Technology of Surface Coating
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Lecture 28
Plasma Spray Process

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Plasma spray process and we shall discuss today this topic and this process. Now let us have a quick look to this application area. Now when we review the flame spray process we see mostly it is the temperature restriction and with this temperature restriction of the flame which generates a temperature in the range of 3000 around 3000 then definitely the material of choice are also limited and this materials are mostly metals and alloys with some additives like Tungsten Carbide, Chromium Carbide and some other metal carbides.

So basically it is metal which gets melted but the Carbide doesn't but it is held in the coating or the spread layer in the form of dispersion. So they are not melted but when we require a better property in terms of say wear resistance or thermal shielding, just like a thermal barrier coating then it is no more the metal or alloy immediately it is becoming the another requirement that means it comes from the ceramic family.

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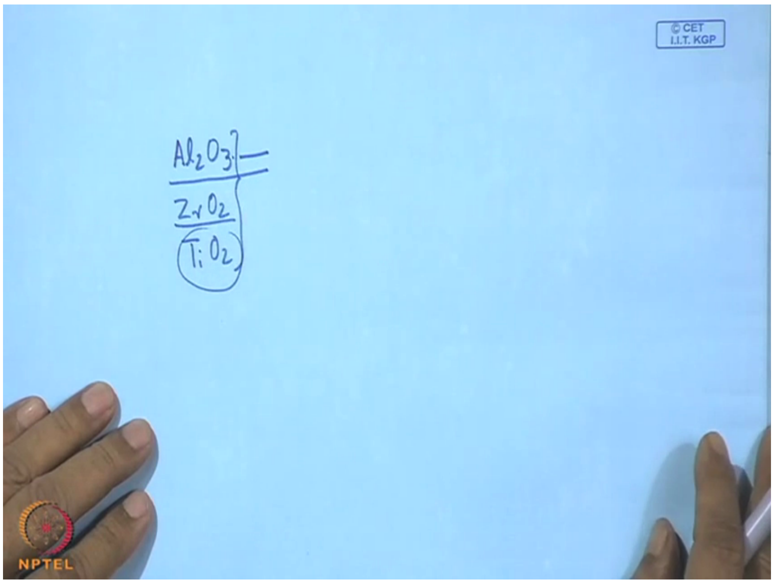

And the ceramic family one immediately the one which comes in our record of mind that is a Aluminium Oxide. Aluminium Oxide, Zirconium Oxide or they are mixture or say Titanium Oxide, so these are some of the Oxides which can be very useful, effective for improving the performance of many mechanical components which are submitted to such areas I mean where it can suffer from thermal damage distortion.

So this heat shielding plus wear resistance say for example Aluminium Oxide that is well-known as a thermal barrier plus also wear resistance. We know this is also used as hard coating in many applications in many wear parts. So Zirconium Oxide, Titanium Oxide, so here the requirement of temperature is rather high and which cannot be very easily which cannot be, it is almost impossible to attend those things either by flame or normal combustion or by striking the electric arc but in that case of course the material has to be conductive but even with flame spray this is almost an impossible task.

So we understand that the requirements are that this temperature but how this energy will be supplied? One may be thermal activation, another maybe plasma activation, so here this plasma activation is important that this requirement of the temperature can be very easily, we can make this thing available by igniting this plasma or by having the whole process within the plasma volume.

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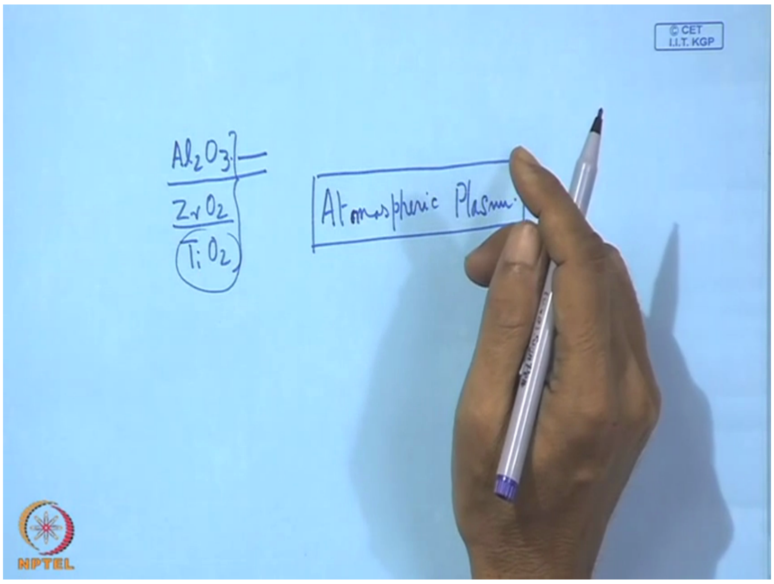

So application area will be those places where we require extreme heat shielding and also where resistance. Now we have some variation in plasma spray, so these variations are namely atmospheric plasma, atmospheric plasma which is carried out an open atmosphere. So this is one type of plasma spray process and let us have a look, how does it work?

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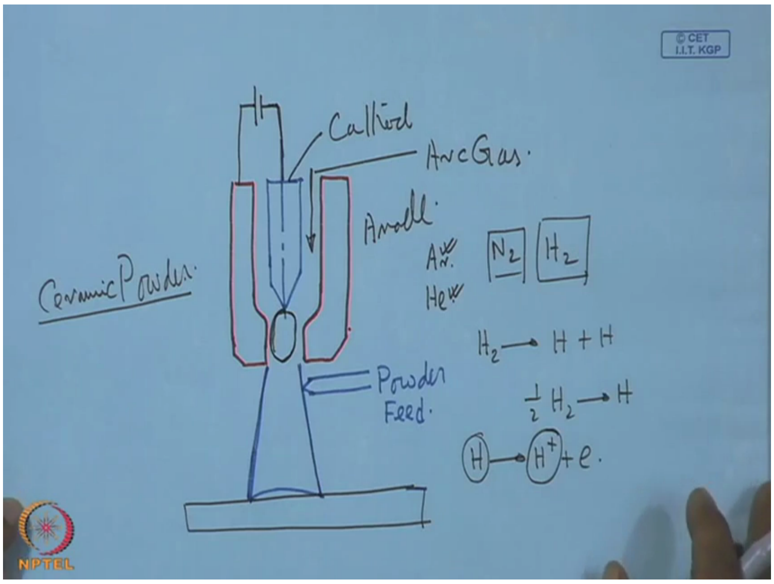

So here also we have to have a nozzle. So basically plasma nozzle that is used for welding, plasma nozzle can be used for cutting. Now this plasma nozzle is used for spraying, so basically we have a centrally located cathode. So this is made of say Tungsten cathode and we have one annular anode and that is usually made of copper. So this is the formation and here this will be, so those are connected.

