

Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 60
Overview & Conclusion

Welcome to the last lecture the 60th lecture of Surface Engineering. We have covered quite a bit and I hope during the course of all these lectures. I have we could arouse sufficient interest in knew about surface engineering and its utility and scopes of application. But, before we wind today I thought I would review the overall scope of surface engineering again, including the scheme of classification because classification is a way of actually addressing the entire subject domain and also take a summary look or bird's eye view. So, that we know exactly what is overall scope and what are the different possibilities of application.

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Surface Dependent Properties

Surface: Structure, Composition, Energy, Properties

Surface dependent properties: Mechanical (hardness, wear, friction (mechanical), corrosion, catalysis, oxidation (chemical), adhesion, reflectivity, emissivity, optical (physical)

Engineering consideration: Design, Life, Performance, Safety, Reliability, Aesthetics, Quality, Cleaning, Environment, Modeling

Surface engineering techniques: Coating, Cladding, Plating, Deposition, Thermal/chemical treatment, Polishing/grinding, Implantation, Diffusional treatment, Surface melting/alloying

Concerned industry: Manufacturing, Automobile, Aerospace, Power/ energy, Chemical/petrochemical, Biomedical, Textile, Defense, Food packaging, Machine/heavy industry, Mining, Electrical/electronics



So, before we talk about surface engineering; obviously, the first and foremost question is what is the surface and what are the surface dependent properties. And if you recall we did say that for any solid whenever we look at the external surface, if the surfaces could be internal as well as external, but we are primarily by surface what we mean essentially is an external surface.

So, for a three-dimensional solid we certainly will have certain external surface or so called solid vapor surfaces and this is where the coordination or the surrounding atoms or ions or molecules the species basically the environment is going to be different. So, there will be at least 1 degree of freedom for any atoms located at the surface then an atom which is in the center or in the interior of the solid.

So, because of these at least 1 degree of freedom there will be certain dangling bonds and the cumulative effect of these dangling bonds give rise to what is known as surface tension per unit length or surface energy per unit area. So, the origin of surface energy as we understand is due to the unsaturated bonds or the cumulative effect of the unsaturated bonds at the surface and this is true for all kinds of solid not only pure solids, not only just metallic ceramic or polymeric solids, but even composites aggregates or all kinds of solids.

But of course, the surface energy varies it depending upon the condition the composition and prior history of the solid and based on that we have different manifestations of surface energy. Now to a large extent the surface energy influences the surface dependent properties. So, as I said we define the surface in terms of its structure the atomic or ionic or molecular aggregate that we are talking about its composition. And there is always a possibility of little variation of the surface composition than the bulk composition, because surface is always prone to absorbing, impurities from the atmosphere around.

We talked about surface energy just now which is a very important characteristic of the surface and obviously, the various forms various types of surface dependent properties. So, there are three major classes of surface dependent properties we have already talked about; one is the mechanical properties namely the hardness where friction on and so on and so forth. We can have properties which are of chemical nature; the corrosion properties, catalysis, oxidation, chemist option, even various kinds of diffusional activities and so on.

So, primarily depend upon the composition and the chemical the Gibbs energy or the chemical potential of the surface. Also we talked about all or we are concerned with various physical properties like the adhesion, reflectivity, emissivity; for example, the optical emission properties or simply the de aesthetics or the appearance of the surface and color and so on.

