Friction and Wear of Materials: Principles and Case Studies
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Lecture – 38
Basics of Ceramics Coating Techniques

Hello, welcome back to this NPTEL course. Today, we will learn about basics of few ceramic coating techniques. We require coating in a tribological application because the coating increases the hardness and so we get a wear resistance. So always these coatings are useful for tribological applications, ceramic coatings are preferred for this kind of applications for their high hardness and abrasion resistance and high temperature sustainability. So today, we will see basics of few thermal spray coating techniques, right.

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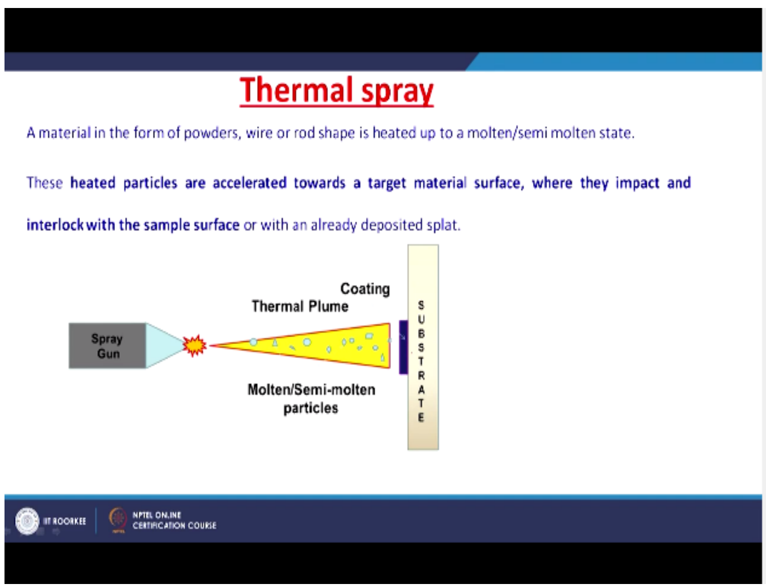

So thermal spray coating techniques are generally used for coating ceramics on a substrate. So in the thermal spray, a material is fed in the form of powders, wires, or rods and this material is heated to a molten or a semi-molten state. The heated particles are accelerated towards a target material surface where the impact and interlock with the sample surface are with already deposited splat and then the coating is formed.

So there is some mechanism for spraying these material. The material may be in the form of powders, wires, or rods. And this material is heated by spraying mechanism and then the heated particles will be accelerated and impact on the substrate. So after impacting, they interlock with each other and as well as the surface and then form a dense coating. So if you look at this thermal spray technique with variation in the moment of this spray gun as well as the distance between the substrate and the spray gun, we can actually have a variation in the coating.

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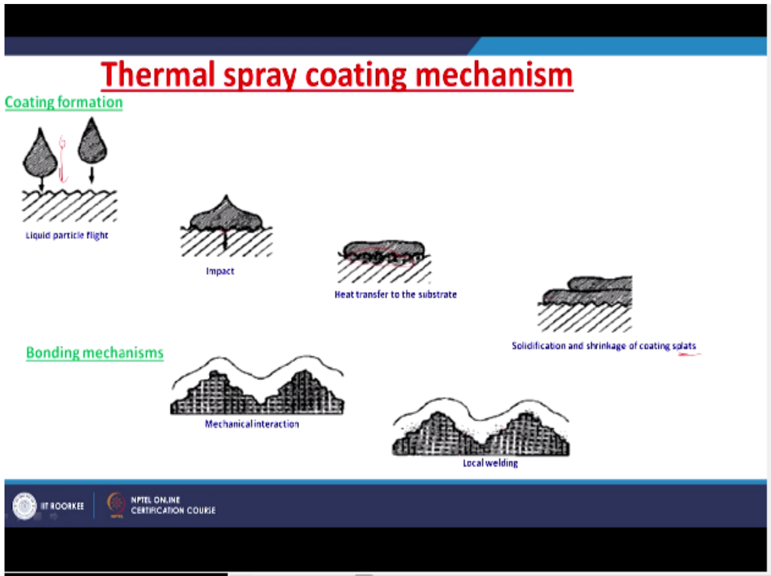

So thermal spray coating is generally done by a mechanism, coating formation mechanism. Initially as I told the particles are heated to a molten or semi-molten state. These particles impinge on the surface and then while impinging, they transfer the heat on to the substrate. In the later stages, they solidify into a coating splat. So solidification and shrinkage of the coating splats are the final result of this coating, right.

So you have a layer by layer structure after coating and this layer consist of such ion splats, right. So these number of such particles will be impacting and then they are bonding on to the surface. While bonding, there is a transfer of heat and then solidification stage, they become a adhered layered structures. So the bonding mechanisms if you see, the bonding is because of the mechanical interaction or the local building happening within this splats.

So it is basically the impinging of the particles. Those are, the particles are molten or semi-molten state. So once they are impinging, they are interlocking with each other and then form a coat. They are strong enough because of their mechanical interaction and then local welding, so they are bonded very strong.