So connectivity is made obviously this way, so this is the positively polarised and this is negatively polarised. So cathode and anode, so here we have the arc gas, so (()) (6:27) will be the arc gas. So this is actually the arc gas and what we have? Within this we have the gas discharge in this zone, we have the gas discharge.

Now as a result of this gas discharge, what is going to happen? Say what are those arc gas? We can have Argon or Nitrogen or Hydrogen or even Helium. However it is prefer to have instead of a mono atomic gas a diatomic gas the idea here is that this enthalpy of formation that is very important in this case because this is going to release energy in the form of heat and this heat will be utilized for melting the powder which is actually a ceramic powder.

So it is actually a ceramic powder that will be melted by the heat generated out of this gas discharge, so what is going to happen? That this H2 that will be become H plus and this neutral, so it may be half H2 to H and then this H will be actually H plus release of this electron.

So this is going to happen here but once that leaves this discharge zone this plasma volume then it will be reversed that means this Hydrogen ion will become by taking one electron that will become atomic Hydrogen and atomic Hydrogen will become molecular Hydrogen and in this process it will start releasing this heat and that is going to happen in this zone outside this discharge zone that is going to happen and here we have the substrate and the powder should be just outside.

So here we must have some powder feeding here, so this is actually the powder feed it will be just outside this and from here we have this spraying of this powder and that is going to impinge on this surface and in this process what happens exactly?

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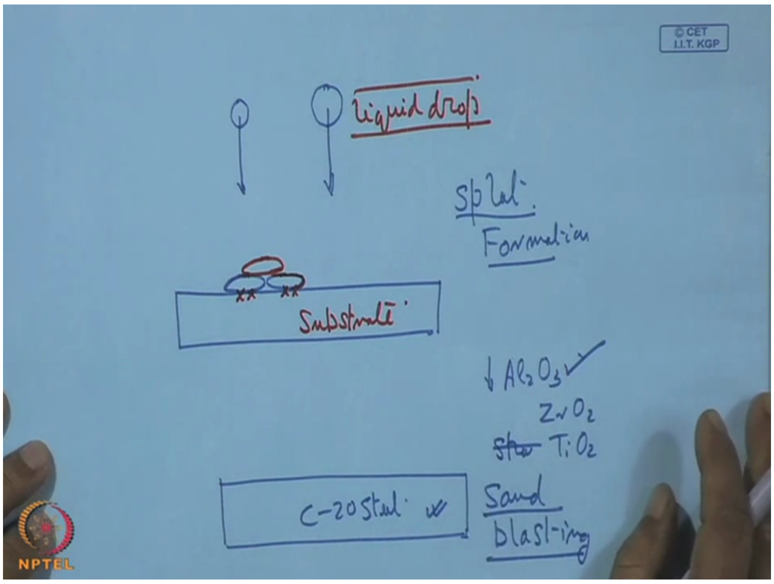

It is actually the liquid will form, so we have droplets of different shape and this droplet will move with a high velocity and then what is going to happen? When it strikes it is called splatting, Splat formation splat formation as it arrives, so we have splat formation and then we had another splat formation over this. So this way it is going to build up the whole thing and then we are going to get a well adherent coating.

So this process the material gets first it's it is impinging on this surface followed by condensation solidification and then adhering either to the substrate surface or to the original surface which is already solidified over this substrate, so this is liquid drop. Now here again the question is how the substrate surface is prepared?

Now basically it is also, it doesn't depend on any chemical bonding. So the surface need to be properly prepared that means decreasing pickling and also then by mechanically roughening the surface that means here we need to have this what we call sandblasting and the sandblasting as usual we need to have this grit sized stream velocity and also the angle of incidence and standardization of the roughness of the surface. So this way we can prepare a very good receptor surface but what happen?

Mostly material build-up in plasma that we have shown already by this splat formation and what happens? Preparation of the substrate surface what we are discussing and this is sandblasting but sometimes since it is ceramic material the chemical compatibility we don't have much chemical compatibility between say this is C-20 steel and here we have Aluminium Oxide or ZrO2 or TiO2 something like that and they may not have very good compatibility.

This material is inert towards this cell towards the surface and it may so happen that material may bounce back and material may not get attached. So in this case though it is moving with high velocity but sticking coefficient that is very poor because of this inertness of the ceramic against this metal.

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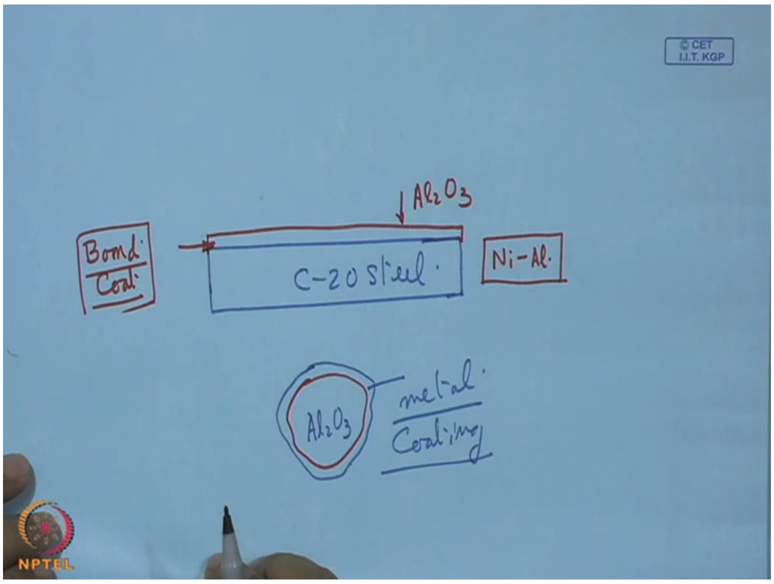

So what is done? In many cases we have to put what we called a bond court. So this is a particular material, so this is a substrate and over the substrate we have a bond court, this is actually metal coating and this can be Nickel Aluminide that is put over the surface, so number 1 this Nickel protects the surface against any possible oxidation and then we have Aluminium on this side.

