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Lecture - 38 Electro and Electroless Deposition Process

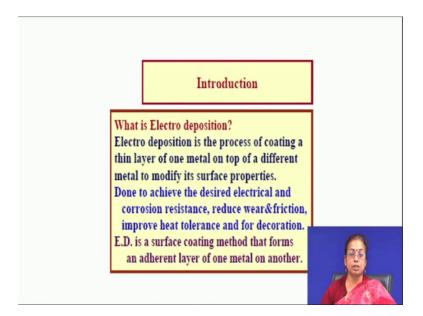
Now, in this talk will come across the electrometric base techniques particularly Electro Deposition techniques and also the solution base techniques like electro less deposition techniques.

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Electro-deposition
Electro-less deposition

So, both their techniques are applied for the development of a very thin coated layer on the surface of the metallic substrate. So, as a name implies in one case we basically use electrolytic current for the deposition purpose, other case it is free from any kind of electrolytic process, it is you do not need to apply any electrolytic electric electrical current for the process to occur.

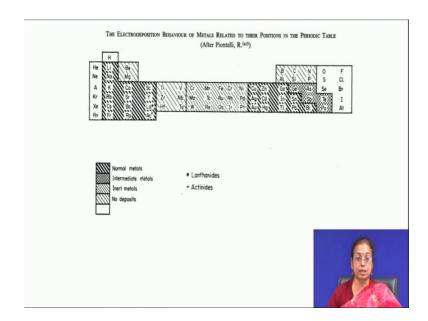
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So, first we will discuss about the electro deposition process. So, it is the process of development of a very thin to moderately thick coating layer on the surface of substrate, for developing the completely another layer on the substrate, for improving the wear resistance, for improving corrosion resistance for improving the aesthetic appearance of the surface as well as for development of completely new kind of component in practice.

So, usually this process is very simple, where we use the component or substrate as the cathode and we pass electrical current. Anode is may anode may be made of the consumable materials consumable anode or it may be made of kind of inert anode and when you pass electrical current what happens is that, there is deposition on the surface of cathode and that deposited layer is actually dependent on the kind of deposition, kind of solution, electrolytic solution you are using and naturally based on your requirement.

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So, as the name implies this is electro deposition and where you need to have the conductive substrate and the metal which you are going to deposit has also to be conductive. So, you will find that for electro deposition, you need to have any kind of you cannot have any kind of substrate. So, basically the substrate have to be highly substrates, you are use used for electro deposition it have to be conductive in nature. So, non conducting surface cannot be used for substrate in electro deposition.

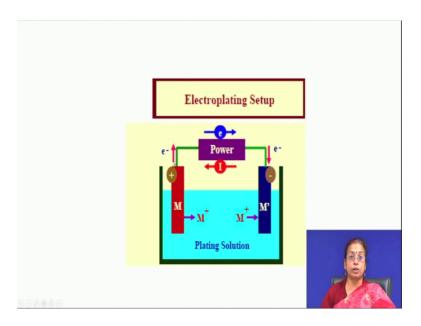
So, usually substrates are highly conducting in nature. So, on the other hand if you talk about deposition, ideally all metallic materials may be deposited by electro deposition technique, but there are certain limitations all metals cannot be deposited by electro deposition techniques. These are the dark hatch colored are the normal metals which are easily electro depositable. So, cross sized metals are the intermediate metals which may be deposited.

And then again light has metals are like inert metals, which may be again deposited and if you talk about the white hatched metal metallic metals there they cannot be deposited they are not depositable. So, you will find that not all metallic materials may be deposited by electro deposition process. So, for the electro deposition to occur first of all the aqueous salt or aqueous electrolyte has to be available unless an until across electrolyte of that metal is available you cannot do electro deposition this is the first requirement.

Second requirement is that when you deposit the metal in the cathode, naturally there is also the process of hydrogen evolution process. So, hydrogen evolution process the kinetics of hydrogen evolution at that potential should not exceed the deposition process that is second requirement, third requirement is that there should not be any oxide formation of the metal ion which you are producing in the electrolyte.

So, these are three important requirements for the materials to get depositable. So, because of that you will find that not all metals can be deposited by the typical way of electro deposition.

