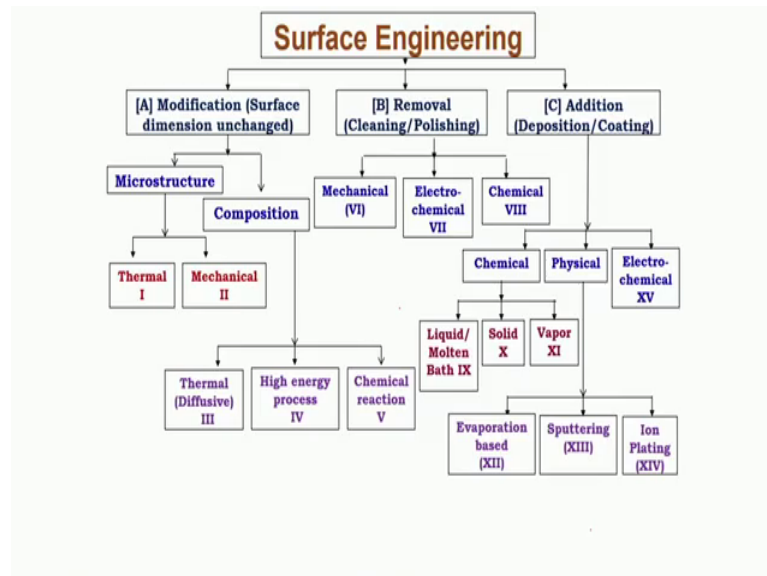


Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 17
Classification of Surface engineering

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Hello and welcome to this 17th lecture of this particular series on Surface Engineering. I hope by now you are familiar with the concept that by surface engineering what we mean is the modification or tailoring of the microstructure and composition or either of them on to the near surface region only leaving the bulk unaffected. So, as I said there are two approaches, we can either change the microstructure or we can change the composition or both. Now there are very many processes available, whenever you actually approach a particular subject matter the first and foremost way of looking at it would be to understand what is the overall scope of the subject.

So, this particular view graph tells you exactly what is in it for the entire course, as this is one snapshot which summarizes the entire scope of the work. And as you can see that there are three approaches three possibilities; one is when we are modifying the surface meaning the modification of the surface composition or the microstructure, but without any change in the overall dimension of the specimen.

For example, the thickness remains what it is and essentially we use either thermal or mechanical activation to change certain parts of the composition and microstructure of the surface alone. So, this is one possibility where we are basically changing only the surface micro structural composition without any major change in dimension.

The next possibility is that, where we actually remove some part of the surface typically in an approach to clean or polish and in the process we actually bring in certain changes in the surface chemistry or the microstructure. We can also do another possibility which is very widely practiced, is based on deposition or coating where we actually add on to the existing dimensions of the surface.

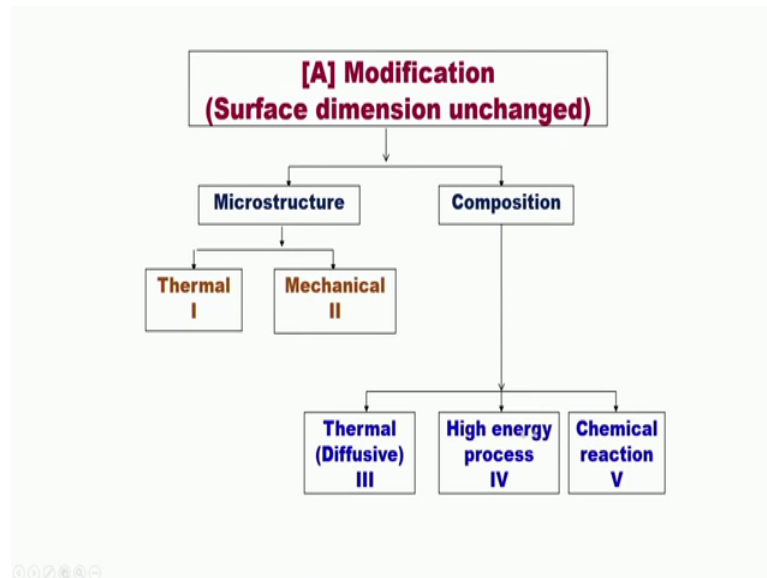
So, in A we do not change the macroscopic dimension of the surface for example, thickness remains what it is. In B the thickness reduces when we remove certain parts from the surface. And in C when we add on and we certainly increase the thickness or certain dimension of the sub of the surface; in all these cases overall we actually would be covering 15 different approaches I will not say very specific techniques.