So this Aluminium can have some kind of compatibility with this incoming Aluminium Oxide, so this choice of bond court, thickness of the bond court these are the 2 very important parameters, how thick this bond court would be and what would be the composition of this bond court?

So these are the 2 important parameters for this material to arrive on the surface with a much better sticking coefficient. So this is actually the bond court but also their some attempts also to use a metal coated Aluminium Oxide, say this is Aluminium Oxide particle this can be also coated with some of the metal and which will be melted and with this metal coating even without having a bond court on the steel there is a fair chance of having good wettability and good sticking coefficient. So it is a metal coating on this Aluminium Oxide particle or Zirconium Oxide particle, it is only to have better adhesion at the time it arrives over this substrate which is a C-20 steel.

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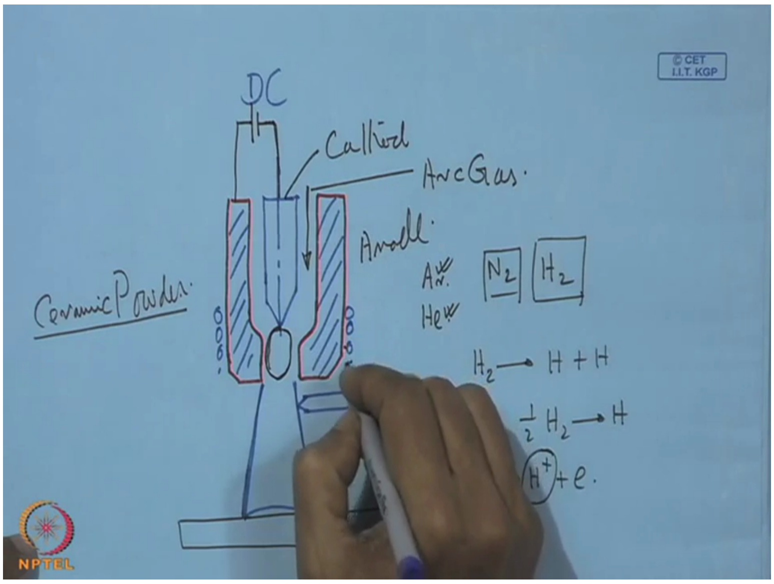

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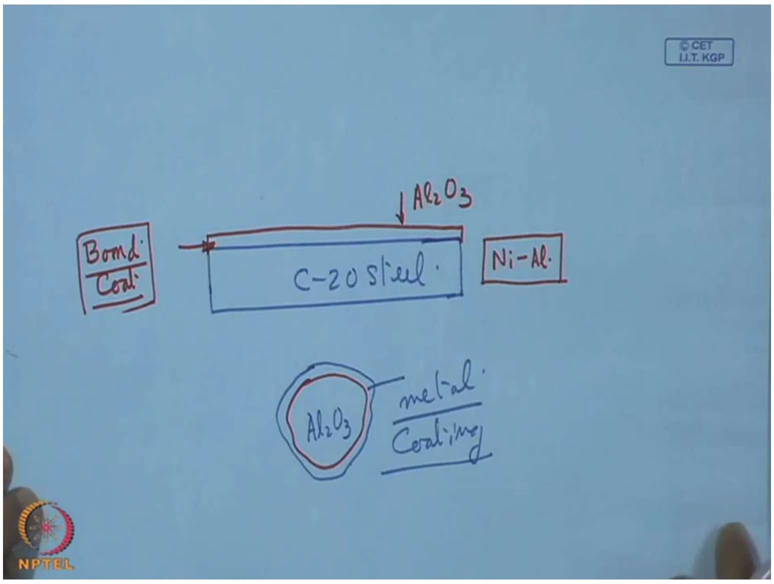

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So here what we see? This is called transferred arc spray. Now what we have shown? In this diagram, this is the copper nozzle and so we have direct polarisation, so it is a DC, so this is positively polarised and this is also water cooled, so there is water-cooled jacket, so this is also water-cooled but when it is actually plasma transferred arc spray, so in that case what we do?

We also polarise the substrate along with this copper nozzle that means outer surface of this nozzle that means the casing is made of copper, so the thing will be like this, so we have the central cathode and then what we have? The nozzle and in this case though we have this connection, so this is negative and here what we have? This is positive, so it is connected like this and then from this point we have made another connection.

So that means this is also from this point, so this is connection, so that means here this arc which was confined only to this nozzle area that is actually extended over this discharged area that is extended up to this surface which was just restricted to this cathode area in front of this cathode in this zone that was the area. Now it is extended to this point, the whole idea here is to have some kind of metallurgical bonding that means allowing this coated material to have some sort of diffusion within the substrate and by that process the top surface of the substrate that may be diluted by this coating material.

So if we have a coating material over this, so that may get diffused into this by this melting, so there will be some dissolution and with this dissolution we can have dilution. However what we can achieve? That is actually the better metallurgical bond between the substrate and the deposited layer that means this coated layer. So here what we see? That this arc, so arc is transferred here and the substrate is also polarised by this process.

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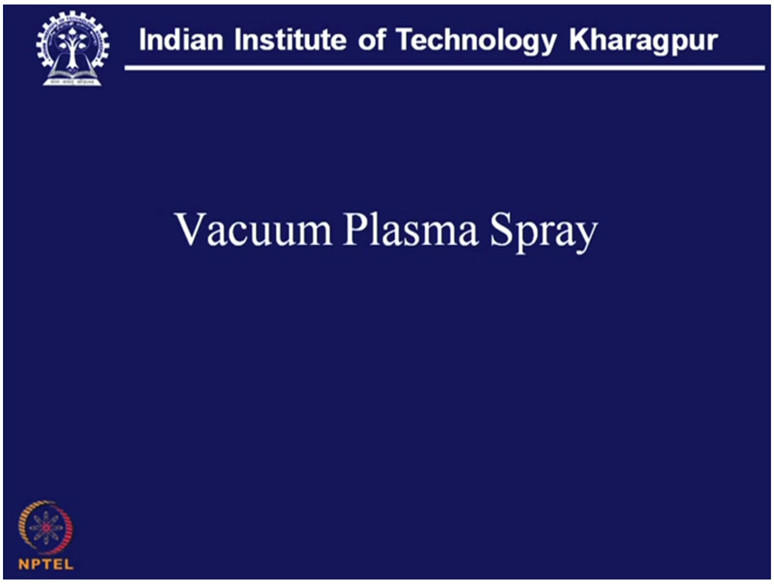

So this is plasma transferred arc but this plasma transferred arc we can also, so these are actually done in open atmosphere but now we can also have vacuum plasma spray. Now vacuum plasma spray has the advantage that the whole substrate is protected against any possible oxidation because of the very presence of oxygen in open atmosphere that we understand.

