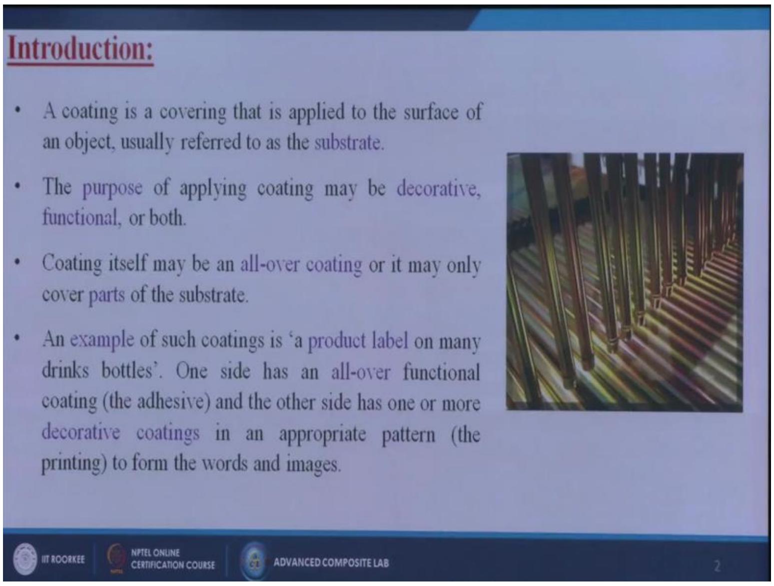
Surface Engineering of Nanomaterials
Dr. Kaushik Pal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology, Roorkee

Lecture - 18
Advanced Coating Practices

Hi. In this lecture we are going to discuss about the Advanced Coating Practices. Till now we are discussing about the different coating practices may be the conventional coating practices, but in this particular lecture we are going to discuss some advanced coating practices which we are going to do on to the substrate so that we can get some better enhanced properties.

So, before going to start let us just know that what is the coating practices, what are the advantages of this coating practices, and what benefits actually we are getting.

(Refer Slide Time: 00:54)



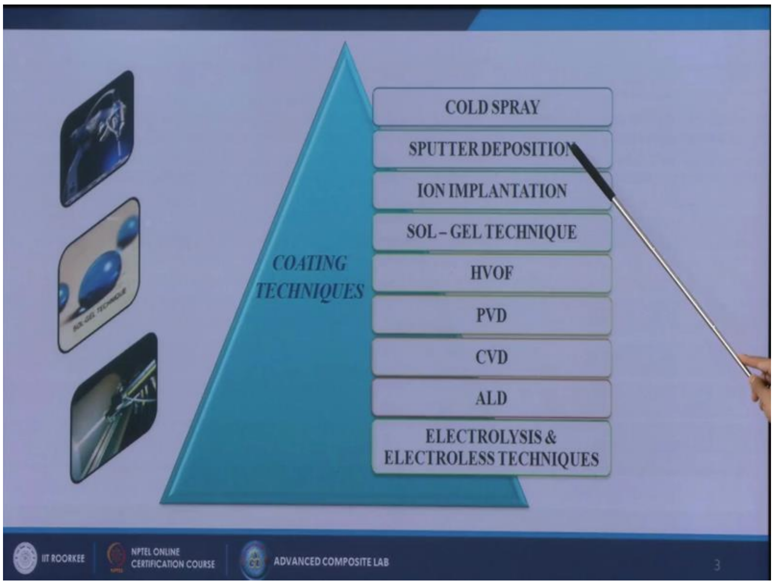
So, coating is a covering that is applied to the surface of an object usually referred to as substrate. So, substrate is nothing but the materials or maybe the metals which we are going to coat; so that is the best one. So, the thing is that either you can incorporate some materials inside the substrate so that we can do make a composites or maybe some kind of blends or maybe the alloys, but here without changing its chemical structure from outside we are giving some kind of layers of materials onto that surface or with that substrate so that we can get some better enhanced properties.

The purpose of applying coating may be decorative, functional or both. So, here the coating generally the decorative, means it should be looking more attractive or we have to make it more lucrative or sometimes it is functional; that means, it can enhance some kind of mechanical properties, some kind of chemical properties, some kind of thermal properties or the both. Coating itself may be an all over coating or it may only cover parts of the substrate. It depends upon us, that depending upon the applications, depending upon the uses either we can do the coating of the entire surface or maybe any specific surface which we want actually, so we can do the coating of that particular surface too.

Then, an example of such coating is a product label on many drinks bottles. One side has an all over functional coatings the adhesives and the other side has one or more decorative coatings in an appropriate pattern when we the print to form the words or images. Suppose, we are taking any kind of drink bottles like Coco-Cola, Thums Up we can see that a label is stick on to the bottle right; one side is the lucrative one where we can see that the name of that bottle drinks what are the contents of that particular drinks what are the price what are the manufacturing date. And the opposite side we are putting some kind of adhesives so that it can stick with the bottle.

So, the both side we can do, we can do by one side or maybe as per our requirement.