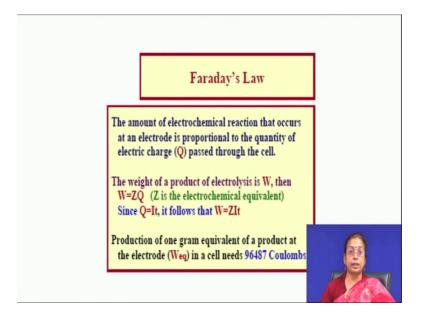
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This is the typical set of our electro deposition process. So, when you use the metal as that typical cathode and your anode may be consumable anode, your may anode maybe not constable conductive anode. So, what you do is that, when you and your electrolyte should contact the electrolyte plating solutions is the source of ions of that metal which you are going to deposit.

And you apply the electrical power supply, the power supply may be your normal DC power supply unit or it may be parts power supply unit and you have to expose for a certain period of time. If you are interested to increase the kinetics of the deposition you have to increase the temperature to a little extent. So, these are the requirement for the electro deposition.

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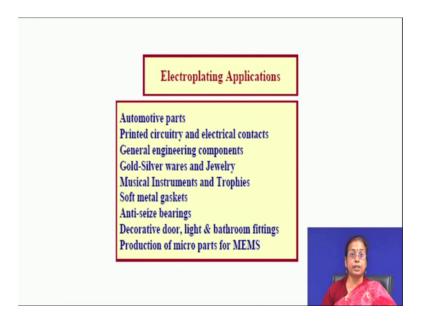


So, now if you quickly go through the deposition rate, deposition rate is very much can be calculated by the application of Faraday's law. So, if you just quickly go through the deposition rate you will find that it follows the typical Faraday's law when it depends on the amount of electrical current that is or current density that you are passing for the electro deposition and that of time and it is also dependent on the electrochemical equivalent of that metal which you are going to deposit.

So, if it is the W which is go which mass of the electrode, mass of the element that you are going to deposit or weight of the electrode weight of the materials which you are going to deposit that is equal to Z I divided Z is nothing, but typically electrochemical equivalent, I is the current density and t is a time. So, this is very important and this gives you typical amount of metal which is going to deposit for a given solution or for a given metal.

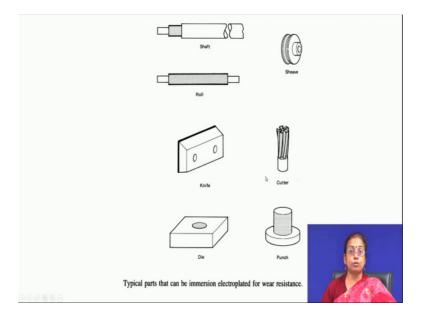
So, this is again a kind of value which gives you information under ideal condition in real condition there are several factors which play important role and which reduces the kinetics of the electro deposition process.

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Now, if you quickly go through the application of the electroplating, it is usually mostly applied for typical aesthetic appearance enhancement purpose, it can we applied for coating for corrosion resistance application, it can also be applied for wear resistance application and it can also be applied for development of the micro parts of the for the MEMS.

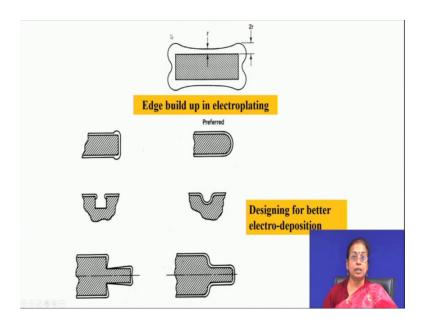
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And one of the biggest limitation of this electro deposition is that, when you electro deposit there is also chance of the charge accumulation along the easies and corners of

the deposited layer. So, when the problem were charged charge a problem of the charge generation is they are charged concentration is there around the corners or sour points you will find that there is actually changing the thickness along the corners and the difference in thickness causes problem.