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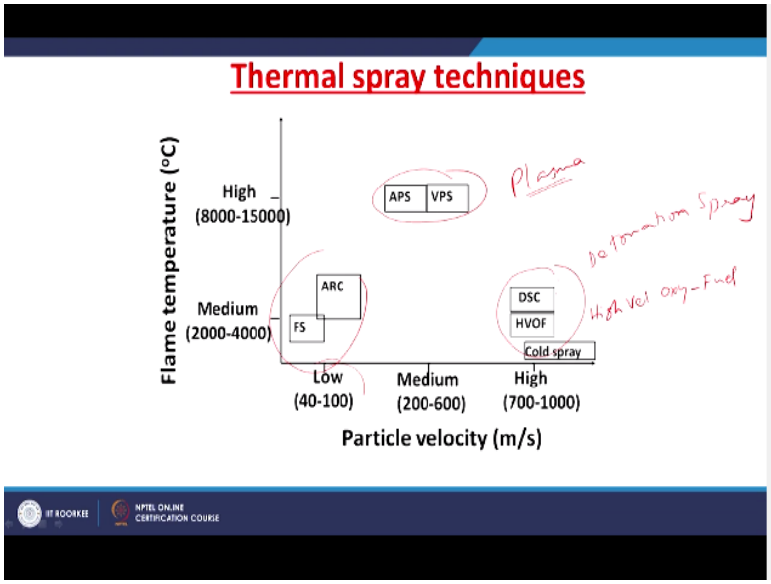

So based on the temperature, that is developed within this flame are the acceleration that is given to these particles, based on these temperature and then acceleration, there are several thermal spray techniques. Namely, the plasma spray technique, either arc plasma or vacuum plasma. There are plasma techniques and then there is an arc technique and then flame spray technique, detonation spray coating and high velocity oxy fuel.

So these are plasma techniques. These plasma techniques actually result into a flame temperature which is more than 8000. So people identified that around maximum of 15,000 Celsius, temperature can be generated in this technique using plasma. Whereas the arc or the flame spray techniques, they can develop a temperature in the flame of around 2000 to 4000 Celsius but the acceleration that is the particle velocity is very less, 40 to 100 m/sec.

The plasma techniques have a high temperature in the flame as well as the medium particle velocity of around 200 to 600 m/sec. Whereas another category of detonation technique, right, detonation spray coating techniques and then high velocity oxy fuel technique, these have a temperatures of around 2000 to 4000 Celsius but a very high particle velocity can be obtained in this technique.

The velocity is around 700 to 1000 m/sec. So these are major categories of thermal spray techniques based on the flame temperature and then particle velocity. So today in this class, we will see very briefly the principles of these different techniques. And we will also see a detonation spray technique, we will also understand this to a larger extent. And because in the few coming lectures, we will see few case studies of the ceramic coatings or ceramic metal coatings done by this detonation spray, right.

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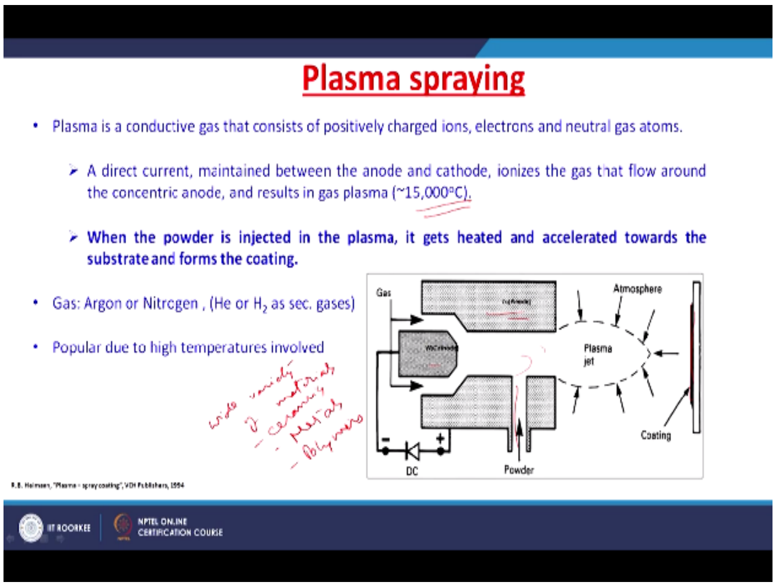

So first plasma spraying technique. The plasma is a generally a conductive gas that consist of positively charged ions, electrons and neutral gas atoms. So you have a plasma that can have a temperature of very high temperatures of around 15,000 Celsius. So how do you produce such a plasma. A direct current maintained between this anode and the cathode ionizes the gas that flow around the concentric anode and results into a plasma.

Thus plasma of around 15,000 Celsius of temperature. So generally the anode is of copper and the cathode is of tungsten. Now when the powder is injected into the plasma, it gets heated and then accelerated towards the substrate and then form a coating. So generally the gas used for generating this plasma is of argon or nitrogen. Argon is generally considered as a low energy plasma.

Whereas nitrogen is for high energy plasma, high temperatures are generated. But if you have the large volumes of plasma, the temperature cannot be much larger, right. The temperature remains same, even the volume of this plasma gas is more. But generally speaking you can actually maintain these temperatures of this plasma around 8000 to 15,000 Celsius by using this different gases or different arrangements of this cathode and anode.

