Introduction to Biomaterials

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Lecture No. # 27
Thermal Spray Coatings

In this lecture we learn about thermal spray coatings. We have learnt how necessary are the coatings to impart certain functionality, because the overall performance of the material is decided by the overall bulk properties of a particular material. So, device of the implant will work based on what the bulk material is composed of; whereas, it is a interaction with the surrounding environment is very, very dictated by the surface. So, we we need to impact certain properties such as corrosion resistance, wear resistance even cytocompatibility. So that is being basically provided by certain coatings. So, in this lecture, we learn we learn about thermal spray coatings how do they impart a surface layer for a bulk material to impart certain functionality.

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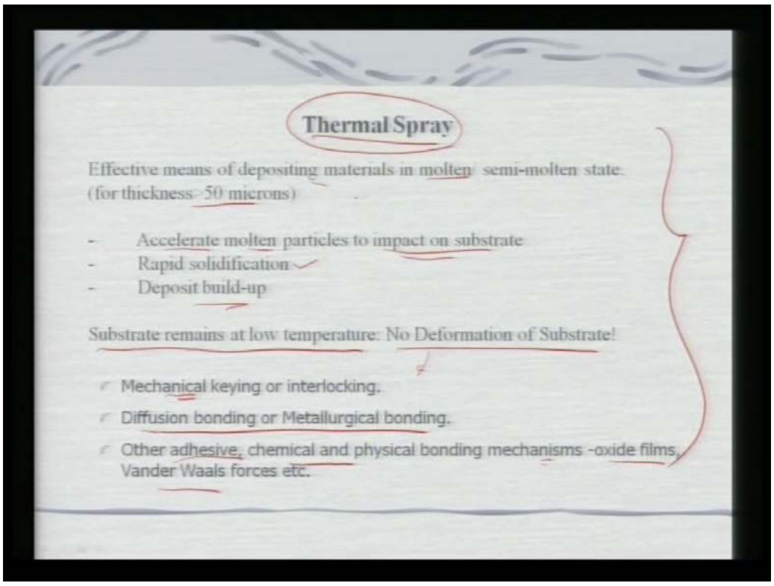

Thermal Spray

Effective means of depositing materials in molten/ semi-molten state (for thickness > 50 microns)

- Accelerate molten particles to impact on substrate
- Rapid solidification
- Deposit build-up

Substrate remains at low temperature: No Deformation of Substrate!

- Mechanical keying or interlocking.
- Diffusion bonding or Metallurgical bonding.
- Other adhesive, chemical and physical bonding mechanisms -oxide films, Vander Waals forces etc.

Thermal spray, it is an effective means of depositing materials either in molten or semi-molten state for achieving thickness which are approximately greater than 5 50 micrometer thick. Essentially more than 90 percent of the coatings for bio biomaterials is basically being utilized by thermal spraying. So, thermal is a very versatile technique in terms of depositing or coating on to a on to an implant surface or a bio biomaterial or an implant or a device material.

In the thermal spraying, the molten particles are accelerated, once they get accelerate once they accelerate then they are impacted on to this on to a substrate. So, they have been heated while they are while they are in flight, so the molten particle they accelerated they impact on a substrate and upon impact for the substrate they undergo rapid solidification which basically results a deposition or the buildup of the coating.

So, the main thing about this particular processes that substrate is maintained at the lower temperature. So, in turn we are not heating the bulk materials. So, the properties of bulk materials they are not altered in any case. So, the bulk material property are what basically remains what what what we really targeted or the overall fabrication of the material of the bulk material remains as it is. So, there is no degradation of the property of the bulk material. And also there is no deformation of the substrate; so that is the plus point of the thermal spraying. The deposition is occurring not because of metallurgical bonding, but because of the mechanical inter locking; so, deposition is occurring by mechanical inter locking of the species all of the molten particles which come impact the substrate and get deposited.

Some sort of diffusion bonding or metallurgical bonding occurs if the temperature is maintained little higher. So, in process, the diffusion is allowed to a certain extent and then it creates also for secondary secondary or secondary bond which is much more stronger that is called diffusion bonding or metallurgical bonding. Other adhesive, chemical and physical bonding mechanisms can also occur such as oxide films, formation of Vander Waal forces, etcetera. So, we can see thermal spraying, it utilizes depositing a material which is generally greater than 50 micrometer and thickness, it accelerates the molten particles let it let it is impact on on a on a substrate and it undergoes rapid solidification to form a final deposition and this deposition is mainly by mechanical interlocking, and eventually because of thermal enhance thermal enhance thermal energy which is being imparted. It can also impart some some sort of a diffusion or metallurgical bonding, and also Vander Waal forces or oxide film formation can also occur during thermal spraying.

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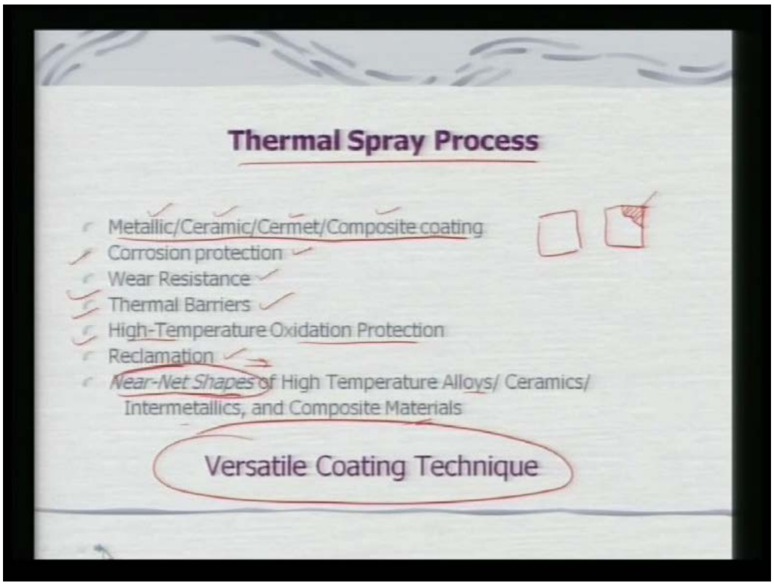

Thermal Spray Process

- Metallic/Ceramic/Cermet/Composite coating
- Corrosion protection
- Wear Resistance
- Thermal Barriers
- High-Temperature Oxidation Protection
- Reclamation
- *Near-Net Shapes* of High Temperature Alloys/ Ceramics/ Intermetallics, and Composite Materials

Versatile Coating Technique

So, thermal spray process is a versatile coating technique, because more than 90 percent of the depositions they are done by thermal spraying. The beauty of thermal spraying is, it can impart metallic coating, ceramic coating, cermet coating or even composite coating. So that is the versatility of the of a thermal spray process, and it can take it can deposit either metallic, ceramic, cermet or a composite coating. It is utilized for corrosion protection by providing a certain ceramic layer, wear resistance to impact wear resistance from particular material, it it can also provide thermal insulation such as thermal barrier coating, it can also provide oxidation protection by providing high temperature oxidation resistance, it can also utilize for reclamation. Reclamation is nothing but repair of a certain damage surface. So, if I need to if a if a particular part is now being damage it will better if it can reclamated instead of making the new part again, so we save the money - the cost as well as time.

So, if I see a damage on this particular material I can reclaim it, I can I can do the reclamation part by thermal spray process, because it is one of the very rapid deposition technique. So, it it can deposited a material to a very high extent couple of kg(s) in an hour. So, we can repair this particular material very quickly. So that is nothing but reclamation. At the same time, we can also provide near-net shapes of high temperature alloys, ceramics, intermetallics and composite materials, which in turn reduces the overall wastage or the scrap which is produced during the processing of a material. Because in any any case we cast a material or we build a particular material, then we need to basically scrape out the excessive material to get to the near-net shape. But in thermal spray process, we can make a negative replica and then we can deposit the material to get a near-net shape. So that minimizes the wastage which in which is basically incurred during the processing of fabrication of a material or a coating.

So, we can see thermal spray process, it can deposit metallics, ceramics, cermet or composite coatings, very well utilize for corrosion, wear, thermal or even high temperature oxidation. It is very well it is very well use utilized for reclamation, because of its high deposition rate, and it can also produce near-net shapes of high temperature alloys, ceramics, intermetallics or even composite materials.

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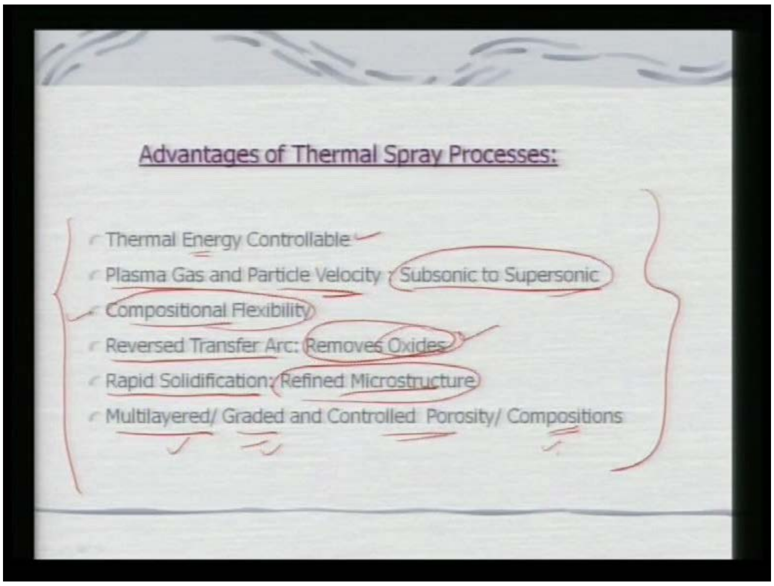

Advantages of Thermal Spray Processes:

- Thermal Energy Controllable
- Plasma Gas and Particle Velocity : Subsonic to Supersonic
- Compositional Flexibility
- Reversed Transfer Arc: Removes Oxides
- Rapid Solidification: Refined Microstructure
- Multilayered/ Graded and Controlled Porosity/ Compositions

The advantage of thermal spray processes include that the thermal energy can be controlled very easily. In case we we can decide what is the kind kind of energy, which is to be applied, so for melting aluminum I might require very low energy, whereas for melting aluminum oxide I might require very high energy. So, I can control the energy input in terms of melting aluminum or aluminum oxide. So, the thermal energy can be controlled in thermal spray process.