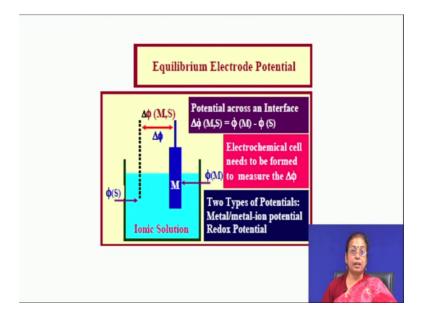
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So, after the electro deposition is over, you have to take out the extra metal and make it uniform in thickness. So, whenever it is important that you do electro deposition of different saved component of thick product or thick electro deposited layer, you have to design the component in such a fashion that there is no chance of accumulation of the charges along the corners or different parts of the component.

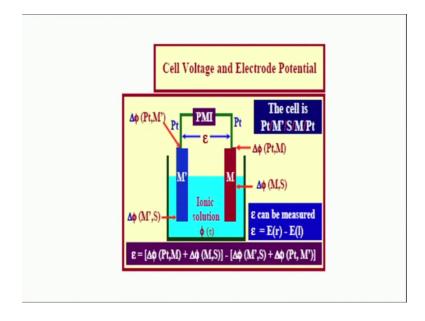
So, otherwise electro deposition is a very good process and can we apply it for any component like shaft, roll, knife, dyes this hard chromium coating for the typical real resistance application. So, it can also be applied for a soft metal gasket, then anti seize bearings, decorative door lights and bathroom fittings can be applied for production of micro parts for MEMS application. So, these are the typical applications of the electro deposition.

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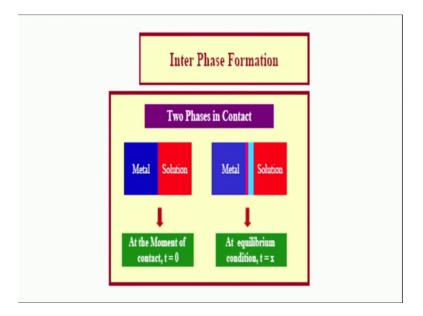


Now, if you quickly go through the electro deposition process in an all real condition, you will find that real condition the Faraday's law is not fallow followed. So, whenever you deep the electrode in an electrolyte containing the metal ions, you will find that there is a potential across an interface. The electrochemical cell needs to be formed to measure the that delta 5 and two types of potentials are there metal nonmetal potential, redox potential.

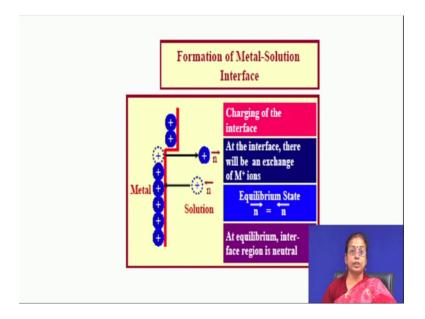
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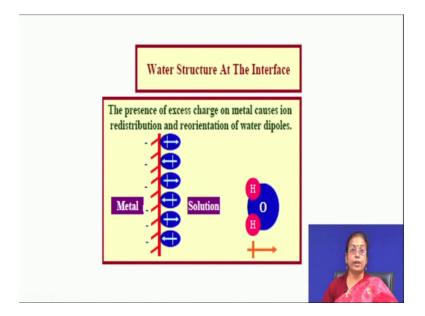


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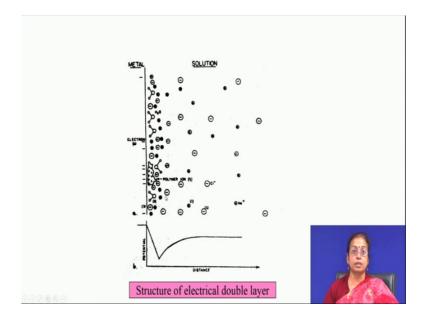
So, when you talk about this charge accumulation naturally, there is always a very thin layer formation that which actually acts as a barrier to subsequent electro deposition, when you do electro deposition in practice. So, that charge accumulation at the interface causes as barrier for subsequent electro deposition process.