And helium or hydrogen are also used as secondary gases to accelerate these particles and to impact on to the substrate. And this technique is very popular because of the high temperatures involved, around 15,000 Celsius temperatures are involved in this. So any material like ceramics, metals, polymers can be coated. So wide variety of materials can be coated, right. So wide variety of materials like ceramics, right; metals; or even polymers can be coated, right.

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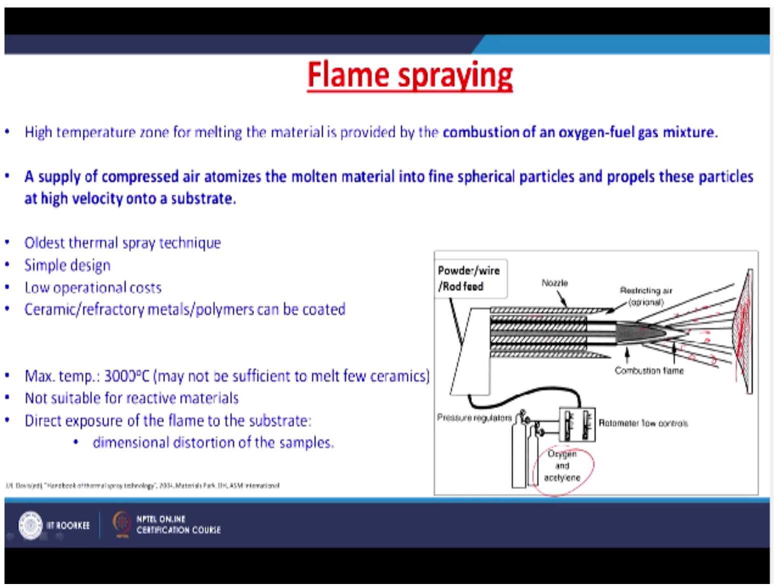

The other technique is a flame spraying technique. So high temperature zone for the melting the material is provided by combustion of an oxygen-fuel gas mixture. So generally the fuel is of acetylene gas. So oxygen and then acetylene gas mixture is given into this chamber where the powder or the wires or the rods are fed into this chamber and then combustion gives a temperature of around 3000 Celsius.

And then these materials are accelerated and then impacted on the substrate to become a coating, right. So a supply of compressed air atomizes this molten material into very fine particles. And those are generally spherical in nature and propels these particles at very high velocity on to the substrate, right. So this is actually the oldest thermal spray technique and very simple in the design and the operation costs are also less compared to the plasma spraying technique.

And you can have a coating of ceramics polymers or refractory metals by using this technique. But regarding this temperature generated is of 3000 Celsius, some ceramics may not be melted, right, particularly the ceramics of high melting temperatures. They may not be melted like borides, carbides, they may not be melted.

For that actually, plasma spraying is better where a very high temperatures of around 15,000 Celsius can be generated in the flame. Whereas this particular simple design flame spraying, a 3000 Celsius temperature maximum can be generated in the flame. So few ceramics may not be melted with this temperature. So it is also not suitable for the reactive materials because of sometime oxidation and other reaction products can be formed.

And direct exposure of the flame on to the substrate that gives a distortion in the dimensions of the samples, right. So these are sometime disadvantages of this flame spraying. But it is generally used because of the simplest design and low operating cost. The other one is the arc spraying. This is wire arc spraying technique.

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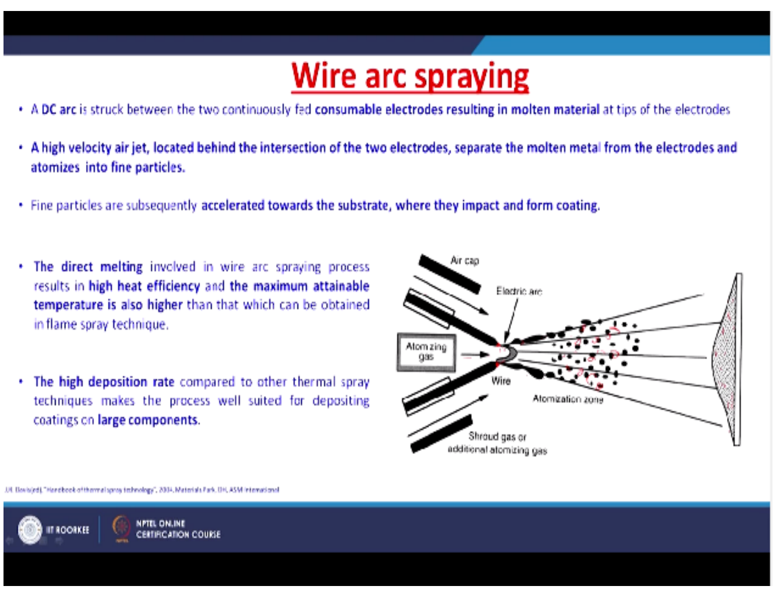

So material is fed in the form of a wire and a DC arc is struck between these consumable wire electrodes that results into a molten material at the tips of this electrodes, right. When there is molten material at the tip of this electrodes, you have very high velocity gas jet located just behind the intersection of these 2 electrodes. This separates this molten material into very fine particles.