However when it is kept within a closed chamber, vacuum chamber it is protected and many delicate job can be handled in the high vacuum atmosphere or in low pressure. So this is done in that vacuum chamber but there is another advantage of that.

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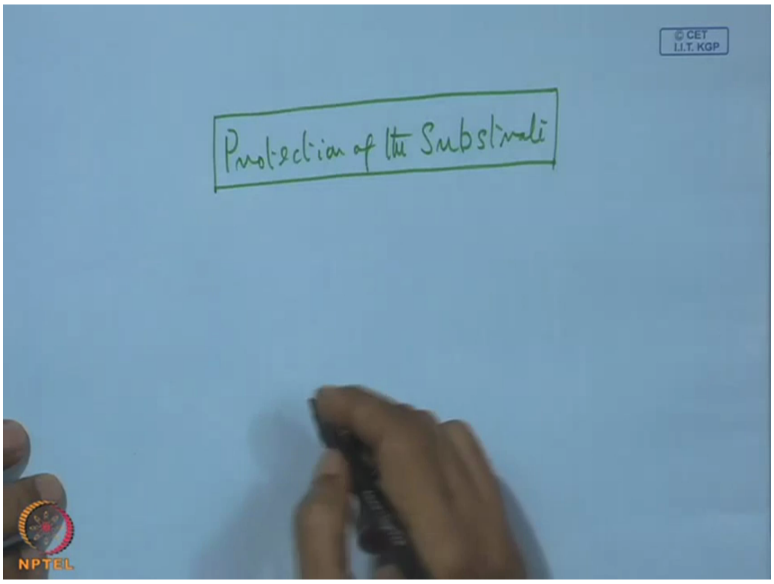

That advantage apart from protecting the surface. So it is basically protection of the substrate that is understandable. However there is another advantage which we have already seen in sputtering process that means in C2 the substrate surface can be clean and without having any contamination we can switch over to the actual deposition process that means we can follow this way that means say for example here we have the centrally located cathode and at the same time here we have the anode and through this arc gas is pass.

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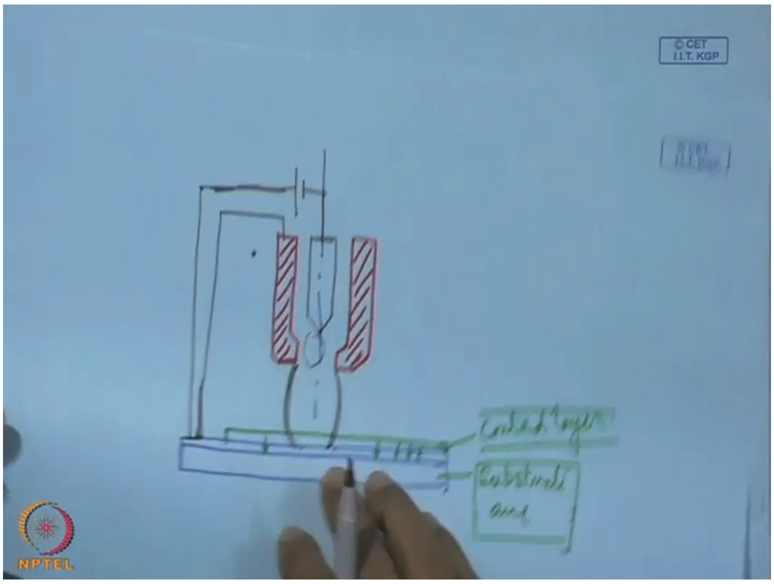

But here we have now the substrate like this. Now the whole thing is put inside a vacuum chamber, the whole thing is inside the vacuum chamber. So what we can do? So what we have done so far? we have connected the positive polarity during this plasma transfer arc process that means here it is positively polarised.

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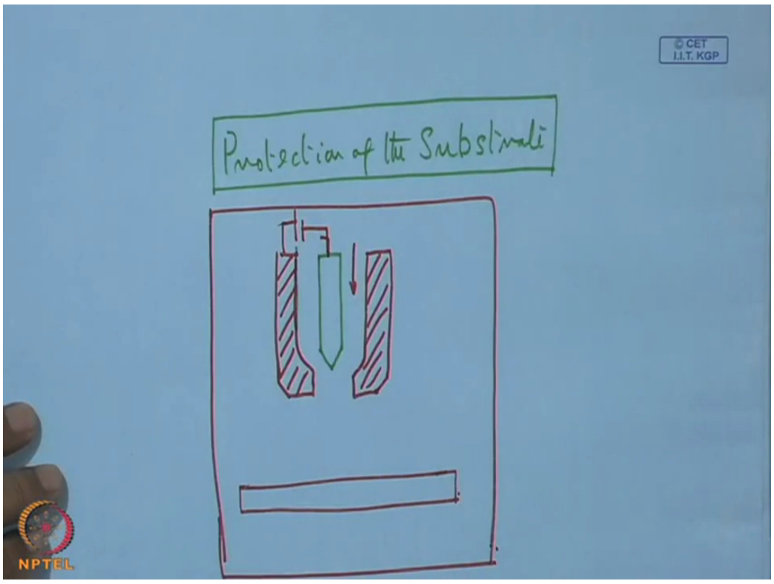

But in this case instead of positive polarisation we can have also a negative polarisation that means a power source which can have a negative polarisation on this surface. So with proper functioning we can have such thing, so that means it is plus and it can be also grounded outside this chamber. So what we see here? That this is actually negatively polarised and we don’t now run this plasma.