Again the plasma gas and particle velocity such as in plasma spraying or even on a hydro high high velocity oxy fuel spraying. We can achieve subsonic to supersonic velocities. So, depending on the kind of kind of deformation we want, if we want thermal energy to play important role or we want to play the impact energy to play vital role, so by plastic deformation or by just the melting and re-solidification, we can control what sort of deformation process we require to deposit a coating.

Also we can impact much much more compositional flexibility. We can play with the powders or wires which are to be deposited, and then we can control what is the feed rate of of those powder particles or the or the or the compositional wires to achieve a gradient coating. So, in that terms we can define the overall composition of flexibility of the coating which is being develop. And in case of electric arc, we can provide this reverse transfer reverse transfer arc which can also provide removal of oxide layer which inherently forms on very reactive materials. So, if we can somehow provide reverse transfer arc we can avoid the deposition of oxide layers. So, in turn we can generate much more smoother interface or much more integrated interface with the coating material.

Again in this process, thermal spray basically is inherently has very high or rapid solidification. So, in turn we get very refine microstructure, and refine microstructure it means that we are we can achieve very drastically improved properties mechanical, corrosion and its wear resistance, so such properties we can achieve via achieving a very refine microstructure. So, in turn what we can get; we can get multilayered structure, we can get a graded structure, also we can control the porosity or the composition. So, that is the advantage of the thermal spray processes. So, we can in case when we require a great porosity, so that the cells can (( )) extend their arms and anchor to the coating material, so that is very, very essential in terms of bio-coatings. So, they need some interaction with the cell surrounding cells. So, cell can extend their arms in the porous and then they can enhance the overall integrity with the device or the implant material.

So, we can see a thermal spray processes, it has it has a controllable energy term that thermal energy can be controlled, we can achieve very high velocities, it can provide its compositional flexibility, it can remove oxides (( )) required to get get an inherent or integrated adherent coating, we can get the refine microstructure that in turn improves the overall properties and we can get either multilayer(s), graded and controlled porosity or even varying compositions.

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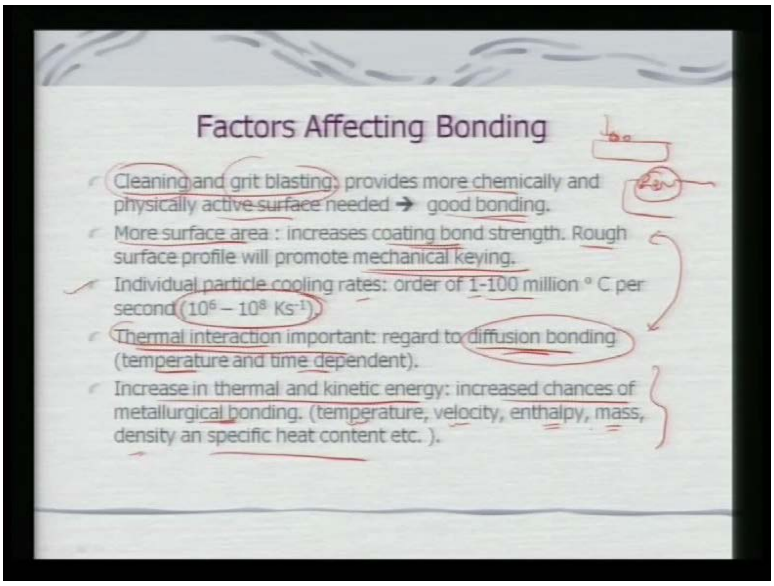

Factors Affecting Bonding

- Cleaning and grit blasting: provides more chemically and physically active surface needed → good bonding.
- More surface area : increases coating bond strength. Rough surface profile will promote mechanical keying.
- Individual particle cooling rates: order of 1-100 million ° C per second ($10^6 - 10^8\ Ks^{-1}$).
- Thermal interaction important: regard to diffusion bonding (temperature and time dependent).
- Increase in thermal and kinetic energy: increased chances of metallurgical bonding. (temperature, velocity, enthalpy, mass, density an specific heat content etc.).

And there is certain factors which define the bonding of this particular coating with the substrate. So, first thing is we are we are going to synthesize the coating in by terms of mechanical bonding. So, the first bond with be which is forming is via mechanical bonding or mechanical inter locking. So, first thing is we need to make the substrate very, very rough in order in order in order to adhere the coating or let the coating get mechanically interlock with the substrate. So, first thing is cleaning and grit blasting, if there is only some already some dirt present on the surface that may not allow the coating to get deposited or may not allow allow it to integrate with the substrate. So, we need to clean the coating and then we need to grit blasting. Grit blasting utilized for roughening the surface. If I very flight surface then it has it has very hard for anything to stick on to it.

But if I have a very corrugated surface or rough surface even entity comes it can basically get locked at certain locations and that will provide it much it much more adherent coating. So that provides more chemically and physically active surfaces that will result in a very good bonding. At the same time, we are providing much enhance surface area and that increases the overall coating bond strength, and also this rough surface provides mechanical interlocking or mechanical keying. So that that is what we we can see here that rougher the surface the better will be the overall mechanical interlocking of this particular material with the substrate.

The refine microstructure can be attained, because the individual particle cooling rates are in the order of around 1 to 100 millions per degree centigrade million degrees centigrade per second. So, we see the cooling rates of the order of 10 to the power 6 to 10 power 8 kelvin’s per second. So that is that is the cooling rate we are talking about it is 10 to power 6 to 10 power 8 kelvin’s per second. It means the cooling rate is very, very drastic as soon as a particular material is heated, it will cool down to room temperature within fraction of a second. The cooling rates are with to the order of very, very high 10 power 6 - 10 power 8 kelvin’s per second. So, they can attain the room temperature in in time period of say less than around couple of micros millisecond. So that is the overall solidification rate we are talking about.

The thermal interaction is very, very important, because that will lead to the eventual diffusion bonding, but that is again dependent on the temperature and time that is imparted to the coating material. So, if you have a sufficient heat available with the bottom most layer, because as soon as we are depositing a material on a substrate, we are also in putting certain heat energy to the substrate. So, eventually we see the overall heating of the substrate material to say couple of 100 degrees up to 100 degrees centigrade or in that particular order. So, we can see the thermal interaction is very, very important as well to decide the overall diffusion bonding which can occur between coating and the substrate material. So, apart from mechanical inter locking we also have a some metallurgical bonding which can generate or it can also lead to Vander Waal force attraction to further made the coating much stronger.

So, providing increase in thermal and kinetic energy, we can increase the chances of metallurgical bonding, so that that is dictated by temperature of the molten particle, velocity of the molten particle, the enthalpy, the mass, density and specific heat content. So, depending on all those parameters we can achieve a relation in the coating properties.

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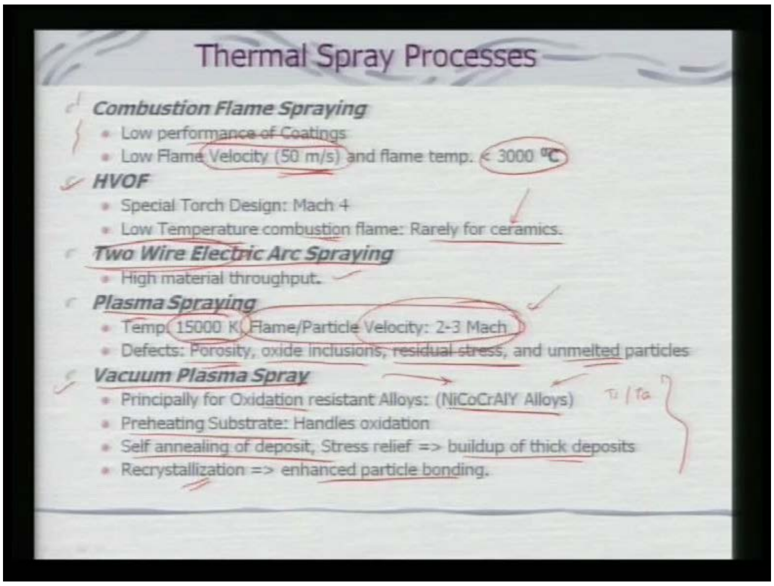

Thermal Spray Processes

Combustion Flame Spraying
- Low performance of Coatings
- Low Flame Velocity (50 m/s) and flame temp. < 3000 °C

HVOF
- Special Torch Design: Mach 4
- Low Temperature combustion flame: Rarely for ceramics.

Two Wire Electric Arc Spraying
- High material throughput.

Plasma Spraying
- Temp. 15000 K, Flame/Particle Velocity: 2-3 Mach
- Defects: Porosity, oxide inclusions, residual stress, and unmelted particles

Vacuum Plasma Spray
- Principally for Oxidation resistant Alloys: (NiCoCrAlY Alloys)
- Preheating Substrate: Handles oxidation
- Self annealing of deposit, Stress relief => buildup of thick deposits
- Recrystallization => enhanced particle bonding.

Ti / Ta

And then certain types of thermal spray processes which are available for deposition; first case first is combustion flame spraying that basically is nothing but combusting a few. But in this case we achieve a very low flame velocity (( )) to the order of 50 meters per second and flame temperature which are lesser than 3000 degrees centigrade. So, the problem with this one is we cannot melt ceramics, ceramics they have very high melting point, so melting ceramics become much more difficult, because of melting the ceramics we need to make it enough molten as well that they become much more (( )) they can be easily deform plastically and then they can get deposited. So that much heat is not available with the combustions flame spraying. So, it provides provides much lower performance of the coating. Also the velocity is very, very low, so the impact it it is not strong enough to fill all the pores which are which might be present on a rough surface.