And these particles are accelerated towards this substrate and then form the coating. So in this technique, the consumable electrode which is a wire electrode and at the intersection of this wire electrode where there is arc is struck. And then there is a molten material just at the tip of this electrode, an atomizing gas will be helping this molten material to form into very fine spherical particles and the particles are impacted on to the substrate to form this coating.

So the direct melting involved in this wire arc spray process results in high heat efficiency. And also the temperature attainable is also higher which can be obtained using flame spraying technique. The high deposition rate compared to other thermal spray techniques makes this process suitable for depositing coatings on large components. So industrial practice, so large components can be deposited by this ceramic, by using this wire arc spraying technique, right.

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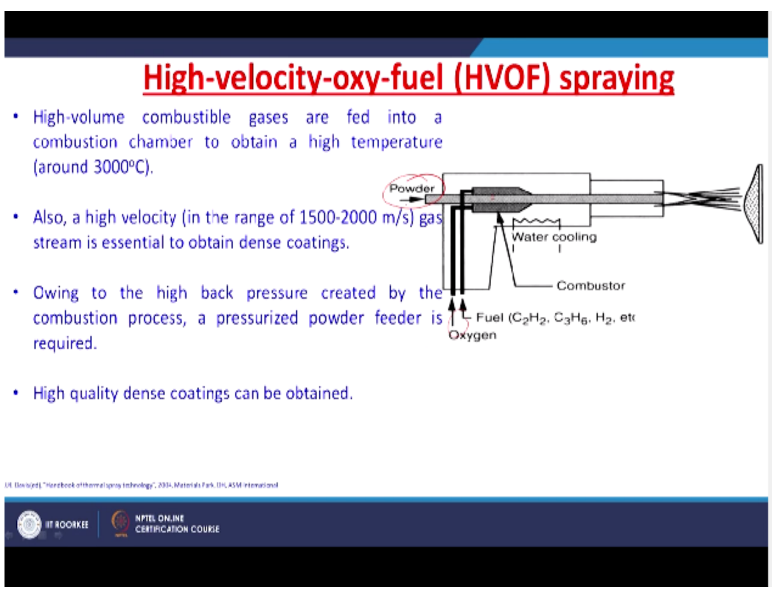

The high velocity oxy fuel spraying technique, here the high volume of combustible gases are fed into the chamber to obtain a temperature of around 3000 Celsius. At the same time, a high velocity gas stream is also required to obtain the dense coatings. So the gas stream will be accelerating this material on to the substrate, right. So this gas stream which is of very high velocity, velocities of around 1500 to 2000 m/sec, such a high velocity gases will be used to accelerate this powder from this flame on to the substrate.

So generally owing to the high back pressure created by the combustion process, the pressurized powder feeder is required, right. And high velocity dense coatings can be obtained by using this high velocity, sorry, high quality dense coatings can be obtained using this high velocity oxy fuel spraying.

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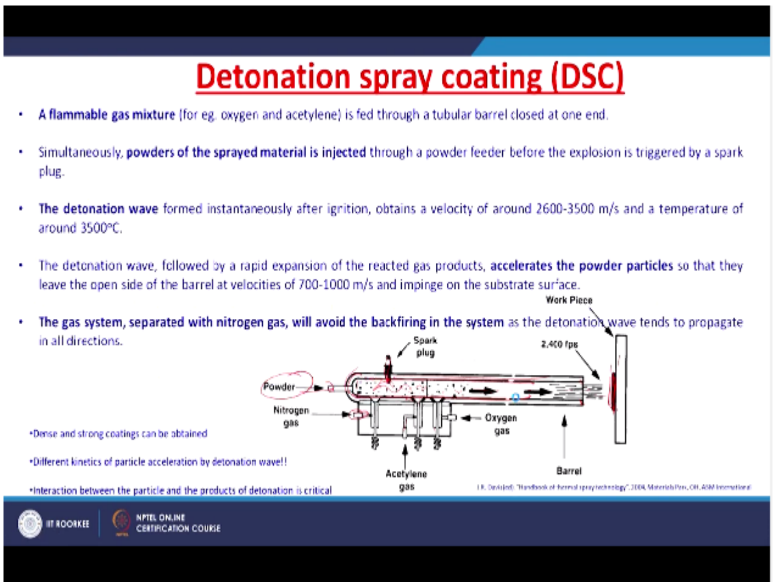

Other one is detonation spray coating. Detonation spray coating is very useful coating for coating a material on to the substrate. The material can be of ceramic or metal or a polymer. So in this detonation spray coating, a flammable gas mixture again, for example oxygen or acetylene is fed to a tubular barrel closed at one end, right. So this gas mixture is fed into this tubular barrel which is closed at one end, right.

And then simultaneously, the powder is also fed and the powder of this sprayed material is injected through a powder feeder before the explosion is triggered by the spark plug, right. Once this explosion is triggered, there is ignition and the ignition gives the detonation wave formed instantaneously after this ignition. So obtains a velocity of 2600 to 3500 m/sec. Such a high velocity and a temperatures of around 3500 Celsius.