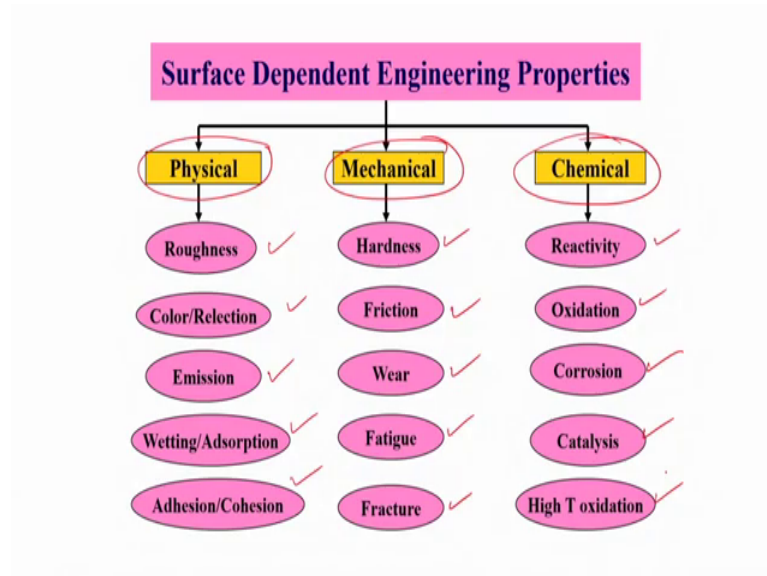
For we need to talk about surface dependent properties for various surface engineering; surface engineering considerations or in general engineering considerations not; so, surfaces are important for various engineering considerations. Be design or life prediction or assessment or the performance properties, safety of the component, its reliability, the aesthetics, the look appearance, the quality, the clean properties environment, an inventory interaction and obviously, a bit of modeling exercises.

Now, there are various surface using techniques I mean just randomly I have picked up a few here we have talked about various coatings, various cladding, processes, plating or deposition then thermal and chemical treatment processes, polishing and grinding, implantation, various diffusional treatments, surface melting surface allowing and so on and so forth, just picked up randomly some of these techniques.

And what are the industries practically all any wherever we use a solid hardware and the surface of the solid is exposed to certain uncontrolled atmosphere; that means, it is not vacuum or it is not an isothermal condition or it is not there is a possibility of change in temperature pressure, moisture content or composition of the environment surrounding the solid. In all such cases there could be a variation of the manifestation of surface dependent properties.

So, all components associated with manufacturing, exercise, automobile industry, aerospace, textile, biomedical applications, chemical and petrochemical, power and energy, production devices, various defense applications, food packaging, machinery and heavy industries, mining operations, electrical and electronic devices almost everything that one can think of.

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So, we as we just now mentioned we divided them into three major classes; physical, mechanical and chemical. For example, roughness, color and reflection, image emissivity or emission characteristics, wettability adsorption, adhesion cohesion all these properties we club them under the physical properties.

Mechanical of course is on the hardness, the friction wear resistance, fatigue properties, even fracture because these are surface dependent the failures mostly initiated the surface. Though to a large extent their bulk properties, but initiation is always at the surface. Similarly; chemical properties in terms of reflectivity, oxidation, corrosion, catalysis, particularly high temperature oxidation processes and so on.

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Surface Engineering Approaches

Dimension: (a) Addition, (b) Modification, (c) Removal

Type of Change: (a) Physical and (b) Chemical

Temperature: At (a) ambient or (b) elevated temperature

Properties: (a) Mechanical, (b) Chemical (c) Functional

Physical state: (a) Solid, (b) Liquid, (c) Gaseous, (d) Plasma

Substrate: (a) Metals and alloys, (b) Semiconductor, (c) Glass, (d) Ceramic, (e) Polymers, (f) Composites/aggregates

Activation: (a) Mechanical, (b) Thermal, (c) Chemical, (d) Electrical, (e) Directed energy beams


Coating-Substrate Interface: (a) Diffused and (b) Sharp

Cost: (a) High capital, low running cost (automated) — *Modern*
(b) Low capital cost, high running cost (labor, utility, etc.) — *Conventional*

Coating dimension: (a) Thick ($> 1 \mu\text{m}$) and (b) Thin ($< 1 \mu\text{m}$)

Hazard: (a) Toxic by-products, (b) Solid waste, (c) Effluent

Objective: (a) SE, (b) Repair, (c) AM (3d printing) *Additive mfg. = Cladding*



Now, how do we approach the entire or the vast field of surfacing engineering and in fact, this is something you know it is not very easy to comprehend the entire scope in one snapshot, but that is exactly what we have tried here. So, in terms of dimension we already classified then in two possibilities where we add on additive type, we only modify do not change the dimension or we remove from the surface typically like polishing grinding.