Second category is high velocity oxy fuel; it is a special torch design which can which can achieve very supersonic velocities to the order of mach 4 which is approximately 1200 meter to up to 2000 meter per second. Though the temperature of this lemma is little lower, because it is again coming from compression, but it is very sufficient impact energy available for deforming a plastically deforming a material soft material such as aluminum, copper, nickel such material. But it is rarely use for ceramics, because the plastic deformation is very limited for ceramics. So, ceramics are inherently heated via or coated via plasma spraying or vacuum plasma spraying. In case of two wire electric arc spraying, we can get very high material throughput, it means we can deposit a very high quantity of a material. At the same time, since we are saying two wire electric arc, it means we need two electrodes to generate an arc. So, one electron material can be nickel, other electron material can be copper; so what we can do, we can produce even bimetallic coatings. Or it can even a more than 1 2 electrodes, so we can again impact much more variation in the composition if required.

Plasma spraying, plasma is nothing but ionized gas, so it can achieve very high temperatures to the exceeding 15000 kelvin. In this case, we achieve particle velocity of around 2 to 3 mach, so molten molten metal particles; they can be accelerated to velocities of generally starting from 200 degrees 200 meters per second to approximately 1000 meters per second. So, they can generate enough velocity, at the same time they very high temperature. So, in this case we can melts ceramics very easily, they can be plastic enough to get reshaped on to the contours of the surface, and the very high velocity as well to fill in the pores, so it can also generate very good coatings. But still they can generate very they can generate certain porosity, they can also have oxide inclusions, they can also have residual stresses and even un-melted particles, because even oxides can form and since the velocity is so high that time may not be sufficient to melt the entire particle. So, we can also achieve some un-melted particles.

We have one more process which is called vacuum plasma spray. So, basically it is utilize for oxidation for avoiding the oxidation of the alloys. So, in certain materials such as nickel, cobalt, chromium, aluminum, yttrium alloy, if we spray them in air some oxidation is is just really is a possibility of this alloy even titanium, tantalum and such metals which are proven to oxidation, those are basically preferred to be spread in like under vacuum condition, so we utilize plasma spraying and a vacuum. So, in this case preheating of substrate that handles oxidation and self annealing of deposit or stress relief can also occur, and in this case we can also build very thick deposits, again if we enhance the re-crystallization it will result enhance particle bonding. So, there are certain advantages of vacuum plasma spraying, but we can avoid oxidation, we can achieve much denser coatings as well, because we are creating plasma which will allow the porosities to be eliminated, and in in turn what we are getting, we are getting very dense coatings of these particular materials.

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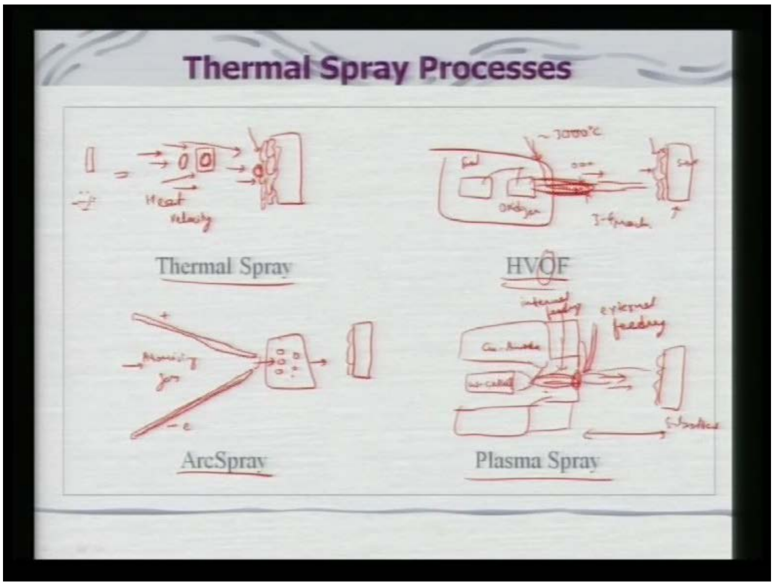

Thermal Spray Processes

Thermal Spray

HVOF

ArcSpray

Plasma Spray

So so in in turn we can see thermal spraying, we have either a solid or a solid billet or may be some powder feed straw that is basically being heated up first so we heated, and once it is heated it becomes a molten droplet, those are now accelerated by via certain media any carrier gas, and then we they they can do impact on a very rough surface. So, we have surface which is very, very rough, mechanically rough, and then this particle this rod getting deposited on to the rough surface as what we called splats. So, we have we had a roughening surface and then we can see the deposition of this material.

In process, the oxidation of these particles the molten particles can also occur and that can lead to oxide formation as well. Some particles they can remain un-melted, because the overall heat which is being required by the by this particles depends on the velocity of this particular droplet. So, if you supply very high velocity, they may not be enough time for it to get acquire enough heat to get melted, and in turn it will just impact on the substrate without getting melted. So that is again thermal spraying. We can also get something called arc by arc spraying. We we have one electrode - positive potential, second electrode - negative potential, and then we have some atomizing gas. And basically an arc is produced between those two electrodes, so we have positive potential, negative potential; it is it can be one kind of wire, it can be different kind of wire, and they can be even same kind of wire.

So, in in turn basically it is producing nothing but arcing will produce the droplet of particles that now impacts on a particle substrate to deposit them as a coating. This is arc spraying and this process as we can see since we utilize two we utilize two electrodes, we can also produce bimetallic coatings or even different kind of materials. We can also have a code wire, so we can do alloying in the core of the wire and still we produce an arc. So, we can control the overall composition of the material as as we increase.

The third part is high velocity oxy fuel, in this case, we have a gas field and then we have a powder powder inlet for letting the powder come. But the overall we we see here is that we accelerate the in case the fuel is the fuel we have certain fuel and this oxide is a this oxygen and then basically fuel and oxygen they combined together, and they are accelerate to a specially designed nozzle that creates the supersonic speeds of this (( )) gases. And in process we get very high velocities to the order of 3 to 4 mach, and that takes the powder particles. And because of mostly because of the plastic deformation we get the coating on the substrate. It is not much because of heat, heat is approximately similar that of a combustion process. So, the temperature approximately 3000 degrees centigrade or so, but it is mainly because of the high impact or the high momentum which is basically being carried over by the molten particles that result the final coating. So, we see the substrate and we get the coating which is very, very fine, it has a minimal porosity because of because of the high deformation which is occurring in the material.

Then we have something called plasma spraying. In this case, we have a tungsten tungsten cathode and a copper anode which is surrounding it, and then a arc is created between tungsten and between the cathode and the anode - copper anode and tungsten cathode. And then the other one more thing in (( )) we have to supply the powder somewhere. So, so in case we we require powder to be fed fed and some location, and then the overall flame which is being generated. So, depending on the residence time of this particular particle it will get molted and it will it will acquire certain heat content.

Same thing happens in plasma spraying that we can either once we generate a plasma, because of the arcing between the copper anode which is surrounding it and the tungsten cathode which generate certain arcing, and that creates a plasma some plasma plume. So, either we can inside the powder particles right at where the plasma is forming, already will fall the form where plasma is forming. So, it means fed within the gun it is called internal feeding, if it is being generated outside it is called external feeding. So, we can either feed the material outside that is called external feeding, it can be generate the fuel can be the the powder can be fed inside the gun that is called internal feeding. That is very essential because for it is very essential for high melting materials, because the high melting materials such as ceramics they require prolong state in the plasma plume. So, if we are adding them as soon as the plasma is as soon as were plasma is forming then it will stain the plasma plume plume for a elongated time. So, certain ceramics such as such as aluminum oxide, (( )), certain ceramics they need to be fed right where the plasma is forming.

But for external feeding, it is basically essential for low melting materials such as magnesium, aluminum and so on. Because if we start feeding the material right where plasma is forming, it is enough time to get melted in splash. Once it splashes it can even choke the nozzle, the nozzle of the gun. So, they need to be fed outside, so still they have enough temperature available to get melted then accelerated by the carrier, and to be taken up by the carrier to get deposited on a substrate. So, we see a substrate, so we require a certain stand of between the between the gun and the substrate material. So that the particles they acquire certain velocity, they acquire certain heat and then they get deposited on to the substrate.

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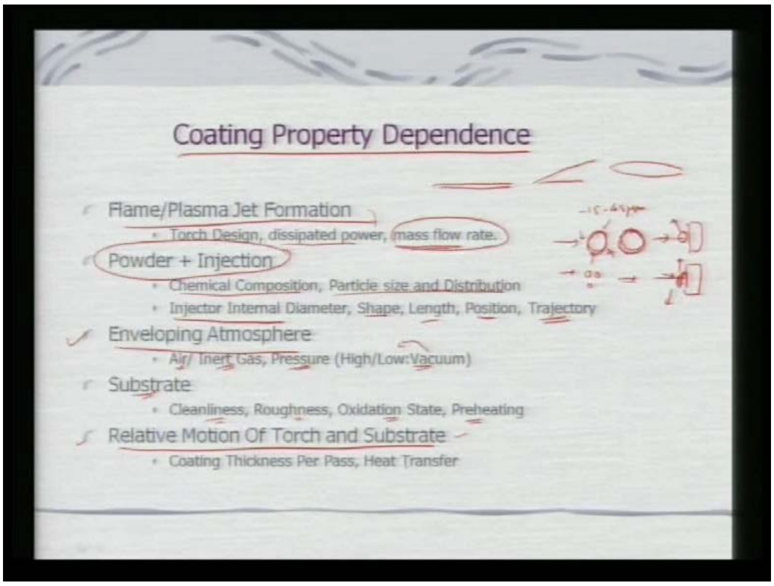

Coating Property Dependence

- Flame/Plasma Jet Formation
  - Torch Design, dissipated power, mass flow rate.
- Powder + Injection
  - Chemical Composition, Particle size and Distribution
  - Injector Internal Diameter, Shape, Length, Position, Trajectory
- Enveloping Atmosphere
  - Air/ Inert Gas, Pressure (High/Low:Vacuum)
- Substrate
  - Cleanliness, Roughness, Oxidation State, Preheating
- Relative Motion Of Torch and Substrate
  - Coating Thickness Per Pass, Heat Transfer

So, the certain property dependence, the coating property dependence; first thing is plasma plasma flame jet formation that basically depends on how we are generating the heat either it is by a flame or it is by plasma. So, there are certain concerns how the torch is being designed. So, once we are forming the plasma whether it is very constructed, so we can get a constructed flame or it is it expanding or it is again constructing like a like an arc like, so so the overall things depends on the overall flame or plasma jet formation. It also depends on how much power we are supplying it or how much is the capability of the gun to to extend certain heat. So, the overall dissipated power, and even how it controls the overall mass flow rate. So, if we want to control very high deposition rates, we need to provide very high capability of the gun to play with high mass flow rates. So, the overall flame and plasma jet formation is being dictated by certain things.