So a detonation wave followed by the rapid expansion of the reacted gas products accelerates this powder particles so that they leave this open side of the barrel at very high velocities of around 700 to 1000 m/sec. And then impinge on to the substrate to form a coating. So the gas system separated generally with nitrogen gas to avoid the backfiring in the system. As the detonation wave tends to propagate in all directions, so we do not have a control on the detonation wave propagation.

The purpose of this gas, nitrogen gas is to avoid this backfiring in the system so that the particles by the help of this detonation wave go only in the forward direction at very high velocity and then impact on the substrate to form the coating. So with this technique, dense and the strong coatings can be obtained. And if you look at the particle accelerate, the kinetics are a bit different than what we found in the high velocity oxy fuel, right.

So the interaction because of the presence of the detonation wave when kinetics are completely different in this detonation spray coating compared with the high velocity oxy fuel technique and then interaction between the particle and the products of detonation is very much critical in this technique.

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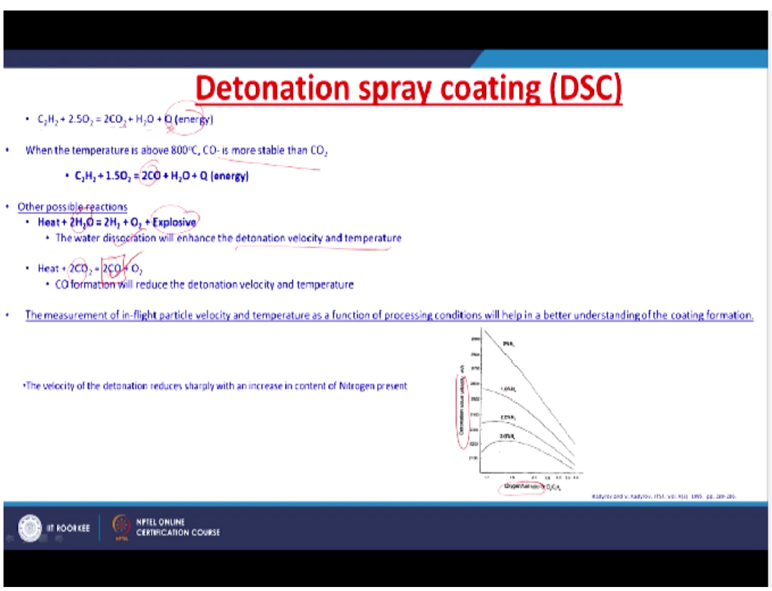

So if you look at this energy released. So the acetylene and then oxygen gas mixture, right, the flammable gas mixture because of this, you get energy, right. If you look at this energy released here, this energy is released as a result of this gas mixture combustion that gives a product of carbon dioxide, H2O and the energy. But when the temperature reaches above 800 Celsius, the carbon monoxide is more stable than the carbon dioxide.

So you will get carbon monoxide, H2O and this energy. And other possible reactions in this condition is this heat generated and also reacts with the H2O to give hydrogen and oxygen + the explosion. So the water dissociation will also enhance the detonation velocity and also the temperature. So we will get high temperature and high velocities because of this water dissociation.

And also this heat may react with this carbon dioxide to give the carbon monoxide and oxygen. Again the formation of such carbon monoxide will reduce the detonation velocity and temperature. So if you look at these 2 reactions, so detonation velocity and temperature can be enhanced by the water dissociation. Whereas these can be reduced by the formation of a carbon monoxide.

So a combination of these reactions will be used for controlling these detonation and then the resultant coating. The measurement of in-flight particle velocity and temperature as a function of processing condition will help in a better understanding of the coating formation. So the velocity processing conditions, for example if you look at these result from a research paper, the detonation wave velocity in m/sec, right and then this fuel ratio, oxygen to fuel ratio used for this coating.

So if you look at this one, as these nitrogen present is increased, the velocity of the detonation reduces sharply, right. So it is 0, 1, 2, 3% nitrogen. So the content of nitrogen is increased. You have, actually there is a sharp decrease in the detonation velocity. So that means if you control the processing conditions, then you can have a better control on the coating as well, right.

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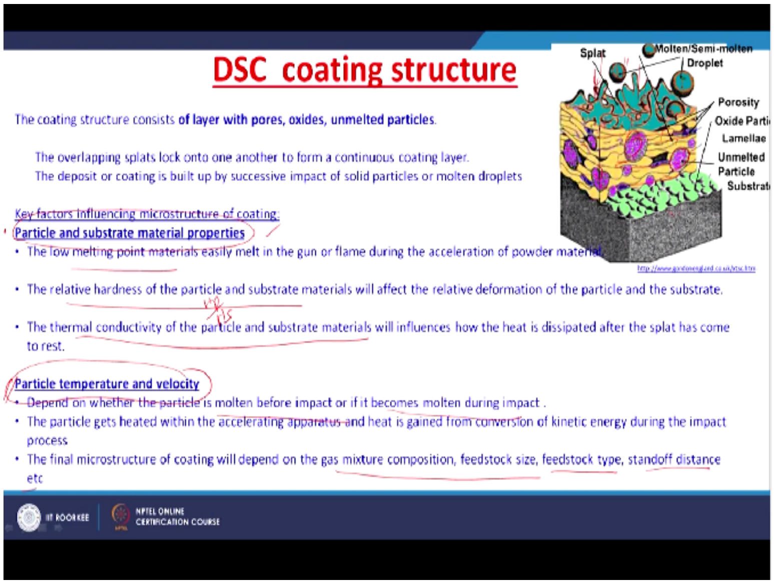

So let us see the coating structure. The coating structure is generally a layered structure but this layer with pores, oxides and unmelted products, right. This unmelted products as well as this layer, right, these are different layers, lamellae and then you can also see sometime pores, right. So these are, this is the substrate, right, on which the coating is being done. So layer by layer the coating is done and these are the molten material or the semi-molten material, those are impacted on this substrate and become a splat, right.