Because these are generic even when I say that I am going to change or modify the surface microstructure using thermal activation or similarly micro structural changes by mechanical activation alone. Then under this 1 and 2 there are quite a number of techniques or processes possible. And in fact, we will be covering more or less all of them, but as I said our approach is scientific.

So, that we first understand the generic principle behind this approach and then certain modifications of one approach to another brings you to from one technique to another. So, we are not going into random description of the various techniques possible we first would like to classify them scientifically.

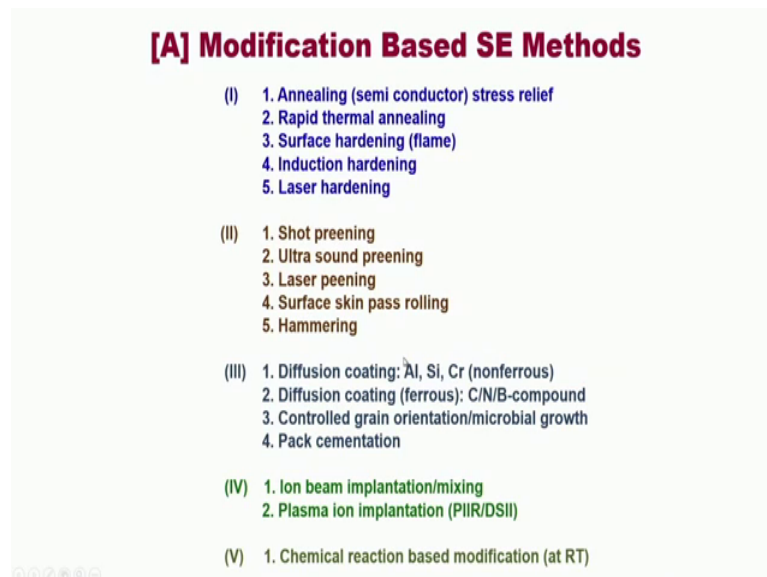
And in this approach for example, under A we have possibilities of thermal or mechanical activation for change in microstructure and similarly compositional changes are possible by using diffusion or high energy processes even chemical reaction for a very thin layer likewise, there are very many possibilities. So, we will go one by one systematically.

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So, first we are talking about approach A where we are changing only the surface micro structure and composition without any major change in dimension of the surface. First when we talk of change of microstructure, as I said already we can do it either by thermal activation or by mechanical activation.

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So, what does it mean? For example, when you are changing the microstructure alone and not changing the composition by thermal activation. Essentially you are exposing the your specimen or the sample to elevated temperature and diffusion may take place

certain phase transformations may take place and in the process the surface actually acquires a slightly different microstructure.

And this could be substantial or this could be marginal for example, when you expose a semiconductor material for annealing or a metallic system for stress relief, you essentially are only changing the state of stress. And in some cases also distribution of the domains or the atomic arrangements on to the surface.

Similarly, the semiconductor materials are often exposed to rapid thermal annealing where, only a certain depth from the surface. So, you actually apply a flash of light which could be a laser light or a thermal flash because of which the surface gets activated thermally up to a very thin distance from the surface towards the core. And only a few atomic layers on the surface undergoes thermally activated diffusion and atomic migration because of which, certain stress relief operations take place or certain reorganization of atoms in small length scale.

In case of steel a very routine and a very standard technique is to harden the surface by way of just heating it either by flame or by induction induct electromagnetic induction or even using an electromagnetic wave called laser. So, that the surface from this from the tip from the top of the surface, unto a small depth from the surface gets heated up. So, within a very short time you actually apply a pulse heating and because of which the surface gets heated up. Now while heat trans transports from surface to the core within a very short distance the temperature comes to a very low level.

So, as a result the bulk of the material remains at room temperature only the surface gets heated up and because of this heating and cooling cycle the microstructure undergoes certain change and in this three cases in particular surface hardening induction hardening and laser hardening the room temperature microstructure which is ferrite, pearlite combination reaches austenite stage.