Again the powder and its injection is also very, very critical, because first thing is chemical composition what sort of chemical composition we want to play with. Also there are certain sizes and distribution of particles. If you make the powder particle very, very big, then may not be enough heat because heat will be will get absorbed by the bulk of material, so they would not be any heat left to melt the surface and then make it plastically deform that may not be possible. If you keep the powder particle very, very small, then because of up on its impact with the substrate (( )) experience is the bow shock. So, the the the overall momentum of the particle may not be enough to overcome the bow shock and it will just get scattered, so it would not lead to any deposition. So, once powder particles is very, very huge, it is not molten enough, it will just impact the substrate and it will bounce off. The powder particles size is very, very fine, it will again it would not be able to overcome the bow shock and it will again just fall off. So, that is the disadvantage with the powder size and distribution. So, we need a certain size, generally which is between 15 to 45 micrometer in diameter.

Again depending on that we also need to say whether we want to have internal feeding, so overall shape length position of that particular injector and also what are the trajectory which is being acquired by the powder powder particles to finally deposit a coating. Second third at most importance is the enveloping atmosphere. So, if we have an air then we have chances of oxidation. So, sometimes we need to maintains either inert gas or we have to maintain low or high pressure, so that depends whether we want to create a vacuum. But then again it makes it makes the process very costly, because we do the entire spraying in a vacuum chamber. So, these these are certain constraints with.

Again substrate cleanliness, its roughness even oxidation state, preheating even the thermal characteristics of the substrate a very, very, very important in terms of dictating the properties of the coating material; so, relative motion of the torch and substrate is also very, very critical, because if we if we are trying to trying to go very slowly basically building of the heat in the material. So, in the in the process we are not really we are not allow allow we are not really if you are moving very high very, very slowly then we just building up heat in the material and much high deposition rates can be achieved, but that might result the overall development of thermal gradients and that can result into crack end. And if you go very slowly we are depositing very, very less material and in that process also we are not allowing the much heat development into the material, and then it might just cool of or it may not the heat may not be sufficient for the material to get deposited on the material.

So in both the cases, we need to somehow maintain or optimize the overall feed rate or the overall motion of the torch and the substrate, so that coatings can be formed very nicely.

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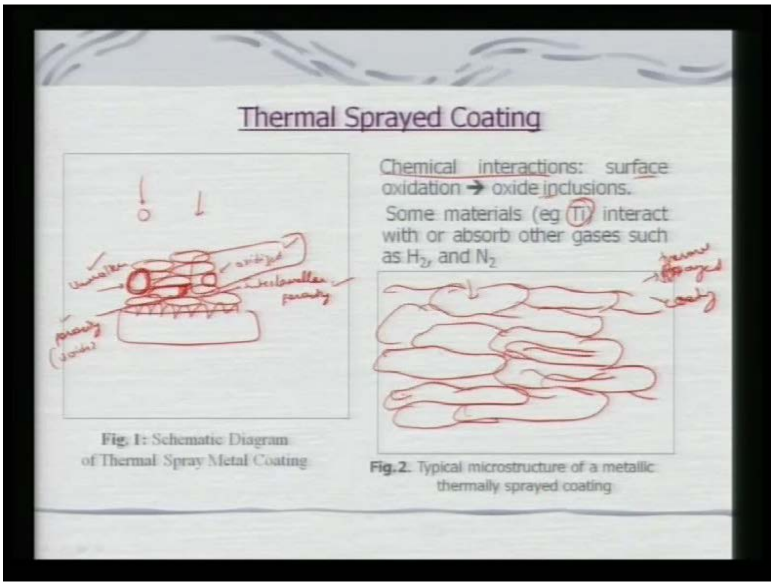

Thermal Sprayed Coating

Chemical interactions: surface oxidation → oxide inclusions.

Some materials (eg Ti) interact with or absorb other gases such as H_2, and N_2

Fig. 1: Schematic Diagram of Thermal Spray Metal Coating

Fig.2. Typical microstructure of a metallic thermally sprayed coating

So, the overall schematic diagram of thermal spray metallic coating. We can see that the in in case of thermal spray coating, we achieve a sort of structure. So, if we have a substrate, substrate is generally very, very rough, so we need to we need to deliberately keep a surface very, very rough. And in process, once a powder particle comes it impact the surface surface it basically flattens up, it flattens in a very rough manner. So, we can see the development of certain splats in between what we can get, we can also get some un-molten particles, because these particles are not heated to large extent they get molted. They they do not they do not get melted; they just remain as it is, so it is un-molten particle.

Once it is acquired enough heat it can also undergo certain oxidation. So, we can see we can also achieve some some particles which are un-molted and un-melted or some which are basically being oxidized. That is again a problem. Inherently since it is forming splats, there is some sort of a some sort of a enter lamellar porosity which is available so we have something called interlamellar porosity. At the same time is surface is very, very rough, it might happen that some of the pores they remain as it is. So, we can also achieve some sort of a porosity in the coating. So, inherently what we are seeing we have un-molted, un-melted particles, some oxidized particles, interlamellar porosity or even certain micro porosity which is available which are nothing but voids and again the surface toughness is essential. So, we can see the overall deflects which can be basically being creped in in the thermal spray coatings.

Again in with certain chemical interactions such as surface oxidation will lead to oxide inclusions that is what we are seeing here, we can get some oxidation of the material such as in reactive materials such as titanium. It can also absorb other gases such as hydrogen and nitrogen, it can form nitrites and hydrides, but typical microstructure of this plasma sprayed or thermal sprayed coatings appears more like this. That it is a very splat kind of a structure. So, it (( )) lamellae's, lamellae lamellae kind of a structure, so we are seen these are nothing but splats which are growing basically one over the other, we can see much deform structure which is more like this. So, this is the overall structure of a plasma sprayed or thermal sprayed thermally sprayed coatings.

We can see stringers or lamellaes which are basically nothing but sprayed splats, so this this is nothing but a typical microstructure of a metallic thermally sprayed coating. So, it is undergoing both; it is undergoing heating and then basically it is spreads out to form a layer over the already existing surface. So and that that deposition is occurring because of the interlocking of this particular sprayed with the existing surface.

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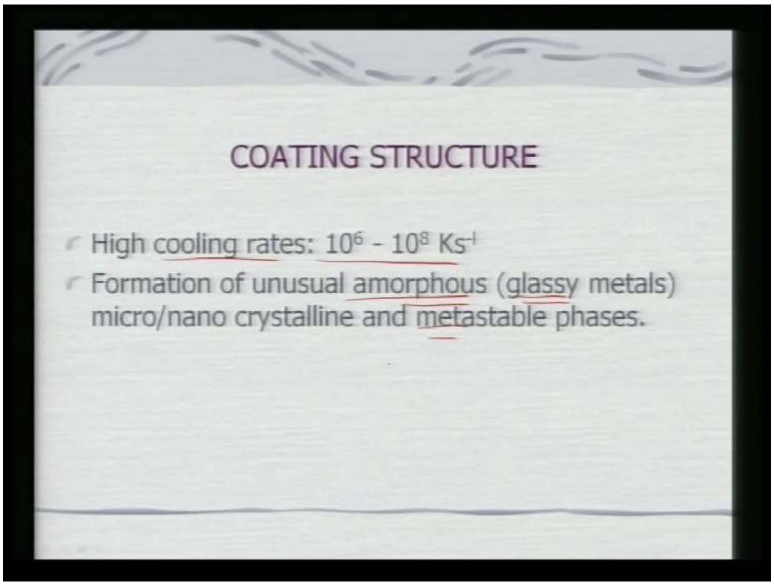

COATING STRUCTURE

- High cooling rates: 10^6 - 10^8 Ks^{-1}
- Formation of unusual amorphous (glassy metals) micro/nano crystalline and metastable phases.

And as we said earlier that the cooling rates are very, very high 10 power 6 - 10 power 8 kelvin per second. So, it is also very useful in terms of creating certain amorphous phases such as glassy metals or glassy ceramics can also be produced. Because glassy metals they can they can be highly degradable. So, if we if we can make those glassy coatings on a on a biomaterial or a or a device material that can basically get dissolved into the body, because of their high dissolution rates. So, we can also basically form metastable or amorphous coatings on a particular implant surface.