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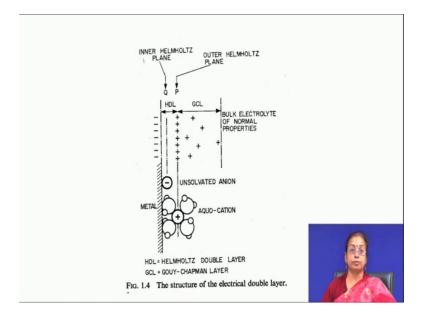
So, when it is there naturally you have to be careful you have to break the layer or otherwise the deposition rate will be slowed down. So, the presence of excess charge on material causes the ion distribution or reorientation of the water dipoles. So, this is very important there is always presence of very thin solvated layer on the surface of the metal when you do electro deposition process.

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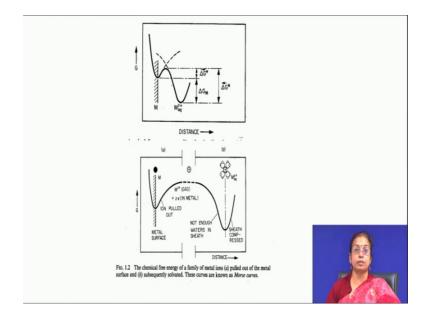
So, because of the solvated layer accumulation, you will find that potential on the surface gradually drops down. So, this casual drop in proposed potential causes the reduction in the kinetics of the electro deposition process.

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This is called a Helmholtz double layer, Helmholtz double layer formation is there then Gouy Chapman layer is outer layer. So, you will find that because of presence of the solvated ions there is always accumulation of charge at the near surface region.

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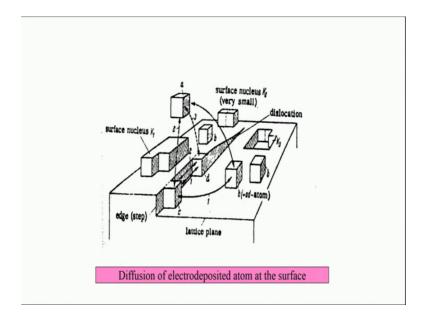
So, the charge or accumulation decreases the weight of the metal which is actually deposited and there is always a difference between the weight which is calculated from Faraday's law and the weight of the metal which is actually deposited and these two differences actually or the ratio between the two gives you the efficiency of the electro deposition process.

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Typical C	omposition	of Nickel Baths	
	Watts	Sulfamate	
Material	Quantity	Quantity	
Nickel Sulfate	250 g/L		
Nickel Sulfamate		350 g/L	
Nickel Chloride	5 g/L	25 g/L	
Boric Acid	25 g/L	80 g/L	
Ferrous Sulfate	8 g/L		
Additives	3 g/L	15 ml/L	
			8

Now, if you quickly go through the bath which are use for example, in case of nickel deposition this is nickel bath. So, you can have the nickel sulfur solution, nickel chloride solution, boric acid is used for usually for as a kind of additives for, changing the brightness of the process you can use solar sulfate as buffer and also you can have different other additives for reaction slow down.

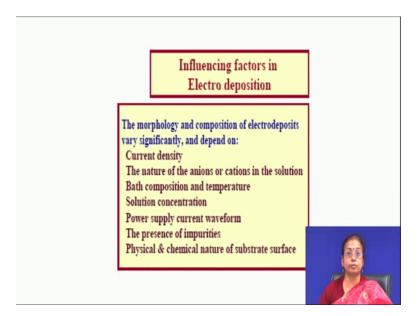
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And when you talk about the electro deposition naturally you will find that deposited layers are in the form of patterns and those atoms can migrate also on the surface because of the presence of several defects on the surface and then migrated atoms say they occupy the defects and corners defects on the sides.

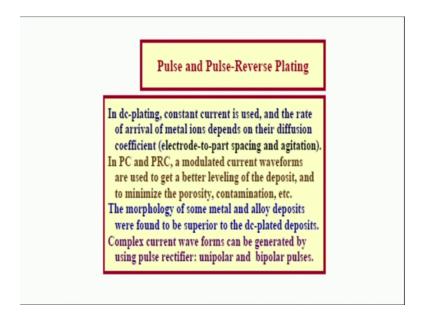
So, defects on the (Refer Time: 12:00) naturally you will find that at the surface if you just clearly see the interface, you will find that at the interference there is atomic level diffusion and that atomic level diffusion actually offers the addition or strength of the coating.