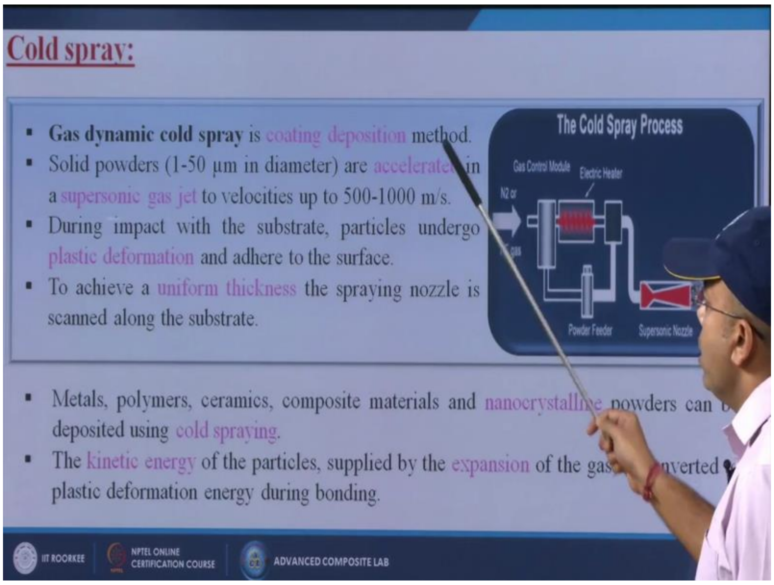
(Refer Slide Time: 03:07)



Then the coating techniques; there are several types of coating techniques are available like. First one is called a cold spray, then the sputter depositions, then anions implantation then sol-gel technique, HVOF is nothing but the high velocity oxygen, PVD is the physical vapour deposition, CVD is the chemical vapour deposition, ALD is the atomic layer deposition and the last one is called the electrolysis and the electroless techniques. So, there are several types of coating techniques are available.

Now in our subsequent slide we are trying to discuss about the cold spray technique. So, in the cold spray technique before going to start these techniques we have to know that what is that technique actually means.

(Refer Slide Time: 03:47)



The gas dynamic cold spray is coating deposition method. Solid powders generally 1 to 50 micrometer, so the powder or maybe the whatever the materials we are going to coat that is into the micrometer range are accelerated in a supersonic gas rate to velocities up to 500 to 1000 meter per second. So, this velocity actually depends upon the substrate whether that much velocity it can sustain or not. So there is a wide range of particles, we are throwing onto the substrate material in a very high velocity depending upon the substrate physical properties and chemical properties. And then these solid powders are sticking on to the substrate itself.

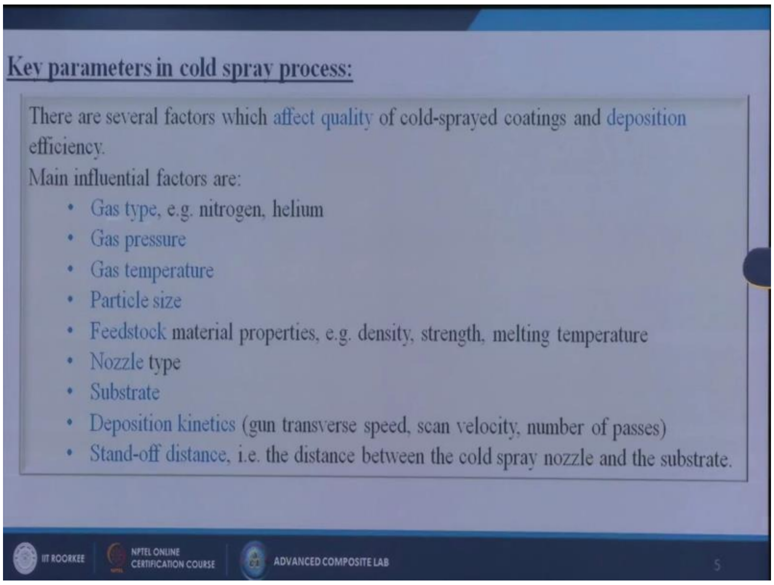
Then during impact with the substrate particles undergo plastic deformations and adhere to the surface. So, when we are throwing those particles from a particular distance it is gathering some kind of kinetic energy and due to that impact that material or maybe that powder is sticking on to the substrate and then it is sticking to that substrate or maybe adhere to the surface itself. To achieve a uniform thickness; the spring nozzle scanned along the substrate. That means, suppose this is the spring nozzle and if I want to coat this material, so I have to put the substrate in a manner so that these gun or maybe these nozzle can go through all around towards its surface so that a uniform coating thickness can be achieved.

So, here generally metals, polymer, ceramics, composite materials, and non crystalline powders can be deposited using the cold spraying process. And the kinetic energy of the particle supplied by the expansion of the gas is converted to plastic deformation energy during bonding. So, here we are using some time that carrier gases, those who are taking the nanopowder from the nozzle to the substrate. So, just it is carrying this powder so that that powder in a high velocity can hit your substrate materials and stick on the surface itself.

So here, generally this one is a schematic diagram where we are putting some kind of nitrogen or maybe the helium gas inside the chamber. Then we are having some kind of electric heater so that, that gas is little bit heated up and then we are having the powder where we are putting the coating materials, then it is mixing together in this particular chamber, then it is some kind of supersonic nozzle through this nozzle it is coming and it is hitting the substrate in a very high velocity. So, mainly this is the principle of this particular technique.

So, here the key parameters in cold spray processes are there are so many factors which are influencing the cold spray technique.

(Refer Slide Time: 06:42)