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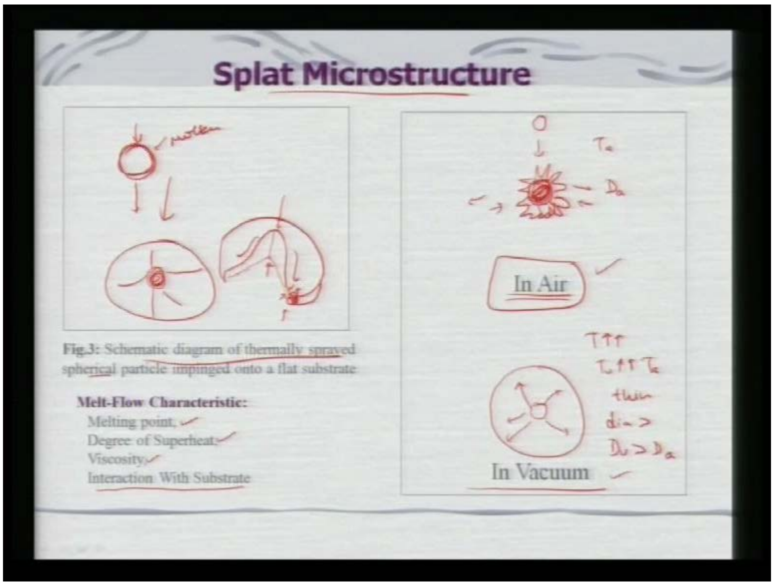

Splat Microstructure

Fig.3: Schematic diagram of thermally sprayed spherical particle impinged onto a flat substrate

Melt-Flow Characteristic:

Melting point,
Degree of Superheat,
Viscosity,
Interaction With Substrate

In Air

In Vacuum

Further we can see the splat microstructure, so as soon as we have a splat, first of all we have a molten molten particles molten particle, it impacts on a substrate and then it basically forms a splat. So, we have center portion which basically now goes on to forming a splat. So, we can see initially the particle the the molten particle was spherical and upon impacting with the substrate it forms a certain rim around it. So, we can see here thicker rim which basically forms and if we take a cross section it appears more like this. We can see that overall thing, so we can see it is it has certain thickness and this thickness is much much higher in the central region. Because here the here was the overall center of gravity for this particular splat, and then the fluids start flowing towards outside, and then it forms a certain rim. So, rim is again it is little thicker, so that is that is what is happening that material starts flowing on the outside and because of the resistance from the air or as soon as it starts solidifying it develop certain mass again little bit here. So, this portion is little thicker than the little inside portion out here. So that is what we can see the schematic diagram of thermally sprayed spherical particle. So, initially we had a molten particle which was spherical and then it forms a splat.

So, this splats deposit over one and another to form or develop the final deposit. And this characteristic of this particular splat is dictated by the melting pointing. If melting point is very, very low there will be much more fluidity available for this splat to basically sprayed; degree of superheat, if we superheat the material again we have high energy or high fluidity available for the splat to sprayed itself; viscosity, if viscosity is very, very high it will it will experience certain friction from the substrate as well as from the surrounding, then it will basically try to construct as a molten particle itself, it may not may not try to sprayed to that extent. Other it is interaction with substrate, if the interfacial energy or the thermal gradients are supportive then it can basically the overall spreading can be dictate dictated by the overall interaction with the substrate. So, substrate and the molten particle they have lower thermal, lower interfacial energy, it will try to sprayed.

Again if the substrate has very high thermal conductivity, it will absorb the heat as soon as possible and again the particle will not get time to sprayed, so again if the certain aspects to the interaction of the molten particle with the substrate. There is one more nice contrast between what happens in air, surrounding air environment and what happens in vacuum. So, this particular powder particle if it tries to impact on a substrate it will develop a splat of certain size with certain stringers like this. So, it will have certain (( )) arms around it but, it will not it will not sprayed to that extent, because it is experiencing certain resistance from air. So, we have molten particle it impacts on a substrate and the atmosphere is air, but it will not basically flow to that extent because of because of its resistance with the air. But in vacuum what is happening, it is not experiencing any resultants; at the same it is also achieving enhanced thermal superheat.

So, what happens in this case, it will try to sprayed out to a very large extent so if we had a splat upon impact at basically spreads to very thin, so it is very thin, the overall diameter is much more than with the in the diameter of air, so diameter in vacuum is much higher than diameter and air. So that part we can observe from here, because it is experiencing very low resistance from the surrounding or the environment. And also it is experiencing much higher heat. So, the temperatures are much higher here, so temperature in vacuum can be much higher than temperatures in air. So, overall we can see the splat microstructure is very different ones it is being deposit in air, only deposit in vacuum.

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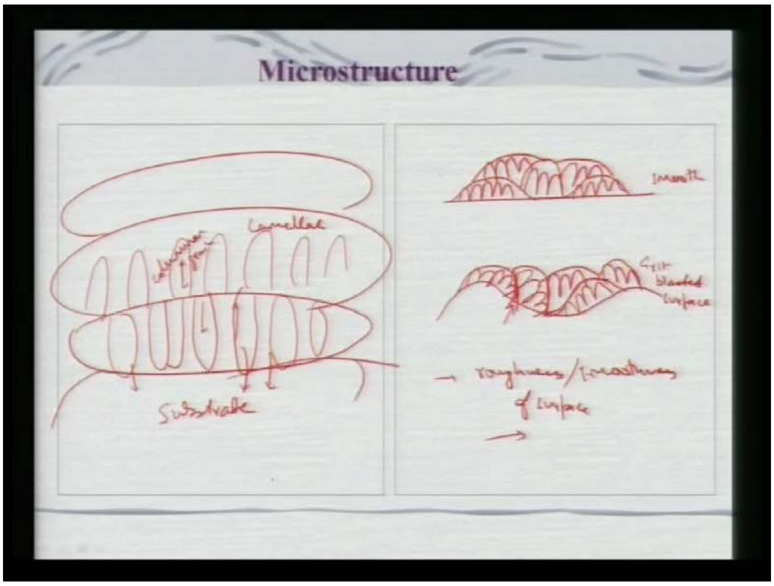

Microstructure

And generally we see the overall microstructure it develops more like this. Just to take you higher high resolutions, so we have a splat; the second layer of splat, third layer of splat and in process we see it forms some sort of columnar grain structure. So, column (( )) heat is being extracted in this direction as soon as this impact this is impact in a substrate, so this is a substrate. The heat is being dissipated in this direction. So, we see the overall growth is also occurring in that particular direction when heat is being extracted, so we can see formation of certain columns like this.

And similarly, the other layer layers also start forming a columnar structure which are more like that. So, generally we can see we have a lamellae structure these are nothing but lamellae, and then we have a columnar grain structure which basically forms in the thermally sprayed processes. And the same time what we can see here is that it also depends on the location or how the surfaces. So, if you have a polish surface then we have a deposit deposited splat, one more splat, then we see the columnar grain like this, this is a smooth surface. If we start taking grit blasted surface then what can happen; we can take we can in the surface will be much more rougher. So, we will see ones splat will basically be form form like this; second splat might form like this and it will have eventual columnar structure. Because depends on whether heat is being extracted, so we have a grit blasted surface.

And consequent splats they will start coming on to the existing surface. So, this is the existing surface I will get the next splat probably like this. Third splat probably like this, next splat probably like this. And in case, this case also now I will get splat like this, again this surface not become refer, though it was initially polished. Now it is becoming much more rougher and I will get consequents development of splat like that. So, it depends on the roughness or smoothness of the of surface. And as we can see the rough surface is providing much good interlocking. So, now it it can provide much good interlocking along the interfaces; so the rougher surface the better interlocking it can provide to the deposit to the deposited coating. So, that is the advantage of this particular, that is a advantage of the surface roughness incase of development of a macrostructure in thermally sprayed coatings.

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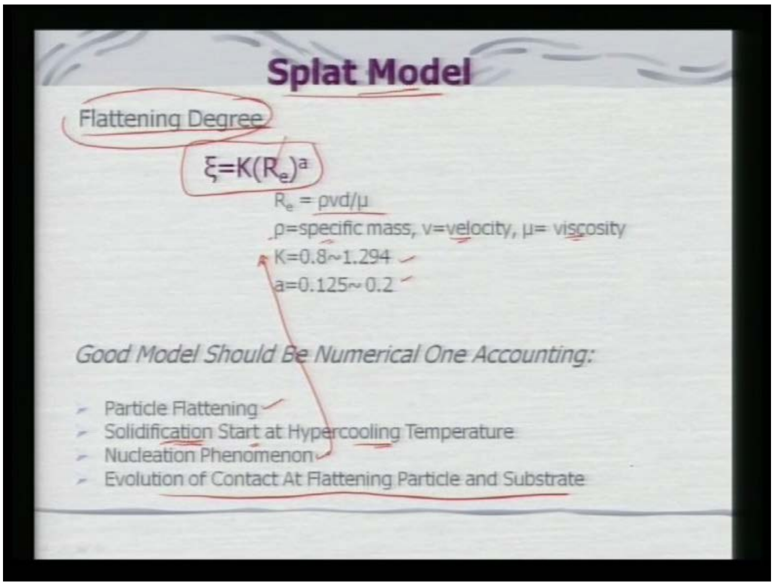

Splat Model

Flattening Degree

$\xi = K(R_e)^a$

$R_e = \rho v d/\mu$

ρ=specific mass, v=velocity, μ= viscosity

K=0.8~1.294

a=0.125~0.2

Good Model Should Be Numerical One Accounting:

- Particle Flattening
- Solidification Start at Hypercooling Temperature
- Nucleation Phenomenon
- Evolution of Contact At Flattening Particle and Substrate

So, one more thing which is inherent to the splatning is the overall flattening degree, because the flattening will decide how much area will be covered to an extent. So, if we have a rough surface, so there is a there are more chances that certain porosity or words can be retained. So, we want to provide much higher degree of flattening or higher degree of filling in those particular pores. So we need to achieve a very good flattening and that flattening is dictated by this particular equation; the flattening is related to a particular constant Reynolds number to a certain again constant. So, we can see that flattening is basically depends on the Reynolds number again it is given by v d rho by mu, so v is the velocity, this is nothing but the overall diameter, and rho is nothing but specific mass, mu is mu is nothing but viscosity.