So, when we coat and deposit or clad when we are doing addition, when we only change the microstructure and not change the composition or sorry, not change the dimension then, we say simply modification or when we remove then we say removal types or processes. The type of changes associated with any surface engineering process would be primarily of two types, when we do not change the composition and change only the microstructure appearance and various other physical attributes we call it physical approaches.

The other one; otherwise in vast majority of surfacing processes we change the composition and we call them chemical surface engineering approaches. And these are physical or chemical methods can be carried out either at ambient temperature or at elevated temperature.

Now, we already said that property wise will be worried about or will be concerned with the mechanical properties, the chemical properties and a vast range of functional

properties; I mean, electrical, electronic various types of physical properties which are of functional measure. In other words which are not dependent on the activation based on mechanical forces or chemical interaction.

So, the way we do surface engineering for example, anything that we want to add on or introduce to the surface, modify the chain surface composition or simply bring the surface to some kind of activation or influence. These things we do in three or four possible ways; one is that we carry out the entire process through solid; so, entirely a solid-state processing for example, of diffusion coating. We can do for example, a liquid I mean, we can immerse the substrate in a liquid medium and then carry out certain divisional process or chemical reaction process essentially in a liquid bath. So, it could be a conversion coating, it could be liquid carburizing or cyanide and so on.

A vast majority of could be done in gaseous state for example, plasma nitride for example, gas nitriding or various gaseous processes or in the vapor state like PVD CVD and so on. We can also do things in the plasma state which actually allows us to clean and as well as to quote, to deposit, to modify, allow diffusion and various processes.

The substrates can be any solid essentially, in one single word is any solid. So, which means it can be the metals and alloys a vast majority of our discussion concerned with metals and alloys, could be semiconductors, could be glass, could be ceramic, polymers even various aggregates and composites. So, can be mixtures of that as large as even concrete for example, so that is why I said aggregates. The activation the reason the driving force where actually the changes come from could be of mechanical nature say for example, say surface rolling or skin pass rolling or sharpening and so on.

Or thermal in nature; a vast majority of them are thermal in nature all these diffusional processes. It could be chemical in nature it could be a chemical reaction various forms of let us say anodizing on or nitriding liquid bath processes or gaseous processes, but changes happen because of the chemical reaction happening at the surface. It could be because of the various electrical forms like; various forms of electrolysis or electrolysis based processes like platings and depositions and so on. It could also we have at the end of the course we did have a number of lectures on ion implantation, laser, plasma, laser or electron beam and so on. So, these are the sources of various surfacing processes happening.

The almost all the surface engineering processes can be broadly divided into two major categories in terms of the coating substrate interface. So, if this is a solid and if this is the coating on top of the solid. So, this interface can either be an interface whereby if I just take a line profile across and then plot the composition, say of the solute element has a function of depth.

We have two possibilities; one is where we have a sharp interface like this. So, this is the coating region where the composition is entirely different than the substrate region or the other possibility could be that we can have and diffuse interface like this. Where the solute atom would have diffused until certain depth from the surface and this is a function this usually is a function of temperature or maybe some other activation.

So, whether the interface solid the substrate deposit interface is diffused or sharp, we can practically divide practically all kinds of surface engineering processes we have discussed so far. Now, the user would be also concerned about the investment the cost. So, one majority of the processes are of the type where the conventional ones are of the type which are low capital cost, but high running cost because of the electricity the various chemicals and so on, labor cost and so on.

So, these are mostly the conventional processes, where as you can also have various other techniques like laser paste, electron beam and so on, where the capital cost is large, but the running cost is fairly low because it is mostly automated. So, these are the so called modern surface engineering processes or techniques.

The coating dimension wise I mean this is a loose classification not a very strict or sacrosanct division anything which has more than a micrometer thick coating we say thick coatings or thick films and so on and anything less than 1 micrometer is generally said thin. So, all these PVD, CVD, sputtering and plating, an implantation all these processes are essentially thin film coating or thin coating technologies. Whereas, cladding or plating or carburizing, nitriding all these are thick coating processes.