So what is done? Just like a sputtering process, here this Argon which is admitted that will be ionised in this zone between this plasma and maybe this anode surface or this wall of this chamber and in this case what happens? This Argon ion that will impinge on this surface and that will clean the surface and after this cleaning we can switch over to the negative polarity and sorry.

Now it should be negatively polarised and this is actually ion etching process, this is actually ion etching process. So that means Argon ions are used for cleaning of the substrate, so it will impinge with high velocity and that will exactly sputtering of the material from the substrate. So if there be any even atomic level, Oxide contamination that can be very easily cleaned by this process and with that we can get a very clean surface.

Now what we can do further to this? Now we can switch over to this positive polarity and with that we can get back to this transferred arc and with that transferred arc, what we can have? We can have this chemical bond formation by having extra energy. Actually what happens? When we have this positively polarised we draw electron on this side, so this electron’s are more efficient in raising the temperature of the substrate and this is exactly done.

And when it is positively polarised, it is Argon ion which will strike this surface and by this impingement by these collision it can remove in atomic scale the top surface layer, if it is oxidised that can be totally removed. So that is the greatest advantage of this vacuum plasma spray process.

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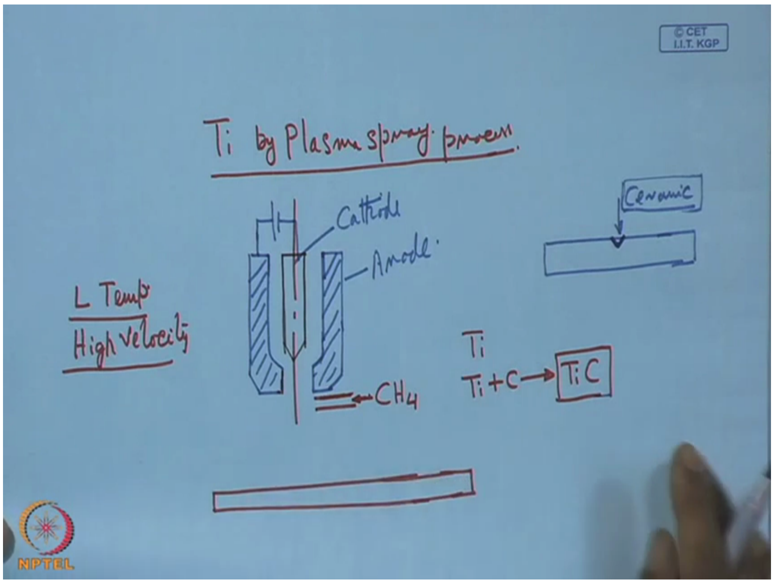

Now this is actually a reactive plasma spraying process. Now in this reactive plasma spraying process what we see? Say we know that Titanium Carbide; we can deposit Titanium by this plasma process. Say deposition of Titanium by process but if we are interested to have deposition of Titanium Carbide then that can be also handled just by this way, we have the centrally located cathode and then, so this way we have the anode-cathode combination, this is the anode.

So here what we see that buy normal route, Titanium can be deposited by having a nozzle somewhere here because in this case it is just the melting of Titanium, it is not high requirement or stringent requirement of temperature. So this can be done but what can be added in the system? We can have something like an entry point of say for example Methane in here.

So Methane will be admitted and with this addition of Methane, here we have Titanium ion and we have also Methane which will be ionised in this case liberating Carbon and finally what we have on this substrate? On the substrate what we have? We have Titanium and at the same time because of this reaction with CH4, we have also Titanium and Carbon and that gives Titanium Carbide.

So it is also possible to use this plasma arc spray process for having a reaction that means to have a reaction during the spray. So during its flight those Titanium will be converted into Titanium Carbide and that will impinge on this surface and that will heat this surface and that will be embedded in the metrics of Titanium. So this is actually what we call Titanium plasma spray process?

Now one thing we know here this is also good to know that this plasma spray process unlike the detonation process, plasma spray process is good for handling ceramic materials because here the temperature is very high but when it is a detonation process though the speed is very high but temperature is low and the substrate material which is actually heated by high velocity. So if we compare this detonation process and plasma process, what we have?

In detonation process, low-temperature and high impingement velocity and with that we cannot use this ceramic material. Now the ceramic material in that case, if we put that can just go with that material with that high velocity and that can hit the substrate and this and that can have some corrosion. So this ceramic material can cause some corrosion on this particular surface of the substrate.

So this ceramic material if we like to deposit ceramic material then this plasma process is a better choice compared to this detonation gun and this detonation gun is used for a soft material. So this is one important thing one can also note. So this is actually Titanium Carbide which is going to hit the surface but here the velocity is not that high compared to that plasma.

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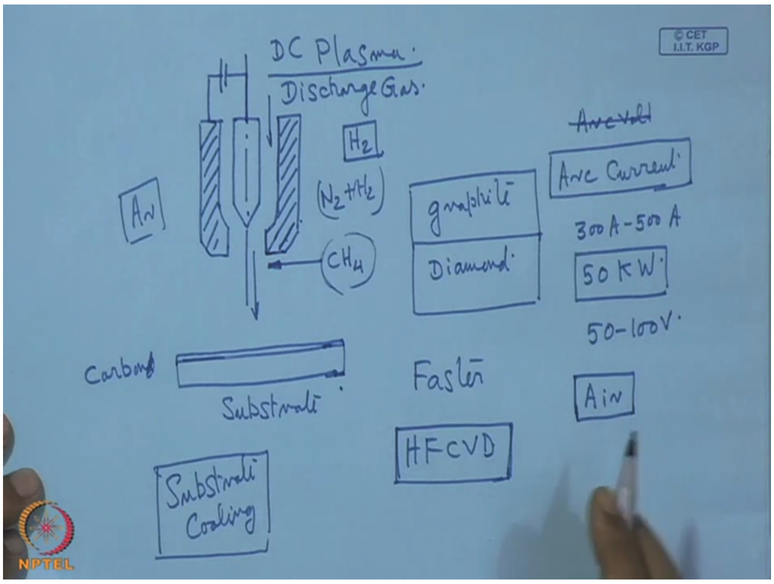

Now comes diamond coating by this plasma spraying process, diamond coating. Now what we see? That with this process this is actually the cathode and here what we have? The anode, so this is a copper anode and that is the Tungsten cathode and we can have this kind of connection between them and what else we have? Here we can have a substrate and this can be used for deposition of diamond that means we have discharged area and here we can have supply of Methane.