So, we can see the v d rho by mu the Reynolds number, and again K and R again the constants with basically are fitting parameters. So, for a good splat model, we need to basically take account of the overall particle flattening again what is what is the sort of solidification start at the hyper cooling temperature, how the nucleation is also occurring; so, nucleation phenomenon also has to be correlates with the overall flattening, because as soon as it starts flattening it also is solidifying. And again we can see the evolution of contact at flattening point and substrate is also very, very critical.

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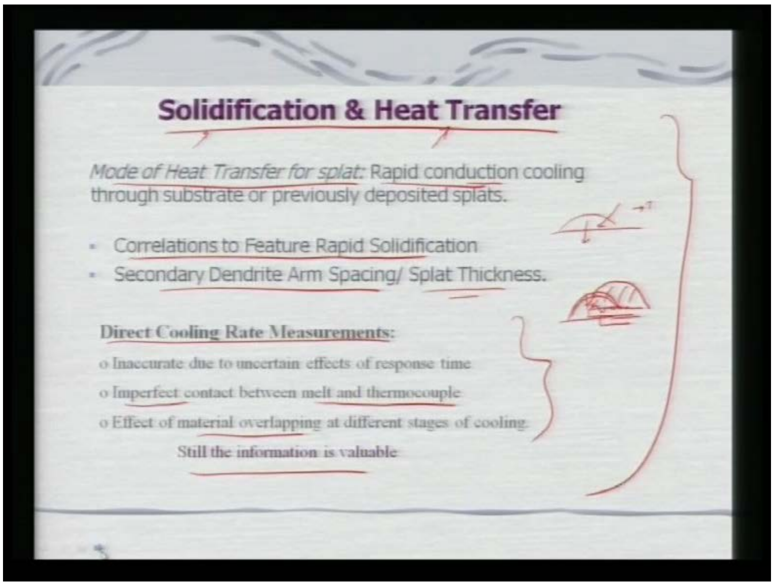

Solidification & Heat Transfer

Mode of Heat Transfer for splat: Rapid conduction cooling through substrate or previously deposited splats.

- Correlations to Feature Rapid Solidification
- Secondary Dendrite Arm Spacing/ Splat Thickness.

Direct Cooling Rate Measurements:

- o Inaccurate due to uncertain effects of response time
- o Imperfect contact between melt and thermocouple
- o Effect of material overlapping at different stages of cooling

Still the information is valuable

The certain certain other concerns as well like the solidification and heat transfer also dictate the overall development of the coating. So, the mode of heat transfer for splat that is that dictates the overall rapid condition, because as soon as splat is being deposited it is experiencing some sort of a conduction, let us conduct the heat for for its solidification. So, it correlates well to the feature of the rapid solidification and that in terms forms the secondary dendrite arm spacing. That also dictates the overall splat thickness. And again the direct cooling rate measurements, they are very, very inaccurate, because we need to put something inside the particular splat to to basically determinate it is temperature and that may not be really feasible.

And so there is also there is imperfect contact between the melt and thermocouple. So, if we have even if we have put a particular thermocouple on a substrate and let the splat deposit on to it, still they would not any be any sufficient contact, so that will again lead to certain inaccuracy in determining the overall temperature. Then again there can be certain material overlapping, so if in case one splat is being deposited, in process second splat might come and just impact here. So, again we are not able to adjust the overall temperature which is being generated, because of this particular splat or the degree of cooling or solidification that is occurring incurred by this particular splat, that may not be really accurate.

But still even if we can measure somehow, what is the overall cooling rate by putting the thermocouple on the substrate itself; still that particular information will also be very, very useful. So that is what is the overall attributes of thermal spraying that we need to say see what is the overall solidification and the heat transfer that is occurring in the splat to result of the final microstructure.

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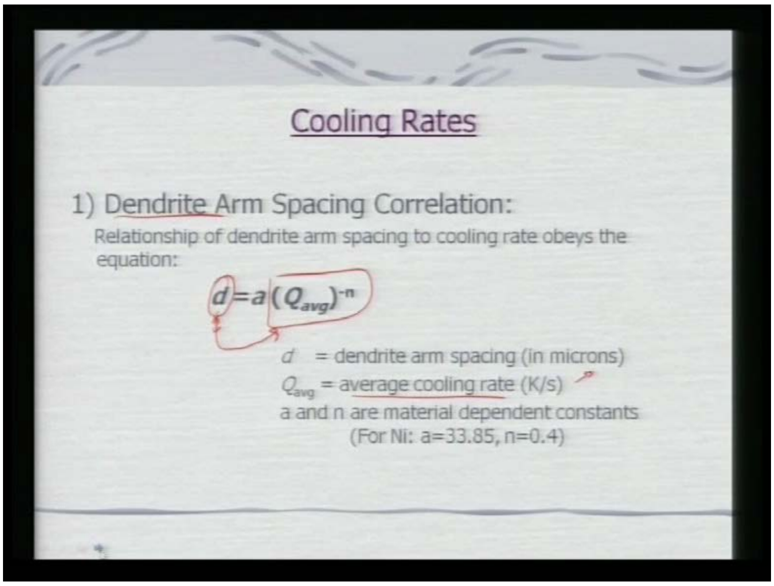

Cooling Rates

1) Dendrite Arm Spacing Correlation:

Relationship of dendrite arm spacing to cooling rate obeys the equation:

$$d = a(Q_{avg})^{-n}$$

d = dendrite arm spacing (in microns)
Q_{avg} = average cooling rate (K/s)
a and n are material dependent constants
(For Ni: a=33.85, n=0.4)

The cooling rates basically can be provided by seeing in term the overall dendrite arm spacing. So, we can see the overall dendrite arm spacing depends on the average cooling rate and that is a inverse proportionality. So, if we have very high cooling rates, the overall dendrite dendrite arm spacing or the or the generated microstructure will be very, very fine. So, we can see the overall dendrite arm spacing or the features of this particular microstructure is inversely proportional to the overall cooling rate, where a and n other material depending constants. So, depending on that it will have a it will have a effect.

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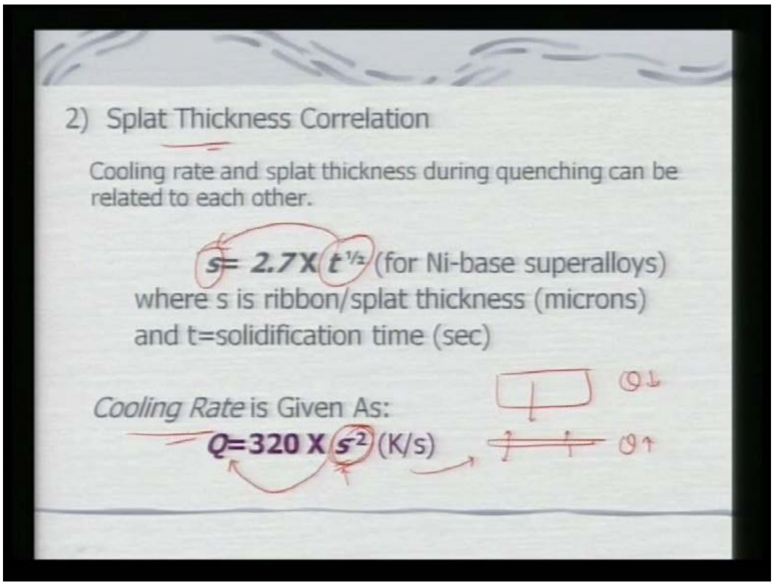

2) Splat Thickness Correlation

Cooling rate and splat thickness during quenching can be related to each other.

$s = 2.7 \times t^{1/2}$ (for Ni-base superalloys)

where s is ribbon/splat thickness (microns)

and t=solidification time (sec)

Cooling Rate is Given As:

$Q = 320 \times s^{-2}$ (K/s)

Again splat thickness, again it is basically being correlated that that splat thickness is basically depended on the overall solidification time. So, higher the solidification time basically, it it basically will result it (( )) certain depends on the overall splat thickness.

Again cooling rate is also given by its depends on the splat thickness of splat is becoming very, very thin; we can achieve very, very high cooling rates. That is again because if I have very thinner splat in compare to the thickness splat, I will lead more time to excavate the heat or take the heat out whereas, in this case may cooling will be very, very rapid. So, as I see if I have very thin splat, I will achieve very high cooling rates, but in this case my cooling rates will be much inferior to that of the second case.

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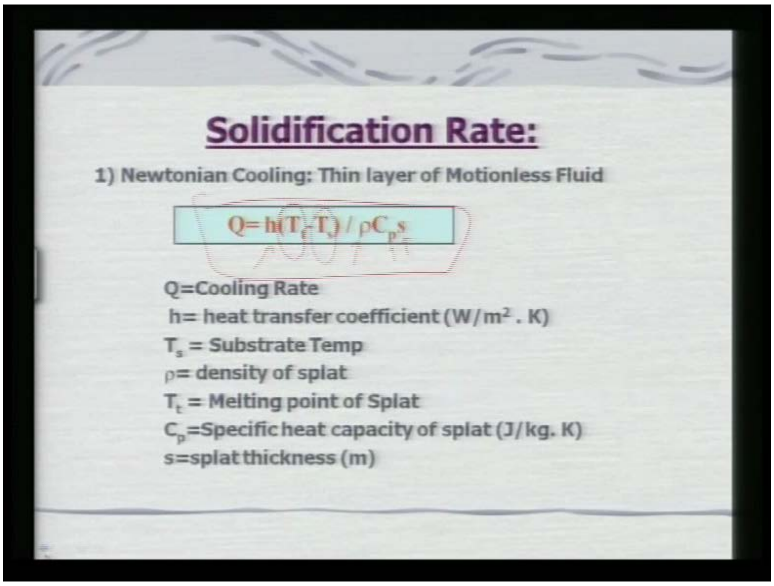

Solidification Rate:

1) Newtonian Cooling: Thin layer of Motionless Fluid

$$\boxed{Q = h(T_f - T_s) / \rho C_p s}$$

Q=Cooling Rate

h= heat transfer coefficient (W/m^2 . K)

T_s = Substrate Temp

ρ= density of splat

T_t = Melting point of Splat

C_p=Specific heat capacity of splat (J/kg. K)

s=splat thickness (m)

So, the overall solidification rate for this sort of Newtonian cooling is basically given by the difference by the difference in the substrate temperature and the melting temperature of the splat. So, we have melting temperature of splat minus the substrate temperature and the certain dependence of the heat transform coefficient, the overall density of the splat, the specific heat and specific specific capacity heat capacity of the splat and the splat thickness. So, we can see the overall solidification rate how it is depended on the properties or material properties and the temperature which is being available.