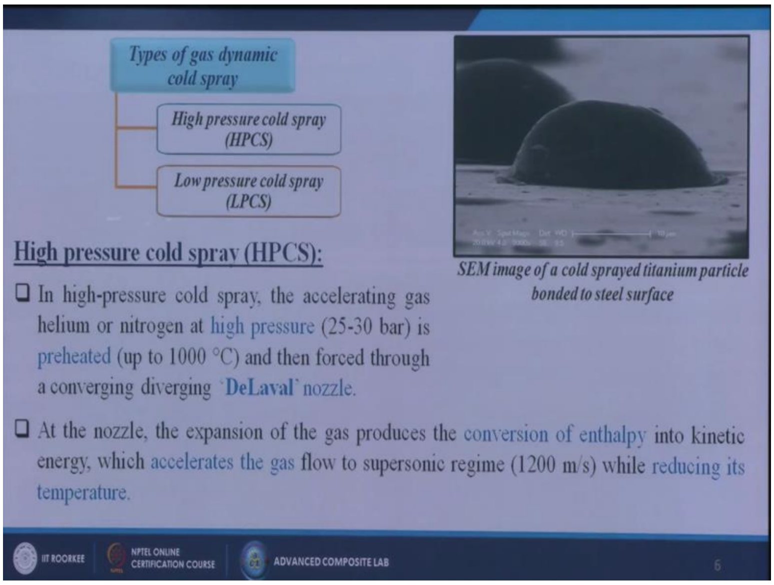
So, there are several factors which affect quality of cold sprayed coatings and deposition efficiency, what are those? First is called the gas type, what type of gas actually we are using, like helium, nitrogen. So, it depends that what is the substrate actually. So, the reactive gas it should not react with the substrate that we have to keep in mind. Then what is the gas pressure. That gas pressure means, how much pressure we are releasing that gas so that that nanoparticle can achieve that much of velocity and it can stick with the substrate itself. Then what is the gas temperature so that, that particles should be little bit melted and it can stick with the substrate itself. Then what is the particle size of those nanoparticles; whether it is too fine so that we can get a uniform coating, if the particle size will be little bit bigger or maybe the coarse grain size then the coating may not be uniform or maybe that surface may not be smooth sometimes we can get some kind of wavy surface too.

Then feedstock material properties like, density, strength, and melting temperature of these particular nanoparticles. Then nozzle type means, what is the size of that nozzle particularly in diameter. If we go for a bigger nozzle diameter so that the area whatever we are covering will be more. If the nozzle size will be less then automatically the particles velocity will be increased, and not only that the area covered area will be less. What are the substrate materials? Whether it is may be it can sustain that pressure or not it can sustain that temperature or not, so that what is the melting temperature of that particular substrate, what is the mechanical strength of that particular substrate so that that powder particle can hit that one, but it will not affect the substrate properties.

Next is the deposition kinetics; gun, transfer speed, scans velocity, number of passes. Means, if we want to increase the thickness of that coating, so several times we have to scan our gun onto the substrate so that the layer by layer coating thickness will be increased, so that the overall coating thickness will be increased. And the last is that standoff distance; then distance is nothing but the distance in between the nozzle and your substrate. So, if we go for a longer distance so automatically that transverse speed sorry, transverse area will be more so that the particle velocity will be reduced. If it will be too close then the particle velocity will be increased, but the covered area will be less. So, it depends upon the standard distance you can increase or decrease the covered area of your particular substrate.

So, here we are going to discuss this cold spray what are the types actually. So, there are two types of cold sprays are available nowadays.

(Refer Slide Time: 09:41)

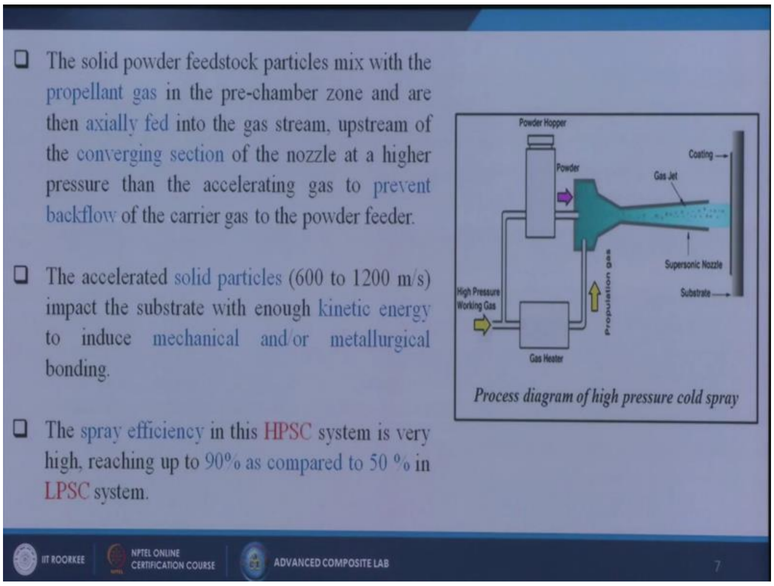


So, first one is called the high pressure cold spray, in a short form it is known as the HPCS; and next one is called that low pressure cold spray, in a short form it is known as the LPCS. Here, first we have to know that; what is the high pressure cold spray. So, from the dream itself you can understand that in that particular technique we are using the high pressure; that means, a high pressure is using to throw these nanoparticles on the substrate itself.

So, in that particular case the accelerating gas helium or nitrogen at high pressure generally 25 to 30 bar we are applying is preheated up to 1000 degree centigrade and then forced through a converging diverging DeLaval nozzle. So, that nozzle is having a particular name, the name of that particular nozzle is known as the DeLaval nozzle. So, at the nozzle the expansion of the gas produced the conversion of enthalpy into kinetic energy which accelerates the gas flow to supersonic regime 1200 meter per second while reducing its temperature. So, that the gas is getting that much of accelerating velocity so that that nanoparticles is flowing onto the substrate in a very high velocity.

And right hand side corner it is an SEM image or maybe the scanning electron microscopy image that this is the substrate on which this powder is throwing in high velocity and it is sticking with the surface of that particular substrate. So, SEM image of a cold sprayed titanium particle bonded to steel surface. So, this is made by the steel and here generally we are using the titanium particle. So, 1 particle, 2 particle, 3 particle like that so all the particle will come in a one space and they will make heat and after that we will get a final coating layer or may be the uniform layer of that coating materials on to the substrate itself.