There are certain hazards involved, like any process we have to be very careful about possibilities of certain toxic byproducts for example, if you are dealing with hexagonal chromium or dealing with phosphine or phosphine kind of reactive gases, even chloride ions or there could be emission of for example, in CVD processes you generally have a byproduct which is halide gas. So, you have you cannot throw it open in the air, even in a

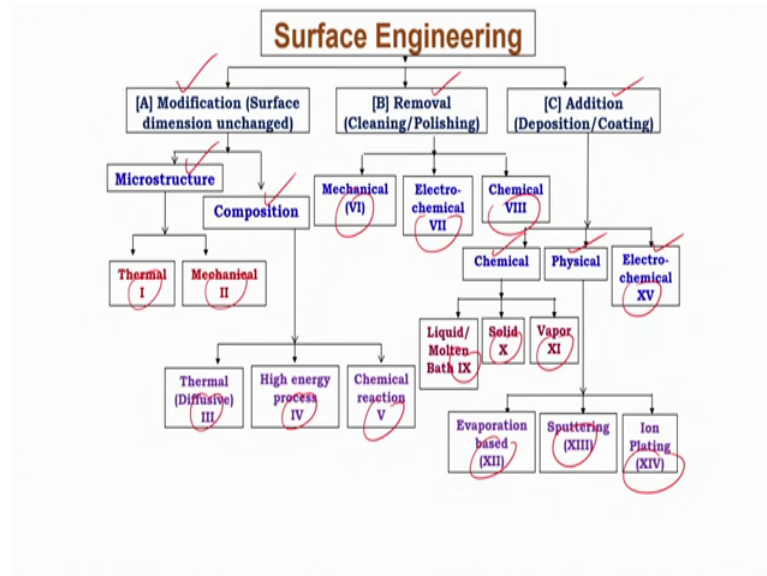
various kind of liquid bath processes or gaseous bath processes we do deal with toxic byproducts.

So, one has to be careful about those things there could be also quite a bit of large amount of solid waste generated. All these divisional coating processes when the pack is exhausted its not defusing more, then these packs can be actually I mean over a period of time you tend to accumulate a lot of pack. So, it is important that we try to reuse them or recharge and reuse them then there could be also liquid effluent all these acids and other kinds of byproducts.

So, the overall objective of surface engineering so to say and the overall scope I would say is I mean, all these techniques I have starting all the way from simple hot dip coating to all the way very sophisticated ion implantation. All these surface engineering processes all these techniques basically could be used for various surface engineering applications. They could also be useful for various repair, refurbishment and reclamation jobs and most importantly this is the modern approach of or the modern scope of graduating surface engineering to the wider scope of application which is essentially additive manufacturing.

So, this additive manufacturing as I said is nothing but it essentially is a larger version or a modified version of cladding. So, you actually develop layer by layer and eventually develop a 3D product and hence it is called 3D printing or nothing but additive manufacturing.

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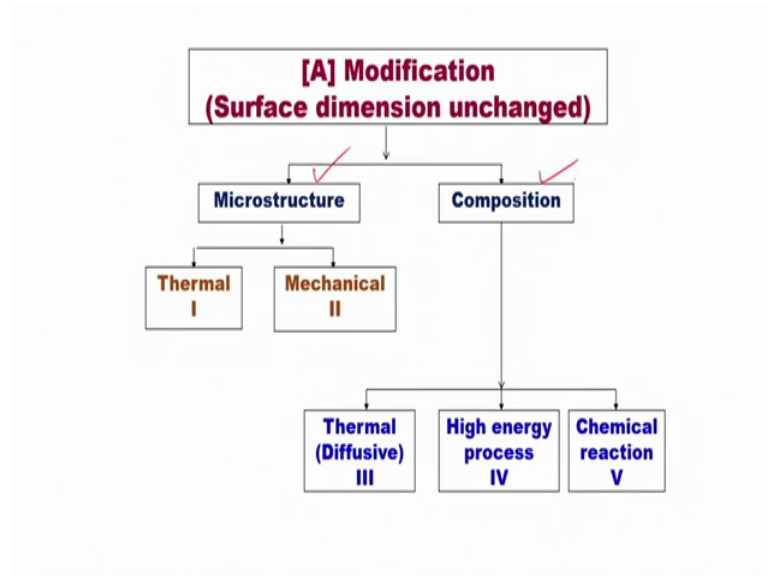


So, the overall scope; I mean, let us be I mean this is something I am just repeating which probably was part of one of the earlier lectures very early lectures. So, this we have already discussed know, the modification which is only changing the surface microstructure or composition without change in dimension.

