$$2HCl(g)+Ni(substrate)\rightarrow NiCl_2(s)+H_2(g)$$

Since $\Delta G^0_{NiCl_2} > \Delta G^0_{HCl}$ *, substrate attack reaction may not occur*

Ta-Ni solid solution at the coating-substrate interface contributes to improved adhesion

- *Low temperature causes insufficient coating-substrate inter-diffusion*
- *High temperature promotes alloying at the interface*

Now we go to this substrate attack reaction, CVD of tantalum, chemical vapor deposition of tantalum on nickel. Here we see that in this reaction, nickel chloride can form but as per the statement of this reaction nickel chloride can form, but if we consider the respective free energy of formation, nickel chloride cannot form. But still it is observed, quite an interesting observation that this coating of tantalum on nickel is not very adherent.

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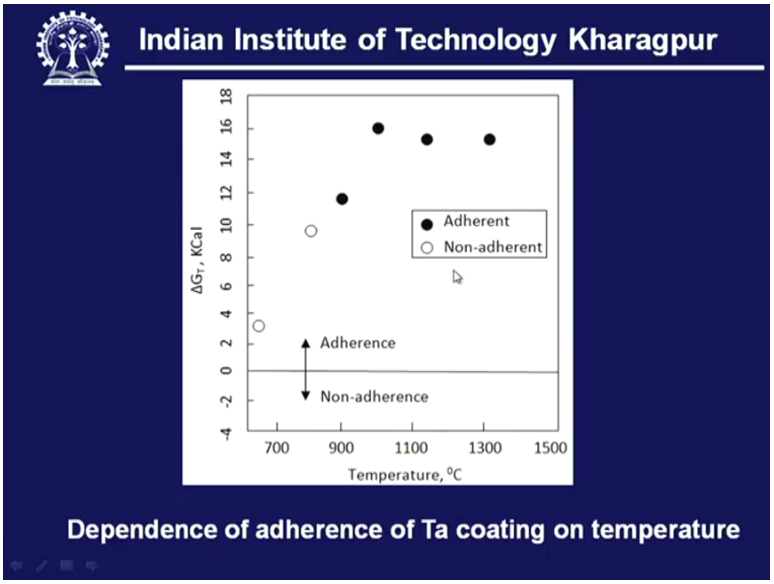

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Dependence of adherence of Ta coating on temperature

In this case, what we find that in this case actually non-adherence is because of the poor alloy formation between the coating and the substrate. But if we raise this temperature, we can get an adherent coating and this is promoted by the cross-diffusion of coating and the substrate from both the sides. So it is not the question of attack by the reaction product but it is just lack of alloy formation between the coating and the substrate.

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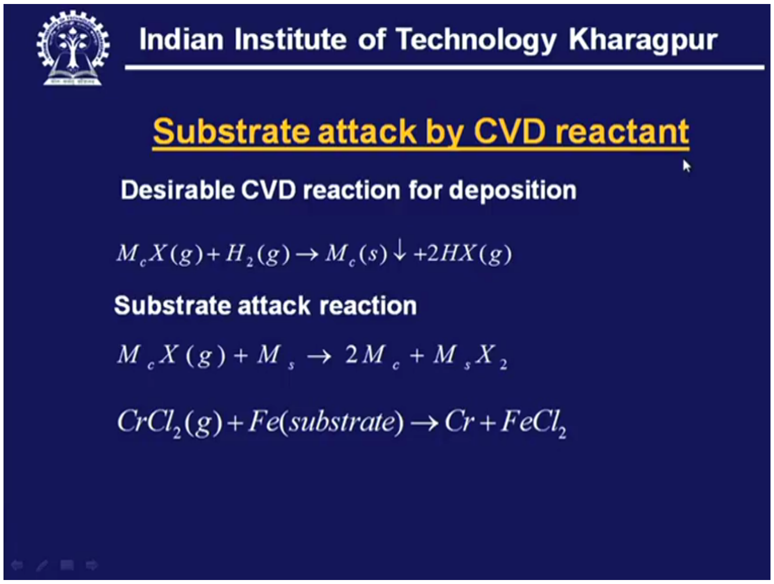