And then subsequently austenite is quenched by self quenching to room temperature and in the process we see transformation of austenite into martensite and as a result the surface gets hardened. So, this is a standard technique for hardening the steel surfaces, on the other hand when you talk of changing a similar micro structural modification of the surface only by mechanical activation without changing the composition.

So, you can do essentially when you imagine any piece of metal and when you heat not thermally heat when you actually, impact or hit with a hammer or for that matter some other techniques, then you actually I am sorry about this spelling mistake here it should have been peening shot peening.

So, this when you hit with either a hammer or with ultrafine spherical objects at very high velocity the impact actually changes the surface and introduces certain density of dislocation. So, this could be purely because of mechanical activation; similarly you can also create a certain shock wave on to the surface by way of laser peening.

So, essentially you confine the surface with some coating and then, when you apply the laser suddenly the coating material expands at a very high rate and in the process creates certain compressive stress onto the surface. You can also do skin pass rolling where the deformation degree of deformation from the surface is very limited onto a very small depth from the surface or you simply can beat the surface with a hammer.

And then create a small deformation layer in all these 5 processes the essence of the micro structural change is related to increasing the dislocation density onto the surface. And as a result of which you actually end up creating residual compressive stress onto the surface, which actually is beneficial for improving the fatigue strength or for that matter any situation where ever one anticipate certain crack growth or crack propagation.

So, the crack propagation will be reduced and in some cases even prevented when the degree of residual stress onto the surface is fairly large. So, in under approach A using the techniques under 1 and 2 we are only changing the microstructure and not the composition. On the other hand we actually can also now move on to another possibility where we do not change the dimension of the surface, but we change the composition; and that can be thermally act through thermally activated process, through high energy processes or taking recourse to some chemical reaction which is confined only to the surface region.

For example, you can quote a material with elements like aluminum, silicon and chromium these are particularly useful for both ferrous and non ferrous substrates. The advantage is that these elements actually create an solute rich layer onto the surface which when exposed to high temperature, preferentially creates oxides of these elements

which are very not only very stable and having very high melting temperature but also are quite adherent to the substrate.

As a result you create a thermal protection system onto the underlying substrate. So, this is possible with let us say these kind of non ferrous elements, similar protection is also possible on metallic systems by way of introducing the interstitial elements like carbon, boron or nitrogen which in turn can create their compound, so interstitial compounds which are extremely hard and wear resistant. So, this is how you can actually create a boride layer or a carbide or a nitride layer onto the surface to protect from any amount of mechanically activated degradation of the surface.

We also can apply thermal activation for control grain orientation or even microbial growth onto the surface, so that the surface composition again very thin region undergoes certain change in composition. And as a result there could be a certain amount of protection or some other activities or the properties are enhanced. We can also do a pack cementation which is very similar to diffusion coating essentially, this is a completely a solid state process.

So, wherein you actually pack the component inside a box and then expose the box or subject the box to a high temperature so that the diffusion takes place, but this here the diffusion pack contains not just the diffusant, but also certain activators and catalysts and so on. The other approach wherein, we are changing the composition of the near surface region without changing the dimension could be for example, using the high energy ion beam which can be either implanted or mixed intermixed.

Now, here essentially you are now instead of like in case of shot peening or ultrasound peening, you actually in shot peening in particular you are throwing small spherical objects at very high velocity. And in the process creating residual compressive stress by increasing the dislocation density on to the surface. In case of ion beam implantation you actually are shooting atoms you actually are energizing accelerating the atoms and from the gun when you shoot these atoms they find their way they make their way into the surface up to a certain depth.