(Refer Slide Time: 11:44)



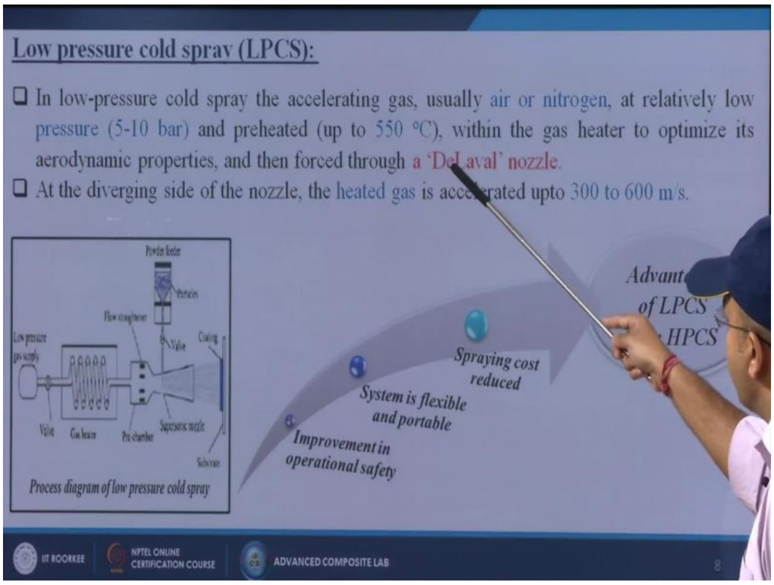
The solid powder feedstock particles mix with the propellant gas in the pre chamber zone and are then axially fed into the gas stream, upstream of the converging sections of the nozzle at a higher pressure than the accelerating gas to prevent backflow of the carrier gas to the powder feeder. Here just we are simply applying one non return valve which will allow the particle to go forward, but when they will mix properly they will not come to the back portion itself. The accelerated solid particles generally 600 to 1200 meter per second impact the substrate with enough kinetic energy to induce mechanical or metallurgical bonding or maybe sometimes both. The spray efficiency in the HPSC systems is very high reaching up to 90 percent as compared to 50 percent in the LPSC; LPSC is nothing but the low pressure cold spray techniques.

So, in this particular case this is the process diagram for the high pressure cold spray where we are applying the high pressure working gas over here, we are having the heating arrangement over there for which we are hitting that gas up to 1000 degree centigrade, then the gas is coming into this chamber. We are putting the coating powder into this chamber. Then powder and this gas is mixing into these sections. Here we are putting some kind of non return valve so that the powder should not go back into this powder hopper or maybe that mixture of powder and gas should not come to the gas heater. Then, after mixing we are allowing this materials mixture of gas and particles through throw in a high pressure so that it can heat on to the substrate and it can make it uniform coating to the substrate itself.

Next one we are going to discuss about the low pressure cold spray. In the low pressure cold spray from the name itself we can understand that here we are using very very low pressure than the high pressure itself. If you remember for the high pressure we have applied the pressure from 25 to 30 bar, but in this particular case we are applying the pressure from 5 to 10 bar only. And that time we are using that preheated gas up to 1000 degree centigrade, but in this case we are preheating these gases up to 550 degree centigrade.

So, in the low pressure case we are reducing the gas temperature as well as the pressure of that particular gas, otherwise everything is the same.

(Refer Slide Time: 14:19)



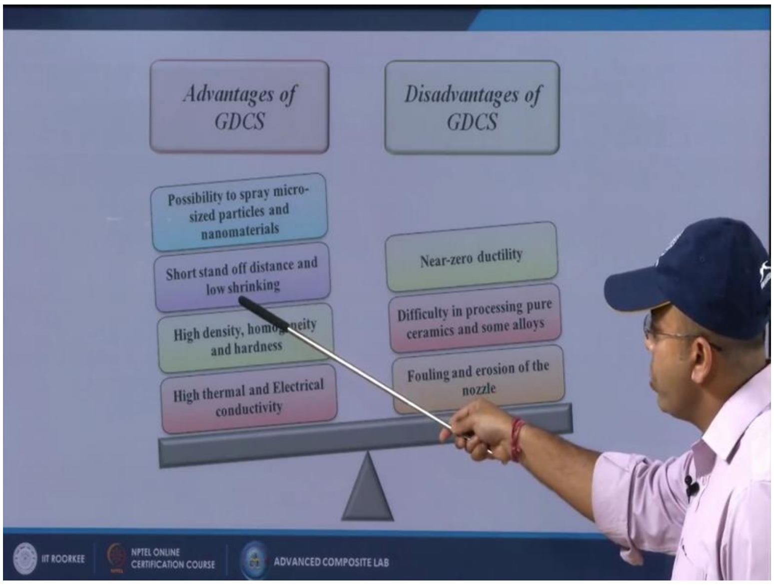
Then after mixing these two again it is coming through the DeLaval nozzle and directly it is depositing on to the substrate. At the diverging side of the module the heated gas is accelerated up to 300 to 600 meter per second that time it reached up to 1200 meter per second.

So, here from this particular case you can see that accelerated velocity is reducing that is why it is called the low pressure cold spray process. So, in this particular case the application is almost same like the high pressures, here just simple instead of high pressure gas we are supplying the low pressure gas, then we are having some valve, then we are having that gas heater; that means, this heated gas should not come out or maybe should go back to its again the gas pressure assembly. Then after that we are having some pre chamber that is known as the flow straightener also we are putting over here. Then we are putting the powder material or maybe that coating material inside it. Here the gas and powder both are mixing properly. Here also we are putting some kind of non return valve so that the powder only comes to in these directions it should not go back.

Then we are having that DeLaval nozzles or maybe that supersonic nozzles by which they are mixing of gas and powder is directly coming and it is depositing onto the substrate itself. Only the basic difference in between the HPCS or maybe that LPCS is that, that in one case we are using the high pressure another case we are using the low pressure and one case we are heating the gas up to 1000 degree centigrade, in one case we are hitting the gas up to 550 degree centigrade. And the thing is that it only depends upon what type of substrate you are using; whether your substrate can sustain up to 1000 degree centigrade or we can sustain up to 550 degree centigrade, whether they are pressure is from 25 to 30 bar, whether it can be sustained by them your substrate or not; if not then we have to go for that low pressure cold spray technology.