Or it can be removal based where we do cleaning, polishing, grinding and so on or we do addition which could be through the chemical method, through physical method or electrochemical method. So, more or less all these as you realize they all of these can be actually a physical type or chemical type, where we are not changing the composition or where we are changing the composition.

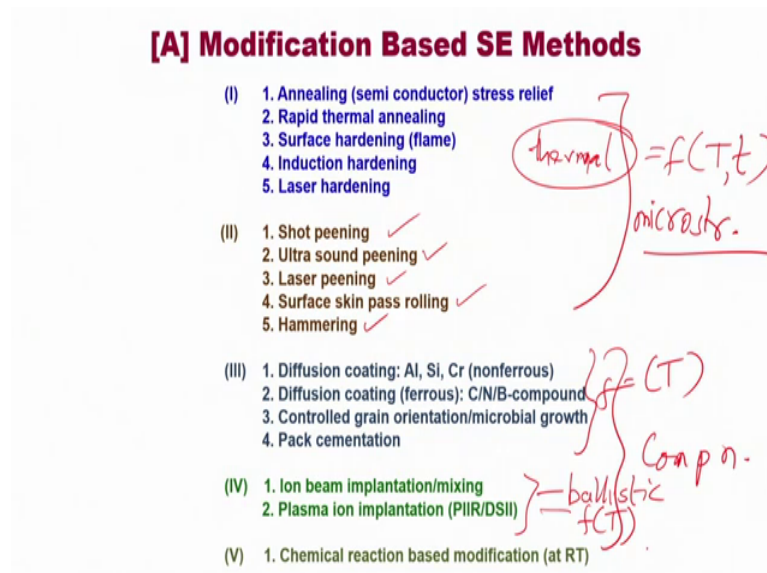
So, when we are doing the modification; so, let us say all these altogether I had these all together from I, II, III, IV likewise we kept on making various forms of changes and then all these put together we have identified some XIV different variants of surface engineering approaches. And they all essentially address the same philosophy tale at the surface microstructure and over composition.

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So, in terms of dimensional changes where surface dimension is not changed, but only we modify as I said, we can change only the microstructure or composition and these are the different methods.

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And if we go deeper then these are the techniques we have discussed in various times, anything starting from a needling, rapid thermal annealing, surface hardening, induction hardening, laser hardening or any other hardening process. So, it this is basically a thermal process, all these are essentially at thermally activated process. So, where we so,

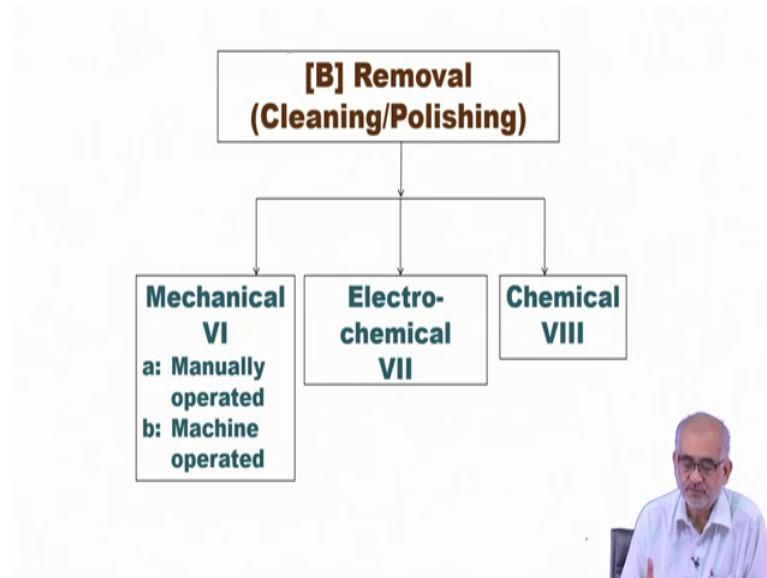
essentially is a function of temperature and time and essentially we change the atomic aggregate on the surface or the thin films. So, that certain properties be a function of functional or say conductivity or maybe strength and so on can be tailored.