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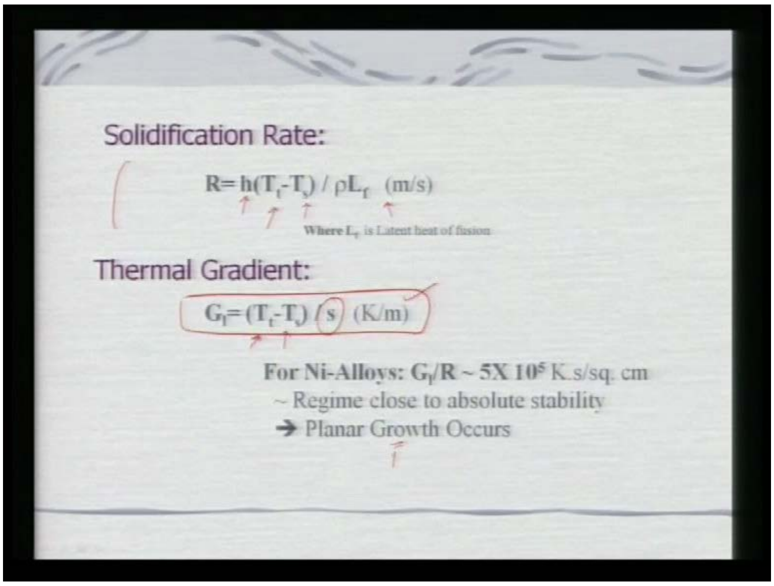

Solidification Rate:

$$R = h(T_t - T_s) / \rho L_f \quad (m/s)$$

Where L_f is Latent heat of fusion

Thermal Gradient:

$$G_l = (T_t - T_s) / s \quad (K/m)$$

For Ni-Alloys: $G_l/R \sim 5X\ 10^5$ K.s/sq. cm

~ Regime close to absolute stability

→ Planar Growth Occurs

So, we can see that melting temperature and the splat temperature, and the the overall coefficient of the overall coefficient of heat transfer is basically been given by h. And then we can see the thermal gradient finally, which comes out to be is the difference between the melting in the substrate temperature divided by the splat thickness. So, we get certain components in terms of kelvin per meter that that is the thermal gradient and the solidification rate is being given above. So, first certain regimes we can see the overall the overall interplay of solidification rate and thermal gradients, it will result to generation of certain micro structural features and that will dictate the overall performance of a particular material.

So, depending on whether we are getting cellular microstructure or the planar growth is occurring or dendrite kind of growth is occurring that is being dictated by the thermal gradient as well as the interfacial velocity.

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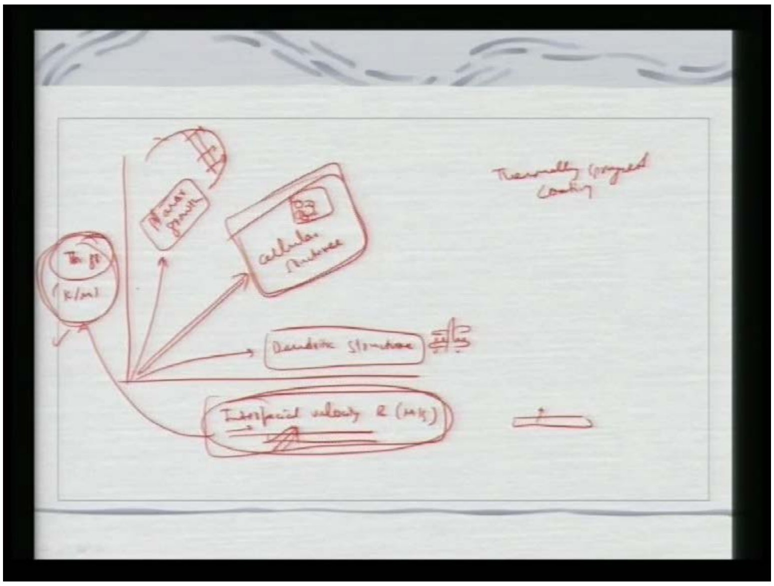

So, we can see if I have if I have, so I can see overall, if I have the interfacial velocity, certain time r that will be in meter per second, and then I have a thermal gradient thermal gradient that will be in kelvin's per meter. So, we can see I can get if I if I can cool them if I can cool them material very, very rapid while achieving a very slow interfacial cooling, slow interfacial velocity, I will get something which is called a planar growth.

And in other case, if I am able to get very high interfacial velocities, whereas I I keep my thermal gradient very, very minimal what I get is some sort of a dendrite structure. But if I keep my interfacial velocity impart with the thermal gradient what I get is some sort of a very refine microstructure which is called a cellular structure. So, what I am getting is if I keep my thermal gradient very, very high while minimizing my interfacial velocity velocity, so the solidification is not occurring at that particular higher rate, but whereas, I have very high thermal gradient available. So, what I am getting? I am getting the entire material is getting transformed or solidified, so I am getting much closure or planar growth of the material.

If I am keeping my interfacial velocity very, very high while not providing it enough thermal energy the gradient not enough thermal gradient then what I get is nothing but a dendrite structure. So, I achieve some sort of a dendrite structure with secondary arms, primary arms and so on. In this case, I am getting very (( )) microstructure, because I am getting a very planar growth, so the entire interface basically starts growing in a similar fashion. But in this case I get very refine microstructure. So that is the advantage of the interplay between the thermal gradient and the interfacial velocity. So, by controlling them I can achieve a very refine microstructure. So that is the overall play with the thermally sprayed coatings.

So, depending on the kind of gradients are provide whether it is a interfacial velocity or thermal gradient, I can interplay with the overall material properties to provide provide the thinness of the splat to let it achieve very high solidification rate, I can supply very high thermal gradients to it by enhancing the cooling rate and so on. So, I can somehow control the overall structure by utilizing previous material parameters as well as the spraying parameters.

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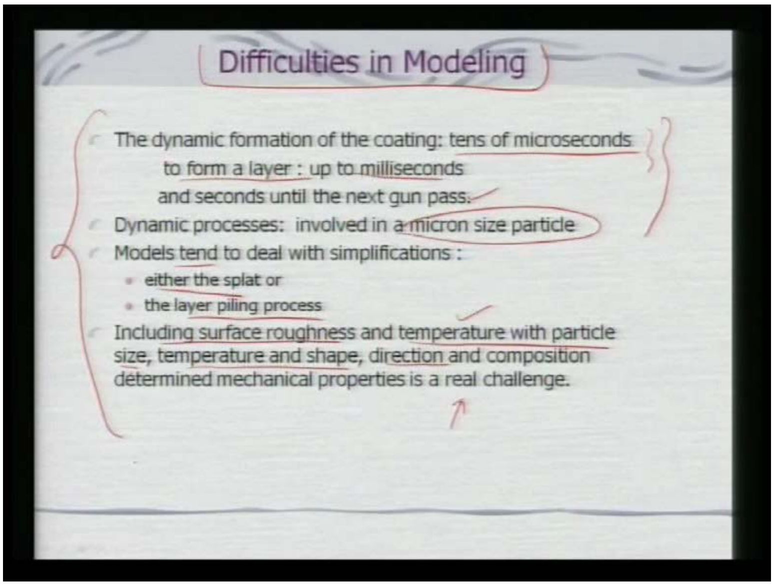

Difficulties in Modeling

- The dynamic formation of the coating: tens of microseconds
  - to form a layer : up to milliseconds
  - and seconds until the next gun pass.
- Dynamic processes: involved in a micron size particle
- Models tend to deal with simplifications :
  - either the splat or
  - the layer piling process
- Including surface roughness and temperature with particle size, temperature and shape, direction and composition determined mechanical properties is a real challenge.

Again the problem if we can modulate very, very nicely that will be very, very good. But the overall problem is the entire process is occurring in tens of microseconds. So, splat it gets heated up, molten, accelerates and impacts on a on a substrate within tens of microseconds. So the so the process is very, very rapid and basically the layer is form in couple of milliseconds, and again it is only few seconds by next pass basically will come.

So, the overall processes very, very dynamic, and the particle size we are talking about is the micron size particle. So, the overall grit makes the process very, very, very complicated. So, the model we have to deal with certain simplifications, so just we can deal only this splat or we can only deal with the piling of the splat to form a layer. Because we are seeing two scales; one is the splat level, second thing is the overall again the micro structural part, so we have certain lamellas, then it is forming some columnar structure and again there is a deposition of all those splats. So, we are talking 2 or 3 orders of hierarchy in this particular structure.

So, it also includes certain roughness, we can also have melting, we can also have un-melted particles, we can have temperature with splat temperature is also variable, particle size is a variable, temperature and shape, direction composition, so we can see there are so many variables which are inherent in the modeling of a of a splat to result a coating. So that is that means processes very, very complicated and very, very dynamic and that creates difficulty in effectively modeling it.