Here, are the advantages of LPCS over HPCS. First is that improvement in operational safety. Of course, here we are applying no pressure, low temperature so it is good for the operator it should not be very very hazardous or maybe some kind of explosions can be taken away. Then next is that system is flexible and portable, because we have to generate the low pressure and low temperature, so the system is totally portable and flexible and spraying cost is reduced; because we are not increasing the temperature, we do not need any kind of high pressure pump so that it can generate a high pressure, so automatically the spraying cost will be reduced, so these all at the advantage that for which we can go for LPCS than the HPCS.

(Refer Slide Time: 17:26)

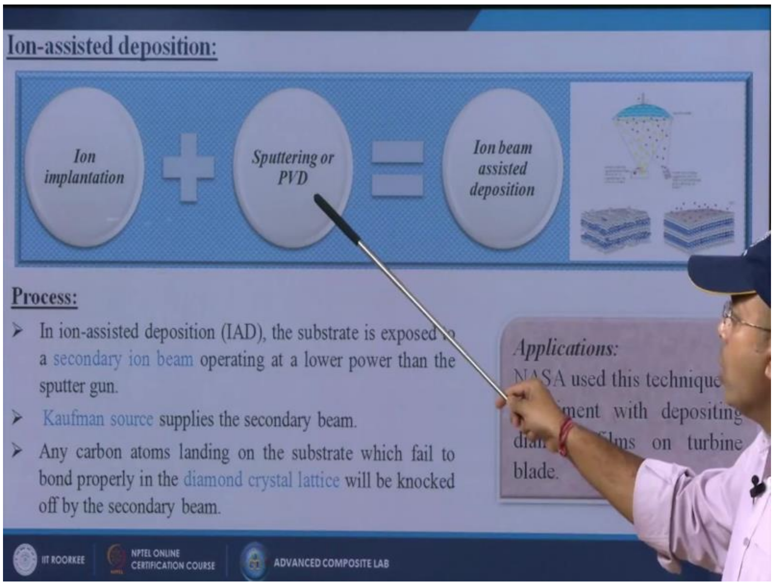


Next, it is a good study about that advantage of the GDCS. And the disadvantage of the GDCS: first one is called a possibility to spray micro sized particles and nanomaterials, short standoff distance and no shrinkage. That means, when we are doing the coating the particle is heating the substrate materials, but if the dimension of that particular substrate will be changed then it is very very difficult because our material properties material size diamonds on everything will be changed. So, that is why here for this particular case the shrinkage is very very minimum; that means, distortion of your substrate will be very very less, not only that short stand up distance. That means, the distance from your nozzle and your substrate should be very very less.

And high density homogeneity and hardness can be achieved in this particular case. High thermal and electrical conductivity can be achieved in this particular case, but of course there is certain kind of disadvantages also present. First one is called that near zero ductility can be observed by these techniques, difficulty in processing pure ceramics and some alloys are possible; fouling and illusions of the nozzle, because your particle is continuously coming through this nozzle. So if there is we are applying some kind of particles which are having the ablative in nature they can rub your nozzle so that the nozzle diameter can be increased or maybe that the nozzle that particle will heat inside your nozzle, so that maybe some poles or cracks can be possible inside your nozzle; so, these all at the disadvantage of these particular techniques.

Next techniques we are going to discuss are about the anions assist depositions. If you remember in our some previous lectures we have already discussed about the anions implantation. But in this particular lecture we are going to discuss that is anions assisted depositions which is nothing but a composition of two techniques or rather it is a mixture of two techniques; one is called the anions implantation another one is called the sputtering or the PVD technique.

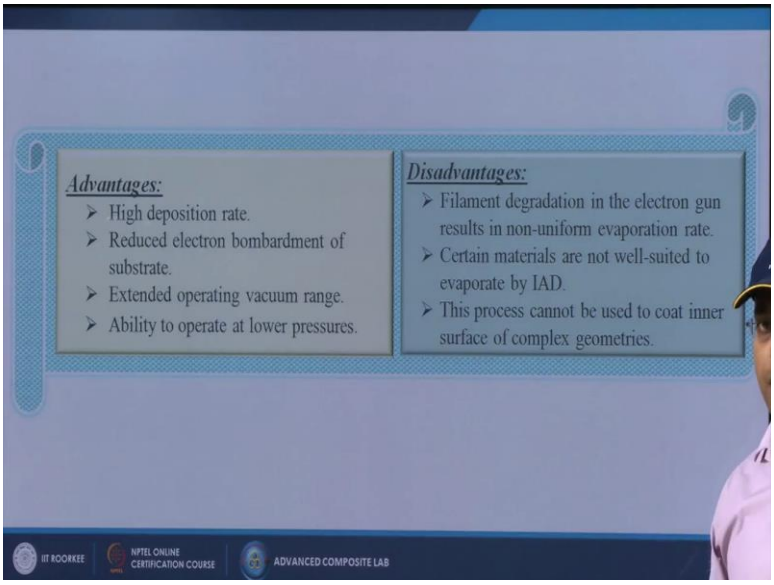
(Refer Slide Time: 19:29)



So, anions implantation and sputtering techniques, together is giving you the anions beam assisted depositions. What is the process? In anions assisted depositions generally in the short form it is known as the IAD, if the substrate is exposed to a secondary anions beam operating at a lower power than the spatter gun. Kaufman source supplies the secondary beam. Any carbon atoms landing on the substrate which failed to bond properly in the diamond crystal lattice will be knocked off by the secondary beam.