So the splat interaction that results into a sometime layer. So that means the overlapping splats lock on to one another to form a continuous coating layer, right. the deposit or coating is built up of by successive impact of such solid particles or molten droplets. So you have a layered structure but the microstructure of such coating is influenced by mainly the particle and the substrate material properties and the particle temperature and velocity.

Particle substrate and material properties, the low melting point materials generally melt easily in the gun or in the flame during the acceleration of the powder material, right. So the material property, that is melting point is very important. And also other important property, relative hardness of the particle and the substrates. If you know this particle hardness and the substrate material hardness, the relative hardness, the particle to the substrate, relative hardness will affect the relative deformation of the particle and the substrate.

So other important properties, the thermal conductivity, right, so the thermal conductivity of the particle and the substrate will also influence how the heat is dissipated after this splat has come to the rest position, right. How the dissipation of this heat is done so that means the thermal conductivity of this particle as well as substrate are also very important.

So the melting point of the materials and the relative hardness of the particle and the substrate, thermal conductivity of the particle and substrate, these are very important properties that can influence the structure of this coating. So coming to the other factor, particle temperature and velocity combination, it all depends on whether the particle is molten before impact, if it becomes molten during impact.

So it all depends on whether the particle is molten before impact or if it becomes molten during impact. The particle gets heated within this accelerating apparatus and the heat is gained from the conversion of kinetic energy during the impact process. So the final microstructure of the coating will depend on the gas mixture composition, feedstock size, feedstock type, as well as the standoff distance, etc.

That means if you control the standoff distance, the distance between the gun and the substrate or the size of this feedstock, right, or the type of this feedstock, either wire, rod, or a particle, powder, or the mixture of this gas which is used for combustion, so the final microstructure will depend on all these factors, right. So categorizing the factors which influences the microstructure of the coating, these are the properties of this particle and substrate and then temperature and velocity, right.

So these are main important factor that influences the microstructure of this coating.

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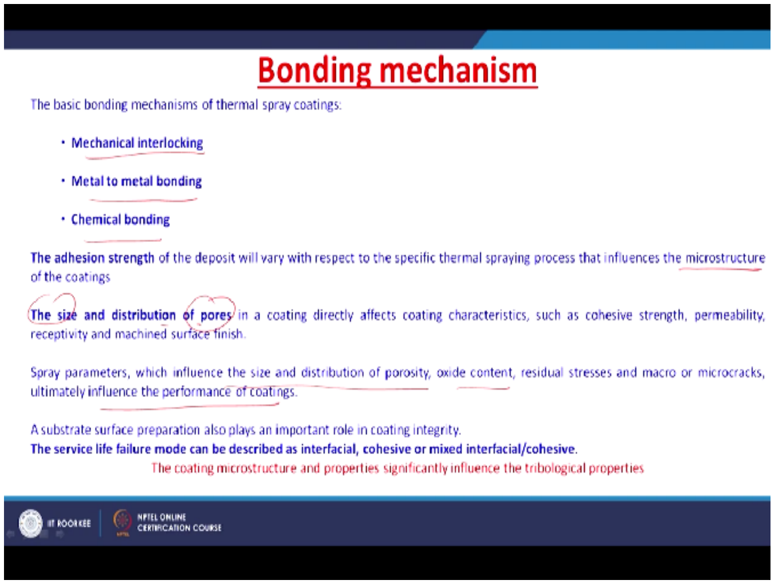

If we look at the bonding mechanism of this thermal spray coatings, generally the bonding is possible just by mechanical interlocking, the metal to metal bonding, or a chemical bonding, right. So the adhesion strength of this deposit will vary with respect to the specific thermal spraying technique that influences the microstructure of the resultant coating.

And the distribution and the size of the pores in a coating directly affects the coating characteristics such as the strength, permeability, receptivity and machined surface finish. So porosity, the distribution of this pores and the size also very important factor in generating a strong bond of this coating. Spray parameters which influence the size and distribution of porosity, oxide contents, residual stresses and cracking, microcracking or a macrocracking, that influence the performance of the coatings, right.

The microstructure is influenced by with respect to the thermal spraying process that we have seen here, the temperature and velocity, the properties of this particles and the substrate, right. Spray parameters influence the size and distribution of porosity, oxide content, the residual stresses, oxide content and cracking and then finally influence the performance of coating. So a substrate surface preparation also plays an important role in coating integrity.