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Now, if you quickly go through the factors which influencing the electro deposition, they are current density the nature of anions are cations in this initial bath composition and temperature solution concentration, power supply current waveform, presence of impurities and physical and chemical nature of the substrate surface these are important.

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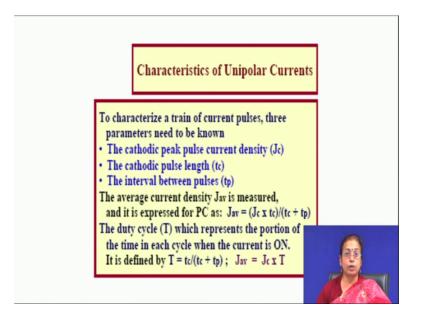


So, now if you talk about the different type of parameters which influence the electro deposition kinetics, they are first important parameters influencing the kinetics of electro deposition are current density and time and apart from current density and time the bath

composition additives they are also important parameter and finally, the kind of current you are using whether it is in DC mode or pulse mode that also influences says the process to a large extent. So, that particular current can be applied in two different modes; one is pulse current another one is pulse (Refer Time: 13:14) current.

So, in dc plating the constant current is used and the rate of arrival of metal ion depends on their diffusion coefficient and in pulse that pulse reverse rating a modulated current waveform is used and that particular modulated pulse waveform basically offers very nice leveling and also cleaner deposition and also minimize the porosities and contamination on the surface. The morphology of some metal and alloy deposits were found to be superior to be dc plated deposit, the complex current wave form can be generated by pulse rectifier. So, you can use different pulse rectifier for complex current reform generation.

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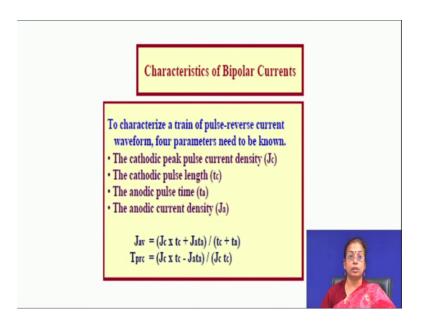
So, whenever you talk about unipolar current naturally, you have two important unipolar current that will sit basically now changes with time and it is only in that you are that you are saved cathode excess cathode and or maybe you sometimes stop the cathodic reaction. So, you either current is very high value your current is 0. So, in this unipolar current what you do is that, in the cathode or in the anode the current density is either maximum or 0 and there are two important parameters; one is cathodic peak pulse

current density another one is cathodic pulse length and interval between the pulses these are important parameters.

So, average current density maybe measured by knowing these all values like if you have the current density of the cathode is Jc and if you cathodic pulse length tc. So, in that case current density in the cathode averaged conducive in the cathode is equal to Jc into tc divided by tc plus tp. On the other hand the duty cycle is nothing, but tc divided by tc plus tp. So, this is actually these are the two important parameters; one is average current density in the cathode, another one is that typical time of duty cycle or time of cathodic interact time of the deposition actually.

So, these two parameters finally, gives you information about the overall time actually that is overall time or overall current that is showing on the cathode.

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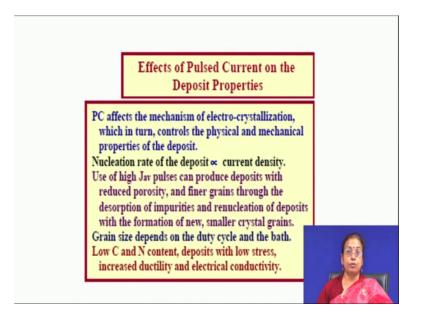
So, on the other hand if you talk about the bipolar current that we seen cathode is acting cathode and anode simultaneously. So, there are two important parameters like cathodic pulse peak pulse current density, cathodic pulse length, then anodic pulse time and anodic current density.

These are four important parameters and naturally J average is equal to the cathodic current density and time for cathode there are no time for which it is cathode plus cathodic current density time for cathodic and anodic current density into time for which

it is a anode divided by total time like to plus ta. On the other hand if you talk about the duty cycle, it its equal to Jc to to minus Jat a divided by Jc to.

So, these two parameters when there then total current that is flowing over the system you get information by multiplying that cathode the average current with that of average duty cycle.