Now what happens? This stream of gas which is, here we have the discharge gas which can be also Hydrogen. Now what happens? This from Methane by this high-energy flow of this material in the substrate direction we can have deposition of Carbon separating this Hydrogen. So here we have deposition of Carbon in the form of a layer, so it is actually carbon. So this plasma wheel cause dissociation and with this energy available the Methane will be transformed into Carbon and that Carbon arrives here.

Now this Carbon can arrive in 2 forms, one is graphite another is diamond. Now it depends upon whether it is hot filament or this DC plasma jet, this is DC plasma jet. This DC plasma jet can be also used for this deposition of diamond but there are 2 chances either graphite or diamond. So if graphite forms then that is most undesirable thing and to remove that one we have continuous supply of Hydrogen and etching rate of graphite is much more compared to that of diamond.

So naturally diamond will be, etching rate of diamond will not be that fast. So diamond will be retain their in much more quantity compared to graphite. So the whole idea is that if there is any graphite form that should be removed by this chemical etching with the help of Hydrogen and this way we can also use this DC plasma discharge for deposition of diamond. Now in contrast to hot filament CVD this DC diamond discharge process, diamond formation process that is a faster process compared to hot filament CVD process.

So this is a process of immediate interest for diamond deposition. Now this will be good for those places which are flat and which are with simple geometry flat surfaces square block, rectangle something like that where deposition of diamond by using this torch will be easy because it is a directed process. It is directed and it is according to this stream velocity which will be intercepted by the substrate surface and deposition will be met.

However if we like to have this process on a complex geometry in that case definitely this hot filament CVD will be a better choice. Now for this DC plasma deposition, what are those process parameters? One is very important that is the arc current or say arc voltage, sorry arc current or power of the machine. So arc current in all routine application it can go straight to 300 ampere to 500 ampere and it can be just 50 kilowatts machine but voltage wise the voltage is rather low it can be between 50-100 volts it can operate.

Then comes one very important thing that powder feeder, normally powder is fed by air as the carrier gas but here the quality of air that is also one important issue and this air has to be number 1 because the source of will be a compressor and from this air which is coming out of a compressor delivered by compressor that should be filtered from all sort of oil which may be the contamination from the compressor then this filtering is done followed by drying in air dryer.

So this filtering and air drying is essential stage to get one quality air and that that should be a metered quantity and there is a vibratory feeder which is also used for feeding the powder in the metered quantity than also comes the discharge gas it is sometimes we use Nitrogen and Hydrogen or sometimes it is also Argon alone but as we have said that Nitrogen, Hydrogen being diatomic gas that is of immediate interest because the conductivity of Hydrogen is also very high and at the same time this enthalpy of formation that is also very high.

So these are the 2 issues one has to also consider then comes the stand of distance, what is the stand-off distance? And then what is the angle of incidence that means at which angle the material is thrown and material is striking because of the simple reason that here the dense coating has to be formed and it is not just a follow-up heating process. So during this process the entire adhesion bond formation has to take place then another thing is also very important cooling of the substrate.

Substrate cooling, the whole idea here is that substrate should not be allowed to be distorted and there to maintain uniformity of the temperature over the entire surface that is also one of the point one has to look in, so this controlling of the substrate temperature that is also one of the parameter then abrasive size the material which is being deposited here that size is also one parameter.

Normally say a grain size, 50 micron or 100 micron that is a size which can be used but if we have a lower size than handling this by these air in that powder feeder that becomes little complicated task because of the absorption of moisture in the system, so that has to be also taken care of by this process.

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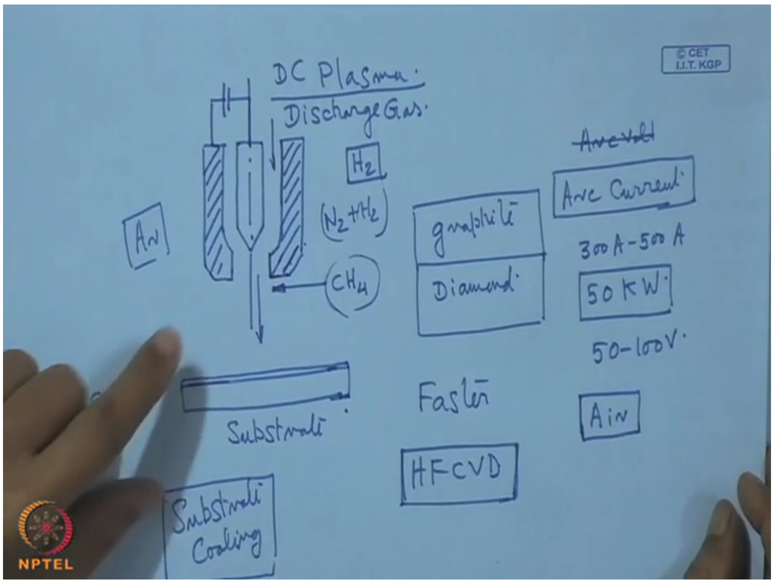

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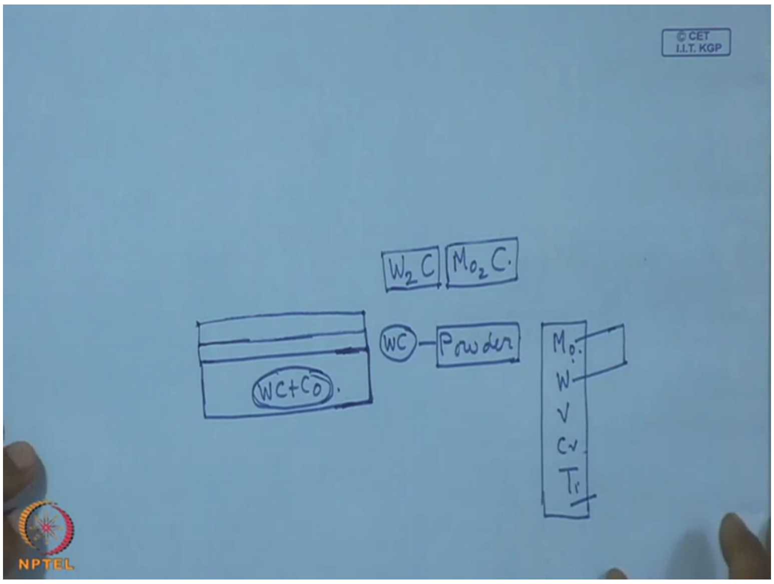