So, simple the powder it is coming, it is hitting your substrate, then you are applying the secondary anions beam which is giving a temperature so that the any unbounded nanoparticles it can stick properly onto the substrate itself. What are the applications? NASA uses this technique to experiment with depositing diamond films on the turbine blades. So, these all are the advanced applications which we are going to do by these anions assisted deposition techniques.

(Refer Slide Time: 20:38)

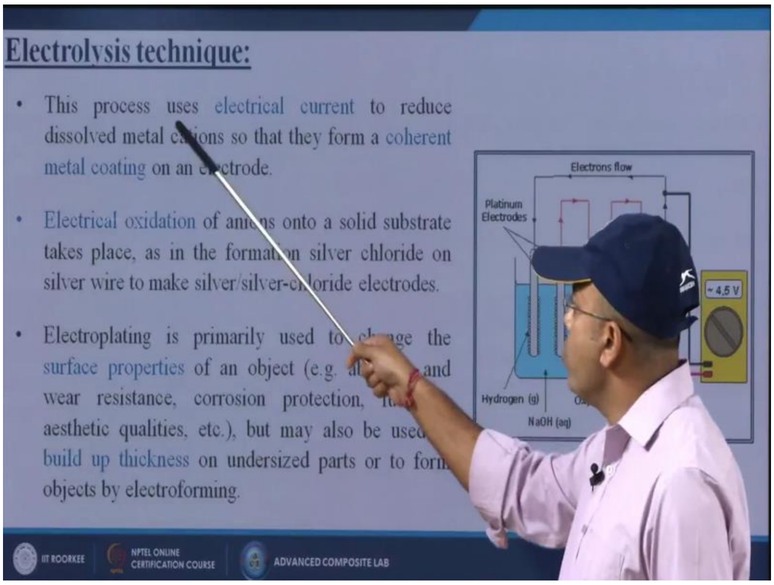


What is the advantages of this techniques? High deposition rate reduced electron bombardment of the substrate, because we are not going to disturb our substrate by any kind of electron bombardment so that it can change its shape and size; extended operating vacuum range, ability to operate at lower pressure. So, these all are the advantages for these particular techniques.

And what are the disadvantages: filament degradation in the electron gun results in non uniform evaporation rates, because as the time is going on the filament is continuously glowing so after certain time the lifespan of the filament will be reduced, so the filament will not properly giving the particular temperature. Or maybe certain materials are not well suited to evaporate by the anions assisted depositions IAD process. This process cannot be used to coat in a surface of complex geometries. Means, there is a disadvantage that it can only coated the outer surface it cannot go inside any complex ships.

Next one is called the electrolysis techniques. So, this process from the name itself you can understand that here we are trying to apply some kind of electrical current. That means, we have to put the potential difference in between the two electrodes and by which we can do the coating.

(Refer Slide Time: 22:00)



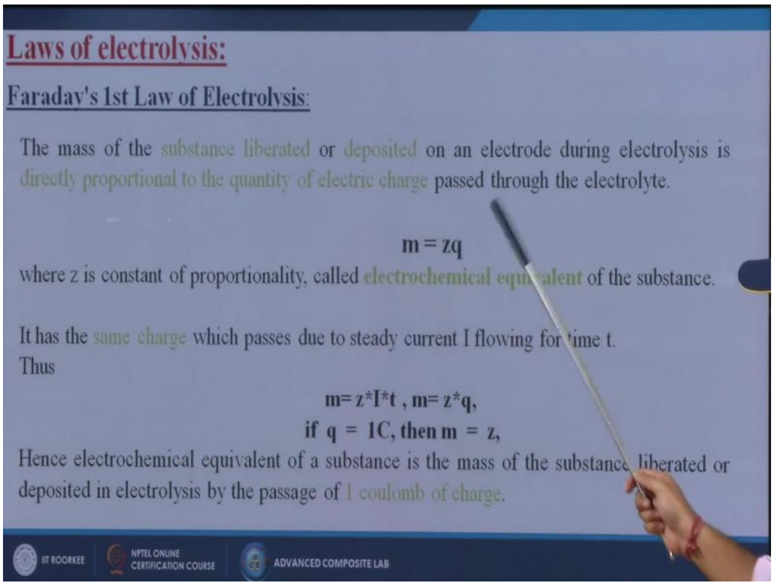
So, in this particular case this process uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating to an electrode. In this particular case we are applying the electrical current on to our substrate, and due to that we are putting these materials into some electrolytic solutions. And then when you are putting the current or maybe we are giving the current or maybe we are applying the current to those electrodes that chemical reaction is going on. Then from that particular self suppose I want to do the coating of some copper material, I can take some copper sulfate solutions.

So, when I am applying these currents the copper sulfate it will give you the copper anions which will simply deposit onto your substrate material. So, just I am giving one examples. So, here the electrical oxidation of anions onto a solid substrate takes place, as in the formation silver chloride on silverware to make silver silver-chloride electrodes. So, here on the silver substrate just we are going to give a silver coating or maybe that silver chloride coating onto that substrate itself.

Electroplating is primarily used to change the surface properties of an object; like abrasions and wear resistance, corrosion productions, lubricity, aesthetic equalities etcetera. But may also be used to build up thickness on underside pass or perform objects by the electro forming. Sometimes not only that we can increase or decrease the coating thickness, sometimes we have made some samples, but it is maybe less size; so just increasing the dimension of that we can do this kind of electroplating over there so that it can achieve the proper dimensions.

So, before going to tell that technology behind this we have to primarily see that; what are the laws of electrolysis actually? So, we already we have gone through this kind of laws in our class 12th standards, but again just to give a reminder of this I am once again telling this laws.