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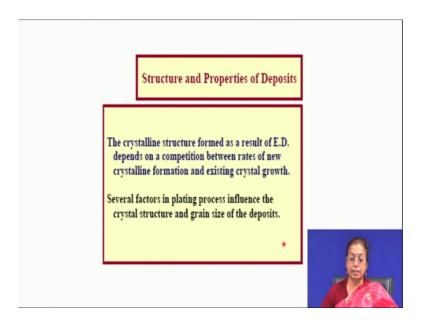
So, now if you talk about the pulse current on deposited property, it is having certain advantages over DC current for example, if you think of about electro deposition process you will find that, electro deposition is active till the or maybe you can say that total any deposition process consists of two stages; one is nucleation and growth second one is growth.

So, usually nucleation rate of the electrode deposition process is proportional to that of current density. So, when you talk about electron nucleation rate it is proportional to that of current density. So, as it is proportional to that of current density naturally you will find that higher the current density higher will be the nucleation rate of the deposition.

On the other hand if you talk about growth rate; growth rate is proportional to time for time of the interaction or duty cycle. So, if you go on increasing the current density and decrease the duty cycles, you will find that the growth will be restricted. So, if you are interested to have very find deposited layer on the surface of any substrate, you should increase the typical current density and you should decrease the duty cycle.

So, these two things can be independently varied in case of pulse or pulse reverse mode on the other hand in DC mode you cannot really vary these all things and brain size depends on duty cycle of the bath. So, this is very important that you should use the pulse current in and pulse reverse current so, that you get the required grain size and also required properties in the coated layer .

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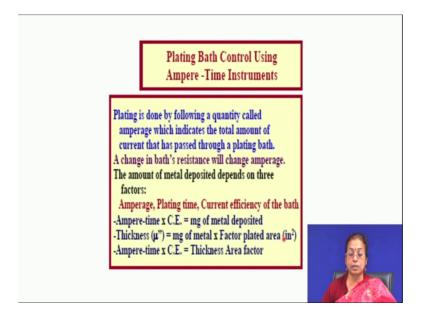
So, it is naturally your ultimate structure will be dependent on the current density and duty cycle combinations, it is very important that you fix them up, fix them up or you optimize them properly.

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Usually, if you talk about dc electro deposition process, there you get very large columnar grains or density grains. On the other hand if you talk about the electro deposition where pulse a pulse reverse mode, your deposition structure is highly uniform it is compact in nature.

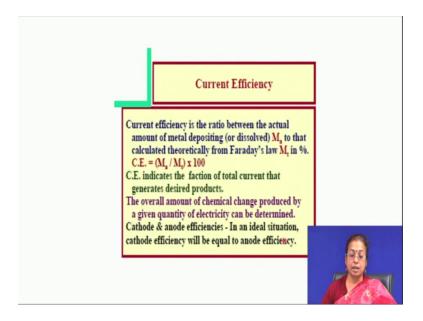
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So, the thickness of the deposited layer and also its microstructure can easily be controlled by controlling these parameters. On the other hand if you are interested to control the other factors like your leveling of the bath, if you are interested to control the

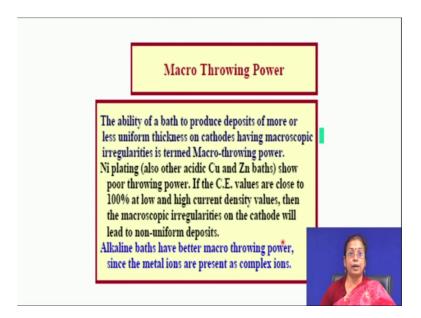
or minimize the charge density along the corners, you have to go for typical other kind of equipment that is ampere time instrument, where you basically want fixing up an amperes and time and also you can choose the bath composition in order to have proper leveling of the bath.

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So, usually if you add some complex reagent in the bath, usually it reduces the kinetics of the deposition and by this process he basically level the structure for it to a very large extent. And current efficiency is also very important; current efficiency equal to a date of which it is deposited in that and also date of a which at least it is deposited as for the Faraday's law and to that of the rate at which it is actually deposited the ratio of actual deposited layer to that of the same which is experimentally or your theoretically calculated by Faraday's law these two ratio gives you information about current efficiency.