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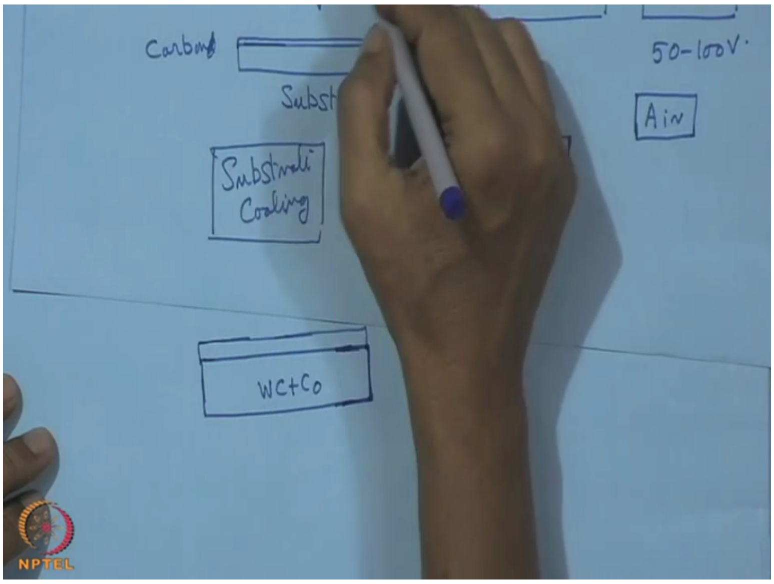

Now this coating of diamond which we have just mentioned here, that we can also extend this process this way that means normally what we see? That on a substrate we have to deposit diamond and then this can be have a transition, say we have Tungsten Carbide Cobalt and from there we can have a deposition of just Tungsten Carbide by this plasma spray process by allowing Tungsten Carbide as a feeder from this side and gradually Tungsten Carbide and Carbon that proportion can be adjusted that means here we have Tungsten Carbide and also that deposition of Carbon from this Methane and finally what we can get here? Pure diamond coating.

So that means first we have Tungsten Carbide Cobalt and then this is Tungsten powder which can be also deposited by this plasma spray process and in the process we can also initiate flow of Methane, so it will be going to be a mixture of Tungsten Carbide of its diamond particle, so that will be an embedded, so it is a dispersion and finally we can also have a diamond built up over this.

So this way we can also see that this effect of Cobalt detrimental effect of Cobalt that can be also eliminated and we can have a fairly transition between Tungsten Carbide cobalt, Tungsten Carbide and also Tungsten Carbide diamond and Tungsten Carbide diamond to pure diamond, so this way fine transition is possible but while choosing this deposition technology with this DC plasma discharge process using Methane as the source of carbon, definitely one has to look for those materials which are good candidate for this diamond formation and for this what we can see?

That this material like Molybdenum, Tungsten and then Vanadium, Chromium, Titanium lot of materials can be tried but in that list what we can see that Molybdenum and Tungsten they are most preferred materials in the whole process because of the simple reason that Molybdenum, Tungsten are good Carbide former but they are less prone to oxidation compared to Titanium or Chromium, not only that what can be seen?

That density of nucleation on Molybdenum and Tungsten that comes out to be very high and this is because of some matching with this Carbide of W2C and Mo2C type Carbide which is not just possible with Titanium or other material. So this W2C or Molybdenum M2C these Carbides are formed over this when this Methane comes over this surface and immediately this type of Carbide is formed over which this high-density diamond nucleation is possible.

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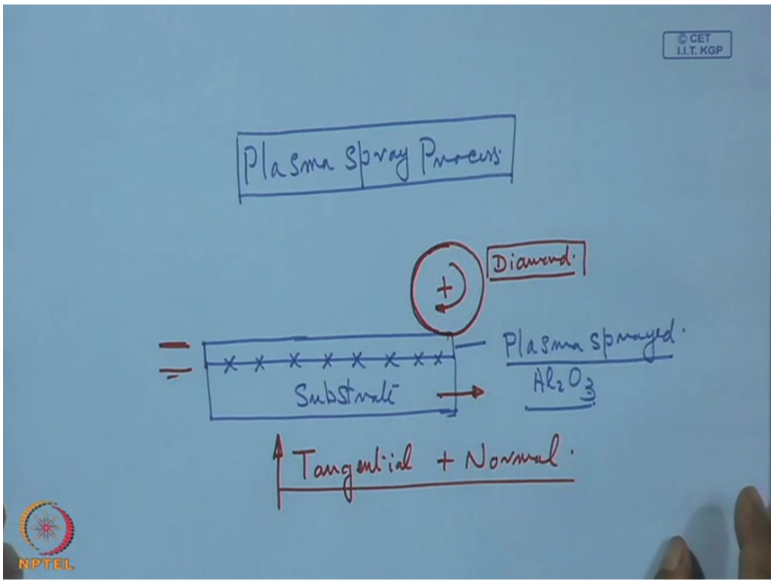

So this Molybdenum and Tungsten that facilitates formation of such kind of Carbide and that follows nucleation with high-density of diamond. Now one thing is also important when it is a plasma spray process this adhesion part is very important because here we don’t have exactly a chemical bond formation just by melting a part of the substrate surface. So this bond formation or adhesion which is developed at this interface that can be checked there are certain ways of checking this because it is a very hard material.

So it is actually plasma sprayed and this is the substrate, this is the plasma sprayed say Aluminium Oxide. Now this how is the adhesion with this surface? For that we can also conduct a test which is called almost like grinding and this is done this way, okay. This is done this way that we have one grinding wheel here and this grinding wheel is made of diamond, it is a fine grain of diamond.

And with this grinding wheel we can grind say it is a thick layer and these are the materials which are not far micron level deposition but it is actually in the millimetre level deposition 5, 6 millimetre is quite routine thing, so that it can serve as a wear resistance coating and also as a thermal barrier shield, so in this case what we can do? Over the surface can have a proper grinding action with certain feed and high table speed?