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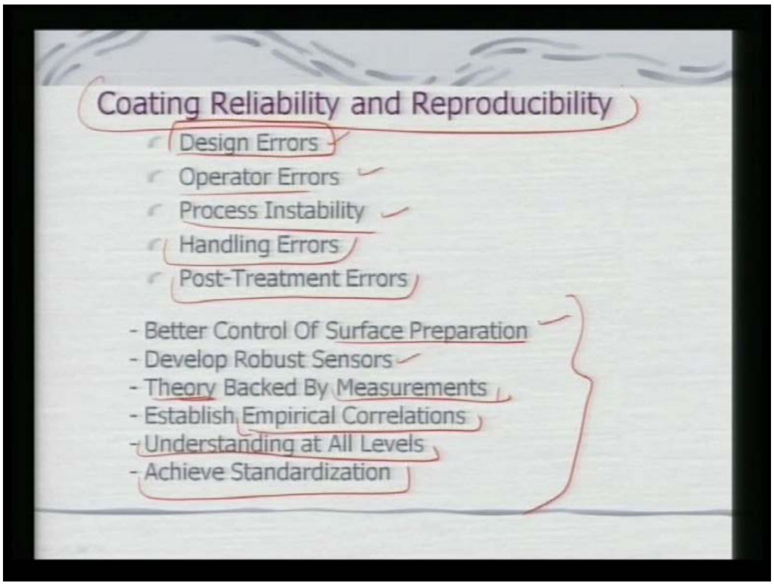

Coating Reliability and Reproducibility

- Design Errors
- Operator Errors
- Process Instability
- Handling Errors
- Post-Treatment Errors

- Better Control Of Surface Preparation
- Develop Robust Sensors
- Theory Backed By Measurements
- Establish Empirical Correlations
- Understanding at All Levels
- Achieve Standardization

Again the reproducibility and reliability of the coatings also also essential components in terms of designing the biomaterials, because if we want to create coating it needs to be what we are intending it to be, so but again there are all these factors such as the the controlling rate, the microstructure, even the parameters of the gun, so we have to play a lot with them to in order to understand it to be able to model it, and to understand it better, we need to basically create some sort of process map to see where we can fit in our coating requirements, and where we can choose the parameters from.

So there are many errors associated which as which can be design errors, some operator errors, they can be also process instability that is being inherent with the process, so there is a fluctuation in the voltage or there is fluctuation in the moment of the gun, they can be handling errors, so even when when we when we utilizing particular material, if we shake it a little bit, the heavier material will settle down, where is a lighter material will basically float up.

So in deposition, first the heavier material will just get deposited, so second time if you do the same coating, the same parameters we might get some very different result; again there can be post treatments those errors can also can creep in, also the kind of surface preparation, so we have to get better control of the surface preparation, sensors also should be very, very robust, and again we have to have the theory, but I should backed by the experimental results of the measurements to back the theory, and somehow establish certain certain empirical correlations, they may not be exactly in nature, but they have to be empirical in nature, so not back by not exactly being that that what is being credit by the theory, but what we are actually seeing.

And then we require and nice understanding at all the levels, starting from the splat splat formation of splat, its stunning down generation of microstructure, and the layering of this particular splats to result overall deposition to finally achieve a standardized procedure of deposing the coating and achieving the controlled structure as well as thickness of those particular coatings with certain specified requirements, so that is what is required in terms of getting a particular coating with a with a nice reliability and reproducibility.

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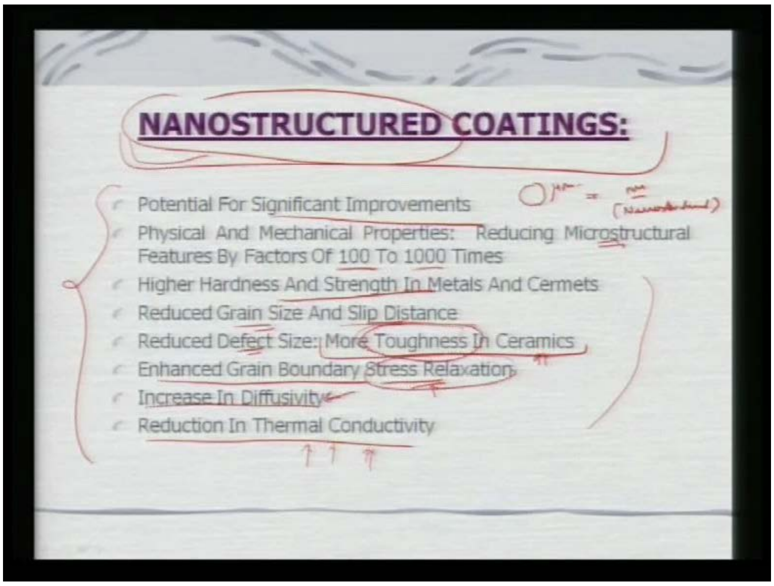

NANOSTRUCTURED COATINGS:

- Potential For Significant Improvements
- Physical And Mechanical Properties: Reducing Microstructural Features By Factors Of 100 To 1000 Times
- Higher Hardness And Strength In Metals And Cermets
- Reduced Grain Size And Slip Distance
- Reduced Defect Size: More Toughness In Ceramics
- Enhanced Grain Boundary Stress Relaxation
- Increase In Diffusivity
- Reduction In Thermal Conductivity

μm = nm (Nanostructured)

And recently a new term has come into picture, which is called nanostructure coating; it has come to (( )), because it has a potential for significant improvement, it can basically nanostructure is nothing but reducing the overall micro structural features by 100 to 1000 times; so generally, we have a structure in terms of structure, which is thicker enough in terms of micrometer range, if we can make them into nanometer range, it means we are getting nanostructured coatings.

It has mired advantages such as it can have higher hardness and strength, it reduced grain size basically reduces a slip distance, so eventuality, we can also reduce the defect size and that can provide much toughness in ceramics. So if you are making hydroxyapatite coating on a on a particular surface, and if we can retain the size or the microstructure micro structural features in the size range of couple of nanometers, we can achieve much enhanced toughness; and that is the criticality of any ceramic component that we want to get maximum toughness out of it.

So if we are if we are able to achieve a very fine grain size, we can enhance its toughness; again if we can make the material much more amorphous such as in glasses, that is again a boon, in case we want if we want to make that particular glass dissolve it time, so for biodegradable components, we can again utilizes particular process, so instead of making nano, we can also make amorphous coatings. And since we have enhanced grain boundary, it it leads to stress relaxation, because now this fine grains can align themselves, they can orient themselves, they can rotate themselves to result a stress relaxation; at the same time, they also increase in diffusivity, that also is a that also is good, because it will result in a uniform microstructure, uniform composition throughout; and also it create it also result in the in a reduction in the thermal conductivity, because we have now very high defect regions, so there is much more of grain boundary area, so much more vacant area, which is nothing but an insulator, so we can achieve much reduce thermal conductivity by refining the grains.

So if you want to provide a thermal production we can also go for this nanostructured coating. And also since the grains are very, very fine, we can also achieve very uniform corrosion properties; so instead of observing a pitting such as which is being observed in as a steel, we can avoid this particular feature ones we utilize the nanostructured coating. So we can see nanostructured coating, they have potential for significant improvements, they can provide much higher hardness and strength by reducing the grain size and slip distance, they can provide much enhanced toughness in ceramics, and they can also lead to stress relaxation, they can increase the diffusivity, also they can reduce the thermal conductivity. So those are the certain advantages of nanostructued coatings, mainly because of their enhanced toughness in ceramics, these are being targeted for.

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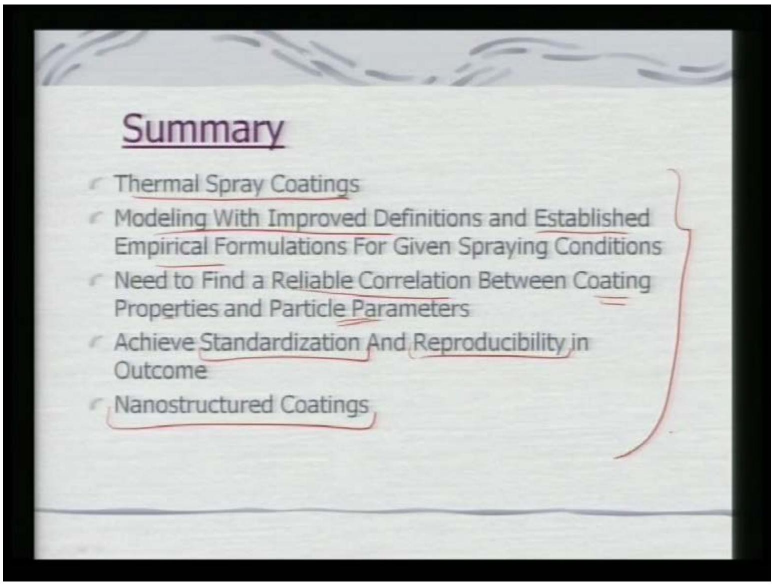

Summary

- Thermal Spray Coatings
- Modeling With Improved Definitions and Established Empirical Formulations For Given Spraying Conditions
- Need to Find a Reliable Correlation Between Coating Properties and Particle Parameters
- Achieve Standardization And Reproducibility in Outcome
- Nanostructured Coatings

So in summary, we can see that the thermal spray coating they emerge as a two for coating by implant material or a device material, to provide certain functionally to it, that is basically the interaction of this implant or the device material with the surrounding tissues; so it can provide a compatibility, it can be either arrangement of certain pours or certain chemical composition to provide to provide it friendliness with the surrounding material or surrounding environment, but again modeling with the improved definitions are required, and it is required that we establish certain empirical formulations for certain spraying conditions, and come up come up with a process map to select certain property with certain functionality or the micro section.

And we will to find a reliable correlation between coating properties and the particle parameters of the processing parameters so we can finally, achieve some standardization and reproducibility, so that is highly required for for achieving a good and reproducible coating again and again, and recently nanostructure coatings have emerged, which can provide much enhanced toughness and enhanced mechanical properties to a surface coating. And again by again we can see by controlling the thermal gradient and the interfacial velocity, we can somehow control the microstructure, and end process we can also control the we can we can evolve with some empirical co relations of the processing itself, and now we can join these two in order to achieve the maximum benefiting properties for a biomaterial coating with this I end my lecture. Thank you.