So, current efficiency is very important because each if it is high then naturally you can say that the rate of deposition is very high hindrances quite minimum.



On the other hand if it is known actually is fine that, very hindrances are there while moving the ions. Now last one is macro throwing power. So, it is nothing, but the ability of a birth to produce deposits of more or less uniform thickness over macroscopic irregularities, this term as macro throwing power it is very important term actually.

So, lower is the macro throwing power naturally you find that, it is a ability of whether two deposit uniform the higher is the macro throwing power naturally higher will be the uniform deposited layer. So, macro throwing power is very important. So, if you go on adding for example, nickel plating shows poor macro throwing power. So, though it is having very high deposition rate, but for macro throwing power; that means, when you deposit the nickel by electrodeposition process, naturally if you have soft corners in the component they are deposition thickness will be go lower than that of deposition thickness will be higher than that of rest of the part.

So, deposition thickness if you are interested to have very fine uniformly deposited layer, you have to go on having the bath or solution which basically offers no macro throwing power. So, macro throwing power is higher macro throwing power. So, macro throwing power is power is very important. And usually you can enhance the macro throwing power, but you receive the rate of the deposition by addition of different complex reagent in the solution.

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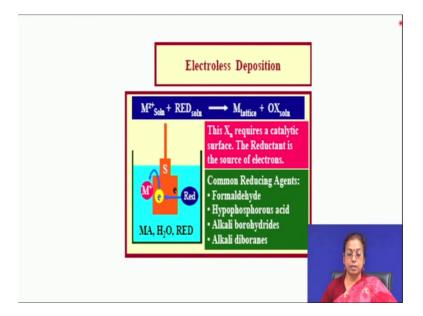
Uniform Electrodeposit Through The Use of Complex Baths

- In most complex baths, the deposition potentials
 are amenable to hydrogen evolution which
 competes with metal deposition such that C.E.
 falls as current density is increased. This results in
 a more uniform deposit on cathodic macro
 irregularities.
- When the ions are complexed, they encounter high concentration polarization (CP). If the CP is high, the micro throwing power is rather poor.
- The ability to produce a deposit over a surface including recesses is called covering power.

So, if you use complex baths like by why the application of complex bath, the deposition potential basically are amenable to hydrogen evolution which computes a metal deposition process and the cathodic efficiency falls as current density is increased, this results in more uniform deposit on cathodic macro irregularity. So, this is very important because in the cathode you have also hydrogen evolution.

So, if you have very high macro throwing power deposition rate is very slow because of hydrogen revolution that basically levels your deposits. So, macro throwing power is a very interesting parameter which is important for leveling the deposition.

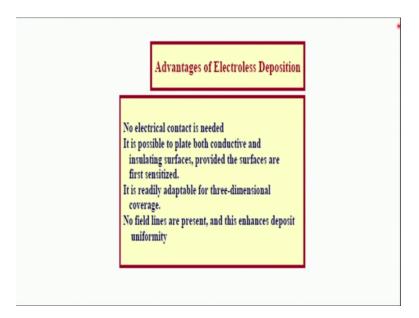
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So, next type of deposition is electroless deposition process. So, electroless deposition you do not need to pass in electrical current where, but you do add reducing agent in order to change the metal ions to its metal act on to its act on. So, usually electroless deposition techniques are very much this technique is very much powerful technique for development of the coating on nonmetallic materials, particularly non metallic materials like odot or maybe polymers or ceramic materials for metalizing them.

Or otherwise metallic materials which otherwise is difficult to code deposit on for example, aluminium, magnesium, this stainless steel on which deposition is very difficult there you can use the electroless deposition process.

So, the basic purpose processes is a easy actually. So, where you basically in the solution you are a reducing agent and common reducing agents are formaldehyde hypo phosphorous acid, alkali borohydrides and alkali diboranes. So, these particular agents when you add naturally the metal ions gets reduced to its metal atom and it get deposited onto the surface of the substrate.