So we have to prepare a substrate for the efficient coating. It must be rough enough so that it can adhere these coating or the splats very easily. And finally the surface life failure mode can be described as interfacial, cohesive, or mixed interfacial or cohesive. So finally relating to these tribological performance, the coating microstructure and properties significantly influences the behavior in the wear conditions and then result into the performance. So the coating microstructure and property is significantly influences the tribological properties.

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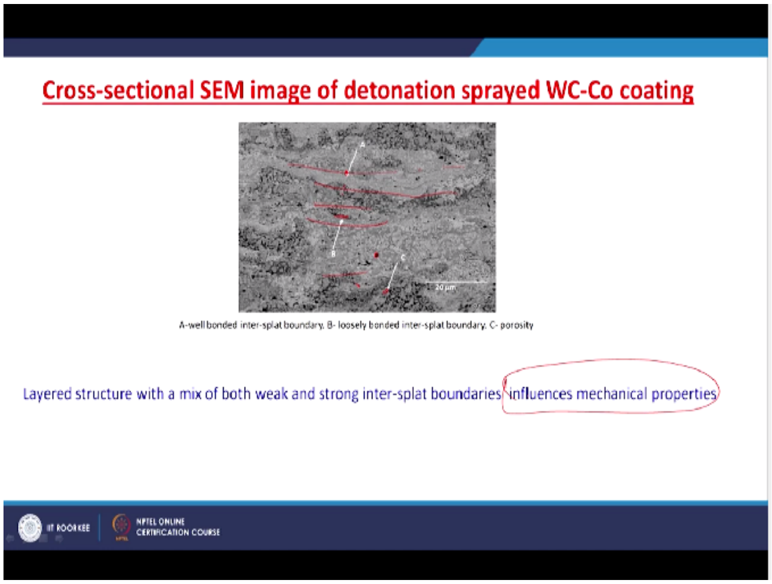

So if you look at this cross-sectional SEM image of detonation sprayed tungsten carbide coating, so you can see the layered structure, right. At the same time, you can also see a well-bonded inter-splat boundary, right or you can see a weakly bonded inter-splat boundary. So both boundaries of strongly bonded or weakly bonded boundaries are possible in this layered structure. At the same time, you also have sometime porosity, right. So this porosity or this boundary of this inter-splats, these may be treated as a defect, right.

So the defect for example cracks, right. They generate a crack and then when they actually, these cracks coalesce each other and then form a size which is longer than or equal to the critical size which is required for the brittle fracture. Then you will actually see a brittle fracture of this coating layer that leads to failure of this entire coating and substrate system. So the microstructure says the layered structure with a mix of both weak and strong inter-splat boundaries, so that influences the mechanical properties.

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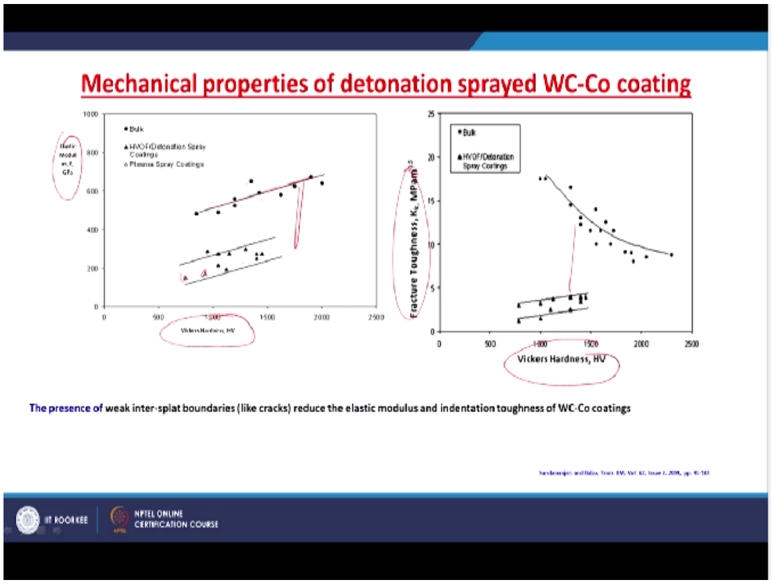

Let us see one study on the mechanical properties of detonation sprayed tungsten carbide cobalt coating, right. If you look at this one, this is the elastic modulus in gigapascal. This is Vickers hardness. Again this is the fracture toughness and Vickers hardness, right. If you look at this, data obtained from the bulk tungsten carbide cobalt, right. Whereas this data is obtained for the coatings of this tungsten carbide cobalt.

The coating is done by either plasma spray coating technique or by the HVOF or detonation spray coating. But if you look at this one, the mechanical properties, the elastic modulus is less in case of coatings as compared in case of bulk tungsten carbide cobalt alloys. Similarly, the fracture toughness is also much lower in case of coatings then compared again to bulk tungsten carbide cobalt material.

So the reason behind this again the defects. The defects in the form of inter-splat boundaries. The presence of such weaker inter-splat boundaries, so like cracks, right. So they propagate easily because that is a weaker region in the coating structure. So the presence of weak inter-splat boundaries like cracks, they reduce the elastic modulus and fracture toughness of this tungsten carbide cobalt coatings, right.