There could be also processes which are mechanically activated so, you essentially heat the surface with stream of hard spheres or allow ultrasonic wave to heat the surface and create a shock wave at very high frequency for a very short duration, but creating a certain force pulses onto the surface. So, that the surface undergoes very thin layer of deformation and in the process create a residual compressive stress on the surface. This could be also through skin pass rolling or simply hammering and so on and so forth.

Then there these three the groups of III, IV and V here we attaining composition; so, this is these two are only changing microstructure and here we are changing the composition as well and how are we changing either by thermally activated diffusion. So, these processes are a function of temperature; so, temperature determines what will be the depth of penetration these two plasma, ion implantation and ion beam implantation, they are basically through these are ballistic processes whereas, plasma ion implantation is also dependent on temperature.

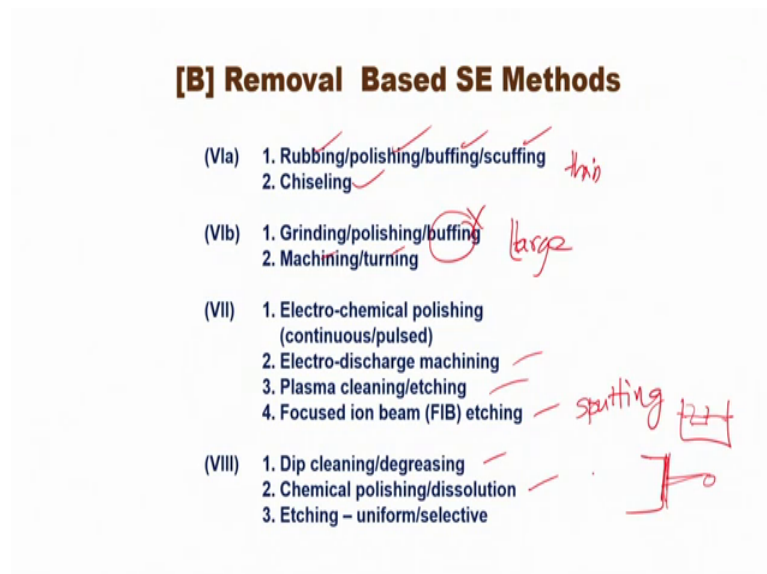
So, we modify the surface composition and hence certain properties depend on surface. There are vast majority of chemical reaction based modification we do not where we do not necessarily change the surface dimension significantly, though there could always be a little bit of changes or certain surface ripples can be formed because of surface tension forces. But the whole process is depending on chemical reaction or chemical changes say anything starting from anodizing to various kinds of conversion coatings and so on.

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We need to clean the surface or remove.

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So, we can do anything like say rubbing, polishing, buffing, scuffing, chiseling heavier or when we deserve here that the amount of material removal is a thin or small and here the material removal is large. So, we can think of grinding, polishing or machining turning and so on, buffing is not quite correct because generally the material removal is very small here. We can also remove materials and clean the surface and make it truly

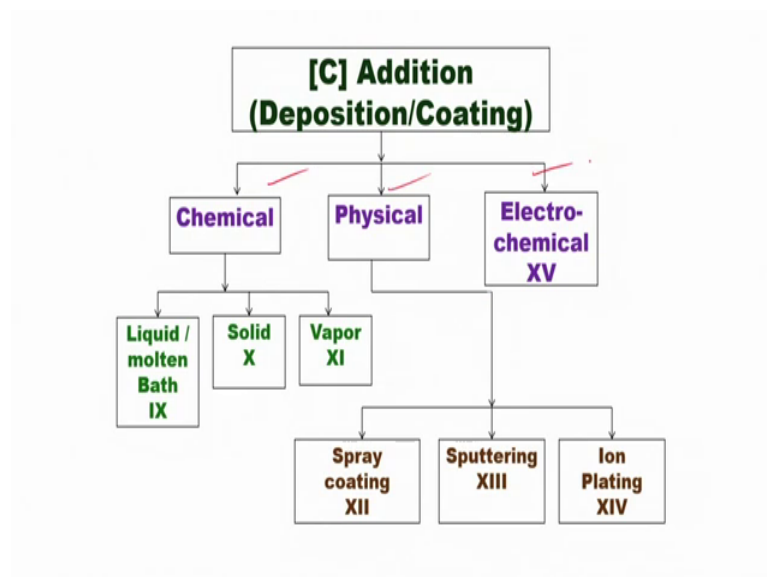
polished by way of electrochemical means where basically the dissolution from anode will remove ions selectively and in a controlled manner.