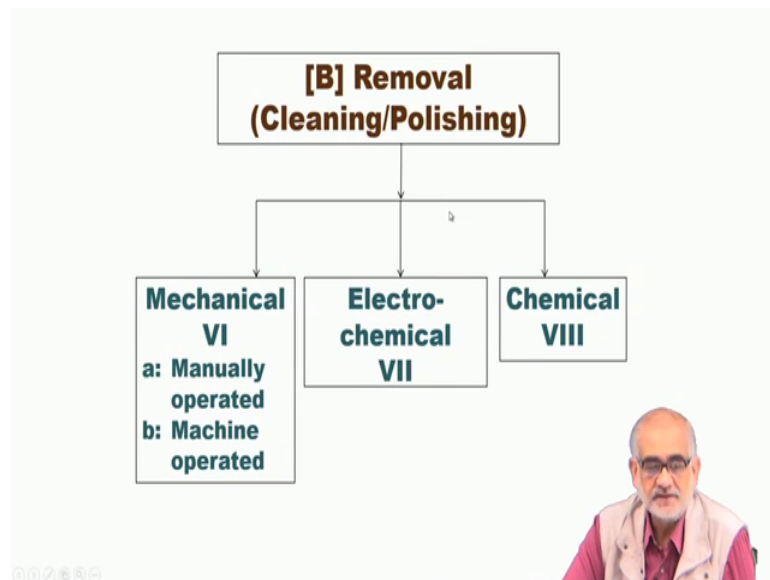
And actually what happens in the process is somewhat similar to the a cascading effect we see on a carrom board or a billiard board when one object hits, one of the frontal coins then in turn that coin hits another and another and so on.

So, you actually see a chain reaction or a cascading reaction and in the process, the ions which are implanted onto the surface reaches up to a certain depth, below the surface and over a period of time, the overall composition of the near surface region which could be just few atomic layers from the surface gets modified.

We can do a similar implantation in a plasma environment and this is typically called a plasma immersion implantation processes. And these are certain characteristics which are fairly beneficial for non line-of sight implantation, I must clarify that when you talk of ion beam implantation you essentially modify exactly the point that you are seeing so, its called line of sight process; whereas, in plasma immersion processes it need not be exactly the line of sight process.

Finally we can also change the surface composition by very thin chemical reaction layer, created at room temperature by way of certain very specific chemical reagents. So, this is what we have just discussed the modification of surface dimension, surface without changing the dimension.

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The next would be when we are ready to remove a part of the surface and this essentially is a process where which can be again through mechanical activation or mechanical means by removal by electrochemical means or removal simply by chemical attack.

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[B] Removal Based SE Methods

- (Via)
 1. Rubbing/polishing/buffing/scuffing
 2. Chiseling
- (Vib)
 1. Grinding/polishing/buffing
 2. Machining/turning
- (VII)
 1. Electro-chemical polishing (continuous/pulsed)
 2. Electro-discharge machining
 3. Plasma cleaning/etching
 4. Focused ion beam (FIB) etching
- (VIII)
 1. Dip cleaning/degreasing
 2. Chemical polishing/dissolution
 3. Etching – uniform/selective



So, in these three approaches, you are talking about. So, this approach based on removal of material from the surface, one can divide the mechanically activated processes into two parts; which are manual or machine driven.

So, for example, we would have seen the artisans, who create excellent or aesthetically very nice looking brasswares or stonewares or various kinds of metallic objects maybe a statue or and so on and so forth. We would have seen them bringing up an excellent luster onto the surface by way of very controlled polishing even buffing and so on. So, these are manual processes, similarly the stone statues the artisans who work with stone or such very hard and brittle objects they are known to chisel certain portions from the surface and in the process they bring in the right kind of a contour they want or even the exact luster or size and dimensions and so on.

So, these are manually driven processes. We can also do a similar thing of removal of material by way of grinding or polishing or buffing these are all machine driven processes. And we can also actually remove very controlled amount by exactly using a lathe or machining or turning or drilling and so on. So, these are also processes which allows you to do surface engineering by way of removal of material from the surface.

And by now I hope you understand that when we talk of surface engineering, we actually are talking about all kinds of all possible kinds of engineering materials, which can be simply a metal piece or a semiconductor chip or it can be a polymeric object, it can be a

ceramic product, it can be refractory, it can be a tool, it can be even a stone or it can be a brass wear or a cast metal or any of these.

So, what whichever solid has engineering objective or is used for engineering purpose or engineering utility; if we are taking care of their life, their design, their aesthetics or their protection or their reliability or safety issues by way of changing the surface micro structure and composition, we certainly call it surface engineering.

Now, removal based surface engineering methods can also employ electrochemical means. So, for example, it can be simply electrochemical polishing or removal from the surface, electro polishing either it can be continuous or it can be through pulsed mode. We can do electro discharge machining, similarly we can do plasma cleaning and etching we can do focused ion beam etching and so on and so forth.