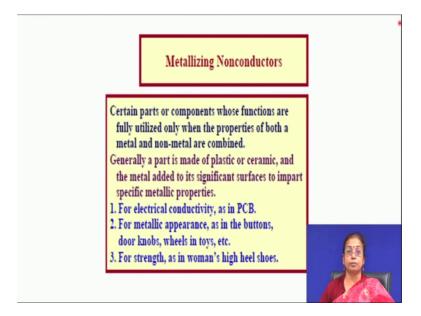


So, here I you do not need to add in electrical contact. So, it is electrical contact list process. So, you can apply this particular deposit without any electrical contact and hints this is an important process for deposition on conductive as well as non conductive material.

So, if you are interested to do electro deposition on non conductive material or those metals which otherwise is difficult to be used as electro deposition substrate, there if you first to electrolyte deposition and then deposit the thin nickel layer electrolyte deposited nickel layer or copper layer, then if you a use it as substrate for subsequent electro deposition your deposition rate becomes very high.

So, it is readily available for three dimensional coverage, there is no field lines are present and the deposition is almost uniform. This is a very useful technique, but heats the efficiency is much lower than that of the same for electrodeposition or kinetics of the process is quite slow. Because in this case you are wishing basically using reducing agent to cause metal atoms and whatever metal atoms are produced they are distributed non uniformly all throughout the surface some of the metal at (Refer Time: 25:58) less you are lost in the environment. So, actual deposited metals is much lower than that of the same which you are generating by the process of the ionization.

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So, were this technique is mostly applied for ionization of the conductor, metallizing of conductor non conductors like for electrical conductivity in PCB for metallic appearance as in the buttons, door, knobs, wheels in toys. For strength actually certain parts of the component which functions are fully utilized when the properties of both metal and non metals are combined.

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And usually nonmetallic materials are deposited by electroless deposition. So, this is very useful technique for and also a kind of important technique to deposit a very thin deposited layer by electrodeposition where the substrate is non conductive.

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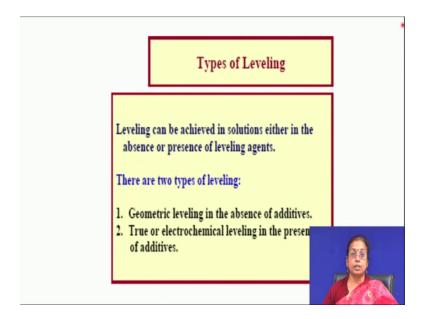
So, one of the important process which is which plays very important role in electrodeposition is that evolution of hydrogen actually. So, hydrogen evolution is a competitive process. So, in the cathode there is hydrogen evolution as well. So, whenever you talk about electrodeposition or electroless deposition, naturally atomic hydrogen they are basically they may get diffused in.

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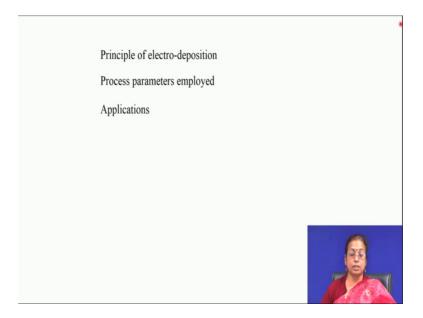
So, if you are interested to get read of the particular hydrogen, you can also go for annealing operation so, that hydrogen is no more there.

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So, this is very important process.

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So, in this particular process we discussed about electrodeposition decision as well as electroless deposition, we have also discussed about the chemical conversion and electro chemical conversion process. So, both the processes are all the processes are very important particularly if you talk about conversion coating, they are mostly used for changing the appearance of the surface for protection against corrosion and also as a base for subsequent painting of operation.

On the other hand electrode electroless deposition may be used for only metalic deposition on the surface of the substrate may be metal or nonmetal. The metal deposition which occurs may be for corrosion resistance application may be for wear resistance application and usually this deposited layer is having some kind of bonding with the substrate at the interface there is only the also diffusion process. On the other hand in the chemical conversion coating the converted the substrate itself is converted to its compound.

So, the interface is very adherent in nature, on the other hand in electro and electroless deposition process there is a very soft interface. So, whenever you talk about the application of the electrodeposition you have to also think of the interface very nicely because interfacial adherence must be at a very higher level and where you need to apply very high strength or fatigue fluctuating load on the component you need not apply electrode deposited substrate.

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So, you have to be very careful in doing the application of the product which you are depositing by electrodeposition technique.

Thank you very much.