So, it will remove the surface asperities and eventually make the surface more flat and less rough, it can be through the electro discharge machining this is not first surface cleaning or polishing, but this is for pure machining operation. It one can do plasma cleaning or plasma etching or even use an ion beam for etching and cleaning even say for example, use sputtering that is also one way of cleaning the surface.

When we reverse the polarity you actually eject atoms from the surface and that is how you clean the surface by it sputter cleaning. You can do a deep cleaning or decreasing in a chemical bath for large components you can do chemical polishing or dissolution where you actually may have a jet incident onto the surface.

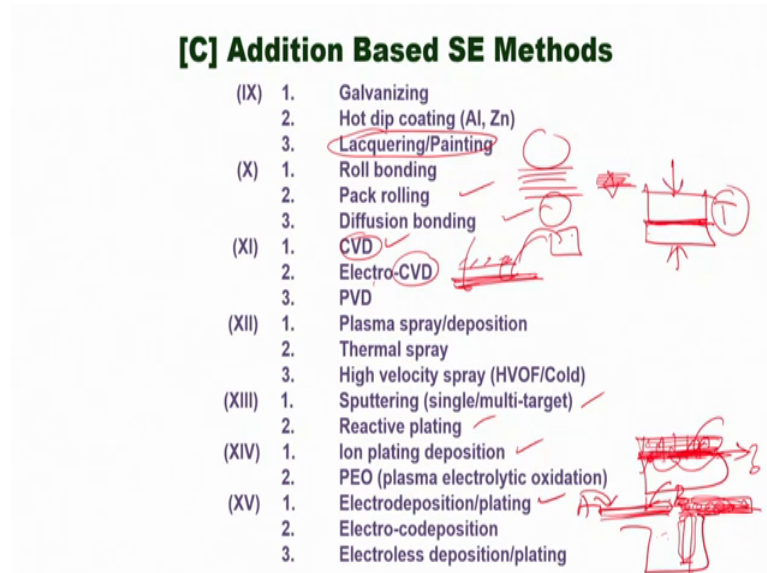
So, if this is a solid surface and here is the nozzle and from the nozzle you throw a jet and you move the jet up and down or vary the angle of incidence and then you can clean the surface. You can do etching where essentially you will have certain chemical reagent and you will put the sample into the bath for a certain period of time and you remove. But, remember this etching can be chemical like this, it can be also through iron or through heat tinting by simply heating or giving certain preferential chemical attack onto the surface so, all possibilities exist.

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In the addition processes, we actually can do various kinds of chemical, physical and electrochemical methods apply them.

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For example, galvanizing, hot dip coating, lacquering and painting. So, this is something which we have not discussed much in the course, but its nevertheless very very important for anything from a large wall of a building to very sophisticated electronic device or even decorative pieces. So, you basically may apply a transparent or translucent molecular coating so, that the surface of the metal or the semiconductor does not get exposed to atmosphere directly.

You can also do roll bonding so, you actually can have multiple foils and then let it pass through the roll and then eventually what comes out will be thinner than this, but this process in the process you actually make them bond well within this thickness. You can do back rolling can do diffusion bonding where you have by diffusion bonding what you mean is you actually have only two foils or two plates and you apply very heavy pressure and exposed to a certain temperature. So, that this interface allows inter phase diffusion and forms a fairly strong bond.

You can do deposition in the form of chemical vapor deposition or electro chemical vapor deposition or plasma assisted deposition processes. So, when you change the composition or you actually create a composite surface with a different or a coating with a different composition than the substrate you call it chemical vapor deposition

processes, otherwise you can also do you can do change the composition. But when a chemical reaction takes place into that in the atmosphere in the vapor state and then get deposited on to the surface you call it CVD processes.