So this whole sample will be put on a table and on the table of the grinding machine and then the wheel this will be moved in this direction, so we have certain theft of cut, so with that there will be some tangential force. So there will be some tangential force and also some normal force. So depending upon this adhesion what can be done? Gradually the depth of cut can be increased and as a result of that what's going to happen? This tangential force that will go up.

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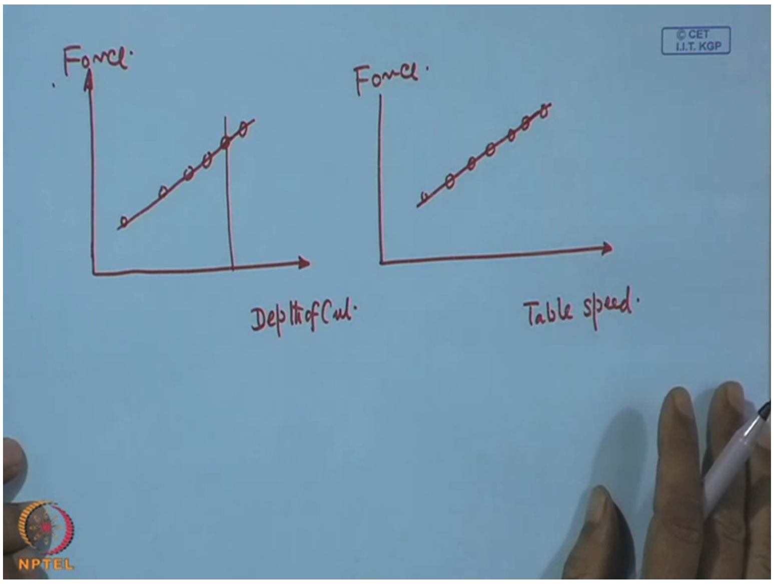

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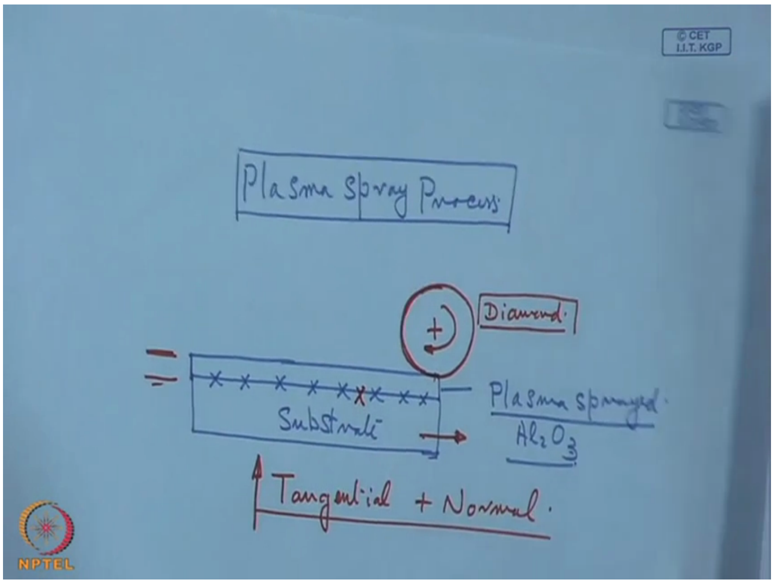

Now if we find that the whole layer can be removed by gradual grinding without having any interface failure then we can record a particular force and from that we can say up to this point that means we can, this is the force, grinding force and this is say depth of cut and by increase of depth of cut this force will keep on rising. However if this force doesn't cause any flaking of this coating then we understand that this is strongly adhering and the bond is quite strong.

So it is quite satisfactory but we can find that, if it is possible or if it is the case that at certain point apart or whole of this chunk gets removed as a whole, as a layer leaving that interface and exposing the substrate in that case we can say that is the limit and that causes the removal of this coating, this is one way of doing the thing but also we can do just by keeping a particular depth of cut and we can record the force.

We have to increase the force and here we can increase the table speed, we can increase the table speed. So force will keep on increasing just by increasing the table speed and here also we need not increase the depth of cut, keeping a particular depth of cut if we increase the table speed and if we see that the coating survives over the entire period of cut and having a particular force level up to which the coating is integrated with the substrate that we can also say that the adhesion is good.

Adhesion is quite satisfactory up to that level of force but if it is not the case then definitely we have to take some measure, so that we can improve the situation it can be either having a proper bond coat having proper substrate preparation particularly the mechanical working of a substrate, mechanical preparation of the substrate and also having proper cohesion in the coating.

So this way we can also check the adhesion of this coating, otherwise checking the adhesion of this rough coating the surface is quite rough, so rough coating is just not possible with conventional scratch tester.

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So with this we can make a summary of the discussion that plasma spray is basically meant for all material to be deposited we need which are having high melting point and it is mostly the ceramic material to give some example it is Aluminium Oxide, Zirconium Oxide, Titanium Oxide these are the some material of immediate interest for engineering use, they can be used as thermal shield and also in many cases as wear resistant material.

Now this thermal plasma spray that can be used as an open atmosphere process or a vacuum deposition process, now in open atmosphere we can also extend this arc to this substrate thereby getting extra heat on the substrate surface, so that there may be some kind of melting of the substrate surface and facilitating dilution of the coating with the substrate and having a metallurgical type of bond which leads to better adhesion.

We can also have vacuum plasma spray, this is to protect the substrate surface but the greatest advantage of vacuum plasma spray is that by having negative polarisation of the substrate we can invite the Argon ion just like a normal sputtering process leading to ion etching and this will lead to absolute cleaning of the substrate inside the chamber and which can be followed immediately by the actual deposition process.

Now this plasma spray process can be extended for reaction plasma spray process for example we can have Titanium powder as the material for deposition but having this Methane in the chamber in the system we can also have spray and reaction that means Titanium during this spray process it also gets converted into Titanium Carbide grain and then we can have a dispersion of Titanium Carbide grain in a metrics of Titanium, enhancing its hardness and wear property.

Similarly deposition of diamond that is one of the very special processes of plasma spray using this process. Now this process can be used for diamond deposition but making a transition from Tungsten Carbide Cobalt to finally a diamond surface using the same DC plasma's torch and the adhesion of this process by normal scratch tester, since the surface appears to be rough it cannot be done but some grinding technique using a fine diamond wheel that can be used effectively to assess, numerically assess the adhesion of the coating.