So, for example, this is very very precise, but its confined to a very small region. In fact, we are talking about less than certainly less than micrometer. So, we are talking about anything between ten nanometer to about hundred or a few hundred nanometers. So, something can be as small and as precise as ion beam etching or on the other hand something could be as large and wide like electro polishing where we actually are removing from a fairly large surface area.

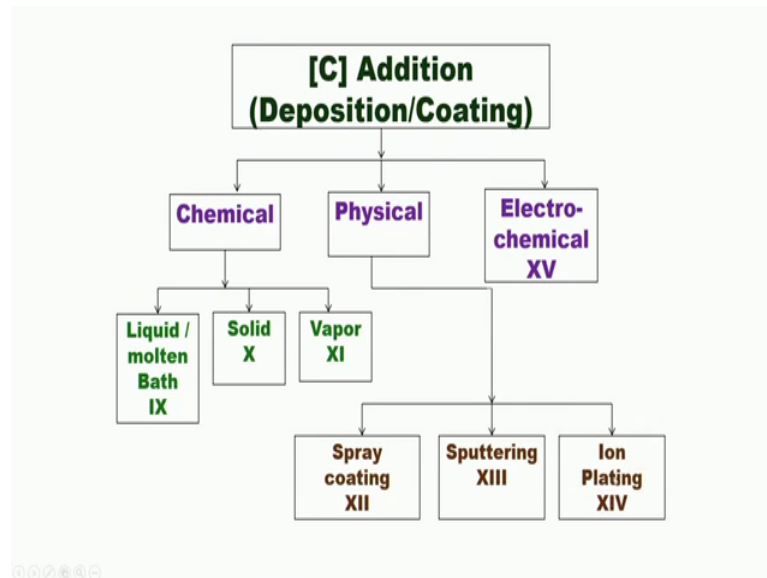
But for talking about surface area or typical industry industrial practices, we actually can also go in certain kinds of hot dipping processes. Say for example, when we and now when we move into the chemical processes where, in case of electrochemical processes we need electrolyte we need two electrodes anode and cathode and we certainly expect ionic transport within the cell and electronic transport outside the cell.

So, essentially we have a complete galvanic cell there, but in case of chemical methods we do not necessarily employ a situation where transport takes transport involves a movement of electrons and ions, but certainly there are dissolution by way of some chemical which attacks control actually employs control attack onto the surface.

So, what we can do dip cleaning or degreasing I mean this is very common in mechanical devices particularly automobiles or any moving parts, we can do chemical polishing or dissolution which removes for example, certain oxides or certain undesirable substances from the surface. And we also can do etching which is very

controlled and selective can be both uniform etching, where we actually remove from the entire surface area or we can remove selective removal, we can employ a selective removal by way of etching when certain constituents onto the surface they are attacked and not the rest. So, this is how we actually can do surface engineering by way of remove removing materials from the surface.

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We can also now think of another possibility which is, in my opinion one of the large one of the most widely employed approaches is when we add on materials to the surface. So, when we coat or deposit and that we can do through one of these three possible approaches by way of chemical deposition or physical deposition or electrochemical deposition.

There is hardly any precise distinction between these two terms, but their generally accepted convention is to mention or invoke deposition when the deposit layer is fairly thin and by way of thin, again the convention says it should be less than a millimeter.

Whereas, when you are talking about, coating you actually are referring to situations where you can build up materials not only millimeter, but actually several millimeters; but then this is a distinction which is very loose and not very precise. I must also mention here that when we talk of these coatings or deposition processes this actually though it is surface engineering.

But this actually is the precursor of now which is a fairly exciting possibility in manufacturing engineering called additive manufacturing, where we build in layer by layer and eventually create a complete component. So, there this the additive manufacturing process is essentially based on the foundation is laid by the science behind edition assisted surface engineering anyway.

So, when we talk of deposition or coating through chemical means we can do it through molten bath, we can do it through entirely through solid state or we can employ deposition from the vapor state. Similarly when we talk of physical, when we are not changing the composition at the surface whatever comes from in the vapor or from the liquid gets deposited onto the surface.

So, without any change from the precursor change between the precursor and the deposit, this can be done through spray coating through sputtering through iron plating. And it is one modification of the so called plating processes, where we are plating not from liquid state or aqueous solution, but from the vapor state. Finally, we can also certainly add on materials by way of electrochemical deposition.