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Substrate attack by CVD reactant

Desirable CVD reaction for deposition

$$M_cX(g)+H_2(g)\rightarrow M_c(s)\downarrow +2HX(g)$$

Substrate attack reaction

$$M_cX(g)+M_s\rightarrow 2M_c+M_sX_2$$

$$CrCl_2(g)+Fe(substrate)\rightarrow Cr+FeCl_2$$

Now this is also another important issue we have to look in. This is the substrate attack by the CVD reactant. It is not actually the reaction product, it is actually the metal donor halide. This is the metal donor halide, say for example tantalum pentachloride or molybdenum pentachloride or we have chromium chloride. So these are the metal donor halide, they directly attacks this particular substrate.

So in this case what happens, this chromium chloride it does not wait for hydrogen for reduction, so it is actually reduced by the element of the substrate and the substrate becomes a chloride. And that becomes also one reason of non-adherence of the coating. So this case we have to also be careful that how to avoid this kind of reaction to choose a particular layer on that surface so that the metal donor halide which is the reactant of the CVD, it does not directly attack the substrate.

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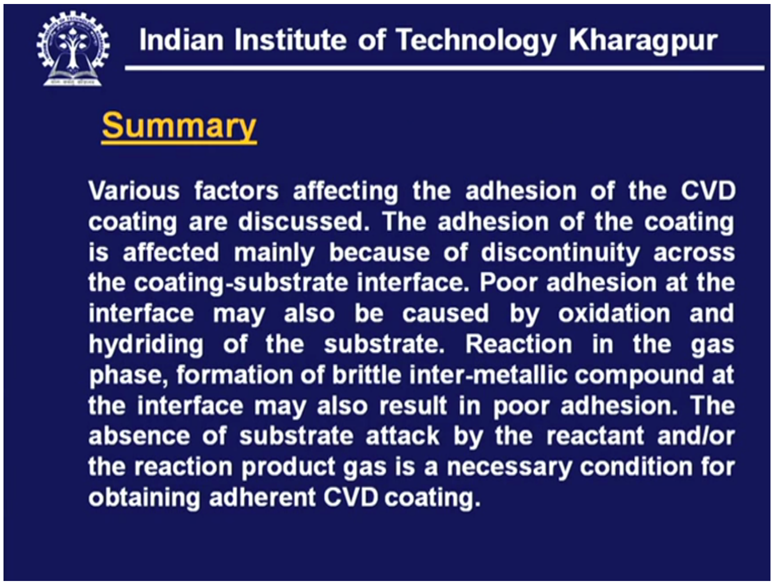

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Summary

Various factors affecting the adhesion of the CVD coating are discussed. The adhesion of the coating is affected mainly because of discontinuity across the coating-substrate interface. Poor adhesion at the interface may also be caused by oxidation and hydriding of the substrate. Reaction in the gas phase, formation of brittle inter-metallic compound at the interface may also result in poor adhesion. The absence of substrate attack by the reactant and/or the reaction product gas is a necessary condition for obtaining adherent CVD coating.

So we come to this summary of this discussion. Just various factors affecting adhesion of the CVD coating are discussed. Adhesion of the CVD coating is affected mainly because of the discontinuity across the coating-substrate interface. They are mainly mechanical in nature, it can be thermal, it can be also chemical whatever we see that, apart from this poor adhesion is also caused by hydride formation on the substrate or even by oxide formation.

Reaction in the gas phase which leads to homogeneous nucleation, that is also one of the principal cause of poor adhesion. So here heterogeneous nucleation should be promoted. One of the main important issue, one of the necessary condition one has to fulfill that to stop the attack of the reaction product of CVD on the substrate surface and for that, appropriate conditions of CVD at the very initial stage of the process should be taken into consideration.

It has been also found that this substrate attack may be also caused not only by the reaction product of CVD but also by the reactants of the CVD. And in this case, if it is a reduction reaction, in that case hydrogen does not participate. It is the substrate material which actively participates and reduces the metal from the halide donor but itself it becomes a chloride.