But in PVD of course, everything comes from the vapor state, but there is no change in composition between the target from which these vapor come and the coating which eventually forms on to the surface. So, in CVD you have a chemical reaction proceeding the deposition or at the surface accompanying the deposition and hence the deposit has a different composition than the precursors, but in PVD, you have the same composition as the target.

Your various forms of spray processes thermal spray or plasma spray or deposition also various high velocity processes like HV or for cold spray. Similarly, you can have processes like sputtering which is through one form of CVD PVD, but under the influence of certain potential difference where you direct a certain agencies to actually scoop out atoms from the target and then those atoms are deposited onto the substrate.

So, unlike PVD the thermal activation is not the key here, it is basically those ions particularly organ ions which actually scoop out atoms from the surface and then deposit elsewhere. So, that is the process, we can also in the process you can have multiple targets and make them react in the vapor state and deposit. Somewhat very similar to CVD, but the difference being that what you plate, what you deposit actually is because of surface reaction happening on to the surface.

We can have ion plating depositions, ion assisted deposition you can have plasma electrolytic oxidation so, you take a substrate and then you allow a selective oxidation from the surface. So, that metallic grains here these metallic grains here actually get selectively oxidized and this oxide and the metallic substrate below are fairly compatible so, there is no immediate equation expected or anticipated.

Normally, when you deposit by laser thermal spray or plasma spray an oxide layer on top a thick coating of oxide layer, compositionally structurally they are so different than the substrate this interface is always a question always a suspect. Whereas, when you do oxidation of the surface and allow oxides to grow like this from the bottom then the compatibility is much better. One can do electro deposition or plating or you can even do

co-deposition so, you can for example, create a surface with an alloy layer by way of depositing A and B either simultaneously or most often they are done sequentially.

So, you have a very thin layer of A and then very thin layer of B or you pulse in such high frequency that in the process you do not necessarily create one layer of A and one layer of B, you actually within the layer itself you will have A B A B so on. And because of high surface diffusion diffusivity, they tend to intermix and form an alloyed coating onto the surface. You can also do electroless deposition or electroless plating where the whole process is essentially because of certain catalytic effect.

So, if you have a bath and if you have if you dip a particular so, without application of any potential difference so, there is no completed circuit, there is no electrically closed circuit, but yet when you dip certain metal. Because of the auto catalytic effect, immediately the ions which are available in the bath will have a tendency to deposit onto this and then form a coating so, that is electroless coating.

So, this is the overall scope of the entire surface engineering course that we have discussed. Now I must tell you that you have to I mean I must admit that there are multiple textbooks available, but there is no single textbook as on date which can cover the entire scope of surface engineering that we have discussed in this course.

So, you have to refer to various sources, various resources including the certain good literature available in the internet, but I would strongly advise you to rely more upon the reviewed resources including technically, technical papers published in the journals, but otherwise textbooks or reference books, handbooks, even internet sources this could be very good material for your self study.

And always whenever you face any difficulty, you are free to write to me an email or we probably soon will have an open discussion session and there you can raise your questions. But, please send your questions beforehand so, that I have a short and composed reply ready for you.

But overall I would end up saying that any solid any hardware primarily if it is a solid substance solid substrate and is in contact with atmosphere either at room temperature or elevated temperature or is undergoing certain interaction which is of mechanical origin or thermal origin or chemical origin or there are various forms of activations possible.

So, under such influences the failure or degradation of the circuit of the component is most likely to happen from the surface. So, how do you protect the surface and in the process the entire component the bulk that is all about surface engineering.

So, again approaches are very different and what is important is that you understand the philosophy, you understand the mechanism, you understand the driving force for certain processes why they are happening. And also understand the various forms of surface dependent properties, and the way they can be improved upon or they can be safeguarded and that is all which is included in surface engineering.

So, I wish you learnt reasonably well and I could make you interested in the subject and hopefully you will be able to this knowledge in your profession and certainly serve the society in a very very effective manner.

So, thank you very much and wish you all the very best.