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[C] Addition Based SE Methods

- (IX) 1. Galvanizing
2. Hot dip coating (Al, Zn)
3. Lacquering/Painting
- (X) 1. Roll bonding
2. Pack rolling
3. Diffusion bonding
- (XI) 1. CVD
2. Electro-CVD
3. PVD
- (XII) 1. Plasma spray/deposition
2. Thermal spray
3. High velocity spray (HVOF/Cold)
- (XIII) 1. Sputtering (single/multi-target)
2. Reactive plating
- (XIV) 1. Ion plating deposition
2. PEO (plasma electrolytic oxidation)
- (XV) 1. Electrodeposition/plating
2. Electro-codeposition
3. Electroless deposition/plating

So, if you now just go one by one. So, this is these are the processes which are essentially deposition from the liquid state. So, what will have is here, a very well known technique called galvanizing.

Now, this galvanizing essentially is it can be for example, hot dip coating or it can be lacquering or it can be painting this one part which actually I will add on to the slide is which is missing. Here is the so called overlays or the weld overlays including cladding. So, you actually can add on to much thicker layers onto the surface by way of this kind of add on or deposition processes where you can add on thick coatings.

You can do in the solid state you can have roll bonding, you can back rolling, you can have diffusion bonding. Wherein actually in roll bonding you actually allow two separate layers to be rolled together mostly in the cold rolling condition and the two layers or the two thin sheets can diffuse and bond with each other. And then in the process you actually cover one layer one sheet with another which is thinner.

And that is how you can protect the thicker one. So, you can do either by similar roll bonding or pack rolling you can also do diffusion bonding where, the two layers can actually bond with each other through thermally activated diffusional process. You can do for example, now these were the chemical changes. So, essentially we were able to change.

So, first one what we saw was through the liquid or molten bath the second one is solid state and then now we can also do such chemical changes onto the surface by way of depositing from the vapor state. And this could be chemical vapor deposition, this could be electro chemical vapor deposition or it can be simply physical vapor deposition. The differences being of course, that in CVD your there is a difference between the composition that you develop onto the surface.

Because the deposition also includes certain limited level of reaction happening either in the vapor state or after arriving on to the surface mostly at the vapor state itself. So, what you deposit is composition wise slightly different than the precursor, the same thing can happen in electro chemical vapor deposition, but in physical vapor deposition you there is no change in composition from the precursor onto the surface what you deposit.

So, this is how you actually all these process of 9, 10, 11 are processes where you are actually changing adding on to the materials by changing the composition of the surface. You can also create another you can create a new surface or add on material by way of spray coating.

But here you do not necessarily change the composition onto the surface, say for example, you can use plasma spray or plasma deposition, you can use thermal spray you can use high-velocity spray. And these are slightly different than most of the techniques we have discussed so far. In so called high velocity spray, the spray velocity of the particles that are impinging onto the surface can be close to supersonic or maybe even greater than supersonic speed.

So, speed wise this actually would be only second to the unimplantation speed otherwise all other processes that we have discussed. So, far all other spray or the depositing processes they are fairly low velocity processes. We can also have a situation where we have this sputtering or we can have reactive plating, we can have iron plating, now in sputtering and reactive plating we actually are talking about change which is only physical in nature.

Similarly we can have these iron plating deposition processes or plasma electrolytic oxidation processes. So, we are changing the composition here and through a certain chemical reaction which essentially converts certain species onto the surface into its oxide layer. Now we finally, we can also think of electrochemical processes, where we actually are depositing the material or the plating the material we can do electro co deposition where we can actually deposit multiple cations onto the same surface having a different anodes, but a single cathode.

We can also coat materials by way of electro less deposition or plating electro less plating processes. So, overall let me go back to the main slide and this is how we actually can summarize the entire process of surface engineering. The entire approach of surface engineering, as I said in the beginning by these kind of various processes.

So, again I must emphasize that whenever we talk of one of these for example, electrochemical or a chemical process under each of these approaches there are multiple techniques possible. And with this summary slide we should be able to take a bird's eye view and in one snapshot capture all possible approaches for the so called surface engineering of engineering solids.

Thank you very much.