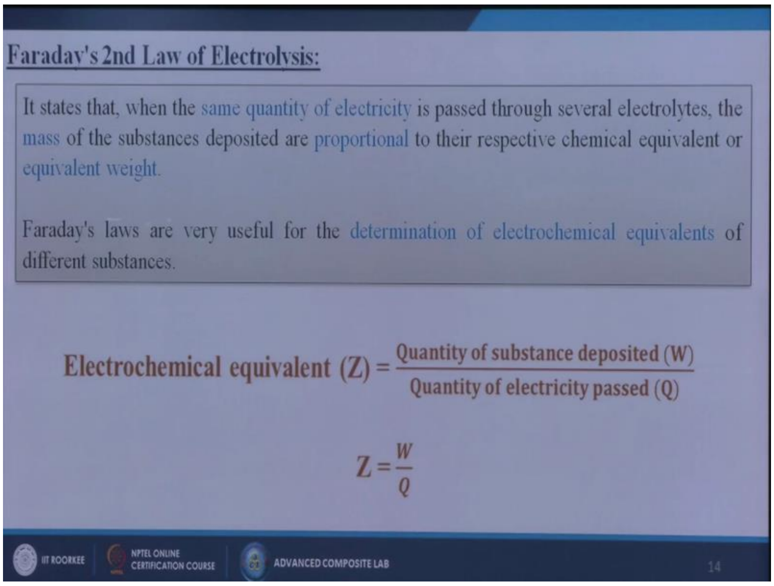
(Refer Slide Time: 24:28)



First one is called the Faraday's 1st Law of Electrolysis. So, based on these laws just we are doing the electroplating onto our sample. So, here the mass of the substrate liberated or deposited on an electrode during electrolysis is directly proportional to the quantity of electric charge passed through the electrolyte.

That is small name equal to z into q; where q is the charge, m is the mass of your particular material, where j is constant of proportionality called electrochemical equivalent of the substance. Then it has the same charge which passes due to steady current I flowing for time T. Thus, m is equal to z into I into t, m equal z into q; if equal to one coulomb then m equal to z. Hence, the electrochemical equivalent of a substance is the mass of the substance liberated or deposited in electrolysis by the passage of one coulomb of charge. So, this is the general standard calculations by which we can calculate; what is the coating thickness how much material can deposit on to that material for over up time

(Refer Slide Time: 25:31)

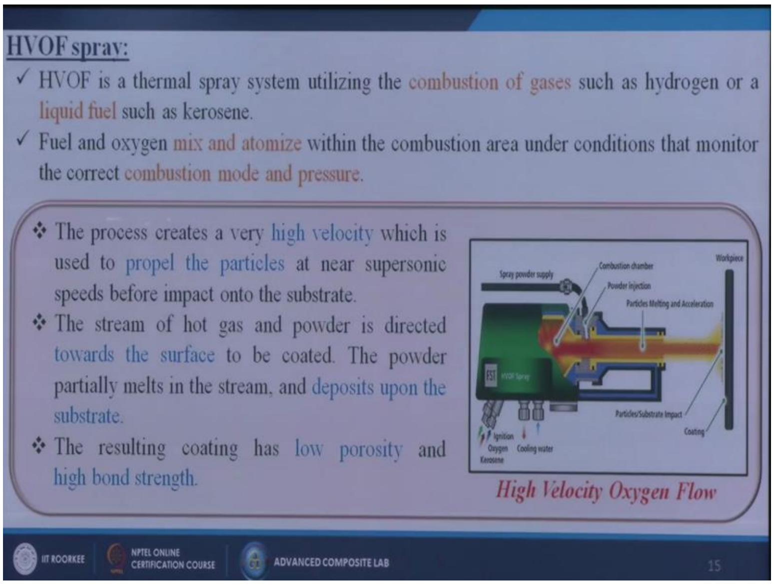


Next, is also the important laws which also associated with this electrolytic depositions. So, that is also the Faraday's 2nd Law of Electrolysis; which states that when the same quantity of electricity is passed from several electrolytes the mass of the substance deposited are proportional to their respective chemical equivalent or maybe the equivalent weight. So, when you are applying the different current, different voltage or to a particular material or maybe to a particular electrolyte the deposition rate is totally different.

Faraday's laws are very useful for the determination of electrochemical equivalents of different substance. So, here the electrochemical equivalent what he has given Z equal to quantity of substance deposited-W divided by quantity of electricity passed-Q. So, simple Z equal to W by Q. So, this is the 2nd Law of Faraday's principle.

So, next one what we are going to deliver is called the HVOF; in a short form it is known as the HVOF, if we go for the bottom name that is known as the high velocity oxygen flow. So, in this particular case it is also one kind of latest technology by which we are modified our substrate or maybe our materials.

(Refer Slide Time: 26:37)



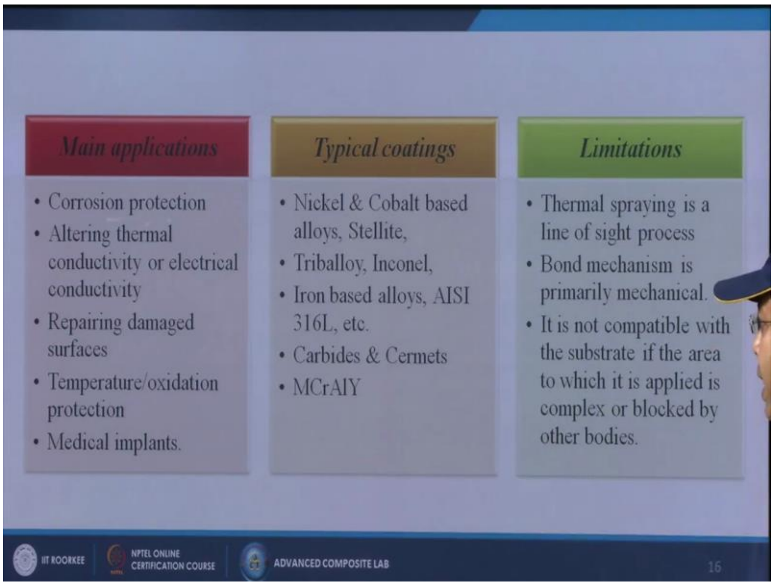
So, HVOF is a thermal spray system utilizing the combustion of gases such as hydrogen or a liquid fuel such as kerosene. Fuel and oxygen mix an atomized within the combustion area under conditions that monitor the correct combustion mode and pressure. Then the process creates a very high velocity which is used to propel the particles at near supersonic speeds before impact onto the substrate. So, it is giving a very very high pressure to that particle so that it can give a huge impact onto that substrate so that it can stick with the substrate surface.