So inherently there are certain inter-splat boundaries, they behave like a defect. And because of the presence of such defects, the mechanical properties are inferior compared to bulk materials, right. And finally, these coatings performance is generally influenced by the decarburization. Generally, at high temperatures, the tungsten carbide is dissolved in the cobalt, right.

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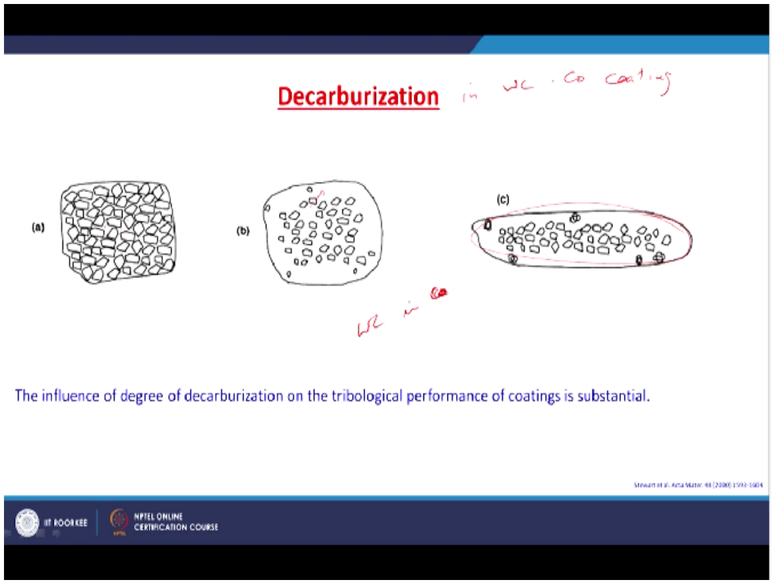

When the tungsten carbide is dissolved in the cobalt, right and then you have a dissociation of tungsten and carbon as well. So if you look at this one, the influence of the degree of carburization on the tribological performance, this is much substantial, right. We will see in separate case studies about the decarburization influence on the tribological performance of these tungsten carbide cobalt, decarburization in tungsten carbide cobalt coatings.

So this is generally reported as a major issue in the tungsten carbide cobalt. So this decarburization can be controlled by changing this oxygen to fuel ratio, right. So we will see in some example case studies with different oxygen to fuel ratios, the decarburization can be changed. So look at this one. This is the tungsten carbide cuboids and then the cobalt, this is the cobalt binder, right.

At high temperatures during coating this tungsten carbide will dissolve. And then when they are impacting, so they will become like a lens shaped like a splat, right. So they coalesce each other and then form a lens shape. So you have a flat lens shape coating on this one, on this substrate. So the decarburization has to be controlled to improve the tribological performance, right. But we will see these in some other case studies, right.

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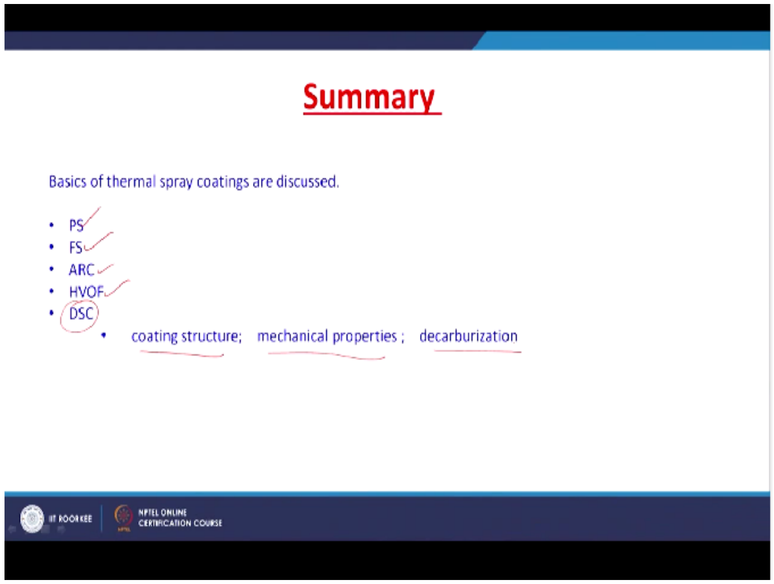

Finally summarizing this today's class, basics of thermal spray coatings are discussed. Mainly the basic principles of plasma spray, the flame spray, wide arc coating technique and high velocity oxy fuel are discussed. In addition to that, the detonation spray coating is discussed a bit elaborately. Mainly concerning the coating structure, the properties and then decarburization.

The coating structure of this detonation spray coated material consist of layered structure having all these pores or oxide materials or unmelted materials in between them. And because of that, they are inferior in the mechanical properties compared to bulk materials. So you have to control the decarburization occurring at high temperatures during this flame, in the flame where the tungsten carbide, for example the tungsten carbide can be dissolved into the cobalt phase.

And then this decarburization results into inferior mechanical properties, that result into inferior performance in the wear conditions. So controlling the decarburization is also an important issue to have a better performance in the wear conditions for this tungsten carbide cobalt. We will see in sometime in case studies about all these issues, okay. Thank you for attending this lecture.