The system of hot gas and powder is directed towards the surface to be coated. The powder partially melts in the stream and deposit upon the substrate. The resulting coating has no porosity and the high bond strength, because huge particle in high velocity it is giving impact onto that substrate so that any virgin surface of that particular material is not possible, so that we can getting a coating of less porosity and high bond strength.

So, here is the schematic view of this particular technology. Here this one is known as the totally HVOF spray which is known as the high velocity oxygen fuel spray nozzle, where we are putting some kind of cooling water arrangements so that it is jacketed throughout the gun, because when we are generating a high temperature of heat there is the always chance of a hazardness. So, just for the safety precautions we are putting a cooling water jacket outside this gun or maybe the nozzle.

Here in this particular case we are putting the oxygen and kerosene so that they will burn inside, they will produce high temperature inside that gun, and through this nozzle we are putting the spray powder inside. So, when this powder is getting heated by this mixing of oxygen and kerosene, so after that they are acting a very high velocity by which that particles is melting accelerated and then it is giving a high impact onto the workpiece. Here, you can see this workpiece, it can rotate it can put into any directions or maybe sometimes it is into the fixed positions the gun can rotate and gun can go into any direction so that uniform coating of that coating materials can be achieved onto the substrate or onto the materials.

(Refer Slide Time: 29:14)



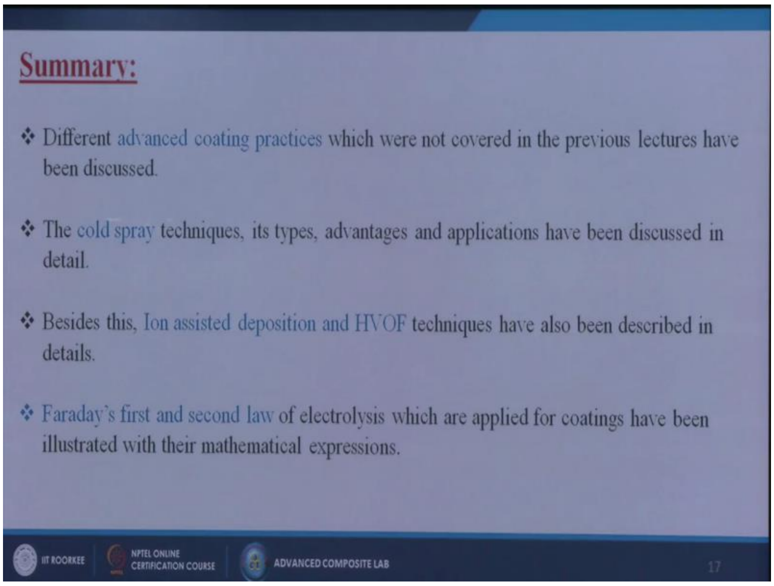
So, here the main applications of these techniques is first one is called the corrosion protections we can put any materials which is corrosion resistance onto the substrate itself. Altering thermal conductivity or electrical conductivity suppose my substrate is electrical non conducting material if I quote any material which can be electrical conductive, so by quoting those materials I can make my substrate from a non conductive or insulator to the conductive one. Next is that repairing the damaged surface suppose I am having any cracks or ports inside our surface or maybe that surface of our particular material I can change, I can do the modification on that particular zone. Temperature or oxygen protection can be done made for medical implants like any kind of knee replacement or may be any kind of joint replacement we can use this kind of techniques.

Then typical coatings generally nickel and cobalt based alloys or maybe the stay light coating can be possible. Triballoy inconel can be done, iron based alloys, AISI 316L etc can be done, carbides and cermets a material can be done or maybe that MCrA1Y that kind of material. So, all these are the hardest materials and not only that these materials are having a numerous applications so that we can do the coating of these kinds of materials onto our substrate.

What are the limitations? Thermal spring is a line of sight process bond mechanism is primarily mechanical because we are heating it due to that connect kinetic energy it is sticking on to that substrate itself by the impact energy. So, primarily the bond mechanism is little bit mechanical, it is not compatible with the substrate if the area to which it is applied this complex or blocked by other bodies because this type of coatings cannot go inside only it can do on to the substrate, a surface of that particular substrate which is open and not only that for very complexes it is not good one.

Next, in the summary here actually we have discussed different types of advanced coating practices which are not covered in the previous lectures have been discussed. The cold spray techniques mainly we have discussed over here, we have discussed about the high pressure cold spray low pressure cold spray techniques, we have given the brief example of these kinds of techniques what are the disadvantages what is the advantages of this kind of techniques.

(Refer Slide Time: 31:46)



Besides that we have discussed about the Ion assisted deformations, then high velocity oxygen, flow techniques have also been described in these particular details and for electrolysis techniques we have discussed about the Faraday's principle which includes first and second Faraday's laws and how this loss can be useful and how to measure the thickness of that particular coating and the amount of coating thickness we can achieve by applying this kind of laws.

Thank you.